Two Main Chain Polymeric Metal Complexes as Dye Sensitizers for Dye-Sensitized Solar Cells Based on the Coordination of the Ligand Containing 8-Hydroxyquinoline and Phenylethyl or Fluorene Units with Eu(III)

LIFEN XIAO, YUAN LIU, QIAN XIU, LIRONG ZHANG, LIHUI GUO, HAILIANG ZHANG, CHAOFAN ZHONG

Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry of Education, Xiangtan University, College of Chemistry, Xiangtan, Hunan 411105, People's Republic of China

Received 6 December 2009; accepted 27 January 2010 DOI: 10.1002/pola.23961 Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Two novel main chain polymeric metal complexes containing 8-hydroxyquinoline europium complexes and phenylethyl or fluorene units: 1,4-Dioctyloxy-2,5-bis[2-(8-hydroxyquinoline)-vinyl]-benzene Eu(III) (3) and 2,7-bis[2-(8-hydroxyquinoline)vinyl]-9,9'-diocthylfluorene Eu(III) (4) with donor–acceptor- π -conjugated structure (D- π -A) have been synthesized and investigated as dye sensitizers for dye-sensitized solar cells dyes (DSSCs). They have been determined and studied by FT-IR, TGA, DSC, GPC, Elemental analysis, UV–vis absorption spectroscopy, photoluminescence spectroscopy, cyclic voltammetry, and application in dyesensitized solar cells (DSSCs) as dye sensitizers. On the basis of optimized dye and molecular structure, they have shown solar-to-

INTRODUCTION Organic electron donor–acceptor– π -conjugated (D– π -A) compounds are of interest owing to the possibility of attaining multiple redox states (*p*-type or *n*-type doping).^{1–5} Importantly, donor–acceptor conjugated polymer systems have been widely studied for their potential applications in organic electronics and optoelectronics, including light-emitting diodes, field-effect transistors, and photovoltaic cells.^{6–10} Among them, polymer solar cells (PSCs) are more attractive because of the importance of solar energy utilization and its advantages, such as low cost, light weight, easy preparation, and the possibility to fabricate flexible.^{11,12}

Currently, dye-sensitized solar cells (DSSCs) as the most promising alternatives for the photovoltaic conversion of solar energy have attracted much interesting attention because the groundbreaking work by O'Regan and Grätzel¹³ due to their high efficiency, potential low-cost, and simple assemble technology, and so forth.¹⁴ The main components of a DSSC are a nanocrystalline oxide semiconductor electrode, a photosensitizer, a redox electrolyte, and a counter electrode.¹⁵ Among them, the photosensitizers play a crucial role for the DSSCs to get higher solar-to-electricity conversion efficiency (η) and have been actively researched by scientists around the world, whose common design is to link the electron electricity conversion efficiency 2.25% for **3** ($J_{sc} = 4.77 \text{ mA cm}^2$, $V_{oc} = 630 \text{ mV}$, FF = 0.75) and 3.04% for **4** ($J_{sc} = 6.33 \text{ mA cm}^2$, $V_{oc} = 640 \text{ mV}$, FF = 0.75), under the illumination of AM1.5G, 100 mW/ cm². The IPCE of **3** and **4** are 30% and 46% at 400 nm, respectively. Besides, they showed good stabilities with thermal decomposition temperatures at 280 °C and 225 °C, respectively, which are suitable for DSSCs. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 1943–1951, 2010

KEYWORDS: 8-hydroxyquinoline; DSSCs; dyes/pigments; fluorene; functionalization of polymers; metal-polymer complexes; phenylethyl; polymeric metal complexes

donor and the electron acceptor by a conjugated spacer.¹⁶ Although ruthenium complexes are appropriate as photosensitizers and the high solar-to-electric power conversion efficiencies more than 11% has been achieved with DSSCs,¹⁷ their extensive application would be confined by the limited availability and environmental issues.¹⁸ Thus, the commercial application of the organic dyes in DSSCs is promising.

Up-to-now, a profound change in philosophy and a huge extension of possible structures has taken place. Many researchers are eager to design functional crosslinked polymer, which is also an attractive tool to construct well-organized π -conjugated materials and have actually been advanced to be among the most frequently used π -conjugated materials.¹⁹ For the further development of functional crosslinked polymers, studies on the polymers with various electron-accepting units and electrondonating units are helpful for a better understanding of the relationship between the chemical structures and properties of the polymers. The changes in physical properties of these polymers strongly depended on the nature of both the π -conjugation and the type of D-A substitution.²⁰⁻²⁵ In most cases, electroactive monomers, such as thiophene,²⁶ carbazole,^{19,27} and triarylamine¹⁹ are essential for electro-polymerization. Then, in the past few years, these structures came up as highly

Correspondence to: C. Zhong (E-mail: zhongcf798@yahoo.com.cn)

Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 48, 1943–1951 (2010) © 2010 Wiley Periodicals, Inc.



SCHEME 1 Molecular Structures of DB8QB-Eu(III) (3) and B8QDF-Eu(III) (4).

promising conjugated materials, because of the introducing of the organic functional groups, which can be applied in organic electronic devices.²⁸

Based on the report that the complexable and π -conjugated crosslinked polymers do not decrease, the injection into the TiO₂ electrode and J_{sc} is comparable with the other materials. So, if the design of the crosslinked metal polymers is possible, their applications in the DSSCs would be potentially better than the other materials.²⁹ To the best of our knowledge, the reports on the crosslinked coordination polymers and their electrochemical properties are still rare.

