

## Supplementary Information

### Dye-sensitized solar cells based on functionally separated D- $\pi$ -A fluorescent dye with aldehyde as electron-accepting group

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#### Experimental Section:

**General:** Melting points were measured with a Yanaco micro melting point apparatus MP model. IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer by ATR method. High-resolution mass spectral data were acquired on a Thermo Fisher Scientific LTQ Orbitrap XL. <sup>1</sup>H NMR spectra were recorded on a Varian-400 (400 MHz) or Varian-500 (500 MHz) FT NMR spectrometer. Absorption spectra were observed with a Hitachi U-2910 spectrophotometer and fluorescence spectra were measured with a HORIBA FluoroMax-4 spectrofluorometer. The fluorescence quantum yields in solution were determined by a Hamamatsu C9920-01 equipped with CCD by using a calibrated integrating sphere system ( $\lambda_{\text{ex}} = 384 \text{ nm}$  for both **YJY-1** and **YJY-2**). Cyclic voltammetry (CV) curves were recorded in acetonitrile/ $\text{Bu}_4\text{NClO}_4$  (0.1M) solution with a three-electrode system consisting of  $\text{Ag}/\text{Ag}^+$  as reference electrode, Pt plate as working electrode, and Pt wire as counter electrode by using a AMETEK Versa STAT 4 potentiostat. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of **YJY-1** and **YJY-2** were evaluated from the spectral analyses and the CV data. The HOMO energy level was evaluated from the  $E_{1/2}^{\text{ox}}$ . The LUMO energy level was estimated from the  $E_{1/2}^{\text{ox}}$  and an intersection of absorption and fluorescence spectra (429 nm; 2.89 eV for both **YJY-1** and **YJY-2**), which correspond to the energy gap between the HOMO and the LUMO.

**Preparation of 4''-bromo-3'-nitro-[1,1':4',1''-terphenyl]-4-carbaldehyde (1):** To a mixture of 4,4'-dibromo-2-nitro-biphenyl (5.0 g, 14.0 mmol), 4-formylphenylboronic acid (2.1 g, 14.0 mmol), and  $\text{Pd}(\text{PPh}_3)_4$  (1.13 g, 0.98 mmol) under an argon atmosphere was added aqueous 1M  $\text{Na}_2\text{CO}_3$  (12.4 mL) and DMF (60 ml) and stirred for 18 h at 100 °C. After concentrating

under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The organic extract was dried over MgSO<sub>4</sub>, filtrated, and concentrated. The residue was chromatographed on silica gel (dichloromethane–hexane = 2 : 1 as eluent) to give **1** (3.47 g, yield 65 %) as a light yellow solid; M.p. 176–177 °C; IR (ATR):  $\nu_{\square}$  = 1694, 1517, 1346 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, acetone-d<sub>6</sub>)  $\delta$  = 7.41 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 1H), 8.08–4.12 (m, 4H), 8.19 (dd, *J* = 2.0 and 8.0 Hz, 1H), 8.36 (d, *J* = 2.0 Hz, 1H), 10.15 (s, -CHO) ppm; <sup>13</sup>C NMR (125 MHz, acetone-d<sub>6</sub>)  $\delta$  = 123.10, 123.60, 128.69, 130.80, 131.07, 131.96, 132.71, 133.43, 135.10, 137.18, 137.41, 141.26, 144.32, 192.52 ppm (one aromatic carbon signal was not observed owing to overlapping resonances); HRMS (APCI): *m/z* (%):[M+H<sup>+</sup>] calcd for C<sub>19</sub>H<sub>13</sub>NO<sub>3</sub>Br, 382.00733; found 382.00729.

**Preparation of 2-(4''-bromo-3'-nitro-[1,1':4',1''-terphenyl]-4-yl)-1,3-dioxolane (2):** A solution of **1** (5.54 g, 14.50 mmol), ethylene glycol (2.02 ml, 36.26 mmol), and *p*-toluenesulfonic acid monohydrate (2 mg) in toluene (30 mL) was refluxed by using Dean-Stark apparatus under an argon atmosphere. After 16 h, the reaction mixture was washed with 10% NaOH aq. and extracted with dichloromethane. The organic extract was dried over MgSO<sub>4</sub>, filtrated, and concentrated. The residue was compound **2** (5.94 g, yield 96 %) as a light green solid; M.p. 183–186 °C; IR (ATR):  $\nu_{\square}$  = 1533, 1355, 1083 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>)  $\delta$  = 4.02–4.16 (m, 4H), 5.84 (s, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.66–7.71 (m, 3H), 7.86 (d, *J* = 8.4 Hz, 2H), 8.10 (dd, *J* = 2.0 and 8.0 Hz, 1H), 8.26 (d, *J* = 2.0 Hz, 1H) ppm; <sup>13</sup>C NMR (125 MHz, acetone-d<sub>6</sub>)  $\delta$  = 65.98, 103.89, 122.94, 123.14, 127.76, 128.35, 130.82, 131.62, 132.66, 133.25, 134.25, 137.39, 139.45, 140.13 ppm (two aromatic carbon signals were not observed owing to overlapping resonances); HRMS (APCI): *m/z* (%):[M+H<sup>+</sup>] calcd for C<sub>21</sub>H<sub>17</sub>NO<sub>4</sub>Br, 426.03355; found 426.03400.

