

The thesis entitled “*Design and Synthesis of Novel Organic Materials Having Potential Applications for Organic Light Emitting Diodes and Chemosensors*” has been divided into FIVE chapters. Each chapter is further sub-divided into the following sections: introduction, results and discussion (synthesis, photophysical, electrochemical, thermal and electroluminescent properties), conclusions, references and spectroscopic data.

Chapter 1: Introduction to Organic Light Emitting Diodes (OLEDs) and Chemosensors & Literature Survey.

OLEDs:

Organic light emitting diodes (OLEDs) have attracted considerable attention in both scientific and commercial applications, since the pioneering work by Tang and VanSlyke in 1987, because of their characteristic low driving voltage, high brightness, full-colour emission, fast response time, wide viewing angle and self-emitting properties. Extensive research has been carried out to promote OLEDs in commercial applications, such as flat-panel displays and solid-state lighting resources, due to their low cost. OLEDs have been successfully utilized in mobile phones, computers, car stereos, digital cameras, wrist watches and white solid-state lighting *etc.* Many researchers were attracted by this research interest due to demands for full-color flat-panel displays have been increased in the development of different display technologies. One of the greatest break-through technologies in the field of displays is that of the organic light emitting diode (OLED), which constitute a new and exciting emissive display technology.

In the OLEDs the light is generated through the process of electroluminescence(EL), This phenomenon arises from the electron-hole recombination that occurs when a voltage is applied to semiconductor materials sandwiched between two electrodes. In between these two electrodes, semiconductor materials were deposited as layers. Such are usually hole-transporting, emissive, and electron-transporting layers. When a voltage is applied, electrons are injected from the cathode into the electron-transporting layer, while holes are injected into the hole-transporting layer. The charges travel through the respective transport layers until they recombine and produce the excitons, which then decay while releasing energy in the form of light In recent years, tremendous progress has been made in the development

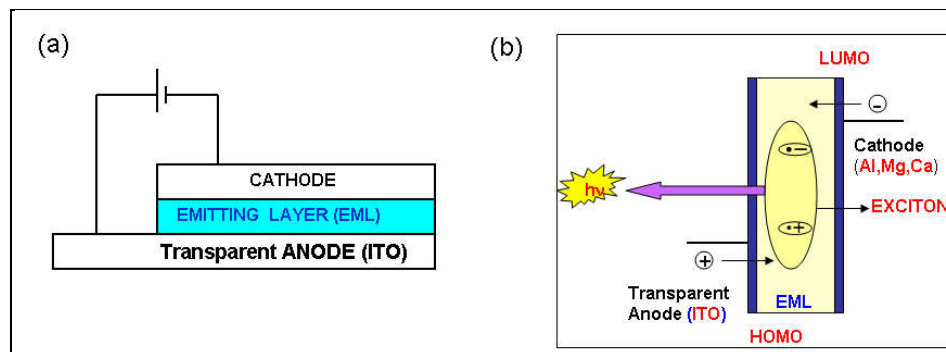
of organic light-emitting diode (OLED) science and technology, The first efficient OLEDs were fabricated using fluorescent emitters such as tris-(8-hydroxyquinoline) aluminum (Alq3). In these devices only the singlet excitons contributed to the devices light output. Since theoretical estimations predict the formation of singlet exciton for each triplet excitons, then the theoretical limit for fluorescence-only devices was a 25% theoretical internal efficiency. Recently, phosphorescent OLEDs (PHOLEDs) have attracted much attention due to the use of singlet and triplet excitons, which theoretically allows the upper limit for internal quantum efficiency to be 100%. The high theoretical quantum efficiency, up to 100% internal efficiency that can be achieved, is due to the quantum statistic (75% excitons are triplet) and intersystem crossing from singlet to triplet excited states

The most basic structures of OLEDs, which have been widely reported in the literature, are multi layer fluorescent emitters and phosphorescent organic light emitting devices (PHOLEDs). To reduce the complexity and overall cost, and to increase the extent of OLED commercialization, several organic light-emitting materials possessing electron or hole transporting characteristics, or even both properties in a single molecule, are being developed, such that their devices can be simplified to a double or even single-layer device architecture. The electro chemiluminescence (ECL) properties including color purity is extremely sensitive to the dopant concentration (usually <5%), and triplet–triplet annihilations.

The present chapter describes the basic introduction of OLEDs and evolution of organic electroluminescence phenomenon and its potential applications. Details of the basic structure of OLED, device operation and mechanism of single layer and multilayered configurations are illustrated. It also describes about the small molecule based hole transporting materials, electron transporting materials, emitting materials along with charge transporting property, fluorescent emitters and delayed fluorescence concept. Though the OLEDs are developing rapidly but still the organic materials are required with improved efficiency, color purity as well as long lifetime and stability. Organic emitting materials with charge transport property and bipolar nature can reduce the device complexity and cost. Hence, it is a challenging to researchers to develop such type of compounds which can bring OLEDs into commercialization. The objective of this thesis is to understand, electronic and optical properties and morphological stability are varying with the chemical structure of

organic compounds. This also explains the design, synthesis and electronic properties of series of newly synthesized materials and their applicability in OLEDs. Figure 1. shows the single layer device structure (a), and operating principle (b) of OLEDs.

Figure 1: Single layer device structure, and operating principle.



Chemosensors:

Transition metal and P-block metal ions play a vital role in human life, occupy an important position in biology. These metal ions like iron, zinc, copper, aluminum, chromium, and manganese absolutely necessary for human life. Iron is present in many proteins and enzymes either for structural purposes or as part of a catalytic site. It is the most abundant intracellular metal ion and plays an important role in a variety of vital cell functions, i.e., oxygen metabolism and electron transfer processes to DNA and RNA syntheses. Especially Iron (III) functions as oxygen carrier in hemoglobin and plays vital roles in enzyme catalysis and cellular metabolism. Even though Fe^{3+} is essential, it can be toxic because of its ability to promote oxidation of lipids, proteins and other cellular components. The deficiency as well as overload of Fe^{3+} ion concentration may lead to several disorders and health issues such as Alzheimer disease, anemia, diabetes, hemochromatosis, cancers and dysfunction of organs such as heart, pancreas and liver.

Zinc is the second most abundant transition metal in humans. The Zn^{2+} ions play several roles in a variety of physiological, pathological processes, DNA binding and recognition, catalytic centers and neural signal transmission. It is as the structural cofactor in metalloproteins. Zn^{2+} ions are vital for many cellular processes such as apoptosis, DNA synthesis, neurotransmission, gene expression, modulation of diverse

ion channels, and signal transduction. Clinically, diverse Zn^{2+} based compounds have been used as tumor photosensitizers, antibacterial/antimicrobial and anticancer agents, radioprotective agents, and antidiabetic insulin mimetics. It was located mainly in muscle and bone, deficiency of Zn metal ion can lead to type I and type II diabetes diseases, neural malfunction, Alzheimer's disease and cancers. a variety of physiological and pathological processes.

Copper is the third most abundant transition metals in the human body, Copper plays a vital role in biological, environmental, and chemical systems. Cu element is essential for both plants and animal, including humans. The Cu^{2+} ions play an important role in several physiological responses, biological processes (redox catalysts) that involve electron transfer reactions and oxidation of various organic substrates. Excess concentration of copper causing damage to liver. It is leads to both Indian childhood cirrhosis (ICC), and non-Indian childhood cirrhosis (NICC). Excess concentrations of Cu^{2+} can also lead to Alzheimer's and Wilson's diseases.

