Synthesis, Characterization and Properties of Hyperstructured Molecules and Polymers Based on Inorganic-Organic Hybird Core Containing Phosphorous

A Thesis Submitted for the Degree of

DOCTOR OF PHILOSOPHY

By

KHEVATH PRAVEEN KUMAR NAIK

(08CHPH17)

School of Chemistry
University of Hyderabad
Hyderabad 500046, Andhra Pradesh, India
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DEDICATED

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WELL WISHERS

STATEMENT

I hereby declare that the matter manifested in this thesis,**“SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF HYPERSTRUCTURED MOLECULES AND POLYMERS BASED ON INORGANIC-ORGANIC HYBRID CORE CONTAINING PHOSPHOROUS”** is the result of research carried out by me in the Department of Chemistry, Hyderabad Central University, India under the supervision of Dr. K. Muralidharan.

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

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CERTIFICATE

Certified that the work contained in the thesis entitled **“SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF HYPERSTRUCTURED MOLECULES AND POLYMERS BASED ON INORGANIC-ORGANIC HYBRID CORE CONTAINING PHOSPHOROUS”** has been carried out by **Mr. K. Praveen Kumar Naik** under my supervision and the same has not been submitted elsewhere for any degree.

Dr. K. Muralidharan

(Thesis supervisor)

Dean

School of Chemistry

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K.PRAVEEN KUMAR NAIK
HCU, Hyderabad

CONTENTS

CHAPTER 1

LIST OF ACRONYMS

HRMS	High Resolution Mass Spectroscopy
MALDI	Matrix Assisted Laser Desorption Ionization
DSC	Differential Scanning Calorimetry
Tg	Thermogravimetric Analysis
NMR	Nuclear Magnetic Resonance
UV-Vis	Ultra Violet Visible
MHz	Mega Hertz
SPE	Solid Polymer Electrolyte
TPA	Two Photon Absorption
LiTFSI	Lithium bis-trifluromethanesulfonimide
NLO	Nonlinear Optics
$LiClO_4$	Lithium perchlorate
DMAc	N, N–dimethylacetamide
THF	Tetrahydrofuran
KPF_6	Hexafluropottasium phosphate

SYNOPSIS

Name of the Student: K. Praveen Kumar Naik

Registration Number: 08chph17

School/Department: School of Chemistry

Degree for which submitted: Ph.D

Thesis Supervisor: Dr. K. Muralidharan

THESIS TITLE: "SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF HYPERSTRUCTURED MOLECULES AND POLYMERS BASED ON INORGANIC-ORGANIC HYBRID CORE CONTAINING PHOSPHOROUS".

This thesis deals with the synthesis, characterization and application of new inorganic-organic hybrid hyperstructured molecules which were built on inorganic heterocyclic rings as core. The thesis also deals with the polyethers containing phosphorous. Property and application studies on these hyperstructured molecules and polymers include luminescence, NLO properties and Li-ion conductivities. The thesis is divided into four chapters.

CHAPTER 1: GENERAL INTRODUCTION

This chapter presents a concise review on the concept of dendrimer and their structure property relationships and applications. The application of hyperstructured molecule based on inorganic-organic core moieties, (known as hybrimer) towards the designing of electroluminescent materials, solid electrolytes for Li- ion batteries and their role in non-linear optics has been described here. This sets the stage for the scope of work carried out in the current thesis.

Figure 1: Hyperstructured molecule based on organic and inorganic core moities

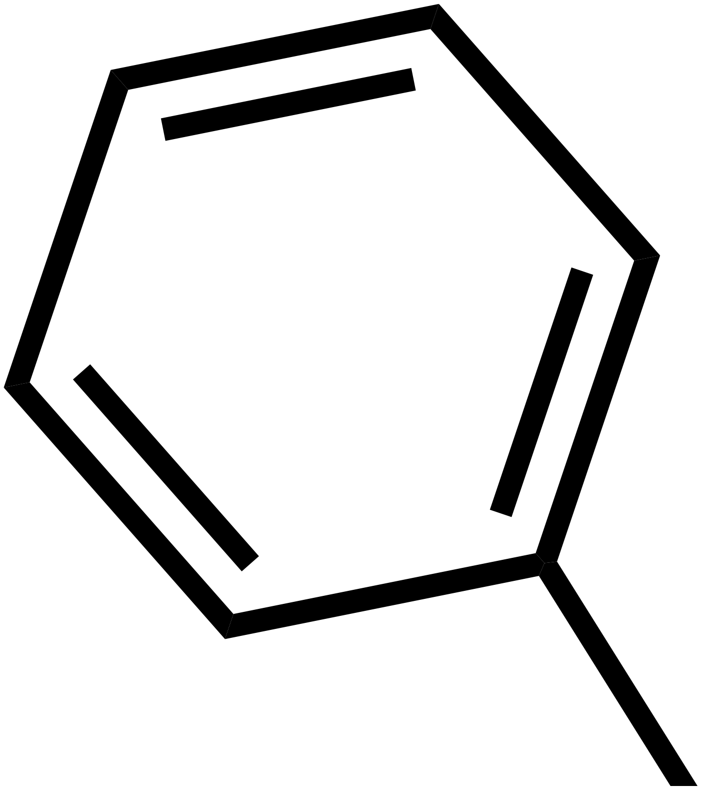
CHAPTER 2: REACTIVITY STUDY ON CYCLOCARBAPHOSPHAZENES AND SYNTHESIS OF HYPERSTRUCTURED MOLECULES USING CYCLOCARBAPHOSPHAZENE AND CYANURIC CHLORIDEAS CORES

This chapter describes the reactivity and applications of cyclocarbaphosphazenes.Compared to the known reactivity of the carbaphosphazenes, we observed a difference in the reactions of dicarbaphosphazenes with 1-methyl imidazole and potassium fluoride (Schemes 1 and 2).This reactions study also explained the non-existence of perfluorinated cyclocarbaphosphazene. The results obtained from these reactions are described in this chapter. Apart from the reactivity study, the cyclocarbaphosphazene and cyanuric chloride were used as core moieties to produce inorganic-organic hybrid hyperstructured molecules known as hybrimers. These molecules were synthesized, in which all chlorine atoms were replaced by simple nucleophilic substitution.

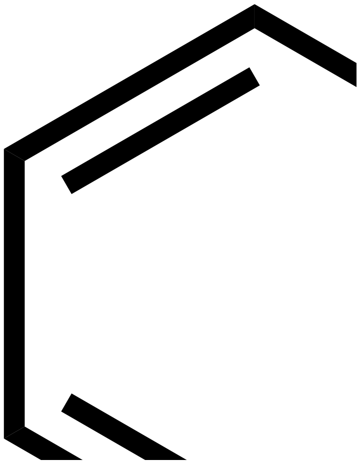
Scheme 1: Reaction of carbaphosphazene with potassium fluoride

[redacted]

Scheme 2: Reaction of cyclocarbaphosphazene with *N*-methylimidazole



Scheme 3: Synthesis of hyperstructured molecule based on carbaphosphazene core.



Scheme 4: Synthesis of hyperstructured molecule based on cyanuric chloride core.

CHAPTER 3: SYNTHESIS OF HYPERSTRUCTURED MOLECULES BASED ON CYCLOPHOSPHAZENE CORE AND THEIR NON-LINEAR OPTICAL PROPERTIES, Li-ION CONDUVTIVITIESAND FLOURESCENT STUDIES

This chapter highlights the construction of hyperstructured molecules taking a cyclotriphosphazene which is a robust inorganic planar non-delocalized cyclic ring consisting of alternate N and P atoms. The hyperstructured molecules were synthesized through simple nucleophilic substitution reaction and it is characterized by MALDI and HRMS and their purity was checked by $^{31}P\{^{1}H\}$ NMR.

Scheme 5: Synthesisof hyperstructured molecules based on cyclophosphazene core.

The present chapter is mainly focused on the studies of Li- ionconductivity and nonlinear optical properties of hyperstructured molecule. The conductivity of one of the hyperstructured molecules (H_7) was found to be 10^{-4} Scm^{-1}. After exposing to moisture it was decreased to 10^{-5} Scm^{-1}. The fluorescence quantum yield of the hyperstructured H_9molecule was found to be 10%.The two photon absorption and three photon absorption of hyperstructured $\mathbf{H_7}$ molecule and hyperstructured $\mathbf{H_8}$ molecule were also determined.

CHAPTER 4: SYNTHESIS OF INORGANIC-ORGANIC HYBRID POLYETHER CONTANING PHOSPHORUS AND THEIR Li-ION CONDUCTIVITIES

Synthesis of phosphorus containing polyethers and their lithium-ion conductivities for the potential use as solid polymer electrolyte (SPE) in high-energy density lithium-ion batteries have been described. Copolymerization of butyl bis(hydroxymethyl)phosphine oxide with three different dibromo monomers were carried out to produce three novel phosphorous containing polyethers (**P1**-**P3**). These polymers were obtained via nucleophilic substitution reactions and were characterized by ^{1}H, ^{31}P NMR spectral data and gel permeation chromatography. SPEs were prepared using polyethers (**P1** and **P2**) with various amounts of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). The lithium-ion conductivity of **SPE2** containing 40 wt% of LiTFSI was 2.1×10^{-5} S cm^{-1} at room temperature and 3.7×10^{-4} S cm^{-1} at 80°C.

Scheme 6: Synthesis of the inorganic-organic hybrid polyethers

CHAPTER 1

GENERAL INTRODUCTION

Abstract:

This chapter presents a concise review on the concept of dendrimer and their structure property relationship and applications. The application of hyperstructured molecule based on organic and inorganic core moieties, (known as hybrimer) towards the designing of electroluminescent materials, solid electrolytes for Li- ion batteries and their role in non-linear optics has been described here. This sets the stage for the scope of work carried out in the current thesis.

Hyperstructured molecule based on organic and inorganic core moieties

1.1. Dendrimers

The design of molecules for various applications in different field is the most challenging one. The challenge can be met with well-known macromolecules known as Dendrimers. Dendrimers are molecules having big size and represents a family of highly branched, fractal–like macromolecule of defined three dimensional shapes and topology which can be prepared with narrow molecular weight distribution [1].The branch of dendrimer was introduced by Voegtle, Tomalia and Newkome [2].The study of these dendrimer expands to all areasincluding theory, synthesis, characterization of structures, properties, and investigations of potential applications as the structure of these materials has great impact on physical and chemical properties [3].The basic moieties of the dendrimer consists of core where the dendrons (originates like a tree), internal cavity, terminal functional group branching center, from where dendrons are generated **(figure-1.1)** [4].

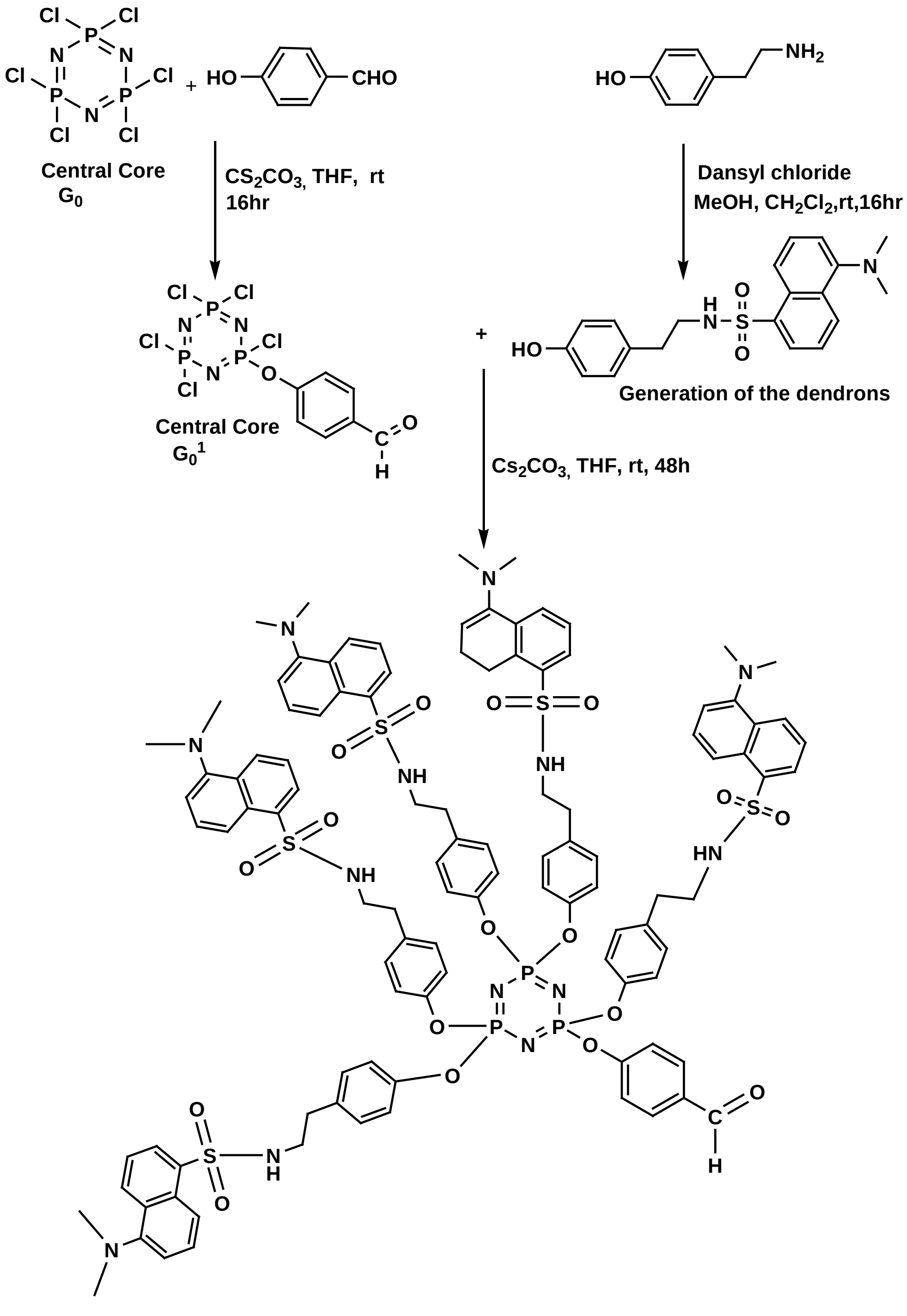
Figure 1.1: Global scheme of dendrimer

1.2. Synthetic Approach for Dendrimers

Two main complementary synthetic strategies were developed for the construction of dendrimer in a stepwise manner, through divergent and convergent approach [5]. Both these synthetic strategies have their own advantages and disadvantages. The **figures 1.2 and 1.3** depict a schematic explanation of both the approaches.

Figure 1.2: Schematic representation for the convergent synthesis of dendrimers

In convergent approach, initially the growing arm polymeric branch, known as dendrons are generated and attached to the multifunctional core molecule and the dendrimeris constructed stepwise; starting from the end groups and propagates towards the central core **(Figure1.2)**. This approach allows easy molecular design, great flexibility, and compatibility with standard purification, and ideal yields which allows the chemist, to offer a number of unique opportunities for the precise construction of nanoscale structure. Therefore convergent approach is very much significant where synthetic and functional versatility reflects the purest synthetic approach for macromolecules known today. For example, in **scheme1.1**, the dendrons were generated and attached to the cyclophosphazene core to get G_1 generation by nucleophilic substitution reaction [6].



Scheme 1.1: Synthesis of fluorescent material based on cyclophosphazene as central core via convergent method

In divergent approach, the dendrons grow outwards from the multifunctional core molecule, where branching is continued through a series of repetitive addition and activation steps which multiply the number of branches **(Figure-1.3)**. The generation of the core proceeds from the central core to the periphery. This method is characterized by rapid increase in the number of reactive groups at the periphery of the growing of macromolecule. The major drawback of this approach is that structure defects arises due to side reactions and incomplete reaction of the end group, to avoid these defect large quantity of reagents are required, which causes some difficulties in the purification of the final product. For example, in **scheme 1.2**, the dendrimer starts from a cyclophosphazene core, the branches or arms were extended up to G_1 generation by simple nucleophilic substitution reaction. The G_2 generation was achieved by doing coupling reaction in presence of palladium as the catalyst [7].

Figure 1.3: Schematic representation for the divergent synthesis of dendrimers

1.3. Inorganic Heterocyclic Compounds and Hybrimers

Many dendritic polymer possessing organic, inorganic, organometallic functionalities have been synthesized during the last decade are known as hybrimers. These inorganic-organic hybrid materials may minimize the amount of packing materials and also reduces the number of dyads [8]**.** The influence of organic and inorganic, hybrids known as hybrimers, has not only find application as precursors for inorganic polymers, but also in finding the unique heterocyclic frame work useful for novel reactions and applications. The synthesis of new inorganic-organic hybrid macromolecules attracted a wide spread current interest and intense research because they possess useful electrical, optical, thermal, and biomedical characteristics. The two entirely different classes of well-studied heterocyclic compounds are cyclophosphazene and cyanuric chloride, the former known to be inorganic heterocycles, while the latter is organic and aromatic heterocycles [9].

Scheme 1.2: Synthesis of dendrimer based on cyclophosphazene as central core via divergent method

The unique inorganic skeleton with alternating nitrogen and phosphorus atoms and a wide variety of side group is phosphazene, which form a broad class of small molecule and high polymeric compound. Much investigation has been made on the chemistry of inorganic heterocyclic like cyclictriphosphazenes and organic heterocyclic like s-triazenes(cyanuric chloride) [10]. One of the robustic inorganic heterocyclic ring with alternate P=N bond system is hexachlorocyclophosphazene with six labile groups that can be substituted with desired groups like pyrazoles, pyridine, hydrazones, hydrazine moieties have been synthesized and extensively studied for their metal complexing properties [11]. The cyclotriphosphazene, (CP) is well documented, due to their unique structural frame work, reactivity of the P-Cl bonds and orientation of substituents around the heterocycle, which make them to be useful as stables core for dendrimer synthesis [12], scaffolds for multicenter ligand [13] and design of unique supra molecular networks [14] and as supramolecular chemistry [15]. The optical and electronics properties are dependent on dendrons and not the CP cores. Being stable and inert the CP cores does not break down under the rather aggressive chemical conditions used during the synthesis. CP is an interesting class of materials that offer access to solution processable dendrimeric materials which are completely due their three dimensional architecture that minimizes aggregation due to pi-pi stacking [16] that is useful in photonic application with phosphorescent molecule like pyren [17].

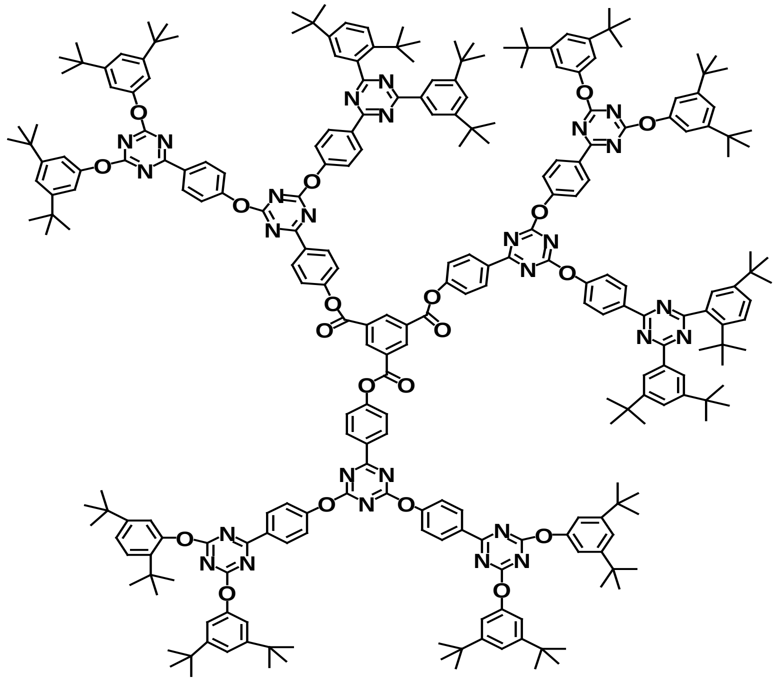


Figure 1.4: Structural diversity dendrimerbased on cyanuric chloride

Cyanuric chloride is the trimer of cyanogen chloride, and much of the chemistry is developed due to the high stability of the ring stabilized by resonance [18]. Most of the dendrimer was synthesized by taking cyanuric chloride as core, either by convergent or divergent approach. The incorporation of this core into dendrimers provides opportunities [19] (a) to exploit different reactivity of triazine, due to the three chlorine atoms which can be easily replaced by nucleophilic substitution reaction, (b) Significant structural diversity dendrimers can be prepared [20] (c) For molecular recognition domains are introduced [21].

The chemistry of cyclocarbaphosphazene can be considered as the linking heterocycles between cyclophosphazenes and s-triazines as they contain both P-N and C-N moieties as part of their ring framework. Their structures, properties, and reaction behavior can be linked to both cyanuric chloride as well as pure inorganic heterocyclic compounds such as cyclophosphazenes **(figure1.5).** The presence of carbon atom in carbocyclophosphazene makes its different in the reactivity of C-Cl and P-Cl bonds which shows interesting selectivity in their substitution reaction which recently has been the subject of detailed investigations [22]. However, the formation of the dendrimer from terachlorodicarbophosphazene and diphenylcarbophosphazene as core is not yet reported [23, 24].

Figure 1.5: Schematic representation of structural transformation of an inorganic heterocyclic compound to the organic heterocyclic compound.

1.4. Structure Property Relationship and Applications of Dendrimers

Due to the well-defined three dimensional sizes, shape and topology, and combining functional units, this dendrimeric material has been much focused on their discovery and development for the potential use for the variety of applications **(Figure 1.6)**. Some of the interesting structure property relationships are discussed below.

i. Due to their size, shape, flexibility and surface chemistry which can be precisely controlled at the molecular level, dendrimers are widely used in the construction of nanostructure and various self-assemblies.
ii. The morphology and structure of these macromolecules is controlled due to their three dimensional scaffolds which control the electronic process, tenability, interfacial effects and inter and intramolecular cross linking band gap [25]**.**
iii. The large surface of the dendrimer, due to their globular shape that can be decorated with chromophore, helps in efficient capture of photons and absorption [26].

iv. The dendrimer, whose molecular weight lies in the range of 1000-10000 $gmol^{-1}$ are found to be very advantageous, since their properties lies intermediate between polymer and small molecules [24]. With controlled molecular weight and high regularity, these dendrimers can be obtained in both the approach, either convergent or divergent approach [27].

