Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information

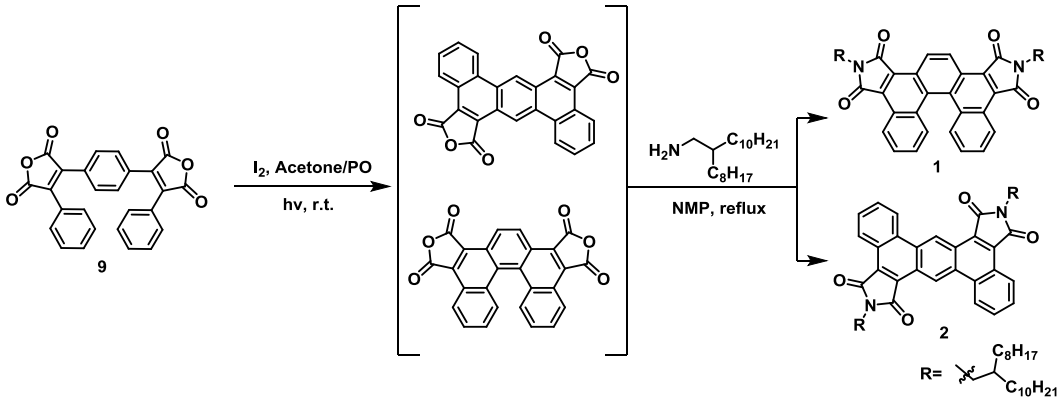
Syntheses of Polycyclic Aromatic Diimides via Intramolecular Cyclization of Maleic Acid Derivatives

Ranran Wang, Ke Shi, Kang Cai, Yikun Guo, Xiao Yang, Jie-Yu Wang, Jian Pei,* Dahui Zhao*

Beijing National Laboratory for Molecular Sciences, Center for the Soft Matter Science and Engineering and the Key Laboratory of Polymer Chemistry and Physics of the Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China

Table of contents

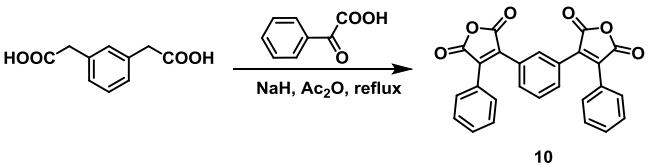
I. Synthetic Procedures and Characterization Data



1 & **2**: A photochemical reactor charged with compound **9** (500.0 mg, 1.2 mmol), I_2 (670.6 mg, 2.6 mmol), acetone (40 mL), and propylene oxide (PO, 40 mL) was flushed with N_2 for 10 min and sealed. The reddish brown solution was irradiated with a high-pressure mercury light at room temperature for 12 hours. The mixture was then concentrated and filtered to offer a dull yellow powder mixture. The mixture was dried in oven and mixed with 2-octyldodecan-1-amine (714.2 mg, 2.4 mmol) in *N*-methyl-2-pyrrolidone (NMP, 20 mL), and the suspension was refluxed overnight. The cooled mixture was poured into water and extracted with dichloromethane (DCM). The organic portion was dried over anhydrous Na_2SO_4 and solvents were then removed under reduced pressure. The crude product was purified with column chromatography of silica gel, eluted with DCM/PE (1⁄6-1⁄4 v/v) to afford the yellow products **2** (51.4 mg, 4.4%) and **1** (457.4 mg, 39% for two steps).

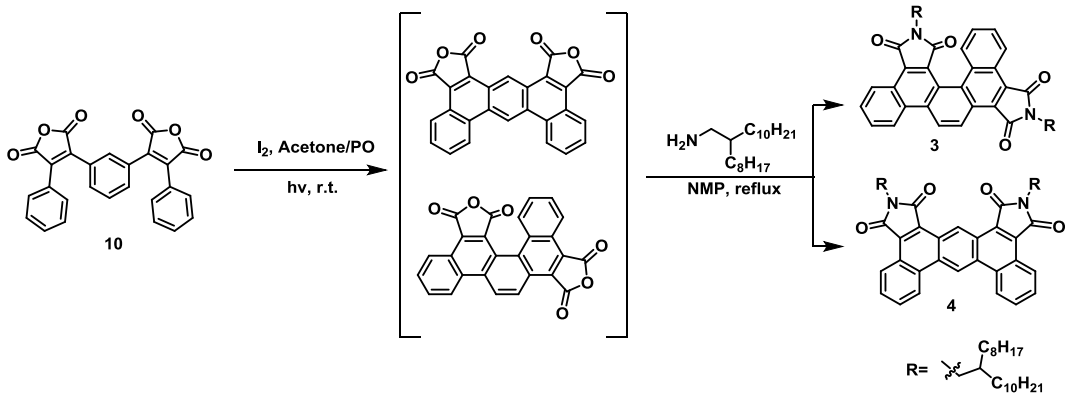
1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.12 (s, 2H), 9.09 (m, 2H), 8.08 (m, 2H), 7.65 (m, 2H), 7.27 (m, 2H), 3.72 (d, J = 7.2 Hz, 4H), 1.99 (br, 2H), 1.41-1.22 (m, 64H), 0.86-0.83 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ169.7, 169.5, 133.7, 130.3, 129.5, 128.7, 128.5, 127.4, 127.1, 126.2, 125.4, 125.1, 42.4, 37.3, 31.9, 31.6, 30.05, 30.02, 29.68, 29.65, 29.60, 29.3, 26.4, 22.7, 14.1. HR-ESI MS: Calcd. for $C_{66}H_{93}N_2O_4$ ($M + H^+$): 977.7130; Found: 977.7103. Elem. Anal.: Calcd. For $C_{66}H_{92}N_2O_4$: C, 81.10%; H, 9.49%; N, 2.87%; Found: C, 81.02%; H, 9.51%; N, 2.91%. m.p.: 109.6 ^{o}C

