

## Supporting Information

### **High performance solid-state dye-sensitized solar cells based on organic blue-colored dyes**

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## 1. Experimental section

### 1.1. Materials and reagents

Fluorine-doped SnO<sub>2</sub> conducting glass (FTO glass, transparency > 90%, sheet resistance 15 Ω/square was obtained from the Geao Science and Educational Co. Ltd. of China. Chlorobenzene (anhydrous 99.8%), acetonitrile (anhydrous 99.8%), Bis(trifluoromethane)sulfonimide lithium salt (Li-TSFI, 99.95%), tetra-n-butyl ammonium hexafluorophosphate (TBAPF<sub>6</sub>), 4-tert-butylpyridine (t-BP), and lithium iodide were bought from Sigma-Aldrich and iodine (99.999%) was purchased from Alfa Aesar. Dye **LEG4** was provided by Dyemaco AB. Spiro-OMeTAD was purchased from Luminescence Technology Corp. All chemicals and reagents were purchased from suppliers and used without further purification. Tetrahydrofuran (THF) and toluene was dried with sodium under argon before use. 5,8-dibromo-2,3-diphenyl pyrido[3,4-b]pyrazine, 5,8-dibromo-2,3-diphenyl quinoxaline, (4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl) tributylstannane and N-(2',4'-bis((2-ethylhexyl)oxy)-[1,1'-biphenyl]-4-yl)-4,4-dimethyl-N-(2, 2'', 4, 4''-tetrakis (2-ethylhexyl)oxy)- [1,1':3',1''-terphenyl]-4'-yl)-2-(trimethylstannyl)-4H-indeno[1,2-b]thiophen-6-amine were synthesized according to the literatures.<sup>1, 2</sup>

### 1.2. Instruments and characterization

A Brücker AM 400 spectrometer was employed to record <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra with TMS as the internal standard and a HITACHI-80 mass spectrometer was used to obtain the high resolution mass spectra. The UV-Vis spectra of the dyes in CH<sub>2</sub>Cl<sub>2</sub> solution and on TiO<sub>2</sub> films were performed on a Shimadzu UV-260 UV-Vis spectrometer. Cyclic voltammetry measurements were performed on dyes using a Versastat II electrochemical workstation (Princeton applied research) with a three-electrode system, in which glassy carbon as the working electrode, Pt wire as the counter electrode, and Ag/AgCl as the reference electrode with ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) as the external standard. The supporting electrolyte was 0.1 M TBAPF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub>. The scan rate was 50 mV/s.

**Liquid-state DSCs:** The current-voltage (*J-V*) photovoltaic characterization was measured under the illumination of AM 1.5 G simulated solar light by using a 450 W xenon lamp (Oriel), a Schott K113 Tempax sunlight filter (PräzisionsGlas & Optik GmbH), and a Keithley 2400 source meter. The setup consisting of SR830 lock-in amplifier, a 300 W xenon lamp (ILC Technology) and a Gemini-180 double monochromator (Jobin-Yvon Ltd.) were used to obtain the Monochromatic incident photon-to-current conversion efficiency (IPCE) spectra. A Zahner IM6e Impedance Analyzer (ZAHNER-Elektrik GmbH & CoKG, Kronach, Germany) was employed to measure the electrochemical impedance spectroscopy (EIS) in dark. The frequency range was 0.1 Hz-100 kHz and the applied bias was from -0.50 V to -0.90 V and from -0.50 V to -0.85 V with cobalt and iodine electrolytes, respectively. The magnitude of the alternating signal was 10 mV.

**Solid-state DSCs:** Current-Voltage characteristics were recorded by applying an external potential bias to the cell while recording the generated photocurrent with a Keithley model 2400 digital source meter. The light source was a 300 W

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collimated xenon lamp (Newport) calibrated with the light intensity to  $100 \text{ mW}\cdot\text{cm}^{-2}$  at AM 1.5 G solar light condition by a certified silicon solar cell (Fraunhofer ISE). The prepared sDSC samples were masked during the measurement with an aperture area of  $0.126 \text{ cm}^2$  (diameter 4 mm) exposed under illumination. IPCE spectra were recorded on a computer-controlled setup comprised of a xenon lamp (Spectral Products ASB-XE-175), a monochromator (Spectral Products CM110) and a Keithley multimeter (Model 2700). The setup was calibrated with a certified silicon solar cell (Fraunhofer ISE) prior to measurements. Electron lifetime was measured by the custom-made “toolbox setup” using a white-light-emitting diode (Luxeon Star 1W) as light source. The solar cell device samples used in photoinduced absorption (PIA) measurements were prepared as described above except the Ag contact layer. PIA spectra were recorded in a lab constructed setup<sup>3</sup>. A 20W tungsten-halogen lamp, filtered up to 530 nm, generated the white probe light. A square-wave modulated (on-off) green light source (Lasermate GML532-100FLE, 532nm) was used for excitation. The transmitted probe light was focused onto a monochromator and detected by a UV-enhanced silicon and germanium photodiode detector.  $6.1 \text{ mW}\cdot\text{cm}^{-2}$  light intensity and 9.3 Hz modulation frequency were used for the blue LED excitation.

### 1.3. Fabrication of dye-sensitized solar cells

**Liquid-state DSCs:** For cobalt electrolyte, the FTO glass was immersed into 40 mM  $\text{TiCl}_4$  aqueous solution at  $70 \text{ }^\circ\text{C}$  for 30 min and sintered at  $450 \text{ }^\circ\text{C}$  for 30min in advance to form a compact  $\text{TiO}_2$  layer. Then the  $\text{TiO}_2$  films consisting of a  $4 \text{ }\mu\text{m}$  layer of Dyesol 90-T  $\text{TiO}_2$  paste and a  $4 \text{ }\mu\text{m}$  scattering layer were coated on the treated FTO conducting glass by screen-printing, followed by sintered gradually up to  $500 \text{ }^\circ\text{C}$  and kept at this temperature for 30 min before cooling. While for iodine electrolyte, four  $4 \text{ }\mu\text{m}$  layers of Dyesol 90-T  $\text{TiO}_2$  paste and a  $4 \text{ }\mu\text{m}$  scattering layer were screen-printed onto the well-cleaned FTO glass and sintered gradually up to  $500 \text{ }^\circ\text{C}$  for 30 min. After cooling down to the room temperature, the obtained photoanodes for both electrolytes were immersed into 40 mM  $\text{TiCl}_4$  aqueous solution at  $70 \text{ }^\circ\text{C}$  for 30 min and sintered at  $450 \text{ }^\circ\text{C}$  for 30 min after washed with redistilled water and anhydrous ethanol. The cooled photoanodes were placed into 5 mM CDCA bath in  $\text{CH}_3\text{CH}_2\text{OH}$  for 30min in advance, and then placed into  $3\times 10^{-4} \text{ M}$  dye bath in  $\text{CH}_2\text{Cl}_2$  solution for 2 h and 4 h with cobalt and iodine electrolytes, respectively. Then the photoanodes were washed with anhydrous ethanol and  $\text{CH}_2\text{Cl}_2$ , respectively. The dye-sensitized photoanodes were sealed with platinized counter electrodes by a hot-melt film (25- $\mu\text{m}$ -thick Surlyn, Dupont). The electrolytes were injected into the cells from the drilled holes in the counter electrodes and finally sealed the holes with a UV-melt gum. The cobalt electrolyte consisted of 0.25 M  $[\text{Co(II)(bpy)}_3]\text{TFSI}_2$ , 0.06 M  $[\text{Co(III)(bpy)}_3]\text{TFSI}_3$ , 0.05 M LiTFSI, and 0.5 M 4-tert-butylpyridine in acetonitrile and the iodine electrolyte consists of 0.05 M  $\text{I}_2$ , 0.1 M LiI, 0.5 M GuSCN, 0.5 M TPB, 0.6 M BMII, 0.1 M DMPII. The active area of all liquid-state DSCs is  $0.12 \text{ cm}^2$ .

**solid-state DSCs:** Fluorine-doped tin-oxide (FTO) coated glass substrates ( Pilkington TEC15) were pre-treated as previously reported.<sup>4</sup> A compact  $\text{TiO}_2$  blocking layer was deposited onto the surface of a pre-cleaned FTO substrate by spray pyrolysis on a hotplate at  $450 \text{ }^\circ\text{C}$  using an airbrush. The solution used in the spray pyrolysis was 0.2 M Ti-isopropoxide, 2 M

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acetylacetone in isopropanol. In all electrode preparations 10 spray cycles were used as standard parameter. Nanoporous TiO<sub>2</sub> films were coated on the compact TiO<sub>2</sub> layer by screen-printing of a diluted TiO<sub>2</sub> paste (Dyesol DSL 18NR-T) with terpineol (2:1, mass ratio). The thickness of the film is ca. 2.2 μm, as measured with a DekTak profilometer. After sintering the TiO<sub>2</sub> film on a hotplate at 500 °C for 30 min, the film was cooled to room temperature and immersed in 0.02 M aqueous TiCl<sub>4</sub> at 70 °C for 30 min. The film was then rinsed by deionized water and then annealed on a hotplate at 500 °C for 30 min. After cooling to 90 °C, the film was immersed for 3 h in 0.1 mM solution (tert-butanol: acetonitrile=1:1) of **S4**, **S5** and **LEG4**, and then the sensitized electrodes were rinsed by ethanol and dried. Subsequently, the HTM solutions were prepared by dissolving the Spiro-OMeTAD in chlorobenzene at a concentration of 150 mM, with addition of LiTFSI (20 mM, from a stock solution in acetonitrile with concentration of 0.5 M), t-BP (200 mM, from a stock solution in chlorobenzene with concentration of 1.0 M) and 4% 1,1,2,2-tetrachloroethane (TeCA) solvent (volume ratio relative to chlorobenzene). The Spiro-OMeTAD solution was left on the sensitized electrode for 30 s and then followed by spin-coating for 30 s with 2000 rpm. All of the Spiro-OMeTAD solutions were prepared in glove box under nitrogen atmosphere; chlorobenzene and acetonitrile were deaerated by bubbling with dry nitrogen for half hours before introducing into glove box environment. The Spiro-OMeTAD solution was stored in glove box for aging over night before using. Subsequently, a 200 nm thick. Ag back contact was deposited onto the organic semiconductor by thermal evaporation in a vacuum chamber with a base pressure of about 10<sup>-6</sup> bar, to complete the device fabrication.

#### 1.4. Synthesis of sensitizers

*5-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)-8-bromo-2,3-diphenylpyrido[3,4-b]pyrazine (1a)*: Under an argon atmosphere, 5,8-dibromo-2,3-diphenylpyrido[3,4-b]pyrazine (484 mg, 1 mmol) and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (35 mg, 0.05 mmol) were dissolved in anhydrous toluene (25 mL) and heated to 50 °C. Then a solution of (4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)tributylstannane (1.1 mmol) was injected in toluene slowly. The mixture was heated to 120 °C for 11 h before cooling down to the room temperature. The raw product was extracted using EA and water. The organic layers were combined and dried by anhydrous Na<sub>2</sub>SO<sub>4</sub>. After evaporating under reduced pressure and the residue was purified by column chromatography with CH<sub>2</sub>Cl<sub>2</sub>/PE (1:2 by volume) to give **1a** as red solid (666.9 mg, 87.6% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (TMS, ppm): δ = 8.79 (s, 1H), 8.53 (m, 1H), 7.61 (d, 4H, J = 8 Hz), 7.39-7.29 (m, 6H), 7.18 (d, 1H, J = 4 Hz), 6.91 (d, 1H, J = 4 Hz), 1.93-1.79 (m, 4H), 1.35-1.18 (m, 5H), 0.91-0.77 (m, 14H), 0.67-0.64 (m, 5H), 0.71-0.58 (m, 6H), 0.53-0.50 (m, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz), δ (TMS, ppm): 158.72, 155.92, 152.75, 152.36, 147.21, 143.27, 140.95, 138.73, 136.97, 136.75, 136.01, 133.79, 132.80, 129.23, 129.18, 128.94, 128.51, 127.95, 127.39, 127.36, 126.23, 125.40, 121.36, 114.38, 52.51, 42.26, 34.18, 33.21, 33.07, 30.91, 30.41, 29.17, 28.69, 28.65, 28.36, 27.50, 27.46, 27.14, 26.39, 26.32, 25.77, 21.73, 21.68, 16.30, 13.11, 13.04, 12.94, 12.58, 9.64, 9.58. HRMS (ESI) m/z: [M + H]<sup>+</sup> calcd for C<sub>44</sub>H<sub>49</sub>BrN<sub>3</sub>S<sub>2</sub>, 762.2551; found, 762.2526.

