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Branched and linear alkoxy chains-wrapped push-pull porphyrins for developing efficient dye-sensitized solar cells

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ABSTRACT

Four alkoxy-wrapped push-pull porphyrin dyes containing the phenothiazine derived donor and the ethynylbenzoic acid acceptor have been designed, synthesized and used as sensitizers for fabricating efficient dye-sensitized solar cells (DSSCs). Branched or linear alkoxy chains were introduced to the *ortho*-positions of the *meso*-phenyl moieties to suppress the dye aggregation and charge recombination. The effect of alkoxy chains were investigated in the absence and presence of an additional electron-withdrawing benzothiadiazole unit. In the former cases, almost identical photovoltaic efficiencies of ~8.3% were achieved for both the branched and the linear alkoxy chains, while in the latter cases, the planar benzothiadiazole unit induces serious dye aggregation and charge recombination, resulting in lower efficiencies of 6.46% and 7.50% for the linear and branched chains, respectively, even though broader absorption was achieved. The relatively higher efficiency achieved for the dyes with branched chains may be related to the better effect of suppressing the dye aggregation and charge recombination. Furthermore, the coadsorption approach was employed, and a highest efficiency of 9.62% was achieved for the dye that features branched chains and the benzothiadiazole unit. These results compose a novel approach for developing efficient DSSCs by combining the coadsorbent with a porphyrin dye containing both the additional benzothiadiazole acceptor and branched alkoxy chains.

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1. Introduction

Dye-sensitized solar cells (DSSCs), as one class of promising techniques for solar-to-electricity conversion, have aroused intensive research interest over the past two decades, showing the advantages of low manufacturing cost and decent photovoltaic efficiency [1–3]. As the “light-harvester”, the sensitizer plays a crucial role in DSSCs. Since the pioneering work on ruthenium-complex-sensitized solar cells by Grätzel and co-workers [1], great efforts have been devoted to seeking for efficient, low-cost, stable and eco-friendly sensitizers [4–11].

As a class of natural dyes found in the photosynthesis systems, porphyrins have inspired chemists to exploit their applications in DSSC devices [12]. Featured with relatively strong absorption, porphyrin dyes often exhibit excellent light harvesting. In addition, up to four *meso*-positions and eight β -positions are available for

structural modification [13,14]. Thus, many porphyrin derivatives have been synthesized and demonstrated to be good candidates as DSSC sensitizers [15–21], and efficiencies up to *ca.* 13% have been achieved using cobalt-based electrolytes [22,23].

It is noteworthy that most of the efficient examples of porphyrin dyes have been designed using the “alkoxy-wrapped” push-pull structures [24,25]. Specifically, the porphyrin cores are tethered with an electron donor and an electron acceptor/anchoring group at two opposite *meso*-positions, respectively, thus promoting the electron injection process. Meanwhile, the other two *meso*-positions are substituted with phenyl moieties with long alkoxy chains attached at the *ortho* positions with the purpose to improve the solubility and reduce the π - π aggregation of the dyes, as well as preventing the unfavorable charge recombination between the injected electrons in TiO₂ and the oxidized redox mediator in the electrolyte, and the photovoltaic performances of the dyes have been demonstrated to be related to the lengths of alkoxy chains [24]. Based on these backgrounds, it is envisioned that branched alkoxy chains may be bulkier than linear ones and may be more effective in preventing aggregation and in blocking the oxidized

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redox mediator from approaching TiO₂ [26–28], and thus herein, we will focus on investigating the effects of linear and branched alkoxy chains on the photovoltaic behavior of DSSCs based on porphyrin dyes.

Four porphyrins **XW18–XW21** (Fig. 1) were thus designed and used as DSSC dyes. All of them possess the identical phenothiazine derived donor, which has been demonstrated to be an efficient donor by us and other groups [29–32]. **XW18** and **XW19** contain linear octyloxy and branched 2-ethylhexyloxy chains, respectively. On this basis, a benzothiadiazole (BTD) unit was further introduced as an additional electron withdrawing group for broadening the spectral response [33]. Thus, **XW20** and **XW21** were also designed and synthesized. As a result, the cells based on **XW18–XW21** exhibit photovoltaic efficiencies of 8.32%, 8.28%, 6.46%, and 7.50%, respectively. After coadsorption with CDCA, **XW21** exhibits a highest PCE of 9.62% among the four dyes. These results indicate that the aggravated dye aggregation effect induced by the BTD unit may be well suppressed by the coexistence of the branched alkoxy chains and the coadsorbent, and thus high DSSC efficiencies may be achieved.

2. Experimental section

2.1. Materials and instrumentation

All reagents and solvents were obtained from commercial sources and used as received unless otherwise noted. DMF was dried over 4 Å molecular sieves. Tetrabutylammonium hexafluorophosphate (TBAPF₆) was vacuum-dried for 48 h. The transparent FTO conducting glass (fluorine-doped SnO₂, transmission >90% in the visible range, sheet resistance 15Ω/square) and the TiO₂ paste were purchased from Geao Science and Educational Co. Ltd. The FTO conducting glass was washed with a detergent solution, deionized water, acetone and ethanol successively under ultrasonication for 20 min before use.

