

A Novel Conjugated Polymer Consists of Benzimidazole and Benzothiadiazole: Synthesis, Photophysics Properties, and Sensing Properties for Pd²⁺

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ABSTRACT: A conjugated polymer PPBIBTE based on benzimidazole and benzothiadiazole was synthesized through palladiumcatalyzed sonogashira cross-coupling reaction. The chemical structures of the monomers and the polymer were indicated by ¹H NMR, and investigation of photophysics properties and sensing optical properties for metal ions were observed by ultravioletvisible and photoluminescence spectroscopy. PPBIBTE showed remarkable selectivity for Pd²⁺ by "turn-off" fluorescence sensing progress. In addition, the Stern–Volmer and Benesi-Hildebrand plots were used to reveal the interaction between the polymer and Pd^{2+} , while job's method was applied to calculate the determination of stoichiometry. The results demonstrate that PPBIBTE can utilize static quenching for Pd^{2+} by forming a 1:1 complex. And it is a potential sensing material as fluorescence chemosensor for Pd^{2+} with high selectivity and sensitivity. © 2020 Wiley Periodicals, Inc. J. Polym. Sci. **2020**

KEYWORDS: benzimidazole; benzothiadiazole; conjugated polymer; fluorescence quenching; synthesis

INTRODUCTION In the past decades, fluorescence chemosensors based on conjugated polymers (CPs) as sensing materials have rapidly developed in energy, chemical engineering, environmental protection, biochemistry and medical treatment fields with their outstanding properties.¹⁻⁴ These materials have received intensive attention because of their favorable selective and sensitive ability, environment-friendly biocompatibility, and fluorescence amplification effect. Compared with a small organic compound fluorescence probe, the delocalized π -electronic conjugated "molecular wires" effect can help CPs display unique signal amplification effect by the facile energy migration along the polymer backbone upon light excitation.⁵ Therefore, CPbased fluorescence chemosensors can realize an efficient fluorescent quenching at very low concentrations of quencher, even the binding of one acceptor site in polymer backbone can result in efficient quenching of the main chain.⁶

Particularly, the fluorescence properties and sensing ability of CP-based fluorescence chemosensors are determined by chromophore and recognition site in the polymer. The design of polymer molecule components plays a significant role in adjusting the ability of selectivity for fluorescence chemosensors, and introducing different functional recognition sites in the polymer backbone and side chains can realize effective detection for ions, small molecules, and biomacromolecules.^{7,8} The recognition site can realize

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detection with these objects by the formation of a covalent bond from chemical reactions and weak interactions involve coordination, hydrogen bond, electrostatic attraction and Van der waals' force.⁹ For example, in metal ions detection, the oxygen atom in the crown ether structure unit can be used as the complex site for metal ions, especially for alkali metal ions.¹⁰ And the coordination between heteroatom and metal ions can be especially useful in this type of chemosensors with specific coordination.¹¹

In respect of fluorescence chemosensors, nitrogen heterocyclic rings were widely used in CPs with their various photoelectric properties and it can realize efficiently ions detection because of the lone pair electrons in nitrogen atom. During the past few years, 2,1,3-Benzothiadiazole (BT) has been widely used as the acceptor in Donor-Acceptor type copolymers due to its good electron-withdrawing ability. The planar structure of benzothiadiazole can enhance the capacity of π - π stacking between molecules and facilitate intramolecular charge transport property which ensures the polymers have high mobility of charge carriers. With these excellent photoelectric properties, this unit is extensively used to form materials for photoactive layer in solar cells.^{12,13} Meanwhile, this unit can be applied in fluorescence chemosensors as fluorophore because of its strong and stable fluorescence. In previous work, benzimidazole unit was extensively applied in small molecule fluorescent probes due to its characteristic fluorescence in various organic solvents,^{14–17} and their fluorescence properties can be affected by various factors like metal ions with coordination. For CPs, this unit was frequently joint with fluorene, pyridine, thiophene, and other neutral rings or rich electron rings to form CPs used as LED materials with shorter absorption in UV-vis spectrum and cyan or blue fluorescence.^{18–20} However, there is no sufficient research for CPs which containing benzimidazole unit applied in fluorescence chemosensors.²¹

Palladium is one of the metal ions in the platinum group which is largely applied as a catalyst in drug synthesis, automobile exhaust purification, and jewelry industry because of its physicochemical properties.^{22,23} However, the final products in those industries are difficult to completely remove palladium element which comes from the catalyst. The extensive use and abundant waste of palladium have raised plenty of pollution to water sources and soils, and cause severe effects and damage to plants, animals, and humans.^{24,25} Especially for humans, excess palladium can get the trigger to serious allergic reactions for eyes and skin in vitro, and it could destroy DNA, coordinate with thiol-containing amino acids, bind to vitamin B6, trigger protein denaturation, and damage several cellular processes in vivo.^{26,27} Therefore, the simple and convenient measurement material is urgently needed to develop and apply in palladium detection and analysis.

In our work, we report the synthesis and characterization of the 4,7-diethynyl-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole (Monomer 1) and 5-bromo-2-(4-bromophenyl)-1-octylbenzimidazole (Monomer 2), getting the ideal CP PPBIBTE. Introduction of long alkyl groups improves the dissolving capacity of the polymer in organic solvents. Compared with other benzimidazole-based CPs, we can expand the absorption range and improve the fluorescence property by using benzothiadiazole unit. PPBIBTE can emit stable and strong yellow-green fluorescence, this chemosensor material displayed a highly sensitive response toward Pd²⁺ over other competitive cations.

