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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  $\beta$ -positions are available for

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http://dx.doi.org/10.1016/j.dyepig.2016.10.041 0143-7208/© 2016 Elsevier Ltd. All rights reserved. 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  $\pi$ - $\pi$  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

2

redox mediator from approaching  $TiO_2$  [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 dves. 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 hexa-fluorophosphate (TBAPF<sub>6</sub>) was vacuum-dried for 48 h. The transparent FTO conducting glass (fluorine-doped SnO<sub>2</sub>, transmission >90% in the visible range, sheet resistance 15Ω/square) and the TiO<sub>2</sub> 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.

<sup>1</sup>H NMR and <sup>13</sup>C 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 TBAPF<sub>6</sub> (Aldrich) as the supporting electrolyte, the sensitizer attached to a nanocrystalline TiO<sub>2</sub> 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<sup>-1</sup>.

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  $\rm cm^{-2}$  using a Newport Oriel PV reference cell system (model 91150 V). *I–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  $CH_2Cl_2$  (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.

additional 1 h. The mixture was basified with Et<sub>3</sub>N (3 mL) and filtered with silica. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> (2:1, v:v) as the eluent. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/MeOH gave compound **3b** as purple powders (1.3 g, yield: 27%). mp 70–72 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.11 (s, 2H, *meso*-H), 9.23 (d, *J* = 4.8 Hz, 4H, pyrrolic), 8.96 (d, *J* = 4.8 Hz, 4H, pyrrolic), 7.71 (t, *J* = 8.4 Hz, 2H, phenyl), 7.02 (d, *J* = 8.4 Hz, 4H, phenyl), 3.79–3.66 (m, 8H), 0.88–0.76 (m, 4H), 0.45–0.29 (m, 16H), 0.29–0.18 (m, 16H), 0.18–0.12 (m, 12H), 0.03 to –0.04 (m, 12H), -2.99 (s, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  160.24, 147.62, 144.88, 130.58, 130.28, 129.92, 119.87, 111.40, 104.94, 103.76, 70.90, 38.44, 29.71, 29.49, 28.13, 22.77, 22.11, 13.24, 10.29. HRMS (ESI, *m/z*): [M+H]<sup>+</sup> calcd for C<sub>64</sub>H<sub>87</sub>N<sub>4</sub>O<sub>4</sub>, 975.6722; found, 975.6720.

### 2.2.2. Synthesis of compound 4b

To a stirred solution of porphyrin **3b** (2.0 g, 2.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (300 mL) was added a solution of NBS (730 mg, 4.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL). After the reaction was quenched with acetone (15 mL), the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> (3:1, v:v) as the eluent. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/MeOH gave **4b** as purple powders (2.1 g, yield: 91%). mp 98–100 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.48 (d, *J* = 4.8 Hz, 4H, pyrrolic), 8.78 (d, *J* = 4.4 Hz, 4H, pyrrolic), 7.70 (t, *J* = 8.4 Hz, 2H, phenyl), 6.98 (d, *J* = 8.4 Hz, 4H, phenyl), 3.74 (m, 8H), 0.97–0.73 (m, 4H), 0.48–0.30 (m, 16H), 0.30–0.13 (m, 28H), 0.06–0.00 (m, 12H), -2.58 (s, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  160.04, 130.23, 119.78, 114.10, 104.70, 102.13, 70.86, 38.53, 29.61, 28.15, 22.88, 22.16, 13.29, 10.41. HRMS (ESI, *m/z*): [M+Na]<sup>+</sup> calcd for C<sub>64</sub>H<sub>84</sub>Br<sub>2</sub>N<sub>4</sub>NaO<sub>4</sub>, 1153.4752; found, 1153.4748.

### 2.2.3. Synthesis of compound 5b

To a solution of **4b** (1.8 g, 1.6 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (300 mL) was added Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (7.0 g, 32 mmol) in MeOH (100 mL). The mixture was refluxed for 12 h. Then the mixture was poured into water, extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with water and dried over Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvents gave the target product **5b** as purple powders (1.6 g, yield: 87%). mp 145–147 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.62 (d, *J* = 4.8 Hz, 4H, pyrrolic), 8.89 (d, *J* = 4.8 Hz, 4H, pyrrolic), 7.70 (t, *J* = 8.4 Hz, 2H, phenyl), 6.99 (d, *J* = 8.4 Hz, 4H, phenyl), 3.84–3.63 (m, 8H), 0.89–0.80 (m, 4H), 0.46–0.28 (m, 16H), 0.28–0.10 (m, 28H), 0.06–0.00 (m, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  160.03, 151.48, 149.69, 132.75, 132.63, 130.03, 120.41, 115.06, 104.74, 103.84, 70.82, 53.39, 38.55, 29.60, 28.14, 22.90, 22.20, 13.34, 10.43. HRMS (ESI, *m/z*): [M+Na]<sup>+</sup> calcd for C<sub>64</sub>H<sub>84</sub>Br<sub>2</sub>N<sub>4</sub>NaO<sub>4</sub>, 1153.4752; found, 1153.4748.

### 2.2.4. Syntheses of compounds 6a and 6b

### General synthetic procedures for **6a** and **6b**.

To a degassed solution of compound **5a** or **5b** (600 mg, 0.50 mmol) and 3-ethynyl-10-hexyl-7-(4-(hexyloxy)phenyl)-10*H*-phenothiazine (290 mg, 0.60 mmol) in THF (250 mL) and Et<sub>3</sub>N (50 mL) were added Pd<sub>2</sub>(dba)<sub>3</sub> (230 mg, 0.25 mmol) and AsPh<sub>3</sub> (306 mg, 1.0 mmol). The mixture was degassed, re-filled with N<sub>2</sub>, and allowed to stir at 60 °C for 6 h, then the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> (5:2, v:v) as the eluent. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/MeOH gave compound **6a** or **6b** as dark green pastes.

**6a.** 104 mg, yield: 13%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.65 (d, J = 4.8 Hz, 2H, pyrrolic), 9.60 (d, J = 4.8 Hz, 2H, pyrrolic), 8.88 (d, J = 4.8 Hz, 2H, pyrrolic), 8.85 (d, J = 4.8 Hz, 2H, pyrrolic), 7.79–7.73 (m, 2H, phenyl), 7.70 (t, J = 8.4 Hz, 2H, phenyl), 7.46 (d, J = 8.8 Hz,

2H, phenyl), 7.40–7.33 (m, 2H, phenyl), 7.01 (d, J = 8.4 Hz, 5H, phenyl), 6.96 (d, J = 8.0 Hz, 1H, phenyl), 6.93 (d, J = 8.8 Hz, 2H, phenyl), 3.97 (t, J = 6.8 Hz, 4H), 3.85 (t, J = 6.4 Hz, 8H), 1.92 (s, 2H), 1.84–1.74 (m, 2H), 1.57–1.44 (m, 4H), 1.39–1.30 (m, 8H), 1.02–0.92 (m, 12H), 0.85–0.76 (m, 8H), 0.66–0.56 (m, 9H), 0.56–0.44 (m, 28H), 0.44–0.34 (m, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.91, 158.43, 152.23, 151.34, 150.53, 149.03, 145.08, 143.32, 135.55, 132.54, 132.32, 132.21, 130.76, 130.03, 129.89, 127.41, 125.50, 125.44, 124.58, 124.44, 120.76, 118.17, 115.60, 115.15, 115.06, 114.77, 105.17, 104.77, 99.96, 95.03, 92.76, 68.61, 68.08, 47.75, 31.60, 31.51, 31.33, 31.26, 29.71, 29.22, 28.66, 28.61, 28.57, 26.86, 26.69, 25.72, 25.24, 22.65, 22.62, 22.25, 14.06, 14.04, 13.82. MS (MALDI-TOF, *m/z*): [M+H] calcd for C<sub>96</sub>H<sub>119</sub>BrN<sub>5</sub>O<sub>5</sub>SZn, 1596.7407; found, 1596.202.

