

## *Supporting Information for*

# **Improvement of Dye-Sensitized Solar Cells' Performance through Introducing Different Heterocyclic Groups to Triarylamine Dyes**

Ze-Min Ju,<sup>a</sup> Hai-Lang Jia,<sup>a</sup> Xue-Hai, Ju,<sup>b</sup> Xing-Fu Zhou<sup>c</sup>, Zhi-Qiang Shi,<sup>a</sup> He-Gen Zheng\*<sup>a</sup> and Ming-Dao Zhang\*<sup>a,d</sup>

*<sup>a</sup>State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, P. R. China, E-mail: zhenghg@nju.edu.cn. Fax : 86-25-83314502.*

*<sup>b</sup>School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, P. R. China.*

*<sup>c</sup>State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing University of Technology, Nanjing 210009, P. R. China.*

*<sup>d</sup>Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control, School of Environmental Science and Engineering, Nanjing University of Information Science & Technology, Nanjing 210044, Jiangsu, P.R. China.*

## **EXPERIMENTAL SECTION**

### **Materials**

All reagents and chemicals were purchased from commercial suppliers. N, N-dimethylformamide (DMF), 1,2-dichloroethane and tetrahydrofuran (THF) were distilled with CaH<sub>2</sub>, while acetonitrile was distilled with P<sub>2</sub>O<sub>5</sub>. Other chemicals and reagents were used as received without further purifications.

### **Fabrication of DSSCs**

The dye-sensitized solar cells (DSSCs) devices were fabricated with working electrodes based on TiO<sub>2</sub> nanoparticles (NP) and Pt-coated counter electrodes reported elsewhere.<sup>S1</sup> For the working electrode, a paste composed of P25 TiO<sub>2</sub>

nanoparticles prepared with a sol-gel method<sup>S2</sup> for the transparent nanocrystalline layer was coated on a TiCl<sub>4</sub>-treated FTO glass substrate to obtain the required thickness on repetitive screen printing. Crystallization of TiO<sub>2</sub> films was performed with a programmed procedure: (1) heating at 275 °C for 5 min; (2) heating at 325 °C for 5 min; (3) heating at 375 °C for 5 min; (4) heating at 450 °C for 15 min and (5) heating at 500 °C for 15 min. The resulting layer had a transparent layer (thickness ~ 10 μm), which were treated again with TiCl<sub>4</sub> at 70 °C for 30 min and sintered at 500 °C for 30 min. After that, they were immersed in a 20 mM CDCA bath in ethanol solution for 8 h and then in a 3×10<sup>-4</sup> M dye bath in CH<sub>2</sub>Cl<sub>2</sub> solution for 16 h at room temperature. The electrode was then rinsed with CH<sub>2</sub>Cl<sub>2</sub> and dried. To prepare the counter electrode, the Pt counter electrodes were prepared on spin-coating drops of H<sub>2</sub>PtCl<sub>6</sub> solution onto FTO glass and heating at 500 °C for 15 min. The dye-adsorbed TiO<sub>2</sub> electrodes and the Pt counter electrodes were assembled into a sealed sandwich-type cell by heating with a Surlyn film as a spacer between the electrodes. A drop of the electrolyte solution was placed in the drilled hole of the counter electrode and was driven into the cell via vacuum backfilling. Finally, the hole was sealed using additional Surlyn and a cover glass (0.1 mm thickness). The electrolyte introduced into the cell is composed of 0.6 M 1,3-dimethylimidazolium iodide (DMII), 50 mM LiI, 30 mM I<sub>2</sub>, 0.5 M tert-butylpyridine and 0.1 M guanidinium thiocyanate (GuNCS) in a solvent mixture of 85% acetonitrile with 15% valeronitrile by volume.<sup>S3</sup> An Al foil was taped at the back side of each counter electrode to reflect unabsorbed light back to the photoanode. DSSCs based on single dye with soaked 16 h and 32 h are similar to the frond of the method, while those soaked 16+16 h need to soak twice according to the above method.