EXPERIMENTAL

Measurements

¹H NMR and ¹³C NMR measurements were carried out on a Bruker Advance II-400 MHz spectrometer with tetramethylsilane as the internal reference. HRMS spectra were recorded on a Waters Q-Tof Premier. Gel permeation chromatography (GPC) was determined by Waters E2695 GPC, with THF as mobile phase and PS as the reference in 35 °C. UV-vis spectra were performed on an Analytik Jena Specord200Plus UV-vis spectrophotometer. Photoluminescence (PL) spectra were recorded on a Hitachi F-4600 luminescence spectrophotometer. All spectra were measured at room temperature. TGA was carried out with a TA Series SDT Q600 at a heating rate of 20 °C min⁻¹ in a nitrogen flow. DSC was conducted using a TA Series DSC2000 at a heating/cooling rate of 10 °C min⁻¹ in a nitrogen flow. Molecular architecture of the monomers and polymer was optimized by using RB3LYP and 6-31 g(D) basis sets by Gaussian 09 software package. A frequency calculation was performed on the optimized geometries to ensure a local minimum was found. Cyclic voltammetry (CV) was performed on a CHI440 Electrochemical Workstation. The polymer was dissolved in degassed dichloromethane (conc. 10^{-3} M). CH₂Cl₂ containing 0.1 M tetrabutylammonium perchlorate (Bu₄NClO₄) was used as the supporting electrolyte, with glassy carbon electrode as the working electrode, Pt electrode as the counter electrode and Ag/AgCl as the reference electrode. The sweep rate was 50 mV/s.

Materials

All of the metal salts in analytical grade were purchased from domestic chemical companies and used without further purification. Dimethyl-formamide (DMF) was purified by distillation under vacuum. Other chemicals were used directly without further purification.

Synthesis

The synthetic routes of Monomer 1, Monomer 2, and PPBIBTE are illustrated in Scheme 1. The synthesis of compound 1,2,3,4 was prepared according to references 28–30.

1,2-Bis-Octyloxy-Benzene (1)

Under argon atmosphere, to a solution of catechol (6.60 g, 0.06 mol) in dry DMF (44 mL) was added 1-bromooctane (0.138 mol, 23.8 mL) and K_2CO_3 (25.05 g, 0.177 mol). The mixture was stirred at 100 °C for 2 days. After cooling to room temperature, 100 mL water was added. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 . The combined organic phase was dried over anhydrous magnesium sulfate. After filtration, the solvent was removed by rotary evaporator. The residue was chromatographically purified on silica gel column eluting with CH_2Cl_2 : Petroleum ether (1:6, v:v) to afford 1 as a colorless oil. Yield: 17.20 g (86.0%). ¹H NMR (400 MHz, CDCl₃) δ 6.97–6.86 (m, 4H), 4.03 (t, *J* = 6.6 Hz, 4H), 1.96–1.75 (m, 4H), 1.60–1.25 (m, 20H), and 0.94 (t, *J* = 6.7 Hz, 6H).

1,2-Dinitro-4,5-Bis-Octyloxy-Benzene (2)

The solution of compound 1 (13.38 g, 0.04 mol) in dichloromethane (110 mL) was added dropwise into 65% nitric acid (0.26 mol, 11.76 mL). Then, sulfuric acid (0.16 mol, 8.52 mL) was added dropwise into the mixture. The mixture was stirred for 1.5 h at room temperature. When the reaction was completed, the mixture was poured into crushed ice, and the aqueous layer was extracted with CH_2CI_2 . The combined organic layer was dried over anhydrous magnesium sulfate. After filtration, the solvent was removed by rotary evaporator. The crude product was purified by recrystallization from ethanol to afford a yellow solid. Yield: 10.50 g (61.9%). ¹H NMR (400 MHz, CDCI₃) δ 7.30 (s, 2H), 4.10 (t, *J* = 6.5 Hz, 4H), 1.93–1.81 (m, 4H), 1.55–1.21 (m, 20H), 0.89 (t, *J* = 6.8 Hz, 6H).



SCHEME 1 Synthetic routes of monomers and polymer.

5,6-Bis-Octyloxy-Benzo [1,2,5] Thiadiazole (3)

Under argon atmosphere, a mixture of compound 2 (2.54 g, 6 mmol) and Sn(II)Cl₂ (10.83 g, 48 mmol) in ethanol (90 mL) and conc. HCl (36 mL) was stirred at 85 °C overnight. After cooling to room temperature, the crude product was filtered and washed with water and methanol. Finally, the product was dried at room temperature under a stream of argon over a few hours and used directly. Yield: 1.15 g (44%). Subsequently, to a mixture of 4,5-bis(octyloxy)benzene-1,-2-diaminium chloride (1.15 g, 2.64 mmol) and triethylamine (2.64 mmol, 3.72 mL) in dichloromethane (44 mL) was slowly added a solution of thionyl chloride (5.28 mmol, 0.38 mL) in dichloromethane (5.4 mL) under argon atmosphere. Then, the mixture was heated to reflux for 6 h. After cooling to room temperature, the solvent was removed by rotary evaporator followed by trituration in water stirring for 30 min. The product was filtered and dissolved in dichloromethane, and the solution was dried over anhydrous magnesium sulfate. After filtration, the solvent was removed by rotary evaporator. The crude product was chromatographically purified on silica gel column eluting with EtOAc: hexanes (1:9, v:v) to afford an off-white solid. Yield: 0.684 g (66.0%). ¹H NMR (400 MHz, $CDCl_3$) δ 7.13 (s, 2H), 4.09 (t, J = 6.6 Hz, 4H), 1.95–1.87 (m, 4H), 1.61-1.23 (m, 20H), 0.89 (t, J = 6.9 Hz, 6H).

