

# Investigation of the Photophysical Properties of Semiconducting Organic Materials for Electronic Applications

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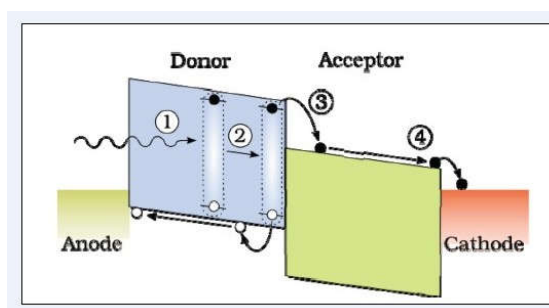
## *Chapter 1*

# Introduction

## 1.1. General

The global demands for low cost renewable energy resources intensify our interest for the discovery of new routes for conversion of energy into electricity. Solar cells are one of the attractive methods for utilizing inexhaustible clean energy from sun. Organic photovoltaic technology is developing as a potential competitor to conventional silicon based technology. Organic semiconducting materials have been now extensively used as building blocks for electronic devices. Polymer solar cells will be the next generation photovoltaics because of their compatibility with flexible substrate, low manufacturing cost and wide range of applications [1,2].

A class of organic solar cell that has inspired significant academic and industrial excitement is the bulk heterojunction solar cells [1,2,3]. These are based on heterojunction resulting by the contact of a donor and acceptor material. In organic heterojunction solar cells, the generation of photocurrent is a cascade of four steps: generation of excitons (electrically neutral bound electron hole pair) by light absorption, diffusion of exciton to the heterojunction, dissociation of the excitons into free charge carrier, and transport of these carriers to the contacts [1-4].



**Figure 1.1.** Energy diagram of an organic solar cell with a donor-acceptor interface.

When electron donor absorbs light an electron goes from highest occupied molecular orbital (HOMO) of the donor material to lowest unoccupied molecular orbital (LUMO) of the donor material. Then the electron in the LUMO level of the donor transfer to the LUMO of the acceptor. It is understood that the relative position of donor LUMO and acceptor LUMO is crucial for the efficient charge transfer [1,2] . It appears that a minimum energy difference of 0.3 eV is required to affect the exciton splitting and charge dissociation. An ideal polymer would have a minimum energy difference between the LUMOs. Generally organic semiconducting polymers are used for the fabrication of bulk heterojunction solar cells. Recently power conversion efficiency of 5-6% has been reported for the bulk heterojunction solar cells [1].

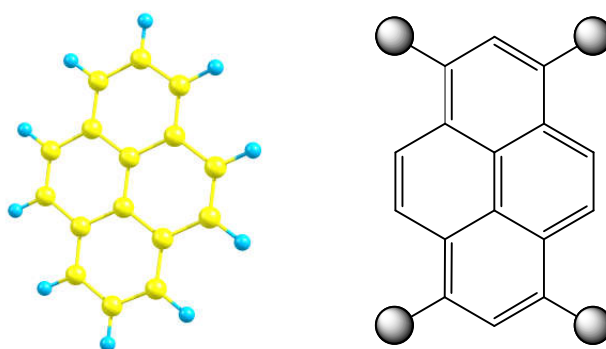
Scientist all over the world putting tremendous efforts to push the efficiencies of organic solar cells to a value that is competent with their inorganic counter parts. The efficiency can improve by controlling the morphology of active layer, optimizing the band gap of polymer to enhance the  $V_{OC}$ .  $V_{OC}$  is the difference between the highest occupied molecular orbital of donor and lowest unoccupied molecular orbital of the acceptor. As  $V_{oc}$  increases the efficiency of the device will also increases, so we can improve the  $V_{oc}$  of the device by carefully matching the band gap of donor and acceptor systems. Therefore one of the methods to improve the efficiency of solar cells is to design conjugated oligomers / polymers having optimum band gap and thus increase the  $V_{oc}$  of the device [1,3].

Film morphology has also a drastic effect on the efficiency of the device. Rough surface and presence of voids may resist the movement of excitons. Surface morphology is

related to the rate of evaporation of solvent which depends in turn on the speed of rotation used in spin coating, condition of processing and surface of underlying support.

## 1.2. Pyrene Based Organic Photovoltaics

Pyrene is an organic molecule with attractive optical and electrical properties. Photochemists are very much interested in Pyrene. Its unique properties have motivated researches from many scientific areas, making Pyrene a most suitable chromophore in fundamental and applied photochemical research. Pyrene acquired great attention as an important organic semiconductor for application in OLEDs, OFETs and also in photovoltaic devices such as bulk heterojunctions (BHJS).



**Figure 1.2.** Tetra (1,3,6,8) substituted Pyrene

The electronic properties of the Pyrene can be tuned by introducing specific substituent groups at Pyrene ring. Fluorescent blue OLEDs based on Pyrene derivatives have shown excellent performance among the reported ones [5,6]. Similarly fabrication of light emitting field effect transistors using Pyrene derivatives has also been very attractive.

Recently bulk heterojunction solar cells based on Pyrene donor has highest reported value of power conversion efficiency [7-9].

