

# **Nano-/Micro-Scale Organic Paramagnetic Materials: Synthesis, Characterization, Self-Assembly, Optical Wave Guiding and Device Structure**

A Thesis Submitted for the Degree of

**Doctor of Philosophy**



by

**PRAMITI HUI**

**School of Chemistry**

**University of Hyderabad**

**Hyderabad 500 046**

**India**

**September 2014**

**Devoted to my beloved parents**

# CONTENTS

|                  |     |
|------------------|-----|
| Declaration      | I   |
| Certificate      | II  |
| Acknowledgements | III |

|                  |                                                        |           |
|------------------|--------------------------------------------------------|-----------|
| <b>Chapter 1</b> | <b>Introduction</b>                                    | Page 1-80 |
| 1.1              | Introduction to Magnetism                              | 1         |
| 1.2              | Electron Spin Resonance (ESR) Spectroscopy             | 6         |
| 1.2.1            | Nuclear Hyperfine Interactions                         | 7         |
| 1.2.2            | The EPR of Biradical Systems                           | 9         |
| 1.2.3            | Exchange Coupling                                      | 12        |
| 1.2.4            | Dipole-Dipole Coupling                                 | 13        |
| 1.2.5            | Determination of Electronic Ground State of Biradicals | 14        |
| 1.3              | Magnetic Force Microscopy (MFM)                        | 15        |
| 1.3.1            | MFM Images of Nano/Micro Poly-radical Structures       | 17        |
| 1.4              | Stable Radicals                                        | 19        |
| 1.4.1            | Survey of Stable Radicals                              | 19        |
| 1.4.1.1          | <i>Triphenylmethyl Radical</i>                         | 19        |
| 1.4.1.2          | <i>Nitroxide Radicals</i>                              | 20        |
| 1.4.1.3          | <i>Phenalenyl Radicals</i>                             | 21        |
| 1.4.1.4          | <i>Phenoxy Radicals</i>                                | 22        |

|                                                                  |    |
|------------------------------------------------------------------|----|
| <i>1.4.1.5 Thiazyl Radicals</i>                                  | 23 |
| <b>1.4.2 Nitronyl Nitroxide (NN), Oxoverdazyl (OVZ) Radicals</b> | 24 |
| <i>1.4.2.1 Nitronyl Nitroxides (NN)</i>                          | 24 |
| <i>1.4.2.2 Verdazyl Radicals</i>                                 | 26 |
| <b>1.5 Properties of Stable Radicals</b>                         | 31 |
| <b>1.6 Organic Radical Based Ferromagnets</b>                    | 34 |
| <b>1.7 Topological Rules for High Spin (HS) State</b>            | 36 |
| <b>1.7.1 Very High Spin Radical Polymers</b>                     | 40 |
| <b>1.8 Introduction to Nanoscience and Technology</b>            | 42 |
| <b>1.9 Assembly of Molecular Nanomaterials</b>                   | 43 |
| <b>1.9.1 J-aggregation and H-aggregation</b>                     | 44 |
| <b>1.10 Fabrication Methods of Nanomaterials</b>                 | 46 |
| <b>1.10.1 Reprecipitation Method</b>                             | 46 |
| <b>1.10.2 Solvent Evaporation Method</b>                         | 46 |
| <b>1.10.3 Vapor Deposition Method</b>                            | 47 |
| <b>1.10.4 Sonochemistry</b>                                      | 48 |
| <b>1.11 Nanomaterials with Diverse Morphologies</b>              | 49 |
| <b>1.11.1 Nano Vesicles</b>                                      | 50 |
| <b>1.11.2 Nano Tubes</b>                                         | 52 |
| <i>1.11.2.1 Driving Force, Formation Mechanism of Soft tubes</i> | 53 |

|                                                              |    |
|--------------------------------------------------------------|----|
| <i>1.11.2.2 Magnetic Inorganic 1-D Nanostructures</i>        | 54 |
| <b>1.12 A Brief Overview of Soft Lithographic Techniques</b> | 56 |
| <b>1.12.1 Types of Soft Lithography Techniques</b>           | 57 |
| <i>1.12.1.1 Replica Molding (RM)</i>                         | 57 |
| <i>1.12.1.1.1 Microtransfer Molding (<math>\mu</math>TM)</i> | 57 |
| <i>1.12.1.1.2 Micromolding in Capillaries (MIMIC)</i>        | 58 |
| <i>1.12.1.1.3 Lithographically Controlled Wetting (LCW)</i>  | 59 |
| <i>1.12.1.2 UV-Molding</i>                                   | 59 |
| <i>1.12.1.3 Embossing (Imprinting)</i>                       | 60 |
| <i>1.12.1.4 Printing</i>                                     | 60 |
| <i>1.12.1.4.1 Microcontact Printing</i>                      | 60 |
| <i>1.12.1.4.2 Nanotransfer Printing</i>                      | 61 |
| <b>1.13 Magnetic Compound Lithography</b>                    | 62 |
| <b>1.14 Optical Wave Guiding</b>                             | 63 |
| <b>1.14.1 Total Internal Reflection (TIR)</b>                | 64 |
| <b>1.14.2 Optical Wave Guiding in 1D Structures</b>          | 65 |
| <b>1.15 Aims of the Thesis</b>                               | 68 |
| <b>References</b>                                            | 71 |

|                  |                                                                                                                                                                                                                                                                          |             |
|------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|
| <b>Chapter 2</b> | <b>Syntheses, Optical, Magnetic and Raman Studies of Doublet and Triplet Nitronyl Nitroxide (NN) and Oxoverdazyl (OVZ) Radicals Appended to 2,6-Bispyrazolyl Pyridine (BPP) and a Novel Spin Cross-Over <math>\text{Fe}^{\text{II}}(\text{BPP-OVZ})_2</math> Complex</b> | Page 81-110 |
| <b>2.1</b>       | <b>Abstract</b>                                                                                                                                                                                                                                                          | 82          |
| <b>2.2</b>       | <b>Introduction</b>                                                                                                                                                                                                                                                      | 82          |
| <b>2.3</b>       | <b>Results and Discussions</b>                                                                                                                                                                                                                                           | 84          |
| <b>2.3.1</b>     | <b>Syntheses and <math>^1\text{H}</math>-NMR Characterization of Paramagnetic Ligands</b>                                                                                                                                                                                | 84          |
| <b>2.3.2</b>     | <b>The Single Crystal X-ray Structure of Radical R1</b>                                                                                                                                                                                                                  | 89          |
| <b>2.3.4</b>     | <b>Optical Properties of Radicals (R1-R6)</b>                                                                                                                                                                                                                            | 89          |
| <b>2.3.5</b>     | <b>X-Band ESR Spectroscopy Studies of Radicals</b>                                                                                                                                                                                                                       | 90          |
| <b>2.4</b>       | <b>Synthesis and Characterization of Spin Cross-Over (SCO) <math>[\text{Fe}^{\text{II}}(\text{R4})_2](\text{ClO}_4)_2</math> Complex (C1)</b>                                                                                                                            | 95          |
| <b>2.4.1</b>     | <b>Variable Temperature Magnetic Susceptibility Measurement and Raman Spectroscopy Studies</b>                                                                                                                                                                           | 96          |
| <b>2.4.2</b>     | <b>X-Band ESR Spectroscopy Studies of Radical R4 and Complex C1</b>                                                                                                                                                                                                      | 98          |
| <b>2.4.3</b>     | <b>Self-Assembly of Radical R4 and Complex C1</b>                                                                                                                                                                                                                        | 98          |
| <b>2.5</b>       | <b>Conclusions</b>                                                                                                                                                                                                                                                       | 100         |

|                                                                   |     |
|-------------------------------------------------------------------|-----|
| <b>2.6 General Experimental Procedures</b>                        | 101 |
| 2.6.1 General Procedure for NN Radicals                           | 101 |
| 2.6.2 General Procedure for OVZ Radicals                          | 102 |
| 2.6.3 General Procedure for Aldehyde                              | 103 |
| 2.6.4 General Procedure for Tetrazanes                            | 105 |
| 2.6.5 Preparation of 4,4,5,5-tetramethylimidazolidine Derivatives | 107 |
| 2.6.6 $\text{Fe}^{\text{II}}(\text{ClO}_4)_2$ Complex (C1)        | 108 |
| References                                                        | 109 |

|                                                        |                                                                                                                                                      |              |
|--------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------|--------------|
| <b>Chapter 3</b>                                       | <b>Shape-Defined and Shape-Shifting Paramagnetic Organic Nano-/Micro-Structures Derived from Doublet State Nitronyl Nitroxide Radical Derivative</b> | Page 111-126 |
| <b>3.1 Abstract</b>                                    |                                                                                                                                                      | 112          |
| <b>3.2 Introduction</b>                                |                                                                                                                                                      | 112          |
| <b>3.3 Results and Discussions</b>                     |                                                                                                                                                      | 114          |
| 3.3.1 Synthesis of Paramagnetic Ligand                 |                                                                                                                                                      | 114          |
| 3.3.2 Fabrication of Nanostructure                     |                                                                                                                                                      | 114          |
| 3.3.3 The Single Crystal X-ray Structure of Radical R1 |                                                                                                                                                      | 119          |
| 3.3.4 Optical Properties of Radical R1                 |                                                                                                                                                      | 120          |
| 3.3.5 X-Band ESR Spectroscopy Studies of Radical R1    |                                                                                                                                                      | 121          |

|                                         |     |
|-----------------------------------------|-----|
| 3.3.6 Magnetic Force Microscopy Studies | 123 |
| <b>3.4 Conclusions</b>                  | 125 |
| <b>References</b>                       | 126 |

**Chapter 4**     **Light Propagation in High-Spin Organic**     Page 127-  
**Microtubes Self-Assembled from Triplet State**     161  
**Macrocycles Carrying Oxo-Verdazyl**  
**Biradicals**

|                                                   |     |
|---------------------------------------------------|-----|
| <b>4.1 Abstract</b>                               | 128 |
| <b>4.2 Introduction</b>                           | 128 |
| <b>4.3 Result and Discussions</b>                 | 130 |
| 4.3.1 Syntheses of Paramagnetic Ligands           | 130 |
| 4.3.2 <sup>1</sup> H-NMR Characterization         | 132 |
| 4.3.3 Optical Properties of Ligands               | 134 |
| 4.3.4 X-Band ESR Spectroscopy Studies of Radicals | 135 |
| 4.3.5 Self-Assembly Studies                       | 136 |
| 4.3.6 Formation Mechanism of a Micro Tube         | 137 |
| 4.3.7 Optical Wave Guiding Studies                | 138 |
| 4.3.8 Micro Raman Spectra                         | 140 |
| <b>4.4 Conclusions</b>                            | 141 |

|                  |                                                                                                                        |              |
|------------------|------------------------------------------------------------------------------------------------------------------------|--------------|
|                  | <b>4.5 General Experimental Procedures</b>                                                                             | 142          |
|                  | <b>4.5.1 Experimental Section</b>                                                                                      | 142          |
|                  | <b>References</b>                                                                                                      | 160          |
| <b>Chapter 5</b> | <b>2D Ordering of Paramagnetic Nano-Cone Square Lattice from Nitronyl-Nitroxide Biradicals on a Flexible Substrate</b> | Page 162-170 |
|                  | <b>5.1 Abstract</b>                                                                                                    | 163          |
|                  | <b>5.2 Introduction</b>                                                                                                | 163          |
|                  | <b>5.3 Results and Discussions</b>                                                                                     | 164          |
|                  | <b>5.3.1 ESR Studies</b>                                                                                               | 167          |
|                  | <b>5.4 Conclusions</b>                                                                                                 | 169          |
|                  | <b>References</b>                                                                                                      | 169          |
|                  | <b>Conclusions</b>                                                                                                     | 171          |
|                  | <b>Appendix A (Methods)</b>                                                                                            | 175          |
|                  | <b>Appendix B (Instrumentation)</b>                                                                                    | 175          |
|                  | <b>Publications &amp; Presentations</b>                                                                                | 179          |
|                  | <b>Presentations in Conferences and Symposiums</b>                                                                     | 180          |
|                  | <b>CV</b>                                                                                                              | 181          |

## **DECLARATION**

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the School of Chemistry, University of Hyderabad, Hyderabad under the supervision of Assoc. Prof. Dr. Rajadurai Chandrasekar.

In keeping with the general practice of reporting scientific observations, due acknowledgements have been made wherever the work described is based on the findings of other investigators. Any omission or error that might have crept in is regretted.

Pramiti Hui

## CERTIFICATE

This is to certify that the work described in this thesis entitled “**Nano-/Micro-Scale Organic Paramagnetic Materials: Synthesis, Characterization, Self-Assembly, Optical Wave Guiding and Device Structure**” has been carried out by Ms. Pramiti Hui (Reg. No. 08CHPH38), under my supervision and the same has not been submitted elsewhere for any degree.

Prof. M. Durga Prasad  
Dean  
School of Chemistry  
University of Hyderabad  
Hyderabad 500 046

Assoc. Prof. Dr. R. Chandrasekar  
**(Thesis Supervisor)**  
School of Chemistry  
University of Hyderabad  
Hyderabad 500 046

## ACKNOWLEDGEMENTS

It is my great pleasure to express my sincere gratitude to my research supervisor Assoc. Prof. Dr. Rajadurai Chandrasekar, for his constant guidance, encouragement and continuous support during my research work. I have been motivated most by his dedication to the research, innovative ideas and a very high degree of discipline and sincerity. Any discussion with him has always been very inspiring and rejuvenating. I am thankful to him for the freedom he gave me in carrying out my research and the time he spent in trying to explain various facts and concepts.

I thank present and former Deans and faculty members of the School of Chemistry for their support and help on various occasions. I thank all the faculty members for their co-operation whenever required. I thank all non-teaching staff, School of Chemistry for their cooperation.

I also sincerely acknowledge Dr. Ahamad Mohiddon for his valuable and timely assistance during Raman imaging and optical waveguiding measurements on SNOM instrument (CFN, UoH) and thank Mr. Durgaprasad (Centre for Nanotechnology, UOH) for his help with TEM experiments. I would also like to express my sincere gratitude to central instrumental laboratory (CIL), UoH especially Mr. Ch. Suresh for his help with ESR experiments, Mr. Pavan for his help with SEM experiments.

I thank CSIR, New Delhi, for providing the financial support; Center for Nanotechnology, University of Hyderabad for the TEM, SNOM and CIL for SEM and ESR.

I am deeply indebted to all my teachers right from my School to the University for the excellent training I received throughout my academics.

It is a great pleasure to thank my lab mate and husband Dr. Supratim Basak, for his excellent support, encouragement, companion, keeping ebullient atmosphere and timely help both inside and outside the lab. I am extremely thankful to all my lab mates Chandrasekhar, Narayana, Ajay and my juniors Krrishna, Ramudu, Radhika and Anjana for their support help and cooperation and maintaining a lively environment in the lab. I thank all research scholars of School of Chemistry and friends for the cheerful and

enlivening atmosphere they maintained and for making my stay in the campus unforgettable.

I am at a loss of words to express gratitude to my parents Shri. Pranam Kumar Hui and Smt. Jharna Hui and my grandparents Late Shri. Bishnu Pada Hui and Late Smt. Bhanumati Hui. The way I grew up, the values I imbibed, the education I received and the person I am now is all due to them. I am grateful to my caring and loving sisters Pratiti and Paramita who has always been an ardent listener and a strong support to me. I would like to acknowledge all my relatives for their love and encouragement.

**Pramiti Hui**

## LIST OF ACRONYMS

|                          |                                             |
|--------------------------|---------------------------------------------|
| $\mu\text{m}$            | Micrometer                                  |
| $^1\text{H}$             | Proton                                      |
| Å                        | Armstrong                                   |
| AO                       | Atomic Orbital                              |
| AF                       | Antiferromagnetic Coupler                   |
| AFM                      | Atomic Force Microscope                     |
| $\text{CDCl}_3$          | Deuterated Chloroform                       |
| $\text{CH}_2\text{Cl}_2$ | Dichloromethane                             |
| $\text{CH}_3\text{CN}$   | Acetonitrile                                |
| $\text{CHCl}_3$          | Chloroform                                  |
| cm                       | Centimeter                                  |
| D                        | Deuterium                                   |
| DCM                      | Dichloromethane                             |
| DMSO                     | Dimethyl Sulfoxide                          |
| EBL                      | Electron Beam Lithography                   |
| EDXS                     | Energy Dispersive X-Ray Spectroscopy        |
| EPR                      | Electron Paramagnetic Resonance             |
| ESR                      | Electron Spin Resonance                     |
| EtOH                     | Ethanol                                     |
| FC                       | Ferromagnetic Coupler                       |
| FESEM                    | Field Emission Scanning Electron Microscope |
| h                        | Hour                                        |
| $\text{H}_2\text{O}$     | Water                                       |
| $hfc$                    | Hyperfine Coupling                          |
| HS                       | High Spin                                   |
| Hz                       | Hertz                                       |
| $h\nu$                   | Light                                       |
| IN                       | Iminonitroxide                              |
| IR                       | Infrared                                    |
| $\text{K}_2\text{CO}_3$  | Potassium Carbonate                         |
| LCW                      | Lithographically Controlled Wetting         |
| LPEF                     | Long Pass Edge Filter                       |
| LS                       | Low Spin                                    |
| mmol                     | Milli Mole                                  |
| MeOH                     | Methanol                                    |
| MHz                      | Megahertz                                   |
| MIMIC                    | Micro Moulding in Capillaries               |
| min                      | Minute                                      |
| MFM                      | Magnetic Force Microscopy                   |
| mW                       | Milliwatt                                   |

|                                    |                                                |
|------------------------------------|------------------------------------------------|
| nm                                 | Nanometer                                      |
| NMR                                | Nuclear Magnetic Resonance Spectroscopy        |
| NN                                 | Nitronylnitroxide                              |
| OVZ                                | Oxo-Verdazyl                                   |
| Pd(PPh <sub>3</sub> ) <sub>4</sub> | Tetrakis(Triphenylphosphine)Palladium (0)      |
| RT                                 | Room Temperature                               |
| SAED                               | Selected Area Electron Diffraction             |
| SCO                                | Spin Cross Over                                |
| SEM                                | Scanning Electron Microscope                   |
| T                                  | Temperature                                    |
| TEM                                | Transmission Electron Microscope               |
| THF                                | Tetrahydrofuran                                |
| UV-Vis                             | Ultraviolet-Visible                            |
| <i>zfs</i>                         | Zero-Field-Splitting                           |
| $\Delta$                           | Heat                                           |
| $\delta$                           | NMR Chemical Shift Reported in ppm             |
| $\Delta\lambda$                    | Change in Wavelength of Emission or Absorption |
| $\lambda$                          | Wavelength                                     |
| $\lambda_{\text{max}}$             | Wavelength of Emission or Absorption Maximum   |
| $\pi$ - $\pi$                      | Pi-Pi                                          |

## List of Symbols

|                  |                                                    |
|------------------|----------------------------------------------------|
| <b>A</b>         | Hyperfine Splitting Tensor                         |
| $a_{\text{iso}}$ | Isotropic Hyperfine Splitting (Fermi Contact Term) |
| $a$              | Hyperfine Coupling                                 |
| $a_{\text{H}}$   | Proton Hyperfine Splitting                         |
| $a_{\text{N}}$   | Nitrogen Hyperfine Splitting                       |
| $c$              | Concentration                                      |
| $C$              | Curie Constant                                     |
| $r$              | Distance                                           |
| $D$              | Zero-Field-Splitting Parameter                     |
| $DI$             | Double Integrated EPR Signal Intensity             |
| <b>g</b>         | g Tensor                                           |
| $g_{\text{n}}$   | Nuclear g Factor                                   |
| $g_{\text{e}}$   | Electron g Factor                                  |
| $h$              | Planck's Constant                                  |
| $B$              | Magnetic Field Strength                            |
| $H$              | Spin Hamiltonian                                   |
| $I$              | Nuclear Spin Quantum Number                        |
| $\hat{I}$        | Nuclear Spin Operator                              |
| $J$              | Spin-Spin Exchange Coupling Energy                 |
| $J$              | Total Angular Momentum                             |

|                 |                                          |
|-----------------|------------------------------------------|
| $L/G$           | Lorentzian- Gaussian Ratio               |
| $M$             | Magnetization                            |
| $M_s$           | Electron Spin Quantum Number             |
| $k_B$           | Boltzmann Constant                       |
| $M_I$           | Nuclear Spin Quantum Number              |
| $N_A$           | Avogadro Number                          |
| $S$             | Spin Quantum Number                      |
| $\hat{S}$       | Electron Spin Operator                   |
| $T$             | Temperature                              |
| $\beta_e$       | Bohr Magneton                            |
| $\Delta B_{PP}$ | Difference in Peak to Peak Width         |
| $\Delta E_{ST}$ | Singlet-Triplet Energy Difference        |
| $\epsilon$      | Extinction Coefficient                   |
| $\Theta$        | Weiss Constant                           |
| $\nu$           | Frequency                                |
| $\chi_M$        | Molar Magnetic Susceptibility            |
| $ \psi(0) ^2$   | Unpaired Electron Density at the Nucleus |

## Conversion Factors (EPR)

| <b>dB</b> | <b><math>\mu\text{Watt}</math></b> | <b><math>\sqrt{\mu\text{Watt}}</math></b> | <b>dB</b> | <b><math>\mu\text{Watt}</math></b> | <b><math>\sqrt{\mu\text{Watt}}</math></b> |
|-----------|------------------------------------|-------------------------------------------|-----------|------------------------------------|-------------------------------------------|
| 40        | 20.1                               | 4.4833                                    | 23        | 1010                               | 31.7805                                   |
| 39        | 25.3                               | 5.02991                                   | 22        | 1270                               | 35.63706                                  |
| 38        | 31.9                               | 5.64801                                   | 21        | 1600                               | 40                                        |
| 37        | 40                                 | 6.32456                                   | 20        | 2000                               | 44.72136                                  |
| 36        | 50.4                               | 7.0993                                    | 19        | 2530                               | 50.29911                                  |
| 35        | 63.6                               | 7.97496                                   | 18        | 3180                               | 56.39149                                  |
| 34        | 80                                 | 8.94427                                   | 17        | 4000                               | 63.24555                                  |
| 33        | 101                                | 10.04988                                  | 16        | 5040                               | 70.99296                                  |
| 32        | 127                                | 11.26943                                  | 15        | 6350                               | 79.68689                                  |
| 31        | 160                                | 12.64911                                  | 14        | 8010                               | 89.4986                                   |
| 30        | 201                                | 14.17745                                  | 13        | 10100                              | 100.49876                                 |
| 29        | 250                                | 15.81139                                  | 12        | 1270                               | 35.63706                                  |
| 28        | 320                                | 17.88854                                  | 11        | 16000                              | 126.49111                                 |
| 27        | 400                                | 20                                        | 10        | 20100                              | 141.77447                                 |
| 26        | 510                                | 22.58318                                  | 9         | 25300                              | 159.05974                                 |
| 25        | 640                                | 25.29822                                  | 8         | 31800                              | 178.32555                                 |
| 24        | 800                                | 28.28427                                  | 7         | 40100                              | 200.24984                                 |
|           |                                    | --                                        | 6         | 50400                              | 224.49944                                 |

## Conversion Factors for Energy Units

|                        | <b>cm<sup>-1</sup></b>   | <b>MHz</b>             | <b>aJ</b>                  | <b>eV</b>                 | <b>kJ/mol</b>             | <b>kcal/mol</b>          | <b>K<br/>(Kelvin)</b>    |
|------------------------|--------------------------|------------------------|----------------------------|---------------------------|---------------------------|--------------------------|--------------------------|
| <b>cm<sup>-1</sup></b> | 1                        | $2.997925 \times 10^4$ | $1.986447 \times 10^{-5}$  | $1.239842 \times 10^{-4}$ | $1.196266 \times 10^{-2}$ | $2.85914 \times 10^{-3}$ | 1.438769                 |
| <b>MHz</b>             | $3.33564 \times 10^{-5}$ | 1                      | $6.626076 \times 10^{-10}$ | $4.135669 \times 10^{-9}$ | $3.990313 \times 10^{-7}$ | $9.53708 \times 10^{-8}$ | $4.79922 \times 10^{-5}$ |
| <b>aJ</b>              | 50341.1                  | $1.509189 \times 10^9$ | 1                          | 6.241506                  | 602.2137                  | 143.9325                 | $7.24292 \times 10^4$    |
| <b>eV</b>              | 8065.54                  | $2.417988 \times 10^8$ | 0.1602177                  | 1                         | 96.4853                   | 23.0605                  | $1.16045 \times 10^4$    |
| <b>kJ/mol</b>          | 83.5935                  | $2.506069 \times 10^6$ | $1.660540 \times 10^{-3}$  | $1.036427 \times 10^{-2}$ | 1                         | 0.239006                 | 120.272                  |
| <b>kcal/mol</b>        | 349.755                  | $1.048539 \times 10^7$ | $6.947700 \times 10^{-3}$  | $4.336411 \times 10^{-2}$ | 4.184                     | 1                        | 503.217                  |
| <b>K<br/>(Kelvin)</b>  | 0.695039                 | $2.08367 \times 10^4$  | $1.380658 \times 10^{-5}$  | $8.61738 \times 10^{-5}$  | $8.31451 \times 10^{-3}$  | $1.98722 \times 10^{-3}$ | 1                        |

## 1.1 Introduction to Magnetism:

Magnetism and its effect is the essential part of our life and it plays an imperative role in many technologies.<sup>1</sup> People have been aware of the magnetic phenomena since 2600 B.C and the Chinese had used lodestone compass for navigation in the 12<sup>th</sup> century.<sup>2</sup> Although the preliminary knowledge of magnetism was known from the beginning of the 19<sup>th</sup> century, it has only been truly understood after the emergence of quantum mechanics (exchange interactions) in the early 20<sup>th</sup> century. Since then several magnetic materials (magnetic refrigeration, plastic magnet etc) have been woven into our daily life. Scientists have also discovered several magnet based phenomena such as spintronics, or spin-based electronics, spin glass, single molecular magnet, quantum magnet and so on. Great discoveries related to magnetism have been revolutionizing the present day electronic and magnetic storage based technologies.

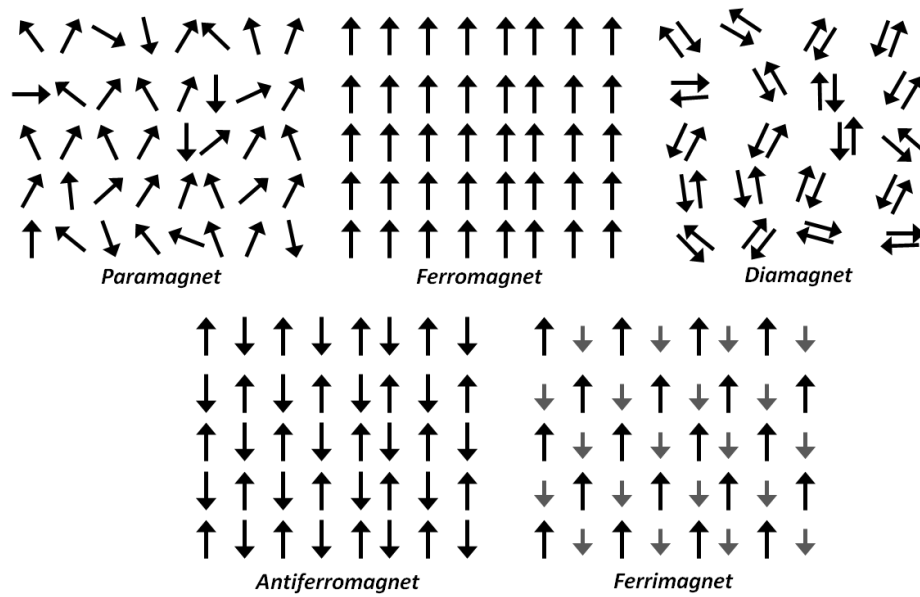


**Figure 1.1** Types of magnets.

There are five main types of magnetism: diamagnetism, paramagnetism, ferromagnetism, ferrimagnetism and antiferromagnetism (Fig. 1.1).<sup>3</sup> Diamagnetism involves a closed-shell system in which electrons are paired, such as the pairing of two electrons to form a bond (no paramagnetic moment). Paramagnetism involves an open-shell system where electron spins are arbitrary and capable of swiftly orienting and reorienting (no net magnetic moment). When exposed to an external magnetic field, all the electrons in a paramagnet will align, and re-orient randomly when the field is

removed.<sup>4</sup> The other three types of magnetic materials are special types of paramagnets. All have an ordering temperature and involve an open-shell system. The temperature below which spontaneous spin alignment occurs is called the ordering temperature. These materials behave as paramagnets above their ordering temperatures. Ferromagnetism is the parallel alignment of the electrons in three dimensions, resulting in a permanent magnetic moment. The ordering temperature for a ferromagnetic material is called the Curie temperature ( $T_C$ ). When the electron spins align themselves in an antiparallel fashion antiferromagnetism occurs, resulting in no permanent magnetic moment. Ferrimagnetism is similar to antiferromagnetism as the electron spins are paired antiparallel, but a net magnetic moment is observed as the spin values of the spin carriers are different. The ordering temperature for antiferromagnetic and ferrimagnetic materials is called the Neél temperature ( $T_N$ ).

One of the parameters which evaluate magnetic communication between paramagnetic species is magnetic exchange (or) spin-spin coupling ( $J$ ). Most of the paramagnetic molecules are typically sufficiently large and far apart that their spin-spin exchange coupling energy  $J$  is smaller compared to the coupling breaking thermal energy ( $J \ll k_B T$ ). Quantitatively the term  $J$  represents the nature (sign) and strength (magnitude) of the magnetic coupling between paramagnetic building blocks. Their spins do not couple, but instead form a very weak *paramagnet*. When the spins are closer,  $J$  can be sufficiently large to enable an efficient parallel or antiparallel alignment, this increase or decrease the magnetic susceptibility ( $\chi$ ).

Magnetic materials act differently in presence of a magnetic field. A sample must acquire the ability to create a magnetic dipole when located in an external magnetic field or electric field. Spin magnetism is due to electron spins, which give rise to angular momentum and thus the magnetic moment. All the materials contain electrons and the response of these electrons in a magnetic field depends upon their orientation in the material. A sample has a molar magnetic moment ( $M$ ) which varies with the applied field ( $B$ ) according to the magnetic susceptibility, ( $\chi$ ) of the material. This relationship is given by the following equation.<sup>5</sup>

$$\chi = M/B \quad \dots\dots 1$$

The observed magnetic susceptibility ( $\chi_{\text{obs}}$ ) is made up of many components, but the two main ones are diamagnetic susceptibility ( $\chi_{\text{dia}}$ ) and paramagnetic susceptibility ( $\chi_{\text{para}}$ ).<sup>6</sup>

$$\chi_{\text{obs}} = \chi_{\text{dia}} + \chi_{\text{para}} \quad \text{.....2}$$

Molar magnetic susceptibility,  $\chi_M$ , is a often has temperature dependence (T) which is given by the following equation.

$$\chi_M = N_A g^2 \beta_e^2 / 3k_B T [S(S+1)] \quad \text{.....3}$$

The molar susceptibility of a paramagnetic substance is proportional to temperature (T), i.e.,<sup>6</sup>

$$\chi_M = C/T \quad \text{.....4}$$

Where C is the Curie constant, which is given by,

$$C = N_A \beta_e^2 g^2 S(S+1) / 3k_B \text{ [or] } C = 0.125 g^2 S(S+1) \text{ cm}^3 \text{ K /mol}^{-1} \quad \text{.....5}$$

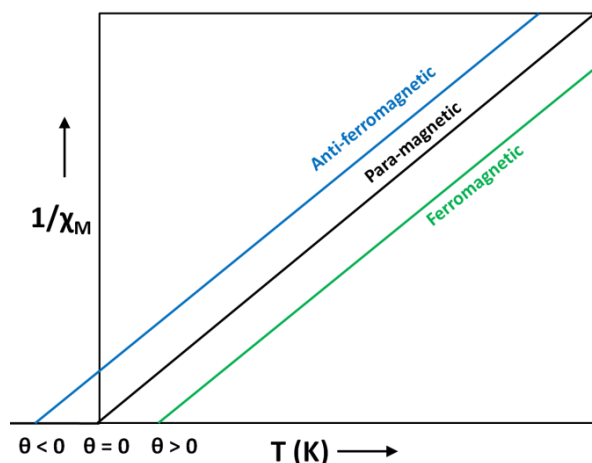


**Figure 1.2** A plot of inverse  $\chi_M$  as a function of temperature. For  $\theta = 0$  ideal paramagnetic behavior exists,  $\theta > 0$  ferromagnetic interactions exists and  $\theta < 0$  antiferromagnetic interactions exists.

Where  $N_A$  is Avogadro's number,  $\beta_e$  is a constant unit called the Bohr magneton (BM) ( $9.27400968(20) \times 10^{-24} \text{ JT}^{-1}$ ),  $k_B$  is Boltzmann constant ( $1.3806488(13) \times 10^{-23} \text{ JK}^{-1}$ ). The Curie constant is useful to identify the spin concentration of the sample ( $C = 0.375 \text{ emu K/mol}$  for  $S = 1/2$ ).

Magnetic materials, possessing interacting individual magnetic moments or spins, follow the

Curie-Weiss law,

$$\chi = \frac{C}{(T-\theta)} = \frac{N g^2 \beta_e^2 S(S+1)}{3k_B (T - \frac{zJ'S(S+1)}{3k_B})} \quad \text{.....6}$$

$$\theta = z J S(S+1) / 3k_B \quad \text{.....7}$$

Where  $\theta$  is the Weiss constant in temperature units, a characteristic property of the material. It takes into account of the total dipole-dipole exchange interactions  $J$ , the number of nearest neighbors ( $z$ ) and the spin quantum number ( $S$ ). When  $\theta$  is zero, the

material is a true paramagnet and follows the Curie law. The value of  $\theta$  signifies the interaction between the intra molecular spins. If  $\theta$  is negative, it indicates an antiferromagnetic interaction and a positive value points out a ferromagnetic interaction (Fig. 1.2).

In substances with interacting magnetic moments and where the orbital contribution to the magnetic moment is significant, the molar susceptibility is given by

$$\chi_M = N_A \beta_e^2 g^2 J(J+1) / 3k_B (T-\theta) \quad \text{.....8}$$

Here the resultant total angular momentum (J) is given by,

$$J(J+1) = L(L+1) + S(S+1) \quad \text{.....9}$$

The quantum number L is the resultant orbital angular momentum of all unpaired electrons present in the atom (i.e. L is zero for a completely filled orbital). In the compounds made of first row transition metal series, the orbital contribution to the magnetic moment is small, such that  $J = S$ . The effective magnetic moment  $\mu_{\text{eff}}$  is  $g\sqrt{s(s+1)}$  or  $\mu_{\text{eff}}^2 = g^2 S(S+1)$ . After taking into account of all the constants, the generalization of eqn. 8 is as follows,

$$\chi_M = [N_A \beta_e^2 / 3k_B] \mu_{\text{eff}}^2 / (T-\theta) \approx 0.125 \mu_{\text{eff}}^2 / (T-\theta) \quad \text{.....10}$$

This allows us to calculate the  $\mu_{\text{eff}}$  of an ion or radical, which can be rewritten as,

$$\mu_{\text{eff}} = \sqrt{8\chi_M(T-\theta)} \quad \text{.....11}$$

When a ferromagnetic material is placed within a coil of wire carrying an electric current (solenoid), the magnetic field strength  $B$  is caused by the current. The magnetic field  $B$  forces some or all of the atomic magnets in the material to align with the field. The induced magnetization ( $M$ ) depends upon the applied field ( $B$ ). When the current ( $i$ ) increases slowly,  $B$  and  $M$  also increase linearly with  $i$ . Initially at point **a**, the domains are randomly oriented (Fig. 1.3). As  $B$  increases the domains align more and more until at point **b**, they are nearly all aligned. At this point the material is said to be "saturated" with almost 98% full saturation. The external field is decreased by reducing the current in the solenoid. As the current is reduced to zero, shown in the point **c**, the domain does not become random. Some permanent magnetism remains and this value is called the *remanence*, *residual induction*, or *retentivity*, which is very high for permanent magnets. If the current is then reversed in direction, the domains are turned around. The value of  $B$

for which  $M$  is zero is called the *coercive force* (point **d**). As the reverse current increases further, the domains get saturated in the opposite direction (point **e**). Finally if again the

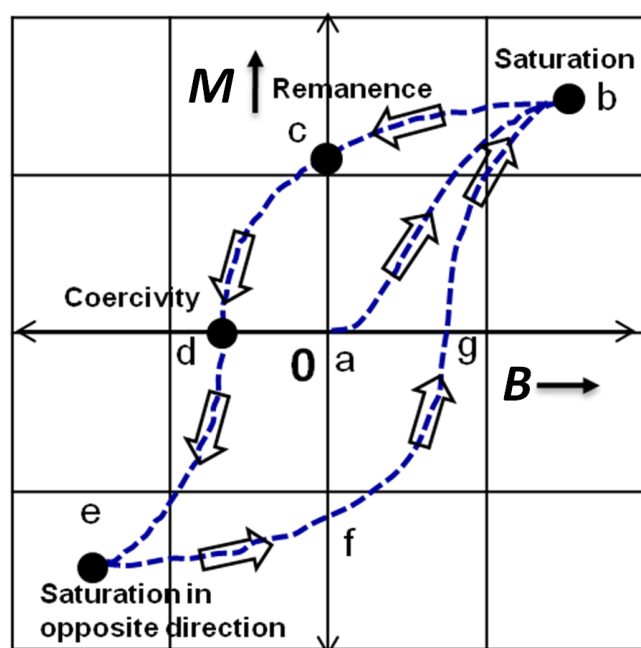


**Figure 1.3** Hysteresis curve of a ferromagnetically ordered material with a memory.

current is reduced to zero and then increased in the original direction, the total field follows the path **e**→**f**→**g**→**b** to again reach the saturation point **b**. Here the field did not pass through the origin (point **a**) in this cycle, i.e., the curves do not retrace themselves in the same path giving *hysteresis*. If the cycle is continued, the graph of the  $M$  versus  $B$  appears as a complete loop, known as a *hysteresis loop*. The energy lost as heat (*hysteresis loss*), in reversing the magnetization of the material is

proportional to the area of the hysteresis loop. Therefore, normally the cores of transformers are made of materials with narrow hysteresis loops to reduce the energy loss in the form of heat. Once the magnetic domains are reoriented, it takes some energy to turn them back again. This property of ferromagnetic materials is useful as a magnetic "memory". Some ferromagnetic materials retain the imposed magnetization indefinitely (for several hundred years) and are called as "permanent magnets".

Conventional magnetic materials are metals or alloys and oxides of cobalt, nickel and iron. The manufactures of these materials take high temperature metallurgic routes for their production. These materials do not offer significant opportunity to tune shape, size and density, properties essential to decrease the size of modern devices. Organic molecule-based magnets are attractive alternatives to general hard magnets. Organic stable radicals play an important role to the development of molecule based magnet materials. For example, material based on organic radical building blocks can be easily tuned or perturbed chemically, electronically, photochemically and magnetically have potential use in devices. In the miniaturization of electronic devices the demand for new

materials, exhibiting improved properties, increases compared to existing benchmarks. Organic radical crystals rely on close intermolecular contacts between radicals in the solid-state. There are many examples of radical crystals that are ferromagnetic at cryogenic temperatures which will be discussed in the next sections. This thesis work mainly deals with paramagnetic organic stable radicals. One of the most important tools to characterize the paramagnetic compound or radical is electron spin resonance (ESR) or electron paramagnetic resonance (EPR) spectroscopy. Therefore a brief introduction will also be given about this important technique in the following section.

## 1.2 Electron Spin Resonance (ESR) spectroscopy:

The principle of ESR spectroscopy is very similar in concept to the more familiar nuclear magnetic resonance (NMR) technique. Both deal with the interaction between electromagnetic radiation and magnetic moments. In the case of ESR, the magnetic moments arise from electrons rather than nuclei. In ESR a crucial point to be considered is that a magnetic moment  $\mu_e$  is always related with the electron spin angular momentum, where  $\mu_e$  is proportional to spin quantum number  $S$ , meaning that  $\mu_e$  and  $S$  are vectors parallel to each other. They have opposite orders because the proportionality constant is negative. This is written as the product of two factors  $g$  and  $\beta_e$ .<sup>7</sup>

$$\mu_e = g \beta_e S \quad \text{.....12}$$

Where  $g$  is a number called the Landé factor or simply the  $g$  factor. For a free electron the value of  $g$  is 2.0023193043617(15).  $g$  is the magnitude of the electron Zeeman factor for the species considered and  $\beta_e = -|e|h/4\pi m_e = -9.27400949(80) \times 10^{-24} \text{ JT}^{-1}$ , where  $m_e$  is the electron mass  $9.10938291 \times 10^{-31} \text{ kg}$ ;  $e$  is the electron charge;  $h = 6.626 \times 10^{-34} \text{ Js}$  is the Planck constant; and  $\beta_e$  is the atomic unit of the magnetic moment, which is called the Bohr magneton. When  $\beta_e < 0$ , to avoid confusion about the sign, generally the absolute value of  $\beta_e$  is used in several equations. Consider a simple  $S = 1/2$  radical (one unpaired electron; doublet state). The linkage of magnetic moment with the electron spin is the reason for having an energy separation between  $\alpha$  and  $\beta$  electron spin states when the electron is exposed to magnetic field. The multiplicity rule tells how many spin states are present,  $2S + 1 = 2(1/2) + 1 = 2$ , where  $S$  is total spin. There are two spin states for a one electron system,  $\alpha$  and  $\beta$ , with the spin quantum numbers  $M_s = +1/2$  and  $M_s = -1/2$  respectively.<sup>8</sup> Because the energy of a magnetic moment  $\mu_e$  is given by the scalar product

between  $\mu_e$  and  $B$ , the electron spin energy will depend on the orientation of  $\mu_e$  with respect to  $B$ :

$$E = -\mu_e \cdot B = g \beta_e |S \cdot B| \quad \text{.....13}$$

$$E = \pm \frac{1}{2} g \beta_e B \quad \text{.....14}$$

$$\Delta E = g \beta_e B \quad \text{.....15}$$

### 1.2.1 Nuclear Hyperfine Interactions:

The interaction of an electron spin with surrounding nuclear spins is called hyperfine interaction or hyperfine coupling (*hfc*). It is extremely useful in EPR spectroscopy, as information on the direct magnetic environment of the electron spin can be gained. Nuclei with an odd number of protons and nuclei with an odd number of neutrons possess the property of nuclear spin angular momentum  $I$ . Examples are hydrogen  $^1\text{H}$  with  $I = \frac{1}{2}$  and nitrogen  $^{14}\text{N}$  with  $I = 1$ . The interaction of an unpaired electron with magnetic nuclei gives rise to nuclear hyperfine interactions. These hyperfine

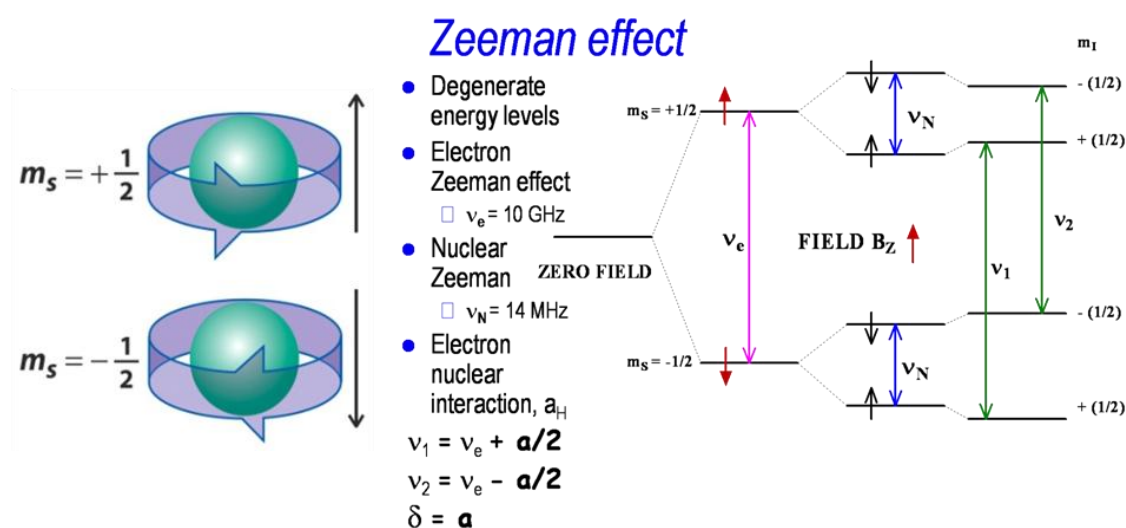


Figure 1.4 The Zeeman effect or splitting.

interactions originate from two processes, the isotropic or *Fermi contact interaction* and anisotropic or *dipolar interaction*. The latter corresponds to the classical dipole-dipole interaction between the magnetic dipoles of the electron and the nucleus. The contribution to the Hamiltonian is given by<sup>9</sup>

$$H_{HF} = \sum_{i=1}^N S A_i I_i = H_F + H_{DD} \quad \text{.....16}$$

Where,  $A$  is the hyperfine interaction tensor. The sum runs over all pair wise interactions of the electron with respective nuclear spins. The hyperfine interaction Hamiltonian

consists of two parts: the isotropic Fermi contact and the electron-nuclear dipole-dipole coupling, called  $H_F$  and  $H_{DD}$ , respectively.

The Fermi contact interaction is isotropic and is readily observed in solution state ESR studies. Spin-Hamiltonian ( $H$ ) depends on the contributions from the electron-Zeeman ( $H_{EZ}$ ) and the hyperfine interaction ( $H_{HF}$ ). Higher order terms for instance nuclear Zeeman and Quadrupole are generally not measured. The splitting of the electron spin energy level into two levels in the presence of a magnetic field is called the Zeeman Effect, and the interaction of an electron magnetic moment with an external applied magnetic field is called the electron Zeeman interaction. The Zeeman Effect is represented graphically in [figure 1.4](#). The spin Hamiltonian which only considers the spin-dependent contributions and the complete electronic terms, for the unpaired electron of an organic radical in a magnetic field experiencing isotropic hyperfine interaction is given by

$$H = H_{EZ} + H_{HF} + \text{higher order terms} \quad \text{.....17}$$

$$H = H_{ZE} + H_{HF} = g_e \beta_e B_0 S_Z + \sum_{i=1}^N S A_i I_i \quad \text{.....18}$$

In liquid solution the Fermi contact interaction ( $H_F$ ) is the only contribution to the hyperfine interaction:

$$H_F = \sum_{i=1}^N a_{iso,i} S_i I_i \quad \text{.....19}$$

Where  $a_{iso}$ , is the isotropic hyperfine coupling constant for the respective nucleus i:

$$a_{iso} = \frac{2\mu_0}{3\hbar} g_e \beta_e g_N \beta_N |\Psi_0(0)|^2 \quad \text{.....20}$$

Here,  $\mu_0$  is the vacuum permeability,  $g_N$  and  $\beta_N$  are the nuclear g-factor and the nuclear magneton, respectively, and  $|\Psi_0(0)|^2$  is the electron spin density at the nucleus. The isotropic hyperfine coupling originates from non-vanishing electron spin density at the s-orbitals (indeed, also from higher orbitals but only in an indirect manner) of the atom. Hence, this mechanism works through direct contact between the unpaired electron and the nucleus, hence called, “*contact interaction*”.

In contrast, the dipole-dipole interaction ( $H_{DD}$ ) is given by,

$$H_{DD} = \sum_{i=1}^N S_i T_i I_i \quad \text{.....21}$$

Here the dipolar coupling tensor  $T$  acts through space. For isotropic rotation in liquid solution this term averages to zero.

For example, X-band EPR spectrum of dilute and oxygen free solutions of the nitronyl nitroxide monoradical ( $\leq 10^{-3}$  M) exhibits a five-line pattern ( $\Delta M_s = \pm 1$  transitions) with an intensity ratio of 1:2:3:2:1 due to the hyperfine coupling (*hfc*) of the NN electron spin with two equivalent nitrogen ( $^{14}\text{N}$ ) nuclei at RT. Simulation of the experimental spectrum showed that the nitrogen *hfc* values of mono nitroxide radicals are in the range of  $a_{\text{N}} = 7.40 - 7.41$  G. The *g*-value of radicals are normally close to 2.0066 - 2.0065. The liquid solution state ESR spectrum of OVZ monoradical displayed a strong nine-line pattern ( $\Delta M_s = \pm 1$  transitions) with an intensity ratio close to 1:4:10:16:19:16:10:4:1. Simulation of the experimental spectrum showed the following *hfc* values:  $a_{\text{N1}} = 6.41$  G,  $a_{\text{N2}} = 5.35$  G and  $a_{\text{H}} = 1$ . The isotropic *g*-values of radicals are in the range of 2.0063 - 2.0071, respectively (Fig. 1.5).

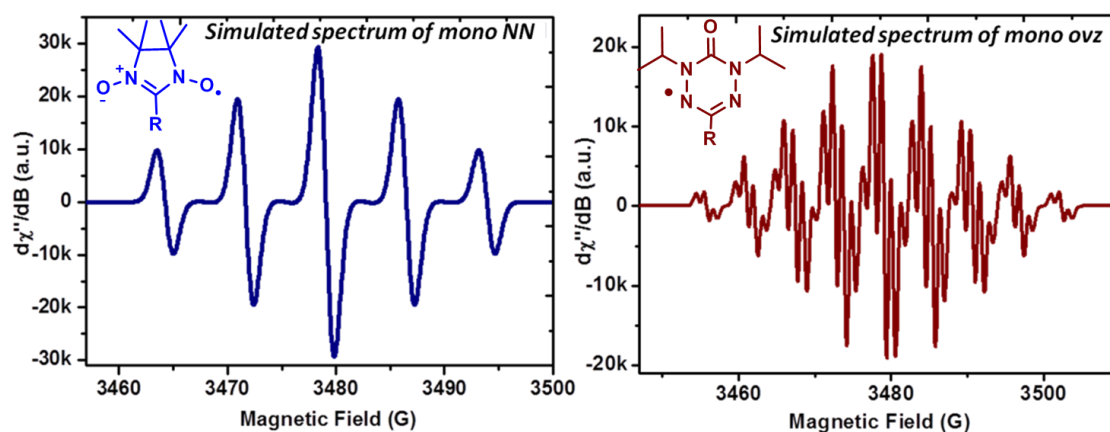


**Figure 1.5** Simulated isotropic X-band EPR spectra ( $\Delta M_s = \pm 1$ ) of mono-NN and -OVZ radicals at RT.

### 1.2.2 The EPR of Biradical Systems:

One of the important branches of stable free radical research is molecules carrying two or more unpaired electrons. A molecule containing diradical or polyradical gives rise to many interesting interactions, compared to simple monoradicals. The extent of spin-spin interaction of unpaired electrons is very interesting parameter to study. The two unpaired electrons of a biradical can be aligned antiparallel ( $\uparrow\downarrow$ ) or parallel ( $\uparrow\uparrow$ ) giving rise to singlet [ $S = 0$ ;  $2(0)+1=1$ ] and triplet [ $S = 1$ ;  $2(1)+1 = 3$ ] spin states, respectively. The triplet state has three spin states,  $M_s = +1, 0, -1$ , but only two allowed transitions as shown in figure 1.6. The magnetic field of the other electron in the system, which is a dipole-dipole interaction, is described by zero-field splitting (*zfs*) or “fine structure”.<sup>10</sup> *zfs* is the removal spin microstate degeneracy of systems with  $S > \frac{1}{2}$  in the absence of an applied magnetic field. EPR spectra of the biradicals in solution have a characteristic

pattern that is dissimilar from those observed in the simple  $S = \frac{1}{2}$  systems, and therefore the understanding the theoretical background of it is necessary. The excited states of a magnetic system are usually described in terms of a spin-Hamiltonian as earlier shown in

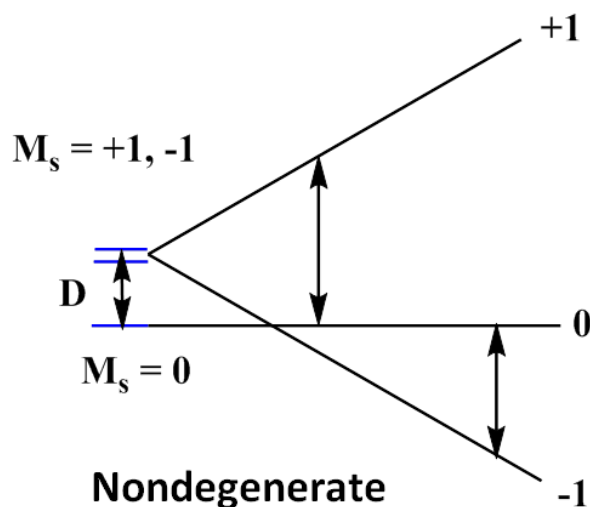


Figure 1.6 Zero field splitting (zfs) of a biradical.

the case of  $S = \frac{1}{2}$  systems. The phenomenological spin-Hamiltonian, for two interacting spins, is modified into the equation:

$$H = g\beta B_0 S_{a,b} - 2JS_a S_b + \sum_{ij} a_{Nij} \times (S_a I_{Nij} + S_b I_{Nij}) + S_a \cdot \mathbf{D} \cdot S_b \quad \dots\dots 22$$

The term  $2JS_a S_b = H_{\text{exch}}$  represents the electron-exchange interaction, also named Heisenberg-Dirac-van Vleck Hamiltonian, HDVV,  $S_a$  and  $S_b$  the electron-spin operators and  $J$  the isotropic electron-exchange coupling constant. Since  $\mathbf{D}$  is traceless, the fine structure is typically described only by two energetic parameters  $D$  and  $E$ , which for a triplet are  $D = 3D_z/2$  and  $E = (D_x - D_y)/2$ . So

$$H = g\beta B_0 S_{a,b} + D(S_z^2 - S(S+1)/3) + E(S_x^2 - S_y^2) \quad \dots\dots 23$$

Frozen state ESR studies of bridged bi- and oligoradicals are important to characterize the high spin patterns from the fine structure transitions ( $\Delta M_S = \pm 1$ ). Additionally,  $\Delta M_S = \pm 2$  and sometimes  $\Delta M_S = \pm 3$  forbidden transitions also can be observed with a relative intensities which follow the ratio  $1:(D/B_0)^2:(D/B_0)^4$ , respectively. A typical spectral simulation for a quartet state ( $S = 3/2$ ) at X-band is shown in [figure 1.7](#).<sup>10a</sup> The splitting between the two ESR transitions depends on  $D$  and on the orientation of the molecule with respect to the magnetic field. The splitting will be large ( $2D$ ) when  $B$  is parallel to  $z$  and small ( $D$ ) when  $B$  is parallel to  $x$ . For a randomly oriented ensemble of molecules the

ESR spectrum will represent a sum spectrum over all possible orientations of the molecules with respect to the magnetic field. In addition to the two allowed  $\Delta M_S = \pm 1$

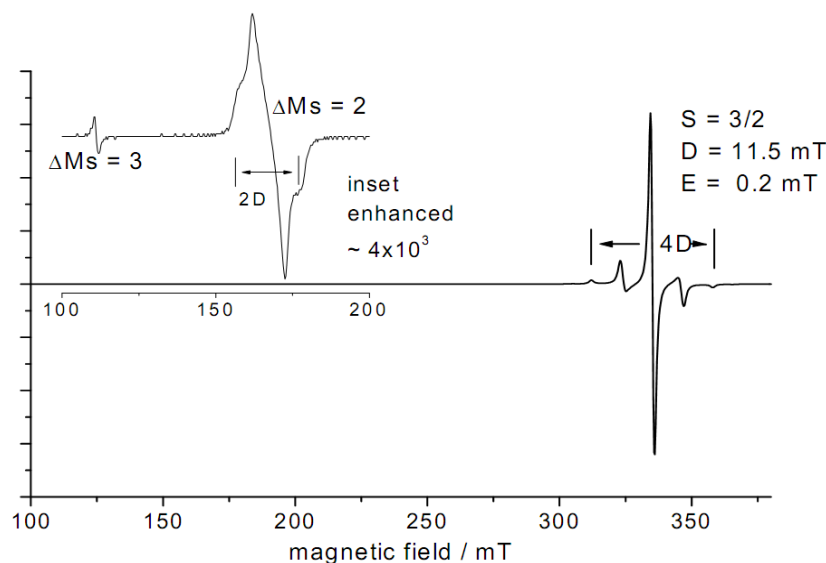


**Figure 1.7** Simulated X- band EPR spectrum for  $S = 3/2$  system with  $D' = 0.01075 \text{ cm}^{-1}$ ,  $E' = 0.00019 \text{ cm}^{-1}$ , and  $g = 2.003$  at 9.4 GHz. ( $B_{\text{res}} = 335 \text{ mT}$ ). Ref 10a.

transitions, the ESR spectrum of a triplet state molecule often exhibits a ‘*forbidden*’  $\Delta M_S = \pm 2$  transition which occurs at approximately half of the normal magnetic field. For a triplet state molecule with axial symmetry  $\Delta M_S = \pm 2$  transitions are expected at  $B_z = \hbar\nu/(2g\beta_e)$  and  $B_x = [(\hbar\nu)^2 - D^2]^{1/2}/(2g\beta_e)$ . Under cubic field (or isotropic samples)  $\Delta M_S = \pm 2$  cannot be observed by a microwave field of any polarization and is strictly forbidden.

The relationship between the intramolecular radical distance and the  $zfs$  parameter or fine structure ( $D$ ) with a point-dipole the approximation is by Mukai and co-workers

$$D = 3/4g^2\beta_e^2 \sum [r_{ij}^2 - 3m_{ij}^2] \rho_i \rho_j / r_{ij}^5 \quad \text{.....24}$$

Where  $r_{ij}$  is the distance between the atoms  $i$  and  $j$ ,  $m_{ij}$  is the distance vector along the axis, which give rise to the largest dipole-dipole interaction, and  $\rho_i$  and  $\rho_j$  are the spin-densities on atom  $i$  and  $j$ . According to the point-dipole approximation, the  $D$  value in axial systems is related with the averaged radical distances as:

$$D \text{ (MHz)} = 77924 (g_{\text{obs}} / g_e) / r^3 \quad \text{.....25}$$

Here the value of  $r$  (in Å) is considered as an averaged through-space separation. Therefore, increase of the intramolecular radical distances causes rapid decrease of the  $zfs$  component.

### 1.2.3 Exchange Coupling:

If the two electron spins  $S_a = \frac{1}{2}$  and  $S_b = \frac{1}{2}$  are considered as individual paramagnetic centers, there is still possibility for significant overlap of the two SOMOs for the two electrons to exchange. This *exchange interaction* leads to a splitting between the singlet state ( $S = 0$ ) and the triplet state ( $S = 1$ ) of the coupled system. If this splitting is so small that transitions between the singlet and triplet state can be excited in an EPR experiment, it is more convenient to treat the system in terms of two individual spins that are coupled to each other. In general at intra radical distances larger than 5-10 Å the individual spin treatment is applied.

The energy difference between the singlet and triplet state is given by the following exchange integral

$$\Delta E = {}^1E - {}^3E \equiv J = e^2 \int dr_1 \int dr_2 \frac{\Psi_1^*(r_1)\Psi_2^*(r_2)\Psi_1(r_2)\Psi_2(r_1)}{|r_1 - r_2|} \quad \dots\dots 26$$

Where  $\Psi_1$  and  $\Psi_2$  are the wave functions of the two unpaired electrons. For negative  $J$ , the singlet state is lower in energy, the orbital overlap is bonding and the interaction is *antiferromagnetic*. Positive  $J$  corresponds to a lower-lying triplet state, i.e., antibonding orbital overlap and results in *ferromagnetic* interaction.

The second contribution to  $J$  arises because of through-space interactions, which varies with the radical separation,  $\langle r \rangle$ . This is a magnetic interaction based on the magnetic dipole moment generated by the unpaired spins (dipolar spin-spin interaction).

$$J = J_0 \exp [-\alpha (\langle r \rangle - d)] \quad \dots\dots 27$$

Where  $d$  stands for the minimum distance-approach and  $J_0$  and  $\alpha$  are empirical values. Approximately the exchange interaction decays exponentially with distance  $r$  between the paramagnetic centers. The decay rate depends on the conductivity of the medium between the centers and on the presence or absence of a conjugated network of bonds between them. If conjugation is weak with the isolating matrix, exchange coupling is much smaller than the dipole-dipole coupling through space at distances longer than 15 Å.

Exchange interactions between two unpaired electrons depend on the relative energies of the two singly occupied molecular orbitals (SOMOs). If two unpaired electrons stay in degenerate or nearly degenerate orbitals there are two possible spin state configurations, parallel and antiparallel. In a low spin diradical, the coupling between unpaired electrons is antiferromagnetic and the total spin is  $S = 0$ . This is said to have a

singlet ground state. In a high spin diradical, the coupling between unpaired electrons is ferromagnetic and the total spin is  $S = 1$ . This is said to have a triplet ground state. If the ground state of a diradical is singlet then the excited state will be a triplet and vice-versa. The strength of the interaction between the two unpaired electrons is represented by  $J$  (exchange interaction). The magnitude of this interaction is proportional to the energy difference between the ground and excited states. If the interaction is ferromagnetic, then  $J$  is positive and if it is antiferromagnetic, then  $J$  is negative.

#### 1.2.4 Dipole-Dipole Coupling:

The dipole-dipole coupling between two electron spins is comparable to coupling between two nuclear spins. The dipole-dipole coupling term of the spin Hamiltonian is given by

$$H_{DD} = S \cdot \mathbf{D} \cdot S_b = \frac{1}{r^3} \cdot \frac{\mu_0}{4\pi\hbar} \cdot g_1 g_2 \beta_e^2 [S_1 S_2 - \frac{3}{r^2} (S_1 r)(S_2 r)] \quad \dots\dots 28$$

As described for the dipolar contribution to the hyperfine interaction, the dipolar coupling between electron spins in the fast motion limit is averaged to zero and exchange interaction through direct exchange is the dominant electron-electron interaction mechanism (Fig. 1.8). In high viscosity liquid solution, nonetheless, the dipolar interaction between electrons is not negligible any longer. In recent years, the measurement of dipolar couplings between electrons has become a dominant tool to extract information on distance distributions of nitroxide spin probes in frozen solution or in solids in biological studies.

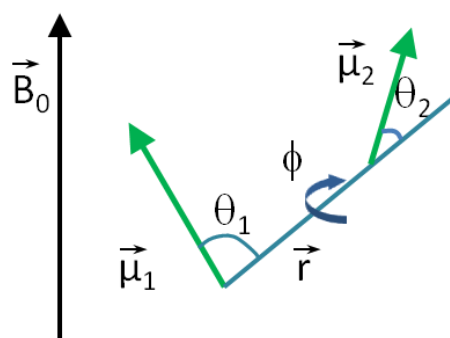


**Figure 1.8** Representation of Coupling between two magnetic moments  $\mu_1$  and  $\mu_2$  in a general orientation with respect to the external magnetic field  $B_0$  and definition of the angles  $\theta_1$ ,  $\theta_2$ , and  $\phi$  that parameterize this interaction. Note that these angles totally depend on the orientation of the molecule in the magnetic field. Ref 7.

### 1.2.5 Determination of Electronic Ground State of Biradicals:

The transition energies concerned in ESR spectroscopy are small ( $\Delta E = g\beta_e B = 6.252 \times 10^{-24}$  J at X-band) in relative to the thermal energy  $k_B T$ . As a result, all spin sublevels are populated at temperatures above 0 K resulting in a Boltzmann distribution of spins between the upper and lower spin sublevels. Since the ESR spectrometer probes the (small) variation between the populations in the upper and lower spin sublevels, the ESR signal intensity is temperature dependent. The Boltzmann distribution  $\frac{N_i}{N_0} = e^{-\frac{\Delta E}{k_B T}}$  describes the population ratio of two spin sublevels separated by  $\Delta M_S = \pm 1$ . Because  $g\beta_e B \ll k_B T$  at ordinary temperatures it follows that  $\exp(-\Delta E/k_B T) \approx 1 - \Delta E/k_B T$ . Consequently, the populations of the two spin levels (separated by  $\Delta M_S = \pm 1$ ) are almost equal and a simple calculation shows that  $\frac{1}{2}N(1 + \Delta E/2k_B T)$  are in the low spin state and  $\frac{1}{2}N(1 - \Delta E/2k_B T)$  are in the high spin state. The EPR signal intensity (I) of a  $\Delta M_S = \pm 1$  transition is proportional to the variation in population,  $N_A g\beta_e B/2k_B T$ , and accordingly linear with the reciprocal temperature. This is equivalent to the Curie law for magnetization:

$$I = C/T \quad \text{.....29}$$

Where C is the Curie constant. With the purpose of analyzing the tendency in the magnetic properties of the isolated molecules, the temperature dependence of the  $\Delta M_S = \pm 2$  transitions has to be recorded down to cryogenic temperature. When the product of doubly integrated ESR signal intensity times temperature (DI·T) increases upon decreasing temperature, it indicates that the ground states is absolutely the triplet ( $S = 1$ ), and the singlet ( $S = 0$ ) have to be connected with thermally accessible excited states. For two interacting spins  $S = \frac{1}{2}$  system, fitting the DI·T data with the Bleaney-Bowers model where DI is represented as

$$DI = \chi_{EPR} \propto \{(2Ng^2\beta_e^2/3k_B T) \times [1/3 + \exp(-2J/k_B T)]\} \quad \text{.....30}$$

In principle, the ground state of a high-spin molecule can be determined from variable temperature ESR measurements. A linear increase of the intensity of the ESR signal with the inverse temperature, according to Curie's law normally indicates that there is no thermal population or depopulation of the spin state of the molecule in that temperature range. The interpretation of Curie-law behavior of the ESR signal intensity may have dual solution. Either the high-spin state (triplets  $S = 1$ ) is the lowest energy state separated by a

considerable difference compared to the thermal energy  $k_B T$  from the low-spin state (singlets  $S = 0$ ), or the energy difference with the lower spin state is extremely small. In the latter case the low-spin and high-spin states are degenerate and a change in temperature does not change the thermal equilibrium between these states.

ESR is the tool to characterize the magnetic properties of paramagnetic compound in bulk or in solution state. To image the magnetic domain of paramagnetic or ferromagnetic nano structures in the solid state, magnetic force microscopy (MFM) technique is used.

### 1.3 Magnetic Force Microscopy (MFM):

The most outstanding quality of scanning force microscopy (SFM) is its ability to detect various types of short and long range atomic, molecular interactions. Magnetic force microscopy (MFM) uses a magnetic tip coated with ferromagnetic film (e.g., CoCr or NiFe). MFM brings the advantages of AFM into the magnetic materials. MFM is non-destructive technique and requires minimal sample preparation. This microscopy generally used to characterize the domain configuration in ferromagnetic materials such as thin films grown by physical techniques or ferromagnetic nanostructures.<sup>11</sup> It is an important method to separate the topography and the magnetic signal by scanning with a magnetic at a lift distance ( $z$ ) of 25–50 nm from the sample such that the long range tip–sample interactions dominant (Fig. 1.9). Most recently, MFM used to detect weak magnetic fields from low dimensional complex systems for instance organic nanomagnets, superparamagnetic nanoparticles, carbon-based materials, etc.

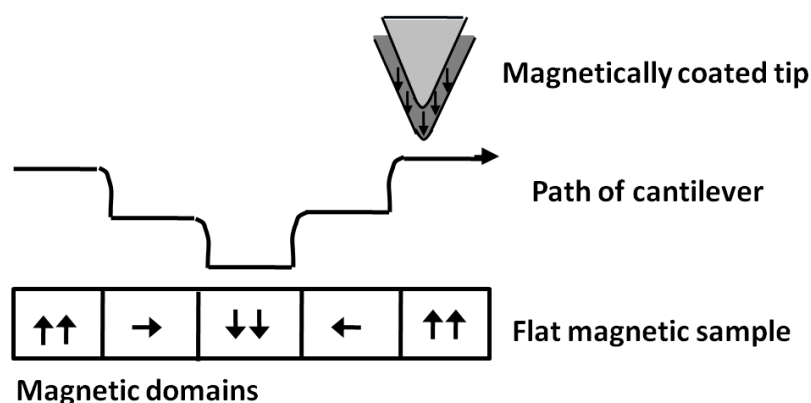


**Figure 1.9** MFM image scanning of a paramagnetic sample.

MFM imaging mode is derived from tapping mode AFM. MFM images are measured by local magnetic interaction between a conductive tip and the sample and the

spatial variation of magnetic field within the sample surface. This technique senses the changes in the resonant frequency of the cantilever modified by the magnetic interaction with the sample surface. The use of tip with a magnetic covering or a tip consisting exclusively of a magnetic material in MFM allows to resolve the magnetization distribution in different ferromagnetic micro and nanostructures and also to study features of magnetization and magnetic exchange in these objects. Though, the interaction between a magnetic tip and a magnetic field created by surface structures is rather complex. Consequently it is often tricky to understand experimental MFM images. The cantilever's resonance frequency and phase change are considered to generate the MFM image with the strength of the magnetic field gradient. MFM can be used to image both physically occurring and purposely written domain structures in magnetic materials.

MFM can be done by dual scanning in lifted mode, by independently measuring topography and magnetic forces. Because the magnetic forces interact at greater distances than Van der Waals forces, this information can be separated from surface topography simply by increasing the tip-to-sample distance. The lift mode allows the imaging of moderately weak but long-range magnetic interactions while minimizing the influence of topography. Usually measurements are taken in two passes across each scan line; each pass consists of one trace and one retrace. In the first pass, topographical data is collected in the tapping mode. The tip is then raised to the lift scan height and subsequently a second trace and retrace cycle is performed while maintaining a constant separation between the tip and the local surface topography. Magnetic interactions are identified during this second pass. Since the surface profile data is not included in the frequency signal, the topography is virtually absent from the MFM image (Fig. 1.10).

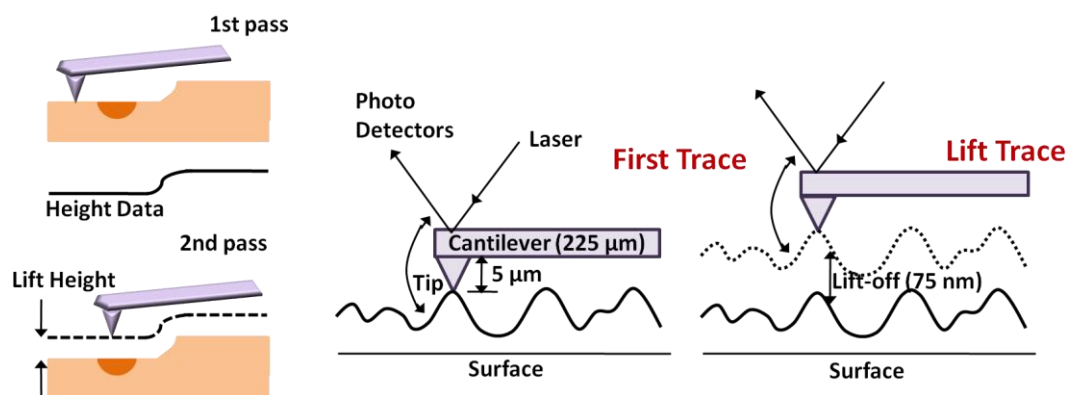


**Figure 1.10** Lifted-mode scanning in MFM.

During the second scan, tip is not forced mechanically by the piezoactuator and no feedback is required. Whilst the magnetic tip moves over a magnetic field gradient from the sample, it is either dragged towards or repelled away from the sample, depending on the magnetic moment direction of the sample. The deflection (or frequency change) of the cantilever, compared to the magnetic field strength, can be calculated by using the standard light-lever system. The magnetic force microscope functions on the basis of directing the interaction between the magnetic tip and the magnetic field produced by surface ferromagnetic structures. The oscillating mode of the microscope is broadly used to increase the sensitivity. For small oscillations and weak interactions the following expression holds.

$$\Delta\varphi = -\frac{Q}{k} \frac{\partial F_z}{\partial z} \quad \text{.....31}$$

Where  $\Delta\varphi$  is the phase shift due to the control of magnetic forces,  $Q$  is the cantilever quality factor,  $k$  is the elasticity constant of the cantilever, and  $\frac{\partial F_z}{\partial z}$  is the Z component of the magnetic force gradient influencing the MFM tip in the given point of the spatial location of the tip. According to eqn. 31, the phase shift is analogous to the magnetic force gradient, so all over the examined surface it is enough to estimate the gradient values in every point of the tip location where the tip is located during scanning.

MFM can be used to estimate magnetic materials and devices or to locate and map magnetic defects on a variety of materials and surfaces. Applications of MFM imaging are: 1) Data recording/storage media,<sup>12</sup> 2) nanoparticles (e.g. biological separation and purification),<sup>13</sup> 3) thin films,<sup>14</sup> 4) detection of magnetic beads,<sup>15</sup> 5) biological magnetic sensing<sup>16</sup>. MFM is well-matched with imaging in fluids or in air, or imaging under controlled environments (e.g. pressure, temperature etc).

### 1.3.1 MFM Images of Nano/Micro Poly-radical Structures:

Recently, MFM technique has been applied to generate molecular image and to study the magnetic response of the high spin polyphenoxyl radical organic radical polymers. For AFM study the dilute dichloromethane solution of the poly radical (molecular weight =  $3.2 \times 10^4$  g/mol) was transferred to a HOPG surface and dried (Fig. 1.11). The AFM showed ca. 35 nm sized particle of the high spin polyphenoxyl aggregates. The MFM on the molecular position clearly specified a magnetic gradient response. The three-dimensional interpretation of the MFM topography demonstrates

“holes” ascribed to the magnetic molecules or an attraction of the magnetized MFM tip to the polyradicals. When the tip was magnetized in the opposite direction this MFM image was inverted. After 1 day of the measurement the MFM images of the polyradical molecule disappeared. This corresponded to inactivation of the radical under ambient conditions.<sup>17</sup>

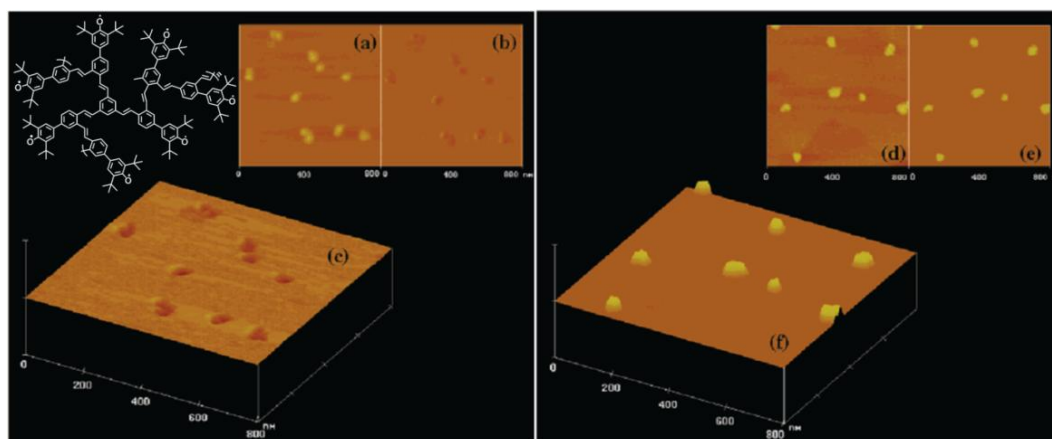


**Figure 1.11** Force microscopy images of a polyradical with a molecular weight of  $3.2 \times 10^4$  g/mol: (a) the AFM image. (b) The MFM image obtained immediately after AFM in the same scan area. (c) The 3D-MFM topography. (d-f) Force microscopy images of polyradical taken under the same conditions as Figure a-c, except using a MFM tip magnetized in the opposite direction. Ref 17.

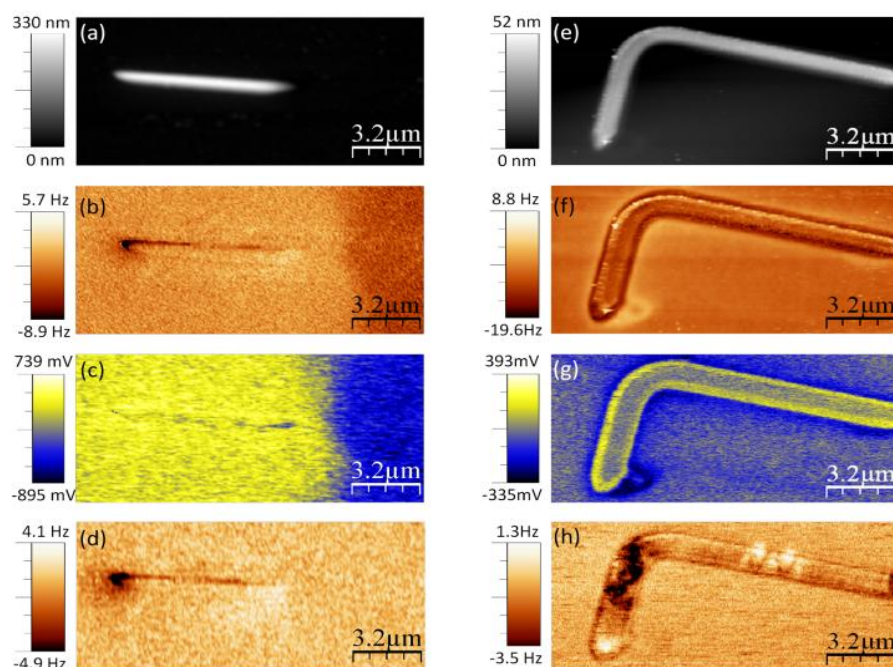


**Figure 1.12** Topography of (a) Co nanowires and (e) L-shaped Co nanostructure. (b) and (f) frequency shift images measured without KPFM acquired at a retrace distance of 30 nm and 25 nm, respectively. (c and g) surface potential images obtained by the KPFM technique. (d and h) MFM images (frequency shift) of the

Co nanostructures measured when the KPFM bias correction was switched on. The oscillation amplitudes were (a–d)  $A = 5$  nm and (e–h)  $A = 8.5$  nm. Ref 15b.

To evidently discriminate the origin of the tip–sample forces, in 2011, Asenjo and coworkers,<sup>15b</sup> have proposed a combined Kelvin probe force microscopy (KPFM) and MFM method. The KPFM technique permits compensating in real time the electrostatic forces between the tip and the sample by minimizing the electrostatic contribution to the frequency shift signal. This is a grand challenge in samples with low magnetic moment. They studied an array of Co nanostructures that exhibit high electrostatic interaction with the MFM tip. By using both of the KPFM/MFM system they were able to separate the electric and magnetic interactions between the tip and the sample (Fig. 1.12).

## 1.4 Stable Organic Radicals:

Almost all the organic molecules follow valence bond theory (VBT), thereby they obey the octet rule and as a result they are diamagnetic. Radicals, atoms or molecules with one or more unpaired electrons, are usually highly reactive<sup>18</sup> transient species. Kinetically and thermodynamically favorable decomposition pathways (e.g., dimerization, hydrogen abstraction, redox processes) make most radicals difficult to study. Hence there is no rule of thumb for the classification of radicals as stable or persistent. According to Ingold definition,<sup>19</sup> “a stable radical is defined as the one that can be isolated and handled as a pure compound, they are sufficiently long lived so that conventional spectroscopic analysis can be carried out.” Some examples of the latter class are even stable in water and air. Some important and most studied stable organic radicals are briefly reviewed here.

### 1.4.1 Survey of Stable Radicals:

**1.4.1.1 Triphenylmethyl Radical:** Prior to 20<sup>th</sup> century organic radicals were believed to be unstable intermediates which cannot be isolated and studied. But in 1900 Gomberg<sup>20</sup> synthesized the first organic free radical i.e. triphenylmethyl (TMP) radical (Fig. 1.13). Since then, many relatives of stable or persistent radicals have been synthesized. TMP radical was accidentally made during the attempted reduction of triphenylchloromethane<sup>21</sup> in the presence of

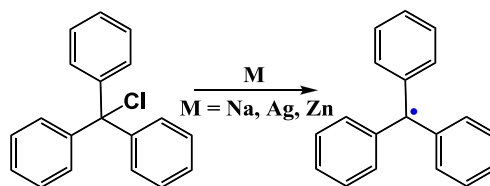


**Figure 1.13** Synthesis of triphenylmethyl radical (TMP).

zinc metal. This radical is stable in dilute, deoxygenated solutions. It is in equilibrium with dimeric species linked by a  $\sigma$ -bond between the central carbon of one radical and the *para*-phenyl carbon of another. The existence of such a dimer is proof that the unpaired electron does not reside on the central carbon entirely, but is delocalized to the *ortho*- and *para*-phenyl positions. This is reflected in the  $\pi$ -SOMO structure (Fig. 1.14). The ESR spectrum showed a well resolved proton hyperfine structure with 196 lines. These lines arise from a 1:3:3:1 quartet splitting of  $a_H = 2.86$  G from the 3 *para*-protons, a 1:6:15:20:15:6:1 septet of  $a_H = 2.61$  G from the 6 *ortho*-protons and a further  $a_H = 1.14$  G septet from the six *meta*-protons. The  $^{13}\text{C}$  splitting in the methyl position is  $a_{^{13}\text{C}} = 26$  G. The g-factor of TMP is 2.0026.

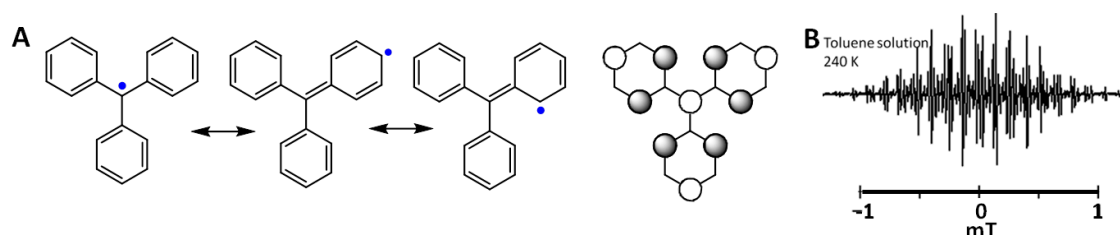


**Figure 1.14** (A) Resonance structures of Gomberg's triphenylmethyl (TPM) radical and its  $\pi$ -SOMO delocalization. (B) ESR spectrum of a TPM radical in toluene at 240 K.

Many polychlorinated trityl radicals have been reported displaying outstanding stability (Fig. 1.15). More recently, it has been shown that trityl radicals with chlorine atoms only at the *ortho*-positions are also exceptionally stable.

