

Efficient co-sensitization of dye-sensitized solar cells by novel porphyrin/triazine dye and tertiary aryl-amine organic dye



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ABSTRACT

A novel porphyrin dye ZnP-triazine-(gly)₂, consisting of a zinc-metallated porphyrin unit covalently linked through its peripheral aryl-amino group with a 1,3,5-triazine group which is functionalized by two carboxylic acid groups of glycine moieties, has been synthesized. Photophysical and electrochemical measurements, as well as theoretical DFT calculations, suggest that the compound exhibits appropriate light absorption characteristics and frontier molecular orbital levels for use as sensitizer in dye-sensitized solar cells (DSSCs). The ZnP-triazine-(gly)₂ based solar cell was found to exhibit a power conversion efficiency (PCE) value of 4.72%. A significant improvement of the overall photovoltaic efficiency of the solar cell was achieved up to 7.34% upon co-sensitization with a tertiary aryl-amine D with two ethynyl-pyridine substituents and cyano-acetic acid anchoring group, which exhibits complementary light absorption characteristics with the porphyrin dye. The higher PCE value of the co-sensitized solar cell is attributed to its enhanced short circuit current (J_{sc}), which is due to improved light harvesting efficiency, reduced porphyrin aggregation, and faster electron injection and charge collection, as well as its enhanced open circuit voltage (V_{oc}), which is due to increased electron density in the TiO₂ conduction band of the photoanode. These results are in accordance with electrochemical impedance spectra (EIS) of the solar cells, which revealed higher charge recombination resistance (R_{rec}), longer electron lifetime (τ_e), and shorter electron transport time (τ_d) for the co-sensitized solar cell.

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1. Introduction

Since the pioneering work of O'Regan and Grätzel in 1991 [1], dye-sensitized solar cells (DSSCs) have gained lot of attention in academic and industrial communities as alternatives to conventional silicon based solar cells, owing to their low cost and easy fabrication process combined with high power conversion efficiencies (PCE) [2]. In such a device, a dye anchored onto the surface of a nanocrystalline TiO₂ electrode absorbs solar radiation and injects the photoexcited electrons into the TiO₂ conduction band. Playing a key role in the light harvesting and electron injection processes, highly efficient sensitizers are needed for future application in DSSCs. Along these lines, a variety of DSSC sensitizers, including ruthenium-polypyridyl based dyes [3], metal free dyes [4], and

porphyrins [5,6], have been synthesized and studied in an effort to get highly efficient solar cells and to get information about their structure-efficiency relationship. In particular, many studies have been focused on improving some of their key properties including (i) enhancement of their light capturing ability, (ii) prevention of aggregates formation, and (iii) decrease of charge recombination tendency at the TiO₂/dye/electrolyte interface of the device.

Among the various types of DSSC sensitizers, porphyrins, the synthetic analogues of the natural light-capturing chlorophylls, are found to be very efficient, due to their intense Soret absorption band (400–450 nm) and moderate Q absorption bands (550–650 nm), which cover the visible and near infrared (NIR) region of solar spectrum. Moreover, they offer the advantage of tuning their optical and electrochemical properties by simply modifying their chemical structure. For example, recently, Grätzel and co-worker reported a highly efficient porphyrin sensitizer, functionalized with two bis-(ortho-alkoxy)-wrapped meso-phenyl groups for decrease of dye aggregation, an ethynyl benzoic acid

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anchoring group, and a benzothiadiazole bridge between the ethynyl and benzoic acid moieties, which resulted in the unprecedented PCE of 13% [5g].

The tendency of porphyrin dyes to aggregate on the TiO₂ surface due to π -interactions between the adjacent macrocycles causes self-quenching of excited states, which subsequently reduces charge injection efficiency increasing electron recombination [7,5f]. An effective way to control the π -stacked aggregation and the resulting charge recombination is the utilization of sensitizers with two anchoring units into a spiro configuration, similar to Ru sensitizers [8]. Sensitizers of this type have the potential to strengthen their binding onto the TiO₂ surface and increase their absorbed amount, which in turn induces efficient electron injection resulting in an improvement of DSSC performance [8–10]. Indeed, when two or more organic dyes with double or multiple anchoring groups have been used as sensitizers, DSSCs with enhanced photoresponses, and stabilities were obtained [9a,11].

Aiming to functionalize a porphyrin sensitizer with two binding sites for attachment onto the TiO₂ surface, a 1,3,5-triazine moiety was employed. The chemical and electronic structure of 1,3,5-triazine facilitates the synthesis of π -conjugated multi-chromophores dyes and allows the mediation of electronic phenomena, resulting in enhanced electron injection and transportation rates [12–14]. A triazine-based metal-free organic dye with a D- π -A structure reported by Liu et al. was used as DSSC sensitizer resulting in a PCE value of 3.63% [15]. Our research group has utilized triazine as scaffold for the construction of porphyrin dyads and triads yielding DSSCs with moderate PCE values [16]. Triazine-bridged porphyrin arrays have been also incorporated by Luechai et al. [17] and recently by us [18] as electron donors in bulk heterojunction solar cells.

Combining the well-documented advantages of triazine as a bridging unit together with the presence of two anchoring units in the same sensitizer, herein we describe the facile synthesis of the porphyrin dye ZnP-triazine-(gly)₂ (Scheme 1) in which a zinc porphyrin is covalently linked through a peripheral aryl-amino group to 1,3,5-triazine that is functionalized by two glycine anchoring units. The ZnP-triazine-(gly)₂ sensitized solar cell showed a moderate PCE value of 4.72%. Interestingly, its photovoltaic performance was almost doubled reaching 7.34%, when a tertiary aryl-amine organic dye D (Scheme 1) with the donor-acceptor molecular architecture was used as co-sensitizer.

