Supporting Information

Aggregation-free branch-type organic dye with a twisting molecular architecture for dye-sensitized solar cells

Youhei Numata, Ashraful Islam, Han Chen, and Liyuan Han*

Experimental Section

General

4,4′-Dibromobenzophenone (1a), 4-(N,N-diphenylamino)phenylboronic acid, 5-formylthiophene-2-boronic acid, and other chemicals were purchased from chemical companies. 2-Bromothiophene-5-methylphosphoryl diethyl1 and 2,7-Diiodofluorenone2 were synthesized according to the literature method. All chemicals were used as received from chemical companies without further purification. Anhydrous solvents were degassed by Ar bubbling for 20 min before use. All syntheses were carried out under argon atmosphere unless stated. Column chromatography was performed using with Wakogel-C300 as a stationary phase. Work functions of the dyes adsorbed onto TiO2 film was measured using with AC-3E Photoemission yield spectrometer (RIKEN KEIKI). The 1H and 13C NMR measurements were performed by a DRX-600 spectrometer (Bruker BioSpin).
4,4′-Bis(p-(N,N-diphenylamino)phenyl)benzophenone (2a)

To a suspension of 1a (868 mg, 2.553 mmol), 4-(N,N-diphenylamino)phenylboronic acid (1.48 g, 5.106 mmol) and Cs$_2$CO$_3$ (4.5 g, 13.811 mmol) in toluene (30 mL), MeOH (20 mL), and H$_2$O (2 mL), a solution of [Pd(dba)$_2$] (dba = dibenzylideneacetone) (73 mg, 0.128 mmol) and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (XantPhos) (73 mg, 0.128 mmol) in toluene (6 mL) and MeOH (4 mL) was added and stirred for 8 h at 85 °C. A reaction mixture was cooled to room temperature and precipitate was removed by filtration. The residual solid was washed with CH$_2$Cl$_2$, and the organic solutions were combined. The solution was extracted with water three times, dried over anhydrous MgSO$_4$, filtrate and the solvent was evaporated to dryness. The mixture was purified by silica gel column chromatography with CH$_2$Cl$_2$ and n-hexane 1:1 mixture as eluent. The yellow fraction was collected and dried over to give 2a as a bright yellow solid (1.31 g, 77%). $^1$H NMR (600 MHz, CD$_2$Cl$_2$, δ): 7.87-7.88 (d, 4H), 7.72-7.71 (d, 4H), 7.58-7.57 (d, 4H), 7.31-7.28 (t, 8H), 7.14-7.13 (m, 12H), 7.08-7.06 (t, 4H), 6.79-6.77 (m, 2H); $^{13}$C NMR (150 MHz, CD$_2$Cl$_2$): 195.77, 148.58, 147.89, 144.82, 136.38, 133.64, 131.03, 129.77, 128.30, 126.58, 125.19,
123.77, 123.67; Anal. calcd for C_{49}H_{36}N_{2}O: C 87.99, H 5.43, N 4.19; Found: C 87.82, H 5.70, N 3.98%.

5-Bromo-2-(2,2-bis(p-(N,N-diphenylamino)biphenyl)-1-vinyl)thiophene (3a)

A solution of diethyl 5-bromothien-2-ylmethylphosphonate (281 mg, 0.897 mmol) in THF (40 mL) was cooled to –78 °C. 2.0 M lithium diisopropylamide solution in n-pentane (0.54 mL) was slowly added. The mixture was stirred for 2 h at the temperature, and then, a solution of 2a (600 mg, 0.897 mmol) in THF (10 mL) was slowly added. The mixture was slowly warmed up to room temperature and stirred for 8 h. A reaction mixture was cooled to room temperature and precipitate was removed by filtration. The residual solid was washed with CH_{2}Cl_{2} and the organic solutions were combined. The solution was extracted with water three times, dried over anhydrous MgSO_{4}, filtrate and the solvent was evaporated to dryness. The mixture was purified by silica gel column chromatography with CH_{2}Cl_{2} and n-hexane 1:1 mixture as an eluent. The yellow fraction was collected and dried over to give 3a as vivid lemon yellow solid (605 mg, 81%). \(^1\)H NMR (600 MHz, CD_{2}Cl_{2}, δ): 7.76-7.75 (d, 2H), 7.64-7.63 (d, 2H), 7.54-7.52 (d, 2H), 7.50-7.48 (d, 2H), 7.40-7.39 (d, 2H), 7.33-7.32 (d, 2H), 7.30-7.26 (m, 9H), 7.17-7.16 (d, 2H), 7.15-7.13 (dd, 4H), 7.11-7.09 (m, 6H), 7.07-7.03 (q, 4H), 6.88-6.87 (d, 1H), 6.82-6.81 (d, 1H); \(^13\)C NMR (150 MHz, CD_{2}Cl_{2}): 148.08, 148.03, 147.97, 147.82, 143.65, 141.03, 140.25, 140.07, 139.99, 137.76, 134.66, 134.53, 131.08, 129.71, 129.70, 129.62, 129.48, 128.08, 127.91, 127.87, 127.56, 126.75, 124.90, 124.24, 124.09, 123.47, 120.79, 113.76; HRMS(FAB), m/z: calcd for C_{54}H_{39}BrN_{2}S, 826.2017; found: 826.2020.

