

# 論文内容の要旨

## 1. Research background

The development of conductive polymers has interested scientists from many fields including chemistry, physics and material science for decades due to their excellent properties such as high conductivity, light weight, flexibility, and electrochemical. Polythiophene and its derivatives are promising as candidates for conjugated polymers and have played important roles in many applications such as energy storage systems, organic thermoelectric device, organic light emitting diodes, organic field-effect transistor, and organic electronic devices. A better understanding of the syntheses, properties and characterizations of thiophene is crucial and high priority for performance enhancement and improving new prospects for next-generation materials.

Although  $\text{FeCl}_3$  oxidative polymerization is the simplest method for synthesis of poly(3-hexylthiophene), some issues concerning the previously proposed mechanism remain to be solved. In addition, enhancement of the polyolefin properties via conjugated polymers will allow for potential applications such as the use of solar energy as a heating source for desalination or preparation of capacitor electrodes. Furthermore, “green” electronic, a novel scientific term, has now emerged as a “hot” area of research aiming at the incorporation of natural compounds and conductive polymers. Research in this regard would open up easy and efficient routes for the production of novel materials with interesting and advantageous properties such as biodegradability, biocompatibility, and sustainability.

Therefore, the goal of this dissertation includes the following targets:

- To propose new insights into the mechanism of oxidative polymerization of 3-hexylthiophene
- To carry out catalytic oxidative polymerization of 3-hexylthiophene
- Synthesis of conjugated copolymers based on 3-hexylthiophene and the application of the so-obtained material for ionic detection and fluorescence control
- Modification of the polypropylene surface through grafting poly(3-hexylthiophene)
- Surface functionalization of biomaterials with poly(3-hexylthiophene)
- Photoluminescence control of the biomaterial through novel oxidative polymerization

All desired objectives were accomplished, with the most important contribution being the oxidative polymerization, a facile and efficient method for the preparation and build-up of a conducting layer on the surface of polypropylene as well as the biomaterials. This method has the advantages of simple manipulation, mild conditions, and ease for industrial-scale production

## 2. New insights into the mechanism of oxidative polymerization of 3-hexylthiophene.

Although there are many proposed mechanism for 3-hexylthiophene oxidative polymerization, the evidence analysis for these hypothesis are still indefinite and insufficient. In this section, we discuss a series of oxidative polymerization employing various ratios of  $\text{FeCl}_3/3\text{HT}$  in the range 1:10 to 1:1, which were conducted to determine the role of the molar ratio in determining the yield and molecular weight (as shown in Figure 1).

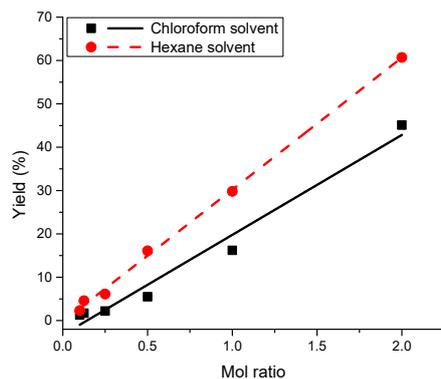


Figure 1: Polymer yield as a function of different molar ratio of  $\text{FeCl}_3$  and 3HT

Although, MALDI TOF MS is a powerful tool for the characterization of synthetic polymers, it is inappropriate for the detection of small molecules with molar mass under 500 Da because of the use of an organic matrix. In contrast, Surface-assisted Laser desorption/Ionization time of light mass spectrometry (SALDI TOF MS) using inorganic nanoparticle as an organic matrix-free can easily detect low-molecular-weight compounds. Therefore, using SALDI TOF MS with titanium dioxide as the matrix, in the first time, the structure of oligomer (such as dimer, trimer, tetramer and pentamer) was confirmed, providing new insights into the mechanism of oxidative polymerization (as shown in Figure 2). The structure of 3-hexylthiophene oligomer also are confirmed by  $^1\text{H}$  NMR as indicated in Figure 3.

