



# Novel polymeric metal complexes as dye sensitizers for Dye-sensitized solar cells based on poly thiophene containing complexes of 8-hydroxyquinoline with Zn(II), Cu(II) and Eu(III) in the side chain

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, PR China

## ARTICLE INFO

### Article history:

Received 26 November 2009  
Received in revised form 4 February 2010  
Accepted 8 February 2010  
Available online 12 February 2010

### Keywords:

Dye-sensitized solar cells  
Polymeric metal complexes  
Thiophene  
8-Hydroxyquinoline

## ABSTRACT

Novel polymeric metal complexes as dye sensitizer for dye-sensitized solar cells (DSSCs) based on poly thiophene containing complexes of 8-hydroxyquinoline with Zn(II), Cu(II), and Eu(III) in the side chain have been synthesized according to the Stille coupling method and characterized by FTIR, GPC, and Elemental analysis. The UV–vis absorption spectroscopy, photoluminescence spectroscopy, cyclic voltammetry, and the applications in dye-sensitized solar cells (DSSCs) are also determined and studied. The DSSCs fabricated by PZn(Q)<sub>2</sub>-co-3MT, PCu(Q)<sub>2</sub>-co-3MT, and PEu(Q)<sub>3</sub>-co-3MT exhibit good device performance with a power conversion efficiency of up to 0.56%, 0.78%, and 1.16%, respectively, under simulated AM 1.5 G solar irradiation (100 mW/cm<sup>2</sup>). They possess excellent stabilities and their thermal decomposition temperatures are 340 °C, 400 °C, and 540 °C, respectively, indicating polymeric metal complexes are suitable for the fabrication processes of optoelectronic devices.

© 2010 Elsevier Ltd. All rights reserved.

## 1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted considerable attentions due to the most promising low cost.<sup>1–3</sup> Up to now, DSSCs based on metal-free organic dyes,<sup>4–7</sup> porphyrin dyes,<sup>8–10</sup> metal-phthalocyanine,<sup>11,12</sup> and natural dyes<sup>13,14</sup> have been reported and developed. Although the efficiencies of DSSCs have not yet approached the theoretical limit and are not competitive with the silicon-based solar cells, organic dyes have their own advantages,<sup>15</sup> such as low cost, high absorption coefficient and easy control of redox potentials of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels. Importantly, the champion data of power conversion efficiency obtained for metal complexes, which are based on ruthenium-containing metallorganic dyes adsorbed on nanocrystalline TiO<sub>2</sub> is 11.3–11.5%,<sup>16</sup> showing the promising potential in the application. However, the ruthenium dyes that are facing the problem of environmental issues will limit the large-scale application of this type solar cells.<sup>17</sup>

Polythiophenes (PTs) are good candidates for donor or  $\pi$ -conjugated unit in polymer solar cells (PSCs).<sup>18–20</sup> Even since the first synthesis in 1986,<sup>21,22</sup> poly(3-alkylthiophenes) (PATs) have attracted increasing interest owing to the significant improvement in

solubility. Recently, many scientists are paying a good deal of attention to thiophene-linked different functionalized group derivatives for dye-sensitized solar cells.<sup>17,23–25</sup> Among them, C217 has been demonstrated to show photo conversion efficiency ( $\eta$ ) up to 9.8% under AM 1.5 irradiation and an excellent stability.<sup>26</sup>

For further development of highly efficient dyes in DSSCs, the dye must fulfill the following criteria: a donor- $\pi$ -conjugation-linkage-acceptor (D- $\pi$ -A) structure required for a wide range absorption extending to the near-infrared or infrared region, which is due to produce a large photocurrent response. In addition, suitable energy levels and location of the HOMO and LUMO orbitals of the photosensitizer are required to match the iodine/iodide redox potential and the conduction band edge level of the TiO<sub>2</sub> semiconductor.<sup>27,28</sup> Based on the previous reports of organic dyes used in DSSCs so far, an oligothiophene moiety was successfully selected as the conjugation unit of the dye molecule between the donor and acceptor groups, resulting in maximum absorption bands shifting to the longer wavelength.<sup>29</sup>

It is well known that metal chelates of 8-HQ derivatives are most super materials as an electro transporter, especially, the introduction of functional group substituting in the 5-position of 8-hydroxyquinoline have been used in many fields.<sup>30,31</sup> Although the report of their application as dye sensitizer for dye-sensitized solar cells is rare, there is no doubt that chemical modifications between PTs and 8-HQ may satisfy application requirements to make an effective way to suppress charge recombination and hence to improve open-circuit photovoltage ( $V_{oc}$ ).

\* Corresponding author. Tel.: +86 731 5829202; fax: +86 731 58292447.  
E-mail address: [zhongcf798@yahoo.com.cn](mailto:zhongcf798@yahoo.com.cn) (C. Zhong).

According to the above-mentioned points, we have designed and synthesized three D- $\pi$ -A dyes possessing a metal-8HQ as an acceptor (A), methyl-functionalized oligothiophenes as a  $\pi$ -conjugation linkage, and a thiophene as a donor group (D), which are shown in Scheme 1. Moreover, the optical properties, thermal properties, and photovoltaic properties of polymeric metal complexes are also investigated in this paper.

## 2. Results and discussion

### 2.1. Synthesis and characterization

Scheme 2 outlines synthetic route of the ligand: D8QTH, which was synthesized by the Wittig reaction and Figure 1 gives the corresponding  $^1\text{H}$  NMR spectra. The vinyl proton peaks appeared at around 7.0–7.25 ppm and the hydrogen proton of thiophene locating at the 3 position is observed at 7.30 ppm, 8.81 ppm, 8.50–8.52 ppm, 7.77–7.79 ppm, 7.48–7.66 ppm are attributed to the hydrogen protons of 8-hydroxyquinoline, but there is no detectable signal for the OH group in  $\text{CDCl}_3$ .<sup>32</sup>

