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Summary

Molecular recognition chemistry synonymously referred as supramolecular chemistry encompasses the systems formed by the discrete number of molecular subunits or components held together by non-covalent interactions. It is truly inspired from biological systems where essential of life such as self-replication, information processing and metabolism occurs thorough the specific interaction/recognition between the molecules. The molecular recognition operates both at microscopic as well as macroscopic levels. A bimolecular reaction starts with the recognition event whether it takes place in solid/liquid or gas phase. On the other hand, it gives rise to supramolecular architects or polymers through self-assembly. Hence, the scope of molecular recognition has now become much broader as it finds applications in diverse fields such as sensing, drug delivery, medical imaging, organic electronics, supramolecular polymers, stimuli responsive materials, crystal engineering, photodynamic therapy, photocatalysis etc. Taking the inspiration from biological systems, numerous synthetic receptors like crown ethers, cryptands, calixarenes, thiacalixarenes, porphyrins, spherands, cyclodextrins etc. have been reported to explore the molecular recognition behaviour of natural receptors toward various guests.

Among the various polyaromatic hydrocarbons, triphenylene and pyrene derivatives find wide applications in the material as well as supramolecular chemistry. Triphenylene is most commonly exploited as central core in discotic liquid crystals (DLCs) and these liquid crystalline materials finds application in the fabrication of organic light emitting diodes, photovoltaic cells, photoconductors and gas sensors. Triphenylene derivatives also find application in sensing of neutral guests. On the other hand, pyrene derivatives are extensively used in molecular probes, organic electronic devices, fluorescent labeling of biomolecules etc. Keeping in view the significance of triphenylene and pyrene derivatives in supramolecular and material chemistry, in the present investigation we have designed and synthesized triphenylene and pyrene based derivatives and evaluated their molecular recognition behaviour toward different analytes. For convenience in presentation, the work carried out in the present investigation has been divided into three chapters.
Chapter 1: Introduction and Review of Literature

This chapter deals with the introduction and review of literature about the various triphenylene and pyrene based derivatives. The importance of their role in material chemistry and molecular recognition is thoroughly reviewed. From the detailed review of literature the following conclusions have been drawn:

1. Most of the triphenylene and pyrene derivatives exhibit hexagonal columnar mesophases which finds immense utilization in material chemistry as liquid crystalline materials. These derivatives are used in the fabrication of organic electronic devices such as organic light emitting diodes (OLEDs), organic field effect transistors (OFETs), photovoltaic cells, one dimensional conductors, gas sensors etc.

2. Triphenylene and pyrene derivatives are important motifs for the preparation of mesoporous covalent organic frameworks (COFs) and metal organic frameworks (MOFs). These materials are important due to their potential applications in light harvesting, energy transfer etc.

3. The semiconducting coordination network of these derivatives showed better electronic properties and charge carries mobilities as compared to molecular semiconductors.

4. The metal complexes of triphenylene and pyrene derivatives have been used as homogenous catalysts which show high catalytic efficiency due to π-π stacking between ligand and substrate.

5. The triphenylene and pyrene derivatives also find application in supramolecular chemistry where these derivatives with suitable functional groups/binding sites
are explored for the detection of analytes of chemical and biological interest such as neutral guests, metal ions and anions. Pyrene derivatives have also been used for the detection of electron deficient nitroaromatic explosives whereas utilization of triphenylene derivatives for detection of nitroaromatics is not explored much.

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

Development of fluorescent chemosensors for the detection of anions and reactive oxygen species (ROS) is an active area of research as they play a significant role in various chemical, biological and environmental processes. In this context, metal ensemble based detection of anions has gained considerable interest as they induce geometrical preorganization which results in the better molecular complementarity towards anions. Moreover, several fluorescent chemosensors have been reported in literature for the detection of ROS. This chapter deals with the design and synthesis of triphenylene based receptors 3 and 7. The chemosensing metal ensembles of these derivatives find application in the detection of biologically important anions and reactive oxygen species. This chapter is divided into two sections:

Section 2.1: Aggregates of Triphenylene Based Chemosensing Ensemble for Sensitive Detection of Cyanide Ions in Aqueous Medium

Among the various anions, cyanide ion is toxic to the living beings as it halts the cellular respiration by inhibiting respiratory enzyme cytochrome c oxidase. However it is still used in many industrial processes such as gold mining, electroplating, metallurgy etc. which can lead to contamination of water resources. Hence, designing of fluorescent chemosensors for trace detection of CN$^-$ ions is an area of immense research interest. Keeping this in view, we have designed and synthesized star shaped triphenylene derivative 3 having six pyridine moieties at its periphery. Derivative 3 serve as potent chemosensor for Cu$^{2+}$ ions. Further, copper ensemble of derivative 3 acts as turn-on chemosensor for CN$^-$ ions in aqueous medium. Derivative 3 was synthesized by palladium catalyzed Suzuki-Miyaura cross coupling of pyridine-3-boronic ester 2 with hexabromotriphenylene 1 (Scheme 2.1). Derivative 3 exhibits blue
fluorescence in mixed alcoholic aqueous medium. Among the various metal ions tested, derivative 3 showed quenching of emission in the presence of Cu$^{2+}$ ions. This quenching of fluorescence is attributed to the formation of non-fluorescent H-aggregates in the presence of Cu$^{2+}$ ions as evaluated by UV-vis, fluorescence, scanning electron microscope (SEM) and powder x-ray diffraction (XRD) studies.

