Fluorescent Nano Materials and Their Sensing Ability Towards Organic Pollutants

A Dissertation

Presented in Partial Fulfillment of the Requirements for The Degree of

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ACKNOWLEDGEMENT

Thanks God for the wisdom and perseverance that He has been bestowing upon me during this research work.

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September, 2013 The Author

ABSTRACT

Synthesis of 1,3-bis(1-butylbenzimidazol-2-yl)benzene (L-2), 2,5-bis(1-butylbenzimidazol-2-yl)thiophene(L-4), 2,5-bis(1-octylbenzimidazol-2-yl)thiophene (L-5), tetrarhenium metallacycles $[\{Re(CO)_3\}_2(\mu\text{-dhaq})(\mu\text{-N–N})]_2$ (L-6) and $[\{Re(CO)_3\}_2(\mu\text{-thaq})(\mu\text{-N–N})]_2$ (L-7), (N–N= 2,5-bis(1-octylbenzimidazol-2-yl)thiophene, H_2-dhaq= 1,4-dihydroxy-9,10-anthraquinone and H_2-thaq= 1,2,4-tri hydroxy-9,10-anthraquinone) were described in the present study. Metallacycles L-6 and L-7 underwent aggregation in THF-water mixtures and the morphology of the aggregate depends on the fraction of water. Compounds L-6 and L-7 formed granular or spongy spheres in THF solution, while they formed micron size rods in a THF-water mixture containing 40% and 30% water respectively. Besides, higher water content of 80% afforded amorphous materials. The micron size rods of L-6, L-7 showed better photoluminescence (PL) over granular or spherical aggregates, while PL is totally quenched in case of amorphous aggregates. Synthesized compounds showed sensing ability towards picric acid (PA) and 1-chloro-4-nitrobenzene. The absorbance spectra showed significance changes and photoluminescence was quenched on addition of nitroaromatics to the solutions of the sensing compounds. Binding properties were studied by Beneshi-Hildebrand and Stern-Volmer plots and found that the compounds had significant binding with nitroaromatics. This class of compounds may be applied for developing sensors for nitroaromatic pollutants in aqueous system.

List of Abbreviations

PL	Photoluminescence
PA	Picric acid
THF	Tetrahydrofuran
DCM	Dichloromethan
H	Host
G	Guest
FONs	Fluorescence Organic Nano Materials
HPS	Hexaphenylsilole
AIE	Aggregation-induced emission
AIEE	Aggregation-induced emission enhancement
SEM	Scanning electron microscopy
FESEM	Field emission scanning electron microscopy
TEM	Transmission electron microscopy
VD	Vapor deposition
VDSA	Vapor-driven self-assembly
NPs	Nanoparticles
CT	Charge transfer
NAC	Nitro-aromatic compound
TNT	Trinitrotoluene
DNT	Dinitrotoluene
GMCO	Graphene oxide–methyl cellulose hybrid
OMC	Ordered mesoporous carbon
NHCs	N-heterocyclic carbenes

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Declaration

It is herewith certified that Reg. No.: 270, M. Phil, Session: 2009-2010, Department of Applied Chemistry and Chemical Engineering, University of Dhaka, Bangladesh, has carried out her M. Phil thesis entitled **"Fluorescent Nano Materials and Their Sensing Ability Towards Organic Pollutants"** in the Department of Applied Chemistry and Chemical Engineering, University of Dhaka under our direct supervision. She has successfully carried out her research work and is ready to present her dissertation, which is required in partial fulfillment of her M. Phil degree. This is an original study of the author and no part of the thesis has been submitted to any other University or Institute for any degree.

We have gone through the final draft of the thesis and recommended its submission for her degree of M. Phil in Applied Chemistry and Chemical Engineering.

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Contents

1.1. Luminescence

Luminescence is emission of light by a substance not resulting from heat; it is thus a form of cold body radiation. It can be caused by chemical reactions, electrical energy, subatomic motions, or stress on a crystal. Historically, radioactivity was thought of as a form of "radio-luminescence", although it is today considered to be separate since it involves more than electromagnetic radiation. The term 'luminescence' was introduced in 1888 by Eilhard Wiedemann[1,2]. Several investigators reported luminescence phenomena during the seventeenth and eighteenth centuries. The luminescence properties of benzimidazole have been extensively studied[3-6], but little work has been reported on substituted species, for example thiabendazol and its major metabolite, 5-hydroxythiabe-ndazole were shown to have luminescence properties[7].

Photoluminescence is a form of luminescence process, in which a substance absorbs photons (electromagnetic radiation) and then re-radiates photons. Quantum mechanically, this can be described as an excitation to a higher energy state and then a return to a lower energy state accompanied by the emission of a photon. The period between absorption and emission is typically extremely short, in the order of 10 nanoseconds. Under special circumstances, however, this period can be extended into minutes or hours.
Photoluminescence is formally divided into two categories, fluorescence and phosphores-cence.

1.2. Fluorescence

Fluorescence is a member of the ubiquitous photoluminescence family, in which susceptible molecules emit light from electronically excited states created by either a physical (for example, absorption of light), mechanical (friction), or chemical reason. It is the property of some atoms and molecules to absorb light at a particular wavelength and to subsequently emit light of longer wavelength after a brief interval. It was British scientist Sir George G. Stokes who first described fluorescence in 1852 and was

responsible for coining the term in honor of the blue-white fluorescent mineral fluorite (fluorspar).

In the excited state, the electron has higher potential energy and will relax back to a lower state by emitting photon energy. This is fluorescence can be detected in the spectrum. In most cases, the emitted light has a longer wavelength, and therefore lower energy, than the absorbed radiation. The most striking examples of fluorescence occur when the absorbed radiation is in the ultraviolet region of the spectrum, and thus invisible to the human eye, and the emitted light is in the visible region.

Fluorescence is generally studied with highly conjugated polycyclic aromatic molecules. The catagory of molecules capable of undergoing electronic transitions that ultimately result in fluorescence are known as fluorescent probes, fluorochrom, or simply dyes. Fluorochrom that are conjugated to a larger macromolecule (such as a nucleic acid, lipid, enzyme, or protein) through adsorption or covalent bonds are termed fluorophores. In general, fluorophores are divided into two broad classes, termed- intrinsic and extrinsic. Intrinsic fluorophores, such as aromatic amino acids, neurotransmitters, porphyrins, and green fluorescent protein are those that occur naturally. Extrinsic fluorophores are synthetic dyes or modified biochemicals that are added to a specimen to produce fluorescence with specific spectral properties.

The study of chemical reactions of molecules in electronically excited states produced by the absorption of infrared (700–1000 nanometers), visible (400–700 nm), ultraviolet (200–400 nm), or vacuum ultraviolet (100–200 nm) light known as photochemistry. Bond making and bond breaking as well as electron transfer and ionization are often observed in both organic and inorganic compounds as a consequence of such excitation.
The excited state produced by absorption of a photon is not generally a stable species. After a characteristic lifetime that can vary from femtoseconds (10^{-15} s) to hours, the excited molecule will either relax to its ground-state precursor or undergo a chemical

transformation. The term photo physics is used to describe nonreactive relaxation processes, which include radiative (taking place with the emission of light) and nonradiative (taking place without the emission of light) pathways.

The energies of the lowest singlet and triplet excited states (relative to the ground state) can be obtained from the longest wavelength band of the fluorescence and phosphorescence spectra, respectively. This band is called a 0, 0 band to indicate a transition between the lowest vibrational levels of the lowest-lying states. Singlet and triplet energies can also be determined indirectly by measuring quenching efficiencies. The shift between the 0, 0 bands for absorption and emission in a single molecule is called its Stokes shift. A small Stokes shift is usually observed when the excited state has geometry similar to the ground state. A Jablonski diagram (see illustration) is often used to graphically depict the relationship between competing photo physical processes.

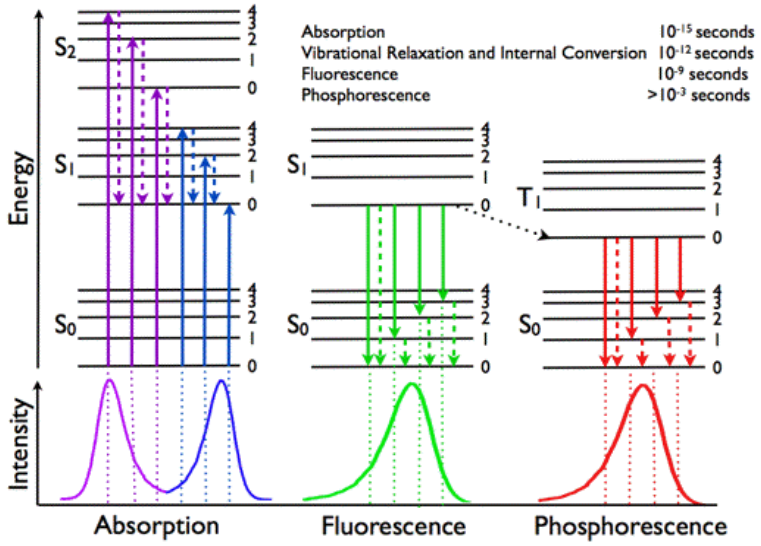


Figure-1 : Jablonski diagram. S terms = singlet states; T terms = triplet states.

1.3. Phosphorescence

Phosphorescence is a form of photoluminescence which is a result of triplet–singlet electronic relaxation (typical lifetime: milliseconds to hours). In which the energy from absorbed photons undergoes intersystem crossing into a state of higher spin multiplicity, usually a triplet state. Once the energy is trapped in the triplet state, transition back to the lower singlet energy states is quantum mechanically forbidden, meaning that it happens much more slowly than other transitions. The result is a slow process of radiative transition back to the singlet state, sometimes lasting minutes or hours. The process of phosphorescence occurs in a manner similar to fluorescence, but with a much longer excited state lifetime.

1.4. Binding property and Quenching

To observe one-to-one binding between host (H) and guest (G) molecule using UV-Visible absorption, Beneshi-Hildebrand method can be used. On the other hand, Stern-Volmer method is used to observe the intermolecular deactivation i.e. quenching of luminescent material.

1.4.1. Beneshi-Hildebrand Method

The Beneshi-Hildebrand method is a mathematical approach used in physical chemistry for the determination of the equilibrium constant K and stoichiometry of non-bonding interactions. This method has been typically applied to reaction equilibria that form one-to-one complexes, such as charge-transfer complexes and host-guest molecular complexation.

$$H + G \rightleftharpoons HG$$

The theoretical foundation of this method is the assumption that when either one of the reactants (host) is present in excess amounts over the other reactant, the characteristic electronic absorption spectra of the other reactant(trace amount/guest) will be transparent

in the collective absorption/emission range of the reaction system[8]. Therefore, by measuring the absorption spectra of the reaction before and after the formation of the product and its equilibrium, the association constant of the reaction can be determined.

The kinetics of Beneshi-Hildebrand method is –

$$1/\Delta A = 1//(\Delta\varepsilon\ K[H][G]) + 1/(\Delta\varepsilon\ [H])$$

Where, $\Delta A = A_0 - A$ = the change of absorbance before (A_0) and after (A) of HG complex.

$\Delta\varepsilon$ = represents the change in value between ε^{HG} and ε^{G}.

K = the equilibrium constant.

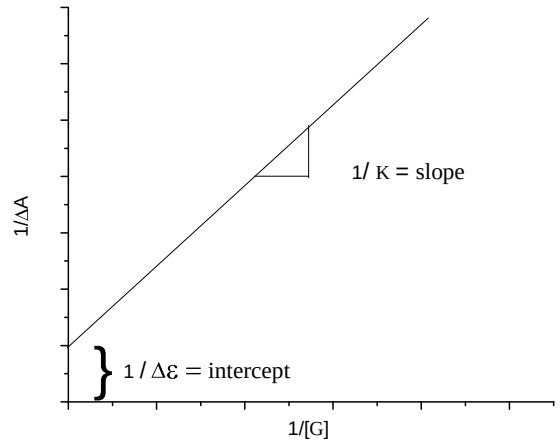


Figure-2 : Beneshi-Hildebrand plot.

Limitations of Beneshi-Hildebrand plot:

1. [H] >> [G] is must ([H] must be almost 10 fold excess than [G]); if not then linearity breaks down to scatter plot.
2. Strongly bound complex formation should be 1:1 product complex; if it is 2:1 weakly bound complex then accuracy would be lost.
3. Only one parameter, K or ε, can be evaluated independently of the other.

1.4.2. Stern–Volmer relationship

The Stern–Volmer relationship, named after Otto Stern and Max Volmer[9] allows us to explore the kinetics of a photophysical intermolecular deactivation process. Processes such as fluorescence and phosphorescence are examples of intramolecular deactivation (quenching) processes. An intermolecular deactivation is where the presence of another chemical species can accelerate the decay rate of a chemical in its excited state. In general, this process can be represented by a simple equation:

$$A^* + Q \rightleftharpoons A + Q$$

Or,

$$A^* + Q \rightleftharpoons A + Q^*$$

Where, A is one chemical species, Q is another (known as a quencher) and * designates an excited state.

1.4.3. Quenching

The process by which an excited state molecule, M*, in an excited singlet or triplet state transfers all or part of its excitation energy to a reaction partner or quencher, Q, is called energy transfer or quenching when the molecule of interest is M.

$$M^* + Q \longrightarrow M + Q^*$$

A number of processes can lead to a reduction in fluorescence intensity, which is referred to as quenching. These processes can occur during the excited state lifetime, for example collisional quenching, energy transfer, charge transfer reactions or photochemistry or they may occur due to formation of complexes in the ground state. There are two quenching processes usually encountered-

1. Collisional (dynamic) quenching
2. Static (complex formation) quenching

1.4.3.1. Collisional (dynamic) Quenching

Collisional quenching occurs when the excited fluorophore experiences contact with an atom or molecule that can facilitate non-radiative transitions to the ground state. Common quenchers include O_2 and acrylamide.

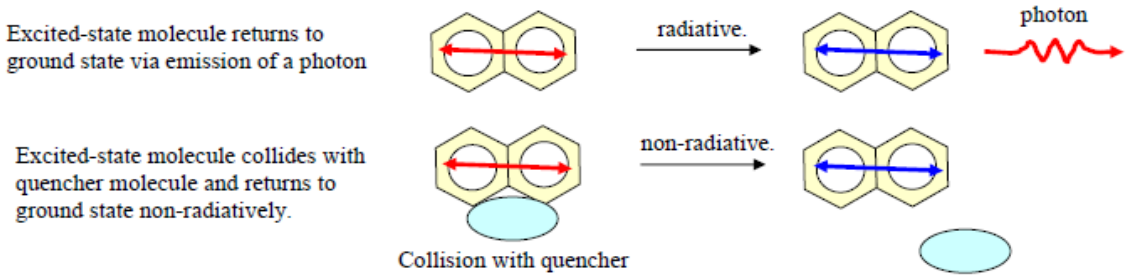


Figure-3 : Collisional quenching.

In the simplest case of collisional quenching, the following relation, called the Stern-Volmer equation, holds:

$$Io/I = K_{sv}[Q] + 1$$

Where, $I_{0,}$ is the intensity, or rate of fluorescence, without a quencher, I, is the intensity, or rate of fluorescence, with a quencher, $K_{sv,}$ is the quencher rate coefficient and Q, is the concentration of the quencher[10].

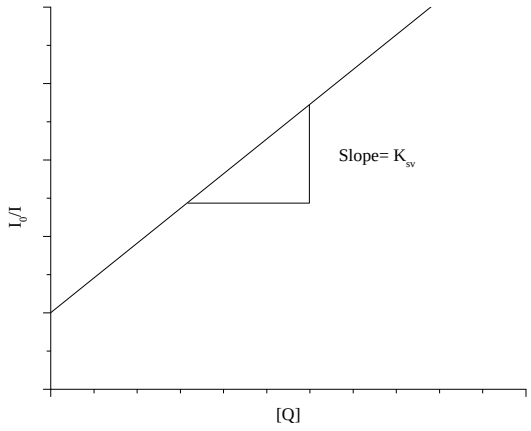


Figure-4 : Stern-Volmer plot for dynamic quenching.

1.4.3.2. Static (complex formation) Quenching

Static quenching only affects the complexed fluorophores. The properties of the uncomplexed fluorophores are not changed.

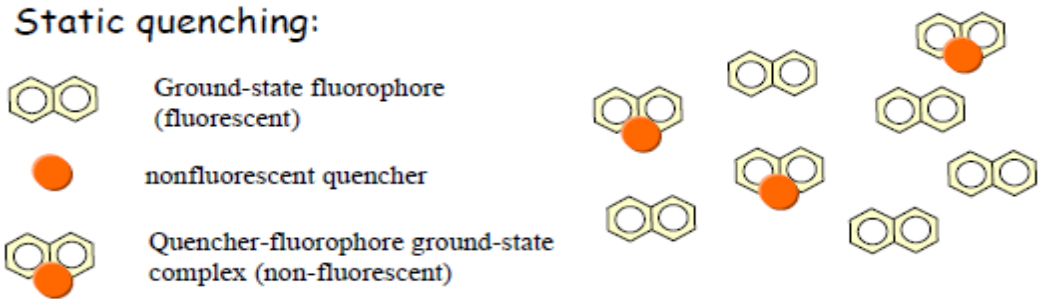


Figure-5 : Static quenching.

In some cases, the fluorophore can form a stable complex with another molecule. If this ground-state is non-fluorescent then we say that the fluorophore has been statically quenched. In such a case, the dependence of the fluorescence as a function of the quencher concentration follows the relation:

$$I_0/I = 1 + Ka\,[Q]$$

Where, Ka is the association constant of the complex. Such cases of quenching via complex formation were first described by Gregorio Weber.

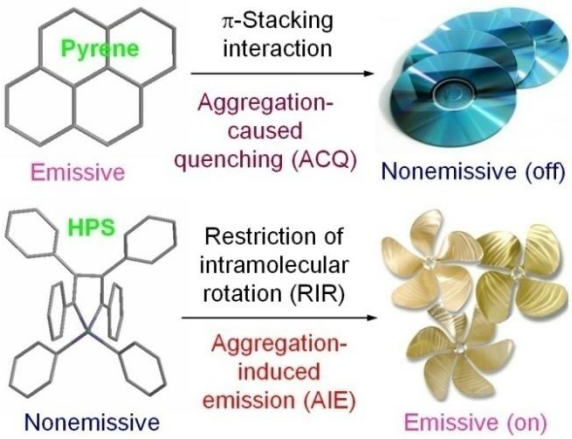
1.5. Fluorescence Organic Nano Materials (FONs)

During the past two decades, more and more research attention has been paid to nanomaterials- those functional materials composed of objects in the range 1–100 nm. If hybrids are neglected, nanomaterials can be divided into two catagories-inorganic nanomaterials and organic nanomaterials. Besides inorganic counterparts, nanomaterials based on traditional functional small organic molecules have been the subject of research interest in recent years, because many routes are introduce for fabricating small organic

compounds into nanostructures. Besides the exploration of the synthetic strategies, much effort has also been made to investigate the unique optical and/or electronic properties of the organic nanomaterials obtained by molecular aggregation in the nanostructures.

One of the example of quenching is aggregation of fluprophor in solvent. Fluorophor aggregation generally quence the light emission. Most of the organic luminogens are highly emissive. But when they undergo aggregation, the luminescence is totally quenched by aggregation or the emission is induced by aggregation. Pentacenequinone derivatives form fluorescent nano aggregates in aqueous media and show aggregation-induced enhancement[11].

Planar luminogens such as pyrene tend to aggregate due to strong π-π stacking interaction, which commonly turns "off" light emission, whereas nonplanar propeller-shaped luminogens such as hexaphenylsilole (HPS) behave oppositely, with their light emissions turned "on" by aggregate formation, due to the restricted intramolecular rotation in the aggregates. The additional thing is hexylphenylsilole (HPS) dissolved in its good solvent is nonemissive. But addition of large amounts of water into the solution causes the silole molecules to aggregate and induces them to emit efficiently. This is "aggregation-induced emission enhencement" (AIEE), because the nonluminescent silole molecules are induced to emit by aggregation.



Scheme-1 : Planar luminogens such as pyrene tend to aggregate just as discs pile, which commonly turns "off" light emission, whereas nonplanar propeller-shaped luminogens such as hexaphenylsilole (HPS) behave oppositely, with their light emissions turned "on" by aggregate formation.

Only a limited number of organic compounds display AIE(aggregation-induced emission) characteristics such as siloles, aminobenzoic acids, arylethene and arylbenzene derivatives. There are two type of aggregate J- aggregate and H- aggregate.

It was found that the optical and electronic properties of organic nanomaterials are fundamentally different from those of their inorganic counterparts, because the intermolecular interactions in organic materials are basically of weak types, such as hydrogen bonds, π-π stacking, van der Waals contacts, and CT(charge transfer) interactions. For organic nanomaterials, a series of unique PL behaviors have been achieved, which resulted from the special aggregation modes of the organic molecules, the crystallinity of the materials, and the deliberate introduction of at least one kind of guest compound into the host material matrices. In the following sections, we introduce the various methods for fabrication of nanopartical and the particular PL (photoluminescence) properties of them, including emission enhancement in amorphous nanostructures, fluorescence narrowing and defect emission from organic crystalline

nanomaterials, size dependent optical properties and tunable and switchable emissions from doped organic nanosystems.

1.6. Methods of FONs preparation

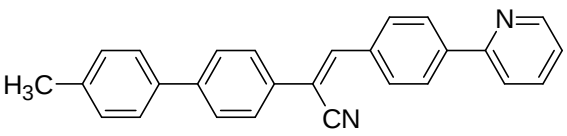
Most of the current works focus on organic nanoparticles with a single chemical composition dispersed in an aqueous system. Of all the preparation methods, reprecipitation is the most facile and commonly used one. Reprecipitation, which is a solvent displacement method, was first reported by Nakanishi and coworkers[12-14]. With this method, a series of organic nanoparticles were successfully fabricated by several groups.

For example, after their pioneer work on this method, Nakanishi and coworkers prepared pyrelene nanoparticles and observed the emissions from both free excitons and self-trapped excitons[15,16].

Horn and coworkers prepared nanoparticles from β-carotene and observed the influence of both supramolecular structure and particle size on the absorption spectra[17].

Majima's group[18] and Barbara's group[19] prepared nanocrystals from perylene and a perylene derivative, respectively, and studied the spectroscopy of single nanoparticles.

Byeong's group[20] prepared colloidal nanoparticals of 1-cyano-trans-1-(4′-methylbiphenyl)-2-[4′-(2′-pyridyl)phenyl]ethylen (Py-CN-MBE) by reprecipitation method where water was added as a nonsolvent to its solution (2×10^{-5} $molL^{-1}$) in THF and observed that after the addition of an 80% volume fraction of water to the THF solution, the suspension was macroscopically homogeneous with no precipitates but had a slightly off-white turbidity as a result of light scattering from the nanoparticles[21] and confirmed the fine spherical structure of nanoparticles by scanning electron microscopy (SEM) image.