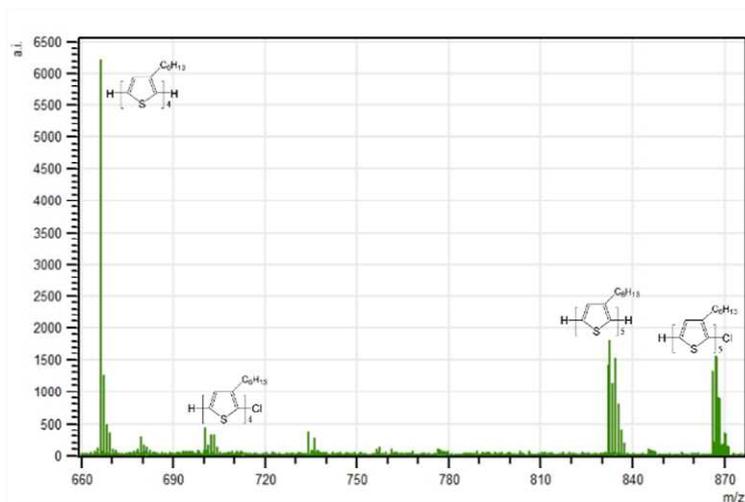


Figure 2: SALDI TOF MS of the 3-hexylthiophene oligomer

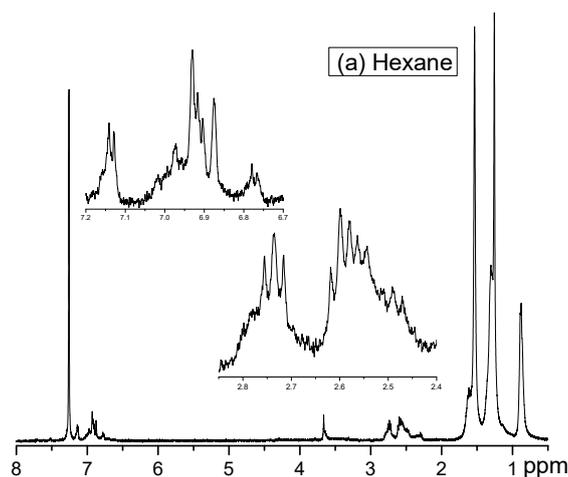


Figure 3:  $^1\text{H}$  NMR of the 3-hexylthiophene oligomer

The stabilizer in the chloroform solvent plays an important role in the oxidative polymerization of the 3HT monomer using  $\text{FeCl}_3$ . The ethanol contained in the chloroform could diminish the coordination between the monomer and  $\text{Fe(III)}$  active sites. When the stoichiometric ratio of  $\text{FeCl}_3/3\text{HT}$  is 1, due to the presence of ethanol, the amount of active  $\text{FeCl}_3$  is insufficient to promote oxidative polymerization of the 3HT monomer in order to obtain P3HT. Under these polymerization conditions, when the reaction is stopped by methanol, there is no black precipitate, and the color of the solution remains yellow, indicating that polymerization did not occur. These results from SALDI TOF MS and  $^1\text{H}$  NMR show that when the stoichiometric ratio of  $\text{FeCl}_3/3\text{HT}$  is 1, oxidative polymerization of 3HT with  $\text{FeCl}_3$  in chloroform (with ethanol as a stabilizer) only produces an oligomer having a regiorandom structure and low molecular weight.

### 3. The catalytic oxidative polymerization of 3-hexylthiophene

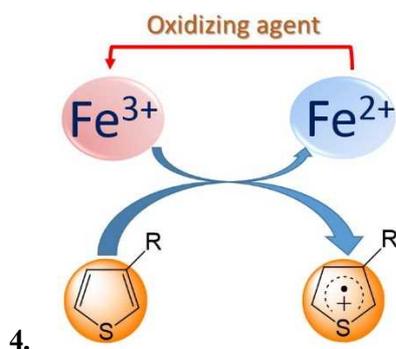


Figure 4. The catalytic oxidative polymerization

In polymerizing 3HT using  $\text{FeCl}_3$  as an oxidizing agent in hexane, it was proven that the yield of the polymer product was influenced when the ratio of  $\text{FeCl}_3$  to 3HT was changed in the range of 1:1 to 1:4. Various oxidative agents ( $\text{Cl}_2$ , BPO,  $\text{H}_2\text{O}_2$ ,  $\text{ZrCl}_4$ , and  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ ) were examined to find an effective oxidizing agent (for  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ ) (as shown in Figure 4).  $\text{Ce}^{4+}$  was the most effective oxidizer for the required reaction, though it is not strong enough to catalyze the chemical coupling oxidative polymerization of 3HT itself.

As  $\text{Ce}^{4+}$  induced a side reaction of 3HT at the 4-position, the structure and properties of P3HT were significantly affected including molecular weight (Table 1), optical properties (Figures 5 and 6) and conductivity. The side reaction of 3HT at the 4-position could result in steric effects due to the torsion angle of the adjacent monomer unit, which would influence the optical properties and the conductivity of P3HT.

**Table 1. Effect of the Ce<sup>4+</sup> into polymerization of 3-hexylthiophene in hexane**

Entry	Sample	Experiment	Oligomer <sup>c</sup>		Polymer <sup>d</sup>	
			M <sub>w</sub> <sup>a</sup> × 10 <sup>3</sup> Da	PDI <sup>b</sup>	M <sub>w</sub> <sup>a</sup> × 10 <sup>3</sup> Da	PDI <sup>b</sup>
1	S1	Fe <sup>3+</sup> /3HT 1:1	4.5	1.4	114	2.2
2	S2	Fe <sup>3+</sup> /3HT/Ce <sup>4+</sup> 1:1:1	5.6	1.3	99	3.8
3	S3	Fe <sup>2+</sup> /Ce <sup>4+</sup> /3HT 1:1:1	1.5	1.4	11	1.9

<sup>a</sup> Determined by Gel-Permeation Chromatography (Polystyrene standard, chloroform as solvent)

