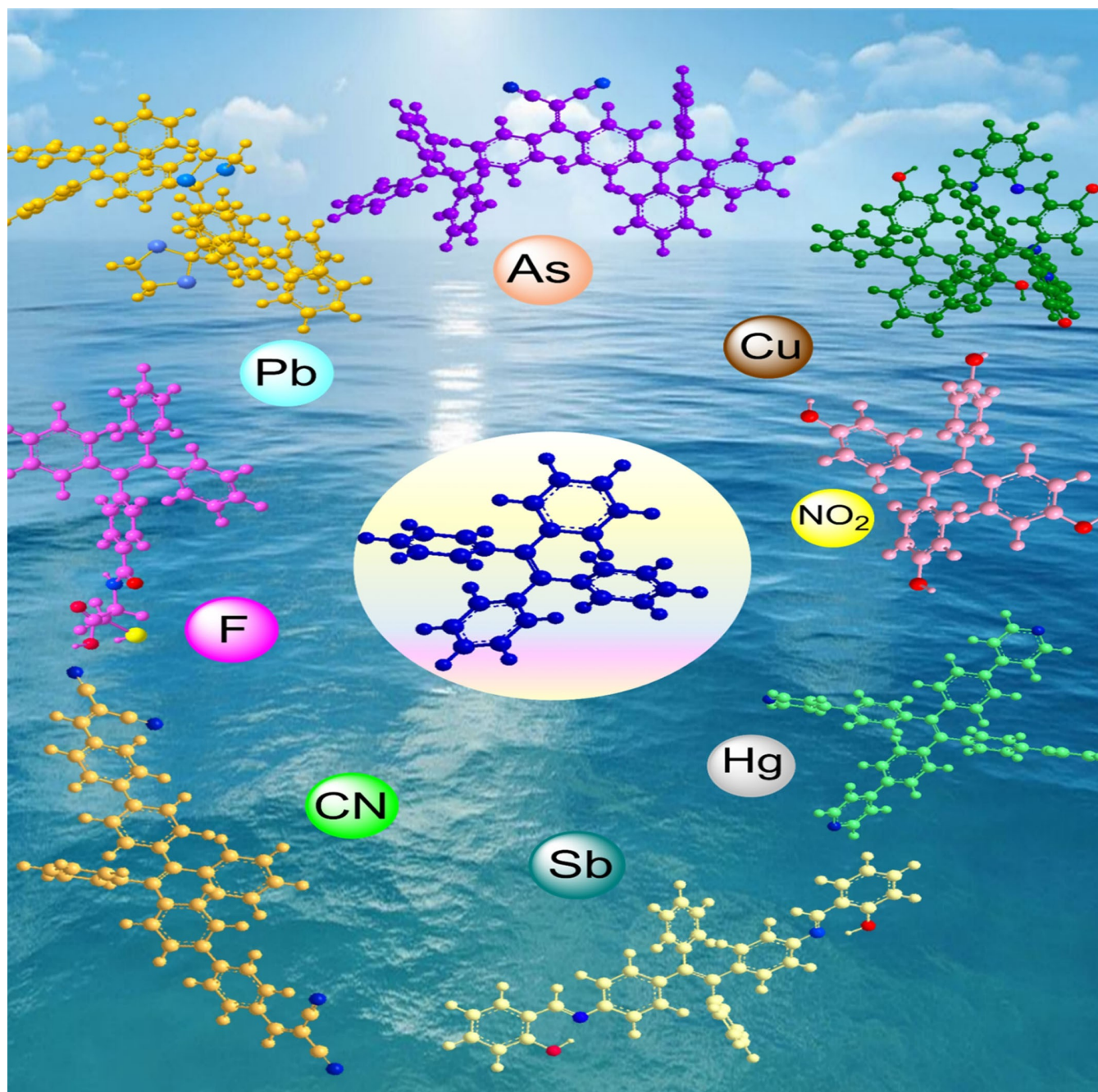


Aggregation Induced Emissive Luminogens for Sensing of Toxic Elements

Geeta A. Zalmi, Vilas K. Gawade, Dinesh N. Nadimetla, and Sheshanath V. Bhosale*^[a]



The major findings in the growing field of aggregation induced emissive (AIE) active materials for the detection of environmental toxic pollutants have been summarized and discussed in this Review article. Owing to the underlying photophysical phenomenon, fluorescent AIE active molecules show more impact on sensing applications. The major focus in current

research efforts is on the development of AIE active materials such as TPE based organic fluorescent molecules, metal organic framework, and polymers that can be employed for the detection of toxic pollutants such as CN^- , NO_2^- , Hg^{2+} , Cd^{2+} , As^{3+} , As^{5+} , F^- , Pb^{2+} , Sb^{3+} ions.

1. Introduction

Ionic species, including anions and heavy metal ions that contaminate resources such as water and various food products, can be very toxic, as they can easily enter into the environment and accumulate in the human body causing severe diseases, which may result into death even at very low concentration. Toxic anions and heavy metal cations often enter the environment as a result of industrial development and increased human activities, thus leading to water pollution. In many regions of the world, water pollution is a major problem in the world.^[1] Various toxic ions that have toxic effect are Al^{3+} , Cr^{3+} , Cd^{2+} , Co^{2+} , Mg^{2+} , Hg^{2+} , Sb^{3+} , As^{3+} , As^{5+} , Cu^{2+} , CN^- , F^- , Br^- , Cl^- . There are different methods that can be employed to detect toxic pollutants such as electro analytical methods, atomic absorption spectroscopy, inductively coupled plasma mass spectrometry, colorimetric methods. Amongst all the available techniques, fluorescent sensing is considered as one of the best methods as it is fast, cost effective, simple and easy to handle. This method can be applied using naked eye detection and low cost of instrumentation. Hence, fluorescent materials have attracted the attention of researchers towards use of the fluorescent dyes such as tetraphenylethene derivatives, Schiff's bases, naphthalene-diimide (NDI), pyrene, conjugated polymer, and various metal organic framework (MOFs). However, many organic dyes show aggregation caused quenching mechanism (ACQ).^[2]

In the ACQ process, the molecule is initially highly emissive in aqueous solution. However, in the aggregated state the molecule exhibits weak emission and generates a detrimental process. Therefore, there is a need of developing simple and efficient fluorescent molecules exhibiting aggregation induced emission characteristics (AIE).^[3,4] Different possible detection mechanisms can be involved such as photoinduced electron transfer (PET),^[5] fluorescence resonance energy transfer (FRET),^[6] intramolecular charge transfer (ICT).^[7] Chelation enhanced fluorescence (CHEF)^[8] and excited state intramolecular proton transfer (ESIPT)^[9] have been reported.

Another phenomenon that came into existence to overcome the ACQ effect is the aggregation induced emission

phenomenon, which was discovered in 2001 by Tang and co-workers. Aggregation induced emission is an unusual phenomenon, exactly opposite to ACQ, in which a molecule is initially non-emissive but becomes highly emissive in the aggregated state. Many research groups have reported AIE-active molecules that can be used for chemical sensing and bio-sensing applications in live cells.^[10,11] In this Review article, we have summarized the various AIE active molecules that can be used for detecting toxic pollutants from the environment such as As^{3+} , CN^- , Hg^{2+} , F^- , Pb^{2+} , Cu^{2+} , Pd^{2+} , Cd^{2+} , NO_2^- , Sb^{3+} and other ions.

The detection of the toxic ions by fluorescent molecule occurs through different chemical reaction via nucleophilic addition and coordination reaction between probe and analyte ion, chemical interaction such as hydrogen bonding and anion π -interaction and physical interaction via electrostatic attraction between cation and anions. Herein are simple fluorescent AIE active molecules discussed for detecting toxic pollutants.

2. AIE Active Molecule for Arsenic Detection

Arsenic (As) is one of the most toxic element and it is found abundantly in the terrestrial crust, especially in ground water, which causes serious global health problems. Arsenic can induce the breaking of DNA producing lesion, increasing the cellular levels of nitric oxide and superoxide and affects the protein phosphorylation binding with thiols.^[12] Nowadays, the contamination level in most of the areas are constantly increasing above permissible limit of 10ppb according to the World health organisation guidelines (WHO).^[13] There are a number analytical techniques that are dependent on expensive large-scale instruments which are time consuming and require series of analysis for determination of Arsenic in real sample such as atomic absorption spectroscopy (AAS),^[14] Inductively coupled plasma (ICP-AES)^[15] and inductively coupled plasma mass spectrometry (ICP-MS)^[16] atomic fluorescence spectroscopy (AFS).^[17] However, the fluorescent methods have attracted the attention of researchers due to easy operation, simple design, high sensitivity, low cost of instrumentation with rapid analysis.^[18]

Herein, Tian and co-workers^[19] have designed a novel aggregation induced (AIE) active molecule by single step reaction combining 3,5-dibromobenzaldehyde with (9-phenyl-9H-carbazol-3-yl)boronic acid via Suzuki reaction. In this example, the AIE active carbazole ring acts as a molecular rotor. The molecule is further combined with cysteine to give compound **2** which has high selectivity and sensitivity towards As^{3+} in aqueous medium. The detection mechanism is shown in

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Figure 1. The thiol group of **2** selectively forms chelate with As^{3+} with ratio of 3:1. The experimental studies showed that compound **2** was highly selective towards As^{3+} with low limit of detection of 1.32 ppb. Further fluorescence studies describe that upon addition of As^{3+} from 0 to 240 ppb in THF/water. Moreover, the fluorescence response to various other ions was carried out in order to study the selectivity such as As^{3+} , Ni^{2+} , Mn^{2+} , Co^{2+} , Pb^{2+} , Cd^{2+} , Cu^{2+} , Al^{3+} , Hg^{2+} , Fe^{3+} , Cr^{3+} and Fe^{3+} . Fluorescence studies revealed that there is enhancement in fluorescence indicating that the molecule **2** was highly selective towards arsenic over other cations. Further the molecule was used for practical application in detecting the As^{3+} in water sample.

Beglan *et al.* synthesized cysteine functionalized derivatives of TPE as the fluorescent AIE active dye for the detection of As^{3+} in aqueous media.^[20] TPE is considered as the important class of AIE active compound and compound was synthesized by reacting the chelating group with TPE core. The molecule was synthesized as shown in Figure 2. TPE-Cys **7** was successfully synthesized by functionalizing TPE core by the treatment of Cys with **5** under basic condition in MeCN- H_2O at room temperature. The molecule was further investigated and showed that the thiol group of Cys represents the binding site

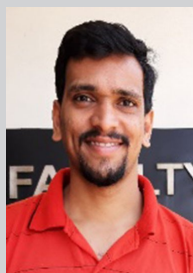
by an As-S bond. It was confirmed that the three Cys groups binds As^{3+} resulting into formation of trigonal pyramidal geometry with symmetric As-(Cys-TPE)₃. TPE moiety being hydrophobic in nature will result in the turn on fluorescence due to π - π aggregation and shows good AIE active characteristics. Diagrammatic representation in which π - π stacking of TPE leads to turn on fluorescence once the As^{3+} interact with TPE-Cys **7**. The selectivity towards arsenite was further confirmed by absorption and fluorescence studies over other ions such as Cu^{2+} , Fe^{2+} , Hg^{2+} , K^+ , Ag^+ , Na^+ , Zn^{2+} , Cd^{2+} and Pb^{2+} this is first compound of TPE to discriminate the As^{3+} the most toxic than As^{5+} .

