Chapter 1

*Introduction and Review of Literature*

The present chapter deals with the brief introduction and review of literature on hexaarylbenezene and hetero-oligophenylene based compounds, synthetic strategies for their preparation, aggregation induced emission enhancement properties, host-guest interaction and their utilization for the construction of microporous organic polymers, photonic devices and organic light emitting diodes.
1.1 Introduction

The derivatives of hexaarylbenzene (HAB) I are important class of aromatic compounds due to their potential applications in the field of science and technology\(^1\) such as molecular scale devices,\(^2\) liquid crystalline materials, molecular receptors,\(^3\) etc. The interesting architectures as well as potential applications of HAB derivatives inspired researchers worldwide for the fabrication of various electronic devices such as photovoltaic cells,\(^4\) semiconductors,\(^5\) light-emitting diodes, sensors and bioimaging agents.\(^6\) HAB and their analogous compounds have non-planar conformations, with large torsional angles between the central and peripheral aryl rings so as to give topology of propeller and toroidal mimic\(^7\) and act as scaffold for the fabrication of proton conducting molecular crystals. The presence of phenyl rotors reduce the conjugation and restrict the general intermolecular π-π and C-H⋯π interactions which led to the higher HOMO-LUMO gap,\(^8\) compact molecular cohesion, improved volatility and higher solubility of HAB derivatives than their planar fused analogous hexa-peri-hexabenzocoronene (HBC) core.

Moreover, HAB derivatives exhibit aggregation induced emission enhancement (AIEE) characteristics due to the presence of peripheral aryl rotors. HAB based molecules are non-fluorescent or weakly emissive in the solution phase, but in the aggregated state, can emit strongly. Thus, aggregates of HAB derivatives display a vast potential in supramolecular chemistry and material chemistry. On the other hand, hetero-oligophenylene (OP) derivatives are attractive candidates for molecular electronics due to their low HOMO-LUMO gap and synthetic flexibility which make them a good candidate to investigate the effect of substituent on their electron transport properties. Further, presence of heteroatoms control the electronic nature of these derivatives without altering the structure.

Keeping in view the important applications of hexaarylbenzene and hetero-oligophenylene derivatives, we designed and synthesized a variety of AIEE (or AIE) active hexaarylbenzene and
hetero-oligophenylene based derivatives and studied their photo-physical and self-aggregation behavior by using UV-vis, fluorescence and NMR spectroscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM), etc. Fluorescent aggregates of these derivatives were then utilized for the detection of various types of analytes such as nitroaromatics, biomolecules and metal ions. Before the presentation of our work, a concise review of literature about the hexaarylbenzene based molecules including hetero-oligophenylene compounds is presented below:

1.2 Literature Reports on Hexaarylbenzene (HAB) Based Molecules

1.2a Synthetic Strategies and Structural Variations

The star shaped HAB molecules due to their conjugated $\pi$-systems possess unique optical and electronic properties which are widely exploited in the field of advanced materials such as organic light-emitting diodes (OLEDs), photovoltaic cells and organic field effect transistors. Further, HAB has tendency to self-assemble to form hollow nanostructures which show a great potential for molecular recognition, molecular transport and reaction catalysis. HAB was first synthesized by Troksen from stilbene in 1663. Bart characterized its structure from single crystal X-ray diffraction analysis. A few representative examples of HAB based derivatives are reviewed below.

Gust et al. reported ortho or meta-substituted HAB derivatives and investigated the possibility of restricted rotation in these substituted HAB derivatives due to steric hindrance caused by ortho- and meta- substituents which lead to large number of stereoisomers. They also reported meta- substituted HAB derivatives and analyzed their rational isomerism by
There are 13 rearrangement modes possible for such molecules demonstrated by mathematical analysis and experimental studies revealed that 16 rotational isomers were possible for highly substituted hexa- and penta-arylbenzenes derivatives. Free energies of activation for isomerization decreased from about 33.0 kcal/mol to about 17.0 kcal/mol for rotations of rings bearing an ortho-methoxy group to meta-substituents.

In HAB derivatives, the central aromatic ring has a persistent involvement in strong C-H⋯π interactions. In this context, Wuest et al.\textsuperscript{17} reported that these interactions could be blocked by adding simple ortho alkyl substituents at the peripheral phenyl groups 4a-d, due to systematic changes caused by ortho alkyl substituents on HAB derivatives in molecular cohesion and packing which were investigated by packing indices, their densities and solubilities, sublimation temperatures and ratios of H⋯H, C⋯H and C⋯C contacts. Thus, ortho substituted HAB derivatives 4a-d have the beneficial effect of altering molecular consistency without varying the
other properties. Kobayashi et al.\textsuperscript{18} prepared hexakis(4-carbamoylphenyl)-benzene derivative 5, by reaction of hexakis-((4-carboxyphenyl)benzene\textsuperscript{19} with thionyl chloride in 1,2-dichloroethane as solvent in the presence of a phase transfer catalyst named as benzyltriethylammonium chloride\textsuperscript{20} and characterized its three-dimensional hydrogen-bonded network, which depends upon different conditions of solvents such as (i) a porous network both in DMSO as well as in 6\textit{n}-PrOH and (iii) non-porous network chain in H\textsubscript{2}O which was due to the difference in solvent polarity resulted into hydrophobic and aromatic \(\pi\)-\(\pi\) interactions. Thus, the hydrogen-bonded 3-dimentional network of derivative 5 was affected by the solvents induced crystallization properties in an organic host lattice.

