Novel Self-assembled Isonicotinic Acid Derivative and Zinc Porphyrin Dyads and Applications in Dye Sensitized Solar Cells

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Abstract
A new self-assemblies based on double-deck dyes ZnTPP-Wi (i = 1–3) were synthesized and applied in dye-sensitized solar cells (DSSCs). Anchoring molecules (Wi i = 1–3) consisting of phenyl carboxyl acid and cyanoacetic acid group. Capping layer dyes zinc meso-tetraphenylporphine (ZnTPP) with anchoring molecules Wi through axially coordination bonds of Zn-to-ligand self-assemblies solar cells devices. We herein report a consisting acylamide and cyanoacetic acid group W3 as an anchoring molecule for the axial coordination with upper zinc porphyrin ZnTPP. W3 was synthesized by introducing acylamide and cyanoacetic acid groups may inhibit adverse dye aggregation and improving electrons are effectively injected into the TiO2 semiconductor surface. Thus, W3 anchoring molecules can be used to fabricate efficient solar cells with ZnTPP porphyrin dye, achieving good photoelectric performance, indicative of their general applicability in fabricating good-performance DSSCs. The assembled modes were also verified by transmission electron microscopy (TEM). The photoelectrochemical efficiencies for dye ZnTPP-W3 are best than those of self-assembly dyes prevailingly ascribed to larger $J_{sc}$ and $V_{oc}$.

Keywords Dye-sensitized solar cells · Zinc porphyrin · Axial coordination · Anchoring molecule

1 Introduction
With the great progress Dye–sensitized solar cells (DSSCs) has made in the last three decades, have attracted much attention due to their supramolecular photosynthetic architectures to mimic the photoinduced energy and electron transfer processes [1–5]. A typical DSSC device consists of a photoanode, a counter electrode, electrolyte, and a dye for light harvesting. Photosensitizers as one of the main components in DSSCs have been well explored. Porphyrins have a broad absorption bands [6–9] and high molar extinction coefficients [10–14] also can serve as efficient sensitizers for DSSCs. To improve the light-harvesting ability of the porphyrin sensitizers is to use an electron donor (D) and electron acceptor (A) group, connected via π bridge, construct D–π–A structure [15]. Commonly used as electron acceptor groups such as carboxyl [16], cyanoacrylic acid [17], salicylic acid [18] and so on. The better electron acceptor groups have also become promising candidates for DSSCs with excellent performance. Although D–π–A zinc porphyrin has many advantages, its development is limited due to its complex structure, difficult synthesis process and low yields.
Porphyrin-based axial coordination self-assemblies, can afford a convenient method for designing and synthesizing of more efficient DSSCs. Utilization of axial metal–ligand coordination construct porphyrin-based donor–acceptor supramolecular assemblies with remarkable photovoltaic performance [19–21]. In this type of assemblies, the porphyrin center metal ion and anchoring molecule N ligand axial coordinated, anchoring molecules as electron acceptor. Sufficient researches indicate that electron transfer between the porphyrin and axial ligand is capable and feasible [20, 21]. D’Souza et al. reported a metal–ligand axial coordination approach to construct a series of (donor)1-(donor)2 porphyrin-based assemblies, its fully proved that this self-assembly can effectively realize photoelectric transfer [22]. Therefore, such as assemblies are widely applied in photovoltaic devices [23–25].

In this paper, three anchored molecules featuring carboxyl and cyanoacrylic acid groups as electron acceptor have been designed and synthesized (denoted as Wi i = 1–3, shown in Scheme 1). Three anchored molecules and zinc meso-tetraphenyl porphyrin (denoted as ZnTPP, shown in Scheme 1) construct axial-coordinated assemblies (described as ZnTPP-Wi, i = 1–3) solar cells. The optical properties, topography, theoretical calculations and the photovoltaic performances of the assemblies are studied to further understand the behavior of the ZnTPP-Wi based dye-sensitized solar cells.

The assembled processes of ZnTPP-Wi on TiO2 surface are as follows: an anchoring molecule (Wi) was immobilized on the TiO2 electrode surface through carboxylic groups, then the desired dye of ZnTPP was bound to the anchoring group through axially coordination bonded from porphyrin central Zn(II) ions of ZnTPP and the N atom of Wi. The detailed assembly approach is shown in Scheme 2.

