Supporting Information

New D-A- π -A organic sensitizers for efficient dye-sensitized solar cells

Xiangguang Li,^{*a*} Zhiwei Zheng,^{*b*} Wei Jiang,^{*a*} Wenjun Wu,^{*b*} Zhaohui Wang^{*a*} and He Tian^{*b*}

^a Beijing National Laboratory for Molecular Sciences, Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.
E-mail: jiangwei@iccas.ac.cn; Fax: +86-10-62653617; Tel: +86-10-62653617
^b Key Labs for Advanced Materials and Institute of Fine Chemicals, East China
University of Science & Technology, 130 Meilong Road, Shanghai, 200237, China.
E-mail:wjwu@ecust.edu.cn; Fax: +86-21-64252288; Tel: +86-21-64250940

Table of Contents

5.	NMR and MS spectra	.23
4.	DSSCs Fabrication and Measurements	.20
3.	Photophysical Properties	.17
2.	Experimental Section	.3
1.	Materials and General Methods	.2

1.Materials and General Methods

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise specified. The solvent DMF from Alfa Aesar was dry and used directly, and THF was distilled over sodium and benzophenone.

¹H NMR and ¹³C NMR spectra were recorded in deuterated solvents using a BRUKER AVANCE III 400 HD (400 MHz), or a BRUKER AVIII 500WB(500 MHz) NMR Spectrometer. NMR chemical shifts are reported in ppm using the residual protonated solvent as an internal standard. Mass spectra (MALDI-TOF-MS) were determined using a Bruker BIFLEX III Mass Spectrometer. High resolution mass spectra (HRMS) were determined on a Bruker Daltonics Inc. BIFLEX III MALDI-TOF or a Waters micromass GCT Mass Spectrometer.

Absorption spectra were measured with a Hitachi (modelU-3010) UV-Vis spectrophotometer in a 1 cm quartz cell. Cyclic voltammetry (CV) was performed using a Zahner IM6e electrochemical workstation at a scan rate of 100 mV s⁻¹, using glassy carbon discs as the working electrodes, Pt wire as the counter electrode, Ag/AgCl electrode as the reference electrode. 0.1 M tetrabutylammonium hexafuorophosphate (*n*-Bu₄NPF₆) dissolved in CH₂Cl₂ (HPLC grade) was employed as the supporting electrolyte. Ferrocene/ferrocenium was employed as an external reference, the energy level of which is assumed to be -4.8 eV below the vacuum level.^{1.2} The LUMO and HOMO levels were estimated from the onset potentials of the first reduction and oxidation waves in CV, respectively. The half-wave potential of oxidation peak of Fc was measured to be 0.48 V against Ag/AgCl.

2.Experimental Section

6*H*-Phenanthro[1,10,9,8-*c*,*d*,*e*,*f*,*g*]carbazole (1) and

3,6-bis(4-bromophenyl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (10) was

synthesized according to the literature.^{3,4}





Scheme S1 Synthesis procedure of ND01-ND04

Synthesis of 2



A mixture of 6*H*-Phenanthro[1,10,9,8-*c*,*d*,*e*,*f*,*g*]carbazole (530 mg, 2 mmol), NaH (72 mg, 3mmol), 2-Ethylhexyl bromide (580 mg, 3mmol) in dry 50 ml THF was stirred at 66 $\$ for 12 h under argon. After cooling to room temperature, the mixture was stirred for 30 min at 0 $\$ before 2 ml of water was added dropwise. The reaction mixture was then poured into water and the product was extracted with dichloromethane. The solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography on silica gel (petroleum ether) to

give695 mg of compound **2** in 92% yield as yellow solids. ¹H NMR (400 MHz, CDCl₃, 298 K) δ = 8.65 (d, 2H), 8.12 (d, 2H), 7.91 (d, 2H), 7.83-7.77 (m, 4H), 4.58-4.54 (m, 2H), 2.25-2.19 (m, 1H), 1.46-1.24 (m, 8H), 0.94 (t, 3H), 0.86 (t, 3H). ¹³C NMR (100 MHz, CDCl₃, 298 K) δ = 132.41, 130.62, 129.01, 125.22, 125.10, 124.70, 123.79, 120.90, 117.55, 113.71, 49.89, 41.65, 31.21, 29.07, 24.56, 23.32, 14.37, 11.11. MS (EI): calcd for [M]⁺, 377; found, 377. HRMS (EI, [M]⁺, 100%): calcd for C₂₈H₂₇N, 377.2144; found, 377.2148. Synthesis of **3**



N-Bromosuccinimide (392 mg, 2.2 mmol) was added to a solution of **2** (755 mg, 2mmol) in N,N-Dimethylformamide (80 mL) under ice-water bath. The mixture was stirred for 0.5 h and quenched with saturated aqueous Na₂CO₃. The mixture was extracted with CH₂Cl₂ for three times. The combined extractions were washed with brine and then dried with Na₂SO₄. After the solvents were removed under vacuum, the crude product was purified by column chromatography on silica gel (petroleum ether) and recrystallized with methanol/dichloromethane to afford 840mg of compound **3** in 92% yield as yellow solids.¹H NMR (400 MHz, DMSO-d₆, 298 K) δ = 8.89 (d, 1H), 8.85(d, 1H), 8.50 (s, 1H), 8.26 (t, 2H), 8.04 (s, 2H), 7.98(t, 1H), 7.88 (t, 1H), 4.71 (d, 2H), 2.19-2.13 (m, 1H), 1.37-1.15 (m, 8H), 0.88 (t, 3H), 0.76 (t, 3H). ¹³C NMR (100 MHz, DMSO-d₆, 298 K) δ = 132.19, 131.38, 129.84, 128.86, 128.20, 127.08, 125.78, 125.65, 124.96, 124.42, 124.09, 123.74, 123.54, 121.99, 121.66, 118.24, 116.43, 115.80, 115.66, 114.54, 49.08, 40.50, 29.94, 27.75, 23.47, 22.42, 13.74, 10.51. MS (EI): calcd for [M]⁺, 455; found, 455. HRMS (EI, [M]⁺, 100%): calcd for C₂₈H₂₆⁷⁹BrN, 455.1249; found, 455.1243.

Synthesis of **4**



A mixture of **3** (456 mg, 1 mmol), $Pd(PPh_3)_4$ (116 mg, 0.1 mmol), 4-Methoxyphenylboronic acid (304mg, 2 mmol) and K_2CO_3 (829 mg, 6 mmol) in 30 mL of THF and 3mL of H_2O was

refluxed for 4 h. After cooling to room temperature, the mixture was extracted with 100 mL of CH₂Cl₂. The extractions were washed with brine and then dried with Na₂SO₄. After removing the solvents by rotary evaporation, the residue was purified by column chromatography on silica (petroleum ether/CH₂Cl₂ =5/1, v/v) and recrystallized with methanol/dichloromethane to give 416 mg of compound **4** in 86% yield as yellow solids. ¹H NMR (400 MHz, CDCl₃, 298 K) δ = 8.68 (dd, 2H), 8.13 (d, 2H), 7.92 (d, 1H), 7.84-7.75 (m, 3H), 7.73 (s, 1H), 7.66 (d, 2H), 7.13 (d, 2H), 4.63-4.51 (m, 2H), 3.95 (s, 3H), 2.27-2.24 (m, 1H), 1.46-1.23 (m, 8H), 0.94 (t, 3H), 0.85 (t, 3H). ¹³C NMR (100 MHz, CDCl₃, 298 K) δ = 159.24, 137.38, 134.86, 132.44, 131.67, 130.84, 130.74, 129.00, 128.31, 125.25, 125.16, 124.97, 124.74, 124.66, 124.55, 123.63, 121.08, 120.85, 117.62, 116.85, 114.29, 114.20, 113.64, 55.69, 49.86, 41.55, 31.17, 28.97, 24.53, 23.32, 14.32, 11.07. MS (EI): calcd for [M]⁺, 483; found, 483. HRMS (EI, [M]⁺, 100%): calcd for C₃₅H₃₃NO, 483.2562; found, 483.2557.