The investigation of effect of alkyl substitution on the photophysical properties of Pyrene chromophore has studied by introducing alkyl groups and trimethylsilyl (TMS) group on the Pyrene ring. It was found that the alkyl substitution enhances the fluorescence quantum yields of Pyrene chromophore to a much greater extent than expected. These substitution effects are mainly caused by  $\sigma$ - $\pi$  conjugation between the butyl groups and Pyrene, which destabilize the HOMO of Pyrene. The alkyl substituents and TMS caused bathochromic shifts in UV visible spectra and enhance the quantum efficiency of Pyrene chromophore. This bathochromic shifts caused by the TMS groups were derived from  $\sigma^*$ - $\pi^*$  conjugations, which were different from  $\sigma$ - $\pi$  conjugation in alkyl Pyrene derivatives. The results were also shows that ubiquitous alkyl groups can be used to tune the photophysical properties of Pyrene chromophore as well as to improve the solubility or prevent the aggregation [10,14].

The quenching of the excited states of Pyrene on SiO<sub>2</sub> by tetra nitro methane (TNM) is studied and the results show that the singlet and triplet excited states of pyrene are quenched on the silica gel surface by co adsorbed TNM by two mechanisms. One is a static mechanism which proceeds very rapidly and the other one is a diffusion of TNM on the silica gel surface. The two factors affecting the diffusion of quenchers on silica surface are the pore size and the temperature pretreatments. At higher temperature it is noted that the rate constant of quenching of silica is rapidly increasing than that for the lower temperature. As the pore size increases from 40 to 50 Å<sup>0</sup> the rate constant decreases. Increasing the pore

size shows significantly increased dynamic fluorescence quenching where the surface area is decreased.

Supra molecular aggregation through  $\pi$ - $\pi$  interactions is found in many polycyclic aromatic hydrocarbons like Pyrene at higher concentrations. Pyrene does not exhibit excimer emission at concentrations of  $10^{-5}$  and below. But at higher concentrations, in the solid state and in non-polar solvents like cyclohexane there are intermolecular  $\pi$ - $\pi$  interactions that bring the two molecules in close proximity which result in excimer emission [13]. These  $\pi$ - $\pi$  interactions results in the formation of molecular aggregates in the solid state and in a non-polar solvents. Solvents with high polarity and strong hydrogen bonding will disrupt the  $\pi$ - $\pi$  interactions resulting in the dissociation of molecular aggregates and hence only monomer emission is observed.

Synthesis of novel pyrene based TQPP (2,1,1bis(1 Methyl Ethyl)-6,7.15.16-Tetrakis(Dodecyloxy)QuinoxalinePhenanthroPhenazine) molecules possessing four long chains of alkyloxyand alkylthio groups of various length are reported. These molecules are found to be forming excimers even at nanomolar concentrations. Compared to the pyrene molecule, such TQPP molecules showed much shorter fluorescence lifetimes, higher radiative rate constants and greater tendencies to excimer formation [12].

In this context we designed and synthesized a series of bay pyrene derivatives namely pyrene benzoxadiazole, pyrene isothiazole and pyrene isothiazole. The photophysical properties such as the absorption and emission properties of these molecules are studied in solution and film state.