3. AIE Active Molecule for Cd^{2+} Detection

Since from last 10 decades there are several sensors have been designed for detection of Cd^{2+} as the cadmium being very toxic to human health and environment. Due to high toxicity and carcinogenic effect Cd^{2+} ions are of major focus as the cadmium on ATSDR's CERCLA priority list of Hazardous substance^[21] The cadmium is extensively used in industries and in agricultural field which have led to water and soil contami-



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Sheshanath Vishwanath Bhosale has received his PhD in supramolecular chemistry from the Freie University Berlin, Germany, under the supervision of Prof. J. H. Fuhrhop in 2004. Dr. Bhosale pursued his postdoctoral studies with Prof. S. Matile at the University of Geneva, Switzerland, funded by a fellowship by the Roche Foundation. After his postdoc he went to Australia, and has been an ARC-APD fellow researcher for five years at Monash University. He has also worked at RMIT University, Melbourne for 6 years as with an ARC-Future Fellowship. Currently, Prof. Bhosale is working at the School of Chemical Sciences, Goa University, India as a UGC-FRP Professor, His research interest in design and synthesis of biomaterials and π -functional materials, especially small molecules for applications in sensing and supramolecular chemistry.

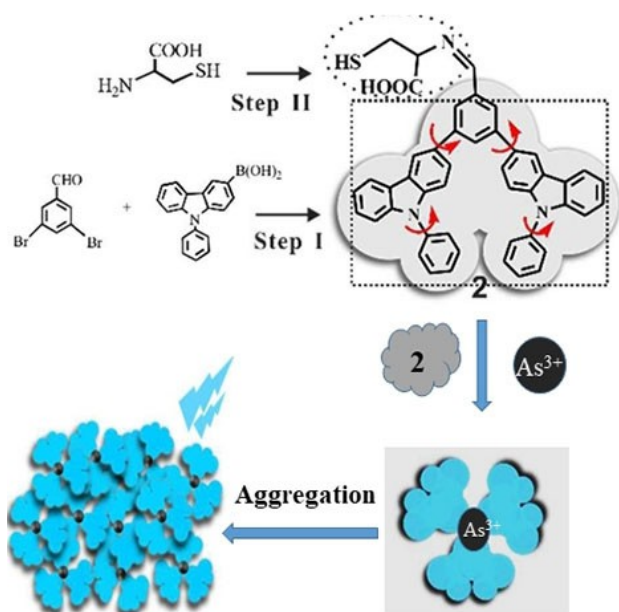


Figure 1. Schematic illustration of the probe and sensing mechanism towards As^{3+} . Reprinted from Ref. [19] with permission of the Royal Society of Chemistry.

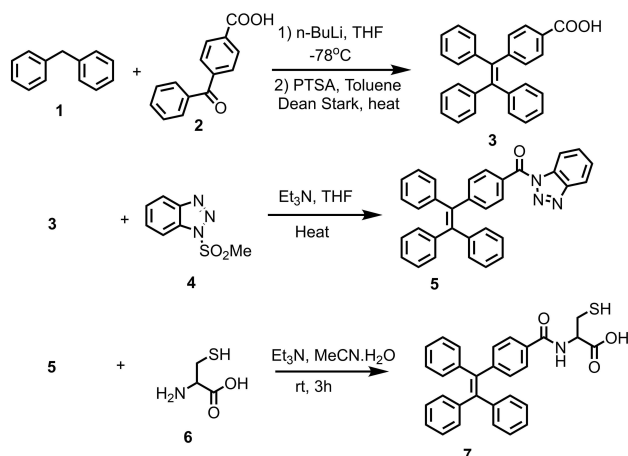


Figure 2. Schematic illustration for the synthesis of the probe TPE-Cys 7.

nation which comes from phosphate fertilizer, metal alloy, Ni–Cd batteries, paint, pigments ceramic. Cadmium also enters the environment through natural sources like erosion and volcanic eruption causing the acute health diseases like the lung cancer, kidney, cancer renal and prostate cancer. Various analytical techniques have been employed but the mostly researcher focus is on developing the sensory materials which selectively detect this toxic species.

Li and co-workers synthesized Y-shaped AIE active diimidazolylbenzene: aggregation and disaggregation molecule for detecting Cd^{2+} and Fe^{3+} ions in aqueous solution.^[22] The Y-shaped dimb molecules shows turn 'ON' fluorescence towards Cd^{2+} ion and 'turn-off' fluorescence for Fe^{3+} ion in MeCN-water (Figure 3). The V-shaped dimb 1,3-diimidazolylbenzene (V-dimb) has two N-atoms which helps in forming the coordination

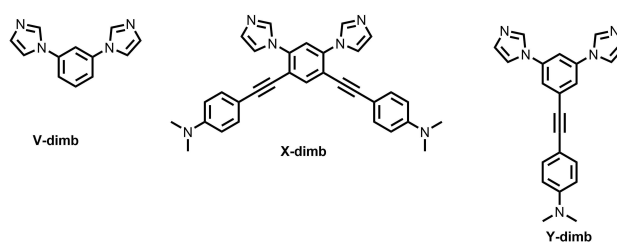


Figure 3. Structure of the Y-shaped dimb AIE active molecules.

polymer. The V-dimb molecule has been already reported that the molecule selectively binds to Ag^{+} ion. X-dimb was synthesized showed good AIE active property but could not recognize any metal ion as two DMAPE group hinders the coordinating polymerisation. However, another molecule Y-dimb was synthesized by reducing the steric hindrance by reacting the DMAPE group at meta position to two imidazole units that facilitates the coordination of metal ion. It was observed that Y-dimb was highly selective towards the Cd^{2+} and Fe^{3+} exhibiting the good AIE active characteristics. The Y-dimb molecule was further utilized for selectivity studies (Figure 4) in fluorescence variation revealed that the molecule was highly selective towards Cd^{2+} ion over other metal ion through aggregation. Y-dimb could not only detect Cd^{2+} but it shows turn off fluorescence towards Fe^{3+} ion by disaggregation.

Another first click triazole bridged cyclodextrin (CD) based AIE active molecule was synthesized for detection of Cd^{2+} detection by Zhang and colleague (Figure 5).^[23] The probe exhibits excellent AIE active property with selective turn on fluorescence response to Cd^{2+} ion in presence over other ions with limit of detection of 0.01 μM .

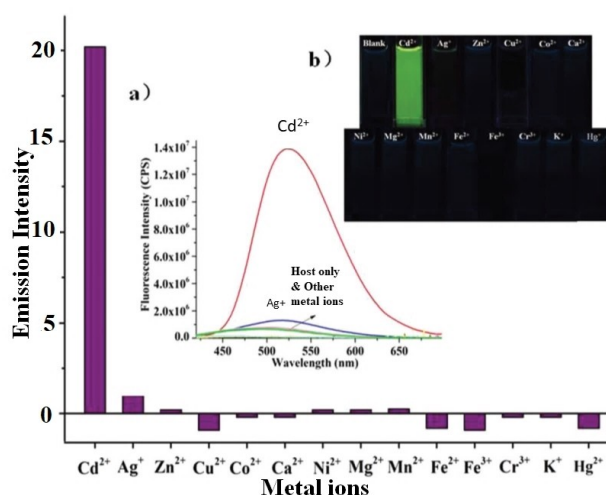


Figure 4. Histogram illustrating the emission intensity. Inset a) represents the fluorescence spectra showing selectivity towards Cd^{2+} in presence over other cations upon variation of Y-dimb (20 μM). Reprinted from Ref. [22] with permission of the Royal Society of Chemistry.

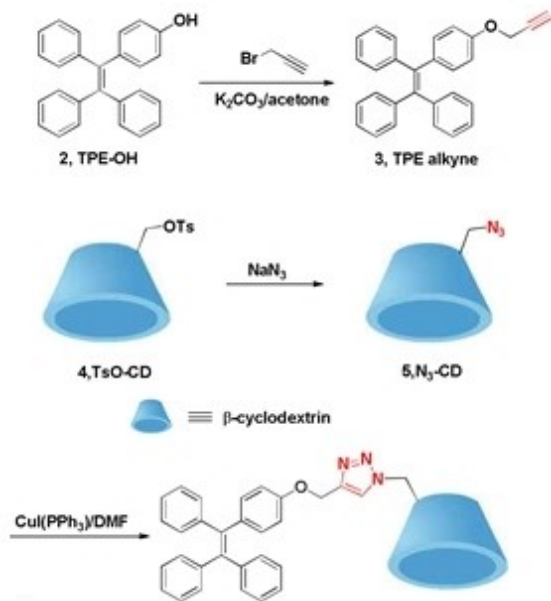


Figure 5. Schematic illustration of TPE-triazole-CD synthesis. Reprinted from Ref. [23] with permission of the Royal Society of Chemistry.

4. AIE Active Molecule for CN^- Detection

Anions play very crucial role in biological systems and chemical processes. Amongst various anions cyanide ion has attained lot of attention due to its high toxicity. Cyanide inhibits the function of enzyme in human by forming the stable complex with cytochrome c oxidase in blood which results in cytotoxic hypoxia and cellular asphyxiation. Cyanide is the most toxic anion and even the smallest amount may result into death. The permissible limit according to World Health Organization (WHO) is $1.9 \mu\text{M}$. Hence, detecting cyanide is very important in today's aspect. Cyanide is widely used in many chemical processes, such as synthetic fibers, plastic manufacturing herbicides and gold extraction process. Hence the accurate and rapid detection method for cyanide is of more importance. There are various methods and solution to detect these toxic anions which rely on analytical instrumentation and other electrochemical methods but due to its high cost and time consuming there is need of developing the simplest method and the simplest method is by the use of fluorescent AIE active molecules for detection. Fluorescent and colorimetric methods have proved to be the most important and found to be successful based on various mechanism such as intramolecular charge transfer (ICT), photo-induced electron transfer (PET), excited state intramolecular proton transfer (ESIPT) and metal ligand charge transfer. However, the chemosensor for cyanide depend mostly on deprotonation approach, hydrogen bonding interaction, nucleophilic addition reaction are the most important approaches in designing the strategy for sensing CN^- .^[24,25] Chen and co-workers designed a novel AIE-active molecule **3** which exhibit turn-off fluorescence towards CN^- upon nucleophilic addition on the vinylic bond of the probe as shown in (Figure 6).^[26] The

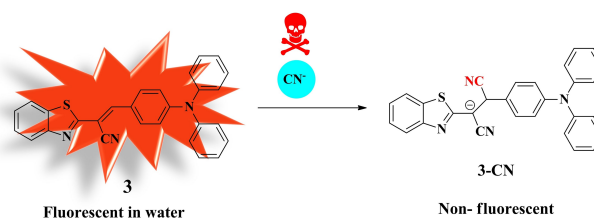


Figure 6. Illustration of sensing of CN^- mechanism pathway for the probe **3**.

probe was synthesized by reacting 2-benzothiazoleacetonitrile and 4-(diphenylamino)-benzaldehyde and showed excellent AIE active property. the probe could detect the cyanide in 100% aqueous medium representing good selectivity and sensitivity towards cyanide with detection limit of 9.44 ppm. However, the absorption and fluorescence studies further confirm the sensing ability of probe towards cyanide which clearly CN^- sensing over other anions such as HSO_3^- , AcO^- , Br^- , Cl^- , I^- , NO_3^- , H_2PO_4^- , HSO_4^- , SO_4^{2-} , F^- , Blank. Moreover, the probe was utilized for biological cell imaging with excellent cellular permeability and very low cytotoxicity and used for preparing test strips which can be used for practical application.

In addition, Chua *et al.* synthesized triphenylethylenyl based donor-acceptor-donor (D–A–D) molecules which display a good AIE-active properties showing good affinity for detection of cyanide.^[27] Triphenylethylene is an AIE active molecule which is similar to TPE as **CS1**, **CS2** and **CS3** (Figure 7). These molecules can be used for detecting CN^-

However, Chen and colleague developed another two novel 2,2'-biindenyl-based derivatives **BDM** and **BDBM** containing dicyanovinyl groups showing solvatochromic and aggregation induced emission enhancement (AIEE) property.^[28] The probe showed high selectivity and sensitivity towards cyanide in aqueous media (Figure 8).

