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# Novel zinc porphyrin sensitizers for dye-sensitized solar cells: Synthesis and spectral, electrochemical, and photovoltaic properties

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ABSTRACT

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### HIGHLIGHTS

### G R A P H I C A L A B S T R A C T

- Synthesis of two novel unsymmetrical zinc porphyrin sensitizers.
- Characterization of prepared compounds.
- Properties of novel zinc porphyrin sensitizers.





Two donor- $\pi$ -spacer-acceptor porphyrin dyes were synthesized for use in dye-sensitized solar cells. The

dyes comprised the same donor (porphyrin derivative) consisting of 3,4,5-trimethoxybenzaldehyde and

acceptor/anchoring group (carboxyl group) but varying  $\pi$ -spacer consisting of a Schiff base structure.

Each of the dyes displayed different adsorption behavior and coverage on the TiO<sub>2</sub> surface. The porphyrin

dyes  $P_{Zn}$ —BIA—COOH studied in this work exhibit red-shifted and broadened electronic spectra respect to the reference  $P_{Zn}$ —COOH as expected. By the introduction of Schiff base unit at the meso positions, the

energy level of  $E_{ox}$  (excited-state oxidation potentials) is significantly shifted to the positive compared

with the reference P<sub>2n</sub>-COOH, indicating a decreased HOMO-LUMO gap. The highest power conversion

efficiency of the two dyes based on DSSCs reached 1.75% under AM 1.5 G irradiation.

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### 1. Introduction

Dye-sensitized solar cells (DSSCs) are currently attracting considerable attention because of their high light-to-electricity conversion efficiencies, ease of fabrication, and low production costs [1]. Ruthenium sensitizers have been distinguished by attain-

ing more than 11% efficiencies because of their intense and widerange absorption of visible light [2,3]. However, the ruthenium dyes that are facing the problem of costs and environmental issues which will limit the large-scale application of DSSCs. In recent years, the complexes derived from common metals or metal-free organic dyes have been attracting increasing attention, owing to their modest cost, large molar absorption coefficients, ease of synthesis and modification and satisfactory stability [4]. Among the alternative dyes, porphyrins show strong absorption and emission in the visible region as well as tunable redox potentials. These

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properties make them as promising candidates for light harvesting dyes for DSSCs. Although many advantages have been put forwarded, porphyrins showed inferior performances compared to those high performance dyes for DSSCs [5–7]. One way to tackle those problems is to elongate the  $\pi$ -system of porphyrin by modifying a  $\beta$  position with olefinic linkage, quinoxaline moiety or naphthyl group [8–10]. Until now, the most efficient porphyrin dye for DSSCs was reported by Grätzel et al. [11] and the porphyrin dye gave the  $\eta$  up to 12.3% for YD2-o-C8+Y123 under one sun and the cobalt-based electrolyte. The breakthrough of the efficiency of porphyrin dyes indicate that porphyrins have the potential to be efficient as higher as the rutheniums were. Another way to improve the performance of porphyrin based DSSCs is to modify porphyrin molecules at meso-position by incorporation of aryl derivatives to extend the  $\pi$ -system. Recently, porphyrins have been recognized as the most promising dyes for such application because of their photochemical and electrochemical stability. strong absorbing ability in the visible region due to  $\pi$ - $\pi$ <sup>\*</sup> transitions of the conjugated macrocycle and high molar extinction coefficient [12-16]. However, the narrow absorption spectra of porphyrins, which poorly matched solar light distribution, limits the performance of porphyrin-sensitized solar cells. In order to solve this problem, many model compounds based on porphyrin have been synthesized for application in DSSCs [17-19].

