

Electronic Supplementary Information

Synthesis of Monolateral and Bilateral Sulfur-Heterocycles Fused Naphthalene Diimides (NDIs) from Monobromo and Dibromo NDIs

Bing Leng,^{*a} Dong Lu,^{a,b} Xueshun Jia,^b Xiaodi Yang^c and Xike Gao^{*a}

^a*Key Laboratory of Synthetic and Self-Assembly Chemistry for Organic Functional Molecules, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China*

^b*Department of Chemistry, Shanghai University, 99 Shangda Road, Shanghai 200444, China and ^cLaboratory of Advanced Materials, Fudan University, Shanghai 200433, China*

Email: gaoxk@mail.sioc.ac.cn; lengbing@sioc.ac.cn

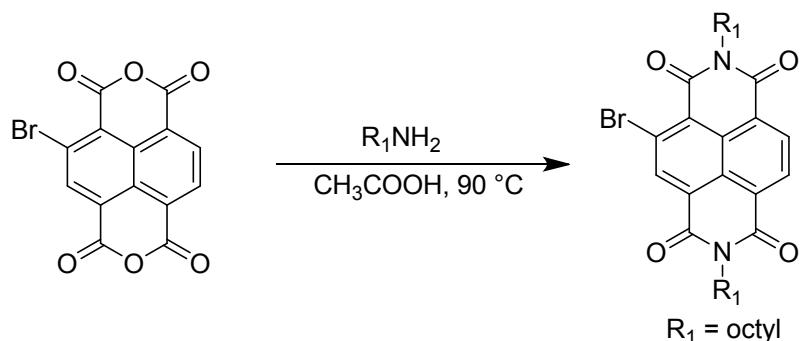
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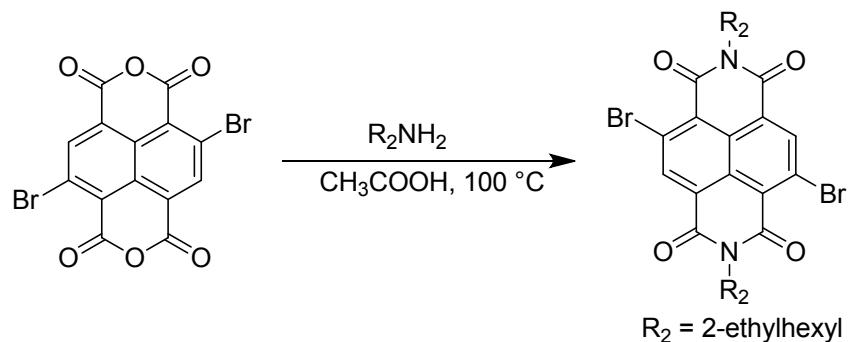
General Information:

Chemical reagents were used as received. 2-Bromo-NDA¹, 2,6-dibromo-NDA¹, 1,1-dicyanoethene-2,2-dithiolate² and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene³ were synthesized according to previously published procedures. ¹H NMR spectra and ¹³C NMR spectra were measured in CDCl₃ on Varian Mercury (300 MHz or 400 MHz) instruments, using tetramethylsilane as an internal standard. Mass spectra (MALDI-TOF) were recorded on a Voyager-DE STR Mass Spectrometer or a Bruker Biflex III MALDI-TOF Spectrometer. Elemental analyses were performed on an Elemental Vario EL III elemental analyzer. Electronic absorption spectra were measured on a U-3900 UV-vis spectrophotometer. Fluorescence spectra were measured on a HITACHI F-2700 fluorescence spectrophotometer. TGA measurements were carried out on a TA Q500 instruments under a dry nitrogen flow at a heating rate of 10 °C/min, heating from room temperature to 500 °C. DSC analyses were performed on a Perkin Elmer Pyris I instruments under nitrogen atmosphere at a heating (cooling) scan rate of 10 °C/min, heating from rt–300 °C. Cyclic voltammetric measurements were carried out in a conventional three-electrode cell using a platinum button working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) reference electrode on a computer-controlled CHI610D instruments.

Synthetic Details

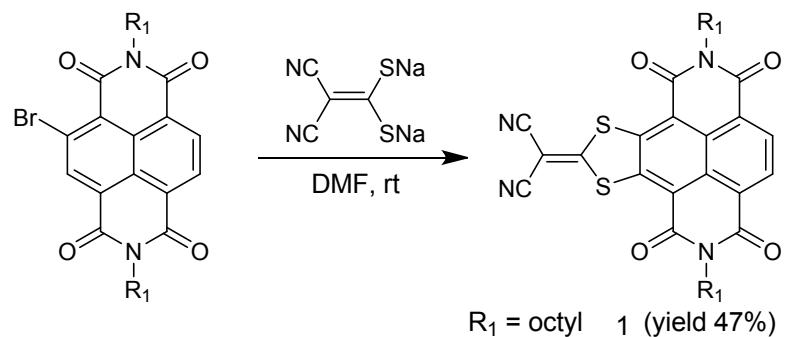


A mixture of 2-bromo-NDA (1 g, 2.9 mmol), n-octylamine (1.4 mL, 8.7 mmol), and acetic acid (30 mL) was stirred at 90 °C for 3 h. The mixture was cooled to room temperature, then the precipitate was collected by filtration, washed with methanol, and dried under vacuum to obtain N,N'-bis-(n-octyl)-2-bromo-NDI as pale yellow solid (yield: 62 %). MS (MALDI-TOF) m/z: 570.1 (M^+). ^1H -NMR (300 MHz, CDCl_3) δ (ppm): 0.86-0.89 (t, $J = 4.5$ Hz, 6H), 1.28-1.38 (m, 20H), 1.73 (m, 4H), 4.17 (m, 4H), 8.74-8.82 (m, 2H), 8.90 (s, 1H). ^{13}C -NMR (100 MHz, CDCl_3) δ (ppm): 14.8, 23.4, 27.8, 27.9, 28.7, 28.8, 29.9, 30.0, 32.5, 41.9, 42.2, 124.6, 126.4, 126.8, 127.6, 129.4, 131.4, 132.4, 139.1, 161.7, 162.4, 162.6, 163.2. Anal. Calcd. For $\text{C}_{30}\text{H}_{37}\text{BrN}_2\text{O}_4$: C, 63.27; H, 6.55; N, 4.92; Found: C, 63.22; H, 6.40; N, 4.70.

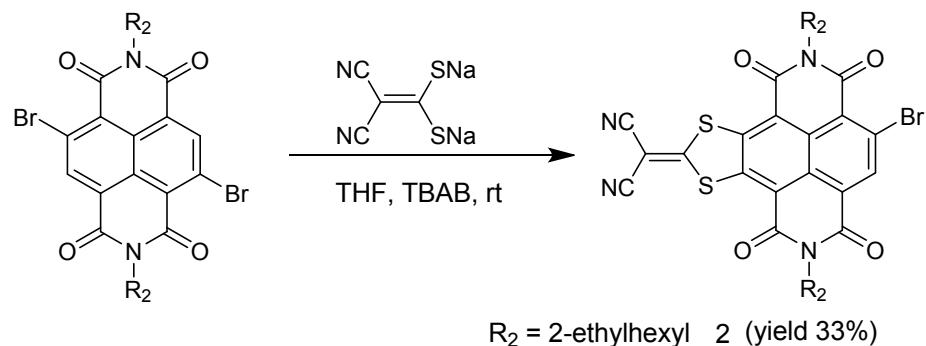


A mixture of 2,6-dibromo-NDA (1 g, 2.35 mmol), 2-ethylhexylamine (1.2 mL, 7.34 mmol), and acetic acid (30 mL) was stirred at 100 °C for 3 h. The mixture was cooled to room temperature, then the precipitate was collected by filtration, washed with methanol, and dried under vacuum to obtain N,N'-bis-(2-Ethylhexyl)-2,6-dibromo-NDI as yellow solid (yield: 50 %). MS (MALDI-TOF) m/z: 649.2 ($\text{M} + \text{H}^+$). ^1H -NMR (300 MHz, CDCl_3) δ (ppm): 0.85-0.94 (m, 12H), 1.28-1.37 (m, 16H), 1.91-1.94 (t, $J = 4.5$ Hz, 2H), 4.09-4.19 (m, 4H), 8.98 (s, 2H). ^{13}C -NMR (100 MHz, CDCl_3) δ (ppm): 10.5, 14.1, 23.1, 23.9, 28.5, 30.6, 37.7, 45.1, 124.0, 125.2, 127.7, 128.4,

139.2, 161.0, 161.2. Anal. Calcd. For $C_{30}H_{36}Br_2N_2O_4$: C, 55.57; H, 5.60; N, 4.32; Found: C, 55.70; H, 5.59; N, 4.35.