Synthesis of **5**



To a stirred solution of **3** (456 mg, 1 mmol) and CuI (19 mg, 0.1 mmol) in DMF (30 mL) was added 1.5 mmol sodium methoxide (30% w/w solution in methanol). The reaction mixture was stirred at 90 °C under argon for 5 h and then diluted with 200 mL water. The resulting mixture was extracted with dichloromethane, washed with brine, and organic layers were dried over anhydrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by column chromatography on silica (petroleum ether/CH₂Cl₂ = 10/1, v/v) and recrystallized with methanol/dichloromethane to give 310 mg of compound **5** in 76% yield as yellow solids. ¹H NMR (400 MHz, DMSO-d₆, 298 K) δ = 8.78 (d, 1H), 8.71 (d, 1H), 8.24 (d, 1H), 8.14 (d, 1H), 7.95 (d, 1H), 7.85-7.78 (m, 3H), 7.53 (s,1H), 4.65 (d, 2H), 4.16 (s, 3H), 2.19-2.16 (m, 1H), 1.38-1.15 (m, 8H), 0.89 (t, 3H), 0.77 (t, 3H). ¹³C NMR (100 MHz, DMSO-d₆, 298 K) δ = 155.24, 132.02, 130.73, 129.39, 129.25, 128.38, 124.79, 124.48, 123.97, 123.73, 123.65, 122.15, 121.88, 121.22, 120.88, 120.41, 116.64, 114.24, 110.02, 94.01, 56.29, 48.81, 40.42, 30.01, 27.80, 23.47, 22.40, 13.71, 10.51. MS (EI): calcd for [M]⁺, 407; found, 407. HRMS (EI, [M]⁺, 100%): calcd for C₂₉H₂₉NO

Synthesis of 6



A mixture of **3** (456 mg, 1 mmol), CuI (9.5 mg, 0.05 mmol), Me₄Phen (24 mg, 0.10 mmol), Cs₂CO₃ (490 mg, 1.5 mmol), and *n*-hexanol (3 mL) as solvent stirred for 24 h at 130 °C. After cooling to room temperature, the mixture was extracted with dichloromethane. The extractions were washed with brine and then dried with Na₂SO₄. After removing solvent under reduced pressure, the residue was purified by column chromatography on silica (petroleum ether/CH₂Cl₂ =5/1, v/v) and recrystallized with methanol/dichloromethane to give 410 mg of compound **6** in 86% yield as yellow solids. ¹H NMR (400 MHz, DMSO-d₆, 298 K) δ = 8.77 (d, 1H), 8.71 (d, 1H), 8.23 (d,1H), 8.14 (d, 1H), 7.94 (d, 1H), 7.84-7.77 (m, 3H), 7.51 (s, 1H), 4.64 (d, 2H), 4.33 (t, 2H), 2.22-2.12 (m, 1H), 1.99-1.92 (m, 2H), 1.64-1.57 (m, 2H), 1.45-1.14 (12H), 0.93-0.83 (m, 6H), 0.77 (t, 3H). ¹³C NMR (125 MHz, DMSO-d₆, 353 K) δ = 154.32, 131.90, 130.70, 129.16, 129.03, 128.15, 124.33, 124.04, 123.60, 123.51, 123.47, 122.31, 121.31, 120.90, 120.53, 119.91, 116.50, 113.73, 110.02, 95.11, 68.79, 48.79, 40.25, 30.55, 30.01, 28.38, 27.64, 24.92, 23.44, 21.85, 21.48, 13.20, 13.06, 10.13. MS (EI): calcd for [M]⁺, 477; found, 477. HRMS (EI, [M]⁺, 100%): calcd for C₃₄H₃₉NO, 477.3032; found,477.3023.

Synthesis of 7



The synthesis method resembles that of compound **3** and the compound was purified by column chromatography on silica gel (petroleum ether) and recrystallized with methanol/dichloromethane to afford compound **7** in 96% yield as yellow solids. ¹H NMR (400 MHz, CDCl₃, 298 K) δ = 8.68 (d, 2H), 8.33 (d, 1H), 8.15 (d, 1H), 8.07 (s, 1H), 7.89 (t, 1H), 7.78 (t, 1H), 7.68 (s, 1H), 7.65 (d, 2H), 7.13 (d, 2H), 4.50-4.47 (m, 2H), 3.95 (s, 3H), 2.22-2.19 (m, 1H), 1.41-1.25 (m, 8H), 0.93 (t, 3H), 0.85 (t, 3H). ¹³C NMR (100 MHz, CDCl₃, 298 K) δ = 159.32,

134.67, 131.63, 130.43, 130.04, 128.01, 127.75, 125.28, 124.73, 124.56, 124.49, 124.22, 121.30, 116.98, 116.62, 116.09, 114.25, 114.03, 55.74, 49.81, 41.39, 31.07, 28.87, 24.49, 23.32, 14.31, 11.05. MS (EI): calcd for $[M]^+$, 561; found, 561. HRMS (EI, $[M]^+$, 100%): calcd for $C_{35}H_{32}^{79}BrNO$, 561.1667; found, 561.1674.

Synthesis of 8



The synthesis method resembles that of compound **3** and the compound was purified by column chromatography on silica gel (petroleum ether) and recrystallized with methanol/dichloromethane to afford compound **8** in 90% yield as yellow solids. ¹H NMR (400 MHz, DMSO-d₆, 298 K) $\delta = 8.81(dd, 2H)$, 8.35 (s, 1H), 8.26 (d, 1H), 8.20 (d, 1H), 7.93 (t, 1H), 7.82 (t, 1H), 7.48 (s, 1H), 4.61 (d, 2H), 4.15 (s, 3H), 2.21-2.08 (m, 1H), 1.39-1.14 (m, 8H), 0.87 (t, 3H), 0.77 (t, 3H). ¹³C NMR (100 MHz, DMSO-d₆, 298 K) $\delta = 155.78$, 132.49, 130.20, 129.69, 128.56, 127.07, 125.56, 124.22, 123.72, 123.27, 123.22, 122.47, 122.10, 121.36, 121.30, 117.86, 116.04, 113.88, 109.53, 93.80, 56.31, 48.82, 40.27, 29.86, 27.67, 23.40, 22.43, 13.73, 10.49. MS (EI): calcd for [M]⁺, 487; found, 487. HRMS (EI, [M]⁺, 100%): calcd for C₂₉H₂₈⁸¹BrNO, 487.1334; found, 487.1343.

