Novel D- π -A dye sensitizers of polymeric metal complexes based on Cd(II) with salicylaldehyde and diaminomaleonitrile: synthesis, characterization, and photovoltaic performance for dye-sensitized solar cells

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Abstract Being a key component of dye-sensitized solar cells, dye sensitizer and its synthesis and application have been extensively researched. In this paper, four novel polymeric metal complexes as dye sensitizers based on Cd(II) with salicylaldehyde and diaminomaleonitrile were functionally designed and synthesized. These dyes use poly(p-phenylenevinylene) or bithiophene phenylenevinylene as electron donor, Cd(II) complex unit as electron acceptor, and ethylenic bond as π linker. They were characterized by FT-IR, ¹H NMR, gel permeation chromatography, and elemental analysis. Their thermal, photophysical, electrochemical, and photovoltaic properties were also investigated by thermogravimetric analysis, differential scanning calorimetry, C-V curves, and J-V curves. All four polymeric metal complexes exhibited some photovoltaic performances. The dyes containing bithiophene (P2, P4) exhibited higher power conversion efficiency (PCE) values than the corresponding polymers without thiophene unit (P1, P3). Dual-core cadmium polymeric metal complexes showed higher PCE than mononuclear cadmium complexes by comparing P4 with P2 as well as P3 with P1. The highest PCE of compound P4 reached 2.07 % ($J_{sc} = 4.22 \text{ mA/cm}^2$, $V_{oc} = 0.71 \text{ mV}$, and FF = 69.1 %) under simulate AM 1.5G solar irradiation.

Keywords Polymeric metal complex · Dye sensitizer · Salicylaldehyde · Diaminomaleonitrile · Cadmium

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Introduction

Energy demands and environmental pollution resulting in global warming have led to a greater focus on renewable energy sources over the past decades. Recently, Michael Grätzel and coworkers reported on high-performance perovskite-sensitized solar cells where a power conversion efficiency of 15 % was achieved with the best device [1]. As a promising renewable energy technology that converts sunlight into electricity, photovoltaics have attracted considerable attention with great potential to solve urgent energy problems [2-4]. DSSCs are the only photovoltaic devices that use molecules to absorb photons and convert them into electric charges without the need of intermolecular transport of electronic excitation [5]. Up to now, DSSCs based on metal-free organic dyes [6, 7], porphyrin dyes [8, 9], metal-phthalocyanine [10], and natural dyes [11, 12] have been developed and reported. Among them, the generation of donor- π -conjugation-linkage-acceptor (D- π -A) sensitizers are impressive and encouraging because the D- π -A structure can help to extend absorption spectra of the dyes, increase the optical absorption coefficient, adjust the HOMO and LUMO energy levels, and the energy gap $\Delta E(\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}})$ of the dye molecules. What's more, excited electrons can easily transfer from the donor to the acceptor with the help of π bridge, and then implant into the semiconductor TiO₂, thus enhancing the transmission of the charge [13].

The disadvantages of small organic dye molecules are their poor charge-transport properties due to the small π conjugated system, and their poor chemical stability, and light stability, especially the thermal stability due to the small molecular weight. As a result, their large-scale study and applications will be affected.

For the above reasons, to synthesize the macromolecular is particularly important. As a kind of plurality of polymers, polymeric metal complexes have received considerable attention for these hybrid materials that provide outstanding physical and chemical properties of both organic and inorganic components, such as unique process ability and easy film-forming ability of polymer, prominent luminescence efficiency, and good thermal stability of metal [14, 15]. Thousands of papers have reported on polymeric metal complexes but articles about their application in dye-sensitized solar cells are quite limited [16, 17]. Therefore, it is worth synthesizing new polymeric metal complexes and studying their photovoltaic properties. However, the high cost and rarity of the ruthenium metal may restrain their extensive application. So, finding cheap substitute metals seems very important. Great efforts have been made to replace Ru-based dyes with metal-free organic dyes [18], such as phenothiazine- [19], indoline- [20], fluorene- [21], triarylamine- [22], thiophene- [23, 24], carbazole- [25, 26], and so on.

