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Two new self-assemblies of two zinc porphyrin with isonicotinic acid by metal–ligand axial coordination and their applications in supramolecular solar cell

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ABSTRACT

Two new self-assemblies based on two zinc porphyrins substituted at the meso-positions with different donor units (denoted as **ZnP1** and **ZnP2**) and isonicotinic acid (**A**) by metal–ligand axial coordination have been designed and immobilized on the double-layer nanostructured TiO_2 film-coated highly transparent FTO conducting glass electrode in a photosynthesis device. These cells were also measured under irradiance of 100 mW cm^{-2} AM 1.5G sunlight. The results reveal that the performance of **ZnP2**-**A** outperforms that of **ZnP1**-**A**. The UV–vis absorption spectra, fluorescence spectra, molecular orbital (MO) patterns, and HOMO–LUMO energy gaps of these assemblies were also investigated to further demonstrate the photovoltaic behavior of these cells.

Inspired by the model of the chromophores of bacterial photosynthetic reaction centers, utilization of the multiporphyrin-based self-assemblies formed by non-covalent interaction (such as π–π stacking and weak van der waals interaction) as sensitizers to mimic the photoinduced energy and electron transfer processes in solar cells have attracted increasing interests recently.[1–6] For example, several groups have constructed zinc(II) porphyrin-based supramolecular assemblies by the coordination bonds of Zn-to-ligand to functionalize carbon nanotubes,[7–9] gold electrode,[10,11] and nanoparticles,[12–15] with an ultimate goal of generating efficient light-energy-harvesting devices employing these assemblies. However, to the best of our knowledge, the reports about the assembly architecture based on zinc porphyrin appended organic acid via metal–ligand axial coordination approach immobilized on nano-structured TiO_2 substrates are very few.[16,17]

Herein, we report two new self-assemblies (described as **ZnP*x*-A**, ***x*** = **1**, **2**) with two zinc porphyrins substituted at the meso-positions with different units (denoted as **ZnP*x***, ***x*** = **1**, **2**, shown in Scheme 1) and isonicotinic acid (denoted as **A**, shown in Scheme 1) by metal–ligand axial coordination, wherein these assemblies were immobilized directly on the double-layer nanostructured TiO_2 film-coated highly transparent FTO conducting glass electrode in a photosynthesis device. To probe into the impact of different donor groups on the photoelectronic performance of their corresponding cells, two different donor units (phenol and benzimidazyl) of these assemblies were introduced. The UV–vis absorption spectra, fluorescence spectra, molecular orbital (MO) patterns, HOMO–LUMO energy gaps, and the photovoltaic performance of these photosynthesis devices are also studied to further understand these assemblies-sensitized solar cells.

The synthetic steps are shown in Supplementary data and **ZnP*x*** are purple solids. The assembled processes of **ZnP*x*-A** on TiO_2 surface are as follows: **A** as anchoring unit was immobilized on the surface of the double-layer nanostructured TiO_2 film-coated highly transparent FTO conducting glass electrode[18] through carboxylic groups, then the desired dye of **ZnP*x*** was bound to the anchoring groups through coordination-bonded from porphyrin central Zn(II) ions of **ZnP*x*** and the N atoms of **A**. The detailed assembly mode is shown in Scheme 2.

The parameters of UV–vis absorption and fluorescence spectra of **ZnP*x*** in solid state and **ZnP*x*-A** on TiO_2 thin film are summarized in Table S1. As shown in Figure 1, these absorption maxima are displayed in the range of 400–480 nm for strong soret (B) bands and 550–630 nm for Q bands, respectively, ascribed to π–π* transitions.[19] The absorption of **ZnP2**-**A** shows slight red-shift relative to that of **ZnP1**-**A**, which showed good agreement with the variation of HOMO–LUMO gaps, probably assigned to the donoring ability of the phenol group over that of the benzimidazyl unit. Interestingly, the absorption of **ZnP*x*-A** pronounces broadening and red-shifts compared with that of **ZnP*x***. Figure 2 compares