To investigate how the structure of Schiff base affects the cell performance of devices, we have designed and synthesized two meso-position modified porphyrin sensitizers with porphyrin moieties as donors, aryl derivatives consisting of Schiff base unit as  $\pi$ -conjugated linkers, and carboxyl group as acceptors or anchoring groups (Fig. 1). The compounds were expected to have broader and intenser absorption than the corresponding porphyrin without Schiff base unit. Herein, we report the synthesis and the spectral, electrochemical, and photovoltaic properties of these porphyrin based sensitizers. For comparison, porphyrin sensitizer P<sub>Zn</sub>–COOH was prepared according to a literature method [20]. Our results indicate that the cell performance of the device using porphyrin P<sub>Zn</sub>–BIA–COOH as sensitizer outperforms the better-reported porphyrin dye. Therefore, P<sub>Zn</sub>–BIA–COOH might be a promising green dye for future colorful DSSC applications.

### 2. Experimental

### 2.1. Materials and reagents

All starting materials were purchased from Aladdin Company. pyrrole were dried and distilled from standard distillation before use. All other solvents and chemicals used in this work were analytical grade and used without further purification. All chromatographic separations were carried out on silica gel (200–300 mesh).

#### 2.2. Analytical measurements

<sup>1</sup>H NMR spectra were recorded with a Varian Inova 400 MHz NMR system. MALDI-TOF mass spectrometric measurements were performed on Bruker Bifiex III MALDI-TOF. UV–vis spectra of the dyes were measured on a Techcomp 2300 spectrophotometer. The PL spectra were obtained using Hitachi F-2500 luminescence spectrometer. Cyclic and differential pulse voltammetry measurements were performed on an electrochemical workstation (CHILK2005A, Tianjin Lanlike Chemistry electronic high-tech Co., Ltd., PR China).

### 2.3. General procedure for preparation and test of solar cells

TiO<sub>2</sub> photoelectrode was prepared by screen-printing methods. TiO<sub>2</sub> photoelectrode (area: ca. 0.8 cm  $\times$  1.2 cm) was prepared by a similar method reported in the literature [21–23]. Nanocrystalline TiO<sub>2</sub> films of 10–15 μm thickness were deposited onto transparent conducting glass (which has been coated with a fluorine-doped stannic oxide layer, thickness of 5 mm, sheet resistance of 19-23  $\Omega$ ). These films were dried at 150 °C for 30 min and then were gradually sintered at 450 °C for 30 min. The sensitizer was dissolved in DMF at a concentration of  $1 \times 10^{-4}$  mol L<sup>-1</sup>. The photoelectrode was dipped into the dye solution immediately after the high-temperature annealing and it was still hot (70 °C) and then kept at room temperature for 24 h so that the dye was adsorbed onto the TiO<sub>2</sub> films. After completion of the dye adsorption, the photoelectrode was withdrawn from the solution and washed thoroughly with ethanol to remove non-adsorbed dye under a stream of dry air or nitrogen.

A sandwich cell was assembled by using the dye anchored TiO<sub>2</sub> films as the working electrode and conducting glass coated with carbon as the counter electrode. The two electrodes were placed on top of each other using a thin polyethylene film  $(50 \,\mu\text{m})$  thick as a spacer to form the space for electrolyte. The empty cell was tightly held, and the edges were heated to 65 °C to seal the two electrodes together. The active surface area of TiO<sub>2</sub> film electrode was ca. 0.96 cm<sup>2</sup>. The electrolyte was introduced into cell through pre-drilled whole of the counter electrode and later covered by cover glass to avoid the leakage of the electrolyte solution. The composition of electrolyte is  $0.05 \text{ mol } L^{-1}$  iodine,  $0.5 \text{ mol } L^{-1}$  LiI in acetonitrile. Photoelectrochemical data were obtained using a 450 W xenon light source focused to give 100 mW cm<sup>-2</sup>, the equivalent of one sun at AM 1.5 (the luminance of the lamp has been normalized and corrected by the supplier), at the surface of the test cell. The solar-to-electricity conversion efficiency ( $\eta$ ) of the DSSCs was calculated from the short-circuit photocurrent density  $(I_{sc})$ , the open-circuit photovoltage  $(V_{oc})$ , the fill factor (ff) and the intensity of the incident light  $(P_{in})$  according to the following equation:



Fig. 1. Molecular structures of porphyrin derivatives used in this study.

$$\eta = \frac{J_{\rm sc} \left( \rm mA \ cm^{-2} \right) \times V_{\rm oc} \left( \rm V \right) \times ff}{P_{\rm in} \left( \rm mW \ cm^{-2} \right)}$$

The IPCE values were plotted as a function of the excited wavelength and defined according to the following equation:

$$IPCE = \frac{1240}{\lambda(nm)} \times \frac{J_{sc} (mA cm^{-2})}{\phi (mW cm^{-2})}$$

where  $J_{\rm sc}$  is the short-circuit photocurrent density generated by monochromatic light,  $\lambda$  is the wavelength of incident monochromatic light, and  $\phi$  is the incident light intensity.