**6b.** 125 mg, yield: 15%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.65 (d, J = 4.8 Hz, 2H, pyrrolic), 9.58 (d, J = 4.8 Hz, 2H, pyrrolic), 8.89 (d, *J* = 4.4 Hz, 2H, pyrrolic), 8.85 (d, *J* = 4.8 Hz, 2H, pyrrolic), 7.81–7.74 (m, 2H, phenyl), 7.71 (t, *J* = 8.4 Hz, 2H, phenyl), 7.48 (d, *J* = 8.8 Hz, 2H, phenyl), 7.41–7.34 (m, 2H, phenyl), 7.06–6.91 (m, 8H, phenyl), 4.03-3.93 (m, 4H), 3.82-3.68 (m, 8H), 1.98-1.87 (m, 2H), 1.85-1.75 (m, 2H), 1.59-1.44 (m, 4H), 1.43-1.30 (m, 12H), 0.92 (t, J = 6.8 Hz, 1.43-1.30 (m, 12H))6H), 0.46–0.31 (m, 16H), 0.31–0.12 (m, 28H), 0.08–0.01 (m, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.02, 158.48, 152.25, 151.45, 150.63, 149.02, 145.11, 143.31, 135.59, 132.39, 132.34, 132.22, 130.75, 130.61, 130.07, 129.91, 127.44, 125.53, 125.46, 124.62, 124.43, 120.50, 118.22, 115.62, 115.21, 114.78, 104.76, 99.84, 94.97, 92.76, 70.84, 70.79, 68.08, 47.74, 38.54, 31.60, 31.50, 29.60, 29.58, 29.24, 28.16, 26.87, 26.69, 25.73, 22.89, 22.64, 22.62, 22.21, 14.05, 14.03, 13.39, 10.44. HRMS (ESI, m/z):  $[M+Na]^+$  calcd for  $C_{96}H_{118}BrN_5NaO_5SZn$ , 1618.7221: found. 1618.7203.

### 2.2.5. Synthesis of compounds **7a** and **7b**

General synthetic procedures for **7a** and **7b**.

To a degassed solution of compound **6a** or **6b** (100 mg, 0.063 mmol) and methyl 4-ethynylbenzoate (30 mg, 0.19 mmol) in dry THF (30 mL) and Et<sub>3</sub>N (6 mL) were added Pd(PPh<sub>3</sub>)<sub>4</sub> (36 mg, 0.031 mmol) and Cul (6 mg, 0.031 mmol) under a nitrogen atmosphere. The mixture was degassed, re-filled with N<sub>2</sub>, and allowed to stir at 60 °C for 16 h, then the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> (3:2, v:v) as eluent. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/MeOH gave compound **7a** or **7b** as dark green powders.

**7a**. 43 mg, yield: 41%. mp 80–82 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.63 (d, I = 4.4 Hz, 2H, pyrrolic), 9.62 (d, I = 4.4 Hz, 2H, pyrrolic), 8.87 (d, J = 4.8 Hz, 2H, pyrrolic), 8.85 (d, J = 4.4 Hz, 2H, pyrrolic), 8.14 (d, J = 8.4 Hz, 2H, phenyl), 7.97 (d, J = 8.4 Hz, 2H, phenyl), 7.81–7.73 (m, 2H, phenyl), 7.71 (t, J = 8.4 Hz, 2H, phenyl), 7.47 (d, *J* = 8.8 Hz, 2H, phenyl), 7.41–7.32 (m, 2H, phenyl), 7.06–6.90 (m, 8H, phenyl), 4.04–3.91 (m, 7H), 3.86 (t, J = 6.4 Hz, 8H), 1.97–1.86 (m, 2H), 1.85-1.75 (m, 2H), 1.51-1.45 (m, 4H), 1.40-1.31 (m, 8H), 1.01-0.91 (m, 12H), 0.88-0.73 (m, 9H), 0.69-0.58 (m, 8H), 0.58-0.46 (m, 28H), 0.45-0.34 (m, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 166.54, 159.92, 158.40, 151.70, 151.41, 150.63, 150.51, 145.04, 143.26, 135.52, 132.18, 132.02, 131.73, 130.90, 130.74, 130.64, 130.33, 130.00, 129.84, 129.48, 129.02, 128.65, 127.38, 125.49, 125.40, 124.50, 124.38, 120.83, 118.10, 115.58, 115.43, 115.11, 114.76, 105.17, 101.15, 98.84, 96.65, 95.31, 94.61, 93.00, 68.63, 68.07, 52.17, 48.67, 47.74, 31.60, 31.50, 31.37, 29.71, 29.21, 28.71, 28.65, 28.61, 26.84, 26.68, 25.71, 25.26, 22.65, 22.62, 22.27, 14.05, 14.03, 13.83. HRMS (ESI, m/z):  $[M+Na]^+$  calcd for  $C_{106}H_{125}N_5NaO_7SZn$ , 1698.8483; found, 1698.8543.

**7b.** 38 mg, yield: 36%. mp 69–71 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.63 (d, *J* = 4.4 Hz, 4H, pyrrolic), 8.88 (d, *J* = 4.4 Hz, 2H, pyrrolic), 8.86 (d, *J* = 4.8 Hz, 2H, pyrrolic), 8.21 (d, *J* = 8.4 Hz, 2H, phenyl), 8.04 (d, *J* = 8.4 Hz, 2H, phenyl), 7.82–7.74 (m, 2H, phenyl), 7.71 (t,

4

*J* = 8.4 Hz, 2H, phenyl), 7.48 (d, *J* = 8.0 Hz, 2H, phenyl), 7.41–7.33 (m, 2H, phenyl), 7.01 (d, *J* = 8.8 Hz, 5H, phenyl), 6.98–6.91 (m, 3H, phenyl), 4.04–3.87 (m, 7H), 3.86–3.66 (m, 8H), 1.97–1.87 (m, 2H), 1.86–1.74 (m, 2H), 1.58–1.44 (m, 4H), 1.39–1.31 (m, 8H), 0.96–0.80 (m, 10H), 0.49–0.32 (m, 16H), 0.31–0.12 (m, 28H), 0.10–0.01 (m, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  166.68, 160.02, 158.49, 151.73, 151.46, 150.79, 150.66, 145.17, 143.29, 135.61, 132.22, 132.14, 131.84, 131.21, 130.81, 130.54, 130.16, 130.10, 129.90, 129.77, 129.34, 128.99, 127.45, 125.54, 125.46, 124.61, 124.41, 120.52, 118.16, 115.70, 115.64, 115.21, 114.79, 104.79, 101.20, 98.79, 96.59, 95.35, 94.72, 92.87, 70.83, 68.09, 52.22, 47.75, 38.57, 31.60, 31.51, 29.71, 29.60, 29.24, 28.20, 26.87, 26.69, 25.73, 22.91, 22.65, 22.62, 22.25, 14.06, 14.04, 13.43, 10.44. HRMS (ESI, *m/z*): [M+H]<sup>+</sup> calcd for C<sub>106</sub>H<sub>126</sub>N<sub>5</sub>O<sub>7</sub>SZn, 1676.8664; found, 1676.8691.

