

Rheniumtricarbonyl-based Helicates and Double Helical Molecules

A Thesis Submitted for the Degree of
DOCTOR OF PHILOSOPHY

By

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April 2022

*Dedicated to
My Mom*

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STATEMENT

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 **Prof. M. Sathiyendiran.**

In keeping with the general practice of reporting scientific observations, due acknowledgments have been made wherever the work described is based on the findings of other investigators.

Hyderabad

April 2022

A handwritten signature in blue ink, appearing to read "Soumya K. R.", is written above the printed name.

Soumya K. R

(16CHPH27)

DECLARATION

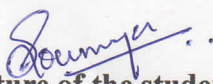
I, Soumya K. R hereby declare that this thesis entitled "*Rheniumtricarbonyl-based Helicates and Double Helical Molecules*" submitted by me under the guidance and supervision of Prof. M. Sathiyendiran is a bonafide research work which is also free from plagiarism. I also declare that it has not been submitted previously in part or in full to this university or any other university or institution for the award of any degree or diploma. I hereby agree that my thesis can be deposited in Shodhganga/INFLIBNET.

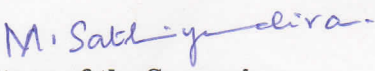
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CERTIFICATE

This is to certify that the thesis entitled “**Rheniumtricarbonyl-based Helicates and Double Helical Molecules**” submitted by **Soumya K. R** bearing registration number 16CHPH27 in partial fulfillment of the requirements for award of the Doctor of Philosophy (Ph.D.) is a bonafide work carried out by her under my supervision and guidance in the School of Chemistry, University of Hyderabad. This thesis is free from plagiarism and has not been submitted previously in part or in full to this or any other University or Institution for award of any degree or diploma. Further, the student has two publications before submission of the thesis for adjudication and has produced evidences for the same in the form of reprints.

Parts of this thesis have been published in the following publications:

1. **Soumya, K. R.**; Arumugam, R.; Shankar, B.; Sathiyendiran, M. *Inorg.Chem.* **2018**, 57, 10718-10725 (**Chapter 2**).
2. Arumugam, R.; Shankar, B.; **Soumya, K. R.**; Sathiyendiran, M. *Dalton Trans.*, **2019**, 48, 7425-7431 (**Chapter 3**).

She has also made presentations in the following conferences:

1. Presented a poster in **Chem-Fest-2017**, March 2017, held at School of Chemistry, University of Hyderabad, India.
2. Presented a poster in **NMSTC (National Meeting of Synthetic and Theoretical Chemists)**, 13-14 October 2017 at School of Chemistry, University of Hyderabad, India.
3. Presented a poster in **Chem-Fest-2018**, 9-10 March 2018 held at School of Chemistry, University of Hyderabad, India.
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5. Presented a poster in **International Conference on Advances in Chemical Sciences and Technologies (ACST)-2019**, 23-25 September 2019 at Department of Chemistry, National Institute of Technology, Warangal, India. (**Best Poster Award**).
6. Presented a poster in **Chem-Fest-2020**, held at School of Chemistry, University of Hyderabad, India.

Further the student has passed the following courses towards the fulfilment of coursework requirement for Ph. D.

Sl. No.	Course No.	Title of the Course	No. of Credits	Grade
1.	CY801	Research Proposal	3	A
2.	CY805	Instrumental Methods-A	3	B
3.	CY806	Instrumental Methods-B	3	B
4.	CY451	Main Group & Inner Transition Elements	3	B

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ACKNOWLEDGEMENTS

I would like to express my heartfelt gratitude to **Prof. M. Sathiyendiran**, my research supervisor for his constant guidance, encouragement, inspiration and motivation. The care and support he has shown gives a true strength and spirit to carry out work. I am grateful to him for giving me the freedom to work in the lab and for his enormous efforts to make our work move smoothly.

I would like extend my sincere thanks to doctoral committee members, Prof. Samar Kumar Das and Prof. K. Muralidharan for their support and concern. I thank present and former deans, School of Chemistry, University of Hyderabad and all the faculty members of school of chemistry for their help and support in various occasions. My special thanks to UGC for providing the fellowship (UGC-JRF), DST and IoE for financial support during the Ph.D. tenure.

I would like to thank all non-teaching members of school of chemistry for their cooperation, especially Mr. Durgesh and Mr. Mahender (NMR, School of Chemistry), Mrs. Asia Parwez and Dr. Manasi Dalai (HRMS, School of Chemistry), Mr. A.V. R. Kumar and Mr. Mahesh Rathod (SC-XRD, School of Chemistry) Mrs. Gomati and Mr. Anand (FTIR, ACRHEM, UoH and School of Chemistry), for their assistance in work with instruments during my research work.

I thank all the seniors from our laboratory and especially Dr. Bhaskaran Shankar and Dr. Ramar Arumugam for their contributions to the area I have worked. I would like to thank Dr. P. Rajakannu, Dr. Sruthi Bayya and Dr. C. Kiran Kumar for their help and suggestions provided during work tenure. I thank my colleagues Ms. Mamina Bhol, Ms. Isha Mishra, Ms. Moon Kedia, Ms. Upasana Phukon, Ms. Reema Borkar, Mr. Vengadesh and Ms. Diya Raveendran for their help and support during my entire Ph.D. I am very thankful to the cooperation and coordination of my lab mates while carrying out the research work. I would like to specially thank Ms. Isha Mishra for her cooperation, help, support, encouragement and motivation she has given me during entire PhD tenure and especially, in the final stages of my work. I also thank all research scholars of school of chemistry for the support and help at various instances.

Apart from my labmates I would like to express my sincere thanks to all my seniors and friends especially, Dr. Anjana K. O, Jyotsna, Kalyani, Suchitra, Radhika, Anju Joseph, Bhuvaneswari, Divya Madhuri, Latha, Priyatharsini, Nanda Kishore, Mujahid, Ishfaq, Asif, Ankit Kumar for making my stay pleasant and memorable. I would like to specially thank Jyotsna Bania, Isha Mishra, Noorul Huda and Kalyani for being with me during tough times and for the care, love, support and encouragement they have given to me.

I am deeply indebted to all my teachers right from my school to the University for the excellent training I received throughout my academics. I would like to thank my teachers, Dr. P. V. Sreenivasan, Dr. Benny Cherian, Dr. Lopez Mathew, Dr. Sheela Kumari Issac, Dr. Simi Pushpan, Mrs. Minu Joys, Dr. Jenish Paul, Mrs. Smita Roy whose teaching have a great impact in pursuing Ph.D. It's a great pleasure to thank my beloved friends, Jisna, Shilpa, Lakshmi, Haseena, Anjumol, Gladiya, Veena, Sarath, Vivek, Sanu and Nikhil Krishna on this special occasion who has given a great support and encouragement. I would like to extend my thanks to all my BSc and MSc friends, Reshma, Mariya, Amrutha, Abhayambika, Jooly, Remya, for their care, support and the positive impact given to me. My special thanks to Fr. Manoj, Sheela aunty and Sosa aunty for their care, love and support during my hardships.

Finally, I would like to express my deep sense of gratitude to my beloved mother Mrs. Omana Raju, whose belief in me had given a great strength and inspiration in pursuing my studies. Thank you mom for being always there for me and for the endless care, love, support and encouragement given to me. I would like to extend my thanks to my beloved father (Mr. M. C. Raju), brothers (Mr. Rajiv K. R and Mr. Sajeesh K. R), sister-in-law (Mrs. Hima Rajiv), niece (Gourinanda) and nephew (Goutham Krishna) for their love, care and support. I could overcome every hurdle in my path only because of their love and affection. Their support and encouragement has led me to this position. I would also like to specially thank my cousin sister, Ms. Neethu Babu for her support and encouragement.

Soumya K. R

COMMON ABBREVIATIONS

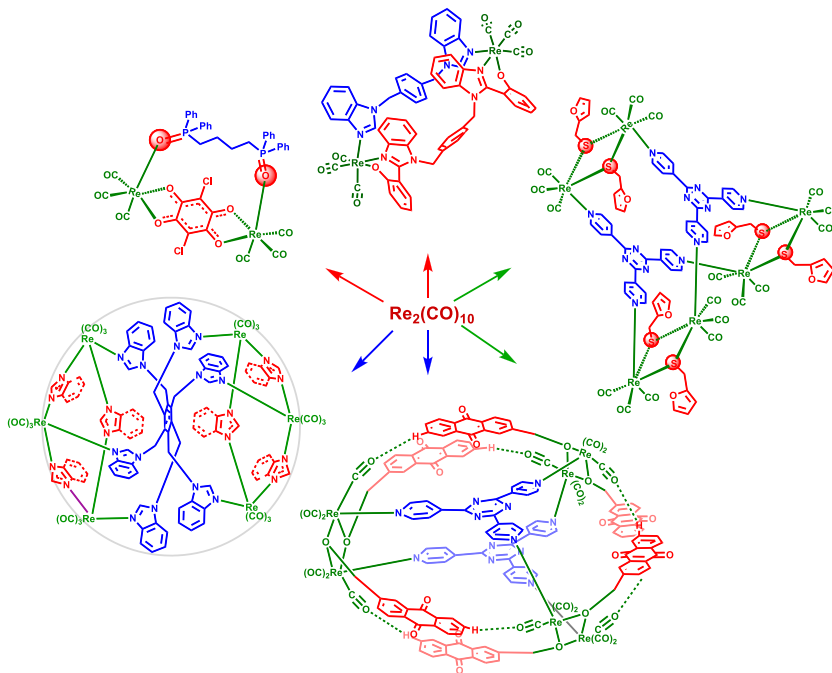
SCCs	Supramolecular Coordination Complexes
<i>fac</i>	facial
2D	Two Dimensional
3D	Three Dimensional
DMSO	Dimethyl sulfoxide
THF	Tetrahydrofuran
DMF	N,N-Dimethylformamide
BCL	Bis-chelating ligand
MLCT	Metal-to-ligand charge transfer
DTE	1,2-dithienylethene
UV	Ultraviolet
ATR-IR	Attenuated Total Reflectance Infrared spectroscopy
FT-IR	Fourier-transform Infrared spectroscopy
NMR	Nuclear magnetic resonance
ESI-TOF-MS	Electrospray Ionization Time-of-Flight Mass Spectrometry
SCXRD	Single Crystal X-Ray Diffraction
SO ₃ ²⁻	Sulfite
SO ₄ ²⁻	Sulfate
Na ₂ SO ₄	Sodium sulfate
NaHSO ₃	Sodium bisulfite
im	imidazole
H ₂ -RBC	Rigid bis-chelating
EA	Ethyl acetate
HR-MS	High resolution mass spectrometry
bim	benzimidazole
H ₂ -FBC	Flexible bis-chelating
DNA	Deoxyribonucleic acid
tbz	Thiabendazole (2-(4-Thiazolyl)benzimidazole)
Me	Methyl

SYNOPSIS

The thesis entitled “**Rheniumtricarbonyl-based Helicates and Double Helical Molecules**” consists of six chapters.

Chapter 1: Introduction

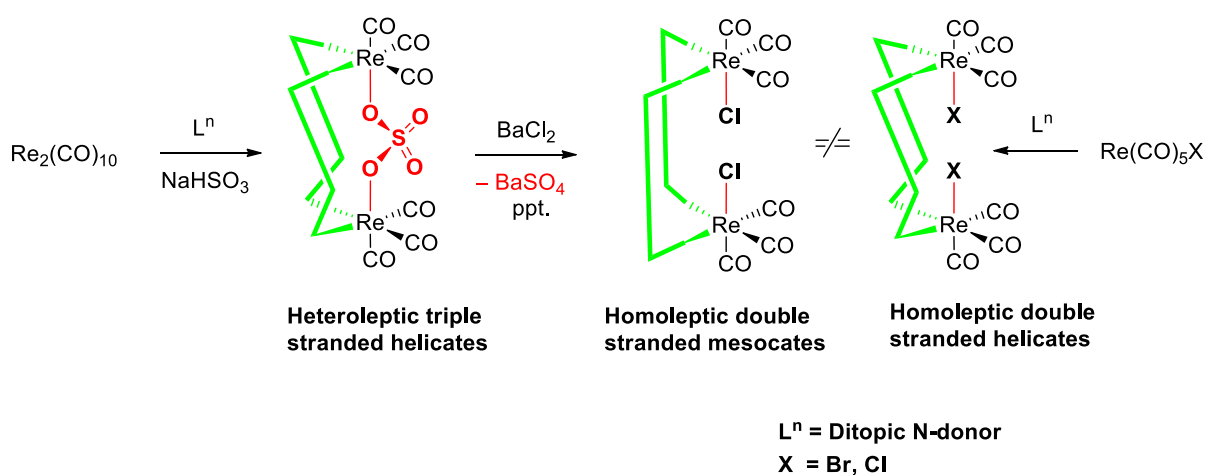
Chapter 1 begins with the general introduction of rheniumtricarbonyl core based supramolecular coordination complexes (SCCs) and their synthesis using various combinations of predesigned ligands (Scheme 1). Further, the developments of coordination-driven self-assembly using *fac*-Re(CO)₃ core and organic building blocks are discussed. The chapter highlights recent reports on well-defined cyclic structures, key design principles and functional properties with the aim to show their utility in building new SCCs using predesigned organic ligands and their potential for various scientific fields. In addition, few synthetic methodologies known earlier are also included here as those approaches can have potential for making new complexes with interesting properties and applications.



Scheme 1. Synthetic route for various Re(I) based SCCs.

Chapter 2: Sulfate donor-based helicates and mesocates

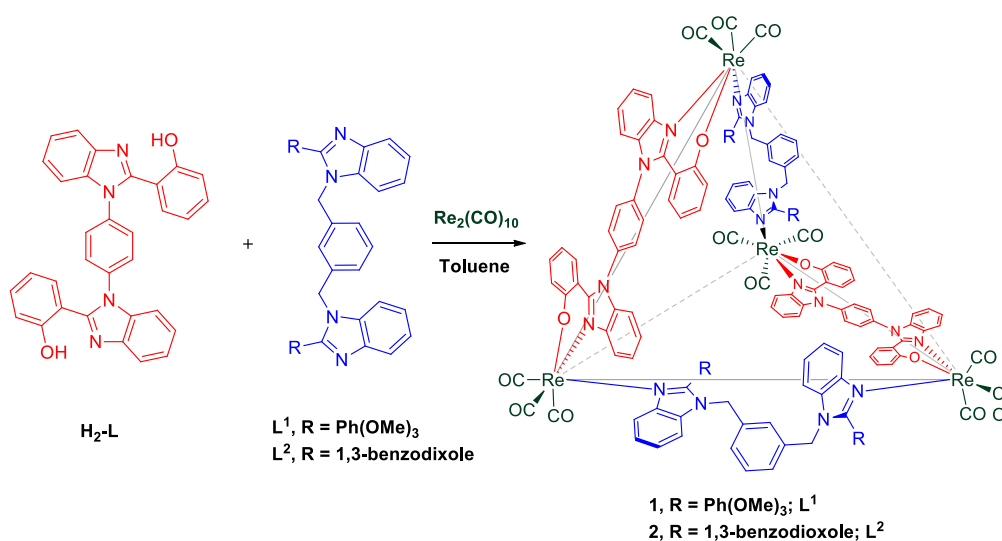
This chapter describes the synthesis and characterization of sulfate donor based *fac*-Re(CO)₃ core containing heteroleptic triple-stranded dinuclear helicates. Further, the transformation of sulfate based heteroleptic triple-stranded helicates to sulfate free homoleptic double-stranded mesocates were discussed. Sulfate donor based supramolecular coordination complexes (SCCs) [*fac*-Re(CO)₃](μ-SO₄)(Lⁿ)₂{*fac*-Re(CO)₃} (**1–3**) were obtained using flexible ditopic N donor ligands (**1**, Lⁿ = L¹; **2**, Lⁿ = L²; **3**, Lⁿ = L³) (n = 1–3), NaHSO₃, and Re₂(CO)₁₀ in a one-pot, multicomponent, coordination-driven self-assembly approach, in which SO₃²⁻ get oxidized to SO₄²⁻ during the reaction and acts as building framework (Scheme 2). Complexes **1–3** were characterized using ATR-IR, ESI-TOF-MS and ¹H NMR spectroscopy. The molecular structures of the complexes **1–3** were confirmed using single crystal X-ray diffraction analysis. The transformation of dinuclear heteroleptic triple stranded helicates to dinuclear homoleptic double stranded mesocates [{Re(CO)₃Cl}₂(Lⁿ)₂] (Lⁿ = L¹, L², L³; **4a–6a**) was achieved by the addition of BaCl₂. The direct reaction of Re(CO)₅X (X = Cl, Br) with L¹/L²/L³ yielded dinuclear homoleptic double stranded helicates [{Re(CO)₃X}₂(Lⁿ)₂] (**4b–6b** and **7–9**).



Scheme 2. Synthesis of heteroleptic and homoleptic helicates/mesocates.

Chapter 3: Rheniumtricarbonyl-based neutral heteroleptic tetrahedrons

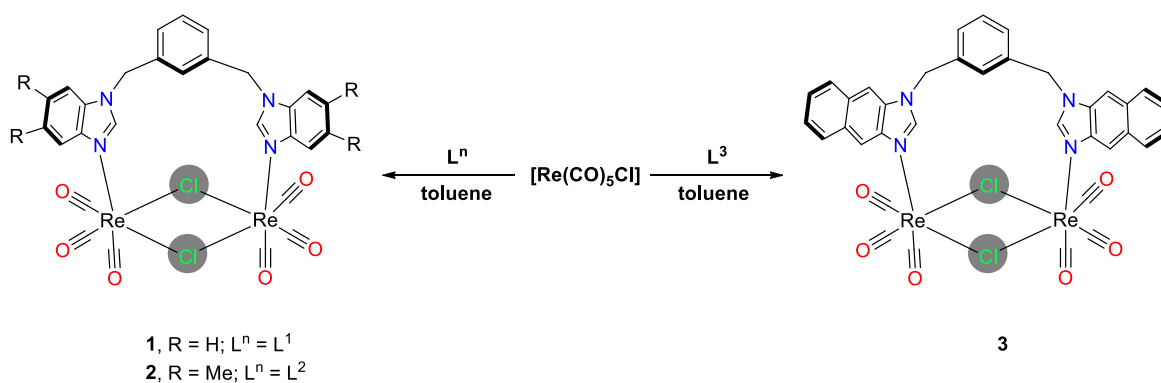
Chapter 3 discusses the synthesis and characterization of *fac*-Re(CO)₃ core based neutral heteroleptic tetrahedrons. Two new flexible ditopic nitrogen donors possessing a xylene spacer and 2-(3,4,5-trimethoxyphenyl)benzimidazole (L¹) / 2-(1,3-benzodioxole)benzimidazole (L²) as a coordinating unit and one rigid bis-chelating ligand consisting of two 2-hydroxyphenylbenzimidazolyl motifs and a central phenylene spacer (H₂-L) were synthesized and further used with Re₂(CO)₁₀ for making a new type of neutral, heteroleptic tetrahedral-shaped supramolecular coordination complexes [{*fac*-Re(CO)₃]₄(Lⁿ)₂(L)₂] (**1–2**) via one-pot approach (Scheme 3). The new ligands and the complexes were characterized using various analytical and spectroscopic methods. The molecular structures of the complexes were determined using single crystal X-ray diffraction analysis, which reveal that four rhenium cores are arranged in the vertices, and four ligands are at the edges of the tetrahedron.



Scheme 3. Synthetic approach for neutral heteroleptic tetrahedrons **1** and **2**.

Chapter 4: Rheniumtricarbonyl-based M_2Cl_2L type metallocycles from ditopic nitrogen donors

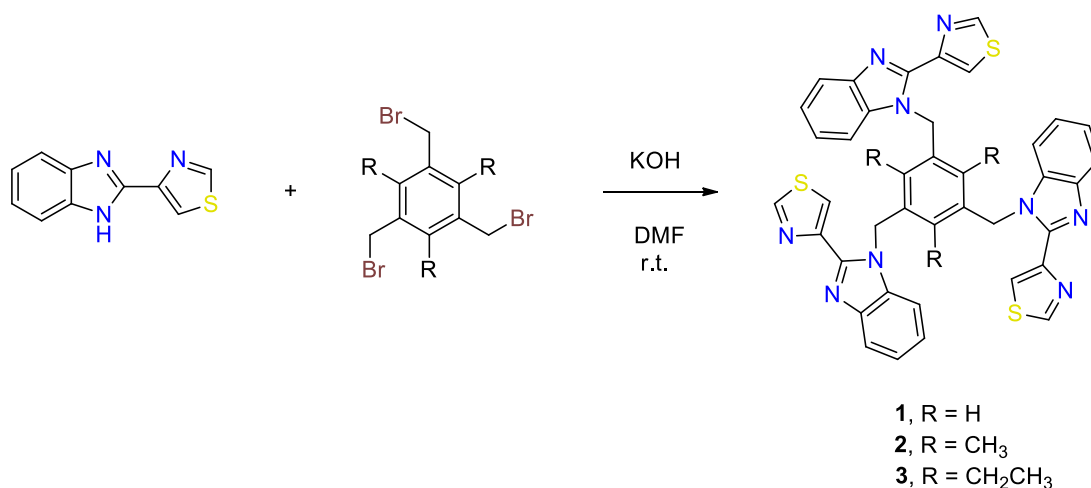
This Chapter contains the synthesis and characterization of *fac*- $Re(CO)_3$ based chloride bridged dinuclear metallocycles. Neutral binuclear metallocycles of the formula *fac*- $[\{ (CO)_3Re(\mu-Cl)_2Re(CO)_3 \} L^n]$ were obtained using $[Re(CO)_5Cl]$ and ditopic flexible nitrogen donor ($L^n = L^1 = \text{bis}(\text{benzimidazol-1-yl})\text{-}m\text{-xylene}$; $L^2 = \text{bis}(5,6\text{-dimethylbenzimidazol-1-yl})\text{-}m\text{-xylene}$, $L^3 = \text{bis}(\text{naphthanoimidazol-1-yl})\text{-}m\text{-xylene}$) in toluene under solvothermal approach (Scheme 4). The metallocycles were characterized by 1H NMR and ESI- Mass analysis. The molecular structures of **1–3** were confirmed by using single crystal X-ray diffraction analysis. The crystal structures of the metallocycles are stabilized by non-traditional intermolecular hydrogen bonding interactions.



Scheme 4. Synthesis of dinuclear metallocycles **1–3**.

Chapter 5: Synthesis of tripodal molecules based on 2-(4-Thiazolyl)benzimidazole

The aim of this work was to synthesize and characterize non-covalent cyclic aromatic trimer containing tripodal molecules using 2-(4-Thiazolyl)benzimidazolyl donor motifs and with or without alkyl substituted benzene spacer. Three tritopic organic molecules (**1–3**) based on 2-(4-thiazolyl)benzimidazolyl (L) terminal motif were synthesized using 1,3,5-tris(bromomethyl)benzene/ 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene/ 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene and 2-(4-thiazolyl)benzimidazole (L-H) (Scheme 5). The molecules were characterized using ESI-MS and ^1H NMR spectroscopic analysis. The molecular structures of two molecules (**2** and **3**) were confirmed by single crystal X-ray diffraction study. Molecule **2** adopts *syn*-conformation with *face-to-face* arrangement in the solid state. Molecule **3** also adopts *syn*-conformation with *edge-to-face* arrangement, in which all the three L units are arranged nearly orthogonal to each other. Two neighboring molecules of **2** interact with each other through non-covalent contacts resulting in double homo stranded helical architecture. ESI-MS analysis indicates that molecule **2** exists as both monomer and dimer (as helix) in solution state as well. Monomer concentrations is predominant than the dimer in the solution. Further, Both molecules **2** and major isomer of **3** have cyclic aromatic trimer motif in which the three benzimidazolyl motifs are arranged in *edge-to-face* fashion and contacts each other through $\text{C-H}\cdots\pi$ interactions.



Scheme 5. Synthesis of tritopic organic molecules **1–3**.

Chapter 6: Conclusion and future prospects

The thesis is summarized, and the possible future direction of the work is also discussed in this chapter. New design principles were developed for the synthesis of various sizes and shapes of *fac*-Re(CO)₃ core based supramolecular coordination complexes which includes helicates, tetrahedron shaped metallocycles and dinuclear metallocycles. The research also provides a way to synthesize double helix molecules which are stabilized *via* weak non-covalent interactions.

Chapter 1

Introduction

1.1. Overview

Supramolecular coordination complexes (SCCs) assembled using coordination-driven self-assembly approaches are well-defined discrete cyclic 2D and/or 3D architectures that can have widespread applications in various fields of chemistry and biology due to the presence of metal complex unit and the arrangement of organic building frameworks [1-28]. The spontaneous formation of the bonds between metal and organic framework units provides several synthetic methodologies to develop these SCCs. Until now, a sequence of discrete supramolecular coordination complexes with different shapes such as triangle, square, rectangle, 2D and 3D architectures through coordination-driven self-assembly approach are reported by several research groups [1-28]. The partially protected facial rheniumtricarbonyl core based SCCs represent a unique class of cyclic assemblies. The most important properties exhibited by these complexes are thermal and kinetic stability, good solubility and metal to ligand charge transfer transitions (MLCT). Re(I)-based cyclic supramolecular architectures with various shapes including dinuclear, trinuclear, tetranuclear squares, rectangles, gondolas, bowls, calixarene, bicycles, hexanuclear prisms, spheroids, wheel and octanuclear prisms are found in literature [10-28]. The dimension, flexibility, shape and intrinsic properties of these SCCs can be easily tuned by modifying the organic ligand framework. The complexes often serve as promising candidates for applications in molecular recognition, catalysis, bio-imaging, sensors, anti-cancer agents and molecular devices [1-9].

The following rhenium carbonyl complexes can be used to self-assemble ionic, neutral, homoleptic and/or heteroleptic supramolecular coordination complexes (Figure 1). Complexes **1-6** are commercially available, whereas, complexes **2-9** can be easily prepared from $\text{Re}_2(\text{CO})_{10}$ using either one-step or two-steps synthetic approach. [3, 29-33].

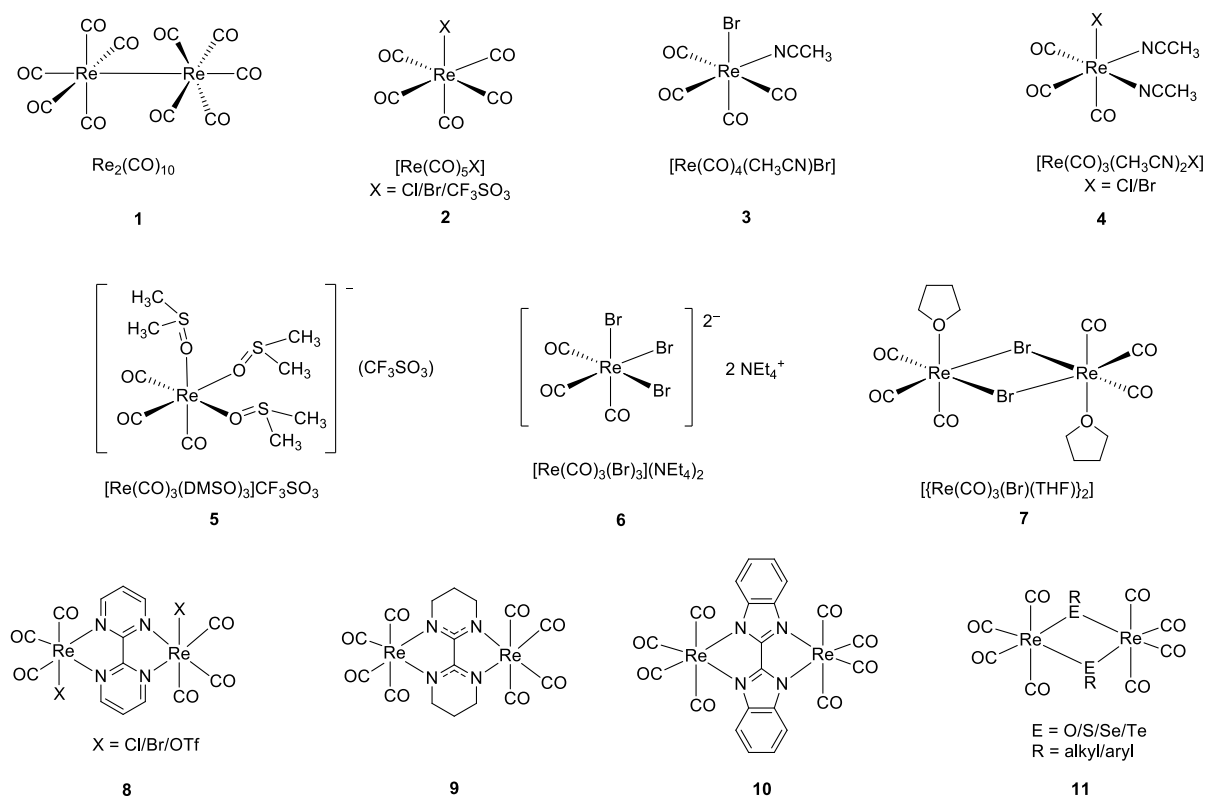


Figure 1. Various rheniumtricarbonyl core based mononuclear and binuclear complexes used for the construction of SCCs.

The following ligands having –N, –O or –S donor sites can be used as sources of anionic building units in making facial rhenium(I)tricarbonyl core-based SCCs (Figure 2) [18, 34-48]. Among bis-chelating ligands, L^1 - L^{20} ; L^1 - L^9 , and L^{15} are good candidates for constructing cavity containing SCCs whereas, L^{10} - L^{14} , L^{16} - L^{20} , and L^{24} - L^{29} can be used for $\pi\cdots\pi$ stacked SCCs [34-48]. Multiple cavities containing SCCs can also be obtained from L^{21} - L^{23} [21-26, 28]. The topology and properties of SCCs such as cavity size, solubility and luminescence can be tuned by modulating the organic functionalities on ligand motifs.

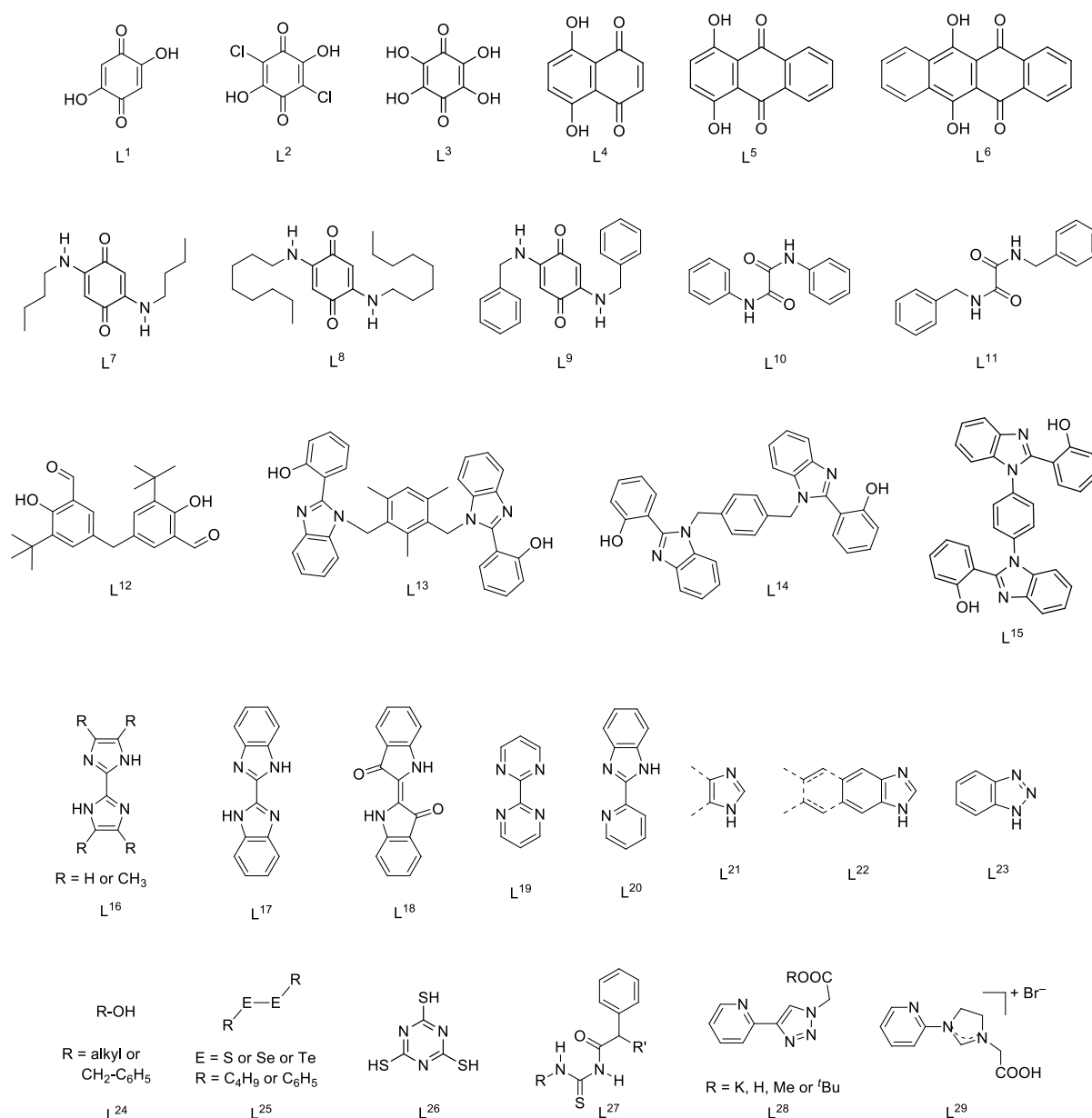


Figure 2. Ligands as structural framework units used for the construction of *fac*-[Re(CO)₃]-core based SCCs.

In general, high reaction temperature is required while using Re₂(CO)₁₀ as metal precursor. Treatment of mononuclear complexes **2-6** and dinuclear complexes **1** and **7-11** with ligands in different solvents (acetone/THF/toluene) yields the formation of desired SCCs with the elimination of carbon monoxide [10-28]. While using halide based complexes, silver trifluoromethanesulfonate is added, this provides silver halide precipitate with the labile triflate

ancillary ligands coordinated to the metal centre [30]. Bromide bridged complexes, triflate based coordination complexes and DMSO coordinated complexes can serve as good metal precursors for making SCCs at room temperature and/or when the thermally unstable ligands are used [29-33]. The facial rheniumtricarbonyl based SCCs are belongs to an excellent and unique class of functional metallomacrocycles exhibiting high stability, solubility and interesting photophysical properties. The research interest for the facial rheniumtricarbonyl core containing SCCs are attributed to their potential applications in various fields of chemistry as well as biology which includes host-guest chemistry, anti-cancer and bio-imaging agents, photocatalysis and sensing applications.

The use of rheniumtricarbonyl as the metal center for the construction of SCCs is ascribed to the various favourable aspects of the rheniumtricarbonyl core. First of all various metal precursor sources such as $\text{Re}_2(\text{CO})_{10}$, $[\text{Re}(\text{CO})_5\text{X}]$ ($\text{X}=\text{Cl}, \text{Br}$), $\text{Re}(\text{CO})_5\text{OSO}_2\text{CF}_3$ and $[\text{Re}(\text{CO})_3(\text{dmsO})_3](\text{CF}_3\text{SO}_3)$ are available for the generation of facial rheniumtricarbonyl core with three vacant positions for coordinating the ligand motifs. The metal sources such as $[\text{Re}(\text{CO})_5\text{Cl}]$ and $[\text{Re}(\text{CO})_5\text{Br}]$ gives the facial rheniumtricarbonyl metal centre with two empty sites for neutral organic coordinating ligands. On the other hand, $\text{Re}_2(\text{CO})_{10}$ gives three vacant sites which requires two coordinating ligands which can provide two-electrons and one anionic ligand capable of donating one-electron (Figure 3).

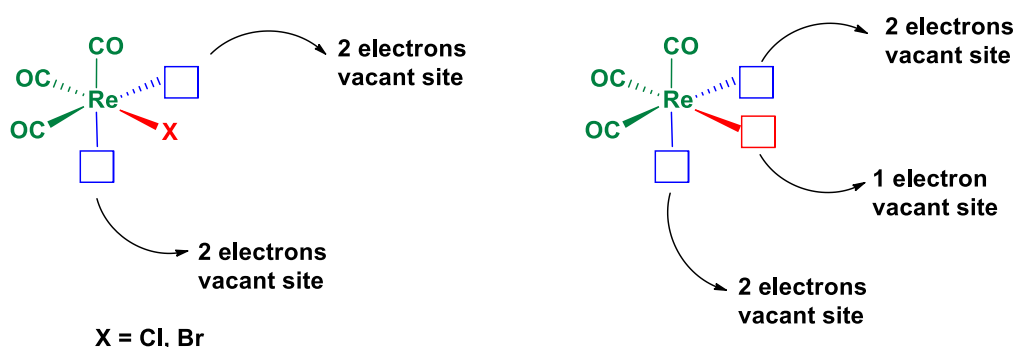


Figure 3. Two types of vacant coordination sites on *fac*- $\text{Re}(\text{CO})_3$ core.

The utilization of various combinations of the predesigned ligands i.e. flexible-rigid or flexible-flexible or rigid-rigid leads to new bonding combinations for making 2D and 3D architectures by one-pot approach using reflux and solvothermal reaction techniques. In general, anionic bis-

chelating ligands with N $\cap$ N-/ O $\cap$ O-/ N $\cap$ O- donors as well as neutral N-donor ligands were used to assemble rhenium(I)tricarbonyl core containing SCCs. Further, IR spectroscopy can be used as the primary characterization tool for the optimization by the in-situ CO stretching frequency.

1.2. Flexible bidentate N-donors with ether, ester or amide functionalities and SCCs

The ligands containing polyether, ester or amide functionalities along with alkyl or aryl spacer motifs bearing pyridyl pendant for coordination to metal centres are ideal choice to construct macrocyclic architectures having various shapes and size (Figure 4). Ligands, L³⁰-L³² can provide crown ether type SCCs, [36, 49, 50] whereas ligands L³³-L⁴⁰ have been utilized to synthesize hammock shaped, rectangular or square like metallacycles [44, 51, 52]. In addition, partial rigidity can be imparted to SCCs by incorporating additional rigid framework (phenyl or biphenyl units) along with polyether, amide or ester functionalities. The incorporation of functional groups and/or spacer that anchors the functional groups in the ligands may play a crucial role in modulating the shape, size and properties of the final assembly.

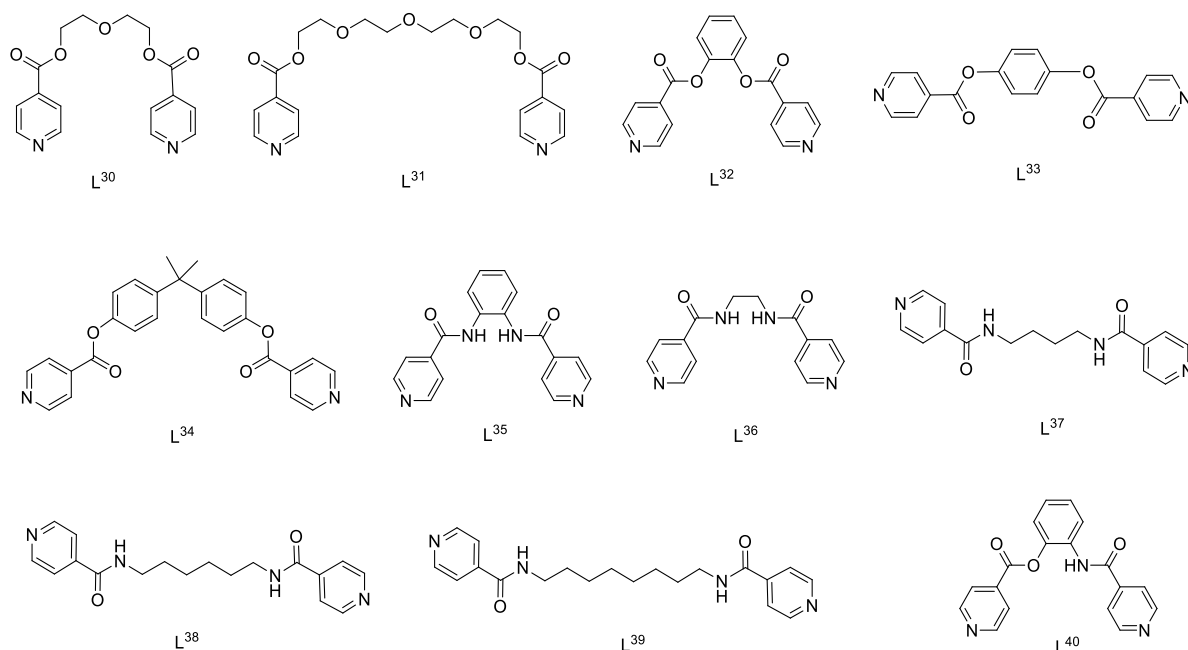


Figure 4. Flexible bidentate ligands with ether, ester and/or amide functionalities as spacer and pyridine as coordinating motifs.

The intrinsic properties associated with $fac-[Re(CO)_3]^+$ and $fac-[Re(CO)_3X]$ (where $X = Cl/Br$) core are suitable to make luminescent SCCs analogous to crown ether type self-assembly which can have potential utility as sensors, catalysts, in host-guest chemistry and can mimic the natural systems [1-28].

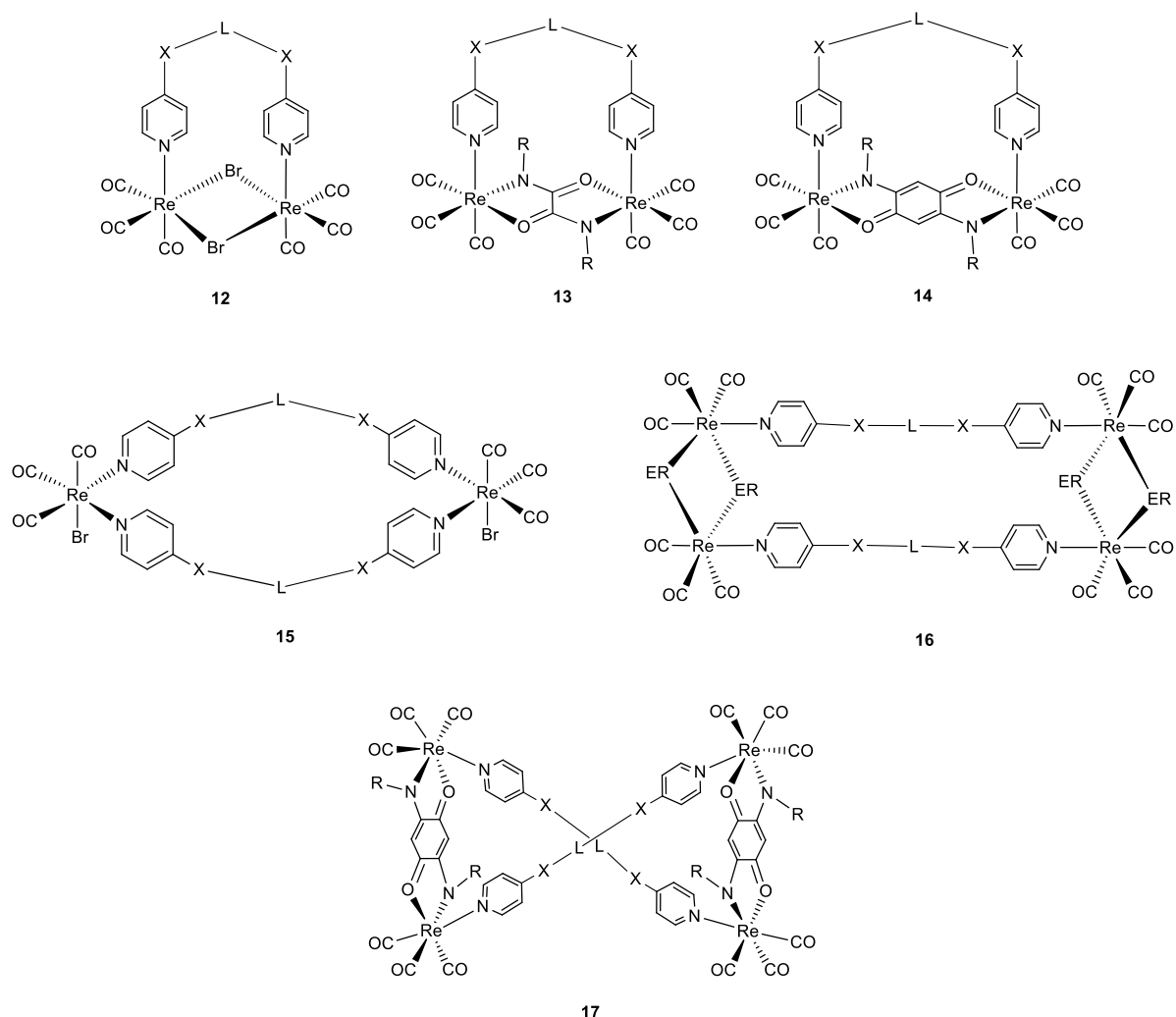


Figure 5. Dinuclear and tetranuclear rhenium core based SCCs.

Five types of SCCs, $fac-[\{Re(CO)_3Br\}_2 L']$ (**12**), $fac-[\{Re(CO)_3(BCL)\}_2 L']$ (**13,14**), $fac-[\{Re(CO)_3Br\}_2 L'_2]$ (**15**), $fac-[\{Re(CO)_3(ER)\}_4 L'_2]$ (**16**), and $fac-[\{Re(CO)_3(BCL)\}_2 L'_2]$ (**17**) (where BCL = bis-chelating ligand ($N^{\wedge}O$) and $L' = X-L-X = N,N$ donors with ether, ester or amide groups), can be self-assembled by simple combination of tricarbonylrhenium(I) complexes and dipyriddy ligands with or without anionic ancillary ligands [49-52]. The

bridging ligands dictate the size of the cavity of the metallacycles in **12-14** [49-52]. The halide-bridged ligands provide the $\pi\cdots\pi$ stacked metallacycles (**12**) without any inner cavity whereas the quinone-based bridging ligands provide the cavity suitable to accommodate the solvent/guest molecules/ions (**13, 14**) [36]. The cavity containing SCCs with recognition units (ether, ester or amide groups) display effective host-guest interactions with aromatic amines *via* non-covalent contacts. The size, shape and properties of the complexes containing alkyl spacers can be varied upon changing the chain length. The complex **15** synthesized using L^{37} - L^{39} exhibits good photophysical properties with MLCT in the region 544-558 nm. The anti-cancer studies for these complexes suggested that upon increasing the chain length, the hydrophobicity increases which results in enhanced anti-cancer activity [52].

1.3. Flexible tritopic N-donor ligands and SCCs

The key factors in self-assembling SCCs are predesigning organic ligands and proper choice of metal precursors. Commonly, rigid ligands are more favourable for constructing SCCs; the coordination angle remains intact during the reaction, and in the final assembly. On contrary, the flexible ligands can have various conformations in solution depending upon the concentration, solvents, and reaction conditions. Although, the coordination angle of flexible organic ligands is less predictable, it provides SCCs with beneficial properties such as adaptability where cavity size can easily shrink or enlarge to have maximum non-covalent interactions. Recently, to control the flexibility of these ligands, rigid ancillary counterparts were used to assemble *fac*- $\text{Re}(\text{CO})_3$ core based SCCs [56-59].

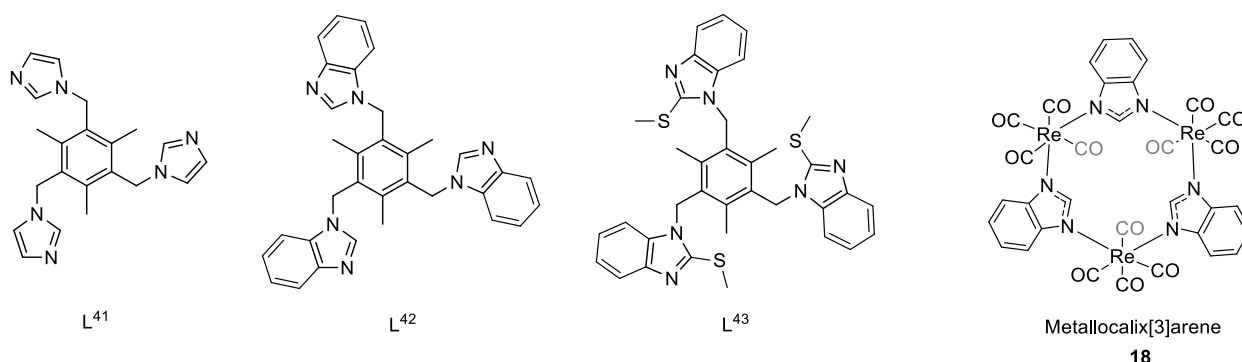
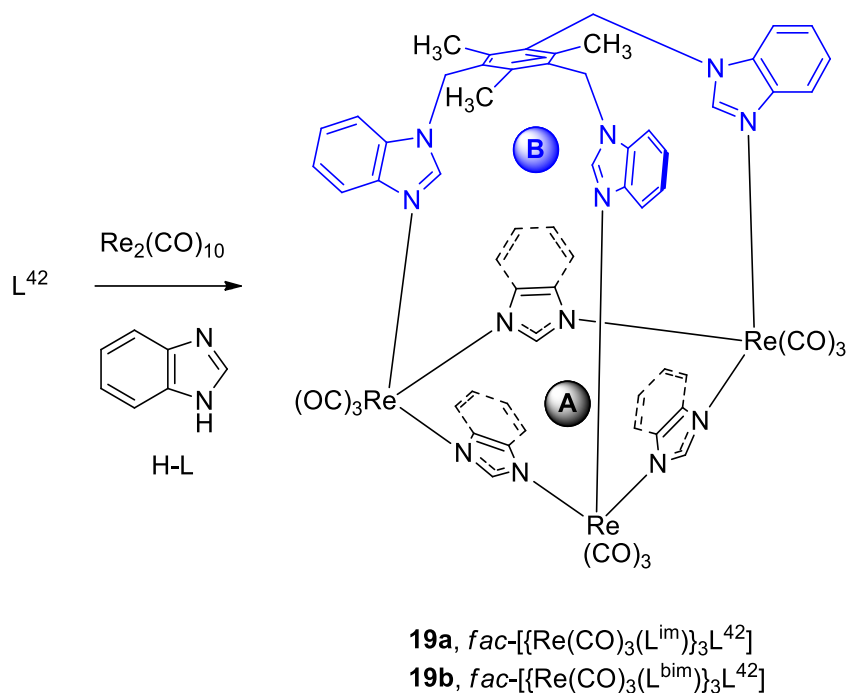


Figure 6. Flexible tritopic N-donors and rheniumtricarbonyl core based SCC.

The flexible tritopic- and poly-topic N-donors can be used to make SCCs with two or more molecular receptor units. For example, trinuclear cages similar to capped metallocalix[3]arene framework can be obtained by using benzimidazolyl-based tritopic ligand, benzimidazole/benzotriazole/imidazole/triazole and $\text{Re}_2(\text{CO})_{10}$ via solvothermal one-pot approach (Scheme 1) [12].



Scheme 1. Synthetic approach for trinuclear cages **19a** and **19b**.

The cages have two cavities, one endo- and one exo-cyclic, suitable to accommodate small anions and neutral guest molecules (Figure 7). The exocyclic cavity not only provides electron deficient three C-H donors but also provide electron rich oxygen from symmetrically arranged three carbonyl units. The molecular structure of the cage (**19a**) with DMSO guest confirms that multiple non-covalent contacts stabilizes the host:guest motif (Figure 8). Both recognition units can be tuned by choosing desired heterocyclic units in tritopic ligands as well as rigid ligands.

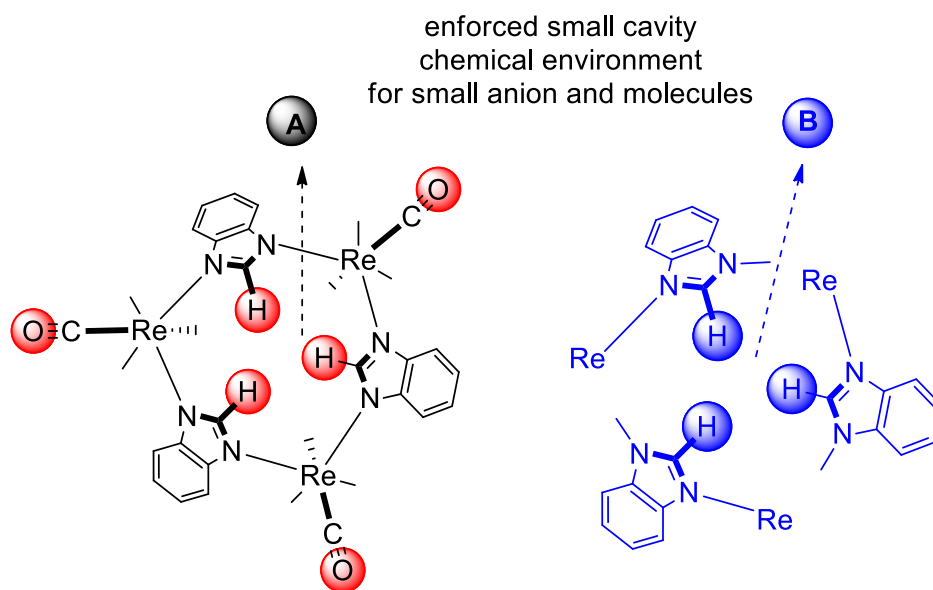


Figure 7. (A) Stereochemical arrangement of three benzimidazolyl units and (B) three benzimidazolate units.

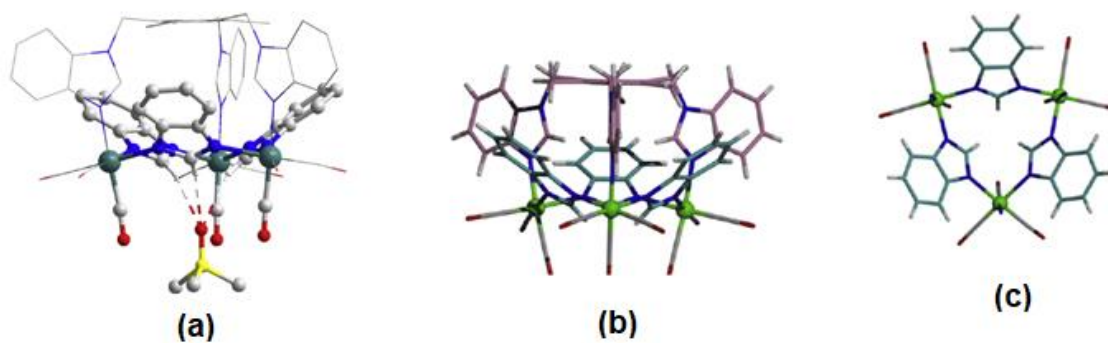
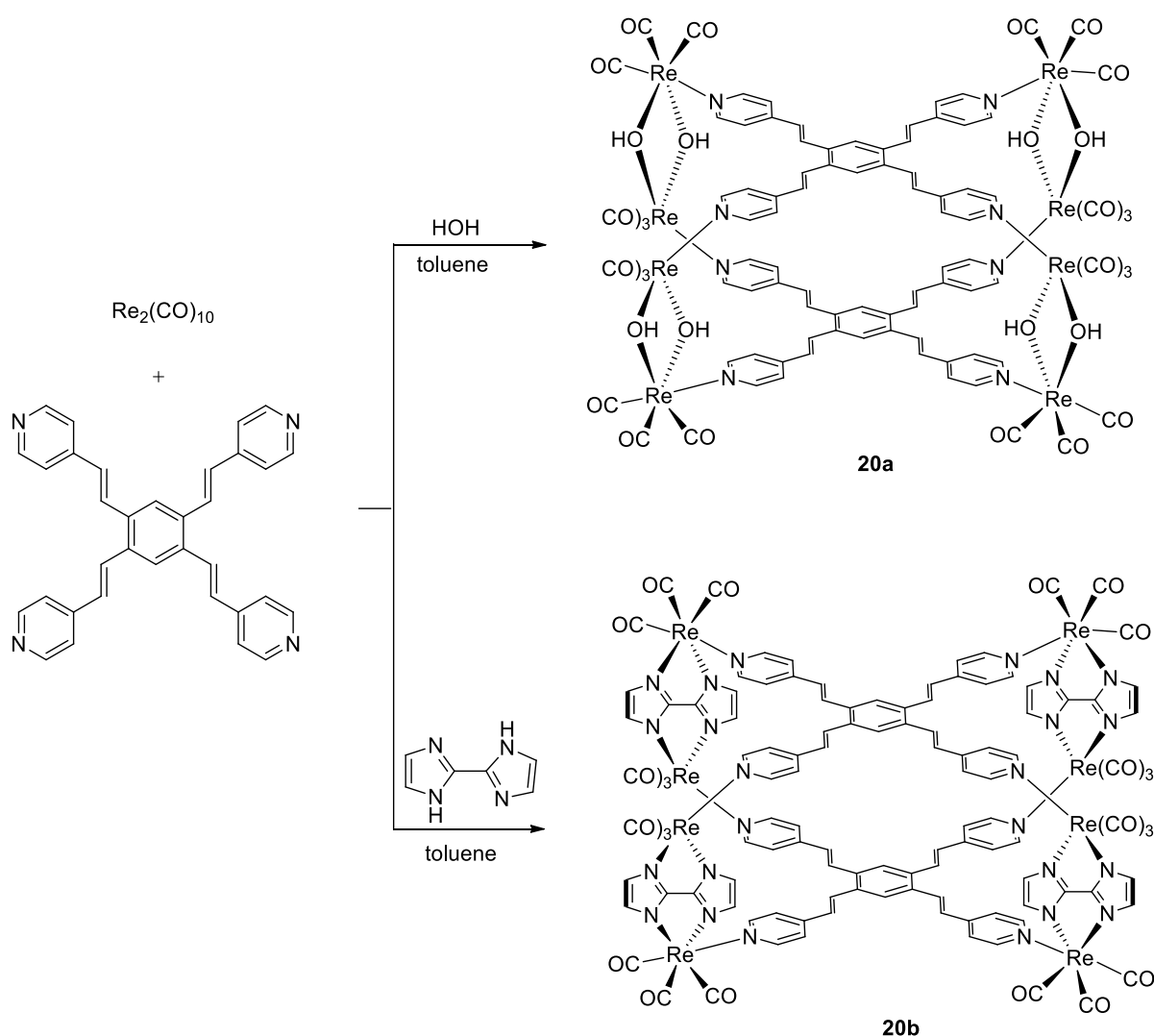


Figure 8. (a) Molecular structure of **19a** with DMSO guest molecule (b) metallocalix[3]arene framework in **19a**. (c) metallocalix[3]arene framework in **19a**.