Particularly, trivalent metal ions like Fe^{3+} or Al^{3+} or Cr^{3+} have their own biological significance and they directly involved in the cell function. Aluminium is the highest abundant metal in the earth crust after oxygen and silicon. Extensive usage of aluminium utensils for cooking/storage and intake of aluminium based pharmaceuticals lead to increase its concentration in the human body. Excess levels of Al^{3+} can cause to adverse physiological effects and may result in Alzheimer's disease, gastrointestinal problems, osteoporosis, anemia, headache, colic, rickets, memory loss and muscle ache. Apart from Fe^{3+} and Al^{3+} , Cr^{3+} also has significant roles on human health. The Cr^{3+} deficiency may result in diabetes, cardiovascular diseases and excess levels of Cr^{3+} can adversely affect on cellular structures. Mercury is one of the most toxic transition metal ions, and can easily pass through biological membranes. On the other hand, fluoride plays a vital role in the treatment of osteoporosis and in the prevention of dental caries. However, exposure to excess levels of fluoride can lead to dental or skeletal fluorosis, or cancer. Hence, design, synthesis and evaluation of fluorescent probes with high sensitivity and selectivity toward Hg^{+2} and F^- are highly desirable.

Due to the potential impact of these ions on human health and the environment, development of techniques for sensing and monitoring these ions has become the focus of numerous studies. Till to date Several techniques like atomic

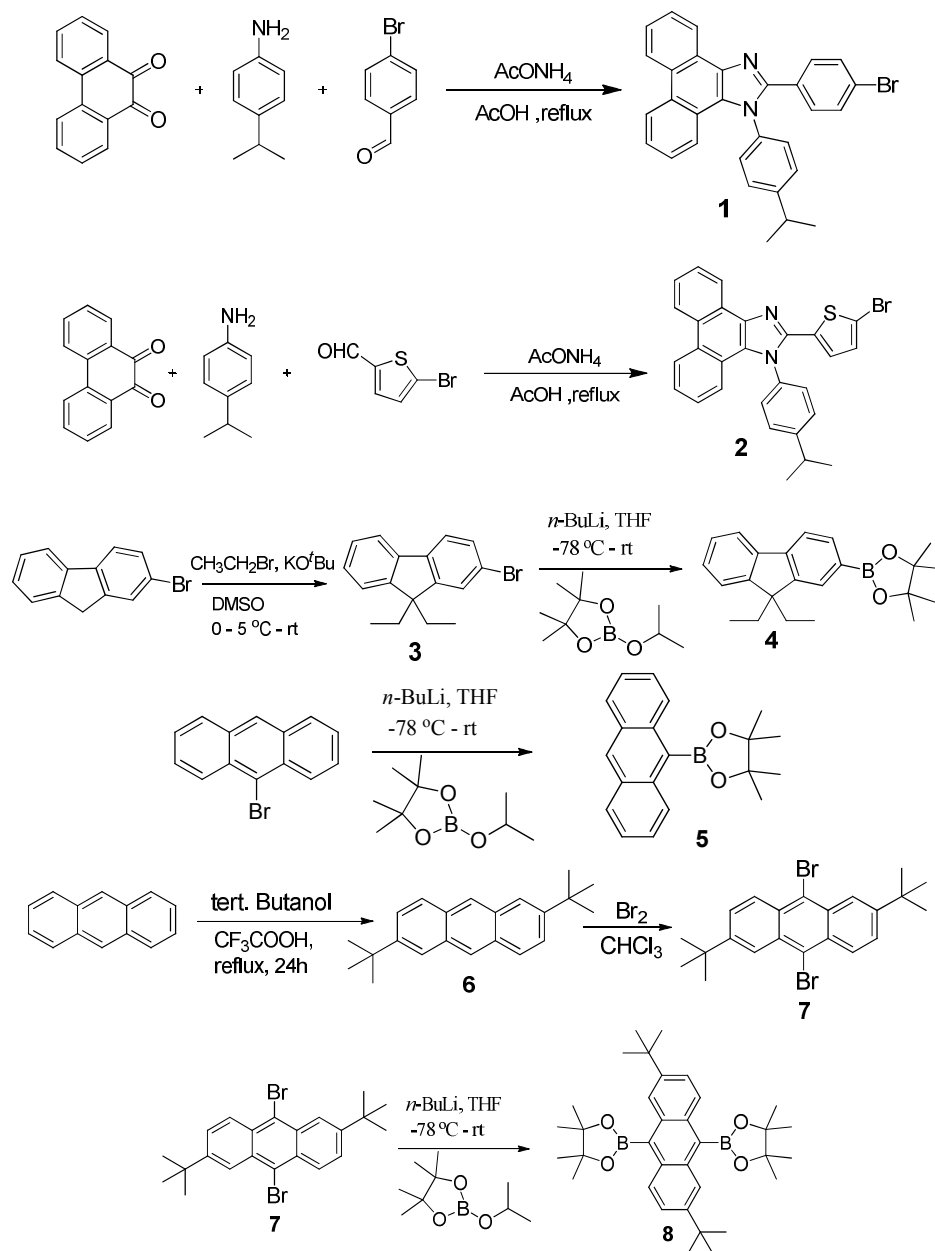
absorption spectroscopy, colorimetry, spectrophotometry, inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), voltammetry, spatially resolved mass spectrometry techniques, electron spectroscopy imaging (ESI) combined with electron energy loss spectroscopy (EELS), and X-ray fluorescence microscopy (XRFM) have been developed for the detection of transition metal ions. Recently, much interest has been focused on the development of MRI and fluorescence probes for the imaging of metal ions in the living cells. Among the above mentioned analytical techniques, fluorescence imaging has received widespread application in biology over other methods because of the experimental simplicity and being easy to perform, portable, and not requiring sophisticated instrumentation. Hence, development of fluorescent chemosensors for the imaging of metal ions has become an emerging area of current research interest. voltammetry have been used for aluminium and iron ions detection. However these methods are costly complicated and not convenient for quick monitoring of Fe^{3+} , Fe^{2+} and Al^{3+} ions. Fluorescent and colorimetric sensors have been particularly attractive due to their simplicity, versatility, sensitivity and real-time monitoring with a quick response time.

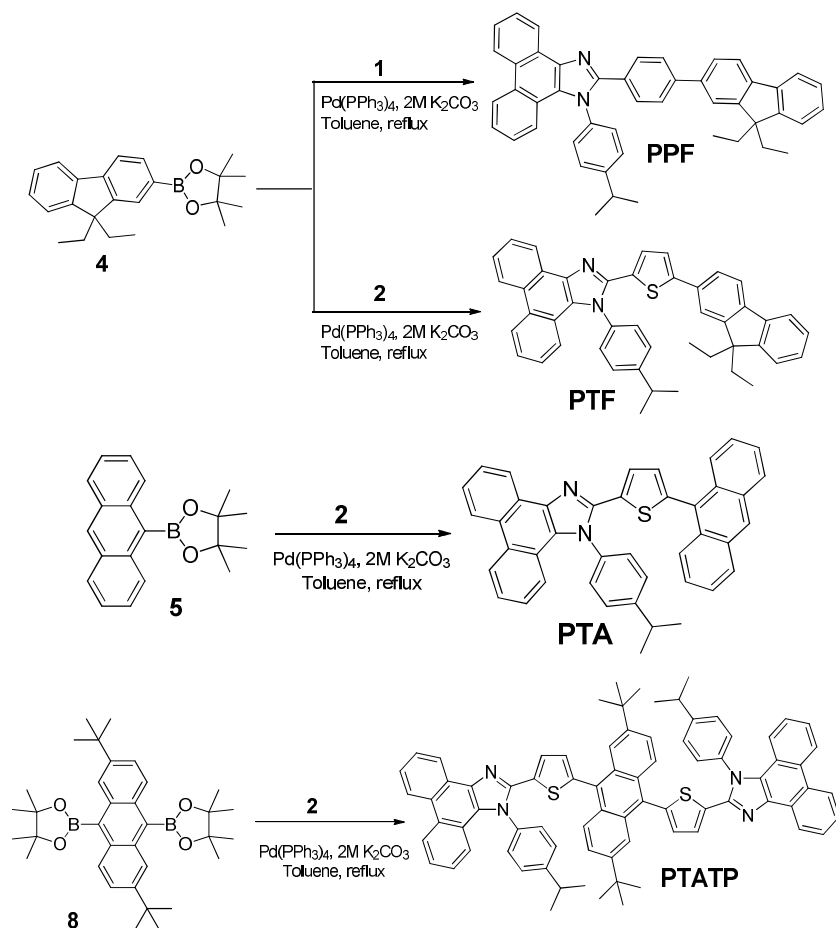
Chapter 2: Delayed Fluorescence Based Phenanthro-imidazoles as OLED Emitters having Electron Transporting Properties.