Zhang and group synthesized TPE based solvatochromic AIE luminogens as supersensitive water detectors in organic solvents and utilized as efficient chemosensors for detection of cyanide in water.^[29] Following TPE derivatives **TPEM** and **TPEBM** contains dicyanovinyl groups possessing solvatochromic effect and excellent AIE characteristics. The molecule was synthesized with TPE as electron donating moiety and diacyanovinyl group

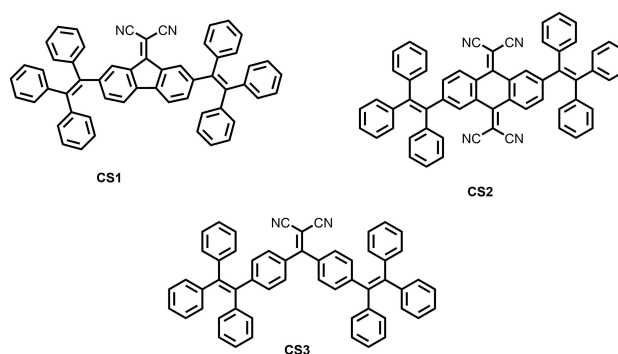


Figure 7. Structures of compound **CS1**, **CS2** and **CS3** for detection of CN^- .

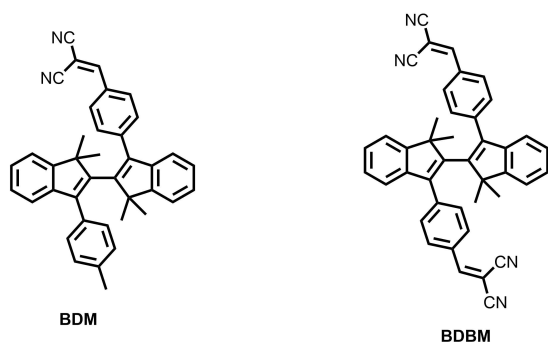


Figure 8. Structures of the probe BDM and BDBM.

as electron accepting moiety (Figure 9). Further the absorption and fluorescence studies revealed that the TPEM and TPEBM were highly selective and sensitive detection of CN^- (Figure 10). In addition similar kind of triphenylamine based AIE active molecule containing dicyanovinyl moiety as acceptor which shows multianalyte sensing towards CN^- , SO_3^- , and Fe^{3+} ion with “turn-off” phenomenon was synthesized by Yang^[30] and co-workers.

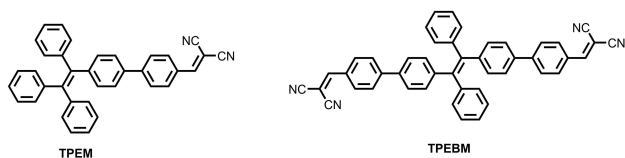


Figure 9. structure of the probe TPEM and TPEBM.

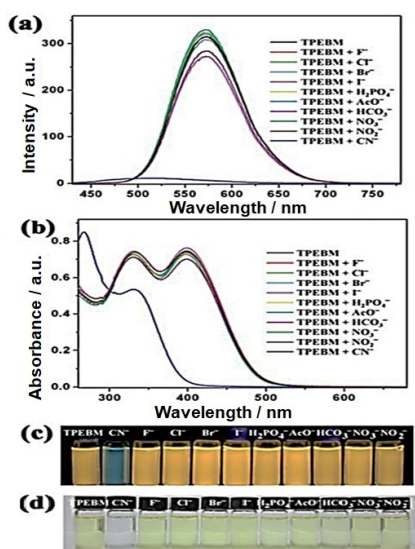


Figure 10. Illustration of (a) fluorescence (b) absorption spectra showing the selectivity towards CN^- ion in presence over other ions 5 eq. CN^- TPEBM in CTAB micelle. (c) Image presenting the colour change upon addition of different ions in TPEBM upon excitation (400 nm) (d) colour change of TPEBM in CTAB micelle naked eye detection in presence over other ions. Reprinted from^[29] with the permission of the Royal Society of Chemistry.

5. AIE Active Molecule for Cu^{2+} Detection

Interestingly, Feng and group synthesized tetraphenylethylene (TPE) Schiff's base self-assembled macrocycle with aggregation induced emission property by condensation reaction of the TPE dialdehyde and 1,2-benzenediamine (Figure 11).^[31] The synthesized Schiff's base aggregated in nanofibers showed high selectivity towards Cu^{2+} . Due to AIE effect gives large Stokes shift to 250 nm. in addition the probe was successfully utilized for detection of $\text{Cu}(\text{II})$ in real water sample and pork juice containing water. as from reported literature it is well known that the imine containing molecules such as Schiff base and hydrazone have strong affinity to bind with copper ions.^[32]

Another approach made by Pannipara and co-workers synthesized probe by reacting 2-hydroxy-1-naphthaldehyde and 5-amino-3-phenylpyrazole in ethanol by adding small amount of acetic acid and the molecule which is used for detecting Cu^{2+} ion. Structure of the receptor as shown in Figure 12a.^[33] The receptor presents AIE behaviour in THF/water with different water fraction the molecule emits strong fluorescence as the water fraction reaches to 90%. Further the absorption and fluorescence studies revealed that the receptor is highly selective and sensitive towards Cu^{2+} over other metal ions (Figure 12b). Absorption studies shows the weak absorp-

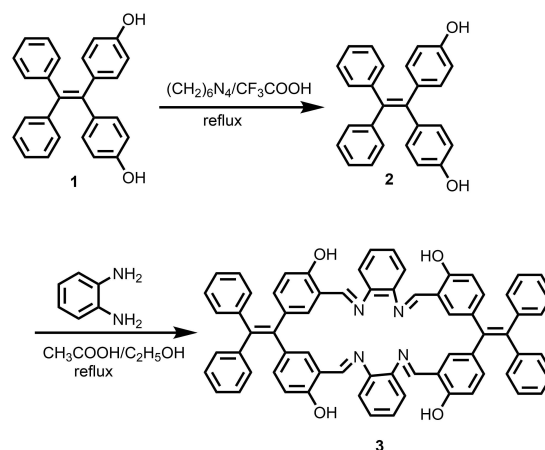


Figure 11. Schematic illustration of the probe used for sensing.

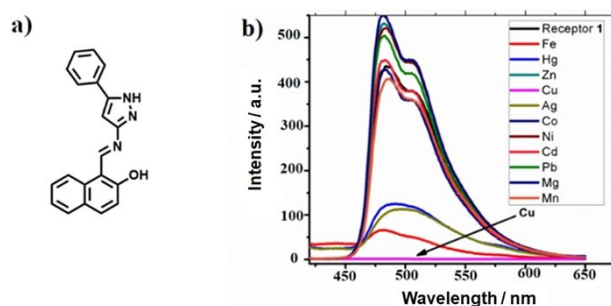


Figure 12. (a) Structure of the molecule used for sensing Cu^{2+} ion and (b) Fluorescence spectra of the molecule representing the quenching of fluorescence upon addition of Cu^{2+} ions. Reprinted from Ref. [33] with the permission of Elsevier.

tion as the water fraction increases in THF. Moreover, the receptor was further used for sensing metal ion over various other ions by studying the emission changes. The receptor shows high selectivity towards Cu^{2+} ion and the quenching efficiency was observed upon addition of Cu^{2+} ion. Quenching phenomenon particularly observed due to paramagnetic nature of Cu^{2+} which shows the chelation enhanced quenching by metal to ligand charge transfer between metal and receptor.

Specifically many more Schiff's base salicylaldehyde based hydrazone AIE active multianalyte sensor was designed by Xu^[34] and co-workers which exhibited excellent AIE activity and found to be highly selective and sensitive towards Al^{3+} and Cu^{2+} . However, Lu^[35] and group designed a novel tetraphenyl-ethylene complex comprising of 4',4'',4''',4''''-(ethene-1,1,2,2-tetrayl)tetrabiphenyl-4-carboxylic acid (H_4ETTC) and dimethyldioctadecylammonium bromide (DOAB) exhibiting enhanced solid state emission through self-assembly strategy. Due to self-assembly and AIE activity the fluorescent ETTC-DOAB complex shows good sensing affinity towards Cu^{2+} ion over other ions (Figure 13).

Recently our group developed and synthesized TPE based probe for copper(II) sensing with thiophenylbipyridine as receptor.^[36] The probe displayed excellent AIE effect with good mechanochromic property. The chromophore represents high selectivity and sensitivity towards Cu^{2+} ions as sensing mechanism occurs via PET with turn OFF-ON process. The turn-off fluorescence observed for probe upon interaction with copper (II) ion. The probe showed high selectivity towards Cu^{2+} ions in presence over other metal ions such as Zn^{2+} , Cd^{2+} , Mg^{2+} , Mn^{2+} , Al^{3+} , Ag^+ , K^+ , Pb^{2+} , Ni^{2+} , Fe^{3+} , Hg^{2+} , Co^{2+} , and Ba^{2+} . Since naked eye detection is easily possible the probe is considered as an excellent tool for sensing application with limit of detection as low as 7.93 nM.

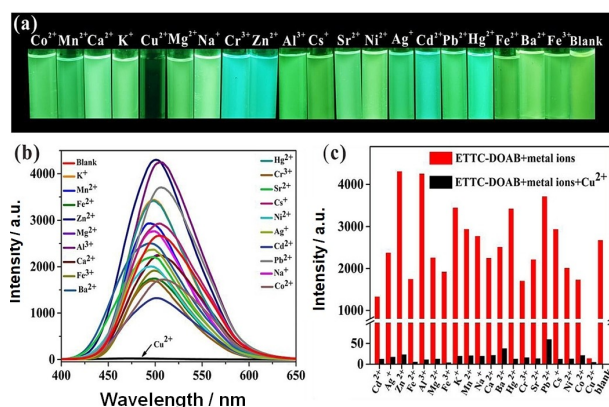


Figure 13. (a) Photograph of ETTC-DOAB complex illustrating the colour change upon addition of Cu^{2+} in presence over various ions under UV light illumination. (b) spectra of ETTC-DOAB complex presenting the selectivity towards Cu^{2+} ion and (c) plot illustrating the emission intensity for ETTC-DOAB complex (red bars) for single ions and (black bars) presenting for ETTC-DOAB, Cu^{2+} ion and other metal ions. Reprinted from Ref. [34] with the permission of Elsevier.

6. AIE Active Molecule for Fluoride Sensing

Detection of anions is of more focus due to wide biological and chemical processes. Due to its simplicity and high detection limit and low-cost fluorescence has proved to be the most efficient. Amongst all anions Fluoride ion is of considerably important for health and environmental issues. Deficiency of fluoride led to increased risk of dental problem and excess of fluoride concentration leads to fluorosis and urolithiasis. However, in this context large number of fluorescent sensors have been developed by applying the simple strategies including supramolecular recognition such hydrogen bonding Lewis acid base interaction and fluoride induced chemical reactions, boron fluoride interaction based chemosensors, and n-n interaction based chemosensors containing thiourea/urea, amide, imidazoline indole pyrrole, schiff's base and other groups which are considered as the binding unit.^[37] Recently TPE and its derivatives are of more interest with remarkable aggregation induced emission characteristics with high fluorescence quantum yield in solid state.^[38,39]

New 'turn-on' fluorescent strategy was developed by Beneci *et al.* based on AIE active phenomenon.^[40] The receptor was synthesized by reacting iodide salt of N-methylpyridinium fused with TPE. Initially this receptor displayed weak fluorescence in the red region but upon addition of fluoride shows fluorescence with blue shift at 470 nm (Figure 14). From this it can be concluded that, the fluorescence intensity may be weaker due to heavy atom effect of iodide which leads to intersystem crossing and quenches the fluorescence. Further the molecule was studied by spectrophotometric method in order to reveal the binding mechanism and to study its selectivity and sensitivity towards the particular analyte. However, the absorption and fluorescence studies showed that the probe shows good selectivity and sensitivity towards fluoride ion.

