

Main Chain Polymeric Metal Complexes Based on Linkage Fluorenevinylene or Phenylenevinylene with Thienyl(8-Hydroxyquinoline)-Cadmium (II) Complexes as Dye Sensitizer for Dye-Sensitized Solar Cells

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ABSTRACT: Dye-sensitized solar cells (DSSCs) have attracted interest from chemists in recent years because of their unique advantages: low cost, simple preparation technologies, and high efficiency. Three main chain polymeric metal complexes F, P1, and P2 connected with thienyl(8-hydroxyquinoline)-Cadmium (II) complexes have been synthesized by Heck coupling and characterized by Gel Permeation Chromatography, Fourier transform infrared, ¹H NMR, thermogravimetric analysis, TGA, UV-vis, cyclic voltammetry, photoluminescence (PL) emission spectra, and the application of dye sensitizers in DSSCs has been studied. The DSSCs exhibited good performance with a power conversion efficiency of up to 1.77%, under simulated air mass 1.5 G solar irradiation. They possess good stabilities, indicating the polymeric metal complexes are suitable for the fabrication processes of optoelectronic devices. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 3104–3112, 2013

KEYWORDS: dyes / pigments; electrochemistry; non-polymeric materials and composites; photochemistry; synthesis and processing

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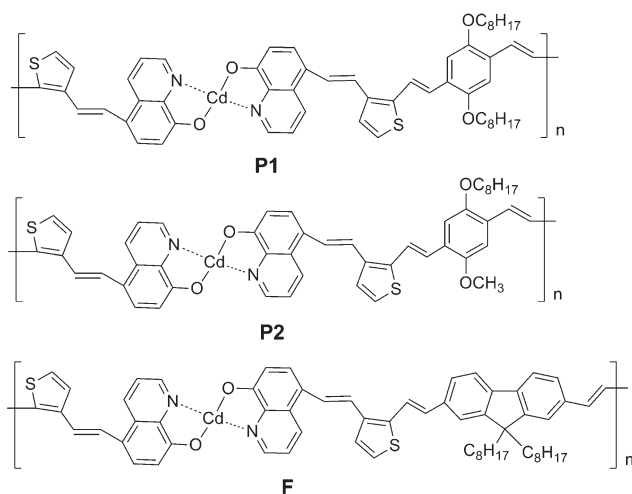
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INTRODUCTION

In the twenty-first century, energy production is one of the biggest challenges of science and technology. Using energy from sunlight by photovoltaic cells is a very important method to solve the growing global energy needs.^{1,2} Dye-sensitized solar cells (DSSCs) have attracted considerable attention due to their relatively small weight, low production cost, short energy pay-back time, high light-to-electrical conversion efficiencies, and so forth.^{3–5} However, as one of the most critical parts in DSSCs, the photosensitizer dyes should be further improved in the area of anchoring groups and electrochemical stability. In this regard, metal-complexes dyes,^{6,7} metal-free organic dyes,^{8,9} porphyrin dyes,^{10,11} and natural dyes^{12,13} have been applied to DSSCs in the past decades. Among them, metal-complexes dyes have broad absorption spectra and favorable photovoltaic properties because they contain central metal ion with ancillary ligands.¹⁴ Ru complexes dyes,¹⁵ are the most widely used metal-complexes dyes, which show suitable excited and ground state energy levels, relatively long excited-state lifetime, and good (electro) chemical stability.¹⁴ Grätzel and co-workers synthesized series of Ru complexes dyes, for example, N3/the black dye, its solar cell efficiency is over 10% under standard measurement conditions.

To some extent, it illustrates that the central metal ion of the complexes is an important part of the overall properties.¹⁵ Besides rare earth metal ions, many attempts have also been made to construct sensitizers with common metal ions, such as Zn,^{16–18} Co,¹⁹ Fe,^{20–22} and Cu.^{23,24} Sauvage and co-workers have discovered that Cu (I) complexes have similar photophysical properties with Ru complexes.²⁵

In conjugated polymers, exciton migration processes and energy transfer are very efficient, so they can be exploited in amplifying sensors response^{26,27} -exciton migration toward dissociation zones in solar cells.²⁸ Various polymers of this type, such as poly(9,9-dialkyl fluorenes) (PFs),^{29–31} poly(phenylene vinylenes),³² poly(thiophenes),^{33,34} poly(carbazoles),^{35,36} and poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene]³⁷ have been designed and investigated.³⁸ Furthermore, the application of polymers containing metal complexes as dye sensitizer in DSSCs is an area of increasing interest. This is partly due to their good solubility and strong absorption onto the surface of TiO₂. Shulz and co-workers³⁹ have recently reported the polyfluorene with Ir complexes in the side chain can enhance solar cell conversion efficiencies, for the longer diffusion length of polymers which showed 0.07% power conversion efficiency (J_{sc}



Scheme 1. The structure of polymeric metal complexes.

= 0.44 mA/cm², V_{oc} = 0.63 mV, FF = 0.19) under standard AM 1.5 G irradiation.

