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# Porphyrin sensitizers containing an auxiliary benzotriazole acceptor for dye-sensitized solar cells: effects of steric hindrance and cosensitization

- 4 Heli Song<sup>*a*</sup>, Weiqiang Tang<sup>*b*</sup>, Shuangliang Zhao<sup>*b*</sup>, Qingyun Liu<sup>*c*</sup> and Yongshu Xie<sup>\*a</sup>
- 5 <sup>a</sup> Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry and Molecular
- 6 Engineering, East China University of Science and Technology, Meilong 130, Shanghai 200237, China.
- 7 <sup>b</sup> School of Chemical Engineering and State Key Laboratory of Chemical Engineering, East China University of
- 8 Science and Technology, Shanghai, 200237, China.
- 9 <sup>c</sup> College of Chemistry and Environmental Engineering, Shandong University of Science and Technology,
- 10 Qingdao, P. R. China.
- 11 \* Corresponding author: Yongshu Xie, E-mail: <u>yshxie@ecust.edu.cn</u>

12 Abstract: Dye-sensitized solar cells (DSSCs) have attracted intensive attention in 13 developing photovoltaic devices for employing solar energy. For developing panchromatic and efficient porphyrin sensitizers, it has been demonstrated to be an 14 effective approach to introduce an electron-withdrawing benzothiadiazole unit as an 15 16 extra electron acceptor. In contrast, the structurally similar benzotriazole moiety 17 remains relatively unknown in this respect. In this work, we have synthesized a novel 18 porphyrin dye containing an extra electron acceptor of benzotriazole. Photophysical 19 and electrochemical investigations revealed red-shifted absorption and a narrower

20	band gap induced by the benzotriazole unit. Thus, a reasonable efficiency of 8.39%
21	has been achieved with a $J_{\rm sc}$ of 17.00 mA·cm <sup>-2</sup> and a $V_{\rm oc}$ of 712 mV. On this basis, to
22	investigate the effect of the dihedral angle between the benzotriazole and the adjacent
23	phenylene ring, one or two methyl groups were attached to the ortho-positions of the
24	phenylene ring. As a result, the enlarged torsion angles induce poor electronic
25	coupling between the LUMO of the dyes and TiO <sub>2</sub> , resulting in lower efficiencies of
26	6.61% and 3.62%, respectively. With the purpose to further improve the efficiencies,
27	coadsorption and cosensitization approaches were employed. And the efficiencies
28	have been successfully elevated to 9.32%, 8.49% and 7.34%, respectively. These
29	results demonstrate the effectiveness of incorporating an auxiliary benzotriazole
30	acceptor into porphyrin dyes on achieving extended light-harvesting wavelength
31	ranges and illustrate the importance of avoiding severe torsion within the acceptor
32	part of the porphyrin dyes. In contrast to the commonly used cosensitizers with
33	absorption peaks lying in the absorption valley between the Soret band and the Q
34	bands of porphyrin dyes (500-600 nm), the utilization of an organic dye with broad
35	absorption in this work has been demonstrated to be effective for improving the
36	efficiencies despite the fact that its absorption peak at 450 nm largely overlaps with
37	the Soret band of the porphyrin dyes. These results provide an alternative approach
38	for developing cosensitizers for porphyrin dyes.

Keywords: Dye-sensitized solar cells; Porphyrin; Sensitizer; Benzotriazole; Steric
hindrance; Cosensitization.

#### 41 **1. Introduction**

Exploitation of new and clean energy sources for future development has 42 43 become one of the major challenges in contemporary society. In this respect, dye-sensitized solar cells (DSSCs) are attractive and promising because of their 44 relatively efficient conversion of sunlight to electricity with the advantages of 45 46 flexibility, easy fabrication and low cost [1,2]. Among the DSSC sensitizers, porphyrins exhibit advantages of high molar absorption coefficients with tunable 47 molecular structures and properties [3,4]. In this respect, a number of excellent 48 49 porphyrin sensitizers like YD2-o-C8, GY50 and SM315 have been developed with efficiencies achieved well above 10% [5-7]. 50

51 Despite the excellent photovoltaic behavior, two inherent drawbacks have been observed for porphyrin dyes. The first is the intrinsic absorption void in the NIR 52 region and the absorption valley between the Soret and Q bands in the range of 53 500-600 nm [8-11]. The other problem is the relatively high tendency for aggregation 54 55 induced by the large conjugated framework, which will lead to quenching of the excited dyes and diminished electron injection [12-14]. To address these problems, 56 57 various approaches reported. have been For example, insertion of а 2,1,3-benzothiadiazole (BTD) unit as an auxiliary electron acceptor has been 58 59 demonstrated to be effective for enhancing the electronic coupling between the porphyrin core and the anchoring group, resulting in relatively panchromatic 60 61 absorption and photo-response [7,15-19]. On the other hand, attachment of alkoxyl or

alkyl chains to appropriate positions can improve dye solubility and reduceaggregation [20-25].

64 In contrast to the widely used BTD unit, the structurally similar benzotriazole (BTz) moiety remains relatively unknown in this respect. In fact, in some cases, the 65 insertion of a BTD unit unfavorably leads to worse photovoltaic performance [26-28], 66 67 and BTz might be advantageous in these cases. In addition, the presence of an additional nitrogen atom facilitates introduction of alkyl chains for suppressing dye 68 aggregation and charge recombination [29]. Herein, we incorporate a BTz unit as the 69 70 auxiliary acceptor to develop a novel porphyrin dye XW33 (Fig. 1), using a 71 phenothiazine-based donor.

72 On the other hand, it is an effective approach to develop porphyrin dyes by 73 borrowing concepts developed for metal-free organic dyes. It has been demonstrated 74 by Li and coworkers that in a certain series of organic dyes, a more twisted spacer neighboring to the anchoring group is favorable for improving  $V_{oc}$  and efficiencies 75 76 (Fig. 1) [30]. By considering this background, XW34 and XW35 (Fig. 1) were 77 synthesized with one or two methyl groups attached at the ortho-positions of the phenylene ring adjacent to the BTz unit. As a result, XW33-XW35 exhibit power 78 79 conversion efficiencies of 8.39%, 6.61% and 3.62%, respectively. These results 80 indicate that the more twisted spacer is unfavorable for the photovoltaic behavior. To 81 improve the cell performance, the porphyrin dyes were coadsorbed with 82 chenodeoxycholic acid (CDCA) and cosensitized with a phenothiazine-based organic

dye **PT-C6** [31], which exhibits a broad absorption peak. Thus, dramatically enhanced efficiencies of 9.32%, 8.49% and 7.34% were achieved for **XW33**, **XW34**, and **XW35** respectively, despite the fact that the absorption peak of **PT-C6** is centered at 450 nm, largely overlapping with the Soret bands of the porphyrin dyes. These successful cosensitization examples indicate that the broad absorption band of **PT-C6** can well compensate for the narrow Soret band of the porphyrin dyes.





Fig. 1 Molecular structures of porphyrin dyes XW33-XW35, the cosensitizer PT-C6 and
organic dyes LI-85 and LI-86 reported by Li and coworkers.

## 92 2. Experimental section

#### 93 2.1 Materials and Instrumentation

All chemical reagents and solvents of analytical grade were purchased and used
without further purification unless otherwise noted. Fluorine-doped SnO<sub>2</sub> conducting
glass (FTO glass, transparency >90% in the visible range, sheet resistance 15
Ω/square) was purchased from the Geao Science and Educational Co. Ltd of China.
TiO<sub>2</sub> paste (18 NR-T and 18 NR-AO) was purchased from Dyesol Ltd.
<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded using a Bruker AM 400

100 spectrometer at 298 K with tetramethylsilane (TMS) as the internal standard. High

101 resolution mass spectroscopy (HRMS) measurements were performed using a Waters 102 spectrometer. Matrix-assisted laser desorption/ionization Premier XE LCT 103 time-of-flight mass spectra (MALDI-TOF-MS) were measured on a Shimadzu-Kratos 104 model Axima CFR+ mass spectrometer using dithranol as the matrix. UV-Vis absorption spectra were measured on a Varian Cary 60 spectrophotometer, and 105 fluorescence spectra were recorded on a Varian Cary Eclipse fluorescence 106 spectrophotometer. The cyclic voltammograms of the dyes were carried out in 107 108 acetonitrile on a Zahner IM6e electrochemical workstation based on a three electrode system using 0.1 M TBAPF<sub>6</sub> (Adamas) as the supporting electrolyte, the sensitizer 109 attached to a nanocrystalline TiO<sub>2</sub> film deposited on the conducting FTO glass as the 110 working electrode, a platinum wire as the counter electrode, and a regular saturated 111 calomel electrode (SCE) as the reference electrode. The scan rate was fixed at 100 112  $mV s^{-1}$ . 113