Yamaguchi et al.\textsuperscript{21} reported the synthesis of 3',4',5',6'-tetrakis(4-hydroxyphenyl)-[1,1':2',1" terphenyl]-4,4"-diol 6 (HPB-OH-1) and 3',4',5',6'-tetrakis(4-hydroxy-3,5-dimethylphenyl)-3,3",5,5"-tetramethyl-[1,1':2',1"-terphenyl]-4,4"-dil 7 (HPB-OH-2) catalyzed by organometallic complex, and their optical properties were investigated before and after deprotonation of the \(-\text{OH}\) groups via treatment with NaH using UV-vis and fluroscence spectroscopy. A red shift was observed in the absorption and emission spectra of derivatives 6 and 7, owing to intramolecular charge transfer (ICT) from the ONa groups to the central benzene core upon deprotonation of – OH groups of derivatives 6 and 7. They also described the synthesis and characterization of five or six different aryl substituted hexaarylbenezene derivatives 8-15, by programmed synthesis using [4+2] cycloaddition and cross-coupling reactions and C–H activation.\textsuperscript{22} The isolation of HAB derivatives 8-15 and their structural–property description was achieved by these methods.

\textbf{1.2b Host-Guest Interactions and Molecular Recognition Chemistry of Hexaarylbenezene and Hetero-oligophenylene Derivatives}

Supramolecular assemblies of organic molecules have been known as good implement for generating well-defined nanosized molecules, which upon binding with metal ions generates metal-modulated assemblies which exhibit potential applications in molecular devices.\textsuperscript{23} in general, individual structures were constructed by metal-induced modulation of assemblies of organic molecules.\textsuperscript{24} However, there are number of reports in which metals binding induced modulation of predesigned hexaphenylbenzene based derivatives which are reviewed below.

Bock et al.\textsuperscript{25} first time reported the two-folds dehydrogenation of hexaphenylbenzene with lithium powder in 1,2-dimethoxyethane (DME) which resulted the formation of two additional C-C bonds as shown in Scheme 1. They crystallized and determined the unexpected lithium ion
complex of HPB [(9,10-diphenyltetrazen[a,c,h,j]anthracene)2-Li(dme)][Li(dme)3]. The experimental and quantum chemical calculations revealed that Li ions initiated deformation of hexaphenylbenzene skeletal which leads to sterically hindered molecular dianion which dynamically caused 2-folds dehydrogenation and formation of C-C bond.

Scheme 1. Lithium powder induced dehydrogenation of HPB and formation of two additional C-C bonds.

Mullen and Woll et al.\textsuperscript{26} reported, a technique for the synthesis of polyaromatic hydrocarbons (PAHs), such as hexabenzocoronene 17, directly from its precursor molecule 16, by thermally initiated cyclodehydrogenation route, after adsorbing precursor on a Copper (Cu) surface. In order to synthesize planar molecule 17, first deposition of precursor 16 onto the Cu (86) surface was carried out in monolayers, which upon heating resulted into complete cyclodehydrogenation and formation of planar molecule 17. The adsorption of HPB molecules 16\textsuperscript{a-b} on Cu surfaces was characterized by X-ray absorption fine structure spectroscopy. They\textsuperscript{27} also demonstrated the capability of polyphenylene dendrimers such as hexaethinyl hexaphenylbenzene 18 and its dendrimer 19, as chemosensors for monitored various volatile organic molecules in the gas phase. Positron Emission Tomography (PET) studies showed that polyphenylene dendrimer was preferably suitable for guest molecules as it contained stable cavities in its core. The crystal structure of dendrimer 19 was investigated, which revealed that its interior cavities easily entrap the solvent molecules. Hence, the presence of internal cavities and affinity to fill these cavities/voids with suitable sized guest molecules, polyphenylene dendrimers were considered as suitable host molecules.

Rabinovitz et al.\textsuperscript{28} described the reduction of hexa(4-n-dodecylbiphenylyl)benzene (HDBB) 20 by series of alkali metal ions in presence of THF as solvent under high vacuum and identified their three reduced states such as dianion, tetraanion and hexaanion by NMR spectroscopy. The NMR studies of hexaanion (HDBB\textsuperscript{6-}) 21 showed an extraordinary deformation of symmetry in presence of alkali metal ions which was interpreted by hindered rotation of the interior phenylene
rings due to twisted conformation of the inner benzene core and the twisted hexaanions 21 exhibited high thermal stability.

Shionoya et al. reported the synthesis of hetero-oligophenylene compounds 22-23 and described the formation of heterotopic sandwich-shaped \( \text{Ag}^{2+} \) complex (\( \text{Ag}^{2+}.22,23 \)) from disk shaped tris(thiazolyl) and hexa(thiazolyl) derivatives 22-23 and three \( \text{Ag}^{+} \) ions. Further, the
intramolecular rotational movement between the coordinatively linked derivatives (22, 23) in trinuclear Ag⁺ complex was driven by the intensive ligand exchange in solution, confirmed by temperature dependent ¹H NMR studies. Such systems which involved intramolecular rotational motion between two coordinatively paired ligands were highly appropriate for the development of metal-induced modulated multicomponent devices at molecular level. Shionoya et al.³⁰ also reported new HPB-based disk-shaped molecule 24, substituted with 3-pyridyl and methyl groups alternately. Upon addition of transition-metal ions such as Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Pd²⁺, Pt²⁺, Cu²⁺, Zn²⁺, Cd²⁺, and Hg²⁺, HPB derivative 24 formed 10 coordination capsules, [M₆(53)₈]¹²⁺, which was due to self-assembly of 24 in presence of metal ions and these formed capsules were structurally equivalent to each other. Furthermore, the voids in the interior of these metal coordinated capsules were effectively filled with anionic ligands because of the site selective substitution of the six CF₃SO₃ ligands coordinated from inner side of these capsules.
Wang et al.\textsuperscript{31} reported star shaped HAB derivatives 25 and 26, substituted with 7-azaindolyl and 2,2'-dipyridylamino groups and characterized them by single-crystal X-ray diffraction studies. Hexa[p-(7-azaindolyl)phenyl]benzene 25 formed extended two-dimensional layered structure through intermolecular $\pi-\pi$ stacking interactions, while molecule hexa[p-(2,2'-dipyridylamino)biphenyl]-benzene 26 formed interpenetrating columnar stacking through self-
assembly on a graphite surface in the solid state. The star shaped molecule 25 showed selective binding behavior with Ag$^{1+}$ and Cu$^{2+}$ ions amongst other metal ions tested and major alteration in the extensive two-dimensional layered structure of 25 was observed after complexation with Ag$^{1+}$ and Cu$^{2+}$ ions. Further, these derivatives are pH sensitive, such as quenching and a red shift in the emission spectra of derivative 25 and 26, respectively was observed at acidic pH. Thus, these star shaped molecules have potential to act as a pH probe.