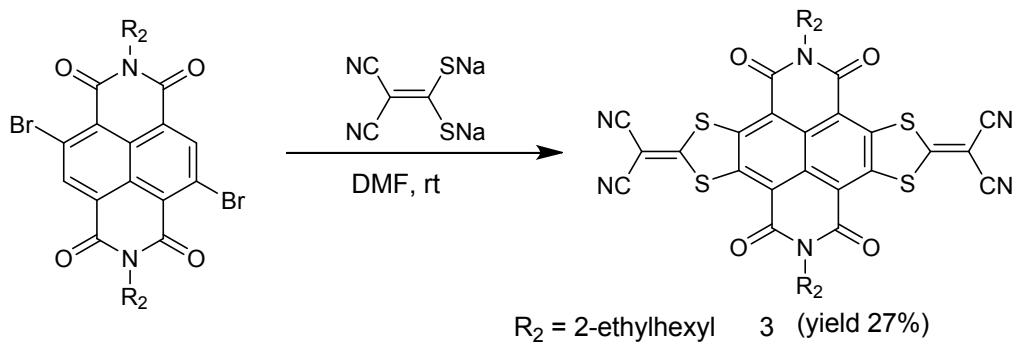


To a solution of N,N' -bis-(n-octyl)-2-bromo-NDI (467 mg, 0.878 mmol) in DMF (20 ml), sodium 1,1-dicyanoethylene-2,2-dithiolate (305 mg, 1.76 mmol) was added, and the mixture was stirred at room temperature for 3h. Then, the solvent was evaporated under reduced pressure, and the residue was purified by column chromatography, using dichloromethane/petroleum (2:1, v:v) as the eluent. 243 mg of 1 was obtained as orange solid (yield: 47 %). MS (MALDI-TOF) m/z: 629.3 ($M + H^+$). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ (ppm): 0.85-0.90 (t, $J = 7.5$ Hz, 6H), 1.29-1.42 (m, 20H), 1.72-1.77 (m, 4H), 4.22-4.27 (t, $J = 7.5$ Hz, 4H), 8.85 (s, 2H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ (ppm): 14.1, 22.6, 27.0, 28.0, 29.2, 31.8, 41.7, 70.4, 111.7, 119.1, 125.7, 125.8, 131.8, 144.1, 161.5, 162.6, 182.8. Anal. Calcd. For $C_{34}H_{36}N_4O_4S_2$: C, 64.94; H, 5.77; N, 8.91; Found: C, 64.94; H, 5.80; N, 8.83.

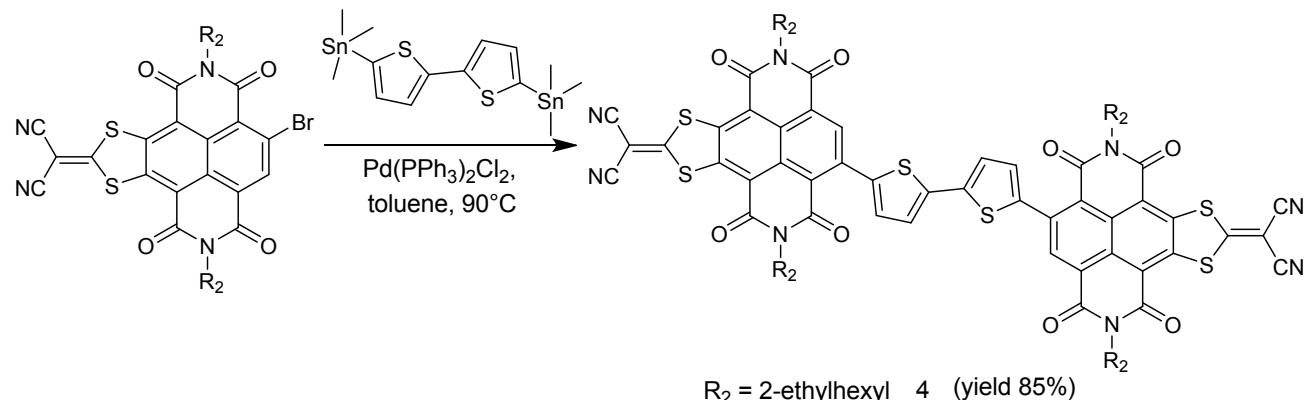


N,N' -bis-(2-Ethylhexyl)-2,6-dibromo-NDI (50 mg, 0.077 mmol) and TBAB (30 mg, 0.093 mmol) were dissolved in THF (10 ml), and sodium 1,1-dicyanoethylene-2,2-dithiolate (14 mg, 0.075 mmol) was added. The mixture was stirred at room temperature for 1h, and then another portion of sodium 1,1-dicyanoethylene-2,2-dithiolate (7 mg, 0.038 mmol) was added. The reaction was monitored continually by TLC until the reaction was completed. After removing

the solvent under reduced pressure, the crude product was purified by column chromatography, using dichloromethane/petroleum (2:1, v:v) as the eluent. 18 mg of 2 was obtained as orange solid (yield: 33%). MS (MALDI-TOF) m/z: 707.2 ($M + H^+$). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ (ppm): 0.90-0.95 (t, $J = 7.5$ Hz, 12H), 1.30-1.37 (m, 16H), 1.95 (m, 2H), 4.20-4.22 (d, $J = 6$ Hz, 4H), 9.08 (s, 1H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ (ppm): 10.5, 10.6, 14.1, 23.0, 23.1, 23.9, 28.4, 28.5, 30.5, 30.6, 37.7, 37.8, 45.5, 45.7, 70.3, 111.8, 118.3, 118.9, 122.9, 124.7, 124.9, 127.7, 129.8, 139.3, 144.0, 145.2, 160.1, 160.9, 162.1, 162.7, 183.0. Anal. Calcd. For $\text{C}_{34}\text{H}_{35}\text{BrN}_4\text{O}_4\text{S}_2$: C, 57.70; H, 4.98; N, 7.92; Found: C, 57.76; H, 4.99; N, 7.93.



$\text{N,N}'\text{-bis-(2-Ethylhexyl)-2,6-dibromo-NDI}$ (100 mg, 0.154 mmol) was dispersed in DMF (10 ml). Under stirring, the sodium 1,1-dicyanoethylene-2,2-dithiolate (86 mg, 0.462 mmol) was added, and the mixture was stirred under room temperature for 5h in ambient condition. Then the solvent was evaporated under reduced pressure, and the residue was purified by column chromatography, using dichloromethane/petroleum (3:1, v:v) as the eluent. 32 mg of 3 was obtained as purple solid (yield: 27%). MS (MALDI-TOF) m/z: 767.0 ($M + H^+$). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ (ppm): 0.93-0.98 (t, $J = 7.5$ Hz, 12H), 1.32-1.42 (m, 16H), 1.95 (m, 2H), 4.23 (m, 4H). Anal. Calcd. For $\text{C}_{38}\text{H}_{34}\text{N}_6\text{O}_4\text{S}_4$: C, 59.51; H, 4.47; N, 10.96; Found: C, 59.78; H, 4.67; N, 10.94.



To a Shchlenk tube equipped with a magnetic stir bar were added compound 2 (20 mg, 0.028

mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (7 mg, 0.014 mmol) and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (1 mg, 0.0014 mmol) under N_2 atmosphere. Anhydrous toluene (3.0 mL) was added to the tube. The reaction mixture was stirred at 90 °C for 22 h. The reaction mixture was then cooled to room temperature. After removing the solvent under reduced pressure, the crude products were purified by column chromatography, using dichloromethane/petroleum (3:1, v:v) as the eluent. 17 mg of **4** was obtained as green solid (yield: 85%). MS (MALDI-TOF) m/z: 1418.5 (M^+). ^1H -NMR (300 MHz, CDCl_3) δ (ppm): 0.93-0.96 (m, 24H), 1.29-1.41 (m, 32H), 1.96 (m, 4H), 4.16-4.22 (t, $J = 9$ Hz, 8H), 7.37 (s, 4H), 8.85 (s, 2H). ^{13}C -NMR (100 MHz, CDCl_3) δ (ppm): 10.6, 14.1, 23.0, 23.1, 24.0, 28.5, 30.6, 37.7, 37.9, 45.4, 70.1, 111.9, 118.8, 119.1, 121.7, 124.2, 125.1, 125.4, 127.4, 130.7, 136.9, 139.8, 140.4, 140.7, 161.3, 161.6, 162.6, 162.9, 183.2. Anal. Calcd. For $\text{C}_{76}\text{H}_{74}\text{N}_8\text{O}_8\text{S}_6$: C, 64.29; H, 5.25; N, 7.89; Found: C, 64.01; H, 5.20; N, 7.72.

References

- 1 M. Sasikumar, Y. V. Suseela and T. Govindaraju, *Asian J. Org. Chem.*, 2013, **2**, 779.
- 2 W. R. Hatchard, *J. Org. Chem.*, 1964, **29**, 660.
- 3 X. G. Guo, F. S. Kim, M. J. Seger, S. A. Jenekhe and M. D. Watson, *Chem. Mater.*, 2012, **24**, 1434.

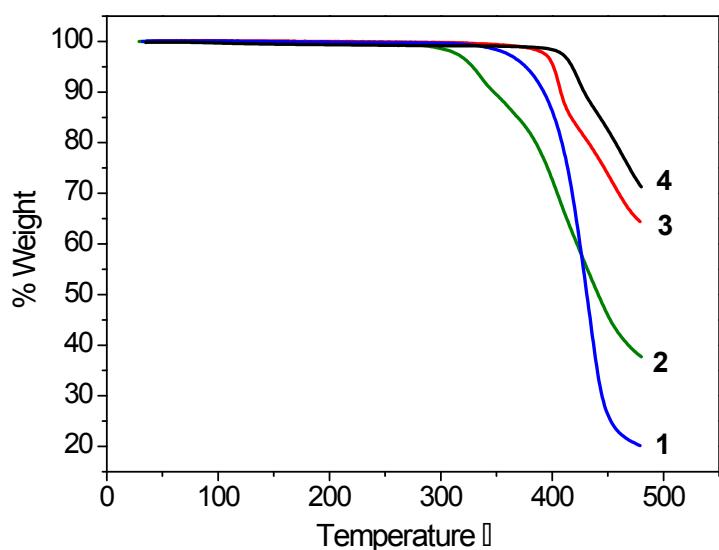


Figure S1. TGA plots of **1**, **2**, **3**, and **4** with a heating rate of 10 °C/min under a nitrogen flow.