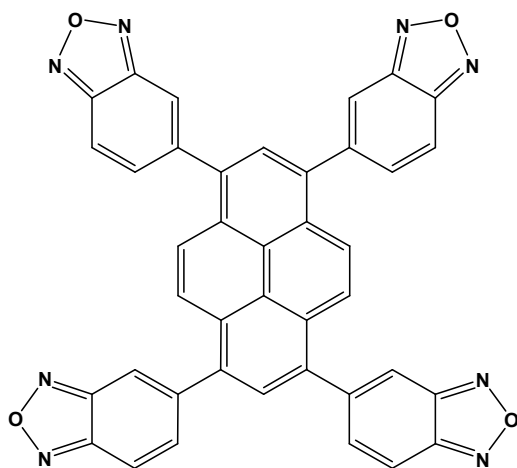


## *Chapter 2*

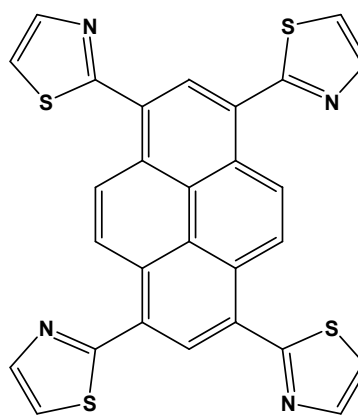
# Materials and Methods

## 2.1. Materials

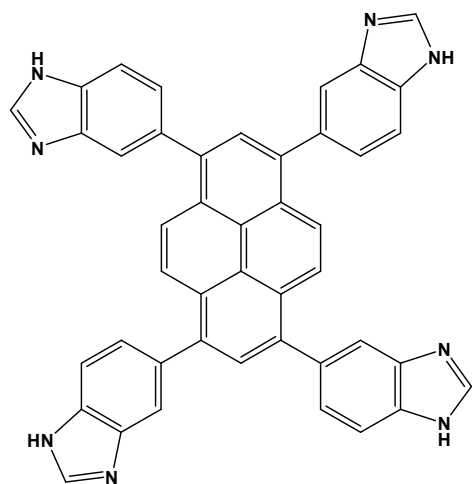
Pyrene, 1*H*-Benzimidazole-5-boronic acid pinacol ester, 2,1,3-Benzoxadiazole-5-boronic acid pinacol ester and 1,3-thiazole-2-boronic acid pinacol ester were purchased from Sigma Aldrich and used without further purification. All reagents and solvents were purchased from commercial suppliers and used without further purification unless otherwise stated. All reactions were carried out under an inert nitrogen atmosphere. Conventional thin film chromatography (TLC) plates (silica gel 60 F254) were used to monitor the progress of the reaction, with spots observed under UV light at 254 and 365 nm. Column chromatography was performed with silica gel 60A. NMR spectra were taken using a 300 MHz Bruker. Absorption spectra were measured on Shimadzu UV-2600 and the fluorescence spectra were recorded in Perkin Elmer LS 55 spectrofluorophotometer. The chemical structures of oligomers are shown in figure 2.1.



**Pyrene benzoxadiazole (PY-1)**



**Pyrene isothiazole (PY-2)**



**Pyrene benzimidazole (PY- 3)**

**Figure 2.1.** Chemical structure of designed pyrene oligomers

The geometry of all systems are optimized using the DFT with 3 parameter hybrid exchange correlation functional B3LYP. The optimized geometries and the frontier orbital of some of the pyrene oligomers calculated using density functional theory at the B3LYP/6-311++G\*\* 5d level.

The pyrene derivatives were synthesized by using two step synthetic method. Initially pyrene was brominated to get tetra bromo pyrene. Tetra bromo pyrene was coupled with the corresponding (Suzuki coupling) boronic acid to yield the final product.

## 2.2. Bromination of Pyrene

Bromine (3.50g, 22.0 mmol) was added drop wise with stirring, to a solution of pyrene (1.0g, 4.90 mmol) in nitrobenzene (20 mL) at 120<sup>0</sup> C. The reaction mixture was then cooled to room temperature to afford a pale green precipitate. This was filtered and the

solid was washed with copious amount of methanol (150 mL). The residue was dried under vacuum to afford 1,3,6,8- tetra bromo pyrene.

### **2.3. Suzuki Coupling**

Pyrene and aryl boronic acid were dissolved in 50 mL of THF and heated to 70°C for 15 minutes under nitrogen atmosphere. About 20 mL of 1M K<sub>2</sub>CO<sub>3</sub> aqueous solution was added followed by addition of 10 mol percentage Pd(PPh<sub>3</sub>)<sub>4</sub>. The contents were heated at 75°C under nitrogen atmosphere for 20- 24 hours. After completion the reaction mixture was diluted with ethyl acetate and extracted with water. The crude product was purified by column chromatography using a mixture of 30% ethyl acetate and 70% hexane as elutant and silica gel as stationary phase.

**Pyrene Benzimidazole derivative <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):** 5.0(s, 4H, NH), 7.48(d, 4H, ArH), 7.71(d, 4H, ArH), 7.76(d, 4H, ArH), 7.92(s, 4H, ArH), 8.08(s, 4H, ArH), 8.26(s, 2H, ArH).

**Pyrene Benzoxadiazole derivative <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):** 7.46(d, 4H, ArH), 7.70(d, 4H, ArH), 7.71(d, 4H, ArH), 7.86(s, 4H, ArH), 8.26(s, 2H, ArH).

**Pyrene 1,3-thiazole (isothiazole) derivative <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):** 7.4(d, 4H, ArH), 7.71(d, 4H, ArH), 8.0(d, 4H, ArH), 8.26(s, 2H, ArH).

### **2.4. Preparation of Thin Film**

Spin coater is used for the preparation of thin films. In spin coater, a small amount of the sample is placed at the centre of the substrate and it is spinned at high speed. Centripetal acceleration causes most of the oligomer to spread leaving a thin film, whose

thin thickness depends on the nature of the resin and the parameters chosen for the spin process.

Pyrene oligomers are individually made soluble in dichlorobenzene and made into a thin film by coating it on a cleaned glass substrate. Spin coating was done using five programs in which program acceleration is done two times. That is, first acceleration with a spin speed of 1900 rpm for 10 seconds and second acceleration with a spin speed of 1990 rpm for 20 seconds. Thin film thus produced is used for studying the absorption, fluorescence and surface morphology.

