Supporting Information:

Cross-Conjugated BODIPY Pigment for Highly Efficient Dye Sensitized Solar Cells

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S1. Measurement

Solar cell Measurement

The current-voltage characteristics were measured using a black metal mask with an aperture area of 0.25 cm^2 under standard AM 1.5 G sunlight (100 mW cm^{-2}, WXS-155S-10: Wacom Denso Co. Japan). Monochromatic incident photon-to-current conversion efficiency (IPCE) spectra were measured with monochromatic incident light of 1×10^{16} photons cm^{-2} under 100 mW cm^{-2} in

direct current mode (CEP-2000BX, Bunko-Keiki). The intensity-modulated photovoltage spectra (IMVS) were measured by a potentiostat (Solartron1287) equipped with a frequency response analyzer (Solartron1255B) at an open-circuit condition based on a monochromatic illumination (420 nm) controlled by Labview system to obtain the photovoltaic response induced by the modulated light. The modulated light was driven with a 10% AC perturbation current super imposed on a DC current in a frequency range from 0.1 to 10^6 Hz. The charge extraction method (CEM) was performed with the same monochromatic light source. The solar respective DSSCs were illuminated at an open-circuit condition for 5 s to attain steady state and then the light source was switched off when the device simultaneously switched to a short-circuit condition to extract the charges generated at the fixed light intensity.

Spectroscopic Measurements

Absorption spectra in solution and in thin films were recorded on a Shimadzu UV-3000 spectrometer. In solid state, the absorption spectra were measured on thin films drop-casted on glass substrates from a 0.5 mg/mL chloroform solution of BODIPY based dyes. The fluorescence emission and excitation spectra were obtained by using a HORIBA JOBIN YVON FLUOROMAX 4. All fluorescence spectra were corrected.

S2. General Methods

All reactions were performed under an atmosphere of dried argon using standard Schlenk tube techniques. All chemicals were used as received from commercial sources unless stated otherwise. THF was distilled from sodium and benzophenone under an Ar atmosphere. DMF was distilled from KOH under an argon atmosphere. ^{1}H NMR (400.1 MHz) and ^{13}C NMR (100.5 MHz) spectra were recorded at room temperature (rt) on a Bruker Advance 400 MHz spectrometer, using perdeuteriated solvents as internal standards. Chromatographic purifications were performed using silica gel (40-63 μm). TLC was performed on silica gel plates coated with fluorescent indicator. Absorption spectra were recorded on a Shimadzu UV-3000 absorption spectrometer. Compound A has been synthesised following the reported work.[1] Cyclic voltammetry (CV) was performed by an ALS electrochemical analyser (ALSE600E). The working, counter, and reference electrode were used Pt disk, Pt wire, and Ag wire, respectively. The ferrocene was used as a reference. A 1 mM of sample in degassed dichloromethane containing $TFPPF_6$ was electrolyzed with a scan rate of 100 mV/s. FT-IR spectra were collected using a Shimadzu IRTracer-100.

S3. Synthetic procedures

Synthesis of Compound 1.

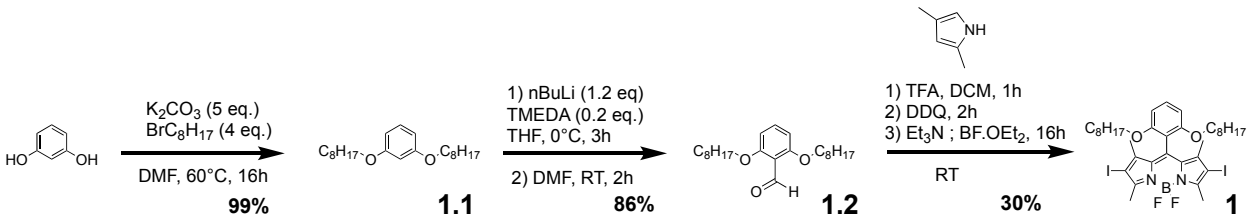
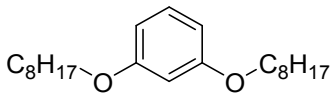


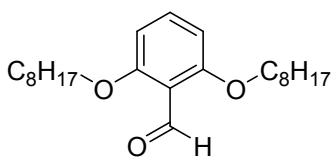
Figure S1. Synthetic route followed for compound **1.**

Compound 1.1



In a dry Schlenck tube under argon atmosphere was placed resorcinol (4.588 g, 41.67 mmol) and dry DMF (150 mL). K_2CO_3 (28.80 g, 208.36 mmol, 5 eq) was added and the mixture was stirred at room temperature for 30 min. Bromooctane (28.8 mL, 166.68 mmol, 4 eq) was added. The mixture was heated at 60 °C overnight. Once cooled down to room temperature, the mixture was washed with water. The aqueous phase was extracted with diethyl ether. The combined organic phase was dried over $MgSO_4$ or absorbent cotton and the solvents were evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, solvent: 90/10 petroleum ether/DCM) and the excess of bromooctane was then distilled under reduced pressure (50 °C, ~10^{-5} bar) to afford compound **1.1** (13.80 g, 41.250 mmol, 99%) as colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7,15 (t, ^{3}J = 8.0 Hz, 1H), 6.50-6.44 (m, 3H), 3.93 (t, ^{3}J= 6.6 Hz, 4H), 1.82-1.72 (m, 4H), 1.49-1.40 (m, 4H), 1.40-1.22 (m, 16H), 0.93-0.86 (m, 6H).

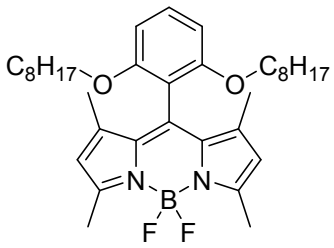
Compound 1.2



In a dry Schlenk flask under argon atmosphere was placed compound **1.1** (5.07 g, 15.16 mmol). Freshly distilled THF (80 mL) and TMEDA (0.54 mL, 3.64 mmol, 0.2 eq) were then added. *n*BuLi (1.6 M, 11.4 mL, 18.18 mmol, 1.2 eq) was added dropwise at 0 °C. The mixture was stirred at room temperature for 3 h. It turned to pale yellow. DMF (2.4 mL, 30.312 mmol, 2 eq) was added dropwise. The mixture was stirred at room temperature for 2 h. It was then washed

with water. The aqueous phase was extracted with dichloromethane. The combined organic phase was dried over $MgSO_4$ or absorbent cotton and the solvents were evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, solvent: 70/30 petroleum ether/DCM) to afford compound **1.2** (4.75 g, 13.09 mmol, 86%) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.53 (s, 1H), 7.36 (t, ^{3}J = 8.4 Hz, 1H), 6.51 (t, ^{3}J = 8.5 Hz, 2H), 4.01 (t, ^{3}J = 6.5 Hz, 4H), 1.86-1.76 (m, 4H), 1.51-1.41 (m, 4H), 1.38-1.21 (m, 16H), 0.90-0.84 (m, 6H).

Compound 1



Compound **1.2** (2.13 g, 5.869 mmol) was placed in a dry flask under argon atmosphere. Distilled DCM (40 mL), 2,4-dimethylpyrrole (1.33 mL, 12.912 mmol, 2.2 eq) and one drop of TFA were successively added. The solution was stirred at room temperature, under light cover for 1 h. It turned to orange and then to red. The mixture was then washed with a solution of NaOH 1M and water. The aqueous phase was extracted with dichloromethane. The combined organic phase was dried over $MgSO_4$ or absorbent cotton and the solvents were evaporated under reduced pressure. Distilled DCM (40 mL) was then added to the crude material. DDQ (1.46 g, 6.456 mmol, 1.1 eq) was added in one portion and the solution turned to dark red. The mixture was stirred at room temperature for 2 h. NEt_3 (4.9 mL, 35.214 mmol, 6 eq) and $BF_3.Et_2O$ (5.9 mL, 46.952, 8eq) were successively added and the solution was left to stir at room temperature overnight. It was then washed several times with water. The aqueous phase was extracted with dichloromethane. The combined organic phase was dried over $MgSO_4$ or absorbent cotton and the solvents were evaporated under reduced pressure. The crude product was purified by two columns chromatography (1st: silica gel, solvent: 50/50 petroleum ether/DCM; 2nd: silica gel, solvent: 50/50 petroleum ether/toluene) to afford compound **1** (1.014 g, 1.746 mmol, 30%) as red oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (t, ^{3}J = 8.4 Hz, 1H), 6.58 (d, ^{3}J = 8.5 Hz, 2H), 5.90 (s, 2H), 3.91 (t, ^{3}J = 6.3 Hz, 4H), 2.54 (s, 6H), 1.61-1.54 (m, 4H), 1.51 (s, 6H), 1.31-1.21 (m, 4H), 1.21-1.09 (m, 16H), 0.86 (t, ^{3}J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.1, 154.0, 141.8, 136.7, 132.0, 130.7, 120.3, 113.3, 105.2, 68.7, 31.9, 29.4, 29.3, 29.2, 25.9, 22.8, 14.7, 14.2, 13.6.

