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As a strong electron donor, indoline has been used in developing organic sensitizers for fabricating efficient dye-sensitized solar cells. Herein we report porphyrin dyes based on modified indoline donors. Firstly, **XW29** and **XW31** featured with a methylphenyl-substituted indoline and a bulkier dialkylfluorene-substituted indoline, respectively, are synthesized. **XW31** exhibits a J<sub>sc</sub> of 22.06 mA·cm<sup>-2</sup> as compared with that of 21.26 mA·cm<sup>-2</sup> for **XW29**. Consequently, **XW31** achieves a higher power conversion efficiency of 10.46% than that of 10.14% for **XW29**. On this basis, to further broaden the spectral response, a benzothiadiazole (BTD) unit is incorporated as the auxiliary electron acceptor to obtain **XW30** and **XW32**, respectively. The IPCE spectra are thus successfully extended to 850 nm. However, due to possibly aggravated dye aggregation, charge recombination and less effective dye regeneration induced by the BTD unit, moderate efficiencies of *ca*. 8.6% are obtained. Through coadsorption, elevated efficiencies of ~9.9% are achieved for **XW30** and **XW32**. These results provide further insights into developing efficient porphyrin dyes by combining the dialkylfluorene moiety with the indoline donor.

# Introduction

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As a type of photovoltaic device, dye-sensitized solar cells (DSSCs) have created booming research interest over the past two decades.<sup>1</sup> Particularly, the quest for highly efficient sensitizing dyes has never stopped. Compared with ruthenium dyes and organic dyes,<sup>2-5</sup> porphyrin dyes have the advantage of relatively strong and broad absorption.<sup>6</sup> In fact, impressive efficiencies have been achieved by porphyrin dyes such as **YD2-o-C8**,<sup>7</sup> **GY50**<sup>8</sup> and the landmark molecule **SM315**.<sup>9</sup>

For designing efficient porphyrin sensitizers, it is essential to broaden the absorption spectra for enhancing  $J_{sc}$  and suppress the unfavorable charge recombination for improving  $V_{\rm oc}$ .<sup>10, 11</sup> The absorption band can be broadened by extending the  $\pi$ conjugation framework and/or strengthening the intramolecular charge transfer (ICT) effect with suitable electron donors, acceptors, and auxiliary acceptors.12-16 However, a large conjugation framework is susceptible to dyeaggregation and charge recombination, which are unfavorable for the photovoltaic performance. To overcome this problem, bulky alkyl chains can be introduced to suppress dye aggregation and charge recombination.17-19

With all the aforementioned considerations in mind, our





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# **Results and Discussion**

#### Synthesis

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The synthetic routes for the dyes are illustrated in Scheme 1. The details can be found in the experimental section. Firstly, the commercially available material 1,2,3,3a,4,8bhexahydrocyclopenta[b]indole successively underwent the Buchwald-Hartwig reaction, bromination and the Sonogashira reaction to obtain the ethynyl derivative of the indoline donor. Then the zinc dibromoporphyrin was utilized as the platform to attach the donor and acceptor to construct the D- $\pi$ -A framework. Finally the target products were obtained by hydrolysis of the esters. All the dyes are air-stable and soluble in common organic solvents such as CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, toluene and THF.

#### **Optical and Electrochemical Properties**

Fig. 2 shows the UV-vis absorption spectra of the four dyes in THF and on TiO<sub>2</sub> films, and the corresponding data are summarized in Table 1. The absorption maxima of XW29 are located around 458 nm and 673 nm. which are red-shifted by 10 nm and 43 nm respectively compared to the reported indoline-based porphyrin dye analogue CM-b<sup>31</sup> (448 nm and 630 nm) without the ethynylene group between the donor and the porphyrin ring, showing the advantage of the ethynylene linkage in light-harvesting. Compared to XW29, a tiny redshift in the Q band can be observed for XW31, and the same trend is observed for XW30 and XW32. These observations indicate that the fluorene substituent on the N-atom of the indoline donor may be slightly more electron-donating than the methylphenyl unit. In contrast to XW29 and XW31, the BTDcontaining dyes XW30 and XW32 exhibit further red-shifted Q bands ( $\Delta\lambda$  = ~20 nm), owing to the strong electronwithdrawing effect of the BTD unit.

For all the four dyes, their absorption spectra on the  $TiO_2$  films are slightly blue-shifted relative to those observed in THF (Table 1) because of a combined effect of deprotonation and aggregation. To make a clear comparison, the normalized solution and film absorption spectra are shown in Fig. S2. As compared with **XW29** and **XW31**, more obvious blue shoulders are observed for the films adsorbed with **XW30** and **XW32**,

denoting a possibly aggravated H-type aggregation<sup>32</sup> induced by the benzothiadiazole unit. It is noteworthy that the broadening character of the film absorption for all the four dyes is favorable for improving the light-harvesting ability.



Fig. 2. Absorption spectra of **XW29-XW32** a) in THF solutions and b) on transparent TiO<sub>2</sub> films (~3 um).

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	Absorption $\lambda_{\max}{}^a$ / nm ( $arepsilon$ , 10 <sup>3</sup> M <sup>-1</sup> cm <sup>-1</sup> )	λ <sub>max</sub> <sup>b</sup> / nm	E <sub>0-0</sub> c / eV	E <sub>ox</sub> <sup>d</sup> / V (vs NHE)	E <sub>ox</sub> *e/ V (vs NHE)				
XW29	458 (239.5), 673 (90.1)	457	1.83	0.83	-1.00				
XW30	467 (171.4), 693 (97.3)	463	1.75	0.84	-0.91				
XW31	455 (218.7), 674 (85.1)	451	1.82	0.85	-0.97				
XW32	468 (164.3), 695 (95.8)	462	1.75	0.86	-0.89				

## Table 1. Optical and Electrochemical Data for XW29-XW32

<sup>*a*</sup> Absorption maxima in THF solutions (3 × 10<sup>-6</sup> M). <sup>*b*</sup> Absorption maxima on transparent TiO<sub>2</sub> films. <sup>*c*</sup> Estimated from the intersection wavelength ( $\lambda_{inter}$ ) of the normalized Q-band absorption and fluorescence emission spectra using the equation  $E_{0-0} = 1240/\lambda_{inter}$ . <sup>*d*</sup>  $E_{ox}$  was measured in acetonitrile using 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as the electrolyte (working electrode: FTO/TiO<sub>2</sub>/dye; reference electrode: SCE; counter electrode: Pt) which was calibrated with ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) as an external reference. <sup>*e*</sup> Estimated from the equation  $E_{0x}^{*} = E_{0x} - E_{0-0}$ .

To confirm the compatibility of the dyes with  $TiO_2$  and the  $I_3$ -/I<sup>-</sup> redox couple in terms of energy levels, cyclic voltammetry curves were checked and the results are shown in Fig. S3, Fig. 3 and Table 1. Apparently, the experimentally determined HOMO energy levels for the porphyrin dyes are located between 0.83 V and 0.86 V (*vs.* NHE), which are more than 0.4 V more positive than the potential of  $I_3$ -/I<sup>-</sup> (~0.4 V *vs.* NHE). Meanwhile, the LUMO levels range between -0.89 V and -1.00 V, which are more negative than the conduction band of TiO<sub>2</sub> (~-0.5 V *vs.* NHE), providing sufficient driving force for electron injection. It should be noted that the HOMO levels of the four dyes here are less positive than those of our previously reported sensitizers based on phenothiazine donors (0.90 V~0.93 V),<sup>33</sup> indicative of the stronger electron donating ability of the indoline donor relative to phenothiazine.