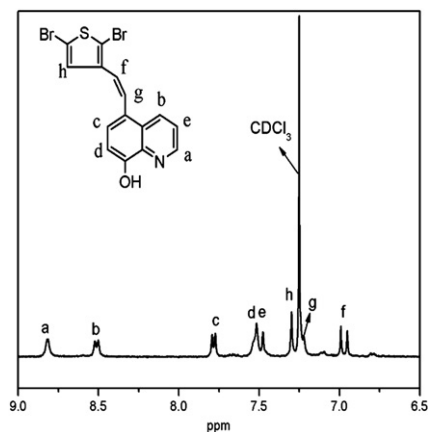
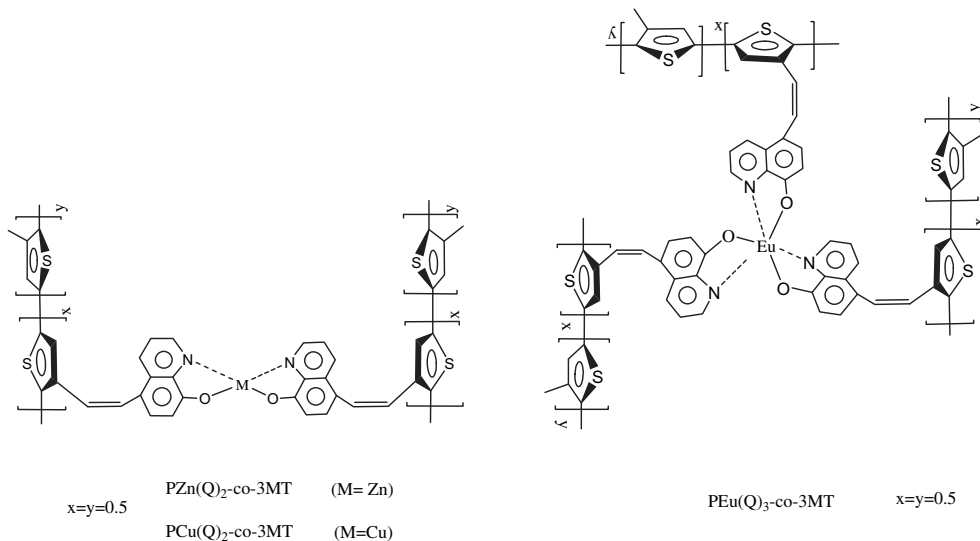
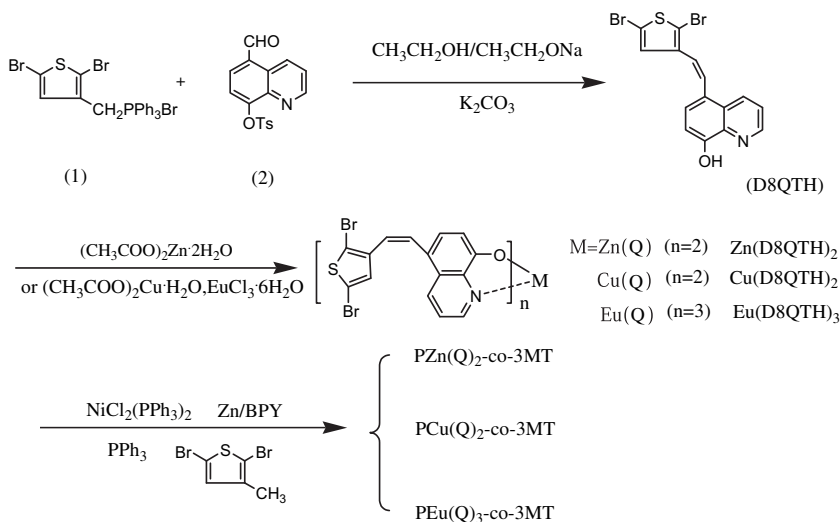


Figure 1.  $^1\text{H}$  NMR spectra of D8QTH in  $\text{CDCl}_3$ .



Scheme 1. Molecular Structures of PZn(Q)<sub>2</sub>-co-3MT, PCu(Q)<sub>2</sub>-co-3MT and PEu(Q)<sub>3</sub>-co-3MT.



Scheme 2. Synthesis of PZn(Q)<sub>2</sub>-co-3MT, PCu(Q)<sub>2</sub>-co-3MT and PEu(Q)<sub>3</sub>-co-3MT.

PZn(Q)<sub>2</sub>-co-3MT, PCu(Q)<sub>2</sub>-co-3MT, PEu(Q)<sub>3</sub>-co-3MT were synthesized by the stille coupling reaction between the metal complexes and 2,5-dibromo-3-methyl-thiophene. The molecular weight determined by GPC is summarized in Table 1. The  $M_n$  of PZn(Q)<sub>2</sub>-co-3MT, PCu(Q)<sub>2</sub>-co-3MT, PEu(Q)<sub>3</sub>-co-3MT synthesized by this method are only 3.9–9.5 K. We thought that steric hindrance of the metal complexes should be the main reason for the low polymerization degree. The obtained polymers are readily soluble in organic solvents, such as DMF, toluene, and DMSO, however, they present poor solubility in some solvent, such as chloroform, dichloromethane and THF.

**Table 1**

Molecular weight and thermal properties of PZn(Q)<sub>2</sub>-co-3MT, PCu(Q)<sub>2</sub>-co-3MT and PEu(Q)<sub>3</sub>-co-3MT

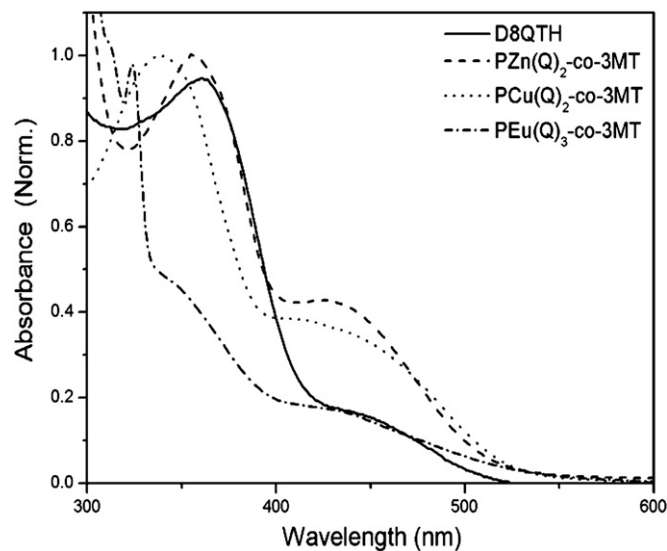
	$\bar{M}_n$ [ $\times 10^3$ ]	$\bar{M}_w$ [ $\times 10^3$ ]	PDI	$T_g^a$ [°C]	$T_d^b$ [°C]
PZn(Q) <sub>2</sub> -co-3MT	3.9	4.2	1.07	156	340
PCu(Q) <sub>2</sub> -co-3MT	4.1	4.3	1.06	168	400
PEu(Q) <sub>3</sub> -co-3MT	9.5	10.6	1.12	202	540

<sup>a</sup> Glass transition temperature, measured from DSC traces of the polymers.

