1.1. Low dimensional materials:

The materials or structures of metal, metal oxide, metal alloy, composite, crystalline form of organic or inorganic materials having either dimension from one nm to thousand micrometer are generally called as low dimensional materials. These materials belong to the intermediate state between bulk materials and single molecules and therefore consist of a huge number of very small particles. The very small particles are named as nanoparticles or microparticles by taking into account the scaling parameter. The ultrafine particles (UFP) named as nanoparticles or microparticles considering the scaling parameter. The word 'nano' is derived from Greek word 'dwarf' which means one billionth (10^{-9}) in dimension. Thus, a nanometer (nm) is 10^{-9} m.

As modern scientist Richerd Feyman presented (1959) a clear concept of nano science by his famous lecture entitled “There’s plenty of rooms at the rooms.” The focus of research shifted molecule or bulk materials to their low dimensional state. The material or structures of inorganic or organic materials having either dimension one nano meter to thousands micrometer are generally called low dimensional materials. The physiochemical properties of many conventional bulk materials changes to their low dimensional structures due to greater surface area per volume than the bulk substances.

The interest of chemists in low dimensional materials is being due to several reasons. The chief reason is the fact that studying nanoparticles and microparticles of various elements and compounds opens up new directions in chemistry that cannot be described in terms of already known relationships and properties of the bulk materials. Many years ago, the earliest civilizations used nanoscale materials for various applications without knowing its scientific aspects. For example, the Mayans used magnesium aluminium silicate clay which contained nanosized channels filled with water. The Mesopotamian civilization used glass embedded with metallic nanoparticles for decorative applications. As time forwarded, the secret science revealed and a new branch of science developed.

1.2. Synthesis of Organic low dimensional materials:

During last decades scientists involved themselves not only in fabrication of new low dimensional materials with desirable applications they also developed many new techniques and designed these to explore interesting properties in nano/micro range. Synthesis of nanoparticles ranging from 1-100 nm and microparticles ranging from 1-100 µm has been intensively pursued over the last 30 years, not only for their scientific interest, but also for their many technological applications. The basic principle for the synthesis of low dimensional materials is to produce a large number of nuclei and to inhibit the growth and aggregation of grains.

Besides inorganic low dimensional materials organic nano/microparticles have also been the subject of intensive research during the last decade. Various chemical methods have been developed to synthesize organic low dimensional material such as (i) reprecipitation (ii) physical vapour deposition (iii) microemulsion (iv) ultra-sonication, (v) Microwave etc.

1.2.1. Reprecipitation Method:

Nakanishi and coworkers [1-3] was first reported that reprecipitation, which is a solvent displacement method. It provides a very easy approach to prepare organic nanoparticles dispersions. The method involves a rapid injection of a small amount of concentrated target compound in a good solvent to excess of a poor solvent. The schematic images of the reprecipitation method are shown in ***Fig. 1.1***. The rapid mixing of the good and poor solvent changes the micro-environment of the target compound molecules. This sudden changes of solubility causes the precipitation, and as the concentration, temperature, and nature of solvent are properly adjusted, stable and dispersed nanocrystal are formed as hydrosol with negative ζ-potential value. The negative ζ -potential is responsible for preventing the particles to aggregate and stabilize the particles as hydrosol due to interparticle repulsion.

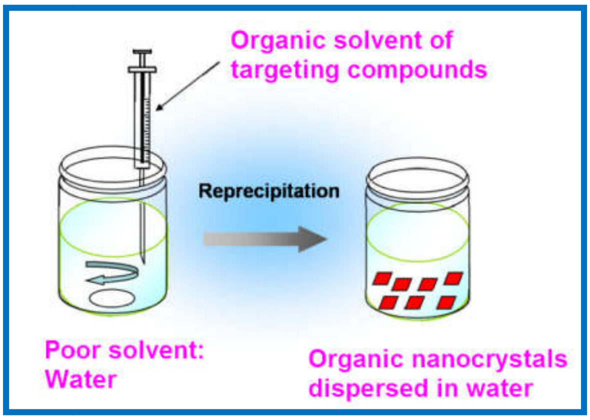


Fig. 1.1: The Scheme of Reprecipitation method

1.2.2. Physical vapour deposition (PVD) method:

Physical vapor deposition (PVD) describes the methods (***Fig. 1.2)*** used to deposit thin films upon the condensation of a vaporized material to various work piece surfaces. This is purely physical processes which require high temperature, vacuum evaporation with subsequent condensation, or plasma sputter bombardment. Yao et al. introduced the adsorbent-assisted PVD method to doped binary organic systems [4].

