Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

N-Annulated perylene–based metal-free organic sensitizers for dye-sensitized solar cells

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1. Materials and Instruments

All chemicals and solvents were purchased from commercial suppliers and used without further purification unless otherwise specified. Starting materials 1 and 5 were synthesized according to literature.[1] ^{1}H and ^{13}C NMR spectra were recorded in deuterated solvents on a Bruker Avance 400 NMR Spectrometer, a Bruker Avance III 500 WB NMR Spectrometer and a Avance 600 NMR Spectrometer. ^{1}H NMR chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard. Mass spectra (MALDI-TOF-MS) were determined on a Bruker BIFLEX III Mass Spectrometer.

2. Optical and Electrochemical Characterization

The absorption spectra of dyes and sensitized films were measured by a Hitachi Model U-3010 UV-Vis spectrophotometer. Cyclic voltammograms (CVs) were recorded on a Zahner IM6e electrochemical workstation using glassy carbon discs as the working electrode, Pt wire as the counter electrode, Ag/AgCl electrode as the reference electrode, and ferrocene/ferrocenium (Fc/Fc^{+}) as an external potential marker for the calibration of potential. 0.1 M tetrabutyl-ammoniumhexafluorophosphate (Bu_4NPF_6) dissolved in CH_2Cl_2 (HPLC grade) was employed as the supporting electrolyte. CH_2Cl_2 was dried over calcium hydride and degassed prior to measurement.

3. DSCs Fabrication and Photovoltaic Performance Measurements

Materials

The FTO conducting glass (FTO glass, fluorine doped tin oxide over-layer, transmission >90% in the visible, sheet resistance 15 U 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. The electrolyte employed was a solution of 0.6 M DMPI, 0.05 M I_2, LiI 0.1 M, 0.5 M TBP in acetonitrile and 3-methoxypropionitrile (v:v = 7 : 3).

Preparation of photovoltaic devices

A screen-printed layer of TiO_2 particles was used as the photo-electrode. A 15 mm thick film of DSL 90T was printed on the FTO conducting glass. The electrodes coated with TiO_2 pastes were gradually heated under an air flow at 325°C for 5min, 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 $TiCl_4$ 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 12 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 H_2PtCl_6 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 TiO_2 electrode and Pt-counter electrode were assembled into a sandwich type cell and sealed with a hot-melt gasket of 25 mm thickness made of the ionomer Surlyn 1702 (DuPont). The size of the TiO_2 electrodes used was 0.12 cm^2 (i.e., 0.3 mm × 0.4 mm). A drop of the electrolyte was put on the hole in the back of the counter electrode, which was introduced into the cell via vacuum backfilling. The hole in the counter electrode was sealed by a film of Surlyn 1702 and a cover glass (0.1 mm thickness) using a hot iron bar.

Photovoltaic performance measurements

The current–density voltage (J–V) characteristics of the DSCs were measured by recording J–V curves using a Keithley 2400 source meter under the illumination of AM 1.5 G simulated solar light (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 photon-to-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 DSCs were per-formed using a Zahner IM6e Impedance Analyzer (ZAHNER-Elektrik GmbH & CoKG, Kronach, Germany). The frequency range is 0.10 Hz–100 kHz. The applied voltage bias is −0.70 V with a magnitude of the alternative signal of 10 mV.

4. Experimental procedures

Synthesis of compound 2:

To a solution of compound 1 (200 mg, 0.38 mmol), $Pd(PPh_3)_4$ (22 mg, 5% equiv), K_2CO_3 (262 mg, 1.90 mmol) in 40 ml THF (1 ml H_2O) was added the dropwise 4-(diphenylamino)phenylboronic acid (110 mg, 0.38 mmol) in 10 ml THF solution under argon. Then the reaction mixture was stirred at 66 ^oC for 12 h. After cooling to room temperature, the reaction mixture was 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:CH_2Cl_2 = 4:1) to yield the yellow solid product (146 mg, 55%). ^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ 0.80-0.83 (m, 6H), 1.19-1.45 (m, 8H), 1.99 (b, 1H), 4.07-4.08 (d, 2H), 7.05-7.08 (t, 2H), 7.24-7.32 (m, 10H), 7.49 (s, 1H), 7.54-7.56 (d, 2H), 7.62-7.70 (m, 3H), 8.07-8.09 (d, 1H), 8.14-8.16 (d, 1H), 8.34-8.36 (d, 1H), 8.40-8.42 (d, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 10.73, 13.97, 22.96, 24.14, 28.50, 30.71, 41.01, 49.48, 113.57, 115.77, 116.26, 116.62, 117.03, 120.93, 120.97, 123.00, 123.45, 124.17, 124.36, 124.41, 124.55, 124.93, 127.39, 127.50, 129.35, 129.69, 130.06, 130.98, 131.18, 132.05, 135.85, 137.38, 146.94, 147.82. MS (MALDI-TOF): m/z (M^+) = 700.4 (calcd for $C_{46}H_{39}BrN_2$, 698.23).

Synthesis of compound 3:

A mixture of compound 2 (200 mg, 0.31 mmol), 5-formyl-2-thiopheneboronic acid (55 mg, 0.35 mmol), $Pd(PPh_3)_4$ (18 mg, 5% equiv), K_2CO_3 (214 mg, 1.55 mmol) in 50 ml dry THF (1 ml H_2O) was stirred at 66 ^oC for 12 h under Argon. After cooling to room temperature, the reaction mixture was 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:CH_2Cl_2 = 1:2) to yield the yellow solid product (181 mg, 80%). ^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ 0.83-0.87 (t, 3H), 0.90-0.94 (t, 3H), 1.25-1.38 (m, 8H), 2.15-2.18 (m, 1H), 4.34-4.36 (d, 2H), 7.10-7.13 (t, 2H), 7.28-7.32 (m, 6H), 7.35-7.39 (t, 4H), 7.52-7.53 (d, 1H), 7.57-7.59 (d, 2H), 7.65 (s, 1H), 7.76-7.80 (m, 2H), 7.82 (s, 1H), 7.88-7.89 (d, 1H), 8.23-8.25 (d, 1H), 8.37-8.39 (d, 1H), 8.59-8.61 (t, 2H), 10.00 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 10.73, 13.95, 22.98, 24.14, 28.51, 30.76, 41.11, 49.61, 113.68, 115.39, 116.15, 118.21, 121.08, 121.28, 123.05, 123.12, 123.37, 124.58, 124.67, 125.21, 126.90, 127.11, 127.68, 127.81, 129.35, 130.18, 130.75, 130.95, 131.29, 133.16, 135.58, 136.94, 138.37, 142.45, 147.08, 147.77, 154.72, 182.73. MS (MALDI-TOF): m/z (M^+) = 730.4 (calcd for $C_{51}H_{42}N_2OS$, 730.3).

Synthesis of NPS-1:

A mixture of 3 (100 mg, 0.14 mmol) with cyanoacetic acid (14 mg, 0.15 mmol) in 10 ml acetonitrile (2 ml $CHCl_3$) was refluxed in the presence of 0.5 ml piperidine for 12 h under Argon. After cooling, the mixture was diluted with dichloromethane, and washed with water and brine, dried over Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (CH_2Cl_2:CH_3OH = 5:1) to yield an red solid product (92 mg, 82%). ^{1}H NMR (DMSO-d_6, 500 MHz, 378 K): δ 0.70-0.73 (t, 3H), 0.83 (b, 3H), 1.15-1.30 (b, 8H), 2.11 (b, 1H), 4.56 (b, 2H), 7.09-7.12 (t, 2H), 7.16-7.19 (t, 6H), 7.35-7.38 (t, 4H), 7.52-7.60 (b, 3H), 7.78 (b, 3H), 7.90 (b, 2H), 8.08 (b, 2H), 8.36 (b, 1H), 8.72 (b, 2H). ^{13}C NMR (DMSO-d_6, 125 MHz, 298 K): δ 10.03, 12.97, 21.79, 23.37, 27.46, 29.87, 48.51, 113.73, 114.87, 115.37, 116.59, 120.99, 122.66, 122.74, 123.60, 123.74, 124.38, 124.87, 126.36, 126.74, 127.46, 129.03, 129.30, 129.74, 130.40, 132.45, 134.78, 136.97, 146.21, 146.90. MS (MALDI-TOF): m/z (M^+) = 797.2 (calcd for $C_{54}H_{43}N_3O_2S$, 797.31). HRMS (MALDI-TOF): m/z (M^+) =797.3068 (calcd for $C_{54}H_{43}N_3O_2S$, 797.3071).

Synthesis of compound 4:

To a solution of 2 (100 mg, 0.14 mmol) in 15 ml dry THF was added dropwise 1.6 M *n*-BuLi in hexane solution (0.1 ml, 0.16 mmol) at -78 ^{o}C under argon. After the mixture was stirred at -78 ^{o}C for 0.5 h, anhydrous DMF (43 mg, 0.58 mmol) was added into the mixture. After it was slowly warm up to room temperature and was stirred for 4 h, the mixture was poured into aqueous NH_4Cl solution. The aqueous layer was extracted with dichloromethane, and the combined organic phase was washed with saturated brine and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified column chromatography on silica gel (petroleum ether:CH_2Cl_2 = 1:3) to yield an orange solid product (59 mg, 65%). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 0.82-0.85 (t, 3H), 0.91-0.95 (t, 3H), 1.23-1.42 (m, 8H), 2.17-2.23 (m, 1H), 4.48-4.49 (d, 2H), 7.08-7.12 (t, 2H), 7.25-7.31 (m, 6H), 7.33-7.37 (t, 4H), 7.59-7.61 (d, 2H), 7.70 (s, 1H), 7.83-7.87 (t, 1H), 7.95-7.99 (t, 1H), 8.14 (s, 1H), 8.25-8.27 (d, 1H), 8.70-8.74 (t, 2H), 9.26-9.28 (d, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 10.78, 13.98, 23.00, 24.22, 28.57, 30.80, 41.26, 49.79, 113.59, 115.85, 121.29, 121.76, 122.13, 123.20, 123.86, 124.10, 124.44, 124.48, 124.72, 124.99, 125.19, 126.93, 127.15, 127.72, 128.60, 129.40, 130.06, 130.34, 130.69, 130.94, 135.08, 135.59, 140.89, 147.42, 147.71, 192.67. MS (MALDI-TOF): m/z (M^+) = 648.8 (calcd for $C_{46}H_{39}BrN_2$, 648.31).

Synthesis of NPS-4:

The product was synthesized according to the procedure as described above for synthesis of **NPS-1**, giving an orange solid of the product **NPS-4** in 66% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, 378 K): δ 0.71-0.73 (t, 3H), 0.85 (b, 3H), 1.15-1.32 (b, 8H), 2.14 (b, 1H), 4.44 (b, 2H), 7.10-7.13 (t, 2H), 7.16-7.20 (m, 6H), 7.35-7.38 (t, 4H), 7.56-7.58 (d, 2H), 7.79 (b, 1H), 7.90 (b, 1H), 8.10-8.11 (d, 1H), 8.27 (b, 1H), 8.59 (b, 1H), 8.75 (b, 2H), 9.10 (b, 1H). ^{13}C NMR (DMSO-d_6, 125 MHz, 378 K): δ 10.03, 12.96, 21.74, 23.50, 27.53, 30.03, 48.51, 113.48, 113.83, 114.67, 118.44, 120.78, 121.32, 122.43, 122.82, 123.37, 123.85, 124.39, 125.05, 126.59, 127.38, 129.04, 129.63, 130.19, 130.41, 133.54, 134.48, 138.07, 146.32, 146.84. MS (MALDI-TOF): m/z (M^+) =715.8 (calcd for $C_{50}H_{41}N_3O_2$, 715.32). HRMS (MALDI-TOF): m/z (M^+) =715.3192 (calcd for $C_{50}H_{41}N_3O_2$, 715.3193).

Synthesis of compound 6:

A mixture of compound 5 (200 mg, 0.44 mmol), 4-(di(*p*-methoxyphenyl)amino))phenylboronic acid (175 mg, 0.50 mmol), $Pd(PPh_3)_4$ (25 mg, 5% equiv), K_2CO_3 (304 mg, 2.20 mmol) in 50 ml dry THF (1 ml H_2O) was stirred at 66 ^oC for 12 h under Argon. After cooling to room temperature, the reaction mixture was 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:CH_2Cl_2 = 2:1) to yield the yellow solid product (233 mg, 78%). ^1H NMR (DMSO-d_6, 500 MHz, 378 K): δ 0.74-0.77 (t, 3H), 0.88-0.91 (t, 3H), 1.17-1.41 (m, 8H), 2.21-2.23 (b, 1H), 4.67-4.69 (d, 2H), 6.96-6.98 (d, 4H), 7.01-7.03 (d, 2H), 7.14-7.16 (d, 4H), 7.52-7.54 (d, 2H), 7.79-7.84 (m, 2H), 7.90 (s, 1H), 7.94-7.99 (m, 2H), 8.12-8.14 (d, 1H), 8.16-8.18 (d, 2H), 8.74-8.77 (t, 2H). ^{13}C NMR (DMSO-d_6, 125 MHz, 298 K): δ 10.13, 13.05, 21.86, 23.45, 27.61, 30.01, 40.31, 48.90, 55.03, 113.83, 113.91, 114.80, 115.25, 116.17, 119.26, 120.42, 120.63, 122.99, 123.54, 123.66, 123.99, 124.16, 124.22, 124.57, 126.22, 127.02, 128.01, 129.39, 129.61, 130.16, 131.69, 131.74, 132.73, 136.46, 140.05, 147.38, 155.63. MS (MALDI-TOF): m/z (M^+) = 680.4 (calcd for $C_{48}H_{44}N_2O_2$, 680.34).

