

Supporting Information:

A novel *N*-fused carbazole-zinc porphyrin-free base porphyrin triad for efficient near-IR dye-sensitized solar cells

Yizhu Liu,^{a,b} Hong Lin,^b Joanne Ting Dy,^a Koichi Tamaki,^a Jotaro Nakazaki,^a Daisuke Nakayama,^a Satoshi Uchida,^a Takaya Kubo,^a and Hiroshi Segawa*^a

^a Research Center for Advanced Science and Technology, The University of Tokyo, 4-6-1, Komaba, Meguro-ku, Tokyo, 153-8904, Japan. Email: csegawa@mail.ecc.u-tokyo.ac.jp.

^b State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing, 100084, P. R. China.

Experimental

General

Standard Schlenk techniques were employed to manipulate oxygen and moisture sensitive chemicals. Starting materials were all commercially available and used as received if not specially mentioned. Dehydrated solvents for reactions, electrochemical measurements and DSC electrolyte preparation, including dichloromethane, toluene, tetrahydrofuran (THF), pyridine and methanol, solvents for column chromatography, including *n*-hexane, dichloromethane, chloroform, ethyl acetate, methanol and acetonitrile, and granular neutral silica gel for column chromatography were purchased from Kanto Chemical. Bis(triphenylphosphino)palladium dichloride, tris(dibenzylideneacetone)dipalladium(0), 1 M tetrabutylammonium fluoride (TBAF) in THF and triphenylarsine were purchased from Tokyo Chemical Industry. Cuprous iodide was purchased from Kojundo Chemical Laboratory. 1,2-Dimethyl-3-propylimidazolium iodide (DMPII) was purchased from Shikoku Chemicals Corporation. Palladium(II) acetate, lithium iodide and 4-*tert*-butylpyridine (TBP) were purchased from Aldrich. Trifluoroacetic acid (TFA), *N*-bromosuccinimide (NBS), 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), 1 M HCl solution, 1 M sodium hydroxide solution, triisopropylsilylacetylene, sodium hydride, calcium hydride, anhydrous sodium sulfate, triethylamine (TEA) and *tert*-butyl chloride were purchased from Wako Pure Chemical and the latter two were distilled over CaH₂ before use. Chloroform for porphyrin annulation was dehydrated by passing through a short column of neutral alumina (Merck 101077, 70-230 mesh). De-ionized water was produced by Millipore Lab Water Purification Systems. 3,5-Di-*tert*-butylbenzaldehyde¹, dipyrromethane², 5-(4-carbomethoxyphenyl)dipyrromethane², 3,6-di-*tert*-butyl-9*H*-carbazole³, and 10-(4-methoxycarbonylphenyl)-5,15-bis(3,5-di-*tert*-butylphenyl)porphyrin⁴ were synthesized according to literature. Chemical shifts for ¹H NMR spectra were recorded by Bruker DX500R against TMS as internal standard. MALDI-TOF mass spectra were recorded by Bruker AutoFLEX. High-resolution mass spectra were recorded by Shimadzu LCMS-8030 Ultra Fast Mass Spectroscopy. FT-IR spectra were acquired using by a IRPrestige-21 IR spectrometer with a KBr pellet. UV-vis absorption spectra of the sensitizer in solution and on TiO₂ film were measured by JASCO V-570 UV/VIS/NIR Spectrophotometer. TiO₂ film for absorption measurement comprises the transparent part of the photoanodes (see **Cell Fabrication** below). Spectrophotometer. Electrochemistry was performed with a three-electrode potentiostat (BAS 100B/W Electrochemical Workstation) in dehydrated dichloromethane which was further deoxygenated by bubbling with prepurified argon. Differential pulse voltammetry was conducted in a home-made two-compartment cell in which saturated calomel electrode (SCE) as reference electrode soaked in saturated KCl solution was separated by a salt bridge with the bulk sample solution where a Pt disk working electrode (BAS) and a Pt wire as counter electrode were settled. Potentials were calibrated with reference to Fc⁺/Fc couple.