5´-(2,2-Bis(p-(N,N-diphenylamino)biphenyl)-1-vinyl)-2,2´-bithiophene-5-carboxaldehyde (4a)
To a mixture of 3a (300 mg, 0.362 mmol), Cs₂CO₃ (180 mg, 0.552 mmol) and 5-formyl-2-thiopheneboronic acid (58 mg, 0.370 mmol) in toluene (20 mL), MeOH (10 mL), and H₂O (2 mL), a solution of [Pd(dba)₂] (9 mg, 0.015 mmol) and XantPhos (9 mg, 0.015 mmol) in toluene (10 mL) and MeOH (5 mL) was added and stirred for 8 h at 85 °C. A reaction mixture was cooled to room temperature and precipitate was removed by filtration. The residual solid was washed with CH₂Cl₂ and the organic solutions were combined. The solution was extracted with water three times, dried over anhydrous MgSO₄, filtrate and the solvent was evaporated to dryness. The mixture was purified by silica gel column chromatography with CH₂Cl₂ and n-hexane 1:1 mixture as an eluent. The orange fraction was collected and dried over to give 4a as vivid orange yellow solid (146 mg, 42%).

1H NMR (600 MHz, CD₂Cl₂, δ): 7.31-7.33 (d, 2H), 7.28-7.25 (t, 4H), 7.09-7.08 (d, 4H), 7.06-7.05 (t, 2H), 7.03 (s, 1H), 7.00-6.99 (d, 2H), 6.96-6.95 (d, 1H), 6.79-6.77 (m, 2H); 13C NMR (150 MHz, CD₂Cl₂): 148.10, 147.84, 145.44, 131.02, 130.88, 129.72, 128.75, 127.58, 126.15, 125.09, 123.66, 123.52, 119.71, 110.69; HRMS (FAB), m/z: calcd for C₅₉H₄₂N₂OS₂, 858.2739; found: 858.2739.

5´-(2,2-Bis(p-(N,N-diphenylamino)biphenyl)-1-vinyl)-2,2´-bithiophene-5-(2-cyanoacrylic acid) (D-1)

A mixture of 4a (100 mg, mmol), cyanoacetic acid (33 mg, 0.384 mmol) and piperidine (few drops) in acetonitrile (30 mL) and CH₃Cl (5 mL) was stirred for 6 h at 60 °C. Resulting mixture was extracted with CH₂Cl₂ and diluted hydrochloric acid, and the organic layer was dried over with MgSO₄. The solvent was removed under vacuum pressure and the residual solid was purified by column chromatography with CH₂Cl₂ and MeOH (v:v 95:5) mixture as an eluent to give D-1 (96 mg, 89%) as dark red solids. 1H NMR (600 MHz, DMSO-d₆, δ): 7.31-7.33 (d, 2H), 7.28-7.25 (t, 4H), 7.09-7.08 (d, 4H), 7.06-7.05 (t, 2H), 7.03 (s, 1H), 7.00-6.99 (d, 2H), 6.96-6.95 (d, 1H), 6.79-6.77 (m, 2H), and a proton of CO₂H could not be
observed; $^{13}$C NMR (150 MHz, DMSO-$d_6$): 184.23, 146.91, 146.85, 146.78, 139.92, 139.74, 138.94, 137.90, 136.67, 136.03, 135.22, 133.44, 133.10, 131.70, 130.26, 129.52, 128.88, 127.73, 127.41, 126.35, 126.08, 124.48, 124.12, 123.21, 123.13, 123.07, 120.25; HRMS (ESI), m/z: [M − H$^+$] calcd for C$_{62}$H$_{42}$N$_3$O$_2$S$_2$, 924.2724; found: 924.2745.