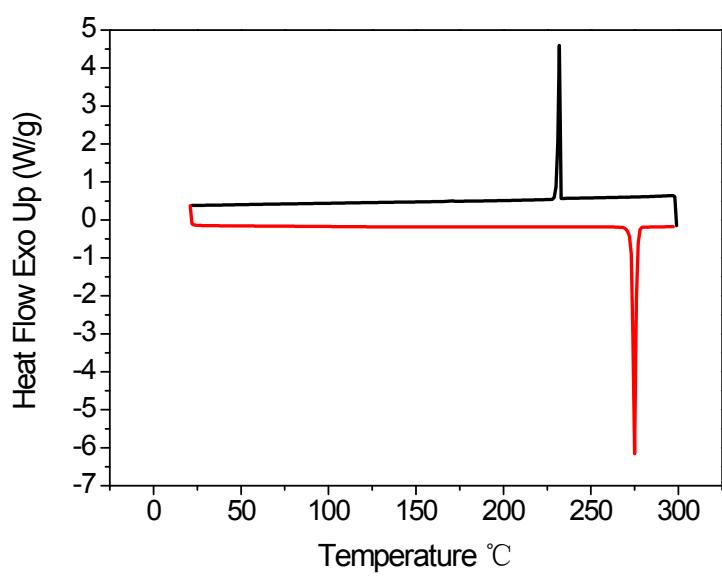


Figure S2. DSC plots of compound 1.

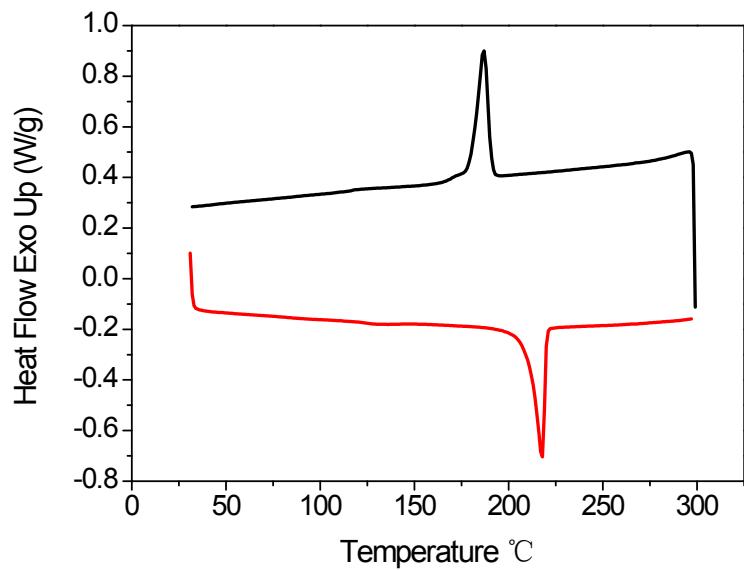


Figure S3. DSC plots of compound 2.

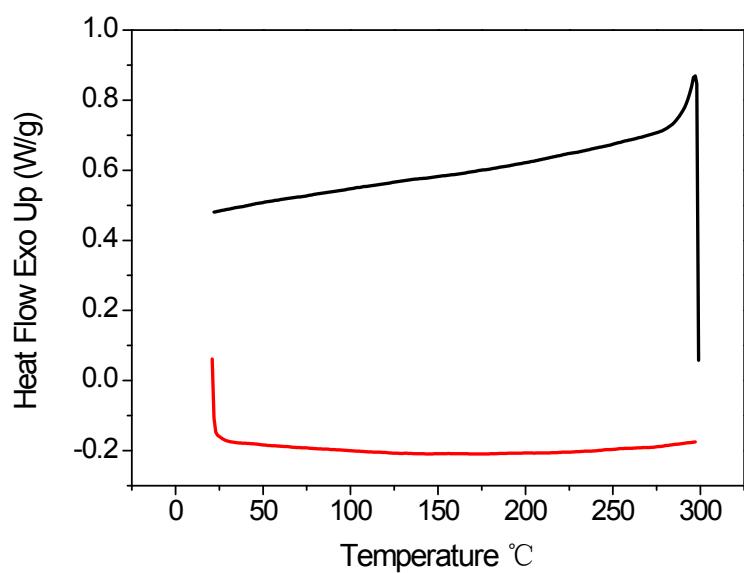


Figure S4. DSC plots of compound 3.

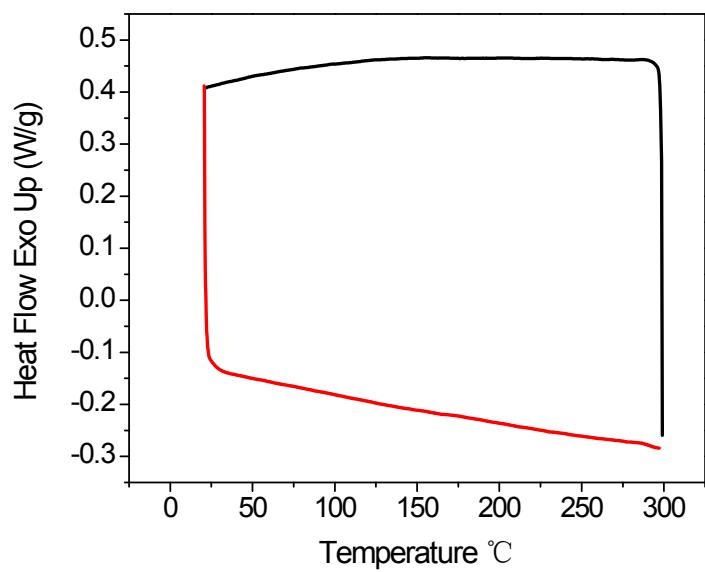


Figure S5. DSC plots of compound 4.

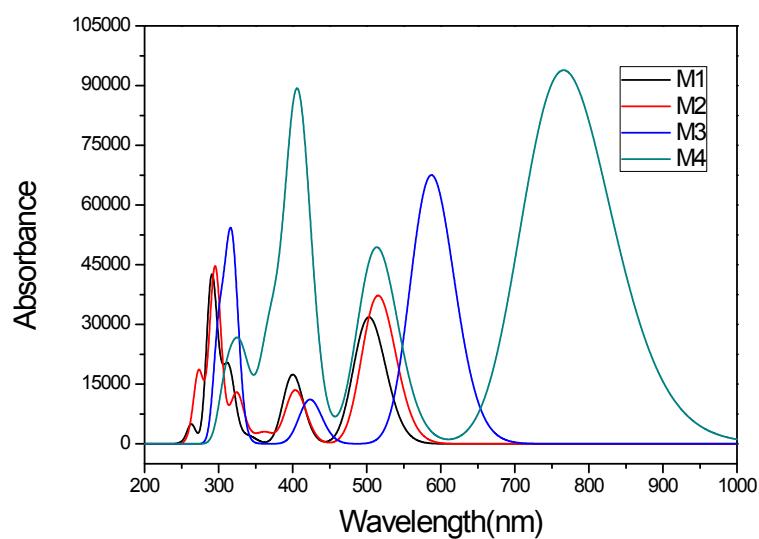


Figure S6. Predicted absorption spectra of **1**, **2**, **3**, and **4**. The absorbance spectra was calculated with the TDDFT/B3LYP/6-31G(d,p) level on DFT/B3LYP/6-31G(d,p) optimized geometries.