Synthesis of compound B

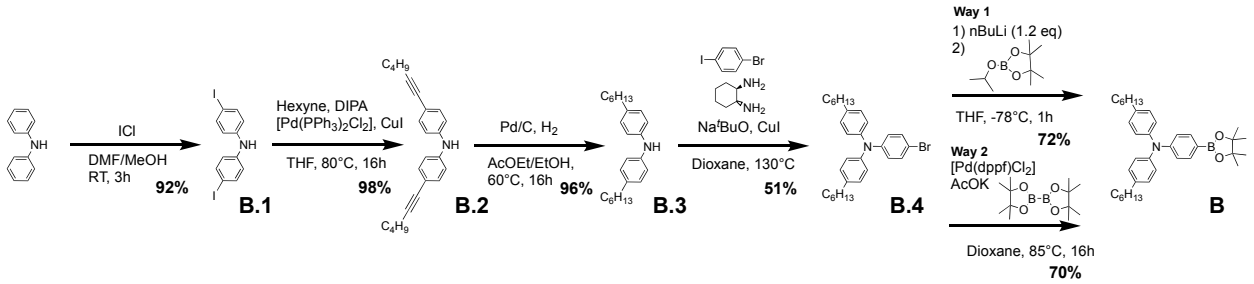
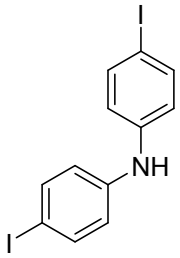


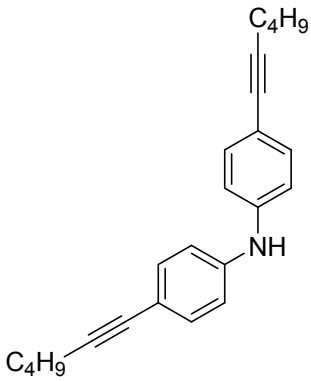
Figure S2. Synthetic route followed for compound **B.**

Compound B.1



Diphenylamine (5.0 g, 29.56 mmol) was placed in a flask with $CHCl_3$ (100 mL). A solution ICl (14.4 g, 88.68 mmol, 3 eq) in MeOH (50 mL) was added dropwise at 0 °C. The solution was then stirred for 3 h at room temperature. The mixture was then washed with a saturated solution of $Na_2S_2O_3$ and water. The aqueous phase was extracted with dichloromethane. The combined organic phase was dried over $MgSO_4$ or absorbent cotton and the solvents were evaporated under reduced pressure. The crude product was first purified by column chromatography (silica gel, solvent: 95/5 petroleum ether/ethyl acetate) and then recrystallized in hot dichloromethane to afford compound **B.1** (11.5 g, 27.32 mmol, 92%) as pale colorless solid. ^{1}H NMR (400 MHz $CDCl_3$): δ = 7.46 (d, ^{3}J = 8.8 Hz, 4H), 6.74 (d, ^{3}J = 8.3 Hz, 4H).

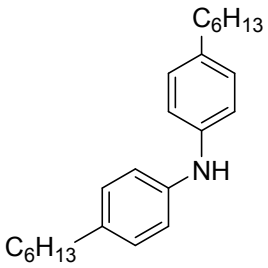
Compound B.2



A solution of compound **B.1** (11.5 g, 27.32 mmol), in THF (200 mL) and DIPA (100 mL) was degased with argon for 1 h. Hexyne (7.9 mL, 68.49 mmol, 2.5 eq), CuI (104 mg, 0.546 mmol, 2% mol) and $[Pd(PPh_3)_2Cl_2]$ (192 mg, 0.274 mmol, 1% mol) were then successively added. The mixture was heated at 80 °C overnight. The mixture was then washed with water. The aqueous phase was extracted with dichloromethane. The combined organic phase was dried over $MgSO_4$ or absorbent cotton and the solvents were evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, solvent: 90/10 petroleum ether/ethyl acetate) to afford compound **B.2** (8.4 g, 25.56 mmol, 93%) as colorless oil.

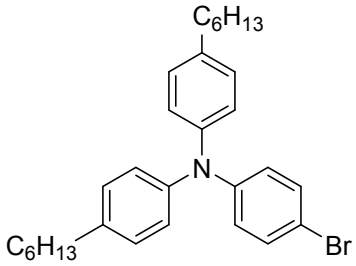
^{1}H NMR (400 MHz $CDCl_3$): δ = 7.30 (d, ^{3}J = 8.7 Hz, 4H), 6.95 (d, ^{3}J = 8.7 Hz, 4H), 5.78 (s, 1H), 2.41 (t, ^{3}J = 7.0 Hz, 4H), 1.66-1.56 (m, 4H), 1.54-1.44 (m, 4H), 0.96 (t, ^{3}J = 7.3 Hz, 6H). ^{13}C NMR (100 MHz $CDCl_3$): δ = 141.9, 132.8, 117.5, 116.6, 89.2, 80.6, 31.1, 22.2, 19.3, 13.8.

Compound B.3



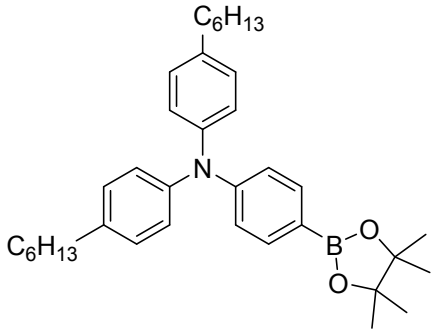
A solution of compound **B.2** (8.4 g, 25.56 mmol) in AcOEt (100 mL), EtOH (100 mL) and water (10 mL) was degased with argon for 20 min. Pd/C 10% (242 mg, 0.227 mmol, 10% mol) was then added and the mixture was degased with argon for 20 min. It was then degased with H_2 for 3 h and then heated overnight at 60 °C under H_2 atmosphere. The mixture was filtered through a pad a celite and the solvents were evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, solvent: 75/25 petroleum ether/DCM) to afford compound **B.3** (8.3 g, 25.56 mmol, 96%) as colorless oil. ^{1}H NMR (400 MHz $CDCl_3$): δ = 7.06 (d, ^{3}J = 8.2 Hz, 4H), 6.97 (d, ^{3}J = 7.9 Hz, 4H), 2.54 (t, ^{3}J = 7.6 Hz, 4H), 1.62-1.55 (m, 4H), 1.39-1.27 (m, 12H), 0.89 (t, ^{3}J = 6.6 Hz, 6H). ^{13}C NMR (50 MHz $CDCl_3$): δ = 141.4, 135.6, 129.3, 118.0, 35.4, 31.9, 31.8, 29.2, 22.8, 14.3.

Compound B.4



A solution of compound **B.3** (751.2 mg, 2.225 mmol), 1-bromo-4-iodobenzene (755.7 mg, 2.671 mmol, 1.2 eq), sodium tert-butoxide (320.7 mg, 3.3375 mmol, 1.5 eq) and (1R,2R)-cyclohexane-1,2-diamine (50.8 mg, 0.445 mmol, 20% mol) in dioxane (10 mL) was degased with argon for 30 min. CuI (42.4 mg, 0.2225 mmol, 10% mol) was then added and the mixture was heated at 130 °C for 24 h. Once cooled down to room temperature, the mixture was washed with water. The aqueous phase was extracted with dichloromethane. The combined organic phase was dried over $MgSO_4$ or absorbent cotton and the solvents were evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, solvent: 100% petroleum ether) to afford compound **B.4** (557.2 g, 1.131 mmol, 51%) as yellowish oil. ^{1}H NMR (400 MHz $CDCl_3$): δ = 7.29 (d, ^{3}J = 8.8 Hz, 2H), 7.08 (d, ^{3}J = 8.3 Hz, 4H), 7.00 (d, ^{3}J = 8.4 Hz, 4H), 6.91 (d, ^{3}J = 8.8 Hz, 2H), 2.58 (t, ^{3}J = 7.7 Hz, 4H), 1.66-1.59 (m, 4H), 1.41-1.29 (m, 12H), 0.94-0.90 (m, 6H). ^{13}C NMR (100 MHz $CDCl_3$): δ = 147.6, 145.2, 138.1, 132.0, 129.4, 124.7, 124.2, 113.8, 35.5, 31.9, 31.6, 29.2, 22.8, 14.2.

Compound B



This compound was prepared in two different ways.