1.4. Neutral flexible tetratopic N-donor ligands and SCCs

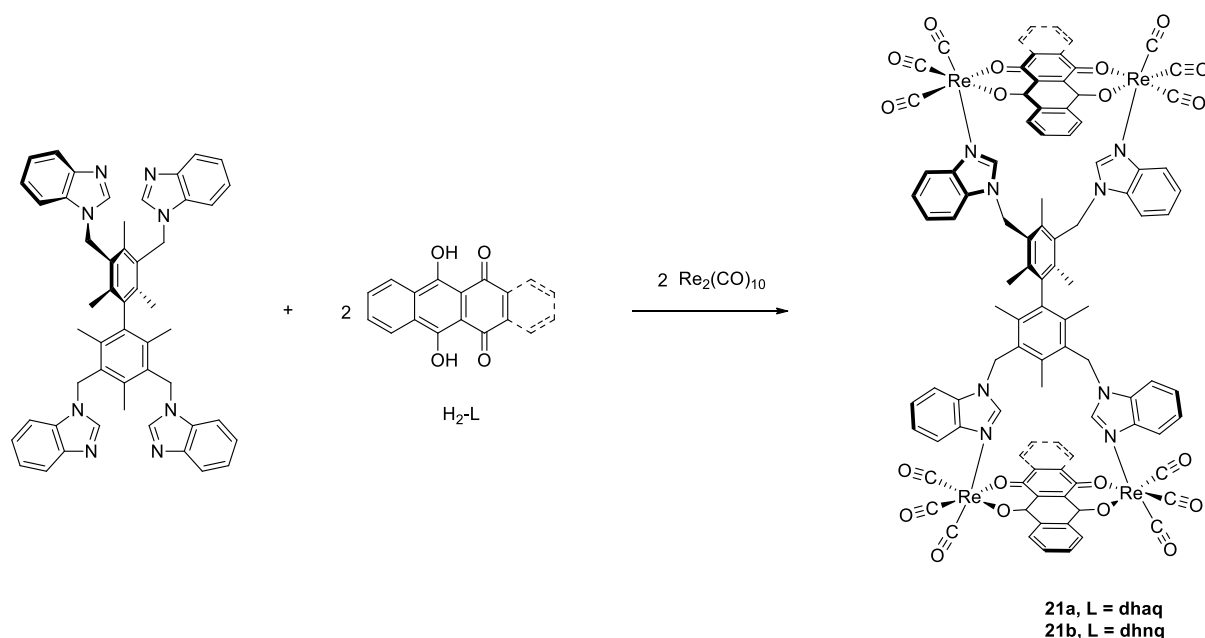
The pyridyl, imidazolyl or benzimidazolyl N-donor ligands are common class of organic building units for making flexible di-, tri-, tetra- or poly-topic ligands. The use of tetratopic ligands with a suitable rigid mono- or bi-dentate donor and Re(I) metal precursor may yield metallacycles having beautiful architecture and appropriate cavity. A vinyl benzene spacer based tetratopic ligand with pyridyl coordinating units upon reaction with water/biimidazole ancillary ligand and $\text{Re}_2(\text{CO})_{10}$ produced neutral π -stacked tetragonal prismatic metallacycles **20a** and **20b** (Scheme 2) [26].



Scheme 2. Synthetic approach for π - π stacked metallacycles, **20a** and **20b**.

The stacked arrangement of the two tetratopic ligands helps in stabilizing the metallacycles through various non-covalent interactions including $\pi\cdots\pi$ stacking, $\text{CH}\cdots\pi$ and H-bonding interactions.

On the other hand, a biphenylene spacer containing tetratopic ligand with benzimidazolyl pendants furnished a bridgeless biscalix[4]arene-shaped metallocavitand **21** upon reacting with quinone ligand unit and $\text{Re}_2(\text{CO})_{10}$ (Scheme 3). The complex consists of two metallocalix[4]arene units lying orthogonal to each other and connected through arene spacer units [15]. Upon changing the coordinating units, the shape and size of the metallacycles can be varied.



Scheme 3. Synthetic approach for bridgeless biscalix[4]arene-shaped metallocavitands **21a** and **21b**.

1.5. Neutral flexible hexatopic N-donor ligands and SCCs

Hexatopic N-donor based ligand motifs serve as a good class of ligands for constructing metallocavitands with larger cavity size that can accommodate larger size guest molecules (Figure 9).

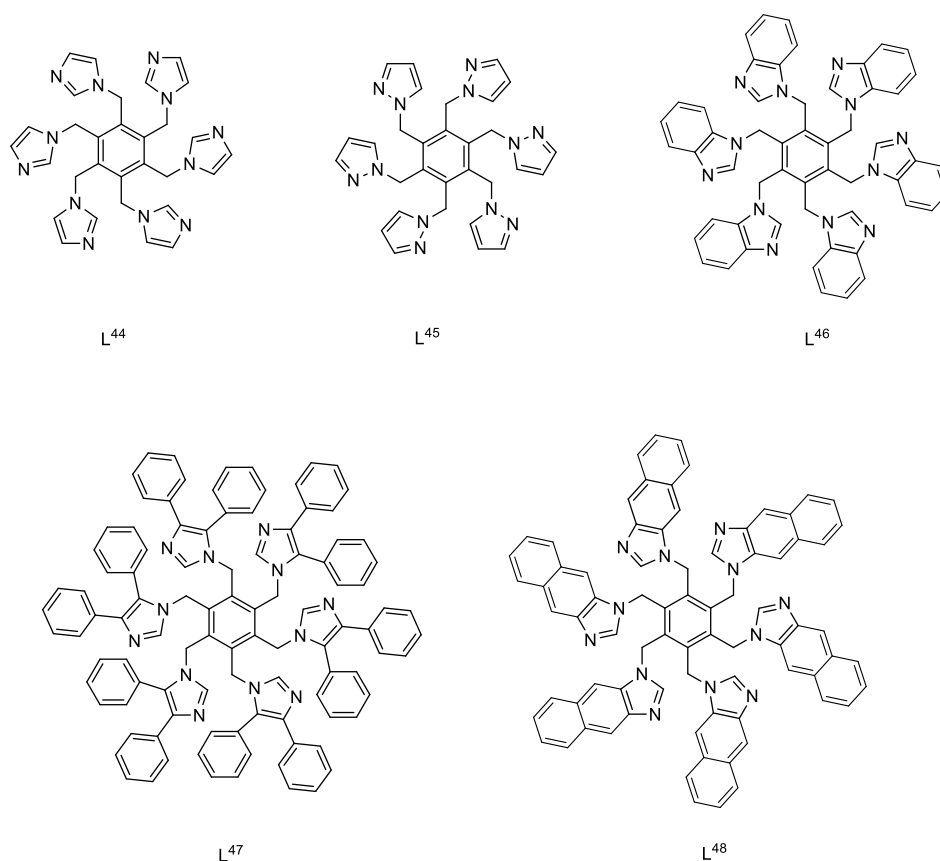


Figure 9. Flexible hexatopic N-donor ligands.

Ligands can be modulated by varying the steric units thereby increasing the arm width of the SCCs for the synthesis of spheroid type metallacycles and metallacycles similar to calix[4]arenes with enlarged interior cavities. Several N⋮N donors like imidazole and its derivatives such as benzimidazole, and naphthanoimidazole are found to be ideal building blocks for constructing these metallocsupramolecules.

A series of neutral hexanuclear heteroleptic metallocavitands possessing multiple exocyclic cavities suitable to host guest molecules can be obtained by the combination of flexible hexatopic ligands, rigid bridging ligand, and $\text{Re}_2(\text{CO})_{10}$ by using simple one-pot approach [28]. These SCCs adopt spheroid-shaped structure. Due to the arrangement of heterocyclic units in the spherical structure, the six calix[4]arene-shaped and two calix[3]arene-shaped exo-cavities are formed (Figure 10).

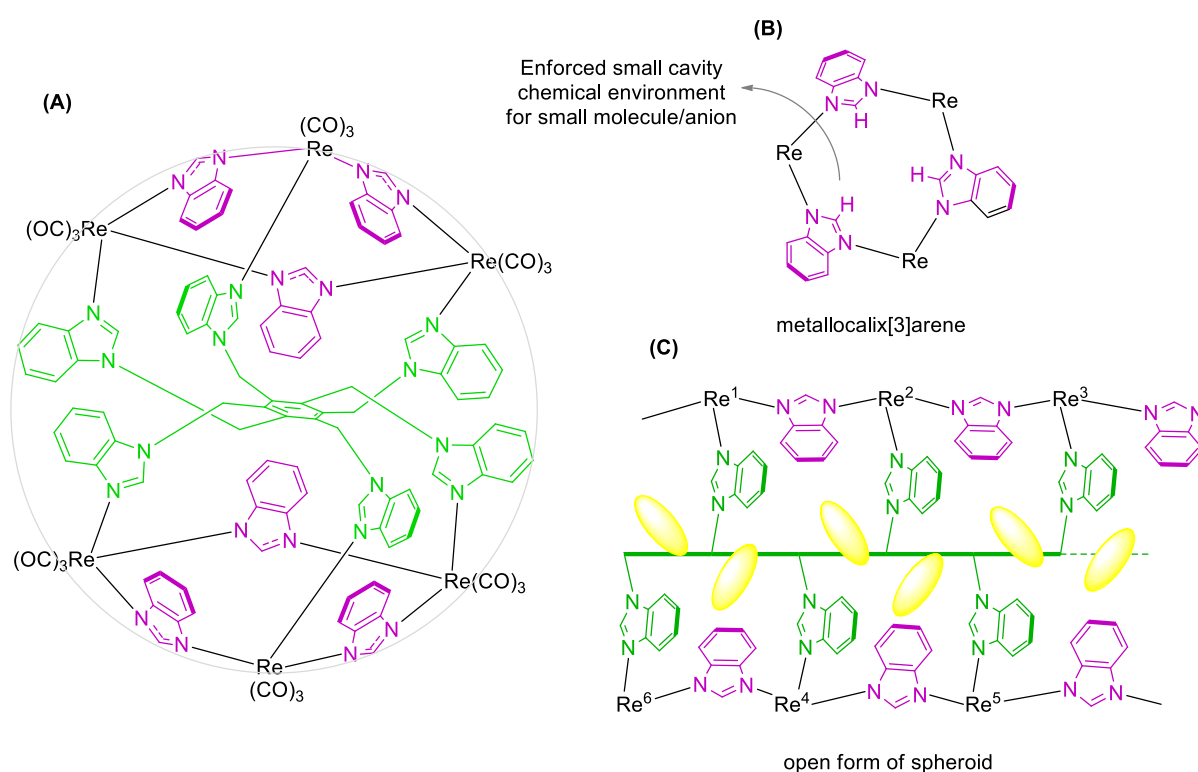


Figure 10. (A) Spheroid cage 22; (B) metallocalix[3]arene motif with enforced small cavity; (C) open form of spheroid showing six metallocalix[4]arene cavities.

The X-ray structures of the SCCs clearly suggest that these SCCs have ability to function as multiple molecular sensors for small molecules. The overall size, cavity width and solubility can be tuned by modulating the hexatopic ligands, in particular 5,6-positions of benzimidazolyl/imidazolyl cores.

1.6. Neutral flexible benzimidazole based ditopic N-donor ligands and SCCs

Benzimidazole and its derivatives-based neutral semi-flexible ditopic N-donors with spacer motif, $[-CH_2-C_6H_3R_3-CH_2-]$ where $R = -H, -Me$ or $-OMe$, are excellent organic building units for making various SCCs such as helicates, mesocates, metallocalix[n]arenes and metallocavitands [21-22, 38-39, 60-62]. The predominantly used flexible ditopic ligands are shown below (Figure 11).

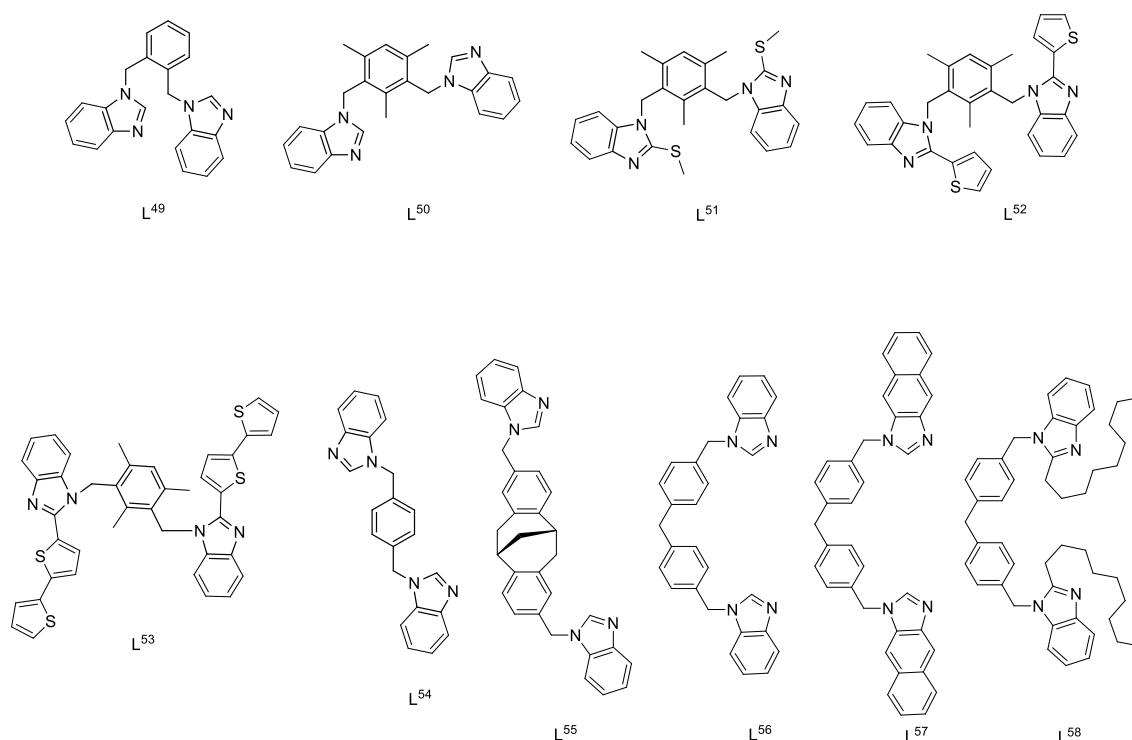
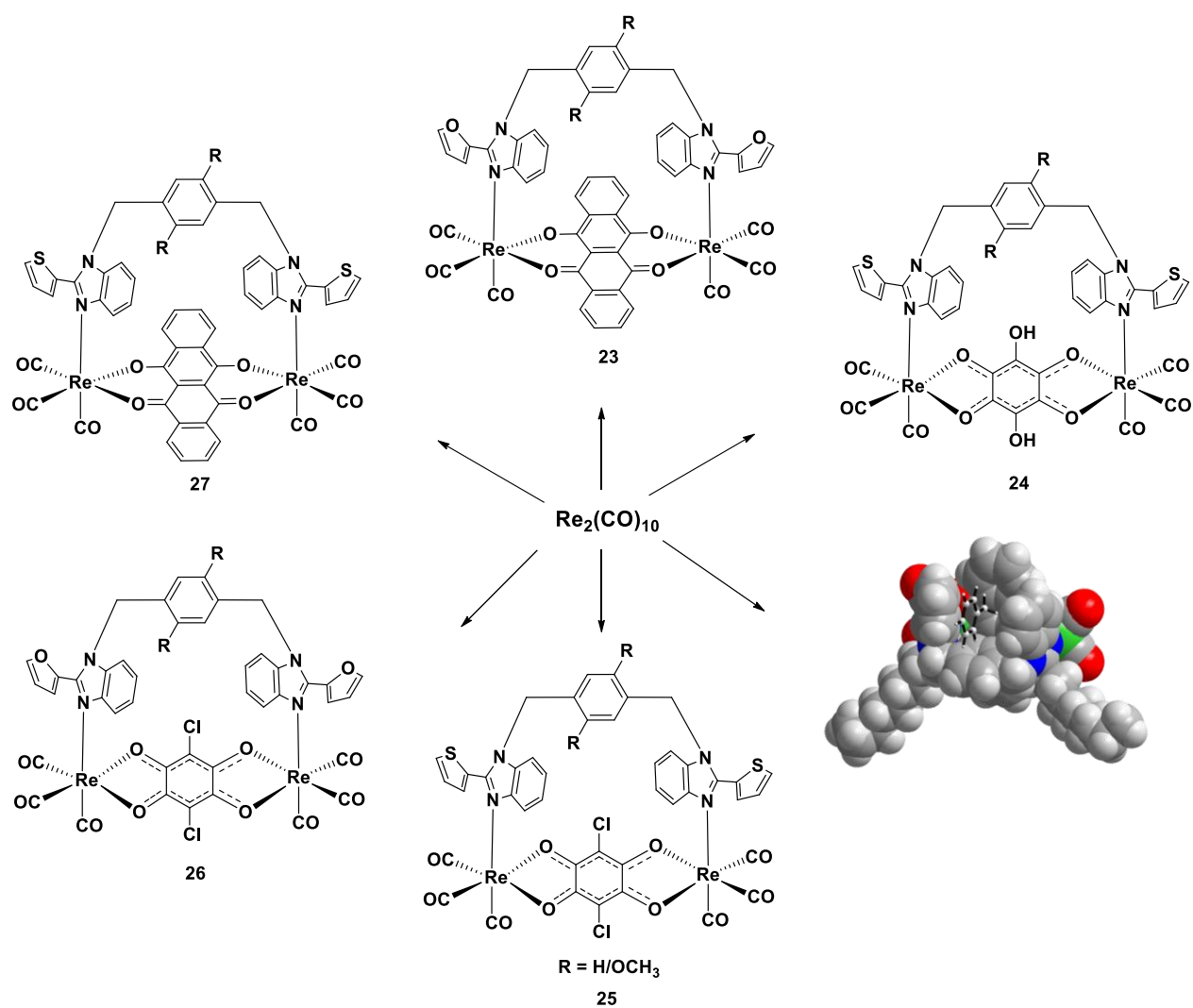


Figure 11. Flexible benzimidazole based ditopic N-donor ligands.

Several simple but elegant neutral heteroleptic dinuclear metallocalix[4]arenes can be obtained by treating $Re_2(CO)_{10}$, dihydroxyquinones and ditopic N-donors by simple one-pot approach (Scheme 4) [22]. Constructing calixarene-shaped SCCs using this approach results in the cone-shaped conformation. Tuning the spacer or benzimidazolyl core by incorporating the substituents provides functional group decorated SCCs without any change in the cone-conformation.



Scheme 4. Synthesis of heteroleptic dinuclear metallocalix[4]arenes.

The cavity in the calixarene-shaped SCCs can accommodate small molecules including toluene [22]. Further, the two benzimidazolyl framework arranged opposite to each other can swing back and forth to have maximum non-covalent interactions with the guest molecules.

As mentioned earlier, flexible ligands offers various conformations in the solution and can have stable conformation after coordinating with metal ions. For example, simultaneous complexation of one flexible bis(monodentate) ligand, one flexible bis(bidentate) unit, and two *fac*-Re(CO)₃ cores forms dinuclear unsaturated double-heterostranded helicate and mesocate (28-30, Figure 12) [38, 60].

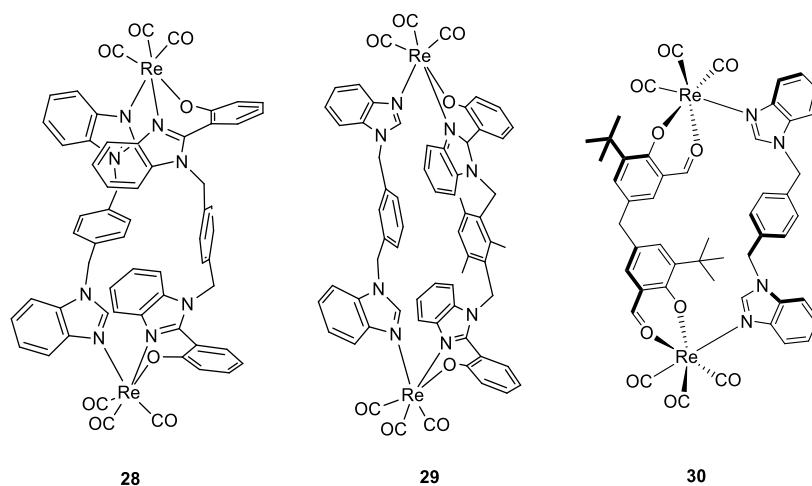


Figure 12. Dinuclear double heterostranded helicate and mesocate.

1.7. Neutral rigid pyridine based ditopic- and tritopic- ligands and SCCs

Neutral rigid ditopic nitrogen donor ligands are highly used as organic building blocks for making molecular squares, $\pi \cdots \pi$ stacked molecular rectangles, cavity containing rectangles, prisms and other 3D-architectures [18, 19, 24-26]. These SCCs can be obtained by the treatment of suitable orthogonal tritopic rhenium acceptor and ditopic nitrogen donors with other rigid ditopic ligands, hydroxyl/chalcogenolato bridge, and bis-chelating ligands.

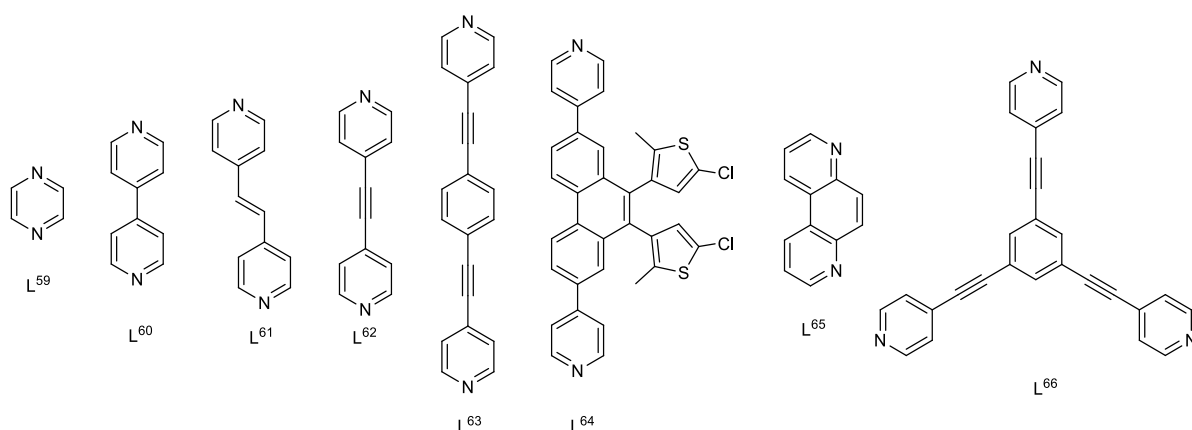
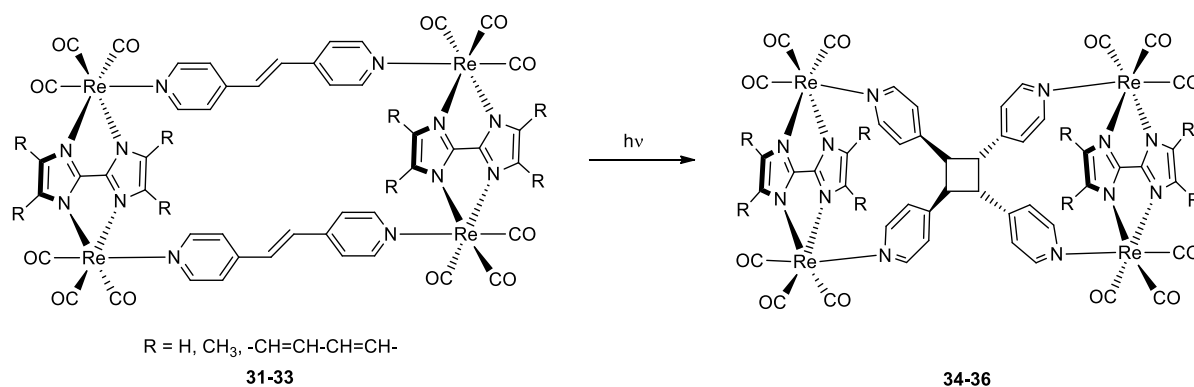


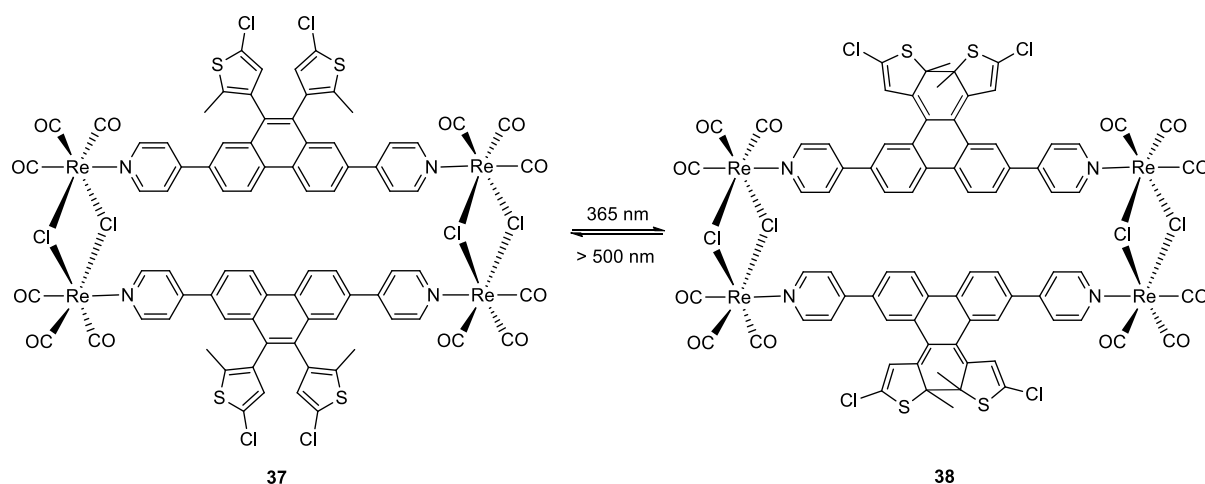
Figure 13. Neutral ditopic and tritopic ligands with pyridyl motifs.

The strategy of synthesising $\pi\cdots\pi$ stacked molecular rectangles is a good method to bring two double bonds in close proximity for undergoing photo induced [2+2] cycloaddition reactions without using any solvent [41]. This was nicely demonstrated in the molecular rectangles (**31-33**) (Scheme 5) containing two *trans*-1,2-bis(4-pyridyl)ethene motif lying parallel to each other.



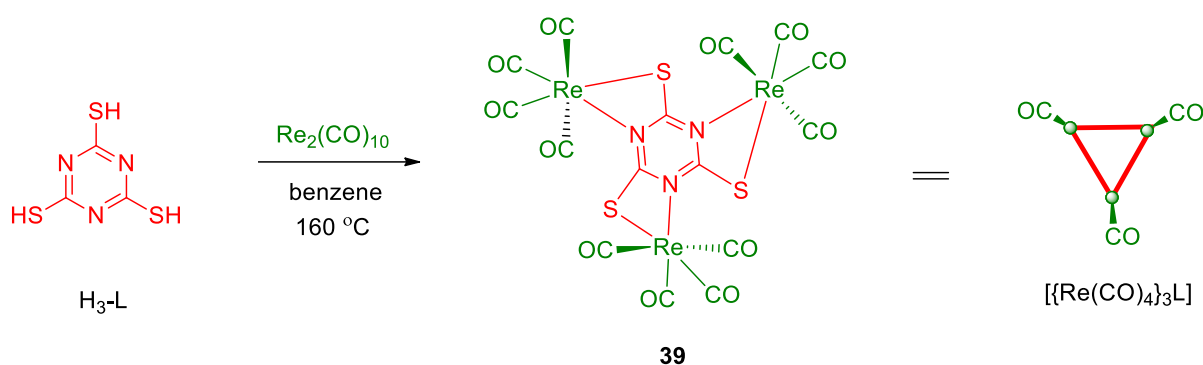
Scheme 5. Photo responsive [2+2] cycloaddition reaction on molecular rectangles.

Photo responsive molecular rectangle (**37**) can be obtained by using rigid photochromic ditopic nitrogen donors possessing photoactive unit as spacer or decorated on the spacer motif [53]. 1,2-dithienylethene (DTE) motif containing molecular rectangle displays reversible photochromic rearrangement in solution and can be interconverted by UV and Visible light (Scheme 6).

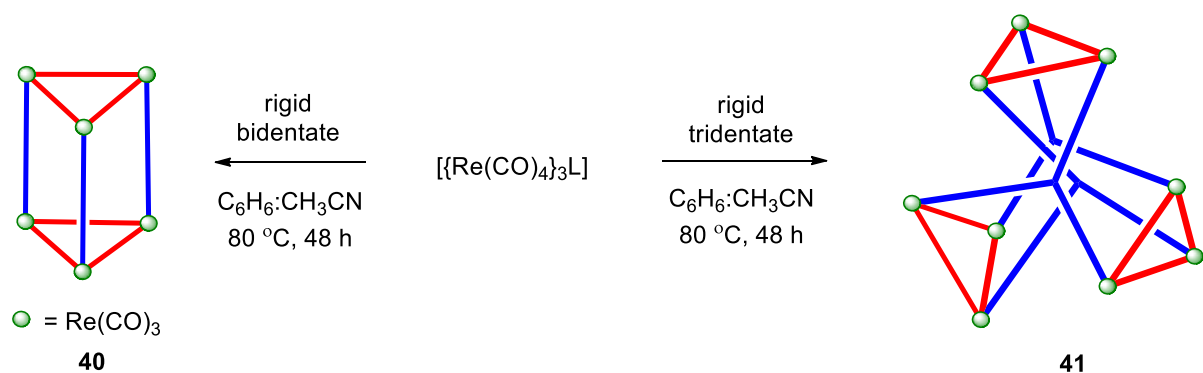


Scheme 6. Photochromic rearrangement in rectangle **37** upon irradiating UV-Vis light.

Trithiocyanuric acid ($\text{H}_3\text{-L}$) is recently introduced as organic framework unit for neutral heteroleptic SCCs [45]. Unlike dihydroxyquinone-based bis-chelating ligands, fully deprotonated trianion L^{3-} acts as tris-chelating motif having four membered chelating cycles. The preparation of the SCCs can be achieved in two-steps synthetic approach. The treatment of $\text{H}_3\text{-L}$ with $\text{Re}_2(\text{CO})_{10}$ in benzene at 160°C yields trinuclear tetracarbonylrhenium(I) complex $[\{\text{Re}(\text{CO})_4\}_3\text{L}]$ (**39**) (Scheme 7). The combination of the complex **39** with rigid bidentate N-donor in the mixture of benzene and acetonitrile at elevated temperature ($\sim 80^\circ\text{C}$) resulted in hexanuclear trigonal prism (**40**) (Scheme 8) [45].



Scheme 7. Synthetic approach for trinuclear tetracarbonylrhenium complex **39**.



Scheme 8. Synthetic approach and schematic representation of trigonal prism **40** and nonanuclear cage **41**.

The width of the prism can be easily varied by changing the length of the bidentate donor. The advantage of this precursor is that three aromatic units can be arranged in an edge-to-face fashion in the trigonal prism structure. Neutral heteroleptic nonanuclear complex **41** hitherto unknown cage can be prepared when the assembly unit is rigid tridentate ligand with coordination angle of 120° with complex **39** under same reaction conditions. Due to triple decker arrangement of the rigid tridentate ligands, the complex **41** acquires triangular star shape (Figure 14) [45].

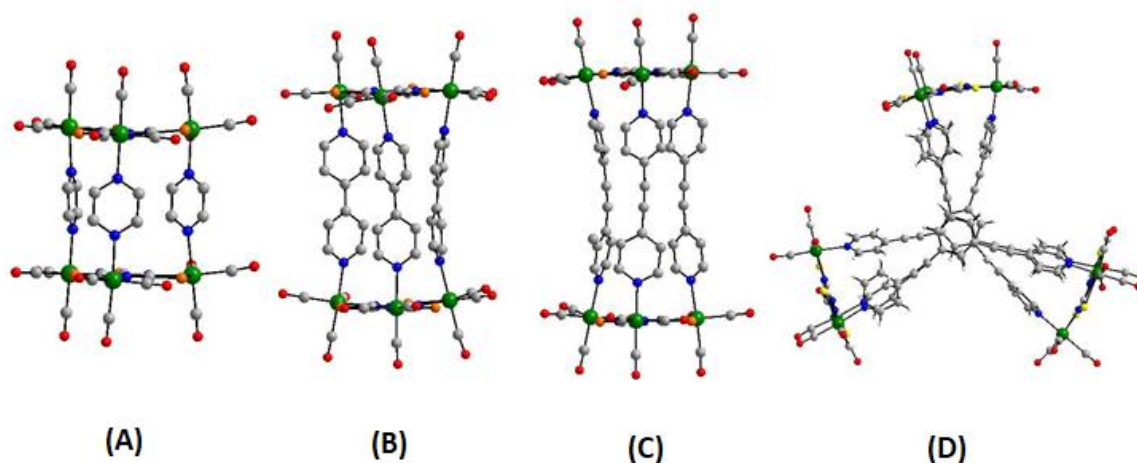


Figure 14. Molecular structure (ball and stick model); (A-C) Prisms, (D) Triangular star.

1.8. Heteroatom donor based ligands and SCCs

Functionalized chelating ligand such as pyridyl-triazole, pyridyl-N-heterocyclic carbene, and benzoylthiourea forms a different class of ligands apart from the usual benzimidazolyl based systems. The planarity/rigidity of the ligands having flexible coordinating arm decides the shape of the complex. The preparation of such type of ligands require multi-step approach, however, new synthetic procedures are now being developed which makes them much easily accessible.

The pyridine-triazole based bifunctional chelating agent with $[\text{Re}(\text{CO})_5\text{Cl}]$ and proper reaction conditions formed a dinuclear complex **42**. The dimeric complex existed as isomers and the structure in which the ligand motifs are parallel contributed maximum to the isomeric ratio [47]. In a similar way, N-heterocyclic carbene based bifunctional ligand with pyridine and carboxylic acid coordinating groups yielded complex **43** by Ag(I) transmetalation protocol using Ag_2O [48]. The strong σ -donating properties, high stability and flexibility of such ligands make their study interesting. Recently, 1-benzoyl-2-thiourea derivative with triazine-2-thione moiety showed unusual binding with facial rheniumtricarbonyl unit *via* thione sulphur atom of triazinethione unit, **44** [46]. The presence of various heteroatoms including -O, -N, -S in benzoylthiourea derivatives provides multitude bonding options with metal ions.

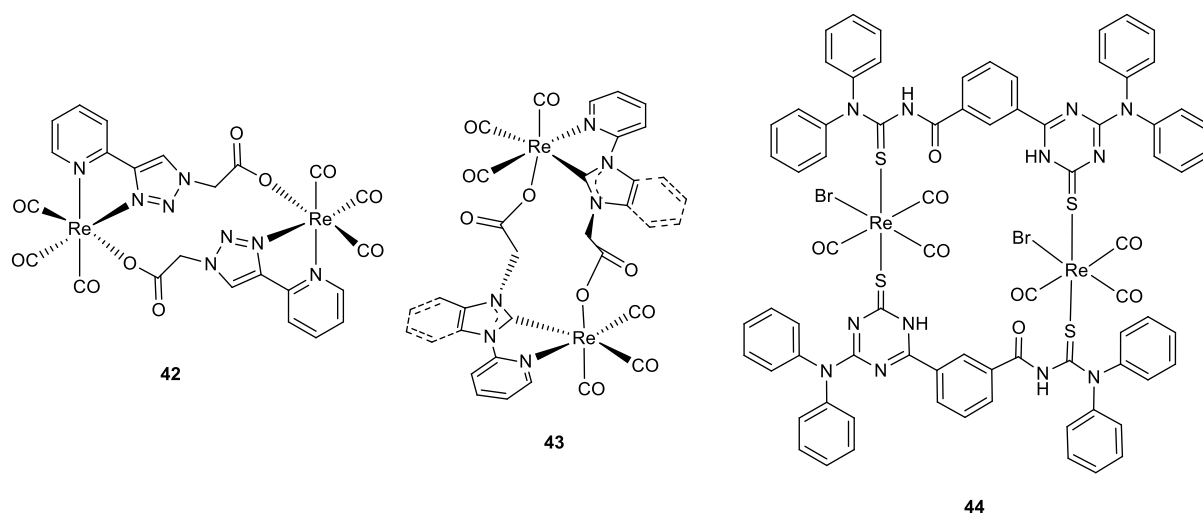


Figure 15. Rheniumcarbonyl based SCCs from unsymmetrical donors.

Phosphine oxide (P=O) donor based neutral ditopic and tetratopic ligands are rarely employed for the construction facial rheniumtricarbonyl core containing SCCs. Recently, countable number of SCCs including binuclear and tetranuclear (**45-49**) (Scheme 9 and Figures 16 and 17) are synthesized by the combination of $\text{Re}_2(\text{CO})_{10}$, dihydroxyquinone-based chelating ligand and di- and tetra-topic phosphine donor in a solvothermal reaction condition.

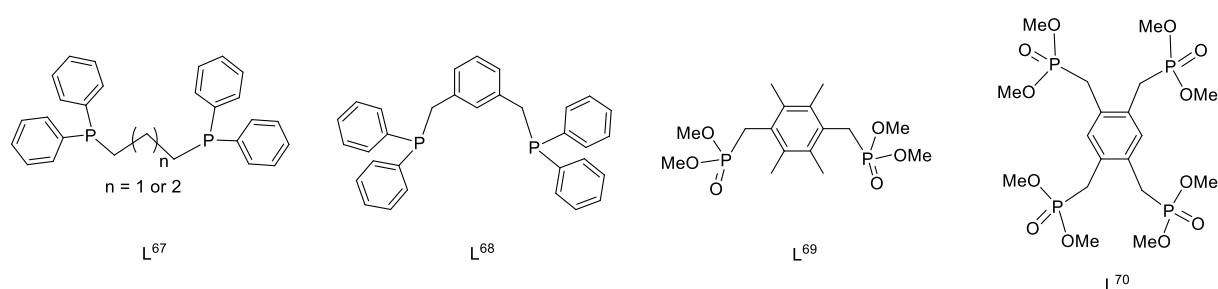
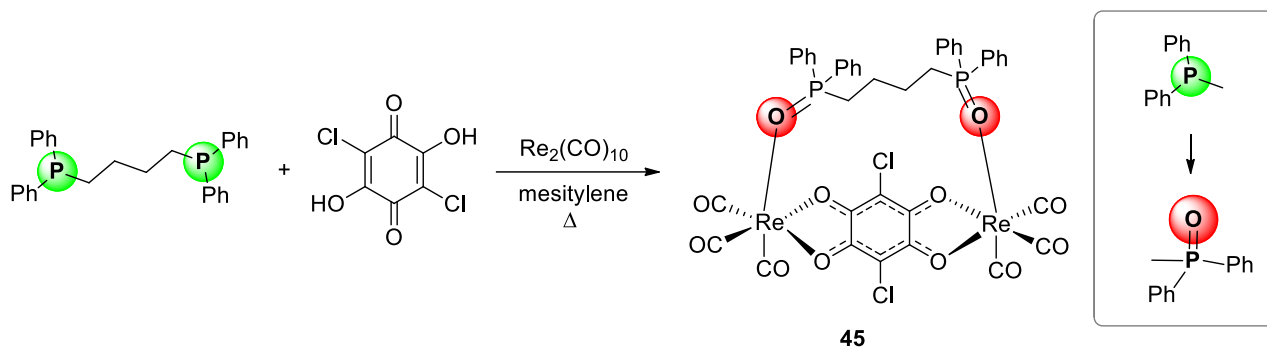


Figure 16. Phosphine oxide donor based ligands.



Scheme 9. Synthetic approach for complex **45**.

The presence of oxygen and moisture in the solvent helps in the transformation of phosphine to phosphine oxide under thermal conditions. Direct use of phosphine oxide donor also results in the formation of similar complexes. These complexes display strong absorption in the visible region with significant red-shift as compared to the N-donors based SCCs.

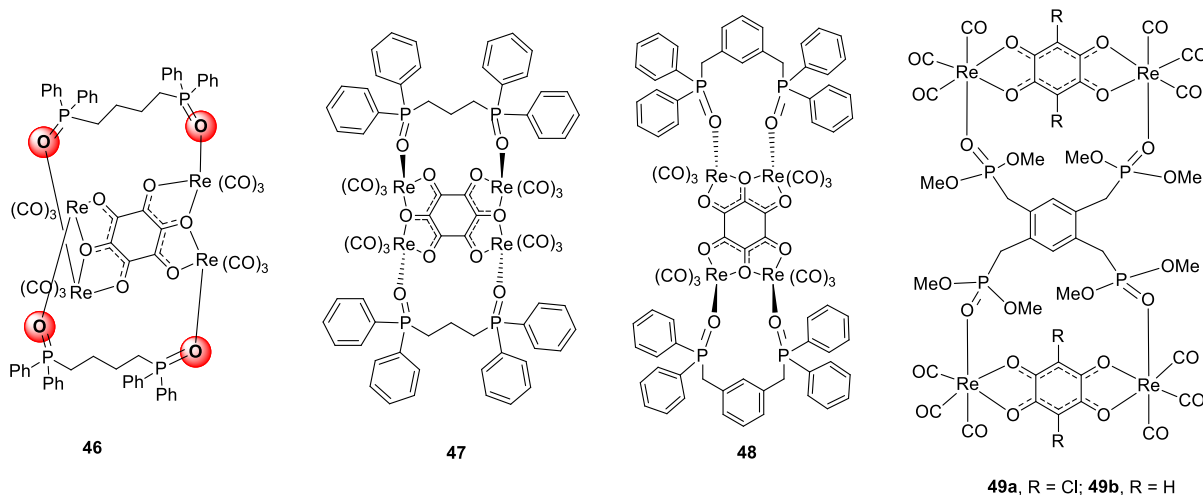
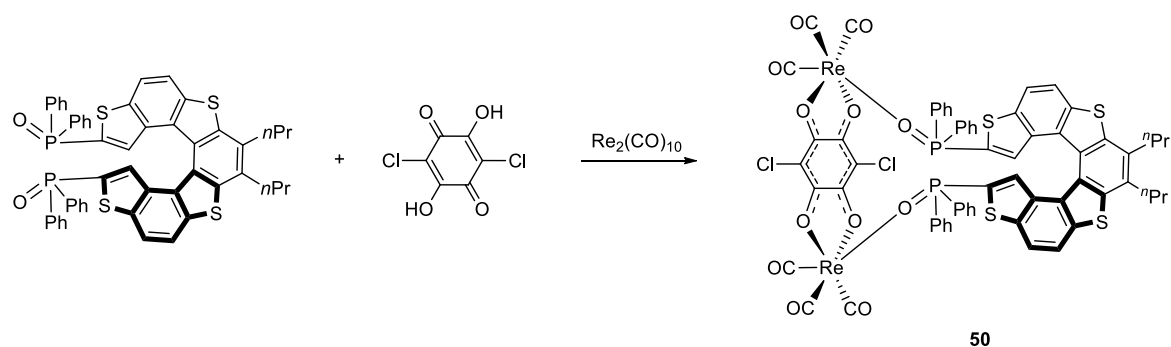


Figure 17. Phosphine oxide donor based tetranuclear SCCs.

Recently, complex **50** containing helicene as spacer with P=O anchors was reported (Scheme 10). The complex serves as a chiral molecule, first example of this kind [54]. The typical helical arrangement of helicene moiety provides a boat-like conformation to the assembly.



Scheme 10. Synthetic approach for complex **50**.

The presence of the spacer motifs; alkyl, aryl or fused aromatic motifs and number of phosphine donors dictate the overall architecture and properties of the SCCs. In the above cases, the ancillary bis-chelating ligands are O $\cap$ O–donors. By changing the bis-chelating donor to tris-/tetrakis-chelating donors, conjoined metallacycles can be obtained. The absorption properties of the P=O donor based SCCs are different from those of complexes obtained using benzimidazole-based nitrogen donors.

The one-pot coordination driven self-assembly approach is a fruitful way to construct Re(I) based SCCs with various sizes and shapes. The physicochemical properties of these complexes can be easily tuned by the careful selection and modification of the coordinated ligands. Most of the complexes presented in this chapter possess rich photophysical and photochemical properties which makes them ideal candidates for applications such as host-guest interaction and molecular recognition, anti-cancer agents, sensors for small molecules and photosensitizers.

1.9. References

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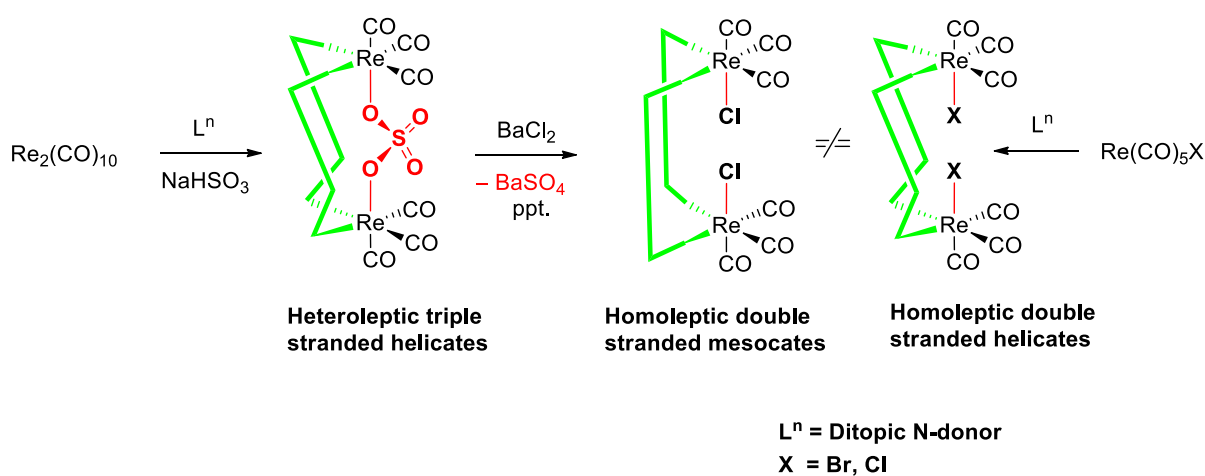
Chapter 2

Sulfate donor-based helicates and mesocates

Abstract

Sulfate donor based supramolecular coordination complexes (SCCs) [$\{fac\text{-Re}(\text{CO})_3\}(\mu\text{-SO}_4)(\text{L}^n)_2\{fac\text{-Re}(\text{CO})_3\}$] (**1–3**) were obtained using flexible ditopic N donor ligands (**1**, $\text{L}^n = \text{L}^1$; **2**, $\text{L}^n = \text{L}^2$; **3**, $\text{L}^n = \text{L}^3$) ($n = 1\text{--}3$), NaHSO_3 , and $\text{Re}_2(\text{CO})_{10}$ in a one-pot, multicomponent, coordination-driven self-assembly approach, in which SO_3^{2-} get oxidized to SO_4^{2-} during the reaction and acts as building framework. Complexes **1–3** were characterized using ATR-IR, ESI-TOF-MS and ^1H NMR spectroscopy. The molecular structures of the complexes **1–3** were confirmed using single crystal X-ray diffraction analysis. The transformation of dinuclear heteroleptic triple stranded helicates to dinuclear homoleptic double stranded mesocates [$\{\text{Re}(\text{CO})_3\text{Cl}\}_2(\text{L}^n)_2$] ($\text{L}^n = \text{L}^1, \text{L}^2, \text{L}^3$; **4a–6a**) was achieved by the addition of BaCl_2 . The direct reaction of $\text{Re}(\text{CO})_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) with $\text{L}^1/\text{L}^2/\text{L}^3$ yielded dinuclear homoleptic double stranded helicates [$\{\text{Re}(\text{CO})_3\text{X}\}_2(\text{L}^n)_2$] (**4b–6b** and **7–9**).

This work has been published in *Inorg. Chem.* **2018**, *57*, 10718-10725.



2.1. Introduction

Several metal-directed synthetic principles are currently available for making well-defined shapes and sizes of supramolecular coordination complexes (SCCs), including helicates and mesocates, which have potential applications in materials and medicinal fields [1-85]. Among the various synthetic approaches, the *fac*-Re(CO)₃ core directed one-pot strategy, i.e., a combination of Re(CO)₅X (X = halide)/ Re₂(CO)₁₀ and organic building units, is a fruitful way to synthesize *fac*-Re(CO)₃ core based SCCs, which have been gaining great interest in molecular recognition, organic transformation, photocatalysts for CO₂ reduction, bio imaging, and anticancer agents [34-78]. Due to their importance, new design principles have been emerging in order to improve the physiochemical properties of SCCs as well as hitherto unexplored molecules. Up to now, the research in this area has mainly been focused on modulating the organic ligands by tuning the denticity and/or spacer to introduce flexibility and decorating framework with functional units [43]. To the best of our knowledge, the hydroxyl (–OH) group and azide anion have been the only ions used as one of the framework units in the Re(I)-based SCCs. As a continuation of the research on progress of Re(I)-based SCCs [66-75], herein, we report the first example of sulfate (SO₄^{2–}) as one of the framework units in neutral heteroleptic *fac*-Re(CO)₃ core based helicate type SCCs. Though the design principles for making various types of helicates are well documented, similar to cavity-containing SCCs [72], examples of rhenium-based helicates are very rare [31-33]. Though the sulfate ion has been gaining research interest in making coordination polymers with auxiliary organic ligands, its use in the SCCs is scarce [21, 22]. The self-assembly of [*fac*-Re(CO)₃](μ-SO₄^{2–})(Lⁿ)₂{*fac*-Re(CO)₃}] (**1–3**) was obtained by the combination of Re₂(CO)₁₀, NaHSO₃, and a neutral flexible ditopic nitrogen donor ((1,3-bis(benzimidazol-1-ylmethyl)benzene (L¹)/1,3-bis(5,6-dimethylbenzimidazol-1-ylmethyl)benzene(L²)/1,3-bis(naphthoimidazol-1-ylmethyl)benzene (L³)). In this approach, NaHSO₃ transforms to tetrahedral SO₄^{2–} during the reaction and acts as part of the framework of SCCs.

2.2. Experimental

Materials and Methods

Starting materials such as $\text{Re}_2(\text{CO})_{10}$, $[\text{Re}(\text{CO})_5\text{Cl}]$, $[\text{Re}(\text{CO})_5\text{Br}]$ (98%, Sigma-Aldrich), sodium bisulfite (Avra), sodium sulfate (Finar), barium chloride (Finar), Acetone (Finar) were purchased. Solvents hexane and toluene were purified using conventional procedures. Ligands (L^1 , L^2) [90] and (L^3) [91] were synthesized as reported in the literature. Sodium Bisulfite (NaHSO_3) (95%, Avra): Crystallized from hot water (1 mL/g). Dried at 100 °C under vacuum for 4 hours. Ligand L^1 was washed several times with distilled hexane and dried at 100°C under vacuum for 2 hours. After purification and drying under vacuum, the compounds were kept in desiccator consisting of blue silica gel as desiccant. ^1H NMR spectra were recorded on Bruker 400 MHz and 500 MHz spectrometers. ATR-IR spectra were recorded on Bruker Tensor-II spectrometer. Elemental analyses were performed on a Flash EA series 1112 CHNS analyzer. The mass spectra were performed on a Bruker maXis mass spectrometer. The Raman spectrum was recorded on a WI-Tec confocal Raman spectrometer equipped with a Peltier-cooled CCD detector.

Synthesis of $[(\text{Re}(\text{CO})_3)_2(\mu\text{-SO}_4)(\text{L}^1)_2]$ (1).

$\text{Re}_2(\text{CO})_{10}$ (100.2 mg, 0.154 mmol), NaHSO_3 (16 mg, 0.154 mmol), L^1 (103.6 mg, 0.306 mmol), toluene (10 mL), and acetone (3 mL) were heated in a solvothermal reactor. Colourless crystals obtained in the solvothermal vessel were filtered and air-dried. Yield: 28% (57 mg). Anal. Calcd for $\text{C}_{50}\text{H}_{36}\text{N}_8\text{O}_{10}\text{Re}_2\text{S}$: C, 45.73; H, 2.76; N, 8.53; S, 2.44. Found: C, 45.82; H, 2.71; N, 8.63; S, 2.48. ESI-MS: 1313.1174 for $[\text{M} + \text{H}]^+$. ^1H NMR (500 MHz, $\text{DMSO-}d_6$): 8.62 (s, 4H, H^2 , benzimidazolyl), 7.67–7.65 (m), 7.49–7.46 (m), 7.36–7.30 (m), 6.82 (s, 2H, H^9 , benzene of L^1) and 5.53–5.43 (dd, 8H, $J = 15$ Hz, $-\text{CH}_2-$). ATR-IR (cm^{-1}): ν 2018 and 1861 (CO).

Synthesis of $[(\text{Re}(\text{CO})_3)_2(\mu\text{-SO}_4)(\text{L}^2)_2]$ (2).

$\text{Re}_2(\text{CO})_{10}$ (100.5 mg, 0.154 mmol), NaHSO_3 (16.1 mg, 0.155 mmol), L^2 (121 mg, 0.307 mmol), toluene (10 mL), and acetone (3 mL) were heated in a solvothermal reactor. Colourless crystals along with a white powder obtained in the solvothermal vessel were washed with distilled hexane and air-dried. Yield: 75%/25% (free ligand and complex) (149 mg) on the basis of ^1H NMR analysis. ATR-IR (cm^{-1}): ν 2014, 1896, and 1866 (CO).

Synthesis of $[(\text{Re}(\text{CO})_3)_2(\mu\text{-SO}_4)(\text{L}^3)_2]$ (3).

$\text{Re}_2(\text{CO})_{10}$ (100.6 mg, 0.154 mmol), NaHSO_3 (16 mg, 0.154 mmol), L^3 (134.3 mg, 0.306 mmol), toluene (10 mL), and acetone (3 mL) were heated in a solvothermal reactor. Colourless crystals and white powder were obtained in the bomb. The mixture was washed with distilled hexane several times to obtain the pure complex and air-dried. Yield: 47% (108.7 mg). Anal. Calcd for $\text{C}_{66}\text{H}_{44}\text{N}_8\text{O}_{10}\text{Re}_2\text{S}$: C, 52.37; H, 2.93; N, 7.40; S, 2.12. Found: C, 52.27; H, 2.89; N, 7.46; S, 2.18. ESI-MS: 1513.2254 for $[\text{M} + \text{H}]^+$. ^1H NMR (500 MHz, $\text{DMSO-}d_6$): 8.92 (s, 4H, H^2), 8.22 (s, 4H, H^4), 8.04–8.02 ($\text{H}^8, ^9$), 7.71–7.39 (m, H^{5-7} and H^{12-14}), 6.96 (s, 2H, H^{11} , benzene of L^3) and 5.57–5.43 (dd, 8H, $J = 15$ Hz, $-\text{CH}_2-$). ATR-IR (cm^{-1}): ν 2009 and 1876 (CO).

Synthesis of $[\{\text{Re}(\text{CO})_3\text{Cl}\}_2(\text{L}^1)_2]$ (4b).

$\text{Re}(\text{CO})_5\text{Cl}$ (100.1 mg, 0.277 mmol), L^1 (94.2 mg, 0.278 mmol), toluene (20 mL), and THF (20 mL) were refluxed for 48 h. The solution volume was reduced to half under reduced pressure. The precipitate was washed with hexane. Yield: 34% (119.7 mg). Anal. Calcd for $\text{C}_{50}\text{H}_{36}\text{Cl}_2\text{N}_8\text{O}_{10}\text{Re}_2$: C, 46.62; H, 2.82; N, 8.70. Found: C, 46.51; H, 2.78; N, 8.65. ESI-MS: 1289.1322 for $[\text{M} + \text{H}]^+$. ^1H NMR (500 MHz, $\text{DMSO-}d_6$): 8.61 (s, 4H, H^2 , benzimidazolyl), 7.80–7.78 (m), 7.55–7.53 (m), 7.39–7.36 (m), 7.29 (s, 2H, H^9 , benzene of L^1), 6.40 (t, $J = 7.6$ Hz, 2H, H^{11}), 6.14 (d, $J = 7.6$ Hz, 4H, $\text{H}^{10,12}$) and 5.58–5.47 (dd, 8H, $J = 16.5$ Hz, $-\text{CH}_2-$). ATR-IR (cm^{-1}): ν 2017, 1915, and 1874 (CO).

Synthesis of $[\{\text{Re}(\text{CO})_3\text{Cl}\}_2(\text{L}^2)_2]$ (5b).

$\text{Re}(\text{CO})_5\text{Cl}$ (100.1 mg, 0.277 mmol), L^2 (110.2 mg, 0.279 mmol), toluene (20 mL), and THF (20 mL) were refluxed for 48 h. The solution volume was reduced to half under reduced pressure. The precipitate was washed with hexane. Yield: 22% (84.8 mg). Anal. Calcd for $\text{C}_{58}\text{H}_{52}\text{Cl}_2\text{N}_8\text{O}_{10}\text{Re}_2$: C, 49.75; H, 3.74; N, 8.00. Found: C, 49.63; H, 3.78; N, 8.15. ESI-MS: 1401.2544 for $[\text{M} + \text{H}]^+$. ^1H NMR (500 MHz, $\text{DMSO-}d_6$): 8.44 (s, 4H, H^2 , methyl benzimidazolyl), 7.55 (s, 4H, H^4), 7.28 (s, 2H, H^9 , benzene of L^2), 7.26 (s, 4H, H^7), 6.21 (t, $J = 7.6$ Hz, 2H, H^{11}), 5.88 (d, $J = 7.65$ Hz, 4H, $\text{H}^{10,12}$) and 5.55–5.39 (dd, 8H, $J = 16.3$ Hz, $-\text{CH}_2-$). ATR-IR (cm^{-1}): ν 2015 and 1875 (CO).

Synthesis of $[\{\text{Re}(\text{CO})_3\text{Cl}\}_2(\text{L}^3)_2]$ (6b).