### 2.4. Synthesis

The synthetic routes to the two porphyrin dyes are shown in Scheme 1. The detailed synthetic procedures were as follows:

### 2.4.1. 5-(4-Nitro) phenyl-10,15,20-tris (3,4,5-trimethoxylphenyl) porphyrin (1)

In a 250 ml three-necked ask, 3,4,5-trimethoxybenzaldehyde (1.96 g, 10 mmol) and 4-nitrobenzaldehyde (0.38 g, 2.5 mmol) were dissolved in 45 ml propionic acid and 10 ml nitrobenzene. The solution was heated to reflux at 125 °C. Pyrrole (0.69 ml, 10 mmol) was then added dropwise and the mixture stirred for another 45 min. After cooling to room temperature, half of the propionic acid was evaporated and C<sub>2</sub>H<sub>5</sub>OH was added. The mixture was cooled over night and filtered under vacuum. The crude product was purified column chromatography (dichloromethane/petroleumether = 2:1 as an eluent). After recrystallization from the mixture of CHCl<sub>3</sub> and  $CH_3OH(1:4, v/v)$ , a desired purple solid of compound **1** was obtained (0.89 g, 10%). <sup>1</sup>H NMR(CDCl<sub>3</sub>, 400 MHz, ppm): 7.07 (d, 2 H, Ar—H), 7.73-7.79 (d, 8 H, Ar-H), 8.05 (d, 2 H, Ar-H), 8.35 (d, 4 H, Ar-H), 8.63 (m, 8 H, pyrrole-H), -2.76 (s, 2 H, N-H), 3.96 (s, 27 H, -OCH<sub>3</sub>). IR (KBr pellet, cm<sup>-1</sup>): 1236 ( $v_{=C-O-C}$ ), 1566 ( $v_{NO2}$ ), 1562 ( $v_{C=C}$  phenyl), 1610 ( $v_{C=0}$  phenyl), 1458 ( $v_{C=H}$  pyrrole), 1001 ( $v_{N-H}$  pyrrole). MALDI-TOF MS calcd. for C<sub>53</sub>H<sub>47</sub>N<sub>5</sub>O<sub>11</sub> 929.98; found 930.19.

## 2.4.2. 5-(4-Amidogen) phenyl-10,15,20-tris (3,4,5-trimethoxylphenyl) porphyrin (**2**)

Under a nitrogen atmosphere, **2** was obtained through restoring the compound **1** (1.43 g, 1.6 mmol) in 36% HCl, and the solvent was heated at 67 °C for 2.5 h. The reductant was SnCl<sub>2</sub>·2H<sub>2</sub>O (0.35 g, 1.6 mmol). When the reaction finished, stronger ammonia water was used to adjust the pH of solution to 7–8. Then the crude product was extracted by dichloromethane and purified using column chromatography (chloroform/cyclohexane = 1:1 as an eluent). A purple solid of compound **2** was obtained (1.18 g, 85%) <sup>1</sup>H NMR(CDCl<sub>3</sub>, 400 MHz, ppm): -2.76 (s, 2 H, N–H), 4.02 (s, 2 H, NH<sub>2</sub>), 7.07 (d, 2 H, Ar–H), 7.73–7.79 (d, 8 H, Ar–H), 8.05 (d, 2 H, Ar–H), 8.35 (d, 4 H, Ar–H), 8.63 (m, 8 H, pyrrole-H), 3.96 (s, 27 H, –OCH<sub>3</sub>). IR (KBr pellet, cm<sup>-1</sup>): 1236 ( $\nu_{C=O-C}$ , 3450 ( $\nu_{N-H}$ ), 1562 ( $\nu_{C=C}$  phenyl), 1610 ( $\nu_{C=O}$  phenyl), 1458 ( $\nu_{C=H}$  pyrrole), 1002 ( $\nu_{N-H}$  pyrrole). MALDI-TOF MS calcd. for C<sub>53</sub>H<sub>49</sub>N<sub>5</sub>O<sub>9</sub> 897.98; found 898.21.