Way 1: A solution of compound **B.4** (358.3 mg, 0.728 mmol), bispinacolborane (203.0 mg, 0.799 mmol, 1.1 eq) and potassium acetate (214.2 mg, 2.181 mmol, 3 eq) in dioxane (10 mL) was degased with argon for 30 min. [Pd(dppf)Cl_2] (119 mg, 0.146 mmol, 20% mol) was then added and the mixture was heated at 95 °C for 24 h. Once cooled down to room temperature, it was then filtered through a celite pad and the solvents were evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, solvent: 80/20 petroleum ether/DCM) to afford compound **B** (274.7 mg, 0.509 mmol, 70%) as colorless oil.

Way 2: Compound **B.4** (2.82 g, 5.431 mmol) was placed in a dry Schlenk tube under argon. Freshly distilled THF (50 mL) was then added. *n*-BuLi (1.6 M, 4.3 mL, 6.877 mmol, 1.2 eq) was added dropwise at -78 °C. The solution turned to red. It was stirred 45 min at -78 °C. Then, Isopropoxyboronic acid pinacol ester (1.5 mL, 7.451 mmol, 1.3 eq) was added dropwise. The solution turned to yellow. It was stirred for 30 min at -78 °C and then at room temperature for 1 h. The solution was quenched with water. The aqueous phase was extracted with dichloromethane. The combined organic phase was dried over $MgSO_4$ or absorbent cotton and the solvents were evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, solvent: 80/20 → 50/50 petroleum ether/DCM) to afford compound **B** (2.24 g, 4.151 mmol, 72%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, ^{3}J = 8.5 Hz, 2H), 6.98 (d, ^{3}J = 8.5 Hz, 4H), 6.93 (d, ^{3}J = 8.5 Hz, 4H), 6.90 (d, ^{3}J = 8.4 Hz, 2H), 2.48 (t, ^{3}J = 7.8 Hz, 4H), 1.56-1.49 (m, 4H), 1.29-1.18 (m, 24H), 0.83-0.80 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.1, 145.1, 138.3, 135.9, 129.3, 125.2, 120.8, 83.6, 35.6, 31.9, 31.6, 29.2, 25.0, 22.8, 14.2.

Synthesis of compound C

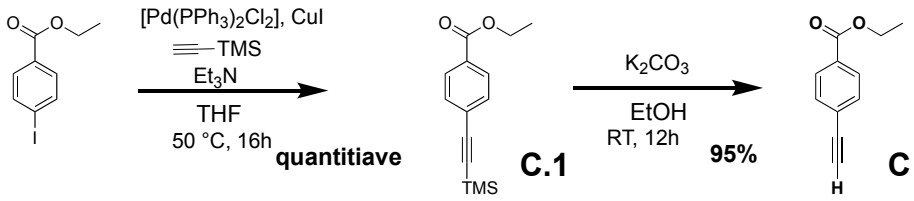
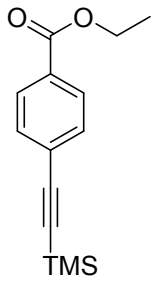


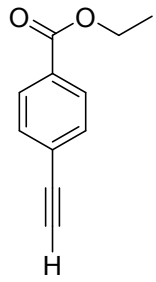
Figure S3. Synthetic route followed for compound **C.**

Compound C.1



A solution of ethyl iodobenzoate (2.30 g, 8.322 mmol) in THF (10 mL) and TEA (10 mL) was degased with argon for 1 h. Ethynyltrimethylsilane (1.2 mL, 8.693, 1.2 eq), CuI (138 mg, 0.724 mmol, 10% mol) and $[Pd(PPh_3)_2Cl_2]$ (254 mg, 0.362 mmol, 5% mol) were then successively added. The mixture was heated at 50 °C overnight. The mixture was then washed with water. The aqueous phase was extracted with dichloromethane. The combined organic phase was dried over $MgSO_4$ or absorbent cotton and the solvents were evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, solvent: 95/5 petroleum ether/ethyl acetate) to afford compound **C.1** (2.03 g, 8.231 mmol, quantitative) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, ^{3}J = 8.6 Hz, 2H), 7.51 (d, ^{3}J = 8.6 Hz, 2H), 4.37 (q, ^{3}J = 7.2 Hz, 2H), 1.39 (t, ^{3}J = 7.2 Hz, 3H), 0.26 (s, 9H).

Compound C



A mixture of compound **C.1** (2.03 g, 8.231 mmol) and potassium carbonate (1.25 g, 9.0574 mmol, 1.1 eq) in EtOH (30 mL) was stirred at room temperature for 2 h. Water and dichloromethane were added. The aqueous phase was extracted with dichloromethane. The combined organic phase was dried over $MgSO_4$ or absorbent cotton and the solvents were evaporated under reduced pressure. Compound **C** was obtained and did not need any further purification (1.36 g, 7.805 mmol, 95 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, ^{3}J = 8.6 Hz, 2H), 7.54 (d, ^{3}J = 8.5 Hz, 2H), 4.38 (q, ^{3}J = 7.1 Hz, 2H), 3.22 (s, 1H), 1.39 (t, ^{3}J = 7.2 Hz, 3H).

Synthesis of *h*-BOD

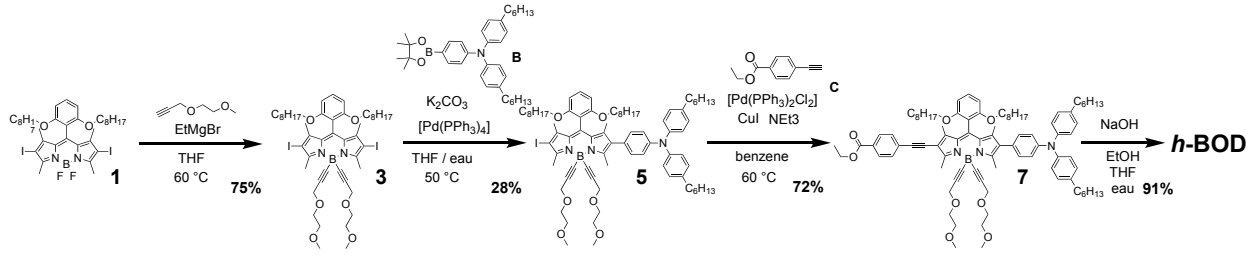
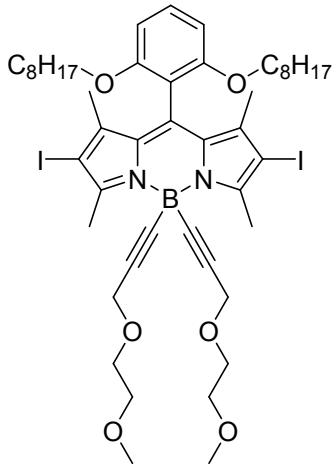


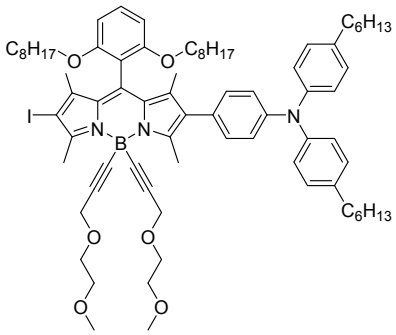
Figure S4. Synthetic route followed for compound ***h*-BOD.**

Compound 3



In a Schlenk tube was added ethylmagnesiumbromide (0.9 M, 2.9 mL, 2.629 mmol, 5 eq) to a stirred solution of 3-(2-methoxyethoxy)prop-1-yne (0.38 mL, 3.1548 mmol, 6 eq) in anhydrous THF. The mixture was stirred at 60 °C for 2 h. The resulting anion was then transferred via cannula to a solution of compound **1** (437.7 mg, 0.5258 mmol) in anhydrous THF. The solution was stirred at 60 °C overnight. A solution of HCl 1M was added, and the solution was extracted with dichloromethane. The organic layer was dried over $MgSO_4$ or absorbent cotton and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, solvent: 90/10 petroleum ether/ethyl acetate) followed by a recrystallization from Et_2O/MeOH to afford compound **3** (401.7 mg, 0.3936 mmol, 75%) as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (t, ^{3}J = 8.4 Hz, 1H), 6.58 (d, ^{3}J = 8.4 Hz, 2H), 4.17 (s, 4H), 3.89 (t, ^{3}J = 6.2 Hz, 4H), 3.68-3.63 (m, 4H), 3.57-3.53 (m, 4H), 3.37 (s, 6H), 2.81 (s, 6H), 1.59-1.51 (m+s, 4H+6H), 1.30-120 (m, 4H), 1.20-1.02 (m, 16H), 0.87 (t, ^{3}J = 7.3 Hz, 6H). ^{13}C NMR (100 MHz $CDCl_3$): δ = 157.0, 154.6, 142.2, 136.8, 131.2, 129.8, 124.8, 113.3, 105.1, 90.7, 85.1, 71.9, 68.9, 68.6, 59.6, 59.0, 32.0, 31.6, 30.4, 30.3, 29.8, 29.8, 29.5, 29.4, 29.0, 25.9, 22.9, 17.6, 16.2, 14.3, 14.2.