Synthesis of 9



The synthesis method resembles that of compound **3** and the compound was purified by column chromatography on silica gel petroleum ether/CH₂Cl₂ =5/1, v/v) and recrystallized with methanol/dichloromethane to afford compound **9** in 92% yield as yellow solids.¹H NMR (400 MHz, DMSO-d₆, 298 K) δ = 8.84 (t, 2H), 8.39 (s, 1H), 8.28 (d, 1H), 8.22 (d, 1H), 7.94 (t, 1H), 7.84 (t, 1H), 7.52 (s, 1H), 4.65 (d, 2H), 4.34 (t, 2H), 2.19-2.12 (m, 1H), 2.01-1.91 (m, 2H), 1.67-1.56 (m, 2H), 1.44-1.13 (m, 12H), 0.96-0.84 (m, 6H), 0.77 (t, 3H). ¹³C NMR (125 MHz, DMSO-d₆, 353 K) δ = 154.93, 132.48, 130.21, 129.51, 128.38, 126.93, 125.15, 123.81, 123.37,

123.17, 123.13, 122.30, 121.97, 121.06, 120.84, 117.47, 116.01, 113.60, 109.57, 94.88, 68.77, 48.83, 40.14, 30.55, 29.89, 28.33, 27.54, 24.91, 23.38, 21.87, 21.49, 13.21, 13.06, 10.11. MS (EI): calcd for $[M]^+$, 557; found, 557. HRMS (EI, $[M]^+$, 100%): calcd for $C_{34}H_{38}^{\ 81}$ BrNO, 557.2116; found,557.2128.

Synthesis of 11



A mixture of **10** (671 mg, 1 mmol), Pd(PPh₃)₄ (58 mg, 0.05 mmol), and K₂CO₃ (1106 mg, 8 mmol) in 30 mL of THF and 4 mL of H₂O were heated to 45 °C under a argon atmosphere for 30 min. A solution of 5-Formyl-2-thiopheneboronic acid (187 mg, 1.2 mmol) in THF (10 mL) was added slowly, and the mixture was refluxed for a further 12 h. After cooling to room temperature, the mixture wasextracted with 50 mL of CH₂Cl₂. The extractions were washed with brine and then dried withNa₂SO₄. After removingthe solvents by rotary evaporation, the residue was purified bycolumn chromatography on silica (petroleum ether/CH₂Cl₂ = 2/1, v/v) and recrystallized with methanol/dichloromethane to give 295 mg of compound **11** in 42% yield as orange red solids. ¹H NMR (400 MHz, CDCl₃, 298 K) δ = 9.88 (s, 1H), 7.76 (d, 2H), 7.70 (d, 1H), 7.65 (d, 2H), 7.55(d, 2H), 7.49 (d, 2H), 7.42 (d, 1H), 3.71 (d, 2H), 3.67 (d, 2H), 1.44-1.32 (m, 2H), 1.20-0.96 (m, 16H), 0.79-0.67 (m, 12H). ¹³C NMR (100 MHz, CDCl₃, 298 K) δ = 182.98, 162.73, 152.87, 148.15, 148.07, 143.57, 137.51, 135.35, 132.23, 130.50, 129.88, 129.34, 127.44, 126.56, 125.87, 125.27, 110.22, 110.00, 45.20, 45.10, 38.75, 30.64, 28.58, 24.10, 23.14, 14.22, 10.72. MS (EI): calcd for [M]⁺, 702; found, 702. HRMS (EI, [M]⁺, 100%): calcd for C₃₉H₄₅⁸¹BrN₂O₃S, 702.2314; found, 702.2296.

Synthesis of 12



A 100 mL Schlenk flask was charged with 3 (456 mg, 1 mmol), PdCl₂(PPh₃)₂ (70 mg, 0.1

mmol), pinacolborane (512 mg, 4 mmol), triethylamine (607 mg, 6 mmol) and 1,2-dichloroethane (40 mL) under argon. The reaction mixture was stirred at 90 °C for 3 hours. After removal of the solvent, the crude product was purified by column chromatography on silica gel (petroleum ether/CH₂Cl₂ = 5/1, v/v) and recrystallized with methanol/dichloromethane to give 453 mg of compound **12** in 90% yield as yellow solids. ¹H NMR (400 MHz, CDCl₃, 298 K) δ = 9.00 (d, 1H), 8.67 (d, 2H), 8.45 (s, 1H), 8.11 (d, 1H), 7.95 (d, 1H), 7.87(t, 1H), 7.83-7.78 (m, 2H), 4.67-4.56 (m, 2H), 2.30-2.24 (m, 1H), 1.51 (s, 12H), 1.46-1.25 (m, 8H), 0.95 (t, 3H), 0.88 (t, 3H). ¹³C NMR (100 MHz, CDCl₃, 298 K) δ = 133.30, 132.82, 132.33, 130.92, 130.60, 128.85, 127.07, 125.28, 125.08, 124.97, 124.86, 124.78, 123.01, 121.01, 120.70, 120.16, 117.53, 113.72, 100.26, 83.88, 49.81, 41.57, 31.09, 28.91, 25.44, 25.41, 24.62, 23.31, 14.39, 11.17. MS (MALDI-TOF): calcd for [M]⁺, 503.3; found, 503.2. HRMS (EI, [M]⁺, 100%): calcd for C₃₄H₃₈BNO₂, 503.2996; found, 503.3004.

Synthesis of 13



The synthesis method resembles that of compound **12** and the compound was purified by column chromatography on silica gel (petroleum ether/CH₂Cl₂ = 3/1, v/v) and recrystallized with methanol/dichloromethane to give compound **13** in 94% yield as yellow solids. ¹H NMR (400 MHz, CDCl₃, 298 K) δ = 9.01 (d, 1H), 8.70 (d, 2H), 8.46 (s, 1H), 8.12 (d, 1H), 7.88 (t, 1H), 7.77(t, 1H), 7.73 (s, 1H), 7.66 (d, 2H), 7.13 (d, 2H), 4.64-4.61 (m, 2H), 3.95 (s, 3H), 2.30-2.26 (m, 1H), 1.51 (s, 12H), 1.47-1.24 (m, 8H), 0.94 (t, 3H), 0.87 (t, 3H). ¹³C NMR (100 MHz, CDCl₃, 298 K) δ = 159.31, 138.52, 134.77, 133.35, 132.81, 132.35, 131.65, 131.15, 130.72, 128.19, 127.04, 125.17, 124.77, 124.46, 122.95, 121.25, 120.70, 120.27, 116.85, 114.31, 114.22, 83.90, 55.72, 49.90, 41.51, 31.04, 28.84, 25.44, 25.42, 24.59, 23.36, 14.40, 11.17. MS (EI): calcd for [M]⁺, 609; found, 609. HRMS (EI, [M]⁺, 100%): calcd for C₄₁H₄₄BNO₃, 609.3414; found, 609.3424. Synthesis of **14**



The synthesis method resembles that of compound **12** and the compound was purified by column chromatography on silica gel (petroleum ether/CH₂Cl₂ = 3/1, v/v) and recrystallized with methanol/dichloromethane to give compound **14** in 86% yield as yellow solids. ¹H NMR (500 MHz, DMSO-d₆, 353 K) δ = 8.86 (d, 1H), 8.77 (d, 1H), 8.71 (d, 1H), 8.41 (s, 1H), 8.26 (d, 1H), 7.84 (t, 1H), 7.81 (t, 1H), 7.48 (s, 1H), 4.67 (d, 2H), 4.19 (s, 3H), 2.23-2.15 (m, 1H), 1.47 (s, 12H), 1.43-1.20 (m, 8H), 0.92 (t, 3H), 0.82 (t, 3H). ¹³C NMR (125 MHz, DMSO-d₆, 353 K) δ = 156.07, 133.13, 131.77, 130.32, 129.24, 129.16, 125.77, 124.34, 123.70, 123.57, 123.38, 122.27, 121.98, 121.62, 120.53, 119.75, 119.17, 109.92, 93.83, 82.90, 56.19, 48.57, 40.34, 29.93, 27.58, 24.38, 24.36, 23.50, 21.84, 13.12, 10.20 MS (EI): calcd for [M]⁺, 533; found, 533. HRMS (EI, [M]⁺, 100%): calcd for C₃₅H₄₀BNO₃, 533.3101; found, 533.3094.

