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**SYNTHESIS AND CHARACTERIZATION OF  
CONJUGATED POLYMERS ORIENTED FOR  
FLUORESCENCE CHEMOSENSOR**

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## Abstract

Conjugated diblock copolymers have been synthesized via the combination of Grignard metathesis method (GRIM) and organo-catalyzed atom transfer radical polymerization reaction (ATRP). Among them, conjugated diblock copolymer of poly(3-hexylthiophene)-*block*-poly(2-(4,6-dichlorotriazin-2-yl)oxy)ethyl methacrylate) (P3HT-*b*-PDCTMA) bears functional reactive triazine chloride groups that act as a platform to react with mercaptan or amine groups via efficient nucleophilic aromatic substitution reactions, and diblock copolymers based on the rod segment of regioregular poly(3-hexylthiophene) (P3HT) and a coil segment of poly(2-(dimethylamino)ethyl methacrylate-*random*-1-pyrenylmethyl methacrylate) (P(DMAEMA-*r*-PyMA)) was examined as a possible chemosensor for trace detection of the trinitrotoluene (TNT) explosive.

On the other hand, the conjugated molecules based on pyrene and dithienopyrrole derivatives including 4-(2-ethylhexyl)-2-(pyren-1-yl)-4H-dithieno[3,2-*b*:2',3'-*d*]pyrrole (EP4HP) and 4-(2-ethylhexyl)-2,6-di(pyren-1-yl)-4H-dithieno[3,2-*b*:2',3'-*d*]pyrrole (EDP4HP) have been successfully synthesized via C-H direct arylation reaction. The conjugated molecules exhibited efficient fluorescence quenching toward herbicide mesotrione as nitroaromatic pesticides that could be promising candidates as the chemosensor for tracing nitroaromatic pesticides.

## INTRODUCTION

In this research, we report the synthesis and characterization of rod-coil diblock copolymers based on P3HT and poly(2-([4,6-dichlorotriazin-2-yl]oxy)ethyl methacrylate (P3HT-*b*-PDCTMA) via organocatalyzed atom transfer radical polymerization (O-ATRP). The P3HT-based rod-coil diblock copolymers can be used as the platform bearing functional triazine dichloride groups. Triazine derivative groups can act as both hydrogen bond donors and acceptors. For instance, substitution reaction of triazine chloride with amines under mild conditions results in amino-triazine moieties with hydrogen bonding and  $\pi$ - $\pi$  interactions that are expected to play an important role in molecular ordering. As such, in this work, rapid amine and mercaptan aromatic substitutions of the triazine chloride side groups of the synthesized P3HT-*b*-PDCTMA were also investigated. This work was envisaged to provide a basis for the future synthetic study of conjugated multiblock structures, such as via grafting of other thiols or amine- end-capped polymer segments to the triazine chloride-bearing block to result in brush terpolymers.

Moreover, in this thesis, we present a diblock copolymer containing the rod segment of regioregular P3HT and the coil segment of 2-(dimethylamino)ethyl methacrylate (DMAEMA) and 1-pyrenylmethyl methacrylate (PyMA). The DMAEMA unit plays a role as a hydrophilic coil in the amphiphilic diblock copolymer which is introduced to improve the compatibility of the copolymer blocks resulting in direct copolymerization. The P3HT-*b*-P(DMAEMA-*r*-PyMA) copolymer was synthesized via the atom transfer radical polymerization method (ATRP) in the presence of CuBr/PMDETA as a catalytic system. The diblock copolymer showed an amphiphilic characteristic and was soluble in co-solvent mixtures of THF and methanol. In addition, P3HT-*b*-P(DMAEMA-*r*-PyMA) showed sensory

properties in tracing explosive TNT compounds through fluorescence quenching due to the Forster resonance energy transfer mechanism.

For mesotrione detector application, the conjugated molecules based on pyrene and 4-(2-ethylhexyl)-2-(pyren-1-yl)-4H-dithieno [3,2-b:2',3'-d]pyrrole have been successfully synthesized via direct arylation reaction. The obtained conjugated molecules have been used for tracing mesotrione compound through FRET with high sensitivity of  $K_{SV}$  of 5570 and 6520  $M^{-1}$  for EP4HP and EDP4HP, respectively. The materials based on the EP4HP and EDP4HP compounds are promising candidates for technical application for mesotrione detection as a chemosensor.

## CHAPTER 1 LITERATURE REVIEW

### 1.1 Structure of Conducting Polymer and Mechanism of Conduction

- Polymers are known to have good insulating properties. Conducting polymers are polymers materials that have metallic and semiconductor characteristics, a combination of properties not exhibited by any other known materials.
- The polymer is a conducting polymer when they have a system of conjugated double bonds that are alternately single and double bond along the backbone of the polymer main chain.
- Sometimes the conducting polymers contain atoms such as nitrogen, sulfur, and oxygen in the main chain. In conducting polymers, the carriers are electrons of conjugated double bonds while the carriers of metal are valence electrons of a half-filled band. The conductivity of a material depends on its electronic energy level structure.
- The electronic ground state of conducting polymers is an insulator with a forbidden energy gap between the valence and conducting bands. The mechanism of conduction of polymeric materials was originally believed by electron transport through the system of conjugated bonds. In conjugated polymer, every bond contains a localized “sigma” ( $\sigma$ ) bond (single plane) which makes a strong chemical bond. In addition, every double bond contains a less strongly localized “pi” ( $\pi$ ) bond (orbitals parallel) that is weaker, the orbitals of the  $\pi$  electrons overlap to form a single delocalized cloud of  $\pi$  electrons over the entire molecules. This means that the delocalized electrons may move around the whole system. However, to make the polymer materials conductive, the polymer material needs to be exposed to the dopant, that process is also called doping. Doping is either the addition of electrons (reduction reaction) or the removal of electrons (oxidation reaction) from the polymer.

## 1.2 Application of Conducting Polymer

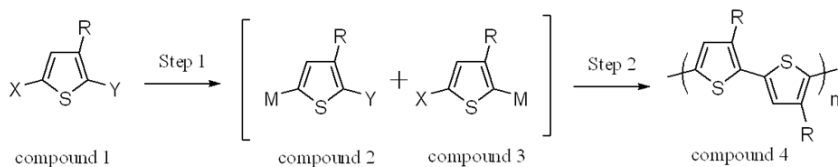
- The utilization of Polymeric Solar Cells (PSCs) effect to generate electricity from solar energy presents an appealing solution to our vital requirement for clean, abundant, and renewable energy sources and protecting the environment. Unfortunately, up to now, only a very small percentage of energy production comes from sunlight, mainly because of the high cost of silicon-based solar cells. PSCs are appreciated as one of the promising candidates for low-cost solar cells. Early work on PSCs was done with a single-component activate layer sandwiched between two electrodes with different work functions. However, the devices based on single-component have given very low power conversion efficiency (PCE is less than 1%) due to poor charge generation and charge transport. Then, a bilayer heterojunction configuration containing a p-type layer for hole transport and an n-type layer for electron transport has been supplemented to improve the PCE of the solar cell devices. However, the performance of bilayer heterojunction devices is greatly limited by a small area of charge-generating interface between donor and acceptor. Therefore, the PCE of bilayer heterojunction solar cells is also less than 1% for PPV/PCBM cells.
- The organic Field-Effect Transistor (OFET) is a 3-terminal device configured like a parallel-plate capacitor. By controlling the voltage on one plate (the gate), a charge can be induced on the other. Then charges are injected from the source electrode and collected across the conducting layer at the drain by applying a voltage. OFETs have made impressive progress during the last decade due to the improvement of the quality of organic semiconductor and dielectric layers as well as promising low-cost manufacturing processes, such as print technique. OFETs become attractive for various applications, not only as flat-panel displays, and electronic paper but also to integrate logic circuitry

into low-cost electronic products such as smart cards, inventory tags, and sensor arrays.

- Since polythiophenes (PTs) possess high conductivity when doped, high electron mobility, solubility in common solvents, excellent thermal and environmental stability, and processibility, they are considered an important class of conjugated polymers. Up to now, PTs have been used in a variety of applications such as PLEDs, SCs, OFET, environmental sensors, electrical conductors... Despite the PT having poor solubility and intractability because of the strong  $\pi$ -stacking interactions between the aromatic rings, PT has excellent thermal stability (42% weight loss at 900°C) and good conductivity ( $1 \times 10^{-1}$  S/cm when doped with iodine).