114 Photovoltaic measurements were performed by employing an AM 1.5 solar 115 simulator equipped with a 300 W xenon lamp (model no. 91160, Oriel). The power of the simulated light was calibrated to 100 mW cm<sup>-2</sup> using a Newport Oriel PV 116 reference cell system (model 91150 V). J-V curves were obtained by applying an 117 118 external bias to the cell and measuring the generated photocurrent with a model 2400 119 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 120 121 monochromatic photon-to-electron conversion efficiency (IPCE) for the solar cells

122	were obtained with a Newport-74125 system (Newport Instruments). The intensity of
123	monochromatic light was measured with a Si detector (Newport-71640). The
124	electrochemical impedance spectroscopy (EIS) measurements of all the DSSCs were
125	performed using a Zahner IM6e Impedance Analyzer (ZAHNER-Elektrik GmbH &
126	CoKG, Kronach, Germany), with the frequency range of 0.1 Hz-100 kHz and the
127	alternative signal of 10 mV. The ZSimpWin software was used to fit the experimental
128	EIS data.
129	2.2 Syntheses of the dyes
130	Compounds 1 [32], 2 [33], 5 [34] and 8 [15] were synthesized according to
131	literature methods.
132	Compound 3 [35]. To a 250 mL flask was added compound 2 (4.0 g, 19 mmol),
133	MeOH (100 mL) and KI (623 mg, 3.8 mmol). The mixture was stirred at 50°C before
134	t-BuOOH (3.9 mL, 70% (aq), 28 mmol) was added dropwise over 30 min. Then the
135	mixture was refluxed for 24 h. After cooling to room temperature, saturated $Na_2S_2O_3$
136	(aq) was added. The mixture was extracted with ethyl acetate, dried over anhydrous
137	Na <sub>2</sub> SO <sub>4</sub> and evaporated in <i>vacuo</i> . The residue was purified by column
138	chromatography on silica gel with petroleum ether / ethyl acetate (15:1, v/v) to afford
139	compound <b>3</b> as a white solid (3.8 g, 84%). <sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) $\delta$ 7.73 (s, 2H),
140	3.90 (s, 3H), 2.46 (s, 6H).
141	Compound 4 [36]. To a 250 mL three-neck flask was added compound 3 (4.5 g,

142 18 mmol), bis(pinacolato)diboron (5.2 g, 20 mmol), 1,4-dioxane (60 mL),

143	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> (519 mg, 0.74 mmol) and KOAc (5.5 g, 56 mmol). The mixture was
144	stirred at 90°C for 24 h under nitrogen. Water was added and the mixture was
145	extracted with dichloromethane and washed with water three times. The combined
146	organic layers were dried over Na <sub>2</sub> SO <sub>4</sub> and evaporated in vacuo. The residue was
147	purified by column chromatography with petroleum ether / ethyl acetate (15:1, v/v) to
148	give the product as a white solid (4.0 g, 75%). <sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) $\delta$ 7.61 (s,
149	2H), 3.89 (s, 3H), 2.43 (s, 6H), 1.40 (s, 12 H).
150	Compound 6a. To a 100 mL three-neck flask was added compound 5 (4.3 g, 11
151	mmol), methyl 4-boronobenzoate (1.0 g, 5.6 mmol) and THF (50 mL). Then
152	$Pd(PPh_3)_4$ (134 mg, 0.116 mmol) and $K_2CO_3$ (6 mL, 2 M aq) were added under
153	nitrogen. The mixture was refluxed for 12 h under nitrogen. The organic layer was
154	extracted with dichloromethane, washed with water, dried over $Na_2SO_4$ and
155	evaporated in vacuo. The residue was purified by column chromatography on silica
156	gel with petroleum ether / dichloromethane (1:1, v/v) to give the product as a
157	colorless oil (1.5 g, 60%). <sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) $\delta$ 8.17 (d, J = 8.8 Hz, 2H,
158	phenyl), 8.08 (d, J = 8.4 Hz, 2H, phenyl), 7.67 (d, J = 7.6 Hz, 1H, phenyl), 7.48 (d, J
159	= 7.6 Hz, 1H, phenyl), 4.79 (t, $J$ = 7.2 Hz, 2H, -NCH <sub>2</sub> -), 3.96 (s, 3H, -OMe), 2.23 –
160	2.08 (m, 2H), 1.46 – 1.34 (m, 4H), 1.30 – 1.20 (m, 6H), 0.87 (t, $J = 6.8$ Hz, 3H). <sup>13</sup> C
161	NMR (101 MHz, CDCl <sub>3</sub> ) δ 166.89, 144.44, 142.61, 141.01, 129.99, 129.62, 129.60,
162	129.19, 128.42, 125.43, 110.55, 57.21, 52.21, 31.71, 30.20, 29.05, 28.95, 26.54, 22.60,
163	14.07. HRMS (ESI, m/z): [M+H] <sup>+</sup> calcd for C <sub>22</sub> H <sub>27</sub> BrN <sub>3</sub> O <sub>2</sub> , 444.1287; found,

164 444.1290.

165	Compound <b>6b</b> . It was synthesized in a similar way with <b>6a</b> except that compound
166	1 was used instead of methyl 4-boronobenzoate. Colorless oil (yield 61%). <sup>1</sup> H NMR
167	(400 MHz, CDCl <sub>3</sub> ) $\delta$ 8.02 (s, 1H, phenyl), 7.95 (dd, $J$ = 7.6, 1.2 Hz, 1H, phenyl), 7.65
168	(d, $J = 7.6$ Hz, 1H, phenyl), 7.42 (d, $J = 8.0$ Hz, 1H, phenyl), 7.14 (d, $J = 7.6$ Hz, 1H,
169	phenyl), 4.72 (t, $J = 7.6$ Hz, 2H, -NCH <sub>2</sub> -), 3.95 (s, 3H, -OMe), 2.25 (s, 3H,
170	phenyl-CH <sub>3</sub> ), 2.14 – 2.02 (m, 2H), 1.37 – 1.29 (m, 4H), 1.28 – 1.18 (m, 6H), 0.86 (t, J
171	= 6.8 Hz, 3H). <sup>13</sup> C NMR (101 MHz, CDCl <sub>3</sub> ) $\delta$ 167.04, 143.83, 143.10, 141.48, 136.75
172	131.63, 130.88, 130.31, 129.86, 128.90, 127.01, 109.96, 57.16, 52.16, 31.67, 30.24,
173	29.02, 28.92, 26.48, 22.59, 20.53, 14.06. HRMS (ESI, m/z): [M+Na] <sup>+</sup> calcd for
174	C <sub>23</sub> H <sub>28</sub> BrN <sub>3</sub> NaO <sub>2</sub> , 480.1263; found, 480.1265.

175 Compound 6c. To a 100 mL Schlenk tube was added compound 5 (1.00 g, 2.57 mmol), compound 4 (895 mg, 3.08 mmol) and DMF (30 mL). Then Pd(PPh<sub>3</sub>)<sub>4</sub> (59 mg, 176 177 0.051 mmol) and K<sub>3</sub>PO<sub>4</sub> (1.36 g, 6.42 mmol) were added under nitrogen. The mixture 178 was stirred at 100°C under nitrogen for 9 h and then poured into water and extracted with dichloromethane. The organic layer was washed with water, dried over 179 anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated in *vacuo*. The residue was purified by column 180 chromatography on silica gel with petroleum ether / dichloromethane (3:2, v/v) to 181 give the product as a colorless oil (450 mg, 37%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.84 182 (s, 2H, phenyl), 7.66 (d, J = 7.6 Hz, 1H, phenyl), 7.02 (d, J = 7.2 Hz, 1H, phenyl), 183 4.70 (t, J = 7.2 Hz, 2H, -NCH<sub>2</sub>-), 3.94 (s, 3H, -OCH<sub>3</sub>), 2.11 - 2.04 (m, 2H, 184

185	-NCH <sub>2</sub> CH <sub>2</sub> -), 2.03 (s, 6H, phenyl-CH <sub>3</sub> ), 1.31 – 1.27 (m, 4H), 1.27 – 1.20 (m, 6H),
186	0.86 (t, $J = 6.4$ Hz, 3H). <sup>13</sup> C NMR (101 MHz, CDCl <sub>3</sub> ) $\delta$ 167.19, 143.98, 142.92,
187	141.10, 136.99, 129.91, 129.58, 129.05, 128.65, 126.73, 109.55, 57.11, 53.44, 52.08,
188	31.63, 30.23, 29.00, 28.87, 26.42, 22.56, 20.58, 14.03. HRMS (ESI, m/z): [M+H] <sup>+</sup>
189	calcd for C <sub>24</sub> H <sub>31</sub> BrN <sub>3</sub> O <sub>2</sub> , 472.1600; found, 472.1601.
190	General synthetic procedure for compounds 7a~7c.
191	To a 100 mL Schlenk tube was added <b>6a~6c</b> (1.0 mmol), THF/Et <sub>3</sub> N (24 mL / 12
192	mL), Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> (5 mol%) and CuI (5 mol%) and charged with nitrogen. Then the
193	mixture was heated at 50°C before trimethylsilylacetylene (4 mmol) was added over
194	15 min via a syringe. The mixture was allowed to reflux for 12 h. The solvents were
195	evaporated and the residue was purified by silica gel column chromatography to get
196	the crude product. To the crude product was added THF/MeOH (20 mL / 20 mL) and
197	KOH (1 eq, 1M aq). The solution was allowed to stir at room temperature for 1 h.
198	Then water was added and the product was extracted with dichloromethane. The
199	organic layers were separated, dried over Na <sub>2</sub> SO <sub>4</sub> and evaporated in <i>vacuo</i> . Silica gel
200	column chromatography was performed to obtain the ethynyl product.