Despite recent advances in DSSCs materials, for example, Zn(II) metal-porphyrins compounds,^{30,31} Ru-sensitized DSSCs exist in which the dye is attached to the TiO₂ via axial ligands^{32–34} or through anchoring groups on the macrocycle periphery,³⁵ research into ligand design for electronic materials has been dominated by the dipyridine and azaindole moiety. Furthermore, practical applications of these compounds in DSSCs would require a new generation of organic ligands that are inexpensive and robust. 8-Hydroxyquinoline (8-HQ) is a chelating ligand with varies properties, which has been extensively exploited in the synthesis of metal complexes. To improve the optoelectronic output of this class of materials, studies involving either 8-HQ or 8-HQ-like species are currently under way.^{36–38} Especially, dendritic derivatives containing 8-hydroxyquinoline have been designed and investigated so far.³⁹

Recently, lanthanide complexes are under active research because of their great potential for applications in optics and electronics.⁴⁰⁻⁴² They combine the outstanding luminescent properties with the remarkable stability of various hosts and these lanthanide complexes could be finely tuned by alternating independently or matching the different groups of D- π -A dyes.⁴¹ Such as Ir(III) complexes are of particular interest due to their promising using as photosensitizers in electroluminescent materials;⁴³ Eu(III) complexes that exhibit both high emission quantum yields and fast radiation rates are desirable electrochemical materials as well.⁴⁴ Addi-

tionally, Eu(III) complexes are designed to meet two criteria: (1) The potential of Eu^{3+} is over the conduction level of TiO_2^{29} and (2) they can be used as energy acceptor units in energy transfer processes.⁴⁵ When compared with other metal complexes via axial ligands, the synthesis of metal polymeric complexes are easier with less steric barrier.⁴⁶ The metal polymeric complexes containing europium could make better electric contact to be good energy acceptor. There is no doubt that chemical modifications between Eu^{3+} and 8-HQ may satisfy application requirements as an acceptor to make an effective way in the application of DSSCs, consequently.

On the basis of the concept of donor- π conjugation bridgeacceptor structure, we here designed and synthesized a kind of new dyes. Among the electron-donating units, phenylethyl⁴⁷⁻⁴⁹ and fluorene⁵⁰ units are very attractive: They not only have low band gap but also are the π -conjugated ring moieties. On the other hand, to synthesize Euq₃-functionalized polymers is typical, combination of phenylethyl or fluorene units to metal polymeric main chain complexes might expand the π -conjugation system, sustain the stability of the dye molecule and would have ability of donor and acceptor simultaneously. The π -conjugated systems between the donor (phenylethyl or fluorene group) and the acceptor (Euq₃) were systematically extended to adjust the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of the dyes (see Scheme 1). Moreover, the solubility in common organic solvents might be enhanced by introducing fluorene and benzene groups at the 5-position of 8-hydroxyquinoline by Wittig-reaction. Especially, their photophysical and electrochemical properties as well as the application in DSSCs were investigated in this article.

EXPERIMENTAL

Materials

All materials were obtained from Shanghai chemical reagent (Shanghai, China) and were used without further

purification. All solvents used in this work were analytical grade. Europium chloride (EuCl₃·6H₂O) was obtained by dissolving Eu₂O₃ (99.99%) in hydrochloric acid followed by successive fuming to remove excess acid and then dissolved in ethanol. 1,4-Bis(bromomethyl)-2,5-dioctyloxybenzene and 2,7-dibromomethyl-9,9'-dioctylfluorene are synthesized according to the methods well-described in the refs. 51 and 52, respectively.

Instrument and Measurements

Nuclear magnetic resonance all ¹H NMR were performed in CDCl₃ and recorded on a Bruker NMR 400 spectrometer, and using TMS (0.00 ppm) as the internal reference. The FT-IR spectra were obtained on a Perkin-Elmer Spectrum One Fourier transform infrared spectrometer by incorporating samples in KBr disks. Thermogravimetric analyses were run on a Shimadzu TGA-7 Instrument in nitrogen atmosphere at a heating rate of 20 K/min from 25 to 900 °C. Differential scanning calorimetry was performed on materials using a Perkin-Elmer DSC-7 thermal analyzer under nitrogen atmosphere at a heating rate of 20 K/min from 25 to 250 °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 was carried out using a Perkin-Elmer 2400 II instrument. Cyclic voltammetry was conducted on a CHI chi630c Electrochemical Workstation, in a 0.1 mol/ $L[Bu_4N]BF_4$ (Bu = butyl) DMF solution at a scan rate of 50 mV/s at room temperature. The working electrode was a glassy carbon rod, the auxiliary electrode was a Pt wire electrode, and Ag/AgCl was used as reference electrode. Gel permeation chromatography (GPC) analyses were done on WATER 2414 system equipped with a set of HT3, HT4, and HT5, *l*-styrayel columns with DMF as an eluent (1.0 mL/min) at 80 °C, calibrated by polystyrene standard.