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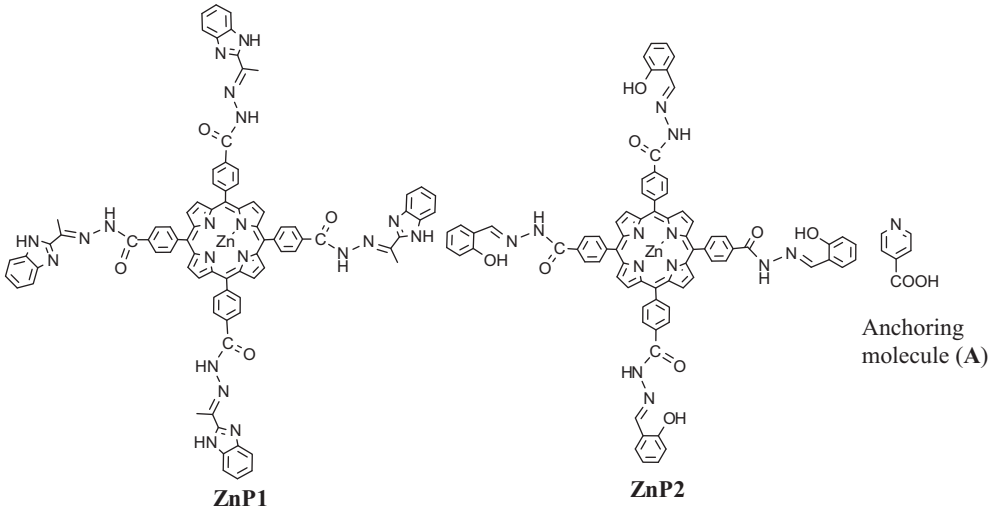
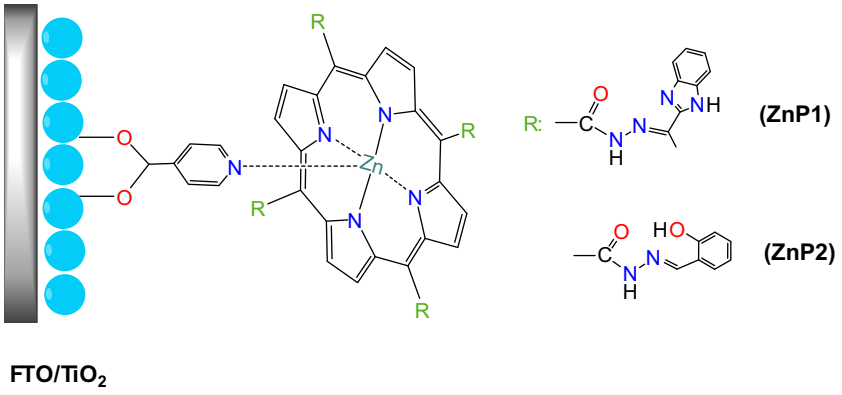


Scheme 1. Structural diagram of **ZnP*x*** and anchoring molecule (**A**).



Scheme 2. The detailed assembly approach of these assemblies on TiO_2 electrode surface.

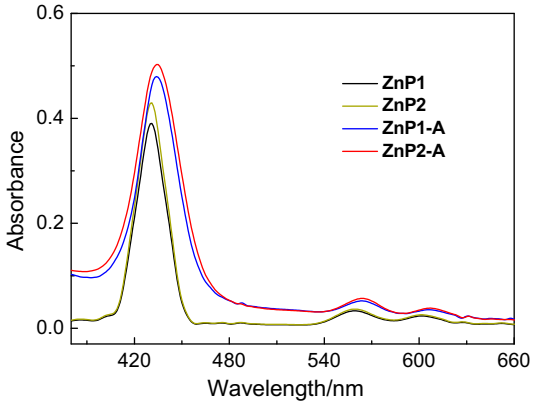


Figure 1. UV–visible spectra of **ZnP*x*** in solid state and **ZnP*x*-A** on TiO_2 thin film.