201 **7a**. Brownish yellow solid (yield 58%, 2 steps). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ 

202 8.18 (d, J = 8.4 Hz, 2H, phenyl), 8.12 (m, J = 8.4 Hz, 2H, phenyl), 7.67 (d, J = 7.2 Hz,

- 203 1H, phenyl), 7.59 (d, J = 7.2 Hz, 1H, phenyl), 4.80 (t, J = 7.2 Hz, 2H, -NCH<sub>2</sub>-), 3.96
- 204 (s, 3H, -OMe), 3.58 (s, 1H, ethynyl), 2.24 2.08 (m, 2H), 1.44 1.34 (m, 4H), 1.33 –
- 205 1.26 (m, 6H), 0.89 0.85 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.88, 145.55,

206	142.34, 141.10, 131.17, 129.97, 129.72, 128.54, 124.38, 111.94, 83.26, 57.09, 52.22,
207	31.72, 30.25, 29.06, 28.98, 26.56, 22.61, 14.08. HRMS (ESI, m/z): [M+Na] <sup>+</sup> calcd for
208	C <sub>24</sub> H <sub>27</sub> N <sub>3</sub> O <sub>2</sub> Na, 412.2001; found, 412.1997.
209	<b>7b</b> . Colorless oil (yield 65%, 2 steps). <sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) $\delta$ 8.03 (s, 1H,
210	phenyl), 7.96 (d, J = 8.0 Hz, 1H, phenyl), 7.65 (d, J = 7.2 Hz, 1H, phenyl), 7.44 (d, J
211	= 8.0 Hz, 1H, phenyl), 7.24 (d, $J = 7.2$ Hz, 1H, phenyl), 4.73 (t, $J = 7.2$ Hz, 2H,
212	-NCH <sub>2</sub> -), 3.95 (s, 3H, -OCH <sub>3</sub> ), 3.56 (s, 1H, ethynyl), 2.26 (s, 3H, phenyl-CH <sub>3</sub> ), 2.13 –
213	2.03 (m, 2H, -NCH <sub>2</sub> CH <sub>2</sub> -), $1.37 - 1.29$ (m, 4H), $1.28 - 1.17$ (m, 6H), $0.86$ (t, $J = 6.8$
214	Hz, 3H). <sup>13</sup> C NMR (101 MHz, CDCl <sub>3</sub> ) δ 167.04, 144.87, 142.83, 141.74, 136.75,
215	132.69, 131.65, 130.91, 130.29, 129.88, 127.00, 126.05, 111.57, 82.86, 79.42, 57.04,
216	52.16, 31.68, 30.29, 29.03, 28.94, 26.50, 22.59, 20.54, 14.06. HRMS (ESI, m/z)
217	$[M+H]^+$ calcd for $C_{25}H_{30}N_3O_2$ , 404,2338; found, 404.2337.
218	<b>7c</b> . Colorless oil (yield 32%, 2 steps) <sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) $\delta$ 7.85 (s, 2H,
219	phenyl), 7.66 (d, J = 7.2 Hz, 1H, phenyl), 7.11 (d, J = 7.2 Hz, 1H, phenyl), 4.71 (t, J =
220	7.2 Hz, 2H, -NCH <sub>2</sub> -), 3.94 (s, 3H, -OCH <sub>3</sub> ), 3.56 (s, 1H, ethynyl), 2.11 – 2.04 (m, 2H),
221	2.03 (s, 6H, phenyl-CH <sub>3</sub> ), $1.32 - 1.26$ (m, 6H), $1.24 - 1.18$ (m, 4H), $0.85$ (t, $J = 6.8$
222	Hz, 3H). <sup>13</sup> C NMR (101 MHz, CDCl <sub>3</sub> ) δ 167.21, 145.01, 142.67, 141.43, 136.92,
223	131.90, 131.10, 129.60, 128.67, 125.78, 111.32, 82.67, 79.41, 57.00, 52.08, 31.64,
224	30.29, 29.70, 29.01, 28.90, 26.45, 22.57, 20.55, 14.04. HRMS (ESI, m/z) [M+H] <sup>+</sup>
225	calcd for C <sub>26</sub> H <sub>31</sub> N <sub>3</sub> O <sub>2</sub> , 418.2495; found, 418.2501.

*General synthetic procedure for compounds* **9a~9c**.

227	To a 100 mL Schlenk tube was added compound $7a \sim 7c$ (0.15 mmol), compound
228	$\boldsymbol{8}$ (110 mg, 0.060 mmol) and THF/Et_3N (30 mL/6 mL). Then Pd(PPh_3)_4 (5 mol%) and
229	CuI (5 mol%) were added under nitrogen. The mixture was allowed to stir at 60°C for
230	24 h. The solvents were evaporated and the residue was purified first on a silica gel
231	column (PE/DCM = 2:3) and then on a preparative silica gel plate (PE/THF = 9:1) to
232	give the crude product, which was recrystallized from DCM/MeOH to give 9a~9c.
233	<b>9a</b> . Dark green tar (yield 40%). <sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) $\delta$ 9.97 (d, $J = 4.4$
234	Hz, 2H, pyrrolic), 9.64 (d, <i>J</i> = 4.4 Hz, 2H, pyrrolic), 8.91 (d, <i>J</i> = 4.4 Hz, 2H, pyrrolic),
235	8.85 (d, <i>J</i> = 4.4 Hz, 2H, pyrrolic), 8.24 (d, <i>J</i> = 8.4 Hz, 2H, phenyl), 8.19 (d, <i>J</i> = 8.8 Hz,
236	2H, phenyl), 8.06 (d, J = 7.2 Hz, 1H, phenyl), 7.82 – 7.67 (m, 5H, phenyl), 7.48 (d, J
237	= 8.8 Hz, 2H, phenyl), 7.41 – 7.34 (m, 2H, phenyl), 7.09 – 6.88 (m, 8H, phenyl), 4.98
238	$(t, J = 7.2 \text{ Hz}, 2\text{H}, -\text{NC}H_2-), 4.04 - 3.92 \text{ (m, 7H, -OC}H_3, -\text{OC}H_2- \text{ and -NC}H_2-), 3.86 \text{ (t, })$
239	J = 6.4 Hz, 8H, -OCH <sub>2</sub> -), 2.42 – 2.31 (m, 2H), 1.97 – 1.87 (m, 2H), 1.85 – 1.75 (m,
240	2H), 1.62 – 1.51 (m, 4H), 1.42 – 1.26 (m, 16H), 1.18 – 1.07 (m, 9H), 1.07 – 0.94 (m,
241	24H), 0.94 – 0.83 (m, 18H), 0.82 – 0.72 (m, 20H), 0.67 – 0.58 (m, 8H), 0.57 – 0.36
242	(m, 24H). <sup>13</sup> C NMR (101 MHz, CDCl <sub>3</sub> ) δ 166.87, 159.97, 158.42, 152.00, 151.40,
243	150.59, 150.55, 146.01, 145.09, 143.26, 142.52, 141.26, 135.54, 132.22, 132.03,
244	131.72, 130.96, 130.80, 130.63, 130.06, 129.82, 129.73, 129.16, 129.02, 128.94,
245	128.08, 127.39, 125.49, 125.41, 124.70, 124.57, 124.42, 120.96, 118.20, 115.57,
246	115.48, 115.09, 114.78, 105.24, 101.22, 100.32, 99.74, 95.38, 93.03, 92.27, 68.71,
247	68.08, 57.06, 52.13, 47.77, 31.82, 31.79, 31.60, 31.51, 30.20, 29.71, 29.45, 29.35,

