Electronic Supplementary Material (ESI) for RSC Advances
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Supplementary Information

N-type organic semiconductor bisazacoronene diimides synthesized by a type of photocylization involving schiff base

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1. Methods

All other reactants were purchased from commercial sources. NMR spectra were measured with a 400MHz Bruker spectrometer using TMS as reference for 1H and 13C NMR. Accurate mass correction is measured with MALDI Tof Mass Spectrometer (MALDI micro MX) and LC/Q-Tof MS Mass Spectrometer. Cyclic voltammetry (CV) and the differential pulse voltammetry (DPV) was performed in 0.05M solution in CH_2Cl_2 with a standard commercial electrochemical analyzer in a three electrode single-component cellunder argon with a scan rate of 100 mV/s. Working electrode: glassy carbon; reference electrode: Ag/AgCl; auxiliary electrode: Pt disk; internal standard: ferrocene (Fc). The energy of Fc/Fc^+ is 5.08 eV relative to vacuum.[S1] UV-vis absorption spectrum is measured with UV-Vis Spectrophotometer (HP8453). Fluorescence spectrum is measured with Fluorescence Lifetime Spectrometer (PTI-700).

2. Experimental Section:

Compound 3,4,9,10-tetra(n-butoxycarbonyl)perylene was synthesized according to literature methods.[S2]

Synthesis of 1

A mixture of 3,4,9,10-tetra(n-butoxycarbonyl)perylene (6.52g, 10 mmol), 60ml CH_2Cl_2, 1.5ml fuming nitric acid of CH_2Cl_2 solution was slow dropped, then stirred 4.5h at room temperature, 9mL Et_3N was added. The crude product was purified by silica gel column chromatography with dichloromethane as eluent. Compound **1** was obtained as red viscous product (5.6g, 80%). HRMS calcd for $C_{40}H_{43}NO_{10}Na$ 720.2785, found : 720.2793 ($[M+Na]^+$, MALDI-TOF-MS); ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 8.10 (q, 3H), 7.97 (d, 1H), 7.80 (d, 1H), 7.62 (d, 1H), 4.42 - 4.32 (m, 8H), 1.81 (dd, 9H), 1.52 (td, 9H), 1.02 (dd, 13H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 168.0, 167.9, 166.8, 146.2, 133.6, 132.3, 132.0, 131.4, 131.3, 130.8, 130.3, 129.9, 129.6, 127.6, 127.5, 125.6, 123.2, 122.7, 66.2, 65.9, 65.8, 65.7, 30.7, 19.4, 13.9 ppm.

Synthesis of 5

A mixture of **1** (3g, 4mmol), 200mg 10% Pa/C, 2MPa H_2 and 50mL THF was heated to 100℃ for 4.5h in the autoclave. After cooling, filtrate to remove Pa/C, the filtrate was evaporated and the crude product was purified by silica gel column chromatography with CH_2Cl_2 and CH_3COOEt as eluent. Compound **5** was obtained as purple viscous product (2.5g, 87%). HRMS calcd for $C_{40}H_{45}NO_8$ 667.3145, found : 667.3154 ($[M]^+$, MALDI-TOF-MS); ^1H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, 1H), 7.89 (dd, 2H), 7.74 (dd, 2H), 7.56 (d, 1H), 7.36 (s, 1H), 4.33 (m, 8H), 1.86 - 1.72 (m, 9H), 1.57 - 1.43 (m, 10H), 1.25 (s, 4H), 1.05 - 0.94 (m, 13H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 169.1, 168.9, 144.0, 134.2, 133.5, 131.4, 130.8, 130.7, 130.3, 130.1, 129.1, 127.5, 126.8, 124.8, 122.3, 121.8, 120.0, 65.6, 65.4, 30.9, 19.5, 14.0 ppm.

Synthesis of 6

A mixture of **5** (2g, 2.99mmol), butyraldehyde (0.7mL, 7.48mmol) was heated to 62℃ for 6h in chloroform under sunlight atmosphere. The mixture was evaporated and the crude product was purified by silica gel column chromatography with dichloromethane and ethyl acetate as eluent. Compound **6** was obtained as blue viscous product (1.1g, 50%). HRMS calcd for $C_{44}H_{51}NO_8Na$ 744.3512, found : 744.3521 ($[M+Na]^+$, LC/Q-Tof-MS); ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 - 7.93 (m, 3H), 7.52 (d, 2H), 7.41 (s, 1H), 6.89 (s, 1H), 4.33 (m, 8H), 1.82 - 0.81 (m, 44H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 168.5, 140.4, 134.1, 131.9, 130.6, 130.3, 129.5, 128.7, 128.6, 128.3, 127.7, 127.6, 126.7, 126.3, 121.9, 120.7, 120.2, 110.1, 65.9, 65.4, 65.3, 60.1, 59.3, 58.8, 58.5, 55.0, 46.1, 44.9, 42.8, 37.3, 36.6, 36.4, 34.5, 34.1, 33.8, 33.1, 32.9, 30.8, 29.8, 22.8, 19.4, 17.3, 14.0, 13.8 ppm.

Synthesis of 4

One step synthesis:

A mixture of **5** (2g, 2.99mmol), butyraldehyde (0.7mL, 7.48mmol) and catalytic amount of iodine was heated to 62℃ for 6h in chloroform under sunlight atmosphere. The mixture was evaporated and the crude product was purified by silica gel column chromatography with dichloromethane and ethyl acetate as eluent. Compound **4** was obtained as yellow viscous product (2g, 93%).

Two steps synthesis:

A mixture of **6** (2g, 2.99mmol) and catalytic amount of iodine was heated to 62℃ for 6h in chloroform under sunlight atmosphere. The mixture was evaporated and the crude product was purified by silica gel column chromatography with dichloromethane and ethyl acetate as eluent. Compound **4** was obtained as yellow viscous product (0.9g, 90%). HRMS calcd for $C_{44}H_{50}NO_8$ 720.3536, found : 720.3483 ($[M]^+$, MALDI-TOF-MS); ^1H NMR (400 MHz, $CDCl_3$) δ 9.00 (q, 1H), 8.89 (d, 1H), 8.49 (q, 1H), 4.50 - 4.40 (m, 4H), 3.72 - 3.64 (m, 1H), 2.16 - 2.05 (m, 1H), 1.93 - 1.81 (m, 4H), 1.71 (s, 1H), 1.64 - 1.48 (m, 4H), 1.18 (t, 2H), 1.03 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 168.6, 168.5, 161.6, 142.6, 133.1, 132.9, 132.5, 131.3, 131.0, 130.8, 129.9, 129.2, 128.7, 127.7, 125.6, 125.6, 125.4, 122.6, 122.2, 121.1, 117.8, 65.9, 37.9, 30.9, 30.9, 30.8, 24.0, 19.5, 19.5, 14.5, 14.0ppm.

Synthesis of 2 (2′)

A mixture of 3,4,9,10-tetra(n-butoxycarbonyl)perylene (6.52g, 10 mmol), 60ml CH_2Cl_2, 3ml fuming nitric acid of CH_2Cl_2 solution was slow dropped, then stirred 4.5h at room temperature, 9mL Et_3N was added. The mixture was evaporated and the crude product was purified by silica gel column chromatography with dichloromethane as eluent. Compound **2 (2′)** was obtained as red viscous product (6.42g, 86%). HRMS calcd for $C_{40}H_{42}N2O_{12}$ 742.2738, found : 742.2736 ([M^+], LC/Q-Tof -MS); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.33 (s, 1H), 8.13 (d, 1H), 8.07 (d, 1H), 8.04 (d, 1H), 8.00 (d, 1H), 4.36 (m, 8H) 1.80 (m, 8H), 1.49 (m, 8H), 1.00 (m, 12H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 167.7, 167.4, 166.5, 166.1, 147.7, 147.2, 133.6, 132.5, 132.2, 131.8, 131.0, 130.2, 129.9, 129.5, 129.0, 128.9, 128.8, 128.3, 127.2, 127.0, 126.7, 125.8, 125.2, 66.6, 66.5, 66.2, 66.1, 30.7, 30.6, 19.4, 19.3, 13.9 ppm.