For data of **2** see below in the Heck reaction route.



10: A mixture of phenylglyoxylic acid (322.4 mg, 2.1 mmol), 2,2'-(1,3-phenylene)diacetic acid (194.2 mg,1 mmol) and NaH (60.0 mg, 2.5 mmol) was stirred in acetic anhydride (5 mL) at room temperature for 15 minutes and then heated at reflux for 3 h. The cooled mixture was poured

into water and the precipitate was collected through vacuum filtration and recrystallized from acetone to give compound **10** (350.0 mg, 82%) as a light yellow powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77-7.37 (m, 14H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 164.3, 139.4, 136.6, 131.9, 131.6, 130.7, 129.7, 129.6, 129.2, 128.3, 126.6. HR-ESI MS: Calcd. for $C_{26}H_{15}O_6$ ($M + H^+$): 423.0863; Found: 423.0859.

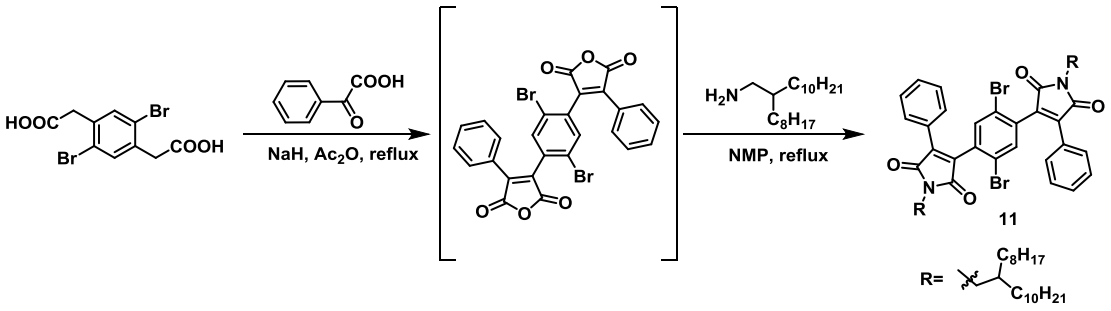


3 & **4**: A photochemical reactor charged with compound **10** (30 mg, 0.07 mmol), I_2 (40.6 mg, 0.16 mmol), acetone (10 mL), and PO (10 mL) was flushed with N_2 for 10 min and sealed. The reddish brown solution was irradiated with a high-pressure mercury light at room temperature for 6 hours. Then the mixture was concentrated and filtered to give a dull yellow powder mixture. The mixture was dried in oven and then mixed with 2-octyldodecan-1-amine (41.7 mg, 0.14 mmol) in NMP (5 mL), and the suspension was refluxed overnight. The cooled mixture was poured into water and extracted with DCM. The organic portion was dried over anhydrous Na_2SO_4 and solvents were then removed under reduced pressure. The crude product was purified with column chromatography of silica gel, eluted with DCM/PE (1/6-1/4, v/v) to afford the yellow products **4** (4.5 mg, 6.5%) and **3** (35.0 mg, 51% for two steps).