248	29.23, 29.16, 29.14, 29.10, 28.73, 28.64, 26.86, 26.78, 26.70, 25.72, 25.29, 22.65,
249	22.62, 14.12, 14.07, 14.03. MS (MALDI-TOF, m/z) [M] calcd for C <sub>136</sub> H <sub>176</sub> N <sub>8</sub> O <sub>7</sub> SZn,
250	2129.2674; found, 2129.1.
251	<b>9b</b> . Dark green tar (yield 39%). <sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) $\delta$ 9.97 (d, $J = 4.4$
252	Hz, 2H, pyrrolic), 9.65 (d, <i>J</i> = 4.8 Hz, 2H, pyrrolic), 8.92 (d, <i>J</i> = 4.8 Hz, 2H, pyrrolic),
253	8.86 (d, $J = 4.4$ Hz, 2H, pyrrolic), 8.10 – 8.03 (m, 2H, phenyl), 8.03 – 7.96 (m, 1H,
254	phenyl), 7.80 – 7.74 (m, 2H, phenyl), 7.74 – 7.67 (t, <i>J</i> = 8.4 Hz, 2H, phenyl), 7.59 (d,
255	J = 8.0 Hz, 1H, phenyl), 7.48 – 7.41 (m, 3H, phenyl), 7.39 – 7.32 (m, 2H, phenyl),
256	7.05 – 6.88 (m, 8H, phenyl), 4.91 (t, $J = 7.2$ Hz, 2H, -NCH <sub>2</sub> -), 3.99 – 3.91 (m, 7H,
257	-OCH <sub>3</sub> , -OCH <sub>2</sub> - and -NCH <sub>2</sub> -), 3.86 (t, $J = 6.4$ Hz, 8H, -OCH <sub>2</sub> -), 2.39 (s, 3H,
258	phenyl-CH <sub>3</sub> ), 2.35 – 2.24 (m, 2H), 1.97 – 1.86 (m, 2H), 1.81 – 1.72 (m, 2H), 1.51 –
259	1.27 (m, 22H), 1.19 – 1.09 (m, 9H), 1.07 – 0.95 (m, 24H), 0.93 – 0.85 (m, 16H), 0.82
260	– 0.73 (m, 20H), 0.67 – 0.59 (m, 8H), 0.56 – 0.37 (m, 24H). <sup>13</sup> C NMR (101 MHz,
261	CDCl <sub>3</sub> ) $\delta$ 167.13, 159.96, 158.42, 151.99, 151.43, 150.60, 150.59, 145.40, 145.10,
262	143.27, 143.18, 142.36, 136.90, 135.54, 132.22, 132.04, 131.70, 131.16, 130.95,
263	130.79, 130.61, 130.47, 130.08, 129.81, 129.62, 128.74, 127.38, 127.02, 126.63,
264	125.48, 125.41, 124.60, 124.44, 121.06, 118.25, 115.58, 115.39, 115.13, 114.78,
265	114.65, 105.30, 101.16, 99.79, 99.68, 95.37, 93.11, 91.89, 68.73, 68.08, 57.05, 52.10,
266	48.28, 47.77, 31.83, 31.75, 31.60, 31.51, 30.26, 29.45, 29.35, 29.23, 29.12, 29.09,
267	28.72, 28.64, 26.88, 26.69, 25.71, 25.27, 22.63, 20.71, 14.08, 14.04, 14.02. MS
268	(MALDI-TOF, m/z) [M] calcd for C <sub>137</sub> H <sub>178</sub> N <sub>8</sub> O <sub>7</sub> SZn, 2143.2831; found, 2143.2.

269	<b>9c.</b> Dark green tar (yield 35%). <sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) $\delta$ 9.96 (d, $J = 4.8$
270	Hz, 2H, pyrrolic), 9.65 (d, <i>J</i> = 4.8 Hz, 2H, pyrrolic), 8.91 (d, <i>J</i> = 4.8 Hz, 2H, pyrrolic),
271	8.85 (d, J = 4.8 Hz, 2H, pyrrolic), 8.08 (d, J = 7.2 Hz, 1H, phenyl), 7.91 (s, 2H,
272	phenyl), 7.80 – 7.74 (m, 2H, phenyl), 7.71 (t, J = 8.4 Hz, 2H, phenyl), 7.51 – 7.45 (m,
273	2H, phenyl), 7.40 – 7.35 (m, 2H, phenyl), 7.31 (d, J = 7.2 Hz, 1H, phenyl), 7.05 –
274	6.92 (m, 8H, phenyl), 4.88 (t, $J = 7.2$ Hz, 2H, -NCH <sub>2</sub> -), 4.03 – 3.93 (m, 7H, -OCH <sub>3</sub> ,
275	-OCH <sub>2</sub> - and -NCH <sub>2</sub> -), 3.86 (t, $J = 6.4$ Hz, 8H, -OCH <sub>2</sub> -), 2.31 – 2.22 (m, 2H), 2.17 (s,
276	6H, phenyl-CH <sub>3</sub> ), 1.96 – 1.88 (m, 2H), 1.85 – 1.76 (m, 2H), 1.48 – 1.41 (m, 4H), 1.40
277	- 1.32 (m, 10H), 1.32 - 1.26 (m, 6H), 1.19 - 1.08 (m, 9H), 1.08 - 0.95 (m, 24H), 0.94
278	– 0.83 (m, 18H), 0.83 – 0.74 (m, 20H), 0.67 – 0.58 (m, 8H), 0.57 – 0.35 (m, 24H). <sup>13</sup> C
279	NMR (101 MHz, CDCl <sub>3</sub> ) δ 167.30, 159.97, 158.43, 152.00, 151.45, 150.62, 145.51,
280	145.12, 143.28, 143.03, 142.05, 137.18, 135.56, 132.23, 132.08, 131.74, 130.97,
281	130.80, 130.63, 130.41, 130.09, 129.83, 129.42, 128.98, 128.71, 127.39, 126.29,
282	125.49, 125.42, 124.61, 124.45, 121.04, 118.23, 115.59, 115.44, 115.13, 114.80,
283	114.33, 105.33, 101.21, 99.77, 99.39, 95.41, 93.03, 91.87, 68.75, 68.09, 57.02, 52.05,
284	47.78, 31.82, 31.72, 31.60, 31.52, 30.27, 29.43, 29.33, 29.22, 29.11, 29.07, 28.70,
285	28.63, 26.89, 26.70, 26.65, 25.72, 25.26, 22.63, 20.70, 14.08, 14.04, 14.03. MS
286	(MALDI-TOF, m/z) [M] calcd for $C_{138}H_{180}N_8O_7SZn$ , 2157.2987; found, 2157.3.

287 *General synthetic procedure for* **XW33~XW35**.

To a Schlenk tube was added compound  $9a \sim 9c$  (0.025 mmol), THF (20 mL) and LiOH·H<sub>2</sub>O (42 mg, 1.0 mmol) in water (2 mL) and then charged with nitrogen. The

290	mixture was stirred at 60°C for 17 h under nitrogen. Water was added and the product
291	was extracted with dichloromethane. The organic layer was separated and dried over
292	Na <sub>2</sub> SO <sub>4</sub> . The solvents were evaporated and the residue was purified on a preparative
293	silica gel plate (DCM/MeOH = 15:1) to obtain the crude product, which was
294	recrystallized from DCM/MeOH to give <b>XW33~XW35</b> .
295	XW33. Dark green powders (yield 75%). <sup>1</sup> H NMR (400 MHz, $CDCl_3$ :
296	DMSO- $d_6 = 1:2$ ) $\delta$ 12.78 (br, 1H), 9.86 (d, $J = 4.4$ Hz, 2H, pyrrolic), 9.52 (d, $J = 4.8$
297	Hz, 2H, pyrrolic), 8.77 (d, <i>J</i> = 4.8 Hz, 2H, pyrrolic), 8.71 (d, <i>J</i> = 4.4 Hz, 2H, pyrrolic),
298	8.34 (d, J = 8.4 Hz, 2H, phenyl), 8.16 (d, J = 8.4 Hz, 2H, phenyl), 8.09 (d, J = 7.2 Hz,
299	1H, phenyl), 7.94 (d, $J = 7.2$ Hz, 1H, phenyl), 7.80 (dd, $J_1 = 10.0$ Hz, $J_2 = 1.6$ Hz, 1H,
300	phenyl), 7.75 – 7.66 (m, 3H, phenyl), 7.48 (d, J = 8.8 Hz, 2H, phenyl), 7.42 – 7.31 (m,
301	2H, phenyl), 7.14 – 6.98 (m, 6H, phenyl), 6.93 (d, J = 8.4 Hz, 2H, phenyl), 5.02 (t, J =
302	6.8 Hz, 2H), 3.95 (t, <i>J</i> = 6.4 Hz, 4H), 3.87 (t, <i>J</i> = 5.6 Hz, 8H), 2.36 (t, <i>J</i> = 7.2 Hz, 2H),
303	1.85 (t, J = 6.8 Hz, 2H), 1.78 – 1.70 (m, 2H), 1.63 – 1.43 (m, 10H), 1.39 – 1.27 (m,
304	16H), 1.17 – 1.06 (m, 10H), 1.03 – 0.88 (m, 46H), 0.78 – 0.69 (m, 16H), 0.65 – 0.53
305	(m, 16H), 0.47 – 0.30 (m, 9H). MS (MALDI-TOF, m/z) [M] calcd for
306	C <sub>135</sub> H <sub>174</sub> N <sub>8</sub> O <sub>7</sub> SZn, 2115.2518; found, 2115.2.