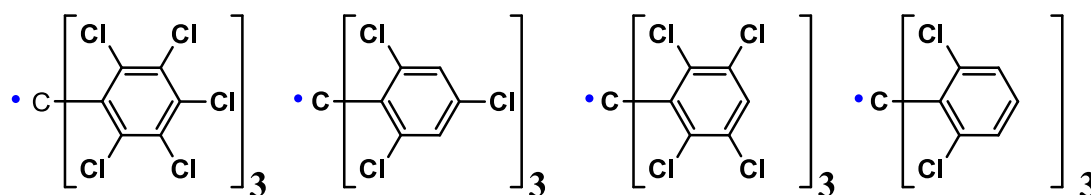


**Figure 1.15** Highly stable polychlorinated trityl radicals.

**1.4.1.2 Nitroxide Radicals:** Piloty and Schwerin synthesized porphyrin oxide, the first organic nitroxide radical in 1901.<sup>22</sup> Because of their trivial-synthesis and excellent stability, nitroxides have been the most studied class of free radicals and exploited in many biological applications. Oxidation of an N,N-disubstituted hydroxylamine with silver oxide or lead oxide gives the corresponding nitroxide radical (Fig. 1.16). Since then many paramagnetic derivatives have

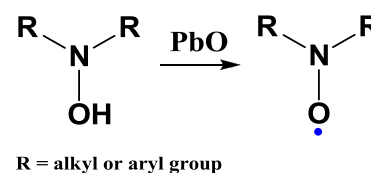


**Figure 1.16** Synthesis of nitroxide radical.

been prepared incorporating this simple radical unit. The stability of these radicals is due to the delocalization of the unpaired electron over the nitrogen and oxygen atoms. Mononitroxide radical gives a triplet EPR spectrum due to the hyperfine coupling interaction

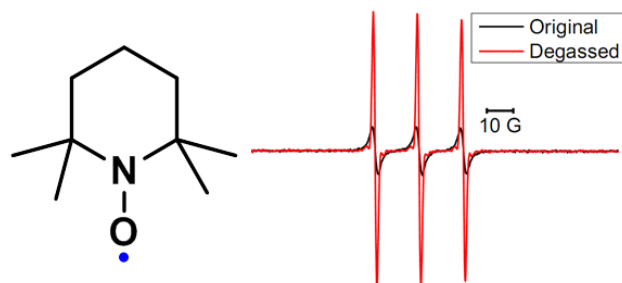


**Figure 1.17** EPR spectrum of TEMPO radical in phenol: air saturated (black), deoxygenated (red).

between the free electron and the nitrogen atom. These lines arise from a 1:1:1 triplet splitting with  $a_N$  of 15.65 G for 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) in  $10^{-2}$  M phenol solution (Fig. 1.17).

**1.4.1.3 Phenalenyl Radicals:** The phenalenyls are a class of carbon-based radicals, which was first synthesized in 1950.<sup>23</sup> The stability of these radicals is entirely as a result of spin delocalization. This class of radical was first synthesized from the precursor phenalene by deprotonation followed by aerial oxidation (Fig. 1.18). The unpaired electron is resonance delocalized over the six  $\alpha$ -carbons in phenalenyl radicals, with very little spin

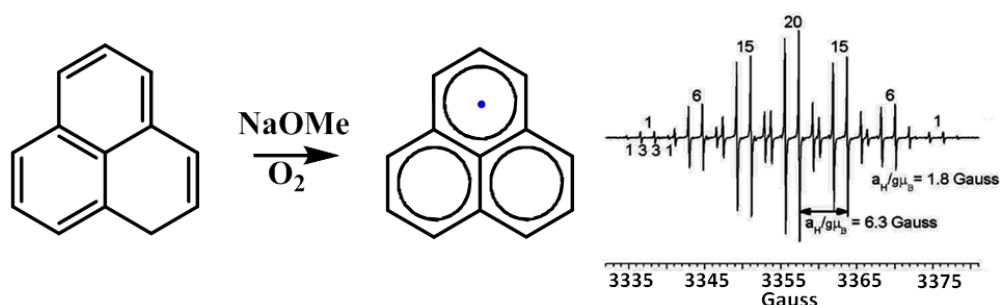


**Figure 1.18** Synthesis of phenalenyl radical and its ESR spectrum recorded at rt in mineral oil.

density found on the central and  $\beta$ -carbons ( $\pi$ -SOMO). Introducing substituents at the  $\beta$ -carbon prevents phenalenyl radicals from  $\sigma$ -dimerization, however such radicals had been shown to form  $\pi$ -dimers. The  $\pi$ -Dimers are face-to-face associated radicals that result

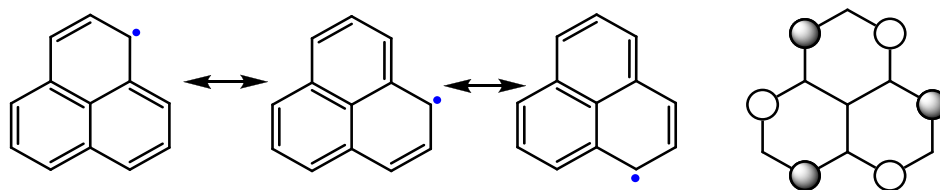


**Figure 1.19.** Resonance structures of phenalenyl radical and its  $\pi$ -SOMO delocalization.

from bonding interactions between  $\pi$ -SOMO orbitals (Fig. 1.19). The resulting dimers contain contacts between monomers shorter than associated Van der Waals Radii, but

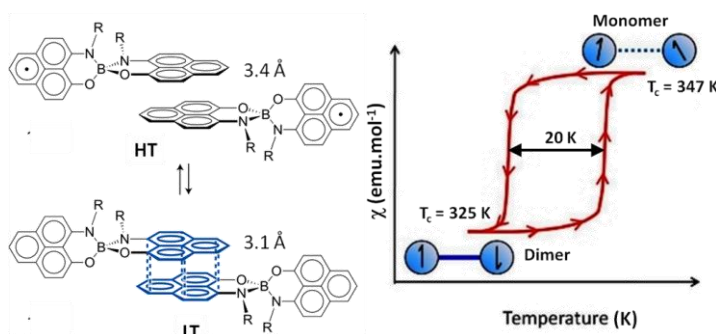


**Figure 1.20** High-temperature form ( $T_c \uparrow = 347$  K) and low-temperature form ( $T_c \downarrow = 325$  K) of spiro-bis(phenalenyl) radical ( $R = n$ -Bu). Its temperature dependence hysteresis curve and paramagnetic susceptibility ( $\chi$ ), Ref 24, 32.

longer than analogous  $\sigma$ -bonds. The perchlorinated derivative is monomeric in both solution and solid states. Earlier Haddon *et al.*<sup>24</sup> have explored the general structure of phenalenyl radical units which are connected to a boron centre in a spiroconjugated manner. The solid-state structure of these radicals is very sensitive to the N-R substituents. Some radicals remain as paramagnetic monomers, others exist as dimers linked by a  $\sigma$ -bond between two carbon atoms and some form co-facially aligned, diamagnetic ' $\pi$ -dimers' in which two phenalenyl units from adjacent molecules stack at a sub-Van der Waals distance (3.1 Å) (Fig. 1.20). One derivative, with  $R = n$ -butyl, has a temperature-dependent structure: at low temperatures (LT) it is a  $\pi$ -dimer whereas at high temperatures (HT) the radicals are unassociated. This compound also displays thermal hysteresis, due to diamagnetic-to-paramagnetic transition with a wide thermal hysteresis loop over the temperature range 325 to 347 K, giving a loop of nearly 20 K (see the plot in Fig. 1.20). It is the CH- $\pi$  interactions in the radical that are responsible for the hysteresis. The hysteresis influences its optical absorption, magnetic susceptibility and electrical conductivity properties.

**1.4.1.4 Phenoxyl Radicals:** Phenoxyl radical was first introduced in the 1920's to rationalize the structure of specific diaryl peroxides.<sup>25</sup> Later it was widely recognized that *ortho*- and *para*-substituents must be present in order to prevent radical decomposition (Fig. 1.21). In 1953 Cook<sup>26</sup> and Muller<sup>27</sup> have prepared for the first time stable

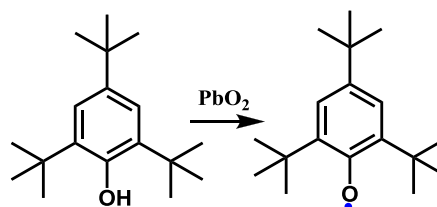


**Figure 1.21.** Synthesis of phenoxyl radical.

phenoxyl, from the corresponding phenol with a series of inorganic oxidizing agents.<sup>28</sup> The unpaired electron is delocalized through resonance, such that the oxygen atom

contains only marginally more spin density than the *ortho*- and *para*-carbons as shown in the  $\pi$ -SOMO (Fig. 1.22).

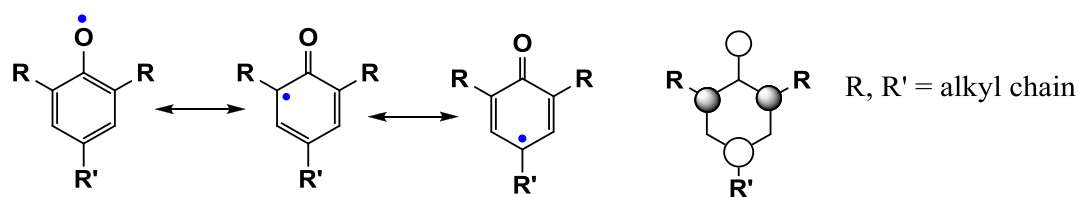


**Figure 1.22** Resonance structures of phenoxyl radical.

Among phenoxyl radicals, the galvinoxyl radical has received much interest due to its unusual magnetic properties and exceptional stability. Like conventional phenoxyl

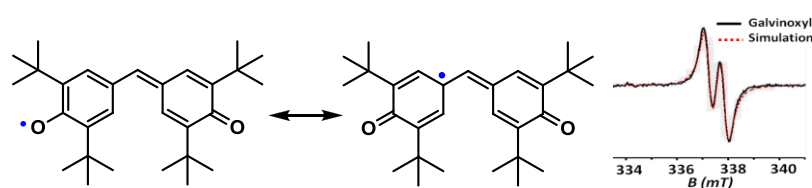


**Figure 1.23** Stability of galvinoxyl radical and its ESR spectra in ethanol solution continuous black line compared with the fitting obtained from blofit dashed red line.

radicals, in galvinoxyl radical, the delocalization of the spin happens onto the *para*-phenyl positions of the phenoxyl ring through resonance (Fig. 1.23). EPR spectrum of a 2.2 mM solution of galvinoxyl in ethanol at room temperature showed a doublet absorption at  $g = 2.00$  with a hyperfine splitting constant of 5.57 G.

**1.4.1.5 Thiazyl Radicals:** Free radicals based on an N-S fragment are the thiazyl radicals. The simplest of these are the thioaminyls, the general structure represented in figure 1.24.<sup>29</sup> Thioaminyl radicals are generally persistent, reversibly forming hydrazine-

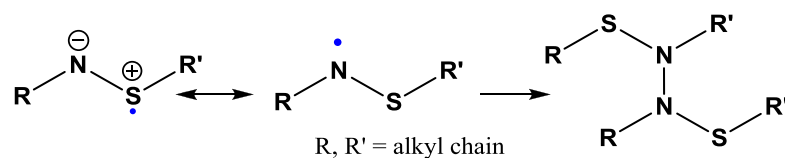


**Figure 1.24** Resonance structures of thiazyls radical.

like dimers in solution. Incorporation of bulky N-substituents (e.g., triphenylmethyl, 2,4,6-trisubstituted phenyl) prevents dimerization and allows the isolation of thioaminyl radicals which are stable towards moisture and oxygen. These radicals can be synthesized by oxidation of the corresponding sulfenamide with  $\text{PbO}_2$  and  $\text{K}_2\text{CO}_3$ . The origin of stability of these radicals is the steric protection afforded by the nitrogen and sulphur bound substituents.<sup>30</sup>

1,2,3,5-dithiadiazolyl (DTDA) radicals (Fig. 1.25) are resonance delocalized thioaminyls, which are stable indefinitely in deoxygenated solutions and in the solid-state. Furthermore, their thermal stability has been demonstrated through their purification by high temperature sublimation under high vacuum condition. DTDA radicals was observed with a typical hyperfine structure associated with coupling to two chemically equivalent  $^{14}\text{N}$  nuclei ( $g_x = 2.002$ ,  $g_y = 2.008$ ,  $g_z = 2.021$ ,  $a_{\text{Nx}} = 14$ ,  $a_{\text{Ny}} < 1$ ,  $a_{\text{Nz}} < 1$  G). The organic radical, 1,3,5-trithia-2,4,6-triazapentalenyl (TTTA),<sup>31</sup> undergo a large first-order magnetic phase transition. The

diamagnetic to paramagnetic transition occurs at 305 K ( $T_{\text{C}}\uparrow$ ), whereas the reverse transition occurs at 230 K ( $T_{\text{C}}\downarrow$ ). The high-

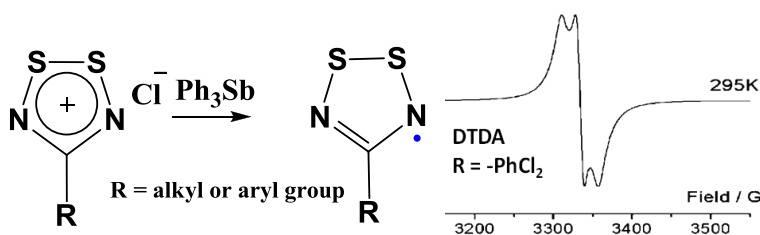


**Figure 1.25** Synthesis of 1,2,3,5-dithiadiazolyl (DTDA) radical and its ESR spectra.

temperature structure consists of a uniform one-dimensional stacking of the paramagnetic radical phase. The low-temperature phase is diamagnetic due to the strong dimerization along the stacking direction. These radicals were proposed for use in thermal sensors, switching units and information storage media based on organic radical crystals (Fig. 1.26).

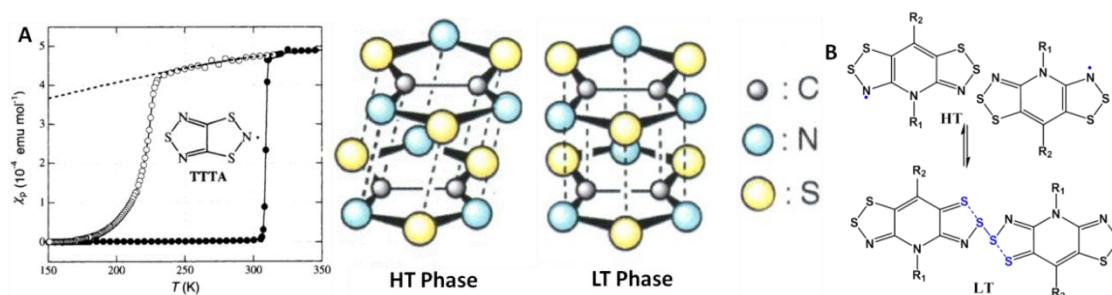


**Figure 1.26** (a) Temperature dependence of the paramagnetic susceptibility ( $\chi$ ), for a polycrystalline sample of TTTA upon cooling (open circles) and upon heating (closed circles). The behavior clearly indicates a first-order phase transition with wide thermal hysteresis:  $T_{\text{C}}\downarrow = 230$  K and  $T_{\text{C}}\uparrow = 305$  K. The dashed curve is the theoretical best fit of the 1D antiferromagnetic chain of  $J/k_{\text{B}} = -320$  K and  $J/k_{\text{B}} = -60$  K. Nearest-neighbor intermolecular arrangements of TTTA in the HT and LT phase. Ref 31 (b) High-temperature form and low-temperature form of bis(1,2,3-dithiazolyl) radical ( $R_1 = \text{Et}$ ,  $R_2 = \text{F}$ ). Ref 32

#### 1.4.2 Nitronyl Nitroxide (NN) and Oxoverdazyl (OVZ) Radicals:

Among radicals, nitronyl-nitroxide (NN) and oxoverdazyl (OVZ) have gained much popularity due to their stability and possible applications in spintronics device, organic battery, etc. These radicals attached to chelating ligand cores are very attractive because

together with magnetic transition metal ions they might offer interesting magnetic properties (*spin-spin* (SS)<sup>33</sup> *exchange coupling* / or *spin cross-over* (SCO) *effect* and the combination of these two interactions. This thesis work is mainly focused on these two organic stable radicals, hence more detailed discussions are presented in the following sections.

**1.4.2.1 Nitronyl Nitroxides (NN):** Mainly common nitroxides are the nitronyl nitroxides, first prepared in 1968 by Boockock and Ullman.<sup>34</sup> Nitronyl (NN) and imino nitroxide (IN) free radicals were described in detail in 1970's by Ullman in his original work.<sup>34</sup> The design and syntheses of stable paramagnetic NN molecules are of interest, due to their possible applications in various areas ranging from molecular magnets,<sup>35</sup> magneto-chemistry,<sup>36</sup> bio-organic chemistry,<sup>37</sup> and bio-inorganic chemistry,<sup>38</sup> and most recently as a material of spintronics device.<sup>39</sup>

Nitronyl nitroxides (NN) are extensively used as building blocks for organic magnetic materials and in spin labeling of small molecules. These radicals continue to receive a great deal of attention as building blocks for purely organic ferromagnetically ordered solids and metal-organic exchange-coupled complexes that exhibit versatile magnetic properties. The fundamental aspects of their electronic structure are well-established in 1991.<sup>40,41</sup> The NN radicals incorporate the necessary features for stability (e.g., no  $\alpha$ -hydrogens) and can thus be made with a wide variety of R groups. The  $\pi$ -SOMO spans both NO groups and has a nodal plane passing through the central carbon atom, although spin polarization leads to nearly negligible spin on this carbon, this can be influenced by electron withdrawing or donating groups (Fig. 1.27). As a result the spin distribution is symmetrically distributed on the two NO groups and is only slightly affected by the substituent R. Recently, Rey *et al.* have synthesized pyrimidinyl nitronyl nitroxides, whose electronic structures are generally quite similar to those of the more familiar imidazoline-based nitronyl nitroxides. Recent experimental and computational studies indicate that there is at least partial delocalization of spin from the ONCNO moiety onto the annelated ring.

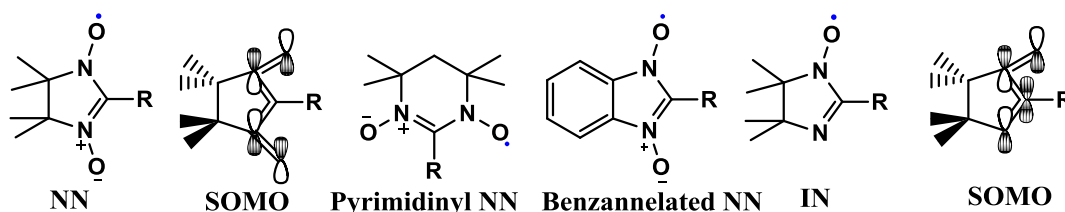


**Figure 1.27** Chemical structure and SOMO of nitronyl nitroxide and imino nitroxide radical.

Nitroxide radicals in which the NO group is conjugated to a C=N moiety, so-called “imino nitroxides” (IN)<sup>34,42</sup> (Fig. 1.27), generally possess higher stability compared to NN. EPR spectroscopy, neutron diffraction and computational studies indicate that spin on the nitroxide nitrogen is comparatively larger than on the imino nitrogen, though the latter nitrogen does possess substantial spin density. In contrast to the NN, the carbon atom (the NCNO moiety) of the imino nitroxides is not necessarily a node of the SOMO, but experimentally negative spin population is observed on this carbon atom. Nevertheless, the effect is less pronounced in the NN radicals. The ESR spectrum of a typical NN is given in figure 1.5.

The traditional “Ullman route” for preparing of NN radicals<sup>34</sup> is the reaction of an aryl or alkyl aldehyde group with 2,3-dimethyl-2,3-bis-(hydroxylamino)butane (BHA) followed by oxidation with NaIO<sub>4</sub> or PbO<sub>2</sub> of the diamagnetic condensation product to get NN radicals. Alternatively, a decade ago, Ovcharenko and Rey *et al.*<sup>43</sup> have developed an elegant “Rey route” for the synthesis of NN radicals by the condensation reaction of 2,3-dimethyl-2,3-dinitrobutane with aryl-aldehydes. They have synthesized 2,3-dimethyl-2,3-diaminobutane by reducing 2,3-dimethyl-2,3-dinitrobutane using tin metal under acidic reflux conditions (Fig. 1.28). In this thesis work, for the preparation of NN radicals (in chapter 2), Rey route has been followed, because synthesis of 2,3-dimethyl-2,3-diaminobutane is easier than BHA. Furthermore BHA easily decomposes to oxime.

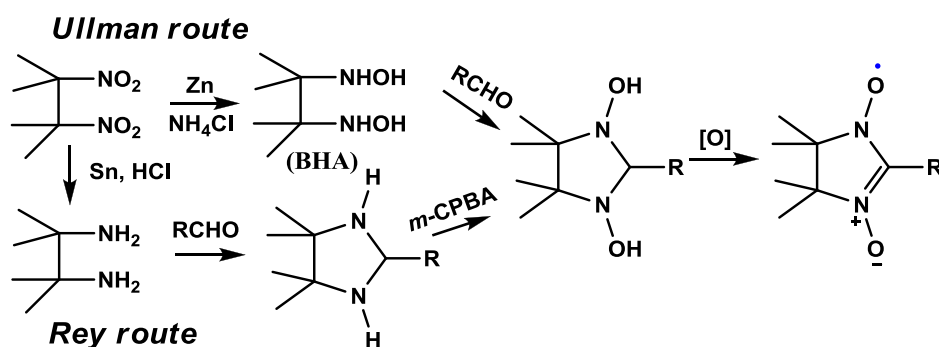


**Figure 1.28** Two different routes for the synthesis of nitronyl nitroxide (NN) radical.

**1.4.2.2 Verdazyl Radicals:** Verdazyls were prepared by Kuhn and Trischmann<sup>44</sup> in 1963 during studies on the alkylation of formazans. Reacting triarylformazan with methyl iodide under strongly basic conditions gave a cyclized product, tetrazine. The tetrazine was readily oxidized in atmosphere to give verdazyl radical. The general structure of a verdazyl radical, consists of a 6-membered heterocyclic ring with four nitrogen atoms at the 1, 2, 4 and 5 positions. The stability of the molecule is attributed to the delocalization

of the unshared electron over the four nitrogen atoms and to the steric shielding provided by the R groups at the 1, 3 and 5 positions. The spin density can be further stabilized via conjugation with any  $\pi$  system the R groups might contain (Fig. 1.29).<sup>45</sup>

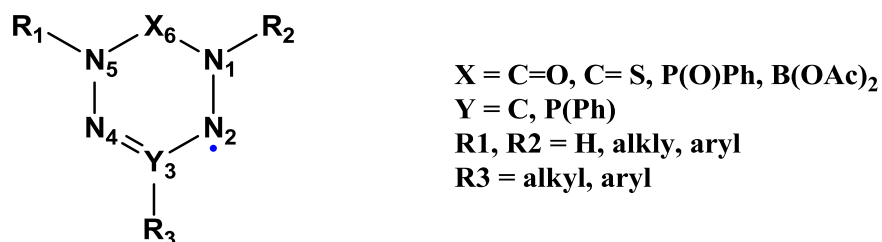


**Figure 1.29** The general structure of a verdazyl radical.

The first category, the Type I verdazyls have a methylene group in the 6 position and phenyl groups at 1 and 5 positions of the ring (numbering shown in Fig. 1.30). These radicals have a half boat structure with the C6 methylene group out of the plane of the tetrazine ring. Type II derivatives have a carbonyl or thiocarbonyl group in position 6. The resonance between the carbonyl and the neighboring nitrogen atoms give this type of verdazyl a planar geometry.

The electronic absorption spectra of verdazyl radicals show characteristic transitions in the visible region. It is the longest wavelength absorptions that are assigned to SOMO to LUMO transitions. Type I verdazyl radicals have a large degree of delocalization through N-phenyl substituents. So they have wavelengths of absorption maxima, or  $\lambda_{\text{max}}$  between 650 and 750 nm. Therefore these derivatives are, typically green. Type II verdazyl radicals have  $\lambda_{\text{max}}$  absorptions between 400 and 600 nm and are typically red, though, some derivatives are orange, maroon or brown. Increasing conjugation at C3 for either Type I or Type II verdazyls leads to a bathochromic shift of  $\lambda_{\text{max}}$ .

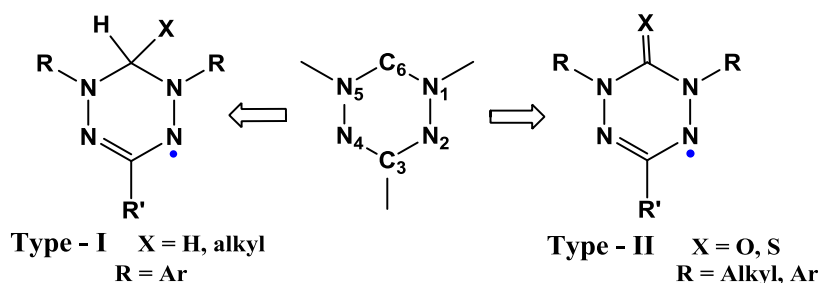


**Figure 1.30** Classification of Verdazyl radicals.

Verdazyl radicals are resonance stabilized hydrazyl radicals that can be isolated, stored and handled without decomposition.<sup>46</sup> Mostly these radicals do not associate, or

dimerize (Fig. 1.31). However, a ferrocene bridged verdazyl diradical has recently been reported to exist as an intramolecular  $\pi$ -dimer in the solid-state but it does not exist in solution, suggesting intermolecular solid-state packing effects.<sup>47</sup> The N-substituents on type I verdazyls are limited to aromatics ( $R = \text{Ar}$ ), while type II verdazyls bearing alkyl and aryl ( $R = \text{Me}$ , *i*-Pr, Ph) N-substituents have been prepared. Recently, it has been shown that verdazyls with N-isopropyl substituents are more stable than their N-methyl counterparts because of hyper conjugation of the alkyl chain proton. EPR spectra and magnetic properties of these radicals have been studied extensively to understand intra and inter spin interaction. Recent efforts also have focused on their use as ligands for transition metals and building blocks for molecule-based magnetic materials.

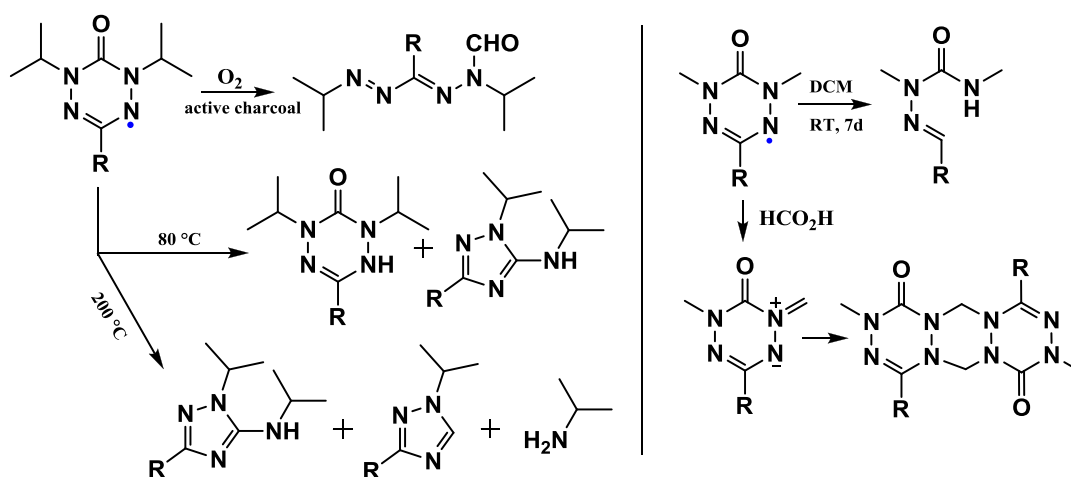


**Figure 1.31** Decomposition, association, or dimerization of verdazyl radicals.

EPR spectra of verdazyl radicals are in general quite complex. Particularly these complex spectra can be observed while long N-alkyl chain is attached with the radicals. The complexity of the spectra of N,N-dimethylverdazyls is increased for heptyl chain. In

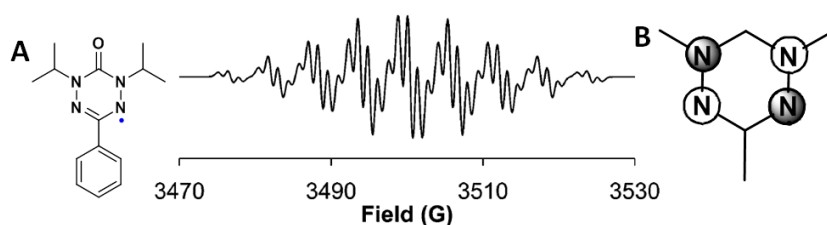


**Figure 1.32** (a) X-band EPR spectrum of phenyl verdazyl in  $\text{CH}_2\text{Cl}_2$ . (b)  $\pi$ -SOMO of a generic verdazyl radical. Ref 49d.

N-heptyl substituted OVZ radicals 36 lines are observed in ESR spectra for both mono and di OVZ radicals instead of nine and thirteen line, respectively

which is discussed in chapter 2. The hyperfine coupling to the protons ( $a_N$ ) is usually 1.17 to 1.36 G. For the spectra of N,N-dimethylverdazyls coupling to the six N-methyl

protons are 5.3 - 5.5 G for radical. The hyperfine coupling to the protons for N,N-di *i*-propylverdazyls is usually 1.30 to 1.56 G. The coupling to the N-alkyl protons is a result of hyperconjugation, which allows spin transfer to the alkyl hydrogen. In the spectrum of N,N'-diphenyl verdazyls, the hyperfine coupling to the aromatic protons is usually too small to resolve, 0.17 to 0.36 G, resulting only in broadening of the nine line pattern imposed by the four nitrogens. The interaction of the unpaired electron with the four nearly equivalent nitrogen atoms of the tetrazane ring gives a dominant nine line EPR pattern. Hyperfine coupling constants,  $a_N$  are typically in the range of 4-7 Gauss, with the three coordinate nitrogens (N1, N5) being slightly larger than the two coordinate nitrogens (N2, N4). The unpaired electron spin resides almost exclusively in a delocalized  $\pi$ -system spanning the four ring nitrogens with a nodal plane bisecting the ring through C3 and C6 (Fig. 1.32B). Only a negligible amount of spin leaks on to the three and six positions of the ring through spin polarization effects. The EPR results have also been supported by molecular orbital calculation. Additional hyperfine coupling is observed between the unpaired electron and the N-bound substituents. The EPR spectrum of phenyl verdazyl monoradical (Fig. 1.32A) contains a dominant nine-line pattern ( $a_{N1} = 5.3$  G), ( $a_{N2} = 6.5$  G) with additional coupling evident to the methyl protons ( $a_H = 1.2$  G) of the isopropyl groups.

1,3,5-triphenylverdazyl radical was accidentally synthesized by Kuhn and Trischmann in 1963 (Fig. 1.33). Their aim was to make an N-alkylformazan, by alkylating triphenylformazan, but they have isolated tetrazane as the main product. It has been confirmed that the alkylated product indeed forms, but cyclizes in solution to form the leucoverdazyl<sup>48</sup> under thermal or basic condition. The tetrazane was subsequently oxidized to the verdazyl radical in oxygen atmosphere.

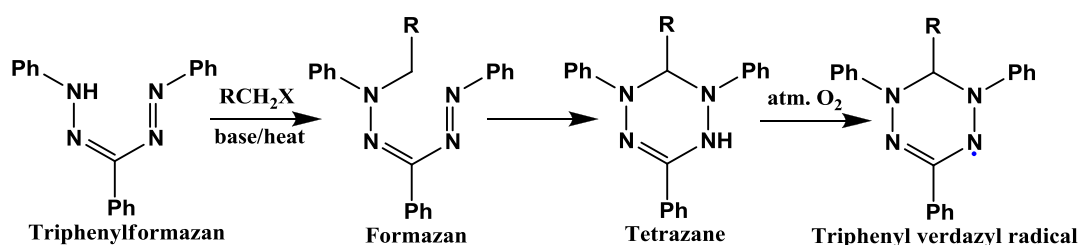


**Figure 1.33** Kuhn and Trischmann's synthetic route towards 1,3,5-triphenylverdazyl radical. Ref 44.

One more route for the preparation of verdazyl radical was reported by Neugebauer and Fischer in 1980. At first bis(hydrazide) was prepared by reacting two

equivalents of 1-methylhydrazine with one equivalent of phosgene.<sup>49</sup> The 1-methylhydrazine reacts exclusively through the N-methyl nitrogen at low temperatures. Two additional equivalents of 1-methylhydrazine were consumed to trap the hydrogen chloride produced as a hydrazine hydrochloride salt. Condensation of bis(hydrazide) with an aldehyde gave the radical precursor 1,5-dimethyl-3-phenyl-1,2,4,5-tetrazane 6-oxide, herein referred to as a tetrazane (Fig. 1.34). This route has the advantage of higher yields compared to the formazan method.<sup>50</sup> A wide range of R-group substituents can be used and, for this reason, 6-oxoverdazyls have also been the major focus of this thesis work. Oxidation of tetrazanes to the corresponding 1,5-dimethyl-6-oxoverdazyls can be achieved with  $\text{FeCl}_3$  in formic acid or  $\text{K}_3\text{Fe}(\text{CN})_6$  in basic condition. Many other organic

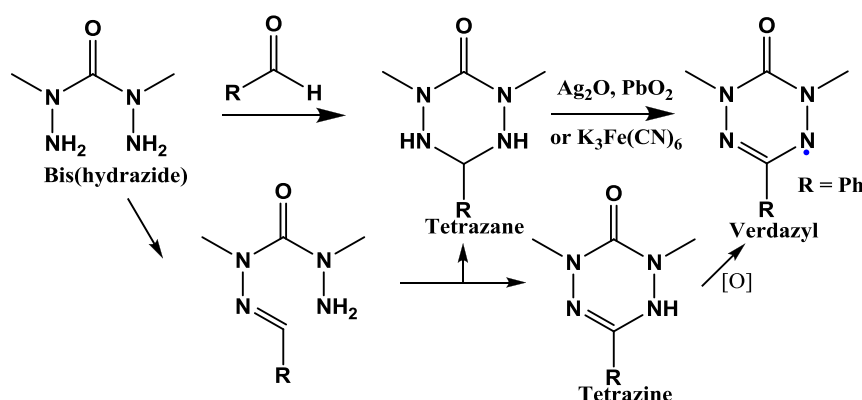


**Figure 1.34** 6-oxoverdazyl radicals reported by Neugebauer and Fischer. Ref 49.

and inorganic oxidants have since been used for a wide range of derivatives including *p*-benzoquinones, periodate,  $\text{PbO}_2$ ,  $\text{AgO}$  and  $\text{Ag}_2\text{O}$ .<sup>51</sup> Generally the hydrazone can be synthesized from the appropriate aldehyde and hydrazine. Reaction of a hydrazine with phosgene or thiophosgene gives the 2-chloroformylhydrazone, which after ring-closure with an aryl aldehyde gives tetrazane. The tetrazanes are oxidized to the corresponding radicals.

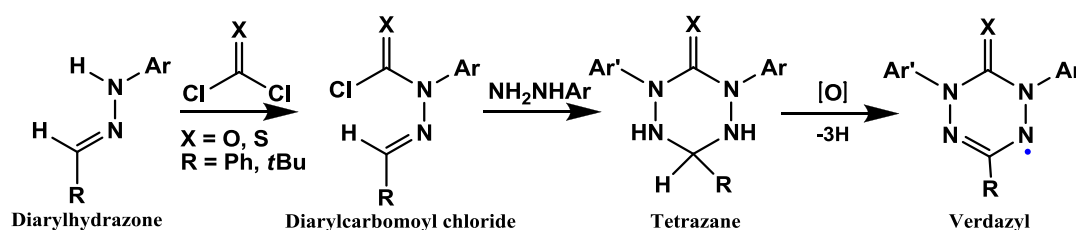


**Figure 1.35** Milcent's synthetic route for preparation of 1,3,5-triaryl-6-oxoverdazyls. Ref 52.

Milcent *et al.* have in the early 1980's developed a methodology for the synthesis of 1,3,5-triaryl-6-oxoverdazyls (Fig. 1.35).<sup>52</sup> This route also proceeds via a tetrazane, but

begins with the reaction of a diarylhydrazine with phosgene to give a diarylcarbomoyl chloride, with subsequent reaction of the product with an arylhydrazine.

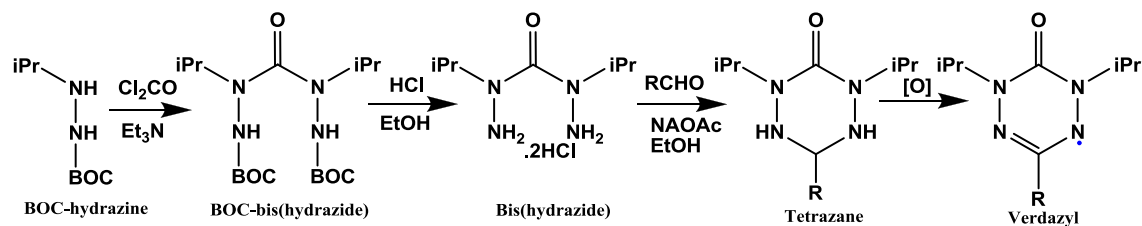


**Figure 1.36** Synthesis of 1,5-diisopropyl-6-oxoverdazyls by Brook and co-workers. Ref 53.

Recently, Brook and co-workers<sup>53</sup> have developed a methodology for the synthesis of 1,5-diisopropyl-6-oxoverdazyls (Fig. 1.36). In this thesis work Brook method has been followed for synthesis of oxo-verdazyl (OVZ) radicals in chapter 2 and 4. In this method instead of phosgene gas, triphosgene solid was used which is easy to handle and safe to use.

## 1.5 Properties of Stable Organic Radicals:

Stable organic radicals have been used broadly to study biological systems through EPR spectroscopy; a technique first introduced in 1944 in Kazan State University by Yevgeny K. Zavoisky and was developed independently at the same time by Brebis Bleaney at the University of Oxford. EPR spectroscopy has long been used to gain structural,<sup>54</sup> dynamic,<sup>55</sup> and reactivity<sup>56</sup> information in systems containing stable radicals. EPR spectroscopy is one kind of nuclear magnetic resonance (NMR) spectroscopy of the paramagnetic analogues.<sup>57</sup> The detection limit of EPR spectroscopy<sup>58</sup> is much lower than NMR spectroscopy, allowing for observation of paramagnetic species at concentrations as low as  $10^{-9}$  M. Stable radicals have also found useful in probing the kinetics and mechanisms of radical-induced polymerizations,<sup>59</sup> radical rearrangement reactions,<sup>60</sup> and homolytic dissociation as a so-called “*radical trap*”.<sup>61</sup> A stable radical is added to a reaction under investigation to trap any reactive radical intermediates that are formed during the reaction. The result is a closed-shell species composed of a stable radical covalently bound to the radical intermediate fragment. This trapping technique is useful for the detection and identification of species that would otherwise be too short-lived or in too low a concentration to detect.

Radicals are exploited as probe molecules in techniques such as spin trapping,<sup>62</sup> spin labeling,<sup>63</sup> and EPR imaging.<sup>64</sup> Spin trapping involves a reaction of a diamagnetic

molecule (radical trap) with a highly reactive radical to generate a new persistent or stable radical. Common spin traps include 2-methyl-2-nitrosopropane, phenyl-tert-butyl nitron and 5,5-dimethyl-2-pyrroline-N-oxide.<sup>65</sup> An example of spin trapping by 5,5-dimethyl-2-pyrroline-N-oxide is shown in [figure 1.37](#). It should be mentioned that spin trapping provides little or no structural information about the trapped species as it is not observed directly, but does provide indirect evidence of the existence of the trapped species.

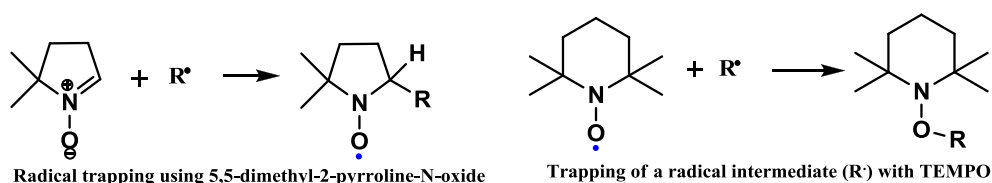


**Figure 1.37** Spin trapping by TEMPO.

Spin labeling is a technique used to study biological systems.<sup>66</sup> A stable radical is integrated into a biological system, and the obtained EPR spectra gives information about the environment around the label (the radical), dynamic processes and hydrophobicity/hydrophilicity. Unfortunately the number of radicals that can be used as spin labels is severely limited by their compatibility with biological systems. Few radicals are soluble in aqueous media and stable over broad pH and temperature ranges.

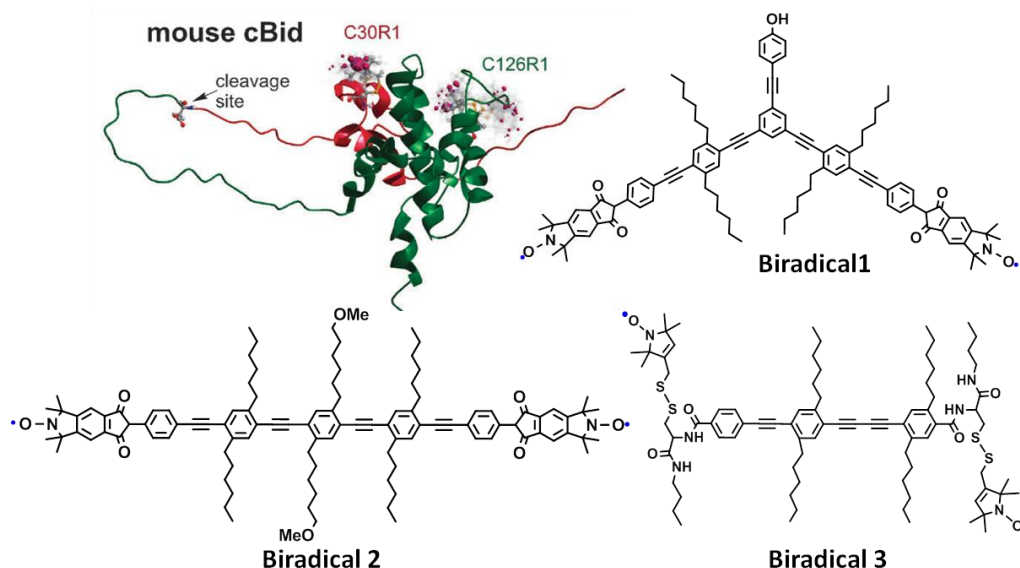


**Figure 1.38** Mouse cBid was spin-labelled at positions 30 and 126 with MTSSL and prepared in the 20  $\mu\text{M}$  Tris buffer, 150 mM NaCl, pH 7.5. The sample was diluted with deuterated glycerol (40% v/v) to 40 mM final concentration. The shape-persistent biradicals 1–3 were dissolved in perdeuterated o-terphenyl at 200  $\mu\text{M}$  concentration. Ref 67.

Jeschke *et al.*<sup>67</sup> have performed the Double Electron–Electron Resonance (DEER) experiment on a pair of nitroxide radicals used as spin markers on the diamagnetic

protein. Due to the very flexible linker connecting the nitroxides with the molecule backbone, not only the interspin distance distribution is very broad, but also mutual orientations of the spin label possible over a broad range of angles. This is one of the important techniques for studying conformational dynamics of proteins. The popularity of DEER is due to its relative ease combined with a high precision in providing distance information on proteins and protein complexes in a mid-to-long distance range of 1.6–1.8 to 6–10 nm. The measurement was done in the water-soluble Bcl-2 protein cBid from mouse. This is spin-labelled with methanethiosulfonate spin label (MTSSL) at the two native cysteines at positions 30 and 126, which was used as a representative of a protein with a pair of labels of moderate flexibility. Several oligo(p-phenyleneethynylene) (oligoPPE) based shape-persistent nitroxide biradicals dissolved in perdeuterated o-terphenyl were used as spin markers (Fig. 1.38). The rigid biradicals **1** and **2** were found suitable using Q-band DEER technique to study geometry of the pairs with high geometrical correlation (as spin labelled DNA for example).

EPR imaging (EPRI)<sup>68</sup> has been emerging as a technique that can provide rich information about systems where a stable radical has been introduced. The technique allows for detection of paramagnetic species within a sample in three dimensions and hence imaging can be done. Although the field is reasonably new, it has been suggested that EPRI may act as a proxy and perhaps complementary technique to nuclear magnetic resonance imaging (NMRI or MRI)<sup>69</sup> in the future. Another use of stable radicals which is technologically important and has possible in industrial applications is living radical polymerization. This technique differs from conventional radical polymerization in that it utilizes a stable free radical to tune polymer structure, giving materials with low polydispersity, controlled molecular weights and defined chain ends.<sup>70</sup>

In neutral closed-shell species, oxidation and reduction actions produce radical cations and radical anions, respectively. Oxidation involves the highest occupied molecular orbital (HOMO) and reduction the lowest unoccupied molecular orbital (LUMO), with both processes leading to the molecule concurrently gaining spin and charge. This confines the utility of neutral closed-shell molecules as reversible, redox active species; a vast majority of the resulting radical ions are highly reactive. These primary differences result in properties that make radicals attractive in applications requiring redox-active species,<sup>71</sup> including alcohol oxidation,<sup>72</sup> conducting materials,<sup>73</sup> metal complexes<sup>74</sup> and redox-switchable systems.<sup>75</sup>

## 1.6 Organic Radical Based Ferromagnets:

Stable paramagnetic species also used as building blocks for designing molecular magnetic materials. Successful achievements in this field, such as purely organic ferromagnetically ordered solids and metal-organic exchange-coupled complexes that exhibit versatile magnetic properties, have triggered the synthesis of hundreds of these

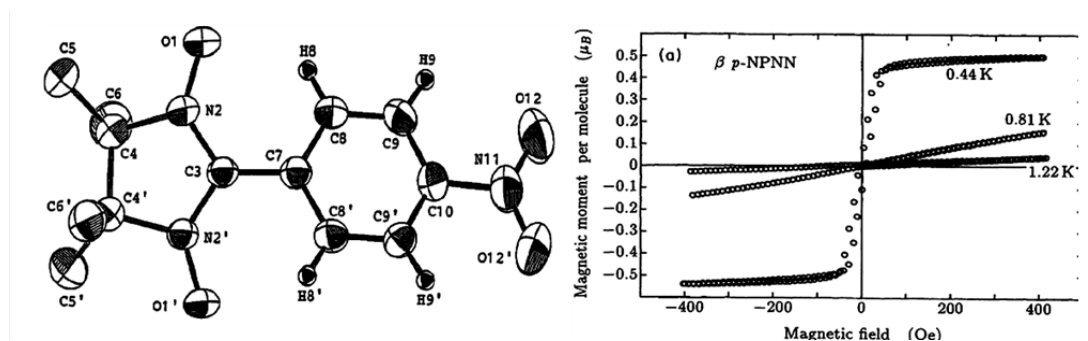


**Figure 1.39** Example of first organic ferromagnet.

free radicals. The first organic ferromagnet p-nitrophenyl-nitronyl nitroxide was made by

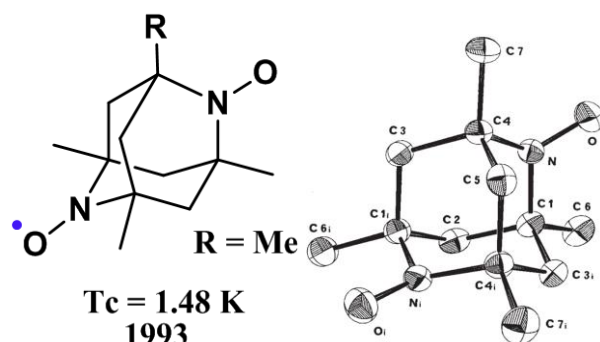


**Figure 1.40** 1,3,5,7-tetramethyl-2,6-diazaadamantane-N,N'-dioxyl and its crystal structure.

magnetization have involved nitroxide radical derivatives as building blocks.<sup>77</sup>

Rassat group<sup>78</sup> have prepared an organic crystalline ferromagnet based on 1,3,5,7-tetramethyl-2,6-diazaadamantane-N,N'-dioxyl (Fig. 1.40). In these radicals when R = CH<sub>2</sub>Me, CH<sub>2</sub>OH they show dominant antiferromagnetic interactions in the bulk state, the diradical R = Me (the most symmetric among the derivatives) is a bulk

the Kinoshita group in 1901 (Fig. 1.39).<sup>76</sup> The thermodynamically most stable  $\beta$ -phase (orthorhombic) undergoes a paramagnetic–ferromagnetic phase transition at  $T_C = 0.6$  K, whereas the  $\gamma$ -phase (triclinic) orders antiferromagnetically at  $T_N = 0.65$  K. Almost all attempts in the design of purely organic radicals systems showing spontaneous

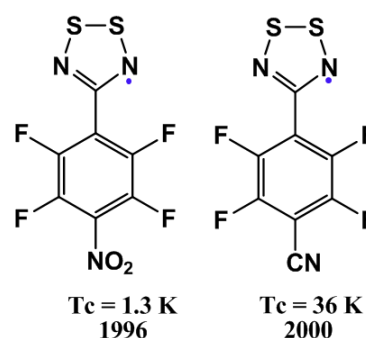


**Figure 1.41** Dithiadiazolyl with -CN and -NO<sub>2</sub> analogue.

ferromagnet with  $T_C = 1.48$  K. As governed by the small magnetic anisotropy of this compound no hysteresis could be observed, which is typical for a “soft” magnet behavior.

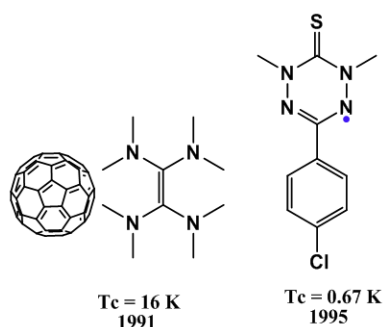


**Figure 1.42** TDAE-C60 and Verdavyl radical ferromagnet.

To date this value of ferromagnetic transition temperature remains the highest among nitroxides. The strength of the exchange interaction between free radical molecules through Van der Waals contacts or through hydrogen-bonding is limited, the  $T_C$  of the crystals among the majority of free radicals is very low (1 K). The dithiadiazolyl -CN analogue (p-NCC<sub>6</sub>F<sub>4</sub>CN<sup>•</sup>SSN<sup>•</sup>,  $\beta$ -phase)<sup>79</sup> exhibits bulk ferromagnetic ordering at exceptional high temperature under ambient pressure at 36 K, although this compound is known as a weak ferromagnet. For the nitro analogue (p-O<sub>2</sub>NC<sub>6</sub>F<sub>4</sub>CN<sup>•</sup>SSN<sup>•</sup>)<sup>80</sup> the  $T_C$  value is only 1.3 K (Fig.1. 41). The main difficulty of utilizing dithiadiazolyl radicals is the lack of sufficient steric protection to inhibit dimerisation. Perfluoraryl groups are commonly used as stabilizing the substituents in aromatic ring. Remarkably, due to the charge transfer interactions between donor and acceptor molecules in purely organic compounds e.g., in tetrakis(dimethylamino) ethylene-C60 (TDAE-C60) a  $T_C$  as high as 16 K could be achieved (Fig. 1.42).<sup>81</sup>

More recently, Miller's group<sup>82</sup> have reported bridging of  $S = 5/2$  Mn<sup>II</sup>(hfac)<sub>2</sub>

(hfac = hexafluoro-acetylacetonate) with  $S = 1/2$  i-propylnitronyl nitroxide to create a linear chain structured ferrimagnet, figure 1.43, with  $T_C = 7.6$  K. The Mn<sup>II</sup>(hfac)<sub>2</sub> bridging to the nitronyl nitroxide can either be *cis* or *trans*, which significantly affects the magnetic properties.

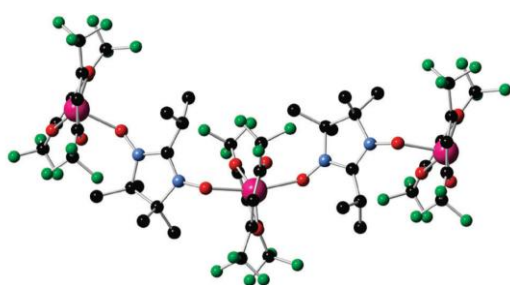


**Figure 1.43** Segment of a uniform 1-D chain of trans-Mn<sup>II</sup>(hfac)<sub>2</sub>-μ-i-propyl nitronyl nitroxide; a ferrimagnet below a  $T_C$  of 7.6 K. Ref 82.

Conventional magnetic materials are mostly based on transition metals, including rare-earth elements. Organic ferromagnets as promising magnetic materials have caught interest due to potential applications such as organic spintronic devices, with logic, communications and data storage. Their

advantages are low cost, light weight and large area production. Some transition metal-free ferromagnetic conducting or semiconducting polymers, such as perchlorate ion

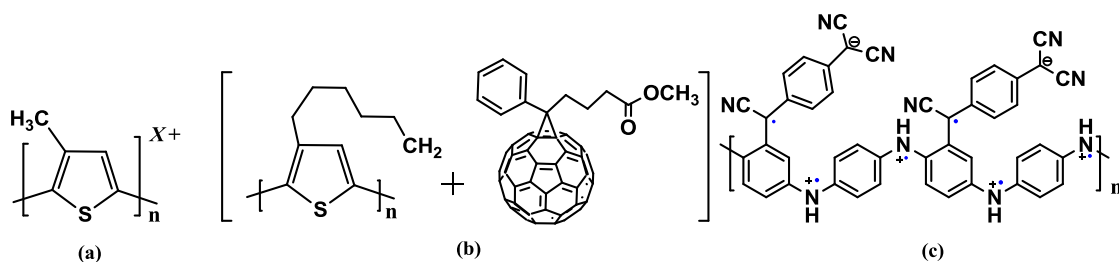


**Figure 1.44** Organic ferromagnets at RT. a) poly(3-methylthiophene) b) poly(3-hexylthiophene) and phenyl-C61-butyricacid methyl ester c) polyaniline:tetracyanoquinodimethane. Ref 83, 84, 85.

(ClO<sub>4</sub><sup>-</sup>) doped with poly(3-methylthiophene)<sup>83</sup>, semiconducting polymer, crystalline phase of poly(3-hexylthiophene)<sup>84</sup> exhibit room temperature (RT) ferromagnetism. Phenyl-C61-butyricacid methyl ester (PCBM) mixed with polyaniline in nanoscale phase separation with tetracyanoquinodimethane (TCNQ). The mixture of polyaniline:tetracyanoquinodimethane (PANiCNQ) showed  $T_C = 350$  K.<sup>85</sup> (Fig. 1.44).

## 1.7 Topological Rules for High Spin (HS) State:

Biradicals are molecules that possess a pair of nonbonding molecular orbitals (NBMOs) that are occupied by two electrons; they are described as non-Kekulé hydrocarbons. These molecules have no resonance structure that pairs the two electrons by forming a new  $\pi$ -bond. Kekulé hydrocarbons, conversely, have resonance structures that pair up all electrons into  $\pi$ -bonds. Non-Kekulé hydrocarbons have been of interest since 1966 when Paul Dowd synthesized trimethylenemethane (TMM) (Fig. 1.45). Some other examples of non-Kekulé hydrocarbons include m-benzoquinodimethane (MBQDM), tetramethyleneethane (TME) and tetramethylenebenzene (TMB). These molecules are interesting because they have either a singlet ( $S = 0$ ) or a triplet ( $S = 1$ ) ground state. Non-Kekulé molecules are fully conjugated but contain at least two atoms that are not  $\pi$ -bonded. In 1950 Longuet-Higgins has proved that an alternant hydrocarbon contains at least  $(N-2T)$  singly occupied non-bonding molecular orbitals (NBMOs), where  $N$  is the number of carbon atoms and  $T$  the maximum number of double bonds that occurs in any resonance structure. Looking at isomeric benzoquinodimethanes, the *ortho*- and *para*- isomer can be represented as a classical Kekulé structure with a total of four double bonds. According to Longuet-Higgins rule,

$$[n\text{NBMO} = (N-2T); S = 0.5 (N-2T)] \quad \dots\dots 32$$

Where,  $N$  is the number of  $\pi$ -centers and  $T$  is the number of double bonds. On the other hand, *meta* isomer can only be drawn in a non-Kekulé fashion, with three double bonds at the most, resulting in two NBMOs each occupied by one unpaired electron. On the basis of Hund's rule, Longuet-Higgins predicts ferromagnetic spin alignment between the unpaired electrons in the NBMOs of a non-Kekulé molecule and a ground-state with a spin quantum number  $S = n/2$ , where  $n$  is the number of unpaired electrons.

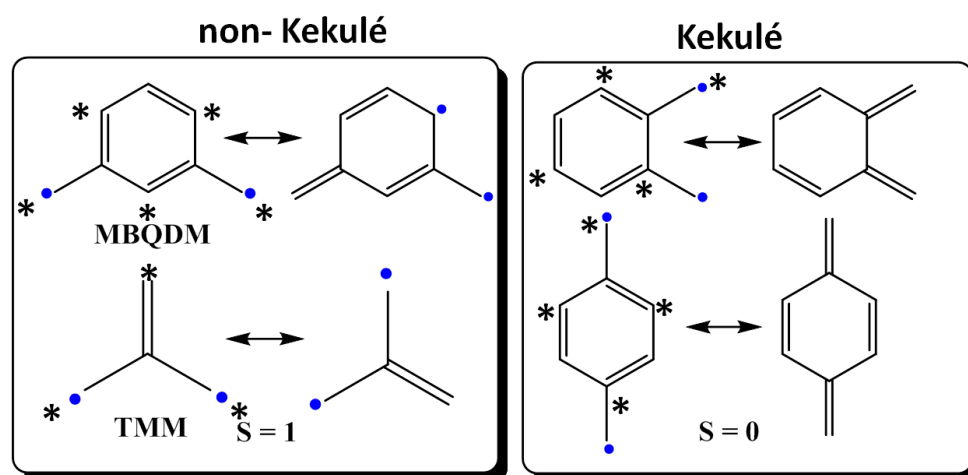


Figure 1.45 Kekulé and non- Kekulé molecules.

Latter, Ovchinnikov developed a valence bond (VB) method for estimating the ground state in non-Kekulé and Kekulé molecules.<sup>86</sup> However, first the molecule must have an alternate hydrocarbon (AH), in which each atom is a part of one of two sets, “starred” or “non-starred” and no atom can have a neighbor of the identical set. The theoretical basis of this method relies on a full MO calculation including configuration interaction, of the sign and magnitude of the spin densities at the carbon atoms. The result of such calculations shows that the starred atoms have a large positive spin density and the unstarred atoms have a small negative spin density. Figure 1.45 shows the star/nonstar labels for TMM and MBQDM. Once all the carbons have been labeled as starred or nonstarred, in which  $N^* \geq N$ , the spin ground state from Ovchinnikov's rule is:

$$S = (N^* - N)/2 \quad \text{.....33}$$

Therefore, if starred atoms are more than nonstarred there is a net spin resulting in a ground state that is not a singlet. If this rule is applied to TMM, there are three starred carbons and one nonstar resulting in  $S = 1$  ground state from the equation 33.

An important goal in the field of organic molecular magnetism is to prepare compounds incorporating more than one unpaired electron with appreciably large

ferromagnetic coupling ( $J$ ) between them, providing a triplet ( $S = 1$ ) or higher ( $S > 1$ ) ground state molecules. In non-conjugated radicals, such as TEMPO, the NO group carrying the unpaired free electron is fairly isolated from the rest of the molecule by saturated hydrocarbon groups and, therefore, carries most of the spin density.

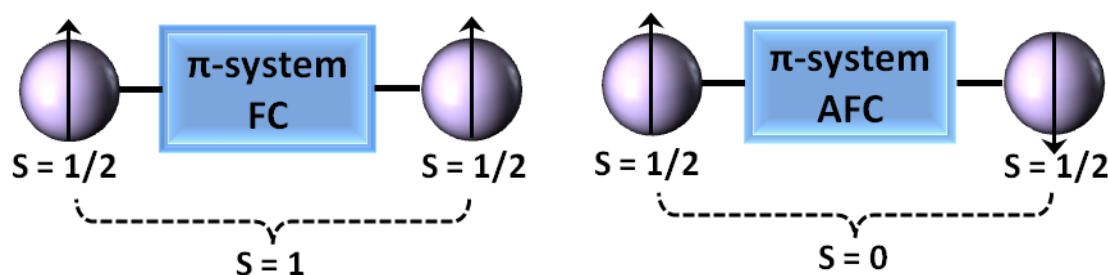


**Figure 1.46** Schematic representation of ferromagnetic and antiferromagnetic spin alignment within a molecule. FC = Ferromagnetic coupling and AFC = Antiferromagnetic coupling.

Therefore, it is necessary to use a "ferromagnetic coupler"<sup>87</sup> or spacer, which offers a pathway for the transmission of the interactions between two or more unpaired electrons within the molecule, leading to extensive delocalization of the free electrons over the aromatic core. Ferromagnetic interactions occur when the electrons have the same spin orientation and conversely, antiferromagnetic coupling is a result of antiparallel spin-spin interactions. The possibility to control the "through bond exchange" in conjugated molecules is the first step towards obtaining bulk magnetic properties (Fig. 1.46). The latest progress in high spin molecules are made from nitroxide radicals with the combination of different radicals in one molecule, so called heterospin molecules.

Iwamura *et al.*<sup>88</sup> have prepared hetero spin molecules by attaching imino nitroxide and/or nitronyl nitroxide radicals to a diphenyl nitroxide radical (Fig. 1.47). All three

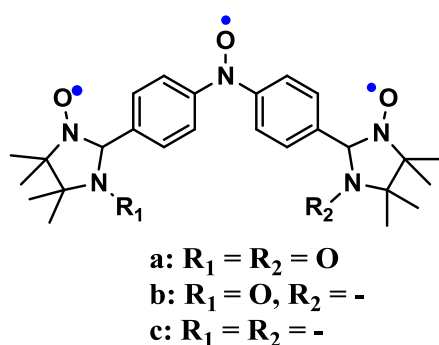


**Figure 1.47** Heterospin nitroxide radicals with a high spin state.

molecules show quartet ground states with an antiferromagnetic intermolecular coupling ( $S = 3/2$ ) in the solid state. The imino nitroxide radicals (b, c) do not have a resonance contribution to the exchange interactions between the radicals in the molecule and thus have a weaker intramolecular ferromagnetic coupling ( $J$ ).

A different and interesting approach has been described by Sugawara *et al.*<sup>89</sup> in which two nitronyl nitroxides were coupled to a thianthrene molecule acting as a ferromagnetic coupler (Fig.

1.48). After oxidation thianthrene is known to generate stable cation radicals, so this molecule is an example of an electronically controllable spin system. The spin states of the neutral forms can be calculated with the spin polarization mechanism, as the lone pair on sulfur acts as a carbon-carbon double bond. The 2,7- and 2,8-isomers have a weak ferromagnetic ( $J = 5.5$  K) and antiferromagnetic ( $J = -1.4$  K) intramolecular coupling, respectively. Surprisingly both the isomers afford ground-state quartet species upon one-electron oxidized triradical state. Interestingly, the mechanism of the spin alignment of these donor radicals in the singly oxidized state is totally different from that in the neutral state.

Takui and co-workers<sup>90</sup> have synthesized the 3,5-pyridine-substituted NN biradicals and its N-alkylated cation salt, to prove the influence of the N-alkylation on the intramolecular exchange interaction (Fig.

1.49). The intramolecular ferromagnetic interaction of the biradical and its cation salt has been found to be  $2J/k_B = 40$  K and  $2J/k_B = 32$  K, respectively. The magnitude of the interaction is reduced only by 20% upon ionization. There is a little influence of the N-

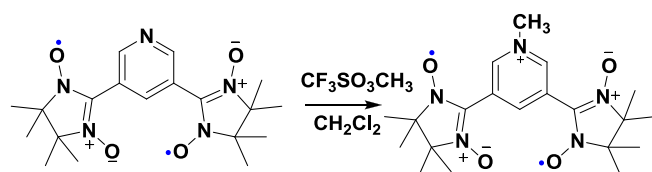


**Figure 1.49.** Pyridine-substituted biradical and its N-alkylated cation salt. Ref 90.

alkylation for the 3,5-pyridine-substituted biradical on the intramolecular exchange interaction. Depending on the substitution pattern, a protonated pyridine can serve as a ferromagnetic couplig unit or an antiferromagnetic coupling unit. Both valence bond and molecular orbital arguments provide qualitative rationalizations of these results.

Rajadurai *et al.*<sup>91</sup> have prepared phenylethynyl spacers carrying NN biradicals attached to the 3,5 and 2,6 positions of the pyridine units (Fig. 1.50a) to observe the influence of the pyridyl nitrogen position on the ground state spin multiplicities. These biradicals showed strong intramolecular exchange coupling ( $J \gg 7 \times 10^{-4} \text{ cm}^{-1}$ ;  $J/a_N \gg 1$ ) within the limit of EPR. The plot of inverse temperature ( $1/T$ ) Vs the  $\Delta Ms = \pm 2$  signal

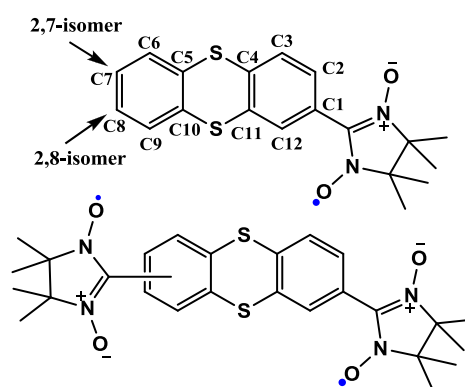


**Figure 1.48** Thianthrene bis(nitronyl nitroxide) radical can perform as a ferromagnetic coupler.

alkylation for the 3,5-pyridine-substituted biradical on the intramolecular exchange interaction. Depending on the substitution pattern, a protonated pyridine can serve as a ferromagnetic couplig unit or an

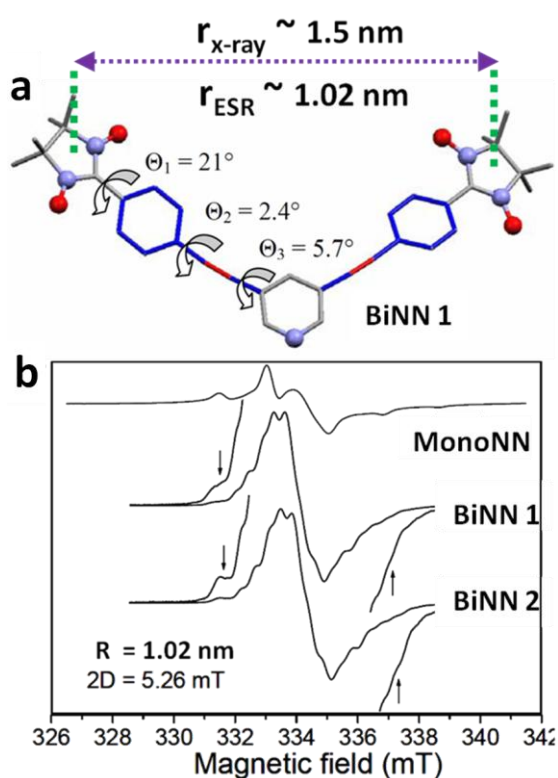


**Figure 1.50** (a) Capped sticks representation of BiNN 1 with torsional angles. (b) ESR spectra ( $\Delta m_s = \pm 1$ ) diradicals in toluene ( $c = 10^{-4} \text{ M}$ ) at 120 K (0.2 mW microwave power) in comparison with monoradical (arrows show the enlarged outermost zfs components). Ref 91.

After applying point-dipole approximation the derived distances for both biradicals were  $r = 1.02 \text{ nm}$ , which is almost close to intra-radical distances of biradicals from crystal structures.

### 1.7.1 Very High Spin Radical Polymers:

True high spin polyradicals are the ultimate goal in the preparation of stable high spin state organic molecules. The polydisperse nature of polymers tends to frustrate the total control over the spin state and clever designs and/or doping procedures are required. Until now all the polyradicals reported are generally possessing lower spin states as compared to monodisperse high spin oligomers, as a consequence of problems associated with the quantitative generation of radicals in a polymer. The pendant radical approach is a promising strategy to overcome the problem of spin defects.

Miura co-workers<sup>92</sup> have prepared two pendant poly(nitroxide radical)s with a poly(1,3-phenylene) backbone. Although polyradical (Fig. 1.51A) ( $n = 18$ ) was stable and 80% of the spins were generated, a low spin state was observed due to the twisting of the

intensity of biradicals follow Curie behavior down to 4 K supporting the triplet ground state or its near-degeneracy with the singlet state. After cryogenic EPR measurements and theoretical studies proved that there was no influence of position of the pyridyl nitrogen on the molecular ground state as well as on zero-field splitting (zfs) values. The crystal structure of both biradicals showed intra-radical distances of 1.54 and 1.47 nm, respectively. The approximate zfs parameter or fine structure ( $D$ ) values taken from the frozen spectra of both biradicals were  $D \sim 0.24 \times 10^{-4} \text{ cm}^{-1}$  (Fig. 1.50b). The monoradical displayed very different anisotropy spectrum with strong asymmetry in the same liquid nitrogen temperature, confirming no monoradical impurity in the biradicals. After applying

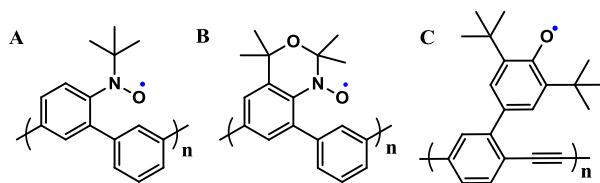


**Figure 1.51** Pendant high spin polymers based on neutral radicals. Ref 92.

observed, but the multiplicity of the ground state was not reported. Nishide and co-workers<sup>93</sup> have prepared phenoxy radicals in combination with a poly(1,4-phenyleneethynylene) backbone (Fig. 1.51C). However, only 60% of the total number of possible radicals was generated.

They have also reported a new radical polymer for use as an anode material in polymer batteries.<sup>94</sup> Their material enables, for the first time, the production of totally

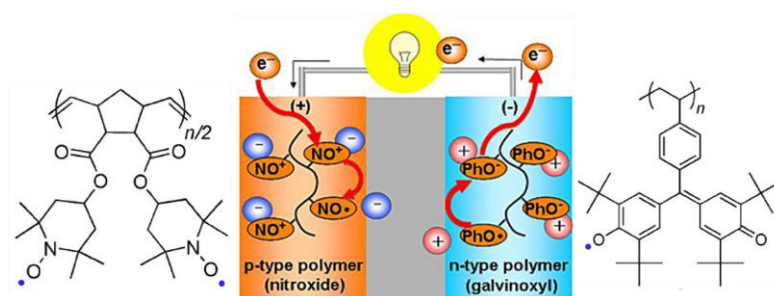


**Figure 1.52.** Schematic diagram of the operation mode of the all-organic batteries. Ref 94.

organic rechargeable batteries, which are paper thin and amenable to roll-to-roll or inkjet processing. The polymer developed by the researchers consists of a simple polystyrene backbone with aryl pendant groups known as ‘galvinoxyl’ groups. This radical gives up its electron under redox conditions, so when placed in a battery arrangement with an electron-accepting polymer (Fig. 1.52), electrons can flow around the circuit to provide power. A galvinoxyl radical is suitable for the n-type electrode-active material. These results are expected to yield wide-ranging applications like to develop a plastic-based, paper-like rechargeable device with radical polymer electrodes, which could be implanted in radio-frequency identification tags, smart cards and electronic paper.

Rajca *et al.* have shown a different strategy to prepare polymers with large magnetic moments and confirmed the ferromagnetic coupling between radical subunits.<sup>95</sup> They have described the preparation and magnetic properties of an organic  $\pi$ -conjugated polymer with very large magnetic moment and magnetic ordering at low temperature.

nitroxide moieties and subsequent antiferromagnetic intramolecular coupling. To prevent the twisting of the nitroxide radical, polyradical (Fig. 1.51B) with cyclic nitroxides was prepared and an intramolecular ferromagnetic interaction was

observed, but the multiplicity of the ground state was not reported. Nishide and co-workers<sup>93</sup> have prepared phenoxy radicals in combination with a poly(1,4-phenyleneethynylene) backbone (Fig. 1.51C). However, only 60% of the total number of possible radicals was generated.

The polymer made of a large density of cross-links and alternating connectivity of radical units with unequal spin quantum numbers ( $S$ ), macrocyclic  $S = 2$  and, cross-linking  $S = \frac{1}{2}$  modules, which allows large net  $S$  values for either ferromagnetic or antiferromagnetic exchange couplings between the modules. In the highly cross-linked polymer, usually an efficient resultant magnetic moment  $S$  of about 5000 and slow reorientation of the magnetization was found at a small magnetic field ( $< 1$  Oe) and temperature below 10 K (Fig. 1.53). This magnetic behavior is equivalent to that of insulating spin glasses and blocked superparamagnets.<sup>96</sup>

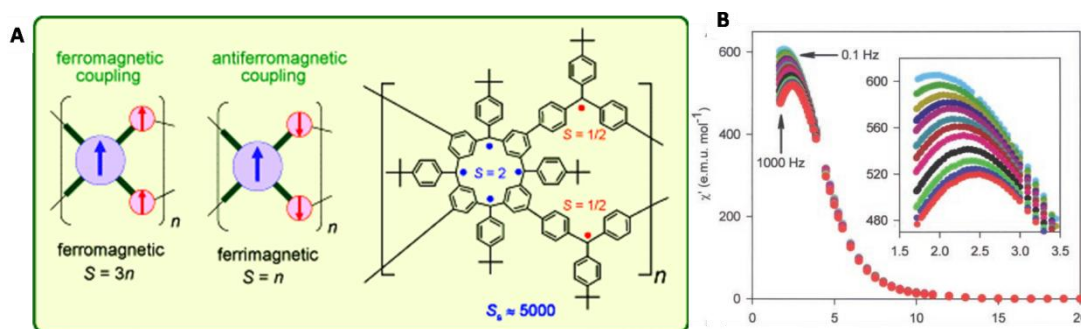


**Figure 1.53** (a) Polymer with ferromagnetic or antiferromagnetic exchange couplings between macrocyclic  $S = 2$  and, cross-linking  $S = \frac{1}{2}$  modules, the resultant magnetic moment  $S$  of about 5000. (b) Temperature dependence of the ac susceptibility  $\chi'$  of the polymer measured in the zero applied field. The ac driving field is 0.1 Oe and the frequencies are 1000, 800, 500, 250, 100, 50, 25, 10, 5, 2, 0.5 and 0.1 Hz. Ref 96.

## 1.8 Introduction to Nanoscience and Technology:

The most important discoveries of the twentieth century are mainly associated with nuclear power engineering, information technology, space exploration, nanoscience and technology, semiconducting and microprocessor technology. All the inventions and discoveries of fundamental sciences have made breakthrough contribution in applied science and technology, which influences our day to day life. Nanoscience and technology is one of the dominant research areas of 21<sup>st</sup> century. Nanotechnology is defined as: “the design, characterization, production and application of materials, devices and systems by controlling shape and size at the nanoscale”.<sup>97</sup> Recent growth in nanoscience and nanotechnology has given rise to a new generation of functional organic nanomaterials with controlled morphology and well-defined properties, which enable a broad range of applications. Richard Feynman in his famous lecture entitled “*There’s Plenty of Room at the Bottom*” talked about the possibility of nanoscale maneuvering of atoms. He predicted the possibility to create new matter at the atomic and molecular level by arranging atoms. Assembly of molecules to create functional soft materials nano/micro

scale is also one of the emerging areas in nano materials science. Molecular self-assembly is the spontaneous structurally dissimilar association of molecules triggered by non-covalent bonds, which aggregates under equilibrium conditions into stable structures. Self-assembly is also rising as a new strategy in chemical synthesis, with the potential of producing nanoscale structures with dimensions of 1 to 100 nanometers. Soft materials exist in different forms; for example, self-assembled organic nano-tubes, nanofibers, gels, liquid crystals and polymers.

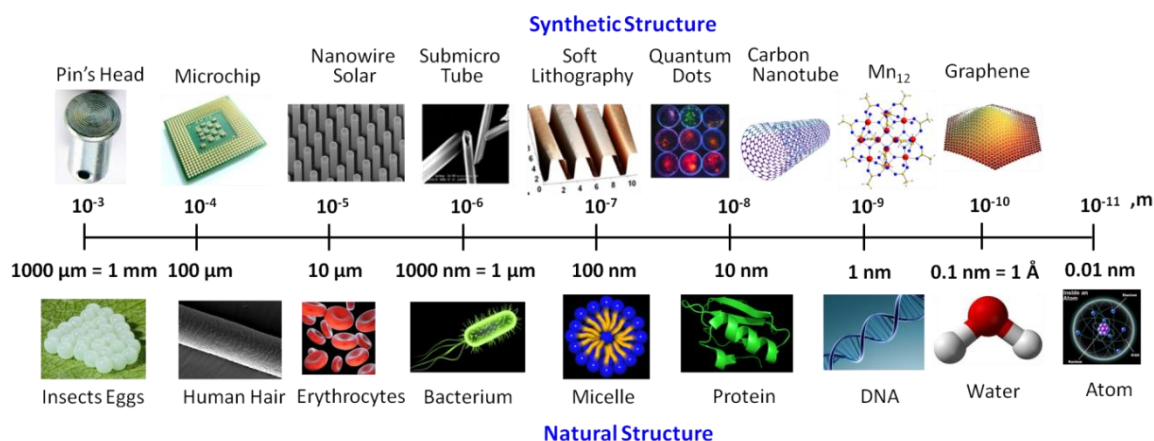


**Figure 1.54** Comparison of the size domains of naturally existing and manmade systems.

Organic nanomaterials built from small functional molecules are interesting due to their potential applications in nanoscale devices as well as their unique optical and electronic properties. As they are usually assembled from molecular units with weak intermolecular interactions, such as hydrogen bonds,  $\pi$ - $\pi$  stacking and Van der Waals force and so they have high structural tunability, reaction activity and processability that provide great opportunities to miniaturized optoelectronic components. These weak interactions allow for more facile fabrication of high class organic nanostructures using mild condition compared to inorganic counterparts. The variety of energy/electron transfer processes in organic semiconductors breaks the routine limitations of traditional photonic and electronic devices. Organic nanomaterials have already appeared to play increasingly an important role in many opto-electronic applications, such as nanolasers, optical waveguides, light-emitting devices, solar cells and smart sensors.

## 1.9 Assembly of Molecular Nanomaterials:

The controlled synthesis of nanomaterial is one of the most important and challenging topics of nanoscience and nanotechnology. Great efforts have been devoted

to the successful development of well-defined nanostructures constructed by the self-assembly of functional,  $\pi$ -conjugated molecules (Fig. 1.54). However, controlling the structure and function of micro/nanomaterials through an understanding of the role of size, shape, architecture, composition, hybridization, molecular engineering, assembly and microstructure is a difficult task.<sup>98</sup> Researchers continue to face great challenges in the construction of well-defined organic compounds that aggregate into larger molecular materials such as nano-wires, tubes, rods, particles, vesicles, sheets, walls, films and other structural arrays. The fabrication of molecular materials can be visualized in terms of two well defined steps - synthesis of the desired building blocks (molecules) from appropriate precursors (atoms/molecules) and then assembling them to form the materials of interest. A variety of methods including simple crystallization, host-guest complexation, intercalation, self assembly using layer-by-layer methodology, deposition by Langmuir-Blodgett method, electric field induced poling of doped polymers and organic molecular beam deposition technique can be employed for the fabrication of molecular materials. Molecular self-assembly is a process that involves the spontaneous organization of molecules mostly under thermodynamic equilibrium conditions into structurally well-defined and stable arrangements through primarily weak, noncovalent interactions. Designing the molecules and supramolecular entities with specific shape and architecture which causes them to aggregate into desired structures is the key issue here.

### 1.9.1 J-aggregation and H-aggregation:

Molecules assemble via J-aggregation (J for Jelly, one of the first workers who investigated these shifts) or H-aggregation (H for hypsochromic) during self-assembly process. H-aggregation is assigned by a blue shift of the absorption maximum of the compounds which indicates parallel interaction modes of the chromophores. By contrast, J-aggregation is confirmed by a red-shifted absorption band occurring due to interaction of the chromophores in a head to tail fashion. H-aggregation was observed at concentrations below the critical micelle concentration (cmc).<sup>99</sup> H-aggregation has been observed in mono-layers, LB films, bilayers, membranes and vesicles.<sup>100</sup> The self-association of molecules in solution or at the solid liquid interface is a frequently encountered incident. In nano chemistry, strong intermolecular Van der Waals like attractive forces exist between the molecules. The J-band and H-band have been elucidated by molecular exciton coupling theory, i.e., coupling of transition moments of the constituent molecules. H-aggregates are based on a sandwich-type intermolecular

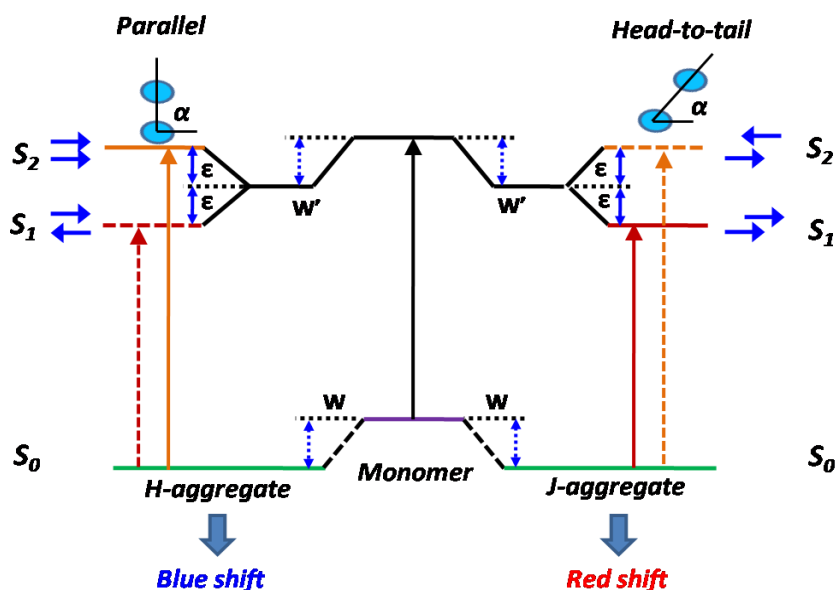


**Figure 1.55** Schematic representation of the relationship between chromophore arrangement and spectral shift based on the molecular exciton theory.

association (parallel or plane-to-plane stacking)<sup>101</sup> and characterized by light absorption at higher energies compared to the isolated molecules. J-aggregates are composed of molecular assemblies with a head-to-tail intermolecular association (end-to-end formation) and absorb light of lower energies with respect to the isolated dye molecules giving rise to the bathochromic (red) shift in the absorption band. For a simple dimer, the transition energies are given by eqn. 34.

$$\Delta E_{\text{dimer}} = \Delta E_{\text{monomer}} + D \pm \epsilon \quad \dots 34$$

Where  $\Delta E$  represents the transition energy to the excited state of the dimer or monomer,  $D$  is the dispersion energy given by  $W - W'$  in figure 1.55 and  $\epsilon$  is the interaction energy. From eqn. 34, it is clear that for a dimer, the excited energy state has two possible levels.<sup>102</sup>  $\alpha$  is the angle between the dipole vector of the molecule and the vector connecting the centers of the two molecules. The energy states are  $S_0$ ,  $S_1$  and  $S_2$ .

## 1.10 Fabrication Methods of Nanomaterials:

Over the last few decades, there has been a strong activity in the field of molecular nanomaterials resulting in the development of a wide range of protocols for the fabrication of nanostructures based on small molecules. A brief overview covering several of these techniques is presented here.