In this study, a series of D– π –A polymeric metal complexes, which use metaldiaminomaleonitrile as an acceptor (A), ethylenic bond as a π -conjugation linkage, and poly(*p*-phenylenevinylene) (PPV) or bithiophene phenylenevinylene as donor group (D), have been synthesized and used as sensitizers in the dye-sensitized solar cells. The structure of **P4** is shown in Scheme 1, and the synthetic routes of the four polymeric metal complexes (**P1–P4**) are shown in Scheme 2. Moreover, the thermal, optical, and photovoltaic properties of those polymeric metal complexes have also been investigated.



Scheme 1 Chemical structure of polymeric metal complex P4

Experimental

Materials

 $NiCl_2(PPh_3)_2$, salicylaldehyde, diaminomaleonitrile (DAMN) and 3-methylthiophene-2-carbaldehyde were obtained from Aldrich Chemical Co. and used as received. *N*,*N*-dimethylformamide was dried by distillation over CaH₂ and methanol was dried over molecular sieves and freshly distilled prior to use. The other materials were common commercial-grade materials and used as received. All chemicals used were of an analytical grade. Solvents were purified with conventional methods.

Instruments and measurements

¹H NMR were performed in CDCl₃ and recorded on a Bruker Avance 400 spectrometer. Gel permeation chromatography (GPC) analyses were measured by a WATERS 2414 system equipped with a set of HT₃, HT₄, and HT₅, 1-Styragel columns with THF as eluent and polystyrene as standard. The FT-IR spectra were obtained on a Perkin-Elmer Spectrum One Fourier transform infrared spectrometer by incorporating samples in KBr pellets. Thermogravimetric analyses (TGA), differential scanning calorimetry (DSC), and elemental analysis were performed on a Shimadzu TGA-7 instrument, Perkin-Elmer DSC-7 thermal analyzer, and Perkin-Elmer 2400 II instrument, respectively. UV-visible spectra of all the polymers were taken on a Lambda 25 spectrophotometer. Photoluminescent spectra (PL) were taken on a Perkin-Elmer LS55 luminescence spectrometer with a xenon lamp as the light source. Cyclic voltammetry (CV) was conducted on a CHI630C Electrochemical Workstation using a three-electrode system in a $[Bu_4N]BF_4$ (0.1 M) DMF solution at a scan rate of 100 mV/s. A glassy carbon rod, a Pt wire electrode, and a saturated calomel electrode (SCE) were used as working electrode, auxiliary electrode, and reference electrode, respectively.



Scheme 2 Synthetic route of the monomers and polymeric metal complexes P1-P4

Fabrication of DSSCs

The DSSCs devices with a sandwich structure in this paper are based on TiO_2 semiconductors. Titania paste was prepared following the procedure: fluorine-doped

SnO₂ conducting glass (FTO) was cleaned and immersed in aqueous 40 mmol/l TiCl₄ solution at 70 °C for 30 min. The 20–30-nm particles 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 was done three times to obtain a TiO₂ film of 10–15 μ m thickness. After cooling to 100 °C, the TiO₂ films were soaked in 0.5 mmol/l dye samples in DMF solution and maintained under dark for 24 h at room temperature. The films were then cleaned by anhydrous ethanol. After drying, electrolyte containing LiI (0.5 mol/l), I₂ (0.05 mol/l) and 4-*tert*-butylpyridine (0.5 mol/l) was dripped on the surface of TiO₂ electrodes. A Pt foil was used as counter electrode and 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 an intensity of 100 mW/cm², which was generated by a 500-W Xe lamp passing through an AM 1.5 G filter with an effective area of 0.2 cm².