307 XW34. Dark green powders (yield 92%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub> :
308 DMSO-d<sub>6</sub> = 1:2) δ 12.86 (br, 1H, -COOH), 9.85 (d, J = 4.8 Hz, 2H, pyrrolic), 9.52 (d,
309 J = 4.4 Hz, 2H, pyrrolic), 8.74 (d, J = 4.8 Hz, 2H, pyrrolic), 8.69 (d, J = 4.4 Hz, 2H,
310 pyrrolic), 8.24 - 8.20 (m, 1H, phenyl), 8.09 (d, J = 7.2 Hz, 1H, phenyl), 7.93 (d, J =

511	8.0 Hz, 1H, phenyl), 7.80 (d, $J = 8.0$ Hz, 1H, phenyl), 7.75 – 7.66 (m, 3H, phenyl),
312	7.61 – 7.45 (m, 4H, phenyl), 7.44 – 7.34 (m, 2H, phenyl), 7.19 – 7.00 (m, 6H, phenyl),
313	6.93 (d, $J = 8.8$ Hz, 2H, phenyl), 4.93 (t, $J = 6.2$ Hz, 2H, -NCH <sub>2</sub> -), 4.01 – 3.92 (m, 4H,
314	-OCH <sub>2</sub> - and -NCH <sub>2</sub> -), 3.86 (t, $J = 5.6$ Hz, 8H, -OCH <sub>2</sub> -), 2.36 (s, 3H, phenyl-CH <sub>3</sub> ),
315	2.31 – 2.21 (m, 2H), 1.88 – 1.77 (m, 2H), 1.76 – 1.68 (m, 2H), 1.53 – 1.39 (m, 8H),
316	1.38 – 1.29 (m, 10H), 1.29 – 1.23 (m, 7H), 1.14 – 1.06 (m, 8H), 1.04 – 0.94 (m, 24H),
317	0.93 - 0.84 (m, 22H), 0.80 - 0.70 (m, 20H), 0.63 - 0.48 (m, 16 H), 0.41 - 0.29 (m,
318	8H). MS (MALDI-TOF, m/z) [M] calcd for C <sub>136</sub> H <sub>176</sub> N <sub>8</sub> O <sub>7</sub> SZn, 2129.2674; found,
319	2129.3.
320	<b>XW35</b> . Dark green powders (yield 70%). <sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> :DMSO- $d_6$
320 321	<b>XW35</b> . Dark green powders (yield 70%). <sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> :DMSO- $d_6$ = 1:2) $\delta$ 12.65 (br, 1H, -COO <i>H</i> ), 9.86 (d, <i>J</i> = 4.4 Hz, 2H, pyrrolic), 9.53 (d, <i>J</i> = 4.4 Hz, 2H)
<ul><li>320</li><li>321</li><li>322</li></ul>	<b>XW35</b> . Dark green powders (yield 70%). <sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> :DMSO- $d_6$ = 1:2) $\delta$ 12.65 (br, 1H, -COO <i>H</i> ), 9.86 (d, <i>J</i> = 4.4 Hz, 2H, pyrrolic), 9.53 (d, <i>J</i> = 4.4 Hz, 2H, pyrrolic), 8.78 (d, <i>J</i> = 4.4 Hz, 2H, pyrrolic), 8.72 (d, <i>J</i> = 4.8 Hz, 2H, pyrrolic),
<ul><li>320</li><li>321</li><li>322</li><li>323</li></ul>	<ul> <li>XW35. Dark green powders (yield 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>:DMSO-d<sub>6</sub></li> <li>= 1:2) δ 12.65 (br, 1H, -COOH), 9.86 (d, J = 4.4 Hz, 2H, pyrrolic), 9.53 (d, J = 4.4 Hz, 2H, pyrrolic), 8.78 (d, J = 4.4 Hz, 2H, pyrrolic), 8.72 (d, J = 4.8 Hz, 2H, pyrrolic), 8.11 – 8.06 (m, 2H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.76 – 7.66 (m, 3H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.76 – 7.66 (m, 3H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.76 – 7.66 (m, 3H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.76 – 7.66 (m, 3H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.76 – 7.66 (m, 3H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.76 – 7.66 (m, 3H, phenyl), 7.76 – 7.66 (m, 3H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.76 – 7.66 (m, 3H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.76 – 7.66 (m, 3H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.76 – 7.66 (m, 3H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.76 – 7.66 (m, 3H, phenyl), 7.76 – 7.66 (m, 3H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.76 – 7.66 (m, 3H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.76 – 7.66 (m, 3H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.76 – 7.66 (m, 3H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.76 – 7.66 (m, 3H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.76 – 7.66 (m, 3H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.76 – 7.66 (m, 3H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.76 – 7.66 (m, 3H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.76 – 7.66 (m, 2H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.76 – 7.66 (m, 2H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.76 – 7.66 (m, 2H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.76 – 7.66 (m, 2H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.76 – 7.66 (m, 2H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.76 – 7.66 (m, 2H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.76 – 7.66 (m, 2H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.76 – 7.66 (m, 2H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.84 – 7.88 – 7.88 – 7.88 – 7.88 – 7.88 – 7.88 – 7.88 – 7.88 – 7.88 – 7.88 – 7.88 – 7.88 – 7.88 – 7.88 – 7.88 – 7.88 – 7.88</li></ul>
<ul><li>320</li><li>321</li><li>322</li><li>323</li><li>324</li></ul>	<ul> <li>XW35. Dark green powders (yield 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>:DMSO-d<sub>6</sub></li> <li>= 1:2) δ 12.65 (br, 1H, -COOH), 9.86 (d, J = 4.4 Hz, 2H, pyrrolic), 9.53 (d, J = 4.4 Hz, 2H, pyrrolic), 8.78 (d, J = 4.4 Hz, 2H, pyrrolic), 8.72 (d, J = 4.8 Hz, 2H, pyrrolic), 8.11 – 8.06 (m, 2H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.76 – 7.66 (m, 3H, phenyl), 7.49 (d, J = 8.4 Hz, 2H, phenyl), 7.44 – 7.32 (m, 3H, phenyl), 7.15 – 6.99 (m, 6H, 7.49 (d, J = 8.4 Hz, 2H, phenyl), 7.44 – 7.32 (m, 3H, phenyl), 7.15 – 6.99 (m, 6H, 7.49 (d, J = 8.4 Hz, 2H, phenyl), 7.44 – 7.32 (m, 3H, phenyl), 7.15 – 6.99 (m, 6H, 7.49 (m, 2H, phenyl), 7.44 – 7.32 (m, 3H, phenyl), 7.15 – 6.99 (m, 6H, 7.49 (m, 2H, phenyl), 7.44 – 7.32 (m, 3H, phenyl), 7.15 – 6.99 (m, 6H, 7.49 (m, 2H, phenyl), 7.44 – 7.32 (m, 3H, phenyl), 7.15 – 6.99 (m, 6H, 7.49 (m, 2H, phenyl), 7.44 – 7.32 (m, 3H, phenyl), 7.15 – 6.99 (m, 6H, 7.49 (m, 2H, phenyl), 7.44 – 7.32 (m, 3H, phenyl), 7.15 – 6.99 (m, 6H, 7.49 (m, 2H, phenyl), 7.44 – 7.32 (m, 3H, phenyl), 7.15 – 6.99 (m, 6H, 7.49 (m, 2H, phenyl), 7.15 – 6.99 (m, 6H, 7.49 (m, 2H, phenyl), 7.44 – 7.32 (m, 3H, phenyl), 7.15 – 6.99 (m, 6H, 7.49 (m, 2H, phenyl), 7.15 – 6.99 (m, 6H, 7.49 (m, 2H, phenyl), 7.44 – 7.32 (m, 3H, phenyl), 7.15 – 6.99 (m, 6H, 7.49 (m, 2H, phenyl), 7.15 – 6.99 (m, 6H, 7.49 (m, 2H, phenyl), 7.15 – 6.99 (m, 6H, 7.49 (m, 2H, phenyl), 7.15 – 6.99 (m, 6H, 7.49 (m, 2H, phenyl), 7.15 – 6.99 (m, 6H, 7.49 (m, 2H, phenyl), 7.15 – 6.99 (m, 6H, 7.49 (m, 2H, phenyl), 7.41 – 7.30 (m, 2H, phenyl), 7.15 – 6.99 (m, 2H, phenyl), 7.41 – 7.30 (m, 2H, phenyl), 7.15 – 6.99 (m, 2H, phenyl), 7.41 – 7.30 (m, 2H, phenyl), 7.15 – 6.99 (m, 2H, phenyl), 7.41 – 7.30 (m, 2H, phenyl), 7.15 – 6.99 (m, 2H, phenyl), 7.41 – 7.30 (m, 2H, phenyl), 7.15 – 6.99 (m, 2H, phenyl), 7.41 – 7.30 (m, 2H, phenyl), 7.15 – 6.99 (m, 2H, phenyl), 7.41 – 7.30 (m, 2H, phenyl), 7.15 – 6.90 (m, 2H, phenyl), 7.41 – 7.30 (m, 2H, phenyl), 7.15 – 7.41 (m, 2H, phenyl), 7.41 – 7.41 (m, 2H, phenyl), 7.41 – 7.41 (m, 2H, phenyl), 7.41 – 7.41 (m, 2H, phenyl), 7.41</li></ul>
<ul> <li>320</li> <li>321</li> <li>322</li> <li>323</li> <li>324</li> <li>325</li> </ul>	<b>XW35</b> . Dark green powders (yield 70%). <sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> :DMSO- $d_6$ = 1:2) $\delta$ 12.65 (br, 1H, -COO <i>H</i> ), 9.86 (d, <i>J</i> = 4.4 Hz, 2H, pyrrolic), 9.53 (d, <i>J</i> = 4.4 Hz, 2H, pyrrolic), 8.78 (d, <i>J</i> = 4.4 Hz, 2H, pyrrolic), 8.72 (d, <i>J</i> = 4.8 Hz, 2H, pyrrolic), 8.11 – 8.06 (m, 2H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.76 – 7.66 (m, 3H, phenyl), 7.49 (d, <i>J</i> = 8.4 Hz, 2H, phenyl), 7.44 – 7.32 (m, 3H, phenyl), 7.15 – 6.99 (m, 6H, phenyl), 6.94 (d, <i>J</i> = 8.4 Hz, 2H, phenyl), 4.90 (t, <i>J</i> = 6.4 Hz, 2H, -NC $H_2$ -), 4.02 –
<ul> <li>320</li> <li>321</li> <li>322</li> <li>323</li> <li>324</li> <li>325</li> <li>326</li> </ul>	<b>XW35</b> . Dark green powders (yield 70%). <sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> :DMSO- $d_6$ = 1:2) $\delta$ 12.65 (br, 1H, -COO <i>H</i> ), 9.86 (d, <i>J</i> = 4.4 Hz, 2H, pyrrolic), 9.53 (d, <i>J</i> = 4.4 Hz, 2H, pyrrolic), 8.78 (d, <i>J</i> = 4.4 Hz, 2H, pyrrolic), 8.72 (d, <i>J</i> = 4.8 Hz, 2H, pyrrolic), 8.11 – 8.06 (m, 2H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.76 – 7.66 (m, 3H, phenyl), 7.49 (d, <i>J</i> = 8.4 Hz, 2H, phenyl), 7.44 – 7.32 (m, 3H, phenyl), 7.15 – 6.99 (m, 6H, phenyl), 6.94 (d, <i>J</i> = 8.4 Hz, 2H, phenyl), 4.90 (t, <i>J</i> = 6.4 Hz, 2H, -NCH <sub>2</sub> -), 4.02 – 3.93 (m, 4H, -NCH <sub>2</sub> - and –OCH <sub>2</sub> -), 3.88 (t, <i>J</i> = 5.6 Hz, 8H, –OCH <sub>2</sub> -), 2.31 – 2.21 (m, 3H)
<ul> <li>320</li> <li>321</li> <li>322</li> <li>323</li> <li>324</li> <li>325</li> <li>326</li> <li>327</li> </ul>	<b>XW35</b> . Dark green powders (yield 70%). <sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> :DMSO- $d_6$ = 1:2) $\delta$ 12.65 (br, 1H, -COO <i>H</i> ), 9.86 (d, <i>J</i> = 4.4 Hz, 2H, pyrrolic), 9.53 (d, <i>J</i> = 4.4 Hz, 2H, pyrrolic), 8.78 (d, <i>J</i> = 4.4 Hz, 2H, pyrrolic), 8.72 (d, <i>J</i> = 4.8 Hz, 2H, pyrrolic), 8.11 – 8.06 (m, 2H, phenyl), 7.84 – 7.78 (m, 2H, phenyl), 7.76 – 7.66 (m, 3H, phenyl), 7.49 (d, <i>J</i> = 8.4 Hz, 2H, phenyl), 7.44 – 7.32 (m, 3H, phenyl), 7.15 – 6.99 (m, 6H, phenyl), 6.94 (d, <i>J</i> = 8.4 Hz, 2H, phenyl), 4.90 (t, <i>J</i> = 6.4 Hz, 2H, -NCH <sub>2</sub> -), 4.02 – 3.93 (m, 4H, -NCH <sub>2</sub> - and –OCH <sub>2</sub> -), 3.88 (t, <i>J</i> = 5.6 Hz, 8H, –OCH <sub>2</sub> -), 2.31 – 2.21 (m, 2H), 2.14 (s, 6H, phenyl-CH <sub>3</sub> ), 1.92 – 1.81 (m, 2H), 1.80 – 1.70 (m, 2H), 1.55 – 1.40