2,7-Diiodo-9-fluorenone (1b)

1b was synthesized according to the literature method.$^2$ A suspension of 9-fluorenone (1.8 g, 0.01 mol) and N-iodosuccinimide (4.5 g, 0.02 mol) in H$_2$SO$_4$ (50 mL) was stirred for 4 h at 40 ºC. The resulting mixture was poured into ice and cooled to room temperature. The ocher solid was filtrated and washed with water. The crude product was dissolved in benzene, the solution was passed through a short alumina column, and the solvent was evaporated under vacuum pressure. The solid was dissolved in minimal amount of CH$_2$Cl$_2$, a little amount of n-hexane was added, and cooled in refrigerator for overnight. 1b was obtained as vivid yellow crystals (2.4 g, 56%). $^1$H NMR (600 MHz, CDCl$_3$, δ): 7.96 (d, 2H), 7.83 (dd, 2H), 7.27 (d, 2H).

2,7-(Bis(p-(N,N-diphenylamino)phenyl)fluorenone (2b)

2b was synthesized by the same method of 2a using 1b (740 mg, 1.729 mmol) instead of 1a. Vivid red solid (990 mg, 86%). $^1$H NMR (600 MHz, CD$_2$Cl$_2$, δ): 7.86 (d, 2H), 7.73 (dd, 2H), 7.61 (d, 2H), 7.54 (q, 4H), 7.29 (t, 8H), 7.12 (d, 12H), 7.06 (t, 4H); $^{13}$C NMR (150 MHz, CD$_2$Cl$_2$): 193.54, 147.83, 147.51, 142.58, 141.44, 135.24, 133.31, 132.55, 129.33, 127.36, 124.67, 123.37, 123.24, 122.01, 120.78; HRMS (ESI), m/z: [M + H]$^+$ calcd for C$_{49}$H$_{35}$N$_2$O, 667.2744; found: 667.2751.

5-Bromo-2-[2,7-(bis(p-(N,N-diphenylamino)phenyl))-9H-fluoren-9-ylidene)methyl]thiophene (3b)
3b was synthesized by the same method of 3a (300 mg, 0.450 mmol) using 2b instead of 2a. Vivid orange solid (270 mg, 73%). 1H NMR (600 MHz, CD2Cl2, δ): 8.37 (d, 1H), 7.94 (d, 1H), 7.78 (d, 1H), 7.75 (d, 1H), 7.62 (m, 2H), 7.59 (d, 2H), 7.47 (d, 2H), 7.29 (m, 10H), 7.16-7.11 (m, 13H), 7.0 (t, 4H); 13C NMR (150 MHz, CD2Cl2): 114.8, 148.06, 147.77, 147.70, 141.34, 140.72, 140.16, 140.06, 139.65, 137.89, 137.31, 137.25, 135.43, 135.17, 131.06, 130.49, 129.71, 128.04, 127.88, 127.82, 127.61124.32, 124.88, 124.21, 124.18, 123.46, 122.83, 120.62, 120.43, 118.83, 118.58, 114.63; HRMS (FAB), m/z: calcd for C54H37BrN2S, 824.1861; found: 824.1884.

5-[2,7-(Bis(p-(N,N-diphenylamino)phenyl)-(9H-fluoren-9-ylidene)methyl)-2,2’-bithiophene-5’-carboxaldehyde (4b)

4b was synthesized by the same method of 4a using 3b (290 mg, 0.351 mmol) instead of 3a. Vivid orange red solid (185 mg, 61%). 1H NMR (600 MHz, CD2Cl2, δ): 9.86 (s, 1H), 8.53 (d, 1H), 7.97 (d, 1H), 7.80 (d, 1H), 7.77 (d, 1H), 7.70 (s, 1H), 7.63 (s+d+dd, 1+1H), 7.61 (d, 2H), 7.54 (dd, 1H), 7.51 (d, 2H), 7.45 (d, 1H), 7.33 (d, 1H), 7.31-7.27 (m, 8H), 7.16 (d, 2H), 7.14 (d, 4H), 7.12-7.10 (d+d, 4+2H), 7.06 (q, 4H); 13C NMR (150 MHz, CD2Cl2): 182.84, 148.08, 148.01, 147.78, 147.71, 146.44, 141.34, 140.84, 140.23, 140.03, 139.63, 138.24, 137.88, 137.76, 137.28, 135.15, 131.77, 129.72, 128.04, 127.92, 127.83, 127.65, 127.04, 125.13, 124.92, 124.89, 124.21, 124.13, 123.49, 123.47, 123.09, 120.68, 120.48, 118.89, 118.71; HRMS (FAB), m/z: calcd for C59H40N2OS2, 856.2582; found: 856.2574.