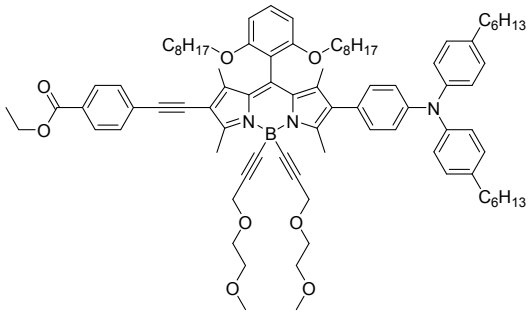
Compound 5



A solution of compounds **3** (401.7 mg, 0.3936 mmol), **B** (212.4 mg, 0.3936 mmol, 1.0 eq) and K_2CO_3 (108.9 mg, 0.7872 mmol, 2 eq) in THF (10 mL) and water (1 mL) was degased with argon for 30 min. [$Pd(PPh_3)_4$] (46 mg, 0.0394 mmol, 10% mol) was added to the solution. It was stirred at 45 °C overnight. The mixture was diluted with dichloromethane and washed with water. The aqueous phase was extracted with dichloromethane. The combined organic phase was dried over $MgSO_4$ or absorbent cotton and the solvents were evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, solvent: 95/5→80/20 petroleum ether/ethyl acetate) to afford compound 4.27 (144.9

mg, 0.1109 mmol, 28%) as a red solid. 280.7 mg (70%) of starting material **5** were also collected. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, ^{3}J = 8.5 Hz, 2H), 7.32 (t, ^{3}J = 8.3 Hz, 1H), 7.08- 6.97 (m, 10H), 6.58 (d, ^{3}J = 8.3 Hz, 2H), 4.19 (s, 4H), 3.91 (t, ^{3}J = 6.2 Hz, 4H), 3.70-3.64 (m, 4H), 3.57-3.53 (m, 4H), 3.36 (s, 6H), 2.81 (s, 3H), 2.73 (s, 3H), 2.58-2.52 (m, 4H), 1.65-1.56 (m, 8H), 1.54 (s, 3H), 1.47 (s, 3H), 1.37-1.19 (m, 32H), 0.92-0.80 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.2, 152.3, 147.8, 147.2, 145.5, 139.4, 138.6, 132.3, 132.2, 131.6, 131.3, 130.0, 129.8, 129.6, 129.2, 129.0, 128.7, 126.7, 126.5, 124.7, 124.6, 124.1, 122.1, 119.2, 114.2, 105.1, 93.8, 87.0, 71.9, 68.7, 68.5, 64.8, 61.3, 61.1, 59.8, 59.1, 36.7, 35.5, 35.0, 34.7, 34.4, 32.1, 32.0, 31.9, 31.6, 31.6, 31.2, 30.5, 30.3, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 28.8, 26.0, 22.9, 14.5, 14.5, 14.4, 14.3.

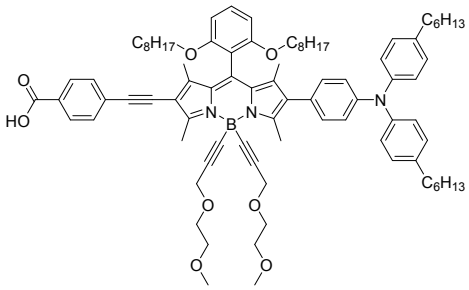
Compound 7



A solution of compounds **5** (190.0 mg, 0.1454 mmol) and **C** (51.0 mg, 0.2909 mmol, 2 eq) in benzene (5 mL) and NEt_3 (5 mL) was degased with argon for 30 min. CuI (6 mg, 0.0315 mmol, 20% mol) and $[Pd(PPh_3)_2Cl_2]$ (10 mg, 0.0142 mmol, 10% mol) were then successively added. The solution was heated at 60 °C overnight. The mixture was diluted with dichloromethane and washed with an HCl 1M solution and water. The aqueous phase was extracted with dichloromethane. The combined organic phase was dried over $MgSO_4$ or absorbent cotton and the solvents were evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, solvent: 90/10 petroleum ether/ethyl acetate) to afford compound **7** (141.9 mg, 0.1049 mmol, 72%) as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, ^{3}J = 8.4 Hz, 2H), 7.47 (d, ^{3}J = 8.4 Hz, 2H), 7.33 (t, ^{3}J = 8.4 Hz, 2H), 7.09-8.98 (m, 12H), 6.59 (d, ^{3}J = 8.4 Hz, 2H), 4.38 (q, ^{3}J = 7.3 Hz, 2H), 4.20(s, 4H), 3.92 (t, ^{3}J = 6.3 Hz, 4H), 3.71-3.64 (m, 4H), 3.58-3.51 (m, 4H), 3.36 (s, 6H), 2.89 (s, 3H), 2.75 (s, 3H), 2.55 (t, ^{3}J = 7.7 Hz, 4H), 1.65 (s, 3H), 1.63-1.55 (m, 8H), 1.50 (s, 3H), 1.44-1.08 (m, 32H), 1.40 (t, ^{3}J = 7.2 Hz, 3H), 0.89 (t, ^{3}J = 6.6 Hz, 6H), 0.78 (t, ^{3}J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.4, 157.3, 156.3, 147.2, 145.5, 139.2, 137.9, 134.1, 131.6, 131.0, 130.9, 129.6, 129.5, 129.3, 129.2, 129.0, 127.0, 124.7, 122.1, 113.7, 113.5, 105.2, 95.1, 90.8, 87.4, 72.0, 68.8, 68.6, 61.2, 59.8, 59.1, 35.6, 32.0, 31.9, 31.6, 29.5, 29.4, 29.2, 26.0, 22.8, 22.8, 15.4, 15.1, 14.5,

14.2, 12.5, 12.3.

Compound *h*-BOD



Compound **7** (141.9 mg, 0.1049 mmol) was placed in a flask with THF (3 mL),EtOH (1 mL) and water (1 mL). NaOH (168 mg, 4.196 mmol, 40 eq) was added and the solution was stirred until the starting material totally disappeared. The mixture was diluted with dichloromethane and washed with an HCl 1M solution and water. The aqueous phase was extracted with dichloromethane. The combined organic phase was dried over $MgSO_4$ or absorbent cotton and the solvents were evaporated under reduced pressure. The crude product purified by column chromatography (silica gel, solvent: 95/5 ethyl acetate/acetic acid) to afford compound ***h*-BOD** (26.6 mg, 0.0200 mmol, 19%) as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, ^{3}J = 8.3 Hz, 2H), 7.50 (d, ^{3}J = 8.4 Hz, 2H), 7.33 (t, ^{3}J = 8.4 Hz, 1H), 7.08-6.99 (m, 12H), 6.60 (d, ^{3}J = 8.5 Hz, 2H), 4.20 (s, 4H), 3.92 (t, ^{3}J = 6.3 Hz, 4H), 3.70-3.65 (m, 4H), 3.57-3.53 (m, 4H), 3.36 (s, 6H), 2.89 (s, 3H),2.75 (s, 3H), 2.55 (t, ^{3}J = 7.8 Hz, 4H), 1.66 (s, 3H), 1.63-1.54 (m, 8H), 1.50 (s, 3H), 1.38-1.07 (m, 32H), 0.90-0.85 (m, 6H), 0.78 (t, ^{3}J =7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.6, 157.2, 156.5, 154.5, 147.1, 145.5, 139.1, 137.8, 137.1, 134.3, 134.1, 131.6, 131.0, 129.9, 129.3, 128.9, 126.8, 124.7, 122.0, 113.5, 113.3, 105.1, 95.0, 90.7, 88.0, 71.9, 68.7, 68.6, 63.2, 59.8, 59.1, 35.5, 32.1, 32.0, 31.9, 31.6, 29.9, 29.5, 29.4, 29.2, 29.2, 26.0, 22.9, 22.8, 15.4, 15.1, 14.3, 12.5, 12.3. FT-IR: *ν*/cm^{-1} = 1232 (C-O), 1251 (C-O), 1693 (C=O).

Synthesis of *cc*-BOD.