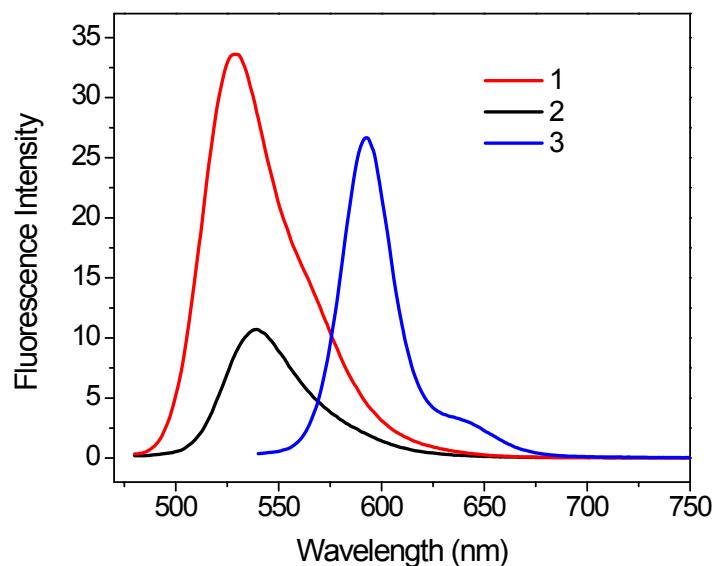
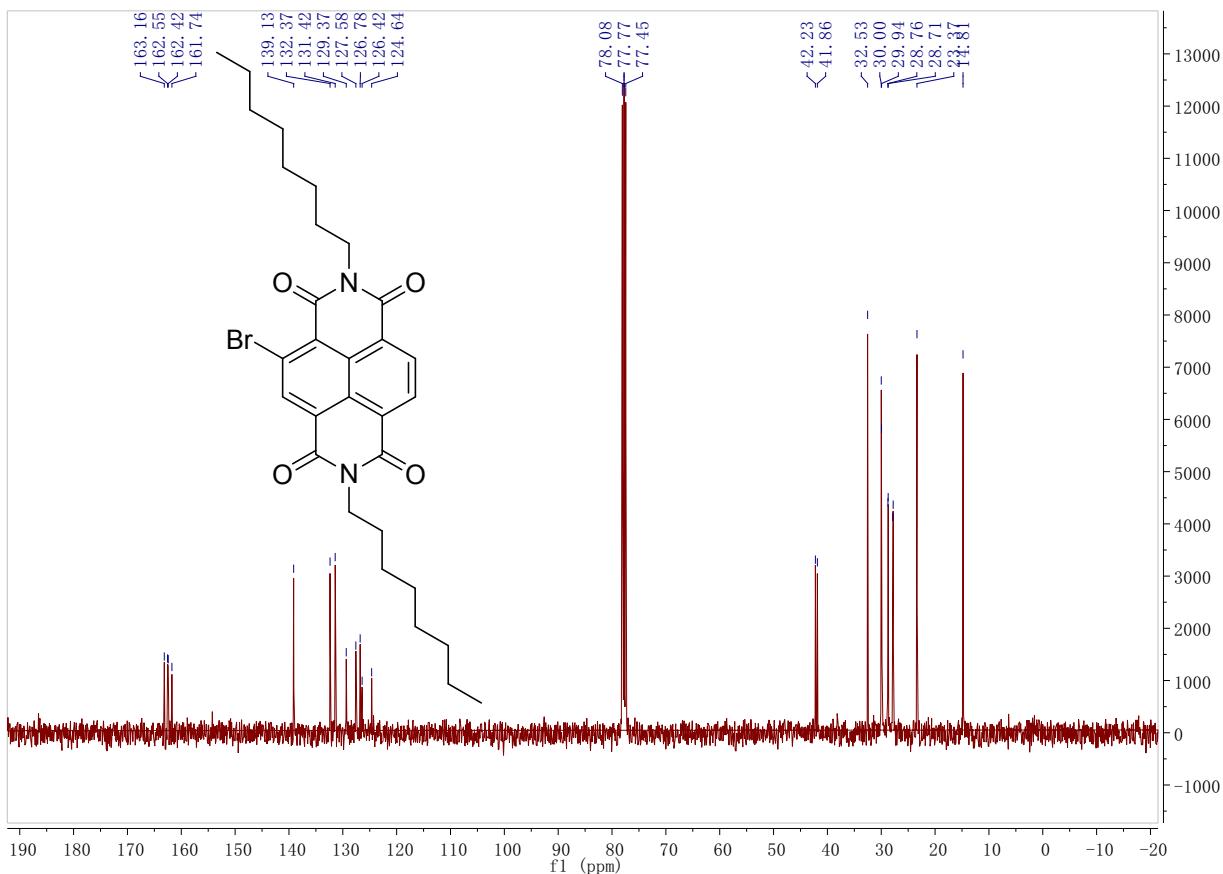
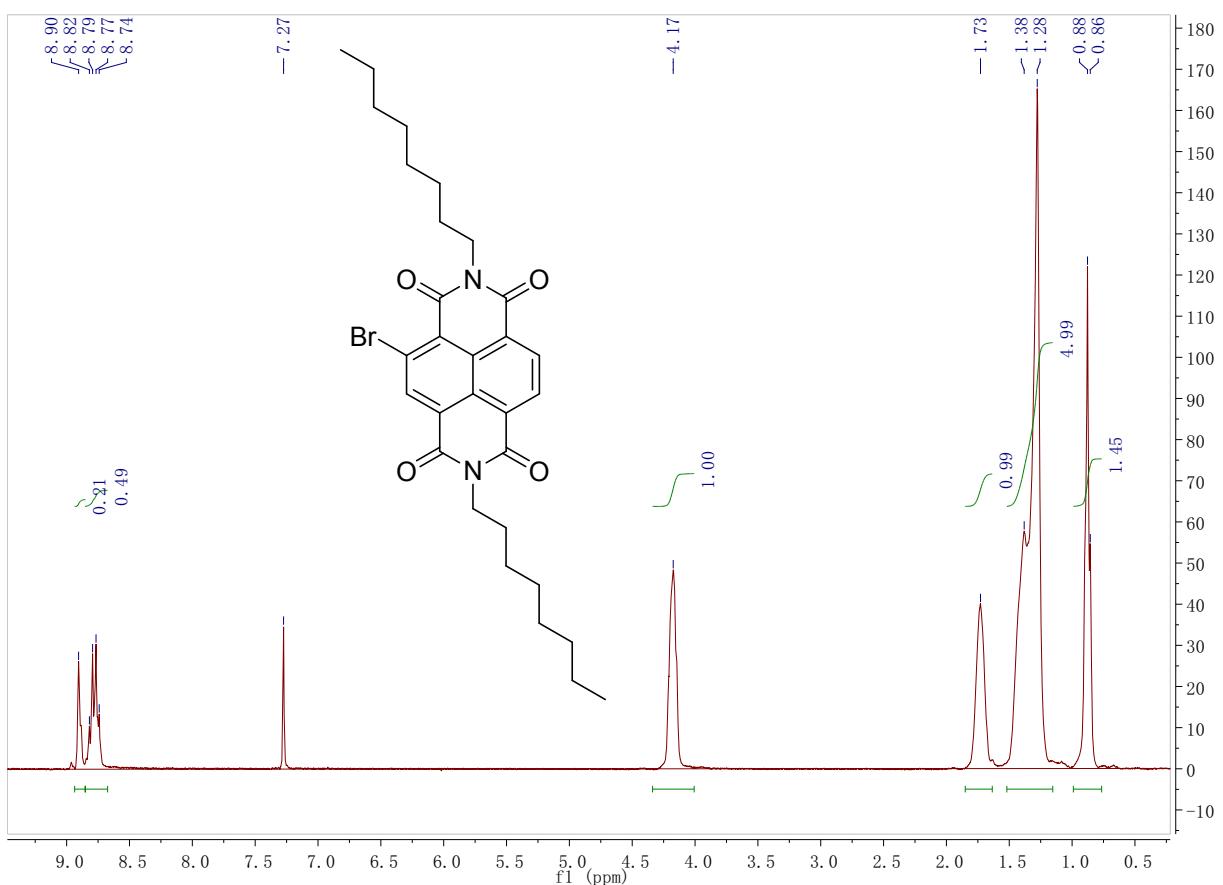