## **Theoretical Analysis**

Density functional theory (DFT) calculations were performed to gain insight into the molecular energy levels and frontier molecular orbital distributions of the porphyrin dyes, using the Gaussian 09 program package<sup>34</sup> at the B3LYP/6-31G\* level.<sup>35-37</sup> As shown in Fig. 4, the HOMOs of the four dyese are mainly distributed on the indoline donor and the operphyrin occer, while the LUMOs are delocalized through the porphyrin core and the acceptor part. The appropriate charge separation and overlapping characteristics may facilitate the electron transfer from the donor to the acceptor and subsequent injection into the TiO<sub>2</sub> conduction band.



Fig. 4 Frontier molecular orbital profiles and energy levels of XW29-XW32 calculated by DFT.

#### **Device Performance**

DSSC devices were fabricated based on the porphyrin dyes. Iodine-based electrolyte was used throughout the study. The corresponding J-V curves are shown in Fig. 5 and the photovoltaic parameters are summarized in Table 2.



Fig. 5 a), b) *J-V* curves and c), d) IPCE action spectra of devices based on individual dyes of **XW29-XW32** in the absence/presence of 1 mM CDCA.

Table 2 Photovoltaic parameters of the devices based on porphyrin dyes XW29-XW32 under simulated AM 1.5G full irradiation (100 mW·cm<sup>-2</sup>). The active areads, OLAC embra the average values of four parallel devices. The last column shows the dye loading amount.

Dyes	CDCA	V <sub>oc</sub>	J <sub>sc</sub>	J <sub>SC</sub> <sup>IPCE</sup> a	J <sub>sc</sub>	FF	PCE <sup>c</sup>	Dye loading
	[mM]	[mV]	[mA·cm⁻²]	[mA·cm <sup>-2</sup> ]	error <sup>b</sup>	[%]	[%]	[nmol·cm <sup>-2</sup> ]
XW29	0	716 ± 4	$21.26 \pm 0.41$	18.97	12%	66.6 ± 0.3	$10.14 \pm 0.13$	97
	1	701 ± 1	$22.00 \pm 0.10$	18.38	20%	65.0 ± 0.6	$10.04 \pm 0.14$	86
XW30	0	678 ± 1	19.67 ± 0.29	16.59	19%	65.1 ± 1.0	8.68 ± 0.09	149
	1	688 ± 1	$21.48 \pm 0.16$	17.92	20%	66.8 ± 0.4	9.87 ± 0.13	127
XW31	0	720 ± 4	22.06 ± 0.30	19.99	10%	65.8 ± 1.0	10.46 ± 0.19	114
	1	696 ± 1	$21.98 \pm 0.31$	18.44	19%	65.0 ± 0.3	9.94 ± 0.17	59
XW32	0	677 ± 2	20.13 ± 0.20	17.26	17%	64.7 ± 0.4	8.82 ± 0.14	167
	1	688 ± 1	21.89 ± 0.16	18.38	19%	65.9 ± 0.5	9.94 ± 0.03	125

<sup>*a*</sup> The calculated J<sub>sc</sub> values by wavelength integration of the standard AM1.5G irradiation and the measured IPCE data. <sup>*b*</sup> The relative deviation between the measured J<sub>sc</sub> and the calculated J<sub>sc</sub> values. <sup>*c*</sup> The original data can be found in Table S1 and Table S2.

It is obvious that XW29 and XW31 featuring the ethynylbenzoic acid acceptor afforded high efficiencies exceeding 10%, with  $V_{oc}$  values of 716 mV and 720 mV, and  $J_{sc}$ values of 21.26 mA·cm<sup>-2</sup> and 22.06 mA·cm<sup>-2</sup>, respectively. These values are comparable to those for the porphyrin dyes with indoline donors reported by You and coworkers.<sup>31</sup> In contrast, benzothiadiazole-containing dyes XW30 and XW32 afforded lower Voc values of 678 mV and 677 mV as well as lower J<sub>sc</sub> values of 19.67 mA·cm<sup>-2</sup> and 20.13 mA·cm<sup>-2</sup>, respectively, resulting in lower PCEs of 8.68% and 8.82%, respectively. The lower Voc values observed for XW30 and XW32 relative to XW29 and XW31 may be ascribed to the aggravated dye aggregation and charge recombination effects induced by the auxiliary BTD unit (vide infra). The difference in J<sub>sc</sub> can be reflected in their IPCE spectra (Fig. 5c). Devices based on XW29 and XW31 exhibit high IPCE plateaus, while those based on XW30 and XW32 exhibit broad but lower IPCEs. Such a trend has also been observed in our previous systems.<sup>38</sup> It should be noted that the IPCE tails of XW30 and XW32 extend beyond 850 nm, possibly indicative of relatively serious dyeaggregation.39

As a special note, the  $J_{sc}$  values obtained from the J-V curves are deviated within 20% compared to the theoretical values calculated from integrating the IPCE curves (Table 2), which is rather large, but still within a reasonably acceptable range.<sup>40</sup> Theoretically, the deviation can be mainly ascribed to the following three reasons: 1) The reflection and absorption of the FTO glass may account for *ca*. 10%~15% loss in the IPCE;<sup>41, <sup>42</sup> 2) The full irradiation applied in the *J*-V test generates more electrons and enables more efficient charge transport/ collection than the wavelength-dependent light in the IPCE measurement;<sup>43</sup> 3) The full irradiation includes near-infrared light and thus generates heat and an increase in temperature would lead to an increase in  $J_{sc}$ ,<sup>43, 44</sup> while the wavelengthdependent light in the IPCE measurement barely exerts such an effect.</sup>

It is known that the IPCE is mainly governed by four factors: light-harvesting efficiency (LHE), electron injection efficiency ( $\varphi_{inj}$ ), charge collection efficiency ( $\eta_{coll}$ ) and dye regeneration efficiency ( $\eta_{reg}$ ).<sup>7</sup> According to the absorption spectra on transparent TiO<sub>2</sub> films (Fig. 2b) and by considering the thicker films with additional scattering layers used in the DSSC

devices, it is anticipated that XW30 and XW32 with broader absorption would have slightly higher LHE values in comparison to XW29 and XW31.9, 42 We then estimated the injection efficiencies by means electron of the photoluminescence (PL) decay measurements using the timecorrelated single-photon counting (TCSPC) technique.<sup>45</sup> The values were estimated to be 85%, 92%, 81% and 94%, respectively (Fig. S4). We also estimated the charge collection efficiencies from the electrochemical impedance spectroscopy (EIS) analysis by using the equation  $\eta_{\text{coll}} = (1 + R_{\text{tr}}/R_{\text{rec}})^{-1}$ .<sup>46-48</sup> The corresponding values at a bias potential of -0.70 V were estimated to be 99% for XW29 and XW31 and 97% for XW30 and XW32, respectively (Fig. S5 and Table S3). The lower charge collection efficiencies for XW30 and XW32 may indicate more serious charge recombination which may be derived from their longer molecular lengths and possibly more tilted adsorption orientation on the TiO<sub>2</sub> surface (vide infra). It is obvious that the different effects of the above-mentioned three factors on the IPCE of the dyes with or without BTD are in trade-off relationships, and the lower charge collection efficiencies of XW30 and XW32 might not fully rationalize the relatively lower IPCE and J<sub>sc</sub> values obtained for these two dyes. Hence, consistent with the lower  $J_{sc}$  values for XW30 and XW32, relatively lower dye regeneration efficiencies are assumed for these two BTD-containing dyes, which is in accordance with the reported results indicating that the longer molecular conjugation lengths of the dyes are correlated with inferior dye regeneration efficiencies for the porphyrin-based DSSCs.49

