

Synthesis of conjugated polymers bearing pendant bipyridine ruthenium complexes



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ABSTRACT

Conjugated polymers bearing pendant bipyridine groups, **PM1PT-x**, were synthesized in high yield from a carefully designed dibromocarbazole monomer **M1** using a Suzuki coupling reaction with a phenothiazine diborate monomer. **PM1PT-x**, where **x** is the mole percentage of **M1** in the total feed of dibromo-monomers and varied to levels of 25%, 50%, 75% and 100%, was reacted with a ruthenium complex to yield conjugated polymers bearing pendant bipyridine ruthenium complexes, **PM1PT-x-Ru**. The introduction of ruthenium complexes extended the absorption of **PM1PT-x-Ru** to the visible light region. Furthermore, these polymers demonstrated sufficient stability and suitable energy levels to potentially be highly efficient photoactive materials for polymeric solar cells.

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1. Introduction

Polymeric materials have played increasingly important roles in meeting the requirements of modern society due to their tunable optoelectronic properties, flexibility, ease of processing and good cost efficiency [1–5]. For synthetic chemists, it is important to design new strategies to simplify the synthesis of functional polymers in order to increase development in corresponding applications. With an increasing demand for cheap renewable energy sources, synthetic polymers have been thoroughly explored as photovoltaic materials [6–8] in recent years. In comparison with their traditional inorganic counterparts, polymeric solar cells (PSCs) have the potential advantage of fabrication on flexible and lightweight substrates using roll-to-roll solution processing, providing cost-effective production [9–11]. However, their power conversion efficiency (PCE), the most important parameter for solar cells, is still insufficient for many practical applications. The relatively mismatched and narrow absorption band of most polymers is one of the main reasons for the low PCE [12–14].

It is well known that some transition metal complexes show strong broad absorption in the visible light region, and these complexes have been frequently used as photosensitizers in dye-sensitized solar cells [15–20]. In literature, several strategies

incorporating transition metal complexes into organic conjugated polymers to improve their optical absorption have also been found, as shown in Chart 1. In most of these strategies, transition metal complexes were incorporated in the polymer main chain (types a and b, Chart 1). However, the charge transfer ability of the conjugated main chain would be affected by the blocking of the embedded metal complexes, which may decrease the PCE in some instances [21–24]. An alternative approach is to link the metal complexes to the side chain of the conjugated polymers through a flexible linkage (type c, Chart 1), which allows for simultaneous extended absorption and high PCE because the charge transfer ability of the main chain and the light harvesting ability of the metal complex would not interfere with each other. However, this approach is rarely used in literature [25,26], possibly due to difficulty in synthesis. As reported in the literature [25], no polymer was obtained directly by the polymerization of monomers containing a metal complex. Thus, it is vital to develop an appropriate and simple way to synthesize this type of polymer.

In this paper, we prepared a series of conjugated polymers, **PM1PT-x-Ru**, with metal complexes linked as pendant groups via a flexible chain. The conjugated main chains consisted of carbazole and phenothiazine moieties, giving the polymers good hole-transporting ability [27,28]. The ruthenium complex, which is one of the most studied metal complexes in this area due to its potential in solar energy conversion [15,29], is linked to the conjugated main chain via a flexible spacer. Thus, the light harvesting ability of ruthenium complexes is combined with the excellent charge