Cell Fabrication

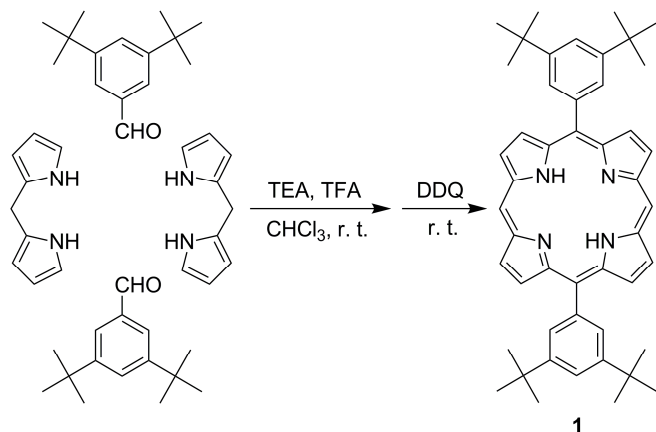
TiO₂ films as photoanodes were prepared by repeatedly screen printing TiO₂ pastes (Solaronix) onto F-doped SnO₂ (FTO, Nippon Sheet Glass) substrates. Typically, 4 layers of TSP, 4 layers of DSP and 2 layers of RSP pastes were screen printed, calcined, treated with TiCl₄ solution at 70 °C for 30 min and calcined once again. TSP paste contains exclusively 13-nm TiO₂

nanoparticles while DSP and RSP pastes contains or is completely composed of scattering 400-nm TiO₂ nanoparticles, respectively. Therefore, only the 4 layers printed from TSP paste is transparent, which are used for measuring UV-vis absorption spectra of DTBC on TiO₂. The calcination programme was as follows: (1) heating at 200 °C for 10 min; (2) heating at 500 °C for 30 min; (3) cooling down. After the second calcination, when the temperature went down to 80 °C, the films were immediately immersed into the chloroform/methanol (2/1) solutions containing 0.2 mM sensitizers and 2 mM chenodeoxycholic acid (CDCA) and kept at 30 °C for 3 hrs. After dye loading, the films were taken out, rinsed with ethanol and sandwiched with commercially available Pt counter electrodes (Geomatec Co., Ltd) with electrolyte filled in the gap separated by a 30- μ m spacer (Himilan). The electrolyte contained 0.1 M LiI, 25 mM I₂, 0.6 M DMPII and 0.2 M TBP in acetonitrile. The active area of the cells was 0.16 cm².

Photovoltaic characterization

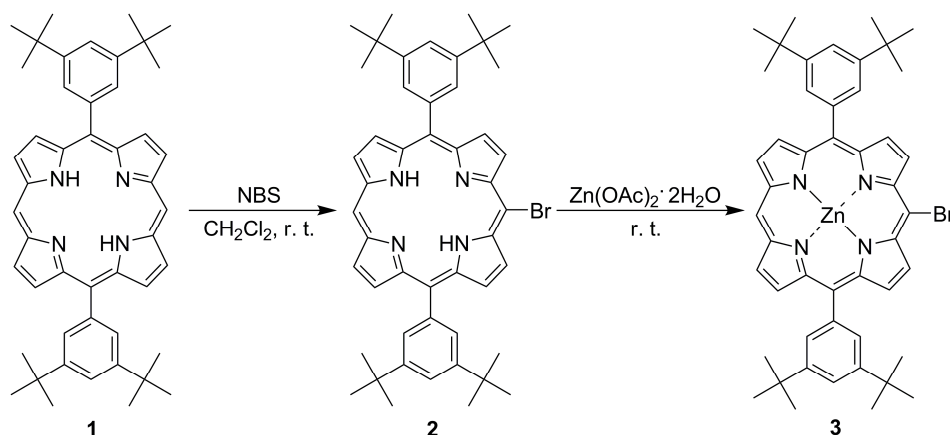
The current-voltage characteristics of the cells were measured with an AM 1.5 solar simulator (CEP-25TF, Bunkoukeiki Co., Ltd). The light intensity was calibrated by a standard silicon cell (BS-520 S/N 235, Bunkoukeiki Co., Ltd). Data were collected by source meter (Keithley 2400) and light-to-electricity conversion efficiency (η) was obtained according to equation $\eta = J_{sc} V_{oc} FF / P_{in}$, where J_{sc} is the short-circuit photocurrent density, V_{oc} the open-circuit voltage, FF the fill factor and P_{in} the incident radiation power. The incident monochromatic photon-to-current conversion efficiency (IPCE) spectra were measured by IPCE measurement system (SM-250E, Bunkoukeiki Co., Ltd). A standard silicon solar cell (SiPD S1337-1010BQ, Bunkoukeiki Co., Ltd) was used as reference and the IPCE values were obtained by comparing the current ratio and the IPCE value of the reference cell at each wavelength.

