



# Synthesis of asymmetric zinc phthalocyanine with bulky diphenylthiophenol substituents and its photovoltaic performance for dye-sensitized solar cells



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## ARTICLE INFO

### Article history:

Received 30 August 2015

Received in revised form 27 January 2016

Accepted 9 February 2016

Available online 11 February 2016

### Keywords:

Asymmetric zinc phthalocyanine

Conversion efficiency

Dye-sensitized solar cell

Red/near-IR light absorption

## ABSTRACT

Asymmetric zinc phthalocyanine derivative (**Zn-tri-PcNc-9**) bearing one carboxylic and six bulky diphenylthiophenol groups was synthesized as a sensitizer for dye-sensitized solar cells. The obtained **Zn-tri-PcNc-9** exhibits strong and expanded Q-band absorption peak (at ~741 nm) in the red/near-IR light (600–800 nm) range, and its photovoltaic performance in sensitizing TiO<sub>2</sub>-based solar cell can be significantly improved by using chenodeoxycholic acid (CDCA) as co-adsorbent due to the retarded charge recombination. Under an optimal sensitization condition, the corresponding solar cell exhibits an efficiency of 3.61%, which is improved by 144% as compared to the solar cell without CDCA. Moreover, **Zn-tri-PcNc-9**-sensitized solar cell shows a maximum incident photo-to-current conversion efficiency of 31.6% at ~730 nm, red-shifted by ~20 nm as compared to that (~710 nm) of its O-substituted analog (**Zn-tri-PcNc-8**) bearing six diphenylphenoxy groups, suggesting an effective solution to expand the red/near-IR responsive range of the ZnPc-sensitized solar cell, and also demonstrating a possibility for future panchromatic sensitizing agents in dye-sensitized solar cells.

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## 1. Introduction

Due to the growing global energy crisis and environmental problems, dye-sensitized solar cells (DSSCs) applying nanosized TiO<sub>2</sub> film electrode have attracted increasingly attention since the pioneering work of O'Regan and Grätzel was reported in 1991 [1]. A relatively high power conversion efficiency (>10%) can be attained by using Ru-bi(poly)pyridyl complexes such as N3, N719 and black dye as sensitizer [2], but the spectral responsive ability of those Ru-based complexes falls away dramatically once the incident light wavelength is longer than 650 nm [3]. Even the porphyrin-sensitized solar cells with the record efficiency (~13%) in the field of DSSCs are still lack of the light absorption at  $\lambda > 650$  nm [4–6]. Nevertheless, ~50% of the available solar radiation energy is in the spectral region with  $\lambda > 650$  nm, and thus the development of novel dyes with broader spectral responsive range (especially in the red/near-IR region) is an attractive topic in the field of DSSCs [7,8].

Among various dyes designed for DSSCs, zinc phthalocyanine (ZnPc) derivatives with large  $\pi$ -conjugated systems and outstanding chromophores, which have intense absorption in the UV/blue

(Soret-band) and the red/near-IR (Q-band) spectral regions, have been considered as promising choice for the utilization of red/near-IR region of the solar spectrum even though the conversion efficiencies of most ZnPc-sensitized solar cells are remaining low as compared to the counterpart sensitized by Ru-based complexes [9–12]. The major limiting factors for the low efficiency are the general dye aggregate tendency due to the molecular  $\pi$ - $\pi$  stacking and the lack of electronic directionality of the symmetric ZnPcs during the energy transfer processes [9–12]. Introducing bulky electron-pushing peripheral substituents was proven to be the best compromise to get ZnPcs with good solubility and low molecule aggregates [11–14], and an efficient electron transfer from the excited ZnPc molecules to TiO<sub>2</sub> conduction band (CB) would be anticipated through an intramolecular electron “push-pull” character afforded by the electron-pushing/withdrawing peripheral groups [12–14]. Certain anchoring groups such as carboxylic can supply the required electronic directionality from the excited ZnPc molecules to TiO<sub>2</sub> through a good electronically coupling between the the lowest unoccupied molecular orbital (LUMO) of the dye and the Ti 3d orbital of TiO<sub>2</sub> [15,16]. For example, asymmetric ZnPcs bearing carboxylic group(s) and bulky substituents (as electron-pushing groups) with effective red/near-IR light response (such as TT1 [9], PCH001 [10], and PcS18 [13]) were designed for creating an electronic directionality while retarding