8-Hydroxyquinoline (8-HQ) is a chelating ligand with various properties, which has been extensively applied in the synthesis of metal complexes. Although large-scale use as a dye sensitizer of DSSCs, photosensitizers free of rare metals are desirable, the wide metal chelates of 8-HQ availability are of great interest in this respect.^{40–42} Thiophene and 8-hydroxyquinoline may satisfy application requirements to make an effective way to suppress charge recombination and hence to improve open-circuit photovoltage (V_{oc}). Polythiophene-containing complexes of 8-hydroxyquinoline with Zn (II), Cu (II), Eu (III) in the side chain have been synthesized and their device efficiency is up to 0.56%–1.16% under simulated air mass 1.5 G solar irradiation.⁴³

The synthesis, characterization, and photovoltaic properties of three novel main chain polymeric metal complex dyes, which contain the thienyl(8-hydroxyquinoline)–Cadmium (II) complexes as an acceptor (A), have been described in this investigation. Specifically, two phenylenevinylene copolymers (namely **P1** and **P2** with octyloxy and methoxy side groups) and one fluorenevinylene copolymer **F** carried octyl side groups as a donor group (D), can enhance the solubility of polymeric metal complexes. All polymeric metal complexes were successfully synthesized by the Heck coupling (Scheme 1). In addition, the optical properties, thermal properties, and photovoltaic properties of polymeric metal complexes are also investigated in this article.

EXPERIMENTAL

Materials

2-bromo-3-methylthiophene (**1**),⁴⁴ 2-bromo-3-bromomethylthiophene (**2**),⁴⁵ 5-formyl-8-tosyloxy quinoline (**4**),⁴⁶ 1,4-Divinyl-2,5-dioctyloxy benzene (**M-1**),⁴⁷ 2-methoxy-5-octyloxy-1,4-xylylene-bis(triphenylphosphonium bromide) (**6**),⁴⁸ and 2,7-bis(triphenylphosphonium)-9,9'-dioctylfluorene dibromide (**7**)⁴⁸ were prepared according to known literature procedures. All initial materials were obtained from Shanghai chemical reagent Co. (Shanghai China), and were used without further purification.

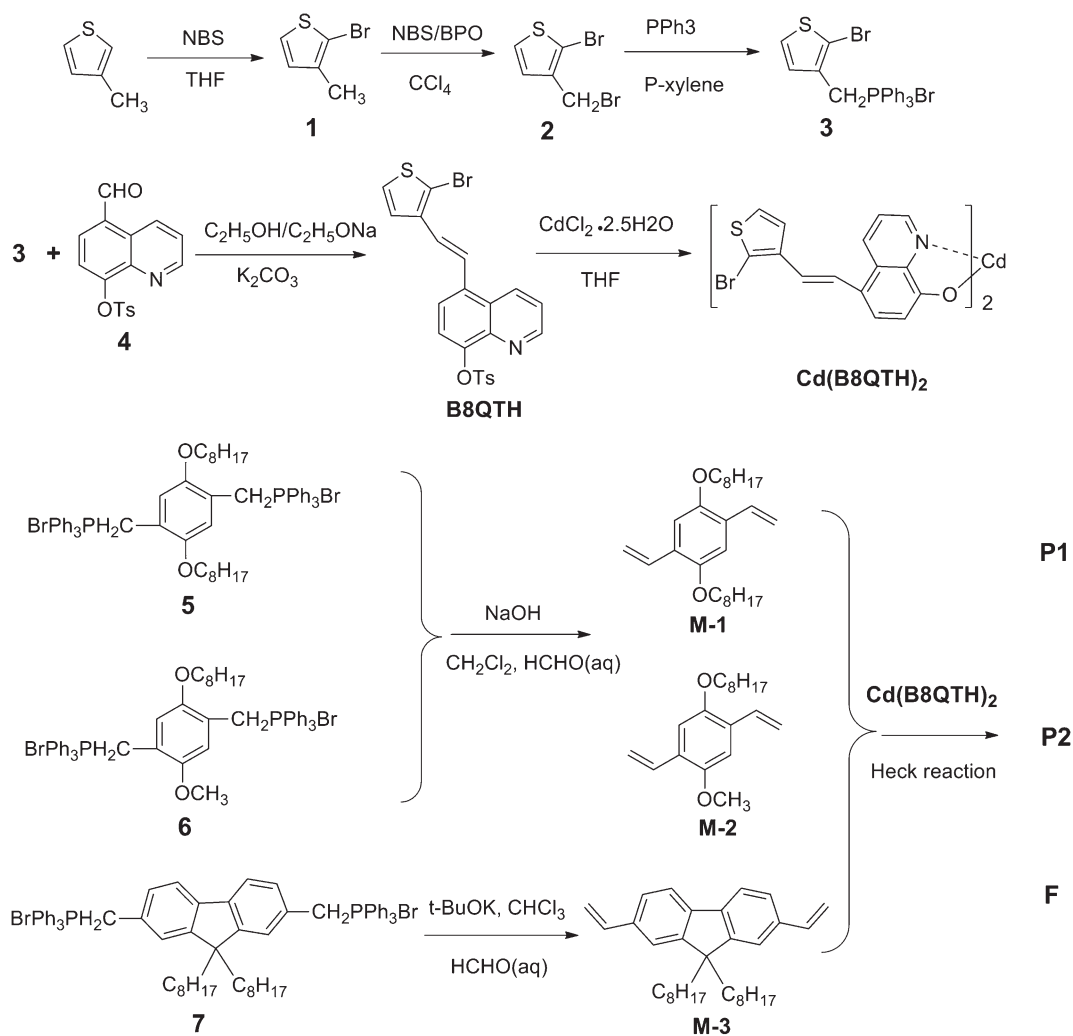
All solvents used in this work were analytical grade. *N,N*-Dimethylformamide (DMF) and tetrahydrofuran (THF) were dried by distillation over CaH₂. Triethylamine was purified by distillation over KOH. All other reagents and solvents from commercial market were used as they supplied.