Synthesis of compound 7:

To the solution of compound 6 (200 mg, 0.29 mmol) in 200 ml CH_2Cl_2 added NBS (55 mg, 0.31 mmol), and the mixture was stirred at room temperature for 1 h. The solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography on silica gel (petroleum ether:CH_2Cl_2 = 3:1) to yield the yellow solid product (1.27 g, 90%). ^1H NMR (DMSO-d_6, 500 MHz, 298 K): δ 0.74-0.77 (t, 3H), 0.88-0.91 (t, 3H), 1.15-1.42 (m, 8H), 2.17-2.23 (m, 1H), 3.79 (s, 6H), 4.67-4.69 (d, 2H), 6.97-6.98 (d, 4H), 7.01-7.03 (d, 2H), 7.15-7.17 (d, 4H), 7.52-7.53 (d, 2H), 7.82-7.86 (t, 1H), 7.91 (s, 1H), 7.95-7.98 (t, 1H), 8.16-8.17 (d, 1H), 8.26-8.28 (d, 1H), 8.40 (s, 1H), 8.82-8.85 (m, 2H). ^{13}C NMR (DMSO-d_6, 125 MHz, 298 K): δ 10.08, 13.02, 21.85, 23.35, 27.48, 29.86, 40.19, 48.94, 55.01, 113.92, 114.79, 115.64, 115.84, 117.60, 119.13, 121.26, 121.36, 121.26, 121.36, 123.37, 123.53, 123.62, 124.10, 124.44, 125.29, 126.26, 126.85, 126.97, 128.94, 129.69, 130.13, 131.16, 132.11, 132.39, 137.32, 139.97, 147.49, 155.65. MS (MALDI-TOF): m/z (M^+) = 758.3 (calcd for $C_{48}H_{43}BrN_2O_2$, 758.25).

Synthesis of compound 8:

The product was synthesized according to the procedure as described above for synthesis of compound 4, giving a yellow solid of the product **8** in 76% yield. ^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ 0.84-0.91 (m, 6H), 1.22-1.36 (m, 8H), 2.09 (b, 1H), 3.87 (s, 6H), 4.22-4.23 (d, 2H), 6.96-7.20 (b, 9H), 7.56 (b, 3H), 7.72-7.77 (m, 3H), 7.85 (b, 1H), 8.20 (b, 2H), 8.51 (b, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 10.72, 13.95, 22.98, 24.13, 28.53, 30.77, 41.12, 49.64, 55.49, 113.54, 114.77, 115.41, 116.03, 118.28, 120.06, 121.05, 121.26, 123.10, 124.54, 124.63, 124.83, 125.21, 126.82, 126.91, 127.81, 130.18, 130.81, 131.27, 133.28, 136.96, 138.72, 140.83, 142.52, 154.80, 156.03, 182.74. MS (MALDI-TOF): m/z (M^+) = 790.3 (calcd for $C_{53}H_{46}N_2O_3S$, 790.32).

Synthesis of NPS-2:

The product was synthesized according to the procedure as described above for synthesis of **NPS-1**, giving a red solid of the product **NPS-2** in 80% yield. ^1H NMR (DMSO-d_6, 400 MHz, 298 K): δ 0.63-0.68 (b, 6H), 1.01-1.10 (b, 8H), 1.91 (b, 1H), 3.72 (s, 6H), 4.24 (b, 2H), 6.90-6.91 (b, 6H), 7.06-7.07 (b, 4H), 7.32 (b, 2H), 7.55-7.67 (b, 4H), 7.90-8.01 (b, 4H), 8.30-8.38 (b, 2H), 8.61 (b, 2H). ^{13}C NMR (DMSO-d_6, 150 MHz, 298 K): δ 10.35, 13.67, 22.37, 23.33, 27.61, 29.79, 40.32, 48.37, 55.22, 113.74, 114.96, 115.51, 116.68, 119.05, 121.41, 123.01, 123.76, 124.15, 124.63, 125.26, 126.30, 126.77, 127.89, 129.50, 129.97, 130.54, 130.88, 132.37, 132.53, 136.00, 136.27, 137.44, 140.07, 141.79, 147.61, 149.13, 155.81. MS (MALDI-TOF): m/z (M^+) = 857.33 (calcd for $C_{54}H_{43}N_3O_2S$, 857.33). HRMS (MALDI-TOF): m/z (M^+) =857.3276 (calcd for $C_{54}H_{43}N_3O_2S$, 857.3282).

Synthesis of compound 9:

The product was synthesized according to the procedure as described above for synthesis of compound 4, giving a yellow solid of the product **9** in 66% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 0.83-0.87 (t, 3H), 0.93-0.97 (t, 3H), 1.23-1.44 (m, 8H), 2.24-2.27 (m, 1H), 3.84 (s, 6H), 4.55-4.56 (d, 2H), 6.90-6.92 (d, 4H), 7.12-7.14 (d, 2H), 7.20-7.22 (d, 4H), 7.32-7.33 (d, 1H), 7.42-7.43 (d, 1H), 7.51-7.55 (m, 3H), 7.69-7.70 (d, 1H), 7.73 (s, 1H), 7.78-7.82 (t, 1H), 8.83-7.87 (t, 1H), 7.91 (s, 1H), 8.25-8.27 (d, 1H), 8.46-8.48 (d, 1H), 8.69-8.72 (m, 2H), 9.89 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 11.01, 14.02, 23.05, 24.36, 28.05, 30.81, 41.36, 49.36, 55.39, 113.61, 114.71, 115.09, 116.31, 117.90, 120.15, 121.10, 121.21, 123.54, 123.91, 124.35, 124.50, 124.78, 124.81, 125.10, 126.71, 126.80, 127.47, 127.56, 127.93, 128.02, 130.23, 130.77, 130.88, 131.58, 133.16, 133.55, 135.26, 137.44, 138.42, 140.97, 141.48, 146.25, 147.46, 147.96, 155.89, 182.55. MS (MALDI-TOF): m/z (M^+) = 872.3 (calcd for $C_{57}H_{48}N_2O_3S_2$, 872.31).

Synthesis of NPS-3:

The product was synthesized according to the procedure as described above for synthesis of **NPS-1**, giving a red solid of the product **NPS-3** in 82% yield. ^{1}H NMR (DMSO-d_6, 500 MHz, 378 K): δ 0.73-0.76 (t, 3H), 0.86-0.89 (t, 3H), 1.17-1.39 (m, 8H), 2.17-2.19 (m, 1H), 3.79 (s, 6H), 4.60-4.62 (d, 2H), 6.95-6.96 (b, 2H), 6.97-6.99 (b, 2H), 7.00 (b, 1H), 7.02 (b, 1H), 7.13-7.14 (b, 2H), 7.15-7.16 (b, 2H), 7.46-7.47 (d, 1H), 7.49-7.50 (m, 3H), 7.59-7.60 (d, 1H), 7.69-7.70 (d, 1H), 7.78-7.81 (t, 1H), 7.83 (s, 1H), 7.84-7.88 (t, 1H), 8.10-8.13 (m, 3H), 8.43-8.45 (d, 1H), 8.75-8.78 (t, 2H). ^{13}C NMR (DMSO-d_6, 125 MHz, 298 K): δ 10.08, 13.01, 21.84, 23.39, 27.51, 29.91, 40.22, 48.70, 55.01, 113.68, 114.78, 115.02, 116.37, 119.17, 120.88, 120.94, 122.86, 123.68, 123.77, 123.93, 124.28, 124.81, 125.55, 126.22, 126.44, 126.86, 126.90, 127.81, 129.42, 129.79, 130.10, 131.07, 132.41, 132.50, 134.38, 134.99, 135.80, 137.16, 140.00, 143.27, 147.42, 155.53.MS (MALDI-TOF): m/z (M^+) = 939.5 (calcd for $C_{60}H_{49}N_3O_4S_2$, 939.32). HRMS (MALDI-TOF): m/z (M^+) =939.3151 (calcd for $C_{60}H_{49}N_3O_4S_2$, 939.3159).

5. CVs of the dyes NPS-1~NPS-4

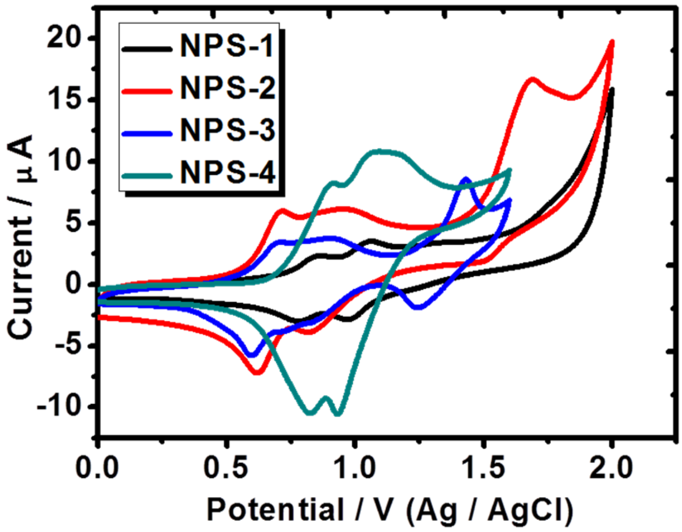


Figure S1. CVs of the five dyes in CH_2Cl_2 solution, scan rate=100 mV / S.

6. Calculated HOMOs and LUMOs of the dyes NPS-1~NPS-4

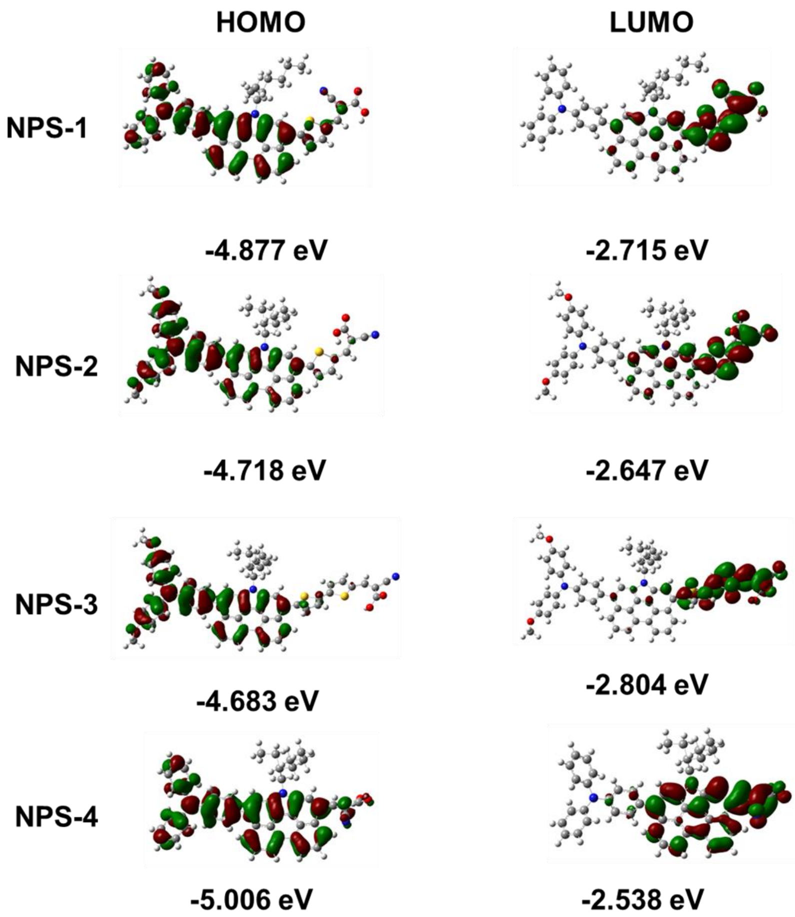


Figure S2. Calculated HOMO and LUMO profiles and energy levels of the dyes **NPS-1~NPS4**.

7. Electron lifetime τ_n of the cells as a function of Capacitance

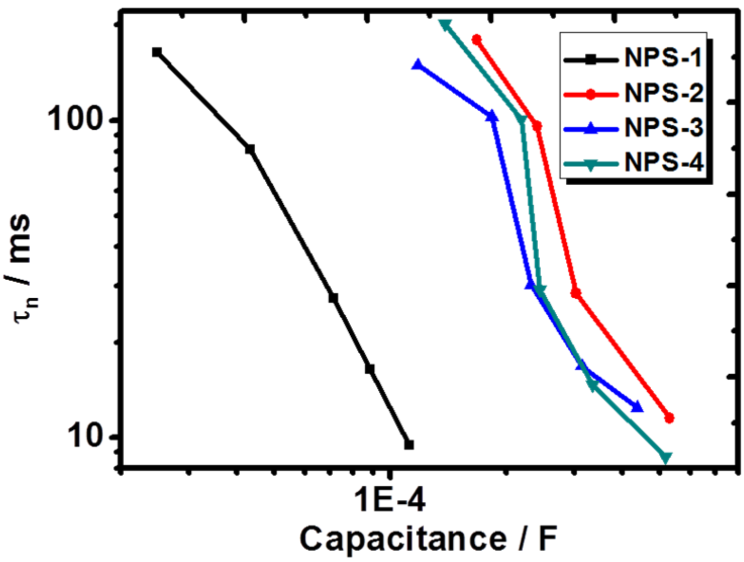


Figure S3. Electron lifetime τ_n of the cells as a function of Capacitance.