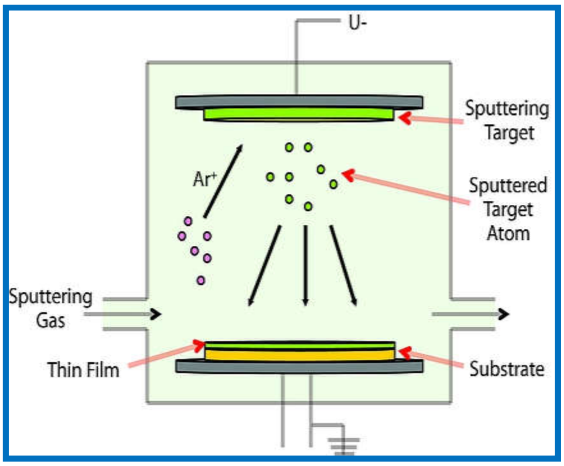


Fig. 1.2: The Scheme of Physical vapor deposition method

1.2.3. Microemulsion Method:

Among the different methods the microemulsion (***Fig. 1.3****)* is a very versatile and reproducible method to produce particles with controlled and narrow size distribution. Microemulsions are homogeneous in macroscale and micro heterogeneous in nanoscale dispersion of two immiscible liquids where nanosized domains of one or both liquids are stabilized by an interfacial film of surface active molecules. The essential distinction between normal emulsion and microemulsion is the size and stability of particles. Microemulsions are optically isotropic, thermodynamically stable and have ultralow interfacial tension to solubilize both aqueous and oil-soluble compounds. The size of the nanoparticles depends on different parameters such as water surfactant ratio R= [H_2O]/[surfactant], concentration of the organic molecules etc. Nano/micro size particles synthesized using this method remain stable for months. Different solvents may be used to solubilize the organic molecules, and the solvents are considered as a carrier vector for which do not influence the precipitation in a significant way [5].

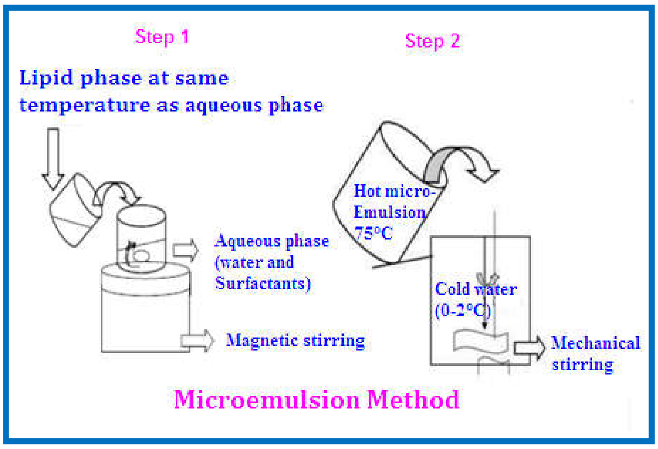


Fig. 1.3: The Scheme of Microemulsion method

1.2.4. Ultra-Sonication Method:

Nano/micro crystals with definite morphologies and optical propertieswere effectively fabricated from an organic functional low molecular weight compound, through an ultra-sonication technique ***(Fig. 1.4)***. In a typical fabrication, silicon or quartz wafers with an area of 1x1 cm2 were first suspended in organic molecule solutions with a variety of solvents and concentrations. The solutions were subsequently put into a commercial ultrasonic cleaning bath in the open. The solvents volatilized as the sonication proceeded, and the organic molecules assembled into nano/micro crystals spontaneously on the surfaces of the substrates. Yao et al. undergoes controllable synthesis through sonication technique for the fabrication of 2,4,5-triphenylimidazole nanoparticles [6]. Sonication method can prove the indispensability for formation of well-defined lophine nanocrystals.

Fig. 1.4: The Scheme of Ultra-Sonication method

1.2.5. Microwave Method:

The microwave processing (***Fig. 1.5***) of nanoparticles results in rapid heating of the reaction mixtures, particularly in water. The precipitation of particles from the solutions tends to be rapid and nearly simultaneous. This process leads to very small particle sizes and narrow size distributions within the solution and it offers the additional benefit of requiring very short reaction times.1,1,4,4-Tetraphenyl-1,3-butadiene nanocrystals were fabricated by the microwave method. [7].

1.3. Stabilization of Microparticles:

1.3.1. Soft Template Method:

The template method is a straight forward approach where the target materials are allowed to grow according to the patterns of the templates.

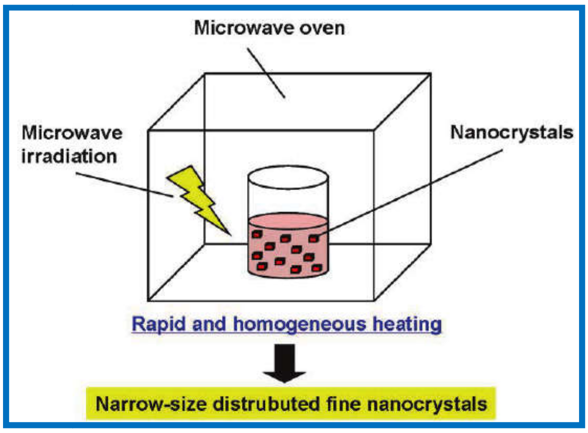


Fig. 1.5: The Scheme of Microwave method

This strategy provides an easy way for the fabrication of nanomaterials with desired size and shape, and has been widely applied in the synthesis of 1D nanostructures. Templates adopted in this method can be generally divided into two sorts: soft and hard ones. The-called soft templates ***(Fig. 1.6)*** are those which can be dissolved in the solution phase, including surfactant micelles, [8] complexes, [9] biomolecules, [10] and copolymers [11]. It is well known that as the concentration of surfactant reaches the critical micelle concentration (CMC) [12] micelles (or inverse micelles) with different shapes, such as spherical or rodlike, are formed. These can be used as soft templates for the synthesis of nanostructures. Yao and coworkers reported nanofibers of 1,3-diphenyl-2-pyrazoline (DP) using CTAB micelles [13] as soft template.