Synthetic procedures

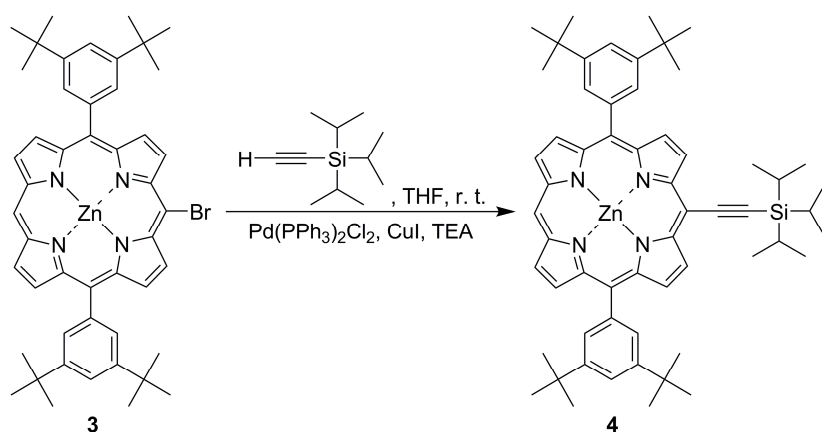


1: 3,5-di-*tert*-butylbenzaldehyde (0.746 g, 3.42 mmol) and dipyrromethane (0.5 g, 3.42 mmol) were dissolved in 650 mL of pre-dehydrated chloroform, and the solution was purged with dry argon for 1 hr. TFA (215 μ L, 2.81 mmol) was added by syringe quickly and the solution was stirred in dark under argon atmosphere at room temperature for 3 hrs. After that, DDQ (1 g, 4.41 mmol) was added and the solution was stirred for further 30 min before quenched by TEA (3 mL, 21.5 mmol). The solvent was evaporated and the crude product was eluted through a short pad of silica gel by chloroform to remove most of the tar. The mixture was further purified by flash column chromatography twice using *n*-C₆H₁₄/CH₂Cl₂ (volume ratio 2/1) as the eluent and reprecipitated

over methanol to give pure product **1** (0.551 g, 46.9%) as dark brown red solid. δ_{H} (500 MHz; CDCl_3 ; TMS) 10.32 (2 H, s), 9.40 (4 H, d, $J=4.3$ Hz), 9.14 (4 H, d, $J=4.3$ Hz), 8.15 (4 H, s), 7.85 (2 H, d, $J=1.4$ Hz), 1.58 (36 H, s), -3.01 (2 H, s).

