Chapter-1

Introduction and Review of Literature

Abstract:

This chapter deals with brief introduction and review of literature about various types of triphenylene and pyrene based derivatives. In addition, the potential applications of these triphenylene and pyrene based derivatives in material and supramolecular chemistry have been thoroughly reviewed. The objectives of present thesis are planned on the basis of these literature reports.
1.1 Introduction

Molecular recognition chemistry synonymously referred as supramolecular chemistry encompasses the systems formed by discrete number of molecular subunits or components held together by non-covalent interactions such as hydrogen bonding, hydrophobic forces, metal co-ordination, van der waals forces, π-π interactions electrostatic and/or electromagnetic effects. Biological systems are also driven by the molecular recognition processes and many essential functions occurs through interaction/recognition between the molecules such as base pairing in DNA double helix, antigen-antibody interactions, DNA-protein interactions, RNA-ribosomes interactions, sugar-lectin interactions etc. Molecular recognition operates both at microscopic as well as macroscopic level. Hence, the scope of molecular recognition has now become much broader as it finds applications in host-guest chemistry, supramolecular assemblies, drug delivery, bioinspired complexes, photochemical and electron transfer devices, photodynamic therapy, stimuli responsive materials, etc. The supramolecular recognition chemistry aims at designing the artificial molecular recognition units to understand the nature’s specific interactions toward various guests. One of the earliest examples of artificial supramolecular systems that exhibit molecular recognition was that of crown ethers which selectively bind specific cations. Thereafter, a number of synthetic receptors were synthesized such as cryptands, spherands, calixarenes, thiacalixarenes, porphyrins, cyclodextrins etc. which act as molecular recognition reagents. Molecular recognition also plays a significant role in self-organization or self-assembly of molecules where small molecules give rise to larger units as a result of these supramolecular interactions. Various nanoarchitects such as nanoparticles, nanotubes, nanorods etc. are also formed as a result of these supramolecular interactions. Self-assembly is also commonly observed in conjugated planar aromatic molecules due to the π-π interactions between their aromatic cores. The self-assembly of these planar molecules give rise to various nanosized architects which find applications in organic electronic devices, supramolecular polymers, gas sensors and molecular receptors. Among the various discotic molecules, triphenylene and pyrene derivatives find vast applications in the field of supramolecular and material sciences.
Chemistry. Triphenylene derivatives find major applications in the fabrication of liquid crystalline materials, as one dimensional photoconductors, organic light emitting diodes, photovoltaic solar cell, gas sensors etc.\textsuperscript{19} On the other hand, pyrene derivatives have been extensively exploited as molecular probes, fluorescent labels,\textsuperscript{20} organic electronic devices etc.\textsuperscript{21} High quantum yield and strong excimer emission of pyrene derivatives have been utilized for supramolecular design, probing structural properties of macromolecular system, sensing of environmental parameters and guests of chemical and biological interest.\textsuperscript{22} Keeping in view the significance of triphenylene and pyrene derivatives, in the present study, we have designed and synthesized triphenylene and pyrene based receptors. The molecular recognition behaviour of these receptors was studied toward various analytes such as metal ions, anions and nitroaromatic explosives by various spectroscopic and analytical techniques \textit{viz.} UV-vis spectroscopy, fluorescence spectroscopy, time resolved fluorescence spectroscopy, NMR spectroscopy, IR spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), dynamic light scattering (DLS) etc. but before presenting the results of our findings, a brief review of literature on triphenylene and pyrene based derivatives is discussed below.

1.2 Literature reports on triphenylene derivatives

Triphenylene, a polyaromatic hydrocarbon in which three benzene rings fused to form fourth common ring was first isolated from pyrolytic products of benzene by Schmidt and Schultz\textsuperscript{23} and first synthesized by aldol trimerization of cyclohexanone in early twentieth century.\textsuperscript{24} Triphenylene derivatives form discotic liquid crystals (DLC) and their liquid crystalline behaviour was discovered by Chandrashekhar \textit{et al.} in 1977.\textsuperscript{25} Liquid crystals are unique functional materials which possess both order and mobility ranging from molecular to macroscopic levels. DLC is a class of liquid crystals. 

![Triphenylene](image-url)
crystals, formed by the self-organization of disc shaped molecules, in which flat rigid aromatic core is surrounded by six or eight flexible aliphatic chains. The majority of DLCs form columnar mesophase in which the disc shaped molecules are stacked one upon the other to form the columns. Triphenylene derivatives also find applications in organic electronic devices such as organic light emitting diodes (OLEDs), organic field effect transistors (OFETs), organic photovoltaic cells, solar cells. Apart from this, triphenylene derivatives are also used as molecular recognition reagents, metal organic frameworks (MOFs), covalent organic frameworks (COFs), hybrid nanomaterials and gas sensors.

Among triphenylene derivatives, symmetrically substituted triphenylene derivatives are the most widely studied liquid crystalline materials. These derivatives are substituted with different substituents with ether or ester linkages. The liquid crystalline behaviour and other properties of these derivatives are strongly influenced by the nature of the substituents.

Kohmoto et al.\textsuperscript{26} reported the triphenylene based room temperature discotic nematic (N\textsubscript{D}) liquid crystals, 1a-c. These triphenylene derivatives exhibit N\textsubscript{D} phase at room temperature, however, phase transformation from N\textsubscript{D} to hexagonal columnar mesophase (Col\textsubscript{h}) was observed upon the addition of alkali metal ions. The liquid crystalline behaviour of derivatives 1a-c was investigated by differential scanning calorimetry (DSC), polarized optical microscopy (POM) and powder X-ray diffraction (XRD) studies. The powder XRD analysis of 1a showed one broad reflection peak. However, addition of 1 mol. equiv. of LiOTf caused the phase transition from N\textsubscript{D} to Col\textsubscript{h} as shown by three reflection peaks in powder XRD spectra.
Uchida et al. synthesized triphenylene derivative 2 with six 4-tetradecyloxyazobenzene units connected with propylene ester linkage and evaluated their photo and thermally induced liquid crystalline phase transition behaviour. The liquid crystalline phase transitions among three phases (Colr, SmA and Iso) were controlled by photo-irradiation which was accompanied by change in shape of molecule between rod and disc. Derivative 2 exhibits smectic A (SmA) and rectangular columnar mesophase (Colr) in an enantiotropic way i.e. it can behave both as rod and disc like molecules depending upon the thermal condition. The photoisomerism of azo benzene unit from trans to cis form with 365 nm UV irradiation induces the phase transition with the decrease in phase transition temperature.

Preece et al. synthesized mono, di, tri and hexa carbazole-triphenylene hybrid materials, 3-7 with alkyl and carboxylic spacer of varying lengths. These derivatives in their pure state did not show liquid crystalline behaviour, however, upon doping with trinitroflorenone (TNF) these derivatives exhibited hexagonal columnar mesophase as
shown by differential scanning calorimeter (DSC), polarized optical microscope (POM) and powder X-ray diffraction (XRD) studies. The mesophases exist below room temperature and mesophase clearing temperature was found to depend upon the chain length separating the carbazole and triphenylene moieties, degree of TNF doping and nature of ether or ester linkage. Highest clearing point was observed for 2:1 complex of triphenylene and TNF.

