Supporting Information

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

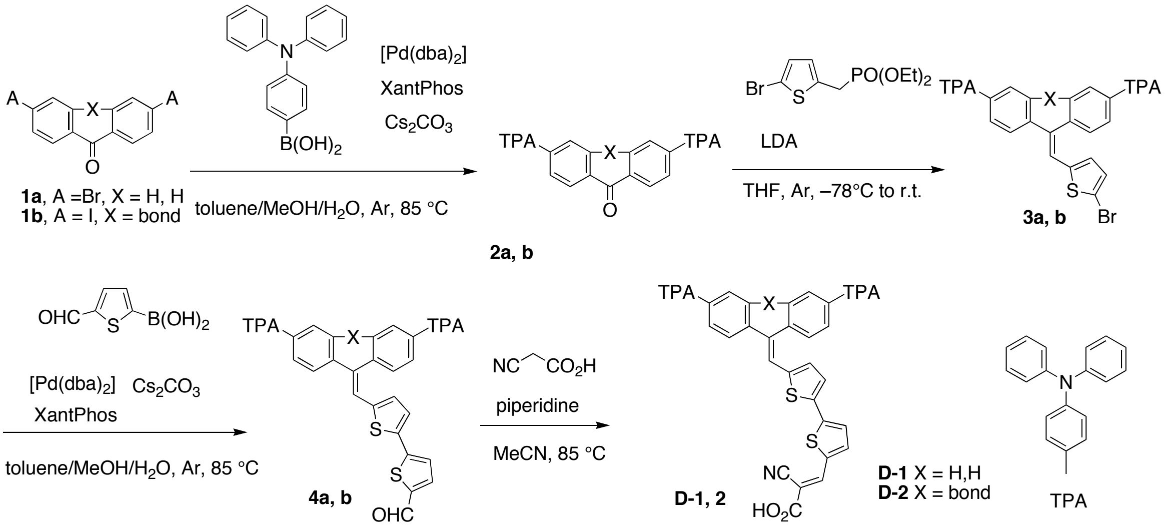
*Youhei Numata, Ashraful Islam, Han Chen, and Liyuan Han**

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-Bromothiopene-5-methylphosphoryl diethyl[1] and 2,7-Diiodofluorenone[2] 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 TiO_2 film was measured using with AC-3E Photoemission yield spectrometer (RIKEN KEIKI). The ^1H and ^{13}C NMR measurements were performed by a DRX-600 spectrometer (Bruker BioSpin).

Synthesis



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_2CO_3 (4.5 g, 13.811 mmol) in toluene (30 mL), MeOH (20 mL), and H_2O (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_2Cl_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_2Cl_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_2Cl_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_2Cl_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 $C_{49}H_{36}N_2O$: 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_2Cl_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_2Cl_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_2Cl_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_2Cl_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 $C_{54}H_{39}BrN_2S$, 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), Cs_2CO_3 (180 mg, 0.552 mmol) and 5-formyl-2-thiopheneboronic acid (58 mg, 0.370 mmol) in toluene (20 mL), MeOH (10 mL), and H_2O (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 CH_2Cl_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_2Cl_2 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, CD_2Cl_2, 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); ^{13}C NMR (150 MHz, CD_2Cl_2): 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 $C_{59}H_{42}N_2OS_2$, 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 CH_3Cl (5 mL) was stirred for 6 h at 60 °C. Resulting mixture was extracted with CH_2Cl_2 and diluted hydrochloric acid, and the organic layer was dried over with $MgSO_4$. The solvent was removed under vacuum pressure and the residual solid was purified by column chromatography with CH_2Cl_2 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-d_6, 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 CO_2H 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, 124.10, 123.21, 123.13, 123.07, 120.25; HRMS (ESI), *m*/*z*: [M – H$^+$] calcd for $C_{62}H_{42}N_3O_2S_2$, 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_2SO_4 (50 mL) was stirred for 4 h at 40 °C. 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_2Cl_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_2Cl_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_2Cl_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 $C_{49}H_{35}N_2O$, 667.2744; found: 667.2751.

5-Bromo-2-[2,7-(bis(*p*-(*N*,*N*-diphenylamino)phenyl))-(9*H*-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%). ^{1}H NMR (600 MHz, CD_2Cl_2, *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); ^{13}C NMR (150 MHz, CD_2Cl_2): 1148.08, 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 $C_{54}H_{37}BrN_2S$, 824.1861; found: 824.1884.