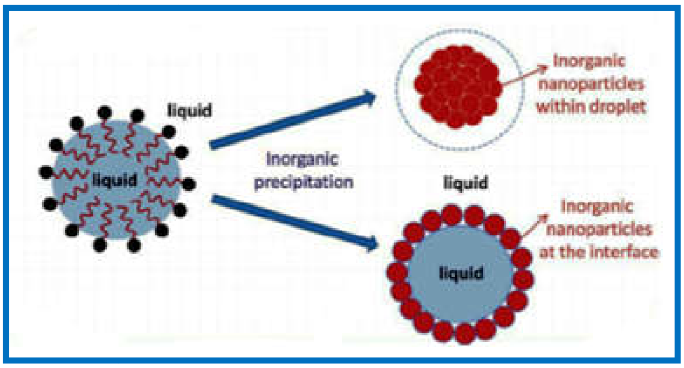


Fig. 1.6: The Scheme of Soft Template Method

1.3.2. Hard Template Method:

The synthesis of nanostructures on hard templates (***Fig. 1.7)*** has been developed in various fields of nanotechnology and it has become one of the most important methods in the preparation of 1D inorganic nanomaterials [14,15]. Possin first used this technique to fabricate semiconductor nanowires in the 1970s [16]. In recent years, this technique has also been applied to synthesize 1D nanomaterials from small organic molecules. Yao's group reported the preparation of perylene [17] and dibenzoylmethane (DBM) [18] nanotubes through the dip-and-dry method followed by heating to increase the crystallinity.

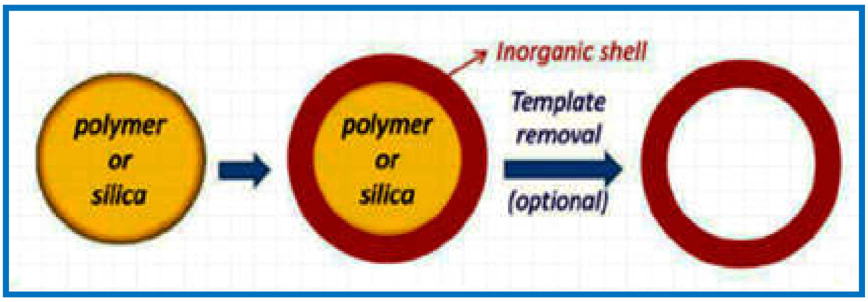


Fig. 1.7: The Scheme of Hard Template Method

1.4. AIEE based low dimensional materials:

Light is of essential importance to the universe and human beings. Photoluminescence is one of the possible physical effects resulting from interaction of light with matter. Low dimensional fluorescent metal or inorganic semiconductor particles have attracted considerable interests due to their unique photophysical properties originating from quantum-size effects. They have been extensively investigated for various applications like fluorescent biological markers, optical sensors, photovoltaic cells and light-emitting diodes (LED) etc. As far as the application is concerned, fluorescent organic materials (FOM) are expected to hold the higher potentials because FOM allow much more variability and flexibility in molecule synthesis and their morphology controlled aggregations.

About half century ago, Förster and Kasper discovered that the fluorescence of pyrene was weakened with the increasing concentration in solution. Studies have shown that the fluorescence of many aromatic luminophores became weaker or even completely quenched in concentrated solutions or in the solid state (***Fig. 1.8***). This common photo physical phenomenon in widely known as aggregation-caused quenching (ACQ) of light emission [19]. This effect was found to be caused by the molecules especially those with disc-like shapes, experience strong π-π stacking interactions to form excimers/exciplexes during the collision interactions between the excited and unexcited aromatic molecules, which are now known to be common to most aromatic hydrocarbons and their derivatives [20]. The ubiquitous concentration quenching effect has forced researchers to study and utilize fluorophores in solution phase but that causes many problems. Numerous processes have been developed and many approaches have been employed to prevent the luminophores from aggregating, but these efforts have met with only limited success. Chromophore aggregation is an intrinsic natural process, as luminophore molecules are located in close vicinity in the condensed phase.

Exactly opposite to the ACQ effect, In 2001, Tang and Park et al. discovered a new class of materials which are non-emissive in good solvent but they become strongly emissive in their aggregated state upon excitation. This phenomenon is known as Aggregation induced emission (AIE). in 2001 Tang and Park observed a unique luminogen system in which luminogen plays a constructive instead of destructive role in the luminescence process [21, 22]. Hexaphenylsilole (HPS) is nonemissive when its molecules are dissolved in a good solvent, such as tetrahydrofuran (THF) or a THF/water mixture with a fraction of water (f_w) lower than 80%. Its fluorescence is turned on when f_w reaches ~80% (***Fig. 1.9***). As water is a poor solvent of the hydrophobic siloles luminogen, addition of water to THF cause the siloles molecules to aggregate in aqueous media [23]. As the light emission occurs through aggregate formation, they used the term aggregation induced emission enhancement (AIEE) for the emission. In the past decade, a large variety of molecules with propeller shapes has been found to show the AIEE effect, indicating that AIEE is a general photophysical event.