Rathore et al.$^{32}$ reported the 2,5 dimethoxytolyl-substituted symmetrical as well unsymmetrical hexaarylbenzene based rotamers 27 and 28. In compound 28, six 1-e$^{-1}$ oxidations were occurred reversibly due to electronic coupling of aryl groups in circular manner spanned around 320 mV, whereas, in case of symmetrical rotamer 27 no 1-e$^{-1}$ oxidations were occurred, as the ethereal oxygen at juxtaposition were utilized for binding with single K$^{+}$ ions which was confirmed by X-ray crystallography and $^1$H NMR spectroscopy. Moreover, the binding of K$^{+}$ ions with 27 was controlled by electrochemical oxidation reversibly. Thus, these HPB-based symmetrical and unsymmetrical rotamers satisfying the essential criteria for the construction of an electrochemical K$^{+}$ ion sensors.$^{33}$

Bhalla et al.$^{34}$ reported the design and synthesis of a star-shaped quinoline substituted hexaphenylbenzene derivative 29. HPB derivative 29 showed significant fluorescence enhancement selectively upon binding with zinc ions among various metal ions tested. Further, derivative 29 showed emission enhancement upon binding with Zn$^{2+}$ ions in the PC-3 cells without the extracellular addition of Zn$^{2+}$ ions, which allowed this HPB derivative a capable candidate as biosensor. In addition to this, Zn$^{2+}$-ensemble of star-shaped HPB derivative 29 displayed highly sensitive and selective response toward H$_2$PO$_4^-$ ions and adenosine monophosphate (AMP). A multichannel molecular keypad was constructed by using three inputs of Zn$^{2+}$ ions, H$_2$PO$_4^-$ ions and AMP, based on fluorogenic response of 29 towards Zn$^{2+}$ ions, H$_2$PO$_4^-$ and AMP, respectively. They also described the design and synthesis of hexa and di rhodamine substituted HPB derivatives 30 and 31.$^{35}$ In which the rodhamine appended phenyl rotors were twisted around their own axis and hindered the electron conjugation between acceptor and donor moieties, hence, resulted into Through Bond Energy Transfer (TBET) phenomenon. Derivative 30 displayed emission enhancement in presence of Hg$^{2+}$ ions, via through bond energy transfer process in polar solvent such as methanol, however efficient fluorescence energy transfer occurred in solution of derivative 31 in THF and acetonitrile in presence of Hg$^{2+}$ ions which leads to emission enhancement at 550 nm in fluorescence spectra.
Recently Bhalla et al. first time reported the facile synthesis of iron oxide nanoparticles by utilizing aggregates of HPB derivative. Hexaphenylbenzene appended azaindole derivative exhibited aggregation induced emission enhancement properties due to presence of phenyl rotors and fluorescent spherical aggregates were formed in mixed aqueous media. Fluorescent aggregates of HPB derivative displayed highly selective ratiometric response towards Fe ions among various metal ions and served as stabilizer and reactor for the preparation of α-Fe₂O₃ nanoparticles. Moreover, these in situ generated α-Fe₂O₃ nanoparticles exhibited excellent catalytic efficiency in photodegradation of Rhodamine B dye as well as palladium and copper free Sonogashira cross coupling.

1.2c Hexaarylbenzene Based Molecules as Redox or Photo-active centers

![Hexaarylbenzene (HAB) π-π interactions “(toroidal delocalization)”]

_Scheme 2._ Toroidal delocalization over hexaarylbenzene.

Design and synthesis of 3-dimensional (3D) organic framework containing multiple redox-active chromophores has attracted increasing attention from the viewpoint of application to molecular devices. HAB has been regarded as one of the potential 3D topologies and is expected to exhibit exceptional electronic features, because of having propeller-like conformation, which results π-π interaction between the aryl rings facing each other, and sextuple gathering of the π-π interactions hence, lead to so-called ‘toroidal delocalization’.

Guzei et al. reported the synthesis and successful isolation of soluble hexa and tetra trityl cations by using readily available starting materials based on HPB and tetraphenylmethane scaffold. The co-crystallization of these polytrityl cations were explored with a variety of nonnucleophilic anions for usage as catalysts for polymerization reactions as well as with redox-active spherical polyoxometalate (poly)anions. These polytrityl cations also embrace potential for the preparation of polytrityl radicals, which may possess interesting magnetic properties.

Rathore et al. described a versatile synthesis of a dendritic structure in which six tetraphenylethylene moieties are connected to a central benzene ring in such a way that the phenyl rings of each tetraphenylethylene is also part of the propeller of the hexaphenylbenzene core. Multiple oxidation waves as well as an intense charge-resonance transition in the near-IR
region was observed in its cyclovoltammogram and cation radical spectrum, which suggested that a single hole delocalizes via electron transfer over six identical redox-active centers. A dendritic hexaaryl and hexaferrocenylbenzene donors (37 and 38) in which six ferrocene moieties are connected at the vertices of the propeller of the HPB core was also synthesized. The molecular structure of 37 and 38 was analyzed by X-ray crystallography. Both hexaaryl and hexaferrocenylenzene donors 37 and 38 undergo reversible six-electron oxidation at a constant potential confirmed by cyclic voltammetry. The ejection of six electrons was further confirmed by redox titrations (which are equivalent to coulometry) using stable aromatic oxidants.

Rathore et al. also reported the synthesis of a dendritic hexanaphthylbenzene derivative 39 in which the six naphthyl groups are connected to the central benzene ring in a propeller-shaped arrangement. The observation of an intense charge resonance transition and multiple oxidation waves in cation radical of derivative 39 gave evidence that a single hole was mobilized via electron transfer over identical six redox-active centers which were cofacially arranged with a
minimal overlap of the naphthyl moieties in a circular array, which opened new class of intervalence materials in which a hole hops over multiple (circularly arrayed) redox centers for potential applications in the preparation of photonic devices contributing towards the emerging area of molecular electronics and nanotechnology.