Py-CN-MBE

Pricipitation Method

80% H20, 20%THF

Slightly off-white turbidity because of nanopartical formation

Scheme -2: Nanopartical formation of (Py-CN-MBE) by reprecipitation method.

a) b)

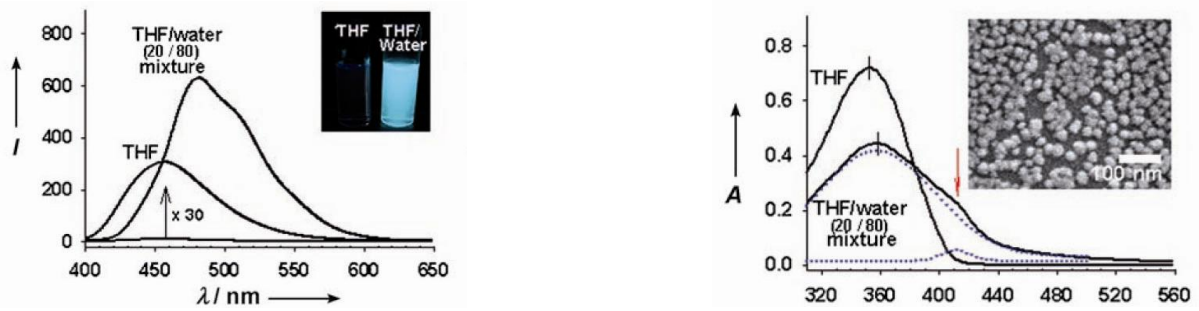


Figure-6 : a) Photoluminescence (PL) spectra of the Py-CN-MBE solution after nanoparticle formation. Insets: the fluorescence emission changes of the Py-CN-MBE solution after nanoparticle formation under illumination by UV light at 365 nm. b) UV/Vis absorption spectra of the Py-CNMBE solution after nanoparticle formation. Blue dotted lines show the peak separation of Py-CN-MBE nanoparticles in the case of 80% water addition and exposure to dichloromethane vapor for 20 s. Insets: SEM images of the Py-CN-MBE colloidal nanoparticles obtained with the reprecipitation method.

Vapor deposition (VD) is also a facile and feasible method for preparing nanomaterials and has achieved great success in fabricating organic nanostructures. Byeong-Kwan and

coworkers[20] also fabricated a photopatterned FONs arrays of 1-cyano-trans-1-(4′-methylbiphenyl)-2-[4′-(2′-pyridyl)ethylene (Py-CN-MBE), which is based on the principles of vapor-driven self-assembly (VDSA) and they found that this molecule has strong nanoparticle formation capability through self-assembly with concomitant fluorescence turn-on (so-called aggregation-induced emission enhanced (AIEE)[22-24].

a) b)

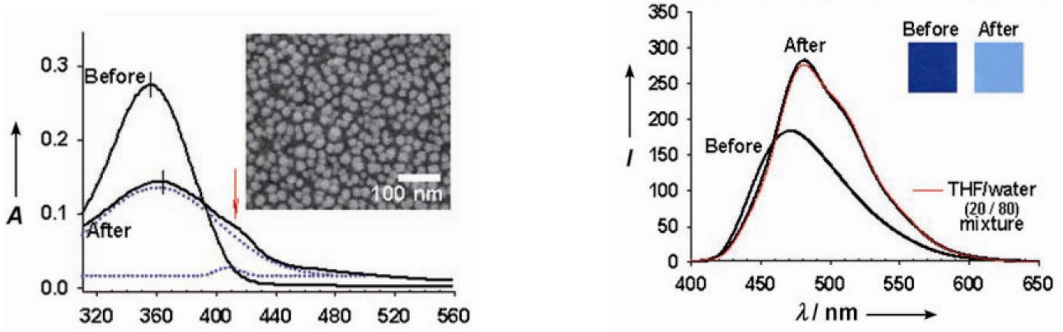
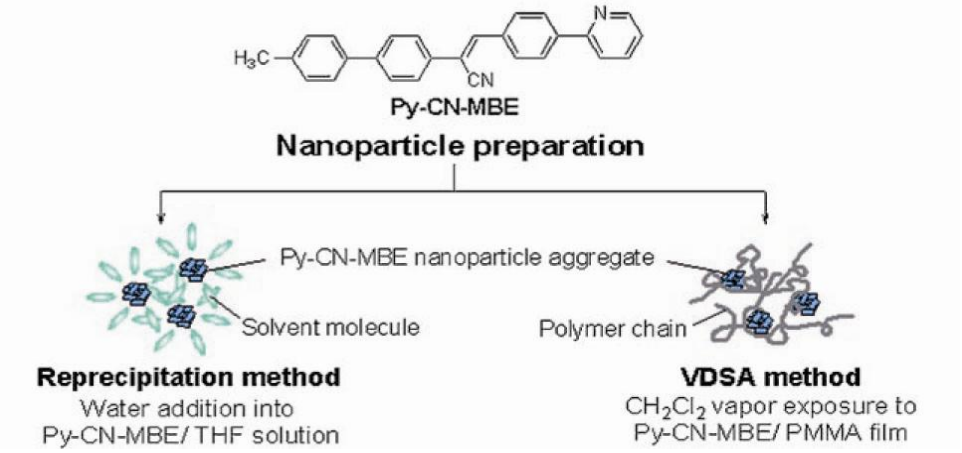
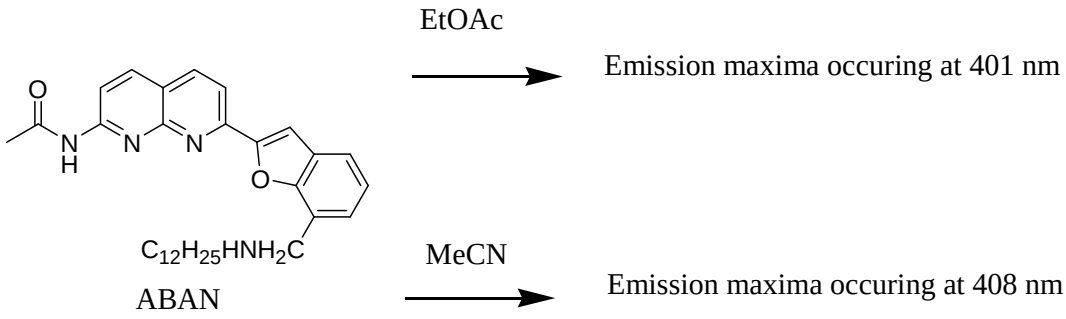


Figure-7 : a) UV/Vis absorption spectra of the Py-CN-MBE/PMMA film after nanoparticle formation. Blue dotted lines show the peak separation of Py-CN-MBE nanoparticles in the case of 80% water addition and exposure to dichloromethane vapor for 20 s. Insets: SEM images of the Py-CN-MBE colloidal nanoparticles obtained with the VDSA process. b) Photoluminescence (PL) spectra of the Py-CN-MBE/PMMA film after nanoparticle formation. Insets: the fluorescence emission changes of the Py-CN-MBE/PMMA film after nanoparticle formation under illumination by UV light at 365 nm.



Scheme-3 : Preparation of nanoparticals of 1-cyano-trans-1-(4′-methylbiphenyl)-2-[4′-(2′-pyridyl)phenyl]ethylen(Py-CN-MBE).

Yeh-Yang Sun and coworkers[25] fabricated nanoparticals of enthynyl-linked benzofuran -naphthyridine compounds (ABAN) by reprecipitation method [13,24,26] and observed that the emission spectra of the benzofuran-naphthyridine linked molecules were solvent sensitive. The fluorescence of ABAN displayed red shifts as the polarity of aprotic solvents increased, e.g., the emission maxima occurring at 401 and 408 nm in EtOAc and MeCN, respectively. That means as the polarity of the solvent increased, the fluorescence peak underwent a bathochromic shift.



Scheme-4 : The emission maxima of ABAN in various solvent.

They also investigated the photophysical properties of the benzofuran-naphyridine linked molecules in H_2O-THF solutions and showed that the fluorescence intensity increased remarkably in H_2O-THF solutions with appropriate fractions of water and determined the morphology of nanoparticles by scanning electron microscopy (SEM).

a) b)

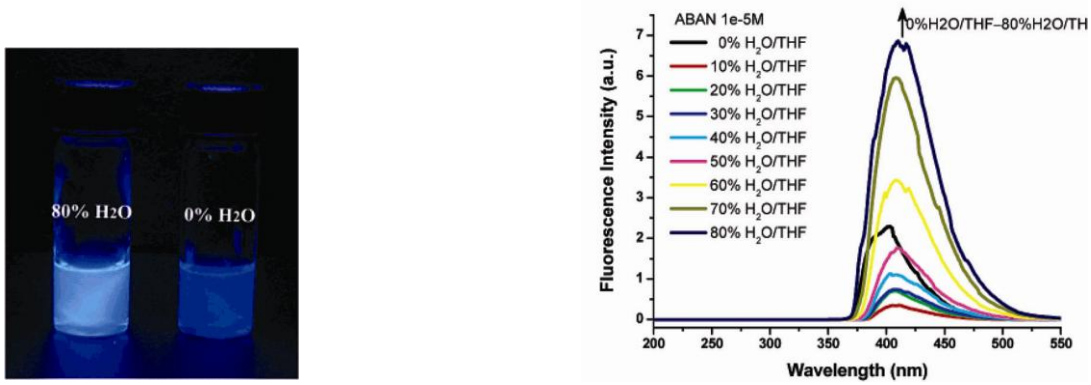


Figure-8 : Fluorescence properties of compound (ABAN) in H_2O-THF solution. (a) Enhanced fluorescence of compound (ABAN) in H2O-THF solution (v/v, 4:1) with excitation at 378 nm. (b) Emission spectra of ABAN in H_2O-THF solution (1×10^{-5} M).

Ai-Dong's group[27] fabricated nanoparticals of 1,3,5-triphenyl-2-pyrazoline (TPP) doped with 4-(dicyanomethylene)-2-methyl-6-(p-dimethyl-aminostyryl)-4H-pyran (DCM) by simple reprecipitation method[12] and investigated that the fluorescence emission from the nanoparticals can be tuned by changing the content of DCM and confirm the size of those nanoparticals are spherical with a mean size of about 30-40 nm by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM).

TPP DCM

Figure-9 : Schematic structures of TPP (left) and DCM (right) molecules.

a) b)

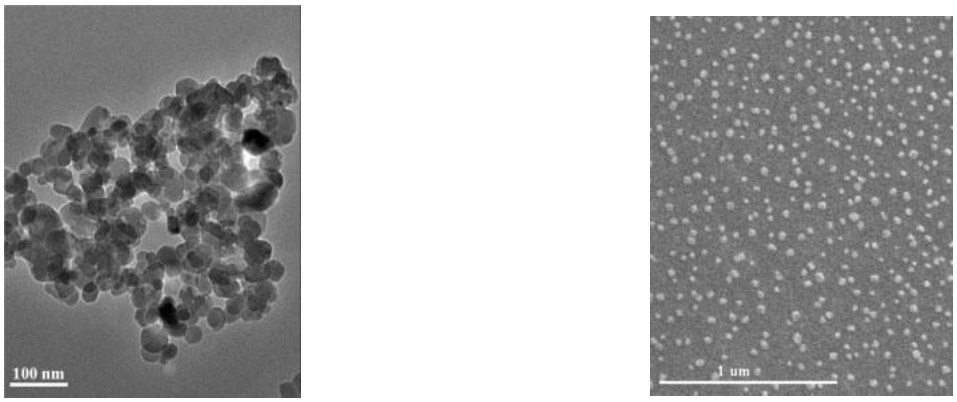
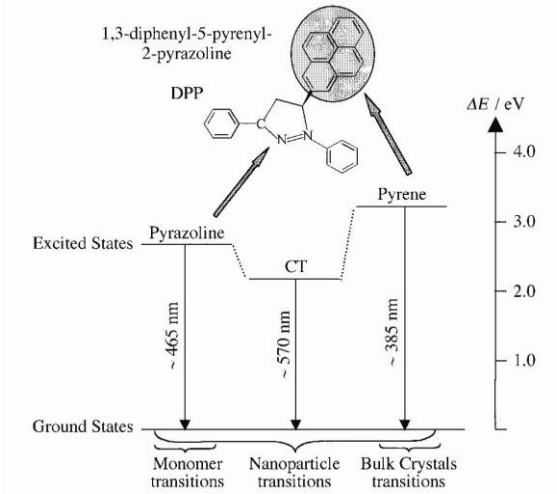


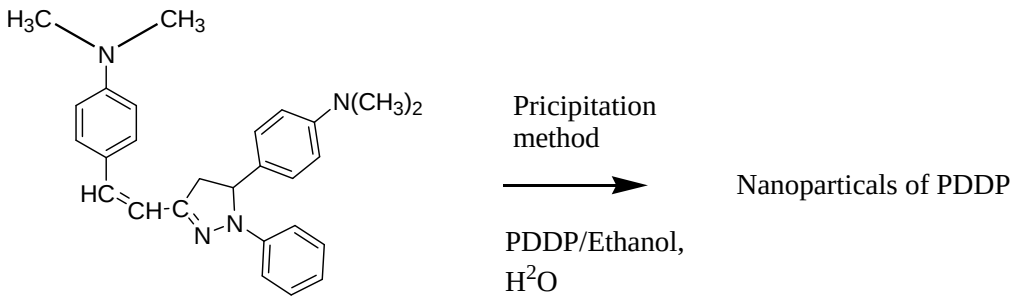
Figure -10 : a)TEM & b)FESEM images of DCM-dopped TPP NPs.

Hongbing Fu, B. H. Loo and coworkers[28] synthesized 1,3-diphenyl-5-pyrenyl-2-pyrazoline (DPP) nanoparticles by reprecipitation method and they found that DPP nanoparticles exhibit multiple emissions from both pyrene and pyrazoline groups and from a CT (charge transfer) complex between pyrene and pyrazoline.Where they molecularly disperse the solution of DPP in a water miscible solvent, acetonitrile and mixed vigorously with an aqueous phase. Mixing the solvent and water phases change the character of the solvent and induced the nucleation and growth of DPP nanoparticles.



Scheme-5 : The emission transitions for DPP in monomers, nanoparticles, and bulk crystals.

Nanoparticles of 1-phenyl-3-((dimethylamino)styryl)-5-((dimethylamino)phenyl)-2-pyrazoline (PDDP) ranging from tens to hundreds of nanometers were fabricated by using the reprecipitation method by Hong-Bing Fu and Jian-Nian Yao[26b]. They were injected quantities of PDDP/ethanol solution($1x10^{-3}$ $molL^{-1}$) into 10 µl of water.



PDDP

Scheme-6 : Nanoparticles formation of PDDP.

They observed that their absorption and emission depended on particle size. As the nanoparticle size increases from 20 to 310 nm the absorption and fluorescence observed to shift to longer wavelength.

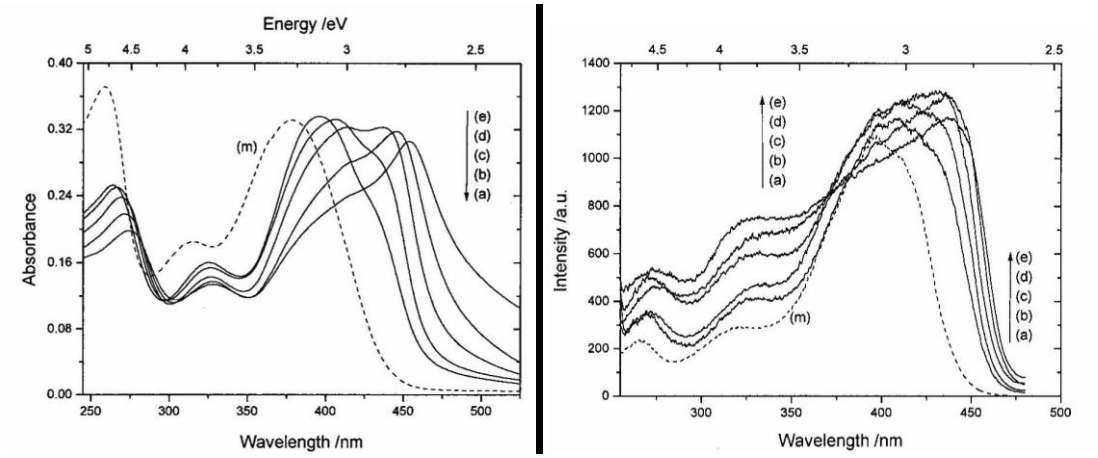


Figure-11 : UV-visible absorption spectra and fluorescence emission spectra of PDDP nanoparticles dispersions in water with different sizes: (a) 20 nm, (b) 50 nm, (c) 105 nm (d)190 nm and (e) 310 nm. (m) The spectrum of the PDDP/ ethanol solution (1.0×10^{-5} $molL^{-1}$).

They also confirm the size of nanoparticals by FESEM.

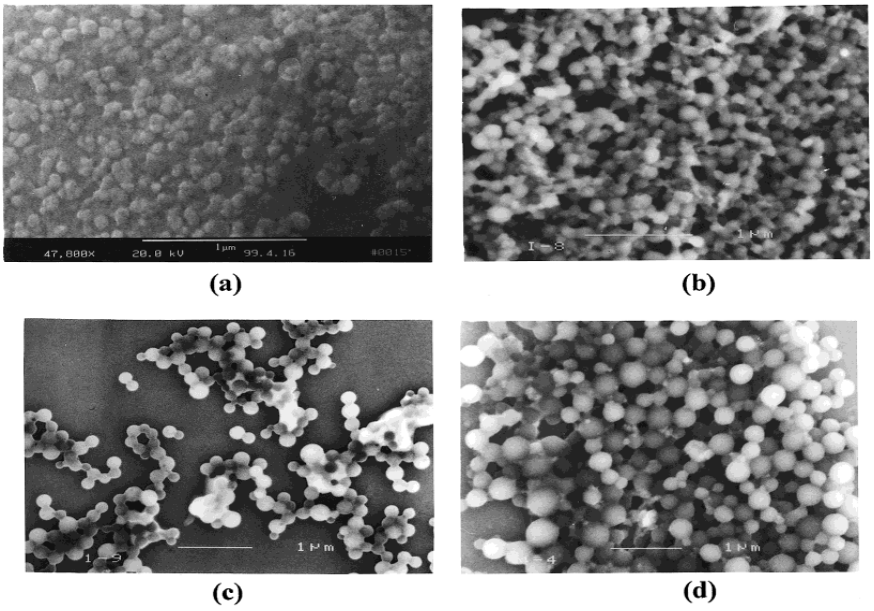
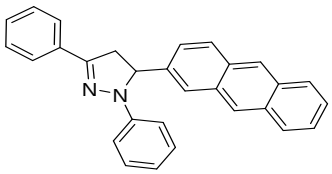


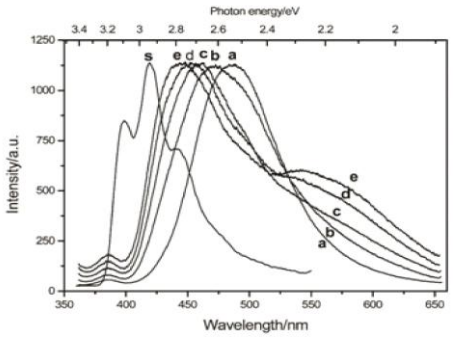
Figure-12 : FESEM photographs of PDDP nanoparicles: (a) 50 nm, (b) 105 nm, (c) 190 nm, and (d) 310 nm.

Debao Xiao, Lu Xi and their group[29] prepared organic nanoparticles of 1,3-diphenyl-5-(2-anthryl)-2- pyrazoline (DAP) ranging in average diameters from 40 to 160 nm through the reprecipitation method. The average diameters of the particles were controlled by variation of the aging time. They found that DAP nanoparticles exhibit the size-dependent optical properties, which demonstrated that the nanoparticle emission in the blue light region from pyrazoline chromophore shifts to shorter wavelengths with increasing particle size.



DAP

Naonparticals formed by pricipitaton method



Flourescence emission of the pyrazoline chromophor was blue shifted with in-crease in the particle size.

Scheme-7 : Fluorescence emission spectra of DAP nanoparticle dispersions with different sizes and DAP solution in acetonitrile. Line s, the spectrum of DAP solution; a, 40 nm; b, 60 nm; c, 90 nm; d, 120 nm; e, 160 nm. The excitation wavelength is at 350 nm.

Nanoparticle dispersion of 1-(4-chlorobenzoyl)-3-(5-(pyrid-4-yl)-1,3,4-thiadiazol-2-yl) thiourea was prepared by a simple reprecipitation method by Al-Kaysi group[30].

Longtian Kang and coworkers[31] fabricated organic core/diffuse-shell nanorods of 1,5-diphenyl-3-(naphthalene-4-yl)-1H-pyrazoline (DPNP) and 2,5-bis(2-(N-hexadecylpyridi-nium-4-yl)-vinyl)pyrrole iodide by two steps: (i) the preparation of uniform DPNP nano-rods by a simple reprecipitation method; (ii) the adsorption of dye on the surface of DPNP nanorods through hydrophobic interactions, which presents fluorescence resonan-ce energy transfer from the core to shell components and they observed that the nanorods of DPNP have an average width of 200 nm by SEM.

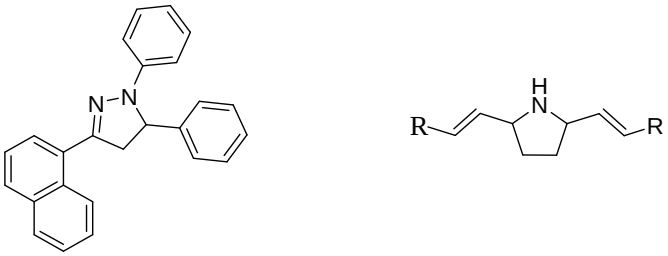


Figure-13 : Structures of DPNP (left) and Dye (right).

Similarly, Yao and co-workers[31] have successfully fabricated organic core/diffuse shell 1,5-diphenyl-3-(naphthalene-4-yl)-1H-pyrazoline (DPNP) nanorods by reprecipitation.

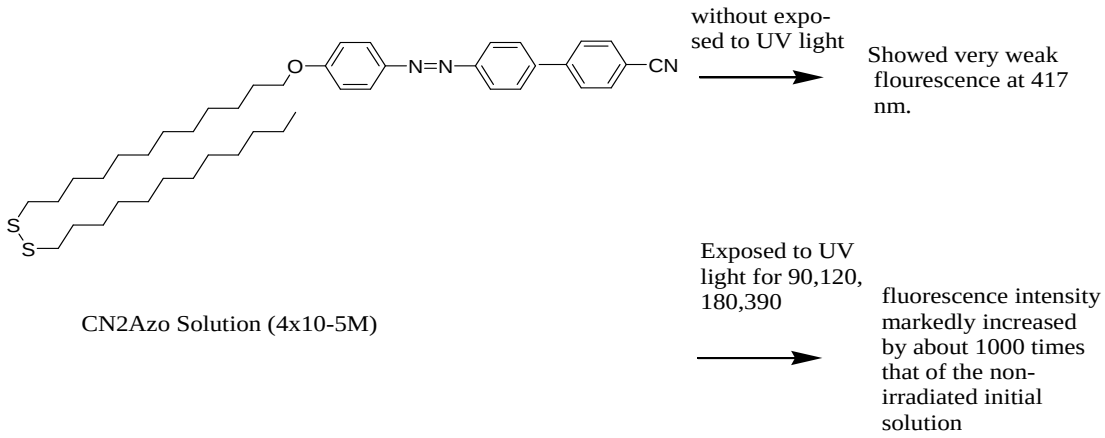
Among them molecular self-assembly is another strategy for nanofabrication that involves designing molecules and supramolecular entities[32]. The assembly of organic molecules to nanostructures needs the driving forces from the molecules themselves and sometimes initiation from the surroundings.

