Supporting Information

Spirally Configured *cis*-stilbene/Fluorene Hybrids as Bipolar, Organic Sensitizers for Solar Cell Applications

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Gerenal Procedures: ¹H NMR and ¹³C NMR spectra were recorded on Bruker AV-400 (400 MHz ¹H, 100 MHz ¹³C) spectrometers in deuterochloroform with chloroform and deuterodimethyl sulfoxide with dimethyl sulfoxide as an internal reference unless otherwise stated. Chemical shift are reported in ppm (δ). Coupling constants J are reported in Hz. High-resolution mass spectra were measured on a Finnigan MAT 95S spectrometer. Analytical TLC was performed on Merck silica gel plates with QF-254 indicator. Column (flash) chromatography was performed using 32-63 um silica gel. Absorption spectra were measured on a HP-8453 Diode Array spectrometer using spectrophotometric grade solvents. Emission spectra (10 µM) were measured on an Aminco-Bowman Series 2 luminescence spectrometer upon excitation at the absorption maxima in the same solvent. Cyclic Voltammetry (CV) measurements were carried out in 1.0 mM of substrate in anhydrous degassed solvents containing 0.1 M tetrabutylammonium hexafluorophosphate ($Bu_4N^+PF_6$) as a supporting electrolyte on a Chinstruments CH1604A potentiostat. Platinum electrode was used as a counter electrode and carbon electrode was used as a working electrode and Ag/AgCl as a reference electrode. All reagents were purchased from ACROS, ALDRICH, and TCI with purification in advance before use. Solvents for extraction and chromatography were reagent grade. Dichloromethane, methanol, acetonitrile and chloroform were dried over CaH₂ before use. THF, toluene, and 1,2-dimethoxyethane (DME) were dried over Na with benzophenone-ketyl intermediate as an indicator. All reactions The were run under argon. starting material 3,7-dibromo-5,5-spirofluorenyl-5H-dibenzo[a,d]cycloheptene (i.e., 3,7-dibromo-STIF) were prepared by following the literature procedure reported by us.¹



Figure S1. The synthesis of *N*-**STIF-TCA** dyes **1-5 3-Bormo-7**-(*N*,*N*-**diphenylamino**)-**5**,**5**-spirofluorenyl-5H-dibenzo-[a,d]cycloheptene (IIb)²



To a 25-mL, two necked, round-bottomed flask was placed **I** (500 mg, 1 mmol), Pd₂(dba)₃ (18 mg, 0.02 mmol), sodium *tert*-butoxide (144 mg, 1.5 mmol), 1,1-bis(diphenylphosphino)ferrocene (26 mg, 0.04

mmol), and diphenylamine (186 mg, 1 mmol) in toluene (10 mL). The whole reaction mixture was refluxed for 8 h and then quenched with saturated aqueous NaHCO₃ (20 mL) The aqueous layer was separated and extracted with CH₂Cl₂ (3 × 20 mL). The combined organic layers were dried (MgSO₄), filtered, and evaporated. The crude residue was purified by column chromatography (CH₂Cl₂/hexanes, 1/3) on silica gel to give **IIb**, which was further re-crystallized from CH₂Cl₂/*n*-hexanes to afford 282 mg (48 %) of pure **IIb**: mp: 256 °C (DSC); M.W.: 588.53; ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, *J* = 7.8, 2H), 7.62 (d, *J* = 7.5, 2H), 7.29-7.23 (m, 6H), 7.19-7.14 (m, 6H), 7.02-6.99 (m, 5H), 6.91-6.88 (m, 6H), 6.77 (d, *J* = 12.1, 1H), 6.52 (d, *J* = 2.2, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 151.7, 148.6, 146.9, 138.7, 135.8, 133.5, 133.2, 133.1, 131.6, 130.1, 129.7, 129.2, 127.9, 127.6, 126.9, 125.0, 123.4, 123.3, 120.1, 119.9, 65.55; FAB-MS (MALDI-TOF) 588.0 (M⁺, 56); HR-MS calcd for C₃₉H₂₆BrN: 587.1249, found: 587.1238; IR (KBr) v 3058 (w), 3019 (w), 1586 (s), 1552 (w), 1492 (s), 1447 (m), 1420 (w), 1397 (w), 1334 (m), 1266 (m), 1230 (w), 1154 (w), 1074 (w), 1028 (w); TLC *R*_f 0.40 (CH₂Cl₂/hexanes, 1/3).

3-Bormo-7-(*N*-methyl-*N*-phenylamino)-5,5-spirofluorenyl-5H-dibenzo-[a,d]cycloheptene (IIa)



Ha (45 %): m.p. 188-190 °C; M.W. 526.47; ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, J = 7.7, 2H), 7.68 (d, J = 7.6, 2H),