Kochi et al. synthesized a series of different aryl-donor groups around a central benzene ring in order to evaluate the intramolecular movement of electrons around redox centers. Upon p-doping of various hexaarylbenezend arrays or one electron oxidation, the unique charge-resonance absorption bands were observed which provide quantitative measures of the
reorganization energy ($\lambda$) and the electronic coupling element that are mandatory for the evaluation of the activation barrier for electron-transfer self-exchange. Furthermore, the Marcus-Hush treatment of the experimental spectral behavior correctly predicted the potential shift close to the experimental value on consideration of the entropy contribution. The hexadonor cation radical is also thermodynamically more favourable to reduce the barrier for hole hopping between six anilinyl sites.

Mullen et al.$^{44}$ demonstrated a crystalline organic material 43 ($p$-6PA-HPB) in which proton conductivity is not a water-based diffusion process unlike in common amorphous polymer electrolytes. The columnar structure of 43 contains peripheral groups which are proton conducting and an insulating core due to which it conduct proton inversely. The Proton conductivity through this crystalline material became possible because of the amphoteric character, high concentration, and aggregation/preorganization of the phosphonic acid groups, and also because of the transport pathways within from the self-assembled columns. Besides, immobilized water in the crystal hydrate has been another assistance to proton transport. In contrast to state of the art polymers and inorganic crystals, compound 43 provide high temperature-independent proton conductivity, which fulfilled one of the requisites for new separator materials in FC systems.

Akita et al.$^{45}$ discussed about the synthesis of series of peripheral thienyl iron substituted hetero-oligophenylenecompounds 44-46 and toroidal delocalization between the peripheral aryl units due to communication between two metal centres. This study entitled the HAB system to serve as a promising 2D wiring device like ethylene and benzene skeleton and generates toroidal interaction for dominant communication pathway for the HAB complexes 45 and 46. Multiple metallated HAB complexes.

Browne and Feringa et al.$^{46}$ reported the straight synthesis, redox- and photochemistry of star-shaped symmetric HPB derivatives 47 a,b appended with dithienylethene groups through cyclotrimerization induced by cobalt catalyst. Dithienylethenes groups were appended owing to their significant electro- and photochromic properties which could be tuned up via modification. Interestingly, due to twisted topology of HPB core no intramolecular interaction was observed within dithienylethene groups which allows the straightforward synthesis of various flexible scaffold in which photo/redox-active groups were approved in high level of order and preservation of molecular properties.
1.2d Hexaarylbenzene Based Polymers of Intrinsic Microporosity

Microporous organic polymers (MOP) having pore size less than 2 nm are of increasing interest due to their prospective applications in sensors, heterogeneous catalysis, gas storage, CO₂ capture, and gas separation. HAB has an interesting structural unit for the construction of MOP due to its rigidity and propeller mimic shape, which arise due to mutual steric interactions of the peripheral phenyl groups. Pascal et al. prepared a very large HPB based cyclophane (C₁₄₅H₉₅O₈S₄) from commercial starting materials in which two 1,3-bis(pentaphenylphenyl)benzene subunits were tethered in order to form the final macrocycle. The X-ray analysis showed that the crystal of cyclophane have large central cavities which form wide, solvent containing channels. He also described the synthesis and crystal structure of a macrocyclic oligophenylene. A polyphenyl-substituted or “phenylog” of tetraphenylene derivative, contains a large interior voids which were packed to form solvated and highly porous crystals as determined by X-ray analysis. Computational studies demonstrated that supertetraphenylene adopts stable conformations in the crystal which essentially prohibited the thermal isomerization of “screw” hexaphenylenes to “crown” hexaphenylenes.
Mckeown et al.\textsuperscript{50} described the synthesis of microporous polymers 50 and 51, and discussed the their intrinsic microporosity on the basis of their solid state inefficient packing.\textsuperscript{51} The nitrogen adsorption isotherm studies concluded that the intrinsic microporosity of compound 51 was greater than 50 and could be used for preparing robust solvent cast films of high gas permeability. Moreover, these cyclic oligomers could also be used as optical sensors due to their high fluorescent nature.\textsuperscript{52}

Han et al.\textsuperscript{53} prepared HAB-based porous organic polymers (HPOP) 52 and 53 through palladium catalyzed C-C coupling. The BET specific surface area for these polymers varies between 742
and 898 m² g⁻¹ confirmed by nitrogen sorption isotherms and their adsorption capacity at 1.13 bar and 50 K, for hydrogen was up to 1.5 wt % investigated by gravimetric hydrogen adsorption isotherms. Hence, compound 52 and 53, due to their unique electronic feature could be taken as a promising building block for designing porous polymers with special properties.

Zheng et al.⁵⁴ have reported interesting topological structures based on HAB (H₂O)₂(COOH)₃(54) supramolecular synthon. The topology of HAB based derivative 54 from nonprotic solvent was continuously interdigitation of 36-hcb layers. The hydrogen bonding between carboxyl groups were adjusted by weak hydrophobic interactions to fulfill close packing of organic tectons. The well-defined connection geometry of the (H₂O)₂(COOH)₃ synthon and reserved hydrogen bonding strength, guided the self-assembly of 54 in a nonprotic solvent. This illustrated the considerable influence of the intrinsic structure of organic tectons in solid-state crystal formation.

Smaldone et al.⁵⁵ reported a series of porous organic polymers (POPs) 55a-c based on hexaphenylbenzene core with different peripheral substituents. The distinct gas sorption properties were observed for HPB-POPs 55 a-c depending on substituent size and the extent of conjugation in the monomer core structure of compound 55. The tert-butyl substituted POP 55 c showed enhanced overall porosity as well as storage capacity than other porous organic polymers 55 a and b.
McKeown et al.\textsuperscript{56} reported the synthesis and characterization of a series of novel methyl, bromide, and nitrile substituted HAB-based polymers \textbf{56 a-c} (HAB-PIM) of intrinsic microporosity. The gas permeability of these compounds were investigated by their successful formation of thin films and it varied with solvent polarity such as significant increase in gas permeability was observed for films cast from THF than methanol, due to an increase in the diffusion coefficient. This varied gas permeability, diffusivity and solubility of these polymers thus confirmed their characteristic dual mode sorption behavior as a function of the feed pressure.