Synthesis of 15



The synthesis method resembles that of compound **12** and the compound was purified by column chromatography on silica gel (petroleum ether/CH₂Cl₂ = 3/1, v/v) and recrystallized with methanol/dichloromethane to give compound **15** in 96% yield as yellow solids. ¹H NMR (400 MHz, DMSO-d₆, 298 K) δ = 8.86 (d, 1H), 8.82 (d, 1H), 8.75 (d, 1H), 8.40 (s, 1H), 8.25 (d, 1H), 7.90-7.79 (m, 2H), 7.55 (s, 1H), 4.71 (d, 2H), 4.37 (t, 2H), 2.17-2.11 (m, 1H), 2.01-1.94 (m, 2H), 1.66-1.58 (m, 2H), 1.44 (s, 12H), 1.41-1.17 (m, 12H), 0.94-0.88 (m, 6H), 0.81 (t, 3H). ¹³C NMR (125 MHz, DMSO-d₆, 353 K) δ = 155.29, 133.21, 131.78, 130.33, 129.26, 129.17, 125.75, 124.33, 123.69, 123.58, 123.42, 122.25, 122.23, 121.58, 120.55, 119.74, 119.19, 109.88, 94.75, 82.90, 68.75, 48.56, 40.36, 30.55, 29.99, 29.94, 28.33, 27.60, 24.91, 24.38, 24.36, 23.51, 21.84, 21.49, 13.21, 13.11, 10.20. MS (EI): calcd for [M]⁺, 603; found, 603. HRMS (EI, [M]⁺, 100%): calcd for C₄₀H₅₀BNO₃, 603.3884; found,603.3890.





A mixture of **11** (112 mg, 0.16 mmol), Pd(PPh₃)₄ (18 mg, 0.016 mmol), and K₂CO₃ (221 mg, 1.6 mmol) in 10 mL of THF and 0.8 mL of H₂O were heated to 45 °C under a argon atmosphere for 30 min. A solution of 12 (106 mg, 0.21 mmol) in THF (5 mL) was added slowly, and the mixture was refluxed for a further 12 h. After cooling to room temperature, the mixture was extracted with 50 mL of CH₂Cl₂. The extractions were washed with brine and then dried with Na₂SO₄. After removing the solvents by rotary evaporation, the residue was purified by column chromatography on silica (petroleum ether/CH2Cl2 =1/3, v/v) and recrystallized with methanol/dichloromethane to give 115 mg of compound 16 in 72% yield as red solids.¹H NMR $(500 \text{ MHz}, \text{DMSO-d}_6, 353 \text{ K}) \delta = 9.96 \text{ (s, 1H)}, 8.84-8.76 \text{ (m, 2H)}, 8.21 \text{ (d, 1H)}, 8.11-8.06 \text{ (m, 3H)},$ 8.04-7.96 (m, 8H), 7.92 (d, 2H), 7.88-7.80 (m, 3H), 4.69 (d, 2H), 3.86(d, 2H), 3.79 (d, 2H), 2.28-2.18 (m, 1H), 1.50-1.10 (m, 26H), 0.91-0.73(m, 18H). ¹³C NMR (125 MHz, DMSO-d₆, 353 K) δ = 183.30, 161.44, 161.37, 150.68, 147.81, 146.38, 143.69, 142.62, 137.96, 135.13, 134.35, 132.08, 131.42, 129.83, 129.22, 129.08, 128.43, 127.99, 126.57, 126.52, 125.96, 125.86, 124.81, 124.46, 124.33, 123.96, 123.62, 122.83, 120.84, 120.72, 115.98, 114.68, 113.82, 109.24, 108.82, 48.89, 44.15, 44.07, 40.32, 38.05, 37.92, 30.01, 29.75, 29.66, 27.61, 27.54, 27.44, 23.46, 23.26, 23.23, 21.85, 21.66, 21.63, 13.09, 13.05, 13.02, 10.11, 9.81. MS (MALDI-TOF): calcd for [M]⁺, 997.5; found, 997.5. HRMS (MALDI-TOF, [M]⁺, 100%): calcd for C₆₇H₇₁N₃O₃S, 997.52107; found, 997.52062.

Synthesis of 17



The synthesis method resembles that of compound 16 and the compound was purified by column chromatography on silica (petroleum ether/ $CH_2Cl_2 = 1/3$, v/v) and recrystallized with

methanol/dichloromethane to give compound **17** in 70% yield as red solids. ¹H NMR (500 MHz, DMSO-d₆, 353 K) $\delta = 9.97$ (s, 1H), 8.86 (t, 2H), 8.14-8.08 (m, 5H), 8.06 (d, 2H), 8.01 (d, 3H), 7.96 (s, 1H), 7.94 (d, 2H), 7.89-7.83 (m, 3H), 7.65 (d, 2H), 7.19 (d, 2H), 4.77 (d, 2H), 3.92 (s, 3H), 3.90-3.85 (m, 2H), 3.83-3.78 (m, 2H), 2.32-2.22 (m, 1H), 1.50-1.10 (m, 26H), 0.92 (t, 3H), 0.84-0.72 (m, 15H). ¹³C NMR (125 MHz, DMSO-d₆, 353 K) $\delta = 183.34$, 161.46, 161.39, 158.51, 150.69, 147.83, 146.40, 143.71, 142.64, 138.01, 136.78, 135.05, 134.38, 133.11, 132.10, 131.50, 130.59, 129.86, 129.59, 129.10, 128.46, 127.07, 126.59, 126.53, 126.01, 125.91, 124.59, 124.41, 123.85, 123.68, 122.88, 120.98, 116.07, 115.23, 114.73, 114.14, 113.83, 109.26, 108.83, 54.97, 48.87, 44.17, 44.09, 40.30, 38.07, 37.93, 29.95, 29.75, 29.66, 27.54, 27.44, 23.43, 23.26, 23.23, 21.88, 21.66, 21.63, 13.10, 13.03, 10.13, 9.83. MS (MALDI-TOF): calcd for [M]⁺, 1103.6; found, 1103.5. HRMS (MALDI-TOF, [M]⁺, 100%): calcd for C₇₄H₇₇N₃O₄S, 1103.56293; found, 1103.56276.