Synthesis

Synthesis of 5-bromo-2-hydroxybenzaldehyde (1) [27]

A carbon tetrachloride solution (20 ml) of liquid bromine (2.6 ml, 0.05 mol) was dropped into an ethanol solution (20 ml) of salicylaldehyde (5.2 ml, 0.05 mol). The reaction system was allowed to cool to 12-15 °C. After the dropwise addition, the reaction was continued for 2 h at room temperature. The white precipitate was collected by filtration, washed with dried ethanol repeatedly; a white solid was obtained (7.04 g, yield 70 %). FT-IR (KBr, cm⁻¹): 3,218, 2,880, 1,669, 1,462, 696. ¹H NMR (400 MHz, CDCl₃, d, ppm): 10.934 (s, 1H), 9.847 (s, 1H), 7.678 (s, 1H), 7.597 (d, 1H), 6.926 (d, 1H). Mp 105–106 °C.

Synthesis of 2-amino-3-(5-bromo-2-hydroxybenzylideneamino)maleonitrile (2) [28]

An ethanol solution (100 ml) of 5-bromo-2-hydroxybenzaldehyde (1) (0.9548 g, 4.75 mmol) was dropped into an ethanol solution (20 ml) of DAMN (0.5027 g, 4.65 mmol), and the mixture was refluxed for 16 h. The yellow solution was cooled in ice to give fine yellow needles, which were filtered off, washed with cooled ethanol, and dried under vacuum (0.5414 g, yield 40 %). FT-IR (KBr, cm⁻¹): 3,407, 3,298, 3,200, 2,249, 2,208, 1,620, 1,473, 1,278, 649. Anal. Calcd for $C_{11}H_7BrN_4O$ (2): C, 45.39; H, 2.42; Br, 27.45; N, 19.25; O, 5.50. Found: C, 45.62; H, 2.24; N, 19.43. MS: Calcd for $C_{11}H_7BrN_4O[M]^+$ 291.10; found, 292.33.

Synthesis of L1 [28]

5-bromo-2-hydroxybenzaldehyde (1) (0.8463 g, 4.21 mmol) and CdCl₂·2.5H₂O (0.4795 g, 2.10 mmol) were dissolved together in refluxing ethanol (100 ml) to give a clear colorless solution. DAMN (0.229 g, 2.12 mmol), dissolved in ethanol (25 ml), was added dropwise and refluxing continued for 4 h. Precipitated dark

yellow solid, filter, washed with ethanol, and dried under vacuum (1.1047 g, yield 90 %). Anal. Calcd for $C_{18}H_8Br_2N_4O_2Cd$: C, 36.99; H, 1.38; N, 9.59. Found: C, 36.35; H, 1.33; N, 9.97; FT-IR (KBr, cm⁻¹): 3,041 (=C–H), 2,921, 2,853, 1,591 (C=N), 2,172 (C = N), 1,051 (C–O–M), 816 (Ar–H), 490 (N–M).

Synthesis of L2 [16]

CdCl₂·2.5H₂O (0.6278 g, 2.75 mmol) was dissolved in methanol (50 ml) with stirring and refluxing. 2-amino-3-((E)-5-bromo-2-hydroxybenzylideneamino) maleonitrile (2) (0.8005 g, 2.75 mmol) dissolved in methanol (75 ml) was then added and the mixture was refluxed for 11 h to give a khaki-brown precipitate, which was filtered off, washed with methanol, and dried under vacuum. Yield: 1.059 g (96 %). Anal. Calcd for $C_{22}H_{10}Br_2N_8O_2Cd_2$: C, 32.91; H, 1.26; N, 13.95. Found: C, 32.36; H, 1.64; N, 13.46. FT-IR (KBr, cm⁻¹): 3,040 (=C–H), 2,976, 2,919, 1,578 (C=N), 2,375, 2,165 (C = N), 1,120 (C–O–M), 816 (Ar–H), 492 (N–M).