7.34-7.26 (m, 4H), 7.24-7.15 (m, 6H), 7.02 (t, J = 7.4, 2H), 6.91 (t, J = 7.3, 3H), 6.72 (d, J = 11.2, 2H), 6.42 (d, J = 2.2, 1H), 3.02 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) 8 152.9, 152.2, 149.4, 147.9, 142.9, 142.1, 138.8, 136.1, 133.7, 133.5, 133.2, 133.0, 131.9, 131.7, 130.1, 129.3, 129.2, 128.9, 128.7, 128.0, 127.7, 127.6, 127.4, 127.1, 126.9, 123.7, 123.4, 123.2, 122.9, 121.6, 120.2, 120.0, 118.5, 118.0, 115.6, 115.2, 65.9, 39.7; FAB-MS (MALDI-TOF) 525.1 (M⁺, 56); HR-MS cald for C₃₄H₂₄BrN: 525.1092, found: 525.1090; IR (KBr) v 3059 (w), 3026 (w), 2882 (w), 2814 (w), 1644 (w), 1604 (m), 1588 (s), 1548 (m), 1494 (s), 1479 (m), 1446 (m), 1404 (w), 1348 (s), 1302 (w), 1263 (m), 1221 (m), 1173 (w), 1112 (m), 1087 (w), 1026 (w); TLC *R*_f 0.40 (CH₂Cl₂/hexanes, 1/3)

3-Bormo-7-(*N*-phenyl-1-naphthalenamino)-5,5-spirofluorenyl-5H-dibenzo-[a,d]cycloheptene (IIc)



Hc (46 %): m.p. 244 °C (DSC); M.W. 638.59; ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 8.2, 1H), 7.72 (d, J = 8.2, 1H), 7.61 (d, J = 8.5, 1H), 7.51-7.44 (m, 5H), 7.31

(t, J = 7.7, 1H), 7.26-7.23 (m, 3H), 7.18-7.11 (m, 6H), 7.01 (d, J = 7.3, 1H), 6.96-6.91 (m, 4H), 6.90 (d, J = 2.2, 1H), 6.83 (t, J = 7.4, 2H), 6.72 (d, J = 12.2, 1H), 6.15 (d, J = 2.2, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 151.7, 148.9, 147.2, 142.8, 142.6, 142.1, 138.6, 135.9, 135.3, 133.5, 133.2, 133.1, 131.6, 130.9, 130.1, 129.1, 128.9, 128.4, 127.7, 127.3, 127.1, 126.7, 126.5, 126.4, 126.2, 126.1, 124.0, 123.2, 122.7, 121.7, 121.1, 119.9, 117.5, 65.53; HR-MS cald for C₄₃H₂₈BrN: 637.1405, found: 637.1361; IR (KBr) v 3057 (w), 3030 (w), 1588 (s), 1549 (m), 1491 (s), 1446 (m), 1389 (m), 1329 (w), 1302 (m), 1272 (m), 1222 (w), 1156 (w), 1112 (w), 1082 (w), 1017 (w); TLC *R*_f 0.38 (CH₂Cl₂/hexanes, 1/3)

3-Bormo-7-(*N*,*N*-di-2-(9,9-dimethyl)fluorenyl)-5,5-spirofluorenyl-5H-dibenzo-[a, d]cycloheptene (IId)



IId (42 %): m.p. 271-272 °C; M.W. 820.85; ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, J = 7.8, 2H), 7.67 (d, J = 7.3, 2H), 7.56-7.51 (m, 4H), 7.39 (d, J =7.4, 2H), 7.34 (t, J = 7.3, 2H), 7.30-7.25 (m, 6H), 7.21 (t, J = 7.0, 1H), 7.13-7.08 (m, 3H), 6.99-6.95 (m, 4H), 6.92-6.79 (m, 5H), 6.54 (d, J = 1.8, 1H),

1.34 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 155.0, 153.6, 152.2, 148.5, 146.7, 142.2, 141.0, 139.0, 138.8, 136.7, 134.4, 133.0, 132.0, 131.2, 130.3, 128.7, 128.0, 127.6, 127.2, 127.1, 127.0, 126.5, 124.5, 123.7, 122.5, 120.5, 120.3, 120.0, 119.4, 119.0, 66.0, 46.78, 27.0; HR-MS cald for C₅₇H₄₂BrN: 819.2501, found: 819.2512; IR (KBr) v 3059 (w), 2958 (m), 2922 (w), 2858 (w), 1591 (s), 1552 (w), 1487 (m), 1447 (s), 1311 (s), 1270 (w), 1225 (w), 1155 (w), 1086 (w), 1023 (w); TLC $R_{\rm f}$ 0.30 (CH₂Cl₂/hexanes, 1/3)

3-Bormo-7-(iminostilbenyl)-5,5-spirofluorenyl-5H-dibenzo-[a,d]cycloheptene (IIe)



He (44 %): m.p. 230-232 °C; M.W. 612.56; ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, J = 7.8, 2H), 7.61 (d, J =7.6, 2H), 7.31-7.20 (m, 9H), 7.14-7.10 (m, 3H), 7.04-6.97 (m, 3H), 6.92 (d, J = 2.0, 1H), 6.82 (d, J =

12.1, 1H), 6.68 (s, 2H), 6.63 (d, J = 12.1, 1H), 6.08 (dd, J = 11.0, 2.5, 1H), 5.97 (d, J = 2.5, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 152.7, 149.6, 142.7, 142.4, 141.6, 138.6, 136.1, 135.9, 133.8, 133.0, 131.5, 130.3, 130.1, 129.9, 129.83, 129.77, 128.9, 128.0, 127.7, 127.6, 127.4, 127.1, 127.0, 126.9, 126.7, 121.2, 119.9, 113.2, 110.8, 65.7; EI-MS (70 eV) 611.2 (M⁺, 74); HR-MS cald for C₄₁H₂₆BrN: 611.1249, found:

611.1244; IR (KBr) v 3058 (w), 3022 (w), 1643 (w), 1602 (m), 1589 (s), 1548 (m), 1502 (m), 1486 (m), 1445 (m), 1368 (w), 1331 (m), 1303 (m), 1265 (m), 1222 (w), 1160 (w), 1114 (w), 1083 (w), 1033 (w), 1006 (w); TLC *R*_f 0.36 (CH₂Cl₂/hexanes, 1/3).

cis-4-Bormo-9-(N,N-diphenylamino)stilbene (IIf)



To a 25-mL, two necked, round-bottomed flask was placed *cis*-4,4'-bis(dibromo)stilbene³ (338 mg, 1 mmol), $Pd_2(dba)_3$ (18 mg, 0.02 mmol), sodium *tert*-butoxide (144 mg, 1.5 mmol), 1,1-bis(diphenylphosphino)-

ferrocene (26 mg, 0.04 mmol), and diphenylamine (186 mg, 1 mmol) in toluene (10 mL). The whole reaction mixture was refluxed for 8 h and then quenched with saturated aqueous NaHCO₃ (20 mL) The aqueous layer was separated and extracted with CH₂Cl₂ (3×20 mL). The combined organic layers were dried (MgSO₄), filtered, and evaporated. The crude residue was purified by column chromatography (EtOAc/hexanes, 1/10) on silica gel to give **IIf**, which was further re-crystallized from CH₂Cl₂/*n*-hexanes to afford 171 mg (40 %) of pure **IIf**: mp: 55-60 °C; M.W. 426.35; ¹H NMR (400 MHz, CDCl₃) δ 7.39 (d, *J* = 8.4, 2H), 7.29-7.20 (m, 7H), 7.12 (d, *J* = 8.0, 2H), 7.06-7.01 (m, 4H), 6.97-6.94 (m, 3H), 6.56 (d, *J* = 11.6, 1H), 6.45 (d, *J* = 11.6, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 147.5, 147.4, 146.9, 146.6, 136.6, 131.4, 130.5, 130.4, 130.3, 129.7, 129.6, 129.3, 129.2, 128.5, 127.5, 124.6, 124.5, 123.1, 122.9, 122.8, 122.6, 120.7; HR-MS calcd for C₂₆H₂₀BrN: 425.0799, found: 425.0794; IR (KBr) v 3034 (w), 1590 (s), 1505 (m), 1491 (s), 1406 (w), 1325 (m), 1278 (s), 1175 (w), 1153 (w), 1107 (w), 1071 (w), 1028 (w), 1010 (w); TLC *R*_f 0.53 (EtOAc/hexanes, 1/10).

3-(*N*,*N*-Diphenylamino)-7-(2-formylthiophenyl)-5,5-spirofluorenyl-5H-dibenzo-[a ,d]cycloheptene (IIIb)^{4,5}



To a 25-mL, two necked, round-bottomed flask was placed **IIb** (600 mg, 1 mmol), PdCl₂(dppf) (22 mg, 0.03 mmol), K₂CO₃ (207 mg, 1.5

mmol), 5-formyl-2-thiopheneboronic acid (235 mg, 1.5 mmol) in methanolic toluene (toluene/MeOH = 1/1, 10 mL), The reaction mixture was refluxed for 12 h and then quenched with saturated aqueous NaHCO₃ (20 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (3 \times 20 mL). The combined organic layers were dried (MgSO₄), filtered, and evaporated. The crude residue was purified by column chromatography on silica gel (CH₂Cl₂/hexanes, 2/1) to give **IIIb**, which was further re-crystallized from CH₂Cl₂/*n*-hexanes to afford 386 mg (80 %) of pure **IIIb**: m.p. 281 °C (DSC); M.W. 619.77; ¹H NMR (400 MHz, CDCl₃) δ 9.77 (s, 1H), 7.82 (d, J = 7.8, 2H), 7.64 (d, J = 7.6, 2H), 7.56 (d, J = 4.0, 1H), 7.46 (dd, J = 9.7, 1.8, 1H), 7.37 (d, J = 8.0, 1H), 7.30 (d, J = 8.0, 1H), 7.22-7.15 (m, 6H), 7.08-6.98 (m, 5H), 6.96 (d, J)= 3.8, 2H), 6.92-6.89 (m, 5H), 6.86 (d, J = 12.1, 1H), 6.63 (d, J = 2.2, 1H); ¹³C NMR (100 MHz, CDCl₃) & 182.6, 154.2, 151.9, 148.8, 146.9, 142.0, 141.8, 138.8, 138.0, 137.3, 134.1, 133.4, 132.6, 132.0, 130.0, 129.2, 128.0, 127.5, 127.0, 126.9, 125.6, 124.7, 123.5, 123.4, 123.3, 120.2, 119.8, 65.9; HR-MS cald for C₄₄H₂₉NOS: 619.1970, found: 619.1976; IR (KBr) v 3064 (w), 3027 (w), 2795 (w), 1664 (s), 1585 (s), 1547 (w), 1492 (s), 1445 (s), 1400 (w), 1334 (m), 1267 (m), 1224 (m), 1174 (w), 1149 (w), 1060 (w), 1020 (w); TLC $R_{\rm f}$ 0.30 (CH₂Cl₂/hexanes, 1/1)

3-(*N*-Methyl-*N*-phenylamino)-**7-**(**2-**formylthiophenyl)-**5**,**5-**spirofluorenyl-**5**H-dibenzo-[a,d]cycloheptene (IIIa)