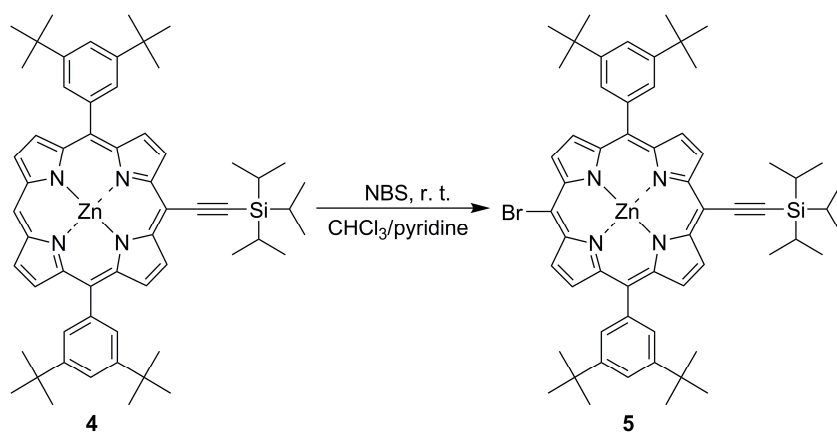


3: **1** (201 mg, 0.29 mmol) was dissolved in 150 mL of CH_2Cl_2 , to which NBS (37.5 mg, 0.21 mmol) was added and the reaction was carried out in dark under room temperature for 80 min before quenched by acetone. Solvent was evaporated and the mixture was purified by flash column chromatography using $n\text{-C}_6\text{H}_{14}/\text{CH}_2\text{Cl}_2$ (volume ratio 3/1) as eluent to give **2** (145 mg, 64.8%) as purple solid. **2** was directly metallated without further purification or structural characterization, namely, **2** (145 mg, 0.19 mmol) was dissolved in 25 mL of CHCl_3 and 5 mL of CH_3OH , and zinc acetate dihydrate (279 mg, 1.27 mmol) was added. The solution was stirred in dark at room temperature for 4 hrs. The solvent was then evaporated and the crude product was purified by flash column chromatography using $n\text{-C}_6\text{H}_{14}/\text{CHCl}_3$ (volumn ratio 1/3) as eluent and reprecipitated over methanol to give **3** (148 mg, 61.2%) as brown red solid. δ_{H} (500 MHz; $\text{CDCl}_3/d\text{-pyridine}$; TMS) 10.10 (1 H, s), 9.75 (2 H, d, $J=4.6$ Hz), 9.28 (2 H, d, $J=4.3$ Hz), 9.01 (4 H, t, $J=5.9$ Hz), 8.05 (4 H, s), 7.81 (2 H, s), 1.55 (36 H, s).

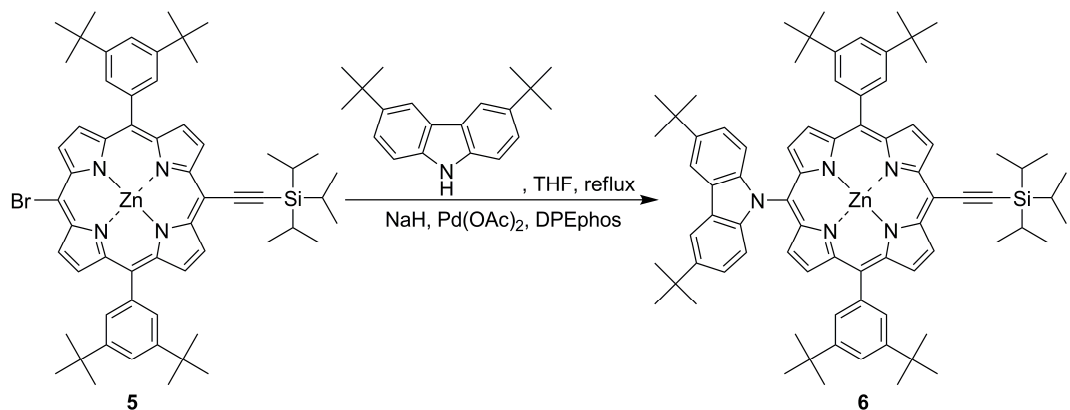


4: In a 100 mL Schlenk tube was dissolved **3** (148 mg, 0.18 mmol) in 49.5 mL of dehydrated toluene and 9.5 mL of distilled TEA and three freeze-pump-thaw cycles were performed to thoroughly exchange the air the system to dry argon atmosphere. $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (14.46 mg, 20.6 μmol), CuI (4.55 mg, 23.9 μmol) and triisopropylsilylacetylene (0.79 mL, 3.55 mmol) were then added and the solution was stirred in dark under argon at room temperature for 3 hrs. After

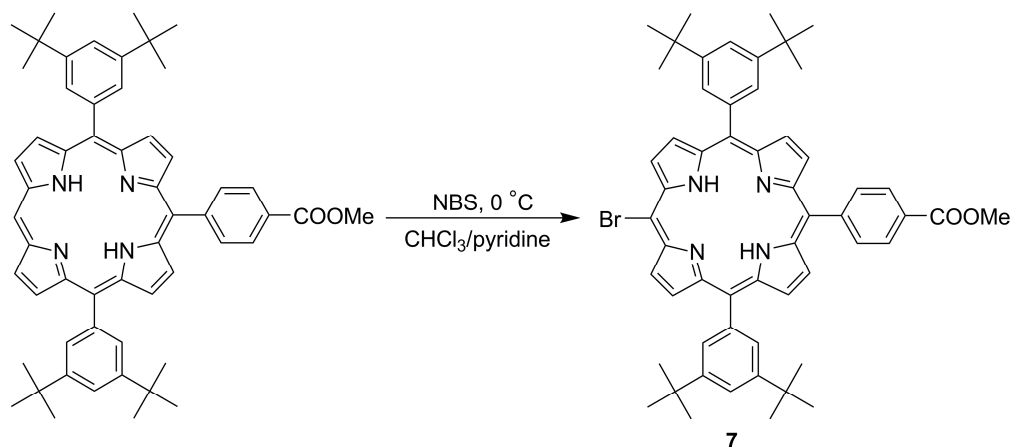
evaporation of the solvents, the crude product was purified by flash column chromatography using $n\text{-C}_6\text{H}_{14}/\text{CH}_2\text{Cl}_2$ (volume ratio 1/1) as eluent and reprecipitated over methanol to give **4** (137 mg, 82.3%) as purple solid. δ_{H} (500 MHz; $\text{CDCl}_3/d\text{-pyridine}$; TMS) 10.22 (1 H, s), 9.86 (2 H, d, $J=4.6$ Hz), 9.36 (2 H, d, $J=4.4$ Hz), 9.09 (2 H, d, $J=4.6$ Hz), 9.08 (2 H, d, $J=4.4$ Hz), 8.08 (4 H, d, $J=1.4$ Hz), 7.83 (2 H, s), 1.56 (36 H, s), 1.45 (21 H, m).