Synthesis of 2,2'-(2,5-bis(octyloxy)-1,4-phenylene)bis(ethene-2,1-diyl)bis(2-bromo-4-methylthiophene) (a) and PPV (b)

These monomers were synthesized according to the published literature [29]. PPV yield (%): 75 %. ¹HNMR (CDCl₃, δ , ppm): 0.882 (t, 6H), 1.38–1.82 (m, 24H), 3.93 (t, 4H), 5.35 (d, 2H), 5.72 (d, 2H), 6.98 (s, 2H), 7.00–7.07 (dd, 2H). a Yield (%): 73 %. ¹HNMR (CDCl₃, δ , ppm): 7.69-7.67 (d, 4H), 7.535 (s, 2H), 7.470 (d, 4H), 6.960 (s, 2H), 4.016 (d,4H), 2.325 (s, 6H), 1.87 (m, 4H), 1.256–1.303 (m, 24H), 0.889 (m, 6H).

Synthesis of polymeric metal complex P1

The polymeric metal complex **P1** was synthesized by using the Heck coupling method, according to the literature [30]. A flask was charged with a mixture of metal complex **L1** (0.1754 g, 0.3 mmol), 1,4-bis(octyloxy)-2,5-divinylbenzene (0.116 g, 0.3 mmol), Pd(OAc)2 (0.0024 g, 0.012 mmol), triethylamine (3 ml), 3-*o*-tolyl phosphine (0.0220 g, 0.072 mmol) and DMF (8 ml). The flask was then pumped into a vacuum and purged with N₂. The mixture was heated at 90 °C for 24 h under N₂. Afterwards, it was filtered after being cooled to room temperature and the filtrate was then poured into methanol. The yellow precipitate was filtered and washed with cold methanol to afford a light yellow solid. (Yield: 0.1486 g, 51 %). FT-IR (KBr, cm⁻¹): 3,045 (=C-H), 2,928, 2,854, 1,651 (C=N), 2,326 (C=N), 1,209 (C-O-M), 827 (Ar-H), 494 (N-M). Et al. Calcd for [C₄₄H₄₈N₄O₄. Cd]: C, 65.30; H, 5.98; N, 6.92; Found: C, 64.52; H, 5.98; N, 6.92; Mn = 8.9 kg/ mol, PDI = 1.36.

Synthesis of polymeric metal complex P2

The copolymer was synthesized by Yamamoto coupling method according to the literature [31, 32]. L1 (0.1169 g, 0.2 mmol), bis(triphenylphosphine) nickel(II) chloride (0.13 g, 0.2 mmol), a (0.1474 g, 0.2 mmol), zinc (0.065 g, 1 mmol), triphenylphosphine (0.1045 g, 0.4 mmol), and a little bipyridine (0.003 g, 0.019 mmol) were dissolved in DMF (7.5 ml) under nitrogen. The mixture was then stirred at 90 °C for 48 h. The yellow solid was precipitated into a large excess of ethanol solution. The crude product was washed with ethanol, distilled water, and THF sequentially, and then dried in vacuum at 65 °C for 1 day to afford pale yellow solids (0.148 g, 56 %). FT-IR (KBr, cm⁻¹): 3,042 (=C–H), 2,921, 2,852, 1,663 (C=N), 2,328 (C=N), 1,220 (C–O–M), 822 (Ar–H), 492 (N–M). Anal. Calcd for [C₅₄H₅₆N₄O₄S₂Cd]: C, 64.75; H, 5.64; N, 5.59; S, 6.40. Found: C, 63.96; H, 5.26; N, 6.23; S, 6.93; Mn = 8.1 kg/mol, PDI = 1.57.