Current research in the field of organic light emitting devices is focused on designing third generation materials which use the photo physical phenomenon of thermally activated delayed fluorescence (TADF). Organic light emitting devices under electrical current generate approximately 25% singlets and 75% triplets. Hence it is argued that OLEDs prepared using fluorescent materials can achieve 25% quantum efficiency where as a compound having fluorescence and phosphorescence emission can theoretically result in obtaining 100% efficiency. However, phosphorescent OLEDs have some disadvantages including lower electrolchemiluminescence (ECL) efficiency under high current. Enormous amount of efforts are being made to improve the efficiency of the device using triplet to singlet energy transfer which results in delayed fluorescence. Delayed fluorescence can be obtained from two different processes i.e., reverse intersystem crossing (RISC) from the lowest triplet to singlet excited state (E-type, $T \rightarrow S$ upconversion, or

thermally activated delay fluorescence) or triplet-triplet annihilation (TTA, P-type, T→S upconversion). Even though fluorescent materials have been widely studied, TADF materials remain quite rare. TADF has been observed in certain dyes, fullerenes, porphyrin derivatives and metal complexes.

Scheme 1: Synthetic route for key intermediates.



Scheme 2: Synthetic route for the target compounds.

Photophysical, electrochemical and thermal properties for all four compounds are studied in detail. The photoluminescence spectra of all compounds indicated their emission in blue region with good fluorescence quantum yields (**Table 1**). All the synthesized compounds are thermally stable at higher temperatures.

Table 1. UV-Vis absorption, and fluorescence data of Phenanthrene derivative compounds.

S.NO	Compound	λ_{abs}^a (nm)	Film ^b (nm)	λ_{em}^a (nm)	Film ^b (nm)	$E_g^{\text{opt } c}$ (eV)	Φ_f^d
1	PPF	362,337,270	372,351	426,407	438	3.2	0.6
2	PTF	395,260	434(sh),408	470,444	486	2.9	0.73
3	PTA	390,373,354	395,378	526	500	2.9	0.19

4	PTATP	403,385,369	412,383,371	507	516	2.9	0.56
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^a Recorded in chloroform at rt (10 μ M sol.). ^b Recorded in thin film state. ^c Optical band gap estimated from the absorption threshold. ^d Fluorescence quantum yields measured in cyclohexane, relative to 9,10-diphenyl anthracene ($\Phi = 0.9$ in cyclohexane).

Table 2. Thermal analysis data of Phenanthrene derivative compounds obtained from TGA and DSC measurements.

S.NO	COMPOUND	T _d (°C) ^a	T _m (°C) ^b	T _g (°C) ^c
1	PPF	429.1	163.7	114.2
2	PTF	398.3	233.8	107.7
3	PTA	412.1	241.8	121.4
4	PTATP	498.8	380.8	205.7

^a T_d: Decomposition temperature. ^b T_m: Melting point. ^c T_g: Glass transition temperature.

In summary, in this chapter a series of four small organic molecules (**PPF**, **PTF**, **PTA** & **PTATP**), have reported the design and synthesis of phenanthroimidazole derivatives. Final step of target molecule was prepared by adopting Pd(0)-catalyzed Suzuki-Miyaura coupling reaction. Optical, thermal and electrochemical properties were evaluated for the same. The four molecules exhibited good thermal properties like high T_d and high T_g. Electrochemical properties evaluated for these compounds indicate that these can act as good electron transporters cum emitters. Delayed fluorescence, observed for **PPF** and **PTF** originates from intra-molecular triplet to singlet energy transfer and this phenomenon provides a new design principle that, one can harvest triplets produced electrochemically to fluorescing singlets in OLEDs. The new phenanthroimidazole compounds reported in this work possess all qualities to be used as materials for making OLEDs.

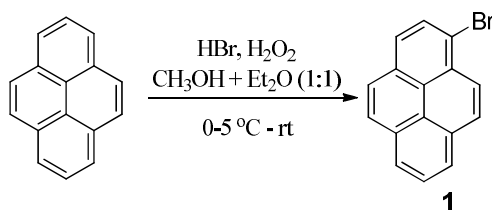
Chapter 3: Synthesis and Characterization of new Pyrene Derivatives end-capped with Phenyl Quinoline as Efficient Electron Transporting Blue Emitters for Non-Doped OLEDs

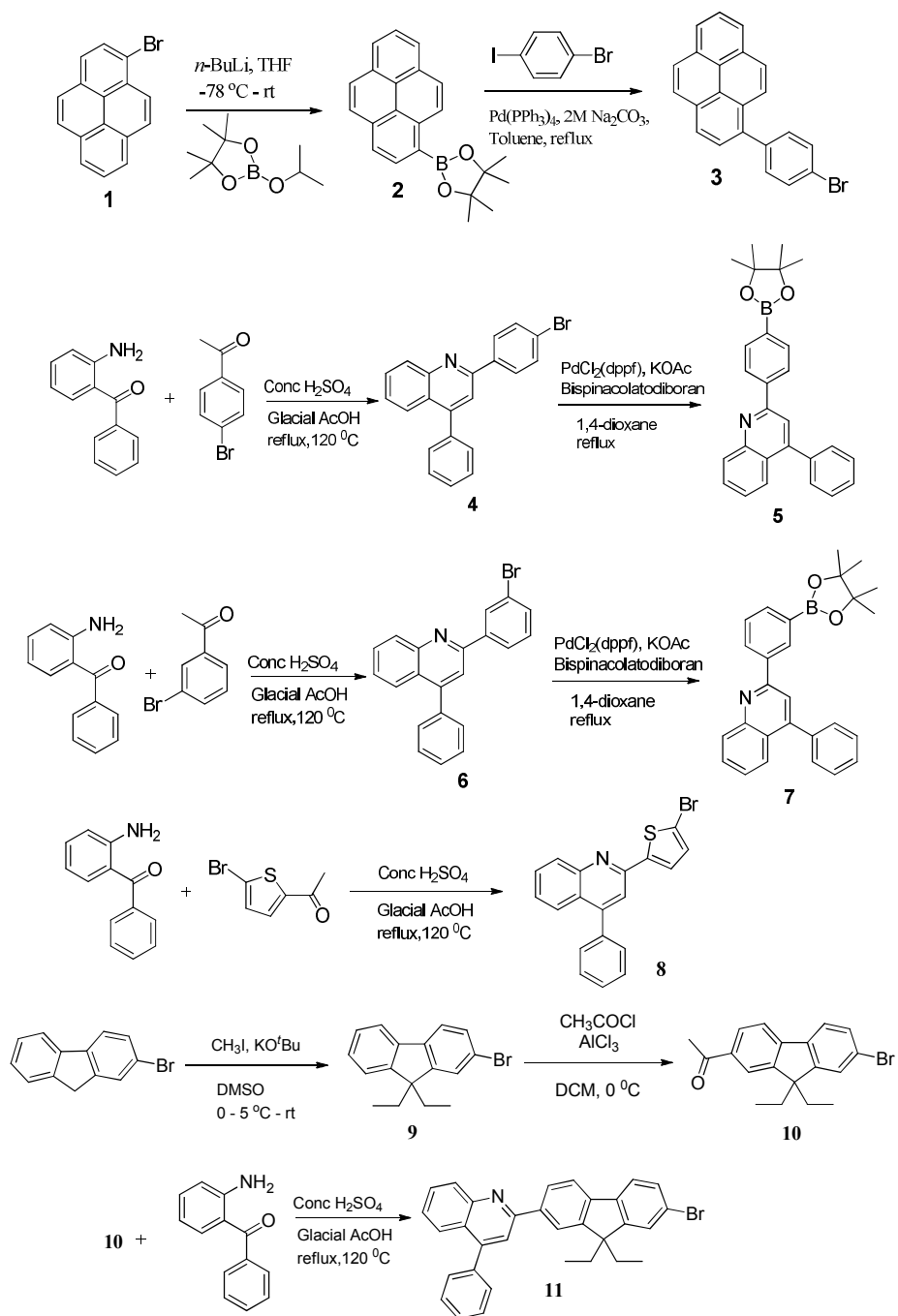
Ever since the invention of organic light emitting diodes (OLEDs) by OLED pioneers Tang and VanSlyke in 1987, were introduced organic light emitting diodes (OLEDs) having applications in flat panel displays and solid-state lighting resources.