Synthesis of 7(7′)

A mixture of **2 (2′)** (6.42g, 8.64mmol), 400mg 10% Pa/C, 3MPa H_2 and 100mL THF was heated to 100℃ for 6h in the autoclave. After cooling, filtrate to remove Pa/C, the filtrate was evaporated and the crude product was purified by silica gel column chromatography with CH_2Cl_2 and CH_3COOEt as eluent. Compound **7(7′)** was obtained as purple viscous product (4.96g, 84%). HRMS calcd for $C_{40}H_{46}N_2O_8$ 682.3254, found : 682.3218 ([M^+], MALDI-TOF-MS); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, 3H), 7.72 (d, 1H), 7.67 (d, 1H), 7.48 (d, 3H), 7.11 (s, 3H), 6.96 (s, 1H), 4.31 (m, 16H), 1.80 (m, 16H), 1.52 (m, 16H), 1.03 (m, 24H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 169.5, 169.2, 168.9, 168.8, 144.3, 142.7, 133.8, 133.4, 132.6, 132.2, 131.9, 131.0, 129.9, 129.8, 128.3, 127.1, 126.0, 123.7, 126.0, 123.7, 122.0, 121.6, 120.1, 119.8, 114.3, 112.7, 65.5, 65.4, 65.3, 30.9, 29.2, 22.8, 18.9, 14.5, 14.4, 14.4, 14.3, 14.0, 11.6ppm.

Synthesis of 8(8′)

A mixture of **7(7′)** (2g, 2.93mmol), butyraldehyde (2.1mL, 29.29mmol) and catalytic amount of iodine was heated to 62℃ for 6h in chloroform under sunlight atmosphere. The mixture was evaporated and the crude product was purified by silica gel column chromatography with dichloromethane and ethyl acetate as eluent. Compound **8(8′)** was obtained as yellow viscous product (2.1g, 90%). HRMS calcd for $C_{48}H_{54}N_2O_8Na$ 809.3778, found : 809.3801 ([M+Na]$^+$, LC/Q-Tof MS); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (s, 1H), 9.59 (s, 1H) , 9.52 (s, 1H), 9.49 (s, 1H), 4.59 (s, 8H), 4.00 (s, 4H), 2.30 (s, 8H), 1.62 (d, 8H), 1.29 (s, 6H), 1.06 (s, 12H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 168.9, 168.7, 163.7, 163.4, 142.0, 132.8, 132.7, 131.8, 131.0, 130.8, 130.1, 129.2, 127.1, 126.5, 124.2, 122.9, 122.7, 121.7, 121.6, 121.2, 117.3, 116.7, 66.3, 66.2, 66.1, 38.6, 31.0, 30.9, 24.0, 23.9, 20.0, 14.7, 14.0 ppm.

Synthesis of 9(9′)

Compound **8(8′)** (300 mg, 0.38mmol) was added to 3mL Chlorosulfonic acid gradually and the mixture was stirred for 4 h at room temperature. Then the mixture was added to ice. After filtration, compound 9(9′) was yielded as dark solid (190 mg, 95%). M.p.: 213.2-215.3℃.

Synthesis of Bisaza CBIs 3 (3')

A mixture of 9(9′) (68mg, 0.13mmol), long-chain amine (120mg, 0.65mmol) was heated to 115℃ for 4h in xylene under an argon atmosphere. After cooling, the crude product was purified by silica gel column chromatography with CH_2Cl_2 and n-hexane as eluent. Compound Bisaza **CBIs 3 (3')** was obtained as yellow viscous product. **3a(3a′) :** 51mg (46%). HRMS calcd for $C_{56}H_{69}N_4O_4$ 861.5319, found : 861.5243 ([M+H]$^+$, MALDI-TOF-MS); ^{1}H NMR (400 MHz, CF_3COOD) δ 10.63 (d, 2H), 10.21 (d, 2H), 4.31 (s, 8H), 2.22 (s, 4H), 1.74 (s, 4H), 1.15 (m, 42H), 0.58 (s, 6H); ^{13}C NMR(100 MHz, CF_3COOD) δ 171.4, 170.9, 167.5, 149.3, 137.5, 135.5, 134.8, 134.5, 133.4, 132.6, 132.4, 130.7, 129.8, 129.4, 128.2, 127.7, 126.2, 125.3, 124.6, 44.9, 33.5, 31.1, 30.9, 29.5, 28.6, 27.7, 24.3, 14.5, 14.2 ppm; **3b(3b′) :** 55mg (41%). HRMS calcd for $C_{68}H_{93}N_4O_4$ 1029.7197, found : 1029.7219 ([M+H]$^+$, MALDI-TOF-MS); ^{1}H NMR (400 MHz, CF_3COOD) δ 10.65 (d, 2H), 10.216 (d, 2H), 4.33 (s, 8H), 2.25 (s, 4H), 1.78 (s, 4H), 1.23 (m, 64H), 0.60 (s, 8H); ^{13}C NMR(100 MHz, CF_3COOD) δ 170.9, 170.7, 165.2, 165.0, 137.3, 136.4, 132.5, 131.3, 130.5,130.3, 129.3, 127.5, 126.4, 126.0, 125.2, 44.7, 33.3, 31.0, 30.7, 29.3, 28.4, 27.5, 23.9, 22.2, 14.3 ppm.

3. Reference:

S1: Mo X., Chen H., Shi M. and Wang M., *Chem. Phys. Lett.* **2006**, *417*, 457.
S2: Thompson B., Kim Y. and Carley T. and Reynolds J., *J. Org. Chem.* **2006**, *128*, 12714.

4. Electrochemical properties of 4 and Bisaza CBIs 3 (3').

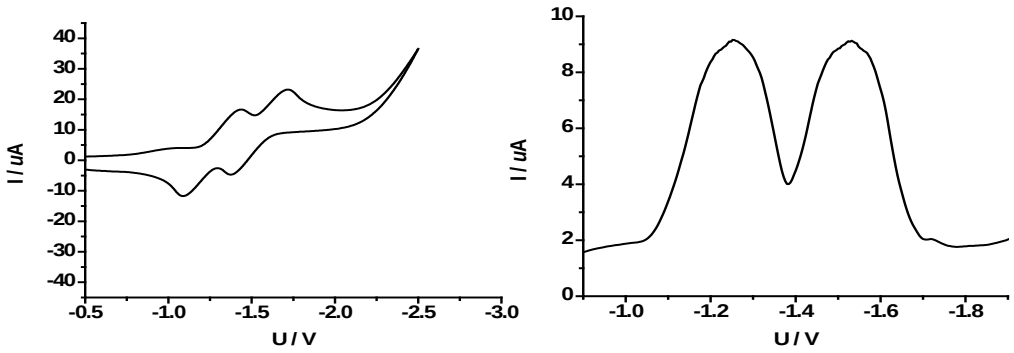


Figure S1. Cyclovoltammograms (left) and DPV (right) of **4** in dichloromethane.

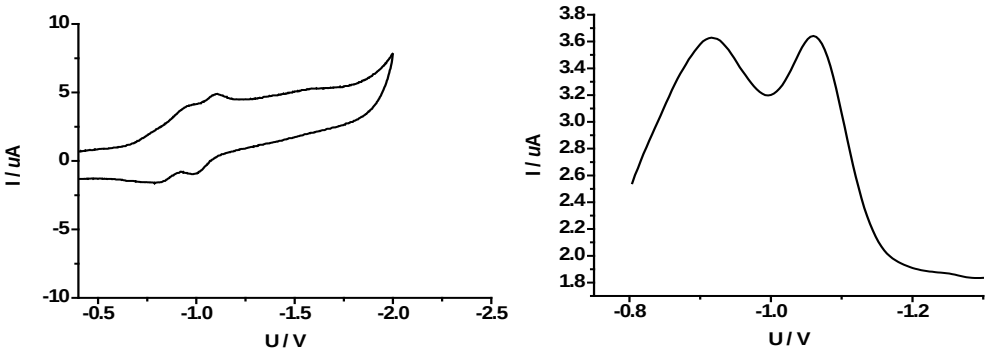


Figure S2. Cyclovoltammograms (left) and DPV (right) of **Bisaza CBI 3a (3a')** in dichloromethane.