### 1.10.1 Reprecipitation Method:

The reprecipitation method had been developed by Nakanishi and co-workers in 1992 (Fig. 1.56).<sup>103</sup> After that various organic nanostructures of different classes of molecules have been fabricated using the reprecipitation method by several groups.<sup>104,105</sup> It is a solvent-exchange process – the intended compound is dissolved in a good solvent

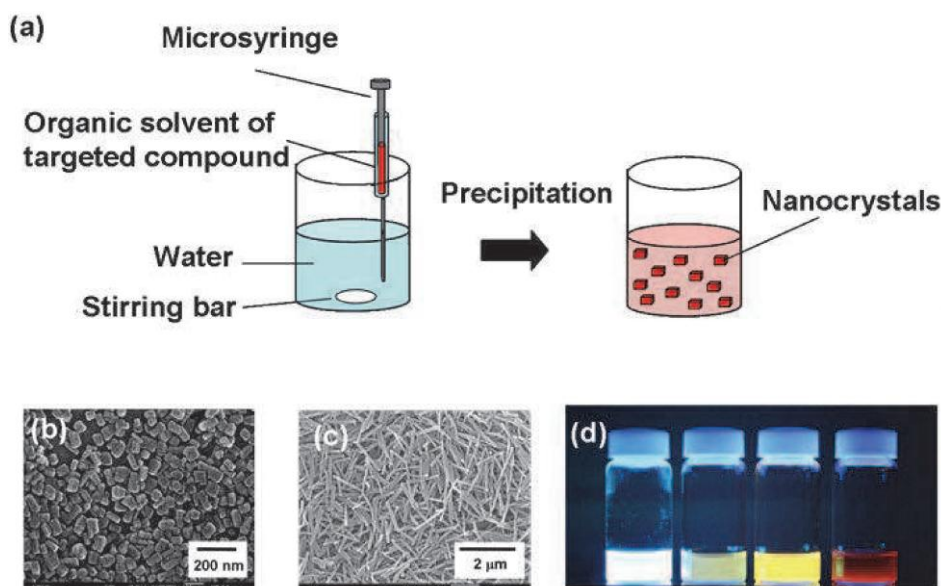


**Figure 1.56** (a) Scheme of the reprecipitation method. (b, c) Size controlled organic phthalocyanine nanocrystals. (d) Fluorescence of organic nanocrystals in water. Ref 104.

and microquantities of the solution is injected rapidly into excess of a stirred second liquid which while miscible with the first liquid, and acts as a nonsolvent or poor solvent for the compound of interest. The good solvent disperses and the sudden change in the surroundings of the molecules causes aggregation leading to the formation of nano/microstructures dispersed homogeneously in the poor solvent.

### 1.10.2 Solvent Evaporation Method:

Techniques based on controlled solvent evaporation provide another approach to fabricate molecular nanostructures from solution that exploit the principles of self-assembly. Solvent evaporation techniques can be classified into three major categories: (a) drop casting, (b) spin coating, and (c) zone casting. The polarity and volatility of the solvent, the concentration of solutions, the chain-length dependence in amphiphilic derivatives and the nature of the surface onto which solutions are to be casted play vital role in the formation of nanostructures through drop casting technique.

### 1.10.3 Vapor Deposition Method:

Vapor deposition (VD) or thermal evaporation of small organic molecules is one of the facile methods for preparing nanomaterials. This process can be classified in two types chemical vapor deposition (CVD) and physical vapor deposition (PVD). The procedure involves sublimation of a material onto a substrate, generally in vacuum (Fig. 1.57).

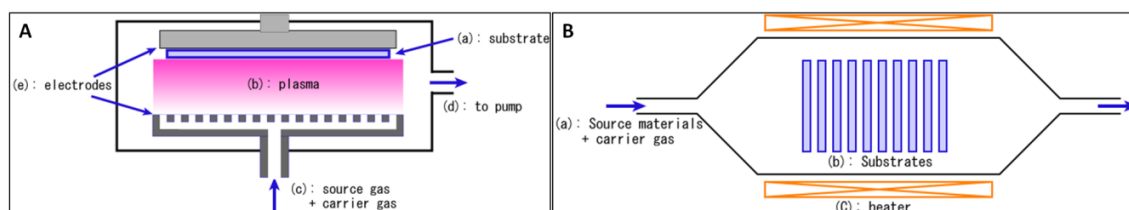


**Figure 1.57** Chemical vapor deposition (CVD) system: (a) Plasma assisted CVD (b) Thermal CVD.

This technique is applicable only to the molecules that can sublime and are stable at the sublimation temperatures. Besides the properties of the molecule itself, the principal factors that affect the size and morphology of the nanoparticles produced by this technique are the rate of evaporation, the nature of the substrate and the temperature at which the substrate is held during the deposition.<sup>106</sup> Chemical vapor deposition (CVD) is

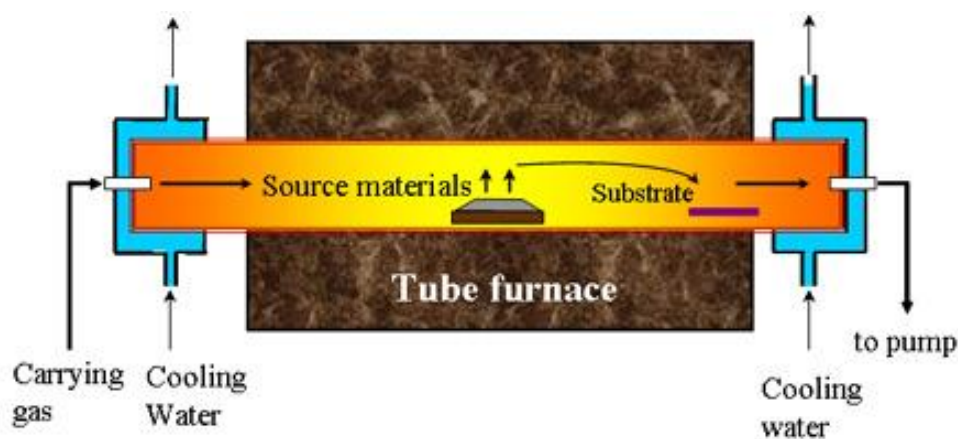


**Figure 1.58** Physical vapor deposition (PVD) system for synthesis of nanostructures. Ref 106.

a deposition process where chemical precursors are transported in the vapor phase to decompose on a heated substrate to form a film. The films may be epitaxial, polycrystalline or amorphous depending on the materials and reaction conditions (Fig. 1.58). Physical vapor deposition (PVD) describes a variety of vacuum deposition methods used to deposit thin film by the condensation of a vaporized form of the desired material onto various work piece surfaces.

### 1.10.4 Sonochemistry:

Ultrasonic waves play an important role in self-assembly of nanostructure. The influence of sonic waves travelling through liquids was first described by Wood and Loomis in 1927. It causes high-energy chemical reactions, sometimes with the emission of light. The origin of sonochemistry and sonoluminescence is acoustic cavitation, i.e. the formation, growth and implosive collapse of bubbles in liquids because of high-intensity sound. The collapse of bubbles originated by cavitation which produces extreme local heating and high pressures, with very short lifetimes (Fig. 1.59). Thus, cavitation can create unexpected physical and chemical conditions in otherwise cold liquids. The chemical effects of ultrasound do not arise from a direct interaction with molecular species. Ultrasound spans the frequencies of roughly 15 kHz to 1 GHz, with the sound velocities in liquids usually about  $1,500 \text{ ms}^{-1}$  and acoustic wavelengths range from roughly 10 to  $10^{-4} \text{ cm}$ .

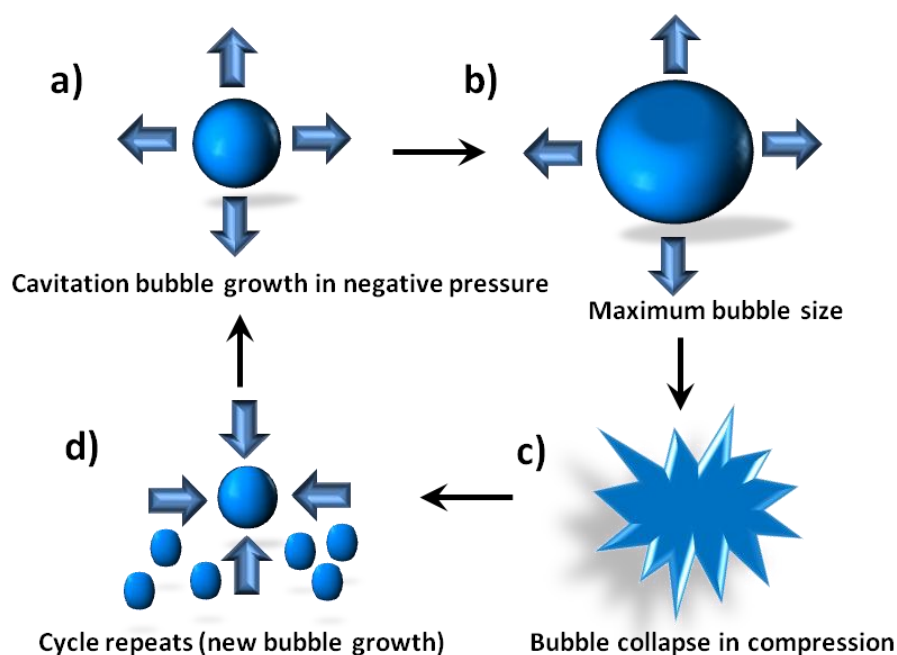


**Figure 1.59** Mechanism involved in the sonication process.

The related phenomena can occur when liquids containing solids are irradiated with ultrasound. Here the cavitations occur near an extensive solid surface and cavity collapse in non-spherical manners and forces high-speed jets of liquid into the surface. The major surface is damaged by high heat due to these jets and associated shock waves. Alternatively, ultrasonic irradiation of liquid–powder suspensions produces high velocity inter-particle collisions. Cavitations and the shock waves it creates in slurry can accelerate

solid particles to high velocities. The resultant collisions are capable of inducing striking changes in surface morphology, composition and reactivity.

Ultrasound treatment leads to collapse of the vesicles and subsequent formation of crystalline nano particles. The main mechanism of sonication is based on the cavitation phenomenon which includes the whole procedure of creation, expansion and collapsing of vesicles throughout liquid phase when negative pressure is applied to the medium during sonication. The ultrasound waves were thought to cleave the intra-molecular  $\pi$ -stacking interactions of the complexes, inducing rapid and spontaneous aggregation through interpenetrating stacking interactions. Ultrasound treatment leads to collapse of the vesicles and formation of dense bilayer structures. It has been reported by Suslick (1989) that under high intensity power ultrasonication, particles suspended in the medium move towards each other at very high velocities (of the order of 150 m/s). When these particles have a collision with each other, so much heat is produced that local melting occurs and particles get fused to each other. In this process, micro jets seem to be the cause of the high velocities attained by the particles.<sup>107</sup>

### 1.11 Nanomaterials with Diverse Morphologies:

Conjugated organic molecules are interesting building blocks for nano materials because of their structures and their electronic, electrical, magnetic, optical, biological and chemical properties. Such nanoscale materials could serve as the potential component for device fabrication. The recent progress lies in the construction of nanostructures formed through the aggregation of organic conjugated molecules and the investigation of their functional properties.<sup>108</sup> Organic conjugated molecular materials, such as organic semiconductors, with a delocalized  $\pi$ -electron system have an inherent wide band gap. Aggregated nanostructures of organic molecules have attracted significant attention during the past decade due to their promising applications in light-emitting diodes,<sup>109</sup> sensors,<sup>110</sup> photovoltaic cells,<sup>111</sup> field emitters,<sup>112</sup> and field-effect transistors.<sup>113</sup> Currently a demanding effort is to develop methods for producing organic aggregate materials with low-dimensionality such as nanowires, nanotubes and nanorods, for exploitation in optoelectronic and nanoelectronic devices. Recently, scientists have developed various techniques for synthesizing and characterizing many new organic semiconductor nanowires, nanotubes and other nanostructures with at least one of the dimensions in nanoscale. Researcher's center of attention is mainly on identifying new properties and

understanding the structure-properties relationships. However, still, the design and synthesis of novel aggregate nanostructures from conjugated organic molecules with well-defined morphology size and controlled properties is a challenging task in nanoscience and nanotechnology.<sup>114</sup>

Nanomaterials can be classified as zero-dimensional (0-D), one-dimensional (1-D), two-dimensional (2-D) and three-dimensional (3-D) materials based on their dimensions (Fig. 1.60). 0-D nanomaterials possess all the x, y, z dimensions within the nanoscale. The most common representation of zero-dimensional nanomaterial is nanoparticles. In case of 1-D material one of the dimensions is outside the nanoscale e.g.

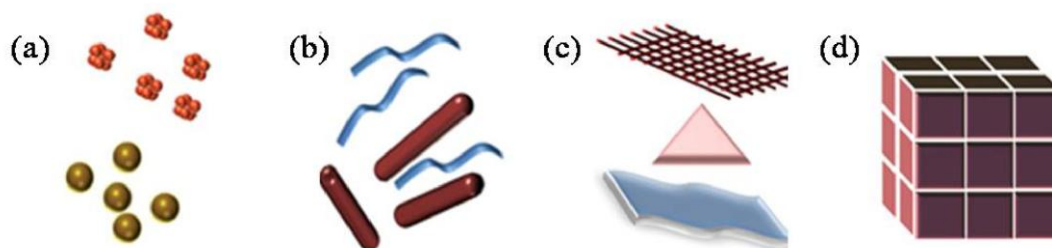


**Figure 1.60** Classification of Nanomaterials (a) 0D spheres, particles and clusters. (b) 1D nanofibers, wires, tubes and rods. (c) 2D films, plates and networks. (d) 3D nanomaterials. Ref. 115.

length, such as nanotubes, nanorods and nanowires. 2-D materials are those where two of the dimensions are not confined to the nanoscale viz. nanofilms, nanolayers and nanocoatings. Three dimensional materials are not confined to the nanoscale in any dimension, but characterized by having three arbitrarily dimensions above 100 nm.<sup>116</sup>

### 1.11.1 Nano Vesicles:

The term “vesicle” refers to hollow-structured spherical materials (HSMs) formed in aqueous solution by the self-assembly of amphiphilic molecules. While the core of the vesicle contains water, its outer shell is composed of a bilayer of the amphiphiles. HSMs, a kind of unique morphology, have been of great interest in the past decade because of the hollow vesicular architecture.<sup>117</sup> The structures have low density, large void space, large specific surface area and good biocompatibility, HSMs present promising application prospects in various fields, such as adsorption and storage, catalysis when catalytically active species are incorporated in the core and/or shell, controlled drug release, targeted drug delivery and simultaneous diagnosis and therapy of cancers when the surface and/or core of the HSMs are functionalized with functional ligands and/or nanoparticles and so on. As multifunctional vesicles have a wide application in many fields; designing these

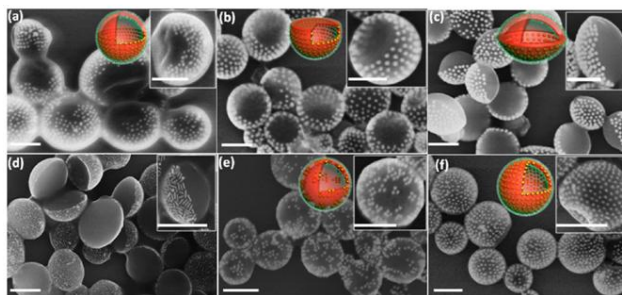


**Figure 1.61** (a) SEM images of the co-assembly of binary mixtures of MAMs and NAPAMs into hybrid vesicles with defined shape, morphology and surface pattern. (b) Spherical hybrid Patchy vesicles. (c) Spherical, (d) hemispherical. (e) disk-like shapes depending on the assembly parameters. (f) HVs with uniform distribution of NPAMs in the membrane. Ref 120.

vesicles is still a challenge. Magnetic and fluorescent vesicles were also obtained by embedding hydrophobic core-shell biocompatible magnetic nanoparticles (MNPs) made of iron oxide ( $\gamma\text{-Fe}_2\text{O}_3$  or  $\text{Fe}_3\text{O}_4$ ) and quantum dots (CdSe/ZnS) in the membrane.<sup>118</sup> The amphiphiles that form the vesicles is a surfactant molecule with a small head, hydrophilic to water and a long tail that is hydrophobic to water. When

surfactants like molecules self-assemble, it forms generally a spherical vesicular structure or film depending upon the size of head. If the entropy of the system is  $S$  and energy  $E$ , then the system likes to have a minimum value for the quantity  $G = E - TS$ , where  $G$  is the free energy of the system. If two surfactant molecules come close to each other the tails of these molecules are as close to each other to lower the energy. In other words, by reducing their interaction with water and increasing the entropy. The head of the molecules prefer to far away from each other because heads are usually charged. So they lower the energy by staying away from each other.<sup>119</sup>

Y. Lie and co-workers<sup>120</sup> have presented a new strategy to fabricate hybrid vesicles with well-defined shape, morphology and surface pattern by co-assembling molecular amphiphiles (MAMs) of block copolymers (BCPs) including inorganic nanoparticle (NP) amphiphiles (NPAMs) (Fig. 1.61). The assembly of binary mixtures produced unique hybrid Janus-like vesicles with different shapes, patchy vesicles and heterogeneous vesicles. The experimental and computational studies point out that the formation of different nanostructures is due to the interaction between the dimension mismatch of the two types of amphiphiles, the entanglement of polymer chains and the mobility of NPAMs. In addition, the entropic attraction between NPAMs plays a leading role in controlling the lateral phase separation of the two types of amphiphiles in the membranes. The multiple different amphiphiles are utilized to construct discrete assemblies and in the self-assembly of structurally complex functional materials. Recently, Ye *et al.*<sup>121</sup> have fabricated biodegradable polymeric poly(lactic-co-glycolic

acid) (PLGA) vesicles by encapsulating inorganic imaging agents (superparamagnetic iron oxide nanoparticles), manganese-doped zinc sulfide (Mn:ZnS) quantum dots (QDs) and the anticancer drug busulfan via an emulsion-evaporation method. The water-dispersible, biocompatible, drug deliverable and superparamagnetic polymer vesicles exhibited excellent colloidal stability at a range of physiological pH conditions and very high relaxivity, demonstrating ultra-sensitivity for magnetic resonance imaging and promising potential applications in nanomedicine.

### 1.11.2 Nano Tubes:

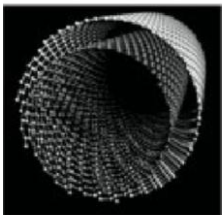
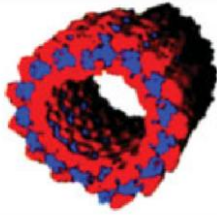
| Physical                                                                          | Supramolecular                                                                    | Chemical                                                                          | Biological                                                                          |
|-----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
|  |  |  |  |
| Multi-Wall CNT                                                                    | Graphite NT                                                                       | Lipid NT                                                                          | Microtubule                                                                         |
| i.d. = 1 ~ 10 nm<br>o.d. = 2 ~ 20 nm                                              | i.d. = 14 nm<br>o.d. = 17 nm                                                      | i.d. = 10 nm<br>o.d. = 40 ~ 50 nm                                                 | i.d. = 15 nm<br>o.d. = 25 nm                                                        |
| Carbon Atom                                                                       | Hexabenzocoronene<br>Amphiphile                                                   | Amphiphile                                                                        | Tubulin                                                                             |

**Figure 1.62** Representative nanotube structures with a hollow cylinder of ca. 10 nm wide. The profiles are classified on the basis of physical, chemical and biological view-points. The bottom column indicates the building block that makes up the tubular assemblies. The images of the carbon nanotube and the microtubule are adopted from NEC Corporation and National Partnership for Advanced Computational Infrastructure (NPACI), respectively.

After the development of carbon nanotubes (CNTs),<sup>122</sup> the one-dimensional (1D) nanostructures (nanowires, nanotubes and nanoribbons)<sup>123</sup> have attracted great attention among the scientists. The 1-D nanostructures have one dimension in the range of 1-100 nm and unlimited in the other dimension. These one dimensional structures have fascinating physical properties and many potential technological applications. The quantum mechanical effects can only occur when their size goes down to certain characteristic lengths, such as the Bohr radius ( $a_0$ ), the wavelength of incandescent light and the phonon mean-free path. The quantum mechanical effects are apparent in their optical, magnetic and electronic properties. These physical properties, along with unique transport features in the longitudinal direction and large surface-to-volume ratio, make 1D nanostructures attractive in both basic research and engineering applications (Fig. 1.62).

Further, encapsulations of guest molecules within self-assembled tubes have been attracting great interest for the development new functional materials with desired drug delivery.

Minghua Liu *et al.*<sup>124</sup> have presented a simple approach for the encapsulation of functional species within self-assembled organic nano tubes through instant gelation. Based on their unique geometric characteristics, 1D nanostructures are believed to play an important role as next generation building blocks for electronic,<sup>125</sup> photoelectronic devices, chemical or biological sensors, energy harvesting, storage, conversion and so on.<sup>126</sup> From a synthetic point of view, it is highly desirable to develop a simple route for fabricating 1D nanostructures in large scale at low cost. On the other hand, in order to transfer the intrinsic nanoscale features of individual 1D nanostructures into macroscopic scale and to realize practical applications, researchers need to investigate highly efficient and scalable assembly methods to transfer 1D nanostructures into functional macroscopic architectures.<sup>127</sup>

**1.11.2.1 Driving Force and Formation Mechanism of Soft tubes:** Generally, the self-

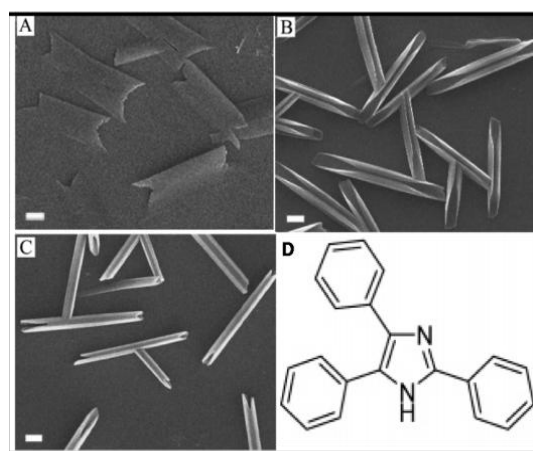


**Figure 1.63** Rolling mechanism involved in the growth of submicrotubes. SEM images of TPI submicrotubes ripened for different time prepared at 25 °C. (A) Without ripening. (B) Ripened for 5 min. (C) Ripened for 30 min. (D) Chemical structure of 2,4,5-triphenylimidazole (TPI). All the scale bars correspond to 250 nm.

assembly of  $\pi$ -conjugated aromatics that form 1-D nanostructures like wires, rods, belts and tubes takes place via supramolecular interactions<sup>128</sup> (Van der Waals interaction, hydrogen bond, coordination bond and  $\pi$ - $\pi$  stack). Controlling and understanding the growth<sup>129</sup> of an organic soft matter into a shape-defined nanotubular configuration (cylindrical, hexagonal,<sup>130</sup> rectangular,<sup>131</sup> and parallelepipedic<sup>132</sup>) is itself a challenging area. In the last decade, much attention has been paid to the development of crystalline one-dimensional (1D)  $\pi$ -conjugated organic/inorganic micro- or nanostructures

for their promising applications in electronic and optoelectronic devices.<sup>133</sup> There are several ways have been discussed in the literature for the formation of tubules. The growth of single crystalline submicrotubes for a small organic functional molecule, 2,4,5-

triphenylimidazole (TPI), shows their evolution from lamellar structures through the rolling mechanism (Fig. 1.63).<sup>134</sup> The SEM characterizations indicated that the tubes were obtained from the rolling from two-dimensional sheet-like structure. SEM images displayed the growth of the submicrotubes with the time during sonication. At the beginning the TPI molecules have a tendency to form a sheet-like structure (Fig. 1.63A) and the lamellar structures are partly rolled at the two sides after 5 min ripening (Fig. 1.63B). Finally the hollow tubes are formed after ripened for 30 min in ultrasound (Fig. 1.63C). This suggests that the formation of the tubes is result of curling of sheet-like structure.

There are reports available for the formation of rod like structures and etching or dissolution by solvents through the inner core of the structures. Etching starts at the center of the solid nanorods, continues towards the interior along the length axis and thus gradually converts the solid nanorods to microsemitubes and finally to completely hollow tubular structures (Fig. 1.64).<sup>135</sup> A simplistic route to produce single crystal [2-(p-dimethylamino phenyl)ethenyl]phenylmethylenepropanedinitrile (DAPMP) microtubes was reported with a typical rectangular cross section. DAPMP is an

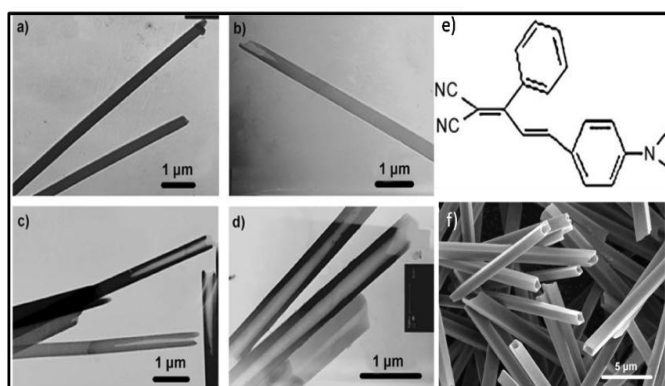


**Figure 1.64** Etching mechanism involved in the formation of microtube. TEM images of DAPMP samples obtained after stirring for (a) 1 min. (b) 10 min. (c) 30 min. (d) 4 h. (e) Chemical structure of DAPMP. (f) SEM images of microtubes. Ref 135.

intramolecular-charge-transfer compound and is recognized as an ideal compound for nonlinear optical materials. The formation of this microtube is characterized by etching mechanism.

**1.11.2.2 Magnetic Inorganic 1-D Nanostructures:** Tenne and co-workers have prepared inorganic nanotubes composed of molybdenum and tungsten sulfides.<sup>136</sup> The synthesis of BN nanotubes has also received much attention because of its structural resemblance with graphite.<sup>137</sup> In the last few years, nanotubes of several inorganic materials including binary oxides, nitrides, halides as well as metals and non-metallic elemental materials have been prepared and studied. Magnetic nanotubes attracted great interest because of

their strong magnetic responsiveness and wide applications like magnetic resonance imaging, environmental remediation and so on. One of the challenging

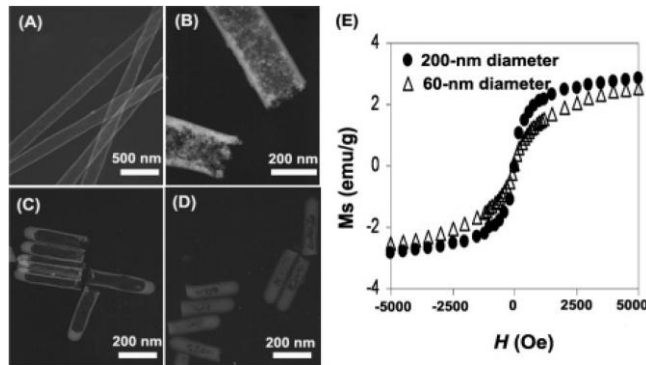


**Figure 1.65** Transmission electron micrographs (TEM) of silica nanotubes (A, B) 200 nm. (C, D) 60 nm diameter. silica nanotubes (A, C) without magnetite. (B, D) magnetic nanotubes (MNTs) with magnetite. (E) room-temperature magnetization curves of MNTs. Ref 140.

applications. Korneva *et al.*<sup>138</sup> have produced magnetic nanotubes by filling carbon nanotubes with paramagnetic iron oxide nanoparticles via chemical vapor deposition. Zhang *et al.*<sup>139</sup> have synthesized magnetic poly(cyclotriphosphazene-co-4,40-sulfonyldiphenol) (PZS) nanotubes with magnetic phases embedded in the walls by ultrasonic irradiation via an in situ template approach. Lee *et al.*<sup>140</sup> have synthesized silica nanotubes by using porous alumina film as template (60 and 200 nm pore diameters) with a layer of magnetite ( $\text{Fe}_3\text{O}_4$ ) nanoparticles on the inner surface of the nanotube (Fig. 1.65).

Cao *et al.*<sup>141</sup> have been reported the preparation and growth mechanism of Ni, Co and Fe nanotubes. The Curie temperatures of ferromagnetically ordered Fe, Co and Ni tubes are 1043 K, 1403 K and 631 K, respectively. In fact the nanotubes are constructed from non-layered materials of the metal and the tubular growth is directed by the current in the template-based electrodeposition process. Ordered magnetic Ni nanotubes have been prepared by utilizing electrodeposition by adding an amphiphilic triblock copolymer to the electrodeposition solution.<sup>142</sup> The tubes are about 50 nm in wall thickness, 60 mm in length and an outer diameter of 250 nm.

Ferromagnetic  $\gamma\text{-Fe}_2\text{O}_3$  nanotubes have been produced by a template based procedure with the help of a high magnetic field.<sup>143</sup> The prepared nanotubes are polycrystalline in nature, with a cubic spinel structure, lengths of about 30  $\mu\text{m}$ , a wall thickness of 20 nm and a diameter in the range of 300–400 nm.  $\alpha\text{-Fe}_2\text{O}_3$  is first produced

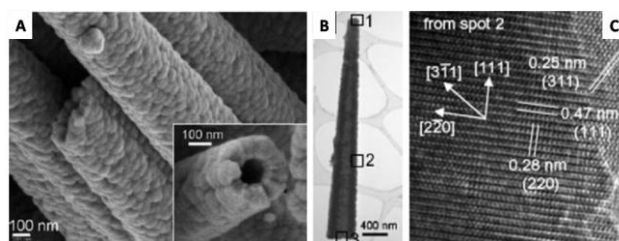


**Figure 1.66** (a) FE-SEM images of needle-like  $\text{Co}_3\text{O}_4$  nanotubes. (b) Low-magnification TEM image of an individual needlelike  $\text{Co}_3\text{O}_4$  nanotube. (c) HREM images taken from spots 2. Ref 144.

at 500 °C by thermal decomposition of  $\text{Fe}(\text{NO}_3)_3$  inside the porous alumina template and then  $\alpha\text{-Fe}_2\text{O}_3$  is transformed into  $\gamma\text{-Fe}_2\text{O}_3$  in the presence of a high magnetic field. Needle-like  $\text{Co}_3\text{O}_4$  nanotubes have been prepared by employing a one-step self-supported topotactic transformation of nano needles of  $\beta\text{-Co}(\text{OH})_2$  (Fig. 1.66).

The nanotubes are 10 mm long with a variable diameter in the range of 150–400 nm.<sup>144</sup>  $\text{Fe}_3\text{O}_4$  and  $\text{Co}_3\text{O}_4$  nanotubes are stable in aqueous solutions and are used in magnetic resonance imaging (MRI).

## 1.12 A Brief Overview of Soft Lithographic Techniques:

The interest of unconventional techniques for nanofabrication has grown exponentially in recent years due to the requirements in micro/nanoscale structures for photonics,<sup>145</sup> microfluidics,<sup>146</sup> biotechnology,<sup>147</sup> and electronics.<sup>148</sup> In some areas, the fabrication processes involve using or modifying conventional tools which have been used in micro-electronics such as photolithography,<sup>149</sup> or electron-beam lithography.<sup>150</sup> There are several drawbacks in these conventional tools, (i) the equipment setup cost is high; (ii) the fabrication process is mostly limited to two dimension material; (iii) the materials to be processed is limited (viz. silicon or metallic); (iv) ultraflat substrates are required; and (v) achieving high resolution is challenging. One of the alternative lithography techniques is called soft lithography. This technique uses organic soft materials such as polymers or self assembled monolayers to perform replication and pattern transfer. Soft lithographic methods use elastomeric stamps, molds and conformable photomasks as patterning elements. Soft lithography provides many advantages that are unavailable with conventional techniques such as patterning at molecular scale resolution ( $\sim 1$  nm),<sup>151</sup> ability to form three-dimensional (3D) structure directly in a single step,<sup>152</sup> experimental simplicity, economy and applicability to large areas.

### 1.12.1 Types of Soft Lithography Techniques:

Soft lithographic techniques can be divided into four major categories i) replica molding, ii) UV molding, iii) embossing and iv) printing, each consists of sub-groups of techniques.

**1.12.1.1 Replica Molding (RM):** Replica molding is a process in which replication of the pattern from a rigid master or soft master takes place into a polymer called poly(dimethylsiloxane) (PDMS). First a photo or thermally curable prepolymer is poured onto the master. The liquid prepolymer takes the shape of the master and it is

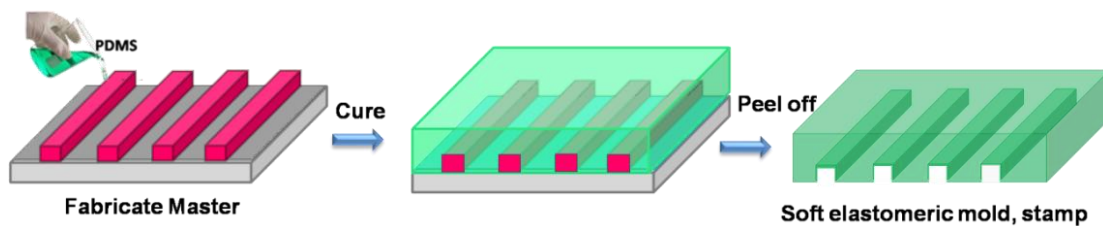


**Figure 1.67** Schematic illustration of the procedure involved in the fabrication of 'soft' elements (stamp) for soft-lithography.

solidified/cured by UV radiation or suitable temperature through cross linking, making the polymer solid. Peeling off the mold from the master creates a reverse replica of the master. The schematic representation of the process described in [figure 1.67](#). The use of a soft PDMS mold as a master in molding has advantages, such as low surface energy of the PDMS mold, allowing the release easily. It is possible to transfer 30 nm lateral features from a diffraction grating by replica molding.<sup>153</sup> The smallest features replicated till now using PDMS are  $\sim 3$  nm wide structures<sup>154</sup> and  $\sim 0.5$  nm vertical deflections.<sup>155</sup> Replica molding against a rigid mold has been used for the mass-production such as compact disks (CDs),<sup>156</sup> diffraction gratings,<sup>157</sup> holograms<sup>158</sup> and micro-tools.<sup>159</sup> Three techniques related to RM are: i) microtransfer molding ( $\mu$ TM), ii) micromolding in capillaries (MIMIC) and iii) lithographically controlled wetting (LCW).

**1.12.1.1.1 Microtransfer Molding ( $\mu$ TM):** In this process at first a liquid pre-polymer, such as polyurethane (PU) or thermally curable epoxy is placed on the patterned surface of the mold (PDMS) and the excess pre-polymer is removed. The most general procedure for removing excess polymer is to scrape it away using a piece of flat PDMS; alternatively, with appropriate structures,

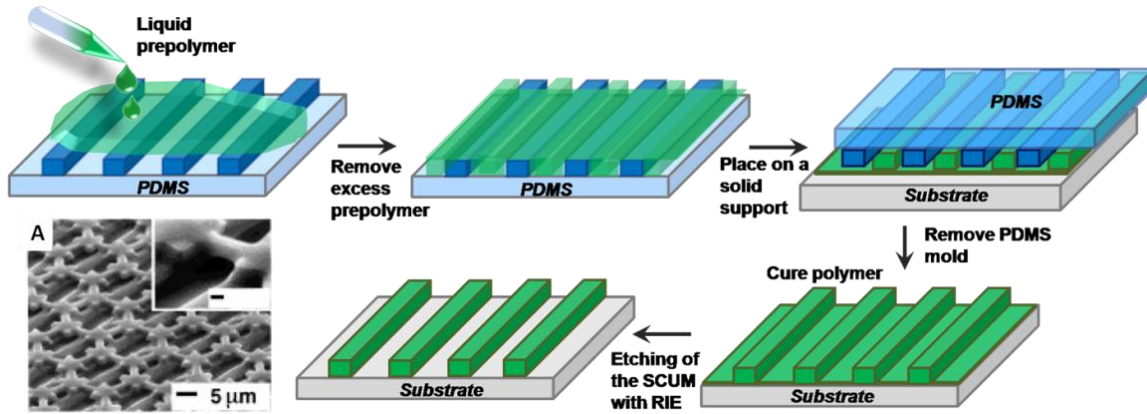


**Figure 1.68** Schematic illustration of the procedure involved in the fabrication of 'soft' elements by microtransfer molding ( $\mu$ TM). (A) SEM images of polymeric microstructures fabricated by  $\mu$ TM. Ref 160.

the excess polymer can be removed by blowing it off from the surface of the mold with a brisk stream of nitrogen. The filled mold is placed in contact with a substrate. The prepolymer is then fully cured thermally or photochemically and the mold is peeled away (Fig. 1.68). It can be used for building 3D microstructures by stacking several layers.  $\mu$ TM has applications in gratings,<sup>160</sup> polymeric waveguides<sup>161</sup>, tissue engineering<sup>162</sup> etc.

**1.12.1.1.2 Micromolding in Capillaries (MIMIC):** In MIMIC, an elastomeric PDMS mold surface protrusions is placed against the substrate surface to form channels. The open ends of channels are filled with liquid ink, which will be sucked into the channels by capillary forces. Materials from the solution can also be deposited (thermal or UV curing

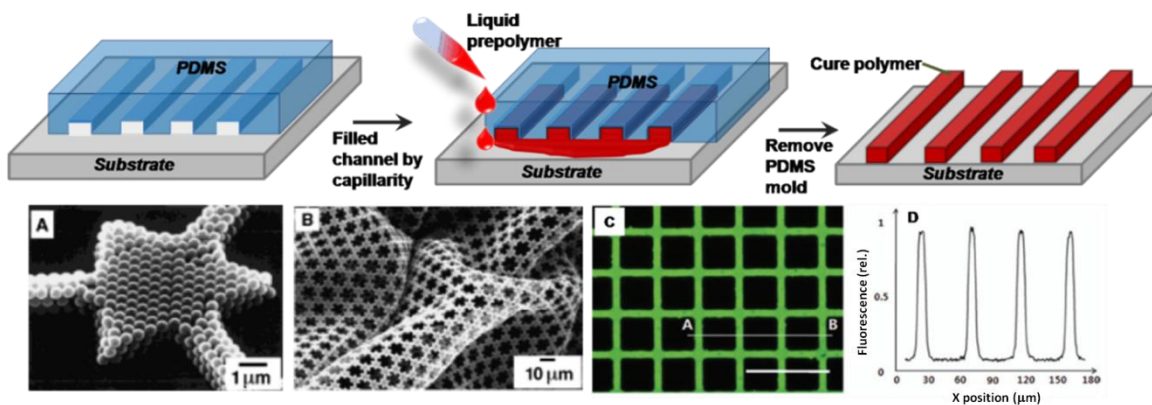


**Figure 1.69** Schematic illustration of the procedure for fabricating 'soft' elements by Micromolding in Capillaries (MIMIC). (A) SEM images of patterned microstructures of polymer beads fabricated by MIMIC from their solutions in water. (B) SEM images of polymeric microstructures fabricated by MIMIC from prepolymer of polyurethane without solvents. (C) Fluorescence images. (D) Fluorescence Intensity profiles of 10 mm-wide grid FITC-labeled poly-L-lysine (PLL-FITC), which was patterned with micromolding in capillaries (MIMIC) (Scale bar is 100 nm). Ref 164.

of polymer or deposition of colloids, salts). After deposition the elastomeric mold is peeled off (Fig. 1.69).<sup>163</sup> The only serious restriction of MIMIC is the need for a hydraulic

network between channels, so they can be filled. Gas from the closed end of the capillaries can escape by diffusing into the PDMS. The rate of filling is depending on the interfacial free energy and the viscosity of liquid.<sup>164</sup>

**1.12.1.1.3 Lithographically Controlled Wetting (LCW):** This technique involves placing an elastomeric stamp on a drop of ink solution spread on the surface; the stamp's protrusions come into contact with the surface, protecting these areas gives a thin layer cell in the recesses. Because the ink solution

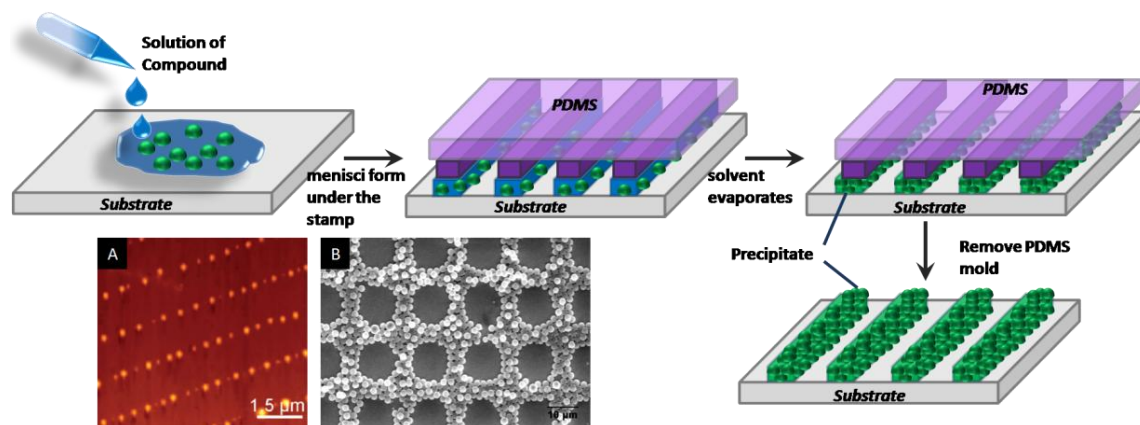


**Figure 1.70** Schematic illustration of the procedure for fabricating 'soft' elements by Lithographically Controlled Wetting (LCW). (A) AFM image of patterned  $\text{Mn}_{12}$  SMM on Si(100) wafer surface. Ref 165. (B) SEM image of PS particles assembled into a square pattern on glass with dimensions similar to the deposition templat, the home constructed TEM grid cell. Ref 166.

only reacts with the surface under the stamp recesses, a patterned substrate is obtained as a negative replica of the elastomeric stamp. LCW exploits the capillary forces of menisci established under the protrusions of a stamp placed in contact with a liquid film. In the space confined by each meniscus, the self-organization of the deposited solute forms highly ordered structures that replicate the motif of the stamp protrusions (Fig. 1.70). Compared with other printing methods, LCW is universal for soluble materials, as it does not require any chemical binding or other specific interactions between the solute and the surface.<sup>165, 166</sup>

**1.12.1.2 UV-Molding:** Ultraviolet-molding (UV-molding) technique differs slightly from the three RM techniques. It usually uses a rigid master, even though a soft PDMS master can be used as well. The curing in MIMIC and  $\mu\text{TM}$  is usually done with a rise in temperature, but for UV-molding UV radiation is utilized and thus a UV-curable prepolymer is used. The prepolymer is casted onto a master and a transparent substrate is

placed on top of it, resembling  $\mu$ TM technique. In figure 1.71, a process is presented, in which the UV radiation is exposed to the prepolymer mixture through a transparent substrate.

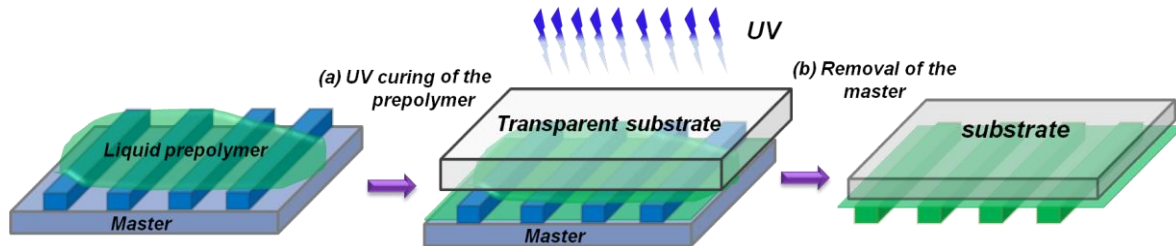


**Figure 1.71** Ultraviolet-molding (UV-molding).

**1.12.1.3 Embossing (Imprinting):** Embossing is the procedure of imprinting a pattern into a primarily flat solid surface by pressing a mold and softening the surface. Conventional embossing uses a rigid master (for example, a master made of nickel or  $\text{SiO}_2$ ) to imprint relief structures into a thermoplastic polymer (for example, polycarbonate or PMMA) that has been thermally softened.<sup>167</sup> It is a simple and cost effective process and is the standard for manufacturing replicas of holograms, diffraction gratings and compact disks (CDs). This technique can also be used for microelectronic circuitry or information storage.<sup>168</sup> Embossing techniques can be divided into two categories i) nanoimprint lithography (NIL), which uses a rigid master and ii) solvent assisted micro molding (SAMIM) (Fig. 1.72), which uses a soft mold as a master. In this process a thin layer, typically 10 nm, of

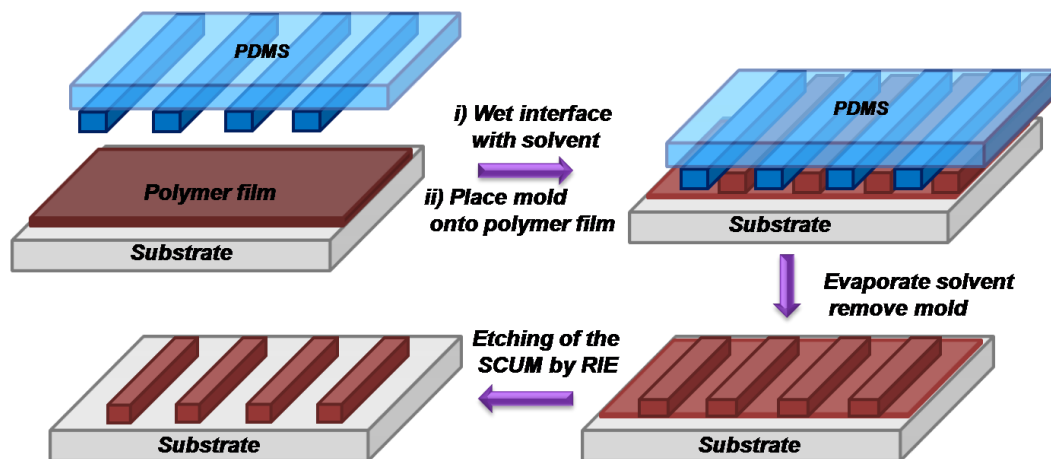


**Figure 1.72** Solvent assisted micro molding (SAMIM).

polymer is left between the features as in replica molding. This can be removed by O<sub>2</sub> reactive-ion etching (RIE).

**1.12.1.4 Printing:** Printing includes material transfer from the mold onto the substrate either physically or chemically. It can be subdivided in following two categories.

**1.12.1.4.1 Microcontact Printing:** In microcontact printing the surface features of a stamp can be patterned onto a substrate. The stamp is inked with a suitable solution and placed in contact with the substrate to be printed. The stamp makes a conformal contact with the

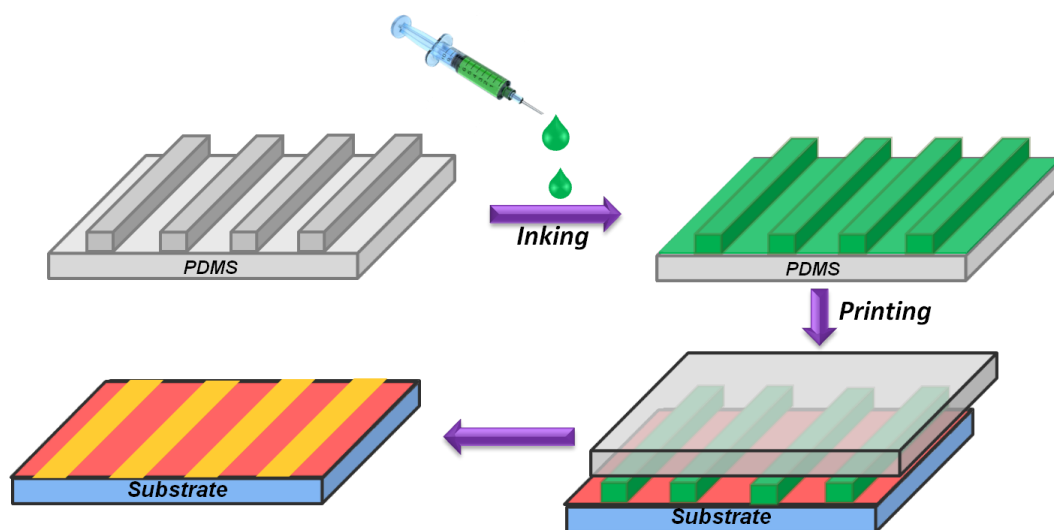


**Figure 1.73** Micro contact printing ( $\mu$ CP).

substrate, so that only the projecting features of the stamp touch the surface and in an ideal case the ink is transferred only at these areas. For the stamp material usually PDMS is used. The pattern of the original master is thus transferred onto the substrate (Fig. 1.73). The best-known example of microcontact printing is the printing of self assembled monolayer (SAM) of alkanethiolates onto the areas of a film of noble and near-noble metals. The first  $\mu$ CP was originally used as a method to pattern gold developed by Whitesides and his coworkers.  $\mu$ CP has been broadly used by researchers in differing fields to pattern water,<sup>169</sup> organic solvents,<sup>170</sup> DNA,<sup>171</sup> proteins,<sup>172</sup> metals,<sup>173,176,209a</sup> polymers,<sup>174</sup> and cells.<sup>175</sup>

**1.12.1.4.2 Nanotransfer Printing:** Nanotransfer printing (nTP) is an additive technique of printing micro- and nanoscale features onto a substrate, without etching steps. Nanotransfer printing (nTP) is conceptually very similar to microcontact printing ( $\mu$ CP). In both the cases high-resolution stamps are used to generate patterns of their relief

structure. nTP technique relies on the principle of surface chemistry. Here chemically modified surfaces act as interfacial "release" or "glue" layers to aid in transfer printing nanostructured metal ink from relief features ("stamp") to a surface of interest. Rogers *et al.*<sup>176</sup> have developed this method and similar approach has been followed by other groups.<sup>177</sup> This method is quite practical to fabricate complex structures in large stacks of nanochannels, which are difficult to fabricate by following in conventional ways.

### 1.13 Magnetic Compound Lithography:

Mannini *et al.* have reported the characterization of the monolayer obtained both by self-assembling and microcontact printing of a paramagnetic di-alkyl sulfide nitronyl nitroxide derivative, 11-decyl sulfanyl-undecanyl nitronyl nitroxide (Fig. 1.74A). There the sulfide unit attaches the molecule to the gold surface via Ag-S bond formation. The

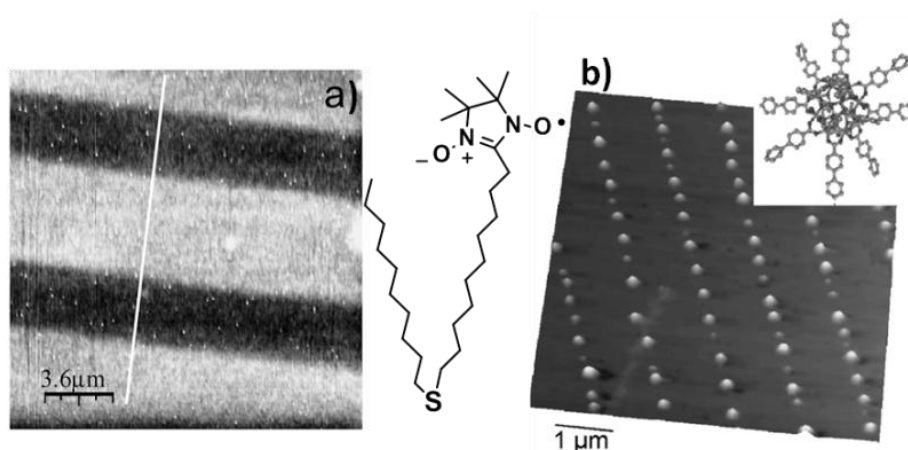


**Figure 1.74** (a) AFM image of 11-decyl sulfanyl-undecanyl nitronyl nitroxide microcontact printed in stripes on gold with a PDMS stamp. Ref 178. (b) AFM image of  $\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CC}_{12}\text{H}_9)_{16}(\text{H}_2\text{O})_4$  printed on  $\text{SiO}_x$  surface by LCW. Ref 179.

two long alkyl chains have been introduced to enhance the packing order of the molecules in a self assembled monolayer structure.<sup>178</sup> Cavallini *et al.* have fabricated arrays of single-molecule magnets derived from  $\text{Mn}_{12}$  complexes  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CC}_{12}\text{H}_9)_{16}-(\text{H}_2\text{O})_4]$  in nanometer scale aggregates (Fig. 1.74B). It can be patterned on large areas by self-organization supported by stamps on a surface in a dewetting regime. The size and distance of the molecular aggregates are controlled by deposition and capillary forces. The method suggested the possibility to patterning of single-molecule magnets for ultra-high-density magnetic storage and quantum computing.<sup>179</sup>

In 2011, Wernsdorfer and co-workers have presented an original spin-valve device wherein a non-magnetic molecular quantum dot which is made of a single-walled

carbon nanotube (SWCNT) in contact with non-magnetic electrodes.<sup>180</sup> This SWCNT coupled through supramolecular interactions to TbPc<sub>2</sub> single-molecule magnets (Pc = phthalocyanine) (Fig. 1.75). Their localized magnetic moments lead to a magnetic field, the resultant magnetoresistance ratios equal to 300% at temperatures less than 1 K, depending on the electrical transport through the single-walled carbon nanotube. This experiment demonstrated the functionality of a supramolecular spin valve without magnetic leads in new spintronic devices with quantum properties. The essential part of molecular spintronics is to resolve the spin character of molecular orbitals interacting

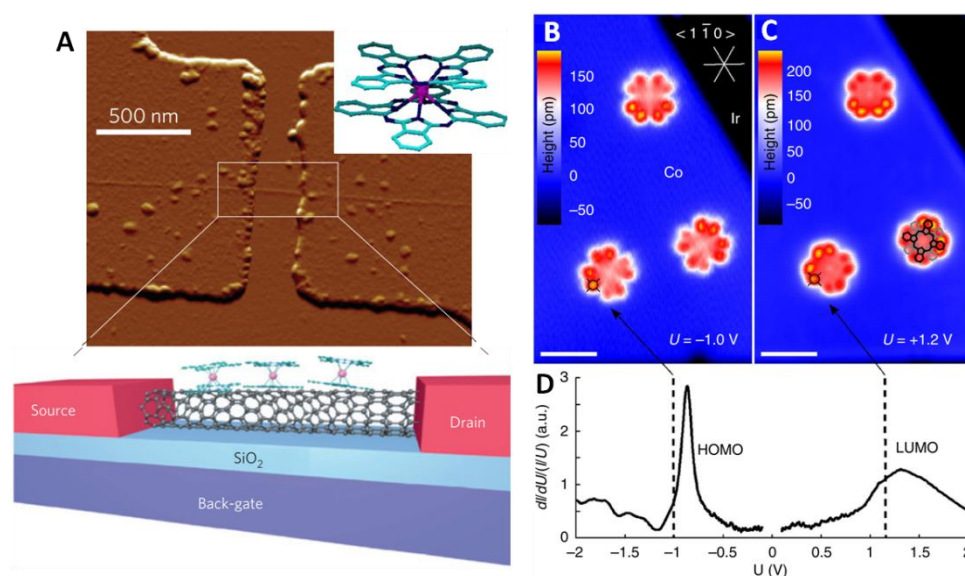


**Figure 1.75** (a) Top, atomic force micrograph of the supramolecular spin valve. The single-walled nanotube lies on a SiO<sub>2</sub> surface supported by a back gate and is connected to palladium source and drain electrodes. d, Bottom, scheme of the supramolecular spin-valve architecture. Inset TbPc<sub>2</sub> structure. (b, c) spin-averaged STM topographs of three TbPc<sub>2</sub> molecules on cobalt islands on Ir. The bias voltage is chosen to image either the HOMO (b) or the LUMO (c). In c, one molecule is overlaid with a model of TbPc<sub>2</sub> with the upper Pc ring drawn in black and the lower one in grey. White scale bars correspond to 2 nm. (d) spin-averaged differential tunnelling spectroscopy, normalized by dividing by  $I/U$ . Ref 180.

with ferromagnetic leads. They have also shown the direct real-space images of spin-split molecular orbitals of a single-molecule magnet adsorbed on a ferromagnetic nanostructure. The magnitudes of the spin-splitting as well as the charge state of the adsorbed molecules were determined quantitatively.

### 1.14 Optical Wave Guiding:

Optical fiber can be used as a medium for telecommunication and computer networking because it is flexible and can be bundled as cables. It is especially advantageous for long-distance communications, because light propagates through the

fiber have many application in electrical cables, remote sensing, medical sciences and so on.

### 1.14.1 Total Internal Reflection (TIR):

Total internal reflection is a phenomenon that happens when a propagating wave strikes a medium boundary at an angle larger than a particular critical angle with respect to the normal to the surface. It can only happen when light travel from optically denser to a rarer medium. The principle behind the fiber optics is total internal reflection. The light can be transmitted inside the optical fiber with almost no loss because of TIR. The condition of TIR satisfies even when the light pipe is bent into a complicated shape. So the light transmitted from one end to the other end practically undiminished except small losses due to reflection at the ends and absorption within the fiber.

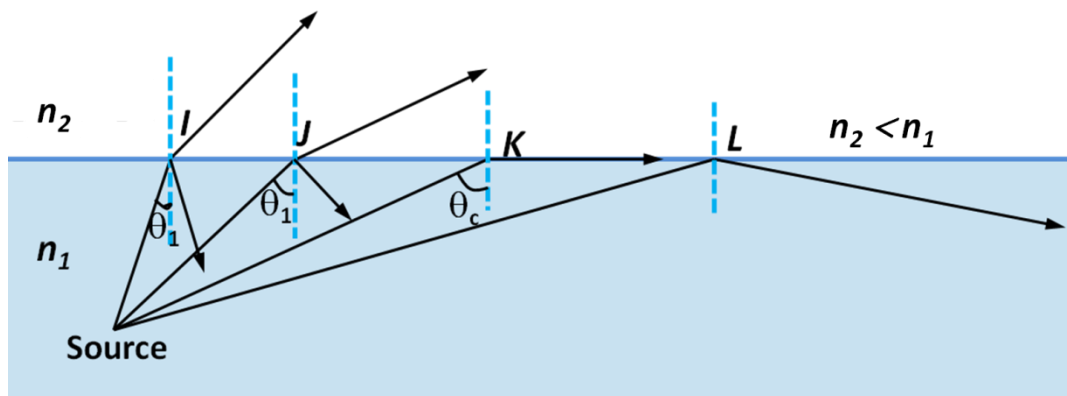


**Figure 1.76** Since  $n_1 < n_2$ , lights rays are totally internally reflected if the incident angle  $\theta_1 < \theta_c$ , as for rays I and J, only a part of the light is reflected, and rest is refracted.

When a ray of light is incident at the interface of two media (like air and glass), the ray undergoes partial reflection and partial refraction as shown in figure 1.76. The vertical dotted line represents the normal to the surface. The angles  $\theta_1$  and  $\theta_c$  represent the angles that the incident ray make with the normal. If a ray is incident at the boundary of a rarer medium ( $n_2 < n_1$ ), the ray will bend away from the normal. The angle of incidence, for which the angle of refraction is  $90^\circ$ , is known as the critical angle and is denoted by  $\theta_c$ .

$$\theta_1 = \theta_c = \sin^{-1} \frac{n_2}{n_1} \quad \dots\dots 35$$

Thus, when the angle of incidence exceeds the critical angle (i.e., when  $\theta_1 > \theta_c$ ), there is no refracted ray and total internal reflection occurs.

### 1.14.2 Optical Wave Guiding in 1D Structures:

Charles K. Kao first time proposed the possibility of optical telecommunication using high purity silica glass fibers for long range optical communication in 1960.<sup>181</sup> He was honored with Nobel Prize in physics in 2009 for his "*groundbreaking achievements concerning the transmission of light in fibers for optical communication*".



**Figure 1.77** Silicon optical fiber.

Silicon optical fibers are much thicker than human hair ( $> 60 \mu\text{m}$ ) and the refractive index ( $n$ ) of the core is greater the cladding hence light is longitudinally transmitted within the core by total internal reflection (TIR). After discovery of the silicon optical fiber, scientists have extensively studied waveguiding behavior of several diamagnetic compounds (Fig. 1.77). They can be classified into three category i) organic<sup>182</sup> ii) inorganic<sup>183</sup> and iii) semiconducting.<sup>184</sup> Organic based waveguides can further be sub divided into two category a) small molecule based and b) polymer based.<sup>185</sup> Organic waveguides have been attracting a vast attention among the scientific community due to their easy structure tunability. Photonic-crystal waveguides<sup>186</sup> are based on the influence of periodic variation in the dielectric constant which is present in a material on the photonic modes. Organic wave guides are further classified into active<sup>188-190</sup> or passive<sup>193-194</sup> based on the nature of optical wave it propagates. The mechanism of active organic wave guides is electronic excitation of pi-conjugated organic solids which leads to the propagation of coupled exciton-polariton (Exciton: electron-hole pair; Polariton: coupling of the electromagnetic radiation with exciton pair). Passive organic waveguides propagates most of the source input light directly to output end along the 1D organic solid.

Organic wave guides from small molecules can play an essential role in many miniaturised device applications, i.e., in opto-electronic applications and integrated photonic circuits replacing classical inorganic materials. Although waveguides are essential in guiding light along nanoscale photonic devices, they suffer from optical losses caused by the coupling of light into the waveguide as well as inefficient light propagation along their lengths. Optical fibers for example rely on the total internal reflections of light at the interface between the fiber core and its cladding materials.

Although this works very well for the relatively large optical fibers, they are less advantageous on the scale of integrated photonic circuits, where the light reflected from the internal surface of the waveguide interacts with the device substrate, significantly increasing losses. Therefore, rather than using solid waveguides, hollow microtubes may serve as better alternatives because they offer a tighter confinement of light. The air medium inside the hollow tubes illustrates a significant role for reducing the optical losses. Now, researchers have developed a synthetic process to achieve the self-assembly of tubular waveguide structures from light-emitting dye compounds. The length and diameter of the tubes can be controlled during the preparation process.

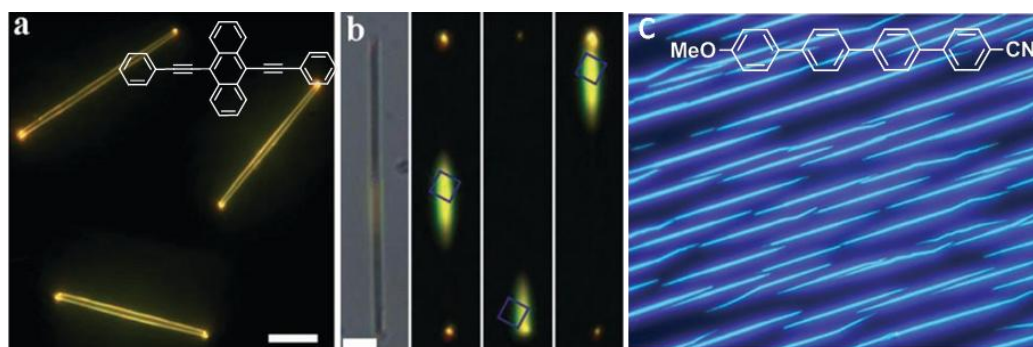


**Figure 1.78** (a) PL microscopy image of some isolated 9,10-bis(phenyl-ethynyl)anthracene (BPEA) tubes excited with blue light (460–490 nm). Scale bars are 20 mm. (b) Bright-field image and micro-area PL images obtained by exciting the identical tube at three different positions. Scale bar is 10 mm. Ref 191. (c) Organic nanofibers from *para*-phenylenes.  $135 \times 100 \text{ mm}^2$  fluorescence microscopy image (excitation wavelength 365 nm) of mutually parallel, blue-light-emitting methoxy-cyano-p-quaterphenyl-ene (MOCNP4) fibers on muscovite mica. Ref 187.

Rubahn,<sup>187</sup> Takazawa,<sup>188a,b</sup> Yao<sup>189</sup> groups have extensively studied the guided photoluminescent (PL) behaviour along extended organic solids (fibres and tubes) which are called active organic optical wave guides.<sup>190</sup> Here, the wave length of the output light is longer than the input light due to electronic excitation of molecular building blocks and resultant fluorescence. To couple light efficiently with the waveguides, a laser beam having excitation at the absorption region of the wave guiding material is used. The laser light is absorbed and consequently emitted at the low energy region, which then propagates along the waveguide. The losses in light propagating along the tubes are found to be much smaller than for comparable solid microrods. Unlike for solid waveguides the main losses are not related to the substrate but are due to the continued absorption and reemission of the light along the path.

Yao and co-workers<sup>191</sup> have prepared hollow tubular structures from a low-molecular-weight organic compound (9,10-bis(phenylethynyl) anthracene, BPEA). The

PL image shown in [figure 1.78A](#) indicates that BPEA microtubes display yellow emission, with a very bright luminescence output at both ends and relatively weaker emission from the bodies of the tubes. [Figure 1.78B](#) shows the PL images at different points along a single BPEA microtube and the excitation laser beam. This clarifies that the tubes absorb the excitation light and propagate the PL emission toward the ends.

Rubahn *et al.* have worked on the active wave guiding properties of linear *para*-phenylene compound, which was self-assembled by following bottom-up approach ([Fig. 1.78C](#)). They designed molecular building blocks with specific optoelectronic properties which are grown via directed self-assembly arrays of morphologically controlled light-

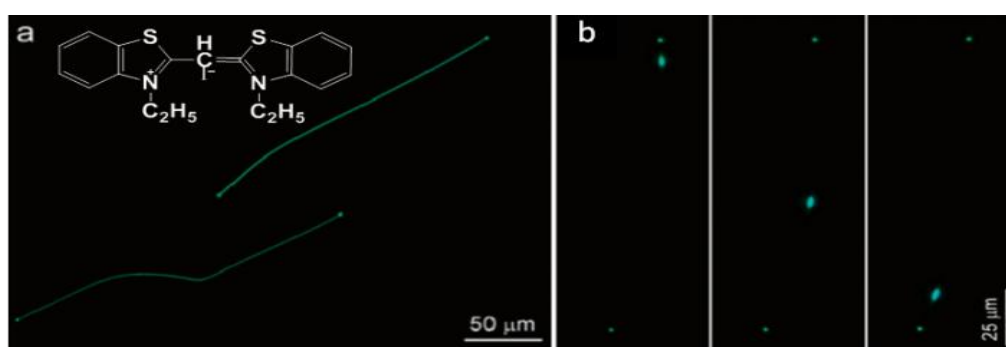


**Figure 1.79** (a) PL images of TC fibers on glass substrate. (b) PL images of the fiber obtained by exciting identical fibers at three different positions. Ref 192.

emitting organic nanofibers on template surfaces. The fibers were transferred from the growth substrate to device platforms either as single entities or as ordered arrays. Takazawa *et al.*<sup>192</sup> have produced fiber shaped nano structure, prepared by the self-assembly of thiacyanine (TC) dye molecules in solution by H-aggregates with lengths of up to 300 μm. Photoluminescence (PL) images and spatially resolved PL spectra of the fibers are studied onto a glass substrate expose that the fibers act as single-mode optical waveguides ([Fig. 1.79](#)). Yao and Yongsheng's groups have developed a fabrication technique to achieve organic nanorods, nanowires and nanotubes, to exploit them for integrated photonic elements and optoelectronic nanodevices. They have adopted methods like liquid-phase assembly, vapor deposition and template based synthesis for achieving 1D nanostructures from small organic functional molecules.

Chandrasekar and co-workers have for the first time reported on the nano/micro scale passive wave guiding organic solids obtained from self-assembled small molecules.<sup>193</sup> Passive organic wave guides function almost similar to commercial optical fibers. They have also demonstrated the potential utility (*remote sensing*) of the guided

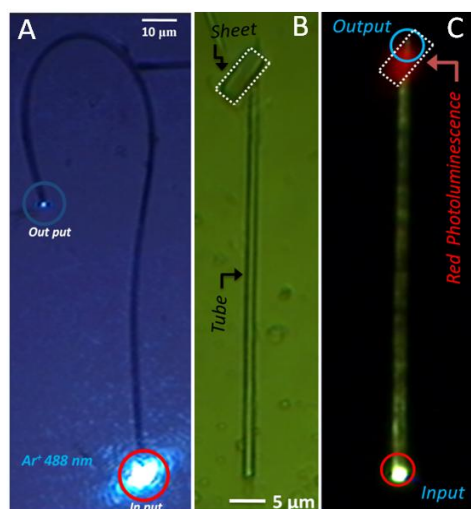


**Figure 1.80** (a) Passive optical wave guiding behavior of a bent organic submicro tube. (b, c) Remote electronic excitation of a porphyrin derivative nano-sheet located at ca. 60 μm away from the 488 nm laser source through a linear submicro tubular waveguide. Ref 193.

tetratolylporphyrin and the propensity of wave guiding nanosheet acting as a wavelength filter.<sup>194</sup>

### 1.15 Aims of the Thesis:

Stable organic radical are becoming very attractive in materials science, due to their high stability and unique properties. Stable radicals have been known for over a century and have been used as spin labeling, spin trapping, EPR imaging, molecular magnets, conducting materials and as well as ligands, stoichiometric reagents, catalysts, and organic battery. Both nitronyl nitroxide (NN) and oxo-verdazyl (OVZ)

radicals are the most studied stable organic radicals. Although there are many research papers highlighting their syntheses and magnetic properties, relatively a few reports of research aimed specifically at the self-assembly and function studies. This thesis work is

laser light along the submicroscale tubes to excite a porphyrine nano-sheet kept 60 microns away from the input source laser (Fig. 1.80). Importantly, to precisely control the optical signal propagation distance from the input point to out points, they have developed a laser ablation method to control of longitudinal optical wave propagation distance along the nanotubes at predetermined length scales precisely to control the light propagation length, to get multiple outputs and estimate of the optical wave transmission efficiency. Recently they have presented the input light dependent guided fluorescent (FL) light propagation paths in hexagonal nanosheet of meso-

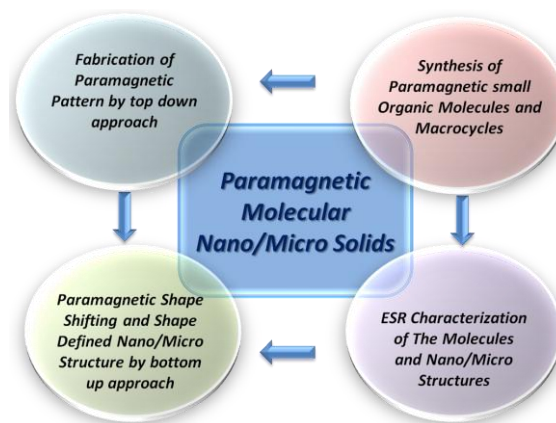


**Figure 1.81** General over-view of this thesis work.

focused on the design and syntheses of new stable NN and OVZ radical appended to various coupling units and their structure-property, self-assembly and nano-functional aspects. In detail, this thesis presents, in addition to syntheses and EPR spectroscopic studies, development of a simple nano-fabrication protocol (both top-down and bottom up approaches) for paramagnetic nanostructures, and optical waveguiding 1D paramagnetic solids. Attempts also have been made to investigate not only to fundamental properties but also on the application-driven studies. Throughout the thesis for the nano-characterizations advanced tools such electron microscopy (SEM, TEM, FESEM), energy dispersive x-ray analysis (EDS), selected area electron diffraction (SAED), atomic force microscopy (AFM), magnetic force microscopy (MFM), and laser confocal Raman microscopy/spectroscopy, were employed. The general approach of the thesis is presented in the [figure 1.81](#).

The introduction part in Chapter 1 provides a short summary of magnetism, basic ESR spectroscopic studies applied to stable radicals and magnetic force microscopy studies. The latter part extensively reviews various stable radical structures, their synthesis using topological rules and ESR spectroscopy investigations. Since the main focus of this thesis is transforming paramagnetic molecules into functional organic nano/micro solids, some basics of nanoscience and technology, its current status, and various nano/micro fabrication methods are also provided. The end part of this chapter provides brief literature review on organic photonics and in particular focuses on optical waveguiding 1D nano/micro structures.

Combining spin-spin (SS) exchange coupling with spin cross-over effect (SCO) by preparing appropriate paramagnetic ligand and SCO complex is not an easy task. It also requires topological design strategy to prepare a stable triplet-state diradicals. For this purpose, attempts have been made to synthesize mono and diradicals composed of both a verdazyl and nitronyl nitroxides, to investigate the SS exchange interactions and the *zfs* using ESR spectroscopy (see Chapter 2). Tridentate 2,6-bispyrazolylpyridine carrying a paramagnetic radical(s) was used for the preparation of Fe(II) complex, displaying spin cross-over effect. Thus these molecules would serve as a fundamental model system for magnetic materials.

The overall goal of this thesis is to further examine the material properties of radicals and explores their potential utility in nano chemistry. The controlled reversible transformation of paramagnetic nano-/micro solids from one shape/dimension to another

and vice versa is a challenging task and attempt towards this direction is given in chapter 3. This includes preparation of paramagnetic nano-vesicles, nano-particles and nano-pores films on glass surfaces. Shape shifting property induced by solvent and sonication also another important subject, and this chapter also presents our successful attempt to shift the shape of nano vesicles into nano particles and vice versa. These paramagnetic nano-/micro solids might find interesting applications in wide areas of materials science and biology involving paramagnetism. Molecule based magnetism can be studied in paramagnetic nanostructures. Vesicles can be exploited for biosensing, drug delivery and detection of cancer cell using magnetic resonance imaging (MRI) technique. Porous film has the potential for the filtration of paramagnetic particles depending upon their sizes.

Till now paramagnetic organic structures are not exploited for the fabrication of nano paramagnetic solids. Hence preparation of paramagnetic photonic organic nano/micro structures via bottom-up approach was aimed. This chapter 4, deals with the preparation of two ring shaped paramagnetic shape persistent molecules carrying OVZ (mono and di) radicals and their self-assembly, submicrotubes formation, growth mechanism and photonic properties. These 1D solids can be used in the miniaturized devices having dual functions such as photonics and paramagnetism. Additionally, a novel waveguiding mode Raman spectroscopy is presented to map/image nano/micro scale molecular defects of the self-assembled solids. Paramagnetic photonic organic nano/micro structures have many applications in information processing and unique optoelectronic properties.

For nano scale information processing, fabrication of magnetic nano structures is necessary. Chapter 5 demonstrates the use of a top-down approach to fabricate paramagnetic 2D nano-cone arrays from a high-spin state ( $S = 1$ ) bi-nitronyl nitroxide radical on a hard (glass) and flexible (polymer) substrates. Embedding the patterns in polymer film makes it easy to handle, flexible, portable, which is necessary for device fabrication in a spintronic application. Organic molecules are lighter atoms and better alternative for spintronics device applications. Finally this can be extended to a wide variety of paramagnetic molecules, such as monoradicals, weakly coupled biradical systems, single molecule magnets and also for spin cross-over systems for use in quantum logic devices.

## References:

1. (a) Faraday, M. *Experimental Researches in Electricity* **1839**, 1. (b) Faraday, M. *Experimental Researches in Electricity* **1844**, 2.
2. Epstein, A. J.; Miller, J. S. *Synth. Met.* **1996**, 80, 231.
3. (a) Coronado, E.; Delhaes, P.; Gatteschi, D.; Miller, J. S., Eds. *Molecular Magnetism: From Molecular Assemblies to the Devices*; Kluwer Academic Publishers: Dordrecht, the Netherlands **1996**, 321. (b) Turnbull, M. M.; Suimoto, T.; Thompson, L. K. *Molecular-Based Magnetic Materials*, ACS Symposium series **1996**.
4. Carlin, R. L. *Magneto-chemistry*, Springer-Verlag, **1985**.
5. Kahn, O. *Molecular magnetism*, VCH, New York, **1993**.
6. Hurd, C. M. *Contemp. Phys.* **1982**, 23, 469.
7. (a) Bersohn, M.; Baird, J. C. *An Introduction to Electron Paramagnetic Resonance*; W. A. Benjamin, Inc.: New York, **1966**. (b) Weil, J. A.; Bolton, J. R.; Wertz, J. E. *Electron Paramagnetic Resonance – Elementary Theory and Practical Applications*, John Wiley & Sons, **1994**. (c) Porio, M. M.; Freed, J. H. *EPR and Advanced Resonance Spectroscopy*, Plenum Press, **1979**. (d) Mabbs, F. E.; Collison, D. *Studies in Inorganic Chemistry 16, Electron Paramagnetic Resonance of d Transition Metal Compounds*, Elsevier, **1992**. (e) Scheffler, K.; Stegmann, H. B.; Elektronenspinresonanz, Organische Chemie in Einzeldarstellungen, 12, Springer-Verlag. **1970**. (f) Welner, W. Jr. *Magnetic Atoms and Molecules*, Scientific and Academic edition, **1983**. (g) Schweiger, A.; Jeschke, G. *Principles of pulse paramagnetic resonance*, Oxford University Press, **2001**.
8. Hanna, M. *Quantum Mechanics in Chemistry*; The Benjamin/Cummings Publishing Company, Inc.: Menlo Park, CA, **1981**.
9. Atherton, N. M. *Principles of Electron Spin Resonance*, Ellis Horwood, New York, **1993**.
10. (a) Baumgarten, M. "High spin molecules directed towards molecular magnets", in "EPR of free radicals in solids, Trends in methods and application", A. Lund, M. Shiotani (eds), Kluwer, **2003/2004**, chapt. 13, 491-528. (b) El-Sayed, M. A. *Pure Appl. Chem.* **1970**, 24, 475.
11. (a) Martin, Y.; Wickramasinghe, H. K. *Appl. Phys. Lett.* **1987**, 50, 1455. (b) Rugar, D.; Mamin, H. J.; Guethner, P.; Lambert, S. E.; Stern, J. E.; McFadyen, I.; Yogi, T. *J. Appl. Phys.* **1990**, 68, 1169. (c) Porthun, S.; Abelman, L.; Lodder, C. J. *Magn. Magn. Mat.* **1998**, 182, 238. (d) Hartmann, U. *Ann. Rev. Mater. Sci.* **1999**, 29, 53. (e) Rasa, M.; Kuipers, B. W. M.; Philipse, A. P. *J. Coll. Interf. Sci.* **2002**, 250, 303.
12. Xiu, F.; Wang, Y.; Kim, J.; Hong, A.; Tang, J.; Jacob, A. P.; Zou, J.; Wang, K. L.; *Nat. Mater.* **2010**, 9, 337.
13. Neves, C. S.; Quaresma, P.; Baptista, P. V.; Carvalho, P. A.; Araujo, J. P.; Pereira, E.; Eaton, P. *Nanotechnology* **2010**, 21, 305706.
14. Ho, K. M.; Li, P. *Langmuir* **2008**, 24, 1801.
15. (a) Fu, L.; Liu, X.; Zhang, Y.; Dravid, V. P.; Mirkin, C. A. *Nano Lett.* **2003**, 3, 757. (b) Jaafar, M.; Iglesias-Freire, O.; Serrano-Ramón, L.; Ibarra, M. R.; Teresa de, J. M.; Asenjo, A. *Beilstein J. Nanotechnol.* **2011**, 2, 552.
16. Mora, C. V.; Davison, M.; Wild, J. M.; walker, M. M. *Nature* **2004**, 432, 508.
17. Nishide, H.; Ozawa, T.; Miyasaka, M.; Tsuchida, E. *J. Am. Chem. Soc.* **2001**, 123, 5942.
18. Moss, R. A.; Platz, M. S.; Jones, M.; Eds, Jr. *Reactive Intermediate Chemistry*, Wiley-Interscience: New York, **2004**.

19. Brokenshire, J. L.; Mendenhall, G. D.; Ingold, K. U. *J. Am. Chem. Soc.* **1971**, *93*, 5278.
20. Gomberg, M. *J. Am. Chem. Soc.* **1900**, *22*, 757.
21. (a) Ballester, M.; Molinet, C.; Castener, J. *J. Am. Chem. Soc.* **1960**, *82*, 4254. (b) Julia, L.; Ballester, M.; Riera, J.; Castaner, J.; Ortin, J. L.; Onrubia, C. *J. Org. Chem.* **1988**, *53*, 1267.
22. (a) Piloty, O.; Schwerin, B. *Ber. Dtsch. Chem. Ges.* **1901**, *34*, 1870. (b) Holden, A. N.; Yager, W. A.; Merity, F. R. *J. Chem. Phys.*, **1951**, *19*, 1319. (c) Wieland, H.; Offenbacher, M. *Ber. Dtsch. Chem. Ges.* **1914**, *47*, 2111.
23. (a) Sogo, P. B.; Nakazaki, M.; Calvin, M. *J. Chem. Phys.* **1957**, *26*, 1343. (b) Reid, D. H. *Tetrahedron* **1958**, *3*, 339.
24. Haddon, R. C.; Sarkar, A.; Pal, S. K.; Chi, X.; Itkis, M. E.; Tham, F. S. *J. Am. Chem. Soc.* **2008**, *130*, 13683.
25. Goldschmidt, S.; Schmidt, W. *Chem. Ber.* **1922**, *55*, 197.
26. Cook, C. D. *J. Org. Chem.* **1953**, *18*, 261.
27. Muller, E.; Ley, K. *Naturforsch* **1953**, *8b*, 694.
28. Musso, H. *Angew. Chem.* **1963**, *75*, 965.
29. (a) Miura, Y.; Asada, H.; Kinoshita, M. *Chem. Lett.* **1978**, 1085. (b) Miura, Y.; Isogai, M.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 751. (c) Miura, Y.; Isogai, M.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3065. (d) Miura, Y.; Katsura, Y.; Kinoshita, M. *Chem. Lett.* **1977**, 409. (e) Miura, Y.; Katsura, Y.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1121.
30. (a) Miura, Y.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1142. (b) Miura, Y.; Tanaka, A.; Hirotsu, K. *J. Org. Chem.* **1991**, *56*, 6638.
31. Fujital, W.; Awaga, K. *Science* **1999**, *286*, 261.
32. Hicks, R.G. *Nature Chem.* **2011**, *3*, 189.
- 33 (a) Min, K. S.; Weyhermuller, T.; Wieghardt, K. *Dalton Trans.* **2004**, 178. (b) Gutlich, P.; Hauser, A.; Spiering, H. *Angew. Chem.Int. Ed.* **1994**, *33*, 2024. (c) Gutlich, P.; Goodwin H. A. (Eds), *Spin Crossover in Transition Metal Compounds I*, Topics in Current Chemistry Series, Springer-Verlag, Berlin, Heidelberg, **2004**, 233. (d) Gutlich, P.; Goodwin H. A. (Eds), *Spin Crossover i Transition Metal Compounds II*, Topics in Current Chemistry Series, Springer-Verlag, Berlin, Heidelberg, **2004**, 234. (e) Gutlich, P.; Goodwin H. A. (Eds), *Spin Crossover in Transition Metal Compounds III*, Topics in Current Chemistry Series, Springer-Verlag, Berlin, Heidelberg, **2004**, 235.
34. (a) Osiecki, J. H.; Ullman, E. F. *J. Am. Chem. Soc.* **1968**, *90*, 1078. (b) Ullman, E. F.; Osiecki, J. H. *J. Org. Chem.* **1970**, *35*, 3623. (b) Ullman, E. F.; Osiecki, J. H.; Boocock, D. G. B.; Darcy, R. *J. Am. Chem. Soc.* **1972**, *94*, 7049.
35. (a) Caneschi, A.; Gatteschi, D.; Lalioti, N. *Angew. Chem.Int. Ed.* **2001**, *40*, 1760. (b) Bobko, A. A.; Bagryanskaya, E. G.; Reznikov, V. A. *Free. Radic. Biol. Med.* **2004**, *36*, 248. (c) Bogani, L.; Sangregorio, C.; Sessoli, R.; Gatteschi, G. *Angew. Chem. Int. Ed.* **2005**, *44*, 5817. (d) Hirel, C.; Li, L.; Brough, P. *Inorg. Chem.* **2007**, *46*, 7545.
36. (a) Luneau, D.; Rey, P. *Coord. Chem. Rev.* **2005**, *249*, 2591. (b) Cambi, L.; Szego, L. *Ber. Dtsch. Chem. Ges. B* **1931**, *64*, 2591. (c) Tamura, M.; Nakazawa, Y.; Shiomi, D. *Chem. Phys. Lett.* **1991**, *186*, 401. (d) Banister, A. J.; Bricklebank, N.; Lavender, I. *Angew. Chem. Int.* **1996**, *35*, 2533. (e) Benelli, C.; Gatteschi, D. *Chem. Rev.* **2002**, *102*, 2369. (f) Caneschi, A.; Gatteschi, D.; Rey, P. *In The Chemistry and Magnetic Properties of Metal Nitronyl Nitroxide Complexes*; Lippard, S. J., Ed.; John Wiley & Sons: New York, **1991**, 39.

