Electronic Supplementary Information:

Ethynyl-linked Push–pull Porphyrin Hetero-dimers for Near-IR Dye-Sensitized Solar Cells: Photovoltaic Performances versus Excited-state Dynamics

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Synthesis

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, acetonitrile and methanol, solvents for column chromatography, including *n*-hexane, dichloromethane, chloroform, ethyl acetate and methanol, carbazole and granular neutral silica gel for column chromatography were Kanto Chemical. Bis(triphenylphosphino)palladium purchased from dichloride $(Pd(PPh_3)_2Cl_2),$ tris(dibenzylideneacetone)dipalladium(0) $(Pd_2(dba)_3)$, bis(2diphenylphosphinophenyl)ether (DPEphos), 1 M tetrabutylammonium fluoride (TBAF) in THF and triphenylarsine (AsPh₃) were purchased from Tokyo Chemical Industry. Cuprous iodide (CuI) was purchased from Kojundo Chemical Laboratory, 1.2-Dimethyl-3-propylimidazolium iodide (DMPII) was purchased from Shikoku Chemicals Corporation. Indium chloride (InCl₃), palladium(II) acetate (Pd(OAc)₂), lithium iodide (LiI) 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-tertbutylbenzaldehyde¹, dipyrromethane², 5-(4-carbomethoxyphenyl)dipyrromethane², 3,6-3 di-*tert*-butvl-9H-carbazole 5-bromo-10,15,20-tris(3,5-di-tertbutylphenyl)porphyrinatozinc(II)⁴ and 10-(4-methoxycarbonylphenyl)-5,15-bis(3,5-di*tert*-butylphenyl)porphyrin⁵ 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. Electrospray ionization high-resolution mass spectra (ESI-HRMS) were recorded by Shimazu LCMS-IT-TOF Ultra Fast Mass Spectroscopy.

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, 2.81mmol) 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. $\delta_{\rm H}(500 \text{ MHz}; \text{CDCl}_3; \text{TMS})$ 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 $n-C_6H_{14}/CH_2Cl_2$ (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 CHCl₃ and 5 mL of CH₃OH, 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*-C₆H₁₄/CHCl₃ (volumn ratio 1/3) as eluent and reprecipitated over methanol to give **3** (148 mg, 61.2%) as brown red solid. $\delta_{\rm H}(500 \text{ MHz}; \text{CDCl}_3/d$ -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. 20.6 µmol), $Pd(PPh_3)_2Cl_2$ (14.46) mg, CuI (4.55 mg, 23.9 umol) 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- C_6H_{14}/CH_2Cl_2 (volume ratio 1/1) as eluent and reprecipitated over methanol to give 4 (137 mg, 82.3%) as purple solid. $\delta_{\rm H}(500 \text{ MHz}; \text{CDCl}_3/d\text{-pyridine}; \text{TMS})$ 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: 5 was synthesized according to literature method⁶ 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%). $\delta_{\rm H}(500 \text{ MHz}; \text{CDCl}_3/d\text{-pyridine}; \text{TMS})$ 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: **6a** and **6b** were synthesized according to literature.⁶ For **6c**, the same catalyst-base system was adopted except for augmented NaH equivalence relative to carbazole (8 eqv.) and elongated reaction time (40 hrs). Yields: **6a** 39%, $\delta_{\rm H}(500 \text{ MHz}; \text{CDCl}_3/d$ –pyridine; TMS) 9.74 (2 H, d, *J*=4.5 Hz), 9.27 (2 H, d, *J*=4.5 Hz), 8.94 (2 H, d, *J*=4.6 Hz), 8.80 (2 5