For example, Shelnutt and coworkers prepared porphyrin nanotubes by ionic self-assembly of two oppositely charged porphyrins in aqueous solution and investigated the photocatylytic behavior of the nanotubes[33].

With a similar method of self-assembly, Zhang and coworkers also prepared tubular structures of an intramolecular charge-transfer compound;[34] Wang and coworkers obtained luminescent nanowires from several quinacridone derivatives;
[35] while Zang and coworkers prepared nanofibers and nanobelts from several kinds of small conjugated molecules[36-38].

Mina Han and Masahiko Hara[39] prepared highly fluorescent self-assembled spherical aggregates of an azobenzene derivatives [12-{4-(4c-cyanobiphenylazo)phenoxy}dodecyl] dodecyldisulfide (CN2Azo), consisting of a photoisomerizable azobenzene core coupled directly to biphenyl fluorophore as a head segment and a long alkyl chain as a tail seg-

ment and describe the highly fluorescent self-assembled spherical aggregates of azobenzene molecules without a specific ionic component under UV light illumination, even though azobenzene itself is negligibly fluorescent in nonirradiated initial solution.



Scheme-8 : Upon irradiation with UV light, change in emission intensities of CN2Azo.

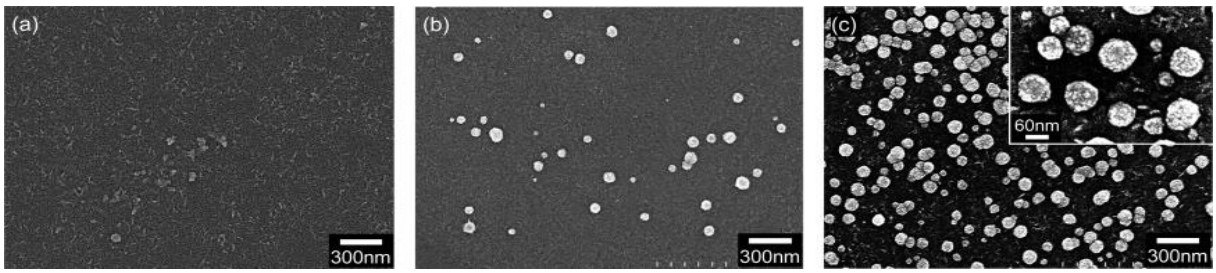


Figure-14 : SEM images of CN2Azo (4×10^{-5} M) after exposure to UV light (a) for 120 min, (b) 180 min, and (c) for 390 min. (Inset) magnified SEM images.

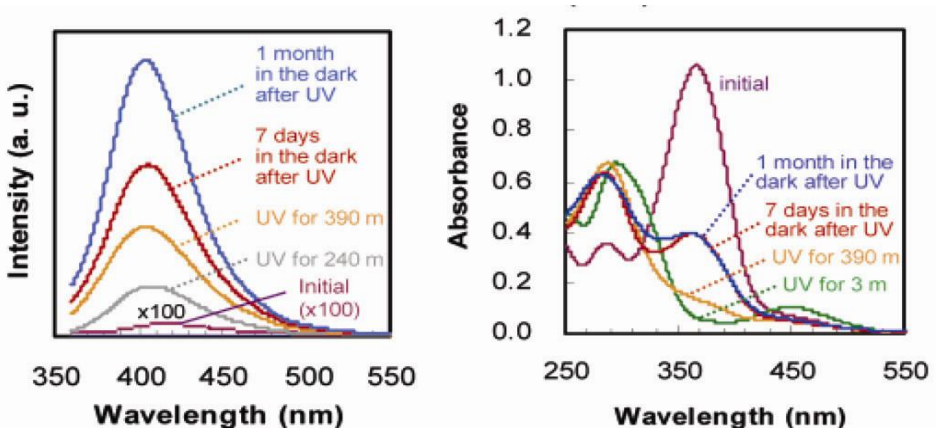
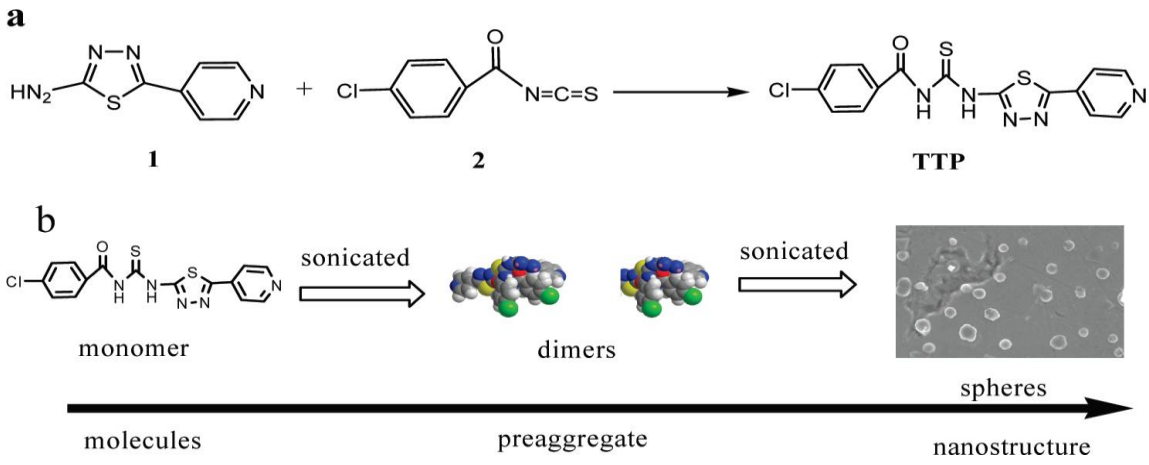


Figure-15 : (a) Emission spectra of CN2Azo (4×10^{-5} M) in dichloromethane at ambient temperature (325 nm excitation). (b) Changes in UV-vis absorption spectra of CN2Azo (4×10^{-5} M) in dichloromethane.

Takazawa and coworkers induced the selfassembly of 3-ethyl-2-[(3-ethyl-2(3H)-benzothiazolylidene)-methyl]benzothiazolium iodide to form wire structures by cooling the hot solutions, and then studied the optical waveguiding behavior of the wires[40,41]. Shimizu and coworkers fabricated nanotubes by the self-assembly of amphiphilic molecules in solutions[42].

Haibing Li and Huijuan Yan[43] found that 1-(4-chlorobenzoyl)-3-(5-(pyrid-4-yl)-1,3,4-thiadiazol-2-yl)thiourea (TTP) molecules readily self-assembled into colloidal nanoparticles as a result of reprecipitation when water was added as a nonsolvent to its solution in THF. They observed that the fluorescence intensity of TTP increased remarkably in H_2O/THF solutions with appropriate fractions of water and they determined the size and morphology of TTP nanomaterials by SEM.



Scheme-9 : (a) Synthesis of TTP and (b) Representation for the formation processes of nanoscale materials of TTP.

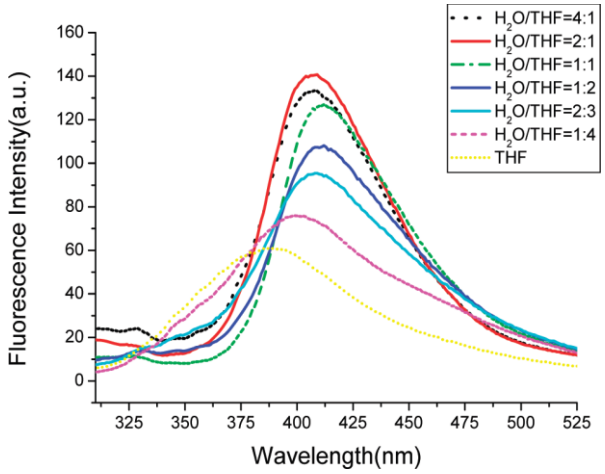


Figure -16 : Fluorescence spectra of the TTP in solutions with different ratios of H_2O/THF.

Debuigne and co-workers have reported the preparation of cholesterol, rhovanil, and rh-odiarome nanoparticles by microemulsions[44].

1.7. Application of FONs

Nanoparticals determine our life in the form of protein complexes and other cell components, as viruses, colloidal particles in drinking water, surface water and sea water, and as aerosols. They have been found to use as dispersion colors and as adhesives; in industry they play an important role in the formulation of pigments and in the production of catalysts. Numerous attempts are being made to deliver nanoparticulate forms of pharmaceutically active compounds specifically to the desired site of the action in the body. Finally nanoparticles find use as quantum dots with special properties for electronic components. Beyond these practical aspects there is scientific interest in nanoparticles owing to their special properties which lie between the properties of molecules and those of bulk material.

During the past few years organic nanomaterials have been increasingly studied because of their unique optical and optoelectronic properties as well as their potential applications in nanoscale devices[22,26b,45a,45b,46,47]. Hongbing Fu and coworkers synthesized 1,3-diphenyl-5-pyrenyl-2-pyrazoline (DPP) is used as a model compound, in the light emitting layer of an electroluminescent device, because of its strong, blue pyrazoline fluorescence[48].

Monodisperse polystyrene nanomaterials and microspheres[49,50] have been widely documented for the construction of photonic crystals.

Micro/nanostructured conductive polymers, such as polyaniline[51] and polypyrrole[52], attracted growing attention because of their good electrical conductivity, redox properties, environmental stability, and potential applications in sensors[53], biomedicine[54], actuators[55], etc.

Nanostructures based on semiconductor conjugated polymers, such as polyfluorene (PF), polythiophene (PT), polyphenylenevinylene (PPV) are attracting significant research interest, owing to their many novel optoelectronic properties and applicat- ions such as field effect transistors[56], optically pumped lasers[57], photodetectors [58], and electroluminescent diodes[59].

Fluorescent organic nanoparticles (FONs) have become the subject of ever-increasing attention in recent years, because of their large diversity in molecular structure and optical properties that are of potential use in optoelectronics and biologics[22,25,26b,26d,27,39,60,61,62,63]. Byeong-Kwan and co-workers[20] develop a new approach to the fabrication of photopatterned assemblies of FONs on the surfaces of solid substrates, which is based on the principles of vapor-driven self-assembly (VDSA) and patternwise photoacid generation to explore the collective properties of FONs as well as to realize practical device applications. This technology has the potential advantage to eliminate the difficulties of transferring preformed colloidal FONs onto fixed locations on substrates, thereby opening up a new approach to the realization of practical optoelectronic nanodevice applications of FONs.

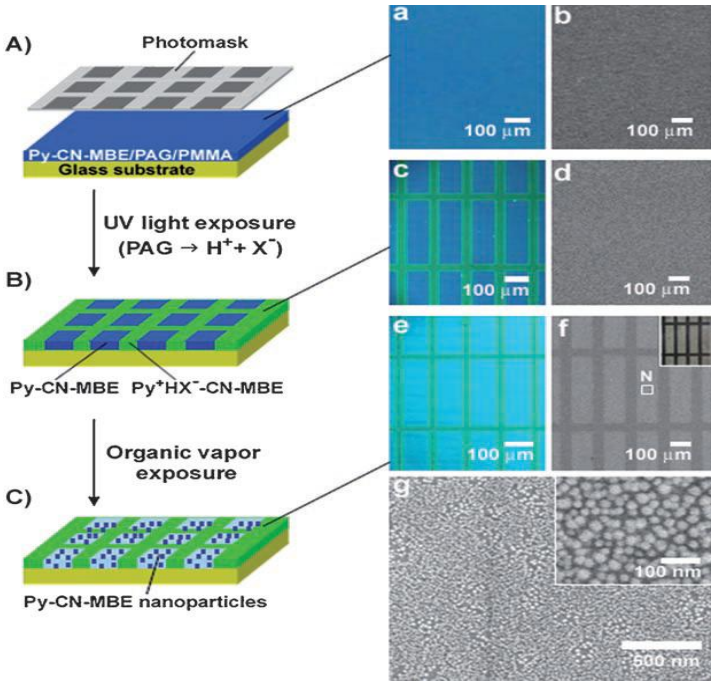


Figure-17 : Photopatterned array of Py-CN-MBE nanoparticles. A–C) Schematic diagram of the procedure for photopatterning Py-CNMBE nanoparticles. a–g) Fluorescence emission and SEM images at each step. The inset photo in (f) shows a microscope image of the patterned array of Py-CN-MBE nanoparticles, obtained with a platinum- sputtering treatment.

Organic low-dimensional nanostructures used as nanoscale building blocks have attracted considerable research interest in the development of novel nanodevices[68].

Organic nanomaterials used as light-emitting candidates have attracted in the development of novel optoelectronic devices and full color flat panel displays due to their advantages such as high luminescence efficiencies[65]. Recently, a study has been reported on the changes in the emission spectra of organic nanoparticles[15,28,66]. For example, perylene nanoparticles were found to exhibit size-dependent emission[15] because of the reduction of the barrier from S-exciton to F-exciton states in the nanoparticles. In light of the fact that pyrazoline derivatives have been widely used as optical brightening agents for textiles and paper because of their strong

fluorescence[67,68] and as the hole-conducting medium in photoconductive materials[69,70] and electroluminescence (EL) devices, Debao Xiao and group has investigated the size-dependent optical properties of the nanoparticles from a series of pyrazoline compounds.The following scheme displays some field emission scanning electron microscope images of the as-prepared DAP nanoparticles, in which the average sizes were 60 nm (A) and 160 nm (B), respectively. These results confirm that the particles are unambiguously amorphous. Such an amorphous character of DAP nanoparticles should be profitable to the light-emitting efficiency because of the reduction in quenching from the internal conversion process which is dominant in the crystalline systems[65]

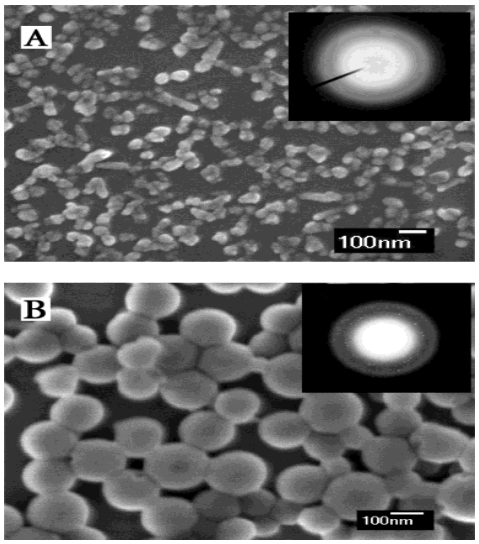


Figure-18 : Field emission SEM images of DAP nanoparticles with average diameters of (A) 60 nm and (B) 160 nm. The insets are electron diffraction patterns of the corresponding particles.

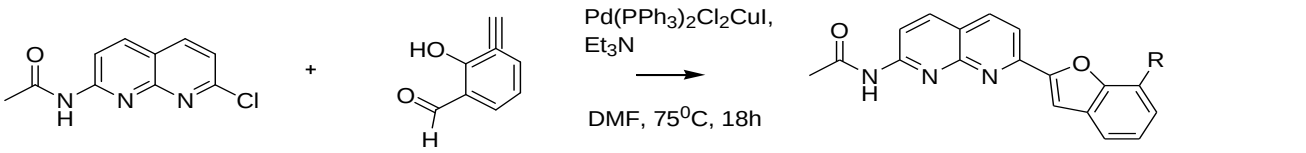
The development of fluorescent sensors with high selectivity and sensitivity for heavy and transition metal ions has always been of particular interest[71]. As mercury and its derivatives are widely used in industry and they have inherent high toxicity, the detection of Hg^{2+} is attracting particular attention[72,73]. Some fluorescent Hg^{2+} sensors have been explored[74], including polymers[75], foldamers[76], biomolecules[77-79], and small

molecules[80-82]. Nanoparticles of organic materials could have interesting applications in the pharmaceutical field because the microemulsions can be potential systems for drug delivery[83]. Nanospheres and nanocapsules are already used to entrap a drug or adsorb it[84-86]. Organic π-conjugated molecules play special and key roles in conductance,superconductance, magnetic, optical, and photo-electronic conversion, and luminescence[87].

Carotenoids nanoparticals is used as active compounds in pharmaceuticals and cosmetics or as coloring agents in the foodstuffs and animal feeds[88-91]. Monitoring pH in biological tissue or cells *via* fluorescence spectroscopy has become a widespread research area, including fluorescent nanoparticles with physically[92,93] or covalently entrapped dyes[94-97] and fiber-optics[98,99]. The nanosensors are based on materials such as polyacrylamide[92,94,97,99], silica[93], phospholipid-coated or amino-modified polystyrene[95,96] and methacrylate hydrogels[98].

Among the nanostructures formed by the self-assembly of specifically designed molecules,has proved to be particularly interesting for applications such asnanowires, gels, and biomemetic systems[100,51].

It has been shown that 2-acetamino-1,8-naphthyridine (AN) derivatives bind via triple hydrogen bondings with guanine (G)[101] preferably over other nitrogenous bases of adenine, cytosine, thymine, and uracil. This property of AN-G complexation has been demonstrated in supramolecular chemistry[113], HPLC separation[102], molecular sensing[103], and mapping of the guanine sequence in DNA[104]. For the development of molecular sensors having the core structure of naphthyridine[105], Yeh-Yang sun and their group intended to prepare 2-acetamido-7-(3-formyl-2-hydroxyphenyl) ethynyl-1,8-naphthyridine (compound **X**) via the Sonogashira coupling reaction5 of 2-acetamido-8-chloro-1,8- naphthyridine1bwith3-ethynyl-2-hydroxybenzaldehyde.



ABAN

Scheme-10 : Synthesis of the Benzofuran-Naphthyridine Linked Compound ABAN.

Among a variety of nanostructured materials, nanoparticles have attracted much attention because of their wide-spread applications in biology[106], for example Au- or conjugated Au- nanoparticles are fabricated and applied for monitoring bioreactions[107] and recognition of biomolecules[108]. Other applications include detection of hazardous organic and radioactive materials[109], toxic cations and anions[110], and pH[111]. Due to their intrinsic localized surface plasmon (LSP) resonance, photophysical and electrochemical properties, metal nanoparticles are widely explored for the development of colorimetric[107, 109a, 109b, 109c, 110c, 111], fluorometric[108d, 108c, 110a, 110b, 110d] and electrochemical [108a, 113a] sensors. Up to now, nanoparticles that consist of metals e.g. Au and Au-conjugates[107-110], Ag[112], Pd[113], inorganic semiconductors[114], (e.g. PbS, ZnS, CdS, CuS, CdSe), metal oxides or metal oxide composites[115], and silica[116] have been widely reported. A few reports are available on nanoparticles of transition metal complexes[117], and coordination polymers[118], where the morphology of the nano- and microparticles of coordination polymers are generally controlled by employing different ligating solvents which block the growth of the particle in some direction[118a,118d,117c].

Rhenium-complexes are extensively studied because of their outstanding photophysical and electrochemical properties[119] and found a wide range of applications as functional materials such as in OLED[120], in opto-electronic polymers[121], and in biology for binding proteins[122], and DNA[123], for biological labeling[124], and as biological probe[125]. Rhenium complexes also demonstrated the ability to sense cations and anions[126], pH[127], oxygen[128] and selective molecular recognition[129].

Surprisingly, studies on the formation of micro- or nanoparticles based on rhenium complexes are lacking so far. Only our group has previously revealed that Re(I) metallacyles undergo aggregation induced emission enhancement[130], thus, an efficient methodology for the fabrication of micro- or nanoparticles and demonstration of their application for sensing purposes will add new tools for the materials scientists.

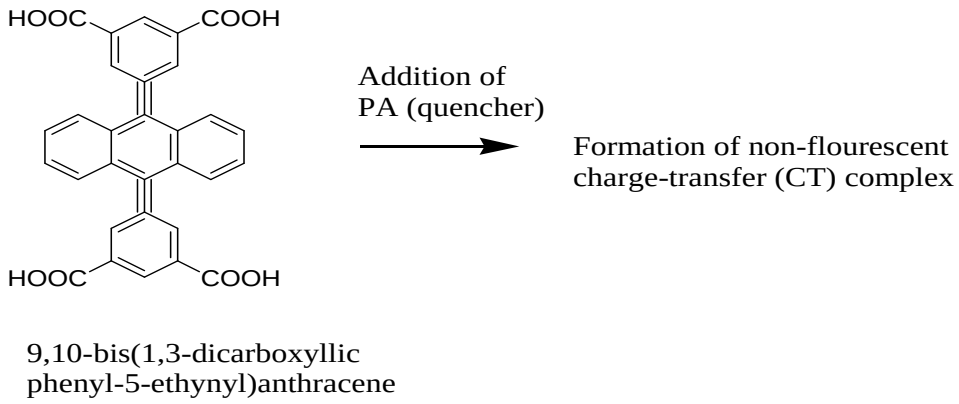
1.8. Nitroaromatic compounds and their detection

Nitroaromatic compounds (NAC) such as trinitrotoluene (TNT), dinitrotoluene (DNT), and picric acid (PA) are considered as environmental contaminants and toxic to living organisms[131-133]. They are well-known primary constituents of many unexploded land mines worldwide and used as dyes, pesticides and explosives and the factory sites that produce such chemicals are highly contaminated with these substances. Further, soil and groundwater of war zone and military facilities can contain toxic levels of these compounds and their degradation products. Polymers[134], siloles[135], metallo-porphyrins[136] and aromatic compounds containing fused ring systems[137] are already reported to show efficient NACs sensing ability. Beside these various fluorescent chemosensors, fluorescent polymers, and nanoparticles have been developed for detection of nitroaromatics[8,138-151]. The concern over the adverse effects of nitroaromatics on environment and health provide the sufficient impetus to develop cost efficient, selective, portable, fast, and sensitive method for detection of nitroaromatics[152-154] Currently, a wide range of instrumental techniques are being employed to detect explosives such as TNT (2,4,6-trinitrotoluene), DNT (2,4-dinitrotoluene) and PA (picric acid), which are the primary constituents of many unexploded land mines worldwide[155]. Among these competing methods, fluorescence quenching based detection of explosives has grown enormously owing to its high sensitivity, easy visualization and real-time monitoring with fast response time[156]

A few reports on florescence quenching of Re(I) metallacycles by aromatic nitro compounds are reported[157,158]. Herein we report a simple one-step method to

synthesize tetrarhenium metallacycles employing bis-benzimidazolylthiophene as a ditopic N-heterocyclic clip and 1,4-dihydroxy- and 1,2,4-trihydroxy-9,10-anthraquinones as bis-chelating bridging ligands. We also document a simple precipitation methods for the fabrication of micron-sized particles of the synthesized matallacyles and their ability to sense nitroaromatic compounds.