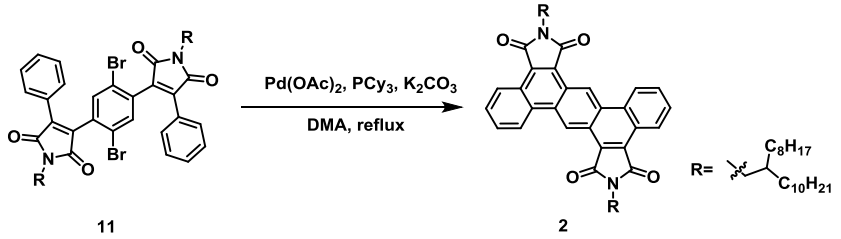
3: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 9.26 (s, 1H), 9.18 (d, J = 8.0 Hz, 1H), 8.80 (d, J = 9.2 Hz, 1H), 8.76 (m, 1H), 8.37 (d, J = 8.0 Hz, 1H), 7.91-7.87 (m, 2H), 7.76 (t, J = 7.6 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 3.73 (d, J = 6.8 Hz, 2H), 3.56-3.42 (m, 2H), 1.97 (br, 1H), 1.86 (br, 1H), 1.43-1.22 (m, 64H), 0.89-0.83 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 169.63, 169.60, 168.1, 135.3, 134.9, 132.9, 130.7, 130.3, 130.2, 129.8, 129.4, 128.7, 128.5, 127.9, 127.5, 126.22, 126.20, 126.1, 125.80, 125.76, 125.5, 125.3, 124.1, 123.4, 120.0, 116.4, 42.3, 37.34, 37.29 31.9, 31.6, 31.5, 30.1, 30.0, 29.63, 29.57, 29.3, 26.6, 26.4, 22.7, 14.1. HR-ESI MS: Calcd. for $C_{66}H_{93}N_2O_4$ ($M + H^+$): 977.7130; Found: 977.7154. Calcd. For $C_{66}H_{92}N_2O_4$: C, 81.10%; H, 9.49%; N, 2.87%; Found: C, 81.05%; H, 9.62%; N, 2.90%. m.p.: 100.2 ^{o}C

4: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.33 (s, 1H), 9.38 (s, 1H), 8.98 (d, J = 3.9 Hz, 2H), 8.61 (d, J = 3.9 Hz, 2H), 7.75-7.72 (m, 4H), 3.62 (d, J = 4.5 Hz, 4H), 1.97 (br, 2H), 1.48-1.22 (m, 64H), 0.86-0.81 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6, 169.2, 132.4, 131.4, 129.4, 128.9, 128.1, 127.2, 126.8, 125.5, 124.1, 123.9, 123.0, 116.7, 42.4, 37.2, 31.9, 31.6, 30.1, 29.9, 29.7, 29.3, 26.5, 22.7, 14.1.

HR-ESI MS: Calcd. for $C_{66}H_{93}N_2O_4$ ($M + H^+$): 977.7130; Found: 977.7152. Calcd. For $C_{66}H_{92}N_2O_4$: C, 81.10%; H, 9.49%; N, 2.87%; Found: C, 80.99%; H, 9.52%; N, 2.83%. m.p.: 86.6 °C



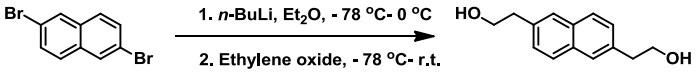
11: A mixture of phenylglyoxylic acid (230.7 mg, 1.5 mmol), 2,2'-(2,5-dibromo-1,4-phenylene)-diacetic acid (176 mg, 0.5 mmol) and NaH (36 mg, 1.5 mmol) was stirred in acetic anhydride (10 mL) at room temperature for 15 minutes and then heated at refluxed for 3 h. The cooled mixture was poured into water and the precipitate was collected through vacuum filtration and dried in oven. The powder was mixed with 2-octyldodecan-1-amine (297.6 mg, 1.0 mmol) in NMP (10 mL) and the mixture was refluxed overnight. The cooled mixture was poured into water and extracted with DCM. The organic portion was dried over anhydrous Na_2SO_4 and solvents were then removed under reduced pressure. The crude product was purified with column chromatography of silica gel, eluted with DCM/PE (1/3, v/v) to afford **11** (398.3 mg, 70% for two steps). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51-7.35 (m, 12H), 3.56 (d, J = 7.2 Hz, 4H), 1.86 (br, 2H), 1.25 (br, 64H), 0.89-0.85 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ170.2, 170.1, 169.4, 169.0, 139.01, 138.96, 135.1, 134.9, 134.8, 134.3, 133.9, 133.7, 130.7, 130.6, 129.7, 129.6, 128.82, 128.78, 128.5, 128.4, 128.2, 122.7, 122.5, 42.9, 36.9, 36.9, 31.9, 31.5, 30.0, 29.9, 29.96, 29.91, 29.63, 29.61, 29.58, 29.53, 29.31, 29.28, 26.4, 26.3, 26.2, 22.6, 14.1. HR-ESI MS: Calcd. For $C_{66}H_{95}Br_2N_2O_4$ ($M + H^+$): 1139.5638; Found: 1139.5663.