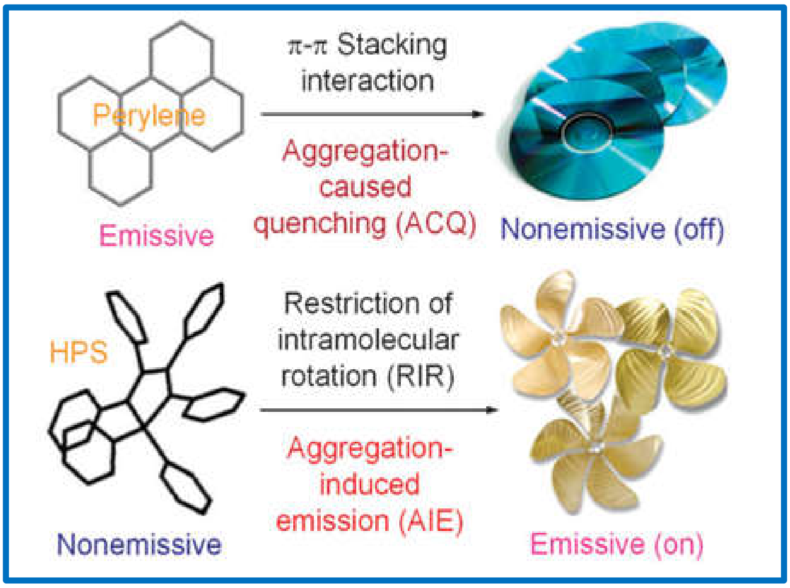


Fig. 1.8: Schematic representation of ACQ and AIE effect respectively.

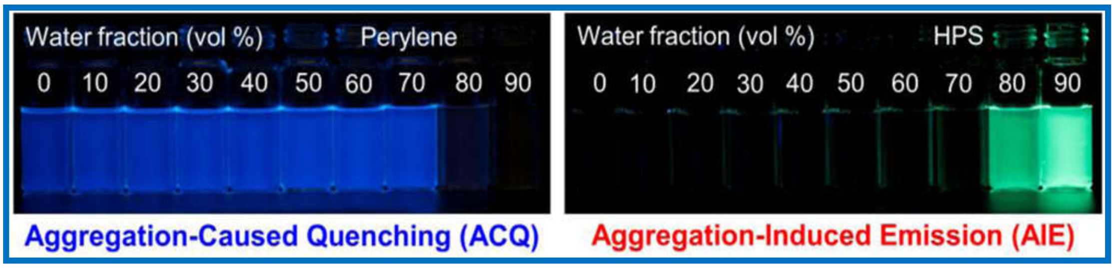
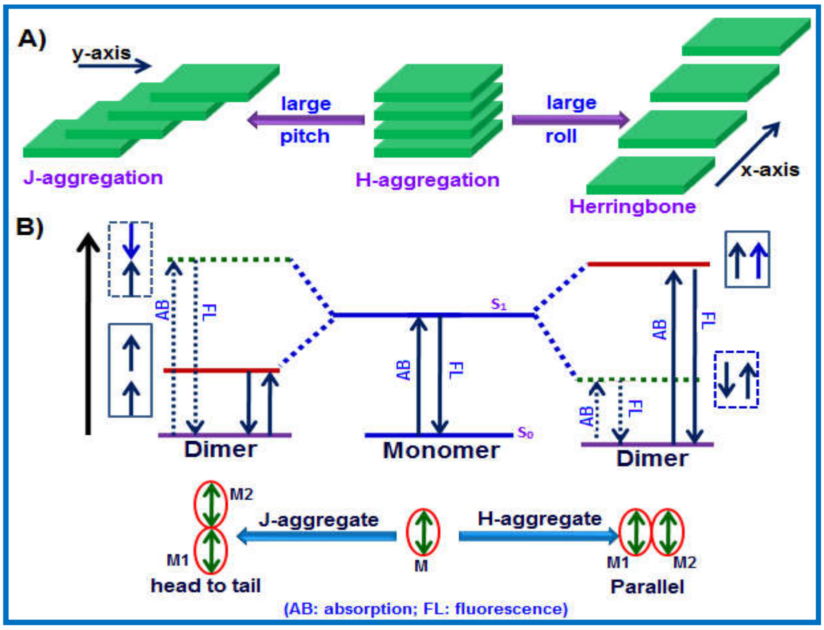


Fig. 1.9: Fluorescence photographs of solutions or suspensions of (left) perylene (20µM) and (right) hexaphenylsilole (HPS; 20µM) in THF/water mixtures with different fractions of water (f_w), showing typical ACQ and AIEE effects, respectively.

1.5. Principle of AIE/AIEE:

One broadly accepted AIE/AIEE mechanism is that the non-radiative decay, which is mostly contributed by energy redistribution to intramolecular rotational motion and can be blocked upon aggregation due to the restriction of movements [24]. This process can be further supported by supramolecular packing (***Scheme 1.1***) like J-aggregation [25], dimer stacking [26], herringbone stacking [27] and even weakly coupled H-aggregation [28] resulting in strong luminescence in solid state. Moreover, there exists a special kind of AIE active compounds and draws significant attention, are intramolecular charge transfer (ICT) materials [29]. For ICT luminophores, several mechanisms are possible including restricted twisted ICT [30] and intermolecular charge-transfer [29], formation of dimer [31] or a combination of these.



Scheme 1.1: A) Schematic representation of the structural description of Herringbone as well as H- and J-aggregates in terms of relative translation of molecules. B) Exciton splitting in J-aggregate and H-aggregate.

1.6. Mechanism of AIEE phenomena:

The invention of the AIEE concept in 2001, researchers has shown persistent desire for learning the genuine mechanistic causes for the AIEE phenomena. A number of mechanistic pathways have been hypothesized, including conformational planarization, J-aggregate formation, E/Z isomerization, TICT and ESIPT. None of them can be fully supported by the experimental data. To avoid these wrong interpretations, the experimental and theoretical works were done to provide solid proof to the three main hypotheses for the mechanistic aspects of the AIEE effects, *i.e.* RIR, RIV and RIM.