Interestingly, another TPE based molecules was synthesized accidentally when attempts were made for preparing diamino-TPE by Nadimetla *et al.* which is the simplest and easiest TPE cyclic urea-based proton transfer signalling unit for selective and sensitive detection of fluoride ion. The expected product was diamino-TPE compound rather the final product formed was cyclic urea compound (Figure 15a).^[41] The final product was further characterised and utilized for sensing application. It was observed that the cyclic urea compound showed prominent response to fluoride ion in presence over various anions AcO^- , NO_3^- , H_2PO_4^- , HSO_4^- , I^- , CN^- , Cl^- and F^- . Optical studies have

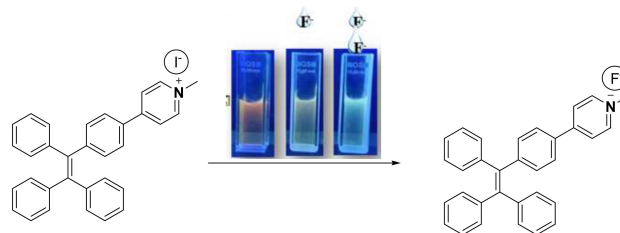


Figure 14. Schematic illustration of sensing mechanism of the probe for F^- . Reprinted from Ref. [40] with the permission of Elsevier.

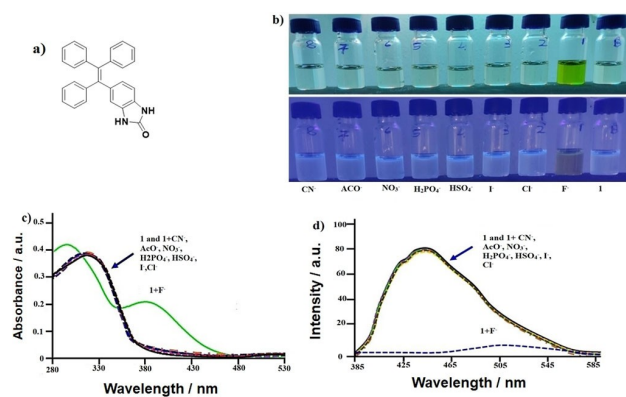


Figure 15. Photograph (a) represents structure of the cyclic urea probe, (b) illustrating the colour change showing the selectivity towards F^- ion presence over other ions using cyclic urea probe. (c) absorption spectra of the probe and (d) fluorescence spectra of the cyclic urea probe. Reprinted from^[41] with the permission of Wiley-VCH.

confirmed that the upon addition of fluoride to receptor in DMSO it shows prominent colour change was observed which confirm high selectivity towards fluoride (Figure 15b). Further to study the binding mode of the cyclic urea receptor. The absorption and fluorescence studies were carried, which particularly shows promising results for detecting F^- ion in aqueous medium (Figure 15c). The UV/Vis spectra show that upon addition of various anions in 5 equivalents, except fluoride all other anions show strong absorption band at 330 nm and only fluoride ion shows shift in absorption band of about 55 nm i.e. upon adding fluoride ion a significant red shift was observed at 385 nm with appears of new peak which shows that the cyclic urea receptor detect the fluoride ion. 1H -NMR titration was carried out upon addition of 5 equiv. F^- there is hydrogen bond interaction with N–H group with two hydrogen fluoride to form the hydrogen difluoride complex. Fluorescence studies were also carried out for further confirmation (Figure 15d). Thus, this cyclic urea-based sensor can be applied in real practical application.

Chen and co-workers designed another multifunctional AIE active molecule with donor-acceptor-donor (D-A-D) type tetraphenylethylene (TPE) derivative (TPEOSi) which shows AIE activity, intramolecular charge transfer (ICT) character with excellent mechanochromic behaviour.^[42] In this Si–O bond is sensitive receptor fluoride detection (Figure 16). Along with AIE characteristic and mechanochromic property TPESiO has good ionic detecting ability. Further, the fluorescence and absorption studies showed that molecule can be effectively used for detecting fluoride in presence over other ions with LOD 3.9×10^{-7} and 1.09×10^{-7} M.

In another example 'turn-on' fluorescent probe was developed by Du *et al.* based on the fluorophore of 2(2'-hydroxyphenyl) benzothiazole (HBT) with aggregation induced emission (AIE) properties.^[43] The synthesized probe PBT is highly selective and sensitive towards F^- . The probe shows typical AIE-characteristics due to ESIPT^[44] and restriction of intramolecular motion (RIM) as represented in Figure 17. The probe was successfully developed as fluorescent and excellent PBT sensor

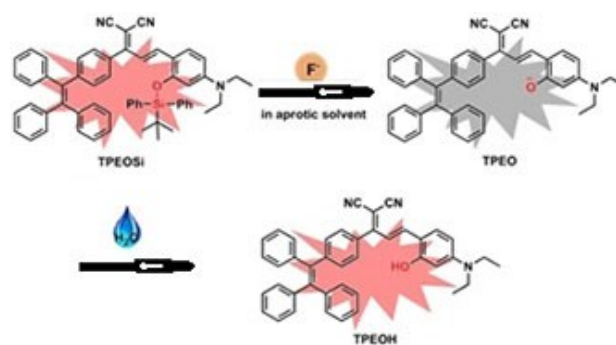


Figure 16. Figure illustrating the molecular structure and representing the sensing mechanism of TPESiO with F^- and water.

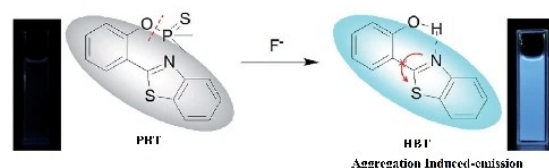


Figure 17. Schematic representation of response of probe PBT towards F^- .

utilized for determining the F^- . Initially the specificity of PBT sensor towards fluoride was investigated over various anions such as Cl^- , Br^- , I^- , HCO_3^- , CO_3^{2-} , NO_2^- , NO_3^- , SO_3^{2-} , SO_4^{2-} , AcO^- , S^{2-} , ClO_4^- , HPO_4^{2-} , CN^- , N_3^- and it was observed that the probe showed high selectivity towards F^- ion. Hence the synthesized probe can be utilized for determining F^- ion in water sample. Limit of detection of the probe found to be 3.8 nM. Therefore, there is need of developing such simplest and cost-effective methods that can be easily available and can be utilized for detection these toxic elements from the environment.

7. AIE Active Molecule for Pd^{2+} Detection

Conjugated polymers due to its excellent electronic and optical properties have attracted the attention of many researchers especially the polymers that displayed aggregation induced emission characteristics and found to be promising fluorescent chemosensory material for ions. Because of their rigid conformation, conjugated polymer has high tendency to aggregate in solution and in solid state.^[45] Since luminescent conjugated polymer has excellent sensitivity it has wide application in various filed. This conjugated polymer can be applied for sensing gases, ions, biomolecules and detecting explosive. However, AIE active molecules successfully solves the quenching problem therefore AIE active molecules are widely used in most of the fields. Amongst all the AIE active luminogens, TPE derivatives have been extensively studied because of its facile synthesis, easy functionalization and high fluorescence quantum yield.^[46,47]

Palladium finds its wide application in chemical and petroleum industry but as the Pd^{2+} increases it has harmful

effect on environment and biological system also increases. There are several methods developed to assess toxic pollutant. The use of fluorescent materials is advantageous owing to their low cost and non-destructive nature. Furthermore, Liu^[48] and co-workers have synthesized AIE active conjugated polymer from conventional, ω -diene by acyclic diene metathesis (ADMET)^[49] polymerization which is used for selective detection of Pd^{2+} in aqueous solution (Figure 18).

The fluorescent CP was synthesized by linking two diene monomers M1 (1,2-diphenyl-1,2-bis(4-vinylphenyl) ethane) (DBVE) and 4,4'-(2,2-diphenylethene-1,1-diyl) bis(vinylbenzene) (DDBV) on tetraphenylethene (TPE) unit through two different modes. Moreover, in order to increase the solubility three other dienes were linked as comonomer (M2) for ADMET copolymerisation such as 1,9-decadiene (C10) linear alkene, 2,7-divinyl-9,9-dinonylfluorene (Flu) and 1,4-dihexyl-2,5-divinylbenzene (Ben) are planar conjugated dienes. More importantly TPE being AIE active fluorescent molecule incorporated by hydrocarbon polymer can be effectively used for detecting Pd in aqueous solution based on dynamic quenching mechanism. Therefore, the synthesized molecule can be effectively utilized for environmental detection of Pd which is considered the most toxic pollutant. Many pyridine functionalised tetraarylethene were synthesized which have been used for various applications. However, Mukherjee *et al.* designed mono-pyridine functionalised triarylethene with AIE active property found promising for selective and sensitive detection towards Pd^{2+} and Fe^{3+} ion.^[50]

8. AIE Active Molecule for Pb^{2+} Detection

Lead (Pb) toxicity is a worldwide environmental issue which has resulted into a public health issue. In fact, Pb^{2+} and its derivatives are considered as the extremely toxic contaminant and even at very low concentration has a cumulative effect especially on children's health.^[51,52] Fluorescent sensing has received more attention because of high sensitivity, low background noise, ease of operation and low cost of instrumentation.^[53] Hence "turn-on" and "turn-off" detection strategies can be applied for detecting Pb^{2+} ion. In this regard, Li and group reported a label

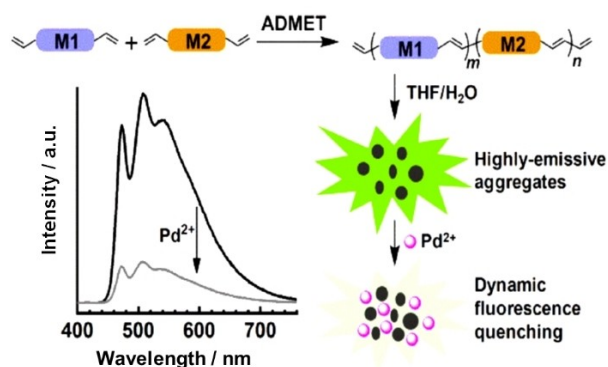


Figure 18. Illustration of the conjugated polymer showing high selectivity towards Pd^{2+} . Reprinted from Ref. [49] with the permission American Chemical Society.

free turn on fluorescence approach for Pb^{2+} . Mechanism of the Pb^{2+} sensing as shown in Figure 19.^[54]

It is studied that the label free thrombin aptamer (TBA, GGTTGGTGTGGTTGG) is a recognition unit for detecting Pb^{2+} ion which has a stable G4 structure when mixed with Pb^{2+} . In overall mechanism, compound 1 acts as an AIE active molecule. Nuclease S1 represents a single-stranded specific endonuclease which hydrolyses single-stranded DNA (ssDNA) and RNA. Importantly, in the absence of Pb^{2+} , nuclease S1 can easily degrade single-stranded TBA into mono- or oligonucleotides. However, there is no aggregation-induced emission activity when compound 1 is added as TBA fragments do not induce aggregate formation, hence resulting in weak fluorescence. But in the presence of Pb^{2+} , TBA forms a stable G4 structure which blocks the hydrolysis that occurs due to nuclease S1. It is expected to give an aggregate when compound 1 is added due to electrostatic interaction between the ammonium cation of 1 and the negative phosphate anions of G4, and possible hydrophobic interaction between nucleosides and the aryl ring in compound 1, thus the fluorescence intensity enhances. Therefore, it is considered that the intensity is directly proportional to the amount of Pb^{2+} . However, in order to display the selectivity approach towards Pb^{2+} , absorption and fluorescence studies were performed, which showed that as the concentration of Pb^{2+} increases, the fluorescence intensity also increases, thus the CP was highly selective towards Pb^{2+} over other ions. The limit of detection was found to be 60 nM. Hence the synthesized label-free molecule gives fluorescence "turn-on" detection of Pb^{2+} with an allosteric G4 (TBA). This AIE active probe was found promising, easy to use, and cost-effective. Its good selectivity and sensitivity allow for wide application potential for environmental monitoring and remediation.

Further, Khandre *et al.* synthesized a TPE-based aggregation-induced emission (AIE) turn-on fluorescent chemodosimeter for the selective detection of Pb^{2+} ion (Figure 20).^[55] The synthesized chemodosimeter consists of tetraphenylethene phosphate monoester residues which have a strong affinity towards lead ion in 95% water-THF by "turn-on" fluorescence response with high selectivity and sensitivity with a limit of detection in the range of 10 ppb.