Based on the preceding results, we then used CDCA as the coadsorbent to suppress the dye-aggregation and charge recombination. The porphyrin dyes responded differently to CDCA (Table 2). **XW30** and **XW32** afforded improved PCEs of approximately 9.9%, as a result of ~10 mV of  $V_{\rm oc}$  increase and 1.7~1.8 mA·cm<sup>-2</sup> of  $J_{\rm sc}$  increase, which agrees well with the elevated IPCE plateaus (Fig. 5c and 5d). On the contrary, for **XW29** and **XW31**, CDCA unfavorably deteriorated their photovoltaic performance, especially in terms of  $V_{\rm oc}$ .

To further understand the device performance, the dye loading amounts were estimated spectroscopically by desorbing the dyes into 0.1 M solutions of NaOH in THF/H<sub>2</sub>O, and the results are shown in Table 2. Interestingly, the

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dialkylfluorene-substituted molecules showed slightly higher loading amounts than their methylphenyl-substituted analogues. This observation may be related to the fact that the additional alkyl chains attached to the fluorene unit might improve the dye solubility and thus facilitate the dye-uptake.<sup>32</sup> A higher loading amount is beneficial for light-harvesting and can improve  $J_{sc}$  if the aggregation is not obviously aggravated. Thus, it may partly account for the higher  $J_{sc}$  of **XW31** with respect to XW29 device. On the other hand, much higher dyeloading amounts were observed for XW30 and XW32 relative to XW29 and XW31. However, lower J<sub>sc</sub> values were observed for XW30 and XW32, probably indicating over-loading of the dyes. After coadsorption with CDCA, the loading amounts for all the four porphyrin dyes decreased because of the competing adsorption of CDCA. Apparently, XW31 and XW32 show more dramatic decrease of loading amounts as compared to XW29 and XW30, which could be rationalized by their bulkier structure.

# Charge Extraction and Transient Photovoltage Decay Measurements

To further understand the  $V_{oc}$  variations for the DSSCs based on the four porphyrin dyes, charge extraction (CE) and transient photovoltage decay (TPD) measurements were carried out.

As shown in Fig. 6a, at a certain open-circuit photovoltage, the amount of charge extracted from different devices are almost the same, implying similar positions of TiO<sub>2</sub> conduction band edges for the devices. On the other hand, the electron half-lifetimes  $(t_{1/2}^{TPD})$  are quite different (Fig. 6b). For the individual dye sensitized devices, the electron half-lifetimes for the devices of XW29 and XW31 are much longer than those of XW30 and XW32, indicative of less charge recombination of XW29 and XW31, which is consistent with the EIS results (Fig. S5). These results indicate that XW30 and XW32 might suffer from more serious charge recombination due to a possibly more tilted adsorption geometry associated with their extended conjugation lengths.<sup>50</sup> After coadsorption with CDCA, devices based on XW30 and XW32 exhibit slightly prolonged electron half-lifetimes, while those based on XW29 and XW31 show decreased electron half-lifetimes, which are in accordance with the trend of their  $V_{\rm oc}$  variations. It could be deduced that CDCA helps relieve the more serious aggregation and charge recombination problems in the devices of XW30 and XW32, while it causes over-competing adsorption in those of XW29 and XW31.



Fig. 6 a) Correlation between the charge stored in a dye-grafted titania film ( $Q^{CE}$ ) and the open-circuit photovoltage ( $V_{OC}$ ) measured with the charge extraction (CE) method and b) Comparison of electron half-lifetimes ( $t_{1/2}^{TPO}$ ) measured with the small-pulse transient photovoltage decay (TPD) against  $Q^{CE}$ .

# Conclusions

With the purpose to develop efficient DSSCs, we have developed a series of indoline-based porphyrin dyes by simultaneously modifying the electron donor and acceptor. Specifically, methylphenyl and dialkylfluorene moieties were respectively introduced into the indoline donor. For the acceptor, the versatile ethynylbenzoic acid unit was used in the absence or presence of the auxiliary benzothiadiazole (BTD) acceptor. For XW29 and XW31 without the additional BTD acceptor, high efficiencies exceeding 10% were achieved. Compared with XW29, the introduction of the dialkylfluorene unit in XW31 is favorable for improving the dye solubility and elevating both the photovoltage and the photocurrent. As a result, a higher PCE of 10.46% was achieved for XW31 relative to 10.16% for XW29. By introducing the auxiliary benzothiadiazole (BTD) acceptor, the absorption spectra of XW30 and XW32 were successfully extended, showing striking IPCE wavelengths beyond 850 nm. In spite of the favorable absorption, XW30 and XW32 exhibit lower efficiencies of 8.68%, and 8.82%, respectively, probably due to more serious aggregation and charge recombination problems and less effective dye regeneration. Fortunately, upon coadsorption with CDCA, the corresponding efficiencies were improved to 9.87% and 9.94%, respectively. In summary, these results provide further insights into developing efficient porphyrin dyes by combining the dialkylfluorene moiety with the indoline donor.

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### Materials and instrumentation

All reagents and solvents were purchased from commercial sources of analytical grade and used as received unless otherwise noted. Fluorine-doped SnO<sub>2</sub> conducting glass (FTO glass, transparency >90% in the visible range, sheet resistance 15 $\Omega$ /square) was purchased from the Geao Science and Educational Co. Ltd of China. TiO<sub>2</sub> paste (18NR-T and 18NR-AO) was purchased from Dyesol Ltd.