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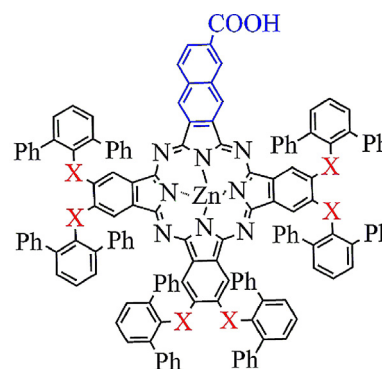
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the dye molecule aggregates, and the asymmetric ZnPc derivatives with one carboxylic and six 2,6-diisopropylphenoxy units (PcS18) showed a high efficiency of 5.9% [13].

More recently, an asymmetric ZnPc derivative (PcS20) containing propoxy groups in the 2 and 6 positions of peripheral phenoxy units and one carboxylic group showed a record efficiency (up to 6.4%) in the field of ZnPc-sensitized solar cells [14]. The above investigations indicated that bulky peripheral units as electron-pushing groups with large steric hindrance can efficiently inhibit the ZnPc molecule aggregates, which can inhibit the charge recombination and improve the photovoltaic performance of DSSCs [7,13,14]. Moreover, Ince and co-workers introduced thiophene into ZnPc molecule to synthesize near-IR absorbing, “push–pull”, bisthiophene-substituted ZnPc derivatives with an efficiency of 2.0%, and found that the absorption ability of Q-band can be improved due to the strong electron-pushing capability of S atoms, which can effectively enhance the electron cloud density of the dye molecules, and then causing the enhanced and expanded Q-band absorption [17]. Besides the molecular engineering of ZnPc sensitizers for efficient DSSCs based on the “push–pull” concepts of ZnPc’s substituents, co-adsorbents such as chenodeoxycholic acid (CDCA) can also prevent the ZnPc dye molecule aggregates, and then promote the dye regeneration and/or the electron injection kinetics by co-grafting of dye and CDCA as mixed monolayer onto the TiO<sub>2</sub> film surface [3,15–18]. It is a benefit to the retard of the charge recombination and the improvement of the ZnPc-sensitized cell’s performance.

Inspired by the above breakthrough on ZnPc dyes, we have designed and synthesized series of asymmetric ZnPc derivatives (**Zn-tri-PcNc-x**) containing tribenzonaphtho-condensed porphyrazine with one or two carboxylic groups, which showed a Q-band redshift to the near-IR region due to the expanded p-conjugated macrocycle by introducing an additional benzo group to the ZnPc framework [19–23]. It was found that the steric hindrance of the three *tert*-butyl (tBu) groups in **Zn-tri-PcNc-2** as dye is too small to effectively retard to the ZnPc molecular  $\pi$ – $\pi$  stacking, which causes the enhanced self-quenching of the dye excited singlet state, and then the decreased efficiency of the TiO<sub>2</sub>-based solar cells [17,18,21], and therefore asymmetric ZnPc derivatives bearing six bulky diphenylphenoxy substituents and two (**Zn-tri-PcNc-4**) or one (**Zn-tri-PcNc-8**) carboxylic group(s) were synthesized based on the “push–pull” concepts of ZnPc’s substituents [22,23]. It was found that the solar cell sensitized by **Zn-tri-PcNc-4** yielded a 3.22% efficiency, higher than that (3.01%) of the solar cell sensitized by **Zn-tri-PcNc-8** [22,23]. Moreover, **Zn-tri-PcNc-4** showed a much higher efficiency (3.22%) than that (1.30%) of its S-substituted analog (**Zn-tri-PcNc-5**) bearing six diphenylthiophenol groups in sensitizing TiO<sub>2</sub>-based solar cell, but **Zn-tri-PcNc-5** exhibited stronger red/near-IR light absorption and an obvious redshift in the Q-band as compared with **Zn-tri-PcNc-4** [22]. The possible reason of the decreased efficiency of **Zn-tri-PcNc-5** is the molecular orbital shift to negative direction afforded by S atoms instead of O atoms in the six substituents of **Zn-tri-PcNc-4**, which leads to insufficient driving force for the electron injection [22].