Figure 1.6: Applications of dendrimers

v. The introduction of bulky substituents in a dendrimer hinders the packing of these molecules and imparts amorphous behavior. This structure creates a microenvironment to avoid dipole-dipole and intermolecular interaction and prevents self-quenching effect, especially where flurophores possess highly concentration dependent emissions and have an inherent tendency to aggregate in the solid state [28].

vi. The linear or branched dendrimers provides a space for the incorporation of specific components which serve as a hole injecting, hole transporting, electron transporting or hole blocking materials, which gives a route to find their application towards the area of organic electronic device like organic solar cell, light emitting electrochemical cell, organic optical detectors, organic receptors, and organic electroluminescent device.

vii. The dendrons are generated with triarylamine and carbazole as precursor, which are well known to be hole transporting materials and found to be suitable for application in organic electronic device and NLO properties.

1.5. Dendrimers for Electroluminescence Devices

In the past few decades, there has been tremendous interest in the development of fluorescent materials, for a wide range of applications especially related to biology and device technologies. Some of the important applications are chemical sensors, biological labeling, medical diagnostics, DNA sequencing, forensics, genetic analysis, cellular and molecular imaging, fluorescentlamps, lasers, light emitting diodes and displays. Dendrimers based on electro active polymers are of current interest for designing material devices for photonic applications. The photo physical properties of dendrimers like exciton and charge localization phenomena, generation dependent carrier mobility and cross linking phenomenon are also a broad fundamental interest. The ultimate properties of the dendrimer can be determined by individual dendrimers and dendrimeric functional groups at polymer chain ends or in well-defined segments, providing controlled material system.Based on this criteria, many report and attempt have been done by incorporating chromophore functional group into the periphery,the branching units and the interior core of a dendrimer using either divergent or convergent approach. The advantages of dendrimersfor electroluminescence devices are listed below.

i. The major role of dendrimers is that, its properties combine the small molecules and polymer for photonic applications.
ii. When compared to the polymers, the purity can be achieved by using simple chromatographic techniques, to form uniform films by spin coating technique, thus overcoming the high cost of vacuum deposition which is important for electroluminescent device.
iii. Due to their monodisperse in nature, these macromolecules are soluble in common solvent and allows synthetic versatility for tuning charge transport and emissive.
iv. The three dimensional architecture dendrimer it provides opportunities for precisely placing charge-carrier transporting units by generation and also helps in preventing interactions between adjacent conjugated moieties that prevent the formation of aggregate or excimers that are known to reduce the device efficiency.

1.5.1. Cores for designing electroluminescent dendrimers

Luminescent core

The luminescent dendrimer mainly consists of three units, an emissive core, dendrons, and peripheral groups. The well-defined and modular construction enables the processing and electronic properties to be tuned independency. For designing dendrimer structure, the core plays the major role for developing generations (like G_1,G_2). They can be designed to possess conjugate cores for an efficient emission and for charge transport and appropriate terminal group or chain for good processibility. In the **figure–1.7**, perylenebis(dicarboximides) is the luminescent core decorated with specific functional group (like carbazole) at the periphery.It is constructed by flexible frechet-type poly(arylther) dendrimers, which plays an important role in carrier-tansport injection and light harvesting for core chromophore. The well aligned energy level of carbazole-naphthalene dicaboximide-perylenebis(dicarboximide) flourophores, the naphthalene dicarboximide unit can play a role in cascade energy transfer from the carbazole to the core perylenebis(carboximide) unit.

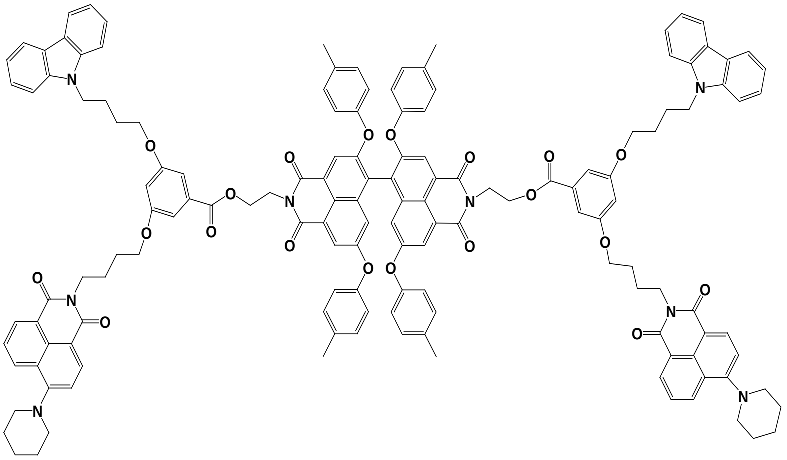


Figure 1.7: Perylenebis(dicarboximides) luminescent core target dendrimer

Non luminescent core

In case non-luminiscent core, like cyclophosphazene non optical or electronic contribution was observerd. Recent work by Sundarraysudhakar and Allan sellinger designed nano composite dendrimer cyclic phosphazene cores. The use of insulating cyclophosphazene cores combined with hole-transport/emissive properties of peripherally attached arylaminopyrene. Since there is no electronic effect from the core, it provides a platform for improving the material properties such as high glass transistion temperature, thermal and chemical stability, monodispersity solubility and high purity. Apart from these benefit, these cyclophosphezene is well studied in both linear as well as cyclic form because of their diverse properties such as excellent hydrolytic stability, thermal stability, flame retardant properties and liquid crystalline behavior to name few.

Figure 1.8: Flourescent (A) and Phosphorescent (B) hyperstructured moieties based on cyclophosphazene core

1.6. Solid Electrolytes for Li-ion Batteries and Dendrimers

A battery can be defined in a simple manner which converts chemical energy into electrical energy or electrical energy into chemical energy. To perform this task, electrolytes perform crucial role,in the transfer of ion in the chemical reduction-oxidation reaction occurring at electrodes of an electro chemical cell resulting in electrical energy. Lithium is the most attractive anode material since it has the highest reduction potential (-3.0 V versus standard hydrogen electrode) and has the lowest density (0.534 g/cm^3). Highest reduction potential of lithium anode is able to afford high cell voltage when it is combined with cathodes. Moreover, the light weight, lithium metal provides high specific capacity of about 3.86 Ah/g [29, 30, 31].The following features are made the lithium based batteries particularly suitable for electronic applications.

- *High cell voltage:* The high energy density is attributable to the operating voltage of lithium batteries (3-4 V). As a result, compared with aqueous batteries, number of cells in a battery pack can be reduced by a factor of 2 or 3.
- *Low temperature performance:* Lithium batteries can function even at temperatures of around -40°C because of low freezing point of non-aqueous solvents. The conductivity of lithium batteries at cold temperature is far better than the previous aqueous batteries.
- *Long shelf life:* The storage limits of lithium batteries are in the range of 5-10 years. The self-discharge is restricted might be due to the formation of SEI on lithium.

The lithium metal is both ductile and malleable. Freshly cut shiny surface of lithium rapidly turns greyish-white to grey or black in air. So the assembly of lithium batteries should be done in ‘Dry rooms’. Handling of lithium is comparatively safer than other alkali metals. The efficient internal energy supply, their storage and conversion is one of the challenging demands which can be overcome by the development of rechargeable lithium ion batteries, considered to be electrochemical storage of Green energy, for mobile and portable electric and electronic device.

Primary battery based on lithium

Some of the potential primary non-aqueous batteries using lithium anode are lithium-manganese dioxide battery, lithium–carbon monofluoride battery and lithium- thionyl chloride. The Li-$(CF_X)_n$ is a 2.8V battery combining a lithium anode and a carbon monoflouride $(CF_X)_n$ cathode. In all primary lithium batteries, lithium act as anode and the discharge reaction at anode as follows.

$$nLi + (CF)_n \longrightarrow ne^{\ominus} + nLiF$$

	Cathode	Electrolyte	Operating voltage (V)	Specific energy (Wh/ kg)	Energy density (Wh/L)
Li-(CFX)n	(CFX)n	organic liquid	2.8	235	330-580

Reaction at cathode $(CF)_n + ne^{\ominus} \longrightarrow nC + nF^{\ominus}$

Over all reaction $nLi + (CF)_n \longrightarrow nC + nLiF$

Figure 1.9: Electrochemical reactions and energy parameters of lithium-carbon monoflouride battery

Secondary batteries based on lithium

Due to the portability and usability over a period, secondary batteries are more advantageous than primary batteries; hence it is used in automobiles and utilization of electricity from photovoltaic devices especially in night. The four important second batteries bases on lithium are tabulated in **table 1.1**.Among the four types of battery lithium oxygen battery is given more importance, due to their high energy density.In case of lithium sulfur batteries, although it possess high theoretical specific energy,it suffers from the dendrite formation, cycling efficiency, safety issue, decomposition of electrolytes, blocking of porous electrode by produced solid product such as Li_2O_2, LIO and Li_2S.

Table 1.1: Properties of secondary lithium ion batteries

Type of battery	Operating Voltage(V)	Theoretical specific energy (Wh/Kg)	Theoretical Energy density (Wh/L)
Lithium-ion	3.8	387	1015
Non-aqueous Li-O_2	3.0	3505	3436
Aqueous Li-O_2	3.2	3582	2234
Li-S	2.2	2567	2199

Electrolytes for Li-ion batteries

The electrolytes used in the Li-ion batteries can be liquid or solid and they are selected depending on the need. The most effective electrolyte for non-aqueous battery is liquid electrolyte. It consists of lithium salts dissolved in aprotic organic solvents. Widely used lithium salts are $LiPF_6$, $LiAsF_6$, $LiBF_4$, $LiClO_4$, $LiAlCl_4$ $LiCF_3SO_3$, lithium trifluoromethanesulphonate (lithium triflate), $LiN(SO_2CF_3)_2$, LiTFSI (lithium imide) and $LiC(SO_2CF_3)_3$ (lithium methide) [32, 33]. The commonly used organic solvents include cyclic esters (propylene carbonate, ethylene carbonate, γ-butyrolactone), linear esters, cyclic ethers (2-methyltetrahydrofuran, 1,3-dioxolane), linear ethers**,** amides and sulphoxides [34]. The solvent used for electrolyte should have low melting point, high boiling point, low vapour pressure and wide operating temperature range. Further, high permittivity and low viscosity are desirable for the solvent to ensure higher ionic conductivity of electrolyte solution. However; solvents with high dielectric constants have generally high viscosity even at room temperature, resulting in slow transfer of lithium ions, *i.e.*, low ionic conductivity in electrolytes. Hence, the solvents with low viscosity are mixed with the solvents described above in order to lower the viscosity of electrolyte system and to increase ionic conductivity [31, 32]. The common solvents used to decrease the viscosity are tetrahydrofuran, dimethoxyethane, diethyl carbonate (DEC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) **(Figure 1.10).**

Figure 1.10: Structures of organic solvent used in non-aqueous batteries as electrolyte

Solid Polymer Electrolytes (SPE)

The use of liquid electrolyte has several disadvantages with regard to long term performance and safety. Organic electrolytes is found to be uncontrolled in large batteries, due to high flammability, abrupt leakage when mechanical forces are applied (in car accidents) and uncontrolled discharge (short circuits) may lead to ignition**.** Hence the replacement of the liquid electrolyte with a thin polymer membrane is highly desirable. Therefore, much effort has been focused to develop solvent free ionic conducting polymer electrolytes over the last decades [35]. Albeit **SPE**s have more advantages over organic liquid electrolyte, the lithium-ion conductivity of **SPE**s is much lesser than the organic liquid electrolyte (~ 10^{-3} S cm^{-1}) by a factor of 1/10 – $1/10^3$. Since the room temperature ionic conductivity of poly(ethylene oxide) (PEO) is too low (10^{-7} S cm^{-1}) for practical applications, advanced SPEs are in demand to improve their performance and efficiency [36, 37]. Though various SPEs are under study, polysiloxanes presented in **Table 1.2** showed good lithium-ion conductivity. The flame retardant and high ionic conductivity of polyphosphazenes are very attractive especially in the potential application of larger batteries as **SPE**s. However, both of these polymers exist as liquid at room temperature. Thus, there is an urgent need to find alternative non-flammable electrolytes having good ionic conductivity that are stable.

Table 1.2: Structures of various polymers based on carbon backbone and their lithium-ion conductivities

Entry	**Polymer host**	**Repeat unit**	**Lithium salt**	**Conductivity S cm^{-1} at RT**
1	Poly(oxymethylene)		$LiClO_4$	~ 10^{-8}
2	Poly(ethylene oxide)		$LiClO_4$	~ 10^{-7}
			$LiCF_3SO_3$	1.1×10^{-6}
3	Poly(propylene oxide)		$LiClO_4$	~ 10^{-8}
			$LiCF_3SO_3$	2.2×10^{-6}
4	Poly(oxymethylene-oligo-oxyethylene)		$LiCF_3SO_3$	3.0×10^{-5}
5	Poly(β-propiolactone)		$LiClO_4$	3.5×10^{-6}
6	Poly(ethylene adipate)		$LiCF_3SO_3$	~ 10^{-6}
7	Poly[(2-methoxy) ethyl glycidyl ether]		$LiClO_4$	~ 10^{-5}
8	Poly(methoxy poly(ethylene glycol)methacrylate)		$LiCF_3SO_3$	2.0×10^{-6}
9	Poly (methoxyethoxy ethyl methacrylate)		$LiClO_4$	3.3×10^{-6}

According to the conventional theory, amorphous polymers exhibit ionic conductivity whereas crystalline polymers most likely behave as insulator. The ionic conductivity in amorphous polymer is due to the movement of ions, ensued by the local segmental motion of the polymer chain particularly above its glass transition temperature (Tg). Above Tg, the superstructure of polymers has disordered and flexible environment. Since the polymer chains are in constant motion above its Tg, a vacant space would continually create and disappear, through which an ion move by coordination. It means, an ion has to wait to find a new coordination site and a free volume for hopping. This clearly describes the rate of ion transport depends on local chain dynamics of polymer. Our interest is creating a fixed perpetual free space through which the ion would move without delay. It would improve the mobility of ion leading to higher ionic conductivity. For that, we have chosen to synthesize materials with a needed structural framework for better lithium ion transport **Chapters 3 and 4].**

Dendrimers for solid electrolytes

A new class of macromolecules, dendrimers has been attracting for their highly branched, monodisperse and globular structures. Dendrimers are amorphous in nature which is the crucial requirement for the successful operation of conductivity [38]. Organic and inorganic hybrid materials synthesized by simple nucleophilic substitution reaction recently [39] are promising conducting materials for next generations display. Ionic active polymer based dendrimer are of current interest for developing new generating organic and inorganic hybrid materials. Tomaliaet al. reported the preparation of the carboxylate-terminated PAMAM dendrimers with Group I metals (e.g. Na1, K1, Cs1 or Rb1) for the direct observation and measurement of single dendrimer molecules by electromicrography[40].

The dendrimer and the metal salt are both solid materials and the preparation of dendrmeric salt complex is achieved by the dissolution of the two materials in common solvent such as dry Tetrahydrofuran, Acetonitrlie, followed by a slow removal of the solvent in vacuum. Dendrimers act a host for the solvation of ionic salts during where dendrimer matrix containing heteroatom coordinates to lithium ions [41]. The formation of the complex depends how effectively the dendrimer matrix solvates the ions, and overcomes the lattice energy of the ionic salt, which depends on the Electron pair donor, Acceptor Number and Entropy Number of the matrix. Molecular design of the dendrimer matrix and lithium salt with lower lattice energy is one of the important criteria for obtaining higher conductivity. Attempts have been made to use $LiClO_4$ and $LiCF_3SO_3$, but the best result was obtained with lithium bis-trifluromethanesulfonimide (LiN $(CF_3SO_2)_3$ (often termed as LiTFSI) with its lowered lattice energy has been the most popular one [42].

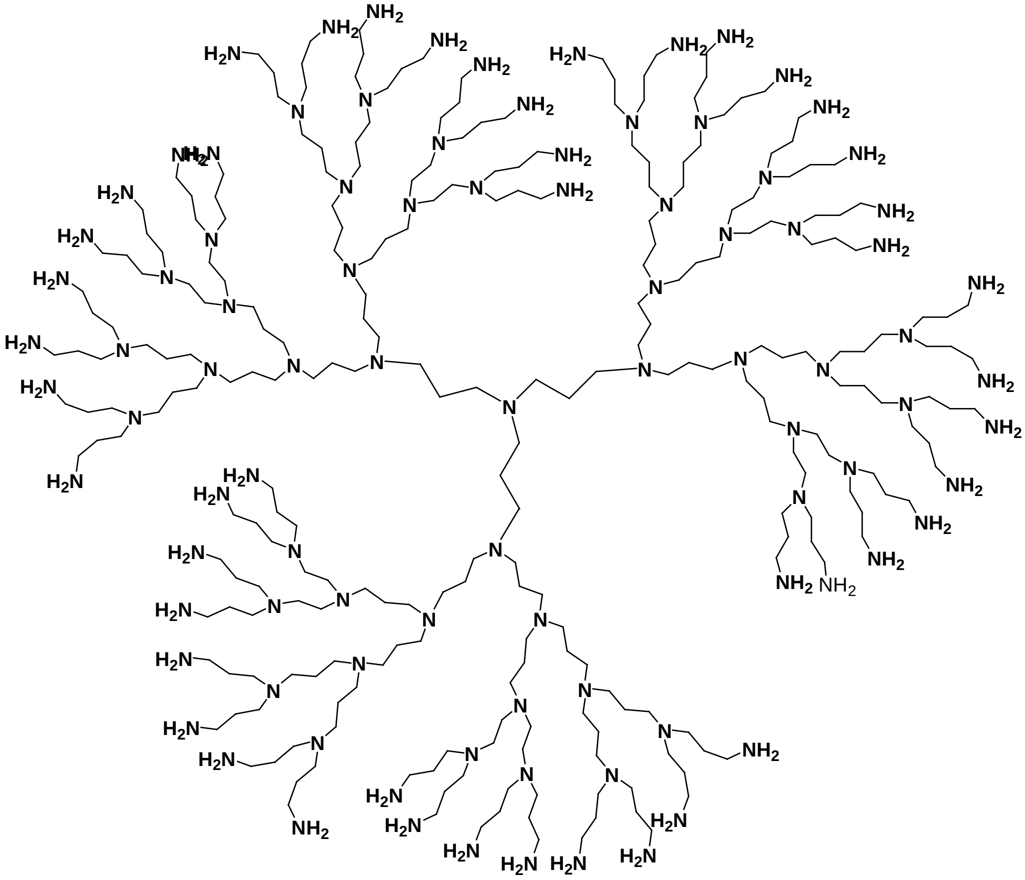


Figure 1.11: Two–dimensional structural representation of the DAB-AM dendrimer exhibiting ionic conductivity

1.7. Role of dendrimer in non-linear optics

Nonlinear optics is the study of phenomena that occur as a consequence of the modification of the optical properties of a material system by the presence of intense light. Typically, only laser light of sufficient intensity can modify the optical properties of a material system. Nonlinear optical phenomena are "nonlinear" in the sense that they occur when the response of a material system to an applied optical field depends on the strength of the optical field in a nonlinear manner.

Due to the promising applications in various fields like three dimensional optical storage data, two photon excited fluorescence microscopy, micro fabrication, two photon up-converted lasing and photodynamictherapy, two photon absorption is gaining importance.The two photon absorption (TPA) process is a third-order nonlinear optical process, in which two photons are absorbed simultaneously via a virtual state. Dendrimers are gaining significant interest towards the synthesis and characterization of many novel and intriguing structures due to their application in two photon absorption,due to its modular architecture, which allows independent tuning of its electrical,optical and processing properties,higher density of effective chromphores as well as strong interchromophore coupling and the formation of delocalized excited state which allows large two photon absorption cross-section.

The design of dendritic architecture, which is important for non-linear optical and light harvesting application, is that due to strong dipole – dipole interaction between the chromphore moieties (with donar-acceptor) make non-centro-symmetric alignment of chromophore moieties under electric field a daunting task during the poling process , due to which beta value increases. To overcome this problem, dendrimer plays a promising molecular topology due to the three dimensional structure in which some isolation groups are bounded to the chromophore moities could decreases the strong intermolecular dipole-dipole interactions and increase the poling efficiency by utilizing the site isolation principle.

Many strategies have been developed, to increase the performance of two photon absorption by increasing the π-conjugation length, introducing electron donor and π-acceptor system, using multipolar and dendritic structures as well as increasing the molecular planarity. To overcome these strategies propeller shaped structure and highly electron rich moiety such as triphenylamine and carbazole are used for the construction of NLO materials to obtain TPA cross-section materials. In triphenylamine, the three N-C bonds and its derivatives lies in one common plane, which supports conjugation through lone pair of electrons on the nitrogen atom. In case of carbazole, a planar group containing two benzene rings linked with a five membered ring with hetero atom provides high overlap of π- orbitals, which is an interesting route to tailor the optical properties. This can be explained by taking the example of hyperbranched tetra substituted carbazole core.

Scheme 1.3: Hyperbranched donor–acceptor polyfluorenes based on 1, 3, 6, 8-tertsubstituted carbazole core.

NLO measurements of hyperstructured molecules

These molecules show strong absorption in region 380 nm to 450 nm due to π-π* transition of their conjugated background which [43], plays major role in two photon absorption process. The absorption spectra are shown below.