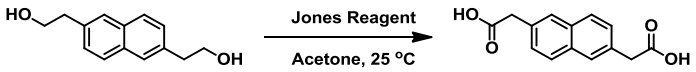
11 2

2: Compound **11** (391.7 mg, 0.34 mmol), palladium diacetate (31.4 mg, 0.14 mmol), tricyclohexylphosphine (67.9 mg, 0.24 mmol) and potassium carbonate (469.2 mg, 3.4 mmol) were stirred at reflux in dry *N*,*N*-dimethylacetamide (DMA, 5 mL) under nitrogen atmosphere overnight. After cooling to room temperature, the mixture was diluted with DCM and washed with water for several times. The organic solution was dried over anhydrous Na_2SO_4 and solvents were then removed under reduced pressure. The crude product was purified with column chromatography of silica gel, eluted with DCM/PE (1/4, v/v) to afford yellow products (210.3 mg, 63%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.10 (s, 2H), 9.04 (d, J = 7.5 Hz, 2H), 8.76 （d, J = 7.5 Hz, 2H),

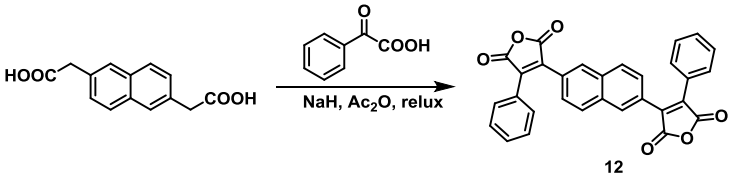
7.85-7.76 (m, 4H), 3.60(d, *J* = 7.5 Hz, 4H), 1.95 (br, 2H), 1.40-1.20 (m, 64H), 0.86-0.83 (m, 12H).[13]C NMR (75 MHz, $CDCl_3$) δ 169.0, 168.9, 132.0, 130.1, 129.5, 128.5, 127.9, 125.9, 124.5, 123.6, 123.2, 119.4, 41.9, 37.4, 31.92, 31.89, 31.5, 30.1, 29.72, 29.67, 29.4, 26.4, 22.7, 22.6, 14.1. HR-ESI MS: Calcd. for $C_{66}H_{93}N_2O_4$ ($M + H^+$): 977.7130; Found: 977.7152. Elem. Anal.: Calcd. For $C_{66}H_{92}N_2O_4$: C, 81.10%; H, 9.49%; N, 2.87%; Found: C, 80.97%; H, 9.68%; N, 2.85%. m.p.: 137.0 ^oC



2,2'-(naphthalene-2,6-diyl)diethanol: Under nitrogen atmosphere, a suspension of 2,6-diibromonaphthalene (813.0 mg, 2.9 mmol) in dry ethyl ether (20 mL) was cooled to -78 ^oC, and a solution of *n*-butyllithium (4.2 mL, 2 M in hexane, 8.4 mmol) was added dropwise. The suspension was stirred for 2 h. Ethylene oxide (3 mL, 58 mmol) was added, and the light yellow mixture was turned to dark brown solution. The solution was stirred overnight as it was gradually warmed to room temperature. The off-white mixture was poured into 10% aq. HCl (20 mL) and filtered. The filtrate was collected and purified with flash column chromatography of silica gel, eluted with dichloromethane/ethyl acetate (DCM/EA = 4/1, v/v) to afford a white solid (301.0 mg, 48%). [1]H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.66 (s, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 3.95 (q, *J* = 6.0 Hz, 4H), 3.03 (t, *J* = 6.0 Hz, 4H), 1.40 (t, *J* = 6.0 Hz, 2H). [13]C NMR (100 MHz, $CDCl_3$) δ 135.6, 132.4, 127.9, 127.7, 127.3, 63.6, 39.3. HR-ESI MS: Calcd. for $C_{14}H_{16}NaO_2$ ($M + Na^+$): 239.1042; Found: 239.1040.



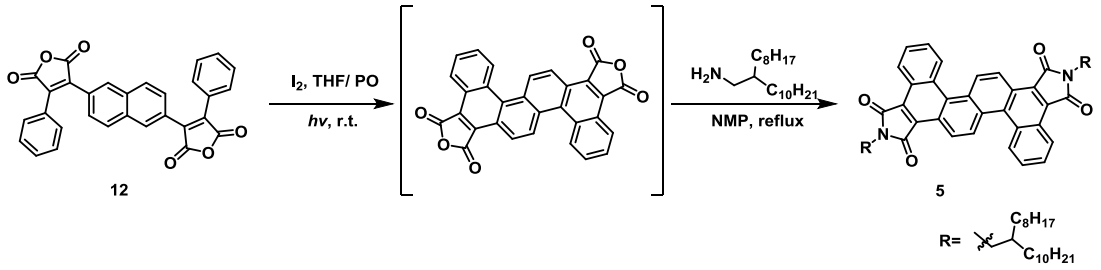
2,2'-(naphthalene-2,6-diyl)diacetic acid: A solution of 2,2'-(naphthalene-2,6-diyl)diethanol (127.8 mg, 0.6 mmol) in acetone (15 mL) was treated with Jones reagent (1 mL, 1.5 mmol) for 15 min at 25 ^oC. Acetone was evaporated and the residue was dissolved in aqueous sodium hydroxide (2 mL, 2 M). The solution was filtered and acidified using concentrated hydrochloric acid. The precipitate was collected and dried to give an off-white solid (120.0 mg, 73%). [1]H NMR (300 MHz, acetone-d_6) δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.80 (s, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 3.80 (s, 4H). [13]C NMR (100 MHz, acetone-d_6) δ 172.7, 133.4, 133.4, 128.9, 128.5, 128.4, 41.4. HR-ESI MS: Calcd. for $C_{14}H_{12}NaO_4$ ($M + Na^+$): 267.0627; Found: 267.0623.