<sup>b</sup> Polydispersity Index, PDI = M<sub>w</sub>/M<sub>n</sub>

<sup>c</sup> Oligomer: the reaction product was Soxhlet extracted with acetone

<sup>d</sup> Polymer: the reaction product was Soxhlet extracted with chloroform

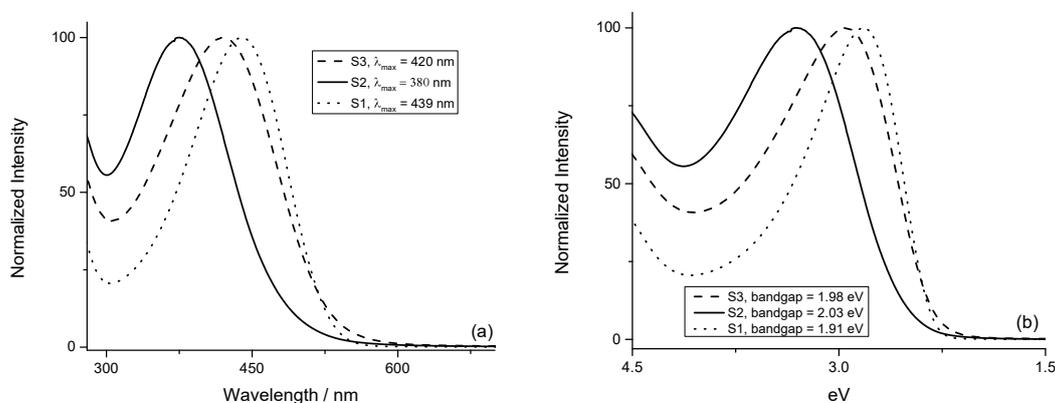


Figure 5. UV-Vis spectra of P3HT (S1, S2, and S3) in chloroform

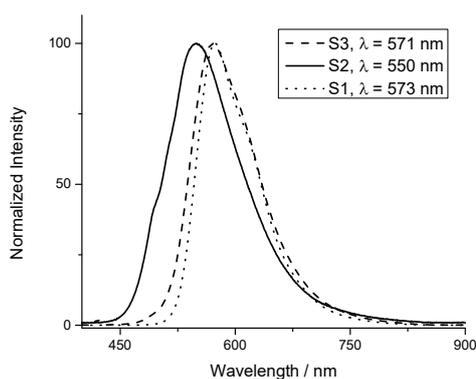


Figure 6. Fluorescence spectra of P3HT samples (S1, S2 and S3) in chloroform

S1 and S3 show similar electrical conductivity (0.9 and 0.6 S/cm), but that of S2 (0.09 S/cm) is lower by about one order of magnitude. Previous works have demonstrated the effect of branched side chains on the physicochemical, photovoltaic, and conductivity properties of conjugated polymer. The difference in conductivity between S1, S2, and S3 is influenced by the side reaction of 3HT at the 4-position which could be related to the torsion angle between adjacent monomer units, resulting in steric hindrance on the π-π stacking of the conjugated polymer chain

## 5. Syntheses, characterization and applications of conjugated polymers

Oxidative polymerization is utilized for the copolymerization of 3-hexylthiophene and some aromatic compound such as fluorene and 9-ethylcarbazole due to its mild reaction condition.

The incorporation of 3HT and fluorene units (as indicated in Figure 7) into the resultant polymer main chain was verified via proton nuclear magnetic resonance ( $^1\text{H}$  NMR) and matrix-assisted laser desorption/ionization mass spectrometry (as shown in Figure 8). During copolymerization, the molar ratios of fluorene and thiophene changed (0 to 100%). Thus, the fluorene content in the copolymers was proportional to that of the fluorene fed into the polymerization reaction mixture. Ultraviolet–visible (UV–Vis) and fluorescence spectra indicated that the absorption and emission peak wavelengths of the resulting copolymer were significantly affected by the fluorene content. The quantum yield determined using the relative method increased from 0.26 to 0.73 with an increase in the fluorene content (as shown in Figure 9). The thermal stability of the copolymers also improved with the presence of fluorene.

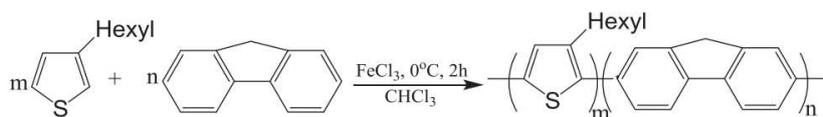


Figure 7. Synthetic scheme for 3-hexylthiophene and fluorene random copolymer

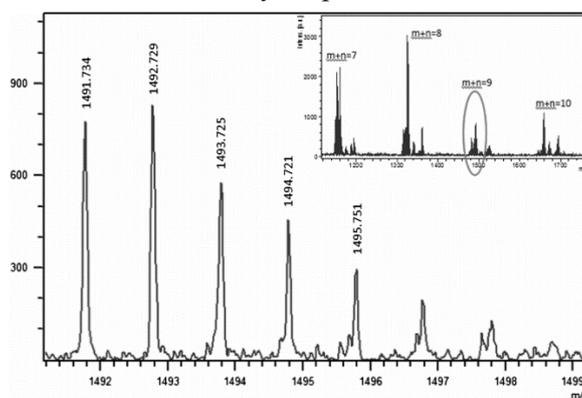


Figure 8. MALDI TOF MS spectra of 3-hexylthiophene/fluorene (50/50) oligomer

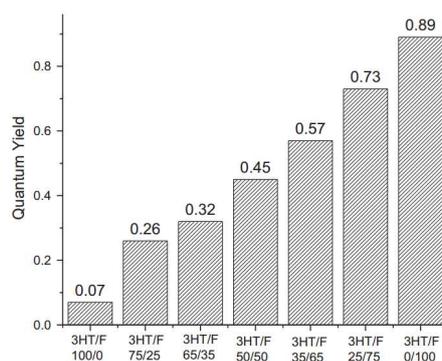


Figure 9. Quantum Yields of 3-hexylthiophene/fluorene random copolymer

Conjugated copolymers based on 9-ethylcarbazole(9EC) and 3-hexylthiophene(3HT) have been synthesized by oxidative polymerization with  $\text{FeCl}_3$  in hexane, and it is confirmed that 9EC and 3HT molecules were built into the polymer main chain (in Figure 10). Although the rate of the 9EC included in copolymers obtained in hexane was high (maximum 47%), the rate of the ones included in copolymers obtained in chloroform and in nitrobenzene were very low (0% in case of chloroform, 5% in case of nitrobenzene). In polymerizing 9EC and 3HT at several temperatures, yield of 3HT/9EC copolymer was 36% at 25 C, but the one was 0% at 0 C. The ratio of 9EC and 3HT unit is shown in Figure 11. The thermal stability of 3HT/9EC copolymer was improved significantly with the presence of 9EC in the polymer

main chain (as indicated in Figure 12). A complex consisting of 3HT/9EC copolymer and tri-n-butylborane (TBB) (1:1) was prepared in THF solution and this complex was confirmed by  $^{11}\text{B}$  NMR. By adding fluoride anion to the complex of 3HT/9EC copolymer and TBB in THF solution, the fluorescence intensity was decreased because of increasing concentrations of fluoride anion (in Figure 13).