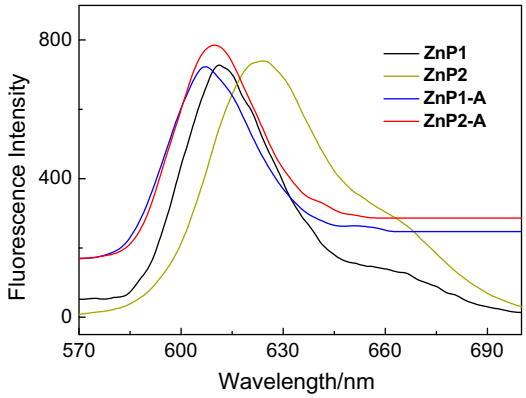


Figure 2. Fluorescence spectra of **ZnP*x*** in solid state and **ZnP*x*-A** on TiO_2 thin film.

the fluorescence spectra of **ZnP*x*** and **ZnP*x*-A**. The results reveal that the latter show blue-shift than the former, especially, the shift range between **ZnP1** and **ZnP1-A** is longer than that of **ZnP2** and **ZnP2-A**, suggesting that the presence of J-aggregation[16] of porphyrin assemblies for **ZnP*x*-A** devices on the TiO_2 surface, and the aggregation of **ZnP1-A** show more than that of **ZnP2-A**.

In order to further understand the electron density distribution within the frontier and other neighboring orbitals of these assemblies, we performed calculations with density functional theory (DFT) using the GAUSSIAN 09 program[20] at the B3LYP/LanL2DZ level. As shown in Figure S1, for **ZnP*x*-A**, the MO patterns of HOMOs are mainly localized at porphyrin cores with slight delocalization to the donor units, while the LUMOs show an electronic distribution on isonicotinic acid groups, signifying the presence of excellent electron-separated status for these assemblies-sensitized devices. Figure 3 shows the energy-levels diagram of these assemblies and TiO_2. The energy gap between the HOMO and LUMO is 2.22 eV for **ZnP1-A**, and 2.15 eV for **ZnP2-A**, to some extent

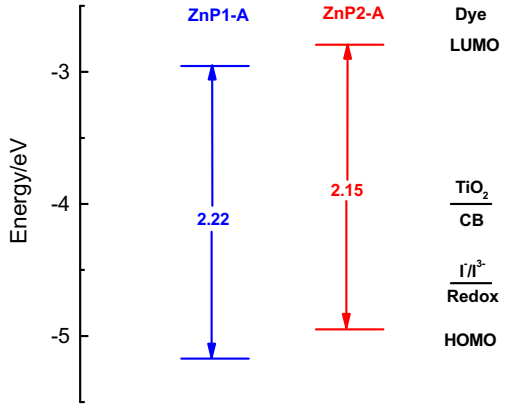


Figure 3. Orbital energy-levels of these assemblies, TiO_2, and electrolyte I^{3-}/I^{-}.

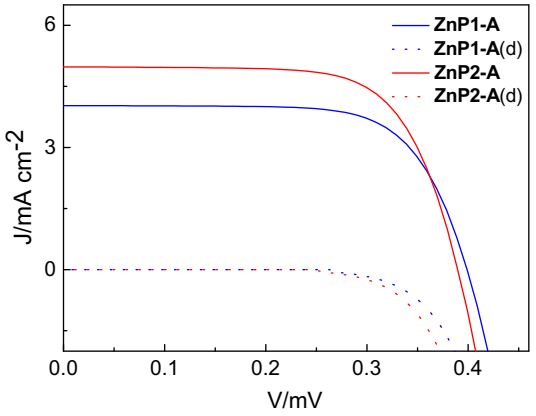


Figure 5. *J–V* characteristics of **ZnP*x*-A**-sensitized SC measured under irradiance of 100 mW cm^{-2} AM 1.5G sunlight (**ZnP*x*-A**) and in the dark (**ZnP*x*-A**(d)).

indicating that the assembly of **ZnP2-A** should have a higher efficiency for corresponding device.[21] Notedly, the LUMO levels of these assemblies above that of the conducting band (CB) of TiO_2, and the HOMO levels below that of the electrolyte I^{3-}/I^{-}, suggest that electron injection from LUMO of these assemblies to the CB of TiO_2 should be capable and feasible and the excited state of these assemblies could be reduced smoothly by the electrolyte.