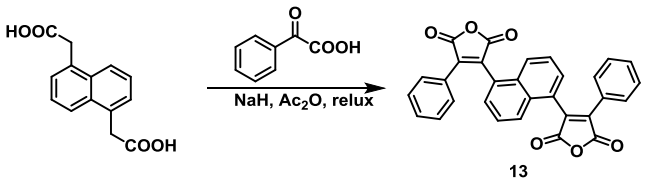
12

12: A mixture of phenylglyoxylic acid (273.2 mg, 1.8 mmol), 2,2'-(naphthalene-2,6-diyl)diacetic acid (222.1 mg, 0.9 mmol) and NaH (48.0 mg, 2.0 mmol) was stirred in acetic anhydride (5 mL) at

room temperature for 15 minutes and then heated to refluxed for 3 h. The cooled mixture was poured into water and the precipitate was collected through vacuum filtration and recrystallized from acetone to give compound **12** (340.1 mg, 79%) as a bright yellow powder. ^{1}H NMR (300 MHz, acetone-d_6) δ 8.30 (s, 2H), 8.01 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 6.6 Hz, 4H), 7.54-7.45 (m, 8H). HR-ESI MS: Calcd. for $C_{30}H_{17}O_6$ ($M + H^+$): 473.1020; Found: 473.1029.

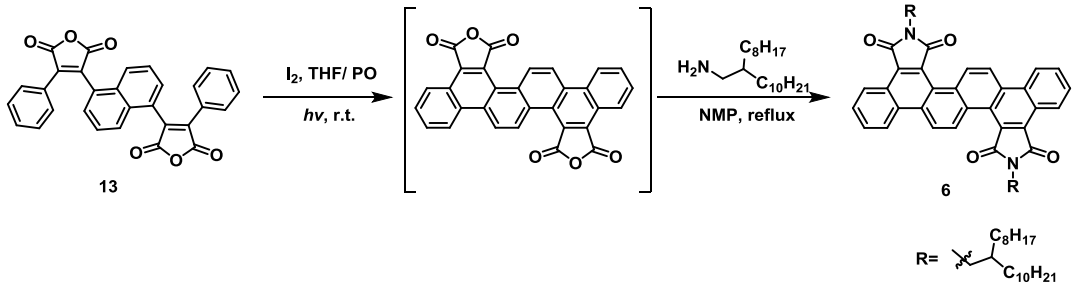


5: A photochemical reactor charged with compound **12** (43.3 mg, 0.09 mmol), I_2 (50.8 mg, 0.2 mmol), tetrahydrofuran (THF, 10 mL), and PO (1 mL) was flushed with N_2 for 10 min and sealed. The red-brown solution was irradiated with high pressure mercury light at room temperature for 6 hours. Then the mixture was concentrated and filtered to give an orange powder. The powder was dried in oven and mixed with 2-octyldodecan-1-amine (80.3 mg, 0.27 mmol) in NMP (10 mL), and the mixture was refluxed overnight. The cooled mixture was poured into water and extracted with DCM. The organic portion was dried over anhydrous Na_2SO_4 and solvents were then removed under reduced pressure. The crude product was purified with column chromatography of silica gel, eluted with DCM/PE (1/4, v/v) to afford the product as a yellow tacky material (40.0 mg, 43% for two steps). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.13 (d, J = 8.1 Hz, 2H), 8.83 (d, J = 8.7 Hz, 2H), 8.66 (d, J = 8.7 Hz, 2H), 8.62 (d, J = 8.1 Hz, 2H), 7.77-7.66 (m, 4H), 3.56 (d, J = 7.2 Hz, 4H), 1.94 (br, 2H), 1,38-1.22 (m, 64H), 0.87-0.82 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ169.7, 169.4, 132.3, 131.2, 130.9, 129.0, 128.8, 128.2, 127.4, 126.6, 125.8, 124.5, 122.2, 42.1, 37.2, 31.9, 31.5, 30.0, 29.9, 29.63, 29.58, 29.5, 29.3, 26.4, 22.7, 14.1. HR-ESI MS: Calcd. for $C_{70}H_{95}N_2O_4$ ($M + H^+$): 1027.7286; Found: 1027.7284. Elem. Anal.: Calcd. For $C_{70}H_{94}N_2O_4$: C, 81.82%; H, 9.22%; N, 2.73%; Found: C, 81.75%; H, 9.35%; N, 2.70%.

