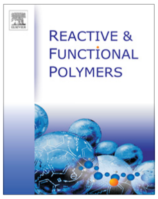
Reactive & Functional Polymers 90 (2015) 7–14

Contents lists available at ScienceDirect

Reactive & Functional Polymers

journal homepage: www.elsevier.com/locate/react



Synthesis of conjugated polymers bearing pendant bipyridine ruthenium complexes

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ARTICLE INFO

Article history:
Received 22 November 2014
Received in revised form 25 February 2015
Accepted 26 February 2015
Available online 22 March 2015

Keywords:
Conjugated polymer
Ruthenium complex
Carbazole
Phenothiazine

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.

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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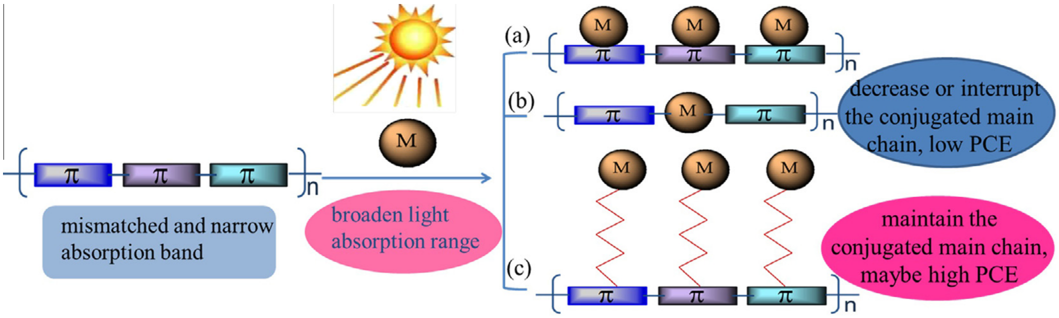


Chart 1. The original idea of this work and different types of conjugated polymers containing metal complexes.

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 $[RuCl_2(p\text{-cymene})]_2$ 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

^{1}H 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 °C min^{-1} with a nitrogen flow from room temperature to 600 °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

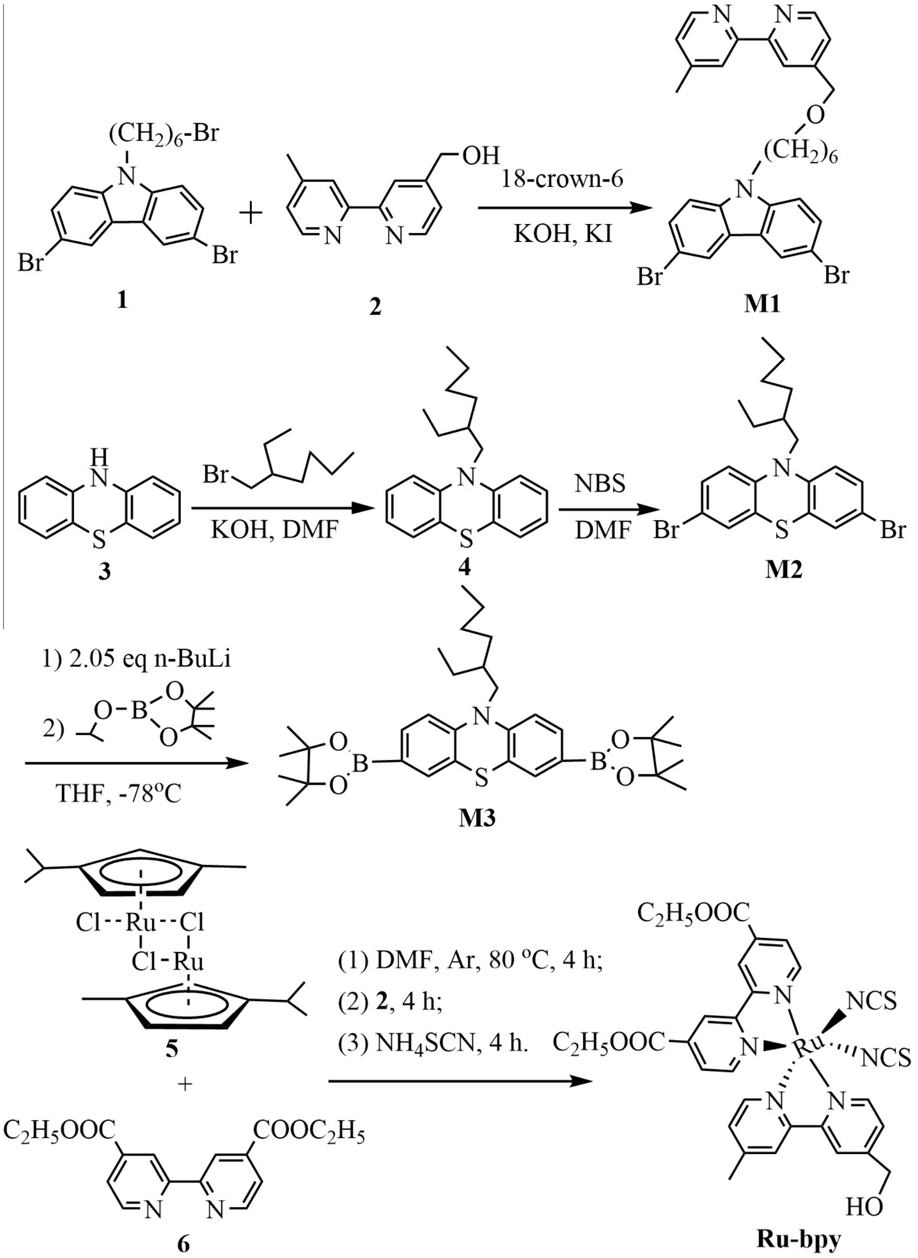
The synthesis of different intermediates and monomers are presented in Scheme 1. The monomer **M1** is a dibromo-carbazole linked with a bipyridine group *via* a flexible spacer, which was carefully designed and not previously reported. A low molar mass ruthenium complex, **Ru-bpy**, was also synthesized 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 °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%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.63 (d, J = 4.9 Hz, 1H, ArH), 8.50 (d, J = 4.9 Hz, 1H, ArH), 8.32 (s, 1H, ArH), 8.23 (s, 1H, ArH), 8.13 (d, J = 1.5 Hz, 2H, ArH), 7.53 (dd, J = 8.7, 1.6 Hz, 2H, ArH), 7.29 (d, J = 4.7 Hz, 1H, ArH), 7.24 (s, 2H, ArH), 7.12 (d, J = 4.8 Hz, 1H, ArH), 4.56 (s, 2H, Ar—CH_2O—), 4.24 (t, J = 7.1 Hz, 2H, —CH_2N), 3.48 (t, J = 6.3 Hz, 2H, —CH_2O—), 2.44 (s, 3H, Ar—CH_3—), 1.83 (m, 2H, —CH_2—), 1.60 (m, 2H, —CH_2—), 1.49–1.27 (m, J = 10.4 Hz, 4H, —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 $[C_{30}H_{29}N_3OBr_2 + H]$ 608.39; found 608.07. Anal. Calcd for $C_{30}H_{29}N_3OBr_2$: 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 °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 °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 ^{1}H NMR spectrum, the product of **Ru-bpy** could be recognized as a mixture of stereoisomers. ^{1}H NMR (400 MHz, DMSO, δ, ppm): 9.50 (d, J = 5.5 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