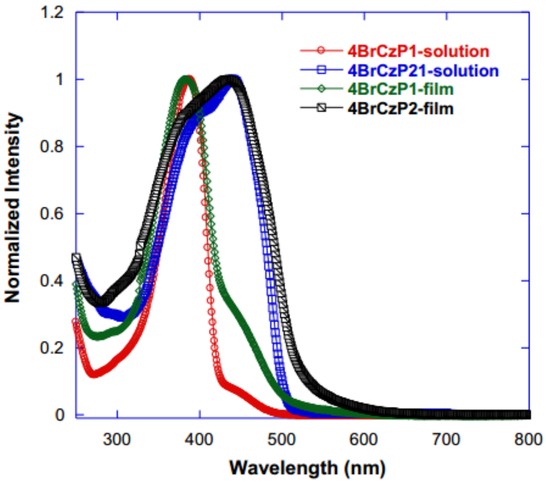
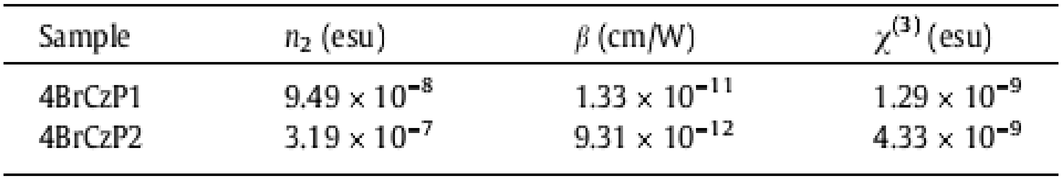


Figure 1.12: UV spectra of the hyperstructured molecules

The third order nonlinear optical properties of the materials were studied using Z-scan technique with femtosecond Ti: sapphire laser with delivering pulses of 140 fs at 800 nm. The molecules show two photon absorption and nonlinear refraction behaviour at 800 nm excitation. The two photon absorption co-efficient (β) values are in the order of 10^{-11} cm/W for 4BrCzP1 and 4BrCzP2. The samples show positive nonlinear refraction (self focusing) and the values are $9.49\text{x}10^{-8}$esu and $3.19\text{x}10^{-7}$ esu for 4BrCzP1 and 4BrCzP2 samples respectively.

The third order nonlinear susceptibility values are obtained from the two photon absorption co-efficient (β) and nonlinear refraction co-efficient (n_2) and the obtained third order nonlinear susceptibility values are in the order of 10^{-9}esu for both the molecules.



Sample	n_2 (esu)	β (cm/W)	$\chi^{(3)}$ (esu)
4BrCzP1	9.49×10^{-8}	1.33×10^{-11}	1.29×10^{-9}
4BrCzP2	3.19×10^{-7}	9.31×10^{-12}	4.33×10^{-9}

The linear or branched dendrimers provides a space for the incorporation of specific components which serve as hole injecting, hole transporting, electron transporting or hole blocking materials, which gives a route to find their application towards the area of organic electronic device like organic solar cell, light emitting electrochemical cell, organic optical detectors, organic receptors, and organic electroluminescent device. Based on the earlier report, the dendrons are generated with triarylamine and carbazole as precursor, which are well known to be hole transporting materials and found to be suitable for application in organic electronic device and NLO properties.

1.8. Scope of the Thesis

Considerable interest have been made in the development of amorphous materials which has outstanding applications in electronic devices like organic light emitting diodes, photo voltaic cells and field effect transistor. Charge transporting materials are classified into p-type (hole transporting), n-type (electron transporting) depending upon the kind of charge carrier transporter. The charge transport in condensed organic system, in general, depends on both the molecules themselves and the way they are assembled in the condensed phase. Due to the low ionization potential of carbazole and triarylamine derivatives, they are known to be photo conducting materials with high mobility.

Figure 1.13: Derivatives of carbazole and triarylamine as hole transporting material

Triarylamine System

Triphenylamine, a starburst structure which can be engineered to meet the requirements of ideal donor with a strong electron donating ability, due low ionization potential [44] which facilitates the formation of holes and contributes to suppress the charge recombination and dye aggregation. The hole transporting and photoconducting properties of the triarylamine system due to its structural unit, which can be incorporated into small molecule and polymers (dendrimers, copolymers, homopolymers)**.** The basic properties of the triarylamines system that is easy oxidizability of the amine nitrogen atom and the ability to transport positive charges which makes them an efficient hole transporting materials. The oxidized radical cation **(Figure- 1.14)** states of triarylamines have found application as hole transport components in photoconductors and light emitting device due their electrical conductivity and electroluminescent properties**.**

Figure 1.14: The unstable radical cation of the unsubstituted triphenyl system undergoing dimerization

Compounds with triarylamine functionality have been extensively investigated due to their favorable redox and optical properties that have facilitated experimental and theoretical analyses of electron transfer [45].

Carbazole system

One of the fundamental structures in the field of electrical and optical materials is carbazole. In our system, we specifically targeted carbazole precursors for the generation of dendrimers due to attractive features like low cost, and environmental stability provided by the fully aromatic unit. They can be easily modified at the 3, 6, or 9 positionsand on the nitrogen atom with a wide range of functional groups permitting a better solubility and a fine tuning of the electronic and optical properties. Carbazole due to their moderate high oxidative potential, during which cations and dications are formed **(Figure-1.15)** and make them promising as hole transporting materials (HTM) and their high triplet energy level makes efficient role in phosphorescence [46].The planarity and rigidity of carbazole derivative plays a key role in exhibiting intense luminescence, making it possible to prepare high performance deep-blue OLED materials [47].

Figure 1.15: Electrochemical oxidation of *N*-alkyl carbazole

1.9 Focus of the thesis

The actual focus of the thesis is defined as follows.

1. Reactivity study on carbophosphazene
2. Synthesizing of hybrimers having phosphorous using cyclophosphazene, and carbaphospahazeneas cores and comparison with cyanuric chloride
3. Synthesis of polyethers containing phosphorus
4. A comparative study of the chemiluminecent properties of hybrimers
5. Study of NLO properties of hybrimers
6. Study of Li-ion conductivity of hybrimers and polymers

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CHPTER 2

REACTIVITY STUDY ON CYCLOCARBAPHOSPHAZENES AND SYNTHESIS OF HYPERSTRUCTURED MOLECULES USING CYCLOCARBAPHOSPHAZENE AND CYANURIC CHLORIDE AS CORES

Abstract:

Reactions of dicarbaphosphazenes with N-methyl imidazole and fluoride ion have been studied. In contrast to earlier observations of dealkylation reactions, these reactions with imidazole led to quaternized products. Attempted fluorination of dicarbaphosphazene led to rupture of the phosphazene ring explaining the non-existence of fluorinated analog of carbaphosphazenes.

Apart from the reactivity study, six inorganic-organic hybrid hyperstructured molecules (hybrimers) based on cyanuric chloride, diphenyl substituted carbaphosphazene and dicarbaphosphazene were synthesized. The molecular structures of these molecules $H_1 - H_6$ were characterized using standard techniques including ^1H, ^{13}C and ^{31}PNMR spectroscopy and HRMS.

2.1.INTRODUCTION

2.1.1. Cyclic phosphazene compounds

Heterocyclic compounds formed by alternating P=N moieties are always fascinating because of their interesting reaction products [1, 2,3] and their application in various fields. Particularly, potential applications of P=N ring systems for use as lubricants and as high energy materials have been described [4]. The most extensively studied inorganic ring systems are cyclophosphazene due to their nucleophilic and polymerization reaction at the phosphorus center which have generated rich chemistry in six-membered ($N_3P_3Cl_6$) and eight-membered ($N_4P_4Cl_8$) rings. In a recent report, the tribological properties of cyclophosphazene derivatives were [5] compared with those of poly(fluoroalkoxy)phosphazenes that are excellent lubricants for aircraft gas turbine engines. Other work examines the potential application of ionic liquids derived from cyclophosphazenes as additives in water lubrication of silicon nitride ceramics [6].

Dicarbaphosphazenes have been suggested as additives as high temperature lubricants when substituted with perfluoroalkyl chains [7]. The chemistry of inorganic heterocyclic compound like hexachlorocyclophosphazene, carbaphosphazene, diphenylcarbaphosphazene, and organic heterocyclic compound like cyanuric chloride has been well established. Structurally typical organic heterocyclic compound cyanuric chloride (s-triazines) transforms to complete inorganic heterocyclic through carbaphosphazene **(figure 1.5)**. Mono and dicarbaphosphazene can be obtained by replacing one or two carbon by phosphorus respectively from cyanuric chloride. The common feature of these inorganic and organic heterocyclic is that, they can easily undergoes nucleophilic substitution reaction by organic moieties, making them as new organic-inorganic macromolecules, which is an area of widespread current interest.

2.1.2. Reactivity ofcarbaphosphazene

The cyclic carbaphosphazenes are interesting due to the robust nature of NP ring and high reactivity of two different reactive sites. The P-Cl and C-Cl bonds in this ring offer a variety of synthetic possibilities through nucleophilic substitution reactions. Following are few interesting reactions of the carbaphosphazene showing regioselectivity in the nucleophilic substitution reactions. For example, the reactions of carbaphosphazene with symmetrical and unsymmetrical trialkylamines were found to be quiet interesting [8]. The reactions with aliphatic amines were reported to cleave the C–N bond leading to dealkylation of amines [9, 10]. These dealkylated amines are substituted on carbon of the carbaphosphazene ring. The dealkylated products in these reactions depend on the stability of the alkyl cation formed. When the cyclocarbaphosphazene was reacted with diethylmethylamine, the bulkier ethyl cleaved over the methyl group (**Scheme 2.1**). Similarly, in the (**scheme 2.2)**, the cleavage of bulkier group that is isopropyl group occurred due to the sterically hindered and non-nucleophilic base, ethylisopropylamine as well it is methyl analogue methylisopropylamine gave only the monosubstituted carbaphosphazene derivativets [11].

Scheme 2.1: Reaction of dicarbaphosphazene with secondary amine

Scheme 2.2: Reaction of dicarbaphosphazene with tertiary amine

While the above reactions in the **schemes 2.1 and 2.2** explained the preferential reactivity of amines with C-Cl bonds, the oxygen nucleophiles react preferentially with P-Cl bonds. The reaction of carbaphosphazene (**Scheme 2.3**) with a diol[CF_2CH_2OH]$_2$ in presence of tri-n-propylamine resulted in the simultaneous formation of a seven-membered spirocycle on the phosphorous atom, and the substitution dialkylamino group on the carbon atoms[12].This reaction was utilized to introduce redox system like ferrocene, which is electrochemically and chemically reversible, to bind on cyclocarbophosphazene [13]. For this purpose a stable ferrocene derived diol was reacted with butyl lithium at -78 °C in THF and then reacted with cyclocarbophosphazene (**Scheme 2.4**). It was found that both the chlorines on phosphorus were replaced through simple nucleophilic substitution reaction while chlorine on carbon involved in dealkylation reactions.

Scheme 2.3: Reaction of dicarbaphosphazene with diol

Scheme 2.4: Reaction of ferrocenediol with amine substitutedcarbaphosphazene

Apart from the nucleophilic substitution reactions, carbaphosphazenes played a role as a facilitator in few reactions. For example, carbaphosphazene along with the dimethylsulfoxide was used for the oxidation of primary and secondary alcohols to the corresponding aldehyde and ketone respectively under a mild condition and in good yield [14]. The P-Cl and C-Cl bonds of the carbaphosphazene in principle bring out the reaction, but there was an increased preference for the C-Cl bond over the P-Cl bonds in the oxidation of alcohol. This was proved by blocking the C-sites with diethylamino group which resulted in no reaction. Blocking the active P-sites on the heterocyclic ring with phenyl group yielded aldehydes in a less yield. In the presence of dimethylformide, carbaphosphazene is used for the conversion of alcohols to alkyl chloride. The role of DMF is more or less catalytic in nature in the conversion of alcohols to alkylchloride.

2.1.3. Macromolecules from carbaphosphazenes

Apart from all these substitution reactions, cyclophosphazenes and cyclocarbaphosphazenes undergo polymerization by ring opening [15]. Cyclophosphazene undergoes polymerization at higher temperature in vacuo, whereas carbaphosphazene undergoes polymerization at lower temperature (**Scheme 2.5**) because of the increasedring strain which arise from the replacement of a skeletal phosphorus atom by the smaller carbon atom.Synthesis of the polymer provides an opportunity to synthesize a variety of organic-inorganic hybrid polymers by replacing the chlorine atom through nucleophilic substitution reactions. These polymers are purified by the combination of tetrahydrofuran and hexane as solvent by precipitation method. `The macromolecules obtained from the carbaphosphazenes are found to possess useful electrical, optical, thermal, or biomedical characteristics or that functions as precursor to ceramic materials.

Scheme 2.5: Polymerization of hexachlorocyclophosphazene and monocarbaphosphazene

Many derivatives of cyclocarbaphasphazeneshave prepared and their properties were well studied.It was observed that halogenated carbaphosphazene were quite sensitive to moisture, while the substituted heterocycles were quite stable against decomposition in the presence of moisture. Earlier research showed stereo and regio specificity in nucleophilic substitution on carbaphosphazene with respect to P–Cl and C–Cl bonds. To our surprise, similar reactivity differences of the perfluorinated cyclic carbaphosphazenes with their chloro analogs have not been explored. Further, in spite of versatility in the reactions on cyclic and polymeric carbaphsophazenes, no dendrimer/hybrimer was constructed on carbaphosphazene core. Therefore, we were interested in preparing fluorinated carbaphosphazene and dendrimers using carbaphosphazenes. For this purpose, we have chosen two different carbaphosphazenes with one having both reactive P-Cl and C-Cl bond, while another having only reactive C-Cl bonds.

The present chapter describes about the results obtained from the reactions of dicarbaphosphazenes with 1-methyl imidazole and potassium fluoride and the syntheses of hybrimers usingcyclocarbaphosphazenes and cyanuric chloride as core moieties by simple nucleophilic substitution. Cyanuric chloride was also included for study because of the possibility for comparison in the reactivities as well as the properties of the derived products.

2.2. RESULTS AND DISCUSSION

2.2.1. Reactivity study on carbaphosphazenes

As discussed in the section **2.1.2**, the reactions of carbaphosphazenes with aliphatic amines were reported to cleave the C–N bond leading to dealkylation of amines [16,17]. These dealkylated amines are substituted on carbon of the carbaphosphazene ring. The dealkylated products in these reactions depend on the stability of the alkyl cation formed. It should be noted that similar reaction with a bicyclic amine such as DABCO, opened one of the bicyclic rings to yield an adduct [16]. Hence with the aim to synthesize an imidazole derivative of carbaphosphazene, we reacted dicarbaphosphazene**1** (1:2) and diphenyl- substituted dicarbaphosphazene, $N_3P(Ph_2)(CCl)_2$(1:2) with 1-methyl imidazole. Analogous to earlier reports demethylation (carbon–nitrogen bond cleavage) and subsequent substitution of imidazole on carbon of the carbaphosphazene was expected. However, the results from the reactions were different leading to quaternized products **3** and **4** instead of dealkylation (**Scheme 2.7**). It is also of interest to observe that the same reactions also proceed to completion under microwave irradiation at room temperature within 5 min.

Scheme 2.6: Reaction of cyclocarbophosphazene with *N*-methylimidazole

The reaction of sodium imidazole with compound **2** followed by quaternization with MeI in THF at room temperature also led to a compound **3a** which is similar to **4** where iodide has replaced chloride (**Scheme 2.6**). However, reactions of compound **2a** with $CF_3(CF_2)_nCH_2CH_2I$ (n = 2,4,6) at 60°C did not give rise to quaternization at the imidazole group. Vigorous conditions and prolonged reaction times led to decomposition of the carbaphosphazene ring. Phosphorus bearing electron donating groups adjacent to the nitrogen in the carbaphosphazene ring could increase its basicity. This nitrogen with enhanced basicity may compete with nitrogen of imidazole to react with alkyl halides. The competition could potentially lead to rupture of the carbaphosphazene ring. This is in agreement with the participation of the electron pair on the nitrogen of carbaphosphazene in the mechanism which was suggested in rationalizing the dealkylation of alkyl amines [16,17, 18].

The basicity of the carbaphosphazene nitrogen may be reduced by substituting the chlorine atoms on phosphorous with fluorine atoms. Therefore, in a typical reaction dicarbaphosphazene (1) and KF were placed in a Schlenk tube inside a dry box and freshly dried acetonitrile was added to it. The tightly closed tube was maintained at 30°C or heated to 70°C in another reaction. In each case, after 4 h the tube was connected to an evacuated vacuum line equipped with a pressure gauge.

Scheme 2.7: Reaction of carbophosphazene with potassium fluoride

All of the gaseous products evolving from the tube were condensed in another schlenk tube connected to the vacuum line. The gas phase IR, and ^{31}P and ^{1}H NMR (dissolved products in $CDCl_3$) spectra of the condensed materials were recorded. This reveals no gaseous or sublimable products other than acetonitrile were obtained from the reaction which was confirmed by the ^{1}H and ^{31}P NMR spectra. Analysis of ^{31}P and ^{19}F NMR spectra of the nonvolatile residue of reaction mixture surprisingly showed the formation of KPF_6 (**Scheme 2.7**). This was confirmed by the presence of a doublet in the ^{19}F NMR and a heptet in the ^{31}P NMR spectra. The reaction also gave rise to a solid material which settled at bottom of the reaction vessel and which was insoluble in organic solvents and water and, therefore, was impossible to characterize. However, IR spectrum of the insoluble materials did not show any known characteristic peaks. It is well known that the sodium and potassium fluorides are used to fluorinate P–Cl bonds in chlorocyclophosphazene and thionylphosphazenes **[2a].** The S–Cl bond in thionylphosphazene requires a strong fluorinating agent like potassium fluorosulfate [18]. Fluorination of the C–Cl bond in cyanuric chloride has been achieved using potassium fluoride. Based on these results we expected potassium fluoride in acetonitrile to fluorinate dicarbaphosphazene completely. However, the result shows the unprecedented rupture of the carbaphosphazene skeleton. Similar instability of cyclic and linear phosphazenes with respect to the reaction with nucleophiles leading to cleaved products has been reported earlier [19, 20].

2.2.2. Synthesis of hyperstructured molecules

The synthesis of hybrimer macromolecules has current interest because of their potential application in electrical, optical, thermal and biomedical fields. Synthesis of the hyperstructured molecules based on cyanuric chloride as core is well established. Carbaphosphazenes in which phosphorus, nitrogen, and carbon form the core of the ring are hybrid inorganic-organic heterocyclic compounds. Their structures, properties, and reaction behavior can be linked to both cyanuric chloride as well as pure inorganic heterocyclic compounds such as cyclophosphazenes. However, the synthesis of the hyperstuctured molecules based on carbaphosphazenes and diphenylcarbaphosphazenes has been not attempted.

The triarylamines, due to their ideal donor character with a strong electron donating ability and suppressing charge recombination and dye aggregation, are widely used in hole transporting materials and light emitters in the fields of optoelectronics such as organic solar cells, non-linear materials and in organic light emitting diodes. Apart from this, these moieties have many favorable properties such as redox, ion transfer process and photochemical behavior with their excellent electronic properties. Similarly, the carbazoles are also used as optical functional moieties due to their rigid framework and high charge mobility with interesting optical and electronic properties. Carbazole substituted on aromatic amine possess electron donating property which can be used as nonlinear optical chromophore. Though these compounds can transport holes inherently, the electronic properties can be changed according to the application by functionalizing with other electron donors. Apart from these they can impart thermal and orientation stability to the corresponding system.

Based on these properties, our interest was to produce hyperstructured molecules using carbaphosphazene as a core combining both triarylamine and carbazole. However, as discussed in the **section 2.1.2**, there exist considerable differences in the reactivities of P-Cl and C-Cl bonds in the carbaphosphazene ring. Further, the P-Cl bonds are known for their sensitivity to moisture and any nucleophilic attack. In the case of cyanuric chloride, the synthesis of hyperstructured molecule can be achieved by simple replacement of the chlorine atom via simple nucleophilic substitution reaction by convergent method. Keeping this view in the mind, (4-hydroxyphenyl)diphenylamine and 4,4’-di(carbazol-9-yl)-4”-hydroxytriphenylamine were grafted on it using respective sodium salts (**Schemes 2.9 and 2.10**) to obtain H_1 and H_2 respectively. Respective sodium salts were prepared *in-situ* by reacting either (4-hydroxyphenyl)diphenylamine or 4,4’-di(carbazol-9-yl)-4”-hydroxytriphenylamine with NaH in THF at reflux temperature (**Scheme 2.8**). After that a calculated quantity of cyanuric chloride was added it and the reaction was continued for further 24 hours at reflux temperature of THF.

Scheme 2.8: Preparation of sodium salts of (4-hydroxyphenyl)diphenylamine and 4,4’-di(carbazol-9-yl)-4”-hydroxytriphenylamine

Scheme 2.9: Synthesis of Hyperstructured $\mathbf{H_1}$ molecule

Scheme 2.10: Synthesis of hyperstructured $\mathbf{H}_2$ molecule

After testing and standardizing the reaction conditions to produce hyperstructured molecules by reacting with C-Cl bonds in cyanuric chloride the reaction was further extended to build hyperstructured molecules based on carbaphosphazene core. Since the P-Cl bonds are highly reactive, P-diphenyl substituted carbaphosphazene, where the phosphorous sites were blocked for any reactions, was selected for making new variety of dendrimers. Accordingly, the reactions of sodium salts **(Scheme 2.9)** of (4-hydroxyphenyl)diphenylamineand 4,4’-di(carbazol-9-yl)-4”-hydroxytriphenylamine with P-diphenyl substituted carbaphosphazene yielded the hyperstructured molecules $\mathbf{H}_3$ and $\mathbf{H}_4$ respectively (**Schemes 2.11 and 2.12**).

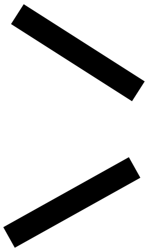
Scheme 2.11: Synthesis of hyperstructured $\mathbf{H}_3$ molecule

Scheme 2.12: Synthesis of hyperstructured $\mathbf{H_4}$ molecule

Encouraged by the stability of $\mathbf{H_3}$ and $\mathbf{H_4}$ molecules, we have synthesized two more hyperstructured molecules by simple nucleophilic substitution reaction on dicarbaphosphazne through convergent method. For this purpose, all the chlorine atoms of the carbaphosphazene were replaced using sodium salt of(4-hydroxyphenyl)diphenylamineand 4,4’-di(carbazol-9-yl)-4”-hydroxytriphenylamine to yield the hyperstructured molecules $\mathbf{H_5}$ and $\mathbf{H_6}$ (**Schemes 2.13 and 2.14**). Here also the sodium salts were synthesized in-situ according to the reaction mentioned in the scheme 2.9.