Synthesis

1,4-Bis(triphenylphosphoniomethyl)-2,5-dioctyloxybenzene dibromine (a1)

A solution of 1,4-bis(bromomethyl)-2,5-dioctyloxybenzene (2.6 g, 0.011 mol) and triphenylphosphine (7.4 g, 0.028 mol) in 150 mL of dried *p*-xylene was stirred at reflux for 12 h. The reaction system was then allowed to cool to room temperature and the white precipitate was collected by filtration, washed with dried ether and acetone repeatedly followed by drying. ¹H NMR (400 MHz, CDCl₃, δ): 7.60–7.75 (m, 30H), 6.72 (s, 2H), 5.31–5.34 (d, 4H), 3.00 (t, 4H), 1.58 (d, 4H), 1.04–1.31 (m, 20H), 0.89–0.92 (t, 6H).

2,7-Bis(triphenylphosphoniomethyl)-9,9'-dioctylfluorene dibromine (a2)

With the same manner with 1a, a white solid (1.9 g, yield 75%). ¹H NMR (CDCl₃, δ , ppm): 7.73–7.80 (m, 24H), 7.62–7.67 (t, 6H), 7.37–7.40 (d, 2H), 7.03–7.05 (d, 2H), 7.00 (s, 2H), 5.46–5.50 (d, 4H), 1.46 (t, 4H), 1.09–1.23 (m, 24H), 0.82–0.90 (t, 6H).

5-Formyl-8-tosyloxyquinoline (b)

5-Formyl-8-hydroxyquinoline (synthesized according to the ref. 53) (15 mmol, 2.6 g) was dissolved in methylene chloride (80 mL), TsCl (18 mmol, 3.2 g) was added in the solution in one portion under the ice-water and then stirred at ambient temperature. After 12 h, the solution was poured the cool water. The organic layer was collected and dried over anhydrous MgSO₄, the removal of solvent gave a yellow solid compound (5.1 g, yield 98%). ¹H NMR (CDCl₃, δ , ppm): 10.29 (s, 1H), 9.75 (d, 1H), 9.57–9.60 (d, 1H), 8.01–8.06 (d, 1H), 7.80–7.82 (d, 1H), 7.58–7.59 (d, 2H), 7.40–7.42 (d, 2H), 7.35–7.40 (d, 1H), 0.85–0.88 (t, 3H).

1,4-Dioctyloxy-2,5-bis(8-hydroxyquinoline-vinyl) benzene (DB8QB) (1)

1,4-Bis(triphenylphosphoniomethyl)-2,5-dioctyloxybenzene dibromine (9.72 g, 0.01 mol) and 5-formyl-8-tosyloxyquinoline (6.92 g, 0.02 mol) were dissolved in 100 mL of anhydrous enthanol. Under an ice-water bath, EtONa (2 g sodium in 20 mL of anhydrous enthanol) was added into the solution. After 30 min, the solution was stirred for 12 h. Then added some K₂CO₃ and refluxed for 8 h. The yellow solid was collected at the end of the condensation reaction and washed with distilled water and ethanol. After dried in vacuum at 45 °C for 1 day, compound **1** was obtained as a pale yellow solid (3 g, yield 45%). ¹H NMR (CDCl₃, δ , ppm): 8.80 (s, 2H), 8.56-8.58 (d, 2H), 7.74-7.76 (d, 2H), 7.66-7.70 (d, 2H), 7.48-7.50 (d, 2H), 7.34-7.38 (d, 2H), 7.19-7.21 (d, 2H), 7.07 (d, 2H), 3.73-4.01 (t, 4H), 2.18-2.25 (d, 4H), 1.23-1.57 (m, 20H), 0.83–0.90 (m, 6H). FT-IR (KBr, cm⁻¹): 3411 (0–H), 2915, 2856 (aromatic and vinylic C-H), 1638 (C=N), 1529 (C=C), 962 (CH=CH trans). Anal. Calcd. for $[C_{44}H_{52}O_4N_2]$: C, 78.54; H, 7.79; N, 4.16; Found: C, 78.01; H, 8.08; N, 4.58.

2,7-Bis[2-(8-hydroxyquinoline)-vinyl]-9,9'-diocthylfluorene (B8QDF) (2)

2,7-bis[2-(8-hydroxyquinoline)-vinyl]-9,9'-diocthylfluorene (B8QDF) (2) was obtained by the same way with compound **1** using 2,7-bis(triphenylphosphoniomethyl)-9,9'-dioctylfluorene dibromine and 5-formyl-8-tosyloxyquinoline, a yellow solid. (3.6 g, yield 49%). ¹H NMR (CDCl₃, δ , ppm): 8.46 (s, 2H), 8.40 (d, 4H), 8.30 (d, 4H), 7.80–7.90 (m, 6H), 7.53–7.54 (m, 6H), 7.50 (d, 2H), 7.23 (d, 2H), 2.43–2.46 (t, 4H), 1.08–1.26 (m, 24H), 0.78–0.83 (t, 6H). FT-IR (KBr, cm⁻¹): 3366 (O–H), 2928, 2864 (aromatic and vinylic C–H), 1579 (C=N), 1520 (C=C), 960 (CH=CH trans). Anal. Calcd. for [C₅₁H₅₆O₂N₂]: C, 84.03; H, 7.74; N, 3.84; Found: C, 83.69; H, 7.98; N, 4.03.