**Preparation of 4''-(1,3-dioxolan-2-yl)-2'-nitro-*N,N*-diphenyl-[1,1':4',1''-terphenyl]-4-amine (3):** To a mixture of **2** (5.88 g, 13.70 mmol), diphenylamine (4.67 g, 27.57 mmol), and Pd(OAc)<sub>2</sub> (0.15 g, 0.69 mmol), and *t*-BuONa (1.66 g, 17.23 mmol) under an argon atmosphere was added (*t*-Bu)<sub>3</sub>P (1M in toluene, 1.38 ml, 1.38 mmol) and toluene (200 ml) and stirred for 4 h at 100 °C. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The organic extract was dried over MgSO<sub>4</sub>, filtrated, and concentrated. The residue was chromatographed on silica gel (dichloromethane–hexane = 1 : 1 as eluent) to give **3** (6.37 g, yield 90 %) as an orange powder; M.p. 72–73 °C; IR (ATR):  $\nu_{\square}$  = 1588, 1519, 1481, 1271 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, acetone-d<sub>6</sub>)  $\delta$  = 4.02–4.15 (m, 4H),

5.83 (s, 1H), 7.08 (d,  $J = 8.5$  Hz, 2H), 7.09–7.14 (m, 6H), 7.32 (d,  $J = 8.5$  Hz, 2H), 7.34–7.38 (m, 4H), 7.63 (d,  $J = 8.5$  Hz, 2H), 7.68 (d,  $J = 8.0$  Hz, 1H), 7.84 (d,  $J = 8.5$  Hz, 2H), 8.05 (dd,  $J = 2.0$  and 8.0 Hz, 1H), 8.18 (d,  $J = 2.0$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR (125 MHz, acetone- $d_6$ )  $\delta = 66.05, 104.00, 122.99, 123.34, 124.57, 125.84, 127.76, 128.40, 129.79, 130.48, 131.13, 131.32, 133.21, 134.93, 139.70, 140.03, 141.42, 148.34, 149.09$  ppm (one aromatic carbon signal was not observed owing to overlapping resonances); HRMS (APCI):  $m/z$  (%): $[\text{M}+\text{H}^+]$  calcd for  $\text{C}_{33}\text{H}_{27}\text{N}_2\text{O}_4$ , 515.19653; found 515.19635.

**Preparation of 7-(4-(1,3-dioxolan-2-yl)phenyl)-*N,N*-diphenyl-9*H*-carbazol-2-amine (4):**

To a mixture of **3** (6.28 g, 12.21 mmol) and  $\text{PPh}_3$  (8.0 g, 30.52 mmol) under an argon atmosphere was added *o*-dichlorobenzene (110 ml) and stirred for 26 h at 160 °C. After concentrating under reduced pressure, the residue was chromatographed on silica gel (dichloromethane–hexane = 2 : 1 as eluent) to give **4** (3.73 g, yield 63 %) as a light yellow solid; M.p. 246–248 °C; IR (ATR):  $\nu_{\square} = 3383, 1593, 1489, 1327, 1244$   $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ )  $\delta = 4.01\text{--}4.14$  (m, 4H), 5.81 (s, 1H), 6.95 (dd,  $J = 2.0$  and 8.5 Hz, 1H), 7.01–7.06 (m, 2H), 7.09–7.14 (m, 4H), 7.17 (d,  $J = 2.0$  Hz, 1H), 7.28–7.32 (m, 4H), 7.50 (dd,  $J = 1.5$  and 8.0 Hz, 1H), 7.57 (d,  $J = 8.0$  Hz, 2H), 7.74–7.76 (m, 3H), 8.04 (d,  $J = 8.5$  Hz, 1H), 8.12 (d,  $J = 8.0$  Hz, 1H), 10.25 (s, -NH) ppm;  $^{13}\text{C}$  NMR (125 MHz, acetone- $d_6$ )  $\delta = 65.95, 104.27, 107.71, 109.89, 117.92, 119.42, 119.82, 120.83, 121.74, 123.46, 123.60, 124.80, 127.77, 128.05, 130.15, 138.27, 138.54, 142.07, 142.69, 143.54, 147.29, 149.32$  ppm; HRMS (APCI):  $m/z$  (%): $[\text{M}+\text{H}^+]$  calcd for  $\text{C}_{33}\text{H}_{27}\text{N}_2\text{O}_2$ , 483.20670; found 483.20654.