![Scheme 2.1 Synthesis of triphenylene derivative 3](image)

The formation of H-aggregates was also confirmed by carrying out temperature dependent UV-vis and fluorescence studies. Further by coordination complex displacement approach these non-fluorescent H-aggregates served as potent ‘turn-on’ chemosensor for CN$^-$ ions. The detection limit of derivative 3 for Cu$^{2+}$ ions was found to be 1.5×10^{-6} M and that of copper ensemble for CN$^-$ ions was found to be 0.026 ppm which is much lower than that of maximum limit of CN$^-$ ion in drinking water as allowed by US EPA (0.2 ppm). Further, the practical application of cooper ensemble of derivative 3 for the detection of CN$^-$ ions was realized by making its solution coated test strips which showed the instant detection of CN$^-$ ions.

**Section 2.2: Zinc Ensemble of Triphenylene Derivative Having Imine Moieties as Chemosensors for Reactive Oxygen Species (ROS): Application as Oxidation Inhibitor**

Introduction of imine moiety in the organic scaffold provides the binding sites for the recognition of soft metal ions. Development of fluorogenic chemosensors for soft metal ion such as zinc is of considerable interest as it plays an important role in variety of biological processes. Zinc is the second most abundant transition element present in the body and is found either in free or sequestered form in various parts of the body such as brain, spermatozoa, pancreas and vesicles of presynaptic neurons. Zinc
also has anti-oxidizing property, as its deficiency increases the production of reactive oxygen species (ROS). In this context, we have designed and synthesized triphenylene receptor 7 having imine moieties. Derivative 7 show selective turn-on response towards Zn$^{2+}$ ions among various metal ions tested. Zinc ensemble of derivative 7 served as antioxidant towards Dakin oxidation of β-hydroxynapthaldehyde.

Reactive oxygen species (ROS) are the oxygen containing chemically reactive species which play vital role in cell signaling, gene expression and homeostasis. They are broadly classified into two categories; radical and non-radical species. The radical species include superoxide (O$_2^-$), hydroxyl (OH), peroxyl (RO$_2^-$), alkoxyl (RO$^-$), hydroperoxyl (HO$_2^-$) while non-radical ROS include hydrogen peroxide (H$_2$O$_2$), hypochlorous acid (HOCl), ozone (O$_3$), singlet oxygen (¹O$_2$) and peroxynitrite (ONOO$^-$). During oxidative stress, the level of ROS increases which results in pathogenesis of several diseases such as cardiovascular disease, cancer, neurological disorders, diabetes mellitus and ageing. Hence, the regulation of generation of ROS is highly important. In this context, antioxidants are the compounds which protect our body by scavenging the ROS. Among various metal ions, zinc acts as an antioxidant and scavenges the ROS formed by other metal ions such as Cu$^{2+}$ ions and Fe$^{3+}$ ions. Earlier, a variety of artificial zinc receptors showing biomimetic applications have been reported in literature, however, zinc ensemble showing antioxidant activity has not been reported in the literature. Thus, in this present section we have designed and synthesized quinoline appended triphenylene receptor 7 having imine linkages which was synthesized by palladium catalyzed Suzuki-Miyaura coupling of boronic ester 4 with hexabromotriphenylene 1 followed by the condensation of the product 5 with quinoline-2-carboxaldehyde (Scheme-2.2).
Derivative 7 acts as selective turn-on chemosensor for Zn$^{2+}$ ions. Further the zinc ensemble of receptor 7 has been evaluated for its anti-oxidizing property as a mimic for zinc metalloenzymes. For evaluating the antioxidant activity, we have taken β-hydroxynapthaldehyde 8 as a template and carried out its Dakin oxidation (Scheme-2.3) with H$_2$O$_2$ and observed its fluorescence behavior in the presence and absence of zinc ensemble of derivative 7 (Zn-7). β-hydroxy naphthaldehyde 8 showed an emission due to fast keto-enol tautomerism (Scheme 2.3a) involving the phenomenon of excited state intramolecular proton transfer (ESIPT). Upon the addition of H$_2$O$_2$, quenching in the fluorescence emission was observed (Figure 2.1). This quenching is ascribed to the oxidative conversion of 8 to species 10 in which the inhibition of ESIPT makes photoinduced electron transfer (PET) operational and as a result emission gets quenched (Scheme 2.3b). Further to observe the anti-oxidant property of Zn-7, we performed the fluorescence titration of derivative 8 with H$_2$O$_2$ under similar conditions in the presence of Zn-7. We observed that in the presence of Zn-7, the rate of oxidation of 8 is decreased and the amount of H$_2$O$_2$ required to quench the fluorescence is larger (1300 µl) than in the absence of Zn-7. This may be ascribed to the fact that hydroperoxide anions (HOO$^-$) generated during the reaction (which are responsible for the oxidation) show preferential binding to the charged zinc centre of Zn-7 (Scheme 2.4). Further, anti-oxidant activity of zinc ensemble was found to be even better than five commercially available antioxidants viz. propyl gallate (PG), butylated hydroxyl toluene (BHT), butylated hydroxyl anisole (BHA), α-tocopherol (TP) and sodium ascorbate.
Chapter 3: Triphenylene and Pyrene Based Derivatives as Sensitive Chemosensors for Nitroaromatic Explosives