1.6.1. Restriction of intramolecular rotation (RIR):

Fundamental physics teaches us that any movement, whether it is microscopic or macroscopic, requires energy. Molecular motions include rotations and vibrations. Tetraphenylethene (TPE) is a well-studied AIEEgen (***Fig. 1.10***) in which four phenyl rings are linked to a central ethene through single bonds and have freedom to rotate against the ethene stator. The isolated molecules of TPE can undergo active intramolecular rotations, which serves as a relaxation channel for the excited states to non-radiatively decay to the ground state. In aggregate state, however, the intramolecular rotations are restricted due to physical constraint, which blocks the non-radiative channels and opens the radiative pathway [32]. Arylenevinylene luminogens containing big dibenzosuberene terminals and anthracene cores [33, 34] are non-planar in conformation and propeller-like in shape and show increased AIEE effect.

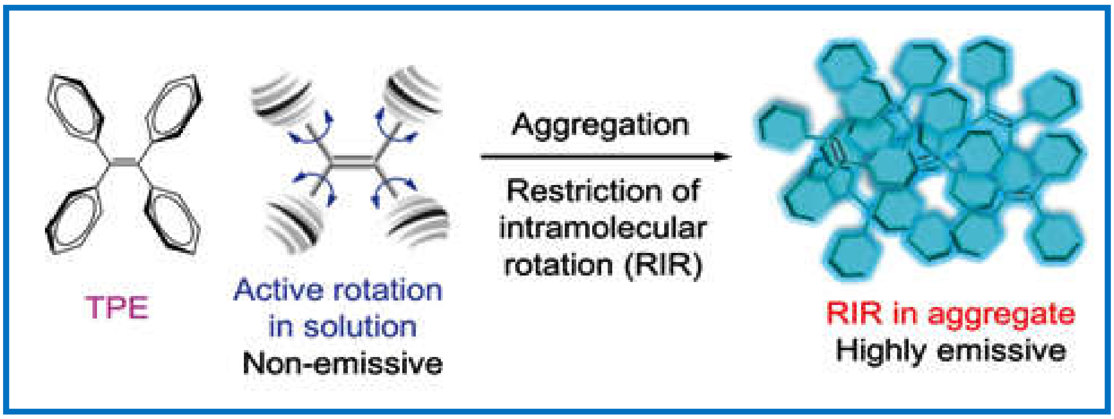


Fig. 1.10: Propeller-shaped tetraphenylethene (TPE) is non-luminescent in a dilute solution but becomes emissive in aggregated state, due to the restriction of intramolecular rotation (RIR).

The above analysis implies restricted intramolecular rotation is responsible for the AIEE process of molecular rotor systems.

1.6.2. Restriction of intramolecular vibration (RIV):

As the AIEE study advances, new AIEEgens are discovered, whose AIEE processes cannot be explained by the RIR mechanism. 10,10′,11,11′-tetrahydro-5,5′-bidibenz-7-annulenylidene (THBA) and 5,5′-bidibenzo-7-annulenylidene (BDBA) is such examples [35,36]. THBA has no rotable units, as its phenyl rings are locked by central C=C bond.

However, it is non-emissive in solution but highly luminescent in its aggregate. So RIV is considered to be responsible for the AIEE effect of this molecule.

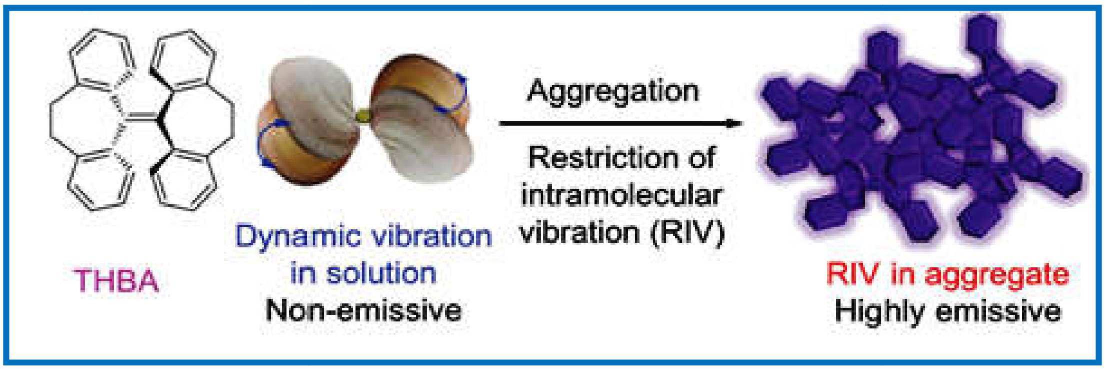


Fig. 1.11: Shell like THBA is non-luminescent in a dilute solution but becomes emissive in aggregated state, due to the restriction of intramolecular vibration (RIV).

Further investigations justify that the vibrational motions of the phenyl rings are the source of redistribution of excitation energy. QM/MM modeling results clearly show that THBA has six normal modes of vibration where the significant amounts of excited energy (~5679cm^{-1}) are distributed. In comparison, for THBA in the cluster, there are only three normal modes consuming significant amounts of excited-state energy (~4016cm^{-1}). In the cluster, the decrease in the number of normal vibrational modes and a loss of ~30% of the exciton energy due to RIV enables THBA to decay radiatively, leading to the observed AIEE effect (***Fig. 1.11***).