37. (a) Zhang, J.; Zhao, M.; Cui, G.; Peng, S. *Bioorgan. Med. Chem.* **2008**, *16*, 4019. (b) Samuni, Y.; Gamso, J.; Samuni, A. *Antioxid. Redox Signal.* **2004**, *6*, 587. (c) Marx, L.; Schollhorn, B. *New J. Chem.* **2006**, *30*, 430.
38. Mathieu, C.; Mercier, A.; Witt, D. *Free Radic. Biol. Med.* **1997**, *22*, 803.
39. (a) Mas-Torrent, M.; Crivillers, N.; Mugnaini, V.; Ratera, I.; Rovira, C.; Veciana, J. *J. Mater. Chem.* **2009**, *19*, 1691. (b) Collauto, A.; Mannini, M.; Sorace, L.; Barbon, A.; Brustolon M.; Gatteschi D. *J. Mater. Chem.* **2012**, *22*, 22272.
40. (a) Ressouche, E.; Boucherle, J. X.; Gillon, B. *J. Am. Chem. Soc.* **1993**, *115*, 3610. (b) Zheludev, A.; Barone, V.; Bonnet, M. *J. Am. Chem. Soc.* **1994**, *116*, 2019.
41. Dooley, B. M.; Bowles, S. E.; Storr, T.; Frank, N. L. *Org. Lett.* **2007**, *9*, 4781.
42. Petrov, P.; Fokin, S.; Romanenko, G. *Mendeleev Commun.* **2001**, 179.
43. Hirel, C.; Vostrikova, K. E.; Pècaut, J.; Ovcharenko, V. I.; Rey, P. *Chem. Eur. J.* **2001**, *7*, 2008.
44. (a) Kuhn, R.; Trischmann, H. *Angew. Chem. Int. Ed.* **1963**, *2*, 155. (b) Kuhn, R.; Neugebauer, F. A.; Trischmann, H. *Monatsh. Chem.* **1966**, *97*, 525.
45. (a) Neugebauer, F. A. *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 455. (b) Polumbrik, O. M.; *Russ. Chem. Rev.* **1978**, *47*, 767. (c) McConnachie, G.; Neugebauer, F. A. *Tetrahedron* **1975**, *31*, 555. (d) Neugebauer, F. A.; Jenne, M. *Chem. Ber.* **1969**, *102*, 3082.
46. (a) Goldschmidt, S. *Ber. Deutsch. Chem. Gesel.* **1920**, *B53*, 44. (b) Goldschmidt, S.; Euler, K. *Ber. Deutsch. Chem. Gesel.* **1922**, *B55*, 616. (c) Goldschmidt, S.; Wolf, A.; Wolffhardt, E. *Ann. Chem.* **1924**, *427*, 194. (d) Goldschmidt, S.; Bader, J. *Ann. Chem.* **1929**, *473*, 137. (e) Goldschmidt, S.; Renn, K. *Ber. Deutsch. Chem. Gesel.* **1922**, *B55*, 628.
47. Koivisto, B.D.; Ichimura, A.S.; McDonald, R.; Lemaire, M.T.; Thompson, L.K.; Hicks, R.G. *J. Am. Chem. Soc.* **2006**, *128*, 690.
48. Yang, A.; Kasahara, T.; Chen, E. K. Y. *Eur. J. Org. Chem.* **2008**, 4571.
49. (a) Kornuta, P. P.; Bobkov, V. N.; Polumbrik, O. M.; Markovskii, L. N. *Zh. Obshch. Khim.* **1978**, *48*, 697. (b) Neugebauer, F. A.; Fischer, H. *Z. Naturforsch.* **1980**, *B35*, 250. (c) Kornuta, P. P.; Bobkov, V. N.; Polumbrik O. M.; Markovskii, L. N. *Zh. Obshch. Khim.* **1981**, *51*, 2449. (d) Hicks, R. G.; Hooper, R. *Inorg. Chem.* **1999**, *38*, 284. (e) Hicks, R. G.; Ohrstrom, L.; Patenaude, G. W. *Inorg. Chem.* **2001**, *40*, 1865.
50. (a) Nineham, A. W. *Chem. Rev.* **1955**, *55*, 355. (b) Brunner, H. *Tetrahedron*, **1971**, *27*, 3611.
51. (a) Neugebauer, F. A. *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 724. (b) ) Neugebauer, F. A.; Fischer, H.; Siegel, R. *Chem. Ber.* **1988**, *121*, 815.
52. Milcent, R.; Barbier, G.; Capelle, S.; Catteau, J. P. *J. Heterocycl. Chem.* **1994**, *31*, 319.
53. Parè, E. C.; Brook, D. J. R.; Brieger, A.; Badik, M.; Schinke, M. *Org. Biomol. Chem.* **2005**, *3*, 4258.
54. Gualtieria, G.; Colacicchia, S.; Sgattonic, R.; Giannoni, M. *Appl. Radiat. Isot.* **2001**, *55*, 71.
55. Odom, B.; Hanneke, D.; D'Urso, B.; Gabrielse, G. *Phys. Rev. Let.* **2006**, *97*, 030801.
56. (a) Bruckner, A. *Chem. Soc. Rev.* **2010**, *39*, 4673. (b) Meiuauudeau, P.; Vedrin, J. C. *J. Chem. Soc. Faraday Trans. 2*, **1976**, *72*, 472.
57. (a) Purcell, E.M.; Torrey, H.C.; Pound, R. V. *Phys. Rev.* **1946**, *69*, 37. (b) Bloch, F.; Hansen, W.W.; Packard, M. *Phys. Rev.* **1946**, *69*, 127. (c) Ernst, R.R.; Anderson, W.A. *Rev. Sci. Instrum.* **1966**, *37*, 93.
58. (a) Zavoisky, E. *J. Phys. USSR*, **1945**, *9*, 211. (b) Blume, R. *J. Phys. Rev.* **1958**, *109*, 1867.

59. Islamova, R. M.; Puzin, Y. I.; Fatykhov, A. A.; Monakov, Y. B. *Polym. Sci., Ser. B*, **2006**, *48*, 130. (b) Braunecker, W. A.; Matyjaszewski, K. *Prog. Polym. Sci.* **2007**, *32*, 93.
60. (a) Bamford, H.; Barb, W. G.; Jenkins, A. D.; and Onyon, P. F. *The Kinetics of Vinyl Polymerization by Radical Mechanisms. Butterworths, London*, **1958**. (b) Sciannamea, V.; Jerome, R.; Detrembleur, C. *Chem. Rev.* **2008**, *108*, 1104. (c) Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.*, **1995**, *117*, 5614.
61. (a) Solomon, D. H.; Rizzardo, E.; Cacioli, P. *European Patent* **1985**, 135280. (b) Fairfull-Smith, K. E.; Blinco, J. P.; Keddle, D. J. *Macromolecules* **2008**, *41*, 1577. (c) Moad, G.; Rizzardo E.; Solomon, D. H. *Macromolecules* **1982**, *15*, 909.
62. (a) Janzen, E. G. *Acc. Chem. Res.* **1971**, *4*, 31. (b) Ebel, C.; Ingold, K. U.; Michon J.; Rassat, A. *Tetrahedron Lett.* **1985**, *26*, 741. (c) Janzen E. G.; Blackburn, B. J. *J. Am. Chem. Soc.* **1968**, *90*, 5909.
63. (a) Burr, M.; Koshland, Jr. D. E. *Proc. Nat. Acad. Sci. USA*, **1964**, *52*, 1017. (b) Berliner, L. J. *Spin labeling. Theory and Applications, Academic Press, New York*, **1976**.
64. Rozantsev, E. G. *Free Nitroxyl Radicals*, Plenum Press, New York, **1970**.
65. (a) Likhtenshtein, G. I. *Spin Labeling Methods in Molecular Biology*, John Wiley & Sons, Inc., New York, **1976**. (b) Berliner, L. J.; Reuben, J. *Spin Labeling: Theory and Applications, Biological Magnetic Resonance*, Plenum Publishing Corp., New York, **1989**, 8.
66. (a) He, G.; Samouilov, A.; Kuppusamy, P.; Zweier, J. L. *Mol. Cell Biochem.* **2002**, *234*, 359. (b) Khramtsov, V. V.; Grigořev, I. A.; Foster, M. A. *Cell. Mol. Biol.* **2000**, *46*, 1361. (c) Lurie, D. J. *Br. J. Radiol.* **2001**, *74*, 782. (d) Nicholson, I.; Robb, F. J.; McCallum, S. *J. Phys. Med. Biol.* **1998**, *43*, 1851.
67. Polyhach, Y.; Bordignon, E.; Tschaggelar, R.; Gandra, S.; Godt, A.; Jeschke, G. *Phys. Chem. Chem. Phys.* **2012**, *14*, 10762.
68. (a) Hyodo, F.; Matsumoto, K.-I.; Matsumoto, A. *Cancer Res.* **2006**, *66*, 9921. (b) Goodson, B. J. *Magn. Reson.* **2002**, *155*, 157. (c) Schroder, L.; Lowery, T. J.; Hilty, C. *Science* **2006**, *314*, 446. (d) Bowers, C. R.; Weitekamp, D. P. *Phys. Rev. Lett.* **1986**, *57*, 2645.
69. (a) Chung, T. C.; Hong, H. *ACS Symp. Ser.* **2003**, *854*, 481. (b) Hoye, A. T.; Davoren, J. E.; Wipf, P. *Acc. Chem. Res.* **2008**, *41*, 87. (c) Krishna, M. C.; DeGraff, W.; Hankovszky, O. H. *J. Med. Chem.* **1998**, *41*, 3477.
70. (a) Haddon, R. C.; Wudl, F.; Kaplan, M. L. *J. Am. Chem. Soc.* **1978**, *100*, 7629. (b) Morita, Y.; Nishida, S.; Kawai, J. *Pure Appl. Chem.* **2008**, *80*, 507. (c) Prokofev, A. I.; Solodovnikov, S. P.; Nikiforov, G. A.; Ershov, V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1971**, 324.
71. (a) Neiman, M. B.; Rozantsev, E. G.; Mamedova, Y. G. *Nature* **1962**, *196*, 472. (b) Bobbitt, J. M.; Bruckner, C.; Merbouh, N. *Org. React.* **2009**, *74*, 106.
72. (a) Haddon, R. C. *Nature* **1975**, *256*, 394. (b) Cordes, A. W.; Haddon, R. C.; Oakley, R. T. *Adv. Mater.* **1994**, *6*, 798.
73. (a) Eaton, S. S.; Eaton, G. R. *Coord. Chem. Rev.* **1978**, *26*, 207. (b) Drago, R. S. *Coord. Chem. Rev.* **1980**, *32*, 97. (c) Eaton, S. S.; Eaton, G. R. *Coord. Chem. Rev.* **1988**, *83*, 29. (d) Volodarsky, L. B.; Reznikov, V. A.; Ovcharenko, V. I. *CRC Press, Inc., Boca Raton* **1994**. (e) Iwamura, H.; Inoue, K. in *Magnetism: Molecules to Materials II. Molecule-Based Materials*, (eds J. S. Miller and M. Drillon), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim **2001**, 61–108.
74. (a) Ruiz-Molina, D.; Veciana, J.; Palacio, F.; Rovira, C. *J. Org. Chem.* **1997**, *62*, 9009. (b) Barth, J. V.; Constantini, G.; Kern, K. *Nature* **2005**, *437*, 671. (c) Gates, B. D.; Xu, Q.; Stewart, M. *Chem. Rev.* **2005**, *105*, 1171. (d) Shukla, A. D.; Das, A.; van der Boom, M. E. *Angew. Chem. Int. Ed.* **2005**, *44*, 3237.
75. (a) Morita, Y.; Okafuji, T.; Satoh, M. *Jpn. Kokai Tokkyo Koho*, **2007**. (b) Nishida, S.; Morita, Y.; Moriguchi, M. Molecular crystalline secondary batteries: properties of phenalenyl-based multi-stage redox systems as

cathode active organic materials. Presented at the 1<sup>st</sup> Russian-Japanese Workshop “Open Shell Compounds and Molecular Spin Devices”, Novosibirsk, Russia, June 30–July 2, **2007**. (c) Preliminary results on molecular crystalline secondary batteries based on closed-shell electron-donor and-acceptor molecules as cathode-active materials are reported. Y. Morita, S. Nishida, N. Akutagawa, Molecular crystalline secondary batteries: novel secondary batteries based on organic molecules as cathode-active materials. Presented at the 19th Symposium on Fundamental Organic Chemistry, Osaka, Japan, October 3–5, C28, **2008**.

76. (a) Kinoshita, M. *Phil. Trans. R. Soc. Lond. A* **1999**, 357, 2855. (b) Itoh, K.; Kinoshita, M.; Eds. *Molecular Magnetism*; Gordon and Breach: Kodansha, **2000**, 1.

77. Mukai, K.; Konishi, K.; Nedaki, K.; Takeda, K. *J. Magn. Mater.* **1995**, 140, 1449.

78. Chiarelli, R.; Novak, M. A.; Rassat A.; Tholence, J. L. *Nature* **1993**, 363, 147.

79. Carretta, P.; Gatteschi, D.; Lascialfari, A. *Physica B*. **2000**, 94.

80. Banister, A. J.; Bricklebank, N.; Lavender, I.; Rawson, J. M.; Gregory, C. I.; Tanner, B. K.; Clegg, W.; Elsegood, M. R. J.; Palacio, F. *Angew. Chem.* **1996**, 108, 2648.

81. Allemand, P.-M.; Khemani, K. C.; Koch, A.; Wudl, F.; Holczer, K.; Donovan, S.; Grüner, G.; Thompson, J. D. *Science* **1991**, 253, 301.

82. Miller, J. S. *Chem. Soc. Rev.* **2011**, 40, 3266.

83. Nascimento, O.R.; Oliveira, A.J.A.; Pereira, E.C.; Correa, A.A.; Walmsley, L. *J. Phys. Condens. Matter.* **2008**, 20, 35214.

84. Yang, B.; Xiao, Z.; Yuan, Y.; Jayaraman, T. V.; Shield, J. E.; Skomski, R.; Huang, J. *Polymer* **2013**, 54, 490.

85. Zaidi, N. A.; Giblin, S.R.; Terry, I.; Monkman, A.P. *Polymer* **2004**, 45, 5683.

86. Ovchinnikov, A. A. *Theor. Chim. Acta.* **1978**, 47, 297.

87. (a) Chiarelli, R.; Novak, M. A.; Rassat, A.; Tholence, J. L. *Nature* **1993**, 363, 147. (b) Shultz, D. A.; Boal, A. K.; Lee, H.; Farmer, G. T. *J. Org. Chem.* **1999**, 64, 4386. (c) Shultz, D. A.; Fico Jr., R. M.; Lee, H. *J. Am. Chem. Soc.* **2003**, 125, 15426. (d) Rajadurai, C.; Enkelmann, V.; Zoppellaro, G.; Baumgarten, M. *J. Phys. Chem. B* **2007**, 111, 4327. (e) Rajadurai, C.; Enkelmann, V.; Ikorskii, V.; Ovcharenko, V. I.; Baumgarten, M. *Inorg. Chem.* **2006**, 45, 24.

88. Tanaka, M.; Matsuda, K.; Itoh, T.; Iwamura, H. *J. Am. Chem. Soc.* **1998**, 120, 7168.

89. Izuoka, A.; Hiraishi, M.; Abe, T.; Sugawara, T.; Sato, K.; Takui, T. *J. Am. Chem. Soc.* **2000**, 122, 3234.

90. Hayakawa, K.; Shiomi, D.; Ise, T.; Sato, K.; Takui, T. *J. Mater. Chem.* **2006**, 16, 4146.

91. Rajadurai, C.; Ivanova, A.; Enkelmann, V.; Baumgarten, M. *J. Org. Chem.* **2003**, 68, 9907.

92. Oka, H.; Tamura, T.; Miura, Y.; Teki, Y. *Polym. J.* **1999**, 31, 979.

93. Nishide, H.; Maeda, T.; Oyaizu, K.; Tsuchida, E. *J. Org. Chem.* **1999**, 64, 7129.

94. Suga, T.; Ohshiro, H.; Sugita, S.; Oyaizu, K.; Nishide, H. *Adv. Mater.* **2009**, 21, 1627.

95. Rajca, A.; Rajca, S.; Wongsriratanakul, J. *J. Am. Chem. Soc.* **1999**, 121, 6308.

96. Rajca, A.; Wongsriratanakul, J.; Rajca, S. *Science* **2001**, 294, 1503.

97. Ramsden, J.; *nanotechnology* ISBN 978-87-7681-418-2, **2009**. (b) Whitesides, G. M.; Mathias, J. P.; Seto, C. T. *Science* **1991**, 254, 1312.

98. (a) Zang, L.; Che, Y.; Moore, J. F. *Acc. Chem. Res.* **2008**, *41*, 1596. (b) Grimsdale, A. C.; Mullen, K. *Angew. Chem. Int. Ed.* **2005**, *44*, 5592. (c) Bong, D. T.; Clark, T. D.; Granja, J. R.; Ghadiri, M. R. *Angew. Chem. Int. Ed.* **2001**, *40*, 988.
99. (a) Cornil, J.; Beljonne, D.; Calbert, J.-P.; Brédas, J.-L. *Adv. Mater.* **2001**, *13*, 1053. (b) Gierschner, J.; Ehni, M.; Egelhaaf, H.-J.; Milián Medina, B.; Beljonne, D.; Benmansour, H.; Bazan, G. C. *J. Chem. Phys.* **2005**, *123*, 144914.
100. Kuiper, J. M.; Engberts, J. B. F. N. *Langmuir* **2004**, *20*, 1152.
101. (a) An, B.-K.; Kwon, S.-K.; Jung, S.-D.; Park, S. Y. *J. Am. Chem. Soc.* **2002**, *124*, 14410. (b) Karpfen, A.; Choi, C. H.; Kertesz, M. *J. Phys. Chem. A* **1997**, *101*, 7426. (c) Babu, S. S.; Kartha, K. K.; Ajayaghosh, A. *J. Phys. Chem. Lett.* **2010**, *1*, 3413. (d) Karpfen, A.; Choi, C. H.; Kertesz, M. *J. Phys. Chem. A* **1997**, *101*, 7426.
102. Como, E. D.; Loi, M. A.; Murgia, M.; Zamboni, R.; Muccini, M. *J. Am. Chem. Soc.* **2006**, *128*, 4277.
103. Kasai, H.; Nalwa, H. S.; Oikawa, H.; Okada, S.; Matsuda, H.; Minami, N.; Kakuta, A.; Ono, K.; Mukoh, A.; Nakanishi, H. *Jpn. J. Appl. Phys.* **1992**, *31*, L1132.
104. Baba, K.; Kasai, H.; Okada, S.; Oikawa, H.; Nakanishi, H. *Opt. Mater.* **2002**, *21*, 591. (b) Masuhara, H.; Nakanishi, H.; Sasaki, K., Eds.; *Springer: Berlin* **2003**, 17-31.
105. Zhao, Y. S.; Fu, H.; Peng, A.; Ma, Y.; Xiao, D.; Yao, J. *Adv. Mater.* **2008**, *20*, 2859.
106. (a) Balzar, F.; Rubahn, H. *Adv. Funct. Mater.* **2005**, *15*, 17. (b) Ng, A. M.; Djurišić, A. B.; Tam, K.; Kwok, W.; Chan, W.; Tam, W. Y.; Phillips, D. L.; Cheah, K. *Adv. Funct. Mater.* **2008**, *18*, 566.
107. (a) Suslick, K. S.; Doktycz, S. J. *Chem. Mater.* **1989**, *1*, 6. (b) Suslick, K. S.; Schubert, P. F.; Goodale, J. W. *IEEE Ultrason. Symp. Proc.* **1981**, *2*, 612.
108. (a) Liang, H.-W.; Liu, J.-W.; Qian, H.-S.; Yu, S.-H. *Acc. Chem. Res.* **2013**, *46*, 1450. (b) Wang, C.; Wang, Z.; Zhang, X. *Acc. Chem. Res.* **2012**, *45*, 608.
109. Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.
110. Liu, X.; Xu, Y.; Jiang, D. *J. Am. Chem. Soc.* **2012**, *134*, 8738.
111. Sun, Y.; Welch, G. C.; Leong, W. L.; Takacs, C. J.; Bazan, G. C.; Heeger, A. J. *Nat. Mater.* **2012**, *11*, 44.
112. Zhang, L.; Wang, K.; Qian, X.; Liu, H.; Shi, Z. *Acs Appl. Mater. Interfaces* **2013**, *5*, 2761.
113. Wu, W.; Liu, Y.; Zhu, D. *Chem. Soc. Rev.* **2010**, *39*, 1489.
114. (a) Lv, J.; Liu, H.; Li, Y. *Pure Appl. Chem.* **2008**, *80*, 639. (b) Zhou, W.; Li, Y.; Zhu, D. *Chem. Asian J.* **2007**, *2*, 222.
115. Sajanalal, P. R.; Sreeprasad, T. S.; Samal, A. K.; Pradeep T. *Nano Rev.* **2011**, *2*, 5883.
116. (a) Huang, C.; Wen, L.; Liu, H.; Li, Y.; Liu, X.; Yuan, M.; Zhai, J.; Jiang, L.; Zhu, D. *Adv. Mater.* **2009**, *21*, 1721. (b) Ajayaghosh, A.; Praveen, V. K. *Acc. Chem. Res.* **2007**, *40*, 644.
117. Kresge, C.; Leonowicz, M.; Roth, W.; Vartuli, J.; Beck, J. *Nature* **1992**, *359*, 710. (b) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T. W.; Olson, D. H.; Sheppard, E. W. *J. Am. Chem. Soc.* **1992**, *114*, 10834.
118. Seth, A.; Béalle, G.; Santanach-Carreras, E.; Abou-Hassan, A.; Ménager, C.; *Adv. Mater.* **2012**, *24*, 3544.

119. (a) Li, Y.; Li, X.; Li, Y.; Liu, H.; Wang, S.; Gan, H.; Li, J.; Wang, N.; He, X.; Zhu, D. *Angew. Chem. Int. Ed.* **2006**, *45*, 3639. (b) Ringsdorf, H.; Schlarb, B.; Venzmer, J. *Angew. Chem. Int. Ed.* **1988**, *27*, 113. (c) Israelachvili, J. N.; Mitchell, D. J.; Ninham, B. W. *J. Chem. Soc. Faraday Trans. 2* **1976**, *72*, 1525.
120. Liu, Y.; Li, Y.; He, J.; Duelge, K. J.; Lu, Z.; Nie, Z. *J. Am. Chem. Soc.* **2014**, *136*, 2602.
121. Ye, F.; Barrefelt, Å.; Asem, H.; Abedi-Valugerdi, M.; El-Serafi, I.; Sagharian, M.; Abu-Salah, K.; Alrokayan, S.; Muhammed, M.; Hassan, M.; *Biomaterials* **2014**, *35*, 3885.
122. (a) Iijima, S. *Nature* **1991**, *354*, 56. (b) Iijima, S.; Ichihashi, T. *Nature* **1993**, *363*, 603.
123. (a) Schnur, J. M.; Ratna, B. R.; Selinger, J. V.; Singh, A.; Jyothi, G.; Easwaran, K. R. K. *Science* **1994**, *264*, 945. (b) Chung, D. S.; Benedek, G. B.; Konikoff, F. M.; Donovan, J. M. *Proc. Natl. Acad. Sci. U.S.A.* **1993**, *90*, 11341. (c) Fuhrhop, J. H.; Spiroski, D.; Boettcher, C. J. *Am. Chem. Soc.* **1993**, *115*, 1600. (d) Zhao, Y.; Fu, H.; Peng, A.; Ma, Y.; Liao, Q.; Yao, J. *Acc. Chem. Res.* **2010**, *43*, 409. (e) Liu, H.; Li, Y.; Xiao, S.; Gan, H.; Jiu, T.; Li, H.; Jiang, L.; Zhu, D.; Yu, D.; Xiang, B.; Chen, Y. *J. Am. Chem. Soc.* **2003**, *125*, 10794.
124. Cao, H.; Duan, P.; Zhu, X.; Jiang, J.; Liu, M. *Chem. Eur. J.* **2012**, *18*, 5546.
125. Xia, Y.; Yang, P.; Sun, Y.; Wu, Y.; Mayers, B.; Gates, B.; Yin, Y.; Kim, F.; Yan, H. *Adv. Mater.* **2003**, *15*, 353.
126. (a) Hu, J.; Ouyang, M.; Yang, P.; Lieber, C. M. *Nature* **1999**, *399*, 48. (b) Che, G.; Lakshmi, B. B.; Fisher, E. R.; Martin, C. R. *Nature* **1998**, *393*, 346. (c) Collins, P. G.; Zettl, A.; Bando, H.; Thess, A.; Smalley, R. E. *Science* **1997**, *278*, 100. (d) Star, A.; Lu, Y.; Bradley, K.; Gruner, G. *Nano Lett.* **2004**, *4*, 1587.
127. (a) Hu, J.; Odom, T. W.; Lieber, C. M. *Acc. Chem. Res.* **1999**, *32*, 435. (b) Xia, Y.; Yang, P.; Sun, Y.; Wu, Y.; Mayers, B.; Gates, B.; Yin, Y.; Kim, F.; Yan, H. *Adv. Mater.* **2003**, *15*, 353. (c) Wang, Z. L. *Adv. Mater.* **2003**, *15*, 432. (d) Law, M.; Greene, L. E.; Johnson, J. C.; Saykally, R.; Yang, P. *Nat. Mater.* **2005**, *4*, 455.
128. (a) Chandrasekhar, N.; Chandrasekar, R. *J. Org. Chem.* **2010**, *75*, 4852. (b) Chandrasekhar, N.; Chandrasekar, R. *Chem. Commun.* **2010**, *46*, 2915. (c) Basak, S.; Hui, P.; Chandrasekar, R. *Synthesis* **2009**, *23*, 4042. (d) Rajadurai, C.; Fuhr, O.; Kruk, R.; Ghafari, M.; Hahn, H.; Ruben, M. *Chem. Commun.* **2007**, 2636. (e) Rajadurai, C.; Schramm, F.; Brink, S.; Fuhr, O.; Kruk, R.; Ghafari, M.; Ruben, M. *Inorg. Chem.* **2006**, *45*, 10019. (f) Rajadurai, C.; Ruben, M. *European Patent Application*, EP 2053049B1.
129. (a) Medforth, C. J.; Wang, Z.; Martin, K. E.; Song, Y.; Jacobsen, J. L.; Shelnutt, J. A. *Chem. Commun.* **2009**, 7261. (b) Schnur, J. M. *Science* **1993**, *262*, 1669. (c) Harada, A.; Li, J.; Kamachi, M. *Nature* **1993**, *364*, 516. (d) Shimizu, T.; *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 2601. (e) Ajayaghosh, A.; Praveen, V. K. *Acc. Chem. Res.* **2007**, *40*, 644. (f) Nakanishi, T. *Chem. Commun.* **2010**, *46*, 3425. (g) Kimizuka, N.; Kawasaki, T.; Hirata, K.; Kunitake, T. *J. Am. Chem. Soc.* **1995**, *117*, 6360. (h) Mann, S. *Nat. Mater.* **2009**, *8*, 781. (i) Zubarev, E. R.; Sone, E. D.; Stupp, S. I. *Chem. Eur. J.* **2006**, *12*, 7313. (j) Iwamura, R.; Hoeben, F. J. M.; Masuda, M.; Scenning, A. P. H. J.; Meijer, E. W.; Shimizu, T.; *J. Am. Chem. Soc.* **2006**, *128*, 13298. (k) Whitesides, G. M.; Grzybowski, B. *Science* **2002**, *295*, 5564.
130. (a) Seley, D. B.; Nath, M.; Parkinson, B. A. *J. Mater. Chem.* **2009**, *19*, 1532. (b) Wang, F.; Liu, X.; *Chem. Soc. Rev.* **2009**, *38*, 976. (c) Vasileiadis, T.; Dracopoulos, V.; Kollia, M.; Yannopoulos, S. N. *Scientific Reports* **2013**, *3*, 1.
131. (a) Hu, J.; Chen, Z.; Jiang, H.; Sun, Y.; Bandoc, Y.; Golberg, D.; *J. Mater. Chem.* **2009**, *19*, 3063. (b) Liu, J.; Xue, D. *J. Mater. Chem.* **2011**, *21*, 223.
132. Seo, M.; Kim, J. H.; Seo, G.; Shin, C. H.; Kim, S. Y. *Chem. Eur. J.* **2009**, *15*, 612. (g) Seo, M.; Seo, G.; Kim, S. Y. *Angew. Chem. Int. Ed.* **2006**, *45*, 6306.
133. Mullen, K.; Scherf, U. *Organic Light Emitting Devices: Synthesis, Properties and Applications*, Wiley-VCH, Weinheim, **2006**. (b) Li, R.; Hu, W.; Liu, Y.; Zhu, D. *Acc. Chem. Res.*, **2010**, *43*, 529. (c) Klauk, H.

*Organic Electronic*, Wiley-VCH, Weinheim, **2006**. (d) Brabec, C.; Dyakonov, V.; Scherf, U. *Organic Photovoltaics*, Wiley-VCH, Weinheim, **2008**.

134. Zhao, Y. S.; Yang, W.; Xiao, D.; Sheng, X.; Yang, X.; Shuai, Z.; Luo, Y.; Yao J. *Chem. Mater.* **2005**, *17*, 6430.

135. Zhang, X.; Zhang, X.; Shi, W.; Meng, X.; Lee, C.; Lee, S. *Angew. Chem. Int. Ed.* **2007**, *46*, 1525.

136. a) Tenne, R. *Chem. Eur. J.* **2002**, *8*, 5296. b) Deepak, F. L.; Tenne, R. *Cent. Eur. Chem.* **2008**, *6*, 373.

137. Rao, C. N. R.; Nath, M. *Dalton Trans.* **2003**, *1*.

138. Korneva, G.; Ye, H. H.; Gogotsi, Y.; Halverson, D.; Friedman, G.; Bradley, J. C.; Kornev, K. G. *Nano Lett.*, **2005**, *5*, 879–884.

139. Zhang, X.; Huang, X.; Tang, X. *New J. Chem.* **2009**, *33*, 2426.

140. Son, S. J.; Reichel, J.; He, B.; Schuchman, M.; Lee, S. B. *J. Am. Chem. Soc.* **2005**, *127*, 7316.

141. Cao, H.; Wang, L.; Qiu, Y.; Wu, Q.; Wang, G.; Zhang, L.; Liu, X. *Chem. Phys. Chem.* **2006**, *7*, 1500.

142. Bao, J.; Tie, C.; Xu, Z.; Zhou, Q.; Shen, D.; Ma, Q. *Adv. Mater.* **2001**, *13*, 1631.

143. Wang, J.; Ma, Y.; Watanabe, K. *Chem. Mater.* **2008**, *20*, 20.

144. Lou, X. W.; Deng, D.; Lee, J. Y.; Feng, J.; Archer, L. A.; *Adv. Mater.* **2008**, *20*, 258.

145. Cao, J. R.; Lee, P.-T. Choi, S.-J. Shafiiha, R.; Choi, S.-J.; O'Brien, J. D.; Dapkus, P. D. *J. Vac. Sci. Technol. B* **2002**, *20*, 2.

146. Khokhar, A. Z.; Parsons, K.; Hubbard, G.; Rahman, F.; Macintyre, D. S.; Xiong, C.; Massoubre, D.; Gong, Z.; Johnson, N. P.; Rue, R. M.; Watson, I. M.; Gu, E.; Dawson, M. D.; Abbott, S. J.; Charlton, M. D.B.; Tillin, M. *Microelectronic Engineering* **2010**, *87*, 2200.

147. Betancourt, T.; Brannon-Peppas, L. *Int. J. Nanomedicine* **2006**, *14*, 483.

148. Parviz, B. A.; Member, IEEE, Ryan, D.; Whitesides, G. M. *IEEE Trans. Adv. Packag.* **2003**, *26*, 233.

149. (a) Klauk, H.; Gundlach, D.J.; Bonse, M.; Kuo, C.C.; Jackson, T.N. *Appl. Phys. Lett.* **2000**, *76*, 1692. (b) Goodberlet, J.G. *Appl. Phys. Lett.* **2000**, *76*, 667.

150. (a) Fujita, J.; Ohnishi, Y.; Ochiai, Y.; Matsui, S. *Appl. Phys. Lett.* **1996**, *68*, 1297. (b) Robinson, A.P.G.; Palmer, R.E.; Tada, T.; Kanayama, T.; Preece, J. A. *Appl. Phys. Lett.* **1998**, *72*, 1302.

151. Pavel, E.; Jinga, S.I.; Vasile, B.S.; Dinescu, A.; Marinescu, V.; Trusca, R.; Tosa, N. *Opt. Laser Technol.* **2014**, *60*, 80.

152. Staude, I.; Decker, M.; Ventura, M. J.; Jagadish, C.; Neshev, D. N.; Gu, M.; Kivshar, Y. S. *Adv. Mater.* **2013**, *25*, 1260.

153. (a) Xia, Y.; Kim, E.; Zhao, X.-M.; Rogers, J. A.; Prentiss, M.; Whitesides, G. M. *Science* **1996**, *273*, 347. (b) Xia, Y.; McClelland, J. J.; Gupta, R.; Qin, D.; Zhao, X. M.; Sohn, L. L.; Celotta, R. J.; Whitesides, G. M. *Adv. Mater.* **1997**, *9*, 147.

154. Hua, F.; Sun, Y.; Gaur, A.; Meitl, M.; Bilhaut, L.; Rotkina, L.; Wang, J. F.; Geil, P.; Shim, M.; Rogers, J. A.; Shim, A. *Nano Lett.* **2004**, *4*, 2467.

155. Xu, Q.; Mayers, B.; Lahav, M.; Vezenov, D. V.; Whitesides, G. M. *J. Am. Chem. Soc.* **2005**, *127*, 854.

156. (a) Terris, B. D.; Mamin, H. J.; Best, M. E.; Logan, J. A.; Rugar, D. *Appl. Phys. Lett.* **1996**, *69*, 4262.

157. Hutley, M. C. *Diffraction Gratings*. New York: Academic **1982**.

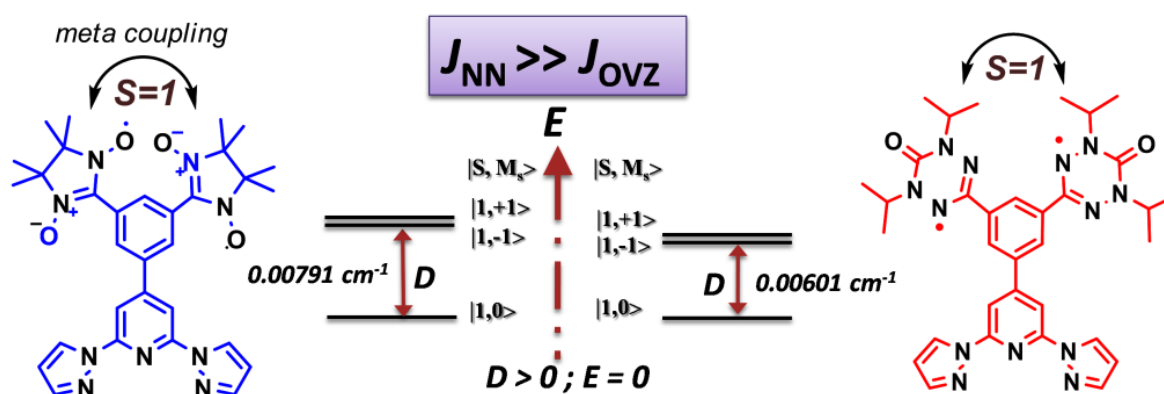
158. Nakano, M.; Nishida, N. *Appl. Opt.* **1979**, *18*, 3073.

159. Kiewit, D. A. *Rev. Sci. Instrum.* **1973**, *44*, 1741.
160. Ohdaira, Y.; Noguchi, K.; Shinbo, K.; Kato, K.; Kaneko, F. *Colloids and Surfaces A: Physicochem. Eng. Aspects* **2006**, *284*, 556.
161. Wiesmann, R.; Kalveram, S.; Rudolph, S.; Johnck, M.; Neyer, A. *Electronics Letters* **1996**, *32*, 2329.
162. Danilevicius, P.; Rekstyt, S.; Balciunas, E.; Kraniauskas, A.; Sirmenis, R.; Baltriukiene, D.; Bukelskiene, V.; Gadonas, R.; Sirvydis, V.; Piskarskas, A.; Malinauskas, M. *Optics & Laser Technology* **2013**, *45*, 518.
163. Xia, Y.; Kim, E.; Whitesides, G. M. *Chem. Mater.* **1996**, *8*, 1558.
164. Hwang, H.; Kang, G.; Yeon, J. H.; Nam, Y.; Park, J.-K. *Lab Chip* **2009**, *9*, 167.
165. Cavallini, M.; Biscarini, F.; Gomez-Segura, J.; Ruiz, D.; Veciana, J. *Nano Lett.* **2003**, *3*, 1527.
166. Celio, H.; Barton, E.; Stevenson, K. J. *Langmuir* **2006**, *22*, 11426.
167. Emmelius, M.; Pawlowski, G.; Vollmann, H. W. *Angew. Chem. Int. Ed.* **1989**, *28*, 1445.
168. Chou, S. Y.; Krauss, P. R.; Renstrom, P. J. *Science* **1996**, *272*, 85. (b) Chou, S. Y.; Krauss, P. R.; Renstrom, P. J. *Appl. Phys. Lett.* **1995**, *67*, 3114.
169. (a) Kumar, A.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1498. (b) Wilbur, J. L.; Kumar, A.; Biebuyck, H. A.; Kim, E.; Whitesides, G. M. *Nanotechnology* **1996**, *7*, 452.
170. Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 2790.
171. (a) Lange, S. A.; Benes, V.; Kern, D. P.; Horber, J. K. H.; Bernard, A. *Anal. Chem.* **2004**, *76*, 1641. (b) Thibault, C.; Berre, V. L.; Casimirius, S.; Trevisiol, E.; Francois, J.; Vieu, C. *J. Nanobiotechnol.* **2005**, *3*, 7.
172. (a) James, C. D.; Davis, R. C.; Kam, L.; Craighead, H. G.; Isaacson, M.; Turner, J. N.; Shain, W. *Langmuir* **1998**, *14*, 741. (b) Bernard, A.; Delamarche, E.; Schmid, H.; Michel, B.; Bosshard, H. R.; Biebuyck, H. *Langmuir* **1998**, *14*, 2225.
173. (a) Wilbur, J. L.; Kumar, A.; Kim, E.; Whitesides, G. M. *Adv. Mater.* **1994**, *6*, 600. (b) Loo, Y. L.; Willett, R. L.; Baldwin, K. W.; Rogers, J. A. *Appl. Phys. Lett.* **2002**, *81*, 562.
174. (a) Ghosh, P.; Lackowski, W. M.; Crooks, R. M. *Macromolecules* **2001**, *34*, 1230. (b) Arrington, D.; Curry, M.; Street, S. C. *Langmuir* **2002**, *18*, 7788.
175. (a) Mrksich, M.; Dike, L. E.; Tien, J.; Ingber, D. E.; Whitesides, G. M. *Exp. Cell Res.* **1997**, *235*, 305. (b) Singhvi, R.; Kumar, A.; Lopez, G. P.; Stephanopoulos, G. N.; Wang, D. I. C.; Whitesides, G. M.; Ingber, D. E. *Science* **1994**, *264*, 696.
176. (a) Loo, Y.-L.; Willett, R. L.; Baldwin, K. W.; Rogers, J. A. *J. Am. Chem. Soc.* **2002**, *124*, 7654. (b) Jeon, S.; Menard, E.; Park, J.-U.; Maria, J.; Meitl, M.; Zaumseil, J.; Rogers, J. A. *Adv. Mater.* **2004**, *16*, 1369.
177. Childs, W. R.; Nuzzo, R. G.; *J. Am. Chem. Soc.* **2002**, *124*, 13583.
178. Mannini, M.; Rovai, D.; Sorace, L.; Perl, A.; Ravoo, B. J.; Reinhoudt, D. N.; Caneschi, A. *Inorg. Chim. Acta.* **2008**, *361*, 3525.
179. Cavallini, M.; Biscarini, F.; Gomez-Segura, J.; Ruiz, D.; Veciana, J. *Nano Lett.* **2003**, *3*, 1527.
180. Urdampilleta, M.; Klyatskaya, S.; Cleuziou, J.-P.; Ruben, M.; Wernsdorfer, W. *Nat. Mater.* **2011**, *10*, 502.
181. Kao, C. K. *Ericsson Rev.* **1979**, *56*, 92.
182. Balzer, F.; Bordo, V. G.; Simonsen, A. C.; Rubahn, H. G. *Appl. Phys. Lett.* **2003**, *82*, 10.

183. (a) Barnes, W. L.; Dereux, A.; Ebbesen, T. W. *Nature* **2003**, 424, 824. (b) Ditlbacher, H.; Hohenau, A.; Wagner, D.; Kreibitz, U.; Rogers, M.; Hofer, F.; Aussenegg, F. R.; Krenn, J. R. *Phys. Rev. Lett.* **2005**, 95, 257403. (c) Sanders, A. W.; Routenberg, D. A.; Wiley, B. J.; Xia, Y. N.; Dufresne, E. R.; Reed, M. A. *Nano Lett.* **2006**, 6, 1822.
184. Tong, L. M.; Gattass, R. R.; Ashcom, J. B.; He, S. L.; Lou, J. Y.; Shen, M. Y.; Maxwell, I.; Mazur, E. *Nature* **2003**, 426, 816.
185. Ma, H.; Jen, A. K. Y.; Dalton, L. R. *Adv. Mater.* **2002**, 14, 1339.
186. Joannopoulos, J. D.; Villeneuve, P. R.; Fan, S. *Nature* **1997**, 386, 143. (b) Joannopoulos, J. D.; Meade, R.; Winn, J. *Photonic Crystals*, Princeton Press, Princeto, NJ, **1995**. (c) Mekis, A.; Chen, J. C.; Kurland, I.; Fan, S. H.; Villeneuve, P. R.; Joannopoulos, J. D. *Phys. Rev. Lett.* **1996**, 77, 3787. (d) Noda, S.; Tomoda, K.; Yamamoto, N.; Chutinan, A. *Science* **2000**, 289, 604.
187. (a) Schiek, M.; Balzer, F.; Al-Shamery, K.; Brewer, J. R.; Lutzen, A.; Rubahn, H. -G. *Small* **2008**, 4, 176. (b) Balzer, F.; Bordo, V. G.; Simonsen, A. C.; Rubahn, H.-G. *Appl. Phys. Lett.* **2003**, 82, 10. (c) Balzer, F.; Bordo, V. G.; Simonsen, A. C.; Rubahn, H.-G. *Phys. Rev. B* **2003**, 67, 115408.
188. (a) Takazawa, K.; Inoue, J.; Mitsuishi, K.; Takamasu, T. *Adv. Mater.* **2011**, 23, 3659. (b) Takazawa, K. *J. Phys. Chem. C*, **2007**, 111, 8671. (c) Takazawa, K. *Chem. Phys. Lett.* **2008**, 452, 168.
189. (a) Zhao, Y. S.; Fu, H. B.; Peng, A. D.; Ma, Y.; Xiao, D. B.; Yao, J. N. *Adv. Mater.* **2008**, 20, 2859. (b) Zhang, C.; Zheng, J. Y.; Zhao, Y. S.; Yao, J. *Adv. Mater.* **2011**, 23, 1380. (c) Zhang, C.; Zou, C. L.; Yan, Y. L.; Hao, R.; Sun, F. W.; Han, Z. F.; Zhao, Y. S.; Yao, J. N. *J. Am. Chem. Soc.* **2011**, 133, 7276. (d) Lei, Y.; Liao, Q.; Fu, H.; Yao, J. *J. Am. Chem. Soc.* **2010**, 132, 1742.
190. (a) R. G. Ulbrich and G. W. Fehrenbach, *Phys. Rev. Lett.* **1979**, 43, 963. (b) S. Chu and S. Wong, *Phys. Rev. Lett.* **1982**, 48, 738. (c) L. C. Andreani, G. Panzarini and J. M. Gerard, *Phys. Rev. B Condens. Matter.* **1999**, 60, 13276. (d) J. I. Inoue, *Eur. Phys. J. B*, **2013**, 86, 70.
191. Zhao, Y. S.; Xu, J. J.; Peng, A. D.; Fu, H. B.; Ma, Y.; Jiang L.; Yao, J. N. *Angew. Chem. Int. Ed.* **2008**, 47, 7301.
192. Takazawa, K.; Kitahama, Y.; Kimura, Y.; Kido, G. *Nano Lett.* **2005**, 5, 1293.
193. (a) Chandrasekhar, N.; Mohiddon, Md. A.; Chandrasekar, R. *Adv. Optical Mater.* **2013**, 1, 305. (b) Basak, S.; Chandrasekar, R. *J. Mater. Chem. C* **2014**, 2, 1404. (c) Chandrasekar, R. *Phys. Chem. Chem. Phys.* **2014**, 16, 7173.
194. Chandrasekhar, N.; Basak, S.; Mohiddon, M. A.; Chandrasekar R. *ACS Appl. Mater. & Interfaces* **2014**, 6, 1488.

# 2

## Syntheses, Optical, Magnetic and Raman Studies of Doublet and Triplet Nitronyl Nitroxide (NN) and Oxoverdazyl (OVZ) Radicals Appended to 2,6-Bispyrazolylpyridine (BPP) and a Novel Spin Cross-Over $\text{Fe}^{\text{II}}(\text{BPP-OVZ})_2$ Complex



## 2.1 Abstract:

*This chapter presents the syntheses of a series of nitronyl nitroxide (NN), and oxoverdazyl (OVZ) based mono-, and bi-radicals attached to 4-phenyl-2,6-bispyrazolylpyridine (bpp) coupling unit, their optical, electron spin resonance (ESR) spectroscopy and computational studies. A correlation between the spin density polarization and the zero-field splitting (zfs) was made for the NN and OVZ based biradicals. The ESR spectroscopy revealed that the axial zfs parameter of the NN biradical ( $|D/hc| = 0.00719 \text{ cm}^{-1}$ ) is lower than the OVZ biradical ( $|D/hc| = 0.00601 \text{ cm}^{-1}$ ). Additionally both biradicals displayed forbidden half-field transitions ( $\Delta M_s = \pm 2$ ;  $g_{av} \sim 4.01$ ) at 170 K demonstrating their triplet nature. The cryogenic ESR measurements of the two biradicals showed a Curie behaviour of the  $\Delta M_s = \pm 2$  signal intensities ( $\chi_{EPR}$ ) down to 4.2 K. A comparative analysis showed that the ground state spin multiplicity of NN biradicals is probably triplet ( $S = 1$ ) and for OVZ biradicals the singlet and triplet states are nearly degenerate.*

*To combine the SCO effect with SS exchange coupling, complex  $[\text{Fe}^{\text{II}}(\mathbf{R4})_2](\text{ClO}_4)_2$  **C1**, was prepared, where **R4** is a mono-OVZ radical connected to a bpp unit. The variable temperature magnetic susceptibility and Raman measurements indicated the operating SCO effect in **C1**, with an estimated  $T_{1/2}$  value over 300 K. Self-assembly studies of **R4** and **C1** exhibited the formation of microrods and nanocrystals, respectively.*

## 2.2 Introduction:

The design and syntheses of paramagnetic molecules are of interest, due to their possible applications in various areas ranging from magneto-chemistry,<sup>1,2</sup> bio-organic chemistry,<sup>3</sup> and bio-inorganic chemistry.<sup>4</sup> Among stable radicals, nitroxides, nitronyl-nitroxide (NN) and oxoverdazyl (OVZ) have gained much interest due to high stability, and their ability to coordinate with *d* and *f* block elements. Particularly, these radicals attached to chelating ligand cores<sup>5,6</sup> are very attractive due to the possibility to synthesize paramagnetic and high-spin ligands which might give interesting magnetic properties such as *spin-spin* (SS) *exchange coupling*<sup>1-6</sup> or *spin cross-over* (SCO) *effect*<sup>7</sup> and the combination of these two interactions upon coordination with Fe(II) and Fe(III) ions. SCO Fe(II) complexes acts as perfect inorganic switches by changing their spin state reversibly from HS ( $t_{2g}^4; e_g^{*2}$ ) to LS ( $t_{2g}^6; e_g^{*0}$ ) w.r.t.

temperature, pressure, light, and electric field.<sup>8g,h</sup> Particularly, understanding the relationship between the zero-field splitting (*zfs*), spin density distribution and SS exchange interaction requires, a comparative investigation of these parameters<sup>4d</sup> in two different *meta* bridged biradicals<sup>8</sup> connected to the same coupling units (CU). To achieve these properties synthesis of a series of paramagnetic molecules carrying mono

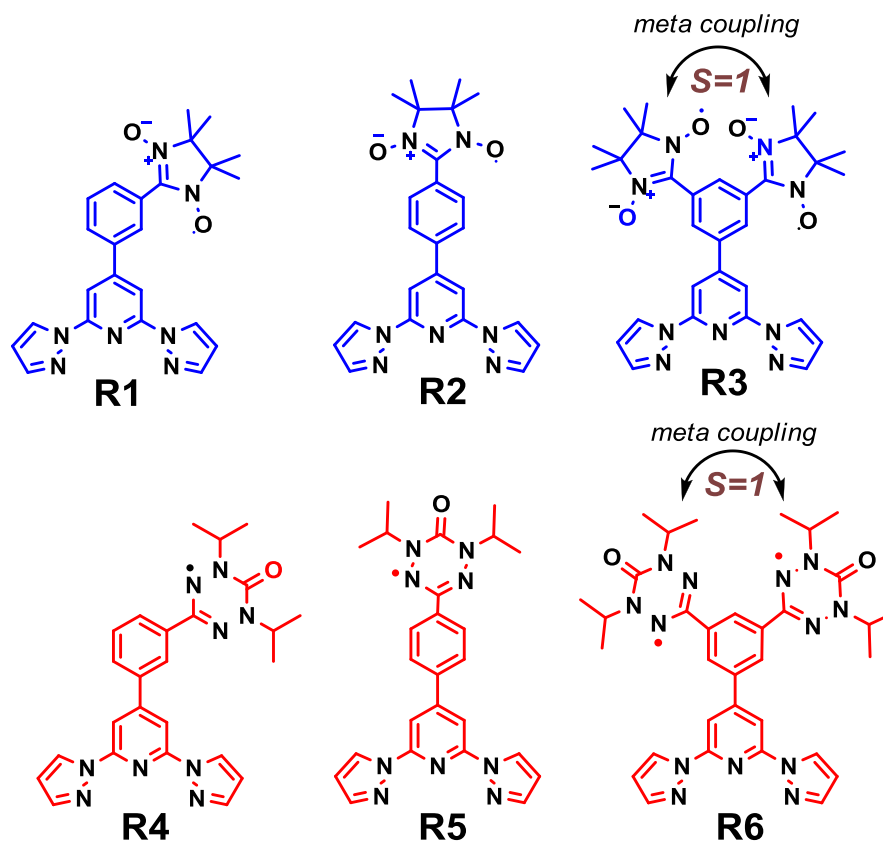
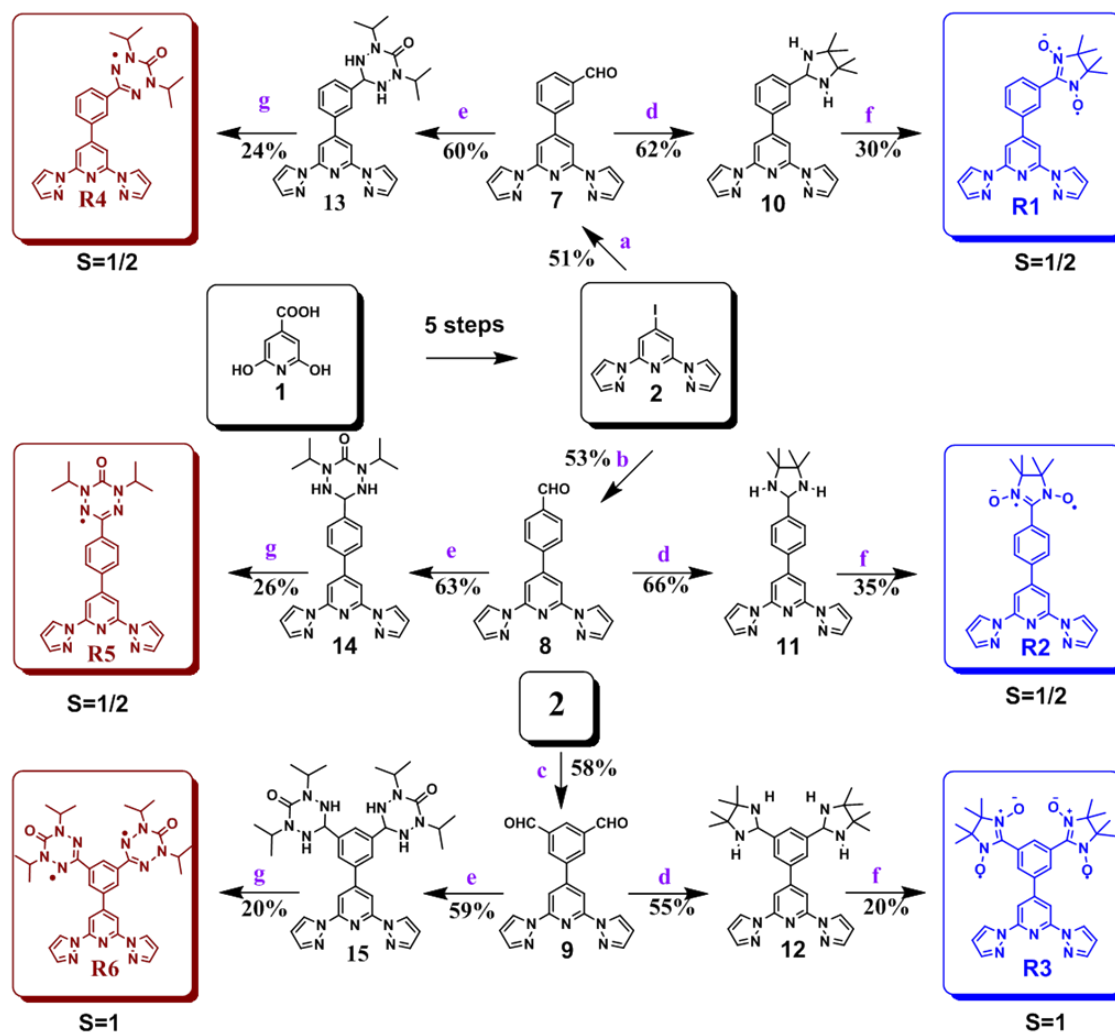


**CHART 2.1** Nitronyl-Nitroxide (NN) and Oxo-Verdazyl (OVZ) based mono and di-radicals decorated to 2,6-Bispyrazolylpyrines (**R1-R6**).

and biradicals (**R1-R6**) based on NN and OVZ radical units connected to 4-phenyl-2,6-bispyrazolylpyridine (bpp) coupling unit was envisioned (Chart 2.1). These radicals also include two *m*-phenylene bridging type NN and OVZ type biradicals (**R3** and **R6**), leading to non-Kekule' structures for high-spin ground-state formation.<sup>8</sup>

This chapter presents the preparation of mono and biradicals, their optical and ESR spectroscopic investigations. A detailed investigation to unravel the intramolecular magnetic properties, i.e. the interplay between spin polarization, dipolar coupling strengths and the ground state spin properties will be also discussed.<sup>4d</sup> Preparation of SCO complex from one of the mono OVZ radicals and its investigations using variable

temperature Raman, ESR spectroscopy and self-assembly properties will also be presented.



**Scheme 2.1** Syntheses of Nitronyl-Nitroxide (NN) and Oxo-Verdazyl (OVZ) based mono and di-radicals attached to 2,6-bispyrazolylpyrines (**R1-R6**). *Reagents and conditions:* (a-c) [Pd(PPh<sub>3</sub>)<sub>4</sub>] / 3-formylphenyl-boronic acid for **7**, 4-formylphenyl-boronic acid for **8**, 3,5-di-formylphenyl-boronic acid for **9** / 1,4-dioxane / Na<sub>2</sub>CO<sub>3</sub>/ 3 d / 70° C. (d) 2,3-diamino-2,3 dimethylbutane (**3**) / CHCl<sub>3</sub> / 2 d / 60 °C. (e) 2,4-diisopropylcarbohydrazide bishydrochloride (**4**) / sodium acetate / EtOH / 15h / RT. (f) *m*-CPBA / NaIO<sub>4</sub> / CH<sub>2</sub>Cl<sub>2</sub> / H<sub>2</sub>O / 0 °C / 1h. (g) benzoquinone / toluene / 60 °C.

## 2.3 Results and Discussions:

### 2.3.1 Syntheses and <sup>1</sup>H-NMR Characterization of Paramagnetic Ligands:

It is important to mention here that the synthesis of NN radical is not straightforward. The traditional Ullman condensation route<sup>9</sup> has a series of limitations i.e. the reaction of an aryl or alkyl aldehyde group with 2,3-dimethyl-2,3-bis-(hydroxylamino)butane (BHA) followed by oxidation of the diamagnetic condensation

product to get NN radicals. Here the synthesis of BHA from 2,3-dimethyl-2,3-bis-(nitro)butane is very sensitive to reaction conditions such as the quality and particle size of the zinc dust used in the reduction reaction. In most of the cases the synthesis is very delicate and often not reproducible. Alternatively, a decade ago, Ovcharenko and Rey *et al.* have developed an elegant “diamino route” for the synthesis of NN radicals by the condensation reaction of 2,3-dimethyl-2,3-dinitrobutane with aryl-aldehydes bypassing the preparation of BHA.<sup>10</sup>

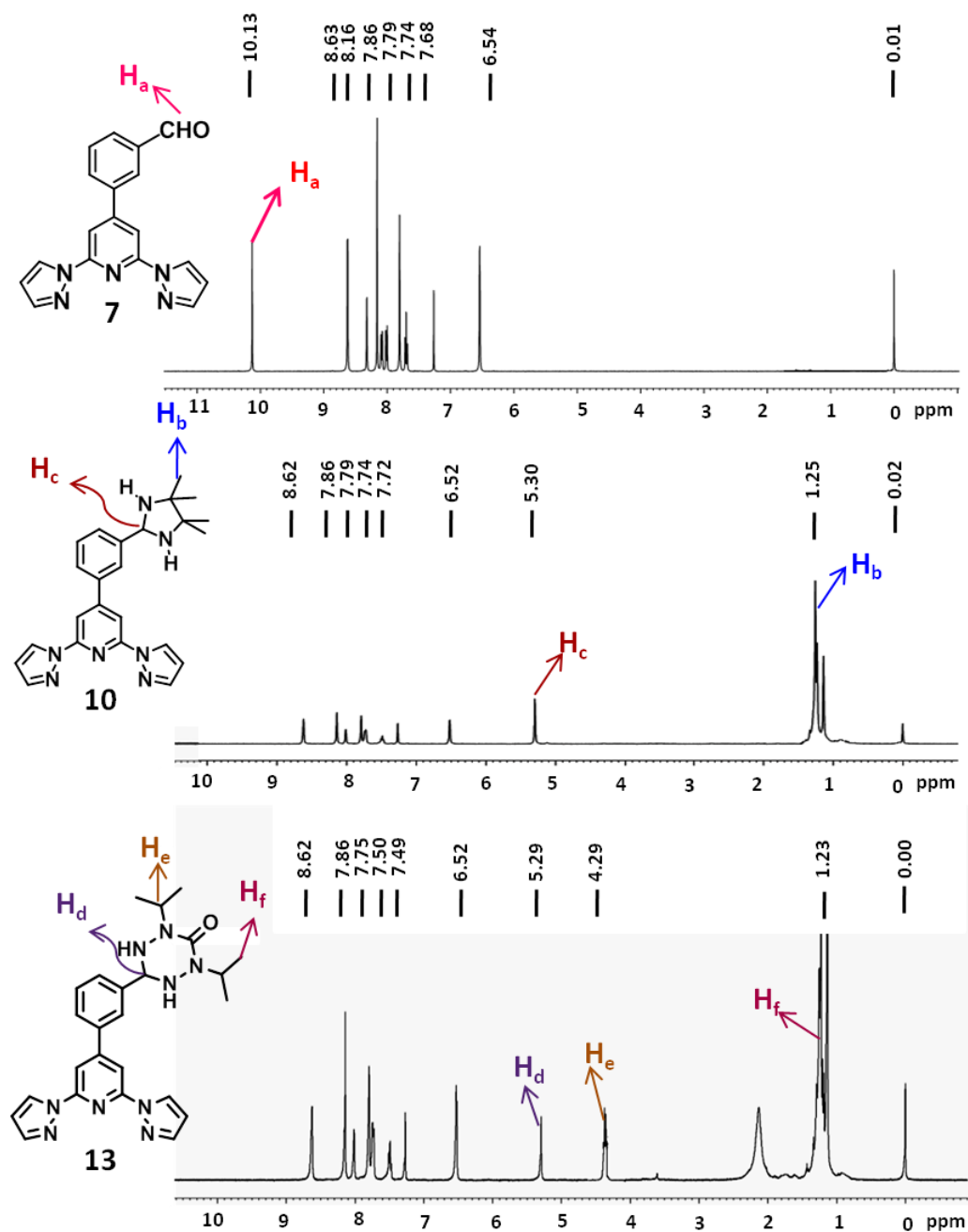


**Figure 2.1** Comparative <sup>1</sup>H-NMR spectra of radical precursors **10** and **13** obtained from the corresponding aldehyde **7**.

Based on this alternative procedure 2,3-dimethyl-2,3-diaminobutane was synthesized by reducing 2,3-dimethyl-2,3-dinitrobutane using tin metal under acidic reflux conditions.

For the syntheses (Scheme 2.1) of NN and OVZ based mono (**R1-R3**) and biradicals (**R4-R6**) the main precursor is the mono- and di-aldehyde functionalized bpp (**7-9**). Compounds **7-9** were prepared under Suzuki cross-coupling conditions by reacting 4'-iodo-2',6'-dipyrazolyl-pyridines<sup>7e</sup> with the corresponding boronic acid derivative of

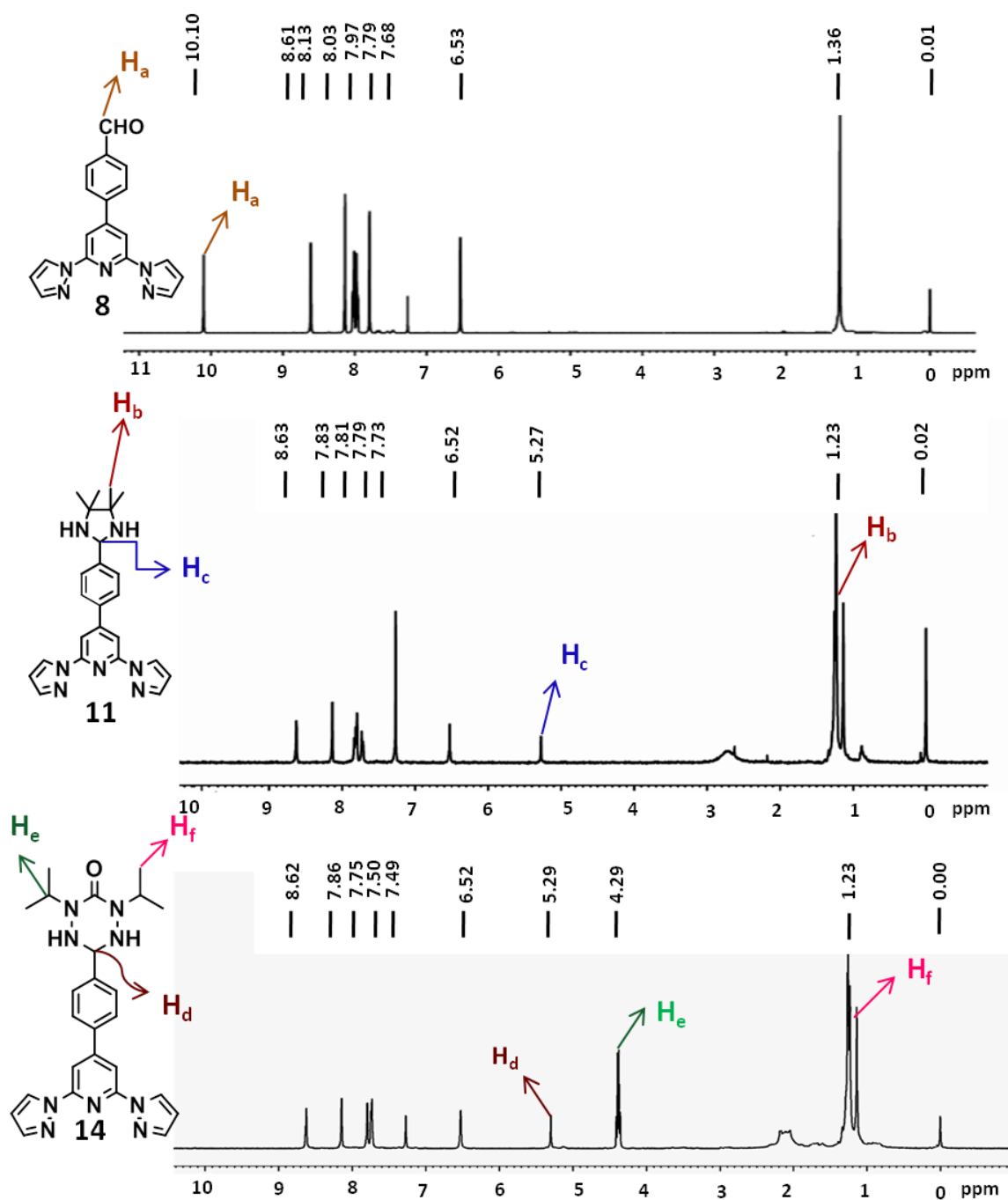


**Figure 2.2** Comparative  $^1\text{H}$ -NMR spectra of radical precursors **11** and **14** obtained from the corresponding aldehyde **8**.

mono or dialdehydes in modest yields of ca. 55%. The formation of aldehyde was confirmed from the  $^1\text{H}$ -NMR chemical shifts of the proton ( $-\text{CHO}$ ) at the range 10.5-9.8 ppm (see Fig. 2.1-2.3 top spectra for compounds 7-9). The five-member imidazolidine ring derivatives (**10-12**) were prepared by reacting the aldehyde precursor (**7-9**) with 2,3-dimethyl-2,3-diaminobutane at 60 °C under inert atmosphere in very good yields (81%).

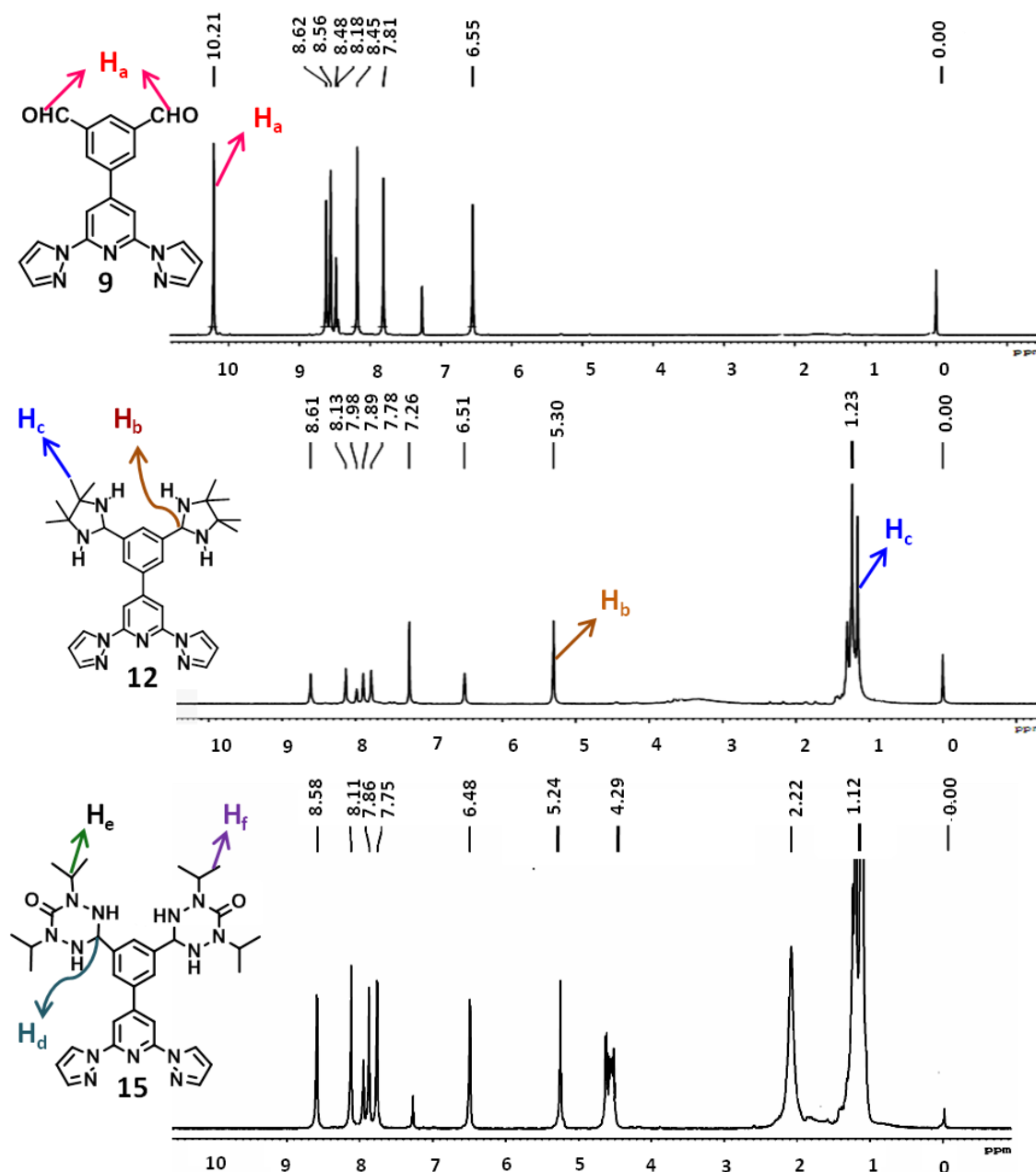


**Figure 2.3** Comparative  $^1\text{H}$ -NMR spectra of radical precursors **12** and **15** obtained from the corresponding aldehyde **9**.

The  $^1\text{H}$ -NMR chemical shifts of the proton attached to tertiary carbon ( $\text{N}-\text{CH}-\text{N}$ ) typically in the range of 5.27-5.30 ppm confirmed the formation of the five member

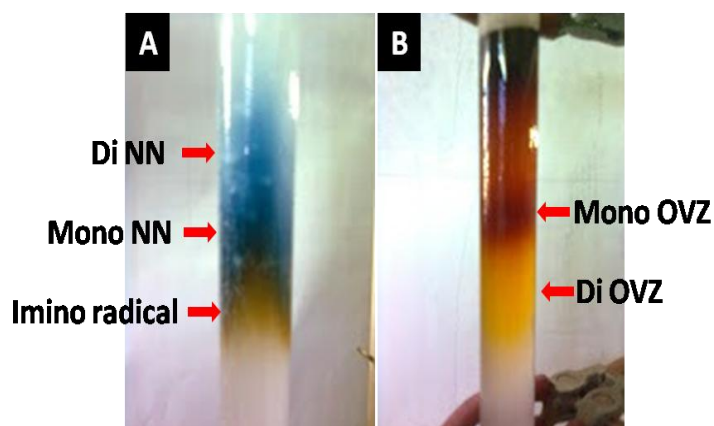


**Figure 2.4** Separation of mono and di radicals by column chromatography, (a) for NN radical. (b) for OVZ radical.

treatment of respective compounds (**10-12**) with *m*-CPBA followed by oxidation with  $\text{NaIO}_4$  to get blue color NN radicals (**R1-R3**).

The OVZ-based mono (**R4** and **R5**) and *m*-phenylene type diradicals (**R6**) were also prepared from **7-9**, respectively. Brook's procedure was employed to synthesize *N,N'*-diisopropyl substituted OVZ radicals (**R4-R6**),<sup>21</sup> because this method gives higher OVZ stability during the synthesis compared to its *N,N'*-dimethyl substituted analogs. Reaction of 2,4-diisopropylcarbohydrazide bis-hydrochloride with the appropriate aldehyde precursors in reflux ethanol formed the mono (**13** and **14**) and bistetrazanes (**15**). The  $^1\text{H}$ -NMR spectra confirmed the formation of tetrazane six-member rings in **13-15** by displaying characteristic chemical shifts in the range of 5.23-5.3 ppm (see Fig. 2.1-2.3 bottom spectra for compounds **13-15**). The tetrazenes were finally oxidized with benzoquinone under reflux condition to get brown-red color mono (**R4** and **R5**) and dioxoverdazyl radicals (**R6**). The LC-MS analyses further established the formation of radicals by exhibiting *m/z* peaks at 469 for **R4** and **R5**, 649 for **R6**.

The purifications of these NN radicals were always carried out on neutral alumina ( $\text{Al}_2\text{O}_3$ ) since they decompose when silica ( $\text{SiO}_2$ ) was used compared to the OVZ radicals which are stable in silica (Fig. 2.4). The colors of nitronyl nitroxide (NN) and oxo verdazyl (OVZ) radicals are deep blue and brown, respectively (Fig. 2.4 and 2.5). Micro crystals were obtained for NN and OVZ by slow evaporation of  $\sim 10^{-3}$  M solution of toluene. The toluene solution was stored inside

imidazolidine moiety (see Fig. 2.1-2.3 middle spectra for compounds **10-12**).

Furthermore LC-MS analyses also confirmed the formation of five-member ring by displaying *m/z* peaks at 414 for **10** and **11** and 541 for **12**. Finally the introduction of 1,3-diol in the five member imidazolidine moiety was carried out by

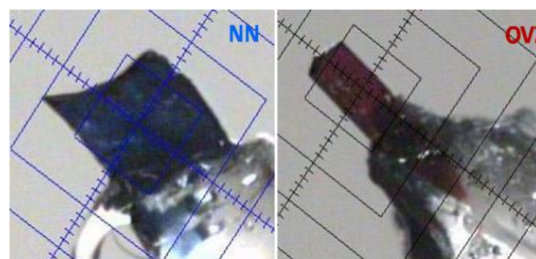


**Figure 2.5** NN and OVZ single crystals at RT.

Micro crystals were obtained for NN and OVZ by slow evaporation of  $\sim 10^{-3}$  M solution of toluene. The toluene solution was stored inside

refrigerator in a crystallisation tube for around 1 month and small plate like crystals were grown on the wall of the tube.

### 2.3.2 Single Crystal X-ray Structure of R1:

The single crystal X-ray structure (monoclinic; P21/c) of **R1** showed that the torsion angles ( $\Phi$ ) between the phenyl ring and the NN radical plane are  $27.60^\circ$  (C9-C8-C18-N7), and  $28.59^\circ$  (C7-C8-C18-N6) (Fig. 2.6). Furthermore the phenyl ring and the chelating unit 2,6-bispyrazolylpyridine are in near planar configuration ( $\Phi = ca. 24^\circ$ ). A clear intra-molecular analysis will be presented in Chapter 3, Section 3.3.3.

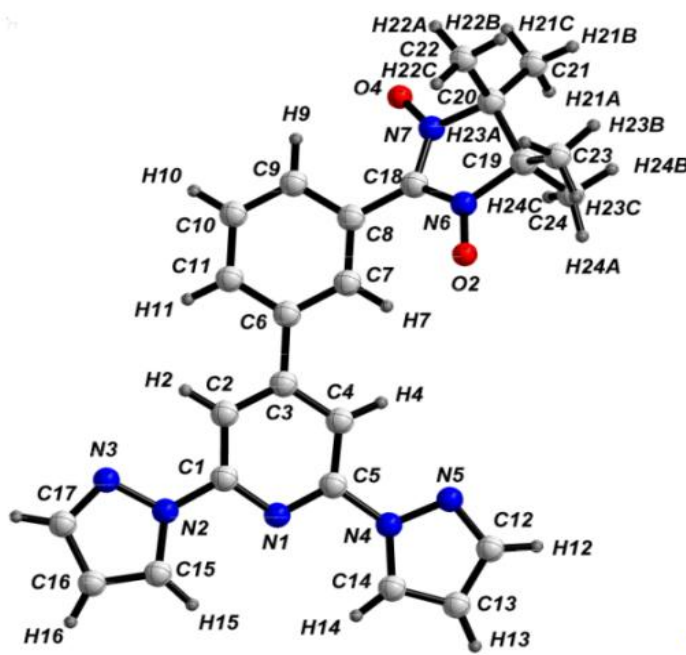


Figure 2.6 ORTEP plot (50 % probability ellipsoid) of mono-NN radical **R1**.

### 2.3.3 Optical Properties of Radicals (R1-R6):

The UV–Vis absorption studies of NN radicals (**R1–R3**) in toluene showed characteristic bands for the  $n\text{-}\pi^*$  transitions in the visible range ( $\lambda_{\text{max}} \sim 600$  nm) with very low extinction coefficient together with the vibronic coupling (Fig. 2.7). The electronic spectra of OVZ radicals (**R4–R6**) displayed distinguished features corresponding to verdazyl radicals. Radicals **R4–R6** displayed high energy bands at 360, 367 and 374 nm, respectively together with broad low energy bands from 400–650 nm range. In toluene solution of NN radical showed blue color and OVZ brown color (Fig. 2.7 inset).

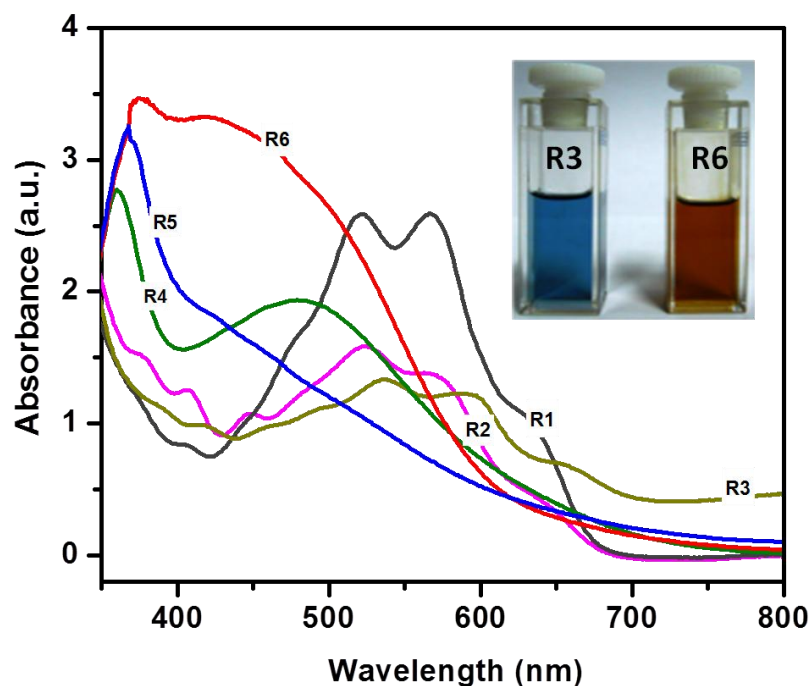


**Figure 2.7** UV-Vis spectra of NN and OVZ radicals **R1-R6**. Inset shows the color of the radicals **R3** and **R6**.

### 2.3.4 X-Band ESR Spectroscopy Studies of Radicals (**R1-R6**):

X-band ESR spectroscopy studies were carried out to understand the intramolecular magnetic properties of the radicals **R1-R6** (Fig. 2.8 and 2.9). At room temperature the mono NN radicals (**R1** and **R2**) (toluene;  $c \sim 10^{-4}$  M) exhibited a five-line pattern ( $\Delta M_s = \pm 1$ ; intensity ratio of 1:2:3:2:1) (Fig. 2.9, top) and NN biradical **R3** showed a nine line spectrum ( $\Delta M_s = \pm 1$ ; close to 1:4:10:16:19:16:10:4:1) due to the hyperfine coupling (*hfc*) of the NN electron spin(s) with two (for **R1** and **R2**) and four (for **R3**) equivalent nitrogen ( $^{14}\text{N}$ ) nuclei (Fig. 2.8A). Simulation<sup>12</sup> of the experimental spectra showed that the nitrogen *hfc* values of **R1** and **R2** are  $a_N = 7.40$  G and 7.41 G, respectively. The isotropic  $g_{\text{iso}}$  value of radicals **R1-R3** are 2.0066, 2.0065 and 2.0071, respectively. In the case of **R3**, due to the strong exchange coupling (*J*) within the EPR limits, the simulation perfectly fits by assuming four nitrogens with half the monoradical hyperfine coupling with  $J \gg 7 \times 10^{-4} \text{ cm}^{-1}$  ( $J/a_N \gg 1$ ). At room temperature OVZ radicals **R4** and **R5** displayed a strong nine-line pattern ( $\Delta M_s = \pm 1$  transitions; intensity ratio close to 1:4:10:16:19:16:10:4:1). Simulation of the experimental spectra showed the following *hfc* values  $a_{N1} = 6.41$  G,  $a_{N2} = 5.35$  G and  $a_H = 1.13$  G for **R4** and  $a_{N1} = 6.20$  G,  $a_{N2} = 5.20$  G and  $a_H = 1.13$  G for **R5** (Table 2.1). Interestingly, biradical **R6** only showed a nine line spectrum with an intensity ratio analogous to **R4** and **R5** (The *zfs* spectrum of **R6** showed only a tiny fraction of monoradical impurity (Fig. 2.8D). For our surprise a

few literatures which reported the ground state spin multiplicity of OVZ biradicals did not disclose their isotropic  $hfc$  pattern.<sup>2f,g</sup> In our case, the obtained nine line spectrum (Fig. 2.8B) of **R6** showed that probably the SS exchange coupling is  $J \geq 0$ . The isotropic  $g$ -values of radicals **R4-R6** are 2.0063, 2.0065 and 2.0071, respectively.

