

# Photocatalytic Activity of Polycyclopentadithiophene Derivatives

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## PREFACE

This work was carried out under the supervision of Professor Masataka Kubo, Division of Applied Chemistry, Graduate School of Engineering, Mie University, from October 2021 to October 2024.

The main objective of this thesis is to investigate the synthesis and evaluate the photocatalytic activity of various compounds of Polycyclopentadithiophene derivatives. Through a systematic exploration of their synthesis processes and subsequent assessment of their photocatalytic capabilities, the thesis aims to contribute to the understanding of these compounds' potential applications in harnessing solar energy for catalytic processes.

This thesis consists of two chapters. The first chapter describes the synthesis of poly(4,4'-(((4H-cyclopenta[2,1-b:3,4-b']dithiophene-4,4-diyl)bis(ethane-2,1-diyl))bis(oxy))bis(4-oxobutanoic acid)) (PCPDT-CO<sub>2</sub>H), elucidating the steps involved in the synthesis and its photocatalytic activity. The second chapter describes the synthesis and subsequent assessment of the photocatalytic activity of Poly(4,4-dihexylcyclopenta[2,1-b:3,4-b']dithiophene) (PDiHexCPDT).

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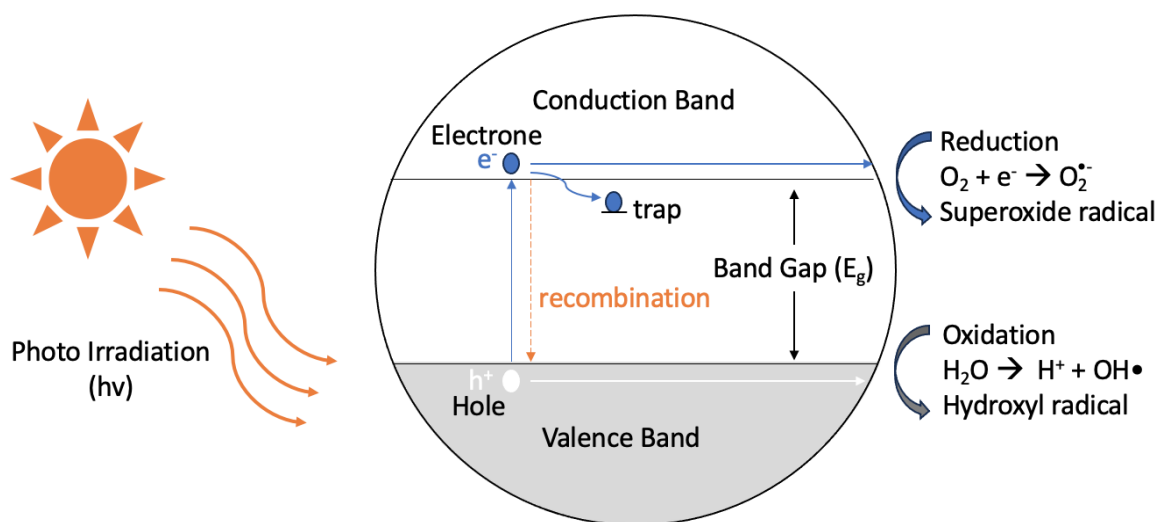
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### General Summary

## General Introduction

In the quest for sustainable solutions to pressing environmental challenges and the pursuit of efficient energy utilization, photocatalysis has emerged as a promising avenue.<sup>1</sup> Photocatalysis is a process that leverages light to accelerate chemical reactions in the presence of a catalyst. Central to photocatalysis is the use of materials capable of absorbing light and subsequently driving chemical transformations. Typically, these materials are semiconductors, which can generate electron-hole pairs upon light irradiation, leading to various redox reactions on their surfaces.

The basic principle of photocatalysis involves the absorption of photons by a photocatalyst, which excites electrons from the valence band to the conduction band, leaving behind holes in the valence band. These electron-hole pairs can migrate to the surface of the photocatalyst and participate in oxidation and reduction reactions. These processes are illustrated in Figure A.



**Figure A** Photocatalytic mechanism for photocatalyst

In water splitting, the photogenerated holes oxidize water to produce oxygen, while the electrons reduce protons to generate hydrogen.<sup>2</sup> Harnessing the power of sunlight to drive chemical reactions, photocatalysis offers potential applications in environmental remediation, energy conversion and the synthesis of valuable chemicals.<sup>3</sup>

Photocatalysis holds significant promise in environmental applications, particularly in the degradation of pollutants. Organic pollutants, including pesticides, pharmaceuticals and dyes, are persistent in water and soil, posing severe risks to human health and ecosystems. Traditional methods for treating such pollutants, like adsorption and chemical oxidation, often fall short in terms of efficiency and sustainability. Photocatalytic processes, on the other hand, can completely mineralize these contaminants into harmless end-products such as carbon dioxide and water.<sup>4</sup> This capability is particularly significant for the degradation of recalcitrant compounds that resist conventional treatment methods.<sup>5</sup>

Air purification is another domain where photocatalysis demonstrates significant importance. Photocatalytic materials can effectively break down volatile organic compounds (VOCs) and other airborne pollutants into less harmful substances under light exposure. This application has profound implications for indoor air quality, where VOCs emitted from household products and building materials can cause adverse health effects.<sup>6</sup> Moreover, photocatalytic air purifiers can operate under ambient conditions, making them energy efficient and practical for widespread use.

In the realm of renewable energy, photocatalysis offers a promising approach to hydrogen production through water splitting. Hydrogen is regarded as a clean fuel with high energy content, and its production via photocatalytic water splitting represents a sustainable alternative to fossil fuels. Semiconductors such as titanium dioxide ( $\text{TiO}_2$ ) and cadmium sulfide (CdS) have been extensively studied for this purpose. The process involves the absorption of light to

generate electron-hole pairs, which then participate in redox reactions to produce hydrogen and oxygen.<sup>7</sup> Enhancements in photocatalyst design, including doping and the development of nanostructures, have significantly improved the efficiency of hydrogen production.<sup>8</sup>

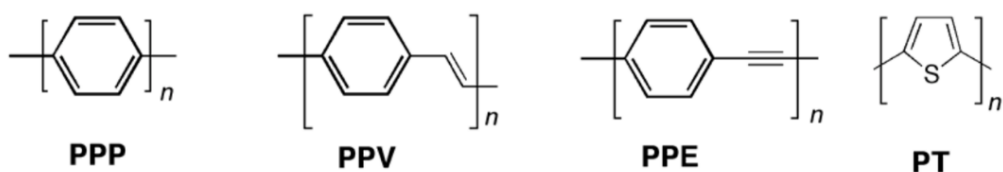
Beyond environmental and energy applications, photocatalysis is vital in various industrial processes. Photocatalytic reactions can be utilized for the selective oxidation of organic compounds, which is crucial in the synthesis of fine chemicals and pharmaceuticals. For instance, the selective oxidation of alcohols to aldehydes or ketones under mild conditions using photocatalysts is an area of active research.<sup>9</sup> This approach not only offers greener synthesis routes but also reduces the need for harsh chemicals and conditions traditionally required in these reactions.

The importance of photocatalysis is further underscored by its potential to contribute to sustainable development goals. By providing clean air and water, reducing reliance on fossil fuels and promoting greener industrial processes, photocatalysis aligns with global efforts to mitigate climate change, reduce pollution, and ensure the availability of clean resources for future generations.<sup>10</sup>

Despite its vast potential, the widespread adoption of photocatalytic technologies faces challenges. Issues such as the recombination of photogenerated charge carriers, the limited absorption of visible light by many photocatalysts, and the stability of these materials under operational conditions need to be addressed. Ongoing research aims to overcome these barriers through the development of advanced materials and innovative reactor designs.<sup>11</sup> Enhancing the efficiency of light absorption and charge separation, improving the stability of photocatalysts, and scaling up laboratory successes to industrial applications are critical areas for future research. Moreover, the design of photocatalysts that can operate under natural sunlight with high efficiency continues to be a primary goal.

Traditional photocatalysts like titanium dioxide (TiO<sub>2</sub>) have been widely studied due to their strong oxidative power, stability and non-toxicity. Since its discovery for photocatalytic applications in the 1970s, TiO<sub>2</sub> has been extensively researched and utilized in various environmental and energy-related fields, including water purification, air purification and hydrogen production.<sup>3</sup> The photocatalytic activity of TiO<sub>2</sub> is primarily attributed to its ability to generate electron-hole pairs upon exposure to ultraviolet (UV) light. When TiO<sub>2</sub> is irradiated with light energy greater than or equal to its band gap (approximately 3.2 eV for anatase TiO<sub>2</sub>), electrons in the valence band are excited to the conduction band, leaving behind holes in the valence band. These electron-hole pairs can initiate redox reactions with adsorbed substances on the TiO<sub>2</sub> surface. However, TiO<sub>2</sub> is primarily activated by ultraviolet (UV) light, which constitutes only a small fraction of the solar spectrum. This limitation has spurred the search for new materials that can utilize visible light, which is more abundant. Recent advancements have introduced conjugated polymers and other novel materials that exhibit enhanced visible light absorption and catalytic activity.

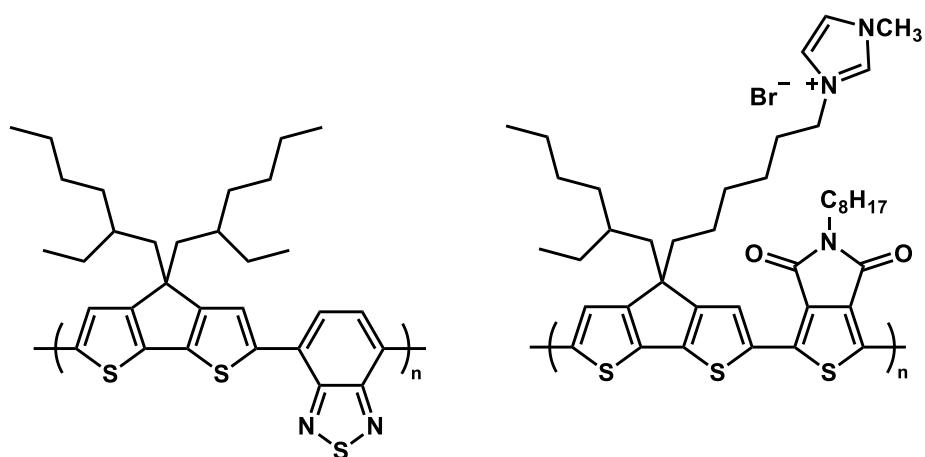
Conjugated polymers have gained significant attention since their discovery in 2001.<sup>12</sup> Conjugated polymers are unique among all polymers due to their backbone, which is comprised of alternating double and single bonds. Since the electrons in these extended  $\pi$ -conjugated systems delocalize along several monomer units, these materials can be considered intrinsic semiconductors. This is the reason that a lot of research is being done to create these materials so they can be used in applications that presently use standard semiconductors. In contrast to traditional inorganic semiconductors, which are only available in Si, Ge, and Group III-V and Group II-VI alloys, conjugated polymers have an infinite number of accessible chemical structures, good mechanical strength, and ease of processing (Figure B).<sup>13</sup> Therefore, it could be able to chemically modify conjugated polymers to change their characteristics.



**Figure B** Four common types of conjugated polymers

Conjugated polymers have shown promising photocatalytic properties. These materials exhibit unique properties due to their conjugated structure, which allows for efficient light absorption and electron transport. Previous studies have demonstrated that these materials can generate reactive oxygen species under visible light, making them suitable for photocatalytic applications. For instance, Mukhta et al. reported that conjugated polymers could effectively absorb visible light and generate hydroxyl radicals, which induce various oxidative reactions.<sup>14</sup> Dong et al. further highlighted the potential of these polymers in photocatalysis, demonstrating their efficiency in producing phenols from arylboronic acids under mild conditions.<sup>15</sup>

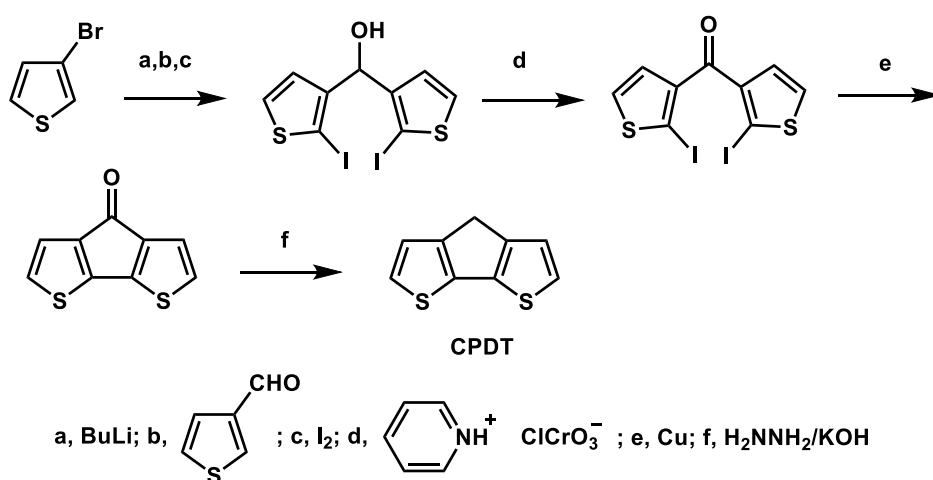
We are interested in conjugated polymer composed of 4H-cyclopenta[2,1-b:3,4-b']dithiophene, cyclopentadithiophene (CPDT) as a new type of photocatalyst. Some CPDT-based polymers were reported to be good candidates as solar cell materials,<sup>16,17</sup> meaning that CPDT-based polymers can absorb sunlight efficiently.



