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Self-assemblies formed by isonicotinic acid analogues axially coordinating with zinc porphyrin via pyridyl unit: synthesis and application in dye sensitized solar cells

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Abstract

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A novel zinc porphyrin **ZnP** bearing a 1,3,5-triazine-2,4-diamine unit has been designed and synthesized in good yield to construct axial-coordinated assemblies (denoted as **ZnP-Ai, i = 1, 2, 3 and 4**) with different isonicotinic acid analogues (assigned as **A1, A2, A3** and **A4**) through zinc-to-ligand axial coordination approach. Then these assemblies were grafted onto TiO₂ electrode surface to build dye sensitized solar cells. The performance of these cells also was examined. Photoelectrochemical measurements illustrate that all the assemblies based cells have certain capabilities to export photocurrent. Especially, the **ZnP-A2** assembly with a cyanoacrylic acid group based solar cell has the highest conversion efficiency of 0.81% with a J_{SC} of 3.0 mA/cm², a V_{OC} of 0.38 V, and a FF of 0.71 among these assemblies based solar cells. Additionally, the UV–Vis absorption, fluorescence spectra, density functional theory (DFT) calculations, transmission electron microscopy (TEM) and electrochemical impedance spectra (EIS) were performed to determine the photoelectric behavior as well as morphological structure on the TiO₂ surface modified by these assemblies.

Keywords: anchoring molecule; zinc porphyrin; axial coordination; solar cell.

1. Introduction

Solar energy is highly expected to solve the environmental and climate problems caused by consumption of fossil fuel, as a kind of clean and renewable energy with its' abundant natural resource on earth. Among the various ways utilizing solar energy, dye sensitized solar cells (DSSCs) firstly reported by Grätzel and co-workers in 1991 [1] are promising photovoltaic devices converting solar energy to electricity and attracted much more attentions. In this type of solar cells, dyes play a dominated role in photocurrent generating [2-5]. For the past decades, variety of dyes including ruthenium complexes [6-9], mental-free organic dyes [10,11] and porphyrin based dyes [2,3,12, 13] have been developed and applied in DSSCs and show excellent conversion efficiency.

Porphyrins are high-potential candidates of the dyes applied in DSSCs due to their strong light-harvesting ability in the visible region, high photochemical and electrochemical stabilities as well as tunable molecular structures [14-18]. In particular, such porphyrins commonly feature a donor- π bridge-accepter (D- π -A) structure and are attached onto TiO₂ surface through covalently linking via anchoring groups containing a carboxylic or cyanoacrylic group [19]. However, the complicated and high-cost syntheses of these asymmetrical porphyrins limit their extensive application.

Utilization of axial metal-ligand coordination appears to be an effective and alternative approach to facilely construct porphyrin based donor-acceptor supramolecular assemblies with remarkable photoelectric properties [20-24]. In this type of assemblies, ligand coordinated with a mental ion in the porphyrin center at the axial place as electron acceptor. Sufficient researches indicate that electron transfer between the porphyrin and axial ligand is capable and feasible [21-25]. Axial-bonding approach can afford a conveniently method for designing and synthesizing of more elaborate porphyrin assemblies having diverse structures and functions. Therefore,

such axial-coordinated assemblies are widely studied and applied in photocurrent generation and photocatalysis due to their excellent advantages [25-28].

Herein, we have designed and synthesized a novel zinc porphyrin **ZnP** bearing a 1,3,5-triazine-2,4-diamine unit in good yield to form such axial-coordinated assemblies (noted as **ZnP-Ai**, i = 1, 2, 3 and 4) with different ligands or anchoring groups (signed as A1, A2, A3 and A4). Then these assemblies were grafted on to TiO₂ electrode surface and the performance of their corresponding DSSCs are tested. The molecule structures and coordination mode are shown in **Scheme 1**. The triazine unit was employed to the porphyrin due to its' excellent photoelectric and electrochemical properties [29-31] in photoelectric devices and the long alkyl chain was introduced to the meso position of the porphyrin for enhancing solubility and reducing dye aggregation.