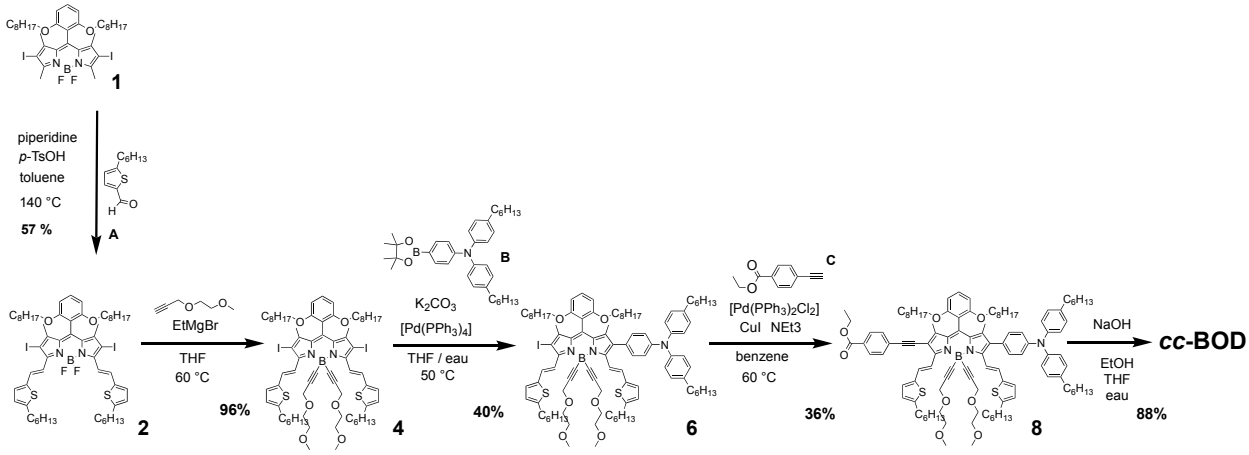
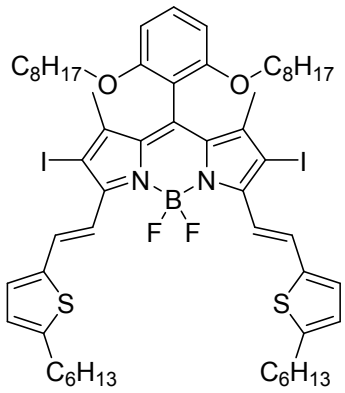


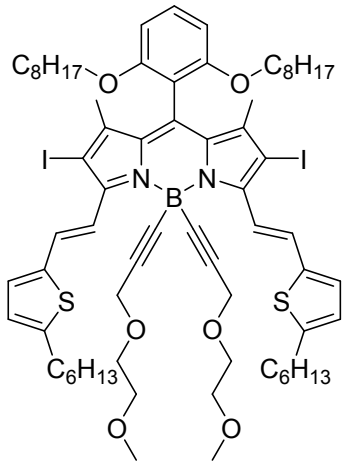
Figure S5. Synthetic route followed for compound ***cc*-BOD.**

Compound 2



A solution of compound **1** (229.2 mg, 0.2754 mmol), 5-hexylthiophene-2-carbaldehyde (216.2 mg, 1.1014 mmol, 4 eq) and a crystal a *p*TsOH in toluene (5 ml) and piperidine (1 ml) was refluxed at 140 °C and the solvents were evaporated until dryness. The mixture was diluted with dichloromethane and washed with water. The aqueous phase was extracted with dichloromethane. The combined organic phase was dried over $MgSO_4$ or absorbent cotton and the solvents were evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, solvent: 80/20 petroleum ether/DCM) to afford compound **2** (185.2 mg, 0.1558 mmol, 57%) as a green solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (d, ^{3}J = 16.3 Hz, 2H), 7.39 (d, ^{3}J = 16.1 Hz, 2H), 7.36 (t, ^{3}J = 8.3 Hz, 1H), 7.09 (d, ^{3}J = 3.5 Hz, 2H), 6.74 (d, ^{3}J = 3.6 Hz, 2H), 6.60 (d, ^{3}J = 8.5 Hz, 2H), 3.91 (t, ^{3}J = 6.2 Hz, 4H), 2.84 (t, ^{3}J = 7.6 Hz, 4H), 1.77-1.67 (m, 4H), 1.61-1.53 (m+s, 4H+6H), 1.45-1.29 (m, 12H), 1.24-1.06 (m, 20H), 0.91 (t, ^{3}J = 6.9 Hz, 6H), 0.81 (t, ^{3}J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3, 148.9, 144.4, 140.8, 139.4, 133.8, 133.3, 132.0, 131.4, 129.1, 125.4, 117.3, 114.2, 113.3, 105.2, 83.1, 68.9, 53.6, 34.0, 32.1, 32.0, 31.7, 31.6, 31.5, 30.8, 29.8, 29.5, 29.5, 29.4, 29.1, 28.9, 26.1, 22.9, 22.8, 22.7, 16.5, 14.3, 14.2.

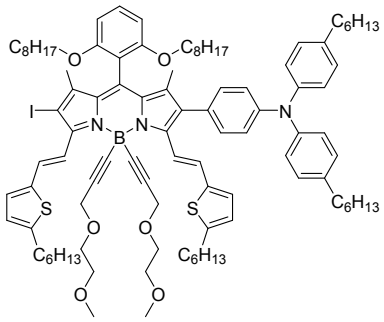
Compound 4



In a Schlenk tube was added ethylmagnesiumbromide (0.9 M, 2 mL, 1.799 mmol, 5 eq) to a stirred solution of 3-(2-methoxyethoxy)prop-1-yne (0.26 mL, 2.158 mmol, 6 eq) in anhydrous THF. The mixture was stirred at 60 °C for 2 h. The resulting anion was then transferred via cannula to a solution of compound **2** (427.7 mg, 0.3597 mmol) in anhydrous THF. The solution was stirred at 60 °C overnight. Water was added, and the solution was extracted with dichloromethane. The organic layer was dried over $MgSO_4$ or absorbent cotton and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, solvent: 90/10 petroleum ether/ethyl acetate)

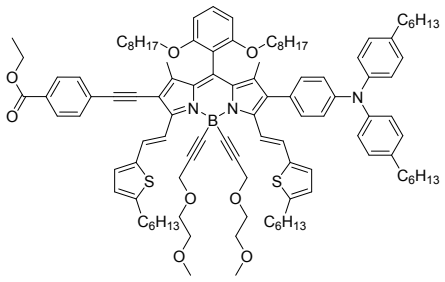
to afford compound **4** (476.8 mg, 0.3462 mmol, 96%) as a green solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, ^{3}J = 16.4 Hz, 2H), 7.96 (d, ^{3}J = 16.3 Hz, 2H), 7.36 (t, ^{3}J = 8.4 Hz, 1H), 7.07 (d, ^{3}J = 3.6 Hz, 2H), 6.75 (d, ^{3}J = 3.6 Hz, 2H), 6.59 (d, ^{3}J = 8.4 Hz, 2H), 4.15 (s, 4H), 3.90 (t, ^{3}J = 6.2 Hz, 4H), 3.60-3.56 (m, 4H), 3.31-3.27 (m, 4H), 3.27 (s, 6H), 2.85 (t, ^{3}J = 7.8 Hz, 4H), 1.78-1.67 (m, 4H), 1.62-1.53 (m+s, 4H+6H), 1.45-1.03 (m, 26H), 0.91 (t, ^{3}J = 6.7 Hz, 6H), 0.81 (t, ^{3}J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.4, 148.4, 148.0, 145.1, 143.2, 141.0, 131.8, 130.0, 128.1, 125.3, 124.9, 120.9, 119.7, 106.2, 105.2, 81.7, 71.8, 68.8, 68.2, 59.4, 58.9, 32.1, 31.7, 30.8, 30.5, 29.8, 29.6, 29.5, 29.1, 29.0, 26.1, 22.9, 22.8, 16.6, 14.3, 14.2.

