

## *Supporting information*

### **Effects of the structural optimization on the performance of dye-sensitized solar cells: spirobifluorene as a promising building-block to enhance $V_{oc}$**

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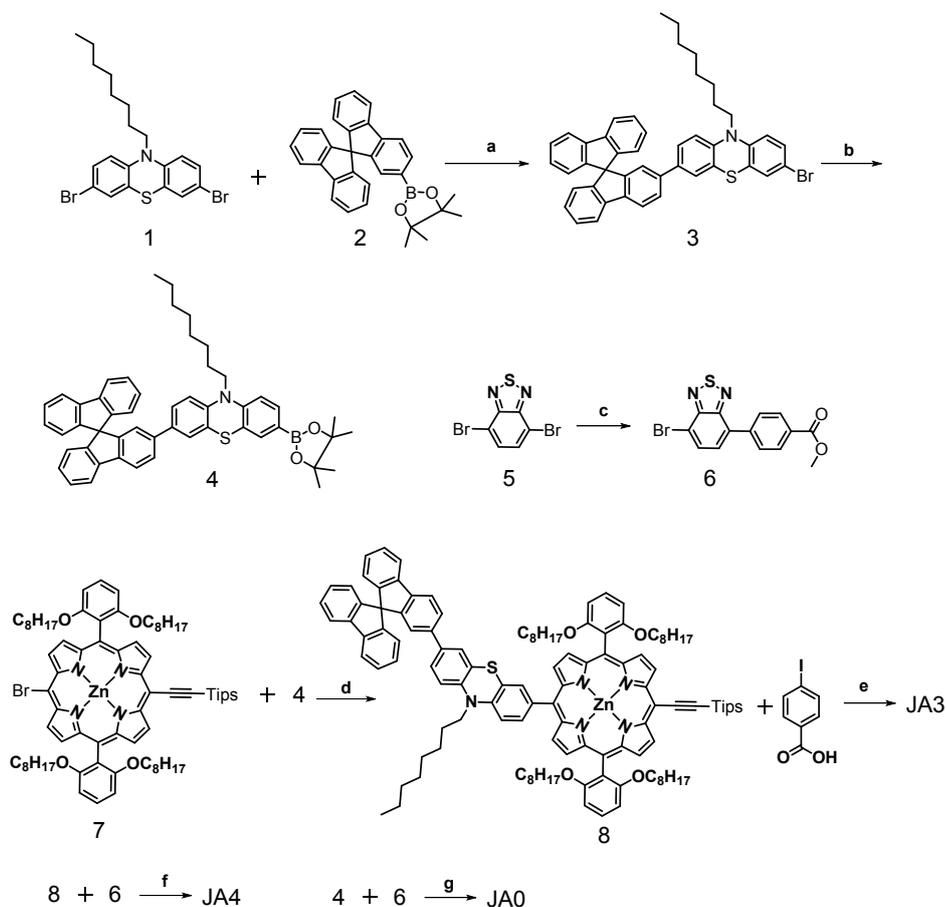
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## **General information**

All solvents were treated by standard methods before use and all chemicals were purchased from commercial suppliers and used without further purification unless indicated otherwise. *N, N*-Dimethylformamide (DMF) and tetrahydrofuran (THF) were dried and distilled from CaH<sub>2</sub>.

The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker DRX (300, 400 MHz) NMR spectrometer with tetramethylsilane (TMS) as the internal standard. The mass spectra were measured in ESI Mass Spectrometer (LCQ Fleet).

## Synthesis of the dyes



**Scheme S1** synthesis procedure of **JA3**, **JA4** and **JA0**. Reagents and conditions: a) Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>O, 1, 4-dioxane, 90°C; b) bis(pinacolato)diboron, Pd(dppf)Cl<sub>2</sub>, KOAc, DMF, 80°C; c) Methyl 4-boronobenzoate, Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>O, 1, 4-dioxane, 90°C; d) Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>O, 1, 4-dioxane, 90°C; e) i: TBAF, THF; ii: Pd<sub>2</sub>(dba)<sub>3</sub>, AsPh<sub>3</sub>, Et<sub>3</sub>N, THF, reflux; f) i: TBAF, THF; ii: Pd<sub>2</sub>(dba)<sub>3</sub>, AsPh<sub>3</sub>, Et<sub>3</sub>N, THF, reflux; iii: EtOH, H<sub>2</sub>O, NaOH; g) i: Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>O, 1, 4-dioxane, 90°C; ii: EtOH, H<sub>2</sub>O, NaOH.

