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PII:	\$0277-5387(16)30219-4
DOI:	http://dx.doi.org/10.1016/j.poly.2016.06.002
Reference:	POLY 12040
To appear in:	Polyhedron
Received Date:	25 March 2016
Accepted Date:	1 June 2016



Please cite this article as: Y. Wu, J-C. Liu, W-B. Guo, R-Z. Li, N-Z. Jin, Three horizontal anchor porphyrins for dye-sensitized solar cells: An optical, electrochemical and photovoltaic investigation, *Polyhedron* (2016), doi: http://dx.doi.org/10.1016/j.poly.2016.06.002

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# Three horizontal anchor porphyrins for dye-sensitized solar cells: An optical, electrochemical and photovoltaic investigation

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#### Abstract

Porphyrins are promising DSSC sensitizers focused on novel anchoring. Herein, three horizontal anchor zinc porphyrins have been designed, synthesized, and well-characterized. Their optical, photovoltaic, theory calculation and electrochemical performances in dye-sensitized solar cells were investigated. Absorption spectra indicated the stronger H-aggregation in *ortho* carboxylic acid anchor porphyrin (*o*-ZnPA) than that in *meta* carboxylic acid anchor porphyrin (*m*-ZnPA) on the surface of TiO<sub>2</sub> nanoparticles. The photoelectric conversion efficiency studies showed a significantly enhanced photovoltaic behavior for *meta* carboxylic acid anchor porphyrin (*m*-ZnPA) compared to *meta* tetrazolium anchor porphyrin (*m*-ZnPTz). The infrared spectroscopies, theory calculations and the electrochemical impedance spectroscopies revealed that carboxylic acid anchoring binding modes could increase the efficiency of electron injection.

**Keywords** dye-sensitized solar cells, zinc porphyrin dye, horizontal, anchoring group

#### 1. Introduction

Solar energy, as an environmental friendly and continual energy sources, solves the energy problems worldwide [1-3]. Dye-sensitized solar cells (DSSCs) have attracted extensive attentions in view of inexpensive materials, easy processing, and minimal environmental impact [4-6]. As such, it is the most feasible technology for the conversion of solar energy directly into electricity. In order to improve the photoelectric conversion efficiency of the dye-sensitized solar cells, selecting the appropriate photosensitizers play a crucial role. In typical DSSCs, usually using Ru polypyridyl complex [7], organic sensitizers [8-10] and zinc porphyrin dyes [3,11] as photosensitizers, respectively. Porphyrins are especially promising DSSC sensitizers due to their structural can be used to collect solar energy and achieve photoinduced electron and energy transfer [12-16]. Thus, numerous zinc porphyrin dyes have been reported based on a donor- $\pi$ -acceptor (D- $\pi$ -A) architecture, such as SM315 [17], with the anchoring group of 4-ethynyl benzothiadiazole benzoic acid attached at the *meso* position exhibited remarkably high efficiency (13%).

Generally, the porphyrin sensitizers are linked to the TiO<sub>2</sub> semiconductor through anchoring groups, such as carboxyl groups, which provide electron injection to the TiO<sub>2</sub> electrode surfaces. Recently, some researchers made to developing novel anchoring groups, which improve the photoelectric efficiency. For example, salicylic acid was reported as an anchoring group for zinc porphyrin dyes [18]. 8-hydroxylquinoline was used as an anchoring group for metalloporphyrin sensitized solar cells [19]. Coutsolelos's group introduced a series of pyridine into porphyrin dyes as an anchoring group [20,21]. Hiroshi Imahori's group reported that tropolone is a robust anchoring group for porphyrin sensitized solar cells [22]. The above are single anchoring group, a typical porphyrin dye with four benzoic acids as anchoring groups was reported by Rochford et al [23]. The four anchoring groups are in the meta or ortho position on the *meso*-phenyl rings of the porphyrin macrocycle, which is called horizontal anchor porphyrin.

In this paper, three horizontal anchor zinc porphyrins (m-ZnPA, o-ZnPA,

m-ZnPTz, shown in Scheme 1) have been designed and synthesized. They include carboxyl and tetrazole groups as anchoring groups. The optical, electrochemical, theoretical calculations and the photovoltaic performances of the assemblies are studied to further understand the behavior of the dye-sensitized solar cells.