1.6.3. Restriction of intramolecular motion (RIM):

In a system, where both RIR and RIV are involved, the luminogen must be AIEE active by restricting intramolecular motion (RIM). 10-hexyl-3,7-bis(7-phenylbenzo[1,2,5]thiadiazol-4-yl)-10H-phenothiazine (PTZ-BZP) which has a nonplanar butterfly-like conformation, is non-emissive in solution but exhibits bright red emission in presence of water, clearly showing an AIEE effect [37]. In the isolated state, there are two major channels consuming its excited-state energy: (i) the rotational motions of the phenyl and benzothiadiazole rings unit and (ii) the vibrational motions of the phenothiazine core. The aggregate formation confines the intramolecular motions of the rotatable and vibratable units and it turns to show emission. The RIM process hence accounts for the AIEE attribute of this compound. 11,11,12,12,-Tetracyano-9,10-anthraquinodimethane, Oxacalixarene 33 are the example of AIEE active molecule whose emission is enhanced by RIM mechanism [38,39]. So the RIM mechanism is the unification of the RIR and RIV mechanisms. A simple, fundamental idea of RIM is that the RIR and RIV mechanisms are not mutually exclusive, rather can work together to bring about the AIEE phenomenon.

1.7. Basic Parameters of AIEE Study:

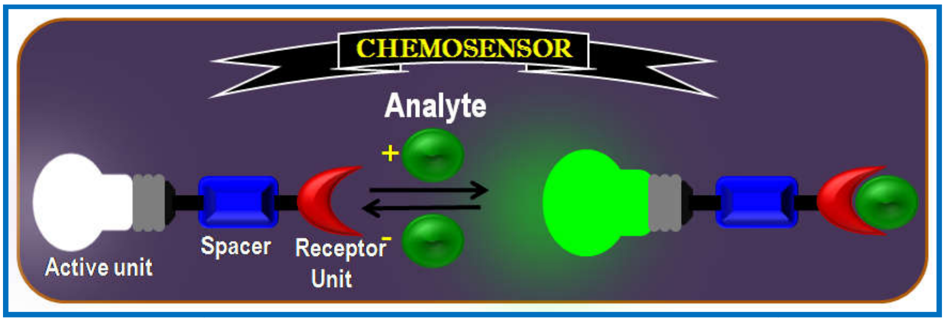
As AIEE is a relatively new concept, there are hardly any literature or systematic rule like those for fluorescent chemosensor (FC) and OLED to qualify this kind of behavior. Commonly used method is to detect the PL intensity of AIEE active molecule in a series of water-organic mixture (v/v%) solvent, keeping the concentration of molecule same. The organic solvent should be highly water-miscible, in this thesis, THF, DMF, MeOH and ETOH are chosen because they mix well with water and provide good solubility for the probe molecule. Plot of PL intensity ratio (I/I_0) i.e PL intensity in bad solvent (I) to the same at good solvent (I_0) as a function of solvent fraction ratio is a good indicator of AIEE behaviour. By comparing each intensity (I) over the initial one (I_0) measured in pure CH_3CN, DMF, MeOH, ETOH and THF solutions, the plot of I/I_0 can be presented to show the percentage enhancement of emission.

Other PL data such as low-temperature photoluminescence, solid photoluminescence or even crystal photoluminescence can also be carried out to know the variations in PL intensity and the shift of emission wavelength from other solvent system and aggregated states could help to have a better understanding on the AIE mechanism. In addition, the typical method to determine the involvement of twisted intra-ligand charge transfer is to perform a series of UV and/or PL measurements for the same compound in solvents with various polarities. Thus, many further supplementary theoretical investigations are used by scientists to predict the details of AIE mechanism. Such as DFT calculations and single-crystal x-ray diffraction are used to predict the possible transition mechanism and intermolecular interaction. Now we discuss about the concept of chemosensor.

1.8. Concept of Chemosensor

To acquaint with the difference between harmful and useful compounds, or to monitor the environment by searching for heavy metal pollutants in waters or the presence of bacteria in drinking water, can only be are achievements only accomplished with the help of man-made sensors. Among the great variety of sensors synthesized by man are those which help us to detect chemical species. This particular type is called a chemical sensor. Two different processes that are essential in chemical sensing are molecular recognition and signal transduction. There are usually three components that constitute a chemosensor (***Scheme***

1.2): a receptor, a spacer and an active unit. Now we discuss briefly about the fluorescent chemosensor and mechanisms of signal transduction elaborately.



Scheme 1.2: Schematic representation showing binding of analyte (guest) by a chemosensor (host), producing a complex accompanying with change in optical properties.

1.9. Fluorescent Chemosensor:

Out of numerous analytical techniques, fluorescence would be preferable to its versatility, high selectivity/sensitivity, reliability and reproducibility, low limit of detection (LOD), low cost, noninvasiveness, and potential application in real-time and real-space analysis [40-42]. A diversity of optical chemosensors, fluorescent chemosensors are used for the detection of trace amounts of cations, anions or small molecules by determination of physical or chemical parameters through the measurement of changes in fluorescence property. So, appropriate knowledge is needed to understand the sensor-metal ion interactions.

1.10. Mechanisms of Signal Transduction:

In the process of molecular detection, interaction between receptor and analyte causes a distinct change in the conformation or chemical structure of the receptor should trigger marked change of photophysical property of signal transducer parts by some means of signal transduction mechanisms. As a result, the change observed in absorption or emission properties could be detected by a spectroscopic instrument. Some general signal transduction mechanisms, including Photoinduced Electron Transfer (**PET**), Intramolecular Charge Transfer (**ICT**), Excited-State Intramolecular Photon Transfer (**ESIPT**) and Fluorescence Resonance Energy Transfer (**FRET**) have been severely studied in the sensing community. To know the detailed working principle for sensor development, a brief introduction on these signal transduction mechanisms will be presented.