Scheme 1. Structures of axial coordination-bond-assisted self-assemblies on TiO₂ electrode surfaces

2. Experimental Section

Supplementary Materials completely described the specific synthetic procedures of **ZnP** and **A2-A4** as well as device fabrication methods. The sensitized titania electrode was assembled as the following procedures: A circular TiO_2 electrode (~0.28 cm²) was primarily stained by immersing it into a solution containing anchoring molecule (~2 mM) in **DMF** overnight, the unbounded molecules were washed out by ethanol, then the electrode was immersed into a dye solution containing **ZnP** (~0.2 mM) in CHCl₃/CH₃OH for 2 h and washed by acetonitrile solution three times. After dried by air flow, the sensitized titania electrode was fabricated to cells according to the methods specified in Supplementary Materials.

UV-vis spectra were obtained on a UV-2550 spectrometer. Fluorescence spectra were measured by LS-55 (PE USA Inc) fluorescence spectrophotometer at room temperature. Transmission electron microscopy (TEM) (Hitachi Model H-900) was carried out to characterize the morphology and particle feature. 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 (the equivalence of one sun at AM 1.5G) by using a metal mask with an aperture area of 0.158 cm². The details of photoelectrochemical measurements were illustrated in our previous article [32]. The electrochemical impedance spectrum (EIS) experiments were performed by applying a bias voltage at -0.7 V under the dark using a CHI660 electrochemical workstation, with a frequency range of 0.1Hz –100 kHz and ac amplitude of 10 mV. The obtained spectra were fitted with ZSimpWin software in terms of an appropriate equivalent circuit [33].

3. Results and discussion

3.1. UV-visible absorption and fluorescence spectra.

The UV-visible absorption spectra and fluorescence spectra of ZnP in CHCl₃ solution and the assemblies ZnP-Ai ($i = 1 \sim 4$) adsorbed onto TiO₂ films are shown in

Fig.1a and **b** separately, detailed absorption and emission maximum wavelength numbers are summarized in **Table S1**. As shown in **Fig.1a**, these assemblies on TiO₂ thin-films (2.5µm) exhibit typical porphyrin spectra [34]: strong Soret bands (B-bands) appear in the region of 400-500 nm while Q bands locate in the long wavelength region of 550-650 nm, attributed to π - π * transitions. The absorption bands of these assemblies on TiO₂ surface are slightly shifted to the lower wavelength along with broadening Soret and enhanced Q bands compared with that of their respective porphyrin **ZnP**.



Fig. 1. Normalized UV-vis absorption spectra (a) and emission spectra (b) of ZnP in CHCl₃ solution and ZnP-Ai adsorbed onto TiO₂ films. The emission spectra were measured by exciting at 420 nm

When jointing ZnP onto TiO₂ surface via anchoring molecules, the fluorescence spectra of the assemblies are weakened and blue shifted. These shifts should be

assigned to the side-to-side J-aggregation of porphyrins [35,36]. The weakened fluorescence intensities indicated the existence of electronic coupling behavior between **ZnP** and anchoring molecules through zinc-to-ligand axial coordination.

3.2. Density functional theory (DFT) calculations.

In order to further understand the electron density distribution of **ZnP-Ai** assemblies within the frontier and other neighboring orbitals, DFT calculations were performed using the Gaussian 09 program [37] at the B3LYP/LanL2DZ level of theory for the ground state geometry optimization. The butoxyl groups in **ZnP** was simplified to a methoxy group for a less uncomplicated calculation process. As shown in **Fig. 2**, the molecule orbital (MO) patterns of the assemblies are in accordance with the Gouterman's four-orbital model with a slight deviation [34], suggesting that, from another respect, the electronic adsorption should attribute to π - π * transitions. Delocalization of the MO patterns at the HOMO and LUMO orbitals can be assigned to the lowered symmetry and the extended π -conjugation of the assemblies.

Importantly, the electrons of HOMO and LUMO orbitals concentrated at the top porphyrin cores and bottom anchoring molecules respectively, which are similar to the result of the reported [38] based on experiment observations and calculations of a series of zinc porphyrins. Such an electron-separated state may translate to a push–pull tendency of the assemblies upon photoexcitation, a favorable merit for electron transferring. It is worthy noticed that in the LUMO+1 level of **ZnP-A2** assembly, electron densities extremely diverged to the carboxylic group in **A2** molecule, indicating that electron injection from the excited **A2** based assembly to TiO₂ conduction band (CB) can be more effective and guaranteeing a better cell performance when applied in solar cells [39,40]. This inference can be further demonstrated by the calculated energy level depicted in **Fig. 3**.