Instrument and Measurements

Nuclear Magnetic Resonance All ¹H NMR was performed in CDCl₃ and recorded on a Bruker NMR 400 spectrometer, and using TMS (0.00 ppm) as the internal reference. The Fourier transform infrared (FT-IR) spectra were obtained on a Perkin–Elmer Spectrum one FTIR spectrometer by incorporating samples in KBr pellets.⁴⁹ Thermogravimetric analysis were run on a Shimadzu TGA-7 Instrument in nitrogen atmosphere at a heating rate of 20°C/min from 25 to 600°C.⁴⁹ Differential Scanning Calorimetry was exploited on materials by using a Perkin–Elmer DSC-7 thermal analyzer in nitrogen atmosphere at a heating rate of 20°C/min from 25 to 300°C. UV-Vis spectra were taken on a Lambda 25 spectrophotometer. Photoluminescent spectra were taken on a Perkin–Elmer LS55 luminescence spectrometer with a xenon lamp as the light source. Elemental analysis for C, H, and N were carried out on a Perkin–Elmer 2400 II instrument. Cyclic Voltammetry was conducted on a CHI chi630c Electrochemical Workstation, in a 0.1 mol/L [Bu₄N]BF₄ (Bu = butyl) DMF solution at a scan rate of 100 mV/s at room temperature. The working electrode was a glassy carbon rod. The auxiliary electrode was a Pt wire electrode, and saturated calomel electrode (SCE) was used as reference electrode. Gel Permeation Chromatography (GPC) analysis were done on WATER 2414 system equipped with a set of HT3, HT4, and HT5, 1-styragel columns with THF as an eluent (1.0 mL/min) at 80°C, being calibrated by polystyrene standard.

DSSCs Fabrication

Titania paste was prepared from P25 (Degussa AG, Germany) following a literature procedure.⁵⁰ Fluorine-doped SnO₂ conducting glass (FTO) were cleaned and immersed in aqueous 40 mM TiCl₄ solution at 70°C for 30 min, then washed with water and ethanol, and sintered at 450°C for 30 min. The 20–30 nm particles size TiO₂ colloid was coated onto the above FTO glass by sliding glass rod method, and obtained a TiO₂ film of 10–15 μm thickness. After dried, the TiO₂-coated FTO glass was sintered at 450°C for 30 min, then treated with TiCl₄ solution and calcined at 450°C for 30 min again. Then cooled to 100°C, the TiO₂ electrodes were soaked in 0.5 mM the dye-sensitized samples dyes **F**, **P1** and **P2** in DMF solution, and then were kept at room temperature under dark for 24 h. And 3-methoxypropionitrile solution containing LiI (0.5M), I₂ (0.05M), and 4-tert-butyl pyridine (0.5M) was used as the electrolyte. A Pt foil was clipped onto the top of the TiO₂ and was used as working electrode. The dye-coated semiconductor film was illuminated through a conducting glass without a mask. And photoelectron chemical performance of the solar cell was measured by using a Keithley 2602 Source meter under the control of the computer. The cell parameters were obtained under an incident light with intensity 100 mW/cm², which was generated by a 500W Xe lamp passing through an AM 1.5G filter with an effective area of 0.16 cm².



Scheme 2. Synthesis of monomers and polymeric metal complexes.

Synthesis

5-Bromo-3-methylthiophene (**1**) and 5-bromo-3-bromomethylthiophene (**2**) were synthesized according to the published literature.⁵¹

Synthesis of 2-Bromo-3-(thienyl Methyl Triphenylphosphonium Bromide) (**3**)

2-Bromo-3-bromomethyl thiophene (**2**) (3.9 g, 14.9 mmol) and triphenylphosphine (3.8 g, 14.9 mmol) were dissolved in 100 mL of dried p-xylene and refluxed under nitrogen. The solution was refluxed for 12 h. After cooling to room temperature, the white precipitate was collected by filtration, washed with dried ether and acetone repeatedly followed by drying, then the white solid was obtained. (6.36 g, yield 83%) ^1H NMR (400 MHz, CDCl_3 , δ , ppm): 7.65–7.83 (m, 15H), 7.19 (d, 1H), 6.95 (d, 1H), 5.55(d, 2H).

Synthesis of 2-Bromo-3-[2-(8-hydroxyquinoline)-vinyl]thiophene (**B8QTH**)

2-Bromo-3-thienyl methyl triphenylphosphonium bromide (**3**) (0.518 g, 10 mmol) and 5-formyl-8-tosyloxy quinoline (**4**) (3.46 g, 10 mmol) were dissolved in 200 mL of anhydrous ethanol.

Under an ice-water bath, NaOEt (0.4 g sodium in 20 mL of anhydrous ethanol) was added into the solution. After 30 min, the solution was stirred for 12 h at an ambient temperature. Then the solution was added potassium carbonate (0.21 g, 15 mmol) and refluxed for 8 h. The yellow solid was collected at the end of the condensation reaction and washed with distilled water and icy methanol. After dried in a vacuum at 45°C , the compound was obtained as pale yellow solid (2.0 g, yield 60%). ^1H NMR (400 MHz, CDCl_3 , δ , ppm): 8.82 (s, 1H), 8.53–8.55 (d, 1H), 7.80–7.82 (d, 1H), 7.62 (s, 1H), 7.58 (s, 1H), 7.51–7.54 (d, 1H), 7.33 (s, 1H), 7.23–7.25 (d, 1H), 7.08–7.12 (d, 1H). FT-IR (KBr, cm^{-1}): 3356 (O–H), 3092, 2939 (aromatic and vinylic C–H), 2900 (aliphatic C–H), 1664 (C=N), 1557 (C=C), 1451 (thiophene C–H), 786 (thiophene C–S). Anal. calcd for $[\text{C}_{15}\text{H}_{10}\text{SONBr}]$: C, 54.23; H, 3.03; N, 4.22; S, 9.65; Found: C, 54.15; H, 3.38; N, 4.48; S, 9.46.