IIIa (75 %): m.p. 227-229 °C; M.W. 557.70; ¹H NMR (400 MHz, CDCl₃) δ 9.77 (s, 1H), 7.94 (d, J = 7.8, 2H), 7.69 (d, J = 7.6, 2H), 7.57 (d, J = 4.0, 1H), 7.45 (dd, J = 9.7, 1.8, 1H), 7.36-7.32 (m, 3H), 7.25-7.17 (m, 6H), 7.05 (t, J = 7.3, 1H), 6.97 (d, J = 4.0, 2H), 6.93 (d, J = 7.2, 2H), 6.80 (d, J = 12.1, 1H), 6.73 (dd, J = 10.8, 2.4, 1H), 6.51 (d, J = 2.4, 1H), 3.04 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 182.5, 154.4, 152.3, 149. 6, 147.8, 142.0, 141.9, 141.7, 138.9, 138.3, 137.4, 134.4, 133.8, 132.5, 131.7, 129.3, 128.7, 128.1, 127.7, 127.5, 127.1, 126.9, 124.7, 123.9, 123.5, 123.4, 120.2, 117.8, 115.0, 66.2, 39.6; HR-MS cald for C₃₉H₂₇NOS: 557.1813, found: 557.1802; IR (KBr) v 3058 (w), 3021 (w), 2801 (w), 1662 (s), 1603 (m), 1586 (s), 1545 (w), 1494 (s), 1445 (s), 1393 (w), 1347 (m), 1263 (w), 1224 (m), 1110 (w), 1060 (w), 1023 (w); TLC *R*_f 0.33 (CH₂Cl₂/hexanes, 1/1).

3-(*N*-Phenyl-1-naphthalenamino)-7-(2-formylthiophenyl)-5,5-spirofluorenyl-5Hdibenzo-[a,d]cycloheptene (IIIc)



IIIc (80 %): m.p. 261-262 °C; M.W. 669.83; ¹H NMR (400 MHz, CDCl₃) δ 9.75 (s, 1H), 7.91 (d, J = 8.2, 1H), 7.74 (d, J = 8.2, 1H), 7.63 (d, J = 8.5, 1H), 7.52-7.50 (m, 4H),

7.45-7.40 (m, 2H), 7.34-7.31 (m, 2H), 7.23-7.09 (m, 7H), 7.03-6.78 (m, 10H), 6.24 (d, J = 2.2, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 182.5, 154.2, 151.8, 149.1, 141.9, 137.3, 134.2, 133.4, 132.5, 129.3, 129.1, 127.7, 127.29, 127.25, 127.0, 126.7, 126.5, 126.4, 126.13, 126.06, 124.0, 123.4, 123.3, 122.8, 121.0, 119.9, 117.4, 65.8; EI-MS (70 eV) 669.4 (M⁺, 100); HR-MS cald for C₄₈H₃₁NOS: 669.2126, found: 669.2131; IR (KBr) v 3056 (w), 3019 (w), 2801 (w), 1665 (s), 1587 (s), 1548 (w), 1491 (s), 1445 (s), 1391 (m), 1305 (m), 1271 (m), 1224 (m), 1149 (w), 1107 (w), 1057 (w); TLC *R*_f 0.30 (CH₂Cl₂/hexanes, 1/1).

3-(N,N-Di-2-(9,9-dimethyl)fluorenyl)-7-(2-formylthiophenyl)-5,5-spirofluorenyl-5

H-dibenzo-[a,d]cycloheptene (IIId)



IIId (75%): m.p. 339-340 °C; M.W. 852.09; ¹H NMR (400 MHz, CDCl₃) δ 9.75 (s, 1H), 7.83 (d, J = 7.8, 2H), 7.68 (d, J = 7.2, 2H), 7.58-7.52 (m, 5H), 7.46 (dd, J = 7.9, 1.6, 1H), 7.40-7.33 (m, 5H), 7.30 (d, J = 7.4, 2H), 7.19-7.0 (m, 4H),

7.03-6.86 (m, 10H), 6.65 (d, J = 2.0, 1H), 1.34 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 182.5, 155.0, 154.1, 153.6, 151.7, 149.0, 146.5, 142.0, 141.8, 141.7, 138.9, 138.8, 138.0, 137.3, 134.7, 134.2, 133.3, 132.6, 132.1, 129.93, 129.86, 128.0, 127.4, 127.0, 126.93, 126.87, 126.6, 124.7, 124.3, 123.8, 123.5, 122.5, 120.6, 120.1, 119.4, 119.1, 65.9, 46.8, 27.0; HR-MS cald for C₆₂H₄₅NOS: 851.32229, found: 851.314; IR (KBr) v 3064 (w), 3026 (w), 2801 (w), 1663 (s), 1603 (m), 1587 (s), 1546 (w), 1494 (s), 1445 (s), 1393 (w), 1347 (m), 1264 (w), 1224 (m), 1172 (w), 1110 (w), 1059 (w), 1023 (w); TLC *R*_f 0.28 (CH₂Cl₂/hexanes, 1/1)

3-(Iminostillbenyl)-7-(2-formylthiophenyl)-5,5-spirofluorenyl-5H-dibenzo-[a,d]-cycloheptene (IIIe)