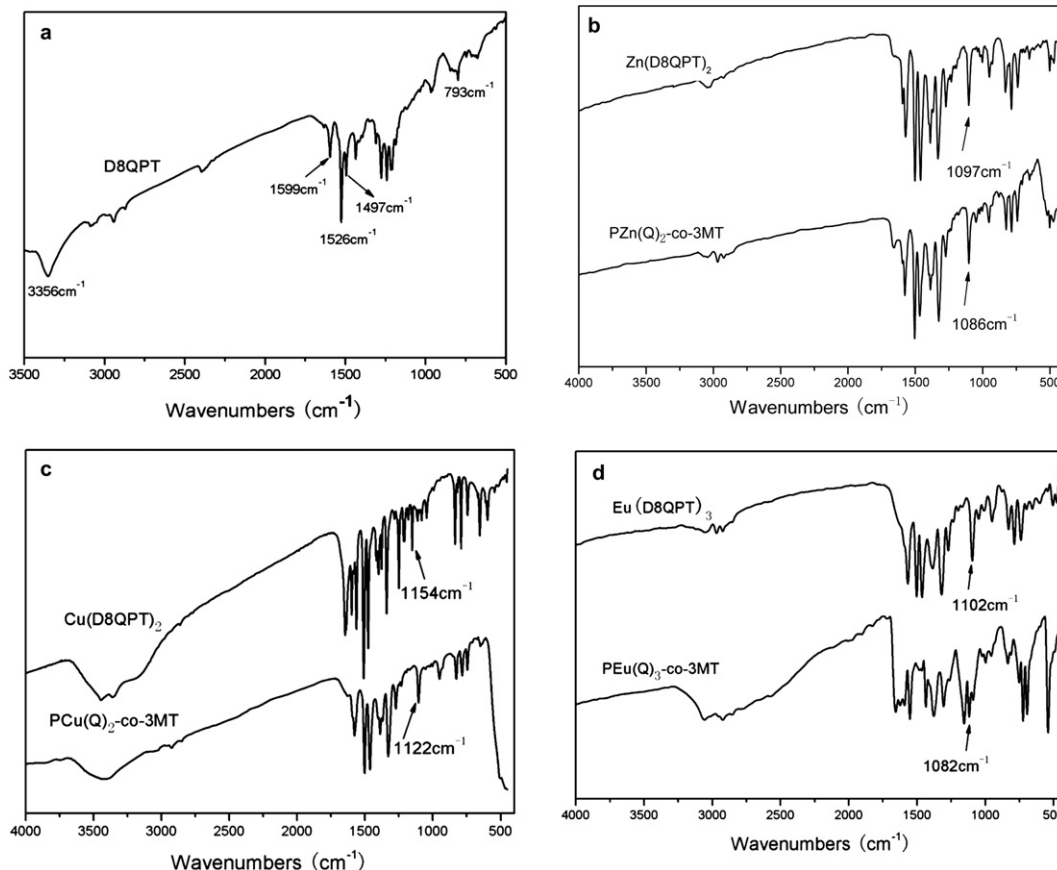
<sup>b</sup> The data were obtained from TGA of the polymers. In both case (DSC and TGA), the data were measured under N<sub>2</sub> atmosphere at a heating rate of 20 °C/min.

Figure 2a shows IR spectra of the D8QTH, a sharp absorption peak at 3356 cm<sup>-1</sup>, which corresponds to O–H stretching of 8-hydroxyquinoline and aromatic and vinylic C–H at 3092 and 2939 cm<sup>-1</sup>, respectively. The peaks at 1494 and 793 cm<sup>-1</sup> are the characteristic absorption peaks of thiophene; the peak at 1599 cm<sup>-1</sup> is due to C=N stretching vibration; and the peak at 1526 cm<sup>-1</sup> is caused by C=C stretching vibration.

Figure 3b–d show IR spectra of Zn(D8QTH)<sub>2</sub>, PZn(Q)<sub>2</sub>-co-3MT, Cu(D8QTH)<sub>2</sub>, PCu(Q)<sub>2</sub>-co-3MT, Eu(D8QTH)<sub>3</sub>, PEu(Q)<sub>3</sub>-co-3MT. The presence of broad absorption band in the region 3450–3360 cm<sup>-1</sup> is probably due to the existence of lattice and/or coordinated water in the molecule, and make it difficult to see the bands due to the O–H stretching vibrations, which would appear in this region.



**Figure 3.** Normalized absorption spectra of the D8QTH, PZn(Q)<sub>2</sub>-co-3MT, PCu(Q)<sub>2</sub>-co-3MT and PEu(Q)<sub>3</sub>-co-3MT in DMF solution.



**Figure 2.** FTIR spectra of D8QTH (a), Zn(D8QTH)<sub>2</sub>, PZn(Q)<sub>2</sub>-co-3MT(b), Cu(D8QTH)<sub>2</sub>, PCu(Q)<sub>2</sub>-co-3MT(c), Eu(D8QTH)<sub>3</sub>, PEu(Q)<sub>3</sub>-co-3MT (d).

The metal complexes and polymeric metal complexes have similar bands, but they have shown red shifts. There are sharp absorption bands at 1097, 1154, 1102  $\text{cm}^{-1}$  for the  $\text{Zn}(\text{D8QTH})_2$ ,  $\text{Cu}(\text{D8QTH})_2$ , and  $\text{Eu}(\text{D8QTH})_3$ , respectively, which should be associated with C–O vibrations at the C–O–M site.<sup>33</sup> With increasing the length of the polymers, the peaks of the corresponding polymeric metal complexes show red-shift comparing with the metal complexes, and the C–Br stretching vibration observed at 573, 538, 590  $\text{cm}^{-1}$  for  $\text{Zn}(\text{D8QTH})_2$ ,  $\text{Cu}(\text{D8QTH})_2$ , and  $\text{Eu}(\text{D8QTH})_3$ , respectively, are disappeared in the corresponding polymeric complexes, which is the evidence of the success of polymerization.

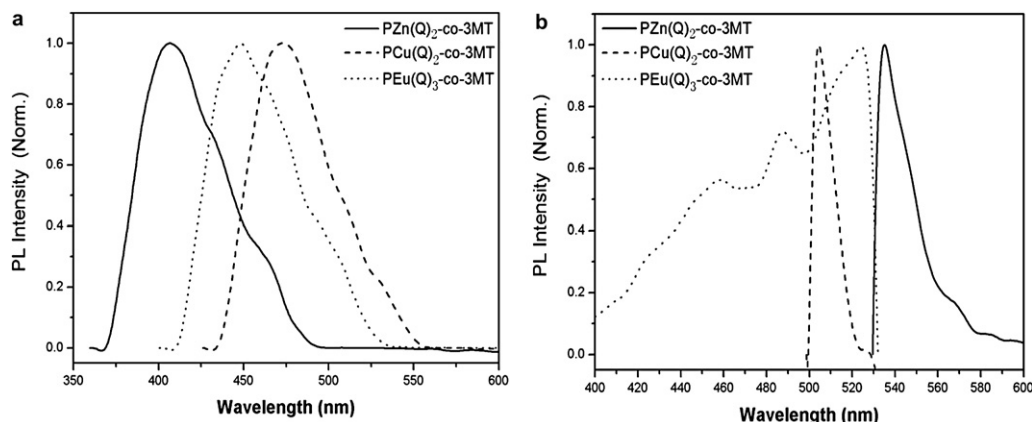
## 2.2. Photophysical properties

The UV–vis absorption spectra could provide a good deal of information on the electronic structures of the polymeric metal complexes. The absorption spectra of the ligand and the polymeric metal complexes in DMF solution are shown in Figure 3 and the corresponding optical data of the polymeric metal complexes are summarized in Table 2. The ligand D8QTH shows a UV–vis normalized absorption peak in DMF located at 360 nm, corresponding to the  $\pi$ – $\pi^*$  electron transitions of the conjugated molecules, which was observed in the intramolecular charge transfer (ICT) between the rings of 8-hydroxyline and thiophene. In comparison with D8QTH, The absorption peak of  $\text{PZn}(\text{Q})_2$ -co-3MT,  $\text{PCu}(\text{Q})_2$ -co-3MT,  $\text{PEu}(\text{Q})_3$ -co-3MT is 356, 337 and 323 nm, respectively, which show blue shifts of the high energy  $\pi$ – $\pi^*$  transitions with respect to the corresponding complex, which can be attributed to the electron donating 3-methyl group in the polymers. The other weak and broad band is in the visible region (430–480 nm) that can be assigned to MLCT or d–d transition and the overlap of the  $\pi$ – $\pi^*$  transitions of the 3-methyl thiophene. An additional weak band at 362 nm was observed in  $\text{PEu}(\text{Q})_3$ -co-3MT, corresponding to direct singlet–triplet absorption, leading to the Eu-centered <sup>3</sup>MLCT states, this behavior could be another clue about the formation of the two charge-transfer bands in the europium complex.