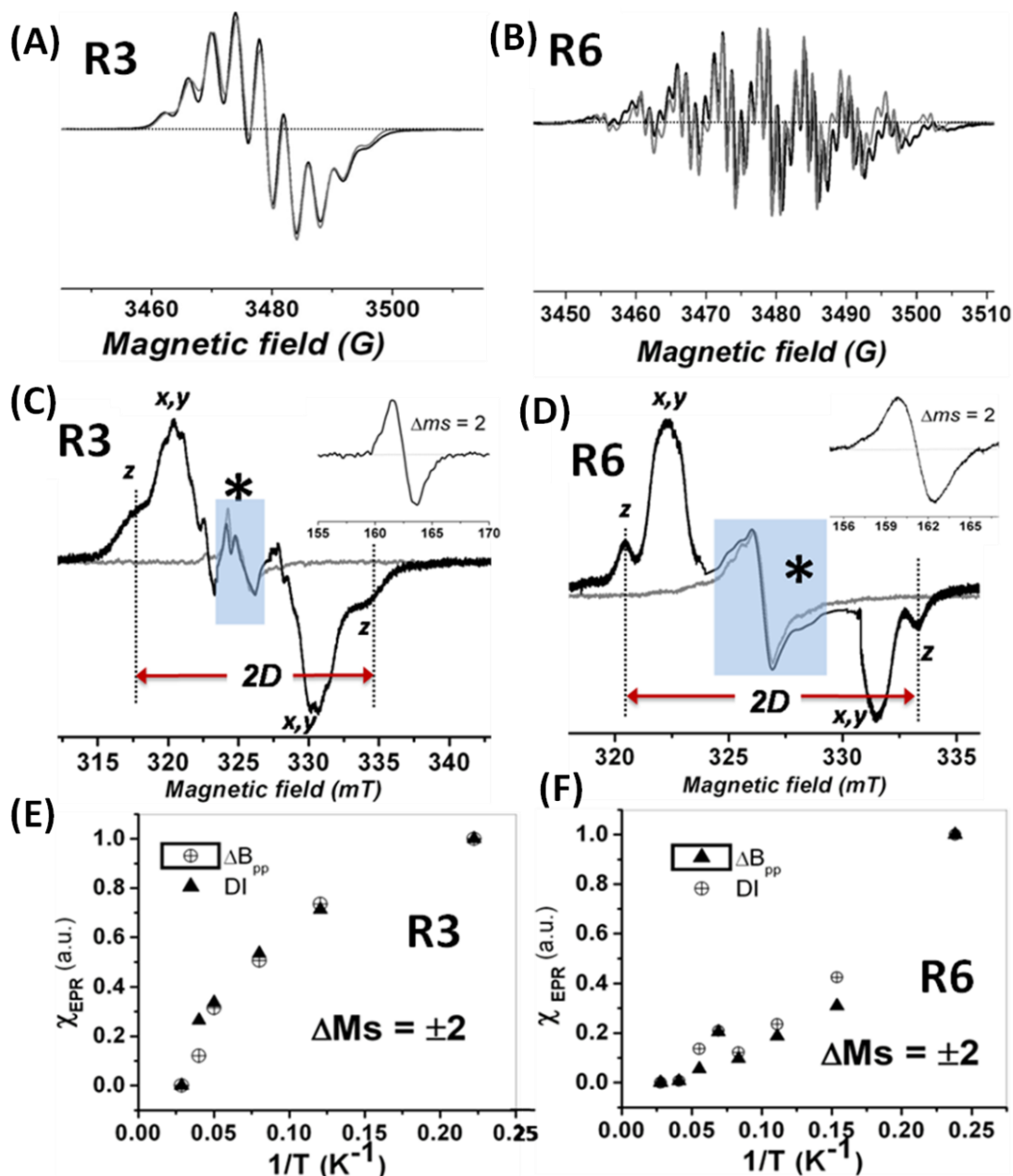


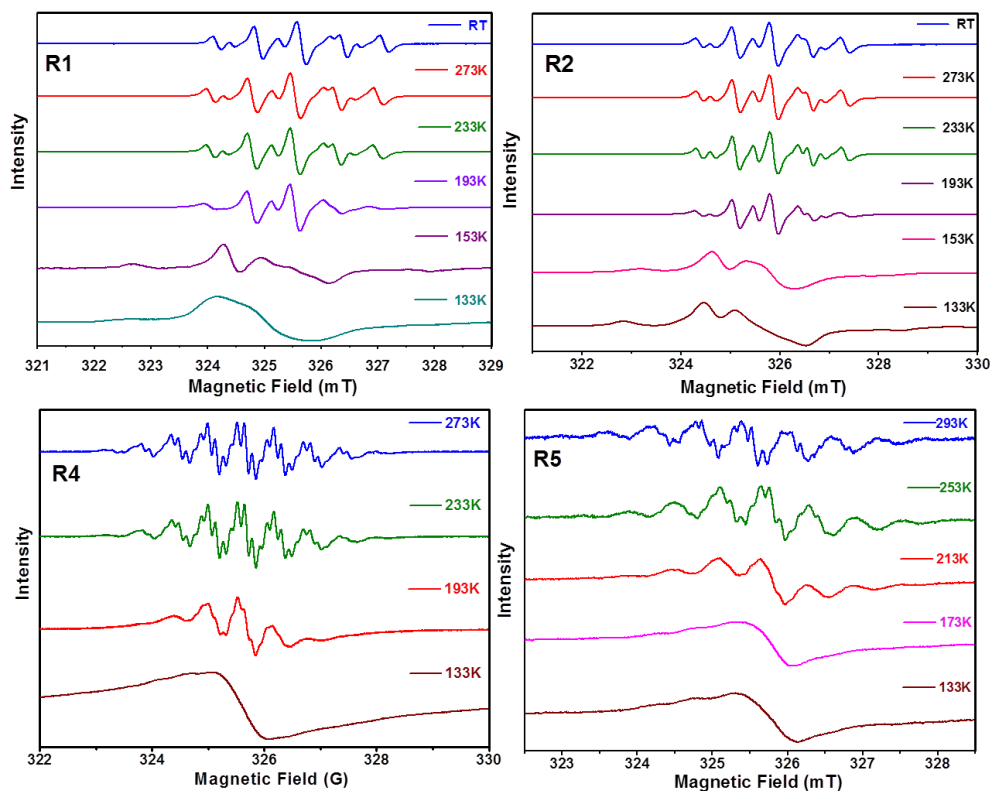
**Figure 2.8** Isotropic ESR spectra of biradicals: (A) **R3** and (B) **R6** in toluene. Experiment (black line) and simulation (gray line). The anisotropic frozen state  $zfs$  spectra of biradicals: (C) **R3** and (D) **R6** are shown in black lines. The asterix (\*) marks and blue shaded regions denote the contribution of the monoradical impurity in **R3** and **R6**. For comparison the monoradical spectra of **R1** and **R4** are plotted in gray lines together with the spectra of **R3** and **R6**, respectively. The inset show the forbidden  $\Delta M_s = \pm 2$  transitions. Temperature dependence of the doubly integrated signal intensities ( $\chi_{EPR}$ ) and the peak-to-peak signal intensities ( $\Delta B_{pp}$ ) of the  $\Delta M_s = \pm 2$  (Curie plot) transitions of (E) **R3** and (F) **R6**.

The triplet nature of biradical **R3** was clearly apparent from its *zfs* pattern obtained from the frozen state (toluene;  $c \sim 10^{-4}$  M; 170 K) axial spectrum with an unusual resolution of nitrogen hyperfine coupling (Fig. 2.8C). The measured *zfs* parameter (2D) value of **R3** is 15.4 mT ( $|D/hc| = 0.00719 \text{ cm}^{-1}$ ). By applying a point-dipole approximation, from the experimental D value, the distance of separation of *ca.*  $r = 7.12 \text{ \AA}$  between two NN units was estimated for biradical **R3**. Interestingly, biradical **R6** also displayed an axial *zfs* pattern at 170 K with a 2D value of 12.86 mT ( $|D/hc| = 0.00601 \text{ cm}^{-1}$ ) proving its biradical nature (Fig. 2.8D). From the D value, an intra-spin distance of separation (*r*) of *ca.*  $7.56 \text{ \AA}$  was calculated between the two OVZ units. For comparison the frozen state monoradical spectra of **R1** and **R4** are plotted together with the *zfs* spectra of biradicals **R3** and **R6**, respectively (gray lines in Fig. 2.8C, D). Furthermore the triplet nature of biradicals **R3** and **R6** were supported by the appearance of forbidden half-field transitions ( $\Delta M_s = \pm 2$ ;  $g_{av} \sim 4.01$ ) at 170 K (Fig. 2.8C, D insets).

To study the temperature dependency of the  $\Delta M_s = \pm 2$  transitions signal intensities of **R3** and **R6** was followed down to 4.2 K. The measurements were repeated at different microwave powers in order to ensure that the signals were not saturated, by plotting the observed doubly integrated signal intensities with respect to the square root of the microwave power used. For both **R3** and **R6**, the plot of the doubly integrated  $\Delta M_s = \pm 2$  intensity ( $\chi_{\text{EPR}}$ ) versus inverse temperature (Fig. 2.8E, F) increased strongly while approaching cryogenic temperature. The strong increase in the  $\chi_{\text{EPR}}$  value clearly suggested the increase in the triplet state population with decrease of temperature following Curie pattern. This finding points out that, for biradicals **R3** and **R6**, the ground state spin multiplicity is probably ferromagnetically coupled ( $J > 0$ ) triplet ( $S = 1$ ) state or the triplet state which is nearly degenerate ( $J \geq 0$ ) with the singlet state ( $S = 0$ ). But it is clear from the obtained *hfc* pattern that the *J* value of **R3** is definitely greater than zero, whereas for **R6** it should be close to zero. This result demonstrated that the NN biradicals in **R3** is more strongly spin-spin (SS) exchange coupled than OVZ biradicals in **R6**. Variable temperature ESR spectra of (NN) **R1**, **R2** and (OVZ) **R4**, **R5** recorded at low microwave power in diluted frozen solutions  $10^{-3}$  M are shown in Figure 2.9. Upon lowering the temperature only there is a large broadening of peaks, with no change in peak-positions, and total spectral widths was observed, hence no *J* modulation is implicated in the temperature range analyzed.

**Table 2.1:** Estimated  $zfs$  parameters (for the biradical systems), hyperfine coupling constants and  $g$  values for mono and biradicals.

| <i>ESR Parameters</i>      | <i>NN radical</i> |             | <i>OVZ radical</i>                                         |                                                            |
|----------------------------|-------------------|-------------|------------------------------------------------------------|------------------------------------------------------------|
|                            | <b>R1</b>         | <b>R3</b>   | <b>R4</b>                                                  | <b>R6</b>                                                  |
| $J$                        | -                 | $J \gg a_N$ | -                                                          | $J \sim 0$                                                 |
| $a_N$ (G)                  | 7.4               | 3.75        | $a_{N1} = 6.41$ G,<br>$a_{N2} = 5.35$ G,<br>$a_H = 1.13$ G | $a_{N1} = 6.20$ G,<br>$a_{N2} = 5.20$ G,<br>$a_H = 1.13$ G |
| $g_{iso}$                  | 2.0066            | 2.0071      | 2.0063                                                     | 2.0068                                                     |
| 2D (mT)                    | -                 | 15.4        | -                                                          | 12.86                                                      |
| $r$ (Å)                    | -                 | 7.12        | -                                                          | 7.56                                                       |
| $D/hc$ (cm <sup>-1</sup> ) | -                 | 0.00719     | -                                                          | 0.00601                                                    |
| $\Delta B_{pp}$ (mT)       | 1.5               | 2.17        | 1.94                                                       | 2.28                                                       |

**Figure 2.9** Top: ESR spectra ( $\Delta M_s = \pm 1$ ) of **R4** and **R5** ( $c = 10^{-3}$  M in toluene) at 273 – 133 K. Bottom: ESR spectra ( $\Delta M_s = \pm 1$ ) of **R1** and **R2** ( $c = 10^{-3}$  M in toluene) at 298 – 133 K.

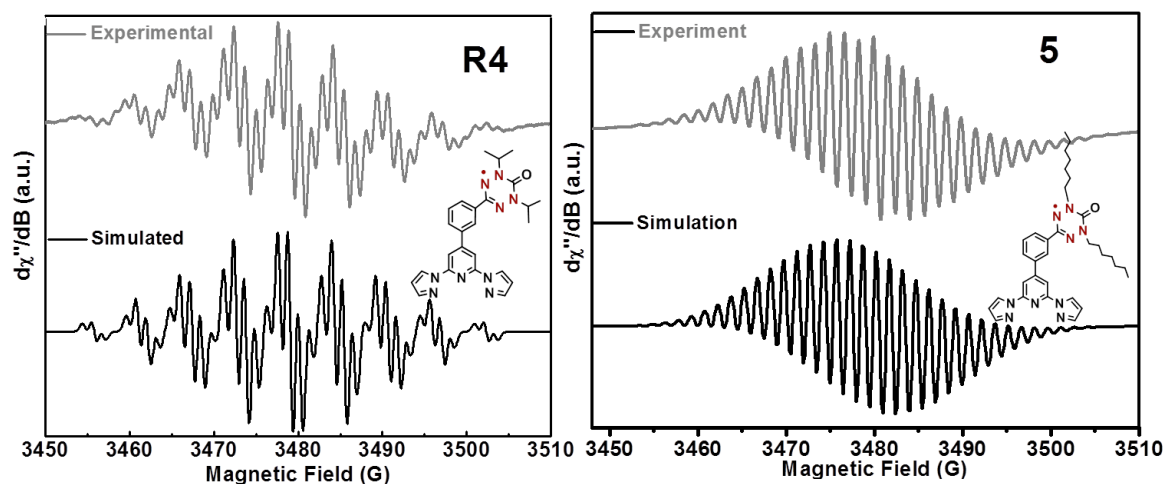


**Figure 2.10** ESR spectra ( $\Delta Ms = \pm 1$ ) of **R4** and **5** ( $c = 10^{-3}$  M in toluene) at RT.

**Table 2.2:** Estimated hyperfine coupling constants of N and H atoms after the attachment of heptyl chains in OVZ unit instead of isopropyl chain.

|           | <b>R4</b>                                               | <b>5</b>                                                                                                          |
|-----------|---------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------|
| $a_N$ (G) | $a_{N1} = 6.41$ G, $a_{N2} = 5.35$ G,<br>$a_H = 1.13$ G | $a_{N1} = 4.50$ G, $a_{N2} = 4.0$ G,<br>$a_{H1} = 1.5$ G, $a_{H2} = 1.3$ G,<br>$a_{H3} = 1.4$ G, $a_{H5} = 1.2$ G |
| $g_{iso}$ | 2.0063                                                  | 2.0069                                                                                                            |

Alkyl chains play a very important role in distributing unpaired electron spin densities as evidenced by the high resolution ESR spectra. Compared to isopropyl group, for long alkyl chains the difference between hyperfine coupling constant of N-atoms is small (Table 2.2), as one can see disappearance of nine line pattern and appearance of multiple lines with narrow spacing. An effective model for the spin density distribution mechanism is *hyperconjugation*, which provides a direct link of the methyl hydrogen atoms with electrons in the  $\pi$ -system (Fig. 2.10).

## 2.4 Synthesis and Characterization of Spin Cross-Over (SCO) $[\text{Fe}^{\text{II}}(\text{R4})_2](\text{ClO}_4)_2$ Complex (C1):

Nihei *et al* have reported for the first time preparation of Fe(II) SCO complex from a organic nitronyl nitroxide radical carrying tridentate bpp ligand.<sup>11</sup> To study the effect of

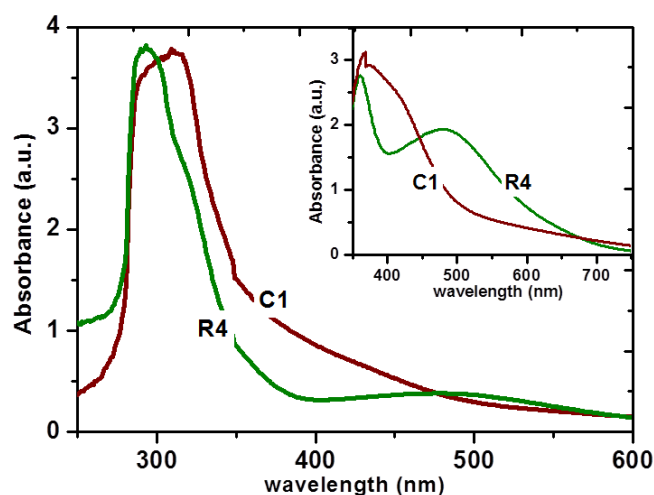
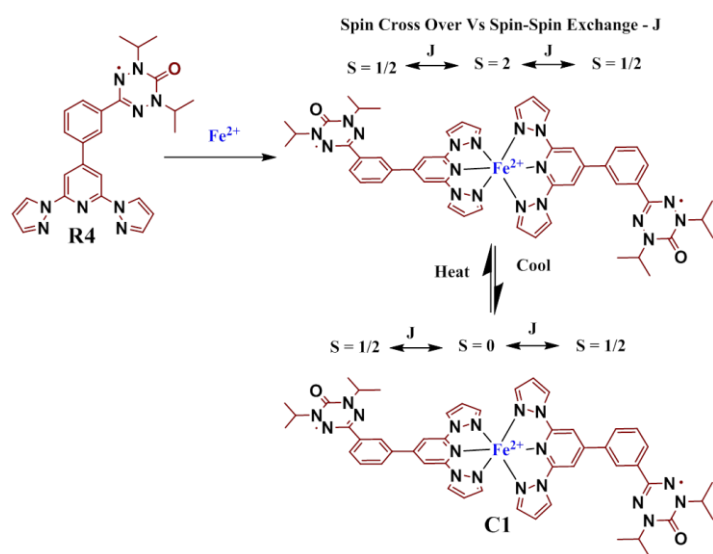


**Figure 2.11.** UV-Vis spectra of OVZ radical **R4** and complex **C1**. Inset shows the low energy bands of the radicals **R4** and complex **C1**.

paramagnetic doublet state ligand on the SCO property complex  $[\text{Fe}^{\text{II}}(\text{R4})_2](\text{ClO}_4)_2$  (**C1**) was synthesized from OVZ radical (**R4**) (Scheme 2.2). Attempts to get the single crystals suitable for x-ray diffraction in various solvents were unsuccessful. But, based upon our earlier studies and others, it is expected that in **C1** the central

Fe(II) ion is coordinated octahedrally by two tridentate ligands totally carrying two

oxoverdazyl radicals (Scheme 2.2).<sup>7b</sup> The formation of complex **C1** was confirmed by LCMS and elemental analysis. The UV-Vis absorption studies of **R4** and **C1** displayed distinguished features corresponding to verdazyl radical and its Fe(II) complex in toluene. Radical **R4** displayed characteristics  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  transition bands in the UV ( $\lambda_{\text{max}} \sim$



**Scheme 2.2.** Synthesis of  $[\text{Fe}^{\text{II}}(\text{R4})_2](\text{ClO}_4)_2$  complex (**C1**).

290 nm) and visible ( $\lambda_{\text{max}} \sim$

490 nm) ranges, respectively.

The broad low energy visible bands from 400-700 nm range vanished upon complex **C1** formation. The high energy absorption band (at 293 nm) of **R4** also shifted to 311 nm in complex **C1** (Fig. 2.11). The Raman spectra of **R4** and complex **C1** showed marked difference in the

band positions indicating the complex formation. A variation in the peak intensity and shifts were observed in **R4** and **C1**. For example the  $984\text{ cm}^{-1}$  peak intensity increased and shifted to  $1015\text{ cm}^{-1}$  in complex (**C1**) compared to radical (**R4**). The peaks appeared at  $1463$  and  $1562\text{ cm}^{-1}$  corresponding to **R4** were shifted to low frequency  $1410$  and  $1501\text{ cm}^{-1}$  in the complex, due to the complex formation (Fig. 2.15D and 2.16F).

#### 2.4.1 Variable Temperature Magnetic Susceptibility Measurement and Raman Spectroscopy Studies:

To study the SCO effect of Fe(II) ion octahedrally coordinated to two mono-OVZ radical carrying ligands and to explore any possible exchange interaction of Fe(II) with the radical centres, temperature dependent magnetic susceptibility of complex **C1** was performed. For the magnetic studies a quantum design vibrating sample magnetometer (VSM-SQUID) set-up operating in the temperature range of  $340 \leftrightarrow 2\text{ K}$  with an applied

DC magnetic field of  $0.5\text{ T}$  was employed (Fig. 2.12).

Compound **C1** showed a reversible ST behavior in the temperature range of  $340 \leftrightarrow 2\text{ K}$ . At  $340\text{ K}$  the product of the molar magnetic susceptibility and temperature ( $\chi T$ ) is  $2.93\text{ emu K mol}^{-1}$ , which is lower than the expected value for a HS Fe(II) ion in the  $S = 2$  state.

At high temperature, a spin-only value of  $6.00\text{ emu K mol}^{-1}$  is expected for the complex **C1** (HS state Fe(II) ion and two doublet radicals centers) in the uncoupled spin states. This experimental magnetic moment showed that the thermally saturated HS state is situated much above  $340\text{ K}$ , which was the upper limit of the experimental set up. Upon cooling the  $\chi T$  value sharply decreased till  $\sim 300\text{ K}$  and below this temperature the  $\chi T$  value dropped in a sluggish manner to reach a minimum value of ca.  $1.81\text{ emu K mol}^{-1}$  at  $61\text{ K}$  and further it decreased steeply to a value of  $0.63$

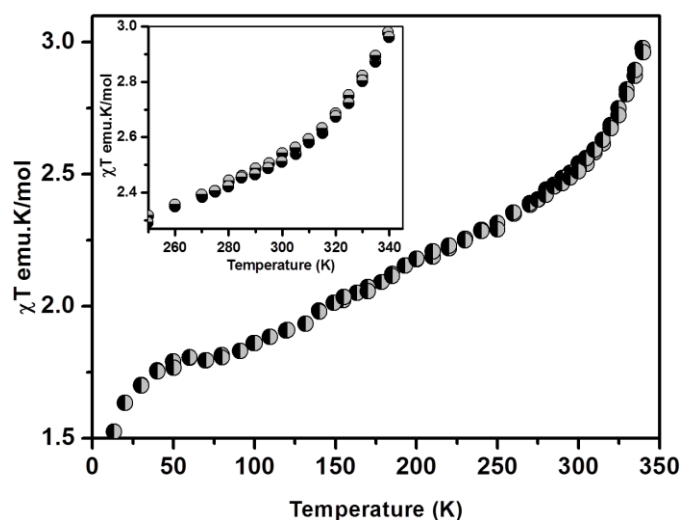


**Figure 2.12** The  $\chi T$  vs  $T$  plot for the complex **C1** measured in the temperature range of  $2\text{--}320\text{ K}$  in the ( $\downarrow$ ) cooling and ( $\uparrow$ ) heating mode cycles with an applied DC magnetic field of  $0.5\text{ T}$ .

$\text{mol}^{-1}$  is expected for the complex **C1** (HS state Fe(II) ion and two doublet radicals centers) in the uncoupled spin states. This experimental magnetic moment showed that the thermally saturated HS state is situated much above  $340\text{ K}$ , which was the upper limit of the experimental set up. Upon cooling the  $\chi T$  value sharply decreased till  $\sim 300\text{ K}$  and below this temperature the  $\chi T$  value dropped in a sluggish manner to reach a minimum value of ca.  $1.81\text{ emu K mol}^{-1}$  at  $61\text{ K}$  and further it decreased steeply to a value of  $0.63$

emu K mol<sup>-1</sup> at 2 K. From the experimental data, without a clear-cut HS state value, one can safely presume that the  $T_{1/2}$  value is above 300 K.

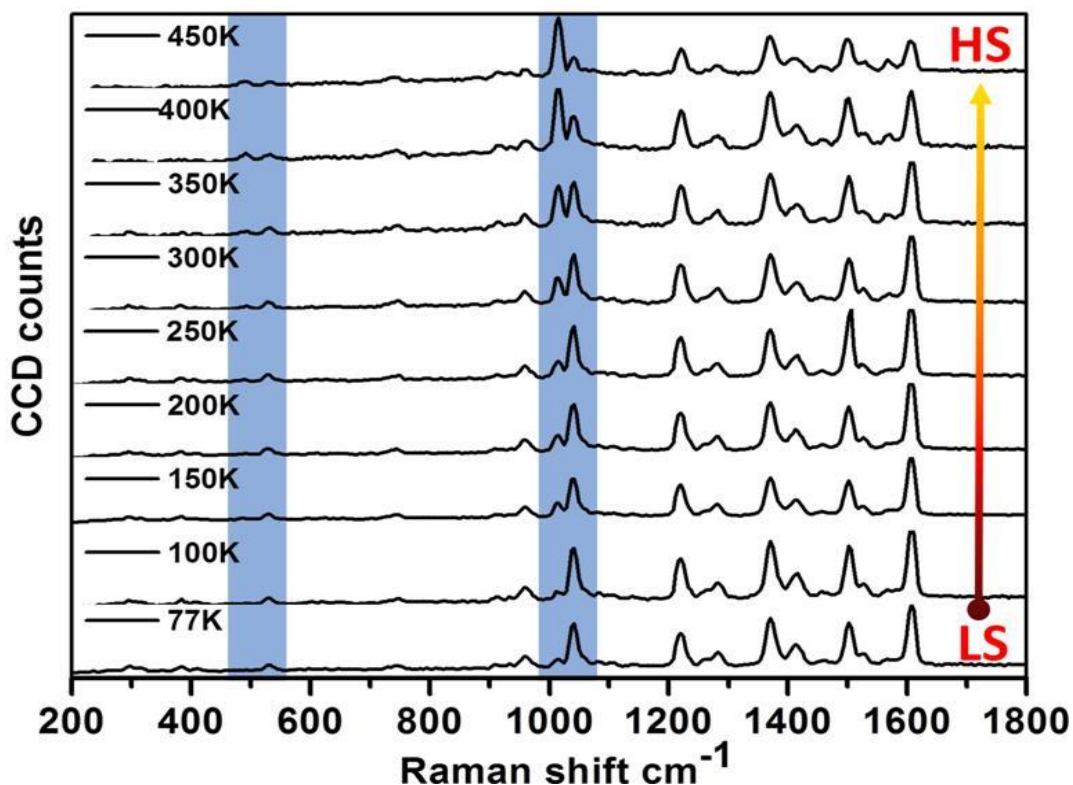


**Figure 2.13** Variable temperature confocal Raman micro spectroscopic data of pellet sample of complex **C1**. Excitation wavelength  $\lambda_{\text{ex}} = 532$  nm laser.

To further confirm the SCO event, variable temperature Raman spectroscopy measurements were performed. Normally during the LS to HS conversion, the average Fe-N bond distance increases to a value of  $\sim 2.1$  Å from  $\sim 1.9$  Å, respectively as a result of the population of the anti-bonding  $e_g^*$  orbital in the HS state ( $t_{2g}^4; e_g^{*2} \leftrightarrow t_{2g}^6; e_g^{*0}$ ). Hence Raman spectroscopy is an effective tool to study the frequency change associated with the bond polarization modulation during the SCO effect. For the Raman measurements a 532 nm laser (Nb:YAG) was used for excitation and the sample was kept in a particular temperature for 20 min. At each temperature four spectra were collected at different points and the average is presented in [Figure 2.13](#). As one can see during the temperature induced HS  $\leftrightarrow$  LS spin-crossover event of **C1**, in the LS state two marker bands i.e. a weak and a strong peaks positioned at  $1015\text{ cm}^{-1}$  and  $1041\text{ cm}^{-1}$ , respectively showed pronounced intensity variation in the HS state ([Fig. 2.13](#)). Additionally, a new band appeared in the HS state at  $480\text{ cm}^{-1}$ . This observed intensity variation and new bands confirmed a significant structural variation associated with SCO effect. It also suggested that the metastable HS state is in the range of 450 K.

### 2.4.2 X-Band ESR Spectroscopy Studies of Radical **R4** and Complex **C1**:

X-band ESR spectroscopy studies were carried out to understand the intramolecular magnetic properties of the radical **R4** and complex **C1**. The biradical nature of complex **C1** was clearly apparent from the forbidden half-field transitions ( $\Delta M_s = \pm 2$ ) appeared in the region  $g_{av} \sim 4.01$  recorded in the frozen state (toluene;  $c \sim 10^{-4}$  M; 170 K). Both **R4** and **C1** showed a broad spectrum in the frozen state. The ESR studies of **R4** and **C1** in toluene solution at 120 K showed diverse peak-to-peak ( $\Delta B_{pp}$ ) and  $g$  values (Fig. 2.14). The  $\Delta B_{pp}/g$  values are as follows: **R4**: 2.79 mT/2.0063 and **C1**: 1.5 mT/2.1120.

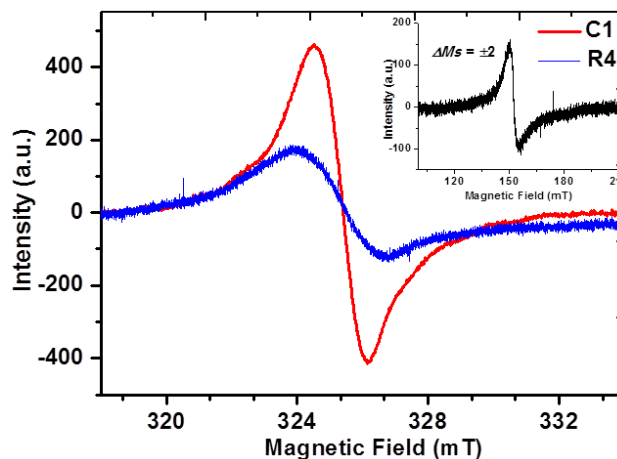


**Figure 2.14.** ESR spectra of radical (**R4**) and complex (**C1**) in toluene recorded at 120 K. The inset shows complex **C1** forbidden  $\Delta M_s = \pm 2$  transitions.

### 2.4.3 Self-Assembly of Radical **R4** and Complex **C1**:

To study the aggregation behaviour of radical **R4** and complex **C1** on glass surface a bottom up approach was undertaken. In a typical procedure, at room temperature addition of  $H_2O$  (1 mL) to acetonitrile (2 mL) solution of **R4** ( $2.16 \times 10^{-3}$  M) formed self-assembled aggregates. The solution was drop-casted on a glass substrate at room temperature followed by slow evaporation to get rod like nano structure. Here possibly the aggregation is mediated by the C-H $\cdots$ N hydrogen bond interactions,<sup>7e</sup> although to verify this single crystal x-ray structure is needed. The confocal microscopy, SEM and TEM images showed formation of 1D elongated solid microrods of **R4** with width in the range of ca. 1-2  $\mu m$  and length of ca. 10-20  $\mu m$  (Fig. 2.15A and B). Selected area electron diffraction (SAED) image showed bright and clear diffraction spots indicating the crystalline nature of the microrods (Fig. 2.15C, inset). The Raman spectrum of the radical microrods further confirmed that indeed the microrods are composed of **R4** (Fig. 2.15D).

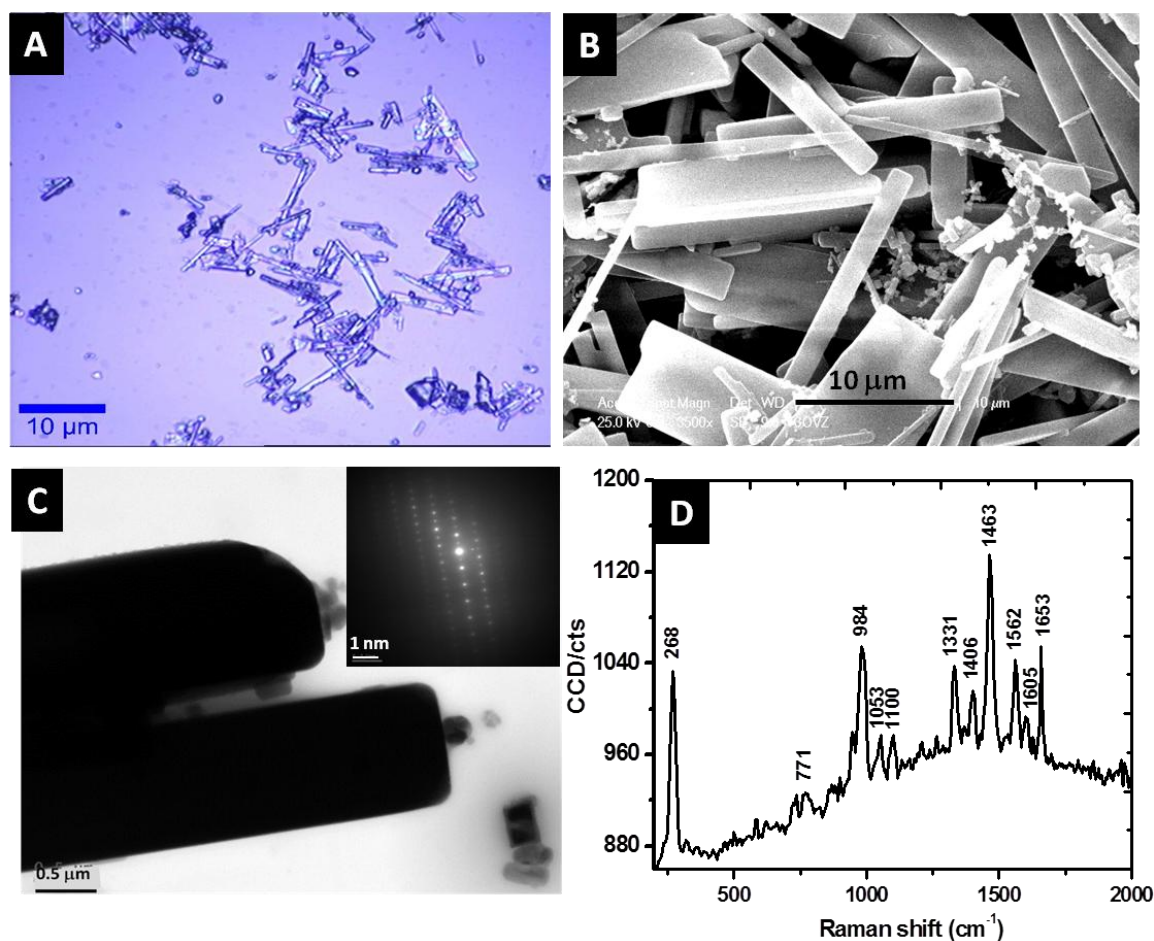


**Figure 2.15** A) Confocal images of microrod grown from **R4** in acetonitrile/H<sub>2</sub>O. B) SEM micrographs of micro rod. C) Bright-field TEM micrographs. Inset shows the SEAD pattern of micro rod. D) Raman spectrum of the microrod.

To prepare nanosolids composed of **C1**, a clear carbon disulphide solution of complex **C1** (5 mg in 2 mL) was drop-casted on a clean glass substrate at room temperature followed by slow evaporation. The confocal microscopy, SEM and TEM images showed formation of nearly cubical shaped microcrystal of **C1** (Fig. 2.16). SEM measurements of the micro crystals illustrated an average diameter of ca. 5-10  $\mu\text{m}$ . The SAED pattern displayed a clear electron diffraction patterns from the nanocrystals demonstrating their crystalline nature (Fig. 2.16C, inset). The Raman imaging/spectroscopy (633 nm laser) of a single micro crystal composed of complex **C1**, showed HS state peaks indicating the statistical spin distribution of the different microcrystals. Interestingly, the appearance of a very strong band at 1015  $\text{cm}^{-1}$  and complete disappearance of 1041  $\text{cm}^{-1}$  band indicated the anisotropic nature of single crystal Raman measurements in comparison to isotropic studies performed on bulk (powder) measurements.

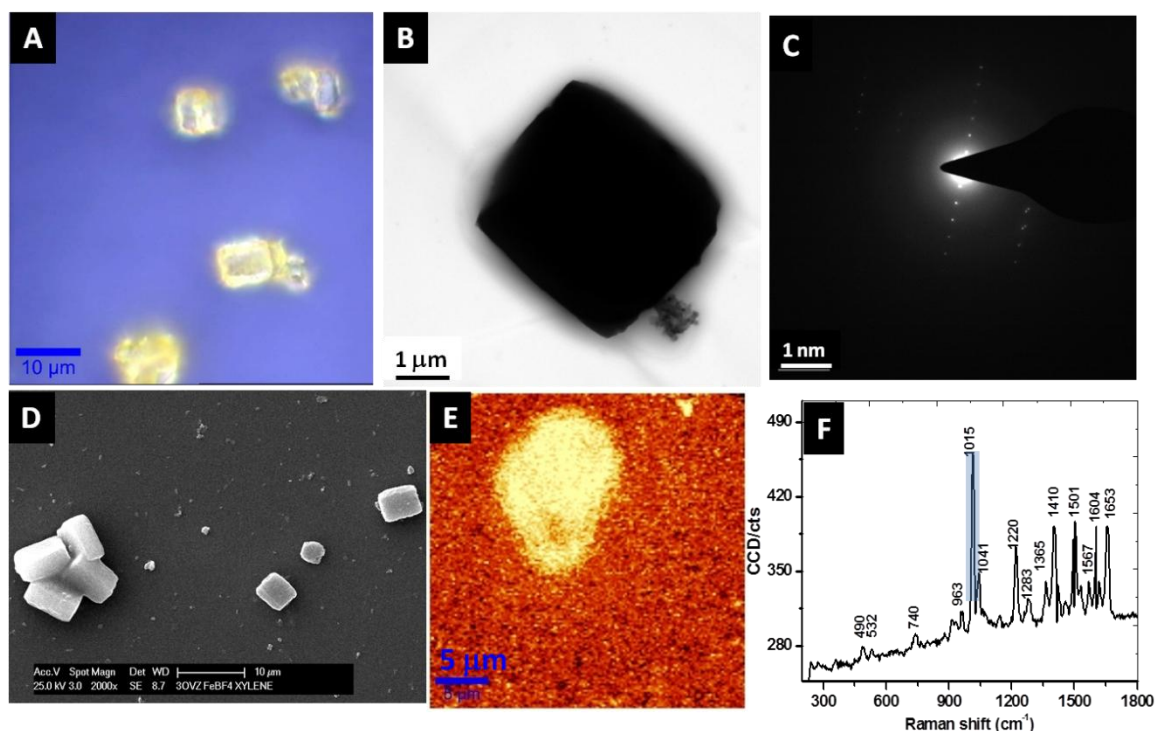


**Figure 2.16** A) Confocal images of microcrystals grown from **C1** in  $\text{CS}_2$  solution. B) Bright-field TEM micrographs. C) The SAED pattern shows the crystalline nature of microcrystals. D) SEM micrographs of microcrystals. E) Raman imaging corresponding to marker peak  $1020\text{ cm}^{-1}$  shown in F. F) Raman spectrum of a HS state single microcrystal.

## 2.5 Conclusions:

Recently, Eaton and Neese *et al.*<sup>4d</sup> have reported that at shorter spin distances or in delocalized systems the use of point-dipole approximation is inadequate. Most of the time the intra-radical distance derived from the experimental  $zfs$  is inconsistent with the X-ray structure. Moreover the SS contribution to the  $zfs$  parameter dictates the  $zfs$  when  $S \geq 1$ . In our present case, to study the *relative* difference in  $D$  values, two types (NN and OVZ) of biradicals (**R3** and **R6**) connected to same 4-phenyl-2,6-bispyrazolylpyridine coupling unit were synthesized. The obtained difference in the  $D$  and  $r$  values (calculated via point-dipole approximation) between the two types of biradicals (NN and OVZ) attached to the same molecular backbone (**R3** and **R6**) is  $0.00118\text{ cm}^{-1}$  and ca.  $0.44\text{ \AA}$ , respectively. This significant difference in  $D$  value clearly confirmed the variation in the spin density distributions and the dipolar coupling strengths of NN and OVZ radicals due to their structural disparity (SOMOs and nodal planes). From the computational studies it is clear that in **R3** the spin density wave is more delocalized into the whole molecular backbone there by reducing the average  $r$  value between the two spins (larger  $D$  value) compared to **R6** (smaller  $D$  value). Additionally since the amount of spin density wave propagation is

also related to the SS exchange interaction ( $J$ ), this obtained results demonstrated that the NN biradicals in **R3** is relatively strongly exchange coupled than that of OVZ biradicals in **R6** i.e.  $J_{\text{NN}} > J_{\text{OVZ}}$ .

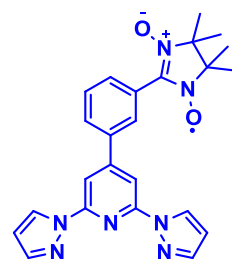
To combine the SCO effect with SS exchange coupling, complex  $[\text{Fe}^{\text{II}}(\text{R4})_2](\text{ClO}_4)_2$  **C1** was prepared. The variable temperature magnetic susceptibility and Raman measurements indicated the operating SCO effect in **C1**, with a  $T_{1/2}$  value over 300 K. Self-assembly studies of **R4** and **C1** exhibited the formation of microrods and nanocrystals, respectively.

## 2.6 General Experimental Procedures:

### 2.6.1 General Procedure for NN Radicals:

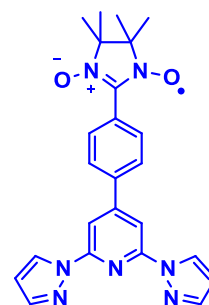
#### 2,6-di(pyrazol-1-yl)-4-(4-(1-oxy-3oxo-4,4,5,5-tetramethylimidazolidin-2-

yl)phenyl)pyridine (**R1**): A solution of *m*-chloroperbenzoic acid (mCPBA) (100 mg) in methylene chloride (5 mL) was added drop-wise to a mixture of 4,4,5,5-tetramethylimidazolidine **10** (30 mg) and saturated solution of  $\text{NaHCO}_3$  (1 mL) in an ice bath. The blue color which developed slowly is a clear indication of the formation of nitronyl-nitroxide radical. The reaction further continued for an hour, subsequently, a solution of  $\text{NaIO}_4$  in water (10 mL) was added drop-wise and stirred for 30 min. The blue organic layer was separated, and the aqueous layer was extracted with dichloromethane ( $3 \times 30$  mL). The organic layers were combined, dried over  $\text{MgSO}_4$  and the solvent was evaporated under reduced pressure to get blue solid of **R1** (Yield: 8 mg, 30%). EPR (in toluene  $c \sim 10^{-4}$  M, RT,  $\nu = 9.14166$  GHz, 0.998 mW power, 1 scan): five lines,  $g_{\text{iso}} = 2.0067$ ,  $a_{\text{N}} = 7.40$  G. UV-Vis (in toluene  $c = 5 \times 10^{-3}$  M):  $\lambda_{\text{abs}}$  ( $\epsilon$ ) 537 nm ( $667 \text{ M}^{-1} \text{ cm}^{-1}$ ), 314 nm ( $1482 \text{ M}^{-1} \text{ cm}^{-1}$ ). FT-IR (KBr): 3233, 2982, 2922, 1754, 1654, 1556, 1464, 1391 (N-O), 1262, 1221, 1088, 945, 874, 831, 749, 651, 517,  $440 \text{ cm}^{-1}$ .



#### 2,6-di(pyrazol-1-yl)-4-(3-(1-oxy-3oxo-4,4,5,5-

tetramethylimidazolidin-2-yl)phenyl)pyridine (**R2**): (Yield: 8 mg, 35%). EPR (in toluene;  $c \sim 10^{-4}$  M, RT,  $\nu = 9.13782$  GHz, 0.998 mW power, 1 scan): five lines,  $g_{\text{iso}} = 2.0066$ ,  $a_{\text{N}} = 7.41$  G. UV-Vis (in toluene  $c = 5 \times 10^{-3}$  M):  $\lambda_{\text{abs}}$  ( $\epsilon$ ) 567 nm ( $1296 \text{ M}^{-1} \text{ cm}^{-1}$ ), 300 nm ( $\epsilon =$



6970  $\text{M}^{-1} \text{cm}^{-1}$ ). FT-IR (KBr): 3253, 2982, 2931, 1734, 1654, 1526, 1464, 1390, 1265, 1224, 1188, 945, 834, 831, 749, 680, 567, 443  $\text{cm}^{-1}$ .

#### 4-(3,5-bis(1-oxy-3oxo-4,4,5,5-tetramethylimidazolidin-2-yl)phenyl)-2,6-di(1H-

pyrazol-1-yl)pyridine (**R3**): (Yield: 8 mg, 20%). EPR (in

toluene  $c \sim 10^{-4} \text{ M}$ , RT,  $\nu = 9.13829 \text{ GHz}$ , 0.998 mW power, 1

scan): nine lines,  $g_{\text{iso}} = 2.0071$ . UV-Vis (in toluene  $c = 5 \times 10^{-3}$

M):  $\lambda_{\text{abs}} (\epsilon)$  592 nm ( $524 \text{ M}^{-1} \text{cm}^{-1}$ ), 303 nm ( $2007 \text{ M}^{-1} \text{cm}^{-1}$ ). FT-

IR (KBr): 2924, 2854, 1734, 1616, 1560, 1521, 1466, 1394, 1261,

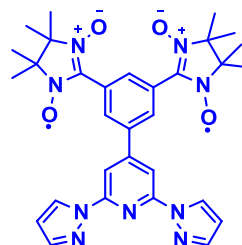
1124, 1039, 952, 862, 788, 540  $\text{cm}^{-1}$ . EPR (in toluene  $c \sim 10^{-4} \text{ M}$ ,

$\nu = 9.14572 \text{ GHz}$ , 0.998 mW power, 1 scan):  $g_{\text{iso}} = 2.0071$ ,  $|D/hc|$

$= 0.00719 \text{ cm}^{-1}$ ,  $\Delta M_s = \pm 2$  transition  $g_{\text{av}} \sim 4.01$ . Elemental analysis: calcd for

$\text{C}_{31}\text{H}_{35}\text{N}_9\text{O}_4$  (597.67): N, 21.09; found C, 62.15; H, 5.95; N, 21.32; requires C, 62.30; H,

5.90.



#### 2.6.2 General Procedure for OVZ Radicals:

##### 6-(3-(2,6-di(pyrazol-1-yl)pyridin-4-yl)phenyl)-2,4-diisopropyl -3-oxoverdazyl (**R4**):

In a typical procedure, 6-(3-(2,6-di(pyrazol-1-yl)pyridin-4-yl)phenyl)-2,4-diisopropyl-

1,2,4,5-tetrazinan-3-one **13** (100 mg, 1 mmol) was heated with

benzoquinone (82 mg, 1.5 mol) in 5 mL toluene for 30 min at 40

$^{\circ}\text{C}$ . After consumption of the starting material, as monitored by

TLC, the resulting solution was cooled, filtered and the solvent

was evaporated. Chromatography of the solid residue on silica

gel using  $\text{CH}_2\text{Cl}_2\text{:EtOAc}$  (9:1) gave a brown crystalline solid of

**R4**. (Yield: 25 mg, 24%). LCMS calcd ( $m/z$ ): 468.53, found

468.4. UV-Vis (in toluene):  $\lambda_{\text{abs}}$  360 and 374 nm. FT-IR (KBr):

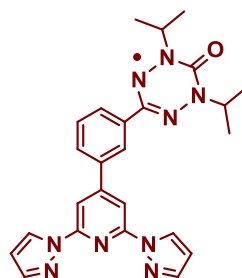
3243, 2984, 2932, 1734, 1634, 1516, 1464, 1373, 1262, 1221, 1088, 945, 874, 831, 760,

681, 527, 448  $\text{cm}^{-1}$ . EPR (in toluene  $c \sim 10^{-4} \text{ M}$ , RT,  $\nu = 9.14577 \text{ GHz}$ , 0.998 mW power,

1 scan): nine lines,  $g_{\text{iso}} = 2.0063$ ,  $a_{\text{N1}} = 6.41 \text{ G}$ ,  $a_{\text{N2}} = 5.35 \text{ G}$  and  $a_{\text{H}} = 1.13 \text{ G}$ . Elemental

analysis: calcd for  $\text{C}_{25}\text{H}_{26}\text{N}_9\text{O}$  (468.53): found C, 64.17; H, 5.48; N, 26.88; requires C,

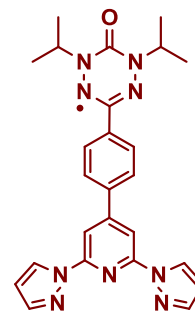
64.09; H, 5.59; N, 26.91.



**6-(4-(2,6-di(pyrazol-1-yl)pyridin-4-yl)phenyl)-2,4-diisopropyl-3-oxoverdazyl (R5):**

(Yield: 27 mg, 26%). LCMS calcd ( $m/z$ ): calcd 468.53; found 469.05.

UV-Vis (in toluene):  $\lambda_{\text{abs}}$  400-650 nm. FT-IR (KBr): 3243, 2984, 2932, 1734, 1634, 1516, 1464, 1373, 1262, 1221, 1088, 945, 874, 831, 760, 681, 527, 448  $\text{cm}^{-1}$ . EPR (in toluene  $c \sim 10^{-4}$  M, RT,  $\nu = 9.14808$  GHz, 0.998 mW power, 1 scan): nine lines,  $g_{\text{iso}} = 2.0063$ ,  $a_{\text{N1}} = 6.20$  G,  $a_{\text{N2}} = 5.20$  G and  $a_{\text{H}} = 1.13$  G. Elemental analysis: calcd for  $\text{C}_{25}\text{H}_{26}\text{N}_9\text{O}$  (468.53): found C 64.15, N 26.78, H 5.48; requires C, 64.09; H, 5.59; N, 26.91.

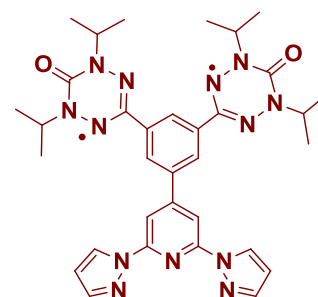
**6-(3,5-(2,6-di(pyrazol-1-yl)pyridin-4-yl)phenyl)-2,4-diisopropyl-3-oxoverdazyl (R6):**

(Yield: 19 mg, 20%). LCMS calcd ( $m/z$ ): calcd 649.74; found

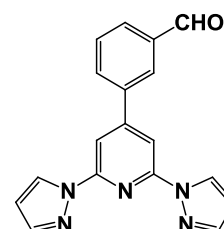
648.75. UV-Vis (in toluene):  $\lambda_{\text{abs}}$  360 and 480 nm. FT-IR (KBr): 3246, 2982, 2936, 1736, 1634, 1555, 1470, 1370, 1258, 1223, 1101, 949, 874, 831, 762, 679, 527, 448  $\text{cm}^{-1}$ .

EPR (in toluene  $c \sim 10^{-4}$  M,  $\nu = 9.14808$  GHz, 0.998 mW power, 1 scan): *zfc* spectrum  $g_{\text{iso}} = 2.0071$ ,  $|D/hc| = 0.00601$   $\text{cm}^{-1}$ ,  $\Delta M_s = \pm 2$  transition at  $g_{\text{av}} \sim 4.01$ . Elemental analysis:

calcd for  $\text{C}_{33}\text{H}_{39}\text{N}_{13}\text{O}_2$  (649.75): found: C 61.22, N 27.86, H 6.16; requires C, 61.00; H, 6.05; N, 28.02.

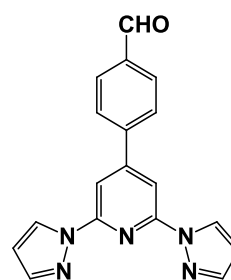
**2.6.3 General Procedure for Aldehyde:**

**3-(2,6-di(pyrazol-1-yl)pyridin-4-yl)benzaldehyde (7):** In a 100 mL flask, 1,4-dioxane (20 mL) and 2M  $\text{Na}_2\text{CO}_3$  (5 mL) were taken together and  $\text{N}_2$  gas was bubbled through the solution for 30 min. To this mixture, 4'-iodo-2',6'-dipyrazolylpyridine (200 mg, 0.5932 mmol), 3-formylphenylboronic acid (97 mg, 0.652 mmol), 2M  $\text{Na}_2\text{CO}_3$  (5 mL) and  $\text{Pd}(\text{PPh}_3)_4$  (50 mg, 0.049 mmol) were added and heated to 70  $^\circ\text{C}$  for 3 days under nitrogen atmosphere. The solvent was removed by using a rotary evaporator and the remaining residue was treated with water and extracted with  $\text{CH}_2\text{Cl}_2$  solvent ( $3 \times 50$  mL). The separated organic layer was dried over  $\text{MgSO}_4$  and the solvent was removed by evaporation. The obtained light greenish solid residue was washed with methanol to remove the soluble impurities and to get a



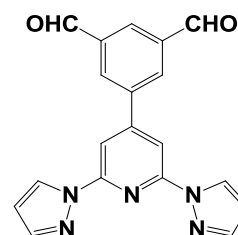
white color powder of **7** (Yield: 100 mg, 53%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3\text{-}d_1$ , 298 K)  $\delta$ : 10.15 (s, 1H, -CHO), 8.62-8.61 (d, 2H), 8.31-8.30 (t, 1H), 8.15 (s, 2H), 8.09-8.06 (m, 1H), 8.01-8.0 (m, 1H), 7.8 (d, 2H), 7.71-7.67 (t, 1H), 6.54-6.53 (q, 2H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3\text{-}d_1$ , 298 K)  $\delta$ : 191.7, 152.7, 150.8, 142.6, 138.5, 137.2, 133.0, 130.5, 129.9, 128.6, 127.3, 108.2, 107.3 ppm. LCMS calcd  $m/z$  = 315.33, found 316.11. Elemental analysis: calcd for  $\text{C}_{18}\text{H}_{13}\text{N}_5\text{O}$  (315.33): C, 68.56; N, 22.21; H, 4.16. Found: C, 68.65; H, 4.09; N, 22.45. FT-IR (KBr):  $\nu$  in  $\text{cm}^{-1}$  = 3432, 2963, 1699 (-CHO), 1618, 1562, 1522, 1470, 1399, 1262, 1036, 949, 862, 799, 540.

**4-(2,6-di(pirazol-1-yl)pyridin-4-yl)benzaldehyde (8).** In a 100 mL flask, 1,4-dioxane (20 mL) and 2M  $\text{Na}_2\text{CO}_3$  (5 mL) were taken together and  $\text{N}_2$  gas was bubbled through the solution for 30 min. To this mixture, 4'-iodo-2',6'-dipirazolyl-pyridine (200 mg, 0.5932 mmol), 4-formylphenylboronic acid (97 mg, 0.652 mmol), 2M  $\text{Na}_2\text{CO}_3$  (5 mL) and  $\text{Pd}(\text{PPh}_3)_4$  (50 mg, 0.049 mmol) were added and heated to 70 °C for 3 days under nitrogen atmosphere. The solvent was removed by using a rotary evaporator and the remaining residue was treated with water and extracted with  $\text{CH}_2\text{Cl}_2$  solvent ( $3 \times 50$  mL). The separated organic layer was dried over  $\text{MgSO}_4$  and the solvent was removed by evaporation. The obtained light greenish solid residue was washed with methanol to remove the soluble impurities and to get a white color powder of **8** (Yield: 92 mg, 51%).  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3\text{-}d_1$ , 298 K)  $\delta$ : 10.10 (s, 1H, -CHO), 8.61 (d, 2H), 8.13 (d, 2H), 8.03-7.95 (m, 4H), 7.79 (s, 2H), 6.53 (m, 2H) ppm.  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3\text{-}d_1$ , 298 K)  $\delta$ : 191.6, 152.7, 150.8, 143.2, 142.6, 136.9, 130.4, 128.0, 127.3, 108.2, 107.5 ppm. LCMS calcd  $m/z$  = 315.33, found 316.10, Elemental analysis calcd for  $\text{C}_{18}\text{H}_{13}\text{N}_5\text{O}$  (315.33): C, 68.56; N, 22.21; H, 4.16. Found: C, 68.55; H, 4.19; N, 22.25. FT-IR (KBr):  $\nu$  in  $\text{cm}^{-1}$  = 2963, 2917, 28589, 1703 (-CHO), 1620, 1557, 1466, 1395, 1262, 1209, 1032, 937, 792.



**5-(2,6-di(pirazol-1-yl)pyridin-4-yl)isophthalaldehyde (9):**

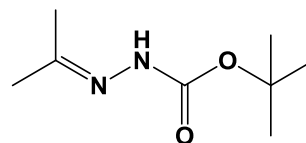
Similar procedure for the synthesis of **8** was applied. 4'-iodo-2',6'-dipirazolyl-pyridine (150 mg, 0.44 mmol), 3,5-diformylphenyl boronic acid (78 mg, 0.44 mmol) and  $\text{Pd}(\text{PPh}_3)_4$  (50 mg, 8%). White color powder of **9** (Yield: 125 mg, 58%).  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3\text{-}d_1$ , 298 K)  $\delta$ : 10.21 (s, 2H, -CHO), 8.62-8.56 (d,



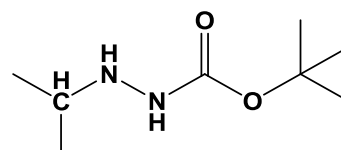
4H), 8.48 (s, 1H), 8.18 (s, 2H), 7.81 (s, 2H), 6.55 ppm.  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3\text{-d}_1$ , 298 K)  $\delta$ : 190.4, 151.3, 151.0, 142.8, 139.8, 137.9, 133.1, 131.2, 127.3, 108.4, 107.2 ppm. LCMS calcd  $m/z$  = 343.34, found 344.0. Elemental analysis: calcd for  $\text{C}_{19}\text{H}_{13}\text{N}_5\text{O}_2$  (343.34): C, 66.47; H, 3.82; N, 20.40. Found: C, 66.32; N, 20.54; H, 3.88. FT-IR (KBr):  $\nu$  in  $\text{cm}^{-1}$  = 3403, 2919, 1698 (-CHO), 1616, 1464, 1397, 1262, 1020, 801.

#### 2.6.4 General Procedure for Tetrazanes:

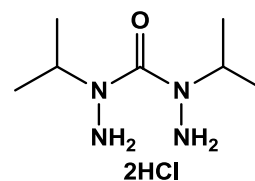
**Synthesis of tert-Butyl-2-isopropenylhydrazenecarboxylate (16):** Tert-butoxy carbazate (2.0 g, 15.1 mmol) was added to dry acetone (10 mL) at RT for 12 h. The resulting mixture was evaporated to get white precipitate (Yield: 2 g, 73%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3\text{-d}_1$ , 298 K),  $\delta$ : 1.38 (s, 9H), 1.94 (s, 6H), 7.0 (s, 1H) ppm.



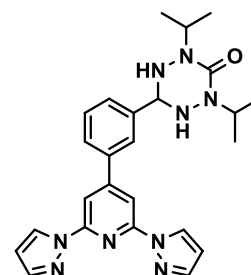
**Synthesis of tert-Butyl-2-isopropylhydrazenecarboxylate (17).** Sodium borohydride (1 g, 26.5 mmol) was added to (16) (1.5 g, 5.29 mmol) in ethanol (150 mL) and the mixture was refluxed for 6 h. The resulting mixture was evaporated, and 60 mL of water and 23.3 mL of 1M HCl aq. was added to the residue. The crude product was extracted with dichloromethane and purified by recrystallization from dichloromethane / hexane (1:1) (Yield: 1 mL, 66%).  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3\text{-d}_1$ , 298 K)  $\delta$ : 1.07 (d, 6H), 1.38 (s, 9H, tert-butyl), 2.0 (t, 1H), 2.97 (sept, 1H), 1.0 (d, 1H) ppm.



**2,4-diisopropylcarbohydrazide bis-hydrochloride (3) :** Synthesized from 17 as per the procedure reported by Parè *et al.*<sup>21</sup>

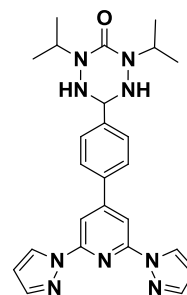


**6-(3-(2,6-di(pyrazol-1-yl)pyridin-4-yl)phenyl)-2,4-diisopropyl-1,2,4,5-tetrazinan-3-one (13).** In a typical procedure, 2,4-diisopropylcarbohydrazide bishydrochloride (162 mg, 0.889 mmol) and 3-(2,6-di(pyrazol-1-yl)pyridin-4-yl)benzaldehyde (7) (200 mg, 0.624 mmol) were dissolved in the minimum amount of ethanol. To this solution sodium acetate (102 mg, 1.304 mmol) was added and the solution was allowed to stir at room temperature for 15 h. Then the mixture was filtered, evaporated and the residue was recrystallized from

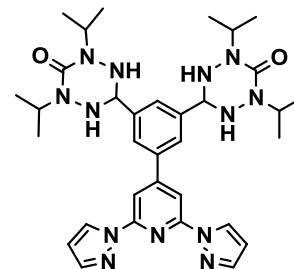


heptane to give a tetrazane derivative **13** (Yield: 87 mg, 60%).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3-d_1$ , 298 K)  $\delta$ : 8.62-8.61 (d, 2H), 8.13 (s, 2H), 8.01 (s, 1H), 7.79-7.72 (m, 4H), 7.51-7.49 (d, 1H), 6.53-6.52 (q, 2H), 5.29 (s, 1H), 4.88-4.16 (m, 2H), 1.33-1.14 (m, 12H) ppm.  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3-d_1$ , 298 K)  $\delta$ : 154.4, 150.9, 149.1, 146.5, 142.6, 132.3, 132.2, 131.5, 131.5, 128.6, 128.5, 127.1, 126.5, 122.5, 120.4, 108.1, 107.8, 73.1, 63.0, 31.9, 25.3, 23.5, 23.0, 22.7, 14.1 ppm. LCMS calcd  $m/z$  = 471.56, found 471.30, Elemental analysis: calcd for  $\text{C}_{25}\text{H}_{29}\text{N}_9\text{O}$  (471.56): C, 63.68; H, 6.20; N, 26.73. Found: C, 63.48; H, 6.25; N, 26.59. FT-IR (KBr):  $\nu$  in  $\text{cm}^{-1}$  = 2982, 1722, 1647, 1574, 1418, 1256, 1105, 1051, 772, 652, 623, 457.

**6-(4-(2,6-di(pyrazol-1-yl)pyridin-4-yl)phenyl)-2,4-diisopropyl-1,2,4,5-tetrazinan-3-one (14):** Compound **(14)** was synthesized by above tetrazane procedure. 2,4-diisopropylcarbonohydrazide bishydrochloride (81 mg, 0.468 mmol), 4-(2,6-di(pyrazol-1-yl)pyridin-4-yl)benzaldehyde (**8**) (100 mg, 0.312 mmol), and sodium acetate (51 mg, 0.624 mmol) were used (Yield: 93 mg, 63%).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3-d_1$ , 298 K)  $\delta$ : 8.62(d, 2H), 8.14 (d, 2H), 7.79 -7.72 (m, 6H), 6.52 (m, 2H), 5.30 (s, 1H), 4.33-4.13 (m, 2H), 1.33-1.14(m, 12H) ppm.  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3-d_1$ , 298 K)  $\delta$ : 154.4, 150.6, 142.3, 137.5, 129.2, 127.7, 127.2, 126.5, 125.5, 107.9, 107.5, 72.2, 62.1, 31.9, 25.3, 23.6, 22.7, 14.1 ppm. LCMS calcd  $m/z$  = 471.56, found 472.00. Elemental analysis: calcd for  $\text{C}_{25}\text{H}_{29}\text{N}_9\text{O}$  (471.56): C, 63.68; H, 6.20; N, 26.73. Found: C, 63.58; H, 6.25; N, 26.45. FT-IR (KBr):  $\nu$  in  $\text{cm}^{-1}$  = 3435, 3289, 3165, 2999, 1701, 1642, 1566, 1414, 1049, 1013, 924, 810, 650, 623, 523, 465.



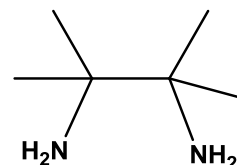
**6,6'-(5-(2,6-di(pyrazol-1-yl)pyridin-4-yl)-1,3-phenylene)bis(2,4-diisopropyl-1,2,4,5-tetrazinan-3 one) (15):** Compound **15** also was synthesized by same procedure as described above. 2,4-diisopropylcarbonohydrazide bishydrochloride (152 mg, 0.87 mmol), 5-(2,6-di(pyrazol-1-yl)pyridin-4-yl)isophthalaldehyde (**9**) (100 mg, 0.343 mmol), and sodium acetate (72 mg, 0.87 mmol) were used (Yield: 111 mg, 59%).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3-d_1$ , 298 K)  $\delta$ : 8.59 (s, 2H), 8.11 (s, 2H), 7.9 (s, 1H), 7.86 (s, 2H), 7.76 (s, 2H), 6.49 (m, 2H), 5.24 (s, 2H), 4.88-4.14 (m, 4H), 1.23-1.05 (m, 24H) ppm.  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3-d_1$ , 298 K)  $\delta$ : 153.9, 150.6, 149.9, 147.1, 145.8, 142.7, 136.5, 127.2, 108.0, 107.2, 73.0, 63.6, 31.9, 25.3, 23.6, 22.7, 14.2 ppm. LCMS calcd  $m/z$  =



655.80, found 655.6. Elemental analysis: calcd for  $C_{33}H_{45}N_{13}O_2$  (655.80): C, 60.44; H, 6.92; N, 27.77. Found: C, 60.58; H, 6.85; N, 27.45. FT-IR (KBr):  $\nu$  in  $\text{cm}^{-1}$  = 3436, 3289, 2980, 2936, 2878, 1738, 1707, 1642, 1564, 1412, 1250, 1155, 1046, 1013, 920, 853, 789, 646, 530.

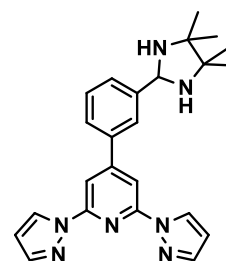
### 2.6.5 Preparation of 4,4,5,5-tetramethylimidazolidine Derivatives (4):

**2,3-diamino-2,3-dimethylbutane** : Synthesized from 2,3-dinitro-2,3-dimethylbutane as per Ray's procedure.<sup>10</sup>



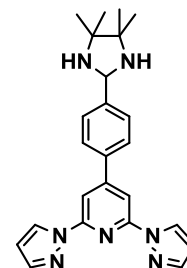
### 2,6-di(pyrazol-1-yl)-4-(4-(4,4,5,5-tetramethylimidazolidin-2-yl)phenyl)pyridine (10):

In a typical procedure, a solution of 3-(2,6-di(pyrazol-1-yl)pyridin-4-yl)benzaldehyde (**7**) (200 mg, 0.63 mmol) in chloroform (10 mL) was added drop wise to a clear solution of 2,3-diamino-2,3-dimethylbutane (100 mg, 0.86 mmol) in chloroform (20 mL). The reaction mixture was left under stirring for 2 days under argon at 60 °C. The TLC confirmed the complete consumption of **7** ( $R_f$  = 0.57; 3:2 DCM:Hexane). The solution was directly dried with  $\text{Na}_2\text{SO}_4$  and evaporated in vacuo to get compound **10** as a white powder (Yield: 163 mg, 62%).  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ - $d_1$ , 298 K)  $\delta$ : 8.63 (s, 2H), 8.18 (s, 2H), 7.84, 7.82, 7.8, 7.73, 6.53 (s, 2H), 5.27 (s, 1H), 1.25, 1.23, 1.13 ppm.  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ - $d_1$ , 298 K)  $\delta$ : 153.9, 150.6, 145.8, 142.4, 136.5, 127.2, 108.0, 107.2, 73.0, 63.0, 31.0, 25.3, 23.6, 14.2 ppm. LCMS calcd  $m/z$  = 413.52, found 414.25. Elemental analysis: calcd for  $C_{24}H_{27}N_7$  (413.52): C, 69.78; H, 6.52; N, 23.81. Found: C, 69.58; H, 6.51; N, 23.85. FT-IR (KBr):  $\nu$  in  $\text{cm}^{-1}$  = 3335, 2978, 2919, 2855, 1615, 1541, 1460, 1391, 1273, 1171, 694.



### 2,6-di(pyrazol-1-yl)-4-(3-(4,4,5,5-tetramethylimidazolidin-2-yl)phenyl)pyridine(11):

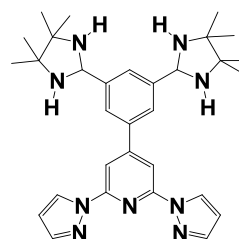
A solution of 4-2,6-di(pyrazol-1-yl)pyridin-4-yl-benzaldehyde (**8**) (200 mg, 0.634 mmol) in chloroform (10 mL) was added drop-wise to a solution of 2,3-diamino-2,3-dimethylbutane (110 mg, 0.952 mmol) in chloroform (20 mL) in a round bottom flask. The reaction mixture was heated at 60 °C for 2 d under argon to get a light turbid solution. The TLC confirmed the complete consumption of **8** ( $R_f$  = 0.55; 3:2 DCM:Hexane). The solution was directly dried with  $\text{Na}_2\text{SO}_4$  and evaporated in vacuo to get compound **11** as a white powder (Yield: 172 mg, 66%).  $^1\text{H}$ -



NMR (400 MHz,  $\text{CDCl}_3$ - $d_1$ , 298 K)  $\delta$ : 8.62, 8.14, 8.01, 7.79, 7.74, 7.72, 6.52, 5.30, 1.34, 1.25, 1.23, 1.14 ppm.  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ - $d_1$ , 298 K)  $\delta$ : 154.4, 150.6, 145.2, 144.0, 142.3, 140.5, 139.0, 137.5, 129.2, 127.6, 127.2, 126.5, 125.5, 108.0, 107.5, 97.2, 87.3, 73.1, 63.0, 31.5, 31.0, 25.3, 24.0, 23.1, 14.1 ppm. LCMS calcd  $m/z$  = 413.52, found 413.65. Elemental analysis: calcd for  $\text{C}_{24}\text{H}_{27}\text{N}_7$  (413.52): C, 69.71; H, 6.58; N, 23.71. Found: C, 69.58; H, 6.51; N, 23.85. FT-IR (KBr):  $\nu$  in  $\text{cm}^{-1}$  = 3335, 2978, 2919, 2855, 1615, 1541, 1460, 1391, 1273, 1171, 694.

**4-(3,5-bis(4,4,5,5-tetramethylimidazolidin-2-yl)phenyl)-2,6-di(1H-pyrazol-1-yl)pyridine (12):** Compound (12) was synthesized by following

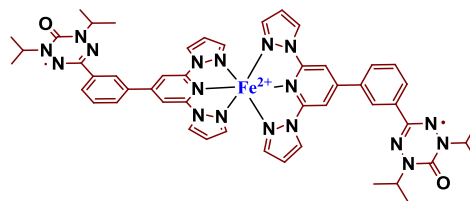
the above condensation procedure. 5-(2,6-di(pyrazol-1-yl)pyridin-4-yl)isophthalaldehyde (**9**) (200 mg, 0.583 mmol) and 2,3-diamino-2,3-dimethylbutane (192 mg, 1.748 mmol) were used (Yield: 172 mg, 55%).  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ - $d_1$ , 298 K)  $\delta$ : 8.61, 8.133, 7.99, 7.9, 7.8, 6.52, 5.3, 1.30, 1.24, 1.2, 1.16 ppm.  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ - $d_1$ , 298 K)  $\delta$ : 154.5, 150.6, 142.3, 137.7, 127.2, 125.7, 125.1, 108.0, 73.4, 63.3, 25.4, 24.5, 23.6 ppm. LCMS calcd



$m/z$  = 539.72, found 540.8. Elemental analysis: calcd for  $\text{C}_{31}\text{H}_{41}\text{N}_9$  (539.72): C, 68.99; H, 7.66; N, 23.36. Found: C, 68.81; H, 7.58; N, 24.31. FT-IR (KBr):  $\nu$  in  $\text{cm}^{-1}$  = 3337, 2969, 2932, 2855, 1721, 1617, 1561, 1466, 1397, 1208, 1169, 1042, 938, 862, 758.

**2.6.6  $\text{Fe}^{\text{II}}(\text{ClO}_4)_2$  Complex (C1):** A solution of  $\text{Fe}^{\text{II}}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (21.7 mg, 0.08 mmol) in degassed acetonitrile (5 ml) was added to the brown solution of **R4** (80 mg, 0.17 mmol) in acetonitrile (5 ml) and stirred for 2 h at

50 °C under nitrogen atmosphere to obtain dark brown solution. After that the reaction mixture was cooled and 100 mL of diethyl ether was added to it to get deep brown colored precipitated. The mixture was then left as such



for 6 hours until all the precipitate settled down. Then the organic solution was decanted to get pure brown color powder of complex **C1**. (Yield: 32 mg, 37%). EPR (in toluene  $c \sim 10^{-4}$  M, 120 K,  $\nu$  = 9.24557 GHz, 0.998 mW power, 1 scan): one broad line,  $g_{\text{iso}}$  = 2.1120,  $\Delta M_s = \pm 2$  transition ( $g = 4.01$ ); Raman spectrum peaks: 490, 532, 740, 963, 1015, 1041, 1220, 1283, 1365, 1410, 1501, 1567, 1604, 1653  $\text{cm}^{-1}$ . LCMS calcd ( $m/z$ ): calcd

992.91; found 993.93. Elemental analysis: calcd for  $C_{50}H_{52}FeN_{18}O_2$  (992.91): found C, 60.35; H, 5.21; N, 25.43; requires C, 60.48; H, 5.28; N, 25.39.

**Table 2.3:** Crystal data and structure refinement for **R1** (CCDC: 768145)

|                                           |                                                                                                                         |
|-------------------------------------------|-------------------------------------------------------------------------------------------------------------------------|
| <b>Empirical formula</b>                  | $C_{24} H_{24} N_7 O_2$                                                                                                 |
| <b>Formula weight</b>                     | 442.50                                                                                                                  |
| <b>Temperature</b>                        | 100(2) K                                                                                                                |
| <b>Wavelength</b>                         | 0.71073 Å                                                                                                               |
| <b>Crystal system, space group</b>        | Monoclinic, P2(1)/c                                                                                                     |
| <b>Unit cell dimensions</b>               | a = 14.584(2) Å    alpha = 90 deg.<br>b = 10.5609(14) Å    beta = 109.665(2) deg.<br>c = 15.240(2) Å    gamma = 90 deg. |
| <b>Volume</b>                             | 2210.4(5) Å <sup>3</sup>                                                                                                |
| <b>Z, Calculated density</b>              | 4, 1.330 Mg/m <sup>3</sup>                                                                                              |
| <b>Absorption coefficient</b>             | 0.089 mm <sup>-1</sup>                                                                                                  |
| <b>F(000)</b>                             | 932                                                                                                                     |
| <b>Crystal size</b>                       | 0.36 x 0.22 x 0.16 mm                                                                                                   |
| <b>Theta range for data collection</b>    | 1.48 to 26.04 deg.                                                                                                      |
| <b>Limiting indices</b>                   | -17 ≤ h ≤ 18, -12 ≤ k ≤ 13, -18 ≤ l ≤ 18                                                                                |
| <b>Reflections collected / unique</b>     | 22106 / 4347 [R(int) = 0.0980]                                                                                          |
| <b>Completeness to theta = 26.04</b>      | 99.8 %                                                                                                                  |
| <b>Absorption correction</b>              | Semi-empirical from equivalents                                                                                         |
| <b>Max. and min. transmission</b>         | 0.9859 and 0.9686                                                                                                       |
| <b>Refinement method</b>                  | Full-matrix least-squares on F <sup>2</sup>                                                                             |
| <b>Data / restraints / parameters</b>     | 4347 / 0 / 302                                                                                                          |
| <b>Goodness-of-fit on F<sup>2</sup></b>   | 1.042                                                                                                                   |
| <b>Final R indices [I &gt; 2sigma(I)]</b> | R1 = 0.0651, wR2 = 0.1373                                                                                               |
| <b>R indices (all data)</b>               | R1 = 0.1084, wR2 = 0.1542                                                                                               |
| <b>Largest diff. peak and hole</b>        | 0.321 and -0.332 e.Å <sup>-3</sup>                                                                                      |

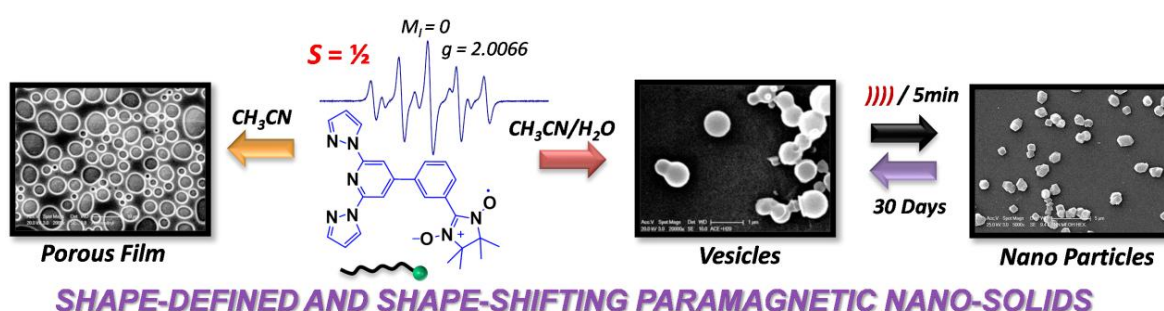
## References

- (a) Iwamura, H.; Koga, N. *Acc. Chem. Res.* **1993**, *26*, 346. (b) Rajca, A. *Chem. Rev.* **1994**, *94*, 871. (c) Lahti, P. M. Ed. *Magnetic Properties of Organic Materials*; Marcel Dekker: New York, **1999**, 1. (d) Itoh, K.; Kinoshita, M.; Eds. *Molecular Magnetism*; Gordon and Breach: Kodansha, **2000**, 1.
- (a) Rajca, A.; Wongsriratanakul, J.; Rajca, S. *Science* **2001**, *294*, 1503. (b) Rajca, S.; Rajca, A.; Wongsriratanakul, J.; Butler, P.; Choi, S. *J. Am. Chem. Soc.* **2004**, *126*, 6972. (c) Rajca, A.; Wongsriratanakul, J.; Rajca, S. *J. Am. Chem. Soc.* **2004**, *126*, 6608. (d) Rajca, A.; Wongsriratanakul, J.; Rajca, S.; Cerny, R. L. *Chem.-Eur. J.* **2004**, *10*, 3144. (e) Fukuzaki, E.; Nishide, H. *J. Am. Chem. Soc.* **2006**, *128*, 996. (f) Brook, D. J. R.; Yee, G.T. *J. Org. Chem.* **2006**, *71*, 4889. (g) Gilroy, J. B.; McKinnon, S. D. J.; Kennepohl, P.; Zsombor, M.S.; Ferguson, M. J.; Thompson, L.K.; Hicks, R. G. *J. Org. Chem.* **2007**, *72*,

8062. (h) Parè, E. C.; Brook, D. J. R.; Brieger, A.; Badik, M.; Schinke, M. *Org. Biomol. Chem.* **2005**, *3*, 4258. (i) Taylor, P.; Lahti, P. M. *Chem. Commun.* 2004, 2656. (j) Ali, Md. E.; Vyas, S.; Datta, S. N. *J. Phys. Chem. A* **2005**, *109*, 6272. (k) Ali, Md. E.; Datta, S. N. *J. Phys. Chem. A* **2006**, *110*, 2776. (l) Parè, E. C.; Brook, D. J. R.; Brieger, A.; Badik, M.; Schinke, M. *Org. Biomol. Chem.* **2005**, *3*, 4258.
3. (a) Hustedt, E. J.; Beth, A. H. *Annu. Rev. Biophys. Biomol. Struct.* **1999**, *28*, 129. (b) Eaton, S. S.; Eaton, G. R. *Biol. Magn. Reson.* **2000**, *19*, 1. (c) Altenbach, C.; Oh, K.-J.; Trabanino, R.; Hideg, K.; Hubbell, W. *Biochemistry* **2001**, *40*, 15471. (d) Hanson, P.; Millhauser, G.; Formaggio, F.; Crisma, M.; Toniolo, C. *J. Am. Chem. Soc.* **1996**, *118*, 7618. (e) Hilger, D.; Polyhach, Ye.; Padan, E.; Jung, H.; Jeschke, G. *Biophys. J.* **2007**, *93*, 3675. (f) Jeschke, G. *Biochim. Biophys. Acta* 2005, 1707, 9.
4. (a) Marlin, D. S.; Bill, E.; Weyhermüller, T.; Bothe, E.; Wieghardt, K. *J. Am. Chem. Soc.* **2005**, *127*, 6095. (b) Ghosh, P.; Bill, E.; Weyhermüller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **2003**, *125*, 3967. (c) Mukherjee, C.; Pieper, U.; Bothe, E.; Bachler, V.; Bill, E.; Weyhermüller, T.; Chaudhuri, P. *Inorg. Chem.* **2008**, *47*, 8943. (d) Riplinger, C.; Kao, J. P. Y.; Rosen, G.M.; Kathirvelu, V.; Eaton, G. R.; Eaton, S. S.; Kutateladze, A.; Neese, F. *J. Am. Chem. Soc.* **2009**, *131*, 10092.
5. (a) Rajadurai, C.; Ivanova, A.; Enkelmann, V.; Baumgarten, M. *J. Org. Chem.* **2003**, *68*, 9907. (b) Rajadurai, C.; Ostrovsky, S.; Falk, K.; Enkelmann, V.; Haase, W.; Baumgarten, M. *Inorg. Chim. Acta*, **2004**, *357*, 581. (c) Rajadurai, C.; Fuhr, O.; Enkelmann, V.; Baumgarten, M. *J. Phys. Org. Chem.* **2006**, *19*, 257. (d) Rajadurai, C.; Enkelmann, V.; Zoppellaro, G.; Baumgarten, M. *J. Phys. Chem. B*, **2007**, *111*, 4327.
6. (a) Zoppellaro, G.; Ivanova, A.; Enkelmann, V.; Geies, A.; Baumgarten, M. *Polyhedron* **2003**, *22*, 2099. (b) Zoppellaro, G.; Enkelmann, V.; Geies, A.; Baumgarten, M. *Org. Lett.* **2004**, *6*, 4929. (c) Stroh, C.; Turek, P.; Rabu, P.; Ziessel, R. *Inorg. Chem.* **2001**, *40*, 5334. (d) Stroh, C.; Ziessel, R. *Tet. Lett.* **1999**, *40*, 4543. (e) Romero, F. M.; Luneau, D.; Ziessel, R. *Chem. Commun.* **1998**, 551. (f) Luneau, D.; Romero, F. M.; Ziessel, R. *Inorg. Chem.* **1998**, *37*, 5078. (g) Shiomi, D.; Ito, K.; Nishizawa, M.; Sato, K.; Takui, T.; Itoh, K. *Synth. Met.* **1999**, *103*, 2271. (h) Osanai, K.; Okazawa, A.; Nogami, T.; Ishida, T. *J. Am. Chem. Soc.* **2006**, *128*, 14008. (i) Hicks, R. G.; Lemaire, M. T.; Thompson, L. K.; Barclay, T. M. *J. Am. Chem. Soc.* **2000**, *122*, 8077. (j) Barclay, T. M.; Hicks, R. G.; Lemaire, M. T.; Thompson, L. K. *Chem. Commun.* **2000**, 21, 2141. (k) Fokin, S.; Ovcharenko, V.; Romanenko, G.; Ikorskii, V. *Inorg. Chem.* **2004**, *43*, 969. (l) Oshio, H.; Yaginuma, T.; Ito, T. *Inorg. Chem.* **1999**, *38*, 2750.
7. (a) Gutlich, P.; Goodwin, H. A. *Spin Crossover in Transition Metal Compounds. In Topics in Current Chemistry*; Eds.; Springer: Berlin, **2004**, 233. (b) Chandrasekhar, N.; Chandrasekar, R. *Dalton Trans.* **2010**, 39, 9872. (c) Rajadurai, C.; Qu, Z.; Fuhr, O.; Gopalan, B.; Kruk, R.; Ghafari, M.; Ruben, M. *Dalton Trans.* **2007**, 3531. (d) Rajadurai, C.; Fuhr, O.; Kruk, R.; Ghafari, M.; Hahn, H.; Ruben, M. *Chem. Commun.* **2007**, 2636. (e) Rajadurai, C.; Schramm, F.; Brink, S.; Fuhr, O.; Kruk, R.; Ghafari, M.; Ruben, M. *Inorg. Chem.* **2006**, *45*, 10019. (f) Holland, J. M.; McAllister, J. A.; Lu, Z.; Kilner, C. A.; Thornton-Pett, M.; Halcrow, M. A. *Chem. Commun.* **2001**, 577.
8. (a) Ishida, T.; Iwamura, H.; *J. Am. Chem. Soc.* **1991**, *113*, 4238. (b) Kanno, F.; Inoue, K.; Koga, N.; Iwamura, H. *J. Phys. Chem.* **1997**, *97*, 13267. (c) Inoue, K.; Iwamura, H. *J. Am. Chem. Soc.* **1994**, *116*, 3173. (d) Inoue, K.; Iwamura, H. *Adv. Mater.* **1996**, *8*, 73. (e) Borden, W. T.; Iwamura, H.; Berson, J. A. *Acc. Chem. Res.* **1994**, *27*, 109. (f) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587. (g) Solanki, N. K.; Leech, M. A.; McInnes, E. J. L.; Zhao, J. P.; Mabbs, F. E.; Feeder, N.; Howard, J. A. K.; Davies, J. E.; Rawson, J. M.; Halcrow, M. A. *J. Chem. Soc. Dalton Trans.* **2001**, 2083. (h) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, ISBN-10: 006042995X, Prentice Hall; 4 edition **1997**.
9. Osiecki, J. H.; Ullman, E. F. *J. Am. Chem. Soc.* **1968**, *90*, 1078.
10. Hirel, C.; Vostrikova, K. E.; Pècaut, J.; Ovcharenko, V. I.; Rey, P. *Chem. Eur. J.* **2001**, *7*, 2008.
11. Nihei, M.; Maeshima, T.; Kose, Y.; Oshio, H. *Polyhedron* **2007**, *26*, 1993.
12. WINEPR-SIMfonia programme was used for the simulation of the experimental ESR spectra.