Compound 6



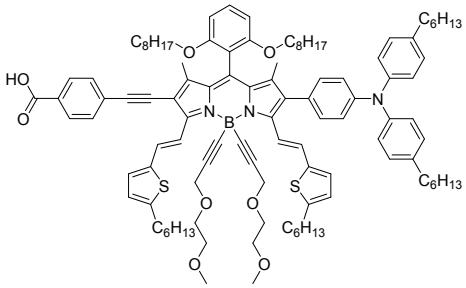
A solution of compounds **4** (186.3 mg, 0.1353 mmol), **B** (73.0 mg, 0.1353 mmol, 1.0 eq) and K_2CO_3 (22.4 mg, 0.1624 mmol, 1.2 eq) in THF (5 mL) and water (1 mL) was degased with argon for 30 min. [$Pd(PPh_3)_4$] (15.6 mg, 0.135 mmol, 10% mol) was added to the solution. It was stirred at 50 °C for 48 h. The mixture was diluted with dichloromethane and washed with water. The aqueous phase was extracted with dichloromethane. The combined organic phase was dried over $MgSO_4$ or absorbent cotton and the solvents were evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, solvent: 90/10 petroleum ether/ethyl acetate) to afford compound **6** (90.0 mg, 0.0541 mmol, 40%) as a green solid. 47.0 mg (25%) of starting material **4** were also collected. ^{1}H NMR (400 MHz, C_6D_6): δ = 8.69 (d, ^{3}J = 16.1 Hz, 1H), 8.65 (d, ^{3}J = 16.1 Hz, 1H), 7.20-7.12 (m overlapping with solvent, 5H), 7.07 (d, ^{3}J = 3.6 Hz, 1H), 7.02-6.95 (m, 7H), 6.88 (d, ^{3}J = 16.3 Hz, 1H), 6.80 (d, ^{3}J = 8.5 Hz, 2H), 6.52 (d, ^{3}J = 3.4 Hz, 1H), 6.50 (d, ^{3}J = 3.6 Hz, 1H), 6.40 (d, ^{3}J = 8.4 Hz, 2H), 4.36 (s, 4H), 4.04 (t, ^{3}J = 4.04 Hz, 4H), 3.94-3.81 (m, 4H), 3.71-3.57 (m, 4H), 3.44 (t, ^{3}J = 4.9 Hz, 4H), 3.20 (s, 6H), 2.97 (t, ^{3}J = 7.6 Hz, 4H), 2.60-2.40 (m, 12H), 1.87 (s, 3H), 1.72 (s, 3H), 1.57-1.04 (m, 44H), 0.96-0.84 (m, 18H). ^{13}C NMR (100 MHz, C_6D_6): δ = 172.7, 158.0, 152.7, 151.6, 148.6, 147.3, 146.2, 141.9, 140.6, 139.3, 138.9, 137.8, 136.2, 134.8, 133.1, 132.0, 131.8, 131.1, 130.9, 129.7, 125.6, 125.5, 125.2, 124.9, 124.7, 124.7, 123.6, 120.3, 120.0, 114.5, 105.4, 72.2, 69.1, 64.5, 59.8, 58.7, 36.8, 35.8, 35.2, 34.6, 34.4, 34.3, 32.5, 32.4, 32.1, 32.0, 31.9, 31.9, 31.9, 31.5, 30.8, 30.5, 30.2, 30.2, 30.1, 30.1, 30.0, 29.9, 29.7, 29.6, 29.4, 29.4, 29.2, 29.1, 26.3, 23.3, 23.1, 23.0, 16.7, 14.5, 14.4, 14.3.

Compound 8



A solution of compounds **6** (131.3 mg, 0.0790 mmol) and **C** (20.6 mg, 0.1184 mmol, 1.5 eq) in benzene (5 mL) and NEt_3 (5 mL) was degased with argon for 30 min. CuI (3 mg, 0.0158 mmol, 20% mol) and $[Pd(PPh_3)_2Cl_2]$ (6 mg, 0.0079 mmol, 10% mol) were then successively added. The solution was heated at 60 °C for 6 h. The mixture was diluted with dichloromethane and washed with an HCl 1M solution and water. The aqueous phase was extracted with dichloromethane. The combined organic phase was dried over $MgSO_4$ or absorbent cotton and the solvents were evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, solvent: 90/10 petroleum ether/ethyl acetate) followed by a recrystallization from Et_2O/MeOH to afford compound **8** (48.2 mg, 0.0282 mmol, 37%) as a green solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (d, ^{3}J = 16.0 Hz, 1H), 8.10 (d, ^{3}J = 16.1 Hz, 1H), 8.02 (d, ^{3}J = 7.9 Hz, 2H), 8.00 (d, ^{3}J = 16.2 Hz, 1H), 7.52 (d, ^{3}J = 8.3 Hz, 2H), 7.34 (t, ^{3}J = 8.3 Hz, 1H), 7.13-6.98 (m, 13H), 6.80 (d, ^{3}J = 3.5 Hz, 1H), 6.76 (d, ^{3}J = 3.5 Hz, 1H), 6.71 (d, ^{3}J = 3.5 Hz, 1H), 6.60 (d, ^{3}J = 8.5 Hz, 2H), 6.60 (d, ^{3}J = 16.0 Hz, 1H), 4.39 (q, ^{3}J = 7.1 Hz, 2H), 4.21 (s, 4H), 3.94 (t, ^{3}J = 6.2 Hz, 4H), 3.70-3.61 (m, 4H), 3.30 (t, ^{3}J = 4.4 Hz, 4H), 3.26 (s, 6H), 2.90-2.80 (m, 4H), 2.56 (t, ^{3}J = 7.7 Hz, 4H), 1.79-1.67 (m, 4H), 1.70 (s, 3H), 1.64-1.54 (m, 8H), 1.42 (s, 3H), 1.46-1.08 (m, 40H), 0.95-0.84 (m, 12H), 0.73 (d, ^{3}J = 6.6 Hz, 6H).

Compound *cc*-BOD



Compound **8** (45.1 mg, 0.0264 mmol) was placed in a flask with THF (2 mL), EtOH (0.5 mL) and water (0.5 mL). NaOH (1.6 mg, 0.0396 mmol, 1.5 eq) was added and the solution was stirred for 2 h. The mixture was diluted with dichloromethane and washed with an HCl 1M solution and water. The aqueous phase was extracted with dichloromethane. The combined organic phase was dried over $MgSO_4$ or absorbent cotton and the solvents were evaporated under reduced pressure. The crude product was washed with pentane and Et_2O to afford compound ***cc*-BOD** (39.0 mg, 0.0232 mmol, 88%) as a green solid. ^{1}H NMR

(400 MHz, $CDCl_3$): δ = 8.27 (d, ^3J = 15.9 Hz, 1H), 8.09 (d, ^3J = 16.1 Hz, 1H), 8.07 (d, ^3J = 8.4 Hz, 2H), 7.99 (d, ^3J = 16.0 Hz, 1H), 7.54 (d, ^3J = 8.3 Hz, 2H), 7.34 (t, ^3J = 8.3 Hz, 1H), 7.11-7.01 (m, 13H), 6.80 (d, ^3J = 3.5 Hz, 1H), 6.76 (d, ^3J = 3.5 Hz, 1H), 6.71 (d, ^3J = 3.5 Hz, 1H), 6.60 (d, ^3J = 8.5 Hz, 2H), 6.60 (d, ^3J = 16.0 Hz, 1H), 4.21 (s, 4H), 3.93 (t, ^3J = 6.4 Hz, 4H), 3.69-3.61 (m, 4H), 3.30 (t, ^3J = 4.5 Hz, 4H), 3.26 (s, 6H), 2.90-2.80 (m, 4H), 2.56 (t, ^3J = 7.8 Hz, 4H), 1.79-1.67 (m, 4H) 1.70 (s, 6H), 1.65-1.56 (m, 8H), 1.42 (s, 3H), 1.46-1.08 (m, 40H), 0.95-0.84 (m, 12H), 0.73 (d, ^3J = 6.6 Hz, 6H). ^{13}C NMR (100 MHz $CDCl_3$): δ = 157.5, 151.1, 148.9, 148.4, 147.9, 145.5, 141.4, 141.1, 137.7, 137.3, 134.0, 133.8, 132.4, 132.3, 131.4, 130.7, 130.4, 129.9, 129.3, 128.7, 128.6, 127.3, 125.4, 124.4, 123.3, 119.4, 113.7, 111.6, 108.6, 105.0, 96.0, 91.6, 84.6, 71.8, 68.7, 68.2, 59.5, 58.9, 35.5, 32.1, 31.9, 31.8, 31.7, 31.7, 30.8, 29.8, 29.6, 29.5, 29.4, 29.2, 29.2, 29.1, 26.1, 22.9, 22.8, 14.2. FT-IR: ν/cm^{-1} = 1250 (C-O), 1688 (C=O).

^1H NMR traces.