The field has developed rapidly, and efficiency of OLEDs has increased steadily, making OLEDs promising alternative to many of today's display and technologies. Subsequently, this field becomes a fascinating technology to the area of research in field of chemistry, material science and physics in human life. After that worthwhile scrutiny has been made for commercial applications in displays and solid state lightings, for flat panel displays is becoming very promising. Although Primary color (RBG) emitting materials are all important for full-color displays, only red (orange) and green emissions have sufficient efficiencies and lifetimes to be of commercial value. The wide band gaps of the blue emitters will lead to larger energy gaps between their LUMO levels and their HOMO level, due to this blue OLEDs show relatively poor performance compared to red and green OLEDs. Hence, the development of blue emitting materials with high efficiencies is more prominent. Pyrene is one of the most promising moiety for organic semiconducting device applications because of its high fluorescence quantum yield, thermal stability and more active positions to develop different derivatives. Pyrene-derivatives have been widely affianced as active layers in various optoelectronic applications such as, OLED, organic photo voltaics (OPV), organic field effect transistors (OFET),*etc.* The Phenyl quinoline moiety incorporated to materials have been extensively used as emitting with ET property.

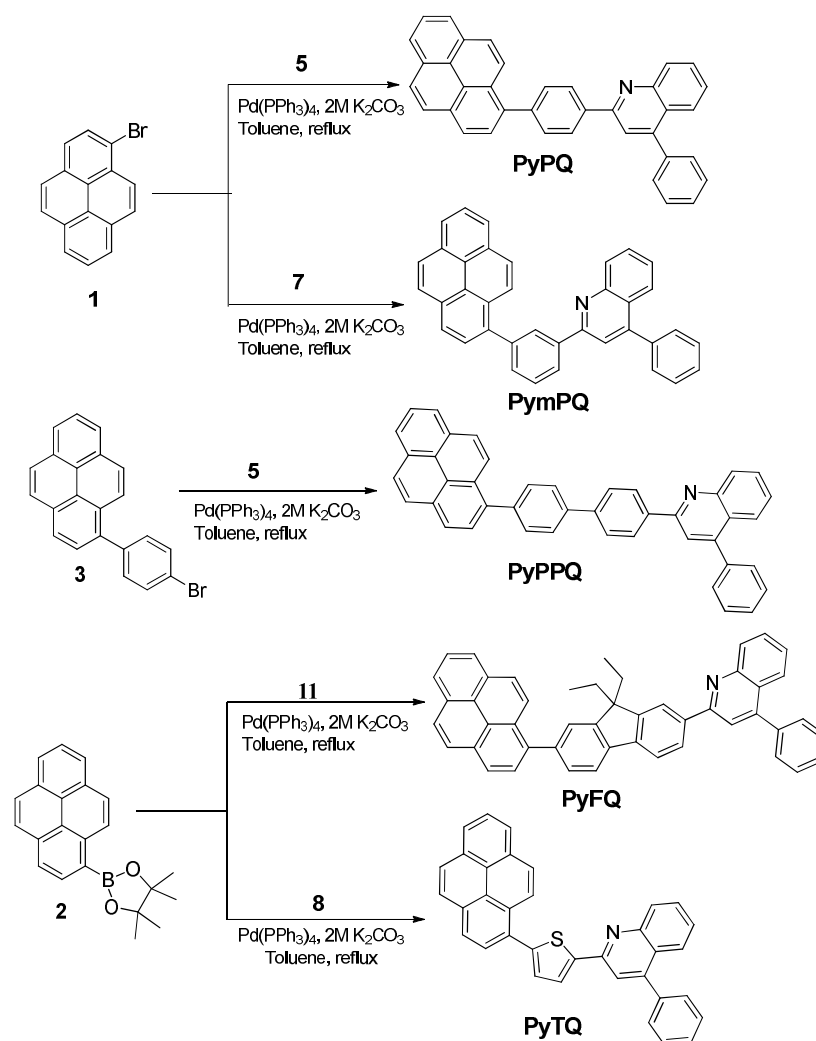
The present chapter deals with an aim to develop efficient electron transporting blue-emitters, five new pyrene derivatives (Scheme 4) appended with Phenyl-Quinoline moiety have been investigated. In this series, pyrene is employed as an emitter and Pheny-Quinoline is incorporated for better electron-transport property and various spacers were used to understand the structure property relationship. The synthetic details are illustrated in **Scheme 3 and 4**.

Scheme 3: Synthetic route for key intermediates





Scheme 4: Synthetic route for five target compounds



The photophysical, electrochemical and thermal properties of the synthesized target compounds are explored. Photophysical properties indicate that all the compounds are emitting in blue region with excellent fluorescent quantum yields (0.59-1.0, **Table 3**). To have a deeper understanding of the electrochemical properties, cyclic voltammetry measurements are performed and the results obtained indicate that the results are in accordance with the adjacent layers for efficient charge injection. By incorporating Phenyl-Quinoline moiety to pyrene, all the synthesized compounds exhibited excellent thermal stability (T_d in the range of 396-438 °C and T_g in between 91-125 °C), which is useful to form good films with better morphology to improve the device efficiency.

Table 3: UV-Vis absorption, and fluorescence data of Pyrene derivative compounds.

S.NO	compound	$\lambda_{\text{abs}}^{\text{a}}$ (nm)	Film ^b (nm)	$\lambda_{\text{em}}^{\text{a}}$ (nm)	Film ^b (nm)	$E_g^{\text{opt c}}$ (eV)	Φ_f^{d}
1	PyPQ	281,350	372	436	468	3.16	1.0
2	PyPPQ	288,351	371	435	462	3.29	0.7
3	PymPQ	281,346	352	388	467	3.37	0.70
4	PyFQ	280,364	372	430	453	3.11	1.0
5	PyTQ	280,383	404	473	479	2.86	0.59