H, d, *J*=4.5 Hz), 7.99 (4 H, s), 7.77 (2 H, s), 7.23 (4 H, d, *J*=9.0 Hz), 6.73 (4 H, d, *J*=9.0 Hz), 3.69 (6 H, s), 1.52 (36 H, s), 1.44 (21 H, m); **6b** 41.6%, $\delta_{\rm H}(500$ MHz; CDCl₃/*d*-pyridine; TMS) 9.76 (2 H, d, *J*=4.5 Hz), 9.30 (2 H, d, *J*=4.5 Hz), 8.97 (2 H, d, *J*=4.6 Hz), 8.82 (2 H, d, *J*=4.5 Hz), 8.01 (4 H, s), 7.77 (2 H, s), 7.24 (4 H, d, *J*=9.0 Hz), 7.16 (4 H, d, *J*=9.0 Hz), 1.52 (36 H, s), 1.44 (21 H, m), 1.22 (18H, s); **6c** 34.9%, $\delta_{\rm H}(500$ MHz; CDCl₃/*d*-pyridine; TMS) 9.80 (2 H, m), 8.97 (2 H, m), 8.72 (2 H, m), 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 reprecepitated over methanol to give 7 (80.5 mg, 89.6%) as brown solid. $\delta_{\rm H}(500 \text{ MHz}; \text{CDCl}_3; \text{TMS})$ 9.69 (2 H, m), 8.94 (2 H, m), 8.85 (2 H, m), 8.73 (2 H, m), 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%). $\delta_{\rm H}(500 \text{ MHz}; \text{CDCl}_3/d$ –pyridine; TMS) 9.63 (2 H, m), 8.90 (2 H, m), 8.80 (2 H, m), 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).



General: 6 (a-c) was dissolved in dehydrated THF and 1 M TBAF in THF 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 Na₂SO₄. After removal of the solvents, the crude product **9** was transfer together with **8** into a Schlenk tube which was thoroughly dried on vacuum line for 1 hr. Dehydrated THF and distilled TEA were then added and three freeze–pump–thaw cycles were performed to thoroughly exchange the air in the system to dry argon atmosphere. $Pd_2(dba)_3$ and AsPh₃ 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 $CHCl_3/CH_3OH$ (volume ratio 15/1) as eluent to give the titled compound.

The general procedure was applied to **6a** (17.9 mg, 15.5 µmol; THF for deprotection 5.4 mL; 1 M TBAF in THF 87 µL, 87 µmol; 8 20.5 mg, 23.1 µmol; THF 10.9 mL; TEA 2.2 mL; Pd₂(dba)₃ 4.5 mg, 4.9 µmol; AsPh₃ 12.5 mg, 40.8 µmol) to give BMPA (17.4 mg, 62.3%) as black brown solid. $\delta_{\rm H}(500 \text{ MHz}; \text{CDCl}_3/d\text{-pyridine}; \text{TMS})$ 10.42 (2 H, d, J=4.1 Hz), 10.36 (2 H, d, J=4.5 Hz), 9.17 (2 H, d, J=4.2 Hz), 9.10 (2 H, d, J=4.5 Hz), 9.02 (2 H, d, J=4.4 Hz), 8.85 (2 H, d, J=4.5 Hz), 8.74 (2 H, d, J=4.5 Hz), 8.71 (2 H, d, J=4.4 Hz), 8.38 (2 H, d, J=7.7 Hz), 8.26 (2 H, d, J=8.1 Hz), 8.06 (4 H, s), 8.01 (4 H, s), 7.77 (2 H, s), 7.74 (2 H, s), 7.20 (4 H, d, J=9.2 Hz), 6.68 (4 H, d, J=9.0 Hz), 3.68 (6 H, s), 1.57 (36 H, s), 1.55 (36 H, s), -1.93 (2 H, s); m/z (MALDI-TOF) 1805.23 (M⁺). 1804.89); ESI-HRMS 903.9474 $([M+2H]^{2+},$ $C_{119}H_{121}N_9O_4Zn$ requires m/zC₁₁₉H₁₂₃N₉O₄Zn calculated 903.9503).