Scheme 2.13: Synthesis of hyperstructured $\mathbf{H_5}$ molecule

Unlike cyclophosphazenes, carbaphosphazene show an increased tendency to undergo partial saturation of the ring double bond. However, after prolonged reaction time, under reflux condition in the presence THF as solvent, we observed that all the chlorine atoms of the carbaphosphazene were substituted with 4-(hydroxy)diphenylamine and 4,4’-Di(carbazol-9-yl)-4”-hydroxytriphenylamine. The reaction of (4-Hydroxyphenyl) diphenylamine and 4, 4’-di(carbazol-9-yl)-4”-hydroxytriphenylamine with carbaphosphazene, in presence of strong base like sodium hydride favors for the generation of nucleophile, generally proceeds with a step wise substitution of chlorine atoms with the initial reactions on the C-Cl bonds.



Scheme 2.14: Synthesis of hyperstructured H_6 molecule

The molecular structures of these molecules H_1 – H_6 were characterized using standard techniques including ^{1}H, ^{13}C and ^{31}PNMR spectroscopy and HRMS. The ^{1}H NMR spectra of these compounds were complex and showed improper splitting patterns because of the difference in the spatial orientation of bulky triaryl amino and carbozole groups on both sides of the plane of the rings. For example, the hyperstructured H_1 and H_2 molecules (where the cyanuric chloride was core),the starting material had only a peak at 173 ppm in ^{13}C NMR. But, once the hyperstructured molecule was formed all the dendron peaks appeared along with major peak indicating the C-O bond formation.

Wherever ^{31}P NMR was possible, the purity of the carbophosphazene based materials can be analyzed by single peak obtained. For example, the ^{31}P NMR spectrum showed one major peak at δ 25.61ppm for hyperstructured $\mathbf{H_5}$, whereas the starting material showed a peak at δ 54.78ppm. This major shift in the ^{31}P NMR spectrum indicated a complete substitution on the cyclophosphazene core by the individual dendrons and no other side product formation. In the case of hyperstructured $\mathbf{H_3}$ and $\mathbf{H_4}$ molecules, (diphenyl substituted carbophosphazene as core) a single sharp was obtained but without much difference from the starting materialas in both the case phosphorous attached with the phenyl rings was not disturbed.

Apart from NMR spectra, the HRMS of all these molecules were obtained which confirmed the structure and purity of the hyperstructured molecules. But with the increase in generation, we obtained the fragmented peaks due to the moderate oxidative potential of carbazole where cations and dications were formed. For example, in the case of $\mathbf{H_1}$ molecule, we got exact mass in HRMS whereas in the case of $\mathbf{H_2}$ molecule we got fragment mass only because of the increases generation. The formation of hyperstructures molecules was further proved with C, H, N analysis where theoretical and experimental values were matching well.

These hyperstructured molecules $\mathbf{H_1} – \mathbf{H_6}$were found to be monodisperse *i.e.*there was no partially substituted product formed in the reactions. Therefore they were soluble in common organic solvent such as chloroform, dichloromethane and tetrahydrofuran. Interestingly, the substitution of these bulkier groups on these carbaphosphazene was found to provide hydrolytical and thermal stability over the unsubstituted carbaphosphazene which degrade slowly when exposed to moisture.

2.3. SUMMERY AND CONCLUSION

The reactivity of dicarbaphosphazenes and their utility to construct hyperstructured molecules are described. Compared to the known reactivity of the carbaphosphazenes, we observed a difference in the reactions of dicarbaphosphazenes with 1-methyl imidazole and potassium fluoride. This reactions study also explained the non-existence of perfluorinated cyclocarbaphosphazene and instability of the carrbaphosphazene core for vigorous reactions. Apart from the reactivity study, the cyanuric chloride, diphenylsubstitutedcarbaphosphazene and dicarbaphosphazenewere used as core moieties to produce inorganic-organic hybrid hyperstructured molecules known as hybrimers. These molecules were synthesized in reactions in which all chlorine atoms were replaced by simple nucleophilic substitution. These hybrimers were found to be hydrolytically stable.

2.4. EXPERIMENTAL SECTION

Materials

Commercially available reagents cyanuric chloride, carbazole, diphenylamine, methoxyiodomethane, copper powder, triehyleneglycoldimethylether, copper iodide, potassium iodide, potassium iodate, N-methyl imidazole, diphenylamine, sodium hydride were purchased from Aldrich. Pottasium carbonate, glacialacetic acid and deuterated $CDCl_3$ were obtained from SRL, India and used as such without any further purification. All the solvents like tetrahyrofuran, dichloromethane, were dried according to standard literature procedures. Standard air free conditions were maintained throughout the reaction by maintaining under the nitrogen atmosphere through standard vacuum –line schlenk techniques. The precursors dicarbaphosphazene, P-diphenyl substituted dicarbaphosphazene**,** 4,4'-di(carbazol-9-yl)-4"-hydroxytriphenylamine and (4-Hydroxyphenyl)diphenylamine were prepared according to literature procedures.

Instrumentation

^{1}H, ^{13}C(400 MHz) and ^{31}P NMR (162 MHz) data were performed on a Bruker Avance-400 MHz FT NMR spectrometer at room temperature using $CDCl_3$ as solvent. All NMR chemical shift are reported in parts per million; downfield shifts are reported as positive values from tetramethylsilane (TMS) as standard at 0.00 ppm. IR spectra were recorded on a JASCOFT/IR-5300 spectrometer with KBr pellets. Elemental analyses were performed on an EA1112, Thermo Finnigan, France. High resolution mass spectroscopy (HRMS) was performed on a Bruker Maxis HRMS mass spectrometer. Analytical thin-layer chromatography was performed using Kieselgel 60F-254 plates from Merck. Column chromatography was carried out on Merck silica gel (60-120 mesh).

Reaction of KF with compound carbophosphazene

The carbophosphazene(0.52g, 0.2 mmol) and potassium fluoride (0.51g, 8.7mmol) were placed in a schlenk tube inside a dry box and freshly dried acetonitrile (20 ml) was added to it. The tightlyclosed tube was maintained at 30 ºC or heated to 70 ºC in another reaction for 4 h. All of the gaseous products evolving from the tube were condensed in another schlenk tube connected to the vacuum line. The gaseous products were then transferred to IR gas cell and spectrum was recorded. The gaseous products were condensed in a NMR tube, and ^{31}P and ^{19}F NMR were recorded. Then the reaction mixture was filtered using frit. The acetonitrile was evaporated from the filtrate to yield white solid which was characterized as KPF_6 via IR.

Synthesis of compound-3

In a typical reaction carbaphosphazene (0.137 g, 0.43 mmol) was dissolved in dry THF (15ml) and two equivalents of 1-methylimidazole dissolved in THF (25 ml) were added to it. The mixture was stirred at 65 ºC for 6 h. Then it was filtered under a nitrogen atmosphere using a frit. The solid was washed with ethylacetate (50 ml) to yield compound **3**.

Synthesis of compound-4

Diphenylcarbaphosphazene (0.386 g, 1.61 mmol) was dissolved in dry THF (20 ml) and two equivalents of 1-methylimidazole (0.25 ml, 3.22 mmol) dissolved in THF (20 ml) was added to it. The mixture was heated at 65ºC for 6 h. Then it filtered under a nitrogen atmosphere using a frit. The reaction mass was washed with ethylacetate to yield compound **4**.

Synthesis of 2a and 3a

Compound 2 (0.27 g, 0.838 mmol) was dissolved in dry THF (30 ml) and added to sodium salt of imidazole (0.15 g, 1.75 mmol).The mixture was stirred for 6 h at reflux condition. Then it was filtered under a nitrogen atmosphere using a frit. The solid was washed with ethyl acetate to yield compound 2a. Compound 2a (0.11g, 0.28 mmol) was dissolved in dry THF and two equivalents of methyl iodide (0.56mmol.035ml), dissolved in THF (25 ml) was added to it.The mixture was stirred for 6 h at reflux condition. Then it wasfiltered under a nitrogen atmosphere using a frit. The solid was washed with ethyl acetate to yield compound 3a.

Common synthetic procedure for hyperstructured molecules, H1 – H_6.

The Dendron, either (4-hydroxyphenyl)diphenylamine or 4,4’-di(carbazol-9-yl)-4”-hydroxytriphenylamine was dissolved in dry THF (20 ml) and cooled to 0 ºC. Then sodium hydride was added, allowed to warm to room temperature and then started refluxing under nitrogen atmosphere for 24h. During reflux, THF solution (20 ml) of core moieties (calculated quantity of cyanuric chloride, diphenylcarbaphosphazene, dicarbaphosphazene) was added to the reaction mixture under the protection of dry nitrogen and refluxing was continued for another 24 h. The exact mole ratio and amounts of core moieties used for the synthesis is provided in the table 2.1. After the reaction mixture was cooled and filtered via frit. The filtrate was evaporated and the residue was purified by neutral Al_2O_3 column chromatography (70: 30, HEXANE - DCM).

***Table 2.1**: Mole ratio of dendrons used to synthesize the hyperstructured molecules H_1 – H_6.*

Hyperstructured molecules	**Cores**	**Dendrons**	**Mole ratio of the base (NaH)**	**Reaction time**
H_1	cyanuric chloride 0.08 g, 0.46 mmol	[(4-ydroxylphenyl)diphenylamine] 0.30 g, 0.13 mmol	0.06 g 0.27 mmol	48h
H_2	cyanuric chloride 0.02 g, 0.11 mmol	[4,4-di(carbazol-9-yl)4-hydroxytriphenyl amine] 0.20 g, 0.33 mmol	0.01 g 2.67 mmol	72h
H_3	diphenyl carbaphosphazene 0.37 g, 1.15 mmol	[(4-hydroxyphenyl)diphenylamine] 0.5 g, 2.31 mmol	0.11 g, 4.62 mmol	48h
H_4	diphenyl carbaphosphazene 0.91 g, 5.92 mmol	[4,4-di(carbazol-9-yl)4-hydroxytriphenyl amine] 0.70g, 1.18 mmol	0.056 g 2.36 mmol	72h
H_5	Carbaphosphazene 0.11 g, 0.46 mmol	[(4-hydroxyphenyl)diphenylamine] 0.40 g, 1.85 mmol	0.08 g, 3.7 mmol	48h
H_6	carbaphosphazene 0.96 g, 4.05 mmol	[4,4-di(carbazol-9-yl)4-hydroxytriphenyl amine] 0.20 g, 0.33 mmol	0.08 g 0.67 mmol	72h

2.5 SPECTRAL DATA

KPF_6	
^{31}P NMR (162 MHz, $CDCl_3$): ^{19}F NMR (400 MHz, $CDCl_3$):	heptet (-135.42 to -157.37 ppm) doublet (-72.05 to -73.99 ppm)

Compound 3		
Yield	:	94%
IR(KBr) v_{max} cm^{-1}	:	1556, 1437, 1375, 1361, 1437, 1375, 1361, 1286, 1147, 1124, 997, 842.
^{1}H NMR (400MHz, $CDCl_3$)	:	10.18 (s, 2H), 8.40 (s, 2H), 7.85(s, 2H), 3.85 (s, 6H).
^{31}PNMR (162MH,$CDCl_3$)	:	7.77 ppm.
^{13}CNMR (100.62MHz, $CDCl_3$)	:	154.33, 137.24, 124.70, 118.96, 36.76.

Compound 4		
Yield	:	93%
IR(KBr) v_{max} cm^{-1}	:	3655, 3317, 3175, 2972, 1805, 1745, 1620, 1585, 1533, 1423, 1367, 1350, 1238, 1157, 1157, 1124, 1084, 1157, 1124, 1084, 1030, 910, 852.
^{1}H NMR (400MHz, CDCl$_3$)	:	10.66(s, 2H), 8.68(s, 2H),7.95-7.88(m, 8H), 7.75(s, 4H), 3.99(s, 6H).
^{31}PNMR (162MHz, CDCl$_3$)	:	42.06 ppm
^{13}CNMR (100.62MHz, CDCl$_3$)	:	159.68,138.70,135.42,132.04,131.91, 130.22,130.09, 128.36,127.06, 125.18, 119.71 36.99.

Dendrimer H_1		
Yield	:	72%
IR(KBr) v_{max} cm^{-1}	:	3052, 2926, 2849, 1567, 1495, 1369, 1304, 1276, 1205, 1084, 843, 810, 745,
^{1}H NMR (400MHz, $CDCl_3$)	:	7.22-7.09(m), 7.07-7.02(m)
^{13}CNMR (100.62MHz, $CDCl_3$)	:	173.80, 147.63, 146.53, 145.72, 129.33, 124.18, 123.01, 122.00.
HRMS	:	859.3371 $(M+H)^+$
Anal.calcd. for $C_{57}H_{42}N_6O_3$: C, 76.45; H,4.99; N,7.43%	:	Found: C, 76.58; H, 4.89; N, 9.65%.

Dendrimer H_2		
Yield	:	70%
IR(KBr) v_{max} cm^{-1}	:	3046, 2920, 2849, 1561, 1512, 1452, 1364, 1315, 1227, 1106, 1008, 832, 745, 717.
^{1}H NMR (400MHz, $CDCl_3$)	:	8.10-8.08(m), 7.47-7.25(m)
^{13}CNMR (100.62MHz, $CDCl_3$)	:	173.94, 147.48, 146.28, 140.87, 132.46, 128.04, 125.76, 124.77, 123.29.122.87, 120.35, 119.91, 109.74.
HRMS	:	803.56 (after fragmentation)
Anal. calcd. for $C_{129}H_{84}N_{12}O_3$: C, 83.74; H, 4.58; N, 9.08 %	:	Found : C, 83.65; H, 4.62; N, 9.21%.

Dendrimer H$_3$		
Yield	:	72%
IR(KBr) v_{max} cm^{-1}	:	3063s, 3030s, 1583s, 1501s, 1315s, 1271s, 1200s, 1172s, 947s, 876s, 832s, 750s, 695s, 641s, 619s, 519.
^{1}H NMR (400MHz, CDCl$_3$)	:	7.152-7.113(m), 7.023-6.913(m)
^{31}PNMR (162MHz, CDCl$_3$)	:	43.731 ppm.
^{13}CNMR (100.62MHz, CDCl$_3$)	:	170.62, 152.85, 133.25, 133.23, 131.15, 130.89, 130.71, 130.62, 129.871, 129.10, 128.99, 128.99, 124.65, 122.23.
HRMS	:	771.77
Anal.Calcd.for $C_{50}H_{38}N_5O_2P$: C, 77.81; H,4.96; N,9.07%	:	Found: C, 77.91; H, 4.89; N, 9.15%

Dendrimer H_4		
Yield	:	73%
IR(KBr) v_{max} cm^{-1}	:	3063s, 3030s, 1583s, 1501s, 1315s, 1271s, 1200s, 1172s, 947s, 876s, 832s, 750s, 695s, 641s, 619s, 519.
^{1}H NMR (400MHz, $CDCl_3$)	:	8.19-8.18(d), 7.76-7.66(m), 7.59-7.43(m), 7.34-7.25(m)
^{31}PNMR (162MHz, $CDCl_3$)	:	40.50ppm.
^{13}CNMR (100.62MHz, $CDCl_3$)	:	171.30, 168.80, 147.93, 146.62, 144.54, 133.56, 132.34, 131.11, 131.00, 130.20, 129.17, 129.03, 128.11, 125.93, 125.48, 124.84, 123.31, 123.06, 120.36, 119.91.
HRMS	:	1432.7568 $(M+H)^+$
Anal.Calcd.for : $C_{98}H_{66}N_9O_2P$: C, 82.16; H,4.64; N,8.80%		Found: C, 82.12; H, 4.52; N, 8.45%

Dendrimer H_5		
Yield	:	72%
IR(KBr) v_{max} cm^{-1}	:	3063s, 3030s, 1583s, 1501s, 1315s, 1271s, 1200s, 1172s, 947s, 876s, 832s, 750s, 695s, 641s, 619s, 519.
^{1}H NMR (400MHz, $CDCl_3$)	:	7.152-7.113(m), 7.023-6.913(m)
^{31}PNMR (162MHz, $CDCl_3$)	:	25.61 ppm.
^{13}CNMR (100.62MHz, $CDCl_3$)	:	147.63, 147.40, 144.90, 129.41, 129.30, 124.52, 124.29, 124.26, 124.22, 124.09, 123.36, 123.03, 122.24, 122.24, 121.53, 121.49.
HRMS	:	1138.4361 $(M+H)^+$
Anal. Calcd. for : $C_{74}H_{56}N_7O_4P$: C, 78.08; H,4.96; N,8.61%		Found: C, 78.12; H, 4.52; N, 8.45%

Dendrimer H_6		
Yield	:	73%
IR(KBr) v_{max} cm^{-1}	:	3046, 2985, 2931, 2843, 1594, 1501, 1457, 1364, 1309, 1227, 1200, 1106, 904.
^1H NMR (400MHz, $CDCl_3$)	:	8.17-8.136(m), 7.98-7.11(m).
^{31}PNMR (162MHz, $CDCl_3$)	:	32.69 ppm.
^{13}CNMR (100.62MHz, $CDCl_3$)	:	146.15,141.05,140.89, 140.65, 140.62,130.05, 128.09, 127.96, 127.66, 126.01, 125.90,125.86, 125.44, 125.80, 125.73, 125.66, 125.55,125.44, 125.49, 125.11, 116.92, 112.84, 109.78.
HRMS	:	803.55 (after fragmentation)
Anal.Calcd.for : $C_{170}H_{112}N_{15}O_4P$: C, 83.01; H,4.59; N,8.54%		Found: C, 83.12; H, 4.52; N, 8.45%

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CHAPTER 3

SYNTHESIS OF HYPERSTRUCTURED MOLECULES BASED ON CYCLOPHOSPHAZENE CORE AND THEIR NON-LINEAR OPTICAL PROPERTIES, Li-ION CONDUVTIVITIES AND FLOURESCENT STUDIES

Abstract

Cyclophosphazene based hyperstructured molecules were synthesized through simple nucleophilic substitution reactions. All these molecules were characterized multinuclear NMR, MALDI and HRMS spectral data.The absorption and fluorescence behaviors, nonlinear optical properties and the Li-ion conductivities of these molecules were studied taking one or two molecules as representative for any of these properties. The highest fluorescence quantum yield of these molecules was found to be 10%. One of the hyperstructred molecules showed highest Li-ion conductivity of 10^{-4} Scm^{-1}. Two of the molecules showed nonlinear refraction.

3.1. INTRODUCTION

Hyperstructured molecules (ordendrimers) based on new generation hybrimer materials are of current interest for developing devices and other photonic and electro active applications[1]. These hyperstructured molecules potentially combine the properties of both small molecules and polymers and hence find application in various fieldslike organic light-emitting diodes, nonlinear optics and solar cells [2]. Compared to the polymerswhere synthetic approach and purification are somewhat problematic, the hyperstructured molecules are preferred. Further, the polymers contain chains of various lengths whereas the hyperstructured molecules are mono-dispersed because it contains well defined macromolecular structure. The properties of the hyperstructured macromolecule can be controlled by individual dendrimeric functional groups because of well-defined segments [3]. For example, the formation of aggregates or excimers which reduces the efficiency of a device can be overcome by designing a hyperstructured molecule with an architecture which prevents the interaction between adjacent conjugated moieties.Therefore, several attempts have been made for the incorporation of various branching units and functional units at the periphery of hyperstructured molecules by various synthetic methodologies [4].

Linear and cyclicphosphazenes consisting of alternate N and P atoms have been studied much by several groups due to their diversifying properties such as excellent hydrolytic stability, flame retardant properties and liquid crystalline behavior [5]. The versatility of the cyclophosphazene is proved by the greater stability of the phosphorus-nitrogen backbone and ability to undergo substitution with the retention of the ring structure. Several regioselective routes are available for the introduction of organofunctional side groups on the cyclophosphazene by involving P-O, P-C, and P-N bond formation [6, 7, 8, 9]. Because of the versatile chemistry, a variety of phosphazene materials have been produced for various potential applications **(figure 3.1).**

Over the past decades, the robust inorganic ring cyclophosphazene with a planar non-delocalized cyclicring become a mature class of core material for hybrimer. Use of hexachlorocyclosphosphazene as starting material for dendrimer synthesis has been exploited by several researchers because the six labile chlorines can be substituted with the desired group by astraight forward chemistry [10]. After the complete substitution, because of the projection of substituent groups above and below the plane of cyclophosphazene, a rigid spherical like structure can be produced. The rigid sphere like three dimensional architecture minimize the aggregation and introduce amorphous property to the material which is important for conductivity and organic light emitting devices.

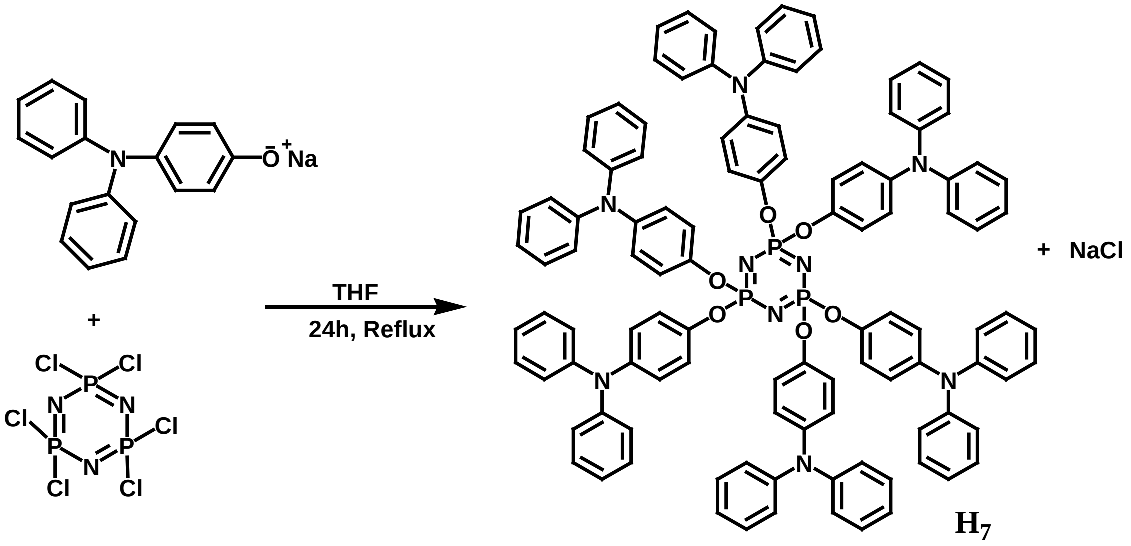
Figure 3.1: The potential applications of cyclophosphazene as stable core

Interestingly, the cyclophosphazenecore does not show any effect on optical and electronic properties. The property of the materials is mostly dependent on the dendrons. Due to the potential application of carbazole and triarylamine in electrochemical devices, hole transport layer, microcavity photoconduction, electroxerography and as photovoltaic compounds which can provide a very efficient matrix for current carrier transport, these materials have been employed as dendronds in the synthesis of hyperstructured molecules [11]. The present chapter mainly highlights the construction of hyperstructured molecules taking cyclotriphosphazene as core where the dendrons containing triarylamine and carbazolemoieties are substituted by simple nucleophilic substitution reaction as building blocks. The nonlinear optical properties, fluorescence andthe Li-ion conductivities of these molecules are studied taking one or two molecules as representative for any of these properties.