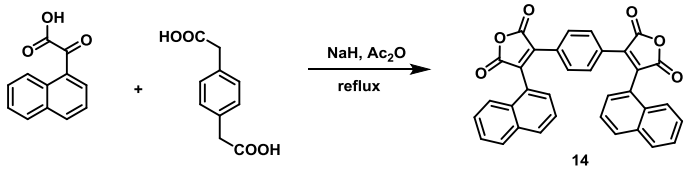


13: A mixture of phenylglyoxylic acid (94.6 mg, 0.6 mmol), 2,2'-(naphthalene-1,5-diyl)diacetic acid (73.3 mg, 0.3 mmol) and NaH (16.8 mg, 0.7 mmol) was stirred in acetic anhydride (4 mL) at room temperature for 15 minutes and then heated at refluxed for 3 h. The cooled mixture was poured into water and the precipitate was collected through vacuum filtration and recrystallized from acetone to give compound **13** (113.0 mg, 80%) as a bright yellow powder. ^{1}H NMR (300

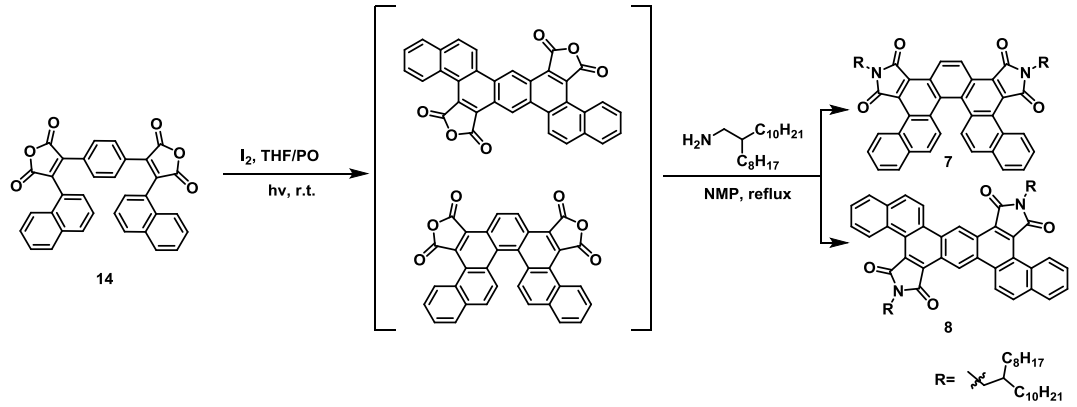
MHz, acetone-d_6) δ: 8.12 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 7.2 Hz, 2H), 7.56-7.36 (m, 12H). HR-ESI MS: Calcd. for $C_{30}H_{17}O_6$ ($M + H^+$): 473.1020; Found: 473.1017.



6: A photochemical reactor charged with compound **13** (50.0 mg, 0.1 mmol), I_2 (55.9 mg, 0.2 mmol), tetrahydrofuran (THF, 10 mL), and PO (1 mL) was flushed with N_2 for 10 min and sealed. The red-brown solution was irradiated with high-pressure mercury light at room temperature for 12 hours. Then the mixture was concentrated and filtered to give an orange powder. The powder was dried in oven and then mixed with 2-octyldodecan-1-amine (59.5 mg, 0.2 mmol) in N-methyl-2-pyrrolidone (NMP, 10 mL), and the mixture was refluxed overnight. The cooled mixture was poured into water and extracted with DCM. The organic solution was dried over anhydrous Na_2SO_4 and solvents were then removed under reduced pressure. The crude product was purified with column chromatography of silica gel, eluted with DCM/PE (1/4, v/v) to afford the yellow product (35.9 mg, 35% for two steps). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.34 (d, J = 9.0 Hz, 2H), 9.30 (m, 2H), 8.75 (m, 2H), 8.71 (d, J = 9.0 Hz, 2H), 7.85-7.80 (m, 4H), 3.68 (d, J = 7.5 Hz, 4H), 1.99 (br, 2H), 1.46-1.13 (m, 64H), 0.88-0.82 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ169.69, 169.67, 133.6, 133.0, 131.8, 129.8, 129.7, 128.9, 128.8, 128.0, 126.3, 126.0, 123.6, 119.7, 42.6, 37.2, 31.9, 31.7, 30.1, 29.70, 29.65, 29.6, 29.4, 26.4, 22.7, 14.1. HR-ESI MS: Calcd. for $C_{70}H_{95}N_2O_4$ ($M + H^+$): 1027.7286; Found: 1027.7274. Elem. Anal.: Calcd. For $C_{70}H_{94}N_2O_4$: C, 81.82%; H, 9.22%; N, 2.73%; Found: C, 81.65%; H, 9.21%; N, 2.55%. m.p.: 106.5 ^{o}C