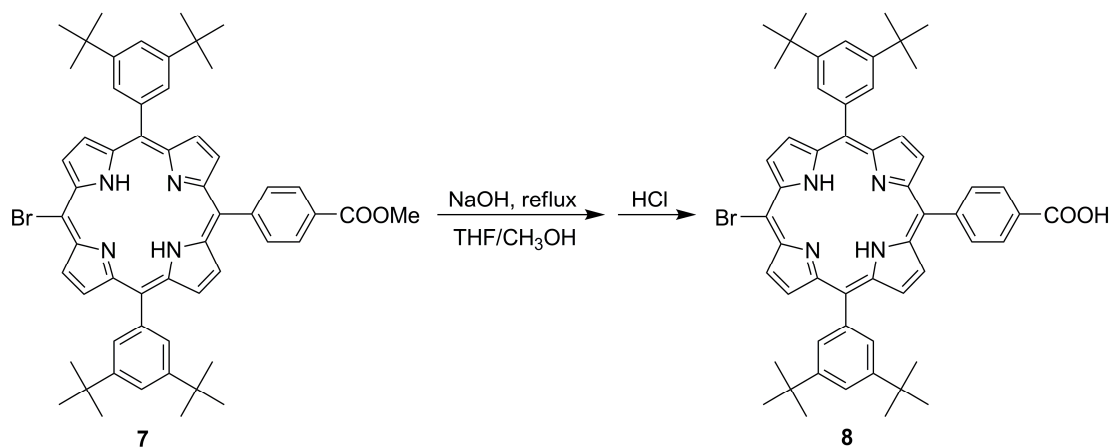
5 was synthesized according to literature method⁵ except for augmented NBS equivalence relative to **4** (1.2 eqv.) and elongated reaction time (15 min) and was obtained as purple solid (yield 65.3%). δ_{H} (500 MHz; $\text{CDCl}_3/d\text{-pyridine}$; TMS) 9.77 (2 H, d, $J=4.5$ Hz), 9.72 (2 H, d, $J=4.6$ Hz), 8.99 (2 H, d, $J=4.6$ Hz), 8.96 (2 H, d, $J=4.6$ Hz), 8.03 (4 H, d, $J=1.5$ Hz), 7.82 (2 H, s), 1.55 (36 H, s), 1.45 (21 H, m).