Scheme 1. Synthesis of the monomers **M1–M3** and the model compound **Ru-bpy**.

(m, 4H, ArH), 7.30 (s, 2H, ArH), 7.19 (d, J = 11.2 Hz, 2H, ArH), 7.06 (s, 2H, ArH), 5.89 (s, 1H, —OH), 5.64 (s, 1H, —OH), 4.90 (s, 2H, Ar—CH_2—), 4.61 (s, 2H, Ar—CH_2—), 4.51 (s, 2H, —CH_2—), 4.37 (d, J = 7.0 Hz, 2H, —CH_2—), 2.68 (s, 3H, Ar—CH_3), 2.41 (s, 3H, Ar—CH_3), 1.45 (t, J = 6.7 Hz, 6H, —CH_3), 1.30 (dd, J = 17.5, 11.4 Hz, 6H, —CH_3). IR (KBr disc): ν (SCN): 2102 cm^{-1}, ν (COO): 1723 cm^{-1}, ν (C=N): 1613 cm^{-1}, ν (C=C): 1400 cm^{-1}.

2.4. Synthesis of polymers bearing pendant bipyridine groups, ***PM1PT-x***

Some carbazole-based copolymers have been synthesized upon Suzuki coupling reaction between dibromo-monomers and diborate monomer using palladium as catalyst [35,36]. Jayakannan et al. [37] reported that polymers obtained using $Pd(OAc)_2$ as catalyst contain chains with various combinations of end groups. While using $Pd(PPh_3)_4$ the number of different end groups was significantly reduced. Therefore, the conjugated polymers bearing pendant bipyridine groups *via* a flexible spacer, **PM1PT-x**, were synthesized using a Suzuki coupling reaction of the dibromo-monomers **M1** and **M2** in different molar ratios with the diborate monomer **M3** using $Pd(PPh_3)_4$ as catalyst. The resulting polymers were named as **PM1PT-x**, with x-values of 25, 50, 75 and 100, representing the molar percentage of **M1** in the total feed dibromo-monomers.

Taking **PM1PT-25** as an example, the typical synthetic procedure was as follows. **M1** (0.152 g, 0.25 mmol), **M2** (0.352 g, 0.75 mmol), **M3** (0.563 g, 1.00 mmol), tetrakis(triphenylphosphine)palladium (0) (26 mg) and tetrabutylammonium bromide (0.200 g) were mixed in a Schlenk tube under argon atmosphere. THF (20 mL) was added and the mixture was degassed by freeze-pump-thaw cycle three times. Cesium carbonate aqueous solution (2.00 g in 3 mL water) was added and the mixture was heated at 60 °C for 7 days. Then, the mixture was dropped into methanol and filtered.

The polymer was dissolved in THF and re-precipitated from methanol three times, and finally dried in vacuum oven overnight. **PM1PT-25** was obtained as a pale yellow powder (0.547 g, Yield: 83.2%). ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 8.73–6.78 (ArH), 4.63–4.49 (Ar—CH$_2$O—), 4.39–4.20 (carbazole—NCH$_2$—), 3.86–3.64 (phenothiazine—NCH$_2$—), 3.56–3.38 (—CH$_2$O—), 2.52–2.35 (Ar—CH$_3$), 2.11–1.15 (—CH$_2$—), 0.98–0.73 (—CH$_3$). $M_w = 6.36 \times 10^3$, $PDI = 1.94$ (GPC). Anal. Calcd for ($C_{42.5}H_{49.5}N_{2.5}O_{0.25}S_{1.75}$): C, 77.92; H, 7.32; N, 5.35. Found: C, 77.81; H, 7.08; N, 5.17.