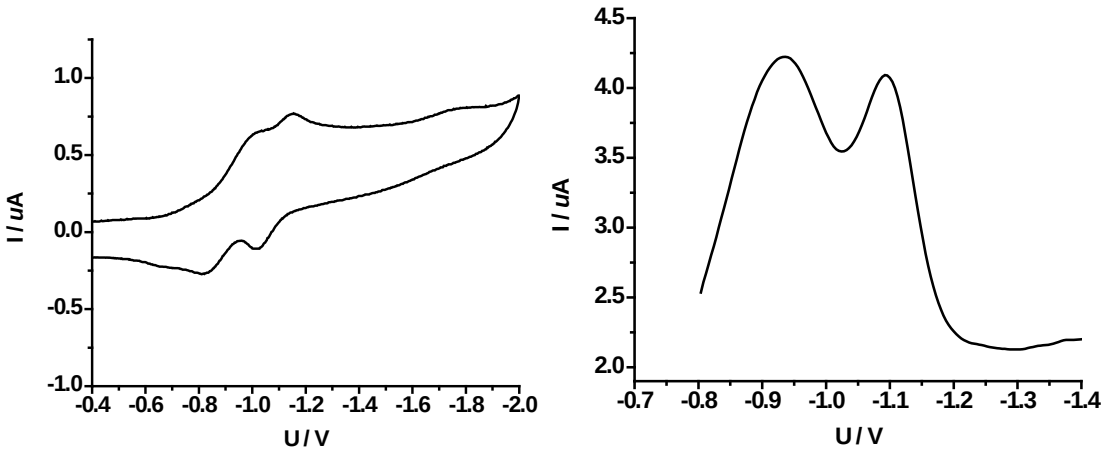
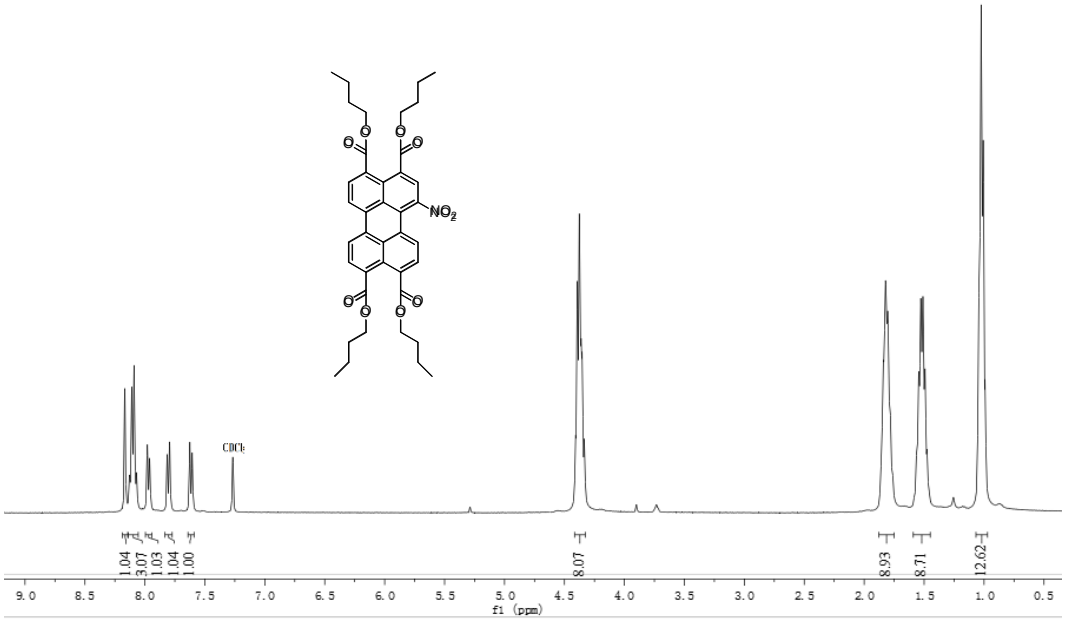


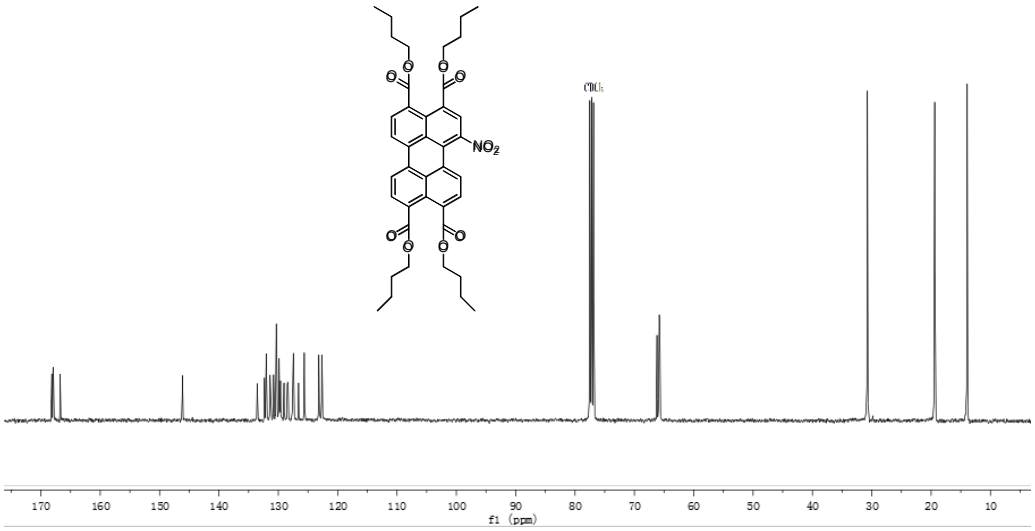
Figure S3. Cyclovoltammograms (left) and DPV (right) of **Bisaza CBI 3b (3b')** in dichloromethane.

5. Copy of NMR Spectrum

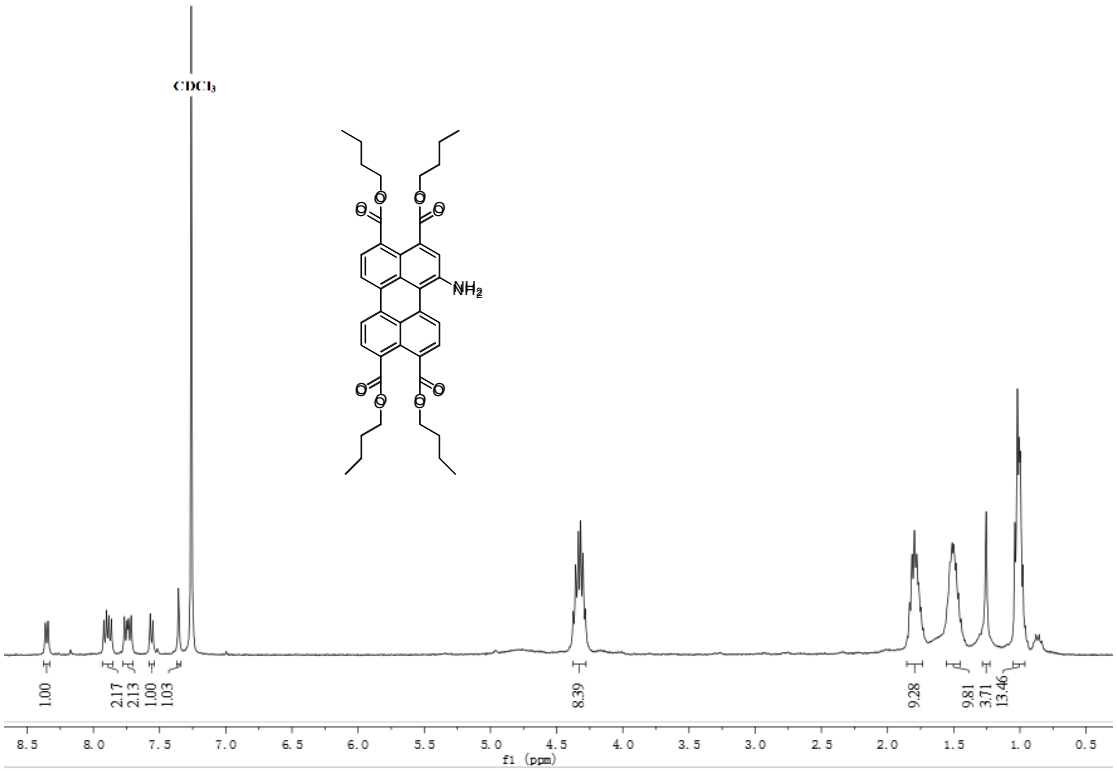
^{1}H NMR (400MHz) spectrum of compound **1** in $CDCl_3$