Herein, we designed a novel asymmetric ZnPc derivative (**Zn-tri-PcNc-9**) bearing single carboxylic group (Scheme 1), it is similar to **Zn-tri-PcNc-8** but bearing six diphenylthiophenol substituents as electron-pushing groups instead of the six diphenylphenoxy groups [23], and investigated its photovoltaic properties in DSSCs. It is found that **Zn-tri-PcNc-9** only yields a 1.48% efficiency in sensitizing TiO<sub>2</sub>-based solar cell, much lower than that (3.01%) of its O-substituted analog (**Zn-tri-PcNc-8**), but the addition of CDCA as a co-adsorbent can reduce the dye molecule aggregates and improve the electron injection efficiency. Under an optimal dye sensitization condition in the presence of 1.87 mM CDCA, the corresponding solar cell exhibits the maximum



**Zn-tri-PcNc-8: X=O; Zn-tri-PcNc-9: X=S**

**Scheme 1.** Molecular structures of asymmetric ZnPc derivative (**Zn-tri-PcNc-9**) and its O-substituted analog (**Zn-tri-PcNc-8**, refer to Ref. [23]).

efficiency of 3.61%, which is improved by 144% as compared with the solar cell fabricated under the same condition in absence of CDCA. The effects of CDCA concentration in the dye solution on the photoelectrochemical behaviors of those electrodes and their corresponding solar cells were investigated in detail.

## 2. Experimental

### 2.1. Dye syntheses

All solvents and reagents are of pure quality and used as received unless otherwise stated. Amyl alcohol was distilled from sodium, and dichlorobenzene for voltammetric studies was freshly distilled from CaH<sub>2</sub> under N<sub>2</sub>. Column chromatography was carried out on silica gel columns (Merck, Kieselgel 60, 70–230 mesh) with the indicated eluents. Preparative thin-layer chromatography (TLC) was performed on glass plates (20 cm × 20 cm) with GF-254 silica gel.

**Zn-tri-PcNc-9** was prepared via a mixed cyclic tetramerization using 1:6 of 6-carboxymethyl-2,3-dicyanonaphthalene (Ligand 1) and 4,5-bis([1,1':3',1''-terphenyl]-2'-ylthio) phthalonitrile (Ligand 2) followed by ester hydrolysis with Na and methanol as shown in Scheme 2. Ligand 1 and 2 were prepared according to our previous literatures [19,22].

**Zn-tri-PcNc-9a:** 1,8-Diazabicyclo[5.4.0] undec-7-ene (DBU) (0.25 mL) was added into a suspension of Ligand 1 (23.6 mg, 0.10 mmol), and Ligand 2 (388.8 mg, 0.60 mmol), and zinc acetate (66 mg, 0.30 mmol) in pre-treated *n*-pentanol (5 mL). The mixture was stirred at 120 °C under N<sub>2</sub> for 8 h, and then the solvent was removed under reduced pressure. The resultant solid was subjected to silica gel column chromatography with CH<sub>2</sub>Cl<sub>2</sub> as a solvent. The second, greenish-blue band contained the desired **Zn-tri-PcNc-9a**. Yield: 25.0 mg, 10.8%. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz):  $\delta$  = 8.10–8.30 (m, 4H), 7.90–8.10 (m, 4H), 7.60–7.90 (m, 4H), 7.40–7.60 (m, 19H), 7.20–7.40 (m, 25H), 6.90–7.20 (m, 33H), 0.80–1.20 (m, 111H); TOF-MS (*m/z*) calcd. for C<sub>150</sub>H<sub>100</sub>N<sub>9</sub>O<sub>2</sub>S<sub>6</sub>Zn [M+H]<sup>+</sup> 2301.56, found 2300.71.

**Zn-tri-PcNc-9:** The obtained **Zn-tri-PcNc-9a** (50 mg, 0.022 mmol) was dissolved in methanol (125 mL), and then metallic Na (0.5 g) was added. The mixture was stirred at 50 °C for 7 days, and then the solvent was evaporated under reduced pressure. The obtained solid was redissolved in water and the pH was adjusted to 3.0 with diluted HCl solution. The precipitate was filtered and dried under reduced pressure. Yield: 45 mg, 90%. Elemental analysis calcd. for C<sub>145</sub>H<sub>90</sub>N<sub>8</sub>O<sub>2</sub>S<sub>6</sub>Zn: C 77.98, H 4.03, N 5.02. Found: C 78.03, H 4.11, N 4.97; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz):  $\delta$  = 7.30–7.40 (M, 4H), 7.20–7.30 (m, 12H), 7.12–7.20 (m, 14H), 7.02–

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