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Introduction

Dye-sensitized solar cells (DSSCs), as an alternative energy technology, have received much attention for worldwide scientists and engineers owing to their low costs, ease of fabrication, and minimal environmental impact.¹⁻⁵ It is well-known that porphyrins dyes play a key role in this type of DSSC, in which they used to collect solar energy, achieve photoinduced electron and transfer solar energy into electricities.⁶ Zinc porphyrin dyes have been reported based on a donor– π –acceptor (D– π –A) architecture, such as SM315, which exhibited remarkably high efficiencies up to 13%.⁷ These porphyrin dyes were linked to surface of TiO₂ through anchoring groups such as carboxyl,⁸ salicylic acid,⁹ pyridine,¹⁰ tropolone,¹¹ to enable the porphyrin ring plane almost to be vertical. Additionally, Rochford *et al.*¹² reported a typical horizontal porphyrin with four benzoic acids as anchoring group to bind onto the TiO₂ electrode surface.

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In this work, employing the meta-mediated assembling strategy for organizing different metal ions (M, M = Zn^{2+} , Cd^{2+} and Co^{2+}) horizontal anchor porphyrins (MPA) and two antennas molecules (Lx, x = 1, 2) on the nanostructured TiO₂ electrode surfaces have been prepared, resulting in a ZnPA+Lx assembled approach. Further, the assemblies were absorbed on the semiconducting TiO₂ electrode surfaces by the carboxylic groups of horizontal anchor porphyrin, and their photovoltaic performances in solar cells were performed under an irradiance of 100 mW cm⁻² AM 1.5G solar simulator. The photoelectric conversion efficiency of the solar cells sensitized by the dyes with triphenylamine group antenna molecule (L2) were obviously enhancement when compared to that sensitized by the dye with dimethylamino group antenna molecule (L1). The results were also verified by the transient photovoltage decay, theory calculations and optical performance. In addition, the assembled modes of the assemblies immobilized on TiO₂ electrode surfaces were also verified by transmission electron microscopy.

Porphyrin-based self-assemblies, as energy/electron/holecarrier agents, have also attracted much attention because they can generate efficient charge separation and carrier of separated charges in their corresponding photoelectrochemical devices.¹³⁻¹⁷ Up to now, a series of surface-fabrication methods have been reported. Imahori *et al.* presented a Pd-mediated stepwise self-assembly of zinc porphyrin on the SnO₂ electrode surface.¹⁸ D'Souza *et al.* reported a metal–ligand axial coordination approach to construct a series of (donor)₁– (donor)₂ porphyrin-based assemblies.¹⁹ Our recent work mainly focuses on zinc porphyrin derivatives appended organic acid *via* metal–ligand axial coordination attached to the TiO₂ electrode surfaces,^{20,21} which use of vertical anchors molecular. To the best our knowledge, the document of organization assemblies of horizontal anchor porphyrins are very few.

Herein, we designed and synthesized horizontal anchor porphyrins with different metal ions (\mathbf{M} , $\mathbf{M} = \mathbf{Zn}^{2+}$, \mathbf{Cd}^{2+} and \mathbf{Co}^{2+}) (denoted as **MPA**, shown in Scheme 1), which selecting metal-mediums of \mathbf{Zn}^{2+} can construct horizon anchor porphyrin molecules on the TiO₂ electrode surface. Further, such a novel self-assembly (described as **ZnPA+Lx**, $\mathbf{x} = 1$, 2) with two antenna molecule (denoted as \mathbf{Lx} , $\mathbf{x} = 1$, 2, shown in Scheme 1) and horizontal anchor zinc porphyrin by metal-ligand axial coordination was constructed, wherein these assemblies were immobilized directly on the double-layer nanostructured TiO₂ and fabricated into solar cells. The optical properties, topography, theoretical calculations, transient photovoltage decay and the photovoltaic performances of the assemblies are studied to further understand the behavior of the **ZnPA+Lx** based dye-sensitized solar cells.