$\text{Re}(\text{CO})_5\text{Cl}$ (100.2 mg, 0.277 mmol), L^3 (121.2 mg, 0.276 mmol), toluene (20 mL), and THF (20 mL) were refluxed for 48 h. The solution volume was reduced to half under reduced

pressure. The precipitate was washed with hexane. Yield: 85%/15% (free ligand: complex) (189.1 mg) on the basis of the ^1H NMR analysis. ATR-IR (cm^{-1}): ν 2019, 1909, and 1888 (CO).

Synthesis of $[(\text{Re}(\text{CO})_3)_2(\text{Br})_2(\text{L}^1)_2]$ (7).

$\text{Re}(\text{CO})_5\text{Br}$ (100.7 mg, 0.248 mmol), L^1 (167.2 mg, 0.494 mmol), toluene (10 mL), and acetone (3 mL) were heated in a solvothermal reactor. The white powder obtained in the bomb was filtered and air-dried. Yield: 14% (46.3 mg). Anal. Calcd for $\text{C}_{50}\text{H}_{36}\text{Br}_2\text{N}_8\text{O}_{10}\text{Re}_2$: C, 43.61; H, 2.64; N, 8.14. Found: C, 43.58; H, 2.56; N, 8.21. ESI-MS: 1377.0226 for $[\text{M} + \text{H}]^+$. ^1H NMR (500 MHz, $\text{DMSO}-d_6$): 8.66 (s, 4H, H^2 , benzimidazolyl), 7.80 (d, $J = 7.5$ Hz), 7.56 (d, $J = 7.25$ Hz), 7.41–7.36 (m), 7.32 (s, 2H, H^9 , benzene of L^1), 6.45 (t, $J = 7.6$ Hz, H^{11}), 6.20 (d, $J = 7.65$ Hz, $\text{H}^{10,12}$) and 5.59–5.49 (dd, 8H, $J = 15.9$ Hz, $-\text{CH}_2-$). ATR-IR (cm^{-1}): ν 2022, 1913, and 1870 (CO).

Synthesis of $[(\text{Re}(\text{CO})_3)_2(\text{Br})_2(\text{L}^2)_2]$ (8).

$\text{Re}(\text{CO})_5\text{Br}$ (100.8 mg, 0.248 mmol), L^2 (98.1 mg, 0.249 mmol), toluene (10 mL), and acetone (3 mL) were heated in a solvothermal reactor. The white powder obtained in the bomb was filtered and air-dried. Yield: 41% (152.8 mg). Anal. Calcd for $\text{C}_{58}\text{H}_{52}\text{Br}_2\text{N}_8\text{O}_{10}\text{Re}_2$: C, 46.78; H, 3.52; N, 7.52. Found: C, 46.65; H, 3.47; N, 7.61. ESI-MS: 1489.1529 for $[\text{M} + \text{H}]^+$. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): 8.46 (s, 4H, H^2 , methyl benzimidazolyl), 7.52 (s, 4H, H^4), 7.31 (s, 2H, H^9 , benzene of L^2), 7.27 (s, 4H, H^7), 6.24 (t, $J = 7.4$ Hz, 2H, H^{11}), 5.91 (d, $J = 8.6$ Hz, 4H, $\text{H}^{10,12}$) and 5.54–5.39 (dd, 8H, $J = 16$ Hz, $-\text{CH}_2-$). ATR-IR (cm^{-1}): ν 2018, 1905, and 1874 (CO).

Synthesis of $[(\text{Re}(\text{CO})_3)_2(\text{Br})_2(\text{L}^3)_2]$ (9).

$\text{Re}(\text{CO})_5\text{Br}$ (100.2 mg, 0.247 mmol), L^3 (108 mg, 0.246 mmol), toluene (20 mL), and THF (20 mL) were refluxed for 48 h. The solution volume was reduced to half under reduced pressure. The precipitate was washed with hexane. Yield: 85%/15% (free ligand: complex) (135 mg) on the basis of the ^1H NMR analysis. ATR-IR (cm^{-1}): ν 2018, 1908, and 1883 (CO).

X-ray crystallography

The crystals of **1–3** were obtained directly from the solvothermal vessel. The structures of **1–3** were confirmed with single crystal X-ray analysis. Intensity data of crystals of **1–3** were collected on a Bruker D8 Quest diffractometer [$\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$]. The structures were solved by direct methods using SHELXS-97 [92-95] and refined using the SHELXL-2014/7 program (within the WinGX program package) [93,94]. Non-H atoms were refined

anisotropically. Some of the lattice solvent molecules could not be modeled, and hence their contribution to the intensities was excluded using the SQUEEZE option in PLATON [92-95].

Table 1. Crystal Data for the Structure determinations of **1** – **3**.

	1	2	3
Formula	C ₅₀ H ₃₆ O ₁₀ Re 2N ₈ S	C ₅₈ H ₅₂ O ₁₀ Re ₂ N ₈ S	C ₆₆ H ₄₄ O ₁₀ Re ₂ N ₈ S
Formula weight	1313.35	1425.53	1513.55
Crystal system			
Space group	Monoclinic	Monoclinic	Monoclinic
<i>a</i> (Å)	P 21/c	I 2/a	I 2/a
<i>b</i> (Å)	13.9869(4)	23.3385(11)	23.6512(11)
<i>c</i> (Å)	19.2913(6)	15.6231(8)	15.6268(8)
α (deg)	18.5930(6)	31.5334(15)	32.6550(16)
β (deg)	90	90	90
γ (deg)	94.445(10)	98.161(3)	94.420(3)
<i>V</i> (Å ³)	90	90	90
<i>Z</i>	5001.8(3)	11381.3(10)	12033.1(10)
<i>T</i> (K)	4	8	8
λ (Å)	295(2)	100(2)	100(2)
<i>D</i> _{calc} (gcm ⁻³)	0.71073	0.71073	0.71073
μ (mm ⁻¹)	1.744	1.664	1.671
R1 ^a [<i>I</i> > 2 σ (<i>I</i>)]	4.943	4.352	4.122
wR2 ^b (all data)	0.0359	0.0672	0.0434
GooF	0.0761	0.1409	0.1152
	0.939	1.094	1.015

$$^a R_1 = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|, \quad ^b wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$$

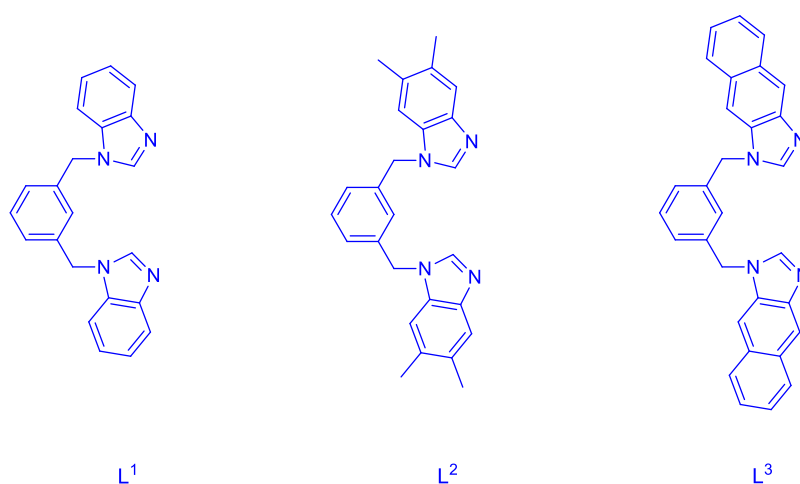
Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes **1-3**

Compound	Re...Re	Coordinated S–O	Uncoordinated S–O
1	6.499	1.505 and 1.503	1.450 and 1.428
2	6.624	1.477 and 1.535	1.442 and 1.512
3	6.539	1.477 and 1.529	1.461 and 1.454

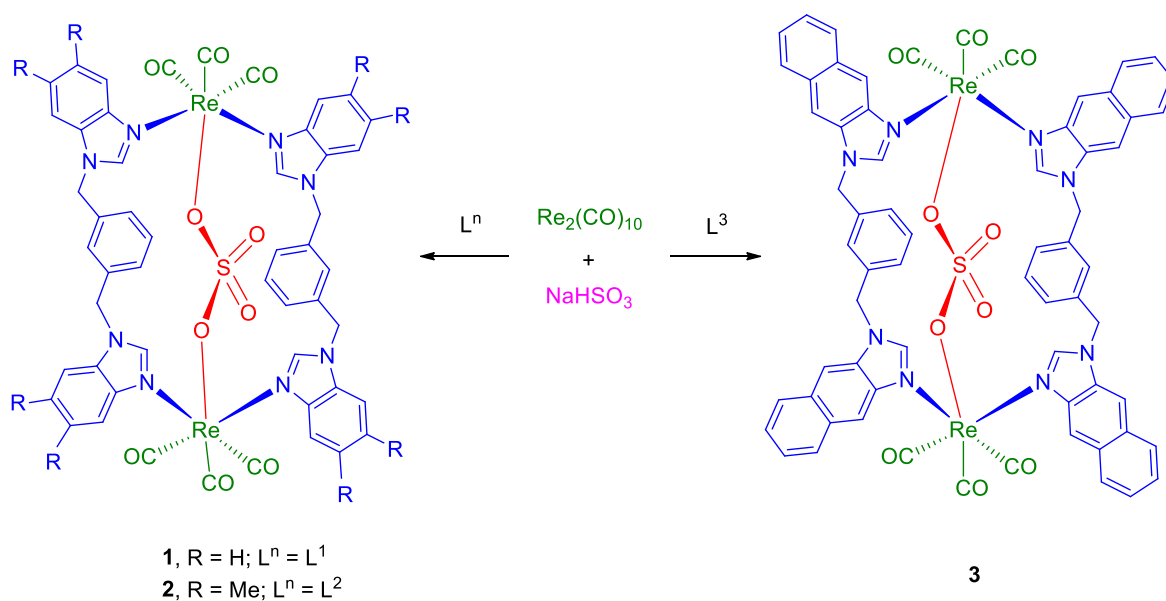
2.3. Results and discussion

Synthesis and characterization of complexes 1-3

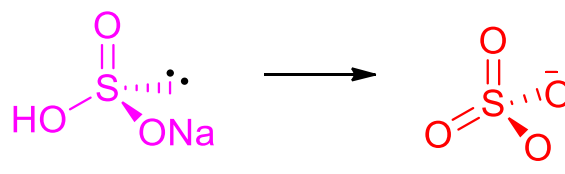
Complexes **1-3** were prepared by treating $\text{Re}_2(\text{CO})_{10}$, NaHSO_3 , and $\text{L}^1/\text{L}^2/\text{L}^3$ in a toluene-acetone solvent mixture under solvothermal conditions (Scheme 1). In this approach, NaHSO_3 transforms to tetrahedral SO_4^{2-} during the reaction and acts as part of the framework of SCCs (Scheme 2).

**Figure 1.** Ditopic N-donor ligands

Ditopic nitrogen donor ligands $\text{L}^1/\text{L}^2/\text{L}^3$ have been used in coordination chemistry as one of the structural frameworks for SCCs, coordination polymers and metal-organic frameworks (Figure 1) [47,48].



Scheme 1. Synthetic approach for complexes 1-3



Scheme 2. Transformation of NaHSO_3 to SO_4^{2-}

The complexes **1-3** are air and moisture stable and soluble in polar organic solvents. The ATR-IR spectrum of **1** displays strong bands at 2018 and 1861 cm^{-1} , characteristics of *fac*- $\text{Re}(\text{CO})_3$ core [34-42]. Three bands observed at 1118, 1009 and 907 cm^{-1} was assigned to SO_4^{2-} unit bridged to metal ions (Figure 2) [79]. The sharp peak observed at 926 cm^{-1} in the Raman spectrum of **1** can be assigned to the S-O vibrations of SO_4^{2-} coordinating unit (Figure 3). In order to understand the source of oxygen for the transformation of sulphite to sulphate, the starting materials such as NaHSO_3 , L^1 , toluene, and acetone were dried and purified using conventional procedures [86,87].

The controlled studies were carried out by reacting $\text{Re}_2(\text{CO})_{10}$, L^1 , and NaHSO_3 in dry toluene-acetone solvent mixture under solvothermal conditions in the presence as well as absence of oxygen (in a glove box). Since acetone may contain traces of isopropyl alcohol, the reaction was also carried out using isopropyl alcohol. The complex was formed when the reactions were done in the presence of air. No complex formation was observed when the reaction was carried out in the absence of oxygen or in the presence of isopropyl alcohol. These results indicate that aerial oxygen is responsible for the transformation of SO_3^{2-} to SO_4^{2-} .

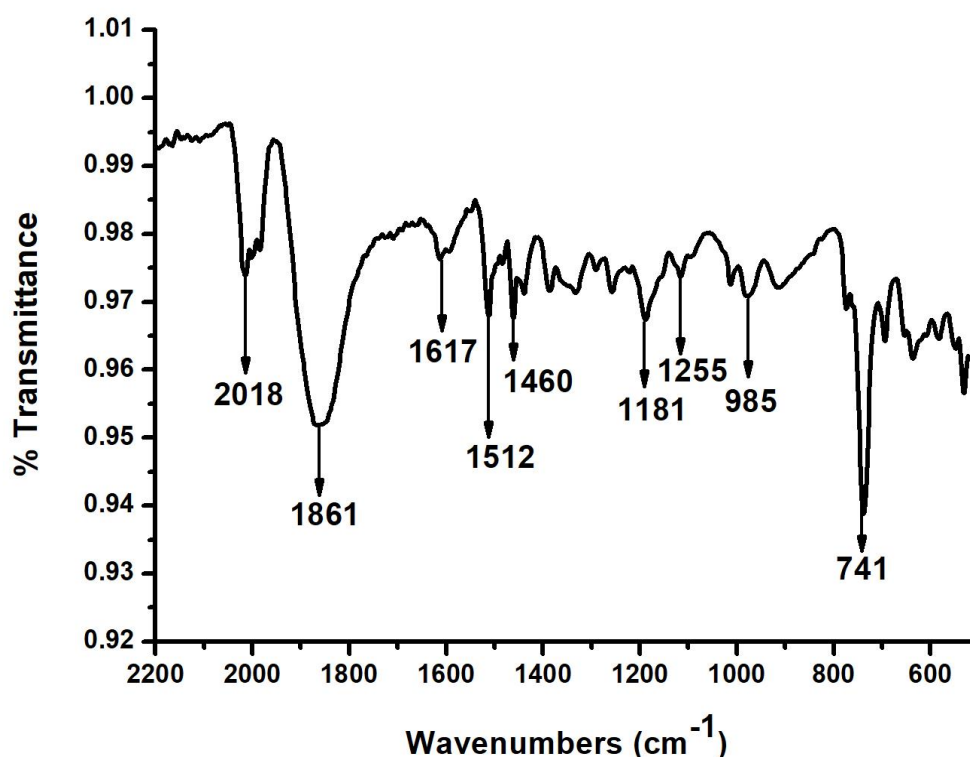


Figure 2. ATR-IR spectrum of **1**

No complex formation was observed upon direct reaction of Na_2SO_4 instead of NaHSO_3 with $\text{Re}_2(\text{CO})_{10}$ and $\text{L}^1/\text{L}^2/\text{L}^3$ i.e., no helicate or mesocate were formed. The reaction yielded a mixture of free ligand and rhenium core, indicating that the complexes cannot be obtained by the direct use of SO_4^{2-} as the template ion.

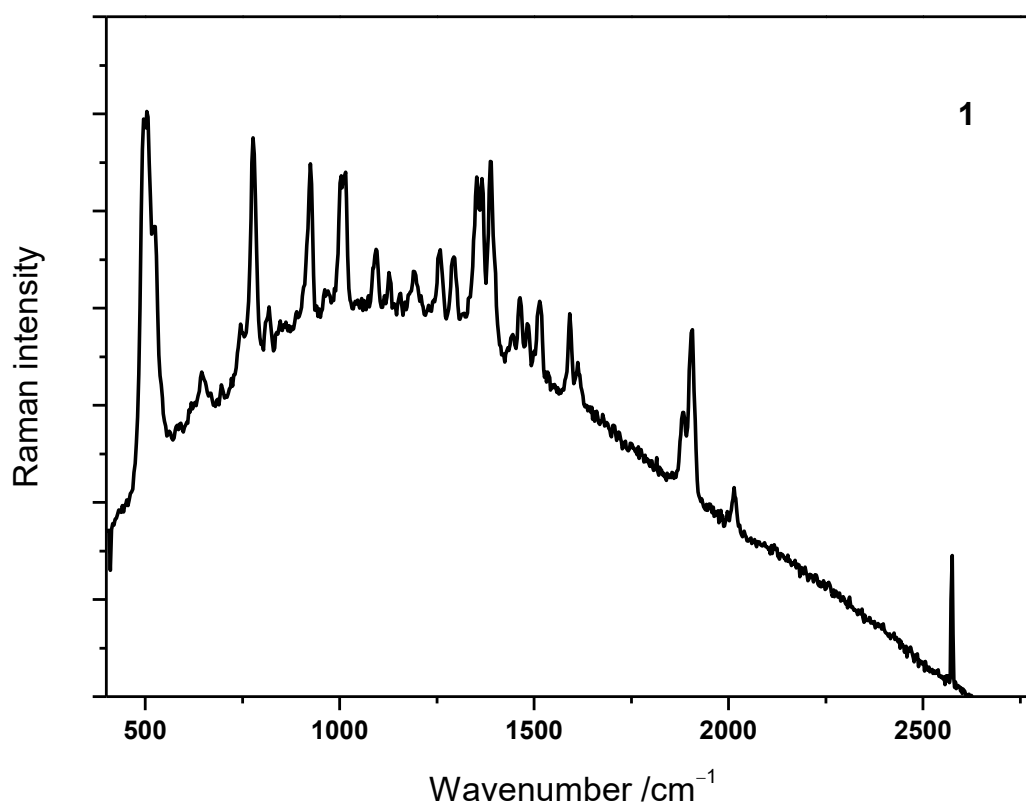


Figure 3. Raman spectrum of **1**

The ^1H NMR spectrum of **1** in $\text{dms-}d_6$ shows a simple pattern with five chemical resonances in the aromatic region (Figure 4). The H^2 proton adjacent to nitrogen was downfield shifted by 0.25 ppm relative to that of uncoordinated L^1 , which can be ascribed to the coordination of the benzimidazolyl tertiary nitrogen to the rhenium core. The H^9 proton of L^1 in **1** appeared as a singlet and was shifted upfield. The same H^9 proton was merged with other aromatic proton signals in the free ligand L^1 . This can be explained by the possibility that the H^9 proton in **1** may be directed over the aromatic face of a neighbouring arene unit and experience the ring current effect [30]. The remaining aromatic protons (H^{4-7} and H^{10-12}) merged together and appeared as three chemical resonances.

The aliphatic methylene protons ($-\text{CH}_2-$) that appeared as a doublet of doublets indicate the rigid nature of the methylene protons in the complex. All observations indicates that L^1 is coordinated with rhenium core and it is rigid in the complex rather than in the free ligand.

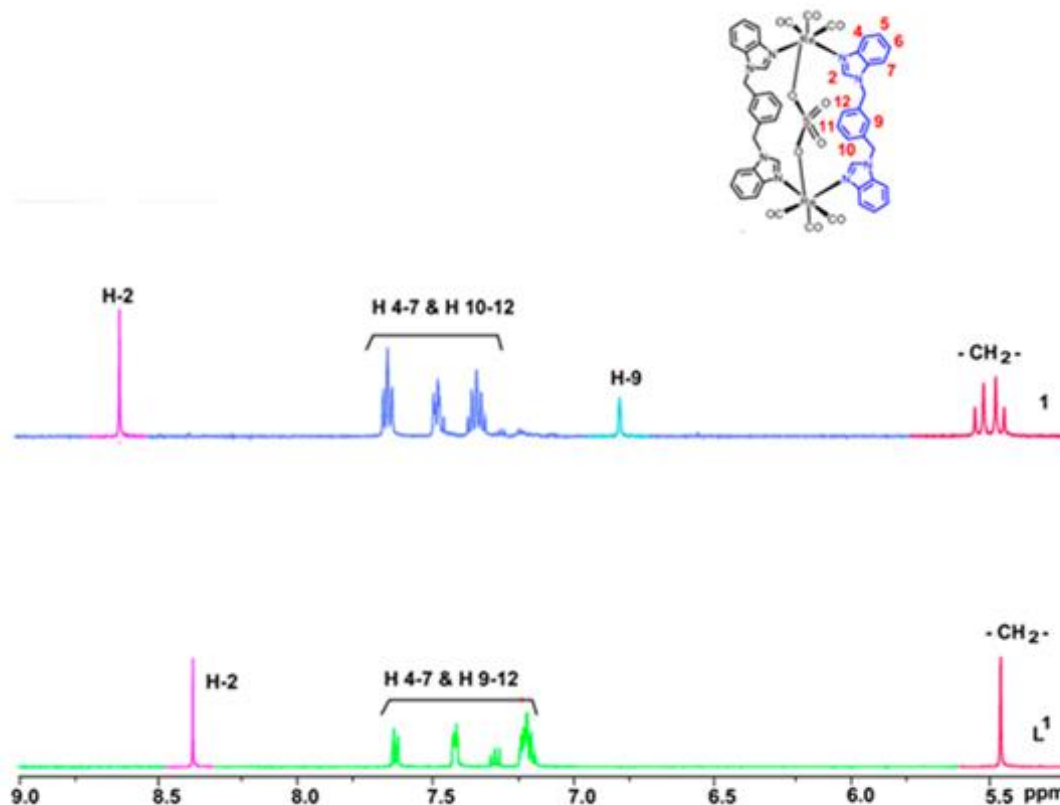


Figure 4. Partial ^1H NMR spectra of L^1 and **1** in $\text{dmsO}-d_6$.

The ^1H NMR spectrum of complex **3** displays a pattern similar to that of **1**, i.e. an upfield shift for H^{11} proton, a downfield shift for the H^2 proton and a multiplet for the $-\text{CH}_2-$ protons, indicating that the arrangements of the ligands in complexes **1** and **3** are similar (Figure 5). The ^1H NMR spectrum of complex **2** shows a considerable amount of free ligand L^2 along with the desired product and the separation of the complex from the mixture was fruitless.

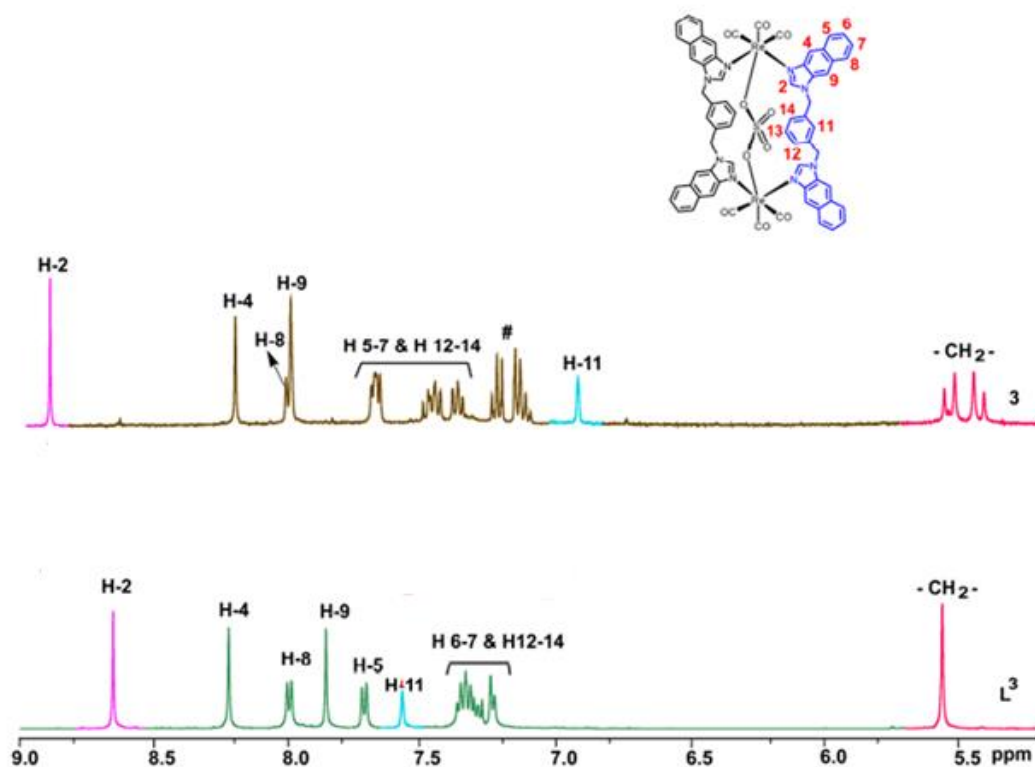


Figure 5. Partial ^1H NMR spectra of L^3 and **3** in $\text{dmsO}-d_6$ (# = toluene).

The formation of **1** was further confirmed by electrospray ionization mass analysis, which displays a molecular ion peak (m/z 1313.1174 for $[\mathbf{1} + \text{H}]^+$) that matches with theoretical value. Complexes **2** and **3** also show the molecular ion peaks m/z 1425.2685 for $[\mathbf{2} + \text{H}]^+$ and m/z 1513.2254 for $[\mathbf{3} + \text{H}]^+$, which confirms the formation of SCCs.

Molecular Structures of Complexes 1–3

The crystals of **1–3** were obtained directly from the solvothermal vessel. The structures of **1–3** were confirmed by single-crystal X-ray analysis (Figure 6). Molecule **1** adopts a helical structure and consists of two *fac*-Re(CO)₃ cores, one SO₄²⁻, and two neutral L¹ ligands. The distance between two rhenium atoms (Re···Re) is 6.499 Å. Two L¹ ligands act as helical molecular clips and wrap around the {Re···Re} core. The helical twist angles of ligands are 25 and 31° i.e., torsion angles of Re1···N2···N1···Re2 and Re1···N4···N3···Re2. Due to this arrangement, two benzimidazolyl units of L¹ in **1** are orthogonal to each other ($\tau = 87$ and 70°). The sulfate dianion takes a syn, anti 2.1100 (μ_2 : η_1 : η_1) [80,81] conformation mode and coordinates two rhenium cores in **1**.

The coordinated S–O distances (1.505 and 1.503 Å) are significantly longer than the uncoordinated S–O distances (1.450 and 1.428 Å). Two different bond lengths for the bridging SO₄²⁻ anion were observed [80,81]. The uncoordinated oxygen atoms in the sulfate anion are directed away from the centre of the molecule. The rhenium atom adopts an octahedral geometry and is surrounded by three facial carbonyl units, one oxygen atom from SO₄²⁻, and two nitrogen donors from two L¹ units. Two benzimidazolyl donors, each from different strands, around each rhenium are arranged in a *cis* fashion.

To the best of our knowledge, rhenium (I)-based SCCs with helicate/ mesocate type structures are very rare [72-75]. Complexes **2** and **3** also adopt structures similar to that of helicate **1** (Figure 6). Though the nitrogen donor ligands in both the complexes adopt a helicate structure, the torsion angles of Re···N···N···Re units in **2** and **3** ($\tau = 12/11^\circ$ for **2** and $14/12^\circ$ for **3**) are smaller than those found in helicate **1**. In the crystal structure of **1**, each molecule is surrounded by six adjacent molecules, two molecules on the Re···Re axis and four molecules on the circular space, which are all held together by multiple non-covalent contacts (C(sp³)-H··· π and edge-to-face C-H··· π , C(sp³)-H···O $\equiv$ C-Re, C(sp²)-H···O(SO₄), C(sp³)-H···O $\equiv$ C-Re, and displaced π ··· π interactions).

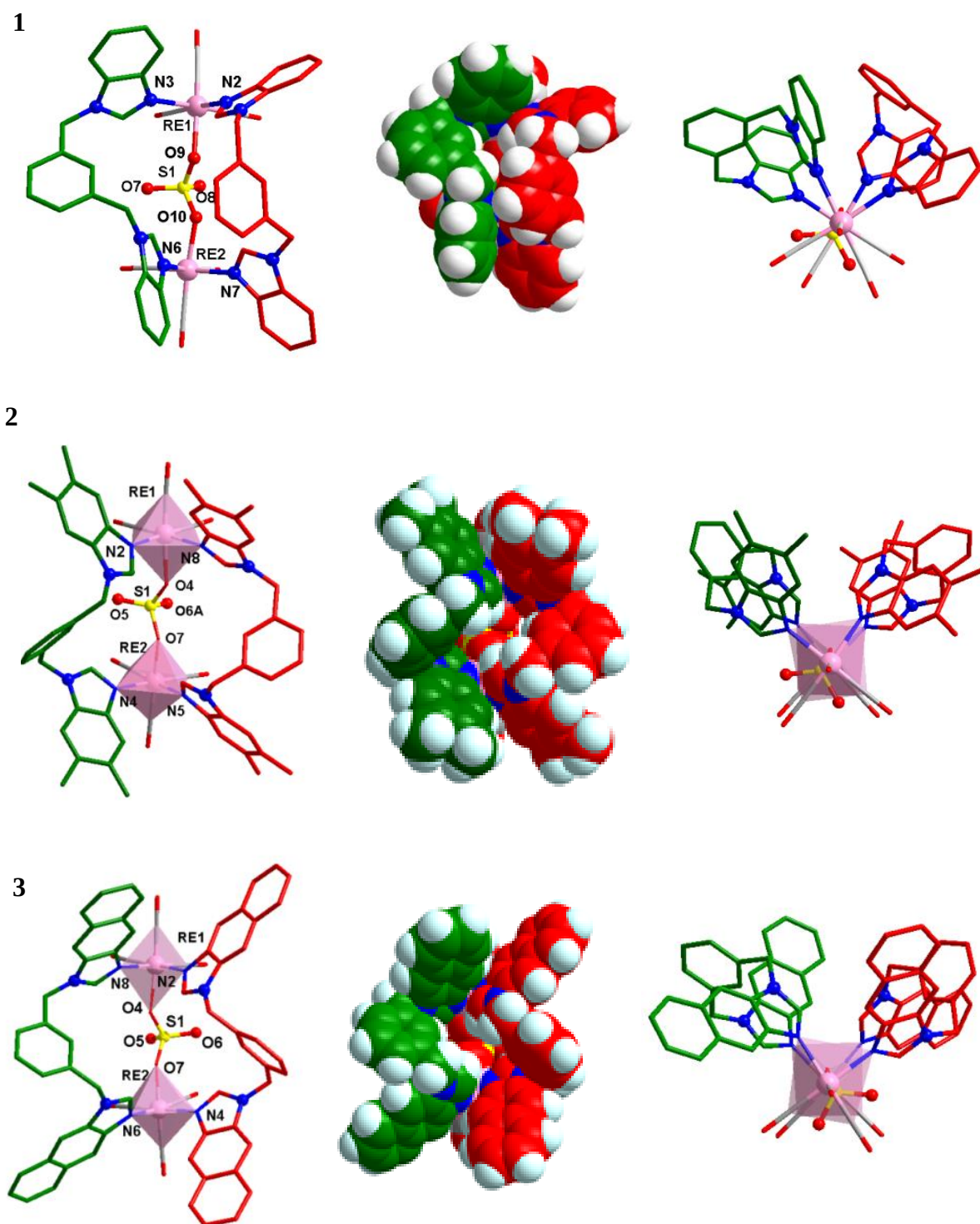
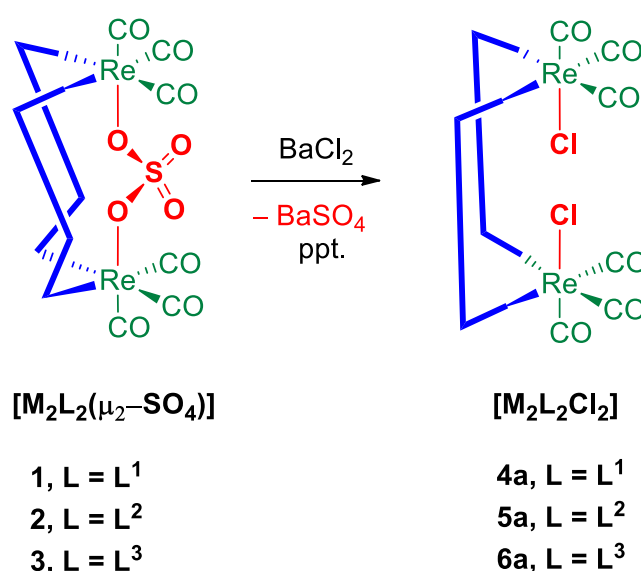


Figure 6. Three different views of the molecular structures of 1–3 showing the helical arrangement of the ligand strands in the complexes (L, green and red stick models; sulfate, ball and stick model, CO, stick models). H atoms are removed for clarity.

Transformation of triple helicates to double mesocates (4a-6a)

The stability of complex **1** was further studied using variable temperature ^1H NMR experiments. Though the chemical shifts for the protons of L^1 in **1** were observed, no additional chemical resonances were observed. In addition, chloranilic acid ($\text{H}_2\text{-CA}$), a well-known dianionic bis-chelator used for the construction of several rhenium based SCCs was added to **1** and heated. The ^1H NMR spectrum of the mixture shows neither an extra peak nor any shift in the resonances, indicating the stable nature of the sulfate coordinated dinuclear structure in solution. However, the sulfate-coordinated complexes **1-3** are unstable in the presence of BaCl_2 . The addition of BaCl_2 to $\text{dms}\text{-}d_6$ solutions of **1-3** resulted in the formation of sulfate free double-homostranded mesocates **4a-6a** (Scheme 3 and Figure 7) along with the formation of BaSO_4 as a white precipitate.



Scheme 3. Synthesis of double stranded homoleptic mesocates

The transformation of **1-3** into **4a-6a** is quantitative on the basis of the ^1H NMR spectroscopic analysis. The solution after the addition of BaCl_2 displays a simple pattern with an upfield/downfield shift for the protons of the ligand motif. The multiplet observed for $-\text{CH}_2-$ protons of SO_4^{2-} -based complex **1** is lost in the Cl -based complex **4a**.

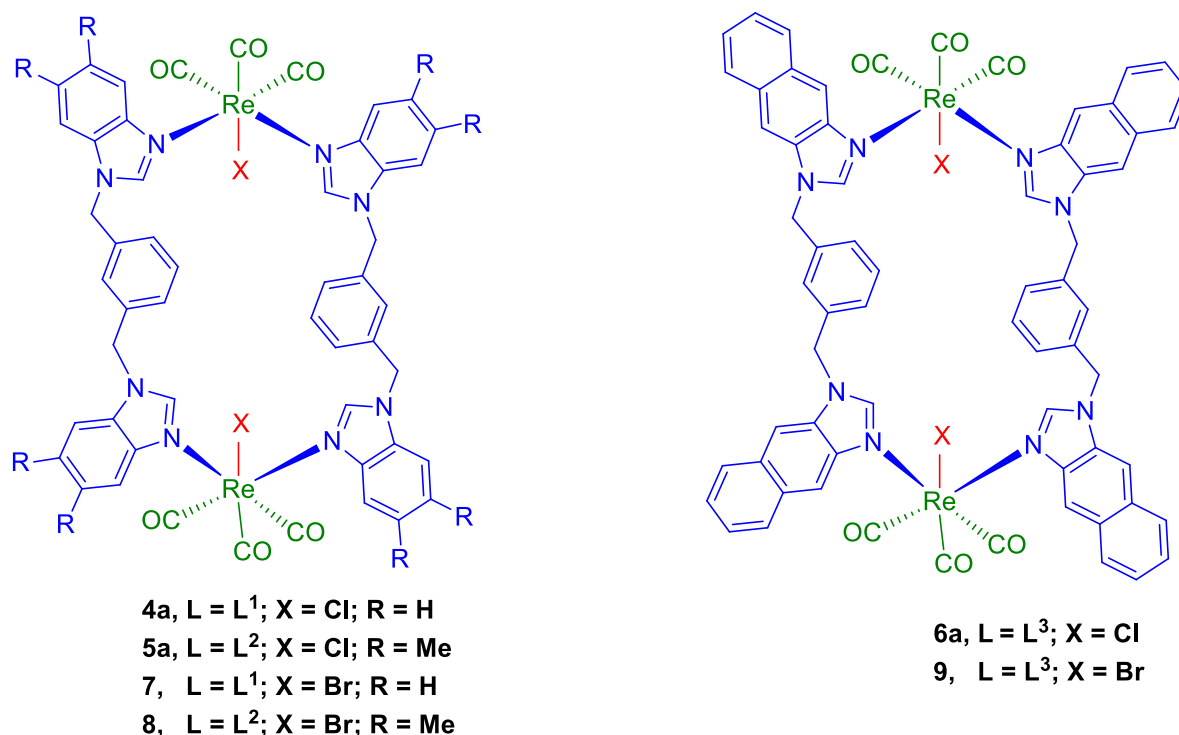


Figure 7. Representation of double-stranded homoleptic mesocates/ helicates.

In particular the 1H NMR spectral pattern of **4a** is completely different from the pattern observed in both complex **1** and ligand L^1 (Figure 8). A similar trend is also observed in case of **6a** (Figure 9). The mixture of complex **2** and ligand L^2 was also treated with $BaCl_2$. The 1H NMR spectrum shows the conversion of complex **2** to complex **5a** without any change in the peak position of L^2 . The formation of complexes **4a-6a** was further supported by ESI-MS analysis. The ESI-MS spectra of **4a-6a** display molecular ion peaks corresponding to the formula $[{Re(CO)_3Cl}]_2(L^n)_2$. The results reveal that the complexes **1-3** completely transformed into complexes **4a-6a**.

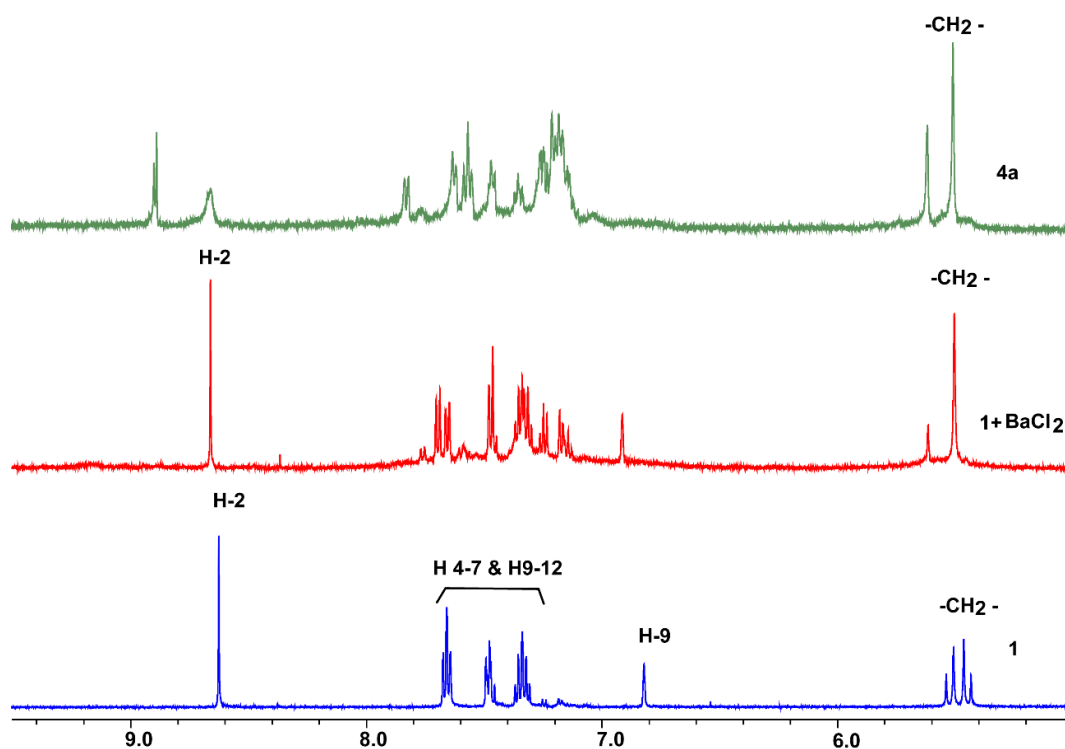


Figure 8. Partial ^1H NMR spectra of **1**, (**1** + BaCl_2) and **4a** in $\text{dmsO-}d_6$. (**1** + BaCl_2 = with less amount of BaCl_2).

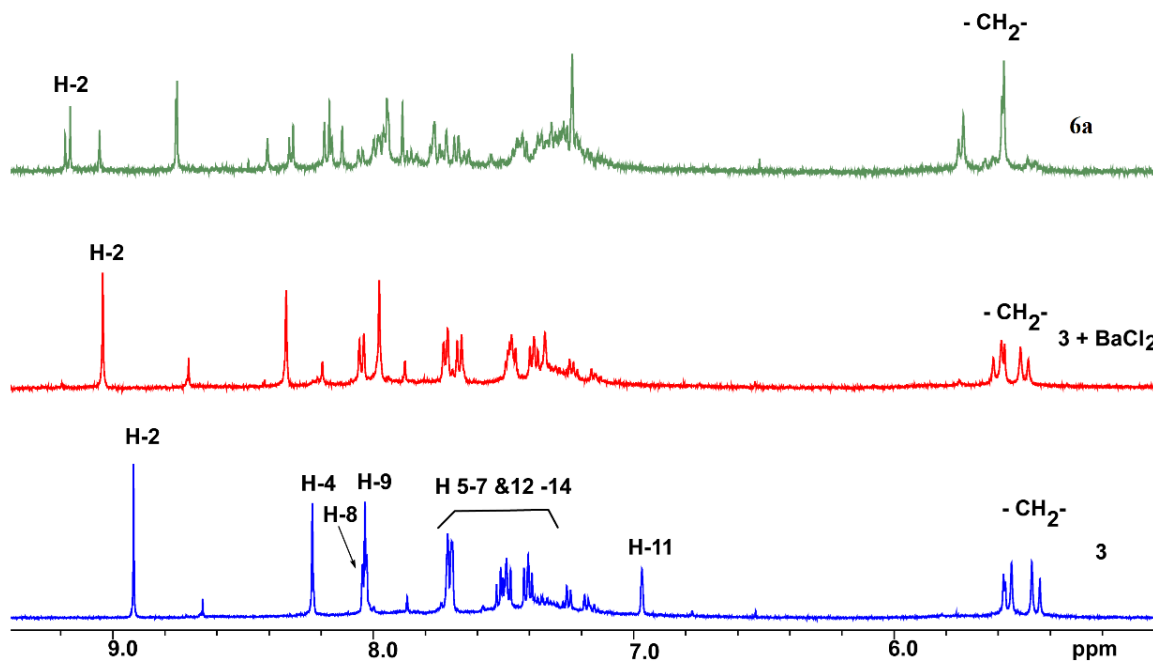
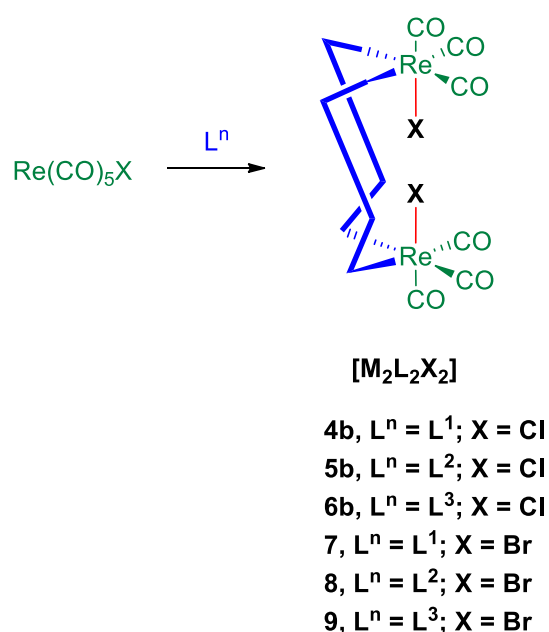


Figure 9. Partial ^1H NMR spectra of **3**, (**3** + BaCl_2) and **6a** in $\text{dmsO-}d_6$. (**3** + BaCl_2 = with less amount of BaCl_2).

Synthesis of double stranded helicates (4b-6b and 7-9)

The direct reaction between $[\text{Re}(\text{CO})_5\text{X}]$ ($\text{X} = \text{Cl}, \text{Br}$) and $\text{L}^1/\text{L}^2/\text{L}^3$ in a toluene/acetone and/or tetrahydrofuran (THF) solvent mixture by solvothermal and conventional methods resulted in the formation of **4b–6b** and **7–9** (Scheme 4 and figure 7) [89]. The ATR-IR spectra of the complexes **4b–6b** and **7–9** exhibit strong bands in the region $2019\text{--}1874\text{ cm}^{-1}$ (Figure 10 and 11) characteristic of *fac*- $\text{Re}(\text{CO})_3$ core.



Scheme 4. Synthesis of double stranded homoleptic helicates

The results of ESI-MS spectral analysis of **4b**, **5b**, **7**, and **8** confirm the formation of $[\{\text{Re}(\text{CO})_3\text{X}\}_2(\text{L}^n)_2]$ ($\text{X} = \text{Cl}, \text{Br}$). The ^1H NMR spectra of **4b** and **5b** are different from those of **4a** and **6a**. In particular the $-\text{CH}_2-$ protons appeared as a multiplet in **4b** and **5b** (Figure 12). Separation of **6b** and **9** from the mixture was fruitless even after several attempts. However, the formation of **6b** and **9** was confirmed by ESI-MS and ^1H NMR spectroscopic analysis. We believe that the complexes **4a**, **6a**, **4b**, and **5b** possess the composition $[\{\text{Re}(\text{CO})_3\text{Cl}\}_2(\text{L}^n)_2]$ and are cyclic in nature. The difference among these complexes may be due to the spatial arrangement of ligands in the complexes. The complexes **4b** and **5b** may possess a helicate type structure, whereas **4a** and **6a** may adopt a mesocate type structure.

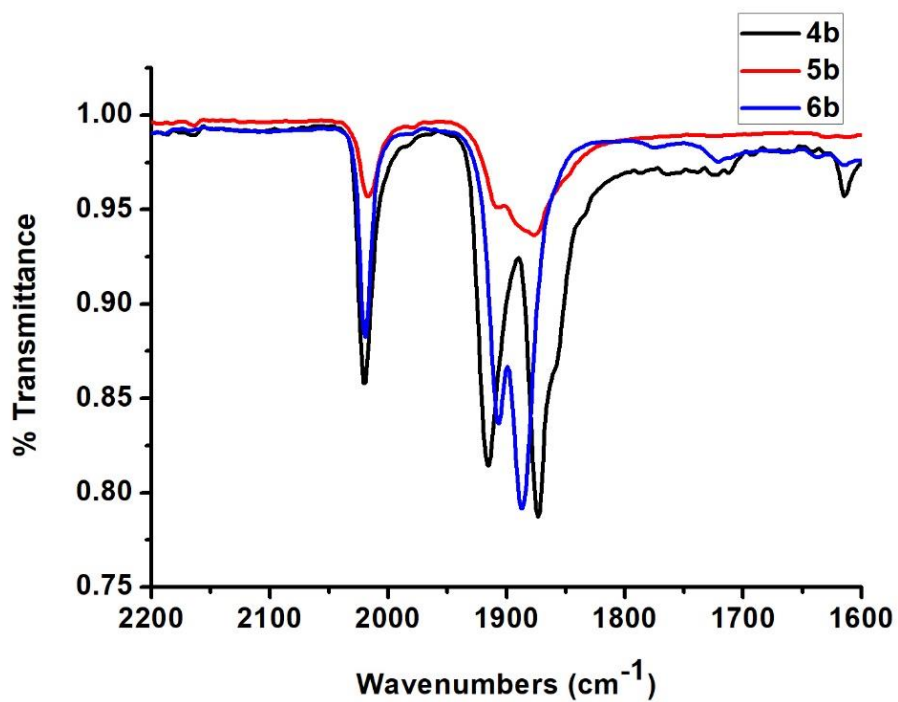


Figure 10. ATR-IR spectra of 4b, 5b and 6b

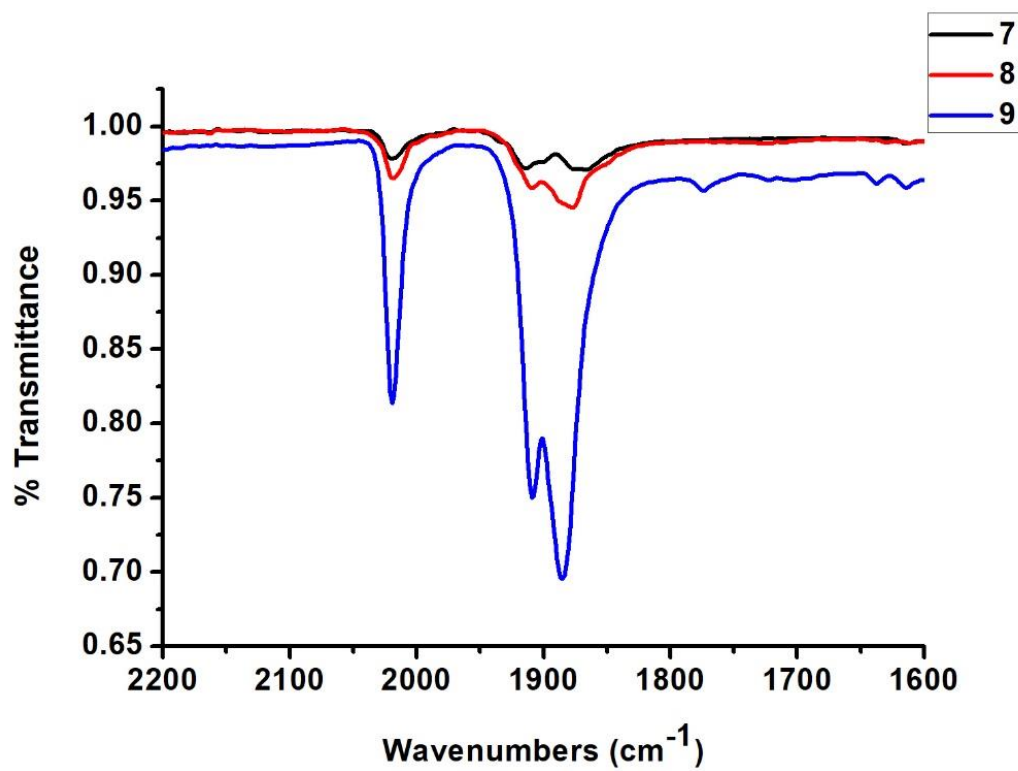


Figure 11. ATR-IR spectra of 7, 8 and 9

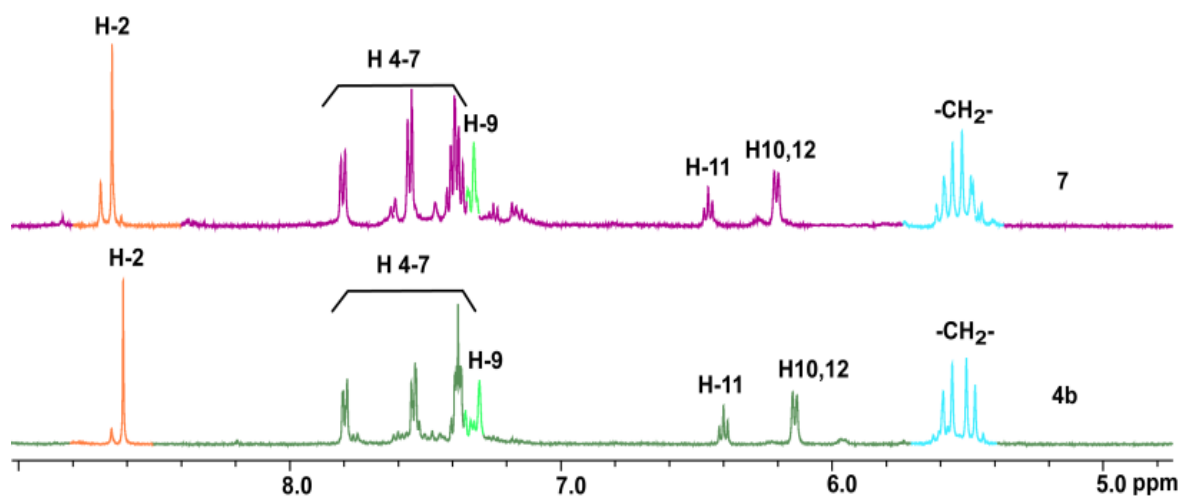


Figure 12. Partial ^1H NMR spectra of **4b** (bottom) and **7** (top) in $\text{dmsO}-d_6$

2.4. Conclusions

In conclusion, the first *fac*- $\text{Re}(\text{CO})_3$ core based SCCs of a sulfate framework ligand are reported and were constructed by spontaneously transforming hydrogen sulfite to sulfate in the presence of neutral nitrogen donors and $\text{Re}_2(\text{CO})_{10}$ using a one-pot, multicomponent, coordination-driven self-assembly process. The results reveal that sulfate ion, a harmless dianion, can be used as one of the basic framework building units to construct SCCs. To the best of our knowledge, the synthetic principle, i.e. spontaneously transforming a sulfite (SO_3^{2-}) to sulfate (SO_4^{2-}) in the presence of a metal source and organic ligand, is the first design principle for making $\text{Re}(\text{I})$ -based SCCs. Two reports on Zn core based SCCs consisting of sulfite and/or sulfate were recently reported [22]. An earlier synthetic principle in which one donor transforms to another donor which further coordinates to metal and forms $\text{Re}(\text{I})$ -based SCCs is a soft ditopic P donor to a hard ditopic $\text{O}=\text{P}$ donor [67]. It is important to mention that research on the transformation and fixation of SO_2 into sulfate by either organic molecules or coordination complexes has been gaining much attention recently due to its risk to human health [21, 22, 82-84]. Addition of BaCl_2 to the SCCs resulted in the transformation of dinuclear heteroleptic triple-stranded helicates to sulfate-free dinuclear neutral homoleptic double-stranded mesocates. The direct reaction of $[\text{Re}(\text{CO})_5\text{X}]$ ($\text{X} = \text{Cl}, \text{Br}$) with ditopic N donors ($\text{L}^1/\text{L}^2/\text{L}^3$) yielded dinuclear homoleptic double-stranded cyclic complexes with the

general formula $[\{\text{Re}(\text{CO})_3\text{X}\}_2(\text{L}^n)_2]$ ($\text{X} = \text{Cl}, \text{Br}$). The ^1H NMR analysis indicates that the difference among these dinuclear homoleptic double stranded cyclic complexes may be due to the spatial arrangement of ligands in the complexes. The results open up a new way to use an inorganic anion to act as a bridging ligand and possibly fix sulfur dioxide in the framework of SCCs.

2.5. References

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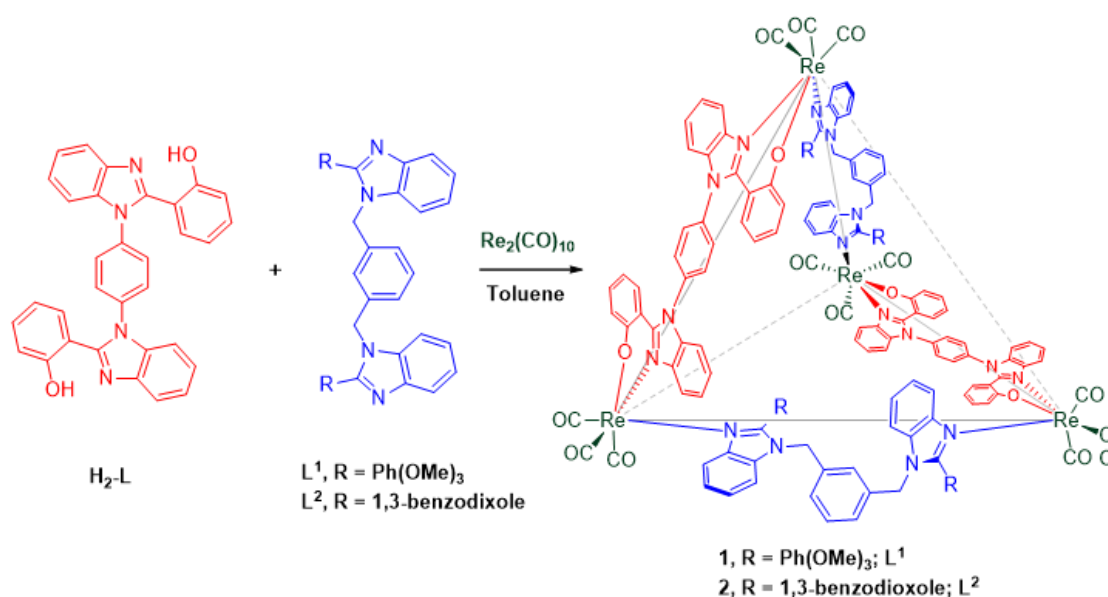
Chapter 3

Rheniumtricarbonyl-based neutral heteroleptic tetrahedrons

Abstract

Two new xylene spacer based ditopic flexible N-donors containing 2-(3,4,5-trimethoxyphenyl)benzimidazole (L^1) / 2-(1,3-benzodioxole)benzimidazole (L^2) as a coordinating unit and one rigid bis-chelating ligand consisting of two 2-(hydroxyphenyl)benzimidazolyl motifs and a central phenylene spacer (H_2-L) were synthesized and further reacted with $Re_2(CO)_{10}$ for the construction of a new type of neutral, heteroleptic tetrahedral-shaped SCCs of the formula $[{\{fac-Re(CO)_3\}_4(L^n)_2(L)_2}]$ (**1-2**) in a one-step synthetic procedure. The newly synthesized ligands and metallacycles were analysed using ESI-Mass and NMR techniques. The crystal structures of the SCCs were verified by SCXRD analysis, which confirms the tetrahedron structure of the SCCs with four rhenium centers arranged in the vertices, and the edges of the tetrahedron are occupied by the four ligands.

This work has been published in *Dalton Trans.*, **2019**, 48, 7425–7431.