¹H NMR and ¹³C NMR spectra were obtained using a Bruker AM 400 spectrometer. HRMS measurements were performed using a Waters LCT Premier XE spectrometer. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was measured using a Shimadzu-Kratos model Axima CFR + mass spectrometer with dithranol as the matrix. UV–Vis

absorption spectra were recorded on a Varian Cary 100 spectrophotometer and fluorescence spectra were recorded on a Varian Cray Eclipse fluorescence spectrophotometer. The cyclic voltammograms of the dyes were obtained in acetonitrile with a Versastat II electrochemical workstation (Princeton Applied Research) using 0.1 M TBAPF₆ (Aldrich) as the supporting electrolyte, the sensitizer attached to a nanocrystalline TiO₂ film deposited on the conducting FTO glass as the working electrode, a platinum wire as the counter electrode, and a regular calomel electrode in saturated KCl solution as the reference electrode. The scan rate was fixed at 100 mV s⁻¹.

Photovoltaic measurements were performed by employing an AM 1.5 solar simulator equipped with a 300 W xenon lamp (model no. 91160, Oriel). The power of the simulated light was calibrated to 100 mW cm⁻² using a Newport Oriel PV reference cell system (model 91150 V). *J–V* curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a model 2400 source meter (Keithley Instruments, Inc. USA). The voltage step and delay time of the photocurrent were 10 mV and 40 ms, respectively. Action spectra of the incident monochromatic photon-to-electron conversion efficiency (IPCE) for the solar cells were obtained with a Newport-74125 system (Newport Instruments). The intensity of monochromatic light was measured with a Si detector (Newport-71640). The electrochemical impedance spectroscopy (EIS) measurements of all the DSSCs were performed using a Zahner IM6e Impedance Analyzer (ZAHNER-Elektrik GmbH & CoKG, Kronach, Germany), with the frequency range of 0.1 Hz–100 kHz and the alternative signal of 10 mV. The ZSimpWin software was used to fit the experimental EIS data of the DSSCs.

2.2. Syntheses of the dyes

Compounds **1a–5a** and **1b–2b** were synthesized according to reported methods [34–37].

2.2.1. Synthesis of compound **3b**

To a degassed solution of compound **2b** (3.63 g, 10.0 mmol) and dipyrromethane (1.46 g, 10.0 mmol) in CH₂Cl₂ (1.5 L) was added trifluoroacetic acid (0.75 mL, 10 mmol). After the solution was stirred at room temperature under dinitrogen for 4 h in the dark, DDQ (3.4 g, 15 mmol) was added and the mixture was stirred for an

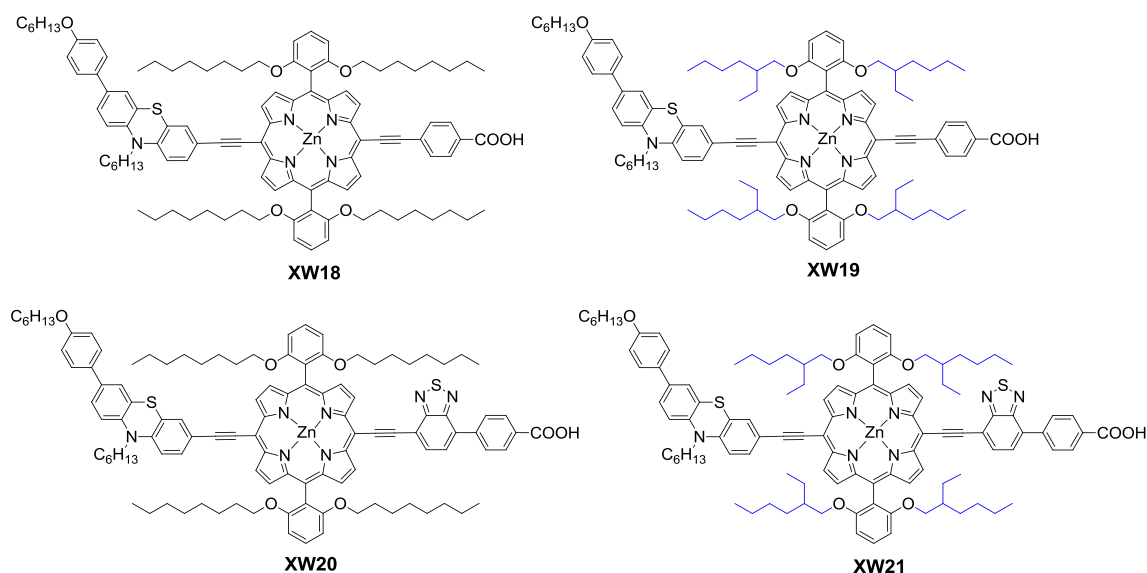


Fig. 1. Molecular structures of dyes **XW18–XW21**.

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