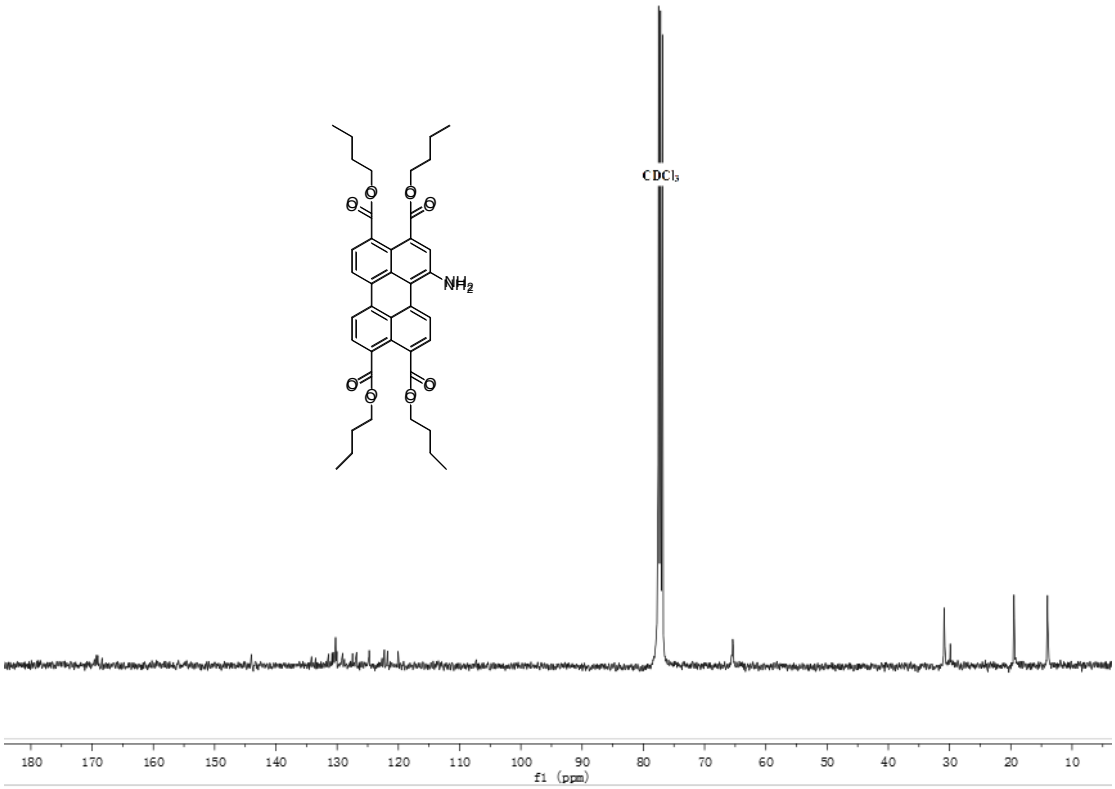
^{13}C NMR (100MHz) spectrum of compound **1** in $CDCl_3$



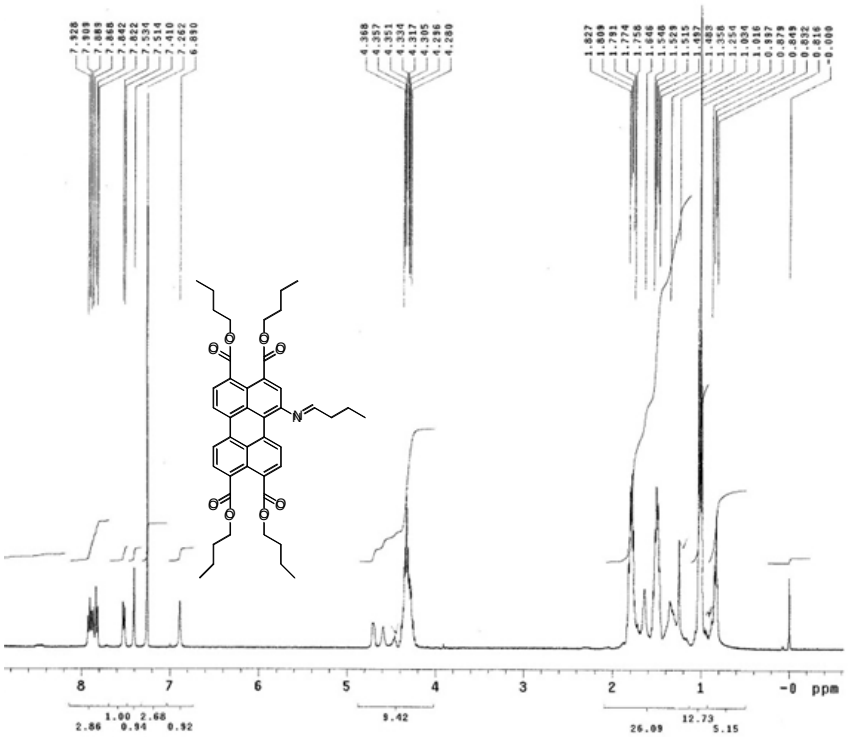
^{1}H NMR (400MHz) spectrum of compound **5** in $CDCl_3$



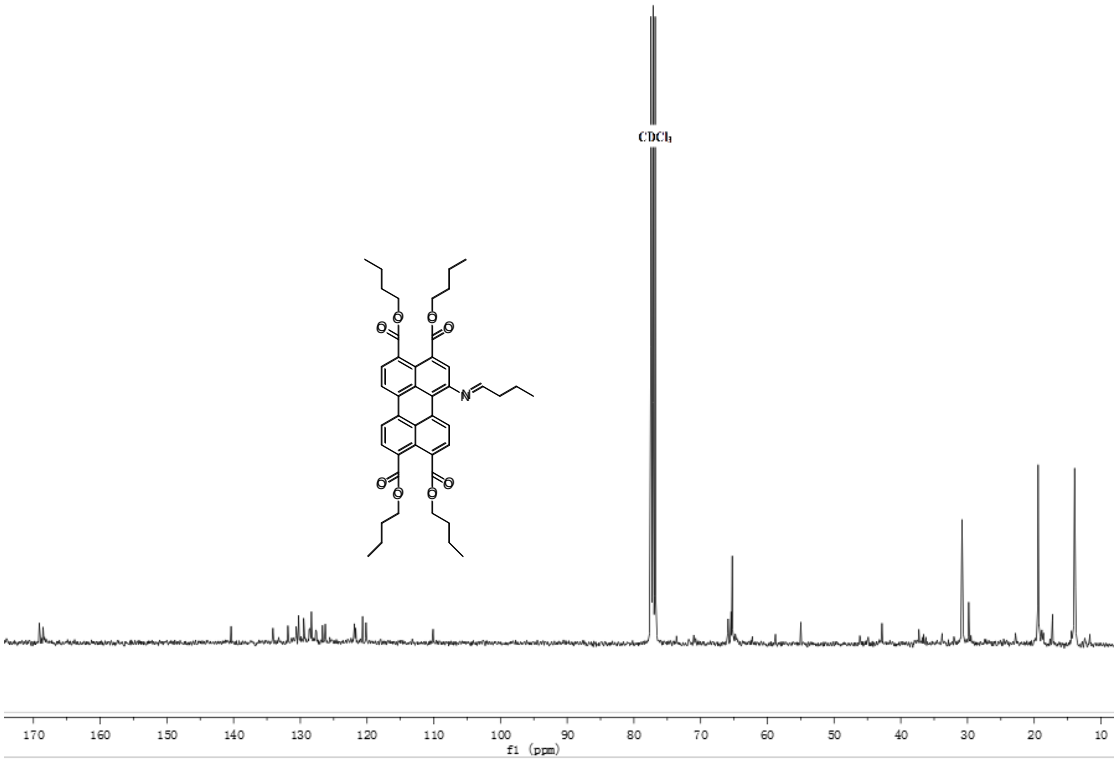
^{13}C NMR (100MHz) spectrum of compound **5** in $CDCl_3$