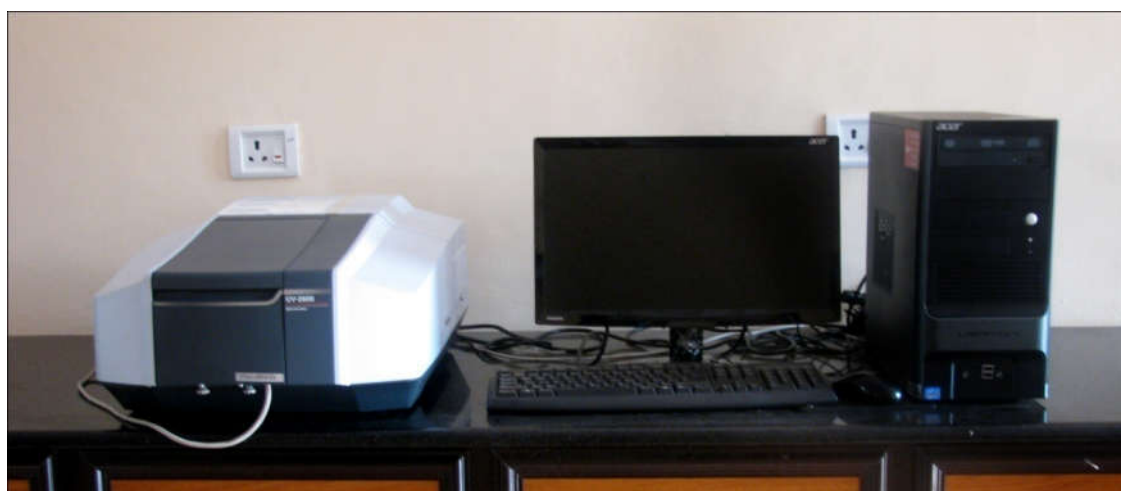


**Figure 2.2.** Spin coating unit

## **2.5. Absorption Spectra**

In UV-visible spectrophotometer by absorbing light electrons will get promoted to the excited state and it obeys Beer-Lamberts law which states that 'when a beam of monochromatic light is passed through a solution of absorbing substance, the rate of decrease of intensity of radiation with thickness of absorbing solution is proportional to the incident radiation as well as the concentration of the solution. That is, the extended of absorption increases with the number of molecules capable of absorbing light. Solid and

solution absorption spectra of both the samples are recorded using the Shimadzu UV-2600 spectrophotometer. The spectral range of the spectrophotometer is adjusted to 200-900 nm. Dichlorobenzene is used as solvent for solution phase absorption spectra for both the compounds.



**Figure 2.3.** UV-Visible spectrophotometer

## **2.6. Fluorescence Spectra**

In fluorescence spectroscopy emission of light takes place when the electrons of the molecule of a compound gets excited by the absorption of UV light, and the emitted light may or may not be visible light. Solution state fluorescence measurements are done for both the compounds. Fluorescence spectra were recorded by using Perkin Elmer LS 55 spectrofluorimeter. A schematic diagram of spectrofluorimeter is shown in figure 2.4.

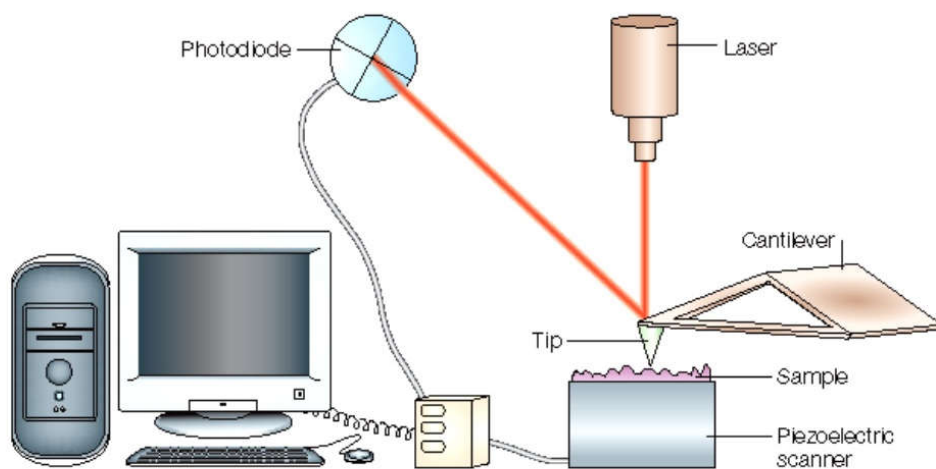


**Figure 2.4.** Fluorescence spectrophotometer

## **2.7. Atomic Force Microscopy [AFM]**

In atomic force microscopy the attractive or repulsive force between a tip and the sample is measured. A pyramidal silicon nitride tip with the radius of curvature of the order  $100\text{\AA}$  is usually used. AFM is measured using two modes, that is, contact mode and non-contact mode. When the tip which is attached to the cantilever is in perpetual contact with the sample then it is said to be on contact mode. In this mode, vertical deflection of the cantilever takes place when the scanner gently traces the tip across the sample and it is measured using some sort of detection apparatus, which indicates the local sample height. In non-contact mode the tip does not touch the sample surface, the topographic images are derived from the measurement of attractive forces.

Morphology of the surface of the two compounds is studied using AFM in tapping mode and schematic diagram of AFM is shown in figure 2.5.