**Figure C** Examples of CPDT-based polymers for solar cell



Figure D shows the synthetic pathway to prepare CPDT. 2-Bromothiophene is lithiated with *n*-butyllithium, followed by reaction with thiophene-2-carbaldehyde and iodine to form bis(2-iodo-3-thienyl)methanol, which is oxidized to bis(2-iodo-3-thienyl)ketone using pyridinium chlorochromate (PCC). The bis(2-iodo-3-thienyl)ketone undergoes cyclization, followed by reduction to yield CPDT.<sup>18</sup> This process effectively synthesizes a CPDT core structure, which is valuable for creating advanced conjugated polymers used in photocatalyst applications.



**Figure D** Synthetic pathway to prepare CPDT

The main motivation for the development of photocatalyst based on CPDT versatile building block for organic electronic materials due to its enhanced photophysical properties, high charge carrier mobility, chemical tunability, and environmental stability.<sup>19</sup> Physically, it has a planar structure, strong optical absorption, thermal stability and variable crystallinity.<sup>20</sup> Chemically, it exhibits aromaticity, can be modified with various substituents, has adjustable solubility, and reactive sites for further functionalization.<sup>21-22</sup> These characteristics make CPDT and its derivatives highly suitable for applications in photocatalysis applications. The purpose of this thesis is to develop novel CPDT-based polymers as photocatalysts, focusing on their ability to harnessing solar energy to drive chemical reactions, offering sustainable solutions for energy and environmental challenges.

## References

1. Y. Paz, *Photocatalysis: Fundamentals and Perspectives*. **2019**, 80-109.
2. M. Kazuhiko, *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*. **2011**, *12*, 237-268.
3. A. Fujishima & K. Honda, *Nature*. **1972**, *238*, 37-38.
4. M. R. Hoffmann, et al. *Chemical Reviews*. **1995**, *95*, 69-96.
5. Y. Zhang, W. Zhang, W. Huang, M. Zhang, *Journal of Environmental Chemical Engineering*. **2014**, *2*, 1041-1048.
6. C. H. Ao, S. C. Lee, J. C. Yu, J. H. Xu, *Applied Catalysis B: Environmental*. **2004**, *54*, 41-50.
7. X. Chen, S. S. Mao, *Chemical Reviews*. **2007**, *107*, 2891-2959.
8. X. Wang, Q. Xu, J. Li, S. Shen, X. Wang, Y. Wang, X. Wang, *Nature Materials*. **2009**, *8*, 76-80.
9. H. Kisch, *Semiconductor Photocatalysis: Principles and Applications*. **2015**, 264.
10. D. S. Bhatkhande, V. G. Pangarkar, A. A. Beenackers, *Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental & Clean Technology*. **2002**, *77*, 102-116.
11. X. Chen, J. Li, M. Grätzel, R. Kostecki, S. S. Mao, *Chemical Society Reviews*. **2012**, *41*, 7909-7937.
12. H. S. Nalwa, *Conducting Polymers and Polymer Electrolytes*. Academic Press. **2001**, 8.
13. T. A. Skotheim, J. R. Reynolds, *Conjugated Polymers: Theory, Synthesis, Properties, and Characterization*. **2006**, *3*, 1-22.
14. B. Mukhta, G. Madras, T. N. G. Row, U. Scherf, S. Patil, *J. Phys. Chem. B*. **2007**, *111*, 7994–7998.

15. X. Dong, H. Huimin, F. Zhang, X. Lang, *Applied Catalyst B: Environmental*. **2022**, 309, 121210.
16. J. You, L. Dou, K. Yoshimura, T. Kato, K. Ohya, T. Moriarty, K. Emery, C.-C. Chen, J. Gao, G. Li, Y. Yang, *Nature Communications* **2013**, 4, 1466.
17. J. Brebels, J. Kesters, M. Defour, G. Pirotte, B. Van Mele, J. Manca, L. Lutsen, D. Vanderzande, W. Maes, *Polymer* **2018**, 137, 303.
18. P. Coppo, M. L. Turner, *J. Mater. Chem.* **2005**, 15, 1123-1133.
19. M. Horie, L. A. Majewski, M. J. Fearn, C. Y. Yu, Y. Luo, A. Song, B. R. Saunders, M. L. Turner, *Journal of Materials Chemistry*. **2010**, 20, 4347-4355.
20. Y. Wang, H. Li, *Journal of Materials Chemistry A*. **2022**, 10, 2137-2150.
21. S. Kim, J. Park, *Advanced Functional Materials*. **2020**, 30, 2003435.
22. T. T. Nguyen, T. Phan, *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*. **2019**, 41, 100317.

## Chapter 1

### Synthesis and Photocatalytic Activity of Poly(4,4'-(((4H-cyclopenta[2,1-b:3,4-b']dithiophene-4,4-diyl)bis(ethane-2,1-diyl))bis(oxy))bis(4-oxobutanoic acid)) (PCPDT-CO<sub>2</sub>H)

#### 1.1 Abstract

Conjugated polymers have garnered substantial interest in the field of photocatalysis owing to their unique electronic structures, facile synthesis routes and tunable properties. In this study, a novel  $\pi$ -conjugated polymer based on cyclopentadithiophene (CPDT) and poly(4,4'-(((4H-cyclopenta[2,1-b:3,4-b']dithiophene-4,4-diyl)bis(ethane-2,1-diyl))bis(oxy))bis(4-oxobutanoic acid)) (PCPDT-CO<sub>2</sub>H), was prepared as a sparingly soluble material. The generation of hydroxyl radicals from PCPDT-CO<sub>2</sub>H in water was confirmed by using coumarin as a hydroxyl radical indicator. Furthermore, PCPDT-CO<sub>2</sub>H was found to catalyze the oxidative hydroxylation of arylboronic acid and the oxidation of benzaldehyde, indicating that PCPDT-CO<sub>2</sub>H can be a promising candidate for metal-free and 100% organic heterogeneous photocatalysts. Overall, this study highlights the synthesis and characterization of a novel PCPDT-CO<sub>2</sub>H and elucidates its exceptional photocatalytic performance. The findings underscore the potential of PCPDT-CO<sub>2</sub>H as a versatile and efficient photocatalyst for environmental remediation, water purification and solar energy conversion applications. Further research endeavors may focus on optimizing the synthesis conditions, exploring additional photocatalytic reactions and integrating PCPDT-CO<sub>2</sub>H into practical devices for real-world applications.

## 1.2 Introduction

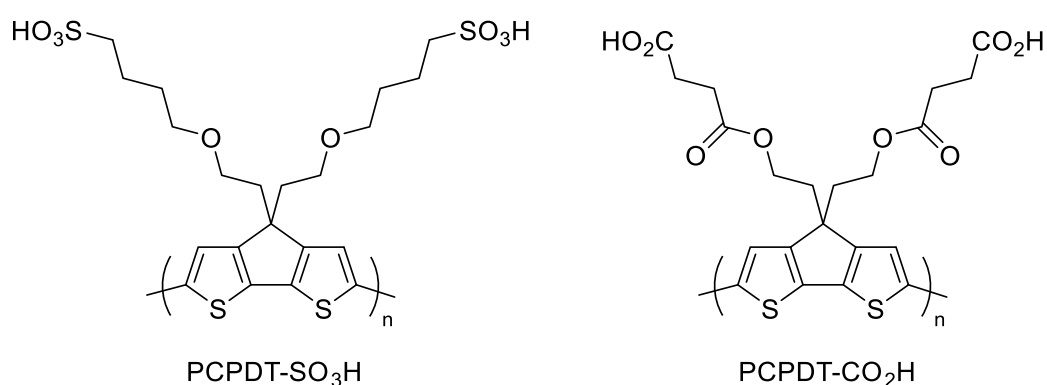
Photocatalysts are highly effective materials that can quickly alter solar energy for various uses. The key characteristic of a photocatalyst is its ability to start and speed up chemical reactions by absorbing photons, without undergoing any long-term changes. For many applications, especially those involving the environment and energy, this characteristic is necessary. The most practical and commonly used photocatalyst is titanium dioxide ( $\text{TiO}_2$ ), due to its chemical stability, abundance, non-toxicity and cost-effectiveness.  $\text{TiO}_2$  and other semiconductor photocatalysts have undergone substantial research for the oxidation of contaminants in water and air.<sup>1-5</sup> Other applications of photocatalysts include solar energy conversion<sup>6-11</sup> and organic synthesis.<sup>12-18</sup> However,  $\text{TiO}_2$  has the disadvantage of not being able to absorb visible light; it can only use ultraviolet (UV) light when exposed to sunlight.  $\text{TiO}_2$  has a relatively wide bandgap, typically around 3.2 to 3.4 electron volts (eV), which limits its electromagnetic spectrum absorption to the UV region.<sup>19,20</sup> This is a significant limitation of the material for practical use.  $\text{TiO}_2$  has a very low solar energy usage efficiency because the proportion of UV radiation to sunlight is only 3–5%. As a result, the research on photocatalysts is focused on the impregnation of  $\text{TiO}_2$  with the ability to respond to visible light and the development of methods that effectively convert visible light into usable energy.<sup>21-24</sup> Numerous modifications, such as ion doping, nano-structuring, and heterojunction construction, have been researched to enhance the photocatalytic capabilities of  $\text{TiO}_2$ .<sup>25,26</sup>

Currently,  $\pi$ -conjugated materials have attracted considerable scientific interest as organic heterogeneous photocatalysts. This is primarily due to their distinctive characteristics and remarkable capacity to effectively capture visible light. The effective visible light absorption is contributed by the extended electron conjugation along the molecular structures of  $\pi$ -conjugated materials. Another attractive characteristic of  $\pi$ -conjugated materials is its tunable properties. By altering the chemical structures of  $\pi$ -conjugated materials, researchers may

precisely control their tunable properties. This tunability allows optimization of their photocatalytic activity for various applications. Representative examples of  $\pi$ -conjugated materials include graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>)<sup>27-29</sup> and conjugated microporous polymers (CMPs).<sup>30-32</sup> These materials are new classes of metal-free catalysts based on earth-abundant carbon materials. A study by Han et al. explores the selection of electron donor for CMP to construct a high-performance polymer catalyst. The researchers discovered that the photocatalytic activity of the resulting polymers is greatly influenced by the geometry of the electron donor. An efficient electron donor for CMP promotes a better charges transmission and light-induced electron/hole separation.<sup>33</sup> CMPs are characterized by a highly conjugated structure, where alternating single and multiple bonds create delocalized  $\pi$ -electron systems. Their versatility, tunability, and ability to generate reactive intermediates make them valuable tools in the field of photocatalysis, contributing to advancements in renewable energy, environmental sustainability, and green chemistry practices.<sup>30-33</sup>

As mentioned above, photocatalysts, starting with titanium dioxide, are being developed into materials with higher performance and environmental compatibility, such as visible light responsive and metal-free types. The design of photocatalysts for wide-range light collection from ultraviolet to NIR regions is an efficient way to accomplish the practical use of photocatalysis since solar light contains around 50% near-infrared (NIR) light. The full utilization of sunlight is valuable in terms of efficient use of energy, and furthermore, near-infrared rays are highly permeable, making them convenient for use as an environmental remediation material. The study of NIR-responsive materials has so far focused on sensitization using NIR-responsive substances including dye molecules and black phosphorus, the surface plasmon resonance effect, up-conversion, and materials with narrow band gaps that act as NIR harvesters.<sup>34-36</sup>

The interest is in 4H-cyclopenta[2,1-b:3,4-b']dithiophene (CPDT)-based self-doped intrinsically conducting polymer as a new candidate for NIR harvesting material because Zotti et al. carried out anodic coupling polymerization of CPDT-based monomers to find that the resulting polymers showed a large absorption at NIR light region.<sup>37-38</sup> Recently, a novel self-doped conducting polymer based on CPDT, poly(4,4'-(((4H-cyclopenta[2,1-b:3,4-b']dithiophene-4,4-diyl)bis(ethane-2,1-diyl))bis(oxy)) bis(butane-1-sulfonic acid)) (PCPDT-SO<sub>3</sub>H)<sup>38</sup> was synthesized. It was found that PCPDT-SO<sub>3</sub>H exhibited a large absorption above 800 nm, which is characteristic for the oxidized conducting state of polythiophenes.<sup>36,38,40</sup> Although PCPDT-SO<sub>3</sub>H may be a potent candidate as a photocatalyst for NIR harvesting, it is difficult to use PCPDT-SO<sub>3</sub>H as a heterogeneous photocatalyst due to its high solubility in water. The idea is to decrease the solubilities is to introduce carboxyl functionalities onto the side chain of the  $\pi$ -conjugated main chain. McCullough et al. reported that poly(3-(2-carboxyethyl)thiophene) exhibits low solubilities in conventional organic solvents.<sup>41</sup> The preparation of poly(4,4'-(((4H-cyclopenta[2,1-b:3,4-b']dithiophene-4,4-diyl)bis(ethane-2,1-diyl))bis(oxy))bis(4-oxobutanoic acid)) (PCPDT-CO<sub>2</sub>H, Figure 1) was reported as a sparingly soluble material. Further, photocatalytic activities of PCPDT-CO<sub>2</sub>H were examined.