3.1. Introduction

The development and synthesis of SCCs with different geometry and dimensions has been progressing over the past three decades because of their appealing frameworks, ease of synthesis by a simple one-pot method, and also due to their significance in the fields of medicine [1-76]. Several metal precursor sources consists of partially protected and naked metal ions are employed to connect the ligand building units in the SCCs, in which the facial rheniumtricarbonyl core directed synthetic approach is found to be the most facile methods for the synthesis of heteroleptic neutral SCCs in a one-step synthetic procedure [48-76]. Examples of such SCCs includes square, rectangle, bowl, helicate, mesocate, spheroid and trigonal-/tetragonal prisms [48-76]. The facial rheniumtricarbonyl core containing heteroleptic or homoleptic tetrahedron shaped SCCs in which four rhenium metal centers are arranged in a tetrahedral geometry, is rare [30-47]. This may be due to the difficulty in predesigning the coordinating ligand motifs for fulfilling the stereoelectronic requirement of the facial rheniumtricarbonyl core, which offers three vacant coordination sites and requires two coordinating ligands capable of donating two electrons and one anionic ligand which can donate one electron. Until now the predesigned ligands, which can be either a combination of rigid-flexible or rigid-rigid or flexible-flexible for the construction rheniumtricarbonyl core containing tetranuclear SCC resulted in the formation of tetranuclear square- or heteroleptic rectangle or zigzag-shaped supramolecular coordination complexes [65-70]. Our research have yielded different types of coordinating ligands for the synthesis of new types of heteroleptic facial rheniumtricarbonyl core based SCCs through various bonding combinations in a one-pot synthetic method [71-76]. The research in this area provided synthetic approaches for the construction of architecturally beautiful neutral, heteroleptic SCCs with potential applications in various fields. Herein, reporting the synthesis of a new class of *fac*-Re(CO)₃ core containing neutral, heteroleptic metallacycles with tetrahedral shape. A combination of bis-chelating rigid ligands having a phenyl spacer (H₂-RBC) and neutral flexible ditopic N-donor ligands (Lⁿ) with Re₂(CO)₁₀ yielded a M₄L₂L'₂-type neutral, heteroleptic tetrahedron with two empty edges in a one-pot method.

3.2. Experimental

Materials and Methods

$\text{Re}_2(\text{CO})_{10}$, o-phenylenediamine, benzaldehyde, piperonal, 3,4,5-trimethoxybenzaldehyde, NaHSO_3 , 1,3-di(bromomethyl)benzene, 1,4-dibromobenzene, copper(I)iodide, 1,10-phenanthroline, Cs_2CO_3 , toluene, acetone and DMF were purchased and used without further purification. 2-(Phenyl)benzimidazole, 2-(3,4,5-trimethoxyphenyl)benzimidazole (L^1), 2-(1,3-benzodioxole)benzimidazole (L^2) were synthesized using previously reported procedures [77-79]. ^1H NMR spectra were obtained from Bruker Avance III 400 and 500 MHz spectrometers. JASCO-5300 FT-IR spectrometer was used to record the FT-IR spectra of the complexes.

Synthesis of rigid bis-chelating ligand $\text{H}_2\text{-RBC}$

The mixture of (2-hydroxyphenyl)benzimidazole (6.0 g, 28.5 mmol), 1,4-dibromobenzene (2.8 g, 11.9 mmol), 1,10-phenanthroline (0.85 g, 4.7 mmol), CuI (0.45 g, 2.4 mmol) and Cs_2CO_3 (16.3 g, 50 mmol) was taken in a Schlenk flask under N_2 atmosphere. Dry DMF (30 mL) was added to the mixture, which was heated under reflux for 48 h. The mixture was extracted using $\text{CHCl}_3/\text{H}_2\text{O}$ three times. The organic layer was separated, washed with brine solution and dried using anhydrous Na_2SO_4 . The solvent was removed using vacuum. The crude $\text{H}_2\text{-RBC}$ was eluted as a white powder using column chromatography using EA/hexane (20/80). The eluted white solid was again separated using column chromatography using the same solvent mixture to obtain pure $\text{H}_2\text{-RBC}$. Yield: 20% (1.18 g). ESI (HR-MS). Calcd for $\text{C}_{32}\text{H}_{23}\text{N}_4\text{O}_2$ $[\text{M} + \text{H}]^+$: m/z 495.1821. Found: m/z 495.1775. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 11.91 (s, 2H, -OH), 7.86–7.84 (m, 2H, H^4), 7.71 (s, 4H, phenylene), 7.41–7.31 (m, 8H, $\text{H}^{5,6,4',5'}$), 7.18 (d, $J = 7.9$ Hz, 2H, $\text{H}^{2'}$), 7.0 (d, $J = 8.2$ Hz, 2H, H^7), and 6.82 (t, $J = 8.0$ Hz, 2H, $\text{H}^{3'}$).

Synthesis of L^1 .

A white powder was obtained by the treatment of 2-(3,4,5-trimethoxyphenyl)benzimidazole (800 mg, 2.8 mmol), 1,3-di(bromomethyl)benzene (371 mg, 1.4 mmol), KOH (320 mg, 5.7 mmol) and DMF (10 mL). Yield: 91% (854 mg). ESI (HR-MS). Calcd for $\text{C}_{40}\text{H}_{39}\text{N}_4\text{O}_6$ $[\text{M} + \text{H}]^+$: m/z 671.2869. Found: m/z 671.2869. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 7.70 (d, $J = 7.84$ Hz, 2H, H^4), 7.32 (d, $J = 7.96$ Hz, 2H, $\text{H}^{10,12}$), 7.24 (t, $J = 7.86$ Hz, 3H, $\text{H}^{5,11}$), 7.18 (t, $J = 7.12$ Hz, 2H, H^7), 6.91–6.88 (m, 6H, $\text{H}^{2',6',6}$), 6.83 (s, 1H, H^9), 5.54 (s, 4H, H^8), 3.70 (s, 6H, -OCH₃) and 3.60 (s, 12H, -OCH₃). ^{13}C NMR (500 MHz, $\text{DMSO}-d_6$) 153.47, 153.36, 142.93, 139.19, 138.41, 136.45, 129.83, 125.63, 125.51, 124.07, 123.10, 122.68, 119.64, 111.09, 106.86, 60.54, 56.16, 47.96.

Synthesis of L^2 .

A white powder was obtained by the treatment of 2-(1,3-benzodioxole)benzimidazole (802 mg, 3.4 mmol), 1,3-di(bromomethyl)benzene (443 mg, 1.7 mmol), KOH (379 mg, 6.8 mmol) and DMF (10 mL). Yield: 85% (831 mg). ESI (HR-MS). Calcd for $C_{36}H_{27}N_4O_4$ $[M + H]^+$: m/z 579.2031. Found: m/z 579.2027. 1H NMR (400 MHz, $DMSO-d_6$): δ 7.67 (d, J = 7.92 Hz, 2H, H^4), 7.27 (d, J = 7.88 Hz, 2H, H^5), 7.22 (t, J = 7.08 Hz, 3H, $H^{7,11}$), 7.15 (t, J = 7.88 Hz, 2H, $H^{10,12}$), 7.09 (d, J = 1.48 Hz, 2H, $H^{2'}$), 6.94–6.90 (m, 4H, $H^{6,5'}$), 6.86 (d, J = 8.04 Hz, 2H, $H^{6'}$), 6.56 (s, 1H, H^9), 6.09 (s, 4H, H_a) and 5.43 (s, 4H, H^8).

Synthesis of 1.

Greenish yellow crystals of **1** were obtained from $Re_2(CO)_{10}$ (100.2 mg, 0.1536 mmol), H_2 -RBC (76 mg, 0.1537 mmol), L^1 (100 mg, 0.1485 mmol), toluene (10 mL), and acetone (2 mL). Yield: 31% (155 mg; crystals). Anal. calcd for $C_{156}H_{116}N_{16}O_{28}Re_4$: C, 54.99; H, 3.43; N, 6.58. Found: C, 55.43; H, 3.38; N, 6.75. ESI (HR-MS). Calcd for $C_{156}H_{117}N_{16}O_{28}Re_4$ $[M + H]^+$: m/z 3408.6464. Found: m/z 3408.6287. FT-IR (KBr, cm^{-1}): ν = 2013(s), 1899 and 1863(s). 1H NMR (400 MHz, $DMSO-d_6$): δ 8.65 (d, J = 8.4 Hz, 4H), 7.99 (d, J = 4H), 7.89 (t, J = 8 Hz, 4H), 7.44–6.96 (t, t, and m, 52 H, compound + toluene), 6.81 (s, 2H), 6.79 (t, J = 7.8 Hz, 2H), 6.31 (d, J = 8.4 Hz, 4H), 6.05 (d, J = 7.2 Hz, 4H), 5.65 (t, J = 7.4 Hz, 4H), 5.51 (d, J = 18.8 Hz, 4H), 5.37 (d, J = 8 Hz, 4H), 5.24–5.19 (t and s, 8H), 4.37 (d, J = 18.8 Hz, 4H), 3.38 (s, 8H, $-OCH_3$) and 3.29 (s, 10H, $-OCH_3$).

Synthesis of 2.

Green crystals of **2** were obtained from $Re_2(CO)_{10}$ (100.3 mg, 0.1537 mmol), H_2 -RBC (76 mg, 0.1537 mmol), L^2 (86.3 mg, 0.1488 mmol) in toluene (10 mL) and acetone (2 mL). Yield: 17% (84 mg; crystals). Anal. calcd for $C_{148}H_{92}N_{16}O_{24}Re_4$: C, 55.15; H, 2.88; N, 6.95. Found: C, 55.21; H, 2.83; N, 7.06. ESI (HR-MS). Calcd for $C_{148}H_{93}N_{16}O_{24}Re_4$ $[M + H]^+$: m/z 3224.4788. Found: m/z 3224.4948. FT-IR (KBr, cm^{-1}): ν = 2017(s), 1899 and 1863(s).

X-ray crystallography

Intensity data of crystals of **1–2** were collected on a Bruker D8 Quest diffractometer [$\lambda(Mo K\alpha) = 0.71073 \text{ \AA}$]. The structures were solved by direct methods using SHELXS-9711 and refined using the SHELXL-2018/3 program (within the WinGX program package) [81,82]. Non-H atoms were refined anisotropically. Two methoxy units in **1** are disordered. Two 1,3-benzodioxole units are disordered in **2**. The majority of the solvent molecules in the complexes could not be modelled correctly, and hence their contribution to the intensities was excluded

using the SQUEEZE option in PLATON [83]. The intensity data of crystal of L^1 were collected on an Oxford CCD X-ray diffractometer (Xcalibur, Eos, Gemini) [$\lambda(\text{Cu K}\alpha) = 1.54184 \text{ \AA}$] and data reduction was performed using CrysAlisPro 1.

Table 1. Twist angles (φ) between two chelating units of RBC and three Re...Re distances in scalene triangle (Δ) in complexes **1** and **2**.

d of Δ ($\text{\AA}$)				
Complexes	φ ($^\circ$)	Re-RBC-Re	Re- L^n -Re	Re...Re
1	72	13.51	14.90	10.63, 11.63
2	87, 78	13.55, 13.47	15.22	11.16

Table 2 . Crystallographic Data of **1** and **2** (the parameters are calculated with/without solvent molecules).

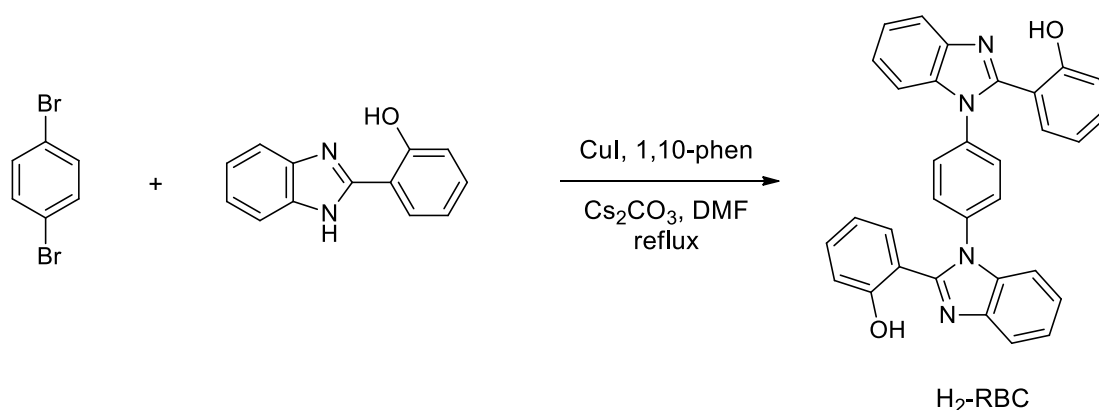
	1	2	2 with solvents
formula	C ₁₅₆ H ₁₁₆ N ₁₆ O ₂₈ Re ₄	C ₁₄₈ H ₉₂ N ₁₆ O ₂₄ Re ₄	C ₁₈₃ H ₉₀ N ₁₆ O ₂₄ Re ₄
<i>M_r</i>	3407.44	3223.17	3641.50
crystal system	Orthorhombic	Orthorhombic	Orthorhombic
space group	<i>Pbcn</i>	<i>Pccn</i>	<i>Pccn</i>
<i>a</i> (Å)	20.942(2)	18.7918(6)	18.7918(6)
<i>b</i> (Å)	23.014(2)	23.7918(7)	23.7918(7)
<i>c</i> (Å)	34.149(3)	35.3639(11)	35.3639(11)
<i>a</i> (deg)	90	90	90
<i>β</i> (deg)	90	90	90
<i>γ</i> (deg)	90	90	90
<i>V</i> (Å ³)	16458(3)	15810.9(8)	15810.9(8)
<i>Z</i>	4	4	4
<i>T</i> (K)	296(2)	296(2)	296(2)
<i>λ</i> (Å)	0.71073	0.71073	0.71073
<i>D_{calc}</i> (gcm ⁻³)	1.375	1.354	1.530
<i>μ</i> (mm ⁻¹)	3.001	3.118	3.128
<i>F</i> (000) goodness- of-fit	6752	6336	7168
R1 ^a /wR2 ^b [<i>I</i> > 2σ(<i>I</i>)]	1.106	1.046	1.079
R1 ^a /wR2 ^b (all data)	0.0858/0.1538	0.0369/0.0793	0.0484/0.1266
Larg. Res. (e Å ⁻³)	0.1358/0.1718	0.0497/0.0858	0.0631/0.1379
	1.560	1.691	1.703

$$^a R_1 = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|, \quad ^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

3.3. Results and discussion

Synthesis and characterization of rigid bis-chelating ligand H₂-RBC

The designed chelating ligand H₂-RBC act as a dianionic bis-chelating unit using its N-atom of benzimidazolyl unit and O-atom of phenolic unit. The insertion of phenylene unit as a spacer in between two benzimidazolyl unit will be useful in (i) charge transfer of electrons between two *fac*-Re(CO)₃(N $\cap$ O) unit, after the coordination of N $\cap$ O unit with Re(I) and (ii) allow to form hydrophobic cavity within the molecules to accommodate guest molecules like toluene. The ligand H₂-RBC was obtained from the reflux reaction of (2-hydroxyphenyl)benzimidazole, 1,4-dibromobenzene, 1,10-phenanthroline, CuI and Cs₂CO₃ in dry DMF solvent under N₂ atm for 48 h. After completion of reaction the mixture was extracted using CHCl₃/H₂O and separated organic layer was dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure. Column chromatography technique was employed to elute the final product using ethyl acetate/hexane (20/80) (Scheme 1). The product shows solubility in organic solvents and was stable in air and moisture.



Scheme 1. Synthesis of rigid bis-chelating ligand H₂-RBC

The purity of the rigid ligand H₂-RBC was confirmed using ¹H NMR analysis. The proton ratio of 2-(2-hydroxyphenyl)benzimidazolyl unit and *p*-phenylene unit was found to be 2:1, confirming the stoichiometry of the ligand. The disappearance of the NH proton signal at 13 ppm and the appearance of two singlets at 7.71 ppm (phenyl) and 11.9 ppm (hydroxyl) indicates the formation of the ligand (Figure 1). The aromatic protons were assigned using ¹H-¹H COSY NMR analysis. The elemental analysis of the ligand was well consistent with the calculated value. The ESI-MS spectrum of H₂-RBC shows a molecular ion peak at 495.17 m/z (Figure 2).

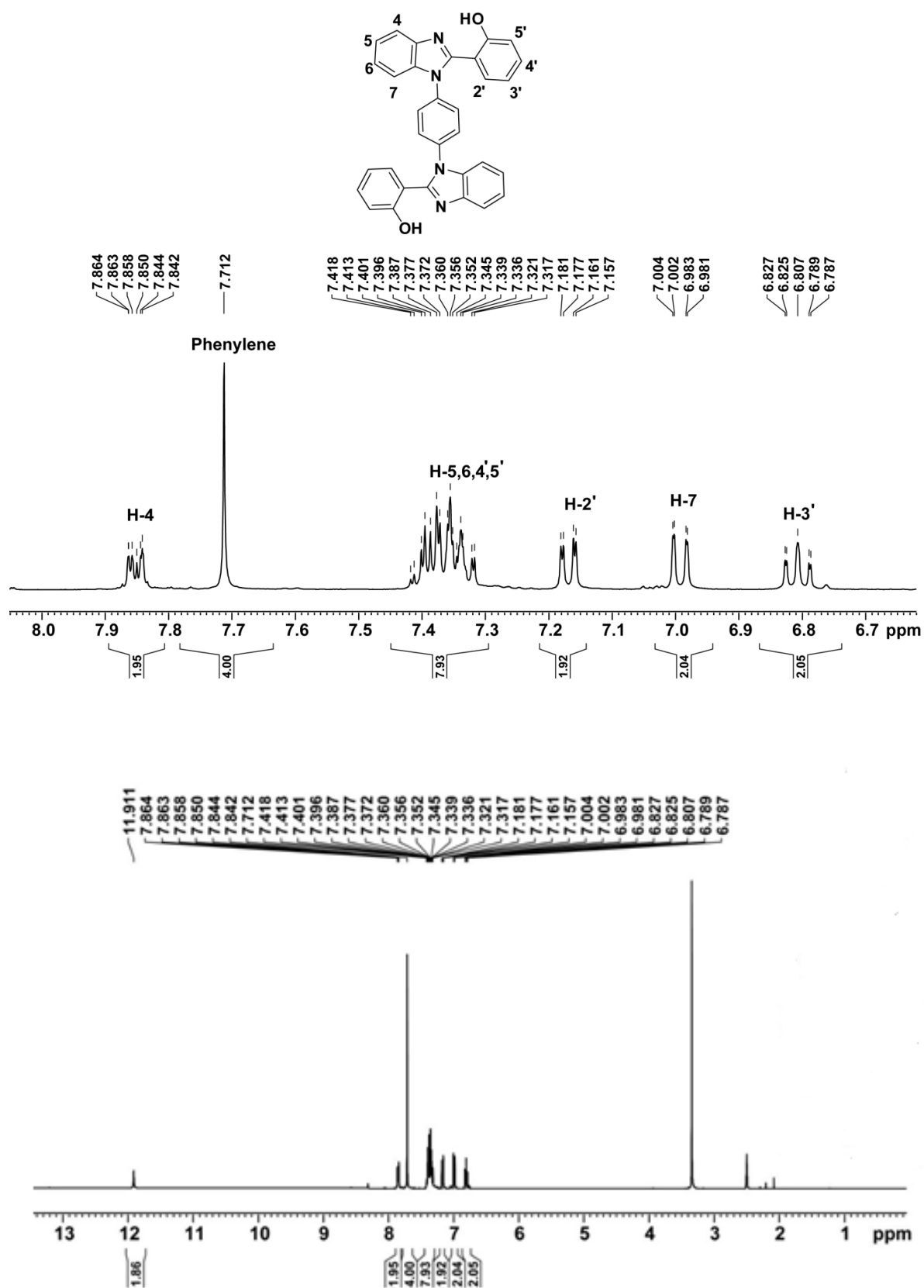


Figure 1. ¹H NMR spectra of H₂-RBC in dmsO-*d*₆.

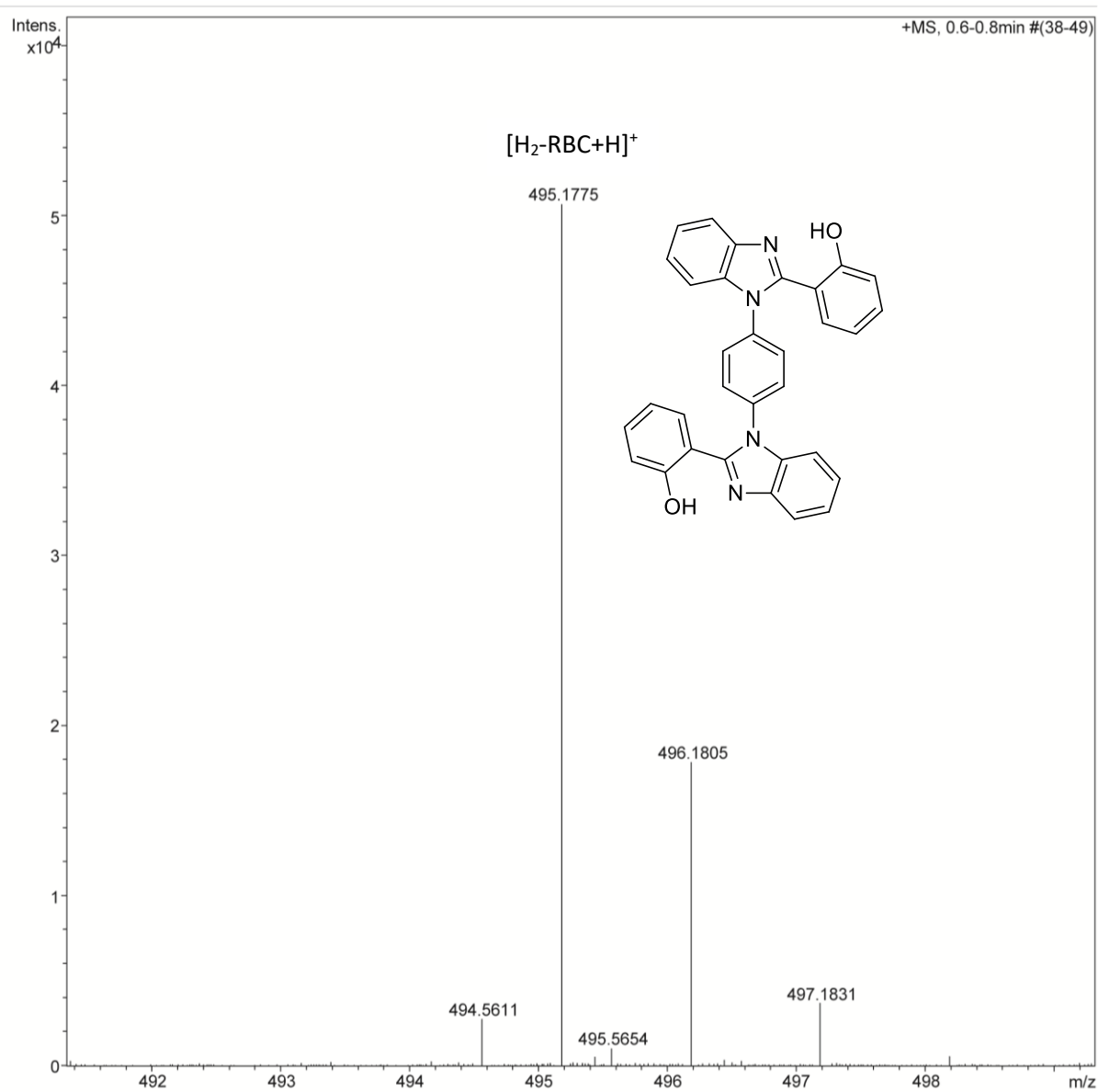
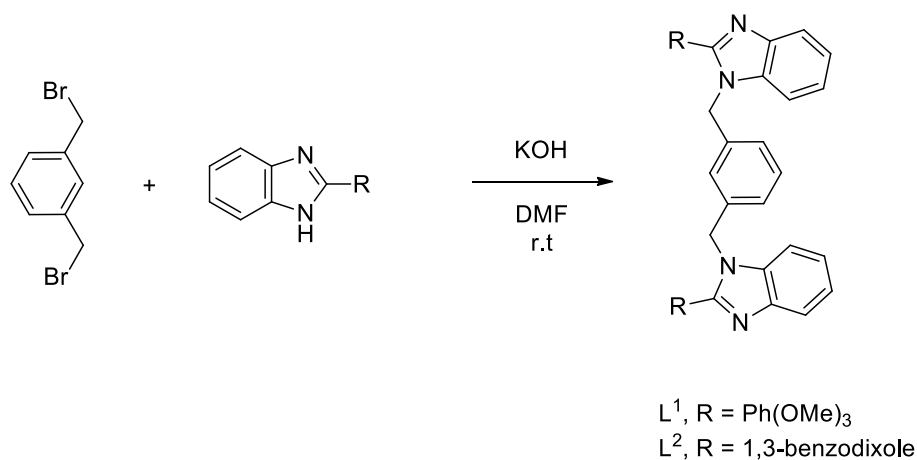


Figure 2. ESI mass spectrum of **H₂-RBC** in positive ion mode.

Synthesis and characterization of flexible ditopic N-donor ligands L^1 and L^2

The crucial aim in designing *m*-directed flexible substituted N-donor ligand is that the flexible nature will allow to form a molecule with accessible cavity. Ligands L^1 and L^2 were synthesized by reacting 2-(3,4,5-trimethoxy)phenylbenzimidazole/2-(1,3-benzodioxole)benzimidazole with 1,3-di(bromomethyl)benzene in the presence of strong base (KOH) in DMF at room temperature (Scheme 2). The synthetic approach used to prepare L^1 and L^2 is similar to that for the benzimidazolyl-based ditopic ligands [77-79].



Scheme 2. Synthesis of flexible ditopic N-donor ligands

The ligands show air-moisture stability and solubility in organic solvents. In the proton NMR spectra of both the ligands L^1 and L^2 , a singlet was observed around ~5.5 ppm which corresponds to the presence of methylene protons. Two doublets and two triplets were observed for the benzimidazolyl protons of both the ligands. This indicates the unsymmetrical nature of the benzimidazolyl protons due to the formation of ligands (Figures 3 and 5). The ESI-Mass spectral analysis of the ligands displayed molecular ion peaks and supporting the product formation (Figures 4 and 6).

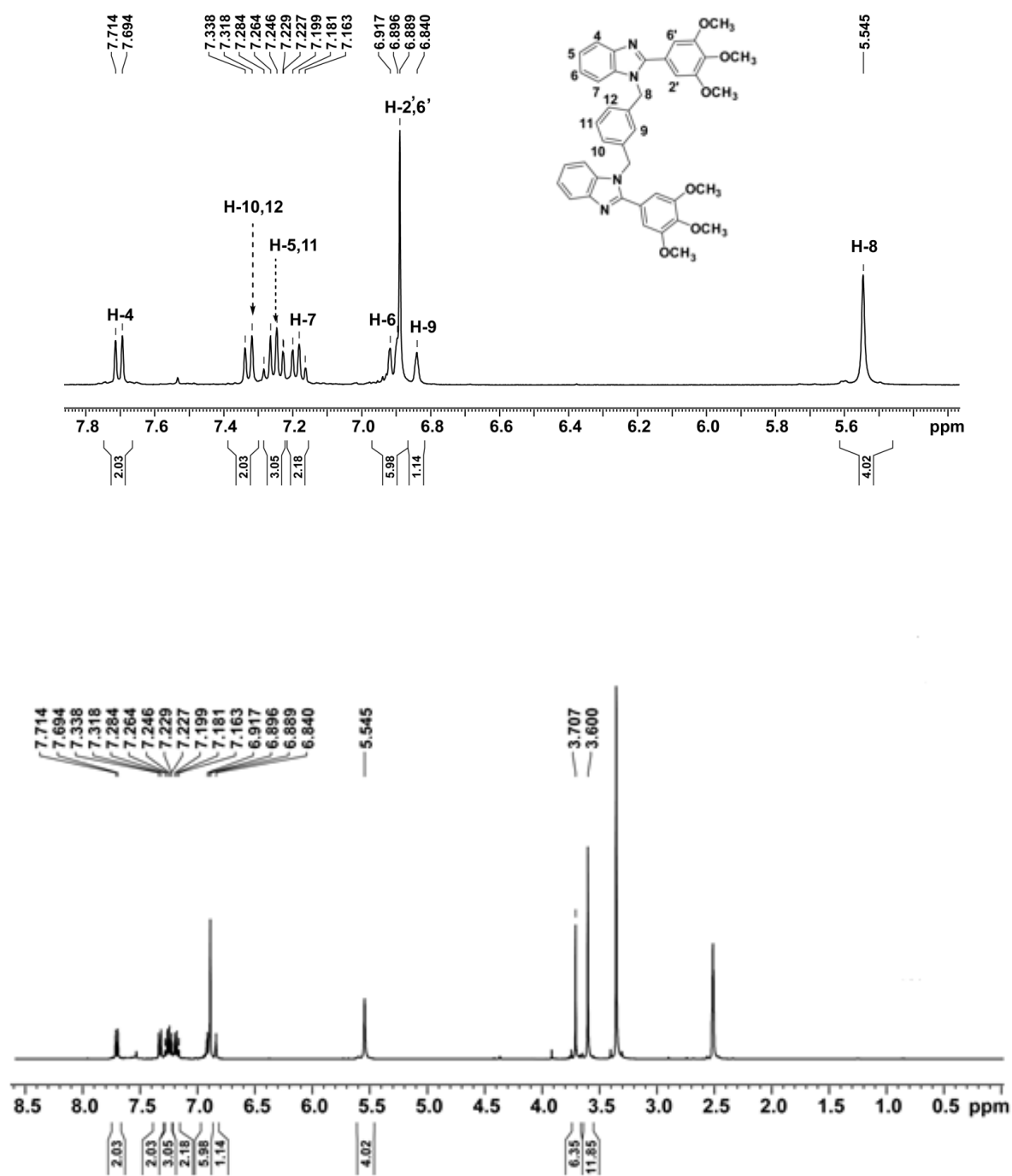


Figure 3. ^1H NMR spectra of L^1 in $\text{dms-}d_6$

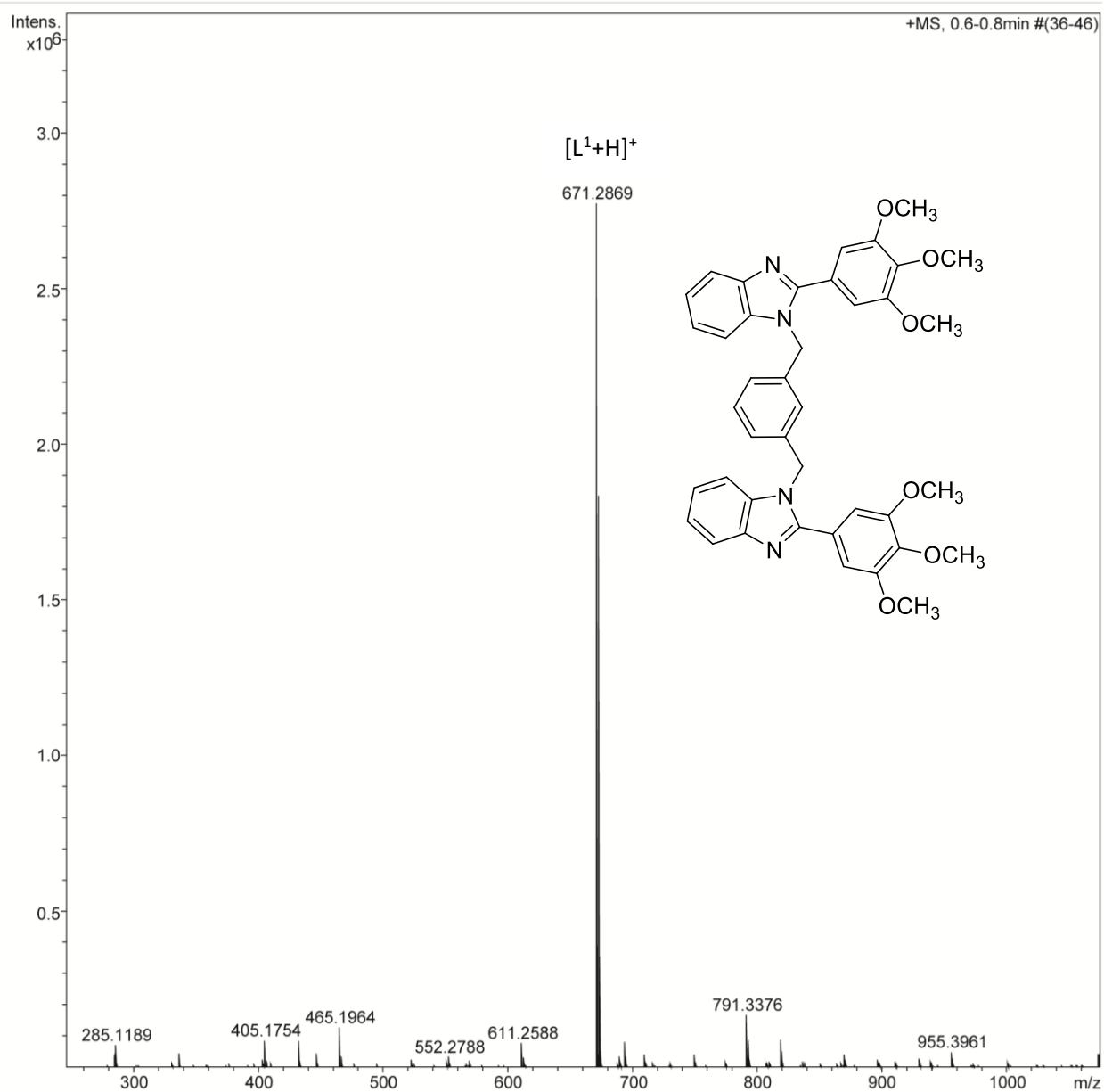


Figure 4. ESI mass spectrum of L^1 in positive ion mode.

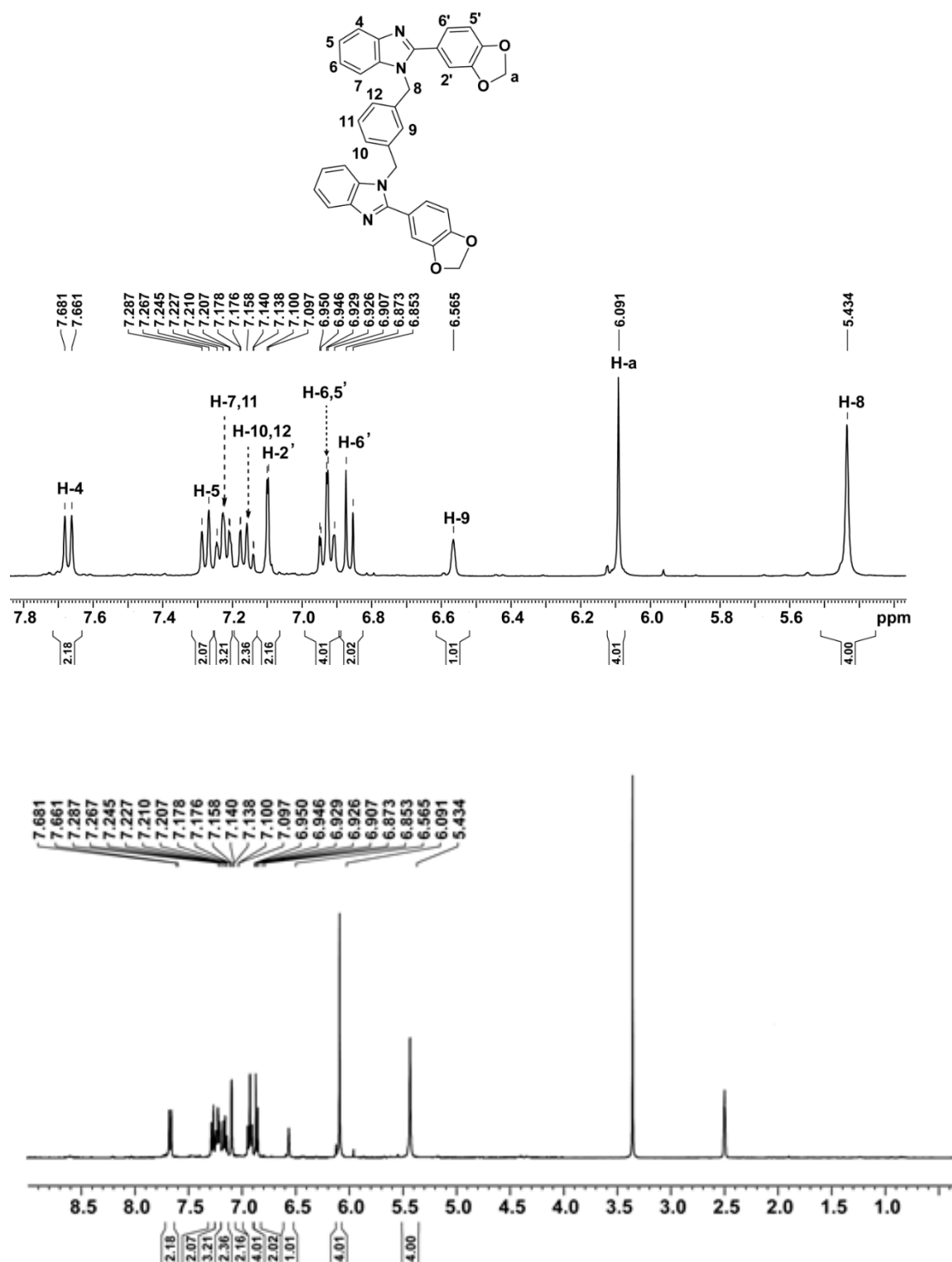


Figure 5. 1H NMR spectra of L^2 in $dmsd-d_6$

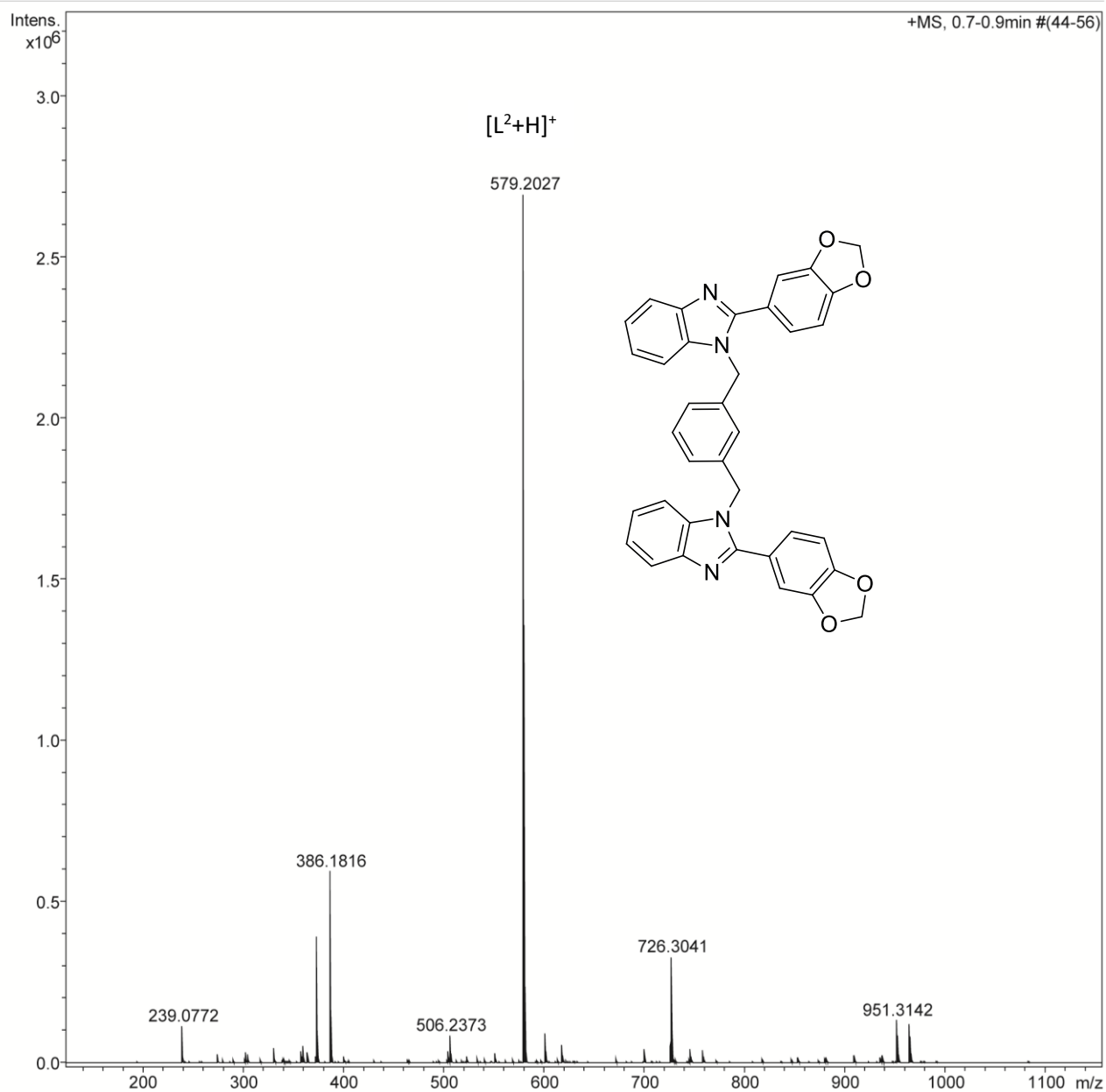


Figure 6. ESI mass spectrum of L^2 in positive ion mode

Molecular structures of ligand L^1 and H_2 -RBC

The molecular structures of L^1 and H_2 -RBC were confirmed using single crystal X-ray diffraction (SCXRD) analysis (Figure 7). The 2-(3,4,5-trimethoxyphenyl)benzimidazolyl motifs in L^1 are *trans* to each other and are perpendicular to the central arene motif. Both nitrogen atoms (N1 and N4) are directed on the same side. The dihedral angle between the two imidazolyl units is 42° . The distance between two nitrogen donor atoms is 11.5 Å (N1...N4) in L^1 .

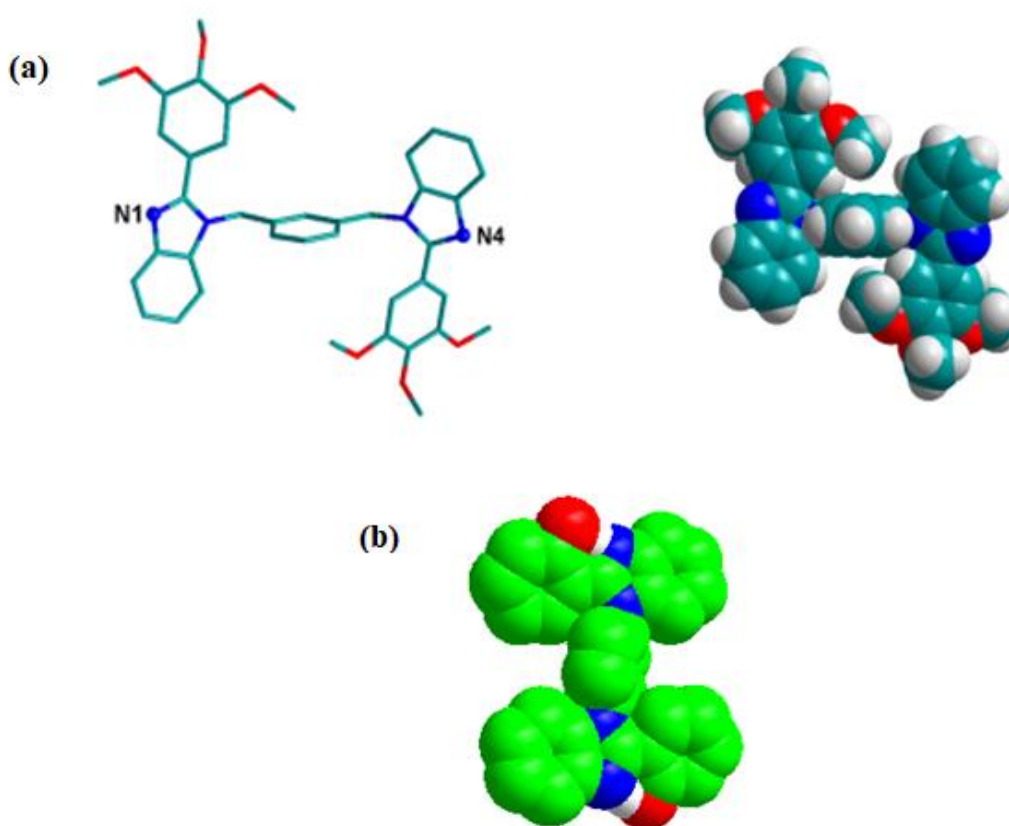
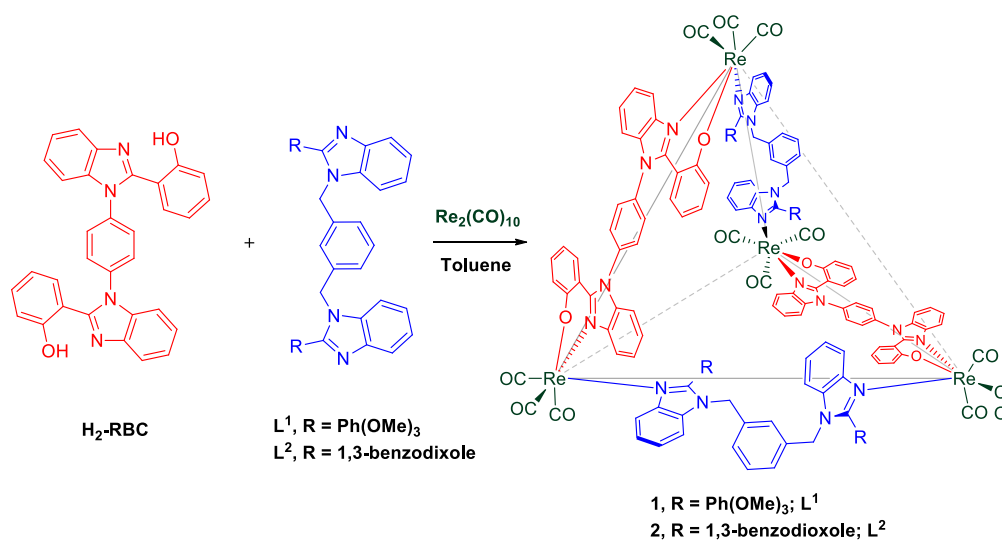


Figure 7. (a) Molecular structures of L^1 and (b) H_2 -RBC (H atoms are removed).

Synthesis and characterization of complexes **1** and **2**

The solvothermal reaction of $\text{Re}_2(\text{CO})_{10}$, rigid bis-chelating ligand $\text{H}_2\text{-RBC}$ and flexible ditopic ligand L^n in toluene resulted in the formation of the SCCs (**1** and **2**) with or without toluene guest molecule(s) (Scheme 3). The metallacycles exhibit air-moisture stability, and moderate solubility in organic solvents. The appearance of three strong bands in the region of 2020–1800 cm^{-1} , in the FT-IR spectra of all the complexes indicating the presence of the rheniumtricarbonyl center in the complexes [71-76].



Scheme 3. Synthetic approach for neutral heteroleptic tetrahedrons (**1** and **2**)

The ^1H NMR spectrum of **1** displays a clear pattern without any decomposition or free ligand impurity (Figure 8). No clear spectrum was obtained for the complex **2**. The ^1H NMR spectrum of **1** in $\text{dms}\text{-}d_6$ showed well distinguished peaks as compared to both the uncoordinated ligands. Considerable upfield and downfield shifts were observed for the protons of the ligands in complex **1**, especially for eight proton peaks present in the region of 6.8 to 4 ppm. In addition, the methylene ($-\text{CH}_2-$) protons signals were appeared as two doublets with coupling constant in accordance with the geminal coupling ($J = 18$ Hz).

Among the two doublets observed for the methylene protons, one appears close to the chemical resonance for the methylene protons of the uncoordinated ligand and the other proton signal shows an upfield shift. These results indicate that the metallacycle **1** maintains the SCC architecture in the solution. The presence of aromatic neighbouring groups resulted in the upfield shift for the protons of the complex as compared to the uncoordinated ligand.

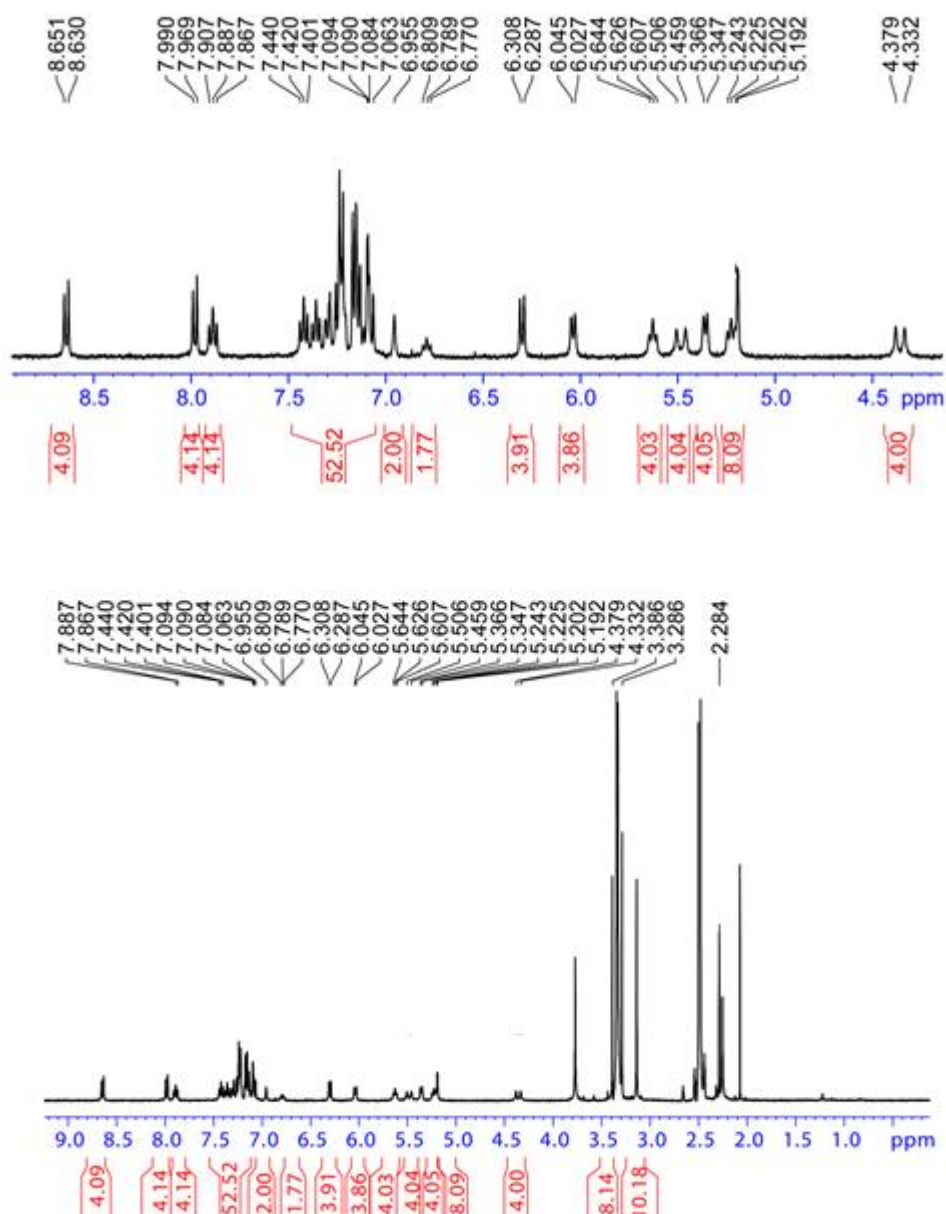


Figure 8. ^1H NMR spectrum of **1** in $\text{dmsO}-d_6$

The results are confirmed by ESI-Mass analysis. The mass spectra of the metallacycles displays a molecular ion peak which match with theoretical values and peaks corresponding to the successive loss of ligand(s) and rheniumtricarbonyl core(s). Moreover, the mass spectra also exhibited the mass corresponds to $[M_2LL^n]$ motif ($M = \text{Re}(\text{CO})_3$) (Figure 9-11).

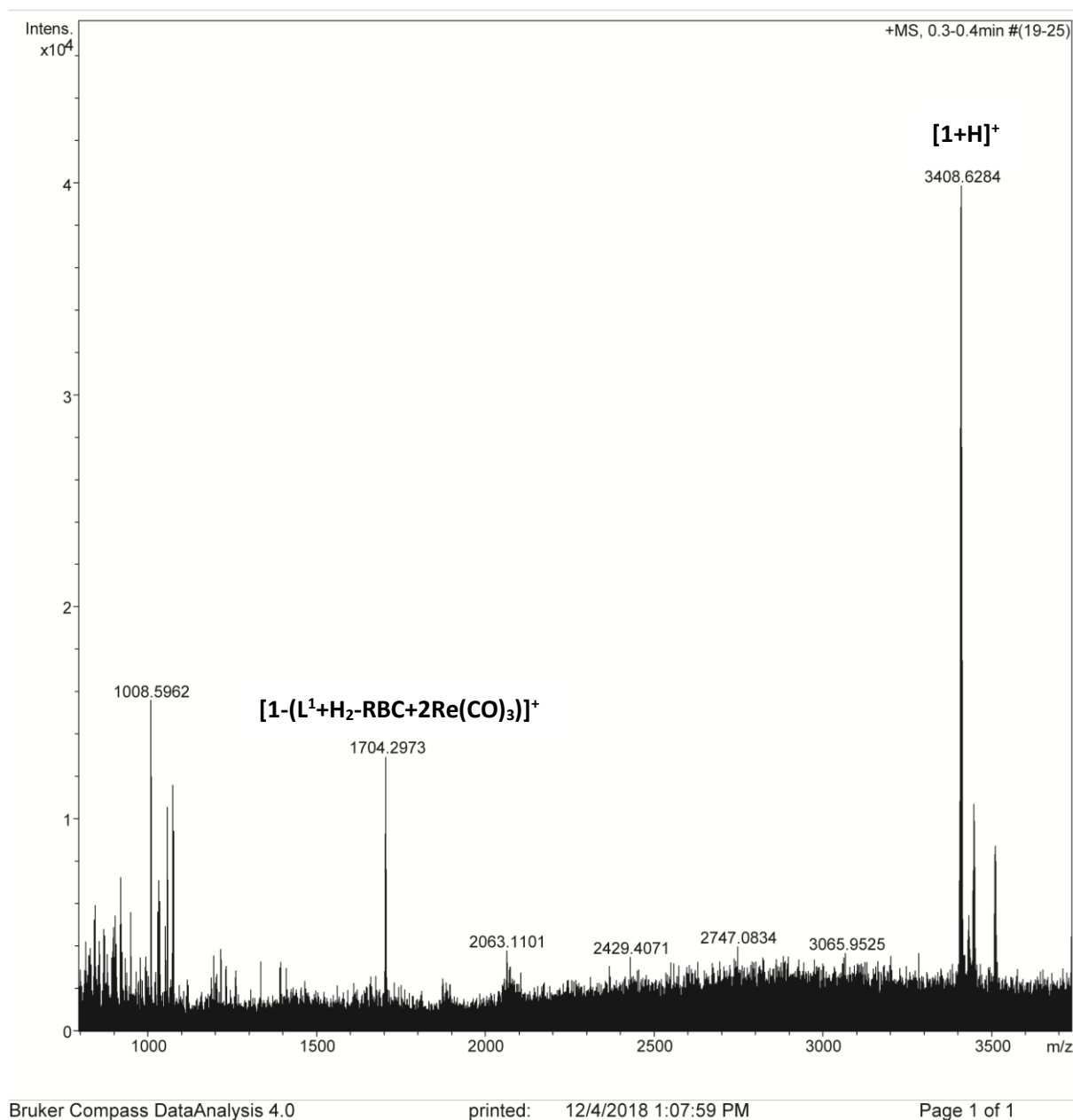


Figure 9. ESI mass spectrum of **1** in positive ion mode.

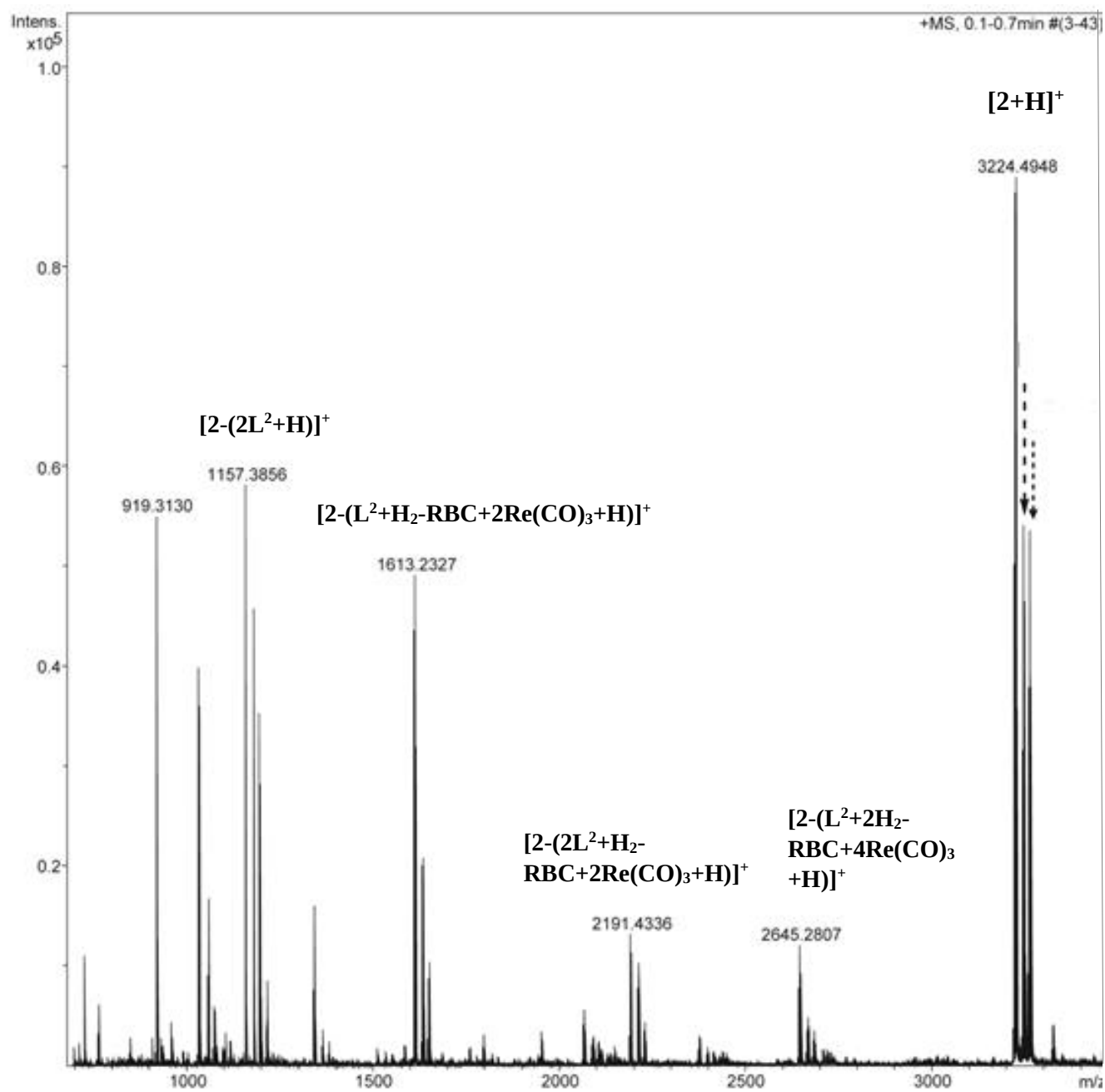


Figure 10. ESI mass spectrum of **2** in positive ion mode.