### 1.3 Synthesis of regioregular poly(3-alkylthiophenes) (rr-P3ATs)

- Generally, P3AT was synthesized by three methods including the McCullough, Rieke, and GRIM method (scheme 1.1).



Method	X,Y	Step 1	M (Ratio 2/3)	Step 2	HT regioregularity
McCullough	H, Br	1, LDA/THF, -40°C, 40 min 2, MgBr <sub>2</sub> .OEt <sub>2</sub> (-60 to -40°C, 40 min)	MgBr (98/2)	Ni(dppp)Cl <sub>2</sub> -5 to rt, 18 h	98-100%
Rieke	Br, Br	1, Zn/THF, -78°C to rt, 4 hours	ZnBr (90/10)	Ni(dppe)Cl <sub>2</sub> 0 to rt, 18 h	97-100%
GRIM	Br, Br	1, R'MgBr/THF, 0 to rt, 1 hour	MgBr (85/15)	Ni(dppe)Cl <sub>2</sub> 0 to rt, 1h	> 99%

Scheme 1. 1. McCullough, Rieke and GRIM methods for synthesis of rr-P3AT



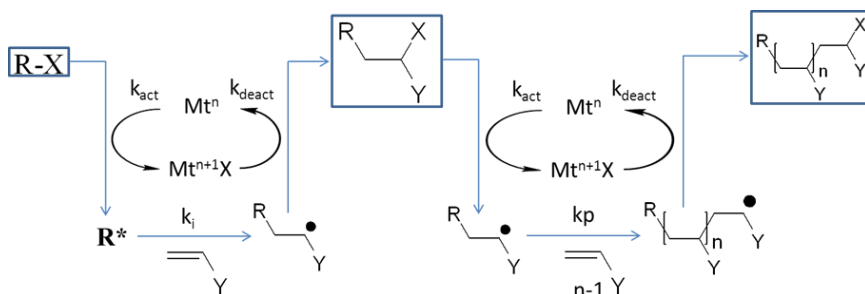
- An advantageous new synthesis for rr-P3AT was reported in 1999, known as the Grignard metathesis (GRIM) method (scheme 1.1). This method gave an excellent strategy to obtain the high rr-P3AT by eliminating of using both cryogenic temperature and highly reactive metals. It offers the easy preparation of rr-P3AT and can scale up to an industrial scale amount of product with high molecular weight rr-P3AT.
- The mechanism of synthesis of rr-P3ATs is based on a transition-metal-catalyzed cross-coupling reaction. The generally accepted mechanism involves a catalytic cycle of three steps: (i) oxidative addition of an organic halide with a metal-phosphine catalyst, (ii) transmetallation between catalyst complex and reactive organometallic reagent (or disproportionation) to generate a diorganometallic complex, and (iii) reductive elimination of the coupled product with the regeneration of the metal-phosphine catalyst. The nickel catalyst is normally used for a polycondensation reaction, it is generally accepted to proceed via a step growth mechanism.

#### 1.4 Poly(3-hexylthiophene) (P3HT)

- Among rr-P3AT, regioregular poly(3-hexylthiophene) (P3HT) is preferred for many organic electronic applications due to its highest hole mobilities, better self-organization in P3HT compared to other polymers in the series as well as good solubility. The highest hole mobilities in conjugated polymers to date have been observed in P3HT (0.05–0.2 cm<sup>2</sup>/Vs)
- The hole mobility as a function of alkyl chain length showed the highest value for P3HT. The hexyl side chain is believed that is optimum for field-effect charge transport because of better self-organization in P3HT. This result indicated that why P3HT is most excellent at using the material in model electronic applications.

### 1.3 Atom Transfer radical polymerization (ATRP)

- Currently, ATRP is the most widely used Controlled radical polymerization (CRP) technique. Controlled synthesis of polymeric materials requires minimization of chain breaking reactions (by transfer and termination) and chain should be grown simultaneously.
- The basic mechanism of ATRP involves homolytic cleavage of an alkyl halide bond R-X (or macromolecular P<sup>n</sup>-X) by a transition metal complex Mt<sup>n</sup>/L (such as CuBr<sub>2</sub>/bpy<sub>2</sub>). The mechanism of ATRP can be illustrated in scheme 1.2.



Scheme 1. 2. General mechanism of ATRP

- ATRP processes depend on many factors including different monomers, initiators, metal catalysts, ligands, solvents, time reaction, temperature, concentration...etc. Therefore, for each particular ATRP, a specific initiator, metal catalysts, ligand, temperature, reaction time, and solvent... should be investigated and selected.

### 1.4 Conjugated polymer for fluorescence sensory application

- A variety of approaches have been investigated for sensors, including enzymatic assays, molecular imprinting coupled with luminescence (using lanthanides), colorimetric methods, surface acoustic waves, and fluorescent organic molecules. The most common ways for detecting OP pesticides are chromatographic methods coupled with different

detectors and different types of spectroscopy, immunoassays, and enzyme biosensors based on the inhibition of cholinesterase activity.

- Today, novel polymers containing special optical response functional groups such as spiro oxazine, pyrene, perylene, or perylene-benzothiazole are one of the most powerful tools for optical sensor materials. However, the synthesis pathway as well as the designed reasonable polymer structure is a big challenge to generate intelligent optical sensors that exhibited their selectivity and sensitive properties.

### **1.5 Aim and objectives**

- In this thesis, we reported the synthesis and characterization of rod–coil diblock copolymers based on P3HT and poly(2-([4,6-dichlorotriazin-2-yl]oxy)ethyl methacrylate (P3HT-b-PDCTMA) via organocatalyzed atom transfer radical polymerization (O-ATRP). The P3HT-based rod–coil diblock copolymers can be used as the platform bearing functional triazine dichloride groups.
- We also synthesized a diblock copolymer containing the rod segment of regioregular P3HT a the coil segment of 2-(dimethylamino)ethyl methacrylate (DMAEMA) and 1-pyrenylmethyl methacrylate (PyMA). The DMAEMA unit plays a role as a hydrophilic coil in the amphiphilic diblock copolymer which is introduced to improve the compatibility of the copolymer blocks resulting in direct copolymerization. The P3HT-b-P(DMAEMA-r-PyMA) copolymer will be synthesized via the atom transfer radical polymerization method (ATRP) in the presence of CuBr/PMDETA as a catalytic system. P3HT-b-P(DMAEMA-r-PyMA) works as sensory property in tracing explosive TNT compounds through a fluorescence quenching due to the Forster resonance energy transfer mechanism.
- Moreover, to extend the research, the conjugated molecules based on pyrene and 4-(2-ethylhexyl)-2-(pyren-1-yl)-4H-dithieno [3,2-b:2',3'-

d]pyrrole (EP4HP) will be synthesized via direct arylation reaction. The conjugated oligomers of 4-(2-ethylhexyl)-2-(pyren-1-yl)-4H-dithieno [3,2-b:2',3'-d]pyrrole will be investigated for tracing mesotrione compound through FRET mechanism. Therefore, the materials based on the EP4HP compound are promising candidates for technical application for mesotrione detection as chemosensors.

## CHAPTER 2 EXPERIMENTAL

### 2.1 Materials

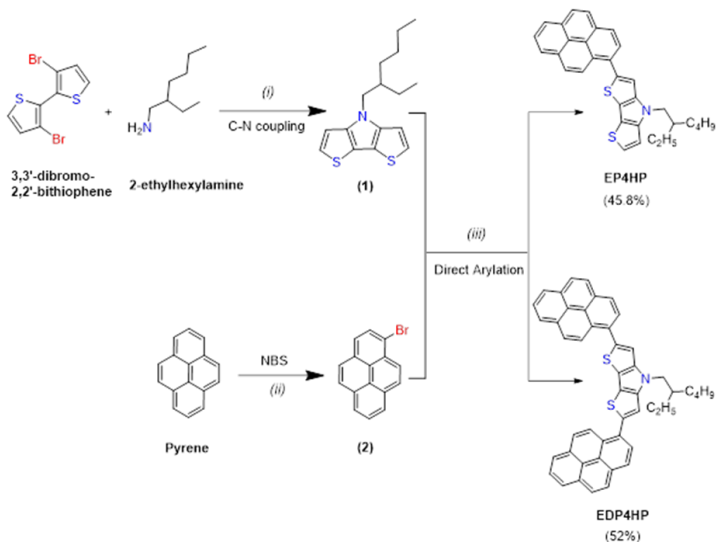
All chemical reagents and starting materials were purchased from Sigma-Aldrich, Acros, Merk, Fisher, and TCI, and were used as received without any further purification unless otherwise specified.