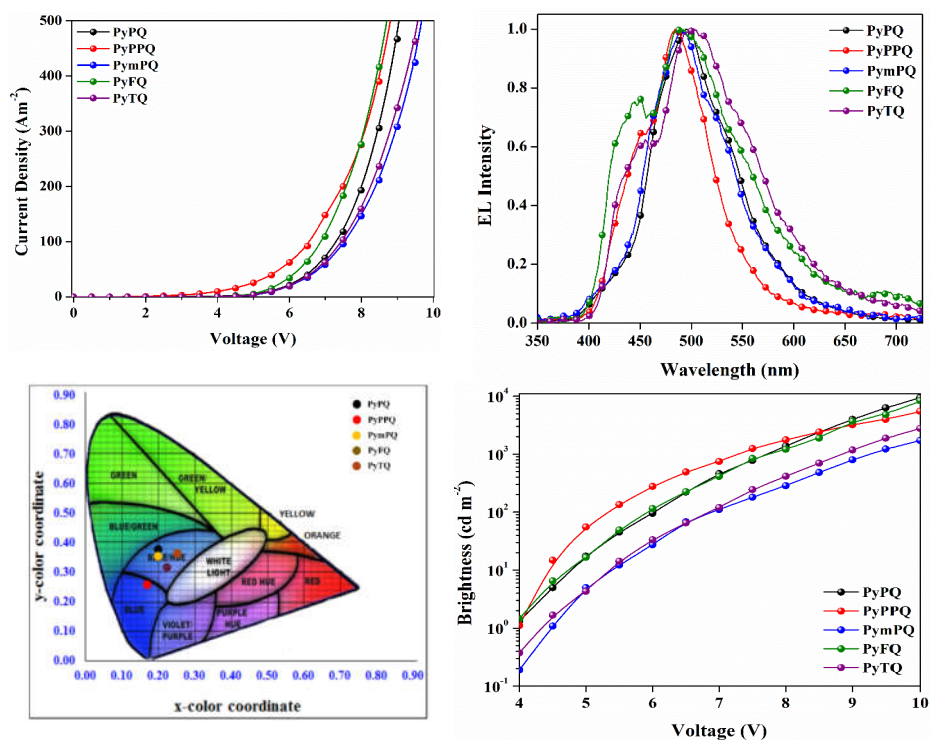
^a Recorded in chloroform at rt (10 μM sol.). ^b Recorded in thin film state. ^c Optical band gap estimated from the absorption threshold. ^d Fluorescence quantum yields measured in cyclohexane, relative to 9,10-diphenyl anthracene ($\Phi = 0.9$ in cyclohexane).

Table 4. Thermal analysis data of Pyrene derivative compounds obtained from TGA and DSC measurements.

S.NO	COMPOUND	T_d ($^{\circ}\text{C}$) ^a	T_m ($^{\circ}\text{C}$) ^b	T_g ($^{\circ}\text{C}$) ^c
1	PyPQ	396.1	255.7	93.6
2	PyPPQ	438.1	284.7	90.7
3	PymPQ	410.2	276.4	91.2
4	PyFQ	438.9	245.2	125.3
5	PyTQ	413.8	223	91.5

^a T_d : Decomposition temperature. ^b T_m : Melting point. ^c T_g : Glass transition temperature.

To test the applicability of these materials in OLED, non-doped OLEDs are fabricated using the target compounds as emitter [configuration: ITO (120 nm)/ α -NPD (30 nm)/ **Pyrene target compound** (35 nm)/BCP (6 nm)/ Alq₃ (30 nm)/ LiF (1 nm)/ Al (150 nm)] as well as electron transporting emitter [ITO (120 nm)// α -NPD (30 nm)/Emissive layer (**Py-compounds**) (45 nm)/LiF (1 nm)/Al (150 nm)]. The electroluminescence (EL) plots of all the compounds are depicted in Figure 2. Among all the compounds, **PyPQ** displayed high current efficiency of 4.63 cd/A, power efficiency of 3.19 lm/W and high brightness 9432 cd/m² as an emitter (Table 4) at applied voltage 100 cd m⁻².

Figure 2: EL plots of pyrene-quinoline derivatives**Table 5:** The EL performance data of compounds as emitters

Device ^a	V_{onset} (V) ^b	L_{max} (cd m ⁻²) ^c	η_c (cd A ⁻¹) ^d	η_p (lm W ⁻¹) ^d	η_{EQE} (%) ^d	λ_{em} (FWHM) (nm) ^e	CIE (α, β) ^g
PyPQ	3.75	9432	4.63	3.19	2.61	495 (60)	(0.204, 0.373)
PyPPQ	3.94	5484	2.88	2.21	2.17	452 ^f , 484 (46)	(0.168, 0.258)
PymPQ	4.34	1714	1.92	1.15	1.14	488 (59)	(0.201, 0.351)
PyFQ	3.72	8390	3.38	2.39	2.19	446 ^f , 490 (92)	(0.227, 0.318)
PyTQ	4.22	2774	1.83	1.12	1.02	455 ^f , 502 (71)	(0.247, 0.371)

^a Device Configuration: ITO (120 nm)/ α -NPD (30 nm)/ **Pyrene** (35 nm)/BCP (6 nm)/ Alq₃ (30 nm)/ LiF (1 nm)/ Al (150 nm).
^b V_{onset} : turn-on voltage at luminance of 1 cd m⁻²
^c L_{ma} : Luminance at 10 V
^d current efficiency (η_c), power efficiency (η_p) and external quantum efficiency (η_{EQE}) at applied voltage 100 cd m⁻²
^e λ_{em} : Emission wavelength maximum. FWHM: full width half maximum at 10 V
^f Shoulder Peak
^g CIE color coordinate

In summary, five novel pyrene-quinoline derivatives as multifunctional emitters have been developed. All the compounds emit in blue region with excellent fluorescence quantum yields. HOMO/LUMO energy levels are appropriate for efficient charge injection. All the compounds are thermally stable over a wide range of temperatures. Non-doped OLEDs are fabricated for the compounds as an emitter as

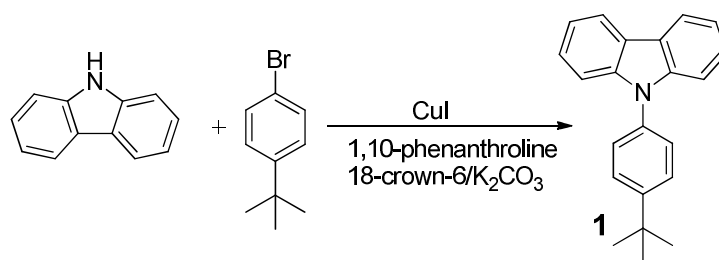
well as an electron transporting emitter to know the applicability of these materials in OLEDs.

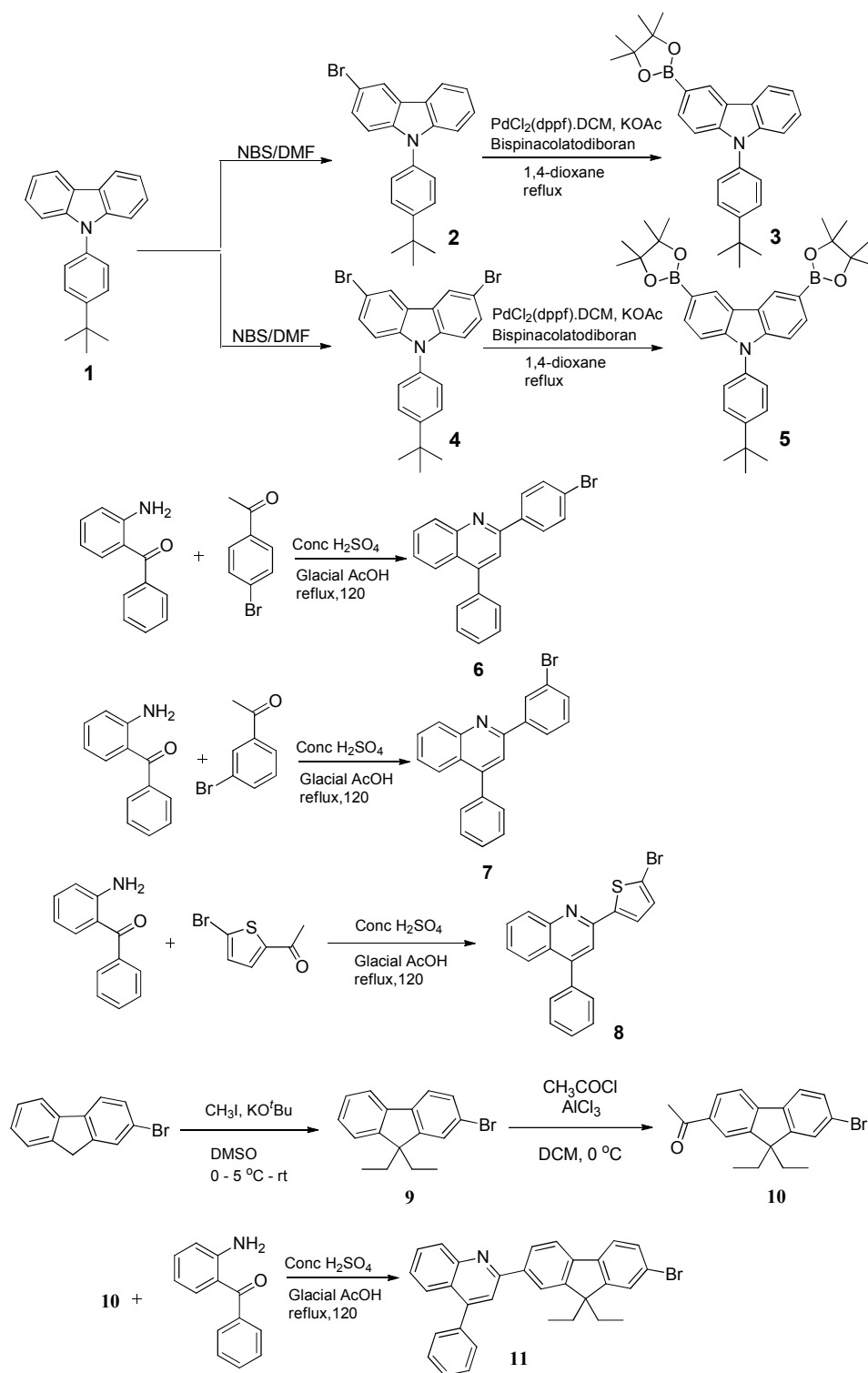
Chapter 4: Synthesis and Characterization of New Carbazole coupled Phenyl-Quinoline Derivatives as Promising Bipolar Materials for Blue Organic Light Emitting Diodes