**Table 2**  
Optical properties of  $\text{PZn}(\text{Q})_2$ -co-3MT,  $\text{PCu}(\text{Q})_2$ -co-3MT and  $\text{PEu}(\text{Q})_3$ -co-3MT

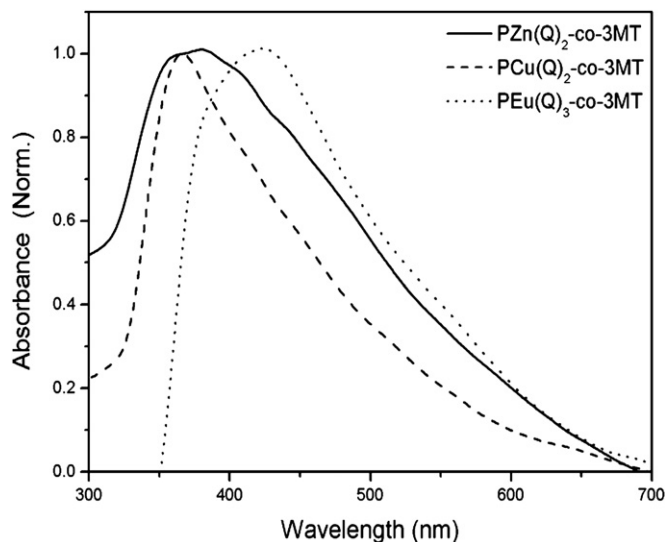
	$\lambda_{\text{max}}^{\text{abs}}$ (nm)		$\lambda_{\text{onset}}^{\text{abs}}$ (nm)		PL (nm)		$E_{\text{g}}^{\text{opta}}$ (eV)
	Solution	Solid	Solution	Solid	Solution	Solid	
$\text{PZn}(\text{Q})_2$ -co-3MT	356	473	530	539	612	2.34	
$\text{PCu}(\text{Q})_2$ -co-3MT	337	442	532	532	607	2.33	
$\text{PEu}(\text{Q})_3$ -co-3MT	323	362,441	534	520	570	2.32	

<sup>a</sup> The optical band gap was obtained from the empirical formula  $E_{\text{g}} = 1240/\lambda_{\text{edge}}$ , in which the  $\lambda_{\text{edge}}$  is the onset value of absorption spectrum in long wave direction.<sup>42</sup>



**Figure 5.** PL spectra of  $\text{PZn}(\text{Q})_2$ -co-3MT,  $\text{PCu}(\text{Q})_2$ -co-3MT, and  $\text{PEu}(\text{Q})_3$ -co-3MT in DMF solution (a) and the solid state (b).

Figure 4 gives the absorption spectra of  $\text{PZn}(\text{Q})_2$ -co-3MT,  $\text{PCu}(\text{Q})_2$ -co-3MT and  $\text{PEu}(\text{Q})_3$ -co-3MT on  $\text{TiO}_2$  films. The absorption spectra of dyes attached to  $\text{TiO}_2$  film are all broadened to the long wavelength, which is attributed to the formation of dye aggregates on the  $\text{TiO}_2$  surface and due to an interaction between the dyes and  $\text{TiO}_2$ ,<sup>34</sup> which would benefit the photoelectrical conversion efficiency of the dye-sensitized solar cells.<sup>35</sup>



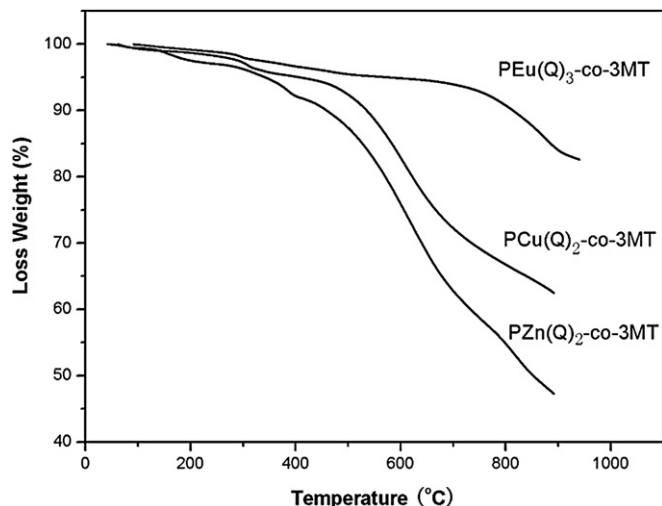
**Figure 4.** Normalized absorption spectra of  $\text{PZn}(\text{Q})_2$ -co-3MT,  $\text{PCu}(\text{Q})_2$ -co-3MT and  $\text{PEu}(\text{Q})_3$ -co-3MT adsorbed on  $\text{TiO}_2$  films.

The photoluminescent spectra of the three polymeric complexes in DMF solution and the solid state are shown in Fig. 5a and Fig. 5b, respectively. The excitation wavelengths were set to the absorption maxima from the UV–vis absorption spectra. It can be seen that the PL peak of  $\text{PZn}(\text{Q})_2$ -co-3MT,  $\text{PCu}(\text{Q})_2$ -co-3MT, and  $\text{PEu}(\text{Q})_3$ -co-3MT is 539, 532, 520 nm, respectively. And in the solid state, they red-shifted by ca. 73, 75, 50 nm in comparison with that of the solution, respectively, indicating that the conformation of the three polymeric metal complexes changed significantly in the solid state.

## 2.3. Thermal stability

The thermal properties of the copolymers were by thermogravimetric (TGA) and differential scanning calorimetric (DSC) analyses and are also reported in Table 1. The TGA (Fig. 6) results reveal

that PZn(Q)<sub>2</sub>-co-3MT, PCu(Q)<sub>2</sub>-co-3MT, and PEu(Q)<sub>3</sub>-co-3MT were thermally stable with 5% weight loss at temperatures of 340 °C, 400 °C, and 540 °C in nitrogen, respectively, which indicate that the polymers are as steadily as ploy(3-alkylthiophene).<sup>36</sup> Obviously, the stability of the polymers is adequate for the fabrication processes of optoelectronic devices.

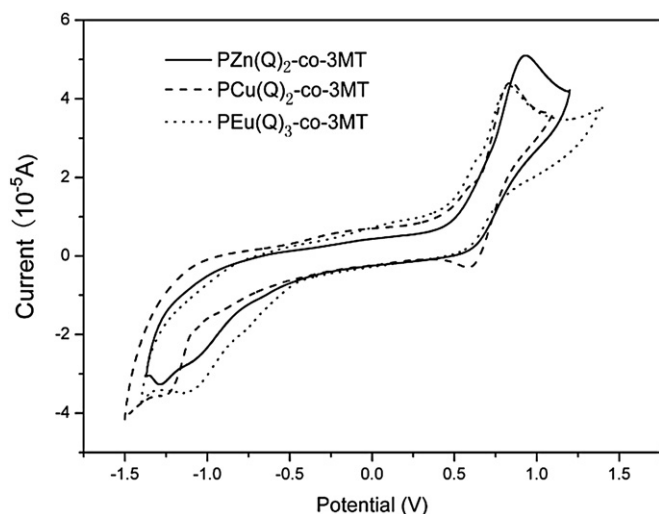


**Figure 6.** TGA plots of PZn(Q)<sub>2</sub>-co-3MT, PCu(Q)<sub>2</sub>-co-3MT and PEu(Q)<sub>3</sub>-co-3MT with a heating rate of 20 °C/min under nitrogen atmosphere.