### 2.4.3. 5-(4-Amidogen) phenyl-10,15,20-tris (3,4,5-trimethoxylphenyl) porphyrin zine (**3**)

In a 250 ml three-necked round-bottomed ask, a mixture of **2** (1.17 g, 1.3 mmol) and Zn (OAc)<sub>2</sub> (0.58 g, 2.6 mmol) in a solution of CHCl<sub>3</sub> (45 ml) and DMF (10 ml) was refluxed for 4.5 h. After cooling to room temperature, the mixture was washed with water. The organic layer was dried over anhydrous MgSO<sub>4</sub> and concentrated. A purple-red solid of compound **3** was obtained (1.07 g, 85%) <sup>1</sup>H NMR(CDCl<sub>3</sub>, 400 MHz, ppm): 4.02 (s, 2 H, NH<sub>2</sub>), 7.07 (d, 2 H, Ar—H), 7.73–7.79 (d, 8 H, Ar—H), 8.05 (d, 2 H, Ar—H), 8.35 (d, 4 H, Ar—H), 8.63 (d, 8 H, pyrrole-H), 3.96 (s, 27 H,  $-OCH_3$ ). IR (KBr pellet, cm<sup>-1</sup>): 1236 (v<sub>=C</sub>-O<sub>-</sub>C), 3450 (v<sub>N-H</sub>), 1562 (v<sub>=C</sub> phenyl), 1610 (v<sub>C=O</sub>)

phenyl), 1458 ( $v_{C=H}$  pyrrole), 1003 ( $v_{N-Zn}$  pyrrole). MALDI-TOF MS calcd. for  $C_{53}H_{47}N_5O_9Zn$  961.35; found 961.42.

## 2.4.4. 5-[p-(4-Carboxyl benzyl idene amino)] phenyl-10,15,20-tris (3,4,5-trimethoxy-lphenyl)porphyrin zine (*P*<sub>Zn</sub>—BIA—COOH)

A 50 ml dichloromethane solution of **3** (1.06 g, 1.1 mmol) and 4formylbenzoic acid (0.25 g, 1.7 mmol) was refluxed at 38 °C in the presence of 0.2 ml acetic acid for 3 h under a nitrogen atmosphere. After cooling to room temperature, the reaction mixture was removed by rotary evaporation and recrystallied from the mixture of CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>OH (1:4, v/v), a purple solid of compound P<sub>Zn</sub>--BIA-COOH was obtained (1.19 g, 98%) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz,  $\delta$  ppm): 7.95 (d, 4 H, Ar-H), 8.22 (d, 12 H, Ar-H), 8.35 (d, 4 H, Ar-H), 8.63 (m, 8 H, pyrrole-H), 8.86 (s, 1 H, -C=NH), 3.96 (s, 27 H, -OCH<sub>3</sub>). IR (KBr pellet, cm<sup>-1</sup>): 1236 (v<sub>=C</sub>-O-C), 1657 (v<sub>C=N</sub> Schiff base), 1562 (v<sub>C=C</sub> phenyl), 1657 (v<sub>C=O</sub> phenyl), 1458 (v<sub>C=H</sub> pyrrole), 1007 (v<sub>N-Zn</sub> pyrrole); MALDI-TOF MS calcd. for C<sub>61</sub>H<sub>51</sub>N<sub>5</sub>O<sub>11</sub>Zn 1095.48; found 1095.45. Elem. Anal. For C<sub>61</sub>H<sub>51</sub>N<sub>5</sub>O<sub>11</sub>Zn Calc: C, 66.88; H, 4.69; N, 6.39. Found: C, 66.92; H, 4.71; N, 6.35.