4,7-Dibromo-5,6-Bis(Octyloxy)Benze[c] [1,2,5] Thiadiazole (4)

To a solution of compound 3 (0.39 g, 1 mmol) in dichloromethane (26.3 mL) and acetic acid (11.6 mL) was slowly added bromine (0.12 g, 7 mmol), and the final solution was stirred in the dark for 48 h at room temperature. When the reaction was completed, the mixture was poured into 40 mL water. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 , the combined organic phase was dried over anhydrous sodium sulfate. After the solvent was removed by rotary evaporator, the crude product was purified by recrystallization from ethanol to afford a white needle-like crystal. Yield: 0.404 g (73.4%). ¹H NMR (400 MHz, CDCl₃) δ 4.18 (t, *J* = 6.6 Hz, 4H), 1.92–1.76 (m, 4H), 1.51–1.19 (m, 20H), 0.98 (t, *J* = 6.9 Hz, 6H).

4,7-Diethynyl-5,6-Bis(Octyloxy)Benzo[c] [1,2,5] Thiadiazole (Monomer 1)

Under argon atmosphere, to a solution of compound 4 (0.55 g, 1 mmol) in triethylamine (14 mL) was added a catalytic amount of CuI (0.0075 g, 0.039 mmol) and $Pd(PPh_3)_2Cl_2$ (0.0140 g, 0.020 mmol). The mixture was carefully stirred for 30 min to deaerate and trimethyl-silylacetylene (0.42 mL, 3 mmol) was added. The final mixture was stirred at 70 °C for



24 h. After the removal of the solvent, the residue was passed through a short silica gel eluting with CH₂Cl₂ to afford a crude product which was chromatographically purified on silica gel column eluting with CH₂Cl₂: Petroleum ether (1:6, v:v) to afford the yellow oil. Subsequently, dissolved the product of the first step in a mixture of methanol (6 mL) and dichloromethane (10 mL) under an argon atmosphere, potassium fluoride (0.22 g, 2.34 mmol) was added and the final mixture was heated to reflux for 4 h. After cooling to room temperature, the solvent was removed by rotary evaporator, and the residue was chromatographically purified on silica gel column eluting with CH₂Cl₂: hexane(1:1, v:v) to afford monomer 1 as a white solid. Gross yield of two-step: 0.176 g (40.0%). ¹H NMR (400 MHz, $CDCl_3$) δ 4.34 (t, J = 6.6 Hz, 4H), 3.82 (s, 2H), 1.96-1.77 (m, 4H), 1.62-1.19 (m, 20H), 0.89 (t, J = 6.7 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 158.84, 151.81, 88.60, 75.87, 75.27, 31.83, 30.29, 29.37, 29.26, 25.92, 22.65, 14.08; HRMS (ESI⁺) $[M + H]^+$: calc'd for C₂₆H₃₇N₂O₂S: 441.2570, found 441.2567.

5-Bromo-2-Nitroaniline (5)

To a solution of 2-nitroaniline (13.81 g, 0.10 mol) in methanol (250 mL) and 40% hydrobromic acid (30 mL) with ice-bath. 30% hydrogen peroxide was slowly added within 15 min. The mixture was stirred overnight at room temperature. When the reaction was completed, the mixture was filtered and the crude product was purified by recrystallization from mixed solvent ethanol/water to afford the final product as an orange needle crystal. Yield: 11.27 g (94.1%) ¹H NMR (400 MHz, CDCl₃) δ 8.27 (d, *J* = 2.3 Hz, 1H), 7.43 (dd, *J* = 8.9, 2.3 Hz, 1H), 6.73 (d, *J* = 8.9 Hz, 1H), 6.09 (s, 2H).

4-Bromobenzene-1,2-Diamine (6)

Under argon atmosphere, to a solution of compound 5 (6.51 g, 30 mmol) in ethanol (45 mL) was added Tin(II) chloride dehydrate (33.85 g, 150 mmol). The mixture was heated to reflux for 15 h. The solvent was removed under vacuum, and the pH of the residue was adjusted to 11–12 by adding sodium hydroxide solution. Then, the mixture was extracted with diethyl ether. The organic phase was dried over anhydrous magnesium sulfate overnight. After filtration, the solvent was removed by rotary evaporator to afford gray pink solid. Yield: 5.26 g (93.7%). ¹H NMR (400 MHz, CDCl₃) δ 6.84 (dd, J = 5.3, 2.2 Hz, 1H), 6.81 (d, J = 2.2 Hz, 1H), 6.58 (d, J = 8.1 Hz, 1H), and 3.37 (s, 4H).