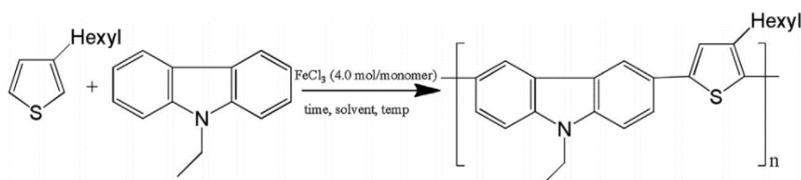


Figure 10. Synthetic scheme for 3-hexylthiophene and 9-ethylcarbazole random copolymer

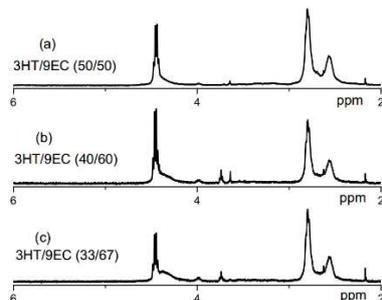


Figure 11.  $^1\text{H}$  NMR spectra of 3-hexylthiophene/9-ethylcarbazole copolymer at different molar ratio

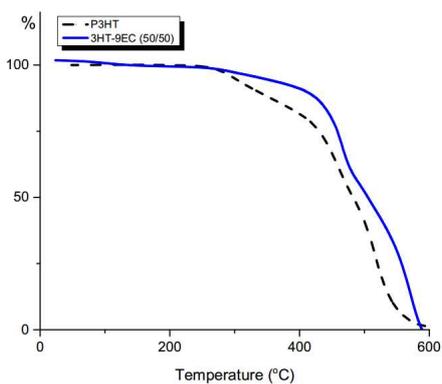


Figure 12. The comparison of TG of P3HT and 3HT/9EC (50/50) copolymer

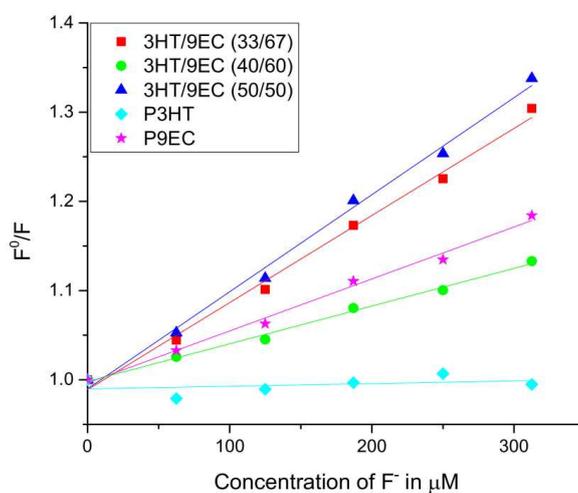


Figure 13. Comparison plot of  $F_0/F$  as a function of the  $\text{F}^-$  anion concentrations with different complexes

## 6. Modification of polyolefin surface through grafting poly(3-hexylthiophene)

Polypropylene (PP) is one of the most important thermoplastic, which present in broad range of applications such as packaging, textile, automotive materials and so forth. However, the highly non-polar nature and low surface energy of PP need to be modified for surface properties improvement such as wettability, adhesion, and dye-ability. The surface modification of PP by  $\pi$ -conjugated polymers is an effective way to increase the functionality of PP which open the door to interesting and potential applications. The outstanding properties of PP, such as high abrasion resistance, chemical inertness, stretchability, and low density make the PP textile industry develop and succeed since the 1950s. During the production and utilization of PP fibers, the surface can become charged easily, which can result in serious problems, such as damage to sensitive electronic equipment. The presence of conducting polymer on the surface of PP promote transfer the static charge which may improve the antistatic properties of PP.

In this section, a new methodology for grafting poly(3-hexylthiophene) P3HT onto PP surfaces (film and powder) is presented, and this process involves two simple reaction steps (as indicated in Figure 14). In the first step, two kinds of monomers are grafted onto the PP surface using triorganoboranes (TBB) and oxygen in the air. In the second step, P3HT is built-up on the PP surface via the chemical oxidative polymerization of modified PP in the first step and 3HT monomers using  $\text{FeCl}_3$  as the oxidant.

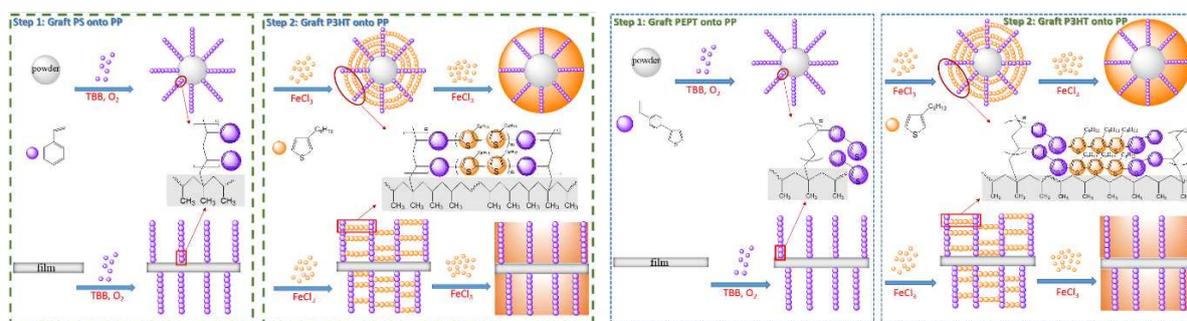


Figure 14. Mechanism grafting of P3HT onto PP film and powder using two-step method with different initial vinyl monomer: styrene (left) and 3-(4-ethenylphenyl)thiophene (right) monomer

The incorporation of 3HT units into PS-g-PP results in absorption and emission peaks appeared in UV-vis and photoluminescence spectra (as shown in Figures 15 and 16).