Cooper \textit{et al.}\textsuperscript{57} first time reported the microporous linear-conjugated polymer \textbf{57}. The combination of the electronic properties as well as compositional difference of both conjugated and microporous linear polymers, allowed the solution of \textbf{57} thin film formation. This soluble linear-conjugated polymer could be utilized for fabrication of devices.

\textbf{1.2e Organic Light Emitting Diodes Based on Hexaarylbenezene}

Organic electroluminescent materials and light-emitting diodes (OLEDs) have been the subject of great research interest because of their potential applications in colorful flat panel displays and white illuminations in solid states. Numerous HAB based conjugated organic molecules have been designed and synthesized to fabricate highly electroluminescent (EL) OLEDs having good thermal properties, longer lifetimes and pure color coordinates ranges same of which are discussed below. Tao \textit{et al.} synthesized HPB based materials \textbf{58 a-c} and \textbf{59 a-c} consisting of amino pyrene substituents. These derivatives possess good charge transport ability and emit high blue light. These HPB derivatives were used for the fabrication of white OLEDs and electrophosphorescent devices.\textsuperscript{58}
Mullen et al.\textsuperscript{59} prepared polyfluorene 60a-b having bulky polyphenylene dendrimer substituents which suppressed the formation of aggregates emitting in longer wavelength and thus polyfluorene emitting in pure blue region. The dendronised polymer 60 was utilized for the construction of the electroluminescent devices and their electrical and luminance characteristics have been found to be comparable with those of alkylated polyfluorenes which indicates that the suppression of aggregation has been achieved without sacrificing the desirable properties of the polyfluorene backbone. A light emitting diode has been established by utilizing molecule 60a-b to produce blue emission with onset voltages below 4 V.

Lin et al.\textsuperscript{60} described hexaarylbenzene based novel energy harvesting molecules 61 a-c featuring triarylamine donors and a dithienyl benzothiadiazole acceptor. These molecules showed efficient intramolecular energy transfer, bipolar characters and bright red fluorescence and were applied as a hole-transporting/emitting layer in OLEDs for the fabrication of novel orange emitting
electroluminescent devices. They also reported the synthesis of a non-planar HAB functionalized benzothiadiazole derivative 62\textsuperscript{61} (HABBTD) and applied it as a red molecular emitter for the fabrication of non-doped organic light-emitting diodes (OLEDs). The HABBTD 62 displayed excellent film-forming properties, good thermal stability, high solubility and weak excited-state solvatochromism in common organic solvents and high stability at different concentrations and in solid states. Red OLEDs were fabricated by HABBTD 62, having emission layers of different thicknesses in a facile non-doped configuration and an enhancement in both efficiency as well as brightness were achieved with increasing thickness of emission layer for the red OLEDs.

Torres \textit{et al.}\textsuperscript{62} reported a transition-metal-catalyzed trimerization reaction of an ethynyl-bridged bisphthalocyanine so as to prepare a benzene-centered, phthalocyanine hexamer 63 and characterized it by different spectroscopic techniques. This trimerization reaction catalyzed by transition-metal represented a superficial method for the synthesis of benzene-centered, sterically-crowded multi-phthalocyanin systems, which served as building blocks for the construction of functional molecular systems.

Tao \textit{et al.} described the synthesis of 1,2,3,4,5,6-hexakis-(9,9-diethyl-9H-fluoren-2-yl)benzene 64 and its utilization for the fabrication of white OLED.\textsuperscript{63} Thermal evaporation was followed for the preparation of device having ITO/NPB (40 nm)/HKEthFLYPh (5 nm)/Alq\textsubscript{3}(50 nm)/Mg:Ag(200 nm) structure. Interestingly, white OLED fabricated from HPB derivative 64 displayed better results as compared to 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) layer.

Li \textit{et al.}\textsuperscript{64} reported a new series of HPB-based hyperbranched conjugated polymers by Suzuki Miyaura cross coupling of compound 65 with 2,5-bis(4-bromophenyl)-1,3,4-oxadiazole and 2,2'- (9,9-dihexyl-9H-fluorene-2,7-diyli)bis(1,3,2-dioxaborinane) which exhibit blue emission and high thermal stabilities in both solutions as well as in solid state. Interestingly, longer wavelength emission at 500-320 nm was not observed due to self-aggregation of polyfluorenes units in their emission spectra after annealing. Two-layer PLED devices (ITO/PEDOT/polymer/ TPBI/Ca/Ag) was fabricated which exhibited good EL efficiency, and maximum efficiency of 0.19. The EL performance was improved noticeably by incorporating this polymeric derivative with oxadiazole groups and electron-transporting units.

They also reported the synthesis of series of polyphenylbenzene derivatives 66-70,\textsuperscript{65} which efficiently emit in blue region and represented a new method for the synthesis of blue-emitters. These blue-emitters 66-70, were efficiently utilized for the fabrication of Non-doped electroluminescence (EL) devices which displayed very good performance with external
quantum efficiency (EQE), power efficiency (PE) and Current efficiency (CE) of 1.6 lmW\(^{-1}\), 2.3\% and 2.0 cdA\(^{-1}\), respectively. Highly improved performance was displayed by doped device fabricated from derivative 66, with CE and EQE values of 4.51 cd A\(^{-1}\) and 3.71\% respectively. Hence, probe 66 was shown to be a promising applicant for the deep-blue emitters OLED.

Lambert et al.\(^{66}\) synthesized hexaarylbenzenes derivatives 71-73 substituted with pyrene as an electron acceptor and triarylamine as an electron donor at different positions, and their charge-transfer states were investigated by optical spectroscopy. The fluorescent properties of these
HAB derivatives were not significantly different from each other and these chromophores showed almost similar fluorescent charge transfer state.