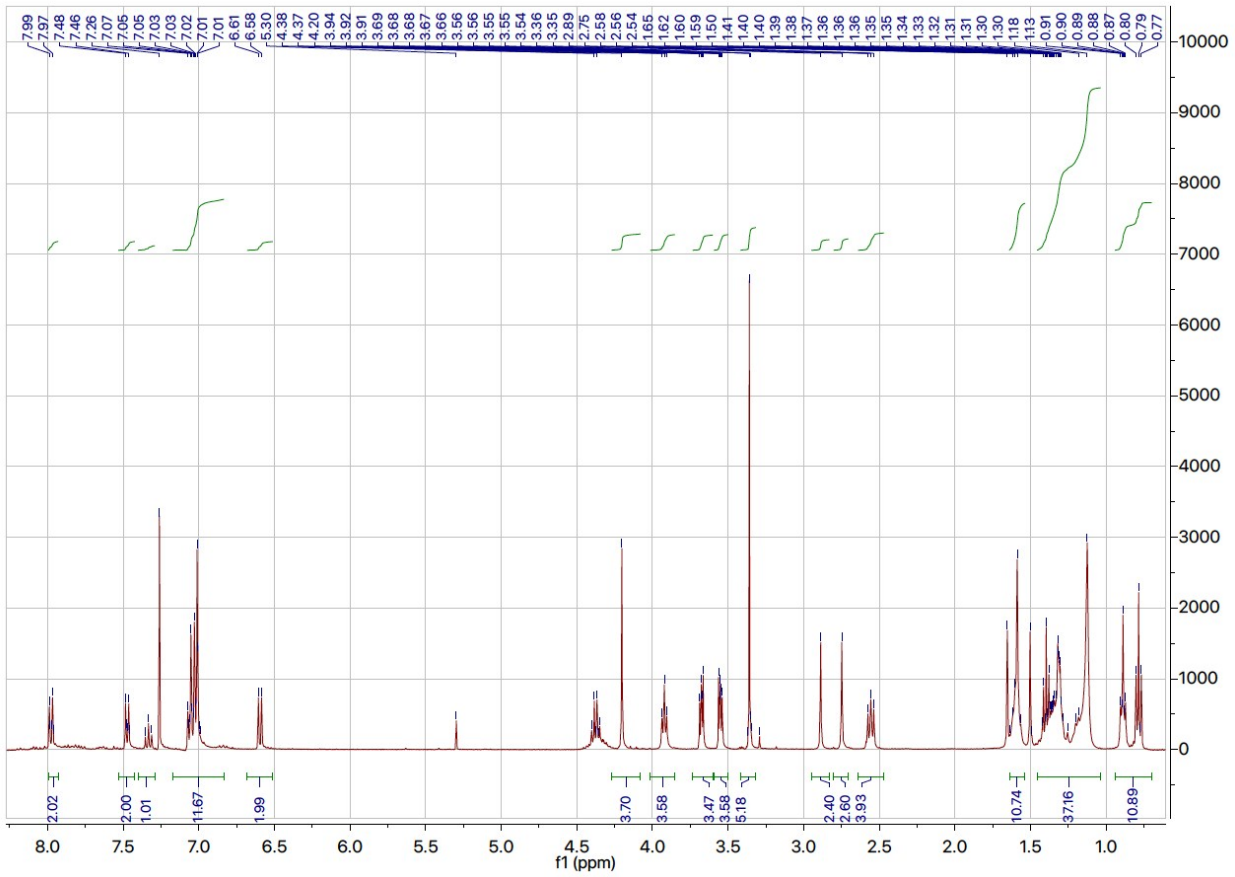


Figure S6. ^1H NMR spectrum of *h*-BOD in $CDCl_3$.

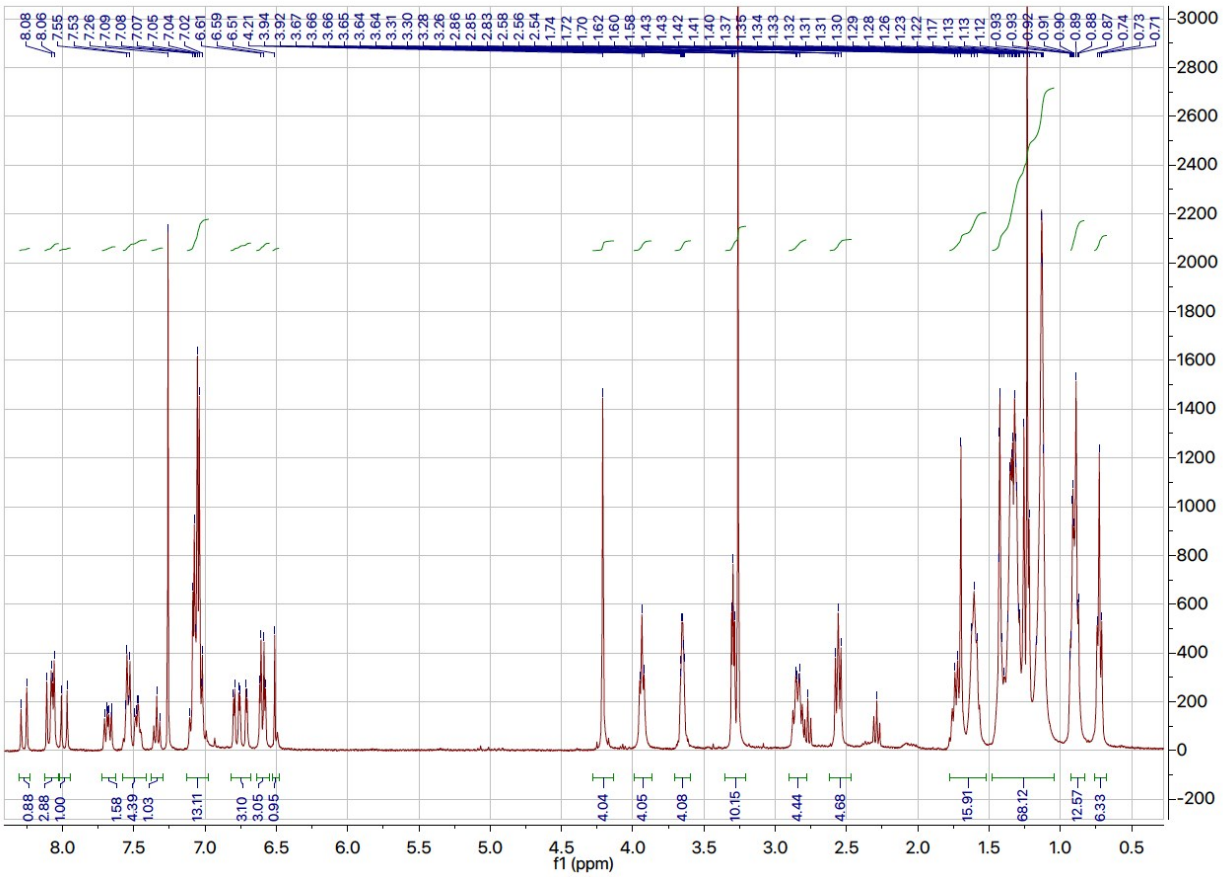


Figure S7. ^{1}H NMR spectrum of *cc*-BOD in $CDCl_3$.

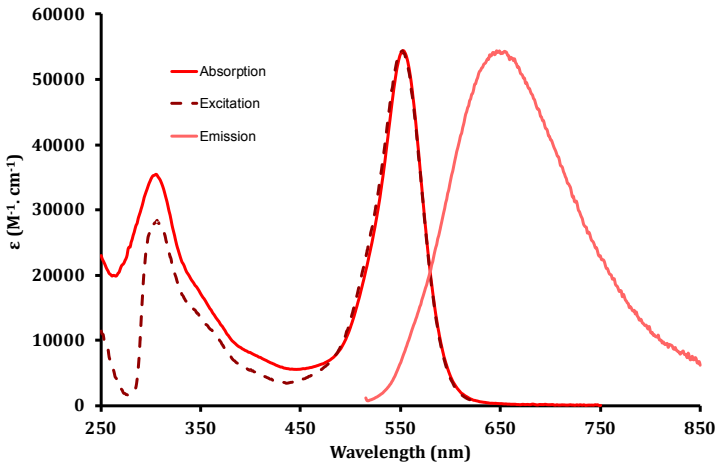


Figure S8. Absorption spectra (orange line), emission spectra (light orange line) and excitation spectra (brown dashed line) in THF ***h*-BOD.**

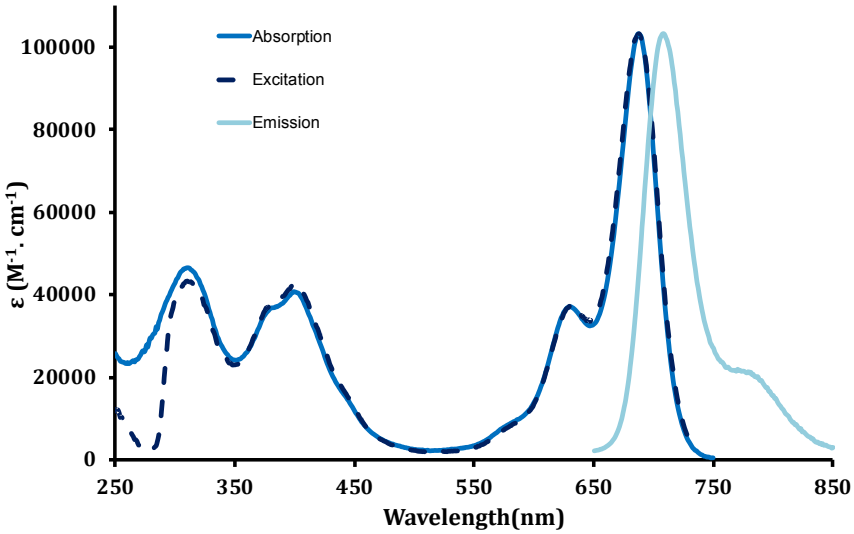


Figure S9. Absorption spectra (blue line), emission spectra (light blue line) and excitation spectra (black dashed line) in THF ***cc*-BOD.**