Molecules which show high proton conductivities at moderate temperature are required for the proton exchange membrane in fuel cells and barrier for the proton conduction can be lowered in liquid crystalline phase as compared to liquid or crystalline phase. In this context, Venkataraman et al.\textsuperscript{29} synthesized triazole modified triphenylene derivatives \textit{8a-c} using ‘click chemistry’. Derivative \textit{8a} and \textit{8b} did not show liquid crystalline behaviour while \textit{8c} showed needle like birefringence in the temperature range 75-140\textdegree{}C. Further, all these three derivatives showed mesomorphic behaviour but minimum ordering was observed in derivative \textit{8a}. The proton conductivities of derivatives \textit{8a-c} were calculated using AC impedance spectroscopy\textsuperscript{30} and it was observed that activation energy barrier for proton conduction was lowered in liquid crystalline state which suggested their use in proton exchange membranes in future.
The conventional discotic liquid crystals contain a rigid aromatic core appended with flexible peripheral chains, however, molecules lacking this flat central core were also found to exhibit liquid crystalline behaviour by the micro-separation of the polar cores from the lipophilic alkyl chains rather than from $\pi-\pi$ stacking of their aromatic cores. Tetraphenylethylene,$^{31}$ triphenylamine derivatives,$^{32}$ octahedral metal complexes,$^{33}$ dendrimers etc. are some of the derivatives which show this behaviour.

Zhang et al.$^{34}$ reported a series of triphenylene dimers 9a-k connected through flexible polymethylene chain ($n = 2$-$12$). The structure of these dimers was confirmed by nuclear magnetic resonance spectroscopy (NMR), fourier transform infrared spectroscopy (FT-IR), high resolution mass spectroscopy (HRMS) and elemental analysis while liquid crystalline behaviour was evaluated by DSC, XRD, and POM techniques. Out of these derivatives, dimers having $n>4$ form highly ordered columnar plastic phase. Derivative 9d was found to exhibit novel rectangular columnar plastic phase and comparable behaviour was observed in derivatives 9e, 9f and 9i-k, in which hexagonal columnar plastic phase was observed at low temperature while ordered hexagonal columnar phase at high temperature. Further, formation of columnar plastic phase was not significantly altered by the introduction of interconnecting alkyl chain. Although no correlation was found between chain length and phase range of the dimers yet these linkages were thought to enhance the mesophases of discotic molecules and obstruct the crystallization. XRD measurement showed that alignment of dimers was
easily tuned by heat treatment and showed ‘face on’ alignment on heating and ‘edge on’
alignment on cooling. Such a controllable alignment is important for the fabrication of
organic electronic devices such as OLEDs, OFETs, OPCs and TFTs.

Zhao et al.\textsuperscript{35} utilized the ‘click chemistry’ for the synthesis of triphenylene
based dimers 10-13 which are composed of two triphenylene discogens connected \textit{via}
triazole ring. The liquid crystalline behaviour of these derivatives was evaluated with
the help of DSC and POM. The results showed that all the dimers exhibit mesophases in
wide range of temperature. The dimers 12 and 13 containing amide bond showed higher
clearing point due to the intermolecular hydrogen bonding. The polarized optical
microscope (POM) images of dimers showed the presence of columnar mesophases.

Kumar \textit{et al.}\textsuperscript{36} reported triphenylene-based benzene-bridged symmetrical
discotic dimers 14-18 in which the two triphenylene units are linked to the central
benzene bridge through ester/ether linkages. Further to evaluate the effect of relative
orientation of two discotic mesogen around benzene bridge on the mesomorphic
behaviour, five benzene bridged dimers with triphenylene units at \( o-, m- \) and \( p- \) positions were synthesized. The liquid crystalline behaviour of these dyads was characterized by DSC, POM and powder XRD studies. None of these dimers showed mesomorphic behaviour but their charge transfer complexes with trinitrofluorenone (TNF), exhibited hexagonal columnar mesophases with distinct optical texture as evaluated by powder XRD analysis.

Paraschiv et al.\(^{37}\) reported discotic liquid crystal 19 based on \( C_3 \) symmetric 1,3,5 benzenetrisamide with three pendant hexaalkoxy triphenylene groups. In this derivative, 1,3,5- benzenetrisamide form the central column to which three triphenylene groups were linked by methylene linkers. The \( \pi-\pi \) stacking of three triphenylene moieties lead to the formation of three columns responsible for the charge migration. The liquid crystalline properties of derivative 19 were evaluated with the help of POM, DSC and XRD techniques. POM of derivative 19 showed ribbon like texture with alternative bright and dark domains at 196 °C when cooled from isotropic state. The powder XRD analysis of derivative 19 at 181 °C showed highly ordered hexagonal columnar mesophase. Further, from XRD studies and molecular modeling it was concluded that strong intermolecular hydrogen bonding and \( \pi-\pi \) stacking resulted in helix like columns of benzenetrisamides. Derivative 19 showed high charge carrier mobility of 0.06
Cm\(^2\)/V.s due to the small rotation between the adjacent stacked triphenylenes groups and short-lived defects in the \(\pi\)-stack.

Zhao et al.\(^{38}\) reported the synthesis of tetraphenylethylene-triphenylene oligomers \(20, 21\text{a}\) and \(21\text{b}\) and studied their aggregation induced emission enhancement (AIEE) and liquid crystalline behaviour. All the derivatives \(20, 21\text{a}\) and \(21\text{b}\) showed
AIEE effect in THF-H$_2$O mixture. The morphology of the aggregates was studied by SEM analysis while the thermal stability and mesomorphic properties were analyzed by using TGA, POM, DSC and XRD techniques. Further, charge transfer complexes of derivative 20 with different mole ratio of electron deficient trinitrofluorene (TNF) showed the presence of hexagonal columnar mesophases. The POM images of these complexes showed typical fan shaped texture. Transition temperature of mesophase to isotropic phase remarkably affected by TNF proportion in the binary mixture and highest clearing point was obtained when TNF concentration was between 67-80 %.

Triphenylene molecules are well known dicotic materials for their self-assembly and charge transporting properties\textsuperscript{39} but most of these derivatives have electron-donating substituent such as –OR or –SR which are used in $p$-type organic semiconductors. Wu \textit{et al.}\textsuperscript{40} synthesized the electron-deficient triphenylene and trinaphthalene carboxamides derivatives 22 and 23. The high electron affinity was
achieved by attaching the electron-withdrawing carboxamide groups. The optical, electronic, thermal and self-assembly properties of these derivatives were investigated in solid state by DSC, POM and XRD. From these studies, it was observed that these derivatives self-assembled into one dimensional columnar structures. Further, the long range ordered columnar phase in these derivatives makes them as potential candidate for \( n \)-type semiconductors in electronic devices.