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*6-(8-bromo-2,3-diphenylpyrido[3,4-b]pyrazin-5-yl)-4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2-carbaldehyde (2a)*: Under an argon atmosphere, Compound **1a** (380.6 mg, 0.5 mmol), was dissolved in anhydrous *N,N*-dimethylformamide (25 mL) in an ice bath for 20 min. Phosphorus oxychloride (0.05 mL, 0.55 mmol) was added with anhydrous *N,N*-dimethylformamide (5 mL) slowly and stirred at 0 °C for 30 min. Then the mixture was heated to 65 °C for 4 h. After cooling, the mixture was poured into ice water. The precipitates were extracted with CH<sub>2</sub>Cl<sub>2</sub> and dried by anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic layer was concentrated under reduced pressure and the crude product was purified by column chromatography with CH<sub>2</sub>Cl<sub>2</sub>/PE (1:1 by volume) to give **2a** as salmon pink solid (361.1 mg, 91.5% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (TMS, ppm): δ = 9.87 (s, 1H), 8.93 (m, 1H), 8.61 (d, 1H, *J* = 4 Hz), 7.71-7.67 (m, 4H), 7.61 (d, 1H, *J* = 4 Hz), 7.50-7.44 (m, 4H), 7.41-7.37 (m, 2H), 2.04-1.97 (m, 4H), 1.29-1.25 (m, 5H), 1.01-0.90 (m, 12H), 0.74-0.71 (m, 5H), 0.63-0.58 (m, 8H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz), δ (TMS, ppm): 182.65, 161.93, 159.16, 157.43, 154.35, 152.56, 148.18, 147.64, 144.24, 144.12, 142.33, 141.98, 137.79, 137.59, 133.79, 130.60, 130.30, 130.21, 129.85, 128.57, 128.49, 126.64, 117.11, 54.05, 43.14, 35.38, 35.34, 34.27, 34.16, 31.48, 30.22, 29.73, 29.47, 28.50, 28.45, 27.50, 27.42, 22.78, 22.73, 14.10, 13.99, 10.69, 10.64. HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>45</sub>H<sub>49</sub>BrN<sub>3</sub>OS<sub>2</sub>, 790.2500; found, 790.2504.

*5-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)-8-bromo-2,3-diphenylquinoxaline (1b)*: Compound **1b** was synthesized in a similar way to compound **1a** by 5,8-dibromo-2,3-diphenylquinoxaline (438 mg, 1 mmol) with (4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)tributylstannane (1.1 mmol). The residue was purified by column chromatography with CH<sub>2</sub>Cl<sub>2</sub>/PE (1:4 by volume) to give **1b** as orange solid (321.6 mg, 42.3% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (TMS, ppm): δ = 8.03 (d, 1H, *J* = 8 Hz), 7.97-7.94 (m, 1H), 7.79 (s, 1H), 7.74-7.67 (m, 4H), 7.44-7.35 (m, 6H), 7.18 (d, 1H, *J* = 4 Hz), 6.97-6.96 (m, 1H), 1.98-1.87 (m, 4H), 1.39-1.25 (m, 2H), 1.01-0.89 (m, 16H), 0.77-0.70 (m, 6H), 0.64-0.58 (m, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz), δ (TMS, ppm): 158.14, 157.13, 153.19, 152.23, 141.88, 138.29, 137.73, 133.11, 130.51, 130.27, 129.31, 129.19, 128.33, 125.89, 125.06, 122.42, 121.86, 121.02, 53.44, 43.36, 35.09, 34.26, 34.12, 28.61, 28.58, 27.40, 22.80, 22.78, 14.10, 14.07, 10.71, 10.61. HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>45</sub>H<sub>50</sub>BrN<sub>3</sub>S<sub>2</sub>, 761.2599; found, 761.2607.

*6-(8-bromo-2,3-diphenylquinoxalin-5-yl)-4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2-carbaldehyde (2b)*: Compound **2b** was synthesized in a similar way to compound **2a** by 5-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)-8-bromo-2,3-diphenylquinoxaline (380 mg, 0.5 mmol) with phosphorus oxychloride (0.05 mL, 0.55 mmol). The residue was purified by column chromatography with CH<sub>2</sub>Cl<sub>2</sub>/PE (1:2 by volume) to give **2b** as orange solid (317.7 mg, 80.6% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (TMS, ppm): δ = 9.85 (s, 1H), 8.07 (d, 1H, *J* = 8 Hz), 8.01-7.98 (m, 1H), 7.80 (s, 1H), 7.72-7.67 (m, 4H), 7.59 (d, 1H, *J* = 4 Hz), 7.47-7.35 (m, 6H), 2.02-1.96 (m, 4H), 1.01-0.90 (m, 18H), 0.76-0.73 (m, 3H), 0.66-0.59 (m, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz), δ (TMS, ppm): 182.53, 161.16, 157.84, 153.56, 152.74, 148.31, 143.30, 142.51, 140.33, 138.07, 137.69, 133.09, 132.73, 130.44, 130.26, 129.45, 128.43, 128.37, 126.57, 122.77, 121.55, 53.91, 43.25, 35.26, 34.26, 29.70, 28.54, 27.50, 27.38, 22.77, 22.73, 14.07, 10.67, 10.59. HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>46</sub>H<sub>50</sub>BrN<sub>2</sub>OS<sub>2</sub>, 789.2548; found, 789.2555.

6-(8-(6-((2',4'-bis(octyloxy)-[1,1'-biphenyl]-4-yl)(2,2'',4,4''-tetrakis(octyloxy)-[1,1':3',1''-terphenyl]-4'-yl)amino)-4,4-dimethyl-4H-indeno[1,2-b]thiophen-2-yl)-2,3-diphenylpyrido[3,4-b]pyrazin-5-yl)-4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2-carbaldehyde (**3a**): Under an argon atmosphere, compound **2a** (157.8 mg, 0.2 mmol) and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (35 mg, 0.05 mmol) were dissolved in anhydrous toluene (20 mL) and heated to 50 °C. Then a solution of N-(2',4'-bis(octyloxy)-[1,1'-biphenyl]-4-yl)-4,4-dimethyl-N-(2,2'',4,4''-tetrakis(octyloxy)-[1,1':3',1''-terphenyl]-4'-yl)-2-(trimethylstannyl)-4H-indeno[1,2-b]thiophen-6-amine (0.25 mmol) was injected in toluene slowly. The mixture was heated to 120 °C and refluxed for 11 h before cooling down. The raw product was extracted with EA. The organic layers were collected and dried by anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the residue was purified by column chromatography with CH<sub>2</sub>Cl<sub>2</sub>/PE (1:1 by volume) to give **3a** as green solid (176.6 mg, 42.6% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (TMS, ppm): 9.87 (s, 1H), 9.16 (s, 1H), 8.60 (d, 1H, J = 8 Hz), 7.87 (s, 1H), 7.79-7.76 (m, 2H), 7.75-7.72 (m, 2H), 7.61 (d, 1H, J = 4 Hz), 7.54 (d, 1H, J = 8 Hz), 7.50-7.44 (m, 5H), 7.42-7.37 (m, 5H), 7.30 (d, 2H, J = 8 Hz), 7.16 (d, 1H, J = 8 Hz), 7.02 (d, 3H, J = 12 Hz), 6.91 (s, 1H), 6.75 (d, 1H, J = 8 Hz), 6.56-6.51 (m, 4H), 6.24 (d, 1H, J = 8 Hz), 6.09 (s, 1H), 3.89-3.83 (m, 8H), 3.67-3.63 (m, 2H), 3.44 (s, 2H), 2.05-1.97 (m, 4H), 1.58 (s, 6H), 1.38-1.32 (m, 24H), 1.29-1.23 (m, 24H), 0.97-0.84 (m, 51H), 0.77-0.74 (m, 12H), 0.64-0.59 (m, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz), δ (TMS, ppm): 189.46, 181.54, 161.20, 158.79, 158.60, 158.51, 156.54, 156.49, 156.24, 156.22, 156.19, 156.11, 155.92, 155.89, 154.53, 152.27, 148.71, 148.56, 147.12, 144.44, 143.62, 143.28, 142.74, 142.45, 140.36, 137.26, 137.03, 136.02, 135.23, 135.17, 134.12, 133.84, 133.41, 130.27, 129.97, 129.90, 129.70, 129.55, 129.45, 129.17, 128.86, 128.80, 128.68, 128.64, 128.58, 128.49, 128.40, 127.49, 127.33, 127.04, 126.50, 125.28, 122.43, 122.34, 122.27, 122.19, 120.33, 120.17, 120.05, 119.35, 104.09, 102.99, 99.19, 99.08, 98.18, 98.08, 76.33, 69.56, 69.48, 69.12, 68.87, 52.93, 44.52, 42.20, 38.45, 38.35, 38.32, 34.35, 34.31, 33.21, 33.12, 29.60, 29.55, 29.47, 28.67, 28.30, 28.10, 28.04, 27.99, 27.92, 27.46, 27.42, 26.45, 26.37, 25.47, 25.15, 24.94, 23.02, 22.88, 22.77, 22.06, 22.02, 21.89, 21.74, 21.70, 21.67, 13.13, 13.09, 13.07, 12.93, 10.25, 10.18, 10.13, 10.10, 10.06, 9.61. HRMS (ESI) m/z: [M + H]<sup>+</sup> calcd for C<sub>136</sub>H<sub>177</sub>N<sub>4</sub>O<sub>7</sub>S<sub>3</sub>, 2074.2779; found, 2074.2788.

6-(8-(6-((2',4'-bis(octyloxy)-[1,1'-biphenyl]-4-yl)(2,2'',4,4''-tetrakis(octyloxy)-[1,1':3',1''-terphenyl]-4'-yl)amino)-4,4-dimethyl-4H-indeno[1,2-b]thiophen-2-yl)-2,3-diphenylquinoxalin-5-yl)-4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2-carbaldehyde (**3b**): Compound **3b** was synthesized in a similar way to compound **3a** by compound **2b** (157.6 mg, 0.2 mmol), N-(2',4'-bis(octyloxy)-[1,1'-biphenyl]-4-yl)-4,4-dimethyl-N-(2,2'',4,4''-tetrakis(octyloxy)-[1,1':3',1''-terphenyl]-4'-yl)-2-(trimethylstannyl)-4H-indeno[1,2-b]thiophen-6-amine (0.25 mmol). The residue was purified by column chromatography with CH<sub>2</sub>Cl<sub>2</sub>/PE (1:1 by volume) to give **3b** as green solid (151.3 mg, 36.5% yield). <sup>1</sup>H NMR (CO(CD<sub>3</sub>)<sub>2</sub>, 400 MHz), δ (TMS, ppm): 9.79 (s, 1H), 8.32 (d, 1H, J = 8 Hz), 8.23-8.19 (m, 1H), 8.14 (d, 1H, J = 4 Hz), 7.97 (d, 1H, J = 4 Hz), 7.91-7.88 (m, 1H), 7.71-7.67 (m, 4H), 7.42-7.40 (m, 1H), 7.37-7.35 (m, 4H), 7.32 (d, 3H, J = 4 Hz), 7.22 (d, 3H, J = 8 Hz), 7.19 (s, 1H), 7.10 (d, 1H, J = 4 Hz), 7.08 (d, 1H, J = 4 Hz), 6.93 (d, 1H, J = 8 Hz), 6.88 (d, 2H, J = 12 Hz), 6.81 (s, 1H), 6.64 (d, 1H, J = 8 Hz), 6.55-6.53 (m, 2H), 6.50-6.45 (m, 2H), 6.18 (d, 1H, J = 4 Hz), 6.11 (s, 1H), 3.83-3.80 (m, 8H), 3.59 (d, 2H, J = 4 Hz), 3.40 (s, 2H), 2.04-2.00 (m, 4H), 1.42-1.33 (m, 12H), 1.27-1.21 (m, 24H), 1.19-1.12 (m, 24H), 0.84-0.77 (m, 24H), 0.75-0.69 (m, 21H), 0.67-0.59 (m, 12H), 0.53-0.50