**Figure 1.1** Chemical structure of PCPDT-SO<sub>3</sub>H and PCPDT-CO<sub>2</sub>H.

### 1.3 Experimental

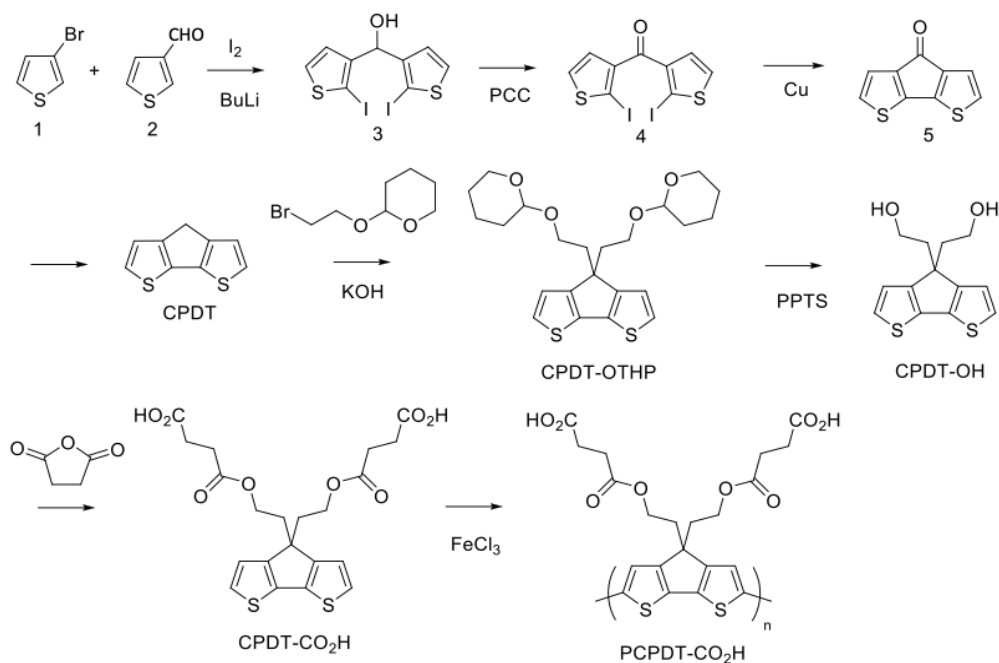
#### *Materials*

2-(2-Bromoethoxy)tetrahydro-2H-pyran and pyridinium p-toluenesulfonate (PPTS) were purchased from Tokyo Chemical Industry. All other reagents were obtained from a commercial source and utilized exactly as it was intended.

#### *Preparation of PCPDT-CO<sub>2</sub>H*

Figure 1.2 shows the synthetic pathway of PCPDT-CO<sub>2</sub>H. The key compound is CPDT. There are some reports regarding preparation of CPDT. We synthesized CPDT by modifying the procedure reported by Pal et al. In order to introduce carboxyl functionalities on the side chains of CPDT, we synthesized CPDT-OTHP that carries hydroxyl functionality masked as the 2-tetrahydropyranyl ether (THP group). This is because THP group is stable under alkaline conditions. After deprotection of THP group, the monomer, CPDT-CO<sub>2</sub>H was prepared by the reaction of CPDT-OH with succinic anhydride. The specific conditions and purification steps may vary based on the synthesis route, but this general procedure outlines the key steps involved in preparing PCPDT-CO<sub>2</sub>H.





**Figure 1.2** Synthetic pathway of PCPDT-CO<sub>2</sub>H.

#### *Preparation of Bis(2-iodo-3-thienyl)methanol (3)*

A 50 mL dry ether was infused with 6.52 g of 3-bromothiophene containing 40.0 mmol. Then it was moved to a low temperature thermostat with a magnetic stirrer and a nitrogen environment set at -78 °C. Using a syringe, 15.0 mL (40.0 mmol) of 2.65 M *n*-butyllithium (*n*-BuLi) was added, and it was stirred for 3 h. A mixture of 4.48 g (40.0 mmol) of 3-thiophenecarbaldehyde with 40 mL of dry ether was added and the mixture was stirred at room temperature for 1 h. The temperature was then decreased to -78 °C and maintained there for almost 12 h. After that, 2.65 M *n*-BuLi was added in 30 mL (80.0 mmol) and stirred for 2 h. The mixture warmed to room temperature after 2 h. It was then stirred for a further hour. A solution containing 32.0 g (126 mmol) of iodine was introduced into a reaction mixture consisting of 200 mL of anhydrous ether. The combination was allowed to react undisturbed for a duration of 16 h. Following the completion of the reaction, the mixture was subjected to extraction using ether. The organic layer underwent two washes with distilled water and three

washes with an aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  solution. Subsequently, the substance was subjected to desiccation using anhydrous magnesium sulphate, followed by the removal of the solvent through the application of reduced pressure. Evaporation gave a brown solid. By loosening and washing with carbon tetrachloride ( $\text{CCl}_4$ ) it becomes a light brown solid. Bis(2-iodo-3-thienyl)methanol was obtained with mass of 8.617g (48.14% of percent yield) and characterized by using NMR and FTIR.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.43 (d,  $J = 6.0$  Hz, 2H), 6.97 (d,  $J = 6.0$  Hz, 2H), 5.76 (s, 1H), 2.26 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 146.8, 131.5, 127.0, 76.84, 71.84; IR (NaCl,  $\text{cm}^{-1}$ ): 3349, 3098, 698, 649.

#### *Preparation of Bis(2-iodo-3-thienyl)ketone (4)*

Under a nitrogen atmosphere, 5.22 g (11.7 mmol) of Bis(2-iodo-3-thienyl) methanol was added to 10 mL of dichloromethane, the mixture was stirred for a while. Then, 3.77 g (17.5 mmol) of chlorochromate (PCC) was added, the mixture was stirred at room temperature for 12 h. After the reaction completed, the mixture was separated into its individual parts using a silica gel column with dichloromethane as the eluent. Bis(2-iodo-3-thienyl)ketone was obtained in a brown solid form with a mass of 6.813g. The percent yield was calculated as 79.6%. The product obtained was characterized by using NMR and FTIR.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.46 (d,  $J = 5.5$  Hz, 2H), 7.04 (d,  $J = 6.0$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 185.7, 143.3, 131.7, 129.9, 81.4; IR (NaCl,  $\text{cm}^{-1}$ ): 3102, 1652, 728, 699.

#### *Preparation of 4H-Cyclopenta[2,1-b:3,4-b']dithiophen-4-one (5)*

4.57 g (10.2 mmol) of Bis(2-iodo-3-thienyl) ketone was added to 32 mL of dimethylformamide (DMF) and the mixture was stirred for a while. Then, 2.0 g (31.2 mmol) of copper powder was added and heated to reflux at 160 °C for 4 h. The reaction was conducted under a nitrogen atmosphere. After the reaction time completed, the solid was removed using celite. Ether was

added to the filtrate and it was washed with distilled water. Anhydrous magnesium sulfate was used to remove remaining water. The solvent was then distilled off under pressure using evaporator. 4H-Cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one was obtained in a reddish purple solid. The mass of product was 2.5866g with percent yield of 88.4%. The product obtained was characterized by using NMR and FTIR. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.03 (d, *J* = 5.5 Hz, 2H), 6.98 (d, *J* = 6.0 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 182.8, 149.3, 142.5, 127.2, 121.8; IR (NaCl, cm<sup>-1</sup>): 3104, 3074, 1699, 691.

#### *Preparation of 4H-Cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CPDT)*

1.75 g (9.1 mmol) of Cyclopenta [2,1-*b*:3,4-*b'*] dithiophen-4-one was added to a mixture of 38 mL ethylene glycol, 1.75 g (31.1 mmol) of potassium hydroxide and 1.56 g (31.1 mmol) hydrazine hydrate. It was then reflux at 180 °C for 24 h under a nitrogen atmosphere. After the completion of reaction time, the temperature was allowed to decrease to room temperature. The desired components were extracted with dichloromethane and washed with water, saturated sodium chloride (*aq.*) and saturated ammonium chloride (*aq.*). Anhydrous magnesium sulfate was used to remove remaining water. The extracted solvent was put under a reduced pressure using evaporator. A brown solid was obtained. The solid was then further purified using silica gel column with hexane as eluent. The CPDT was obtained in a white solid with mass of 1.2600g and 52.3% yield. The product obtained was characterized by using NMR and FTIR. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ): 7.18 (d, *J* = 5.5 Hz, 2H), 7.08 (d, *J* = 6.0 Hz, 2H), 3.53 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ ): 149.7, 138.5, 124.5, 123.0, 31.9; IR (NaCl, cm<sup>-1</sup>): 3089, 687.

*Preparation of 2,2'-(((4H-cyclopenta[2,1-b:3,4-b']dithiophene-4,4-diyl)bis(ethane-2,1-diyl))bis(oxy)) bis(tetrahydro-2H-pyran) (CPDT-OTHP)*

Finely crushed potassium hydroxide (1.0 g) was added to a solution containing CPDT (1.0 g, 5.6 mmol), 2-(2-bromoethoxy)tetrahydro-2H-pyran (2.4 g, 11.2 mmol), and potassium iodide (20 mg) in dimethyl sulfoxide (DMSO) (20 mL). The resulting mixture was stirred for 24 h at room temperature. Dichloromethane was used to extract the reaction mixture after it had been placed into water. After being dried over anhydrous magnesium sulfate, the organic layer was washed with water and placed under reduced pressure to remove the solvent. The product obtained was 0.65g with percent yield of 60.7%. A silica gel column was used to charge the residue, and the eluent used was a mixture of hexane and ethyl acetate (4:1 v/v). In the first band, 2.2 g (90%) of CPDT-OTHP was obtained as a light yellow oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 7.16 (d, *J* = 5.8 Hz, 2H), 6.98 (d, *J* = 5.8 Hz, 2H), 4.26 (t, *J* = 5.9 Hz, 2H), 3.7-2.9 (m, 8H), 2.25 (d, *J* = 7.3 Hz, 4H), 1.8-1.3 (m, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ): 156.5, 136.6, 124.8, 121.7, 98.8, 63.9, 61.6, 49.3, 37.7, 30.4, 25.2, 19.2; IR (NaCl, cm<sup>-1</sup>): 2939, 1120, 1076, 1031, 669; Anal. calcd. for C<sub>23</sub>H<sub>30</sub>O<sub>4</sub>S<sub>2</sub>: C 63.56, H 6.96; found: C 63.39, H 7.06.

*Preparation of 2,2'-(4H-cyclopenta[2,1-b:3,4-b']dithiophene-4,4-diyl)bis(ethan-1-ol) (CPDT-OH)*

PPTS (0.4 g, 1.6 mmol) was added to a solution of CPDT-OTHP (2.0 g, 4.6 mmol) in 40 mL of ethanol, and the mixture was stirred for 5 h at 60 °C. Diethyl ether was used to extract the reaction mixture after it had been placed into water. After being dried over anhydrous magnesium sulfate, the organic layer was washed with water and placed under reduced pressure to remove the solvent. Ethyl acetate was used as the eluent and the residue was charged onto a silica gel column. A white solid weighing 1.0 g (79%) of CPDT-OH was obtained from the first band; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ): 7.32 (d, *J* = 5.2 Hz, 2H), 7.07 (d, *J* = 5.2 Hz, 2H),

3.12 (t,  $J = 6.8$  Hz, 4H), 2.24 (t,  $J = 6.8$  Hz, 4H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 158.0, 137.6, 126.5, 122.6, 59.3, 50.5, 41.4; IR (KBr,  $\text{cm}^{-1}$ ): 3273, 2902, 1451, 1043, 676; Anal. calcd. for  $\text{C}_{13}\text{H}_{14}\text{O}_2\text{S}_2$ : C 58.62, H 5.30; found: C 58.79, H 5.16.

*Preparation of 4,4'-(((4H-cyclopenta[2,1-b:3,4-b']dithiophene-4,4-diyl)bis(ethane-2,1-diyl))bis(oxy)) bis(4-oxobutanoic acid) (CPDT-CO<sub>2</sub>H)*

A mixture of 2,2'-(4H-cyclopenta[2,1-b:3,4-b']dithiophene-4,4-diyl)bis(ethan-1-ol) (CPDT-OH) (0.25 g, 0.94 mmol), succinic anhydride (0.19 g, 1.9 mmol), 4-dimethylaminopyridine (DMAP) (0.23 g, 1.9 mmol), and tetrahydrofuran (THF) (20 mL) was heated under reflux for 48 h. The reaction mixture was added to diluted hydrochloric acid and extracted with ethyl acetate. Anhydrous magnesium sulfate was used to dry the organic layer and the solvent was removed by placing it under reduced pressure. Ethyl acetate was used as the eluent while charging the residue onto a silica gel column. The first band was collected to give 0.44 g (quant) of CPDT-CO<sub>2</sub>H as a viscous green oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.19 (d,  $J = 5.5$  Hz, 2H), 6.99 (d,  $J = 5.5$  Hz, 2H), 3.75 (t,  $J = 6.8$  Hz, 4H), 2.58 (m, 4H), 2.46 (m, 4H), 2.25 (t,  $J = 6.8$  Hz, 4H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 177.7, 177.1, 155.3, 137.3, 125.8, 121.4, 61.7, 49.3, 36.4, 28.9, 28.8; IR (NaCl,  $\text{cm}^{-1}$ ): 2930, 1716; Anal. calcd. for  $\text{C}_{21}\text{H}_{22}\text{O}_8\text{S}_2$ : C 54.07, H 4.75; found: C 54.28, H 4.91.