### 2.2 Synthesis monomers

1-Bromopyrene, 2-bromo-3-hexylthiophene, 2-bromo-3-hexyl-5-iodothiophene, 2-([4,6-dichlorotriazin-2-yl]oxy)ethyl methacrylate (DCTMA), 1-pyrenylmethyl methacrylate (PyMA), 4-(2-ethylhexyl)-4h-dithieno[3,2-b:2',3'-d]pyrrole (EDP), 10-(2-ethylhexyl)-10H-phenoxazine, 10-(4-(hexyl)benzoyl)-10H-phenoxazine were synthesized and characterized by <sup>1</sup>H NMR.

### 2.3 Synthesis of 4-(2-ethylhexyl)-2-(pyren-1-yl)-4h-dithieno[3,2-b:2',3'-d]pyrrole (EP4HP) and 4-(2-ethylhexyl)-2,6-di(pyren-1-yl)-4h-dithieno[3,2-b:2',3'-d]pyrrole (EDP4HP)

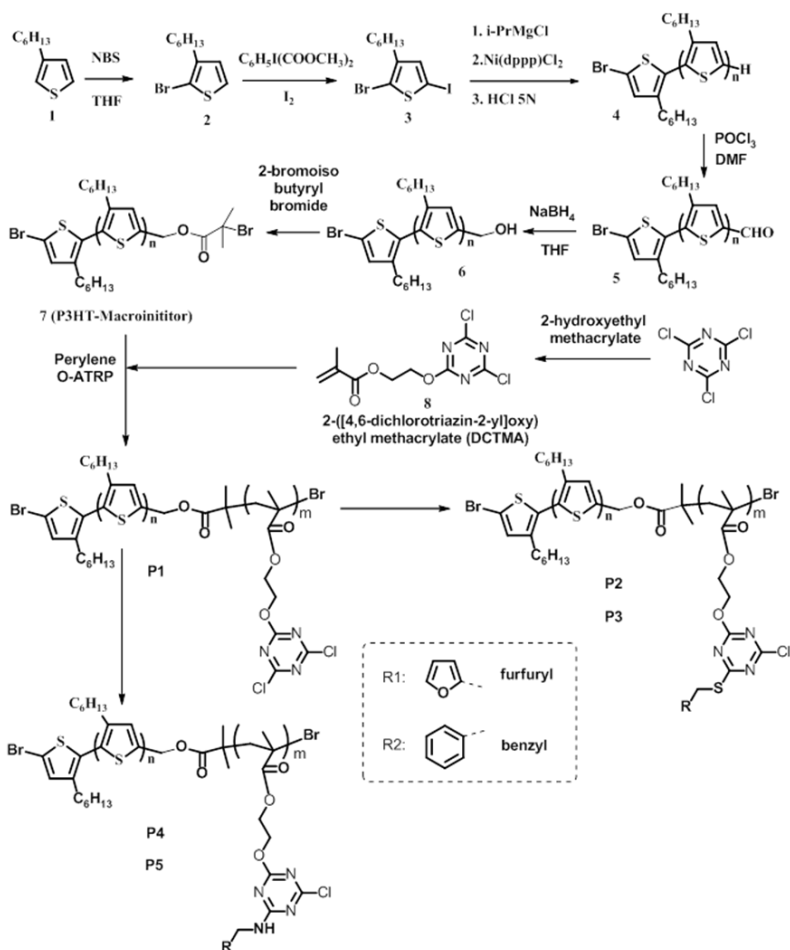
EDP (compound 1) and 1-Bromopyrene (compound 2) were synthesized according to the reported procedure. The synthesis of EP4HP and EDP4HP is described in Scheme 2.1, the Buchwald–Hartwig reaction between 3,3'-dibromo-2,2'-bithiophene and 2-ethylhexylamine catalyzed by Pd<sub>2</sub>(dba)<sub>3</sub> at 110 °C for 24 h afforded compound 1 in a yield of 56%. In the final stage, the reductive elimination of the two coupling 1-Bromopyrene and EDP compound regenerate the catalyst and give the final products of EP4HP and EDP4HP.



Scheme 2.1. Synthesis for the conjugated molecular EP4HP and EDP4HP

## 2.4 Synthesis of conjugated diblock copolymers based on poly(3-hexylthiophene) (scheme 2.2)

- Synthesis of regioregular head-to-tail poly(3-hexylthiophene) with H/Br end group (compound 4)
- Synthesis of regioregular head-to-tail poly(3-hexylthiophene) with CHO/Br end group (compound 5)
- Synthesis of regioregular head-to-tail poly(3-hexylthiophene) with CH<sub>2</sub>OH/Br end group (compound 6)
- Synthesis of bromoester-terminated poly(3-hexylthiophene) (compound 7)
- Synthesis of poly(3-hexylthiophene)-block-poly(2-([4,6-dichlorotriazin-2-yl]oxy)ethyl methacrylate) (P3HT-b-PDCTMA) diblock copolymers (compound P1)



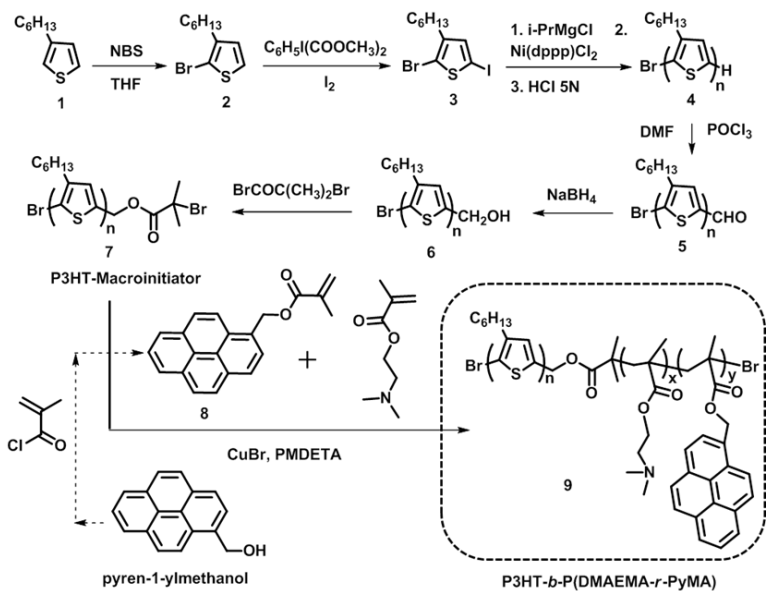
Scheme 2.2. Synthesis of diblock copolymers P3HT-*b*-PDCTMAs.

- Functionalization reaction of poly(3-hexylthiophene)-block-poly(2-[(4,6-dichlorotriazin-2-yl)oxy]ethyl methacrylate) (P3HT-*b*-PDCTMA) diblock copolymer with furfuryl mercaptan (compound P2)
- Functionalization reaction of poly(3-hexylthiophene)-block-poly(2-[(4,6-dichlorotriazin-2-yl)oxy]ethyl methacrylate) (P3HT-*b*-PDCTMA) diblock copolymers with benzyl mercaptan (compound P3)

- Functionalization reaction of poly(3-hexylthiophene)-block-poly(2-([4,6-dichlorotriazin-2-yl]oxy)ethyl methacrylate) (P3HT-*b*-PDCTMA) diblock copolymer with furfurylamine (compound P4)
- Functionalization reaction of poly(3-hexylthiophene)-block-poly(2-([4,6-dichlorotriazin-2-yl]oxy)ethyl methacrylate) (P3HT-*b*-PDCTMA) diblock copolymers with benzylamine (compound P5)

## 2.5 Synthesis of Poly(3-hexylthiophene)-*b*-poly(2-(dimethylamino)ethyl methacrylate-*random*-1-pyrenylmethyl methacrylate) (P3HT-*b*-P(DMAEA-*r*-PyMA)) (compound 9, scheme 2.3)

The synthesis of P3HT-*b*-P(DMAEA-*r*-PyMA) was performed via the ATRP method using the P3HT-macroinitiator. The obtained polymer solution was evaporated and precipitated into the flask of cold methanol. After being isolated via filtration, the resulting block copolymer was dried under vacuum at 50 °C for 24 h.