**Figure 2.5.** Schematic diagram of Atomic Force Microscopy.



## *Chapter 3*

# Results and Discussion

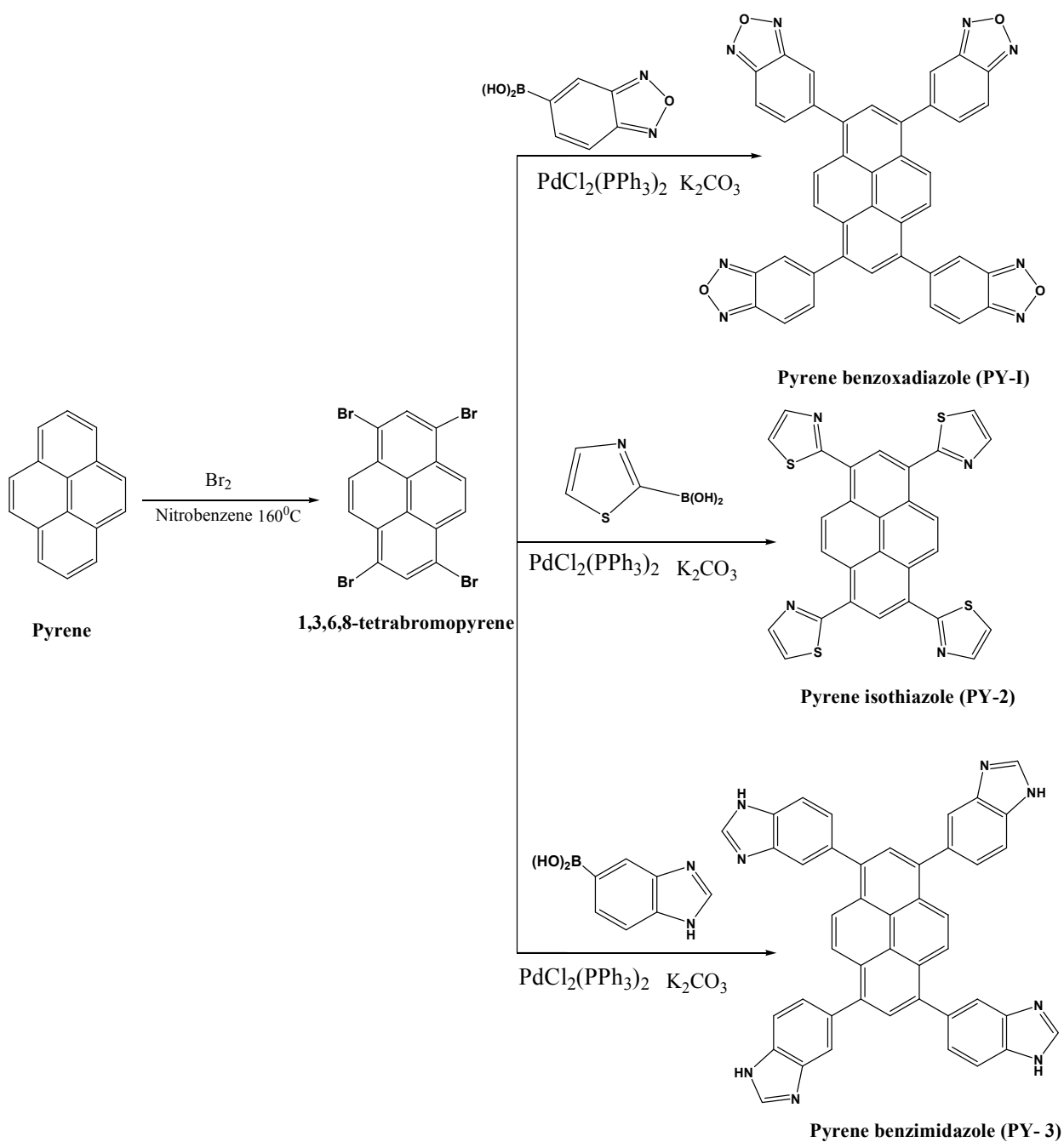
### 3.1. Results and Discussion

Organic materials consisting of the well-known polycyclicplanar aromatic system, pyrene as a core, functionalized with different chromophores as arms can be employed as hole transporting materials in various optoelectronic and electronic devices. Moreover this kind of architecture could facilitate the hole injection by tuning the highest occupied molecular orbital (HOMO) energy level. Therefore, initially we designed some of the pyrene derivatives namely pyrene benzimidazole, pyrene benzoxadiazole and pyrene isothiazole derivatives. These derivatives were synthesized by using two step synthetic method. Initially pyrene was brominated to get tetra bromo pyrene. Tetra bromo pyrene was coupled with the corresponding (Suzuki coupling) boronic acid to yield the final product. The synthetic scheme is shown in scheme 3.1. The NMR data of the pyrene derivatives in CDCl<sub>3</sub> is given below.

**Benzoxadiazole derivative <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):** 7.46(d, 4H, ArH), 7.70(d, 4H, ArH), 7.71(d, 4H, ArH), 7.86(s, 4H, ArH), 8.26(s, 2H, ArH).