The self-assemblies of **ZnP*x*-A** were fabricated into DSSC devices and tested their corresponding photovoltaic properties under irradiance of 100 mW cm^{-2} AM 1.5G sunlight. The photovoltaic parameters are listed in Table 1. The photocurrent action spectra of **ZnP*x*-A**-sensitized solar cells in the wavelength range 300–800 nm shown in Figure 4 are analogous to their respective UV–vis spectra except for broader features, and consistent with the variation of HOMO–LUMO gaps, demonstrating the responsibility of photovoltaic behavior of these assemblies-sensitized solar cells. The maximum value of **ZnP2-A** device approaching 60% is significantly larger than that of the **ZnP1-A** device. As shown in Figure 5, the short-circuit photocurrent density (J_{sc}), open-circuit photovoltage (V_{oc}), fill factor (FF), and overall conversion efficient (η) are found to be 4.03 mA cm^{-2}, 0.40 V, 0.70, and 1.12% for **ZnP1-A** device; 4.98 mA cm^{-2}, 0.30 mV, 0.69, and 1.34% for **ZnP2-A** device. These results suggest that the phenol group increases the IPCE value of latter than the former to enhance the cell behavior of the latter. However, the larger V_{oc} in **ZnP1-A** compared to **ZnP2-A** device is observed, probably assigned to the effect of aggregation.[22] Notedly, the poor efficiency of these assemblies may be assigned to the inefficient absorption of porphyrin molecules on red-NIR optical range.

Table 1
Photovoltaic parameters of **ZnP1-A**/**ZnP2-A**-sensitized solar cells

Dye	J_{sc} (mA cm^{-2})	V_{oc}/V	FF	η (%)
ZnP1-A	4.03	0.40	0.70	1.12
ZnP2-A	4.98	0.30	0.69	1.34

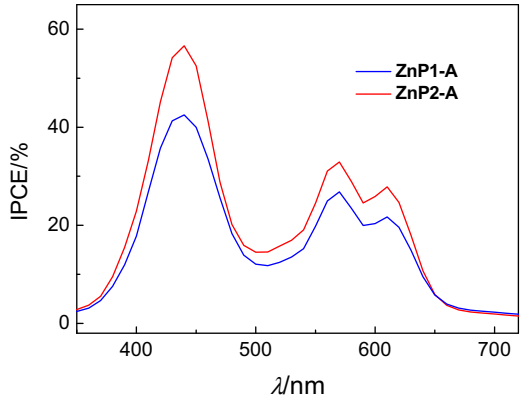


Figure 4. Photocurrent action spectra of **ZnP*x*-A**-sensitized solar cells.

In summary, we have successfully designed and obtained two new self-assemblies based on two zinc porphyrins **ZnP1** and **ZnP2** bound to isonicotinic acid by metal–ligand axial coordination. The UV–vis absorption spectra, fluorescence spectra, and the photovoltaic performance of these photosynthesis devices are also described. Our results reveal that these photosynthesis devices enable attainment of impressive improvement in photocurrent response, especially for **ZnP2-A** based on the substituent of phenol over the **ZnP1-A** substituted with benzimidazyl. Additionally, the molecular orbital (MO) patterns and HOMO–LUMO energy gaps of these assemblies are also studied to further demonstrate these experimental products. Further study about the construction of similar assembly is on process.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.05.043.

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