



Push–pull type porphyrin based sensitizers: The effect of donor structure on the light-harvesting ability and photovoltaic performance



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ARTICLE INFO

Article history:

Received 18 May 2015

Received in revised form

8 June 2015

Accepted 10 June 2015

Available online 23 June 2015

Keywords:

Push–pull
Porphyrin
Anthracene
Carbazole
Solar cell
Organic dye

ABSTRACT

Push–pull type porphyrin-based sensitizers have become promising candidates for high-efficiency dye sensitized solar cells (DSCs). It is of importance to understand the fundamental structure-physical property-photovoltaic performance relationships by varying the donor and acceptor moieties. In this work, two new porphyrin-based sensitizers, WW-7 and WW-8, were synthesized and compared with the known sensitizer YD20. All the three dyes have the same porphyrin core and acceptor group (ethynylbenzoic acid) but their donor groups vary from the triphenylamine in YD20 to *meso*-diphenylaminoanthracene in WW-7 to *N*-phenyl carbazole in WW-8. Co(II/III)-based DSC device characterizations revealed that WW-7 showed enhanced light harvesting ability in comparison to YD20 with improved incident photon-to-collected electron conversion efficiencies (IPCEs). As a result, WW-7 displayed much higher short circuit current (J_{sc} : 13.54 mA cm⁻²) and open-circuit voltage (V_{oc} : 0.829 V), with a power conversion efficiency (η) as high as 7.7%. Under the same conditions, YD20 cell exhibited a power conversion efficiency of 6.6% and the dye WW-8 showed even lower efficiency (η = 4.6%). Detailed physical measurements and theoretic calculations were conducted to understand the difference and reveal how three different donor structures affect their molecular orbital profile, light-harvesting ability, energy level alignment, and eventually the photovoltaic performance.

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1. Introduction

Dye-sensitized solar cells (DSCs) have drawn a rising interest due to the low production cost, good conversion efficiency, ease of fabrication and environmental concerns [1]. Design and synthesis of stable organic dyes with appropriate push–pull structure was proved to be the key to achieve highly efficient DSCs. Based on this principle, various types of organic dyes with donor π -acceptor (D- π -A) system have been investigated [2]. Among these dyes,

push–pull type porphyrin-based sensitizers are considered to be promising candidates for DSCs because of the facile functionality and their excellent light-harvesting properties [3]. In 2011, a zinc porphyrin sensitizer (YD2-*o*-C8) co-sensitized with an organic dye (Y123) using a cobalt-based electrolyte attained a power conversion efficiency (η) of 12.3%, which is superior to those developed based on Ru complexes [4]. Recently, the performance of porphyrin-based sensitizers is improved even higher [5].

For further improvement of the device, it is however highly desirable to develop new dyes with even enhanced light harvesting ability both in the visible (ca. 400–700 nm) and the near infrared (NIR) region (ca. 700–1400 nm) since a significant portion of solar energy falls within this range [6]. Extending the π -conjugation of a sensitizer is a logical and most common way to achieve such a goal. Based on the structure of YD2-*o*-C8, many strategies were applied to design and synthesize porphyrin-based sensitizers with

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extended π -conjugation in order to enhance the light-harvesting ability [7]. Among these attempts, phenylethynyl (PE) group was widely used as π -spacer in the design of porphyrin-based sensitizers in order to extend the π -conjugation and to form a well-defined and rigid structural arrangement [8]. In addition, the choice of donor is critical to achieve good light-harvesting ability and efficient intramolecular charge separation upon photo-irradiation. So far, one of the most often used donors in organic sensitizers is triphenylamine. For example, the porphyrin-based dye YD20 (Fig. 1) gave high power conversion efficiency (η : 8.1%) as reported by Yeh and Diau et al. [8e]. How to further improve the performance is critical and we expect the following modifications on the donor structure could work: (1) replacing the phenyl spacer by a more π -extended anthracene unit will enhance the light-harvesting ability (i.e., “benzannulation” approach, Fig. 1); (2) replacing the diphenylamino unit with a carbazole group could lower down the HOMO energy level and thus enhance dye generation driving force [9a] (i.e., “ring fusion” approach, Fig. 1). So far, the donor moiety of many porphyrin-based sensitizers is mainly limited to diphenylamino groups, and examples of modification with *N*-fused heterocycles are few [9]. Based on these considerations, in this work two new porphyrin dyes, WW-7 and WW-8 were synthesized and compared with the dye YD20 (Fig. 1).