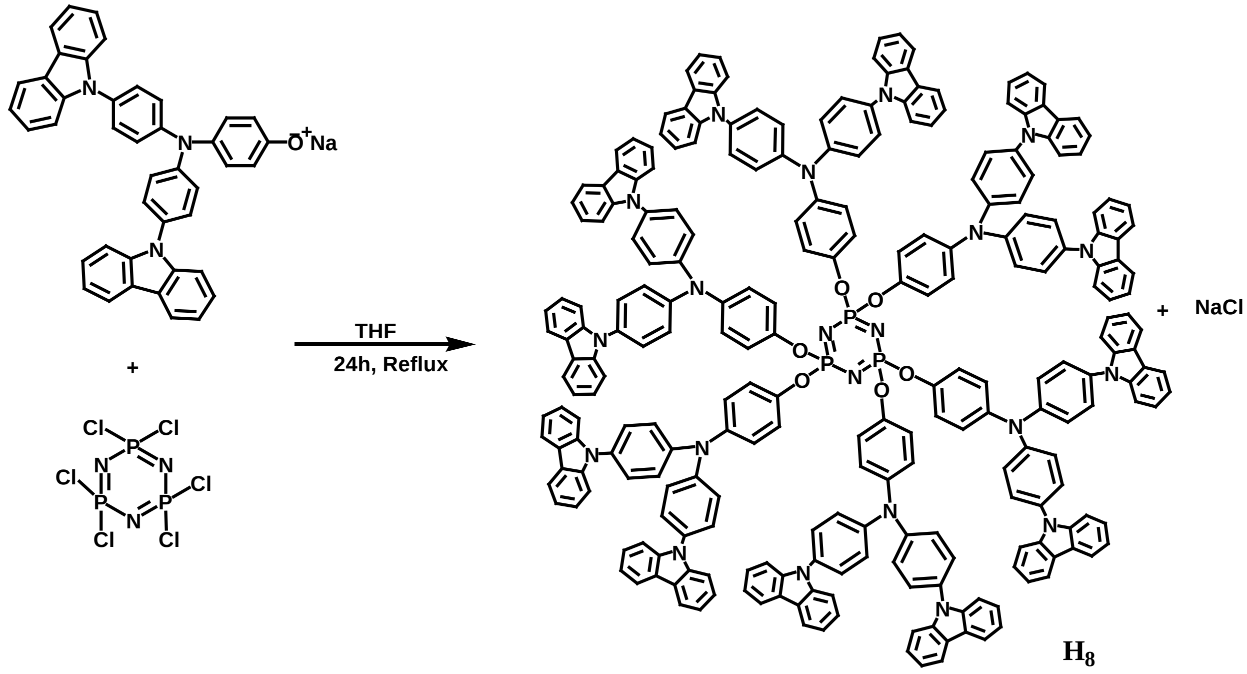
3.2 RESULTS AND DISCUSSION

3.2.1. Synthesis and characterization of H_7 – H_{10}

One of the simple and effective methods for the synthesis hybrid inorganic-organic materials based on phosphazene core is the replacement of chlorine atoms in hexachlorocyclophosphazene. Keeping this view in the mindthe (4-hydroxyphenyl) diphenylamine and 4,4'-di(carbazol-9-yl)-4"-hydroxytriphenylamine were grafted on the hexachlorocyclophosphazenevia simple nucleophilic substitution reaction using the respective sodium salts **(Scheme 2.9).** The **schemes 3.1and 3.2** depict the synthesis of first and second generation dendrimers (**H_7** and **H_8**) by convergent method. By this method the first and second generation dendrimers containing cyclophosphazene as core and triarylamineand carbazole as dendrons were synthesized. These dendrimers having monodisperse nature are found to be highly soluble in common organic solvent such as chloroform, dichloromethane, and tetrahydrofuran which makes them convenient for solution processability.



Scheme 3.1: Synthesis ofhyperstructuredmolecule**H_7**



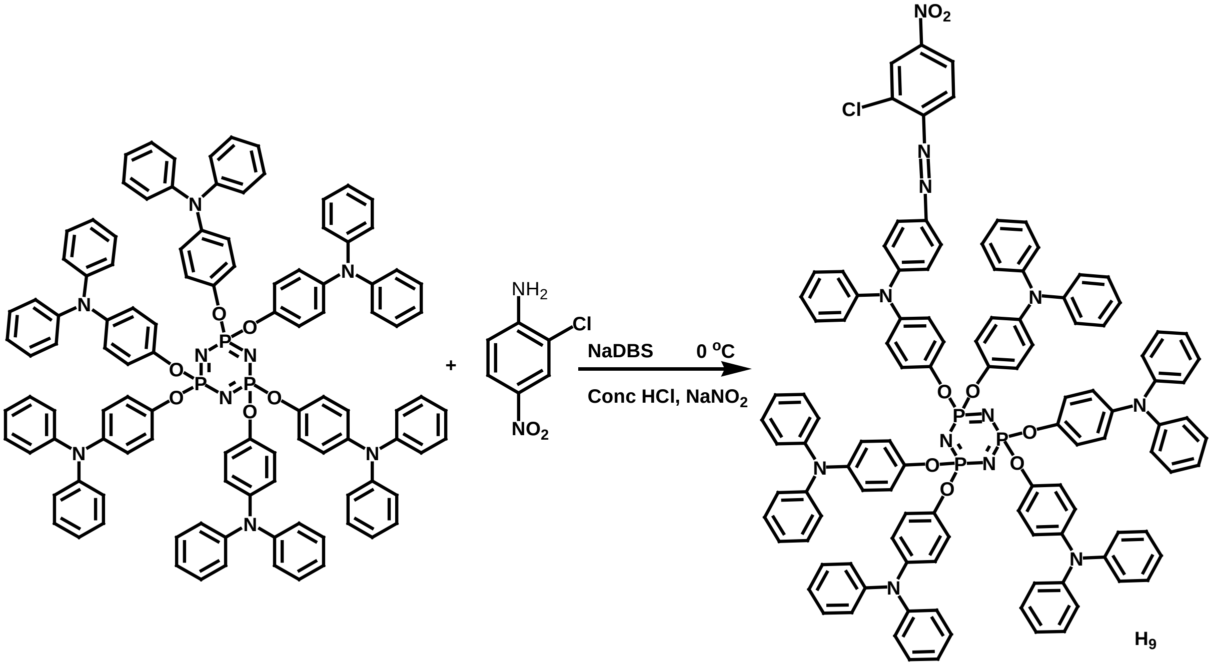
Scheme 3.2: Synthesis ofhyperstructuredmolecule**H_8**

The formation of molecules **H_7** and **H_8** was concluded using standard techniques including ^{1}H, ^{13}C and ^{31}PNMR spectroscopy and HRMS. As mentioned in the chapter 2, with increasing dendrimer generation it was difficult to discern the structure due to complicity in ^{1}H and ^{13}C NMR signal. However, though the splitting pattern was not clearly observed in both thehyperstructured molecules the numbers of protons were matched.In the case of **H_7** it was able to find 64 protons whereas in the case of **H_8**, 84 protons were matched. The high intensity peaks in^{13}C NMR spectra of **H_7** and **H_8** revealed the formation of the hyperstructured moleculesand symmetrical substitution of the dendrons.

More clearly, the chemical structures were further characterized by HRMS (High resolution Mass Spectroscopy) and MALDI-TOF (Matrix–assisted laser desorption ionization time of flight).For hyperstructuredmolecule **H_7**, the HRMS provided the molecular weight as 1697 and an additional peak was observed due to the sodium ion. In the case of hyperstructured **H_8** molecule, due to high molecular weight MALDI was preferred. The MALDI spectrum showed a peak matching the molecular weight 3677 along with the other fragments peaks. The purity of these materials was confirmed by a single peak obtained in ^{31}PNMR spectra and clear MALDI-TOF and HRMS. The ^{31}PNMR spectroscopy showed only astrong peak at δ 9.4 ppm for

H_7 and a δ 9.3 ppm **H_8** indicating the complete substitutions on the cyclophosphazene core by the individual dendrons moieties without any side product formation.

The hyperstructured molecule **H_7** was reacted with 2-chloro 4nitro aniline to provide a withdrawing group to the hole-transporting material so that push–pull effect can be observed **(Scheme 3.3)**. It was observed from the NMR spectral data that the azo substitution has happened at the para position (**H_9**), but we could not get clear HRMS due to the problem in the purification. The cyclophosphazenewas also reacted with 4-bromo-4-hydroxy biphenyl to replace all chlorine atoms to get the G_1generation a precursor to **H_{10}**.This was confirmed by ^{31}PNMR spectrum as there was a single sharp at δ 9.4 ppm. By divergent method the G_1generation was further reacted with carbazole in presence of a catalyst and a base (sodium *tert*-butoxide) to get the G_2 generation molecule **H_8 (Scheme 3.4)** which can be used as hole-transporting material. Formation of this hyperstructured molecule was confirmed by NMR spectra. However, the HRMS showed a major peak along with unassignable additional peaks indicating the presence of impurities.



Scheme 3.3: Synthesis of hyperstructuredmolecule**H_9**

Scheme 3.4: Synthesis of hyperstructuredmolecule **H$_{10}$**

These hyperstructured molecules **H$_7$** and **H$_8$** were quite stable when exposed to moisture. To check the stability, these molecules were dissolved in water and worked up with dichloromethane and then analyzed by ^{31}P NMR and HRMS. It was observed that there was no change in either NMR or HRMS spectrum. This indicated the potential of these molecule for long time stability in open atmosphere, water based reaction for the construction of further generation and safe usage in optoelectronic devices.

3.2.2 Absorption and fluorescence properties of hyperstructured molecules $H_7$and H_8

The absorption and emission properties are the prime requisite for any material to be considered for OLED and NLO applications and hence UV-absorption and fluorescence spectra of **H_7 and H_8** were recorded (**figure 3.2** include the UV absorption spectrum of **H_7 and H_8)**. Both of the molecules showed strong absorption in the region around 300 nm due to π-π* and n- π* transitionof their conjugated background. The hyperstructuredmolecule **H_8** exhibited relative fluorescence at 402 nm and their quantum yield was found to be 10 %, by taking quinine sulphate as standard.

Figure 3.2: Absorption and fluorescence spectra of **H_7**

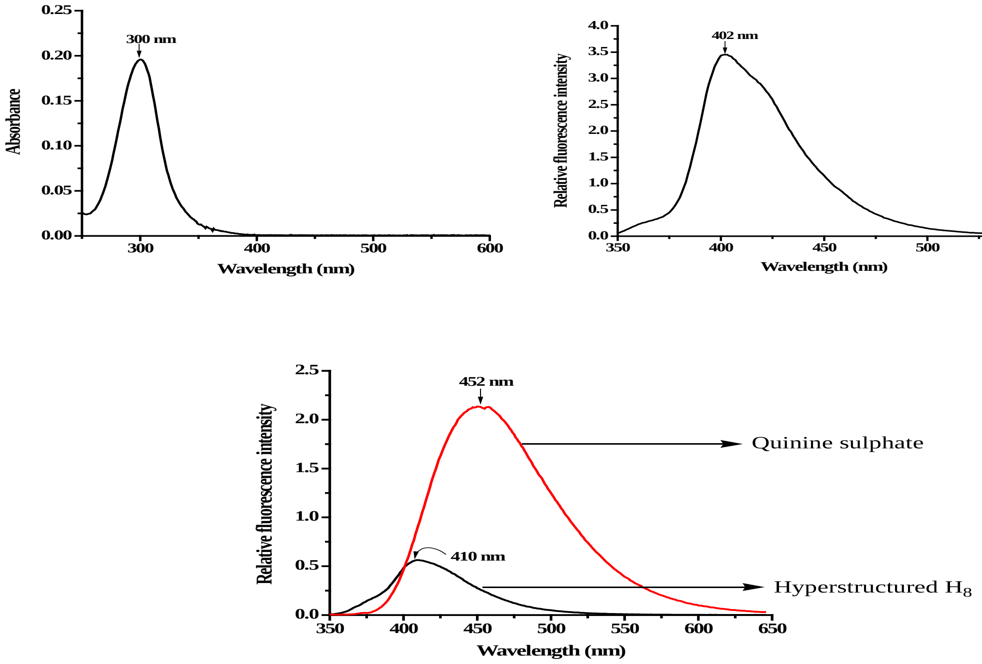
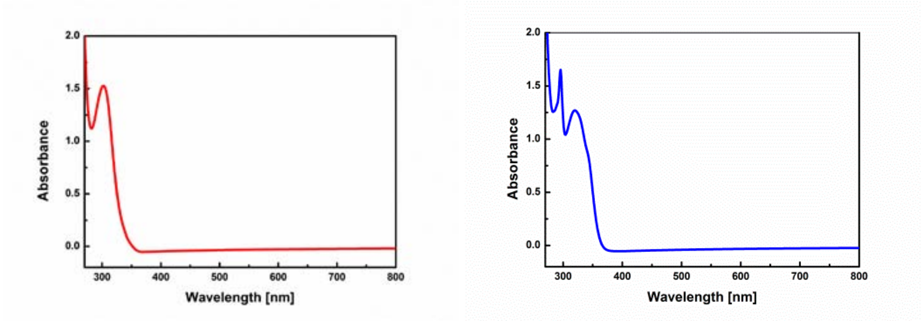


Figure 3.3: Absorption and fluorescencespectra of $\mathbf{H_8}$in comparison with quinine sulphate

3.2.3. Nonlinear optical properties of H_7 and H_8

Nonlinear optics is the study of phenomena that occur as a consequence of the modification of the optical properties of a material system by the presence of intense light. In chapter 1, section **1.7**, the role of dendrimers in non linear optics were discussed. Since the hyperstructured molecules $\mathbf{H_7}$ and $\mathbf{H_8}$ were constructed incorporating triarylamine and carbazole moieties as dendrons and obtained in pure form, we have studied NLO properties of them. The nonlinear optical properties of the samples were studied by Z-scan technique using 800 nm wavelengths, 100 fs pulses with 1 kHz repetition rate. Complete details of NLO measurements are provided in experimental section **(Section 3.4.6)** of this chapter.

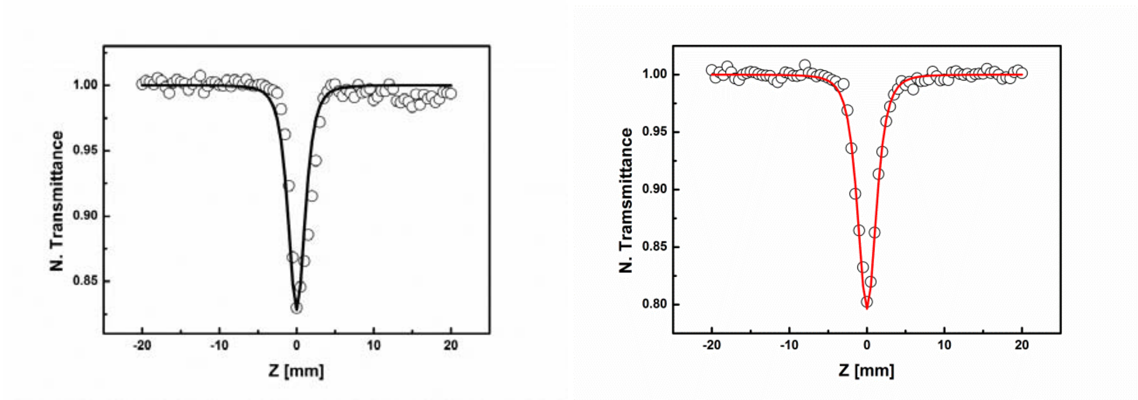
Both the hyperstructured molecules showed absorption peak around 300 nm which plays an important role in the nonlinear optical properties. The linear absorption spectra of $\mathbf{H_7}$ and $\mathbf{H_8}$ molecules are shown in **figure 3.4**.



(a) (b)

Figure 3.4 (a): Absorption spectra of sample $\mathbf{H_7}$ (b): Absorption spectra of sample$\mathbf{H_8}$

The nonlinear absorption curves for the hyperstructured $\mathbf{H_7}$ and $\mathbf{H_8}$under open aperture Z-scan configuration are shown in figure 3.4. It is clear from the Z-scan curves that the optical transmittance falls as the intensity increases indicating that the laser pulse experiences reverse saturable absorption which is attributed to the three photon absorption (TPA). We have extracted nonlinearities of the samples $\mathbf{H_7}$ and $\mathbf{H_8}$ by removing the solvent contributions from the samples by adopting our earlier reports [18].



(a) (b)

Figure 3.5 (a): nonlinear absorption spectra for sample $\mathbf{H_7}$ and (b) nonlinear absorption spectra forsample $\mathbf{H_8}$.The dotted line represents experimental data and the solid lines are theoretical fitting

The Z-scan curves obtained for both the samples indicate a typical nonlinear absorptive response. The nonlinear absorption is indicated by smooth valley shaped curve, that is symmetric about the focal (Z=0) position. The intensities used for the open aperture Z-scan is mode 740 GW/cm^2. The experimental data is fitted using formalism

$$T_{OA(3PA)} = \frac{1}{[1+2\alpha_3 L'_{eff}(I_0/(1+(z/z_0)^2))^2]^{1/2}}$$

Where α_3 is the three photon absorption coefficient, the effective path length for the sample $L'_{eff} = \frac{1-e^{-2\alpha_0 L}}{2\alpha_0}$, α_0 is the linear absorption coefficient, I_0 is the peak intensity, z is the sample position, $z_0 = \frac{\pi\omega_0^2}{\lambda}$ is the Rayleigh range, ω_0 is the beam waist at the focus point (Z=0), λ is the laser beam wavelength.

$$\sigma_{3PA} = \frac{(h\upsilon)^2}{N}\alpha_3$$

Where $N = N_A D$, h is Plank's constant, υ is the laser frequency, N is the number of molecules for unit volume, D is molecular concentration of the compounds, N_A is the Avogadro constant.

Table 3.1: The measured three photon absorption co-efficient (α_3), three photon absorption cross section (σ_3) and nonlinear refraction (n_2) values are in fs regime.

Sample Name	n_2 (cm^2/W)	α_3 (cm^3/W^2)	σ_3(cm^2 s^2/photon^{-2})
H$_7$	4.5x10^{-16}	5.5x10^{-23}	1.13x10^{-76}
H$_8$	2.26x10^{-16}	7.3x10^{-23}	1.89x10^{-76}

The intensity dependent data for the sample **H$_7$** are shown in **figure 3.5**. It is obvious that, as the input intensity increases, the nonlinear absorption get increases up to the damage threshold value. The same behavior has been observed in sample **H$_8$** which is shown in **figure 3.6.**

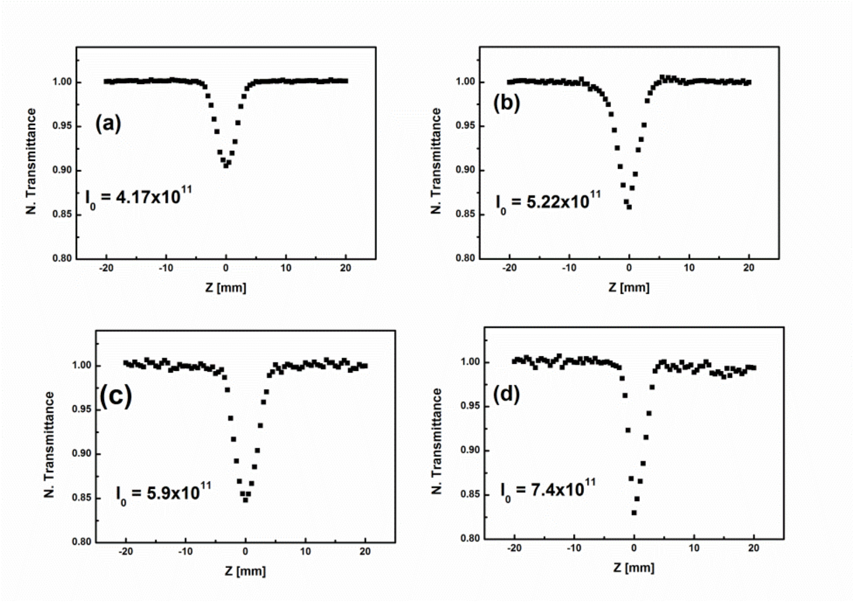


Figure 3.6: The intensity dependant open aperture Z-scan curves for sample $\mathbf{H_7}$

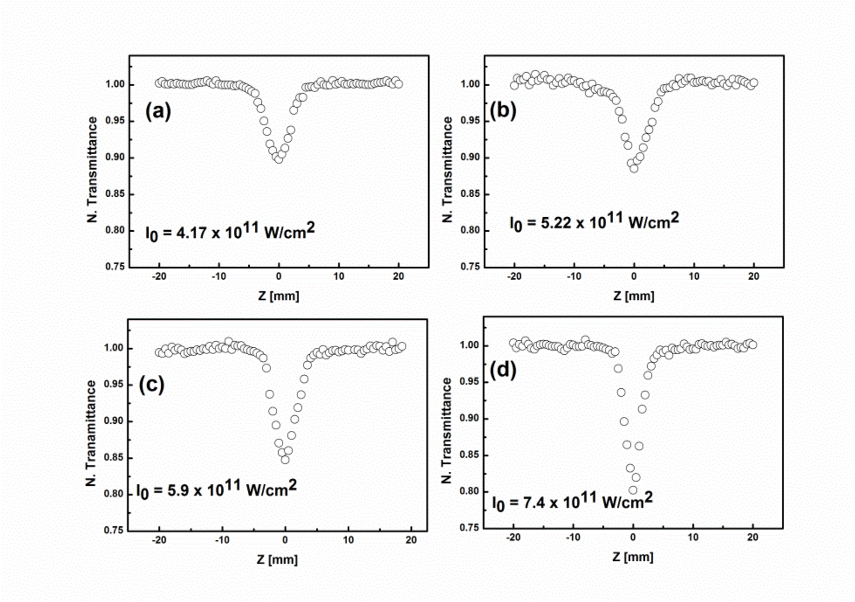


Figure 3.7: The intensity dependentopen aperture Z-scan curves for sample $\mathbf{H_8}$

In order to estimate the nonlinear refractive index of the samples **H_7** and **H_8**, first, the normalized closed aperture transmittance (T_{CA}) was estimated, which is given by the following relation,

$$T_{CA} = 1 - \frac{4\Delta\phi(z/z_0)}{[1+(z/z_0)^2][9+(z/z_0)^2]}$$

where ΔØ is the phase change of the laser beam due to nonlinear refraction, ΔØ value was estimated from the theoretical fits to experimental data. The nonlinear refractive index n_2 was calculated from the relation,

$n_2(cm^2W^{-1}) = \frac{|\Delta\varphi|\lambda}{2\pi I_0 L_{eff}}$ where λ wavelength of the laser beam is, $L_{eff} = 1-e^{-\alpha_0 L} / \alpha_0$ is the effective path length of the sample, L is the sample length, α_0 is linear absorption coefficient, I_0 is peak intensity.