Scheme1. Structure of zinc porphyrin dyes

#### 2. Experimental Section

#### 2.1 General methods

Electronic absorption spectra were measured on a UV-2550 spectrometer. The Luminescence spectrum was measured by an LS-55 (PE USA Inc) fluorescence spectrophotometer at room temperature. 1H NMR (600 MHz) was measured on a Varian Mercury Plus-400 spectrometer. An LS1000 solar simulator (Solar Light Com. Inc., USA) was used to give an irradiance of 100 mW cm<sup>-2</sup> (the equivalent of one sun at AM 1.5G) at the surface of a testing cell. The current-voltage characteristics were obtained by applying external potential bias to the cell and measuring the dark current and photocurrent with a Keithley model 2602 digital source meter. This process was fully automated using Labview 8.0. A similar data acquisition system was used to control the incident photon-to-collected electron conversion efficiency (IPCE) measurement. Under full computer control, light from a 1,000-W xenon lamp was focused through a monochromator onto the photovoltaic cell under testing. A computer-controlled monochromator (Omni  $\lambda 300$ ) was incremented through the spectral range (300-900 nm) to generate a photocurrent action spectra with a sampling interval of 10 nm and a current sampling time of 2 s. IPCE is defined by IPCE( $\lambda$ ) =  $hcJ_{sc}/e\phi\lambda$ , where h is Planck's constant, c is the speed of light in a vacuum, e is the electronic charge,  $\lambda$  is the wavelength (m),  $J_{sc}$  is the short-circuit photocurrent density (mA cm<sup>-2</sup>), and  $\phi$  is the incident radiative flux (mW m<sup>-2</sup>). Photovoltaic performance was measured by using a metal mask with an aperture area of 0.1576 cm<sup>2</sup>. A homemade heating-cooling system was used for temperature dependent J-V measurements. Cyclic voltammetry trials were conducted using a CHI 1140C instrument, with a traditional three-electrode system. The working electrode, reference electrode, and auxiliary electrode was a glassy carbon electrode, Ag/AgCl and Pt electrode, respectively. The electrochemical impedance spectroscopy (EIS) was achieved on a Princeton applied research VMP2 multi potentiastat. The frequency of the AC signal ranged between 0.1 Hz and 100 kHz. The amplitude of the AC signal was 10mV at room temperature.

#### 2.2 Device fabrication

A screen-printed double layer film of interconnected  $TiO_2$  particles was used as the mesoporous negative electrode. A 7 µm thick transparent layer of 20 nm sized titania

particles were first printed on the fluorine-doped SnO<sub>2</sub> (FTO) conducting glass electrode and further coated by a 5 µm thick scattering layer of 400 nm sized titania particles. The film thickness was measured by a benchtop Ambios XP-1 stylus profilometer. The detailed preparation procedures of  $TiO_2$  nanocrystals, pastes for screen-printing, and nanostructured  $TiO_2$  film have been reported by Prof. P. Wang [24]. A cycloidal TiO<sub>2</sub> electrode ( $\sim 0.28 \text{ cm}^2$ ) was stained by immersing it into an ethanol solution containing **ZnPA** (2mM) anchoring molecule overnight. Other TiO<sub>2</sub> electrode was stained by immersing it into DMF solution containing **ZnPTz** (2mM) anchoring molecule overnight. After being washed with acetonitrile and dried by air flow, the sensitized titania electrode was assembled with a thermally platinized FTO electrode. The electrodes were separated by a 35-µm-thick Bynel (DuPont) hot-melt gasket and sealed up by heating. The internal space was filled with a liquid electrolyte using a vacuum backfilling system. The electrolyte-injecting hole on the counter electrode glass substrate, made with a sand-blasting drill, was sealed with a Bynel sheet and a thin glass cover by heating. The electrolyte used contained 50 mM LiI, 30 mM  $I_2$  in acetonitrile solvent. After all these procedures, the cells were located in the over for heating posttreatment at 100°C for 30 min and cooled to room temperature before photoelectrochemical measurements.