2 Experimental

2.1 Materials and Physical Measurements

All solvents and reagents were used directly without further purification as commercially analytical grade. Isonicotinic acid and 4-pyridylcarboxyaldehyde were purchased from Aldrich, pyrrole was distilled prior to use. Electronic absorption spectra were measured on a SHIMADZU UV-2550 spectrometer. 1H NMR (400 MHz) was measured on a Varian Mercury Plus-400 spectrometer. Electrospray ionization (ESI) mass spectra was investigated on a Thermo Fisher-QE mass spectrometer. Surface topography of the self-assembly films on TiO2 electrode surface was imaged using transmission electron microscopy (TEM) (Hitachi Model H-900). The electrochemical impedance spectroscopy (EIS) was achieved on a Princeton applied research VMP2 multi potentiate. The detail synthesis processes are shown in Scheme 3.
2.2 Synthesis

2.2.1 The Synthesis of 4-((isonicotinamido)benzoic Acid (W1)

A similar method was previously reported [26]. A mixture of isonicotinic acid (2.46 g, 20 mmol) and SOCl₂ (20 mL) was refluxed for 2 h then excess SOCl₂ was removed under vacuum. The residue was dissolved in dry dichloromethane (40 mL). To the solution was added 4-aminobenzoic acid (2.74 g, 20 mmol) and then triethylamine (5.6 mL, 40 mmol). The reaction mixture was stirred overnight at ambient temperature and dichloromethane was removed by rotary evaporation, the solid then dissolved in 5% NaOH followed by slowly acidified with conc. HCl. Precipitate appears and filtered, washed with water and dried to give W1 as a light yellow solid. Yield, 63.2% 1H NMR (CDCl₃) δ 10.1 (s 1H), 8.82 (d, 2H), 7.85–8.13 (dd, 6H) HRMS (ESI, m/z): [M + H]+ calcd for C₁₃H₁₀N₂O₃, 243.0; found 243.23.

2.2.2 The Synthesis of (E)-2-cyano-3-(pyridin-4-yl)acrylic Acid (W2)

A similar method was previously reported [24]. Yield, 63.2% 1H NMR (CDCl₃) δ 8.78–8.80 (d 2H), 8.35 (s, 1H), 7.83–7.85 (dd, 2H) HRMS (ESI, m/z): [M + H]+ calcd for C₁₃H₁₀N₂O₂, 243.0; found 243.23.

2.2.3 The Synthesis of (E)-2-cyano-3-(4-(isonicotinamido) phenyl)acrylic Acid (W3)

A was synthesized in a similar procedure as W1 except that 4-aminobenzoic acid was replaced by 4-aminophenol (2.18 g, 20 mmol), a in CH₃OH (5 mL) then cyanoacetic acid (0.065 mmol, 5.5 g), was dissolved in CH₃OH (10 mL) was added under magnetic stirring. The mixture was reacted at ambient temperature for 3 h. White precipitated generated and was filtered off, washed by CH₃OH to give W3 as a white powder in 58.3% yield. 1H NMR (DMSO) δ 10.80 (s 1H), 9.02–9.03 (d, 2H), 8.36–8.38 (d, 2H), 7.57–7.59 (d, 2H), 6.76–6.79 (d, 2H) HRMS (ESI, m/z): [M + H]+ calcd for C₁₆H₁₁N₃O₃, 294.0; found 294.08.

2.2.4 The Synthesis of ZnTPP

A similar method was previously reported. Yield, 27.2% 1H NMR (DMSO) δ 8.75 (s 2H), 8.15–8.17 (m, 2H), 7.78–7.79 (m, 2H), 5.74 (s, 1H), 3.31 (s, 20H), 1.21 (s, 1H) HRMS (ESI, m/z): [M + H]+ calcd for C₄₄H₂₈N₄Zn, 677.0; found 677.16.

The solid with ZnTPP dye was showed by infrared spectroscopies (Fig. S1). The evidenced skeleton vibration absorption of benzene ring and pyrrole ring (over 1440–1636 cm⁻¹). The spectra bands from the benzene ring = C–H plane bending vibration over 1048 cm⁻¹ and...
973 cm\(^{-1}\). The spectra bands from the pyrrole=C-H stretches over 768 cm\(^{-1}\) and 730 cm\(^{-1}\). The 3542 cm\(^{-1}\) is the peak of water.

### 2.3 Device Fabrication

The detailed preparation procedures of TiO\(_2\) nanocrystals, pastes for screen-printing, and nanostructured TiO\(_2\) film have been reported by Wang [27]. A cycloidal TiO\(_2\) electrode (~0.28 cm\(^2\)) was stained by immersing it into a solution containing anchoring molecule (2 mM) in DMF overnight, after removal of the unbound molecules (through three ethanol washings), then the electrode was immersed into a dye solution containing ZnTPP (0.2 mM) in CHCl\(_3\)/CH\(_3\)OH for 2 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 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 oven for heating posttreatment at 100 °C for 30 min and cooled to room temperature before photoelectrochemical measurements.