8. Resistance of the cells as a function of bias voltage

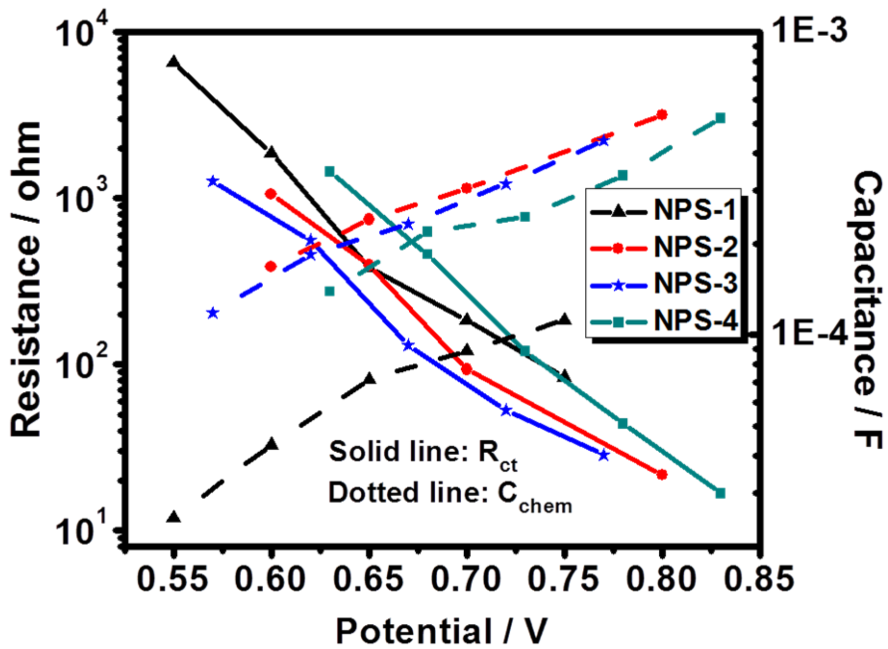


Figure S4. Resistance of the cells as a function of bias voltage.

9. Current of the cells as a function of bias voltage

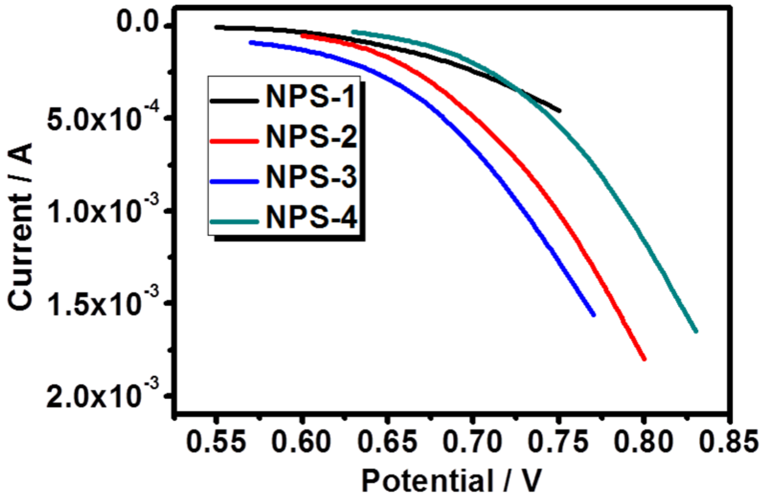


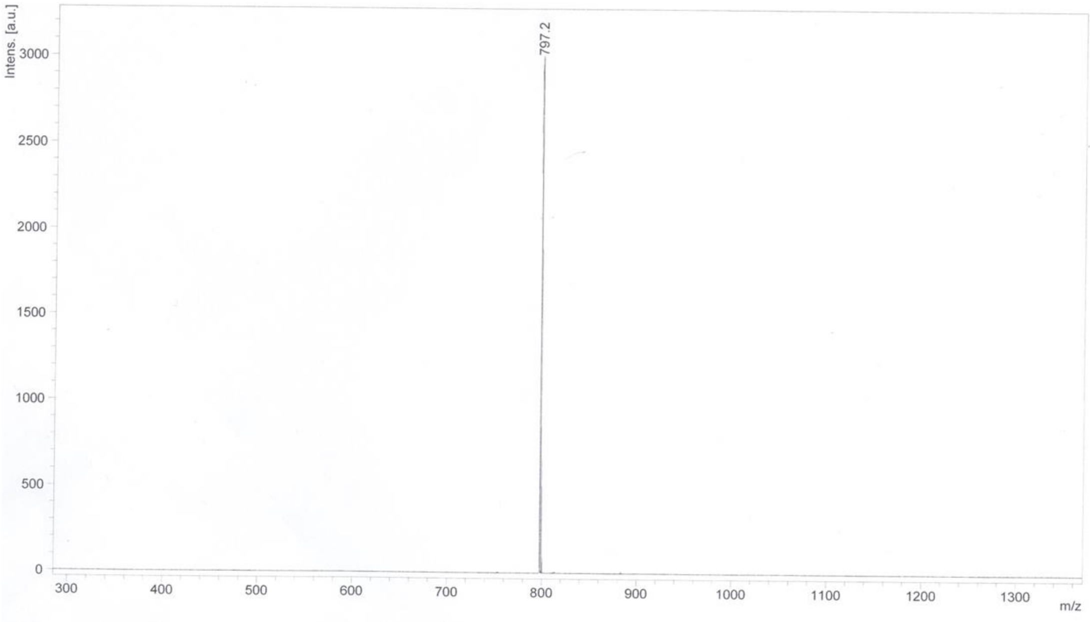
Figure S5. Current of the cells as a function of bias voltage.

10. References

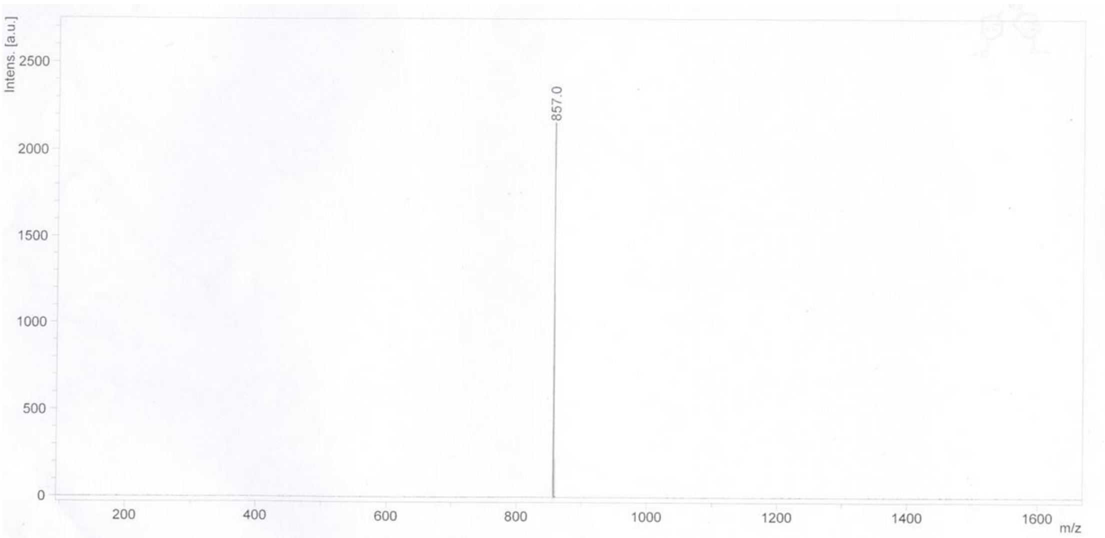
1. (a) Jiang, W.; Qian, H.; Li, Y.; Wang, Z. *J. Org. Chem*. **2008**, *73*, 7369. (b) Li, Y.; Wang, Z. *Org. Lett*. **2009**, *11*, 1385.