Bappaditya Gole and coworkers[159] synthesized a p-electron rich supramolecular polymer 9,10-bis(1,3-dicarboxyllicphenyl-5-ethynyl)anthracene and their analogues which are used as chemosensor for detection of nitroaromatic explosives such as TNT and PA both insolutions aswell as in thin-film. They report that the incorporation of ethynyl groups enriches π-conjugation in 9,10-bis(1,3-dicarboxyllicphenyl-5-ethynyl)anthracene and thereby they exhibit strong fluorescence emission and also observed that the emission intensity is reduced because of theformation of a non-fluorescent charge-transfer (CT) complex between the electron donor (fluoro-phore) and the electronacceptor (quencher).



Scheme-11 : Quenching of 9,10-bis(1,3-dicarboxyllicphenyl-5-ethynyl)anthracene by Picric acid.

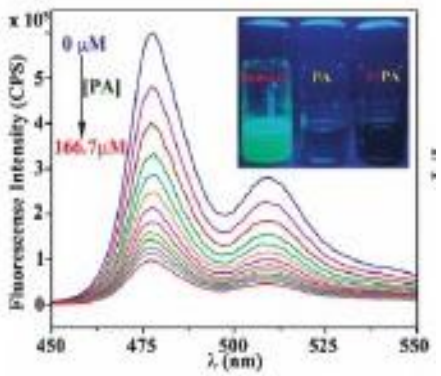


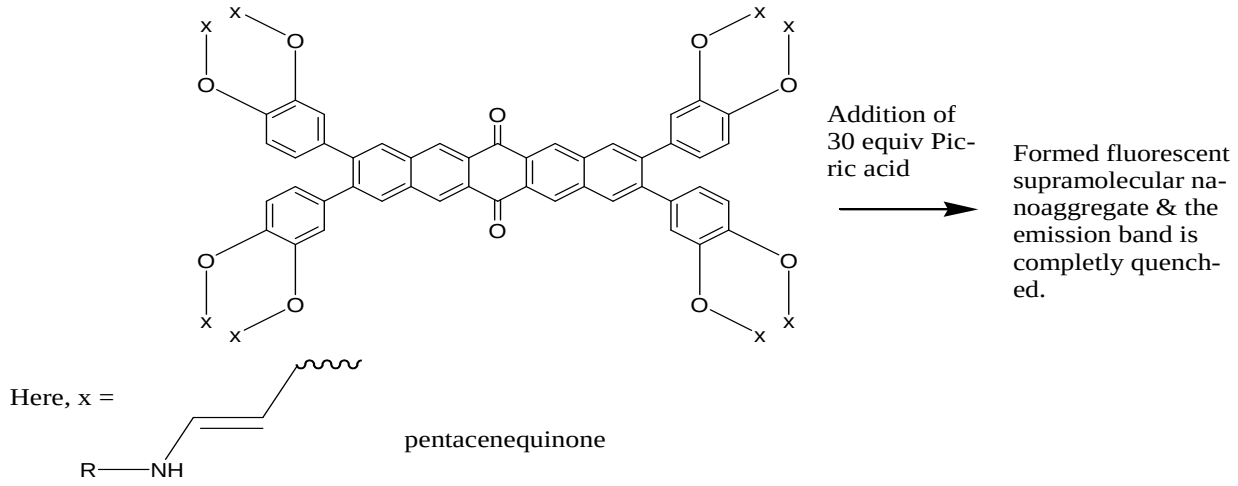
Figure-19 : Reduction in the emission intensity of compound 9,10-bis(1,3-dicarboxylicphenyl-5-ethynyl)anthracene upon gradual addition of PA.

New triphenylene derivatives was synthesized by Vandana and coworkers[160] by using a Suzuki–Miyaura coupling protocol and by a click reaction respectively, serve as potent chemosensors for various electron deficient nitroaromatic explosives, such as picric acid, trinitrotoluene, dinitrotoluene and dinitrobenzene.

Pyrene-functionalized Ru nanoparticles were synthesized by Chen W and coworkers[161] by olefin metathesis reactions of carbene-stabilized Ru nanoparticles with 1-vinylpyrene and 1-allylpyrene (the resulting particles were denoted as Ru=VPy and Ru=APy, respectively) and they examined this sensitive chemosensors for the detection of nitroaromatic compounds, such as 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 1-chloro-nitrobenzene (CNB), and nitrobenzene (NB), by their effective quenching of the nanoparticle fluorescence. They was found that the detection sensitivity increased with increasing nitration of the molecules.

Recently, several fluorescent conjugated polymers[162] and fluorescent nanofibers obtained by molecular self-assembly have been reported as sensing materials for detection of nitroaromatic explosives[163-165] Vandana Bhalla and coworkers reported that pentacenequinone derivative forms fluorescent supramolecular nanoaggregates[11]

in aqueous media that selectively sense picric acid in solution phase[166]. They have chosen pentacenequinone moiety as the motif for preparation of luminescent supramolecular aggregates because of the tendency of 6,13-pentacenequinones to form ordered thin films which make them good candidates for preparation of organic electronic devices[167-169].They carried out fluorescence studies of compound pentacenequinone with picric acid.The following scheme shows that Upon addition of 30 equiv of picric acid, the emission band of pentacenequinone (1.0×10^{-5} M) at 515 nm in toluene/DCM (8:2) is completely quenched.



Scheme-12 : fluorescence studies of compound pentacenequinone with picric acid.

Aniruddha Kundu and coworkers[170] reported on their paper that there is a drastic decrease in PL intensity on addition of nitroaromatics to the GMCO (graphene oxide–methyl cellulose hybrid) system and it is very large (91%) for the addition of picric acid. Thus, the hybrid system acts as a good sensor for the detection of nitro aromatics by instantaneous photoluminescence quenching with a detectable limit of 2 ppm.

Fang Q and coworkers[171] report that an inverted opal fluorescence chemosensor for the ultrasensitive detection of explosive nitroaromatic vapors through resonance-energy-transfer-amplified fluorescence quenching.They fabricated the inverted opal silica film

with amino ligands by the acid-base interaction between 3-aminopropyltriethoxysilane and surface sulfonic groups on polystyrene microsphere templates. Then they chemically anchored the fluorescent dye onto the interconnected porous surface to form a hybrid monolayer of amino ligands and dye molecules and observed that amino ligands can efficiently capture vapor molecules of nitroaromatics such as 2,4,6-trinitrotoluene (TNT) through the charge-transfer complexing interaction between electron-rich amino ligands and electron-deficient aromatic rings.

A sensitive electrochemical sensor has been fabricated by Zang J. and coworkers[172] to detect ultratrace nitroaromatic explosives using ordered mesoporous carbon (OMC) and they reported that as low as 0.2 ppb TNT, 1 ppb 2,4-dinitrotoluene and 1 ppb 1,3-dinitrobenzene can be detected on OMC based electrodes.

Content S and coworkers[173] detect nitroaromatic molecules in air by the quenching of the photoluminescence of porous silicon (porous Si) films. They achieved the detection by monitoring the photoluminescence (PL) of a nanocrystalline porous Si film on exposure to the analyte of interest in a flowing air stream. They quenched the photoluminescence on exposure to the nitroaromatic, presumably by an electron-transfer mechanism and observed detection limits of 500 parts-per-billion (ppb), 2 ppb, and 1 ppb for nitrobenzene, 2.4-dinitrotoluene (DNT), and 2,4,6-trinitrotoluene (TNT), respectively (exposure times of 5 min for each, in air).

1.9. Benzimidazole

Benzimidazole is a bicyclic aromatic compound involves the fusion of a fundamental structural characteristic of six-member benzene fused to five member imidazole.

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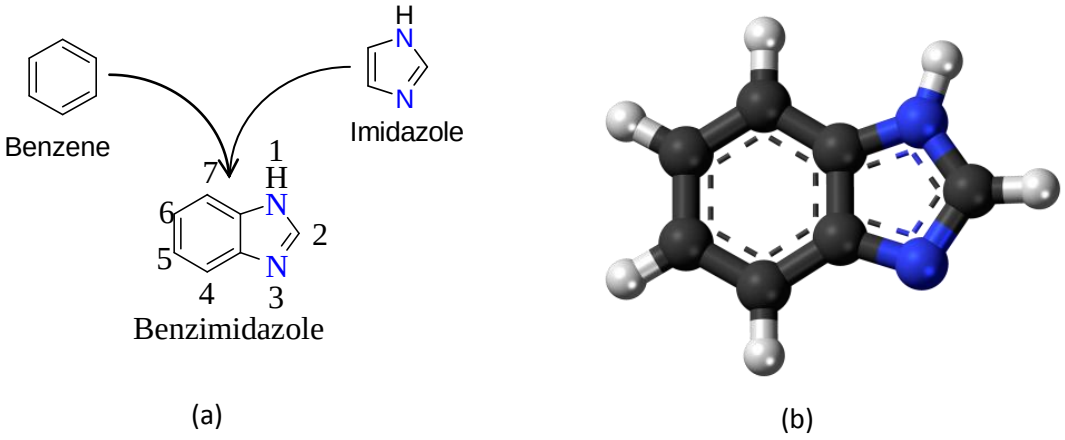


Figure-20 : The Benzimidazole skeleton is the fusion of benzene and imidazole (a), 3D structure of Benzimidazole (b).

This basic '6+5' heterocyclic structure is shared by another class of chemical compounds, the purines. Among the members of this group are several very well-known and important biomolecules, such as adenine and guanine, two of the four nucleic acid bases, uric acid, and caffeine[9].

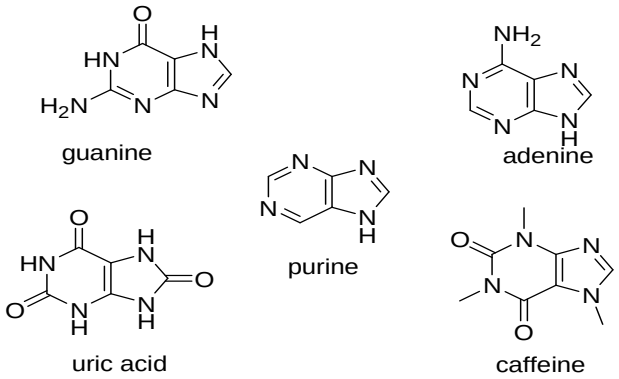


Figure-21 : Purines, which include some of the most well-known biomolecules, share the '6+5' heterocyclic structure with benzimidazoles.

From this fundamental structural similarity, it is not too surprising that benzimidazole containing molecules and benzimidazole derivatives have been found to be biologically active small molecules, such as vitamin B_{12} and a variety of antimicrobial, antiparasitic, and even antitumor agents[9,10].

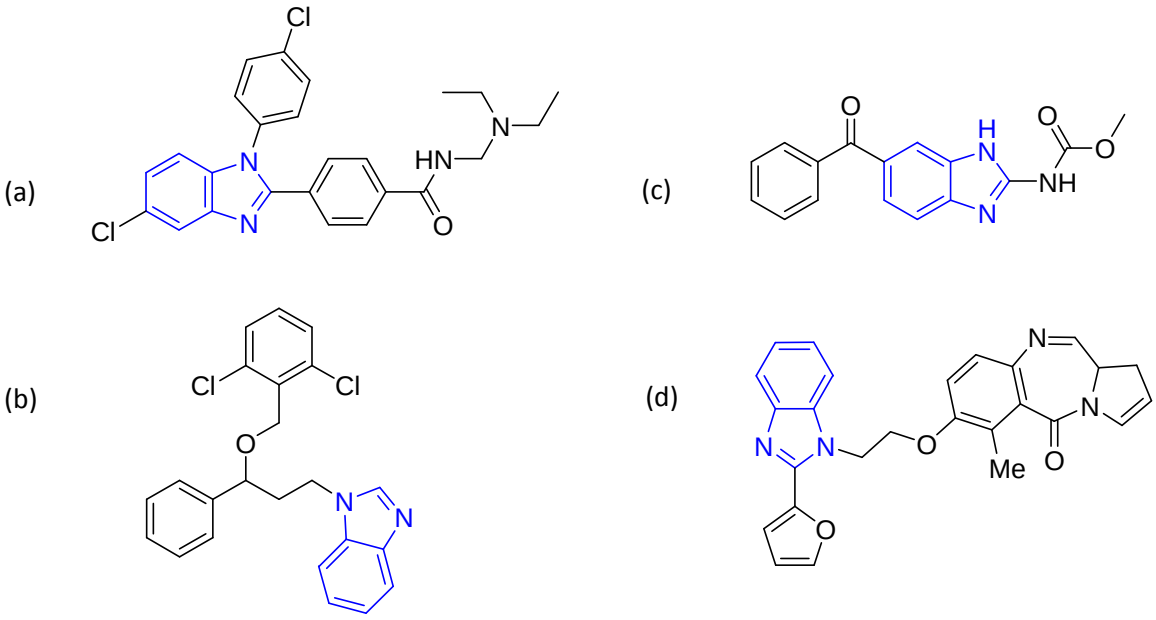
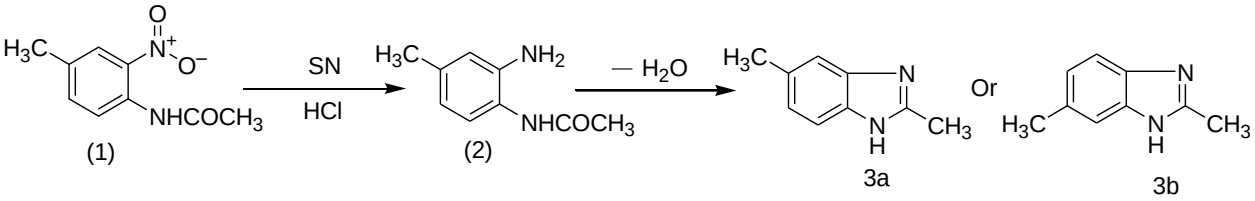


Figure-22 : Examples of antimicrobial (a, b), antiparasitic (c), and antitumor agents (d) containing the Benzimidazole moiety (colored blue).

Aside from their place in biomedical research, benzimidazoles also have a prominent place in organocatalysis, organometallic[174], and materials chemistry[175] for two reasons stemming from their molecular architecture: the imidazole is a precursor to N-heterocyclic carbenes; and the benzene ring provides a convenient scaffold to which additional functionality may be easily added to modify the spatial and electronic characteristics of a benzimidazole derivative.

1.9.1. Synthesis of benzimidazole

The benzimidazole nucleus does not appear to occur very widespread in nature. Historically, the first benzimidazole was prepared in 1872 by Hoebrecker, who obtained 2,5 (or 2,6) di-methyl-benzimidazole (3) by the reduction of 2-nitro-4-methyl-acetanilide (1). Several years later Ladenburg obtained the same compound by refluxing 3, 4-diaminotoluene with acetic acid[176].



Scheme-13 : Synthesis reaction of first synthesized benzimidazole.

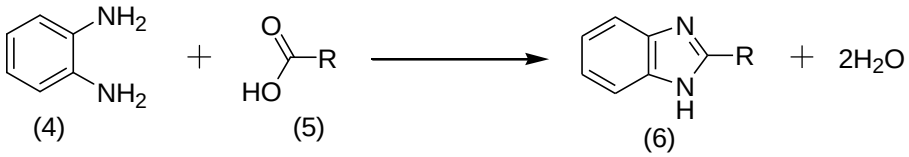
A number of methods developed for the synthesis of benzimidazole derivatives, which include conversion of esters using an aluminum reagent, the reaction between N-ethoxycarbonylthioamides with 1,2-diamines, the reaction of an appropriate 1,2-phenylenediamine with carboxylic acid and its derivative, nitriles, or orthoesters in the presence of a strong acid at elevated temperature. Recently, several methods had introduced, where aldehydes, acid chloride, o-dinitrobenzene, Gold's reagent, and 2-nitroanilines are used as starting materials for this synthesis. Brain and coworker developed a new procedure for the preparation of these compounds by palladium-catalyzed aryl-amination chemistry. Although these methods are suitable for certain synthetic conditions, sometimes, there exist some drawbacks such as long reaction time, high temperature, low yields of products in some cases, use of an additional microwave oven, corrosive reagents and large amounts of solid supports which would eventually result in the generation of a large amount of toxic waste. Moreover more than one step is involved in the synthesis of these compounds in some procedures.

Some common synthetic procedures for benzimidazoles [176].

A. From by Reaction o-phenylenediamine with Carboxylic Acids

a. Monobasic Acids

O-phenylenediamines reacts readily with most carboxylic acids to give 2-substituted benzimidazoles, usually in very good yield. The reaction is carried out usually by heating the reactants together on a steam bath, by heating together under reflux or at an elevated temperature or by heating in a sealed tube.

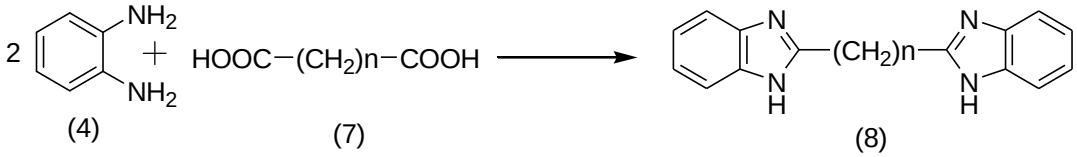


(4) (5) (6)

Scheme-14: Synthesis reaction of benzimidazole from monobasic acids.

b. Dibasic Acids

When dibasic acids react with o-phenylenediamine the products formed depend on the mole ratio of the reactants and the experimental conditions. Two or more moles of the o-phenylenediamines are heated with one mole of the dibasic acid to give bisbenzimidazole as the product.



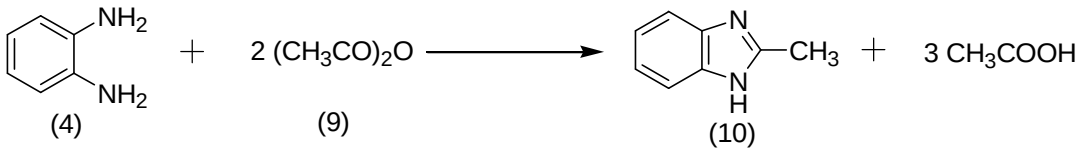
(4) (7) (8)

Scheme-15: Synthesis reaction of Benzimidazole from dibasic acid.

B. By Reaction with acid Anhydrides

a. Anhydrides of Monobasic Acids

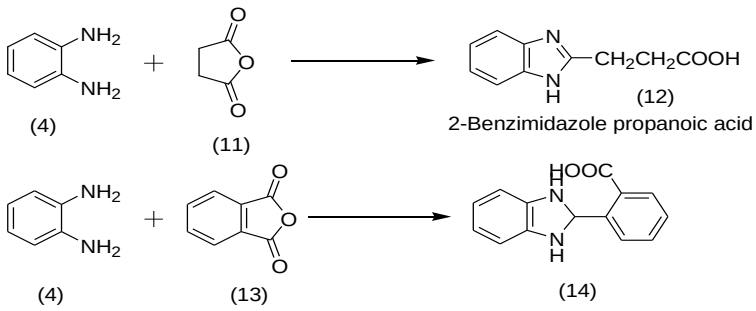
The reaction of acid anhydrides and o-phenylenediamine will lead to benzimidazoles or to N, N'-diacylphenylenediamines depending on the conditions employed. It was formerly thought that o-phenylenediamine yield benzimidazoles with acids and diacyl derivatives with acid anhydrides; however, this was shown to be incorrect. Time appears to be a decisive factor and if the refluxing is continued long enough benzimidazoles may be obtained, usually in good yield. O-phenylenediamines when heated under reflux for several hours with acetic anhydride is completely converted to 2-methylbenzimidazole.



Scheme-16 : Synthesis reaction of benzimidazole from anhydrides of monobasic acid.

b. Anhydrides of Dibasic Acids

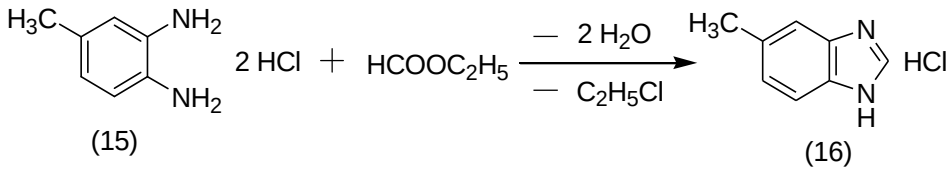
The anhydrides of dibasic acids react as monobasic acids; for example, succinic anhydride with o-phenylenediamines gives β-(2-benzimidazole) propionic acid (12) & phthalic anhydride gives o-(2-benzimidazole) benzoic acid (14). In several cases amides or phthalanils have been obtained as byproducts[10].



Scheme-17 : Synthesis reaction of benzimidazole derivatives from the anhydrides of dibasic acids.

C. By Reaction with Esters

Reaction of o-phenylenediamine with esters also yields benzimidazoles. Von Niementowski first investigated the reaction of esters and o-phenylenediamine to give benzimidazoles. Equimolecular amounts of 3, 4-diaminotoluene dihydrochloride and ethyl formate when heated in a sealed tube for 3 hr. at 225°C give 84 per cent of 5(or 6)-methylbenzimidazole hydrochloride.

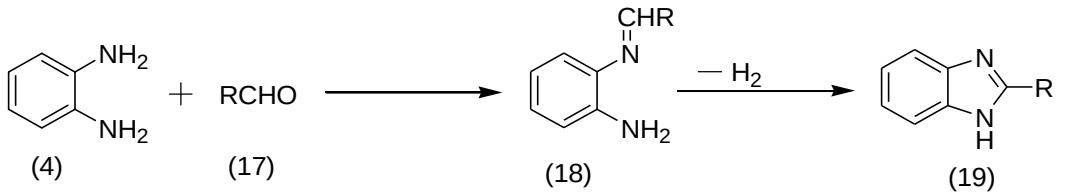


(15) (16)

Scheme-18 : Synthesis reaction of benzimidazole derivatives by the esters.

D. By Reaction with Aldehydes

Under the correct conditions aldehydes may react with o-phenylenediamines to yield 2-substituted benzimidazoles.



(4) (17) (18) (19)

R= phe, phe-derivatives

Scheme-19 : Synthesis of Benzimidazole derivatives by aldehydes.

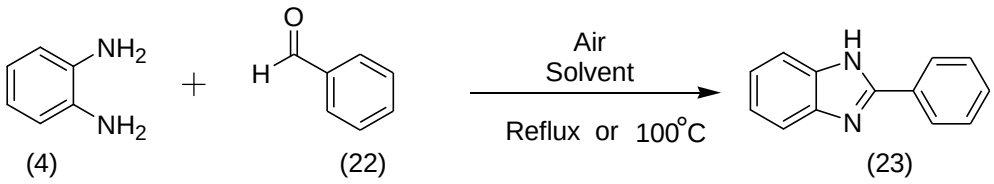
Since an oxidation is involved, the reaction is best carried out under oxidative conditions. This oxidation may be brought about by the air or, more conveniently, by the use of other oxidizing agents such as cupric acetate. This latter reagent was first introduced by Weidenhagen.