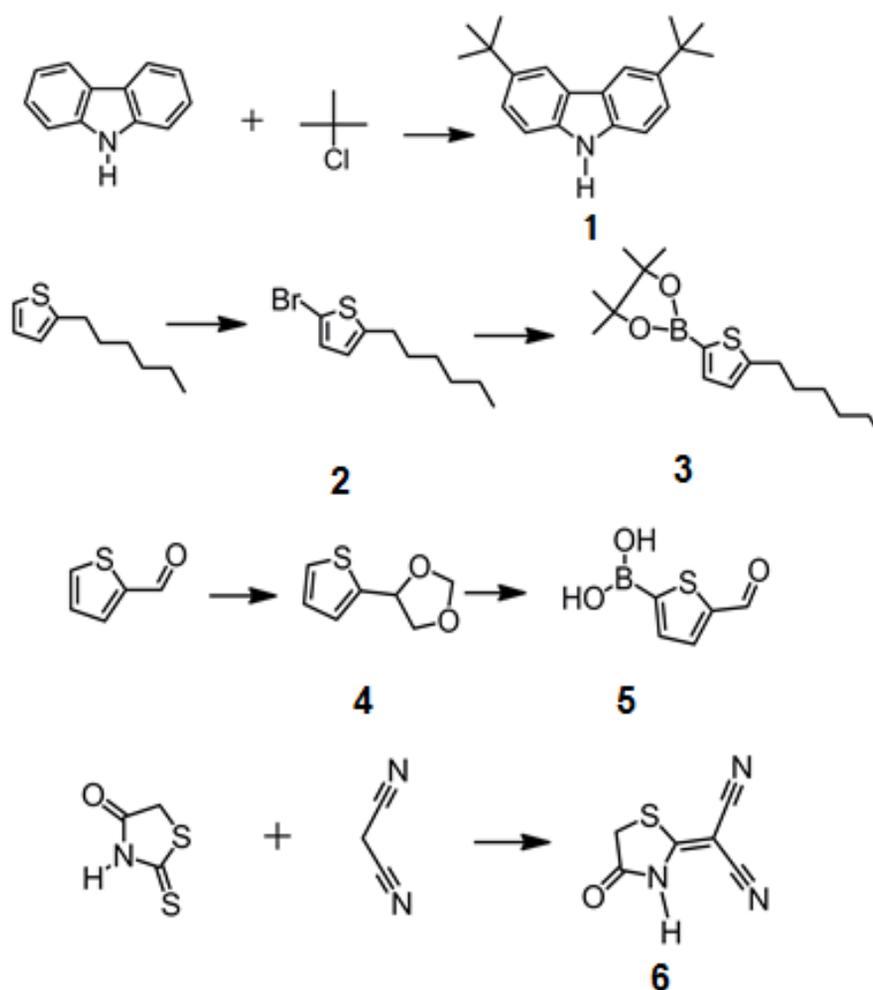
### **Instrumentation**

The molecular structures of TTR1-3 and intermediates were confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and mass spectra, as summarized in the supporting materials. The attenuated total reflection fourier transform infrared (ATR-FTIR) spectra were measured with a Thermo Scientific Nicolet iS10 FT-IR Spectrometer. The <sup>1</sup>H NMR

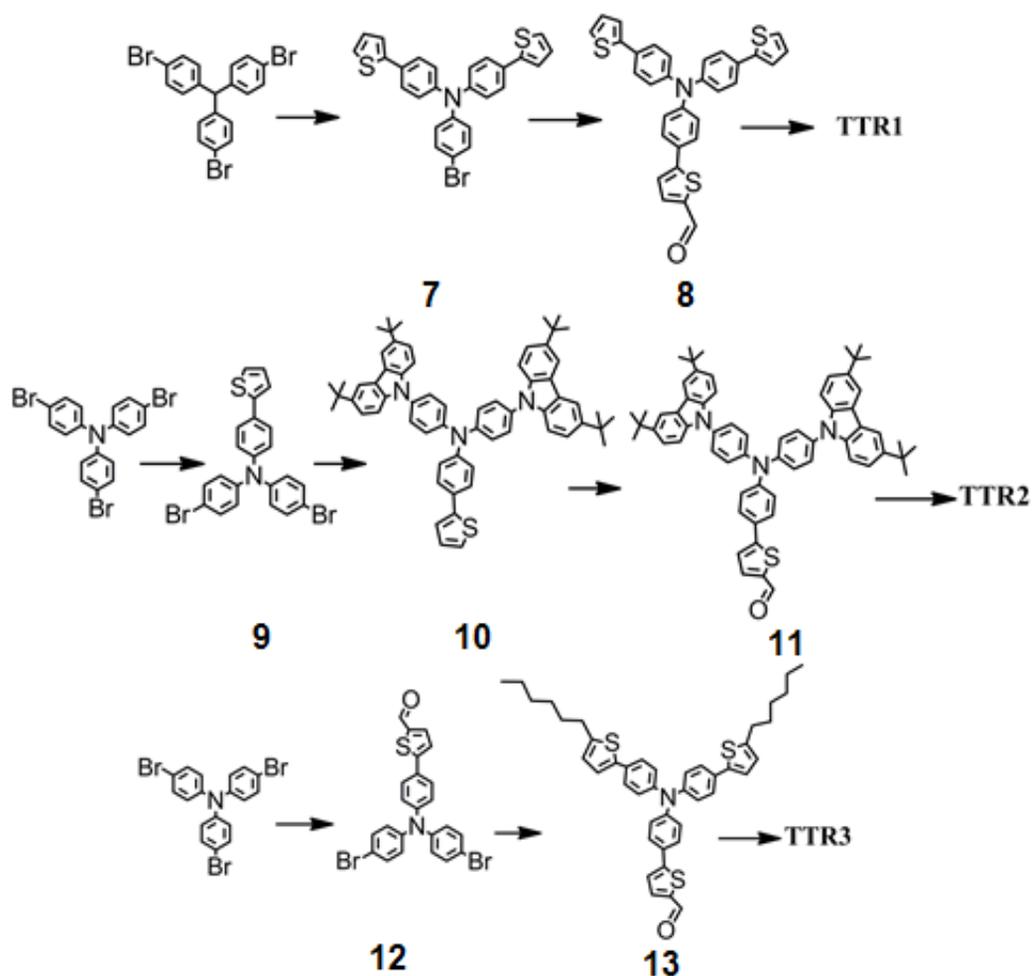
and  $^{13}\text{C}$  NMR spectra were recorded in solution of  $\text{CDCl}_3$  or  $\text{DMSO-}d_6$  on a Bruker DRX (500 MHz) NMR spectrometer with tetramethylsilane (TMS) as the internal standard. MALDI-TOF (matrix-assisted laser desorption ionization time-of-flight) analysis was performed on Bruker Daltonics Ultraflex MALDI TOF/TOF Mass Spectrometer, using  $\alpha$ -Cyano-4-hydroxycinnamic acid as matrix. Electron spray mass spectrometry was measured in Thermo LCQ Fleet Electro-Spray Mass Spectrometer.

## SYNTHESIS

### Synthesis of RD-I, RD-II, CA-I, CA-II and RDA-I



**Scheme S1.** Synthetic routes of the fragment



**Scheme S2.** Synthetic routes of the TTR1, TTR2 and TTR3.

**3,6-di-tert-butyl-9H-carbazole (1).** Carbazole (5.0 g, 0.03 mol) and anhydrous  $\text{AlCl}_3$  (4.0 g, 0.03 mol) were dissolved in  $\text{CH}_2\text{Cl}_2$  (100 mL). When the mixture was cooled to  $0\text{ }^\circ\text{C}$ , a solution of  $t\text{-BuCl}$  (6.6 mL, 0.06 mol) in  $\text{CH}_2\text{Cl}_2$  (20 mL) was added slowly. After that, the ice-bath was removed and the resulting mixture was stirred for 24 h at room temperature. Then, the mixture was poured into water, extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 50\text{ mL}$ ), and dried with anhydrous  $\text{MgSO}_4$ . Solvent was evaporated to afford the crude products, which were recrystallized from petroleum ether twice to give compound **1** as a white solid (4.5 g, yield 54%).  $^1\text{H-NMR}$  (DMSO, 500 MHz):  $\delta$  10.90 (s, 1H), 8.14 (s, 2H), 7.43 (d,  $J = 10.5$ , 2H), 7.36 (d,  $J = 10.5$ , 2H), 1.41 (s, 18H). HRMS-EI ( $m/z$ ): calculated for  $\text{C}_{20}\text{H}_{25}\text{N}$ , 279.1987; found, 279.1989.