### 2.2.6. Synthesis of compounds 7c and 7d

General synthetic procedures for 7c and 7d.

Compound **7c** and **7d** were prepared according to the similar procedure as described for **7a** and **7b** by using methyl 4-(7-ethynylbenzo[c] [1,2,5]thiadiazol-4-yl)benzoate (37 mg, 0.13 mmol) instead of methyl 4-ethynylbenzoate, and dry THF/ piperidine (20 mL/1 mL) was used as the solvent.

7c. 34 mg, yield: 30%.  $^1\text{H}$  NMR (400 MHz, CDCl\_3)  $\delta$  9.93 (d, *J* = 25.4 Hz, 2H, pyrrolic), 9.60 (d, *J* = 12.4 Hz, 2H, pyrrolic), 8.94 (s, 2H, pyrrolic), 8.87 (s, 2H, pyrrolic), 8.25-7.82 (m, 5H, phenyl), 7.80–7.60 (m, 5H, phenyl), 7.48 (d, J = 8.0 Hz, 2H, phenyl), 7.41–7.31 (m, 2H, phenyl), 7.13-6.85 (m, 8H, phenyl), 4.06-3.78 (m, 15H), 1.98-1.86 (m, 2H), 1.86-1.72 (m, 2H), 1.50-1.43 (m, 4H), 1.41-1.32 (m, 8H), 1.12–0.97 (m, 8H), 0.96–0.88 (m, 6H), 0.86–0.72 (m, 8H), 0.70–0.36 (m, 44H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 166.62, 159.97, 158.45, 155.71, 152.51, 152.00, 151.29, 150.63, 150.52, 145.01, 143.26, 140.47, 135.52, 132.22, 131.64, 130.82, 130.75, 129.94, 129.84, 129.25, 129.01, 128.25, 127.84, 127.42, 125.49, 125.41, 124.45, 124.38, 120.84, 118.05, 117.90, 115.62, 115.57, 115.08, 114.79, 105.17, 101.55, 101.30, 98.88, 95.30, 92.99, 92.32, 68.70, 68.10, 53.42, 52.16, 47.77, 31.93, 31.61, 31.51, 31.38, 29.70, 29.32, 29.24, 28.74, 28.69, 28.66, 26.84, 26.69, 25.73, 25.31, 22.66, 22.62, 22.26, 14.13, 14.06, 14.04, 13.81. MS (MALDI-TOF, *m*/*z*): [M+H] calcd for C<sub>112</sub>H<sub>128</sub>N<sub>7</sub>O<sub>7</sub>S<sub>2</sub>Zn, 1810.8608; found, 1810.573.

**7d**. 31 mg, yield: 27%. mp 85–87 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.99 (s, 2H, pyrrolic), 9.63 (s, 2H, pyrrolic), 8.94 (d, *J* = 4.0 Hz, 2H, pyrrolic), 8.86 (d, *J* = 3.2 Hz, 2H, pyrrolic), 8.28 (d, *J* = 6.8 Hz, 1H, phenyl), 8.24 (d, J = 8.0 Hz, 2H, phenyl), 8.16 (d, J = 7.6 Hz, 2H, phenyl), 7.94 (d, *J* = 7.2 Hz, 1H, phenyl), 7.83–7.64 (m, 4H, phenyl), 7.48 (d, J = 8.0 Hz, 2H, phenyl), 7.42–7.33 (m, 2H, phenyl), 7.06-6.92 (m, 8H, phenyl), 4.05-3.91 (m, 7H), 3.86-3.66 (m, 8H), 1.97-1.87 (m, 2H), 1.85-1.75 (m, 2H), 1.41-1.32 (m, 8H), 0.97-0.89 (m, 8H), 0.46-0.34 (m, 16H), 0.33-0.21 (m, 16H), 0.21-0.13 (m, 12H), 0.10-0.01 (m, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 166.84, 160.05, 158.52, 156.12, 153.20, 152.13, 151.40, 150.85, 150.74, 145.19, 143.30, 141.55, 135.62, 132.39, 132.25, 131.77, 131.14, 130.83, 130.70, 130.55, 130.11, 129.90, 129.85, 129.71, 129.10, 128.54, 127.47, 125.55, 125.48, 124.62, 124.43, 120.58, 118.42, 118.16, 115.89, 115.64, 115.22, 114.81, 104.84, 101.72, 101.43, 98.86, 95.42, 92.90, 92.16, 70.88, 68.10, 52.23, 47.76, 38.57, 31.61, 31.51, 29.71, 29.62, 29.25, 28.19, 26.88, 26.69, 25.74, 22.93, 22.65, 22.62, 22.24, 14.06, 14.04, 13.44, 10.45. MS (MALDI-TOF, m/z): [M+H] calcd for C<sub>112</sub>H<sub>128</sub>N<sub>7</sub>O<sub>7</sub>S<sub>2</sub>Zn, 1810.8608; found, 1810.238.

### 2.2.7. Syntheses of XW18-XW21

### General synthetic procedures for XW18-XW21.

To the respective solution of **7a-7d** (27 mg for **7a** or **7b** and 29 mg for **7c** or **7d**, 0.016 mmol) in THF (20 mL) was added LiOH $\cdot$ H<sub>2</sub>O (30 mg, 0.71 mmol) in H<sub>2</sub>O (2 mL). The mixture was degassed, re-filled with N<sub>2</sub>, and allowed to stir at 60 °C for 12 h.

Then water was added and the organic phase was extracted with  $CH_2Cl_2$ . After evaporation of the solvents, the residue was purified by column chromatography on silica gel using  $CH_2Cl_2/MeOH$  (20:1, v:v) as eluent. Recrystallization from  $CH_2Cl_2/MeOH$  gave the target products.