IIIe (72 %): m.p. 343-345 °C; M.W. 643.79; ¹H NMR (400 MHz, CDCl₃) δ 9.76 (s, 1H), 7.77 (d, J = 7.8, 2H), 7.63 (d, J = 7.5, 2H), 7.54 (d, J = 3.8, 2H), 7.40 (d, J = 7.8, 1H),

7.31-7.27 (m, 9H), 7.16 (s, 2H), 7.13 (s, 1H), 7.08 (t, J = 7.6, 2H), 7.02 (d, J = 8.2, 1H), 6.93 (d, J = 3.8, 1H), 6.88 (d, J = 12.1, 1H), 6.71 (s, 1H), 6.69 (s, 2H), 6.09 (s, 1H), 6.07 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 182.5, 154.5, 152.0, 149.9, 142.5, 141.8, 141.7, 141.5, 138.7, 138.4, 137.4, 135.9, 134.6, 133.3, 132.4, 131.5, 130.3, 130.1, 129.9, 129.8, 128.1, 127.8, 127.6, 127.02, 126.99, 126.8, 124.5, 123.3, 120.0,

113.3, 110.9, 66.0; EI-MS (70 eV) 643.3 (M⁺, 100); HR-MS cald for C₄₆H₂₉NOS: 643.1970, found: 643.1967; IR (KBr) v 3064 (w), 3020 (w), 2795 (w), 1663 (s), 1603 (m), 1587 (s), 1547 (m), 1503 (m), 1487 (w), 1444 (s), 1404 (w), 1325 (m), 1266 (w), 1225 (m), 1158 (w), 1114 (w), 1060 (w); TLC *R*_f 0.34 (CH₂Cl₂/hexanes, 1/1).

cis-4-(N,N-diphenylamino)-9-(2-formylthiophenyl)stilbene (IIIf)

IIIf (70%): mp: 103-106 °C; M.W. 457.58; ¹H NMR (400 MHz, CDCl₃) δ 9.89 (s, 1H), 7.73 (d, J = 4.0, 1H), 7.58 (d, J = 8.4, 2H), 7.42-7.39 (m, 2H), 7.31 (t, J = 8.4, 5H), 7.19 (d, J = 8.4, 3H), 7.14 (d, J = 8.0, 2H), 7.08 (t, J = 7.2, 3H), 6.96 (d, J = 8.8, 2H), 6.61 (d, J = 11.4, 1H), 6.52 (d, J = 11.4, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 182.6, 153.9, 147.3, 147.0, 142.0, 139.0, 137.5, 131.3, 130.9, 130.3, 129.7, 129.5, 129.2, 127.6, 127.5, 126.1, 124.6, 123.8, 123.1, 122.4; HR-MS cald for C₃₁H₂₃NOS: 457.1500, found: 457.1507; IR (KBr) v 3033 (w), 2806 (w), 2355 (w), 1664 (s), 1589 (s), 1490 (s), 1447 (s), 1325 (m), 1277 (m), 1224 (m), 1177 (w), 1114 (w), 1057 (w); TLC *R*_f 0.36 (CH₂Cl₂/hexanes, 1/2).

3-(*N*,*N*-Diphenylamino)-7-((thiophenyl-2-yl)acrylic acid)-5,5-spirofluorenyl-5H -dibenzo-[a,d]cycloheptene (Ph₂N-STIF-TCA; dye 2)⁶



To a 25-mL, one necked, round-bottomed flask was placed **IIIb** (344 mg, 0.5 mmol), cyanoacetic acid (85 mg, 1 mmol), piperidine (0.1 mL,

0.05 mmol), and molecule sieve 4Å (300 mg) in a mixed solution of CHCl₃ (5 mL) and CH₃CN (10 mL). The reaction mixture was refluxed for 24 h and then quenched with aqueous CH₃COOH (HOAc/H₂O= 1/9, 20 mL). The aqueous layer was separated and extracted with CH₂Cl₂ (3 × 20 mL). The combined organic layers were dried

(MgSO₄), filtered, and evaporated. The crude residue was purified by column chromatography (EtOAc then MeOH) on silica gel to give 262 mg (77 %) of pure **2**: m.p. 254 °C (DSC); M.W. 686.82; ¹H NMR (400 MHz, d₆-DMSO) δ 8.22 (s, 1H), 7.81 (t, *J* = 8.0, 4H), 7.74 (d, *J* = 3.7, 1H), 7.63 (d, *J* = 7.3, 1H), 7.50 (d, *J* = 8.1, 1H), 7.35-7.21 (m, 8H), 7.12-7.02 (m, 6H), 6.94-6.87 (m, 5H), 6.76 (dd, *J* = 6.5, 1.8, 1H), 6.65 (s, 1H); ¹³C NMR (100 MHz, d₆-DMSO) δ 151.0, 148.0, 146.0, 141.1, 140.9, 138.1, 137.5, 135.3, 133.8, 133.7, 132.8, 131.6, 129.6, 129.4, 129.2, 128.2, 127.7, 126.5, 125.7, 125.0, 124.5, 124.1, 123.9, 121.1, 120.5, 118.6, 65.3; HR-MS cald for C₄₇H₃₀N₂O₂S: 686.2028, found: 686.2064; IR (KBr) v 3058 (w), 3021 (w), 2207 (w), 1692 (br), 1585 (s), 1492 (s), 1442 (m), 1367 (w), 1335 (w), 1321 (w), 1267 (w), 1223 (w), 1088 (w); TLC *R*_f 0.20 (EtOAc)