**2-bromo-5-hexylthiophene (2)** In a 300 mL three-neck flask having a dropping

funnel, 2-hexylthiophene (6.2 g, 37 mmol) was dissolved in DMF (150 mL). Then, a solution obtained by dissolving NBS (6.56 g, 37 mmol) in DMF (15 mL) was added thereto in drops at a room temperature over 10 minutes and thereafter stirred for 12 h at a room temperature. Then a saturated sodium hydrogen carbonate solution (150 mL) was added and then stirred for 30 minutes. Then, hexane (80 mL) was added thereto. Subsequently, a water layer was separated and then extracted with hexane (80 mL  $\times$  2). Then, organic layers were collected, washed with water (100 mL  $\times$  3), and dried with anhydrous magnesium sulfate. After the resulting solution was filtered, a solvent was removed therefrom under a reduced pressure. As a result, compound **2** was obtained in the form of yellow liquid (8.9 g, 98%). (silica gel, methylene chloride: hexane = 1:1);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500MHz):  $\delta$  6.87 (d,  $J = 4.6$ , 1H), 6.55 (s,  $J = 4.5$ , 1H), 2.77 (t,  $J = 9.5$ , 2H), 1.66 (dd,  $J = 9.5$ , 2H), 1.34 (m, 6H), 0.93 (t,  $J = 8.5$ , 3H). HRMS-EI ( $m/z$ ): calculated for  $\text{C}_{10}\text{H}_{15}\text{BrS}$ , 247.0123; found, 247.0126.

**2-(5-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3).** A degassed THF solution (125 mL) containing 2-bromo-5-hexylthiophene (4280 mg, 17.32 mmol) was cooled to  $-70\text{ }^\circ\text{C}$  at which point *n*-butyllithium (8.31 mL, 20.8 mmol) was added dropwise while maintaining the temperature at  $-70\text{ }^\circ\text{C}$ . After the reaction was stirred at this temperature for 45 min, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5.30 mL, 26.0 mmol) was added. The reaction was brought to  $25\text{ }^\circ\text{C}$  and then stirred for 18 h. The addition of methanol (15 mL) turned the reaction opaque white before returning to a clear, colourless solution. The reaction was filtered and solvent removed in vacuo. The crude product was purified using a  $\text{SiO}_2$  plug (hexanes/ $\text{CH}_2\text{Cl}_2$ ; 3:1;  $v:v$ ) to produce a yellow oil **3** in quantitative yield.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500MHz):  $\delta$  7.50 (d,  $J = 5$ , 1H), 6.89 (d,  $J = 5$ , 1H), 2.88 (t,  $J = 10$ , 2H), 1.72 (dd, 2H), 1.33 (m, 18H), 0.91 (d, 3 H). HRMS-EI ( $m/z$ ): calculated for  $\text{C}_{16}\text{H}_{27}\text{BO}_2\text{S}$ , 295.1849; found, 295.1803.

**2-(Thiophen-2-yl)-1,3-dioxolane (4):** A benzene (50 mL) solution of thiophene-2-carbaldehyde (1.35 g, 12.0 mmol), ethylene glycol (3 mL) and *p*-toluenesulfonic acid (0.01 g, 0.06 mmol) was heated to vigorous reflux overnight in a flask equipped

with a Dean-Stark trap to remove water. Then, the solution was poured into a 10% sodium hydroxide solution and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. Afterwards, the mixture was concentrated under reduced pressure to give 2-(thiophen-2-yl)-1,3-dioxolane as a brown liquid (1.79 g, 10 mmol, 95%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 7.37 (m, *J* = 5.2, 1H), 7.30 (m, *J* = 4.5, 1H), 7.04 (s, *J* = 4.0, 1H), 6.16 (s, 1H), 4.17 (m, *J* = 4.6, 2H), 4.07 (d, *J* = 4.6, 2H). HRMS-EI (*m/z*): calculated for C<sub>7</sub>H<sub>8</sub>O<sub>2</sub>S, 157.0258; found, 157.0197.

**5-Formylthiophen-2-yl-2-boronic acid (5):** A THF (30 mL) solution of 2-(thiophen-2-yl)-1,3-dioxolane (1.82 g, 11.66 mmol) was cooled to -78 °C under nitrogen atmosphere and then 2.5 M *n*-butyllithium (7 mL, 17.50 mmol) was added dropwise over 15 min. The mixture was stirred at -78 °C for 1 h and then at -40 °C for 4 h. After cooling back to -78 °C, trimethyl borate (1.39 mL, 12.24 mmol) was added dropwise, and the solution was stirred at room temperature for 24 h. The reaction was quenched by the addition of 2 M HCl and the mixture was extracted with diethyl ether. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. Afterwards, the mixture was concentrated under reduced pressure. The residue was washed by *n*-hexane to obtain 5-formylthiophen-2-yl-2-boronic acid as a pale brown solid (1.65 g, 0.01 mol, 90%). <sup>1</sup>H NMR (DMSO, 500 MHz): δ 9.97 (s, 1H), 8.62 (s, 2H), 8.01 (d, *J* = 4.6, 1H), 7.77 (d, *J* = 4.5, 1H). HRMS-EI (*m/z*): calculated for C<sub>5</sub>H<sub>5</sub>BO<sub>3</sub>S, 154.0258; found, 154.0197.