**XW18**: dark green powders, 22 mg, yield: 83%. mp 220–222 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>: DMSO- $d_6 = 1:2$ )  $\delta$  12.90 (s, 1H, -COOH), 9.55 (d, J = 4.8 Hz, 2H, pyrrolic), 9.54 (d, J = 4.8 Hz, 2H, pyrrolic), 8.75 (d, J = 4.4 Hz, 2H, phenyl), 8.73 (d, J = 4.4 Hz, 2H, phenyl), 8.14–8.09 (m, 2H, phenyl), 8.07 (d, J = 8.4 Hz, 2H, phenyl), 7.81 (d, J = 8.4 Hz, 1H, phenyl), 7.72 (t, J = 8.4 Hz, 3H, phenyl), 7.50 (d, J = 8.8 Hz, 2H, phenyl), 7.72 (t, J = 8.4 Hz, 3H, phenyl), 7.50 (d, J = 8.8 Hz, 2H, phenyl), 7.09–7.02 (m, 5H, phenyl), 6.94 (d, J = 8.8 Hz, 2H, phenyl), 4.02–3.94 (m, 4H), 3.88 (t, J = 6.1 Hz, 8H), 1.09–1.81 (m, 2H), 1.80–1.71 (m, 2H), 1.55–1.42 (m, 4H), 1.38–1.33 (m, 8H), 1.04–0.93 (m, 16H), 0.92–0.89 (m, 5H), 0.84–0.77 (m, 8H), 0.68–0.63 (m, 12H), 0.63–0.56 (m, 16H), 0.51–0.38 (m, 9H). HRMS (ESI, m/z):  $[M+Na]^+$  calcd for C<sub>105</sub>H<sub>123</sub>N<sub>5</sub>NaO<sub>7</sub>SZn, 1684.8327; found, 1684.8343.

**XW19**: dark green powders, 21 mg, yield: 79%. mp 195–197 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>: DMSO- $d_6 = 1: 2$ )  $\delta$  12.87 (s, 1H, -COOH), 9.60–9.45 (m, 4H, pyrrolic), 8.80–8.65 (m, 4H, pyrrolic), 8.18 (d, J = 8.4 Hz, 2H, phenyl), 8.13–8.09 (m, 1H, phenyl), 8.07 (d, J = 8.0 Hz, 2H, phenyl), 7.81 (d, J = 8.4 Hz, 1H, phenyl), 7.72 (t, J = 8.4 Hz, 3H, phenyl), 7.51 (d, J = 8.4 Hz, 2H, phenyl), 7.46–7.32 (m, 2H, phenyl), 7.14 (d, J = 8.8 Hz, 1H, phenyl), 7.05 (d, J = 8.8 Hz, 5H, phenyl), 6.94 (d, J = 8.8 Hz, 2H, phenyl), 3.97 (t, J = 6.4 Hz, 4H), 3.87–3.62 (m, 8H), 1.92–1.81 (m, 2H), 1.80–1.70 (m, 2H), 1.57–1.42 (m, 4H), 1.41–1.29 (m, 8H), 0.97–0.83 (m, 10H), 0.68–0.38 (m, 24H), 0.38–0.13 (m, 32H). HRMS (ESI, m/z):  $[M+Na]^+$  calcd for C<sub>105</sub>H<sub>123</sub>N<sub>5</sub>NaO<sub>7</sub>SZn, 1684.8327; found, 1684.8315.

**XW20**: brown powders, 23 mg, yield: 80%. mp 239–341 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>: DMSO- $d_6 = 1: 2$ )  $\delta$  12.93 (s, 1H, -COOH), 9.91 (d, *J* = 4.4 Hz, 2H, pyrrolic), 9.54 (d, *J* = 4.0 Hz, 2H, pyrrolic), 8.79 (d, *J* = 2.8 Hz, 2H, pyrrolic), 8.71 (d, *J* = 2.8 Hz, 2H, phenyl), 8.46–8.37 (m, 1H, phenyl), 8.25 (d, *J* = 5.2 Hz, 2H, phenyl), 8.18 (d, *J* = 8.0 Hz, 3H, phenyl), 7.82 (d, *J* = 6.0 Hz, 1H, phenyl), 7.78–7.68 (m, 3H, phenyl), 7.52 (t, *J* = 8.4 Hz, 2H, phenyl), 7.47–7.36 (m, 2H, phenyl), 7.20–7.13 (m, 1H, phenyl), 7.09 (t, *J* = 8.0 Hz, 5H, phenyl), 6.99–6.90 (m, 2H, phenyl), 4.07–3.94 (m, 4H), 3.89 (t, *J* = 5.6 Hz, 8H), 1.90–1.78 (m, 2H), 1.79–1.68 (m, 2H), 1.55–1.40 (m, 4H), 1.40–1.29 (m, 8H), 1.06–0.83 (m, 22H), 0.83–0.71 (m, 8H), 0.71–0.49 (m, 28H), 0.48–0.35 (m, 8H). MS (MALDI-TOF, *m*/*z*): [M+H] calcd for C<sub>111H126</sub>N<sub>7</sub>O<sub>7</sub>S<sub>2</sub>Zn, 1796.8452; found, 1796.436.

**XW21**: brown powders, 23 mg, yield: 80%. mp 224–226 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>: DMSO- $d_6$  = 1: 2)  $\delta$  12.85 (s, 1H, -COOH), 9.89 (d, *J* = 4.4 Hz, 2H, pyrrolic), 9.52 (d, *J* = 4.4 Hz, 2H, pyrrolic), 8.85–8.75 (m, 2H, pyrrolic), 8.75–8.67 (m, 2H, pyrrolic), 8.40 (d, *J* = 7.6 Hz, 1H, phenyl), 8.25 (d, *J* = 7.6 Hz, 2H, phenyl), 8.18 (d, *J* = 8.0 Hz, 2H, phenyl), 8.15–8.14 (m, 1H, phenyl), 7.82 (d, *J* = 8.0 Hz, 1H, phenyl), 7.73 (t, *J* = 8.0 Hz, 3H, phenyl), 7.52 (d, *J* = 8.4 Hz, 2H, phenyl), 7.43 (d, *J* = 8.0 Hz, 1H, phenyl), 7.40–7.36 (m, 1H, phenyl), 7.16 (d, *J* = 8.4 Hz, 1H, phenyl), 7.07 (d, *J* = 8.4 Hz, 5H, phenyl), 6.96 (d, *J* = 8.0 Hz, 2H, phenyl), 4.04–3.95 (m, 4H), 3.88–3.66 (m, 8H), 1.92–1.81 (m, 2H), 1.81–1.71 (m, 2H), 1.57–1.43 (m, 4H), 1.42–1.30 (m, 8H), 0.98–0.83 (m, 10H), 0.69–0.38 (m, 24H), 0.38–0.11 (m, 32H). MS (MALDI-TOF, *m*/*z*): [M+H] calcd for C<sub>111</sub>H<sub>126</sub>N<sub>7</sub>O<sub>7</sub>S<sub>2</sub>Zn, 1796.8452; found, 1795.526.

### 2.3. Theoretical approach

The ground state geometries and frontier molecular orbitals of the dyes were computed using the hybrid B3LYP functional and the 6-31G\* basis set [38–40]. For zinc atoms the Los Alamos effective core potential basis set (LANL2DZ) was used [41]. All calculations

were carried out using the Gaussian09 program package [42].