Liu et al.\(^{41}\) prepared the \( n \)-type disk shaped triphenylene-cored fused naphthaleneimide imidazole and peryleneimide imidazole derivatives 24 and 25. The fusion of electron deficient napthaleneimide and peryleneimide to the triphenylene core resulted in the extended conjugation and superior optical properties along with well-aligned frontier energies. The charge carrier mobility of these derivatives was evaluated by field effect transistor and space charge limited-current (SCLC) measurements. The correlation between film morphology and charge transport behaviour was established by X-ray scattering and AFM analysis. The charge carrier mobility of derivative 24 is isotropic due to the more ordered hexagonal packing with edge-on orientation in thin films while that of 25 is anisotropic which is due to the lack of connected pathway to the lateral direction and the molecules are more connected along the vertical direction due to the slipped \( \pi \)-interaction and large domains.
Adachi et al.\textsuperscript{42} have reported the electron transport materials (ETMs) based on
disubstituted triphenylene derivatives 26-29 for their application in organic light
emitting diodes (OLEDs). In these materials, triphenylene core provides the good
electron transport ability while bipyridine units provide the good electron injection
ability due to their electron accepting property. The thin films of these ETMs have
optical anisotropy as shown by ellipsometry measurements. Further out of these ETMs,
the green OLED fabricated with derivative 27 showed considerably lesser driving
voltage and attained lesser power consumption in comparison to conventional OLEDs
containing tris(8-hydroxyquinolinato)aluminum (Alq\textsubscript{3}) and 1,3,5-tris(2-phenyl-1H-
benzo[d] imidazol-1-yl)benzene (TPBi). The operation lifetime of blue OLED
containing derivative 27 is comparable to that of OLED containing TPBi.

The liquid crystals with redox behaviour can be obtained by the introduction of
redox active units on triphenylene. Several attempts were made to synthesize
triphenylene derivatives with both redox and mesomorphic behaviour,\textsuperscript{43} however,
derivatives with both mesomorphic and redox behaviour were not known. In this
context, Yang et al.\textsuperscript{44} recently reported triphenylene-ferrocene dyad 30a-b linked by
long and short conjugated spacers. The electrochemical properties of these dyads were
evaluated by cyclic voltammetry while mesomorphics behaviour was studied by DSC,
XRD and POM techniques. Dyad 30b with long conjugated showed redox property but
did not exhibit mesomorphic behaviour while dyad 30a showed both reversible
electrochemical response as well as ordered hexagonal columnar mesophase.
Wan and co-workers\textsuperscript{45} reported belt shaped, semiconducting, luminescent covalent organic frameworks (COFs) 31 formed by triphenylene and pyrene scaffolds. In this COF, the D$_3$h symmetric triphenylene monomers acted as corners while D$_2$h symmetric pyrene monomers acted as edges to form hexagonal porous skeleton. The SEM image of COFs showed the presence of uniform belts having length in micrometer range. Powder X-ray diffraction (PXRD), theoretical and molecular simulation studies show that COF 31 is crystalline in nature with pores of uniform size formed by eclipsed packing of polymeric network. The mesoporous COF 31 exhibits light harvesting over the wide range of wavelength, energy transfer and migration. In addition, the COF is conductive in nature and possess repetitive ‘on-off’ current switching at room temperature.

Fused aromatic molecules find application in organic semiconductors. However, they have low charge mobility due to the van der waals interactions between molecules. In this context, Xu \textit{et al.}\textsuperscript{46} described a group of 3-dimentional, semiconductive
coordination networks based on 2,3,6,7,10,11-hexakis (alkylthio) triphenylene (HATT) 32a-c and Bi (III) halides. The large polarizable fused π-electron system of triphenylene core enhanced the electroactivity of resultant network. Secondly, symmetrical structure of triphenylene core readily accommodates three pairs of 1,2-bis(alkylthio) groups, capable of binding with metal ions to enhance the electronic interaction between organic-π-system and metal ions. These semiconductive networks possessed flexible network dimensionalities and electronic properties and good solution processible properties. As compared to molecular semiconductors these integrated hybrid networks showed stronger electronic communication and better charge carrier mobilities. Further, Xu et al.\textsuperscript{47} reported semiconductive coordination networks 33a-b based on 2,3,6,7,10,11-hexakis(phenylthio)triphenylene and 2,3,6,7,10,11-hexakis(4-methoxyphenylthio) triphenylene and silver (I) salts. The network structure featured distinct channel like domain which incorporated various solvent molecules as guests which can be removed to produce stable and crystalline apohost network. This 3D network showed strong fluorescence at room temperature due to the electrons of triphenylene moiety. Further, these extended structures crystallized in non-centrosymmetric space groups, thus, making these star shaped molecules useful for forming acentric crystals.

Chen et al.\textsuperscript{48} reported dithiol-functionalized triphenylene (TP-S) modified ZnO nanoparticles (TP-S@ZnO) as effective hybrid solar cell 34 based on the blend of poly(3-hexyl thiophene) and DLC ligand. These hybrid nanoparticles (TP-S@ZnO) possessed well defined dispersability arising from the supramolecular self-assembly of TP-S discs. Attachment of TP-S on ZnO NPs rendered the ZnO NPs to self-assemble, thus, improving the compatibility between poly(3-hexylthiophene) polymer and ZnO NPs which favors the exciton dissociation and charge carrier generation. Powder XRD
and wide angle X-ray diffraction studies (WAXS) showed that modification of ZnO NPs with TP-S under thermal annealing increased the power conversion efficiency of hybrid solar cell from 0.45% to 0.95%.

The aromatic π−π stacking between ligand and substrate is known to improve catalytic efficiency, thus, making the polyaromatic ligands as interesting tools for the designing of efficient homogenous catalysts. Inspired from this, Peris et al. reported the star shaped *tris*(N-heterocyclic carbene) derivative 35 in which three carbenes were connected by π-delocalised polyaromatic system derived from triphenylene. The gold (Au) and palladium (Pd) complexes of tris NHC were evaluated for catalytic activity towards various reactions such as α-arylation of propiophenone with aryl bromides, Suzuki-Miyura coupling and hydroamination of terminal alkynes. It was observed that palladium complex 36 showed excellent activity towards α-arylation and Suzuki-Miyura coupling and Au complex 39 showed better catalytic activity towards hydroamination of terminal acetylenes as compared to trimetallic triptycene *tris* (NHC) complexes 39, 41 and monometallic complexes 40, 41. High catalytic activity with
triphenylene complexes was due to the higher local concentration of the catalytic active species in the trimetallic complexes or due to the \( \pi \)-stacking interactions between the polyaromatic core of triphenylene tris (NHC) and aromatic substrates.