**2-(1,1-dicyanomethylene)-1,3-thiazol-4-one (6).** Compound **6** was prepared according to literature procedures.<sup>S4</sup> An equimolar mixture of rhodanine **1** (2.66 g, 20 mmol), malononitrile (1.32 g, 20 mmol) and sodium acetate (1.64 mg, 20 mmol) in absolute ethanol (40 mL) was refluxed for 12 h. The ensuing precipitate was filtered off and washed with water and ice cooled ethanol. The solid was purified by recrystallization from ethanol to yield a yellowish solid **6** (1.98 g, 60 % yield). <sup>1</sup>H NMR (DMSO, 500 MHz): δ 3.80 (s, 2H). HRMS-EI (*m/z*) calculated for C<sub>6</sub>H<sub>3</sub>N<sub>3</sub>OS, 163.9919; found, 163.9918.

**Bis(4-bromophenyl)-4-(2-thienyl)phenylamine(7)** and **4-Bromophenylbis[4-(2-thienyl)phenyl]amine(9)**. Tris(4-bromophenyl)amine (9.64g, 20 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (1 g, 0.87 mmol), 2-thiopheneboronic acid (5.12 g, 40 mmol) and K<sub>2</sub>CO<sub>3</sub> (12.4 g, 90 mmol) in 250 mL of 1,4-dioxacyclohexane and 50 mL of H<sub>2</sub>O were heated to 95 °C under a nitrogen atmosphere for 18 h. After cooling to room temperature, the mixture was extracted with CHCl<sub>3</sub> (3 × 100 ml). The organic portion was combined and dried over magnesium sulfate, then removed by rotary evaporation. The residue was purified by column chromatography (silica gel, dichloromethane /petroleum ether = 1/200) as eluent to yield **7** (2.72 g) and **9** (4.69 g). For **7**: <sup>1</sup>H NMR( CDCl<sub>3</sub>, 500MHz): δ 7.55 (d, *J* = 5.2, 2H), 7.53 (d, *J* = 4.7, 2H), 7.40 (dd, *J* = 6.0, 2H), 7.28 (d, *J* = 6.5, 4H), 7.13 (d, *J* = 4.5, 2H), 7.10 (d, *J* = 3.6, 4H), 7.04(dd, *J* = 3.6, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 146.5, 146.2, 143.0, 132.9, 129.4, 128.9, 127.2, 126.1, 125.6, 124.8, 123.6, 114.6. HRMS-EI (*m/z*) calculated for C<sub>26</sub>H<sub>18</sub>BrNS<sub>2</sub>, 489.0000; found, 489.0029.

For **9**: <sup>1</sup>H NMR( CDCl<sub>3</sub>, 500MHz): δ 7.00(d, *J* = 5.6, 4H), 7.07(d, *J* = 4.6, 2H), 7.26 (m, *J* = 4.6, 1H), 7.28 (m, *J* = 4.5, 2H), 7.40 (d, *J* = 4.5, 4H), 7.53 (d, *J* = 3.7, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 145.4, 145.1, 143.4, 132.9, 129.7, 128.9, 127.2, 126.1, 125.7, 124.9, 123.7, 115.6. HRMS-EI (*m/z*) calculated for C<sub>22</sub>H<sub>15</sub>Br<sub>2</sub>NS, 484.9327; found, 484.9366.

**5-(4-(bis(4-(thienyl)phenyl)amino)phenyl)thiophene-2-carbaldehyde (8)**. Compound **7** (1.437 g, 3 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (500 mg, 0.435 mmol) and K<sub>2</sub>CO<sub>3</sub> (2.07 g, 15 mmol) in 100 mL of THF and 20 mL of H<sub>2</sub>O were heated to 55 °C under a nitrogen atmosphere for 30 min. A solution of 5-formyl-2-thiopheneboronic acid (0.47 g, 3 mmol) in THF (15 mL) was added slowly, and the mixture was refluxed for further 12 h. After cooling to room temperature, the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 ml). The organic portion was combined and dried over magnesium sulfate, then removed by rotary evaporation. The residue was purified by column chromatography (silica gel, ethyl acetate /petroleum ether = 1/20) as eluent to yield an orange-yellow solid **8** (860 mg, 52.5%). <sup>1</sup>H NMR(DMSO, 500MHz): δ 9.97 (d,

1H), 8.57 (s,  $J = 5.5$ , 2H), 8.03 (d,  $J = 7.2$ , 1H), 7.73 (d,  $J = 5.4$ , 2H), 7.65 (d,  $J = 7.1$ , 4H), 7.53 (d,  $J = 4.0$ , 2H), 7.47(m,  $J = 4.5$ , 2H), 7.12-7.16 (m,  $J = 3.2$ , 5H), 7.10 (d,  $J = 2.5$ , 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  184.2, 153.1, 149.3, 145.9, 143.4, 141.6, 139.8, 129.9, 129.0, 128.0, 127.3, 126.9, 125.8, 125.0, 124.8, 123.8, 123.4. HRMS-EI (m/z) calculated for  $\text{C}_{32}\text{H}_{23}\text{NOS}_2$ , 502.1246; found, 502.1238.

**2-(5-(4-(bis(4-(thienyl)phenyl)amino)benzylidene)-4-oxothiazolidin-2-ylidene) malononitrile (TTR1).** Equimolar quantities of compound **1** (520 mg, 1 mmol) and **2** (165 mg, 1 mmol) in EtOH (50 mL) was stirred under basic conditions (5 drops, 20% aq NaOH solution) and refluxed for further 12 h. The solvent was removed by rotary evaporation, and the crude reaction was purified by column chromatography (silica gel, dichloromethane/EtOH = 20/1) as eluent to yield an red solid **TTR1** (360 mg, 76%).  $^1\text{H}$  NMR( $\text{CDCl}_3$ , 500MHz):  $\delta$  7.81 (s, 1H), 7.73 (d,  $J = 7.8$ , 2H), 7.64 (d,  $J = 6.0$ , 4H), 7.60 (s,  $J = 5.5$ , 2H), 7.52 (d,  $J = 4.5$ , 2H), 7.46 (d,  $J = 3.6$ , 2H), 7.14 (d,  $J = 6.8$ , 1H), 7.13 (m,  $J = 5.4$ , 4H), 7.12-7.09 (m,  $J = 3.2$ , 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  172.5, 162.8, 148.3, 146.3, 145.4, 142.8, 142.0, 139.1, 134.8, 133.1, 128.4, 128.1, 127.5, 125.8, 125.0, 124.5, 124.1, 123.2, 121.9, 118.1, 117.0, 116.6, 109.7, 35.0, 32.3, 29.4. HRMS-EI (m/z)calculated for  $\text{C}_{37}\text{H}_{22}\text{N}_4\text{OS}_4$ , 634.1056; found, 634.1109.