3-(*N*-Methyl-*N*-phenylamino)-7-((thiophenyl-2-yl)acrylic acid)-5,5-spirofluorenyl -5H-dibenzo-[a,d]cycloheptene (MePhN-STIF-TCA; dye 1)



1 (73 %): m.p. 224 °C (DSC); M.W. 624.75;
¹H NMR (400 MHz, d₆-DMSO) δ 8.06 (s,
1H), 7.88 (d, J = 7.6, 2H), 7.82 (d, J = 7.4,
2H), 7.62-7.58 (m, 2H), 7.48 (d, J = 8.0, 1H),

7.38-7.31 (m, 3H), 7.26-7.15 (m, 5H), 7.05-6.99 (m, 3H), 6.95 (d, J = 7.7, 2H), 6.88-6.80 (m, 2H), 6.51 (s, 1H), 3.04 (s, 3H); ¹³C NMR (100 MHz, d₆-DMSO) δ 163.4, 151.4, 149.0, 146.9, 141.1, 140.8, 138.1, 137.9, 134.7, 134.2, 134.0, 132.7, 131.1, 129.3, 128.9, 128.2, 127.6, 127.2, 126.5, 125.9, 124.5, 124.1, 123.3, 120.5, 116.9, 114.6, 65.5; HR-MS cald for C₄₂H₂₈N₂O₂S: 624.1871, found: 624.1883; IR (KBr) v 3075 (w), 3025 (w), 2212 (w), 1695 (br), 1585 (s), 1494 (s), 1437 (m), 1415 (w), 1348 (m), 1266 (w), 1223 (m), 1130 (w), 1108 (w), 1062 (w); TLC *R*_f 0.20 (EtOAc)



3 (78 %): m.p. 233 °C (DSC); M.W. 736.88; ¹H NMR (400 MHz, d₆-DMSO) δ 8.91 (s, 1H), 8.07 (s, 1H), 8.04 (d, *J* = 8.3, 1H), 7.88 (d, *J* =

8.2, 1H), 7.71 (d, *J* = 7.6, 2H), 7.65 (d, *J* = 3.8,

1H), 7.58-7.42 (m, 6H), 7.34 (d, J = 8.4, 2H), 7.24 (q, J = 7.3, 4H), 7.15-7.11 (m, 2H), 6.99-6.91 (m, 8H), 6.75 (dd, J = 8.4, 1.9, 1H), 6.38 (s, 1H); ¹³C NMR (100 MHz, d₆-DMSO) δ 150.9, 148.5, 141.6, 141.0, 137.9, 137.3, 134.9, 132.7, 129.4, 128.6, 128.4, 127.9, 127.4, 127.2, 127.1, 126.5, 126.4, 126.2, 126.1, 123.2, 123.0, 120.3, 116.4, 65.2; HR-MS cald for C₅₁H₃₂N₂O₂S: 736.2184, found: 736.2202; IR (KBr) v 3053 (w), 3021 (w), 2218 (w), 1694 (br), 1584 (s), 1492 (m), 1438 (m), 1390 (m), 1337 (m), 1297 (m), 1270 (m), 1216 (w), 1155 (w), 1076 (w), 1051 (w), 1023 (w); TLC *R*_f 0.20 (EtOAc)

3-(*N*,*N*-Di-2-(9,9-dimethyl)fluorenyl)-7-((thiophenyl-2-yl)acrylic acid)-5,5-spirofluorenyl-5H-dibenzo-[a,d]cycloheptene (Fl₂N-STIF-TCA; dye 4)



4 (77 %): m.p. 239 °C (DSC); M.W. 919.14; ¹H NMR (400 MHz, H d₆-DMSO) δ 8.22 (s, 1H), 7.80-7.65 (m, 11H), 7.53-7.48 (m, 3H), 7.42 (d, *J* = 8.5, 1H), 7.36 (t, *J* = 7.4, 2H), 7.30 (t, *J* = 7.3, 2H),

7.24 (d, *J* = 3.7, 1H), 7.16-7.06 (m, 2H), 7.03 (s, 2H), 7.01-6.91 (m, 8H), 6.63 (s, 1H), 1.29 (s, 12H); ¹³C NMR (100 MHz, d₆-DMSO) δ 154.8, 153.2, 150.8, 148.5, 145.6, 141.1, 140.8, 138.2, 138.1, 137.6, 134.5, 131.5, 129.4, 128.0, 127.4, 127.0, 126.8, 126.5, 124.2, 123.9, 122.6, 121.2, 120.5, 119.6, 119.1, 65.3, 46.3, 26.5; HR-MS cald for C₆₅H₄₆N₂O₂S: 918.3280, found: 918.3387; IR (KBr) v 3058 (w), 3023 (w), 2957 (w), 2207 (w), 1686 (br), 1583 (s), 1487 (m), 1446 (s), 1303 (m), 1269 (m), 1224 (m), 1092 (w), 1085 (w), 1023 (w), 1006 (w); TLC *R*_f 0.20 (EtOAc).