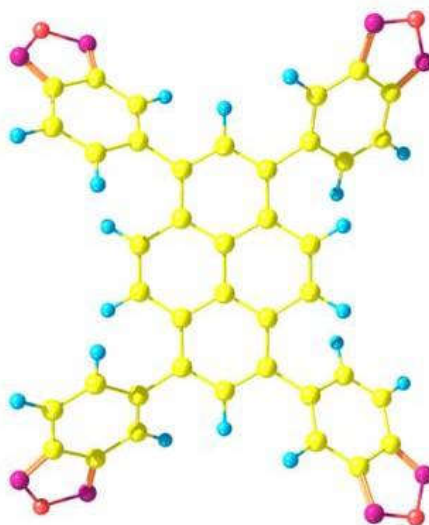
**1,3-thiazole (isothiazole) derivative <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):** 7.4(d, 4H, ArH), 7.71(d, 4H, ArH), 8.0(d, 4H, ArH), 8.26(s, 2H, ArH).

**Benzimidazole derivative <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm):** 5.0(s, 4H, NH), 7.48(d, 4H, ArH), 7.71(d, 4H, ArH), 7.76(d, 4H, ArH), 7.92(s, 4H, ArH), 8.08(s, 4H, ArH), 8.26(s, 2H, ArH).

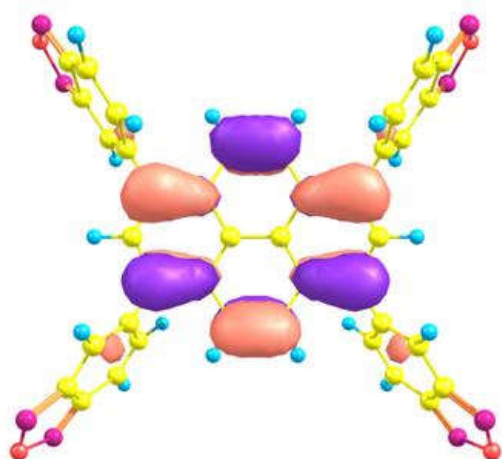


Scheme 3.1. Pyrene Oligomers

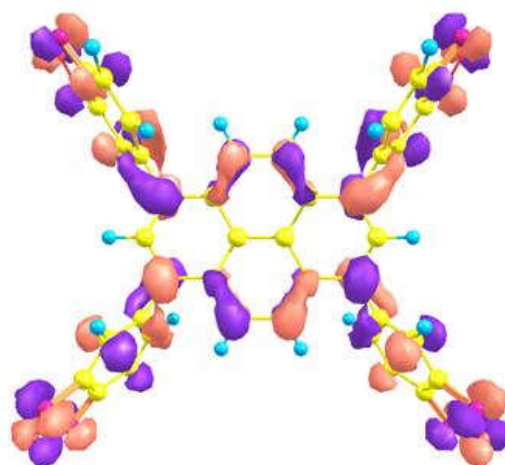
The geometries of all the designed pyrene derivatives were fully optimized by using the density functional theory (DFT) with the three parameter hybrid exchange correlation functional, B3LYP. The optimized geometries and the frontier orbital of the pyrene oligomers calculated using density functional theory at the B3LYP/6-311++G\*\* 5d level is shown in figure 3.1.