5’-(2,7-Bis(p-(N,N-diphenylamino)phenyl)-(9H-fluoren-9-ylidene)methyl)-2,2’-bithiophene-5’-(2-cyanoacrylic acid) (D-2)

D-2 was synthesized by the same method of D-1 using 4b (60 mg, 0.070 mmol) instead of 4a. Dark red solid (48 mg, 75%). 1H NMR (600 MHz, DMSO-d6, δ): 7.86 (d, 2H), 7.73 (q, 2H), 7.61 (d, 2H), 7.54 (q, 4H), 7.29 (t, 8H), 7.12 (m, 12H), 7.06 (t, 4H), and a proton of CO2H
could not be observed; $^{13}$C NMR (150 MHz, DMSO-$d_6$): 162.83, 146.94, 146.84, 146.71, 146.61, 140.30, 139.11, 138.66, 138.39, 137.51, 136.45, 136.04, 134.84, 134.77, 134.18, 139.80, 133.15, 129.50, 127.67, 127.23, 127.08, 126.49, 125.20, 124.19, 123.95, 123.25, 123.12, 123.06, 121.78, 120.75, 120.33, 119.97, 118.63; HRMS (FAB), $m/z$: calcd for C$_{62}$H$_{41}$N$_3$O$_2$S$_2$, 923.2640; found: 923.2606.

Photophysical measurements

Cyclic voltammetry

Reduction and oxidation potentials of the dyes were determined by Electrochemical Analyzer ALS model 624D (ALS Co., Ltd.) using three electrodes cell with a Pt working electrode, Pt wire counter electrode, and Ag/Ag$^+$ reference electrode. Measurements were performed in 0.5 and 1.0 mM CH$_2$Cl$_2$ solutions for D-1 and D-2, respectively. 0.1 M tetra-$n$-butylammonium hexafluorophosphate (TBAPF$_6$) solution in CH$_2$Cl$_2$ was used as the supporting electrolyte. Scan rate was 50 mV/s.

UV-Vis spectra measurement in solutions and on TiO$_2$ film

UV-Vis spectra were measured in dichloromethane solution using UV-3600 UV-VIS-NIR Spectrophotometer (SHIMADZU). The specimens were prepared by same method with cell fabrication described later using 2.3 µm thick TiO$_2$ films. The TiO$_2$ films were sensitized by the immersing in 0.3 mM CHCl$_3$/MeOH (1/1, v/v) dye solutions with or without Deoxycholic acid (0 or 20 mM) as a co-adsorbent for 48 h. Measurements were performed under AM 1.5 irradiation (100 mW cm$^{-2}$) on the specimens with 1.00 cm$^2$ active surface area defined by a metal mask.

DFT calculations
Geometry optimization and calculations for molecular orbital distributions and energy levels of D-1 and D-2 were performed by using B3LYP functional and 6-31G (d,p) basis set implemented in the Gaussian 09 program package.³

Cell Fabrication
The DSC devices were fabricated as follows.⁴ A 12 µm main transparent layer with ca. 20 nm sized titania particles and a 4 µm scattering layer with ca. 400 nm sized titania particles were screen printed on the fluorine-doped tin oxide (FTO) conducting glass substrate. Coating of the titania film was carried out by immersing in 0.3 mM chloroform/MeOH (1/1, v/v) solutions of sensitizers for 45 h. Deoxycholic acid (20 mM) was added into the dye solution as a co-adsorbent to prevent aggregation of the dye molecules. The dye adsorbed TiO₂ film was clipped with a platinized FTO glass used as counter electrode. Finally, the sandwich-type solar cell could be obtained after the injection of an electrolyte consisting of 0.6 mM 1-methyl-3-propylimidazolium iodide, 0.1 mM LiI, 0.2 mM tert-butylpyridine, and 0.05 mM I₂ in acetonitrile.

Photovoltaic Characterization
Incident photon-to-current conversion efficiency (IPCE) spectra were measured by a CEP-200BX spectrometer (Bunko Keiki). The photocurrent-photovoltage (J-V) curves were obtained by a WXS-90S-L2 Super solar simulator (WACOM). Photovoltaic parameters were obtained by the measurements on two different cells of each experimental condition. Measurements were performed under AM 1.5 irradiation (100 mW cm⁻²) on the DSC devices with 0.25 cm² active surface area defined by a metal mask. Important tips in photovoltaic characterization are described in these literatures.⁵
Fig. S1 Cyclic voltammograms for D-1 (red) and D-2 (blue). Conditions, in CH₂Cl₂ solution, reference; vs. Ag/Ag⁺, scan rate; 50 mV/s, supporting electrolyte; 0.1 M TBAPF₆, and dye concentration; 0.5 and 1.0 mM for D-1 and D-2, respectively.
**Fig. S2** Calculated frontier orbital distributions of D-1 and D-2.

**Fig. S3** Calculated energy diagrams of D-1 and D-2.
Fig. S4 $J-V$ curves of D-1 and D-2 dyes adsorbed on TiO$_2$ film without or with DCA (dye: 0.3 mM and DCA: 20 mM in CHCl$_3$/MeOH 1:1 solution).
References