1.10.1. Photo-induced Electron Transfer (PET):

Generally, PET take place from donor centers (e,g. N, O, S, P having lone pairs of electrons) to the HOMO of the excited fluorophore. Lone pair on the donor atoms coordinates to the metal center to prevent PET and turn on the fluorescence. Solvent polarity also influences the PET process. Higher solvent polarity, more easier the electron transfer and consequently more quicker the quenching effect. Fluorescence sensors that work via PET inhibition mechanism generally show no emission band shifting upon binding with the analyte. [43]

1.10.2. Intramolecular Charge Transfer (ICT):

Generally, when a fluorophore is directly attached to a receptor (usually an amino group), without any spacer, to form a u-electron conjugated system with electron rich and electron poor terminals, then ICT from the electron donor to receptor is enhanced upon excitation by light.[44]

1.10.3. Excited State Intramolecular Proton Transfer (ESIPT):

ESIPT process incorporates a fast excited-state proton transfer from a proton donor to an acceptor group mediated by an intermolecular hydrogen bonding. The ESIPT process drastically reduces the chance of photochemical reactions of excited molecules and significantly enhances the photo stability of the molecules. In addition, a large apparent stokes shift may also be observed. Thus, the ESIPT process is very suitable for designing luminescent chemodosimeters with spectral shift for selective detection.[45]

1.10.4. Fluorescence Resonance Energy Transfer (FRET):

Fluorescence Resonance Energy Transfer (FRET) (***Fig. 1.12)*** approach is also applied in designing chemosensor. Usually for FRET system, sufficiently large spectral overlap is necessary between the donor emission and the acceptor absorption, which limits the resolution of double-channel images.[46]

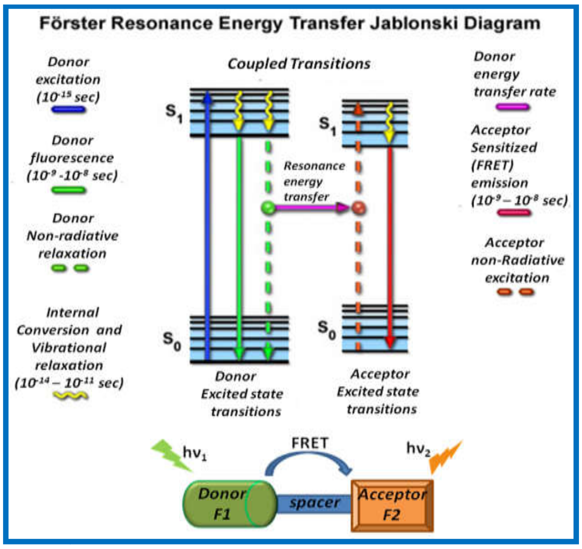


Fig. 1.12: Jablonski diagram illustrating coupled transitions between donor emission and acceptor absorbance in fluorescence resonance energy transfer.

1.11. Development of AIEE based Chemosensor:

Since the discovery of aggregation induced emission enhancement (AIEE) phenomenon, the field has been rising and become one of the most advanced research topics. The AIEE phenomenon provides unique materials which are luminescent in their aggregate state to impact the use of these materials in our day to day, such as sensing, OLED, bioimaging, solar cells and OFET [47-50]. Tang's research group recognized one fundamental mechanism RIR to explain this type of phenomenon. Based on that, some functional groups introduced into a large diversity of AIEE luminogens, which include conjugated stators together with aromatic rotors were developed e.g, chemosensors, bioprobes and solid-state emitters [51-55]. AIEEgens have successfully been used as "turn-on" fluorescence sensors [56-59]. Diverse AIEE based chemosensing systems have been explored for a broad range of analytes, such as ions [60], explosives [61] and fingerprints [62], which are importance for homeland security, water quality control, environmental protection and forensic investigation etc.

Considering the advantages of AIEE probes such as high sensitivity and selectivity Tang et. al. integrated the AIEE concept with the selective recognition of Zn^{2+} ions (***Fig. 1.13***) [63]. Much effort on the application of AIEE luminophores has been given to utilities in optoelectronic and sensory fields [47-50]. Together with high efficiency OLEDs, a large number of AIEE active materials and biological probes have been successfully developed [64].