3-(Iminostilbenyl)-7-((thiophenyl-2-yl)acrylic acid)-5,5-spirofluorenyl-5H-dibenzo [a,d]cycloheptene (IMS-STIF-TCA; dye 5)



5 (72 %): m.p. 306 °C (DSC); M.W. 710.84; ¹H NMR (400 MHz, d₆-DMSO) δ 8.28 (s, 1H), 7.78-7.76 (m, 3H), 7.71 (d, *J* = 7.6,

2H), 7.62 (d, J = 7.7, 1H), 7.45-7.30 (m, 10H), 7.23-7.21 (m, 3H), 7.14-7.12 (m, 3H), 7.03 (s, 1H), 6.93 (d, J = 12.1, 1H), 6.80-6.78 (m, 3H), 6.03-6.00 (m, 2H); ¹³C NMR (100 MHz, d₆-DMSO) δ 163.5, 151.2, 150.9, 149.5, 141.6, 140.9, 140.8, 138.0, 135.3, 134.8, 134.1, 133.4, 132.5, 131.0, 130.2, 130.1, 130.0, 129.3, 128.0, 127.8, 127.6, 127.2, 126.6, 126.2, 125.8, 124.4, 124.1, 120.3, 116.8, 110.3, 65.4; HR-MS cald for C₄₉H₃₀N₂O₂S: 710.2028, found: 711.2131; IR (KBr) v 3032 (w), 3019 (w), 2851 (w), 2207 (w), 1683 (br), 1586 (s), 1487 (m), 1437 (m), 1384 (w), 1331 (w), 1278 (w), 1267 (w), 1223 (w), 1085 (w), 1072 (w); TLC *R*_f 0.20 (EtOAc)

cis-4-(N,N-Diphenylamino)-9-((thiophenyl-2-yl)acrylic acid)stilbene

(cis-Ph₂N-ST-TCA, dye 2')



6 (73 %): mp: 143-146 °C; M.W. 524.63; ¹H NMR (400 MHz, d₆-DMSO) δ 8.32 (s, 1H), 7.85 (d, *J* = 3.2, 1H), 7.72-7.62 (m, 3H), 7.36 (d, *J* = 8.0, 2H), 7.31 (t, *J* = 8.0,

5H), 7.15 (d, *J* = 8.4, 2H), 7.06-6.91 (m, 6H), 6.80 (d, *J* = 8.4, 2H), 6.59 (d, *J* = 11.4, 1H), 6.52 (d, *J* = 11.4, 1H); ¹³C NMR (100 MHz, d₆-DMSO) δ 164.0, 150.4, 147.0, 146.9, 146.6, 143.9, 139.0, 138.4, 138.1, 135.2, 131.2, 130.9, 130.5, 130.3, 129.7,

S14

129.6, 129.4, 129.1, 127.9, 127.1, 126.3, 125.9, 124.8, 124.3, 123.4, 122.7, 122.2, 117.8; HR-MS cald for $C_{34}H_{24}N_2O_2S$: 524.1588, found: 524.1596; IR (KBr) v 3019 (w), 2356 (w), 2218 (w), 1672 (br), 1584 (s), 1505 (m), 1490 (s), 1419 (m), 1325 (m), 1280 (m), 1222 (m), 1110 (w), 1064 (w), 1032 (w); TLC R_f 0.20 (EtOAc).

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Electrode preparation and device fabrication

The photoanodes composed of nanocrystalline TiO₂ were prepared using the sol-gel method reported elsewhere. A paste composed of about 25-nm TiO₂ particles for the transparent nanocrystalline layer was coated on a TiCl₄-treated FTO glass substrate (FTO, 8 Ω/\Box) to obtain the required thickness by repetitive screen printing. To improve the performance of DSSC, one additional scattering layer (particle size 200-600 nm) was screen-printed on the transparent nanocrystalline layer. The TiO2 working electrodes were gradually heated according to a programmed procedure: (1) heating at 80 °C for 15 min; (2) heating at 135 °C for 10 min; (3) heating at 325 °C for 30 min; (4) heating at 375 °C for 5 min; (5) heating at 450 °C for 15 min; (6) heating at 500 °C for 15 min. The resulting layer was composed of 12 µm thickness of transparent layer and 4 µm thickness of scattering layer, which were treated again by TiCl₄ at 70 °C for 30 min and sintered at 500 °C for 30 min. After cooling in air, the sintered TiO₂ films were immersed in dye solutions (for six different organic dyes: 0.3 mM in anhydrous THF at 25 °C for 8 h; containing chenodeoxycholic acid 0.6 mM for dye loading onto the working electrodes). The counter electrode was made by spin-coating the H₂PtCl₆/isopropanol solution onto an FTO glass substrate (FTO, 8 Ω/\Box) (typical size 1.0 × 1.5 cm²) through thermal decomposition at 380 °C for 30 min. The two electrodes were assembled into a cell of sandwich type and sealed with a hot-melt film (SX1170, thickness 25 µm). The electrolyte solution for devices

contains LiI (0.1 M), I_2 (0.05 M), 1-methyl 3-propyl imidazolium iodide (PMII; 0.6 M) and 4-*tert*-butylpyridine (0.5 M) in a solvent mixture containing acetonitrile and valeronitrile (volume ratio, 85:15)

Dye-loading examination

To determine the dye-loading (DL) amount of the **N-STIF-TCA** dyes on TiO_2 films, each dye was desorbed in tetrabutylammonium hydroxide (0.1 M, TBAOH, Fluka) in methanol (2 mL). The absorption spectrum of the solution was recorded with a UV-vis spectrometer (Varian, Cary 50). A calibration curve for **N-STIF-TCA** in 0.1 M TBAOH in MeOH was derived to obtain the absorption coefficient shown in Figure S2. The amounts of dye coverage on TiO_2 films shown in Figure S1 were obtained from the measured absorbances in the spectra (cuvette thickness 2 mm) and the calibrated absorption coefficient of **N-STIF-TCA** according to Beers' law.