11. MALDI-TOF-MS of the dyes NPS-1~NPS-4

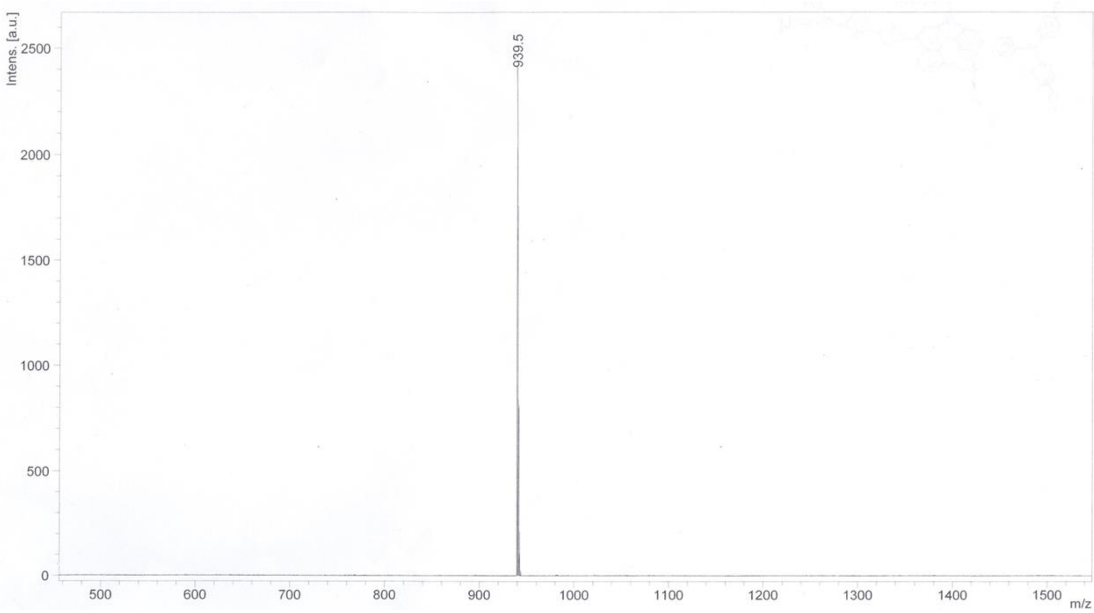
MALDI-TOF-MS of NPS-1



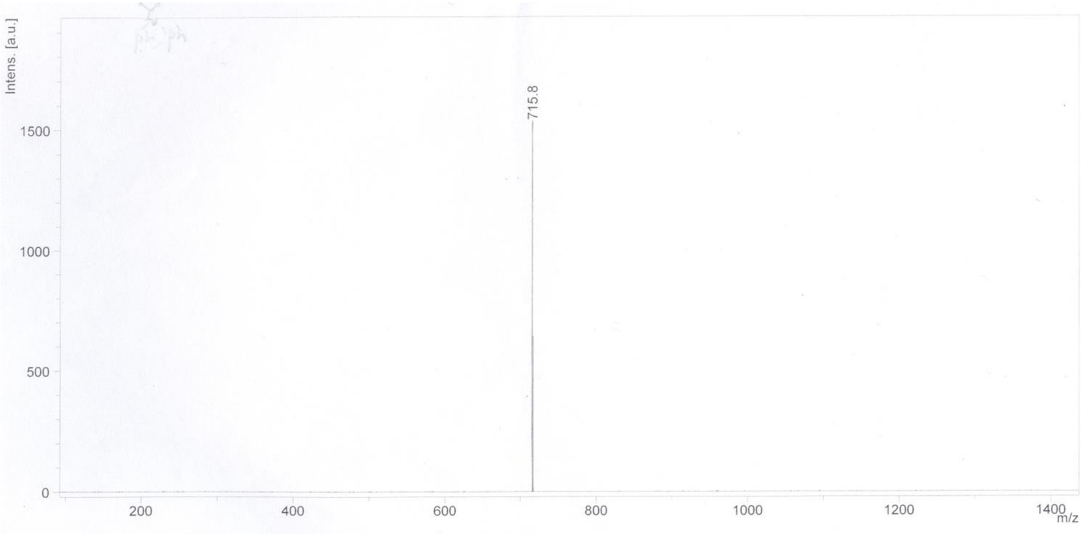
MALDI-TOF-MS of NPS-2



MALDI-TOF-MS of NPS-3

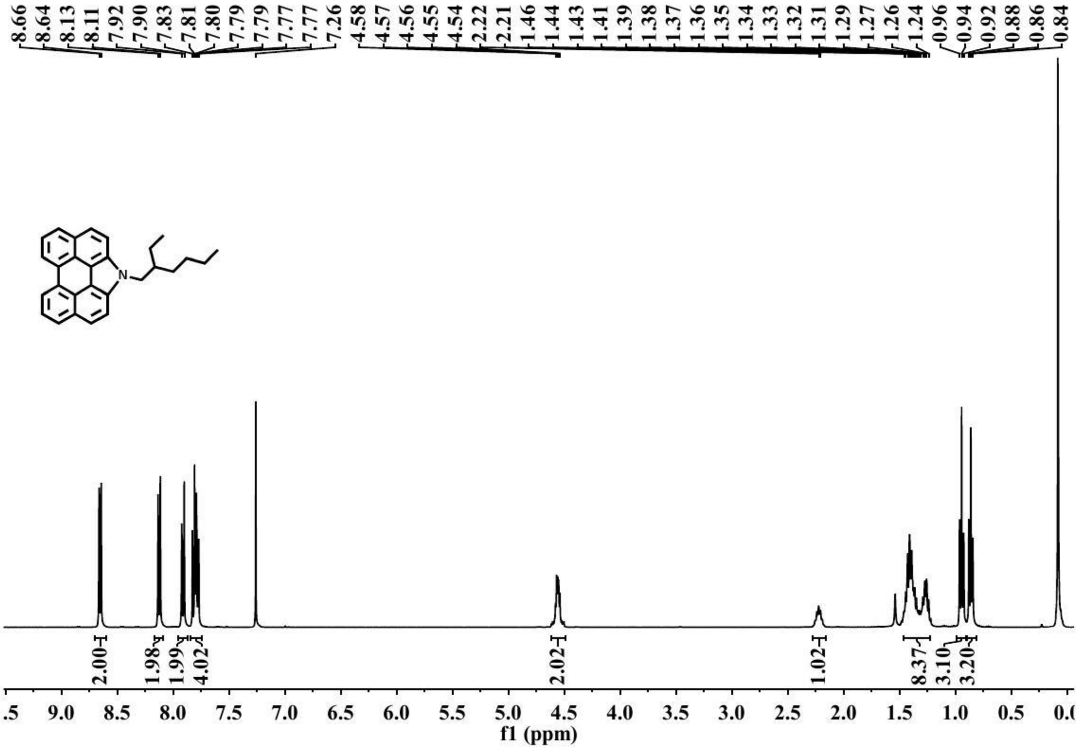


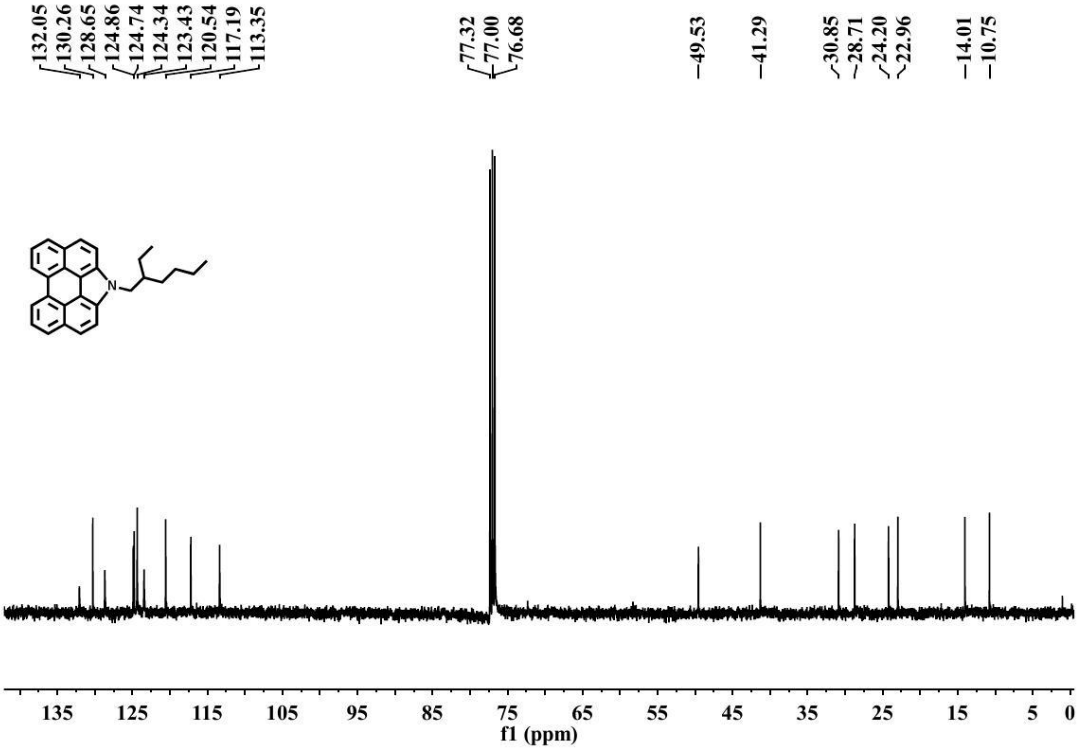
MALDI-TOF-MS of NPS-4



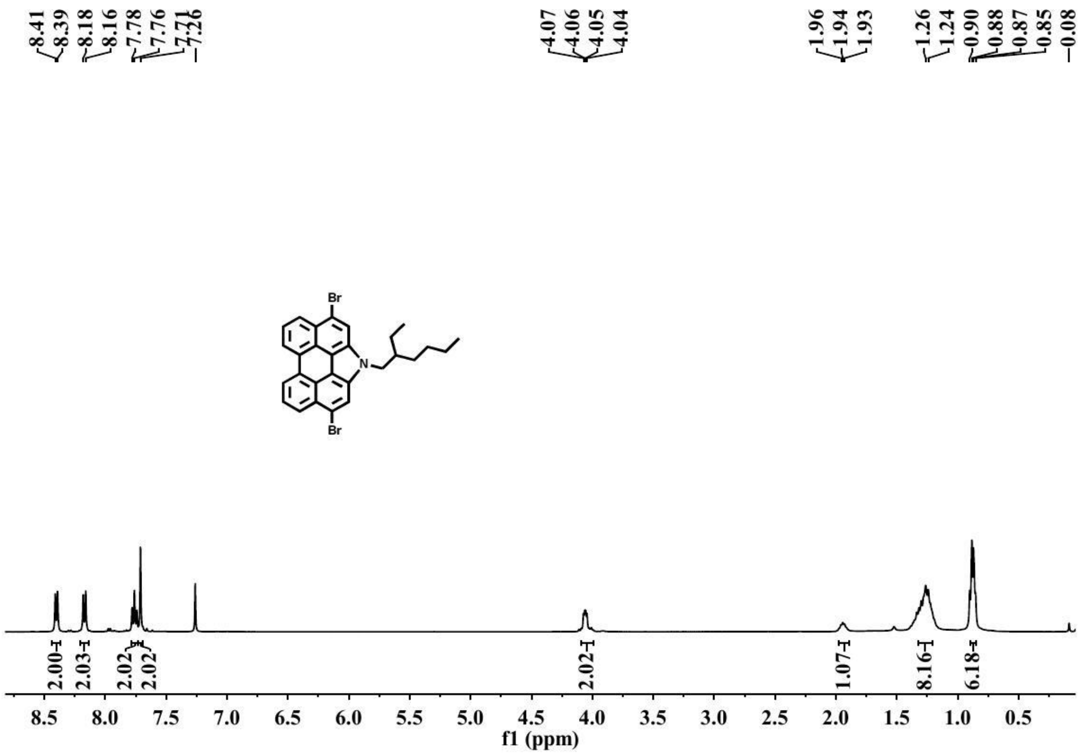
12. ^{1}H and ^{13}C NMR Spectra of Synthetic Compounds

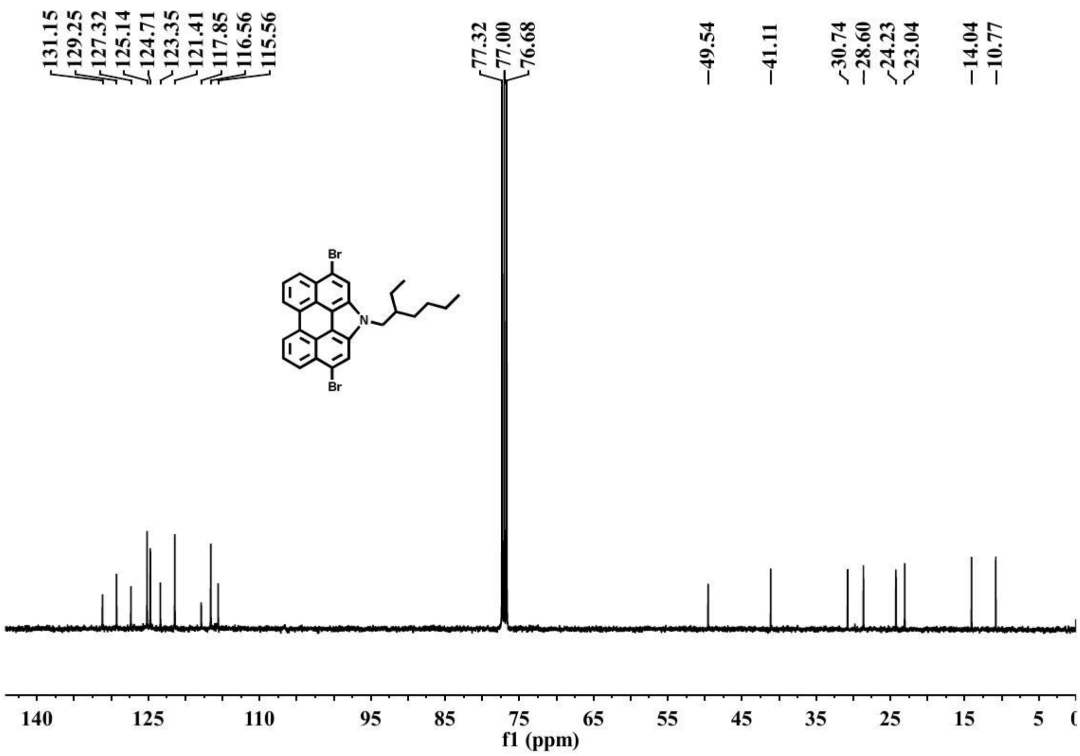
6-alkyl-Phenanthro[1,10,9,8-*c*,*d*,*e*,*f*,*g*]carbazole in $CDCl_3$