Synthesis of **18**



The synthesis method resembles that of compound **16** and the compound was purified by column chromatography on silica (petroleum ether/CH₂Cl₂ =1/3, v/v) and recrystallized with methanol/dichloromethane to give compound **18** in 68% yield as red solids. ¹H NMR (500 MHz, DMSO-d₆, 353 K) δ = 9.97 (s, 1H), 8.82 (d, 1H), 8.78 (d, 1H), 8.30 (d, 1H), 8.11-8.04 (m, 4H), 7.99 (d, 5H), 7.92 (d, 2H), 7.86-7.78 (m, 3H), 7.52 (s, 1H), 4.69 (d, 2H), 4.21 (s, 3H), 3.90-3.84 (m, 2H), 3.83-3.76 (d, 2H), 2.30-2.21 (m, 1H), 1.46-1.10 (m, 26H), 0.93 (t, 3H), 0.83-0.71 (m, 15H). ¹³C NMR (125 MHz, DMSO-d₆, 353 K) δ =183.29, 161.45, 161.36, 155.52, 150.68, 147.89, 146.29, 143.96, 142.61, 137.95, 134.32, 132.91, 132.41, 130.52, 129.79, 129.69, 129.07, 128.98, 128.46, 128.41, 126.58, 126.32, 125.95, 125.85, 124.40, 123.73, 123.60, 123.40, 122.57, 122.05, 121.69, 120.75, 120.38, 116.44, 114.66, 109.94, 109.24, 108.75, 94.02, 56.19, 48.77, 44.15, 44.07, 40.17, 38.04, 37.90, 29.96, 29.75, 29.65, 27.58, 27.53, 27.43, 23.42, 23.25, 23.22, 21.88, 21.64, 21.61, 13.08, 13.06, 13.01, 10.12, 9.81. MS (MALDI-TOF): calcd for [M]⁺, 1027.5; found, 1027.6. HRMS (MALDI-TOF, [M]⁺, 100%): calcd for C₆₈H₇₃N₃O₄S, 1027.53163; found, 1027.53102.

Synthesis of 19



The synthesis method resembles that of compound **16** and the compound was purified by column chromatography on silica (petroleum ether/CH₂Cl₂ =1/3, v/v) and recrystallized with methanol/dichloromethane to give compound **19** in 64% yield as red solids. ¹H NMR (500 MHz, DMSO-d₆, 353 K) δ = 9.97 (s, 1H), 8.81 (d, 1H), 8.78 (d, 1H), 8.30 (d, 1H), 8.11-8.07 (m, 3H), 8.06 (d, 1H), 8.01 (d, 4H), 7.99 (s, 1H), 7.92 (d, 2H), 7.88-7.80 (m, 3H), 7.52 (s, 1H), 4.69 (d, 2H), 4.41 (t, 2H), 3.89-3.84 (m, 2H), 3.83-3.77 (m, 2H), 2.28-2.22 (m, 1H), 2.05-1.98 (m, 2H), 1.69-1.62 (m, 2H), 1.49-1.11 (m, 30H), 0.97-0.91 (m, 6H), 0.83-0.76 (m, 12H), 0.73 (t, 3H). ¹³C NMR (125 MHz, DMSO-d₆, 353 K) δ = 183.32, 161.46, 161.37, 154.75, 150.69, 147.90, 146.31, 143.98, 142.62, 137.98, 134.34, 132.90, 132.52, 130.55, 129.81, 129.72, 129.09, 129.00, 128.48, 128.42, 126.60, 126.33, 125.98, 125.88, 124.42, 123.73, 123.62, 123.44, 122.57, 122.31, 121.67, 120.78, 120.39, 116.47, 114.68, 109.91, 108.76, 95.01, 68.79, 48.78, 44.16, 44.09, 40.21, 38.05, 37.93, 30.57, 29.99, 29.75, 29.66, 28.38, 27.60, 27.53, 27.44, 24.93, 23.44, 23.26, 23.23, 21.88, 21.65, 21.62, 21.50, 13.22, 13.09, 13.06, 13.02, 10.14, 9.83, 9.81. MS (MALDI-TOF): calcd for $C_{73}H_{83}N_3O_4S$, 1097.60988; found, 1097.6. HRMS (MALDI-TOF, [M]⁺, 100%): calcd for $C_{73}H_{83}N_3O_4S$, 1097.60988; found, 1097.60933.

Synthesis of ND01



To a stirred solution of compound **16** (99.8 mg, 0.1 mmol) and cyanoacetic acid (25.5 mg, 0.3 mmol) in acetonitrile (10 mL) and chloroform (5 mL) was added piperidine (59.6 mg, 0.7 mmol). The reaction mixture was refluxed under argon for 12 h and then acidified with 2 M hydrochloric acid aqueous solution (50 mL). The crude product was extracted into dichloromethane, washed

with brine, and dried over anhydrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by column chromatography on silica (CH₂Cl₂/ methanol = 10/1, v/v) and recrystallized with methanol/dichloromethane to give 96 mg of compound **ND01** in 90% yield as red solids. mp>350 °C. ¹H NMR (500 MHz, DMSO-d₆, 353 K) δ =8.82-8.78 (m, 2H), 8.21 (d, 1H), 8.12-8.06 (m, 4H), 8.01-7.94 (m, 4H), 7.91 (d, 4H), 7.88-7.82 (m, 2H), 7.78-7.70 (m, 2H), 4.64 (d, 2H), 3.92-3.85 (m, 2H), 3.84-3.75 (m, 2H), 2.26-2.17 (m, 1H), 1.50-1.11 (m, 26H), 0.92-0.89 (m, 3H), 0.84-0.72 (m, 15H). ¹³C NMR (125 MHz, DMSO-d₆, 353 K) δ = 161.40, 147.59, 146.63, 146.19, 143.54, 139.07, 137.33, 134.98,, 134.76, 134.48, 131.89, 131.24, 129.74, 129.71, 129.15, 129.05, 128.41, 127.93, 127.56, 126.55, 126.39, 125.31, 125.22, 124.76, 124.33, 124.24, 123.86, 123.51, 122.73, 120.70, 120.59, 118.44, 115.82, 114.55, 113.52, 109. 00, 108.74, 48.66, 44.11, 43.98, 40.25, 38.01, 37.84, 29.99, 29.78, 29.66, 27.61, 27.55, 27.44, 23.46, 23.28, 23.24, 21.84, 21.67, 21.63, 13.09, 13.05, 13.02, 10.08, 9.82. MS (MALDI-TOF): calcd for [M]⁺, 1064.5; found, 1064.7. HRMS (MALDI-TOF, [M]⁺, 100%): calcd for C₇₀H₇₂N₄O₄S, 1064.52688; found, 1064.52615.

Synthesis of ND02



The synthesis method resembles that of compound **ND01** and the compound was purified by column chromatography on silica (CH₂Cl₂/ methanol = 10/1, v/v) and recrystallized with methanol/dichloromethane to give compound **ND02** in 92% yield as red solids.mp>350 °C.¹H NMR (500 MHz, DMSO-d₆, 353 K) δ = 8.79 (t, 2H), 8.12-8.05 (m, 5H), 7.96-7.88 (m, 6H), 7.83-7.7.79 (m, 3H), 7.74-7.7.71 (m, 2H), 7.60 (d, 2H), 7.17 (d, 2H), 4.60 (d, 2H), 3.92 (s, 3H), 3.90-3.83 (m, 2H), 3.83-3.76 (m, 2H), 2.24-2.16 (m, 1H), 1.50-1.11 (m, 26H), 0.89 (t, 3H), 0.84-0.72 (m, 15H). ¹³C NMR (125 MHz, DMSO-d₆, 353 K) δ = 161.42, 158.45, 147.60, 146.63, 146.26, 143.54, 139.17, 137.31, 136.56, 134.85, 134.76, 134.51, 133.10, 131.89, 131.31, 130.58, 129.84, 129.69, 129.48, 129.06, 128.43, 127.56, 126.91, 126.52, 126.35, 125.47, 125.28, 124.79, 124.38, 124.22, 123.71, 123.60, 122.74, 120.76, 118.44, 115.90, 115.08, 114.52, 113.74, 113.52,

109.00, 108.73, 54.96, 48.58, 44.10, 43.96, 40.19, 37.99, 37.82, 31.01, 29.95, 29.78, 29,67, 27.56, 27.45, 23.42, 23.28, 23.25, 21.87, 21.67, 21.64, 13.10, 13.03, 10.09, 9.83. MS (MALDI-TOF): calcd for $[M]^+$, 1170.6; found, 1170.6. HRMS (MALDI-TOF, $[M]^+$, 100%): calcd for $C_{77}H_{78}N_4O_5S$, 1170.56874; found, 1170.56897.