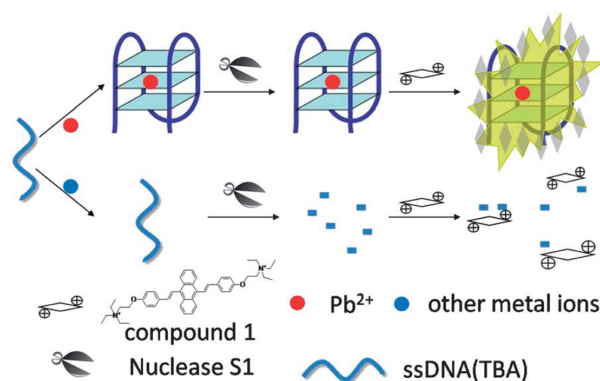


Figure 19. Diagrammatic representation of sensing Pb^{2+} ion. Reprinted from Ref. [53] with the permission of the Royal Society of Chemistry.

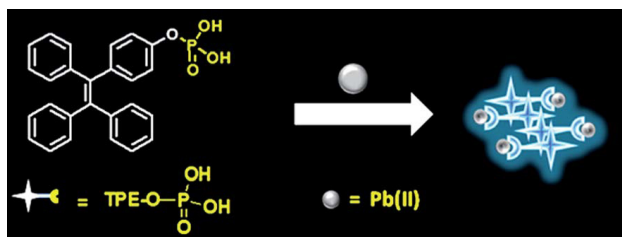


Figure 20. Schematic illustration of the Probe 1 towards Pb^{2+} ions. Reprinted from Ref. [54] with the permission of the Royal Society of Chemistry.

9. AIE Active Molecule for Nitrite Detection

Nowadays, the selective detection and quantification of metal ions is important in many fields including environmental monitoring, clinical toxicology, medical diagnosis and wastewater management. Recently, water and air pollution has been a major problem in many areas due to combustion of fossil fuels used in power plants, vehicles and other incineration processes are the main sources of pollutants. The major contaminant generated from the is nitrite ion which is considered as the primary pollutant which responsible for acid rain smog, depletion of ozone layer and leading to harmful effect on human health.^[56] Nitrite ions, interact with protein acts as important for generation of highly toxic precursor for generation of highly carcinogenic N-nitrosamines. The maximum contaminant level specified by US environmental Protection Agency (EPA)^[57,58] of nitrites is 1 ppm (21.7 μM) and according to world health Organisation (WHO) the specified level is 3 ppm. Excessive consumption may lead to number of health issues such as oesophageal cancer, spontaneous abortion, infant methemoglobinemia, birth defects and so on. Hence determination of nitrite level is of more interest in monitoring drinking water for water quality and for clinical diagnosis.^[59] Most commonly used techniques for detection of nitric oxide involves electrochemical method, gas chromatography, fluorescence and colorimetric method. Colorimetric method is the simplest and most convenient for visual naked analysis of the analytes amongst all reported methods such as chemical and optical methods, ionic methods and electrochemical, methods for detection of nitrite ion.

Our group have developed simple and novel probe based on amino functionalized AIE active TPE probe as selective nitrite ion receptor i.e. tetra-amino tetraphenylethene (TA-TPE) as shown in Figure 21.^[60] The probe is highly selective and sensitive towards nitrite ion through visible colour change in aqueous medium. Mechanism illustrated for detection of nitrite ion and the tetra-amino tetraphenylethene further studied for its selectivity towards nitrite over other ions such as SO_4^{2-} , Cl^- , HSO_3^- , CO_3^{2-} , CH_3COO^- , NO_3^- , and $\text{S}_2\text{O}_3^{2-}$. Further in order to study the selective sensing performance of the receptor TA-TPE the fluorescence and absorption studies were carried out which revealed that absorption peak appears at 301 nm upon addition of different ions SO_4^{2-} , Cl^- , HSO_3^- , CO_3^{2-} , CH_3COO^- , NO_3^- , and $\text{S}_2\text{O}_3^{2-}$ but shifts the absorption band by 30 nm upon addition of the nitrite. Absorption studies displayed that upon incremental

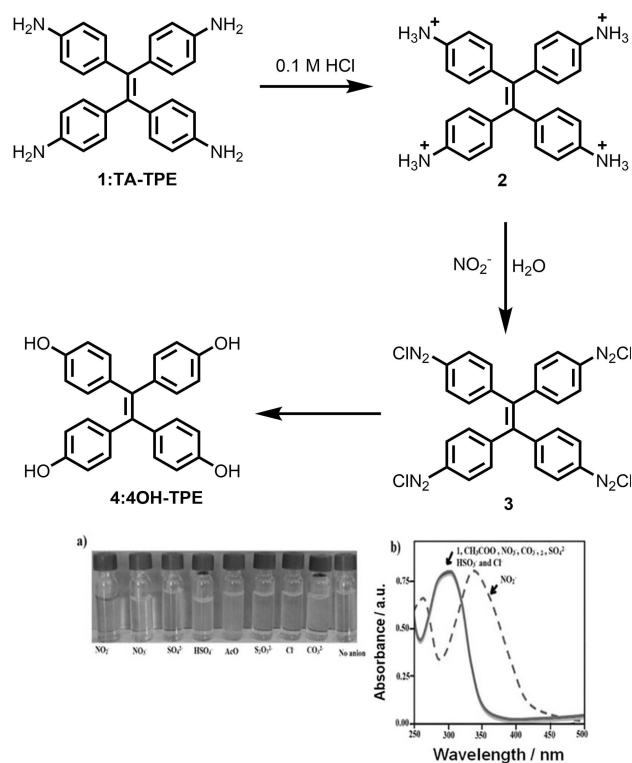


Figure 21. Illustration of mechanistic pathway for detection of nitrite ions using tetra-amino tetraphenylethene. a) photograph presenting the colorimetric response towards nitrite ion over other competitive ions for TA-TPE (1) probe. b) absorption spectra TA-TPE (1) showing the selectivity towards NO_2^- in presence over other ions. Reprinted from Ref. [60] with the permission of the Royal Society of Chemistry

addition of nitrite to receptor there is gradual decrease in intensity of 331 nm peak and isosbestic point at 316 nm. Further the fluorescence studies showed the ability of detecting nitrite ion. As the TA-TPE is protonated showed very weak emission at 510 nm. However, upon incremental addition of nitrite there is 20-fold times enhancement in fluorescence intensity from 0–50 equivalent which indicate that the receptor TA-TPE can detect the trace levels of nitrite ions in solution.

Since this method offers additional benefits such that receptor can be employed for sensitive detection of NO_2^- through reduction step with simultaneous shift in absorption and “turn on” fluorescence hence this method can be considered very useful and environmentally viable. In another example, Chatterjee and co-workers have synthesized a novel AIE-based fluorescent probe for the detection of trace number of nitrites and nitrate ions in water.^[61] The probe was synthesized by McMurry coupling reaction. The synthesized probe undergoes diazotization by reaction with NO_2^- ion followed by coupling with β -naphthol to produce azodye. Probe showed good AIE behaviour highly fluorescent in 3% THF – 0.1 N HCl and the dye produced in the reaction become non fluorescent in solution as well in aqueous solution hence the synthesized probe acts as a “turn off” type of molecular sensor for detection of nitrite in presence over other ions. The probe also works well for detecting nitrate ion under reducing

condition (over Zn dust). Thus, the probe found to be excellent and promising for practical application.

10. AIE Active Molecule for Hg^{2+} Ion Detection

Heavy toxic element such as lead and mercury can pollute soil and water resources, with consequent potential negative effects on ecosystems and on human health.^[62] Mercury is the most toxic and widely distributed element in the environment because of its wide range of application in industry, agriculture, and daily life. Mercury's toxic impact affects the immune, endocrine, and nervous system in living organisms. For instance, methylmercury is a potent neurotoxin for central nervous system and causes serious diseases.^[63] Hence, there is the need of developing convenient, fast, inexpensive and highly accurate and effective methods for the detection of these toxic ions. Over the past few decades, several instrumental techniques were successfully employed for detecting mercury ion such as calorimetry, atomic absorption spectroscopy, and inductively coupled plasma mass spectrometry, an atomic fluorescence spectroscopy (AFS), X-ray absorption spectroscopy (XAS) and other electrochemical; methods however these methods failed to meet necessary requirement give. Hence the use of fluorescent molecules has attracted the interest of researcher towards detecting toxic ions such as naphthalene diimide (NDI),^[64] polymers,^[65] Bipillar^[66] molecules, tetraphenylethene (TPE),^[67] Schiff's base,^[68] Pyrene,^[69,70] triphenylamine^[71] and metal organic framework (MOF's).^[72] Following work focuses on AIE active molecule synthesized by Huang and co-workers which is highly selective and sensitive towards $\text{Hg}(\text{II})$ ion.^[73] However, the same tetra-(pyridylphenyl) ethylene molecule reported by our group earlier which is effectively used for sensing H^+ and ratio metric detection of intracellular pH values.^[74] The molecule displays good AIE activity with fluorescence "turn on". The molecule exhibits fluorescence difference upon addition of Hg^{2+} ion in presence over other ions. Initially at very low concentration of below 4 equiv. the compound was weakly emissive but as the concentration of Hg^{2+} increases there is significant enhancement in fluorescence however compound remaining weakly emissive in presence over other metal ions. It can be interpreted that the compound bearing four-pyridyl group coordinates with Hg^{2+} to form the co-ordinate complex as shown in Figure 22.^[72] Interestingly, the fluorescence of the compound1 can be further increased by addition of HSO_4^- . Here point to be noted that compound do not show any fluorescence but enhancement in fluorescence takes place only in Hg^{2+} . This proves that fluorescence of compound can be switched on by the synergistic interaction of Hg^{2+} and HSO_4^- .

Several research groups have utilized TPE core for synthesizing the fluorescent molecule for detecting Hg^{2+} ions. Interestingly Ruan and co-workers developed a novel AIEgens containing two thioketal moieties (*p*DTPES and *m*DTPES) for detection of Hg^{2+} ions which basically promoted by deprotection reaction as shown in Figure 23.^[75] The luminescence colour change from sky blue to yellow green upon addition of Hg^{2+} ion which can

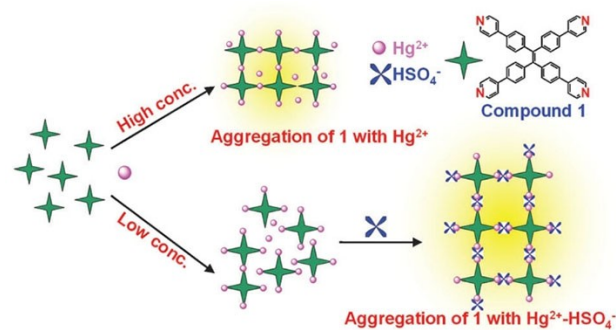


Figure 22. Schematic illustration of the compound showing the fluorescence change upon addition of Hg^{2+} ion. Reprinted from Ref. [72] with the permission of The Royal Society of Chemistry.

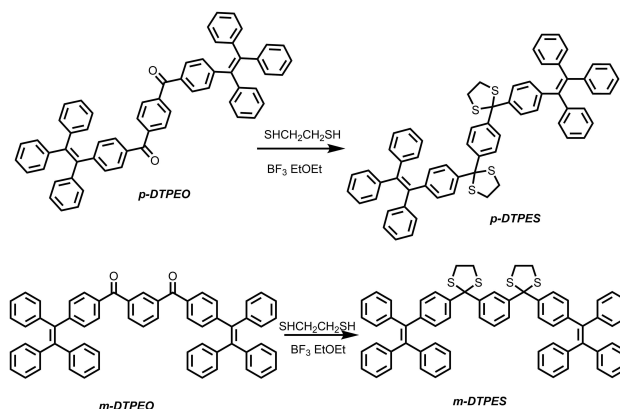


Figure 23. Illustration of schematic pathway of *p*-DTPES and *m*-DTPES for sensing Hg^{2+} .

be observed through naked eye. The probe displayed high selectivity towards Hg^{2+} ions in presence over various ions. Further the probe could be used for real practical application in determining mercury ion in water sample.