Fig. 3 shows the calculated energy level diagram of the assemblies, all the LUMO levels of these assemblies lie above the CB of TiO₂, all the HOMO levels are

lower than the redox energy of Γ/I^{3-} . As suggested in the figure, all assemblies should be efficient to inject electrons to the CB of TiO₂ upon excitati on and the corresponding oxidized molecule can be efficiently reduced by the electrolyte.



Fig. 2. Frontier molecular orbital distributions of ZnP-Ai assemblies under B3LYP/LanL2DZ level.



Fig. 3. Frontier orbital energy distribution of the assemblies.

3.3. Morphological characterization of the TiO_2 nanoparticles modified by assemblies

To gain further insight into the architecture of the assemblies attached onto TiO₂, transmission electron microscopy (TEM) was used to investigate the morphologies of **ZnP-Ai** modified TiO₂ surfaces. **Fig. 4** shows the TEM images of TiO₂ nanoparticles modified with **ZnP-Ai**, as presented in the figure, the surface of TiO₂ nanoparticles were effectively overlaid by a layer of assemblies, demonstrating the well-organized joint of porphyrin **ZnP** onto the TiO₂ surface through axially coordination with anchoring molecules. Simultaneously, the layer thickness was identified to be 1.3 ± 0.1 nm for **ZnP-A1**, 1.2 ± 0.1 nm for **ZnP-A2**, 1.6 ± 0.1 nm for **ZnP-A3** and 1.7 ± 0.1 nm for **ZnP-A4** modified TiO₂ respectively. The layer thicknesses almost match to the molecule heights obtained by computational simulation displayed in **Fig. S1** in supplementary materials, ulteriorly verifying the assembly patterns.



Fig. 4. TEM images of TiO₂ nanoparticles modified with **ZnP-A1** (a), **ZnP-A2** (b), **ZnP-A3** (c) and **ZnP-A4** (d).

3.4. Photovoltaic Properties.

The photovoltaic performance of devices with **ZnP-Ai** assemblies was measured using double-layer TiO₂ films as photoanodes, in combination with Γ/Γ^{3-} as electrolyte, under standard AM 1.5G illumination and under the dark. IPCE spectra of the cells fabricated with **ZnP-Ai** in the wavelength range of 350~650 nm are shown in **Fig. 5**. The photocurrent responses roughly resemble their corresponding absorption spectra and computational energy gaps. The highest IPCE value of 70%, 44%, 33%, 30% were achieved for cells based on assemblies **ZnP-A1**, **ZnP-A2**, **ZnP-A3** and **ZnP-A4**, respectively. Meanwhile, the IPCE values rank in a sequence of **ZnP-A2** > **ZnP-A1** > **ZnP-A3**≈**ZnP-A4**, suggesting that electrons can feasibly transfer to the anchoring molecule upon photoexcitation then bound to TiO₂ surface, this result consists with the DFT calculations. Our previous research [41] revealed that the device without anchoring molecule exhibits obviously lower performance than the assembly-based device. Moreover, **A2** based cell shows the better performance than **A1** based cells under the same testing condition, where **A1** is the best anchor we have found before.



Fig. 5. IPCE values of ZnP-Ai based solar cells.



Fig. 6. Current density-voltage (J-V) characteristics for solar cells based on the assemblies under irradiance of 100 mW·cm⁻² AM 1.5G sunlight (symbols) and in the dark (dotted lines).

The current density-voltage (J-V) plots of the assemblies based solar cells are given in Fig. 6. The detailed parameters are collected in Table 1. The solar cell based on ZnP-A2 exhibits an noticeable conversion efficiency of 0.81% with a J_{SC} of 3.0 mA/cm², a V_{OC} of 0.38 V, and a FF of 0.71. The explanation for the higher short-current density of ZnP-A2 based solar cells can be mainly attributed to the appropriate HOMO-LUMO level and charge separate state as well as more feasible electron transmission along the porphyrin-anchor-TiO₂ pathway compared to other assemblies. The A3 and A4 with amide groups based devices showed lower efficiencies due to their faintish photocurrent response. Compared to the present high-efficiency DSSCs [12-15], the lower overall performances of ZnP-Ai -sensitized solar cells can be mainly attributed to the small amount of porphyrin loaded on TiO₂ surface, reflected by the faint color of modified electrodes and the weak UV-vis absorbing intensities on TiO₂ film.

