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Novel dye sensitizers of polymeric metal complexes with benzodithiophene derivatives as donor and their photovoltaic performance

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Abstract Four novel donor–acceptor (D-A) type conjugated polymeric metal complexes (**P1-P4**) bearing benzodithiophene or carbazole derivative as donors were synthesized, characterized and applied as dye sensitizers in dye-sensitized solar cells (DSSCs). Salicylaldehyde derivative complexes acted as electron acceptors, Zn (II) or Cd (II) was chosen as the coordinated metal ion, and diaminomaleonitrile was ancillary ligand in these structures. The thermal, photophysical, electrochemical and photovoltaic properties of these polymeric metal complexes were investigated by FT-IR, GPC, TGA, DSC, UV–vis absorption spectroscopy, Elemental analysis, cyclic voltammetry (CV), J-V curves and IPCE plots. These polymer dyes exhibit good thermal stability for their application in DSSCs. The DSSC device based on **P2** which containing benzodithiophene derivative as donor and Cd(II) as coordination ion, exhibited the highest power conversion efficiency of 2.43% (J_{sc} = 4.95 mA/cm², V_{oc} =0.71 V, FF=69.3%) under AM 1.5G solar irradiation. It indicates a new way to design dye sensitizers for DSSCs.

Keywords: dye-sensitized solar cell, polymeric metal complex, benzodithiophene

1. Introduction

Dye-sensitized solar cells are considered as one of the most promising next-generation photovoltaic cells, which can perform efficient conversion of solar energy directly into electricity [1]. Since first reported by Grätzel and O'Regan in 1991 with a power conversion efficiency of 7% [2], they have raised a great deal of attentions for their potential advantages of low cost, easy production, flexibility, and transparency in comparison with conventional silicon solar cells [3]. Recently, a high-performance perovskite-sensitized solar cell is reported with the power conversion efficiency over 15% [4].

As a crucial element of DSSCs, the dye sensitizer which is adsorbed on semiconducting TiO₂ anode, plays an important role in the performance of DSSCs. There are mainly two types of dyes, metal-organic dyes and metal-free organic dyes [5]. Ruthenium complex dyes are the typical metal-organic dyes, such as N719 [6], N3 [7], and black dye [8]. To date, a DSSC exhibits an excellent conversion efficiency of 11.5% by using Ru-based dye CYC-B11 [9]. However, the limited resource and high cost impede their development as dye sensitizers. Extensive research has been focused on organic dyes as promising candidates to Ru-based complexes dyes due to the advantage of inexpensive, high molar extinction coefficient and tunable absorption and electrochemical properties [10]. But organic dyes are less stable than metal complexes dyes, which can probably cause the formation of excited triplet states and unstable radicals under light irradiation. Hence, the idea of polymeric metal complexes dyes as metal-organic hybrid polymer materials used for DSSCs has great appeal. The strong interaction between organic and inorganic components creates unique electrochemical, photophysical and photochemical properties, which make these conjugated polymers potential materials for applications in solar energy conversion [11].

Sensitizers for DSSCs often feature push-pull molecular structures [12]. Benzodithiophene derivatives attracted some interest as a common unit in conjugated polymers, they are excellent electron donor materials for the preparation of highly efficient D-A type polymers for photovoltaic devices [13]. Because they have large

planar conjugated structure and form π - π stacking easily, which improves mobility, and the steric hindrance between adjacent units is very small [14]. Carbazole derivatives are also usually used as electron donor in dye molecular due to the electron-rich nitrogen heteroatom [15]. The salicylaldehyde derivatives of aromatic imine-based ligands prepared by condensation reaction between aldehyde and primary amine have been widely used in the synthesis of new coordination complexes [16]. But there are few reports about their use as dye sensitizers for DSSCs.

Accordingly, we report four D-A type polymeric metal complexes dyes for DSSCs. The benzodithiophene or carbazole derivatives are used as electron donor, salicylaldehyde derivatives complex as electron acceptor. Diaminomaleonitrile acts as ancillary ligand. Introduction of CN groups aims to enhance the electron-withdrawing ability of electron acceptor part, and to facilitate the electron injection between the dyes and TiO₂ surface [17]. Zn (II) or Cd (II) is chosen as the coordinated metal ion for their low cost and easy to get. To increase the solubility of these dyes, long aliphatic side chains are incorporated into the dye structures. Moreover, the optical properties, thermal properties, and photovoltaic properties of these polymeric metal complexes are also investigated in this paper.