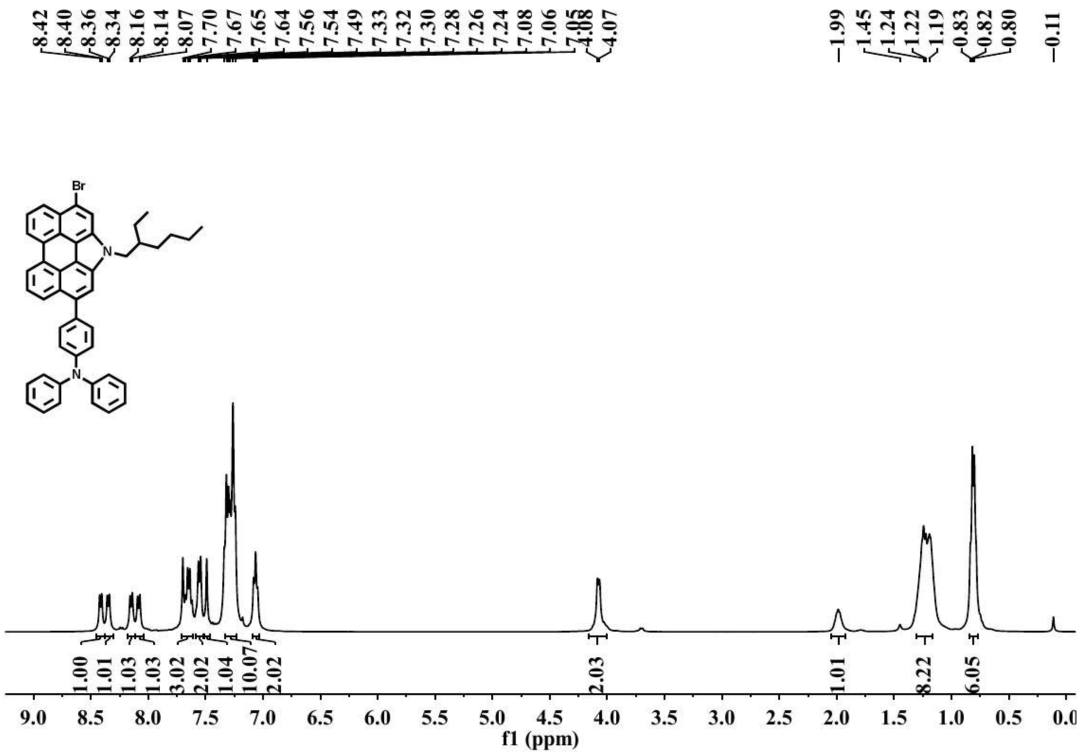


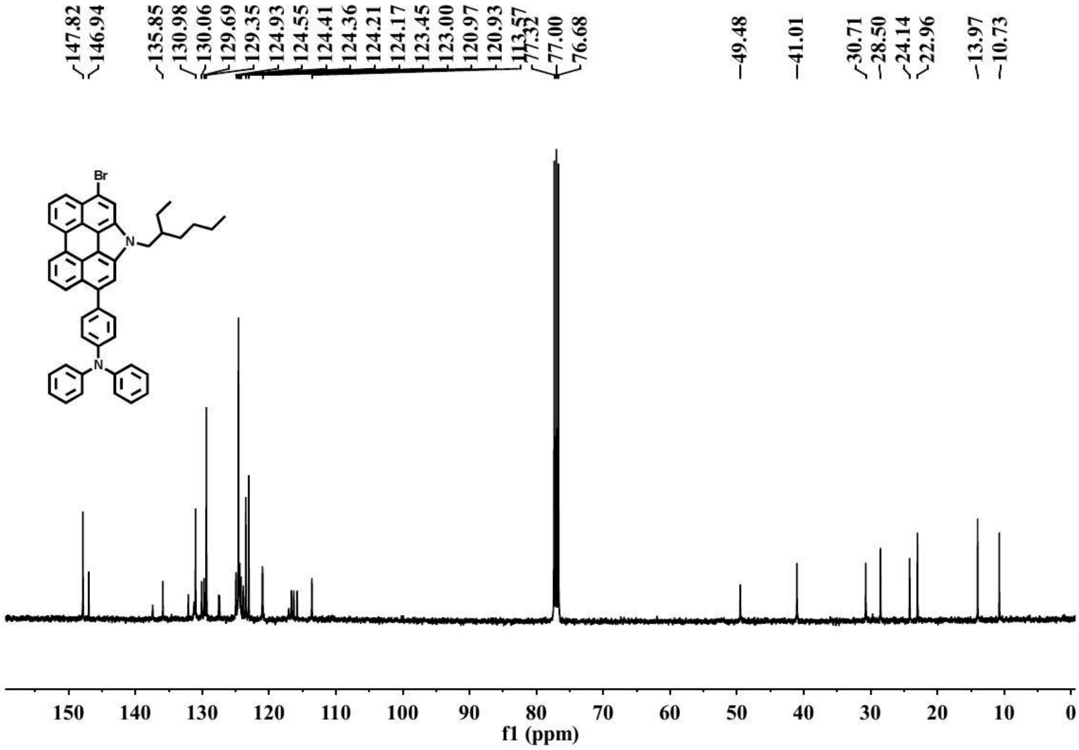
Compound 1 in $CDCl_3$



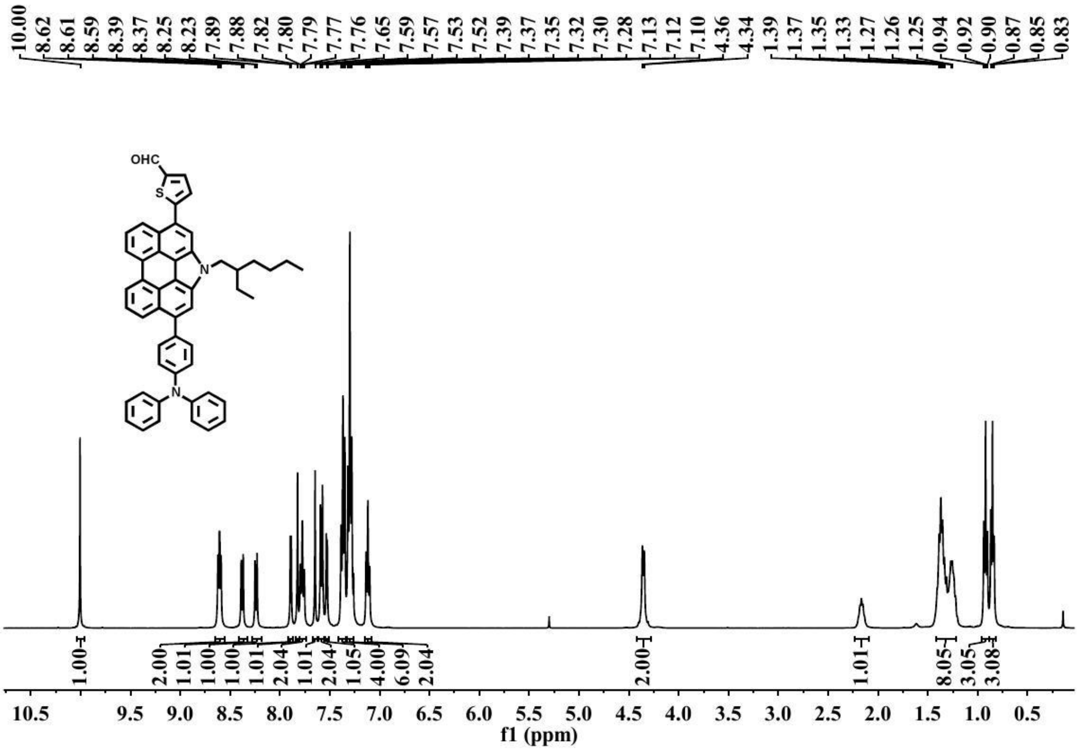


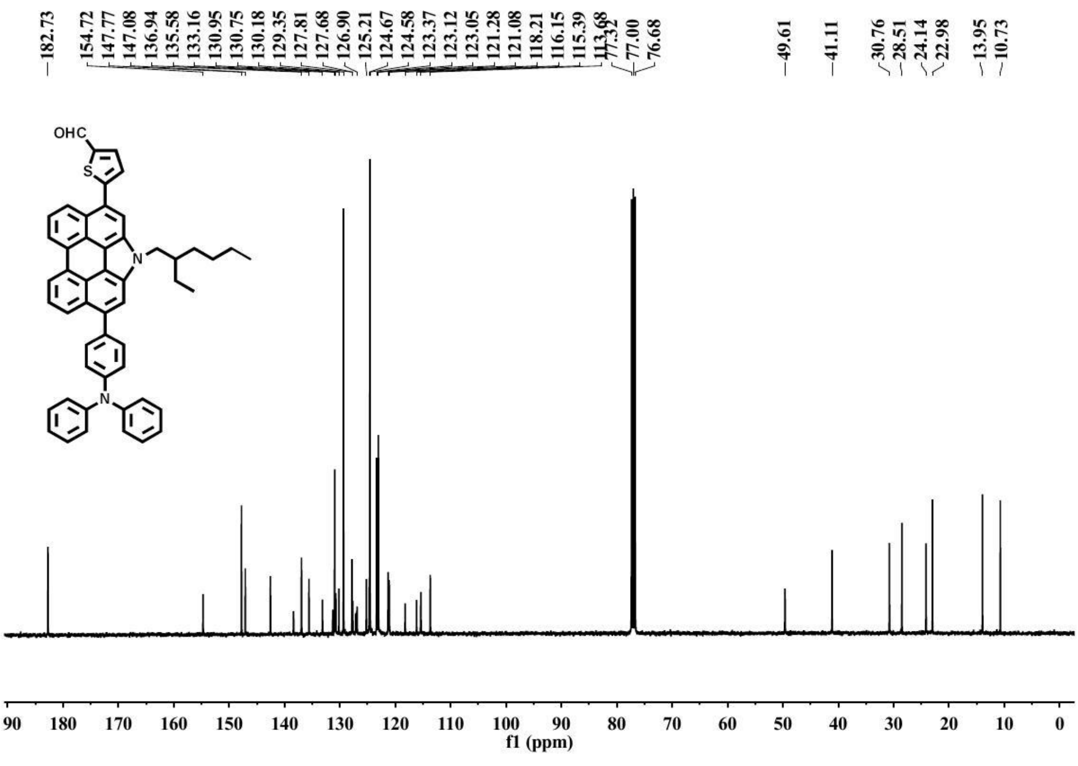
Compound 2 in $CDCl_3$



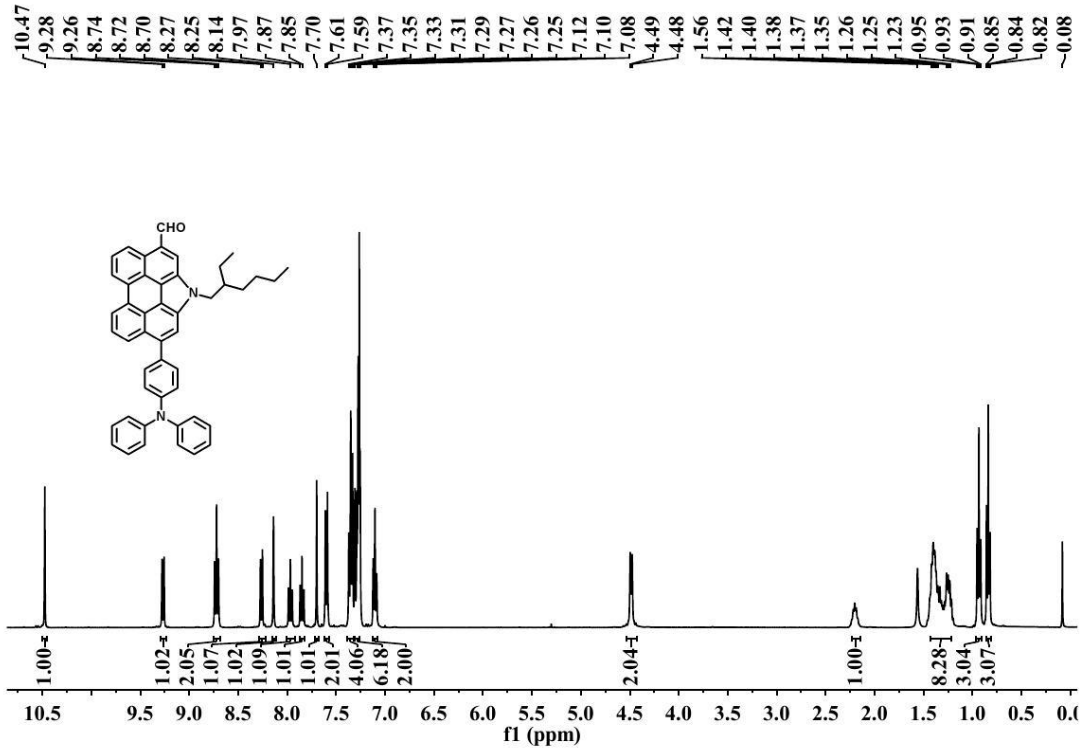


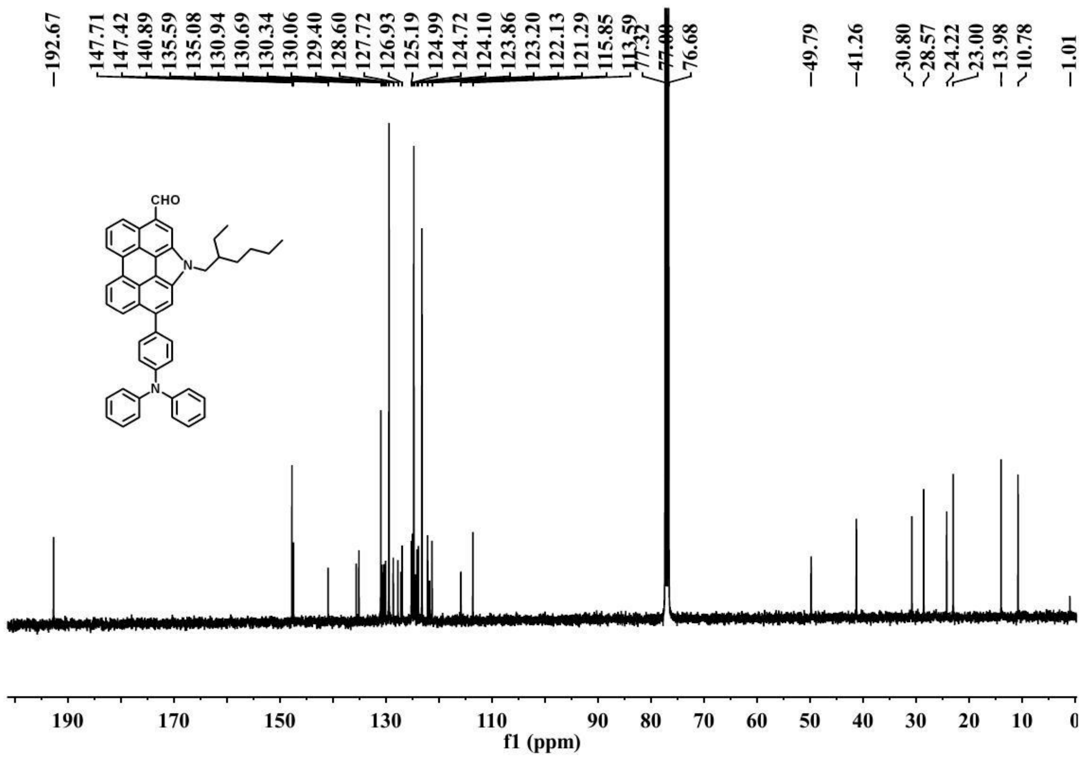