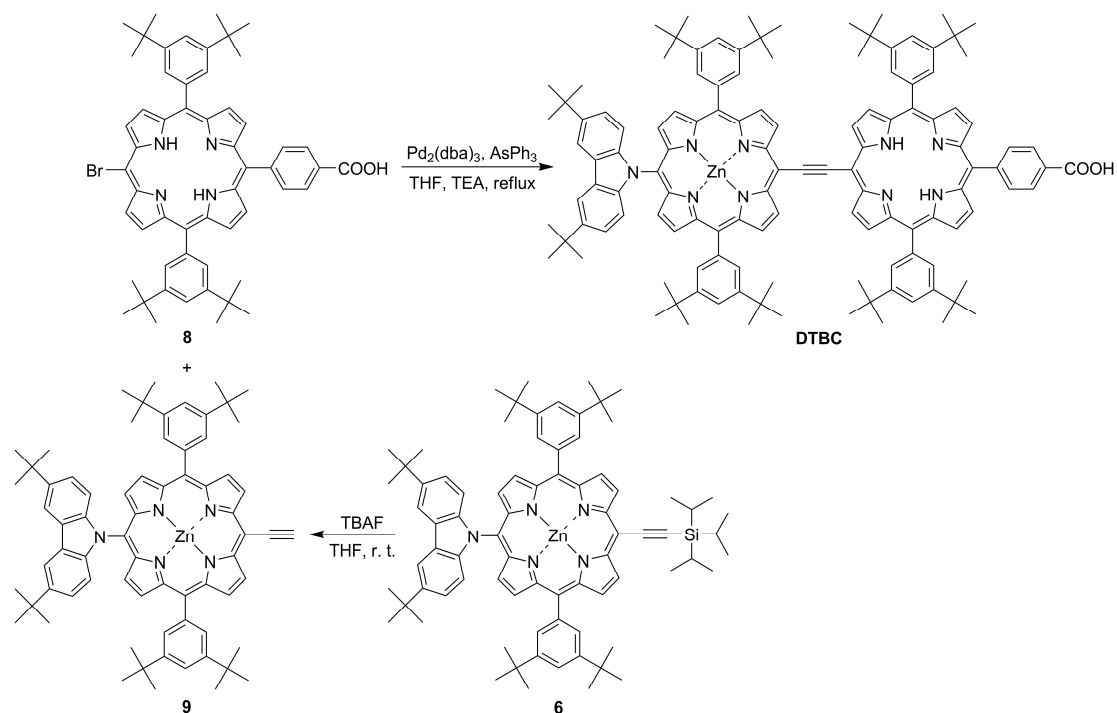
6 was synthesized using the same catalyst-base system according to literature⁵ but with augmented NaH equivalence relative to carbazole (8 eqv.) and elongated reaction time (40 hrs). Yields: 34.9%, δ_{H} (500 MHz; $\text{CDCl}_3/d\text{-pyridine}$; TMS) 9.80 (2 H, s), 8.97 (2 H, s), 8.72 (2 H, s), 8.43 (4 H, d, $J=12.9$ Hz), 7.99 (4 H, s), 7.76 (2 H, s), 7.25 (2 H, s), 6.55 (2 H, s), 1.50 (36 H, s), 1.26 (18 H, s).



7: 10-(4-methoxycarbonylphenyl)-5,15-bis(3,5-di-*tert*-butylphenyl)porphyrin (82 mg, 0.1 mmol) was dissolved in 50 mL of pre-dehydrated chloroform and 5 mL of dehydrated pyridine and the flask was immersed in ice bath. Argon was purged for 15 min and NBS (19.6 mg, 0.11 mmol) was then added. The solution was stirred at 0 °C for 30 min and quenched with acetone. After removal of the solvents the crude product was purified by flash column chromatography using *n*-C₆H₁₄/CH₂Cl₂ (volume ratio 2/3) as eluent and reprecipitated over methanol to give **7** (80.5 mg, 89.6%) as brown solid. δ_{H} (500 MHz; CDCl₃; TMS) 9.69 (2 H, s), 8.94 (2 H, s), 8.85 (2 H, s), 8.73 (2 H, s), 8.42 (2 H, d, *J*=7.3 Hz), 8.27 (2 H, d, *J*=8.1 Hz), 8.05 (4 H, d, *J*=1.6 Hz), 7.82 (2 H, s), 4.10 (3 H, s), 1.54 (36 H, s), -2.70 (2 H, s).



8: **7** (108 mg, 0.12 mmol) was dissolved in 70 mL of THF and 10 mL of methanol, and 12 mL of 1 M NaOH aqueous solution was added by syringe. The solution was refluxed under argon for 2 hrs and cooled to room temperature. The pH value was adjusted to around 4 by 1 M HCl. The mixture was extracted with CHCl₃ twice and dried with anhydrous Na₂SO₄. After removal of the solvent, the crude product was purified by flash column chromatography using CHCl₃/CH₃OH (volume ratio 15/1) and reprecipitated over methanol to give **8** (101.09 mg, 95.1%). δ_{H} (500 MHz; CDCl₃/*d*-pyridine; TMS) 9.63 (2 H, s), 8.90 (2 H, s), 8.80 (2 H, s), 8.71 (2 H, d, *J*=3.6 Hz), 8.39 (2 H, d, *J*=8.0 Hz), 8.21 (2 H, d, *J*=7.6 Hz), 8.0 (4 H, s), 7.78 (2 H, s), 1.50 (36 H, s), -2.76 (2 H, s).