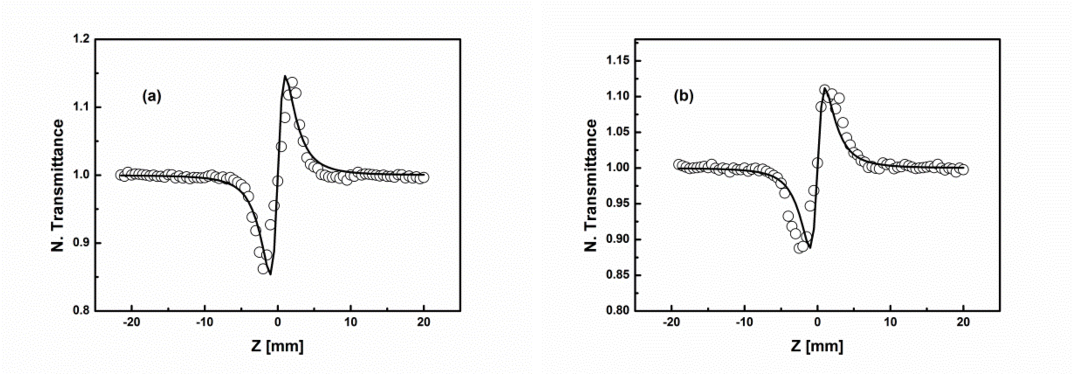


Figure 3.8: The closed aperture Z-scan traces for sample **H_7** (a) and sample **H_8** (b).

The nonlinear refraction of Z-scan curves for samples **H_7** and **H_8** were obtained after dividing the closed aperture Z-scan data by corresponding open aperture Z-scan data as shown in **figure 3.7**. The dotted lines represent the experimental data and the solid lines are theoretical fitting. All the samples show positive nonlinearity. The intensity used for the closed aperture Z-scan measurement was 211GW/cm^2. The obtained nonlinear refractive index for **H_7** and **H_8** molecules are 4.5x10^{-16} cm^2/W and 2.26x10^{-16} cm^2/W respectively.

3.2.4. Li-ion conductivity of hyperstructured molecule H_7

In the chapter 1, **Section 1.6**, we have discussed briefly about the requirement of solid electrolyte for Li-ion batteries and the potential use of dendrimers as solid electrolytes. The important task of an electrolyte is ion transfer, a crucial step in the chemical reduction – oxidation of an electrochemical cell resulting in electrical energy. The conventional theory explained that the amorphous polymers exhibit ionic conductivity whereas crystalline polymers most likely behave as insulator. The ionic conductivity in amorphous polymer is due to the movement of ions, ensued by the local segmental motion of the polymer chain particularly above its glass transition temperature (Tg). Dendrimers are gaining importance due to their amorphous nature which provides flexible backbone and low glass transition temperature. The lower generation of dendrimers contains fewer branching units and adopts flat ellipsoidal structure whereas the higher generation adopts spherical shape. Since the hyperstructured molecules contains heteroatoms like O, P, N, in their structure, and their amorphous form provides flexible in nature which suits for conductivity when mixed with lithium salt. Therefore, it can be expected that the possibility of coordination of hyperstructured molecule with lithium ion would facilitate the solvation [19].

Since we were interested to produce solid electrolytes (**SE**) having phosphorous atom and with good Li-ion conductivity, we prepared solid electrolytes using the molecules $\mathbf{H_7}$. These solid electrolytes were prepared by dissolving $\mathbf{H_7}$with lithium salt (LiTSFI) in THF by varying the lithium salt ratio with two different weight percentages ratios (20% and 30%) to obtain the solid electrolytes; **H7SE-20** and **H7SE-30**. The LiTSFI was selected as Li source due to its proven characteristics as a good candidature Li-ion conductivity studies. Both **H7SE-20** and **H7SE-30** were characterized by using IR, TGA. IR absorption peak for P-O-C group of $\mathbf{H_7}$ appeared at 947 cm^{-1}, but the absorption peak for **SE** was shifted to higher frequency 953cm^{-1}.This shift in frequency supports the interaction of P-O-C group with lithium ion. The TGA analyses revealed that thermal stability of SPE (from 85°C to 180 °C) was increased compared to $\mathbf{H_7}$ which also shows that coordination of the lithium group with $\mathbf{H_7}$.

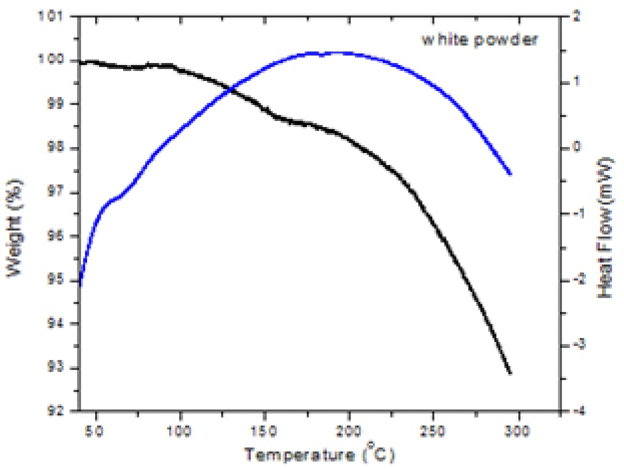


Figure 3.9: TGA plot ofhyperstructured **H_7** molecule.

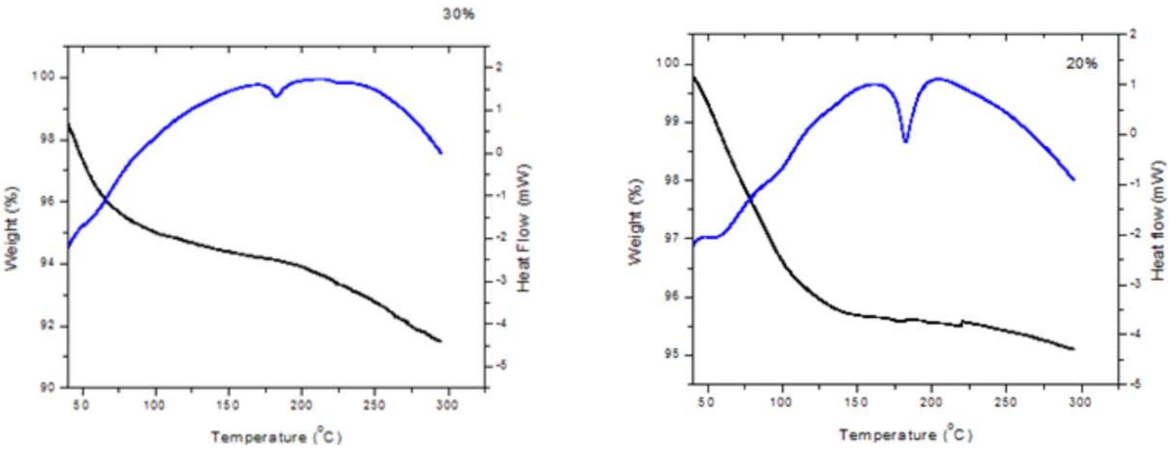


Figure 3.10: TGA plot of **H_7SE-20** and **H_7SE-30**

The conductivity of the **H7SE-20** and **H7SE-30** was studied at various temperatures. At room temperature, the conductivity was found to be 10^{-5} Scm^{-1}. With the increase in temperature, the conductivity started increasing and reached up to 10^{-4} Scm^{-1}, with 20% of lithium salt. When the percentage of the salt increased near to 30% the conductivity decreased and reached up to 10^{-5} Scm^{-1}.With the increase of salt percentage, there is more chance of moisture absorption by lithium salt which results in decrease in conductivity. After exposing the pellet (with 30%) to moisture for several days, the conductivity was studied again which showed that the conductivity didn't change much and it was found to be 10^{-5} Scm^{-1}.It showed that lithium was strongly coordinated to the hyperstructured molecule.

Table 3.2: Li-ion conductivity of **H7SE-20** and **H7SE-30** at various temperatures

Temperature (°C)	Conductivity, σ (S cm^{-1})		
	H7SE-20	**H7SE-30**	**H7SE-30** after exposing to moisture
30	5.81×10^{-5}	3.66×10^{-5}	2.84×10^{-5}
40	8.85×10^{-5}	3.88×10^{-5}	2.01×10^{-5}
50	1.43×10^{-4}	4.00×10^{-5}	1.88×10^{-5}
60	1.35×10^{-4}	3.02×10^{-5}	1.58×10^{-5}
70	1.10×10^{-4}	2.77×10^{-5}	1.55×10^{-5}
80	9.39×10^{-5}	2.23×10^{-5}	1.36×10^{-5}

3.3. SUMMERY AND CONCLUSION

In conclusion, the four cyclophosphazene based hyperstructured molecules were synthesized successfully and they were characterized by standard techniques including multinuclear NMR, HRMS and MALDI spectral data. The major advantage of these hyperstructured molecules is that they were much stable to moisture even up to six month and soluble in common organic solvents which may be useful for solution processability. The absorption and fluorescence behaviors, nonlinear optical properties and the Li-ion conductivitiesof these molecules were studied. The molecule $\mathbf{H_8}$ showed highest fluorescence quantum yield of 10%. Two of the molecules, $\mathbf{H_7}$ and $\mathbf{H_8}$ showed nonlinear refraction with nonlinear refractive indexes 4.5×10^{-16} cm^2/W and 2.26×10^{-16} cm^2/W respectively. The hyperstructred molecule $\mathbf{H_7}$ showed highest Li-ion conductivity of 10^{-4} Scm^{-1}.

3.4. EXPERIMENTAL SECTION

3.4.1. Materials and Instrumentation

Commercially available reagents like hexachlorocyclophosphazenes, carbazole, diphenyl amine, methoxyiodomethane, copper powder, triehyleneglycoldimethylether, potassium iodide, potassiumiodate, cyanuricchloride were purchased from Aldrich. Pottasium carbonate, glacialacetic acid and deuterurated $CDCl_3$ were obtained from SRL, India and used as such without any further purification. The precursors, carbophosphazene, diphenylcarbophosphazene, 4,4'-di(carbazol-9-yl)-4"-hydroxytriphenylamine were prepared according to the standard literature procedure. All the solvents like tetrahyrofuran, dichloromethane, were dried according to standard procedure. Air or moisture-sensitive reactions were maintained throughout the reaction condition, in an inert atmosphere of dry nitrogen using standard schlenk techniques.The dendron (4-hydroxy)diphenylamine, and 4,4-di(carbazol)-4- hydroxytriphenylamine), were purified by using silica gel 60-120 mesh, and the hyperstructured molecule was purified from pure neutral Al_2O_3 column chromatography purchased from SRL company.

^1H, ^{13}C (400MHz) and ^{31}P NMR (162MHz) data were performed on a Bruker Avance-400MHz FT NMR spectrometer at room temperature using $CDCl_3$ as solvent. All NMR chemical shift are reported in parts per million; downfield shifts are reported as positive values from tetramethylsilane (TMS) as standard at 0.00ppm. IR spectra were recorded on a JASCOFT/IR-5300 spectrometer with KBr pellets. UV-Vis spectra were recorded with a Shimadzu 3010 UV/Visible spectrometer NIR spectrometer and JASCO V-670 for nonlinear optics. The fluorescence spectra were recorded on Fluoromax-4 Spectrofluorometerusing DCM as solvent. Elemental analyses were performed on an EA1112, Thermo Finnigan, France. Highresolution mass spectroscopy (HRMS) was performed on a Bruker Maxis HRMS mass spectrometer. The Netzsch STA 409 PC model was used for thermogravimetric and differential thermal analysis (TGA-DTA) to examine the thermal stability.

3.4.2. Common synthetic procedure for the synthesis of H_7 and H_8

The dendron (4-hydroxy)diphenylamine, and 4,4-di(carbazol)-4- hydroxytriphenylamine) was dissolved in dry THF (30 ml) and slowly cool down to $0^{\circ}C$ and then sodium hydride was added and brought down to room temperature and started refluxing under nitrogen atmosphere. 20 ml of a THF solution ofhexachlorocyclotriphosphazene was added to the reaction mixture during the refluxed condition under the protection of dry nitrogen and refluxed. After the reaction mixture is cool down, it was separated via frit and the filtrate part is evaporated and the residue is purified by neutral Al_2O_3 column chromatography (70: 30, HEXANE -DCM).

Table 3.1: *Mole ratio of dendrons used to synthesize the hyperstructured molecules H_7– H_8.*

Hyperstructured molecules	Core	Dendron	Base (NaH)	Reaction time
H_7	cyclophosphazene 0.08 g, 2.96 mmol	[(4- Hydroxy)diphenylamine] 0.32 g, 1.488 mmol	0.07g, 2.96 mmol	48 h
H_8	cyclophosphazene 0.05 g, 0.16 mmol	4,4-di(carbazol-9-yl)-4”-hydroxytriphenylamine 0.07 g, 1.18 mmol	0.05 g, 2.36 mmol	72 h

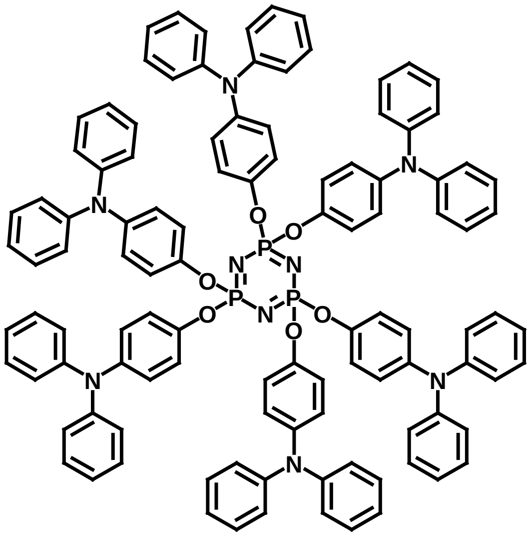
3.4.3. Synthesis of H_9

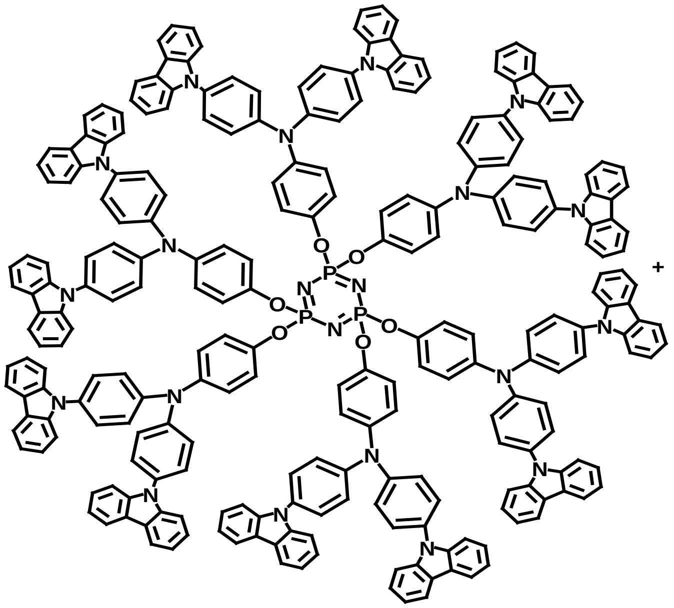
2-chloro-4-Nitroaniline (0.1 g, 0.58mmol) was dissolved in a solution of concentrated HCl (20 ml). The mixture was cooled with an ice bath to lower than 4 °C, and then an aqueous solution containing sodium nitrite (0.08 g, 1.16mmol) was slowly added. The mixture was stirred in the ice bath for 30 min. While the mixture was kept in the ice bath, NaDBS (0.02 g) and a solution of compound hyperstructured **H_7** (0.98 g, 0.58mmol) in dichloromethane (20 ml) were successively added. The resultant mixture was stirred vigorously at room temperature for 24 h. Ethanol (20 ml) was added, and the mixture was heated to remove the dichloromethane layer. The isolated red precipitate was filtered, washed with water, and air-dried. The solid was separated and purified via column chromatography using chloroform on silica gel. However, we could not get pure product.

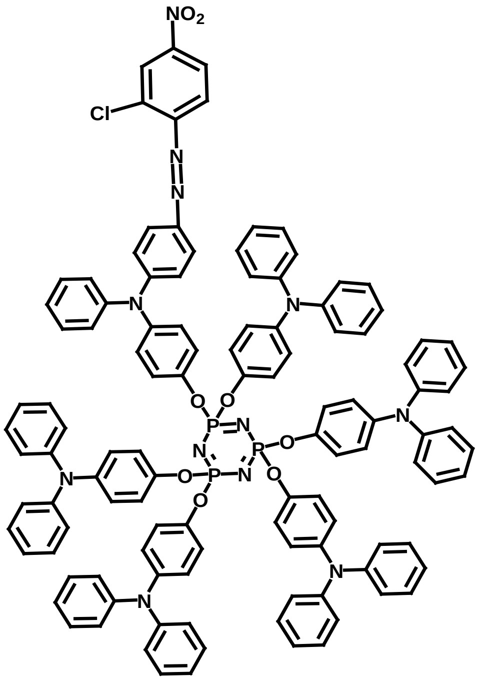
3.4.4. Synthesis of H_{10}

A suspension of K_2CO_3 powder (6.68g, 48.3mmol), 50ml dry THF and 4-bromo-4-hydroxybiphenyl (7.97g, 32mmol) were stirred vigorously at 70 °C for 48 h. A solution of phosphonitrilic chloride trimer (1.39 g, 4.0 mmol) in 25ml of dry THF was then added dropwise to the stirring suspension and allowed to react at 70 °C for 48h. The filtered THF solution was extracted with brine and the organic layer was dried with $MgSO_4$, filtered and concentrated on a rotary evaporator to obtain the crude product that was washed with methanol, dried and used without further purification for the next step. The obtained product (1g, 0.681mmol) was dissolved in toluene further reacted with carbazole (0.67g, 0.041mmol) in presence of the palladium catalyst (1mmol), sodiumtertbutoxide (0.38g, 0.041mmol) as base and refluxed for 48 h. The filtered toluene solution was extracted with brine and the organic layer was dried with $MgSO_4$, filtered and concentrated on a rotary evaporator to obtain the crude product which was purified by column chromatography.

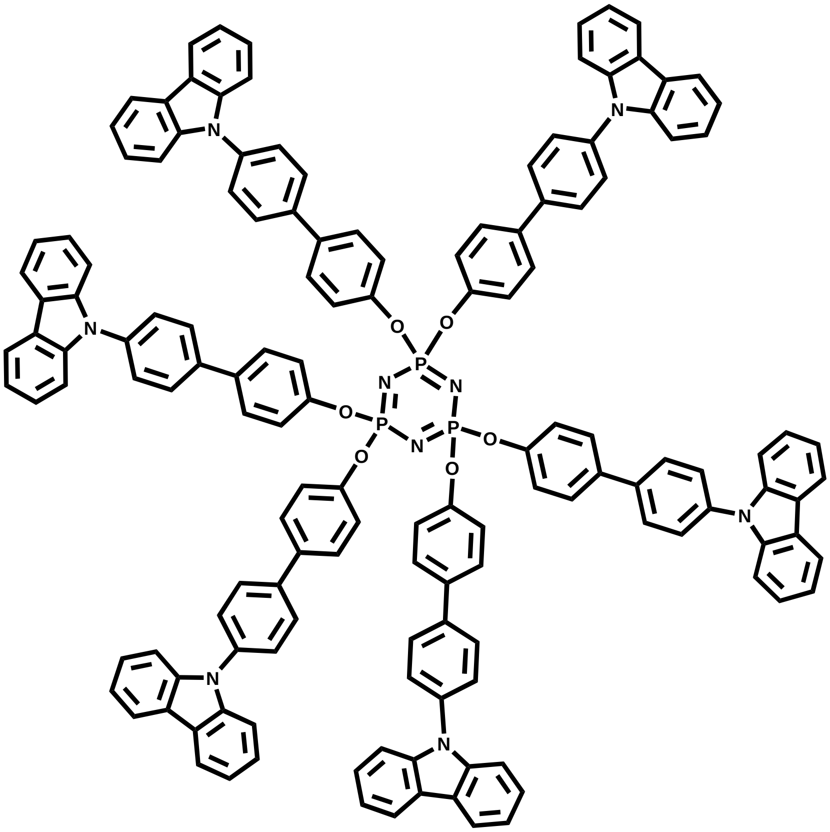
3.4.5. Spectral data

Hyperstructured H_7 molecule 		
Yield	**:**	72%
IR(KBr) ν_{max} cm^{-1}	**:**	3063, 3030, 1583, 1501, 1315, 1271, 1200, 1172, 947, 876, 832, 750, 695, 641, 619**,**
^{1}H NMR (400MHz, $CDCl_3$)	**:**	7.152-7.113(m), 7.023-6.913(m)
^{31}PNMR (162MHz, $CDCl_3$)	**:**	9.41 ppm.
^{13}CNMR (100.62MHz, $CDCl_3$)	**:**	147.64, 145.88, 144.90, 129.25, 124.92, 124.00, 127.74, 121.93.
HRMS	**:**	1696.5626 $(M+H)^+$
Anal.Calcd.for : $C_{108}H_{84}N_9O_6P_3$: C, 76.45; H,4.99; N,7.43%	**:**	Found: C, 76.34; H,4.92; N,7.51%

Hyperstructured H_8 molecule 		
Yield	:	75%
IR(KBr) v_{max} cm^{-1}	:	3463, 3042, 2959, 2356, 1625, 1597, 1562, 1507, 1451, 1333, 1263, 1228, 1174 1102, 1014
^1H NMR (400MHz, $CDCl_3$)	:	8.102-8.065(m), 7.325-7.180(m)
^{31}PNMR (162MHz, $CDCl_3$)	:	9.30 ppm.
^{13}CNMR (100.62MHz, $CDCl_3$)	:	146.23, 140.81, 132.44, 129.54, 128.01, 125.86, 124.62, 123.27,122.38, 122.12 120.31, 119.90, 109.62.
HRMS	:	3677.610 $(M+H)^+$
Anal.Calcd.for : $C_{252}H_{168}N_{21}O_6P_3$: C, 82.27; H,4.60; N,7.99%	:	Found: C, 82.16; H,4.71; N,7.85%

Hyperstructured H_9 molecule 		
^{1}H NMR (400MHz, $CDCl_3$)	**:**	7.95 -7.93(d), 7.06-7.00(m), 6.83-6.80(d)
^{31}PNMR (162MHz, $CDCl_3$)	**:**	8.60 ppm.