1.2f Self-Assembly and Aggregation Induced Emission Enhancement Properties of HAB and Hetero-oligophenylene Based Molecules

Aggregation or self-assembly is the process in which molecules assume a defined arrangement without direction or management from an external source. Molecular self-assembly is a key concept in supramolecular chemistry, as assembly of molecules in such systems is directed through noncovalent interactions such as hydrogen bonding, hydrophobic interactions, Vander-Waals forces, π-π interactions, etc. Further examples of supramolecular assemblies demonstrate that a variety of different shapes and sizes can be obtained using molecular self-assembly.

Percec et al.\textsuperscript{67} prepared hexa(4-alkoxyphenyl)benzenes $74 (n=4-9)$ by PdCl\textsubscript{2}(PhCN)\textsubscript{2} catalyzed cyclotrimerizations of the corresponding 1,2-di(4-alkoxyphenyl)acetylenes. The derivatives $74 (n=6-9)$, formed anisotropic glasses and became fluid as the temperature approaches isotropization. Solidification could be promoted by introducing methyl branches in either the mesogen or the alkoxy substituents in crystalline phase as well as an anisotropic glass.

Mullen et al.\textsuperscript{68} reported discotic molecules with hexaarylbenzene cores $75\text{a-c}$ and hetero-oligophenylene compound $76\text{a-c}$, which have been synthesized by [2+2+2] cyclotrimerization of diarylsubstituted acetylenes. All of these formed mesophases depending on the compositions and aryl length. Their mesomorphic behavior was characterized by differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and X-ray diffraction pattern. Hexakis(4-dodecylphenyl)benzene $75\text{a}$, hexakis(4'-dodecylbiphenyl)benzene ($75\text{b}$) and hexakis[4-(5'-dodecyl-2'-thienyl)phenyl]benzene ($75\text{c}$) were self-assembled to form ordered columnar mesophases which were strongly influenced by intermolecular forces such as dipole–dipole or steric interactions. Compound $77\text{c}$ showed much higher clearing point than $75\text{ a-b}$, which demonstrated the importance of thiophene rings around a hexaphenylbenzene core for the formation of higher ordered mesophases. However, in $75\text{c}$ broad mesophase was observed, which was due to the presence of strong intermolecular interactions induced by dipole resulting from the lone electron pair on the sulfur atom. In $75\text{ a-b}$, the replacement of the phenyl or biphenyl linker with thienyl or bithiienyl moiety as in $76\text{ a-b}$, caused lower transition temperatures and lesser ordered mesophases, owing to the deformation of the packing behavior usually associated with cores encircled by a substituted phenylene unit.\textsuperscript{69}
Kobayashi et al.\textsuperscript{70} reported the synthesis of various types of hexakis(4-functionalized-phenyl)-benzenes 77 a-f and hexakis[4-(4′-functionalized-phenylethynyl)phenyl]benzenes 78 a-f directed to form host molecules for guest-inclusion networks in the solid state. Compounds 77e or 78f
formed 2-dimentional network by utilizing unique I⋯I or CH⋯O=C interactions, respectively confirmed by by X-ray crystallographic analysis. Schenning \textit{et al.} \cite{71} synthesized six-armed star-shaped oligo(p-phenylenevinylene) (OPV) substituted HAB derivative 79 bearing chiral alkyl groups with a central benzene core and characterized its properties by polarization optical microscopy (POM) and X-ray analysis. A well plastic crystalline behavior at room temperature was shown by derivative 79 with well-ordered columnar superstructure and self-assembled into right-handed chiral superstructures via a highly cooperative fashion in polar solvent which was stable even at high temperatures and low concentration. OPV molecule 79 also formed organized monolayers at the liquid-solid interface with chiral hexagonal lattice. These unique properties made the HAB derivative 79 to be potentially useful in the field of supramolecular electronics.\cite{72}

To ensure efficient utilization of solar spectrum, a numerous antenna based molecules have been photosynthesized which transfer excitation to a photoinduced charge separation reaction center after absorbing solar energy. In this context, Gust \textit{et al.} \cite{73} described photoinduced electron transfer process in self-assembled porphyrin-fullerene triad hexaphenylbenzene chromophores 80 and 81. In these chromophores the fullerene unit was coordinated to two zinc porphyrins \textit{via} pyridine groups and the association constant for these molecules were determined by spectroscopic studies. The highly intense electronic interactions among the moieties resulted into rapid photoinduced electron transfer from porphyrin to the fullerene. Compound 81 underwent self-assembly in non-coordinating solvents and self-assembled triad so formed showed similar electron transfer features as that of various covalently linked porphyrin-fullerene frameworks which suggested that these self-assembled constructs would be a functional adjunct to light harvesting antenna complexes for the creation of photosynthetic antenna-reaction center mimics. They also reported an artificial photosynthetic antenna-reaction center complex called molecular heptad 82 that features two bis(phenylethynyl)anthracene, two borondipyrromethene antennas and two zinc porphyrins linked to a hexaphenylbenzene core and an electron acceptor fullerene self-assembled to both porphyrins \textit{via} dative bonds.\cite{74} After absorbing solar energy, the four antennas efficiently transferred its energy to the porphyrins, and then the excited porphyrins donate an electron to the fullerene with a time constant of 3 picosecond to generate a charge separated state with a lifetime of 230 ps which leads to quantum yield one. However, without fullerene excited singlet state of porphyrin donates an electron to a borondipyrromethene. Thus, 82 confirmed the role of antennas, to harvest efficiently light throughout the visible from ultra-
violet wavelengths out to $\sim 353$ nm for a molecular systems.