6-Bromo-2-(4-Bromophenyl)-1H-Benzo[d] Imidazole (7)

A mixture of 4-bromobenzaldehyde (1.11 g, 6 mmol), NaHSO₃ (0.62 g, 6 mmol) and ethanol (25 mL) was stirred for 4 h at room temperature. Subsequently, a solution of compound 6 (1.12 g, 6 mmol) dissolved in DMF (15 mL) was added and the mixture was heated to reflux for 2 h. When the reaction was complete, the solvent was removed under vacuum, EtOAc (20 mL) was added and the mixture was washed with water. The organic phase was dried over anhydrous sodium sulfate. After the solvent was removed by rotary evaporator, the residue was chromatographically purified on silica gel column eluting with EtOAc: petroleum ether (4:1, v:v) to afford 7 as a

white solid. Yield: 1.30 g (61.5%) ¹H NMR (400 MHz, DMSO d_6) δ 13.20 (d, J = 17.5 Hz, 1H), 8.11 (d, J = 6.9 Hz, 2H), 7.90–7.47 (m, 4H), and 7.36 (t, J = 9.4 Hz, 1H).

6-Bromo-2-(4-Bromophenyl)-1-Octyl-1H-Benzo [d]Imidazole (Monomer 2)

Under argon atmosphere, to a solution of compound 7 (1.76 g, 5 mmol) in DMF (20 mL) was added NaH (0.7 g, 17.5 mmol) in ice-bath and stirred for 1.5 h at room temperature. Then the mixture was heated to 40 °C and was slowly added 1-bromooctane (1.16 g, 6 mmol), the final mixture was heated to 80 °C and stirred for 12 h. After the reaction was completed, the cooled solution was added 15 mL water and extracted with CH₂Cl₂. The organic layer was washed by water and dried over anhydrous sodium sulfate. After filtration, the mixture was concentrated under vacuum. The crude product was chromatographically purified on silica gel column eluting with EtOAc: petroleum ether (4:1, v:v) to afford a white solid. Yield: 1.83 g (80.0%). ¹H NMR (400 MHz, DMSO d_6) δ 7.94 (dd, I = 37.5, 1.7 Hz, 1H), 7.82–7.69 (m, 4H), 7.66 (dd, J = 13.0, 8.6 Hz, 1H), 7.41 (ddd, J = 22.0, 8.6, 1.8 Hz, 1H), 4.31 (t, J = 7.3 Hz, 2H), 1.66-1.52 (m, 2H), 1.25-1.01 (m, 10H), 0.82 (t, J = 7.2 Hz, 3H); ¹³C NMR (101 MHz, DMSO- d_6) δ 153.46, 144.25, 134.56, 132.05, 130.73, 129.09, 125.92, 124.58, 122.81, 115.47, 111.31, 44.91, 31.61, 29.67, 28.96, 28.86, 26.56, 22.51, 13.97; HRMS (ESI⁺) [M + H]⁺ calc'd for C₂₁H₂₅Br₂N₂: 465.0359, found 465.0360.

Polymer (PPBIBTE)

Under argon atmosphere, monomer 1 (0.177 g, 0.40 mmol) and monomer 2 (0.186 g, 0.40 mmol) were dissolved in toluene (4 mL). Then CuI (0.0015 g, 0.08 mmol), triphenylphosphine (0.002 g, 0.008 mmol), Pd(PPh₃)₂Cl₂ (0.0281 g, 0.04 mmol), and diisopropylamine (1 mL) were added into the solution. The final mixture was stirred at 105 $^\circ$ C for 24 h and subsequently cooled to room temperature. The resulting mixture was filtered and the filtrate was slowly added into methanol (250 mL) and stirred for 1 h. The precipitate was isolated by filtration followed by washing with hot methanol, and purified through Soxhlet extraction for 24 h by using methanol and CHCl₃, respectively. The methanol fraction was discarded while the CHCl₃ fraction was collected, and the polymer was reprecipitated by adding excess methanol into CHCl₃ fraction to afford a red-brown solid. Yield: 0.174 g (58.4%). ¹H NMR (400 MHz, CDCl₃) δ 8.02–7.29 (m, 7H), 4.72-3.82 (m, 6H), 1.88 (d, 6H), 1.32 (d, 30H), 0.87 (d, 9H). Mw: 15108, Mn: 8025, and Mw/Mn: 1.88 (GPC).

Fluorescence Sensing Analysis

The stock solutions of polymer PPBIBTE in THF was prepared at a concentration of 5×10^{-4} M and diluted with THF before used. The metal ions stock solutions were prepared by dissolving the metal salts in methanol at a concentration of 1×10^{-3} M. The emission spectra were recorded from 350 to 750 nm using 332 nm as excitation wavelength at room temperature. The metal ion solution in 1×10^{-3} M was added with a gradient of 4 µL into the PPBIBTE solution of test sample (2 mL, 2×10^{-5} M) placed in a quartz cell (1 cm width),

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and the fluorescence spectra were recorded by measuring the changes of intensity after mixing for 5 min.