The detection of nitromatic explosives has gained worldwide attention as they possess serious threat to mankind and international peace. Nitroaromatic compounds (NACs) such as picric acid (PA), 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), 1,4-dinitrobenzene (DNB), 4-nitrotoluene (4-NT), 1,4-benzoquinone (BQ), nitromethane (NM) and 2,3-dimethyl-2,3-dinitrobutane (DMNB) are the major constituents of most of the explosives. NACs are also considered as contaminants as they possess high toxicity and mutagenic properties towards humans and wildlife. Hence, sensitive and trace detection of NACs explosives is very important for combating terrorism, maintaining national security and providing environmental safety. In this context, fluorescence based detection of nitroaromatic explosives is of considerable interest due to its high sensitivity, selectivity and real time monitoring with fast response time. Further, as NACs are electron deficient in nature, the fluorescent chemosensors for these should be \( \pi \)-electron rich, planar, conjugated and should have high quantum yield. Keeping this in mind, in the present investigation, we have designed and synthesized various electron rich fluorescent derivatives based on triphenylene and pyrene core which showed sensitive response towards nitroaromatic explosives. The findings of our results have been divided into following sections.

Section 3.1 Carbazole Substituted Triphenylene Derivative for the Sensitive Detection of Nitroaromatic Explosives

In this section, we have designed and synthesized carbazole substituted
triphenylene derivative 12 by palladium catalysed Suzuki-Miyaura coupling of 9-hexyl-9H-carbazol-3-yl-boronic acid 11 with hexabromotriphenylene 1 (Scheme-3.1) in which six N-alkylated carbazole moieties are appended at the periphery of triphenylene core. Here the planar triphenylene core is expected to undergo π-π stacking to form non-fluorescent aggregates whereas incorporation of six bulky N-alkylated carbazole groups at periphery prevents the self-aggregation of molecule thus making the derivative 12 emissive in solution. The derivative 12 exhibits sensitive response toward various nitroaromatic explosives with maximum sensitivity towards picric acid. The mechanism of observed fluorescence quenching with picric acid was attributed to the energy transfer from photo-excited derivative 12 to picric acid as shown by UV-vis and fluorescence studies. Further, time resolved fluorescence and cyclic voltammetry studies showed that quenching was static in nature and a ground state complex was formed. The practical application of derivative 12 was realised by making solution coated test strips which can detect the trace amounts of picric acid in solid state and in the contact mode.

Section 3.2 Rhodamine Substituted Pyrene Derivative as Sensitive Chemosensor for Picric Acid in Mixed Aqueous Medium

Among various nitroaromatic explosives, selective detection of picric acid (PA) is of considerable interest as it possess health hazard to humans as well as wildlife. The acute exposure to picric acid can cause respiratory diseases, skin/eye irritation. Thus, to improve the sensitivity and selectivity of chemosensors toward picric acid we have selected pyrene as central core in the next part of our investigation. Pyrene derivatives possess high quantum yield, good excimer emission and interesting photophysical
properties in comparison to triphenylene derivatives. On the other hand, rhodamine based derivatives are promising chemosensors due to their high quantum yield, absorption and emission at longer wavelength. Further, most of the reported chemosensors shows turn off response towards picric acid while turn-on response is more favorable due to the easy detection of signal over the dark background. In this context, we have designed and synthesized terasubstituted pyrene derivative 17 by condensation of rhodamine acid chloride 16 with pyrene amine 14 (Scheme 3.2) having four rhodamine moieties at the periphery connected through phenyl spacer. Derivative 17 acts as turn-on chemosensor for picric acid due to the spirolactum ring opening of rhodamine moieties. This ring opening of derivative 23 with picric acid further accounts for the colorimetric detection of picric acid. Further, for practical application of derivative 17, the solution coated test strips of derivative 17 was used for colorimetric detection of picric acid.