### 2.3 Synthesis of Porphyrin Dyes

All solvents and reagents were used directly without further purification as commercially analytical grade. The ZnPA porphyrin dyes were synthesized by the modified Lindsey method [25,26], especially, it is reacted with different reactants. Syntheses followed as Scheme 1.



Scheme1. Synthetic protocol for zinc porphyrin dyes

### 5,10,15,20-tetra(3-cyanophenyl) porphyrin (a)

Syntheses of **a** was prepared according to literature [26]. 3-cyanophenyl (0.98g, 7.5mmol) was refluxed in a mixture propionic acid (50mL) and 0.52mL of distilled pyrrole (7.5mmol) was then added dropwise. After complete addition, the reaction mixture was stirred for another 2h and cooled to room temperature. After evaporation under reduced pressure of the solvent to dryness, the solid residue was dissolved in methylene chloride and chromatographed on aluminum oxide. Elution with methylene chloride to give  $\mathbf{a}$  in 18% yield as a purple solid, which was used in the metalation step without further characterization.

### 5,10,15,20-tetra[3-(2,3,4,5-tetrazolyl)phenyl] porphyrin (b)

Syntheses of **b** was prepared according to literature [27]. A solution of

5,10,15,20-tetra(3-cyanophenyl) porphyrin **a** (0.6g, 0.84mmol), NaN<sub>3</sub> (0.48g, 7.34mmol), NH<sub>4</sub>Cl (0.36g, 6.74mmol), and anhydrous DMF (50mL) was heated at 120°C for 2 days. Additional NaN<sub>3</sub> (0.34g, 5.18mmol) and NH<sub>4</sub>Cl (0.22g, 4.1mmol) were added to push the reaction, which monitored by TLC until the reaction was complete. The DMF was evaporated under reduced pressure then cold H<sub>2</sub>O (20mL) was added. The resulting solution was acidified with 6 N HCl then CH<sub>2</sub>Cl<sub>2</sub> (20mL) was added. The resulting precipitate was collected and dried under vacuum to provide **b** in 80% yield as a green solid, which was used in the metalation step without further purification.

#### 5,10,15,20-tetra(2-cyanophenyl) porphyrin (c)

Syntheses of **c** was prepared according to literature. Synthesis method was similar to 5,10,15,20-tetra(3-cyanophenyl) porphyrin. Yield, 10%

#### General Procedure for a and c Metalation

The free base **a** and **c** porphyrins (0.4mmol) was dissolved in CHCl<sub>3</sub> (80mL). A solution of  $Zn(OAc)_2 \cdot 2H_2O$  (1.6mmol) in MeOH (10mL) was added to the porphyrin solution in one portion, and the reaction mixture was refluxed 4h. The solvents were removed in vacuo leaving a purple solid, which was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and washed successively with 5% aqueous NaHCO<sub>3</sub> and water. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed in vacuo. The metaloporphyrins were obtained in 80% yields following silica gel chromatography with dichloromethane/ethyl acetate (95:5) to afford pure metalloporphyrins.

#### General Procedure for metalloporphyrins alkaline hydrolysis

The metalloporphyrins were added 5M NaOH (10mL), then add 8~10mL C<sub>2</sub>H<sub>5</sub>OH, and the reaction mixture heated at 80 °C for 48h, with moist pH paper detecting whether the reaction of ammonia discharged there, until no ammonia gas evolution reaction. Diluted with water, filtration of impurities, and the filtrate neutralized with 6M HCl to precipitate appears. Allowed to stand overnight, with sand core funnel filtration, and dried to obtain the product *m*-ZnPA and *o*-ZnPA. Yield, 73%

*m*-**ZnPA** <sup>1</sup>H NMR (600MHz, DMSO-d<sub>6</sub>)  $\delta$ 13.2(s, 4H), 8.86~8.83(s, 10H), 8.46~8.33(m, 8H), 8.23~8.12(m, 4H), 6.83 (s, 2H). MS (ESI, *m/z*): [M+H]<sup>+</sup> calcd for C<sub>49</sub>H<sub>31</sub>N<sub>4</sub>O<sub>8</sub>Zn, 867.2; found, 868.1