E. Synthesis of 2-Substituted Benzimidazoles

The widespread interest in benzimidazole-containing structures has prompted extensive studies for their synthesis of 2-substituted benzimidazoles. One is the coupling of phenylenediamines and carboxylic acids or their derivatives (nitriles, imidates, or ortho-esters), which often requires strong acidic conditions, and sometimes combines with very high temperatures (i.e., PPA, 180°c) or the use of microwave irradiation[177]. The other way involves a two step procedure that includes the oxidative cyclo-dehydrogenation of aniline Schiffs bases, which are often generated in situ from the condensation of phenylenediamines and aldehydes.

(1) Direct One-Step Air Oxidation Procedure[178]

In this method, various benzimidazoles are synthesized from phenylenediamines and aldehyde using air as the oxidant. The reaction scheme involves:



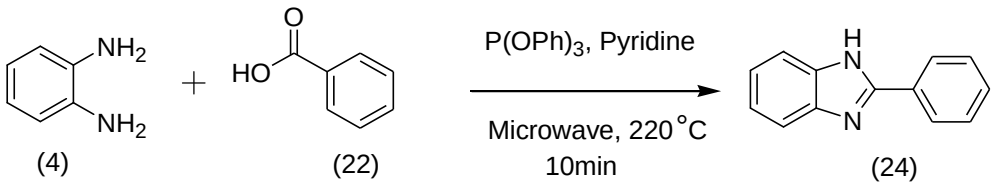
(4) (22) (23)

Scheme-20 : Synthesis reaction of 2-substitued benzimidazole derivatives.

The salient features of this method include a simple procedure, mild conditions, no coupling agents or commercial oxidants/additives used, no waste produced (only by-product being water), easy purification, and high generality.

(2) Microwave Assisted One Step High Throughput Synthesis Process[179]

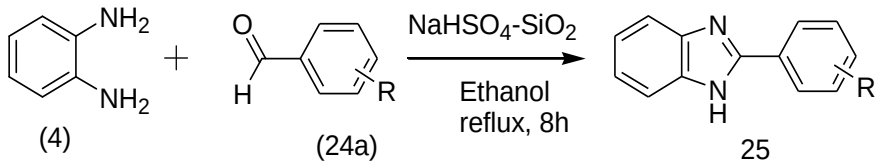
In this process, various benzimidazoles are synthesized from diamines and carboxylic acids under microwave irradiation condition. The reaction scheme involves:



Scheme-21 : Synthesis reaction of benzimidazole derivatives through microwave-assisted process.

(3) $NaHSO_4$-SiO_2 Promoted Synthesis Process[180]

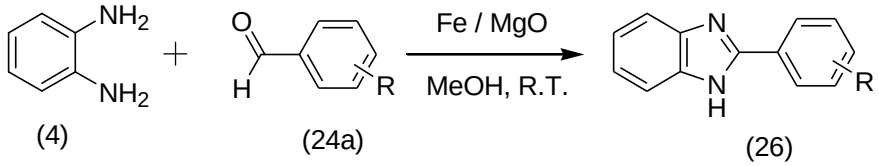
A library of benzimidazole derivatives have been prepared through the reaction of o-phenylenediamine and aldehydes in the presence of catalytic amount of silica supported sodium hydrogen sulphate ($NaHSO_4$-SiO_2) under refluxing in ethanol solvent to obtained excellent yields. This method is simple, convenient, environmental friendly, reusable, efficient and practical.



Scheme-22: Synthesis reaction of $NaHSO_4$-SiO_2 Promoted Synthesis of benzimidazole derivatives.

(4) Cyclization–Oxidation processes[181]

A convenient and straight forward method has been developed for the synthesis of benzimidazole using aryl aldehydes and o-phenylene diamine in the presence of Fe containing Magnesium oxide (Fe/MgO), at room temperature. The salient feature of this method includes mild condition, short reaction time, high yield, easy purification, recyclable catalyst, large scale synthesis and simple procedure. The catalyst can be reused for several cycles without decrease in activity.

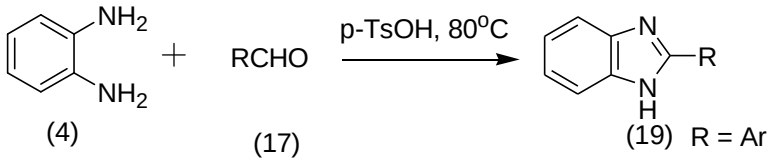


(4) (24a) (26)

Scheme-23 : Synthesis reaction of benzimidazole derivatives through cyclization-oxidation.

(5) p-TsOH Catalyzed Synthesis Process[182]

p-TsOH (20 mol%) was used to be a catalyst for the synthesis of 2-arylsubstituted benzimidazoles efficiently. Simple and convenient procedure, easy purification and shorter reaction time are the advantageous features of this method.



(4) (17) (19) R = Ar

Scheme-24 : Synthesis reaction of benzimidazole derivatives through p-TsOH Catalyzed process.

1.9.2. Characteristics Shown by benzimidazole Derivatives

1.9.2.1. Biological Properties of benzimidazole

Benzimidazoles are remarkably effective compounds both with respect to their inhibitory activity and their favorable selectivity ratio. Extensive biochemical and pharmacological studies have confirmed that benzimidazole molecules are effective against various strains of microorganisms. Benzimidazoles are regarded as a promising class of bioactive heterocyclic compounds that exhibit a range of biological activities. Specifically, this nucleus is a constituent of vitamin-B_{12}. This ring system is present in numerous antiprotozoal[183], antihelmintics[184], anti-HIV[185], anticonvulsant[186], anti-inflammatory[187], antihepatic[188], antineoplastic[189] and antiulcer[190] activities. Now-a-days Infectious microbial diseases are causing problems world-wide, because of

resistance to number of antimicrobial agents (β-lactam antibiotics, macrolides, quinolones, and vancomycin). A variety of clinically significant species of micro-organisms has become health problem globally [191]. In particular, increasing drug resistance among Gram-positive bacteria such as *staphylococci*, *enterococci* and *streptococci* is a significant for health. One way to fight with this challenge is the appropriate usage of the available marketed antibiotics the other is the development of novel antimicrobial agents[192]. Hence, there will always be a vital need to discover new chemotherapeutic agents to overcome the emergence of resistance and ideally shorten the duration of therapy. Due to the structural similarity to purine, antibacterial ability of benzimidazoles are explained by their competition with purines resulting in inhibition of the synthesis of bacterial nucleic acids and proteins[193,194].

1.9.2.2. Photophysical Properties of benzimidazole Derivatives

Benzimidazole has been used as carbon skeletons for N-heterocyclic carbenes (NHCs), which is an extensiton of the well elaborated imidazole system. The NHCs are usually used as ligands for transition metal complexes. They are often prepared by deprotonating an N, N'-disubstituted benzimidazolium salt at the 2-position with a base[195,196]. The luminescence properties of benzimidazole have been extensively studied[197-200], but little work have been reported on substituted species. Thiabendazol and its major metabolite, 5-hydroxythiabendazole shows luminescence properties[201].

1.9.3. Application of benzimidazole & Its Derivatives

Benzimidazoles are the important among the heterocyclic compounds found in several natural and non-natural products such as Vitamin B_{12}[202], marine alkaloid kealiquinone[203], benzimidazole nucleosides[204] etc. Some of their derivatives aremarketed as anti-fungal agents such as Carbendazim[205],anti-helmintic agents such as Mebendazole and thiabendazole[206] and anti-psychotic drug such as Pimozide[207] and other derivatives have been found to possess some interesting bioactivities such as anti-tubercular[208], anti-cancer[209] etc. Besides these applications benzimidazole

derivatives also used in the treatment of HBV infection, in suppressing the proton pump function, and in the textile industry[210]. A large number of patents describe benzimidazole derivatives of use in the textile industry as wetting, emulsifying, foaming, or softening agents or as dispersants for use in dyeing. In the main, these compounds are sulfonated benzimidazoles. Another use is in the treatment of fibers to improve whiteness of the undyed material or as optical bleach. A number of aminobenzimidazoles have been used for the preparation of sulfur and azo dyes of use in the textile industry. Another use has been in the preparation of fluorescent dyes for use in such preparations as inks for marking clothes to be dry-cleaned. Benzimidazole derivatives have wide range of biological actions & industrial applications.

Research on suitable chemical sensors with high sensitivity forthe detection of explosives has attracted much attention in recent time for wide applications in security screening and environment monitoring [211]. Currently, a wide range of instrumental techniques are being employed to detect explosives such as TNT (2,4,6-trinitrotoluene), DNT (2,4-dinitrotoluene) and PA (picric acid), 1-chloro-4-nitrobenzene, which are the primary constituents of many unexploded land mines worldwide[212]. Among these competing methods, fluorescence quenching based detection of explosives has grown enormously owing to its high sensitivity, easy visualization and real-time monitoring with fast response time[213]. The benzimidazole ring is an important pharmacophore in modern drug discovery. In recent years, attention has increasingly been given to the synthesis of benzimidazole derivatives. The synthesis of novel benzimidazole derivatives remains a main focus of medicinal research. Recent observations suggest that benzimidazoles derivatives show easy interactions with nitro-aromatic compound and act as sensor for them. Since now, researchers have been attracted toward designing more potent benzimidazole derivatives having wide diverse of biological activity.

So the objectives of my research can be summarized as following:

1. To synthesis a series of novel benzimidazole derivatives having biological as well as photo physical properties.
2. Synthesis of tetrarhenium complexes applying the benzimidazole derivatives obtained.
3. Nanomaterials fabrication of the benzimidazole derivatives and tetrarhenium complexes.
4. To Study of their photophysical properties (binding and quenching with nitro-aromatic compound).
5. Evaluation of the potency/efficiency of these compounds as sensor for nitro-aromatic compounds.
6. To apply these compounds as chemical sensor.

3.1. Materials and Methods

Caution : Picric acid is explosive in nature and should be handled in small quantities. It also forms shock-sensitive compounds with heavy metals. All reagents were purchased commercially and were used as received without further purification. Tetrahydrofuran (THF) and dichloromethan (DCM) used in this study was of spectroscopic grade and deionized water was used throughout the experiment. Prior to use, the solvents were checked for spurious emissions in the region of interest and found to be satisfactory. ^{1}H NMR spectra were measured on Bruker AC 300 and AMX-500 FT-NMR spectrometers. Infrared spectra were recorded on a Perkin-Elmer Paragon 882 FT-IR spectrometer. Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. Mass data were obtained using a JEOL JMS-700 for FAB or Waters LCT-Premier XE for ESI. Scanning electron microscopy (SEM) experiments were carried out in a JSM-5400 scanning microscope to examine the morphology and microstructure of the aggregated samples. Electronic absorption spectra were recorded on a UV-1700 spectrophotometer. Emission spectra were obtained in THF and DCM solution at ambient temperature with a Hitachi F7000 fluorescence spectrophotometer.

3.2. Synthesis

3.2.1. Synthesis of 1,3-bis(benzimidazolyl)benzene (compound L-1)

1,3-bis(benzimidazolyl)benzene was synthesized following a literature procedure[214] and the product was obtained as brown powder. The melting point of the compound was 250-255^{o} c.

3.2.2. Synthesis of 1,3-bis(1-butylbenzimidazol-2-yl)benzene (compound L-2)

1,3-Bis(2´-benzimidazolyl)benzene (4.00 g, 12.9 mmol) in DMSO (80.0 mL) was cooled to 8 °C on an ice-water bath, KOH (7.20 g, 128.8 mmol) was added, during which, the bath temperature was maintained at 8 ^{o}C. The mixture was stirred for 15 min, 1-bromobutane (8.82 g, 64.4 mmol) was added and the solution then allowed to reach room

temperature and left for 24 h. The mixture was diluted with water (200 mL) and the solution extracted with dichloromethane (2 × 200 mL). The combined organic layer was washed with water (2 × 200 mL), dried ($MgSO_4$), filtered and evaporated under reduced pressure and purified by flash column chromatography on silica gel with hexane-ethylacetate as the eluent, to give a colorless solid (4.86 g, 11.5 mmol, 89%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 0.67 (t, 6H, J = 6.9 Hz, CH_3), 1.05 (sextet, 4H, J = 7.5 Hz, –CH_2–CH_3), 1.59 (quintet, 4H, J = 7.5 Hz, –CH_2–CH_2–CH_3) 4.08 (t, 4H, J = 7.5 Hz, –CH_2–$(CH_2)_2$–CH_3), 7.08 (m, 4H, ArH), 7.23 (m, 2H, ArH), 7.50 (m, 1H, ArH), 7.67 (m, 4H, ArH), 7.92 (s, 1H, ArH). MS (ESI$^+$): *m/z* 423.5 (M + H$^+$). Anal. calcd for $C_{28}H_{30}N_4$.0.5 H_2O: C, 78.02; H, 7.25; N, 12.99. Found: C, 78.21; H, 7.33; N, 13.01.

3.2.3. Synthesis of 2,5-bis(1-butylbenzimidazol-2-yl)thiophene (compound L-4)

2,5-Bis(2′-benzimidazolyl)thiophene (4.00 g, 12.6 mmol) in DMSO (80.0 mL) was cooled to 8 °C on an ice-water bath, KOH (7.10 g, 126.4 mmol) was added, during which, the bath temperature was maintained at 8 ^{o}C. The mixture was stirred for 15 min, 1-bromobutane (12.21 g, 63.2 mmol) was added and the solution then allowed to reach room temperature and left for 24 h. The mixture was diluted with water (200 mL) and the solution extracted with dichloromethane (2 × 200 mL). The combined organic layer was washed with water (2 × 200 mL), dried ($MgSO_4$), filtered and evaporated under reduced pressure and purified by flash column chromatography on silica gel with hexane-ethylacetate as the eluent to give an yellowish solid (4.86 g, 11.5 mmol, 89%, m.p. 105-107^o c). For $C_{26}H_{30}N_4S$: C, 75.51; H, 8.20; N, 10.36; S, 5.93%. Found: C, 70.1456; H, 6.5934; N, 12.4661; S, 8.0406%.

3.2.4. Synthesis of 2,5-bis(1-octylbenzimidazol-2-yl)thiophene compo- und L-5)

2,5-Bis(2′-benzimidazolyl)thiophene (4.00 g, 12.6 mmol) in DMSO (80.0 mL) was cooled to 8 °C on an ice-water bath, KOH (7.10 g, 126.4 mmol) was added, during which, the bath temperature was maintained at 8 ^{o}C. The mixture was stirred for 15 min, 1-bromooctane (12.21 g, 63.2 mmol) was added and the solution then allowed to reach room temperature and left for 24 h. The mixture was diluted with water (200 mL) and the solution extracted with dichloromethane (2 × 200 mL). The combined organic layer was washed with water (2 × 200 mL), dried ($MgSO_4$), filtered and evaporated under reduced pressure and purified by flash column chromatography on silica gel with hexane-ethylacetate as the eluent to give an yellowish solid (4.86 g, 11.5 mmol, 89%). ^{1}H NMR: (300 MHz, $CDCl_3$): 0.83 (t, 6H, J = 7.0), 1.23-1.40 (m, 20H), 1.93 (quintet, 4H, J = 7.5 Hz), 4.42 (t, 4H, J = 7.5 Hz), 7.28-7.33 (m, 4H), 7.37-7.40 (m, 2H), 7.67 (s, 2H), 7.79-7.82 (m, 2H). Cald. For $C_{34}H_{44}N_4S$: C, 75.51; H, 8.20; N, 10.36; S, 5.93%. Found: C, 75.23; H, 8.35; N, 9.95; S, 5.8%. m/e (ES): 541.3 (M^{+} + H).

3.2.5. Synthesis of $[\{Re(CO)_3\}_2(\mu\text{-dhaq})(\mu\text{-1})]_2$ (compound L-6)

A suspension consisting of a mixture of $Re_2(CO)_{10}$ (0.130 g, 0.20 mmol), 1,4-dihydroxy-9,10-anthraquinone (H_2-dhaq, 0.053 g, 0.22 mmol), and L-5 (0.088 g, 0.21 mmol) in *p*-xylene (6 mL) was sealed in a Teflon-lined stainless steel autoclave. The autoclave was placed in an oven maintained at 160 °C for 48 h and then cooled to room temperature to afford black colored crystalline products (0.19 g, 0.079 mmol, 79%). ^{1}H NMR (500 MHz, THF-d^8): 0.75 (12H, t, J = 7.0 Hz, Me), 1.1-1.29 (32H, m), 1.35-1.47 (8H, m), 1.69-1.79 (4H, m, underneath THF), 1.80-1.90 (4H, m),2.26 (s, Me, *p*-xylene guest) 4.17-4.27 (8H, m), 6.86 (4H, s, $H^{5,6}$-bBImth), 7.01 (s, *p*-xylene guest), 7.27-7.29 (8H, dd, 5.9, 3.2, $H^{2,3}$-bBImth), 7.54-7.56 (4H, dd, 5.9, 3.2, H^{4}-bBImth), 7.75 (4H, s, $H^{1,2}$-dhaq), 7.92-

7.94 (4H, dd, 5.8, 5.3, $H^{4,5}$-dhaq), 8.54-8.56 (4H, dd, 5.9, 3.2, H^{1}-bBImth), 8.63-8.65 (4H, dd, 5.8, 5.3, $H^{3,6}$-dhaq) IR (KBr, pellet, cm^{-1}): ν_{CO} 2012.1 (s), 1906.7 (s), 1875.5 (s). MS (FAB, ^{187}Re): *m/z* 2637.2 (M^{+} - H). Anal. Calcd for $C_{108}H_{100}N_8O_{20}S_2Re_4$. 0.5 C_8H_{10}: C, 49.97; H, 3.93; N, 4.16; S, 2.38%. Found: C,49.76; H,4.02; N,4.20; S, 2.36%. UV-vis (10^{-5} M, THF, nm): λ_{max} 231, 281, 403 (MLCT), 609, 661. Emission (THF, nm): λ_{max} 470.

3.2.6. Synthesis of $[\{Re(CO)_3\}_2(\mu\text{-thaq})(\mu\text{-1})]_2$ (compound L-7)

Complex L-7 was synthesized followed a procedure similar to that for 23a using H_2-thaq(1,2,4-trihydroxy-9,10-anthraquinone) instead of H_2-dhaq(1,4-dihydroxy-9,10-anthraquinone). Yield: 80% (0.21 g, 0.080 mmol). ^1H NMR (500 MHz, THF-d8): 0.77 (12H, t, J = 7.2 Hz, Me), 1.18-1.32 (32H, m), 1.35-1.55 (8H, m), 1.69-1.79 (4H, m, underneath THF), 1.85-2.0 (4H, m),2.28 (s, Me, *p*-xylene guest) 4.20-4.30 (8H, m), 6.77 (4H, s, $H^{5,6}$-bBImth), 7.01 (s, *p*-xylene guest), 7.26-7.35 (8H, m $H^{2,3}$-bBImth), 7.52-7.63 (4H, m, H^{4}-bBImth), 7.76-7.80 (4H, m, $H^{1,2}$-dhaq), 7.89-7.97 (4H, m, $H^{4,5}$-dhaq), 8.60 (2H, s, dhaq)., 8.62-8.67 (4H, m, H^{1}-bBImth).IR (KBr, pellet, cm^{-1}): ν_{CO} 2012.7 (s), 1907.0 (s), 1877.0 (s). MS (FAB, ^{187}Re): *m/z* 2669.5 (M^{+} - H). Anal. calcd for $C_{108}H_{100}N_8O_{22}S_2Re_4.C_8H_{10}$: C, 50.17; H, 3.99; N, 4.03; S, 2.31%. Found: C,49.78; H,4.13; N,4.12; S, 1.99%. UV-vis (10^{-5} M, THF, nm): λ_{max} 221, 266, 408 (MLCT), 590, 638. Emission (THF, nm): λ_{max} 470.

3.3. Fabrication of nano particles

3.3.1. Fabrication of nano particles of compound L-6

Aggregates were fabricated by adding 0.5 mL of a stock solution of compound L-6 (2×10^{-4} M, THF) in round bottom flasks containing THF-water mixture of the required ratio (9.5 mL) with vigorous stirring for 30 min. at room temperature to give a final concentration of 1×10^{-5} M . For example, for a 40% water fraction 0.5 mL of the stock

solution of 7a (2×10^{-4} M, THF) was added to 9.5 mL of solvent mixture containing 5.7 mL THF and 3. 8 mL H_2O.

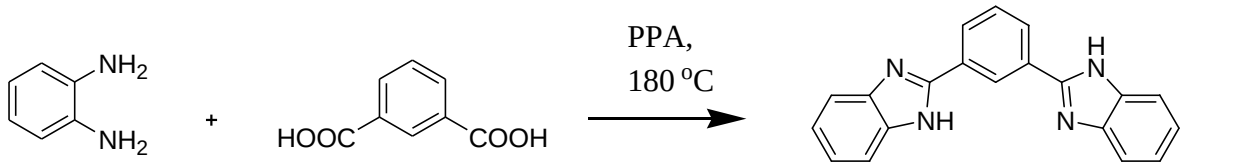
3.3.2 Fabrication of nano particles of compound L-7

Aggregates were fabricated by adding 0.5 mL of a stock solution of compound L-7 (1×10^{-4} M, THF) in round bottom flasks containing THF-water mixture of the required ratio (9.5 mL) with vigorous stirring for 30 min. at room temperature to give a final concentration of 0.5×10^{-5} M . For example, for a 40% water fraction 0.5 mL of the stock solution of 7a (2×10^{-4} M, THF) was added to 9.5 mL of solvent mixture containing 5.7 mL THF and 3. 8 mL H_2O.

4.1. Synthesis

Synthesis of compound L-1 and L-3

1,3-Bis(benzimidazolyl)benzene (L-1) was synthesized by reacting O-phenylenediamine (2 mole) with 1,3-benzenedicarboxylic acid (1 mole) in strong acidic condition and at very high temperature (i.e., PPA, 180^{o} C).Melting point of the compound was 250-255 °C (decompose).

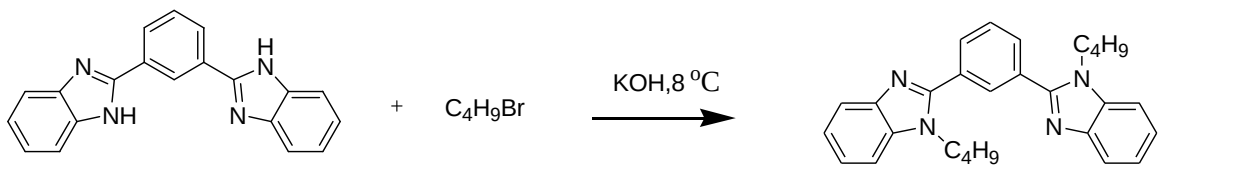


O-Phenylenediamine 1,3-Benzenedicarboxylicacid 1,3-Bis(benzimidazolyl)benzene (L-1)

Scheme-25 : Synthesis of L-1[1,3-bis(benzimidazolyl)benzene].