#### 2.4. Fabrication of solar cells

The procedure for preparation of TiO<sub>2</sub> electrodes and fabrication of the sealed cells for photovoltaic measurements were adapted from that reported by Grätzel and co-workers [43]. A screenprinted double layer of TiO<sub>2</sub> particles was used as the photoelectrode. The detailed procedure was reported in our previous work [44]. The films were then immersed into a 0.2 mM solution of the dyes with or without CDCA in a mixture of toluene and ethanol (1/4, v/v) for 10 h at 25 °C. The counter electrode was also prepared according to the procedure reported in our previous work [44]. Finally, the DSSCs were assembled, with the electrolyte solution containing 0.1 M LiI, 0.05 M I<sub>2</sub>, 0.6 M 1-methyl-3-propyl-imidazolium iodide (PMII), and 0.5 M 4-*tert*-butylpyridine (TBP) in acetonitrile.

### 3. Results and discussion

### 3.1. Syntheses

The synthetic routes for XW18-XW21 are depicted in Scheme 1.

The Zn(II) dibromoporphyrin intermediates **5a** and **5b** were prepared according to reported procedures [34]. Then the donor and acceptor moieties were successively introduced *via* Sonogashira cross-coupling reactions. Finally, the target products were obtained by hydrolysis of the esters. All key intermediates and target products were fully characterized by NMR and MS.

### 3.2. Optical and electrochemical properties

As shown in Fig. 2 and Table 1, all the four dyes feature typical porphyrin absorption characteristics. **XW18** and **XW19** display an intense Soret band around 457 nm and a clearly resolved Q band around 663 nm. As for **XW20** and **XW21**, incorporation of the BTD group results in dramatically broadened absorption and more intense and red-shifted Q-bands around 681 nm. The spectral changes can be rationalized by the strong electron-deficient nature of the BTD unit, which is believed to enhance the electronic coupling between the porphyrin core and the acceptor part. These changes are favorable for light-harvesting and are expected to afford better cell performance.

It should be noted that the absorptions of **XW18** and **XW19** are almost identical, so are those of **XW20** and **XW21**, indicating that the different alkoxy chains only slightly influence the porphyrin



Scheme 1. Synthetic Routes for XW18-XW21. Reaction conditions: (i) 1-bromooctane or 2-ethylhexyl bromide, KOH, DMSO, rt, overnight; (ii) *n*-BuLi, TMEDA, THF, 0 °C, 3 h; then DMF, rt, 2 h; (iii) bis(1H-pyrrol-2-yl)methane, TFA, CH<sub>2</sub>Cl<sub>2</sub>, rt, 4 h; then DDQ, rt, 1 h; (iv) NBS, CH<sub>2</sub>Cl<sub>2</sub>, rt, 1 h; (v) Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O, DCM/MeOH, reflux, 6 h; (vi) 3-ethynyl-10-hexyl-7-(4-(hexyloxy)phenyl)-10H-phenothiazine, Pd<sub>2</sub>(dba)<sub>3</sub>, AsPh<sub>3</sub>, THF/Et<sub>3</sub>N, 55 °C, 6 h; (vii) for **7a** and **7b**: methyl 4-ethynylbenzoate, Pd(PPh<sub>3</sub>)<sub>4</sub>, Cul, THF/Et<sub>3</sub>N, 55 °C, overnight; for **7c** and **7d**: methyl 4-(7-ethynylbenzo[c] [1,2,5]thiadiazol-4-yl)benzoate, Pd(PPh<sub>3</sub>)<sub>4</sub>, Cul, THF/Piperidine, 60 °C, overnight; (viii) LiOH·H<sub>2</sub>O, THF/H<sub>2</sub>O, 60 °C, overnight.



Fig. 2. Absorption spectra of dyes XW18-XW21. (a) in THF solutions, (b) on TiO<sub>2</sub> films (3  $\mu$ m in thickness).

absorption. Upon adsorption onto  $TiO_2$  films, both the Soret band and Q-bands are broadened due to interactions among dye molecules and/or between dyes and nanocrystalline  $TiO_2$ . This observation is also favorable for light-harvesting.

Cyclic voltammetry was employed to investigate the oxidation potentials of the dyes and evaluate the possibility of electron injection and dye regeneration from the thermodynamic point of view (Table 1 and Figure S37). The ground state oxidation potentials ( $E_{\text{ox}}$ ) were estimated to be 0.90 V–0.93 V vs NHE, which are more positive than the potential of I<sub>3</sub>/I<sup>-</sup> (~0.4 V), ensuring sufficient driving force for dye regeneration.  $E_{0-0}$  was calculated to be 1.90 eV for **XW18** and **XW19** and 1.80 eV for **XW20** and **XW21**. The

Table 1
Absorption spectral and electrochemical data for XW18-XW21



Fig. 3. Schematic energy levels of dyes XW18-XW21.

narrower energy gap of **XW20** and **XW21** relative to **XW18** and **XW19** is in accordance with their broader and red-shifted absorption. The excited state oxidation potentials  $(E_{ox}^*)$  were obtained to be in the range of -0.87 V ~ -1.00 V, negative enough for electron injection as compared to that of the TiO<sub>2</sub> conduction band (~-0.5 V) (Fig. 3).

### 3.3. DFT calculations

We employed density functional theory (DFT) calculations to optimize the ground state geometries of the dyes, and the calculated frontier molecular HOMO and LUMO orbitals are shown in Fig. 4. The HOMO electrons of all four dyes are mainly distributed over the donor part and the porphyrin core, while the LUMO electrons are predominantly populated on the acceptor part and the porphyrin core. Especially for **XW20** and **XW21**, the LUMO electrons are strongly pulled to the acceptor part by the electronwithdrawing BTD unit. These observations can be rationalized by enhanced charge-transfer from the donor to the acceptor, which possibly favors the electron injection process.

### 3.4. Photovoltaic performances

The photovoltaic performances of **XW18-XW21** were tested using iodine-based electrolyte. Fig. 5 shows the *J*-*V* curves and IPCE action spectra of the devices and the corresponding photovoltaic parameters are listed in Table 2.

Initially, the TiO<sub>2</sub> films were sensitized with individual porphyrin dyes. **XW18** and **XW19** show comparable performances, with a PCE of ~8.3% and similar  $J_{sc}$  and  $V_{oc}$ . On the other hand, cells based on **XW21** showed  $V_{oc}$  and  $J_{sc}$  of 723 mV, and 15.66 mA cm<sup>-2</sup>,

Dye	$\lambda_{\rm max}$ , nm ( $\epsilon$ , 10 <sup>3</sup> M <sup>-1</sup> cm <sup>-1</sup> ) <sup>a</sup>	$\lambda_{max}$ , nm <sup>b</sup>	<i>E</i> <sub>0-0</sub> , eV <sup>c</sup>	$E_{\rm ox}$ , V <sup>d</sup> (vs NHE)	$E_{\rm ox}^*$ , V <sup>e</sup> (vs NHE)
XW18	457 (255.6), 664 (62.2)	461	1.90	0.92	-0.98
XW19	457 (264.9), 663 (63.9)	460	1.90	0.90	-1.00
XW20	465 (154.2), 682 (86.3)	466	1.80	0.93	-0.87
XW21	465 (173.1), 681 (95.4)	466	1.80	0.91	-0.89

<sup>a</sup> Absorption maxima wavelengths ( $\lambda_{max}$ ) and molar extinction coefficients ( $\varepsilon$ ) in THF solution.

 $^{\rm b}\,$  Absorption maxima wavelengths on 3  $\mu m$  transparent TiO\_2 films.