### Synthesis of compound 3

Under an nitrogen, compound **5** (8 g, 17 mmol), compound **2** (7.5 g, 17 mmol),  $K_2CO_3$  (7.1 g, 51 mmol) and  $Pd(PPh_3)_4$  (0.98 g, 0.85 mmol) were dissolved in 1, 4-dioxane (100 mL) and  $H_2O$  (20 mL). The mixture was heated under  $90^\circ C$  for overnight. The reaction mixture was cooled to room temperature and extracted by EtOAc ( $3 \times 100$  mL). The combined organic layers were washed with brine, dried over  $MgSO_4$ , and evaporated in vacuo. The residue was purified by silica gel column chromatography (PE/EA=10/1) to give the compound **3** (4 g, 33%).  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta_H$  7.83-7.86 (m, 4H), 7.52-7.54 (m, 1H), 7.38 (t,  $J = 7.6$ Hz, 3H), 7.14-7.19 (m, 4H), 7.07-7.12 (m, 3H), 6.85 (s, 1H), 6.70-6.78 (m, 4H), 6.62 (d,  $J = 8$ Hz, 1H), 3.72 (s, 2H), 1.67-1.74 (m, 2H), 1.23-1.37 (m, 10H), 0.84 (t,  $J = 7.2$ Hz, 3H). MS (ESI): Calcd for  $C_{45}H_{38}BrNS$ , 703.19; found, 703.75.

### Synthesis of compound 4

A mixture of compound **3** (2.5 g, 3.55 mmol), bis(pinacolato)diboron (1.35 g, 5.32 mmol) and KOAc (1.04 g, 10.64 mmol) in DMF (40 mL) was added  $Pd(dppf)Cl_2$  (0.29 g, 0.35 mmol) under dinitrogen. The mixture was heated under  $80^\circ C$  for overnight. The reaction mixture was cooled to room temperature and  $H_2O$  (150 mL) was added, the mixture was extracted by EtOAc ( $3 \times 50$  mL). The combined organic layers were washed with brine, dried over  $MgSO_4$ , and evaporated in vacuo. The residue was purified by silica gel column chromatography (PE/EA=10/1) to give the compound **4** (2 g, 75%).  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta_H$  7.84-7.90 (m, 4H), 7.47-7.59 (m, 2H), 7.40 (t,  $J = 6.9$ Hz, 2H), 7.10-7.20 (m, 4H), 6.92-7.06 (m, 3H), 6.89 (s, 1H), 6.73-6.83 (m, 5H), 3.81 (t,  $J = 6.3$ Hz, 2H), 1.74-1.78 (m, 2H), 1.26-1.46 (m, 22H), 0.85-0.91 (m, 3H). MS (ESI): Calcd for  $C_{51}H_{50}BNO_2S$ , 751.36; found, 752.42.

### Synthesis of compound 6

Under an nitrogen, compound **5** (5 g, 17 mmol), Methyl 4-boronobenzoate (3.1 g,

17 mmol),  $K_2CO_3$  (7.1 g, 51 mmol) and  $Pd(PPh_3)_4$  (0.98 g, 0.85 mmol) were dissolved in 1, 4-dioxane (100 mL) and  $H_2O$  (20 mL). The mixture was heated under  $90^\circ C$  for overnight. The reaction mixture was cooled to room temperature and extracted by EtOAc ( $3 \times 50$  mL). The combined organic layers were washed with brine, dried over  $MgSO_4$ , and evaporated in vacuo. The residue was purified by silica gel column chromatography (PE/EA=4/1) to give the compound **6** (2 g, 34%).  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta_H$  8.19 (d,  $J = 8.4$ Hz, 2H), 7.94-7.99 (m, 3H), 7.64 (d,  $J = 7.6$  Hz, 1H), 3.97 (s, 3H).