*Preparation of Poly(4,4'-(((4H-cyclopenta[2,1-b:3,4-b']dithiophene-4,4-diyl)bis(ethane-2,1-diyl))bis(oxy))bis(4-oxobutanoic acid)) (PCPDT-CO<sub>2</sub>H)*

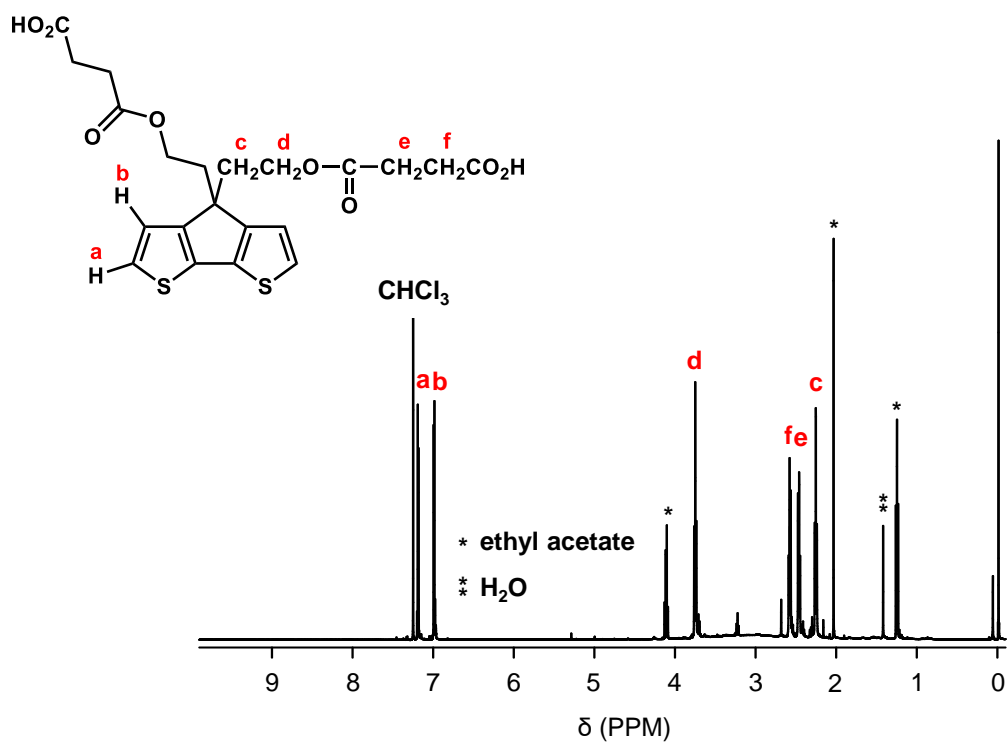
A mixture of CPDT-CO<sub>2</sub>H (0.61 g, 1.3 mmol),  $\text{FeCl}_3$  (5.2 mmol), and chloroform (20 mL) was stirred under nitrogen for 24 h. The reaction mixture was poured into methanol (120 mL) containing a few drops of hydrazine monohydrate. The precipitated polymer was purified by Soxhlet extraction using methanol as a solvent to obtain PCPDT-CO<sub>2</sub>H (0.43 g, 70%) as a black solid with metallic luster.

### *Measurements*

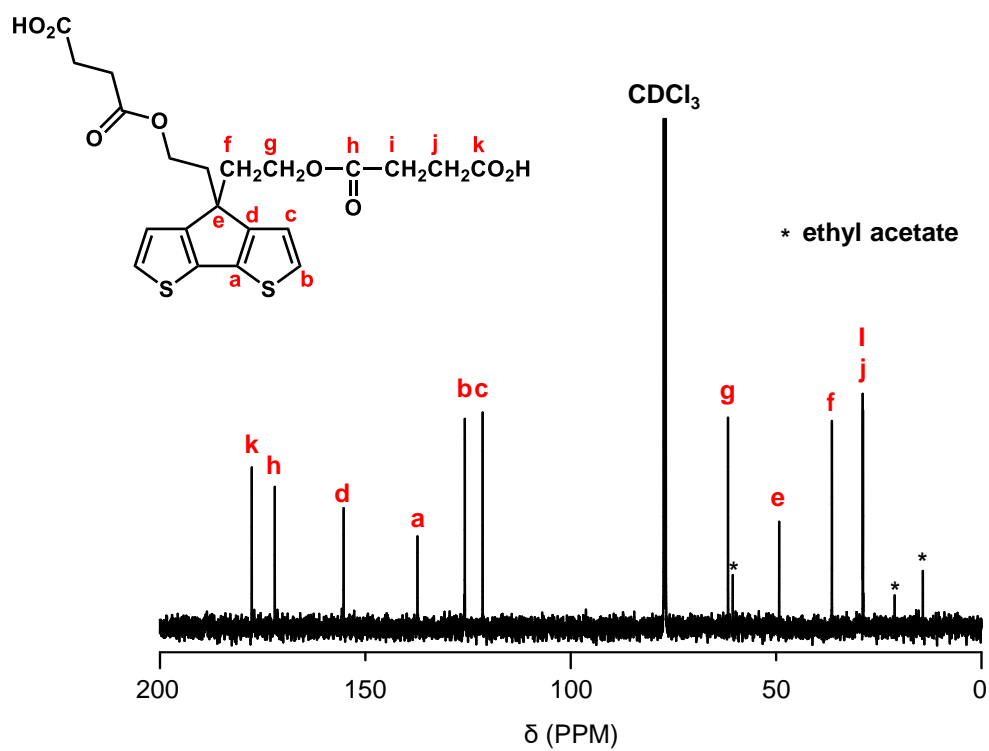
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on a JEOL ECZ500R nuclear magnetic resonance spectrometer. The analysis was conducted at room temperature. The samples were dissolved in  $\text{CDCl}_3$ , with tetramethylsilane (TMS) serving as the internal standard. On the other hand, photoluminescence spectra were recorded on a HAMAMATSU Multi Channel Analyzer PMA-11. The analysis was conducted at the exciting wavelength of 365 nm. Furthermore, infrared spectra were recorded on a JASCO FT/IR-4100 and UV-vis-NIR spectra was analyzed using V-770. Elemental analysis was carried out using YANACO CHN-corder MT-5.

### **1.4 Results and Discussion**

The structure of CPDT- $\text{CO}_2\text{H}$  was confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, as shown in Figure 1.3 and Figure 1.4, respectively. The existence and connectivity of individual functional groups as well as the overall chemical structure of the monomer can be confirmed by comparing the experimental NMR spectra with the expected spectra based on the suggested chemical structure of CPDT- $\text{CO}_2\text{H}$ .



**Figure 1.3**  $^1\text{H}$  NMR spectrum of CPDT- $\text{CO}_2\text{H}$  in  $\text{CDCl}_3$ .

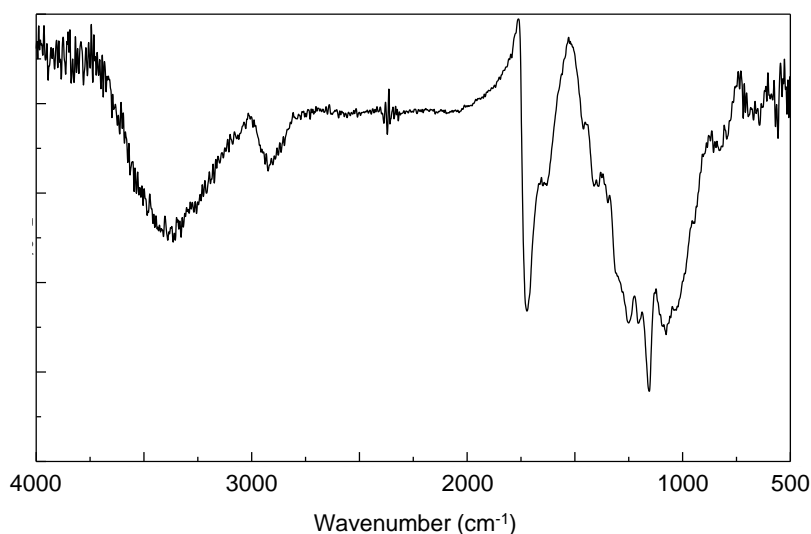


**Figure 1.4**  $^{13}\text{C}$  NMR spectrum of CPDT- $\text{CO}_2\text{H}$  in  $\text{CDCl}_3$ .

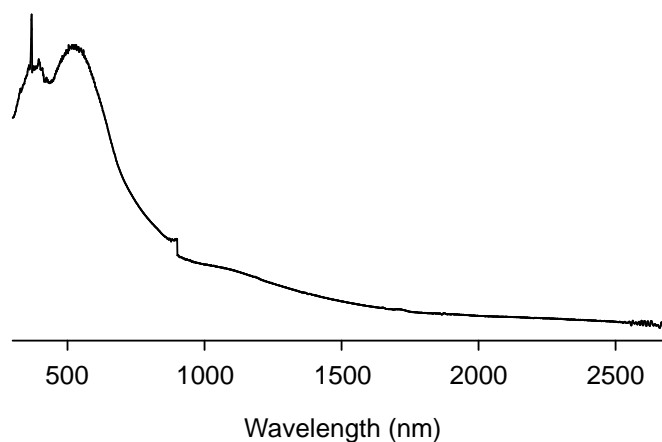
The obtained CPDT-CO<sub>2</sub>H was polymerized in chloroform by oxidative polymerization using FeCl<sub>3</sub> as an oxidant. It is a common strategy for synthesizing certain conjugated polymers through oxidative polymerization.<sup>43,44</sup> This approach is often referred to as chemical oxidative polymerization or oxidative coupling. Oxidative polymerization is a well-established method for the synthesis of conjugated polymers with  $\pi$ -conjugated backbones. It allows for the efficient coupling of monomers to form extended conjugated systems. This method can lead to the formation of high-molecular-weight polymers with desirable properties for applications in organic electronics, photovoltaics, and other fields. The choice of chloroform and FeCl<sub>3</sub> in oxidative polymerization offers good control over the reaction conditions and polymerization process, leading to consistent and reproducible results. The resulting polymer, PCPDT-CO<sub>2</sub>H, was purified by Soxhlet extraction using methanol as the solvent. PCPDT-CO<sub>2</sub>H was obtained as a black solid with metallic luster, a typical physical appearance of self-doped conducting polymers. Figure 1.5 shows the IR spectrum of PCPDT-CO<sub>2</sub>H. The broad OH-band in the region from 3700 to 3100 cm<sup>-1</sup> is due to carboxyl functionalities. The C-H stretching vibrations of methylene moiety are observed around 2920 cm<sup>-1</sup>. The peaks at 1720 and 1630 cm<sup>-1</sup> are due to the C=O stretching of ester and carboxylate, respectively. PCPDT-CO<sub>2</sub>H was partially soluble in THF, but insoluble in hexane, chloroform, acetonitrile, methanol, *N,N*-dimethylformamide (DMF), and water. Therefore, PCPDT-CO<sub>2</sub>H is suitable material for heterogeneous photocatalyst for organic synthesis. Figure 1.6 shows the UV-vis-NIR spectrum of PCPDT-CO<sub>2</sub>H in the solid state. Sharp absorption at around 350 nm is probably due to source changeover between tungsten lamp (visible region) and deuterium discharge lamp (ultraviolet region). The spectrum exhibited a broad continuous absorption from 400 to 800 nm. The optical bandgap was determined to be 1.7 eV. Unlike PCPDT-SO<sub>3</sub>H, PCDT-CO<sub>2</sub>H did not exhibit a large absorption in NIR region. This is probably due to the weaker acidity of



CO<sub>2</sub>H than SO<sub>3</sub>H. Therefore, we examined photocatalytic activities of CPDT-CO<sub>2</sub>H under visible light irradiation conditions.



**Figure 1.5** IR spectrum of PCPDT-CO<sub>2</sub>H.



**Figure 1.6** Solid-state UV-vis-NIR absorption spectrum of PCPDT-CO<sub>2</sub>H.

### *Generation of hydroxyl radical*

The detection of hydroxyl radicals was carried out to better understand and keep track of chemical processes. Coumarin is a commonly used probe for the detection of hydroxyl radicals in heterogeneous photocatalytic reactions.<sup>45</sup> The use of coumarin is based on the ability to undergo a reaction with hydroxyl radicals, leading to the formation of a fluorescent product.