The differential scanning calorimetry (DSC) analysis reveals the glass transitions at 156 °C for PZn(Q)<sub>2</sub>-co-3MT, 168 °C for PCu(Q)<sub>2</sub>-co-3MT, and 202 °C for PEu(Q)<sub>3</sub>-co-3MT during heating, which is noted that the materials may increase the stability of devices.<sup>37</sup> But there was no melting point, suggesting that the polymers are amorphous. The lack of crystallinity in the polymers could serve as a drawback for the use in organic solar cells.<sup>38</sup> Further optimization of the conditions for polymerization reaction and chemical structure of polymers may be necessary to obtain polymers with higher molecular weight and crystallinity.

#### 2.4. Electrochemical properties

Electronic energy level is an important property for organic materials used in solar cells. Figure 7 shows the cyclic voltammograms



**Figure 7.** CV curves of PZn(Q)<sub>2</sub>-co-3MT, PCu(Q)<sub>2</sub>-co-3MT PZn(Q)<sub>2</sub>-co-3MT and PEu(Q)<sub>3</sub>-co-3MT measured in DMF solution containing [Bu<sub>4</sub>N]BF<sub>6</sub>(Bu=butyl) as supporting electrolyte at a scan rate of 100 mV/s.

of PZn(Q)<sub>2</sub>-co-3MT, PCu(Q)<sub>2</sub>-co-3MT, and PEu(Q)<sub>3</sub>-co-3MT. The cyclic voltammetry of complexes were measured in DMF containing [Bu<sub>4</sub>N]BF<sub>6</sub>(Bu=butyl) as supporting electrolyte and SCE reference electrode at a scan rate of 100 mV/s. 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 gap of the polymers were calculated according to the equations.<sup>39,40</sup>

$$\begin{aligned} \text{HOMO} &= -e(E_{ox} + 4.40)(\text{eV}); & \text{LUMO} &= -e(E_{red} + 4.40)(\text{eV}); \\ E_g^{ec} &= e(E_{ox} - E_{red})(\text{eV}) \end{aligned}$$

The values obtained are listed in Table 3. The reduction and oxidation potentials of PZn(Q)<sub>2</sub>-co-3MT were measured to be  $E_{ox}=0.92$  V and  $E_{red}=-1.23$  V, respectively, and the energy band gap was 2.15 eV, the energy value of the HOMO was calculated to be  $-5.32$  eV and the energy value of the LUMO was calculated to be  $-3.17$  eV. In the same case of PCu(Q)<sub>2</sub>-co-3MT and PEu(Q)<sub>3</sub>-co-3MT, their  $E_g$  is 2.05 eV and 1.93 eV, respectively. On the basis of the CV data, the electron accepting ability of the complexes follows the order of PZn(Q)<sub>2</sub>-co-3MT < PCu(Q)<sub>2</sub>-co-3MT < PEu(Q)<sub>3</sub>-co-3MT. And the  $E_g$  of PEu(Q)<sub>3</sub>-co-3MT is more suitable for the fabrication of optoelectronic devices than other two ones.

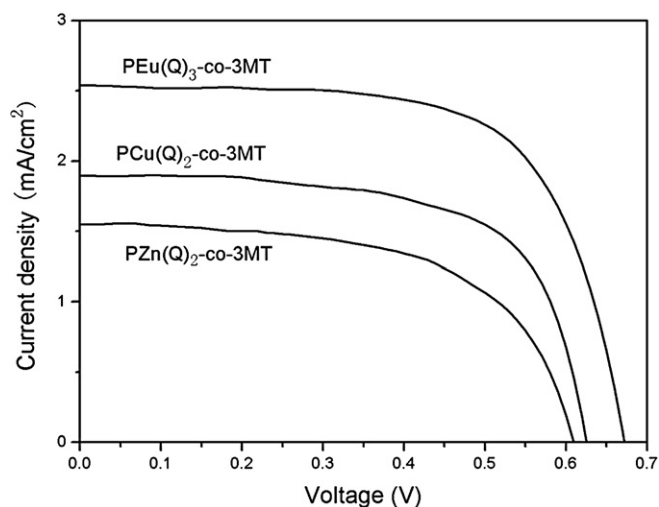
**Table 3**

Cyclic voltammetric results of PZn(Q)<sub>2</sub>-co-3MT, PCu(Q)<sub>2</sub>-co-3MT and PEu(Q)<sub>3</sub>-co-3MT

	$E_{onset}^{ox}$ (V)	$E_{onset}^{red}$ (V)	HOMO (eV)	LUMO (eV)	$E_g^{EC}$ (eV)
PZn(Q) <sub>2</sub> -co-3MT	0.92	-1.23	-5.32	-3.17	2.15
PCu(Q) <sub>2</sub> -co-3MT	0.84	-1.21	-5.24	-3.19	2.05
PEu(Q) <sub>3</sub> -co-3MT	0.83	-1.10	-5.23	-3.30	1.93

#### 2.5. Photovoltaic performances of dye-sensitized solar cells (DSSCs)

Figure 8 shows current density–voltage (J–V) characteristics of devices based on the three polymeric metal complexes. And the corresponding open-circuit voltage ( $V_{oc}$ ), short-circuit current density ( $J_{sc}$ ), fill factor (FF) and power conversion efficiency (PCE) are listed in Table 4. It can be seen that  $V_{oc}$ ,  $J_{sc}$ , FF, and PCE are all increased from PZn(Q)<sub>2</sub>-co-3MT to PEu(Q)<sub>3</sub>-co-3MT. The  $J_{sc}$  based on PEu(Q)<sub>3</sub>-co-3MT reached 2.53 mA/cm<sup>2</sup>, which is nearly 1.7 times of that of the device based on PZn(Q)<sub>2</sub>-co-3MT (1.55 mA/cm<sup>2</sup>); the power conversion efficiency (PCE) based on PEu(Q)<sub>3</sub>-co-3MT



**Figure 8.** J–V curves of DSSCs based on PZn(Q)<sub>2</sub>-co-3MT, PCu(Q)<sub>2</sub>-co-3MT and PEu(Q)<sub>3</sub>-co-3MT in DMSO solution.

reached 1.16%, which is more than two times of that of the device based on PZn(Q)<sub>2</sub>-co-3MT (0.56%). The lower  $J_{sc}$  of PZn(Q)<sub>2</sub>-co-3MT and PCu(Q)<sub>2</sub>-co-3MT might be ascribed to the poor charge separation and transportation. It suggests that the europium complex could make better electric contact than zinc and copper complexes. Weak adsorption onto the surface of TiO<sub>2</sub> and recombination losses due to the short alkyl in the thiophene ring are two major factors that limit the efficiencies of dye-sensitized solar cells (DSSCs). And further work on optimizing the device performance is under investigation.