# 3

## Shape-Defined and Shape-Shifting Paramagnetic Organic Nano-/Micro-Structures Derived from Doublet State Nitronyl Nitroxide Radical Derivative



\*A part of this chapter has been adapted from:

P. Hui and R. Chandrasekar\*  
*Chem. Plus. Chem.* **2012**, *12*, 1062.

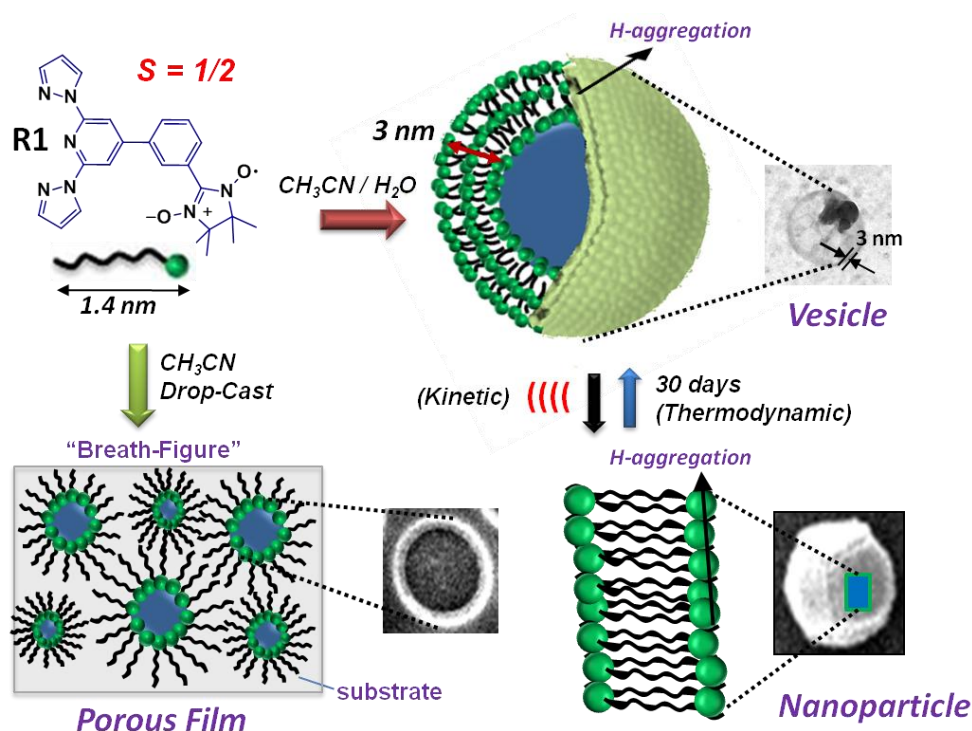
### 3.1 Abstract:

*Nano-/micro-scale paramagnetic porous film, reversibly shape shifting vesicles and nanoparticles were successfully prepared in a controlled manner from a stable nitronyl-nitroxide radical derivative using solvent and ultrasound mediated self assembly. This chapter presents for the first time self assembly of stable paramagnetic nitronyl nitroxide radical **R1** into micro porous film on a silica substrate and nano/micro scale vesicles in acetonitrile/water. These vesicles upon sonication form crystalline metastable nanoparticles (NPs) with facets. The shape-shifting tendency is highly reversible (Vesicles  $\leftrightarrow$  NPs). Single crystal X-ray structure was obtained to understand the non-covalent forces (C-H $\cdots$ O type intermolecular H-bonding interactions) responsible for the self-assembly. Furthermore both vesicles and NPs formed in solution exhibit Tyndall effect demonstrating their stable distribution in solution state. Interestingly, EPR spectroscopy studies of the solution containing vesicles and NPs show different g-values and peak-to-peak width ( $\Delta B_{pp}$ ) values in comparison to a clear acetonitrile solution of **R1** depending upon their aggregation size.*

### 3.2 Introduction:

Hierarchical self-assembly of functional organic building block molecules into organic nano-/micro-solid structures with specific properties (magnetic, electronic, optical and electrical) is one of the active research areas of organic based nanoscience and technology.<sup>1-4</sup> The main driving forces for the self-assembly of organic molecules in solvents are: i) nature of supramolecular interactions (van der Waals interaction, hydrogen bonds, and  $\pi$ - $\pi$  stacking) and ii) type of solvents (polar and non-polar).<sup>1-4</sup> Additionally, during deposition of these self-assembled aggregates at any surfaces/substrates, the final shape, morphology and dimension of nano-/micro-solids can be influenced by the nature of surfaces (SiO<sub>2</sub>, Graphite, Mica etc.,) and external perturbation factors such as temperature, solvent evaporation time, and atmosphere. Until now, most of the reported organic nano-/micro-structures are diamagnetic in nature. In contrary to diamagnetic molecules, self-assembly of stable organic radicals in solution and/or at surfaces (bottom-up) might form functional paramagnetic nano-/micro-solid structures. Particularly, paramagnetic vesicles, nanoparticles, and porous films might find applications in the areas of molecule based magnetism, magnetic resonance imaging (MRI) contrast agents, biosensing, drug delivery, separation of

paramagnetic gas molecules, and organic battery applications. Additionally, controlled reversible transformation of paramagnetic nano-/micro-solids from one shape/dimension to another and vice versa is another challenging task.<sup>1,2,4d</sup> Although sonication induced shape-shifting has been reported earlier,<sup>5</sup> to the best of our knowledge no article has been reported on the solvent(s)/surface/ultrasound assisted assembly of organic radical into diverse shape-defined and shape-shifting nano-/micro-scale objects.



### PARAMAGNETIC NANO-/MICRO-SOLIDS

**Scheme 3.1** Illustration of the formation mechanism of paramagnetic structures from mono nitronyl-nitroxide radical (R1).

This chapter presents versatile methods to generate paramagnetic nano-/micro-scale solid structures such as shape-defined porous film and reversibly shape-shifting vesicles and crystalline nanoparticles and vice versa, from a stable doublet state ( $S=1/2$ ) nitronyl nitroxide (NN) radical attached to 2,6- bispyrazolylpyridine (bpp) unit **R1** (Scheme 3.1).<sup>6</sup> Solvents such as acetonitrile, acetonitrile/water and ultrasonification conditions were employed to prepare these nano-/micro-scale structures solids in solution and at glass surface. The paramagnetic structures were studied by using electron microscopy (SEM/FESEM/TEM), selected area electron diffraction (SAED), atomic force microscopy (AFM), magnetic force microscopy (MFM), confocal Raman

$\mu$ -spectroscopy, powder X-ray diffraction (PXRD), UV/Vis spectroscopy and electron paramagnetic resonance (ESR) spectroscopy.

### 3.3 Results and Discussions:

#### 3.3.1 Synthesis of Paramagnetic Ligand:

Paramagnetic molecule, 2,6-di(pyrazol-1-yl)-4-(3-(1-oxy-3-oxo-4,4,5,5-tetramethylimidazolidin-2-yl)phenyl)pyridine (**R1**) was prepared as per our previously reported procedure (see chapter 2).<sup>6a</sup>

#### 3.3.2 Fabrication of Paramagnetic Nanostructure:

The generation of diverse shape-defined nano-/micro-structures from radical **R1** via self-assembly is a solvent, surface and ultrasound mediated process. The solubility of **R1**, its concentration, solvent polarity and addition of water play a crucial role in shaping the aggregation behaviour and the evolution of ultimate structural morphology. To fabricate paramagnetic porous membrane using a bottom-up approach, a well-known “*breath figure*” (BF)<sup>7b-d</sup> method (discovered in 1957) was adopted. There are many successful methods for fabricating ordered honeycomb structures with suitable pores over a large surface area. Top-down approaches usually involve multiple, complex and expensive steps, and may possibly break the final pattern after exclusion of templates. In 1994, Francois *et al.*<sup>8</sup> have first reported the use of condensed water droplets as a dynamic templates to prepare highly ordered honeycomb-patterned films with two- or three-dimensional hexagonal arrays of pores. In this method a solution of compound is first casted on a solid surface under humid circumstances, and rapid evaporation of the volatile solvent causes a quick drop in the surface temperature under the dew point, which leads to fast condensation and nucleation of water droplets on the surface of the compound solution. During the evaporation of the water droplets, a hexagonal packed pattern develops due to the convectional flow or the capillary force generated at the solution front.<sup>8</sup> After complete evaporation of solvent and water, traces of water droplets remain in the compound film to form honeycomb structures. The two key factors responsible for the formation of honeycomb structure are high humidity and a volatile solvent. Other influencing factors are molecular weight of the compound, air velocity, concentration, evaporation time and nature of substrate.

In a typical procedure, an acetonitrile solution of **R1** ( $c = 2.35 \times 10^{-3}$  M) was drop-casted on a glass substrate at room temperature followed by slow evaporation. The SEM and AFM topography images showed formation of a porous film of **R1** (Fig. 3.1A-E). AFM profile measurements illustrated an average pore diameter of ca. 400 nm - 1  $\mu$ m (Fig. 3.1F) and a film thickness of ca. 670 nm (Fig. 3.1G).

The formation mechanism of porous membrane like structure from **R1** can be interpreted as follows. During the evaporation of acetonitrile solution of **R1** from surface at room temperature, due to the condensation of water droplets and subsequent self-assembly of hydrophilic radical part of **R1** around them, a porous film formed in two dimensions (Scheme 3.1). For the preparation of vesicles, 1 ml of water was injected as a nonsolvent into a clear 2 ml ( $2.35 \times 10^{-3}$  M) CH<sub>3</sub>CN solution of **R1**. The resultant solution was homogeneous and no precipitate was found. Illumination of laser light to the CH<sub>3</sub>CN/H<sub>2</sub>O solution of **R1** displayed a pronounced *Tyndall effect* demonstrating the

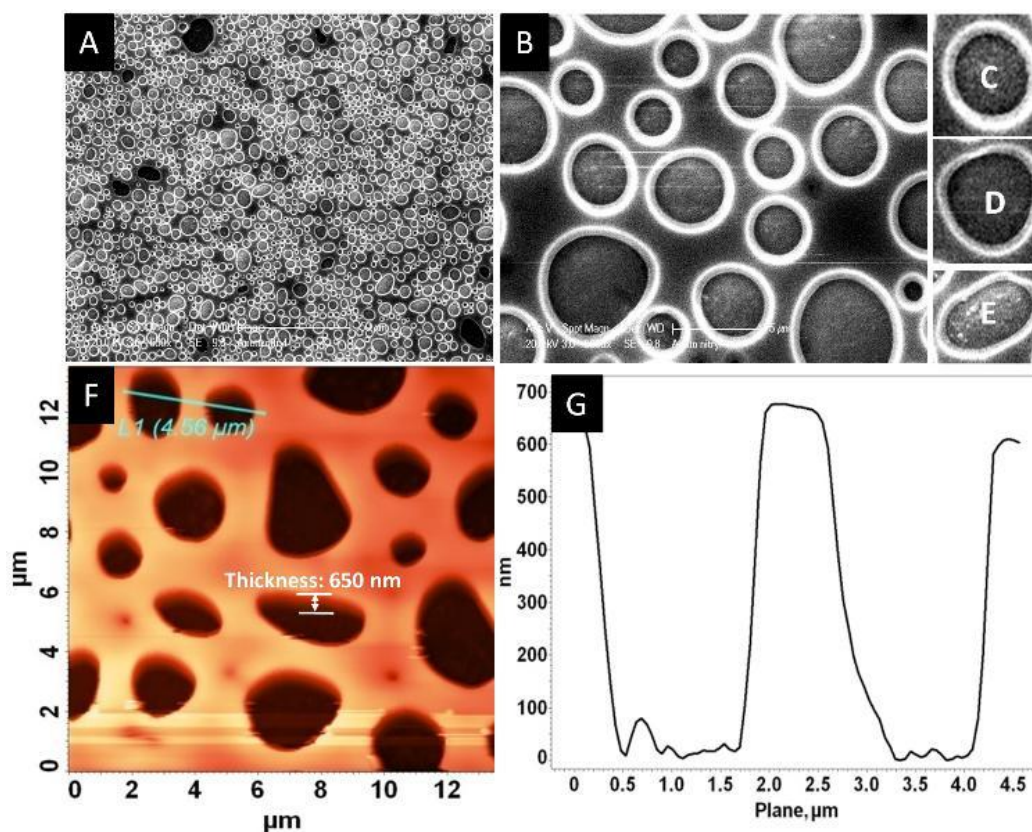


**Figure 3.1** SEM micrographs of porous film produced from **R1** in acetonitrile: A) low magnification image (scale bar is 50  $\mu$ m), B) high magnification image of pores. C-E) Different shapes of pores. AFM topography image: G) AFM thickness and diameter profile of two adjacent pores marked in topography image F) as a white line.

formation of solution stable nanostructures, whereas the same solution before water addition showed no such as a scattering effect (Fig. 3.2A, inset). To investigate the shape of the nano-objects using SEM analysis, two drops of the solution was drop-casted on a glass substrate. The images revealed the presence of isolated vesicles and several interconnected vesicles (Fig. 3.2A and B). The top, side and bottom views of dried vesicles are shown in figure 3.2C-E.

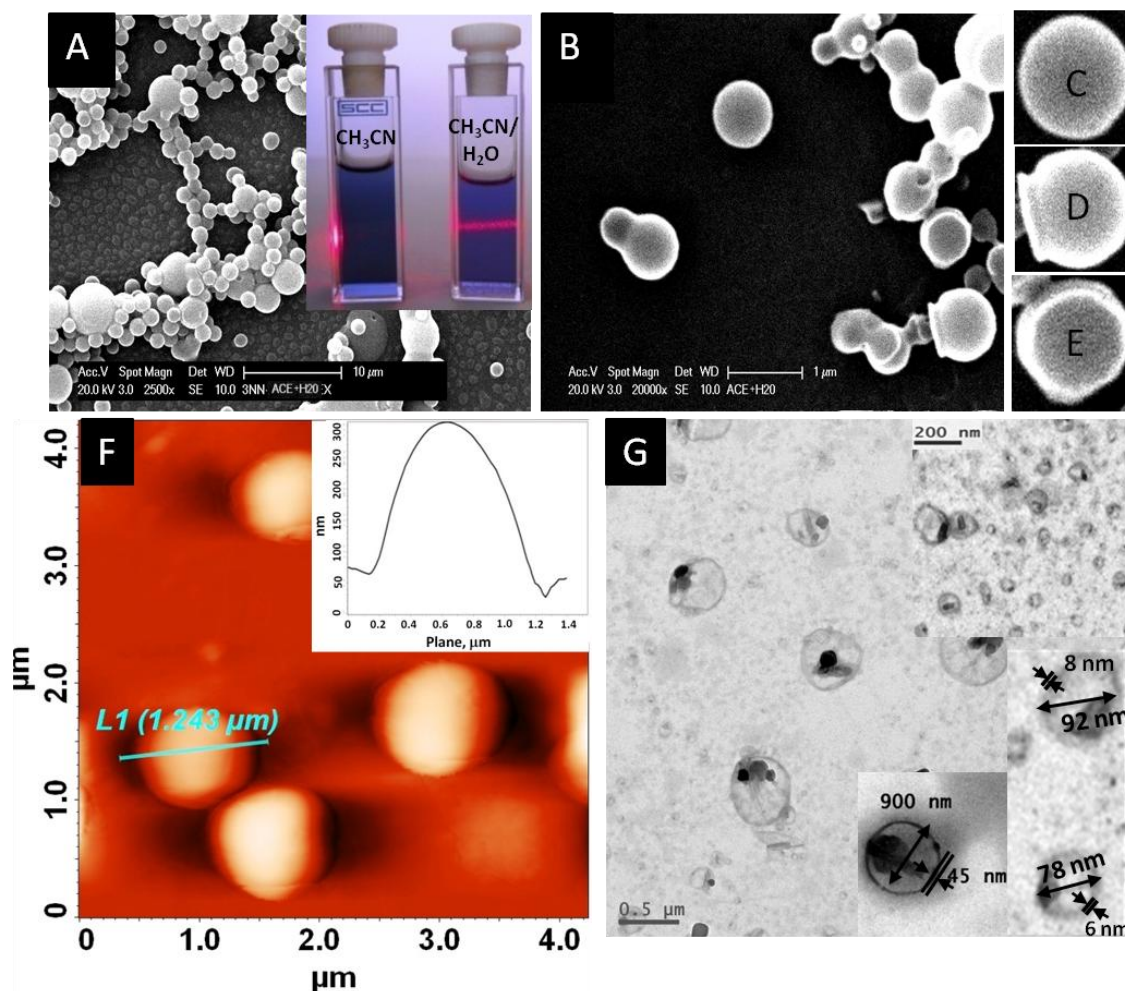


**Figure 3.2** SEM micrographs of vesicle of various sizes grown from **R1** in acetonitrile/H<sub>2</sub>O: A) a chain-like morphology of aggregated vesicles (scale bar is 10  $\mu$ m). The inset shows the *Tyndall effect* displayed by the vesicles in CH<sub>3</sub>CN/H<sub>2</sub>O in comparison with the pure CH<sub>3</sub>CN solution of **R1**. B) magnified-view of vesicles. C-E) Different shapes of dried vesicles. AFM topography image: F) several independent vesicles, inset shows the AFM height and width profile of a vesicle shown in F. Bright-field TEM micrographs: G) several ruptured vesicles. The insets show the diameter and the wall thickness of selected vesicles.

AFM studies of vesicles revealed that the diameter  $\times$  height profiles are in the range of *ca.* 800 nm–*ca.* 1.5  $\mu$ m  $\times$  *ca.* 120–220 nm, respectively (Fig. 3.2F and inset). These deformed disc-like structural profiles of vesicles on the substrate indicated their

soft nature. Furthermore, the bright-field TEM investigation revealed the existence of several nano-vesicles in the range of *ca.* 30-70 nm together with micro-vesicles (Fig. 3.2G). Furthermore the vesicles were ruptured under TEM measurement conditions, due to their soft nature. Additionally, TEM images clearly showed a dark contrast from the walls of the vesicles (Fig. 3.2G inset). Typical wall thicknesses of *ca.* 78 nm and *ca.* 900 nm sized vesicles are in the range of *ca.* 8 nm and *ca.* 45 nm, respectively. The self-assembly of vesicles from **R1** in acetonitrile/water and the size dependent membrane thickness indicated the formation of several lamellar like structures due to the presence of hydrophilic NN group and hydrophobic bpp unit in **R1**.

Surprisingly, sonication (for 5 min) of vesicles in acetonitrile/water converted them into crystalline nanoparticles (NPs). Here it is likely that the ultrasound waves caused cavitation and cleaved the intermolecular H-bonding interactions thereby collapsing

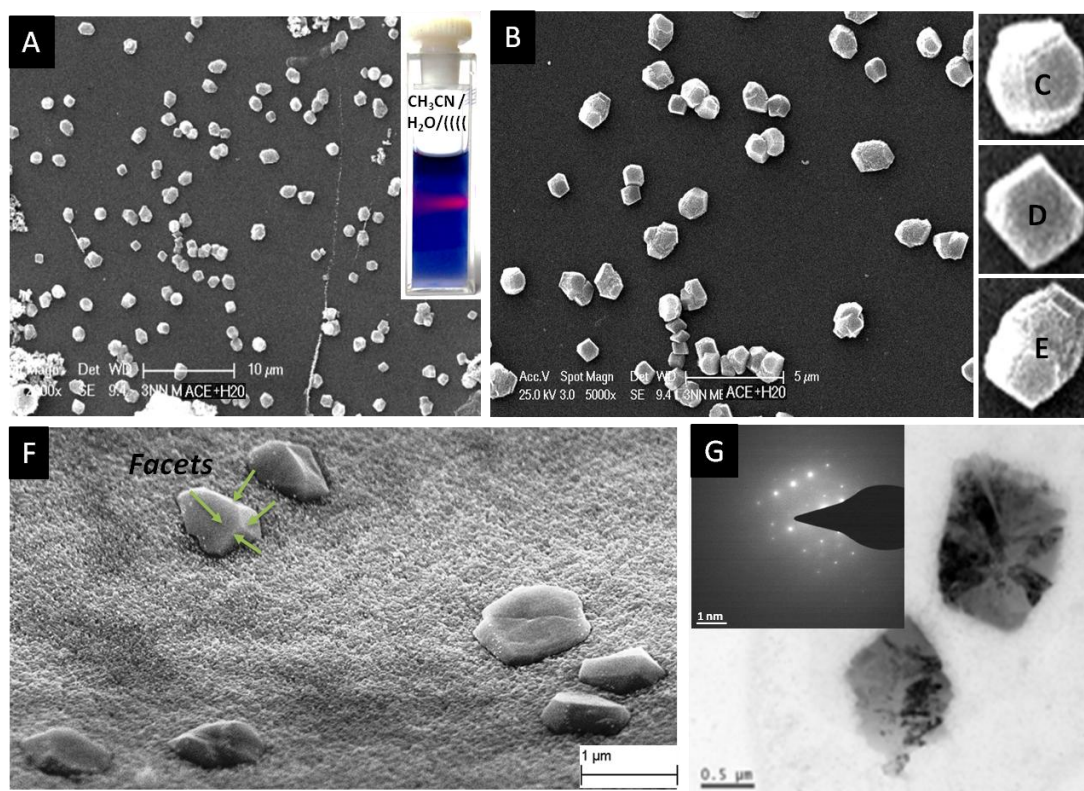


**Figure 3.3** SEM micrographs of paramagnetic nanoparticles of **R1**: A and B) Distribution of nanoparticles in a wide surface coverage area with varying sizes (Scale bar is 10  $\mu\text{m}$  and 5  $\mu\text{m}$ , respectively). The inset in A) shows the *Tyndall effect*. C - E) Different geometries of nanoparticles. F) FESEM image: nanoparticles with crystalline facets. G) Bright-field TEM micrograph of nanoparticles. The inset shows their SAED pattern.

the vesicles, creating nucleation and subsequently forming closely packed metastable high energy crystalline NPs. The NPs were well dispersed in solution and displayed a feeble Tyndall effect. As per Mie scattering theory the spherical vesicles normally display a well pronounced scattering than the much smaller NPs. The SEM images clearly exemplified the complete transformation of vesicles into crystalline NPs of dimension in the range of ca. 600 nm with several facets (Fig. 3.3A-F). TEM studies showed very dark contrasts from the particles indicating their high molecular density. The SAED pattern displayed a clear electron diffraction patterns from the particles demonstrating their crystalline nature (Fig. 3.3G, inset). This finding is further supported by the powder XRD experiments, which showed new diffraction peaks from the NPs at  $14.57^\circ$ ,  $16.11^\circ$ ,  $29.58^\circ$  compared to simulated PXRD spectrum of the single crystals having relatively sharper peaks, whereas vesicles showed a weak and broader peak due to their amorphous nature (Fig. 3.4).

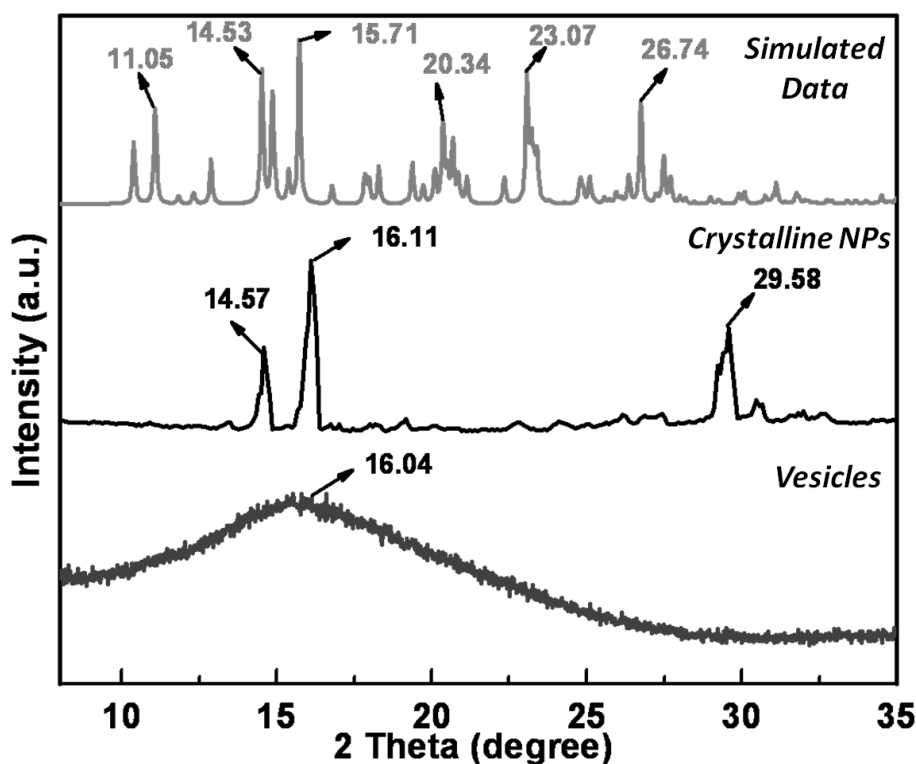


**Figure 3.4** Powder XRD data of crystalline nanoparticles and amorphous vesicles are presented in middle and bottom black lines respectively. Simulated spectrum from the single crystal X-ray structure is shown (top) in grey line.

The NPs are very stable in a dried up state, but when the kinetically stable NPs were kept in the same solution for a month, they reversibly shape-shifted back to thermodynamically stable vesicles (Fig. 3.5). Recently, Abe and his coworkers have

showed that nanoparticles derived from hydrophobic compounds which have polar groups are stable in water without surfactants for a long time.<sup>7</sup> The polar groups induces high negative  $\zeta$  potential in the nanoparticles and due to the electrostatic repulsion of the negative potential particles the flocculation/coalescence of the same is prevented.<sup>9</sup> Hence the stability (ca. 30 days) of the paramagnetic nano-/micro-structures in 2:1 CH<sub>3</sub>CN/water is possibly arises due to a negative Zeta ( $\zeta$ ) potential originated from the polar nitroxide group, with the magnitude possibly in the range of ca. -30 mV.<sup>11</sup>

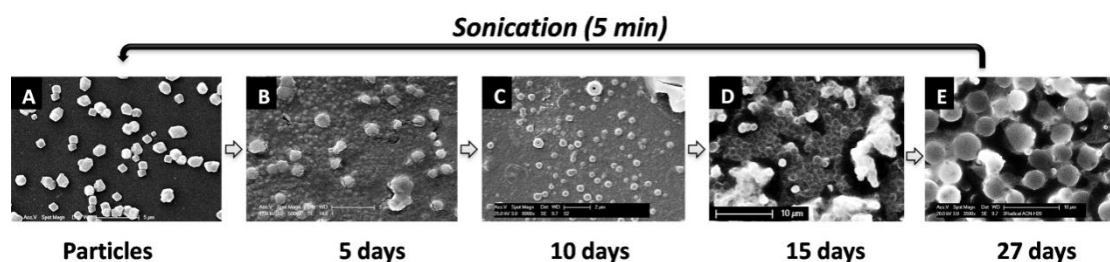


**Figure 3.5** SEM images displaying reversibly shape shifting tendency of thermodynamically stable vesicles into kinetically stable nanoparticles and vice versa.

Furthermore, ultrasonic irradiation causes acoustic cavitation, and bubble collapse produces intense local heating, high pressures, and very short lifetimes; these transient, localized hot spots drive high-energy chemical reactions. Ultrasonic cavitation in liquid–solid systems also has high-energy physical effects, including (i) the improvement of mass transfer, (ii) the disintegration of solids, and (iii) the generation of surface damage at liquid–solid inter-faces. The ultrasound waves were thought to cleave the intra-molecular  $\pi$ - $\pi$  stacking interactions of the compound, inducing rapid and spontaneous aggregation through interpenetrating stacking interactions.

### 3.3.3 The Single Crystal X-ray Structure of Radical R1:

Examination of the single X-ray structure of **R1** showed that the molecule has an unique structural feature for hierarchical supramolecular self-assembly via hydrogen bonding interactions (Fig. 3.6). The NN ring oxygen atom (O2) and (O4) participate in the C-H $\cdots$ O type intermolecular hydrogen bond interactions with the pyrazole ring protons and methyl protons, [O2 $\cdots$ H12 = 2.319 Å; O2 $\cdots$ H15 = 2.303 Å;

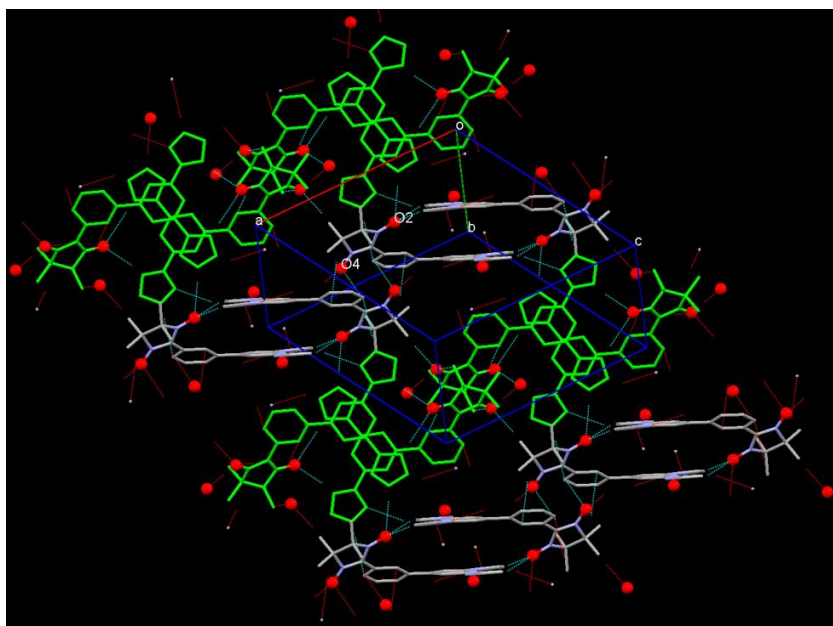


**Figure 3.6** Solid state packing diagram of monoradical **R1**. The red balls show the oxygen atoms. Hydrogen atoms are omitted for clarity.

$O2 \cdots H14 = 2.666 \text{ \AA}$ ;  $O4 \cdots H24C = 2.599 \text{ \AA}$ ;  $O4 \cdots H22B = 2.399 \text{ \AA}$ . The torsion angles ( $\Phi$ ) between the phenyl ring and the NN radical are  $27.60^\circ$  (C9-C8-C18-N7), and  $28.59^\circ$  (C7-C8-C18-N6). Furthermore the phenyl ring and the bpp unit are in near planar configuration ( $\Phi = 24^\circ$ ).

### 3.3.4 Optical Properties of Radical **R1**:

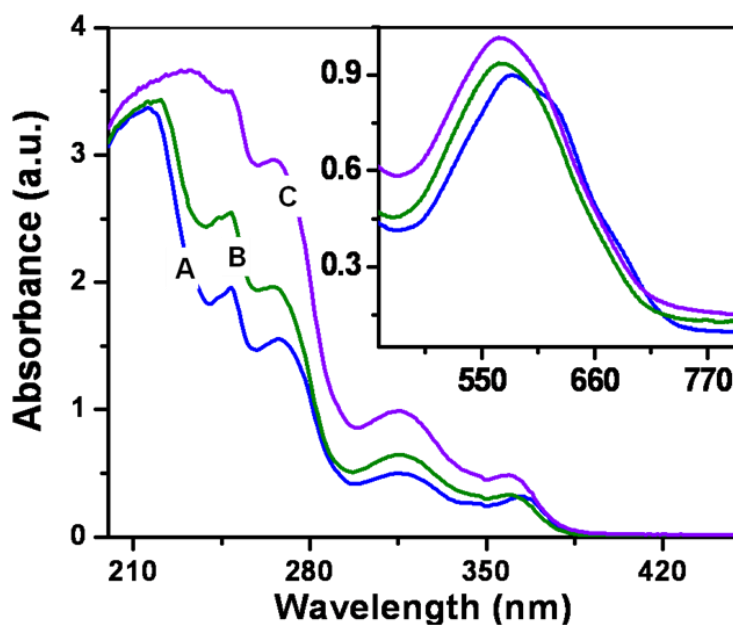


**Figure 3.7** (A) The change in the absorption spectra of a clear acetonitrile solution of **R1**. (B) Due to the formation of vesicles. (C) NPs in acetonitrile/water at room temperature. The inset shows their corresponding shift in the  $n \rightarrow \pi^*$  transition at 450–800 nm region.

The UV-Visible spectra of compound **R1** in CH<sub>3</sub>CN, vesicles and NPs showed characteristic  $n \rightarrow \pi^*$  transitions of a NN radical at 579, 571 and 568 nm, respectively (Fig. 3.7). The absence of broad absorption band at *ca.* 470 nm ( $n \rightarrow \pi^*$ ) ruled out the possibility of imino radical formation due to further oxidation.<sup>6c</sup> Interestingly, the optical spectra of vesicles and NPs in CH<sub>3</sub>CN/H<sub>2</sub>O mixed solvent were shifted towards high energy side compared to a clear solution of **R1** in CH<sub>3</sub>CN. This observed blue shift from vesicles and NPs can be attributed to the formation of H-type aggregates and size reduction. The absorption spectra of radical **R1** in pure acetonitrile showed no shift in peaks upon increasing in concentration indicating no aggregate formation (Fig. 3.8).

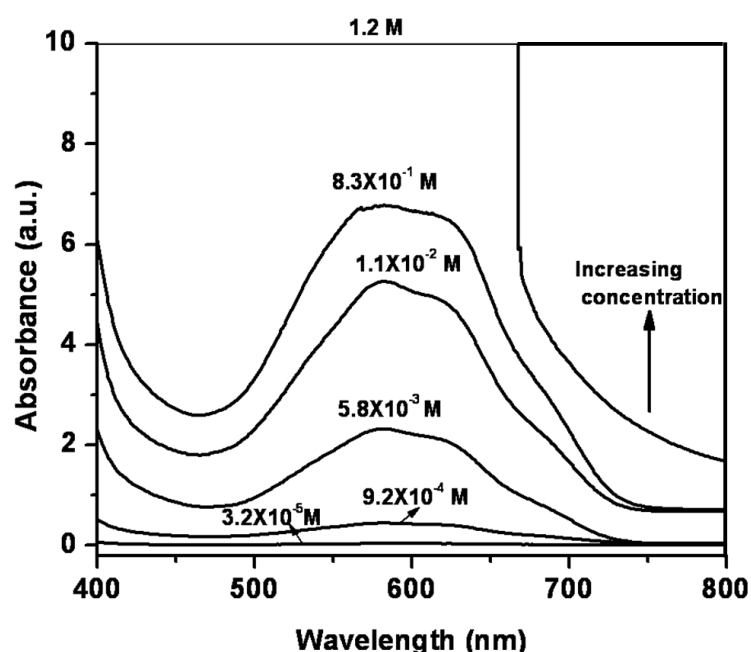


**Figure 3.8** UV-Vis spectra of acetonitrile solution of **R1** at different concentrations.

### 3.3.5 X-Band ESR Spectroscopy Studies of Radical **R1**:

High-resolution isotropic fluid state ESR (X-band) spectrum of an intermolecularly secluded ( $c \ll 10^{-4}$  M) monoradical **R1** recorded in degassed toluene/isopropanol solvent mixture at room temperature is shown in figure 3.9. The spectrum showed a well-resolved five-line pattern ( $\Delta M_s = \pm 1$  transitions) with the isotropic  $g_{iso}$ -value of 2.0066 and nitrogen hyperfine coupling ( $hfc$ ) value of  $a_N = 7.40$  G.<sup>6a</sup> Additionally, each of the five major lines composed of a group of lines due to further

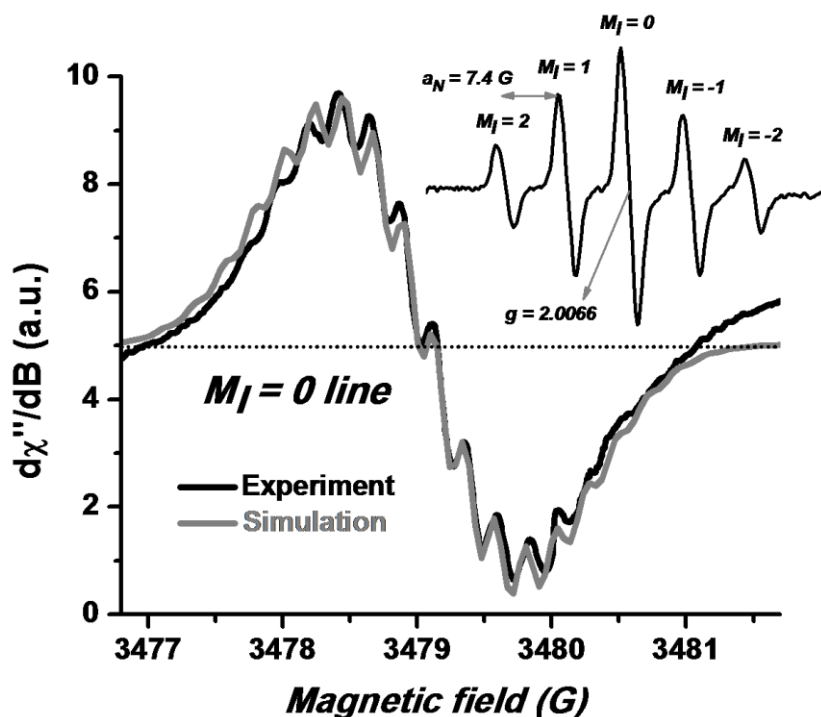


**Figure 3.9** High-resolution isotropic EPR spectra ( $\Delta M_s = \pm 1$  transitions) of radical **R1**. The highly resolved  $M_I = 0$  lines were recorded with the following parameters:  $c \leq 10^{-4}$  M in a toluene/isopropanol mixture, 293 K, and 0.5 mW microwave power. The black and grey lines show the experimental and computer simulated spectrum, respectively.

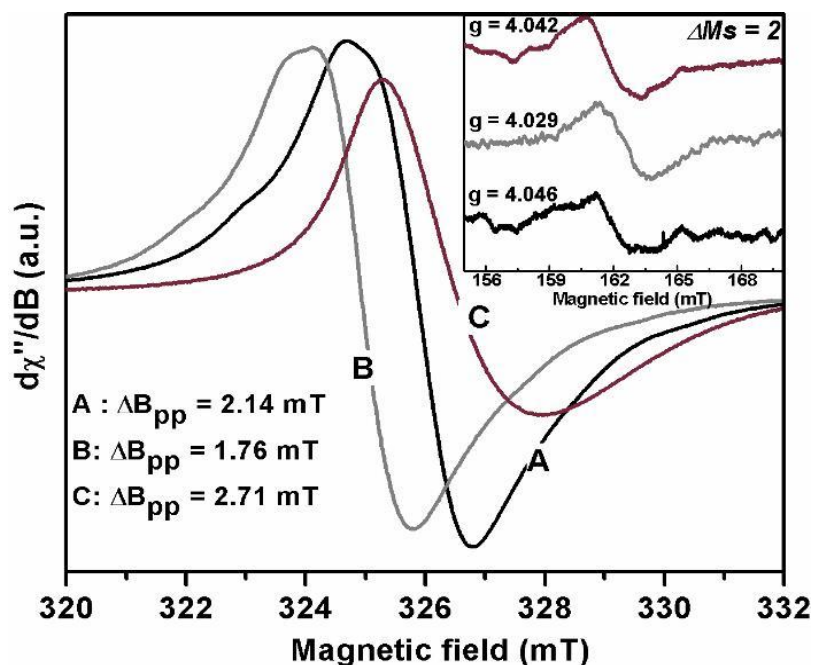


**Figure 3.10** ESR spectra of vesicles (B) and NPs (C) in acetonitrile/water in comparison with clear acetonitrile solution of **R1** (A) recorded at 120 K. The inset shows their corresponding forbidden  $\Delta M_s = \pm 2$  transitions.

$hfc$  with magnetically active nuclei of small spin densities. The group of lines in the central line ( $M_I = 0$ ) of the spectrum was best simulated with the following proton  $hfc$  values:  $a_{H(ortho)} = 0.49$  G;  $a_{H(meta)} = 0.2$  G;  $a_{H(para)} = 0.4$  G;  $a_{H(pyridine)} = 0.41$  G;  $a_{H(Me)} = 0.22$  G;  $a_{H(Pyrazole)} = 0.21$  G. The ESR studies of vesicles (B) and NPs (C) containing solutions at 120 K showed diverse peak-to-peak ( $\Delta B_{pp}$ ) and  $g$  values compared to a clear acetonitrile solution of **R1** (A) (Fig. 3.10). The  $\Delta B_{pp}/g$  values are as follows: A: 2.14 mT/2.0077, B: 1.76 mT/2.0120 and C: 2.71 mT/2.0056. Here, due to bigger size of vesicles the alignment parameter ( $\lambda$ ) of vesicles is higher than NPs.<sup>9</sup> As a result the ESR signals of vesicles and NPs were shifted to lower and higher magnetic field, respectively. Moreover, the typical line shape and broadening of the  $\Delta M_s = \pm 1$  lines and appearance of  $\Delta M_s = \pm 2$  transitions (see Fig. 3.10 inset) indicated the operating spin-spin exchange or magnetic dipole interactions between the spins in the solid state.

### 3.3.6 Magnetic Force Microscopy Studies:

Magnetic force microscopy is a useful technique to map the magnetic domain (if there any) in the nano/micro regime. As mentioned in section 1.3, the lift height ( $z$ ) of the magnetic tip is crucial to isolate the non-magnetic interactions (such as Van der Waals

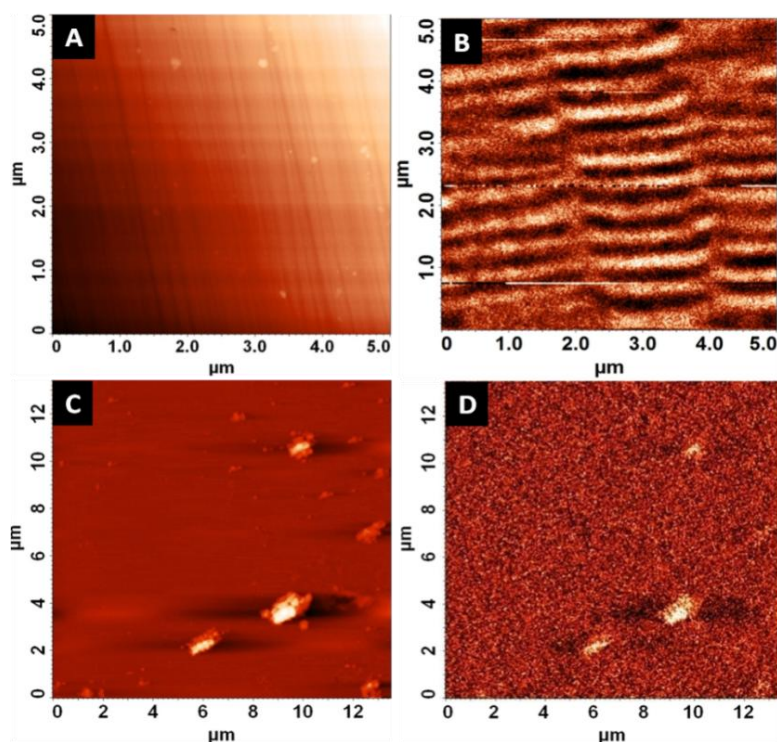


**Figure 3.11** MFM image of hard disk (A) height image, (B) the corresponding MFM phase image. MFM image of a  $\text{Fe}_3\text{O}_4$  nano particles (C) height image, (D) the corresponding MFM phase image.

force, adhesive force, and electrostatic force etc.) from the magnetic forces. Normally these nonmagnetic forces are dominant in the low  $z$  regime. Before the actual measurement, to test, a magnetic hard disk and  $\text{Fe}_3\text{O}_4$  nanoparticles were chosen for MFM imaging. As one can see, the height image (at  $z = 50$  nm) does not show any topographic features, whereas corresponding MFM phase image clearly exhibited magnetic domain of the hard disk (Fig. 3.11 A & B). On the other hand, due to shape,  $\text{Fe}_3\text{O}_4$  nanoparticles show clear topography in the height image (Fig. 3.11 C), and the corresponding phase image (Fig. 3.11 D) shows the possible magnetic interaction from the nanoparticles.

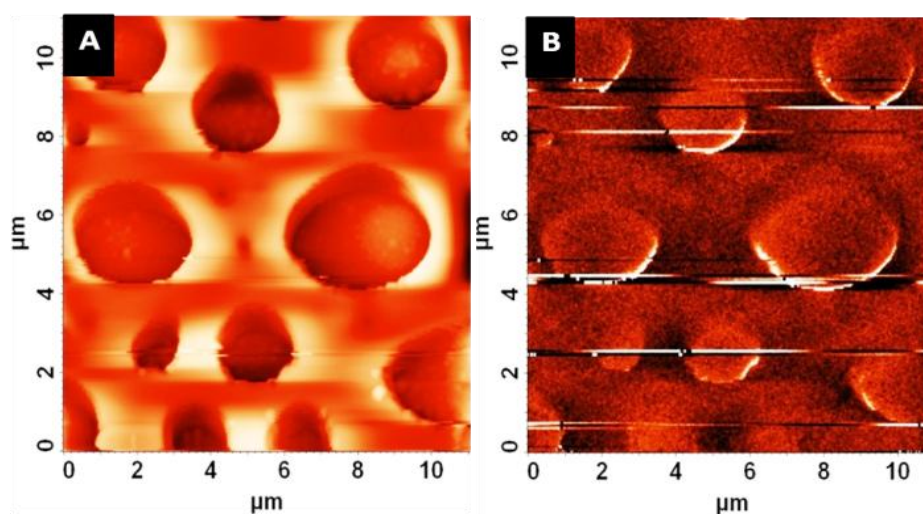


**Figure 3.12** A) MFM height image of a porous film and B) the corresponding MFM phase image of pores (lift height)  $z$ -range topography of 100 nm.

The MFM measurement on the porous film composed of radical **R1** is presented in figure 3.12. The height image of the porous film (Fig. 3.12 A) and the corresponding MFM scanning performed at  $z = 100$  nm, showed phase contrast feature similar to the height profile images. It was found that in the similar lift height even normal AFM tip generated analogous image. One of the most important differences between AFM and MFM is the nature of the force applied on the cantilever. In AFM, the force is originated as a result of a mechanical interaction between two surfaces. In MFM, the force is the interaction with a vector force field and the net force seen by the cantilever at a particular position is the result of the superposition of many magnetic dipoles located both on the sample and on the cantilever. Thus the force on the cantilever depends strongly on the distance between the tip and the scanned surface; this distance is the lift height ( $z$ ). Adjusting this ( $z$ ) parameter does not necessarily improve the MFM image; rather it

samples the magnetic field at a different  $z$  location. To study the effect of different lift heights on the phase images contrasts, for vesicles the height and phase images were collected at  $z = 50, 100, 300,$  and  $500$  nm (Fig. 3.13). As one can see at higher  $z$  values the phase contrast image intensity decreased significantly. But it is hard to conclude that the MFM phase contrast image is a result of tip and sample magnetic interactions. It is also important to mention here that for samples having height in the range of several nm even at larger lift height one cannot eliminate the other non-magnetic interactions from the weak magnetic interactions.

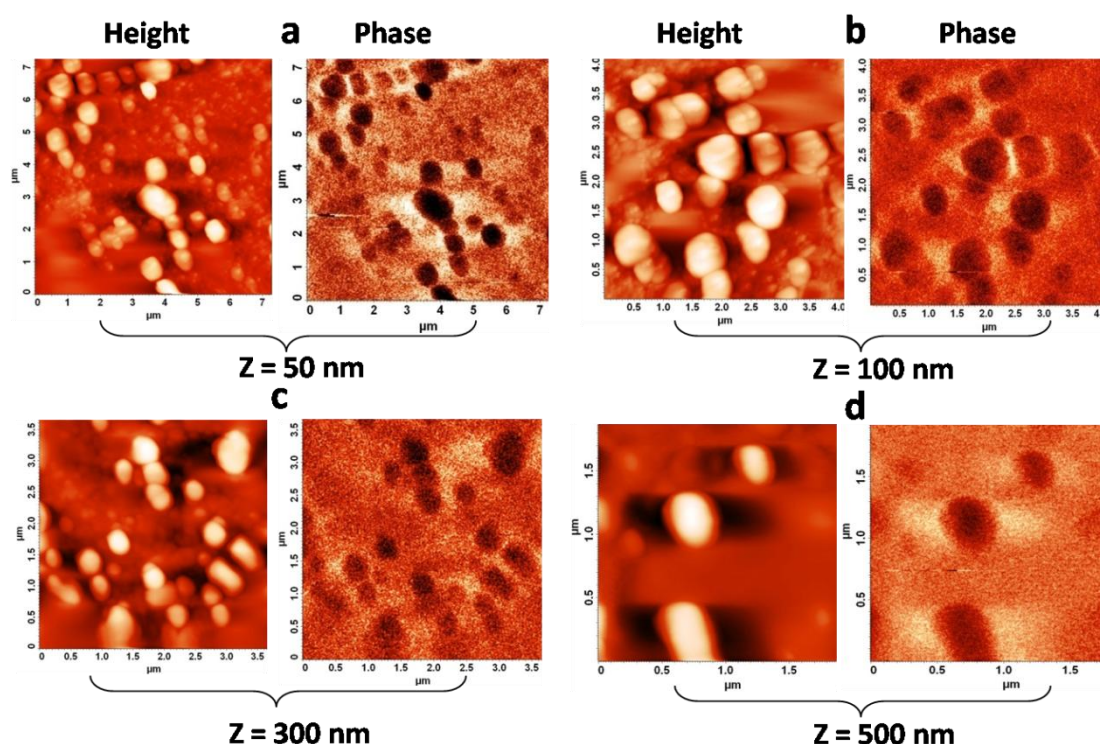


**Figure 3.13** MFM phase and height images of vesicles in different lift height ( $z$ ) of tip.

### 3.4 Conclusions:

In summary, this chapter demonstrated, for the first time, a controlled generation of paramagnetic solid structures such as porous film, vesicles and NPs from an organic NN radical **R1**. The main driving forces behind the aggregation phenomena is C-H $\cdots$ O type intermolecular H-bonding interactions. The development of micro porous film during the evaporation of acetonitrile solution of **R1** was surface/H<sub>2</sub>O condensation assisted process. Interestingly, **R1** formed soft vesicles in acetonitrile/H<sub>2</sub>O via multi-lamellar mechanism. Ultrasonification technique was employed to reversibly shape shift

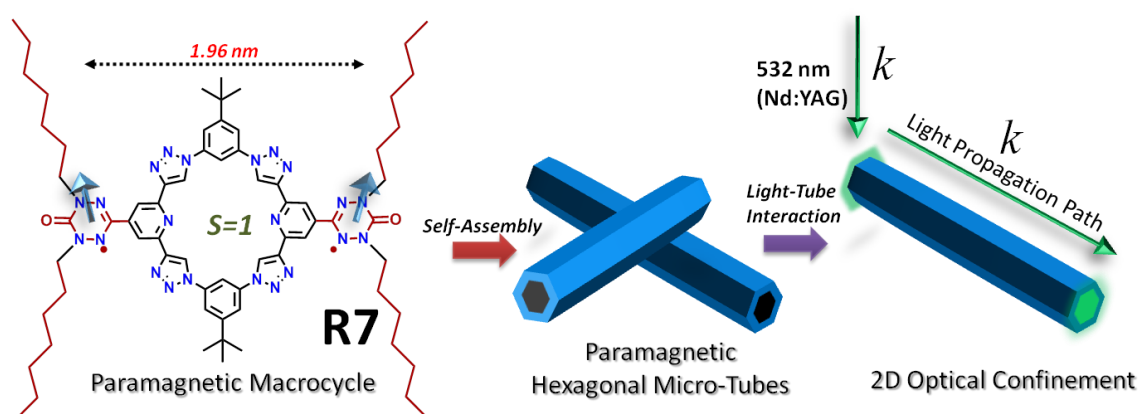
the vesicles into NPs and vice versa in acetonitrile/H<sub>2</sub>O. These paramagnetic nano-/micro-solids might find interesting applications in wide areas of materials science and biology involving paramagnetism.

### References:

1. (a) Whitesides, G. W.; Grzybowski, B. *Science* **2002**, *295*, 2418. (b) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071. (c) Bong, D. T.; Clark, T. D.; Granja, J. R.; Ghadiri, M. R. *Angew. Chem. Int. Ed.* **2001**, *40*, 988. (d) Palmer, L. C.; Stupp, S. I. *Acc. Chem. Res.* **2008**, *41*, 1674. (e) Ajayaghosh, A.; Praveen, V. K. *Acc. Chem. Res.* **2007**, *40*, 644. (f) Ajayaghosh, A.; Praveen, V. K.; Vijayakumar, C. *Chem. Soc. Rev.* **2008**, *37*, 109. (g) Nakanishi, T.; Schmitt, W.; Michinobu, T.; Kurth, D. G.; Ariga, K. *Chem. Commun.* **2005**, 5982. (h) Abraham, S.; Vijayaraghavan, R. K.; Das, S. *Langmuir* **2009**, *25*, 8507. (i) Ramakanth, I.; Shankar, B. V.; Patnaik, A. *Chem. Commun.* **2008**, 4129. (j) Gerlich, S.; Eibenberger, S.; Tomand, M.; Nimmrichter, S.; Hornberger, K.; Fagan, P.; Tüxen, J.; Mayor, M.; Arndt, M. *Nat. Commun.* **2011**, *2*, 263. (k) Babu, S. S.; Prasanthkumar, S.; Ajayaghosh, A. *Angew. Chem. Int. Ed.* **2012**, *51*, 1766.
2. (a) Lim, Y.; Moon, K.-S.; Lee, M. *Chem. Soc. Rev.* **2009**, *38*, 925. (b) Kim, H. J.; Kim, T.; Lee, M. *Acc. Chem. Res.* **2011**, *44*, 72. (c) Cizek, J.W.; Huang, L.; Wang, Y.; Mirkin, C. A. *Small* **2008**, *4*, 206. (d) Yagai, S.; Mahesh, S.; Kikkawa, Y.; Unoike, K.; Karatsu, T.; Kitamura, A.; Ajayaghosh, A. *Angew. Chem. Int. Ed.* **2008**, *47*, 4691. (e) Vijayakumar, C.; Praveen, V. K.; Ajayaghosh, A. *Adv. Mater.* **2009**, *21*, 2059. (f) Hirai, Y.; Babu, S. S.; Praveen, V. K.; Yasuda, T.; Ajayaghosh, A.; Kato, T. *Adv. Mater.* **2009**, *21*, 4029.
3. (a) Shu, L.; Müri, M.; Krupke, R.; Mayor, M. *Org. Biomol. Chem.* **2009**, *7*, 1081. (b) Langner, A.; Tait, S. L.; Lin, N.; Rajadurai, C.; Ruben, M.; Kern, K. *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 17927. (c) Samori, P.; Francke, V.; Muellen K.; Rabe, J. P. *Chem. Eur. J.* **1999**, *5*, 2312. (d) Savariar, E. N.; Krishnamoorthy, K.; Thayumanavan, S. *Nat. Nanotech.* **2008**, *3*, 112.
4. (a) Chandrasekhar, N.; Chandrasekar, R. *Chem. Commun.* **2010**, *46*, 2915 (b) Basak, S.; Chandrasekar, R. *Adv. Funct. Mater.* **2011**, *21*, 667. (c) Narayana, Y. S. L. V.; Chandrasekar, R. *Chem. Phys. Chem.* **2011**, *12*, 2391. (d) Chandrasekhar, N.; Chandrasekar, R. *Angew. Chem. Int. Ed.* **2012**, *51*, 3556. (e) Basak, S.; Hui, P.; Boodida, S.; Chandrasekar, R. *J. Org. Chem.* **2012**, *77*, 3620.
5. (a) Ke, D.; Zhan, C.; Li, A. D. Q.; Yao, J. *Angew. Chem. Int. Ed.* **2011**, *50*, 3715. (b) Isozaki, K.; Takaya, H.; Naota, T. *Angew. Chem. Int. Ed.* **2007**, *46*, 2855. (c) Ke, D.; Zhan, C.; Xu, S.; Ding, X.; Peng, A.; Sun, J.; He, S.; Li, A. D. Q.; Yao, J. *J. Am. Chem. Soc.* **2011**, *133*, 11022. (d) Yu, X.; Liu, Q.; Wu, J.; Zhang, M.; Cao, X.; Zhang, S.; Wang, Q.; Chen, L.; Yi, T. *Chem. Eur. J.* **2010**, *16*, 9099. (e) Wang, Y.; Zhan, C.; Fu, H.; Li, X.; Sheng, X.; Zhao, Y.; Xiao, D.; Ma, Y.; Ma, J. S.; Yao, J. *Langmuir* **2008**, *24*, 7635.
6. (a) Hui, P.; Arif, Khaja. Md.; Chandrasekar, R. *Org. Biomol. Chem.* **2012**, *10*, 2439 (b) Rajadurai, C.; Schramm, F.; Brink, S.; Fuhr, O.; Kruk, R.; Ghafari, M.; Ruben, M. *Inorg. Chem.* **2006**, *45*, 10019 (c) Zoppellaro, G.; Enkelmann, V.; Geies A.; Baumgarten, M. *Org. Lett.* **2004**, *6*, 4929.
7. (a) Kamogawa, K.; Akatsuka, H.; Matsumoto, M.; Yokoyama, S.; Sakai, T.; Sakai, H.; Abe, M. *Colloids Surf. A* **2001**, *180*, 4153. (b) Widawski, G.; Rawiso, M.; Francois, B. *Nature* **1994**, *369*, 387. (c) Spurr, R.T.; Butlin, J.G. *Nature* **1957**, *179*, 1187. (d) Knobler, C. M.; Beysens, D. *Europhys. Lett.* **1988**, *6*, 707.
8. Wiawski, G.; Rawiso, M.; Francois, B. *Nature* **1994**, *369*, 387.
9. An, B.-K.; Kwon, S.-K.; Jung, S.-D.; Park, S. Y. *J. Am. Chem. Soc.* **2002**, *124*, 14410.
10. Trapp, C.; Smith D.; Wasson, J. R. *J. Chem. Phys.* **1969**, *51*, 1419.
11. Fu, H.; Loo, B. H.; Xiao, D.; Xie, R.; Ji, X.; Yao, J.; Zhang, B.; Zhang, L. *Angew. Chem. Int. Ed.* **2002**, *41*, 962.

# 4

## Light Propagation in High-Spin Organic Microtubes Self-Assembled from Triplet State Macrocycles Carrying Oxo-Verdazyl Biradicals



\*A part of this chapter has been adapted from:

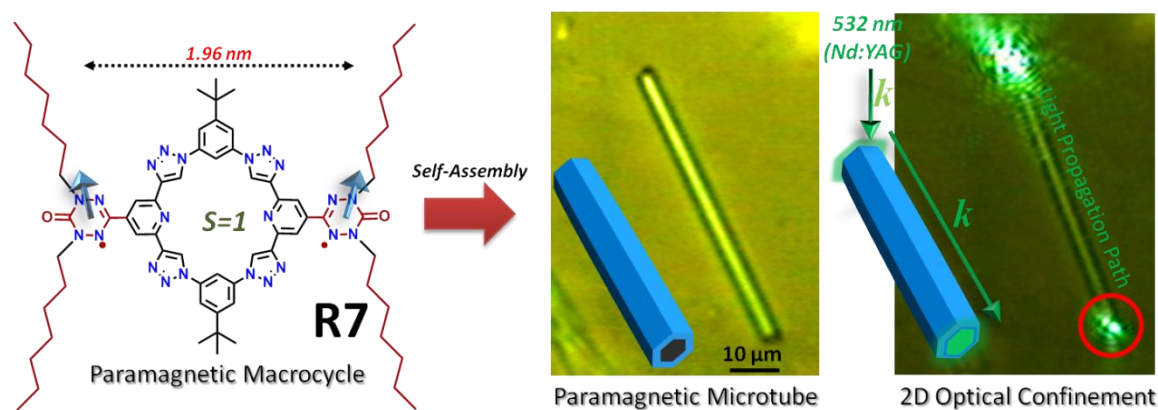
P. Hui, R. Chandrasekar\*  
*Adv. Mater.* **2013**, 25, 2963.

## 4.1 Abstract:

*Mono and dioxo-verdazyl radicals attached to organic shape persistent paramagnetic “Click” macrocycles were successfully synthesized. Frozen state EPR spectroscopy studies of the biradical-macrocycle in toluene ( $c \sim 10^{-4}$  M) displayed an axial zero-field splitting ( $|D/hc| = 7.94 \times 10^{-4} \text{ cm}^{-1}$ ) and a forbidden half field ( $\Delta M_S = \pm 2$ ) transition ( $g = 4.05$ ) at cryogenic temperature supported its triplet ( $S = 1$ ) nature. From the 2D value the estimated distance ( $r$ ) between two OVZ centres is ca. 19 Å. The biradical-macrocycle self-assembled via J-type aggregate forming paramagnetic microtubes. Raman imaging/spectroscopy was used to probe 1D light propagation and photonic properties of the paramagnetic tube. Additionally the wave guiding experiment was used to identify naturally inherited nano-defect sites of the tube.*

## 4.2 Introduction:

Interest in hollow tubular organic nanostructures has been progressively growing since the discovery of carbon nanotubes by Iijima in 1991.<sup>1</sup> Tiny organic tubular objects derived from  $\pi$ -conjugated organic molecules possessing electronic,<sup>2</sup> optical,<sup>3</sup> and magnetic functions may find potential use in miniaturized nano/micro scale soft photonic, conducting and spintronic devices. Hence supramolecular interactions (Van der Waals force, electrostatic, hydrogen bond, metal coordination, and  $\pi$ - $\pi$  stack) mediated self-assembly of nano/micro scale soft tubes from tailor made organic molecules of interest,<sup>1-3</sup> because many functional properties can be readily incorporated into the molecular building block by tailor-made organic synthesis. To date most of the reported organic tubes are all self-assembled from small  $\pi$ -conjugated organic molecules,<sup>4</sup> polymers<sup>5</sup> and peptides.<sup>6</sup> For our surprise, all of them are *diamagnetic* in nature. Some groups also exploited the fluorescent emission property of the *diamagnetic* tubular structures, to confine and guide the fluorescent waves in one dimension via local electronic excitation of the tube.<sup>7</sup> Recently, for the first time, our group has demonstrated the passive optical wave guiding behavior of organic tubes without electronically exciting the molecular units of the tube.<sup>3d</sup> Molecules carrying unpaired electron spins are potential building blocks for the bottom-up fabrication of soft spintronic devices.<sup>8</sup> Hence preparation of paramagnetic tubes from stable and solution processable  $\pi$ -conjugated organic radicals having supramolecular self-assembling properties is very important.



**Scheme 4.1** A 1D paramagnetic organic tube self-assembled from a macrocycle carrying high-spin oxo-verdazyl biradicals **R7** shows optical wave guiding behaviour.

Earlier, Ghadiri *et al.* have self-assembled aliphatic macrocycles with polar functional groups into nanotubular solid structure.<sup>9</sup> Also, several other groups have independently reported numerous diamagnetic  $\pi$ -conjugated shape persistent macrocycles (SPM)<sup>10,11</sup> and some of them form self-assembled solid state aggregates. For radicals having total spin value  $S \geq 1$ , extensive  $\pi$ -conjugation is important to achieve efficient intra spin-spin interaction. Among known stable neutral radicals, oxo-verdazyl type radicals are known for its exceptional stability and easy synthesis.<sup>12,13c</sup> Therefore in this work, a synthetic plan has been made to attach of two stable neutral verdazyl biradicals ( $S = 1$ ) to a SPM composed of eight conjugated ring systems via Click chemistry to study its self-assembly properties.

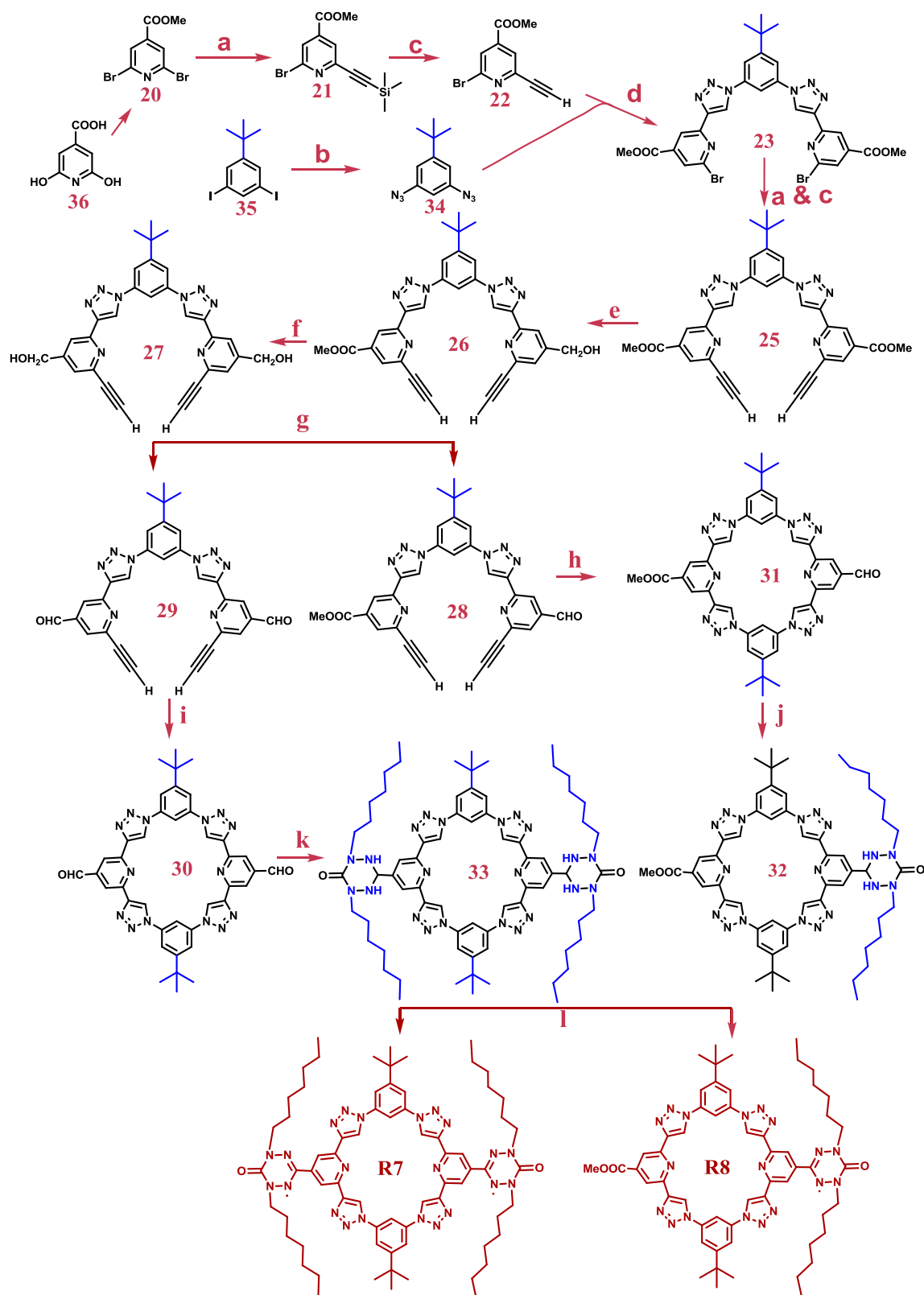
In this chapter, the design, syntheses, UV/Vis and EPR spectroscopy studies of triplet and doublet state diheptylated oxo-verdazyl radicals connected to  $\pi$ -conjugated Click SPMs **R7** and **R8**, respectively and the self-assembly of triplet macrocycle **R7** into paramagnetic microtubes in DCM/hexane will be presented in detail (Fig. 4.7). The self-assembled microtubes were well characterized by using electron microscopy (SEM/FESEM/TEM), atomic force microscopy (AFM), powder X-ray diffraction (PXRD) and confocal Raman microscope (CRM) techniques. For the first time, by exploiting the Raman spectroscopy/imaging option of a transmission mode confocal Raman microscope, the laser light was successfully guided through the tube (Scheme 4.1). Subsequently, a novel method “wave guiding mode Raman imaging” was developed to locate the nano/micro scale spin defect sites inherited during the tube self-assembly process.

## 4.3 Results and Discussions:

### 4.3.1 Syntheses of Paramagnetic SPMs:

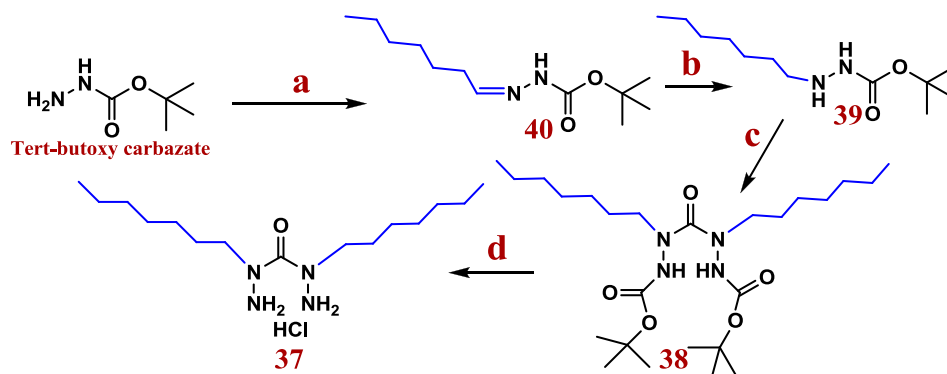
For the syntheses of paramagnetic SPMs, **R7** and **R8**, a *convergent cyclization strategy*<sup>10,11</sup> was adopted (Scheme 4.2). The starting compound 2,6-dibromoisonicotinic acid methyl ester **20** was synthesized from citrazinic acid **36** as per reported method.<sup>11</sup> Selective mono Sonogashira cross-coupling of compound **20** using trimethyl silyl acetylene (TMSA) readily formed compound **21** in 81% yield. Deprotection reaction of the acetylene group of **21** quantitatively converted it into **22** with 99% yield. The Click precursor 3,5-diazido-1-tert-butylbenzene **34** was prepared in three steps from 4-tert-butylaniline.<sup>10e,14</sup> Reaction of the alkyne compound **22** with diazide under Click reaction condition gave clicked dibromo precursor **23** in 92% yield, which was subsequently converted into the TMS-protected diethynyl compound **24** (92%) followed by deprotection to afford **25** in 95% yield. Controlled reduction of the ester group of **25** with sodium borohydride in ethanol gave mono (**26**) and dialcohol (**27**) derivatives in 85% and 70%, yields, respectively. Oxidation of **26** and **27** with pyridinium chlorochromate (PCC) in DCM solvent converted them into mono **28** and dialdehyde **29** derivatives in 65% and 63% yields, respectively. The macrocyclic ring (SPMs) formation reactions of **28** and **29** were successfully carried out under one-pot intermolecular coupling with 3,5-diazido-1-tert-butylbenzene in highly diluted conditions to generate shape persistent macrocycles **30** and **31** with 56% and 41% yields, respectively. The <sup>1</sup>H-NMR and electron spray ionization mass spectrometry (ESI-MS) studies clearly confirmed (for **30**: *m/z* 796.27 [ $M^+ + Na$ ]; for **31**: *m/z* 766.19 [ $M^+ + Na$ ]) the formation of Clicked macrocyclic rings (For <sup>1</sup>H-NMR spectra of **30** and **31** see Fig. 4.1 and 4.2, respectively).

To attach heptylated oxo-verdazyl radicals to macrocyclic aldehydes, a novel 2,4-diheptylcarbo-hydrazide bis-hydrochloride salt **37** was also prepared (in 74% yield) from tert-butoxy carbazate in four steps by following a reported methodology<sup>13c</sup> (Scheme 4.3). At first, the reaction of tert-butoxy carbazate with dry heptaldehyde gave a white precipitate of **40** with 92% yield. The sodium borohydride reduction reaction converted compound **40** into **39** with 80% yield. To a solution of compound **39** in dry toluene, 1 equivalent of dry triethylamine and a solution of 20% phosgene in toluene was reacted to give a crude product of **38**. This crude product was purified by recrystallization from heptane to isolate **38** in 44% yield.



**Scheme 4.2.** Reagents and conditions: (a) Trimethyl silylacetylene /  $[\text{PdCl}_2(\text{PPh}_3)_2]$  / CuI. (b) KF, MeOH / THF, 8 h. (c) 1,3-diazido-5-tert-butylbenzene /  $\text{CuSO}_4$  / Sodium ascorbate / EtOH /  $\text{H}_2\text{O}$  / toluene (7:3:1), Ar. (d)  $\text{NaBH}_4$  / EtOH / 8 h / 80 °C. (e) PCC / DCM / RT / 4 h. (f) 1,3-diazido-5-tert-butylbenzene / CuI / DBU / dry toluene / Ar / 6 h. (g) 2,4-diheptylcarbohydrazide-bishydrochloride (**37**) / sodium acetate / EtOH / 15 h / RT. (h) benzoquinone / toluene / 60 °C.

Compound **38** was mixed with ethanol and conc. hydrochloric acid to get the 2,4-diheptylcarbohydrazone bis-hydrochloride (**37**) as off-white crystals. Further it was recrystallized from n-butanol to give white needles of compound **37** in 74% yield. Reaction of **37** with appropriate macrocyclic aldehyde derivatives (**30** and **31**) in reflux ethanol gave radical precursors mono (**32**) and bistetrazanes (**33**), respectively. The formation of six membered tetrazane moiety is evident from the ESI-MS  $m/z$  peaks which appeared at 1065.66  $[M^+ + Na]$  for **32** and 1303.85  $[M^+ + Na]$  for **33**. The  $^1H$ -NMR spectra further supported the formation of six-member tetrazane ring by displaying characteristic chemical shifts at 5.22 ppm for **32** and **33** (Fig. 4.1 and 4.2). Finally, oxidation of the tetrazane products with benzoquinone under reflux condition, followed by column chromatography on silica gave brown red color mono (**R8**) and dioxo-verdazyl (**R7**) radicals attached to the macrocycles with 27% and 22% yields, respectively. The  $R_f$  value of **R7** and **R8** are 0.21 and 0.17, respectively with 2% MeOH/DCM solvent. ESI-MS analyses of radicals **R7** and **R8** showed  $m/z$  values at 1296.64  $[M^+ + Na]$  and 1061.65  $[M^+ + Na]$ , respectively, supporting the OVZ radical formation.



**Scheme 4.3** Reagents and conditions: (a) Heptaldehyde/toluene / 80 °C / 6h. (b)  $NaBH_4$  / EtOH / 80 °C / 6 h. (c) Triphosgene /  $Et_3N$  / toluene / RT / 2h. (d) HCl / EtOH / 50 °C / 0.5h.

#### 4.3.2 $^1H$ -NMR Spectroscopy Studies:

The formation of tetrazane six-membered rings is evident from the  $^1H$ -NMR chemical shifts of the proton attached to tertiary carbon (N-CH-N), which is typically in the range of 5.23-5.3 ppm. The  $^1H$ -NMR spectra confirmed the formation of tetrazane six-member rings in **32** and **33** by displaying characteristic chemical shifts in the range of 5.24 (Fig. 4.2 for **32**) and 5.22 ppm (Fig. 4.1 for **33**) and the disappearance of aldehyde peaks (10.07 and 10.10 ppm) of **30** and **31**. The formation of heptyl chains in both tertazanes were confirmed by the range of chemical shift from

4.5-4.2 ppm and 1.6-0.91 ppm. The methy-protons in ester group in **31** and **32**, displayed peaks at 4.06 and 4.02 ppm, respectively (Fig. 4.2).

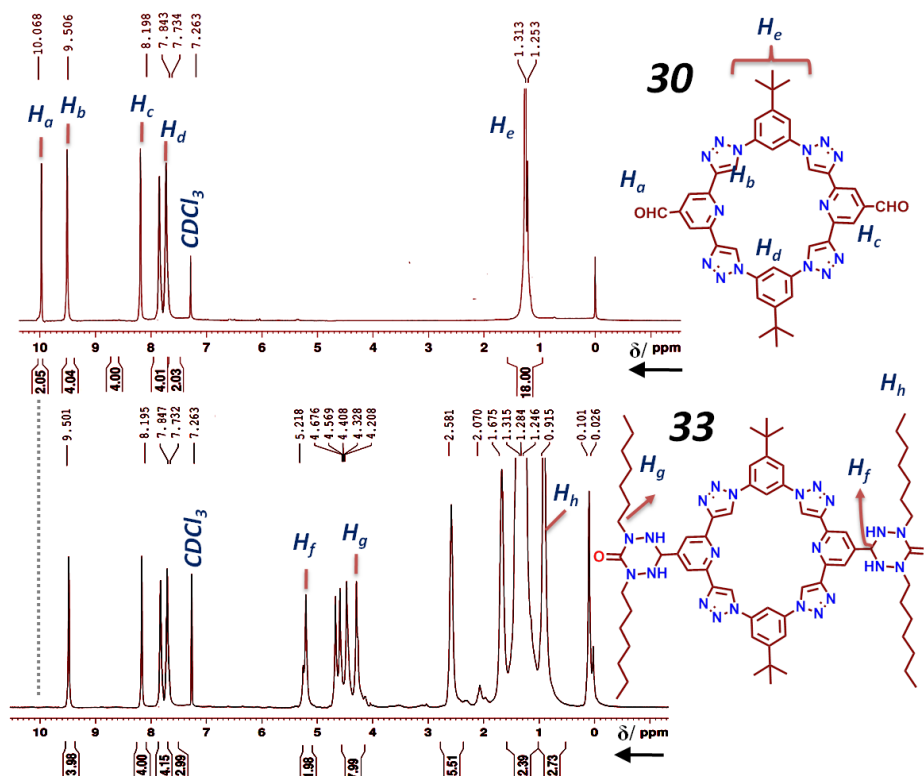


Figure 4.1 Comparative  $^1\text{H}$ -NMR spectra of macrocyclic radical precursor **33** and macrocyclic dialdehyde **30**.

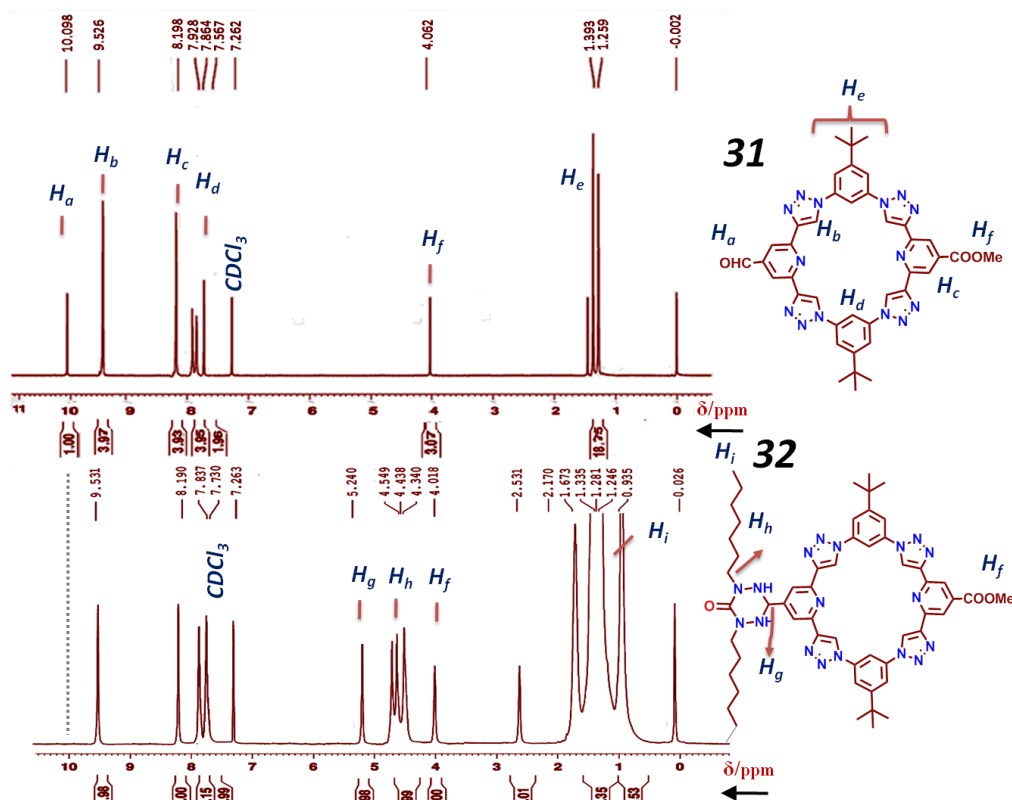


Figure 4.2 Comparative  $^1\text{H}$ -NMR spectra of macrocyclic radical precursor **32** and macrocyclic monoaldehyde **31**.

### 4.3.3 Optical Properties of Paramagnetic SPMs:

The electronic spectra of both diradical-SPM **R7** and monoradical-SPM **R8** showed absorption maxima in the range of 380 nm, and broader weaker visible absorptions at 500-700 nm, which is typical of oxo-verdazyl radicals  $n\text{-}\pi^*$  transition (Fig. 4.3). The effect of concentration on the aggregation behaviour was also studied by UV-vis

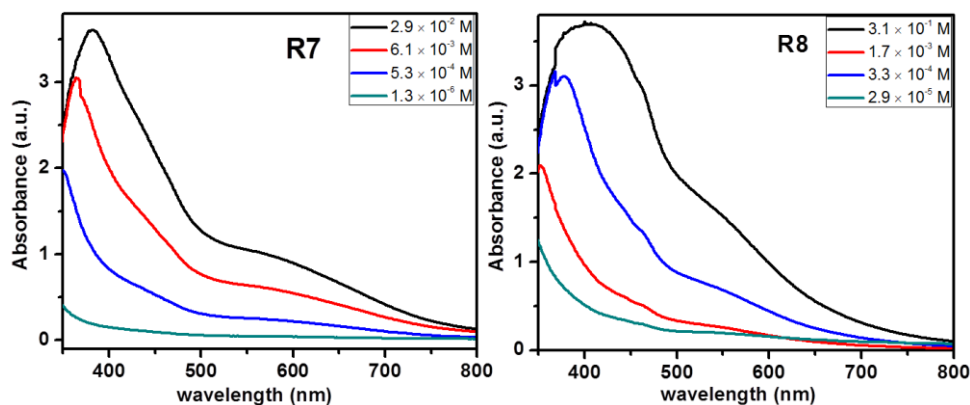


Figure 4.3 UV-Vis spectra of **R7** and **R8** in toluene recorded at RT at variable concentration.