### Zn-5,10,15,20-tetra[3-(2,3,4,5-tetrazolyl)phenyl] porphyrin (m-ZnPTz)

A solution of e (0.4mmol) and Zn(OAc)<sub>2</sub>•2H<sub>2</sub>O (2mmol) in anhydrous DMF (50mL) was heated at reflux for 4~5h. The reaction mixture was allowed to cool to room temperature then DMF was evaporated under reduced pressure. The crude product was silica gel chromatography to give m-ZnPA2. Yield,  $70\%^{1}$ H NMR (600MHz, DMSO-d<sub>6</sub>)  $\delta$  8.65(d, 4H), 8.41~7.97(m, 8H), 6.67~5.71(m, 10H), 5.30(s, 2H) MS (ESI, *m*/z): [M+H]<sup>+</sup> calcd for C<sub>48</sub>H<sub>28</sub>N<sub>20</sub>Zn, 848.2; found, 869

#### 3. Results and Discussion

3.1. Optical and Electrochemical Properties

In order to studied the electronic transition of these dyes. The UV-Vis absorption spectra of these dyes in DMF solutions are shown in Figure 1. All three dyes exhibited the features typical of the porphyrin ring, with absorptions at 400~480nm for intense Soret band (corresponding to the  $\pi$ - $\pi$ \* transitions) and weak Q bands at 550~630nm (corresponding to the energy vibration transition). Compared to the absorption spectra of *m*-**ZnPA** and *o*-**ZnPA**, the spectra of *o*-**ZnPA** and *m*-**ZnPA** red-shifted (~40nm), indicating that the *o*-**ZnPA** are being high steric hindrance,  $\pi$ - $\pi$  stacking interactions lead to extend the absorption to longer wavelengths. Both bands of *m*-**ZnPTz** red-shifted for ca. 5nm relative to those of *m*-**ZnPA**, which can be rationalized by the stronger conjugation effect of the tetrazole group respect to the carboxylic acid. There are three porphyrin dyes absorbed on the TiO<sub>2</sub> thin film (2.5µm) are shown in Figure S1. The absorption spectra of three dyes are broadened may be presence of aggregations on the TiO<sub>2</sub> surfaces. Comparison the solution spectra (Figure 1) show that slightly red-shifted, which is beneficial for improving light-harvesting.



Figure1. UV-vis absorption spectra of three porphyrin dyes in DMF solution

Figure 2 showed the fluorescence spectra of three porphyrin dyes in DMF. Dyes emission spectra were very similar. o-ZnPA is slightly blue-shifted than that of m-ZnPA, which is o-ZnPA being high steric hindrance. Notedly, the spectra (Figure S2) reveal blue shifts and broadening compared to those solution fluorescence spectra (Figure2), ascribed to the occurrence of *J*-aggregations of dye molecules on the TiO<sub>2</sub>

films [28]. Table 1 summarizes the optical data of three porphyrin dyes. Three porphyrin dyes on  $TiO_2$  film digital and presented in Table S1.

The electrochemical properties of these porphyrin dyes were investigated by cyclic voltammetry and presented in Table 1. The oxidation potentials ( $E_{ox}$ ) of dyes were +1.19 V for *m*-ZnPA, +1.16 V for *o*-ZnPA and +1.19 V for *m*-ZnPTz, that were far below the redox potential of  $\Gamma/I_3^-$  (0.4V) to ensure efficient regeneration. The excitation energies ( $E_{0.0}$ ) were determined to be 2.18 eV for *m*-ZnPA, 2.05 eV for *o*-ZnPA and 2.14 eV for *m*-ZnPTz, respectively. The injection potentials ( $E_{s+/s^*}$ ) subtracted the  $E_{0.0}$  from the  $E_{ox}$  of the sensitizers was much higher than the potential of the conducting band of TiO<sub>2</sub> nanoparticles (0.5V) [29].