**Preparation of ethyl 7-(2-(4-(1,3-dioxolan-2-yl)phenyl)-7-(diphenylamino)-9*H*-carbazol-9-yl)heptanoate (5):**

A solution of **4** (1.00 g, 2.07 mmol) in DMF (50 ml) was treated with sodium hydride (60%, 0.15 g, 6.22 mmol) and stirred for 1 h at room temperature. Ethyl 7-bromoheptanoate (2.02 ml, 10.367 mmol) was added dropwise over 30 min and the solution was stirred at room temperature for 5 h. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The organic extract was dried over  $\text{MgSO}_4$ , filtrated, and then concentrated to afford the compound **5** in quantitative yield; IR (ATR):  $\nu_{\square} = 1728, 1594, 1489, 1459$   $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, acetone- $d_6$ )  $\delta = 1.16$  (t,  $J = 7.1$  Hz, 3H), 1.28–1.38 (m, 4H), 1.46–1.54 (m, 2H), 1.79–1.87 (m, 2H), 2.20 (t,  $J = 7.4$  Hz, 2H), 4.00–4.15 (m, 6H), 4.38 (t,  $J = 7.0$  Hz, 2H), 5.81 (s, 1H), 6.93 (dd,  $J = 1.8$  and 8.4 Hz, 1H), 7.02–7.06 (m, 2H), 7.10–7.14 (m, 4H), 7.26 (d,  $J = 1.8$  Hz, 1H), 7.28–7.33 (m, 4H), 7.52 (dd,  $J = 1.5$  and 8.1 Hz, 1H), 7.57 (d,  $J = 8.2$  Hz, 2H), 7.79–7.82 (m, 3H), 8.06 (d,  $J = 8.4$  Hz, 1H), 8.14 (d,  $J = 8.1$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR (100 MHz, acetone- $d_6$ )  $\delta = 14.52, 25.41, 27.40,$

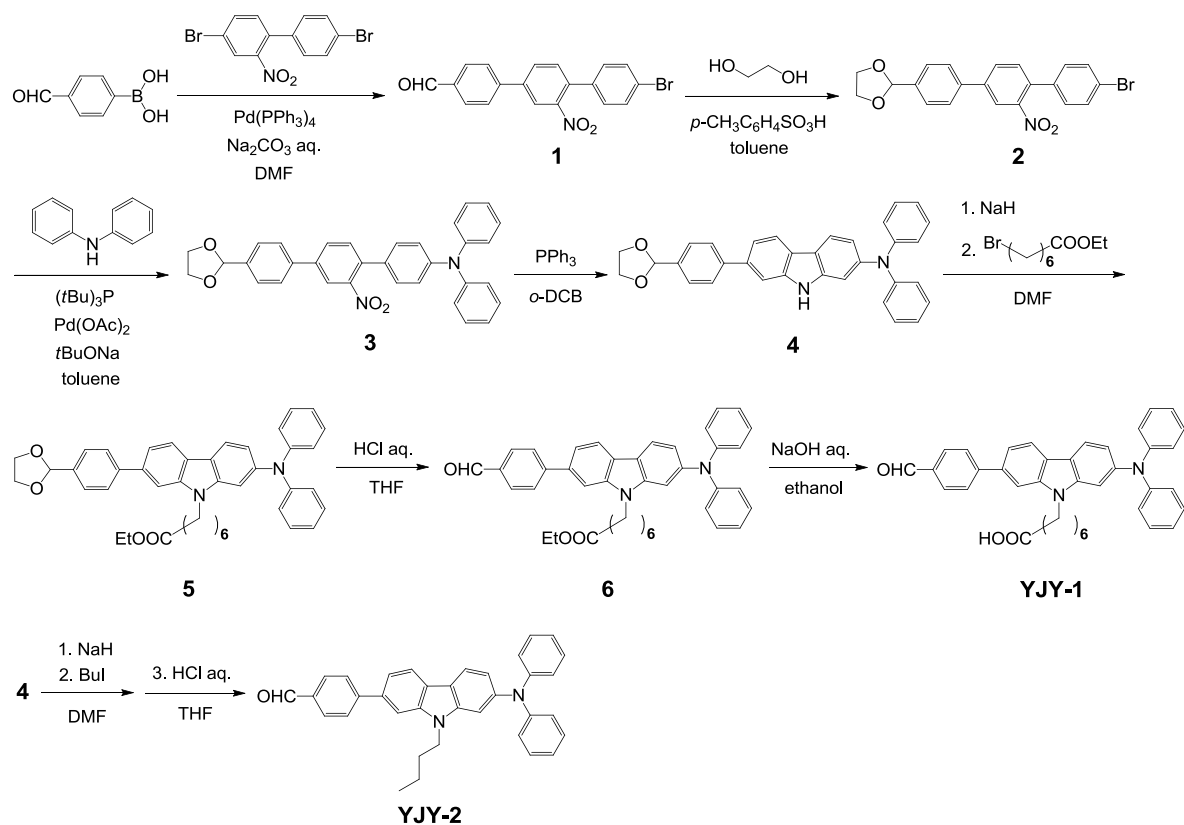
28.80, 33.36, 34.41, 43.11, 60.37, 65.89, 104.19, 106.17, 108.14, 117.86, 119.27, 119.41, 120.89, 121.87, 123.15, 123.38, 124.57, 127.89, 127.97, 130.10, 138.24, 138.57, 142.40, 143.06, 143.50, 147.20, 149.18, 173.50 ppm; HRMS (ESI):  $m/z$  (%): $[M+Na^+]$  calcd for  $C_{42}H_{42}N_2O_4Na$ , 661.30368; found 661.30457.