### Synthesis of compound **8**

Under an nitrogen, compound **4** (1 g, 1.33 mmol), compound **7** (1.21 g, 0.93 mmol)<sup>[S1]</sup>,  $K_2CO_3$  (0.55 g, 3.99 mmol) and  $Pd(PPh_3)_4$  (0.15 g, 0.13 mmol) were dissolved in 1, 4-dioxane (50 mL) and  $H_2O$  (10 mL). The mixture was heated under  $90^\circ C$  for overnight. The reaction mixture was cooled to room temperature and extracted by  $CH_2Cl_2$  ( $3 \times 20$  mL). The combined organic layers were washed with brine, dried over  $MgSO_4$ , and evaporated in vacuo. The residue was purified by silica gel column chromatography (PE/DCM=4/1) to give the compound **8** as a green solid (1.9 g, 78%).  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta_H$  9.63 (d,  $J = 4.8$ Hz, 2H), 8.84 (d,  $J = 4.8$ Hz, 2H), 8.74 (d,  $J = 4.8$ Hz, 2H), 8.70 (d,  $J = 4.8$ Hz, 2H), 7.74-7.80 (m, 6H), 7.61 (t,  $J = 8.4$ Hz, 2H), 7.50 (d,  $J = 6.8$ Hz, 1H), 7.19-7.28 (m, 5H), 7.12 (s, 1H), 7.01 (t,  $J = 7.2$ Hz, 4H), 6.83-6.89 (m, 5H), 6.70 (d,  $J = 7.2$ Hz, 2H), 6.62 (d,  $J = 7.6$ Hz, 1H), 3.94 (s, 2H), 3.72 (s, 8H), 1.90 (s, 2H), 1.44-1.49 (m, 2H), 1.12-1.38 (m, 29H), 0.78-0.86 (m, 11H), 0.63-0.69 (m, 8H), 0.29-0.51 (m, 44H). MS (ESI): Calcd for  $C_{120}H_{141}N_5O_4SSiZn$ , 1840.97; found, 1841.75.

### Synthesis of JA3

To a solution of compound **8** (500 mg, 0.27 mmol) in anhydrous THF (20 mL) was added TBAF (0.6 mL, 1 M in THF). The solution was stirred at room temperature for 30 min under dinitrogen. The mixture was quenched with  $H_2O$  and then extracted

with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried over anhydrous MgSO<sub>4</sub> and the solvent was removed under reduced pressure. The residue and 4-iodobenzoic acid (270 mg, 1.09 mmol) were dissolved in a mixture of anhydrous THF (50 mL) and Et<sub>3</sub>N (12 mL) under dinitrogen, then Pd<sub>2</sub>(dba)<sub>3</sub> (75 mg, 0.081 mmol) and AsPh<sub>3</sub> (166 mg, 0.542 mmol) were added to the mixture. The solution was refluxed for 6 h. The solvent was removed under reduced pressure and was purified by silica gel column chromatography (DCM/MeOH=20/1), then recrystallization from MeOH/Ether to give dye **JA3** as a green solid (230 mg, 47%). <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, 300 MHz) δ<sub>H</sub> 9.69 (d, *J* = 4.5 Hz, 2H), 8.81 (d, *J* = 4.5 Hz, 2H), 8.65-8.69 (m, 4H), 8.37 (d, *J* = 7.8 Hz, 2H), 7.98-8.02 (m, 2H), 7.85-7.91 (m, 6H), 7.66 (t, *J* = 8.7 Hz, 3H), 7.23-7.37 (m, 6H), 7.02-7.11 (m, 8H), 6.92 (s, 1H), 6.70 (d, *J* = 6.5 Hz, 2H), 6.63 (d, *J* = 7.8 Hz, 1H), 4.11 (t, *J* = 6.6 Hz, 2H), 3.85 (s, 8H), 1.94-2.02 (m, 2H), 1.54-1.63 (m, 2H), 1.30-1.46 (m, 8H), 0.87-0.97 (m, 18H), 0.75-0.82 (m, 8H), 0.57-0.67 (m, 37H). <sup>13</sup>C NMR (THF-*d*<sub>8</sub>, 75 MHz) δ<sub>C</sub> 161.24, 152.87, 151.97, 151.28, 150.74, 150.30, 149.96, 145.51, 143.03, 142.66, 141.97, 141.04, 139.49, 139.23, 136.30, 134.49, 133.82, 132.59, 131.83, 131.65, 131.49, 131.28, 131.11, 130.60, 129.81, 128.74, 127.68, 127.16, 126.48, 126.20, 124.99, 123.90, 123.40, 122.73, 122.34, 122.02, 121.39, 121.01, 120.02, 116.70, 115.15, 114.02, 106.58, 105.66, 104.65, 98.78, 96.09, 95.93, 69.14, 48.48, 32.97, 32.63, 30.48, 29.94, 29.87, 28.04, 23.73, 23.40, 14.66, 14.51. MS (ESI): Calcd for C<sub>118</sub>H<sub>125</sub>N<sub>5</sub>O<sub>6</sub>SZn, 1804.86; found, 1803.83.