Synthesis of compound L-2

1,3-Bis(1-butylbenzimidazol-2-yl)benzene (L-2) was synthesized by reacting 1,3-bis(benzimidazolyl)benzene with 1-bromobutane in DMSO and KOH at 8°C for 24 h. In this process N-alkylation of both the secondary amino groups took place. The compound was extracted from DMSO-H_20 mixture with DCM. The combined DCM layers were dried over $MgSO_4$ and DCM was evaporated to afford light yellow to brown power. The product was sufficiently pure for analysis and tests.



1,3-Bis(benzimidazolyl)benzen

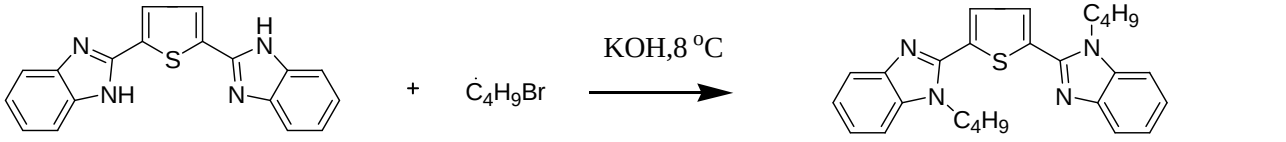
1,3-Bis(1-butylbenzimidazole-2-yl)benzen (L-2)

Scheme-26 : N-Alkylation of of L-2 [1,3-bis(1-butylbenzimidazol-2-yl)benzene].

Compound L-2 were characterized by ^{1}H NMR, elemental analysis, FAB-MS data. The ^{1}H NMR spectra and mass data indicated the formation of compound L-5 in the reaction. The proton^{1}H NMR of this compound showed two triplet at 0.67 and 4.08 which were assigned for methyl protons and N-CH_2 protons, a sextet at 1.05 and a quintet at 1.59 for methylene protons and two multiplets at 7.08 and 7.23 for aromatic protons.

Synthesis of compound L-4

2,5-Bis(1-butylbenzimidazol-2-yl)thiophene (L-4) were synthesized in high yields (89%) by reacting 2,5-bis(2′-benzimidazolyl)thiophene in DMSO with 1-bromobutan and KOH at 8°C for 24 h applying same method as for compound L-2.



2,5-Bis(2'-benzimidazolyl)thiophene

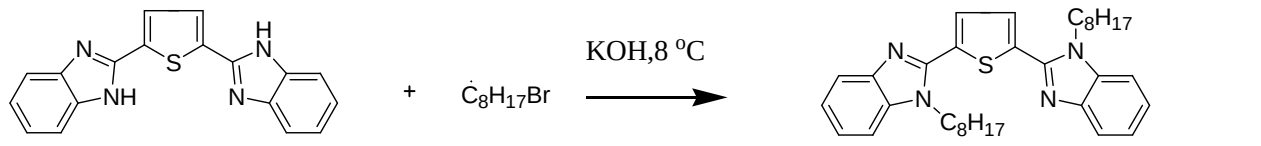
2,5-Bis(1-butylbenzimidazole-2-yl)thiophene (L-4)

Scheme-27 : N-Alkylation of L-4(2,5-bis(1-butylbenzimidazol-2-yl)thiophene).

Compound L-4 was purified by same method as compound L-2 and melting point measured was 105-107^o c (literature m. p. 104-105 °C)[215].

Synthesis of compound L-5

2,5-Bis(1-octylbenzimidazol-2-yl)thiophene (L-5) was obtained in high yield (89%) by reacting 2,5-bis(2´-benzimidazolyl)thiophene with 1-bromooctane in DMSO and KOH at 8°C for 24 h following the same method as for compound L-2.



2,5-Bis(2'-benzimidazolyl)thiophene(L-3)

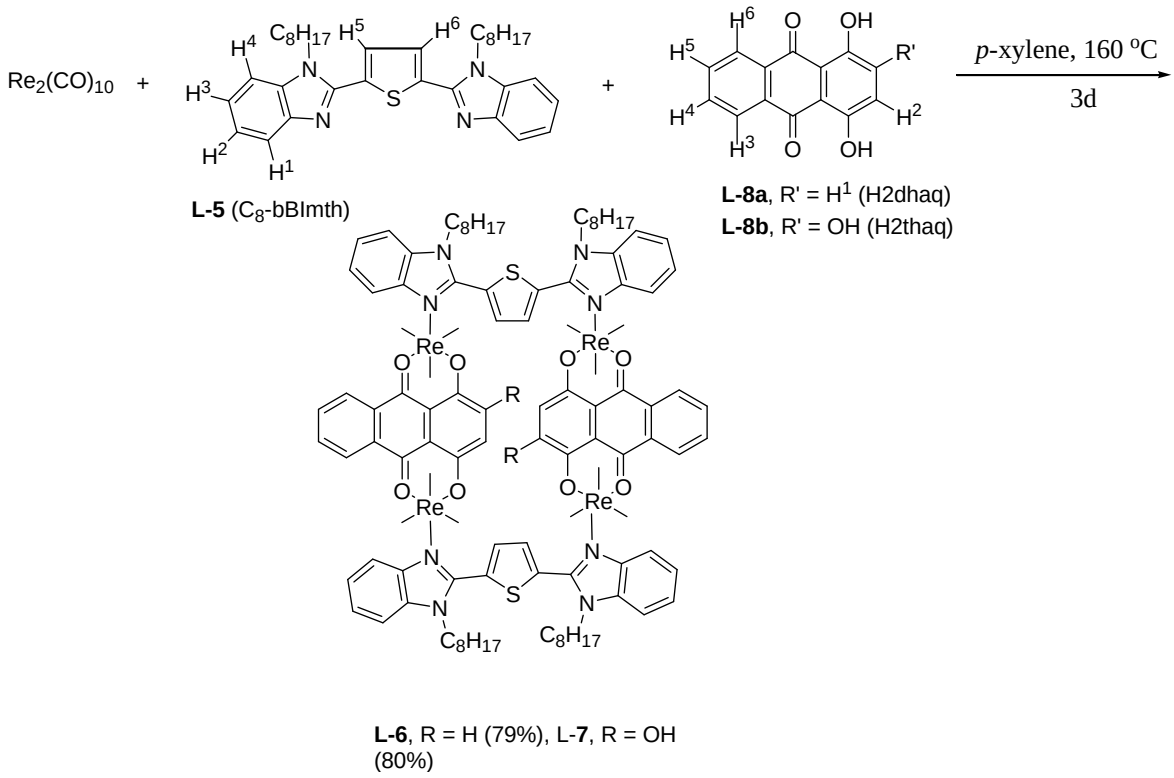
2,5-Bis(1-octylbenzimidazole-2-yl)thiophene (L-5)

Scheme-28 : N-alkylation of L- 5 (2,5-bis(1-octylbenzimidazol-2-yl)thiophene).

Compound L-5 was characterized by ^{1}H NMR, elemental analysis, FAB-MS data. The ^{1}H NMR spectra and mass data indicate the formation of compound L-5 in the reaction. The ^{1}H NMR of this compound showed a singlet at 7.67 attributed for two thiophenyl protons, two triplets at 0.83 and 4.42 and a quintet at 1.93 for methylene protons and a multiplet at 1.23-1.40 and three multiplets at 7.28-7.33, 7.37-7.40 and 7.79-7.82 which were assigned for aromatic protons.

Synthesis of compound L-6 and L-7

Complexes $[\{Re(CO)_3\}_2(\mu\text{-dhaq})(\mu\text{-N–N})]_2$ (L-6**)** and $[\{Re(CO)_3\}_2(\mu\text{-thaq})(\mu\text{-N–N})]_2$ (L-7) (H_2-dhaq = 1,4-dihydroxy-9,10-anthraquinone; H_2-thaq = 1,2,4-trihydroxy-9,10-anthraquinone; N–N = 2,5-bis(1-octylbenzimidazol-2-yl)thiophene were prepared in high yields (79%) by reacting $Re_2(CO)_{10}$, H_2dhaq or H_2-thaq, an *N*-heterocyclic ditopic bridging ligand L-5 in *p*-xylene at 160 °C for 48 h under solvothermal conditions.



Scheme-29 : Solvothermal synthesis of metallacycles L-6 and L-7

Complexes L-6, L-7 were characterized by ^{1}H NMR, IR spectra, FAB-MS data, and microanalyses. The ^{1}H NMR spectra and mass data indicate the possible formation of tetrarhenium metallacycles in the reactions. The proton^{1}H NMR of this compound showed triplet at 0.75 which is assigned for methyl proton, singlet at 6.86 for bBImth proton and at 7.75 for$H^{1,2}$-dhaq proton , singlet at 7.01 for P-xylene guest proton and at 7.75 which assign for $H^{1,2}$-dhaq proton, five multiplets at 1.1-1.29, 1.35-1.47, 1.80-1.90, which account for alkyl protons and three double doublets at 7.93, 8.55,8.64. The IR spectra of all the compounds exhibited strong and characteristic CO stretching vibrations in the range of 2013-1873 cm^{-1} region and were consistent with literature values[216]. X-ray diffraction analyses further confirmed the structures of compounds L-6 and L-7.

4.2. Studies on Binding property

Binding properties of PA with L-2, L-4, L-5, L-6, L-7 were studied using UV-Visible spectroscopy. Different amounts of PA, such as 50, 75, 100, 125, 150, 200, 275 μL of 10^{-3} (M) DCM stock solution was added with 2 mL of the solution of L-2 in DCM (0.25×10^{-4} M), where the final conc. of picric acid were [PA] $\times 10^{-4}$ M = 0, 0.24, 0.36, 0.47, 0.58, 0.69, 0.9, 1.1 and the absorption spectra were recorded immediately. Similarly the binding was monitored by adding different amounts of PA, such as 50, 75, 100, 125, 150, 175, 200, 225, 275, 325 μL 10^{-3} (M) DCM stock solution with 2 mL of the solution of L-4 in DCM (0.25×10^{-4} M), where the final conc. of picric acid were [PA] $\times 10^{-4}$ M = 0, 0.24, 0.36, 0.47, 0.58, 0.69, 0.8, 0.9, 1, 1.1, 1.39 and the absorption spectra were recorded immediately. For L-5 the amounts of PA, such as 25, 50, 60, 70, 80, 90, 100, 120 μL of 10^{-3} (M) DCM stock solution were added with 2 mL of the solution of L-5 in DCM (0.25×10^{-4} M) ,where the final conc. of picric acid were [PA] $\times 10^{4}$ M = 0, 0.12, 0.24, 0.29, 0.33, 0.38, 0.43, 0.47, 0.57 and the absorption spectra were recorded immediately. For L-6 the amounts of PA, such as 50, 75, 100, 150, 175, 225, 375, 450 μL 10^{-4} (M) THF stock solution were added with 2 mL of the solution of L-6 in THF (1×10^{-5} M), where the final conc. of picric acid were [PA] $\times 10^{-5}$ M = 0, 0.24, 0.36, 0.69, 0.8, 1, 1.5, 1.8 and the absorption spectra were recorded immediately. For L-7 the amounts of PA, such as 75, 150, 200, 250, 300, 350 μL 10^{-4} (M) THF stock solution were added with 2 mL of the solution of L-7 in THF (0.5×10^{-5} M) , where the final conc. of picric acid were [PA] $\times 10^{-5}$ M = 0, 0.36, 0.47, 0.69, 0.9, 1.1, 1.3, 1.48 and the absorption spectra were recorded immediately.

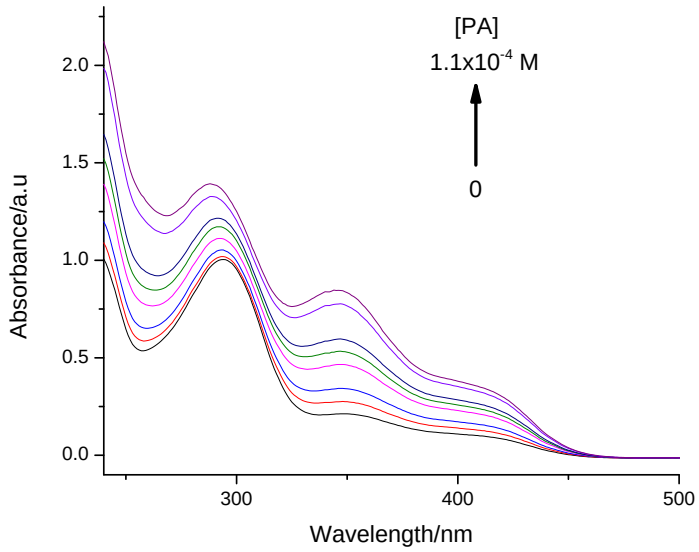


Figure-23 : UV-Visible spectra of L-2 with various amounts PA from bottom, [PA] × 10^{-4} M = 0, 0.24, 0.36, 0.47, 0.58, 0.69, 0.9, 1.1.

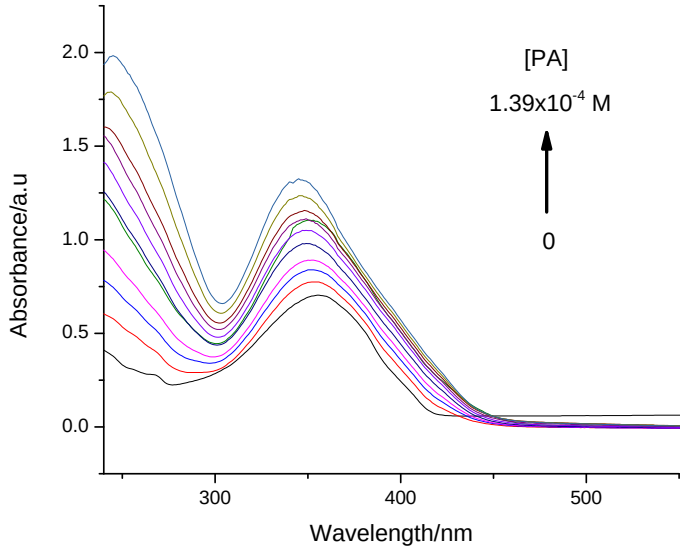


Figure-24 : UV-Visible spectra of L-4 with various amounts PA from bottom, [PA] × 10^{-4} M = 0, 0.24, 0.36, 0.47, 0.58, 0.69, 0.8, 0.9, 1, 1.1, 1.39.

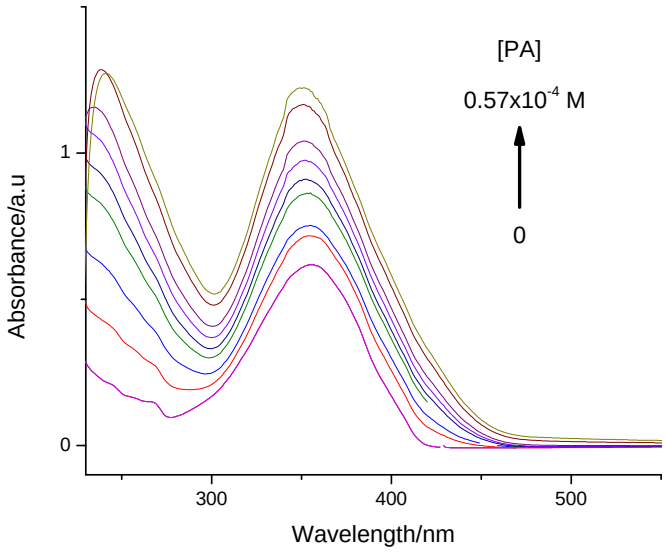


Figure-25 : UV-Visible spectra of L-5 with various amounts PA from bottom, [PA] × 10^{-4} M = 0, 0.12, 0.24, 0.29, 0.33, 0.38, 0.43, 0.47, 0.57.

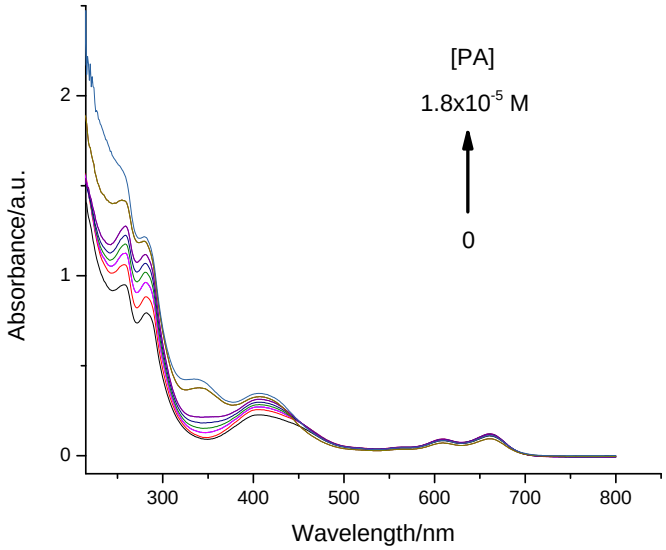


Figure-26 : UV-Visible spectra of L-6 with various amounts PA from bottom, [PA] × 10^{-4} M = 0, 0.24, 0.36, 0.69, 0.8, 1, 1.5, 1.8.

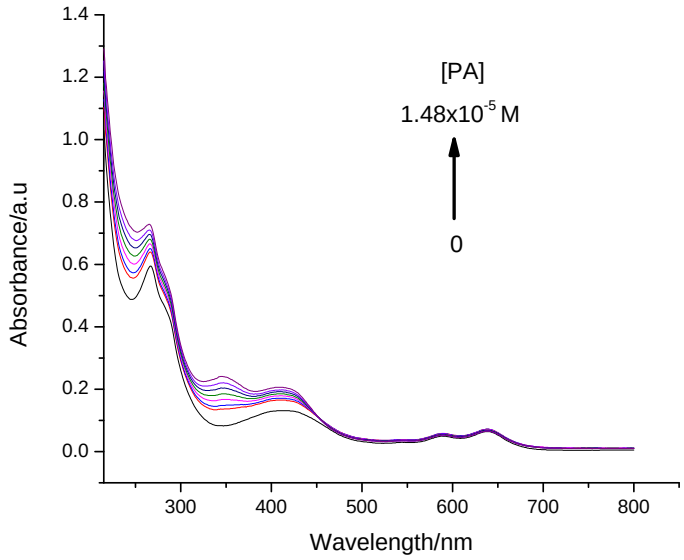


Figure-27 : UV-Visible spectra of L-7 with various amounts PA from bottom, [PA] × 10^{-4} M = 0, 0.36, 0.47, 0.69, 0.9, 1.1, 1.3, 1.48.

The absorption spectrum of L-2, L-4, L-5 in DCM (0.25 × 10^{-4} M) showed an intense band at 300 nm (L-2) and at 350 (L-2, L-4, L-5) corresponding to the π–π* transitions on addition of picric acid (1 × 10^{-3} M).The absorption spectrum of L-6 in THF (1 × 10^{-5} M) showed an intense band at 250 nm with shoulders at 280 nm, corresponding to the π–π* transitions of the dhaq and L-5 ligands and a broad and weak band at 400 nm, assigned to the MLCT transition. In addition, two weak bands appeared at 610 and 660 nm, which are assigned to intraligand transitions of the dhaq moiety. For compound L-7 the bands are situated at 250, 300 (π–π* transitions), 410 (MLCT), and at 590, 630 nm.

Table-6 : Absorption maxima of compound L-2, L-4, L-5, L-6, L-7

Compound	λ_{max} (nm)
L-2	300, 350
L-4	350
L-5	350
L-6	250, 280, 400, 610, 660
L-7	250, 350, 410, 590, 630

1-Chloro-4-nitrobenzene were also used to study the binding properties of L-2. Different amounts such as 50, 75, 100, 125, 150, 175, 225, 275 µL 10^{-3} (M) DCM stock solution of 1-Chloro-4-nitrobenzene were added with 2 mL of the solution of L-2 (0.25×10^{-4} M), where the final conc. of picric acid were [PA] $\times 10^{-4}$ M = 0, 0.24, 0.36, 0.47, 0.58, 0.69, 0.9, 1, 1.1 and the absorption spectra were recorded immediately. The absorption spectrum of L-2 in DCM (0.25×10^{-4} M) showed an intense band at 285 nm(L-2) corresponding to the π–π* transitions.

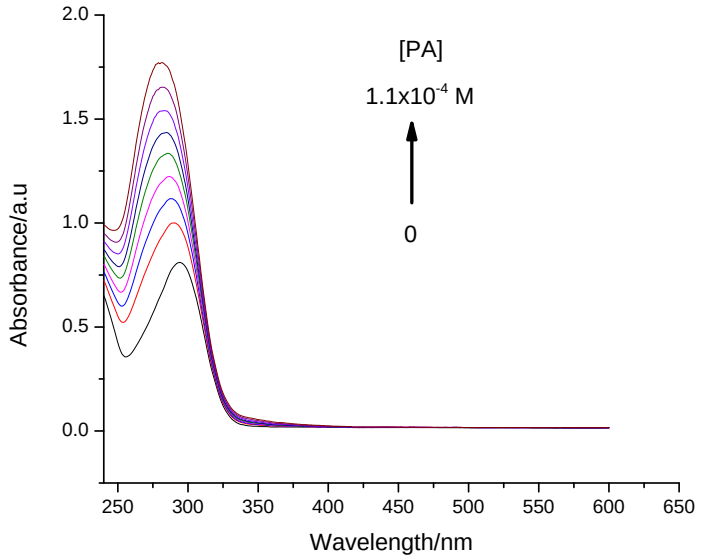


Figure-28 : UV-Visible spectra of L-5 with various amounts of 1-chloro-4-nitrobenzene

fraction from the top, [PA] × 10^{-4} M = 0, 0.24, 0.36, 0.47, 0.58, 0.69, 0.9, 1, 1.

The current observations support that PA forms non-emissive ground state complex with (L-2, L-4, L-5, L-6, L-7). To observe one-to-one binding between host (H) and Guest (G) molecule using UV-Visible absoption , Beneshi-Hildebrand method can be used.

Beneshi-Hildebrand plot is,

$$1/\Delta A = 1//(\Delta\varepsilon K[H][G]) + 1/(\Delta\varepsilon[H])$$

Where ΔA is the difference of absorbance in absence and in the present of host, $\Delta\varepsilon$ is the difference of the molar extinction coefficient in absence and in the present of host, K is the binding constant, and [H], [G] represent host and guest molar concentration respectively.