Synthesis of polymeric metal complex P3, P4

P3 was synthesized with a similar synthetic method as **P1**, **P4** was synthesized with a similar synthetic method as **P2**, **P3**: (Yield: 0.1653 g, 55 %), FT-IR (KBr, cm⁻¹): 3,055 (=C–H), 2,930, 2,853, 1,649 (C=N), 2,331 (C \equiv N), 1,170 (C–O–M), 833 (Ar–H), 492 (N–M). Et al. Calcd for [C₄₈H₅₀N₈O₄Cd₂]: C, 56.09; H, 4.90; N, 10.90; Found: C, 56.62; H, 5.33; N, 11.24; Mn = 9.3 kg/mol, PDI = 1.30. **P4**: (Yield: 0.1464 g, 60 %), FT-IR (KBr, cm⁻¹): 3,046 (=C–H), 2,918, 2,857, 1,580 (C=N), 2,344 (C \equiv N), 1,164 (C–O–M), 820 (Ar–H), 496 (N–M). Et al. Calcd for [C₅₈H₅₈N₈O₈S₂Cd₂]: C, 57.10; H, 4.79; N, 9.81; S, 5.26; Found: C, 57.73; H, 5.32; N, 9.37; S, 5.73; Mn = 8.6 kg/mol, PDI = 1.48.

Results and discussion

Synthesis and characterization

The detailed synthetic routes of the four polymeric metal complexes (**P1–P4**) as well as the monomers are shown in Scheme 2, and the two polymers (**P1**, **P3**) were synthesized by the Heck coupling [33]. The other two polymers (**P2**, **P4**) were synthesized by Yamamoto coupling [32]. The four as-synthesized polymers were readily dissolved in common organic solvents such as DMF and DMSO at room temperature. However, in the other solvents, they exhibit a poor solubility, such as in chloroform and dichloromethane.

Figure 1 shows the ¹H NMR spectra of the 2,2'-(2,5-bis(octyloxy)-1,4-pheny-lene)-bis(ethene-2,1-diyl)bis(2-bromo-4-methylthiophene) (a). The vinyl proton peaks appeared at around 7.67–7.69 ppm, and the hydrogen proton of thiophene locating at the four position is observed at 7.535 ppm. The protons of octyl appeared at 0.889–4.016 ppm. The ¹H NMR shows that monomer was synthesized successfully.

The IR spectra of the ligand monomer (2), metal complex (**L1**, **L2**), and the target polymers (**P1–P4**) are shown in Figs. 2 and 3. As for the monomer 2, absorption peaks at 1,628 cm⁻¹ are due to C=N bond stretching vibration, the absorption peaks at 3,409, 3,298, and 3,197 cm⁻¹ are the characteristic absorption peaks of the amino-group stretching vibration, and the peak at 648 cm⁻¹ is the C–Br stretching vibration absorption peak. From Figs. 2 and 3, the peaks of 1,151 and 1,170 cm⁻¹ are due to C–N-M stretching vibration of metal compound **L1** and **L2**, respectively [34]. Combining with the results of elemental analysis, we can conclude that metal Cd⁺₂ has been successfully coordinated with ligand 2, namely complexes **L1** and **L2** have been successfully synthesized. Due to the introduction of donor unit and extension of the conjugated system, the stretching vibration



Fig. 1 ¹H NMR spectra of a in CDCl₃ solution



Fig. 2 FT-IR spectra of L1, P1, and P2



Fig. 3 FT-IR spectra of 2, L2, P3, and P4

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

\overline{M}_n^a [×103]	\overline{M}_{w}^{a} a [×103]	Ν	PDI	$T_{\rm g}^{\rm b}$ [°C]	$T_{\rm d}^{\rm c}$ [°C]
8.9	12.1	11	1.36	162	323
8.1	12.7	8	1.57	169	375
9.3	12.1	9	1.30	181	350
8.6	12.7	7	1.48	186	420
	$ \overline{M}_{n}^{a} [\times 103] $ 8.9 8.1 9.3 8.6	\overline{M}_n^a [×103] \overline{M}_w^a a [×103] 8.9 12.1 8.1 12.7 9.3 12.1 8.6 12.7	\overline{M}_n^a [×103] \overline{M}_w^a a [×103] N 8.9 12.1 11 8.1 12.7 8 9.3 12.1 9 8.6 12.7 7	\overline{M}_n^a [×103] \overline{M}_w^a a [×103]NPDI8.912.1111.368.112.781.579.312.191.308.612.771.48	\overline{M}_n^a [×103] \overline{M}_w^a a [×103]NPDI T_g^b [°C]8.912.1111.361628.112.781.571699.312.191.301818.612.771.48186