Mullen et al.\textsuperscript{75} described the synthesis of the bulk-phase self-assembly of per-meta-functional HAB molecule 83 bearing six hydrocarbon and fluorocarbon chains and characterized these self-assembled structures by polarized optical microscopy, differential scanning calorimetry (DSC), X-ray scattering, and $^{19}$F magic-angle spinning (MAS) and solid state NMR. Gust et al.\textsuperscript{76} described the synthesis of hexad 84 that displayed similar function as that of the antenna in nonphotochemical quenching (NPQ). NPQ is a process or mechanism which is involved in the thylakoid lumen part of plants in order to protect it from excess sunlight. Upon excitation, the zinc porphyrin moieties of hexad 84 exchanged energy with each other and decayed normally by photophysical processes in an organic media and the excited-state lifetimes was more enough which allowed harvesting of the absorbed energy for charge separation. Whereas, upon addition of acid, rhodamine dye opened up which leads to very fast quenching of the first excited singlet states of zinc porphyrin moieties which ultimate resulted into conversion of excited energy into heat. Thus, Compound 84 provided a straightforward efficient model for the artificial antenna in NPQ.

Bhalla et al.\textsuperscript{77} described the synthesis of new hetero-oligophenylene derivative 85 which displayed aggregation-induced emission enhancement (AIEE) behavior in THF/H$_2$O (2:8) mixture. The AIEE phenomenon was mainly attributed to the restriction of phenyl rotors
which increased the radiative excitons by blocking the non-radiative channels, thus, leads to fluorescence enhancement. The aggregates of probe 85 could detect BSA, DNA, cytochrome c, and lysozyme amongst various other biomacromolecules tested in contrasting modes. In addition to biomolecules, these aggregate were also utilized for the sensing of metal ions and among various metal ions tested aggregates of probe 85 showed selectivity towards Pb$^{2+}$ and Pd$^{2+}$ ions. Two different sequential logic circuits have been constructed based on sensing behavior of aggregates toward biomolecules and metal ions.

Kumar and Bhalla et al.$^{78}$ reported the synthesis of carbazole appended AIEE-active hetero-oligophenylene derivatives 86 and 87. The carbazole moiety was appended with hetero-oligophenylene derivatives because of its hole transporting as well as better electroluminescence properties. Both derivatives exhibited AIEE characteristic i.e both molecules were weakly emissive in good solvent such as THF, whereas upon increasing volume fraction of water in THF, both derivatives resulted into fluorescence enhancement which was attributed to formation
of aggregates. Interestingly, fluorescent aggregates of derivatives 86 and 87 served as chemosensors for selective detection of TNT (trinitrotoluene) among various other nitroexplosive tested such as picric acid (PA), 2,4-dinitrotoluene (DNT), nitrotoluene (NT) and 1,3-dinitrobenzene (DNB). Moreover, dipcoated paper strips of these derivatives were utilized for sensitive detection of TNT in vapour, contact and solution phase.

\[ R = C_{16}H_{33} \]
Gust et al.\textsuperscript{79} synthesized hexad 88 and 89, containing four coumarin chromophores and two porphyrin groups around the central HPB core. Upon excitation, any of the coumarins chromophore transferred its absorbed energy to porphyrin with in 1–10 ps time scale and the quantum yield of singlet energy transfer is unity. The rate constants for energy transfer were constant which followed Forster dipole−dipole mechanism. A fullerene group bearing pyridyl moieties self assembled to form hexad consisting zinc porphyrins resulted into an antenna−reaction center heptad 89. In heptad 89 upon excitation, coumarin chromophore
transferred energy to the porphyrins which was then transferred to fullerene by electron transfer process with in 3 picoseconds.

Hoger et al.\(^8^0\) and coworker reported the synthesis of a new spoked-wheel shaped HPB derivatives 90 and 91 a-b having 4 nm approximate diameter and the optical properties of these derivatives were investigated by comparing with model chromophores by MS and NMR spectroscopy. Compounds 90 and 91 a-b in solution phase self-assembled to form closely packed two dimensional hexagonal arrangement which was confirmed by scanning electron microscopy. The morphology, dimensions and size of the self-assembled structures was investigated by Small-angle X-ray scattering (SAXS) and Dynamic Light Scattering (DLS).

Tang et al.\(^8^1\) reported the design and synthesis of a series of hexaphenylbenzene (HPB)-tetraphenylethene (TPE) adducts 92-96 by Diels–Alder reaction of tetraphenylcyclopentadienone with corresponding acetylenes. These HPB-TPE adducts exhibited aggregation-induced emission properties with up to 60 % quantum yield in solid state fluorescence. The presence of steric hindrance and twisting phenyl groups in TPE-HPB adducts were responsible for AIE behavior.
Bhalla et al.\textsuperscript{82} described the design and synthesis of AIEE-active $p$-hydroxynaphthaldehyde appended HPB derivative 97, which in mixed aqueous media formed emissive nanoaggregates with cyanide ions. The fluorescent aggregates of derivative 97 in the presence of cyanide ions displayed selective and sensitive fluorogenic and colorimetric response towards trinitrotoluene (TNT) with a minimum detection limit of 10.21 ppq. Furthermore, the dip coated paper strips of supramolecular anion ensemble of derivative 97 were utilized for contact mode detection of TNT with minimum detection limit up to attogram level. They also reported the synthesis of amide
appended HPB-based derivative 98 which exhibited AIEE behavior and in mixed aqueous media formed spherical aggregates. As amides groups are well known to form hydrogen-bonds with anions, the binding behavior of aggregates of HPB derivative 98 was investigated with various anions such as F⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, CH₃COO⁻, ClO₄⁻ and H₂PO₄⁻. Interestingly, fluorescent spherical aggregates of HPB derivative 98 suffered deaggregation upon addition of CN⁻ ions and showed highly selective and sensitive “ratiometric” and “colorimetric” response with cyanide ions over other anions tested in aqueous media. Further, anion modulated aggregates of 100 displayed reversible reaction based behavior in presence of TFA or H⁺ ions. Depending upon the behavior of aggregates of 98 towards CN⁻ and TFA or H⁺ ions a sequential memorized logic circuit has been developed. After reporting anion modulated assemblies of hexaphenylbenzene derivative, they have then reported the synthesis of AIEE active pyrene appended hexaphenylbenzene (HPB) derivatives 99 which exhibited selective intermolecular interactions with Hg²⁺ ions amongst various other metal ions tested. Fluorescent 99-Hg²⁺ ensemble were utilized for selective detection of picric acid with minimum detection of limit of 2.29 fg/cm² and acquired nanofibrous like morphology in presence of PA. Further, to investigate the importance of pyrene moieties for the formation of highly cross-linked nanofibrous morphology, AIEE active naphthyl appended HPB derivative 100 as model compound was synthesized. A high selective response towards Hg²⁺ ions was shown by aggregates of derivative 100 and spherical aggregates were formed, but no cross-linked fibrous morphology was observed in presence of PA for Hg²⁺-100 ensemble, which indicated the important role played by pyrene moieties for nanofibrous aggregate formation.
Zhang et al.\(^{85}\) reported the preparation of carbon nano-membrane (CNM) having thickness 0.6 to 1.7 nm, from self-assembled architecture of polyaromatic precursor such as hexaphenylbenzene derivative 101, via cross-linking induced by electrons at low-energy and investigated their mechanical properties by atomic force microscopy (AFM). The stiffness of the precursor molecule 101 was correlated with the so prepared CNM. The deformation profiles and the pressure–deflection relationships were created by finite element method (FEM).