RESULTS AND DISCUSSION

Synthesis and Characterization

The ¹H NMR results of monomer 1, monomer 2, and PPBIBTE were listed in Figure 1. In the spectrum of monomer 1, the proton 9 of the triple bond was easy to recognize with singlet at 3.82 ppm. The proton 8 adjoins with oxygen in alkyl chain was affected by the inductive effect which decreased rapidly with distance and shows as a triplet at 4.34 ppm. Multiplet at 1.77 ppm and 1.62-1.99 ppm is proton 7 and proton 2-6. The proton 1 is farthest from the heteroatom and shows with a triplet in 0.89 ppm. The law of peaks originate from alkyl chain in monomer 2 is the same as monomer 1 and the signals at a range of 7.35-8.88 ppm come from aromatic protons. It can be known from the integral area that the resonance peak of protons 9 and 10 is between 7.70 and 7.80 ppm. The relative positions of bromine atoms and hydrogen atoms in the imidazole ring are different while the ring was synthesized, which will lead to the occurrence of isomers in monomer 2 and PPBIBTE, respectively,²⁰ and the introduction of alkyl chain will further affect the generation of peak signals. Therefore, the signals of aromatic protons 11, 12, and 13 in monomer 2 could appear with splitting. The peak signal of the proton 12 which is far away from the imidazole ring shown in high filed at 7.36–7.45 ppm, it is less affected by the deshielding effect of imidazole compared with protons 11 and 13. Since the introduction of alkyl group increases the effect of electron-donating group of the nitrogen atom and leads to the increase of electron density of proton 13, which result in the chemical shift of proton moves to a high field. Therefore, the peaks at 7.62–7.69 ppm belong to 13 and the peaks at 7.98 and 7.89 ppm are the peak signals of the proton 11. In the spectrum of PPBIBTE, the peaks between 0.75-1.90 and 4.30-4.60 ppm are signals of hydrogens in the alkyl chain. The

isomer ratio of 5-bromo-2-(4-bromophenyl)-1-octyl-benzimidazole and 6-bromo-2-(4-bromophenyl)-1-octy-benzimidazole is about 0.80:0.20 for monomer 2 by calculating the integral areas of splitting peaks in protons 11, 12, and 13, respectively. Similarly, we can calculated the isomer ratio of 5-bromo-2-(4-bromophenyl)-1H-benzo[d]imidazole and 6-bromo-2-(4-bromophenyl)-1H- benzo [d]imidazole for compound 7 is 0.55:0.45. The spectrum of polymer always shows with sharpening wide peaks because of the different chain lengths and various configurations. The protons in conjugated structures are influenced by complex deshielding effects, and a series of peak signals in the range of 7.20-8.00 ppm are all derived from the aromatic ring on the benzimidazole. Comparing these three spectra, the characteristic signal peak of the alkynyl hydrogen in monomer 1 disappeared in the spectrum of PPBIBTE because of the removal of the triple bond hydrogen in the coupling reaction, which proved that the successful polymerization reaction had occurred. The ¹H NMR results show that PPBIBTE was successfully synthesized.

Thermal Analysis

According to thermal analysis of the polymer (Figure 2), it has high thermal stability with no weight loss up to 250 °C and 5% weight loss temperature is 266 °C in TGA curve. Meantime, as it is shown in Figure 2(b), there are no obvious endothermic peaks and exothermic peaks can be observed during the forward scan and reverse scan, indicating that there were no obvious melting and crystallization phenomena during the heating and cooling process. In addition, it can be found that the polymer has a tendency to absorb heat during the heating process, which may be related to the evaporation of the solvent in the sample at high temperature. According to the midpoint of the step in the curve during the heating process, the $T_{\rm g}$ of the polymer was determined to be 103 °C. Therefore, the polymer PPBIBTE has a desirable thermal property for practical applications as a fluorescence sensor.



FIGURE 1¹H NMR spectra of Monomer 1, Monomer 2, and PPBIBTE. [Color figure can be viewed at wileyonlinelibrary.com]





FIGURE 2 (a) TGA and (b) DSC curves of the conjugated polymer PPBIBTE. [Color figure can be viewed at wileyonlinelibrary.com]

Photophysical Properties of Polymers

The UV-vis absorption spectra and fluorescence emission spectra of PPBIBTE in different solvents at the same concentration $(1 \times 10^{-5} \text{ M} \text{ for absorption spectra and } 2 \times 10^{-5} \text{ M} \text{ for emission spectra, calculated by repeating unit}) is shown in Figure 3, and the parameters of absorption and emission$

maxima are listed in Table 1. PPBIBTE show two broad absorption peaks at the range of 300-370 nm and 380-480 nm, respectively. The shorter wavelength peak originates from localized π - π * electron transition of the polymer backbone, while the longer wavelength peak can be attributed to intramolecular charge transfer (ICT) effect between monomer 1 and monomer 2. Meanwhile, the longer wavelength absorption peak intensity is weaker than short one which may indicate the ICT effect is weak in PPBIBTE.³¹ The absorption and emission wavelengths of the thin film were listed in Table 1. Compared with solution, a large red shift for emission wavelength was observed due to the strong intermolecular interaction in solid state. There is no apparent difference between absorption and emission maxima among different solvents. The absorption peak shifts only 4 nm in wavelength from the low-polar solvent (Toluene) to strong polar solvent (DMF) with increasing Dimroth-Reichardt solvent polarities $E_{\rm T}(30)$ = 33.9 kcal/ mol for toluene (from to $E_{\rm T}(30) = 43.2$ kcal/ mol for DMF, $E_{\rm T}$ (30) is polarity index: data from ref. 32), indicating that the electronic and structural nature of the ground and the Franck-Condon excited states does not change much.³³ But the emission intensity in DMF is much less than other solvents which may come from π -stacking of polymer in solution caused by the high permittivity of DMF. Meantime, a bathochromic shift caused by intramolecular charge transfer interaction results in the emission peak shifts 6 nm in wavelength from the Toluene to DMF. Considering the soluble capacity of metal ions and the Stokes shift of polymer in these solvents, THF can be a favorable solvent for sensing properties experiment below.