**Optimized geometry**

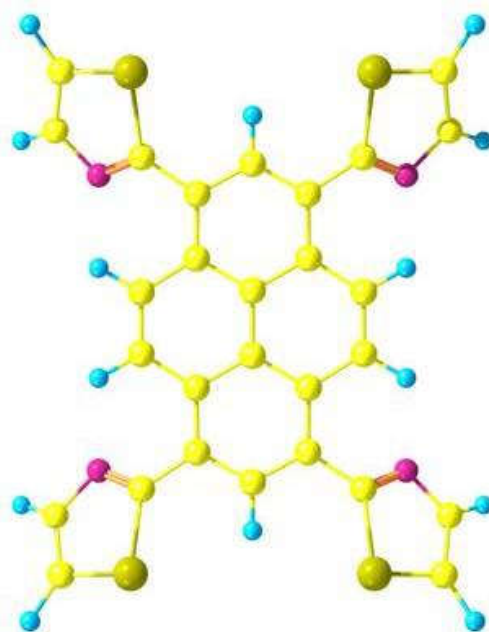


**HOMO**

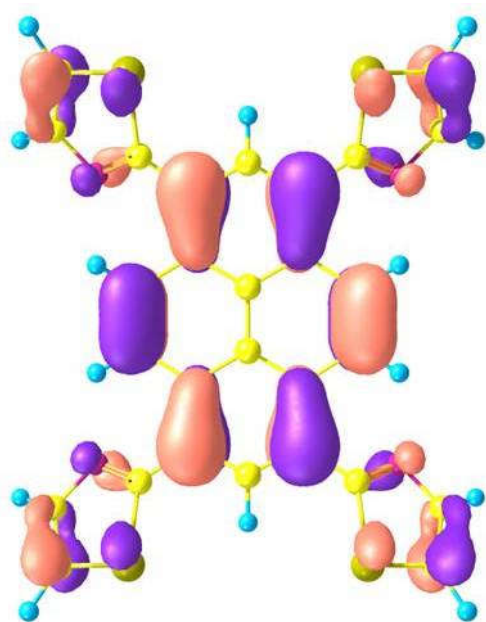


**LUMO**

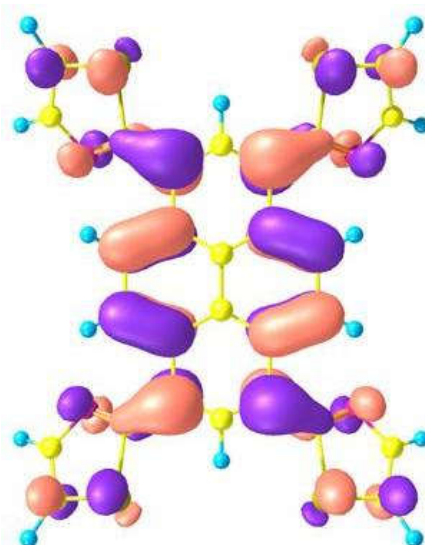
**Pyrene Benzoxadiazole (PY- 1)**



**Optimized geometry**



**HOMO**



**LUMO**

**Pyrene Isothiazole (PY 2)**

**Figure 3.1.** Optimized geometry and frontier orbital of pyrene oligomers.

We also calculated the optical band gap, HOMO, LUMO level and total energy of these oligomers. The results of the theoretical calculation are summarized in table 3.1.

**Table 3.1:** HOMO LUMO, band gap and total energy of pyrene oligomers

<b>Compound</b>	<b>HOMO (eV)</b>	<b>LUMO (eV)</b>	<b>Bandgap (eV)</b>	<b>Energy (eV)</b>
<b>PY 1</b>	-6.13	-2.80	3.33	61881
<b>PY 2</b>	-5.57	-2.69	2.88	78571
<b>PY3</b>	-	-	-	57904

### 3.2. Optical Properties

The absorption spectra of pyrene oligomers in chloroform and thin film is shown figure 3.2 and 3.3. All oligomers have absorption in the range of 350 – 500 nm in solution. In the case of pyrene benzoxadiazole derivative the absorption spectra are characterized with a broad band centered around 395 nm. In pyrene isothiazole derivatives this broad absorption is red shifted and centered on 445 nm. The absorption spectra of benzimidazole derivative characterized with an absorption maxima at 400 nm. As expected the absorption maxima in thin film is red shifted compared to the solution state. In thin film state the absorption spectra of benzoxadiazole derivative the maximum is centered on 406 nm. However in the case of pyrene isothiazole and benzimidazole derivative this is observed at 450 nm and 409 nm respectively.

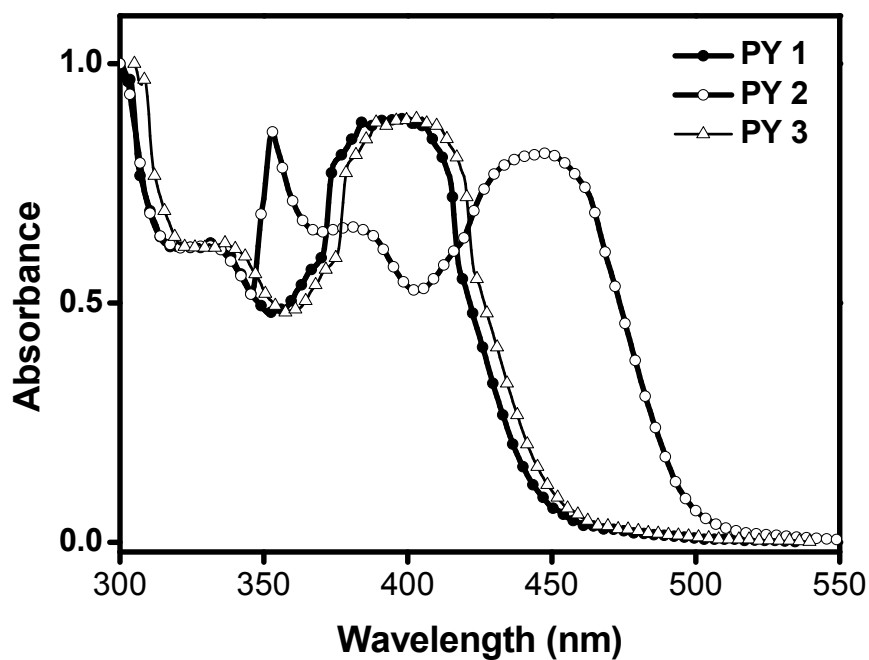


Figure 3.2. Absorption spectra of pyrene oligomers in chloroform.