This fluorescence change can be monitored spectroscopically which allows the study of presence and activity of hydroxyl radicals in photocatalytic systems. The hydroxy radical reacts with coumarin to give umbelliferone, which was used to detect hydroxyl radical by fluorometry. In this work, 0.4 mM coumarin aqueous solution was photo-irradiated in the presence of PCPDT-CO<sub>2</sub>H. The reaction mixture was filtered to remove PCPDT-CO<sub>2</sub>H, and the filtrate was investigated by PL spectrum. Figure 1.7 shows the PL spectra of the coumarin solution before and after photoirradiation. A sharp emission at 365 nm is from UV-LED as an excitation light source. The observed spectra were normalized using this emission at 365 nm. After irradiation, emission at 450 nm was observed, and this emission is coming from umbelliferone, suggesting that hydroxyl radicals were generated when visible light was irradiated. PCPDT-CO<sub>2</sub>H was served as the photocatalyst in the system. PCPDT-CO<sub>2</sub>H absorbs photons from the visible light, creating electron-hole pairs within the material. This absorption of photons is what allows the photocatalyst to become activated. Once activated, PCPDT-CO<sub>2</sub>H can participate in redox reactions. It can transfer electrons from the excited state to nearby molecules or species to generate hydroxyl radicals. The hydroxyl radicals generated by PCPDT-CO<sub>2</sub>H are now available to react with coumarin and produces umbelliferone. This finding shows that PCPDT-CO<sub>2</sub>H can effectively serve as a photocatalyst for harnessing the energy of visible photons to drive chemical reactions.

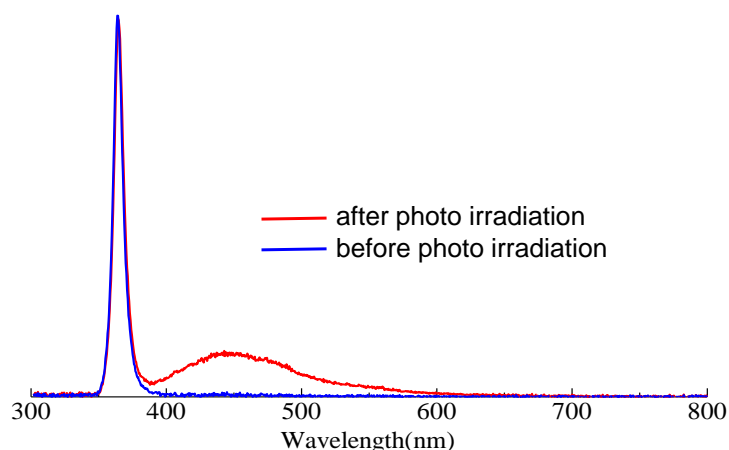
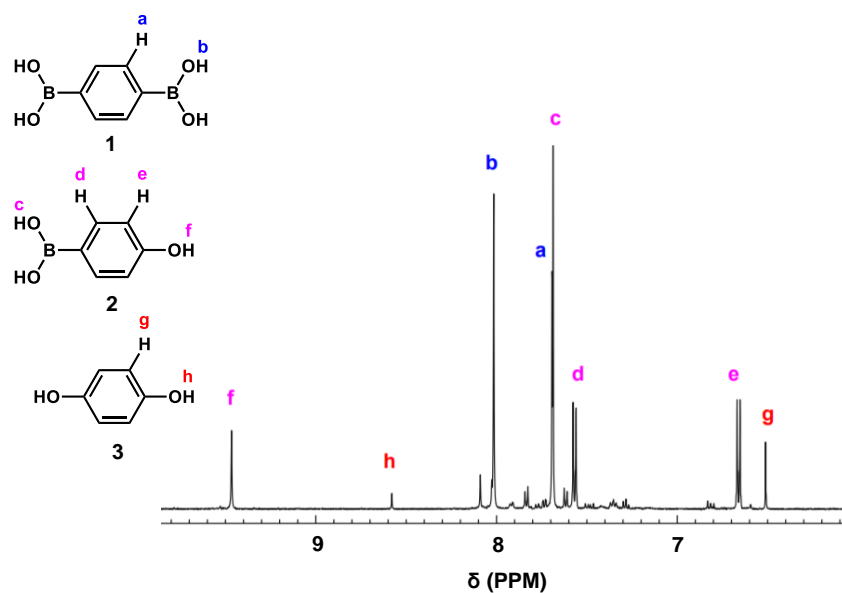


Figure 1.7 PL spectra of aqueous coumarin solution of (blue line) before and (red line) after photo irradiation ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ).

#### *Oxidative Hydroxylation of 1,4-Phenylenediboronic Acid*

Luo et al.<sup>46</sup> and Wang et al.<sup>47</sup> reported that conjugated microporous polymer (CMP) could serve as a reusable and efficient visible light heterogeneous photocatalyst for oxidative hydroxylation of arylboronic acids using molecular oxygen as a green oxidant. Therefore, the photocatalytic activity of PCPDT-CO<sub>2</sub>H in photocatalytic oxidative hydroxylation of arylboronic acid under visible light irradiation were examined. The photocatalytic oxidative hydroxylation of 1,4-phenylenediboronic acid (**1**) was chosen as the model reaction. The boronic acid (**1**) undergoes a hydroxylation reaction to give 4-hydroxyphenylboronic acid (**2**), which is finally converted to hydroquinone (**3**). An example of a <sup>1</sup>H NMR spectrum of the reaction products is shown in Figure 1.8 with peak assignments. The reaction mixtures were composed of hydroquinone (**3**), 4-hydroxyphenylboronic acid (**2**), and unreacted 1,4-phenylenediboronic acid (**1**). The percent composition of the reaction products was determined from the integral ratio of peaks a, e and g. We carried out a series of screening and control experiments. Table 1.1 summarizes the

experimental results. It was obvious that CPDT-CO<sub>2</sub>H, triethylamine, oxygen, and light is essential in this oxidative hydroxylation reaction. These experimental results suggest a reaction mechanism similar to the literature,<sup>46</sup> as shown in Figure 1.9. The charge separation occurs when PCPDT-CO<sub>2</sub>H is irradiated by light, some of its electrons are promoted to higher energy levels. This creates electron-hole pairs in the material. Due to the presence of an electron-rich and electron-deficient regions in the PCPDT-CO<sub>2</sub>H material, the excited electrons can become separated from the holes (electron vacancies). In the presence of oxygen (O<sub>2</sub>), the excited electrons can reduce molecular oxygen to form superoxide anions (O<sub>2</sub><sup>•-</sup>). This process occurs because the excited electrons have enough energy to reduce molecular oxygen to superoxide. The generated superoxide anions (O<sub>2</sub><sup>•-</sup>) can act as reactive intermediates and participate in chemical reactions by reacting with boronic acid. On the other hand, triethylamine acts as a reducing agent and converts the boronic acid moiety to a hydroxyl group. The overall sequence of events involves light absorption, charge separation, superoxide anion generation, and subsequent reaction with the boronic acid. This process is typical in photocatalytic reactions, where light energy is harnessed to drive chemical transformations.



**Figure 1.8** An example of <sup>1</sup>H NMR spectrum of the reaction products (entry 1, Table 1).

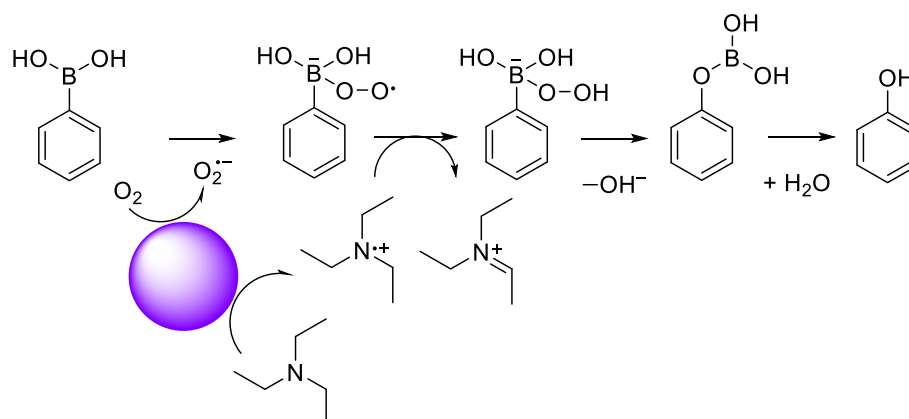
**Table 1.1** Results of Oxidative Hydroxylation of 1,4-Phenylenediboronic acid

entry	Reaction Conditions	Composition (mol%)		
		1	2	3
1	normal <sup>1</sup>	32	58	10
2	w/o PCPDT-CO <sub>2</sub> H	100	0	0
3	in the dark	100	0	0
4	w/o Et <sub>3</sub> N	100	0	0
5	w/o O <sub>2</sub> <sup>2</sup>	95	4	1
6	w/ radical scavenger <sup>3</sup>	97	2	1

<sup>1</sup> **1** = 0.2 mmol; Et<sub>3</sub>N = 0.6 mmol, PCPDT-CO<sub>2</sub>H = 15 mg; DMF = 1 mL; Xe lamp (100 W) = 3 h.

<sup>2</sup> N<sub>2</sub> bubbling.

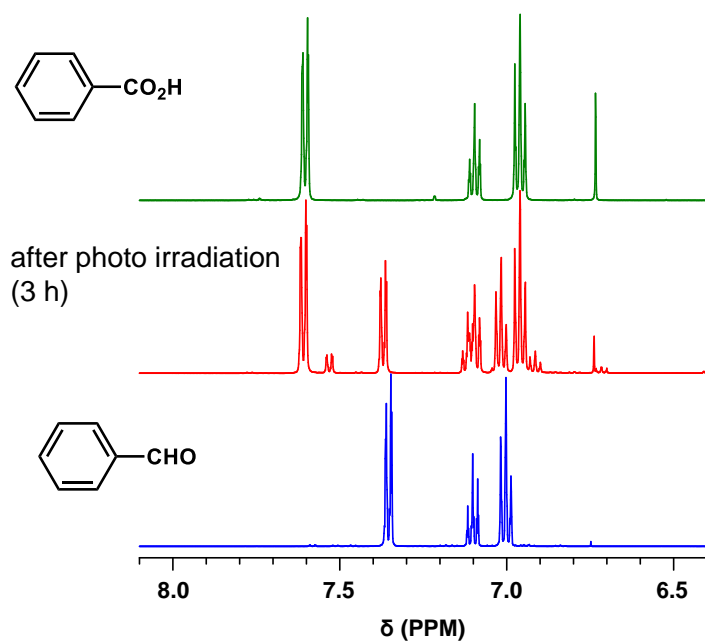
<sup>3</sup> Benzoquinone = 5 mg.

**Figure 1.9** Plausible reaction mechanism for hydroxylation of phenylboronic acid.

### *Oxidation of Benzaldehyde*

PCPDT-CO<sub>2</sub>H can efficiently catalyze the oxidation of benzaldehyde under photoirradiation. PCPDT-CO<sub>2</sub>H was added to a chloroform solution of benzaldehyde. Upon photoirradiation (Xe lamp) of the reaction mixture, the conversion from benzaldehyde to benzoic acid was estimated by <sup>1</sup>H NMR (Figure 1.10). After irradiation of 3 h, the conversion reached 70%. Since benzaldehyde is easily oxidized in the air,<sup>48,49</sup> control experiments were performed.

Under the same irradiation conditions without PCPDT-CO<sub>2</sub>H, the conversion was only 10%. No reaction occurred when PCPDT-CO<sub>2</sub>H was added to the benzaldehyde solution in the dark for 3 h. These experimental results indicated that PCPDT-CO<sub>2</sub>H efficiently catalyzed the oxidation of benzaldehyde under photoirradiation.



**Figure 1.10** <sup>1</sup>H NMR spectra of benzoic acid, benzaldehyde and reaction mixture in CDCl<sub>3</sub>.

## 1.5 Conclusion

The FeCl<sub>3</sub>-based oxidative polymerization of CPDT-CO<sub>2</sub>H was carried out to obtain PCPDT-CO<sub>2</sub>H as a new photocatalyst. It shows a strong, broad absorption in the visible-light region. After photo irradiation of the dispersion of PCPDT-CO<sub>2</sub>H in aqueous coumarin solution, blue emission was observed from the reaction mixtures. The emission comes from umbelliferone, indicating that hydroxyl radicals were generated during photoirradiation. Further, PCPDT-CO<sub>2</sub>H was found to catalyze oxidative hydroxylation of arylboronic acid. Finally, photoirradiation of chloroform solution of benzaldehyde was carried out in the presence of PCPDT-CO<sub>2</sub>H to find that benzaldehyde was oxidized to benzoic acid efficiently. These experiment results indicate that PCPDT-CO<sub>2</sub>H can be a promising candidate for a metal-free 100% organic photocatalyst.

## 1.6 References

1. M. R. Hoffman, S. T. Martin, W. Choi, D. W. Bahnemann, *Chem. Rev.* **1995**, *95*, 69–96.
2. L. Cao, F. Spiess, A. Huang, S. L. Suib, T. N. Obee, S. O. Hay, J. D. Freihaut, *J. Phys. Chem. B* **1999**, *103*, 2912–2917.
3. D. S. Muggli, J. L. Falconer, *J. Catal.* **1999**, *187*, 230–237.
4. F. Soana, M. Strini, L. Cermenati, A. Albini, *J. Chem. Soc., Perkin Trans. 2* **2000**, 699–704.
5. J. Theurich, D. W. Bahnemann, R. Vogel, F. E. Dhamed, G. Alhakimi, I. Rajab, *Res. Chem. Intermed.* **1997**, *23*, 247–274.
6. K. Honda, A. Fujishima, *Nature* **1972**, *238*, 37–38.
7. Z. Zou, J. Ye, K. Sayama, H. Arakawa, *Nature* **2001**, *414*, 625–627.
8. T. Ohno, D. Haga, K. Fujihara, K. Kaizaki, M. Matsumura, *J. Phys. Chem. B* **1997**, *101*, 6415–6419.
9. K. Fujihara, T. Ohno, M. Matsumura, *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 3705–3709.
10. A. J. Bard, M. A.; Fox, *Acc. Chem. Res.* **1995**, *28*, 141–145.
11. T. Tanaka, Y. Furumi, K. Shinohara, A. Tanaka, M. Hara, J. N. Kondo, K. Domen, *Chem. Mater.* **1997**, *9*, 1063–1064.
12. S. Yanagida, Y. Ishimaru, Y. Miyake, T. Shiragami, C. Pac, K. Hashimoto, T. Sakata, *J. Phys. Chem.* **1989**, *93*, 2576–2582.
13. B. Ohtani, J. Kawaguchi, M. Kozawa, S. Nishimoto, T. Inui, K. Izawa, *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1103–1109.