2. Experimental section

2.1. Materials

All starting materials were obtained from Shanghai Chemical Reagent Co. Ltd (Shanghai China) and were used without further purification. DMF and were dried by distillation over CaH₂. All other reagents and solvents were commercially purchased and were used as received. 3,5-dibromosalicylaldehyde (1) [18], 3,6-dibromo-N-otylcarbazole (4) [20] was prepared according to the literature methods.

2.2. Instruments and measurements

¹H NMR spectra were obtained in CDCl₃ and recorded with a Bruker ARX400 (400 MHz) Germany, and the spectra were referenced against tetramethylsilane (δ =0.00 ppm) as the internal standard. FT-IR spectra were recorded using KBr pellets with a Perkin-Elmer Spectrum One FT-IR spectrometer over the range 400–4000 cm⁻¹.

The UV-vis absorption spectra were measured with Lamada 25H spectrometer. Samples were dissolved in DMF and diluted to a concentration of 10^{-5} - 10^{-4} mol L⁻¹. Gel Permeation Chromatography (GPC) analyses were measured by WATER 2414 system equipped with a set of HT₃, HT₄ and HT₅, 1-styrayel columns with DMF as eluent, and polystyrene was used as standard. Elemental analysis for C, H, N was performed on Perkin-Elmer 2400 II instrument under nitrogen atmosphere. Thermogravimetric analyses (TGA) and Differential Scanning Calorimetry (DSC) were performed on Shimadzu TGA-7 Instrument and Perkin-Elmer DSC-7 thermal analyzer at a heating rate of 20 °C min⁻¹ from 25 to 600 °C in nitrogen atmosphere, respectively. Electrochemical redox potentials were obtained by cyclic voltammetry (CV), and conducted on a CHI630C electrochemistry workstation in a [Bu₄N]BF₄ (0.1 mol L⁻¹) CH₃CN solution at a scan rate of 100 mV s⁻¹ at room temperature. The working electrode was a glassy carbon electrode, the auxiliary electrode was a platinum wire electrode and a saturated calomel electrode (SCE) was used as reference electrode.

2.3. Fabrication of DSSCs

The DSSCs devices with sandwich structure in this paper are based on TiO₂ semiconductors. Titania paste was prepared following a procedure: fluorine-doped SnO₂ conducting glass (FTO) were cleaned and immersed in aqueous 40 mmol L⁻¹ TiCl₄ solution at 70 °C for 30 min. The 20–30 nm particles sized TiO₂ colloid was coated onto the above FTO glass by the sliding glass rod method and following sintered at 450 °C for 30 min which has been repeated for three times to obtain a TiO₂ film of 10-15 μ m thickness. After cool to 100 °C, the TiO₂ films were soaked in 0.5 mmol L⁻¹ dye samples in DMF solution and maintained under dark for 24 h at room temperature. Then the film were cleaned by anhydrous ethanol. After drying, electrolyte containing LiI (0.5 mol L⁻¹), I₂ (0.05 mol L⁻¹) and 4-tert-butylpyridine (0.5 mol L⁻¹) was dripped on the surface of TiO₂ electrodes. A Pt foil was used as counter electrode was clipped onto the top of the TiO₂. The dye-coated semiconductor film was illuminated through a conducting glass support without a mask. The photoelectron chemical performance of the solar cell was measured using a Keithley

2602 Source meter controlled by a computer. The cell parameters were obtained under an incident light with intensity 100 mW cm⁻², which was generated by a 500-W Xe lamp passing through an AM 1.5 G filter with an effective area of 0.2 cm^2 .

2.4. Synthesis

2.4.1. Synthesis of 2,4-dibromo-6-((p-tolylimino)methyl)phenol (2) [19]

A ethanol solution of p-toluidine (1.63g, 15mmol) was added in a ethanol solution of (1) (4.22g, 15mmol) while stirring at room temperature. The mixed solution was continue stirred at room temperature for 3h. The formed solid was separated by filtration under reduced pressure, washed with ethanol and dried under vacuum. The crude product was recrystallized from ethanol, resulting in orange crystal solid (4.71g, 85%). FTIR (KBr, cm⁻¹): 3443, 3082, 2968, 1621, 1591, 688. ¹HNMR (CDCl₃, δ , ppm): 14.63 (s, 1H), 8.54 (s, 1H), 7.74 (s, 1H), 7.48 (s, 1H), 7.21-7.24 (m, 4H), 2.40 (s, 3H).