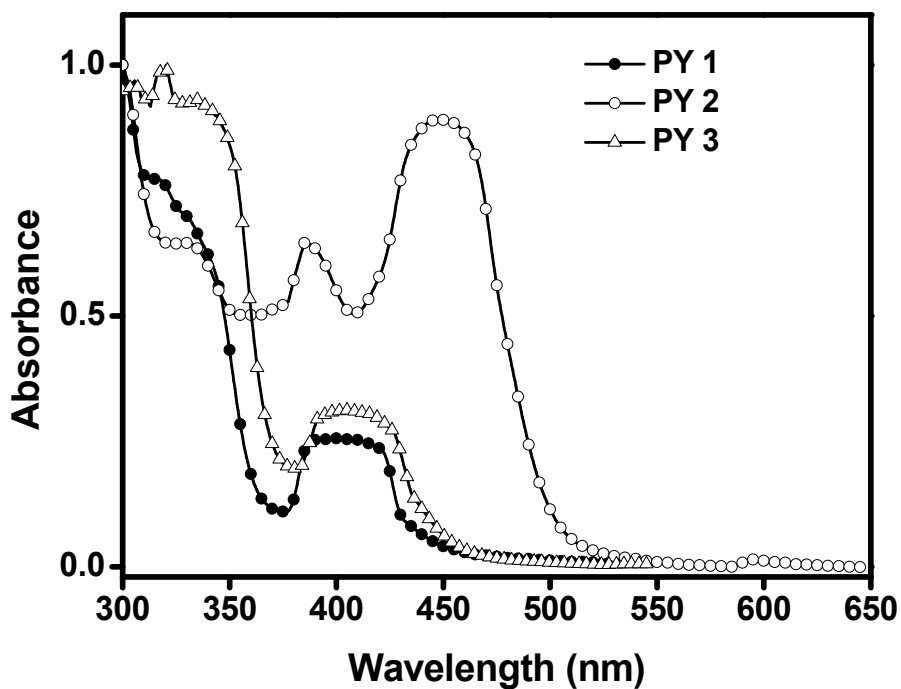
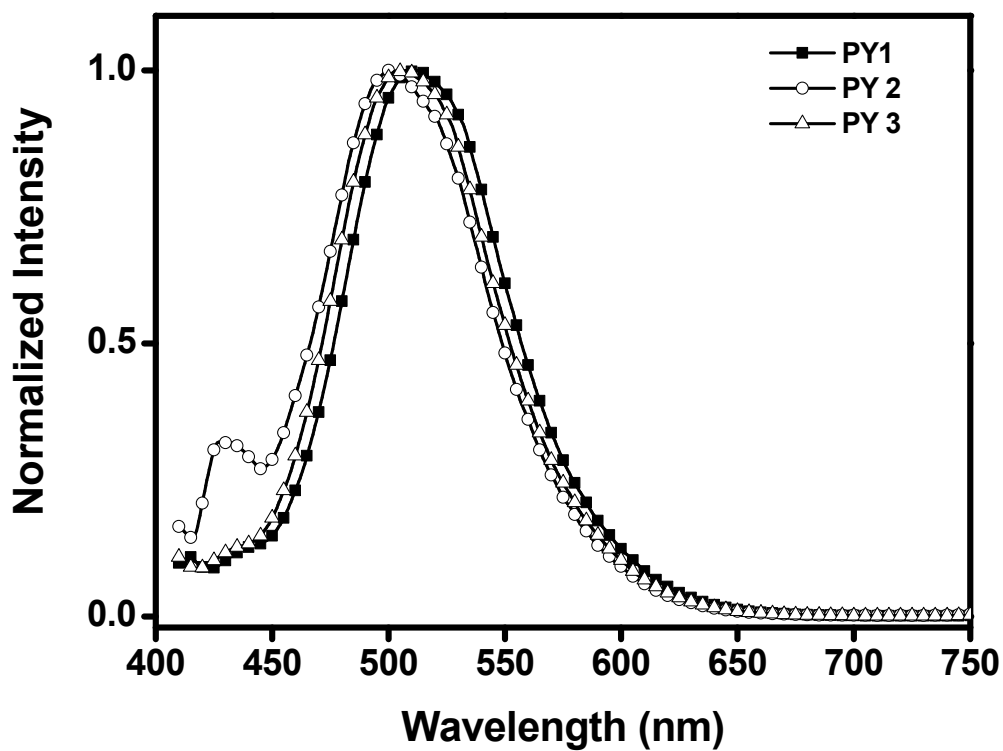


Figure 3.3. Absorption spectra of pyrene oligomers in thin film.

The emission spectra of the pyrene oligomers are shown in figure 3.4. It is observed that the fluorescence spectra of all oligomers have similar characteristics. The emission maxima of benzoxadiazole, isothiazole and benzimidazole derivative are observed at 514 nm, 499 nm and 508 nm respectively. The optical properties of all pyrene oligomers are summarized in table 3.2.



**Figure 3.4.** The fluorescence spectra of pyrene oligomers in chloroform.



**Table 3.2.** Optical properties of pyrene oligomers.

Compound	Absorption (nm)		Emission (nm)
	Solution (Chloroform)	Thin Film	Solution (Chloroform)
PY1	336, 395	320, 406	514
PY2	352, 383, 445	331, 450	430, 491
PY3	337, 400	386, 409	508

### 3.3. Conclusion

In conclusion we designed and synthesized a series of pyrene oligomers namely pyrene benzoxadiazole, pyrene isothiazole and pyrene benzimidazole derivative. The theoretical modelings of all the oligomers are performed by density function theory. Theoretically we calculated the HOMO level, LUMO level, band gap and total energy of these molecules. It is observed that pyrene isothiazole derivative have a small band gap of 2.88 eV. The absorption and emission properties of these oligomers are investigated both in solution and thin film state. All oligomers have very strong absorption in the range of 350 – 500 nm regions. The emission spectra of all these pyrene derivatives is characterized with an emission maximum in the green region. The study of transport properties of these molecules are currently under progress in our laboratory.

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