### Synthesis of **JA4**

To a solution of compound **8** (500 mg, 0.27 mmol) in anhydrous THF (20 mL) was added TBAF (0.6 mL, 1 M in THF). The solution was stirred at room temperature for 30 min under dinitrogen. The mixture was quenched with H<sub>2</sub>O and then extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried over anhydrous MgSO<sub>4</sub> and the solvent was removed under reduced pressure. The residue and compound **6** (284 mg, 0.81 mmol) were dissolved in a mixture of anhydrous THF (50 mL) and Et<sub>3</sub>N (12 mL) under dinitrogen, then Pd<sub>2</sub>(dba)<sub>3</sub> (75 mg, 0.081 mmol) and AsPh<sub>3</sub> (166 mg, 0.542 mmol) were added to the mixture. The solution was refluxed for 6 h. The solvent was

removed under reduced pressure and was purified by silica gel column chromatography (PE/DCM=4/1), then the residue was added in EtOH (10 mL), THF (20 mL) and H<sub>2</sub>O (30 mL), and then added NaOH (0.29 g, 7.31 mmol). The mixture was heated under 90°C for overnight. The reaction mixture was cooled to room temperature and the solvent was evaporated, the residue was acidified with diluted HCl, then filtered and recrystallization from MeOH/Ether to give dye **JA4** as a brown solid (200 mg, 38%). <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, 300 MHz) δ<sub>H</sub> 10.07 (d, *J* = 4.5Hz, 2H), 8.83-8.91 (m, 2H), 8.73-8.80 (m, 2H), 8.62-8.67 (m, 2H), 8.52 (d, *J* = 4.5Hz, 1H), 8.37-8.39 (m, 1H), 8.28-8.33 (m, 2H), 8.21 (d, *J* = 8.1Hz, 2H), 8.11-8.16 (m, 2H), 8.03 (d, *J* = 8.1Hz, 1H), 7.87-7.96 (m, 4H), 7.79-7.84 (m, 3H), 7.63-7.73 (m, 3H), 7.33-7.38 (m, 3H), 7.04-7.13 (m, 8H), 6.73-6.76 (m, 2H), 6.68 (d, *J* = 7.5Hz, 1H), 4.54 (s, 2H), 3.88 (s, 8H), 2.13-2.20 (m, 2H), 1.47-1.51 (m, 2H), 1.30-1.40 (m, 8H), 0.85-0.92 (m, 26H), 0.51-0.72 (m, 37H). <sup>13</sup>C NMR (THF-*d*<sub>8</sub>, 75 MHz) δ<sub>C</sub> 161.27, 157.46, 154.51, 153.42, 152.39, 152.17, 151.58, 151.49, 150.93, 150.38, 149.91, 143.08, 142.57, 142.32, 140.44, 138.80, 138.70, 138.29, 136.91, 135.29, 133.06, 131.80, 130.83, 130.15, 129.82, 128.77, 128.08, 127.67, 127.46, 125.71, 125.03, 122.95, 122.16, 121.62, 121.07, 117.49, 115.92, 114.81, 106.76, 105.67, 104.64, 97.84, 92.84, 69.16, 48.70, 32.99, 32.62, 30.52, 29.89, 27.78, 26.45, 23.73, 23.40, 14.66, 14.46. MS (ESI): Calcd for C<sub>124</sub>H<sub>127</sub>N<sub>7</sub>O<sub>6</sub>S<sub>2</sub>Zn, 1938.86; found, 1938.33.