 $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained using a Bruker AM 400 spectrometer at 298 K with tetramethylsilane (TMS) used as the internal standard. 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 using 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 performed on a Versastat II electrochemical workstation (Princeton Applied Research) using 0.1 M TBAPF<sub>6</sub> (Adamas) 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 cm<sup>-2</sup> using a Newport Oriel PV reference cell system (model 91150 V). J-V curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a model 2400 source meter (Keithley Instruments, Inc. USA). The voltage step and delay time of the photocurrent were 10 mV and 40 ms, respectively. Action spectra of the incident monochromatic photon-toelectron conversion efficiency (IPCE) for the solar cells were with a Newport-74125 obtained 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. TCSPC measurements were performed on a LifeSpec-II fluorescence spectrometer employing an EPL-670 pulsed laser diode and a MCP high speed photomultiplier detector. The details for CE and TPD measurements have been described in previous papers.51,52

#### Syntheses of the dyes

Thestartingmaterial1,2,3,3,3,4,8,b\_chexahydrocyclopenta[b]indolewasDOput Chase of the hase of t

Compound 1a. It was prepared according to a procedure modified from the literature report.31 A mixture of 1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole (5.0 g, 31 mmol), 4-bromotoluene (5.37 g, 31 mmol), Pd(OAc)<sub>2</sub> (176 mg, 0.78 mmol), P<sup>t</sup>Bu<sub>3</sub>·HBF<sub>4</sub> (455 mg, 1.6 mmol) and <sup>t</sup>BuONa (4.2 g, 44 mmol) in toluene (40 mL) was heated at 95°C under N<sub>2</sub> for 9 h. After cooling to room temperature, water was added and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried over anhydrous Na2SO4, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether /  $CH_2Cl_2 = 10$  : 1) to afford **1a** as a colourless oil (7.1 g, 91%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.23 – 7.17 (m, 2H), 7.17 – 7.08 (m, 3H), 7.06 – 6.98 (m, 1H), 6.92 (d, J = 7.6 Hz, 1H), 4.80 - 4.70 (m, 1H), 3.87 -3.78 (m, 1H), 2.34 (s, 3H), 2.09 - 1.98 (m, 1H), 1.96 - 1.84 (m, 2H), 1.84 - 1.75 (m, 2H), 1.70 - 1.61 (m, 1H), 1.58 - 1.49 (m, 1H).

**Compound 1b.**<sup>54</sup> It was prepared as a white solid in a similar way with **1a** using 1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole (5.0 g, 31 mmol) and 2-bromo-9,9-dibutyl-9*H*-fluorene (11.2 g, 31 mmol) as the reactants (12.1 g, 88%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.69 – 7.57 (m, 2H), 7.35 – 7.27 (m, 2H), 7.26 – 7.19 (m, 3H), 7.14 (d, *J* = 7.2 Hz, 1H), 7.10 – 7.03 (m, 1H), 7.03 – 6.96 (m, 1H), 6.79 – 6.68 (m, 1H), 4.90 – 4.80 (m, 1H), 3.92 – 3.80 (m, 1H), 2.12 – 1.78 (m, 7H), 1.72 – 1.61 (m, 1H), 1.27 – 1.21 (m, 1H), 1.16 – 1.01 (m, 4H), 0.93 – 0.81 (m, 3H), 0.73 – 0.62 (m, 8H).

**Compound 2a.** It was prepared according to a procedure modified from the literature method.<sup>55</sup> To a solution of **1a** (6.67 g, 26.7 mmol) in acetone (130 mL) was added an acetone solution (50 mL) of NBS (4.76 g, 26.7 mmol) dropwise at 0°C. Then the mixture was stirred at room temperature for 3 h and then poured into water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in *vacuo*. The residue was purified by column chromatography on silica gel (petroleum ether / CH<sub>2</sub>Cl<sub>2</sub> = 10 : 1) to afford **2a** as a white powder (8.3 g, 94%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.19 – 7.11 (m, 5H), 7.08 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 4.78 – 4.70 (m 1H), 3.82 – 3.74 (m, 1H), 2.32 (s, 3H), 2.07 – 1.96 (m, 1H), 1.93 – 1.71 (m, 3H), 1.69 – 1.60 (m, 1H), 1.56 – 1.44 (m, 1H).

**Compound 2b**.<sup>56</sup> It was prepared as a white powder in a similar way with **2a** using **1b** (5.0 g, 11 mmol) as the starting material (5.7 g, 96%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.67 – 7.58 (m, 2H), 7.34 – 7.28 (m, 2H), 7.26 – 7.23 (m, 1H), 7.23 – 7.17 (m, 3H), 7.15 – 7.10 (m, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 4.90 – 4.81 (m, 1H), 3.87 – 3.78 (m, 1H), 2.11 – 1.78 (m, 8H), 1.73 – 1.64 (m, 1H), 1.60 – 1.46 (m, 1H), 1.18 – 1.00 (m, 4H), 0.78 – 0.56 (m, 10H).

**Compound 3a**. To a solution of **2a** (2.0 g, 6.1 mmol) in THF / Et<sub>3</sub>N (12 mL/48 mL) were added Pd(PPh<sub>3</sub>)<sub>4</sub> (352 mg, 0.30 mmol) and CuI (57 mg, 0.30 mol) under N<sub>2</sub>. The mixture was

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stirred at 50°C under N<sub>2</sub> before trimethylsilylacetylene (3.4 mL, 24 mmol) was added via a syringe over 20 min. Then the mixture was heated at 70°C for 22 h. The solvents were removed in *vacuo* and the residue was purified by flash column chromatography on silica gel (petroleum ether /  $CH_2Cl_2$  = 20 : 1) to afford **3a** as a yellow oil (1.17 g, 55%). $\delta$  7.21 – 7.18 (m, 1H), 7.17 – 7.11 (m, 5H), 6.73 (d, *J* = 8.4 Hz, 1H), 4.79 – 4.72 (m, 1H), 3.79 – 3.70 (m, 1H), 2.32 (s, 3H), 2.03 – 1.91 (m, 1H), 1.90 – 1.80 (m, 2H), 1.78 – 1.68 (m, 1H), 1.66 – 1.58 (m, 1H), 1.53 – 1.42 (m, 1H), 0.23 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  148.16, 139.59, 134.43, 131.76, 131.73, 129.56, 128.01, 120.28, 111.41, 106.62, 106.57, 90.62, 68.90, 44.88, 34.77, 33.39, 24.07, 20.57. HRMS (ESI, *m/z*): [M+H]<sup>+</sup> calcd for C<sub>23</sub>H<sub>28</sub>NSi, 346.1991; found, 346.1990.

**Compound 3b.** It was prepared as a light orange powder in a similar way with **3a** using **2b** (2.0 g, 3.9 mmol) as the starting material (1.2 g, 57%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.67 – 7.60 (m, 2H), 7.34 – 7.28 (m, 2H), 7.27 – 7.26 (m, 1H), 7.25 – 7.18 (m, 4H), 6.85 (d, *J* = 8.0 Hz, 1H), 4.92 – 4.84 (m, 1H), 3.85 – 3.77 (m, 1H), 2.08 – 2.00 (m, 1H), 1.98 – 1.85 (m, 6H), 1.85 – 1.76 (m, 1H), 1.70 – 1.63 (m, 1H), 1.55 – 1.45 (m, 1H), 1.15 – 1.03 (m, 4H), 0.74 – 0.59 (m, 10H), 0.24 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  151.77, 150.13, 147.84, 141.30, 140.72, 135.42, 134.74, 131.79, 128.10, 126.53, 125.96, 122.50, 120.00, 118.76, 118.67, 114.42, 111.75, 107.01, 106.46, 90.87, 69.05, 54.71, 44.95, 39.96, 39.93, 34.75, 33.34, 25.76, 25.74, 24.15, 22.81, 13.63, 13.61. HRMS (ESI, m/z): [M+H]<sup>+</sup> calcd for C<sub>37</sub>H<sub>46</sub>NSi, 532.3400; found, 532.3398.