DTBC: 6 (17.1 mg, 14.1 μmol) was dissolved in dehydrated 5 mL of THF and 1 M TBAF in THF (80 μL , 80 μmol) was added by syringe. The solution was stirred in dark under argon at room temperature for 45 min and quenched with de-ionized water. The mixture was extracted with CH_2Cl_2 twice and dried with anhydrous Na_2SO_4 . After removal of the solvents, the crude product **9** was transfer together with **8** (18.7 mg, 21.1 μmol) into a Schlenk tube which was thoroughly dried on vacuum line for 1 hr. Dehydrated THF (9.9 mL) and distilled TEA (2 mL) were then added and three freeze-pump-thaw cycles were performed to thoroughly exchange the air in the system to dry argon atmosphere. $\text{Pd}_2(\text{dba})_3$ (4.1 mg, 4.4 μmol) and AsPh_3 (11.4 mg, 37.1 μmol) were then added and the solution was refluxed in dark under argon for 3 hrs. After evaporation of the solvents the crude product was purified by flash column chromatography using $\text{CHCl}_3/\text{CH}_3\text{OH}$ (volume ratio 15/1) as eluent to give **DTBC** (13.7 mg, 52.2%) as black brown solid. δ_{H} (500 MHz; CDCl_3/d -pyridine; TMS) 10.39 (2 H, d, $J=4.4$ Hz), 10.35 (2 H, d, $J=4.4$ Hz), 9.11 (2 H, d, $J=4.3$ Hz), 9.08 (2 H, d, $J=4.3$ Hz), 8.83 (6 H, s), 8.73 (2 H, d, $J=4.3$ Hz), 8.56 (2 H, s), 8.50 (2 H, d, $J=7.5$ Hz), 8.27 (2 H, d, $J=8.0$ Hz), 8.10 (4 H, s), 8.07 (4 H, s), 8.01 (2 H, s), 7.80 (2 H, s), 7.76 (2 H, s), 7.22 (2 H, s), 1.52 (36 H, s), 1.51 (36 H, s), 1.47 (18 H, s), -1.92 (2 H, s). m/z (MALDI-TOF) 1855.30 (M^+ , $\text{C}_{125}\text{H}_{131}\text{N}_9\text{O}_2\text{Zn}$ requires 1854.98); ESI-HRMS m/z 928.9961 ($[\text{M}+2\text{H}]^{2+}$, $\text{C}_{125}\text{H}_{133}\text{N}_9\text{O}_2\text{Zn}$ calculated 928.9946). FT-IR (KBr) ν_{max} 3431, 2962, 2925, 2855, 2159, 1696, 1592, 1474, 1364, 1292, 1261, 1248, 1209, 1145, 795 cm^{-1} .

¹ M. J. Plater, S. Aiken and G. Bourhill, *Tetrahedron*, 2002, **58**, 2405.

² J. K. Laha, S. Dhanalekshmi, M. Taniguchi, A. Ambroise and J. S. Lindsey, *Org. Proc. Res. Dev.*, 2003, **7**, 799.

³ V. C. Gibson, S. K. Spitzmesser, A. J. P. White and D. J. Williams, *Dalton Trans.*, 2003, 2718.

⁴ H. Imahori, K. Tamaki, Y. Araki, Y. Sekiguchi, O. Ito, Y. Sakata and S. Fukuzumi, *J. Am. Chem. Soc.*, 2002, **124**, 5165.

⁵ C. Lee, H. Lu, C. Lan, Y. Huang, Y. Liang, W. Yen, Y. Liu, Y. Lin, E. W. Diau and C. Yeh, *Chem. Eur. J.*, 2009, **15**, 1403.

Table S1 Fundamental photophysical and electrochemical properties of **DTBC**

Porphyrin	Absorption ^a λ_{\max}/nm ($\epsilon/10^5 \text{ M}^{-1}\text{cm}^{-1}$)	Emission ^b λ_{\max}/nm	^c E_{0-0}/eV	^d $E_{\text{S}+/ \text{S}}/\text{V}$ (vs. NHE)	^d $E_{\text{S}/ \text{S}^-}/\text{V}$ (vs. NHE)	^e $E_{\text{S}+/ \text{S}^*}/\text{V}$ (vs. NHE)
DTBC	414 (0.86), 430 (0.96), 478 (1.43), 531 (0.13), 575 (0.15), 649 (0.19), 722 (0.38)	740	1.71	+1.04, +1.22, +1.64	-0.75	-0.67

^a Absorption data measured in chloroform-methanol (2/1). ^b Emission data measured in toluene at 298 K. ^c Excitation energy E_{0-0} was estimated from the incept of normalized absorption and emission spectra recorded in toluene. ^d $E_{\text{S}+/ \text{S}}$ and E_{S/ S^-} were directly measured by DPV in degassed dichloromethane using 0.1 M TBAPF₆ as supporting electrolyte. ^e $E_{\text{S}+/ \text{S}^*}$ was calculated by subtracting E_{0-0} from the first $E_{\text{S}+/ \text{S}}$.