Synthesis of $\text{Cd}(\text{B8QTH})_2$

An ethanol solution (10 mL) of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (0.114 g, 0.5 mmol) was dropped into a mixed THF solution (20 mL) of **B8QTH** (0.41 g, 1 mmol). The reaction mixture was neutralized carefully with 1M aqueous sodium hydroxide to slightly acidic

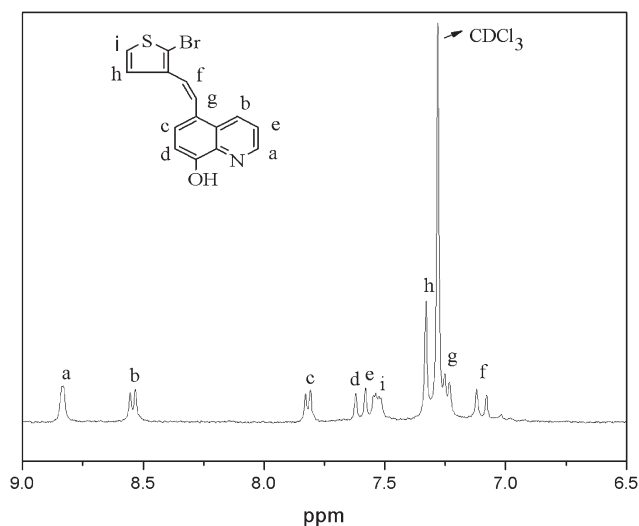


Figure 1. ^1H NMR spectra of B8QTH in CDCl_3 .

pH and was refluxed overnight. And then re-crystallize by ethanol. Filtered, washed with ethanol and water repeatedly, the yellow precipitate was collected. (0.28 g, yield 80%). FT-IR (KBr, cm^{-1}): 3094, 3032 (aromatic and vinylic C—H), 1571 (C=N), 1510 (C=C), 1095 (C—O—M), 515 (N—M). Anal. Calcd for $[\text{C}_{30}\text{H}_{18}\text{S}_2\text{O}_2\text{N}_2\text{BrCd}]$: C, 51.85; H, 2.61; N, 4.03; S, 9.23; Found: C, 51.58; H, 2.73; N, 4.21; S, 9.12.

Synthesis of 1,4-Divinyl-2-methoxyl-5-octyloxy Benzene (M-2)

Under argon atmosphere, a mixture of formaldehyde aqueous (18 mL) and 2-methoxyl-5-octyloxy-1,4-xylylene-bis(triphenyl phosphonium bromide) (**6**) (4.257 g, 4.5 mmol) in dichloromethane (60 mL) was stirred at 0°C , when an aqueous solution of NaOH (20 wt %, 39 mL) was added by dropwise in 1 h. After reaction mixture was stirred for 24 h, the aqueous layer of resulting solution was extracted with dichloromethane for three times. The combined organic layer was washed with water and

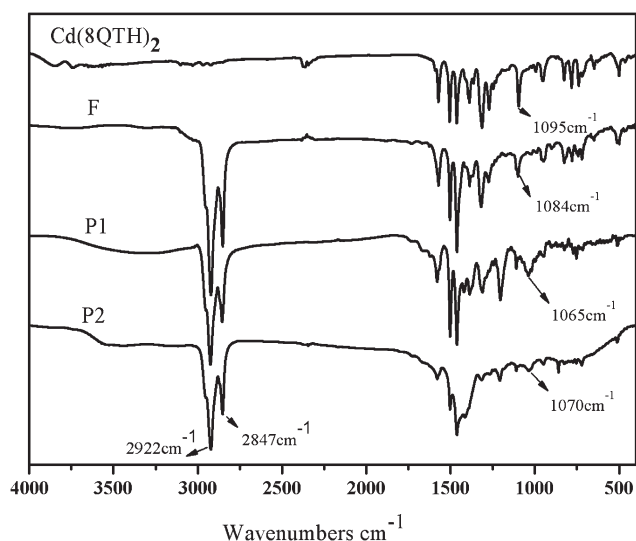


Figure 2. FT-IR spectra of $\text{Cd}(\text{B8QTH})_2$ and polymers F, P1, and P2.

Table I. IR Data of F, P1, and P2

	IR band (cm^{-1})				
	C—H (aliphatic chains)	C=N	C=C	C—O—Cd	N—Cd
$\text{Cd}(\text{B8QTH})_2$		1571	1510	1095	515
F	2925, 2849	1579	1502	1084	503
P1	2925, 2856	1586	1503	1065	508
P2	2922, 2847	1579	1502	1070	509

dried. Subsequently, the solvent was removed by rotary evaporation. The crude product was further purified by column chromatography (eluent: *n*-hexane/dichloro methane = 7:2) to afford light yellow liquid. (0.648 g, yield 50%). ^1H NMR (400 MHz, CDCl_3 , δ , ppm): 7.10–7.03 (m, 2H), 7.01 (s, 2H), 5.78–5.71 (d, 2H), 5.29–5.26 (d, 2H), 3.99–3.98 (t, 2H), 3.85 (s, 3H), 1.85–1.81 (m, 12H), 0.91–0.81 (t, 3H).