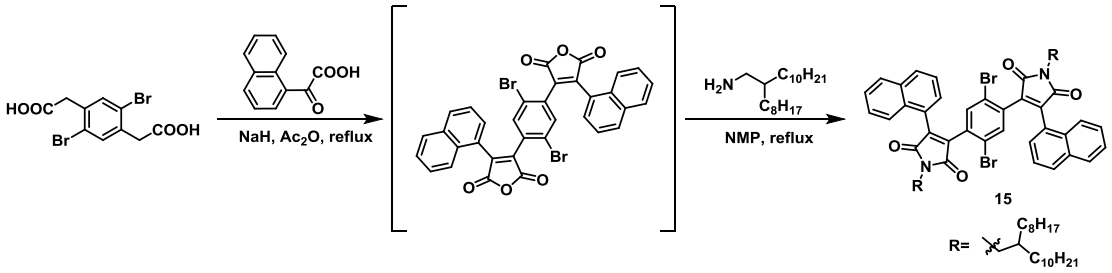
14: A mixture of 2-(naphthalen-1-yl)-2-oxoacetic acid (400.0 mg, 2.0 mmol), 2,2'-(1,4-phenylene)diacetic acid (194.2 mg, 1.0 mmol) and NaH (48.0 mg, 2.0 mmol) was stirred in acetic anhydride (5 mL) at room temperature for 15 minutes and then heated at reflux for 3 h. The cooled mixture was poured into water and the precipitate was collected through vacuum filtration and recrystallized from acetone to give compound **14** (406.5 mg, 78%) as an orange powder. ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.05 (m, 2H), 7.97 (d, J = 8.0 Hz, 2H), 7.77 (br, 2H), 7.59-7.51 (m, 6H), 7.37-7.33 (m, 6H). ^{13}C NMR (100 MHz, acetone-d_6) δ 165.9, 165.6, 134.6, 131.7, 131.1, 130.4, 129.5, 129.2, 127.8, 127.5, 126.5, 126.3, 125.9. HR-ESI MS: Calcd. for $C_{34}H_{19}O_6$ ($M + H^+$): 523.1176; Found: 523.1184.



7 & **8**: A photochemical reactor charged with compound **14** (150.0 mg, 0.28 mmol), I_2 (160.5 mg, 0.63 mmol), tetrahydrofuran (THF, 100 mL), and PO (5 mL) was flushed with N_2 for 10 min. and sealed. The red-brown solution was irradiated with high-pressure mercury light at room temperature for 16 hours. Then the mixture was concentrated and filtered to give an orange powder. The powder dried in oven and then mixed with 2-octyldodecan-1-amine (166.6 mg, 0.56 mmol) in NMP (20 mL), and the mixture was refluxed overnight. The cooled mixture was poured into water and extracted with DCM. The organic portion was dried over anhydrous Na_2SO_4 and condensed under reduced pressure. The crude product was purified with column chromatography of silica gel, eluted with DCM/PE (1⁄4, v/v) to afford **7** (120.1 mg, 40%) and **8** (9.0 mg, 3.0%).

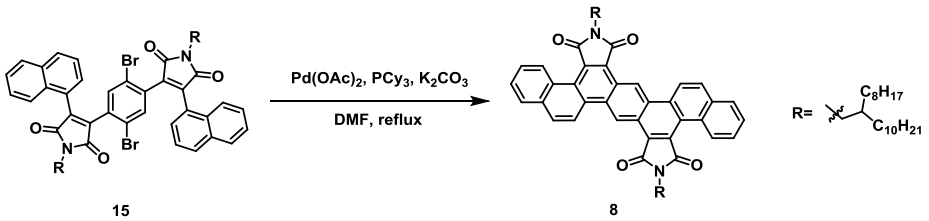
7: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (d, J = 4.0 Hz, 2H), 9.47 (s, 2H), 7.87 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 8.0 Hz, 2H), 7.76 (t, J = 12.0 Hz, 2H), 7.54-7.46 (m, 4H), 3.75 (d, J = 8.0 Hz, 4H), 2.04 (br, 2H), 1.41-1.22 (m, 64H), 0.86-0.82 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ169.3, 169.1, 135.4, 132.7, 130.7, 130.2, 129.5, 129.0, 128.5, 127.7, 127.62, 127.59, 126.9, 126.8, 125.2, 42.9, 37.2, 31.9, 31.7, 30.1, 30.0, 29.7, 29.66, 29.60, 29.3, 26.5, 26.4, 22.7, 14.1. HR-ESI MS: Calcd. for $C_{74}H_{97}N_2O_4$ ($M + H^+$): 1077.7443; Found: 1077.7445. Elem. Anal.: Calcd. For $C_{74}H_{96}N_2O_4$: C, 82.48%; H, 8.98%; N, 2.60%; Found: 82.24%; H, 8.86 %; N, 2.54%. m.p.: 98 ^{o}C