**Preparation of ethyl 7-(2-(diphenylamino)-7-(4-formylphenyl)-9H-carbazol-9-yl)heptanoate (6):** To a compound **5** (1.32 g, 2.07 mmol) under an argon atmosphere was added THF (20 ml) and 3N HCl (25ml), and refluxed for 1 h. The reaction mixture was cooled to room temperature, washed with water, and extracted with dichloromethane. The organic extract was dried over  $MgSO_4$ , filtrated, and then concentrated to afford the compound **6** in quantitative yield; IR (ATR):  $\nu_{\square} = 1723, 1697, 1598, 1492\text{ cm}^{-1}$ ;  $^1H$  NMR (400 MHz, acetone- $d_6$ )  $\delta = 1.16$  (t,  $J = 7.2$  Hz, 3H), 1.28–1.37 (m, 4H), 1.44–1.53 (m, 2H), 1.79–1.89 (m, 2H), 2.19 (t,  $J = 7.4$  Hz, 2H), 4.00–4.06 (q, 2H), 4.39 (t,  $J = 7.0$  Hz, 2H), 6.94 (dd,  $J = 1.9$  and 8.4 Hz, 1H), 7.03–7.07 (m, 2H), 7.11–7.15 (m, 4H), 7.26 (d,  $J = 1.9$  Hz, 1H), 7.29–7.34 (m, 4H), 7.60 (dd,  $J = 1.5$  and 8.1 Hz, 1H), 7.95 (d,  $J = 1.5$  Hz, 1H), 8.01–8.05 (m, 4H), 8.08 (d,  $J = 8.4$  Hz, 1H), 8.18 (d,  $J = 8.1$  Hz, 1H), 10.10 (s, -CHO) ppm;  $^{13}C$  NMR (100 MHz, acetone- $d_6$ )  $\delta = 14.51, 25.39, 27.38, 27.41, 33.36, 34.39, 43.12, 60.37, 105.97, 108.53, 117.85, 119.12, 119.40, 121.06, 122.07, 123.51, 123.97, 124.70, 128.65, 130.13, 130.83, 136.15, 137.26, 142.34, 143.26, 147.57, 148.55, 149.11, 173.49, 192.49$  ppm; HRMS (ESI):  $m/z$  (%): $[M+Na^+]$  calcd for  $C_{40}H_{38}N_2O_3Na$ , 617.27746; found 617.27814.