2. Experimental section

2.1. Materials and instruments

All reagents and starting materials were obtained from commercial suppliers and used without further purification unless otherwise noted. Anhydrous toluene and THF were distilled from sodium-benzophenone immediately prior to use. The ^1H NMR and ^{13}C NMR spectra were recorded in solution of CDCl_3 or $\text{THF}-d_8$ on Bruker DPX 300 or DRX 500 NMR spectrometers with tetramethylsilane (TMS) as the internal standard. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet. MALDI-TOF or APCI mass

spectrometry was used to confirm the mass of compound. The electrochemical measurements were carried out in anhydrous methylene chloride with 0.1 M TBAPF₆ as the supporting electrolyte at room temperature under the protection of nitrogen. A gold stick was used as working electrode, platinum wire was used as counting electrode, and Ag/AgCl (3 M KCl solution) was used as reference electrode. The potential was externally calibrated against the ferrocene/ferrocenium couple. Steady-state UV–vis absorption were recorded on a Shimadzu UV-1700 spectrometer. The solvents used for UV–vis measurements are of HPLC grade (Merck). The synthetic details of WW-7 and WW-8 are described in the [Electronic Supplementary Information](#).

2.2. DSC fabrication and characterization

A 4.2- μm -thick, transparent layer of 25-nm-sized TiO_2 particles was first screen-printed on FTO glass (Nippon Sheet Glass, Solar, 4 mm thick) and further coated with a 5.0- μm -thick second layer of scattering titania particles (WER4-O, Dyesol) to produce a bilayer titania film, which was used later as the negative electrode of a DSC. The preparation procedures of TiO_2 nanocrystals and paste for screen-printing were reported in a previous paper [10]. The film thickness was monitored with a bench-top Ambios XP-1 stylus profilometer. After sintering at 500 °C and cooling to 80 °C, a circular titania electrode ($\sim 0.28 \text{ cm}^2$) was stained by immersing it overnight into a solution of 150 μM dye dissolved in a binary solvent of THF and ethanol (volume ratio, 1/4). The dye-coated titania electrode was then rinsed with acetonitrile and dried by air flow, and was further assembled with a thermally platinumized FTO positive electrode by a 25-mm-thick Surlyn (DuPont) hot-melt gasket and sealed up by heating. The internal space was perfused with an electrolyte with the aid of a vacuum-back-filling system.

Transient photoelectrical experiments were measured with an Autolab-PGSTAT302N electrochemical workstation. The steady and perturbing lights on the photoanode side of a testing cell were supplied with white and red light-emitting diodes, respectively. We used the red light to generate a photovoltage perturbation near the

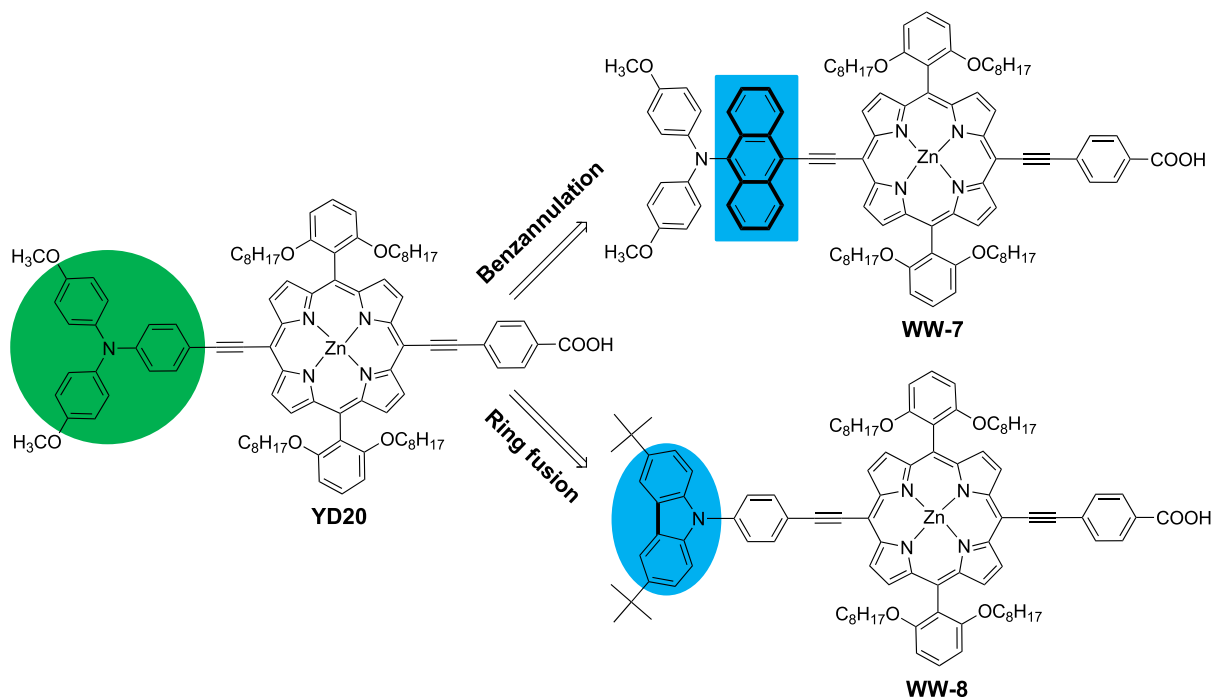


Fig. 1. Structures of WW-7, WW-8 and YD20.

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