2.4.2. Synthesis of C1 [21]

A ethanol solution (30ml) of Zn(CH₃COO)₂·2H₂O (0.35g, 1.5mmol) was slowly dropped into a mixture of (**2**) (0.55g, 1.5mmol) and diaminomaleonitrile (0.16g, 1.5mmol) in ethanol (45ml) with stirring and refluxing. After the solutiom was refluxed for 10h, the reaction system was then allowed to cool to room temperature. The precipitate was collected by filtration, washed with ethanol several times and then dried in vacuum. A brick-red solid was collected (0.57g, 63%). FTIR (KBr, cm⁻¹): 3435(N-H), 3062(=C-H), 2975(C-H), 2221(C=N), 1619(C=N), 1054(C=N-M), 567(N-M). Anal. Calcd. for [C₂₀H₁₇Br₂N₅O₃Zn]: C, 40.01; H, 2.83; N, 11.67. Found: C, 40.78; H, 2.95; N, 11.32%.

2.4.3. Synthesis of C2

With the similar synthetic method for C1 With $Cd(CH_3COO)_2 \cdot 2H_2O$ (0.41g, 1.5mmol) afforded reddish brown solid (0.66g, 68%). FTIR (KBr, cm⁻¹): 3434(N-H), 3063(=C-H), 2978(C-H), 2226(C=N),1626(C=N), 1051(C=N-M), 548(N-M). Anal. Calcd. for [C₂₀H₁₇Br₂N₅O₃Cd]: C, 37.07; H, 2.63; N, 10.81. Found: C, 37.85; H, 2.26; N, 11.27%.

2.4.4. Synthesis of P1

The polymeric metal complex was synthesized by Yamamoto coupling method according to the literature [22]. Under nitrogen atmosphere, metal complex C1 (0.24g, 0.4mmol), bis(triphenylphosphine) nickel(II) chloride (0.26g,0.4mmol). 2,6-dibromo-4,8-bis(2'-ethhylhexyl)oxy)benzodithiophene (3) (0.24g, 0.4mmol), zinc (0.13g, 2mmol), triphenylphosphine (0.21g,0.8mmol), and a little bipyridine (0.006g, 0.038mmol) were dissolved in DMF(15 mL) under nitrogen. Then the mixture was stirring at 90 °C for 48 h. After that, it was filtered after cooled to room temperature and the filtrate was poured into a large excess of ethanol. The precipitate was filtered and washed with cold ethanol, then dried in vacuum for one day to afford brown solid (0.21g, 58%). FTIR (KBr, cm⁻¹): 3431(N-H), 3036(=C-H), 2961, 2925, 2857(C-H), 1606(C=N), 2194(C≡N), 1045(C=N-M), 485(N-M). Anal. Calcd. for [C₄₆H₅₃N₅O₅S₂Zn]: C, 62.44; H, 5.60; N,7.92. Found: C, 61.87; H, 5.73; N, 8.56%. Mn=8.24 Kg/mol, PDI=1.55.

2.4.5. Synthesis of P2

With the similar synthetic method as described for **P1**. A mixture of metal complex **C2**, bis(triphenylphosphine) nickel(II) chloride, monomer **3**, zinc, triphenylphosphine, and a little bipyridine and DMF afforded brown solid (0.19g, 51%). FTIR (KBr, cm⁻¹): 3419(N-H), 3039(=C-H), 2973, 2921, 2862(C-H), 2153(C=N), 1619(C=N), 1047(C=N-M), 488 (N-M). Anal. Calcd. for [C₄₆H₅₃N₅O₅S₂Cd]: C, 59.29; H, 5.69; N,7.52. Found: C, 59.84; H, 6.21; N, 7.15%. Mn=9.37 Kg/mol, PDI=1.47.

2.4.6. Synthesis of P3

With the similar synthetic method as described for **P1**. A mixture of metal complex **C1**, bis(triphenylphosphine) nickel(II) chloride, monomer **4**, zinc, triphenylphosphine, and a little bipyridine and DMF afforded brown solid (0.18g, 63%). FTIR (KBr, cm⁻¹): 3406(N-H), 3059(=C-H), 2961, 2921, 2851(C-H), 2187(C=N), 1612(C=N), 1025(C=N-M), 482(N-M). Anal. Calcd. for $[C_{40}H_{40}N_6O_3Zn]$: C, 66.95; H, 5.58; N, 11.72. Found: C, 67.73; H, 5.86; N, 11.17%. Mn=6.74 Kg/mol, PDI=1.65.