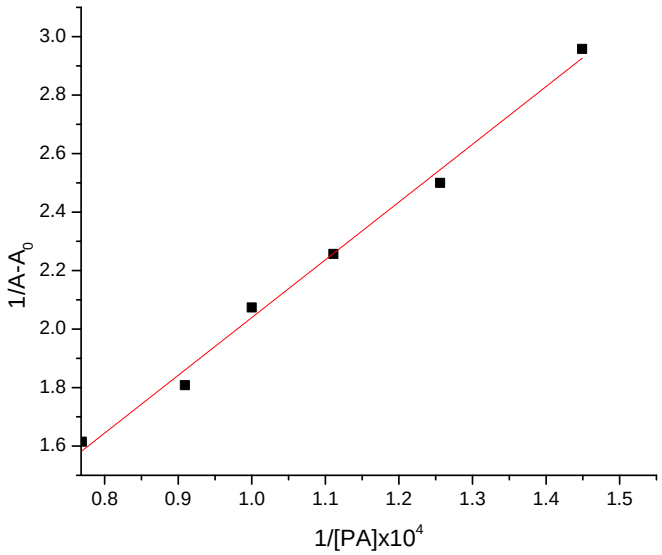


Figure-29 : Beneshi-Hildebrand plot for the binding of L-2 with PA.

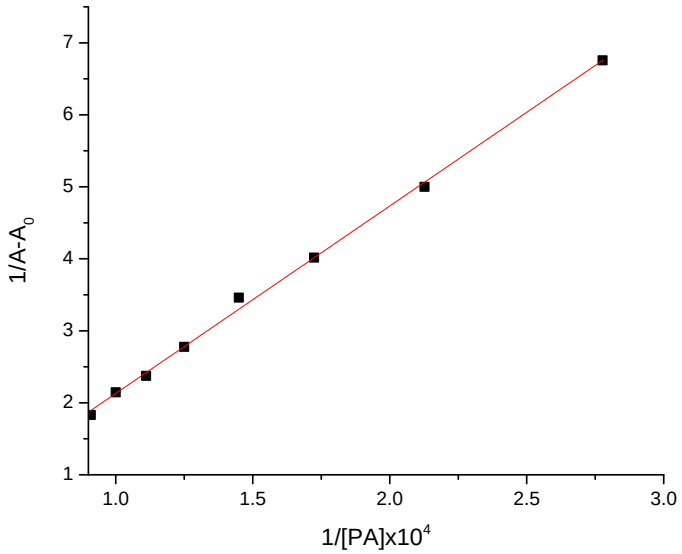


Figure-30 : Beneshi-Hildebrand plot for the binding of L-4 with PA.

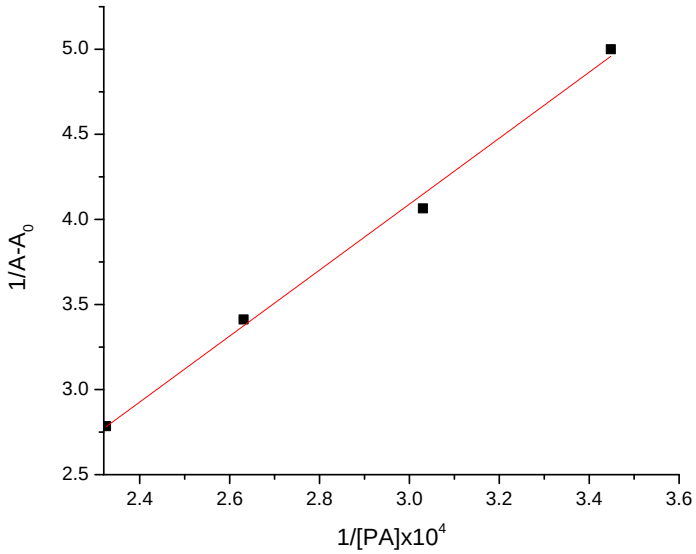


Figure-31 : Beneshi-Hildebrand plot for the binding of L-5 with PA.

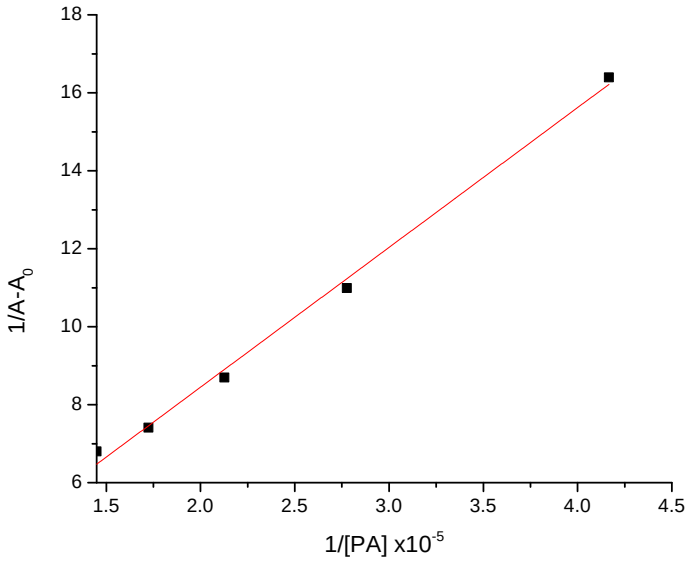


Figure-32 : Beneshi-Hildebrand plot for the bingding of L-6 with PA.

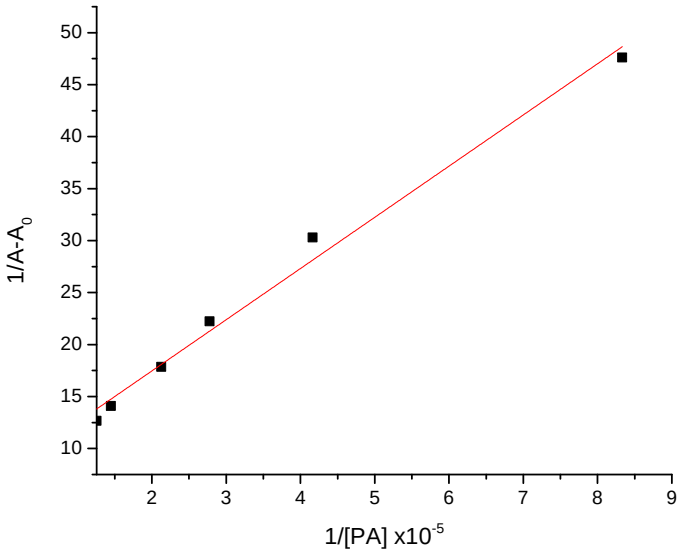


Figure-33 : Beneshi-Hildebrand plot for the bingding of L-7 with PA.

4.3. PL Quenching Study:

Picric acid (PA) were used to study the quenching properties of L-2, L-4, L-5, L-6, L-7 by using fluorescence spectroscopy. The quenching was monitored by adding different amounts, such as 50, 75, 100, 125, 150, 175, 200, 225 μL 10^{-3} M DCM stock solution of quencher(PA) with 2 mL of the solution of L-2 (0.25×10^{-4} M), where the final conc. of picric acid were [PA] $\times 10^{-4}$ M = 0, 0.24, 0.36, 0.47, 0.58, 0.69, 0.9, 1 and the PL spectra were recorded immediately. Similarly different amounts of quencher(PA), such as 25, 50, 75, 100, 125, 150, 175, 200, 275 μL 10^{-3} M DCM stock solution were added with 2 mL of the solution of L-4 (0.25×10^{-4} M), where the final conc. of picric acid were [PA] $\times 10^{-4}$ M = 0, 0.24, 0.36, 0.47, 0.58, 0.69, 0.9, 1.1 and the PL spectra were recorded immediately. For L-5 different amounts of quencher(PA), such as 25, 50, 60, 70, 80, 90, 100, 110, 120, 130 μL 10^{-3} M DCM stock solution were added with 2 mL of the solution of L-5 (0.25×10^{-4} M), where the final conc. of picric acid were [PA] $\times 10^{-4}$ M = 0, 0.12, 0.24, 0.29, 0.33, 0.38, 0.43, 0.52, 0.62 and the PL spectra were recorded immediately . For L-6 the amounts of quencher(PA), such as 0, 125, 175, 225, 275, 300, 325, 375 μL 10^{-4} M THF stock solution of were added with 2 mL of the solution of L-6 in THF (1×10^{-5} M), where the final conc. of picric acid were [PA] $\times 10^{-5}$ M = 0, 0.24, 0.58, 0.8, 1, 1.2, 1.3, 1.39, 1.5 and the PL spectra were recorded immediately. And for L-7 different amounts of quencher(PA), such as 50, 100, 150, 250, 350, 450 μL 10^{-4} M THF stock solution were added with 2 mL of the solution of L-7 in THF (0.5×10^{-5} M), where the final conc. of picric acid were [PA] $\times 10^{-5}$ M = 0, 0.24, 0.47, 0.69 1.1, 1.48, 1.8 and the PL spectra were recorded immediately.

Upon excitation at 355 nm L-2, L-4, L-5 emitted a structureless PL band at 420 nm, 455 nm and L-6, L-7 at 415 nm, 440 nm, which originates from the singlet MLCT excited states as the Stock shift is small (100 nm for L-2, L-4, L-5 and 85 nm for L-6, L-7).

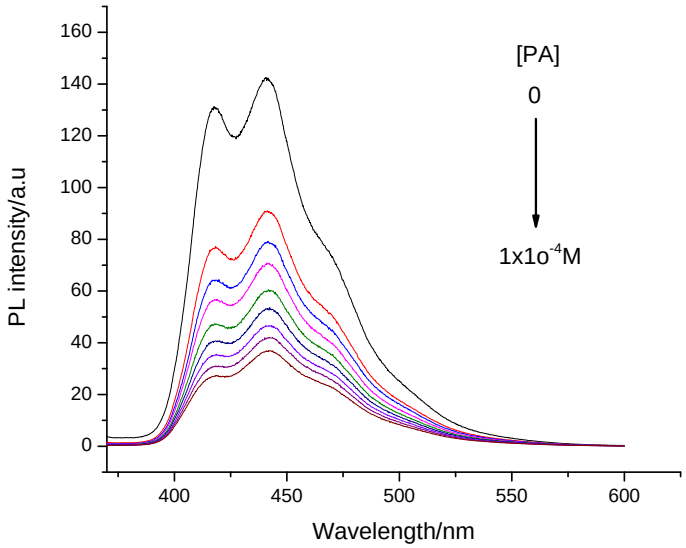


Figure-34 : PL quenching of L-2 by picric acid from top, [PA] × 10^{-4} M = 0, 0.24, 0.36, 0.47, 0.58, 0.69, 0.9, 1.

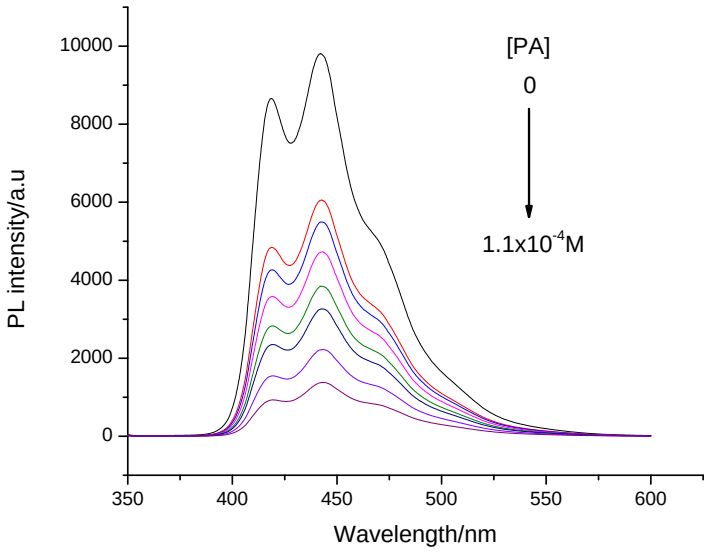


Figure-35 : PL quenching of L-4 by picric acid from top, [PA] × 10^{-4} M = 0, 0.24, 0.36, 0.47, 0.58, 0.69, 0.9, 1.1.

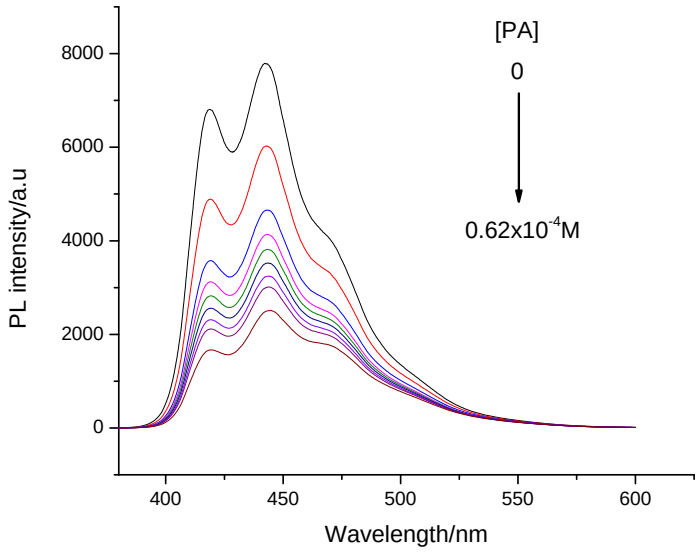


Figure-36 : PL quenching of L-5 by picric acid from top, [PA] × 10^{-4} M = 0, 0.12, 0.24, 0.29, 0.33, 0.38, 0.43, 0.52, 0.62.

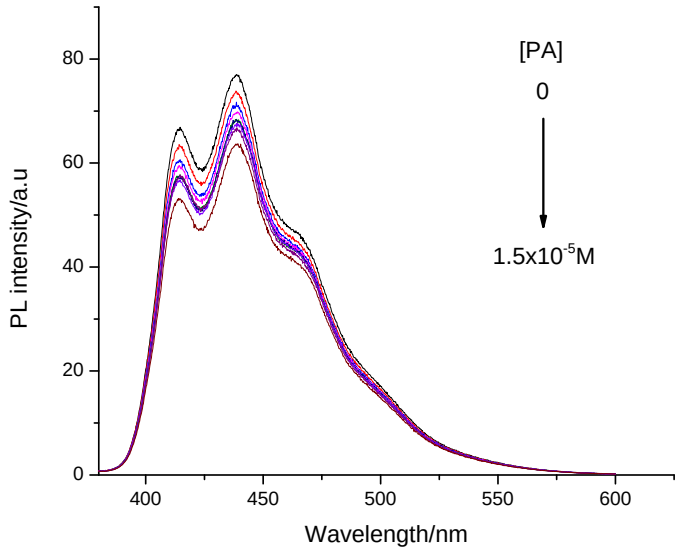


Figure-37 : PL quenching of L-6 by picric acid from top, [PA] × 10^{-5} M = 0, 0.24, 0.58, 0.8, 1, 1.2, 1.3, 1.39, 1.5.

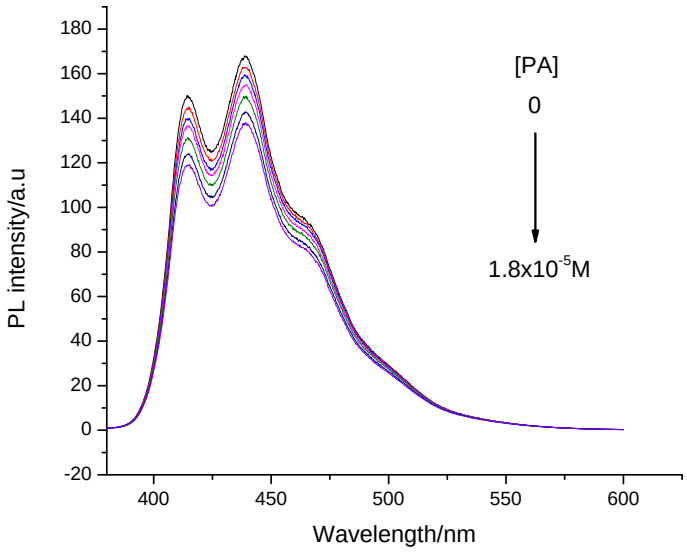


Figure-38 : PL quenching of L-7 by picric acid from top, [PA] × 10^{-5} M = 0, 0.24, 0.47, 0.69, 1.1, 1.48, 1.8.

PL intensity were quenched on addition of PA. Among the compounds studied L-2, L-4, L-5 showed significant quenching, where change is not significant for L-6 and L-7.

The quenching of luminescent material is normally analyzed using the Stern-Volmer equation[8] as long as a linear plot is obtained.

$$Io/I = K_{sv}[Q] + 1$$

According to the equation the Stern-Volmer plot for PL quenching of L-2 and L-5 by picric acid showed linear curvature and L-4, L-6, L-7 showed positive curvature. So modified stern-Volmer were ploted for L-4 and L-7.

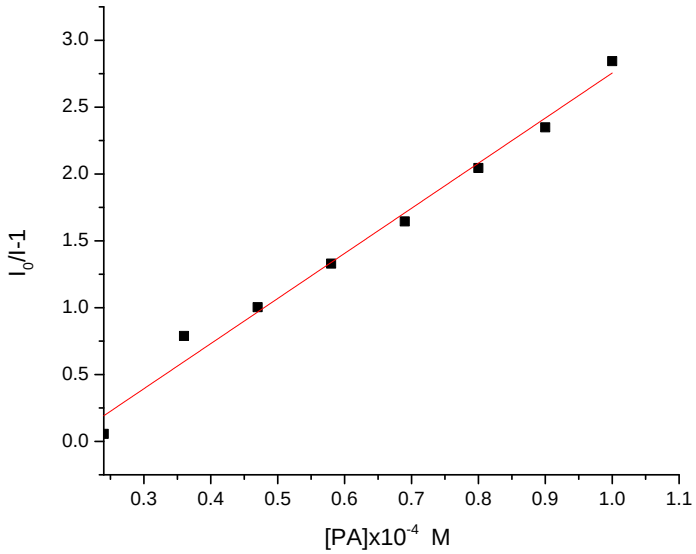


Figure-39 : Stern-Volmer plot for PL quenching of L-2 by PA.

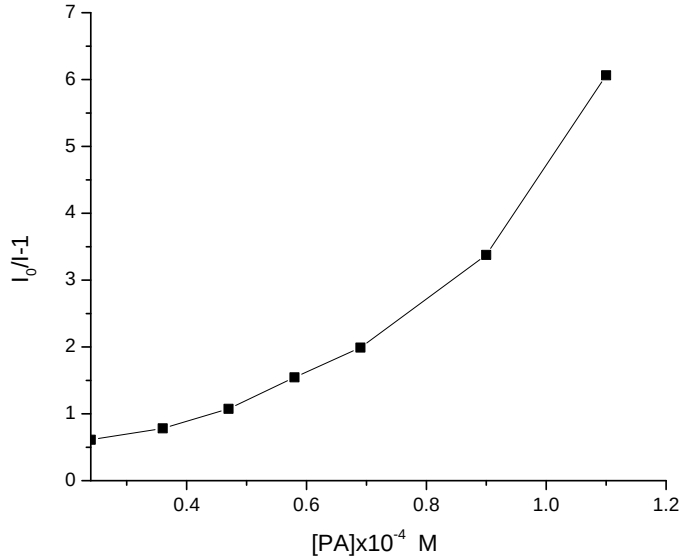


Figure-40 : Stern-Volmer plot for PL quenching of L-4 by PA.

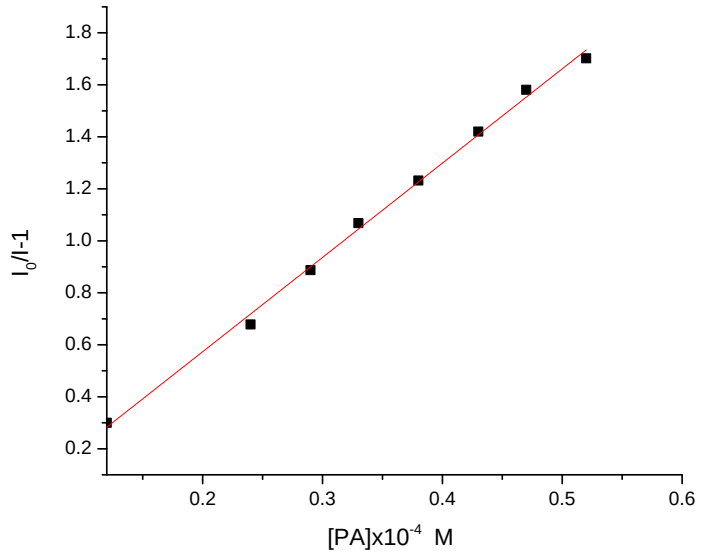


Figure-41 : Stern-Volmer plot for PL quenching of L-5 by PA.

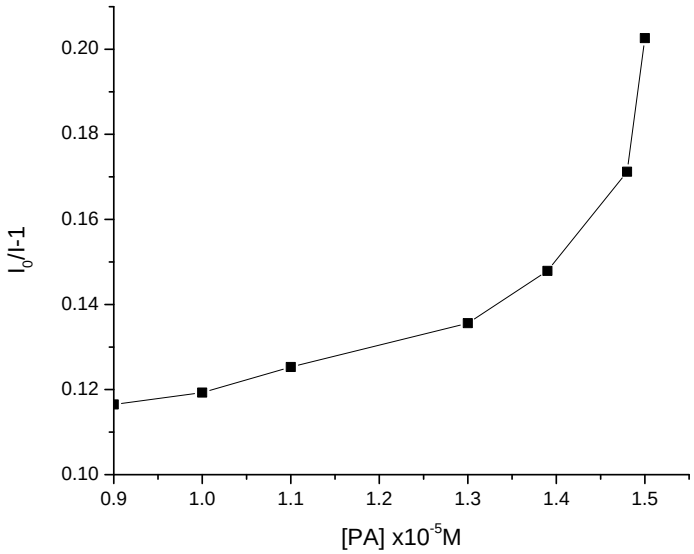


Figure-42 : Stern-Volmer plot for PL quenching of L-6 by PA.

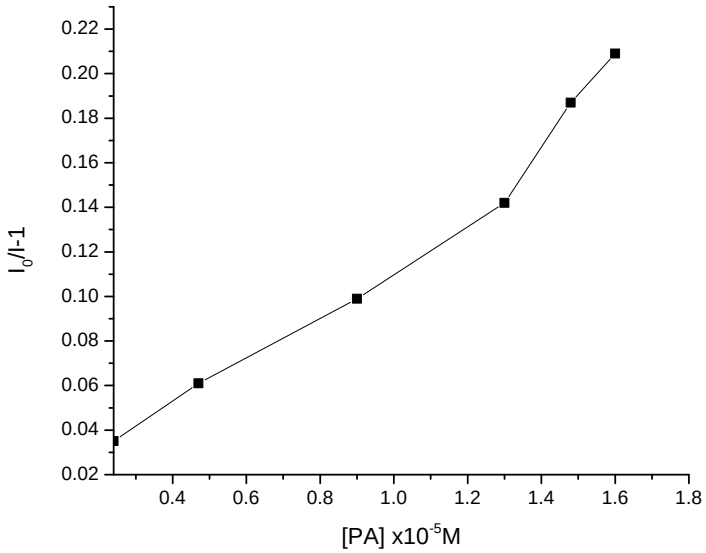


Figure-43 : Stern-Volmer plot for PL quenching of L-7 by PA.

A positive curvature at higher quencher concentration is attributed to the static quenching mechanism at higher quencher concentrations and need modified Stern-Volmer equation[217].

$$(Io/I\text{-}1)/[Q] = (K_s + K_{sv}) + K_s K_{sv}[Q]$$

Where K_s is the formation constant of the ground state 1:1 complex. For L-4, L-7 the plot of $(Io/I\text{-}1)/[PA]$ vs. [PA] produced linear plots and from the intercept the sum of the formation constant K_s and Stern-Volmer constant K_{sv} were obtained.