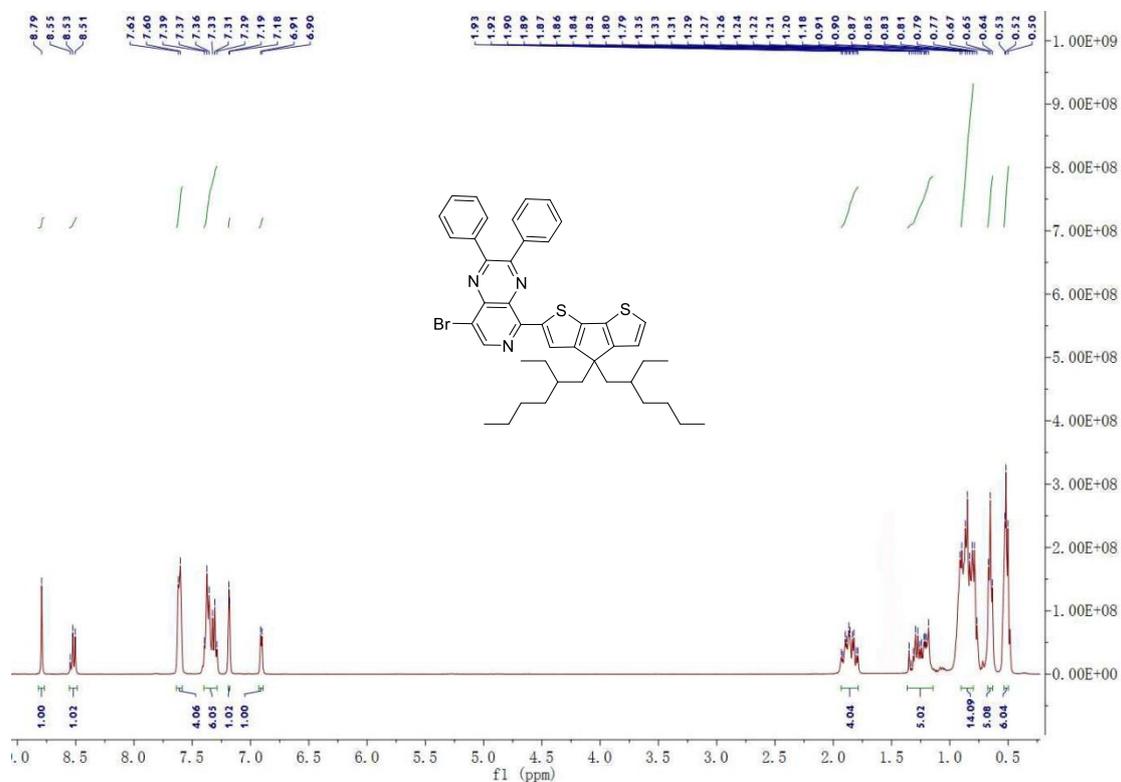
(m, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz), δ (TMS, ppm): 190.58, 159.63, 156.96, 138.57, 130.54, 130.47, 129.77, 129.24, 129.12, 128.43, 128.22, 105.20, 105.14, 105.11, 105.10, 105.08, 105.05, 104.12, 104.08, 100.41, 100.33, 100.28, 100.24, 100.21, 100.20, 100.20, 100.15, 100.12, 99.22, 99.21, 70.64, 70.57, 70.52, 70.16, 53.81, 43.28, 39.52, 39.42, 39.38, 35.33, 35.28, 34.34, 34.31, 34.21, 31.97, 30.66, 30.61, 30.52, 29.74, 29.70, 29.41, 29.17, 29.10, 29.06, 28.99, 28.59, 28.56, 27.59, 27.56, 27.41, 24.08, 23.94, 23.86, 23.83, 23.12, 23.10, 23.09, 23.07, 22.95, 22.82, 22.80, 22.74, 14.20, 14.16, 14.12, 14.10, 11.33, 11.27, 11.20, 11.16, 11.13, 10.74, 10.72, 10.64. HRMS (ESI) m/z: [M + H]<sup>+</sup> calcd for C<sub>137</sub>H<sub>178</sub>N<sub>3</sub>O<sub>7</sub>S<sub>3</sub>, 2073.2827; found, 2073.2832.

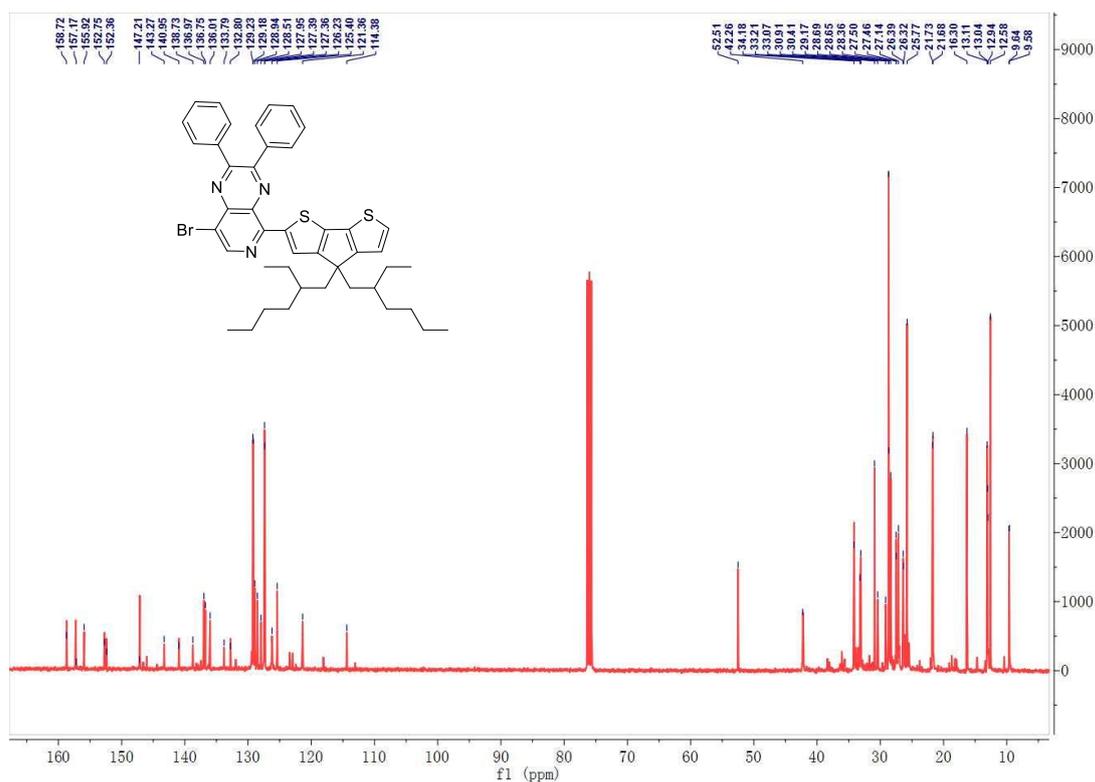
*(E)-3-(6-(8-(6-((2',4'-bis(octyloxy)-[1,1'-biphenyl]-4-yl)(2,2'',4,4''-tetrakis(octyloxy)-[1,1':3',1''-terphenyl]-4'-yl)amino)-4,4-dimethyl-4H-indeno[1,2-b]thiophen-2-yl)-2,3-diphenylpyrido[3,4-b]pyrazin-5-yl)-4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)-2-cyanoacrylic acid (S4)*: Under an argon atmosphere, a mixture of compound **3a** (124.4 mg, 0.06 mmol), 2-cyanoacetic acid (85 mg, 1 mmol) and ammonium acetate (115 mg, 1.5 mmol) in acetic acid (15 mL) and 5 mL THF was heated at refluxed for 10 h before cooling down. The mixture was poured into 200 mL water and stirred for 30 min. The precipitates were collected by filtration and purified by column chromatography with CH<sub>2</sub>Cl<sub>2</sub>/methanol (20:1 by volume) to give **S4** as blue solid (105.3 mg, 82% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (TMS, ppm): 9.11 (s, 1H), 8.50 (d, 1H, J = 4 Hz), 8.27 (s, 1H), 7.82 (s, 1H), 7.70 (d, 2H, J = 8 Hz), 7.67-7.65 (m, 2H), 7.48-7.40 (m, 6H), 7.37-7.33 (m, 4H), 7.31 (d, 2H, J = 8 Hz), 7.24-7.21 (m, 3H), 7.09 (d, 1H, J = 8 Hz), 6.95 (d, 2H, J = 12 Hz), 6.84 (s, 1H), 6.69 (d, 1H, J = 8 Hz), 6.48-6.44 (m, 4H), 6.17 (d, 1H, J = 8 Hz), 6.02 (s, 1H), 3.84-3.75 (m, 8H), 3.58 (s, 2H), 3.36 (s, 2H), 1.96-1.93 (m, 4H), 1.30-1.24 (m, 24H), 1.21-1.19 (m, 36H), 0.90-0.85 (m, 24H), 0.81-0.77 (m, 21H), 0.70-0.66 (m, 12H), 0.57-0.53 (m, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz), δ (TMS, ppm): 178.42, 167.25, 162.18, 158.77, 158.56, 158.50, 156.22, 156.10, 155.90, 145.55, 138.61, 137.09, 136.98, 135.92, 135.59, 135.22, 133.84, 133.37, 133.28, 129.96, 129.71, 129.70, 129.55, 129.46, 129.12, 128.89, 128.86, 128.79, 128.73, 128.67, 128.64, 128.40, 127.64, 127.34, 126.50, 124.50, 122.39, 122.31, 120.30, 115.80, 104.05, 102.95, 99.17, 98.15, 92.32, 69.55, 69.47, 69.09, 52.92, 44.50, 42.19, 42.14, 38.44, 38.42, 38.35, 38.30, 34.37, 33.13, 32.94, 30.90, 29.60, 29.54, 29.45, 28.67, 28.65, 28.64, 28.57, 28.42, 28.34, 28.23, 28.10, 28.05, 28.03, 27.99, 27.92, 27.39, 26.36, 25.15, 23.68, 23.01, 22.87, 22.76, 22.06, 22.04, 22.02, 22.01, 21.88, 21.76, 21.71, 21.67, 13.13, 13.10, 13.06, 13.02, 12.94, 10.25, 10.20, 10.12, 10.09, 10.06, 9.57. HRMS (ESI) m/z: [M + H]<sup>+</sup> calcd for C<sub>139</sub>H<sub>178</sub>N<sub>5</sub>O<sub>8</sub>S<sub>3</sub>, 2141.2838; found, 2141.1890.

*(E)-3-(6-(8-(6-((2',4'-bis(octyloxy)-[1,1'-biphenyl]-4-yl)(2,2'',4,4''-tetrakis(octyloxy)-[1,1':3',1''-terphenyl]-4'-yl)amino)-4,4-dimethyl-4H-indeno[1,2-b]thiophen-2-yl)-2,3-diphenylquinoxalin-5-yl)-4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)-2-cyanoacrylic acid (S5)*: **S5** was synthesized in a similar way to **S4** by compound **3b** (103.6 mg, 0.05 mmol) with 2-cyanoacetic acid (85 mg, 1 mmol) and ammonium acetate (115 mg, 1.5 mmol) in acetic acid (15 mL) and 5 mL THF. The residue was purified by column chromatography with CH<sub>2</sub>Cl<sub>2</sub>/methanol (20:1 by volume) to give **S5** as blue solid (91.6 mg, 85.6% yield). <sup>1</sup>H NMR (CO(CD<sub>3</sub>)<sub>2</sub>, 400 MHz), δ (TMS, ppm): 8.31 (s, 1H), 8.24 (s, 1H), 8.10 (d, 2H, J = 16 Hz), 7.89 (d, 1H, J = 8 Hz), 7.83 (d, 1H, J = 12 Hz), 7.65-7.62 (m, 4H), 7.36 (d, 2H, J = 12 Hz), 7.31-7.26 (m, 7H), 7.19-7.15 (m, 4H), 7.08-7.03 (m, 2H), 6.87 (d, 2H, J = 8 Hz), 6.78 (s, 1H), 6.61 (d, 1H, J = 8 Hz), 6.50 (d, 2H, J = 4 Hz), 6.44-6.40 (m, 2H), 6.14 (d, 1H, J = 8 Hz), 6.07 (s, 1H), 3.78-3.74 (m, 8H), 3.54 (s, 2H), 3.36 (s, 2H), 1.58-1.50 (m, 4H), 1.34-1.27 (m, 12H), 1.23-1.16 (m, 24H), 1.14-1.07 (m, 24H),

0.80-0.73 (m, 27H), 0.71-0.59 (m, 30H), 0.52-0.47 (m, 9H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz),  $\delta$  (TMS, ppm): 166.65, 159.87, 159.64, 159.61, 158.57, 157.30, 157.19, 156.99, 152.41, 152.11, 149.10, 146.48, 146.18, 143.74, 143.52, 139.95, 138.41, 138.38, 136.28, 136.04, 135.01, 134.50, 131.05, 130.93, 130.89, 130.78, 130.64, 129.74, 129.51, 129.35, 129.33, 129.13, 127.91, 127.62, 123.45, 123.35, 122.77, 122.70, 121.39, 120.63, 119.48, 119.45, 117.30, 116.78, 105.16, 104.09, 100.27, 99.26, 70.64, 70.54, 70.24, 70.03, 45.81, 39.52, 39.49, 39.40, 30.67, 30.62, 30.53, 29.75, 29.71, 29.18, 29.09, 29.06, 29.00, 26.15, 24.11, 23.96, 23.91, 23.83, 23.14, 23.12, 23.10, 23.08, 23.02, 14.21, 14.18, 14.15, 11.28, 11.21, 11.19, 11.13. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{140}\text{H}_{179}\text{N}_4\text{O}_8\text{S}_3$ , 2140.2885; found, 2140.2881.