### 2.4.5. 5-(4-Carboxyl) phenyl-10,15,20-tris (3,4,5-trimethoxylphenyl) porphyrin (**5**)

The synthetic procedure for **5** was similar to that for **1**, except that 4-formyl benzoic acid (0.38 g, 2.5 mmol) was used instead of 4-nitrobenzaldehyde. The crude product was purified using silica chromatograph with dichloromethane/cyclohexane mixture (1:1) to give **5** as a purple solid (0.35 g, 15%) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): 7.47 (d, 4 H, Ar—H), 7.54–7.79 (d, 12 H, Ar—H), 8.24 (m, 8 H, pyrrole-H), 3.95 (s, 27 H,  $-OCH_3$ ). IR (KBr pellet, cm<sup>-1</sup>): 1236 ( $\nu_{e-C}$ – $\sigma_{e-C}$ ), 3450 ( $\nu_{N-H}$ ), 1562 ( $\nu_{e-C}$  phenyl), 1458 ( $\nu_{e-H}$  pyrrole), 1008 ( $\nu_{N-H}$  pyrrole). MALDI-TOF MS calcd. for C<sub>54</sub>H<sub>48</sub>N<sub>4</sub>O<sub>11</sub> 928.99; found 929.01.

### 2.4.6. 5-(4-Carboxyl) phenyl-10,15,20-tris (3,4,5-

*trimethoxylphenyl)porphyrin* (*P*<sub>*Zn*</sub>—COOH)

The synthetic procedure for P<sub>Zn</sub>—COOH was similar to that described for **3**, except that **5** (0.02 g, 0.03 mmol) was used instead of **2**. A purple-blue solid of compound P<sub>Zn</sub>—COOH was obtained (0.21 g, 96%) <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): 7.47 (d, 4 H, Ar—H), 7.54–7.79 (d, 12 H, Ar—H), 8.24 (d, 8 H, pyrrole-H), 3.95 (s, 27 H, —OCH<sub>3</sub>). IR (KBr pellet, cm<sup>-1</sup>): 1236 ( $\nu_{=C-O-C}$ ), 3450 ( $\nu_{N-H}$ ), 1562 ( $\nu_{c=C}$  phenyl), 1458 ( $\nu_{c=H}$  pyrrole), 1007 ( $\nu_{N-Zn}$  pyrrole). MALDI-TOF MS calcd. for C<sub>54</sub>H<sub>46</sub>N<sub>4</sub>O<sub>11</sub>Zn 992.36; found 992.34. Elem. Anal. For C<sub>54</sub>H<sub>46</sub>N<sub>4</sub>O<sub>11</sub>Zn calcd.: C, 65.35; H, 4.67; N, 5.65. Found: C, 65.32; H, 4.69; N, 5.63.

### 3. Results and discussion

#### 3.1. Synthesis and chemical characterization

Both the two dyes have been synthesized according to several classical reactions. The synthetic strategy is shown in Scheme 1. Taking  $P_{Zn}$ —BIA—COOH as an example, the dye was synthesized as following steps. First, the starting material, 5-(4-nitro) phenyl-10,15,20-*tris* (3,4,5-trimethoxylphenyl) porphyrin **1**, was obtained from 3,4,5-trimethoxybenzaldehyde in the presence of 4-nitrobenz-aldehyde and pyrrole. Subsequently, compound **1** was converted into 5-(4-amidogen) phenyl-10,15,20-*tris* (3,4,5-trimethoxylphenyl) porphyrin **2** by Tin(II) chloride dehydrate with 36% HCl. Finally, compound **2** was treated with Zn(OAc)<sub>2</sub>, and then reacted with 4-formyl benzoic acid by bonus-elimination reaction to give  $P_{Zn}$ —BIA—COOH.  $P_{Zn}$ —COOH were synthesized by the same procedure as that for  $P_{Zn}$ —BIA—COOH except 4-carboxyl benzyl group was used instead of p-(4-carboxyl benzyl idene amino) phenyl group at the

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Scheme 1. Synthesis of porphyrin dyes.