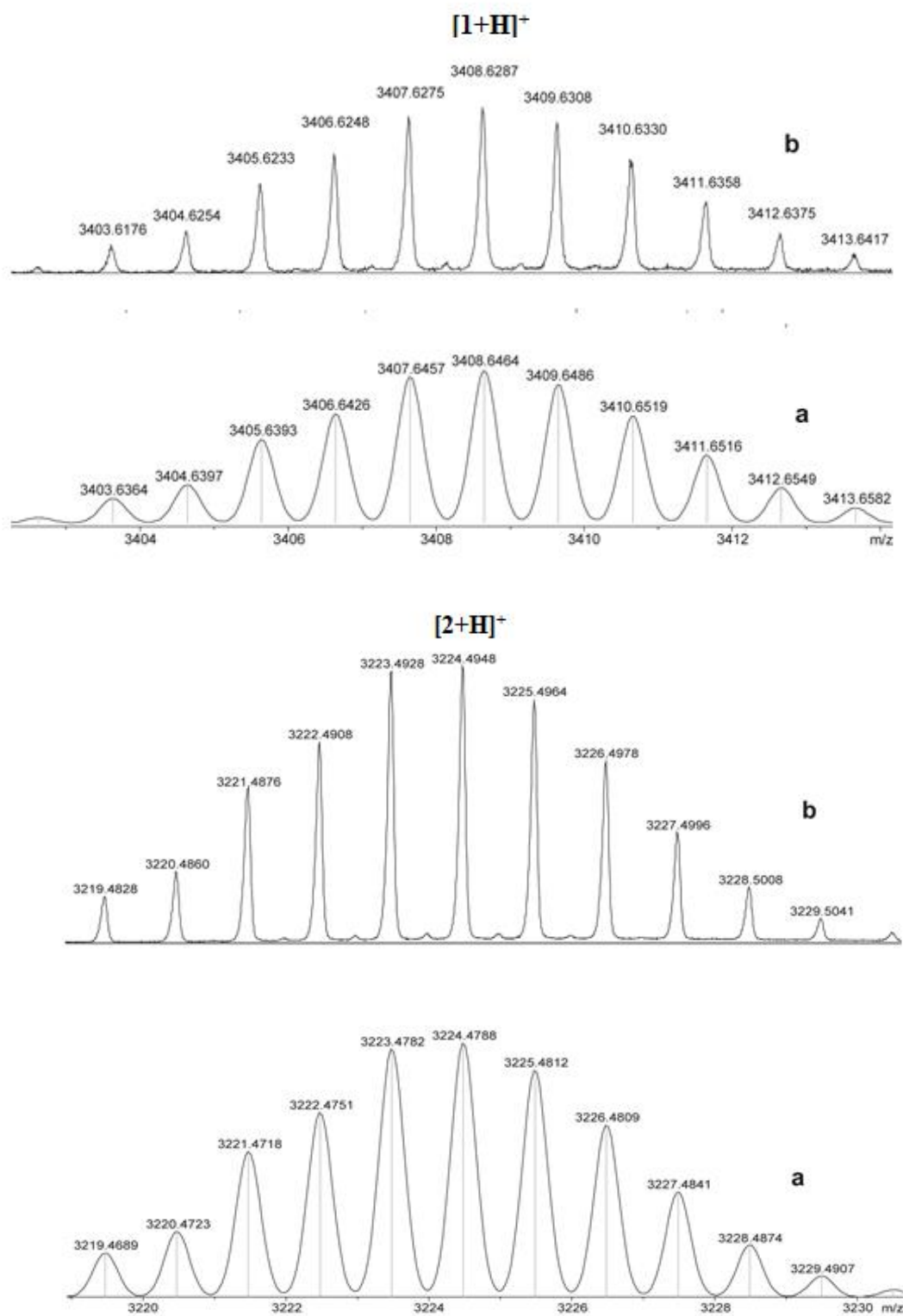


Figure 11. Experimental (a) and calculated (b) ESI-TOF mass spectra of $[1+H]^+$ and $[2+H]^+$

Molecular structures of complexes 1 and 2

The crystal structures of **1** and **2** were determined by SCXRD analysis, which reveal that the complexes acquire $M_4L_2L'_2$ -type SCC framework (Figures 12-14). The complexes **1** and **2** can be considered as a $[4 + 2 + 2]$ assembly of four rheniumtricarbonyl cores, two dianionic rigid ligand ($RBC^{2-} = L^{2-}$) motifs, and two neutral N-donor ligands (L^n). These metallacycles adopts a distorted tetrahedral shape with two empty edges due to the arrangement of four rhenium atoms and four ligand motifs. The four facial rheniumtricarbonyl cores and the four ligand motifs represents the four vertices and four edges of the tetrahedron respectively. Three types of edges are present in the tetrahedra i.e. the shorter edge provided by the RBC ligand ($d(Re \cdots Re) = 13.5 \text{ \AA}$) and the longer edge offered by the flexible L^n ligand ($d(Re \cdots Re) = \sim 15.3 \text{ \AA}$) and the empty edge ($Re \cdots Re$, $d(Re \cdots Re) = \sim 11.2 \text{ \AA}$) (Table 1). As a result of these different edges and two empty edges, the distorted tetrahedron possess scalene triangular faces and each triangular face consists of one rigid ligand edge, one flexible ligand edge and one empty edge (Figures 14 and 15).

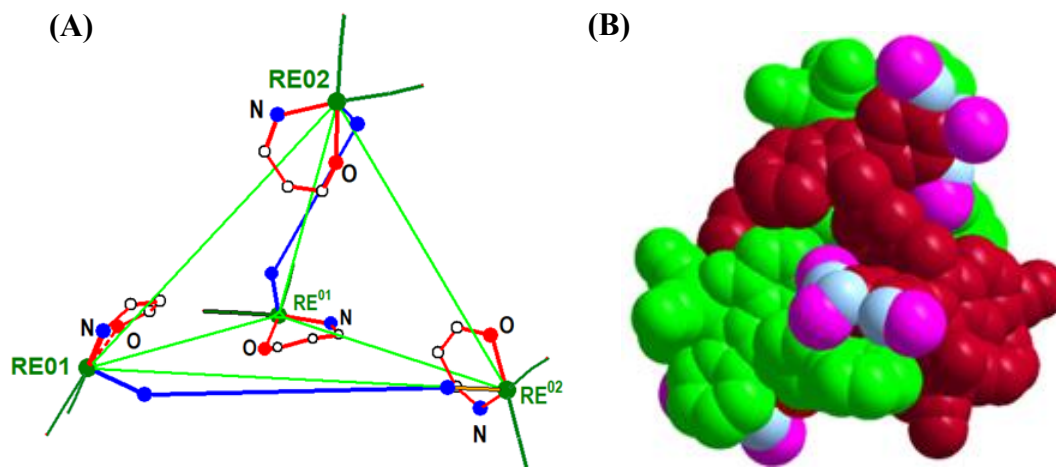


Figure 12. (A) Ball and stick view of **1** (hydrogen atoms are omitted for clarity; Bonds of L^1 are shown in blue; bonds of chelating atoms of RBC are shown in red). (B) Space-filling view of **1**.

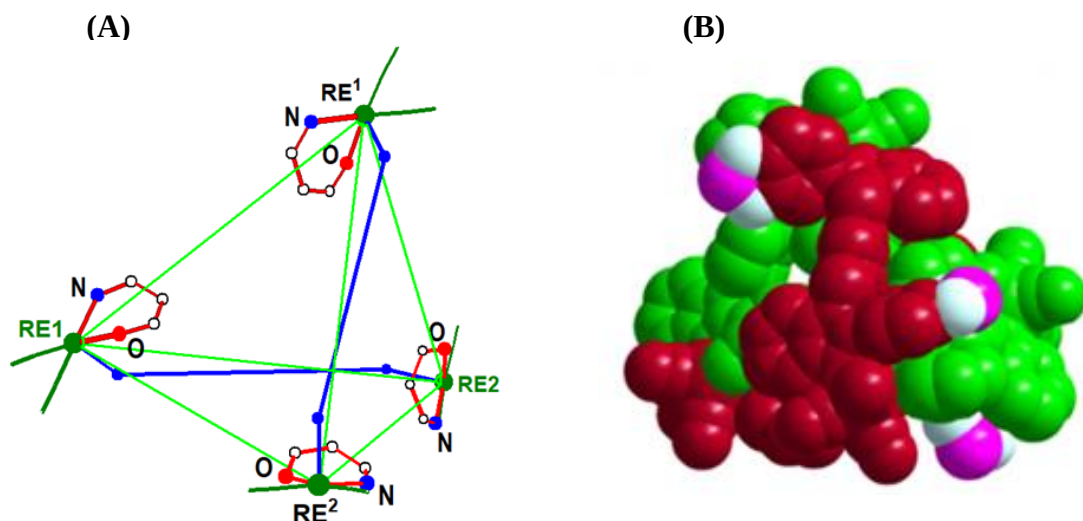


Figure 13. (A) Ball and stick view of **2** (hydrogen atoms are omitted for clarity; Bonds of L^2 are shown in blue; bonds of chelating atoms of RBC are shown in red). (B) Space-filling view of **2**.

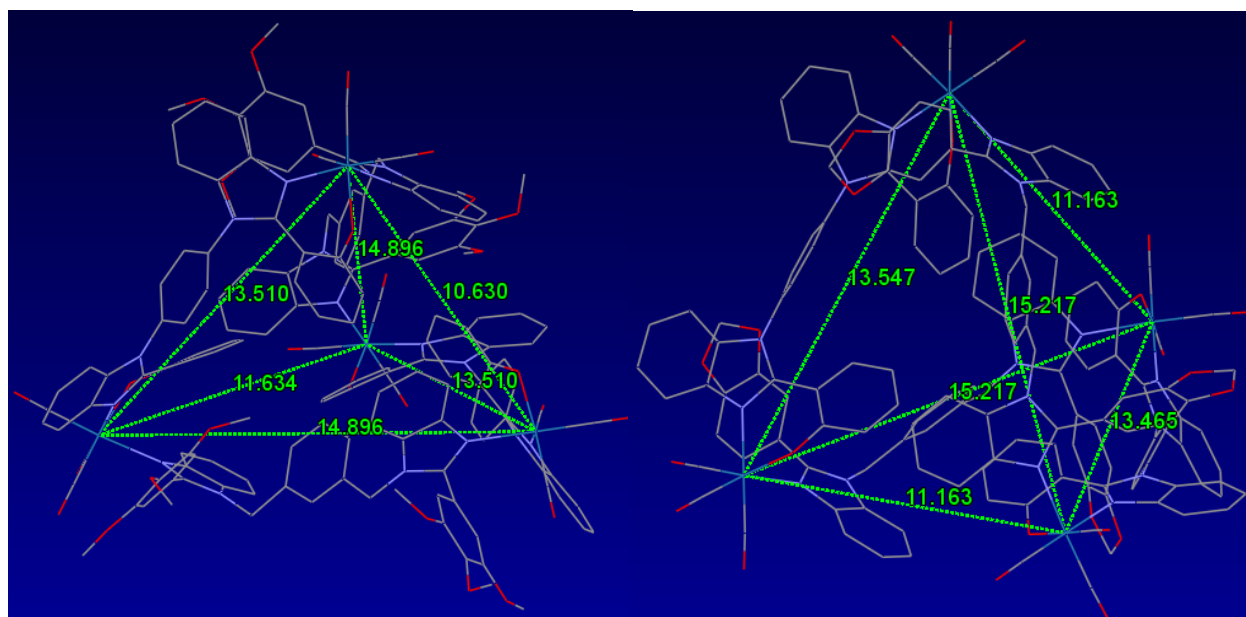


Figure 14. Molecular structures of **1** and **2** showing size of tetrahedron edges.

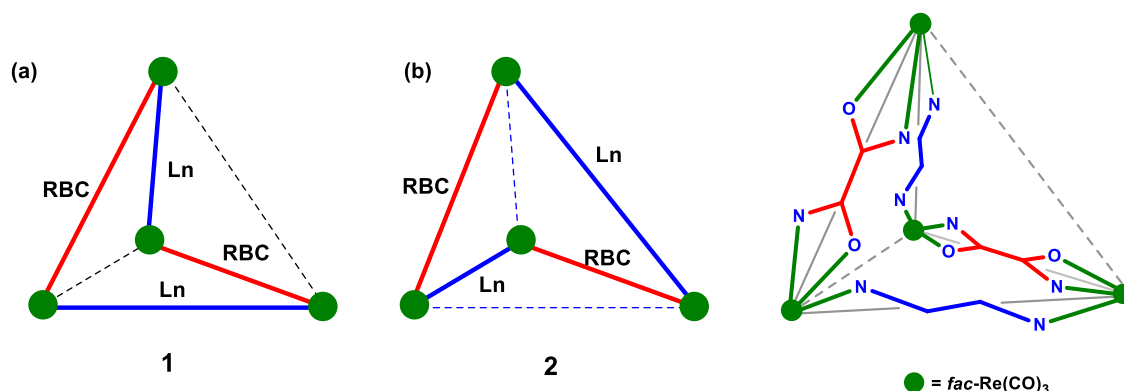


Figure 15. Different edge arrangement of L^n motif (blue) in the tetrahedrons **1** and **2**. Red indicates rigid ligand (RBC), and dotted line indicate missing edge.

The complex **2** is different from that of **1** due to the arrangement of two flexible ligand units in the tetrahedron edges. Both rigid ligand motifs occupy similar edges in both the complexes. The two empty edges in **1** are taken up by L^2 in **2**. The four exo-cavities of **1** were occupied by the methoxy unit of L^1 i.e., one methoxy motif occupy one face of the tetrahedron. Multiple weak C–H $\cdots\pi$ interactions were observed between the methoxy and the phenylene units. Average-to-strong intramolecular $\pi\cdots\pi$ stacking interactions were observed between the benzimidazolyl unit of RBC and the phenyl motif of L^n . Whereas in complex **2**, apart from the intramolecular $\pi\cdots\pi$ stacking interactions, C–H $\cdots\pi$ contacts are also observed between the planar 1,3-benzodioxole ring and the benzimidazolyl unit of the chelating motif.

An earlier report of combination of $\text{Re}_2(\text{CO})_{10}$ with a bis-chelating flexible ligand ($\text{H}_2\text{-FBC}$) and a flexible ditopic nitrogen donor resulted in the formation of a neutral dinuclear unsaturated heteroleptic helicate/mesocate [72]. The use of a rigid bis-chelating ligand resulted in the formation of the tetranuclear tetrahedron instead of a dinuclear helicate or a mesocate. This may be due to the steric hindrance between these two ligands because the distance between two bis-chelating donors either in the rigid $\text{H}_2\text{-RBC}$ ligand ($d(\text{Re-RBC-Re}) = 11.3 \text{ \AA}$) or in the flexible $\text{H}_2\text{-FBC}$ ligand ($d(\text{Re-RBC-Re}) = 13.1 \text{ \AA}$) is comparable [72]. Therefore, we can conclude that the substitution at the 2-position of the benzimidazolyl motif of L^n may play an important role for the formation of a tetrahedron assembly instead of a dinuclear helicate/

mesocate. The attempt to obtain a single crystal of SCC with $\text{Re}_2(\text{CO})_{10}$, $\text{H}_2\text{-RBC}$, and L^{m} is fruitless. Therefore, we suggest that the substituted phenyl at the 2-position of the benzimidazolyl of L^{n} may play a major role for directing from the dinuclear helicate/ mesocate to the tetrahedron assembly. The role of the fused benzene ring of benzimidazole in the ligand (L^{n}) as a steric motif may not be omitted.

3.4. Conclusions

In conclusion, a new type of facial rheniumtricarbonyl core containing heteroleptic tetrahedral-shaped SCCs with two empty edges were synthesized by the combination of $\text{Re}_2(\text{CO})_{10}$, with a bis-chelating rigid ligand (RBC) and a ditopic flexible ligand (L^{n}) with xylene spacer and substituted 2-(phenyl)benzimidazolyl derivatives as coordinating unit in a one-step synthetic method. The tetrahedral shaped metallacycles are neutral and heteroleptic with scalene triangular faces. To the best of our knowledge, this synthetic procedure is the first example for the synthesis of a facial rheniumtricarbonyl core containing heteroleptic tetrahedra. The results open up new a way to construct Re(I) based heteroleptic tetrahedra in a simple one-pot strategy.

3.5. References

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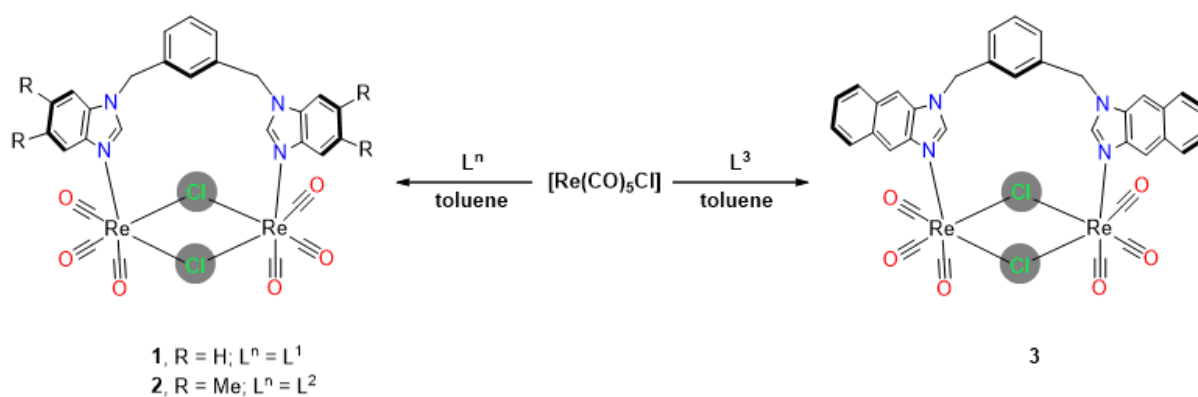
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Chapter 4

Rheniumtricarbonyl-based M_2Cl_2L -type metallocycles from ditopic nitrogen donors

Abstract

Neutral binuclear metallocycles of the formula of $fac-[{(CO)_3Re(\mu-Cl)_2Re(CO)_3}L^n]$ were obtained using $[Re(CO)_5Cl]$ and ditopic flexible nitrogen donor ($L^n = L^1 = \text{bis}((\text{benzimidazol-1-yl)methyl})\text{benzene}$; $L^2 = \text{bis}((5,6\text{-dimethylbenzimidazol-1-yl)methyl})\text{benzene}$, $L^3 = \text{bis}((\text{naphthanoimidazol-1-yl)methyl})\text{benzene}$ in toluene under solvothermal approach. The metallocycles were characterized by 1H NMR and ESI- Mass analysis. The crystal structures of **1-3** were confirmed by using single crystal X-ray diffraction analysis. The crystal structures of the metallocycles are stabilized by non-traditional intermolecular hydrogen bonding interactions.



4.1. Introduction

The construction of rhenium(I)tricarbonyl core based metallocycles have been getting intense research interest day by day owing to their potential applications in various fields [1-36]. Presently, considerable research has been concentrated on the synthesis of small sized Re(I) based metallocycles with π - π stacked motifs using flexible ligands due to their stability and ability to interact with bio-systems. Few semi-rigid ditopic ligands with heterocyclic donors with phenyl spacer are designed and employed. In addition, bis-chelating ligands are used along with semi-rigid ligands to assemble small sized neutral rhenium tricarbonyl based metallocycles. In all the cases, the resulting metallocycles are heteroleptic and neutral in nature. The ditopic ligands so far utilized for the metallocycles contain pyridine donors (Figure 1) [37-40].

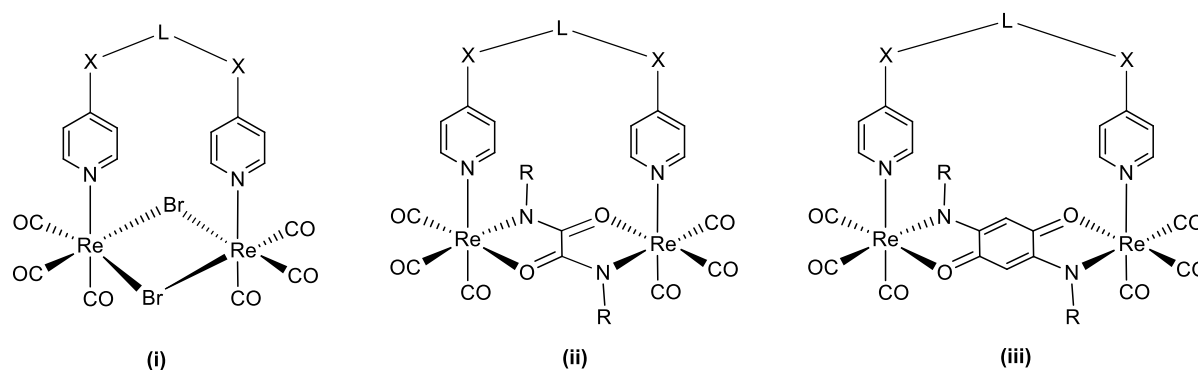


Figure 1. Metallocycles containing pyridine donors

On the other hand, neutral heteroleptic dinuclear metallocycles based on rheniumtricarbonyl cores with internal cavity suitable to accommodate solvent molecules are growing considerably. Most of the cases, these cavity containing metallocycles are self-assembled using semi-rigid ligands containing benzimidazolyl and its derivatives as coordinating unit (Figure 2). To the best of our knowledge, small dinuclear metallocycles with π - π stacked motif assembled using benzimidazolyl and its derivatives are scarce [41-45]. Similarly, hydroxyl ion (OH) and halides (Cl/Br) are well-known bridging ligands and can be used to make dirhenium metallocycles with π - π stacked motif. Though these ions as bridging ligands are highly desirable for making the metallocycles, these ions are employed less frequently.

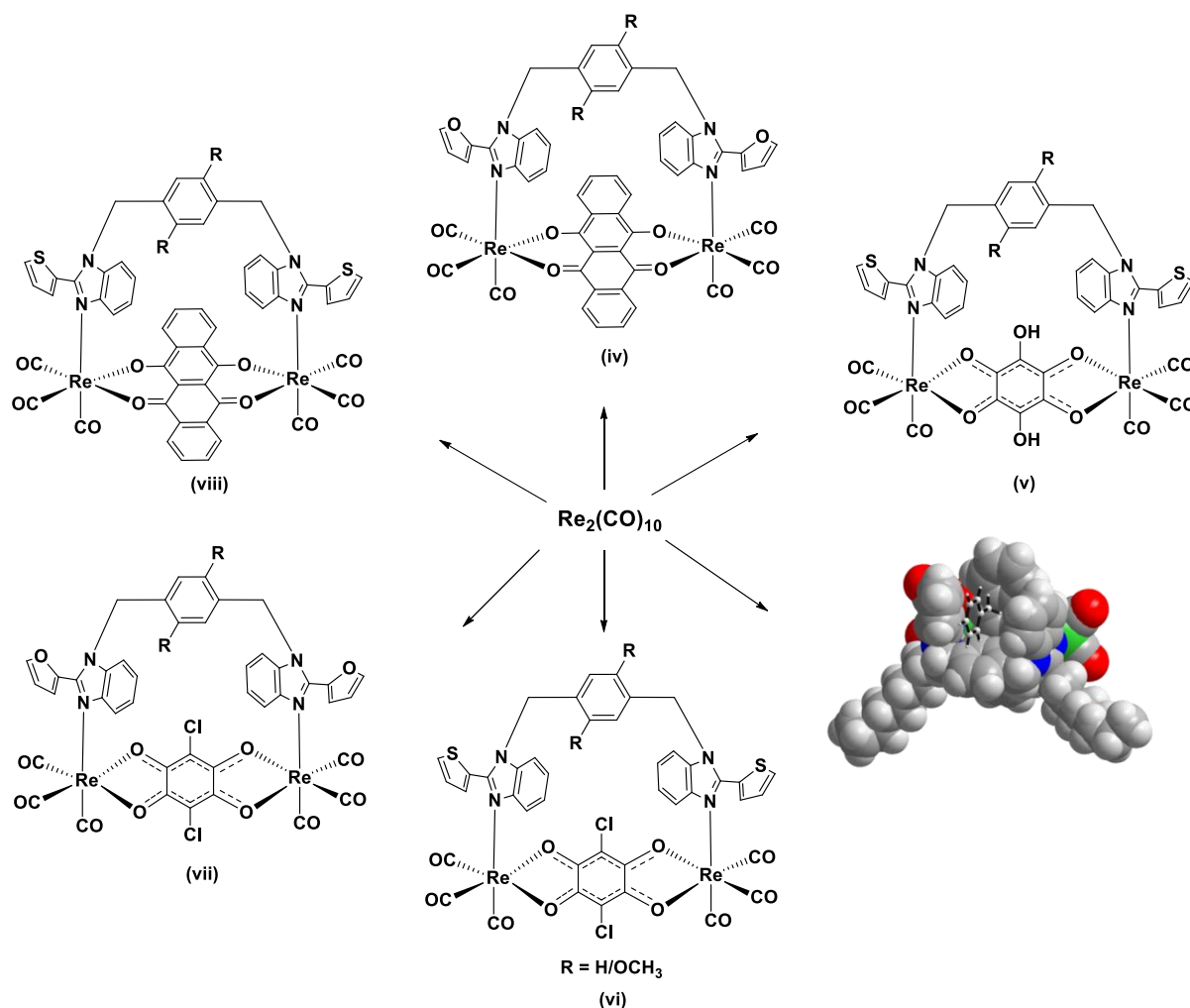


Figure 2. Cavity containing metallocycles assembled using semi-rigid ligands containing benzimidazole and its derivatives as coordinating units.

Recently, our research group has been designing different types of flexible N-donor ligands and utilizing to synthesize different types of facial rheniumtricarbonyl core based metallocycles in the presence of anionic bis-chelating organic ligands [46]. In general, the use of halide ions along with ditopic flexible ligands and rheniumtricarbonyl would result in new type of $\pi \cdots \pi$ stacked metallocycles. Herein, we report a neutral chloride bridged binuclear metallocycles of the formula $\text{fac-}[\{\text{Re}(\text{CO})_3(\mu\text{-Cl})_2\text{Re}(\text{CO})_3\}\text{L}^n]$ (**1-3**). These metallocycles were obtained by the treatment of $[\text{Re}(\text{CO})_5\text{Cl}]$ with ditopic flexible N-donor ligands ($\text{L}^n = \text{L}^1 = \text{bis}((\text{benzimidazol-1-yl})\text{methyl})\text{benzene}$; $\text{L}^2 = \text{bis}((5,6\text{-dimethylbenzimidazol-1-yl})\text{methyl})\text{benzene}$, $\text{L}^3 = \text{bis}((\text{naaphthanoimidazol-1-yl})\text{methyl})\text{benzene}$ in toluene under solvothermal approach. The crystal structures of the metallocycles **1-3** were confirmed by

SCXRD analysis. The molecular structures of these metallocycles are stabilized by non-traditional intermolecular hydrogen bonding interactions.

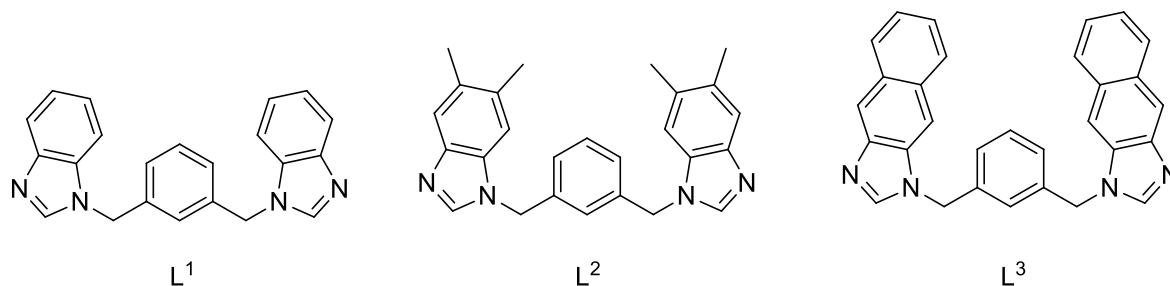


Figure 3. Flexible ditopic nitrogen donor ligands used in this work

4.2. Experimental

Materials and Methods

[Re(CO)₅Cl] (98%, Sigma-Aldrich) was purchased and used as such. The purification of the solvents toluene and hexane was done by the conventional methods. Ligands L^1 , L^2 and L^3 were synthesized according to the previous reports [47, 48]. ATR-IR spectra of the complexes were recorded on Bruker Tensor-II spectrometer. Proton NMR spectra were obtained from a Bruker Avance III 400 and 500 MHz instruments. The mass spectra of all the complexes were recorded in a Bruker maXis mass spectrometer.

Synthesis of fac-[(CO)₃Re(μ-Cl)₂Re(CO)₃]L¹] (1)

Complex **1** was obtained by using a mixture of [Re(CO)₅Cl] (100.4 mg, 0.2775 mmol), L^1 (46.78 mg, 0.1382 mmol) and toluene (10 mL) in a Teflon flask that was placed in a steel bomb. The bomb was kept in an oven maintained at 160 °C for 48 h and then cooled to 30 °C. Colorless crystals of **1** along with violet colored powder obtained in the solvothermal vessel were washed with distilled hexane, filtered and air dried. Yield (crystal and powder): 41% (54.5 mg). IR (KBr, cm⁻¹): 2018 (C≡O), 1885 (C≡O). ESI (HR-MS). Calcd. for C₂₈H₁₉Cl₂N₄O₆Re₂ [M + H]⁺: *m/z* 950.9797. Found: *m/z* 950.9712.

Synthesis of *fac*-[$\{(CO)_3Re(\mu-Cl)_2Re(CO)_3\}L^2$] (2**)**

Complex **2** was obtained by using a mixture of $[Re(CO)_5Cl]$ (100.5 mg, 0.2778 mmol), L^2 (54.53 mg, 0.1382 mmol) and toluene (10 mL) in a Teflon flask that was placed in a steel bomb. The bomb was kept in an oven maintained at 160 °C for 48 h and then cooled to 30 °C. Colorless crystals of **2** along with white colored powder obtained in the solvothermal vessel were washed with distilled hexane, filtered and air dried. Yield (crystal and powder): 80% (112 mg). IR (KBr, cm^{-1}): 2013 (C≡O), 1905 (C≡O), 1875 (C≡O). ESI (HR-MS) Calcd. for $C_{32}H_{27}Cl_2N_4O_6Re_2 [M + H]^+$: m/z 1007.0422. Found: m/z 1007.0392.

Synthesis of *fac*-[$\{(CO)_3Re(\mu-Cl)_2Re(CO)_3\}L^3$] (3**)**

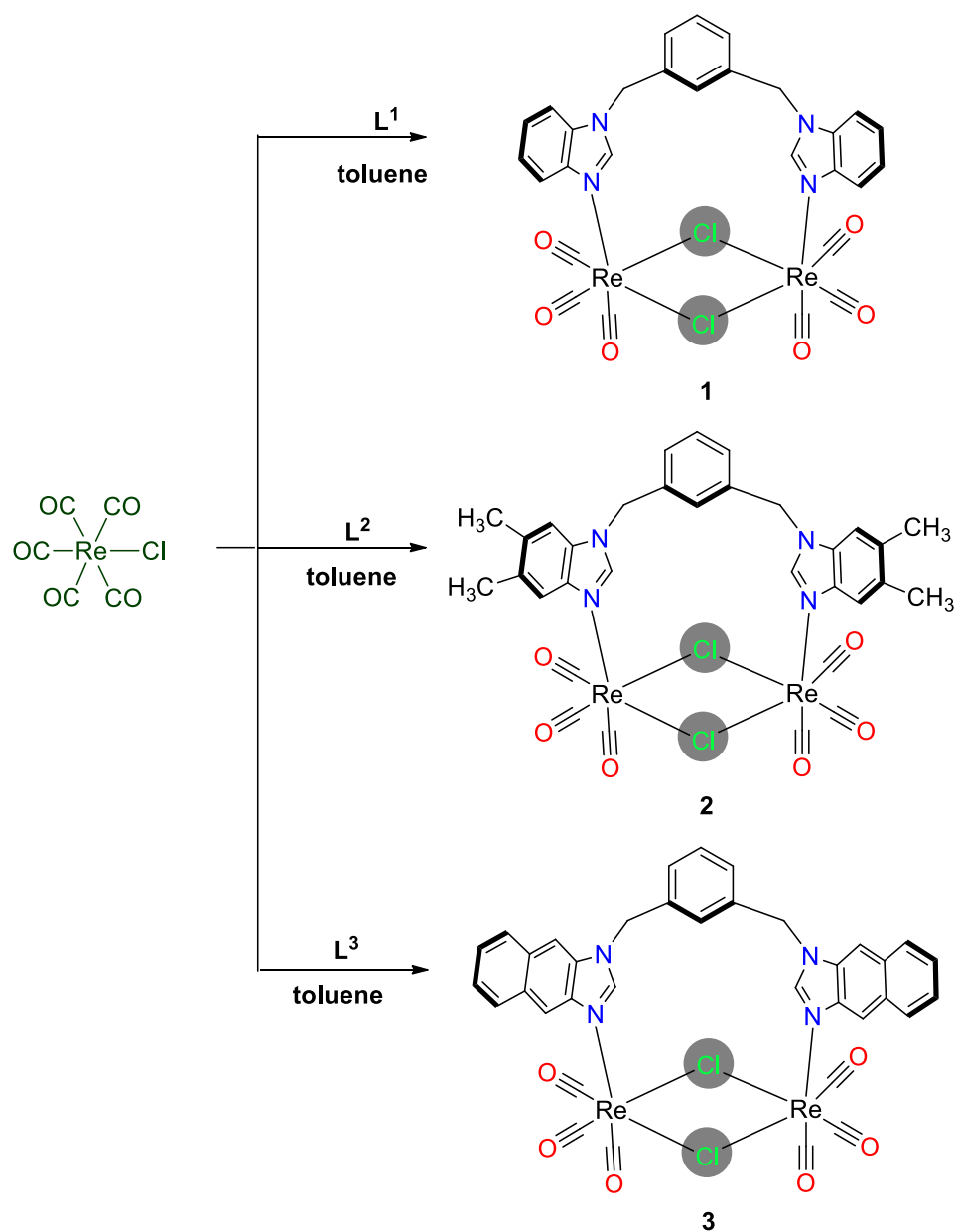
Complex **3** was obtained by using a mixture of $[Re(CO)_5Cl]$ (100.5 mg, 0.2778 mmol), L^3 (121.23 mg, 0.2764 mmol), and toluene (10 mL) in a Teflon flask that was placed in a steel bomb. The bomb was kept in an oven maintained at 160 °C for 48 h and then cooled to 30 °C. Yellow-colored crystals of **3** along with white colored powder obtained in the solvothermal vessel were washed with distilled hexane, filtered and air dried. Yield (crystal and powder): 32% (93.5 mg). IR (KBr, cm^{-1}): 2016 (C≡O), 1882 (C≡O). ESI (HR-MS). Calcd. for $C_{36}H_{23}Cl_2N_4O_6Re_2 [M + H]^+$: m/z 1051.0110. Found: m/z 1051.0131.

X-ray crystallography

Single crystal X-ray data of crystals of **1** and **2** were collected on a Rigaku oxford XtalLAB Synergy [$\lambda(Mo K\alpha) = 0.71073 \text{ \AA}$]. The structures were solved by direct methods using SHELXS-2014/5 (Sheldrick 2014) and refined using the SHELXL-2018/3 (Sheldrick, 2018) program (within the WinGX program package) [49, 50]. Non-H atoms were refined anisotropically.

4.3. Results and discussion**Synthesis and characterization of metallocycles 1-3**

The treatment of $[Re(CO)_5Cl]$, $L^1/L^2/L^3$ (L^1 for **1**, L^2 for **2**, and L^3 for **3**) and toluene under solvothermal reaction vial lead to the formation of compounds **1-3** (Scheme 1). The metallocycles are stable in air and moisture and soluble in organic solvents. The AT-IR spectra of the metallocycles showed two or three strong bands in the region 2019-1890 cm^{-1} , characteristic of facial rheniumtricarbonyl unit in the complexes (Figures 4-6) [51-59].

**Scheme 1.** Synthesis of metallocycles 1-3

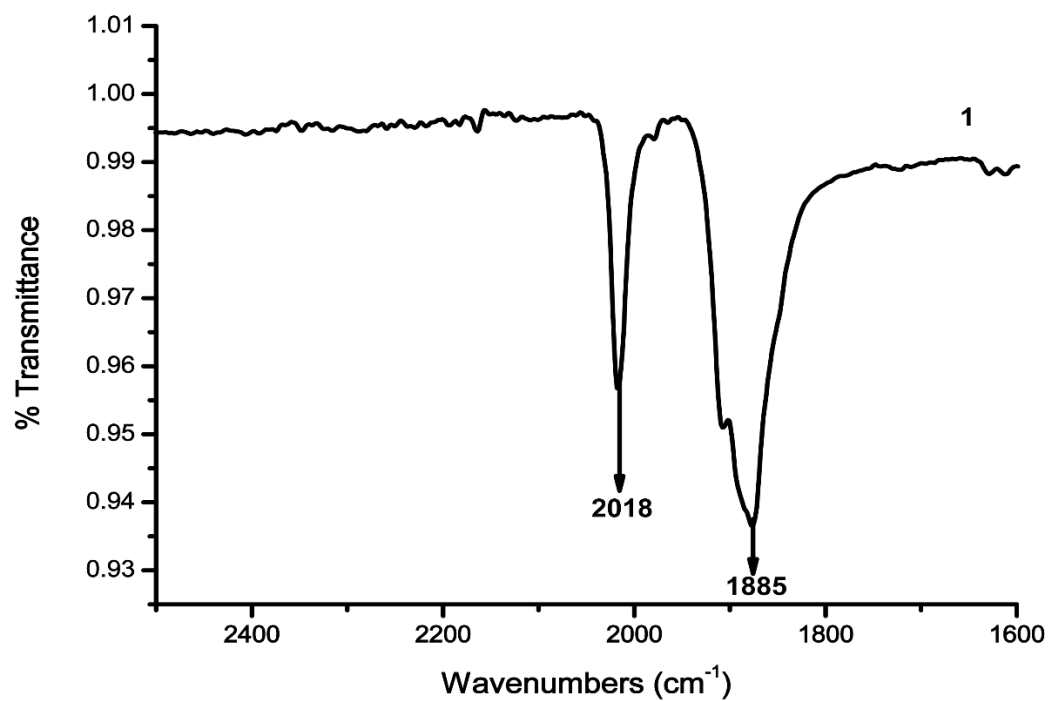


Figure 4. ATR-IR Spectrum of complex 1

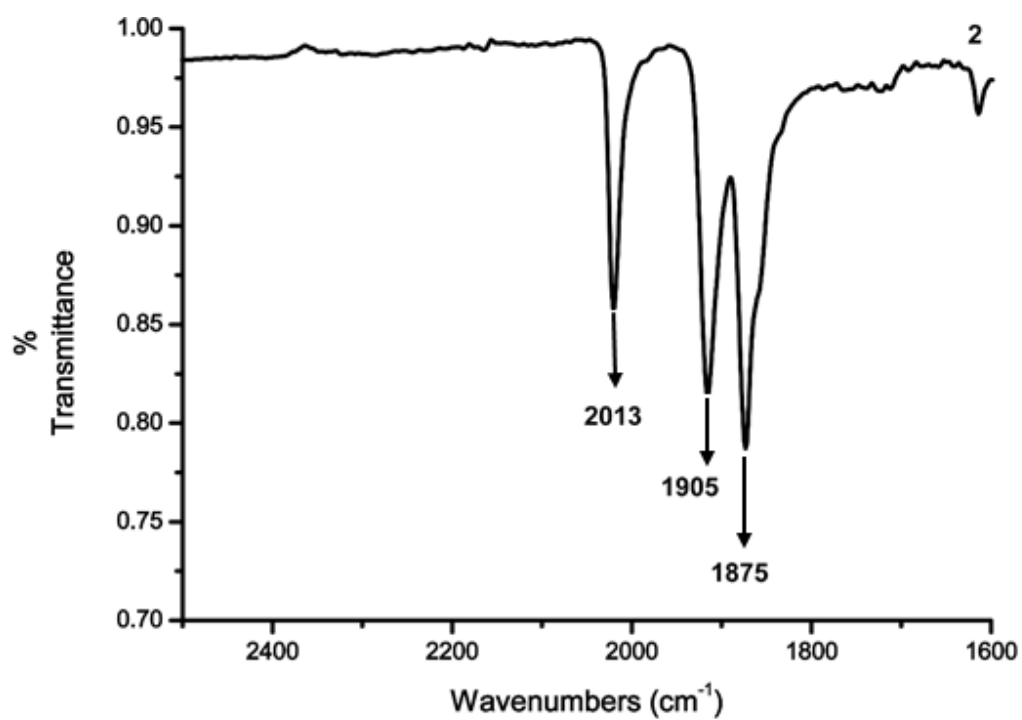


Figure 5. ATR-IR Spectrum of complex 2

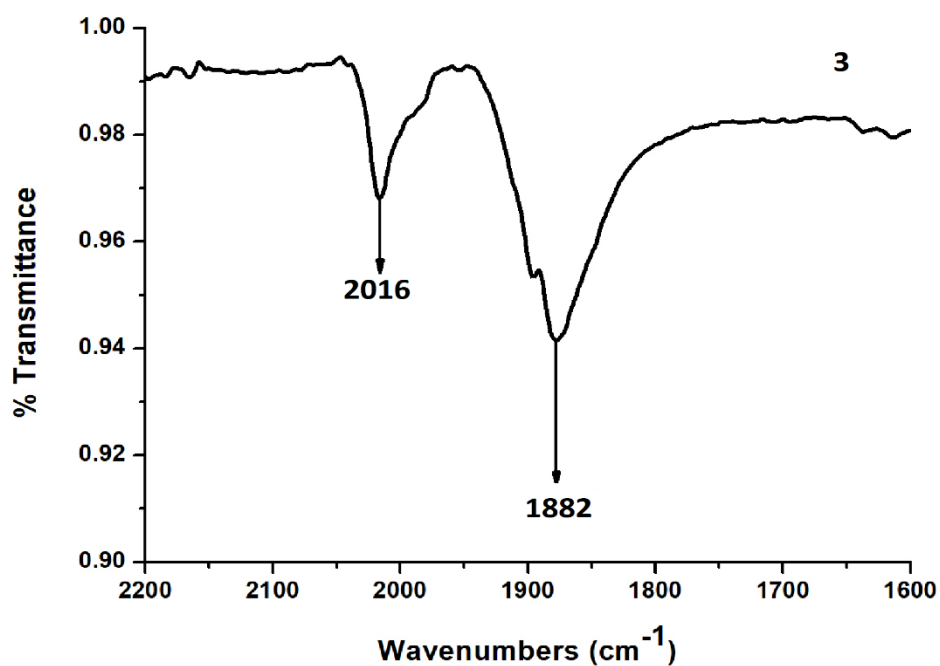


Figure 6. ATR-IR Spectrum of complex 3

The ^1H NMR spectra of the metallocycles displayed complex pattern i.e., more chemical resonances for the ligand framework protons than expected peaks (Figure 7). This may be due to the following changes occur in the solution:

- (i) The presence of various conformers in different ratio, or
- (ii) Some of the dinuclear metallocycles transformed into dinuclear acyclic complexes *via* transformation of bridging chloride to monocoordinated chloride i.e., each rhenium has one coordinated chloride ion, or
- (iii) Mixture of both cyclic and acyclic complexes with different ratio.

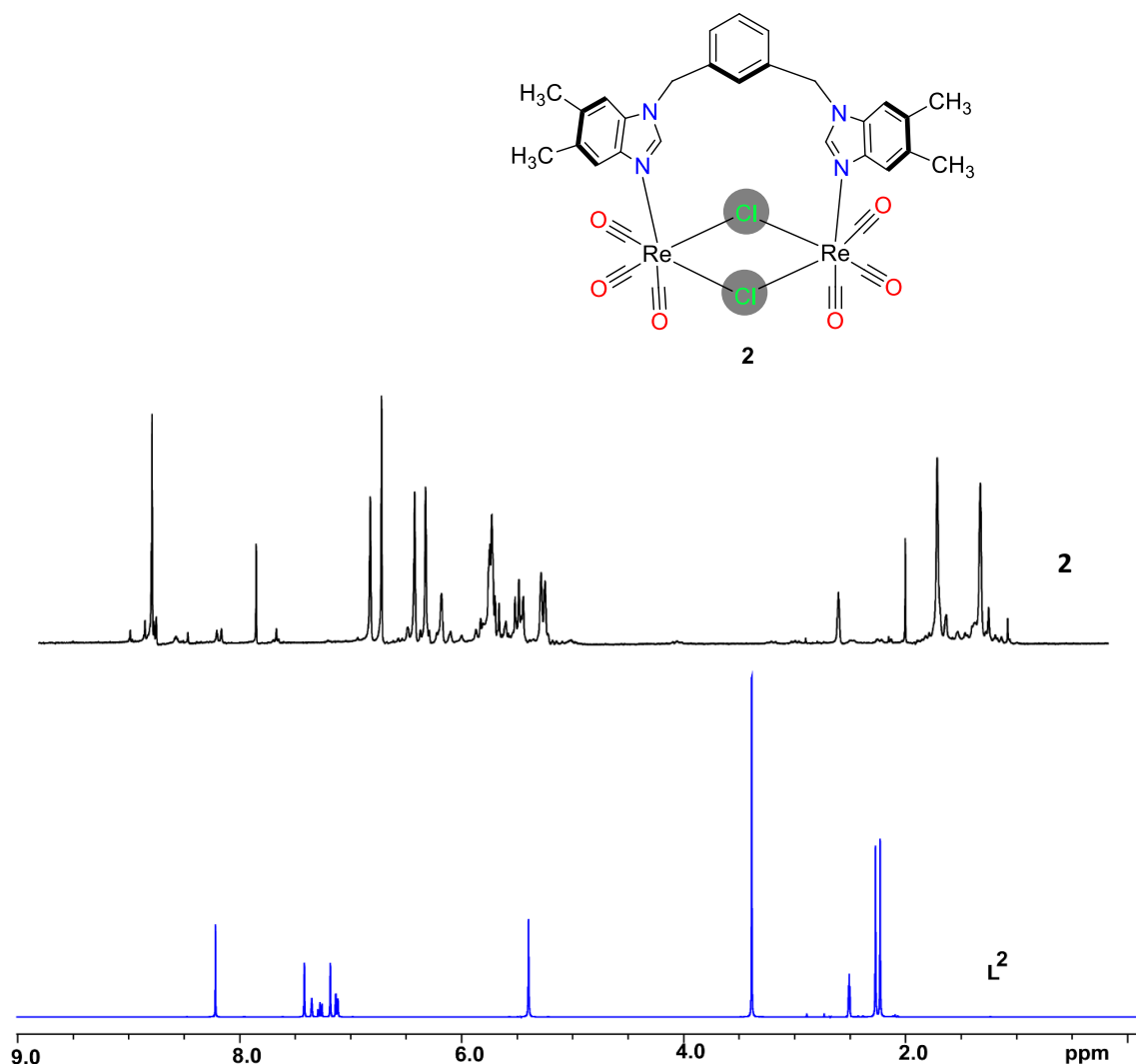


Figure 7. Partial ^1H NMR spectra of **2** and free ligand L^2 in $\text{dmsO-}d_6$.

The formation of the metallocycles **1-3** were supported by the electrospray ionization mass spectrometry which exhibited a molecular ion peak (m/z 950.9797) corresponds to $[\mathbf{1} + \text{H}]^+$ that matches with the theoretical value. Similarly complexes **2** and **3** also exhibit molecular

ion peaks m/z 1007.0422 and m/z 1051.0110 corresponds to $[2 + H]^+$ and $[3 + H]^+$ respectively and confirms the formation of these metallocycles in solution (Figures 8-10).

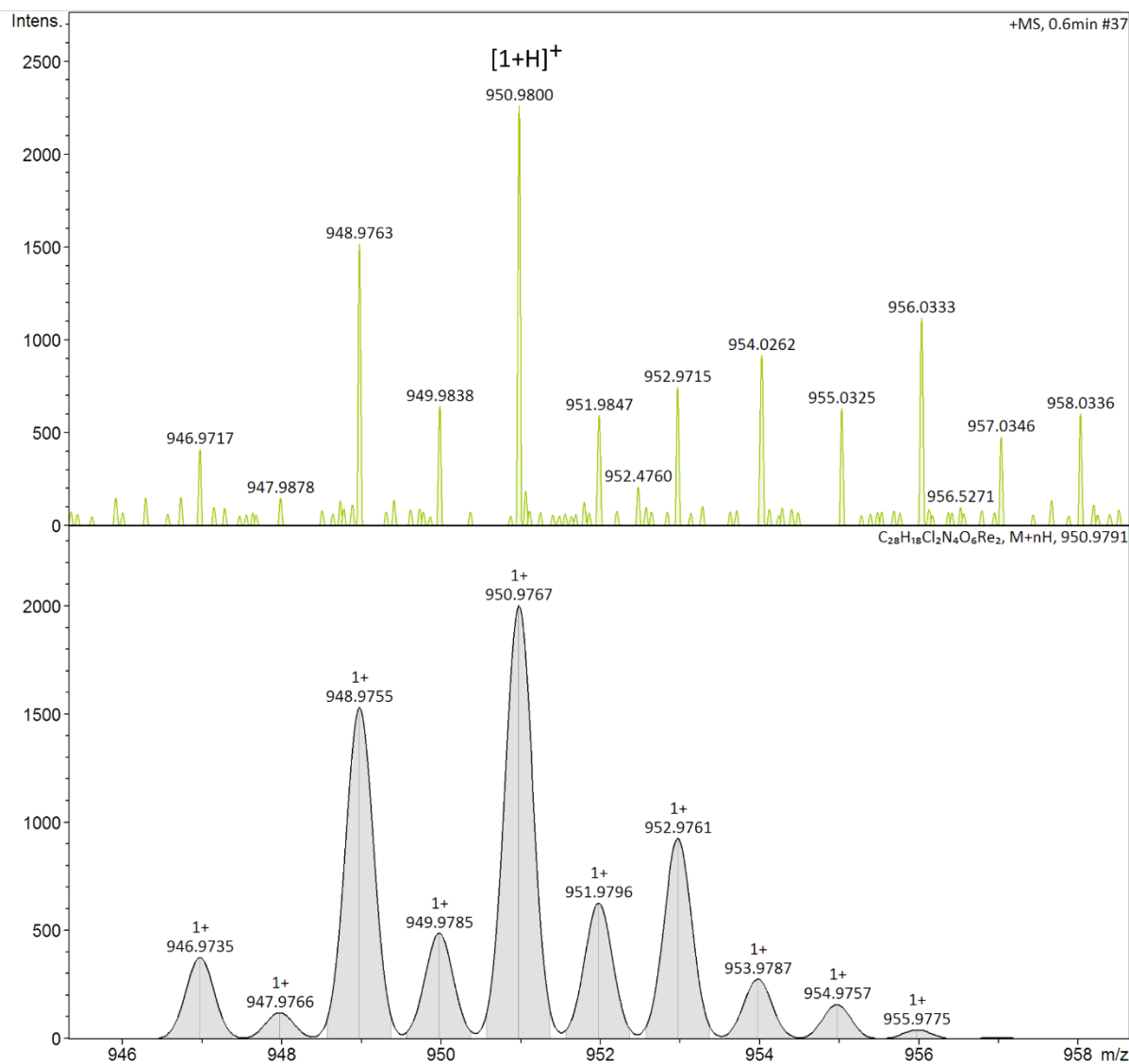


Figure 8. Experimental (top) and calculated (bottom) ESI-TOF-MS spectra of $[1+H]^+$.

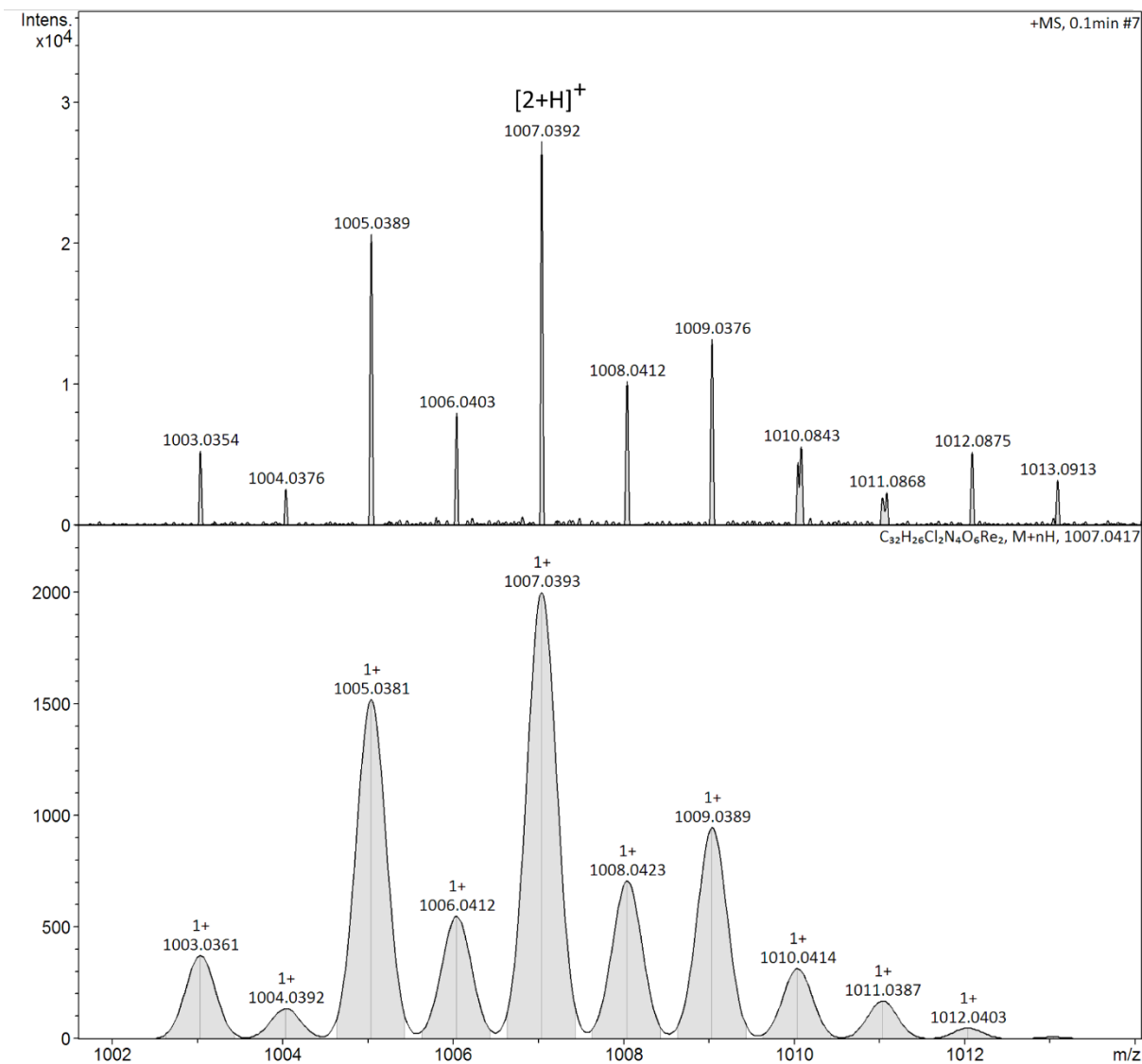


Figure 9. Experimental (top) and calculated (bottom) ESI-TOF-MS spectra of $[2+H]^+$.

