

Effect of carboxyl anchoring groups in asymmetric zinc phthalocyanine with large steric hindrance on the dye-sensitized solar cell performance



Wenye Shi, Bosi Peng, Li Lin, Renjie Li, Jing Zhang^{**}, Tianyou Peng^{*}

College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, PR China

HIGHLIGHTS

- ZnPcs with six diphenylphenoxy and one/two carboxyl groups are used as dyes for DSSCs.
- Effect of carboxyl group number on the ZnPc-sensitized cell property are scrutinized.
- Grafting two carboxyl groups on ZnPc leads to the enhanced photocurrent and efficiency.
- ZnPc with one COOH has a higher open-circuit voltage than its analog with two COOH.

ARTICLE INFO

Article history:

Received 17 October 2014

Received in revised form

11 June 2015

Accepted 17 July 2015

Available online 12 August 2015

Keywords:

Organometallic compounds

Semiconductors

Electrochemical techniques

Electrochemical properties

ABSTRACT

Asymmetric zinc phthalocyanines containing tribenzonaphtho-condensed porphyrazine with six bulky diphenylphenoxy and one or two carboxyl groups are used as sensitizers for dye-sensitized solar cells (DSSCs). It is found that **Zn-tri-PcNc-4** having two carboxyl groups shows a slight redshift in the Q-band absorption but a significantly decreased absorbance as compared with **Zn-tri-PcNc-8** having one carboxyl group, and **Zn-tri-PcNc-4** can be more stably and perpendicularly grafted onto the TiO₂ surface than **Zn-tri-PcNc-8**, which further leads to the differences in the interfacial charge transfer dynamics and dye-loaded amount. **Zn-tri-PcNc-4** with two carboxyl groups grafted onto the TiO₂ electrode surface of DSSC results in a photovoltaic conversion efficiency of 3.22%, higher than that (3.01%) of the analog with one carboxyl group (**Zn-tri-PcNc-8**), which exhibits a lower short-circuit current but much higher open-circuit voltage. The additional carboxyl group in **Zn-tri-PcNc-4** leads to the enhanced dye-loaded amount and the molecular orbital energy level shift toward positive direction, causing more efficient electron injection and higher short-circuit current than **Zn-tri-PcNc-8**; while the two carboxyl groups of **Zn-tri-PcNc-4** would cause more protonation of TiO₂ surface, which possibly leads to the downward shift of TiO₂ conduction band edge, and then to the decreased open-circuit voltage. The present results demonstrate the molecular engineering aspect of ZnPc dyes in which the fine tuning of the energy levels and molecular structures is crucial for high conversion efficiency of DSSCs.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The conversion of sunlight to electricity via dye-sensitized solar cells (DSSCs) has drawn increasing attention due to their relatively low cost and simple production process compared to the traditional Si-based devices [1–5]. Currently, the most used sensitizers are

ruthenium polypyridyl complexes (such as N3, N719 and black dye), giving 10–11% power conversion efficiency under AM1.5 illumination [2,3]. However, the cost and environmental issues of ruthenium complexes are unfavorable for the DSSCs application due to the noble metal ruthenium and toxicity [1]. Although the pure organic dyes with facile molecular tailoring, good cost-effectiveness and high molar absorption coefficients are another kind of promising alternative for DSSCs, the photovoltaic conversion efficiencies of many pure organic dyes are still lower than those of ruthenium complexes [1]. Moreover, the spectral responses of the above complexes and organic dyes fall away

^{*} Corresponding author.

^{**} Corresponding author.

E-mail addresses: jzhang03@whu.edu.cn (J. Zhang), typeng@whu.edu.cn (T. Peng).

dramatically once the light wavelength longer than 650 nm, which results in insufficient absorption in the red/near-IR region of the solar spectrum. Even porphyrin-sensitized solar cells, which gave the record efficiency (~13%) in the field of dye-sensitized solar cells up to now, are also lack of the light absorption above 600 nm [4]. Since ~50% of the available solar radiation energy is in the spectral region with wavelength longer than 700 nm, the development of red/near-IR-light-responsive dyes with high molar extinction coefficient and low cost is compulsory task [5].