Compound 3 in $CDCl_3$



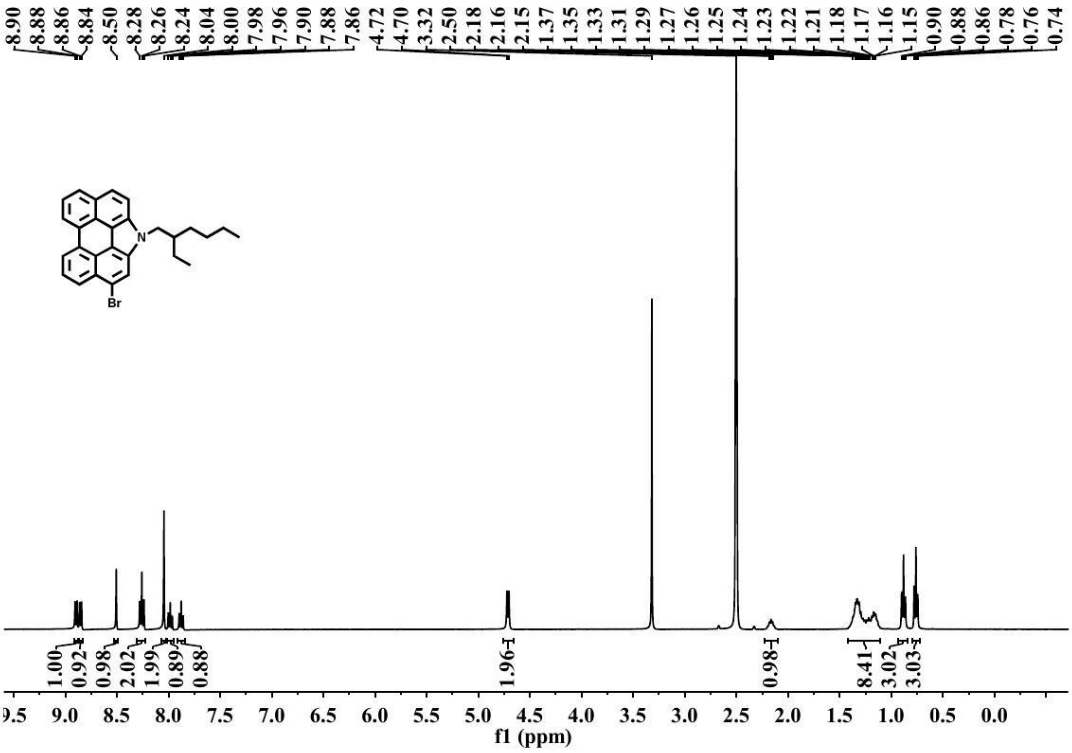


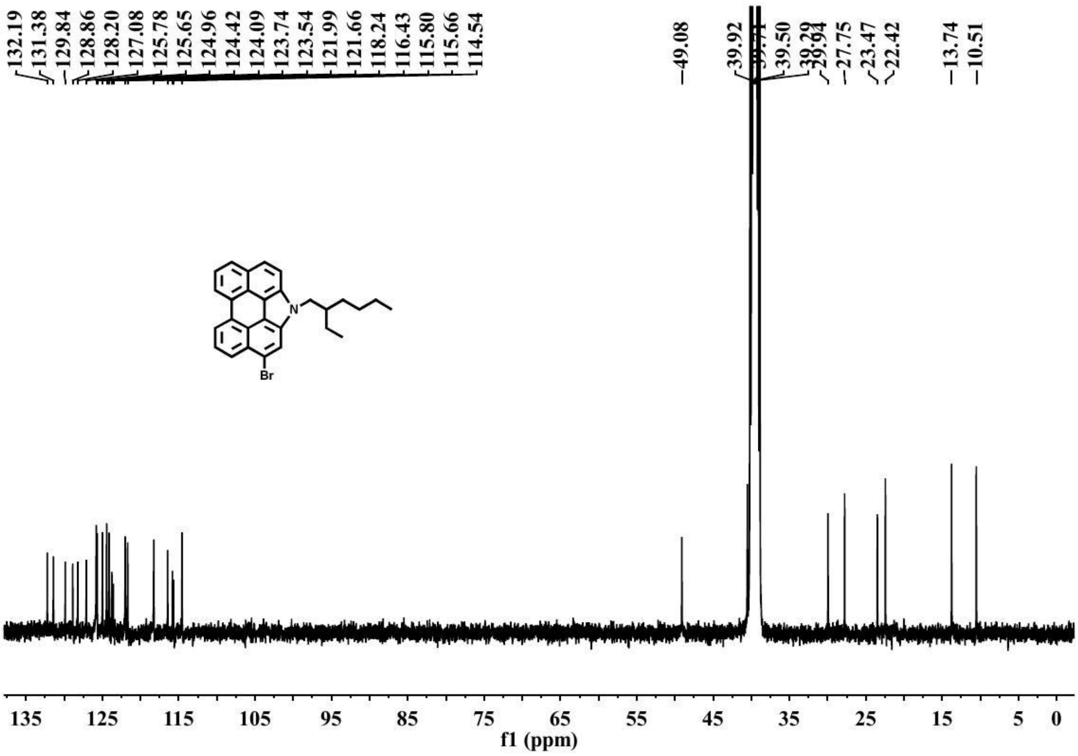
Compound 4 in $CDCl_3$



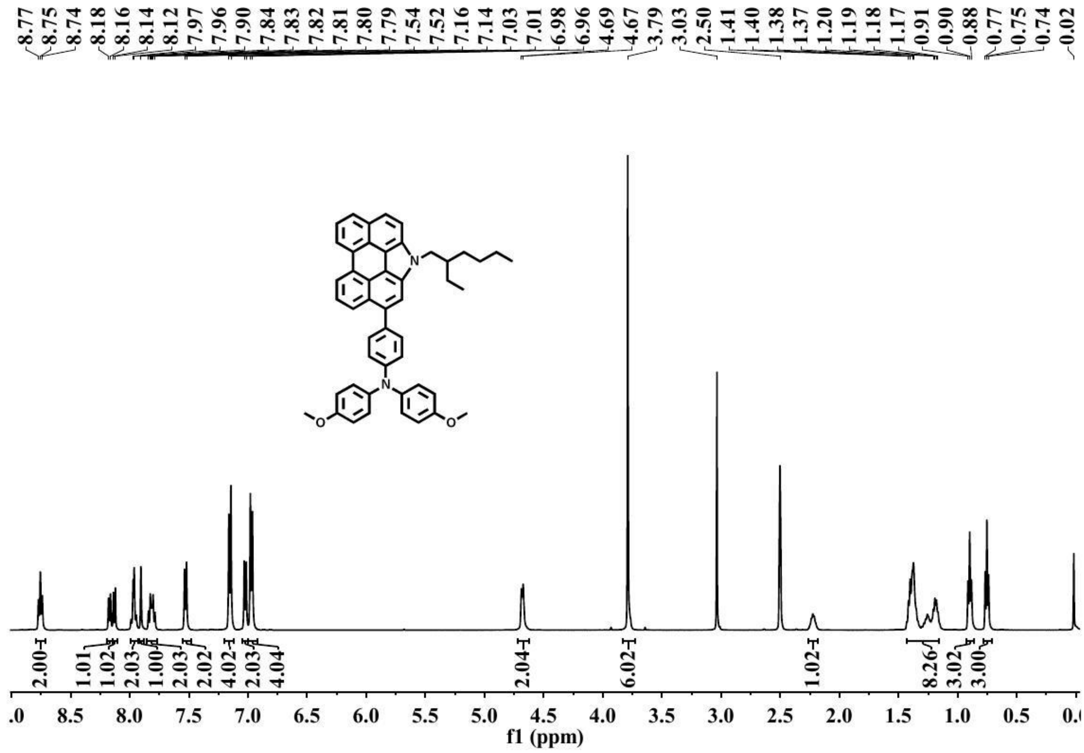


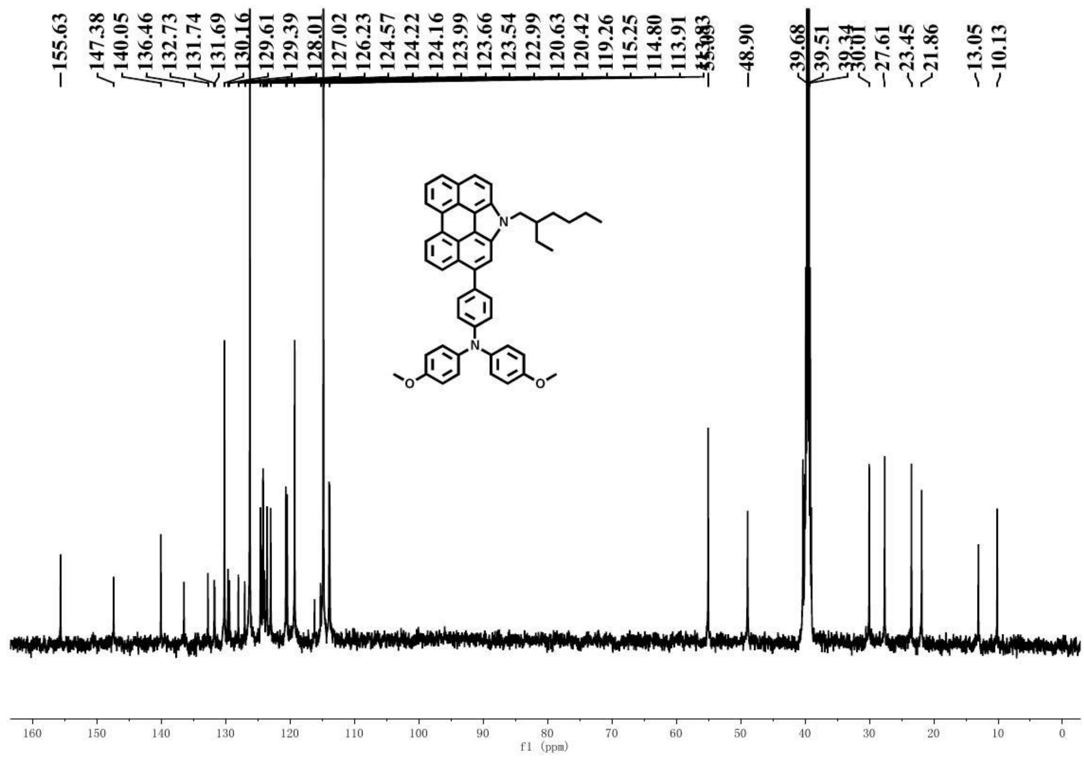
Compound 5 in DMSO-d_6



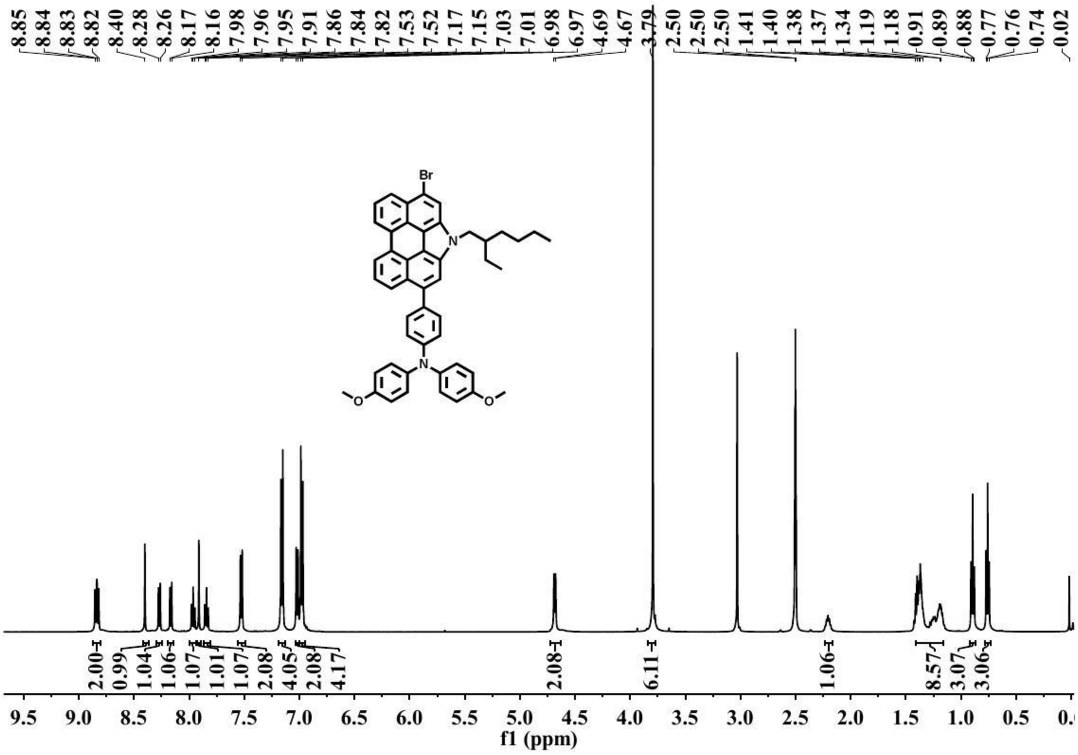


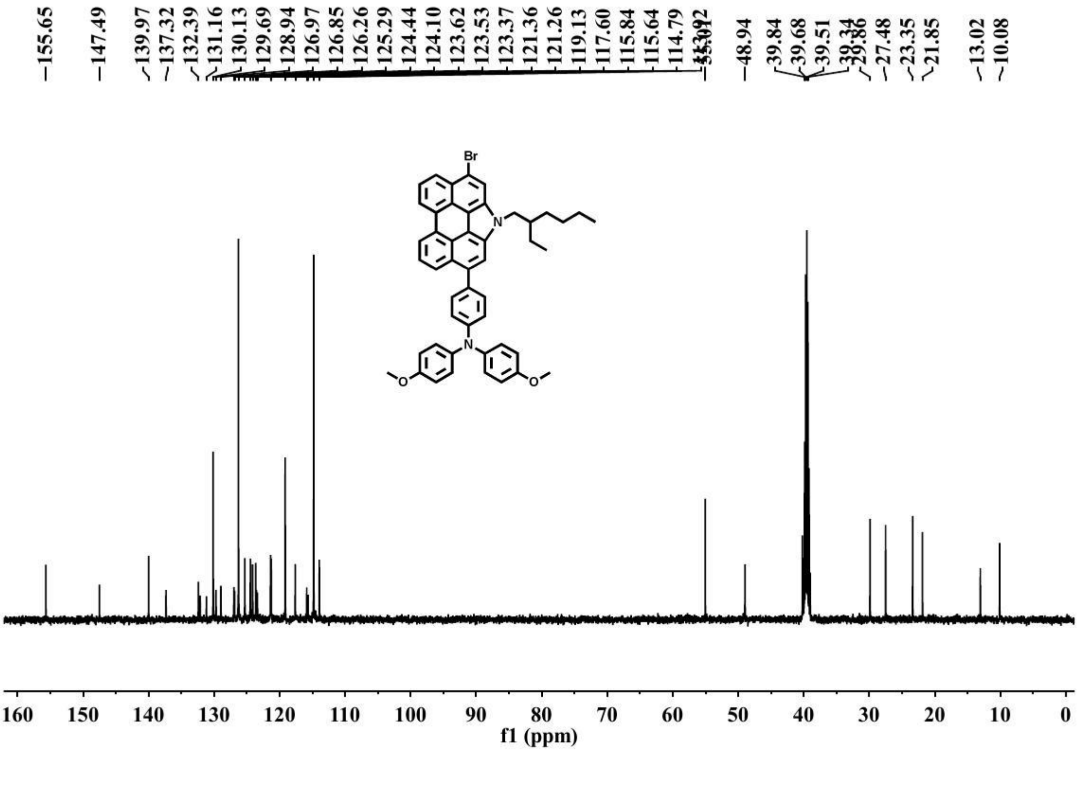