Figure S2: Absorption spectra of dye loading examination for dyes 1-5 and 2'.

Photovoltaic characterization. The current-voltage characteristics were determined with a digital source meter (Keithley 2400, computer-controlled) with the device under one-sun AM 1.5 G irradiation from a solar simulator (SAN-EI, XES-502S) calibrated with a standard silicon reference cell (VLSI standards, Oriel PN 91150V). When the device is irradiated with the solar simulator, the source meter sends a voltage (V) to the device, and the photocurrent (I) is read at each step controlled with a computer via a GPIB interface. The efficiency (η) of conversion of light to electricity is obtained with these relations, $\eta = J_{sc} V_{oc} FF / P_{in}$, in which $J_{sc} (mA cm^{-2})$ is the current density measured at short circuit, and V_{oc} (V) is the voltage measured at open circuit. P_{in} is the input radiation power (for one-sun illumination $P_{in} = 100 \text{ mW}$ cm⁻²) and FF is the fill factor. For all measurements, the DSSC devices were covered with a black mask of aperture area 0.16 cm^2 to ensure the measured photocurrent not being exaggerated. The spectra of the incident photons-to-current conversion efficiency (IPCE) of the corresponding devices were obtained with a system comprising a Xe lamp (PTi A-1010, 150 W), a monochromator (Dongwoo DM150i, 1200 gr/mm blazed at 500 nm), and a source meter (Keithley 2400). A standard Si photodiode (ThorLabs FDS1010) served as a reference to calibrate the power density of the light source at each wavelength. Both photocurrent densities of the target device and the reference Si cell were measured under the same experimental conditions (excitation beam size $\sim 0.08 \text{ cm}^2$) so to obtain the efficiency of the device from a comparison of the current ratio and the value of the reference cell at each wavelength.



Figure S3. (left) Chem Draw and (right) Chem 3D presentations of the X-ray crystal structure for Ph₂N-STIF-FCA which bears a furan spacer conjugated with α -cyano-acrylonitrile as the electron acceptor. The dihedral angel is 22.1° between C=C and flanking phenyl groups in the confined *cis*-stilbene core.

ORTEP drawing (ellipsoids are shown at 30% probability level) and selected crystal data for the X-ray crystal structure of Ph₂N-STIF-FCA (1 H₂O molecule is present in the asymmetric unit and was removed by SQEEZE⁷ program refinement)

The SQUEEZE process removed the contributions of some 143.9 electrons from the reflection file. This then corresponds with 143.9/4 = 36.0 electrons per asymmetric unit, or some 36.0/18 = 2 molecules of H₂O per asymmetric unit. Since there are two independent molecules of Ph₂N-STIF-FCA in the asymmetric unit, the overall correct formulation for this complex would be Ph₂N-STIF-FCA • 1.0 (H₂O).

Crystal data for Ph₂N-STIF-FCA-H₂O (CCDC 871304): C₄₇H₃₁N₃O₂, M_r = 669.75, triclinic, space group P-1, a = 12.7199(3) Å, b = 18.3611(4) Å, c = 19.7203(5) Å, a =63.081(1), β= 84.443(1), γ =74.863(1), V = 3963.0(15) Å³, Z = 4, ρ_{calcd} = 1.123 Mgm⁻³, T = 200(2)K, Bruker Kappa CCD diffractometer, Mo ka radiation (λ = 0.71073), μ = 0.069 mm⁻¹. The structure was solved by SHELXL-86 (Sheldrick, 1986) Solver. All non-hydrogen atoms were refined anisotropically (SHELXS-97; Sheldrick, 1997). Final block-diagonal matrix least-square refinement on F² with all 13945 reflections and 919 variables converged to *R*1 ($I > 2\sigma(I)$) = 0.0583, *w*R2 (all data) = 0.1605, and GOF = 0.841.





¹H and¹³C NMR spectra of **Ha**



¹H and¹³C NMR spectra of **IIb**



¹H and¹³C NMR spectra of **IIc**



¹H and¹³C NMR spectra of **IId**

mqq

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H spectrum of

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¹H and¹³C NMR spectra of **He**



¹H and¹³C NMR spectra of **IIf**



¹H and¹³C NMR spectra of **IIIa**



¹H and¹³C NMR spectra of **IIIb**

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¹H and¹³C NMR spectra of **IIIc**



¹H and¹³C NMR spectra of **IIId**



¹H and¹³C NMR spectra of **IIIe**



H and¹³C NMR spectra of **IIIf**

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¹H and ¹³C NMR spectra of **MePhN-STIF-TCA** (dye 1)

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 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of $\mathbf{Ph_2N}\textbf{-STIF}\textbf{-TCA}$ (dye 2)

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¹H and ¹³C NMR spectra of NpPhN-STIF-TCA (dye 3)

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¹H and ¹³C NMR spectra of **Fl₂N-STIF-TCA** (dye 4)

S32

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¹H and¹³C NMR spectra of **IMS-STIF-TCA** (dye 5)



¹H and ¹³C NMR spectra of *cis*-Ph₂N-STB-TCA (dye 2')