- $329 \qquad (m, \ 44H), \ 0.82 \ \ 0.71 \ (m, \ 20H), \ 0.68 \ \ 0.53 \ (m, \ 16H), \ 0.48 \ \ 0.35 \ (m, \ 8H). \ MS$
- 330 (MALDI-TOF, m/z) [M] calcd for  $C_{137}H_{178}N_8O_7SZn$ , 2143.2831; found, 2143.3.
- 331 **PT-C6.** It was synthesized according to literature procedures [31] as dark red

- 332 powders. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.08 (s, 1H), 7.91 (dd, J = 8.4, 2.0 Hz, 1H,
- 333 phenyl), 7.67 (d, *J* = 2.0 Hz, 1H, phenyl), 7.44 (d, *J* = 8.4 Hz, 2H, phenyl), 7.32 (dd, *J*
- 334 = 8.4, 2.0 Hz, 1H, phenyl), 7.25 (d, J = 2.0 Hz, 1H, phenyl), 6.97 6.83 (m, 4H,
- 335 phenyl), 3.99 (t, J = 6.8 Hz, 2H), 3.89 (t, J = 7.2 Hz, 2H), 1.89 1.74 (m, 4H), 1.53 –
- 336 1.43 (m, 4H), 1.40 1.32 (m, 8H), 0.94 0.86 (m, 6H).
- 337 2.3 Fabrication of the solar cells

The FTO conducting glass was washed with a detergent solution, deionized 338 water, acetone and ethanol successively for 20 minutes under ultrasonication before 339 use. The preparation of the  $TiO_2$  electrodes and fabrication of the cells were adapted 340 from that reported by Grätzel and co-workers [37]. The TiO<sub>2</sub> photoanode was 341 prepared by repetitive screen-printing. Afterwards, the TiO<sub>2</sub> films were heated with a 342 programmed procedure at 275°C for 5 min, 325°C for 5 min, 375°C for 5 min, 450°C 343 344 for 15 min, and 500°C for 15 min. The resulting layers were post-treated with 40 mM TiCl<sub>4</sub> solution at 70°C for 30 min and sintered once again at 450°C for 30 min. Then 345 346 they were immersed in a 0.1 mM solution of the porphyrin dyes in a mixture of 347 CHCl<sub>3</sub> and ethanol (2:3, v/v) for 12 h at 25°C for dye uptake. For coadsorption, chenodeoxycholic acid was added directly into the porphyrin dye solutions. For 348 349 cosensitization, the coadsorbed photoanode was taken out and rinsed with ethanol, 350 and then immersed in a 0.3 mM solution of PT-C6 in a mixture of t-BuOH and acetonitrile (1:1, v/v) for 12 h. For the counter electrode, H<sub>2</sub>PtCl<sub>6</sub> in 2-propanol was 351 352 evenly distributed on FTO glass through spin coating, and the cathode was heated at

353	400°C for deposition of platinum. Eventually, the two electrodes were sealed with
354	thermoplastic Surlyn, and an electrolyte solution was injected through one hole in the
355	counter electrode to complete the fabrication of the sandwich-type solar cells. The
356	electrolyte was composed of 0.1 M LiI, 0.05 M I <sub>2</sub> , 0.6 M 1,
357	2-dimethyl-3-propyl-imidazolium iodide (DMPII) and 0.5 M 4-tert-butylpyridine
358	(TBP) in acetonitrile.
359	2.4 Theoretical calculation details

We employed density functional theory (DFT) calculations to optimize the ground state geometries of the sensitizers, using the hybrid B3LYP functional [38,39] and the 6-31G\* basis set [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].