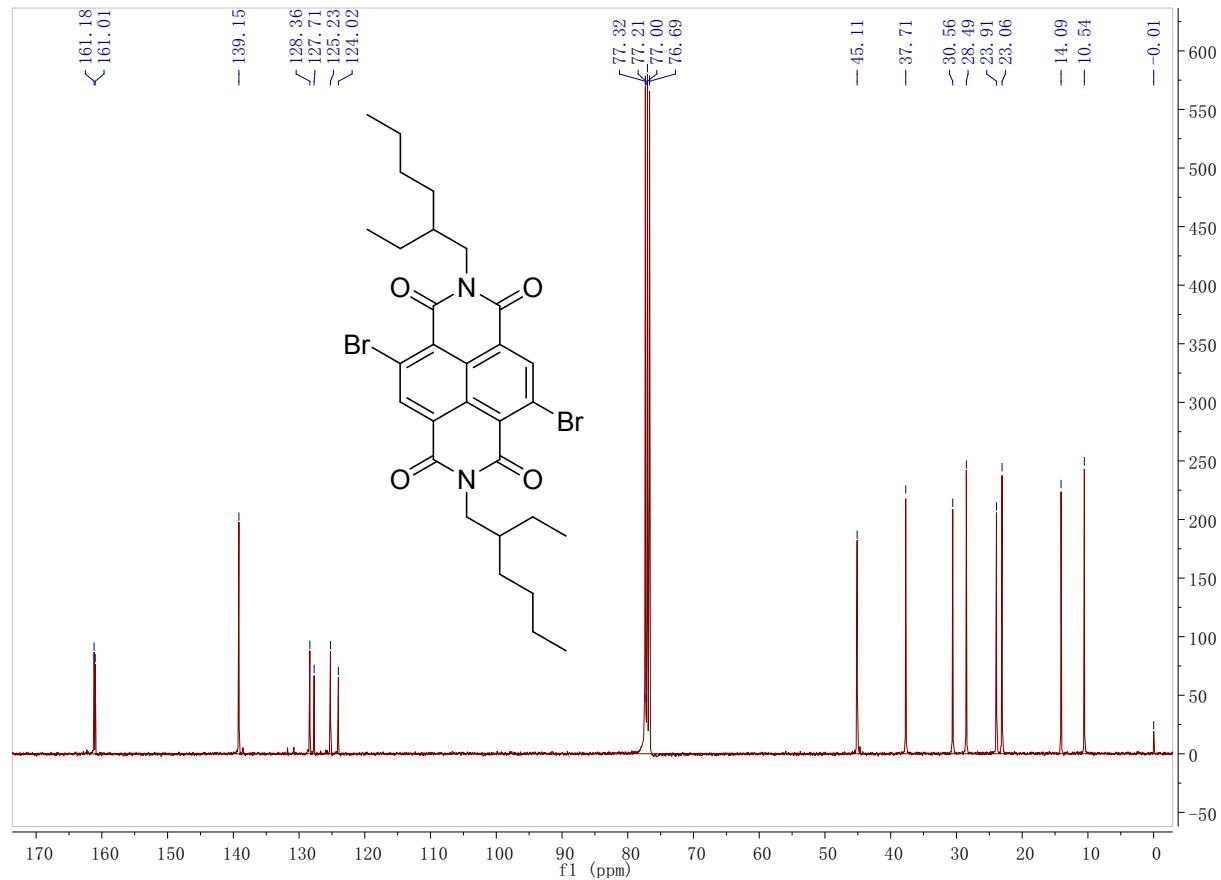
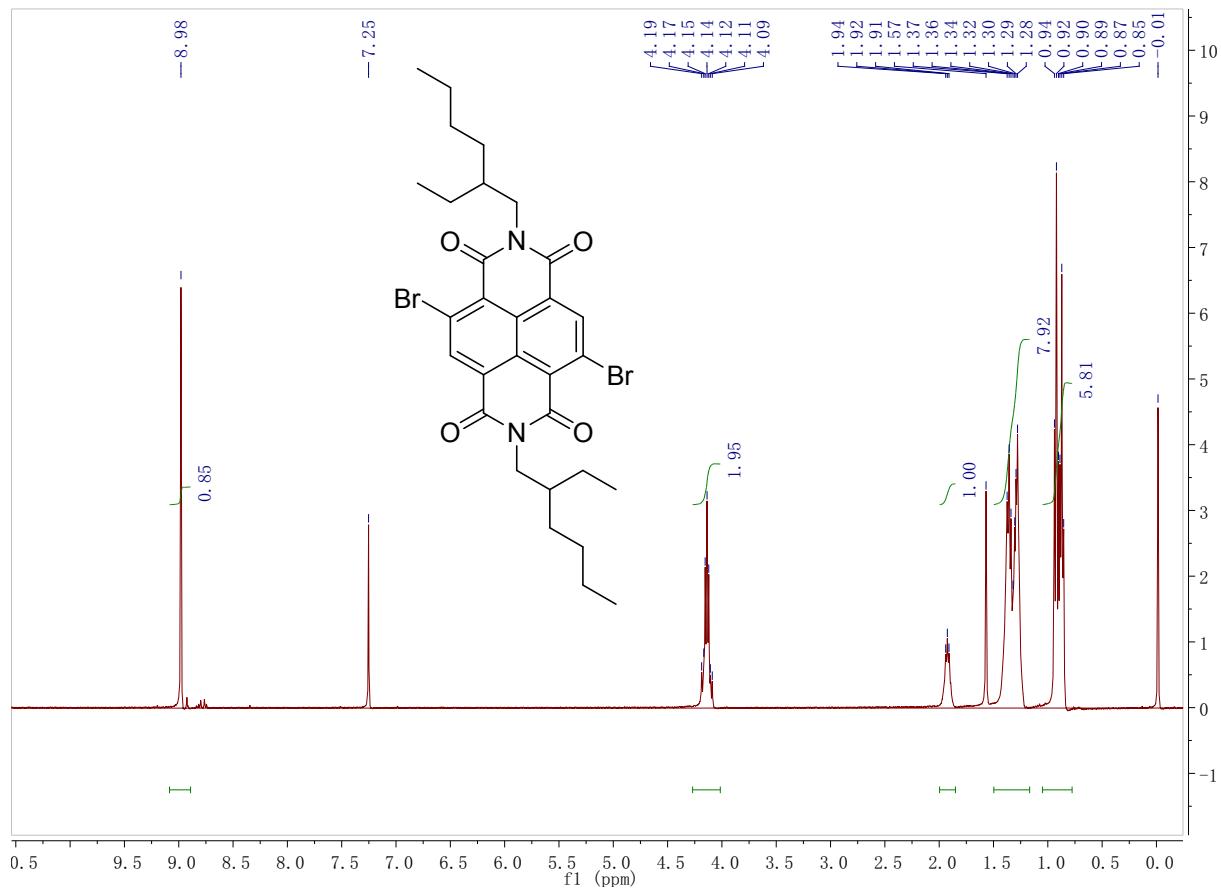
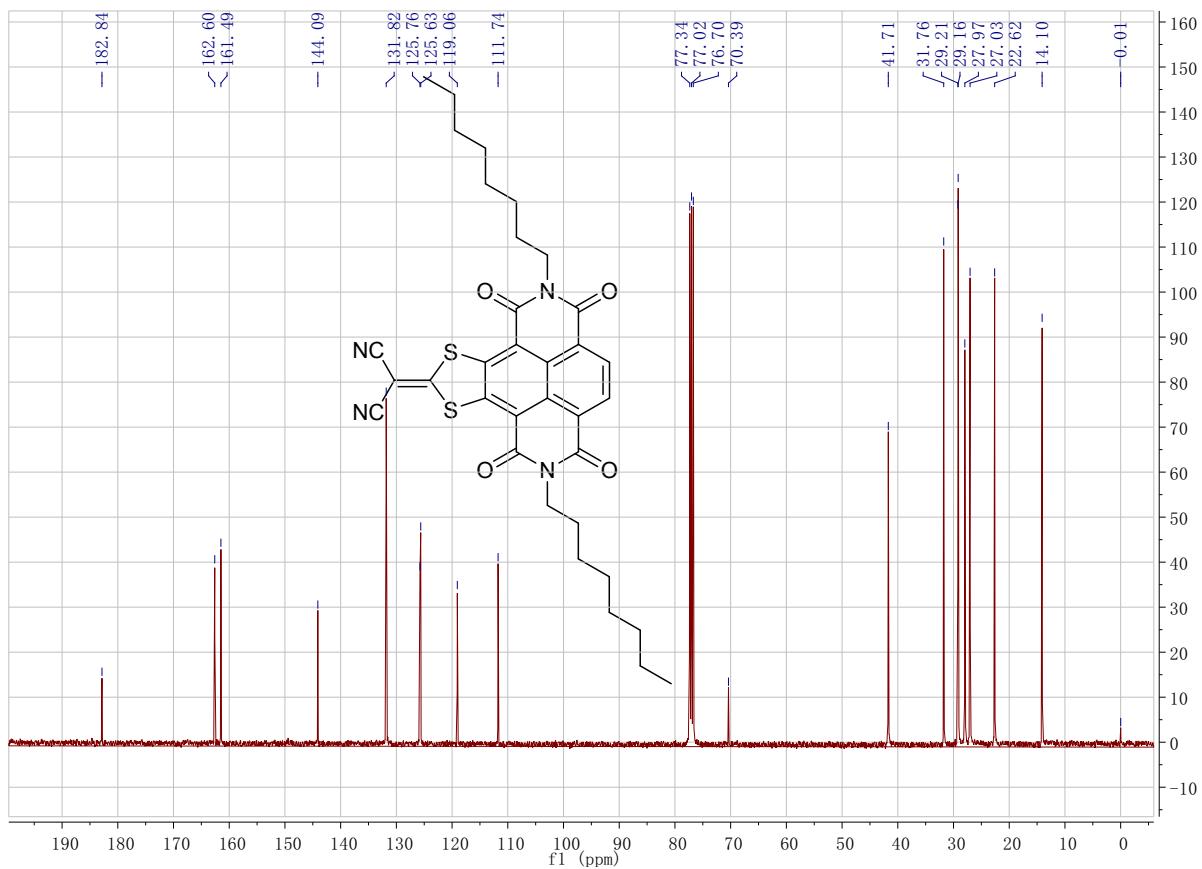