Liquid crystalline nanoscience is a symbiotic association between liquid crystals and nanoscience in which nanomaterials are incorporated into the self-assembly of discotic liquid crystals, thus, providing an opportunity to explore the new hybrid materials and their applications.\(^{51}\) In this regard, Kumar \emph{et al.}\(^{52}\) has reported the CdSe quantum dots-DLC composites \(42\) in which CdSe quantum dots of different sizes were dispersed into the columnar matrix of hexabutyloxytriphenylene DLC. These hybrid materials showed higher conductivity than pure triphenylene. Nature of mesophases did not alter with the insertion of quantum dots however, minor change in their transition temperatures was observed. This composite material found applications in the fabrication of organic electronic devices. The same group also reported the nanocomposites in which gold nanorods were embedded in hexagonal columnar mesophases of hexapentyloxy-triphenylene derivatives \(43\) and showed enhanced conductivity due to the insertion of nanorods into the ribbon like structures\(^{53}\).
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Li et al.\textsuperscript{54} reported the construction of microbelts through the co-assembly of hexapyridylhexaazatriphenylene (HPHAT) 44 and primary alkyl ammoniums with hydrogen bonding as driving force. The extended pocket of hexaazatriphenylene (HAT) with six pyridyl units provided the three hydrogen bond acceptor pockets while primary alkyl ammonium with different chain lengths provided the three hydrogen bond donor NH for binding with N-atom of HPHAT. The addition of dodecylammonium triflate into the chloroform solution of HPHAT resulted in the formation of well-defined microbelts as shown by SEM, TEM and confocal microscopic images. The mechanism of formation of microbelts was investigated on the basis of spectroscopic and crystallographic observations. The \textsuperscript{1}H NMR of HPHAT showed down field shift in the signals of pyridine unit which confirms the intermolecular H-bonding. Sharp peaks in the powder XRD spectra of microbelts suggested the highly crystalline character while diffraction peak with d spacing of 3.8Å revealed the π-π stacking between the HAT molecules. From these observations, it was concluded that mechanism of formation of microbelts involved two steps. First a complex was formed between HPHAT and alkylammoniums by the H-bonding. This complex then self-assembled to form microbelts through the cooperative interactions of π-π stacking of HAT cores and van der waals interactions between the alkyl chains.

\begin{center}
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Li et al.\textsuperscript{55} also reported the formation of microscale structures by the coordinative assembly of hexapyridylhexaazatriphenylene (HPHAT) derivative 44 with transition metal ions. The co-assembly of derivative 44 with Zn\textsuperscript{2+} ions in methanol and chloroform resulted in the formation of microspheres. With monovalent Ag\textsuperscript{+} ions in methanol and chloroform, derivative 44 showed the hollow microtubes. However, in
10% H₂O under same conditions microrods of hexagonal cross section was formed. It was observed that microtubes and microrods could be transformed into each other by adding or removing water to or from the solution. Morphology of microstructures was evaluated with SEM and TEM analysis. The microsphere was also found to encapsulate rhodamine which could be used as carrier materials.

From above literature reports, it is clear that triphenylene derivatives have great applications in the material chemistry, however, there are few reports which showed the recognition behaviour of triphenylene derivatives toward different analytes. Some of the representative examples are discussed below.

Apart from fabrication of microbelts and metal ions assisted nano-architectures through self-assembly, derivative 44 was also utilized for metal ion recognition. In this context, Bu et al.⁵⁶ reported the application of hexapyridylhexaazatriphenylene (HPHAT) derivative 44 for selective fluorescence sensing of Cd²⁺ ions over other metal ions including zinc. Derivative 44 showed weak fluorescence emission at 405 nm but with the addition of Cd²⁺ ions, fluorescence enhancement was observed at 456 nm and colour of the resulting solution became light yellow. However, with zinc colour of the solution changed from colourless to reddish-brown without any fluorescence emission, provided an easy way to discriminate between Cd²⁺ ions and Zn²⁺ ions. The fluorescent enhancement with Cd²⁺ ions resulted from intramolecular charge transfer effect due to the binding of Cd²⁺ ions with N atoms which reduced the electron-withdrawing ability of N-atoms and lowered the electron density of HPHAT.

Further, Han et al.⁵⁷ synthesized two C₂ symmetrical hexaazatriphenylene based derivatives 45 and 46 containing different number of pyridine groups. Both derivatives exhibited selective colorimetric and ratiometric detection of Zn²⁺ ion over alkali, alkaline-earth and transition metal ions. Derivative 45 showed fluorescence emission at 417 nm in acetonitrile however; with addition of Zn²⁺ ions significant fluorescence enhancement was observed at 545 nm. Similar fluorescence enhancement was observed with derivative 46. Derivative 45 showed 1:3 stoichiometry with Zn²⁺ ions as proved by Job’s plot and single crystal X-ray analysis of 45 and 45-Zn²⁺. While Job’s plot of derivative 46 showed 1:2 binding mode with Zn²⁺ ions. Fluorescence enhancement with
Zn$^{2+}$ ions was due to coordination of nitrogen atoms to Zn$^{2+}$ ion reducing the electron withdrawing effect of nitrogen atoms and lowering electron density which resulted in intramolecular charge transfer (ICT) effect. Further, the coordination of Zn$^{2+}$ ions enhanced the plane rigidity which increases the conjugation of whole molecule.

Kocyigit et al.$^{58}$ reported the synthesis of triphenylene derivatives 47-49 having carboxylic acid groups and their Fe/Cr(III) salophen capped complexes. The derivatives 47-49 were synthesized from hexahydroxytriphenylene which were then converted to complexes bridged by carboxylate anions to the chromium or iron center with $[\{\text{Fe/Cr(salophen)}\}_2\text{O}]$ as “ligand complex”. All the complexes were stable at room temperature and were characterized by elemental analysis, thermogravimetric analysis, magnetic susceptibility and FT-IR spectroscopic studies. The magnetic susceptibility studies revealed the hexanuclear structure of Fe(III) and Cr(III) complexes with Fe and Cr in octahedral environment. The FT-IR spectra of these complexes showed the shifting of C=O band either to higher or lower values than their free ligands showing the participation of oxygen in coordination with ligand complexes.
Further, the Kocyigit et al. synthesized triphenylene based Schiff base and studied its complexation behaviour with various transition metal ions such as Co$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, Pd$^{2+}$ and Cd$^{2+}$. These metal complexes were characterized by infrared spectroscopic (IR), magnetic susceptibility and thermal gravimetric analysis (TGA) analysis. The IR spectra of free ligand showed vibration of OH and imine C=N groups at 3400 and 1690 cm$^{-1}$, respectively which were shifted to lower frequencies upon complexation with metal ions. Moreover, the strong band around 3380-3446 cm$^{-1}$ was assigned to coordinated water while bands at 554-532 and 464-479 were attributed to M-N and M-O bonds respectively. The magnetic susceptibility studies showed that Cd(II), Pd(II) and Zn(II) complexes were diamagnetic while Ni (II), Co(II) and Cu(II) were found to be paramagnetic in nature. The magnetic susceptibility values of Co$^{2+}$
complexes suggested the d7 metal ion in square planar while that of Ni2+ and Cu2+ complexes suggested the d8, d9 metal ion, respectively in tetrahedral structure.

Recently, Sakamoto et al.60 reported the synthesis of trinuclear metalladithiolene complexes of derivative 51 with Co, Rh and Ir, 51a-c. The planar structure of the Ir-complex was determined using single crystal diffraction analysis which featured a planar π-conjugated heptacyclic framework. The absorption spectra of these complexes in dichloromethane showed intense band in the visible and NIR region which was assigned to ligand to metal charge transfer (LMCT) transitions. The LMCT transitions of trimetallic complexes were red shifted as compared to that of mononuclear complexes 53a-c. The electronic communication in the reduced mixed-valent state was investigated by means of chemical reduction followed by UV-vis-NIR spectroscopy studies and it was found that mono and divalent reduced Co complexes showed inter valence charge transfer (IVCT) band in NIR region indicating the role of metal nuclei in electronic communication. This fact also proved that π-conjugation among the three metalladithiolene units was transmitted by triphenylene core.