**5-(4-(bis(4-(3,6-di-tert-butyl-9H-carbazolyl)phenyl)amino)phenyl)thiophene (10).** Compound **9** (1.94 g, 4 mmol), Compound **1** (3.516g, 12 mmol),  $\text{K}_2\text{CO}_3$  (2.76 g, 12 mmol) and CuI (0.76 g, 0.4 mmol) 18-Crown-6 (0.1056 g, 0.04 mmol) in 20 mL of 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone were heated to 250 °C under a nitrogen atmosphere for 3 days. After cooling to room temperature, the mixture was extracted with  $\text{CHCl}_3$  (3  $\times$  50 ml). The organic portion was combined and dried over magnesium sulfate, then removed by rotary evaporation. The residue was purified by column chromatography (silica gel, ethyl acetate /petroleum ether = 1/200) as eluent to yield an orange-yellow solid **10** (1.639 g, 45.8%).  $^1\text{H}$  NMR(DMSO, 500MHz):  $\delta$  9.29 (s, 4H), 7.71 (d,  $J = 5.7$ , 2H), 7.60 (d,  $J = 5.7$ , 4H), 7.53 (d,  $J = 2.4$ , 1H), 7.50 (d,  $J = 3.7$ , 4H), 7.47 (t,  $J = 2.3$ , 1H), 7.41 (d,  $J = 4.0$ , 4H), 7.38 (d,  $J = 4.0$ , 4H), 7.30 (d,  $J = 5.6$ , 2H), 7.15 (m,  $J = 5.6$ , 1H), 1.43 (s, 36H).  $^{13}\text{C}$

NMR (CDCl<sub>3</sub>):  $\delta$  146.6, 145.9, 143.6, 142.7, 139.1, 132.7, 129.5, 128.5, 127.7, 121.1, 125.2, 124.9, 123.8, 123.1, 116.5, 109.5, 34.8, 32.2. HRMS-EI (m/z) calculated for C<sub>62</sub>H<sub>63</sub>N<sub>3</sub>S, 881.4756; found, 881.4729.

**5-(4-(bis(4-(3,6-di-tert-butyl-9H-carbazolyl)phenyl)amino)phenyl)thiophene-2-carbaldehyde (11).** To an ice-cooled solution of distilled dimethylformamide (0.329 g, 4.5 mmol) and compound **10** (1.341 g, 1.5 mmol) in dry 1,2-dichloroethane (30.0 mL) under N<sub>2</sub>, phosphorus oxychloride (0.583 g, 3.75 mmol) was added drop wise. The resulting mixture was slowly brought to room temperature and then stirred at 85 °C for 18 h. After refluxing, the solution was cooled to room temperature. Then the solution was poured into a saturated sodium acetate aqueous solution (50 mL), and stirred for 6 h to complete the hydrolysis. The hydrolyzed solution was extracted with dichloromethane (3 × 50 mL). The combined dichloromethane solutions were dried over anhydrous MgSO<sub>4</sub>, and then concentrated by distillation under reduced pressure. After purification by silicagel column chromatography using CH<sub>2</sub>Cl<sub>2</sub>: hexane (v : v, 1 : 10) as eluent, title compound **11** was obtained as yellow liquid. Yield: 1.300 g (67%). <sup>1</sup>H NMR (DMSO, 500 MHz):  $\delta$  9.91 (s, 1H), 8.30 (s, 4H), 8.05 (d, *J* = 2.7, 1H), 7.85 (d, *J* = 4.5, 2H), 7.70 (d, *J* = 2.9, 1H), 7.66 (d, *J* = 4.5, 4H), 7.52 (d, *J* = 4.9, 4H), 7.47 (d, *J* = 4.8, 4H), 7.40 (d, *J* = 5.2, 4H), 7.31 (d, *J* = 4.8, 2H), 1.43 (s, 36H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  184.2, 154.3, 149.6, 146.7, 143.4, 141.9, 139.0, 138.9, 132.2, 130.4, 129.4, 129.1, 124.3, 124.2, 118.9, 117.9, 115.1, 111.7, 35.5, 32.0. HRMS-EI (m/z) calculated for C<sub>63</sub>H<sub>63</sub>N<sub>3</sub>OS, 909.4731; found, 909.4726.

**2-(5-(4-(bis(4-(3,6-di-tert-butyl-9H-carbazolyl)phenyl)amino)benzylidene)-4-oxothiazolidin-2-ylidene)malononitrile (TTR2).** The synthesis method resembles that of compound **TTR-1**, and the compound was purified by column chromatography (silica gel, dichloromethane/EtOH = 20/1) as eluent to yield a red solid **TTR2** (489 mg, 46.3%). <sup>1</sup>H NMR (DMSO, 500 MHz):  $\delta$  8.30 (s, 4H), 7.96 (d, *J* = 6.8, 1H), 7.81 (d, *J* = 5.5, 2H), 7.76 (d, *J* = 4.2, 1H), 7.63 (m, *J* = 5.6, 4H), 7.59 (s, 1H), 7.52 (d, *J* = 4.2, 4H), 7.45 (d, *J* = 4.2, 4H), 7.40 (d, *J* = 3.9, 4H), 7.30 (d, *J* = 4.3,