Synthesis of 2,7-Divinyl-9,9-dioctylfluorene (M-3)

A solution of 2,7-bis(triphenylphosphonium)-9,9'-dioctylfluorene dibromide (**7**) (0.45 g, 0.445 mmol) and 37% formaldehyde solution (0.3 g, 3.56 mmol) in 10 mL of chloroform were added dropwise with a solution of potassium tert-butoxide (0.45 g, 4 mmol) dissolved in 10 mL of EtOH. After being stirred for 5 h, the solution was poured into an excess of ice water. The organic layer was successively washed with water for twice, dried over MgSO_4 and filtered off, followed with solvent removal under reduced pressure. The residue was further purified by column chromatography using *n*-hexane as an eluent to colorless liquid of M-3 (0.177 g, yield: 90%). ^1H NMR (400 MHz, CDCl_3 , δ , ppm): 7.64–7.62 (d, 2H), 7.37–7.41 (m, 4H), 6.78–6.85 (m, 2H), 5.79–5.83 (d, 2H), 5.26–5.28 (d, 2H), 1.95–1.99 (m, 4H), 1.06–1.32 (m, 24H). 0.81–0.96 (t, 6H).

Preparation of Polymeric Metal Complexes

The preparation of F is a typical example for the preparation of polymeric metal complexes.

A flask was charged with a mixture of $\text{Cd}(\text{B8QTH})_2$ (0.1298 g, 0.315 mmol), M-3 (0.0602 g, 0.315 mmol), $\text{Pd}(\text{OAc})_2$ (0.0029 g, 0.013 mmol), tri-*o*-tolyl phosphine (0.0220 g, 0.072 mmol), DMF (8 mL), and triethylamine (3 mL). The flask was degassed and purged with N_2 . The mixture was heated at 90°C for 36 h under

Table II. Molecular Weight and Thermal Properties of F, P1, and P2

	\bar{M}_n^a [$\times 10^3$]	\bar{M}_w^a [$\times 10^3$]	PDI ^a	T_d^b [$^\circ\text{C}$]	T_g^c [$^\circ\text{C}$]
F	35.6	47.6	1.34	370	158
P1	38.5	48.0	1.25	311	115
P2	34.3	43.1	1.26	332	93

^a \bar{M}_n , \bar{M}_w , and PDI of the polymers were determined by GPC using polystyrene standards in THF.

^bThe temperature of degradation corresponding to a 5% weight loss determined by TGA at a heating rate of $10^\circ\text{C}/\text{min}$.

^cGlass transition temperature measured from DSC traces of the polymeric metal complexes.

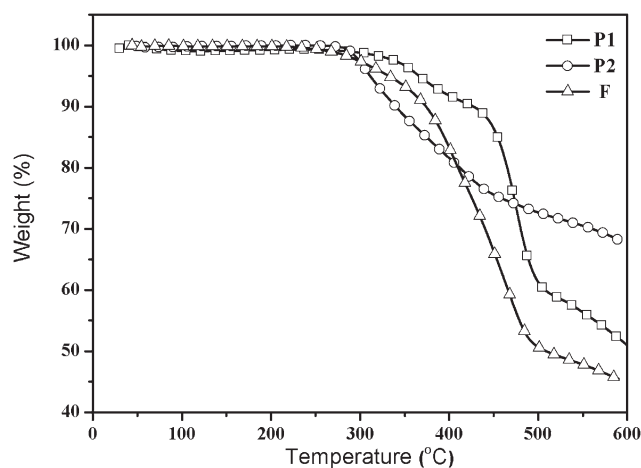


Figure 3. TGA plots of F, P1, and P2 with a heating rate of 20°C/min under nitrogen atmosphere.

N₂. Then, it was filtered and the filtrate was poured into methanol. The purple precipitate was filtered and washed with methanol. The crude product was purified by dissolving in THF and precipitating in methanol (0.14 g, yield 77%). FT-IR (KBr, cm⁻¹): 2926, 2852, 1694, 1590, 1450, 1420, 1336, 1258, 1206, 1188, 1033, 984, 896, 810, 750, 568 et al. Calcd for [C₆₃H₆₂S₂O₂N₂Cd]_n: C, 71.67; H, 5.92; N, 2.65; S, 6.07; Found: C, 71.90; H, 6.01; N, 2.89; S, 6.11.

Polymeric metal complex **P1** was similarly prepared in 69% yield from the reaction of Cd(B8QTH)₂ with **M-1**. FT-IR (KBr, cm⁻¹): 2928, 2852, 1694, 1654, 1590, 1456, 1420, 1338, 1258, 1202, 1132, 1036, 985, 896, 810, 752, 568 et al. Calcd for [C₅₆H₅₈S₂O₄N₂Cd]_n: C, 67.29; H, 5.85; N, 2.82; S, 6.42; Found: C, 67.46; H, 6.03; N, 2.63; S, 6.22.

Polymeric metal complex **P2** was similarly prepared in 79% yield from the reaction of Cd(B8QTH)₂ with **M-2**. FT-IR (KBr, cm⁻¹): 2926, 2854, 1696, 1654, 1592, 1458, 1338, 1258, 1188, 986, 896, 812, 752, 568 et al. Calcd for [C₄₉H₄₄S₂O₄N₂Cd]_n: C, 65.29; H, 4.92; N, 3.11; S, 7.11; Found: C, 66.03; H, 5.12; N, 3.27; S, 7.24.

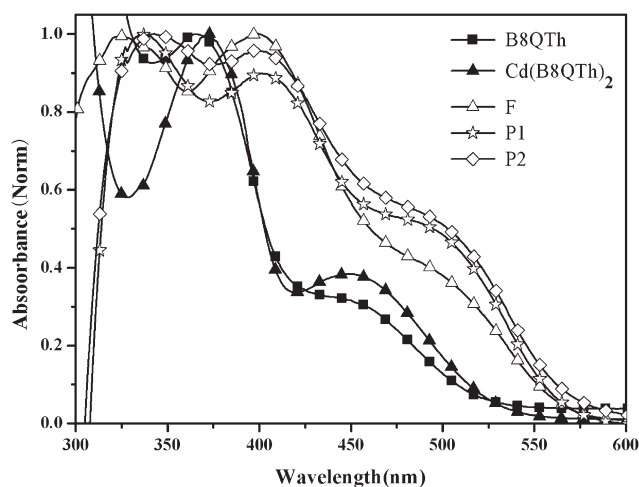


Figure 4. UV-vis absorption spectra of F, P1, and P2 in the THF solution ($1 \times 10^{-5} M$).