Bhalla et al.61 synthesized the triazole appended triphenylene derivative 54 by click reaction. The recognition behaviour of 54 was studied using UV-vis and fluorescence spectroscopy. Among the various metal ions tested, derivative 54 selectively sensed Cu2+ ions. Further, copper ensemble of derivative 54, was used for the selective and sensitive sensing of CN− ions, by displacement approach due to the formation of stable complex between Cu2+ and CN− ions. Formation of this stable complex due to the demetallation of copper ensemble (54.Cu2+) resulted in ‘turn-on’ sensing for CN− ions. Derivative 56 also showed sensitive response with Cu2+ and CN−
ions in bovine serum albumin and blood serum milieu. The practical application of derivative 54 for the detection of Cu$^{2+}$ and CN$^{-}$ ions was realized by using solution coated TLC strips for the solid state detection of Cu$^{2+}$ and CN$^{-}$ ions. By applying the chemodosimetric approach Bhalla et al.$^{62}$ reported the irreversible cyclization of symmetrical and unsymmetrical terphenyls 55a-b to corresponding triphenylenes 56a-b in presence of tetrabutylammonium fluoride (TBAF). The cyclization process was accompanied by drastic colour change and was evaluated with the help of UV-vis, fluorescence and NMR spectroscopy. Based upon these results, they have proposed the mechanism for cyclization; in which F$^{-}$ assisted desilylation of TBS groups provided the optimum negative charge for cyclization,$^{63}$ favored by high conjugation of triphenylene. On the basis of similar mechanism, Bhalla et al.$^{64}$ also reported extended triphenylene derivative, 57 which undergoes the F$^{-}$ induced irreversible cyclization to form supertriphenylene, 58. The formation of supertriphenylene was accompanied by colour change which was investigated by using UV-vis and fluorescence spectroscopy.
Further, the practical application of derivative 57 for detection of F- ions was realized by making the solution coated test-strips of derivative 57 which upon dipping in aqueous solution of KF showed colour change and fluorescence quenching hence account for naked eye detection of F- ions.

Kaner et al.\textsuperscript{65} reported blue fluorescent noanofibrils based on oligotriphenylene derivative 59 as chemosensors for nitroaromatic explosives such as trinitrophenol, nitrobenzene and Fe(III) ions. The highly blue fluorescent oligotriphenylene was synthesized by oxidizing the triphenylene with ferric chloride. The length and diameter of the fibrils was tuned from 0.5 to 5 µm and 50 to 200 nm respectively by controlling the reaction temperature, monomer concentration and doping acid used. Conjugated oligotriphenylene nanofibres exhibited good thermal stability in comparison to triphenylene due to the extended conjugation. The oligotriphenylene also possess high fluorescence quantum yield and stable fluorescence. Strong π-π interaction between the oligotriphenylene molecules is the main driving force for nanofibres formation. Further, UV-vis, fluorescence lifetime studies and molecular simulation studies indicated the static quenching process as an underlying factor for sensing.

Triphenylene derivatives also find application in the detection of neutral molecules and guests of biological interest. Bibal et al.\textsuperscript{66} reported the H-bond acceptor polyphosphorylated triphenylene receptors 60a-b for the selective sensing of catechol. The six bulky (diaryl)phosphinate groups around the central triphenylene disc prevented the core aggregation and favored H-bonding. The polyphosphinated hosts 60a-b showed selective recognition of 1,2-dihydroxybenzene (catechol) moieties 61-63 with 1:2 (host:guest) stoichiometry in chloroform solution. However, no binding was
observed with other aromatic H-bond donors such as phenol, aniline and thiol derivatives. Further, the selective sensing of catechol by derivative 60 was found to take place through two processes. The weak H-bonding between phosphinate groups and hydroxyl groups was confirmed by IR and $^{31}$P NMR studies. From molecular dynamics simulation and recognition experiments it was observed that receptor 60 interact with catechol molecule through H-bond assisted by $\pi-\pi$ interaction between triphenylene core and catechol that could exist in 1:2 complex.

Bibal et al.\textsuperscript{67} also synthesized water soluble multivalent triphenylene derivatives 64a-b. Out of various ammoniums tested such as $\alpha$-aminoacids (glutamate, aspartate and glycine), $\gamma$-amino acids (GABA), nicotine and epibatidine, derivative 64b selectively recognizes acetylcholine and its agonist nicotine in phosphate-buffered water. 1:1 complex was formed between acetylcholine and derivative 64b with binding constant of 94±9M\textsuperscript{-1}. The host: guest interactions were studied by IR spectroscopy which revealed that ion pairing occurs between carboxylate host and ammonium guest, assisted by the desolvatation of the guest ester.
Using the combination of hydrophobic effects and ion pairing, Bibal et al.\textsuperscript{68} have also synthesized triphenylene based receptor 65 for the binding of biological amines; 66-68 \textit{viz.} phenylethyl amines, serotonin, and D-glucosamine in phosphate buffered water. Recognition of these analytes occurred through the hydrophobic effects between the aromatic surfaces and ion pairing between the carboxylate groups of the host and hydroxyl groups of the guests. The strength of host and guest association was found to be dependent upon lipophilicity/hydrophilicity of the guest. Catecholamines and serotonin formed 1:1 complex with receptor 65 with binding constant of 200 M\textsuperscript{-1} while D-glucosamine exhibited binding constant of 90 M\textsuperscript{-1}.

Waldvogel et al.\textsuperscript{69} synthesized trifunctionalized triphenylene ketal 69, 70 for the recognition of alkylated oxopurines such as caffeine 71, theophylline or theobromine. Recognition of caffeine involved the three dimensional surround of guest by the C\textsubscript{3} symmetric cleft of derivative 69 through the non-covalent interactions such as hydrogen bonding and stacking interactions between the electron-rich host and electron-deficient guest. The interaction of host with guest was evaluated with the help of NMR spectroscopy and single crystal X-ray analysis. These studies showed that receptor 69 formed 1:1 complex with caffeine (with binding constant of 35600 M\textsuperscript{-1}) in which the guest molecule was located between the urea functions instead of binding to the open side through $\pi-\pi$ stacking, $\pi$-donor-$\pi$-acceptor or hydrophobic interactions. The preorganized urea moieties, required for H-bonding in 69 increased the binding constant by 200 as compared to flexible derivative 70.
Liu et al.\textsuperscript{70} have reported two star shaped polyelectrolytes based on triphenylene core with six poly[2-(dimethylamino)ethyl meth-acrylate] (PDEM, 72) and poly(acrylic acid) (PAA, 73) arms at the periphery. Both these derivatives were synthesized by atom transfer radical polymerization (ATRP) method and have fluorescence properties which depend upon pH and ionic species. The fluorescence emission of derivative 72 and 73 was decreased with increase in pH without any shift in their wavelength. Derivative 72 ($pK_a = 6.5$) exists in monomeric form at pH<5.2 due to the electrostatic repulsions between highly charged and extended chains thus fluorescence intensity remains constant in the pH range of 2.7 to 5.2; however at pH >8.1 the molecules become uncharged and undergo aggregation due to the hydrophobic forces between the triphenylene scaffold. Thus, fluorescence intensity remains low because of aggregation caused quenching of fluorescence. Similar quenching in fluorescence intensity was observed in derivative 73 with increasing pH, however, here the mechanism of quenching was chain conformation controlled non-radiative relaxation.\textsuperscript{71} Moreover, no
Excimer emission was observed in the whole pH range which indicates the segregation of triphenylene cores from each other due to the steric effect of hydrophobic chains.