### Synthesis of JA0

Under an nitrogen, compound **4** (0.5 g, 0.67 mmol), compound **6** (0.18 g, 0.53 mmol), K<sub>2</sub>CO<sub>3</sub> (0.28 g, 2.0 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (77 mg, 0.07 mmol) were dissolved in 1, 4-dioxane (20 mL) and H<sub>2</sub>O (10 mL). The mixture was heated under 90°C for overnight. The reaction mixture was cooled to room temperature and extracted by CH<sub>2</sub>Cl<sub>2</sub> (3×20 mL). The combined organic layers were washed with brine, dried over MgSO<sub>4</sub>, and evaporated in vacuo, the residue was purified by silica gel column chromatography (PE/CH<sub>2</sub>Cl<sub>2</sub> = 4/1). After evaporated in vacuo, then the residue was added in EtOH (10 mL), THF (20 mL) and H<sub>2</sub>O (30 mL), and then added NaOH (0.27

g, 6.65 mmol). The mixture was heated under 90°C for overnight. The reaction mixture was cooled to room temperature and the solvent was evaporated, the residue was acidified with diluted HCl, then filtered and recrystallization from MeOH/Ether to give dye **JA0** as a red solid (320 mg, 54%). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz) δ<sub>H</sub> 13.16 (s, 1H), 8.01-8.12 (m, 8H), 7.92 (d, *J* = 7.6Hz, 1H), 7.84 (d, *J* = 7.2Hz, 1H), 7.77-7.79 (m, 1H), 7.73 (d, *J* = 2.0Hz, 1H), 7.62-7.67 (m, 1H), 7.37-7.42 (m, 3H), 7.09-7.18 (m, 5H), 7.03 (d, *J* = 8.8Hz, 1H), 6.84-6.88 (m, 1H), 6.78 (s, 1H), 6.63-6.68 (m, 2H), 6.60 (d, *J* = 7.6Hz, 1H), 3.79 (s, 2H), 1.58-1.63 (m, 2H), 1.26-1.31 (m, 2H), 1.05-1.21 (m, 8H), 0.74 (t, *J* = 6.8Hz, 3H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 75 MHz) δ<sub>C</sub> 167.63, 153.47, 149.36, 148.87, 148.48, 144.68, 143.52, 141.65, 141.18, 140.72, 138.91, 134.24, 131.80, 130.88, 129.77, 129.36, 128.30, 127.22, 124.92, 123.84, 120.90, 65.84, 46.84, 31.39, 30.76, 28.92, 28.80, 26.36, 22.33, 14.20. MS (ESI): Calcd for C<sub>58</sub>H<sub>45</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub>, 879.29; found, 879.17.

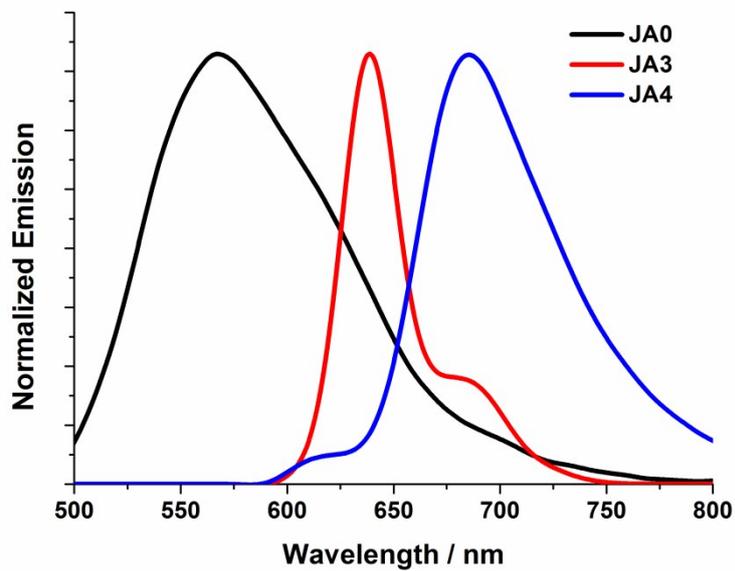


Fig. S1 Emission spectra of JA0, JA3 and JA4 in THF.