2.4.7. Synthesis of P4

With the similar synthetic method as described for **P1**. A mixture of metal complex **C2**, bis(triphenylphosphine) nickel(II) chloride, monomer **4**, zinc, triphenylphosphine, and a little bipyridine and DMF afforded brown solid (0.17g, 55%). FTIR (KBr, cm⁻¹): 3421 (N-H), 3053(=C-H), 2962, 2926, 2856(C-H), 2193(C=N), 1618(C=N), 1041(C=N-M), 495(N-M). Anal. Calcd. for [C₄₀H₄₀N₆O₃Cd]: C, 62.83; H, 5.24; N, 10.99. Found: C, 63.64; H, 5.59; N, 11.28%. Mn=6.48 Kg/mol, PDI=1.52.

3. Results and discussion

3.1. Synthesis and characterization

The detailed synthetic routes of the monomers and the four polymeric metal complexes are depicted in Scheme. 1. The intermediate (2) was prepared by the condensation of 3,5-dibromosalicylaldehyde with p-toluidine in ethanol solution. The target four polymers were obtained by the Yamamoto coupling [22], the reactions were carried out in N_2 atmosphere. The four as-synthesized polymers showed good solubility in DMF and DMSO solvent at room temperature. But they can not be dissolved well in chloroform or other solvents.

Fig. 1 shows the ¹H NMR spectrum of monomer **2**. Signals at 8.54, 2.40 ppm are attributed to proton of H-C=N and methyl, respectively. There is no proton signal of H-C=O that further prove the success of the synthesis of **2**.

The IR spectra of the metal complex (**C1**, **C2**) and the target polymers (**P1-P4**) are shown in Fig. 2. As for **C1**, **C2**, the absorption peaks at 1054cm⁻¹ and 1051 cm⁻¹ are assigned to their C=N-M stretching vibration, respectively [23]. And their N-M stretching vibration peak appeared at 567 cm⁻¹ and 548 cm⁻¹, respectively. While the C=N-M stretching vibration signals of **P1-P4** appear at 1045 cm⁻¹, 1047 cm⁻¹, 1025 cm⁻¹ and 1041cm⁻¹, respectively, and their corresponding N-M stretching vibration peaks appeared at 485 cm⁻¹, 488 cm⁻¹, 482 cm⁻¹ and 495 cm⁻¹, respectively. It is obvious that these kinds of peaks of the polymeric metal complexes show red-shift comparing with the corresponding metal complexes. This is due to the extending of conjugation system after polymerization.

The number average molecular weight and the weight average molecular weight

of the four target polymers dyes (**P1-P4**) are measured by gel permeation chromatography (GPC) and the corresponding data are shown in Table 1. The four polymer dyes have number average molecular weights (M_n) of 8.24, 9.37, 6.74 and 6.48 kg mol⁻¹, respectively, with a PDI in the range of 1.55, 1.47, 1.65, and 1.52, respectively. Changes in the molecular weight further proved an evidence for the successful synthesis of the four target polymers.

3.2. Optical properties

Fig. 3 shows the absorption spectra of **C1**, **C2** and **P1-P4** in DMF solution, and the corresponding data are summarized in Table 2. The light absorption of 356nm and 367nm for metal complexes **C1**, **C2** is mainly due to metal-to-ligand charge transfer. We observe that the maximum absorption peak of **P1–P4** are at 455, 471, 414, and 425 nm, respectively. These strong absorption bands result from intramolecular charge transfer between the electron-donating unit and the electron-accepting moiety. It can be easily found that the maximum absorptions of the polymeric metal complexes (**P1–P4**) are obviously red shifted comparing with corresponding metal complex **C1**, **C2** due to the introduction of the benzodithiophene or carbazole derivatives, and the increase of an effective conjugated chain length.

The normalized photoluminescent (PL) spectra of **P1–P4** in DMF solution are shown in Fig. 4, the excitation wavelengths were set according to the maximal absorption peak of UV–vis spectrum. It can be seen in table 2 that the PL peaks of **P1–P4** are at 526, 551, 502, and 511 nm, respectively, which can be attributed to the π – π * transition of intra-ligand.

3.3. Thermal stability

The thermal properties of these four polymeric metal complexes were studied by TGA and DSC. The results are shown in Fig. 5 and the corresponding data was recorded in Table 1. The results of TGA show the excellent stability of polymers **P1–P4** with 5 % weight loss temperatures (T_d) of 337, 328, 356, and 344 °C under nitrogen, respectively. This is important for the thermal stability of DSSCs. And their glass transition temperature (T_g) are 157, 150, 168, and 162 °C, respectively. There is no fixed melting point which is due to our synthetic method and purification means

that we only obtained the amorphous products. Their high glass transition temperature shows that these polymeric metal complexes will be a valuable material for application in DSSCs.