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A novel self-assembly with horizontal anchor porphyrin for supramolecular solar cells[†]



Scheme 1 Structural diagram of MPA and antenna molecule (Lx, x = 1, 2).

Experimental section

General methods

All solvents and reagents were used directly without further purification as commercially analytical grade. 5,10,15,20-Tetra(3-cyanophenyl) porphyrin (a) was synthesized according to Lindsey's method with slight modification.²² UV-vis spectra were measured on a UV-2550 spectrometer. Luminescence spectrum was measured by an LS-55 (PE USA Inc) fluorescence spectrophotometer at room temperature. ¹H NMR (400 MHz) was measured on a Varian Mercury Plus-400 spectrometer. The detailed synthesis processes are shown in Scheme 3 and 4. Surface topography of the self-assembly films on TiO₂ electrode surface was imaged using transmission electron microscopy (TEM) (Hitachi Model H-900). The current density-voltage (J-V) and incident photon-to-collected electron conversion efficiency (IPCE) were measured under an irradiance of 100 mW cm⁻² (AM (1.5G) by using a metal mask with an aperture area of (0.158 cm^2) . The details of photoelectrochemical measurements were illustrated in our previous article.21 Transient photoelectrical examinations were tested on Autolab-PGSTAT302N electrochemical workstation equipped with ADC10M high-speed module.23

Device fabrication

The detailed preparation procedures of TiO₂ nanocrystals, pastes for screen-printing, and nanostructured TiO₂ film have been reported by Prof. P. Wang.24 A cycloidal TiO₂ electrode (~0.28 cm²) was stained by immersing it into a methanol solution containing ZnPA (2 mM) as anchoring molecule overnight, after removal of the unbound molecules (through three ethanol washings), then the electrode was immersed into a dye solution containing Lx (0.2 mM) in CHCl₃/DMF (85/15, v/v) for 1 h, then, washed by acetonitrile solution three times 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 electrolyteinjecting 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 I₂ in acetonitrile solvent. After all these procedures, the cells were located in the oven for heating post treatment at 100 °C for 30 min and cooled to room temperature before photoelectrochemical measurements.

Synthesis of dyes

General procedure for free base porphyrin (a). 3-Cyanophenyl (0.98 g, 7.5 mmol) was refluxed in a mixture propionic acid (50 mL) and 0.52 mL of distilled pyrrole (7.5 mmol) was then added dropwise. After complete addition, the reaction mixture was stirred for another 2 h 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 a in 18% yield as a purple solid, which was used in the metalation step without further characterization.



Scheme 2 The assembled approach of the assemblies on TiO₂ electrode surfaces.



Scheme 3 Synthesis protocol for anchoring molecule.



Scheme 4 Synthesis protocol for antenna molecule.

General procedure for a metalation (b). The free base a porphyrins (0.4 mmol) was dissolved in CHCl₃ (80 mL). A solution of $M(OAc)_2 \cdot 2H_2O$ (1.6 mmol) (M: $Zn(OA_C)_2 \cdot 2H_2O$; Cd(OAc)₂·2H₂O; Co(OAc)₂·2H₂O) in MeOH (10 mL) was added to the porphyrin solution in one portion, and the reaction mixture was refluxed 4 h. The solvents were removed in vacuo leaving a purple solid, which was dissolved in CH₂Cl₂ and washed successively with 5% aqueous NaHCO₃ and water. The organic layer was dried over Na2SO4, and the solvent was removed in vacuo. The metalloporphyrins were obtained in 80% vields following silica gel chromatography with dichloromethane/ethyl acetate (95:5) to afford pure metalloporphyrins.

General procedure for metalloporphyrins alkaline hydrolysis (c). The metalloporphyrins were added 5 M NaOH (10 mL), then add 8–10 mL C_2H_5OH , and the reaction mixture heated at 80 °C for 48 h, 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 6 M HCl to precipitate appears. Allowed to stand overnight, with sand core funnel filtration, and dried to obtain the product **ZnPA**, **CdPA** and **CoPA**. Yield, 73%.