DB8QB-Eu(III) (3)

A ethanol solution (10 mL) of EuCl₃·6H₂O (0.366 g, 1 mmol) was dropped to a mixed THF solution (20 mL) of DB8QB (2.02 g, 3 mmol). The reaction mixture was neutralized carefully with 1 M aqueous sodium hydroxide until neutral to slightly acidic pH and was refluxed overnight. Then recrystallize by ethanol. Filtered, washed with ethanol and water repeatly, the light-yellow precipitate was collected (1.8 g, yield 83%). FT-IR (KBr, cm⁻¹): 2934, 2844 (aromatic and vinylic C—H), 1630 (C=N), 1499 (C=C), 488 (N—M). Anal. Calcd. for [C₁₃₂H₁₅₆O₁₂N₆Eu]: C, 73.04; H, 7.24; N, 3.87; Found: C, 72.86; H, 7.56; N, 3.71.

B8QDF-Eu(III) (4)

In the same manner as described for **3**, a red solid (1.98 g, yield 85%). FT-IR (KBr, cm^{-1}): 2922, 2850 (aromatic and



SCHEME 2 Synthesis of DB8QB-Eu(III) (3) and B8QDF-Eu(III) (4).

vinylic C—H), 1559 (C=N), 1550 (C=C), 524 (*N*—M). Anal. Calcd. for $[C_{153}H_{162}O_6N_6Eu]$: C, 78.77; H, 7.00; N, 3.60; Found: C, 78.56; H, 7.13; N, 3.45.

RESULTS AND DISCUSSION

Synthesis and Characterization

Scheme 2 outlines synthetic routes of the two ligands DB8QB and B8QDF, which were synthesized by Wittig-reaction. Figure 1(a) gives the ¹H NMR spectra of DB8QB (1), the characteristic signals at around 7.36 and 7.20 ppm can be assigned to the resonance of protons on vinylene group. $-CH_2$ – linked to oxygen is at 3.73 ppm, the signals at 2.18-0.83 ppm correspond to the protons of the long alkyl chain and 7.07 ppm is attributed to the signals of protons of phenyl hydrogen; 8.80 ppm, 8.56-8.58 ppm, 7.74-7.76 ppm, and 7.66-7.70 ppm are attributed to the protons of 8-hydroxyquinoline. Figure 1(b) shows the ¹H NMR spectra of B8QDF (2), the vinyl proton peaks appeared at around 7.50 and 7.23 ppm; 8.46 ppm, 8.40 ppm, 8.30 ppm, and 7.66-7.70 ppm are attributed to the protons of 8-hydroxyquinoline, the protons of fluorene are observed at 7.80-7.90 ppm and 7.53-7.54 ppm. The signals at 2.46-0.78 ppm were attributed to the alkyl of fluorine. Besides, there are no detectable signals for the OH group in CDCl₃ in both of the spectra.⁵⁴

The FT-IR spectra of the polymeric metal complexes **3** and **4** are shown in Figure 2. Upon comparison of the ligands, all the bands of the corresponding complexes are red shift, which is attributed to the extending of π -conjugation after coordinated with metal ions successfully. There are bands appears at 488 cm⁻¹ and 505 cm⁻¹ in polymeric metal com-

plexes **3** and **4**, respectively, which are absent in the free corresponding ligands, can be attributed to metal-nitrogen bonds. 55

Gel permeation chromatography (GPC) studies showed that **3** and **4** have weight-averaged molecular weights at 18 and 23.2 kg/mol (7 and 8 repeating units on average for **3** and **4**, respectively) with a relatively narrow polydispersity index (PDI) between 1.14 and 1.21 for **3** and **4**, respectively (shown in Table 1). As expected, **3** and **4** were soluble in organic solvents such as DMF, toluene, and DMSO, but present poor solubility in THF, DCM, and MeOH. The elemental analysis of the polymeric metal complexes **3** and **4** show that the ratio of europium metal and DB8QB or B8QDF is 1:3. These results, combined with elemental analysis, indicate that the polymers are obtained.

Optical and Thermal Properties of the Polymers

Figure 3 presents the UV-vis absorption spectra of **3** and **4** recorded in solution using DMF as solvent and adsorbed on TiO₂ films. We consider that the spectra of complexes **3** and **4** exhibit λ_{max} at 318 and 393 nm in DMF solution, respectively. We can see both of the dyes with a strong absorption maximum in the visible region absorbed on TiO₂ films corresponding to intramolecular charge transfer absorption. The peaks are located at 436 and 448 nm for **3** and **4**, respectively. The absorption spectra of dyes attached to TiO₂ film are red-shifted compared with those of the corresponding solution spectra, which is attributed to the formation of dye aggregates on the TiO₂ surface and an interaction between the dyes and TiO₂.⁵⁶⁻⁵⁸ This phenomenon would benefit the photoelectrical conversion efficiency of the dye-sensitized



FIGURE 1 ¹H NMR spectra of DB8QB (a), B8QDF (b) in CDCI₃.

solar cells.⁵⁹ At the same time, the spectra become broader than that in solution, which is attributed to a greater amount of absorbed dye on the TiO₂ films, and as a result of the increased intermolecular π - π interaction with expanding π -conjugation.⁶⁰

We also measured the PL spectra of the polymeric metal complexes in DMF solution and the solid state shown in Figure 4. The PL spectra of the polymeric metal complexes show an emission peak at 503 and 458 nm for **3** and **4**, respectively, in DMF solution. It can be seen that the PL peak of **3** and **4** in the solid state is red-shifted by about 70,103 nm to 573 and 561 nm, respectively, in comparison with that of the solution, which is assigned to that the coordination of metal ions enhances the capability of accept-electron of ligands, decreases and steadies the electron transition energy of the intra ligand charge-transfer and indicates that the conformation of the two metal polymeric complexes **3** and **4** changed significantly in the solid state. This pheno-

menon ensures that all photons absorbed by the polymeric metal complexes are useful for the photovoltaic conversion.