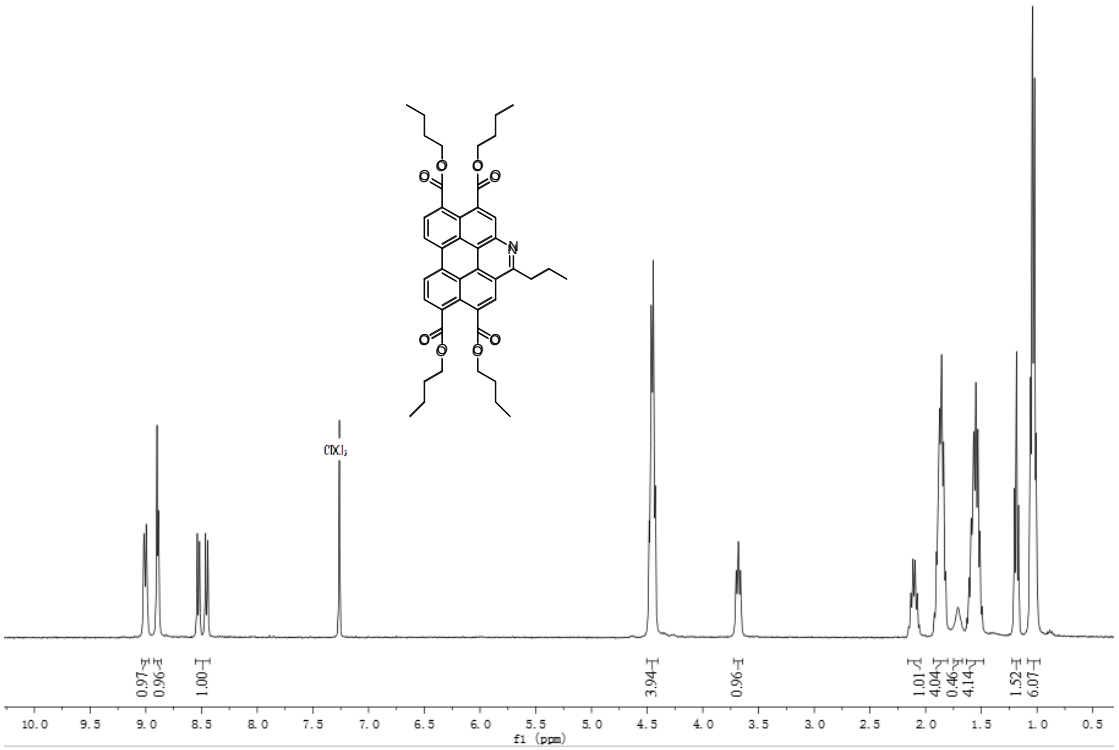
^{1}H NMR (400MHz) spectrum of compound **6** in $CDCl_3$



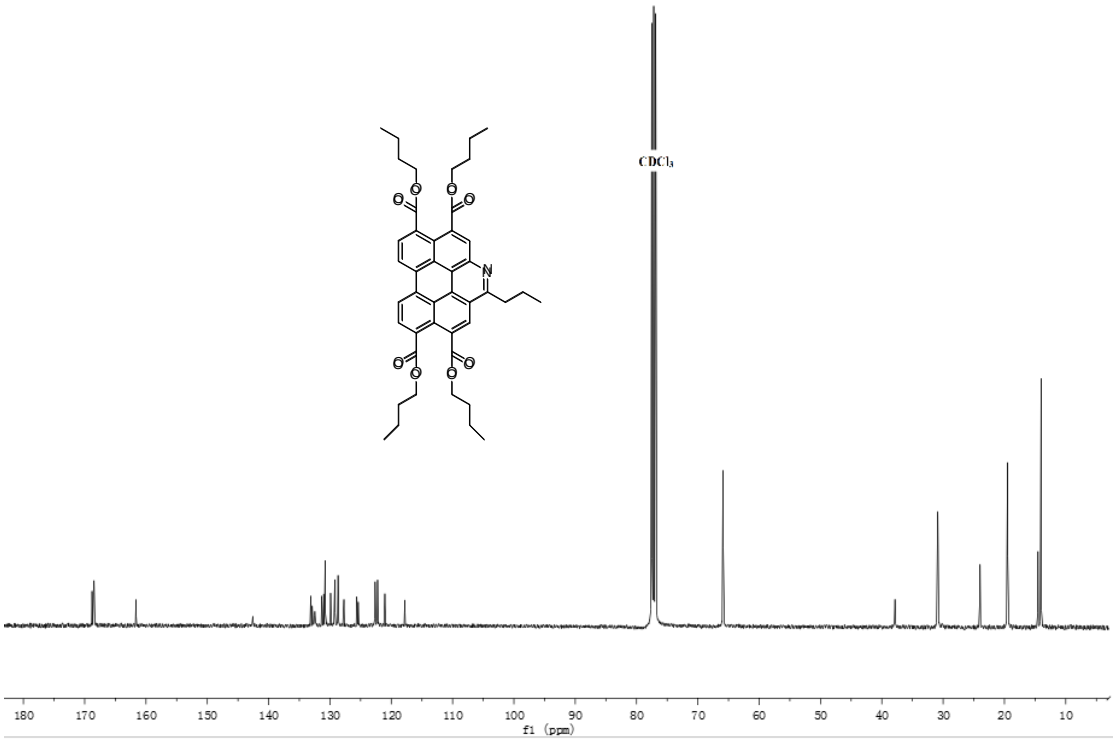
^{13}C NMR (100MHz) spectrum of compound **6** in $CDCl_3$



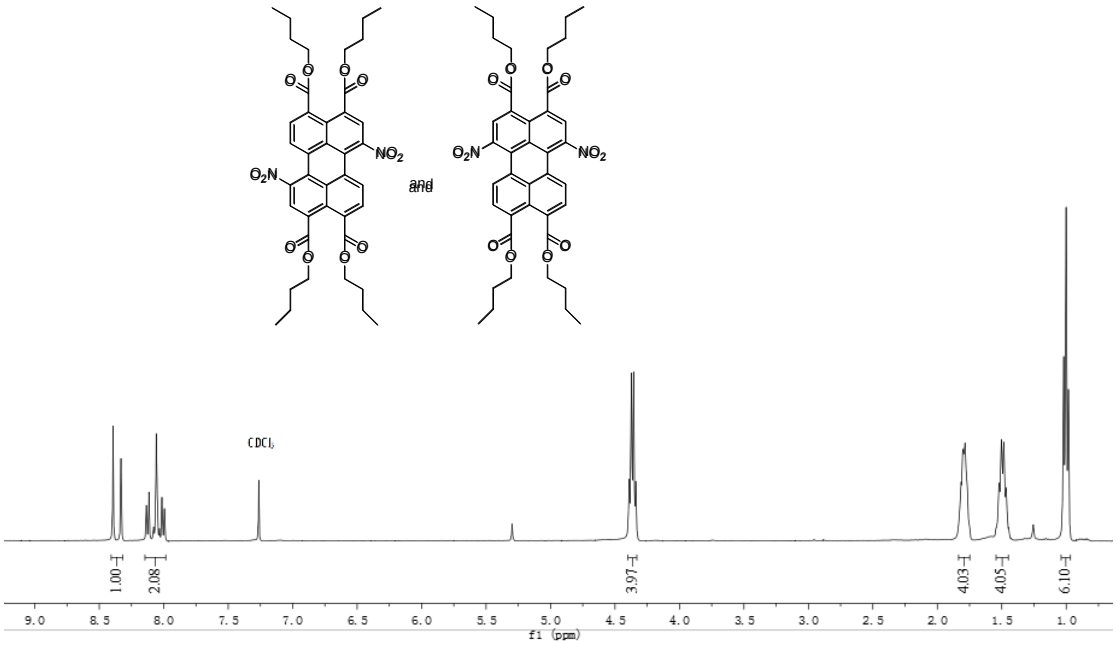
^{1}H NMR (400MHz) spectrum of compound **4** in $CDCl_3$