## 365 3. Results and discussion



Scheme 1. Synthetic routes for XW33-XW35. Reaction conditions: i) KI, *t*-BuOOH, MeOH; ii)
bis(pinacolato)diboron, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, KOAc, 1,4-dioxane; iii) for 6a and 6b: methyl
4-boronobenzoate or 1, Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, THF/H<sub>2</sub>O; for 6c: 4, Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>3</sub>PO<sub>4</sub>, DMF; iv)
Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CuI, trimethylsilylacetylene, THF/Et<sub>3</sub>N; v) KOH (aq), THF/MeOH; vi) Pd(PPh<sub>3</sub>)<sub>4</sub>,
CuI, THF/Et<sub>3</sub>N; vii) LiOH·H<sub>2</sub>O, THF/H<sub>2</sub>O.

372 *3.1 Syntheses of the porphyrin dyes* 

366

The synthetic routes for porphyrin dyes **XW33-XW35** (Fig. 1) are depicted in Scheme 1. The key intermediates **1** and **4** were successfully obtained *via* Pd-catalyzed Miyaura coupling reactions under optimized conditions in high yields (>70%). Afterwards, they were connected to benzotriazole through Suzuki-coupling reactions. Subsequent Sonogashira coupling reactions yielded the ethynyl-substituted acceptor

moieties, which were respectively attached to intermediate 8 to accomplish the
porphyrin dye framework. Final hydrolysis of the esters gave rise to the target
products. All the key intermediates and target dyes were fully characterized with
NMR and MS (Fig. S4-S30).



383



384 Fig. 2 Absorption spectra of XW33-35 and cosensitizer PT-C6 in THF.

The UV-vis absorption spectra of XW33-XW35 in THF are shown in Fig. 2, and 385 386 the corresponding data are summarized in Table 1. The three porphyrin dyes exhibit intense Soret bands with the maxima at 469 nm, 464 nm and 462 nm, respectively, 387 388 and corresponding moderate Q bands at 675 nm, 672 nm and 670 nm, respectively. 389 The successive blue-shifts of the absorption bands from XW33 to XW35 indicate a 390 deteriorated conjugation, which can be easily understood from the increasing steric 391 hindrance associated with the increasing number of methyl groups. Consistently, the 392 estimated energy band gaps ( $E_{0-0}$ ) of XW34 and XW35 are 0.01 eV and 0.02 eV 393 larger than that of **XW33**, respectively (Table 1). It is noteworthy that the Soret and Q 394 bands of XW33 are both 10 nm red-shifted compared to those observed for our

395	previously reported analogue XW10 which does not contain the benzotriazole unit
396	[15]. This observation implies that the incorporation of the benzotriazole unit
397	successfully enhances the push-pull effect and thus achieves a favorable extended
398	spectrum. For the cosensitizer PT-C6, it exhibits a smaller absorption coefficient,
399	However, its absorption peak centered around 450 nm is very broad, which may
400	compensate for the relatively narrow Soret bands of the porphyrin dyes in this region.
401	To evaluate the feasibility of electron injection and dye regeneration processes in
402	terms of energy levels, cyclic voltammetry tests were conducted (Fig. S3), and the
403	estimated energy levels are illustrated in Fig. 3 and Table 1. Apparently, with the
404	increase of steric hindrance from XW33 to XW35, slightly elevated HOMOs and
405	LUMOs were observed. Fortunately, all the three porphyrin dyes have LUMO levels
406	(-0.91 V ~ -0.95 V) higher than the TiO <sub>2</sub> conduction band (~ -0.5 V), and HOMO
407	levels (0.91 V ~ 0.89 V) lower than the $I_3^-/I^-$ (~ 0.4 V) redox shuttle, indicating
408	feasibilities of both electron injection and dye regeneration processes.

409 <b>Table 1</b> . Ab	sorption and e	lectrochemical	data of XW33-	XW35
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Dye	Absorption $\lambda_{max}^{a}/nm$ ( $\varepsilon/10^{3} \text{ M}^{-1} \text{ cm}^{-1}$ )	$\lambda_{\max}^{TiO_2}$ /nm	$E_{0-0}$ <sup>c</sup> /eV	$E_{\rm ox}^{\ \ d}/{\rm V}$ (vs NHE)	$E_{\rm ox}^{*}/{\rm V}$ (vs NHE)
XW33	469 (427.5), 675 (126.9)	470	1.82	0.91	-0.91
XW34	464 (397.3), 672 (102.1)	465	1.83	0.90	-0.93
XW35	462 (435.5), 670 (109.0)	461	1.84	0.89	-0.95

410 <sup>*a*</sup> Absorption maxima in THF solutions  $(2 \times 10^{-6} \text{ M})$ .

411 <sup>*b*</sup> Absorption maxima on transparent  $TiO_2$  films.

412 <sup>*c*</sup> Estimated from the intersection wavelength ( $\lambda_{inter}$ ) of the normalized UV-vis absorption and 413 fluorescence spectra using the equation  $E_{0-0} = 1240/\lambda_{inter}$ .

414  $^{d} E_{ox}$  was measured in acetonitrile using 0.1 M tetra-*n*-butylammonium hexafluorophosphate

415 (TBAPF<sub>6</sub>) as the electrolyte (working electrode: FTO/TiO<sub>2</sub>/dye; reference electrode: SCE; counter

416 electrode: Pt) which was calibrated with ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) as an external reference.

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



418

419 Fig. 3 Schematic energy level diagrams of XW33-XW35.

421 Based on the results shown in the preceding section, it is anticipated that XW33-XW35 can be employed as DSSC dyes. Thus, devices were fabricated firstly 422 using the individual porphyrin dyes and then coadsorbed with CDCA. The results are 423 424 shown in Table 2 and Fig. 4. The  $V_{oc}$  values of devices based on the three individual dyes vary in a small range (704 mV ~ 717 mV), in contrast to the results of Li's 425 system where the  $V_{\rm oc}$  values are dramatically improved by the increased steric 426 427 hindrance [30]. Electrochemical impedance spectroscopy (EIS) results under dark 428 conditions reveal only slightly increased electron lifetimes of XW34 and XW35 in 429 comparison to XW33 (Fig. 4d), implying that the distortion-induced retardation of charge recombination is not as obvious as that observed in Li's system. On the other 430 hand, drastically different  $J_{\rm sc}$  values were observed for devices based on the three 431 dyes. A relatively high  $J_{sc}$  of 17.00 mA·cm<sup>-2</sup> was achieved for **XW33**, while the 432 corresponding values were drastically decreased to 13.28 mA·cm<sup>-2</sup> and 7.43 mA·cm<sup>-2</sup> 433

<sup>420 3.3</sup> Photovoltaic performance

434	for XW34 and XW35, respectively. This large difference was unambiguously
435	reflected in their IPCE spectra (Fig. 4b) with successively lowered IPCE plateaus. As
436	a result, the achieved power conversion efficiencies were found to be in a descending
437	order of $8.39\% > 6.61\% > 3.62\%$ for <b>XW33-35</b> , respectively. Notably, the efficiency
438	achieved for XW33 is higher than that obtained for our previously reported individual
439	dye XW11 (7.8%) and comparable to XW10 (8.6%) [15], and is also higher than that
440	of 5.05% obtained for the reported similar sensitizer DHC-1 [43]. These results
441	clearly indicate the effectiveness of incorporating the benzotriazole unit and the
442	validity of the molecular design. On the other hand, the decreasing efficiencies
443	obtained for XW34 and XW35 show a trend opposite to that observed for the dyes
444	reported by Li and coworkers [30], which will be discussed in more details in section

445 3.4.

446 **Table 2.** Photovoltaic parameters of the solar cells sensitized by **XW33-XW35** in the absence or 447 presence of CDCA under simulated AM 1.5 G full sunlight (100 mW·cm<sup>-2</sup>). The active area is 448  $0.12 \text{ cm}^2$ . The data are based on five parallel devices. The last column shows the dye loading 449 amounts.