PM1PT-50. **M1** (0.304 g, 0.50 mmol), **M2** (0.235 g, 0.50 mmol) and **M3** (0.563 g, 1.00 mmol) were charged for the polymerization. **PM1PT-50** was obtained as a pale yellow powder (0.434 g, Yield: 81.2%). ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 8.68–6.78 (ArH), 4.63–4.49 (Ar—CH$_2$O—), 4.39–4.20 (carbazole—NCH$_2$—), 3.86–3.64 (phenothiazine—NCH$_2$—), 3.56–3.38 (—CH$_2$O—), 2.52–2.35 (Ar—CH$_3$), 2.11–1.12 (—CH$_2$—), 0.98–0.73 (—CH$_3$). $M_w = 4.46 \times 10^3$, $PDI = 1.57$ (GPC). Anal. Calcd for ($C_{45}H_{51}N_3O_{0.5}S_{1.5}$): C, 78.37; H, 7.40; N, 6.10. Found: C, 78.26; H, 7.39; N, 6.07.

PM1PT-75. **M1** (0.456 g, 0.75 mmol), **M2** (0.118 g, 0.25 mmol) and **M3** (0.563 g, 1.00 mmol) were charged for the polymerization. **PM1PT-75** was obtained as a pale yellow powder (0.573 g, Yield: 78.8%). ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm) 8.68–6.78 (ArH), 4.63–4.49 (Ar—CH$_2$O—), 4.39–4.20 (carbazole—NCH$_2$—), 3.86–3.64 (phenothiazine—NCH$_2$—), 3.56–3.38 (—CH$_2$O—), 2.52–2.35 (Ar—CH$_3$), 2.11–1.12 (—CH$_2$—), 0.98–0.73 (—CH$_3$). $M_w = 3.23 \times 10^3$, $PDI = 1.50$ (GPC). Anal. Calcd for ($C_{47.5}H_{52.5}N_{3.5}O_{0.75}S_{1.25}$): C, 78.95; H, 7.27; N, 6.78. Found: C, 78.43; H, 7.31; N, 6.25.

PM1PT-100. **M1** (0.608 g, 1.00 mmol) and **M3** (0.563 g, 1.00 mmol) were charged for the polymerization. **PM1PT-100** was obtained as a pale yellow powder (0.560 g, Yield: 73.6%). ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm) 8.73–6.82 (ArH), 4.63–4.49 (Ar—CH$_2$O—), 4.39–4.20 (carbazole—NCH$_2$—), 3.86–3.64 (phenothiazine—NCH$_2$—), 3.56–3.38 (—CH$_2$O—), 2.52–2.35 (Ar—CH$_3$), 2.19–1.05 (—CH$_2$—), 0.98–0.73 (—CH$_3$). $M_w = 7.78 \times 10^3$, $PDI = 1.98$ (GPC). Anal. Calcd for ($C_{50}H_{54}N_4OS$): C, 79.16; H, 7.12; N, 7.39. Found: C, 78.86; H, 7.08; N, 7.17.

2.5. Synthesis of Ru-containing polymers, *PM1PT-x-Ru*

As shown in Scheme 2, the Ru-containing polymers **PM1PT-x-Ru** were synthesized by adding compound **6**, NH$_4$SCN and **PM1PT-x** in sequence to the DMF solution of Ru-complex **5**. The obtained polymers **PM1PT-x-Ru**, where $x = 25$, 50, 75 and 100, were extracted in a Soxhlet extractor to remove the unreacted low molar mass compounds.

Taking **PM1PT-25-Ru** as an example, compound **6** (0.083 g, 0.30 mmol) was added to a DMF (30 mL) solution of compound **5** (0.087 g, 0.15 mmol) in a flask protected by argon flushing, and stirred at 80 °C for 4 h under reduced light. Subsequently, NH$_4$NCS (0.046 g, 0.60 mmol) was added, and the reaction mixture was refluxed for 4 h. Finally, polymer **PM1PT-25** (0.658 g, 0.25 mmol bipyridine units) was added to the resulting black solution, and the reaction mixture was refluxed for another 4 h. The reaction mixture was cooled to room temperature and added dropwise into 150 mL methanol. The polymer precipitate was collected by filtration and washed with large amount of water, methanol and acetone. The product was further purified by washing it with a mixed solution (methanol/acetone = 1:1) in a Soxhlet extractor for 2 days to remove any residual low molar mass compounds. **PM1PT-25-Ru** was obtained as a brownish black powder (0.627 g, Yield: 80.1%). IR (KBr disc): v (SCN): 2100 cm^{-1}, v (COO): 1720 cm^{-1}. Anal. Calcd for ($C_{47}H_{53.5}N_{3.5}O_{1.25}S_{2.25}Ru_{0.25}$): C, 71.96; H, 6.83; N, 6.25. Found: C, 71.62; H, 6.80; N, 6.09.