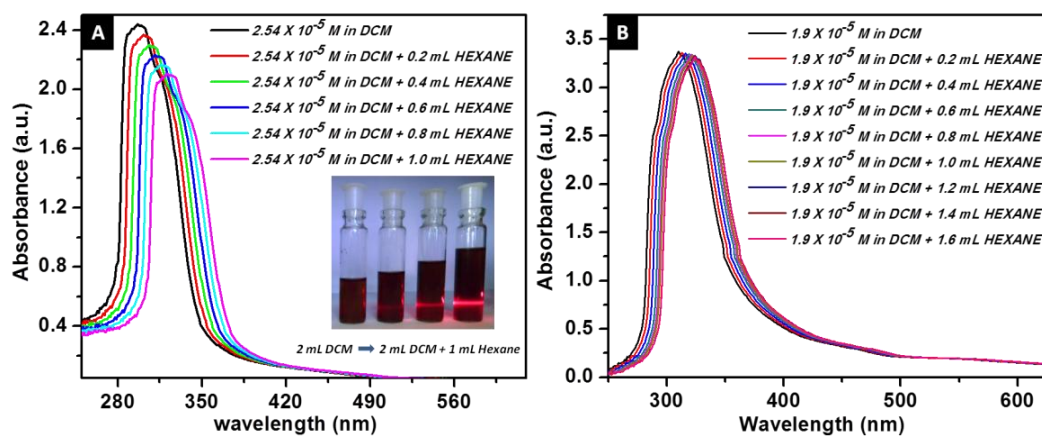


Figure 4.4 UV-Vis spectra of micro structures in DCM/HEX of A) **R7** and B) **R8** recorded at RT in gradual addition of Hexane. Tyndall effect for **R7** is shown in inset of A.

spectroscopy. For example, gradual addition of hexane (in 0.2 ml portion) to a  $2.54 \times 10^{-5}$  M solution of **R7** and  $1.9 \times 10^{-5}$  M solution of **R8** in DCM (2 ml) showed a clear red shifts corresponding to the spectral mark of *J*-aggregation (Fig. 4.4). The absorbance intensity slightly decreased due to aggregation or particle formation. This observation is further supported by Tyndall effect upon signing a laser beam to the aggregated solution. Interestingly upon increasing the addition of hexane to the DCM solution of **R7** the Tyndall effect gradually increased due to increased light scattering from the particles (see

inset of Fig. 4.4A). This result pointed out the formation of nano/micro *J*-aggregates in the solution.

#### 4.3.4 X-Band ESR Spectroscopy Studies of SPM Radicals:

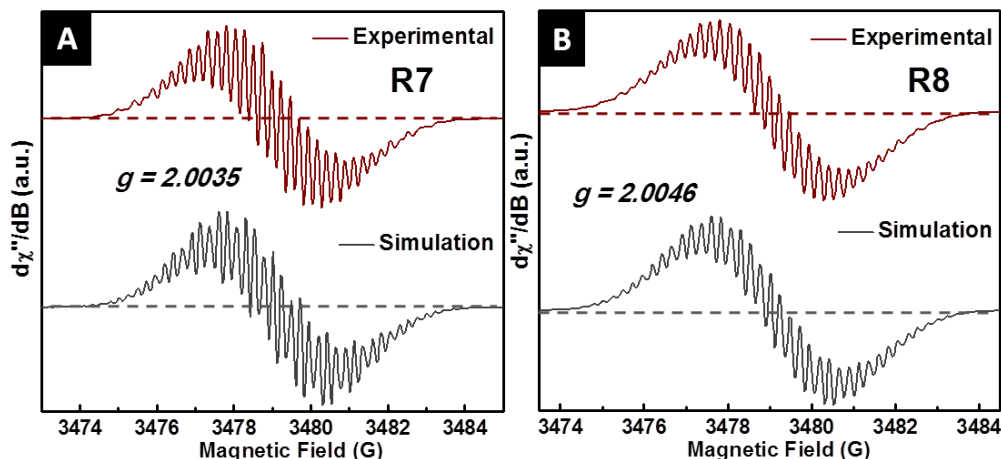


**Figure 4.5** X-band ESR spectra in isotropic liquid state: A) **R7** B) **R8**. The experimental spectra and the corresponding simulations are shown in brown and gray lines, respectively.

X-band ESR spectroscopy studies of SPMs radicals (**R7** and **R8**) were carried out in degassed toluene solutions ( $c \sim 10^{-4}$  M) to probe the intra-molecular magnetic properties. Interestingly, the room temperature spectra of both **R7** and **R8** exhibited a well-resolved  $\Delta M_s = \pm 1$  transition lines (ca. 36-lines) due to the hyperfine coupling (*hfc*) of the OVZ electron spin with two sets of equivalent nitrogen ( $^{14}\text{N}$ ) nuclei and heptyl chain protons ( $^1\text{H}$ ) (Fig. 4.5). Simulations of the experimental spectra of **R7** and **R8** showed the following

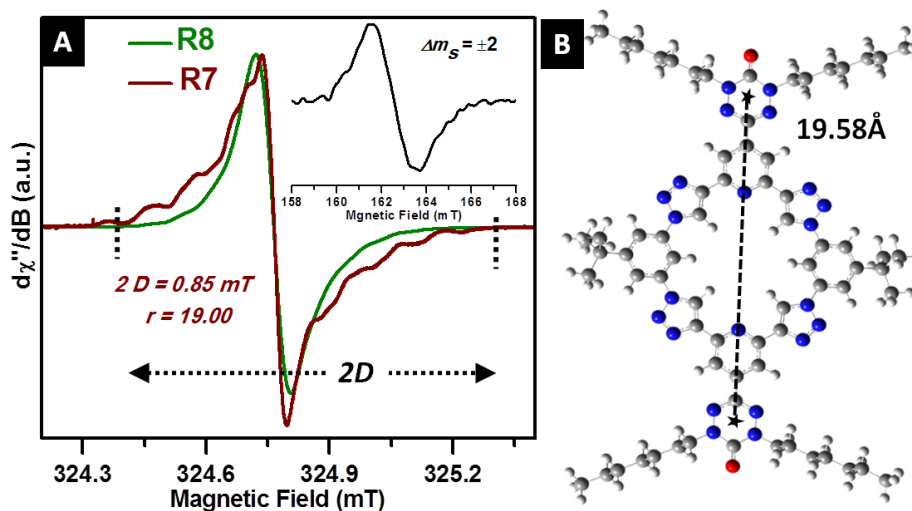


**Figure 4.6** A) Frozen state X-band EPR spectra of **R7** and **R8** at 120 K. The inset shows the forbidden  $\Delta M_s = \pm 2$  transition of **R7**. B) Energy minimized structure (DFT/6-31G) of **R7** and the measured intra-radical distance,  $r = 19.58$  Å.

*hfc* values:  $aN_1 = 0.7$  G,  $aN_2 = 0.5$  G,  $aH_1 = 0.21$  G and  $aH_2 = 0.19$  G for **R7**; and  $aN_1 = 0.7$  G,  $aN_2 = 0.5$  G,  $aH_1 = 0.20$  G and  $aH_2 = 0.21$  G for **R8**. The triplet nature of biradical **R7** was clearly apparent from its frozen state axial zero-field splitting (*zfs*) pattern and the forbidden half-field transition ( $\Delta M_s = \pm 2$ ;  $g = 4.05$ ) signal recorded in toluene ( $c \sim 10^{-4}$  M) at 120 K. The *zfs* spectrum of **R7** exhibited an unusual resolution of nitrogen *hfc* with a  $2D$  value of 0.85 mT ( $|D/hc| = 7.94 \times 10^{-4} \text{ cm}^{-1}$ ) (Fig. 4.6A). For comparison the frozen state spectrum of **R8** ( $S = 1/2$ ) was plotted together with the *zfs* spectrum of **R7** ( $S = 1$ ) (see brown lines in Fig. 4.6A). By applying a point-dipole approximation, from the experimental  $D$  value, the estimated distance ( $r$ ) between the two OVZ centers in **R7** is ca. 19 Å, which is in line ( $r = 19.58$  Å) with the computational (DFT/UB3LYP/6-31G(d)) result (Fig. 4.6B). The slight deviation of the  $r$  value from the theoretical value arise due to the effective delocalization of unpaired spin density within the molecular  $\pi$ -conjugated backbone thus weakening the dipolar interaction.<sup>13c,15</sup>

#### 4.3.5 Self-Assembly Studies:

At room temperature addition of hexane (1 mL) to a DCM (2 mL) solution of **R7** ( $2.16 \times 10^{-3}$  M) formed self-assembled aggregates. The solution containing aggregates was drop-casted on a silica substrate and dried at RT for confocal microscopy, SEM, AFM and optical wave guiding studies. The confocal micrographs indicated the formation of

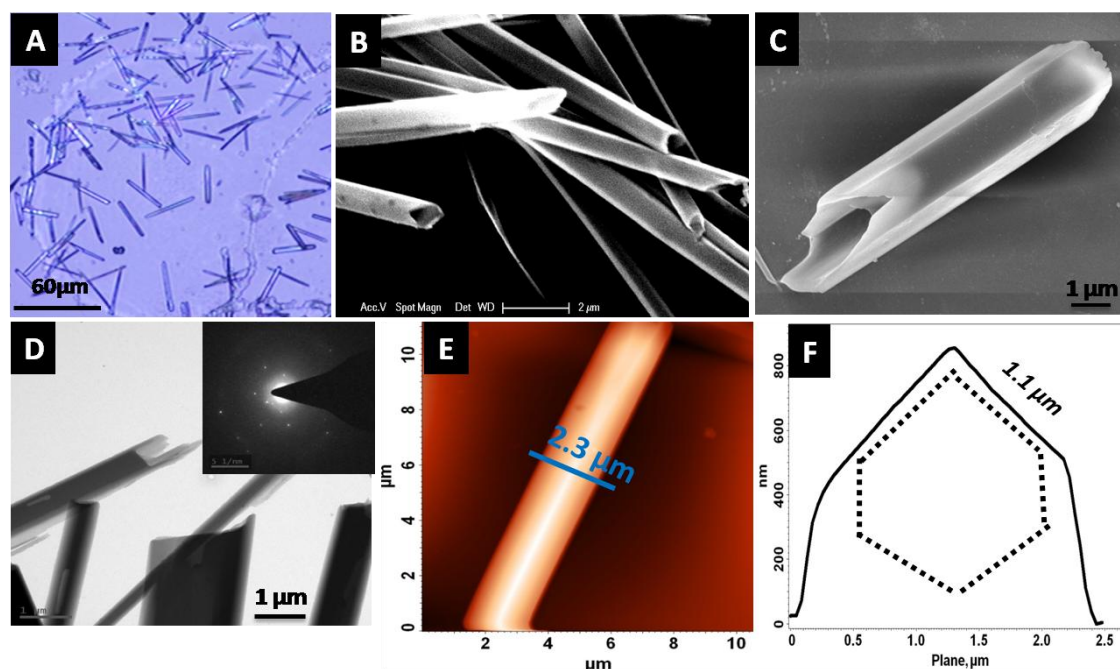


**Figure 4.7** A) Confocal microscopy image of microtubes self-assembled from **R7**. B) SEM micrograph of tubes. C) FESEM image of a hexagonal hollow tube. D) Bright-field TEM micrograph of tubes. The inset shows the SAED pattern. E) AFM image of a tube. F) The corresponding AFM height and width profiles of a tube shown in E.

1D elongated solid state micro aggregates of **R7** (Fig. 4.7A). Electron microscopy studies revealed the tubular nature of the elongated aggregates (Fig. 4.7B-D). The 1D tubes were hexagonal in shape with a circular hollow cross-section extending along their tube axes. The tube lengths were in the range of ca. 10-70  $\mu\text{m}$  with varying diameter of a. 100 nm–2.5  $\mu\text{m}$ . Selected area electron diffraction showed bright diffraction spots indicating the crystalline nature of the tube walls (Fig. 4.7D, inset). AFM studies of a selected tube showed the tube diameter of 2.3  $\mu\text{m}$  (Fig. 4.7E and F). The width of each facet in the hexagonal tube was ca. 1.2  $\mu\text{m}$ , and the thickness of the tube walls was ca. 700 nm.

#### 4.3.6 Formation Mechanism of a Micro Tube:

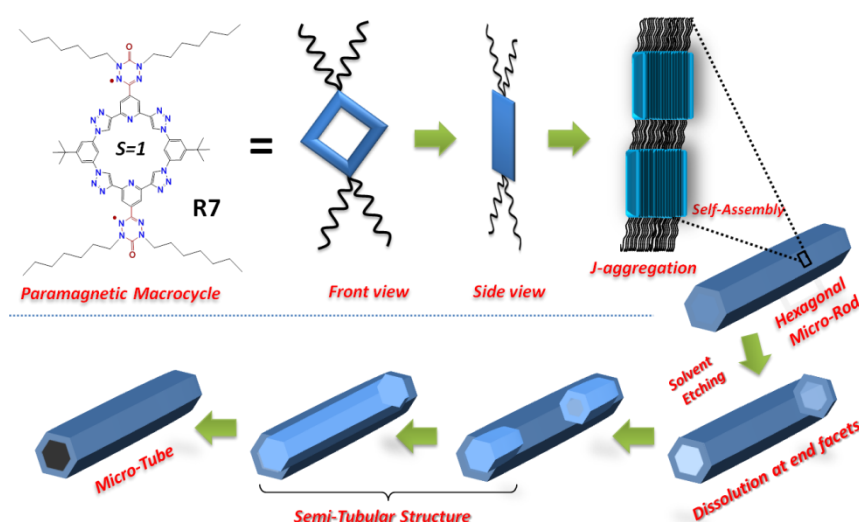


**Figure 4.8** Schematic representation of possible etching mechanism involved in the growth of hexagonal microtubular structure of **R7** in DCM/Hexane.

Aggregation studies pointed out that the tube formation is probably initiated by the stacking (*J*-type) of molecules of **R7** forming crystalline hexagonal rods followed by solvent etching at the high energy facets (growth axis) and subsequent caving in along the axis of the tube forming a hollow tubular structure. The wall thickness depends upon the degree of etching. More etching opened the tubes and formed sheets (Fig. 4.8 and 4.9).<sup>16</sup>

On the basis of SEM analyses, the formation mechanism of microtubes can be explained as follows: First formation of hexagonal microrod of **R7** in DCM/Hexane solution (Fig. 4.8, 4.9A). Then the etching or dissolution of microrod (Fig. 4.9B) by DCM starts at the defective high energy facets (growth axis) of a solid hexagonal rod, which

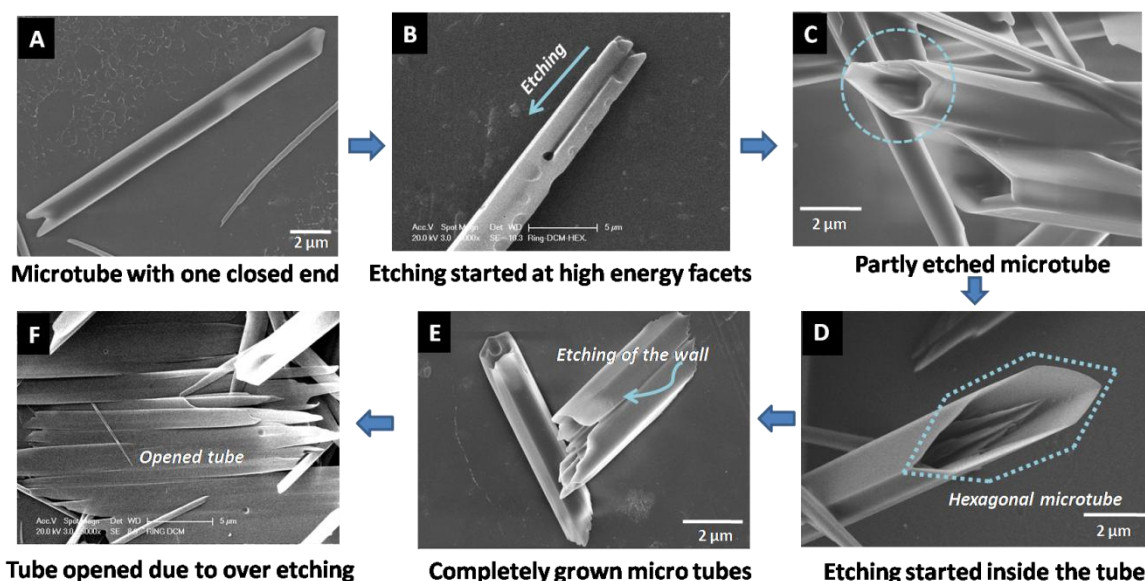


**Figure 4.9** SEM images displaying the etching mechanism involved in the microtube formation.

then continues towards the interior along the length axis (Fig. 4.9C) and thus gradually converts the solid nanorods to microtubes (Fig. 4.9D) and finally into hollow tubular structures (Fig. 4.9E). A high density of defects probably existed at the facets of the rectangular microrods and induced a high etching rate at the edge and resulted in the formation of tubular structures. More etching opened the tubes and formed sheets (Fig. 4.9F).

#### 4.3.7 Optical Wave Guiding Studies:

Furthermore, the tendency of the tubes to propagate optical wave was studied under transmission mode confocal microscope set-up connected to a charge coupled device (CCD) spectrometer (Fig. 4.10). It was expected that the difference in the refractive indices of organic tube ( $n \sim 1.6$ ) and air ( $n = 1$ ) would facilitate effective coupling of the laser light to the tube there by providing good 2D optical

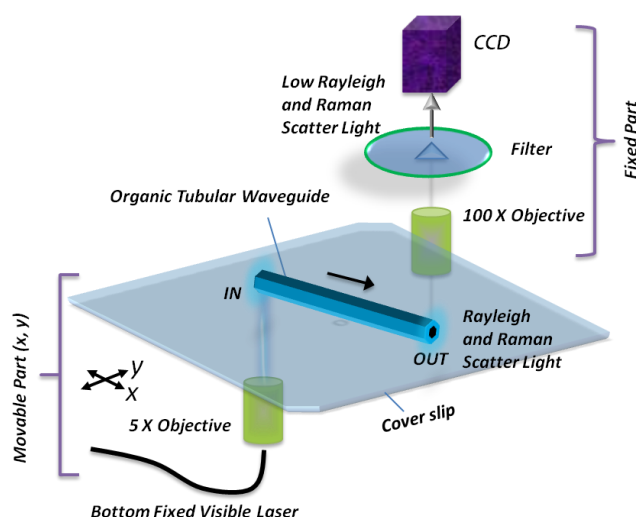


**Figure 4.10** Illustration of the transmission mode confocal microscope set-up connected to a charge coupled device (CCD) spectrophotometer.

confinement by guiding the laser light in 1D. For this *light-organic tube interaction* studies, a visible light laser (532 nm) was employed to circumvent the absorption of a laser light by the molecular building blocks of the tube (Fig. 4.11A). A 532 nm (Nd:YAG) laser beam was bottom fix illuminated through a 5 $\times$  objective at one of the ends of tube kept on a thin glass substrate. From the top, a 100 $\times$  (NA = 0.95) objective was used to collect the scattered

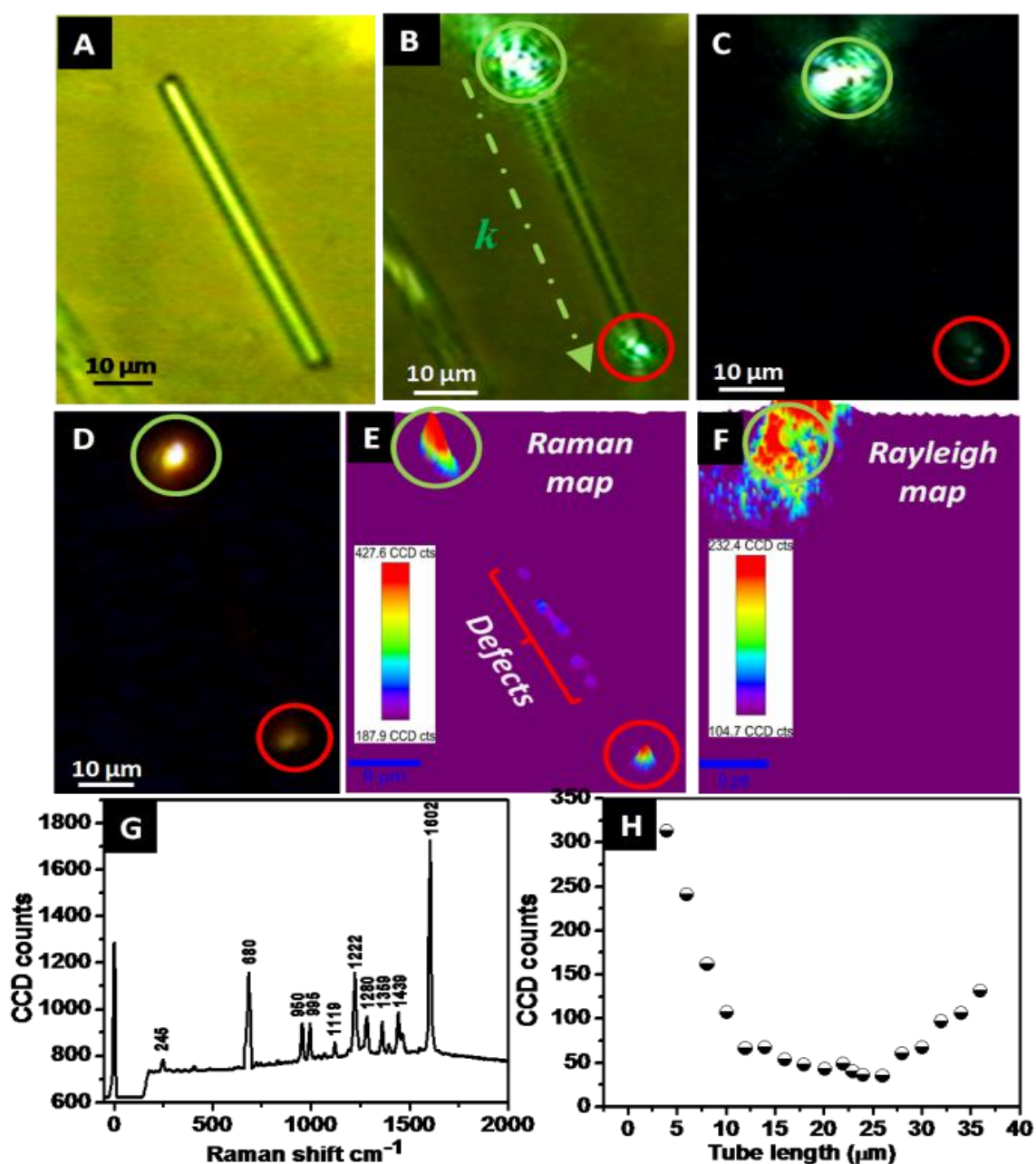


**Figure 4.11** A) Bright-field image of a paramagnetic microtube obtained from R7. B and C) Bright and dark-field images of a tube irradiated at one of the open ends with 532 nm laser, respectively. D) Dark field image of a tube acquired with 570 nm LPEF. E and F) 3D map of Raman and Rayleigh scattered photons along the tube, respectively. G) Raman spectrum of a tube. H) Plot of CCD Raman counts versus tube length. The green dotted arrow in B indicates the light propagation direction ( $k$ ). The green and red circles show the laser input and output points, respectively.

photons by scanning the entire area of the tube. Orthogonal illumination of a green laser beam at one of the open-ends of a tube (*optical coupling point*) showed propagation of guided scattered photons at the opposite end of the tube (Fig. 4.11B and C). While irradiation of laser at the center of the tube showed light propagation to both open-ends features of the tube. Analogous experiments performed on tubes having different length from 10  $\mu\text{m}$  to 60  $\mu\text{m}$  showed similar results. Here, after initial coupling of the laser light to the one of the ends of the tube, due to the interaction of the propagating light with the tube, both elastically (Rayleigh) and inelastically (Raman) scattered photons were generated. Raman spectroscopy is one of the powerful techniques to study the interaction of light with organic solid. Since Raman scattering is a weak process, to record and quantify the feeble Raman signals along the tube, the scattered photons were collected and sent to a CCD spectrophotometer through a 570 nm long pass edge filter (LPEF) to reject *most* of the Rayleigh scattered photons (Fig. 4.11D). Distribution of Rayleigh and Raman signals along the tube was three dimensionally mapped from the scattering spectrum (Fig. 4.11E and G) acquired through a 570 nm LPEF. For Raman mapping, an intense peak at  $1602\text{ cm}^{-1}$  (C=C stretch) was used. Analysis of the Rayleigh map showed its signal *only* at the laser–tube coupling area with no output signal at the opposite tube end (Fig. 4.11F). Whereas the Raman map clearly displayed inelastic signals from the input and output tube exits (Fig. 4.11E). A plot of tube length versus CCD Raman counts showed high Raman intensity at the light input point and moderate intensity at the output.

Importantly, pockets of relatively low intense Raman signals were observed from the body of tube indicated the scattering from the defect sites during the light propagation. The generated intense Raman signal from tube ends and the defective areas clearly pointed out a near parallel orientation of Raman active molecular C=C vibration with the electric field ( $E$ ) of propagating light. This experiment confirmed an efficient propagation of the light along the paramagnetic microtube. Moreover in this *light confinement technique*, direct “source laser” illumination of the entire area of the tube has been avoided (except the input point), hence one can unambiguously trace the *nanoscale defect spin sites* created during the self-assembly process (avoiding source laser induced defects), which is otherwise very difficult to detect and pin-point.

#### 4.3.8 Micro Raman Spectra:

The confocal Raman micro spectroscopy investigations of self-assembled tubular structures showed clear evidence of their formation from compound **R7** by exhibiting

characteristics Raman shifts very similar to the bulk compound (Fig. 4.12). A slight variation in the peak intensity and shifts were observed. For example the  $680\text{ cm}^{-1}$  peak intensity increased in the tube compared to its powder spectrum indicating the increase in the bond polarizability. The peaks appeared at  $930$  and  $1202\text{ cm}^{-1}$  corresponding to the powder state were shifted to high frequency  $950$  and  $1222\text{ cm}^{-1}$  in the tube, probably due to the participation of the particular vibrations in the solid state supramolecular interactions. This result indicated that during the self assembly, molecule **R7** adopted slightly different molecular packing to form tube.

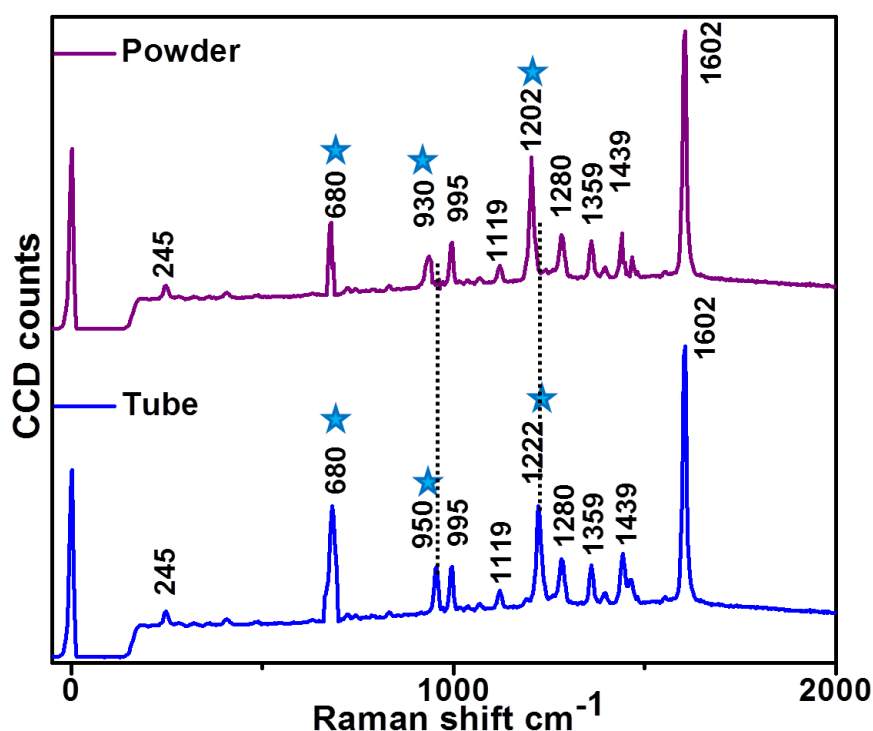


**Figure 4.12** Confocal Raman micro spectroscopic data of powder sample and microtube of biradical **R7**. Excitation wavelength  $\lambda_{\text{ex}} = 633\text{ nm}$  (HeNe Laser).

#### 4.4 Conclusions:

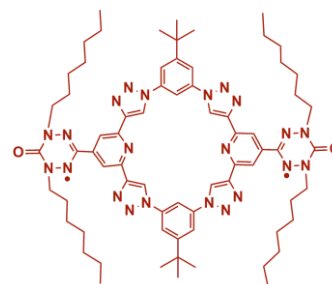
In summary, this chapter demonstrated for the first time, syntheses of shape persistent macrocyclic paramagnetic molecules decorated with stable high-spin state mono and dioxo-verdazyl biradicals. The biradical macrocycle self assembled forming submicro scale paramagnetic organic tubular solids. Laser illumination at one of the open-ends of the tube showed propagation of light to the opposite exit direction. One of the important additional finding in this work is the determination of nano/micro scale spin defect sites in the tube using wave guiding mode Raman spectroscopy. Till now spin-

photon interaction is well-known for ferromagnetic metals but paramagnetic organic materials are not yet recognized.<sup>17</sup> In the same line, these paramagnetic organic tubular solids can also be exploited to understand/establish the spin-photon interactions such as magneto-optical and related effects at cryogenic temperature.

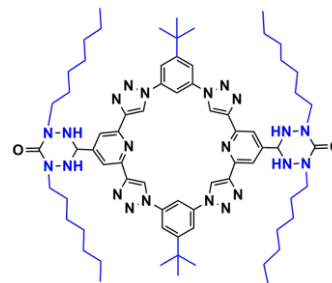
## 4.5 General Experimental Procedures:

### 4.5.1 Experimental Section:

**Biradical-Macrocycle (R7):** In a 100 mL flask tetrazane derivative **33** (300 mg, 0.23 mmol) was heated with 1.5 mol eq. benzoquinone (38 mg, 0.35 mmol) in 5 mL toluene for 30 min at 40 °C. The resulting reaction mixture was cooled and filtered to remove the excess benzoquinone solid residue. The filtrate was evaporated in vacuo to get brown solid residue. During the column chromatography, the residue was purified using silica gel (9:1 CH<sub>2</sub>Cl<sub>2</sub>:MeOH), and the different fractions (25-30 fractions) of column solution was collected. The desired compound was checked by TLC and the isolated fraction ( $R_f = 0.17$ ) was evaporated in vacuo to get brown crystalline solid of **R7** (Yield: 12 mg, 22%). FTIR (KBr disc;  $\nu$  in cm<sup>-1</sup>): 2926, 2854, 1732, 1606, 1556, 1464, 1394, 1261, 1221, 1097, 1016, 970, 949, 862, 802, 725, 659, 611, 524. ESI-MS:  $m/z$  calcd 1273.63, found 1296.64 [ $M^+ + Na$ ]. Anal. Calcd for C<sub>70</sub>H<sub>92</sub>N<sub>22</sub>O<sub>2</sub><sup>••</sup>: C, 66.01; H, 7.28; N, 24.19%. Found: C, 66.06; H, 7.28; N, 24.13%. EPR (in toluene  $c \sim 10^{-4}$  M, RT,  $\nu = 9.14587$  GHz, 0.998 mW power, 1 scan): > 36 lines,  $g_{iso} = 2.0035$ ,  $a_{N1} = 0.7$  G,  $a_{N2} = 0.5$  G,  $a_{H1} = 0.21$  G and  $a_{H2} = 0.19$  G.  $|D/hc| = 0.000794$  cm<sup>-1</sup>,  $\Delta M_s = \pm 2$  transition with  $g_{av} \sim 4.05$ .

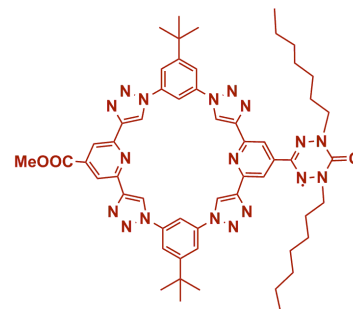


**Bitetrazane-Macrocycle (33):** In a 100 mL flask, 1 mmol of 2,4-diheptylcarbohydrazide bis-hydrochloride (26 mg, 1.63 mmol) and **30** (400 mg, 5.31 mmol) were dissolved in a minimum amount of ethanol. To this solution, 2 mmol of sodium acetate (50 mg) in ethanol was added and the solution was allowed to stir at RT for 15 h. After this period the mixture was filtered, and from the resultant filtrate the solvent was evaporated in vacuo. The obtained residue was recrystallized from heptane to give off-white color tetrazane derivative **33**. (Yield: 32 mg, 38%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>-d<sub>1</sub>, 298 K)  $\delta$ : 9.50 (s, 4H), 8.19 (s, 4H), 7.85 (s, 4H), 7.73 (s, 2H), 5.22 (s, 2H),

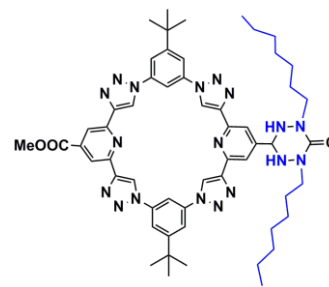


4.67-4.21 (m, 8H), 1.67-1.24 (m, 52H), 0.92 (m, 12H). FTIR (KBr disc;  $\nu$  in  $\text{cm}^{-1}$ ): 2926, 2854, 1732, 1606, 1556, 1464, 1394, 1261, 1221, 1097, 1016, 970, 949, 862, 802, 725, 659, 611, 524. ESI MS:  $m/z$  calcd 1279.83, found 1303.85 [ $\text{M}^+ + \text{Na}$ ]. Anal. Calcd for  $\text{C}_{70}\text{H}_{98}\text{N}_{22}\text{O}_2$ : C, 65.70; H, 7.72; N, 24.08%. Found: 65.72; H, 7.71; N, 24.11%.

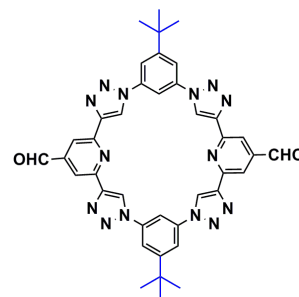
**Monoradical-Macrocyclic (R8):** In a 100 mL flask a tetrazane derivative **32** (500 mg, 0.21 mmol) was heated with 1.5 mol eq. benzoquinone (43 mg) in 5 mL toluene for 30 min at 40 °C. The resulting reaction mixture was cooled and the excess benzoquinone was filtered. The filtrate was evaporated in vacuo to get brown solid residue. Chromatography purification of the residue on silica gel (9:1  $\text{CH}_2\text{Cl}_2$ :MeOH) gave brown crystalline solid of **R8** ( $R_f = 0.21$ ). (Yield: 15 mg, 27%). FTIR (KBr disc;  $\nu$  in  $\text{cm}^{-1}$ ): 3215, 2926, 2752, 1701, 1638, 1558, 1547, 1456, 1394, 1261, 1198, 1016, 956, 792. ESI-MS:  $m/z$  calcd 1038.23, found 1061.65 [ $\text{M}^+ + \text{Na}$ ]. Anal. Calcd for  $\text{C}_{56}\text{H}_{65}\text{N}_{18}\text{O}_3$ : C, 64.78; H, 6.31; N, 24.28%. Found: C, 64.82; H, 6.41; N, 24.31%. EPR (in toluene  $c \sim 10^{-4}$  M, RT,  $\nu = 9.14577$  GHz, 0.998 mW power, 1 scan): 36 lines,  $g_{\text{iso}} = 2.0046$ ,  $a_{\text{N1}} = 0.7$  G,  $a_{\text{N2}} = 0.5$  G,  $a_{\text{H1}} = 0.20$  G and  $a_{\text{H2}} = 0.21$  G.



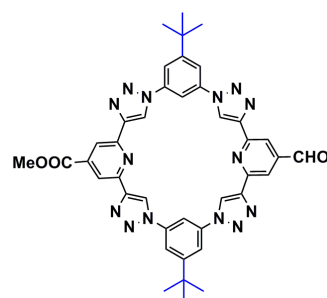
**Monotetrazane-Macrocyclic (32):** In a 100 mL flask, 2,4-diheptylcarbo-hydrazide bis-hydrochloride (300 mg, 0.66 mmol) and **31** (400 mg, 5.62 mmol) were dissolved in the minimum amount of ethanol. To this solution, 2 mmol of sodium acetate (50 mg) in ethanol was added and the solution was allowed to stir at RT for 15 h. After this period the mixture was filtered to remove insoluble impurities, and the solvent from the filtrate was evaporated in vacuo. The obtained off-white solid residue was recrystallized from heptane to give a tetrazane derivative **32**. (Yield: 500 mg, 42%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ - $d_1$ , 298 K)  $\delta$ : 9.53 (s, 4H), 8.19 (s, 4H), 7.84 (s, 4H), 7.73 (s, 2H), 5.24 (s, 1H), 4.55-4.34 (m, 4H), 4.02 (s, 3H), 1.67-1.24 (m, 37H), 0.94 (m, 6H). FTIR (KBr disc;  $\nu$  in  $\text{cm}^{-1}$ ): 2926, 2854, 1732, 1690, 1556, 1464, 1384, 1261, 1221, 1097, 1016, 970, 959, 862, 802, 725, 659, 611, 424. ESI MS:  $m/z$  calcd 1041.26, found 1065.66 [ $\text{M}^+ + \text{Na}$ ]. Anal. Calcd for  $\text{C}_{56}\text{H}_{68}\text{N}_{18}\text{O}_3$ : C, 64.59; H, 6.58; N, 24.21%. Found: 64.62; H, 6.61; N, 24.31%.



**Macrocycle (30):** 1,8-Diaza[5.4.0]bicycloundec-7-ene (DBU) (2.0 mmol, 0.35 mL, 20 equiv) was added to toluene (200 mL), degassed (argon) for 30 minutes and heated to 70 °C while flushing with argon. At 70 °C, CuI (0.03 mmol, 5.7 mg, 0.3 equiv) was added to the mixture. A solution of the diacetylene-3/4- premacrocycle **29** (51 mg, 0.1 mmol, 1.0 equiv) and 3,5-diazido-1-tert-butylbenzene (21.6 mg, 0.1 mmol, 1.0 equiv) in dry toluene:THF (1:1) (50 mL) was added to the solution slowly over 10 h and stirred for additional 4 h under argon. The mixture was then cooled to RT and filtered through a short column of basic Al<sub>2</sub>O<sub>3</sub> to remove the insoluble material, and the filtrate was concentrated in vacuo. The product was purified via flash chromatography on silica gel (50:2:0.3 CH<sub>2</sub>Cl<sub>2</sub>:MeOH:(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N) to afford white solid of **30** (*R<sub>f</sub>* = 0.11 in 5% MeOH/DCM) (Yield: 56 mg, 41%) as a off-white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>-*d*<sub>1</sub>:CD<sub>3</sub>OD-*d*<sub>4</sub> (3:2), 298 K) δ: 10.07 (s, 2H), 9.51 (s, 4H), 8.20 (s, 4H), 7.84 (s, 4H), 7.73 (s, 2H), 1.13-1.25 (s, 18H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>-*d*<sub>1</sub>, 298 K) δ: 191.6, 152.7, 150.8, 143.2, 142.6, 136.9, 130.4, 128.0, 127.3, 108.2, 107.5, 31.1, 30.3 ppm. FTIR (KBr disc; ν in cm<sup>-1</sup>): 3111, 2923, 2853, 1658, 1619, 1564, 1495, 1465, 1396, 1262, 1012, 990, 970, 955, 930, 864, 831, 813, 795, 722, 622, 602. ESI MS: *m/z* calcd 742.30, found 766.19 [M<sup>+</sup> + Na]. Anal. Calcd for C<sub>40</sub>H<sub>34</sub>N<sub>14</sub>O<sub>2</sub>: C, 64.68; H, 4.61; N, 26.40%. Found: 64.65; H, 4.68; N, 26.45%.

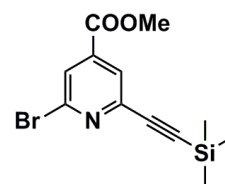


**Macrocycle (31):** Similar to above procedure. Yield: 85 mg 52%, *R<sub>f</sub>* = 0.21. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ: 10.10 (s, 1H), 9.53 (s, 4H), 8.2 (s, 4H), 7.93-7.86 (m, 4H), 7.57 (s, 2H), 4.06 (s, 3H), 1.39-1.26 (m, 18H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>-*d*<sub>1</sub>, 298 K) δ: 191.5, 152.7, 150.8, 143.2, 142.6, 136.9, 130.3, 128.0, 127.3, 108.2, 107.5, 51.4, 31.1, 30.3 ppm. FTIR (KBr disc; ν in cm<sup>-1</sup>): 3113, 2928, 2856, 1730, 1660, 1574, 1469, 1390, 1348, 1305, 1234, 11890, 1099, 1030, 964, 895, 864, 819, 790, 769, 733, 655, 617, 507. ESI MS: *m/z* calcd 772.82, found 796.27 [M<sup>+</sup> + Na]. Anal. Calcd for C<sub>41</sub>H<sub>36</sub>N<sub>14</sub>O<sub>3</sub>: C, 63.72; H, 4.70; N, 25.37%. Found: C, 63.75; H, 4.69; N, 25.40%.

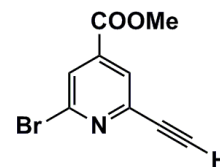


**Methyl 2-bromo-6-((trimethylsilyl)ethynyl)isonicotinate (21):**

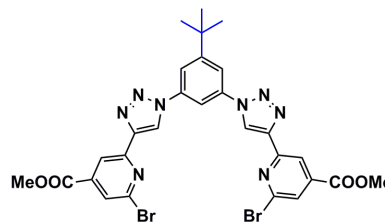
Methyl 2,6-dibromoisonicotinate (2 g, 6.781 mmol) in a round-bottomed flask was charged with freshly distilled, anhydrous diisopropylamine (DIA, 20 mL) and THF (10 mL). To this  $\text{Pd(PPh}_3)_4$  (130 mg, 0.11 mmol), triphenylphosphine (50 mg, 0.19 mmol) and CuI (50 mg, 0.26 mmol) were added. The flask was evacuated and filled with argon for several times. Trimethylsilylacetylene ( $0.69 \text{ g} \cdot \text{mL}^{-1}$ , 0.96 mL, 6.78 mmol) was added under argon by syringe, and the resulting mixture was kept in room temperature for 6 h. The mixture was filtered through a filter paper and the filter paper was washed with THF. The filtrate was concentrated in vacuo and column chromatographed ( $\text{SiO}_2$ , 2:25 EtOAc:Hexane) to get a white solid of **21** (Yield: 1.6 g, 81%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ - $d_1$ , 298 K)  $\delta$ : 7.99 (s, 2H), 3.98-3.97 (m, 3H), 0.29 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ - $d_1$ , 298 K)  $\delta$ : 164.1, 150.1, 142.5, 141.1, 124.8, 124.4, 108.5, 53.1 ppm. FTIR (KBr disc;  $\nu$  in  $\text{cm}^{-1}$ ): 2924, 2853, 1612, 1576, 1547, 1464, 1392, 1261, 1099, 1016, 804. ESI MS:  $m/z$  calcd 312.23, found 336.09 [ $\text{M}^+ + \text{Na}$ ]. Anal. Calcd for  $\text{C}_{12}\text{H}_{14}\text{BrNO}_2\text{Si}$ : C, 46.16; H, 4.52; N, 4.49%. Found: C, 46.15; H, 4.54; N, 4.49%.

**Methyl 2-bromo-6-ethynylisonicotinate (22):**

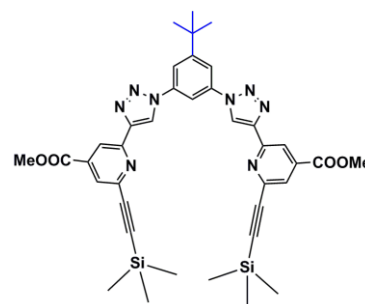
Methyl 2-bromo-6-((trimethylsilyl)ethynyl)isonicotinate (**21**) (1.6 g, 5.13 mmol) was loaded in a 100 mL two-neck round bottom flask containing degassed (1:1) THF:MeOH. To this solution, solid KF (2.1 g, 36.8 mmol) was added under  $\text{N}_2$  atmosphere. After 30 min, the completion of the reaction was confirmed by TLC (1:9 Ethyl acetate:Pet ether) and reaction mixture was concentrated on vacuo. The obtained solid compound was re-dissolved in chloroform and filtered to remove solid red impurities. The filtrate was evaporated to get desired compound as white powder of **22** (Yield: 1.2 g, > 99%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.98-7.81 (s, 2 H), 4.03-3.97 (s, 3H), 3.24 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ - $d_1$ , 298 K)  $\delta$ : 164.1, 150.1, 142.5, 141.1, 124.8, 124.4, 102.4, 51.3 ppm. FTIR (KBr disc;  $\nu$  in  $\text{cm}^{-1}$ ): 3113, 2926, 2854, 1707, 1618, 1574, 1460, 1392, 1261, 1192, 1060, 964, 802, 721, 673, 611, 408. ESI MS:  $m/z$  calcd 240.05, found 263.38 [ $\text{M}^+ + \text{Na}$ ]. Anal. Calcd for  $\text{C}_9\text{H}_6\text{BrNO}_2$ : C, 45.03; H, 2.52; N, 5.83%. Found: 45.05; H, 2.54; N, 5.89%.



**Dibromo-3/4-Oligome (23):** A solution of the 3,5-diazido-1-tert-butylbenzene (1 g, 4.2 mmol), monoacetylene **22** (1.9 g, 9.24 mmol), and sodium ascorbate (0.4 mmol, 88.3 mg), in a 7:3:1 mixture of EtOH:H<sub>2</sub>O:toluene (55 mL) was stirred at RT. To this freshly prepared aqueous solution of CuSO<sub>4</sub> (0.04 mmol, 11.2 mg) was added. Upon addition immediately a sharp color change from pale yellow to intense wine red color observed. During the reaction the intense of color become decreased to pale orange/pink. The course of reaction was monitored by TLC (10:1 CH<sub>2</sub>Cl<sub>2</sub>:MeOH). After disappearance of the starting material in almost 24 h, the solvents from the residue was evaporated in vacuo, and the yellow crude product was purified by column chromatography (SiO<sub>2</sub>; 10:1 CH<sub>2</sub>Cl<sub>2</sub>:MeOH) to isolate white solid of **23** (Yield: 2.61 g, 91%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.57 (s, 2 H), 8.22 (s, 2H), 7.82-7.65 (m, 4H), 7.51 (s, 1H), 4.06 (s, 6H), 1.76-0.96 (m, 9H). <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>-d<sub>1</sub>, 298K) δ: 164.2, 159.1, 154.1, 150.2, 145.5, 142.2, 141.4, 124.9, 124.4, 114.4, 107.8, 107.4, 102.4, 51.3, 33.4, 30.3 ppm. FTIR (KBr disc; ν in cm<sup>-1</sup>): 3437, 3354, 3238, 2920, 2851, 1655, 1575, 1479, 1394, 1190, 983, 920, 871, 808, 713, 632, 459.ESI MS: *m/z* calcd 696.35, found 719.73 [M<sup>+</sup> + Na]. Anal. Calcd for C<sub>28</sub>H<sub>24</sub>Br<sub>2</sub>N<sub>8</sub>O<sub>4</sub>: C, 48.29; H, 3.47; N, 16.09%. Found: C, 48.25; H, 3.50; N, 16.09%.

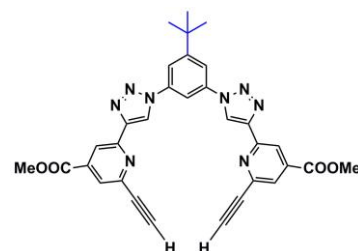


**Di(trimethylsilylethynyl)-3/4-oligomer (24):** Dibromo-3/4-oligomer **23** (2 g, 2.83 mmol), CuI (57 mg, 0.3 mmol), and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (210 mg, 0.3 mmol) were taken in a two neck flask. The flask was degassed under high vacuum and filled with argon three times prior to the addition of degassed freshly distilled THF (30 mL), diisopropylamine (6 mL), followed by drop-wise addition of trimethylsilylacetylene (0.84 mL, 6.0 mmol). The reaction mixture was stirred for 8 h at RT. The volatiles were removed in vacuo and the obtained brown solid was washed with water (3×30 ml), extracted with CH<sub>2</sub>Cl<sub>2</sub> (2×50 mL), and dried using MgSO<sub>4</sub>. The solution mixture was concentrated under reduced pressure to get crude residue. The white solid crude product was purified by column chromatography (SiO<sub>2</sub>, 10:1, CH<sub>2</sub>Cl<sub>2</sub>:MeOH) to afford **24** as a white solid (Yield: 1.92 g, 92%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.47 (s, 2 H), 8.24 (s, 2H), 7.78-7.65 (m, 4H), 7.52 (s, 1H), 4.05 (s, 6H), 1.76-1.25 (m, 9H), 0.21

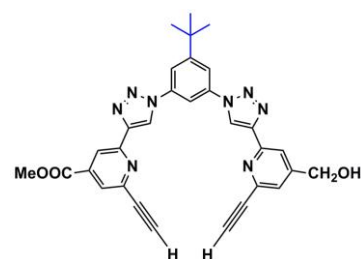


(s, 18H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ - $d_1$ , 298K)  $\delta$ : 164.1, 159.1, 154.1, 150.2, 145.5, 142.4, 141.3, 124.9, 124.4, 114.4, 107.8, 107.3, 93.4, 51.4, 33.4, 30.3 ppm. FTIR (KBr disc;  $\nu$  in  $\text{cm}^{-1}$ ): 3103, 2926, 2851, 1734, 1585, 1568, 1454, 1392, 1263, 1190, 1157, 1053, 1018, 960, 866, 839, 802, 760, 706, 646, 609, 540. ESI MS:  $m/z$  calcd 730.96, found 754.38 [ $\text{M}^+ + \text{Na}$ ]. Anal. Calcd for  $\text{C}_{38}\text{H}_{42}\text{N}_8\text{O}_4\text{Si}_2$ : C, 62.44; H, 5.79; N, 15.33%. Found: C, 62.43; H, 5.78; N, 15.36%.

**Diacetylene-3/4-premacrocycle (25):** A 50 mL flask was charged with **24** (0.5 g, 0.68 mmol), KF (406 mg, 7 mmol), THF (10 mL) and methanol (10 mL) and stirred at RT for 8 h. The volatiles were removed in vacuo and the solid obtained was extracted with  $\text{CH}_2\text{Cl}_2$  (3×50 mL), washed with water (30 mL), dried ( $\text{MgSO}_4$ ) and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (10:1  $\text{CH}_2\text{Cl}_2$ :MeOH) to isolate **25** as a white sticky solid (Yield: 0.32 g, 94%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.46 (s, 2 H), 8.25 (s, 2H), 7.77-7.65 (m, 4H), 7.50 (s, 1H), 3.99 (s, 6H), 3.25 (s, 2H), 1.76-1.22 (m, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ - $d_1$ , 298 K)  $\delta$ : 164.2, 159.1, 154.1, 150.2, 145.5, 142.4, 141.3, 124.9, 124.4, 114.4, 107.5, 99.9, 99.3, 87.4, 51.4, 33.4, 30.3 ppm. FTIR (KBr disc;  $\nu$  in  $\text{cm}^{-1}$ ): 2924, 2853, 1701, 1618, 1572, 1460, 1348, 1306, 1258, 1182, 1030, 962, 891, 816, 795, 773, 703, 665, 534. ESI MS:  $m/z$  calcd 586.60, found 610.02 [ $\text{M}^+ + \text{Na}$ ]. Anal. Calcd for  $\text{C}_{32}\text{H}_{26}\text{N}_8\text{O}_4$ : C, 65.52; H, 4.47; N, 19.10%. Found: C, 65.53; H, 4.48; N, 19.14%.



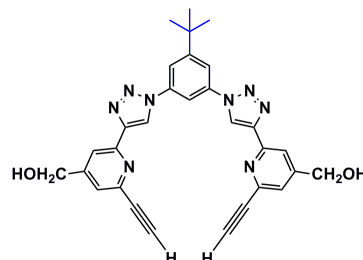
**Diacetylene-3/4-premacrocyclemonoalcohol (26):** Sodium borohydride (0.5 g, 13.5 mmol) was added to compound **25** (1.5 g, 2.55 mmol) in ethanol (150 mL) and the mixture was kept under reflux for 6 h. The resulting mixture was evaporated, and 60 mL of water and 23.3 mL of 1M HCl aq. was added to the residue. The crude product was extracted with dichloromethane and purified by column chromatography ( $\text{SiO}_2$ , 3:2  $\text{CH}_2\text{Cl}_2$ :Hexane) to get white powder of **26** (Yield: 0.76 g, 85%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.72 (s, 2 H), 8.26 (s, 2H), 8.23-7.95 (m, 4H), 7.59 (s, 1H), 4.81 (s, 2H), 4.09 (s, 3H), 3.26 (s, 2H), 1.25 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ - $d_1$ , 298K)  $\delta$ : 164.5, 159.5, 154.2, 151.2, 145.4, 142.3, 141.4, 124.9, 124.4, 114.4, 107.4, 99.8, 99.3, 87.1, 61.6, 51.3, 33.4, 30.3 ppm. FTIR (KBr disc;  $\nu$  in  $\text{cm}^{-1}$ ):



3466, 3434, 3364, 3229, 3113, 2926, 2855, 1650, 1632, 1547, 1487, 1410, 1186, 982, 943, 941, 835, 788, 723, 642, 540. ESI MS:  $m/z$  calcd 558.59, found 582.02 [ $M^+ + Na$ ]. Anal. Calcd for  $C_{31}H_{26}N_8O_3$ : C, 66.66; H, 4.69; N, 20.0%. Found: C, 66.63; H, 4.69; N, 20.04%.

**Diacetylene-3/4-premacrocycedialcohol (27):**

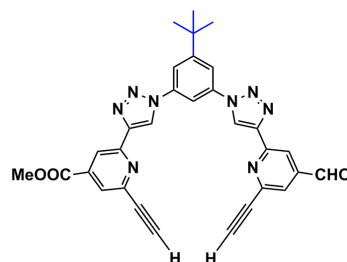
Sodium borohydride (1 g, 26.5 mmol) was added to compound **26** (1.5 g, 2.55 mmol) in ethanol (150 mL) and the mixture was kept under reflux for 6 h. The resulting mixture was evaporated, and 60 mL of water and 23.3 mL of 1M HCl aq. was added to the residue. The crude product was



extracted with dichloromethane and purified by column chromatography from ( $SiO_2$ , 3:2  $CH_2Cl_2$ :Hexane) to get white power of **27** (Yield: 0.76 g, 70%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$ : 8.61 (s, 2 H), 8.13 (s, 2H), 8.02-7.95 (m, 4H), 7.59 (s, 1H), 4.82 (s, 4H), 3.29 (s, 2H), 1.25 (s, 9H).  $^{13}C$  NMR (400 MHz,  $CDCl_3-d_1$ , 298 K)  $\delta$ /ppm: 164.5, 159.5, 154.2, 151.1, 145.4, 142.3, 141.4, 124.9, 124.4, 114.4, 107.4, 99.8, 99.3, 87.1, 61.6, 33.3, 30.3 ppm. FT-IR (KBr)  $\nu$  in  $cm^{-1}$ : 3111, 2926, 2851, 1603, 1595, 1549, 1456, 1414, 1269, 1190, 1130, 962, 851, 793, 768, 663, 623, 540. ESI MS:  $m/z$  calcd 530.58, found 554.06 [ $M^+ + Na$ ]. Anal. Calcd for  $C_{30}H_{26}N_8O_2$ : C, 67.91; H, 4.94; N, 21.12%. Found: C, 67.93; H, 4.91; N, 21.14%.

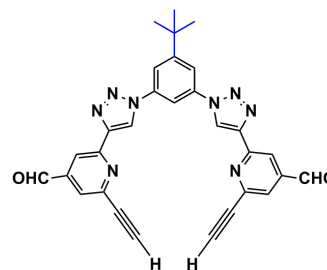
**Diacetylene-3/4-premacrocyclemonoaldehyde (28):**

Pyridiniumchlorochromate (0.6 g, 3 mmol) was added to **26** (1.5 g, 2.85 mmol) in dry DCM (50 mL) and the mixture was stirred for 6 h at RT. The resulting reaction mixture was directly purified on a silica column using dichloromethane as eluent to get white solid of **28** (Yield: 0.76 g, 58%).  $^1H$  NMR (400 MHz,  $CDCl_3-d_1$ , 298K)  $\delta$ :

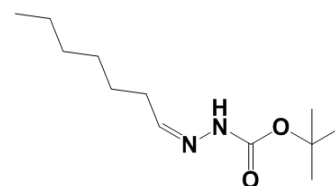


10.06 (s, 1H), 8.71-8.70 (d, 2H), 8.25-8.23 (s, 2H), 8.15-7.94(s, 4H), 4.03 (s, 3H), 3.25 (s, 2H), 1.25 (m, 9H) ppm.  $^{13}C$  NMR (100 MHz,  $CDCl_3-d_1$ , 298K)  $\delta$ : 191.6, 165.7, 160.7, 152.7, 150.8, 143.2, 142.6, 136.9, 130.4, 128.0, 127.3, 87.4, 51.2, 31.1, 30.3 ppm. FTIR (KBr disc;  $\nu$  in  $cm^{-1}$ ): 2926, 2853, 1674, 1685, 1545, 1472, 1408, 1202, 1150, 959, 831, 795, 664. ESI MS:  $m/z$  calcd 556.57, found 580.11 [ $M^+ + Na$ ]. Anal. Calcd for  $C_{31}H_{24}N_8O_3$ : C, 66.90; H, 4.35; N, 20.13%. Found: C, 66.91; H, 4.33; N, 20.16%.

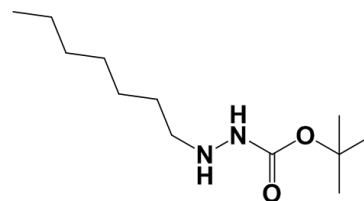
**Diacetylene-3/4-premacrocyclicdialdehyde (29):** Pyridiniumchlorochromate (1.3 g, 6 mmol) was added to **27** (1.5 g, 2.85 mmol) in dry DCM (50 mL) and the mixture was stirred for 6 h at RT. The reaction mixture was directly put on a silica column and purified using dichloromethane as eluent to get white color solid of **29** (Yield: 0.96 g, 63%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 10.1 (s, 2H), 8.5 (s, 2 H), 8.28 (s, 2H), 7.81-7.74 (m, 4H), 7.53 (s, 1H), 3.27 (s, 2H), 1.25 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ , 298 K)  $\delta$ : 191.7, 165.6, 160.8, 152.7, 150.8, 143.2, 142.7, 137.0, 130.4, 128.0, 127.3, 108.3, 107.5, 87.4, 31.2, 30.4 ppm. ESI MS:  $m/z$  calcd 526.55, found 550.05 [ $\text{M}^+ + \text{Na}$ ]. Anal. Calcd for  $\text{C}_{30}\text{H}_{22}\text{N}_8\text{O}_2$ : C, 68.43; H, 4.21; N, 21.28%. Found: C, 68.42; H, 4.23; N, 21.26%. FTIR (KBr disc;  $\nu$  in  $\text{cm}^{-1}$ ): 3059, 2926, 2857, 1687, 1578, 1470, 1379, 1126, 1065, 993, 802, 459.



**Synthesis of tert-butyl 2-heptylidenehydrazinecarboxylate (40).** Tert-butoxy carbazate (2.0 g, 15.1 mmol) was added to dry heptaldehyde (2 mL) in 60 mL toluene at 80 °C and the reaction was stirred for 6 h. Then the resulting mixture was evaporated in vacuo to get white sticky precipitate of **40**. (Yield: 2.3 g, 92%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3\text{-d}_1$ , 298 K),  $\delta$ : 1.25 (m, 3H), 1.49 (s, 8H), 1.80 (s, 10H), 2.27 (m, 2H), 7.40 (s, 1H) ppm.  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3\text{-d}_1$ , 298 K)  $\delta$ : 151.0, 150.7, 93.0, 31.4, 28.7, 28.6, 22.6, 19.7, 14.2, 14.1 ppm. LCMS analysis calcd  $m/z$  = 228.33, found 229.30. Anal. Calcd for  $\text{C}_{12}\text{H}_{24}\text{N}_2\text{O}_2$  (228.33): C, 63.12; H, 10.59; N, 12.27; O, 14.01%. Found: C, 63.55; H, 10.49; N, 12.25%.



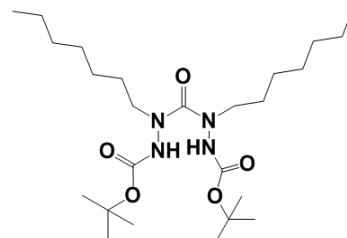
**Synthesis of tert-butyl 2-heptylhydrazinecarboxylate (39).** Sodium borohydride (1 g, 26.5 mmol) was added to compound **40** (1.5 g, 5.29 mmol) in ethanol (150 mL) and the mixture was kept under reflux for 6 h. The resulting crude mixture was evaporated, and 60 mL of water and 23.3 mL of 1M HCl aq. was added to the residue. The crude product was extracted with dichloromethane and purified by recrystallization from 1:1  $\text{CH}_2\text{Cl}_2$ :Hexane to get white solid of **39** (Yield: 1 mL, 80%).  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3\text{-d}_1$ , 298 K)  $\delta$ : 3.29-3.21 (t, 2H), 1.63 (s, 9H, tert-butyl), 1.49 (s, 6H), 0.97 (s, 3H ppm.  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3\text{-d}_1$ , 298 K)  $\delta$ : 154.2, 81.3, 52.1, 31.9, 30.7, 29.7, 29.4, 29.3, 24.3, 22.7, 14.3,



14.1 ppm. LCMS analysis calcd  $m/z$  = 230.35, found 231.35. Anal. Calcd for  $C_{12}H_{26}N_2O_2$ : C, 62.57; H, 11.38; N, 12.16%. Found: C, 62.55; H, 11.19; N, 12.25%.

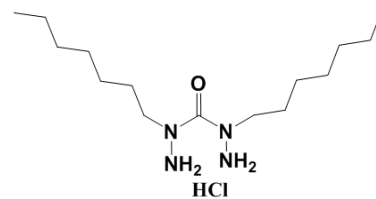
**Synthesis of tert-butyl 2,2'-carbonylbis(2-heptylhydrazinecarboxylate) (38).**

Compound **39** (20.6 g, 0.118 mol) was dissolved in dry toluene and dry triethylamine (11.9 g, 0.118 mol) was added. To this, a solution of 20% phosgene in toluene (31 mL, 0.06 mol) was added dropwise at a rate of less than one drop per second. During addition a copious precipitate of triethylamine hydrochloride is formed. Once addition was complete, the solution was stirred at room temperature for 2 h, filtered and the filtrate evaporated to give the crude product. The crude product was purified by recrystallization from heptane to give white solid of **38** (Yield: 9.75 g, 44%).

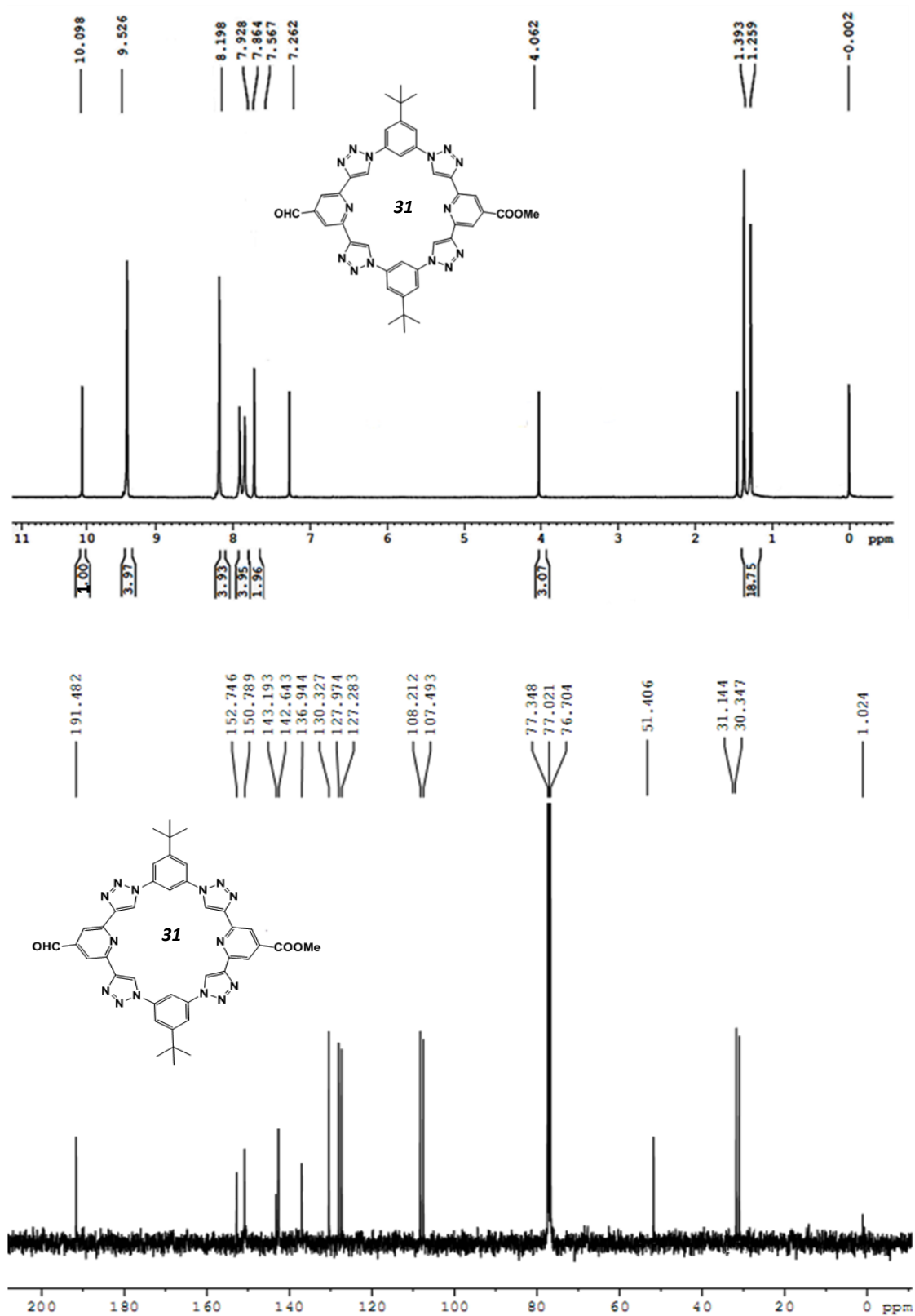


$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3\text{-}d_1$ , 298 K)  $\delta$ : 4.51-4.16 (m, 2H), 2.34 (s, 1H), 1.40-1.29 (m, 22H), 1.24-1.13 (m, 21H) ppm.  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3\text{-}d_1$ , 298 K)  $\delta$ : 154.2, 150.7, 81.3, 50.1, 31.9, 30.7, 29.4, 29.3, 24.3, 22.7, 14.1 ppm. LCMS analysis calcd  $m/z$  = 486.38, found 487.38. Anal. Calcd for  $C_{25}H_{50}N_4O_5$ : C, 61.70; H, 10.36; N, 11.51%. Found: C, 61.55; H, 10.19; N, 11.25%.

**2,4-diheptylcarbonylhydrazide bis-hydrochloride (37):** Compound **38** (0.655 g, 1.75 mmol) was dissolved in 10 mL ethanol and 5 mL concentrated HCl was added to it. Then the mixture was warmed (50 °C) on a hot plate for 0.5 h during which a mild effervescence occurred. The solution was allowed to cool overnight. Removal of the solvent and excess acid under vacuum left the 2,4-diheptylcarbonylhydrazide bis-hydrochloride as off-white crystals (0.426 g, 99%).



The sample was recrystallized from n-butanol to give white needles of **37** (Yield: 450 mg, 74%).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3\text{-}d_1$ , 298 K)  $\delta$ : 4.27-4.22 (m, 2H), 3.65-3.61 (m, 2H), 1.65-1.18 (m, 20H), 0.93-0.89 (m, 6H) ppm.  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3\text{-}d_1$ , 298 K)  $\delta$ : 156.8, 51.3, 31.9, 30.8, 29.7, 29.4, 29.3, 24.3, 22.7, 14.1 ppm. LCMS analysis calcd  $m/z$  = 286.46, found 286.46. Anal. Calcd for  $C_{15}H_{34}N_4O$ : C, 62.89; H, 11.96; N, 19.56%. Found: C, 62.55; H, 12.19; N, 19.25%.



## Display Report

## Analysis Info

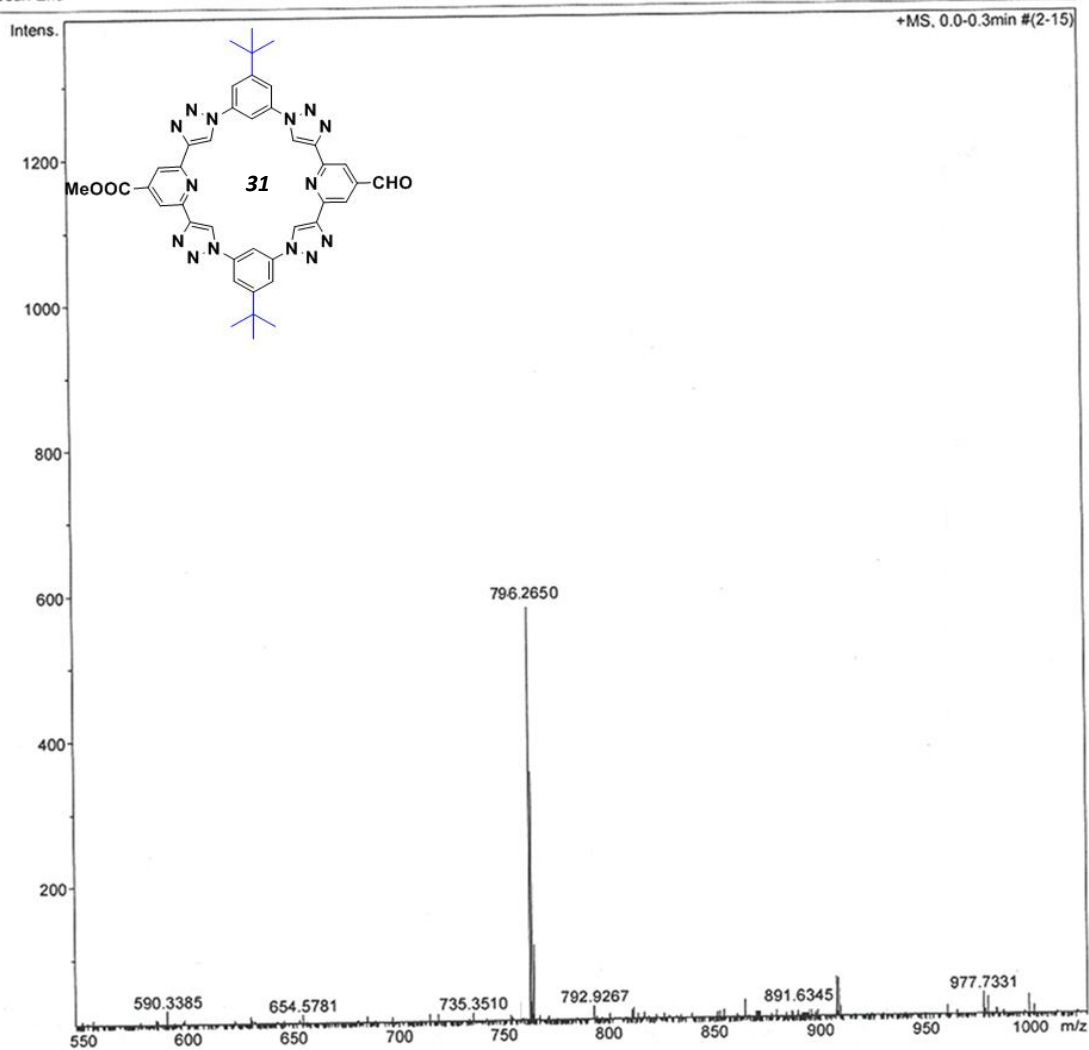
Analysis Name D:\Data\2012\Dr.RC\DEC\PhH-6R.d  
Method tune\_high\_Pos.m  
Sample Name PhH-6-MeOH  
Comment

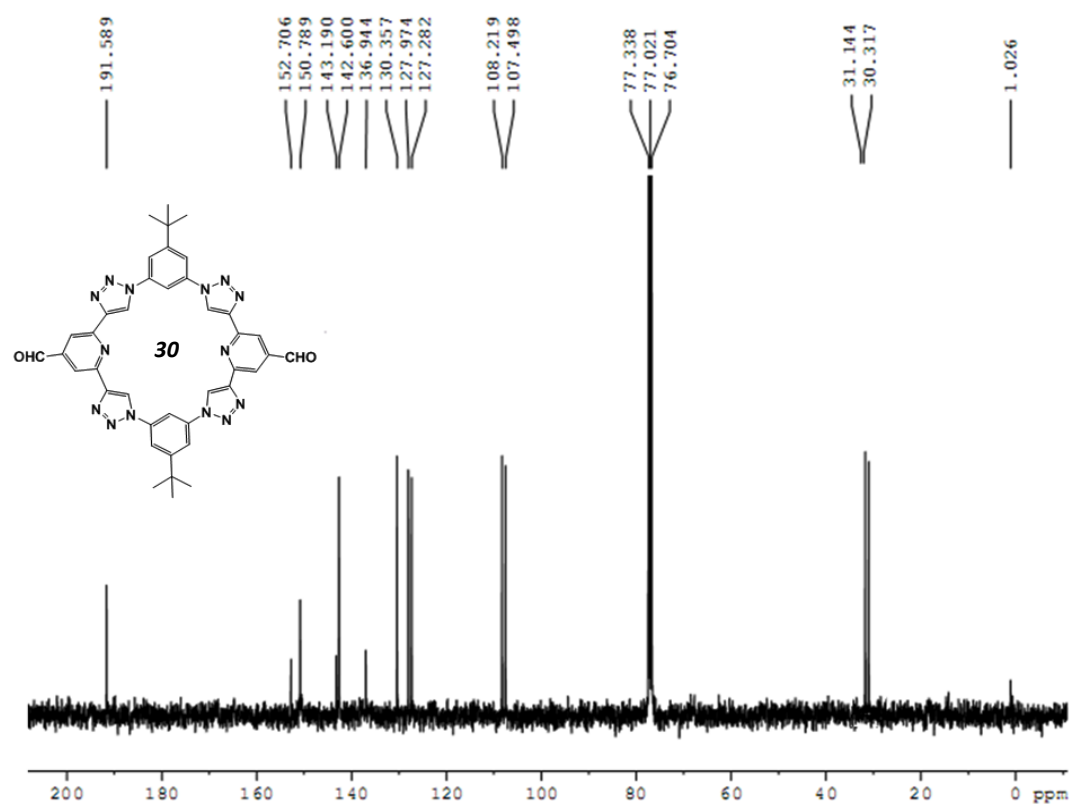
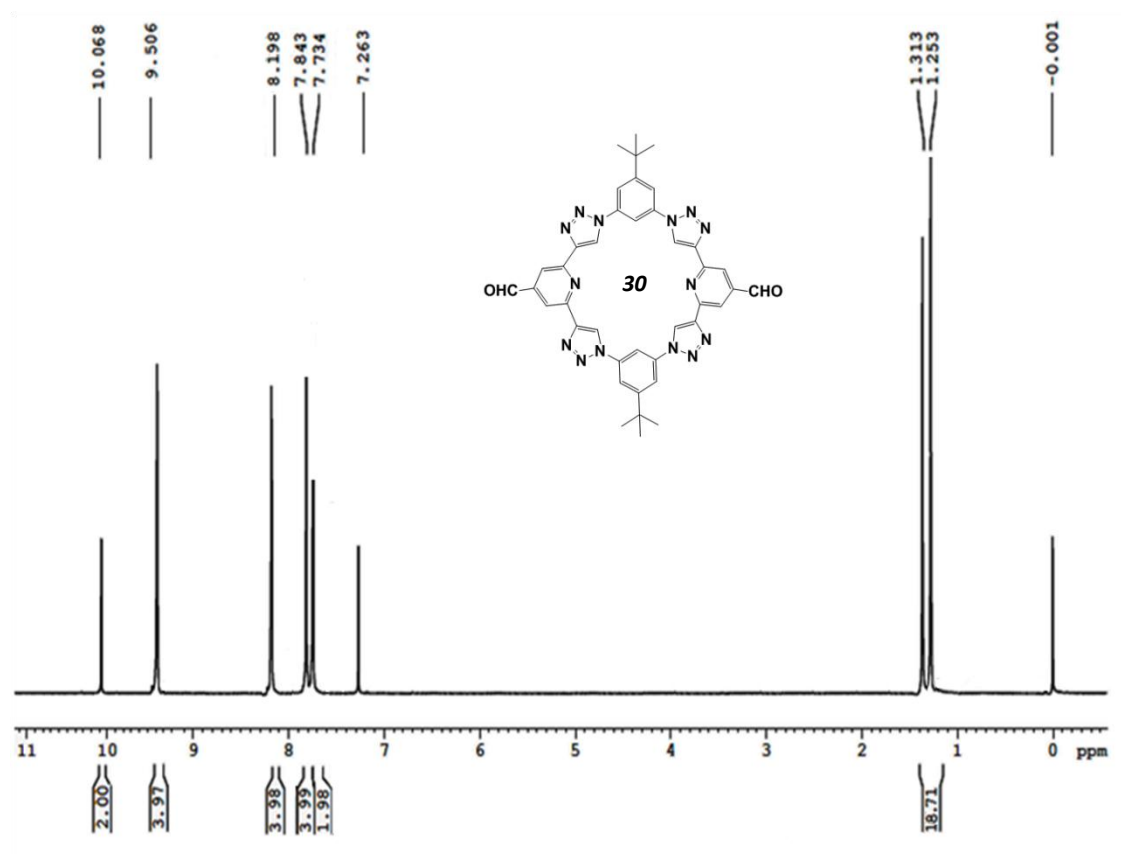
Acquisition Date 07/03/2012 12:39:42 PM

Operator UOH  
Instrument maXis 12138

## Acquisition Parameter

|             |            |                       |            |                  |           |
|-------------|------------|-----------------------|------------|------------------|-----------|
| Source Type | ESI        | Ion Polarity          | Positive   | Set Nebulizer    | 0.3 Bar   |
| Focus       | Not active | Set Capillary         | 4800 V     | Set Dry Heater   | 180 °C    |
| Scan Begin  | 50 m/z     | Set End Plate Offset  | -500 V     | Set Dry Gas      | 4.0 l/min |
| Scan End    | 2500 m/z   | Set Collision Cell RF | 3500.0 Vpp | Set Divert Valve | Waste     |





## Display Report

## Analysis Info

Analysis Name D:\Data\2012\Dr.RC\DEC\PhH-1R.d  
Method tune\_high\_Pos.m  
Sample Name PhH-1-MeOH  
Comment