5-[2,7-(Bis(*p*-(*N*,*N*-diphenylamino)phenyl))-(9*H*-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%). ^{1}H NMR (600 MHz, CD_2Cl_2, *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+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); ^{13}C NMR (150 MHz, CD_2Cl_2): 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 $C_{59}H_{40}N_2OS_2$, 856.2582; found: 856.2574.

5′-(2,7-Bis(*p*-(*N*,*N*-diphenylamino)phenyl)-(9*H*-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%). ^{1}H NMR (600 MHz, DMSO-d_6, *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 CO_2H

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 $C_{62}H_{41}N_3O_2S_2$, 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_2Cl_2 solutions for **D-1** and **D-2**, respectively. 0.1 M tetra-*n*-butylammonium hexafluorophospate ($TBAPF_6$) solution in CH_2Cl_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 ware 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 TiO_2 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, 0.2mM *tert*-butylpyridine, and 0.05 mM I_2 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 cm^2 active surface area defined by a metal mask. Important tips in photovoltaic characterization are described in these literatures.[5]

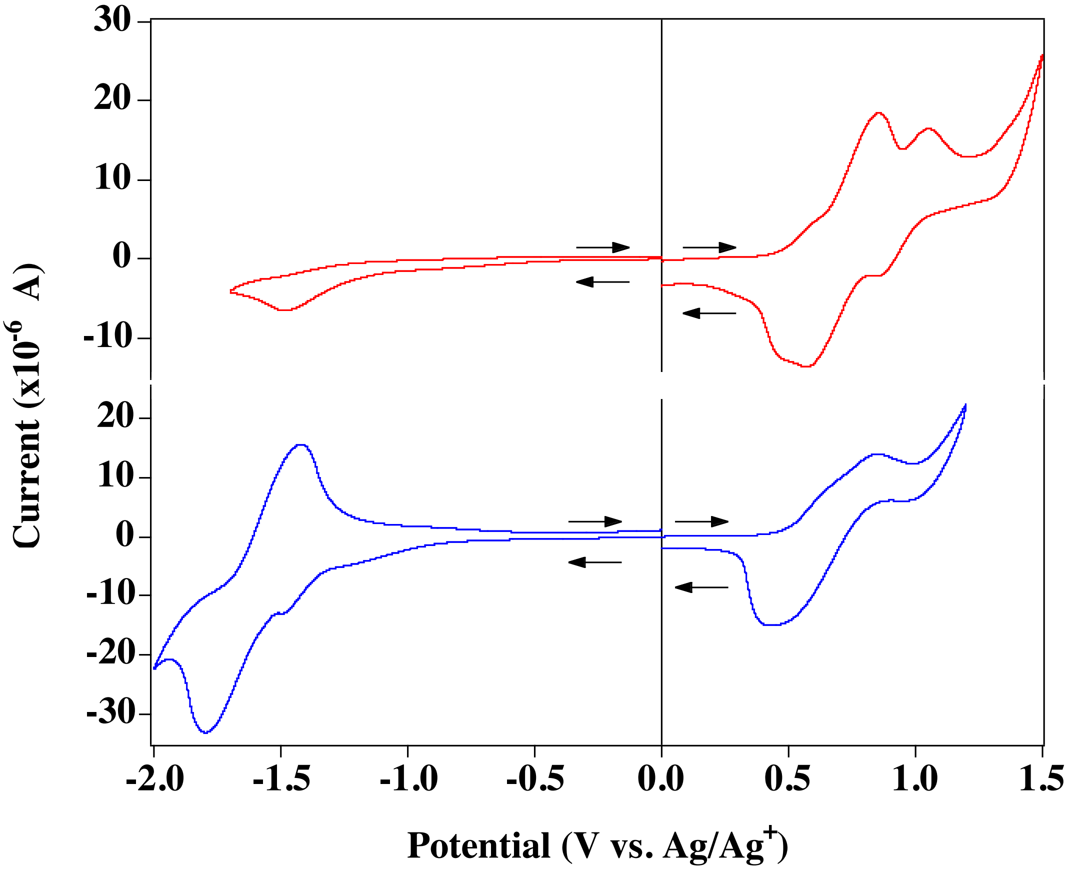


Fig. S1 Cyclic voltammograms for **D-1** (red) and **D-2** (blue). Conditions, in CH_2Cl_2 solution, reference; vs. Ag/Ag^{+}, scan rate; 50 mV/s, supporting electrolyte; 0.1 M $TBAPF_6$, and dye concentration; 0.5 and 1.0 mM for **D-1** and **D-2**, respectively.