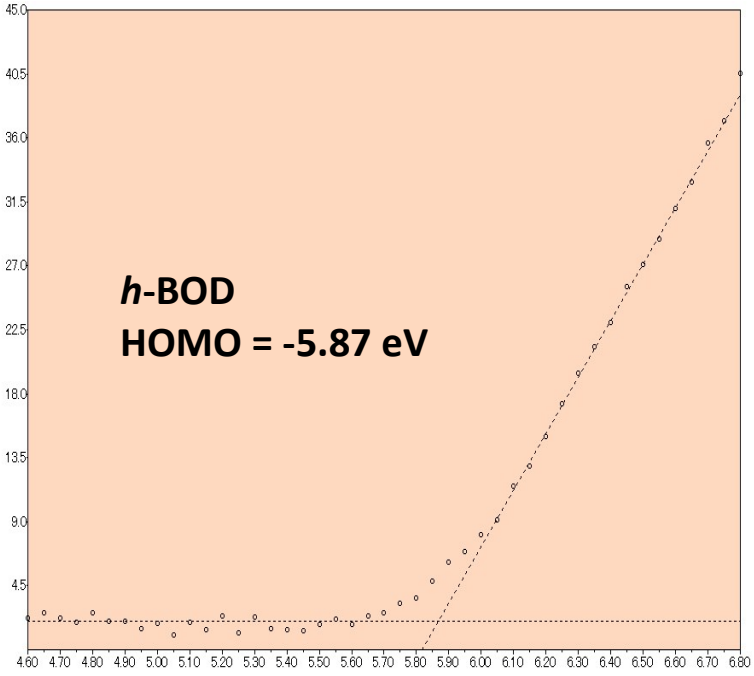


Figure S10. Ionization potential (IP) of *h*-BOD anchored onto TiO_2 film

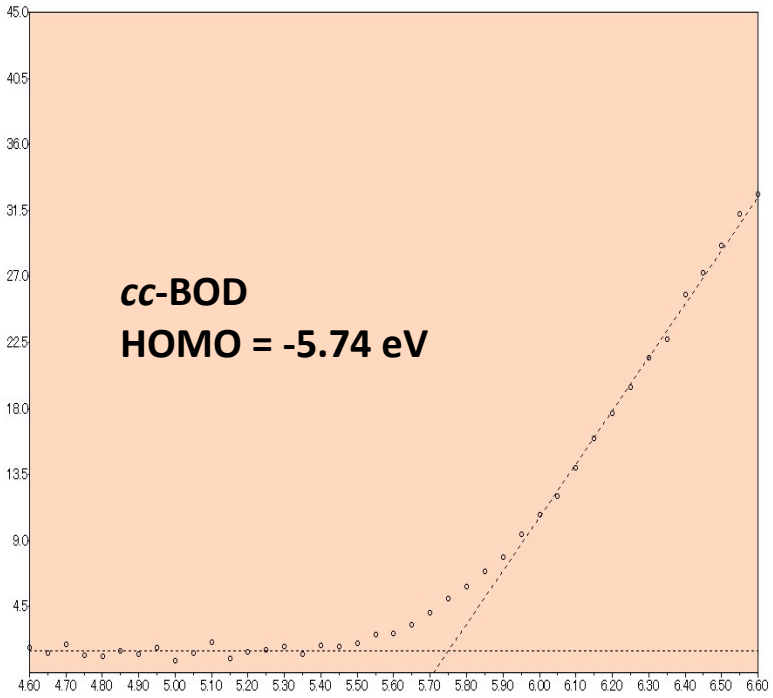


Figure S11. Ionization potential (IP) of *cc*-BOD anchored onto TiO_2 film

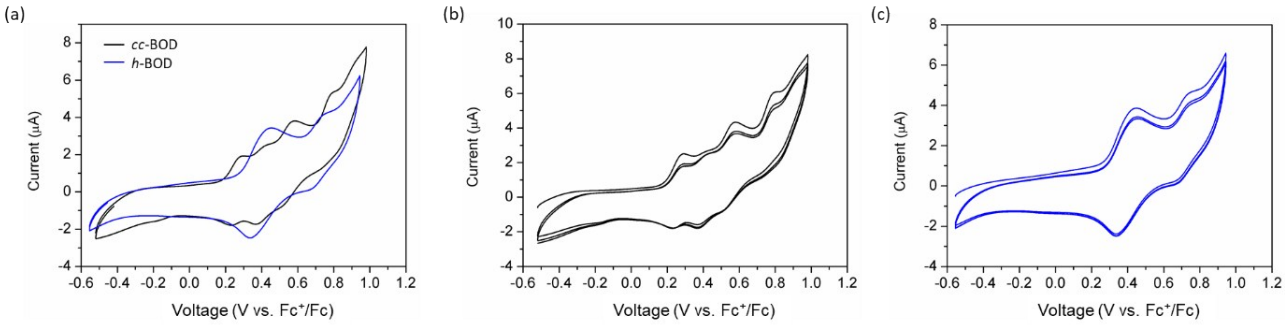


Figure S12. Cyclic voltammograms. [dye] = 1 mM, [$TBPPF_6$] = 0.1 M, 293 K, scan rate 100 mV/s. (a) *cc*-BOD and *h*-BOD. (b) *cc*-BOD. (c) *h*-BOD.

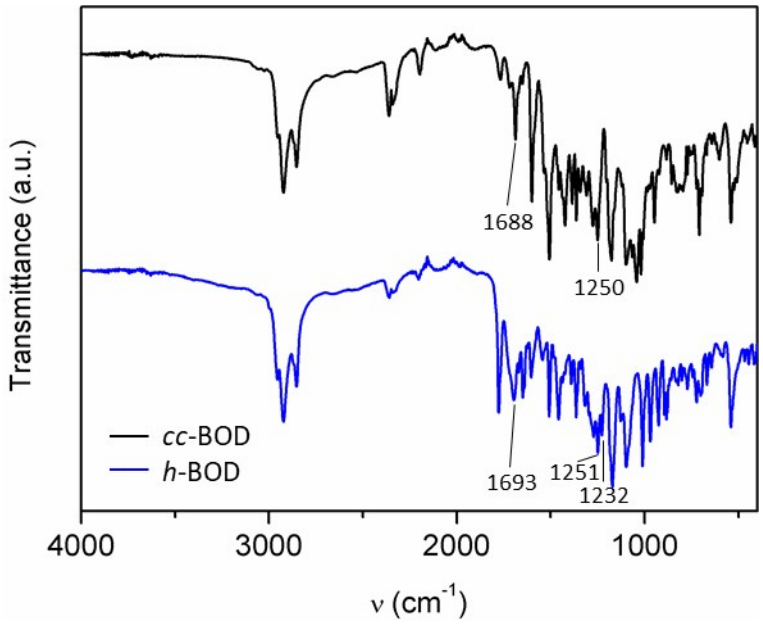


Figure S13. FT-IR spectra of *cc*-BOD and *h*-BOD.

Table S1. Redox characteristics of *cc*-BOD and *h*-BOD.

Samples	E_{ox1} /V vs. Fc^+/Fc	E_{ox2} /V vs. Fc^+/Fc	E_{ox3} /V vs. Fc^+/Fc	E_{ox4} /V vs. Fc^+/Fc	HOMO (eV)[a]
cc-BOD	+0.26	+0.40	+0.55	+0.77	-5.36
h-BOD	+0.36	+0.71	-	-	-5.46

[a] $E_{HOMO} = -(E_{ox[vs.\ Fc+/Fc]}+5.1)$

Table S2. Photovoltaic parameters of the fabricated DSSCs

Dye	Sample	J_{SC} **[mA cm^{-2}]**	V_{OC} **[V]**	***FF***	***η [%]***
h-BOD	1	**9.69**	**0.537**	**0.711**	**3.697**
	2	9.59	0.535	0.718	3.683
	3	9.31	0.540	0.725	3.640
	4	9.67	0.526	0.719	3.658
cc-BOD	1	**15.43**	**0.549**	**0.711**	**6.023**
	2	15.35	0.545	0.699	5.855
	3	15.33	0.544	0.719	5.999
	4	15.30	0.552	0.712	6.019
h-BOD + *cc*-BOD	1	**16.07**	**0.561**	**0.688**	**6.201**
	2	15.93	0.554	0.702	6.196
	3	15.86	0.560	0.698	6.198
	4	15.76	0.559	0.698	6.141

References

1. T. Bura, N. Leclerc, S. Fall, P. Lévêque, T. Heiser, P. Retailleau, S. Rihn, A. Mirloup and R. Ziessel, Journal of the American Chemical Society, 2012, 134, 17404-17407.