 $^{c}$   $E_{0-0}$  was estimated from the wavelength at the intersection ( $\lambda_{inter}$ ) of normalized absorption and emission spectra using the equation  $E_{0-0} = 1240/\lambda_{inter}$ .

<sup>d</sup>  $E_{ox}$  was obtained from the first oxidation potential measured in acetonitrile using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as the electrolyte (working electrode: FTO/TiO<sub>2</sub>/dye; reference electrode: SCE; counter electrode: Pt). The  $E_{ox}$  values were calibrated with ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) as an external reference, and its potential was estimated to be 0.45 V, vs SCE (Figure S37). By comparing this value with that of 0.63 V vs NHE, the  $E_{ox}$  vs. SCE can be converted to that vs. NHE by adding a value of 0.18 V.

<sup>e</sup>  $E_{ox}^*$  was estimated from the equation  $E_{ox}^* = E_{ox} - E_{0-0}$ .

6

H. Song et al. / Dyes and Pigments xxx (2016) 1–9



Fig. 4. Calculated frontier molecular HOMO and LUMO orbitals of XW18-XW21.



Fig. 5. J-V curves (a,b) and IPCE action spectra (c,d) of XW18-XW21-sensitized solar cells with or without CDCA as the coadsorbent.

respectively, both higher than the respective values of 716 mV and 13.36 mA cm<sup>-2</sup> achieved for **XW20**. As a result, a higher efficiency of 7.50% was achieved for **XW21** relative to 6.46% for **XW20**.

It is noteworthy that **XW20** and **XW21** exhibit dramatically redshifted IPCE onset wavelengths triggered by the strong "pulling" effect of the BTD unit. However, their IPCE plateaus are relatively low, especially for **XW20**, which exhibits IPCE values lower than 50% at most of the wavelengths. Considering that IPCE = LHE( $\lambda$ ) ×  $\Phi_{inj}$  ×  $\eta_{coll}$  ×  $\eta_{reg}$  (where LHE( $\lambda$ ) is the light-harvesting efficiency,  $\Phi_{inj}$  is the electron injection yield from the photoexcited dye into TiO<sub>2</sub> conduction band,  $\eta_{coll}$  is the collection efficiency of the photo-generated charge carriers and  $\eta_{reg}$  is the dye regeneration efficiency) [34], the lower IPCE of **XW20** and **XW21** may be ascribed to the following two main reasons: 1. The planar BTD unit aggravates the dye-aggregation problem, causing selfquenching of the excited dyes and in turn lowering the electroninjection yield; 2. Although electron back-transfer may be attenuated by the phenyl spacer inserted between the BTD unit and the carboxyl anchoring group, it couldn't be fully prevented [23,45]. In other words, the electron-trapping effect of BTD may lead to aggravated charge recombination, resulting in lower electron-

7

#### Table 2

Photovoltaic parameters of DSSCs based on **XW18-XW21** under simulated AM 1.5 G full sun illumination (Power 100 mW cm<sup>-2</sup>) using iodine-based electrolyte<sup>a</sup>.

Dyes	CDCA [mM]	$V_{\rm oc} [{\rm mV}]$	$J_{\rm sc} [{\rm mA}\cdot{\rm cm}^{-2}]$	FF [%]	PCE [%]
XW18	0	755 ± 1	$16.42 \pm 0.21$	67.1 ± 0.5	8.32 ± 0.02
	8	$754 \pm 1$	$18.78 \pm 0.17$	$67.2 \pm 0.5$	$9.50 \pm 0.07$
XW19	0	$755 \pm 2$	$16.90 \pm 0.15$	$64.9 \pm 0.2$	$8.28 \pm 0.07$
	8	$742 \pm 2$	$18.54 \pm 0.24$	$68.5 \pm 0.2$	9.42 ± 0.11
XW20	0	$716 \pm 1$	$13.36 \pm 0.28$	$67.6 \pm 0.5$	$6.46 \pm 0.15$
	8	737 ± 1	$18.09 \pm 0.24$	$65.4 \pm 0.3$	8.72 ± 0.11
XW21	0	$723 \pm 3$	$15.66 \pm 0.38$	66.3 ± 1.0	$7.50 \pm 0.06$
	8	$734 \pm 2$	$19.62\pm0.15$	$66.8 \pm 0.5$	9.62 ± 0.11

<sup>a</sup> The parameters were obtained from the average value of three devices.

H. Song et al. / Dyes and Pigments xxx (2016) 1–9



**Fig. 6.** Plots of (a) chemical capacitance ( $C_{\mu}$ ) and (b) electron lifetime ( $\tau$ ) obtained through electrochemical impedance analysis as a function of bias voltages with or without CDCA as the coadsorbent.

collection efficiency of **XW20** and **XW21**. The above two reasons may also account for the fact that the change of the linear chains to the branched ones makes a difference only for the BTD-containing dyes. When branched alkoxy chains were introduced into the BTDcontaining dye **XW20** to afford **XW21**, the severe dye aggregation may be suppressed, and thus an elevated efficiency was observed for **XW21** as compared with **XW20**.

To further improve the DSSC efficiencies, especially for those based on **XW20** and **XW21**, which exhibit quite broad absorption, CDCA was used as a coadsorbent to suppress dye aggregation and charge recombination [46]. As expected, all the dyes display improved performances under an optimized CDCA concentration of 8 mM (see Table S4 for the data of the optimization of CDCA concentrations). Specifically, for **XW20** and **XW21**, the  $J_{sc}$  and  $V_{oc}$  were simultaneously elevated, leading to a drastic improvement in their PCEs; while for **XW18** and **XW19**, an increase of  $J_{sc}$  was accompanied by a slight sacrifice of  $V_{oc}$ . Therefore, their improvement in PCE was relatively small. As a result, benefiting from both BTD and branched chains, the combination of **XW21** with CDCA gives a highest PCE. The final PCEs lie in the order of **XW21** (9.62%) > **XW18** (9.50%)  $\approx$  **XW19** (9.42%) > **XW20** (8.72%).

The different coadsorption behaviors between the dyes in the cases with and without the BTD unit indicate that the dye aggregation for XW18 is not very serious due to its relatively small conjugation framework, and thus when branched alkoxy units were used to afford XW19, the aggregation effect were not obviously affected, and thus similar photovoltaic characteristics were observed for XW18 and XW19. In contrast, XW20 contains a larger conjugation framework due to the presence of the planar BTD unit, which may induce serious dye aggregation effect, and thus it exhibits a lower efficiency relative to XW18 and XW19. When branched alkoxy chains were introduced to afford XW21, the dye aggregation effect may be suppressed, and thus an elevated efficiency was observed for XW21 as compared with XW20. However, its efficiency is still lower than XW18 and XW19 in spite of its broader absorption, indicating that additional approaches are required for further suppressing the dye aggregation effect. Hence, when CDCA was further used as the coadsorbent, a highest efficiency of 9.62% was observed for XW21.