**Compound 4a**. To a solution of **3a** (470 mg, 1.36 mmol) in THF / MeOH (30 mL / 30 mL) was added dropwise an aqueous KOH solution (1 M, 1.36 mL) . The reaction mixture was allowed to stir at room temperature for 4.5 h. Then water was added and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated in *vacuo* to afford the crude product of **4a** as a yellow oil (330 mg), which was extremely unstable on silica gel and was therefore directly used for the next step without further purification.

**Compound 4b**. It was prepared in a similar way with **4a** using **3b** (664 mg, 1.25 mmol) as the starting material and the crude product was obtained as a light orange powder (560 mg), which was also unstable on silica gel and was thus directly used for the next step without further purification.

**Compound 5a**. To a mixture of the zinc dibromoporphyrin (727 mg, 0.51 mmol) and the crude product of **4a** (155 mg) in THF / Et<sub>3</sub>N (200 mL / 50 mL) were added Pd<sub>2</sub>(dba)<sub>3</sub> (234 mg, 0.26 mmol) and AsPh<sub>3</sub> (313 mg, 1.02 mmol) under N<sub>2</sub>. The mixture was allowed to stir at 50°C under N<sub>2</sub> for 4.5 h. Then solvents were removed in *vacuo* and the residue was purified by column chromatography on silica gel (petroleum ether / CH<sub>2</sub>Cl<sub>2</sub> = 2 : 1) and then on a preparative silica gel plate (petroleum ether / THF = 25 : 1) to afford **5a** as a dark green tar (173 mg, 21%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.67 (d, *J* = 4.4 Hz, 2H, pyrrolic), 9.55 (d, *J* = 4.8 Hz, 2H, pyrrolic), 7.75 – 7.64 (m, 4H, phenyl), 7.27 (d, *J* = 8.4 Hz, 2H, phenyl), 7.21 (d, *J* = 8.4 Hz, 2H, phenyl), 7.04 – 6.95 (m, 5H, phenyl), 4.94 – 4.86 (m, 1H, indoline-CH), 4.00 – 3.93 (m, 1H, indoline-CH), 3.83 (t, *J* 

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= 6.4 Hz, 8H,  $-OCH_2$ -), 2.37 (s, 3H, phenylene- $CH_3$ ), 2.20<sub>CTE</sub> 2.110 (m, 1H, indoline- $CH_2$ -), 2.08 – 1.97 (m, 2H, indoline- $CH_2$ -), 0.190 – 1.82 (m, 1H, indoline- $CH_2$ -), 1.77 – 1.70 (m, 1H, indoline- $CH_2$ -), 1.68 – 1.60 (m, 1H, indoline- $CH_2$ -), 1.23 – 1.16 (m, 8H), 1.14 – 1.02 (m, 16H), 0.98 – 0.90 (m, 16H), 0.87 – 0.79 (m, 20H), 0.72 – 0.63 (m, 8H), 0.59 – 0.47 (m, 16H), 0.46 – 0.36 (m, 8H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  159.97, 152.10, 151.08, 150.34, 148.94, 148.16, 139.98, 135.18, 132.16, 131.94, 131.89, 131.83, 131.49, 130.69, 129.85, 129.66, 127.79, 121.13, 120.46, 114.51, 113.47, 107.39, 105.08, 104.09, 100.83, 97.05, 91.15, 69.27, 68.57, 64.56, 45.35, 35.20, 33.74, 31.87, 29.49, 29.38, 29.27, 29.10, 28.76, 28.65, 25.25, 24.46, 23.10, 22.66, 20.84, 14.11. HRMS (FTICR-MS) (m/z): [M+H]<sup>+</sup> calcd. for C<sub>100</sub>H<sub>133</sub>BrN<sub>5</sub>O<sub>4</sub>Zn, 1610.88269; found 1610.88843.

Compound 5b. It was prepared as a dark green tar in a similar way with 5a using the zinc dibromoporphyrin (700 mg, 0.493 mmol) and 4b (245 mg) as the starting materials (159 mg, 18%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.69 (d, J = 4.4 Hz, 2H, pyrrolic), 9.56 (d, J = 4.8 Hz, 2H, pyrrolic), 8.85 (d, J = 4.4 Hz, 2H, pyrrolic), 8.82 (d, J = 4.4 Hz, 2H, pyrrolic), 7.77 - 7.64 (m, 6H, phenyl), 7.38 – 7.26 (m, 5H, phenyl), 7.12 (d, J = 8.0 Hz, 1H, phenyl), 6.99 (d, J = 8.4 Hz, 4H, phenyl), 5.05 - 4.97 (m, 1H, indoline-CH), 4.04 - 3.97 (m, 1H, indoline-CH), 3.83 (t, J = 6.4 Hz, 8H, -OCH2-), 2.25 -2.15 (m, 1H), 2.12 - 2.06 (m, 1H), 2.04 -1.97 (m, 4H), 1.94 - 1.86 (m, 1H), 1.80 - 1.72 (m, 1H), 1.71 -1.61 (m, 1H), 1.21 - 1.03 (m, 30H), 0.99 - 0.90 (m, 16H), 0.87 -0.81 (m, 17H), 0.78 - 0.62 (m, 18H), 0.59 - 0.47 (m, 18H), 0.45 - 0.35 (m, 8H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.97, 152.12, 152.08, 151.11, 150.39, 150.36, 148.97, 147.82, 141.70, 141.04, 135.61, 135.46, 132.21, 131.97, 131.88, 131.49, 130.70, 129.69, 127.87, 126.79, 126.18, 122.75, 121.11, 120.30, 119.00, 118.91, 114.58, 113.82, 107.79, 105.11, 104.16, 100.79, 96.98, 91.31, 69.43, 68.59, 64.63, 55.00, 45.41, 40.27, 40.23, 35.17, 33.68, 31.86, 29.48, 29.37, 29.27, 29.09, 28.75, 28.65, 26.06, 26.03, 25.25, 24.53, 23.15, 23.09, 22.67, 14.12, 13.90, 13.87. HRMS (FTICR-MS) (m/z): [M+H]<sup>+</sup> calcd. for C<sub>114</sub>H<sub>151</sub>BrN<sub>5</sub>O<sub>4</sub>Zn, 1797.0235; found 1797.0241.

