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Photosensitizing triarylamine- and triazine-cored porphyrin dimers for dye-sensitized solar cells

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ABSTRACT

Two novel triarylamine- and triazine-cored porphyrin dimers were synthesized and investigated for their potential in dye-sensitized solar cells (DSSCs). Based on cyclic voltammetric analysis, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the target porphyrins were found to be in an appropriate range in the TiO_2-based DSSC systems. The device studies indicated the photovoltaic effects in the DSSCs based on both materials and the significant effect of their core units on the photovoltaic conversion efficiencies of the devices.

1. Introduction

In solar cell research and development, dye-sensitized solar cells (DSSCs) have achieved great attraction due to the ease of fabrication and cost-competitiveness compared with conventional silicon-based solar devices. The best solar-to-electric power conversion efficiency (PCE) of DSSCs of 12.3% has recently been obtained by the state-of-art donor-π-bridge-acceptor (D-π-A) sensitizers engaging zinc porphyrin core [1]. Owing to their large molar absorption coefficients, and amenability to structural modification allowing the tuning of the electrochemical and photophysical properties, porphyrins play important roles in natural photosynthesis and are gradually gained attention as sensitizers for DSSCs [2–4]. Furthermore, porphyrins have received a great deal interest in various optoelectronic applications, for example photovoltaic cells [5], organic light-emitting diodes (OLEDs) [6], and organic field-effect transistors (OFETs) [7].

In this study, we use porphyrin macrocycles as light harvesting antennae by attaching them via their *meso*-carbons on two of three peripheral sites of an electron donating triarylamine and an electron withdrawing core unit. The remaining site on each core unit is occupied by a carboxyl surface anchoring group in order to obtain the efficient electronic communication between the dye and the TiO_2. Based on this design, high light absorptivity due to the porphyrin antennae combined with efficient charge transfer, provided by the triarylamine and triazine core units, and the covalent attachment of the dyes on TiO_2 surface via the carboxyl group should give photovoltaic effect in the DSSCs based on these dyes. According to our recent studies [8], satisfactory solubility, suitable photophysical and electrochemical properties, sufficient stability upon device fabrication and photovoltaic effect were obtained from a corresponding three-pointed star architecture having three porphyrin rings attached on triarylamine and triazine core units. Therefore, this work aims to demonstrate the synthesis, investigation of photophysical and electrochemical properties, and evaluation of the potential use for dye-sensitized solar cells of this type of materials.

2. Results and discussion

2.1. Synthesis

The synthesis of triarylamine-cored porphyrin dimer started with Sonogashira coupling of compounds **1** [9] and **2** in the presence of bis(triphenylphosphine)palladium(II) dichloride, copper(I) iodide and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in tetrahydrofuran (THF) under nitrogen atmosphere at room temperature

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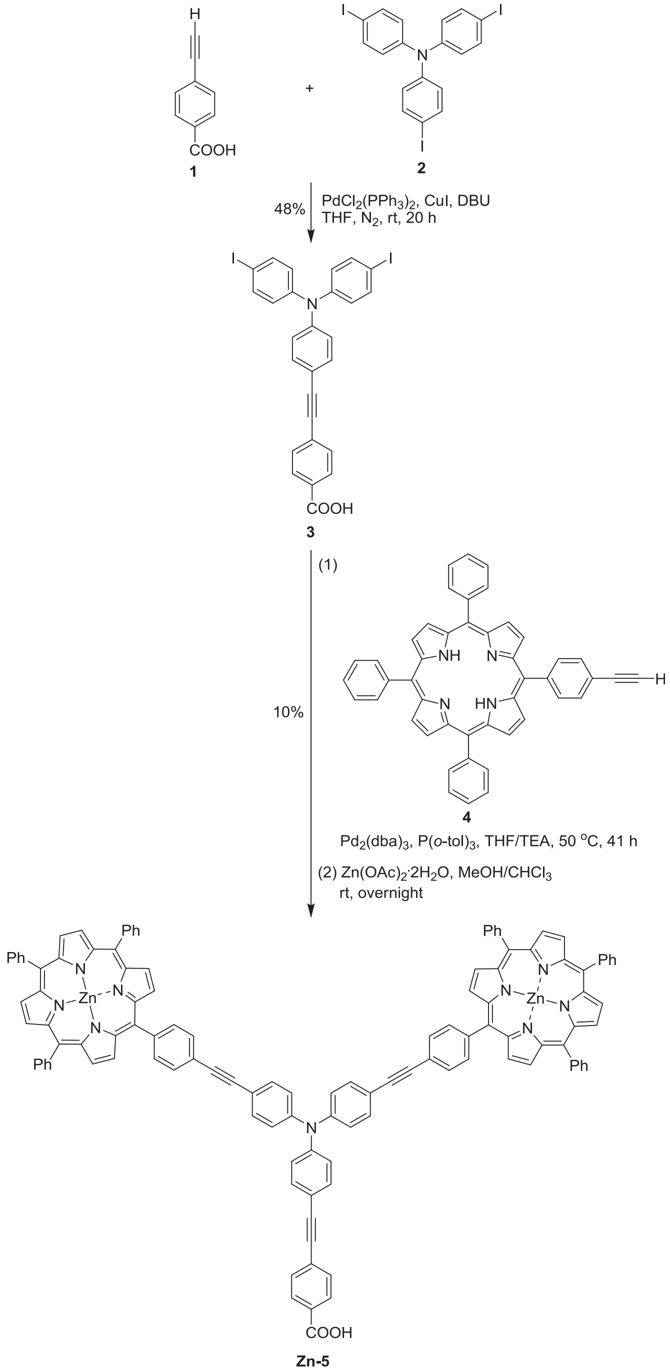
for 20 h, leading to **3** in 48% (Scheme 1) [10]. Then, **3** was coupled with **4** [8b] under catalysis of tris(dibenzylideneacetone)dipalladium(0) and tri(*o*-tolyl)phosphine in THF/(triethylamine) TEA under nitrogen atmosphere at 50 °C for 41 h [11], affording **5** in 12%. Compound **5** was Zn-metallated with $Zn(OAc)_2 \cdot 2H_2O$ in chloroform/methanol overnight [12], resulting in **Zn-5** in 83% yield. A mass spectrum of compound **5** exhibited a molecular ion peak at *m*/*z* 1663.882, while that of **Zn-5** showed a molecular ion peak at *m*/*z* 1791.114. The absence of the emission of **Zn-5** at ~720 nm upon photoexcitation at its maximum absorption, together with the disappearance of the singlet signal of the N–H internal proton of the freebase porphyrin in a range from −2 to −3 ppm in its ^1H nuclear magnetic resonance (NMR) spectrum indicated the complete metallation of the porphyrin ring. Solubility of **Zn-5** was found to be higher than 20 mg/mL in several common organic solvents, such as CH_2Cl_2, $CHCl_3$, toluene, THF, etc., allowing the preparation of DSSCs by our routine wet process.