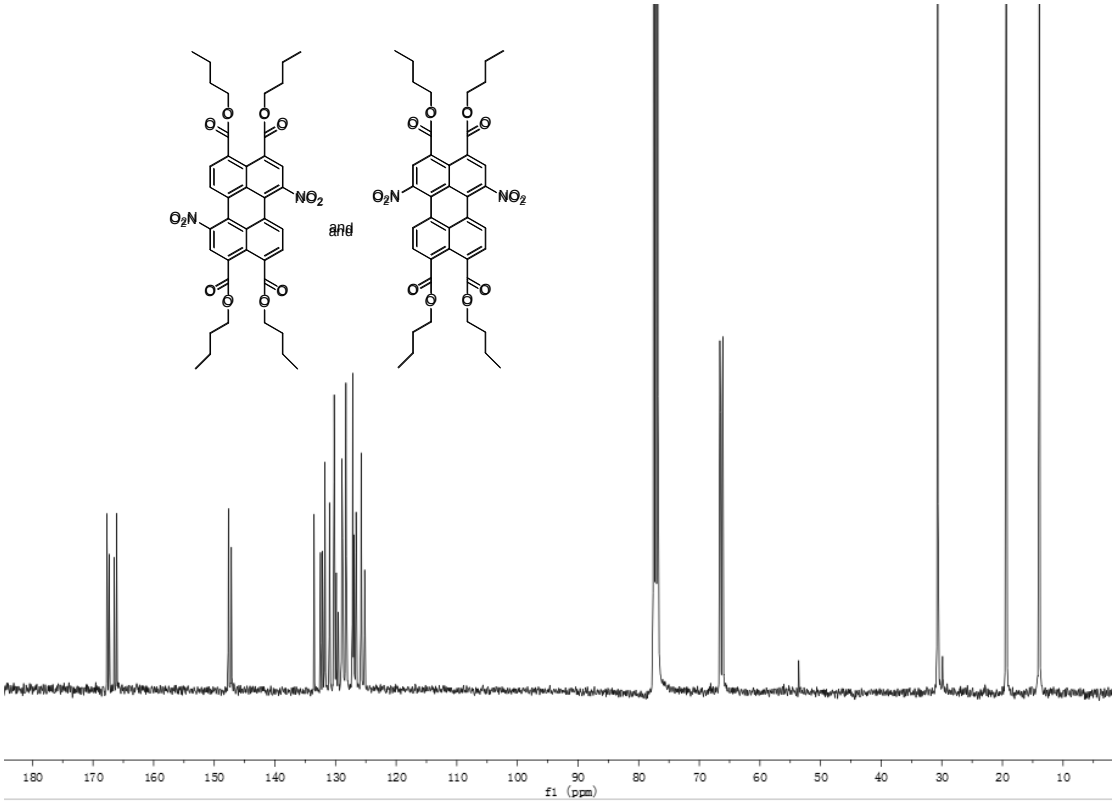
^{13}C NMR (100MHz) spectrum of compound **4** in $CDCl_3$



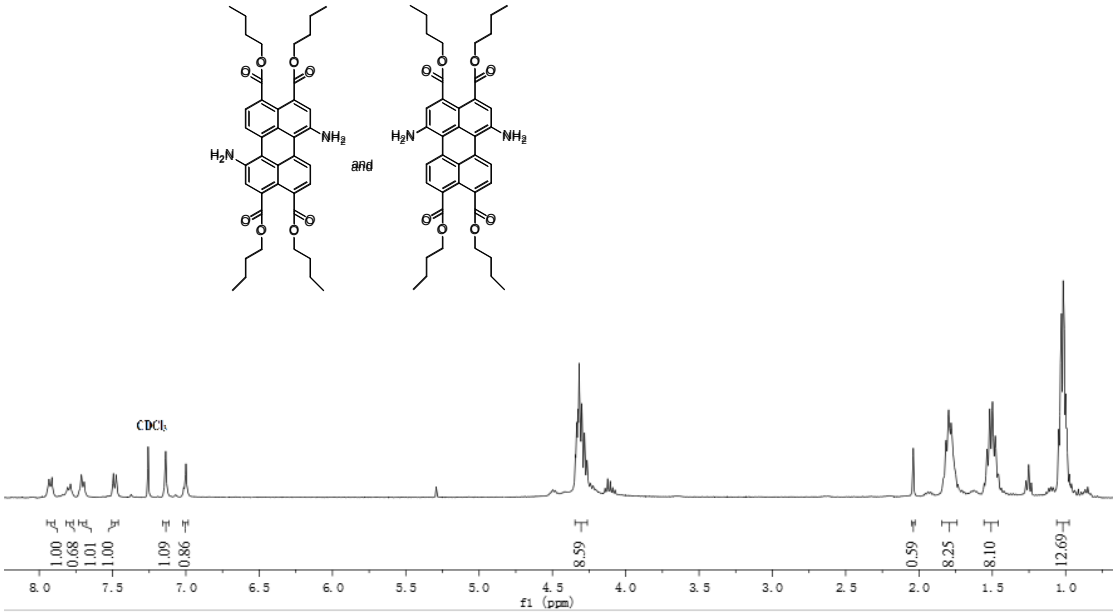
^{1}H NMR (400MHz) spectrum of compound **2 (2′)** in $CDCl_3$



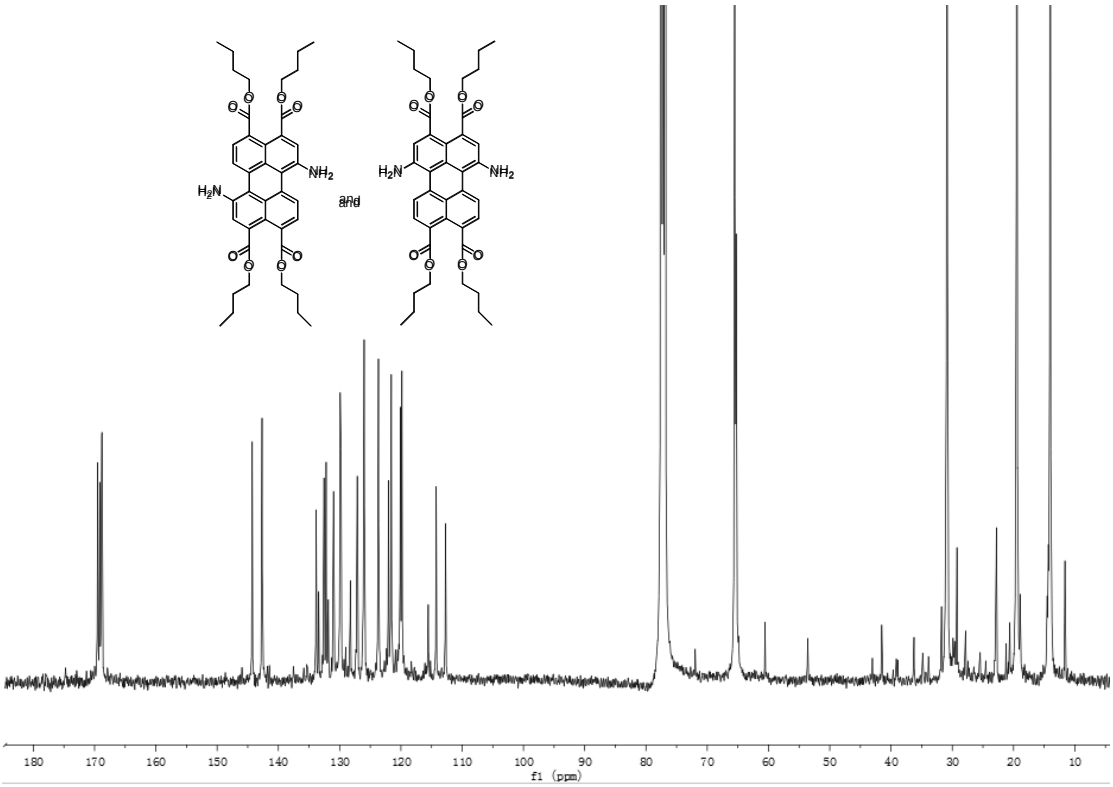
^{13}C NMR (100MHz) spectrum of compound **2 (2′)** in $CDCl_3$