Table III. Optical Properties of F, P1, and P2

Polymer	UV-vis absorbance				E_g^{opta} (eV)	PL (nm)
	THF solution					
	λ_{max} (nm)	λ_{onset} (nm)	λ_{max} (nm)	λ_{onset} (nm)	λ_{max} (nm)	
F	324	401	501	561	2.21	423
P1	342	404	491	564	2.20	457
P2	347	401	496	578	2.14	470

^aThe optical band gap was obtained from the empirical formula $E_g = 1240/\lambda_{edge}$, in which the λ_{edge} is the onset value of absorption spectrum in long wave direction³⁹.

RESULTS AND DISCUSSION

Synthesis and Characterization

Scheme 2 outlines the synthesis route of the ligand **B8QTH**, which was synthesized by the Wittig reaction⁵² and Figure 1 gives the corresponding ¹H NMR spectra. The small but clear signals around 7.08–7.25 ppm are associated with the protons CH=CH group between the thiophene and hydroxyquinoline. The hydrogen proton of thiophene located at the 3 and 4 position is observed at 7.33 ppm and 7.51–7.54 ppm, respectively. 8.82 ppm, 8.53–8.55 ppm, 7.80–7.82 ppm, 7.58 ppm, and 7.62 ppm are attributed to the hydrogen protons of 8-hydroxyquinoline, but there is no detectable signal for the OH group in CDCl₃.⁵³

Three new polymeric metal complexes **F**, **P1**, and **P2** were synthesized by Heck coupling⁵⁴ utilizing the dibromide Cd(B8QTH)₂ as starting material. Polymeric metal complexes were synthesized by the reaction of dibromide Cd(B8QTH)₂ with divinyls **M-3**, **M-1**, and **M-2**, respectively (Scheme 2). Polymeric metal complexes **P2** and **P3** are PPV derivatives with octyloxy and methoxy side groups, respectively, while **F** is fluorine vinylene derivative. The polymeric metal complexes have the donor- π (bridge)-acceptor conjugated (D- π -A) architecture with the electron-rich 9,9-dioctylfluorene, 2-methoxy-5-octyloxy benzene, or 2, 5-dioctyloxy benzene as D unit and the

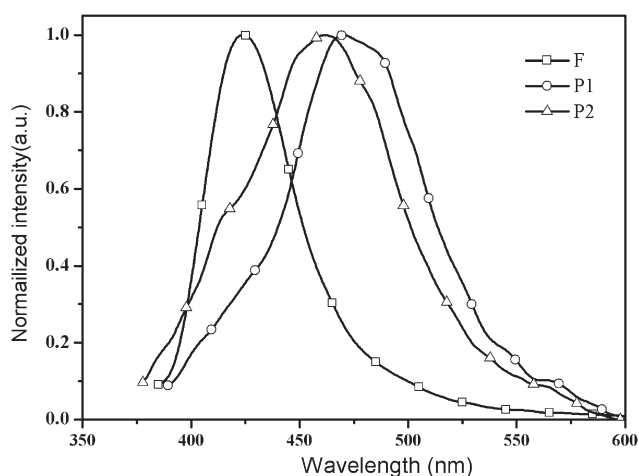


Figure 5. PL spectra of F, P1, and P2 in the THF solution ($1 \times 10^{-5} M$).

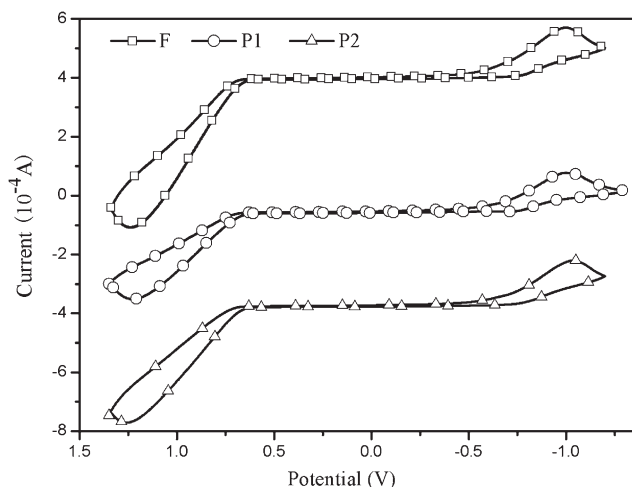


Figure 6. Cyclic voltammograms of **F**, **P1**, and **P2** measured in DMF solution containing $[\text{Bu}_4\text{N}]\text{BF}_4$ ($\text{Bu}=\text{butyl}$) as supporting electrolyte at a scan rate of 100 mV/s.

electron-deficient methal-8Qth as A unit. Even though dibromide $\text{Cd}(\text{B8QTH})_2$ is a metal complex of low solubility, the polymers have good solubility in common organic solvents such as: THF, toluene, DMSO, and DMF. The alkoxy or alkyl side chains and the cyclohexyl rings, which were attached to the metal complexes, enhanced the solubility of polymeric metal complexes.