14. L. Cermenati, C. Richter, A. Albini, *Chem. Commun.* **1998**, 805–806.
15. T. Ohno, T. Kigoshi, K. Nakabeya, M. Matsumura, *Chem. Lett.* **1998**, 27, 877–878.
16. T. Ohno, K. Nakabeya, M. Matsumura, *J. Catal.* **1998**, 176, 76–81.
17. J. Jia, T. Ohno, Y. Masaki, M. Matsumura, *Chem. Lett.* **1999**, 28, 963–964.
18. J. Jia, T. Ohno, M. Matsumura, *Chem Lett.* **2000**, 29, 908–909.
19. A. Fujishima, X. Zhang, D. A. Tryk, *Surf. Sci. Rep.* **2008**, 63, 515– 582.
20. D. Robert, S. Malato, *Sci. Total Environ.* **2002**, 291, 85–97.
21. M. Kitano, M. Matsuoka, M. Ueshima, M. Anpo, *Appl. Catal. A: General* **2007**, 325, 1–14.
22. S. Rehman, R. Ullah, A. M. Butt, N. D. Gohar, *J. Hazard. Mater.* **2009**, 170, 560–569.
23. V. Etacheri, C. D. Valentin, J. Schneider, D. Bahnemann, *J. Photochem. Photobiol. C: Photochem. Rev.* **2015**, 25, 1–29.
24. R. Fagan, D. E. McCormack, D. D. Dionysiou, S. C. Pillai, *Mater. Sci. Semicond. Process.* **2016**, 42, 2–14.
25. S. Zhang, Z. Liu, D. Chen, Z. Guo, M. Ruan, *Chem. Eng. J.* **2020**, 395, 125101.
26. Y. Qin, Y. Guo, Z. Liang, Y. Xue, X. Zhang, L. Yang, J. Tian, *Chin. Chem. Lett.* **2021**, 32, 1523–1526.
27. G. Dong, Y. Zhang, Q. Pan, J. Qiu, *J. Photochem. Photobiol. C: Photochem. Rev.* **2014**, 20, 33–50.
28. J. Wen, J. Xie, X. Chen, X. Li, X. *Appl. Surface Sci.* **2017**, 391, 72–123.

29. M. Ismael, M. J. *Alloys Compd.* **2020**, *846*, 156446.
30. S. Luo, Z. Zeng, G. Zeng, Z. Liu, R. Xiao, P. Xu, H. Wang, D. Huang, Y. Liu, B. Shao, Q. Liang, D. Wang, Q. He, L. Qin, Y. Fu, *J. Mater. Chem. A* **2020**, *8*, 6434–6470.
31. S. Qiao, M. Di, J. Jiang, B. H. Han, *EnergyChem* **2022**, *4*, 100094.
32. J. S. M. Lee, A. I. Cooper, *Chem. Rev.* **2020**, *120*, 2171–2214.
33. C. Han, S. Xiang, M. Ge, P. Xie, C. Zhang, J. Jiang, *Small* **2022**, *18*, 2202072.
34. Y. Wang, L. Wang, Z. Liu, E. Ye, J. H. Pan, G. Guan, Z. Li, *Appl. Catal. A, General* **2022**, *644*, 118836.
35. Y. Yang, H. Tan, B. Cheng, J. Fan, J. Yu, W. Ho, *Small Methods* **2021**, *5*, 2001042.
36. B. Li, Y. Hu, Z. Shen, Z. Ji, L. Yao, S. Zhang, Y. Zou, D. Tang, Y. Qing, S. Wang, G. Zhao, X. Wang, *ACS EST Engg.* **2021**, *1*, 947–964.
37. G. Zotti, S. Zecchin, G. Schiavon, A. Berlin, G. Pagani, A. Canavesi, *Chem. Mater.* **1997**, *9*, 2940–2944.
38. G. Zotti, S. Zecchin, G. Schavon, B. Vercelli, A. Berlin, W. Porzio, *Chem. Mater.* **2004**, *16*, 2091–2100.
39. N. Kumazawa, M. Towatari, T. Uno, T. Itoh, M. Kubo, *J. Polym. Sci., Part A: Polym. Chem.* **2014**, *52*, 1376–1380.
40. M. Chayer, K. Faïd, M. Leclerc, *Chem. Mater.* **1997**, *9*, 2902–2905.
41. R. D. McCullough, P. C. Ewbank, R. S. Loewe, *J. Am. Chem. Soc.* **1997**, *119*, 633–634.
42. B. Pal, W. C. Yen, J. S. Yang, C. Y. Chao, Y. C. Hung, S. T. Lin, C. H. Chuang, C. W. Chen, W. F.; Su, *Macromolecules* **2008**, *41*, 6664–6671.

43. N. Toshima, S. Hara, *Prog. Polym. Sci.* **1995**, *20*, 155–183.
44. K. Yoshimo, S. Nakajima, R. I. Sugimoto, *Jpn. J. Appl. Phys.* **1987**, *23*, 1038–1039.
45. F. Lai, Y. Wang, D. Li, X. Sun, J. Peng, X. Zhang, Y. Tian, T. Liu, *Nano Res.* **2018**, *11*, 1099–1108.
46. J. Luo, X. Zhang, J. Zhang, *ACS Catal.* **2015**, *5*, 2250–2254.
47. Z. J. Wang, R. Li, K. Landfester, K. A. I. Zhang, *Polymer* **2017**, *126*, 291–295.
48. S. Tanaka, T. Enoki, H. Imoto, Y. Ooyama, J. Oshita, T. Kato, K. Naka, *Macromolecules* **2020**, *63*, 2006–2013.
49. G. Martra, S. Coluccia, L. Marchese, V. Augugliaro, V. Loddo, L. Palmisano, M. Schiavello, M. *Catalyst Today* **1999**, *53*, 695–702.

## Chapter 2

### Synthesis and Photocatalytic Activity of Poly(4,4-dihexylcyclopenta [2,1-b:3,4b']dithiophene) (PDiHexCPDT)

#### 2.1 Abstract

PDiHexCPDT was compared with poly(3-hexylthiophene) (P3HexTh) in terms of its photocatalytic performance. The generation of hydroxyl radicals and the oxidative hydroxylation of boronic acid and oxidative coupling of benzylamine were used as model reactions to evaluate PDiHexCPDT photocatalytic capabilities. The results demonstrated that PDiHexCPDT exhibits superior photocatalytic activity under fluorescent light irradiation compared to P3HexTh. PDiHexCPDT exhibited better photocatalytic activity than P3HexTh under fluorescent light irradiation. However, the combination of PDiHexCPDT with P3HexTh improved the photocatalytic activity to 84%. The combination improved the photocatalytic reactivity when the light source was a white LED, which is composed of blue and yellow emissions. The enhanced performance of PDiHexCPDT is attributed to its absorption spectrum, which matches well with the emission spectrum of the light source. Moreover, the study explored the potential of PDiHexCPDT/SiO<sub>2</sub> and PDiHexCPDT/TiO<sub>2</sub> composites and highlights the synergistic effects observed in mixed systems. However, composite formation of PDiHexCPDT with SiO<sub>2</sub> or TiO<sub>2</sub> did not give a high conversion rate. This research sheds light on the promising role of organic  $\pi$ -conjugated polymers as efficient and versatile photocatalysts for sustainable energy applications.

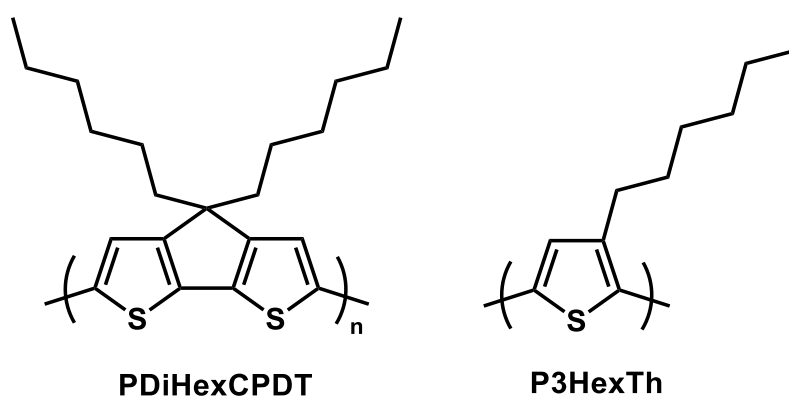
## 2.2 Introduction

The present worldwide energy deficit and environmental issues have arisen as a consequence of population expansion and industrial development. Hence, it is imperative to examine and establish energy systems that are sustainable and ecologically sound. Solar energy is a form of energy that can be supplied endlessly and is cost-free, ecologically beneficial, widely available, and accessible.<sup>1</sup> The use of solar energy by photocatalysis, a process wherein solar energy is transformed into chemical energy, presents a viable and environmentally friendly method that is both cost-effective and sustainable. Since the seminal research conducted by Fujishima and Honda in the 1970s,<sup>2</sup> there has been a significant amount of research and advancement in the field of photocatalysis. This can be supported by the rapid increase witnessed in yearly publications dedicated to this topic. Photocatalysis involves various fundamental processes, including the production of hydrogen by splitting water, the generation of solar energy through carbon dioxide reduction, the breakdown of pollutants, and the synthesis of organic compounds.<sup>3,4</sup>

Titanium dioxide ( $\text{TiO}_2$ ) has received much attention in photocatalyst research because of its advantageous properties, including its cost-effectiveness, enduring stability and eco-friendly nature. However, the bandgap of  $\text{TiO}_2$  is around 3.2 eV, limiting its responsiveness to just ultraviolet (UV) light. It is important to note that UV light comprises only 4% of the overall sun irradiation. Photocatalyst research focuses on enhancing the properties of titanium dioxide to develop efficient techniques for converting visible light into useful energy and to improve titanium dioxide's ability to respond to light.

Organic  $\pi$ -conjugated polymers are widely recognized for their ability to absorb light within the visible spectrum. Consequently, there has been a notable increase in the interest for the potential of unconventional materials as viable substitutes for conventional inorganic

semiconductors in the field of photocatalysis. These characteristics can be attributed to their distinct benefits, such as their cost-effectiveness, exceptional chemical stability and the capacity to adjust their optoelectronic properties at the molecular level.<sup>5,6</sup> The majority of  $\pi$ -conjugated polymers that are utilized for photocatalytic applications such as organic transformation and oxidative coupling of amine are conjugated porous polymers, graphitic carbon nitride and covalent organic frameworks which are insoluble materials. Given the distinct characterization of linear polymers in terms of molecular weight and molecular weight distribution, a comprehensive understanding of the correlation between chemical structure and photocatalytic activity may be achieved. I am interested in conjugated polymer based on 4H-cyclopenta[2,1-b:3,4-b']dithiophene (CPDT) because CPDT-based polymers have been investigated as low bandgap polymers that efficiently absorb sunlight in the long wavelength range.<sup>7-10</sup> As far as I aware, there have been no reports regarding the photocatalytic activity of polymers based on CPDT have been published. Here, the photocatalytic activity of poly(4,4-dihexylcyclopenta[2,1-b:3,4-b']dithiophene) (PDiHexCPDT) was presented. Further, the reactivity of PDiHexCPDT was compared with that of poly(3-hexylthiophene) (P3HexTh) (Figure 2.1).



**Figure 2.1** Chemical structures of  $\pi$ -conjugated polymers investigated in this work

## 2.3 Experimental

### *Preparation of PDiHexCPDT and P3HexTh*

PDiHexCPDT and P3HexTh were produced according to previously reported techniques<sup>11,12</sup> using Grignard metathesis (GRIM) polymerization. To ascertain the molecular weights, gel permeation chromatography (GPC) was employed. The molecular weight of PDiHexCPDT and P3HexTh were determined as  $M_n = 5,850$  ( $M_w/M_n = 1.5$ ) and  $M_n = 8,600$  ( $M_w/M_n = 1.8$ ), respectively, with respect to a polystyrene standard.

### *Preparation of PDiHexCPDT/SiO<sub>2</sub> and PDiHexCPDT/TiO<sub>2</sub> Composites*

PDiHexCPDT/SiO<sub>2</sub> and PDiHexCPDT/TiO<sub>2</sub> composites were prepared according to the following procedure. 50 mg of Silica (SiO<sub>2</sub>) (Merck Silica Gel 60) or titanium dioxide (TiO<sub>2</sub>) (Wako, anatase) was introduced to a mixture of PDiHexCPDT (10 mg) in chloroform (10 mL). The solution was stirred at ambient temperature for a period of 48 hours. Then, the composite was dried under reduced pressure.