### 1.5. Characterization of intermediates and compounds S4, S5





### Elemental Composition Report

Page 1

#### Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

31 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)

Elements Used:

C: 0-44 H: 0-200 N: 0-3 S: 0-2 Br: 0-1

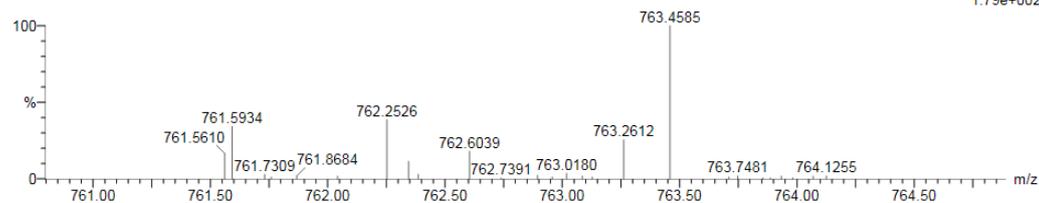
JL-HUA

ECUST institute of Fine Chem

23-Mar-2016

HL-SZJ-503 129 (0.892) Cm (128:130)

22:31:50  
1: TOF MS ES+  
1.79e+002

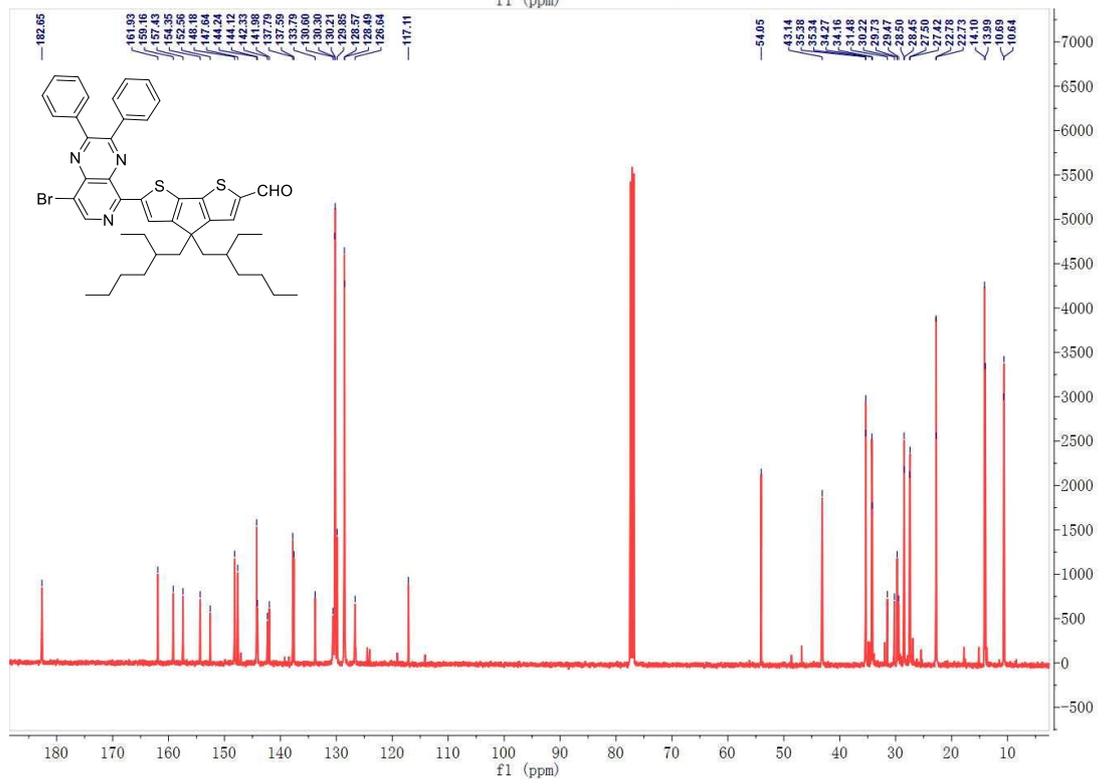
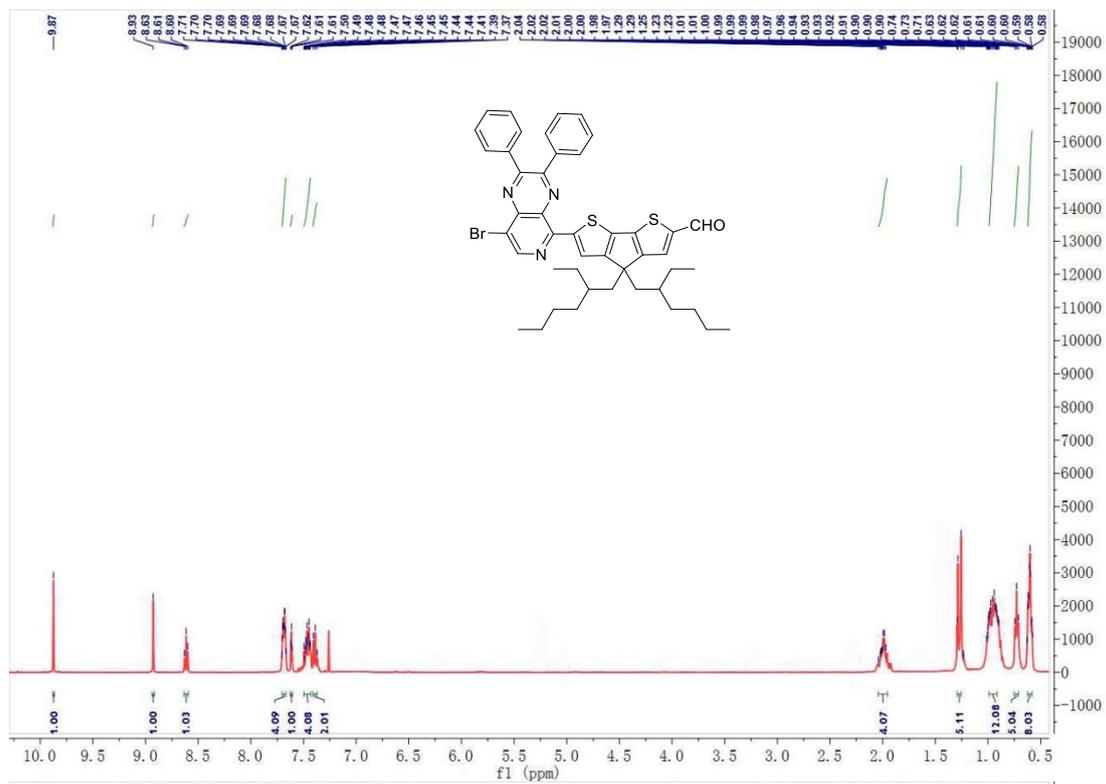


Minimum:

Maximum: 300.0 50.0 -1.5 100.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
762.2526	762.2551	-2.5	-3.3	21.5	78.9	0.0	C44 H49 N3 S2 Br

Fig. S1  $^1\text{H}/^{13}\text{C}$  NMR spectroscopy and HR Mass spectrometry of compound 1a.



## Elemental Composition Report

Page 1

### Single Mass Analysis

Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

393 formula(e) evaluated with 35 results within limits (up to 1 best isotopic matches for each mass)

Elements Used:

C: 0-54 H: 0-50 N: 1-3 O: 0-6 S: 0-2 Br: 0-1

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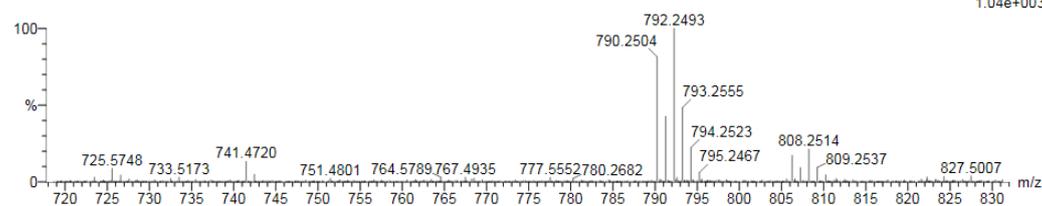
05-Sep-2014

HL-SZJ-114 81 (2.586) Cm (81:84)