#### 3.5. Electrochemical impedance analysis

To further understand the difference in  $V_{oc}$  for the devices based on **XW18-XW21**, electrochemical impedance spectroscopy (EIS) was performed in the dark at a series of bias voltages near their  $V_{oc}$ values. Data were fitted with an equivalent circuit to obtain information about the chemical capacitance ( $C_{\mu}$ ) and electron lifetime ( $\tau$ ). Generally, the maximum attainable  $V_{oc}$  of a DSSC device is determined by the quasi Fermi level of electrons in TiO<sub>2</sub> semiconductor and the potential of the redox species in the electrolyte. Given the same electrolyte used in the test, the  $V_{oc}$  should be only limited by the quasi Fermi level in TiO<sub>2</sub>, which is governed by the TiO<sub>2</sub> conduction band position and the electron injection/charge recombination process [47]. The attained  $C_{\mu}$  and  $\tau$  values provide some perception into these factors, respectively.

The similar  $C_{\mu}$  values at a fixed bias voltage (Fig. 6a) signify negligible differences in the conduction band positions for the four dyes, while the electron lifetimes of **XW18** and **XW19**-based cells are obviously longer than those based on **XW20** and **XW21** (Fig. 6b), indicating that **XW20** and **XW21** suffer from more serious dye-aggregation/charge recombination, which leads to their lower observed  $V_{oc}$  values (*vide supra*). On the other hand, the electron lifetime of **XW21** is slightly longer than that of **XW20**, indicative of the effect of branched chains on suppressing the dye-aggregation/ charge recombination.

After coadsorption with CDCA, the  $C_{\mu}$  values of the cells based on **XW18** and **XW19** were observed to be slightly decreased (Fig. 6a), indicating an upward shift of TiO<sub>2</sub> conduction band edge, which is favorable for improving  $V_{oc}$ . But their electron lifetimes were also decreased (Fig. 6b), resulting in the net effect of slightly decreased  $V_{oc}$  values. On the other hand, cells based on **XW20** and **XW21** showed obviously decreased  $C_{\mu}$  and slightly elevated or almost unchanged electron lifetimes after coadsorption, resulting in their improved  $V_{oc}$  values (*vide supra*).

### 4. Conclusions

In summary, four push-pull porphyrin dyes XW18-XW21 were designed, synthesized and used as DSSC sensitizers. Linear and branched alkoxy chains were used to wrap the porphyrin framework. For the dyes containing the ethynylbenzoic acid group as the acceptor, the changes in the alkoxy chains make little difference in the photovoltaic performance, while for dyes containing the BTD unit as the auxiliary acceptor, branched chains result in obviously better photovoltaic behavior than the linear ones. Finally, by employing CDCA as the coadsorbent, the porphyrin dye containing both BTD and branched chains (XW21) exhibits a highest PCE of 9.62%. This work clearly demonstrates the inherent advantages of the additional BTD acceptor and the possibility of achieving high DSSC efficiencies by combining the coadsorbent CDCA with a porphyrin dye containing both the BTD acceptor and branched alkoxy chains. However, a large amount of CDCA is required for suppressing the dye aggregation/charge recombination for XW21, indicating that the effect of branched chains is still limited. Further structural modification of the

#### H. Song et al. / Dyes and Pigments xxx (2016) 1-9

porphyrin dyes is under way in our laboratory.

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### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2016.10.041.

#### References

- O'Regan B, Gratzel M. A low-cost, high-efficiency solar cell based on dyesensitized colloidal TiO<sub>2</sub> films. Nature 1991;353:737–40.
- [2] Wang SW, Chou CC, Hu FC, Wu KL, Chi Y, Clifford JN, et al. Panchromatic Ru(II) sensitizers bearing single thiocyanate for high efficiency dye sensitized solar cells. J Mater Chem A 2014;2:17618–27.
- [3] Zhang S, Yang X, Numata Y, Han L. Highly efficient dye-sensitized solar cells: progress and future challenges. Energy Environ Sci 2013;6:1443–64.
- [4] Bessho T, Zakeeruddin SM, Yeh CY, Diau EWG, Grätzel M. Highly efficient mesoscopic dye-sensitized solar cells based on donor–acceptor-substituted porphyrins. Angew Chem Int Ed 2010;49:6646–9.
- [5] Lu X, Feng Q, Lan T, Zhou G, Wang ZS. Molecular engineering of quinoxalinebased organic sensitizers for highly efficient and stable dye-sensitized solar cells. Chem Mater 2012;24:3179–87.
- [6] Yao Z, Wu H, Li Y, Wang J, Zhang J, Zhang M, et al. Dithienopicenocarbazole as the kernel module of low-energy-gap organic dyes for efficient conversion of sunlight to electricity. Energy Environ Sci 2015;8:3192–7.
- [7] Kakiage K, Aoyama Y, Yano T, Oya K, Fujisawa Ji, Hanaya M. Highly-efficient dye-sensitized solar cells with collaborative sensitization by silyl-anchor and carboxy-anchor dyes. Chem Commun 2015;51:15894–7.
- [8] Liu YC, Chou HH, Ho FY, Wei HJ, Wei TC, Yeh CY. A feasible scalable porphyrin dye for dye-sensitized solar cells under one sun and dim light environments. [Mater Chem A 2016;4:11878–87.
- [9] Higashino T, Fujimori Y, Sugiura K, Tsuji Y, Ito S, Imahori H. Tropolone as a high-performance robust anchoring group for dye-sensitized solar cells. Angew Chem Int Ed 2015;54:9052-6.
- [10] Wu Y, Zhu WH, Zakeeruddin SM, Grätzel M. Insight into D–A–π–A structured sensitizers: a promising route to highly efficient and stable dye-sensitized solar cells. ACS Appl Mater Interfaces 2015;7:9307–18.
- [11] Guo FL, Li ZQ, Liu XP, Zhou L, Kong FT, Chen WC, et al. Metal-free sensitizers containing hydantoin acceptor as high performance anchoring group for dyesensitized solar cells. Adv Funct Mater 2016. http://dx.doi.org/10.1002/ adfm.201601305.
- [12] Gobeze HB, Das SK, D'Souza F. Femtosecond transient absorption study of supramolecularly assembled metal tetrapyrrole—TiO<sub>2</sub> thin films. J Phys Chem C 2014;118:16660—71.
- [13] Li LL, Diau EWG. Porphyrin-sensitized solar cells. Chem Soc Rev 2013;42: 291-304.
- [14] Chen B, Sun L, Xie YS. Modulation of photovoltaic behavior of dye-sensitized solar cells by electron donors of porphyrin dyes and cosensitization. Chin Chem Lett 2015;26:899–904.
- [15] Urbani M, Grätzel M, Nazeeruddin MK, Torres T. Meso-substituted porphyrins for dye-sensitized solar cells. Chem Rev 2014;114:12330–96.
- [16] Cabau L, Vijay Kumar C, Moncho A, Clifford JN, Lopez N, Palomares E. A single atom change "switches-on" the solar-to-energy conversion efficiency of Znporphyrin based dye sensitized solar cells to 10.5%. Energy Environ Sci 2015;8:1368–75.
- [17] Lu J, Li H, Liu S, Chang YC, Wu HP, Cheng Y, et al. Novel porphyrin-preparation, characterization, and applications in solar energy conversion. Phys Chem Chem Phys 2016;18:6885–92.
- [18] Wang CL, Zhang M, Hsiao YH, Tseng CK, Liu CL, Xu M, et al. Porphyrins bearing a consolidated anthryl donor with dual functions for efficient dye-sensitized solar cells. Energy Environ Sci 2016;9:200–6.
- [19] Li C, Luo L, Wu D, Jiang R, Lan J, Wang R, et al. Porphyrins with intense absorptivity: highly efficient sensitizers with a photovoltaic efficiency of up to 10.7% without a cosensitizer and a coabsorbate. J Mater Chem A 2016;4: 11829–34.
- [20] Kurotobi K, Toude Y, Kawamoto K, Fujimori Y, Ito S, Chabera P, et al. Highly asymmetrical porphyrins with enhanced push-pull character for dye-

sensitized solar cells. Chem Eur J 2013;19:17075-81.