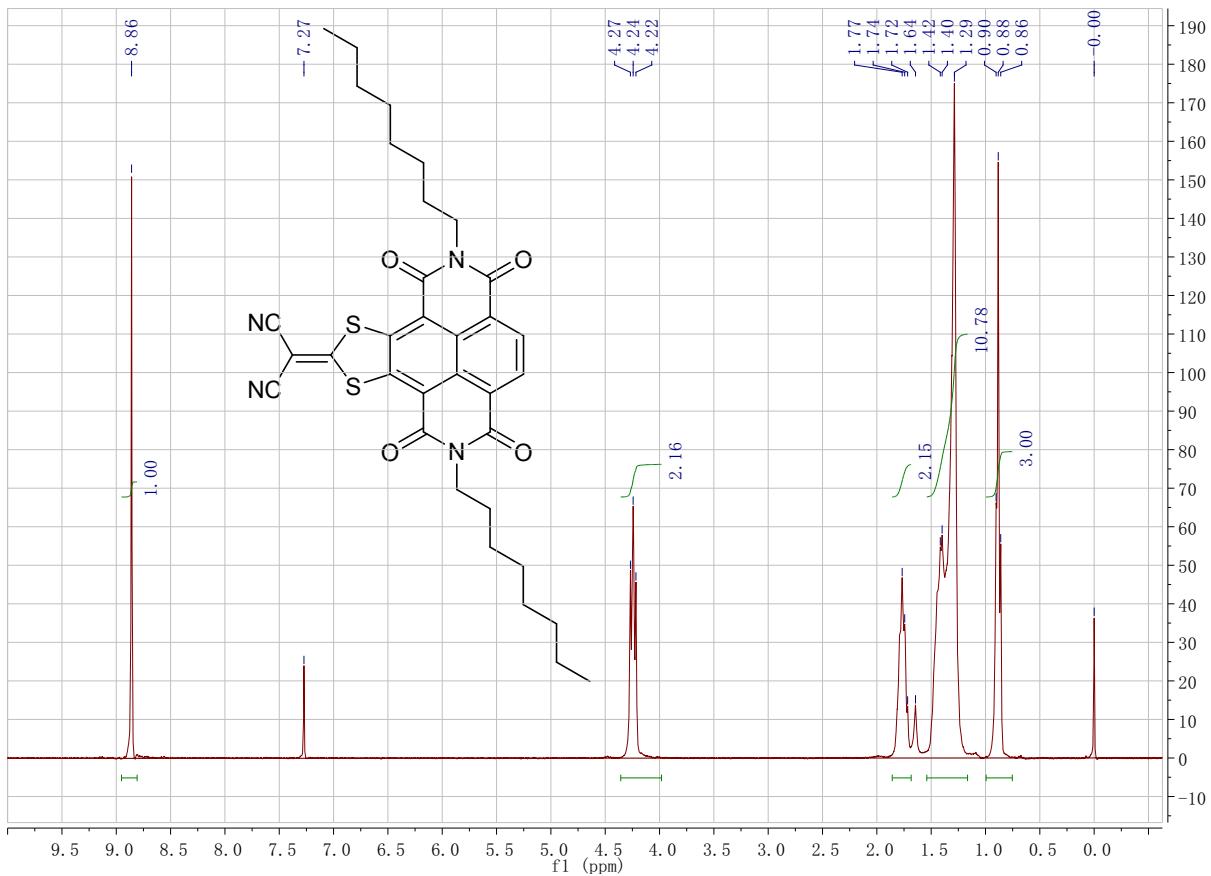
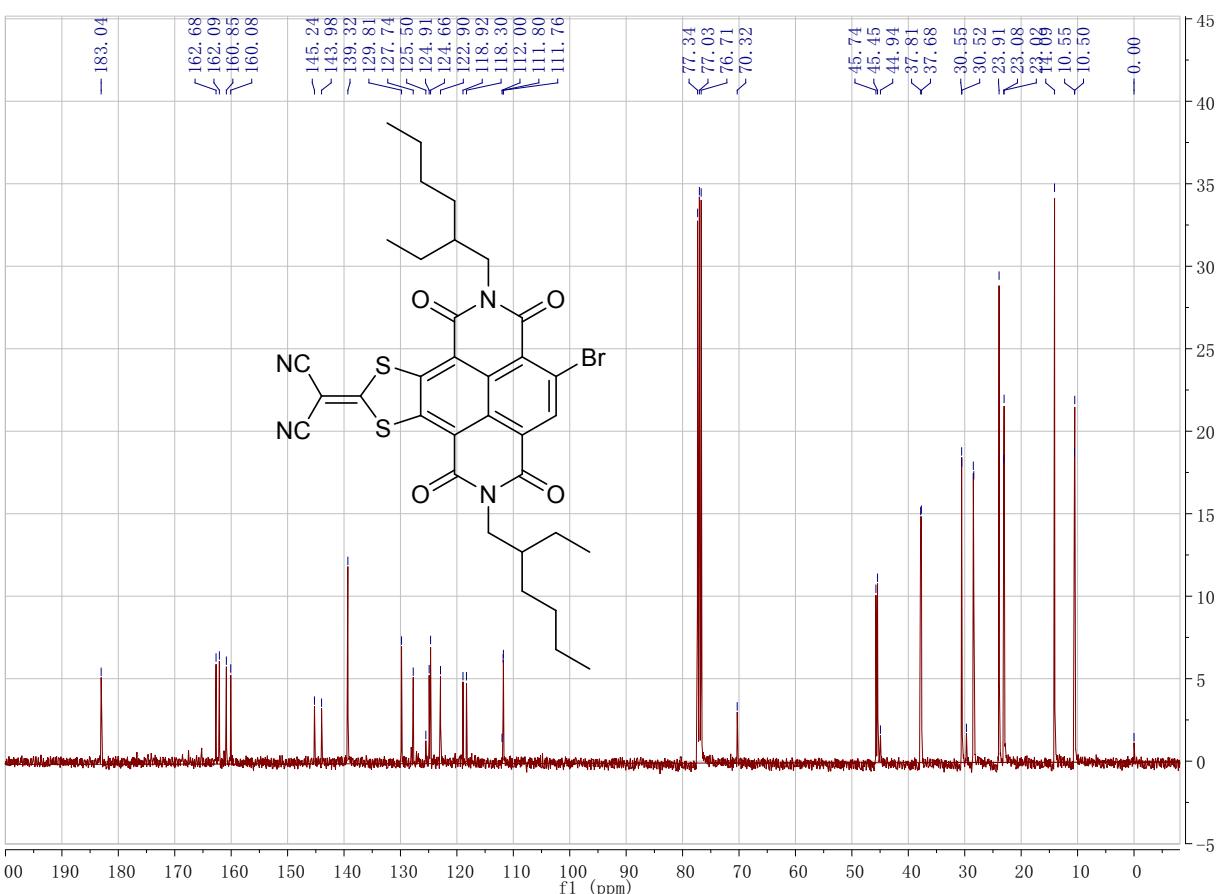
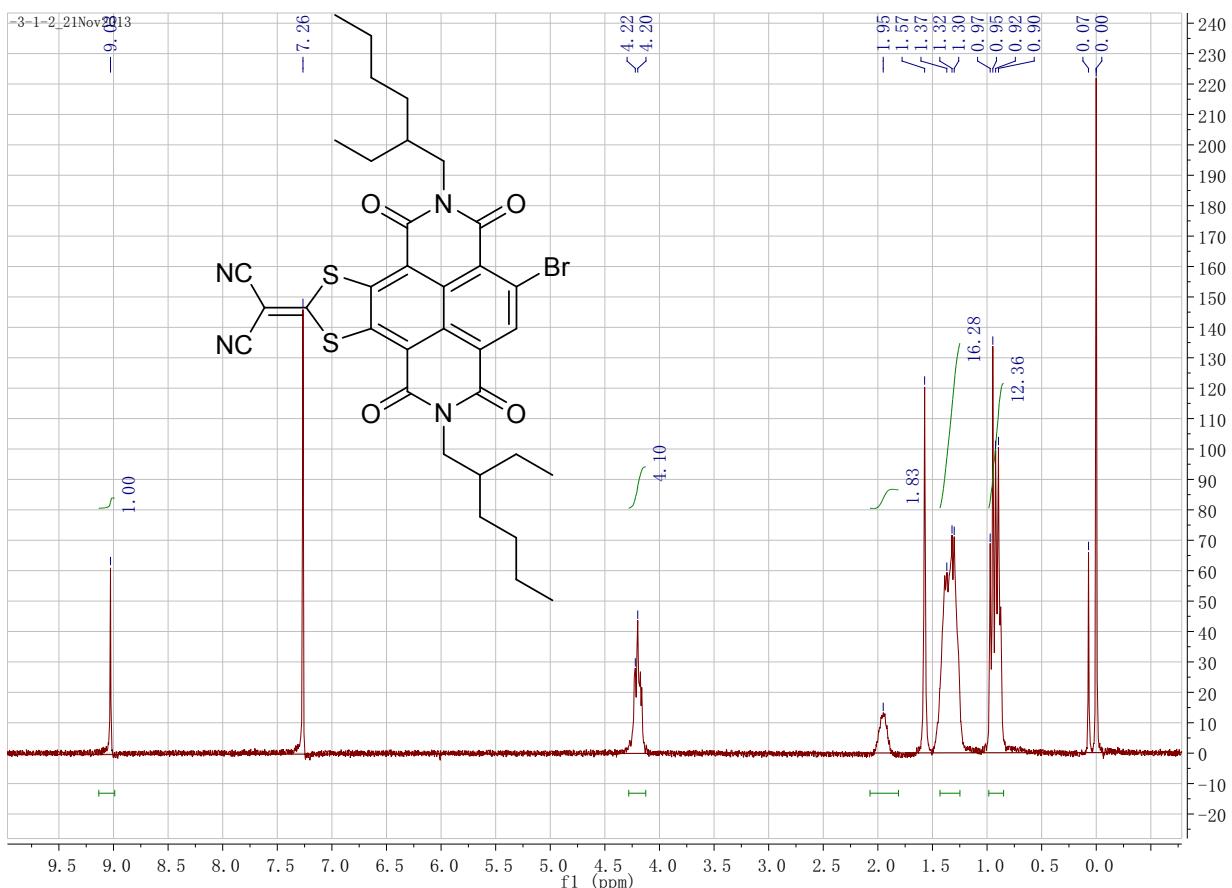