18:41:31

1: TOF MS ES+

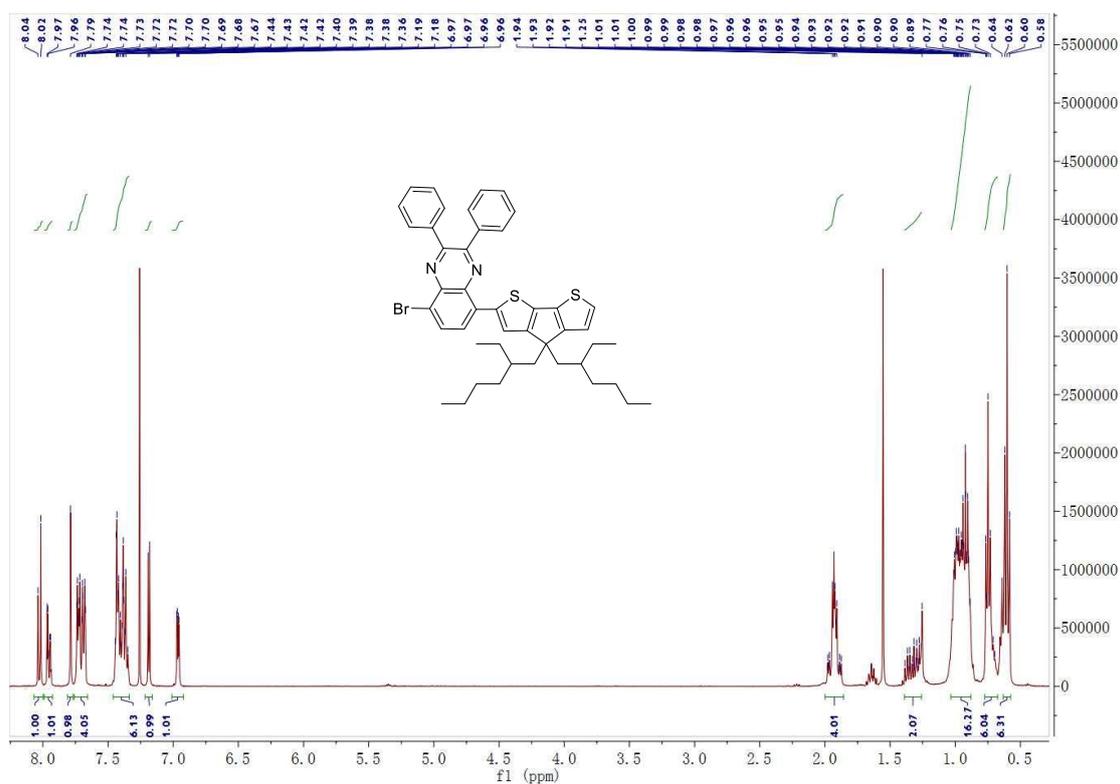
1.04e+003

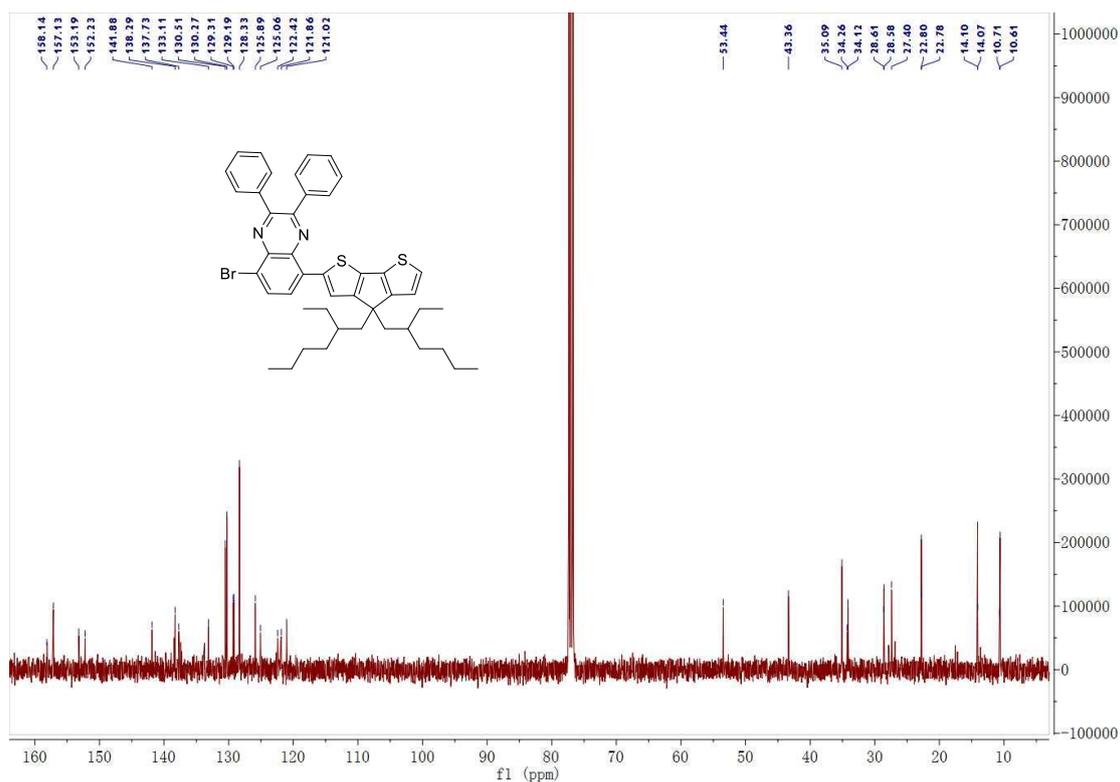


Minimum: -1.5  
Maximum: 100.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
790.2504	790.2500	0.4	0.5	22.5	64.7	0.0	C45 H49 N3 O S2 Br

Fig. S2  $^1\text{H}/^{13}\text{C}$  NMR spectroscopy and HR Mass spectrometry of compound 2a.





### Elemental Composition Report

#### Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

26 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)

Elements Used:

C: 0-46 H: 0-90 N: 0-2 S: 0-2 Br: 0-1

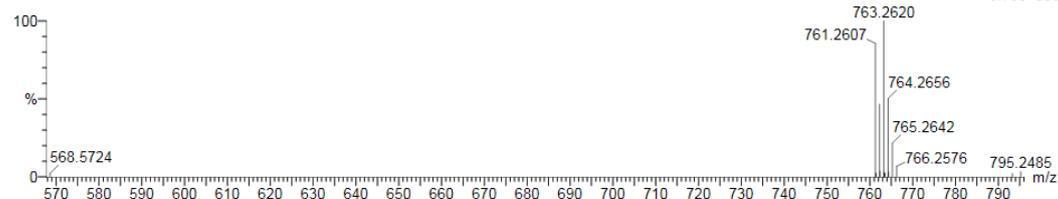
JL-HUA

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Page 1

HL-LX-131 167 (1.124) Cm (164:169)

23-Apr-2015  
21:18:11  
1: TOF MS ES+  
6.78e+003



Minimum: -1.5  
Maximum: 300.0 50.0 100.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
761.2607	761.2599	0.8	1.1	21.5	40.5	0.0	C45 H50 N2 S2 Br

Fig. S3  $^1\text{H}/^{13}\text{C}$  NMR spectroscopy and HR Mass spectrometry of compound 1b.



## Elemental Composition Report

Page 1

### Single Mass Analysis

Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0  
 Element prediction: Off  
 Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

353 formula(e) evaluated with 33 results within limits (up to 1 best isotopic matches for each mass)

Elements Used:

C: 0-54 H: 0-60 N: 1-3 O: 0-6 S: 0-2 Br: 0-1

HUA-JL

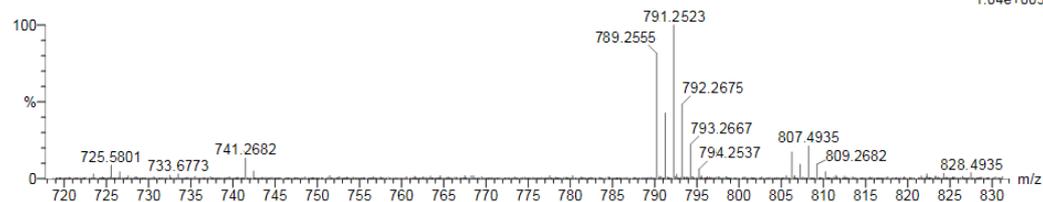
ECUST institute of Fine Chem

04-Sep-2014

18:48:14

1: TOF MS ES+

1.04e+003

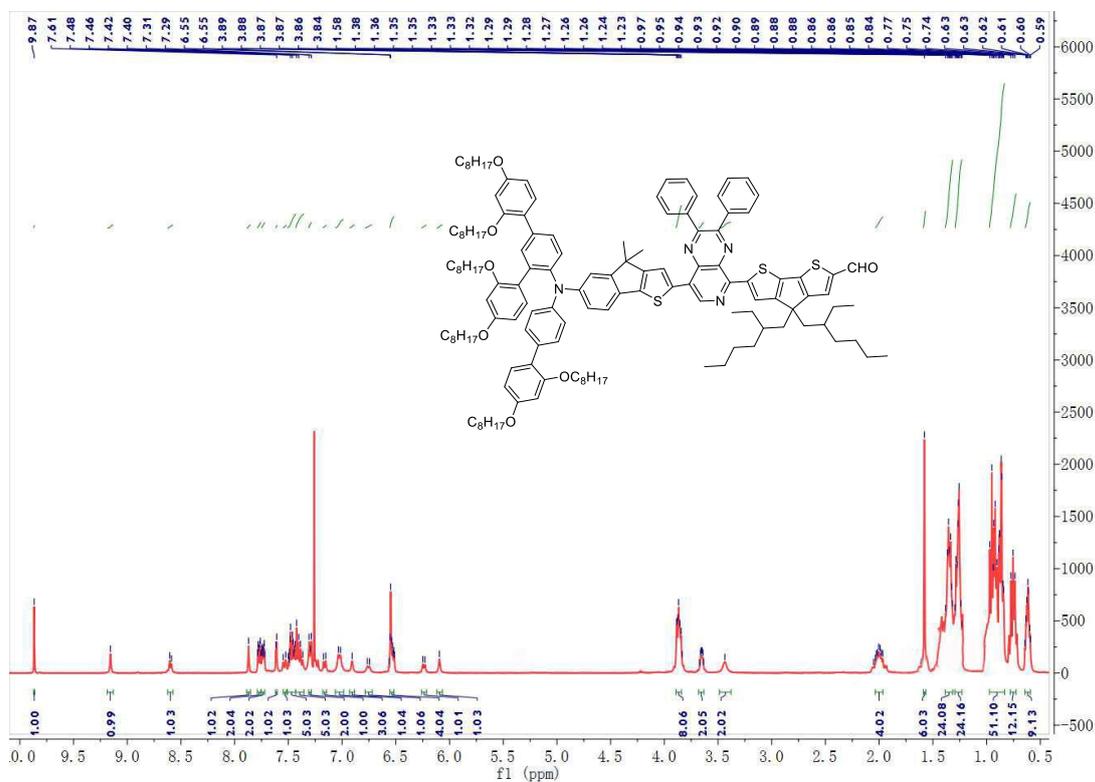


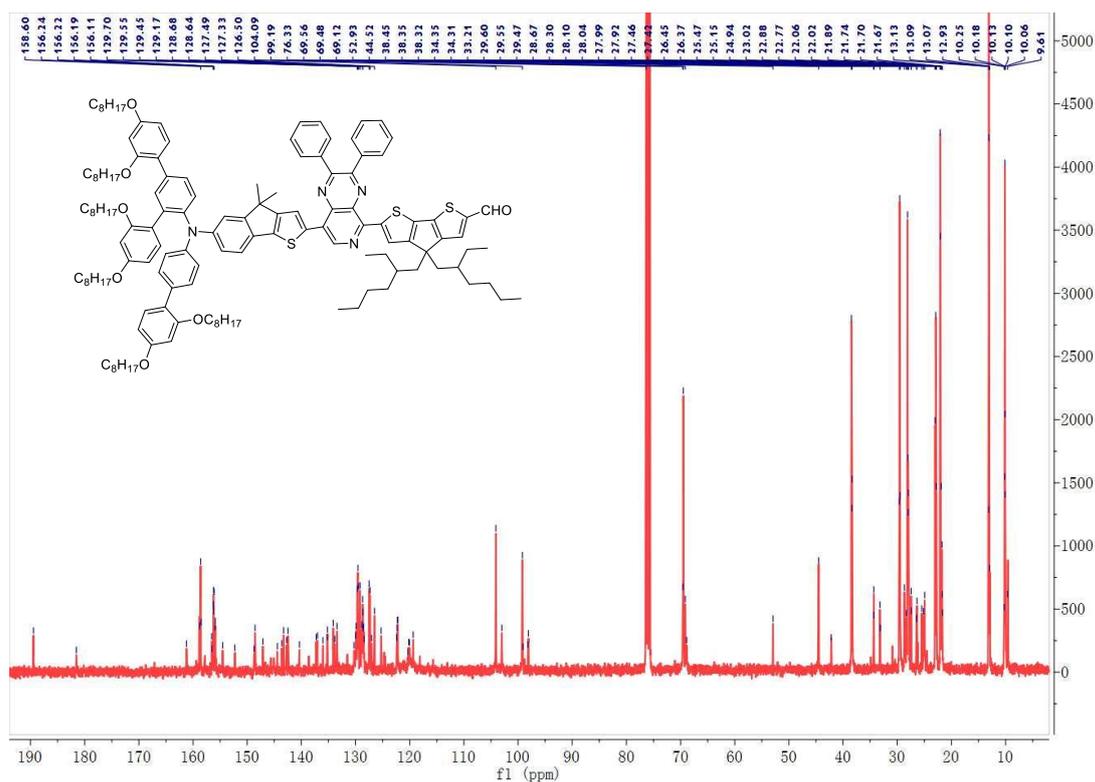
Minimum:

Maximum: 300.0 50.0 -1.5 100.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
789.2555	789.2548	0.4	0.6	25.5	67.7	0.0	C <sub>46</sub> H <sub>50</sub> N <sub>2</sub> O S <sub>2</sub> Br

Fig. S4 <sup>1</sup>H/<sup>13</sup>C NMR spectroscopy and HR Mass spectrometry of compound 2b.