ZnPA. ¹H NMR (600 MHz, DMSO-d₆) δ 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]⁺ calcd for C₄₉H₃₁N₄O₈Zn, 867.2; found, 868.1.

General procedure for antenna molecule dyes L1 and L2. Syntheses of antenna molecule were prepared according to the corresponding literature method.²⁵ Aldehydes and 4-aminopyridine equimolar amounts were mixed in 50 mL toluene under stirring at heating (80–100 °C) for 4 h. After completion of the reaction, the reaction was cooled to room temperature, acetic-acid were added the reaction. The reaction mixture was filtered and recrystallized from methanol. Yields: 86–90%.

L1. ¹H NMR (600 MHz, DMSO-d₆) 3.32 (6H, s), 5.16 (1H, s), 7.26–7.88 (8H, m). MS (ESI, m/z): $[M + H]^+$ calcd for $C_{14}H_{15}N_3$, 225.2; found, 226.1.

L2. ¹H NMR (600 MHz, DMSO-d₆) 5.16 (1H, s), 6.60–6.68 (6H, m), 7.26–7.88 (10H, m). MS (ESI, m/z): $[M + H]^+$ calcd for C₁₄H₁₅N₃, 349.2; found, 350.1.

Results and discussion

The preparation processes of the assemblies on TiO_2 surfaces were as follows: a porphyrin molecule (**ZnPA**) as anchoring group was immobilized on the TiO_2 electrode surface through carboxylic groups: then the antenna molecule of **L***x* was bounded on the porphyrin by axially coordination to the central Zn(II)ion in the anchoring porphyrin **ZnPA** *via* the N atom of **L***x*. The detailed assembly approach is shown in Scheme 2.

Surface topography

In order to further demonstrate the zinc porphyrins are efficiently immobilized on the TiO₂ electrode surfaces, the surface morphologies of the assemblies immobilized on the TiO₂ nanoparticles were performed using a transmission electron microscope (TEM).^{18,26} With respect to the comparison of the height of two ends of the dyad obtained by computational simulation (Fig. 1) and the film thickness identified by TEM analysis (Fig. 2). As shown in Fig. 1, the thicknesses of the selfassembly systems as ZnPA+L1 and ZnPA+L2 are 1.9 nm and 2.1 nm respectively, which are in agreement with the results of TEM shown in Fig. 2, indicating that the assembled mode of the assembly ZnPA+Lx sensitized on TiO₂ electrode surfaces should be described are shown in Scheme 2 and Fig. 1.

UV-visible and fluorescence spectral properties

The UV-vis absorption spectra of ZnPA, ZnPA-f and ZnPA+Lx are shown in Fig. 3 and the corresponding spectroscopic data are summarized in Table 1.

As expected, zinc porphyrin dyes exhibit a typical intense absorbing Soret band within 400-480 nm and moderate absorbing Q bands in a range of 550-630 nm, which are attributed to the π - π * electron transition. In DMF solution, ZnPA showed an intense absorption peak for the Soret band at 425 nm and weak absorption speak for the Q bands at 558 nm and 597 nm. On TiO₂ films, the dyes showed a slight red shift and considerably broadening as compared to those in solution.



Fig. 1 Molecular modeling of ZnPA+Lx on TiO₂ electrode surfaces.



ZnPA+L1 ZnPA+L2 Fig. 2 TEM images of TiO₂ nanoparticles modified with ZnPA+Lx.





1.0

Fig. 3 UV-vis absorption spectra of ZnPA in DMF solution and ZnPA-f, ZnPA+Lx on TiO₂ thin films.

Table 1 The peak wavelength of the UV-vis absorption and fluorescence spectra of ZnPA in DMF solution and ZnPA-f, ZnPA+Lx on the TiO₂ thin films

Dye	Absorption ^{<i>a</i>} λ_{max}/nm	Emission ^{<i>a</i>} λ_{max}/nm	
ZnPA	425, 558, 597	608, 654	
ZnPA-f	428, 557, 595	596, 655	
ZnPA+L1	427, 563, 601	594, 651	
ZnPA+L2	430, 560, 598	596, 652	

^a The absorption and emission data were measured in DMF. Excitation wavelengths/nm: 420.