The thermal stability of the two polymeric metal complexes **3** and **4** were studied by means of thermo gravimetric analyses (TGA) and differential scanning calorimetry (DSC) under nitrogen atmosphere, which are shown in Table 1 and Figure 5. It is seen that **3** and **4** have glass transition temperature, $T_{\rm g}$ of 168 °C and 150 °C, respectively. TGA showed that the 5 wt % loss temperature for **3** and **4** are 280 °C and 225 °C, respectively, suggesting that the polymers may be served as an advantage for the fabrication processes of DSSCs and other optoelectronic devices.

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 voltammetry curves of **3** and **4**. The cyclic



FIGURE 2 FT-IR spectra of DB8QB, DB8QB-Eu(III) (a), B8QDF(2), B8QDF-Eu(III) (b).

 TABLE 1 Molecular Weight and Thermal Properties

 of DB8QB-Eu(III) and B8QDF-Eu(III)

	\overline{M}_{n} (×10 ³)	\overline{M}_{w} (×10 ³)	PDI	Tg ^ª (°C)	<i>T</i> d ^b (°C)
DB8QB-Eu(III)	18	20.5	1.14	168	280
B8QDF-Eu(III)	23.2	28	1.21	150	225

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

^b The data were obtained from TGA of the polymeric metal complexes.

voltammetry of complexes were measured in DMF solution containing [Bu₄N]BF₆(Bu = butyl) as supporting electrolyte and Ag/AgCl as reference electrode at a scan rate of 50 mV/s. The HOMO and LUMO are measured by electrochemical cyclic voltammetry (CV). When Ag/AgCl electrode is used as the reference electrode, the correlation can be expressed as the equation: HOMO = $-e(E_{\rm ox} + 4.40)$ (eV); LUMO = $-e(E_{\rm red} + 4.40)$ (eV).^{61,62} The corresponding data are obtained and tabulated in Table 2. The reduction and oxidation potentials of **3** were measured to be $E_{\rm red} = -1.224$ V



FIGURE 3 Normalized absorption spectra of DB8QB-Eu(III) (3) and B8QDF-Eu(III) (4) in DMF solution (a) and adsorbed on TiO_2 films (b).



FIGURE 4 PL spectra of DB8QB-Eu(III) (3) and B8QDF-Eu(III) (4) in DMF solution and in the solid state.

and $E_{\rm ox} = 0.914$ V, respectively. The energy band gap was 2.038 eV, the energy value of the HOMO was calculated to be -5.314 eV and the energy value of the LUMO was calculated to be -3.276 eV. In the case of **4**, the HOMO and LUMO energy value were calculated as -5.302 eV and -3.404 eV, respectively, with an $E_{\rm g}$ of 1.898 eV. In the comparison of **3**, the HOMO of **4** is higher than **3** resulted from the stronger hole-transporting capacity of **4**, indicating that using strong donors with high HOMO energy levels and strong acceptors with low LUMOs can control the extent of the polymeric metal complexes band gap.

Fabrication of DSSCs

Titania paste was prepared following a procedure: Fluorinedoped 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, sintered at 450 °C for 30 min. The 20–30 nm particles sized TiO₂ colloid was coated onto the above FTO glass by sliding glass rod method to obtain a TiO₂ film of 10–15 μ m thickness. After drying,



FIGURE 5 TGA plots of DB8QB-Eu(III) (3) and B8QDF-Eu(III) (4) with a heating rate of 10 $^{\circ}$ C/min under nitrogen atmosphere.



FIGURE 6 CV curves of DB8QB-Eu(III) (3) and B8QDF-Eu(III) (4) measured in DMF containing $[Bu_4N]BF_6(Bu = butyI)$ as supporting electrolyte at a scan rate of 50 mV/s.

the TiO₂-coated FTO glass were sintered at 450 °C for 30 min, then treated with TiCl₄ solution and calcined at 450 $^\circ$ C for 30 min again. After cooling to 100 °C, the TiO₂ electrodes were soaked in 0.5 mM the dye-sensitized samples dyes ${\bf 3}$ and 4 in DMF solution, then kept at room temperature under dark for 24 h. 3-Methoxypropionitrile solution containing LiI (0.5 M), I₂ (0.05 M), and 4-tert-butyl pyridine (TBP) (0.5 M) was used as the electrolyte. A Pt foil used as counter electrode was clipped onto the top of the TiO_2 using as working electrode. The dye-coated semiconductor film was illuminated through a conducting glass support without a mask. 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 \cdot cm⁻², which was generated by a 500 W Xe lamp passing through an AM 1.5G filter with an effective area of 0.196 cm^2 .