3.4. Electrochemical properties

The electrochemical behaviors of the polymers were investigated by cyclic voltammetry. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the polymers are important for evaluating the possibility of electron transfer from the excited dyes to the conductive band of TiO_2 and the regeneration of dyes. They can be calculated conveniently by the following equations as well as energy gap (E_g) [24]:

HOMO=
$$-e(E_{ox} + 4.40) (eV)$$
 (1)
LUMO= $-e(E_{red} + 4.40) (eV)$ (2)
 E_{g} = HOMO - LUMO (3)

Fig. 6 shows the cyclic voltammetry curves of **P1-P4**, and the data are summarized in Table 2. The oxidation potential values (E_{ox}) of **P1-P4** are 1.15, 1.06, 1.26, and 1.21V, respectively, which can be attributed to the benzodithiophene or carbazole derivatives donor segment. The reduction potential values (E_{red}) of **P1-P4** are -0.96, -0.98, -1.02, and -0.99V, respectively, which can be attributed to the metal-ligand complex acceptor segment. Accordingly, the HOMO energy values of **P1-P4** are -5.55, -5.46, -5.66, and -5.61 eV, respectively, which are are lower than the standard potential of Γ/I_3 ⁻ redox couple (-4.83 eV) [25]. The LUMO energy values are -3.44, -3.42, -3.38, and -3.41 eV, respectively, which are higher than the conduction band of TiO₂ (-4.26 eV). The details are shown in Fig. 7. It indicates that electrons can transfer from the excited dye to the TiO₂ efficiently and can facilitate dyes' regeneration. The electrochemical band gaps (E_g) of **P1-P4** are estimated to be 2.11, 2.04, 2.28 and 2.20 eV, respectively, which are consistent with the optical band gaps, so they are suitable for fabrication of optoelectronic devices.

3.5. Photovoltaic properties

The photocurrent density-voltage (J–V) curves of the DSSCs devices based on the four polymeric metal complexes are reported in Fig. 8. The corresponding datas

are listed in Table 3. It can be seen that the open-circuit voltage (V_{oc}) of **P1-P4** are 0.69, 0.71, 0.64 and 0.67 V, respectively. The corresponding fill factor (FF) are 68.2, 69.3, 64.8, and 64.5. And the short-circuit current density (J_{sc}) follow the order of **P2** (4.95 mA/cm²) > **P1** (4.77 mA/cm²) > **P4** (4.51 mA/cm²) > **P3** (4.43 mA/cm²). This is in accordance with the order of the power conversion efficiency (η) of the four dyes that **P2** (2.43%) > **P1** (2.24%) > **P4** (1.95%) > **P3** (1.84%). We found that polymers containing benzodithiophene derivatives as electron donor show higher J_{sc} values than polymers containing carbazole derivatives, this is due to the stronger electron-donating capability of benzodithiophene than carbazole, which is more conducive to the generation of photocurrent. Besides, the electron transport properties of Cd complexes are better than Zn complexes. Since the radius of Cd(II) is bigger that of Zn(II), the coordination bond between ligands and cadmium is stronger relative to zinc , which lead to the stronger electronic withdrawing ability of the former and facilitate the electron transport in the dye molecules, thus the polymers with Cd ion exhibited better photovoltaic properties than the polymers with Zn ion.

However, J_{sc} values of these materials are still low. This is related to many factors, such as the low charge separation and transportation efficiency, and the narrow absorption spectra of the polymers. It can also be seen from the input photon to converted current efficiency (IPCE) curves as shown in Fig. 9. The IPCE values of the four polymers are relatively low with only 30-40% at 400-450nm. This is not as good as Si which as photovoltaic material with a broader spectral response ranges 400~1100 nm, and the IPCE value can reach to over 80% in the visible spectrum region [26]. But it shows a new way to design dye sensitizers.

4. Conclusions

Four novel D-A polymeric metal complexes dyes containing benzodithiophene or carbazole derivatives as electron donors were designed, synthesized and applied for DSSCs. These dyes exhibit good thermal stability for their application in DSSCs. The strength of the electron-donating group as well as different metal ion greatly influenced the performance of the photovoltaic device. DSSC based on **P2** shows the best power conversion efficiency of 2.43% with a better light absorption and higher

 J_{sc} value among the four dyes studied. The results show that this type of functional materials would be a potential material for DSSCs.