The general procedure was applied to **6b** (20.6 mg, 17 µmol; THF for deprotection 6 mL; 1 M TBAF in THF 95 µL, 95 µmol; **8** 22.5 mg, 25.4 µmol; THF 11.9 mL; TEA 2.4 mL; Pd₂(dba)₃ 4.9 mg, 5.4 µmol; AsPh₃ 13.7 mg, 44.7 µmol) to give **BTBPA** (14.4 mg, 45.5%) as black brown solid. $\delta_{\rm H}(500 \text{ MHz}; \text{CDCl}_3/d$ –pyridine; TMS) 10.40 (4 H, m), 9.33 (2 H, m), 9.17 (2 H, d, *J*=4.1 Hz), 9.14 (2 H, d, *J*=3.9 Hz), 8.89 (4 H, d, *J*=3.8 Hz), 8.76 (2 H, d, *J*=3.7 Hz), 8.52 (2 H, d, *J*=7.0 Hz), 8.37 (2 H, d, *J*=7.5 Hz), 8.15 (4 H, s), 8.11 (4 H, s), 7.85 (2 H, s), 7.81 (2 H, s), 7.29 (4 H, d, *J*=6.7 Hz), 7.20 (4 H, d, *J*=8.6 Hz), 1.57 (36 H, s), 1.55 (36 H, s), 1.52 (18 H, s), -1.94 (2 H, s); *m/z* (MALDI–TOF) 1859.18 (M⁺, C₁₂₅H₁₃₃N₉O₂Zn requires 1858.86); ESI–HRMS *m/z* 930.0006 ([M+2H]²⁺, C₁₂₅H₁₃₅N₉O₂Zn calculated 930.0024).

The general procedure was applied to **6c** (17.1 mg, 14.1 µmol; THF for deprotection 5 mL; 1 M TBAF in THF 80 µL, 80 µmol; **8** 18.7 mg, 21.1 µmol; THF 9.9 mL; TEA 2 mL; Pd₂(dba)₃ 4.1 mg, 4.4 µmol; AsPh₃ 11.4 mg, 37.1 µmol) to give **DTBC** (13.7 mg, 52.2%) as black brown solid. $\delta_{\rm H}(500$ MHz; CDCl₃/*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, m), 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⁺, C₁₂₅H₁₃₁N₉O₂Zn requires 1854.98); ESI–HRMS m/z 928.9961 ([M+2H]²⁺, C₁₂₅H₁₃₃N₉O₂Zn calculated 928.9946).



10: 5-Bromo-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrinatozinc(II) (10.0 mg, 9.8 μmol) and trimethylsilylacetylene (19.3 mg, 98 μmol) were dissolved in 10 mL of 5:1 v/v dehydrated THF/TEA in a 50 mL Schlenk flask, degassed and replaced with Ar atmosphere by freeze–pump–thaw cycles. Then, Pd(PPh₃)₂Cl₂ (2.1 mg, 2.9 μmol) and copper iodide (0.23 mg, 1.2 μmol) were added to the mixture under Ar atmosphere. After stirring overnight at 30 °C, the solvents were removed and the resulting crude product was subjected to silica gel chromatography for purification to elute the desired compound with *n*-hexane/CHCl₃ (3:2 v/v) to give 7 mg (6.8 μmol) of porphyrin. The porphyrin was dissolved in CHCl₃ and treated with 1 M TBAF in THF solution (0.02 mL, 21.3 μmol) and stirred in the dark at rt for 1h. The reaction mixture was extracted with CHCl₃, washed with water and dried over anhydrous Na₂SO₄. The crude product was passed through a silica gel column for purification to give **10** (13 mg, 63%) as purple-green compound. $\delta_{\rm H}(400 \text{ MHz}; \text{CDCl}_3; \text{TMS})$ 1.43 (18 H, two s, 1.46 (36 H, s), 3.93 (1 H, s), 7.70 (1 H, t, *J*=1.6 Hz), 7.73 (2 H, t, *J*=1.6 Hz), 7.97 (2 H, d, *J*=1.6 Hz), 8.00 (4 H, d, *J*=1.6 Hz), 8.88 (4 H, d, *J*=4.8 Hz), 8.96 (2 H, d, *J*=4.8 Hz), 9.62 (2 H, d, *J*=4.8 Hz).