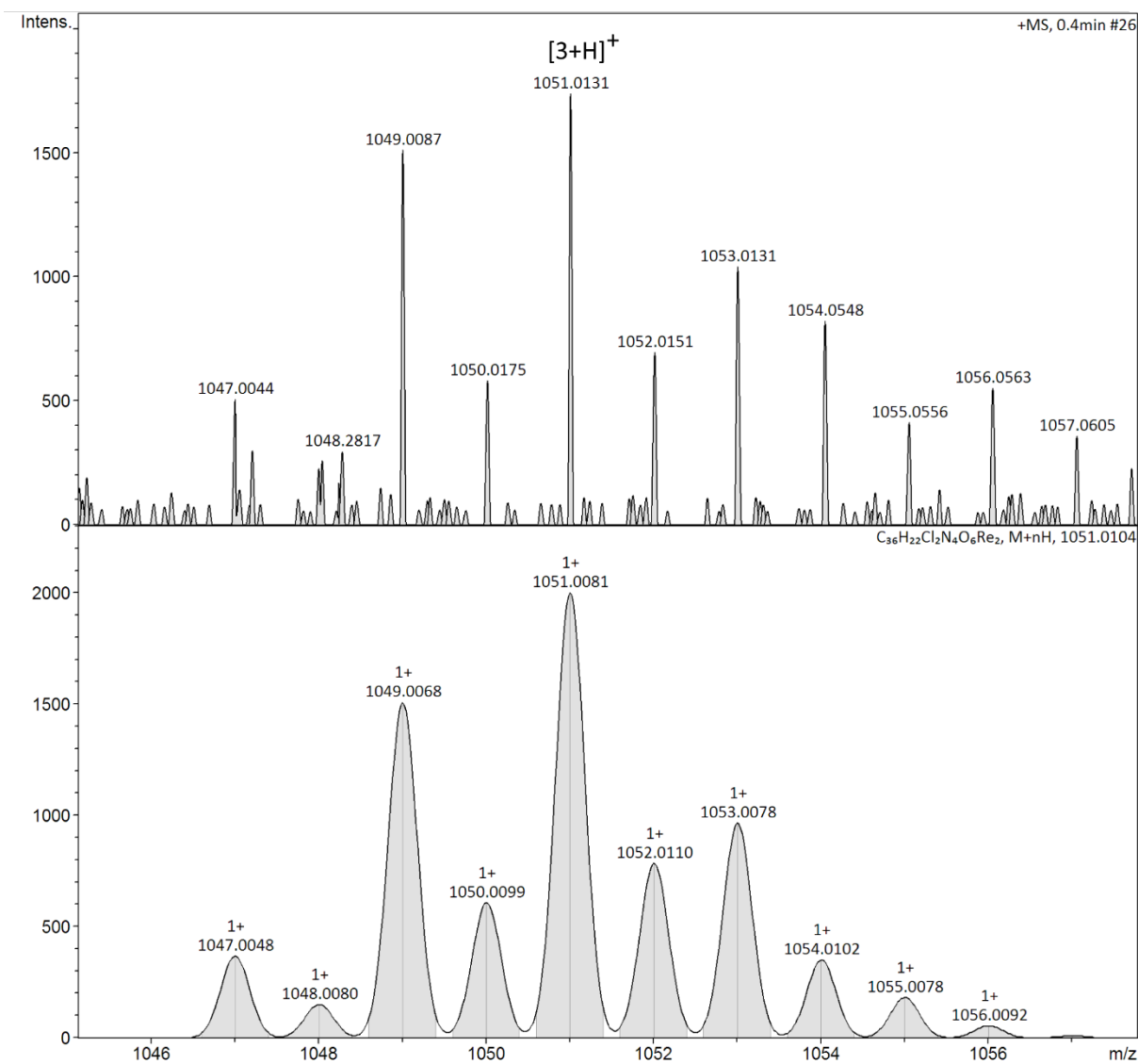


Figure 10. Experimental (top) and calculated (bottom) ESI-TOF-MS spectra of $[3+H]^+$.

Molecular structures of metallacycles 1-3

The crystal structures of metallacycles **1** and **2** were analysed by SCXRD analysis, which reveals that the molecules **1** and **2** take binuclear $M_2Cl_2L^n$ type cyclic structure. These molecules are made up of two *fac*- $Re(CO)_3$ motifs, two chloride ions, and one neutral L^n ligand (Figure 11). The rhenium in the complexes is in an octahedral environment with a C_3Cl_2N -donor surroundings. The two chloride ions bridge two rhenium centers and each chloride ion acts as three electron donors. The Re–Cl bond distances in the metallacycles are in the expected region. The Re–Re distance in the chloride bridged dinuclear assembly $[(CO)_3Re(\mu-Cl)_2Re(CO)_3]$ is ~ 3.8 Å. The dinuclear assembly is further clipped by a neutral ditopic nitrogen donor. The neutral nitrogen donor L^n takes a *syn*-conformation by arranging both the benzimidazolyl motifs on the same side.

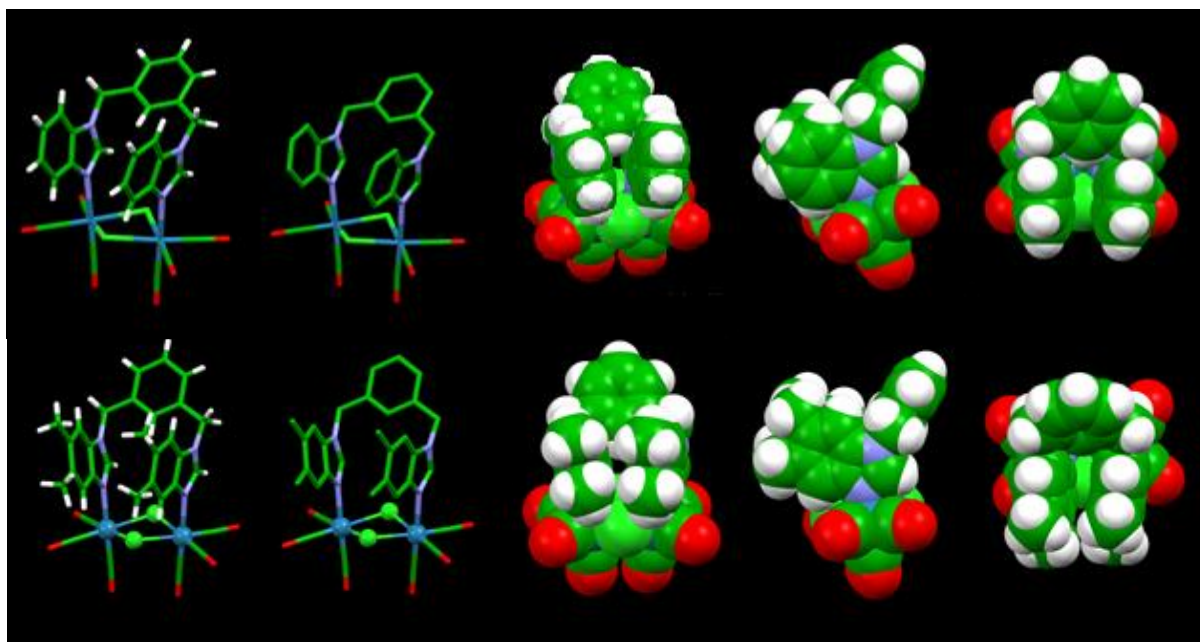


Figure 11. Various views of molecular structures of **1** (top) and **2** (bottom) with and without hydrogen atoms.

The dihedral angle and the distances range between two benzimidazolyl motifs in **1** are $\sim 18.4^\circ$ and ~ 3.9 - 5.0 Å. The data clearly indicates a very weak $\pi \cdots \pi$ stacking interactions or no $\pi \cdots \pi$ stacking interactions exist between the two parallel arranged benzimidazolyl motifs in **1**. The central phenylene spacer of L^1 in complex **1** is arranged in such way that the C^2H portion of six-membered ring directed in the metallacycle and its plane is perpendicular to the two benzimidazolyl motifs. The dihedral angle between the phenylene motif and benzimidazolyl plane is $\sim 83^\circ$. A similar arrangement of neutral nitrogen donor was found in the metallacycle **2**. The

dihedral angle and the distances between two benzimidazolyl motifs in **2** are $\sim 15^\circ$ and ~ 3.68 - 4.86 Å. The data clearly indicates a weak $\pi \cdots \pi$ stacking interactions exist between two parallel arranged 5,6-dimethylbenzimidazolyl motifs in **2**. The central phenylene spacer of L^2 in complex **2** is arranged in such way that the C^1H portion of six-membered ring directed in the metallocycle and its plane is perpendicular to the two benzimidazolyl motifs. The dihedral angle between the phenylene motif and benzimidazolyl plane is $\sim 86^\circ$.

The crystal structures of both the metallocycles were stabilized by intermolecular hydrogen bonding interactions. In particular, the coordinated carbonyl groups involve extensively as hydrogen acceptors. In the crystal structure of **1**, two adjacent molecules interact each other in such a way that the chloride edge of metallocycle directed towards the phenylene edge of the neighbouring metallocycle. It is better to represent these two metallocycles as non-covalent dimer. These two metallocycles interact each other *via* $C-H_{(CH_2)} \cdots O(O \equiv C-Re)$ hydrogen bonds. Four such intermolecular H-bonds stabilizes the dimer molecule. The dimer molecule further interact with neighbouring dimer molecules in the crystal structure *via* H-bonds that occur between hydrogen atoms of phenylene core to oxygen atom of the carbonyl group $C-H_{(Ph)} \cdots O(O \equiv C-Re)$ (Figure 12).

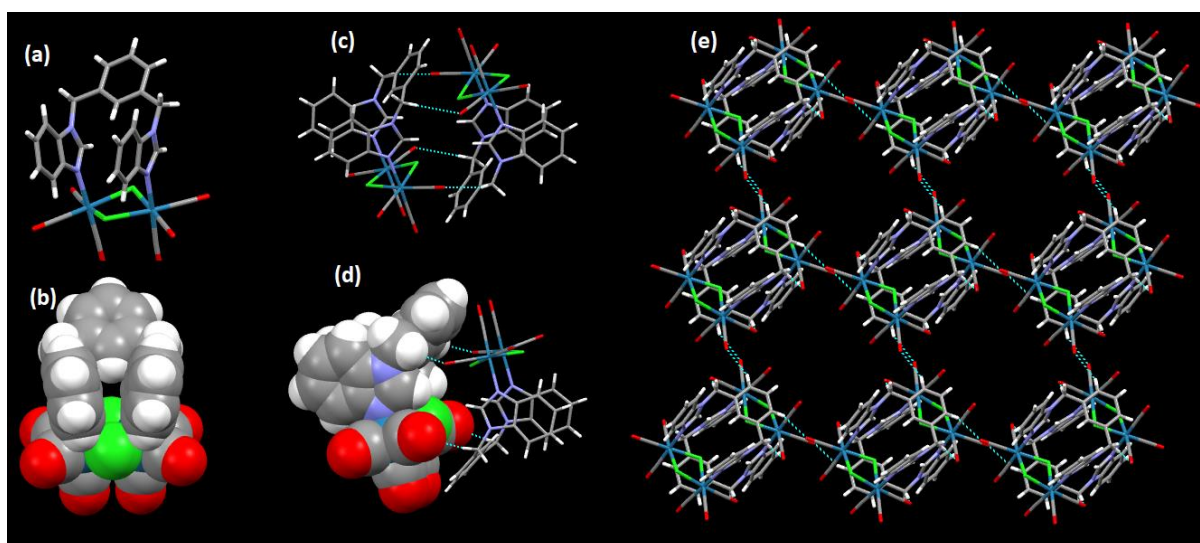


Figure 12. (a) Molecular structure of **1**. (c) Non-covalent dimer of **1** in the crystal structure showing aliphatic $C-H \cdots O \equiv C-Re$ H-bonds. (e) Partial packing diagram (nine dimeric molecules) showing dimer molecules interacting with another dimer molecules *via* aromatic $C-H \cdots O \equiv C-Re$ H-bonds. Color code: C – Gray, H - white, N - Blue, Cl – Bright green, Re - Teal and O – Red.

The crystal structure of metallocycle **2** was stabilized by intermolecular hydrogen bonding interactions similar to that of **1** (Figure 13). Few features in the crystal structure of **2** are discussed below. Two metallocycles are present in the unit cell and are arranged in such a way that two neighbouring dimethylbenzimidazolyl motifs from two different metallocycles are arranged in an anti-cofacial manner. Orthogonal direction to the dimer metallocycles, each metallocycles interact with neighbouring molecules through *face-to-face* $\pi \cdots \pi$ stacking contacts. In this case, the chloride edge of the metallocycle are anti-cofacially arranged. These two metallocycles contact each other through intermolecular C–H $\cdots$ Cl contacts and accepting bifurcated hydrogen bonding interactions between hydrogen atoms (CH₂ and CH (benzimidazolyl)) to oxygen atoms of equatorially coordinated carbonyl atoms of the neighbouring metallocycle. Altogether, six non-covalent contacts found between the dimer. These supramolecular assembly can be considered as [1+1] assembly along the c axis which interact with another dimer assembly that are arranged anti-cofacially *via* intermolecular hydrogen bonds using hydrogen atoms of methyl group of one metallocycles to oxygen atom of carbonyl group. In another direction, the cleft available in the metallocycle is occupied by central phenyl unit of the neighbouring molecules.

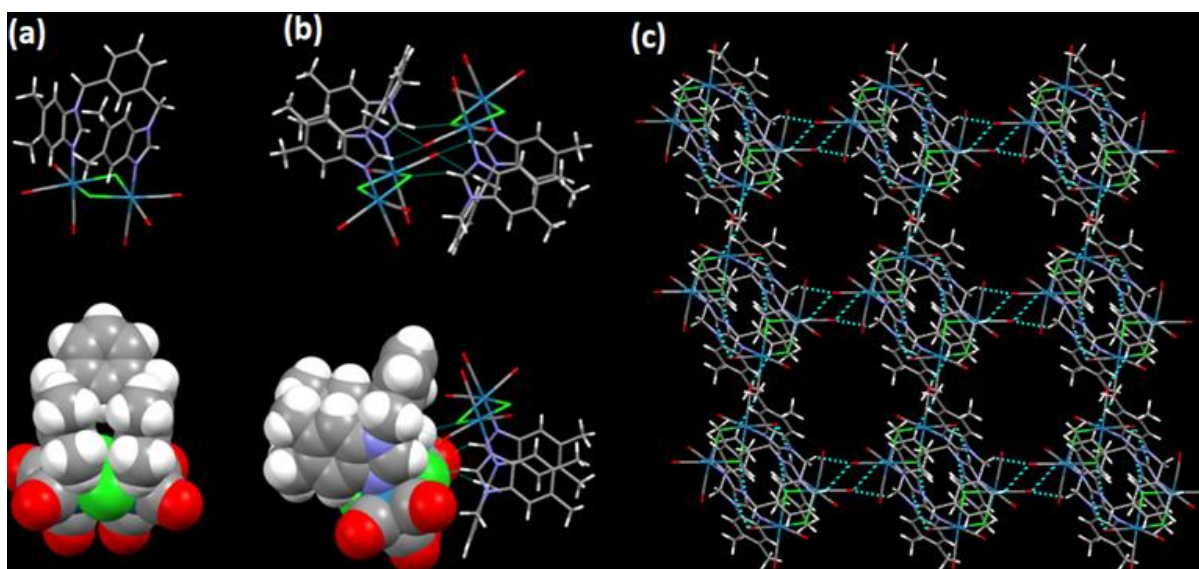


Figure 13. (a) Molecular structure of **2**. (b) Non-covalent dimer of **2** in the crystal structure showing aromatic C–H $\cdots$ O=C–Re H-bonds and C–H $\cdots$ Cl contacts. (c) Partial packing diagram (nine dimeric molecules) showing dimer molecules interacting with another dimer molecules *via* both aliphatic and aromatic C–H $\cdots$ O=C–Re H-bonds. Color code: C – Gray, H - white, N - Blue, Cl – Bright green, Re - Teal and O – Red.

4.4. Conclusions

In conclusion, a neutral chloride bridged small sized metallocycles based on rheniumtricarbonyl core were synthesized using $[\text{Re}(\text{CO})_5\text{Cl}]$, and semi-rigid ditopic ligand containing benzimidazolyl donor. The chloride bridge is responsible in bringing two rhenium cores very close to each other and indirectly allowing to coordinate nitrogen donors to act as *syn*-conformations. Though the distance between two rhenium atoms are very short, the central phenylene core prevents sterically by directing portion of its core towards the center of the metallocycle thus keeping two benzimidazolyl motif away from each other. However, the results provide the simple way to make small sized metallocycles.

4.5. References

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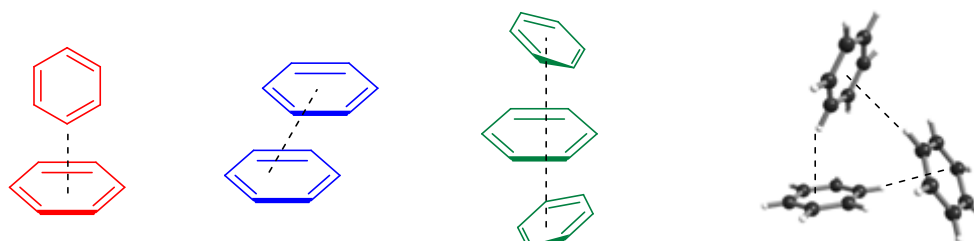
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Chapter 5

Synthesis of tripodal molecules based on 2-(4-thiazolyl)benzimidazole

Abstract

Three tritopic organic molecules (**1-3**) based on 2-(4-thiazolyl)benzimidazolyl (L) terminal motif were synthesized using 1,3,5-tris(bromomethyl)benzene/1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene/1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene and 2-(4-thiazolyl)benzimidazole (L-H). Compounds **1-3** were analysed by ESI-Mass spectrometry and ^1H NMR spectroscopy. The solid state structures of **2** and **3** were also confirmed by SCXRD analysis. However, structure of **1** could not be established due to failure attempt of growing single crystal. Molecule **2** takes a *syn*-conformation with *face-to-face* arrangement in solid state, whereas **3** takes *syn*-conformation with *edge-to-face* arrangement, in which all the three L units are arranged nearly orthogonal to each other. In the crystal structure, neighbouring pair of molecules of **2** interacts each other through non-covalent contacts resulting in double homost stranded helical architecture. ESI-MS analysis indicates that molecule **2** is predominantly present as monomer along with small proportion of the dimer. Further, monomer **2** and **3** in solution have cyclic aromatic trimer motif with *edge-to-face* arrangement of the benzimidazolyl units which are stabilized through aromatic $\text{C-H}\cdots\pi$ interactions.



Non-covalent interactions in aromatic motifs

5.1. Introduction

The design and synthesis of organic molecules-based discrete supramolecules with desired shapes and sizes have been attracted because of their beautiful architectures and potential biomedical applications [1]. Discrete supramolecular aggregates with specific geometries mostly rely on traditional hydrogen bonding interactions [2]. The well-known examples are DNA (Figure 1) and protein macromolecules [3].

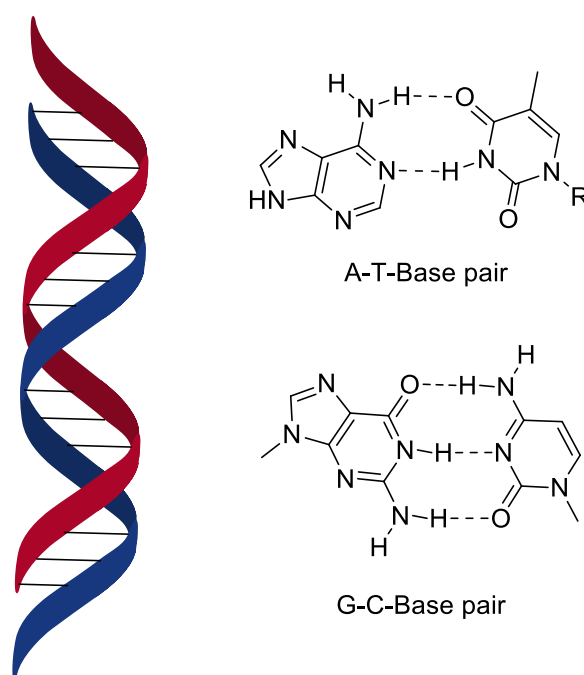


Figure 1. Double helix structure of DNA (left) and hydrogen bonding interactions between the base pairs in DNA (right).

Further, very weak non-covalent interactions between hetero(aromatic) units in biomolecules play a vital role in controlling their structure stabilization including stabilization of DNA, protein structure, protein folding and functions such as protein-protein recognition [4,5]. In particular, aromatic units present as side motifs in biomolecules contact with each other and adopt dimer, trimer and oligomeric aromatic clusters which contribute to the specific structural features (Figure 2) [6]. Aromatic C-H... π (*edge-to-face*) and *face-to-face* π ... π stacking contacts stabilize these aromatic motifs due to the cumulative contacts.

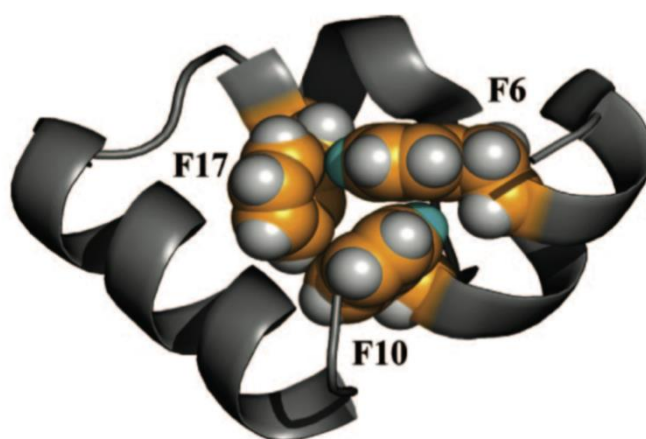


Figure 2. Cyclic aromatic trimer interactions found in the 35-residue villin headpiece subdomain and play vital role for folding of the subdomain.

Large as well as small molecules containing aromatic dimer motif are prevalent. Examples of biomolecules possessing aromatic ladder-type trimer and aromatic cyclic trimers are also known [5]. However, synthetic molecules with non-covalent aromatic cyclic trimer motif are scarce. Attempts to synthesis discrete small molecules with aromatic cyclic trimer and higher order clusters were highly challenging due to difficulty in arranging three or several aromatic motifs with particular orientations and optimal distances (Figure 3).

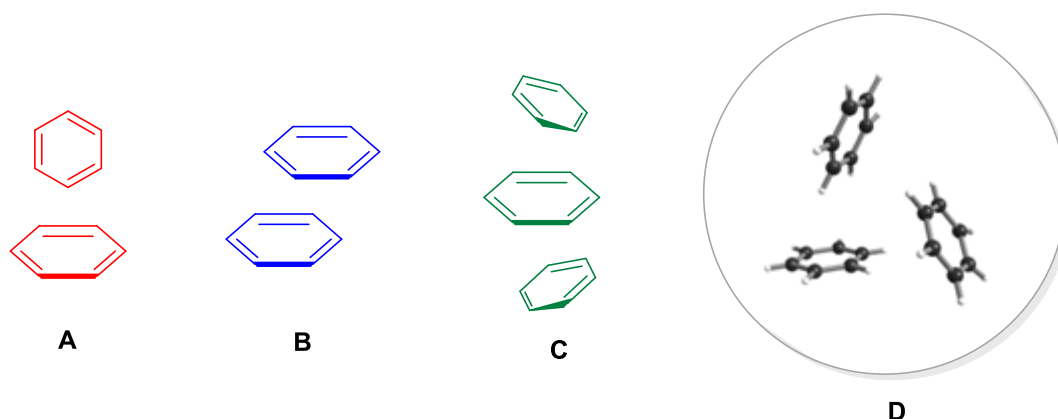
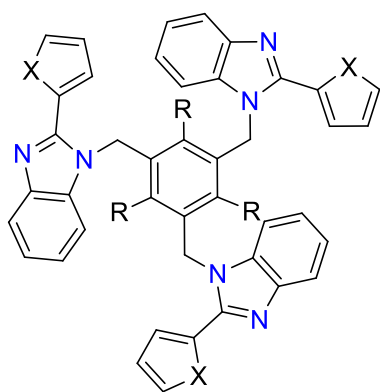


Figure 3. Non-covalent aromatic dimers (A-B), trimer (ladder, C) and cyclic trimer (D).

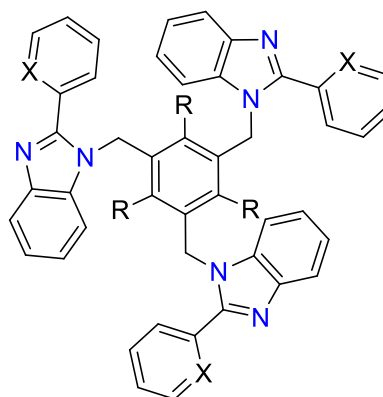
Recently our group introduced a new method in which secondary groups (substituents in benzene core and prosthetic units) in flexible tripodal molecules direct the aromatic motifs to adopt aromatic cyclic trimer motif. The secondary group is placed in the molecule at the second position of the benzimidazolyl motif, and alternate positions of the benzene core (Figure 4 and 5).



Ia, X = O, R = H; **Ila**, X = S, R = H

Ib, X = O, R = CH₃; **Ilb**, X = S, R = CH₃

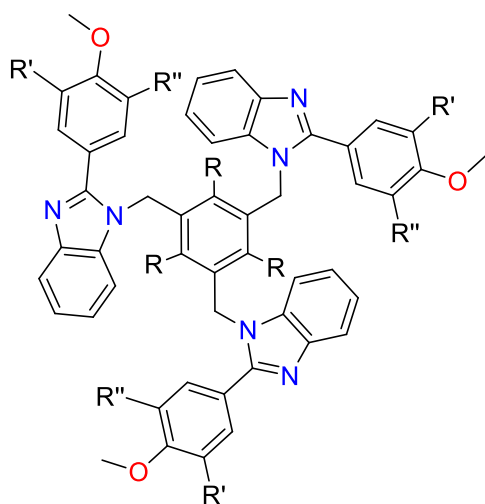
Ic, X = O, R = CH₂CH₃; **Ilc**, X = S, R = CH₂CH₃



IIlb, X = N, R = CH₃

IIlc, X = N, R = CH₂CH₃

IVc, X = CH, R = CH₂CH₃



Va, R = R' = R'' = H

Vb, R = CH₃; R' = R'' = H

Vc, R = CH₂CH₃; R' = R'' = H

Vla, R = H; R' = OCH₃; R'' = H

Vlb, R = CH₃; R' = OCH₃; R'' = H

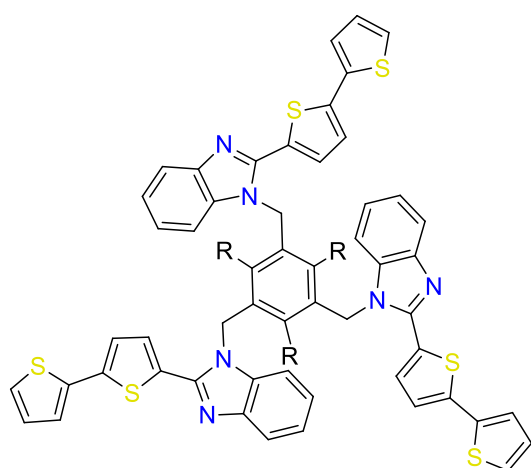
Vlc, R = CH₂CH₃; R' = OCH₃; R'' = H

Vlla, R = H; R' = R'' = OCH₃

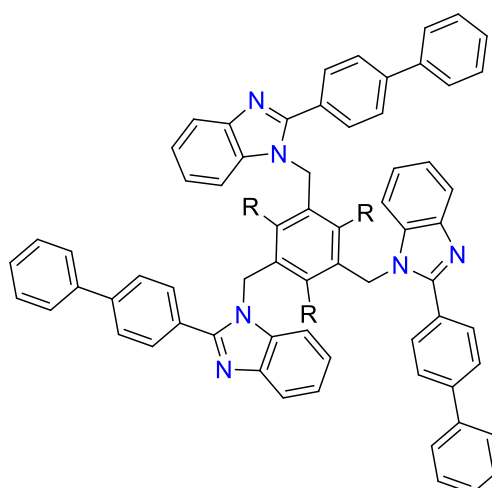
Vllb, R = CH₃; R' = R'' = OCH₃

Vllc, R = CH₂CH₃; R' = R'' = OCH₃

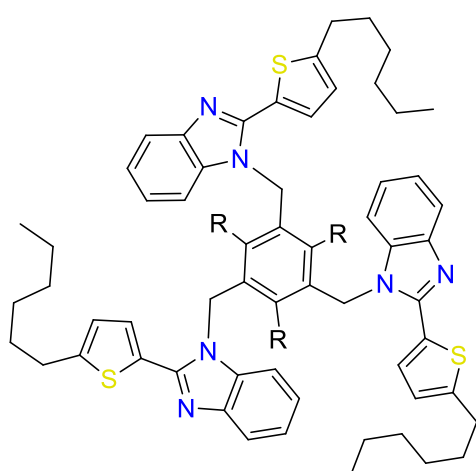
Figure 4. Tripodal molecules containing hetero(arene) substituted benzimidazolyl motifs.



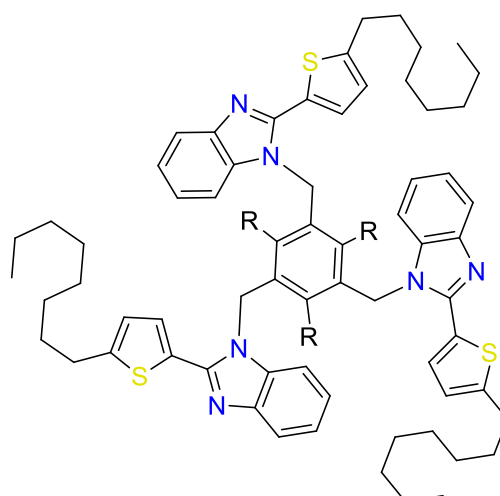
VIIIa, R = H
VIIIb, R = CH₃
VIIIc, R = CH₂CH₃



IXa, R = H
IXb, R = CH₃
IXc, R = CH₂CH₃



Xa, R = H
Xb, R = CH₃
Xc, R = CH₂CH₃



XIa, R = H
XIb, R = CH₃
XIc, R = CH₂CH₃

Figure 5. Tripodal molecules containing hetero(arene) substituted benzimidazolyl motifs

It is important to mention that known tripodal molecules without both the secondary groups likely to exist with any one of the conformations shown in Figure 6 in solution as well in solid state. The nature of solvent and intermolecular interactions also play a vital role in the stabilization of a particular structure.

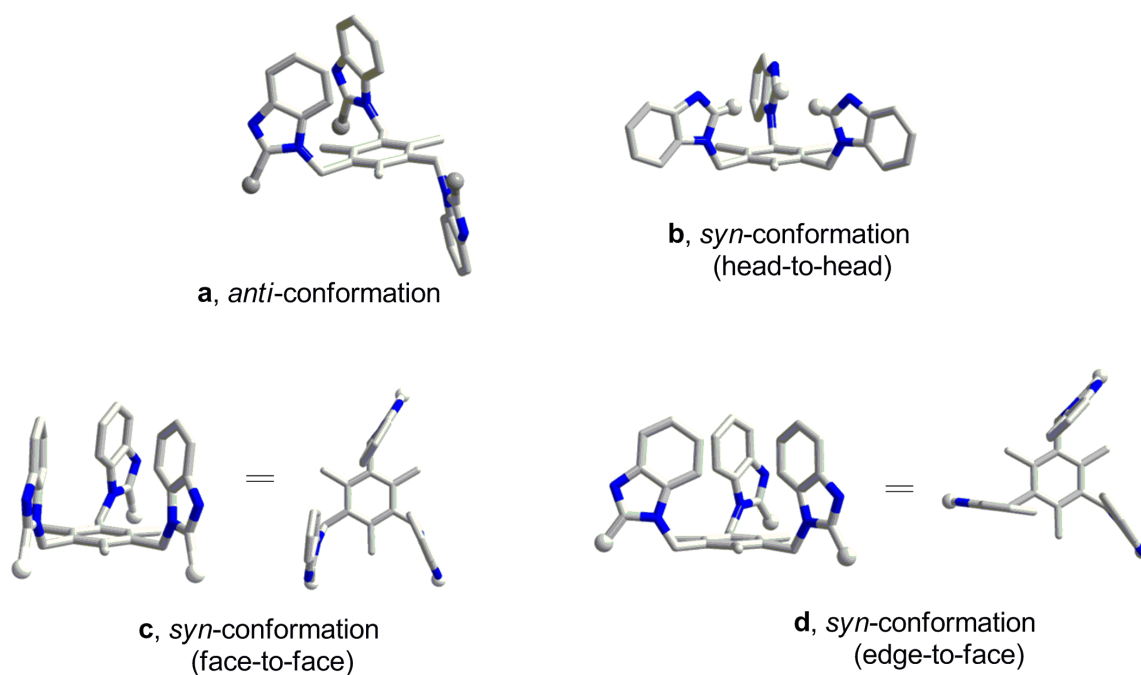


Figure 6. Tripodal molecules (I-XI) can exist in several conformer(s) (a-d) in solution.

The aromatic motifs so far used to prepare tripodal molecules containing non-covalent cyclic trimer motifs are thiophene-/phenyl-/pyridyl-/substituted phenyl-based benzimidazolyl motifs (Figures 5-7) [7-10]. For example, dimethoxyphenyl motif substituted benzimidazolyl with 2,4,6-trimethylbenzene spacer-based tripodal molecule adopts a conformation containing cyclic aromatic trimer motif (Figure 7).

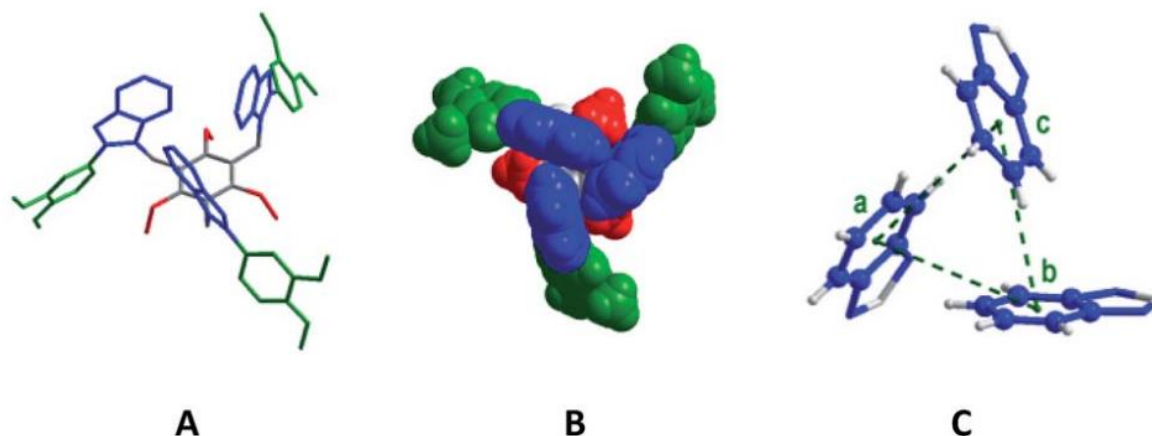


Figure 7. Solid state molecular structure of **VIIc** (A-B). Three benzimidazolyl units of **VIIc** showing aromatic cyclic trimer motif. (H atoms are removed).

To the best of our knowledge, only few reports on molecule having non-covalent cyclic aromatic trimer motif are available in the literature [7-35]. Hence, tuning the structure of the tripodal molecules with non-covalent cyclic aromatic trimer motif will open up new avenues in the modelling of new drug molecules.

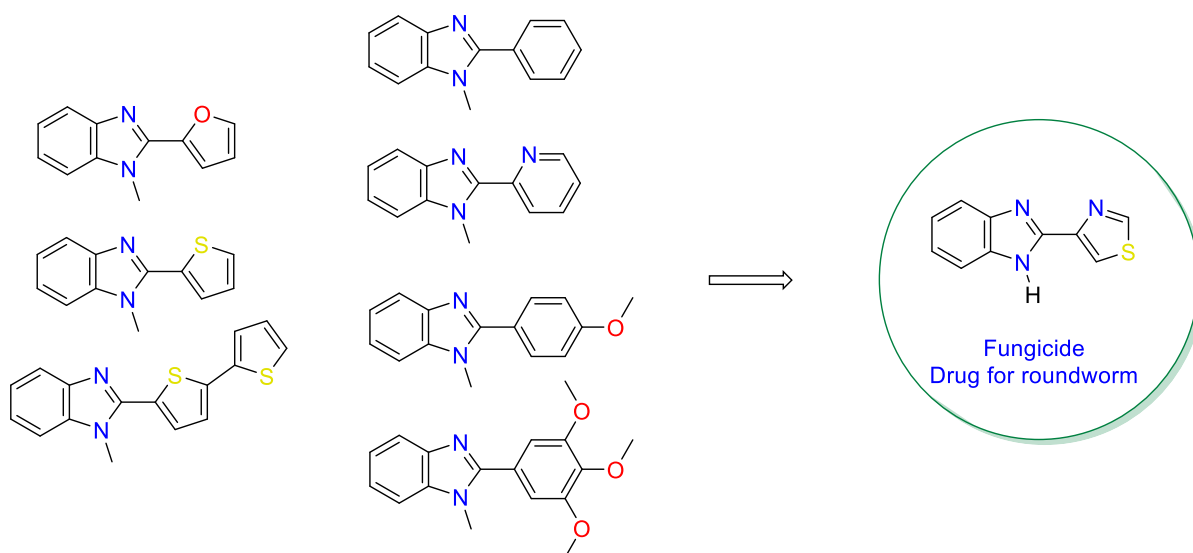


Figure 8. Towards to drug molecule

Herein, three tritopic organic molecules based on thiabendazolyl (L) terminal motif were synthesized using L-H and 1,3,5-tris(bromomethyl)benzene/ 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene/ 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene. These thiabendazole (tbz)-based molecules possess potential medicinal applications since thiabendazole itself is already approved as a drug for treatment of infections caused by round worms in humans and as a fungicide in the treatment of fruits [36].

5.2. Experimental

Materials and Methods

2-(4-Thiazolyl)benzimidazole (tbz), 1,3,5-tris(bromomethyl)benzene, 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene, KOH and dimethylformamide (DMF) were purchased and utilized as received. 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene was synthesized according to the previous reports [37]. ^1H NMR spectra were obtained from BrukerAvance III 400 and 500 MHz instruments. The mass spectra were recorded on a Bruker maXis mass spectrometer.

X-ray crystallography

Single crystal X-ray data of crystals of **2** and **3** were collected on a Rigaku oxford XtalLAB Synergy [$\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$]. The structures were solved by direct methods using SHELXS-2014/5 (Sheldrick 2014) and refined using the SHELXL-2018/3 (Sheldrick, 2018) program (within the WinGX program package) [39-42]. Non-H atoms were refined anisotropically.

1,3,5-Tris(2-(4-thiazolyl)benzimidazol-1-ylmethyl)benzene(1)

A mixture of 2-(4-thiazolyl)benzimidazole (169.17 mg, 0.84 mmol) and KOH (62.88 mg, 1.12 mmol) was stirred in DMF (10 mL) at room temperature for 3h. 1,3,5-Tris(bromomethyl)benzene (100 mg, 0.28 mmol) was added to the reaction mixture and continuously allowed to stir for 72 h. The reaction was quenched by adding ice cold water (200 mL). The powder was collected by filtration. Yield: 92% (220 mg, 0.30 mmol). ^1H NMR (500 MHz, DMSO- d_6): δ 8.84 (d, 3H, $J = 1.91 \text{ Hz}$, H5'), 8.19 (d, 3H, $J = 1.9 \text{ Hz}$, H3'), 7.64 (d, 3H, $J = 8.0 \text{ Hz}$, H4), 7.23-7.17 (m, 6H, H5,6), 7.12 (t, 3H, $J = 7.5 \text{ Hz}$, H7), 6.85 (s, 3H, phenyl), 5.72 (s, 6H, $-\text{CH}_2-$). HRMS (m/z): $[\text{M} + \text{H}]^+$ calc. for $\text{C}_{39}\text{H}_{28}\text{N}_9\text{S}_3$, 718.1630; found: 718.1635.

1,3,5-Tris(2-(4-thiazolyl)benzimidazol-1-ylmethyl)2,4,6-trimethylbenzene(2)

A mixture of 2-(4-thiazolyl)benzimidazole (302.66 mg, 1.50 mmol) and KOH (112.51 mg, 2.0 mmol) was stirred in DMF (10 mL) at room temperature for 3h. 1,3,5-Tris(bromomethyl)2,4,6-trimethylbenzene (200 mg, 0.50 mmol) was added to the reaction mixture and continuously allowed to stir for 72 h. The reaction was quenched by adding ice cold water (200 mL). The powder was collected by filtration. Yield: 80% (475 mg, 0.62 mmol). Yellow crystals of **2** were obtained from chloroform: acetone at room temperature after few days. ^1H NMR (400 MHz, DMSO- d_6): δ 9.25 (d, 3H, $J = 1.75$ Hz, H5'), 8.41 (d, 3H, $J = 1.75$ Hz, H3'), 7.60 (d, 3H, $J = 8.0$ Hz, H4), 7.16 (t, 3H, $J = 7.5$ Hz, H5), 6.61 (t, 3H, $J = 7.5$ Hz, H6), 6.31 (d, 3H, $J = 8.1$ Hz, H7), 6.12 (s, 6H, $-\text{CH}_2-$). HRMS (m/z): $[\text{M} + \text{H}]^+$ calc. for $\text{C}_{42}\text{H}_{34}\text{N}_9\text{S}_3$, 760.2099; found: 760.2098.

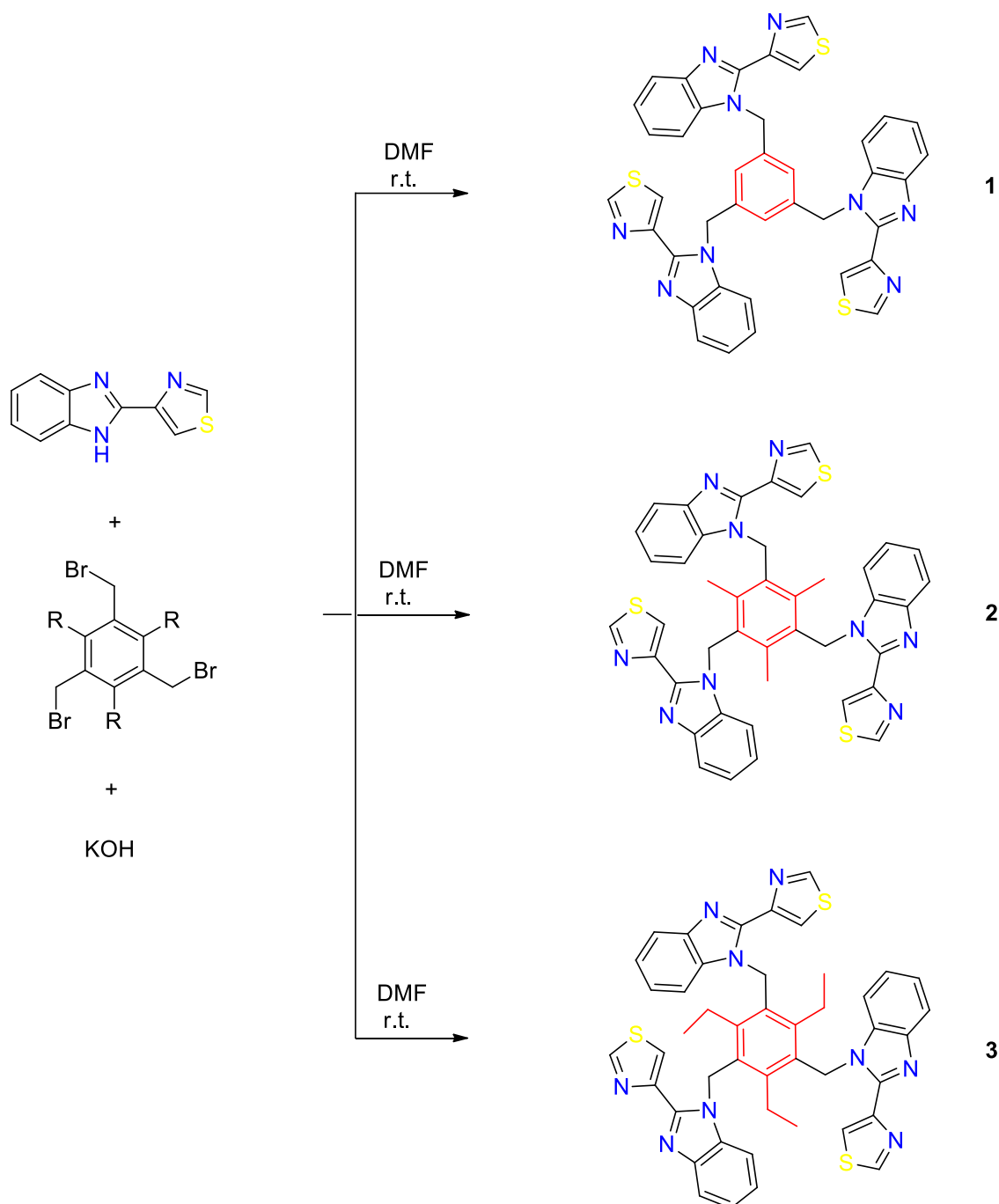
1,3,5-Tris(2-(4-thiazolyl)benzimidazol-1-ylmethyl)2,4,6-triethylbenzene(3)

A mixture of 2-(4-thiazolyl)benzimidazole (136.8 mg, 0.68 mmol) and KOH (50.8 mg, 0.90 mmol) was stirred in DMF (10 mL) at room temperature for 3h. 1,3,5-Tris(bromomethyl)2,4,6-triethylbenzene (100 mg, 0.22 mmol) was added to the reaction mixture and continuously allowed to stir for 72 h. The reaction was quenched by adding ice cold water (200 mL). The powder was collected by filtration. Yield: 93% (194.7 mg, 0.24 mmol). Colourless crystals of **3** were obtained from chloroform: acetone at room temperature after few days. ^1H NMR (500 MHz, DMSO- d_6): δ 9.31 (d, 3H, $J = 2.0$ Hz, H5'), 8.46 (d, 3H, $J = 2.0$ Hz, H3'), 7.62 (d, 3H, $J = 8.0$ Hz, H4), 7.17-7.09 (m, 6H, H5, H6), 6.35 (d, 3H, $J = 8.1$ Hz, H7), 6.09 (s, 6H, $-\text{CH}_2-$). HRMS (m/z): $[\text{M} + \text{H}]^+$ calc. for $\text{C}_{45}\text{H}_{40}\text{N}_9\text{S}_3$, 802.2569; found: 802.2570.

5.3. Results and discussion**Synthesis and characterization of tripodal molecules (1-3)**

The tripodal organic molecules (**1-3**) were synthesized by the reaction of 2-(4-thiazolyl)benzimidazole with 1,3,5-tris(bromomethyl)benzene/1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene/1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene in DMF in the presence of KOH (Scheme 1). The compounds are air stable and are also soluble in CHCl_3 and DMSO.

Further, these compounds were characterized using ESI-MS, ^1H NMR spectroscopic techniques. The molecular structures of **2** and **3** were confirmed by SC-XRD analysis.



Scheme 1. Synthesis of tripodal organic molecules.

The proton NMR spectrum of molecule **1** in $\text{dms-}d_6$ showed distinct signals corresponds to all the protons. In addition to the peaks for protons of tbz, a single sharp peak at 5.72 ppm for methylene ($-\text{CH}_2-$) protons was observed. The disappearance of $-\text{NH}$ proton and appearance of methylene protons suggest the formation of compound **1**. It was further supported by the proton ratio of 6:3:18 (methylene:central phenylene:tbz) in **1** (Figure 9).

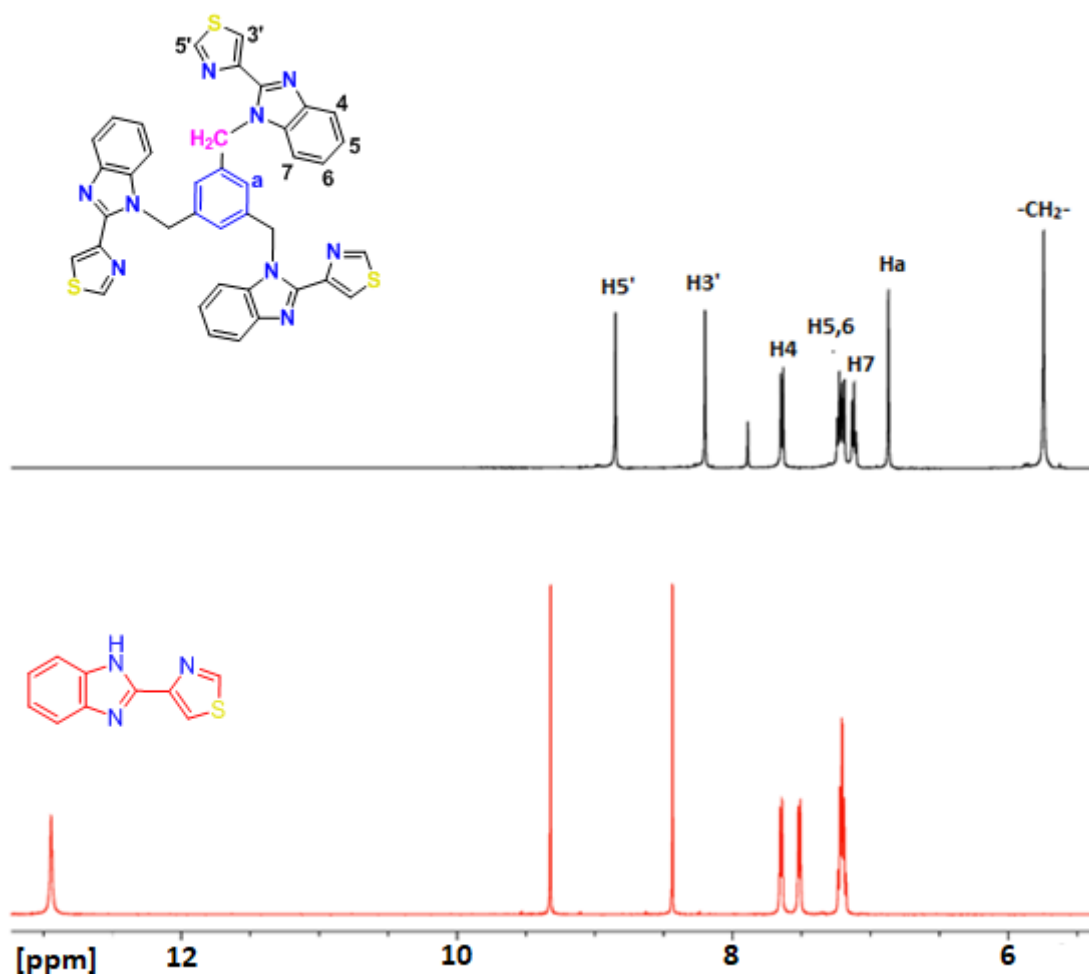


Figure 9. Partial ^1H NMR spectra of **1** and H-tbz in $\text{dms-}d_6$

Significantly, all the protons in **1** were upfield shifted relative to those of free starting materials. The data indicates that the three tbz motifs in **1** experience a similar chemical environment in the DMSO solution. This upfield shift is possible if the molecule **1** adopts either the cylindrical

conformation or undergoes fast flipping (back and forth) with respect to central benzene spacer in the NMR time scale.

Molecule **2** in $\text{dms-}d_6$ displayed well-separated ^1H NMR signals for the protons of thiazolylbenzimidazolyl (tbz) unit relative to those of free H-tbz molecule. The 6:18 proton ratio for methylene and tbz suggests the formation of tripodal molecule **2**. Further, only one type of chemical signal is observed for the three tbz motifs in **2**, revealing the presence of a single isomer (conformer) or the presence of various conformers that undergo a rapid equilibrium in solution on the NMR time scale (Figure 10).

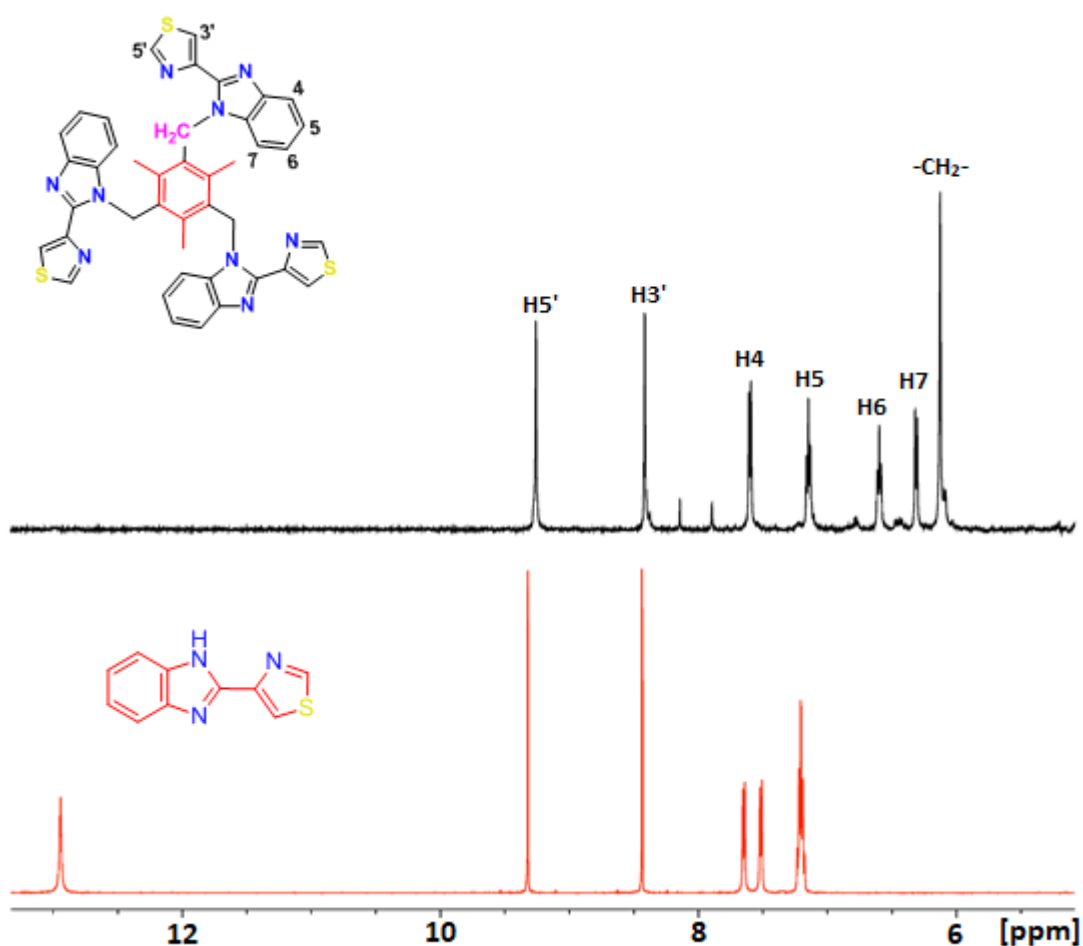


Figure 10. Partial ^1H NMR spectra of **2** and H-tbz in $\text{dms-}d_6$

Among the proton signals, the H6 and H7 signals in **2** are noticeably upfield shifted compared to those of H-tbz. A single set of chemical resonances for all three tbz with upfield shift for H6-7 in **2** suggests that the three benzimidazolyl motifs are arranged in a cyclic manner in which the H6 and H7 are directed toward the face of neighbouring benzimidazolyl. This suggests that tripodal molecule **2** in solution adopts syn-conformation with *edge-to-face* arrangement of three benzimidazolyl motifs from three tbz. A similar ^1H NMR pattern was earlier observed for molecules **Ib**, **Iib**, **IIIb**, **IVb**, **Vb**, **VIb**, **VIIb**, **VIIIb**, **IXb**, **Xb**, and **XIb** in the solution.

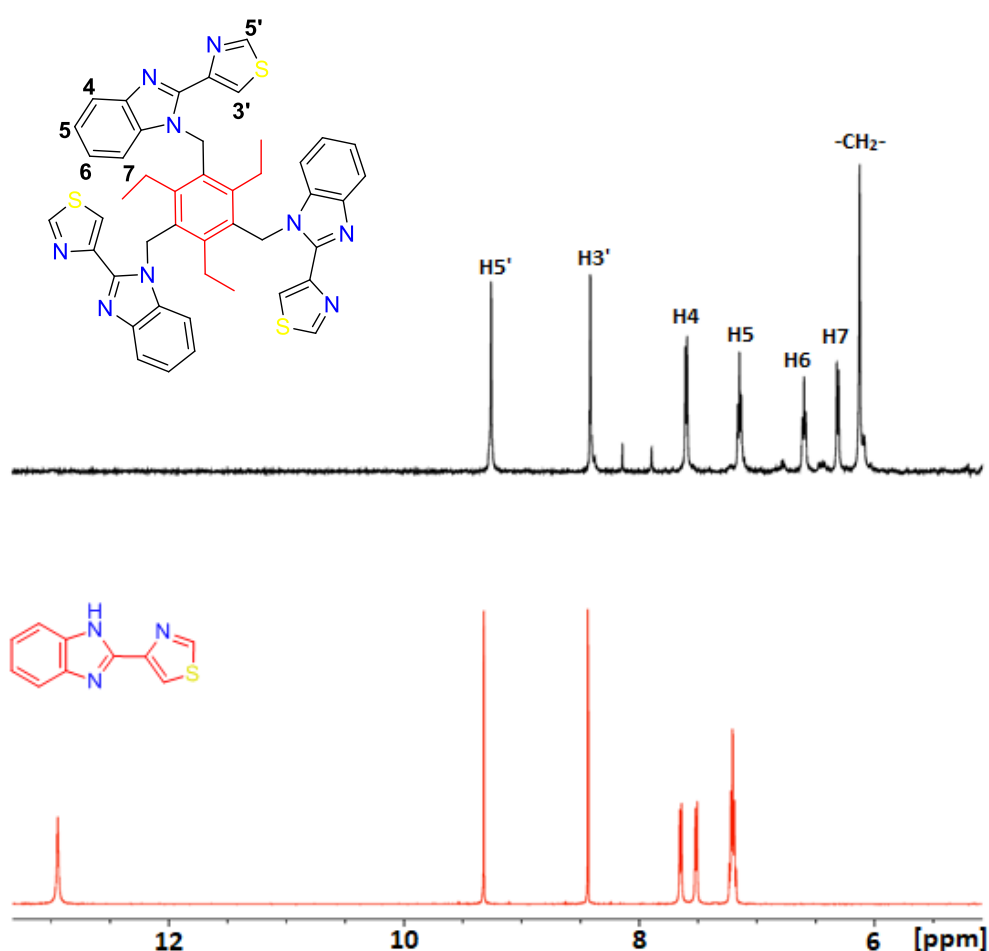


Figure 11. Partial ^1H NMR spectra of **3** and H-tbz in $\text{dmsO}-d_6$

The ^1H NMR spectrum of molecule **3** also displays a similar kind of observations as that of molecule **2** (Figure 11). Similar to tripodal molecule **2**, the H6 and H7 proton signals of the benzimidazolyl motif were upfield shifted and merged. Further, the upfield shift for these

protons in **3** is high in comparison to molecule **2**. The pattern of the remaining protons of **3** is similar to those of molecule **2**. The data reveals that molecule **3** is also adopt *syn*-conformation with *edge-to-face* arrangement of benzimidazolyl motifs. The non-covalent interactions among the aromatic units in the cyclic aromatic trimer motif are greater in **3** than in molecule **2**. The ^1H NMR data of **2** and **3** in solution reveals that both adopt *syn*-conformation with *edge-to-face* arrangement as shown in Figure 12.