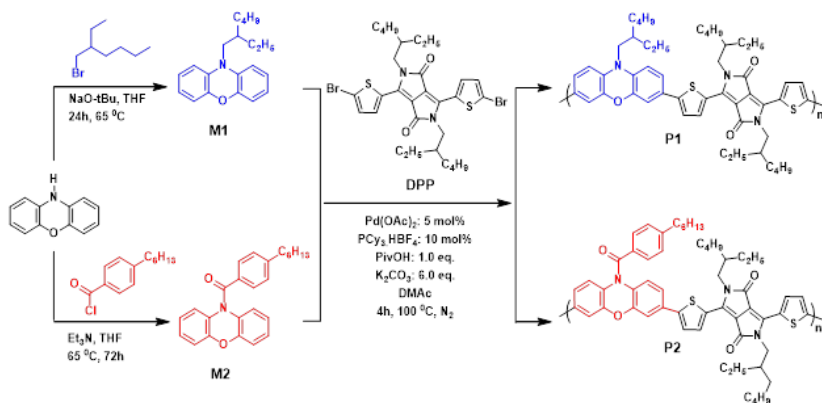


Scheme 2.3. Synthesis of P3HT-*b*-P(DMAEMA-*r*-PyMA) diblock copolymer via ATRP polymerization



## 2.6 Synthesis of donor-acceptor conjugated copolymers poly(alkyl-POZ-DPP) and poly(benzoylalkyl-POZ-DPP) via direct arylation polycondensation (compound P1 and P2, scheme 2.4)

M1 or M2, 3,6-bis(5bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (DPP) and DMAc were added to the reactor for 20 min. The septum was opened and Pd(OAc)<sub>2</sub>, PCy<sub>3</sub>.HBF<sub>4</sub>, PivOH (30.64 mg, 0.3 mmol), and K<sub>2</sub>CO<sub>3</sub> were added. The reactor was heated in a 100 °C oil bath for 4h. After being cooled to room temperature, the reaction mixture was diluted with 30 mL of chloroform. The product was purified by sequential Soxhlet extractions using methanol (6h), acetone (6h), and hexane (6h). The resultant polymer was further purified by dissolving in CHCl<sub>3</sub> and reprecipitating into methanol. The pure copolymers were obtained after drying under a vacuum at 60 °C overnight.



Scheme 2.4. Route of synthesis for the phenoxazine-based monomers and copolymers.

## CHAPTER 3 RESULT AND DISCUSSION

### 3.1 Synthesis of conjugated diblock copolymer P3HT-*b*-PDCTMA

#### 3.1.1 Synthesis and characterization of Poly(3-hexylthiophene)-*b*-poly(2-(4,6-dichlorotriazin-2-yl)oxy)ethyl methacrylate) (P3HT-*b*-PDCTMA)

- The synthesis yield was approximately 82%
- The molecular weight of the homopolymer P3HT was also determined by  $^1\text{H}$  NMR to be  $\sim 9,000$  g/mol
- The optimal content of perylene catalyst should be about 0.5 equivalent with respect to the P3HT-*i*BuBr macroinitiator in order to afford an efficient polymerization process.
- The FT-IR suggested that the PDCTMA segment has been incorporated as a coil segment in diblock copolymers (Figure 3.1).

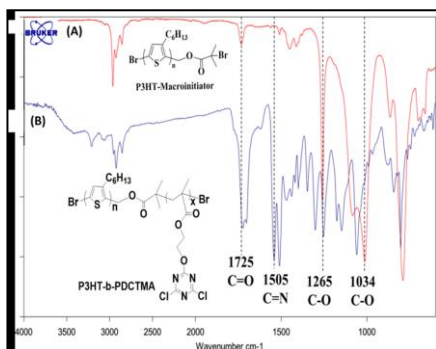


Figure 3.1. FT-IR spectrum of P3HT-macroinitiator (A) and diblock copolymer P3HT-*b*-PDCTMA (B)

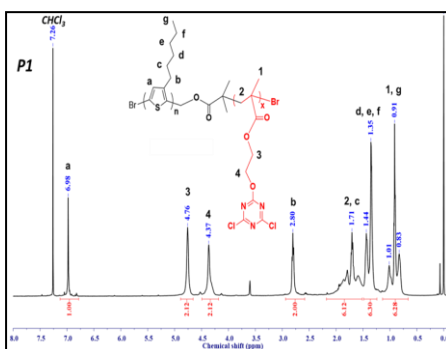


Figure 3.2.  $^1\text{H}$  NMR spectrum of diblock copolymer P3HT-*b*-PDCTMA (P1)

- The  $^1\text{H}$  NMR spectrum of the obtained diblock copolymer P1 showed all characteristic peaks corresponding to its structure (Figure 3.2). The  $M_n$  of P1 was calculated to be  $\sim 18,000$  g/mol based on the  $^1\text{H}$  NMR result, where the composition of the PDCTMA coil block occupied 50% of the copolymer.

### 3.1.2 Functionalization of diblock copolymer P3HT-*b*-PDCTMA (P1-P5) via thiol-triazazine and amine-triazazine substitution reactions

- Table 3.1 presents the reaction conditions and conversions of the functionalization reactions of diblock copolymer P1 with furfuryl mercaptan, benzyl mercaptan, furfuryl amine, and benzyl amine.

Table 3. 1. Functionalization degree of P3HT-*b*-PDCTMA P1 ( $M_n$  GPC = 17,500 g/mol,  $\bar{D} = 1.42$ ) by nucleophilic substitution reaction of the triazine chloride group of P1 in THF at 0 °C for 3 h and subsequently at room temperature for 15 h.

Diblock copolymer product	Nucleophile	Conversion of substitution reaction <sup>a</sup> (%)
P2	Furfuryl mercaptan	95
P3	Benzyl mercaptan	95
P4	Furfurylamine	96
P5	Benzylamine	96

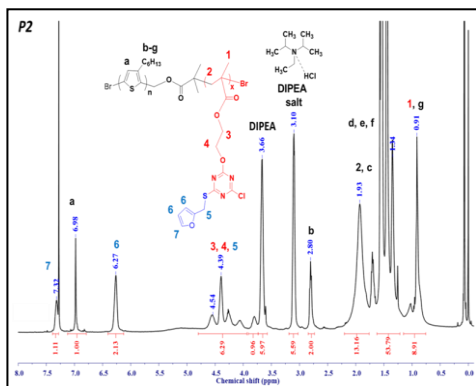


Figure 3.3. <sup>1</sup>H NMR spectra recorded in CDCl<sub>3</sub> of diblock copolymer P2

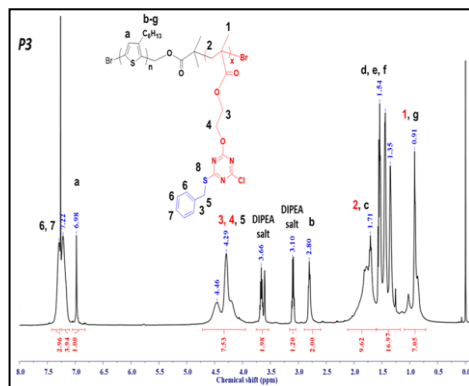


Figure 3.4. <sup>1</sup>H NMR spectra recorded in CDCl<sub>3</sub> of diblock copolymer P3

- The structure of diblock copolymer P2 was confirmed by <sup>1</sup>H NMR, as shown in Figure 3.3. This result indicates that the mercaptan group reacted easily with the triazine chloride side group of the diblock copolymer.

- In the  $^1\text{H}$  NMR spectrum of P3, besides all characteristic peaks of the P3HT and PDCTMA blocks, the benzyl sulfide group showed aromatic peaks at 7.22 and 7.30 ppm (peak “6” and “7”, Figure 3.4), indicating that benzyl mercaptan reacted successfully with triazine chloride.
- The  $^1\text{H}$  NMR spectrum of diblock copolymer P4 appeared to peak at 6.24 ppm and 7.28 ppm attributed to the protons of furan rings (Figure 3.5). This indicates that furfuryl amine reacted successfully with triazine chloride. The  $^1\text{H}$  NMR spectrum of P5 also showed all characteristic peaks expected for the structure of the diblock, with the peak of benzylamine moieties appearing at 7.17 ppm (Figure 3.6).
- Diblock copolymers P1-P5 in solvents of different polarities. Depending on the solvent polarity:  $\text{CH}_2\text{Cl}_2$ , toluene,  $\text{CHCl}_3$ , THF and Ethyl acetate, the diblock copolymers exhibited different solubilities.