The polymer based tetraphenyl ethylene (TPE) based AIE active polymer was developed by Wei and co-workers prepared from tetraphenyl ethene and diamino benzene via click reaction which is employed for detection of Hg^{2+} ions (Figure 24).^[76] A new AIE active polymer sensor was synthesized by incorporating triazole moiety for Hg^{2+} detection in aqueous solution. Polymer showed excellent AIE activity in THF water at 90% of water fraction. Upon binding with Hg^{2+} the polymer exhibits quenching phenomenon over other competing ions by change in colour from cyan to almost no emission resulting in to quenching of fluorescence. The UV-vis and fluorescence studies were performed to study the specificity of the polymer sensor



Figure 24. Schematic illustration of the conjugated polymer sensor.

towards mercury in presence over other ions as shown in Figure 25. Further the interaction of polymer (P1) with triazole was confirmed by means of ^1H NMR spectroscopy which revealed that there is shift of triazole proton to downfield and remaining aromatic protons to up field.

Shi *et al.* synthesized a simple triphenylamine-barbituric acid adduct by Knoevenagel reaction displayed excellent aggregation induced emission enhancement (AIEE) characteristics in a THF- H_2O .^[77] The probe consists of triphenylamine as donor and barbituric acid as acceptor molecule (M1). The specificity of the probe M1 was studied by introducing various metal ions in the probe and it was observed that probe showed excellent selectivity towards Hg^{2+} ions. Herein there is interaction between Hg^{2+} ion with thymine like groups in M1 leading to enhancement in fluorescence. In another example Kala and colleague developed similar carbazole derivative of barbituric acid based AIE active derivative found to be highly selective and sensitive towards detection of Hg^{2+} ion (M2).^[78] Wherein Wang and co-workers also designed the molecules in which anthracene acts as donor and barbituric acid as acceptor by forming mercury (II) barbiturate coordination polymer (M3).^[79] The barbituric acid plays important role in supramolecular chemistry to afford Hg (II) mediated supramolecular self-assemblies. Thus, the fluorescent molecules have wide application in detecting the toxic ions from environmental system (Figure 26).

Many researchers have reported the AIE active fluorophore which display application in various fields such as chemo/biosensor, cell imaging, environment, optical devices etc. Wu and co-workers synthesized a novel AIE probe based on pyrene. Initially probe gives weak green emission with good AIE active

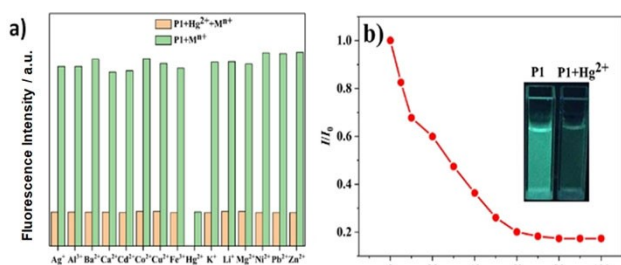


Figure 25. (a) Fluorescence spectral change of polymer (P1) upon increasing addition of Hg^{2+} ions ($1.0 \times 10^{-5} \text{ mol L}^{-1}$ in THF and water $f_w = 90\%$ $\lambda = 320 \text{ nm}$). (b) plot representing the selectivity of polymer (P1) towards Hg^{2+} ions over various ions ($1.0 \times 10^{-5} \text{ mol L}^{-1}$ in THF and water $f_w = 90\%$ $\lambda = 320 \text{ nm}$). Reprinted from Ref. [76] with the permission of Elsevier.

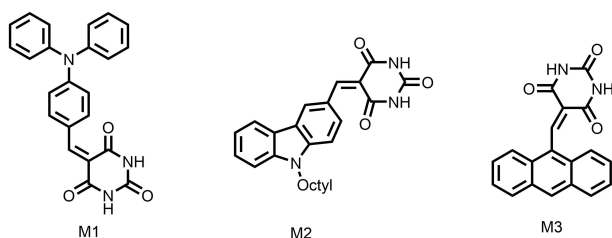


Figure 26. Schematic illustration of the compound M1, M2 and M3.

effect in water/DMF, but upon addition of Hg^{2+} the probe shows colour changes to blue and enhancement in fluorescence emission was observed. The probe can be used for detection of Hg^{2+} and found to be promising in environmental safety and biosystems (Figure 27).^[80]

11. AIE Active Molecules for Hydrazine Detection

Yin and co-workers developed a novel carbazole indandione based red emitting fluorescent sensor (CBI) with aggregation induced characteristics in aqueous medium at 615 nm.^[81] The synthesized molecule was successfully utilized for detection of hydrazine in 100% aqueous medium. The probe showed sensing for N_2H_4 exhibited good AIE activity. Further the sensing of N_2H_4 was studied by fluorescence and absorption which reveals that the molecule was highly selective towards N_2H_4 in presence over other interfering species such as Cys, Hys, GHS, Urea, thiourea, NH_2OH , EDA, PhNH_2 , TEA, NH_3 , $n\text{-BuNH}_2$, Na^+ , Al^{3+} , Cr^{3+} , Cd^{2+} , Co^{2+} , Mg^{2+} , Hg^{2+} , CN^- , F^- , Br^- , Cl^- and AcO^- . The molecule shows quenching of fluorescence when N_2H_4 binds selectively (Figure 28). The molecule was further used for biological cell imaging and interestingly can be applied for analysing water and urine sample. Developed CBI exhibits quick response, excellent selectivity, and great sensitivity with a low detection limit of 1.18 ppb for hydrazine in water, human urine and live cells.

12. AIE Active Molecule for Sb^{3+} Ion Detection

Recently antimony contamination of water sources and other environmental sources have been polluted due to release of toxic waste from industrial waste and various development directly into the water which affects human, plants, animals and other aquatic animals which is of global concern. According to WHO permissible limit 20 $\mu\text{g/L}$ in water if the limit exceeds it may cause serious health issue. In order to detect the Sb^{3+} recently in 2020 Huang and group developed a new TPE-2IPH AIE active fluorogen with high physical and chemical stability for detection of Sb^{3+} (Figure 29).^[82] The probe TPE-2IPH was

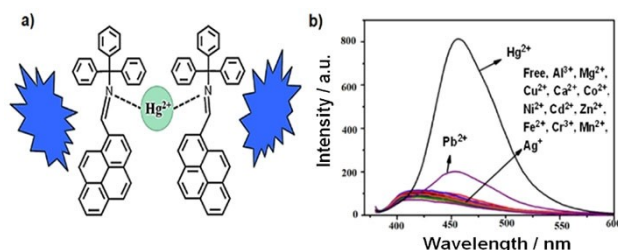


Figure 27. Photograph of most plausible binding mechanism and (b) Fluorescence spectra of the probe showing selectivity towards Hg^{2+} ion in presence over other ions. Reprinted from Ref. [80] with the permission of Elsevier.

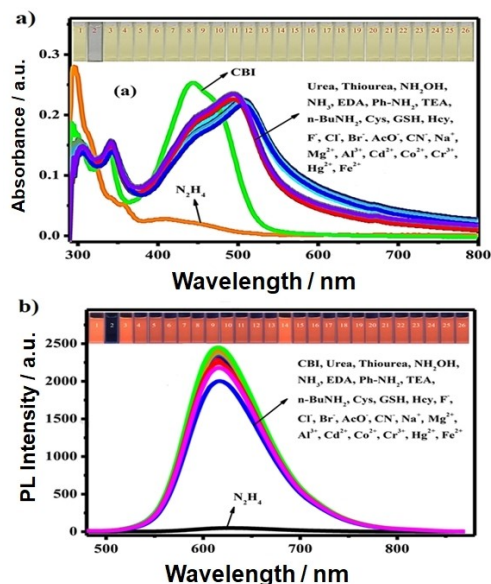


Figure 28. Absorption and fluorescence spectra of the CBI molecule representing selectivity towards hydrazine in presence over other interfering species. Reprinted from Ref. [81] with the permission of the Elsevier.

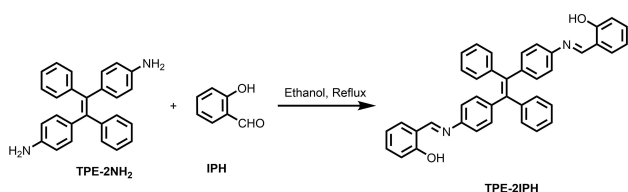


Figure 29. Schematic illustration of the probe TPE-2IPH utilized for selective and sensitive detection of Sb^{3+} .

further studied for specificity and selectivity towards different ions. However, the probe was highly selective and sensitive towards Sb^{3+} shows the excellent AIE activity in THF/water fraction (Figure 30).

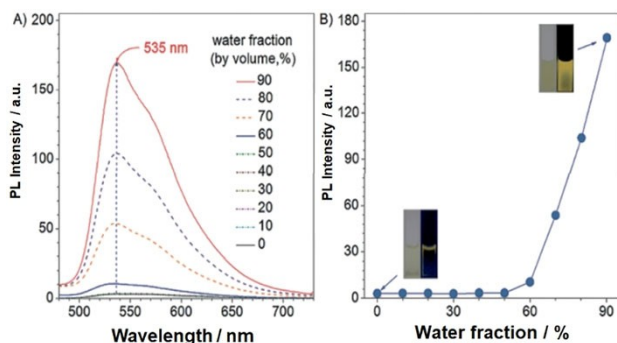


Figure 30. Illustration of fluorescence spectra of TPE-2IPH showing the aggregation induced emission characteristic in THF/Water fraction. (B). Inset: photos of TPE-2IPH under daylight and UV-light illumination ($\lambda_{\text{ex}} = 375 \text{ nm}$). Reprinted from Ref. [82] with the permission of Wiley-VCH.

13. AIE Active Metal Organic Framework for Sensing Toxic Ions

Environment and its compartments are heavily polluted by heavy toxic metals which is of global health concern. Hence in order to minimize the effect of this toxic element there is need of remediation and minimize the release of heavy toxicants in environment.^[83] Luminescent nanomaterials have numerous applications in bioimaging, therapeutic, chemo sensing, light emitting diodes (LEDs) etc. Various fluorescent materials such as quantum dots(Q-dots), metal cluster, rare-earth ion doped nanomaterials, organic dyes, and luminescent metal organic framework (MOFs). However, Q-dots and metal cluster have toxic element needs high crystallinity and a special structure, dye-based materials have low photostability and most of these dyes exhibit aggregation caused quenching (ACQ) phenomenon which inhibits further application.^[84] Many research groups are focusing on luminescent metal organic framework which has wide application in gas storage and separation, desulfurization of fuels, sensing application, catalysis drug delivery and molecular imaging. Recently AIEgens functionalised MOFs have been reported due to its several advantages such as good fluorescence emission efficiency and displays improved sensing performance.^[85] MOFs are crystalline porous coordinating polymeric materials that consists of metal ion or cluster coordinated with organic linkers.^[86] Various MOF based sensing platform for environmental contaminant detection including anions, heavy metal ions, organic compounds and gases.^[87]

Xei and co-workers synthesized AIE-active metal organic framework which has facile synthesis, tunable light emission, ultrasensitive sensing of Cu^{2+} and which has affinity to detect glucose.^[88] This MOFs is synthesized by binding aggregation induced emission (AIEgens) with nanoscale ZIF-8 with good photostability and excellent dispersibility have been fabricated. The AIE active MOF-2(LMOF-2) acts a fluorescence probe for detecting copper ion in 1 to 100 nM range. Furthermore, glucose oxidase catalysed cascade redox reaction of LMOF-2/GOD fluorescent allochroic test strips were developed for visual detection of glucose. Sensing performance of the LMOF was carried out as shown in Figure 31. it was observed that fluorescence intensity quenches upon Cu^{2+} addition however no change in fluorescence intensities in presence over other ions. LMOF has limit of detection around 550 pM in range from 1 nM to 100 nM. Further, the LMOF utilized for detecting Cu^{2+} in water sample.