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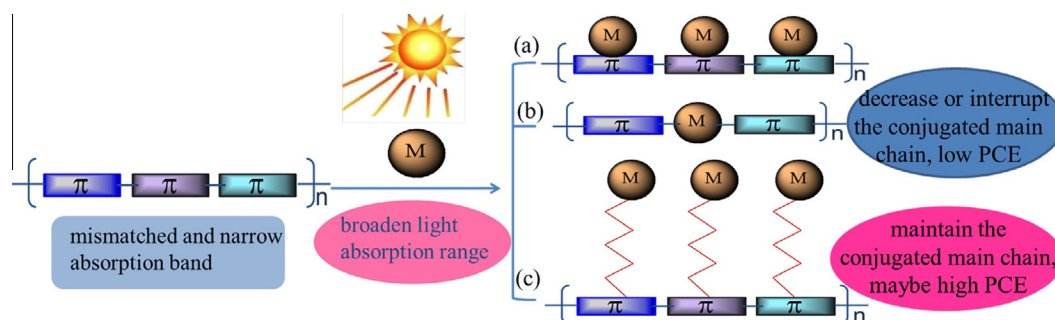


Chart 1. The original idea of this work and different types of conjugated polymers containing metal complexes.

transfer ability of the conjugated backbone in one molecule. Encouragingly, thin films of the obtained polymers showed a broad absorption peak centered at approximately 540 nm. Furthermore, these polymers demonstrated good stability and suitable energy level. Coupled with their extended absorption spectra, these polymers should be suitable candidates for fabricating PSCs. Herein, we present the synthesis and characterization of these polymers.

2. Experiment

2.1. Materials

4,4'-Dimethyl-2,2'-bipyridine and $[\text{RuCl}_2(\text{p-cymene})_2]$ were purchased from Acros. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was purchased from Alfa Aesar. 3,6-Dibromo-9-(6-bromohexyl) carbazole (**1**) [30], 4-hydroxymethyl-4'-methyl-2,2'-bipyridine (**2**) [31], monomers **M2** [32] and **M3** [32], and 2,2'-bipyridine-4,4'-dicarboxydiethylester (**6**) [33] were synthesized according to literature procedures. All other reagents were used as received.

2.2. Instruments

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-400 (400 MHz) NMR spectrometer. FT-IR spectra were conducted with a Nicolet Protégé 460 infrared spectrometer on a KBr disc. Elemental analyses were carried out on an EA 1110 CHNSO elemental analysis system. Mass spectra were recorded on a Micromass Q-ToF mass spectrometer. Gel permeation chromatography (GPC) analysis was performed on an HLC-8220 liquid chromatograph calibrated with polystyrene standards using THF as eluent. Thermogravimetric analysis (TGA) was determined with a NETZSCH DSC-204 calorimeter at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ with a nitrogen flow from room temperature to $600\text{ }^\circ\text{C}$. UV-vis absorption spectra were obtained on a Shimadzu UV-3010 instrument. Cyclic voltammetry (CV) was measured on a RST 3000 electrochemistry workstation with a three-electrode system, consisting of a Teflon-shrouded 3 mm glassy carbon electrode, a saturated calomel electrode and a platinum wire as the working, reference and counter electrodes, respectively. Distilled dimethylformamide (DMF) was used as the solvent, which was deoxygenated with argon prior to the measurement. Then, 0.1 M of tetrabutylammonium tetrafluoroborate (TBABF_4) was used as the supporting electrolyte, and the scan rate of all measurements was 100 mV s^{-1} .

2.3. Synthesis of intermediates and monomers

The synthesis of different intermediates and monomers are presented in Scheme 1. The monomer **M1** is a dibromo-carbazole linked with a bipyridine group via a flexible spacer, which was

carefully designed and not previously reported. A low molar mass ruthenium complex, **Ru-bpy**, was also synthesized as a model compound.