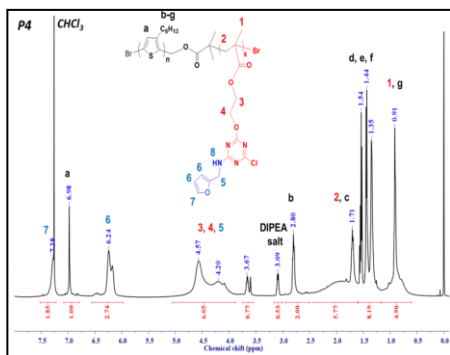


Figure 3.5.  $^1\text{H}$  NMR spectra recorded in  $\text{CDCl}_3$  of diblock copolymer P4

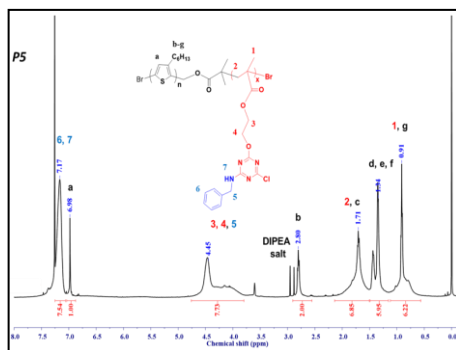


Figure 3.6.  $^1\text{H}$  NMR spectra recorded in  $\text{CDCl}_3$  of diblock copolymer P5

## 3.2 Synthesis of conjugated diblock polymer P3HT-*b*-P(DMAEMA-*r*-PyMA)

### 3.2.1 Synthesis of conjugated diblock polymer P3HT-*b*-P(DMAEMA-*r*-PyMA)

- The FT-IR spectra of the resulting P3HT-*b*-P(DMAEMA-*r*-PyMA) and P3HT-macroinitiator are shown in Figure 3.7. The GPC result in figure 3.8 shows a clear shift of the GPC curve of the diblock copolymer

P3HT-*b*-P(DMAEMA-*r*-PyMA) to a shorter retention time as compared to that of the P3HT-macroinitiator, confirming that the polymerization occurred completely.

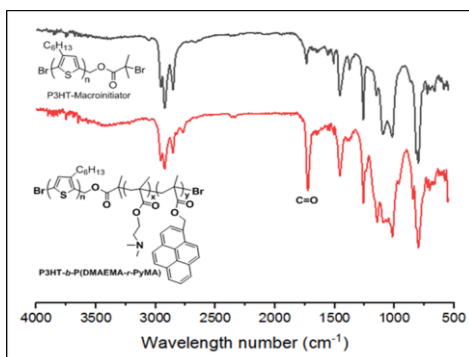


Figure 3.7. FT-IR spectra of P3HT-macroinitiator and diblock copolymer P3HT-*b*-P(DMAEMA-*r*-PyMA)

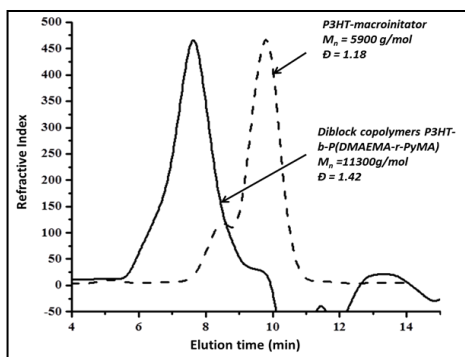


Figure 3.8. GPC traces of P3HT-macroinitiator and diblock copolymer P3HT-*b*-P(DMAEMA-*r*-PyMA)

### 3.2.2 Optical and thermal properties of conjugated diblock copolymer P3HT-*b*-P(DMAEMA-*r*-PyMA) and sensory application

- In the solution of P3HT-*b*-P(DMAEMA-*r*-PyMA) in THF without TNT, the emission of P3HT-*b*-P(DMAEMA-*r*-PyMA) exhibited at 580 nm with an intensity value of 840 a.u.
- The fluorescence intensities were decreased gradually with successive increasing the concentration of TNT. At 0.7 mM of TNT concentration, the emission intensity of P3HT-*b*-P(DMAEMA-*r*-PyMA) was decreased to 200 a.u. This result can be explained by the occurrence of binding between pyrene moieties with the nitro group of TNT that induces energy transfer leading to a fluorescence quenching of P3HT-*b*-P(DMAEMA-*r*-PyMA) (Figure 3.9).

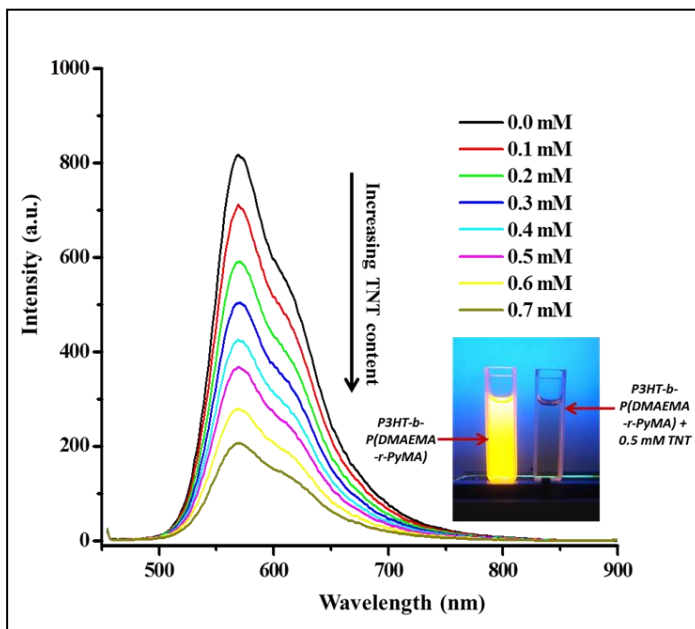


Figure 3.9. Fluorescence spectra of P3HT-*b*-P(DMAEMA-*r*-PyMA) in the presence of explosive TNT compounds

### 3.3 Synthesis of EP4HP and EDP4HP

#### 3.3.1 Synthesis and characterization of EP4HP and EDP4HP

- The FT-IR spectrum of EP4HP and EDP4HP compounds showed bands from 2868 to 3044  $\text{cm}^{-1}$  signed to the C-H stretching vibrations of ethyl -hexyl group and C-H linkage in aromatic structure. The band from 1516 to 1600  $\text{cm}^{-1}$  is corresponding to C=C stretching in aromatic and C-H deformation vibrations. The peaks from 1020 to 1103  $\text{cm}^{-1}$  indicate the existence of C-N. The band from 719  $\text{cm}^{-1}$  to 824  $\text{cm}^{-1}$  are responsible for the C-S stretching vibrations of thiophene structures.
- The structures of the EP4HP and EDP4HP molecules were characterized via  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopies in figure 3.11. The results indicated that the direct arylation cross-coupling has been applied successfully to obtain the molecules of EP4HP and EDP4HP.

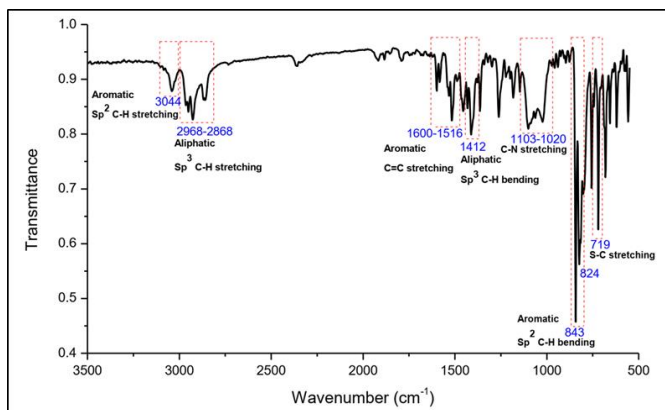


Figure 3.10. FT-IR spectra of the molecules EP4HP and EDP4HP

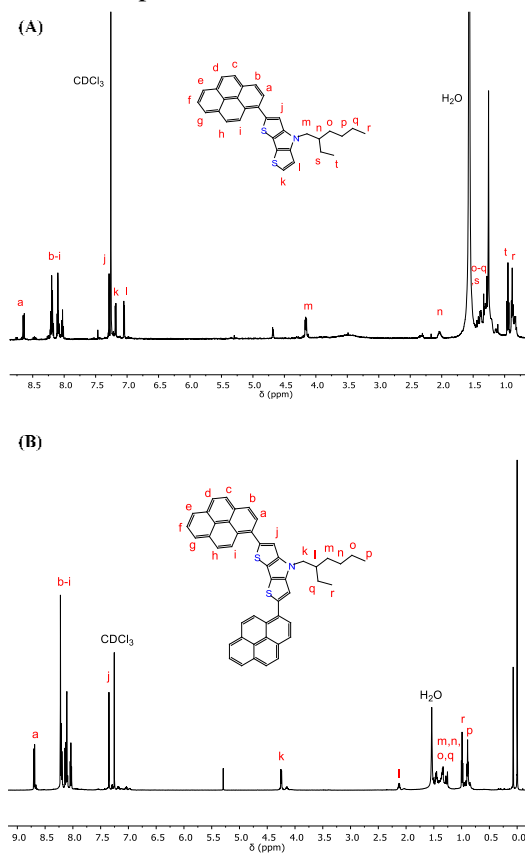


Figure 3.11.  $^1\text{H}$  NMR spectra (500 MHz,  $\text{CDCl}_3$ ) of the molecules EP4HP (A) and EDP4HP (B)