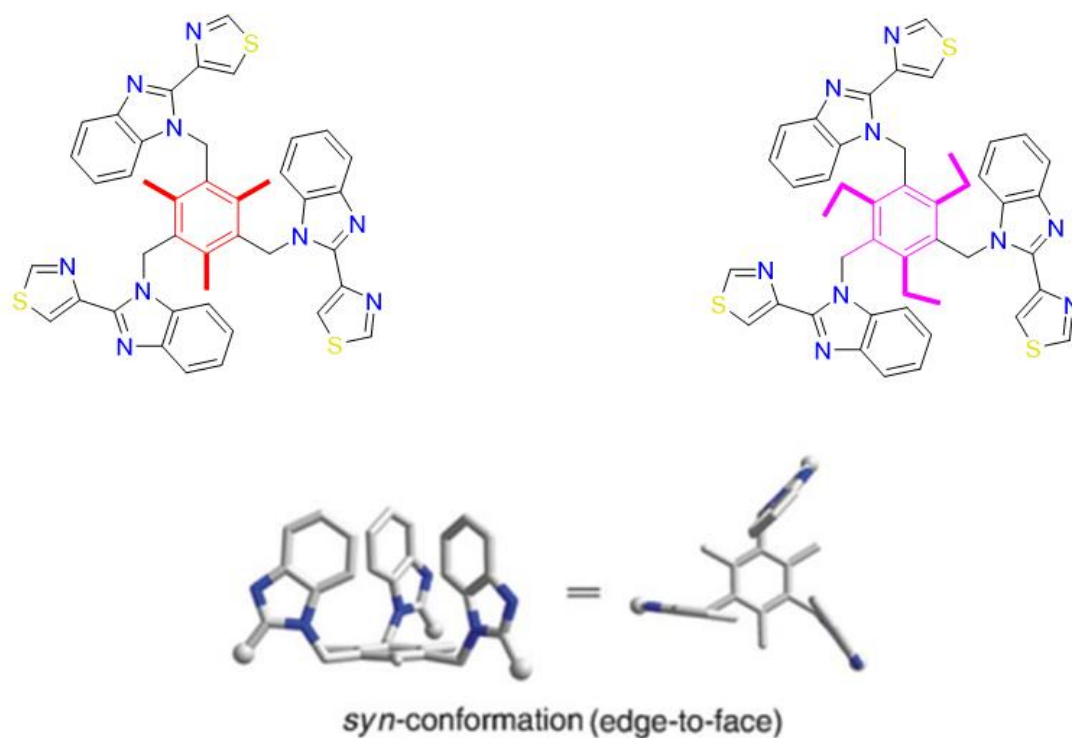


Figure 12. Comparison of molecular structures of **2** and **3** in the solution state

Further, the formation of the tripodal molecules **1-3** was confirmed using ESI-Mass analysis which displays molecular ion peaks, $[\mathbf{1} + \text{H}]^+ = 718.1630$ for **1**; $[\mathbf{2} + \text{H}]^+ = 760.2096$ for **2** and $[\mathbf{3} + \text{H}]^+ = 802.2566$ for **3** (Figure 13-15).

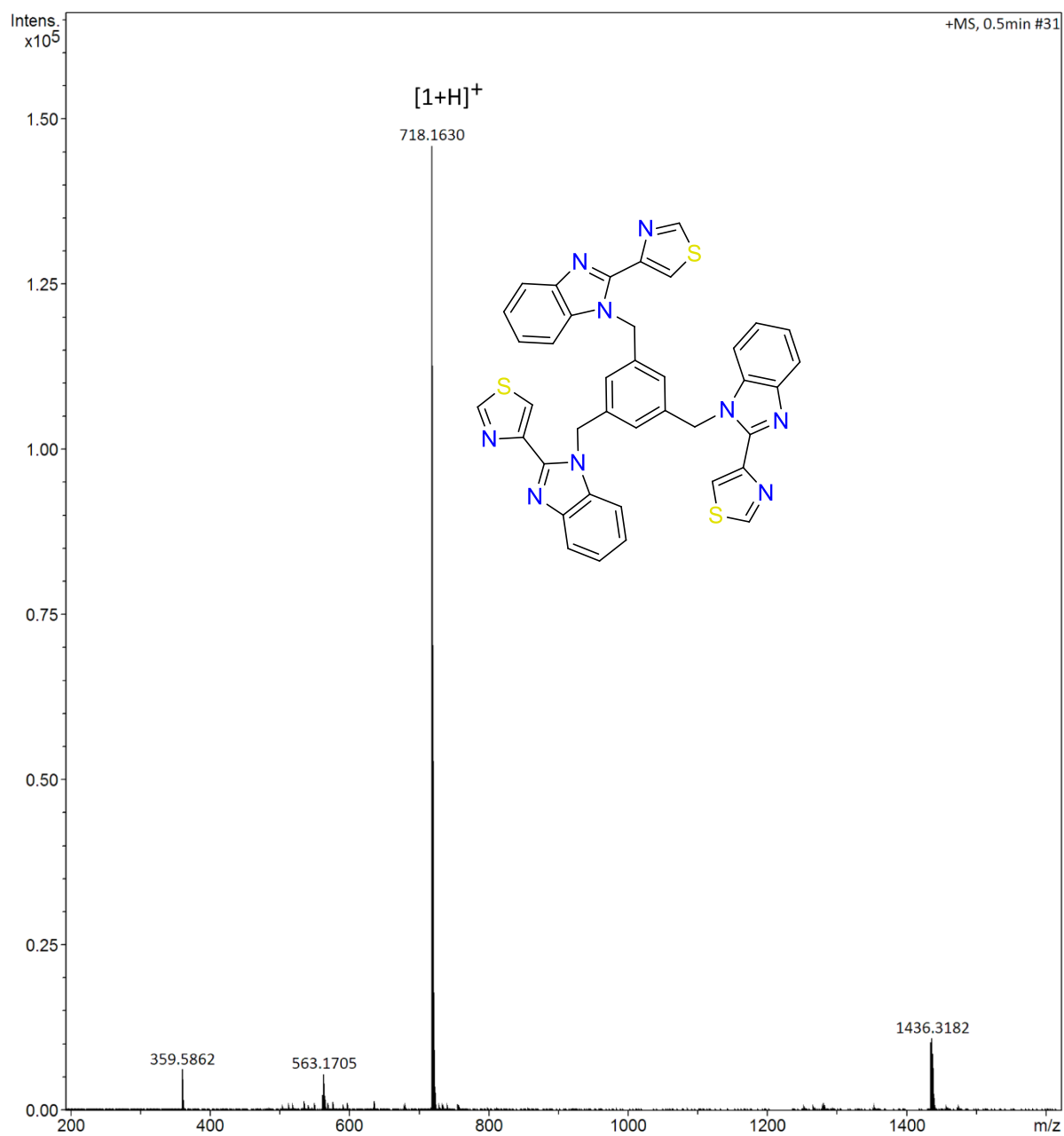


Figure 13. ESI mass spectrum of **1** in positive ion mode

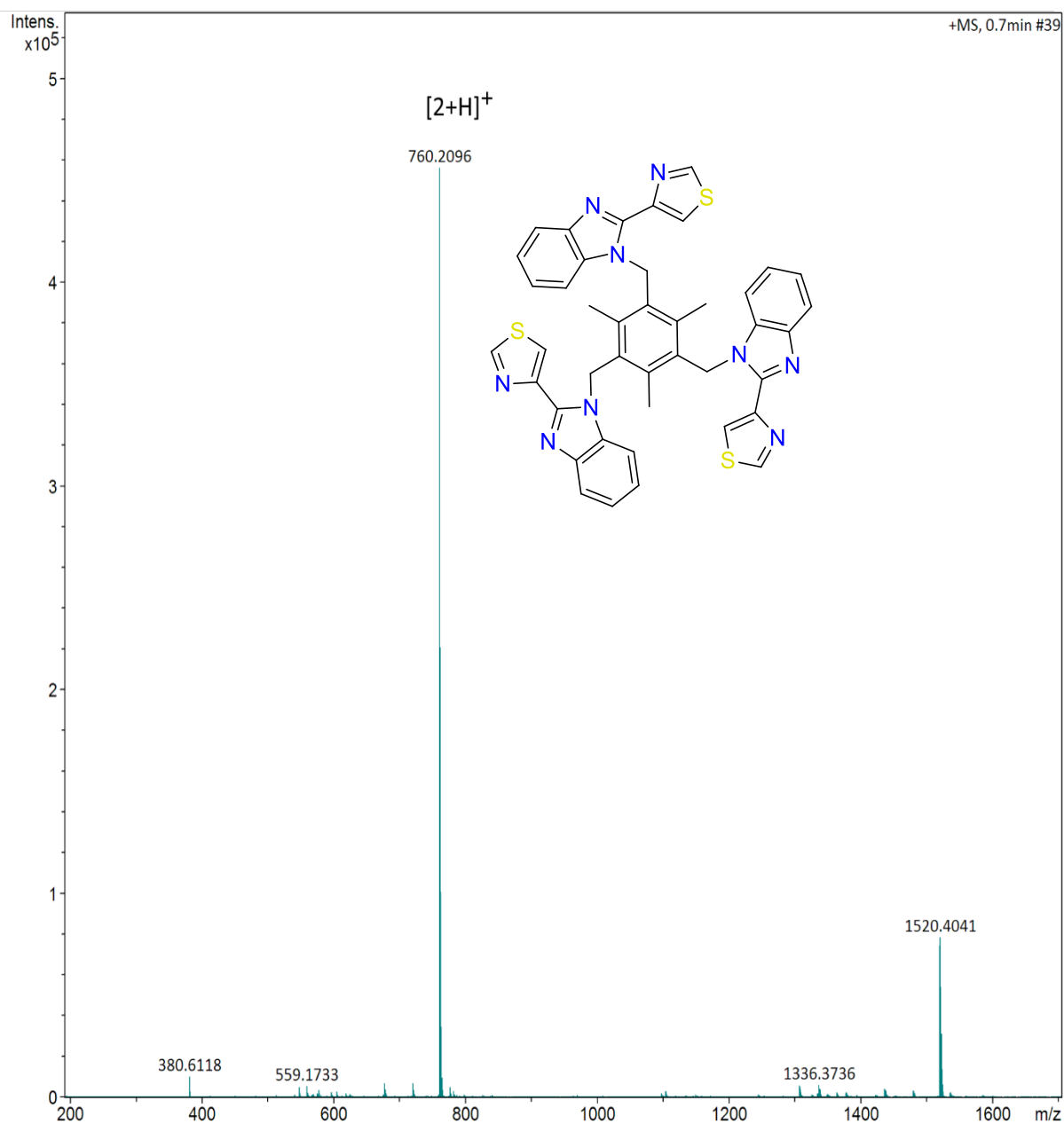


Figure 14. ESI mass spectrum of **2** in positive ion mode.

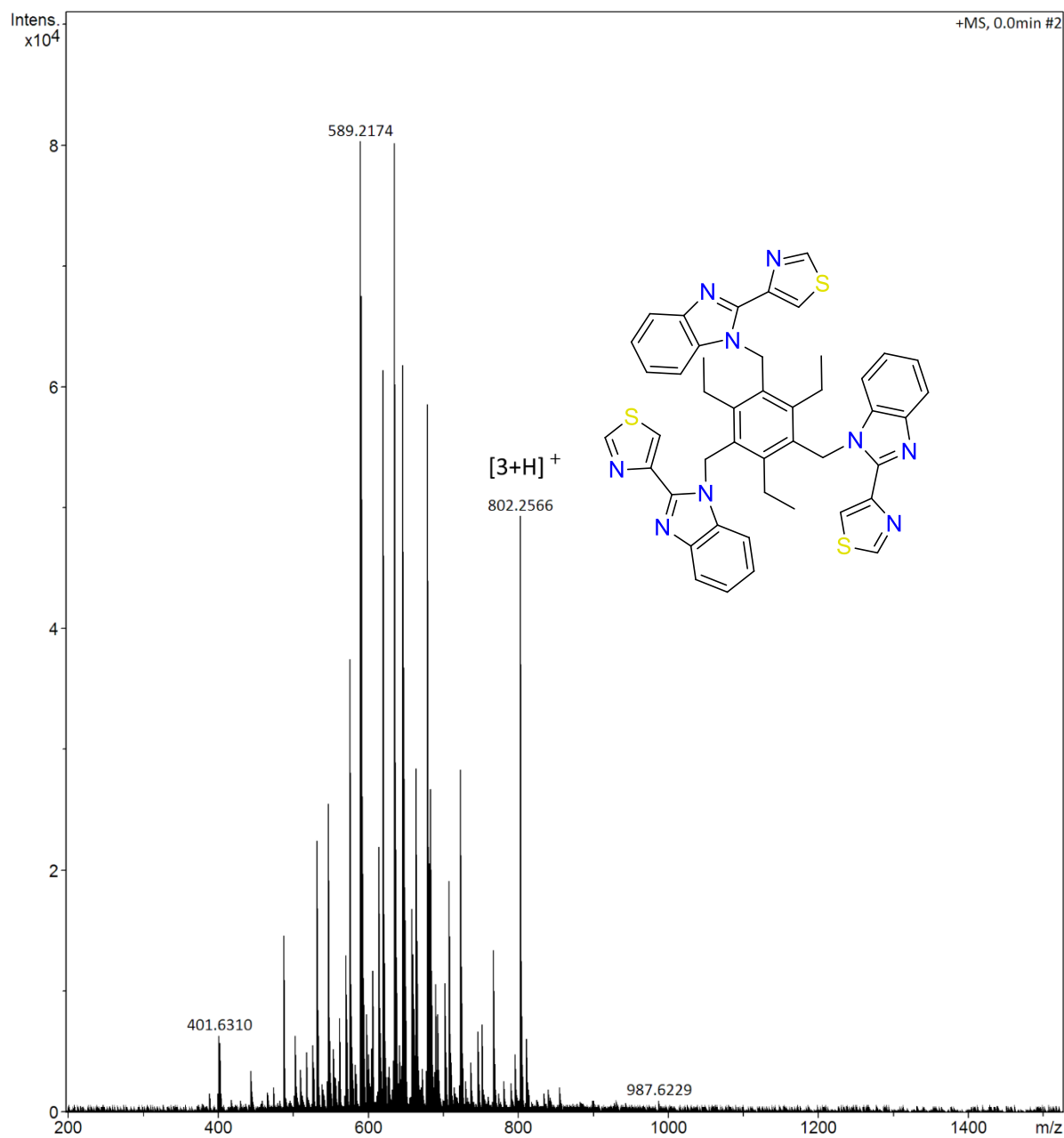


Figure 15. ESI mass spectrum of **3** in positive ion mode.

Molecular structures of tripodal molecules 2 and 3

The molecular structures of **2** and **3** were analysed by SCXRD analysis. However, structure of **1** could not be established due to failure attempt of growing single crystal. The crystal data of **2** shows that it acquires a *syn*-conformation in which all three thiabenzodazolyl motifs are on the same side and are near parallel to each other. In particular, the three thiabenzodazolyl motifs are arranged like Y-shaped fashion. Interestingly, no significant non-covalent interactions was found between any two of the benzimidazolyl motifs.

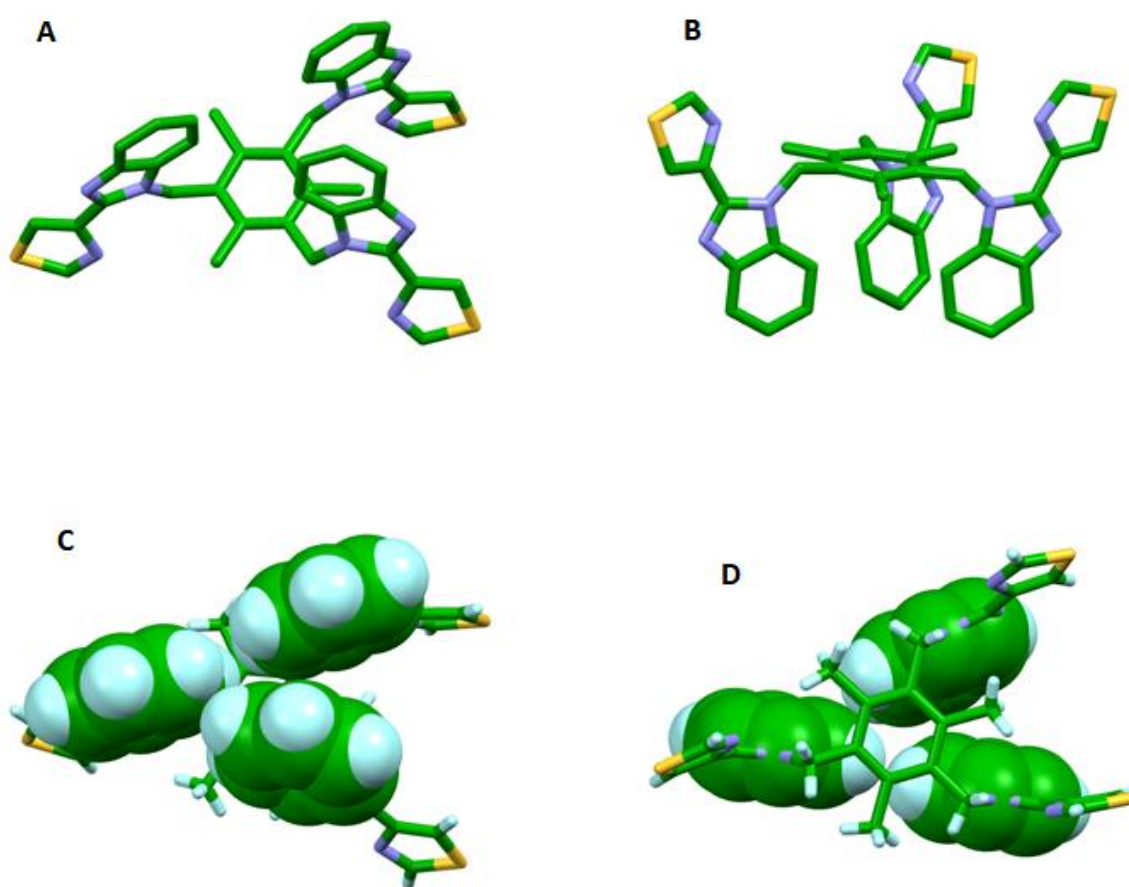


Figure 16. Various views of molecular structure of **2**. Hydrogen atoms are omitted in A and B. Three fused benzene of the benzimidazolyl motifs are shown in space-filling model to reflect the orientation and interactions of these three motifs (C and D).

In the crystal packing of **2**, neighbouring molecules forms a dimer which interact with each other through a weak C–H...N and H...H contacts. Very interestingly, these non-covalent contacts between these pair of molecules results in the double stranded helix (Figure 17). Each dimer further interacts with neighbouring dimers *via* cumulative weak C–H...N and C–H...O interactions. In contrast, to the best of our knowledge, double helices are stabilized by strong hydrogen bonding contacts or strong ion-ion interactions or extended $\pi\cdots\pi$ contacts only [38].

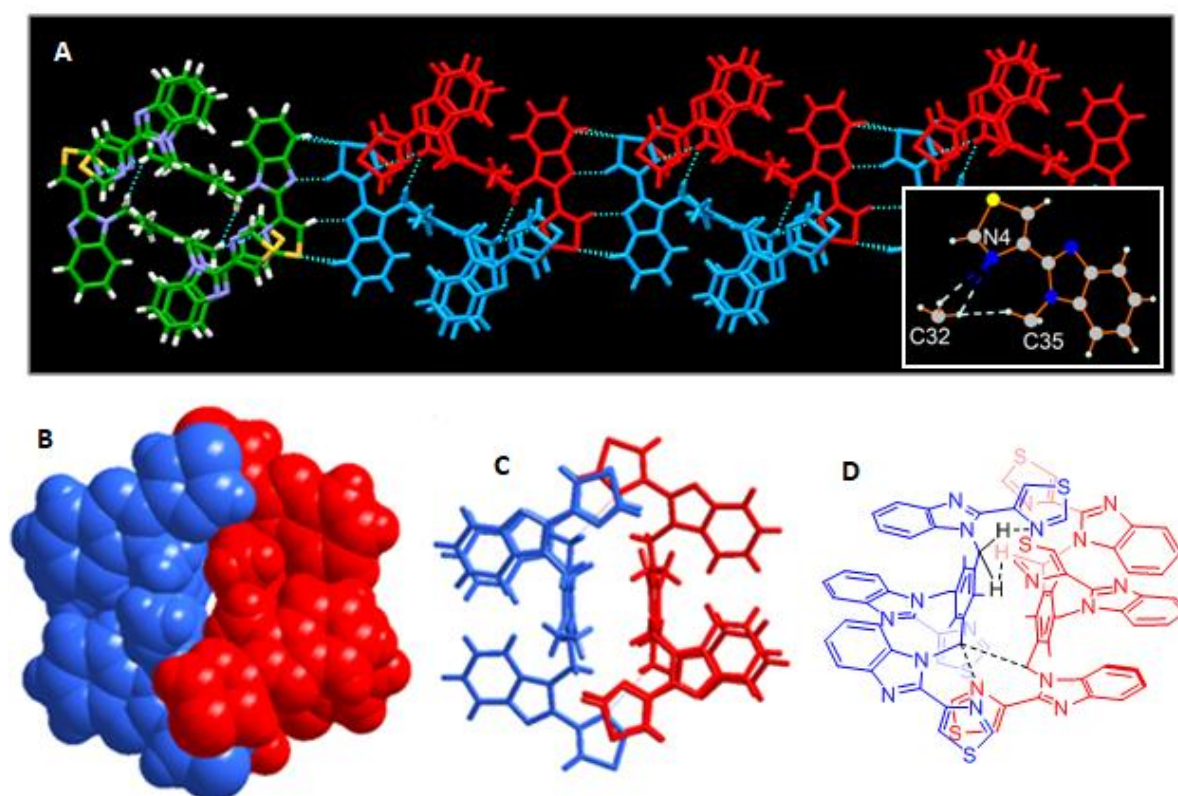


Figure 17. (A) Partial packing diagram of **2**. (B) Double helix of **2**. (C) Chemdraw of double helix **2** (left) and intermolecular contacts between two strands in **2** (right).

In molecule **3**, the three thiabenzodiazolyl motifs are arranged in cyclic aromatic trimer with the edge of benzimidazolyl directed over the face of the neighbouring benzimidazolyl plane. The dihedral angle between these three units are $\sim 62^\circ$, $\sim 59^\circ$ and $\sim 58^\circ$. The three distance of the center of mass (COM) of fused arene motifs of the benzimidazolyl are ~ 5.154 , ~ 5.106 and ~ 5.297 Å. The data indicate that strong *edge-to-face* aromatic interactions exist between these three benzene units of the benzimidazolyl motifs.

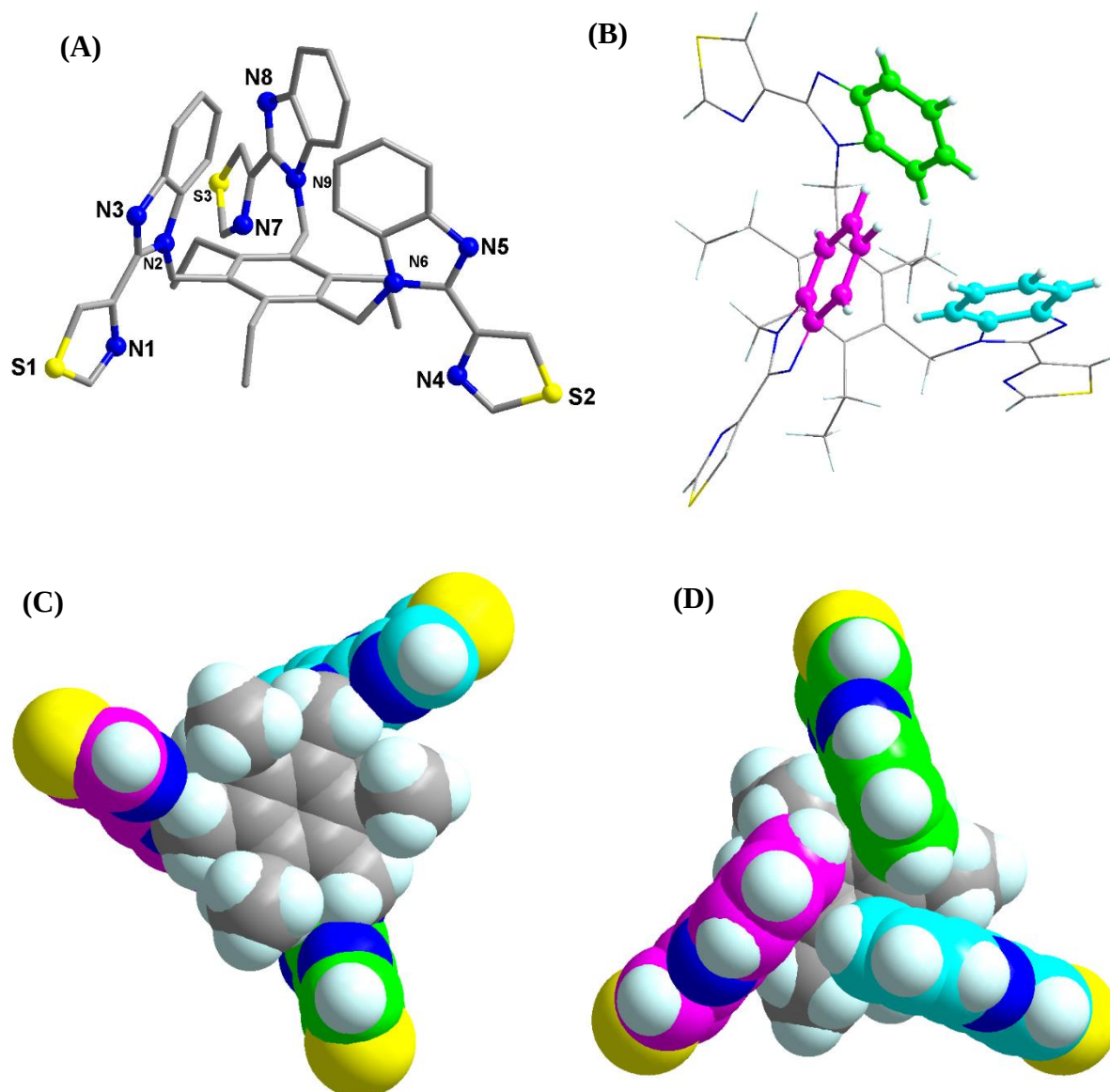


Figure 18. Molecular structure of **3**. (A) Stick model without hydrogen atoms; (B) Three benzene motifs of three thiabenzodazolyl units of **3** shown in different colours showing the cyclic aromatic trimer motif; (C) and (D) Space filling views showing cyclic aromatic trimer motif.

Comparison of the molecular structures of **2** and **3** in solid state reveals that **2** acquire a *syn*-conformation with *face-to-face* arrangement in solid state, whereas **3** takes *syn*-conformation with *edge-to-face* arrangement as shown in Figure 19.

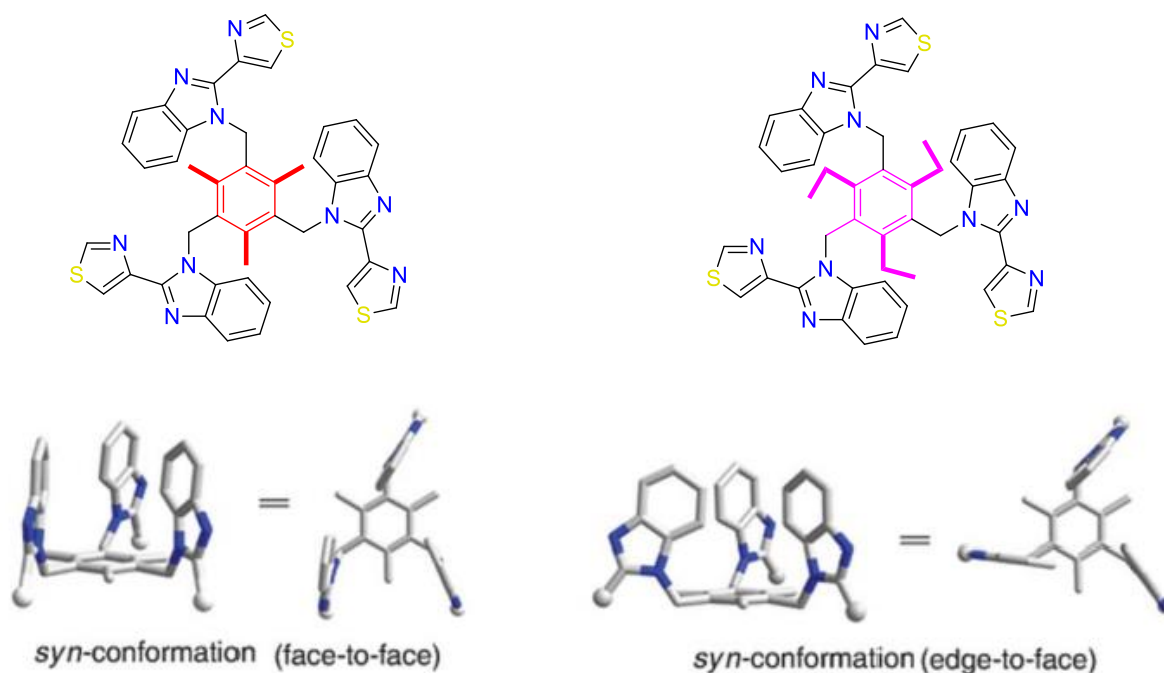


Figure 19. Comparison of molecular structures of **2** and **3** in the solid state

5.4. Conclusions

In conclusion, three tripodal molecules (**1-3**) containing three drug motifs were designed and synthesized. Each tripodal molecule contains three thiabenzodiazolyl drug motifs that are arranged symmetrically. In the solution, these three motifs are arranged in a cylindrical fashion in **1**, and cyclic triangular manner i.e., cyclic aromatic trimer fashion, in **2** and **3**. However, molecules **2** and **3** have different orientation in the solid-state. Molecule **2** takes *syn*-conformation with *face-to-face* arrangement, whereas **3** holds *syn*-conformation with *edge-to-face* in solid state. A key feature of the results of this chapter is that three drug motifs in one molecule with proper orientation can be prepared, which is important in designing new type of bioactive molecules due to the combination of drug with non-covalent cyclic aromatic trimer motif.

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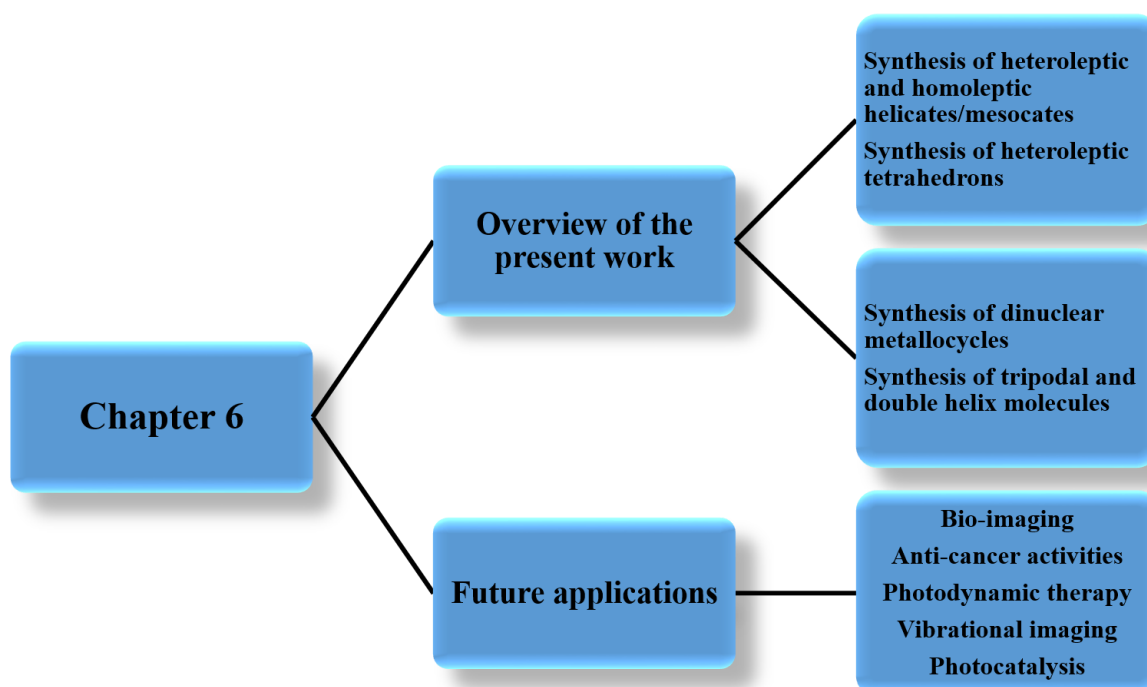
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Chapter 6

Conclusion and future prospects

Abstract

The thesis entitled “Rheniumtricarbonyl-based Helicates and Double Helical Molecules” discusses the synthetic principles for the construction of rhenium(I)tricarbonyl based supramolecular coordination complexes (SCCs) and organic double helical molecules. In this chapter, the importance of the new synthetic approaches developed in this thesis are outlined and the possible future applications of rheniumtricarbonyl core based supramolecular coordination complexes are briefly discussed.



6.1. Overview of the present work

The facial rheniumtricarbonyl core containing supramolecular coordination complexes (SCCs) offer various interesting properties such as thermal and photo-stability, luminescence, kinetic inertness, large Stoke's shifts and membrane permeability [1, 2]. Apart from the metal core, the ligand framework plays a crucial role in improving the properties of these discrete cyclic systems. These SCCs hold utility in various fields of material chemistry and biology including bio-imaging, anti-cancer activity, host-guest chemistry and as molecular devices [3]. The considerable amount of research has been focussed on acyclic systems with *fac*-Re(CO)₃ core whereas only handful of examples are available for Re(I) based cyclic systems that are utilized for biological studies [4]. The synthesis of architecturally elegant supramolecular coordination complexes with varying shapes and dimensions has become an interesting research area owing to their applications in the fields of chemistry and biology.

We have developed a new design principle for the synthesis of inorganic ion, such as SO₄²⁻ containing SCCs and the first *fac*-Re(CO)₃ core based helicates consisting of a sulfate framework unit. The helicates were constructed by the spontaneous transformation of sulfite to sulfate using ditopic nitrogen donor ligand and Re₂(CO)₁₀ *via* one-step synthesis. Further, these sulfate coordinated heteroleptic triple-stranded helicates were successfully transformed to sulfate free homoleptic double-stranded mesocates by the abstraction of sulfate from the coordination sphere using BaCl₂. To the best of our knowledge, the spontaneous transformation of sulfite to sulfate in the presence of metal source and organic ligand is the first design principle for making Re(I) based SCCs.

We also ventured into the development of another new synthetic strategy for assembling heteroleptic tetrahedron shaped SCCs using new bonding combination of a bis-chelating rigid ligand and a ditopic nitrogen donor flexible ligand with Re₂(CO)₁₀ *via* one-pot synthetic approach. The tetrahedron shaped metallacycles are neutral and heteroleptic with scalene triangular faces. According to our knowledge, our research provides a new design principle and the first example of facial rheniumtricarbonyl core based heteroleptic tetrahedron shaped metallacycles.

The organic ligand framework plays a crucial role in altering the properties of the complexes. Further, the focus of the work was to synthesize non-covalent cyclic aromatic trimer molecules using thiabendazolyl motif and benzene spacer with or without alkyl substitution. Due to pharmacological properties of thiabendazole and its use as a drug molecule, it was chosen as

the coordinating ligand motif. The aromatic-aromatic interaction between the biomolecules are known to be significant for the stabilization of protein structure and protein folding. These type of interactions results in the formation of dimers, trimers and higher order clusters which are stabilized by *edge-to-face* or *face-to-face* non-covalent interactions. Among these, aromatic cyclic trimer containing molecules are studied and are considered to be the basic unit for higher order clusters. The design and synthesis of cyclic aromatic trimer containing molecules are very difficult because of the cyclic arrangement of the three aromatic units with proper distances and angles between them. We have successfully synthesized non-covalent cyclic aromatic trimer containing tripodal molecules using thiabendazolyl motifs.

The research work also provided a new synthetic strategy for making double helix molecules from organic molecules i.e., without a metal coordination. The organic tripodal molecule dimer with methyl substituted benzene spacer adopts a double helix structure in the solid state. Literature surveys reveals that artificial double helix molecules were synthesized by implementing strong hydrogen bonding interactions, salt-bridge formations and π - π stacking interactions. We have successfully developed a new way of synthesizing double helix molecules which are stabilized by weak hydrogen bonding and London dispersion interactions.

6.2. Future directions

Rhenium(I)tricarbonyl core containing complexes have been recognized as promising candidates for therapeutic and diagnostic applications. The low spin d^6 electronic configuration of Re(I) makes these complexes kinetically inert which enhances their utility in biology. Apart from the kinetic inertness, these complexes also possess large Stoke's shifts and higher photostability which makes them ideal for applications in bio-imaging. In addition, $\text{Re}(\text{CO})_3$ core containing complexes exhibit strong CO stretching vibrations in the region $1800\text{--}2100\text{ cm}^{-1}$. As this region is transparent in the biological systems, these complexes can also be used for vibrational imaging applications [5]. Many of these complexes shows anti-cancer activities and finds applications in photodynamic therapy and membrane transport. The key advantage of these systems is that the properties of these complexes can be easily tuned by modifying the coordinated ligand motifs.

The development of new synthetic methodologies for the construction of *fac*- $\text{Re}(\text{CO})_3$ core based SCCs encourages the researchers to develop and synthesize architecturally beautiful supramolecular metallacycles with various sizes and shapes which possess potential utility in

the fields of chemistry and biology. The current research in this area focuses on the enhancement of functional properties of these complexes for desired applications [6].

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List of Publications

1. Soumya, K. R.; Arumugam, R.; Shankar, B.; Sathiyendiran, M. Sulfate Donor Based Dinuclear Heteroleptic Triple-Stranded Helicates from Sulfite and Ditopic Nitrogen Donor Ligands and Their Transformation to Dinuclear Homoleptic Double-Stranded Mesocates. *Inorg. Chem.* **2018**, *57*, 10718-10725.
2. Arumugam, R.; Shankar, B.; Soumya, K. R.; Sathiyendiran, M. *fac*-Re(CO)₃-based neutral heteroleptic tetrahedrons. *Dalton Trans.*, **2019**, *48*, 7425-7431.
3. Soumya, K. R.; Sathiyendiran, M. Synthesis of tripodal molecules based on 2-(4-Thiazolyl)benzimidazole. (Manuscript under preparation).
4. Soumya, K. R.; Mishra, I.; Kedia, M.; Phukon, U.; Borkar, R.; Sathiyendiran, M. Rhenium (I)-based supramolecular coordination complexes: Synthesis and functional properties. In *Supramolecular Coordination Complexes Design, Synthesis and Applications*; Shanmugaraju. S., Eds., Elsevier, **2022**.

Poster Presentations

1. Presented a poster in **Chem-Fest-2017**, held at School of Chemistry, University of Hyderabad, India.
Poster Title: Re(I)- based supramolecular coordination complexes.
2. Presented a poster in **NMSTC (National Meeting of Synthetic and Theoretical Chemists)-2017** at School of Chemistry, University of Hyderabad, India.
Poster Title: Re(I)-based supramolecular coordination complexes from in situ hydrogen sulfite oxidation reaction.
3. Presented a poster in **Chem-Fest-2018**, held at School of Chemistry, University of Hyderabad, India.
Poster Title: Triple heterostranded helicates to double homostranded mesocates.
4. Presented a poster in **1st International Symposium on Main-group Molecules to Materials (MMM)-2018** at Department of Inorganic and Physical chemistry, IISc Bangalore, India.
Poster Title: Rhenium-core based helicates/mesocates.
5. Presented a poster in **International Conference on Advances in Chemical Sciences and Technologies (ACST)-2019** at Department of Chemistry, National Institute of Technology, Warangal, India.
Poster Title: Rhenium-core based helicates/mesocates. (**Best Poster Award**).
6. Presented a poster in **Chem-Fest-2020**, held at School of Chemistry, University of Hyderabad, India.
Poster Title: *fac*-Re(CO)₃-based Supramolecular Coordination Complexes.

Rheniumtricarbonyl-based Helicates and Double Helical Molecules

by Soumya K R

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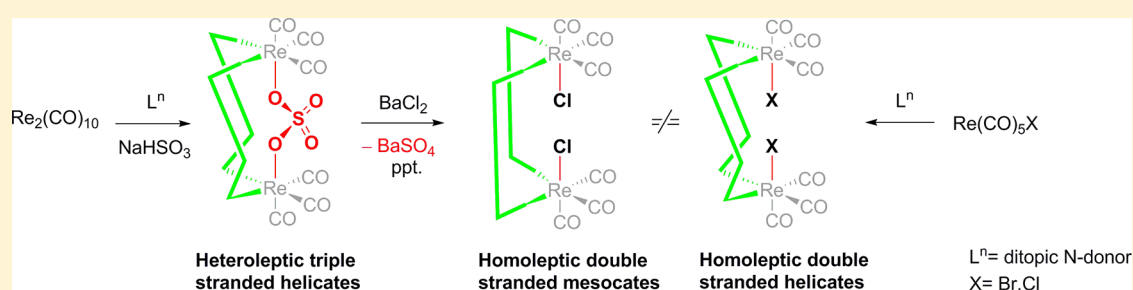
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Sulfate Donor Based Dinuclear Heteroleptic Triple-Stranded Helicates from Sulfite and Ditopic Nitrogen Donor Ligands and Their Transformation to Dinuclear Homoleptic Double-Stranded Mesocates

K. R. Soumya, Ramar Arumugam, Bhaskaran Shankar, and Malaichamy Sathiyendiran*

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Supporting Information



ABSTRACT: Sulfate donor based supramolecular coordination complexes $[\{\text{fac-Re}(\text{CO})_3\}(\mu\text{-SO}_4)(\text{L}^n)_2\{\text{fac-Re}(\text{CO})_3\}]$ (**1–3**) were obtained using ditopic N donors (L^n ; $n = 1–3$), NaHSO_3 , and $\text{Re}_2(\text{CO})_{10}$ in a one-pot, multicomponent, coordination-driven self-assembly approach, in which SO_3^{2-} becomes oxidized to SO_4^{2-} during the reaction and acts as a building framework. Complexes **1–3** were characterized using IR, ESI-TOF-MS, and ^1H NMR spectroscopy. The structures of complexes **1–3** were confirmed using single-crystal X-ray diffraction analysis. The transformation of the dinuclear heteroleptic triple-stranded helicate to the dinuclear homoleptic double-stranded mesocate $[\{\text{Re}(\text{CO})_3\text{Cl}\}_2(\text{L}^n)_2]$ ($\text{L}^n = \text{L}^1, \text{L}^2, \text{L}^3$; **4a–6a**) was achieved by the addition of BaCl_2 . The direct treatment of $\text{Re}(\text{CO})_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) with $\text{L}^1/\text{L}^2/\text{L}^3$ yielded the dinuclear homoleptic double-stranded helicates $[\{\text{Re}(\text{CO})_3\text{X}\}_2(\text{L}^n)_2]$ (**4b–6b** and **7–9**).

INTRODUCTION

Several metal-directed synthetic principles are currently available for making well-defined shapes and sizes of supramolecular coordination complexes (SCCs), including helicates and mesocates, which have potential applications in materials and medicinal fields.^{1–16} Among the various synthetic approaches, the $\text{fac-Re}(\text{CO})_3$ core directed one-pot strategy, i.e., a combination of $\text{Re}(\text{CO})_5\text{X}$ ($\text{X} = \text{halide}$)/ $\text{Re}_2(\text{CO})_{10}$ and organic building units, is a fruitful way to synthesize $\text{fac-Re}(\text{CO})_3$ core based SCCs, which have been gaining great interest in molecular recognition, organic transformation, photocatalysts for CO_2 reduction, bioimaging, and anticancer agents.^{3–12} Due to their importance, new design principles have been emerging in order to improve the physiochemical properties of SCCs as well as hitherto unexplored molecules. Up to now, the research in this area has mainly been focused on modulating the organic ligands by tuning the denticity and/or spacer to introduce flexibility and decorating framework with functional units.⁴ To the best of our knowledge, the hydroxyl ($-\text{OH}$) group and azide anion have been the only ions used as one of the framework units in the $\text{Re}(\text{I})$ -based SCCs. As a continuation of the research on progress of $\text{Re}(\text{I})$ -based SCCs,^{10,11} herein, we report the first example of sulfate (SO_4^{2-}) as one of the framework units in

neutral heteroleptic $\text{fac-Re}(\text{CO})_3$ core based helicate type SCCs. Though the design principles for making various types of helicates are well documented, similar to cavity-containing SCCs,^{11a} examples of rhenium-based helicates are very rare.^{2h–j} Though the sulfate ion has been gaining research interest in making coordination polymers with auxiliary organic ligands, its use in the SCCs is scarce.^{1u,v} The self-assembly of $[\{\text{fac-Re}(\text{CO})_3\}(\mu\text{-SO}_4^{2-})(\text{L}^n)_2\{\text{fac-Re}(\text{CO})_3\}]$ (**1–3**) was obtained by the combination of $\text{Re}_2(\text{CO})_{10}$, NaHSO_3 , and a neutral flexible ditopic nitrogen donor ((1,3-bis(benzimidazol-1-ylmethyl)benzene (L^1)/1,3-bis(5,6-dimethylbenzimidazol-1-ylmethyl)benzene (L^2)/1,3-bis(naphthoimidazol-1-ylmethyl)benzene (L^3)). In this approach, NaHSO_3 transforms to tetrahedral SO_4^{2-} (Scheme 1) during the reaction and acts as part of the framework of SCCs.

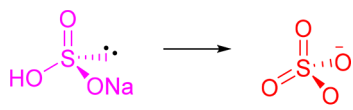
RESULTS AND DISCUSSION

Synthesis and Characterization of 1–3. Complexes **1–3** were prepared by treating $\text{Re}_2(\text{CO})_{10}$, NaHSO_3 , and $\text{L}^1/\text{L}^2/\text{L}^3$ in a toluene–acetone solvent mixture under solvothermal conditions (Scheme 2). Ditopic nitrogen donor ligands $\text{L}^1/\text{L}^2/$

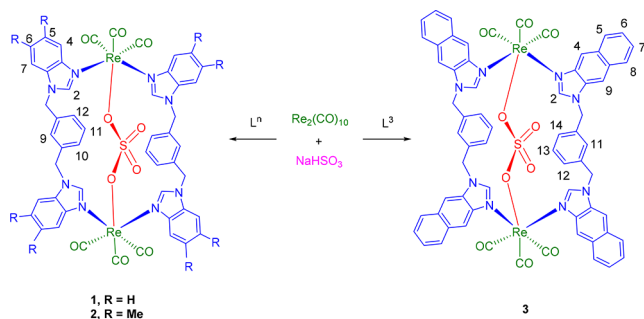
Received: May 16, 2018

Published: August 14, 2018

Scheme 1



Scheme 2. Synthesis of 1–3



L^3 have been used in coordination chemistry as one of the structural frameworks for SCCs, coordination polymers, and metal–organic frameworks.^{4e,f} The products 1–3 are air and moisture stable and soluble in polar organic solvents. The ATR-IR spectrum of 1 displays strong bands at 2018 and 1861 cm^{-1} , characteristic of the *fac*- $\text{Re}(\text{CO})_3$ core.³ Three bands observed at 1118, 1009, and 907 cm^{-1} were assigned to an SO_4^{2-} unit bridged to metal ions (Figures S1–S3 in the Supporting Information).¹³ The sharp peak observed at 926 cm^{-1} in the Raman spectrum of 1 can be assigned to the S–O vibrations of SO_4^{2-} coordinating unit (Figure S4 in the Supporting Information). To understand the source of oxygen for the transformation of sulfite to sulfate, starting materials such as NaHSO_3 , L^1 , toluene, and acetone were dried and purified using conventional procedures.^{17a,b} The controlled studies were carried out by reacting $\text{Re}_2(\text{CO})_{10}$, L^1 , and NaHSO_3 in dry toluene–acetone solvent mixture under solvothermal conditions in the presence as well as the absence of oxygen (in a glovebox). Since acetone may contain traces of isopropyl alcohol, the reaction was also carried out using isopropyl alcohol. The complex was formed when the reaction was done in the presence of air (Figure S6 in the Supporting Information). No complex formation was observed when the reaction was carried out in the absence of oxygen (Figure S7 in the Supporting Information)^{17c,d} or in the presence of isopropyl alcohol (Figure S8 in the Supporting Information). These results indicate that aerial oxygen is responsible for the transformation of SO_3^{2-} to SO_4^{2-} . No complex formation was observed upon direct reaction of Na_2SO_4 instead of NaHSO_3 with $\text{Re}_2(\text{CO})_{10}$ and $L^1/L^2/L^3$: i.e., no helicate or mesocate was formed. The reaction yielded a mixture of free ligand and rhenium core, indicating that the complexes cannot be obtained by the direct use of SO_4^{2-} as the template ion. (Figures S9–S11 in the Supporting Information). The ^1H NMR spectrum of 1 in $\text{DMSO}-d_6$ shows a simple pattern with five chemical resonances in the aromatic region (Figure 1). The H^2 proton adjacent to nitrogen was downfield shifted by 0.25 ppm relative to that of uncoordinated L^1 , which can be ascribed to the coordination of the benzimidazolyl tertiary nitrogen to the rhenium core. The H^9 proton of L^1 in 1 appeared as a singlet and was shifted upfield. The same H^9 proton was merged with other aromatic proton signals in the free ligand L^1 . This can be explained by the possibility that the

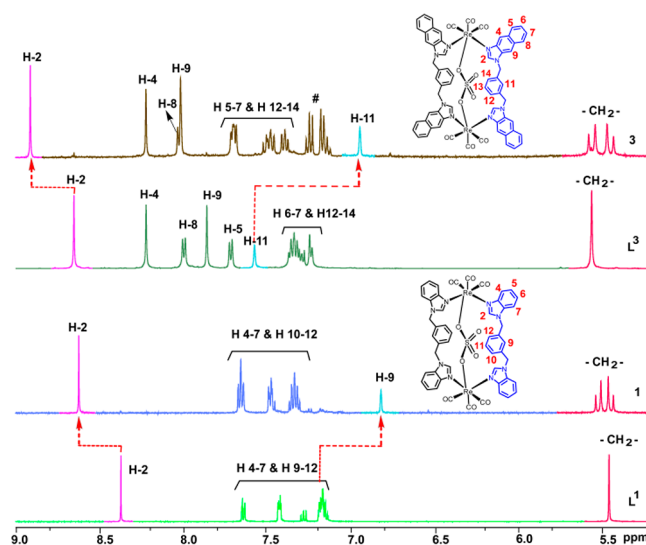


Figure 1. Partial ^1H NMR spectra of L^1 , 1, L^3 , and 3 in $\text{DMSO}-d_6$ (# = toluene).

H^9 proton in 1 may be directed over the aromatic face of a neighboring arene unit and experience the ring current effect.^{2g} The remaining aromatic protons (H^{4-7} and H^{10-12}) merged together and appeared as three chemical resonances. The aliphatic methylene protons ($-\text{CH}_2-$) that appeared as a doublet of doublets indicate the rigid nature of the methylene protons in the complex. All observations indicate that L^1 is coordinated with Re and is rigid in the complex rather than in the free ligand. The ^1H NMR spectrum of complex 3 displays a pattern similar to that of 1, i.e. an upfield shift for the H^{11} proton, a downfield shift for the H^2 proton, a multiplet for the $-\text{CH}_2-$ protons, indicating that the arrangements of ligands in complexes 1 and 3 are similar (Figure 2). The ^1H NMR spectrum of complex 2 shows a considerable amount of free ligand L^2 along with the desired product, and separation of the complex from the mixture was fruitless (Figure S12 in the Supporting Information). The formation of 1 was further confirmed by electrospray ionization mass analysis (Figure S14 in the Supporting Information), which displays a molecular ion peak (m/z 1313.1174 for $[1 + \text{H}]^+$) that matches with the theoretical value. Compounds 2 and 3 also show the molecular ion peaks m/z 1425.2685 for $[2 + \text{H}]^+$ and m/z 1513.2254 for $[3 + \text{H}]^+$ (Figures S15 and S16 in the Supporting Information), which confirm the formation of SCCs.

Crystal Structures of Complexes 1–3. The crystals of 1–3 were obtained directly from the solvothermal vessel. The structures of 1–3 were confirmed by single-crystal X-ray analysis (Figure 2). Molecule 1 adopts a helical structure and consists of two *fac*- $\text{Re}(\text{CO})_3$ cores, one SO_4^{2-} , and two neutral L^1 ligands. The distance between two rhenium atoms ($\text{Re}\cdots\text{Re}$) is 6.499 Å. Two L^1 ligands act as helical molecular clips and wrap around the $\{\text{Re}\cdots\text{Re}\}$ core. The helical twist angles of ligands are 25 and 31° i.e., torsion angles of $\text{Re1}\cdots\text{N2}\cdots\text{N1}\cdots\text{Re2}$ and $\text{Re1}\cdots\text{N4}\cdots\text{N3}\cdots\text{Re2}$. Due to this arrangement, two benzimidazolyl units of L^1 in 1 are orthogonal to each other ($\tau = 87$ and 70°). The sulfate dianion takes a syn, anti 2.1100 ($\mu_2:\eta^1:\eta^1$)¹⁴ conformation mode and coordinates two rhenium cores in 1. The coordinated S–O distances (1.505 and 1.503 Å) are significantly longer than the uncoordinated S–O distances (1.450 and 1.428 Å). Two different bond lengths for

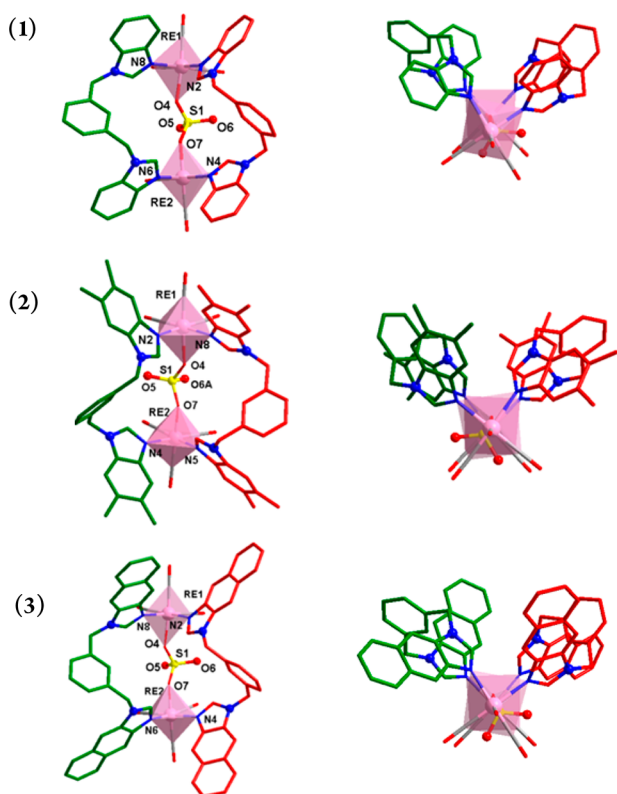


Figure 2. Two different views of the molecular structures of **1–3** (L , green and red stick models; sulfate, ball and stick model, CO, stick models). H atoms are removed for clarity.

the bridging SO_4^{2-} anion were observed¹⁴ (Table S1 in the Supporting Information). The uncoordinated oxygen atoms in the sulfate anion are directed away from the center of the molecule. The rhenium atom adopts an octahedral geometry and is surrounded by three facial carbonyl units, one oxygen atom from SO_4^{2-} , and two nitrogen donors from two L^1 units. Two benzimidazolyl donors, each from different strands, around each rhenium are arranged in a cis fashion. To the best of our knowledge, rhenium(I)-based SCCs with helicate/mesocate type structures are very rare.¹¹

Complexes **2** and **3** also adopt structures similar to that of helicate **1**. Though the nitrogen donor ligands in both the complexes adopt a helicate structure, the torsion angles of $\text{Re}\cdots\text{N}\cdots\text{N}\cdots\text{Re}$ units in **2** and **3** ($\tau = 12/11^\circ$ for **2** and $14/12^\circ$ for **3**) are smaller than those found in helicate **1**. In the crystal structure of **1**, each molecule is surrounded by six adjacent molecules, two molecules on the $\text{Re}\cdots\text{Re}$ axis and four molecules on the circular space, which are all held together by multiple noncovalent contacts ($\text{C}(\text{sp}^3)\cdots\text{H}\cdots\pi$ and edge-to-face $\text{C}\cdots\text{H}\cdots\pi$, $\text{C}(\text{sp}^3)\cdots\text{H}\cdots\text{O}\equiv\text{C}\cdots\text{Re}$, $\text{C}(\text{sp}^2)\cdots\text{H}\cdots\text{O}(\text{SO}_4)$, $\text{C}(\text{sp}^3)\cdots\text{H}\cdots\text{O}\equiv\text{C}\cdots\text{Re}$, and displaced $\pi\cdots\pi$ interactions).

Transformation of Triple Helicates to Double Mesocates. The stability of complex **1** was further studied using variable-temperature ^1H NMR experiments. Though chemical shifts for the protons of L^1 in **1** were observed, no additional chemical resonances were observed. In addition, chloranilic acid ($\text{H}_2\text{-CA}$), a well-known dianionic bis-chelator used for the construction of several Re-based SCCs, was added to **1** and heated. The ^1H NMR spectrum of the mixture shows neither an extra peak nor any shift in the resonances, indicating the stable nature of the sulfate-coordinated dinuclear structure **1** in

solution. However, the sulfate-coordinated complexes **1–3** are unstable in the presence of BaCl_2 . The addition of BaCl_2 to $\text{DMSO}-d_6$ solutions of **1–3** resulted in the formation of sulfate-free double-homostranded mesocates **4a–6a** (Scheme 3 and Figure 3) along with the formation of BaSO_4 as a white precipitate.