^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

absorption peaks of C=N, C–N–M, and N-M bond of all the target polymers stretching vibration absorption peaks have some degree of red-shift, which can prove that the target products have been successfully synthesized combined with the GPC test results (Table 1) and elemental analysis results.

GPC study results of all the target polymers are shown in Table 1. The number average molecular weight of **P1–P4** is 8.9, 8.1, 9.3, and 8.6 kg/mol, and the unit of them is 11, 8, 9, and 7, respectively. All the PDI of polymeric metal complexes are relatively wide (**P1–P4**: 1.36, 1.57, 1.30, and 1.48, respectively). The changes of the molecular weight also proved that the copolymerization has taken place between the monomers, which is further evidence for the synthesis of the target polymers.

Optical properties

Figures 4 and 5 give the UV–Vis and normalized PL spectra of the polymeric metal complexes **P1–P4** (10–5 M in DMF solution), respectively, and the corresponding data are summarized in Table 2.

In Fig. 4, the maximum absorption values of **P1–P4** are at 402, 421, 423, and 446 nm, respectively, and these strong absorption bands result from intramolecular charge transfer (ICT) between the electron acceptor metal-salicylaldehyde unit and the electron-donating alkoxy benzene. These polymers have very weak shoulder absorption peaks in the band 457–500 nm, which is due to the charge transition of the DAMN derivatives and d10 metal ions in the polymer. By comparing **P1** with **P2** as well as **P3** with **P4**, we found that **P2** and **P4** have better UV–Vis absorption, which indicates that adding the thienyl group in polymers can promote the absorption of light. In the later work, we will introduce more electron–donor groups to ensure that the λ max of dyes shift to the red or infrared region and improve the photovoltaic properties.

The normalized photoluminescent (PL) spectra of **P1–P4** in DMF solution are shown in Fig. 5. The excitation wavelengths were set according to the maximum absorption peak of UV–Vis spectrum and the corresponding optical data are also listed in Table 2. It can be seen that the PL peaks of **P1–P4** are at 491, 469, 445, and 431 nm, respectively, which can be attributed to the π - π * transition of intra-ligand.

Thermal stability

As an important part of DSSCs, the dye should have good stability, which can increase the thermal stability of photovoltaic devices. Therefore, the thermal stability study has important implications for DSSCs. TGA and DSC were selected to study the thermal stability of the target product, and the TGA is used to test the target thermal decomposition temperature (Td: 5 % weight loss temperature), while the DSC is used to test target the glass-transition temperature (Tg). The corresponding data are listed in Table 1. The TGA results (Fig. 6) show the Td of the four polymeric metal complexes (**P1–P4**) are at temperatures of 323, 375,



Fig. 4 UV-Vis absorption spectra of L1, L2, and polymeric metal complexes (P1-P4) in DMF solution



Fig. 5 PL spectra of the four polymeric metal complexes (P1-P4) in DMF solution

Polymer	$\lambda_{a}, \max^{d}, \lambda_{a, onset}$	$\lambda_{p, max}^{e}$,	$E_{\rm g, opt}/{ m eV^{f}}$	$E_{\rm ox}$ (V) ^g	$E_{\rm red}$ (V) ^g	HOMO (eV)	LUMO (eV)	$E_{\rm g}, E_{\rm C}/{\rm eV^{h}}$
P1	402,494	491	2.51	1.13	-1.08	-5.53	-3.32	2.21
P2	421,528	469	2.35	1.18	-1.02	-5.58	-3.38	2.20
P3	423,508	445	2.44	1.16	-1.08	-5.56	-3.32	2.24
P4	446,560	431	2.26	1.22	-0.94	-5.62	-3.46	2.16