The synthesis of polymeric metal complexes could be monitored by FT-IR spectroscopy. Figure 2 presents the IR spectra of $\text{Cd}(\text{B8QTH})_2$, **F**, **P1**, and **P2**. The main data are listed in Table I. Absorption peaks at 515, 503, 508, and 509 cm^{-1} can be attributed to metal-nitrogen bonds of $\text{Cd}(\text{B8QTH})_2$, **F**, **P1**, and **P2**, respectively,⁵⁵ the polymers show a red-shift compared with that of the free ligand. There isn't sharp absorption peak at 3356 cm^{-1} for $\text{Cd}(\text{B8QTH})_2$ and polymers, this indicates that there aren't O—H stretching. What's more, it can further indicate that the intramolecular hydrogen bond between **B8QTH** has been broken, which is most probably due to the coordination of Cd with N and O. The metal complexes and polymeric metal complexes have similar bands, but the band at 1084, 1065, 1070 cm^{-1} for **F**, **P1**, and **P2** are shown red shifts compared with dibromide $\text{Cd}(\text{B8QTH})_2$, respectively, which should be associated with C—O vibrations at the C—O—M site.⁵⁶ The polymeric metal complexes **F**, **P1**, and **P2** have similar bands that show common absorptions at 2922 and 2847 cm^{-1} , being associated with the CH_2 asymmetric and symmetric stretching vibration, respectively, which illuminates that alkoxy benzene

Table IV. Cyclic Voltammetric Results of the Polymeric Metal Complexes **F**, **P1**, and **P2**

Polymers	$E_{\text{onset}}^{\text{ox}}$ (V)	$E_{\text{onset}}^{\text{red}}$ (V)	HOMO (eV)	LUMO (eV)	E_g^{EC} (eV)
F	0.933	-0.778	-5.333	-3.622	1.711
P1	1.241	-0.996	-5.641	-3.404	2.237
P2	1.264	-1.036	-5.664	-3.364	2.300

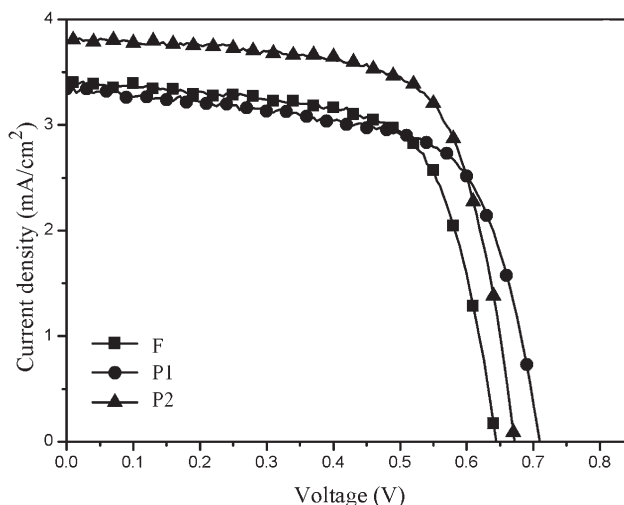


Figure 7. J–V curves of DSSCs based on **F**, **P1**, and **P2** in DMF solution.

and alkyl fluorene have been successfully embedded in the molecular chain. The number-average molecular weights (M_n) determined by GPC were 34.3–38.5 kg/mol with a relatively narrow polydispersity of 1.25–1.34 (Table II). The results prove that the copolymerization took place in the monomers. Combined with elemental analysis, it indicates that the polymeric metal complexes are obtained.

Thermal Properties

The thermal properties of polymeric metal complexes were investigated by thermogravimetric (TGA) and differential scanning calorimetric (DSC) analyses and were also reported in Table II. The TGA (Figure 3) results reveal that **F**, **P1**, and **P2** have good thermal stability with 5%-weight-loss at temperatures (T_d) of 370, 311, and 331 $^{\circ}\text{C}$ in nitrogen. The glass transition temperatures (T_g) of **F**, **P1**, and **P2** are 158, 115, and 93 $^{\circ}\text{C}$, respectively. Good thermal stability and high values of T_g are important parameters for polymers incorporated in PSC devices, because they provide resistance against the deformation or degradation of the active layers.

Optical Properties of the Polymers

The UV-vis absorption spectra of the ligand, metal complex, and the polymeric metal complexes in THF solution are shown in Figure 4. The corresponding optical data of the polymeric metal complexes are summarized in Table III. The ligand **B8QTH** in THF shows an absorption at 365 nm and a shoulder at 445 nm, which are assigned to the intraligand $\pi-\pi^*$ and $n-\pi^*$ electron transfer, respectively.⁵⁷ In contrast to ligand **B8QTH**, the metal complex $\text{Cd}(\text{B8QTH})_2$ shows a remarkably strong absorption band at 450 nm due to the coordination of

Table V. Photovoltaic Performances of DSSCs

Polymer	Solvent	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
F	DMF	3.41	0.645	0.672	1.48
P1	DMF	3.34	0.71	0.660	1.57
P2	DMF	3.80	0.67	0.694	1.77

the non-bonded electron pairs of the N atom with Cd(II).⁵⁸ The shorter wavelength band of complex Cd(B8QTH)₂ is 4 nm red-shifted from 365 to 369 nm. The red-shifted mainly results from the co-ordination of ligand with Cd(II), which weakens the conjugation plane of the complex and lowers the energy of the π^* orbital of the ligand, making the $\pi-\pi^*$ transition occurs at lower energy.⁵⁹ All absorption spectra of the three polymers exhibit two peaks and a shoulder above 450 nm. Compared with complex Cd(B8QTH)₂, the UV-vis absorption of polymers get broadened and cover a large part of the ultraviolet and visible region approximately from 300 to 600 nm. The absorption maximum ($\lambda_{a,max}$) of **F**, **P1**, and **P2** are located at 324, 342, and 347 nm, respectively. The red-shifted absorption maxima of **P1** and **P2** indicate a decrease of the conjugation length relative to **F**.