The broaden absorption bands of ZnPA+Lx may be assigned to the presence leads to the formation of dves aggregates.²⁷ Furthermore, the Q bands of the self-assemblies display slightly red-shifted than that of anchoring porphyrin ZnPA immobilized on TiO_2 thin film (**ZnPA**-**f**). That indicates the assembly dyes enhanced the photoelectronic responses.

Fig. 4 showed the fluorescence spectra of ZnPA in DMF solution and ZnPA-f, ZnPA+Lx absorbed on the TiO₂ thin films (2.5 µm). The emission spectrum of ZnPA+L2 is slightly redshifted than that of ZnPA+L1, which is consistent with the variation of the UV-vis absorption spectra. When jointing Lx onto TiO₂ surface via anchoring porphyrin ZnPA, the spectra of ZnPA-f and ZnPA+Lx are weakened and blue shifted. These reveal blue shifts compared to those of ZnPA, ascribed to the occurrence of J-aggregations of porphyrin molecules on the TiO₂ films.²⁸ The weakened fluorescence intensities indicated the existence of electronic coupling behavior between Lx and through anchoring porphyrin Zinc-to-ligand axial coordination.29,30

Theoretical calculations and energy levels

To provide the electronic structure of the dyes, their geometries and energies were fully optimized by DFT using the Gaussian 09 program at the B3LYP/LANL2DZ level.31,32 The molecule orbital



Fig. 4 Fluorescence spectra of ZnPA in DMF solution and ZnPA-f, ZnPA+Lx on TiO₂ thin films.

(MO) patterns of HOMO and LUMO of dyes were shown in Fig. 5. 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. Fig. 6 reveals the energy-level diagram of these assemblies and conducting band (CB) TiO₂. The LUMO levels of these assemblies above that of the CB of TiO₂, and the HOMO levels below that of the electrolyte I^-/I_3^- . These results confirm assemblies should be efficient to inject electrons to the CB of TiO₂ upon excitation and the corresponding oxidized molecule can be efficiently reduced by the electrolyte.³³

Photovoltaic performance of DSSCs

The assemblies **ZnPA+L***x* were sensitized on the TiO_2 films to serve as working electrodes of DSSC devices for the photovoltaic characterization under irradiance of 100 mW cm⁻² AM 1.5G solar simulator. As shown in Fig. 7, the photocurrent action spectra of **ZnPA+L***x* reveals the energy conversion of B and Q



bands of porphyrin, roughly analogous to their corresponding UV-vis spectra. The maximum IPCE value of **ZnPA+Lx** devices approaching 70%, which is significantly larger than that of anchor porphyrin (**ZnPA**) device and also outperforms those of others assemblies reported by D'Souza and co-workers.¹⁹ Thus, their onset wavelength thresholds (Fig. 7) lie in the order of **ZnPA** < **ZnPA+L1** < **ZnPA+L2**, which is in consistent with the sequence of photocurrent J_{sc} (*vide infra*).

The photocurrent–voltage (*J–V*) curves of DSSCs with **ZnPA**, **ZnPA+L1**, and **ZnPA+L2** were shown in Fig. 8 and the photovoltaic parameters were presented in Table 2. The open-circuit voltages of the cell sensitized by **ZnPA** higher than that of **ZnPA+Lx**, which the assembly cells possess the dye aggregation. Owing to the antenna elements retarded the dye regeneration and then reduced the electron lifetime of the conducting band of titania accordingly, thus this presence could be partially responsible for the reduction of V_{oc} . To be more specific, the J_{sc} values within 3.23–4.08 mA cm⁻² for **ZnPA+Lx** are higher than that of 2.33 mA cm⁻² for **ZnPA**; this may be ascribed to the broadened absorption caused by the enhanced electrondonating ability of the antenna elements relative to the



Fig. 5 Molecular orbitals of ZnPA, ZnPA+L1 and ZnPA+L2.