PM1PT-50-Ru Compound **5** (0.087 g, 0.15 mmol), compound **6** (0.083 g, 0.30 mmol), NH$_4$NCS (0.046 g, 0.60 mmol) and **PM1PT-50** (0.268 g, 0.25 mmol bipyridine units) were charged for the reaction. **PM1PT-50-Ru** was obtained as a brownish black powder (0.403 g, Yield: 85.4%). IR (KBr disc): v (SCN): 2100 cm^{-1}, v (COO): 1720 cm^{-1}. Anal. Calcd for ($C_{54}H_{59}N_5O_{2.5}S_{2.5}Ru_{0.5}$): C, 68.39; H, 6.23; N, 7.39. Found: C, 67.76; H, 6.30; N, 7.29.

PM1PT-75-Ru Compound **5** (0.175 g, 0.30 mmol), compound **6** (0.166 g, 0.60 mmol), NH$_4$NCS (0.092 g, 1.20 mmol) and **PM1PT-75** (0.484 g, 0.50 mmol bipyridine units) were charged for the reaction. **PM1PT-75-Ru** was obtained as a black powder (0.615 g, Yield: 83.6%). IR (KBr disc): v (SCN): 2101 cm^{-1}, v (COO): 1720 cm^{-1}. Anal. Calcd for ($C_{61}H_{64.5}N_{6.5}O_{3.75}S_{2.75}Ru_{0.75}$): C, 65.86; H, 5.80; N, 8.19. Found: C, 65.46; H, 5.96; N, 7.85.

PM1PT-100-Ru Compound **5** (0.175 g, 0.30 mmol), compound **6** (0.166 g, 0.60 mmol), NH$_4$NCS (0.092 g, 1.20 mmol) and **PM1PT-100** (0.381 g, 0.50 mmol bipyridine units) were charged for the reaction. **PM1PT-100-Ru** was obtained as a black powder (0.553 g, Yield: 86.3%). IR (KBr disc): v (SCN): 2102 cm^{-1}, v (COO): 1720 cm^{-1}. Anal. Calcd for ($C_{68}H_{70}N_8O_5S_3Ru$): C, 64.04; H, 5.49; N, 8.78. Found: C, 64.56; H, 5.60; N, 8.09.