### Elemental Composition Report

#### Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

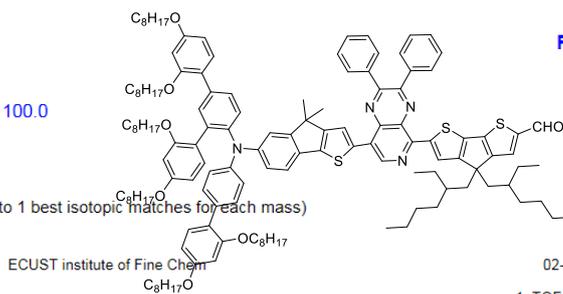
105 formula(e) evaluated with 2 results within limits (up to 1 best isotopic matches for each mass)

Elements Used:

C: 0-136 H: 0-200 N: 0-4 O: 0-7 S: 0-3

GR-CHEN

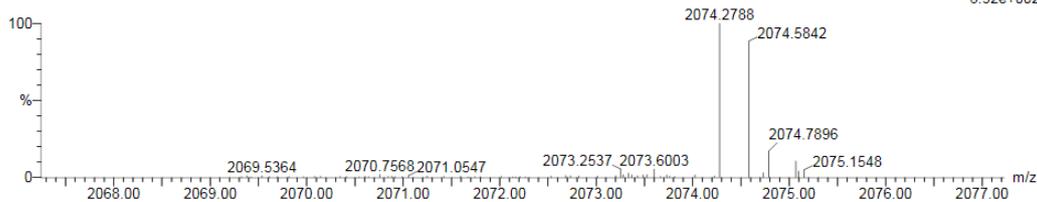
HL-SZJ-313 11 (0.162) Cm (6:16)



Page 1

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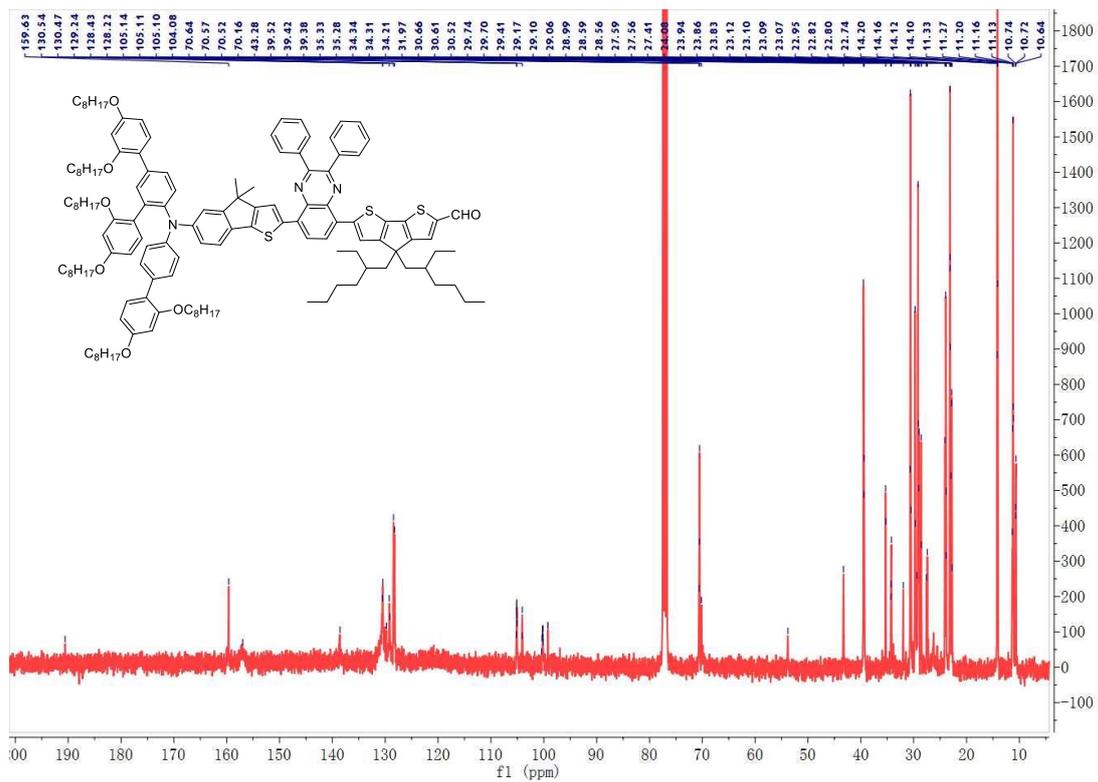
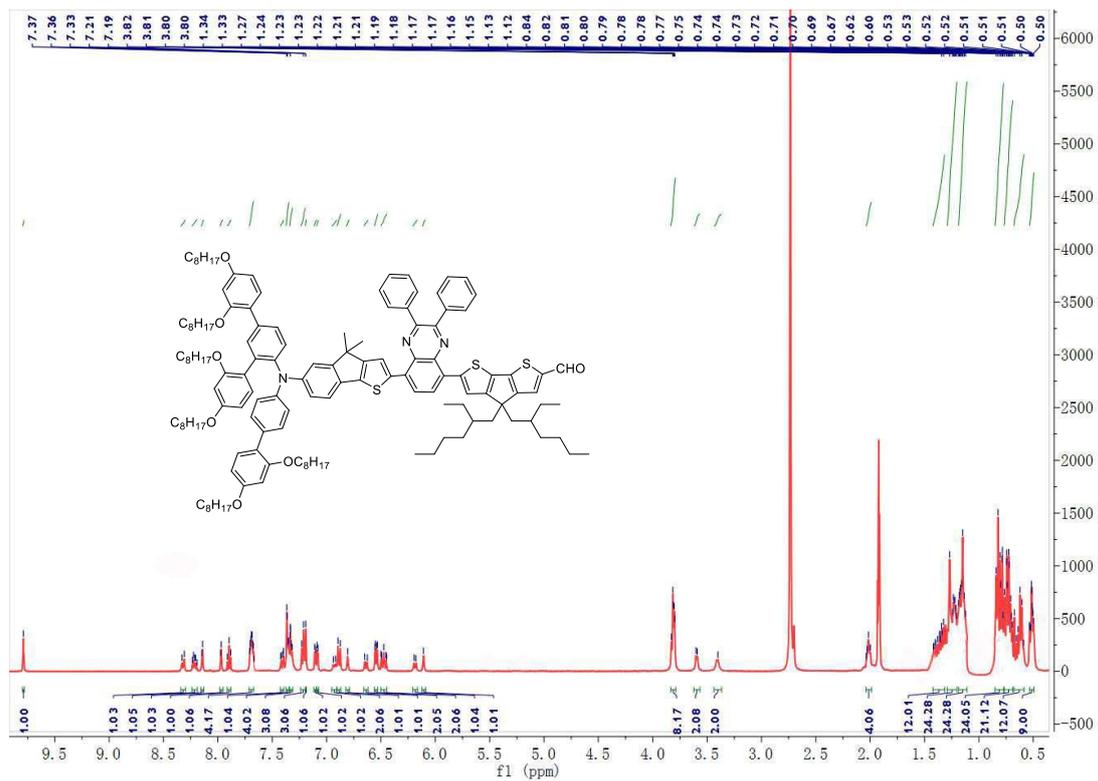
02-Apr-2015  
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1: TOF MS ES+  
8.32e+002



Minimum: 300.0 50.0 -1.5  
Maximum: 300.0 50.0 100.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
2074.2788	2074.2779	0.9	0.4	50.5	75.3	0.0	C136 H177 N4 O7 S3

Fig. S5  $^1\text{H}/^{13}\text{C}$  NMR spectroscopy and HR Mass spectrometry of compound **3a**.



Elemental Composition Report

Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

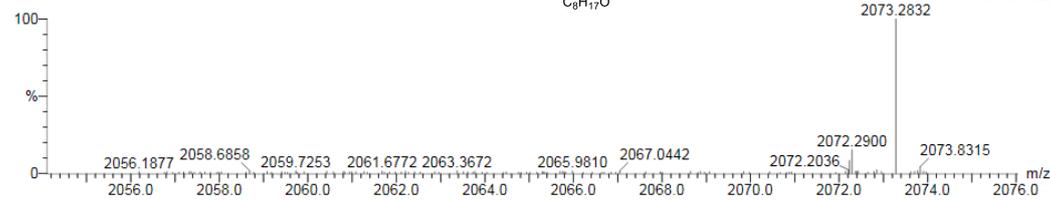
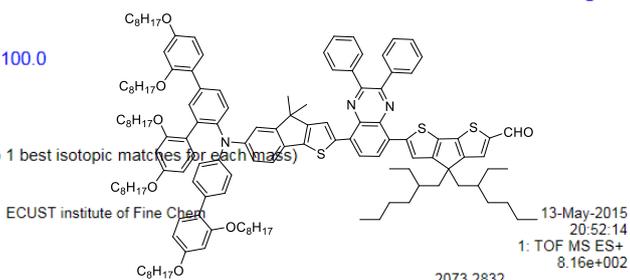
79 formula(e) evaluated with 2 results within limits (up to 1 best isotopic matches for each mass)

Elements Used:

C: 0-137 H: 0-200 N: 0-3 O: 0-7 S: 0-3

JL-HUA

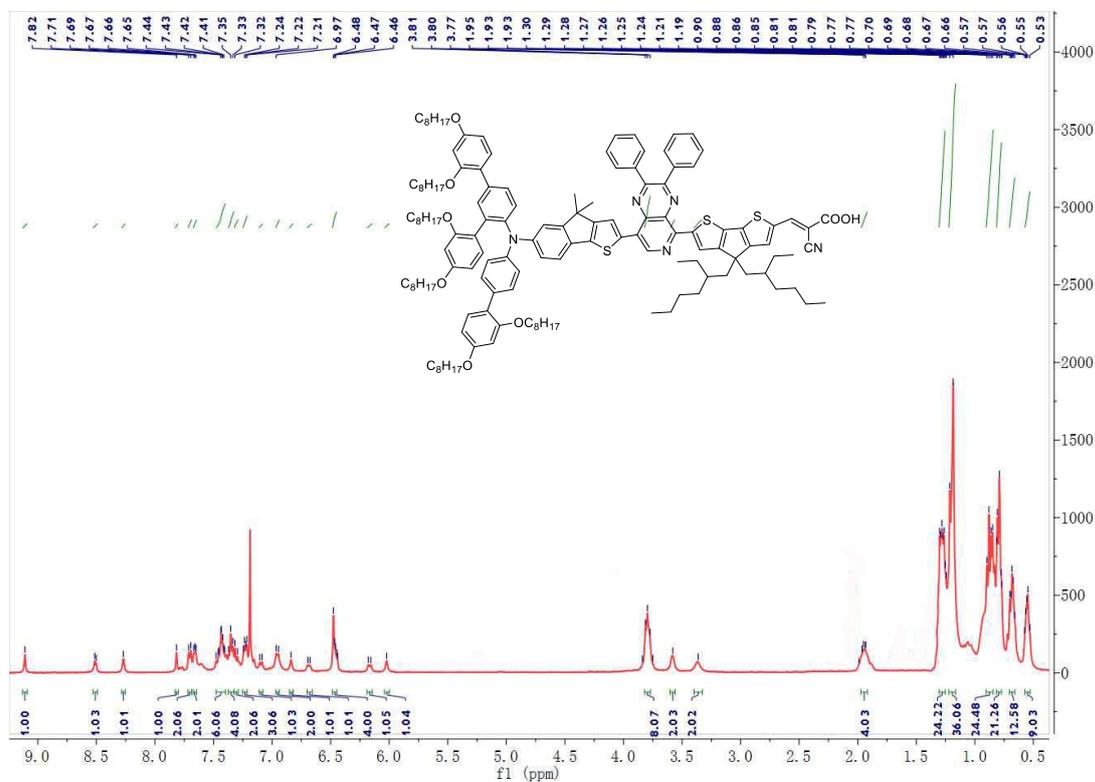
HL-SZJ-433 153 (1.033) Cm (150:160)