Carbazole derivatives are commonly used hole-transporting (HT) and host materials due to their very good HT properties, high triplet energy values and easy chemical manipulation. On the other hand phenyl-quinoline, a nitrogen-containing electron deficient heterocyclic entity facilitates electron injection and transport and exhibits good emission properties. Bipolar emitting materials can reduce the device complexity and cost.

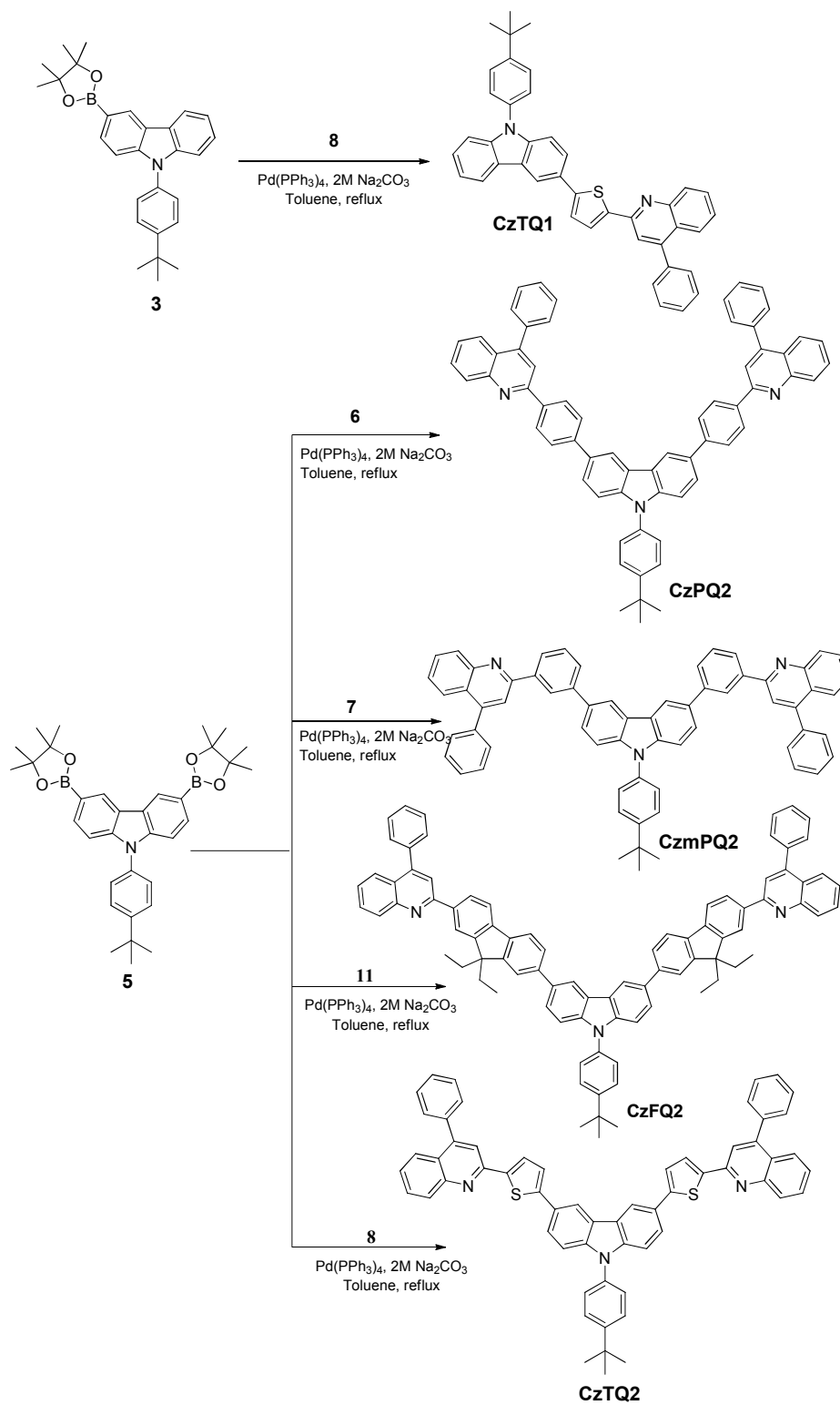
In this chapter the design strategy, synthesis, photophysical, electrochemical and thermal properties of bipolar blue emitting materials composed of carbazole coupled with Phenyl-quinoline moieties (**Scheme 6**) have been described. In this series, carbazole moiety is used as central core owing to its high thermal stability as well as better HT property. Central core Carbazole unit is attached to Phenyl-quinoline moiety to study their affect on hole transport (HT) and electron transport (ET) properties. The Funnel(Y) shaped configuration of the derivatives may further offer improved solubility, high thermal stability, better film formation, structural uniformity and high degree of purity compared with linear organic conjugated oligomers and polymers.

Scheme 5: Synthetic route for intermediates.





Scheme 6: Synthetic route for target compounds.



The absorption and photoluminescence (PL) characteristics of the synthesized materials are studied in solution as well as in thin film states to estimate their photophysical characteristics. The electrochemical properties of the synthesized derivatives are measured using cyclic voltammetry (CV) and the calculated HOMO and LUMO energy values are in the range of 5.37-5.57 eV and 2.49-2.66 eV, respectively.

Thermal stability of the materials is verified using thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements. The observed decomposition temperature (T_d) from TGA and the glass transition temperature (T_g) from DSC are in the range of 457-521 °C and 155-169.5 °C, respectively.

Table 6: Thermal data obtained from TGA and DSC measurements

S.NO	COMPOUND	T_d (°C) ^a	T_m (°C) ^b	T_g (°C) ^c
1	CzPQ2	521.2	294	167.4
2	CzmPQ2	497.6	269.5	155.9
3	CzFQ2	473.8	300.6	161.2
4	CzTQ2	457.6	322.6	169.5
5	CzTQ1	409.4	198.6	120.6

^a T_d : Decomposition temperature. ^b T_m : Melting point. ^c T_g : Glass transition temperature.

In summary, five new ambipolar materials with Carbazole as electron donors and phenyl quinoline as electron acceptor with different spacers, were synthesized. The photophysical, electrochemical and thermal properties of the derivatives were studied to evaluate their suitability as ambipolar emitting materials in OLEDs. The high fluorescence quantum yields, suitable HOMO/LUMO energy levels, and excellent thermal stability of depict them as good candidates for the realization of efficient ambipolar materials for blue OLEDs.