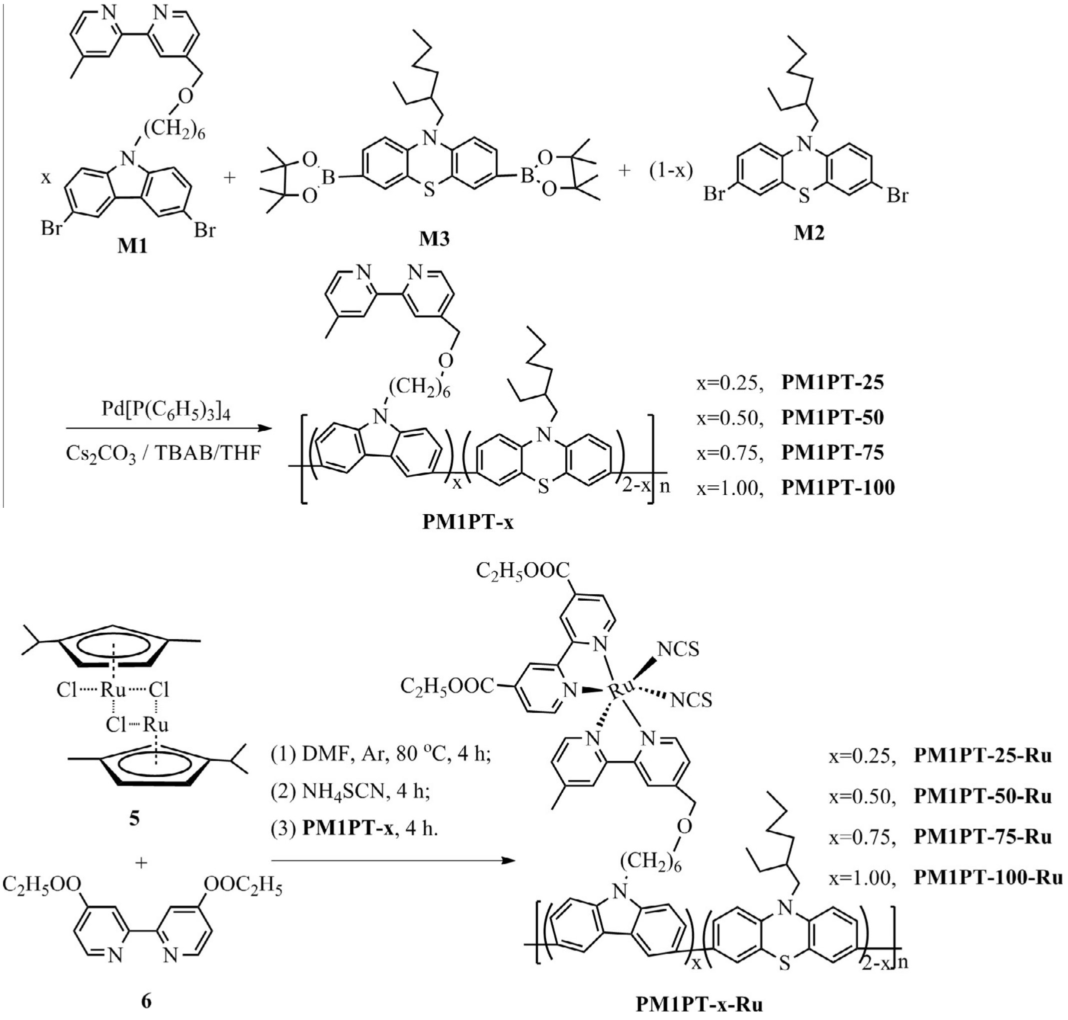
3. Results and discussion

3.1. Synthesis of monomer *M1*

The synthetic routes to the monomers and polymers are presented in Schemes 1 and 2. **M1** was synthesized using a Williamson reaction between compounds **1** and **2** in the presence of potassium hydroxide, potassium iodide and 18-crown-6. When only using strong alkali NaH or weak alkali K$_2$CO$_3$ in DMF without potassium iodide and 18-crown-6, the yield of **M1** was very low. When M1 was synthesized by a Williamson reaction between 6-bromohexyl carbazole and compound 2, then brominated by NBS, the post-treatment of **M1** was very difficult. The ^{1}H NMR spectrum of **M1** is shown in Fig. 1. The peaks at 3.49 ppm and 4.57 ppm may be assigned to the protons of the alkoxy group linked to the hexyl group (—(CH$_2$)$_5$—CH$_2$O—, marked i in Fig. 1) and bipyridine (—OCH$_2$—bpy, marked j in Fig. 1), respectively. Their integrated area ratio was 1:1, which is consistent with the theoretical value, indicating the successful synthesis of **M1**. Furthermore, the chemical structure of **M1** was also confirmed by ^{13}C NMR, elemental analysis and MS measurements.

3.2. Synthesis of polymers bearing pendant bipyridine groups, *PM1PT-x*

The conjugated polymers were prepared by Suzuki polycondensation between the dibromo-monomers **M1** and **M2** and the diborate monomer **M3**. The obtained conjugated polymers were named as **PM1PT-25**, **PM1PT-50**, **PM1PT-75** and **PM1PT-100**, corresponding to the molar percentage of **M1** in the dibromo-monomer feed. Fig. 1 shows the ^{1}H NMR spectra of monomer **M1** and all **PM1PT-x** polymers. In the ^{1}H NMR spectra of the polymers, the chemical shifts were consistent with the proposed polymer structure as demonstrated in Scheme 2, although they demonstrated a tendency for signal broadening due to polymerization. Furthermore, the content of relative monomers was also calculated from the integration ratios of the peaks to be 4.35 ppm (carbazole—NCH$_2$—, marked m in Fig. 1) and 3.83 ppm (phenothiazine—NCH$_2$—, marked n in Fig. 1). The mole ratio of carbazole units to phenothiazine units of **PM1PT-25**, **PM1PT-50**, **PM1PT-75** and **PM1PT-100** were estimated to be 1:7.01, 1:3.02, 0.6:1, and 1:1, respectively, and thus were very close to the calculated values x:(2 − x) expected from the corresponding **M1** in the dibromo-monomer feed (x = 25%, 50%, 75%, and 100%). The integration value of the signals originating from the bipyridine moiety of **M1** is 8.3–8.7 ppm, increasing with the increase of **M1** content in



Scheme 2. Synthesis of polymers **PM1PT-x** and **PM1PT-x-Ru**.

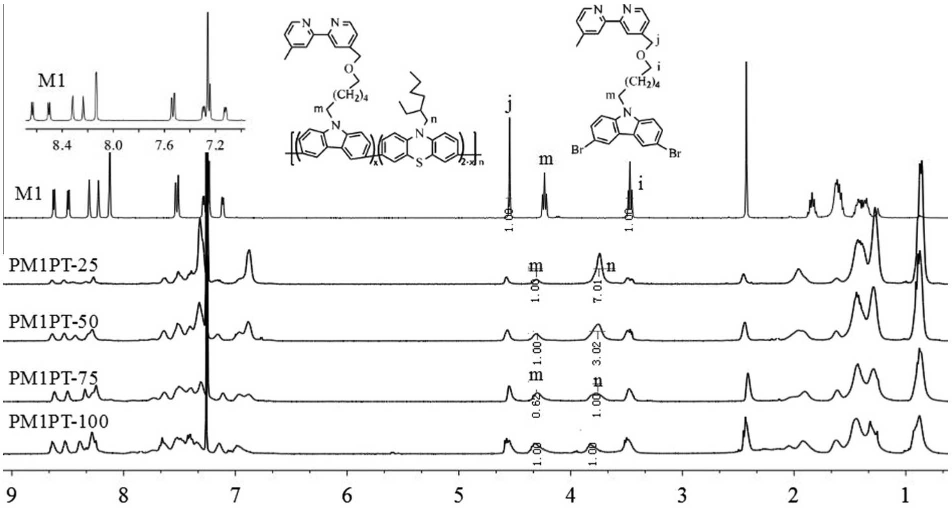


Fig. 1. ^{1}H NMR spectra of monomer **M1** and polymers **PM1PT-x** in $CDCl_3$.

the feed. This is more evident for successful polymerization. Furthermore, all elemental analyses of **PM1PT-x** were consistent with their corresponding calculated values according to the compositional formulae $[C_{(40+10x)}H_{(48+6x)}N_{(2+2x)}O_xS_{(2-x)}]$, where x = 25%, 50%, 75%, and 100%, further confirming the successful polymerization. The data of weight-averaged molecular weight (M_w) and polydispersity index (PDI) measured by GPC were summarized in Table 1. The M_w values ranged from 3230 to

7780, and the *PDI* values were in the range of 1.50–1.98, which are similar to the results of reported polymers prepared through Suzuki polycondensation [38–40].