Zinc phthalocyanines (ZnPs) are well known chromophores for their intense absorption in the UV/blue (Soret-band) and the red/near-IR (Q-band) light regions. Their appropriate redox properties, electrochemical, photochemical and thermal stability, which can be adjusted through rational design of these ZnPc molecular structures, also render them as an excellent option for DSSCs [5–9]. Unfortunately, unimpressive conversion efficiencies of the most ZnPc-sensitized solar cells are mainly due to the strong dye molecule aggregation on the TiO₂ surface and the lack of directionality in the excited state of the symmetric ZnPs [6,7]. Some co-adsorbents such as chenodeoxycholic acid (CDCA) were used to prevent the dye molecule aggregation during the dye sensitization process and promote the dye regeneration and/or the electron injection kinetics by co-grafting of ZnPc dye and CDCA as mixed monolayer onto TiO₂ surface [8,9]. Additionally, some asymmetric ZnPc derivatives (such as PCH001 [6], TT1 [7], and PcS18 [10]) containing bulky peripheral substituent groups with steric hindrance were synthesized for creating effective red/near-IR light response while retarding the molecule aggregation, and the asymmetric PcS18 with one carboxyl and six 2,6-diisopropylphenoxy peripheral units showed an efficiency of 5.9% under one sun condition [10]. Recently, the same group reported another asymmetric ZnPc (PcS20) containing propoxy groups in the 2 and 6 positions of peripheral phenoxy units and one carboxyl group showed a record efficiency (6.4%) in the field of ZnPc-sensitized solar cells [11].

The electronic directionality required for efficient electron transfer from the excited ZnPc to TiO₂ conduction band (CB) can be obtained from the good electronically coupling between the lowest unoccupied molecular orbital (LUMO) of the dye and the Ti 3d orbital of TiO₂, and the carboxyl anchoring group electronically connected to the ZnPc can facilitate the expected electron transfer [7–10]. Except that the anchoring group should be located close to the ZnPc core, the spacer, located between the macrocyclic core and the carboxyl adsorption site, should facilitate the perpendicular localization of the ZnPc molecules onto the TiO₂ surface for an efficient electron injection [7]. Torres and co-workers [5] have used asymmetric ZnPs bearing three tert-butyl and one (TT1) or two (TT9) carboxyl groups to minimize the dye molecule aggregation and induce the electron directionality, and found that TT9 bearing two carboxyl groups connected to ZnPc core can keep it perpendicularly arranged and close enough to the TiO₂ surface, and then resulting in a dramatic improvement in stability as compared with TT1 having one carboxyl group under continuous exposure to light and high temperature [12].

Inspired by the above breakthroughs on ZnPc dyes, we have synthesized novel asymmetric ZnPc derivatives (**Zn-tri-PcNc**) containing tribenzonaphtho-condensed porphyrazine with one carboxyl and three tert-butyl substituent groups (**Zn-tri-PcNc-2**), which showed a Q-band redshift toward the near-IR region stemmed from the expanded π -conjugated macrocycle by introducing an additional benzo group to the benzopyrrole groups of the ZnPc framework [13–15]. Using as sensitizer for TiO₂-based solar cells, **Zn-tri-PcNc-2** showed an efficiency of 2.89% under an optimal dye sensitization condition in the presence of CDCA as co-adsorbent [14,15], while the solar cell without CDCA attained an efficiency of 1.96%, only 68% of the efficiency of the device prepared in the

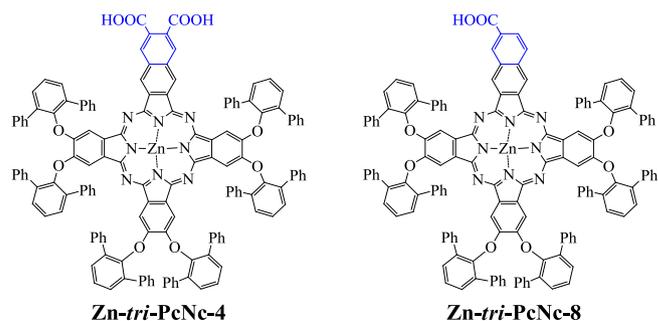
presence of CDCA, primarily because of a loss in the photocurrent of the solar cell [14]. It indicates that the steric hindrance of the three tert-butyl groups in **Zn-tri-PcNc-2** is too small to effectively retard to ZnPc's π - π stacking [8,9].