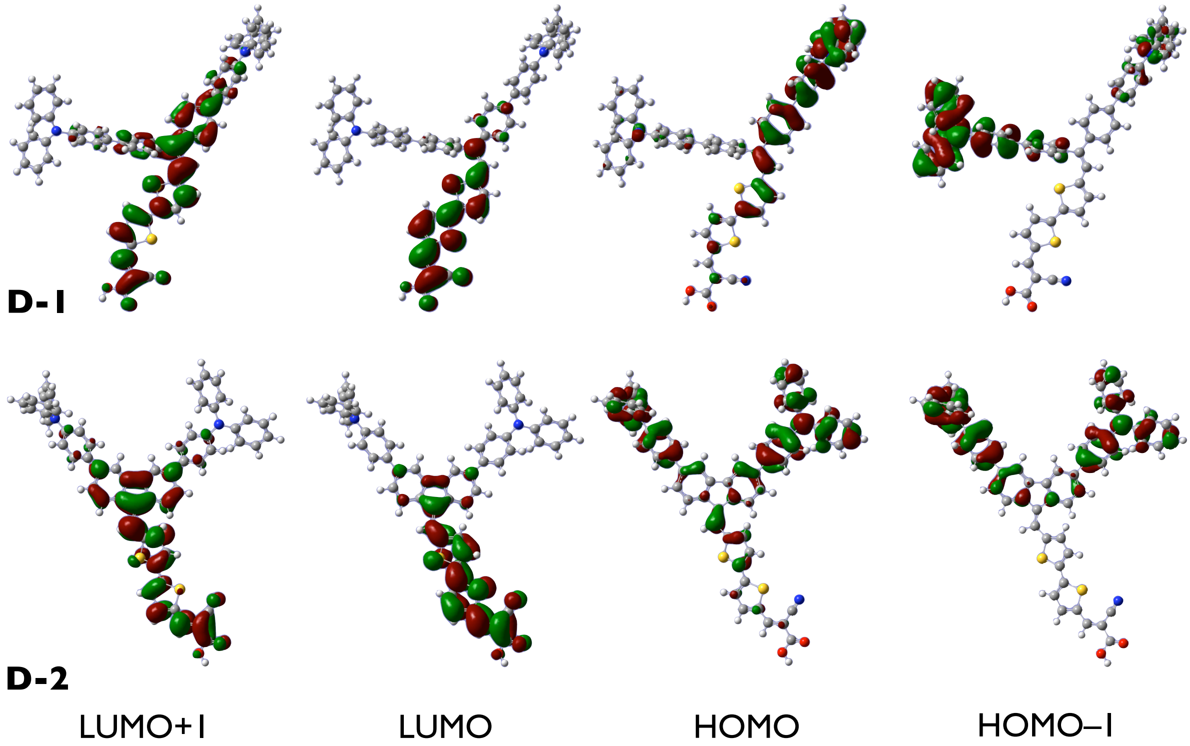


Fig. S2 Calculated frontier orbital distributions of **D-1** and **D-2**.

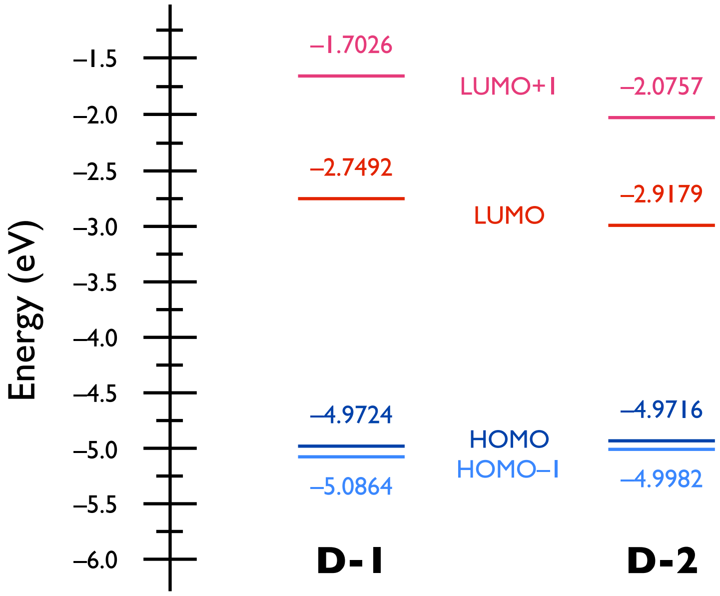


Fig. S3 Calculated energy diagrams of **D-1** and **D-2**.