Table 2 Optical and electrochemical properties of the polymeric metal complexes

 a $\lambda_{a,max},\,\lambda_{a,\mbox{ onset}}$ The maxima and onset absorption from the UV–Vis spectra in DMF solution

^b $\lambda_{p, max}$: The PL maxima in DMF solution

^c $E_{g,opt}$: Optical energy band gap calculated from the formula $E_g = 1,240/\lambda_{a,onset}$ (eV)

^d Values determined by cyclic voltammetry

^e E_g, E_C: Electrochemical band gap estimated from HOMO and LUMO

350, and 420 °C in nitrogen, respectively, which means all of them are steady [35]. From the data of Table 1, we can see that the Tg of the four polymeric metal complexes (P1–P4) follow the order P4 (186 °C) > P3 (181 °C) > P2 (169 °C) > P1 (162 °C), which suggests that polymeric metal complex have binuclear metal hold higher rigidity than that have mononuclear metal. There is no fixed melting point, which is due to our synthetic method, and purification means that we only obtained the amorphous products, and this kind of structure might not be conducive to be used in organic solar cells. The high glass-transition temperature of them shows that these kinds of materials have great application prospects in improving the stability of the dye-sensitized solar cells.



Fig. 6 TGA curves of P1-P4 with a heating rate of 20 °C/min under nitrogen atmosphere



Fig. 7 Cyclic voltammograms for P1-P4 in DMF/0.1 M [Bu₄N]BF₄ at 100 mV/s

Electrochemical properties

Electronic energy level is one of the most important properties for organic materials used in solar cells. Figure 7 shows the cyclic voltammograms of **P1–P4**. The cyclic voltammetry of polymeric metal complexes were measured in DMF containing $[Bu_4N]BF_4$ (Bu = butyl) as supporting electrolyte and saturated calomel electrode (SCE) as reference electrode at a scan rate of 50 mV/s. The lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energy levels of the dyes are crucial properties for materials used in DSSCs. The LUMO,

HOMO, and energy gap (Eg) can be obtained according to Eqs. (1), (2), and (3), respectively [36].

$$HOMO = -e(E_{ox} + 4.40) (eV)$$
 (1)

$$LUMO = -e(E_{red} + 4.40)(eV)$$
(2)

$$E_{g} = HOMO - LUMO$$
(3)

The values obtained are listed in Table 3. The optical band gaps of **P1–P4** are estimated to be 2.51, 2.35, 2.44, and 2.26 eV, respectively. The energy levels of HOMO and LUMO, which are -5.53 and -3.32 eV for **P1**, -5.58 and -3.38 eV for P2, -5.56 and -3.32 eV for **P3**, and -5.62 and -3.46 eV for **P4**, were calculated from the onset oxidation and reduction potential. The electrochemical band gaps of **P1–P4** are estimated to be 2.21, 2.20, 2.24, and 2.16 eV, respectively, which is consistent with the optical band gaps, so they are suitable for fabrication of optoelectronic devices. **P4** exhibits a slightly lower band gap compared with other three polymeric metal complexes (**P1–P3**); this may be due to the stronger electron-donating ability of bithiophene phenylenevinylene units that decreased the energy gap.

Photovoltaic properties

DSSCs devices based on these four polymeric metal complexes were fabricated and tested under the illumination of AM 1.5G, 100 mW/cm² for solar cell applications. Following our conventional practice for these polymeric metal complexes using solution process [37, 38], the active layers were spin-coated from their DMF solutions.

Figure 8 shows the incident photon-to-current conversion efficiencies (IPCE) of the DSSCs devices based on four polymeric metal complexes (**P1–P4**). From Fig. 8, the IPCE values of the dye **P3** and **P4** reach to 31.4 and 34.1 %, respectively, around the band of 450 nm. Though dye **P4** has the maximum IPCE among the four dyes, the results are not as good as the traditional ruthenium dye, which is probably caused by low charge collection efficiency [39].