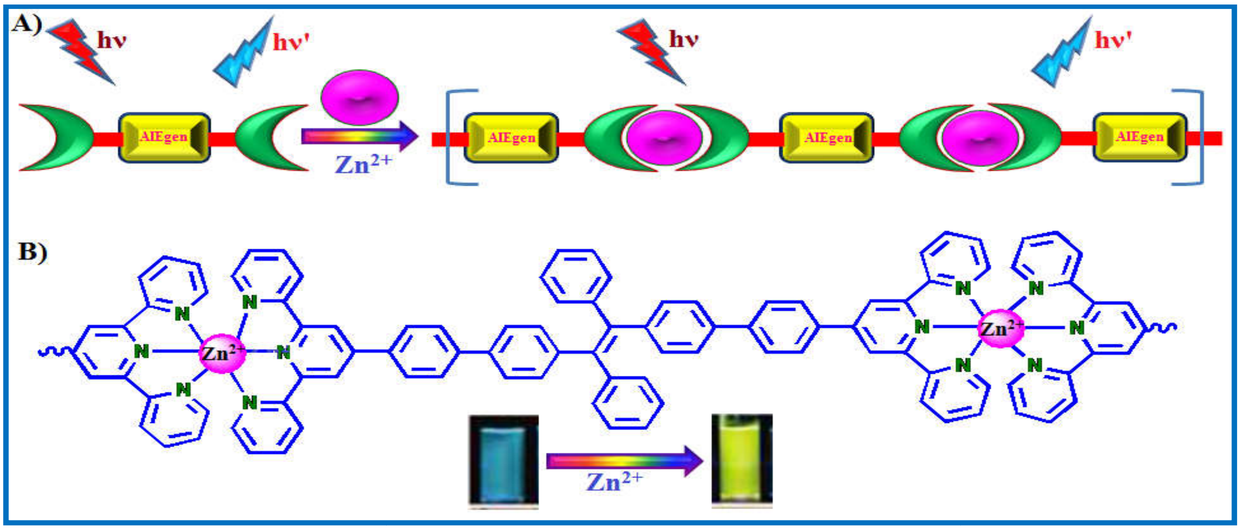
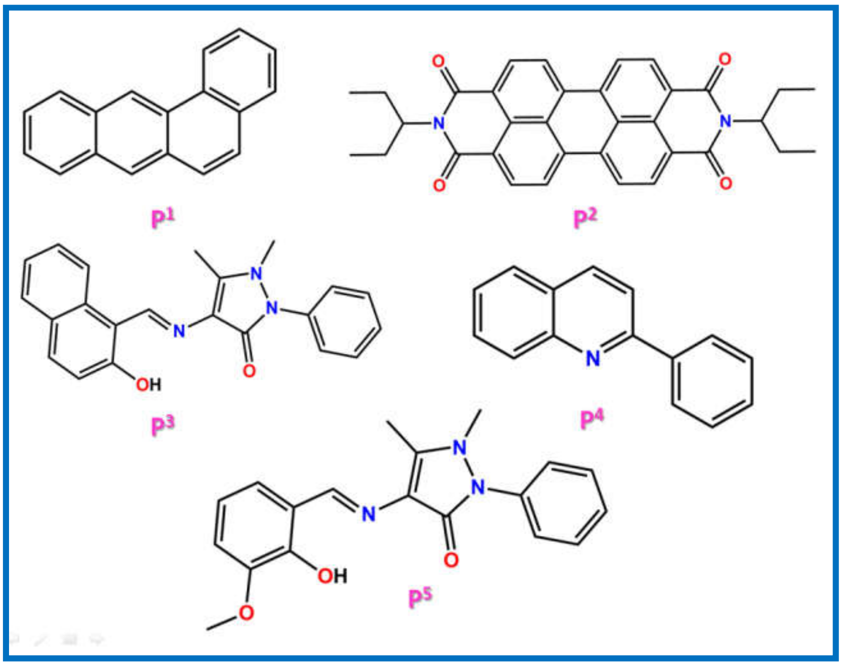


Fig. 1.13: Representative examples of fluorescent chemosensors for Zn^{2+} on the basis of AIEgen. (A) Possible stoichiometry of sensing Zn^{2+} ions. (B) Structure of zinc-bound AIEgen, and photographs of the aqueous solutions of after and before Zn^{2+} taken under UV light illumination at 365 nm.

1.12. Objectives of the Present Thesis Work:

In the earlier sections, a few important ideas related to this work are introduced. By putting together some of these concepts it is possible to define the objective of this thesis. On the basis of above different signal transduction mechanisms and properties of fluorophores, this Ph.D project will aim to synthesis of low dimensional fluorescence organic materials, design and develop novel fluorescent chemosensors that will incorporate Schiff bases with functionality, in order to study receptor/functional groups which can sense a particular analyte. The main focus of this PhD work will be the design of novel materials in such a way that it fulfill most of the basic structural requirements, such as solubility, stability, and aggregation induced emission with high quantum yields. It is also important to mention that we will take account of design prerequisites that will help us to generate target derivatives for supramolecular chemistry, i.e. materials are designed having in mind Pearson's rules of hard and soft donors and acceptors, and the photophysical mechanisms of recognition inherent to analyte binding. In this way, functionalization with different donor atoms will be carried out.

In this thesis, we propose to develop low dimensional fluorescence organic materials and diversity of fluorescent chemosensors for the detection of various biologically and environmentally relevant analytes (Al^{3+}, Zn^{2+} & TNP) by using varied choice of fluorophores usually flat disk-like aromatic molecules (anthracene & naphthalene), some of them looking for novel AIEE properties. In the previous description of numerous categories of AIEE luminogens, the propeller-like molecules consisting of π-conjugated rotors and stators have caught our greatest attention and curiosity, owing to their structural simplicity and great color tunability. On the basis of our mechanistic understanding, we have also developed a large variety of new AIEE active luminogens with emission colours covering the entire visible spectral region which are pursue as chemical sensors, smart nanomaterials, and solid-state emitters. The binding mode toward analytes and signal transduction mechanism would be investigated by the combination of absorption, fluorescence, NMR, SEM, TCSPC methods. The interesting properties of fluorophore containing Schiff base derivatives and low dimensional organic material encouraged us to dedicate our effort to the comprehensive research on the synthetic scheme, photophysical behavior, as well as exploration of their potential modern applications to enrich the whole story of fluorescent chemosensor as well as aggregation-induced emission enhancement. The fluorophores adopted in this research endeavor are listed in ***Scheme 1.3***.



Scheme 1.3: Design of target molecules