Mullen et al.\(^{86}\) reported the synthesis of a series of HPB derivatives 102-104, substituted with one, two and four polyethyleneglycol units as well as ortho-linked trimer of HPB core consisting of two PEG units at para-position and studied their self-assembly and ion conductivity behavior with DSC and X-ray diffraction pattern. For trimer HPB 104 bearing PEG chains, supramolecular columnar organization was observed due to the presence of efficient π–π stacking unlike in other HPB derivatives.

Wang et al.\(^{87}\) reported the synthesis of snowflake-structure of hexa-tetraphenylethene (TPE)-substituted propeller shaped non-planar HPB derivatives 105 and 106, by 6-folds Suzuki-Miyaura coupling of monoboronic acid of TPE with hexabromobenzene. These derivatives exhibit essential aggregation-induced emission (AIE) characteristics. The fluorescence quantum yield as well as piezochromic behavior of derivative 105 was enhanced or tuned up by inserting phenyl rotors as bridged between HPB and TPE moieties so as to synthesize derivative 106 via altering the twisted confirmation. These results demonstrated that the photophysical properties could be considerably tunable based on small molecules through suspicious engineering of these molecular organization.

### 1.3 Followings are the comments Drawn from the Review of Literature

- The strong C-H−−π interactions between the peripheral phenyl groups in HAB derivatives could be blocked by simply substituted ortho-positions by alkyl groups, which efficiently caused changes in molecular organization and packing mode. Upon ortho-substitution of HAB derivatives one could efficiently altered the molecular consistency without varying any other properties.
- Hexaarylbenzenes with five or six distinct substituents could be enabled by programmed synthesis using C-H activation, cross-coupling and [4+2] cycloaddition reactions. This method provides route for the isolation and structure–property description of distinct aryl substituted HAB derivatives.
Hexaarylbenzenes in presence of lithium powder undergoes modulation of central benzene core to a sterically hindered dianion which dynamically leads to a two-fold dehydrogenation and C-C bond formation.

Azaindole appended AIEE active hexaphenylbenzene served as stabilizer as well as reactor for the preparation of α-Fe₂O₃ nanoparticles with tremendous catalytic efficiency in photodegradation of Rhodamine B dye and in palladium, copper and amine free Sonogashira cross coupling.

HAB derivatives has potential 3D topologies which enables π-π interaction between the peripheral aromatic rings would lead to ‘‘toroidal delocalization’’. Hence HAB molecules are found to be redox active and exhibit exceptional electronic features, thus, can be used for fabrication of conducting materials.

HAB derivatives could be efficiently used as a promising building block for designing and construction of microporous organic polymers due to unique electronic features and propeller mimic shape, which arise due to mutual steric interactions of the peripheral phenyl groups.

HAB derivatives possess a good charge transport ability, high $T_g$ and emit blue light, hence can be used in the fabrication of white OLEDs and electrophosphorescent devices.

The star-shaped hexaarylbenzene derivatives bearing chiral alkyl substituents and antenna based chromophores are potentially useful in the field of supramolecular electronics.

Presence of phenyl rotors at peripheral of benzene core are responsible for aggregation induced emission enhancement characteristics in HAB derivatives.

Because of amplified sensing responses and high quantum yield, AIEE or AIE-active HAB-based probes have been efficiently utilized for the detection of nitroaromatic explosive.

Fluorescent nanoaggregates of HAB derivatives have been utilized as chemosensors for sensitive detection of metal ions.

Aggregates of HAB derivatives have been extensively used as bioprobes for quantification and detection of biomolecules in aqueous media.

1.4 Main Objectives of Present Work

Based on the above review of literature, in the present work, we have designed and synthesized a
few hexaarylbenzene (HAB) and hetero-oligophenylene derivatives and evaluated their recognition behaviour toward nitroaromatics, metal ions and biomolecules in the aggregated state. The present section also includes the utilization of aggregates of hexaarylbenzene (HAB) and hetero-oligophenylene derivatives as capping as well stabilizing agent for the preparation of nanoparticles and their catalytic applications. The resultant output of our investigation have been given in following chapters.

Chapter 2 Supramolecular Assemblies of Hexaarylbenzene and Hetero-oligophenylene based Derivatives for the Detection of Nitroaromatics

Chapter 3 Fluorescent Supramolecular Metal Assemblies as ‘No Quenching’ Probe for Detection of Threonine in Nanomolar Range

Chapter 4 Facile Decoration of Multiwalled Carbon Nanotubes with Hetero-oligophenylene Stabilized-Gold Nanoparticles: Visible Light Photocatalytic Degradation of Rhodamine B Dye

Chapter 5 Copper nanoparticles generated from aggregates of a hexaarylbenzene derivative: a reusable catalytic system for ‘click’ reactions

1.5 References


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