# Two self-assemblies of Schiff base porphyrins to modify titanium dioxide electrodes for supramolecular solar cells

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**Abstract** In this work, two Schiff base porphyrins have been successfully synthesized. The metal–ligand axial coordination assembling strategy has been used to organize two assemblies based on the two porphyrins appended isonicotinic acid ligands. Further, the assemblies were absorbed on the semiconducting TiO<sub>2</sub> electrode surfaces by the carboxylic groups of isonicotinic acid ligands, and their photovoltaic performances were performed under irradiance of 100 mW cm<sup>-2</sup> AM 1.5G sunlight. Photoelectrochemical studies show a significantly enhanced photovoltaic behavior for phenol-based zinc porphyrin assembly compared to pyridine-based zinc porphyrin assembly. The UV–Vis absorption, fluorescence spectra, molecular orbital patterns, and HOMO–LUMO energy gaps of the assemblies were also performed to further understand their photovoltaic features. In addition, the assembled modes of the assemblies immobilized on TiO<sub>2</sub> electrode surfaces were also verified by transmission electron microscopy.

Keywords Schiff base porphyrin · Self-assembly · Solar cells

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#### Introduction

Excavation by modern society of fossil fuels leads to global warming, environmental pollution, and other natural disasters, and therefore more and more people focus on renewable energy sources. Solar energy, as one of the several promising clean energy sources, could contribute to a stable energy supply and slow down the ring of these natural disasters. In nature, porphyrin chromophore in chlorophyll can be used to collect solar energy and achieve photoinduced electron and energy transfer [1-5]. Inspired by this intriguing natural principle, much effort has been made to modify the porphyrin unit, with an ultimate goal of using such a natural feature to construct excellent artificial light-harvesting devices in dye-sensitized solar cells (DSSC). It is worthy noticed that the porphyrin-based solar cell has achieved an excellent PCE value with 13 % under simulated air mass 1.5 global sunlight [6]. Porphyrin-based self-assemblies, as energy/electron/hole-carrier agents, have also attracted much attention from worldwide scientists and engineers because they can generate efficient charge separation and transfer the separated charges to their corresponding electrodes [7-11]. We have successfully designed and organized a series of assemblies based on N-heterocyclic porphyrin and acetohydrazide zinc porphyrin derivatives to functionalize the nanostructured  $TiO_2$ electrode surfaces [12–18].

It is well accepted that Schiff base molecules are also considered to be the active materials in polymerization, functional dyes, and pigments in the field of medicine [19]. Schiff bases have been regarded as dye sensitizers in solar cells, and have shown a perfect performance [20–22]. So, to understand the performances of the assemblies with Schiff base porphyrins on the electrode surfaces is an urgent task. In this paper, two novel Schiff-base zinc porphyrins (ZnPx, x = 1 and 2, shown in Scheme 1) have been designed and synthesized. Then, a metal-mediated assembling strategy has been used to construct two new assemblies based on ZnPx appended isonicotinic acid ligands (A) by the coordination bonds of Zn-to-ligand on the semiconducting TiO<sub>2</sub> electrode surfaces, resulting in a ZnPx-A assembled approach. The detailed assembly mode is shown in Scheme 1. The UV–Vis absorption spectra,



Scheme 1 The detailed assembly approach of the assemblies on TiO<sub>2</sub> electrode surfaces

fluorescence spectra, molecular orbital (MO) patterns, HOMO–LUMO energy gaps, and the photovoltaic performances of the assemblies are studied to further understand the behavior of the assemblies-sensitized solar cells.

# Experimental

Materials and physical measurements

All solvents and reagents were used directly without further purification as commercially analytical grade. 5,10,15,20-tetra(para-nitrophenyl)porphyrin (a) was prepared according to the corresponding literature method [23, 24]. 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. <sup>1</sup>H NMR (400 MHz) was measured on a Varian Mercury Plus-400 spectrometer. The detailed synthesis processes are shown in Scheme 1. Surface topography of the self-assembly films on TiO<sub>2</sub> electrode surface was imaged using atomic force microscopy (AFM, Nanoscope III, Digital Instruments Co.) in contact tapping mode. Transmission electron microscopy (TEM) (Hitachi Model H-900) was prepared to characterize the morphology and particle size distribution. 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),  $J_{\rm sc}$  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 0.158 cm<sup>2</sup>. A homemade heating-cooling system was used for temperaturedependent J-V measurements.

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  $SnO_2$  (FTO) conducting glass electrode and further coated by a 5-µm-thick scattering layer of 400-nm-sized titania particles. Film thickness was measured by a benchtop Ambios XP-1 stylus

profilometer. The detailed preparation procedures of TiO<sub>2</sub> nanocrystals, pastes for screen printing, and nanostructured TiO<sub>2</sub> film have been reported by Prof. P. Wang [25]. A cycloidal TiO<sub>2</sub> electrode ( $\sim 0.28 \text{ cm}^2$ ) was stained by immersing it into a methanol solution containing isonicotinic acid (2 mM) as anchoring molecule overnight, after removal of the unbound molecules (through three ethanol washings), then immersing it into a dye solution containing ZnPx (0.2 mM) in DMF for 1 h, and after this, washed by DMF solution three times. After being washed with ethanol 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 I2 in acetonitrile solvent. After all these procedures, the cells were located in the oven for heating posttreatment at 100 °C for 30 min and cooled to room temperature before photoelectrochemical measurements.