Hyperstructured H_8 molecule



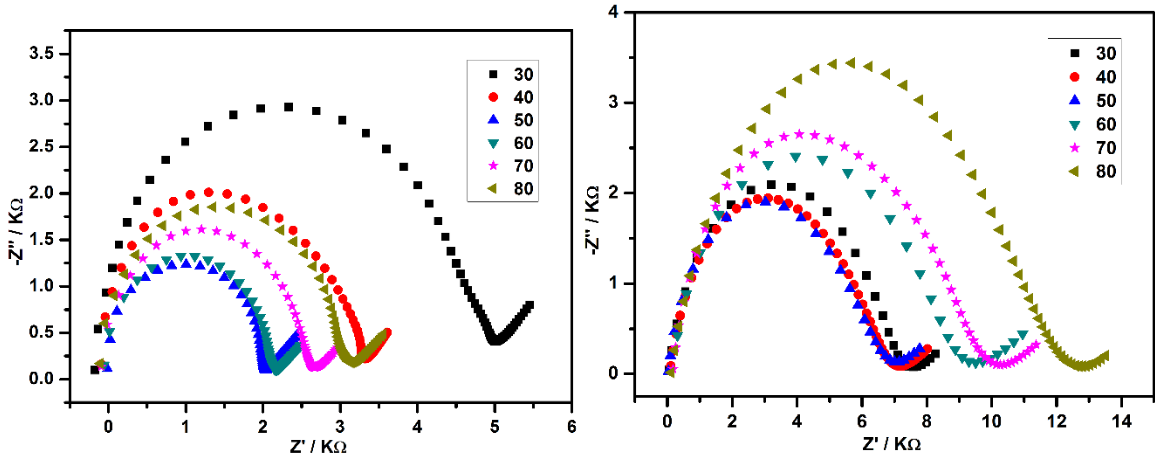
^1H NMR (400MHz, $CDCl_3$)	**:**	8.16-8.09(m), 7.62-7.22(m)
^{31}PNMR (162MHz, $CDCl_3$)	**:**	9.41 ppm.
HRMS	**:**	2141.6256 $(M+H)^+$

3.4.6. Measurement for nonlinear optical properties:

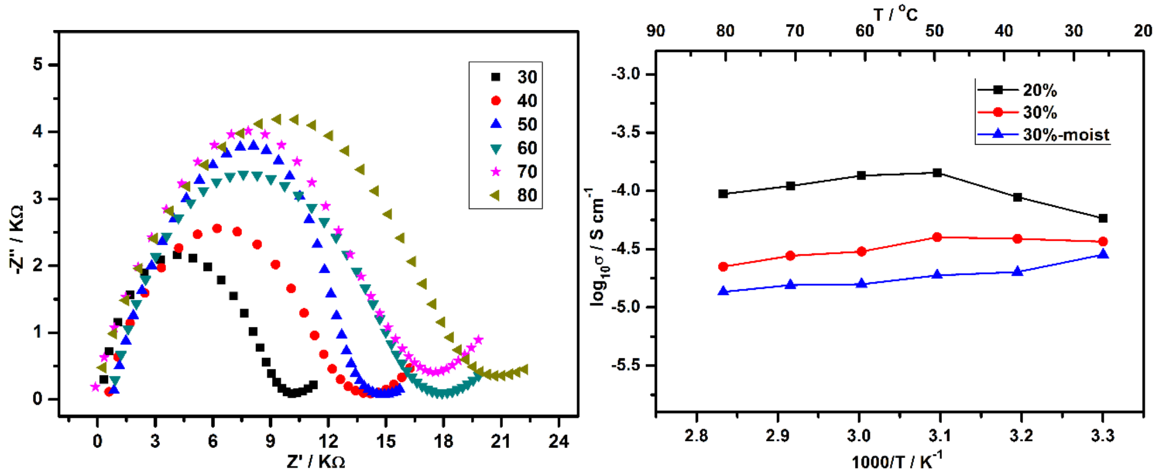
The linear absorption spectra of the samples were measured using UV – Vis spectrophotometer (JASCO V-670).The thickness of the samples used for the absorption measurement was 1 mm thin quartz cell. The third order nonlinear optical properties for hyperstructured molecules were carried out with Z-scan technique using ultrashort laser pulses obtained from a conventional chirped pulse amplification (CPA) system comprising of an oscillator (Maitai, Spectra Physics Inc.) delivering 80 fs, 82 MHz pulse train with pulse energy of 1nJ, at 800 nm and a regenerative amplifier (Spitfire, Spectra Physics Inc.), pumped by a 150 ns, 1kHz, Q-switched Nd:YLF laser. After the regenerative amplifier, we obtained 1 kHz, 110 fs duration pulses with maximum pulse energy of 1mJ. The Z-scan technique is a single beam method was used for measuring both nonlinear absorption and nonlinear refraction [20]. Its operation involves the measurement of sample transmittance at far filed for a tightly focused Gaussian beam as a function of sample position. A lens with focal length of 12 cm was used to focus the Gaussian beam. The sample is moved through the focal region of the laser beam over the length of 80 mm. At the focal point, the sample experiences maximum pump intensity, which gradually decreases in either direction from the focus. The sample solution taken in 1mm quartz cuvette which is smaller than the Rayleigh range of the focussed beam calculated to be ~ 4 mm. The samples were dissolved in chloroform and concentration of the samples used for linear and NLO (nonlinear optical) measurements is $5x10^{-5}$ M.

3.4.7. Impedance measurements for Li-ion conductivity

The impedance measurements of polymer electrolytes were performed in Zahnerzennium electrochemical work station withbuilt in Thales software for data acquisition. The measurements were done in the frequency range of 1 Hz-4 MHz. Initially films were made by dissolving polymer and $LiN(SO_2CF_3)_2$ in THF at room temperature, but the films of SPEs were brittle. Therefore, instead of making films, pellets were made for measurements. The consistency of result was checked by repeating the measurements three times. The specimens in the form of pellets were sandwiched between two gold plated electrodes housed in a homemade cell. For variable temperature measurements, cell was equilibrated at each temperature for 30 min before measuring. The conductivity was calculated according to the equations ¼ d/(ARb), where d is thethickness of the polymer electrolyte disc, A is the surface area of thepellet and Rb is the bulk resistance value which can be obtained from the Nyquist plot [21].



H7SE-20 (1) **H7SE-30 (2)**



H7SE-30moist (3) **Arrhenius plot (4)**

Figure 3.10: Temperature dependent of nyquist plots of **H7SE-20** and **H7SE-30.** The plot (4) explains about the Arrhenius plot of temperature dependence conductivity of **H7SE-20**, **H7SE-30**and exposed **H7SE-30**to moisture.

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CHAPTER 4

SYNTHESIS OF INORGANIC-ORGANIC HYBRID POLYETHER CONTANING PHOSPHOROUS AND THEIR Li-ION CONDUCTIVITIES

Abstract:

Synthesis of phosphorous containing polyethers and their lithium-ion conductivities for the potential use as solid polymer electrolyte (SPE) in high-energy density lithium-ion batteries have been described. Copolymerization of butyl bis(hydroxymethyl)phosphine oxide with three different dibromo monomers were carried out to produce three novel phosphorous containing polyethers (**P1**-**P3**). These polymers were obtained via nucleophilic substitution reactions and were characterized by ^{1}H, ^{31}P NMR spectral data and gel permeation chromatography. SPEs were prepared using polyethers (**P1**and**P2**) with various amounts of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). The lithium-ion conductivity of **SPE2** containing 40 wt% of LiTFSI was 2.1×10^{-5} S cm^{-1}at room temperature and 3.7×10^{-4} S cm^{-1} at 80°C.

4.1 INTRODUCTION

The requirements of energy storage and portability increase the demand for efficient energy storage devices [1]. Rechargeable lithium-ion batteries are the major power sources for portable electronics. At present, the performance of lithium-ion battery for the miniature portable electronic devices is satisfactory. However, the current technology cannot be promoted to automobile batteries due to the potential fire hazard of organic liquid electrolyte present in batteries [2]. Moreover, organic liquid electrolytes suffer from volatility, pressure build-up or even explosion, limited operating temperature range and harmful leakage. The fundamental solution to this problem is substituting the flammable organic liquid electrolyte with non-flammable solid polymer electrolyte (SPE). Besides the safety considerations, other interesting properties such as flexibility, easy manipulation, wide operating temperature range, high electrochemical stability and light weight fabrication gives possibilities for advanced lithium-ion polymer secondary batteries. In addition, both ion conduction and mechanical separation can be attained in a single solid electrolyte membrane. Furthermore, a battery can be fabricated in any desired shape and size due to the flexibility of polymer membranes [3]. Therefore, a better SPE with flame retardant property for high-energy density lithium ion batteries is always been in demand to replace the organic liquid.

Wright and co-workers revealed the ability of poly (ethylene oxide) (PEO) to dissolve inorganic salts and exhibiting ion conduction at room temperature [4]. But, the room temperature ionic conductivity of PEO based polymer electrolyte is too low (10^{-7} S cm^{-1}) for practicable applications. Polyphosphazenes, [7] and polysiloxanes, [8] were good hosts for lithium ion conductivity; accordingly they were reported to have maximum conductivity of 5×10^{-5} S cm^{-1} and 4.5×10^{-4} S cm^{-1}, respectively. However their practical use was hindered because of their jelly nature other properties like mechanical strength.

Our interest is to prepare SPEs having good ionic conductivity with wider operating voltage and flame retardant property. The ionic conductivity in amorphous polymers depends on local segmental motions of polymer chains and such a favourable situation was obtained only at temperatures above T_g [5]. Hence, an amorphous, solid polymer with low glass transition temperature is preferred for ionic conductivity.Many efforts are directed toward synthesizing polymers for lithium ion transport without sacrificing their properties. One such approach is constructing a perfect polymer framework through a crystalline arrangement of polymer chains either by metal organic framework (MOFs) or covalent organic framework (COFs). MOFs and COFs are well-known for applications in gas storage, catalysis and molecular separation; [6] but synthesizing the material by MOF and COF approach for lithium ion transport without sacrificing their desired properties is challenging.

In the chapter 3 **(section 3.2.4.)**, we discussed about the possibility of using hyperstructured molecules having phosphorus for Li-ion conductivity. These molecules facilitated the Li-ion conductivity which was created because of the distorted orientation of bulky groups. Recent work in our research group demonstrated that super structure for facile lithium ion transport can be created by introducing bulky pendent group in polymer chain.The intrinsic porous structure was generated because of the inefficent packing of the polymer chain. Our interest is inducing conformational flexibilities by incorporating phosphorous in the form of C-P-C bonds in the chain. Integration of heteroatoms into the carbon–carbon polymer chain can be an intriguing strategy to tailor the properties to expand the applications of materials. However, incorporation of heavier main group element in the polymer back bone is synthetically challenging. In this scenario, use of substituted bis(hydroxymethyl)phosphine oxides as monomer in a copolymerization reaction could be an interesting choice to obtain polyethers with phosphorous-carbon bonds in the main chain. In this chapter, the polymerization behaviour of butyl bis(hydroxymethyl)phosphine oxide and the influence of phosphorous containing polyethers on ionic conductivity is discussed.

Figure 4.1: Bis(hydroxymethyl)phosphine oxide

4.2 RESULTS AND DISCUSSION

The following methods are generally used to achieve flame retardant property for polymers: a) blending polymers with phosphorous containing molecules; b) covalently attaching phosphorous containing molecules as pendant group to the polymer chains; c) phosphorous containing polymers in which phosphorous present in main chain of polymer [10]. We are interested to synthesize polyethers having phosphorous in the main chain of polymer. It is known that the hydroxymethyl groups of alkyl bis(hydroxymethyl)phosphine $RP(CH_2OH)_2$ behaved like masked $-PH_2$ group. But it behaves as a normal diol when the phosphine was converted to phosphine oxide $RP(O)(CH_2OH)_2$ [11]. A variety of natural and synthetic polymers where phosphorous is in main chain with O-P-O linkages are known. However, polymers with C-P-C linkages are challenging for synthesis. Therefore, use of alkyl substituted bis(hydroxymethyl) phosphine oxide as monomer to produce polyether is attractive methodology to obtain polymers with C-P-C links.

4.2.1 Synthesis of monomer (M1)

While tris(hydroxymethyl)phosphine (**S1**) was treated with 1- iodobutane in methanol, followed by the addition of triethylamine and hydrogen peroxide yielded **M1** as a major product and **M2** as a minor product **(scheme 4.1)**. These compounds were separated by column chromatography. The compound $P(CH_2OH)_3$**S1** was known to release formaldehyde (HCHO) when heated. The HCHO thus formed in turn reacted with unreacted $P(CH_2OH)_3$ similar to well-known wittig reaction forming **M2**. This is also a reason for low yield of **M1**. The structures of **M1** and **M2** were confirmed by ^1H, ^{13}C and ^{31}P NMR spectral data.

Scheme 4.1: Synthesis of butyl bis(hydroxymethyl)phosphine oxide (**M1**)

4.2.2 Synthesis of polyethers (P1-P3)

1,4–bis(bromomethyl)–2,3,5,6–tetramethylbenzene (**M3**) and 1,4–bis(bromomethyl)–2,3,5,6–tetramethoxybenzene (**M4**) were synthesized from durene and 2,5-dihydroxy-1,4-benzoquinone respectively according to the literature procedures [7,8].The butyl bis(hydroxy methyl)phosphine oxide **M1** was copolymerized with different dibromo monomers such as **M3**, **M4** and 1,5–dibromopentane**M5** to obtain polyethers **P1–P3** respectively via nucleophilic substitution reactions **(scheme 4.2)**. The condensation polymers were synthesized in the presence of K_2CO_3 as a base in N, N–dimethylacetamide(DMAc). The polymerization procedure was carried out in two stages. First, toluene was added to the reaction mixture and azeotropic distillation was continued until water that formed during the reaction was removed from the reaction mixture [12]. In the later stage, temperature was increased to 160 °C and polymerization was progressed for required time. All the crude polymers were purified by reprecipitation from THF in hexane.

Scheme 4.2: Synthesis of phosphorus containing polyethers**P1-P3**

Table 4.1: Properties of polyethers**P1-P3**

Entry	Co-monomer	Polymer (**P**)	T_d (°C)	T_g (°C)	M_n (g mol^{-1})	M_w (g mol^{-1})	PDI
1	**M3**	**P1**	308.2	65.1	9414	15156	1.61
2	**M4**	**P2**	279.9	43.4	8420	14230	1.69
3	**M5**	**P3**	240.7	-40.5	10077	16425	1.63

The polyethers**P1** and **P2** are solids while **P3** is liquid and they are readily soluble in chloroform, Tetrahydrofuran and dimethylsulfoxide. The polyethers**P1-P3** was characterized by ^{1}H and ^{31}P NMR spectral data which showed that the data were consistent with the expected molecular structure. The ^{31}P{^{1}H} NMR spectra of polymers **P1-P3** showed a single peak and appeared at δ 44.15, 45.75 and 44.92 ppm respectively. The decomposition temperature (T_d), glass-transition temperature (T_g), molecular weight ($M_n$and M_w) and PDI of polyethers **P1-P3** are listed in **Table 4.1**. The copolymers **P1–P3** have molecular weight (M_w) in the range of 14.2-16.4 kg mol^{-1}. Thermogravimetric analyses (Figure 4.2) revealed the thermal stability of polymers **P1-P3** lies in the range of 240-308 °C. The polymers **P1–P3** are completely amorphous and they did not show any peak corresponds to melting temperature (T_m) on DSC analyses **(Figure 4.3)**.

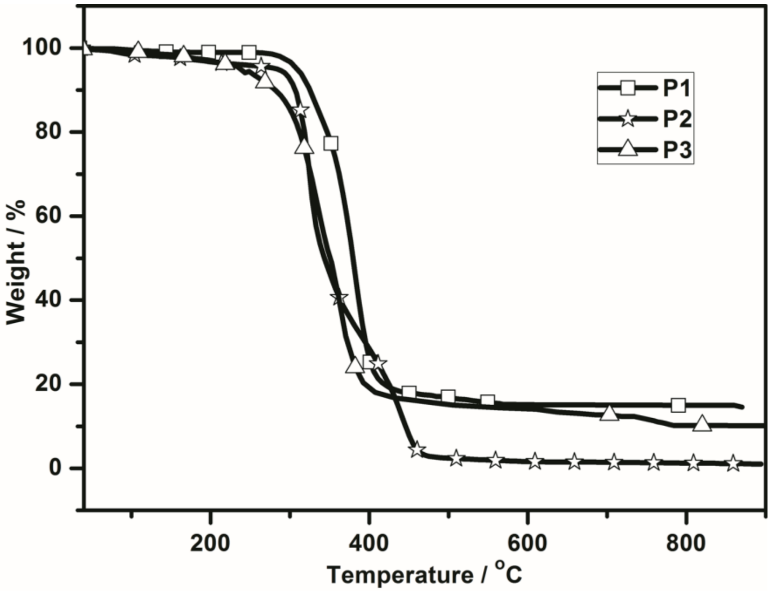

Figure 4.2: TGA plots of polyethers **P1-P3**

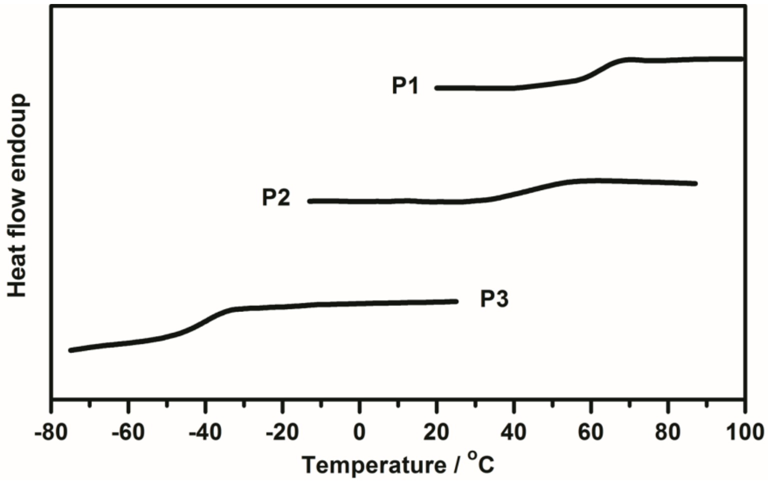

Figure 4.3: DSC plots of polyethers**P1-P3**

4.2.3 Solid polymer electrolyte (SPE)

P1 and **P2** were utilized to prepare **SPE1** and **SPE2** using various amounts of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (10, 20, 30 and 40 wt%). The liquid polymer **P3** was not used to make an electrolyte. The polymers and lithium salt was dissolved in THF at 25 °C and maintained for 12 h. THF was evaporated and dried under vacuum to obtain SPEs. Compared to **P1** and **P2**, thermal stability of **SPE1** and **SPE2** was increased with increasing lithium salt content from 10 wt% of LiTFSI (**10%**) to 40 wt% of LiTFSI **(Figure 4.2and 4.4 ;Tables4.1,4.2 and 4.3)**. Likewise, T_g of **SPE1** and **SPE2** increased continuously with the addition of lithium salt from **10%** to **40% (Figures 4.4 and S2; Tables4.2 and 4.3)**. The rise in T_d and T_g compared to their corresponding polymer might be due to the effective coordination of polymer chains with lithium-ion. Based on the following observations from DSC analyses: (a) absence of peaks matching the melting temperature (T_m) of lithium salt; (b) a singleT_g; (c) increase in T_g with the addition of lithium salt; it was concluded, LiTFSI is completely miscible in **P1** and **P2** that affords a homogeneous amorphous phase and did not exist as aggregates. The absence of melting point of salts is attributable to the solvation of lithium-ions by coordination of polymer.