Compound 6a. To a mixture of 5a (80 mg, 0.050 mmol) and methyl 4-ethynylbenzoate (24 mg, 0.15 mmol) in THF / Et<sub>3</sub>N (24 mL / 4 mL) were added Pd(PPh<sub>3</sub>)<sub>4</sub> (29 mg, 0.025 mmol) and Cul (5 mg, 0.025 mmol) under N2. The mixture was stirred at 60°C under N<sub>2</sub> for 24 h. Then solvents were removed in vacuo and the residue was purified by column chromatography on silica gel (petroleum ether /  $CH_2Cl_2 = 1.2 : 1$ ) and then on a preparative silica gel plate (petroleum ether / THF = 9 : 1) to give the crude product, which was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> / MeOH to give 6a as a dark green solid (40 mg, 48%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.67 (d, J = 4.4 Hz, 2H, pyrrolic), 9.61 (d, J = 4.4 Hz, 2H, pyrrolic), 8.87 (d, J = 4.8 Hz, 2H, pyrrolic), 8.83 (d, J = 4.4 Hz, 2H, pyrrolic), 8.13 (d, J = 8.0 Hz, 2H, phenyl), 7.97 (d, J = 8.0 Hz, 2H, phenyl), 7.76 - 7.63 (m, 5H, phenyl), 7.27 (d, J = 8.0 Hz, 1H, phenyl), 7.21 (d, J = 8.3 Hz, 2H, phenyl), 7.04 – 6.96 (m, 5H, phenyl), 4.94 – 4.87 (m, 1H, indoline-CH), 4.00 – 3.92 (m, 4H, indoline-CH and -OCH<sub>3</sub>), 3.85 (t, J = 6.4 Hz, 8H, -OCH<sub>2</sub>-), 2.37 (s, 3H, phenylene-CH<sub>3</sub>), 2.20 – 2.11 (m, 1H, indoline-CH<sub>2</sub>-), 2.08 – 1.96 (m, 2H, indoline-CH<sub>2</sub>-), 1.89 – 1.80 (m, 1H, indoline-CH<sub>2</sub>-), 1.77 – 1.71 (m, 1H, indoline-CH<sub>2</sub>-), 1.68 – 1.60 (m, 1H,

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indoline- $CH_2$ -), 1.20 – 1.12 (m, 8H), 1.09 – 0.95 (m, 24H), 0.92 – 0.85 (m, 8H), 0.83 – 0.75 (m, 20H), 0.66 – 0.58 (m, 8H), 0.57 – 0.36 (m, 24H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  166.48, 159.93, 151.85, 151.40, 150.52, 150.34, 148.29, 139.87, 135.16, 135.10, 135.04, 132.06, 131.96, 131.61, 131.49, 131.27, 130.85, 130.23, 129.84, 129.80, 129.45, 129.07, 128.57, 128.28, 128.22, 128.16, 127.79, 120.92, 120.54, 115.39, 113.10, 107.31, 105.21, 102.87, 98.51, 97.95, 96.70, 94.56, 90.91, 69.26, 68.66, 52.15, 45.28, 35.23, 33.69, 31.84, 29.70, 29.45, 29.34, 29.23, 29.08, 28.71, 28.63, 25.27, 24.44, 22.64, 20.84, 14.08. HRMS (FTICR-MS) (m/z): [M]<sup>+</sup> calcd. for C<sub>110</sub>H<sub>139</sub>N<sub>5</sub>O<sub>6</sub>Zn, 1690.0011; found 1690.0016.

Compound 6c. It was synthesized in the same procedure as 6a except that 5a (105 mg, 0.065 mmol) and methyl 4-(7ethynylbenzo[c][1,2,5]thiadiazol-4-yl)benzoate (48 mg, 0.16 mmol) were used as the reactants and THF/piperidine (20 mL / 1 mL) were used as the solvents. The product was obtained as a brownish-green solid (35 mg, 29%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.97 (d, J = 4.4 Hz, 2H, pyrrolic), 9.66 (d, J = 4.4 Hz, 2H, pyrrolic), 8.93 (d, J = 4.8 Hz, 2H, pyrrolic), 8.84 (d, J = 4.4 Hz, 2H, pyrrolic), 8.21 (d, J = 7.2 Hz, 1H, phenyl), 8.15 (d, J = 8.4 Hz, 2H, phenyl), 8.05 (d, J = 8.0 Hz, 2H, phenyl), 7.82 (d, J = 7.2 Hz, 1H, phenyl), 7.76 – 7.64 (m, 4H, phenyl), 7.27 (d, J = 8.4 Hz, 2H, phenyl), 7.22 (d, J = 8.4 Hz, 2H, phenyl), 7.06 - 6.97 (m, 5H, phenyl), 4.95 - 4.87 (m, 1H, indoline-CH), 4.03 - 3.93 (m, 4H, indoline-CH and -OCH<sub>3</sub>), 3.87 (t, J = 6.4 Hz, 8H, -OCH<sub>2</sub>-), 2.38 (s, 3H, phenylene-CH), 2.24 - 1.94 (m, 4H), 1.89 - 1.80 (m, 1H), 1.77 - 1.71 (m, 1H), 1.68 - 1.60 (m, 1H), 1.18 - 0.92 (m, 32H), 0.90 - 0.72 (m, 28H), 0.67 - 0.36 (m, 31H). <sup>13</sup>C NMR (101 MHz,  $CDCl_3$ )  $\delta$  166.62, 159.97, 155.76, 152.55, 152.14, 152.08, 151.22, 150.47, 150.39, 150.32, 147.87, 141.64, 141.04, 140.50, 135.62, 135.45, 132.13, 131.58, 131.28, 130.71, 130.59, 129.73, 129.23, 128.94, 128.22, 127.88, 126.80, 126.19, 122.76, 121.06, 120.31, 119.01, 118.95, 118.10, 115.37, 114.61, 113.62, 107.74, 105.19, 102.70, 101.98, 98.33, 97.66, 92.22, 91.34, 69.42, 68.71, 55.01, 52.14, 48.79, 45.37, 40.28, 35.20, 33.65, 31.81, 29.46, 29.37, 29.27, 29.22, 29.13, 28.79, 28.69, 26.07, 26.04, 25.31, 24.53, 23.10, 22.61, 14.06, 13.92, 13.88. HRMS (FTICR-MS) (*m/z*): [M]<sup>+</sup> calcd. for C<sub>116</sub>H<sub>141</sub>N<sub>7</sub>O<sub>6</sub>SZn, 1823.9950; found 1823.9939.

**Compound 6b.** It was synthesized in the same procedure as 6a using 5b (95 mg, 0.053 mmol) as the starting material and it was obtained as a dark green powder (55 mg, 55%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.69 (d, J = 4.4 Hz, 2H, pyrrolic), 9.63 (d, J = 4.4 Hz, 2H, pyrrolic), 8.87 (d, J = 4.8 Hz, 2H, pyrrolic), 8.84 (d, J = 4.4 Hz, 2H, pyrrolic), 8.18 (d, J = 8.4 Hz, 2H, phenyl), 8.01 (d, J = 8.4 Hz, 2H, phenyl), 7.78 - 7.63 (m, 6H, phenyl), 7.38 - 7.27 (m, 5H, phenyl), 7.12 (d, J = 8.0 Hz, 1H, phenyl), 7.01 (d, J = 8.4 Hz, 4H, phenyl), 5.05 - 4.98 (m, 1H, indoline-CH), 4.05 - 3.96 (m, 4H, indoline-CH and –OCH<sub>3</sub>), 3.85 (t, J = 6.4 Hz, 8H, -OCH<sub>2</sub>-), 2.25 - 2.16 (m, 1H), 2.14 - 2.04 (m, 2H), 2.04 - 1.96 (m, 4H), 1.95 - 1.86 (m, 1H), 1.81 - 1.73 (m, 1H), 1.72 - 1.64 (m, 1H), 1.21 - 1.11 (m, 12H), 1.10 - 0.94 (m, 24H), 0.93 - 0.83 (m, 10H), 0.82 - 0.68 (m, 28H), 0.66 - 0.58 (m, 8H), 0.57 - 0.32 (m, 24H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.47, 159.92, 152.07, 151.84, 151.39, 150.52, 150.39, 150.35, 147.92, 141.59, 141.03, 135.65, 135.45, 132.05, 131.59, 131.50, 130.83,