TPE based fluorescent metal organic framework are the focal point of the research. Herein, Jackson and co-workers focused on 1D ribbon metal organic framework and exhibits aggregation induced emission.^[89] The developed network composed of tetrapyrroline tetraphenylethene molecule coordinated to ZnCl_2 nodes and network exhibits enhanced "turn on" fluorescence in presence of methyl substituted volatile organic compounds (VOCs) and similar network shows quenching of fluorescence in presence of nitro-substituted VOCs. This MOF can be utilized as good sensor for sensing volatile organic compounds (VOCs). This work on MOFs have focused more

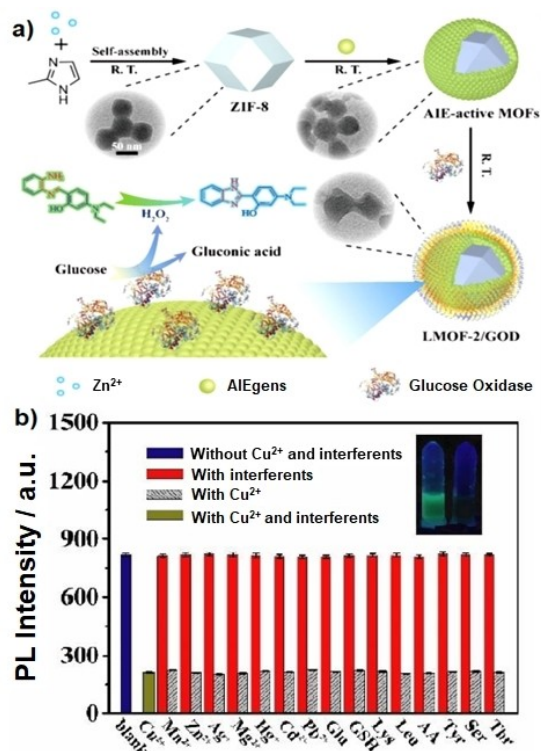


Figure 31. a) Photograph representing the schematic illustration of LMOF for detection of glucose and b) plot showing the selectivity of AIE-active LMOF towards Cu^{2+} ion in presence over other ions and molecules. Reprinted from Ref. [88] with the permission of Royal chemical Society.

detecting methyl and nitro-substituted substances such as 2,4-dinitrotoluene (DNT), 2,4,6-trinitrotoluene (TNT) and so on (Figure 32). In fact, in addition many tetraphenylethene (TPE) and its derivative have been discussed by Jiang and a group wherein co-ordination driven self-assembled supramolecular architecture were developed by selecting organic donors and metal acceptors.^[90] MOFs have been successfully constructed by self-assembly of TPE cored ligands, with metal salts and excellent AIE activity which has explored wide application in the field of fluorescent sensors.

Just to brief that the development and applications of AIE active luminescent material are not only restricted for sensing of toxic pollutants but there are several other advantages that

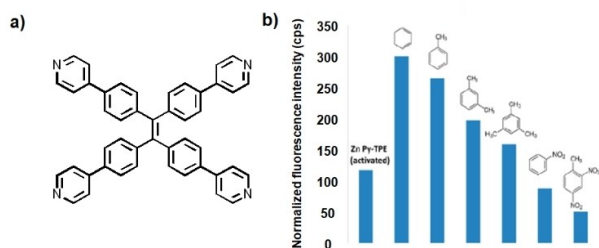


Figure 32. a) Illustration of structure of TPE based MOF tetrapyrroline-tetraphenylethene and b) plot illustrating the fluorescence intensity upon detecting methyl and nitro-substituted substances. Reprinted from Ref. [89] with the permission of the American Chemical Society.

makes them excellent and powerful tool for advanced applications. These luminescent materials can be also utilized for flexible sensing and tracing of body temperature and viscosity which are considered an important parameter for monitoring and maintaining the quality of life. In this regards, Gon group^[91] described the concept of AIE active exciton driven boron boron complexes with excellent luminescent property. The study has illustrated its mechanism and stimuli responsive luminescence with high sensitivity. Important to mention these boron mediated derivatives have shown growing demand and acts as a good platform for sensing and tracing the body temperature and vascular flow.

As we have described earlier, the cysteine substituted to TPE derivative can be used for detection of toxic arsenic element in water. Similarly, Roy *et al.*^[92] explored the functionalization and applications of amino acids and peptide derivatives in arylenediimides for molecular recognition, molecular self-assembly heterostructure and living assembly system. These molecular architectonics not only facilitate in the sensing applications but extensively used in optoelectronics, molecular and nanoelectronics, light and energy harvesting and storage, energy charge transfer, photonics, piezoelectricity, ferroelectricity, catalysis, diagnosis and therapeutics. In addition, there are several AIE active organic semiconducting materials described by Li *et al.*^[93] which are multifunctional platform for wide range of biomedical and for advance bio-photonics application. Moreover, researchers are still exploring advance application in the field of AIE active luminescent material which will give more reproducible and fruitful results for future application.

14. Conclusions and Outlook

In this, review article we have summarised and discussed the different aggregation induced emission (AIE) active molecules used in the detection of environmental toxic pollutants such as CN^- , Hg^{2+} , Cu^{2+} , Pb^{2+} , Sb^{3+} , Pd^{2+} , Cd^{2+} , F^- , NO_3^- , As^{3+} and hydrazine. Among these active molecules are TPE-based derivatives, pyrene, NDI, organic dyes and AIE active metal organic frameworks (MOFs). Developing a strategy for the detection of toxic pollutants is crucial as these substances are highly toxic to human beings and the environment. Fluorescent sensors have attracted significant attention due to their high sensitivity, selectivity, simple use and short response time with low limit of detection. However, detection of this toxic pollutants depends on different photophysical phenomenon such as PET, CHEF, FRET, ICT and ESIPT. Most of the conventional fluorophores exhibits ACQ effect which is considered to be detrimental and limits their usage for further application. Interestingly, another phenomenon was developed in order to overcome the ACQ effect known as AIE. In AIE initially molecule shows weak fluorescence in solution state but exhibit enhancement in fluorescence in aggregated state. Finally, we have summarised the AIE molecules that can be used for detection of toxic pollutants.

Since most of these luminescent materials are highly versatile and many research groups have utilized TPE as the

building block for construction AIE active candidate combining with different receptors for wide range of applications. Nevertheless, these AIE active luminescent materials have not only explored its application in supramolecular sensing, but have also been widely in the therapeutics, optoelectronic and green energy devices, environmental monitoring and so on due to their extraordinary photophysical properties. Despite of the described advances, this luminescent material can be utilized for drug delivery system. Further applications can be found in food safety, which is currently one of the most important parameters in terms of public health all over the world. Therefore, the fundamental design, synthesis, its function and mechanism of AIE active luminogens can find applicability in food analysis for identify potential food adulteration. The food analysis is major concern due severe health effects caused by various toxic cation, anions, food additives, pesticides bacteria and so on. Thus, AIE active material have also shown its extensive application in field of food safety and quality control via sensing approach.

The development of novel AIE active luminescent material and its application in various field will be continued in the future even though plenty of work being reported in the field of AIE active material is applied to sensing of toxic pollutants. We do believe that more work is needed in various aspects of the sensing strategies towards toxic elements. For instance, still very few reports are available for the detection of toxic pollutants such as Pd^{2+} , As^{3+} , Hg^{2+} and Cd^{2+} and other F- block elements. We believe that this is due to lack of appropriate receptors and binding ligands for selective and sensitive detection of these toxic pollutants. It is also necessary to improve the selectivity of fluorescent materials towards the specific and structurally precise receptors or ligands for coordination with toxic analytes. There is still a need of developing simple and cost-effective strategies for design and synthesis of novel fluorescent sensors. Moreover, photostability and solubility are yet another important parameter of AIE-based chemosensors that needs further attention. Importantly, the application of existing AIE active materials should be explored in different directions keeping in mind their good stability and tunable functionalities. Periphery core modification of AIE genes may also contribute to a significant development because it enhances the characteristic of the materials with varying optical and photophysical properties. Even though significant progress has been achieved already, extensive and more insightful research in the field of AIE-active materials is required for further application in the field of supramolecular chemistry, in particularly in self-assembled structures which can be used for selective and accurate sensing in remote areas for real-world applications.

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Conflict of Interest

The authors declare no conflict of interest.

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- [1] A. E. Evans, J. Mateo-Sagasta, M. Qadir, E. Boelee, A. Ippolito, *Curr. Opin. Environ. Sustain.* **2019**, *36*, 20–27.
- [2] D. Ding, K. Li, B. Liu, B. Z. Tang, *Acc. Chem. Res.* **2013**, *46*, 2441–2453.
- [3] H. Wang, E. Zhao, J. W. Y. Lam, B. Z. Tang, *Mater. Today* **2015**, *18*, 365–377.
- [4] G. Chen, W. Li, T. Zhou, Q. Peng, D. Zhai, H. Li, W. Z. Yuan, Y. Zhang, B. Z. Tang, *Adv. Mater.* **2015**, *27*, 4496–4501.
- [5] M. R. Wasielewski, *Chem. Rev.* **1992**, *92*, 435–461.
- [6] R. M. Clegg, *Chapter 1 Förster Resonance Energy Transfer-FRET What Is It, Why Do It, and How It's Done*, Elsevier B. V., **2009**.
- [7] J. Seo, S. Kim, S. Y. Park, *J. Am. Chem. Soc.* **2004**, *126*, 11154–11155.
- [8] M. Ghosh, S. Ta, M. Banerjee, M. Mahiuddin, D. Das, *ACS Omega* **2018**, *3*, 4262–4275.
- [9] J. E. Kwon, S. Y. Park, *Adv. Mater.* **2011**, *23*, 3615–3642.
- [10] X. Cai, B. Liu, *Angew. Chem. Int. Ed.* **2020**, *59*, 9868–9886; *Angew. Chem.* **2020**, *132*, 9952–9970.
- [11] M. Gu, Z. Zeng, M. Xing, Y. Xiong, Z. Deng, S. Chen, L. Wang, *Biotechnol. J.* **2019**, *14*, 1–9.
- [12] J. Ma, M. K. Sengupta, D. Yuan, P. K. Dasgupta, *Anal. Chim. Acta* **2014**, *831*, 1–23.
- [13] H. G. Gorchev, G. Ozolins, *Who* **2004**, *1*, 564.
- [14] Q. Zhang, H. Minami, S. Inoue, I. Atsuya, *Anal. Chim. Acta* **2004**, *508*, 99–105.
- [15] K. Jitmanee, M. Oshima, S. Motomizu, *Talanta* **2005**, *66*, 529–533.
- [16] B. Klaue, J. D. Blum, *Anal. Chem.* **1999**, *71*, 1408–1414.
- [17] Y. Cai, *TrAC Trends Anal. Chem.* **2000**, *19*, 62–66.
- [18] W. R. Cullen, K. J. Reimer, *Chem. Rev.* **1989**, *89*, 713–764.
- [19] X. Tian, L. Chen, Y. Li, C. Yang, Y. Nie, C. Zhou, Y. Wang, *J. Mater. Chem. C* **2017**, *5*, 3669–3672.
- [20] M. Baglan, S. Atilgan, *Chem. Commun.* **2013**, *49*, 5325–5327.
- [21] S. Ellairaja, R. Manikandan, M. T. Vijayan, S. Rajagopal, V. S. Vasantha, *RSC Adv.* **2015**, *5*, 63287–63295.
- [22] C. Li, C. Gao, J. Lan, J. You, G. Gao, *Org. Biomol. Chem.* **2014**, *12*, 9524–9527.
- [23] L. Zhang, W. Hu, L. Yu, Y. Wang, *Chem. Commun.* **2015**, *51*, 4298–4301.
- [24] X. L. Lu, M. Xia, *RSC Adv.* **2016**, *6*, 85787–85794.
- [25] P. B. Pati, *Sens. Actuators B* **2016**, *222*, 374–390.
- [26] X. Chen, L. Wang, X. Yang, L. Tang, Y. Zhou, R. Liu, J. Qu, *Sens. Actuators B* **2017**, *241*, 1043–1049.
- [27] M. H. Chua, H. Zhou, T. T. Lin, J. Wu, J. Xu, *J. Mater. Chem. C* **2017**, *5*, 12194–12203.
- [28] Q. Lin, K. P. Zhong, J. H. Zhu, L. Ding, J. X. Su, H. Yao, T. B. Wei, Y. M. Zhang, *Macromolecules* **2017**, *50*, 7863–7871.
- [29] Y. Zhang, D. Li, Y. Li, J. Yu, *Chem. Sci.* **2014**, *5*, 2710–2716.
- [30] X. Yang, X. Chen, X. Lu, C. Yan, Y. Xu, X. Hang, J. Qu, R. Liu, *J. Mater. Chem. C* **2016**, *4*, 383–390.
- [31] H. T. Feng, S. Song, Y. C. Chen, C. H. Shen, Y. S. Zheng, *J. Mater. Chem. C* **2014**, *2*, 2353–2359.
- [32] L. Tang, J. Guo, Y. Cao, N. Zhao, *J. Fluoresc.* **2012**, *22*, 1603–1608.
- [33] M. Pannipara, A. G. Al-Sehemi, A. Kalam, A. M. Asiri, M. N. Arshad, *Spectrochim. Acta Part A* **2017**, *183*, 84–89.
- [34] Z. H. Xu, Y. Wang, Y. Wang, J. Y. Li, W. F. Luo, W. N. Wu, Y. C. Fan, *Spectrochim. Acta Part A* **2019**, *212*, 146–154.
- [35] L. Lu, X. K. Ren, R. Liu, X. Q. Jiang, L. Y. Geng, J. F. Zheng, Y. Feng, E. Q. Chen, *ChemPhysChem* **2017**, *18*, 3605–3613.
- [36] D. N. Nadimetla, S. V. Bhosale, *New J. Chem.* **2021**, *45*, 7614–7621.
- [37] Y. Zhou, J. F. Zhang, J. Yoon, *Chem. Rev.* **2014**, *114*, 5511–5571.
- [38] D. D. La, S. V. Bhosale, L. A. Jones, S. V. Bhosale, *ACS Appl. Mater. Interfaces* **2018**, *10*, 12189–12216.