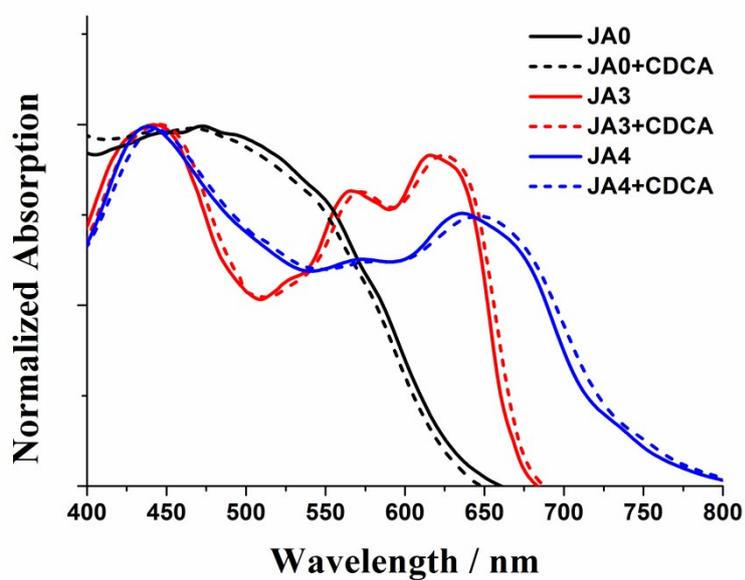
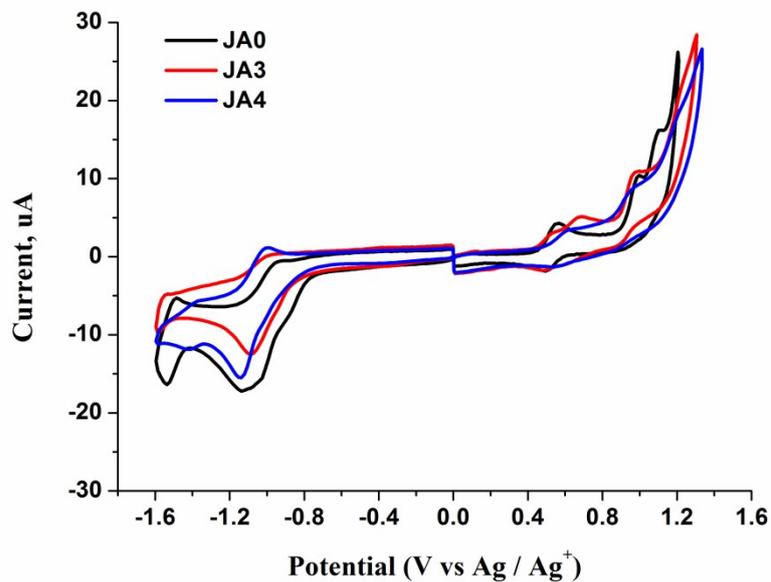
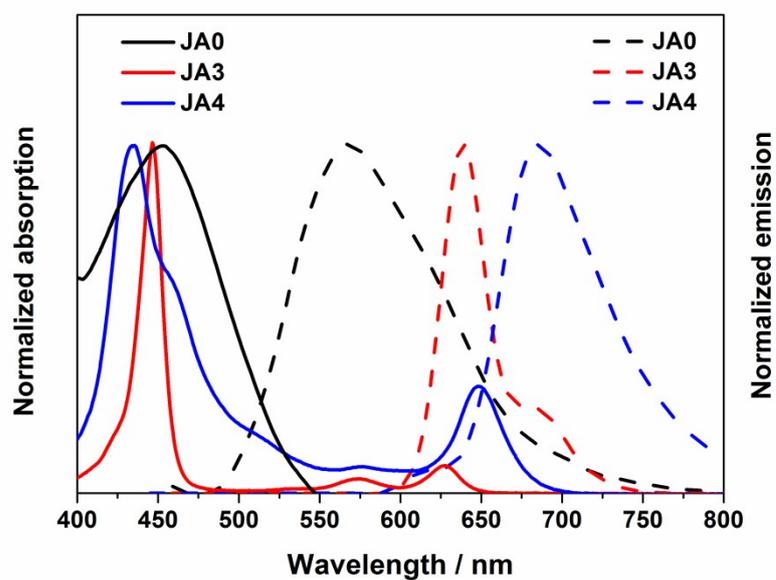