Synthesis of ND03



The synthesis method resembles that of compound **ND01** and the compound was purified by column chromatography on silica (CH₂Cl₂/ methanol = 10/1, v/v) and recrystallized with methanol/dichloromethane to give compound **ND03** in 93% yield as red solids.mp>350 °C.¹H NMR (500 MHz, DMSO-d₆, 353 K) δ = 8.77 (d, 1H), 8.74 (d, 1H), 8.26 (d, 1H), 8.10-8.04 (m, 2H), 8.02 (d, 2H), 7.91 (d, 2H), 7.86-7.82 (m, 4H), 7.79 (dd, 2H), 7.70 (d, 1H), 7.68 (d, 1H), 7.21 (s, 1H), 4.40-4.28 (m, 2H), 4.14 (s, 3H), 3.91-3.83 (m, 2H), 3.79 (d, 2H), 2.15-2.08 (m, 1H), 1.36-1.11 (m, 26H), 0.87 (t, 3H), 0.84-0.76 (m, 12H), 0.73 (t, 3H). ¹³C NMR (125 MHz, DMSO-d₆, 353 K) δ = 161.39, 155.26, 147.67, 146.52, 146.28, 143.75, 139.17, 137.26, 134.66, 134.48, 132.63, 132.07, 130.19, 129.66, 129.58, 129.03, 128.86, 128.39, 127.53, 126.38, 126.22, 125.18, 125.12, 124.20, 123.56, 123.45, 123.22, 122.41, 121.92, 121.48, 120.69, 120.15, 118.41, 116.16, 114.43, 109.63, 108.94, 108.59, 93.35, 55.89, 48.32, 44.04, 43.89, 37.94, 37.77, 29.95, 29.79, 29.66, 27.56, 27.44, 23.40, 23.28, 23.24, 21.85, 21.66, 21.61, 13.06, 13.00, 10.06, 9.81. MS (MALDI-TOF): calcd for [M]⁺, 1094.5; found, 1094.5. HRMS (MALDI-TOF, [M]⁺, 100%): calcd for C₇₁H₇₄N₄O₅S, 1094.53744; found, 1094.53734.

Synthesis of ND04



The synthesis method resembles that of compound **ND01** and the compound was purified by column chromatography on silica (CH₂Cl₂/ methanol = 10/1, v/v) and recrystallized with methanol/dichloromethane to give compound **ND04** in 90% yield as red solids. mp>350 °C. ¹H NMR (500 MHz, DMSO-d₆, 353 K) δ = 8.78 (dd, 2H), 8.28 (d, 1H), 8.11-8.05 (m, 4H), 7.97-7.89 (m, 6H), 7.86-7.79 (m, 2H), 7.77-7.69 (m, 2H), 7.41 (s, 1H), 4.57 (d, 2H), 4.43-4.33 (m, 2H), 3.90-3.84 (m, 2H), 3.82-3.77 (m, 2H), 2.22-2.15 (m, 1H), 2.04-1.98 (m, 2H), 1.70-1.63 (m, 2H), 1.49-1.11 (m, 30H), 0.96 (t, 3H), 0.91 (t, 3H), 0.83-0.76 (m, 12H), 0.73 (t, 3H). ¹³C NMR (125 MHz, DMSO-d₆, 353 K) δ = 161.41, 154.59, 147.67, 146.54, 146.12, 143.79, 138.92, 137.36, 134.72, 134.36, 132.66, 132.23, 130.27, 129.68, 129.62, 129.05, 128.88, 128.40, 127.53, 126.41, 126.25, 125.23, 125.14, 124.24, 123.58, 123.47, 123.28, 122.43, 122.17, 121.50, 120.73, 120.17, 118.48, 116.24, 114.46, 110.77, 109.66, 108.97, 108.64, 94.43, 68.55, 48.43, 44.09, 43.95, 40.21, 37.97, 37.81, 30.61, 29.98, 29.79, 29.66, 28.40, 27.60, 27.56, 27.44, 24.95, 23.43, 23.29, 23.25, 21.87, 21.66, 21.62, 21.52, 13.23, 13.08, 13.06, 13.01, 10.10, 9.81. MS (MALDI-TOF): calcd for C₇₆H₈₄N₄O₅S, 1164.61569; found, 1164.8. HRMS (MALDI-TOF, [M]⁺, 100%): calcd for C₇₆H₈₄N₄O₅S, 1164.61569; found, 1164.61586.



3.Photophysical Properties

Fig. S1 UV-Vis spectra of ND01-ND04 anchored on the 4 µm TiO₂ film.



Fig.S2 UV-Vis spectra of all dyes with (solid lines) and without (dashed lines) CDCA on 4 μ m TiO₂ film.



Fig. S3 CVs of ferrocene, ND01, ND02, ND03 and ND04. Scan rate: 100 mv/s

dye	$\lambda_{max}^{sol.}[nm]$ $(\epsilon \times 10^4 M^{-1} cm^{-1})^a$	$\lambda_{\max}^{ ext{ film }}$ $\left[ext{nm} ight]^b$	E_{g}^{opt} $[eV]^{c}$	LUMO $[eV]^d$	LUMO[V] (vs.NHE) ^e	HOMO[V] (vs.NHE) ^f
ND01	522(4.67) 400(5.73) 298(4.31)	510	2.04	-3.23	-1.27	0.77
ND02	526(3.96) 403(4.39) 301(3.50)	512	2.02	-3.11	-1.39	0.63
ND03	527(3.17) 397(3.80) 303(3.03)	510	1.98	-3.14	-1.36	0.62
ND04	527(3.82) 396(4.69) 304(3.64)	510	1.97	-3.20	-1.30	0.67

Table S1 Optical and electrochemical properties of the dye ND01-ND04

^{*a*} Measured in dilute CHCl₃ solution (1.0 × 10⁻⁵ M);^{*b*} Measured in the film on 4 µm TiO₂;^{*c*} Calculated by the onset of absorption in CHCl₃ solution according to E_g = 1240/ λ_{onset} ; ^{*d*} LUMO was estimated by the onset of reduction peaks and calculated according to E_{LUMO} = -(4.8 + E_{onset}), and measured in CH₂Cl₂ solution *vs*. Fc/Fc⁺, performed in *n*-Bu₄NPF₆/CH₂Cl₂ (0.1 M), scan rate 100 mV s⁻¹; ^{*e*} To convert to the electrochemical scale, the sign has to be inverted and 4.5 eV subtracted;^{5*f*} Estimated from LUMO levels and E_g .



Fig.S4 Calculated HOMO and LUMO profiles and energy levels of ND01-ND04 (B3LYP/6-31G**).