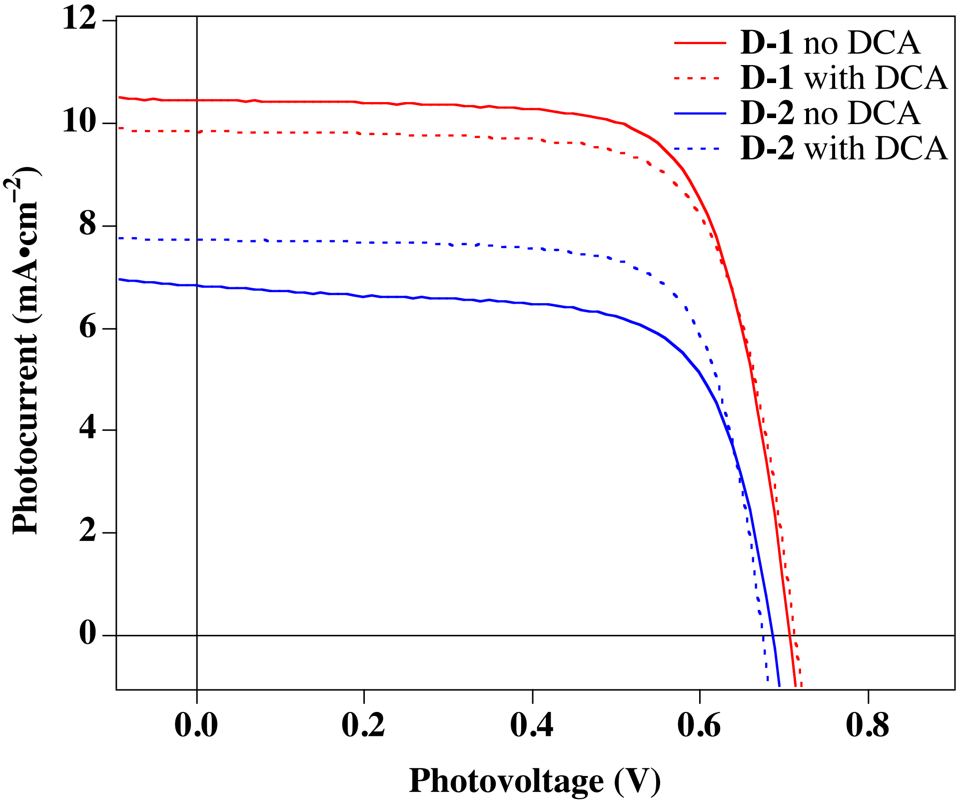


Fig. S4 *J-V* curves of **D-1** and **D-2** dyes adsorbed on TiO_2 film without or with DCA (dye: 0.3 mM and DCA: 20 mM in $CHCl_3$/MeOH 1:1 solution).

References

1 X. Jiang, X. Yang, C. Zhao, K. Jin, L. Sun, *J. Phys. Chem. Soc. C* **2007**, *111*, 9595.

2 F. Dewhurst, P. K. J. Shah, *J. Chem. Soc.* **1969**, *11*, 1503.

3 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision A.02; Gaussian, Inc.: Wallingford, CT (2009).

4 S. Gao, A. Islam, Y. Numata, L. Han, *Appl. Phys. Express* **2010**, *3*, 062301.

5 a) Y. Chiba, A. Islam, Y. Watanabe, R. Komiya, N. Koide, L. Han, *Jpn. J. Appl. Phys.* 2006, 45, L638; b) Y. Chiba, A. Islam, R. Komiya, N. Koide, L. Han, *Appl. Phys. Lett.* **2006**, *88*, 223505-1; c) N. Koide, A. Islam, Y. Chiba L. Han, *J. Photochem. Photobiol. A* **2006**, *182*, 296; d) N. Koide, Y. Chiba, L. Han, *Jpn. J. Appl. Phys.* **2005**, *44(6A)*, 4176; e) L. Han, N. Koide, Y. Chiba, A. Islam, R. Komiya, N. Fuke, A. Fukui R. Yamanaka, *Appl. Phys. Lett.* **2005**, *86*, 213501; f) N. Koide L. Han, *Rev. Sci. Instrum*. 2004, 75, 2828; g) L. Han, N. Koide, Y. Chiba, T. Mitate, *Appl. Phys. Lett.* **2004**, *84*, 2433.