Table1. Absorption/Emission and Electrochemical Properties of Porphyrin Dyes

dye	absorption <sup>a</sup>	emission <sup><i>a</i></sup>	$E_{0-0}^{b} = E_{0x}^{c}$	$\mathrm{E_{s+/s^*}}^d$
	$\lambda_{\max}$ (nm)	$\lambda_{\rm em}$ (nm)	eV (V vs NHE)	(V vs NHE)
m-ZnPA	425, 558, 597	608, 654	2.18 1.19	-0.99
o-ZnPA	465, 603,	606, 656	2.05 1.16	-0.89
m-ZnPTz	430, 562, 601	610, 650	2.14 1.19	-0.95

<sup>*a*</sup> Absorption and emission spectra were measured in DMF solution at room temperature. <sup>*b*</sup>  $E_{0,0}$  was determined from the intersection of normalized absorption and emission spectra. <sup>*c*</sup> The oxidation potentials of dyes were measured in DMF with 0.1M TBAPF<sub>6</sub> with a scan rate of 100mVs<sup>-1</sup> (vs NHE). <sup>*d*</sup>  $E_{s+/s^*}$  was calculated by  $E_{ox}$ - $E_{0,0}$ .



Figure2. Fluorescence spectra of three porphyrin dyes in DMF solution

#### 3.2. FT-IR

The functionalization of TiO<sub>2</sub> thin film with three dyes was showed by infrared spectroscopies (Figure S3). All solid samples evidenced spectra bands from the pyrrole C-H, C=C, and C=N stretches (over 700~1500cm<sup>-1</sup>) of the porphyrin typical spectra [30-32]. Samples of *m*-ZnPA and *o*-ZnPA showed a strong band of the carboxylic acid stretching peak (1690~1700cm<sup>-1</sup>). For all two tetraacid porphyrins bound to TiO<sub>2</sub> films showed the disappearing of the carboxylic acid stretching peak, which concomitant appearance of asymmetric and symmetric stretching modes of the v (CO<sub>2</sub><sup>-</sup>) [33]. This indicated carboxylate groups through chelating or bidentate blinding modes on the TiO<sub>2</sub> surface [34-37]. Samples of *m*-ZnPTz allowed a tetrazole N-N vibrational stretching peak located 1005cm<sup>-1</sup>, which adsorption on TiO<sub>2</sub> films showed the conjugated heterocycle [38].

3.3. Theoretical Calculations and Energy Levels

To gain a better insight into the structure changes affect the photophysical properties and energy levels of frontier molecular orbital, we performed calculations with DFT using the Gaussian 09 program [39] at the B3LYP/LanL2DZ level. As shown in Figure S4, the electrons of the HOMO levels for all the dyes mainly distribute over the porphyrin center framework, while the LUMO orbitals are markedly delocalized over the porphyrin macrocycle turn to the anchoring group. It's worth noting that the LUMO+2 levels for all of distribute anchoring group. The features suggest the presence of excellent electron-separated status for these devices. The energy-levels diagram of three dyes relative to the TiO<sub>2</sub> and the electrolyte  $I/I_3$ are shown in Figure 3. All of the LUMO are higher than the conduction band edge (CB) of TiO<sub>2</sub> (-4.0eV), indicating that efficient electron injection into TiO<sub>2</sub> conduction band from the excited states [40]. The HOMO levels are more negative than the electrolyte  $\Gamma/I_3$ , suggest that electron injection process could thermodynamically accept electrons from I to regenerate the dyes. Notedly, the energy gap between the HOMO and LUMO is almost equal. It is obvious that *m*-ZnPA is lowest energy-levels, which agree with carboxylic acid groups are effective anchor groups.