3.3. Synthesis of Ru-containing polymers, **PM1PT-x-Ru**

The polymers **PM1PT-x-Ru** were prepared by a one-pot post-functionalization method. To avoid the occurrence of inter-chain crosslinking through macromolecular ligand chelation with metal ions, the feeding order of reagents was carefully arranged. First, dichloro-(*p*-cymene) ruthenium (II) dimer and compound **6** in DMF were added to a flask, and then NH_4NCS was added. At this stage, four of the six coordination sites of the ruthenium ion had been occupied by one bipyridine ligand and two thiocyanate ligands, and only two coordination sites were left for the coordination with the pendant bipyridine groups in the polymers **PM1PT-x**. Therefore, crosslinking through inter-chain coordination of macromolecular ligand with ruthenium ion could be avoided effectively. The Ru-containing polymers **PM1PT-x-Ru** were obtained in high yields, above 80%, and show fairly good solubility in some organic solvents, which could be further indication that inter chain coordination was avoided. Thus, by modifying the synthetic procedure, polymers **PM1PT-x-Ru** have been synthesized by a one-pot post-functionalization reaction, which is a novel simplified strategy to prepare this type of conjugated polymers with metal complexes linked to the pendant ligand through a flexible chain.

Fig. 2 is the FT-IR spectra of **PM1PT-x-Ru**. Compared to the metal-free polymers **PM1PT-x**, **PM1PT-x-Ru** have very strong absorption bands at approximately 2100 cm^{-1} and 1720 cm^{-1}, which could be ascribed to the -SCN group and —COO— group stretching vibration of the ruthenium complex, indicating the ruthenium complexes had been successfully introduced into the polymer. Furthermore, the elemental analysis results of **PM1PT-x-Ru** were very close to the theoretical value, indicating that almost all the bipyridine ligands in the polymers **PM1PT-x** have been converted into the corresponding ruthenium complexes.

3.4. Solubility and thermal properties

The metal-free polymers **PM1PT-x** showed good solubility in common organic solvents such as $CHCl_3$, THF, DMF, DMAc and DMSO. After coordinating with the ruthenium complex, the solubility of corresponding **PM1PT-x-Ru** decreased to some extent, but they are still soluble in some polar solvents such as DMF, DMAc and DMSO, indicating again that the modification of the synthetic procedure avoided inter-chain crosslinking of macromolecular ligands.

The thermal stability of the polymers under nitrogen atmosphere was evaluated by thermogravimetric analysis (TGA). Fig. 3(a) shows the TGA curves of ligand polymers **PM1PT-x**, with the temperature at 5% weight loss (T_d) summarized in Table 1. The T_d of **PM1PT-x** was in the range of 317–356 °C. With the content of **M1** units increased, the T_d of **PM1PT-x** showed a tendency to decrease, which might result from the ether linkage between the carbazole and bipyridine moieties in the monomer **M1** [41].

Table 1
Results of GPC, TGA and UV–vis measurements for all **PM1PT-x**.

PM1PT-x	M_w[a]	*PDI*[a]	T_d (°C)[b]	λ_{abs} (nm)[c]
PM1PT-25	6360	1.94	356	283, 370
PM1PT-50	4460	1.57	340	285, 363
PM1PT-75	3230	1.50	331	286, 351
PM1PT-100	7780	1.98	317	286, 338

[a] Estimated by GPC using THF as eluent calibrated by polystyrene standard.
[b] The temperature at 5% weight loss (T_d) determined by TGA under nitrogen atmosphere at a heating rate of 10 °C/min.
[c] The UV–vis absorption in a 2 mg/mL THF solution.

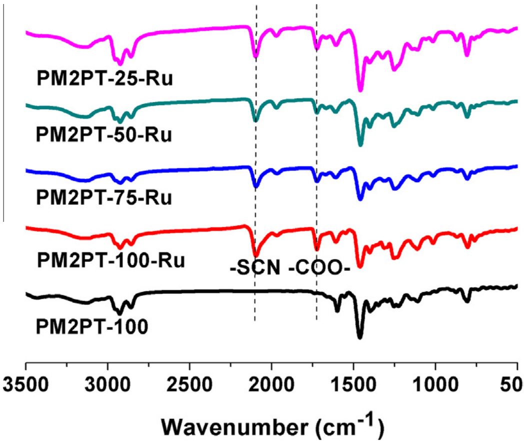


Fig. 2. FT-IR spectra of **PM1PT-x-Ru** (*x* = 25, 50, 75 and 100) in KBr disc.