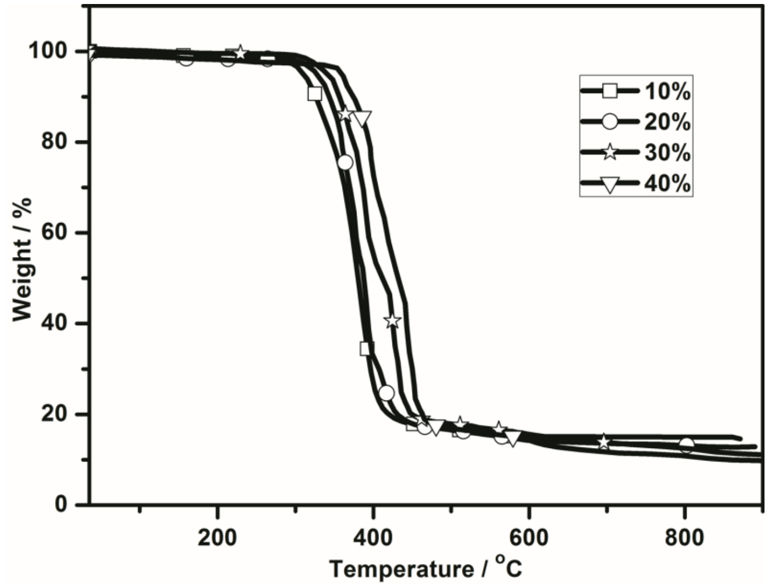

Figure 4.4: TGA plots of **SPE1** (**10%-40%**)

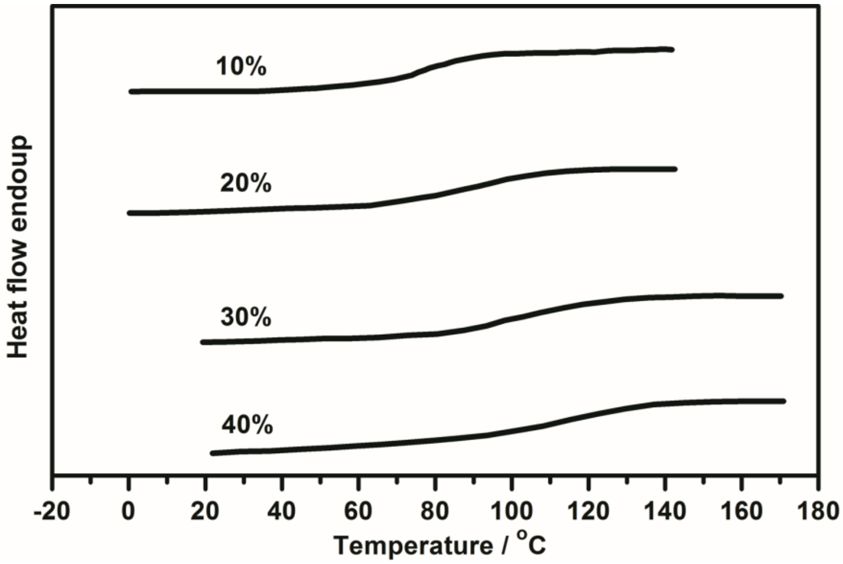

Figure 4.5: DSC plots of **SPE1** (**10%-40%**)

Table4.2:Thermal properties and Li-ion conductivity of **SPE1** (**10%-40%**)

SPEs(wt% of LiTFSI)	**SPE1**			
	Conductivity σ (S cm^{-1})		T_d (°C)	T_g (°C)
	30 °C	80 °C		
SPE (10%)	5.1×10^{-7}	5.6×10^{-6}	324.1	78.9
SPE (20%)	6.5×10^{-7}	8.3×10^{-6}	332.5	86.7
SPE (30%)	9.5×10^{-7}	4.4×10^{-5}	341.6	102.4
SPE (40%)	2.6×10^{-6}	7.3×10^{-5}	355.8	116.2

Table 4.3: Thermal properties and Li-ion conductivity of **SPE2** (**10%-40%**)

SPEs(wt% of LiTFSI)	**SPE2**			
	Conductivity σ (S cm^{-1})		T_d (°C)	T_g (°C)
	30 °C	80 °C		
SPE (10%)	3.2×10^{-6}	2.3×10^{-5}	290.2	52.4
SPE (20%)	6.5×10^{-6}	8.8×10^{-5}	298.1	65.3
SPE (30%)	1.2×10^{-5}	1.4×10^{-4}	310.5	70.6
SPE (40%)	2.1×10^{-5}	3.7×10^{-4}	321.7	78.1

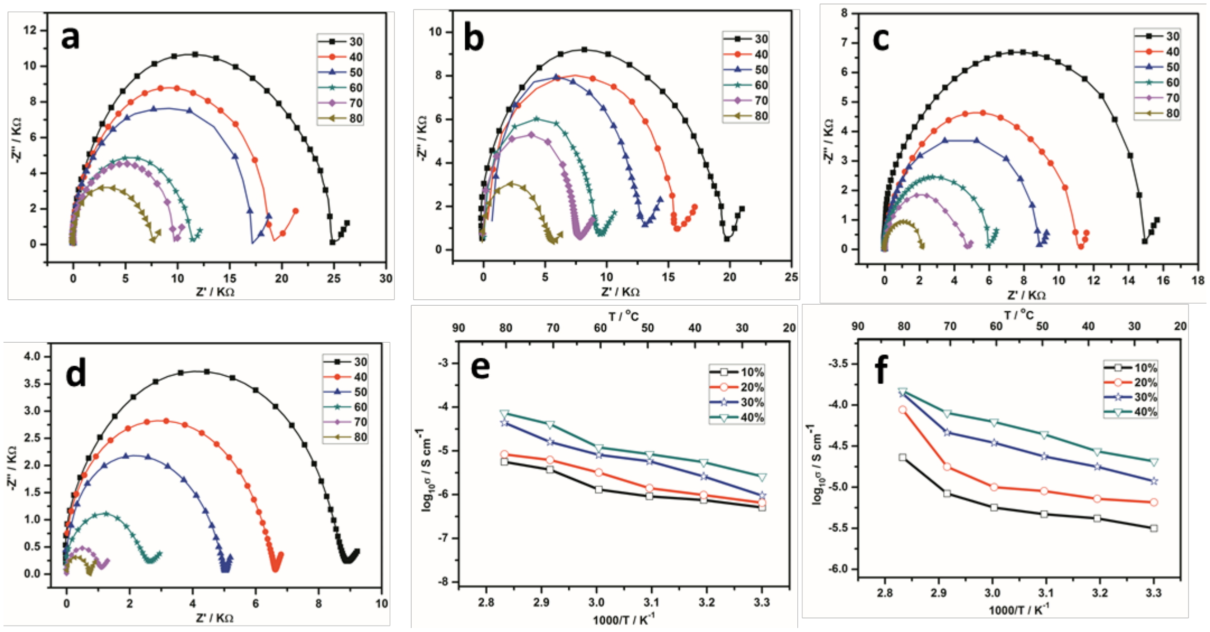

Figure 4.6: Temperature dependent nyquist plots of **SPE1** a) **10%** b) **20%** c) **30%** d) **40%**. Arrhenius plots of temperature dependent conductivities of e) **SPE1** (**10%-40%**) f) **SPE2** (**10%-40%**).

The conductivities of **SPE1** with 10-40 wt% of LiTFSI [**SPE1**(**10%-40%**)] and **SPE2** with 10-40 wt% LiTFSI [**SPE2**(**10%-40%**)] were calculated from the bulk resistance determined from complex impedance spectra [13]. The ionic conductivities at 30 °C and 80 °C of **SPE1**(**10%-40%**) and **SPE2**(**10%-40%**) are listed in **Table 4.2 and 4.3**. **Figure 4.6** shows the temperature dependent nyquist plots of **SPE1** (**10%-40%**) and Arrhenius plots of **SPE1** (**10%-40%**) and **SPE2** (**10%-40%**). While increasing the lithium salt content progressively from **10%** to **40%**, the ionic conductivity of **SPE1** and **SPE2** increased. Further, ionic conductivity of **SPE1** (**10%-40%**) and **SPE2** (**10%-40%**) were increasing with temperature. The room temperature ionic conductivity of **SPE1** (**10%-40%**) and **SPE2** (**10%-40%**) lies in the range of 5.1×10^{-7}- 2.1×10^{-5} S cm^{-1}. The maximum conductivity of 3.7×10^{-4} S cm^{-1} was attained for **SPE2** (**40%**) at 80 °C. Among **SPE1** and **SPE2**, **SPE2** exhibited better ionic conductivity with various amounts of lithium salt and with temperature. The presence of more coordinating group (-OMe) in **P2** as well as low T_g of **P2** compared to **P1** makes a better host polymer for lithium-ion conductivity.

4.3 SUMMERY AND CONCLUSIONS

The phosphorous containing polyethers wherein phosphorous exists in the main chain of polymer with C-P-C links has been synthesized. The utilization of alkyl substituted bis(hydroxylmethyl)phosphine oxide as monomer for polymer synthesis was studied. The completely amorphous, highly stable and flame retardant polymers (**P1-P3**) were obtained by condensation polymerization. The solid polymer electrolytes **SPE1** and **SPE2** were prepared and their ionic conductivity behaviour was examined. The **SPE2** (**40%**), prepared from **P2**, showed the highest conductivity of 3.7×10^{-4} S cm^{-1} at 80 °C. **SPE2** may be a promising SPE having good ionic conductivity with possible flame retardant property that would find potential application in larger batteries.

4.4 EXPERIMENTAL SECTION

4.4.1 Materials and instruments

All manipulations involving air and moisture sensitive compounds were carried out using standard schlenk techniques under the atmosphere of dry nitrogen. All solvents to be used under inert atmosphere were thoroughly deoxygenated using freeze-pump-thaw method before use. They were dried and purified by refluxing over a suitable drying agent followed by distillation under nitrogen atmosphere. The compounds, tris(hydroxymethyl)phosphine (**S1**)[6], 1,4–bis(bromomethyl)–2,3,5,6–tetramethylbenzene[7](**M3**), 1,4–bis(bromomethyl)-2,3,5,6–tetramethoxybenzene [8] (**M4**) were synthesized according to the literature procedures [19]. The compounds, tetrakis(hydroxymethyl)phosphonium chloride (Acros); 1,5–dibromo -pentane (**M5**), 1- iodobutane and lithium bis(trifluoromethanesulfonyl)imide $LiN(SO_2CF_3)_2$ (LiTFSI) were purchased from Aldrich and were used as received without purification. K_2CO_3 (Merck) was dried at 100 °C for 6 h under vacuum prior to use.

Structures of all the products were confirmed by ^{1}H, ^{31}P and ^{13}C NMR spectra. All the NMR spectra were recorded on a BrukerAvance 400 MHz FT NMR spectrometer at room temperature using either $CDCl_3$ or CD_3OD as solvent. The chemical shifts are reported in parts per million (δ) relative to tetramethylsilane as reference for ^{1}H and $^{13}C\{^{1}H\}$ NMR (100 MHz). The $^{31}P\{^{1}H\}$ NMR (162 MHz) spectra referenced to 85% H_3PO_4. The Netzsch STA 409 PC model was used for thermogravimetric and differential thermal analysis (TG-DTA) to examine the thermal stability. The decomposition behaviour of polymers was studied from 30 to 900 °C under the nitrogen flow with a heating rate of 10 °C/min. The temperature of 5% weight loss was chosen as onset point of decomposition (T_d). The glass transition temperatures (T_g) of polyethers were measured on a Differential Scanning Calorimeter (DSC) from PerkinElmer (Pyris Diamond DSC 8000). The measurements were performed at a heating rate of 10 °C/min under the nitrogen. T_g was assigned as the inflection point in the thermogram. The molecular weights of the polymers were determined by Gel Permeation Chromotography (GPC) of Shimadzu 10AVP model equipped with refractive index (RI) detector. The separation was achieved using a Phenogel mixed bed column (300 × 7.80 mm) operated at 30 °C with a flow rate of 0.5 mL/min.

using tetrahydrofuran (THF) as the eluent. The molecular weight and molecular weight distributions were calculated using polystyrene as a standard.

The impedance measurements of polymer electrolytes were performed in Zahnerzennium electrochemical work station with built in Thales software for data acquisition. The measurements were done in the frequency range of 1 Hz to 4 MHz. The specimens in the form of pellets were sandwiched between two gold plated electrodes housed in a homemade cell. For variable temperature measurements, cell was equilibrated at each temperature for 30 min, before measuring. The conductivity was calculated using the equation $\sigma = d/(AR_b)$, where d is the thickness of the polymer electrolyte disc, A is the surface area of the pellet and R_b is the bulk resistance value which can be obtained from the Nyquist plot [9].

4.4.2 Experimental procedure

a) Synthesis of butyl bis(hydroxymethyl)phosphine oxide (**M1**):

The synthesis of **M1** was achieved in three steps as follows: A solution of tris(hydroxymethyl)phosphine (**S1**) (12.60 g, 0.1 mol) in methanol (20 mL) was taken into a 500 mL two necked flask under nitrogen. To this, deoxygenated mixture of 1- iodobutane (37.43 g, 0.2 mol) and methanol (140 mL) was added drop wise at 0 °C for 30 min. The reaction mixture was refluxed for 4 h and the solvent was evaporated under high vacuum to get a viscous oilyproduct.Purification of this product was unsuccessful because it was non-volatile oily liquid.

To the above mixture (25.38 g), dry triethylamine (190 mL) was added in one portion under nitrogen with stirring. The resulting mixture was then heated to 60 °C for 1 h and then allowed to cool to room temperature. The solid $[NHEt_3]Cl$ byproduct was filtered off and triethylamine solvent was distilled out at atmospheric pressure to give a crude product which was then heated to 90 °C for 5 h under reduced pressure. A viscous oily product was obtained.

To the above oily product(10.88 g) in methanol (25 mL), 30% hydrogen peroxide solution (8.3 mL, 72 mmol) was added dropwise at 15 °C and stirred for 2 h. The solution was concentrated under vacuum which was purified by column chromatography on silica gel eluting with CH_2Cl_2/MeOH (6 : 1) to give a clear colorless liquid butyl bis(hydroxy methyl)phosphine oxide(**M1**). (TLC was analyzed by immersing the plate in 5% sulfuric acid in methanol followed by heating using hot-air drier for 2 min. and spots were visualized by naked eye) Yield: 5.40 g, 45%. ^{1}H NMR (CD_3OD): δ 4.86 (s, 2H, –O*H*), 3.97 (dd, *J* = 26.5, 14.1 Hz, 4H, –OC*H*$_2$P), 1.91-1.79 (m, 2H, –PC*H*$_2$CH$_2$), 1.71-1.56 (m, 2H, –C*H*$_2$CH$_2$CH$_3$), 1.53-1.41 (m, 2H, –C*H*$_2$CH$_3$), 0.96 (t, *J* = 7.3 Hz, 3H, –C*H*$_3$). ^{13}C NMR (CD_3OD): δ 58.45 (d, *J* = 79 Hz, –P*C*H$_2$O), 26.39 (d, *J* = 13 Hz, –*C*H$_2$), 24.98 (d, *J* = 4 Hz, –*C*H$_2$), 24.13 (d, *J* = 62 Hz, –*C*H$_2$), 15.07 (s, –*C*H$_3$). ^{31}P NMR (CD_3OD): δ 51.54. EI-MS: *m/z* 333 ($2M^+$+1, base peak). Anal.calcd for $C_6H_{15}O_3P$: C, 43.37; H, 9.10. Found: C, 43.28; H, 9.25. Further continuation of elution yielded tris(hydroxymethyl)phosphine oxide (**M2**). Yield: 1.50 g, 12%. ^{1}H NMR (CD_3OD): δ 4.11 (s, 6H, C*H*$_2$), 2.55 (s, O*H*). ^{13}C NMR (CD_3OD): δ 57.14 (d, *J* = 76 Hz, –*C*H$_2$). ^{31}P NMR (CD_3OD): δ 46.00.

b) General procedure for the copolymerization of **M1** with **M3**−**M5**:

A typical polymerization procedure is as follows. The mixture of $BuP(O)(CH_2OH)_2$ (**M1**) (3 mmol), corresponding co-monomer (**M3**, **M4** or **M5**) (3.3 mmol) and K_2CO_3 (7.2 mmol) in N, N–dimethylacetamide (2.5 mL) was taken in a 100 mL round bottom flask equipped with a Dean-Stark trap. To this, toluene (20 mL) was added as an azeotrope. The reaction mixture was heated to 130 °C for 5 h in order to remove water that formed during the reaction. Then, the reaction mixture was heated to 160 °C and maintained for 30 h. The viscous reaction mixture was poured into ethanol and filtered off. The product was purified by dissolving in THF and reprecipitatingin hexane. This process was repeated for three more times to obtain pure polymers.

***Polymer 1 (P1)** (Copolymer of **M1** and **M3**):* After purification, **P1** was obtained as a white color powder. Yield: 83%. ^{1}H NMR ($CDCl_3$): δ 4.81-4.62 (m, 4H, OC*H*$_2$Ph), 3.98-3.82 (m, 4H, PC*H*$_2$O), 2.45-2.18 (m, 12H, –C*H*$_3$), 1.79-1.65 (m, 2H, –PC*H*$_2$), 1.63-1.50 (m, 2H, –C*H*$_2$), 1.48-1.31 (m, 2H, –C*H*$_2$CH$_3$), 0.88 (t, 3H, –C*H*$_3$). ^{31}P NMR ($CDCl_3$): δ 44.15.

***Polymer 2 (P2)** (Copolymer of **M1** and **M4**):* After purification, **P2** was obtained as a white color powder. Yield: 80%. ^{1}H NMR ($CDCl_3$): δ 4.77-4.56 (m, 4H, OC*H*$_2$Ph), 4.32-3.91 (m, 4H, PC*H*$_2$O), 3.90-3.68 (m, 12H, –OC*H*$_3$), 1.93-1.78 (m, 2H, –PC*H*$_2$), 1.66-1.51 (m, 2H, –C*H*$_2$), 1.48-1.35 (m, 2H, –C*H*$_2$CH$_3$), 0.88 (t, 3H, –C*H*$_3$). ^{31}P NMR ($CDCl_3$): δ 45.75.

Polymer 3 (P3) *(Copolymer of **M1** and **M5**):* After purification, **P3** was obtained as a colorless liquid. Yield: 82%. ^{1}H NMR ($CDCl_3$): δ 3.95-3.68 (m, 4H, OCH_2P), 3.57-3.38 (m, 4H, –CH_2O), 1.86-1.69 (m, 2H, –PCH_2), 1.67-1.50 (m, 6H, –CH_2), 1.48-1.24 (m, 4H, –CH_2), 0.87 (t, 3H, –CH_3). ^{31}P NMR ($CDCl_3$): δ 44.92.

c) General preparation of solid polymer electrolytes **SPE1** and **SPE2**:

The polymers **P1** and **P2** were dried at 60 °C and 40 °C under vacuum for 8 h. $LiN(SO_2CF_3)_2$ was dried at 150 °C under vacuum for 10 h before use. All manipulations were carried out in an MBraun glove box filled with ultrapure nitrogen gas. Electrolytes with different ratio were prepared as follows: the polymer was dissolved in THF with lithium salt and stir for 12 h at 25 °C. After this, THF was evaporated under vacuum and dried the residue at 60 °C for 12 h. The residue was loaded in to a die and then pressed to make a pellet. Specimens of 0.07–0.08 cm thickness and 0.9 cm diameter were obtained for conductivity studies. These pellets were sandwiched between two gold plated electrodes housed in a homemade cell for conductivity studies. The consistency of results was checked by repeating the experiment three times.

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SUMMARY AND CONCLUSION

The cyclotriphosphazene and cyclocarbaphosphazene has the impact on the production of new inorganic-organic macromolecules which have a wide spread current interest.These macromolecules were constructed in the form of polymer or dendrimer. The hyperstructured molecules were constructed by taking molecules having low ionization potential like triarylamine and carbazole and substituting them on either cyclophosphazene or carbaphosphazne core. The polyethers having phosphorus were prepared by copolymerization taking bis(hydroxymethyl)phosphine oxides as one of the monomers.

The reactivity of cyclocarbaphosphazene has been well documented. The unexpected reaction of chlorocyclocarbaphosphazene with 1-methylimidazole lead to the formation of salt and their reaction with potassium fluoride lead to the rupture of the cyclic ring and the formation of hexafluorophosphate. Using the reactivity of Cl-bonds, the dendrons(4-hydroxyphenyl)diphenylamine and 4,4’-di(carbazol-9-yl)-4”-hydroxytriphenylamine were grafted on it by simple nucleophilic substitution reactions. These reactions lead to the formation of hyperstructured molecules which his reported for the first time in case of cyclocarbaphosphazene chemistry.

In our approach, hyperstructured molecules based on well-defined model inorganic heterocycle *i.e* .cyclotriphosphazene were synthesized by simple nucleophilic substitution reaction. The high pure dendrimers were obtained by purification via common chromatographic techniques and found to exhibit photo luminescent behavior. Apart from these, the Li-ion conductivity and nonlinear optical properties of these molecules were also studied. The conductivity was found to be 10^{-4} Scm^{-1} for hyperstructured molecule **H_7**. Two these hyperstructured molecules were found to refract nonlinearly. The fundamental work showed that the cyclotriphosphazene skeleton is a promising candidate as building block for optical materials.

The synthesis of polymers by copolymerization of butyl bis(hydroxymethyl)phosphine oxide with three different dibromo monomers were carried out to produce three novel phosphorous containing polyethers (**P1-P3**) by simple nucleophilic substitution reactions. Lithium ionic conductivities of the polymers were examined by preparing solid polymer electrolytes **SPE1** and **SPE2**. The **SPE2** (**40%**), prepared from **P2**, showed the highest conductivity of 3.7 × 10^{-4} S cm^{-1} at 80 °C. **SPE2** may be a promising SPE having good ionic conductivity with possible flame retardant property that would find potential application in larger batteries.

LIST OF PUBLICATIONS

Publications from thesis

1) “Unexpected reaction of dicarbaphosphazene with N-Methyl imidazole and Potassium fluoride"

Khevath Praveen Kumar Naik and Krishnamurthi Muralidharan, Inorganic Chemica Acta, 2011, 12, 2123-2124.

2) “Phosphorous containing polyether for Li- ion conductivities”

Khevath Praveen Kumar Naik and Krishnamurthi Muralidharan (manuscript submitted).

3) “Synthesis and characterization of cyclophosphazene based hyperstructured molecules and the Li- ion conductivity”

Khevath Praveen Kumar Naik and Krishnamurthi Muralidharan (manuscript under preparation).

4) “Dendrimers having carbazole and triarylamine motif on phosphazene core : and their NLO properties”

Khevath Praveen Kumar Naik and Krishnamurthi Muralidharan (manuscript under preparation).

5) “Synthesis and characterization of hyperstructured molecules based on carbaphosphazene, diphenylcarbaphosphazene and cyanuric chloride”

Khevath Praveen Kumar Naikand Krishnamurthi Muralidharan(manuscript under preparation).

Poster and Oral Presentation

1) Khevath Praveen Kumar Naik and Krishnamurthi Murlidharan“ Synthesis of hyperstructured molecule based on cyclophosphazene , carbophosphazene and cyanuric chloride as core moieties” presented a poster and a talk at In-house symposium, School of Chemistry, University of Hyderabad on 03-04- 2013.

2) Presented a group poster from lab at Modern Trend in Inorganic Chemistry, School of Chemistry, University of Hyderabad on 21-12- 2012.