- Figure 3.12 showed the UV-Vis absorption spectra of molecules EP4HP and EDP4HP in dilute  $\text{CHCl}_3$  solution at different concentrations

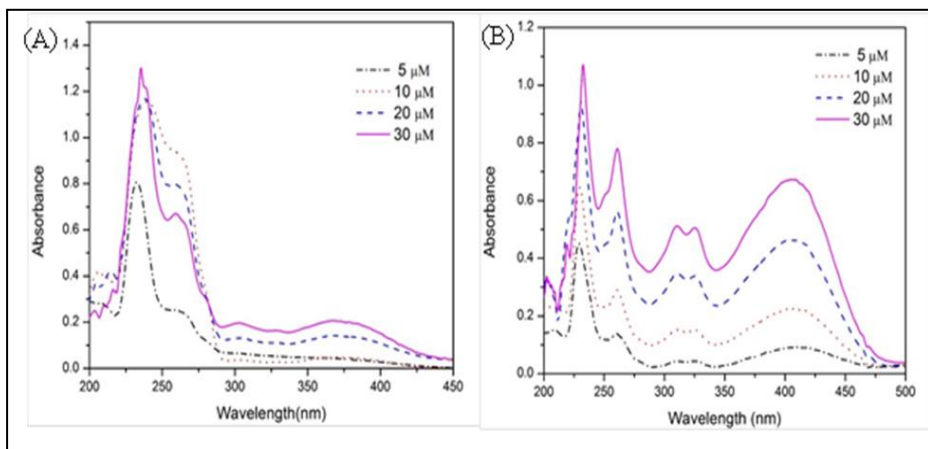


Figure 3.12. UV–vis absorption spectra of EP4HP (A) and EDP4HP (B) at various concentrations in  $\text{CHCl}_3$

### 3.3.2 Application of EP4HP and EDP4HP for tracing mesotrione

- The fluorescence of EP4HP and EDP4HP in solution was excited at the wavelength of 365 nm. The polymer when analyzed for fluorescence is blue. The solutions of EP4HP and EDP4HP in  $\text{CHCl}_3$  were added to different amounts (0 – 75  $\mu\text{M}$ ) of mesotrione, the fluorescence intensities decreased gradually with increasing the concentration of mesotrione compound.
- The binding between mesotrione with EP4HP and EDP4HP causes fluorescence quenching in figure 3.13.



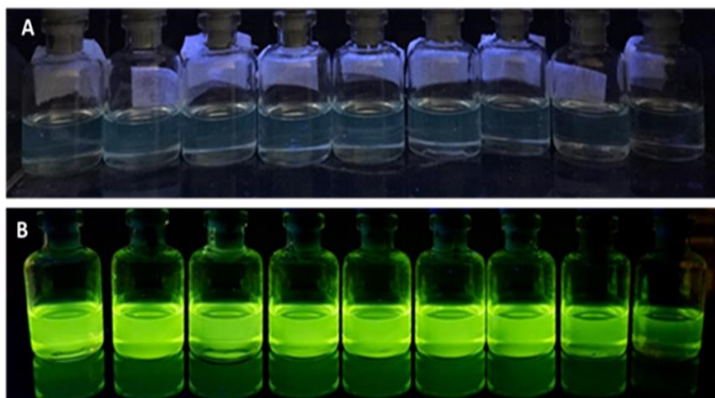


Figure 3.13. Fluorescence quenching of EP4HP in  $\text{CHCl}_3$  ( $1 \mu\text{M}$ ) (A) and EDP4HP in  $\text{CHCl}_3$  ( $1 \mu\text{M}$ ) (B) upon addition of mesotrione ( $0\text{-}75 \mu\text{M}$ ).

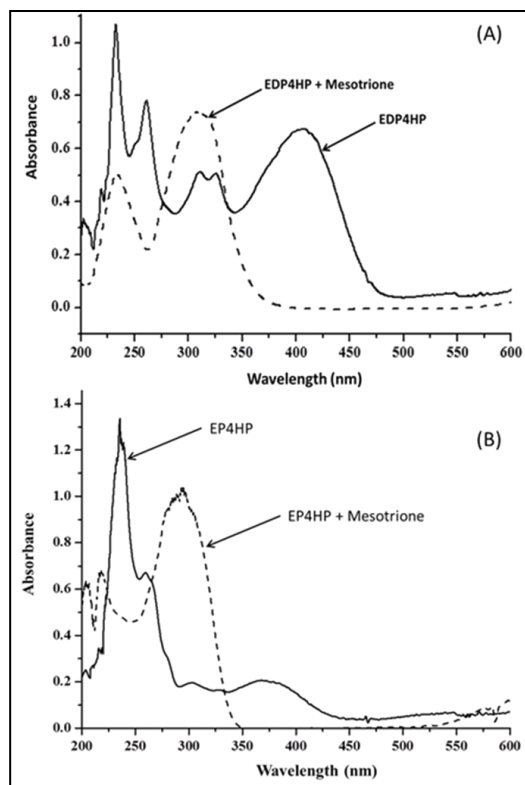


Figure 3.14. UV-vis absorption spectra of EDP4HP/EDP4HP with mesotrione (A) and with mesotrione in  $\text{CHCl}_3$  (B)

- The UV-vis of the EDP4HP solution showed an absorption peak at 410 nm that was red-shift as compared with the absorption of EDP4HP with mesotrione (CM = 1  $\mu$ M) solution which showed the absorption peak at 320 nm in figure 3.14. In the case of EP4HP, the UV-Vis spectra of EP4HP with mesotrione exhibited absorption at 305 nm while the absorption of EP4HP is around 232 nm with a shoulder of 261 nm.

### 3.4 Synthesis of donor-acceptor conjugated copolymers poly(alkyl-POZ-DPP) and poly(benzoylalkyl-POZ-DPP) via direct arylation polycondensation (compound P1 and P2)

#### 3.4.1 Synthesis of monomer 10-(2-ethylhexyl)-10H-phenoxazine (M1) and monomer 10-(4-(hexyl)benzoyl)-10H-phenoxazine (M2)

- The synthesis yield were approximately 86% (M1) and 75% (M2)
- The structure of monomers M1 and M2 was determined via  $^1\text{H}$  NMR in figure 3.15. The presence of these peaks, along with their integral ratios, indicate that the reaction has taken place successfully to give the ethylhexyl-POZ and hexylbenzoyl-POZ monomers.

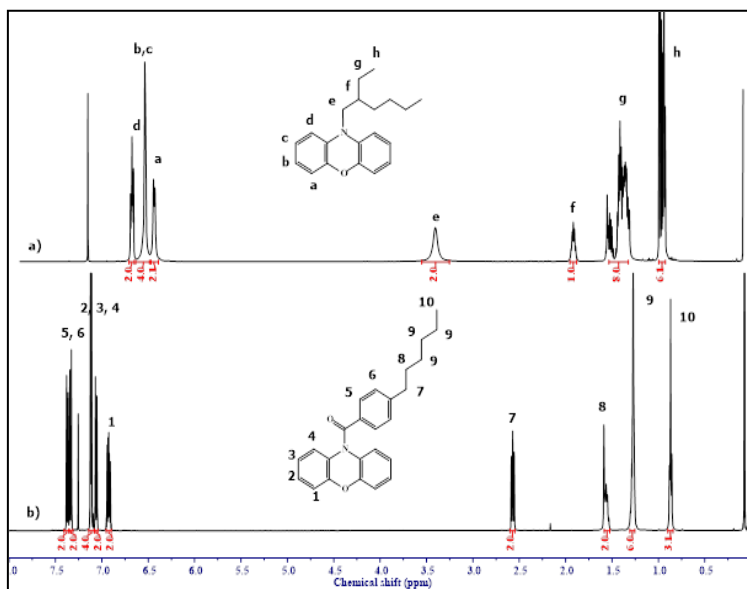


Figure 3.15.  $^1\text{H}$  NMR spectra of monomer M1 (a) and M2 (b) in  $\text{CDCl}_3$ .