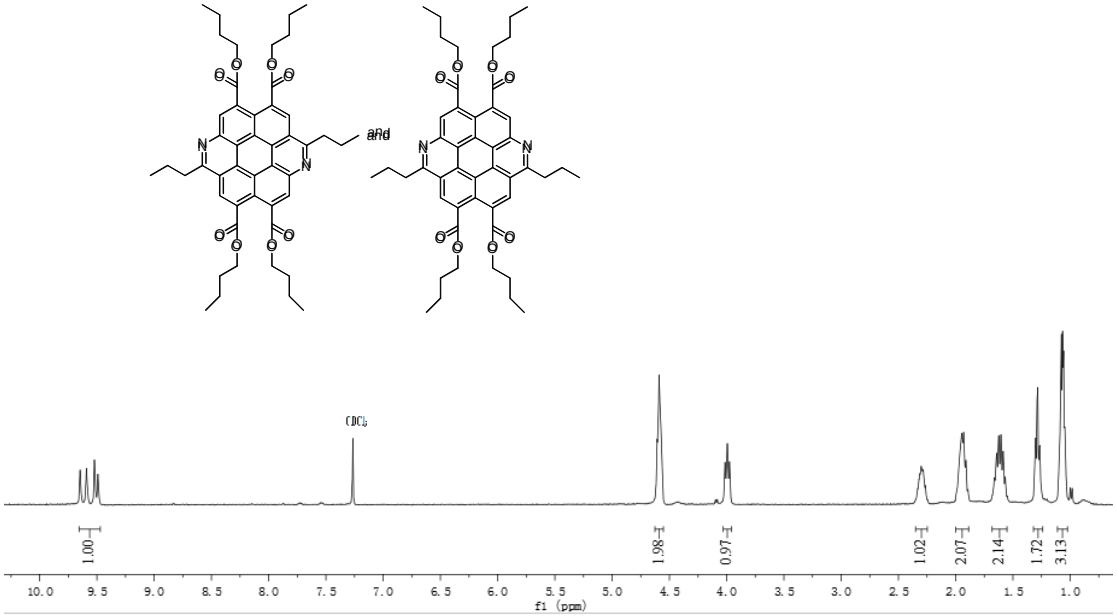
^{1}H NMR (400MHz) spectrum of compound **7 (7′)** in $CDCl_3$



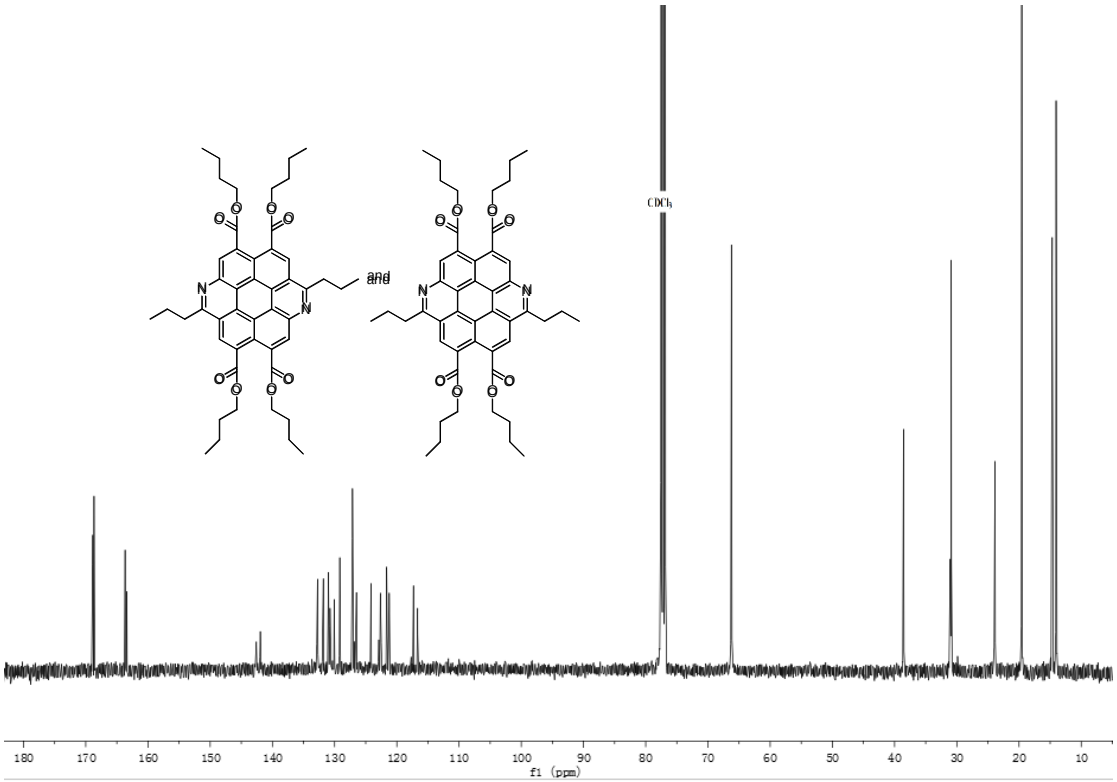
^{13}C NMR (100MHz) spectrum of compound **7 (7′)** in $CDCl_3$



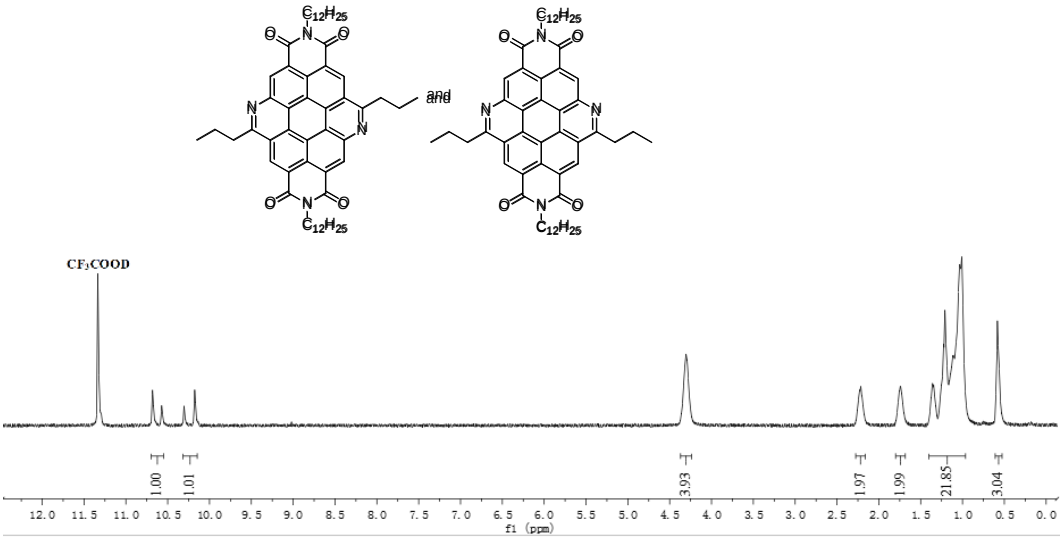
^{1}H NMR (400MHz) spectrum of compound **8 (8′)** in $CDCl_3$