# 130.25, 129.80, 129.44, 129.04, 128.55, $127_{v}85_{Art1}126_{AT}$ 126.20, 122.75, 120.89, 120.30, 119.01; 10.15.39.874.0464, 113.44, 107.71, 105.18, 102.73, 98.55, 97.78, 96.70, 94.56, 91.11, 69.41, 68.65, 55.00, 52.16, 45.33, 40.28, 40.23, 35.20, 33.62, 31.83, 29.45, 29.34, 29.24, 29.23, 29.08, 28.71, 28.63, 26.05, 26.02, 25.27, 24.50, 23.10, 22.64, 14.09, 13.92, 13.88. HRMS (FTICR-MS) (*m/z*): [M]<sup>+</sup> calcd. for C<sub>124</sub>H<sub>157</sub>N<sub>5</sub>O<sub>6</sub>Zn, 1876.1420; found 1876.1401.

Compound 6d. It was synthesized in the same procedure as 6a except that 5b (120 mg, 0.067 mmol) and methyl 4-(7ethynylbenzo[c][1,2,5]thiadiazol-4-yl) benzoate (49 mg, 0.17 mmol) were used as the reactants and THF/piperidine (20 mL / 1 mL) were used as the solvents. The product was obtained as a brownish-green powder (37 mg, 27%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.86 (d, J = 4.4 Hz, 2H, pyrrolic), 9.63 (d, J = 4.4 Hz, 2H, pyrrolic), 8.90 (d, J = 4.4 Hz, 2H, pyrrolic), 8.84 (d, J = 4.4 Hz, 2H, pyrrolic), 7.99 (d, J = 7.2 Hz, 1H, phenyl), 7.80 (d, J = 8.0 Hz, 2H, phenyl), 7.76 – 7.62 (m, 8H, phenyl), 7.43 (d, J = 7.2 Hz, 1H, phenyl), 7.39 - 7.25 (m, 5H, phenyl), 7.10 (d, J = 8.0 Hz, 1H, phenyl), 7.04 (d, J = 8.8 Hz, 4H, phenyl), 5.02 (t, J = 7.0 Hz, 1H, indoline-CH), 4.00 (t, J = 8.0 Hz, 1H, indoline-CH), 3.95 - 3.83 (m, 11H, -OCH\_2- and -OCH\_3), 2.26 – 2.14 (m, 1H), 2.12 – 2.06 (m, 1H), 2.04 - 1.97 (m, 4H), 1.95 - 1.86 (m, 1H), 1.82 - 1.73 (m, 1H), 1.72 - 1.62 (m, 1H), 1.32 - 1.27 (m, 2H), 1.20 - 1.08 (m, 12H), 1.08 - 0.93 (m, 24H), 0.92 - 0.83 (m, 10H), 0.82 -0.71 (m, 27H), 0.69 – 0.63 (m, 8H), 0.62 – 0.45 (m, 24H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  166.56, 159.97, 155.66, 152.40, 152.12, 151.21, 150.47, 150.31, 148.22, 140.27, 139.87, 135.15, 132.19, 131.89, 131.60, 131.33, 130.77, 130.68, 130.58, 130.53, 129.83, 129.76, 129.11, 128.79, 128.04, 127.79, 127.73, 120.93, 120.45, 117.91, 115.49, 113.14, 107.31, 105.15, 102.89, 101.64, 98.41, 97.86, 92.23, 90.98, 69.23, 68.70, 52.13, 45.29, 35.23, 33.70, 31.80, 29.44, 29.35, 29.25, 29.21, 29.12, 28.77, 28.68, 25.33, 24.45, 22.60, 20.85, (FTICR-MS) 14.06. HRMS (*m/z*): [M]+ calcd. for C<sub>130</sub>H<sub>159</sub>N<sub>7</sub>O<sub>6</sub>SZn, 2010.1359; found 2010.1331.

XW29. To a solution of 6a (54 mg, 0.032 mmol) in THF (20 mL) was added a solution of LiOH·H $_2$ O (54 mg, 1.3 mmol) in  $H_2O$  (2 mL). The mixture was stirred at 55°C under  $N_2$  for 18 h. After cooling to room temperature, water was added and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated in vacuo. The residue was then purified on a preparative silica gel plate  $(CH_2Cl_2 / MeOH = 15 : 1)$  to afford the crude product, which was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> / MeOH to give XW29 as a dark green powder (43 mg, 79%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub> : DMSOd<sub>6</sub> = 1:2, v/v) δ 12.94 (br, 1H, -COOH), 9.52 (d, J = 4.4 Hz, 4H, pyrrolic), 8.70 (d, J = 4.4 Hz, 2H, pyrrolic), 8.67 (d, J = 4.4 Hz, 2H, pyrrolic), 8.18 - 8.13 (m, 2H, phenyl), 8.06 (d, J = 8.4 Hz, 2H, phenyl), 7.76 - 7.61 (m, 4H, phenyl), 7.30 - 7.18 (m, 4H, phenyl), 7.06 (d, J = 8.4 Hz, 4H, phenyl), 6.98 (d, J = 8.4 Hz, 1H, phenyl), 5.01 - 4.93 (m, 1H, indoline -CH), 4.00 - 3.94 (m, 1H, indoline -CH), 3.87 (t, J = 6.4 Hz, 8H, -OCH<sub>2</sub>-), 2.34 (s, 3H, phenylene-CH<sub>3</sub>), 2.22 – 2.10 (m, 1H, indoline -CH<sub>2</sub>-), 2.04 – 1.95 (m, 1H, indoline -CH<sub>2</sub>-), 1.92 – 1.81 (m, 2H, indoline -CH<sub>2</sub>-), 1.77 - 1.68 (m, 1H, indoline -CH<sub>2</sub>-), 1.60 - 1.49 (m, 1H, indoline -CH<sub>2</sub>-), 1.21 - 1.12 (m, 8H), 1.11 - 1.01 (m, 16H), 1.01 - 0.87 (m,

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24H), 0.85 – 0.73 (m, 20H), 0.66 – 0.50 (m, 16H), 0.45 – 0.31 (m, 8H). HRMS (FTICR-MS) (m/z): [M]<sup>+</sup> calcd. for C<sub>109</sub>H<sub>137</sub>N<sub>5</sub>O<sub>6</sub>Zn, 1675.9855; found 1675.9836.