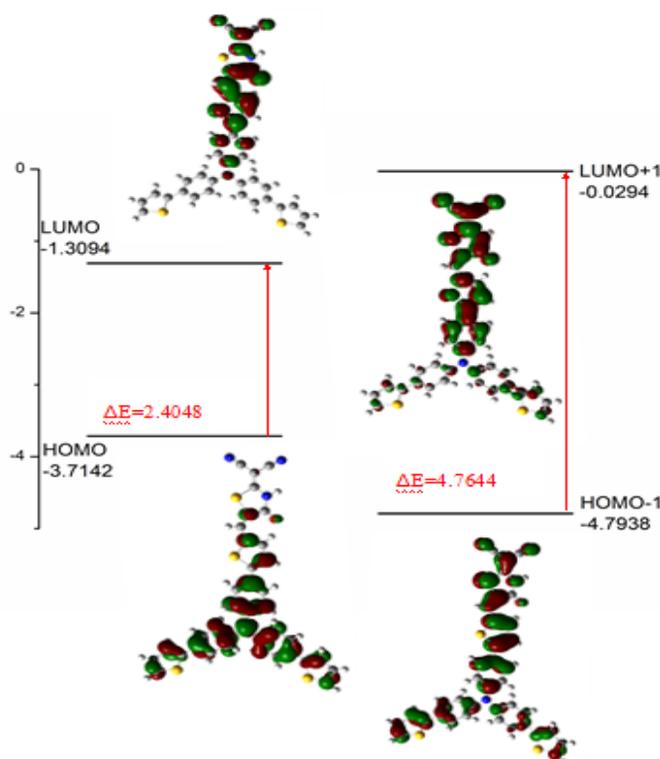
2H), 1.44 (s, 36H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  172.5, 162.8, 148.3, 146.3, 145.4, 142.8, 142.0, 139.1, 134.8, 133.1, 128.4, 128.1, 127.5, 125.8, 125.0, 124.5, 124.1, 123.2, 121.9, 118.1, 117.0, 116.6, 109.7, 35.0, 32.3, 29.4. HRMS-EI ( $m/z$ ) calculated for  $\text{C}_{69}\text{H}_{64}\text{N}_6\text{OS}_2$ , 1056.4689; found, 1056.4672.

**(Bis(4-bromophenyl)phenyl)thiophene-2-carbaldehyde (12).** Tris(4-bromophenyl)amine (4.82 g, 10 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (0.5 g, 0.435 mmol), 5-formyl-2-thiopheneboronic acid (1.56 g, 10 mmol) and  $\text{K}_2\text{CO}_3$  (6.2 g, 45 mmol) in 150 mL of 1,4-dioxacyclohexane and 50 mL of  $\text{H}_2\text{O}$  were heated to 95 °C under a nitrogen atmosphere for 18 h. After cooling to room temperature, the mixture was extracted with  $\text{CHCl}_3$  ( $3 \times 100$  ml). The organic portion was combined and dried over magnesium sulfate, then removed by rotary evaporation. The residue was purified by column chromatography (silica gel, dichloromethane /petroleum ether = 1/100) as eluent to yield **12** (3.26 g, 63.5%).  $^1\text{H}$  NMR(DMSO, 500MHz):  $\delta$  9.89 (s, 1H), 8.03 (d,  $J = 4.4$ , 1H), 7.74 (d,  $J = 3.6$ , 2H), 7.66 (d,  $J = 6.6$ , 1H), 7.51 (t,  $J = 2.6$ , 4H), 7.05 (d,  $J = 6.0$ , 4H), 7.03 (d,  $J = 6.6$ , 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  182.6, 153.9, 148.0, 145.7, 141.7, 137.6, 132.6, 127.5, 127.4, 126.2, 123.27, 123.2, 116.7. HRMS-EI ( $m/z$ ) calculated for  $\text{C}_{23}\text{H}_{15}\text{Br}_2\text{NOS}$ , 512.9246; found, 512.9269.

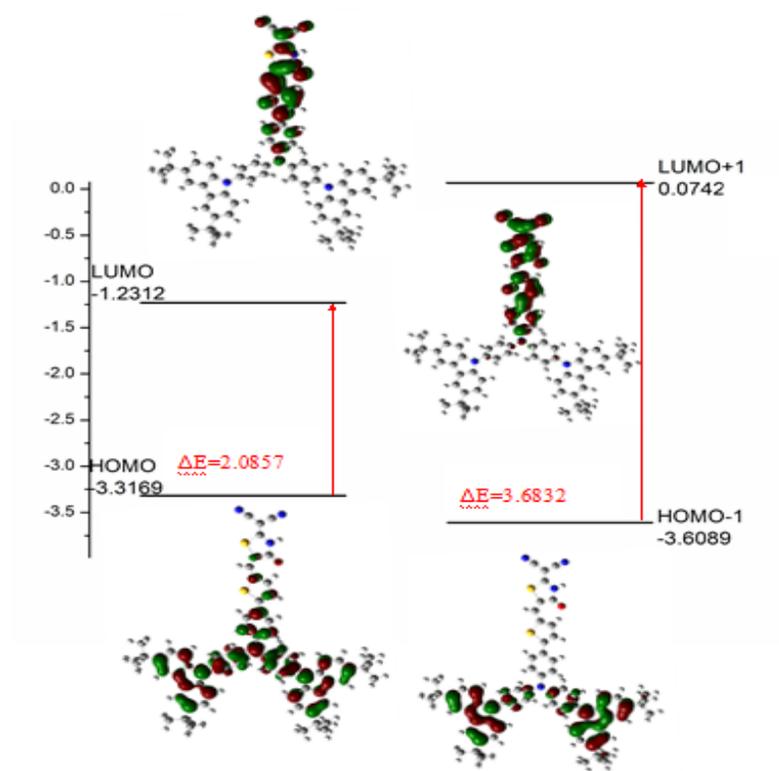
**5-(4-(bis(4-(5-hexylthiophen-2-yl)phenyl)amino)phenyl)thiophene-2-carbaldehyde (13).** Compound **12** (2.052 g, 4 mmol), Compound **3** (3.528 g, 12 mmol),  $\text{K}_2\text{CO}_3$  (2.76 g, 12 mmol) and  $\text{CuI}$  (0.76 g, 0.4 mmol) 18-Crown-6 (0.1056 g, 0.04 mmol) in 20 mL of 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone were heated to 250 °C under a nitrogen atmosphere for 3days. After cooling to room temperature, the mixture was extracted with  $\text{CHCl}_3$  ( $3 \times 50$  ml). The organic portion was combined and dried over magnesium sulfate, then removed by rotary evaporation. The residue was purified by column chromatography (silica gel, ethyl acetate /petroleum ether = 1/200) as eluent to yield an orange-yellow solid **13** (1.728 g, 62.8%).  $^1\text{H}$  NMR(DMSO, 500MHz):  $\delta$  9.86 (s, 1H), 7.72 (d,  $J = 2.5$ , 1H), 7.54 (d,  $J = 3.6$ , 2H), 7.48 (m,  $J = 6.8$ , 4H), 7.32 (d,  $J = 7.4$ , 1H), 7.10-7.14 (d,  $J = 3.6$ , 6H), 7.07 (d,  $J = 7.3$ , 2H), 6.73 (d,  $J = 4.0$ , 2H), 2.81 (t, 4H), 1.70 (dt, 4H), 1.33 (m, 12H),