Scheme 3. Synthesis of Double-Stranded Homoleptic Helicates/Mesocates

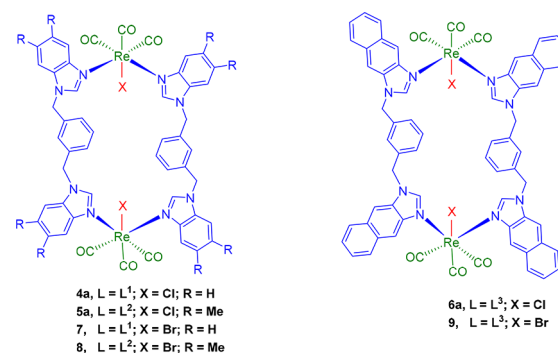
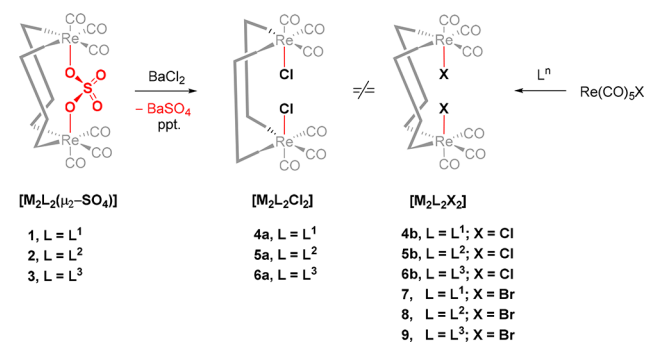


Figure 3. Representation of double-stranded homoleptic mesocates/helicates.

The transformation of **1–3** into **4a–6a** is quantitative on the basis of the ^1H NMR spectroscopic analysis. The solution after the addition of BaCl_2 displays a simple pattern with an upfield/downfield shift for the protons of the ligand motif. The multiplet observed for $-\text{CH}_2-$ protons of SO_4^{2-} -based complex **1** is lost in the Cl-based complex **4a**. In particular the ^1H NMR spectral pattern of **4a** is completely different from the pattern observed in both complex **1** and ligand L^1 . A similar trend is also observed in case of **6a** (Figures S17 and S19 in the Supporting Information). The mixture of **2** and L^2 was also treated with BaCl_2 . The ^1H NMR spectrum shows the conversion of **2** to **5a** without any change in the peak position of L^2 (Figure S18 in the Supporting Information). The formation of complexes **4a–6a** was further supported by ESI-MS analysis (Figures S20–S22 in the Supporting Information). The ESI-MS spectra of **4a–6a** display molecular ion peaks corresponding to the formula $[\{\text{Re}(\text{CO})_3\text{Cl}\}_2(L^n)_2]$. The results reveal that complexes **1–3** completely transformed into complexes **4a–6a**.

Synthesis of Double-Stranded Helicates. The direct reaction between $\text{Re}(\text{CO})_5\text{X}$ ($X = \text{Cl}, \text{Br}$) and $L^1/L^2/L^3$ in a toluene/acetone and/or tetrahydrofuran (THF) solvent mixture by solvothermal and conventional methods resulted in the formation of **4b–6b** and **7–9** (Scheme 3).¹⁸ The ATR-IR spectra of the complexes **4b–6b** and **7–9** exhibit strong

bands in the region 2019–1874 cm^{-1} (Figures S23 and S24 in the Supporting Information) characteristic of *fac*- $\text{Re}(\text{CO})_3$. The results of ESI-MS spectra analysis of **4b**, **5b**, **7**, and **8** confirm the formation of $[\{\text{Re}(\text{CO})_3\text{X}\}_2(\text{L}^n)_2]$ ($\text{X} = \text{Cl}, \text{Br}$) (Figure 5 and Figures S25, S26, and S28 in the Supporting Information). The ^1H NMR spectra of **4b** and **5b** are different from those of **4a** and **6a**. In particular the $-\text{CH}_2-$ protons appeared as a multiplet in **4b** and **5b** (Figure 4). Separation of

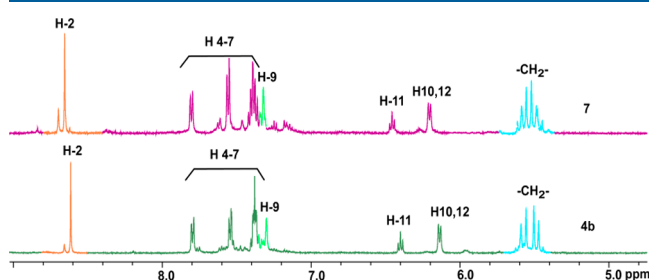


Figure 4. Partial ^1H NMR spectra of **4b** (bottom) and **7** (top) in $\text{DMSO}-d_6$.

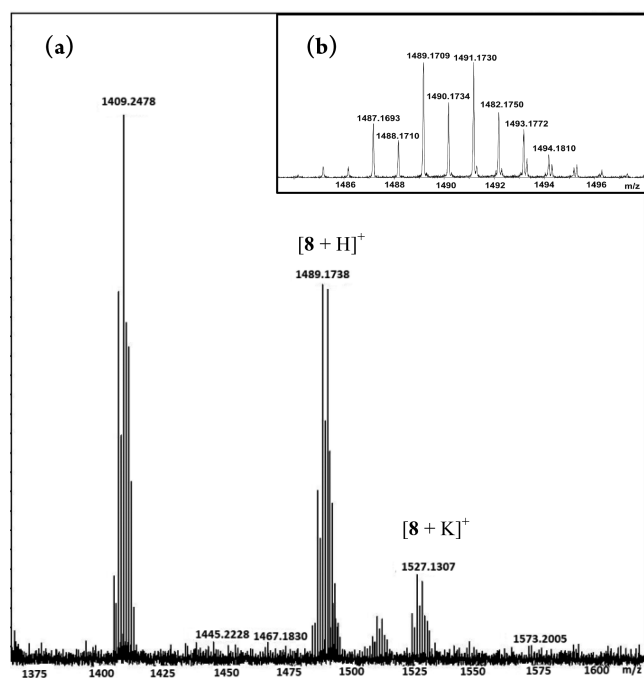


Figure 5. (a) Experimental ESI-TOF mass spectrum of **8** in positive ion mode. (b) Molecular ion peaks of $[\mathbf{8} + \text{H}]^+$.

6b and **9** from the mixture was fruitless even after several attempts. However, the formation of **6b** and **9** was confirmed by ESI-MS and ^1H NMR spectroscopic analysis (Figures S27, S29, S32, and S35 in the Supporting Information). We believe that the complexes **4a**, **6a**, **4b**, and **5b** possess the composition $[\{\text{Re}(\text{CO})_3\text{Cl}\}_2(\text{L}^n)_2]$ and are cyclic in nature. The difference among these complexes may be due to the spatial arrangement of ligands in the complexes. The complexes **4b** and **5b** may possess a helicate type structure, whereas **4a** and **6a** may adopt a mesocate type structure.

CONCLUSION

In conclusion, the first *fac*- $\text{Re}(\text{CO})_3$ core based SCCs of a sulfate framework ligand are reported and were constructed by

spontaneously transforming hydrogen sulfite to sulfate in the presence of neutral nitrogen donors and $\text{Re}_2(\text{CO})_{10}$ using a one-pot, multicomponent, coordination-driven self-assembly process. The results reveal that sulfate ion, a harmless dianion, can be used as one of the basic framework building units to construct SCCs. To the best of our knowledge, the synthetic principle, i.e., spontaneously transforming a sulfite (SO_3^{2-}) to sulfate (SO_4^{2-}) in the presence of a metal source and organic ligand, is the first design principle for making $\text{Re}(\text{I})$ -based SCCs. Two reports on Zn core based SCCs consisting of sulfite and/or sulfate were recently reported.^{1v} An earlier synthetic principle in which one donor transforms to another donor which further coordinates to metal and forms $\text{Re}(\text{I})$ -based SCCs is a soft ditopic P donor to a hard ditopic $\text{O}=\text{P}$ donor.^{10b} It is important to mention that research on the transformation and fixation of SO_2 into sulfate by either organic molecules or coordination complexes has been gaining much attention recently due to its risk to human health.^{1u,v,1s} Addition of BaCl_2 to the SCCs resulted in the transformation of dinuclear heteroleptic triple-stranded helicates to sulfate-free dinuclear neutral homoleptic double-stranded mesocates. The direct reaction of $\text{Re}(\text{CO})_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) with ditopic N donors ($\text{L}^1/\text{L}^2/\text{L}^3$) yielded dinuclear homoleptic double-stranded cyclic complexes with the general formula $[\{\text{Re}(\text{CO})_3\text{X}\}_2(\text{L}^n)_2]$ ($\text{X} = \text{Cl}, \text{Br}$). The ^1H NMR analysis indicates that the difference among these dinuclear homoleptic double-stranded cyclic complexes may be due to the spatial arrangement of ligands in the complexes. The results open up a new way to use an inorganic anion to act as a bridging ligand and possibly fix sulfur dioxide in the framework of SCCs. The construction of SCCs with various organic nitrogen donors and anionic frameworks, in particular sulfate and carbonate, by using sulfite/sulfur dioxide/carbon dioxide is in progress.

EXPERIMENTAL SECTION

General Data. Starting materials such as $\text{Re}_2(\text{CO})_{10}$, $\text{Re}(\text{CO})_5\text{Cl}$, $\text{Re}(\text{CO})_5\text{Br}$ (98%, Sigma-Aldrich), NaHSO_3 (Avra), Na_2SO_4 (Finar), BaCl_2 (Finar), and acetone (Finar) were purchased from the vendors indicated. Hexane, THF, and toluene were purified using conventional procedures. Ligands L^1 , L^2 , and L^3 were synthesized as reported in the literature.^{19–21} ^1H NMR spectra were recorded on Bruker 400 and 500 MHz spectrometers. ATR-IR spectra were recorded on a Bruker Tensor-II spectrometer. Elemental analyses were performed on a Flash EA series 1112 CHNS analyzer. The mass spectra were obtained on a Bruker maXis mass spectrometer. The Raman spectrum was recorded on a WI-Tec confocal Raman spectrometer equipped with a Peltier-cooled CCD detector.

Synthesis of $[\{\text{Re}(\text{CO})_3\}_2(\mu\text{-SO}_4)(\text{L}^1)_2]$ (1**).** $\text{Re}_2(\text{CO})_{10}$ (100.2 mg, 0.154 mmol), NaHSO_3 (16 mg, 0.154 mmol), L^1 (103.6 mg, 0.306 mmol), toluene (10 mL), and acetone (3 mL) were heated in a solvothermal reactor. Colorless crystals obtained in the solvothermal vessel were filtered and air-dried. Yield: 28% (57 mg). Anal. Calcd for $\text{C}_{50}\text{H}_{36}\text{N}_8\text{O}_{10}\text{Re}_2\text{S}$: C, 45.73; H, 2.76; N, 8.53; S, 2.44. Found: C, 45.82; H, 2.71; N, 8.63; S, 2.48. ESI-MS: 1313.1174 for $[\text{M} + \text{H}]^+$. ^1H NMR (500 MHz, $\text{DMSO}-d_6$): 8.62 (s, 4H, H^2 , benzimidazolyl), 7.67–7.65 (m), 7.49–7.46 (m), 7.36–7.30 (m), 6.82 (s, 2H, H^9 , benzene of L^1) and 5.53–5.43 (dd, 8H, $J = 15$ Hz, $-\text{CH}_2-$). ATR-IR (cm^{-1}): ν 2018 and 1861 (CO).

Synthesis of $[\{\text{Re}(\text{CO})_3\}_2(\mu\text{-SO}_4)(\text{L}^2)_2]$ (2**).** $\text{Re}_2(\text{CO})_{10}$ (100.5 mg, 0.154 mmol), NaHSO_3 (16.1 mg, 0.155 mmol), L^2 (121 mg, 0.307 mmol), toluene (10 mL), and acetone (3 mL) were heated in a solvothermal reactor. Colorless crystals along with a white powder obtained in the solvothermal vessel were washed with distilled hexane and air-dried. Yield: 75%/25% (free ligand and complex) (149 mg)

on the basis of ^1H NMR analysis. ATR-IR (cm^{-1}): ν 2014, 1896, and 1866 (CO).

Synthesis of $[\{\text{Re}(\text{CO})_3\}_2(\mu\text{-SO}_4)(\text{L}^3)_2]$ (3). $\text{Re}_2(\text{CO})_{10}$ (100.6 mg, 0.154 mmol), NaHSO_3 (16 mg, 0.154 mmol), L^3 (134.3 mg, 0.306 mmol), toluene (10 mL), and acetone (3 mL) were heated in a solvothermal reactor. Colorless crystals and white powder were obtained in the bomb. The mixture was washed with distilled hexane several times to obtain the pure complex and air-dried. Yield: 47% (108.7 mg). Anal. Calcd for $\text{C}_{66}\text{H}_{44}\text{N}_8\text{O}_{10}\text{Re}_2\text{S}$: C, 52.37; H, 2.93; N, 7.40; S, 2.12. Found: C, 52.27; H, 2.89; N, 7.46; S, 2.18. ESI-MS: 1513.2254 for $[\text{M} + \text{H}]^+$. ^1H NMR (500 MHz, $\text{DMSO}-d_6$): 8.92 (s, 4H, H^2), 8.22 (s, 4H, H^4), 8.04–8.02 ($\text{H}^8, ^9$), 7.71–7.39 (m, H^{5-7} and H^{12-14}), 6.96 (s, 2H, H^{11} , benzene of L^3) and 5.57–5.43 (dd, 8H, J = 15 Hz, $-\text{CH}_2-$). ATR-IR (cm^{-1}): ν 2009 and 1876 (CO).

Synthesis of $[\{\text{Re}(\text{CO})_3\text{Cl}_2(\text{L}^1)_2\}]$ (4b). $\text{Re}(\text{CO})_5\text{Cl}$ (100.1 mg, 0.277 mmol), L^1 (94.2 mg, 0.278 mmol), toluene (20 mL), and THF (20 mL) were refluxed for 48 h. The solution volume was reduced to half under reduced pressure. The precipitate was washed with hexane. Yield: 34% (119.7 mg). Anal. Calcd for $\text{C}_{50}\text{H}_{36}\text{Cl}_2\text{N}_8\text{O}_{10}\text{Re}_2$: C, 46.62; H, 2.82; N, 8.70. Found: C, 46.51; H, 2.78; N, 8.65. ESI-MS: 1289.1322 for $[\text{M} + \text{H}]^+$. ^1H NMR (500 MHz, $\text{DMSO}-d_6$): 8.61 (s, 4H, H^2 , benzimidazolyl), 7.80–7.78 (m), 7.55–7.53 (m), 7.39–7.36 (m), 7.29 (s, 2H, H^9 , benzene of L^1), 6.40 (t, J = 7.6 Hz, 2H, H^{11}), 6.14 (d, J = 7.6 Hz, 4H, $\text{H}^{10,12}$) and 5.58–5.47 (dd, 8H, J = 16.5 Hz, $-\text{CH}_2-$). ATR-IR (cm^{-1}): ν 2017, 1915, and 1874 (CO).

Synthesis of $[\{\text{Re}(\text{CO})_3\text{Cl}_2(\text{L}^2)_2\}]$ (5b). $\text{Re}(\text{CO})_5\text{Cl}$ (100.1 mg, 0.277 mmol), L^2 (110.2 mg, 0.279 mmol), toluene (20 mL), and THF (20 mL) were refluxed for 48 h. The solution volume was reduced to half under reduced pressure. The precipitate was washed with hexane. Yield: 22% (84.8 mg). Anal. Calcd for $\text{C}_{58}\text{H}_{52}\text{Cl}_2\text{N}_8\text{O}_{10}\text{Re}_2$: C, 49.75; H, 3.74; N, 8.00. Found: C, 49.63; H, 3.78; N, 8.15. ESI-MS: 1401.2544 for $[\text{M} + \text{H}]^+$. ^1H NMR (500 MHz, $\text{DMSO}-d_6$): 8.44 (s, 4H, H^2 , methylbenzimidazolyl), 7.55 (s, 4H, H^4), 7.28 (s, 2H, H^9 , benzene of L^2), 7.26 (s, 4H, H^7), 6.21 (t, J = 7.6 Hz, 2H, H^{11}), 5.88 (d, J = 7.65 Hz, 4H, $\text{H}^{10,12}$) and 5.55–5.39 (dd, 8H, J = 16.3 Hz, $-\text{CH}_2-$). ATR-IR (cm^{-1}): ν 2015 and 1875 (CO).

Synthesis of $[\{\text{Re}(\text{CO})_3\text{Cl}_2(\text{L}^3)_2\}]$ (6b). $\text{Re}(\text{CO})_5\text{Cl}$ (100.2 mg, 0.277 mmol), L^3 (121.2 mg, 0.276 mmol), toluene (20 mL), and THF (20 mL) were refluxed for 48 h. The solution volume was reduced to half under reduced pressure. The precipitate was washed with hexane. Yield: 85%/15% (free ligand: complex) (189.1 mg) on the basis of the ^1H NMR analysis. ATR-IR (cm^{-1}): ν 2019, 1909, and 1888 (CO).

Synthesis of $[\{\text{Re}(\text{CO})_3\text{Br}_2(\text{L}^1)_2\}]$ (7). $\text{Re}(\text{CO})_5\text{Br}$ (100.7 mg, 0.248 mmol), L^1 (167.2 mg, 0.494 mmol), toluene (10 mL), and acetone (3 mL) were heated in a solvothermal reactor. The white powder obtained in the bomb was filtered and air-dried. Yield: 14% (46.3 mg). Anal. Calcd for $\text{C}_{50}\text{H}_{36}\text{Br}_2\text{N}_8\text{O}_{10}\text{Re}_2$: C, 43.61; H, 2.64; N, 8.14. Found: C, 43.58; H, 2.56; N, 8.21. ESI-MS: 1377.0226 for $[\text{M} + \text{H}]^+$. ^1H NMR (500 MHz, $\text{DMSO}-d_6$): 8.66 (s, 4H, H^2 , benzimidazolyl), 7.80 (d, J = 7.5 Hz), 7.56 (d, J = 7.25 Hz), 7.41–7.36 (m), 7.32 (s, 2H, H^9 , benzene of L^1), 6.45 (t, J = 7.6 Hz, H^{11}), 6.20 (d, J = 7.65 Hz, $\text{H}^{10,12}$) and 5.59–5.49 (dd, 8H, J = 15.9 Hz, $-\text{CH}_2-$). ATR-IR (cm^{-1}): ν 2022, 1913, and 1870 (CO).

Synthesis of $[\{\text{Re}(\text{CO})_3\text{Br}_2(\text{L}^2)_2\}]$ (8). $\text{Re}(\text{CO})_5\text{Br}$ (100.8 mg, 0.248 mmol), L^2 (98.1 mg, 0.249 mmol), toluene (10 mL), and acetone (3 mL) were heated in a solvothermal reactor. The white powder obtained in the bomb was filtered and air-dried. Yield: 41% (152.8 mg). Anal. Calcd for $\text{C}_{58}\text{H}_{52}\text{Br}_2\text{N}_8\text{O}_{10}\text{Re}_2$: C, 46.78; H, 3.52; N, 7.52. Found: C, 46.65; H, 3.47; N, 7.61. ESI-MS: 1489.1529 for $[\text{M} + \text{H}]^+$. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): 8.46 (s, 4H, H^2 , methylbenzimidazolyl), 7.52 (s, 4H, H^4), 7.31 (s, 2H, H^9 , benzene of L^2), 7.27 (s, 4H, H^7), 6.24 (t, J = 7.4 Hz, 2H, H^{11}), 5.91 (d, J = 8.6 Hz, 4H, $\text{H}^{10,12}$) and 5.54–5.39 (dd, 8H, J = 16 Hz, $-\text{CH}_2-$). ATR-IR (cm^{-1}): ν 2018, 1905, and 1874 (CO).

Synthesis of $[\{\text{Re}(\text{CO})_3\text{Br}_2(\text{L}^3)_2\}]$ (9). $\text{Re}(\text{CO})_5\text{Br}$ (100.2 mg, 0.247 mmol), L^3 (108 mg, 0.246 mmol), toluene (20 mL), and THF (20 mL) were refluxed for 48 h. The solution volume was reduced to half under reduced pressure. The precipitate was washed with hexane.

Yield: 85%/15% (free ligand: complex) (135 mg) on the basis of the ^1H NMR analysis. ATR-IR (cm^{-1}): ν 2018, 1908, and 1883 (CO).

X-ray Crystallography. Intensity data of crystals of 1–3 were collected on a Bruker D8 Quest diffractometer ($\lambda(\text{Mo K}\alpha)$ = 0.71073 Å). The structures were solved by direct methods using SHELXS-97²² and refined using the SHELXL-2014/7 program (within the WinGX program package).^{22b,c} Non-H atoms were refined anisotropically. Some of the lattice solvent molecules could not be modeled, and hence their contribution to the intensities was excluded using the SQUEEZE option in PLATON.²² The crystallographic data of 1–3 are provided in Table S1 in the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b01343.

NMR spectra, ESI-TOF mass spectra, ATR-IR spectra, and Raman spectrum (PDF)

Accession Codes

CCDC 1567135 and 1841541–1841542 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the University of Hyderabad, DST-SERB (EMR/2015/000627), for financial support. K.R.S. thanks the UGC for the award of a Junior Research Fellowship.

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Cite this: *Dalton Trans.*, 2019, **48**, 7425

fac-Re(CO)₃-based neutral heteroleptic tetrahedrons†

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Received 22nd December 2018,
Accepted 11th April 2019

DOI: 10.1039/c8dt05065a

rsc.li/dalton

Four new flexible ditopic nitrogen donors possessing a xylene spacer and 2-phenylbenzimidazolyl or its derivatives as a coordinating unit and one rigid bis-chelating ligand consisting of two 2-hydroxyphenylbenzimidazolyl motifs and a central phenylene spacer were synthesized and further used with Re₂(CO)₁₀ for making a new family of neutral, heteroleptic tetrahedral-shaped supramolecular coordination complexes *via* a one-pot approach. The new ligands and the complexes were characterized using various analytical and spectroscopic methods. The molecular structures of the complexes were determined using single crystal X-ray diffraction analysis, which reveal that four rhenium cores are arranged in the vertices, and four ligands are at the edges of the tetrahedron.

Introduction

The design of supramolecular coordination complexes (SCCs) with various shapes and sizes has been going on during the past three decades due to their beautiful architectures, which can be assembled in a one-step approach, and their importance both in the materials and medicinal fields.^{1–9} Various metal sources including naked metal ions and partially protected metal precursors are used as connectors for ligand structural frameworks in the SCCs. Among the metal sources, a *fac*-Re(CO)₃-directed approach is one of the most versatile methods for making neutral heteroleptic SCCs *via* a one-pot approach.^{6–9} Examples of various types of *fac*-Re(CO)₃-based SCCs are helicate, mesocate, bowl, square, rectangle, trigonal/tetragonal prisms, and spheroid.^{6–9} Surprisingly, the *fac*-Re(CO)₃ core-based homoleptic or heteroleptic tetrahedron *i.e.*, having four metal ions arranged in a tetrahedral topology, is scarce.^{4,5} The lack of a *fac*-Re(CO)₃-based approach for the tetrahedron may be due to the difficulty in predesigning ligands for the stereoelectronic requirement of the *fac*-Re(CO)₃ core, which provides three orthogonal acceptor sites and requires two two-electron donors and one anionic one-electron donor (Fig. 1). Predesigned ligands (rigid–rigid or rigid–flexible or flexible–flexible ligand motifs) for the *fac*-Re(CO)₃ core-based tetranuclear SCC

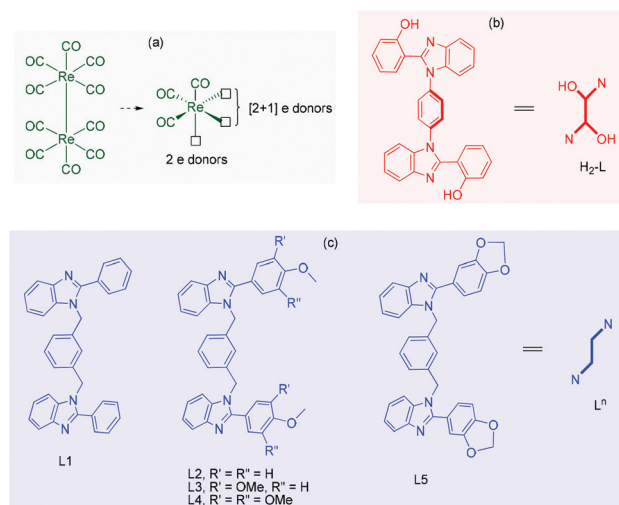
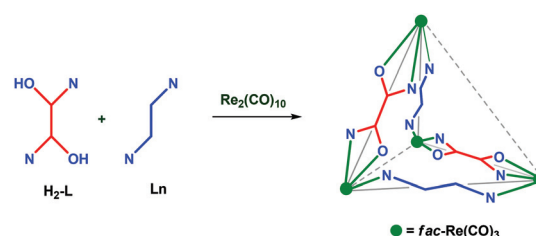


Fig. 1 Chemicals used for the work. (a) Stereoelectronic requirement of the *fac*-Re(CO)₃ core, (b) rigid bis-chelator (H₂-RBC = H₂-L) and (c) N-donor.

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†Electronic supplementary information (ESI) available: Experimental section and crystallographic data of **L4**, and **1–5**. CCDC 1886926, 1885873, 1885870, 1547013, 1885869 and 1885872. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8dt05065a



Scheme 1 Synthetic approach to heteroleptic M₄L₂L'₂-type SCC with a tetrahedral shape (gray) with two missing edges (gray dotted line).

have so far yielded tetranuclear square- or heteroleptic rectangle- or zigzag-shaped 2D-SCCs.⁸ Since 2008, we have been designing various types of ligands for making new types of heteroleptic *fac*-Re(CO)₃-based SCCs *via* new bonding combinations in a one-pot approach.⁹ Our research has been yielding synthetic approaches for neutral heteroleptic SCCs with aesthetically pleasing architectures and which have potential applications in various fields. Herein, we report a new *fac*-Re(CO)₃-based synthetic approach for neutral, heteroleptic tetrahedral-shaped SCCs. The combination of rigid bis-chelating donors with a rigid phenyl spacer and neutral flexible ditopic nitrogen donors with Re₂(CO)₁₀ in a one-pot approach provides a neutral, heteroleptic M₄L₂L'₂-type tetrahedron with two missing edges (Scheme 1).

Results and discussion

Synthesis and characterization of ligands

Neutral phenyl or substituted phenyl at the 2-position of the benzimidazolyl-based ditopic N-donor ligands (L2–L5) were obtained using 1,3-di(bromomethyl)benzene, the corresponding benzimidazole and KOH in DMF.¹⁰ The synthetic approach used to prepare L2–L5 is similar to that for the benzimidazolyl-based ditopic ligands.¹⁰ The ligands are air- and moisture-stable and are soluble in polar organic solvents. The ¹H NMR spectra of L2–L5 showed a single peak around ~5.5 ppm corresponding to methylene protons (see Fig. S2–S5 in the ESI†). The benzimidazolyl protons of all the ligands displayed as well-separated two doublets and two triplets, indicating the unsymmetrical nature of the benzimidazolyl protons due to the formation of ligands. The rigid ligand (H₂-RBC = H₂-L, Fig. 1) was synthesized using 2-hydroxyphenylbenzimidazole (HO-PBz-H) and 1,4-dibromobenzene in the presence of CuI/Cs₂CO₃ in DMF. The sharp singlet at δ 7.71 ppm for the protons of the central phenylene motif, and a 4:18 proton ratio for –C₆H₄– protons and two (HO-PBz) units of protons, confirm the rigid ligand (Fig. S1 in ESI†). The ESI-MS spectra of the ligands (Fig. S6–S10 in ESI†) show molecular ion peaks, further supporting the formation of the product.

The molecular structure of L4 was confirmed using single crystal X-ray diffraction (SCXRD) analysis (Fig. 2).^{11,12} The two 3,4,5-trimethoxyphenylbenzimidazolyl motifs are *trans* to each other and are perpendicular to the central arene motif. Both nitrogen atoms (N1 and N4) are directed on the same side. The dihedral angle between the two imidazolyl units is 42°. The distance between two nitrogen donor atoms is 11.5 Å (N1...N4) in L4.

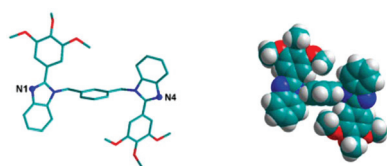
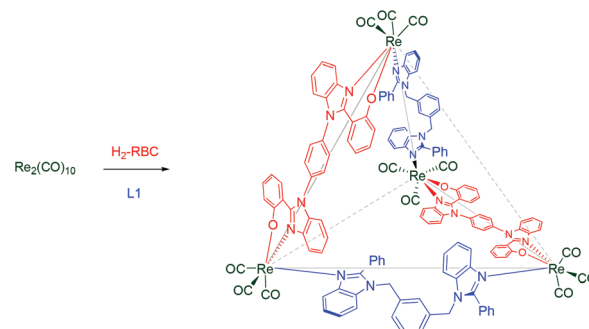


Fig. 2 Molecular structure of L4 (left: H atoms are removed).

Synthesis and characterization of SCCs

The solvothermal heating of Re₂(CO)₁₀, H₂-RBC and Ln and toluene yielded SCCs (1–5) with/without lattice toluene molecule(s) (Scheme 2). The SCCs are air and moisture stable, and moderately soluble in polar organic solvents. The FT-IR spectra of the complexes displayed three strong bands in the region of 2020–1800 cm^{−1}, characteristic of the *fac*-Re(CO)₃ motifs in the asymmetric environment.⁹ The ¹H NMR spectrum of 4 is discussed here due to the clear pattern *i.e.*, without decomposition or free ligand Ln impurity. The ¹H NMR spectra of 1 and 2 indicated that the chemical resonance pattern is similar to that of 4 (Fig. S11–S13 in ESI†). However, there were additional peaks which are similar to the free ligand Ln (L1 for 1 and L2 for 2), which may be due to either decomposition of the complex while heating or the presence of impure ligands. No clear ¹H NMR spectra was obtained for the complexes 3 and 5. The ¹H NMR spectrum of 4 in DMSO-*d*₆ displayed well-separated peaks compared to both the free ligands. Both upfield and downfield shifts were observed for the protons of the ligands of 4. In particular, eight peaks are present in the region of 6.8–4 ppm in 4. However, only one single peak for methylene protons was observed for the uncoordinated L1 ligand in the region. Further, the methylene (–CH₂–) protons appeared as two doublets with coupling constant consistent with geminal coupling (*J* = 18 Hz). Among the two doublets of the methylene protons, one is near the chemical resonance of the methylene protons of the free ligand and the other proton is upfield shifted. The results suggest that complex 4 remains as an SCC structure in the solution and the upfield shift for the protons of the complex compared to the free ligand is due to neighbouring aromatic motifs. All the remaining complexes also displayed a similar pattern like that of 4. The results are further supported by ESI-MS studies. The mass spectra of the complexes show a molecular ion peak with isotopic distribution peaks which match with theoretical values. Further, the mass spectra of the complexes displayed peaks corresponding to the consecutive loss of ligand(s) and Re(CO)₃ core(s). In addition, the mass spectra showed the mass of the [M₂LLn] motif, where M = Re(CO)₃ (Fig. S14–S18 in ESI†).



Scheme 2 Synthesis of 1.

Molecular structures of SCCs

The molecular structures of 1–5 were confirmed by SCXRD studies, which showed that the complexes adopt an $M_4L_2L'_2$ -type SCC architecture (Fig. 3–6 and Fig. S24–S32 in ESI†). The complexes 1–5 can be viewed as a $[4 + 2 + 2]$ assembly of four *fac*- $\text{Re}(\text{CO})_3$ cores, two dianionic ligand ($\text{RBC}^{2-} = \text{L}^{2-}$) motifs, and two neutral nitrogen ligands (L^n). The arrangements of four rhenium atoms and four ligand motifs provide an overall distorted tetrahedron shape with two missing edge units to the

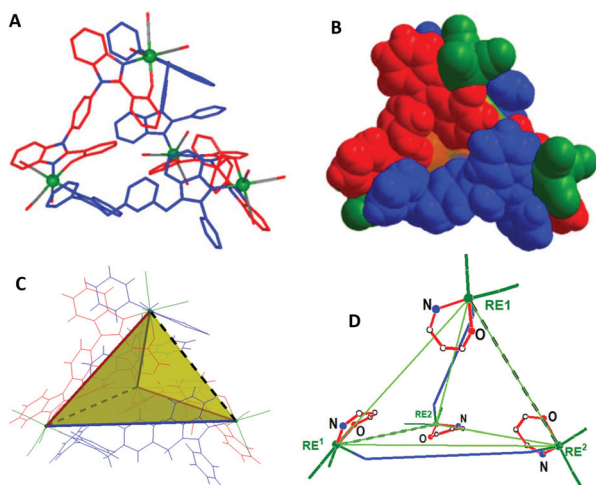


Fig. 3 Various representations of molecular structure of 1 (A–C). Ball and stick model without hydrogen atoms (A) and space-filling view (B). Face view of the highlighted tetrahedron with a thin stick model of 1; two dotted lines represent two missing edges (C). Helical arrangement of ligands in 1; the blue line is L^1 and chelating atoms ($\text{O}–\text{C}–\text{C}–\text{N}$) are shown to indicate a Δ or Λ configuration at each of the four vertices; $\text{Re}^1\text{Re}^1\text{Re}^2\text{Re}^2$ adopts a $\Delta\Delta\Lambda\Lambda$ twisted conformation (D). Color code: red = ligand RBC^{2-} , blue = L^1 , $\text{Re}(\text{CO})_3$ = green or gray (C) and green or red (O).

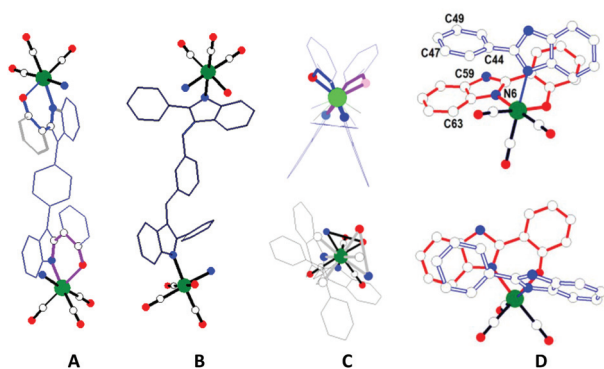


Fig. 4 Helical arrangement of a dinuclear anionic ligand (A)- and a neutral ligand (B) in 1. Two chelating ($\text{O}–\text{C}–\text{C}–\text{N}$) atoms are colored in blue and in purple (A and C) to show the difference clearly in the top-view (C). Top view with two chelating motifs of A (top, C) and the neutral motif of B (bottom, C) highlighted. Intramolecular π – π stacking interactions between the phenyl of the N donor and the arene motif of the phenoxybenzimidazolyl motif (D). Hydrogen atoms are omitted. C = gray, N = blue, O = red, Re = green.

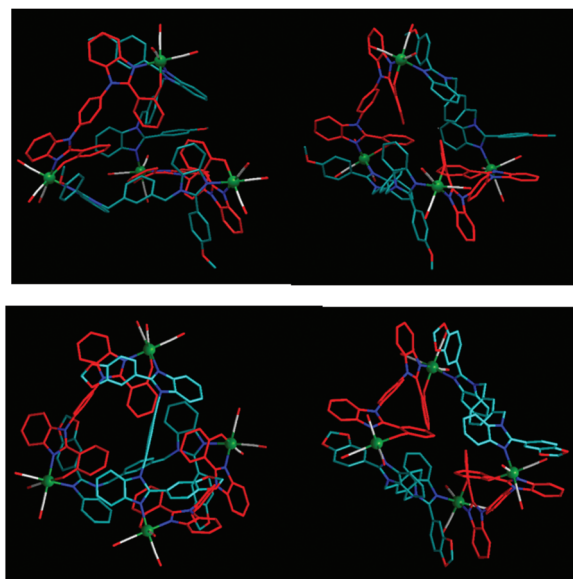


Fig. 5 Two views of the molecular structures of 2 (top) and 5 (bottom). Carbon atoms of the rigid ligand are shown in red, C atoms of the flexible ligand are shown in aqua. H atoms are omitted for clarity. Color code: C = gray for CO, N = blue, O = red and Re = green.

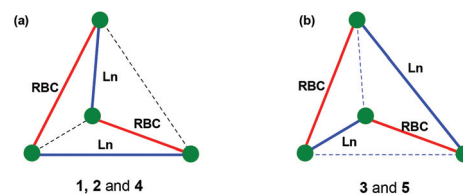


Fig. 6 Different edge arrangement of the Ln motif (blue) in the tetrahedrons 1–5. Red indicates a rigid ligand (RBC), and the dotted line indicates a missing edge.

complexes. The four *fac*- $\text{Re}(\text{CO})_3$ cores are considered as the four vertices and the four ligand motifs are represented as the four edges of the tetrahedron in the complexes. Three types of edges are present in the tetrahedra (the rigid RBC ligand provides shorter edge $\{\text{Re}–\text{RBC}–\text{Re}, d_{(\text{Re}\cdots\text{Re})} = 13.5 \text{ \AA}\}$, the flexible L^n offers longer edge ($\text{Re}–\text{L}^n–\text{Re}, d_{(\text{Re}\cdots\text{Re})} = \sim 15.3 \text{ \AA}$) and the missing edge ($\text{Re}\cdots\text{Re}, d_{(\text{Re}\cdots\text{Re})} = \sim 11.2 \text{ \AA}$) (Table 1). Due to the different edges and two missing edges, the distorted tetrahedron has scalene triangular faces. Each scalene triangular face (Δ) has one anionic ligand edge, one neutral ligand edge and one missing edge (Fig. 3c and Fig. S28–S32 in ESI†, Table 1).

The arrangement of the four ligands in the complexes provides a helical SCC architecture (Fig. 4, 5 and Table 1). For example, the two chelating motifs of the RBC strand ($\text{Re}–\text{RBC}–\text{Re}$) in 1 are twisted with respect to each other with a twist angle of RBC *i.e.*, the angle between the planes of the two $\text{Re}–\text{O}(\text{chel})–\text{N}(\text{chel})$ units, of $78/87^\circ$. The flexible L^1 takes a *syn*-conformation with an *anti*-cofacial arrangement of two phenyl-

Table 1 Twist angles (φ) between two chelating units of RBC and three Re...Re distances in a scalene triangle (Δ) in **1**–**5**. The parameters were calculated without the solvent

Comp.	φ ($^\circ$)	d of Δ ($\text{\AA}$)		
		Re-RBC-Re	Re-Ln-Re	Re...Re
1	78, 87	13.6, 13.54	15.27	11.28
2	74, 81	13.48	15.10	11.33
3	70, 74	13.50	14.91	11.63, 10.46
4	72	13.51	14.90	10.63, 11.63
5	87, 78	13.55, 13.47	15.22	11.16

benzimidazolyl units and is arranged in a helical fashion in **1** (Fig. 3–6 and Fig. S28–S32 in ESI†).

The four Re...Re distances in **1** are mentioned in Table 1. The rhenium core adopts a distorted octahedral geometry and is surrounded by three carbon atoms from three carbonyl ligands, NNO from chelating units and N from neutral benzimidazolyl motif. The bond distances between Re–C, Re–N_(bbenz), Re–N_(chel), and Re–O_(chel) are normal in **1** and consistent with values found for dinuclear *fac*-Re(CO)₃-based helicates/mesocates possessing similar coordinating cores *i.e.* a hydroxyphenylbenzimidazolyl chelating unit, a benzimidazolyl motif, and three CO units.^{9d}

The complexes **2** and **4** are almost similar to that of **1** (Fig. 5). The four methoxy (OCH₃) groups of the L2 motif are directed away from the tetrahedron **2**. However, the complexes **3** and **5** differ from those of **1**, **2**, and **4** with respect to the arrangement of two neutral ligand motifs in the tetrahedron edges (Fig. 5 and 6). Both anionic ligand motifs take similar edges in all the complexes. The two missing edges in **1** and **4** are now occupied by Ln in **2**, **3** and **5** as shown in Fig. 6. The four *exo*-cavities present in the four faces of the tetrahedra of **3** and **4** were occupied by the methoxy unit of Ln *i.e.*, one methoxy motif sits one face of the tetrahedron. Multiple weak C–H... π contacts were found between the OCH₃ and the framework (phenylene units) of the cavity.

It is worth mentioning that the number of methoxy units, (OCH₃), in the complexes is increased from complex **2** to complex **4** *i.e.*, four (OCH₃) units in **2**, eight (OCH₃) units in **3**, and twelve (OCH₃) units in **4**. Moderate-to-strong intramolecular π ... π stacking interactions were found between the benzimidazolyl unit, in particular the imidazolyl motif, of RBC and the phenyl motif of Lⁿ (dihedral angle = 13.6°; and $d_{\text{C63-C47/C59-C49/N6-C44}} = 3.44/3.5/3.8$ Å for **1**). Four such π ... π stacking interactions are found in all the complexes. In the case of complex **5**, in addition to the intramolecular π ... π stacking interactions, the C–H... π contacts are found between the planar 1,3-benzodioxole ring and the benzimidazolyl unit of the chelating motif.

It is worth mentioning that the bis-chelating ligand (H₂-RBC = HO₂N–C₆H₄–N₂OH, where N₂OH is 2-(2-hydroxyphenyl)-benzimidazolyl) used in this work is rigid, whereas the ditopic N donor Ln is flexible (Ln = N–CH₂–C₆H₄–CH₂–N, where N = 2-(phenyl) benzimidazolyl). A similar bis-chelating flexible

ligand (H₂-FBC = HO₂N–CH₂–C₆H₄–CH₂–N₂OH, where R = H or Me) *i.e.*, a methylene unit incorporated as a connector for the chelating motif (HO₂N) and spacer (C₆H₄) and a flexible ditopic nitrogen donor (L^m = N–CH₂–C₆H₄–CH₂–N, where N = benzimidazolyl) provided neutral dinuclear unsaturated heteroleptic helicate/mesocate with Re₂(CO)₁₀.^{9d} The formation of the tetranuclear tetrahedron instead of dinuclear helicate/mesocate while using the rigid bis-chelating ligand may be due to the steric hindrance between these two ligands since the distance between two bis-chelating donors either in the rigid H₂-RBC ligand ($d_{\text{(Re-RBC-Re)}} = 11.3$ Å) or in the flexible H₂-FBC ligand ($d_{\text{(Re-RBC-Re)}} = 13.1$ Å) is comparable.^{9d} The attempt to obtain a single crystal of SCC with Re₂(CO)₁₀, H₂-RBC, and L^m is fruitless. Therefore, we suggest that the phenyl/substituted phenyl at the 2-position of the benzimidazolyl of Ln may play a major role for directing from the dinuclear helicate/mesocate to the tetrahedron assembly. The role of the fused benzene ring of benzimidazole in the ligand (Ln) as a steric motif may not be omitted.¹³

Conclusions

A family of the *fac*-Re(CO)₃ core-based heteroleptic tetrahedra with two missing edges was obtained using new bonding combinations *i.e.* Re₂(CO)₁₀, a rigid bis-chelating donor possessing a phenyl spacer, a flexible ditopic nitrogen donor possessing a xylene spacer and 2-phenylbenzimidazolyl or its derivatives coordinating unit *via* a one-pot approach. The tetrahedra are neutral, heteroleptic, and possess scalene triangle faces. To the best of our knowledge, the reported synthetic approach is the first example of a design approach for making *fac*-Re(CO)₃-based tetrahedra. The result provides a way to prepare *fac*-Re(CO)₃-based heteroleptic tetrahedra with a tunable exterior *via* a simple one-pot method. The construction of *fac*-Re(CO)₃-based tetrahedra with similar building units by tuning the spacer is in progress.

Experimental details

General data

The starting materials, Re₂(CO)₁₀, *o*-phenylenediamine, benzaldehyde, piperonal, *p*-anisaldehyde, 3,5-dimethoxybenzaldehyde, 3,4,5-trimethoxybenzaldehyde, NaHSO₃, 1,3-di(bromomethyl)benzene, 1,4-dibromobenzene, copper(i) iodide, 1,10-phenanthroline, cesium carbonate, toluene, acetone and dimethylformamide (DMF) were procured from commercial sources and used as received. 2-Phenyl-1*H*-benzimidazole, 2-(4-methoxyphenyl)-1*H*-benzimidazole, 2-(3,5-dimethoxyphenyl)-1*H*-benzimidazole, 2-(3,4,5-trimethoxyphenyl)-1*H*-benzimidazole, 2-(1,3-benzodioxole)-1*H*-benzimidazole and **L1** were synthesized using procedures reported in the literature.¹⁰ ¹H NMR spectra were recorded on Bruker Avance III 400 and 500 MHz spectrometers. FT-IR spectra were recorded on a JASCO-5300 FT-IR spectrometer. Elemental analyses were performed on a

Flash EA series 1112 CHNS analyser. The ES mass spectra were recorded on a Bruker maXis mass spectrometer.

Synthesis of H₂-RBC. The mixture of (2-hydroxyphenyl)-1H-benzimidazole (6.0 g, 28.5 mmol), 1,4-dibromobenzene (2.8 g, 11.9 mmol), 1,10-phenanthroline (0.85 g, 4.7 mmol), CuI (0.45 g, 2.4 mmol) and Cs₂CO₃ (16.3 g, 50 mmol) was taken in a Schlenk flask under a N₂ atmosphere. Dry DMF (30 mL) was added to the mixture, which was heated under reflux for 48 h. The mixture was extracted using CHCl₃/H₂O three times. The organic layer was separated, washed with brine solution and dried using anhydrous Na₂SO₄. The solvent was removed using vacuum. The crude H₂-RBC was eluted as a white powder using column chromatography using EA/hexane (20/80). The eluted white solid was again separated using column chromatography using the same solvent mixture to obtain pure H₂-RBC. Yield: 20% (1.18 g). ESI (HR-MS). Calcd for C₃₂H₂₃N₄O₂ [M + H]⁺: *m/z* 495.1821. Found: *m/z* 495.1775. ¹H NMR (400 MHz, DMSO-*d*₆): δ 11.91 (s, 2H, -OH), 7.86–7.84 (m, 2H, H⁴), 7.71 (s, 4H, phenylene), 7.41–7.31 (m, 8H, H^{5,6,4',5'}), 7.18 (d, *J* = 7.9 Hz, 2H, H²), 7.0 (d, *J* = 8.2 Hz, 2H, H⁷), and 6.82 (t, *J* = 8.0 Hz, 2H, H³).

General synthetic approach for L2–L5

A mixture of KOH and phenylbenzimidazole in DMF was stirred at room temperature for 2 h. 1,3-Di(bromomethyl)benzene was added to the solution. The reaction mixture was stirred for 24 h. The reaction was quenched by adding ice water (~100 mL). The powder was collected by filtration, washed with hexane and dried.

Synthesis of L2. A white powder was obtained by the treatment of 2-(4-methoxyphenyl)-1H-benzimidazole (800 mg, 3.6 mmol), 1,3-di(bromomethyl)benzene (471 mg, 1.8 mmol), KOH (400 mg, 7.1 mmol) and DMF (10 mL). Yield: 61% (600 mg). ESI (HR-MS). Calcd for C₃₆H₃₁N₄O₂ [M + H]⁺: *m/z* 551.2447. Found: *m/z* 551.2456. ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.69 (d, *J* = 7.92 Hz, 2H, H⁴), 7.39 (d, *J* = 8.8 Hz, 4H, H^{2',6'}), 7.29 (d, *J* = 7.92 Hz, 2H, H⁵), 7.24 (t, *J* = 7.32 Hz, 3H, H^{7,11}), 7.17 (t, *J* = 7.08 Hz, 2H, H^{10,12}), 6.96 (d, *J* = 7.72 Hz, 2H, H⁶), 6.88 (d, *J* = 8.84 Hz, 4H, H^{3',5'}), 6.54 (s, 1H, H⁹), 5.42 (s, 4H, H⁸) and 3.7 (s, 6H, -OCH₃). ¹³C NMR (500 MHz, DMSO-*d*₆) 160.65, 153.68, 143.17, 138.14, 136.18, 130.81, 129.68, 125.57, 123.92, 122.81, 122.63, 122.50, 119.53, 114.51, 111.22, 55.72, 47.73.

Synthesis of L3. A white powder was obtained by the treatment of 2-(3,5-dimethoxyphenyl)-1H-benzimidazole (800 mg, 3.1 mmol), 1,3-di(bromomethyl)benzene (415 mg, 1.5 mmol), KOH (353 mg, 6.3 mmol) and DMF (10 mL). Yield: 98% (941 mg). ESI (HR-MS). Calcd for C₃₈H₃₅N₄O₄ [M + H]⁺: *m/z* 611.2658. Found: *m/z* 611.2651. ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.71 (d, *J* = 7.84 Hz, 2H, H⁴), 7.32 (d, *J* = 7.92 Hz, 2H, H⁷), 7.27–7.16 (m, 5H, H^{5,10–12}), 6.87 (d, *J* = 7.4 Hz, 3H, H^{6,9}), 6.75 (d, *J* = 2.16 Hz, 4H, H^{2',6'}), 6.61 (s, 2H, H^{4'}), 5.50 (s, 4H, H⁸), 3.64 (s, 12H, -OCH₃). ¹³C NMR (400 MHz, DMSO-*d*₆) 160.90, 153.36, 142.93, 138.23, 136.33, 132.18, 129.86, 125.57, 124.42, 123.22, 122.70, 119.77, 111.26, 107.30, 102.39, 55.68, 47.94.

Synthesis of L4. A white powder was obtained by the treatment of 2-(3,4,5-trimethoxyphenyl)-1H-benzimidazole (800 mg,

2.8 mmol), 1,3-di(bromomethyl)benzene (371 mg, 1.4 mmol), KOH (320 mg, 5.7 mmol) and DMF (10 mL). Yield: 91% (854 mg). ESI (HR-MS). Calcd for C₄₀H₃₉N₄O₆ [M + H]⁺: *m/z* 671.2869. Found: *m/z* 671.2869. ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.70 (d, *J* = 7.84 Hz, 2H, H⁴), 7.32 (d, *J* = 7.96 Hz, 2H, H^{10,12}), 7.24 (t, *J* = 7.86 Hz, 3H, H^{5,11}), 7.18 (t, *J* = 7.12 Hz, 2H, H⁷), 6.91–6.88 (m, 6H, H^{2',6',6'}), 6.83 (s, 1H, H⁹), 5.54 (s, 4H, H⁸), 3.70 (s, 6H, -OCH₃) and 3.60 (s, 12H, -OCH₃). ¹³C NMR (500 MHz, DMSO-*d*₆) 153.47, 153.36, 142.93, 139.19, 138.41, 136.45, 129.83, 125.63, 125.51, 124.07, 123.10, 122.68, 119.64, 111.09, 106.86, 60.54, 56.16, 47.96.

Synthesis of L5. A white powder was obtained by the treatment of 2-(1,3-benzodioxole)-1H-benzimidazole (802 mg, 3.4 mmol), 1,3-di(bromomethyl)benzene (443 mg, 1.7 mmol), KOH (379 mg, 6.8 mmol) and DMF (10 mL). Yield: 85% (831 mg). ESI (HR-MS). Calcd for C₃₆H₂₇N₄O₄ [M + H]⁺: *m/z* 579.2031. Found: *m/z* 579.2027. ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.67 (d, *J* = 7.92 Hz, 2H, H⁴), 7.27 (d, *J* = 7.88 Hz, 2H, H⁵), 7.22 (t, *J* = 7.08 Hz, 3H, H^{7,11}), 7.15 (t, *J* = 7.88 Hz, 2H, H^{10,12}), 7.09 (d, *J* = 1.48 Hz, 2H, H²), 6.94–6.90 (m, 4H, H^{6,5'}), 6.86 (d, *J* = 8.04 Hz, 2H, H^{6'}), 6.56 (s, 1H, H⁹), 6.09 (s, 4H, H^d) and 5.43 (s, 4H, H⁸).

General synthetic approach for 1–5

A mixture of Re₂(CO)₁₀, Lⁿ and H₂-RBC in toluene in a Teflon flask was placed in a steel bomb. The bomb was placed in an oven maintained at 160 °C for 48 h and then cooled to 25 °C. The resulting crystalline products were separated by filtration, washed with distilled hexane and air-dried.

Synthesis of 1. Greenish yellow crystals of **1** were obtained from Re₂(CO)₁₀ (100.2 mg, 0.1536 mmol), H₂-RBC (76.3 mg, 0.1542 mmol), **L1** (73.2 mg, 0.1492 mmol), toluene (10 mL) and acetone (2 mL). Yield: 26% (120 mg; crystals). Anal. calcd for C₁₄₄H₉₂N₁₆O₁₆Re₄: C, 56.76; H, 3.04; N, 7.35. Found: C, 56.69; H, 3.12; N, 7.41. ESI (HR-MS). Calcd for C₁₄₄H₉₃N₁₆O₁₆Re₄ [M + H]⁺: *m/z* 3048.5194. Found: *m/z* 3048.7418. FT-IR (KBr, cm⁻¹): ν = 2017(s), 1898 and 1862(s).

Synthesis of 2. Greenish yellow crystals of **2** were obtained from Re₂(CO)₁₀ (100.5 mg, 0.154 mmol), H₂-RBC (76.4 mg, 0.1545 mmol), **L2** (82 mg, 0.1498 mmol), toluene (10 mL) and acetone (2 mL). Yield: 12% (56 mg; crystals). Anal. calcd for C₁₄₈H₁₀₀N₁₆O₂₀Re₄: C, 56.12; H, 3.18; N, 7.08. Found: C, 56.27; H, 3.12; N, 7.23. ESI (HR-MS). Calcd for C₁₄₈H₁₀₁N₁₆O₂₀Re₄ [M + H]⁺: *m/z* 3168.5618. Found: *m/z* 3168.8069. FT-IR (KBr, cm⁻¹): ν = 2013(s), 1903 and 1862(s). ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.56 (d, *J* = 8.6 Hz, 4H), 8.58 (d, *J* = 8.56 Hz, 4H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.62–7.14 (t, m, 32 H, compound + toluene), 6.9 (m, 9H), 6.19 (d, *J* = 7.2 Hz, 4H), 5.98 (d, *J* = 8.7 Hz, 4H), 5.76 (t, *J* = 7.4 Hz, 4H), 5.4 (m, 8H), 5.3 (m, 8H), 5.58 (d, *J* = 18.2 Hz, 4H) and 3.76 (s, 6H).

Synthesis of 3. Greenish yellow crystals of **3** were obtained from Re₂(CO)₁₀ (100.8 mg, 0.1548 mmol), H₂-RBC (76.2 mg, 0.1541 mmol), **L3** (91 mg, 0.1488 mmol), toluene (10 mL) and acetone (2 mL). Yield: 22% (109 mg; crystals). Anal. calcd for C₁₅₂H₁₀₈N₁₆O₂₄Re₄: C, 55.53; H, 3.31; N, 6.82. Found: C, 55.43; H, 3.38; N, 6.75. ESI (HR-MS). Calcd for C₁₅₂H₁₀₉N₁₆O₂₄Re₄

$[M + H]^+$: m/z 3288.6041. Found: m/z 3288.7196. FT-IR (KBr, cm^{-1}): $\nu = 2012(\text{s})$, 1900 and 1867(s).

Synthesis of 4. Greenish yellow crystals of **4** were obtained from $\text{Re}_2(\text{CO})_{10}$ (100.2 mg, 0.1536 mmol), $\text{H}_2\text{-RBC}$ (76 mg, 0.1537 mmol), **L4** (100 mg, 0.1485 mmol), toluene (10 mL), and acetone (2 mL). Yield: 31% (155 mg; crystals). Anal. calcd for $\text{C}_{156}\text{H}_{116}\text{N}_{16}\text{O}_{28}\text{Re}_4$: C, 54.99; H, 3.43; N, 6.58. Found: C, 55.43; H, 3.38; N, 6.75. ESI (HR-MS). Calcd for $\text{C}_{156}\text{H}_{117}\text{N}_{16}\text{O}_{28}\text{Re}_4 [M + H]^+$: m/z 3408.6464. Found: m/z 3408.6287. FT-IR (KBr, cm^{-1}): $\nu = 2013(\text{s})$, 1899 and 1863(s). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 8.65 (d, $J = 8.4$ Hz, 4H), 7.99 (d, $J = 4\text{H}$), 7.89 (t, $J = 8$ Hz, 4H), 7.44–6.96 (t, t, and m, 52 H, compound + toluene), 6.81 (s, 2H), 6.79 (t, $J = 7.8$ Hz, 2H), 6.31 (d, $J = 8.4$ Hz, 4H), 6.05 (d, $J = 7.2$ Hz, 4H), 5.65 (t, $J = 7.4$ Hz, 4H), 5.51 (d, $J = 18.8$ Hz, 4H), 5.37 (d, $J = 8$ Hz, 4H), 5.24–5.19 (t and s, 8H), 4.37 (d, $J = 18.8$ Hz, 4H), 3.38 (s, 8H, $-\text{OCH}_3$) and 3.29 (s, 10H, $-\text{OCH}_3$).

Synthesis of 5. Green crystals of **5** were obtained from $\text{Re}_2(\text{CO})_{10}$ (100.3 mg, 0.1537 mmol), $\text{H}_2\text{-RBC}$ (76 mg, 0.1537 mmol), **L5** (86.3 mg, 0.1488 mmol) in toluene (10 mL) and acetone (2 mL). Yield: 17% (84 mg; crystals). Anal. calcd for $\text{C}_{148}\text{H}_{92}\text{N}_{16}\text{O}_{24}\text{Re}_4$: C, 55.15; H, 2.88; N, 6.95. Found: C, 55.21; H, 2.83; N, 7.06. ESI (HR-MS). Calcd for $\text{C}_{148}\text{H}_{93}\text{N}_{16}\text{O}_{24}\text{Re}_4 [M + H]^+$: m/z 3224.4788. Found: m/z 3224.4948. FT-IR (KBr, cm^{-1}): $\nu = 2017(\text{s})$, 1899 and 1863(s).

X-ray crystallography

Intensity data of crystals of **1–5** were collected on a Bruker D8 Quest diffractometer [$\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$]. The structures were solved by direct methods using SHELXS-97¹¹ and refined using the SHELXL-2018/3 program (within the WinGX program package).^{11b,c} Non-H atoms were refined anisotropically. Two methoxy units in **3** and **4** are disordered. Two 1,3-benzodioxole units are disordered in **5**. The majority of the solvent molecules in the complexes could not be modelled correctly, and hence their contribution to the intensities was excluded using the SQUEEZE option in PLATON.^{11d} The intensity data of crystal of **L4** were collected on an Oxford CCD X-ray diffractometer (Xcalibur, Eos, Gemini) [$\lambda(\text{Cu K}\alpha) = 1.54184 \text{ \AA}$] and data reduction was performed using CrysAlisPro 1.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank the University of Hyderabad and the DST-SERB (EMR/2015/000627) for financial support. Dedicated to Prof. V. Chandrasekhar on the occasion of his 60th birthday.

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