### 3 Results and Discussion

#### 3.1 Photophysical Properties

The UV–vis absorption spectra for ZnTPP dye in CHCl\(_3\) solution, the ZnTPP-f and assembled dyes (ZnTPP-Wi i=1–3) absorbed onto TiO\(_2\) films are displayed in Fig. 1 and the data are summarized in Table S1. In general, all these dyes have two absorption bands at ca. 400–450 nm and ca. 550–650 nm, corresponding to typical porphyrin spectra. Compared with the absorption spectrum of ZnTPP in CHCl\(_3\), the assembled dyes ZnTPP-Wi corresponding spectrum on the TiO\(_2\) film is slightly broadened and red shifted, which may be related to the J-aggregation of the assembled dye molecules on the TiO\(_2\) film [28, 29]. Furthermore, the Q bands of the self-assemblies display slightly red-shifted than that of porphyrin ZnPTPP immobilized on TiO\(_2\) thin film ZnTPP-f. These characters are favorable for enhancing the light-harvesting ability.

The light harvesting efficiency (LHE) will quantify this capability of a device to absorb photons, as LHE (λ) is the incident light-harvesting efficiency for photons with wavelength λ (nm), (LHE = (1−10^{-A}), with A being the absorbance of the film) [30]. As all films display very similar absorption spectra (Fig. 1), LHE were assumed likewise to be similar for all dyes, but on the other hand, cyanoacetic acid group can expect that it would favorably improve the LHE of the dye. As Fig. 2, indeed, going from ZnTPP-W2 and ZnTPP-W3, the introduction of cyanoacetic acid anchoring group causes assembled systematic important redshifts and broadening. For ZnTPP-W3 has a higher LHE, which is the key factor for higher short circuit current density (\(J_{sc}\)).

![Fig. 1 UV–Vis absorption spectra of ZnTPP in CHCl\(_3\) solution and ZnTPP-f, ZnTPP-Wi on TiO\(_2\) thin films](image1)

![Fig. 2 Light harvesting efficiency of the self-assemblies dyes TiO\(_2\) electrodes](image2)
3.2 Density Functional Theory (DFT) Calculations

The energy-optimized structures, electronic distribution, and energy levels of HOMO–LUMO of all three self-assemblies dyes were theoretically calculated using the Gaussian 09 program package with the functional basis set of the B3LYP/6-31G level [31, 32]. As can be seen from Fig. 3, the HOMOs for three self-assemblies dyes (ZnTPP-Wi) are completely located on the top porphyrin cores and the LUMO is delocalized over the bottom anchoring molecules respectively, which is very important for efficient electron injection from the excited state of the sensitizer to the conduction band of the TiO2 semiconductor. The HOMO energy levels of all dyes are almost at 0.35 V owing to the presence of the same top porphyrin molecular structures. These values are more negative than the redox potential of the I−/I3− couple (−4.60 eV), assuring sufficient dye regeneration [33]. The LUMO values of the dyes are also slightly more positive than the conduction band of TiO2 (−4.00 eV), resulting in a diminished driving force for charge injection into TiO2 [34, 35]. The HOMO–LUMO gap of the three sensitzers are 2.46 eV (ZnTPP-W1), 2.17 eV (ZnTPP-W2) and 2.02 eV (ZnTPP-W3), and the order is ZnTPP-W1 > ZnTPP-W2 > ZnTPP-W3.

3.3 Morphological Characterization

The surface morphologies of ZnTPP-Wi (i = 1–3) sensitized on the TiO2 electrode surfaces were performed using transmission electron microscopy (TEM), the characteristic method well-established by some other researchers [36, 37]. With respect to the comparison of the length of two ends of the dyad obtained by computational simulation (Fig. S1) and the film thickness identified under TEM analysis (Fig. 4). The film thicknesses almost match to the computational values, indicating that the assemble modes of ZnTPP-Wi immobilized onto the TiO2 electrode surfaces should be similar to those of Scheme 2.

Fig. 3 Energy diagram of three assemblies dyes calculated using the B3LYP/6-31G level

Fig. 4 TEM images of TiO2 nanoparticles modified with ZnTPP-Wi (i = 1–3)

Fig. 5 J–V characteristics of ZnTPP-Wi (i = 1–3)
3.4 Photovoltaic Properties

The photovoltaic performance of DSSCs using an iodine electrolyte under standard AM 1.5 irradiation (100 mW cm\(^{-2}\)). The photocurrent density–voltage (J–V) curves of the devices and the detailed performance parameters are given in Fig. 5 and Table S2, respectively. The short-circuit current density (\(J_{sc}\)) decreased in order ZnTPP-W3 (3.69 mA/cm\(^2\)) > ZnTPP-W2 (2.78 mA/cm\(^2\)) > ZnTPP-W1 (2.65 mA/cm\(^2\)), which indicated that the presence of the cyanoacetic acid anchoring group had a significant effect on electron injection. The open-circuit voltage (\(V_{oc}\)) of the devices decreased in the order ZnTPP-W3 (0.41 V) > ZnTPP-W2 (0.37 V) > ZnTPP-W1 (0.35 V), which the ZnTPP-W3 device exhibited a higher power conversion efficiency. By comparing these photovoltaic parameters and analyzing anchor molecular structure, we can conclude cyanoacetic acid group and longer molecular structure can effectively inhibit the electron aggregation between the upper porphyrin and TiO\(_2\) surface. Our previous research [38] revealed that the device without anchoring molecule exhibits obviously lower performance than the assembly-based device.