### 3.4.2 Synthesis of polymers poly(alkyl-POZ-DPP) (P1) and poly(benzoylalkyl-POZ-DPP) (P2)

- The synthesis yield were approximately 82% (P1) and 85% (P2)
- The molecular weights were approximately 28000 gmol<sup>-1</sup> (P1) and 41500 gmol<sup>-1</sup> (P2)

### 3.4.3 Structure of polymers poly(alkyl-POZ-DPP) (P1) and poly(benzoylalkyl-POZ-DPP) (P2)

- Figure 3.16 shows the FT-IR spectra of the obtained these copolymers, a peak at 1689 cm<sup>-1</sup> appears in the spectrum of the P2 attributed to the stretching vibration of the carbonyl groups (C=O) having higher intensity than of the P1.

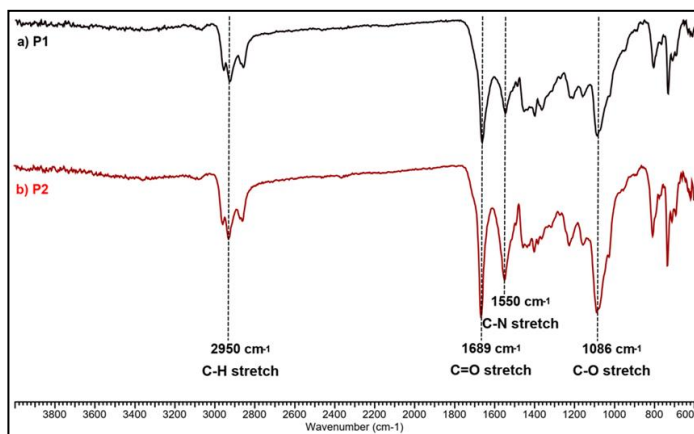


Figure 3.16. Comparative FT-IR spectra of P1 (a) and P2 (b)

- Figure 3.17 showed the <sup>1</sup>H NMR spectra of the alternating copolymers, P1 and P2, which were in good agreement with the polymers' structures. The spectrum of P1 showed resonances in the range of 7.5 - 7.8 ppm that can be attributed to the protons in the phenoxazine ring

and peaks at 9.0 ppm and 7.3 ppm which is attributable to the protons in the DPP ring.

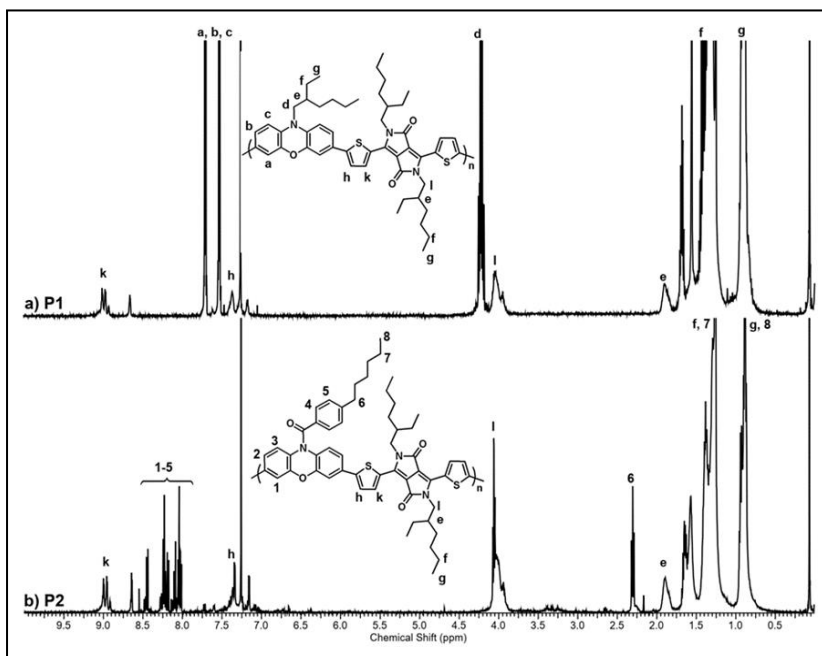


Figure 3.17.  $^1\text{H}$  NMR spectra of P1 (a) and P2 (b) in  $\text{CDCl}_3$

#### 3.4.4 Optical Properties of polymers poly(alkyl-POZ-DPP) (P1) and poly(benzoylalkyl-POZ-DPP) (P2)

- The UV–vis absorption spectra of the two polymers P1 and P2 were recorded in figure 3.18. The UV spectrum of P1 and P2 polymers in chloroform exhibit a strong absorbance with  $\lambda_{\text{max}}$  at 700 nm and 710 nm, respectively.
- The UV–vis spectra of thin films of all polymers show absorption throughout the visible region. There is significant absorption extending into the near-IR region (as far as ca. 900 nm). The 92 nm red shift in  $\lambda_{\text{max}}$  observed for the P2 polymer compared to P1 is due to the branched alkyl/benzoyl of group substitutions on phenoxazine. P2 films exhibit

slightly red-shifted absorption and a lower  $E_g^{\text{opt}}$  of 1.43 eV, whereas P1 films exhibit blue-shifted absorption and a higher  $E_g^{\text{opt}}$  of 1.46 eV.

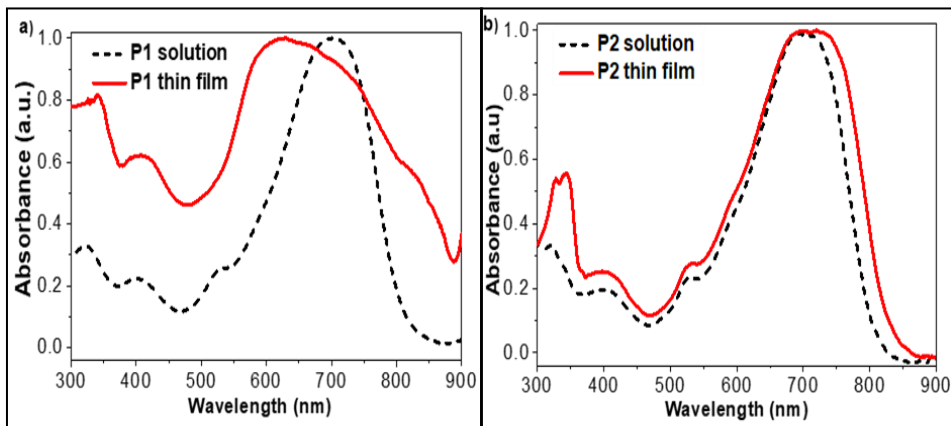


Figure 3.18. UV-vis absorption spectra of P1 (a) and P2 (b) in  $\text{CHCl}_3$  solution and thin film on a quartz substrate

## CHAPTER 4 CONCLUSION

### 4.1 Summary of current work

- The P3HT-*b*-PDCTMA diblock copolymers have been synthesized successfully via the combination of the GRIM method, end group modifications, and ATRP of 2-([4,6-dichlorotriazin-2yl]oxy)ethyl methacrylate. The use of P3HT-*b*-PDCTMA bearing triazine chloride groups as a platform to react with thiol and amine nucleophiles has been investigated. The aromatic nucleophilic substitution reactions between triazine chloride and amine/thiol compounds have been demonstrated to be a straightforward and efficient tool for coupling functional groups.
- A rod coil diblock copolymer P3HT-*b*-P(DMAEMA-*r*-PyMA) based on P3HT as rod segment and P(DMAEMA-*r*-PyMA) as a coil segments has been successfully synthesized via the combination of the GRIM method and ATRP polymerization methods. P3HT-*b*-P(DMAEMA-*r*-PyMA) was well characterized to determine its chemical structure and optical properties. The obtained diblock copolymer exhibited a controlled molecular weight of 11300 g/mol with a narrow dispersion index of 1.42. The diblock copolymers P3HT-*b*-P(DMAEMA-*r*-PyMA) showed the sensory property in tracing explosive TNT compounds through a fluorescence quenching due to the Forster resonance energy transfer mechanism.
- The conjugated molecules based on pyrene and 4-(2-ethylhexyl)-2-(pyren-1-yl)-4H-dithieno [3,2-*b*:2',3'-*d*]pyrrole have been successfully synthesized in the first time via direct arylation reaction. The obtained molecules have been used for tracing mesotrione compounds through FRET with high sensitivity of  $K_{SV}$  of 5570 and 6520 M<sup>-1</sup> for EP4HP and EDP4HP, respectively. The materials based on the EP4HP and

EDP4HP compounds are promising candidates for technical application for mesotrione detection as a chemosensor.