Fig. 3(b) shows the TGA curves of the Ru-containing polymers **PM1PT-x-Ru** and the model compound **Ru-bpy** with the temperature at 5% weight loss (T_d) summarized in Table 2. The T_d values of **PM1PT-x-Ru** are in the range of 220–282 °C, much lower than those of the ligand polymer **PM1PT-x**. This decrease may possibly be due to the prior detachment of the thiocyanate ligands on the ruthenium complex [41]. With the increase in Ru content, the T_d of **PM1PT-x-Ru** also showed a tendency to decrease. Fortunately, the thermal stability of these Ru-containing polymers is much better than the model compound **Ru-bpy**, indicating the contribution of the conjugated polymeric main chain. Furthermore, this observation also indicated that our strategy to prepare this type of polymer was successful in some sense; otherwise, the thermal stability of the obtained polymers would be similar to that of the model compound **Ru-bpy**.

3.5. UV–vis absorption spectra

Fig. 4(a) shows the UV–vis absorption spectra of **PM1PT-x** in THF solution. A strong absorption peak centered at 285 nm and a shoulder peak in the range of 325–440 nm were observed. The peak at 285 nm resulted from the absorption of bipyridine-centered transitions. The shoulder peak may be assigned to the absorption of the conjugated main chain. With the increase of the carbazole moieties in **PM1PT-x**, the shoulder peak shifted from 370 nm to 338 nm, indicating the decreased effective conjugation length.

Fig. 4(b) shows the UV–vis absorption spectra of **PM1PT-x-Ru**, **PM1PT-100** and **Ru-bpy** in films. The polymer thin films were prepared by spin-coating a DMF solution (6 mg/mL) onto indium-tin-oxide (ITO) coated glass substrates at a rotating speed of 1200 RPM at room temperature, then drying the coated glass substrates in the oven. Compared with **PM1PT-100**, **PM1PT-100-Ru** showed a new broad peak centered at 528 nm with the full width at half maximum (FWHM) of 163 nm. This new peak of **PM1PT-100-Ru** is similar to the absorption peak at 556 nm of the model compound **Ru-bpy**, which was ascribed to the metal-to-ligand charge transfer (MLCT) of Ru-complex linked to the polymer chain [22,29]. The MLCT absorption peak is due to the promotion of an electron from the metal-centered d orbital to an unfilled ligand-centered π^* orbital. This result also indicated that the ruthenium complex moieties have been successfully incorporated into the polymer chain. Therefore, the objective of enhancing the photosensitivity of the polymeric materials into the visible region

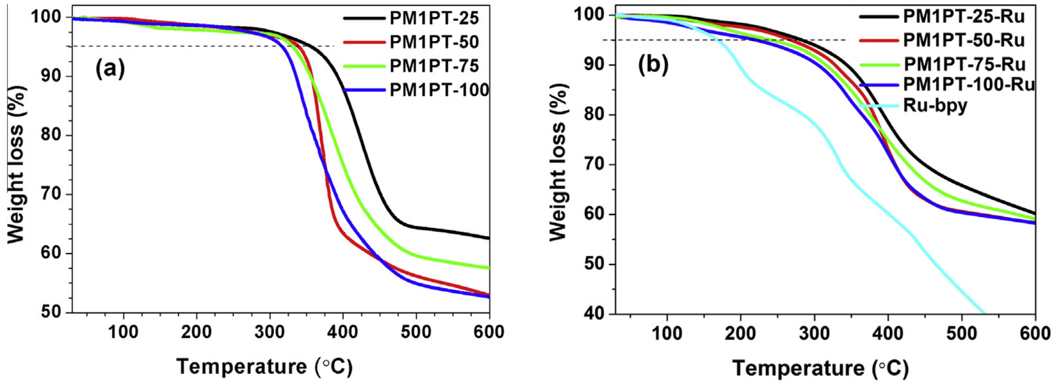


Fig. 3. The TGA curves of **PM1PT-x** (a), **PM1PT-x-Ru** and **Ru-bpy** (b) under nitrogen atmosphere at a heating rate of 10 °C min^{-1}.

Table 2
Data of TGA, UV–vis and CV measurements for **PM1PT-x-Ru** (x = 25, 50, 75, 100) and **Ru-bpy**.

PM1PT-x-Ru	T_d (°C)[a]	λ_{abs} (nm)[b]	E_{onset}^{ox}	E_{onset}^{red}	HOMO (eV)[c]	LUMO (eV)[c]	E_g (eV)[d]
PM1PT-25-Ru	282	298, 350, 550	0.60	−0.79	−5.34	−3.95	1.39
PM1PT-50-Ru	268	298, 349, 546	0.61	−0.75	−5.35	−3.99	1.36
PM1PT-75-Ru	241	298, 347, 540	0.62	−0.74	−5.36	−4.00	1.36
PM1PT-100-Ru	220	298, 346, 528	0.69	−0.73	−5.43	−4.01	1.42
PM1PT-100	317	296, 351	0.73	−0.74	−5.47	−4.00	1.47
Ru-bpy	170	297, 341, 555	0.64	−0.43	−5.38	−4.31	1.07

[a] Determined by TGA under nitrogen atmosphere at a heating rate of 10 °C/min.
[b] The UV–vis absorption maxima in solid film.
[c] Tested in 0.1 M DMF-$TBABF_4$ solution at 100 mV s^{-1} scan rate.
[d] Calculated by $E_g = (E_{LUMO} - E_{HOMO})$ eV.

was realized through the introduction of ruthenium complexes. The above characteristic d–π* MLCT transitions of all **PM1PT-x-Ru** polymers appeared at approximately 540 nm with FWHM in the range of 156–163 nm. The intensity of the MLCT bands increased with the increase in ruthenium complex content in **PM1PT-x-Ru**. In addition, the absorption maximum of the MLCT band shifted to shorter wavelengths when the ruthenium content increased, which was mainly attributed to the presence of intra- and inter-chain charge transfer complexes (CTC) in the condensed film state [42].