The photoluminescence (PL) spectra of **F**, **P1**, and **P2** in the diluted THF solution are shown in Figure 5. It can be seen that the PL peaks of **F**, **P1**, and **P2** are at 423, 457, and 470 nm respectively. **P1** and **P2** had comparable $\lambda_{f,max}$ which supports that the length of the alkoxy side chains did not influence their emission considerably. In contrast, the $\lambda_{f,max}$ of **P1** and **P2** was significantly red-shifted by 34 and 47 nm, respectively, relative to **F** because of the presence of the electron donating alkoxy side groups that usually causes a bathochromic shift.⁶⁰ The corresponding optical data of the polymeric metal complexes are summarized in Table III.

Electrochemical Properties

The electrochemical behaviors of the obtained polymers were investigated by cyclic voltammetry, which is an important property for organic materials used in solar cells. Figure 6 shows the cyclic of **F**, **P1**, and **P2**. The cyclic voltammetry of complexes were measured in DMF solution containing [Bu₄N]BF₄ (Bu = butyl) as supporting electrolyte and SCE as a reference electrode at a scan rate of 100 mV/s. The HOMO and LUMO are measured by electrochemical cyclic voltammetry (CV).

From the onset oxidation potentials (E_{ox}) and the onset reduction potentials (E_{red}) of the polymers, HOMO and LUMO energy levels as well as the energy gaps of the polymers were calculated according to the equations:⁶¹ HOMO = $-e(E_{ox} + 4.40)$ (eV); LUMO = $-e(E_{red} + 4.40)$ (eV); $E_g = e(E_{ox} - E_{red})$ (eV). The electrochemical measurements and calculated energy levels of polymers are listed in Table IV. The reduction and oxidation potentials of **F** were measured to be $E_{red} = -0.938$ eV and $E_{ox} = 1.249$ eV, respectively. The energy band gap was 2.187 eV, and the energy value of the HOMO was calculated to be -5.333 eV, and the energy value of the LUMO was calculated to be -3.622 eV. In the same case of **P1** and **P2**, their E_g is 2.237 eV and 2.300 eV, respectively. Based on the CV data, the electron accepting ability of the complexes follows the order of **F** < **P1** < **P2**, which shows **F** has stronger hole-transporting capacity and can control the extent of the polymeric metal complexes' band gap.

Photocurrent–Voltage Measurements

Figure 7 shows the irradiation source for the photocurrent density–voltage (J–V) measurement of the DSSCs devices based on the three polymeric metal complexes **F**, **P1**, and **P2**. And the corresponding open-circuit voltage (V_{oc}), short-circuit current

density (J_{sc}), fill factor (FF), and power conversion efficiency (η) are listed in Table V. It shows that the V_{oc} values of **F**, **P1**, and **P2** dyes are 0.645 V, 0.71 V, and 0.67 V, respectively, and the corresponding FF values are 0.672, 0.66, and 0.694. However, the J_{sc} values increased from 3.28 mA/cm² for **F** to 3.80 mA/cm² for **P2**. The power conversion efficiency based on **P2** reached 1.77%, which is higher than that of the device based on **F** (1.48%) and **P1** (1.57%).

Polymeric metal complexes **P2**-containing methoxy shows long-lived charge separation. As discussed in the UV-vis absorption spectra section, **P2** has the higher power conversion efficiency than **F** and **P1**, making it has greater adsorption and aggregation of the dyes on the TiO₂ surface. The adsorption modes of dyes on TiO₂ surfaces are very important for the DSSCs efficiency.⁶² Therefore, in order to obtain a high η value, the dyes must be absorbed on the surface of the TiO₂ intimately.

Although the power conversion efficiency of **F**, **P1**, and **P2** is relatively low in the device, we believe this type of functional conjugated material would be a potential material for solar cell and it would provide a new way to synthesize dye for DSSCs. And further work on optimizing the device performance is under investigation.

CONCLUSIONS

In summary, a series of novel main chain polymeric metal complexes, comprising thienyl(8-hydroxyquinoline)–Cadmium (II) Complexes with D- π -A structure, which are selected based on the prominent metal to ligand charge transfer (MLCT) band. Polymeric metal complexes **P1** and **P2** have octyloxy and methoxy in side groups, respectively, and **F** has octyl side groups. Polymeric metal complexes **F**, **P1**, and **P2** can be soluble in common organic solvents due to their long alkyl side groups. Increasing the number of thiophene units can further extend the π -conjugation, which can also increase the short circuit photocurrent, as the result of the red-shifted absorption of the sensitizer loaded TiO₂ film.⁶³ But the red-shifted absorption of the **F**, **P1**, and **P2** is not that obvious, so the J_{sc} of them are still small, which can lead to the power conversion efficiency of DSSCs based on **P2** (1.77%), **F** (1.48%), and **P1** (1.57%) are low. The three materials show good stability, and their thermal decomposition temperatures are 370, 311, and 331°C, respectively. These results strongly indicate the importance of their further investigation as new solar cell materials. Although the conversion efficiency is not very high now, there is no doubt that this type of functional conjugated material would be a potential material for solar cell. As the next work, our group will try to synthesize functional polymer materials with one anchoring group such as cyano, ester, acid chloride, acetic anhydride, carboxylate salt, or amide groups for strong adsorption onto the surface of TiO₂. We firmly believe that next investigation will be reported in the near future.

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