Acquisition Date 07/03/2012 12:39:42 PM

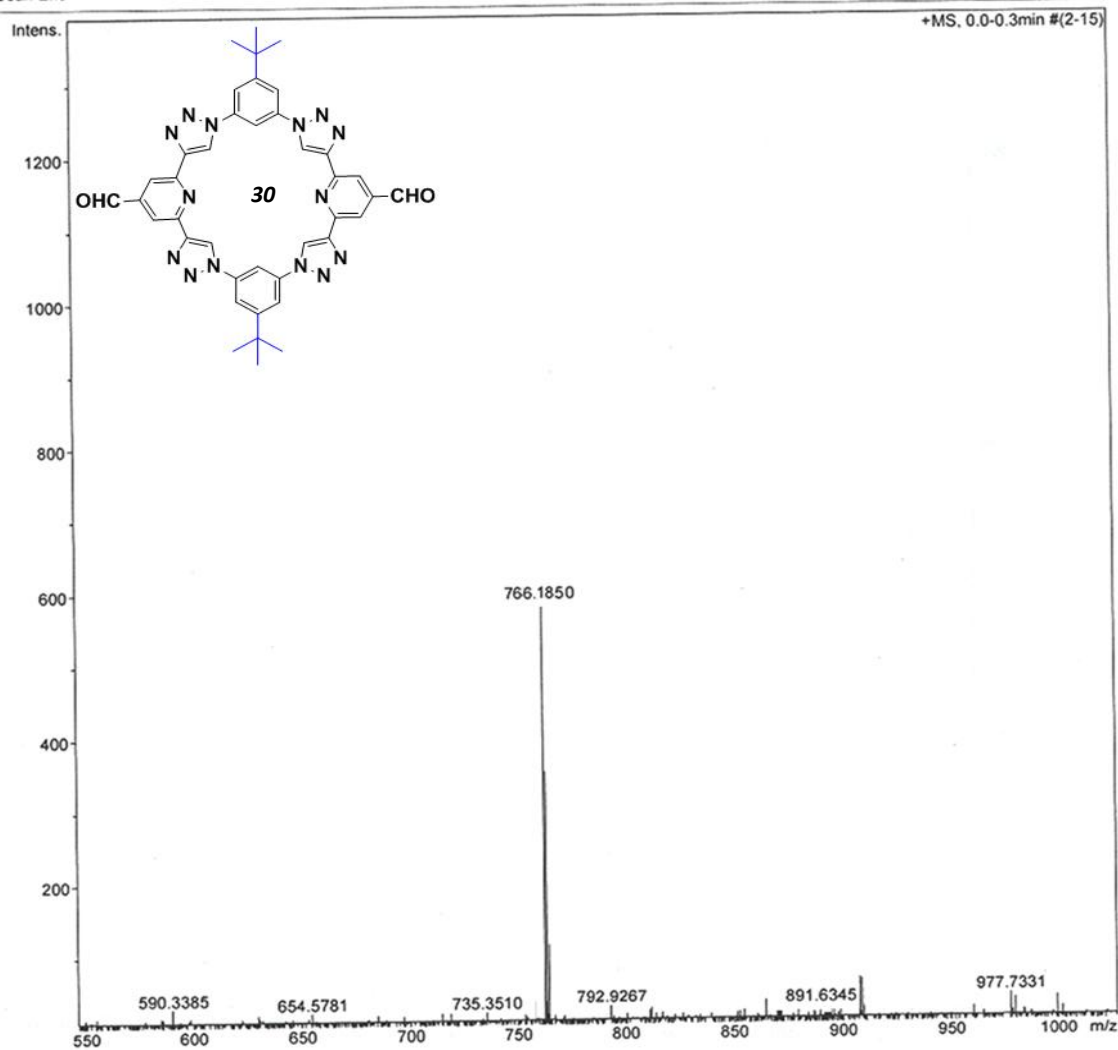
Operator UOH  
Instrument maXis 12138

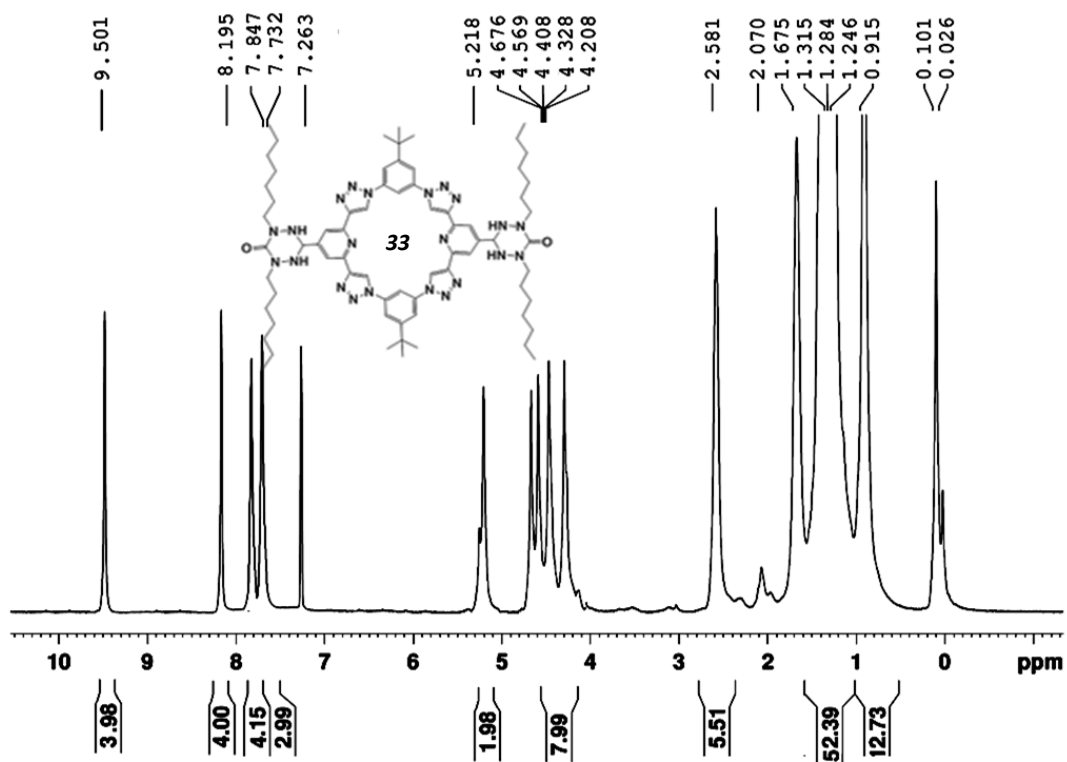
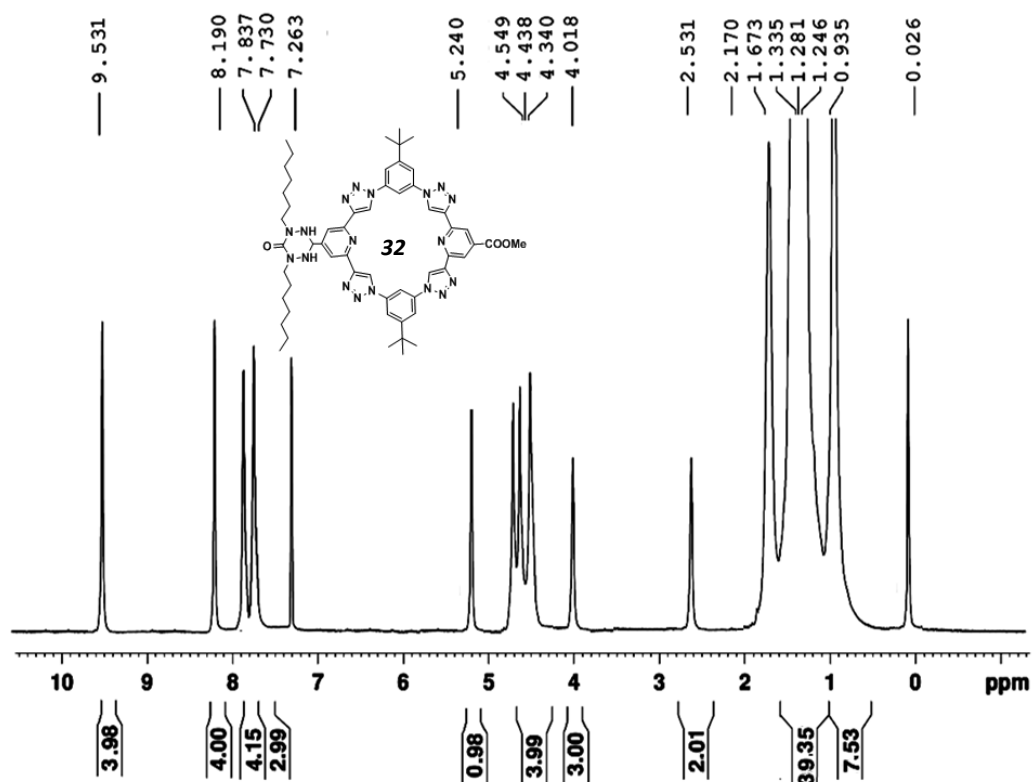
## Acquisition Parameter

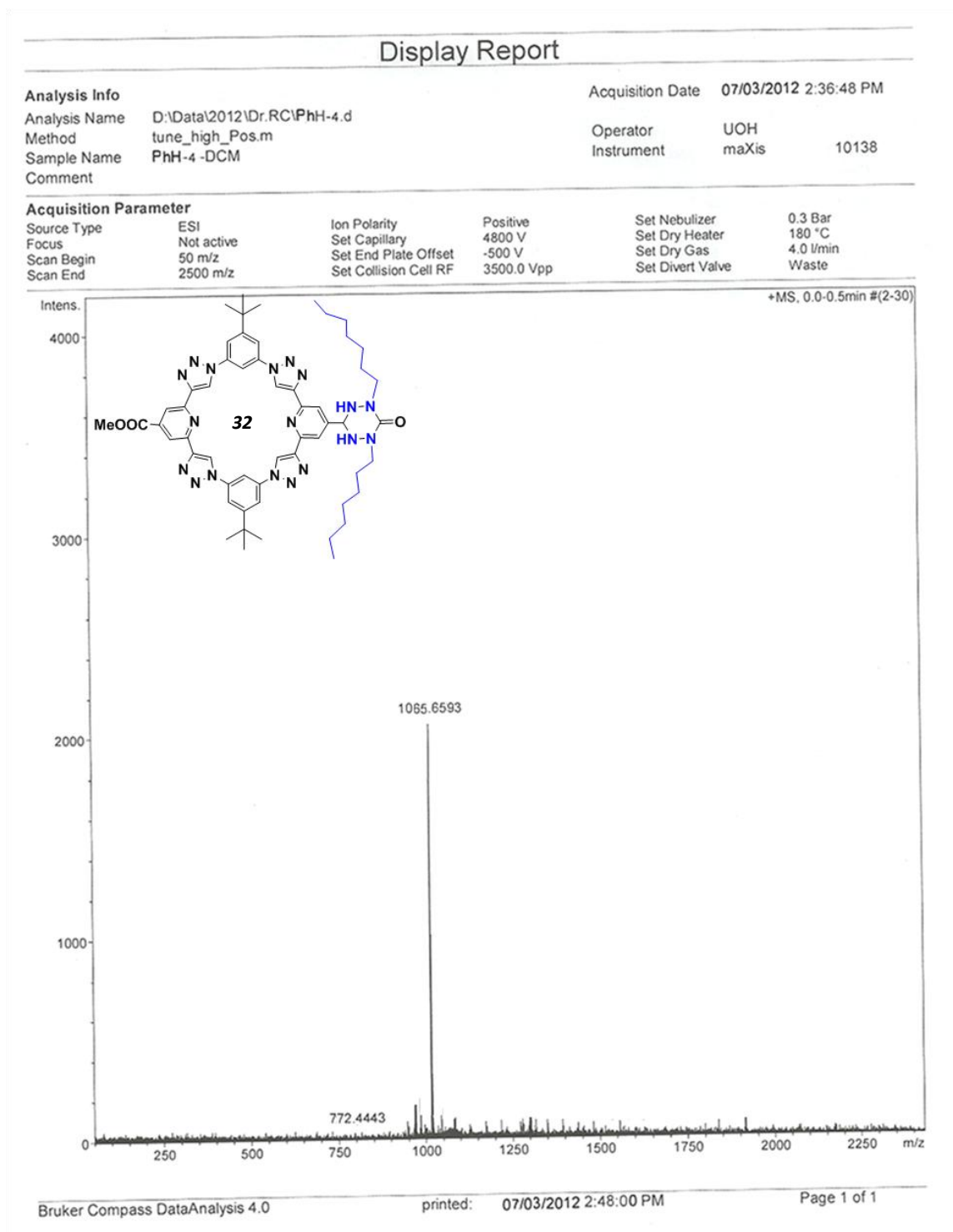
Source Type ESI  
Focus Not active  
Scan Begin 50 m/z  
Scan End 2500 m/z

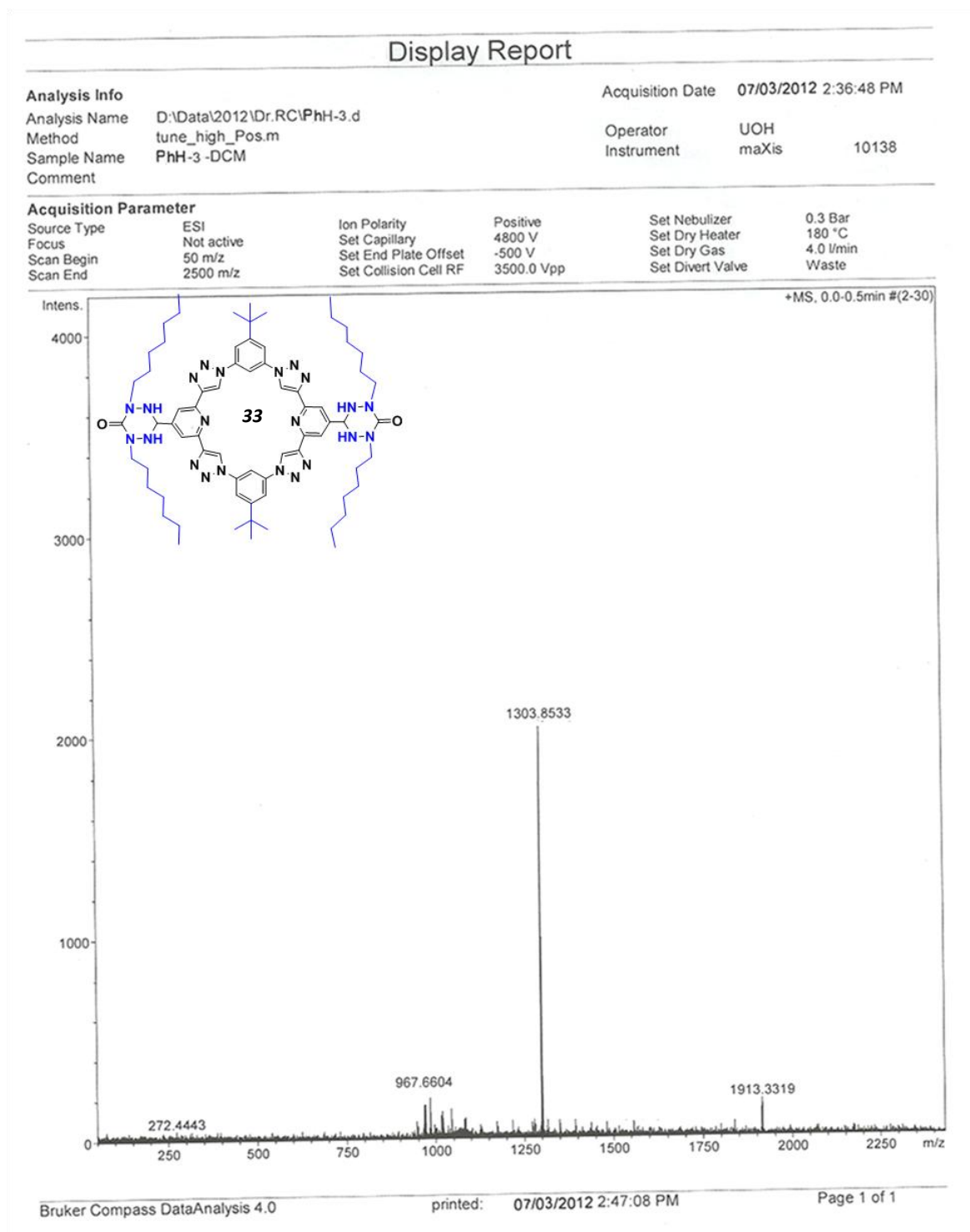
Ion Polarity Positive  
Set Capillary 4800 V  
Set End Plate Offset -500 V  
Set Collision Cell RF 3500.0 Vpp

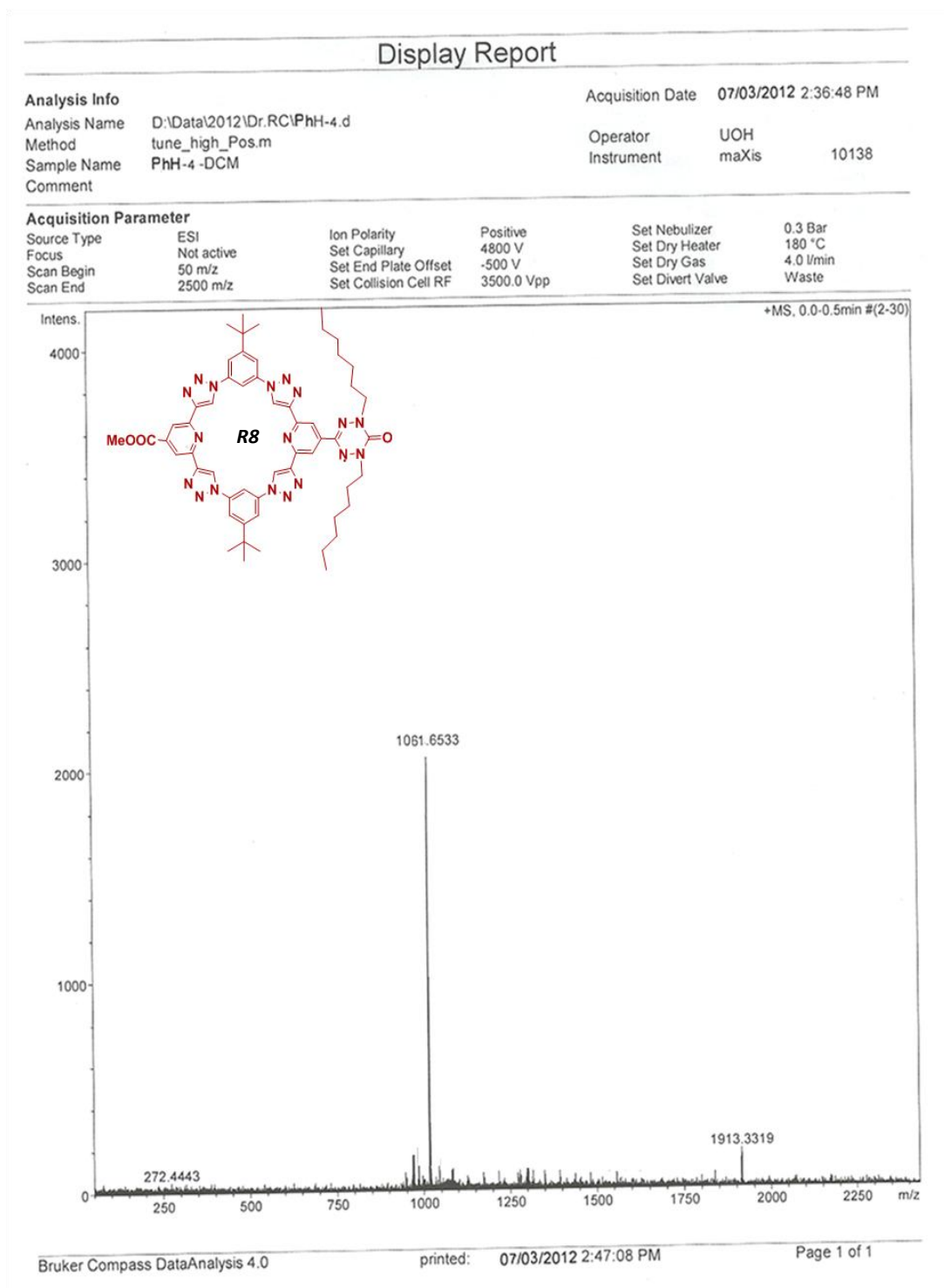
Set Nebulizer 0.3 Bar  
Set Dry Heater 180 °C  
Set Dry Gas 4.0 l/min  
Set Divert Valve Waste

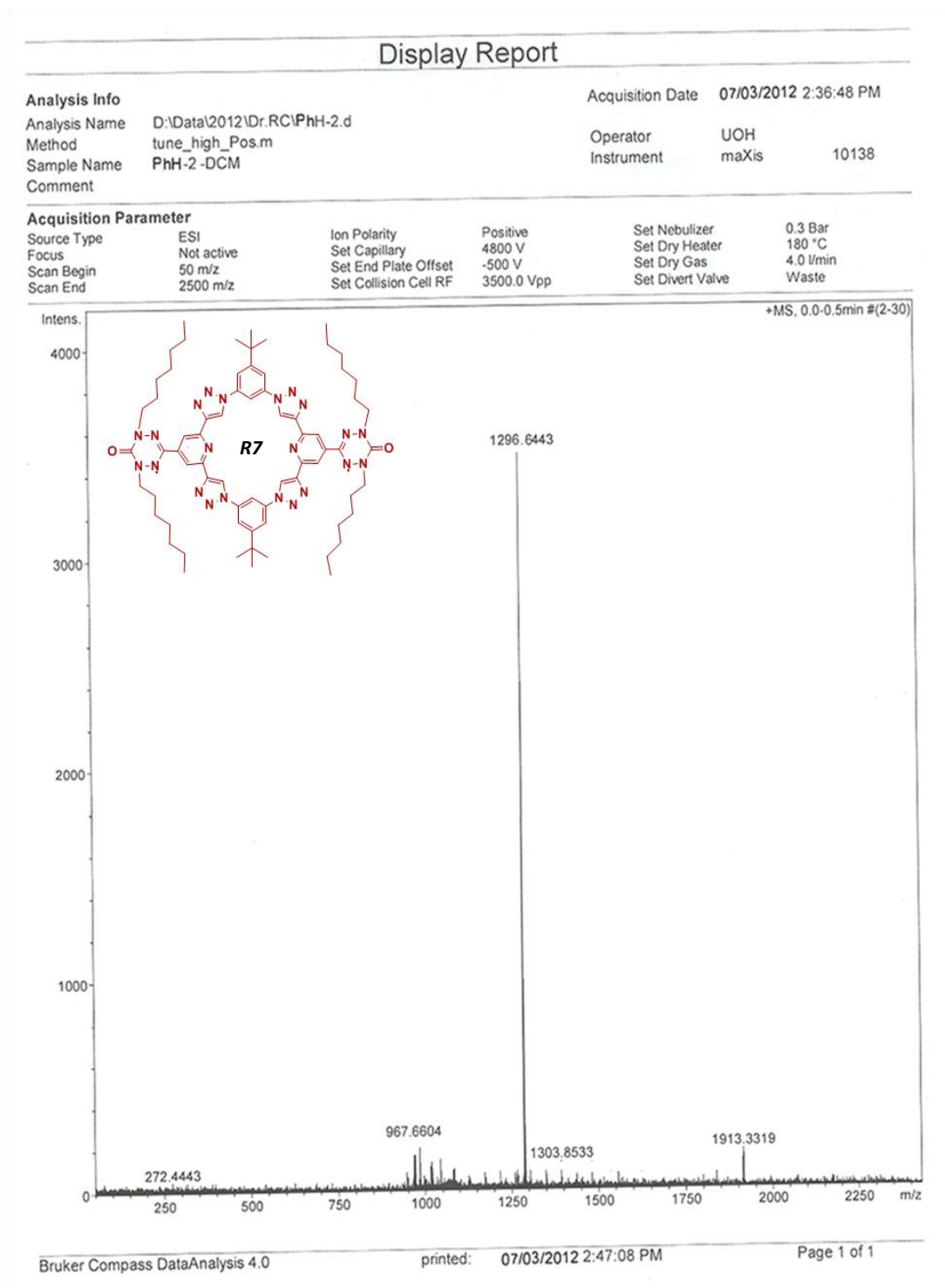












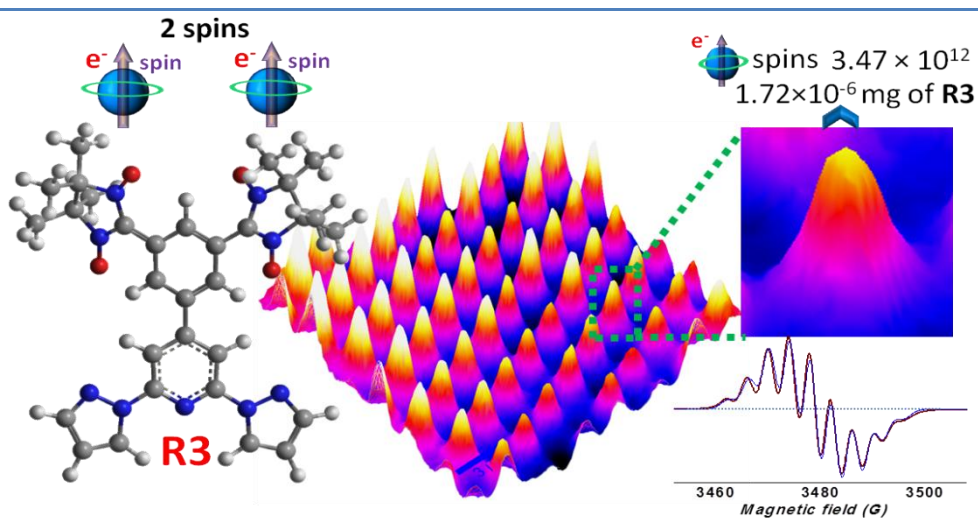
## References

1. Iijima, S. *Nature* **1991**, *354*, 56.
2. (a) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071. (b) Babu, S. S.; Praveen, V. K.; Ajayaghosh, A. *Angew. Chem. Int. Ed.* **2012**, *51*, 1766. (c) Srinivasan, S.; Babu, S. S.; Praveen, V. K.; Ajayaghosh, A. *Angew. Chem. Int. Ed.* **2008**, *31*, 5746. (d) Srinivasan, S.; Praveen, V. K. Philip, R.; Ajayaghosh, A. *Angew. Chem. Int. Ed.* **2008**, *31*, 5750.
3. (a) Zhao, Y. S.; Fu, H.; Peng, A.; Ma, Y.; Liao, Q.; Yao, J. *J. Acc. Chem. Res.* **2010**, *43*, 409. (b) Chandrasekhar, N.; Chandrasekar, R. *Chem. Commun.* **2010**, *46*, 2915. (c) Basak, S.; Chandrasekar, R. *Adv. Funct. Mater.* **2011**, *21*, 667. (d) Chandrasekhar, N.; Chandrasekar, R. *Angew. Chem. Int. Ed.* **2012**, *51*, 3556.
4. (a) Zhao, Y. S.; Yang, W.; Xiao, D.; Sheng, X.; Yang, X.; Shuai, Z.; Luo, Y.; Yao, J. *Chem. Mater.* **2005**, *17*, 6430. (b) Diaz, N.; Simon, F.-X.; Schmutz, M.; Rawiso, M.; Decher, G.; Jestin, J.; Mésini, P. *J. Angew. Chem. Int. Ed.* **2005**, *44*, 3260. (c) Pantos, G. D.; Pengo, P.; Sanders, J. K. M. *Angew. Chem. Int. Ed.* **2007**, *46*, 2238. (d) Seo, M.; Kim, J. H.; Seo, G.; Shin, C. -H.; Kim, S. Y. *Chem. Eur. J.* **2009**, *15*, 612. (e) Seo, M.; Seo, G.; Kim, S. Y. *Angew. Chem. Int. Ed.* **2006**, *45*, 6306. (f) Wu, D.; Zhi, L.; Bodwell, G. J.; Cui, G.; Tsao, N.; Müllen, K. *Angew. Chem. Int. Ed.* **2007**, *46*, 5417.
5. (a) Savariar, E. N.; Krishnamoorthy, K.; Thayumanavan, S. *Nat. Nanotech* **2008**, *3*, 112. (b) Feng, X.; Liang, Y.; Zhi, L.; Thomas, A.; Wu, D.; Lieberwirth, I.; Kolb, U.; Müllen, K. *Adv. Mater.* **2009**, *19*, 2125.
6. (a) Yan, X.; He, Q.; Wang, K.; Duan, L.; Cui, Y.; Li, J. *Angew. Chem. Int. Edn.* **2007**, *46*, 2431. (b) Leclair, S.; Baillargeon, P.; Skouta, R.; Gauthier, D.; Zhao, Y.; Dory, Y. L. *Angew. Chem. Int. Edn.* **2004**, *43*, 349.
7. (a) Balzer, F.; Bordo, V. G.; Simonsen, A. C.; Rubahn, H.-G. *Phys. Rev. B.* **2003**, *67*, 115408. (b) Zhao, Y. S.; Fu, H.; Peng, A.; Ma, Y.; Liao, Q.; Yao, J. *Acc. Chem. Res.* **2010**, *43*, 409. (c) Takazawa, K.; Kitahama, Y.; Kimura, Y.; Kido, G. *Nano Lett.* **2005**, *5*, 1293. (d) Yanagi, H.; Morikawa, T. *Appl. Phys. Lett.* **1999**, *75*, 187. (e) Zhao, Y. S.; Xu, J. J.; Peng, A. D.; Fu, H. B.; Ma, Y.; Jiang, L.; Yao, J. N. *Angew. Chem. Int. Ed.* **2008**, *47*, 7301.
8. (a) Urdampilleta, M.; Klyatskaya, S.; Cleuziou, J. -P.; Ruben, M.; Wernsdorfer, W. *Nature Mater.* **2011**, *10*, 502. (b) Candini, A.; Klyatskaya, S.; Ruben, M.; Wernsdorfer, W.; Affronte, M. *Nano Lett.* **2011**, *11*, 2634. (c) Klyatskaya, S.; Galan Mascaros, J. R.; Bogani, L.; Hennrich, F.; Kappes, M.; Wernsdorfer, W.; Ruben, M. *J. Am. Chem. Soc.* **2009**, *131*, 15143.
9. Ghadiri, R.; Granja, J. R.; Milligan, R. A.; McRee, D. E.; Khazanovich, N. *Nature* **1993**, *366*, 324.
10. (a) Venkataraman, D.; Lee, S.; Zhang, J.; Moore, J. S. *Nature* **1994**, *374*, 591. (b) Zhang, W.; Moore, J. S. *Angew. Chem. Int. Ed.* **2006**, *45*, 4416. (c) Zhao, D.; Moore, J. S. *Chem. Commun.* **2003**, 807. (d) Grave, C.; Schluter, A. D. *Eur. J. Org. Chem.* **2002**, 3075. (e) Li, Y.; Flood, A. H. *Angew. Chem. Int. Ed.* **2008**, *47*, 2649. (f) Meudtner, R. M.; Hecht, S. *Angew. Chem. Int. Ed.* **2008**, *47*, 4926. (g) Juwarker, H.; Lenhardt, J. M.; Pham, D. M.; Craig, S. L. *Angew. Chem. Int. Edn.* **2008**, *47*, 3740.
11. (a) Höger, S. *Chem. Eur. J.* **2004**, *10*, 1320. (b) Shu, L.; Müri, M.; Krupke, R.; Mayor, M. *Org. Biomol. Chem.* **2009**, *7*, 1081. (c) Shu, L.; Mayor, M. *Chem. Commun.*, **2006**, 4134. (d) MacLachlan, M. J. *Pure Appl. Chem.* **2006**, *78*, 873.
12. (a) Iwamura, H.; Koga, N. *Acc. Chem. Res.* **1993**, *26*, 346. (b) Rajca, A. *Chem. Rev.* **1994**, *94*, 871. (c) *Magnetic Properties of Organic Materials*, ed. Lahti, P. M.; Marcel Dekker, New York **1999**, pp. 1–713. (d) *Molecular Magnetism*, ed. Itoh, K.; Kinoshita, M.; Gordon, Breach, Kodansha, **2000**, pp. 1–337. (e) Baumgarten, M. High spin molecules directed towards molecular magnets, in *EPR of Free Radicals in Solids, Trends in Methods and Application*, ed. A. Lund and M. Shiotani, Kluwer, **2003/2004**, Ch. 12, pp. 491–528. (f) *Stable Radicals: Fundamentals and Applied Aspects of Odd-Electron Compounds*, Hicks, R. G. ed., John Wiley & Sons, Ltd.: Wiltshire, **2010**. (g) Parè, E. C.; Brook, D. J. R.; Brieger, A.; Badik, M.; Schinke, M. *Org. Biomol. Chem.* **2005**, *3*, 4258.
13. (a) Amb, C. M.; Rasmussen, S. C. *J. Org. Chem.* **2006**, *71*, 4696. (b) Chandrasekhar, N.; Chandrasekar, R. *J. Org. Chem.* **2010**, *75*, 4852. (c) Hui, P.; Arif, K. Md.; Chandrasekar, R. *Org. Biomol. Chem.* **2012**, *10*, 2439. (d) Hui, P.; Chandrasekar, R. *Chem. Plus. Chem.* **2012**, *12*, 1051.

14. Miura, Y.; Ushitani, Y.; Inui, K.; Teki, Y.; Takui, T.; Itoh, K. *Macromolecules* **1993**, *26*, 3698.
15. Riplinger, C.; Kao, J. P. Y.; Rosen, G. M.; Kathirvelu, V.; Eaton, G. R.; Eaton, S. S.; Kutateladze, A.; Neese, F. *J. Am. Chem. Soc.* **2009**, *131*, 10092.
16. Zhang, X.; Zhang, X.; Shi, W.; Meng, X.; Lee, C.; Lee, S. *Angew. Chem. Int. Ed.* **2007**, *46*, 1525.
17. De Hall, H. *J. de phys.* **1971**, *C1*, 590.

# 5

## 2D Ordering of Paramagnetic Nano-Cone Square Lattice from Nitronyl-Nitroxide Biradicals on Hard and Flexible Substrates



## 5.1 Abstract:

*Using a top-down approach paramagnetic 2D nano-cone arrays from a high-spin state ( $S = 1$ ) bi-nitronyl nitroxide radical were fabricated on hard (glass) and flexible (polymer) substrates. The height and width at half height (W) profile of the cones are  $115 \text{ nm} \times 750 \text{ nm}$ , respectively. The nano-cones formed a 2D square lattice pattern and each cone was separated from one another by about  $1.4 \text{ }\mu\text{m}$ . Electron spin resonance (ESR) spectroscopy studies of the nano-cones formed on the polymer substrate ( $1 \text{ mm}^2$ ) revealed that the approximate spin concentration of each cone is  $3.47 \times 10^{12}$  spins. Further cryogenic measurements down to  $4.2 \text{ K}$  indicated the Curie-like behavior of the  $\Delta M_s = \pm 2$  transitions from the cones composed of biradicals.*

## 5.2 Introduction:

Controlled organization of molecular magnetic materials on surfaces is one of the crucial and challenging steps in realizing miniaturized soft spintronic devices. The first miniaturization of data storage device using ultra thin film deposition of magnetic molecules by Langmuir-Blodgett method was started by Pomerantz and co-workers.<sup>1</sup> Latter, techniques like soft lithography and self assembled monolayers (SAM) allowed one to fabricate 2D lattice of molecules. Particularly stable organic radicals are one of the promising candidates for quantum logic devices, in patterned magnetic media, resonance imaging, magnetic logic devices and magnetic random access memory technologies, molecular spin based quantum information processing, and spintronics applications.<sup>2</sup> After the discovery of ferromagnetic ordering in the  $\beta$ -crystals of organic *p*-nitrophenyl nitronyl nitroxide (NN) by Kinoshita *et al.*<sup>3</sup> NN have been widely studied for their intrinsically interesting magnetic properties.

To accomplish the objective of designing the storage media based on NN radical, one obviously requires an ability to handle these radicals down to the nano scale and to organize them in ordered 2D arrays. Arrays of domains with a characteristic size and position can definitely be addressed and read differentially by a magnetic head or by magnetic scanning probes. In the past, nano/micro patterning of fluorescent molecules, organic semiconductors, biomolecules, polymers, dendrimers, spin crossover compounds, metals had been carried by electron beam lithography,<sup>4</sup> photolithography,<sup>5</sup> and also by some soft lithographic<sup>6</sup> techniques like polymeric masks,<sup>7</sup> micro moulding in capillaries (MIMIC),<sup>8</sup> lithographically controlled wetting (LCW),<sup>9</sup> micro transfer moulding,<sup>10</sup> etc.

Previously the 1D patterning of NN has been carried out by micro-contact printing,<sup>11</sup> and by forming SAM on a gold surface.<sup>12</sup> Recently, the fabrication of 1D fluorescent microstripes<sup>13</sup> and optically transparent flexible 1D and 2D spin cross-over patterns<sup>14</sup> by using MIMIC and LCW techniques had been reported. But fabrication of diverse 2D patterns/domains with definite shape and geometry is still a challenging problem. For this development of cost effective yet simple polymer mold preparation technique is required, which can facilitate the fabrication of 2D nano structures composed of NN radical at surfaces.

### 5.3 Results and Discussions:

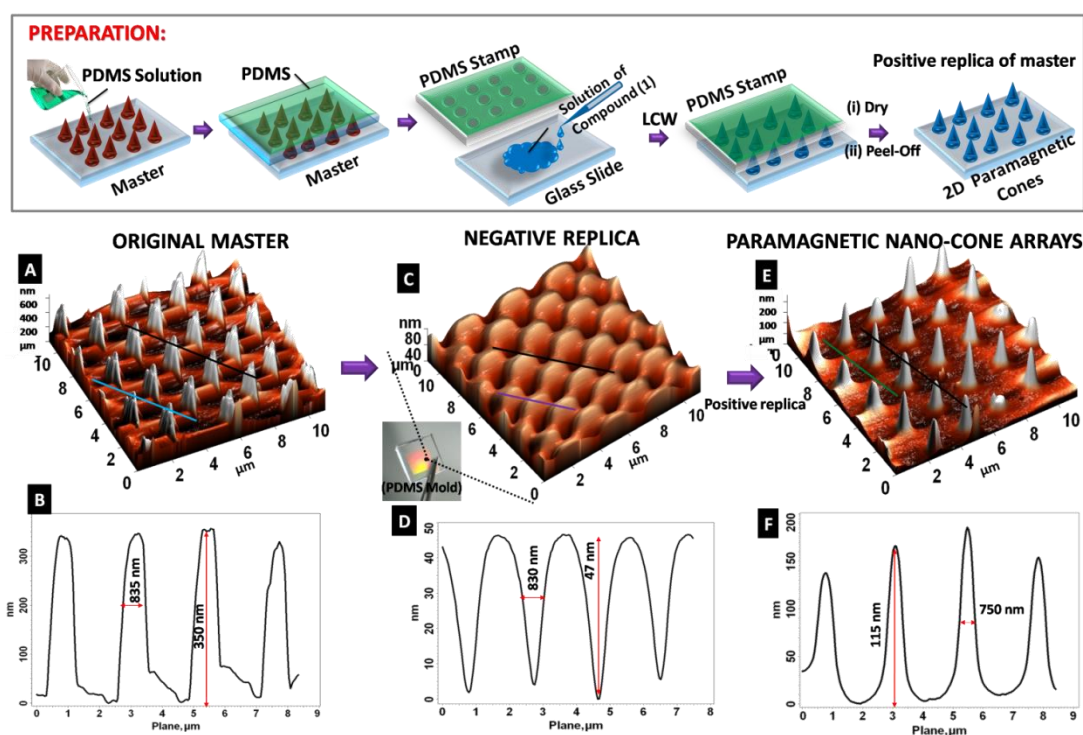


**Figure 5.1** Schematic representation of lithographically controlled wetting (LCW) technique used for the fabrication of paramagnetic solid structures from binitronyl-nitroxide radical derivative (**R3**): A) AFM image of paramagnetic cones formed using the PDMS mould. B) Its corresponding height and width profiles. C) AFM image of PDMS mould displaying negative replica of a master. D) Its corresponding height and width profiles. E) AFM images of cones composed of **R3**. F) Its corresponding height and width profiles. The inset shows the picture of the PDMS mould.

This chapter presents the utility of a novel poly(dimethylsiloxane) (PDMS) stamp to create 2D nano-cone like cubic lattice from a acetonitrile solution of NN biradicals appended to 2,6-bispyrazolyl pyridine molecule (**R3**), by following the top-down LCW technique.<sup>15</sup> The paramagnetic nano-cone lattice was thoroughly characterized by

scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), optical and confocal Raman imaging/microscopy techniques. Finally the spin concentration and spin ground state of lithographically fabricated nano-cones were also determined by performing electron spin resonance (EPR) spectroscopy down to liquid Helium temperature (Fig. 5.4).

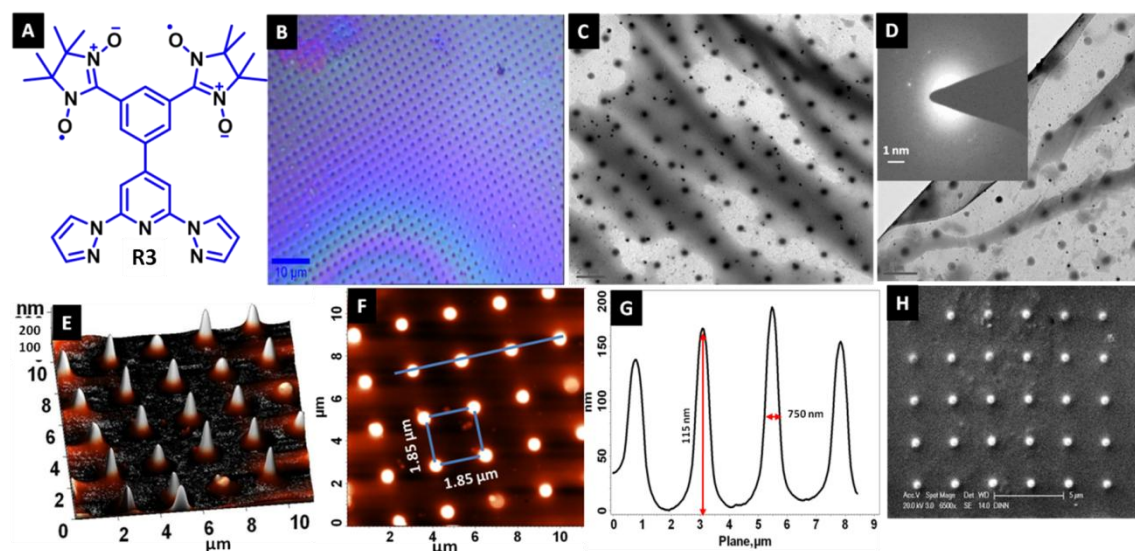


**Figure 5.2** (A) Chemical structure of high spin state NN biradicals appended to 2,6-bispyrazolyl pyridine (**R3**). (B) Confocal microscopy image of nano-cone arrays composed of **R3**. (C and D) Bright-field TEM micrographs of nano-cones formed on a poly(styrene) film. The inset shows the SAED pattern. (E) 3D projection of AFM image of nano-cones. (F) 2D AFM image of figure shown in E. (G) The corresponding height and width profiles of cones shown in F. (H) SEM image of nano-cones.

To create nano pattern, at first a novel elastomeric PDMS stamp consists of negative replica of 2D arrays of nano-cones was fabricated by replica molding of PDMS on the commercially available AFM standard (master) (Fig. 5.1A). AFM image of a commercial AFM standard (NTMDT-TGT 1) showed that each cone is well separated from each other by  $\sim 1.6 \mu\text{m}$  gap and each cone height and width are about *ca.* 350 nm and *ca.* 835 nm, respectively (Fig. 5.1B). AFM topography of the PDMS stamps showed cone like holes of *ca.* 830 nm diameter (on the surface) and *ca.* 47 nm depth, each separated by *ca.* 1.5  $\mu\text{m}$  gap (Fig. 5.1C and D). The calculated diameter of cones and their separation distance from each other in the PDMS stamp were nearly matched with the original master, except the depth profile. The experimentally estimated depth of each cone in the mold (*ca.* 47 nm; Fig. 5.1D) was less than the master (*ca.* 350 nm; Fig. 5.1B), because the AFM tip was unable to reach to the narrow bottom of the cone, which lead to an

inaccurate measurement. Before LCW technique, the PDMS stamp was cleaned by using hexane and sonicated in ethanol for 20 min.

Nano-patterning of biradical **R3** was carried out by drop casting 20  $\mu\text{L}$  of a 2 mg/mL solution in acetonitrile on glass slide. Prior to use the glass slides was cleaned by sonication in electronic-grade water (Milli-Q-pure quality), in acetone, and 2-propanol (for 2 min each). Adopting LCW technique, on top of this solution the PDMS stamp was carefully placed and uniformly loaded with a weight of 5 g. After 30 min the solution was naturally dried and the PDMS mould was carefully peeled-off (See Fig. 5.1 Top box). AFM investigation of patterned surface or positive replica of master (Fig. 5.1E and 5.2E) showed the formation of 2D cones arrays. AFM profile analyses indicated that each cone height (H) and width at half height (W) profiles were *ca.* 115 nm and *ca.* 750 nm, respectively (Fig. 5.1F and 5.2G). Each cone of the square lattice was well separated from each other by *ca.* 1.85  $\mu\text{m}$  (Fig. 5.1F and 5.2G).

After the successful fabrication of the 2D nano-cone lattice on a hard glass substrate, attempts were made to embed the nano-cone arrays in a transparent polymer film. Embedding the patterns in polymer film provides, flexibility, portability and also suitable for easy to handle foldable future spintronic applications. For this optically transparent polystyrene (PS) was selected as a substrate, since it is easy to handle and dissolves in most of the organic solvents except acetonitrile. Here the choice of the solvent is important, since the polymer should not dissolve in the solvent used for the fabrication of diradical (**R3**) pattern. For the fabrication, at first a solution of PS in toluene was prepared by dissolving 125 mg of PS in 2 mL of toluene. A thin layer of PS was fabricated on a clean and smooth glass substrate of dimension (1.2 cm  $\times$  1.5 cm) by drop casting of 100  $\mu\text{L}$  of the polymer solution. Upon evaporation of the solvent a free standing thin film of thickness around 5-6  $\mu\text{m}$  was obtained. Subsequently, 2D cones composed of compound **R3** were fabricated on the top of the PS layer. The formation of cones was easily observed by confocal optical microscope (Fig. 5.2B) and SEM micrographs (Fig. 5.2H). Similarly for the TEM studies the nano-cone lattice composed of **R3** was prepared on a PS film formed on a carbon coated TEM grid. TEM micrograph showed clear dark and gray contrasts for the cones and polymer film, respectively (Fig. 5.2C). Further the TEM image indicated the flexibility of the paramagnetic cones formed on the PS film (Fig. 5.2D). Selected area electron diffraction (SAED) pattern of the nano-cones showed diffraction spots indicating their crystalline nature (Fig. 5.2D inset).

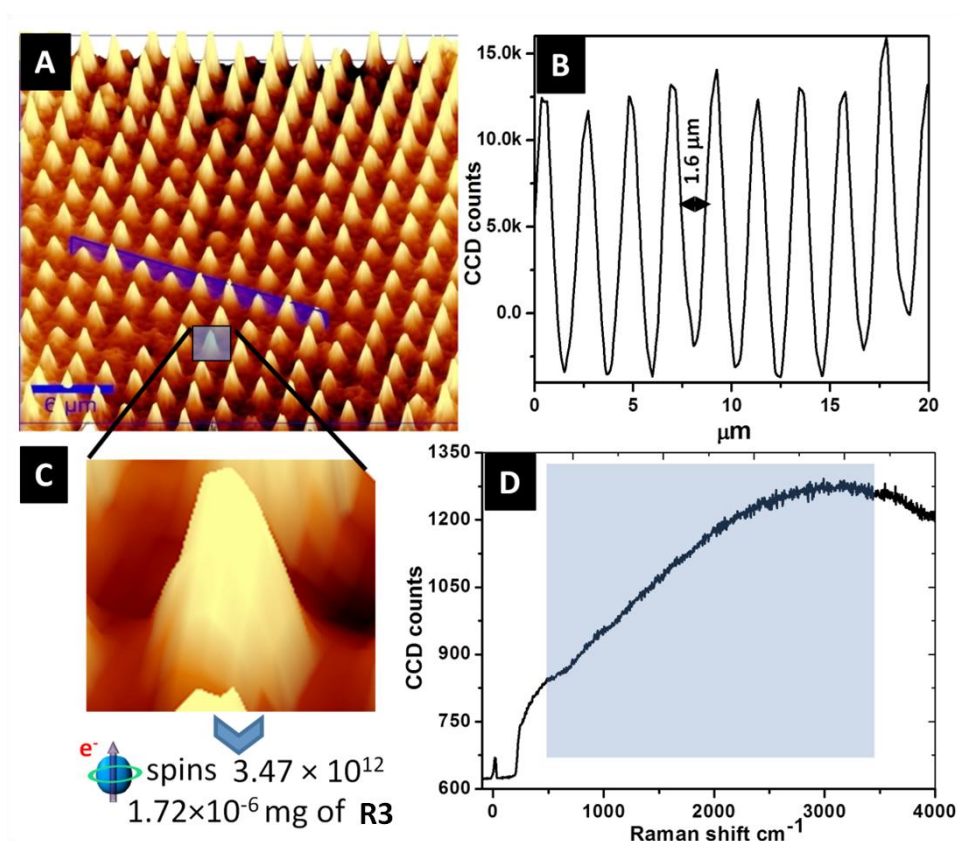


**Figure 5.3** (A) Raman image of nano-cone lattice. (B) CCD counts versus width profile of image A. (C) High resolution image of one single cone. (D) Confocal Raman micro spectroscopic data of nano-cone lattice composed of biradical **R3**. Excitation wavelength  $\lambda_{\text{ex}} = 488 \text{ nm}$  ( $\text{Ar}^+$  Laser).

To confirm the composition of the nano-cones confocal Raman imaging technique was performed (Fig. 5.3). For Raman imaging a  $20 \mu\text{m} \times 20 \mu\text{m}$  area was selected and the laser was illuminated using a  $100\times$  ( $\text{NA} = 0.95$ ) objective. The experiment was carried out at very low laser power ( $\text{Ar}^+$  488) to avoid the damage of the nano-cones. As the result, no clear Raman frequency shift was observed from the sample except a broad inelastic signal. The 3D Raman image generated from the broad band spectrum confirmed the presence of nano-cone 2D square lattice (Fig. 5.3D). The CCD counts from each cone were almost the same, confirming the uniform molecular distribution of **R3** (Fig. 5.3B). These cones were also well separated from each other at a (full width half maximum) distance of  $1.6 \mu\text{m}$ .

### 5.3.1 ESR Spectroscopy Studies:

The magnetic properties of the flexible nano-cone arrays were explored by using X-band EPR spectroscopy measurements down to liquid He temperature. The spin concentration of each nano-cone can be estimated by comparing it with the identical

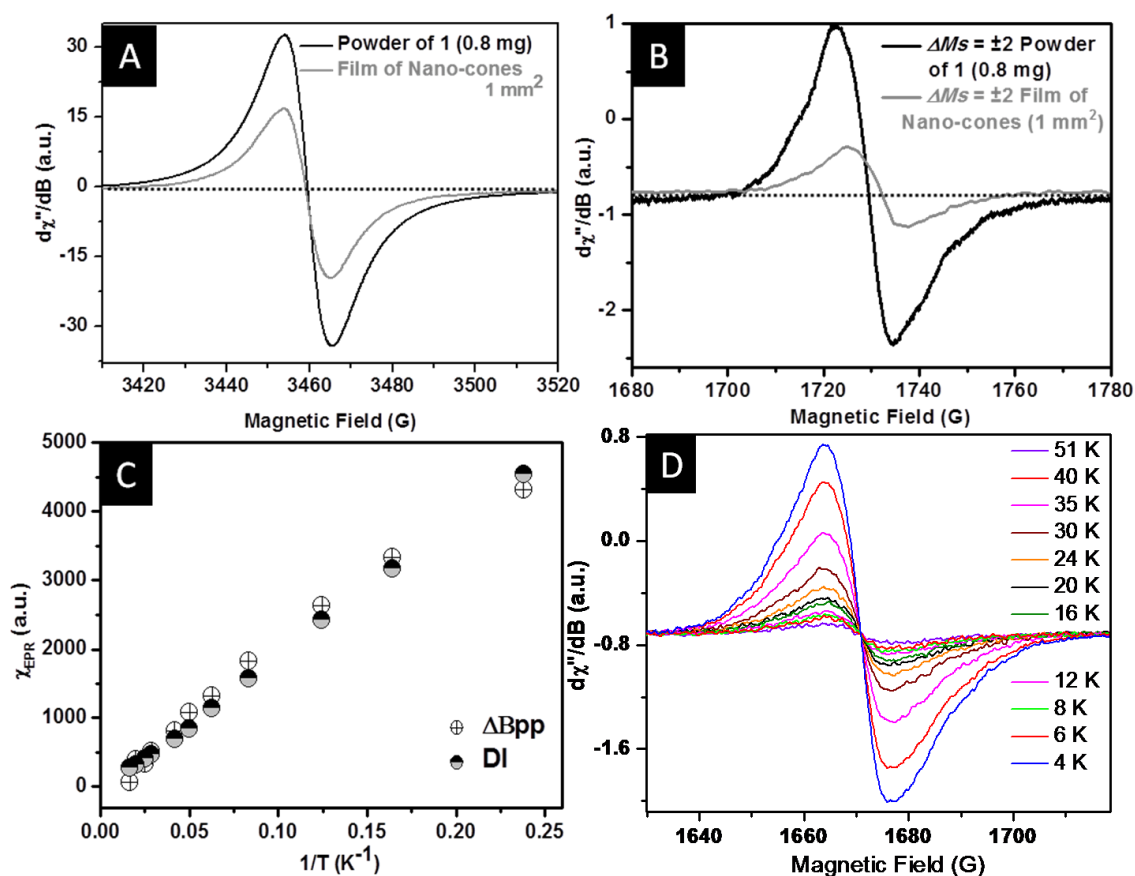


**Figure 5.4** A) Frozen state EPR (X-band) spectra of powder form of **R3** and nano-cones arrays formed in PS film at 120 K. B) The forbidden  $\Delta M_s = \pm 2$  transition of **R3** and nano-cones arrays formed in PS film. C) Temperature dependence of the doubly integrated signal intensities ( $\chi_{EPR}$ ) and the peak-to-peak signal intensities ( $\Delta B_{pp}$ ) of the  $\Delta M_s = \pm 2$  (Curie plot) transitions of film. D) Variable temperature ESR spectra of **R3** ( $c \sim 10^{-3}$  M in toluene) displaying  $\Delta M_s = \pm 2$  at 50.9 – 4.2 K. Experimental parameters for (C): 9.51392 GHz Frequency, 100 kHz modulation frequency, 0.6 G modulation amplitude,  $2 \times 10^4$  power gain, 84 sec sweep time, 41 msec time constant, and 0.1 mW power.

sample of known weight. The number of unpaired electron spins in the sample is proportional to area under the ESR spectrum under non-saturation condition (at low microwave power). To measure the spin concentration at first the ESR spectrum of 0.8 mg of solid powder of **R3** was collected at room temperature and the area under the signal was calculated (Fig. 5.4A). Then, using the same instrumental parameters, ESR spectrum of a 1 mm<sup>2</sup> size PS embedded nano-cone pattern was recorded and the area under the spectrum was calculated by similar signal integration. For similarity, the two ESR experiments were carried out at very low micro-wave power (0.1 mW) to avoid power saturation. Both bulk powder and film composed of nano-cones showed  $\Delta M_s = \pm 1$  and  $\Delta M_s = \pm 2$  transitions (Fig. 5.4A and B). By comparing the spectra of powder and film composed of nano-cones, the weight of the di-NN radical **R3** on the film was determined, which was 0.43 mg (see Fig. 5.4A for a rough estimation). The number of nano-cones in

1 mm<sup>2</sup> area of the PS film was roughly estimated as  $\sim 25 \times 10^4$ ; hence each cone consists of  $1.72 \times 10^{-6}$  mg of **R3**. In other words, for a biradical, the number of spins in each cone is  $3.47 \times 10^{12}$ .

Furthermore the temperature dependency of the  $\Delta M_s = \pm 2$  transitions signal intensities of 2D nano-cone lattice formed on the PS film was carried out down to 4.2 K (Fig. 5.4C). These measurements were also done at low microwave powers in order to ensure that the signals were not saturated. The plot of the doubly integrated ( $\chi_{\text{EPR}}$ ) and the peak-to-peak ( $\Delta B_{\text{pp}}$ ) signal intensities of the  $\Delta M_s = \pm 2$  signal versus inverse temperature showed a strong increase of the  $\chi_{\text{EPR}}$  and  $\Delta B_{\text{pp}}$  down to cryogenic temperature (Fig. 5.4C). The strong increase in the  $\chi_{\text{EPR}}$  value clearly suggested the increase in the triplet state population with decrease of temperature in accordance with Curie-like magnetic behavior. Similarly, the variable temperature ESR spectra of **R3** ( $c \sim 10^{-3}$  M in toluene) displayed an increase in the  $\Delta M_s = \pm 2$  signal intensity from 51 K to 4.2 K is shown in figure 5.4D.

## 5.4 Conclusions:

This chapter demonstrated the fabrication strategy to generate nano-cone 2D lattice on hard and soft substrates. Both optimization and controlling the number of spins of paramagnetic nanostructures were successfully carried out. This presented general methodology can be extended to a wide variety of paramagnetic molecules, such as monoradicals, weakly coupled biradical systems, single molecule magnets and also for spin cross-over systems.

## References:

1. Pomerantz, M.; Pollak, R. A. *Chem. Phys. Lett.* **1975**, *31*, 602.
2. (a) Iwamura, H.; Koga, N. *Acc. Chem. Res.* **1993**, *26*, 346-351; (b) Rajca, A. *Chem. Rev.* **1994**, *94*, 871; (c) Lahti, P. M. Ed. *Magnetic Properties of Organic Materials*; Marcel Dekker: New York **1999**, 1-713; (d) Minamoto, M.; Matsushita, M. M.; Sugawara, T. *Polyhedron* **2005**, *24*, 2263; (e) Mitsutaka, O.; Yasutaka, K.; Takeshi, T.; Kizashi, Y. *Polyhedron* **2005**, *24*, 2330; (f) Atsumi, H.; Maekawa, K.; Nakazawa, S.; Shiomi, D.; Kitagawa, K. S. M.; Takui, T.; Nakatani, K. *Chem.-Eur. J.*, **2012**, *18*, 178. g) Sato, K.; Nakazawa, S.; Rahimi, R.; Ise, T.; Nishida, S.; Yosh, T.; Mori, N.; Toyota, K.; Shiomi, D.; Yakiyama, Y.; Mo, Y.; Kitagawa, M.; Nakasuji, K.; Nakahara, M.; Hara, H.; Hofer, P. C. P.; Takui, T. *J. Mater. Chem.* **2009**, *19*, 3739.
3. Tamura, M.; Nakazawa, Y.; Shiomi, D.; Nozawa, K.; Hosokoshi, Y.; Ishikawa, M.; Takahashi, M.; Kinoshita, M. *Chem. Phys. Lett.* **1991**, *186*, 401.

4. Agusti, G.; Cobo, S.; Gaspar, A. B.; Molnar, G.; Moussa, N. O.; Szilagyi, P. A.; Palfi, V.; Vieu, C.; Munoz, M. C.; Real, J. A.; Bousseksou, A. *Chem. Mater.* **2008**, *20*, 6721.
5. Klauk, H.; Gundlach, D. J.; Bonse, M.; Kuo, C. C.; Jackson, T. N. *Appl. Phys. Lett.* **2000**, *76*, 1692. (b) Goodberlet, J. G. *Appl. Phys. Lett.* **2000**, *76*, 667.
6. Quintero, C. M.; Guralskiy, I.; Salmon, L.; Molnár, G.; Bergaud, C.; Bousseksou, A. *J. Mater. Chem.* **2012**, *22*, 3745.
7. (a) Thibault, C.; Molnar, G.; Salmon, L.; Bousseksou, A.; Vieu, C. *Langmuir* **2010**, *26*, 1557. (b) Kaehr, B.; Shear, J. B. *J. Am. Chem. Soc.* **2007**, *129*, 1904.
8. (a) Xia, Y.; Kim, E.; Whitesides, G. M. *Chem. Mater.* **1996**, *8*, 1558. (b) Hwang, H.; Kang, G.; Yeon, J. H.; Nam, Y.; Park, J. -K. *Lab Chip*, **2009**, *9*, 167.
9. (a) Xia, Y. N.; Whitesides, G. M. *Annu. Rev. Mater. Sci.* **1998**, *28*, 153. (b) Cavallini, M.; Bergenti, I.; Milita, S.; Kengne, J. C.; Gentili, D.; Ruani, G.; Salitros, I.; Meded, V.; Ruben, M. *Langmuir* **2011**, *27*, 4076.
10. (a) Ohdaira, Y.; Noguchi, K.; Shinbo, K.; Kato, K.; Kaneko, F. *Colloids and Surfaces A: Physicochem. Eng. Aspects* **2006**, *284*, 556. (b) Wiesmann, R.; Kalveram, S.; Rudolph, S.; Johnck, M.; Neyer, A. *Electro. Lett.* **1996**, *32*, 2329.
11. (a) Kumar, A.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1498. (b) Wilbur, J. L.; Kumar, A.; Biebuyck, H. A.; Kim, E.; Whitesides, G. M. *Nanotechnology* **1996**, *7*, 452. (c) Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 2790. (d) Lange, S. A.; Benes, V.; Kern, D. P.; Horber, J. K. H.; Bernard, A. *Anal. Chem.* **2004**, *76*, 1641. (e) Thibault, C.; Berre, V. L.; Casimirius, S.; Trevisiol, E.; Francois, J.; Vieu, C. *J. Nanobiotech.* **2005**, *3*, 7.
12. (a) Mannini, M.; Sorace, L.; Gorini, L.; Piras, F.M.; Caneschi, A.; Magnani, A.; Menichetti, S.; Gatteschi, D. *Langmuir* **2007**, *23*, 2389. (b) Mas-Torrent, M.; Crivillers, N.; Mugnaini, V.; Ratera, I.; Rovira, C.; Veciana, J. *J. Mater. Chem.* **2009**, *19*, 1691.
13. Basak, S.; Hui, P.; Boodida, S.; Chandrasekar, R. *J. Org. Chem.* **2012**, *77*, 3620.
14. Basak, S.; Hui, P.; Chandrasekar, R. *Chem. Mater.* **2013**, *25*, 3408.
15. (a) Hui, P.; Arif, K. Md.; Chandrasekar, R. *Org. Biomol. Chem.* **2012**, *10*, 2439. (b) Hui, P.; Chandrasekar, R. *Chem. Plus. Chem.* **2012**, *12*, 1051.

# 6

## 6.1 Conclusions:

This thesis entitled “*Nano-/Micro-Scale Organic Paramagnetic Materials: Syntheses, Characterization, Self-Assembly, Optical Wave Guiding and Device Structures*” described the syntheses of several mono and di radicals of 2,6-bis(pyrazol-1-yl)pyridine (BPP) derivatives and macrocycles. It presented the exploitation of their self-assembling properties to create nano/micro scale molecular tubes, arrays and patterns possessing unique photonic and magnetic properties. The ultimate aim of the thesis is to create paramagnetic molecular solids down to nano/micro domains (Fig. 6.1). Hence in the beginning much attention has been paid to synthesize of mono and di radicals to study their spin-spin exchange and dipolar coupling, which are described in *chapters 2 and 4*.

Later we have adopted *top-down* and *bottom-up* nano technological approaches to achieve our goals. *Chapter 3 and 4* provides a general bottom-up approach for fabrication of paramagnetic organic porous film, vesicles, nano particles and rectangular nano/micro tubes using the NN and OVZ radicals. Then by following *top-down* technique we have developed a methodology to fabricate paramagnetic nano/micro patterns and arrays on an optically transparent polymer film towards future spintronics device applications, which are discussed in *chapter 5*.

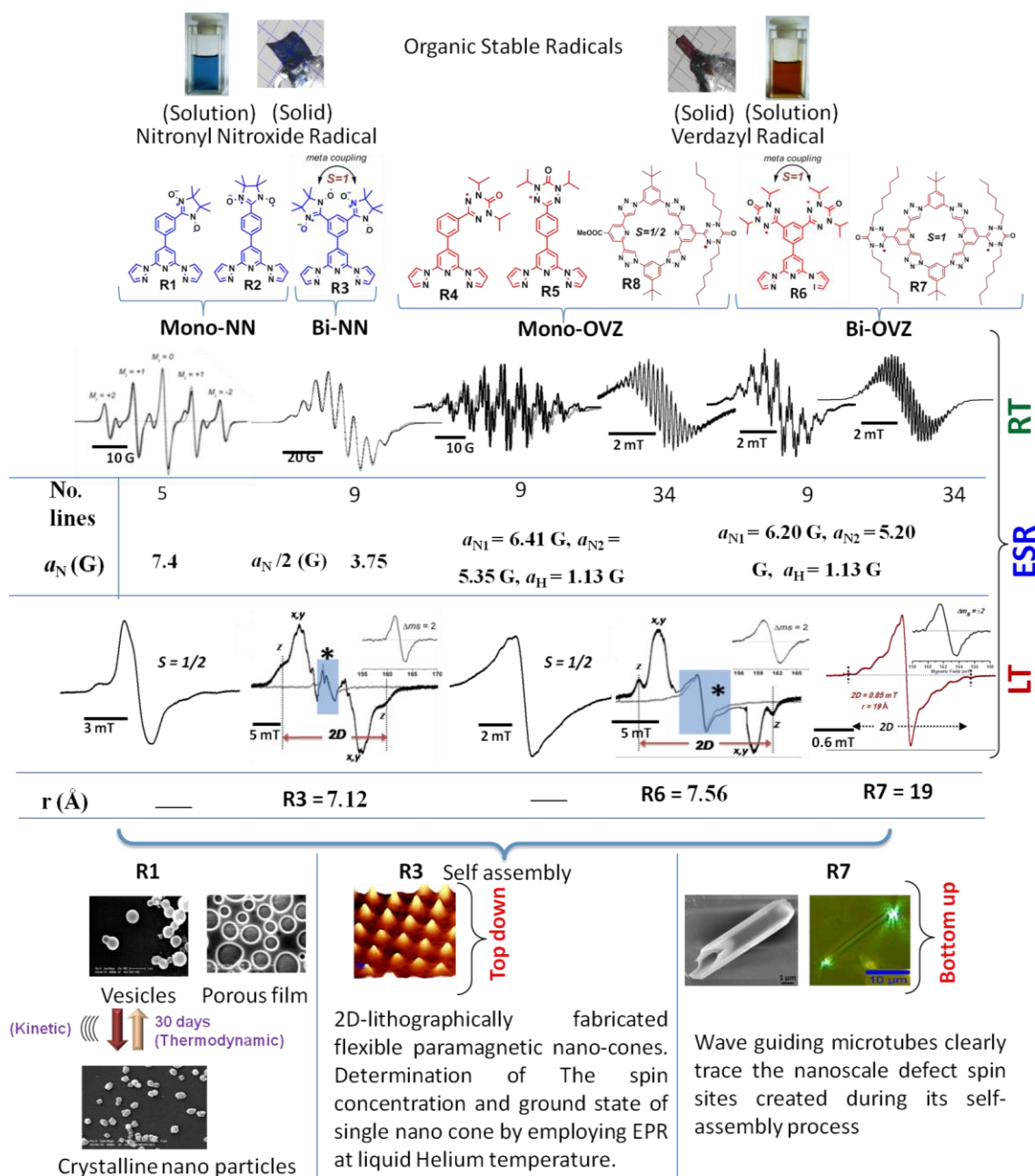


**Figure 6.1** Summary of the thesis.

Chapter 2 presented the synthesis of a series of nitronyl nitroxide (NN), and oxoverdazyl (OVZ) based mono-, and bi-radicals attached to 4-phenyl-2,6-bispyrazolylpyridine coupling unit, their optical, and electron spin resonance (ESR) spectroscopy studies. A connection between the spin density polarization and the zero-field splitting (zfs) was made for the NN and OVZ based biradicals. A comparative analysis showed that the ground state spin multiplicity of NN biradicals is probably triplet ( $S = 1$ ) and for OVZ biradicals it is nearly degenerate singlet ( $S = 0$ ) triplet states. The difference in the  $D$  and  $r$  values between the two types of biradicals attached to the same unsaturated molecular backbone (**R3** and **R6**) are

$0.00118\text{ cm}^{-1}$  and ca.  $0.44\text{ \AA}$ , respectively. It is clear that in **R3** the spin density wave is more delocalized into the whole molecular backbone compared to biradical **R6**. Additionally since the amount of spin density wave propagation is also related to the SS exchange interaction ( $J$ ), this obtained results demonstrated that the NN biradicals in **R3** is relatively strongly exchange coupled than that of OVZ biradicals in **R6** i.e.  $J_{\text{NN}} > J_{\text{OVZ}}$ . To combine the SCO effect with SS exchange coupling, a  $[\text{Fe}^{\text{II}}(\text{R4})_2](\text{ClO}_4)_2$ , (**C1**) was prepared. The variable temperature magnetic susceptibility and Raman measurements indicated the operating SCO effect in **C1**, with a  $T_{1/2}$  value over 300 K. Self-assembly studies of **R4** and **C1** exhibited the formation of microrods and nanocrystals, respectively.

In *chapter 3* nano-/micro-scale paramagnetic porous film, reversibly shape shifting vesicles and nanoparticles were successfully prepared in a controlled manner from a stable nitronyl-nitroxide radical derivative using solvent and ultrasound mediated self assembly. this chapter demonstrated, for the first time, controlled generation of paramagnetic solid structures such as porous film, vesicles and NPs from an organic NN radical **R1**. The main driving forces behind the aggregation phenomena is C-H $\cdots$ O type intermolecular H-bonding interactions. The development of micro porous film during the evaporation of acetonitrile solution of **R1** was surface/H<sub>2</sub>O condensation assisted process. Interestingly, **R1** formed soft vesicles in acetonitrile/H<sub>2</sub>O via multi-lamellar mechanism. Ultrasonification technique was employed to reversibly shape shift the vesicles into NPs and vice versa in acetonitrile/H<sub>2</sub>O. These paramagnetic nano-/micro-solids might find interesting applications in wide areas of materials science and biology involving paramagnetism.

An original and innovative technique to probe the optical wave guiding tendency of the tubes is described in *chapter 4*. Mono and dioxo-verdazyl radicals attached to organic shape persistent paramagnetic “Click” macrocycles were successfully synthesized. This chapter demonstrated for the first time, synthesis of shape persistent macrocyclic paramagnetic molecules decorated with stable high-spin state mono and dioxo-verdazyl biradicals. The biradical macrocycle self assembled forming submicro scale paramagnetic organic tubular solids. Laser illumination at one of the open-ends of the tube showed propagation of light to the opposite exit direction. One of the important additional finding in this work is the determination of nano/micro scale spin defect sites in the tube using wave guiding mode Raman spectroscopy. Till now spin-photon interaction is well-known for ferromagnetic metals but paramagnetic organic materials are not yet recognized. On the same

line, these paramagnetic organic tubular solids can also be exploited to understand/establish the spin-photon interactions such as magneto-optical and related effects at cryogenic temperature.

Using a top-down approach paramagnetic 2D nano-cone arrays from a high-spin state ( $S = 1$ ) bi-nitronyl nitroxide radical were fabricated on hard (glass) and flexible (polymer) substrates. The height and width at half height (W) profile of the cones are  $115 \text{ nm} \times 750 \text{ nm}$ , respectively. The nano-cones formed a 2D square lattice pattern and each cone was separated from one another by about  $1.4 \text{ }\mu\text{m}$ . Electron spin resonance (ESR) spectroscopy studies of the nano-cones formed on the polymer substrate ( $1 \text{ mm}^2$ ) revealed that the approximate spin concentration of each cone is  $3.47 \times 10^{12}$  spins. Further cryogenic measurements down to  $4.2 \text{ K}$  indicated the Curie-like behavior of the  $\Delta M_s = \pm 2$  transitions from the biradicals composing the cones. This chapter demonstrated the optimization and controlling the number of spins of paramagnetic nanostructures. This presented general methodology can be extended to a wide variety of paramagnetic molecules, such as monoradicals, weakly coupled biradical systems, single molecule magnets and also for spin cross-over systems.

## Appendix A

### Materials

|                                                    |                               |
|----------------------------------------------------|-------------------------------|
| [Pd(PPh <sub>3</sub> ) <sub>4</sub> ]              | Aldrich, 99%                  |
| Citrazinic acid                                    | Aldrich, 98%                  |
| Cu(I)I                                             | Avra Synthesis Pvt. Ltd. 98%  |
| Eu(tta) <sub>3</sub> ·3H <sub>2</sub> O            | Acros, 98%                    |
| 1,3-diazido-5-tert-butylbenzene                    | Aldrich, 97%                  |
| Fe(ClO <sub>4</sub> ) <sub>2</sub>                 | Aldrich, 98%                  |
| HIO <sub>3</sub>                                   | Sigma Aldrich, 99.5%          |
| I <sub>2</sub>                                     | Finar Reagents, 99.5%         |
| KI                                                 | Merck Chemicals Pvt. Ltd. 99% |
| LiOH                                               | Avra Synthesis Pvt. Ltd. 98%  |
| NaN <sub>3</sub>                                   | Avra Synthesis Pvt. Ltd. 98%  |
| NaNO <sub>2</sub>                                  | Merck Chemicals Pvt. Ltd. 99% |
| POCl <sub>3</sub>                                  | Avra Synthesis Pvt. Ltd. 98%  |
| PPh <sub>3</sub>                                   | Avra Synthesis Pvt. Ltd. 98%  |
| Pyrazole                                           | Aldrich, 98%                  |
| Trifloro acetic acid                               | Aldrich, 99%                  |
| (COCl) <sub>2</sub>                                | Avra Synthesis Pvt. Ltd. 98%  |
| Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> | Aldrich, 99%                  |
| Trimethyl silylacetylene                           | Avra Synthesis Pvt. Ltd. 98%  |
| CuSO <sub>4</sub>                                  | Merck Chemicals Pvt. Ltd. 99% |
| Sodium ascorbate                                   | Merck Chemicals Pvt. Ltd. 99% |
| DBU                                                | Aldrich, 99%                  |
| PCC                                                | Finar Reagents, 99.5%         |
| Triphosgene                                        | Avra Synthesis Pvt. Ltd. 98%  |
| NaBH <sub>4</sub>                                  | Avra Synthesis Pvt. Ltd. 98%  |
| Benzoquinone                                       | Merck Chemicals Pvt. Ltd. 99% |
| Formylphenyl-boronic acid                          | Aldrich, 99%                  |
| <i>m</i> -CPBA                                     | Aldrich, 99%                  |
| NaIO <sub>4</sub>                                  | Aldrich, 99%                  |
| Sodium acetate                                     | Avra Synthesis Pvt. Ltd. 98%  |

## Appendix B

### Instrumentation

#### *Nuclear Magnetic Resonance Spectroscopy*

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. Spectra were recorded using the solvent peaks as the internal standard.

### *Mass Spectroscopy*

Shimadzu LC-MS 2010A equipment was used to record the mass spectra of the isolated compounds following atmospheric pressure chemical ionization (APCI) technique. The mass spectra of high molecular weight compounds were recorded on a Electrospray ionization time-of-flight (ESI-TOF) instrument, HRMS, (Bruker Daltonik, GmbH, Bremen Germany, Microtof Control, Compass 1.3 Microtof S.R3, version 3.0 SR2 Build 66).

### *Elemental Analysis*

Elemental analysis was carried out on a Thermo Finnigan Flash EA-1112 series CHNS analyzer.

### *Infrared Spectroscopy*

FT-IR spectra were recorded on a JASCO FT/IR-5300 or Nicolet 5700 FT-IR. Solid samples were recorded as KBr pellets.

### *Electronic Spectroscopy*

Absorption spectra were recorded on a Shimadzu UV-3600 UV-Vis-NIR Spectrophotometer or Cary 100 Bio UV-Visible spectrophotometer.

### *Transmission Electron Microscopy*

TEM images were obtained on a TECNAI G2 FEI F12 TEM at an accelerating voltage of 120 kV. Samples were prepared by placing a drop of the samples on a polymer (polyvinyl formvar) – coated copper grid (200 mesh) and air drying.

### *Scanning Electron Microscopy*

SEM and FESEM images were recorded on a Philips XL30 ESEM and a HITACHI S-4300SE/N FESEM respectively using beam voltages of 20 kV. The samples were fixed on aluminum platforms using carbon tapes; a conducting connection was made between samples and aluminum platform by silver paint. Samples were coated with a thin layer (3 – 5 nm) of sputtered gold prior to imaging.

*Atomic force microscopy*

Atomic Force Microscopy (AFM) imaging was carried out on NT-MDT Model Solver Pro M microscope using a class 2R laser of 650 nm wavelength having maximum output of 1 mW. All calculations and image processing was carried out by a software NOVA 1.0.26.1443 provided by the manufacturer. The images were recorded in a semi-contact mode using a noncontact mode tip purchased from NT-MDT, Moscow. The dimensions of the tip are as follows: Cantilever length = 95 ( $\pm 5$ )  $\mu\text{m}$ , Cantilever width 30 ( $\pm 5$ )  $\mu\text{m}$ , and Cantilever thickness = 1.5-2.5  $\mu\text{m}$ , Resonate frequency = 140-390 kHz, Force constant = 3.1-37.6 N/m, Chip size = 3.4 $\times$ 1.6 $\times$ 0.3 mm, Reflective side = Au, Tip height = 14-16  $\mu\text{m}$ , Tip curvature radius = 10 nm, and Aspect ratio 3:1-5:1.

*Magnetic Force Microscopy*

Magnetic Force Microscopy (MFM) imaging experiments were carried out on a NT-MDT Model Solver Pro M microscope using a class 2R laser of 650 nm wavelength having maximum output of 1 mW. All calculations and image processing was carried out by a software NOVA 1.0.26.1443 provided by the manufacturer. The images were recorded in a semi-contact mode using a tip side coated with CoCr supplied by NT-MDT, Moscow was used. The quality of the MFM tips was checked by imaging a hard drive.

*Confocal Raman Micro Spectroscopy Studies*

Raman spectra of the samples were recorded on a WI-Tec confocal Raman spectrometer equipped with a Peltier-cooled CCD detector. Using a 600 grooves/mm grating BLZ = 500 nm, the integration time was typically 2.0000 s. Ten accumulations was performed for acquiring a single spectrum. For imaging the integration time was typically 2.000 s, keeping in mind that the x or y resolution is  $\sim 250$  nm four points per line and four line per image was taken for imaging of a  $1\mu\text{m} \times 1\mu\text{m}$  area. A He-Ne 633 nm or Argon-Ion 488nm laser was used as an excitation source for the Raman scattering. All measurements were done at ambient conditions.

*Bulk Magnetic Studies*

The temperature dependent magnetic susceptibility of complexes in the powder state was measured on a Quantum Design vibrating sample magnetometer (VSM-SQUID) setup in the temperature range of 340 $\leftrightarrow$ 2 K at continuous cooling ( $\downarrow$ ) and heating ( $\uparrow$ )

cycles with an applied direct current (DC) magnetic field of 0.5 T. Heating and cooling rate of the sample was kept at a 10 K interval in sweep mode.

#### *Electron Spin Resonance Spectroscopy (ESR) Studies*

X-band EPR spectra were recorded on a JEOL instrument JES-AV-200 as well as on a Bruker-ER073 spectrometer equipped with an EMX microX source. For data analysis Xenon 1.1b.60 software provided by the manufacturer was used. During the liquid helium measurement the temperature was controlled by a temperature controller supplied by Oxford instruments (ITC 503S). Simulations were performed by using SIMFONIA program.

#### *Powder X-ray Diffraction*

Powder X-ray diffraction pattern was recorded on a Philips Model PW 1830 Powder X-ray Diffractometer. CuK $\alpha$  radiation was used.

#### *Computation*

Computational studies (DFT; B3LYP) were performed to determine the spin density distribution patterns of radicals.

#### *Single Crystal X-ray Diffraction: Data Collection, Solution and Refinement*

The X-ray intensity data of crystals were collected on a Bruker Nonius SMART APEX CCD area detector system equipped with a graphite monochromator and a MoK $\alpha$  fine-focus sealed tube ( $\lambda = 0.71073 \text{ \AA}$ ) operated at 1750 W power (50 kV, 35 mA). All data were collected at 298K. The detector was placed at a distance of 6.003 cm from the crystal; exposure time (10-20 sec/frame) was set based on the data quality. The frames were integrated with the Bruker SAINT Software package using a narrow-frame integration algorithm. Data were corrected for absorption effects using the multi-scan technique (SADABS). The structure was solved and refined using the direct method analysis in Bruker SHELXTL Software Package.

## RESEARCH PUBLICATIONS

1. Basak, S.; **Hui, P.**; Chandrasekar, R. "Regio-Selective Synthesis of Brominated and Iodinated 2',6'-Bispyrazolyl Pyridine Units"  
*Synthesis*, **2009**, 23, 4042-4048.
2. **Hui, P.**, Khaja. Md. Arif, and Chandrasekar, R. "Syntheses, Optical and Intramolecular Magnetic Properties of Mono- and Di-Radicals Based on Nitronyl Nitroxide and Oxoverdazyl Groups Appended to 2,6-Bispyrazolylpyridine Core"  
*Org. Biomol. Chem.* **2012**, 10, 2439-2446. **(Chapter 2)**
3. Basak, S.; **Hui, P.**; Boodida, S.; Chandrasekar, R. "Micro-Patterning of Metallo-Polymers: Syntheses of Back-to-back Coupled Octylated 2,6-Bis(pyrazolyl)pyridines Ligands and their Solution Processable Coordination Polymers"  
*J. Org. Chem.* **2012**, 77, 3620-3626.
4. **Hui, P.** and Chandrasekar, R. "Shape-Defined and Shape-Shifting Paramagnetic Organic Nano-/Micro-Structures Derived from Doublet State Nitronyl Nitroxide Radical"  
*Chem. Plus. Chem.* **2012**, 12, 1062- 1065. **(Chapter 3)**
5. **Hui, P.** and Chandrasekar, R. "Light Propagation in High-Spin Organic Microtubes Self-Assembled from Shape Persistent Macrocycles Carrying Oxo-Verdazyl Biradicals"  
*Adv. Mater.* **2013**, 25, 2963-2967. **(Chapter 4)**
6. Basak, S.; **Hui, P.**; Chandrasekar, R. "Flexible and Optically Transparent Polymer Embedded Nano/Micro Scale Spin Cross-Over Fe(II) Complex Patterns/Arrays"  
*Chem. Mater.* **2013**, 25, 3408-3413.
7. **Hui, P.** and Chandrasekar, R. "2D Ordering of Paramagnetic Nano-Cone Square Lattice from Nitronyl-Nitroxide Biradicals on Hard and Flexible Substrates" (*is in Preparation*). **(Chapter 5)**

## PRESENTATIONS IN CONFERENCES AND SYMPOSIUMS

1. **Hui, P.;** Chandrasekar, R. "Paramagnetic Nano/Micro Structures: Syntheses, Optical and Magnetic Properties of Stable Nitronyl Nitroxide and Oxoverdazyl Radicals"

Poster presented in FICS, IITG, Dec 2-4, 2012, Guwahati, India. (**BEST POSTER AWARD**)

2. **Hui, P.;** Chandrasekar, R. "Syntheses, Optical and Magnetic Properties of Nitronyl Nitroxide and Oxoverdazyl Radicals"

Poster presented in Chemfest-2011, 8<sup>th</sup> Annual In-House Symposium held at University of Hyderabad, Hyderabad, India.

3. **Hui, P.** "An ordered fabrication of two-dimensional paramagnetic square lattices and waveguiding of paramagnetic tube"

Delivered an oral presentation as well as a poster presentation in Winter School-2013 on Frontiers in Material Science organized by JNCASR-Cambridge-SSL winter school, Dec 2-6, 2013, Bangalore, India. (**1<sup>st</sup> PRIZE FOR ORAL PRESENTATION**)

4. **Hui, P.** "Paramagnetic Organic Nano-/Micro-Structures from Nitronyl-Nitroxide and Oxoverdazyl Radicals"

Delivered an oral presentation as well as a poster presentation in CHEMFEST-2013 held in University of Hyderabad, Hyderabad, India.

5. **Hui, P.** "Functional (Photonic and Magnetic) Nano/micro Scale Solids for use in Magnetic/Opto-Electronic/Sensing Devices"

Oral presentation at Dr. K. V. Rao 9th Annual Research Award Program, Hyderabad, India, on March 15, 2014. (Received "**WINNER AWARD**")

6. **Hui, P.;** Chandrasekar, R. "Light Propagation in High-Spin Organic Microtubes Self-Assembled from Triplet State Macrocycles Carrying Oxoverdazyl Biradicals"

Poster presented Directions in Materials Science held in JNCASR during 30<sup>th</sup> Nov-1<sup>st</sup> Dec, 2013.

## Pramiti Hui

[pramitibhu@gmail.com](mailto:pramitibhu@gmail.com)/ [ch08ph38@uohyd.ernet.in](mailto:ch08ph38@uohyd.ernet.in)

### Personal Details:

|                |                  |
|----------------|------------------|
| Name           | Pramiti Hui      |
| Father's name  | Pranam Kumar Hui |
| Nationality    | Indian           |
| Sex            | Female           |
| Marital Status | Married          |



### Education:

- 2009- 2014: **PhD in Materials Chemistry**, School of Chemistry, University of Hyderabad , India.
- 2006-2008: **M.Sc (Chemistry)**, Department of Chemistry, Banaras Hindu University, Varanasi, India.
- 2002-2005: **B.Sc (Chemistry Hons)**, Midnapur College (Vidyasagar University), WB, India.
- 2000-2002: **12<sup>th</sup> (Intermediate)**, WBCHSE,WB, India.

### Awards and Recognitions:

- *WINNER AWARD for oral presentation at Dr. K. V. Rao-2014, Annual Research Award Program, Hyderabad, India, on May 22, 2014.*
- *1<sup>st</sup> award for oral presentation in winter school-2013 on Frontiers in Material Science organized by JNCASR-Cambridge-SSL winter school Dec 2-6, 2013.*
- *Best poster award in FICS held at IITG on Dec 2-4, 2012.*
- *2010 – 2013 Awarded as a Senior Research Fellow (SRF) from Council of Industrial Scientific Research (CSIR), New Delhi, India.*
- *2008–2010 Awarded as a Junior Research Fellow (JRF) from CSIR, New Delhi, India.*
- *Jun. 2008 Qualified All India level Junior Research Fellowship and Lectureship awarded by CSIR-JRF (NET), New Delhi, India.*
- *Qualified IIT JAM 2006 All India level.*