#### Synthesis of porphyrins

### The synthesis of b

5,10,15,20-tetra(para-nitrophenyl)porphyrin (a) (1.82 mmol, 1.45 g) was dissolved in HCl (60 ml) and then stannous (25 mmol, 5.64 g) in HCl under argon. The mixture was refluxed 1 h at 65 °C. Mixture in an ice bath the reaction was 0.5 h, and neutralized with aqueous ammonia and filtered, the crude product was column using chloroform as eluent chromatography to give b. Yield, 19 %.<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.74(s, 2H), 5.58(s, 8H), 6.98–7.01(m, 8H), 7.84–7.86(m, 8H), 8.88(s, 8H).

### The synthesis of c

b (0.14 mmol, 0.094 g) and Zn(CH<sub>3</sub>COO)<sub>2</sub> (1.08 mmol, 0.198 g) were dissolved a mixture of methanol and chloroform under argon. The mixture was refluxed 4 h at 65 °C. After completion of the reaction, the solvent was removed, the crude product by column chromatography with dichloromethane to give c. Yield, 65 %. <sup>1</sup>H NMR (400 MHz,  $d_6$ -DMSO):  $\delta$  5.46(s, 8H), 6.95–6.97(m, 8H), 7.79–7.81(m, 8H), 8.83(s, 8H).

### The synthesis of ZnP1

c (0.133 mmol, 0.0,979 g) and 2-pyridinecarboxaldehyde (1.2 ml) were dissolved in DMF (20 ml) under argon. The mixture was refluxed 24 h at 80 °C. After the reaction was cooled to room temperature, water was added to give the crude product that was filtered, washed with water and methanol, and the cake was washed and dried to obtain ZnP1. Yield, 46 %. <sup>1</sup>H NMR (400 MHz,  $d_6$ -DMSO):  $\delta$  2.73(s, 4H),

7.61–7.62 (m, 4H), 7.78–7.80 (m, 8H), 8.05–8.09 (m, 4H), 8.82–8.90 (m, 8H), 8.35–8.36 (m, 4H), 8.99–9.10 (m, 4H). ESI–MS: *m/z* 1,093 [M + H]<sup>+</sup>.

## The synthesis of ZnP2

ZnP2 was synthesized in a similar procedure as ZnP1 except that 2-pyridinecarboxaldehyde (1.2 ml) was replaced by salicylaldehyde (1.2 ml). Yield, 43 %. <sup>1</sup>H NMR (400 MHz,  $d_6$ -DMSO):  $\delta$  7.50 (s, 4H), 7.83 (s, 12H), 7.85–7.87 (m, 8H), 8.21–8.23 (m, 8H), 8.91 (s, 8H), 9.31–9.34 (m, 4H), 13.31 (s, 4H). ESI–MS: m/z1,153 [M + H]<sup>+</sup> (Scheme 2).



#### Scheme 2 Synthesis of the porphyrins

#### **Results and discussion**

The assembled processes of the assemblies on  $TiO_2$  surfaces were as follows: a molecule as anchoring group was immobilized on the  $TiO_2$  electrode surface through carboxylic groups; then the desired dye of ZnPx was bound on the a unit by the coordination-bonded from porphyrin central Zn(II) ion of ZnPx and the N atom of A. The detailed assembly approach is shown in Scheme 1.

In order to further demonstrate the Schiff base porphyrins efficiently immobilized on TiO<sub>2</sub> electrode surfaces, the surface morphologies of the assemblies immobilized on the TiO<sub>2</sub> nanoparticles were performed using a transmission electron microscope (TEM). Compared to the length of two ends of the assembly obtained by computational simulation (Fig. 1) and the film thickness identified under TEM analysis (Fig. 2), we can observe that the distances between the two ends of assemblies (~1.9 nm for ZnP1-A and ~1.8 nm for ZnP2-A) are equal to the film thicknesses from the direct TEM observations, indicating that the assembled mode of the assembly ZnPx-A sensitized on TiO<sub>2</sub> electrode surfaces should be described as shown in Scheme 1 and Fig. 1.