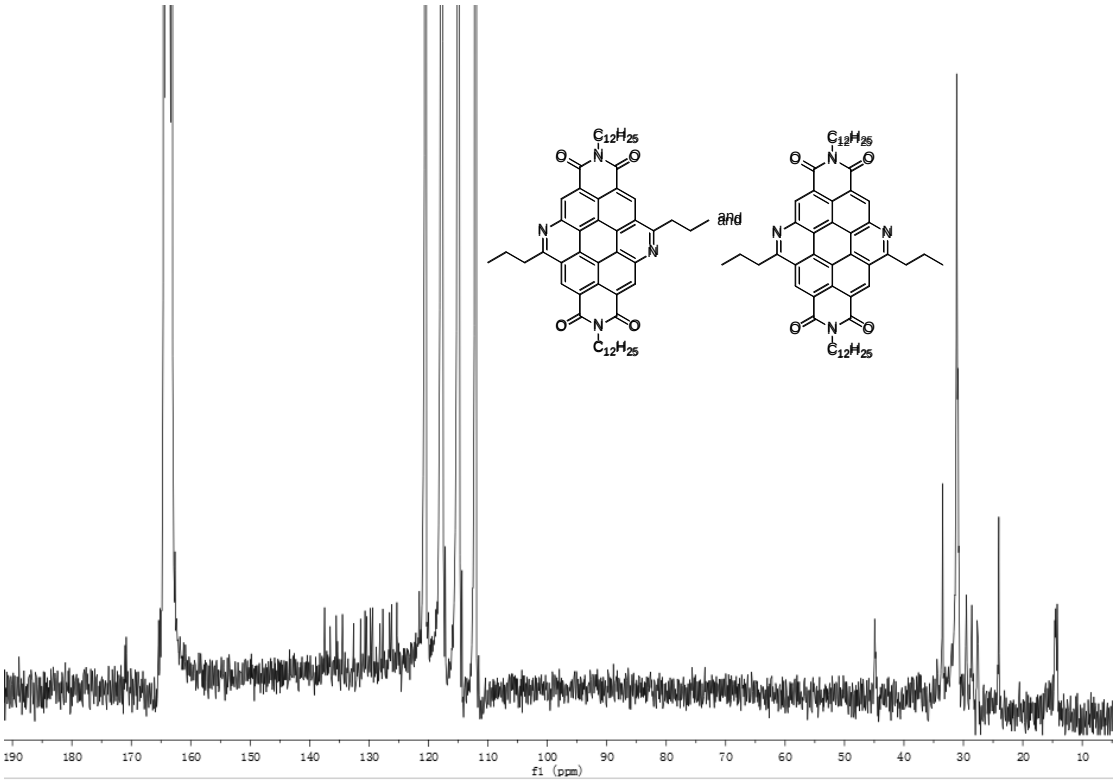
^{13}C NMR (100MHz) spectrum of compound **8 (8′)** in $CDCl_3$



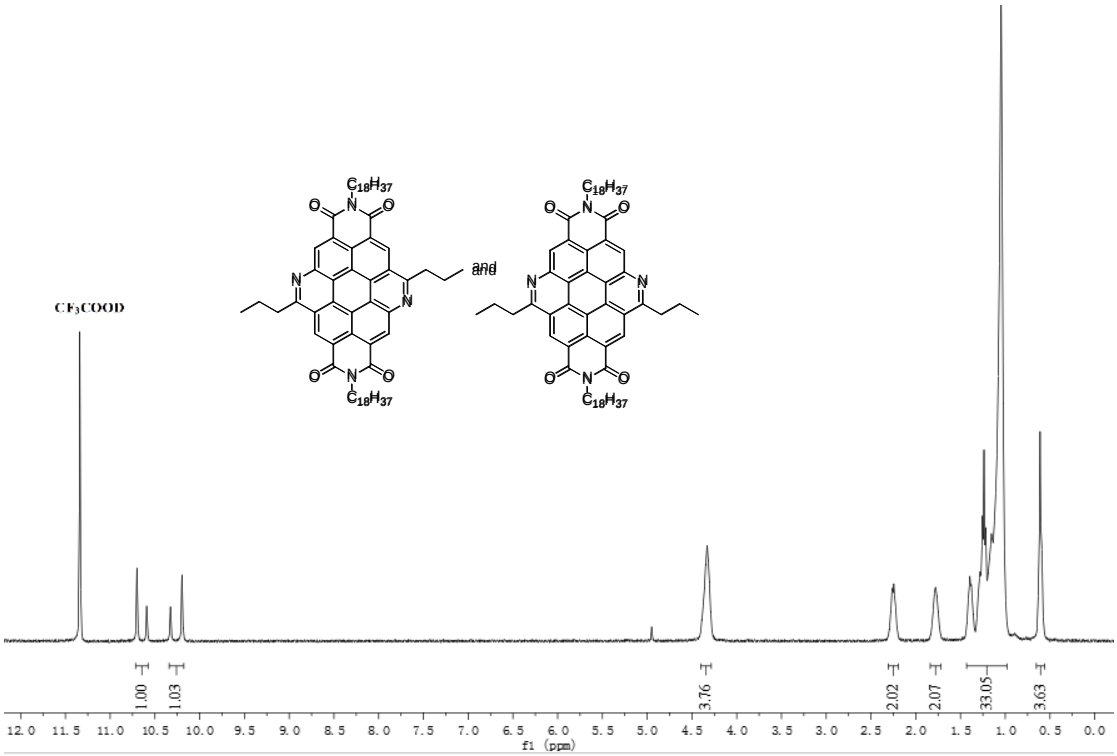
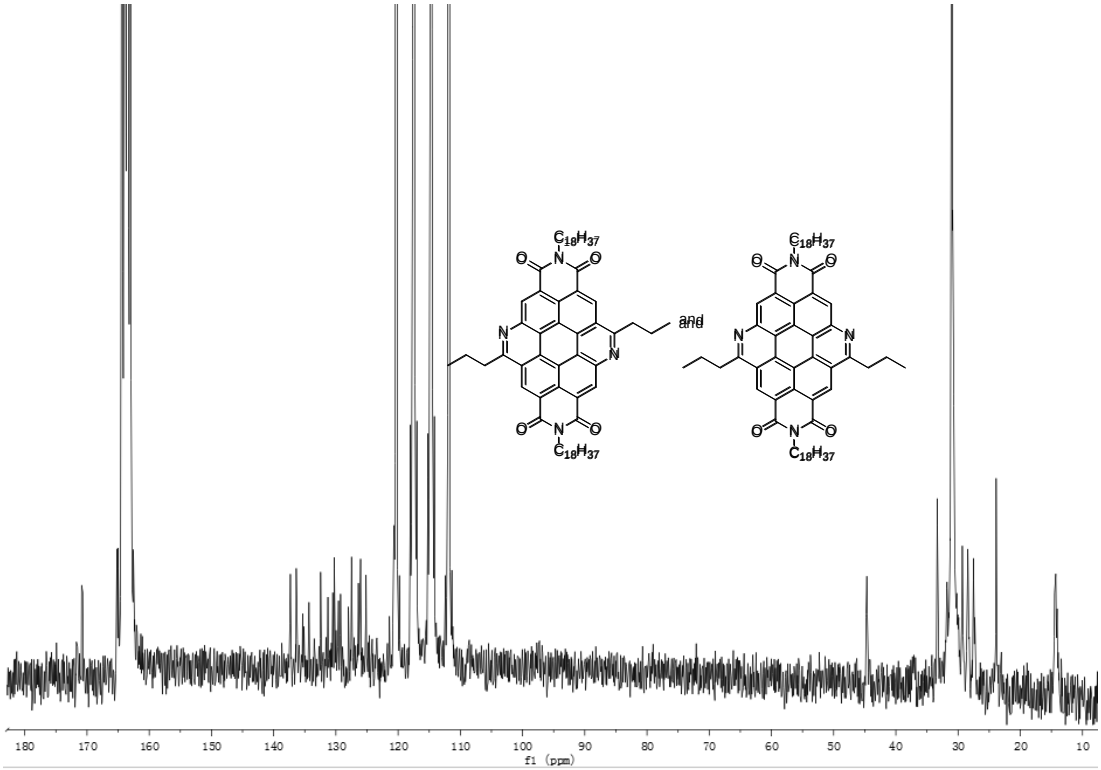
^{1}H NMR (400MHz) spectrum of compound Bisaza-**CBI 3a** (**3a'**) in CF_3COOD



^{13}C NMR (100MHz) spectrum of compound Bisaza-**CBI 3a** (**3a'**) in CF_3COOD



^{1}H NMR (400MHz) spectrum of compound Bisaza-**CBI 3b** (**3b'**) in CF_3COOD



^{13}C NMR (100MHz) spectrum of compound Bisaza-**CBI 3b** (**3b'**) in CF_3COOD