0.90 (t, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  183.6, 148.9, 146.8, 143.9, 142.2, 139.3, 135.9, 130.5, 129.7, 129.4, 129.1, 128.6, 127.8, 126.7, 124.3, 124.2, 41.3, 33.9, 33.8, 29.9, 24.2, 14.6. HRMS-EI ( $m/z$ ) calculated for  $\text{C}_{42}\text{H}_{43}\text{NOS}_3$ , 673.2546; found, 673.2559.

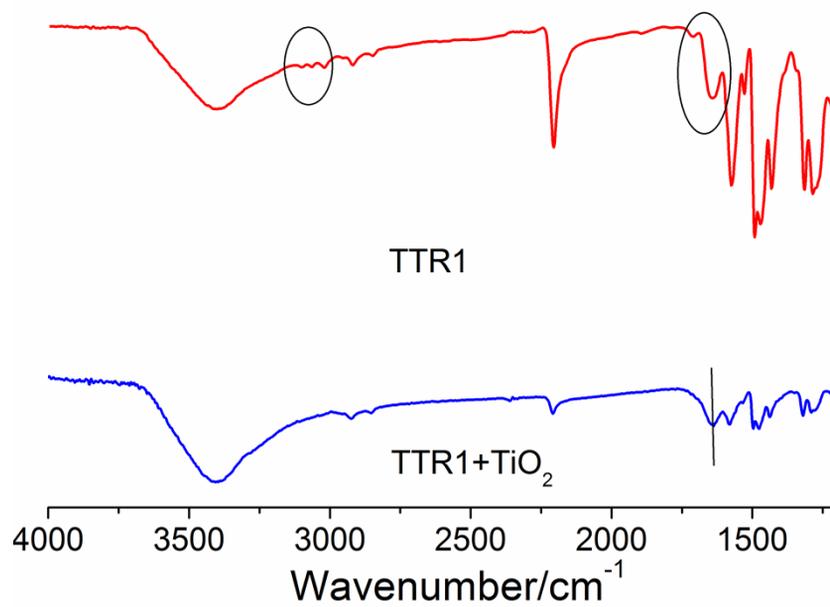
**2-(5-(2-(5-hexylthiophen-2-yl))phenylamino)benzylidene)-4-oxothiazolidin-2-ylidene)malononitrile (TTR3).** The synthesis method resembles that of compound **TTR1**, and the compound was purified by column chromatography (silica gel, dichloromethane/EtOH = 20/1) as eluent to yield a red solid **TTR3** (396 mg, 47.4%).  $^1\text{H}$  NMR(DMSO, 500MHz):  $\delta$  7.73-7.69 (d,  $J = 7.1$ , 3H), 7.58-7.54 (d,  $J = 6.8$ , 6H), 7.25 (d,  $J = 6.8$ , 2H), 7.11-7.05 (t,  $J = 7.3$ , 6H), 6.83 (d,  $J = 4.5$ , 2H), 2.79 (d, 4H), 1.63 (d, 4H), 1.29 (t, 12H), 0.87 (d, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  180.1, 178.6, 147.9, 147.3, 145.8, 145.0, 140.8, 138.5, 134.5, 129.8, 127.8, 127.3, 126.7, 126.2, 125.1, 124.2, 123.9, 123.2, 121.0, 118.2, 117.1, 95.9 31.531.4, 29.9, 28.6, 22.6, 14.5. HRMS-EI ( $m/z$ ) calculated for  $\text{C}_{49}\text{H}_{46}\text{N}_4\text{OS}_4$ , 835.2616; found, 835.2621.



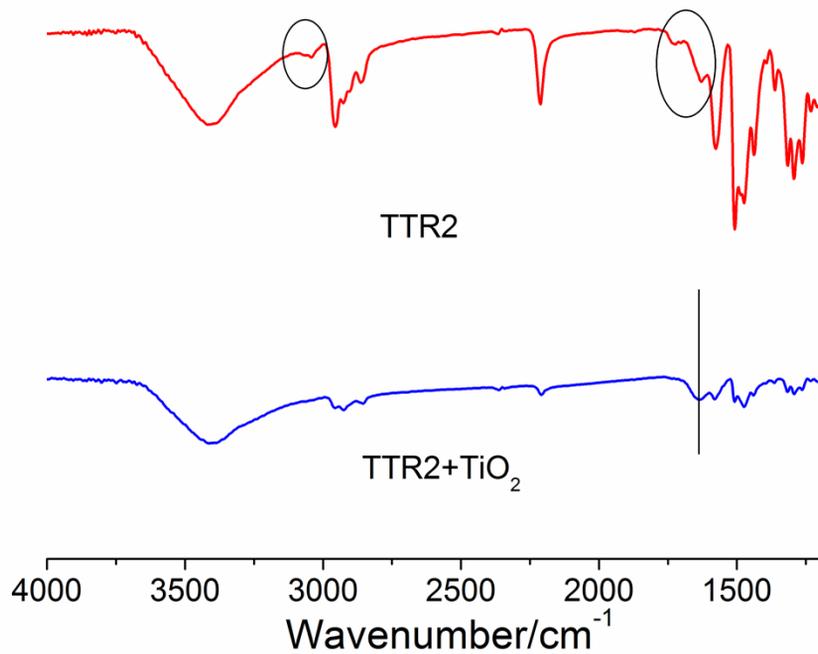
**Fig. S1** Calculated HOMO, HOMO-1, LUMO and LUMO+1 levels for TTR1.