XW30. It was synthesized in the same procedure as XW29 using 6c (60 mg, 0.033 mmol) as the starting material, and it was obtained as a brownish-green powder (50 mg, 83%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub> : DMSO- $d_6$  = 1 : 2)  $\delta$  12.93 (br, 1H, -COOH), 9.88 (d, J = 4.8 Hz, 2H, pyrrolic), 9.52 (d, J = 4.4 Hz, 2H, pyrrolic), 8.77 (d, J = 4.4 Hz, 2H, pyrrolic), 8.68 (d, J = 4.4 Hz, 2H, pyrrolic), 8.38 (d, J = 7.2 Hz, 1H, phenyl), 8.25 (d, J = 8.4 Hz, 2H, phenyl), 8.17 (d, J = 7.2 Hz, 2H, phenyl), 8.13 (d, J = 7.2 Hz, 1H, phenyl), 7.76 – 7.68 (m, 3H, phenyl), 7.66 (d, J = 8.4 Hz, 1H, phenyl), 7.27 (d, J = 8.4 Hz, 2H, phenyl), 7.22 (d, J = 8.4 Hz, 2H, phenyl), 7.07 (d, J = 8.4 Hz, 4H, phenyl), 6.98 (d, J = 8.4 Hz, 1H, phenyl), 5.01 - 4.94 (m, 1H, indoline-CH), 4.00 - 3.94 (m, 1H, indoline-CH), 3.88 (t, J = 5.6 Hz, 8H, -OCH<sub>2</sub>-), 2.35 (s, 3H, phenylene-CH<sub>3</sub>), 2.22 – 2.12 (m, 1H, indoline-CH<sub>2</sub>-), 2.02 – 1.96 (m, 1H, indoline-CH<sub>2</sub>-), 1.92 - 1.82 (m, 2H, indoline-CH<sub>2</sub>-), 1.77 - 1.69 (m, 1H, indoline-CH<sub>2</sub>-), 1.60 - 1.50 (m, 1H, indoline-CH<sub>2</sub>-), 1.15 - 1.07 (m, 8H), 1.04 - 0.85 (m, 40H), 0.81 - 0.70 (m, 20H), 0.66 - 0.52 (m, 16H), 0.44 - 0.34 (m, 8H). HRMS (FTICR-MS) (*m*/*z*): [M]<sup>+</sup> calcd. for C<sub>115</sub>H<sub>139</sub>N<sub>7</sub>O<sub>6</sub>SZn, 1809.9794; found 1809.9759.

**XW31**. It was synthesized in the same procedure as **XW29** using **6b** (64 mg, 0.034 mmol) as the starting material, and it was obtained as a dark green powder (49 mg, 78%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub> : DMSO- $d_6 = 1 : 2$ , v / v)  $\delta$  13.02 (br, 1H, -COOH), 9.57 – 9.49 (m, 4H, pyrrolic), 8.70 (d, J = 4.4 Hz, 2H, pyrrolic), 8.67 (d, J = 4.0 Hz, 2H, pyrrolic), 8.17 (d, J = 8.0 Hz, 2H, phenyl), 8.05 (d, J = 8.0 Hz, 2H, phenyl), 7.82 – 7.66 (m, 6H, phenyl), 7.42 – 7.24 (m, 5H, phenyl), 7.15 – 7.00 (m, 5H, phenyl), 5.14 – 5.04 (m, 1H, indoline -CH), 4.04 – 3.97 (m, 1H, indoline -CH), 3.93 – 3.78 (m, 8H, -OCH<sub>2</sub>-), 2.24 – 2.16 (m, 1H), 2.08 – 1.97 (m, 5H), 1.96 – 1.88 (m, 2H), 1.79 – 1.72 (m, 1H), 1.61 – 1.54 (m, 1H), 1.18 – 0.92 (m, 52H), 0.82 – 0.53 (m, 46H), 0.43 – 0.30 (m, 8H). HRMS (FTICR-MS) (m/z): [M]<sup>+</sup> calcd. for C<sub>123</sub>H<sub>155</sub>N<sub>5</sub>O<sub>6</sub>Zn, 1862.1263; found 1862.1248.

XW32. It was synthesized in the same procedure as XW29 using 6d (55 mg, 0.027 mmol) as the starting material, and it was obtained as a brownish-green powder (46 mg, 85%). <sup>1</sup>H NMR (400 MHz,  $CDCl_3$  : DMSO- $d_6$  = 1 : 2)  $\delta$  12.93 (br, 1H, -COOH), 9.88 (d, J = 4.4 Hz, 2H, pyrrolic), 9.54 (d, J = 4.4 Hz, 2H, pyrrolic), 8.77 (d, J = 4.8 Hz, 2H, pyrrolic), 8.68 (d, J = 4.0 Hz, 2H, pyrrolic), 8.39 (d, J = 7.2 Hz, 1H, phenyl), 8.25 (d, J = 8.0 Hz, 2H, phenyl), 8.18 (d, J = 7.6 Hz, 2H, phenyl), 8.13 (d, J = 7.6 Hz, 1H, phenyl), 7.84 – 7.63 (m, 6H, phenyl), 7.42 – 7.22 (m, 5H, phenyl), 7.14 - 7.00 (m, 5H, phenyl), 5.13 - 5.04 (m, 1H, indoline-CH), 4.05 - 3.98 (m, 1H, indoline-CH), 3.89 (t, J = 5.6 Hz, 8H, -OCH<sub>2</sub>-), 2.26 - 2.15 (m, 1H), 2.09 - 1.97 (m, 5H), 1.96 -1.89 (m, 2H), 1.80 - 1.71 (m, 1H), 1.64 - 1.54 (m, 1H), 1.17 -1.06 (m, 12H), 1.05 - 0.85 (m, 40H), 0.84 - 0.51 (m, 46H), 0.46 0.32 (m, 8H). HRMS (MALDI-TOF, m/z) calcd for C<sub>129</sub>H<sub>157</sub>N<sub>7</sub>O<sub>6</sub>SZn, 1996.1208; found, 1996.1202.

#### **Fabrication of Solar Cells**

The FTO conducting glass was washed with a detergent solution, deionized water, acetone and ethanol successively

for 20 minutes under ultrasonication before use The preparation of the TiO2 electrodes and fabrieation/of the cells were adapted from that reported by Grätzel and co-workers.<sup>57</sup> The photoanode was prepared by repetitive screen-printing. Afterwards, the TiO<sub>2</sub> films were heated with a programmed procedure at 275 °C for 5 min, 325 °C for 5 min, 375 °C for 5 min, 450 °C 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 they were immersed in a 0.1 mM solution of the dyes in a mixture of CHCl<sub>3</sub> and ethanol (2:3, v/v) for 10 h at 25 °C for dye loading. For coadsorption, chenodeoxycholic acid was added into the dye solution as above mentioned. For the counter electrode, H<sub>2</sub>PtCl<sub>6</sub> in 2-propanol solution was uniformly distributed on FTO glass through spin coating, and the cathode was heated at 400 °C for deposition of platinum. Eventually, the two electrodes were sealed with thermoplastic Surlyn, and an electrolyte solution was injected through one hole in the counter electrode to complete the sandwich-type solar cells. The electrolyte was composed of 0.1 M Lil, 0.05 M I<sub>2</sub>, 1.0 M 1, 2-dimethyl-3-propyl-imidazolium iodide (DMPII) and 0.5 M 4tert-butylpyridine (TBP) in acetonitrile.

# Conflicts of interest

There are no conflicts to declare.

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A high power conversion efficiency exceeding 10% was achieved for novel porphyrin sensitizers with modified indoline donors.