**Preparation of 7-(2-(diphenylamino)-7-(4-formylphenyl)-9H-carbazol-9-yl)heptanoic acid (YJY-1):** To a solution of **6** (1.23 g, 2.07 mmol) in ethanol (300 ml) was added dropwise aqueous NaOH (0.40 g, 10 mmol, 100 mL) with stirring at 75 °C. After further stirring for 10 h under reflux, the solution was acidified to pH 4 with 2M HCl, and concentrated under reduced pressure. The residue was dissolved in dichloromethane, and washed with water. The organic extract was concentrated under reduced pressure. The resulting residue was subjected to reprecipitation from dichloromethane–hexane to give **YJY-1** (0.94 g, yield 80 %) as a yellow powder; M.p. 180–181 °C; IR (ATR):  $\nu_{\square} = 1714, 1697, 1598, 1492\text{ cm}^{-1}$ ;  $^1H$  NMR (500 MHz, acetone- $d_6$ )  $\delta = 1.31$ –1.34 (m, 4H), 1.48–1.54 (m, 2H), 1.82–1.86 (m, 2H), 2.22 (t,  $J = 7.5$  Hz, 2H), 4.40 (t,  $J = 7.0$  Hz, 2H), 6.95 (dd,  $J = 2.0$  and 8.5 Hz, 1H), 7.04–7.07 (m, 2H), 7.12–7.15 (m, 4H), 7.27 (d,  $J = 2.0$  Hz, 1H), 7.30–7.34 (m, 4H), 7.61 (dd,  $J = 1.5$  and 8.0 Hz, 1H), 7.96 (d,  $J = 1.5$  Hz, 1H), 8.02–8.06 (m, 4H), 8.08 (d,  $J = 8.5$  Hz, 1H), 8.18 (d,  $J = 8.0$  Hz, 1H), 10.10 (s, -CHO) ppm;  $^{13}C$  NMR (125 MHz, acetone- $d_6$ )  $\delta = 25.45, 27.51, 29.46, 29.51, 34.04, 43.20, 106.02, 108.59, 117.89, 119.17, 119.45, 121.11, 122.12, 123.58, 124.03, 124.77,$

128.71, 130.19, 130.90, 136.21, 137.32, 142.40, 143.32, 147.64, 148.61, 149.17, 174.59, 192.56 ppm; HRMS (APCI):  $m/z$  (%): $[M+H^+]$  calcd for  $C_{38}H_{35}N_2O_3$ , 567.26422; found 567.26379.

**Preparation of 4-(9-butyl-7-(diphenylamino)-9H-carbazol-2-yl)benzaldehyde (YJY-2):** A solution of **4** (0.26g, 0.54 mmol) in DMF (30 ml) was treated with sodium hydride (60%, 0.04 g, 1.63 mmol) and stirred for 3 h at room temperature under an argon atmosphere. 1-iodobutane (0.31 ml, 2.72 mmol) was added dropwise over 30 min and the solution was stirred at room temperature for 10 h. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The organic extract was dried over  $MgSO_4$ , filtrated, and concentrated. Next, to a solution of the residue in THF (20 ml) was added 3N HCl (6 ml), and refluxed for 1 h at room temperature. The reaction mixture was washed with water, and extracted with dichloromethane. The organic extract was dried over  $MgSO_4$ , filtrated, and then concentrated. The residue was chromatographed on silica gel (dichloromethane as eluent) to give **YJY-2** (0.24 g, yield 91 %) as a yellow powder; M.p. 187–189 °C; IR (ATR):  $\nu_{\square}$  = 1694, 1596, 1492  $cm^{-1}$ ;  $^1H$  NMR (400 MHz, acetone- $d_6$ )  $\delta$  = 0.86 (t,  $J$  = 7.4 Hz, 3H), 1.26–1.34 (m, 2H), 1.75–1.84 (m, 2H), 4.39 (t,  $J$  = 7.0 Hz, 2H), 6.95 (dd,  $J$  = 1.7 and 8.4 Hz, 1H), 7.03–7.08 (m, 2H), 7.11–7.14 (m, 4H), 7.25 (d,  $J$  = 1.7 Hz, 1H), 7.28–7.34 (m, 4H), 7.61 (dd,  $J$  = 1.2 and 8.1 Hz, 1H), 7.95 (d,  $J$  = 1.2 Hz, 1H), 8.02–8.07 (m, 4H), 8.09 (d,  $J$  = 8.4 Hz, 1H), 8.19 (d,  $J$  = 8.1 Hz, 1H), 10.10 (s, -CHO) ppm;  $^{13}C$  NMR (100 MHz, acetone- $d_6$ )  $\delta$  = 14.11, 20.95, 31.83, 42.99, 105.93, 108.53, 117.81, 119.11, 119.38, 121.05, 122.06, 123.52, 123.96, 124.72, 128.64, 130.11, 130.85, 136.17, 137.25, 142.36, 143.24, 147.57, 148.57, 149.10, 192.51 ppm; HRMS (ESI):  $m/z$  (%): $[M+Na^+]$  calcd for  $C_{35}H_{30}N_2ONa$ , 517.22503; found 517.22467.



**Scheme S1.** Synthesis of D- $\pi$ -A fluorescent dye sensitizers **YJY-1** and **YJY-2**.