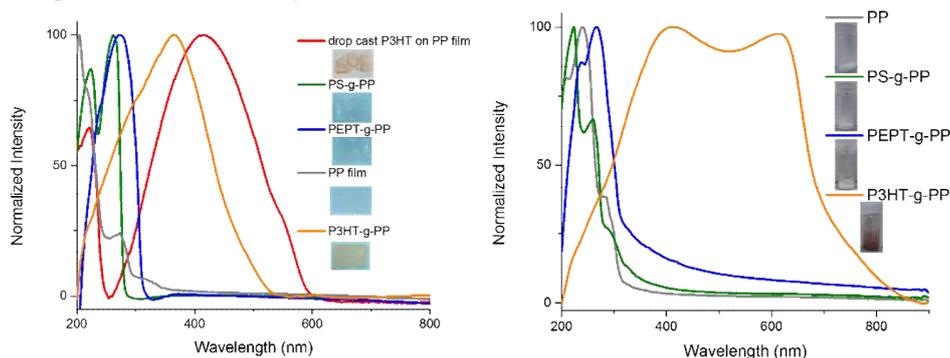


Figure 15. UV-Vis spectra of PP, PEPT-g-PP, PS-g-PP and P3HT-g-PP in film (left) and powder (right)

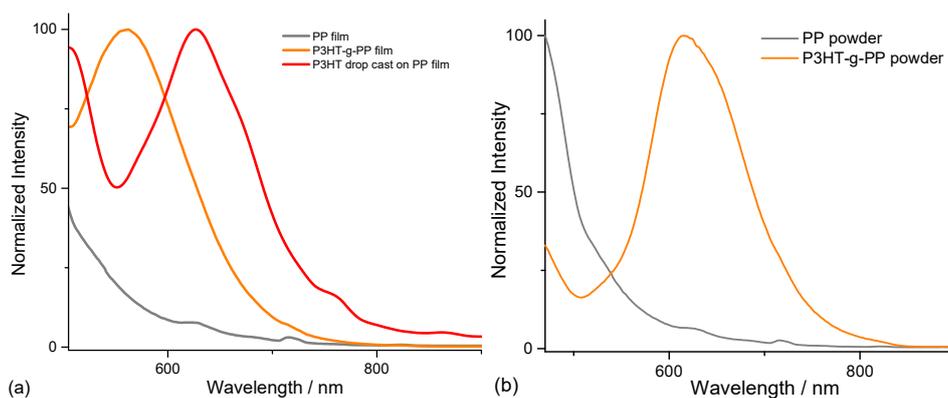


Figure 16. Photoluminescence spectra of PP, P3HT-g-PP in film (a) and powder (b)

The thermal stability of PP was significantly improved by grafting P3HT onto the PP surface (Figure 17).

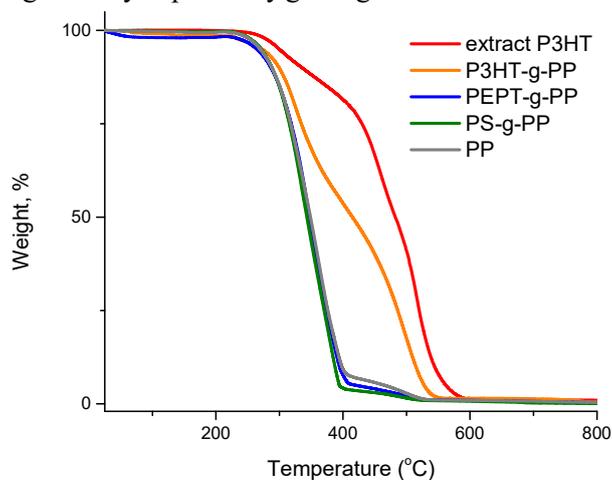


Figure 17. TGA curves of PP, PEPT-g-PP, PS-g-PP, P3HT-g-PP and P3HT

The doping of the surface with I<sub>2</sub> extended the  $\pi$ -conjugation and reduced the band gap energy.

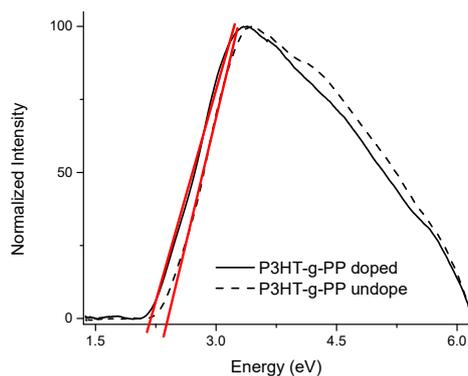


Figure 18. UV-Vis spectra of the undoped and doped P3HT-g-PP films

The presence of sulfur, originating from the monomeric heterocyclic compound 3HT, was detected by TEM-EDX analysis.

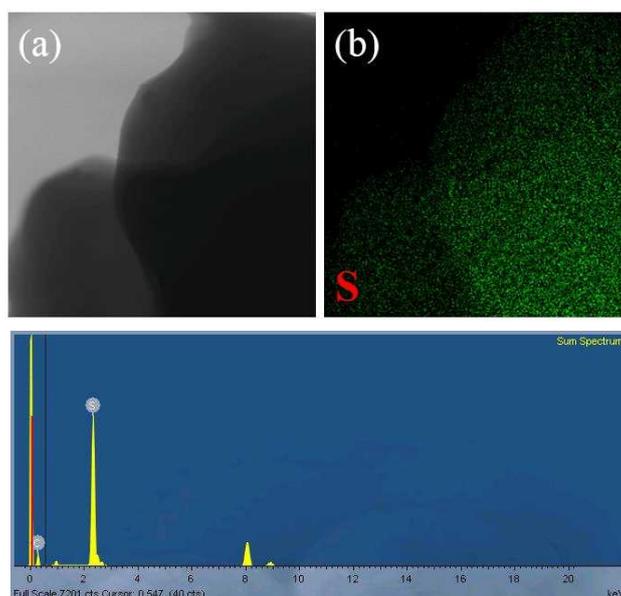


Figure 19. The EDX mapping images (a), (b) and EDX spectrum of P3HT-g-PP powder

The electrical conductivity (around 0.02 S/cm) of the grafted powder indicates that the P3HT layer was well grafted onto the surface of the PP.

#### 7. Surface functionalization of biomaterial substrates with poly(3-hexylthiophene)

Recently, advances in the research combining conjugated polymers and biomaterials have driven new interest in enhancing the novel functionalities of materials and further opening the scope of applications such as biosensor, bioelectronics, tissue engineering, and biofuel cell.