4.DSSCs Fabrication and Measurements

Materials

The FTO conducting glass (FTO glass, fluorine doped tin oxide over-layer, transmission >90% in the visible, sheet resistance 15 Ω square⁻¹) was obtained from the Geao Science and Educational Co. Ltd. of China. Titania pastes of DSL 90T were purchased from Dyesol. Lithium iodide was from Fluka and iodine, 99.999%, was from Alfa Aesar.

Preparation of photovoltaic devices

A screen-printed layer of TiO₂ particles was used as the photoelectrode. A 15 μ m thick film of DSL 90T was printed on the FTO conducting glass. The electrodes coated with TiO₂ pastes were gradually heated under an air flow at 325 °C for 5 min, 375 °C for 5 min, 450 °C for 15 min and

500 °C for 15 min. Before immersion in the dye solution, these films were immersed into a 40 mM aqueous TiCl₄ solution at 70 °C for 30 min and washed with water and ethanol. Then the films were heated again at 450 °C for 30 min followed by cooling to 80 °C and dipping into a 3 × 10^{-4} M solution of dye in acetonitrile for 18 h at room temperature. To prepare the counter electrode, the Pt catalyst was deposited on the cleaned FTO glass by spin coating with a drop of H₂PtCl₆ solution (0.02 M in 2-propanol solution) with heat treatment at 400 °C for 15 min. A hole (0.8 mm diameter) was drilled on the counter electrode by a drill-press. The perforated sheet was cleaned by ultrasound in an ethanol bath for 10 min. As for the assembly of DSSCs, the dye-covered TiO₂ electrode and Pt-counter electrode were assembled into a sandwich type cell and sealed with a hot-melt gasket of 25 µm thickness made of the ionomerSurlyn 1702 (DuPont). The size of the TiO₂ electrodes used was 0.12 cm² (*i.e.*, 3 mm × 4 mm). A drop of the electrolyte was put on the hole in the back of the counter electrode was sealed by a film of Surlyn 1702 and a cover glass (0.1 mm thickness) using a hot iron bar.

Electrolytes

The electrolyte employed was a solution of 0.5 M MPII (1-methyl-3-propyl-imidazolium iodide), 0.05 M I_2 , 0.1 M LiI, 0.1 M GuSCN (guanidiniumthiocyanate) and 0.5 M 4-tertbutylpyridinein acetonitrile and 3-methoxypropionitrile (v:v= 7 : 3).

Photovoltaic performance measurements

The current–density voltage (J-V) characteristics of the DSSCs were measured by recording J-V curves using a Keithley 2400 source meter under the illumination of AM 1.5 G simulated solarlight (Newport-91160 equipped with a 300 W Xe lamp and an AM 1.5 G filter). The incident light intensity was calibrated to 100 mW cm⁻² with a standard silicon solar cell (Newport 91150V). Action spectra of the incident monochromatic photonto-electron conversion efficiency (IPCE) for the solar cells were obtained with a Newport-74125 system (Newport Instruments). The intensity of monochromatic light was measured with a Si detector (Newport-71640). The electrochemical impedance spectroscopy (EIS) measurements of all the DSSCs were performed using a ZahnerIM6e Impedance Analyzer (ZAHNERElektrik GmbH &CoKG, Kronach, Germany). The

frequency range is 0.10 Hz-100 kHz. The applied voltage bias is -0.60 V with a magnitude of the alternative signal of 10 mV.

Table S2 Photovoltaic performance of DSSCs based on **ND01-ND04** dyes with liquid electrolyte under irradiation of AM 1.5 G simulated solar light (100 mW cm⁻²)

Dye	$J_{ m SC}$	$V_{\rm OC}$	FF	PCE	Absorbed Dye
	$[\mathrm{mAcm}^{-2}]$	[mV]		[%]	$[mol cm^{-2}]$
ND01	15.29	675	0.723	7.46	4.63×10 ⁻⁷
ND02	17.14	698	0.694	8.30	5.57×10 ⁻⁷
ND03	14.60	639	0.717	6.69	6.71×10 ⁻⁷
ND04	15.59	643	0.699	7.01	5.65×10 ⁻⁷

Table S3 Photovoltaic performance of DSSCs based on **ND01-ND04** dyes with liquid electrolyte under irradiation of AM 1.5 G simulated solar light (100 mW cm⁻²)

		-			
Dye	CDCA	$J_{ m SC}$	$V_{\rm OC}$	FF	PCE
	[mM]	$[mA cm^{-2}]$	[mV]		[%]
ND01	0	14.55	651	0.695	6.58
	10	15.29	675	0.723	7.46
ND02	0	15.97	649	0.696	7.21
	10	17.14	698	0.694	8.30
ND03	0	12.67	605	0.677	5.19
	10	14.60	639	0.717	6.69
ND04	0	12.90	632	0.683	5.57
	10	15.59	643	0.699	7.01

Additional References:

- 1. Q. Sun, H. Wang, C. Yang, Y. Li, J. Mater. Chem., 2003, 13, 800.
- 2. K.Cai, J. Xie and D. Zhao, J. Am. Chem. Soc., 2014, 136, 28.
- 3. W. Jiang, H. Qian, Y. Li and Z. Wang, J. Org. Chem., 2008, 73, 7369.
- 4. A. R. Rabindranath, Y. Zhu, I. Heim and B. Tieke, Macromolecules, 2006, 39, 8250.
- 5. D. Cahen, G. Hodes, M. Grätzel, J. F. Guillemoles, I. Riess, J. Phys. Chem. B, 2000, 104, 2053.

5, NMR and MS spectra

¹H NMR Spectrum of 2 in CDCl₃ at 400 MHz





HRMS of compound 2



Elemental Composition Report

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions 8 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Minimum:	80.00				-1.5		
Maximum:	100.00		200.0	10.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
377.2148	100.00	377.2144	0.4	1.2	16.0	1	C28 H27 N







HRMS of compound 3



Elemental Composition Report

Multiple Mass Analysis: 2 mass(es) processed Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron lons 54 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)

Minimum	80.00				-15					
Maximum:	100.00		200.0	10.0	50.0					
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Form	ula		
455.1243	100.00	455.1249	-0.6	-1.2	16.0	1	C28	H26	Ν	79Br
457.1231	98.61	457.1228	0.3	0.6	16.0	1	C28	H26	N	81Br

¹H NMR Spectrum of 4 in CDCl₃ at 400 MHz





HRMS of compound 4



Elemental Composition Report

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron lons 4 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Minimum:	80.00				-1.5				
Maximum:	100.00		200.0	10.0	50.0				
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula		
483.2557	100.00	483.2562	-0.5	-1.1	20.0	1	C35 H33	Ν	0

^1H NMR Spectrum of 5 in DMSO-d_6at 400 MHz





HRMS of compound 5



Elemental Composition Report

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions 32 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Minimum:	80.00				-1.5				
Maximum:	100.00		200.0	10.0	50.0				
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula		
407.2244	100.00	407.2249	-0.5	-1.3	16.0	1	C29 H29	N /	0

¹H NMR Spectrum of 6 in DMSO-d₆at 400 MHz





HRMS of compound 6



Elemental Composition Report

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron lons 152 formula(e) evaluated with 4 results within limits (up to 50 closest results for each mass)

Minimum:	80.00				-1.5		
Maximum:	100.00		200.0	10.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
477.3023	100.00	477.3032	-0.9	-1.8	16.0	4	C34 H39 N O