2.3.1. Synthesis of monomer **M1**

A mixture of compound **1** (0.976 g, 2.00 mmol), compound **2** (0.400 g, 2.00 mmol), potassium hydroxide (0.281 g, 5.00 mmol), potassium iodide (13 mg), 18-crown-6 (11 mg), and DMF (20 mL) was stirred at $105\text{ }^\circ\text{C}$ for 24 h under argon. The mixture was then poured into water and extracted using CHCl_3 , followed by washing with water. The organic phase was separated and dried overnight with anhydrous MgSO_4 . Solvents were removed by evaporation, and the obtained residue was purified by silica gel column chromatography using a mixed solvent of hexane, ethyl acetate and triethylamine (1:1:0.01, v/v/v) as eluent to give a white powder of **M1** (1.060 g, Yield: 87.3%). ^1H NMR (400 MHz, CDCl_3 , δ , ppm): 8.63 (d, $J = 4.9\text{ Hz}$, 1H, ArH), 8.50 (d, $J = 4.9\text{ Hz}$, 1H, ArH), 8.32 (s, 1H, ArH), 8.23 (s, 1H, ArH), 8.13 (d, $J = 1.5\text{ Hz}$, 2H, ArH), 7.53 (dd, $J = 8.7, 1.6\text{ Hz}$, 2H, ArH), 7.29 (d, $J = 4.7\text{ Hz}$, 1H, ArH), 7.24 (s, 2H, ArH), 7.12 (d, $J = 4.8\text{ Hz}$, 1H, ArH), 4.56 (s, 2H, Ar- CH_2O -), 4.24 (t, $J = 7.1\text{ Hz}$, 2H, $-\text{CH}_2\text{N}$), 3.48 (t, $J = 6.3\text{ Hz}$, 2H, $-\text{CH}_2\text{O}$ -), 2.44 (s, 3H, Ar- CH_3 -), 1.83 (m, 2H, $-\text{CH}_2-$), 1.60 (m, 2H, $-\text{CH}_2-$), 1.49–1.27 (m, $J = 10.4\text{ Hz}$, 4H, $-\text{CH}_2-$). ^{13}C NMR (100 MHz, CDCl_3 , δ , ppm): 156.3, 155.8, 149.3, 149.0, 148.3, 139.3, 129.1, 124.8, 123.5, 123.3, 122.1, 121.9, 119.4, 112.0, 110.4, 71.4, 70.8, 43.2, 29.5, 28.8, 27.0, 26.0, 21.2. MS (ES-TOF) Calcd for $[\text{C}_{30}\text{H}_{29}\text{N}_3\text{OBr}_2 + \text{H}]$ 608.39; found 608.07. Anal. Calcd for $\text{C}_{30}\text{H}_{29}\text{N}_3\text{OBr}_2$: C, 59.33; H, 4.81; N, 6.92. Found: C, 59.16; H, 4.83; N, 6.89.

2.3.2. Synthesis of the model compound, **Ru-bpy**

The synthesis of the low molar mass ruthenium complex **Ru-bpy** was conducted similarly to as described in literature [34]. Compound **2** (60 mg, 0.30 mmol) was added to a DMF (30 mL) solution of compound **5** (87 mg, 0.15 mmol) in a flask protected by argon flushing, and stirred at $80\text{ }^\circ\text{C}$ for 4 h without exposure to light. Subsequently, compound **6** (83 mg, 0.30 mmol) was added and the reaction mixture was stirred at $140\text{ }^\circ\text{C}$ for 4 h. Finally, an excess of NH_4NCS (46 mg, 0.60 mmol) was added to the resulting deep black solution and the reaction continued for another 4 h at the same temperature. Subsequently, the reaction mixture was cooled to room temperature and the solvent was removed. Water was added to resuspend the precipitate, which was collected and washed with water and ethanol several times, and then dried under vacuum to yield a black powder of **Ru-bpy**. (136 mg, Yield: 83.1%). From the ^1H NMR spectrum, the product of **Ru-bpy** could be recognized as a mixture of stereoisomers. ^1H NMR (400 MHz, DMSO, δ , ppm): 9.50 (d, $J = 5.5\text{ Hz}$, 2H, ArH), 9.21 (m, 2H, ArH), 9.09–8.97 (m, 4H, ArH), 8.68 (s, 2H, ArH), 8.52 (s, 2H, ArH), 8.36 (m, 2H, ArH), 8.03–7.78 (m, 4H, ArH), 7.74–7.54

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