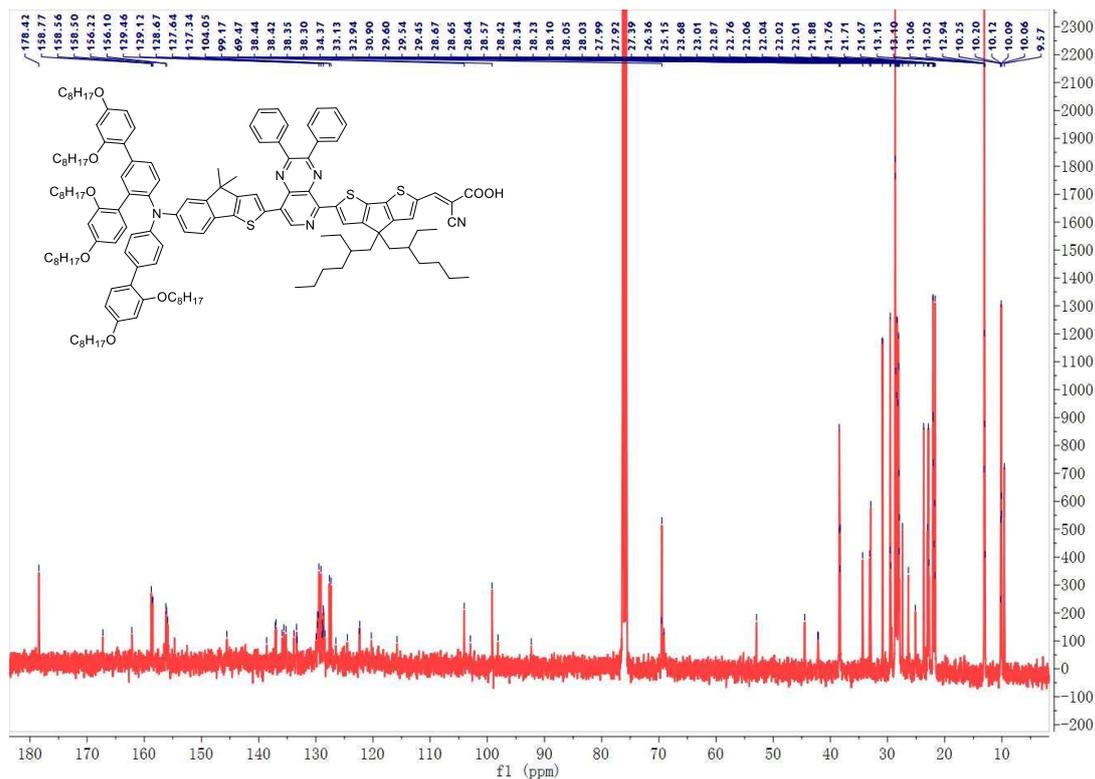


Minimum: -1.5  
Maximum: 300.0 50.0 100.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
2073.2832	2073.2827	0.5	0.2	50.5	53.1	0.0	C137 H178 N3 O7 S3

Fig. S6 <sup>1</sup>H/<sup>13</sup>C NMR spectroscopy and HR Mass spectrometry of compound 3b.





### Elemental Composition Report

#### Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

153 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)

Elements Used:

C: 0-139 H: 0-200 N: 0-5 O: 0-8 S: 0-3

JL-HUA

HL-SZJ-401 4 (0.203) Cm (4)



Minimum: -1.5  
Maximum: 300.0 50.0 100.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
2141.1890	2141.2838	-94.8	-44.3	53.5	23.0	0.0	C139 H178 N5 O8 S3

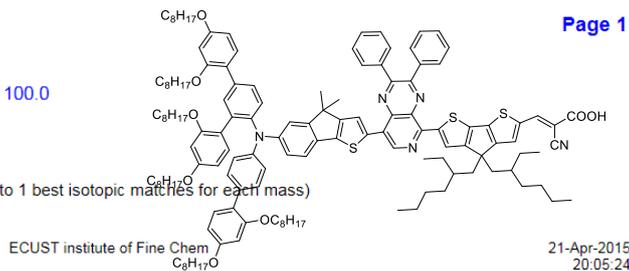
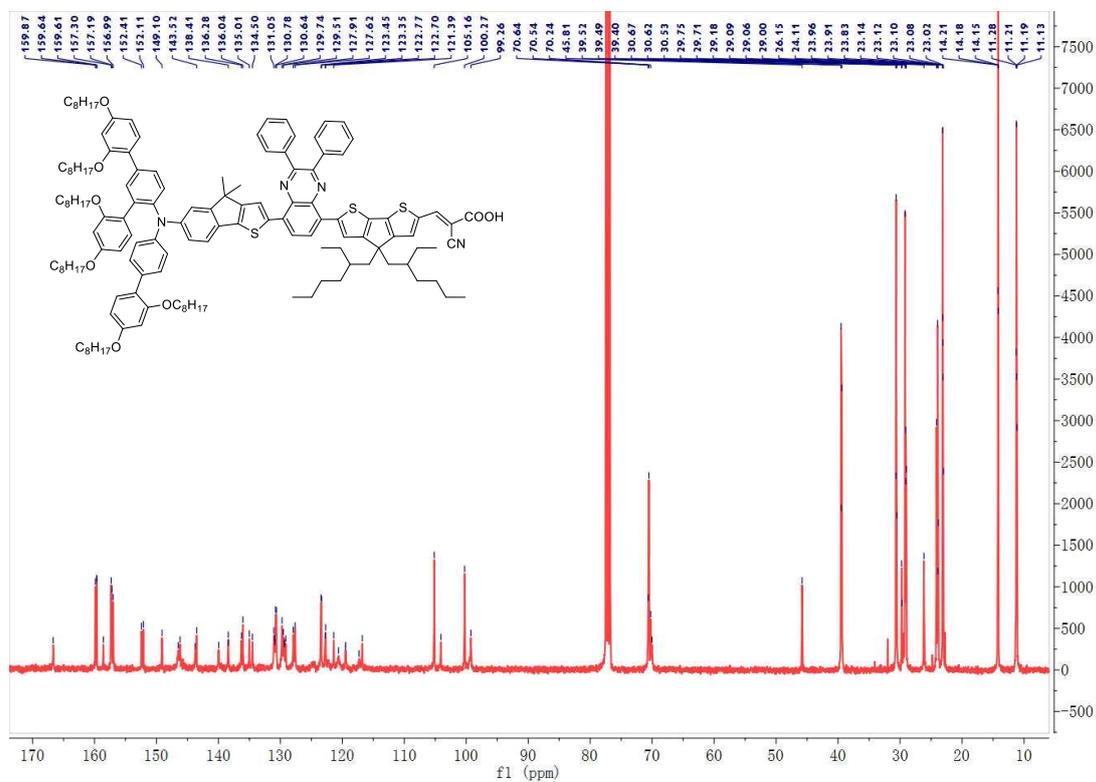
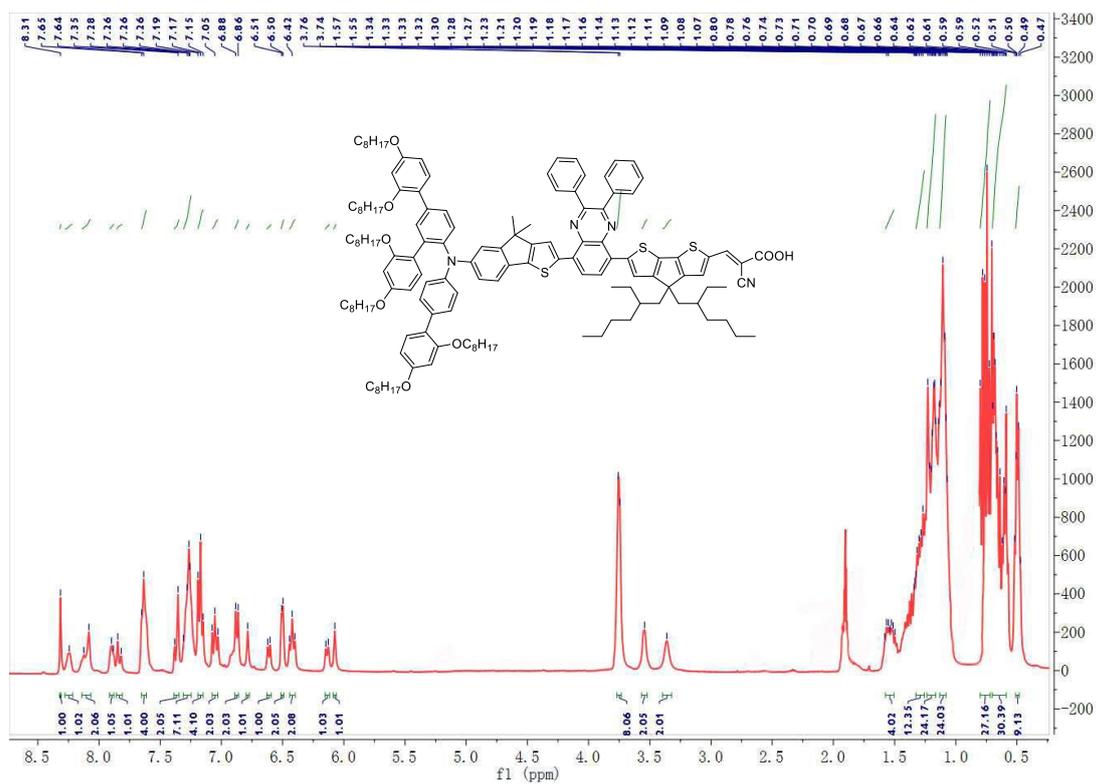


Fig. S7  $^1\text{H}/^{13}\text{C}$  NMR spectroscopy and HR Mass spectrometry of compound S4.



## Elemental Composition Report

### Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0  
Element prediction: Off  
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

121 formula(e) evaluated with 2 results within limits (up to 1 best isotopic matches for each mass)

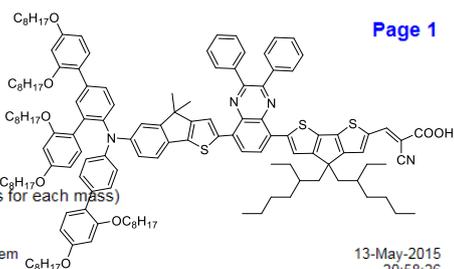
Elements Used:

C: 0-140 H: 0-200 N: 0-4 O: 0-8 S: 0-3

JL-HUA

HL-SZJ-434 80 (0.583) Cm (75:82)

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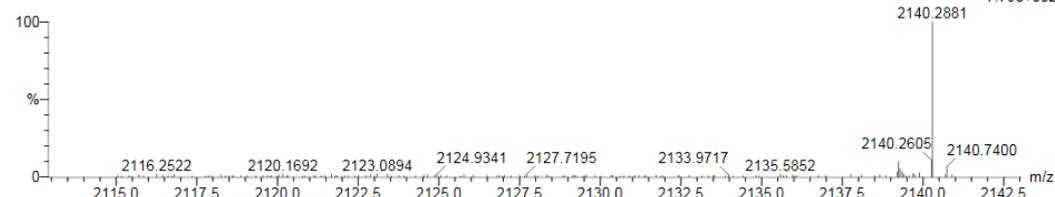


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1: TOF MS ES+

7.79e+002



Minimum:

Maximum: 300.0 50.0 -1.5 100.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
2140.2881	2140.2885	-0.4	-0.2	53.5	39.9	0.0	C140 H179 N4 O8 S3

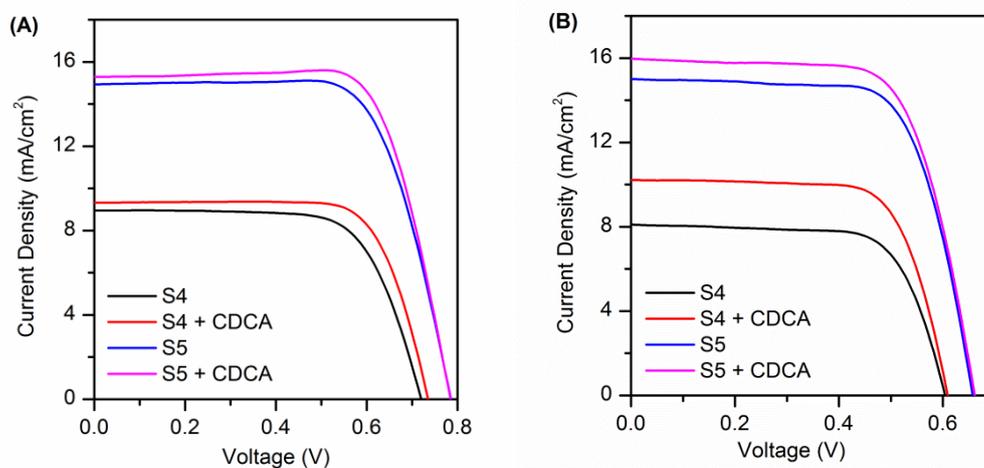
Fig. S8  $^1\text{H}/^{13}\text{C}$  NMR spectroscopy and HR Mass spectrometry of compound **S5**.