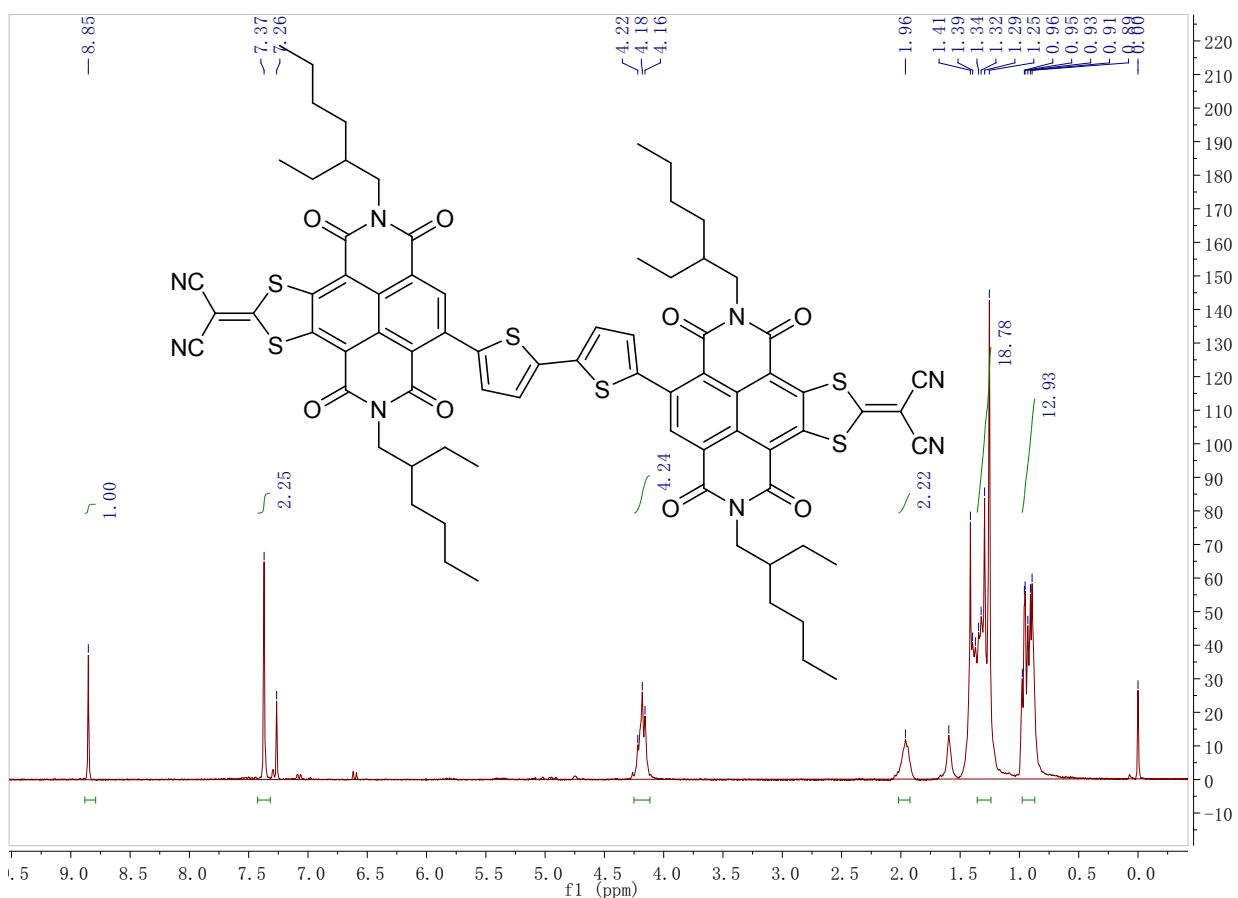
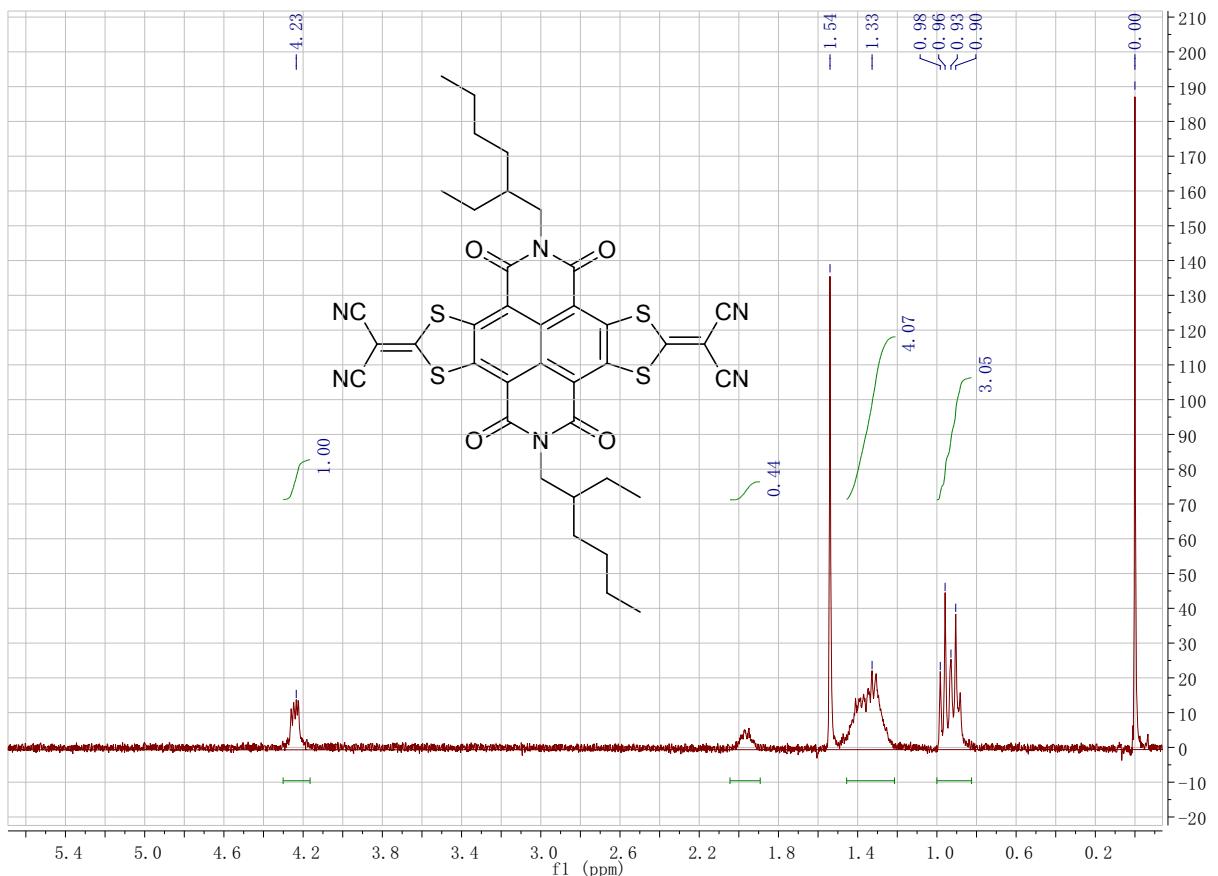
Figure S7. Fluorescence spectra of compound **1**, **2** and **3**.