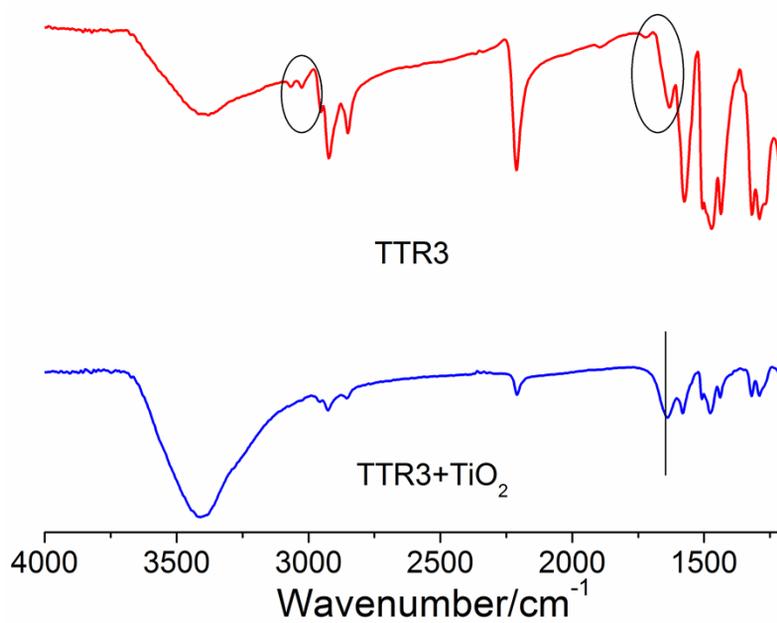
**Fig. S2** Calculated HOMO, HOMO-1, LUMO and LUMO+1 levels for TTR2.



**Fig. S3** FTIR spectra of TTR1 powders and the dyes adsorbed on TiO<sub>2</sub>.

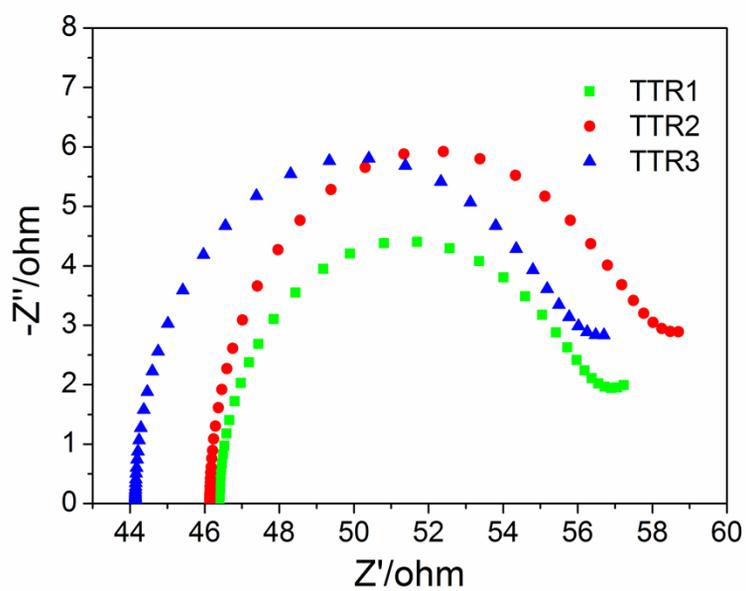


**Fig. S4** FTIR spectra of TTR2 powders and the dyes adsorbed on TiO<sub>2</sub>.



**Fig. S5** FTIR spectra of TTR3 powders and the dyes adsorbed on TiO<sub>2</sub>.

**Fig. S6** Cyclic voltammogram of the reduction behavior of the dyes were measured in dry  $\text{CH}_2\text{Cl}_2$  containing 0.1 M tetrabutylammonium hexafluorophosphate ( $\text{TBAPF}_6$ ) as supporting electrolyte (working electrode, glassy carbon; reference electrode,  $\text{Ag}/\text{Ag}^+$  ; counter electrode, Pt).



**Fig. S7** EIS Nyquist for TTR1-3 based DSSCs in absence of CDCA under illumination of  $100 \text{ mW cm}^{-2}$  simulated AM1.5 solar light.

**Table S1.** The results generated from the EIS experiments.

| Dye  | $R_{\text{rec}}^a/\Omega$ | $R_{\text{rec}}^b/\Omega$ |
|------|---------------------------|---------------------------|
| TTR1 | 16.24                     | 9.41                      |
| TTR2 | 20.38                     | 12.24                     |
| TTR3 | 23.26                     | 12.07                     |

<sup>a,b</sup>EIS Nyquist for DSSCs based on TTR1-3 in presence (a) and absence (b) CDCA measured in the dark at a forward bias of  $-0.7$  V.

**Table S2.** Adsorption amount per unit area of TiO<sub>2</sub> film.

| Dye  | With CDCA <sup>a</sup><br>mol cm <sup>-2</sup> | 16h <sup>b</sup><br>mol cm <sup>-2</sup> | 32h <sup>b</sup><br>mol cm <sup>-2</sup> | 16+16h <sup>b</sup><br>mol cm <sup>-2</sup> |
|------|--|--|--|---|
| TTR1 | $1.429 \times 10^{-7}$                         | $1.476 \times 10^{-7}$                   | $1.537 \times 10^{-7}$                   | $1.600 \times 10^{-7}$                      |
| TTR2 | $1.38 \times 10^{-7}$                          | $1.396 \times 10^{-7}$                   | $1.468 \times 10^{-7}$                   | $1.524 \times 10^{-7}$                      |
| TTR3 | $1.403 \times 10^{-7}$                         | $1.418 \times 10^{-7}$                   | $1.507 \times 10^{-7}$                   | $1.572 \times 10^{-7}$                      |

<sup>a</sup>Adsorption quantity of DSSCs with CDCD coadsorbant soaking 16 h.

<sup>b</sup>Adsorption quantity of DSSCs based on single dye soaking 16 h, 32 h, 16+16 h.

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