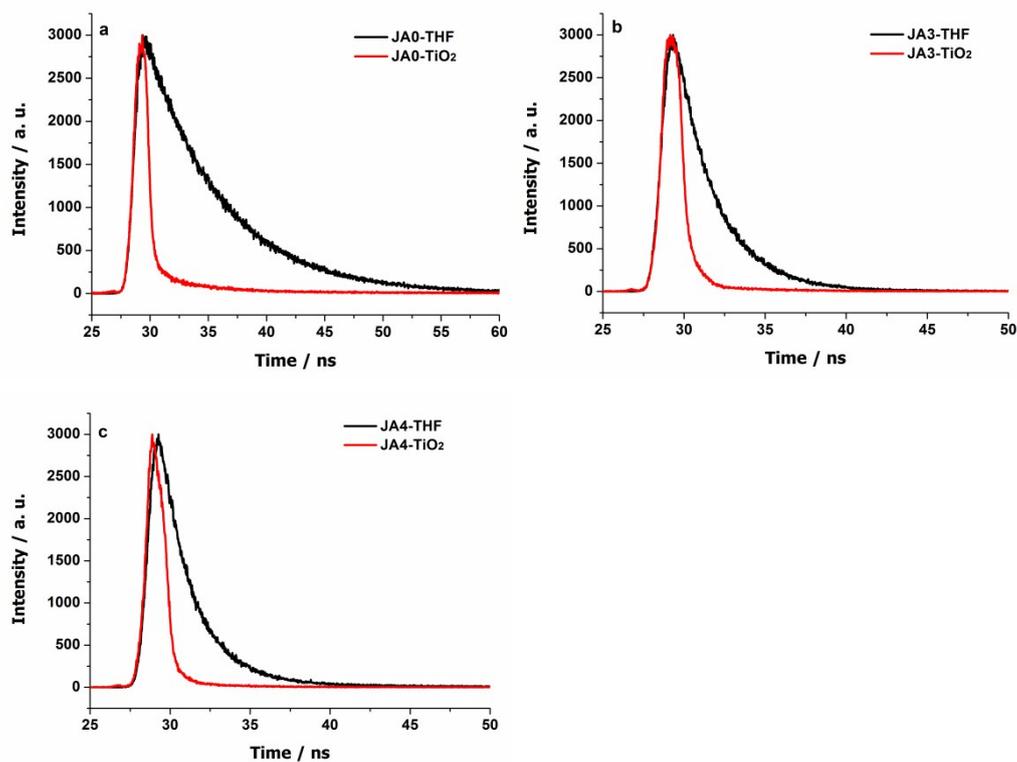
Fig. S2 Absorption spectra of JA0, JA3 and JA4 anchored on TiO<sub>2</sub> films with and without CDCA (10 mM).



**Fig. S3** Cyclic voltammogram of **JA0**, **JA3** and **JA4** in DMF, 0.1 M TBAPF<sub>6</sub>, glassy carbon electrode as working electrode, Pt as counter electrode, Ag/Ag<sup>+</sup> as reference electrode, scan rate: 100 mV s<sup>-1</sup>, calibrated with ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) as an external reference.



**Fig. S4** The normalized absorption spectra (solid lines) and emission spectra (broken lines) of **JA0**, **JA3** and **JA4**.



**Fig. S5** Fluorescence decay curves of dyes in THF (black line) and dyes adsorbed onto TiO<sub>2</sub> surface (red line), (a) **JA0**, (b) **JA3**, (c) **JA4**

## References

- [S1] A. Yella, H. W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W. G. Diau, C. Y. Yeh, S. M. Zakeeruddin, M. Grätzel, *Science*, 2011, **334**, 629.