### *Hydroxyl Radicals Generation Experiment*

10 mg of PDiHexCPDT was introduced to a 0.4 mM aqueous solution of coumarin with a volume of 3 mL. For 20 hours, the combination was exposed to radiation from a 100 W Xe lamp at room temperature. A fluorescence spectrophotometer was used to examine the filtrate following the polymer's removal by filtration.

### *Oxidative Hydroxylation of 4-Carboxylphenylboronic acid*

In a typical example, 4-carboxylphenylboronic acid (0.2 mmol, 33 mg) and *N,N*-diisopropylethylamine (DIPEA) (1 mmol, 130 mg) were dispersed in a 4 mL solution consisting of acetonitrile and water in a volume ratio of 4:1. At ambient temperature,

PDiHexCPDT (5 mg) was introduced. For a duration of 48 hours, the mixture was subjected to illumination from a white LED bulb (6 W). Following immersion in ether, the reaction mixture was subsequently washed with water. The organic layer was subjected to vacuum distillation to eliminate the solvents. To ascertain the degree of conversion,  $^1\text{H}$  NMR was used to examine the resulting residue.

#### *Oxidative Coupling of Benzylamine*

Illustratively, a mixture of benzylamine (0.4 mmol, 43 mg), PDiHexCPDT (10 mg), and acetonitrile (8 mL) was irradiated with a fluorescent light (27 W) at ambient temperature for 24 h. Polymer was separated by filtration. To get rid of the solvent, the filtrate that was left over was put under lower pressure. The extent of conversion was determined by analyzing the residue using  $^1\text{H}$  NMR.

#### *Measurements*

In this study, JEOL A-500 nuclear magnetic resonance (NMR) spectrometer was utilized to determine molecular structure of a material on an atomic level.  $^1\text{H}$  spectra were obtained at the temperature of the surrounding environment. The samples were dissolved in  $\text{CDCl}_3$  solution. As an internal standard, tetramethylsilane (TMS) was used respectively. In order to conduct gel permeation chromatography (GPC), this experiment involved the utilization of a Tosoh HLC-8020 chromatograph. The chromatograph is consisting of a number of polystyrene gel components which are Tosoh TSK gel G2500H and G3000. It is also equipped with dual-mode detectors that are both refractive and ultraviolet. The eluent utilized in this experiment was tetrahydrofuran (THF). It was dispensed at a pace of 1.0 mL/min. Polystyrene standards were used to create the calibration curves that were utilized in the GPC analysis. PMA-11 HAMAMATSU Multi-Channel Analyzer was used to measure the photoluminescence spectra. The reading of photoluminescence spectra was captured at an exciting wavelength of 365 nm.



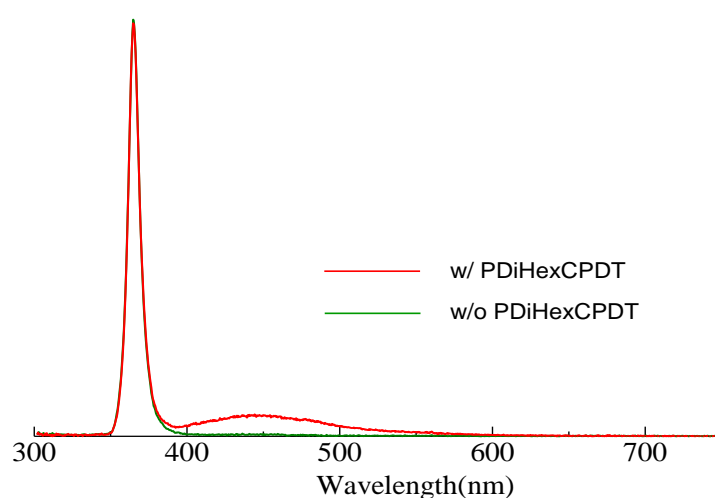
## 2.4 Results and Discussion

### *Hydroxyl Radicals Generation*

The investigation initially focused on the formation of hydroxyl radicals from an aqueous dispersion of PDiHexCPDT when exposed to visible light. Hydroxyl radicals are highly reactive species that play a crucial role in various photocatalytic processes, including the degradation of organic pollutants and the oxidation of organic compounds. Detecting and quantifying the generation of hydroxyl radicals is essential for evaluating the photocatalytic activity of materials. The generation of hydroxyl radicals can be detected using a fluorescence probe method with coumarin.<sup>13</sup> Coumarin, a nonfluorescent compound, reacts with hydroxyl radicals to produce umbelliferone, a fluorescent product. The nonfluorescent compound known as coumarin effectively seizes hydroxyl radicals, resulting in the production of umbelliferone, a substance that exhibits blue fluorescence when stimulated by light at an excitation wavelength of 365 nm.

In this study, the fluorescence spectra of the reaction products were analyzed to detect hydroxyl radicals. The emission at a wavelength of 365 nm was generated using an ultraviolet light-emitting diode (UV-LED) as the excitation light source. The measured spectra were standardized by normalizing them to the emission at 365 nm. As shown in Figure 2.2, blue fluorescence was observed from the mixture of PDiHexCPDT and coumarin, indicating the generation of hydroxyl radicals upon photoirradiation. In contrast, no fluorescence was detected when the polymer was dispersed in pure water, confirming that the fluorescence was specifically due to the reaction between coumarin and hydroxyl radicals generated by the photoexcited PDiHexCPDT.

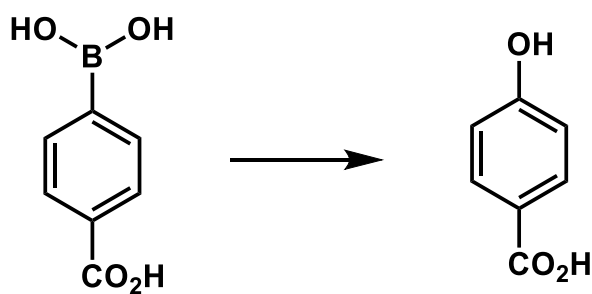
This method of detecting hydroxyl radicals provides a reliable way to assess the photocatalytic activity of PDiHexCPDT. The results demonstrate that PDiHexCPDT is capable of generating hydroxyl radicals under visible light irradiation, which is a key factor in its potential application for environmental remediation and organic synthesis. The ability to produce hydroxyl radicals suggests that PDiHexCPDT can facilitate the degradation of organic pollutants and drive oxidation reactions, making it a promising material for photocatalytic applications.



**Figure 2.2** Fluorescence spectra of the reaction products ( $\lambda_{\text{ex}} = 365 \text{ nm}$ )

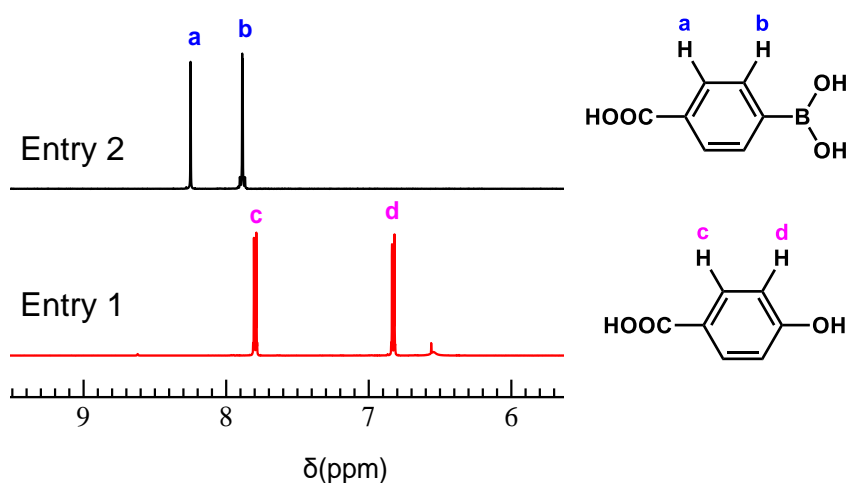
#### *Oxidative Hydroxylation of Arylboronic Acid*

The oxidative hydroxylation of arylboronic acids is an important reaction in organic chemistry, allowing the introduction of hydroxyl groups into aromatic compounds, which can be further utilized in various chemical transformations and applications. Nailwal et al. reported the process of adding hydroxyl groups to arylboronic acids through oxidation using a covalent organic framework as a heterogeneous photocatalyst.<sup>14</sup> Inspired by this work, we evaluated the photocatalytic activity of PDiHexCPDT towards the oxidative hydroxylation of 4-carboxyphenylboronic acid, converting it to 4-hydroxybenzoic acid (Figure 2.3).



**Figure 2.3** Oxidative hydroxylation reaction of 4-carboxyphenylboronic acid

The experimental setup for the oxidative hydroxylation reaction involved several key components, PDiHexCPDT as the photocatalyst, N,N-diisopropylethylamine (DIPEA) as the sacrificial electron donor, oxygen and visible light. The reaction mixture was irradiated with a white LED lamp (6 W) for 48 hours. The conversion of 4-carboxyphenylboronic acid to 4-hydroxybenzoic acid was monitored using  $^1\text{H}$  NMR spectroscopy. Figure 2.4 shows examples  $^1\text{H}$  NMR spectra of the reaction products with peak assignments. The conversion was calculated based on the integral ratio of peaks a and c corresponding to the starting material (4-carboxyphenylboronic acid) and the product (4-hydroxybenzoic acid).



**Figure 2.4** Examples of  $^1\text{H}$  NMR of the reaction products

Table 2.1 summarizes the results. The oxidative hydroxylation reaction necessitates the presence of PDiHexCPDT, DIPEA, oxygen, and light. The experimental results support the reaction mechanism described in the literature<sup>15</sup>, where charge separation occurs when PDiHexCPDT is irradiated by light, and a superoxide anion is generated from the oxygen in the reaction system, which reacts with the boronic acid. Conversely, the tertiary amine functions as a reducing agent, transforming the boronic acid group into a hydroxyl group.

**Table 2.1** Results of Oxidative Hydroxylation of 4-Carboxyphenylboronic Acid

Entry	Reaction Conditions	Conversion (%)
1	normal <sup>a</sup>	100
2	w/o PDiHexCPDT	0
3	in the dark	0
4	w/o DIPEA	0
5	w/o oxygen <sup>b</sup>	0
6	w/ radical scavenger <sup>c</sup>	6

<sup>a</sup> 4-carboxyphenylboronic acid = 0.2 mmol; DIPEA = 1 mmol, PDiHexCDT = 5 mg; CH<sub>3</sub>CN/H<sub>2</sub>O (4:1 v/v) = 4 mL; white LED lamp (6 W) = 48 h. <sup>b</sup> N<sub>2</sub> bubbling. <sup>c</sup> Benzoquinone = 5 mg.

The reaction mechanism involves the formation of hydroxyl radicals upon light irradiation of the photocatalyst, which then oxidize the arylboronic acid. The key steps in this reaction include the following. When PDiHexCPDT is irradiated with visible light, it absorbs the photons, leading to the excitation of electrons and the generation of electron-hole pairs. The excited electrons react with oxygen molecules in the system to form superoxide anions. The superoxide anions and other reactive oxygen species generated in the process oxidize the arylboronic acid to the corresponding 4-hydroxybenzoic acid.

To further compare the photocatalytic activity of PDiHexCPDT with different supports, we conducted another set of experiments using PDiHexCPDT/SiO<sub>2</sub> and PDiHexCPDT/TiO<sub>2</sub> composites. Table 2.2 shows the results, indicating that PDiHexCPDT/TiO<sub>2</sub> exhibits higher efficiency in converting 4-carboxyphenylboronic acid to 4-hydroxybenzoic acid compared to PDiHexCPDT/SiO<sub>2</sub>. This suggests that there might be some beneficial interactions between the conjugated polymer and TiO<sub>2</sub>, enhancing the photocatalytic performance.

**Table 2.2** Results of Oxidative Hydroxylation<sup>a</sup> of 4-Carboxyphenylboronic Acid

Entry	Catalyst (mg)	Conversion (%)
1	PDiHexCPDT/SiO <sub>2</sub> (30)	21
2	PDiHexCPDT/TiO <sub>2</sub> (30)	33

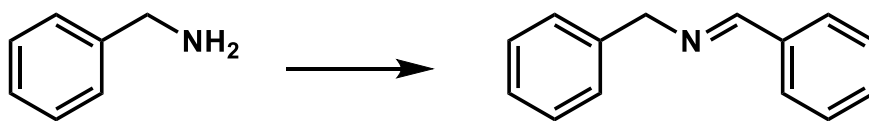
<sup>a</sup> 4-carboxyphenylboronic acid = 0.2 mmol; DIPEA = 1 mmol, CH<sub>3</sub>CN/H<sub>2</sub>O (4:1 v/v) = 4 mL; White LED lamp (6 W) = 48 h.

These findings highlight the potential of PDiHexCPDT and its composites as effective photocatalysts for oxidative hydroxylation reactions, offering a pathway to develop efficient and sustainable photocatalytic processes for organic synthesis and environmental applications.