DTBP: In a 50 mL Schlenk flask, 10 (12 mg, 12.5 µmol) and 7 (22.5 mg, 25 µmol) were dissolved in 12 mL of 5:1 v/v dehydrated THF/TEA, degassed and replaced with Ar atmosphere by freeze-pump-thaw cycles. Then, Pd₂(dba)₃ (2.1 mg, 2.0 µmol) and AsPh₃ (5.9 mg, 15 µmol) were added to the mixture under Ar atmosphere. After stirring at 50°C for 1 hr, the solvents were removed and the resulting crude product was subjected to silica gel chromatography for purification to elute the desired compound with nhexane/CHCl₃ (3:2 v/v). It was then dissolved in 18 mL of 2:1 THF/EtOH, to which was added 2 mL of 1 M NaOH aqueous solution. After refluxing for 2 hr at 80°C, the solution was cooled down and 1 mL of 1 M HCl was added. The reaction mixture was extracted with $CHCl_3$ and washed with H_2O_2 , then dried over anhydrous Na_2SO_4 . The crude product was subjected to column chromatography on silica gel using CH₂Cl₂/THF (9:1 v/v) as eluent to give **DTBP** (12 mg, 80%) as a black brown compound. $\delta_{\rm H}$ (500 MHz; CDCl₃/dpyridine; TMS) 10.41 (4 H, d, J=4.5 Hz), 9.12 (4 H, q, J=4.4 Hz), 8.84 (2 H, d, J=4.7 Hz), 8.75 (2 H, d, J=4.4 Hz), 8.71 (2 H, d, J=4.6 Hz), 8.57 (1 H, s), 8.51 (2 H, d, J=7.9 Hz), 8.42 (4 H, m, J=4.6 Hz), 8.29 (2 H, d, J=7.9 Hz), 8.12 (4 H, s), 8.04 (4 H, d, J=1.5 Hz), 7.82 (2 H, s), 7.75 (2 H, s), 1.54 (36 H, s), 1.50 (36 H, s), 1.48 (18 H, s), -1.93 (2 H, s); m/z (MALDI-TOF) 1764.22 (M⁺, C₁₁₉H₁₂₈N₈O₂Zn requires 1764.95); ESI-HRMS m/z $884.4832 ([M+2H]^{2+}, C_{119}H_{130}N_8O_2Zn \text{ calculated } 884.4812).$

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Figure S1. UV–visible absorption spectra of DTBC on transparent Al₂O₃ and TiO₂ films.



Figure S2. Normalized absorption and emission spectra of **BMPA** (absorption: solid line; emission: square \Box), **BTBPA** (absorption: dashed line; emission: circle \circ), **DTBC** (absorption: short dot line; emission: triangle \triangle) and **DTBP** (absorption: dash-dot line; emission: lozenge \diamond).



Figure S3. Differential pulse voltammetry (DPV) spectra of ethynyl-linked heteroporphyrin dimers in de-aerated dichloromethane, with 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte.



Figure S4. Mono-exponential fitting of decay data of the four sensitizers in toluene solution. The red smooth lines represent the fitted curves. The black fluctuating lines represent the residuals of fittings.



Figure S5. Bi-exponential fitting of decay data of the four sensitizers on Al_2O_3 films immersed in acetonitrile solution containing 0.1 M LiI and 0.2 M TBP. The red smooth lines represent overall fitted curves. The magenta smooth lines represent the faster fitted components. The cyan smooth lines represent the slower fitted components. The black fluctuating lines represent the residuals of fittings.



Figure S6. Bi-exponential fitting of decay data of the four sensitizers on TiO_2 films immersed in acetonitrile solution containing 0.1 M LiI and 0.2 M TBP. The red smooth lines represent overall fitted curves. The magenta smooth lines represent the faster fitted components. The cyan smooth lines represent the slower fitted components. The black fluctuating lines represent the residuals of fittings.