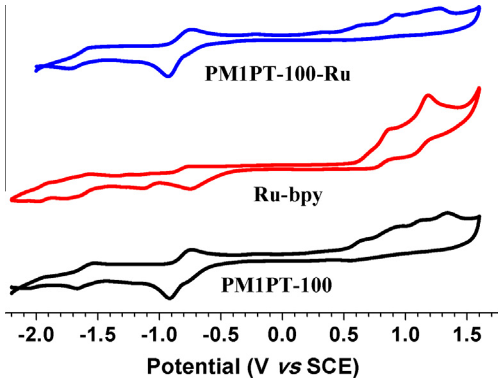


Fig. 5. CV curves of **PM1PT-100-Ru**, **Ru-bpy** and **PM1PT-100** dissolved in 0.1 M DMF-$TBABF_4$ with a scanning rate of 100 mV s^{-1}.

3.6. Electrochemical properties

Fig. 5 shows the cyclic voltammetry (CV) curves of **Ru-bpy**, **PM1PT-100**, and **PM1PT-100-Ru**, which were measured by CV using SCE as reference electrode in 0.1 M DMF-$TBABF_4$ solution at 100 mV s^{-1} scanning rate. The HOMO/LUMO energies were calculated from the oxidation and reduction potentials according to an empirical formula, $E_{HOMO} = -(E_{on}^{ox} + 4.74)$ (eV), $E_{LUMO} = -(E_{on}^{red} + 4.74)$ (eV) [43], and summarized in Table 2. The quasi-reversible oxidation waves of **Ru-bpy** complex could be assigned to the Ru(II/III) couple [26], and the reversible reduction waves could be assigned to the ligand-centered reduction of substituted bipyridines. The HOMO/LUMO of **Ru-bpy** was evaluated to be

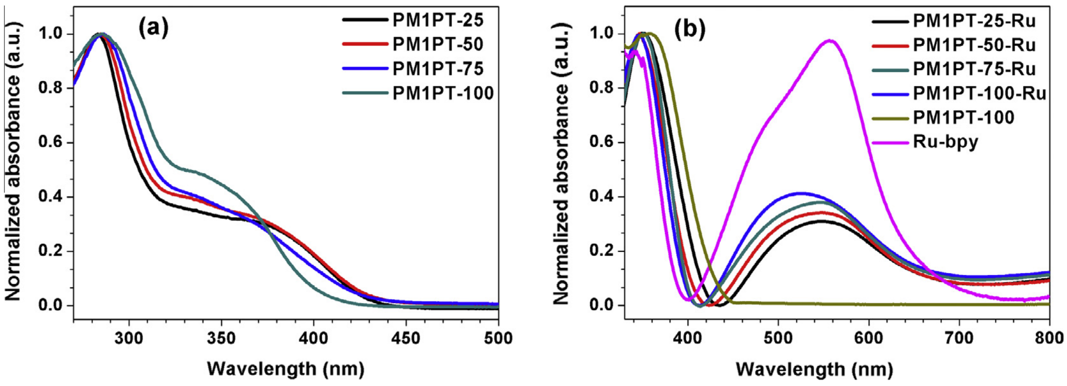


Fig. 4. UV–vis absorption spectra of **PM1PT-x** in THF solution (a) and **PM1PT-x-Ru**, **PM1PT-100** and **Ru-bpy** in films (b).

-5.38 eV and -4.31 eV, respectively. As for polymers **PM1PT-100** and **PM1PT-100-Ru**, their HOMO energy levels were -5.47 eV and -5.43 eV, respectively. The band gaps of **PM1PT-100** and **PM1PT-100-Ru** were calculated to be 1.47 eV and 1.42 eV, respectively. As listed in Table 2, all the E_g of **PM1PT-x-Ru** were in the range of 1.36–1.42 eV, which was consistent with the data reported in literature [44]. This result also suggested that ruthenium complexes were successfully introduced into the polymer chain and the obtained **PM1PT-x-Ru** possessed lower band gap and lower HOMO energy level [45].

4. Conclusion

A series of conjugated polymers **PM1PT-x** with pendant bipyridine groups were synthesized successfully *via* Suzuki coupling polycondensation using carbazole and phenothiazine as the main chain moieties. Through a one-pot post-functionalization reaction, ruthenium complexes were introduced into the polymer through a flexible spacer in high yields, which lead to a new simplified strategy to synthesize this special type of conjugated polymers with metal complex linked pendant groups through a flexible chain. Furthermore, after the incorporation of ruthenium complexes, the obtained Ru-containing polymers **PM1PT-x-Ru** exhibited broad absorption in the visible region, and possessed a narrow electrochemical band gap (approximately $1.36 \sim 1.42$ eV) and low HOMO energy level (about $-5.47 \sim -5.34$ eV), indicating that they are suitable candidates as photosensitive materials for solar cells.

Acknowledgement

We are grateful for the financial support of National Natural Science Foundation of China (NSFC) (20774088, 20874091, 21274133).

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