Sensing Properties of PPBIBTE

To investigate the response performance of PPBIBTE in THF at the concentration of 2×10^{-5} M with different metal ions (including Pd²⁺, Fe³⁺, Mg²⁺, Sn²⁺, Co²⁺, Zn²⁺, Cu²⁺, Mn²⁺, Ni²⁺, Cr³⁺, Fe²⁺, Hg²⁺, and Cd²⁺) at the same concentration which is the fluorescence-quenching extreme limit of Pd²⁺, the selective behavior is shown in Figure 4(a). Upon addition of these metal ions, it can be observably found that Pd²⁺ can cause instantly and mostly quenching of the polymer while Cu²⁺, Fe³⁺, and Co²⁺ only lead to a slight quenching of the polymer and other common metal ions (Mg²⁺, Sn²⁺, Zn²⁺, Mn²⁺, Ni²⁺, Cr³⁺, Fe²⁺, Hg²⁺, and Cd²⁺) only exhibit negligible effect to the

TABLE 1 Photophysical Parameters of PPBIBTE in Thin Film and Different Solvents

Thin film							
Absorption λ _{max} (nm)	Emission λ _{max} (nm)	Solvent	Absorption λ _{max} (nm)	Excitation λ _{ex} (nm)	Emission λ _{max} (nm)	Stokes shift λ(nm)	E _T (30) kcal/mol
454	602	DMF	434	328	518	84	43.2
		THF	436	332	517	81	37.4
		EtOAc	433	328	509	76	38.1
		CH_2CI_2	433	331	519	86	40.7
		CHCl ₃	433	331	520	87	39.1
		Benzene	437	334	513	76	34.3
		Toluene	438	334	512	74	33.9



FIGURE 3 UV-vis spectra and fluorescence spectra of PPBIBTE in different solvents. [Color figure can be viewed at wileyonlinelibrary.com]

fluorescence intensity. To further study the interaction between palladium ion and the polymer, the fluorescence spectra of PPBIBTE in THF with different concentrations of Pd^{2+} is shown in Figure 4(b).

When the concentration of Pd^{2+} in the solution increases from 0 to 2×10^{-5} M with a gradient of 2×10^{-6} M, the fluorescence intensity of the polymer decreased obviously and regularly at a significant extent. Subsequently, there is no visible fluorescence can be observed with the Pd^{2+} at the concentration of 2×10^{-5} M, and the maximum intensity of fluorescence emission in the fluorescence spectra reduced from 6992 to only 177 and almost 97 percent of fluorescence is quenched. Meanwhile, the fluorescence spectra did not change regularly and there is no significant effect on the fluorescence intensity of polymer with other metal ions in the same experiment.

To further study the recognition ability of PPBIBTE to Pd^{2+} , the values of I_0/I_1 for each metal ions are calculated and compared in Figure 5(a), where I_0 and I_1 are the fluorescence intensities of PPBIBTE in the absence and the saturated concentration of metal ions, respectively. All the concentrations of these metal ions are 2.0×10^{-5} M which is the fluorescence quenching extreme limit of Pd^{2+} . As shown in Figure 5(a), the I_0/I_1 value of Pd²⁺ is almost 40 while the I_0/I_1 values of the remaining ions are all approximately equal to 1. Meanwhile, the competition experiment was carried out in Figure 5(b) to evaluate the interference from other metal ions. To the solution of PPBIBTE/metal system was subsequently added Pd²⁺, no significant interference was observed and the fluorescence was still extremely and rapidly quenched, illustrating the favorable anti-interference ability toward Pd²⁺. The results indicate the polymer has no ability to recognize these metal ions except Pd²⁺.

In the processing of the test, the fluorescence change of each mixed solution can be observed preliminarily and obviously with naked eyes. For developing a convenient, effective, low-



FIGURE 4 (a) The fluorescence spectra of polymer solution with different metal ions. (b) The fluorescence spectra of polymer solution with Pd^{2+} in different concentrations from 0 to 2×10^{-5} M. [Color figure can be viewed at wileyonlinelibrary.com]

costing, and a timely sensing method, the solution of PPBIBTE and a mixed solution of the polymer with different metal ions were prepared and placed under the daylight and the ultraviolet light in Figure 6. Both the concentration of polymer and metal ions are 2.0×10^{-5} M. In this photo, these solutions do not have any observable difference from each other under the daylight. Under the ultraviolet light, the blank polymer solution on the far left presents a strong yellow-green color, and it is noticeable that the fluorescence of PPBIBTE disappeared with the concentration of Pd²⁺ in 2.0×10^{-5} M while other metal ions showed no visible fluorescence change. The result is coinciding with the recognition experiment above which is further confirmed that PPBIBTE have strong specificity for Pd²⁺ recognition.