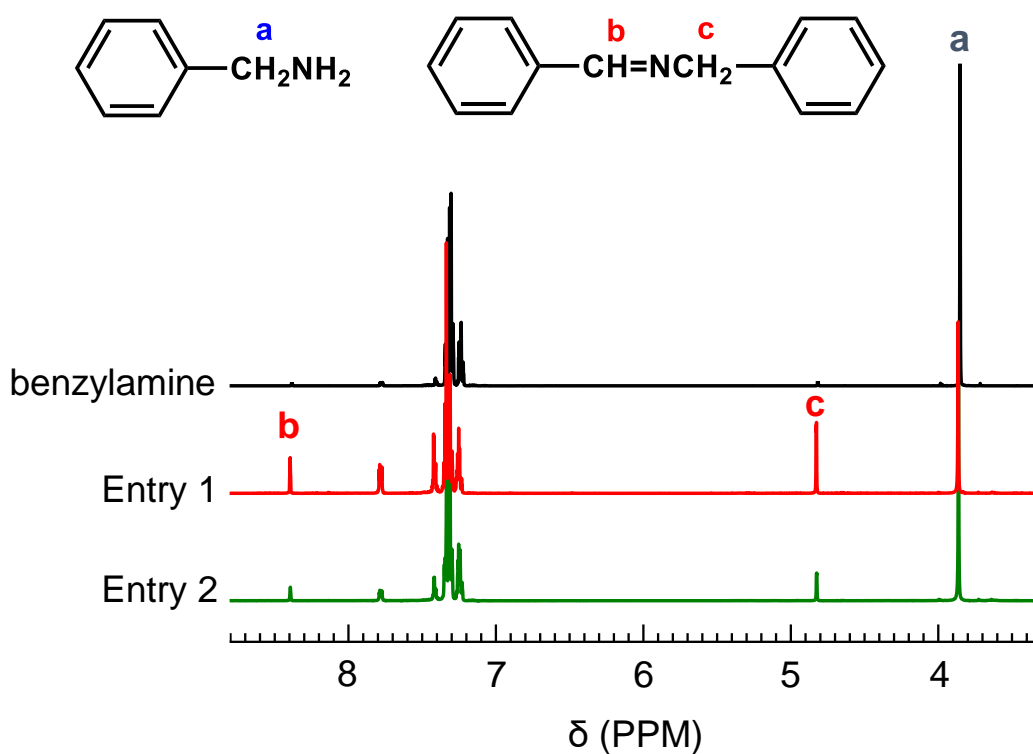
#### *Oxidative Coupling of Benzylamine*

Alzard et al. reported that benzylamine is converted to N-benzylidenebenzylamine by a photocatalytic oxidative coupling reaction (Figure 2.5).<sup>16</sup> The reaction was carried out using two different photocatalysts, PDiHexCPDT and P3HexTh, under two light sources, fluorescent light and white LED. The efficiency of the reaction was monitored using <sup>1</sup>H NMR spectroscopy, and conversion rates were calculated based on the integral ratio between specific peaks in the NMR spectra. Figure 2.6 shows examples of <sup>1</sup>H NMR spectra of the reaction products together

with that of benzylamine. The conversion was calculated based on the integral ratio between peaks a and c. Table 2.3 summarizes the results.



**Figure 2.5** Oxidative coupling of benzylamine



**Figure 2.6** Examples of  $^1\text{H}$  NMR of the reaction products

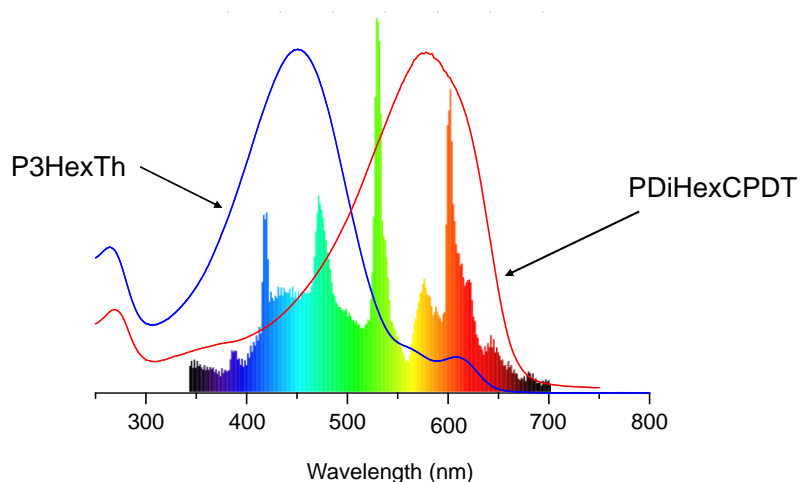
**Table 2.3** Results of Oxidative Coupling of Benzylamine under Various Conditions

Entry	Light Source	Catalyst (mg)	Conversion (%)
1	fluorescent light <sup>a</sup>	PDiHexCPDT (10)	29
2	fluorescent light	P3HexTh (10)	11
3	white LED <sup>b</sup>	PDiHexCPDT (10)	62
4	white LED	P3HexTh (10)	15
5	white LED	PDiHexCPDT/SiO <sub>2</sub> (10)	15
6	white LED	PDiHexCPDT/TiO <sub>2</sub> (10)	13
7	white LED	PDiHexCPDT (5) and P3HexTh (5)	84

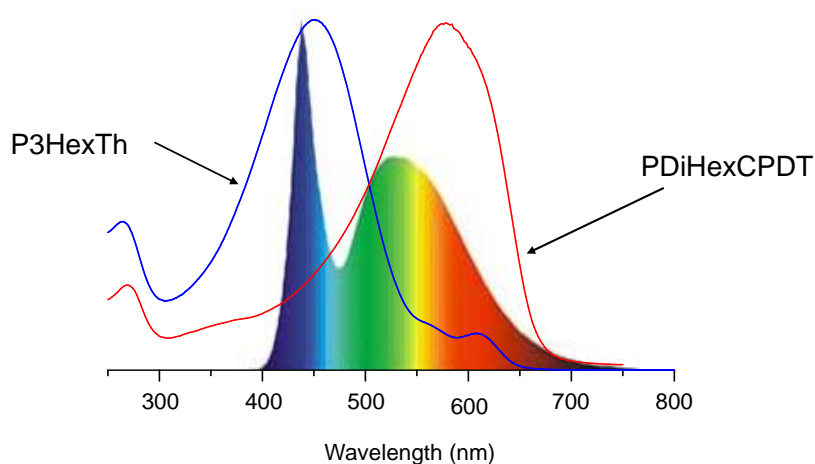
<sup>a</sup> 27 W, 2 h. <sup>b</sup> 6 W, 24 h.

Under fluorescent light, PDiHexCPDT (Entry 1) showed a higher conversion rate (29%) compared to P3HexTh (Entry 2) (11%). This can be reasonably explained by considering the matching between the emission spectrum of the light source and the polymer's absorption spectrum, as shown in Figure 2.7. PDiHexCPDT can efficiently absorb the emissions at 475, 535, and 604 nm, whereas P3HexTh only utilizes the emissions at 415 and 475 nm. PDiHexCPDT have a narrower band gap compared to P3HexTh, making it more suitable for visible light absorption. Furthermore, PDiHexCPDT have superior electron and hole mobility, facilitating the separation of charge carriers and reducing the chances of recombination. Meanwhile, when using a white LED, PDiHexCPDT again showed superior performance (62%) compared to P3HexTh (15%). The white LED emits a broader spectrum of light, and PDiHexCPDT, with its narrower band gap, is better suited for absorbing visible light across this range. Composites of PDiHexCPDT with SiO<sub>2</sub> or TiO<sub>2</sub> did not enhance the conversion rate significantly (15% and 13%, respectively). This suggests that the pure PDiHexCPDT catalyst

is more effective than its composites, possibly due to better electron and hole mobility in the pure form, which facilitates more efficient charge separation and transfer. Interestingly, mixing PDiHexCPDT and P3HexTh resulted in a remarkable increase in conversion rate to 84%. This synergistic effect can be explained by the complementary absorption spectra of the two catalysts. PDiHexCPDT efficiently absorbs emissions at 475, 535, and 604 nm, while P3HexTh absorbs well at 415 and 475 nm (Figure 2.8). The combined PDiHexCPDT and P3HexTh can therefore harness a broader range of the light spectrum from the white LED, leading to enhanced photocatalytic activity. This factor determines the effectiveness of the combined photocatalyst in harnessing light energy to drive chemical reactions.



**Figure 2.7** Emission spectrum of fluorescent light and absorption spectra of polymers



**Figure 2.8** Emission spectrum of white LED and absorption spectra of polymers



## 2.5 Conclusion

The photocatalytic activity of PDiHexCPDT was demonstrated through examination of the oxidative hydroxylation of 4-carboxyphenylboronic acid and the oxidative coupling of benzylamine. PDiHexCPDT showed better photocatalytic activity than P3HexTh under fluorescent light irradiation. The difference in the photocatalytic reactivity between PDiHexCPDT and P3HexTh was reasonably explained by considering the polymer's absorption spectrum. The combination of PDiHexCPDT and P3HexTh improved the photocatalytic reactivity when the light source was a white LED, which is composed of blue and yellow emissions. These results suggest that PDiHexCPDT holds potential as a metal-free photocatalyst composed entirely of organic materials, which makes it a promising option in this field. Since organic  $\pi$ -conjugated polymers can be freely designed, they are interesting materials which show high reactivity depending on the type of light source. Further studies on photocatalytic efficiency and stability are now undergoing.

## 2.6 References

1. J. Mosinger, K. Lang, P. Kub'at, *Top. Curr. Chem.* **2016**, 370, 135.
2. A. Fujishima, K. Honda, *Nature* **1972**, 238, 37.
3. X. Yang, D. Wang, *ACS Appl. Energy Mater.* **2018**, 1, 6657.
4. X. Chen, S. Shen, L. Guo, S. S. Mao, *Chem. Rev.* **2010**, 110, 6503.
5. C. Dai, B. Liu, *Energy Environ. Sci.* **2020**, 13, 24.
6. C. Zhao, Z. Chen, R. Shi, X. Yang, T. Zhang, *Adv. Mater.* **2020**, 32, 1907296.
7. M. L. Turner, P. Coppo, *J. Mater. Chem.* **2005**, 15, 1123.
8. Y. Zhang, J. Zou, C. C. Cheuh, H. L. Yip, A. K. Y. Jen, *Macromolecules* **2012**, 45, 5427.
9. Albrecht, S.; Janietz, S.; Schindler, W.; Frisch, J.; Kurpiers, J.; Kniepert, J.; Inal, S.; Pingel, P.; Fostiropoulos, K.; Koch, N.; Neher, D.; Fluorinated Copolymer PCPDTBT with Enhanced Open-Circuit Voltage and Reduced Recombination for Highly Efficient Polymer Solar Cell. *J. Am. Chem. Soc.* **2012**, 134, 14932.
10. Y. Li, J. Zou, H. L. Yip, C. Z. Li, Y. Zhang, C. C. Chueh, J. Intemann, Y. Xu, P. W. Liang, Y. Chen, A. K. Y. Jen, *Macromolecules* **2013**, 46, 5497.
11. P. Coppo, D. C. Cupertino, S. G. Yeates, M. L. Turner, *Macromolecules* **2003**, 36, 2705.
12. R. S. Loewe, P. C. Ewbank, J. Liu, L. Zhai, R. D. McCullough, *Macromolecules* **2001**, 34, 4324.
13. K. Hirano, T. Kobayashi, *Ultrasono. Sonochem.* **2016**, 30, 18.
14. Y. Nailwal, A. D. D. Wonanke, M. A. Addicoat, S. K. Pal, *Macromolecules* **2021**, 54, 6595.

15. J. Luo, X. Zhang, J. Zhang, *ACS Catal.* **2015**, *5*, 2250.

16. R. H. Alzard, L. A. Siddig, A. S. Abdelhamid, A. Alzamy, *ACS Omega* **2022**, *7*, 36689.

## General Summary

In Chapter 1, PCPDT-CO<sub>2</sub>H was synthesized via FeCl<sub>3</sub>-based oxidative polymerization. The polymer displayed strong, broad absorption in the visible-light region, making it an effective photocatalyst under visible light. It catalyzed the oxidative hydroxylation of arylboronic acid and efficiently oxidized benzaldehyde to benzoic acid under photoirradiation, underscoring its potential as an efficient photocatalyst. Meanwhile in Chapter 2, PDiHexCPDT was synthesized, it exhibited significant photocatalytic activity in the oxidative hydroxylation of 4-carboxyphenylboronic acid and the oxidative coupling of benzylamine. Interestingly, the composite of PDiHexCPDT and P3HexTh outperformed the photocatalytic reactivity of PDiHexCPDT alone.

Both PCPDT-CO<sub>2</sub>H and PDiHexCPDT are promising CPDT-based photocatalysts composed entirely of organic materials, with high photocatalytic efficiency under visible light. Their broad absorption spectrum allows them to harness a wide range of wavelengths from natural or artificial light sources, making them highly effective under visible light, which is the most abundant and accessible portion of the solar spectrum. As fully organic materials, PCPDT-CO<sub>2</sub>H and PDiHexCPDT are derived from ubiquitous material and potentially sustainable sources. This organic composition not only reduces the environmental footprint but also makes these materials more accessible and less expensive to produce.

In summary, PCPDT-CO<sub>2</sub>H and PDiHexCPDT are highly promising photocatalysts due to their high efficiency in photocatalytic reactivity. Their ability to function effectively under visible light, coupled with their potential as ubiquitous, sustainable materials, makes them interesting candidate for further studies. Ongoing research into their photocatalytic efficiency, long-term stability and scalability will be crucial in unlocking their full potential and expanding their applicability across different domains.

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