Fig. 7 IPCE action spectra of porphyrin-sensitized solar cells.



Fig. 8 J–V curves of porphyrin-sensitized solar cells.

Table 2 Photovoltaic performance of DSSCs based on porphyrin dyes

Dye	$J_{ m sc}~({ m mA~cm}^{-2})$	$V_{\rm oc}$ (V)	FF (%)	η (%)
ZnPA	2.33	0.38	69.5	0.61
ZnPA+L1	3.23	0.35	63.2	0.71
ZnPA+L2	4.08	0.36	64.5	0.95

anchor porphyrin in **ZnPA**. The highest J_{sc} of 4.08 mA cm⁻² achieved for **ZnPA+L2** due to the presence of the triphenylamine group. As a result, **ZnPA+L1** and **ZnPA+L2** demonstrate DSSC efficiencies of 0.71% and 0.95%, respectively, higher than that of **ZnPA**.

Charge extraction and transient photovoltage decay

To examine the interfacial energetic and dynamic origins of the $V_{\rm oc}$ variation,³⁴ charge extraction (CE) and transient photovoltage decay (TPD) measurements were performed on the assembly devices with **ZnPA+L1** and **ZnPA+L2**. As illustrated in Fig. 9a, the dye alternation from **ZnPA+L1** to **ZnPA+L2** does not affect the conduction-band edge and the distribution of trap states of titania with respect to the electrolyte.³⁵ However at a given $Q^{\rm CE}$, photo-injected electrons in titania, the electron half lifetime ($t_{1/2}^{\rm TPD}$) for the **ZnPA+L1** device is much shorter than the **ZnPA+L2** cell (Fig. 9b), mirroring the same tendency of $V_{\rm oc}$.

The effect of different metal-mediums in solar cells

To further selecting suitable metal-mediums for anchor porphyrin (**MPA**), the performances of the **MPA** series dyes were investigated by photophysical and photovoltaic methods (Fig. S1–S6†), and the photovoltaic parameters were displayed in Table 3. The cell performance of **ZnPA** demonstrated the highest photoelectric conversion efficiency than others. As seen in Table 3, the devices of **ZnPA** display significantly enhanced conversion efficiency, roughly consistent with the variation of HOMO–LUMO gaps, UV-vis and fluorescence spectra. In



Fig. 9 (a) Plots of charges extracted from a dye-grafted titania film (Q^{CE}) versus V_{oc} ; (b) plots of electron half-lifetimes $(t_{1/2}^{TPD})$ as a function of Q^{CE} .

Dye	$J_{\rm sc}$ (mA cm ⁻²)	$V_{\rm oc}$ (V)	FF (%)	η (%)
ZnPA	2.33	0.38	69.5	0.61
CdPA	0.54	0.23	61.6	0.07
CoPA	0.41	0.20	51.0	0.04

conclusion, when the metal-mediums of **Zn** can construct horizon anchor porphyrin molecules on the TiO_2 electrode surface to improve electron injection efficiency and preserve the photoexcited energy.^{15,36}

Conclusion

In summary, the horizontal anchor porphyrins with different metal ions and antennas molecules have been designed and synthesized. The zinc ion could be used successfully for horizontal anchor porphyrin. Further, we have successfully designed and obtained a novel type assembly based on antennas molecules appended horizontal anchor porphyrin (**ZnPA**) *via* metal-ligand axial coordination and modified the nano-structured TiO_2 electrode surface. The optical, photovoltaic, transient photovoltage decay and theory calculations of these assemblies are also prepared. In addition, the assembly devices afford more effective transmission channel of the charge separated state than mono-horizontal anchor porphyrin, which is exhibits a better photovoltaic performance. This work provides a basis for further investigation in supramolecular solar cells.

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