Photocurrent-Voltage Measurements

Figure 7 shows the irradiation source for the photocurrent density-voltage (*J*-*V*) measurement of the DSSCs devices based on the two polymeric metal complexes **3** and **4**. 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 3. It can be seen that The V_{oc} values of **3** and **4** dyes are 0.63 V and 0.64 V, respectively, and the corresponding FF values are both 0.75. However, the J_{sc} values increased from 4.77 mA/cm² for **3** to 6.33 mA/cm² for **4**. The power conversion efficiency based on **4** reached

 TABLE 2 Cyclic Voltammetric Results of the Polymeric Metal

 Complexes

	E ^{ox} onset (V)	E ^{red} onset (V)	HOMO (eV)	LUMO (eV)	E ^{EC} (eV)
DB8QB-Eu(III)	0.914	-1.124	-5.314	-3.276	2.038
B8QDF-Eu(III)	0.902	-0.996	-5.302	-3.404	1.898



FIGURE 7 J-V curves of DSSCs based on DB8QB-Eu(III) (3) and B8QDF-Eu(III) (4) in DMF solution.

3.04%, which is higher that of the device based on 3 (2.25%).

The low I_{sc} is ascribed to the low charge separation and transportation efficiency, which results from the long distance between donor and acceptor⁶³ and can be seen from the input photon to converted current efficiency (IPCE) curves as shown in Figure 8. The maximum external quantum efficiency of 3 and 4 are only 30% and 46% at 400 nm, respectively. It should be noted that 3 and 4 still show weak IPCE response at the range of long wavelength region. As discussed in the UV-vis absorption spectra section, the higher power conversion efficiency of 4 result in greater adsorption than 3 and aggregation of the dyes on the TiO_2 surface, which lead to less efficient electron injection⁶⁴ to TiO₂ because of quenching of the excited state and thus may not give a satisfactory η value. Also, we speculate **4** suppress the charge recombination, resulting in elongation of the electron lifetime. So, to obtain a high η value, a suitable π -conjugated length should be adapted to the dyes.

The power conversion efficiency is relatively low in the device, and further work on optimizing the device performance is under investigation.

CONCLUSIONS

In summary, we reported the synthesis and characterization of two novel europium complexes: 1,4-Dioctyloxy-2,5-bis[2-(8-hydroxyquinoline)-vinyl]-benzene Eu(III) (3) and 2,7-bis[2-(8-hydroxyquinoline)-vinyl]-9,9'-diocthylfluorene Eu(III) (4)

TABLE 3 Photovoltaic P	erformances of DSSCs
------------------------	----------------------

Polymer	Solvent	Illumination Time (min)	J _{sc} (mA/cm²)	V _{oc} (V)	ff	η (%)
DB8QB-Eu(III)	DMF	2	4.77	0.63	0.75	2.25
B8QDF-Eu(III)	DMF	2	6.33	0.64	0.75	3.04



FIGURE 8 Input photon to converted current efficiency (IPCE) curves of DSSCs based on DB8QB-Eu(III) (3) and B8QDF-Eu(III) (4).

containing 8-hydroxyquinoline europium complexes with phenylethyl or fluorene units. The two materials have showed good stabilities and their thermal decomposition temperatures are 280 °C and 225 °C, respectively. They also exhibit the good open-circuit voltage, fill factor, and power conversion efficiency under simulated AM. 1.5G illumination (100 mW/cm²). These results strongly indicate the importance of their further investigation in DSSCs.

However, there are many challenges to surmount, J_{sc} and IPCE are very low based on both the materials, the light absorption, electron injection efficiency, and adsorption affinities on the TiO_2 are the main reasons that we cannot obtain outstanding η . One or two anchoring groups such as carboxylic acid or sulfonic acid groups should be introduced in the structure for good solubility and strong adsorption onto the surface of $TiO_2^{.65,66}$ Accordingly we should find the further structural optimization with broad spectral coverage, excellent charge separation, and transportation are expected to produce more efficient photosensitizers. We managed to enhance the solubility of the polymeric metal complexes able to evaluate the absorption spectra in several solvents and to bring out the adequate structural modifications that will optimize the properties of the polymeric metal complexesbased DSSCs. Our work toward these directions are underway.

This work was financially supported by the Open Project Program of Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry of Education, China (No. 09HJYH10).

REFERENCES AND NOTES

1 Beaujuge, P. M.; Ellinger, S.; Reynolds, J. R. Adv Mater 2008, 20, 2772–2776.

2 Beaujuge, P. M.; Ellinger, S.; Reynolds, J. R. Nat Mater 2008, 7, 795–799.

3 Steckler, T. T.; Zhang, X.; Hwang, J.; Honeyager, R.; Ohira, S.; Zhang, X.-H.; Grant, A.; Ellinger, S.; Odom, S. A.; Sweat, D.; Tanner, D. B.; Rinzler, A. G.; Barlow, S.; Bredas, J.-L.; Kippelen, B.; Marder, S. R.; Reynolds, J. R. J Am Chem Soc 2009, 131, 2824–2826.

4 Wu, Z.; Chen, Z.; Du, X.; Logan, J. M.; Sippel, J.; Nikolou, M.; Kamaras, K.; Reynolds, J. R.; Tanner, D. B.; Hebard, A. F.; Rinzler, A. G. Science 2004, 305, 1273–1276.