**Table 4**  
The data of Photovoltaic Performances of DSSCs

	Solvent	Illumination time (min)	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	ff	$\eta$ (%)
PZn(Q) <sub>2</sub> -co-3MT	DMSO	8	1.55	0.61	0.59	0.56
PCu(Q) <sub>2</sub> -co-3MT	DMSO	8	1.872	0.63	0.65	0.78
PEu(Q) <sub>3</sub> -co-3MT	DMSO	10	2.531	0.68	0.67	1.16

### 3. Conclusions

In this paper, we have successfully synthesized three novel polymeric metal complexes comprising thiophene and 8-hydroxyquinoline with D- $\pi$ -A structure based on poly thiophene containing complexes of 8-hydroxyquinoline with Zn(II), Cu(II), and Eu(III) in the side chain and applied them in dye-sensitized solar cells (DSSCs). The three materials based on PZn(Q)<sub>2</sub>-co-3MT, PCu(Q)<sub>2</sub>-co-3MT, and PEu(Q)<sub>3</sub>-co-3MT have good stabilities and their thermal decomposition temperatures are 340 °C, 400 °C, and 540 °C, respectively. The power conversion efficiencies of them are 0.56%, 0.78%, and 1.16%, respectively, suggesting their potential in DSSCs applications. The results may open up the possibility of controlling not only the gap band but also the semiconducting properties of novel materials. Overall, the present results highlight the potential of the conjugated polymeric metal complexes as models for DSSCs, as well as a new class of functional conjugated materials.

However, there are some shortcomings and improvements of the polymeric metal complexes as dye sensitizer for dye-sensitized solar cells: (1) Due to the solubility limits, the exact structure of the polymeric metal complexes can not be determined and the UV-vis spectra of the corresponding film can not be obtained because of the poor film-forming at room temperature. (2) The absorption region of the polymeric metal complexes is not wide enough and should be a red shift in comparison of the ligand. (3) One or two anchoring groups, such as carboxylic acid or sulfonic acid groups and long alkyls should be introduced in the structure for good solubility and strong adsorption onto the surface of TiO<sub>2</sub>.<sup>41</sup> To improve the solubility and get better photovoltaic materials, we still have much work to do and the next investigation will be reported in future.

### 4. Experimental section

#### 4.1. Materials and instruments

NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, 3-methyl thiophene, and NBS were obtained from Aldrich Chemical Co. and used as received. *N,N*-Dimethylformamide was dried by distillation over CaH<sub>2</sub>, ethanol was dried over molecular sieves and freshly distilled prior to use. The other materials were common commercial grade and used as received. All chemicals used were of an analytical grade. Solvents were purified with conventional methods.

All <sup>1</sup>H NMR were performed in CDCl<sub>3</sub> and recorded on a Bruker NMR 400 spectrometer, and using TMS (0.00 ppm) as the internal

reference. Infrared (FTIR) spectra were recorded on KBr pellets 250 mg of dried KBr and 2 mg of lyophilized samples with a Perkin-Elmer Spectrum One Fourier transform infrared spectrometer over the 4000–450 cm<sup>-1</sup> range, at a rate of 16 nm/s. Thermogravimetric analyses were run on a Shimadzu TGA-7 Instrument in nitrogen atmosphere at a heating rate of 20 K/min from 25 °C to 900 °C. Differential Scanning Calorimetry was performed on materials using a Perkin-Elmer DSC-7 thermal analyzer in nitrogen atmosphere at a heating rate of 20 °C/min from 25 °C to 250 °C. UV-vis spectra were taken on a Lambda 25 spectrophotometer. Samples were dissolved in DMF and diluted to a concentration (10<sup>-4</sup>–10<sup>-5</sup> M). 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, metal ion, and chlorine ion were measured by chemical method. Gel Permeation Chromatography (GPC) analyses were done on WATER 2414 system equipped with a set of HT3, HT4, and HT5, I-styragel columns with DMF as an eluent (1.0 mL/min) at 80 °C, calibrated by polystyrene standard. Cyclic voltammetry was conducted on a CH Instruments chi630c Electrochemical Workstation, in a 0.1 mol/L[Bu<sub>4</sub>N]BF<sub>4</sub> (Bu=butyl) DMF solution at a scan rate of 100 mV/s at room temperature. The working electrode was a glassy carbon electrode, the auxiliary electrode was a Pt wire electrode, and saturated calomel electrode (SCE) was used as reference electrode.

#### 4.2. General procedures for fabrication of the DSSCs devices

Titania paste was prepared following a procedure: Fluorine-doped SnO<sub>2</sub> conducting glass (FTO) was cleaned and immersed in aqueous 40 mM TiCl<sub>4</sub> 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 TiO<sub>2</sub> colloid was coated onto the above FTO glass by sliding glass rod method to obtain a TiO<sub>2</sub> film of 10–15  $\mu$ m thickness. After drying, the TiO<sub>2</sub>-coated FTO glass were sintered at 450 °C for 30 min, then treated with TiCl<sub>4</sub> solution and calcined at 450 °C for 30 min again. After cooling to 100 °C, the TiO<sub>2</sub> electrodes were soaked in 0.5 mM the dye-sensitized samples dyes in dimethyl sulfoxide (DMSO) solution, then kept at room temperature under dark for 24 h. An 3-methoxypropionitrile solution containing LiI (0.5 M), I<sub>2</sub> (0.05 M), and 4-*tert*-butylpyridine (TBP) (0.5 M) was used as the electrolyte. A Pt foil used as counter electrode was clipped onto the top of the TiO<sub>2</sub> using as working electrode. And photoelectrochemical performance of the solar cell was measured using a Keithley 2602 Source meter controlled by a computer. The cell parameters were obtained under an incident light with intensity 100 mW/cm<sup>2</sup>, which was generated by a 150 W Xe lamp passing through an AM 1.5 G filter.

#### 4.3. Synthesis

2,5-Dibromo-3-triphenylphosphoniomethylbromo-thiophene (1): A solution of 2,5-dibromo-3-bromomethylthiophene (synthesized according to the lit.<sup>42</sup>) (6.7 g, 20 mmol) and triphenylphosphine (6.3 g, 24 mmol) 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, the white solid was obtained (9.3 g, yield 83%) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.68–7.85 (m, 15H), 6.94(s, 1H), 5.57, and 5.63 (d, 2H).

5-Formyl-8-tosyloxyquinoline (2): 5-formyl-8-hydroxyquinoline (synthesized according to the lit.<sup>43</sup>) (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

into the cool water. The organic layer was collected and dried over anhydrous  $\text{MgSO}_4$ , a yellow solid compound was obtained after the removal of solvent. (5.1 g, yield 98%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 10.26(s, 1H), 9.75(d, 1H), 9.55–9.61 (d, 1H), 8.00–8.06 (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).