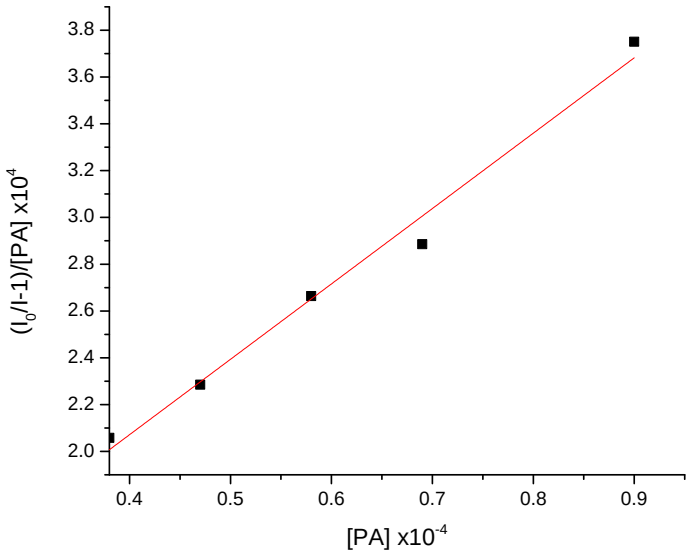


Figure-44 : Modified Stern-Volmer plot for the PL quenching of L-4 by PA.

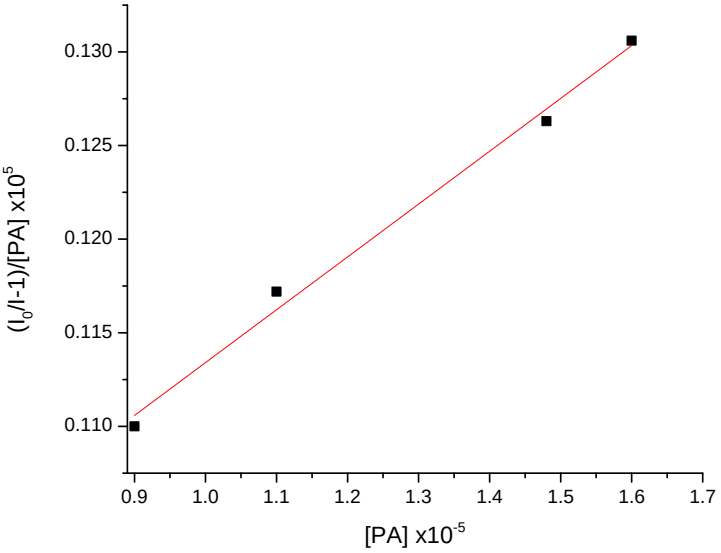


Figure-45 : Modified Stern-Volmer plot for the PL quenching of L-7 by PA.

In this case K_s is also considered as the static quenching constant[218], which was obtained from Beneshi-Hildebrand plot using equation.

Table-25 : Dynamic and Static Stern-Volmer constants for L-2, L-4, L-5, L-6, L-7.

Compound	K_{sv} , M^{-1}	K_s , M^{-1}
L-2	3.37312	0.0327
L-4	18.397[a]	0.1751
L-5	3.62719	0.8900
L-6		0.3563
L-7	0.01824[a]	1.5470

Here, a = K_{sv} for modified Stern-Volmer plot.

4.4. Absoption and Flourescence spectroscopy of nanomaterials of L-6 and L-7

Aggregates of L-6 were fabricated by adding 0.5 mL of a stock solution of compound (2 × 10^{-4} M, THF) in round bottom flasks containing THF-water mixture of the required ratio (9.5 mL) with vigorous stirring for 30 min. at room temperature to give a final concentration of 1 × 10^{-5} M . Similarly aggregates of L-7 were also fabricated by adding 0.5 mL of a stock solution of compound (1 × 10^{-4} M, THF) in round bottom flasks containing THF-water mixture of the required ratio (9.5 mL) with vigorous stirring for 30 min. at room temperature to give a final concentration of 0.5 × 10^{-5} M .

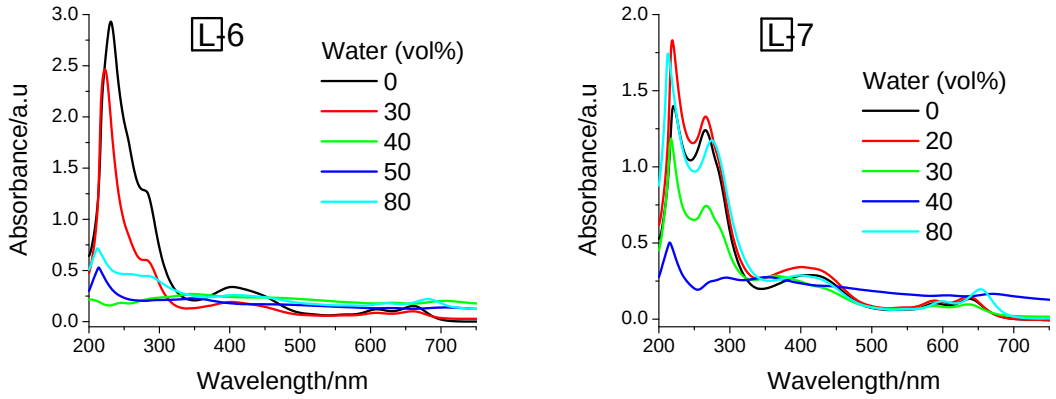


Figure-46 : UV/visible spectra of L-6 and L-7 with various water fractions.

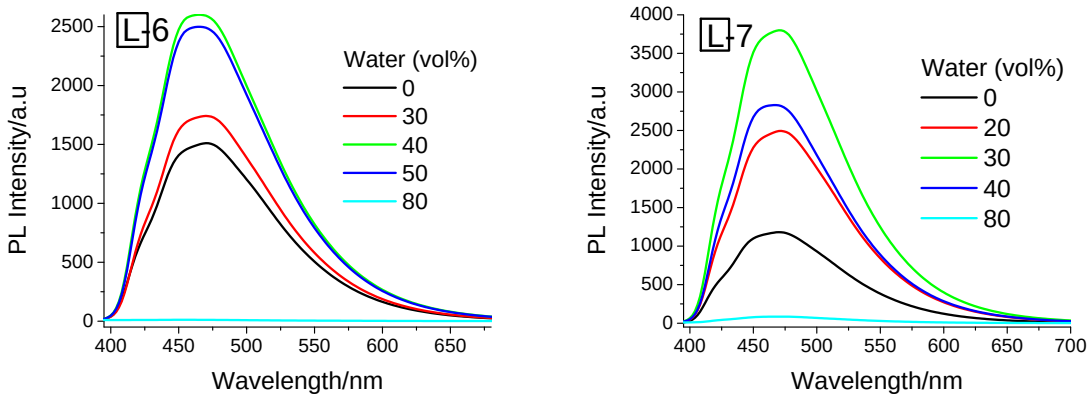


Figure-47 : PL spectra of L-6 and L-7 with various water fractions.

4.5. Spectral properties of aggregates

Aggregates of different morphologies were fabricated by simple precipitation method. A dilute solution of the compound in THF was added drop-wise to THF-water mixture of a required composition with vigorous stirring for 30 min. Solutions of compounds L-6 and L-7 in 40% and 30% water content precipitated on standing, while solutions with lesser or higher water contents were macroscopically homogenous and visually clear without precipitation. For compound L-6 the UV-vis bands at 231 and 281 nm are blue shifted by 10-20 nm upon addition of increased amount of water [Figure 46]. The MLCT band and

the bands at 609, 661 nm was blue shifted slightly (up to 40% water) and then red shifted. Similar shifts of UV-vis bands were observed for compounds L-7 [Figure-46]. The red shift in the UV-vis spectra can be attributed to aggregation analogous to J-aggregation[219]. Moreover, tailing of the UV-vis absorption spectra into the visible region was observed, which is a common feature of aggregated particles[220], due to the Mie effect. The PL spectra of aggregated particles of L-6 showed slight blue shift with increasing water fraction, while the change is not significant for L-7**.**

4.6. Morphology of the aggregates

The formation of aggregates of compound L-6, L-7 was confirmed by SEM analysis (Figure-48). SEM samples were prepared by casting a drop of a sample solution onto an individual copper holder and coated with gold. In THF solution L-6 formed granular type aggregates admixture with some nanorods, while L-7 in THF formed spongy speheres composed of nanorods. In a solution containing 40% water, L-6 produced open-ended micron size rods of wide lengths (3.8–8.8 μm), while L-7 in solution with a water content of 30% afforded smaller micron size rods (1.1–3.1 μm). In 80% water content both L-6 and L-7 afforded amorphous aggregates. The intermolecular interactions in aggregates are not clear to us. Presumably, the presence of four alkyl chains in the periphery of the metallacycle imparts sufficient hydrophobicity to drive the aggregation process[221]. The morphology change as a function of water content can be due to two reasons: (a) Re–CO···H–O type hydrogen bonding between the carbonyl ligand and water could play a crucial role in nanoparticle formation, since a coordinated carbonyl ligand has been reported to be a hydrogen bond acceptor[222], (b) rapid nucleation of the aggregation process in the solvent with a higher water (a non solvent) content offers the aggregates little opportunity to grow and thus smaller particles are formed[223].

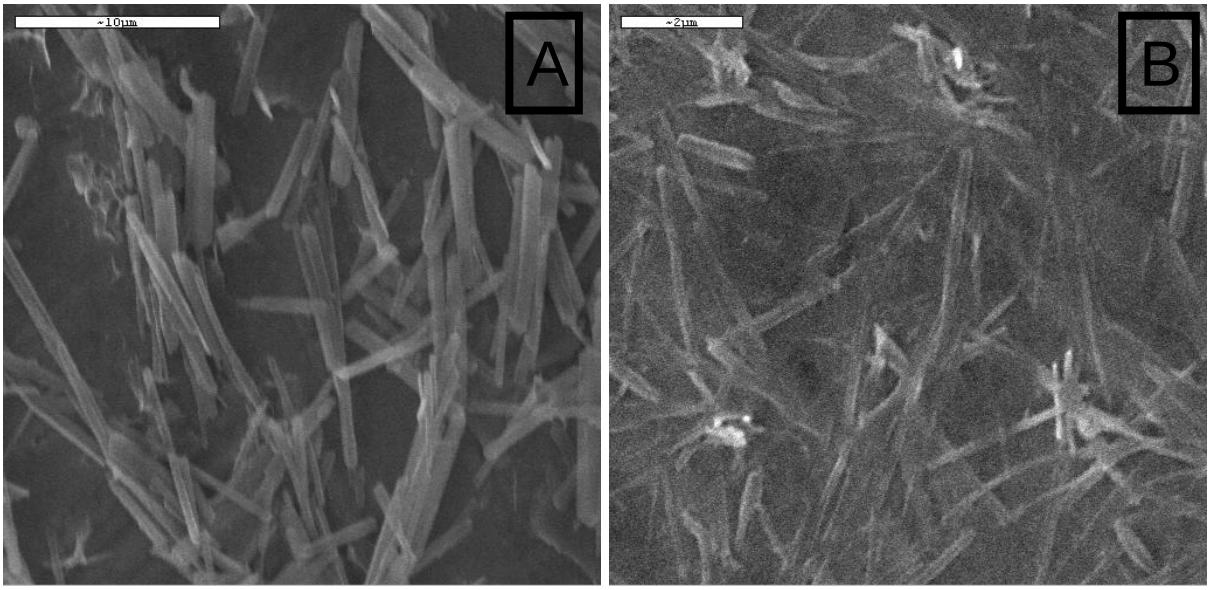


Figure-48 : SEM images of aggregated particles of L-6 (A) and L-7 (B) in water fraction 40% and 30% respectively.

Increased environmental awareness and societal needs serve as a catalyst for developing new method to detect organic pollutants. From this panorama, this investigation involved synthesis of various benzimidazole derivatives such as 1,3-bis(benzimidazolyl)benzene (L-1) by reacting O-phenylenediamine with dicarboxylic acid in strong acidic condition and at very high temperature (i.e., PPA, 180°C). N-alkylated derivatives such as 1,3-bis(1-butylbenzimidazol-2-yl)benzene(L-2), 2,5-bis(1-butylbenzimidazol-2-yl) thiophene (L- 4) and 2,5-bis(1-octylbenzimidazol-2-yl)thiophene compound L-5) were obtained by N-alkylation of amino groups. Rhenium(I) metallacycles $[\{Re(CO)_3\}_2(\mu\text{-dhaq})(\mu\text{-1})]_2$ (L-6) $[\{Re(CO)_3\}_2(\mu\text{-thaq})(\mu\text{-1})]_2$ (L-7) were synthesized under solvothermal condition. The binding and quenching of them with nitro-aromatic compounds such as picric acid (PA) and 1-chloro-4-nitrobenzene were also investigated. Present study demonstrated that compounds L-2, L-4, L-5, L-6, L-7 showed better sensing ability towards picric acid and 1-chloro-4-nitrobenzene. It was also observed that rhenium(I) metallacycles L-6 and L-7 underwent aggregation in THF-water mixtures and the morphology of the aggregate depends on the water fraction. Thus L-6 and L-7 formed granular or spongy spheres in THF solution, while they formed micron size rods in a THF-water mixture containing 40% and 30% water respectively. Higher water content of 80% afforded amorphous materials. The micron size rods of L-6 and L-7 showed better photoluminescence (PL) over granular or spherical aggregates, while PL is totally quenched in case of amorphous aggregates.

In reference to the previous observations it was revealed that PA formed ground state complexes with the compounds L-2, L-4, L-5, L-6, L-7). To observe binding between hosts [L-2, L-4, L-5, L-6, L-7] and guests [PA] UV-Visible absorption spectroscopy was employed and Beneshi-Hildebrand was applied. The Stern-Volmer plot for PL quenching of L-2 and L-5 by picric acid showed linear fit and L-4, L-6, L-7 showed positive curvature. The positive curvature is attributed to the involvement of both static and dynamic quenching.

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Appendix

Experimental Data

Table-1 : Observation of binding of L-2 with PA by UV-Visible spectroscopy

Vol. of PA (10^{-3} M) added (µl) With 0.25 x 10^{-4}(M) L-2	Final conc. of [PA] × 10^{-4} [M]
0	0
50	0.24
75	0.36
100	0.47
125	0.58
150	0.69
200	0.9
275	1.1

Table-2 : Observation of binding of L-4 with PA by UV-Visible spectroscopy.

Vol. of PA (10^{-3} M) added (µl) With 0.25 x 10^{-4}(M) L-4	Final conc. of [PA] × 10^{-4} [M]
0	0
50	0.24
75	0.36
100	0.47
125	0.58
150	0.69
175	0.8
200	0.9
225	1
275	1.1
325	1.39

Table-3 : Observation of binding of L-5 with PA by UV-Visible spectroscopy

Vol. of PA (10^{-3} M) added (µl) With 0.25 x 10^{-4}(M) L-5	Final conc. of [PA] × 10^{-4} [M]
0	0
25	0.12
50	0.24
60	0.29
70	0.33
80	0.38
90	0.43
100	0.47
120	0.57

Table-4 : Observation of binding of L-6 with PA by UV-Visible spectroscopy.

Vol. of PA (10^{-4} M) added (µl) With 1 x 10^{-5}(M) L-6	Final conc. of [PA] × 10^{-5} [M]
0	0
50	0.24
75	0.36
150	0.69
175	0.8
225	1
375	1.5
450	1.8

Table-5 : Observation of binding of L-7 with PA by UV-Visible spectroscopy.

Vol. of PA (10^{-4} M) added (µl) With 0.5 x 10^{-5}(M) L-7	Final conc. of [PA] × 10^{-5} [M]
0	0
75	0.36
125	0.58
150	0.69
200	0.9
250	1.1
300	1.3
350	1.48

Table-6 : Absorption maxima of compound L-2, L-4, L-5, L-6, L-7.

Compound	λ_{max} (nm)
L-2	300, 350
L-4	350
L-5	350
L-6	250, 280, 400, 610, 660
L-7	250, 350, 410, 590, 630

Table-7 : Observation of binding of L-2 with 1-chloro-4-nitrobenzene by UV-Visible spectroscopy.

Vol. of 1-chloro-4-nitrobenzene (10^{-3} M) (µl) added With 0.25 x 10^{-4} (M) L-2	Final conc. of [1-chloro-4-nitrobenzene] x 10^{-4} [M]
0	0
50	0.24
75	0.36
100	0.47
125	0.58
150	0.69
200	0.9
225	1
275	1.1

Table-8 : Data for Benesi-Hildebrand plot [Compound : L-2]

Final [PA] x 10^{-4} M	1/[PA] x 10^{4} M	Absorbence(A)	$1/\Delta A=1/A-A_0$
0.69	1.449	1.112	2.958
0.8	1.256	1.174	2.5
0.9	1.111	1.217	2.257
1	1	1.256	2.074
1.1	0.909	1.327	1.808
1.3	0.769	1.393	1.615

Table-9 : Data for Benesi-Hildebrand plot [Compound : L-4]

Final [PA] x 10^{-4} M	1/[PA] x 10^{4} M	Absorbence(A)	$1/\Delta A=1/A-A_0$
0.36	2.777	0.839	6.756
0.47	2.127	0.891	5
0.58	1.724	0.940	4.016
0.69	1.449	0.980	3.460
0.8	1.256	1.051	2.777
0.9	1.111	1.112	2.375
1	1	1.157	2.145
1.1	0,909	1.237	1.831
1.3	0.769	1.326	1.574

Table-10 : Data for Benesi-Hildebrand plot [Compound : L-5]

Final [PA] x 10^{-4} M	1/[PA] x 10^{4} M	Absorbence(A)	$1/\Delta A=1/A-A_0$
0.29	3.448	0.818	5
0.33	3.03	0.864	4.065
0.38	2.631	0.911	3.412
0.43	2.325	0.977	2.785

Table-11 : Data for Benesi-Hildebrand plot [Compound : L-6]

Final [PA] x 10^{-5} M	1/[PA] x 10^{5} M	Absorbence(A)	$1/\Delta A=1/A-A_0$
0.24	4.166	1.126	16.393
0.36	2.777	1.153	10.989
0.47	2.127	1.177	8.695
0.58	1.724	1.197	7.407
0.69	1.449	1.209	6.802

Table-12 : Data for Benesi-Hildebrand plot [Compound : L-7]

Final [PA] x 10^{-5} M	1/[PA] x 10^{5} M	Absorbence(A)	$1/\Delta A=1/A-A_0$
0.12	8.333	0.616	47.61
0.24	4.166	0.628	30.30
0.36	2.777	0.640	22.22
0.47	2.127	0.651	17.857
0.69	1.449	0.666	14.084
0.8	1.256	0.674	12.658

Table-13: Observation of quenching of L-2 with PA by fluorescence spectroscopy.

Vol. of PA (10^{-3} M) added (µl) With 0.25 x 10^{-4}(M) L-2	Final conc. of [PA] × 10^{-4} [M]
0	0
50	0.24
75	0.36
100	0.47
125	0.58
150	0.69
225	1

Table-14: Observation of quenching of L-4 with PA by fluorescence spectroscopy.

Vol. of PA (10^{-3} M) added (µl) With 0.25 x 10^{-4}(M) L-4	Final conc. of [PA] × 10^{-4} [M]
0	0
50	0.24
75	0.36
100	0.47
125	0.58
150	0.69
275	1.1

Table-15: Observation of quenching of L-5 with PA by fluorescence spectroscopy.

Vol. of PA (10^{-3} M) added (µl) With 0.25 x 10^{-4}(M) L-5	Final conc. of [PA] × 10^{-4} [M]
0	0
25	0.12
50	0.24
60	0.29
70	0.33
80	0.38
90	0.43
110	0.52
130	0.62

Table-16: Observation of quenching of L-6 with PA by fluorescence spectroscopy.

Vol. of PA (10^{-4} M) added (µl) With 1 x 10^{-5}(M) L-6	Final conc. of [PA] × 10^{-5} [M]
0	0
50	0.24
125	0.58
175	0.8
225	1
275	1.2
300	1.3
325	1.39
375	1.5

Table-17: Observation of quenching of L-7 with PA by fluorescence spectroscopy.

Vol. of PA (10^{-4} M) added (µl) With 0.5 x 10^{-5}(M) L-7	Final conc. of [PA] × 10^{-5} [M]
0	0
50	0.24
100	0.47
150	0.69
275	1.1
350	1.48
450	1.8

Table-18 : Data of Stern-Volmer plot for PL quenching of L-2 by PA.

[PA] x 10^{-4} M	$I_0/I-1$
0.24	0.0556
0.36	0.788
0.47	1.003
0.58	1.329
0.69	1.645
0.8	2.044
0.9	2.348
1	2.844

Table-19 : Data of Stern-Volmer plot for PL quenching of L-4 by PA.

[PA] x 10^{-4} M	$I_0/I-1$
0.24	0.612
0.36	0.782
0.47	1.074
0.58	1.545
0.69	1.991
0.9	3.376
1.1	6.064

Table-20 : Data of Stern-Volmer plot for PL quenching of L-5 by PA.

[PA] x 10^{-4} M	$I_0/I-1$
0.12	0.3
0.24	0.678
0.29	0.887
0.33	1.068
0.38	1.232
0.43	1.420
0.47	1.581
0.52	1.702

Table-21 : Data of Stern-Volmer plot for PL quenching of L-6 by PA.

[PA] x 10^{-5} M	I_0/I-1
0.9	0.1165
1	0.1193
1.1	0.1253
1.3	0.1356
1.39	0.1479
1.48	0.1712
1.5	0.2026

Table-22 : Data of Stern-Volmer plot for PL quenching of L-7 by PA.

[PA] x 10^{-5} M	I_0/I-1
0.24	0.035
0.47	0.061
0.9	0.099
1.3	0.142
1.6	0.209
1.8	0.220

Table-23 : Data of Modified stern-Volmer plot for the PL quenching of L-4 by PA.

[PA] x 10^{-4}M	$(I_0/I-1)/[PA] \times 10^5$M
0.36	2.0578
0.47	2.2851
0.58	2.6637
0.69	2.8855
0.9	3.7511

Table-24 : Data of Modified stern-Volmer plot for the PL quenching of L-7 by PA.

[PA] x 10^{-5}M	$(I_0/I-1)/[PA] \times 10^5$M
0.9	0.11
1.1	0.1172
1.48	0.1263
1.6	0.1306

Table-25 : Dynamic and Static Stern-Volmer constants for L-2, L-4, L-5, L-6, L-7.

Compound	K_{sv}, M^{-1}	K_s, M^{-1}
L-2	3.37312	0.0327
L-4	18.397[a]	0.1751
L-5	3.62719	0.8900
L-6		0.3563
L-7	0.01824[a]	1.5470

Here, a = K_{sv} for modified Stern-Volmer plot.