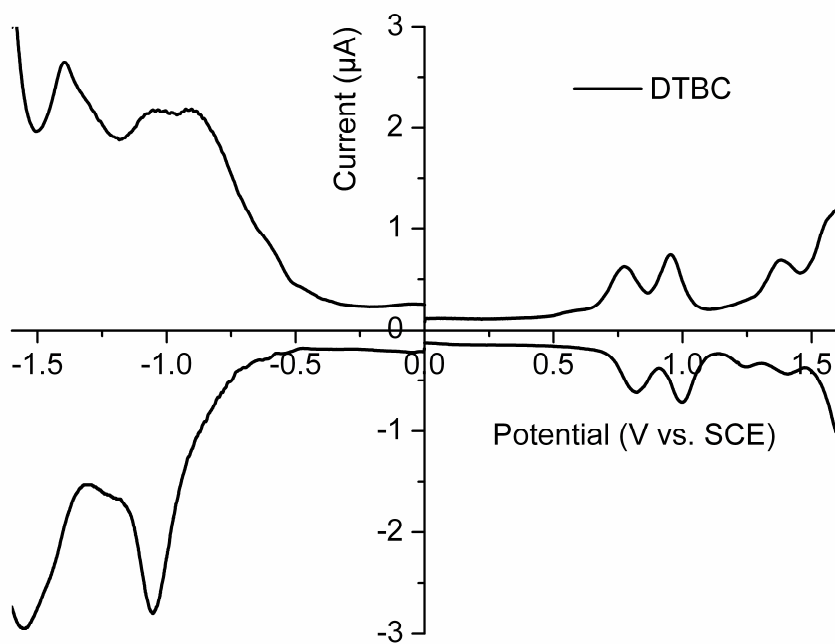


Fig. S1 Differential pulse voltammetry (DPV) spectra of **DTBC** in de-aerated dichloromethane, with 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte.

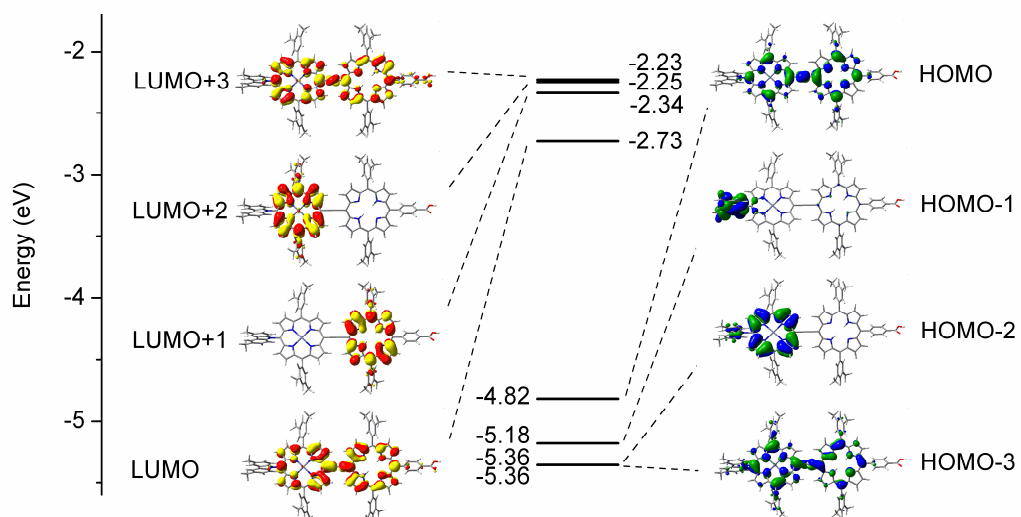


Fig. S2 Energy levels and molecular orbital distribution of **DTBC** calculated at the B3LYP/6-31 G level of theory. *Tert*-butyl groups have been simplified into methyl groups for calculation convenience.