Surface functionalization of cellulose with poly(3-hexylthiophene) (P3HT) was conducted with  $\text{FeCl}_3$  as an oxidant in three different solvents: acetonitrile, chloroform, and hexane. Of these three solvents, hexane best promoted the grafting P3HT to cellulose with a high grafting ratio and molecular weight. The maxima of the UV-vis absorption and fluorescent spectra (in Figures 20 and 21), observed at around 500 and 600 nm, respectively, represented the build-up of the conjugated chain length formed by the grafting of P3HT onto the cellulose surface.

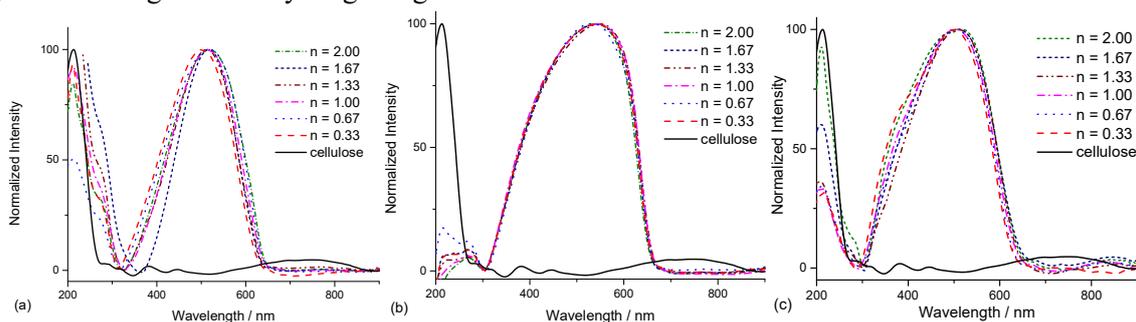


Figure 20. UV-Vis spectra of cellulose and P3HT-g-cellulose

(a) synthesis in chloroform

(b) synthesis in hexane

(c) synthesis in acetonitrile

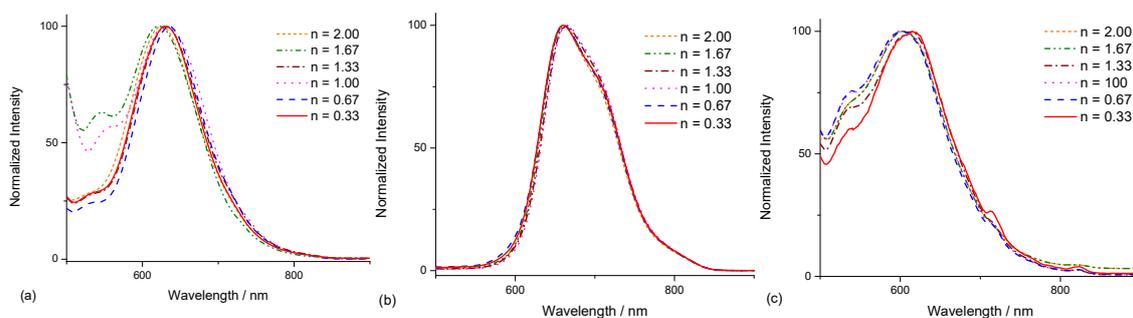


Figure 21. Fluorescence spectra of cellulose and P3HT-g-cellulose

- (a) synthesis in chloroform      (b) synthesis in hexane      (c) synthesis in acetonitrile

As shown in Figures 22 and 23, the HOMO level of cellulose as determined by photoemission yield spectroscopy decreased from 4.83 to 4.67 eV after modification with P3HT, as well as the grafting P3HT onto the surface of cellulose provided super-hydrophobic property with a lotus effect.

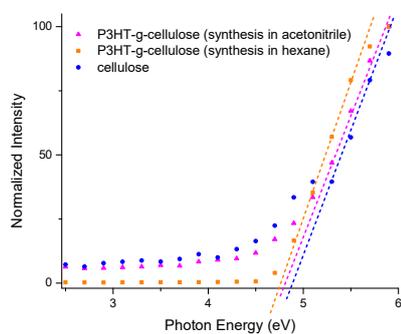


Figure 22. PYS spectra of cellulose, P3HT-g-cellulose

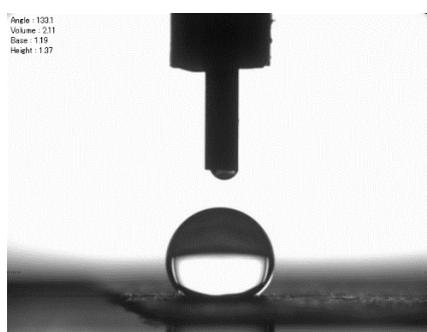


Figure 23. Illustration of contact angle formed by water drop on a surface of P3HT-g-cellulose paper

The conductivity of cellulose also improved significantly, from  $10^{-9}$  to  $10^{-6}$  S/cm when P3HT was present on the surface. The thermal stability and crystallinity of cellulose decreased slightly upon graft polymerization with P3HT in Figure 24.

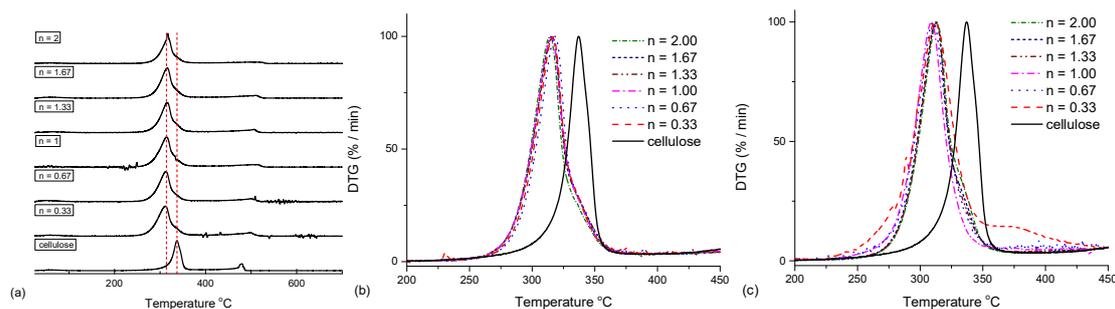


Figure 24. DTG curves of cellulose and P3HT-g-cellulose

- (a) synthesis in chloroform      (b) synthesis in hexane      (c) synthesis in acetone