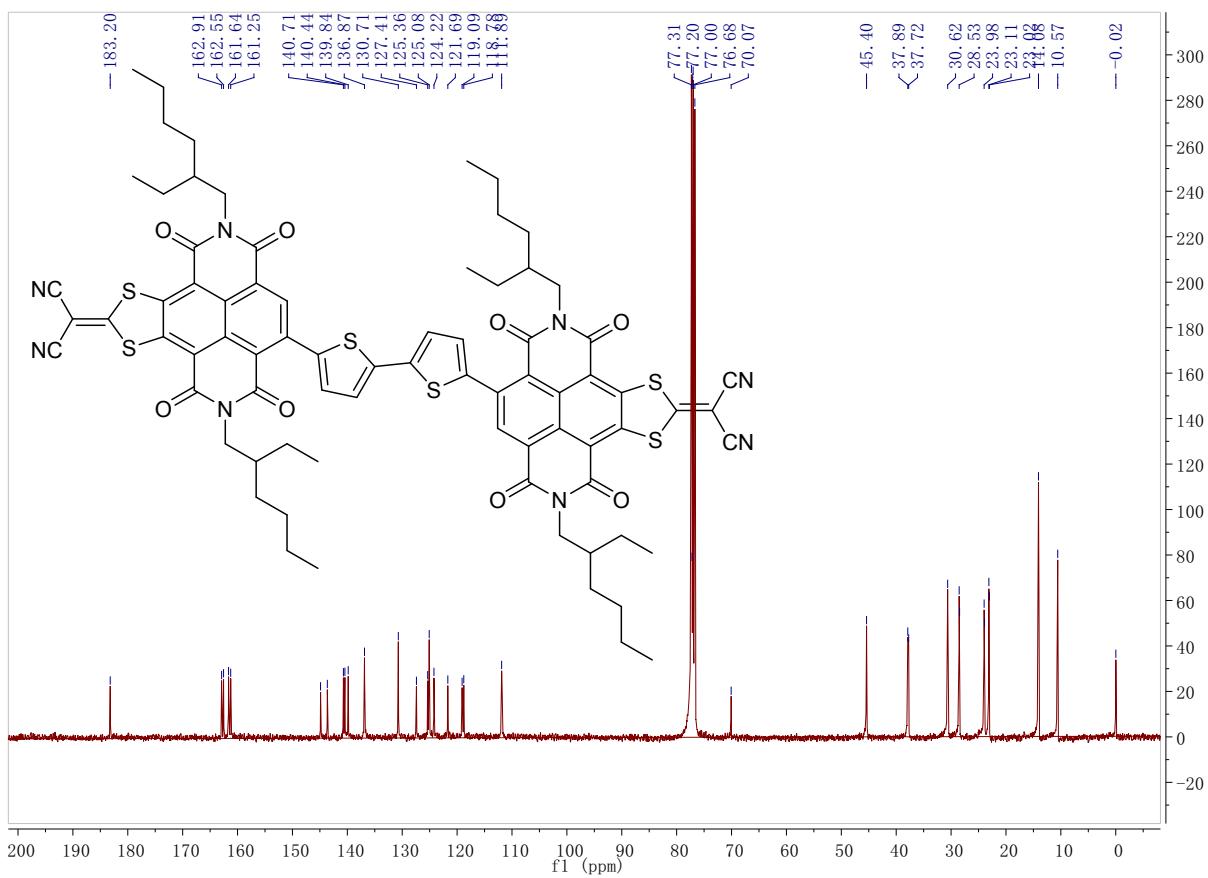






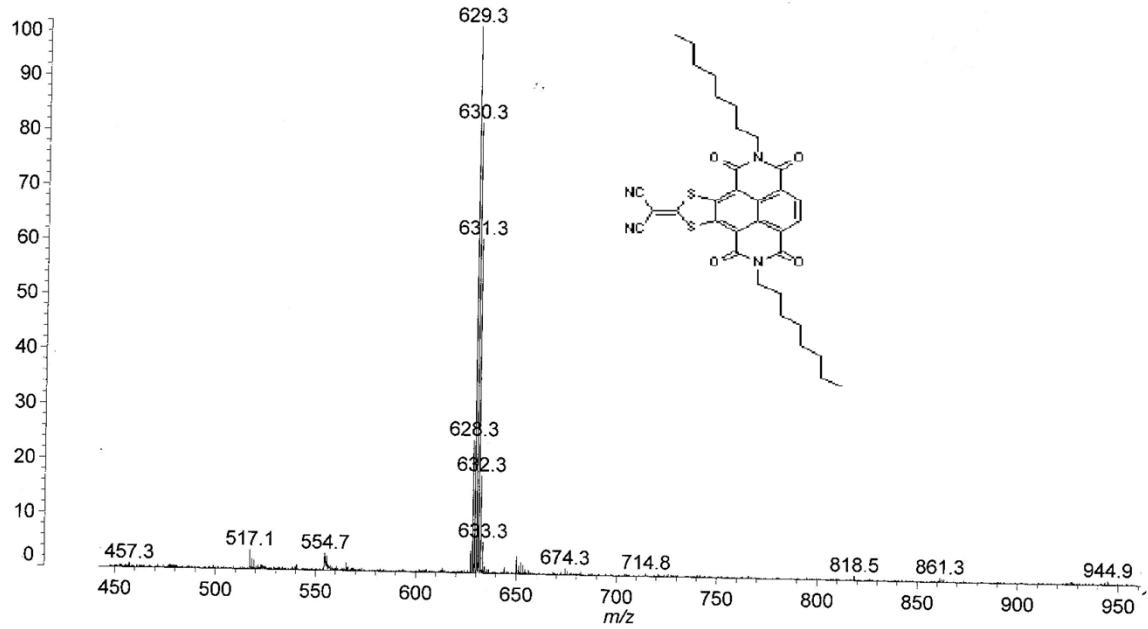






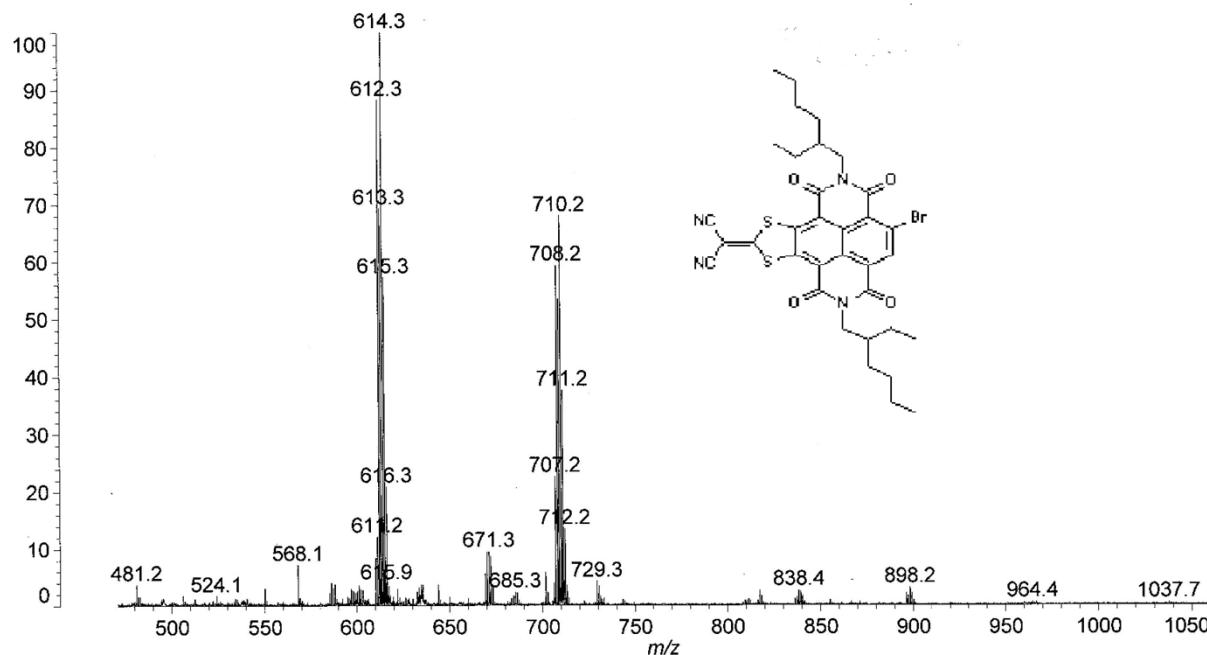
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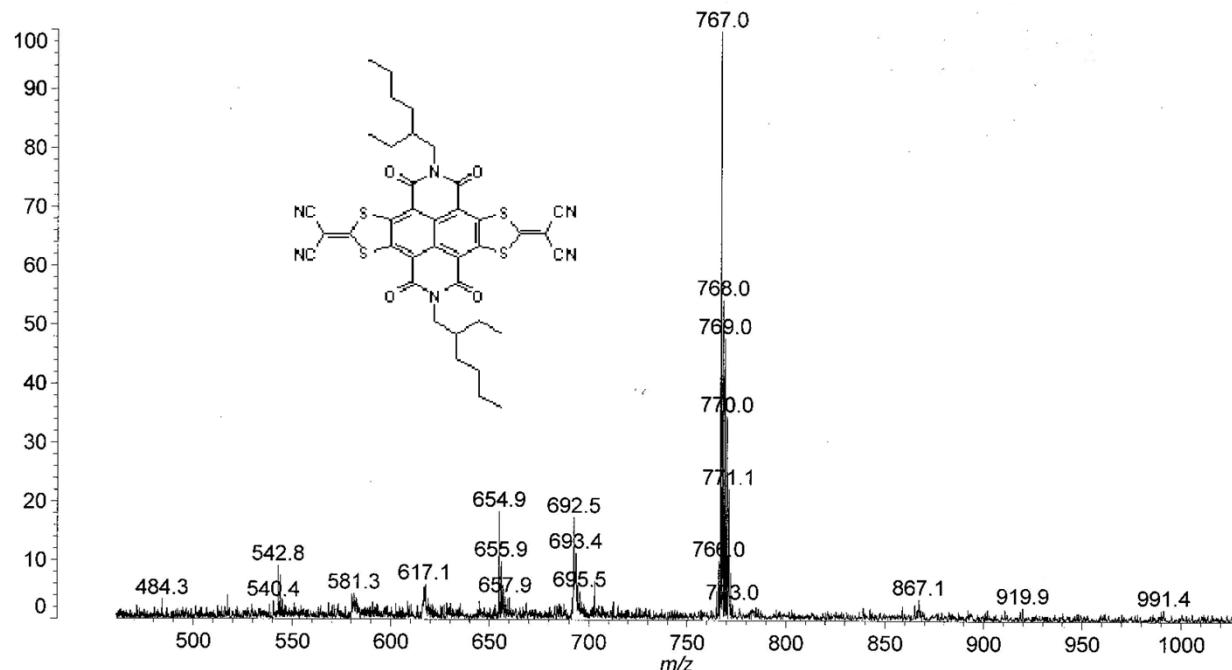
LB-3-1

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LB-3-25

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LB-3-44

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