The incident photon-current conversion efficiencies (IPCEs) for these dyes in DSSCs are plotted in Fig. 6. All dyes exhibited broad optical response range from 350 to 700 nm, which maximum IPCE peaks of 45% for ZnTPP-W1, and 47% for ZnTPP-W2, and 76% for ZnTPP-W3. ZnTPP-W3 exhibited stronger absorption response, whose DSC device possessed outstanding light capturing ability and then obtained higher \(J_{sc}\) value. The IPCE response of ZnTPP-W1 was lower, which is attributed to the conventional anchor group of benzoic acid. Therefore, the cyanoacetic acid anchor group of ZnTPP-W3 improved its light harvesting ability, which resulted in improved current density.

APCE is the absorbed photo to current conversion efficiency and shows how efficient the numbers of absorbed photons are converted into current [16, 30]. APCE values provide further insight into the properties of the device, which originates by dividing the IPCE number by the LHE and the results are depicted in Fig. S2. The maximum APCE value, decreases in the order ZnTPP-W3 (85%) > ZnTPP-W2 (55%) > ZnTPP-W1 (50%). Thus, the superior performance of ZnTPP-W3 cell, mainly arises from the relative larger integrated APCE value.

3.5 Electrochemical Impedance Spectroscopy Analysis

The electrochemical impedance spectroscopy (EIS) under dark was often measured to study the electron recombination dynamics of the DSSCs, electron recombination rate has an important influence on the open-circuit voltage (\(V_{oc}\)), we measured the EIS under the applied voltage of – 0.6V [39–42]. The equivalent circuit was presented in Fig. 7c, \(R_s\), \(R_{ct}\), \(R_{ct}\), and \(C\) represent series resistances, charge transfer resistances, Nernst diffusion resistances and double layer capacitance, respectively. Nyquist plots of DSSCs are shown in Fig. 7a, the larger semicircle at the intermediated frequency reflected the charge transfer resistance (\(R_{ct}\)) at the TiO\(_2\)/dye/electrolyte interface. It is clear that radius of the large semicircle of ZnTPP-W3 is largest than that of other cell devices. It indicates that the cyanoacetic acid group is effective in TiO\(_2\)/dye/electrolyte interface modification, and this implies that the cyanoacetic acid effectively reduces the electron recombination rate, giving rise to a higher \(V_{oc}\) [43, 44]. In generally, a high charge transfer resistance will lead to a long electron lifetime. We analyzed the electron lifetimes of the devices by bode phase plots (Fig. 7b). The electron lifetime (\(\tau\)) can be calculated by \(\tau = 1/(2\pi f)\) [45, 46]. The bode phase plots show that ZnTPP-W3 based device have longest electron lifetime compared to other cells. This is explaining the DSSCs based on ZnTPP-W3 has the highest \(V_{oc}\).

4 Conclusion

In this work, we report the synthesis, fundamental properties, and photovoltaic performance in DSSC of three new anchoring molecules (Wi, i = 1–3) and zinc meso-tetraphenylporphine (ZnTPP). A novel type assembly based on ZnTPP appended anchoring molecules (Wi, i = 1–3) via metal−ligand axial coordination and modified the nano-structured TiO\(_2\) electrode surface. The photovoltaic
properties studies show that ZnTPP-W3 outperforms others in the series with a PCE of 1.15%. Superior PCE of ZnTPP-W3 may be attributed to the greater $J_{sc}$ and $V_{oc}$ values. A greater $J_{sc}$ is consistent with a broadened and red-shifted spectrum with cyanoacetic acid group and longer molecular structure. EIS measurements suggest that the higher $V_{oc}$ of the ZnTPP-W3 cell may be attributed to a greater charge recombination resistance. As to remedy the possible issue of high-performance self-assembly cells, synthesis of more suitable for molecular structure.

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Fig. 7 EIS spectra of DSSCs based on porphyrin dyes: a Nyquist plots in the dark. b Bode phase plots in the dark. c The equivalent circuit

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Declarations

Competing interest The authors have not disclosed any competing interests.

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