The common mechanism of fluorescence quenching can be divided into dynamic quenching and static quenching, and it has been reported that benzimidazoles derivatives can form complexes with Pd^{2+} . Therefore, it is speculated that the







FIGURE 5 (a) Comparison of I_0/I_1 of PPBIBTE with different metal ions in THF (Metal ions concentration = 2.0×10^{-5} M). (b) Fluorescence spectra histogram of competition experiments for PPBIBTE in THF. (Black bar: free PPBIBTE or PPBIBTE + other metal ions; Red bar: PPBIBTE + other metal ions + Pd²⁺; PPBIBTE or Metal ions concentration = 2.0×10^{-5} M). [Color figure can be viewed at wileyonlinelibrary.com]

fluorescence quenching between the polymer and palladium ion may be caused by the static quenching of the polymermetal ion complexes formed by the binding of N atoms in imidazole of the polymer and Pd^{2+,34,35} The color and UV-vis spectra of the mixed solution will change because the ground state complex generated during the static quenching process, comparing the UV-vis spectra of polymer solution $(2 \times 10^{-5} \text{ M})$ containing Pd²⁺ in the solution increasing from 0 to 2×10^{-5} M with a gradient of 5×10^{-6} M in Figure 7. The right bottle which contains both polymer and Pd²⁺ in 2×10^{-5} M is slightly darker than the polymer solution in the illustration. As shown in Figure 7, with the increase of Pd^{2+} concentration in the solution, both absorption peaks intensity of the mixed solution decrease and show a hypochromatic shift. While the short-wavelength absorption peak exhibited a blueshift from 331 to 327 nm, and the long-wavelength absorption peak moved from 435 to 427 nm. The formation of an MD-A complex through metal ion (M) binds with a Donor-Acceptor structure molecule at the donor site, which will decrease the donor strength and restrain ICT. On the other hand, the formation of a D-AM complex by metal-acceptor binding will facilitate ICT.36,37 Therefore, the colorimetric result shows that there is an interaction between the donor unit and Pd²⁺ with the quenching type "static quenching."

In order to further investigate the interaction between polymer and metal ions, Job's method which is often used in analytical chemistry to determine the stoichiometry of the combination of substances was adopted to study the binding properties by using eq 1.

$$F_{\rm job} = (1 - x)F_0 - F$$
 (1)

where x is the molar fraction of Pd^{2+} , F_0 and F are the fluorescence intensities of polymer solution in the absence and presence of Pd^{2+} , respectively. In this method, the total volume molar concentration of the two components should be kept at a certain value while the molar fraction of any component is variable. The total concentration by the addition of the polymer and Pd^{2+} was 2×10^{-5} M, and the molar fraction of Pd^{2+} in the mixture was 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0, respectively. As shown in Figure 8, the Job's plot reached a turning point when the molar fraction of Pd^{2+} was about 0.5, which indicated that the complex binding ratio between PPBIBTE and Pd^{2+} is 1:1.



FIGURE 6 The color comparison of PPBIBTE with different metal ions under the daylight and the ultraviolet light. [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 7 The UV-vis spectra of polymer solution containing Pd^{2+} in different concentrations and the color comparison of the polymer solution and polymer solution containing Pd^{2+} at the concentration of 2×10^{-5} M. [Color figure can be viewed at wileyonlinelibrary.com]

The Stern–Volmer analysis is commonly used to explore the quenching or enhancement process of fluorescence sensors; it has specific equations for both dynamic and static mechanisms,³⁸ for static quenching between PPBIBTE and Pd² ⁺ satisfy the following eq 2:

$$ln\frac{F_0}{F} = e^{K_{SV}[Q]} - 1$$
 (2)

where F_0 and F are the fluorescence intensities of polymer solution with the absence and presence of Pd²⁺, respectively. K_{sv} is the Stern-Volmer quenching constant and [Q] is the concentration of Pd²⁺. The plots and non-linear fitting results obtained in this experiment according to eq 2 are shown in Figure 9(a). It can be investigated that the plots in these concentrations of Pd²⁺ conform to the Perrin model of static quenching, 39 which further indicate that the quenching type between the polymer and palladium ions is static quenching. Metal ions will continuously cooperate with polymer molecules and form polymer-metal complexes with increasing concentration. Until the concentration of Pd²⁺ reaches 2×10^{-5} M, the metal ions and polymer molecules are completely combined to form 1:1 complex. The K_{SV} quenching constant values about 7.80×10^4 M⁻¹, $R^2 > 0.99$ of the nonlinear fitting result proves that the fitting equation coincides with static quenching type between PPBIBTE and Pd²⁺.