Scheme 1. Synthesis of triarylamine-cored porphyrin dimer **Zn-5**.

The synthesis of triazine-cored porphyrin dimer relied on arylamination of compound **6** [13] and cyanuric chloride in the presence of K_2CO_3 in THF at room temperature for 10 h (Scheme 2) [14]. The separation of the freebase dimer from other arylamination products and impurities was efficiently achieved by a three-column process: firstly, a silica column was used to remove unreacted compound **6** and other polar byproducts; secondly, sized-exclusion chromatography (SEC) separated the freebase dimer from unavoidable mono- and tri-substituted byproducts; and finally, another silica column was utilized to remove of impurities possibly coming from SEC. The formation of the freebase porphyrin dimer was confirmed by it mass spectrum showing a molecular ion peaks at *m*/*z* 1371.742. The subsequent Zn-metallation of compound **7** with $Zn(OAc)_2 \cdot 2H_2O$ [12] led to compound **Zn-7** quantitatively. The disappearance of the characteristic singlet signal of the N–H internal proton in its ^1H NMR spectrum and an emission peak at ~720 nm upon the excitation at its maximum absorption indicated the completion of the reaction, which is similar to those observed for **Zn-5**. Moreover, the formation of **Zn-7** was proved by matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) that exhibited a molecular ion peak at *m*/*z* 1498.714. After that, another arylamination of compound **Zn-7** was performed in the presence of **8** [15] and K_2CO_3 in refluxing THF for 8 h to obtain **Zn-9** in 47% yield. Mass spectrometry confirmed the formation of **Zn-9** by showing its molecular ion peak at *m*/*z* 1599.636. Like **Zn-5**, the solubility on **Zn-9** was found to be higher than 20 mg/mL in several common organic solvent, *e.g.* CH_2Cl_2, $CHCl_3$, toluene, THF, etc.

2.2. Electrochemistry

Shown in Fig. 1 are cyclic voltammograms obtained with a glassy carbon electrode at a scan rate of 100 mV s^{-1}. Curves A and B, recorded for the oxidation of 0.5 mM compound **Zn-5** in a dichloromethane solution containing 0.10 M (tetra-*n*-butylammoniumhexafluorophospate) TBAP, reveal two successive quasireversible redox couples with the first anodic and cathodic peak potentials of 0.50 V and 0.41 V; and the second anodic and cathodic peak potentials of 0.81 V and 0.72 V, respectively. The differences between the anodic and cathodic peak potential (ΔE_p) of both redox couples are approximately 90 mV, implying that each oxidation process in medium-polar dichloromethane is possibly involved with one electron. In voltammetric theory, ΔE_p for a reversible redox couple has a value close to 59/n mV at 25 °C [16]. Curve B shows that no additional peak corresponding to the oxidation can be observed in the accessible potential window of this system. This electrochemical behaviour of compound **Zn-5** is expected for zinc porphyrin-based compounds attached to arylamine units [1,17]. According to the previously reported publication that investigated the spectral and electrochemical properties of triarylamine-bound zinc porphyrin and its related compounds in a tetrahydrofuran solution at −20 °C with thin-layer spectroelectrochemistry and cyclic voltammetry, the first oxidation occurs at the triarylamine moiety and the second one corresponds to the porphyrin oxidation [17]. Despite slight differences in the compound structure and experimental conditions (*i.e.*, studied temperature, solvent, and electrolyte), the oxidation of these zinc porphyrins takes place in the same potential region with the deviation of the peak positions less than 300 mV.

In the reduction domain (curve D), where the potential was negatively scanned from 0.00 V to −2.10 V, two cathodic waves of