1.3 Literature reports on pyrene derivatives

Pyrene consists of four fused benzene rings and it is considered as fruiutfly of photochemists.\(^7\) It was discovered by Laurent in 1837 from the residue of destructive distillation of coal tar.\(^7\) It possess excellent fluorescence properties such as exceptionally long fluorescence lifetime,\(^7\) higher tendency to form excimer,\(^7\) high quantum yield and sensitivity of excitation spectra to microenvironment changes.\(^7\) Due to these properties pyrene is one of the most thoroughly investigated chromophores and finds applications in the diverse fields ranging from supramolecular chemistry to material chemistry. Pyrene labels have been used for the synthesis of fluorescent sensor for the recognition of various guests such as metal ions\(^7\) or anions,\(^7\) organic molecules\(^7\) and gases.\(^8\) They are also used as biological markers in structure elucidation of proteins and peptides,\(^8\) DNA binding,\(^8\) cell membranes.\(^8\)

Electrophilic substitution of pyrene readily takes place at 1, 3, 6 and 8 positions hence _mono_ and _tetra_ substituted pyrenes derivatives are easily accessible. Out of these 1,3,6,8 substituted pyrene derivatives finds many applications such as liquid crystals,\(^8\) organic light emitting diodes,\(^8\) field effect transistors,\(^8\) fluorescent labeled polymers,\(^8\) metal-organic framework,\(^8\) photoactive polypeptides\(^8\) and genetic probes.

Sankararaman _et al._\(^9\) reported the synthesis and photophysical properties of 1,3,6,8 _tetra_ substituted pyrene derivatives\(^7\) and\(^7\) containing acetylinic units. The presence of acetylene units shifts the absorption and emission of these derivatives into
visible region which makes them as suitable candidates for the making of light emitting devices. The fluorescence quantum efficiencies of tetra ethenyl derivatives 74 and 75 were found to be comparable to pyrene, however, in the case of 74e it was found to be low owing to the deactivation of the excited state resulting from the free rotation of phenyl groups.

Zhu et al.\textsuperscript{91} synthesized two butterfly shaped pyrene derivatives 76 and 77 by Suzuki-Miyura coupling protocols and used them in thin film transistors. These derivatives showed strong solid state fluorescence due to the twisted structure and were packed in herringbone arrangement similar to that of pentacene. The thermogravimetric measurements show that derivatives 76 and 77 are thermally stable upto 388 and 428 °C respectively. Thin films of derivatives 76 and 77 were deposited on SiO\textsubscript{2} by high vacuum evaporation at room temperature while their OFET devices were fabricated on SiO\textsubscript{2}/Si substrate using top contact geometry. No FET performance was observed in the device fabricated from derivative 76 however derivative 77 showed p-type performance with hole mobility of 3.7×10\textsuperscript{-3} cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1}, on-off ratio of 10\textsuperscript{4} and threshold voltage of -21V, hence, can be used as an active layer in p-type field effect transistors.

Lee et al.\textsuperscript{92} reported the electron transport materials based on tetrasubstituted pyrene derivatives viz. 1,6-dipyridin-3-y1-3,8-dinaphthalen-1-ylpyrene 78 and 1,6-dipyridin-3-y1-3,8-dinaphthalen-2-ylpyrene 79 for their application in blue OLED. The
OLED fabricated using these materials showed higher external quantum efficiency than materials using tris-(8-hydroxyquinolinato)aluminum (Alq3) as electron transport material due to the efficient balanced charge recombination in the emissive layer. The electron mobilities are also three time higher than that in Alq3. The high power efficiency of these materials was ascribed to the low electron injection barrier and high electron mobility.

Pyrene is the most attractive \( \pi \)-centre for two-photon materials due to its planar structure. Kim and Cho *et al.*\(^9\) have synthesized a series of [4-(N,N-dimethylamino)phenylethynyl]pyrene derivatives 80a-e and studied their two-photon absorption characteristics. The two photon cross section \( \delta_{\text{max}} \) of these derivatives was measured by two-photon-induced fluorescence measurement technique. The comparison of \( \delta_{\text{max}} \) values with related compound showed that efficiency of pyrene as \( \pi \)-centre in two photon materials was comparable to that of anthracene. The \( \delta_{\text{max}} \) values of these derivatives increased with increase in number of substituents and had maximum value of 1150 GM for *tetra*-substituted derivative. Further, the two photon action cross section \( \Phi_{\delta_{\text{max}}} \) value of derivative 80e was found to be comparable to most efficient two photon materials.\(^{94}\)
Araki et al.\textsuperscript{95} reported the 1,3,6,8 tetraphenylpyrene derivative, \textit{81} with four hexylamide units showing peizochromic-luminescence. Peizochromism is the tendency of certain materials to change colour by the application of pressure or mechanical grinding and its return to the original colour by heating and recrystallization process. This phenomenon of showing colour change or fluorescence change is known as peizochromic luminescence. These materials find application in optical recording or strain or pressure sensing systems. In these materials presence of two different pressure dependent states or metastable states are necessary.\textsuperscript{96} The derivative \textit{81} showed white colour and blue emission (B-form) however upon grinding the colour of the powder changed to yellow with strong green luminescence (G-form).

P. Sonar et al.\textsuperscript{97} synthesized tetra-functionalized pyrene based derivatives, \textit{82a-d} and developed solution processible organic light emitting diodes (OLEDs). Introduction of various moieties such as phenylene, bithiophene, theinothiophene and benzothiadiazone- thiophene have a substantial effect on the resultant optoelectronic and thermal properties. Out of these four derivatives, OLED based upon 1, 3, 6, 8-tetrakis (4-butoxyphenyl) pyrene \textit{82b} showed deep blue emission, low turn-out voltage and maximum brightness.
Stylianou et al.\textsuperscript{98} synthesized the permanent, microporous, fluorescent metal organic framework (MOF) based upon tetra-benzoate functionalized pyrene derivative \textit{83} with In (III) as inorganic component. The MOF [In$_2$(OH)$_2$(TBAPy)].guest displayed 54 \% total accessible volume with excellent thermal stability.

Gingras et al.\textsuperscript{99} synthesized a series of pyrene cored polysulphurate dendrimers \textit{84a-c} with poly (thiophenylene) groups. These dendrimers display remarkable photophysical and redox properties which were regulated by the length of their branches. Thus, on increasing the dendrimer generation the absorption band showed red shift alongwith the increase in absorption. Quantum yield, fluorescence lifetime and half-wave potential also increases with dendrimer generation. Further, all the dendrimers undergo two successive one electron reversible electrochemical oxidation processes with AuCl$_4^-$ in dichloromethane.