The photocurrent density-voltage (J-V) curves are reported in Fig. 9 and the corresponding photovoltaic performance is summarized in Table 3. We can see from Table 3 that the V_{oc} values of **P1**, **P2**, **P3**, and **P4** are 0.52, 0.64, 0.58, and

 Table 3
 Photovoltaic parameters of devices with sensitizers P1–P4 in DSSCs at full sunlight (AM 1.5 G, 100 wM/cm²)

Polymer	Solvent	$J_{\rm sc}~({\rm mA/cm}^2)$	$V_{\rm oc}~({ m V})$	FF (%)	η (%)
P1	DMF	3.76	0.52	69.7	1.36
P2	DMF	4.09	0.64	63.2	1.65
P3	DMF	3.86	0.58	68.3	1.53
P4	DMF	4.22	0.71	69.1	2.07



Fig. 8 IPCE plots for the DSSCs based on the four polymeric metal complexes (P1-P4)



Fig. 9 J-V curves of DSSCs based on dyes (P1-P4) under the illumination of AM 1.5, 100 mW/cm²

0.71 V, respectively. The corresponding FF values are 69.7, 63.2, 68.3, 69.1. The J_{sc} values follow the order P4 ($J_{sc} = 4.22 \text{ mA/cm}^2$) > P2 ($J_{sc} = 4.09 \text{ mA/cm}^2$) > P3 ($J_{sc} = 3.86 \text{ mA/cm}^2$) > P1 ($J_{sc} = 3.76 \text{ mA/cm}^2$). We can find that the J_{sc} values of the target polymers (P2, P4) containing bithiophene PPV as donor are higher than the corresponding target polymers (P1, P3) only containing PPV. The reason for this is mainly that introduction of more thiophene units can improve electron-donating ability, and this is more conducive to the generation of photocurrent. Besides, the electronic conductivity of dual-core cadmium complexes is better than mononuclear cadmium complexes. However, J_{sc} values of these materials are still low; the low J_{sc} is related to low electron transfer efficiency and charge separation

and narrow absorption spectra in the region of visible light. The J_{sc} value has great influence on the power conversion efficiency. Device based on **P4** reached the highest power conversion efficiency of 2.07 % than that of the devices based on **P1** (1.36 %), **P2** (1.65 %), **P3** (1.53 %).

Conclusions

In this paper, four polymeric metal complexes containing salicylaldehyde and diaminomaleonitrile units with Cd(II) were synthesized and used as sensitizers in DSSCs. The polymeric metal complexes have higher V_{oc} and FF values. The results show that the introduction of a thiophene and cyano group to the molecular skeleton is conducive to broaden the spectral absorption range of polymeric metal complexes. Increasing the number of metal ions in the ligand also can promote the absorption of light. All the LUMO energy level of the complexes is higher than the LUMO level of TiO₂, which makes the electrons transfer to the TiO₂ smoothly. These results strongly indicate that the polymeric metal complexes will achieve further applications in DSSCs.

Though **P4** containing binuclear metal and more thiophenes shows better optical and photovoltaic properties, there are also some shortcomings and improvements of the polymeric metal complexes used as dye sensitizers for dye-sensitized solar cells: (1) For the low solubility, the polymeric metal complexes cannot be well dissolved in DMF; in the PV testing, those complexes could not have more adsorption. (2) The absorption region of the polymeric metal complexes is not wide enough and so they have a low IPCE value. (3) To get good solubility, long alkyls should be introduced in the structure. (4) For strong adsorption onto the surface of TiO₂, one or two anchoring groups, such as carboxylic acid or sulfonic acid groups, should also be introduced in the structure. In order to improve the solubility and get better photovoltaic materials, we still have much work to do and we will report the next investigation in the future.

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