Herein, similar asymmetric ZnPc derivatives bearing two (**Zn-tri-PcNc-4**) or one (**Zn-tri-PcNc-8**) carboxyl and six bulky diphenylphenoxy substituent groups (Scheme 1) are selected as dyes for DSSCs. Their synthetic pathways, experimental procedures and characterizations on composition, structure and property were reported elsewhere [16,17]. Experimental results indicate that **Zn-tri-PcNc-4** bearing two carboxyl groups shows a slight Q-band redshift in the red/near-IR region but a significantly decreased absorbance as compared with **Zn-tri-PcNc-8** bearing one carboxyl group, and the solar cell sensitized with **Zn-tri-PcNc-4** yielded a 3.22% efficiency, higher than that (3.01%) of the solar cell sensitized with the analog (**Zn-tri-PcNc-8**) with one carboxyl group. The grafting of ZnPc dye onto TiO₂ surface through two carboxylic groups resulted in significantly higher short-circuit photocurrent but much lower open-circuit voltage as compared with the analog (**Zn-tri-PcNc-8**) bearing the same six diphenylphenoxy and only one carboxyl groups, demonstrating the influence of anchoring group number on the ZnPc-sensitized solar cell performance. The frontier molecular orbitals of the compounds calculated by using density functional theory (DFT) and the experimental data were used to explain the above experimental phenomena.

2. Experimental

2.1. Dye synthesis and characterization

All solvents and reagents are of pure quality and used as received unless otherwise stated. **Zn-tri-PcNc-4**/**Zn-tri-PcNc-8** were prepared via a mixed cyclic tetramerization by using 6:1 of 4,5-bis([1,1':3',1''-terphenyl]-2'-yloxy) phthalonitrile and 1,3-dioxo-2-phenyl-2,3-dihydro-1H-benzo[f] isoindole-6,7-dicarbonitrile /6-carboxymethyl-2,3-dicyano-naphthalene followed by ester hydrolysis with Na and methanol similar to the previous report [13]. The obtained asymmetric ZnPs and their corresponding intermediates were fully characterized by elemental analysis and spectroscopic techniques, such as matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS), ¹H NMR, IR, UV-vis and fluorescence spectroscopy in our previous literatures [16,17]. For example, **Zn-tri-PcNc-4** (Yield: 98 mg, 98%. ¹H NMR (DMSO-d₆, 300 MHz): δ = 9.50 (s, 2H), 7.76 (s, 13H), 7.53–7.48 (m, 30H), 7.17–7.12 (m, 12H), 7.07–7.04 (m, 22H), 6.93 (s, 6H), 6.80 (s, 3H), 6.13 (s, 2H). TOF-MS (*m/z*) calcd. for C₁₄₆H₉₀N₈O₁₀Zn: [M+H]⁺ 2181.70, found 2182.20. Elemental analysis calcd. for C₁₄₆H₉₀N₈O₁₀Zn 0.5 CH₂Cl₂: C 79.11, H 4.12, N 5.04, found: C 79.18, H 4.10, N 5.04) [16]; **Zn-tri-PcNc-8** (Yield: 90 mg,



Scheme 1. Molecular structures of asymmetric ZnPc derivatives (**Zn-tri-PcNc-4** and **Zn-tri-PcNc-8**).

Download English Version:

<https://daneshyari.com/en/article/1521088>

Download Persian Version:

<https://daneshyari.com/article/1521088>

[Daneshyari.com](https://daneshyari.com)