In our next work, we will design new conjugated polymeric metal complexes dyes with much stronger electron-donating units so as to make the maximum absorption red-shift, and further improving J_{sc} value. Besides, more suitable metal ions should be found to tune the molecule structure and broaden absorption spectra, and thus to obtain outstanding energy conversion efficiency.

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Fig. 3

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more and more than properties of the polymetre metal comprehes.							
Polymer	$\overline{M}_n^{a} [\times 10^3]$	$\overline{M}_{w}^{a}[\times 10^{3}]$	PDI	Ν	$T_g^{b}[^{\mathrm{o}}\mathrm{C}]$	$T_d^{c}[^{o}C]$	
P1	8.24	12.15	1.47	9	157	337	
P2	9.37	13.07	1.39	10	150	328	
P3	6.74	11.13	1.65	9	168	356	
P4	6.48	9.86	1.52	8	162	344	

Table 1		
Molecular weights and thermal	properties of the polymeric metal	complexes

^a Determined by gel permeation chromatography using polystyrene as standard.

^b Determined by DSC with a heating rate of 20 °C/min under nitrogen.

^c The temperature at 5% weight loss under nitrogen.

Table 2

Optical and electrochemical properties of the polymeric metal complexes.

Polymer	$\lambda_{a,max}$ $(nm)^{a}$	PL (nm) ^b	$E_{ox}(V)^{c}$	$E_{red}(V)^{c}$	HOMO (eV)	LUMO (eV)	$E_{g,EC}\!/\!eV^{~d}$
P1	455	526	1.15	-0.96	-5.55	-3.44	2.11
P2	471	551	1.06	-0.98	-5.46	-3.42	2.04
Р3	414	502	1.26	-1.02	-5.66	-3.38	2.28
P4	425	511	1.21	-0.99	-5.61	-3.41	2.20

^a The maxima absorption from the UV–vis spectra in DMF solution.

^b The PL maxima in DMF solution.

^c Values determined by cyclic voltammetry.

^d Electrochemical band gap estimated from HOMO and LUMO.

Table 3

Photovoltaic parameters of devices with sensitizers **P1-P4** in DSSCs at full sunlight (AM 1.5 G, 100 wM cm⁻²).

Polymer	Solvent	J_{sc} (mA / cm ²)	$V_{oc}(V)$	FF (%)	η (%)
P1	DMF	4.77	0.69	68.2	2.24
P2	DMF	4.95	0.71	69.3	2.43
P3	DMF	4.43	0.64	64.8	1.84
P4	DMF	4.51	0.67	64.5	1.95

Figure Legends:

- Scheme. 1. Synthesis of the monomers and polymeric metal complexes P1-P4.
- **Fig. 1.** ¹H NMR spectra of 2 in CDCl₃ solution.
- Fig. 2. FT-IR spectra of C1, C2, P1-P4.
- **Fig. 3.** UV-vis absorption spectra of **C1**, **C2** and polymeric metal complexes **P1-P4** in DMF solution.
- Fig. 4. PL spectra of polymeric metal complexes P1–P4 in DMF solution.
- Fig. 5. TGA curves of P1-P4 with a heating rate of 20 °C/min under nitrogen atmosphere.
- Fig. 6. Cyclic voltammograms for P1-P4 in CH₃CN/0.1 M [Bu₄N]BF₄ at 100 mV/s.
- Fig. 7. HOMO and LUMO energy levels of the polymers.
- **Fig. 8.** J-V curves of DSSCs based on dyes (**P1-P4**) under the illumination of AM 1.5, 100 mW cm⁻².
- Fig. 9. Spectra of incident photon-to-current conversion efficiencies (IPCE) for DSSCs based on dyes (P1-P4).







P3: M= Zn(II) P4: M= Cd(II)

Graphical abstract

Highlights

- Four novel polymeric metal complexes are designed and synthesized for being used as dyes of dye-sensitized solar cells (DSSCs). The results show that they exhibit some photovoltaic performance, and pave a potential way for researching and developing dyes.
- The dyes with benzodithiophene derivatives as donor (P1, P2) show better photovoltaic performance than that with carbazole derivatives as donor (P3,P4). This show a new way to design and synthesize polymeric metal complexes for being used as dyes.
- The four polymers were investigated by UV–vis absorption spectroscopy and PL spectroscopy, which lays a foundation for further photochemical research.