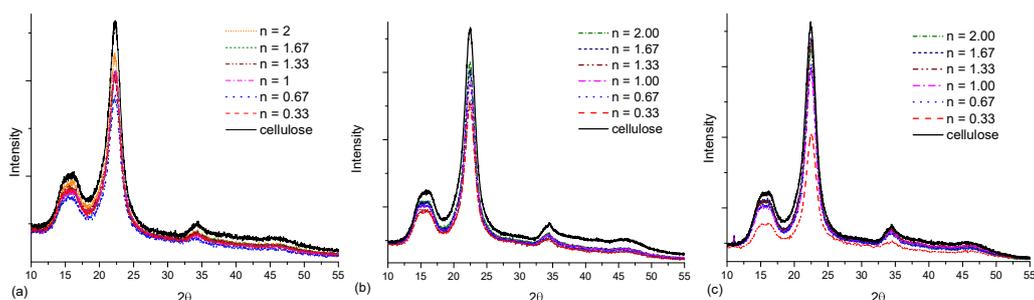


Figure 25. XRD patterns of cellulose and P3HT-g-cellulose

(a) synthesis in chloroform      (b) synthesis in hexane      (c) synthesis in acetonitrile

The modification of the surface of chitin and chitosan have been grafted successfully with P3HT, using same method. The illustrated images of grafted chitin and chitosan are described in Figure 26. Introducing the P3HT layer in the surface helped to enhance the conductivity of chitin and chitosan. The S element from 3HT unit was detected by TEM-EDX. The absorption and emission peaks in the range from 500 to 600 nm is an evidence of  $\pi$ - $\pi^*$  conjugation from 3HT unit, grafted to chitin and chitosan. The modified chitin and chitosan display high water contact angles imply that the hydrophilic nature of chitin and chitosan turned to hydrophobicity after the grafting with P3HT. The thermal stability of grafted cellulose was found to depend on its crystallinity. The thermal stabilities of the P3HT-g-chitin and P3HT-g-chitosan were slightly lower than that of chitin and chitosan themselves, while the thermal decomposition behavior of a simple mixture of a P3HT with chitin and chitosan were superior to that of chitin/chitosan alone.



Figure 26. Images of chitin and P3HT-g-chitin (left); chitosan and P3HT-g-chitosan (right)

## 8. Photoluminescence control of biomaterials through novel oxidative polymerization

In this chapter, the surface of those polysaccharides were chemically modified to control its photoluminescence with a series of conducting polymers, including fluorene (F) and 3-hexylthiophene (3HT), through oxidative polymerization with  $\text{FeCl}_3$ . In this report, P3HT and PF are used as conjugated polymers because of their unique properties, including high solubility, high efficiency emission in a wide variety of colors, low operating voltage, performance enhancement of organic light-emitting diode (OLEDs), high photoluminescence quantum efficiencies, and thermal stability. The images of obtained products are described in Figure 27.



Figure 27. Images of the (3-hexylthiophene and fluorene) copolymers grafted

(a) cellulose      (b) chitin      (c) chitosan

This approach is an interesting method to create a biomaterial with innovative optical properties. The desired blue-/red-shifted absorption and emission of grafted cellulose/chitin/chitosan can be manipulated by different feeding ratios of the 3HT/F units. (as shown in Figures 28 and 29)

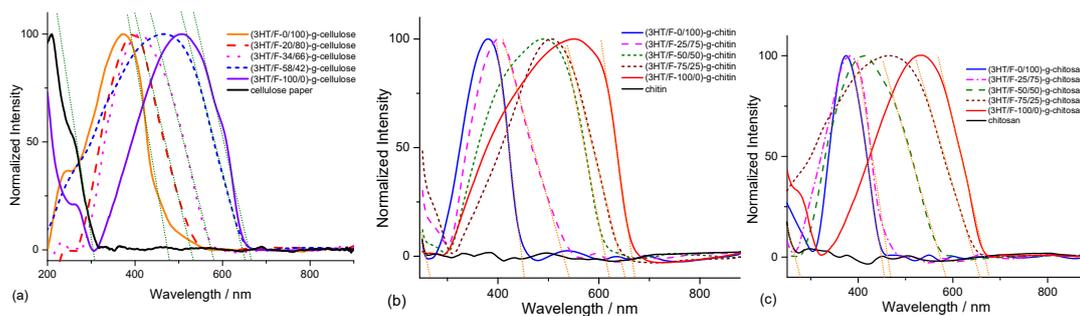


Figure 28. UV-Vis spectra of (a) cellulose and grafted cellulose, (b) chitin and grafted chitin; (c) chitosan and grafted chitosan

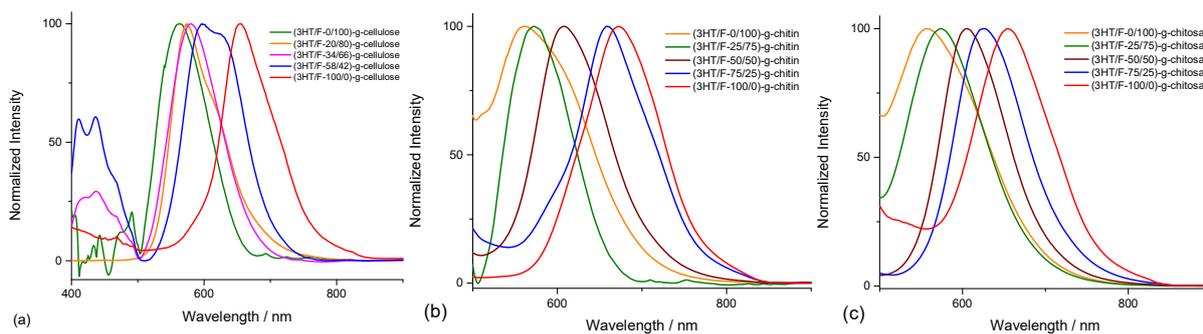


Figure 29. Fluorescence spectra of (3HT/F) copolymer grafted to cellulose (a), chitin (b) and chitosan (c)

In Figure 30, the quantum yield of (3HT/F)-g-cellulose/chitin/chitosan increased with an increase in the fluorene unit.