Section 3.3 Aggregates of Triphenylene Derivatives Having AIEE Characteristics for the Sensitive Detection of Picric Acid

Disc shaped molecules often form aggregates due to the π-π stacking interactions, experience the decrease in emission intensity in concentrated solution and in solid state. This is due to the non-radiative decay of aggregates of these molecules known as aggregation caused quenching effect (ACQ). Triphenylene derivatives are known for their high charge carrier mobilities due to the efficient π-π stacking between their molecules. However, in most of the triphenylene derivatives this π-π stacking
results in the formation of non-luminescent aggregates due to the ACQ effect hence limits their use in organic electronic devices such as OLEDs. On the other hand, aggregation induced emission enhancement effect (AIEE) suppresses the intermolecular quenching and induce/increases the emission intensity by blocking the non-radiative decay through restriction of rotation or torsion of intermolecular bond. Thus, keeping this in view in next part of investigation, we were interested in the development of fluorescent supramolecular assemblies based on triphenylene derivatives by utilizing AIEE phenomenon. In this context, we have designed and synthesized extended triphenylene derivative 19 having six nitrile groups at periphery by palladium catalyzed Suzuki-Miyuara coupling of 4-cyanophenyl boronic acid 18 with hexabromotriphenylene 1 (Scheme-3.3). This derivative showed emission enhancement in mixed aqueous media.

We also studied the AIEE characteristics of derivative 5. These derivatives with rotatable C-C/C-N bonds show AIEE phenomenon due to the combined effect of slipped packing of molecules in aggregated state, restriction of rotation and aggregation driven growth of aggregates. Further, the fluorescent aggregates of these derivatives serve as potent chemosensors for nanomolar detection of picric acid. Out of these two, derivative 5 showed selective and more sensitive response towards the detection of picric acid with highest Stern-Volmer constant and lower detection limit. The solution coated test strip of derivative 5 can detect femtogram level of picric acid.

Further, presence of amino groups prompted us to investigate the binding behaviour of derivative 5 towards various metal ions. Earlier, various small molecules/polymers having amino groups have been reported for the preparation of gold nanoparticles. Gold nanoparticles find numerous applications in catalysis, drug
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delivery, gene therapy, sensing etc. Among these, the catalytic activity has widespread application in reduction reactions, C-C/C-N/C-O bond formation, cyclization, hydroformylation etc. Keeping this in view, we have evaluated the binding behaviour of aggregates of derivative 5 towards different metal ions in mixed aqueous medium by UV-vis and fluorescence spectroscopy. Among the various metal ions tested, the aggregates of derivative 5 exhibits sensitive response towards Au$^{3+}$ ions and served as reactors and stabilizers for preparation of gold nanoparticles without the addition of any reducing agent. The formation of gold nanoparticles was further confirmed by transmission electron microscope (TEM), powder X-ray diffraction (XRD) and energy dispersive X-ray spectroscopic techniques. Further, these amine stabilized gold nanoparticles smoothly reduce 4-nitrophenol to 4-aminophenol at room temperature.

Section 3.4 Aggregates of Gallic Acid Substituted Triphenylene Derivative for the Sensitive Detection of Trinitrotoluene in Aqueous Medium and in Vapour Phase

Among various nitroaromatic compounds (NACs), trinitrotoluene (TNT) is widely used as an explosive and is a constituent of unexploded landmines worldwide. TNT is also considered as environmental pollutant as it can contaminate the ground water of war zone, thus, posing a serious threat to human health. Moreover, trinitrotoluene is carcinogenic in nature and its continuous exposure results in headache, skin irritation, anemia and abnormal liver function. Hence, development of chemosensors for trace detection of TNT is important for security as well as environmental safety. Keeping this in mind, in next part of investigation we have designed and synthesized gallic acid substituted extended triphenylene derivative 21 by the condensation of alkylated gallic acid chloride 20 with triphenylene based amine 5 (Scheme-3.4).

Derivative 21 with six trialkoxyphenyl groups at the periphery connected via amide bonds to extended triphenylene core undergoes self-assembly to form ‘not quenched’ fluorescent porous aggregates due to the slipped arrangement of the molecules in aqueous media. Further, these fluorescent aggregates served as selective and efficient chemosensor for trinitrotoluene (TNT) over the other nitroaromatics. The efficient fluorescence quenching with TNT is attributed to the charge transfer
phenomenon from aggregates of derivative 21 to electron deficient TNT. Further, derivative 21 also showed vapour phase detection of TNT due to the quick penetration and diffusion of vapours of TNT into the pores of aggregates. Detection up to attogram level of TNT by dip strips of derivative 21 shows its practical utility.