Fig. 2. UV-vis absorption spectra of porphyrins in DMF solution.

meso position. The structures of the two dyes were verified by 1H NMR, IR, and MOLDI-TOF mass spectra.

### 3.2. Optical and electrochemical properties

The UV–vis absorption spectra of  $P_{Zn}$ –BIA–COOH and  $P_{Zn}$ –COOH in DMF solution are shown in Fig. 2, and the peak positions and molar absorption coefficients ( $\varepsilon$ ) of Soret and Q bands of porphyrin dyes are listed in Table 1. The UV–vis absorption spectra of  $P_{Zn}$ –COOH exhibits a strong Soret band at 423 nm and two moderate Q-bands at 559 and 600 nm. However,  $P_{Zn}$ –BIA–COOH showed broad and moderate strong absorption peak at 431 nm and stronger absorption peak at 564 nm, which are broader and red-shifted than that of  $P_{Zn}$ –COOH. As seen on the UV–vis absorption spectrum, the Soret band of  $P_{Zn}$ –BIA–COOH at 431 nm are red-shifted about 8 nm compared to  $P_{Zn}$ –COOH. The molar extinction coefficients ( $\varepsilon$ ) of Soret bands are  $1.83 \times 10^5$  mol L<sup>-1</sup> cm<sup>-1</sup> for  $P_{Zn}$ –BIA–COOH and  $1.94 \times 10^5$  mol L<sup>-1</sup> cm<sup>-1</sup> for  $P_{Zn}$ –COOH. These results indicate that  $P_{Zn}$ –BIA–COOH and  $P_{Zn}$ –COOH have relatively strong light harvesting ability, respectively, both of which are much higher than that of Ru(dcbpy)<sub>2</sub> (NCS)<sub>2</sub> (N<sub>3</sub> dye: ca.1.6 × 10<sup>4</sup> mol L<sup>-1</sup> cm<sup>-1</sup>) [24].

The steady-state fluorescence spectra of  $P_{Zn}$ —BIA—COOH and  $P_{Zn}$ —COOH were measured in DMF by exciting at the peak position of the Soret band (Fig. 3) and the wavelengths for emission maxima are listed in Table 1. From the intersection of the normalized absorption and emission spectra, the zero-zero excitation energies ( $E_{0-0}$ ) are determined to be 2.88 eV for  $P_{Zn}$ —BIA—COOH and 2.93 eV for  $P_{Zn}$ —COOH. The redox potentials of the porphyrin dyes were obtained by cyclic voltammetry and differential pulse voltammetry (Fig. 4), and the corresponding data are summarized in Table 2 [26]. The oxidation potentials of  $P_{Zn}$ —BIA—COOH and  $P_{Zn}$ —COOH (1.195 and 0.937) are both higher than the redox potential (0.2 V vs. SCE) of the iodide/triiodide couple. This could lead to fast dye regeneration, avoiding the geminate charge recombination between oxidized dye molecules and photoinjected electrons in the nanocrystalline titania film. As shown in Table 2, the excited-state



Fig. 3. PL spectra of P<sub>Zn</sub>-BIA-COOH and P<sub>Zn</sub>-COOH in DMF solution.



**Fig. 4.** Cyclic voltammograms and differential pulse voltammerty for  $P_{Zn}$ -BIA-COOH and  $P_{Zn}$ -COOH in DMF solution, measured at a scan rate of 100 mV s<sup>-1</sup>.

oxidation potentials of two porphyrin dyes are more negative than the equivalent potential of the TiO<sub>2</sub> conduction band edge (-0.74 V vs. SCE), and the  $E_{\rm gap}$  ranges from 0.71 to 0.76 eV. Assuming that energy gap of 0.2 eV is necessary for efficient electron injection these driving forces are sufficiently large for effective electron injection [25]. It is noted that the measured electrochemical HOMO/LUMO gaps are 2.19 and 2.52 eV for P<sub>Zn</sub>—BIA—COOH and P<sub>Zn</sub>—COOH, which are broader than the above mentioned optical gaps. This difference is a common feature of organic optoelectronic materials and may be related to the solvent effect.