Accordingly, the above researches prove that polymer molecules can form a 1:1 complex with Pd^{2+} , and the association constant *K* is determined by the following Benesi-Hilderbrand eq 3:

$$\frac{1}{F_0 - F} = \frac{1}{K \times (F_0 - F_{\min}) \times [Q]^n} + \frac{1}{F_0 - F_{\min}}$$
(3)



FIGURE 8 Job's plot of a 1:1 complex formed between PPBIBTE and Pd²⁺. [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 9 (a) The plot of ln (F_0/F) versus the concentrations of Pd²⁺; (b) The Benesi–Hildebrand plot of PPBIBTE with Pd²⁺. [Color figure can be viewed at wileyonlinelibrary.com]





FIGURE 10 Two primary repeating units configuration of PPBIBTE and energy-level diagram which showing band gap and topographical representation of monomers and different polymer repeat units. [Color figure can be viewed at wileyonlinelibrary.com]

where F_0 and F are the fluorescence intensities in the absence and presence of Pd^{2+} , and F_{min} is the minimum fluorescence intensity in the presence of Pd^{2+} , [Q] is the concentration of Pd^{2+} and n is the stoichiometric ratio of fluorescence molecules to quencher which is 1 between PPBIBTE and Pd^{2+} . The association constant K was evaluated graphically in Figure 9 (b) by plotting $1/(F_0 - F)$ against $1/[Pd^{2+}]$ and obtained from the slope and intercept of the line, and the value is about $1.78 \times 10^4 \text{ M}^{-1}$. Both the association constant and quenching constant are higher than what has been reported,^{40,41} and the polymer has realized the specificity detection of palladium ions. These results indicate that polymer PPBIBTE has a good recognition for Pd^{2+} .

Theoretic Calculation

To provide an insight into the molecular architecture of the monomers and model compound of polymer, the molecular simulation was carried out for these molecules with a chain length of n = 1 using density functional theory at the RB3LYP/6-31g(D) level with the Gaussian 09 program package. The asymmetric structure of the benzimidazole unit can result in different repeat units in the polymer main chain, and two primary atomic arrangements are listed in Figure 10. Using the theoretic calculation to get the molecular orbital configuration and band gap of monomers and the polymer repeat units. It is obvious to observe that the LUMO of P-repeat unit-1 and P-repeat unit-2 were mainly located in the benzothiadiazole unit, and the orbital morphology was consistent with the LUMO of monomer 1, suggesting that the LUMO formation of the polymer was determined by benzothiadiazole unit and the band gaps can be reduced in

this situation compared with monomer 2. Meanwhile, the HOMO of both repeat units are roughly distributed throughout the molecular chain, while the HOMO of P-repeat unit-2 are more uniform, which indicates that the intramolecular charge is transferred from the benzimidazole unit to the benzothiadiazole unit.⁴²

Electrochemical Properties

In order to investigate the electronic properties of PPBIBTE and make comparisons of HOMO, LUMO, and $E_{\rm g}$ levels between practical and theoretical results, the CV experiment which is an important electrochemical method for measuring the oxidation and reduction potentials for CPs was performed. All the potentials are reported versus Ag/Ag⁺ with the ferrocene/ferrocenium couple as an internal standard. The onset potentials of CV plot can be used to determine the HOMO, LUMO, and band gap energy levels. Onset potentials were defined as the potential at which 10% or 20% of the current value at the peak potential was reached.⁴³ As it shown in Figure 11, the oxidation potential (E_{ox}^{onset}) is 0.67 V versus Ag/Ag⁺ while the onset reduction potential ($E_{\rm red}^{\rm onset}$) is -0.60 V versus Ag/Ag⁺. From the $E_{\rm ox}^{\rm onset}$ and $E_{\rm red}^{\rm onset}$ of the polymers, the HOMO and LUMO energy levels of the PPBIBTE can be calculated from the following eqs 4 and 5 (Figure 11):^{44,45}

$$E_{\rm HOMO} = -e \left(4.71 + E_{\rm ox}^{\rm onset} \right) \tag{4}$$

$$E_{\rm LUMO} = -e \left(4.71 + E_{\rm red}^{\rm onset} \right) \tag{5}$$



FIGURE 11 Cyclic voltammogram of PPBIBTE film on a glassy carbon electrode in $0.1 \text{ M Bu}_4\text{NCIO}_4$, CH_2Cl_2 solution. [Color figure can be viewed at wileyonlinelibrary.com]

Therefore, the HOMO energy level of PPBIBTE is -5.38 eV while the LUMO energy level is -4.11 eV. Thus, the band gap (Eg) is 1.27 eV for PPBIBTE. These MO results of polymer was in agreement with the theoretic result. But the LUMO energy level of polymer obviously decreases with the increasing chain length compared with repeat unit, which indicates the strong electron-withdrawing ability of benzothiadiazole.

CONCLUSIONS

In summary, we have successfully synthesized, characterized, and developed a readily available conjugated polymer PPBIBTE. This polymer can exhibit favorable dissolving capacity in conventional organic solvents. The GPC result shows that it has appropriate molecular weights. PPBIBTE can be a novel fluorescence "turn-off" chemosensor with a higher selectivity for Pd²⁺ in THF solution over other metal ions. The fluorescence intensity was significantly quenched about 97% with the addition of 20 µM of Pd2+. The Stern-Volmer, Benesi-Hildebrand plots and job's method collectively proved that the fluorescence quenching originated the 1:1 PPBIBTE-Pd²⁺ complex, with quenching constant values about $7.80\times10^4\:M^{-1}$ and association constant values about 1.78×10^4 M⁻¹. The theoretic calculation indicates that the LUMO and band gap of PPBIBTE can be determined by benzothiadiazole unit. This result can approve that benzothiadiazole in the main chain can affect the photoelectrical properties of polymers and improve its sensing ability.

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