5 Steckler, T. T.; Abboud, K. A.; Craps, M.; Rinzler, A. G.; Reynolds, J. R. Chem Commun 2007, 46, 4904–4906.

6 Zhu, Y.; Yen, C.-T.; Jenekhe, S. A.; Chen, W.-C. Macromol Rapid Commun 2004, 25, 1829–1834.

7 Thompson, B. C.; Fréchet, J. M. J Angew Chem Int Ed Engl 2008, 47, 58–77.

8 Blouin, N.; Michaud, A.; Gendron, D.; Wakim, S.; Blair, E.; Neagu-Plesu, R.; Belletête, M.; Durocher, G.; Tao, Y.; Leclerc, M. J Am Chem Soc 2008, 130, 732–742.

9 Wong, W.-Y. Macromol Chem Phys 2008, 209, 14-24.

10 Hancock, J. M.; Gifford, A. P.; Champion, R. D.; Jenekhe, S. A. Macromolecules 2008, 41, 3588–3597.

11 Sommer, M.; Thelakkat, M. Eur Phys J Appl Phys 2006, 36, 245–249.

12 Kim, M.-S.; Kim, J.-S.; Cho, J.; Stein, M.; Guo, L. J.; Kim, J. Appl Phys Lett 2007, 90, 123113.

13 O'Regan, B.; Grätzel, M. Nature 1991, 353, 737-740.

14 Wang Y. Sol Energy Mater Sol Cells 2009, 93, 1167–1175.

15 Hara, K.; Dan-oh, Y.; Kasada, C.; Ohga, Y.; Shinpo, A.; Suga, S.; Sayama, K.; Arakawa, H. Langmuir 2004, 20, 4205–4210.

16 Thomas, K. R. J.; Hsu, Y.-C.; Lin, J. T.; Lee, K.-M.; Ho, K.-C.; Lai, C.-H.; Cheng, Y.-M.; Chou, P.-T. Chem Mater 2008, 20, 1830–1840.

17 Thampi, K. R.; Bessho, T.; Gao, F.; Zakeeruddin, S. M.; Wang, P.; Grätzel, M. In 23rd European PhotoVoltaic Solar Energy Conference and Exhibition, Valencia, Spain, September 1–4, 2008.

18 Li, G.; Jiang, K.-J.; Li, Y.-F.; Li, S.-L.; Yang, L.-M. J Phys Chem C 2008, 112, 11591–11599.

19 Son, H.-J.; Han, W.-S.; Han, S. J.; Lee, C.; Kang, S. O. J Phys Chem C 2010, 114, 1064–1072.

20 Steybe, F.; Effenberger, F.; Beckmann, S.; Kramer, P.; Glania, C.; Wortmann, R. Chem Phys 1997, 219, 317–331.

21 Steybe, F.; Effenberger, F.; Gubler, U.; Bosshard, C.; Gunter, P. Tetrahedron 1998, 54, 8469–8480.

22 Raimundo, J. M.; Blanchard, P.; Gallego-Planas, N.; Mercier, N.; Ledoux-Rak, I.; Hierle, R.; Roncali. J. J Org Chem 2002, 67, 205–218.

23 Casado, J.; Pappenfus, T. M.; Miller, L. L.; Mann, K. R.; Ortí, E.; Viruela, P. M.; Pou-Amérigo, R.; Hernández, V.; López Navarrete, J. T. J Am Chem Soc 2003, 125, 2524–2534.

24 Ruiz Delgado, M. C.; Hern, V.; Casado, J.; López Navarrete, J. T.; Raimundo, J.-M.; Blanchard, P.; Roncali, J. Chem** sEur J 2003, 9, 3670–3682.

25 Raposo, M. M. M.; Fonseca, A. M. C.; Kirsch, G. Tetrahedron 2004, 60, 4071–4078.

26 Collis, G. E.; Campbell, W. M.; Officer, D. L.; Burrell, A. K. Org Biomol Chem 2005, 3, 2075–2084.

27 Chen, C.-Y.; Pootrakulchote, N.; Wu, S.-J.; Wang, M.; Li, J.-Y.; Tsai, J.-H.; Wu, C.-G.; Zakeeruddin, S. M.; Grtzel, M. J Phys Chem C 2009, 48, 20752–20757.

28 Mishra, A.; Ma, C.-Q.; Bäuerle, P. Chem Rev 2009, 109, 1141–1276.

29 Nakashima, T.; Satoh, N.; Albrecht, K.; Yamamoto, K. Chem Mater 2008, 20, 2538–2543.

30 Allegrucci, A.; Lewcenko, N. A.; Mozer, A. J.; Dennany, L.; Wagner, P.; Officer, D. L.; Sunahara, K.; Moric, S.; Spiccia, L. Energy Environ Sci 2009, 2, 1069–1073.

31 Umeyama, T.; Takamatsu, T.; Tezuka, N.; Matano, Y.; Araki, Y.; Wada, T.; Yoshikawa, O.; Sagawa, T.; Yoshikawa, S.; Imahori, H. J Phys Chem C 2009, 113, 10798–10806.

32 Nazeeruddin, M. K.; Humphry-Baker, R.; Grätzel, M.; Murrer, B. A. Chem Commun 1998, 719–720.

33 Yanagisawa, M.; Korodi, F.; He, J.; Sun, L.; Sundstrom, V.; Akermark, B. J Porphyr Phthalocyanines 2002, 6, 217–224.

34 O'Regan, B. C.; Lopez-Duarte, I.; Martinez-Diaz, M. V.; Forneli, A.; Albero, J.; Morandeira, A.; Palomares, E.; Torres, T.; Durrant, J. R. J Am Chem Soc 2008, 130, 2906–2907.