**4.3.1. 2,5-Dibromo-3-[2-(8-hydroxyquinoline)-vinyl]thiophene (D8QTH).** 2,5-Dibromo-3-triphenylphosphoniomethylbromo-thiophene (0.597 g, 10 mmol) and 5-formyl-8-tosyloxyquinoline were dissolved in 200 mL of anhydrous ethanol. Under an ice-water bath,  $\text{NaOEt}$  (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 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 vacuum at  $45^\circ\text{C}$ , the compound was obtained as pale yellow solid (2.1 g, yield 50%).  $^1\text{H}$  NMR( $\text{CDCl}_3$ ,  $\delta$ , ppm): 8.81(s, 1H), 8.50–8.52 (d, 1H), 7.77–7.79 (d, 1H), 7.48–7.66 (d, 2H), 7.30(s, 1H), 7.22–7.25 (d, 1H), 6.95–6.99 (d, 1H). FTIR (KBr,  $\text{cm}^{-1}$ ): 3356(O–H), 3092, 2939 (aromatic and vinylic C–H), 2900 (aliphatic C–H), 1599 (C=N), 1526 (C=C), 1494 (thiophene C–H), 793(thiophene C–S). Anal. Calcd for  $[\text{C}_{15}\text{H}_{10}\text{SONBr}_2]$ : C, 43.72; H, 2.44; N, 3.40; S, 7.78. Found: C, 44.15; H, 2.58; N, 3.58; S, 7.46.

$\text{Zn}(\text{D8QTH})_2$ : A ethanol solution (10 mL) of  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (0.11 g, 0.5 mmol) was dropped to a mixed THF solution (20 mL) of D8QTH (0.41 g, 1 mmol). The reaction mixture was neutralized carefully with 1 M aq sodium hydroxide until neutral to slightly acidic pH and was refluxed overnight. And then re-crystallize by ethanol. Filtered, washed with ethanol and water repeatedly, the yellow precipitate was collected. (0.8 g, yield 83%). FTIR (KBr,  $\text{cm}^{-1}$ ): 3035, 2927 (aromatic and vinylic C–H), 1579 (C=N), 1496 (C=C), 1097 (C–O–M). Anal. Calcd for  $[\text{C}_{30}\text{H}_{18}\text{S}_2\text{O}_2\text{N}_2\text{Br}_4\text{Zn}]$ : C, 40.59; H, 2.04; N, 3.16; S, 7.22. Found: C, 40.21; H, 2.18; N, 3.28; S, 7.12.

$\text{Cu}(\text{D8QTH})_2$ : In the same manner as described for  $\text{Zn}(\text{D8QTH})_2$ , Yield(%): 86%, a red solid. FTIR (KBr,  $\text{cm}^{-1}$ ): 3149, 2872(aromatic and vinylic C–H), 1578 (C=N), 1514 (C=C), 1472,793 (thiophene),1154 (C–O–M). Anal. Calcd for  $[\text{C}_{30}\text{H}_{18}\text{S}_2\text{O}_2\text{N}_2\text{Br}_4\text{Cu}]$ : C, 40.68; H, 2.05; N, 3.16; S, 7.24. Found: C, 41.01; H, 2.36; N, 3.21; S, 7.14.

$\text{Eu}(\text{D8QTH})_3$ : With the similar synthetic method as  $\text{Eu}(\text{D8QTH})_3$ . Yield(%): 80%, a yellow solid. FTIR (KBr,  $\text{cm}^{-1}$ ): 3055, 2966, 2926 (aromatic and vinylic C–H), 1579 (C=N), 1509 (C=C), 1102 (C–O–M). Anal. Calcd for  $[\text{C}_{45}\text{H}_{27}\text{S}_3\text{O}_3\text{N}_3\text{Br}_6\text{Eu}]$ : C, 39.02; H, 1.96; N, 3.03; S, 6.94; Found: C, 38.75; H, 2.01; N, 2.98; S, 6.85.

Poly[2,5-dibromo-3-[2-(8-hydroxyquinoline)-vinyl]thiophene-Zn-co-3-methyl-thiophene] PZn(Q)<sub>2</sub>-co-3MT: The copolymer was synthesized by Yamamoto coupling method according to the lit.<sup>44</sup>  $\text{Zn}(\text{D8QTH})_2$  (0.355 g,0.4 mmol), bis(triphenylphosphine) nickel(II) chloride (0.26 g,0.4 mmol), 3-methyl thiophene (synthesized according to the lit.<sup>42</sup>) (0.205 g,0.8 mmol), zinc (0.13 g,2 mmol), triphenylphosphine (0.209 g,0.8 mmol), and a little bipyridine (0.006 g,0.038 mmol) were dissolved in DMF(15 mL) under nitrogen. Then the mixture was stirring at  $90^\circ\text{C}$  for 48 h. The yellow solid were precipitated into a large excess of methanol solution. The crude product was washed with methanol, distilled water, and THF sequentially, then dried in vacuum at  $60^\circ\text{C}$  for one day to afford pale yellow solids (0.25 g, 59%) FTIR (KBr,  $\text{cm}^{-1}$ ): 3063, 2972, 2907 (aromatic and vinylic C–H), 1578 (C=N), 1488 (C=C), 1086 (C–O–M). Anal. Calcd for  $[\text{C}_{40}\text{H}_{26}\text{S}_4\text{O}_2\text{N}_2\text{Zn}]$ : C, 63.12; H, 3.45; N, 3.68; S, 16.87. Found: C, 63.42; H, 3.26; N, 3.88; S, 17.13;  $M_n=3.9$  K,  $M_w/M_n=1.07$ .

$\text{PCu}(\text{Q})_2$ -co-3MT: With the similar synthetic method as  $\text{Zn}(\text{D8QTH})_2$  to afford red solids(0.27 g, 64%). FTIR (KBr,  $\text{cm}^{-1}$ ): 3025, 2925, 2862 (aromatic and vinylic C–H), 1578 (C=N), 1504 (C=C), 1122 (C–O–M). Anal. Calcd for  $[\text{C}_{40}\text{H}_{26}\text{S}_4\text{O}_2\text{N}_2\text{Cu}]$ : C, 63.34;

H, 3.46; N, 3.69; S, 16.91; Found: C, 63.25; H, 3.38; N, 3.48; S, 17.26;  $M_n=4.1$  K,  $M_w/M_n=1.06$ .

$\text{PEu}(\text{Q})_3$ -co-3MT: With the similar synthetic method as  $\text{Zn}(\text{D8QTH})_2$  to afford yellow solids(0.51 g, 61%). FTIR (KBr,  $\text{cm}^{-1}$ ): 3075, 2935, 2846 (aromatic and vinylic C–H), 1558 (C=N),1499 (C=C), 1082 (C–O–M). Anal. Calcd for  $[\text{C}_{60}\text{H}_{39}\text{S}_6\text{O}_3\text{N}_3\text{Eu}]$ : C, 60.34; H, 3.29; N, 3.51; S, 16.11. Found: C, 61.03; H, 3.18; N, 3.38; S, 16.92;  $M_n=9.5$  K,  $M_w/M_n=1.12$ .