| bl | e  | 1   |
|----|----|-----|
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UV, PL spectral data of porphyrin dyes.

| Dyes                      | $\lambda_{abs}^{a}$ ( $\epsilon$ , 10 <sup>5</sup> mol L <sup>-1</sup> cm <sup>-1</sup> ) | $\lambda_{em}^{b}(nm)$ | $\lambda_{int}^{c}(nm)$ | $\Gamma^{\rm d}~(10^{-9}~{ m mol}~{ m cm}^{-2})$ |
|---------------------------|---|------------------------|-------------------------|--|
| P <sub>Zn</sub> -BIA-COOH | 431 (1.83), 564 (0.19), 606 (0.09)<br>423 (1.94), 559 (0.24), 600 (0.09)                  | 609, 660<br>609, 659   | 548<br>546              | 1.83   |

<sup>a</sup> Absorption spectra was measured in DMF solution.

<sup>b</sup> Wavelengths for emission spectra in DMF solution by exciting at Soret wavelength.

<sup>c</sup> Measured by the intercept of the normalized absorption and emission spectra.

<sup>d</sup> Dye loading density was obtained on TiO<sub>2</sub> film.

| Table 2  |                           |
|--|---------------------------|
| Electrochemical data for porphyrin dyes and driving forces for electron-transfer processes | on the TiO <sub>2</sub> . |

| Dyes                      | $E_{0-0}{}^{a}(eV)$ | $E_{ox}^{b}(V)$ | $E_{red}^{c}(V)$ | $E_{ox}^{*d}(V)$ | $\Delta G_{ing}^{e} (eV)$ | $\Delta G_{reg}^{f}(eV)$ |
|---------------------------|---------------------|-----------------|------------------|------------------|---------------------------|--------------------------|
| P <sub>Zn</sub> —BIA—COOH | 2.88                | 1.195           | -0.764           | -1.685           | -0.945                    | -0.995                   |
| P <sub>Zn</sub> -COOH     | 2.93                | 0.937           | -0.841           | -1.993           | -1.253                    | -0.737                   |

<sup>a</sup> Determined from the intercept of the normalized absorption and emission spectra.

<sup>b</sup> First oxidation potentials (vs. SCE).

<sup>c</sup> First reduction potentials (vs. SCE).

 $^{d}$  Excited-state oxidation potentials approximated from  $E_{ox}$  and  $E_{0-0}$  vs. SCE).

 $^2$  Driving forces for electron injection from the porphyrin excited singlet state  $E_{ox}^*$  to the conduction band of TiO<sub>2</sub> (-0.74 V vs. SCE).

<sup>f</sup> Driving forces for regeneration of the porphyrin radical cation by  $I^-/I_3^-$  redox couple (+0.2 V vs. SCE).

### 3.3. Photovoltaic properties of porphyrin-sensitized TiO<sub>2</sub> solar cells

DSSCs were fabricated using two dyes as the sensitizers, with an effective area of 0.96  $cm^2$ , single-layer  $TiO_2$  film with 10–15  $\mu m$ thickness on ITO, and the electrolyte composed of 0.5 M LiI, 0.05 M I<sub>2</sub>, and 0.5 M 4-tert-butyl-pyridine (TBP) in 3-methoxypropionitrile in methanol solution. The photovoltaic performance of the porphyrin-sensitized TiO<sub>2</sub> cells was obtained under optimized conditions which the dyes were taken out and illuminated for 30 min after immersing in DMF for 15 min. Fig. 5 shows the J-V curves of DSSCs based on Pzn-BIA-COOH and Pzn-COOH. The detailed parameters ( $J_{sc}$ ,  $V_{oc}$ , ff, and  $\eta$ ) are summarized in Table 3. The DSSC based on P<sub>Zn</sub>-BIA-COOH dye shows a better comprehensive properties with an open-circuit voltage ( $V_{oc}$ ) of 0.49 V, a short-circuit photocurrent density  $(J_{sc})$  of 5.5 mA cm<sup>-2</sup>, and a fill factor (*ff*) of 0.65, corresponding to a solar-to-electricity conversion efficiency ( $\eta$ ) of 1.75% under AM 1.5 irradiation (100 mW cm<sup>-2</sup>), while  $P_{Zn}$ —COOH sensitized one yields  $\eta = 1.06\%$  with  $V_{oc} = 0.40$  V,  $J_{\rm sc}$  = 4.0 mA cm<sup>-2</sup>, and *ff* = 0.66. It is easy to see that the  $V_{\rm oc}$  of P<sub>Zn-</sub> -COOH dye is lower than that of P<sub>Zn</sub>-BIA-COOH which may be explained by dark current voltage curves of DSSCs.