35 Yanagisawa, M.; Korodi, F.; Bergquist, J.; Holmberg, A.; Hagfeldt, A.; Akermark, B.; Sun, L. J Porphyr Phthalocyanines 2004, 8, 1228–1235.

36 Chen, C. Y.; Wu, S. J.; Wu, C. G.; Chen, J. G.; Ho, K. C. Angew Chem Int Ed Engl 2006, 118, 5954–5957.

37 Hou, J. H.; Tan, Z. A.; Yan, Y.; He, Y. J.; Yang, C. H.; Li, Y. F. J Am Chem Soc 2006, 128, 4911–4916.

38 Chang, F.; Park, S.; Kim, H. Bull Korean Chem Soc 2008, 29, 1327.

39 Zhang, L.; You, C.; Chen, J.; Yang, G.; Li, Y. Acta Phys Chim Sin 2006, 3, 326–329.

40 Wua, W.-N.; Tanga, N.; Yana, L. Spectrochim Acta Part A 2008, 71, 1461–1465.

41 Kido, J.; Okamoto, Y. Chem Rev 2002, 102, 2357–2368.

42 Carlos, L. D.; Ferreira, R. A. S.; de Zea Bermudez, V.; Ribeiro, S. J. L. Adv Mater 2009, 21, 509–534.

43 Evans, R. C.; Doublas, P.; Winscom. C. J Coord Chem Rev 2006, 250, 2093–2126.

44 Hasegawa, Y.; Yamamuro, M.; Wada, Y.; Kanehisa, N.; Kai, Y.; Yanagida, S. J Phys Chem A 2003, 107, 1697–1702.

45 Welter, S.; Salluce, N.; Belser, P.; Groeneveld, M.; De Cola, L. J Coord Chem Rev 2005, 249, 1360–1371.

46 Satoh, N.; Nakashima, T.; Yamamoto, K. J Am Chem Soc 2005, 127, 13030–13038.

47 Zhao, G.; Wu, G.; He, C.; Bai, F. O.; Xi, H.; Zhang, H. X.; Li, Y. J Phys Chem C 2009, 113, 2636–2642.

48 Tao, Y.; Wang, Q.; Shang, Y.; Yang, C.; Ao, L.; Qin, J.; Ma, D.; Shuai, Z. Chem Commun 2009, 77–79.

49 Egbea, D. A. M.; Nguyenb, L. H.; Carbonnierc, B.; Mühlbacherd, D.; Sariciftci, N. S. Polymer 2005, 46, 9585–9595.

50 Kim, D.; Lee, J. K.; Kang, S. O.; Ko, J. Tetrahedron 2007, 63, 1913–1922.

51 Detert, H.; Schollmeyer, D.; Sugiono, E. Eur J Org Chem 2001, 15, 2927–2938.

52 Chen, B.; Wu, Y.; Wang, M.; Wang, S.; Sheng, S.; Zhu, W.; Sun, R.; Tian, H. Eur Polym J 2004, 40, 1183–1191.

53 Clemo, G. R.; Howe, R. J Chem Soc Dalton 1955, 3552–3553.

54 Massimo, L. D.; Annarita, G.; Iolinda, A.; Alessandra, C.; Mauro, G.; Sandra, B.; Mario, A.; Francesco, L. J Chem Soc Dalton Trans 2004, 16, 2424–2431.

55 Pagadala, R.; Ali, P.; Meshram, J. S. J Coord Chem 2009, 62, 4009–4017.

56 Li, S.-L.; Jiang, K.-J.; Shao, K.-F.; Yang, L.-M. Chem Commun 2006, 2792–2794.

57 Liang, M.; Wu, W.; Cai, F.; Chen, P.; Peng, B.; Chen, J.; Li, Z. J Phys Chem C 2007, 11, 4465–4472.

58 Li, G.; Jiang, K. J.; Li, Y. F.; Li, S. L.; Yang, L. M. J Phys Chem C 2008, 30, 11591–11599.

59 Guo, M.; Diao, P.; Ren, Y. J.; Meng, F. S.; Tian, H.; Cai, S. M. Sol Energy Mater Sol Cells 2005, 88, 23.

60 Hara, K.; Miyamoto, K.; Abe, Y.; Yanagida, M. J Phys Chem B 2005, 50, 23776–23778.

61 Bertho, S.; Haeldermans, I.; Swinnen, A.; Moons, W.; Martens, T.; Lutsen, L.; Vanderzande, D.; Manca, J.; Senes, A.; Bonfiglio, A. Sol Energy Mater Sol Cells 2007, 91, 385–389.

62 Hou, J.; Huo, L.; He, C.; Yang, C.; Li, Y. Macromolecular 2006, 39, 594–603.

63 Odobel, F.; Blart, E.; Lagrée, M.; Villieras, M.; Boujtita, H.; Murr, N. E.; Caramori, S.; Bignozzi, C. A. J Mater Chem 2003, 13, 502–510.

64 Wenger, B.; Grätzel, M.; Moser, J. E. J Am Chem Soc 2005, 35, 12150–12151.

65 Nazeerudin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Müller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. J Am Chem Soc 1993, 115, 6382–6390.

66 Wang, Z.-S.; Li, F.-Y.; Huang, C.-H. J Phys Chem B 2001, 105, 9210.