Chapter 5: Design and synthesis of Rhodamine based Chemosensors

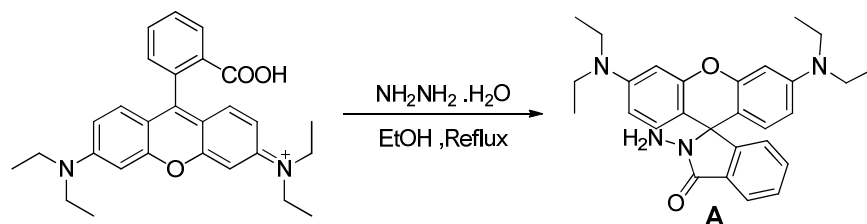
A novel FRET 'off-on' fluorescent probe for the selective detection of Fe^{3+} , Al^{3+} & Cr^{3+} ions and

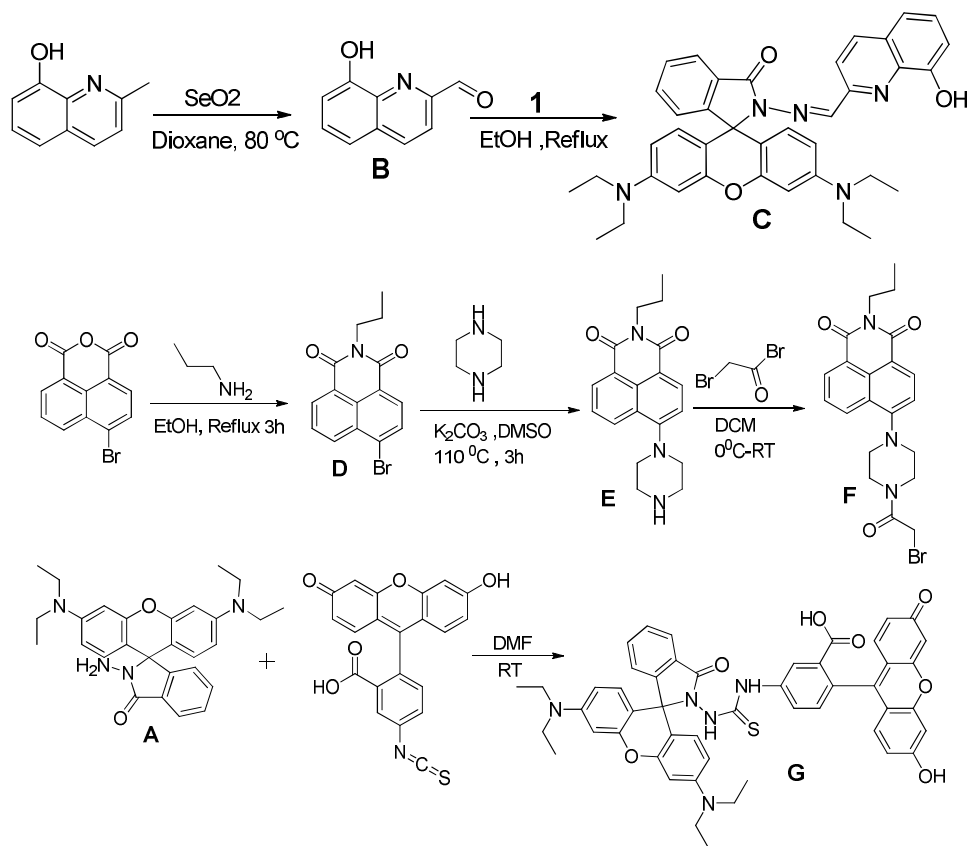
A two fluorophore embedded probe for collective and ratiometric detection of Hg^{2+} and F^- ions

Transition metal ions play a vital role in human life. Particularly, trivalent metal ions like Fe^{3+} or Al^{3+} or Cr^{3+} have their own biological significance and they directly involved in the cell function. Iron (III) functions as oxygen carrier in hemoglobin, and plays vital roles in enzyme catalysis and cellular metabolism. The deficiency as well as overload of Fe^{3+} ion concentration may lead to several disorders. Aluminium is the highest abundant metal in the earth crust. Extensive usage of aluminium utensils for cooking/storage and intake of aluminium based pharmaceuticals lead to increase its concentration in the human body. Excess levels of Al^{3+} can cause to adverse physiological effects and may result in Alzheimer's disease, gastrointestinal problems, osteoporosis, anemia, headache, colic, rickets, memory loss and muscle ache. Apart from Fe^{3+} and Al^{3+} , Cr^{3+} also has significant roles on human health. The Cr^{3+} deficiency may result in diabetes, cardiovascular diseases and excess levels of Cr^{3+} can adversely affect on cellular structures.

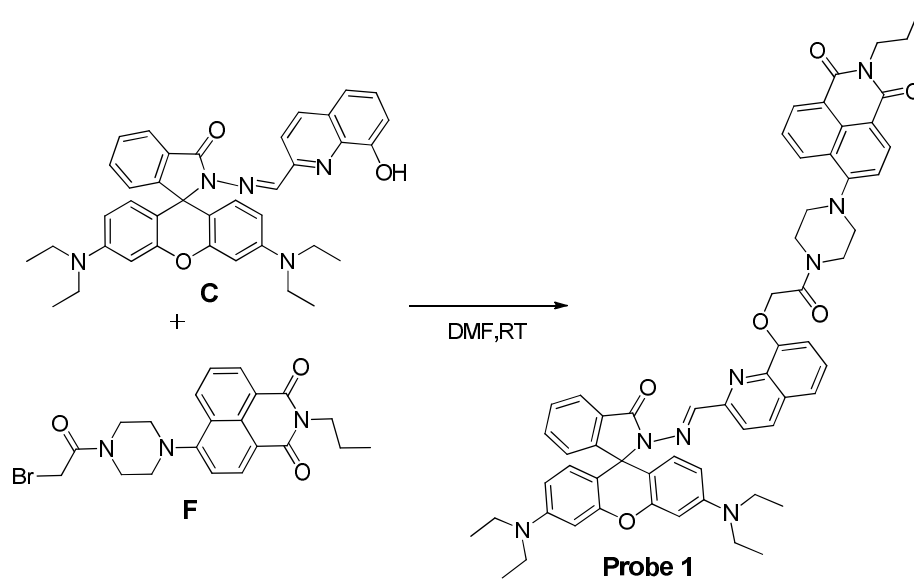
Development of fluorescent probes for the selective detection of toxic ions is a developing area of research. Mercury is one of the most toxic transition metal ions, and can easily pass through biological membranes. On the other hand, fluoride plays a vital role in the treatment of osteoporosis and in the prevention of dental caries. However, exposure to excess levels of fluoride can lead to dental or skeletal fluorosis, or cancer. Hence, design, synthesis and evaluation of fluorescent probes with high sensitivity and selectivity toward Hg^{+2} and F^- are highly desirable. Desulfation followed by cyclisation reaction of thiourea has been widely exploited for the development of Hg^{+2} selective chemodosimeters. Fluoride ion selective cleavage of Si-O linkage has been extensively applied for designing fluoride selective chemosensors. Here it is imperative to develop new fluorescent probes for individual and collective detection of Hg^{+2} and F^- ions in aqueous and biological samples. In this chapter we reported a two fluorophore-embedded fluorescent probe 2, for simultaneous detection of Hg^{+2} and F^- ions.

Scheme 7: Synthesis of key intermediates.





Scheme 8: Synthetic route for target dyad probes 1 & 2.