- [39] S. Peng, J. Wen, M. Hai, Z. Yang, X. Yuan, D. Wang, H. Cao, W. He, *New J. Chem.* **2019**, *43*, 617–621.
- [40] M. Bineci, M. Bajlan, S. Atilgan, *Sens. Actuators B* **2016**, *222*, 315–319.
- [41] D. N. Nadimetla, G. A. Zalmi, S. V. Bhosale, *ChemistrySelect* **2020**, *5*, 8566–8571.
- [42] P. Chen, H. Zhu, L. Kong, X. Xu, Y. Tian, J. Yang, *Dyes Pigm.* **2020**, *172*, 107832.
- [43] M. Du, B. Huo, M. Li, A. Shen, X. Bai, Y. Lai, J. Liu, Y. Yang, *RSC Adv.* **2018**, *8*, 32497–32505.
- [44] K. Dhanunjayarao, V. Mukundam, K. Venkatasubbaiah, *J. Mater. Chem. C* **2014**, *2*, 8599–8606.
- [45] T. Wang, N. Zhang, W. Bai, Y. Bao, *Polym. Chem.* **2020**, *11*, 3095–3114.
- [46] H. Huang, K. Wang, W. Tan, D. An, X. Yang, S. Huang, Q. Zhai, L. Zhou, Y. Jin, *Angew. Chem. Int. Ed.* **2004**, *43*, 5635–5638; *Angew. Chem.* **2004**, *116*, 5753–5756.
- [47] R. Balamurugan, J. H. Liu, B. T. Liu, *Coord. Chem. Rev.* **2018**, *376*, 196–224.
- [48] X. Liu, T. Chen, F. Yu, Y. Shang, X. Meng, Z. R. Chen, *Macromolecules* **2020**, *53*, 1224–1232.
- [49] Y. Qin, M. A. Hillmyer, *Macromolecules* **2009**, *42*, 6429–6432.
- [50] A. Mukherjee, M. Chakravarty, *New J. Chem.* **2020**, *44*, 6173–6181.
- [51] G. Donzelli, A. Carducci, A. Llopis-Gonzalez, M. Verani, A. Llopis-Morales, L. Cioni, M. Morales-Suárez-varela, *Int. J. Environ. Res. Public Health* **2019**, *16*, 1–14.
- [52] H. Needleman, *Annu. Rev. Med.* **2004**, *55*, 209–222.
- [53] R. Zhou, B. Li, N. Wu, G. Gao, J. You, J. Lan, *Chem. Commun.* **2011**, *47*, 6668–6670.
- [54] X. Li, B. Xu, H. Lu, Z. Wang, J. Zhang, Y. Zhang, Y. Dong, K. Ma, S. Wen, W. Tian, *Anal. Methods* **2013**, *5*, 438–441.
- [55] D. G. Khandare, H. Joshi, M. Banerjee, M. S. Majik, A. Chatterjee, *RSC Adv.* **2014**, *4*, 47076–47080.
- [56] N. Adarsh, M. Shanmugasundaram, D. Ramaiah, *Anal. Chem.* **2013**, *85*, 10008–10012.
- [57] T. Information, I. S. Distributed, S. For, T. H. E. Purpose, D. Peer, R. Under, A. Information, S. Not, B. E. Construed, T. O. Represent, a N. Y. Agency, **2003**.
- [58] J. G. M. M. Smeenk, *Environ. Sci. Technol.* **1983**, *17*, 21–23.
- [59] Z. Xue, Z. Wu, S. Han, *Anal. Methods* **2012**, *4*, 2021–2026.
- [60] Anuradha, K. Latham, S. V. Bhosale, *RSC Adv.* **2016**, *6*, 45009–45013.
- [61] A. Chatterjee, D. G. Khandare, P. Saini, A. Chattopadhyay, M. S. Majik, M. Banerjee, *RSC Adv.* **2015**, *5*, 31479–31484.
- [62] G. Wei, N. Lin, Y. Gu, X. Ren, G. Zhao, S. Guang, J. Feng, H. Xu, *Sens. Actuators B* **2020**, *321*, 128532.
- [63] L. Chen, L. Chan, X. Fu, W. Lu, *ACS Appl. Mater. Interfaces* **2013**, *5*, 284–290.
- [64] S. Mukherjee, P. Thilagar, *Chem. Commun.* **2013**, *49*, 7292–7294.
- [65] Y. Shan, W. Yao, Z. Liang, L. Zhu, S. Yang, Z. Ruan, *Dyes Pigm.* **2018**, *156*, 1–7.
- [66] Q. Lin, X. M. Jiang, X. Q. Ma, J. Liu, H. Yao, Y. M. Zhang, T. B. Wei, *Sens. Actuators B* **2018**, *272*, 139–145.
- [67] L. N. Neupane, E. T. Oh, H. J. Park, K. H. Lee, *Anal. Chem.* **2016**, *88*, 3333–3340.
- [68] W. Fang, G. Zhang, J. Chen, L. Kong, L. Yang, H. Bi, J. Yang, *Sens. Actuators B* **2016**, *229*, 338–346.
- [69] C. B. Bai, P. Xu, J. Zhang, R. Qiao, M. Y. Chen, M. Y. Mei, B. Wei, C. Wang, L. Zhang, S. S. Chen, *ACS Omega* **2019**, *4*, 14621–14625.
- [70] X. Yang, Z. Zhao, H. Ran, J. Zhang, L. Chen, R. Han, X. Duan, H. Sun, J. Y. Hu, *Dyes Pigm.* **2020**, *173*, 107881.
- [71] X. Wen, L. Yan, Z. Fan, *Spectrochim. Acta Part A* **2020**, *241*, 118664.
- [72] F. C. Pigge, *J. Mol. Eng. Mater.* **2013**, *01*, 1340009.
- [73] G. Huang, G. Zhang, D. Zhang, *Chem. Commun.* **2012**, *48*, 7504–7506.
- [74] A. Rananaware, R. S. Bhosale, H. Patil, M. Al Kobaisi, A. Abraham, R. Shukla, S. V. Bhosale, S. V. Bhosale, *RSC Adv.* **2014**, *4*, 59078–59082.
- [75] Z. Ruan, Y. Shan, Y. Gong, C. Wang, F. Ye, Y. Qiu, Z. Liang, Z. Li, *J. Mater. Chem. C* **2018**, *6*, 773–780.
- [76] G. Wei, Y. Jiang, F. Wang, *Tetrahedron Lett.* **2018**, *59*, 1476–1479.
- [77] W. Shi, S. Zhao, Y. Su, Y. Hui, Z. Xie, *New J. Chem.* **2016**, *40*, 7814–7820.
- [78] K. Kala, N. Manoj, *RSC Adv.* **2016**, *6*, 22615–22619.
- [79] J. Wang, L. Zhang, Q. Qi, S. Li, Y. Jiang, *Anal. Methods* **2013**, *5*, 608–611.
- [80] Y. Wu, X. Wen, Z. Fan, *Spectrochim. Acta Part A* **2019**, *223*, 117315.
- [81] P. Yin, Q. Niu, T. Li, T. Wei, J. Chen, X. Qin, *J. Mol. Liq.* **2020**, *316*, 113845.
- [82] Y. Huang, J. Lin, L. Wang, Z. Cao, Y. Wang, M. Wu, *Zeitschrift fur Anorg. und Allg. Chemie* **2020**, *646*, 47–52.
- [83] C. W. Abney, J. C. Gilhula, K. Lu, W. Lin, *Adv. Mater.* **2014**, *26*, 7993–7997.
- [84] S. Y. Lim, W. Shen, Z. Gao, *Chem. Soc. Rev.* **2015**, *44*, 362–381.
- [85] J. Dong, P. Shen, S. Ying, Z. J. Li, Y. Di Yuan, Y. Wang, X. Zheng, S. B. Peh, H. Yuan, G. Liu, Y. Cheng, Y. Pan, L. Shi, J. Zhang, D. Yuan, B. Liu, Z. Zhao, B. Z. Tang, D. Zhao, *Chem. Mater.* **2020**, *32*, 6706–6720.
- [86] S. C. Vardali, N. Manousi, M. Barczak, D. A. Giannakoudakis, *Molecules* **2020**, *25*, DOI 10.3390/molecules25030513.
- [87] X. Fang, B. Zong, S. Mao, *Nano-Micro Lett.* **2018**, *10*, DOI 10.1007/s40820-018-0218-0.
- [88] S. Xie, Q. Liu, F. Zhu, M. Chen, L. Wang, Y. Xiong, Y. Zhu, Y. Zheng, X. Chen, *J. Mater. Chem. C* **2020**, *8*, 10408–10415.
- [89] S. L. Jackson, A. Rananaware, C. Rix, S. V. Bhosale, K. Latham, *Cryst. Growth Des.* **2016**, *16*, 3067–3071.
- [90] B. Jiang, C. W. Zhang, X. L. Shi, H. B. Yang, *Chinese J. Polym. Sci. (English Ed.)* **2019**, *37*, 372–382.
- [91] M. Gon, K. Tanaka, Y. Chujo, *Bull. Chem. Soc. Jpn.* **2019**, *92*, 7–18.
- [92] B. Roy, T. Govindaraju, *Bull. Chem. Soc. Jpn.* **2019**, *92*, 1883–1901.
- [93] J. Li, K. Pu, *Chem. Soc. Rev.* **2019**, *48*, 38–71.

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