- [21] Li Z, Li Q, Molecular engineering and cosensitization for developing efficient solar cells based on porphyrin dyes with an extended  $\pi$  framework. Sci China Chem 2014;57:1491.
- [22] Yella A, Mai CL, Zakeeruddin SM, Chang SN, Hsieh CH, Yeh CY, et al. Molecular engineering of push—pull porphyrin dyes for highly efficient dye-sensitized solar cells: the role of benzene spacers. Angew Chem Int Ed 2014;53:2973–7.
- [23] Mathew S, Yella A, Gao P, Humphry-Baker R, CurchodBasile FE, Ashari-Astani N, et al. Dye-sensitized solar cells with 13% efficiency achieved through the molecular engineering of porphyrin sensitizers. Nat Chem 2014;6:242–7.
- [24] Wang CL, Lan CM, Hong SH, Wang YF, Pan TY, Chang CW, et al. Enveloping porphyrins for efficient dye-sensitized solar cells. Energy Environ Sci 2012;5: 6933–40.
- [25] Ripolles-Sanchis T, Guo BC, Wu HP, Pan TY, Lee HW, Raga SR, et al. Design and characterization of alkoxy-wrapped push-pull porphyrins for dye-sensitized solar cells. Chem Commun 2012;48:4368–70.
- [26] Hung WI, Liao YY, Lee TH, Ting YC, Ni JS, Kao WS, et al. Eugenic metal-free sensitizers with double anchors for high performance dye-sensitized solar cells. Chem Commun 2015;51:2152–5.
- [27] Jia HL, Zhang MD, Yan W, Ju XH, Zheng HG. Effects of structural optimization on the performance of dye-sensitized solar cells: spirobifluorene as a promising building block to enhance Voc. J Mater Chem A 2016;4:11782–8.
- [28] adi Jr FM, Kang X, O'Neil D, Pajares G, Getmanenko YA, Szymanski P, et al. Near-infrared asymmetrical squaraine sensitizers for highly efficient dye sensitized solar cells: the effect of  $\pi$ -bridges and anchoring groups on solar cell performance. Chem Mater 2015;27:2480–7.
- [29] Hua Y, Chang S, Huang D, Zhou X, Zhu X, Zhao J, et al. Significant improvement of dye-sensitized solar cell performance using simple phenothiazine-based dyes. Chem Mater 2013;25:2146–53.
- [30] Lin RYY, Wu FL, Li CT, Chen PY, Ho KC, Lin JT. High-performance aqueous/ organic dye-sensitized solar cells based on sensitizers containing triethylene oxide methyl ether. ChemSusChem 2015;8:2503–13.
- [31] Sun X, Wang Y, Li X, Agren H, Zhu W, Tian H, et al. Cosensitizers for simultaneous filling up of both absorption valleys of porphyrins: a novel approach for developing efficient panchromatic dye-sensitized solar cells. Chem Commun 2014;50:15609–12.
- [32] Xie Y, Tang Y, Wu W, Wang Y, Liu J, Li X, et al. Porphyrin cosensitization for a photovoltaic efficiency of 11.5%: a record for non-ruthenium solar cells based on iodine electrolyte. J Am Chem Soc 2015;137:14055–8.
- [33] Tang Y, Wang Y, Li X, Ågren H, Zhu WH, Xie Y. Porphyrins containing a triphenylamine donor and up to eight alkoxy chains for dye-sensitized solar cells: a high efficiency of 10.9%. ACS Appl Mater Interfaces 2015;7:27976–85.
- [34] Yella A, Lee HW, Tsao HN, Yi C, Chandiran AK, Nazeeruddin MK, et al. Porphyrin-sensitized solar cells with cobalt (II/III)–Based redox electrolyte exceed 12 percent efficiency. Science 2011;334:629–34.
- [35] Lee CY, Hupp JT. Dye sensitized solar cells: TiO<sub>2</sub> sensitization with a bodipyporphyrin antenna system. Langmuir 2010;26:3760–5.
- [36] Chen ZK, Lee NHS, Huang W, Xu YS, Cao Y. New phenyl-substituted PPV derivatives for polymer light-emitting Diodes–Synthesis, characterization and Structure–Property relationship study. Macromolecules 2003;36:1009–20.
- [37] Sasaki K, Nomura K. Photoelectric conversion element and dye-sensitized solar cell. PCT Int Appl 2013; WO 2013089087 A1 20130620.
- [38] Becke AD. Density-functional thermochemistry. III. The role of exact exchange. J Chem Phys 1993;98:5648–52.
- [39] Lee C, Yang W, Parr RG. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys Rev B 1988;37:785–9.
- [40] Hehre WJ, Ditchfield R, Pople JA. Self-consistent molecular orbital methods. XII. further extensions of gaussian-type basis sets for use in molecular orbital studies of organic molecules. J Chem Phys 1972;56:2257–61.
- [41] Hay PJ, Wadt WR. Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. J Chem Phys 1985;82: 270–83.
- [42] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian 09 revision A. 2. Wallingford, CT: Gaussian, Inc; 2009.
- [43] Ito S, Murakami TN, Comte P, Liska P, Grätzel C, Nazeeruddin MK, et al. Fabrication of thin film dye sensitized solar cells with solar to electric power conversion efficiency over 10%. Thin Solid Films 2008;516:4613–9.
- [44] Wang Y, Chen B, Wu W, Li X, Zhu W, Tian H, et al. Efficient solar cells sensitized by porphyrins with an extended conjugation framework and a carbazole donor: from molecular design to cosensitization. Angew Chem Int Ed 2014;53:10779–83.
- [45] Chai Z, Wu M, Fang M, Wan S, Xu T, Tang R, et al. Similar or totally different: the adjustment of the twist conformation through minor structural modification, and dramatically improved performance for dye-sensitized solar cell. Adv Energy Mater 2015:5. http://dx.doi.org/10.1002/aenm.201500846.
- [46] Shi J, Chai Z, Tang R, Hua J, Li Q, Li Z. New triphenylamine-based sensitizers bearing double anchoring units for dye-sensitized solar cells. Sci China Chem 2015;58:1144.
- [47] Ning Z, Fu Y, Tian H. Improvement of dye-sensitized solar cells: what we know and what we need to know. Energy Environ Sci 2010;3:1170–81.