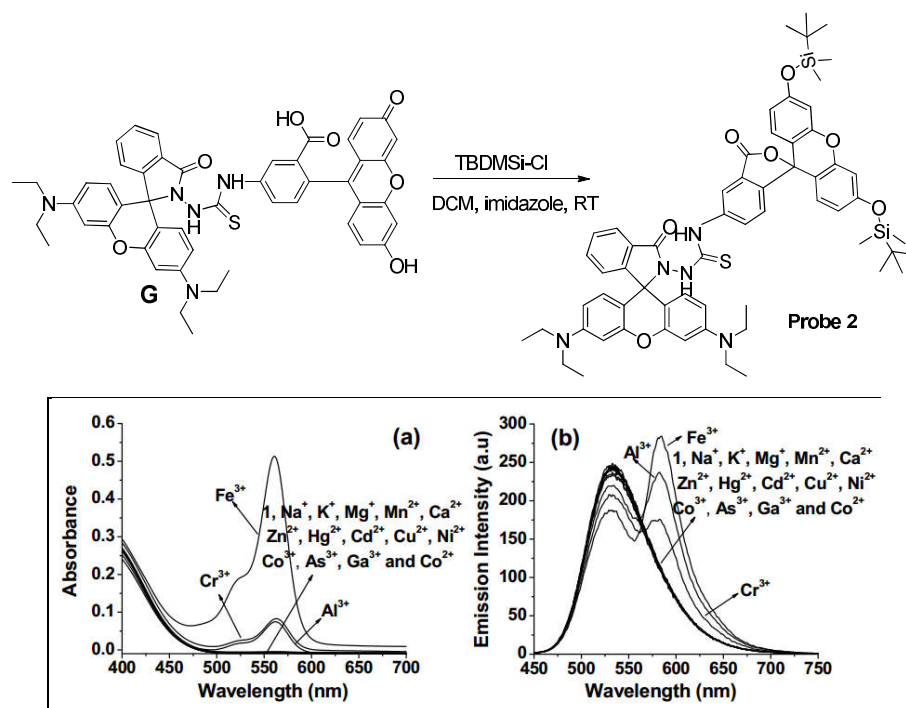


Fig. 3. Metal ion (10 μM) induced variations in the (a) absorbance and fluorescence (b) spectra of **1** (10 μM); Excitation wavelength: 400 nm.

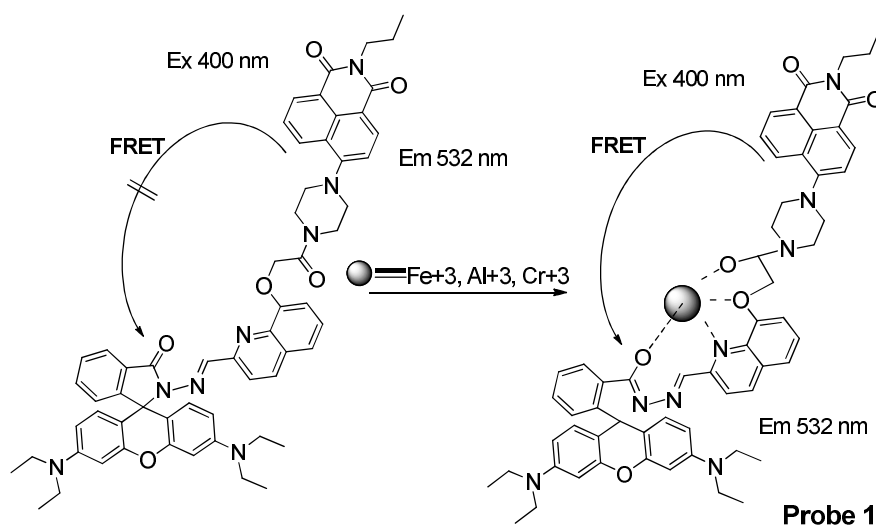
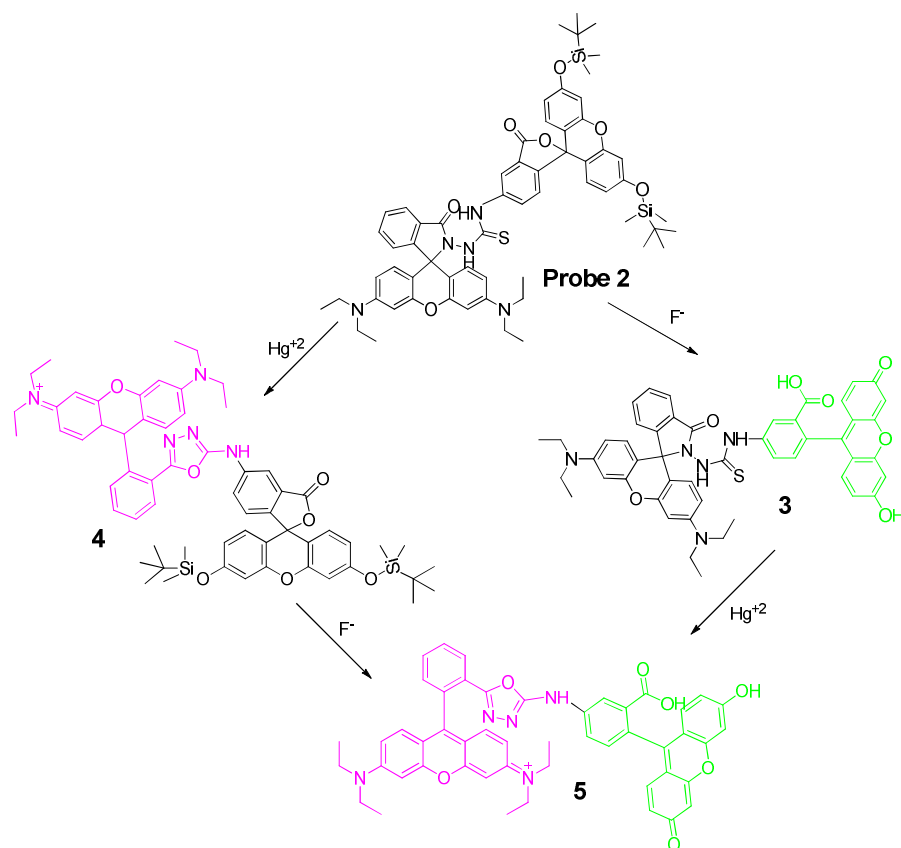


Fig.4 Schematic representation of the trivalent metal ion induced FRET in Probe1.



Scheme 8: The mechanistic aspects involved in the detection of Hg^{+2} and F^- using **Probe 2**

In summary, we have reported the design, synthesis and metal ion sensing properties of an ultrafast Förster resonance energy transfer rhodamine-naphthalimide dyad probe **1**. Among various metal ions, Fe^{3+} or Al^{3+} or Cr^{3+} selectively opens the spirolactam ring of the rhodamine moiety of the probe and facilitates the FRET from naphthalimide moiety to rhodamine. The dyad probe is highly selective to Fe^{3+} or Al^{3+} or Cr^{3+} ions and the presence of other monovalent or divalent ions do not affect the detection process. The probe can detect these trivalent metal ions even at sub-micromolar quantities. The dyad probe **1** is stable at physiological pH, non-toxic under experimental conditions, and probe **1** is the first of its kind that can be used for the FRET based ratiometric detection of Fe^{3+} or Al^{3+} or Cr^{3+} ions present in the aqueous and biological samples. And probe **2** is the first of its kind that can be used for the simultaneous and ratiometric detection of both Hg^{+2} and F^- ions in both aqueous and biological systems. Based on two fluorophore embedded approach, we have developed a new fluorescein-rhodamine conjugate **2** useful for the

simultaneous detection of both F⁻ and Hg⁺² ions selectively even in the presence of competitive ions. The versatility of the probe **2** to transform into **3**, **4** and **5** with respect to the presence of F⁻ and Hg⁺² in isolation and in combination permits both linear and ratiometric detection of these ions at ppb levels. Further, the probe **2** is cell membrane permeable, stable at physiological pH and non-lethal under the experimental conditions, and hence, could be used for the detection and imaging of W138 normal lung fibroblast cells contaminated with F⁻ and Hg⁺² ions. We hope that the two fluorophore embedded approach demonstrated in this communication will help augment the design and development of new multi-analyte probes.