Figure3. Energy-level diagram of three porphyrin dyes

#### 3.4. Photovoltaic Performance of DSSCs.

The photovoltaic properties of the devices sensitized by three porphyrin dyes were tested by iodine electrolyte and under irradiance of 100mW cm<sup>-2</sup> AM 1.5G sunlight. The incident photo-to-current conversion efficiency (IPCE) spectra of the new porphyrin dyes sensitized devices in the wavelength range 300-700nm can be seen in IPCE values Figure 4. The order of of dyes is as follows: *m*-ZnPA>*m*-ZnPTz>*o*-ZnPA. The IPCE of dyes reveal the energy conversion of Soret and Q bands of porphyrin, roughly analogous to their corresponding UV-Vis spectra. Compared with *m*-ZnPA, the introduction of additional tetrazole group in *m*-**ZnPTz** slightly red-shift. The phenomenon is consistent with the UV-Vis absorption spectrum. More impressively, o-ZnPA has a weak broadening of 460nm~500nm. However, *o*-ZnPA sensitized cell reveal lowest IPCE, assigned to the dye-aggregation on the TiO<sub>2</sub> electrode surface [41]. Therefore, o-ZnPA J-V curve and electrochemical impedance spectroscopy were not investigation. The detailed data of short-circuit photocurrent density  $(J_{sc})$ , open-circuit photovoltage  $(V_{oc})$  and fill factor (FF) for these cells are shown in Table S2 and Figure 5. The  $J_{sc}$  increased in the order of *m*-ZnPTz<*m*-ZnPA, which this trend was also consistent with IPCE spectra. Introduction of the tetrazolium as anchor groups is favorable for extending its conjugation length and preventing the dye-aggregation on the  $TiO_2$  electrode surface, thus *m*-ZnPTz shows the highest open voltage ( $V_{oc}$ ) of 453mV. Whereas, *m*-ZnPA sensitized device shows highest short-circuit photocurrent density  $(J_{sc})$  and total photoelectronic conversion efficiency  $(\eta)$ . The performance of these dyes with the

carboxylic acid group as the anchoring group is superior than that with the tetrazolium group as the anchoring group.







**Figure5.** *J-V* characteristics of DSSCs sensitized by three porphyrin dyes

3.6. Electrochemical Impedance Spectroscopy

To further understand the interfacial charge transportation in the DSSC devices was investigated by electrochemical impedance spectroscopy, which was carried out at different applied potentials under dark conditions [42-45]. Figure 6 showed the Nyquist plots of the DSSCs base on dyes *m*-ZnPA and *m*-ZnPTz. Nyquist plots have three semicircles, and the large semicircle at intermediated frequency reflected the interfacial charge transfer resistance ( $R_{ct}$ ) at the TiO<sub>2</sub>/dye/electrolyte interface. The fitted  $R_{ct}$  values of *m*-ZnPTz-based devices are much larger than *m*-ZnPA-based devices. In other words, the larger  $R_{ct}$  meant a slower charge recombination rate; as a

result, the electron recombination at the TiO2/dye/electrolyte interface can be efficiently suppressed, leading to a higher  $V_{oc}$  for DSSCs sensitized with *m*-ZnPTz [23,46].



Figure6. Electrochemical impedance spectroscopy (EIS) of DSSCs based on three porphyrin dyes

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#### 4. Conclusion

In conclusion, three new dyes of horizontal anchor zinc porphyrins using carboxyl and tetrazole as anchoring groups have been designed and synthesized. The optical, photovoltaic and electrochemical performance in dye-sensitized solar cells were investigated. Our results reveal enhanced photovoltaic behavior for *m*-ZnPA porphyrin dye. The carboxyl horizontal anchor porphyrin could enhance the efficiency electron injection from dyes to the TiO<sub>2</sub> nanoparticles. To improve the photoelectric conversion efficiency of use *m*-ZnPA as horizontal anchor groups for self-assembling, which is our future research and the results will be reported in due course.

#### Acknowledgments

The National Natural Science Foundation of China (No. 21461023) has supported this work. We are very grateful to Prof. Peng Wang (Changchun Institute of Applied Chemistry, Chinese Academy of Sciences) for supplying device fabrication and measurement of solar cells. We also acknowledge the support of Gansu Computing Center of china.

#### Supplementary material

Supplementary figure and data associated with this article can be found, in the online version.

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### **Graphical Abstract-Pictogram**



### **Graphical Abstract**

Horizontal anchor zinc porphyrins have promising DSSC sensitizes. The UV-vis absorption spectra, fluorescence spectra, and the photovoltaic performance of these photosynthesis devices are described. Our results reveal that these DSSC devices have impressive photoelectric conversion efficiency, especially for the assembly based on carboxylic group horizontal anchor porphyrin.