2. Experimental section

2.1. Materials and techniques

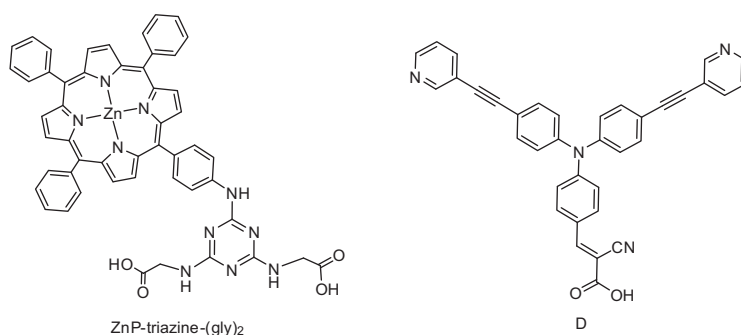
All manipulations were carried out using standard Schlenk techniques under nitrogen atmosphere. 2,4,6-Trichloro-1,3,5-triazine (cyanuric chloride), diisopropylethylamine (DIPEA), glycine

methylester hydrochloride, Zn(CH₃COO)₂·2H₂O, Na₂SO₄, KOH and other chemicals and solvents were purchased from usual commercial sources and used as received, unless otherwise stated. Tetrahydrofuran (THF) was freshly distilled from Na/benzophenone. 5-(4-Aminophenyl)-10,15,20-triphenyl-porphyrin H₂[TPP-NH₂] [19] were prepared according to literature procedures. The synthesis of compound D is described in SI.

Synthesis of 5-(4-{3,5-[glycine-methylester]triazinyl}-amino phenyl)-10,15,20-triphenyl-porphyrin (1): To a THF solution (2 mL) of cyanuric chloride (14.6 mg, 0.079 mmol) and DIPEA (17 μ L, 0.095 mmol) a THF solution (6 mL) of H₂[TPP-NH₂] (50 mg, 0.079 mmol) was added, under Ar at 0 °C. The mixture was stirred at 0 °C and, upon reaction completion (monitored by TLC), it was left to warm at room temperature. Next, a THF solution (4 mL) of glycine methyl ester hydrochloride (20 mg, 0.16 mmol) and DIPEA (33 μ L, 0.19 mmol) was added and the mixture was stirred at room temperature overnight. The volatiles were removed under reduced pressure and the residue was diluted in CH₂Cl₂ and purified by column chromatography (silica gel, CH₂Cl₂/MeOH 0–1%) resulting in a purple solid. This was transferred into a Schlenk flask under Ar and an excess of DIPEA (0.3 mL, 1.9 mmol) was added. After stirring the mixture at room temperature for 30 min, an excess of glycine methyl ester hydrochloride (100 mg, 0.79 mmol) was added and the mixture was heated at 80 °C in a closed system for 5 days. The volatiles were removed under reduced pressure and after dilution in CH₂Cl₂, the residue was purified by column chromatography (silica gel, CH₂Cl₂/MeOH 0–1%). Compound **1** was isolated as purple solid. Yield: 27 mg (38%). ¹H NMR (300 MHz, CDCl₃): δ_H (ppm) 8.94 (m, 3H), 8.85 (s, 5H), 8.22 (m, 6H), 8.16 (d, *J* = 8.4 Hz, 2H), 8.00 (s br, 3H), 7.76 (s, 9H), 5.93 (s br, 2H), 4.28 (s br, 4H), 3.80 (s, 6H), –2.76 (s, 2H). HRMS (MALDI-TOF): *m/z* calcd for C₅₃H₄₂N₁₀O₄, 882.3390 [M]⁺: found 882.3405. UV-vis (CH₂Cl₂), λ/nm ($\epsilon \times 10^{-3}/M^{-1} cm^{-1}$): 419 (788.2), 515 (32.2), 552 (17.0), 591 (9.7), 647 (8.3). Anal. Calcd for C₅₃H₄₂N₁₀O₄: C, 72.09; H, 4.79; N, 15.86. Found: C, 71.92; H, 4.86; N, 15.77.

2.2. Synthesis of 5-(4-{3,5-[glycine]-triazinyl}-aminophenyl)-10,15,20-triphenyl-porphyrin zinc or ZnP-triazine-(gly)₂(2): Metallation

To a CH₂Cl₂ solution (12 mL) of **1** (50 mg, 0.056 mmol) a 20-mL MeOH solution of Zn(CH₃COO)₂·2H₂O (125 mg, 0.56 mmol) was added and the reaction mixture was stirred at room temperature overnight. The organic phase was washed with H₂O (3 \times 10 mL), dried with Na₂SO₄ and the solvent was removed under reduced pressure. The crude product **1-Zn** was purified by column chromatography (silica gel, CH₂Cl₂/MeOH 0–1%) resulting in 49 mg of a purple solid (yield: 93%). ¹H NMR (300 MHz, CDCl₃): δ_H (ppm) 9.02 (s br, 2H), 8.95 (m, 6H), 8.22 (s br, 6H), 8.13 (d, *J* = 8.1 Hz,



Scheme 1.

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