## Acknowledgements

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

- Gratzel, M. *Nature* **2001**, *414*, 338.
- Hagfeldt, A.; Gratzel, M. *Acc. Chem. Res.* **2000**, *33*, 269.
- Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Muller, E.; Liska, P.; Vlachopoulos, N.; Gratzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382.
- Mende, L. S.; Bach, U.; Baker, R. H.; Horiuchi, T.; Miura, H.; Ito, S.; Uchida, S.; Gratzel, M. *Adv. Mater.* **2005**, *17*, 813.
- Miyashita, M.; Sunahara, K.; Nishikawa, T.; Uemura, Yu; Koumura, N.; Hara, K.; Mori, A.; Abe, T.; Suzuki, E.; Mori, S. *J. Am. Chem. Soc.* **2008**, *130*, 17874.
- Kitamura, T.; Ikeda, M.; Shigaki, K.; Inoue, T.; Anderson, N. A.; Ai, X.; Lian, T.; Yanagida, S. *Chem. Mater.* **2004**, *16*, 1806.
- Mosurkal, R.; He, J. A.; Yang, K.; Samuelson, L. A.; Kumar, J. J. *Photochem. Photobiol., A* **2004**, *168*, 191.
- Nazeeruddin, K.; Baker, R. H.; Officer, D. L.; Campbell, W. M.; Burrell, A. K.; Gratzel, M. *Langmuir* **2004**, *20*, 6514.
- 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.
- Lee, M. W.; Lee, D. L.; Yen, W. N.; Yeh, C. Y. *J. Macromol. Sci., Pure Appl. Chem.* **2009**, *46*, 730.
- Markus K. R. Fischer; López-Duarte, I.; Martijn M. Wienk; Victoria Martínez-Díaz, M.; René A. J. Janssen; Bäuerle, P.; Torres, T. *J. Am. Chem. Soc.* **2009**, *131*, 8669.
- Rawling, T.; Austin, C.; Buchholz, F.; Colbran, S. B.; McDonagh, A. M. *Inorg. Chem.* **2009**, *48*, 3215.
- Dai, Q.; Rabani, J. *New J. Chem.* **2002**, *26*, 421.
- Lai, W. H.; Su, H. Y.; Teoh, G. L. *J. Photochem. Photobiol., A* **2008**, *195*, 307.
- Kathiravan, A.; Renganathan, R. *J. Colloid Interface Sci.* **2009**, *335*, 196.
- Thampi, K.R.; Bessho, T.; Gao, F.; Zakeeruddin, S.M.; Wang, P.; Grätzel, M. 23rd European PhotoVoltaic Solar Energy Conference and Exhibition: Valencia, Spain, Sept. 1–4, 2008.
- Chen, R.; Yang, X.; Tian, H.; Wang, X.; Hagfeldt, A.; Sun, L. *Chem. Mater.* **2007**, *19*, 4007.
- Sang, K. L.; Nam, S. C.; Joong, H. K.; Koeng, S. L.; Hong, K. S.; Hwang, D. H.; Christoph, J. B. *Thin Solid Films* **2006**, *158*, 511.
- Shen, P.; Liu, Y.; Huang, X.; Zhao, B.; Xiang, N.; Fei, J.; Liu, L.; Wang, X.; Huang, H.; Tan, S. *Dyes Pigm.* **2009**, *83*, 187.
- Wu, S.-h.; Chen, C.-Y.; Chen, J.-G.; Li, h.-Y.; Tung, Y.-L.; Ho, K.-C.; Wu, C.-G. *Dyes and Pigments*. **2010**, *84*, 95.
- Sato, M.; Tanaka, S.; Kaeriyama, K. *J. Chem. Soc., Chem. Commun.* **1986**, 873.
- Jen, K. Y.; Miller, G. G.; Elsenbaumer, R. L. *Chem. Commun.* **1986**, 1346.
- Wang, Z.-S.; Koumura, N.; Cui, Y.; Takahashi, M.; Sekiguchi, H.; Mori, A.; Kubo, T.; Furube, A.; Hara, K. *Chem. Mater.* **2008**, *20*, 3993.
- Wang, Z.-S.; Koumura, N.; Cui, Y.; Miyashita, M.; Mori, S.; Hara, K. *Chem. Mater.* **2009**, *21*, 2810.
- Liu, Y.; Xiang, N.; Feng, X.; Shen, P.; Zhou, W.; Weng, C.; Zhao, B.; Tan, S. *Chem. Commun.* **2009**, 2499.
- Zhang, G.; Bala, H.; Cheng, Y.; Shi, D.; Lv, X.; Yu, Q.; Wang, P. *Chem. Commun.* **2009**, 2198.
- Chaoyan Li; Xichuan Yang; Ruikui Chen; Jingxi Pan; Haining Tian; Hongjun Zhu; Xiuna Wang; Anders Hagfeldt; Licheng Sun. *Sol. Energy Mater. Sol. Cells.* **2007**, *91*, 1863.
- Qin, P.; Yang, X.; Chen, R.; Sun, L.; Marinado, T.; Edvinsson, T.; Boschloo, G.; Hagfeldt, A. *J. Phys. Chem. C* **2007**, *111*, 1853.
- Hara, K.; Wang, Z.-S.; Sato, T.; Furube, A.; Katoh, R.; Sugihara, H.; Dan-oh, Y.; Kasada, C.; Shinpo, A.; Suga, S. *J. Phys. Chem. B* **2005**, *109*, 15476.
- Xie, J.; Ning, Z.; Tian, H. *Tetrahedron Lett.* **2005**, *46*, 8559.
- Saylam, A.; Seferoglu, Z.; Ertan, N. *Dyes and Pigments*. **2008**, *76*, 470.
- La Deda, M.; Grisolia, A.; Aiello, I.; Crispini, A.; Ghedini, M.; Belviso, S.; Amati, M.; Lelj, F. *J. Chem. Soc., Dalton Trans.* **2004**, *16*, 2424.
- Robert, G.; Charles, H.; Freiser, R.; Friedel, L.; Hilliard, E.; Johnston, W. D. *Spectrochimica Acta* **1956**, *8*, 1.
- Li, S.-L.; Jiang, K.-J.; Shao, K.-F.; Yang, L.-M. *Chem. Commun.* **2006**, 2792.
- Guo, M.; Diao, P.; Ren, Y. J.; Meng, F. S.; Tian, H.; Cai, S. M. *Sol. Energy Mater. Sol. Cells* **2005**, *88*, 23.
- Ng, S.; Xu, J. M.; Chan, H. S. O. *Synth. Met.* **2000**, *110*, 31.

37. 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.
38. CRC: Boca Raton, *Organic Photo Voltaics: mechanisms, Materials and Devices*; Sun, S. S., Sariciftci, R. S., Eds.; CRC: Boca Raton, FL, 2005.
39. Cho, N. S.; Hwang, D.-H.; Jung, B.-J.; Lim, E.; Lee, J.; Shim, H.-K. *Macromolecules* **2004**, *37*, 5265.
40. Li, Y.; Cao, Y.; Gao, J.; Wang, D.; Yu, G.; Heeger, A. J. *Synth. Met.* **1999**, *99*, 243.
41. Wang, Z.-S.; Li, F.-Y.; Huang, C.-H. *J. Phys. Chem. B* **2001**, *105*, 9210.
42. Hou, J.; Huo, L.; He, C.; Yang, C.; Li, Y. *Macromolecules* **2006**, *39*, 601.
43. Clemo, G. R.; Howe, R. *J. Chem. Soc. Dalton* **1955**, 3552.
44. An, B. K.; Kim, Y. H.; Shin, D. C.; Park, S. Y.; Yu, H. S.; Kwon, S. K. *Macromolecules* **2001**, *34*, 3993.