1,3,6,8-tetra(thio)pyrenes known as good organic p-conductors,\textsuperscript{100} form complexes with thiophilic metal ions and charge transfer complexes with organic molecules. However, its electronic and physiochemical properties can be modulated by appending the metal binding units. In this context, Gingras et al.\textsuperscript{101} also reported tetra(phenylthio) pyrene cored multichromoporic system \textit{85} appended with four terpyridine units which possess strong chelating activity towards various metal ions.\textsuperscript{102} This system exhibited high quantum yield and quantitative energy transfer upon exciting the terpyridine unit. Further, binding of Fe$^{2+}$, Zn$^{2+}$ and Nd$^{2+}$ leads to formation of oligometric structure with 2:1 stoichiometry in which metal ion bridging the terpyridine units from two different molecules.
Thomas et al.\textsuperscript{103} have reported the synthesis, photophysical and electroluminescent properties of the mono, and tetra fluorenone substituted pyrene derivatives 86 -90. The optical properties of these derivatives were found to be dependent upon number of chromophores present on pyrene nucleus. The mono substituted derivatives showed blue emission while tetrasubstituted derivatives showed greenish blue emission. The derivatives end capped with diphenyl amine moieties shows more red shift in their absorption and emission profile and were found to be more thermally stable. Further, the derivatives with acetylene linkage between the pyrene and fluorene chromophores showed better optical, electrical and thermal properties as compared to the derivatives without acetylenic linkages. The amine containing molecules showed positive solvatochromism in their fluorescence emission spectra owing to the more polar nature of the excited state which was ascribed to the effective charge migration from diphenylamine donor to central pyrene $\pi$-acceptor. Further, these
derivatives were used as efficient dopants in multilayered organic light emitting diodes with CBP (4,4'-bis(9H-carbazol-9-yl)biphenyl) as host and exhibited colour purity over wide range of voltage.

Apart from fluorescent materials several groups have tried to synthesize the fluorescent columnar liquid crystals based on pyrene core functionalized at 1,3,6,8 positions. In this context, Geerts et al.\textsuperscript{104} have synthesized derivatives, 91a-j having different aromatic substituents. The nature, number, size of side chain and polarity around the core has been varied but none of these derivatives showed desired liquid crystalline behaviour.

Geerts et al.\textsuperscript{105} also reported that incorporation of acetylene spacer between pyrene core and phenyl moiety resulted in the formation of hexagonal and rectangular columnar mesophases. Tetrakis(trisalkoxy-phenylethynyl)pyrene showed fluorescent discotic liquid crystals over the large temperature range. Derivative 92 possesses strong luminescence in solution, crystal and liquid crystalline state. The fluorescent quantum yield was found to be 70% in dichloromethane solution and 62% in solid state. High solid state quantum yield was attributed to the rotated chromophores allowing the lowest optical transition. Thermotropic properties of the mesogen were studied by DSC, POM and XRD analysis. Derivative 92 possess enantiotopic hexagonal columnar (Col\(_h\)) mesophase over the large temperature range. Further, nature of the intermolecular interactions and their effect on the quantum yield and spectral properties were studied by carrying out concentration and temperature dependent UV-vis and fluorescence studies and quantum-mechanical calculations.
Muccini and Ziessel et al.\textsuperscript{106} reported \textit{di} and \textit{tetra} \textit{N}-(4-ethynylphenyl)-3,4,5-tris(hexadecyloxy) benzamide substituted pyrene derivatives \textit{93} and \textit{94}, respectively. Out of these derivatives the \textit{di}-substituted derivative \textit{93} showed gelation in DMF, toluene and cyclohexane but did not show any mesomophic behaviour. The morphology of supramolecular gel was characterized by (SEM) and laser scanning confocal microscopy (LSCM). SEM analysis of the gel showed the presence of interlocked fibers which were extended over several micrometer distances while LSCM image of gel showed that excimer formation of pyrene units was efficiently prevented by 3D architecture. Further, this organogel was used as active layer in organic field effect transistor which showed good bulk electron and hole charge mobilities. On the other hand, the \textit{tetra}-substituted pyrene derivative \textit{94} did not show any gelation but exhibited liquid crystalline mesophase from room temperature to 200\textdegree C. The liquid crystalline behaviour was studied by XRD and POM analysis which revealed the presence of columnar mesophases with hexagonal symmetry. The POM images showed the flower like motifs with six petals reflect the six-fold symmetry of Col\textsubscript{h} mesophase.

Pyrene is also known to perform electronic communication between two metal centres. In this context, Zhong \textit{et al.}\textsuperscript{107} reported the electronic coupling between two cyclometalated ruthenium centers bridged by 1,3,6,8-\textit{tetra}(2-pyridyl)pyrene \textit{95} – \textit{96} which was studied by electrochemical and spectroscopic studies. Cyclic voltametric and
differential pulse voltammetric studies showed the stepwise oxidation of two metal centers of the dimetalllic complexes. The splitting of 210 mV between two redox bands of bisruthenium complex showed the efficient electronic coupling by planar tetrapyridylpyrene ligand, which was supported by appearance of intervalence charge transfer transition in the NIR region.

![Chemical structure](image)

Tang et al.\textsuperscript{108} reported efficient solid state emitter 97 in which the attachment of tetraphenylethylene units at 1,3,6,8 positions of pyrene core resulted in the aggregation induced emission enhancement (AIEE). The derivative 97 showed proficient solid state photoluminescence (Φ=70%) and high thermal stability (T\textsubscript{d} = 485°C). The multilayered green OLED fabricated from derivative 97 showed high current (12.3 cd A\textsuperscript{-1}) and power efficiency (7.01 mW\textsuperscript{-1}), low turn-on voltage (3.6V), high luminescence (36300 cd m\textsuperscript{-2}) and high η\textsubscript{ext} of 4.65% at 6V. Moreover the device showed superior performance than similar devices using Alq\textsubscript{3} as emitter.

![Chemical structure](image)

Mukherjee et al.\textsuperscript{109} have synthesized a series of electron rich molecules, 98-102 containing trimethylsilyl functionalities and utilized these derivatives for the sensing of nitroaromatic explosives. The presence of TMS functionalities prevented the self-quenching in these molecules due to excimer formation due to the π-π interaction and
increases the emission intensity of the fluorophores. Out of these, tetrasubstituted pyrene derivative 102 showed colorimetric response towards TNT while the thin films of derivatives 101 and 102 on quartz plate showed significant quenching of fluorescence with saturated vapors of nitroaromatic explosives.

By modifying their initial design 102, Mukherjee et al.\textsuperscript{110} synthesized supramolecular polymers based on fluorophores 103-105 for the detection of nitroaromatic explosives. These fluorophores which behaved as discrete fluorophore in solution form infinite supramolecular polymer network in solid state by intermolecular hydrogen bonding between their hydroxyl groups. These fluorophores showed high fluorescence quenching response with nitroaromatic explosives through the formation of charge-transfer complex by \( \pi-\pi \) interaction of their aromatic cores. Further the thin films of these fluorophores were utilized for the sensitive and reversible vapour phase sensing of DNT.