Table 1. Photovoltaic parameters of ZMP-AI -sensitized solar cen.					
Dye	$J_{SC}/\mathrm{mA}\cdot\mathrm{cm}^{-2}$	V_{OC} /V	FF	$\eta/\%$	
ZnP-A1	2.20	0.32	0.69	0.49	
ZnP-A2	3.00	0.38	0.71	0.81	
ZnP-A3	1.73	0.33	0.70	0.40	
ZnP-A4	1.69	0.28	0.67	0.32	

We also investigated the dark current of these cells to inspect the charge recombination on the TiO₂ surface. As presented in Fig. 6, an obviously increased

dark current for the cells based on ZnP-A1, ZnP-A3 and ZnP-A4 at a given potential bias was observed, suggesting a facilitated charge recombination of electrons in titania with Γ/I^{3-} electrolyte. As is well known, seriously charge recombination can result in a lower V_{OC} [42], the higher V_{OC} value of ZnP-A2 was caused by the lower charge recombination rate at the dye/TiO₂/electrolyte interface, which was further surveyed by EIS measurements.



Fig. 7. Impedance spectra of ZnP-A1 and ZnP-A2 fabricated solar cells, the lines of a and b show theoretical fits using the equivalency circuits c.

EIS measurement was conducted to deeply understand the V_{OC} variation in solar cells based on **ZnP-A1** and **ZnP-A2** at a forward bias of -0.70 V in the dark. The

Nyquist plots (a), Bode plots (b) and equivalent circuit (c) are shown in **Fig. 8**. The R_s , R_{CT} , and C represent series resistances, charge transfer resistances at the dye/TiO₂/ electrolyte interface and double layer capacitance, respectively. In the Nyquist plots, the larger semicircle located in the middle-frequency region is refer to the charge transfer process at the dye/TiO₂/electrolyte interface [43]. **ZnP-A2** based cells display higher charge recombination resistance (R_{CT}) value than the **ZnP-A1**, indicating a slow rate of charge recombination at the dye/TiO₂/electrolyte interface. The larger R_{CT} , in other words, represented the restraining charge recombination between the injected electron in the TiO₂ and oxidized species in the electrolyte. Usually, a high charge recombination resistance will lead to a long electron lifetime reflected by the phase degree peaks in bode plots moved to lower frequency. It can be noticed in **Fig. 8b** that **ZnP-A2** based solar cells have longer electron lifetime in associated with its' higher V_{OC} value compared to **ZnP-A1** based cells, in agreement with its' electron density distribution, HOMO-LUMO levels and photocurrent responses.

4. Conclusions

successfully synthesized a novel porphyrin ZnP have bearing we 1,3,5-triazine-2,4-diamine unit and jointed onto TiO₂ electrode surfaces through axially coordinating with anchoring groups (A1, A2, A3 and A4) bonded on the TiO_2 surfaces. The effects of different anchoring molecules in the solar cells fabricated by these self-assemblies were investigated, and the results suggest that the ZnP-A2 assemblies immobilized onto nanostructured TiO₂ surfaces using Zn-to-ligand axial coordination significantly improved photovoltaic performance. Additionally, the optical properties, molecular orbital (MO) distributions, HOMO-LUMO energy gaps of these assemblies are also considered and further demonstrate the experimental results. The morphological characteristics of the TiO₂ nanoparticles modified by these assemblies were also investigated by transmission electron microscopy (TEM) and computational simulations. EIS measurements indicate that ZnP-A2 based cells exhibit higher charge recombination resistance and longer electron lifetime than the **ZnP-A1** based cells, resulting a higher V_{OC} value. Overall, this work provides a new type of self-assembly different from other porphyrin-based sensitizers and has developed a facile method for fabricating solar cells.

Appendix A. Supplementary material

Supplementary material of this article can be found, in the online version, at...

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A novel zinc porphyrin **ZnP** bearing a 1,3,5-triazine-2,4-diamine unit have been designed and synthesized to construct axial-coordinated assemblies with different anchoring groups. Then these assemblies were grafted onto TiO_2 electrode surface and their corresponding solar cells were successfully fabricated. The performance of these devices were studied and discussed.

Highlights

1. Axial-coordinated self-assemblies based on a novel zinc porphyrin (ZnP).

2. Isonicotinic acid analogues (A1, A2, A3 and A4) act as anchoring molecules.

3. Their performance in dye sensitized solar cells was tested.

4. All the assemblies based cells have certain capabilities to export photocurrent.

5. ZnP-A2 Improved photocurrent generation of with cyanoa