The parameters of UV–Vis absorption and fluorescence spectra of ZnPx in DMF solution and ZnPx-A absorbed on the TiO<sub>2</sub> thin films (2.5  $\mu$ m) are summarized in Table S1. As shown in Fig. 3, all dyes exhibit the maxima of the spectra characteristic of porphyrin attributed to  $\pi$ – $\pi$ \* transitions in the range of 400–480 nm for strong Soret (B) bands and 550–630 nm for Q bands. Comparison of the film with the solution spectra show that the absorption bands of films are slightly red-shifted and considerably broadening B bands from those of solution spectra. The broaden absorption bands may be assigned to the presence of porphyrin aggregations on the TiO<sub>2</sub> surfaces [12, 26]. It is worthy noticed that the absorption maxima of ZnP2-A are slightly red-shifted than those of ZnP1-A, signifying the existence of enhanced photovoltaic performance for ZnP2-A-sensitized solar cell. Figure 4 displays the fluorescence spectra of ZnPx in DMF solution and ZnPx-A absorbed on the TiO<sub>2</sub> thin films (2.5  $\mu$ m). The emission spectrum of ZnP2-A is slightly red-shifted than that of ZnP1-A, which is consistent with the variation of the UV–Vis absorption spectra. Notedly, the spectra of ZnPx-A reveal blue shifts



Fig. 1 Molecular modeling of the assemblies on the TiO<sub>2</sub> electrode surfaces



Fig. 2 TEM images of TiO<sub>2</sub> nanoparticles modified by the assemblies

![](_page_6_Figure_3.jpeg)

Fig. 3 UV–Vis spectra of ZnPx in DMF solution and ZnPx-A on  $TiO_2$  thin films

![](_page_6_Figure_5.jpeg)

Fig. 4 Fluorescence spectra of ZnPx in DMF solution and ZnPx-A on TiO<sub>2</sub> thin films

compared to those of ZnPx, ascribed to the occurrence of J-aggregations [12] of porphyrin molecules on the  $TiO_2$  films.

To gain insight into the electron density distribution within the frontier and other close-lying of the assemblies, we performed calculations with density functional theory (DFT) using the Gaussian 09 program [27] at the B3LYP/LanL2DZ level. As shown in Fig. S1, the MO patterns of HOMOs are mainly localized at porphyrin cores with slight delocalization to the neighboring donor units, and the LUMOs show electronic distribution on A groups. These features suggest the presence of excellent electron-separated status for these assemblies-sensitized devices. Figure 5 reveals the energy-level diagram of these assemblies and the conducting band (CB) TiO<sub>2</sub>. The energy gap between the HOMO and LUMO is 2.32 eV for ZnP1-A, and 2.25 eV for ZnP2-A. The LUMO levels of the assemblies are above that of the conducting band (CB) of TiO<sub>2</sub>, indicating that the LUMO levels of the assemblies should all be capable of the electron injection to the CB of TiO<sub>2</sub>.

The assemblies were fabricated into DSSC devices and measured their respective photovoltaic performances under irradiance of 100 mW cm<sup>-2</sup> AM 1.5G sunlight. The photocurrent action spectra of the assemblies-sensitized solar cells in the wavelength range of 300–800 nm are shown in Fig. 6. The behaviors of photocurrent responses roughly resemble corresponding UV–Vis spectra, especially for the features of broadened spectra. The maximum value of ZnP2-A device over 20 % is significantly larger than that of the ZnP1-A device, suggesting that the phenol unit may serve as a potential donor group to ensure the excellent performance of the corresponding zinc porphyrin dye for DSSC. This behavior is also consistent with the result reported by our work [17]. As shown in Fig. 7, the short-circuit photocurrent density ( $J_{sc}$ ), open-circuit photovoltage ( $V_{oc}$ ), fill factor (FF) and overall conversion efficient ( $\eta$ ) are found to be 1.20 mA/cm<sup>2</sup>, 0.27 V, 0.65, and 0.21 % for ZnP2-A device. Due to the faint color of sensitized electrodes and the smaller UV–Vis absorbing intensities, ZnPx-A-sensitized cells show the lower photovoltaic performances compared to the high-efficiency DSSCs [28, 29].

![](_page_7_Figure_4.jpeg)

![](_page_8_Figure_1.jpeg)

Fig. 6 Photocurrent action spectra of ZnPx-A-sensitized solar cells

![](_page_8_Figure_3.jpeg)

Fig. 7 J-V characteristics of ZnP2-A-sensitized SC measured under irradiance of 100 mW cm<sup>-2</sup> AM 1.5G sunlight (ZnP2-A) and in the dark condition [ZnP2-A(d)]

## Conclusions

In summary, we have successfully designed and obtained two new self-assemblies based on two Schiff base porphyrins bound to isonicotinic acid by metal–ligand axial coordination on the nanostructured  $TiO_2$  electrode surfaces. The UV–Vis absorption, fluorescence spectra, and the photovoltaic performances of these assemblies are also prepared. Our results reveal significantly enhanced photovoltaic behavior for phenol-based zinc porphyrin assembly. This feature indicates the phenol entity may be used as a potential substituent applied into the sensitizers. To improve the solar cells' efficiency of such an assembly, our further study about the

assemblies based on porphyrin acid derivatives serving as the anchoring groups is on process.

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