Dyes	V <sub>oc</sub>	$J_{ m sc}$	FF	PCE	Dye loading
	[mV]	$[mA \cdot cm^{-2}]$	[%]	[%]	[nmol·cm <sup>-2</sup> ]
XW33	$712 \pm 1$	$17.00\pm0.29$	$69.3\pm0.3$	$8.39\pm0.12$	114
XW33 + CDCA	721 ± 2	$18.71\pm0.46$	$68.7\pm0.8$	$9.27\pm0.15$	97
XW34	717 ± 2	$13.28\pm0.09$	$69.5\pm0.4$	$6.61\pm0.06$	120
XW34 + CDCA	$729\pm2$	$14.85\pm0.55$	$68.5\pm1.0$	$7.42\pm0.19$	89
XW35	$704 \pm 1$	$7.43\pm0.12$	$69.3\pm0.6$	$3.62\pm0.05$	96
XW35 + CDCA	$719\pm3$	$8.24\pm0.71$	$69.4 \pm 1.0$	$4.11\pm0.29$	53



451 Fig. 4 a) *J-V* curves, b) IPCE spectra, c) capacitance and d) electron lifetimes of the DSSCs
452 based on XW33-XW35 in the absence or presence of CDCA coadsorption.

450

453 After coadsorption with CDCA, devices based on all the three dyes showed 454 slightly improved  $V_{oc}$  and obviously improved  $J_{sc}$ , resulting in elevated efficiencies of 9.27%, 7.42% and 4.11%, respectively. EIS measurements indicated prolonged 455 electron lifetimes induced by coadsorption with CDCA (Fig. 4d). Meanwhile, dye 456 loading amounts were estimated by comparing absorption of desorbed dye solutions 457 with that of their standard solutions. As expected, the competing adsorption of CDCA 458 caused diminished porphyrin dye uptake (Table 2). In view of the improved  $V_{oc}$  and 459 460 prolonged electron lifetimes, it can be concluded that the presence of CDCA is favorable for forming a more compact adsorption layer on TiO<sub>2</sub> and thus reduces 461 charge recombination, and CDCA is also favorable for suppressing the dye 462 463 aggregation on the TiO<sub>2</sub> film.

464 3.4 Theoretical analysis

465 In order to reveal the underlying reason for the strikingly different photovoltaic 466 performance of the three dyes, density functional theory (DFT) calculations were employed to obtain the optimized ground state geometries of the dyes, and the 467 calculated frontier molecular orbitals of HOMO and LUMO are shown in Fig. 5. As 468 469 expected, the increasing steric hindrance induced by the introduced methyl groups causes dramatically aggravated torsion between BTz and the adjacent phenylene ring, 470 which can be clearly evidenced by the increasing dihedral angles of 30.5°, 48.3° and 471 77.2° for XW33-XW35, respectively. Meanwhile, the LUMO electron distributions 472 are also seriously affected. As can be clearly observed in Fig. 5, while the LUMO 473 474 electrons of XW33 are reasonably distributed over the porphyrin core and the whole acceptor part including the anchoring carboxylic group, those of XW34 and XW35 475 seem to be separated from the anchoring group because of the relatively large dihedral 476 angles. Especially for XW35, there is very little electron distribution on the 477 carboxylic anchor, which is indicative of poor electronic coupling between the LUMO 478 479 of **XW35** and the  $TiO_2$ , resulting in poor electron injection [44], which may account for the drastically lowered  $J_{sc}$  values observed for XW34 and XW35. This 480 observation is in sharp contrast to the results reported by Li and coworkers [30]. 481

25



## 482



## 484 *3.5 Cosensitization*

485 **Table 3**. Photovoltaic parameters for the cosensitized solar cells under simulated AM 1.5 G full 486 sunlight (100 mW·cm<sup>-2</sup>). The active area is  $0.12 \text{ cm}^2$ . The data are based on five parallel devices.

487 The last two columns show the dye loading amounts.

Dyes	$V_{ m oc}$	$J_{ m sc}$	FF	PCE	Porphyrin	PT-C6
	[mV]	$[mA \cdot cm^{-2}]$	[%]	[%]	loading	loading
					[nmol·cm <sup>-2</sup> ]	[nmol·cm <sup>-2</sup> ]
PT-C6	$735\pm2$	$13.71\pm0.29$	68.6 ± 1.3	$6.91\pm0.12$	_	339
XW33 + CDCA + PT-C6	$733\pm3$	$18.93\pm0.11$	$67.2\pm0.5$	$9.32\pm0.09$	41	137
XW34 + CDCA + PT-C6	$737 \pm 3$	$17.12\pm0.21$	$67.3\pm0.7$	$8.49\pm0.12$	26	166
XW35 + CDCA + PT-C6	$740 \pm 4$	$14.50\pm0.11$	$68.6\pm0.5$	$7.34\pm0.05$	16	191





488

491 To further improve the photovoltaic performance, especially to compensate for the intrinsic drawback of XW34 and XW35, a stepwise cosensitization method was 492 carried out using a previously reported metal-free organic dye PT-C6 [31], which was 493 494 selected in this work because of its relatively high  $V_{oc}$  of 735 mV as well as its broad absorption. In addition, it is easily synthesized and the possibility of using it as a 495 496 cosensitizer for porphyrin dyes has been elucidated [45]. As shown in Table 3 and Fig. 6, all the cosensitized devices exhibit further improved  $V_{oc}$  and  $J_{sc}$  as compared with 497 those coadsorbed with CDCA. As a result, improved PCEs of 9.32%, 8.49% and 498 499 7.34% are achieved for XW33-XW35, respectively. It is noteworthy that more 500 pronounced enhancement of efficiencies was observed for XW34 and XW35 as 501 compared with XW33. To further insight into these results, dye loading amounts were

502 estimated by desorbing the dyes from TiO<sub>2</sub> photoanodes into basic THF solutions 503 followed by measuring the absorbance. Although the dye-loading amounts reveal a 504 dominating role of **PT-C6** instead of the **XW** porphyrin dyes in the cosensitization 505 systems, the role of the porphyrin dye is still indispensable because typical porphyrin characters in the long wavelength range of 650 ~ 750 nm can be clearly observed in 506 the IPCE spectra (Fig. 6b). In addition, EIS analysis indicates further prolonged 507 electron lifetimes upon cosensitization (Fig. 6d). Hence, the finally achieved 508 efficiencies are higher than those based solely on PT-C6 or the corresponding 509 porphyrin dyes, which may be ascribed to the densely packed dye adsorbing layer and 510 511 the broad absorption peak of **PT-C6**, although its peak largely overlaps with the Soret 512 band of the porphyrin dyes.

#### 513 **4. Conclusions**

In conclusion, porphyrin sensitizers XW33-XW35 featuring an alkyl-substituted 514 515 benzotriazole unit as the auxiliary acceptor have been designed, synthesized and used as DSSC sensitizers, among which XW33 exhibits the highest performance of 8.39%. 516 517 Introduction of the electron-withdrawing benzotriazole unit induces red-shifted 518 absorption, which is favorable for light-harvesting. The steric hindrance associated with the ortho-methyl groups in XW34 and XW35 induces enlarged torsion angles, 519 leading to slightly prolonged electron lifetimes and retarded charge recombination. 520 521 However, the aggravated torsion induces poor electronic coupling between the LUMO

522 electrons and TiO<sub>2</sub>, resulting in poor electron injection, and low  $J_{sc}$  values. As a result, 523 lower efficiencies of 6.61% and 3.62% were obtained for XW34 and XW35, 524 respectively. Bv coadsorption with CDCA and cosensitization with a phenothiazine-based organic dye PT-C6, elevated efficiencies of 9.32%, 8.49% and 525 7.34% were achieved for XW33-XW35, respectively. 526

527 These results demonstrate the effectiveness of incorporating a benzotriazole unit 528 as the auxiliary acceptor in extending the absorption, and elucidate the importance of 529 avoiding severe torsion within the acceptor part of the porphyrin dyes. Furthermore, 530 cosensitization with the spectrally broad and high-photovoltaged cosensitizer PT-C6 531 is effective in achieving higher efficiencies despite the fact that its absorption peak at 532 450 nm largely overlaps with the Soret band of the porphyrin dyes, which is in 533 contrast to most commonly used cosensitizers whose absorption peaks lie in the 534 absorption valley between the Soret band and the Q bands of porphyrin dyes. These 535 results provide further insight into developing efficient cosensitizers for porphyrin 536 dyes.

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# 679 Graphical abstract:



# 682 Highlights:

683 1. Absorption of porphyrins extended by introducing an auxiliary benzotriazole

684 acceptor.

- 685 2. The importance illustrated for avoiding severe torsion within the acceptor part.
- 686 3. The narrow Soret band of porphyrins compensated by a broad band of the

687 cosensitizer.

688 4. An achieved efficiency of 9.32%.