- Two novel low-bandgap conjugated donor-acceptor copolymers based on phenoxazine with ethylhexyl/hexyl benzoyl side chain and diketopyrrolopyrrole were successfully synthesized by Pd-catalyzed direct arylation coupling polycondensation with high Mn (up to 41500 g/mol) and high yield (>80%). Interestingly, the phenoxazine-based polymers with hexyl benzoyl side chains have higher molecular weights than those with branched ethylhexyl side chains. The benzoyl substitution also resulted in a broadening and redshift of the solid-state absorption spectra of the corresponding copolymer compared to the nonbenzoyl counterpart giving rise to lower optical bandgaps.

## 4.2 Contributions of this thesis

The goal of this thesis aims to synthesize novel diblock conjugated copolymers and novel small conjugated molecules and new donor-acceptor conjugated copolymers which can be applied in sensory applications for tracing the toxic and dangerous chemical compounds such as TNT explosives and organophosphates (OP) chemical.

- The novel diblock copolymers P3HT-*b*-PDCTMA based on poly(3-hexylthiophene) have been synthesized successfully via a combination of GRIM and ATRP methods. In addition, the diblock copolymers P3HT-*b*-PDCTMA can be used as platform polymers to create the serial of functional diblock copolymers due to the post-polymerization of P3HT-*b*-PDCTMA with thiol and amine compounds.
- A rod coil diblock copolymer P3HT-*b*-P(DMAEMA-*r*-PyMA) has been synthesized successfully via the combination of the GRIM method and ATRP polymerization methods. In addition, the diblock copolymer P3HT-*b*-P(DMAEMA-*r*-PyMA), the first time, the diblock copolymers

P3HT-*b*-P(DMAEMA-*r*-PyMA) can be applied as a fluorescence sensor for detector TNT explosive compound.

- The novel conjugated molecules of 4-(2-ethylhexyl)-2-(pyren-1-yl)-4H-dithieno [3,2-*b*:2',3'-*d*]pyrrole (EP4HP) and 4-(2-ethylhexyl)-2,6-di(pyren-1-yl)-4H-dithieno[3,2-*b*:2',3'-*d*]pyrrole (EDP4HP) were synthesized in the first time. Moreover, the 4-(2-ethylhexyl)-2-(pyren-1-yl)-4H-dithieno [3,2-*b*:2',3'-*d*]pyrrole (EP4HP) and 4-(2-ethylhexyl)-2,6-di(pyren-1-yl)-4H-dithieno[3,2-*b*:2',3'-*d*]pyrrole (EDP4HP) have been used for tracing mesotrione compound through FRET with high sensitivity of  $K_{SV}$  of 5570 and 6520  $M^{-1}$ , respectively.
- Novel low-bandgap conjugated donor-acceptor copolymers poly(alkyl-POZ-DPP) and poly(benzoylalkyl-POZ-DPP) based on phenoxazine with ethylhexyl/hexyl benzoyl side chain were successfully synthesized by direct arylation coupling polycondensation in high yields (>80%).



## LIST OF PUBLICATIONS

1. Thao Thanh Bui, Tam Huu Nguyen, Hai Le Tran, Chau Duc Tran, Duong Thanh Le, Dai Ngoc Dao, Thao Phuong Le Nguyen, Luan Thanh Nguyen, Le Thu Thi Nguyen, Thiet Quoc Nguyen, Son Thanh Cu, Mai Ha Hoang, Tsutomu Yokozawa, Ha Tran Nguyen, “Synthesis of rod–coil conjugated diblock copolymers, poly(3-hexylthiophene)-block-poly(2-(4,6-dichlorotriazin-2-yl]oxy ethyl methacrylate) and click chemistry”, *Chemical Papers*, 2023, pp. 1-18 (IF=2.2, Q3).
2. Thao Thanh Bui, Tam Huu Nguyen, Bao Kim Doan, Le-Thu Thi Nguyen, Chau Duc Tran and Ha Tran Nguyen, “Phenoxazine and diketopyrrolopyrrole based donor-acceptor conjugated polymers: synthesis and optical properties”, *Polimeros*, 2023, Vol 33, No. 1, pp. 1-7 (IF=1.3, Q3).
3. Thao Phuong Le Nguyen, Thao Thanh Bui, Cam Hong Thi Nguyen, Duong Thanh Le, Tam Huu Nguyen, Le Thu Thi Nguyen, Quoc Thiet Nguyen, Mai Ha Hoang, Tsutomu Yokozawa, Ha Tran Nguyen\*, “Diblock copolymers poly(3-hexylthiophene)-block-poly(2-(dimethylamino)ethyl methacrylate-random-1-pyrenylmethyl methacrylate), controlled synthesis and optical properties”, *Journal of Polymer Research*, 2023, Vol 30, No. 292, pp. 1-11 (IF=2.8, Q2)
4. Tam Huu Nguyen, Thao Thanh Bui, Thao Phuong Le Nguyen, Ngoc Xuan Dat Mai, Bao Kim Doan, Tam Hoang Luu, Le-Thu T. Nguyen, Chau Duc Tran, Hai Le Tran, Son Thanh Cu, Minh Nghia Phan, Quoc-Thiet Nguyen, Ha Tran Nguyen, “Synthesis and characterization of hyperbranched conjugated polymers based on triphenylamine, phenoxazine, and benzothiadiazole for optoelectronic applications”, *Optical Materials: X*, 2023, Vol 20, pp. 10270 (IF: not yet, Q2)
5. Bao Kim Doan, Cam Hong Thi Nguyen, Thao Thanh Bui, Tung Viet Tuan Tran, Ha Phuong Ky Huynh, Quoc Thiet Nguyen, Son Thanh Cu,

- Le Thu Thi Nguyen, Chau Duc Tran, Phong Thanh Mai, Hai Le Tran and Ha Tran Nguyen, “Synthesis of Conjugated Molecules Based on Dithienopyrrole Derivatives and Pyrene as Chemosensor for Mesotrione Detection”, *Journal of the Brazilian Chemical Society*, 2022, Vol 33, No. 9, pp. 1106-1116 (IF=1.4, Q3)
6. Thao Thanh Bui, Dat Hung Tran, Hai Minh Phan, Dai Ngoc Dao, Quoc Thiet Nguyen, Son Thanh Cu, Ha Tran Nguyen, “Synthesis and Optical Properties of Conjugated Copolymers based on Phenoxazine and Fluorene for an Activated Layer in Polymeric Solar Cell Applications”, *Science & Technology Development Journal*, 2022, Vol 25, No. 3, pp. 1-9.
  7. Thao Phuong Le Nguyen, Thao Thanh Bui, Bao Kim Doa, Linh Phuong Bui, Tam Hoang Luu, Chau Duc Tran, Tung Viet Tuan Tran, Tsutomu Yokozawa, Ha Tran Nguyen, “Synthesis of a conjugated molecular triad based on 9,9-dioctyl-9H-fluorene for fluorescence sensing to determine mesotrione”, *Vietnam Journal of Science and Technology*, 2023, <https://doi.org/10.31276/VJSTE>, Vol 65, No. 1, pp.14-18.
  8. Cam H. T. Nguyen, Thao Phuong Le Nguyen, Thao Thanh Bui, Bao Kim Doan, Tam Hoang Luu, Chau Duc Tran, Thuy Thu Truong, Tung Viet Tuan Tran, Hai Le Tran, Xuan Van Mai, Ha Tran Nguyen, “Effect of Applied Voltage on the Electrochemical Copolymerization of Thiophene and Dithenopyrrole Derivatives”, *Science & Technology Development Journal*, 2023, Vol 26, No. 2, pp.1-8.