Compound 6 in DMSO-d_6



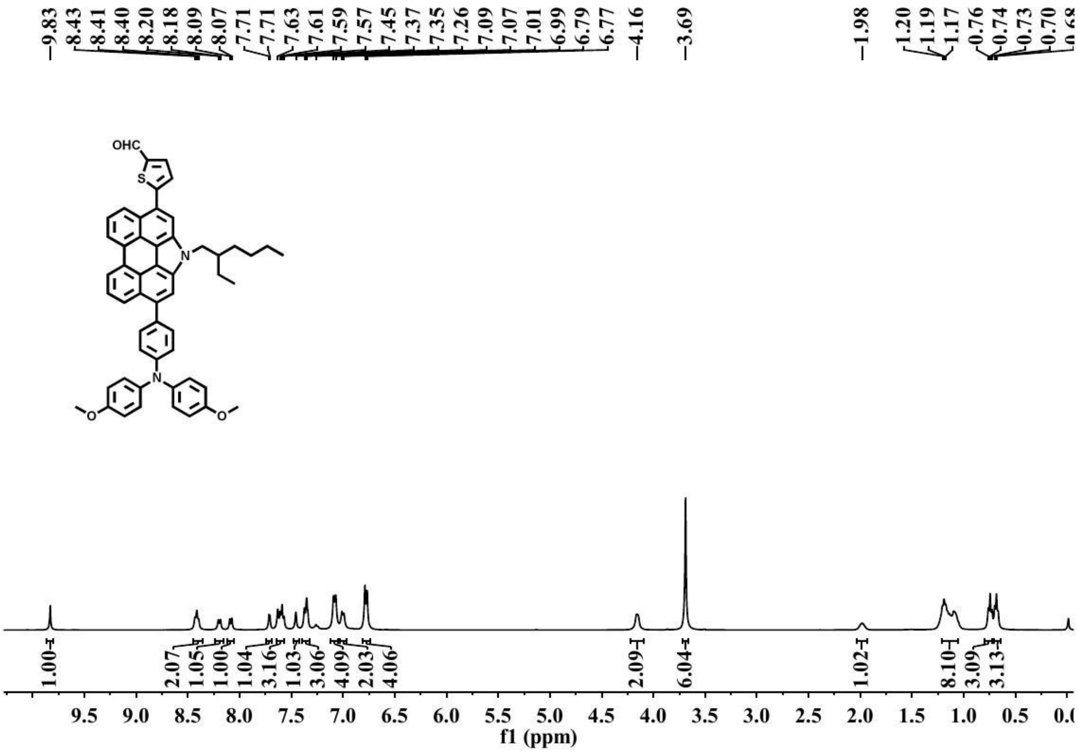


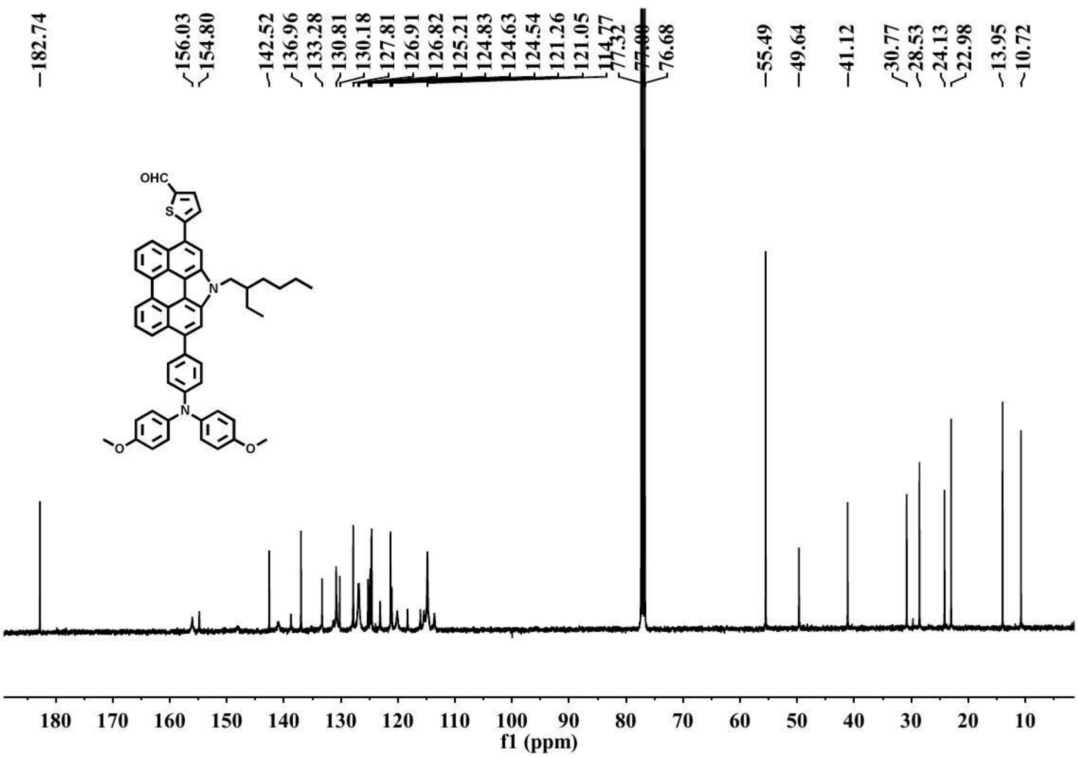
Compound 7 in DMSO-d_6



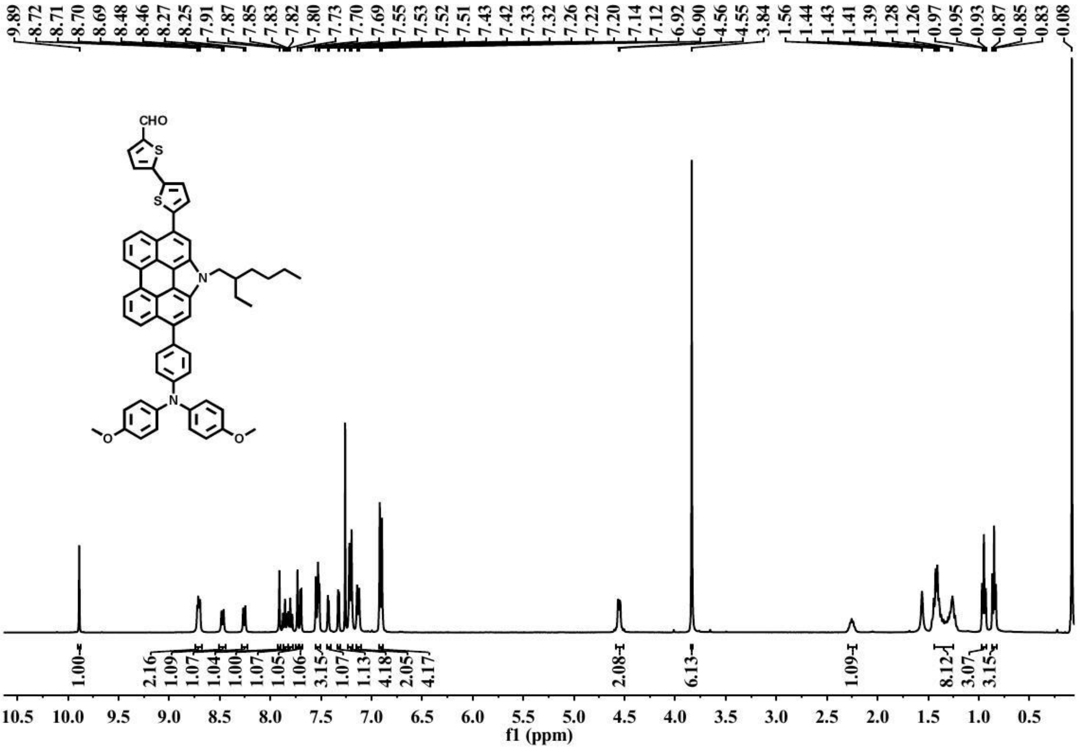


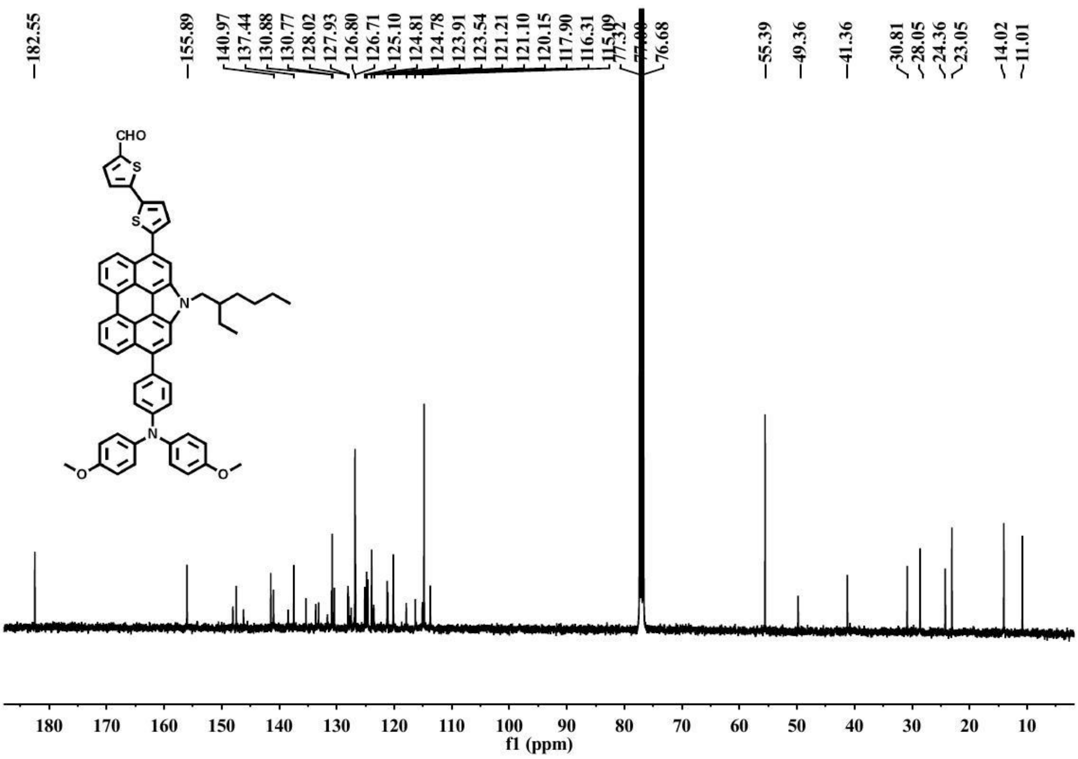
Compound 8 in $CDCl_3$



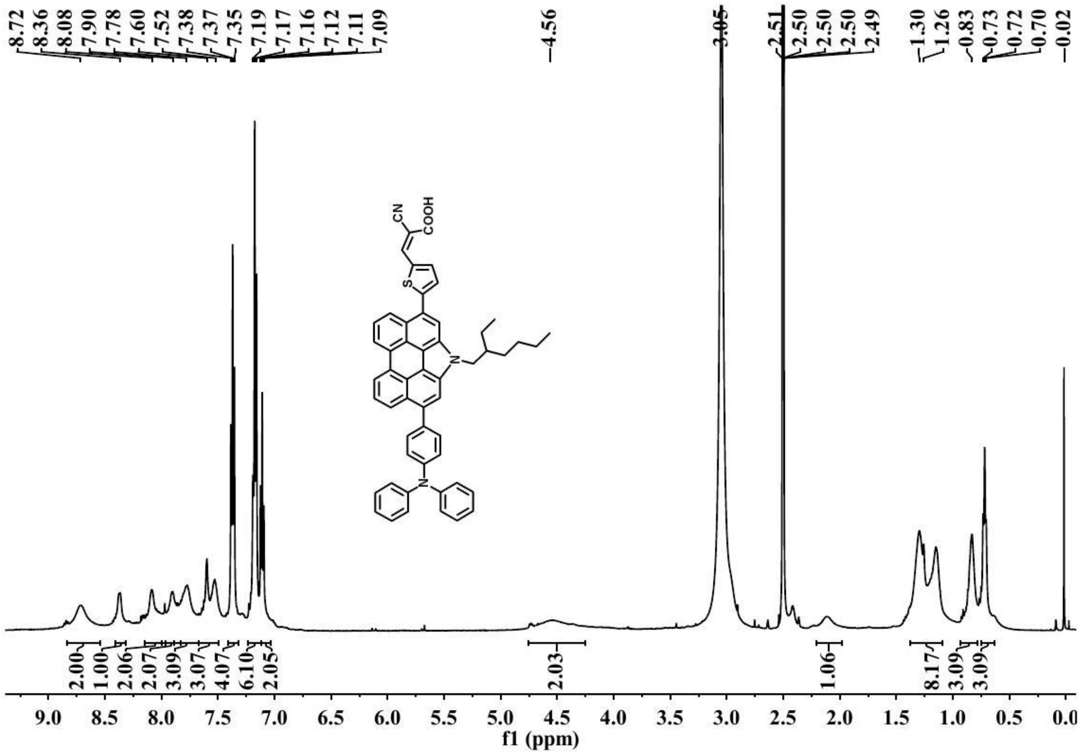