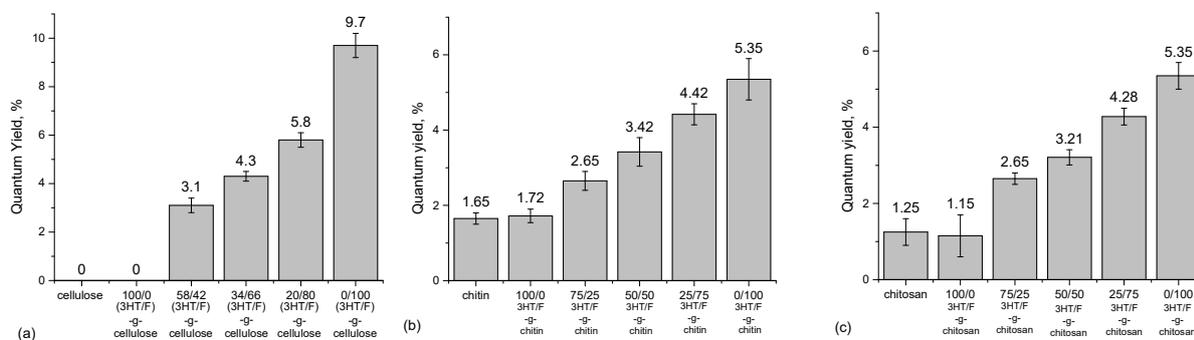


Figure 30. Quantum yields of (a) cellulose and grafted cellulose, (b) chitin and grafted chitin; (c) chitosan and grafted chitosan

The crystallinity of cellulose, chitin, and chitosan decreased slightly after graft polymerization of PF and P3HT (Figure 31).

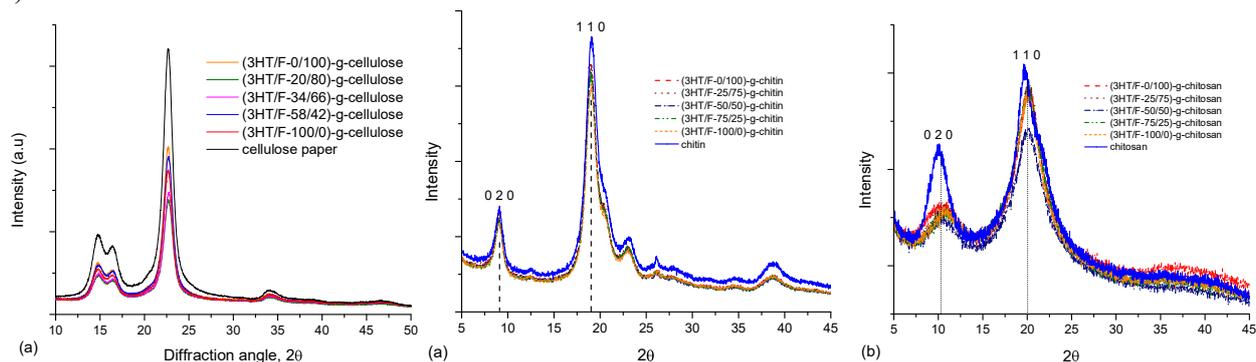


Figure 31. XRD pattern of (a) cellulose and (3HT/F)-g-cellulose, (b) chitin and (3HT/F)-g-chitin; (c) chitosan and (3HT/F)-g-chitosan

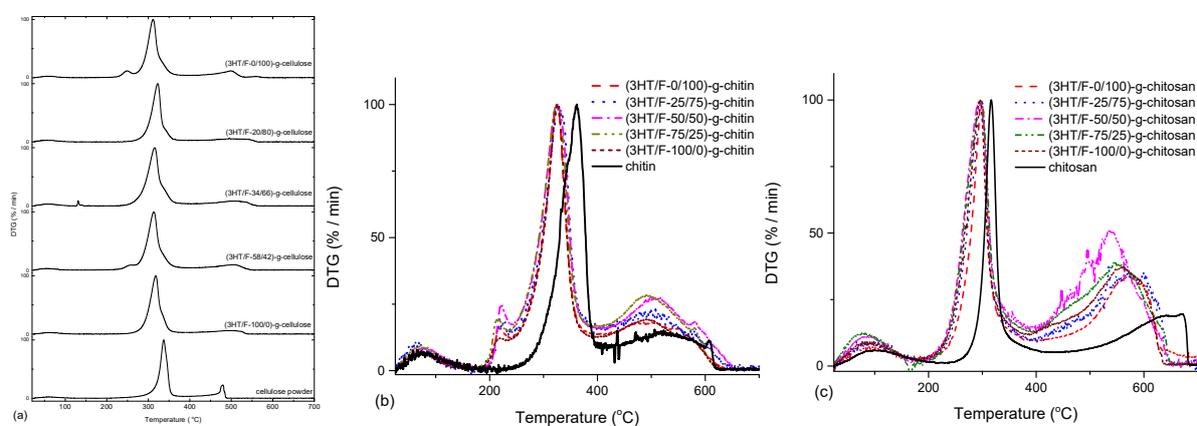


Figure 32. Derivative thermogravimetric (DTG) of (a) cellulose and grafted cellulose, (b) chitin and grafted chitin, and (c) chitosan and grafted chitosan

The thermal stability of the (3HT/F)-g-cellulose/chitin/chitosan was slightly lower than that of cellulose/chitin/chitosan (in Figure 32).