The \( \pi-\pi \) interaction mechanism for the sensing of nitroaromatic explosives was also exploited by Kim et al.\textsuperscript{111} They reported the dipyrenylamido-calix\[4\]arene--[15]\crown\-5 derivative, 106 as fluorescent chemosensor for detection of trinitroaromatic explosives such as TNT and TNB. Upon the addition of these
trinitroaromatic compounds, quenching of monomer as well as excimer emission was observed due to the formation of charge transfer complex between pyrene and nitroaromatics. Further, charge transfer complex formation was confirmed from UV-vis, fluorescence and $^1$H NMR spectroscopic studies. The single crystal X-ray structure of TNT complex of derivative 106 further confirmed the proposed charge transfer mechanism which showed a closed stacked interaction between the electron rich planar pyrene units and electron deficient TNT in solid state. The detection limit of derivative 106 for TNT was found to be 1.1 ppb which is less than 2.0 ppb, the maximum acceptable limit of TNT in drinking water as established by US EPA\textsuperscript{112}.

Sukwattanasinitt \textit{et al.}\textsuperscript{113} reported four triskelion shaped fluorophores 107, 108, 109 and 110 based on electron rich triphenylamine core coupled with polynuclear
aromatic hydrocarbon (PAHs) units such as planar pyrene or bowl shaped corannulene units through triazole or acetylene linkers for the detection of TNT explosives. Out of these four, derivatives with triazole linker show more sensitivity towards TNT than with acetylene linkers as shown by their higher Stern-Volmer constants which indicate the role of triazole bridge for increasing the quenching efficiency and hence detecting ability up to ng cm\(^{-2}\) level.

Fang et al.\(^{114}\) reported the sensing of TNT with fluorescent film of pyrene containing conjugated polymer in aqueous medium. The two new conjugated polymers containing poly(pyrene-co-phenyleneethynylene)s units, \(^{111}, 112\) of different compositions were synthesized and the, fluorescent films were fabricated from these polymers onto the glass substrate which were found to show highly sensitive and selective response towards TNT (with Stern-Volmer constant of \(3.65 \times 10^4\) M\(^{-1}\)) without any interference from other nitroaromatics such as picric acid dinitrotoluene, nitrobenzene. However, there was negligible change in the fluorescence emission of film deposited from parent polymer poly(phenyleneethylene), \(^{113}\). The efficient quenching of pyrene-copolymer with TNT was ascribed to the \(\pi-\pi\) interaction between the pyrene and TNT. The fluorescence lifetime studies showed the static nature of quenching. Moreover the films were used for the supersensitive detection of TNT in ground water and sea water.

Colquxoan et al.\(^{115}\) synthesized pyrene functionalized copolymer \(^{114}\) by the side chain functionalization of copolymer, poly(maleic anhydride-alt-1-octadecene) for the detection of nitroaromatic compound 3,5-dinitrobenzonitrile (DNB). Detection of nitroaromatic involved the formation of charge transfer complexes by \(\pi-\pi\) stacking of
electron rich pyrene moiety and electron deficient nitroaromatics which was evaluated with the help of, UV-Vis, fluorescence and $^1$H NMR spectroscopy. The appearance of deep orange colour upon mixing copolymer 114 with DNB and the upfield shifting of aromatic protons in $^1$H NMR showed the formation of charged transfer complex. Moreover, the spin casted film of 114 showed prompt fluorescence quenching upon exposure to the vapors of 3,5-dinitrobenzonitrile.

Chen et al. $^{116}$ reported pyrene functionalized ruthenium nanoparticles, 115a-b as potent chemosensor for nitroaromatic explosives such as such as 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 1-chloronitrobenzene (CNB), and nitrobenzene (NB). Synthesis of these nanoparticles involves the olefin metathesis of carbone stabilized Ru nanoparticles with 1-vinylpyrene (Ru=VPy) and 1-allylpyrene (Ru=APy). The pyrene moieties were bound to ruthenium surface through conjugated Ru=carbene $\pi$ bonds$^{117}$ and the resulting nanoparticles
showed similar response as pyrene conjugated polymers toward nitroaromatic explosives sensing. Out of these two, Ru=VPy NPs displayed much higher sensitivity than Ru=APy NPs and pyrene monomers towards nitroaromatic explosives which showed nanomolar detection limit for TNT. The enhanced sensitivity of immobilized fluorophore on NPs was due to the increased collision frequency between fluorophores and quenchers. Additionally, extended intra-particle conjugation also provided the effective pathways for energy/electron transfer and therefore amplified the analyte binding events.

1.4 Observations drawn from review of literature

From the detailed review of literature, following conclusions were drawn

1. Triphenylene and pyrene core have great potential in material chemistry owing to their role as liquid crystalline materials. Most of the triphenylene derivatives form stable columnar mesophase due to their \( \pi-\pi \) stacking. The presence of large aromatic core further enhances the stability of mesophases. Interesting fluorescence properties of these derivatives enable them to be used in fabrication of organic electronic devices such as OLEDs, FETs, photovoltaic cells etc.

2. Triphenylene and pyrene derivatives are also used in the fabrication of mesoporous covalent organic frameworks (COFs) and metal organic framework (MOFs) which find potential application in light harvesting, energy transfer, gas storage/absorption etc.

3. The semiconducting coordination networks based on triphenylene and pyrene scaffold show better charge carrier mobilities and electronic properties as compared to molecular semiconductors.

4. The metal complexes designed on triphenylene or pyrene scaffold show good catalytic activity due to the efficient stacking between these molecules and aromatic substrate.

5. Apart from material chemistry, these triphenylene and pyrene derivatives also find applications in supramolecular chemistry where these derivatives with suitable functional groups have been exploited for the recognition of various
analytes of chemical and biological interest such as metal ions, anions, neutral guests etc. Various pyrene derivatives have been used for the detection of nitroaromatic explosives whereas utilization of triphenylene derivatives for detection of nitroaromatics is not much explored

1.5 Objectives of Present Work

Based upon above observations, in the present work we have designed and synthesized triphenylene and pyrene based fluorescent receptors and evaluated their recognition behaviour towards various analytes such as metal ions, anions, reactive oxygen species and nitroaromatic explosives by the use of various spectroscopic techniques. To facilitate the presentation of work, the results of our findings are divided in following chapters.

Chapter 2: Metal Ensembles of Triphenylene Based Derivatives for the Sensing of Anions and Reactive Oxygen Species (ROS)

Chapter 3: Triphenylene and Pyrene Based Derivatives as Sensitive Chemosensors for Nitroaromatic Explosives

1.6 References:


(c) Templer, R. H.; Castle, S. J.; Curran, A.
(d) Pokhrel, M. R.;  
23  
24  
Mannich, C. Ber. 1907, 40, 159.  
25  
26  
27  
28  
29  
30  
31  
(a) Higuchi, H.; Mitani, I.; Kikuchi, H.; The 23rd International Liquid Crystal Conference, P-1.50, Krakow, Poland, July, 2010, pp. 11; (b) Schreivogel, A.;  
32  
33  
34  
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52 Kumar, S.; Sagar, L. K. Chem. Commun. 2011, 47, 12182.
Chapter 1 Introduction and Review of Literature

70 Chen, F.; Li, C.; Wang, X.; Liu, G.; Zhang, G. Soft Matter 2012, 8, 6364
71 Pu, K.; Shi, J.; Cai, L.; Li, K.; Liu, B. Biomacromolecules 2011, 12, 2966


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