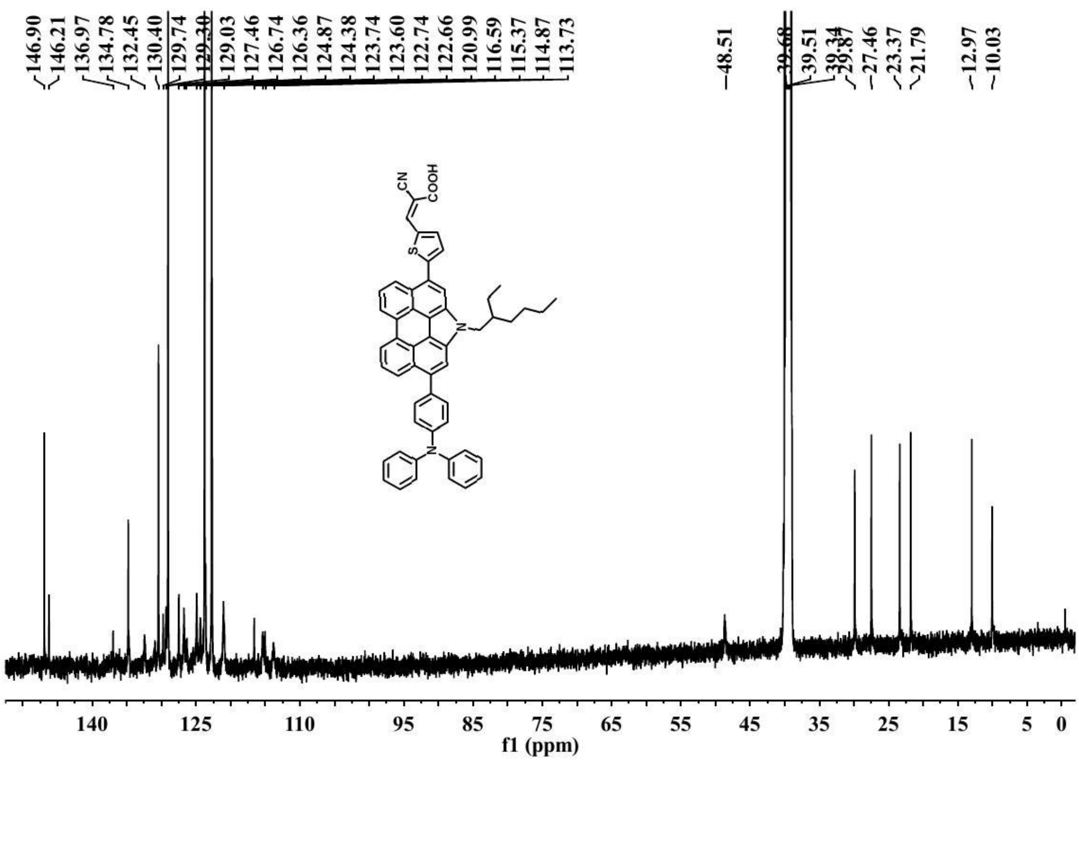
Compound 9 in $CDCl_3$



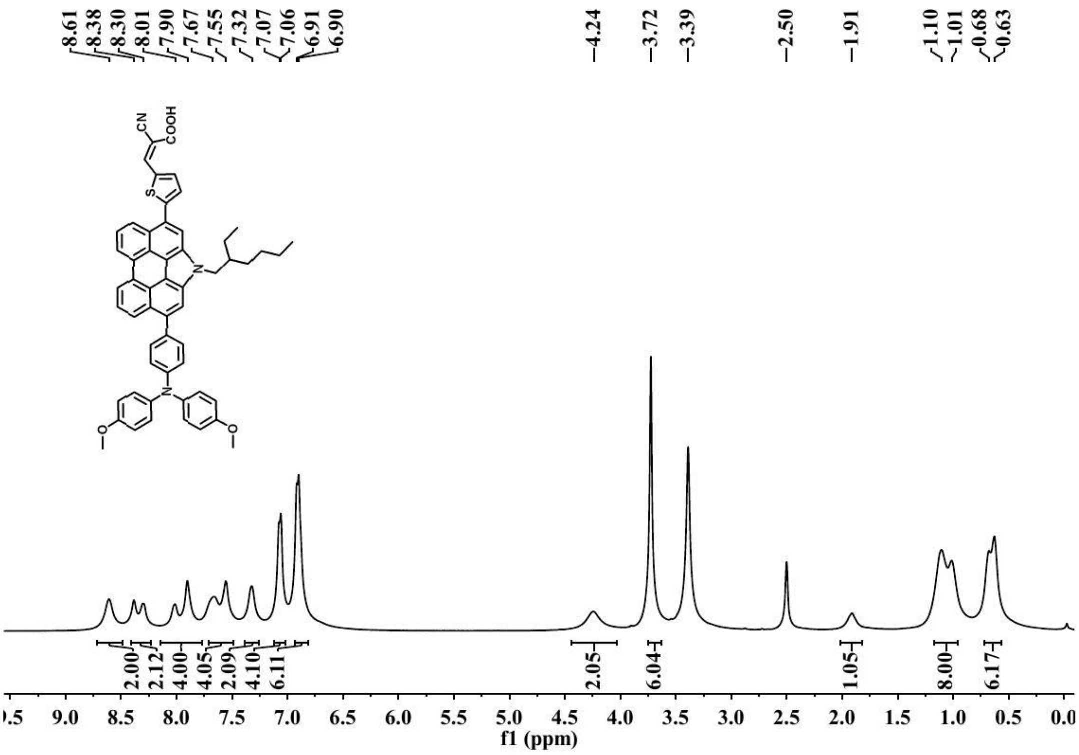


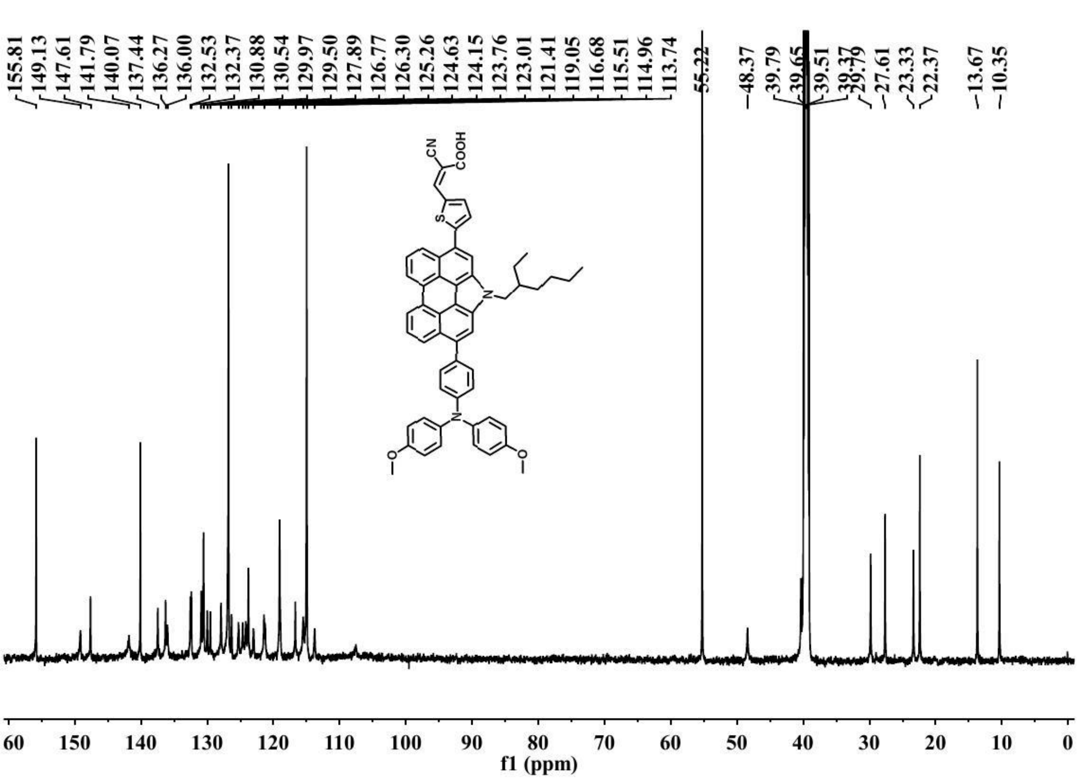
NPS-1 in DMSO-d_6



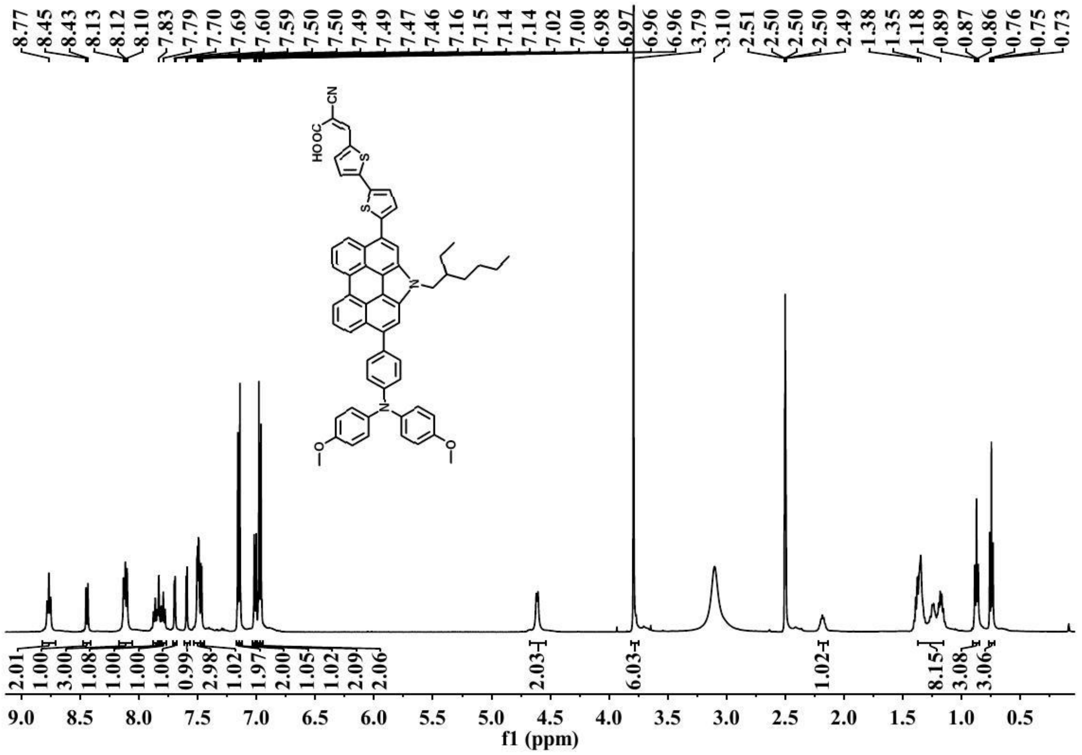


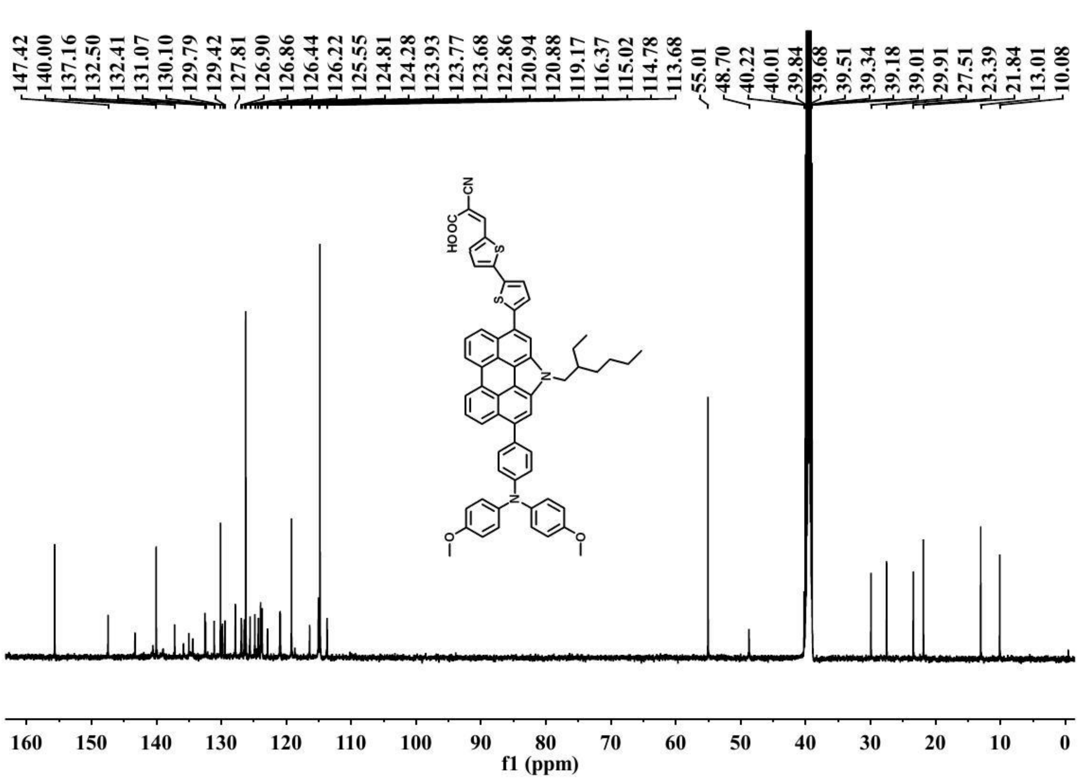
NPS-2 in DMSO-d_6





NPS-3 in DMSO-d_6





NPS-4 in DMSO-d_6