To a large extent, the two porphyrin dyes display rather similar  $V_{oc}$  and ff values. The different  $\eta$  values of the two porphyrin-sensitized primarily result from the difference of  $J_{sc}$ . Because the surface density of the dye-sensitized TiO<sub>2</sub> films is an important factor to determine the photocurrent generation. From Tables 1 and 3, we can see that the low  $J_{sc}$  of  $P_{Zn}$ —COOH sensitized TiO<sub>2</sub> cell compared to that of the  $P_{Zn}$ —BIA—COOH Sensitized cells mainly results from the low surface density of TiO<sub>2</sub>/P<sub>Zn</sub>—COOH. It seems that the higher electron collection efficiency of  $P_{Zn}$ —BIA—COOH determined by the moderate surface density of TiO<sub>2</sub>/Dyes is suitable for preparing high efficient DSSCs. Given the similar driving forces of two porphyrin dyes, the influence of electron injection efficiency in the  $\eta$ 



Fig. 5. Photocurrent density-voltage characteristics for DSSCs based on the two dyes.

| Table 3   |
|---|
| Photovoltaic performance of DSSCs for the two porphyrin dyes. |

| Dyes                      | $J_{\rm sc}~({\rm mA/cm}^2)$ | $V_{\rm oc}\left({\sf V}\right)$ | ff   | η%   |
|---------------------------|------------------------------|----------------------------------|------|------|
| P <sub>zn</sub> —BIA—COOH | 5.5                          | 0.49                             | 0.65 | 1.75 |
| P <sub>zn</sub> —COOH     | 4.0                          | 0.40                             | 0.66 | 1.06 |

values is excluded. However, the biggest difference between the two dyes is their orientation on the TiO<sub>2</sub> surface.  $P_{Zn}$ —BIA—COOH will be tilted due to the C=C bond. This will result in different dye loading density and different electron injection rate. Therefore, the enhanced light-harvesting ability and higher electron collection efficiency of  $P_{Zn}$ —BIA—COOH probably lead to the higher  $\eta$  value than  $P_{Zn}$ —COOH.

### 4. Conclusions

In summary, we have successfully synthesized two porphyrin sensitizers (P<sub>Zn</sub>-BIA-COOH and P<sub>Zn</sub>-COOH) in which porphyrin unit act as electron-donating moiety and carboxyl group as electron-accepting moiety. By introducing the  $\pi$ -spacer consisting of a Schiff base unit, the light absorption of P<sub>Zn</sub>—BIA—COOH has been broadened and slightly red-shifted compared to that of P<sub>Zn</sub>-COOH. Therefore, Pzn-BIA-COOH exhibits the maximum power conversion efficiency of 1.75% with  $J_{sc}$  = 5.5 mA cm<sup>-2</sup>,  $V_{oc}$  = 0.49 V and ff= 0.65. Since electron injection efficiencies of the two porphyrin dyes are more or less similar, the light-harvesting ability and electron collection efficiencies of porphyrin sensitizers have strong influence on the photovoltaic performances. Our results demonstrate the necessity and importance of modifying  $\pi$ -spacers in D- $\pi$ -A structure of porphyrin dyes. Inspired by the natural light-harvesting ability of porphyrin derivatives, further structural modification of mesosubstituted porphyrin for broadening the spectral absorption is anticipated to give some new porphyrin dyes with even better performances.

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