¹H NMR Spectrum of 7 in CDCl₃ at 400 MHz





HRMS of compound 7



Elemental Composition Report

Multiple Mass Analysis: 2 mass(es) processed Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions 66 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)

Minimum:	80.00			10.0	-1.5			
Maximum: Mass	100.00 RA	Calc. Mass	200.0 mDa	PPM	DBE	Score	Formula	
561.1674	100.00	561.1667	0.7	1.2	20.0	1	C35 H32 N O	79Br
563.1655	91.78	563.1647	0.8	1.5	20.0	1	C35 H32 N O	81Br

¹H NMR Spectrum of 8 in DMSO-d₆at 400 MHz





HRMS of compound 8



Elemental Composition Report

Multiple Mass Analysis: 2 mass(es) processed Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron lons 120 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)

Minimum: Maximum:	80.00 100.00		200.0	10.0	-1.5 50.0					
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula			
485.1360	98.73	485.1354	0.6	1.2	16.0	1	C29 H28	N	0	79Br
487.1343	100.00	487.1334	0.9	1.9	16.0	1	C29 H28	N	0	81Br







HRMS of compound 9



Elemental Composition Report

Multiple Mass Analysis: 2 mass(es) processed Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions 43 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)

Minimum:	80.00				-1.5				
Maximum:	100.00		200.0	10.0	50.0				
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula		
555.2144	95.86	555.2137	0.7	1.3	16.0	1	C34 H38	NO) 79Br
557,2128	100.00	557 2116	12	21	16.0	1	C34 H38	NC) 81Br

¹H NMR Spectrum of 11 in CDCl₃ at 400 MHz



¹³C NMR Spectrum of 11 in CDCl₃ at 100 MHz





HRMS of compound 11



Elemental Composition Report

Multiple Mass Analysis: 2 mass(es) processed Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron lons 717 formula(e) evaluated with 4 results within limits (up to 50 closest results for each mass)

Minimum	80.00				-15						
Maximum:	100.00		200.0	10.0	50.0						
Mass	RA	Calc. Mass	mDa	PPM	DBE	Scor	e Form	ula			
700.2326	92.14	700.2334	-0.8	-1.2	18.0	1	C39	H45	N2	03	S
702.2296	100.00	702.2314	-1.8	-2.5	18.0	1	C39	H45	N2	03	S

laximum:	100.00		200.0	10.0	50.0							
lass	RA	Calc. Mass	mDa	PPM	DBE	Scor	re Form	ula				
00.2326	92.14	700.2334	-0.8	-1.2	18.0	1	C39	H45	N2	03	S	79Br
02.2296	100.00	702.2314	-1.8	-2.5	18.0	1	C39	H45	N2	03	S	81Br

¹H NMR Spectrum of 12 in CDCl₃ at 400 MHz







Elemental Composition Report

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions 28 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)

Minimum:	80.00				-1.5						
Maximum:	100.00		200.0	10.0	50.0						
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Form	nula			
503.3004	100.00	503.2996	0.8	1.7	17.0	1	C34	H38	в	Ν	02

¹H NMR Spectrum of 13 in CDCl₃ at 400 MHz





HRMS of compound 13



Elemental Composition Report

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron lons 7 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Minimum	80.00				-15					
Maximum:	100.00		200.0	10.0	50.0					
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula			
609.3424	100.00	609.3414	1.0	1.6	21.0	1	C41 H44	Ν	03	В



¹H NMR Spectrum of 14 in DMSO-d₆ at 500 MHz



HRMS of compound 14



Elemental Composition Report

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions 32 formula(e) evaluated with 3 results within limits (up to 50 closest results for each mass)

Minimum:	80.00				-1.5		
Maximum:	100.00		200.0	10.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
533.3094	100.00	533.3101	-0.7	-1.4	17.0	1	C35 H40 B N O3

¹H NMR Spectrum of 15 in DMSO-d₆ at 400 MHz





HRMS of compound 15



Elemental Composition Report

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions 9 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Minimum:	80.00				-1.5				
Maximum:	100.00		200.0	10.0	50.0				
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula		
603.3890	100.00	603.3884	0.6	1.0	17.0	1	C40 H50	BN	03

¹H NMR Spectrum of 16 in DMSO-d₆ at 500 MHz



$^{13}\mathrm{C}$ NMR Spectrum of 16 in DMSO-d_6 at 125 MHz





HRMS of compound 16



¹H NMR Spectrum of 17 in DMSO-d₆ at 500 MHz





HRMS of compound 17



¹H NMR Spectrum of 18 in DMSO-d₆ at 500 MHz



$^{13}\mathrm{C}$ NMR Spectrum of 18 in DMSO-d_6 at 125 MHz





HRMS of compound 18



 Meas.m/z
 #
 Formula
 Score
 m/z
 err [ppm]
 Mean err [ppm]
 mSigma
 rdb
 e⁻ Conf
 N-Rule

 1027.53102
 1
 C 68 H 73 N 3 O 4 S
 100.00
 1027.53163
 0.59
 0.15
 34.0
 34.0
 odd
 ok

¹H NMR Spectrum of 19 in DMSO-d₆ at 500 MHz



$^{13}\mathrm{C}$ NMR Spectrum of 19 in DMSO-d_6 at 125 MHz





HRMS of compound 19



 Meas.m/z
 # Formula
 Score
 m/z
 err [ppm]
 Mean err [ppm]
 mSigma
 rdb
 e⁻ Conf
 N-Rule

 1097.60933
 1
 C 73 H 83 N 3 O 4 S
 100.00
 1097.60988
 0.50
 0.50
 373.1
 34.0
 odd
 ok

¹H NMR Spectrum of ND01 in DMSO-d₆ at 500 MHz



$^{13}\mathrm{C}$ NMR Spectrum of ND01 in DMSO-d_6 at 125 MHz





HRMS of compound ND01



 Meas.m/z
 # Formula
 Score
 m/z
 err [ppm]
 Mean err [ppm]
 mSigma
 rdb
 e⁻ Conf
 N-Rule

 1064.52615
 1
 C 70 H 72 N 4 O 4 S
 100.00
 1064.52688
 0.68
 0.68
 391.4
 37.0
 odd
 ok

¹H NMR Spectrum of ND02 in DMSO-d₆ at 500 MHz



$^{13}\mathrm{C}$ NMR Spectrum of ND02 in DMSO-d_6 at 125 MHz





HRMS of compound ND02



 Meas. m/z
 # Formula
 Score
 m/z
 err [ppm]
 Mean err [ppm]
 mSigma
 rdb
 e⁻Conf
 N-Rule

 1170.56897
 1
 C 77 H 78 N 4 O 5 S
 100.00
 1170.56874
 -0.19
 -0.85
 59.1
 41.0
 odd
 ok

¹H NMR Spectrum of ND03 in DMSO-d₆ at 500 MHz





HRMS of compound ND03



 Meas. m/z
 # Formula
 Score
 m/z
 err [ppm]
 Mean err [ppm]
 mSigma
 rdb
 e⁻ Conf
 N-Rule

 1094.53734
 1
 C 71 H 74 N 4 O 5 S
 100.00
 1094.53744
 0.09
 -0.54
 19.9
 37.0
 odd
 ok

¹H NMR Spectrum of ND04 in DMSO-d₆ at 500 MHz



$^{13}\mathrm{C}$ NMR Spectrum of ND04 in DMSO-d_6 at 125 MHz





HRMS of compound ND04