## 2. Photovoltaic performance of **S4**, **S5** based liquid-state DSCs

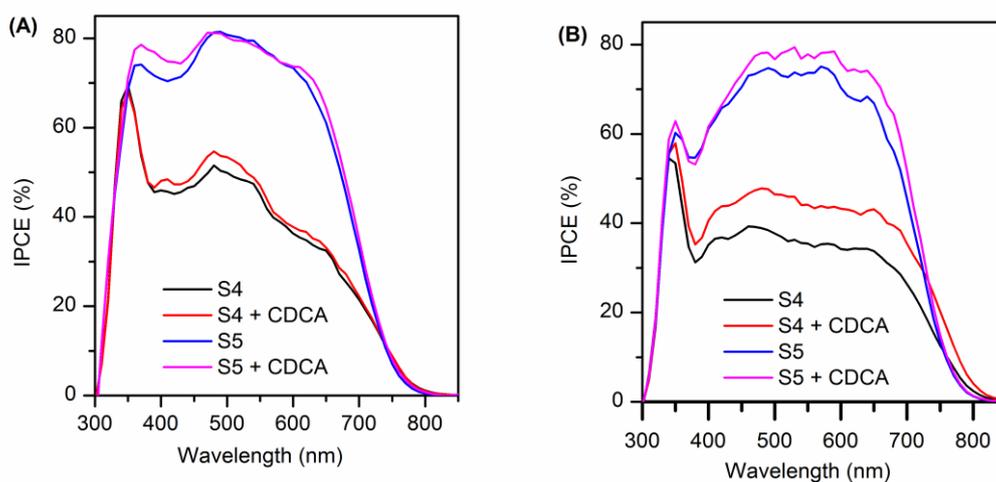
Fig. S9 shows the IPCE spectra of **S4** and **S5** based devices together with cobalt and iodine electrolytes. The IPCE spectra of devices based on **S4** are slightly broader than the corresponding spectra of **S5** in both types of electrolytes, which is in agreement with their UV-Vis absorption spectra. However, the IPCE plateau of **S4**-based devices is much lower than that of **S5**, where the curve of **S5**-sensitized devices reach over 70% and that of **S4**-based devices is less than 50% in the range 350-700 nm. This difference can be attributed to the much higher molar extinction coefficient of the dye **S5**. The higher IPCE plateau predicts that **S5**-based devices should render higher  $J_{sc}$ .

The current-voltage characteristics curves of all cells based on the two types of electrolytes were investigated under standard AM 1.5G conditions ( $100 \text{ mW cm}^{-2}$ ). The  $J$ - $V$  curves of DSCs based on **S4** and **S5** with cobalt and iodine based electrolytes are shown in Fig. S10. The detailed photovoltaic data are listed in Table S3. For the DSCs based on the cobalt electrolyte, the PCE recorded for **S4**-based cells was 4.46 % with a  $J_{sc}$  of  $8.94 \text{ mA/cm}^2$ , a  $V_{oc}$  of 721 mV, and an  $FF$  of 0.69. While replacing the PP unit with the QT unit, caused an improvement of  $J_{sc}$  by about  $6 \text{ mA/cm}^2$  and an  $V_{oc}$  enhancement by 60 mV. The PCE of **S5**-based solar cell reached 8.31%. The higher  $J_{sc}$  of **S5**-based devices is in accordance with the IPCE spectra. Using CDCA as coadsorbent a highest PCE of 8.85% was obtained with **S5**-based cells. Besides, for iodine-based cells, the  $J_{sc}$ s of both **S4** and **S5** based devices were somewhat higher than those based on the cobalt electrolyte. This can be attributed to the higher driving force for dye regeneration in the cells based on the iodine electrolyte. Due to the higher redox potentials in the iodine electrolyte, the  $V_{oc}$ s obtained were lower than those from cobalt-based devices for both dyes. Finally, for iodine-

based DSCs containing the coadsorbent CDCA, the best PCE of **S5**-based cell was recorded to 7.29% with a  $J_{sc}$  of 15.97 mA/cm<sup>2</sup>, a  $V_{oc}$  of 660 mV, and an FF of 0.69.



**Fig. S9** Current-voltage characteristics of DSCs based on **S4** and **S5** with cobalt electrolyte (A) and iodine electrolyte (B).



**Fig. S10** IPCE action spectra for DSCs based on **S4** and **S5** with cobalt electrolyte (A) and iodine electrolyte (B).

**Table S1** Photovoltaic performance of the **S4** and **S5**-based liquid-state DSCs

Dye	Electrolyte	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (mV)	FF	$\eta$ (%)
S4	I <sup>-</sup> /I <sub>3</sub> <sup>-</sup>	8.11	605	69.71	3.42
S4+CDCA	I <sup>-</sup> /I <sub>3</sub> <sup>-</sup>	10.23	610	71.17	4.44
S5	I <sup>-</sup> /I <sub>3</sub> <sup>-</sup>	15.03	657	70.25	6.83
S5+CDCA	I <sup>-</sup> /I <sub>3</sub> <sup>-</sup>	15.97	660	69.15	7.29
S4	Co(bpy) <sub>3</sub> <sup>2+/3+</sup>	8.94	721	69.28	4.46
S4+CDCA	Co(bpy) <sub>3</sub> <sup>2+/3+</sup>	9.32	736	73.41	5.04
S5	Co(bpy) <sub>3</sub> <sup>2+/3+</sup>	14.93	782	71.15	8.31
S5+CDCA	Co(bpy) <sub>3</sub> <sup>2+/3+</sup>	15.29	784	73.89	8.85

### 3. EIS measurements for liquid-state DSCs

Fig. S11A displays the charge transfer resistance ( $R_{ct}$ ) and chemical capacitance ( $C_{chem}$ ) of **S4** and **S5** based DSCs as a function of IR drop potential with  $[Co(bpy)_3]^{2+}/[Co(bpy)_3]^{3+}$  redox electrolyte. The  $R_{ct}$  values of **S5** based devices are higher than that of devices based on **S4**, which suggests less charge recombination in **S5** based devices, resulting in a higher  $V_{oc}$ . The  $C_{chem}$  of the DSCs based on both dyes show only minor differences, indicating no significant alteration of the substrate conduction band energy level. Cell based on the  $I^-/I_3^-$  redox electrolyte, the  $R_{ct}$  and  $C_{chem}$  as a function of bias voltage are illustrated in Fig. S11B. As for  $R_{ct}$ , it is similar to the results obtained for the  $[Co(bpy)_3]^{2+}/[Co(bpy)_3]^{3+}$  electrolyte. However, the  $C_{chem}$  s of **S5** based DSCs are larger than those of **S4** based devices, indicating an upward shift of the  $TiO_2$  conduction band leading to a higher  $V_{oc}$ .

As well known, the  $V_{oc}$  is associated with the electron lifetime ( $\tau_n$ ), which in turn is related to the charge transfer resistance, and it can be estimated from the equations of  $\tau_n = R_{ct} \times C_{chem}$ . The electron lifetime ( $\tau_n$ ) of **S4** and **S5** based DSCs with either  $[Co(bpy)_3]^{2+}/[Co(bpy)_3]^{3+}$  and  $I^-/I_3^-$  redox electrolytes are shown in Fig. S12. The  $\tau_n$  of **S5** based devices is much longer than those of **S4** sensitized DSCs, irrespective of electrolyte, indicating less charge recombination and suggesting a higher  $V_{oc}$  of the devices based on **S5**. This is consistent with the  $V_{oc}$  trend of the devices observed in the  $I$ - $V$  studies.

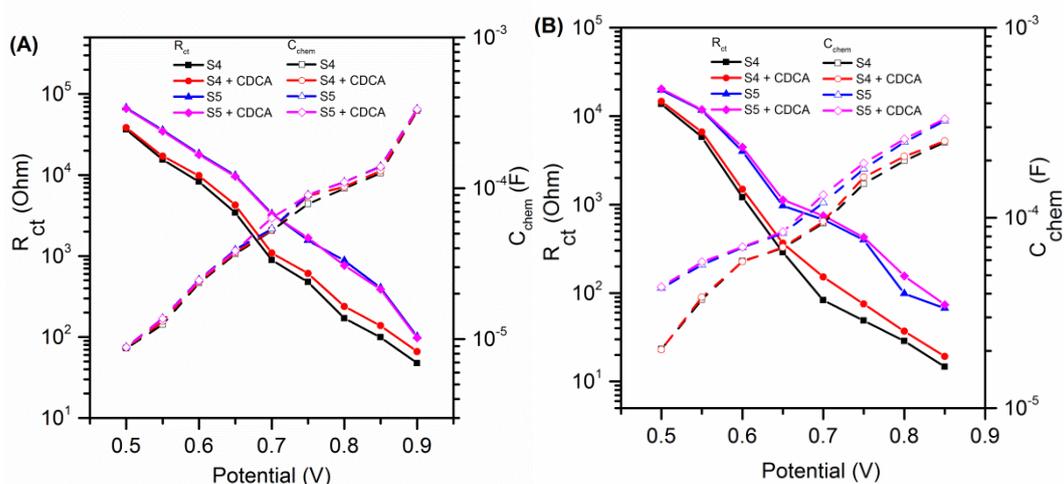
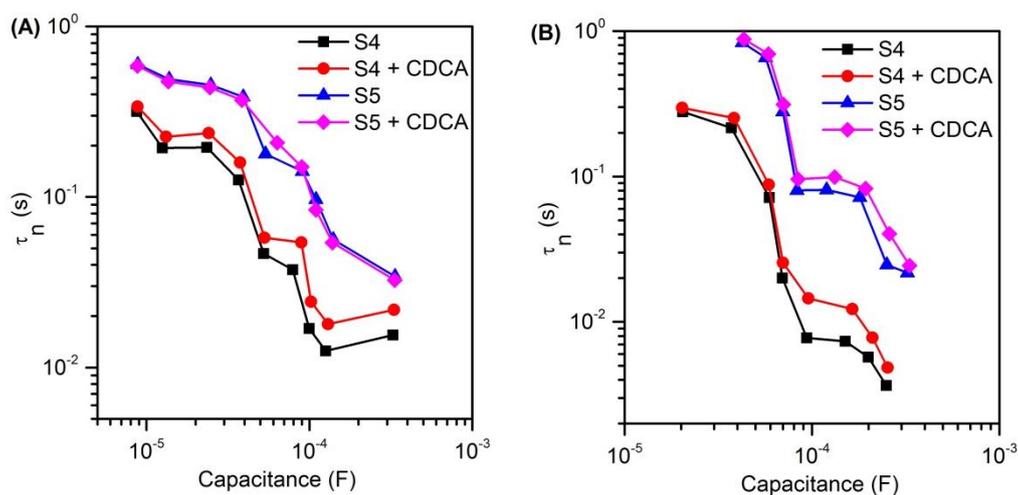


Fig. S11 The charge transfer resistance ( $R_{ct}$ ) and chemical capacitance ( $C_{chem}$ ) plotted against the IR drop potential of **S4** and **S5** based DSSCs extracted from the EIS measurement with cobalt electrolyte (A) and with iodine electrolyte (B).



**Fig. S12** The electron lifetime ( $\tau_n$ ) of DSSCs based on **S4** and **S5** as the function of chemical capacitance ( $C_{\text{chem}}$ ) during the EIS measurement with cobalt (A) and iodine electrolyte (B).

#### 4. References

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- (2) (a) X. Y. Zhang, J. Y. Mao, D. Wang, X. Lin, J. B. Yang, Z. J. Shen, W. J. Wu, J. Li, H. Ågren and J. L. Hua, *ACS Appl. Mater. Interfaces* 2015, **7**, 2760; (b) J. B. Yang, P. Ganesan, J. Teuscher, T. Moehl, Y. J. Kim, C. Y. Yi, P. Comte, K. Pei, T. W. Holcombe, M. K. Nazeeruddin, J. L. Hua, S. M. Zakeeruddin, H. Tian and M. Grätzel, *J. Am. Chem. Soc.* 2014, **136**, 5722; (c) J. Y. Mao, J. B. Yang, J. Teuscher, T. Moehl, C. Y. Yi, H. B. Robin, P. Comte, C. Grätzel, J. L. Hua, S. M. Zakeeruddin, H. Tian and M. Grätzel, *J. Phys. Chem. C* 2014, **118**, 17090.
- (3) J. W. Schultze and A. Thyssen, *Synthetic Met.* 1991, **43**, 2825.
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