For data of **8** see below in the Heck reaction route**.**



15: A mixture of 2-(naphthalen-1-yl)-2-oxoacetic acid (300.0 mg, 1.5 mmol), 2,2'-(2,5-dibromo-1,4-phenylene)diacetic acid (262.4 mg, 0.75 mmol) and NaH (36.0 mg, 1.5 mmol) was stirred in acetic anhydride (5 mL) at room temperature for 15 minutes and then heated at refluxed for 3 h. The cooled mixture was poured into water and the precipitate was

collected through vacuum filtration and dried with oven to give a yellow powder. The powder was mixed with 2-octyldodecan-1-amine (446.3 mg, 1.5 mmol) in NMP (20 mL) and the mixture was refluxed overnight. The cooled mixture was poured into water and extracted with DCM. The organic portion was dried over anhydrous Na_2SO_4 and condensed under reduced pressure. The crude product was purified with column chromatography of silica gel, eluted with DCM/PE (1⁄3, v/v) to afford compound **15** (500.0 mg, 54% for two steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 8.0 Hz, 2H), 7.43-7.24 (m, 12H), 3.58 (d, J = 8.0 Hz, 4H), 1.89 (br, 2H), 1.89-1.21 (m, 64H), 0.88-0.84 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 168.9, 141.5, 137.9, 135.0, 133.6, 133.3, 130.9, 130.6, 128.6, 126.3, 125.8, 125.2, 125.1, 122.1, 43.1, 37.0, 31.9, 30.0, 29.70, 29.66, 29.65, 29.59, 29.4, 26.4, 22.7, 14.1. HR-ESI MS: Calcd. For $C_{74}H_{99}Br_2N_2O_4$ (M + H^+): 1239.5951; Found: 1239.5997.



15 8

8: Compound **15** (243.9 mg, 0.2 mmol), palladium diacetate (18.0 mg, 0.08 mmol), tricyclohexylphosphine (39.3 mg, 0.14 mmol) and potassium carbonate (276.4 mg, 2.0 mmol) were stirred at reflux in dry *N*,*N*-dimethylformamide (DMF, 2 mL) under nitrogen atmosphere overnight. After cooling to room temperature, the mixture was extracted with DCM and washed with water for several times. The organic solution was dried over anhydrous Na_2SO_4 and solvents were then removed under reduced pressure. The crude product was purified with column chromatography of silica gel, eluted with DCM/PE (1⁄4, v/v) to afford red product (188.1 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.51 (s, 2H), 9.45 (d, J = 8.0 Hz, 2H), 8.86 (d, J = 8.0 Hz, 2H), 8.16 (d, J = 12.0 Hz, 2H), 8.00 (d, J = 8.0 Hz, 2H),7.77-7.69 (m, 4H), 3.56 (d, J = 8.0 Hz, 4H), 1.97 (br, 2H), 1.39-1.18 (m, 64H), 0.84-0.79 (m, 12H).^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 168.8, 133.14, 133.09, 131.3, 130.8, 129.9, 129.7, 128.8, 127.8, 127.7, 127.5, 126.4, 124.2, 123.8, 121.1, 120.7, 42.5, 37.1, 31.93, 31.91, 31.6, 30.2, 29.74,29.72, 29.68, 29.0, 29.37, 26.4, 22.7, 14.1. HR-ESI MS: Calcd. for $C_{74}H_{97}N_2O_4$ (M + H^+):1077.7443; Found: 1077.7466. Elem. Anal.: Calcd. For $C_{74}H_{96}N_2O_4$: C, 82.48%; H, 8.98%; N, 2.60%; Found: C, 82.41%; H, 8.99%; N, 2.52%. m.p.: 195.6 ^{o}C.

II. DFT Calculations

For DFT calculation, all long alkyl substituents were replaced with methyl groups to simplify the calculations. Molecular orbitals and energies were obtained at optimized geometries. Quantum-chemical calculations were performed with the Gaussian03 package[1] and the orbital images were prepared using Gaussview.[2] The DFT calculations were performed at the B3LYP level of theory with a 6-31G* basis set.[3,4]

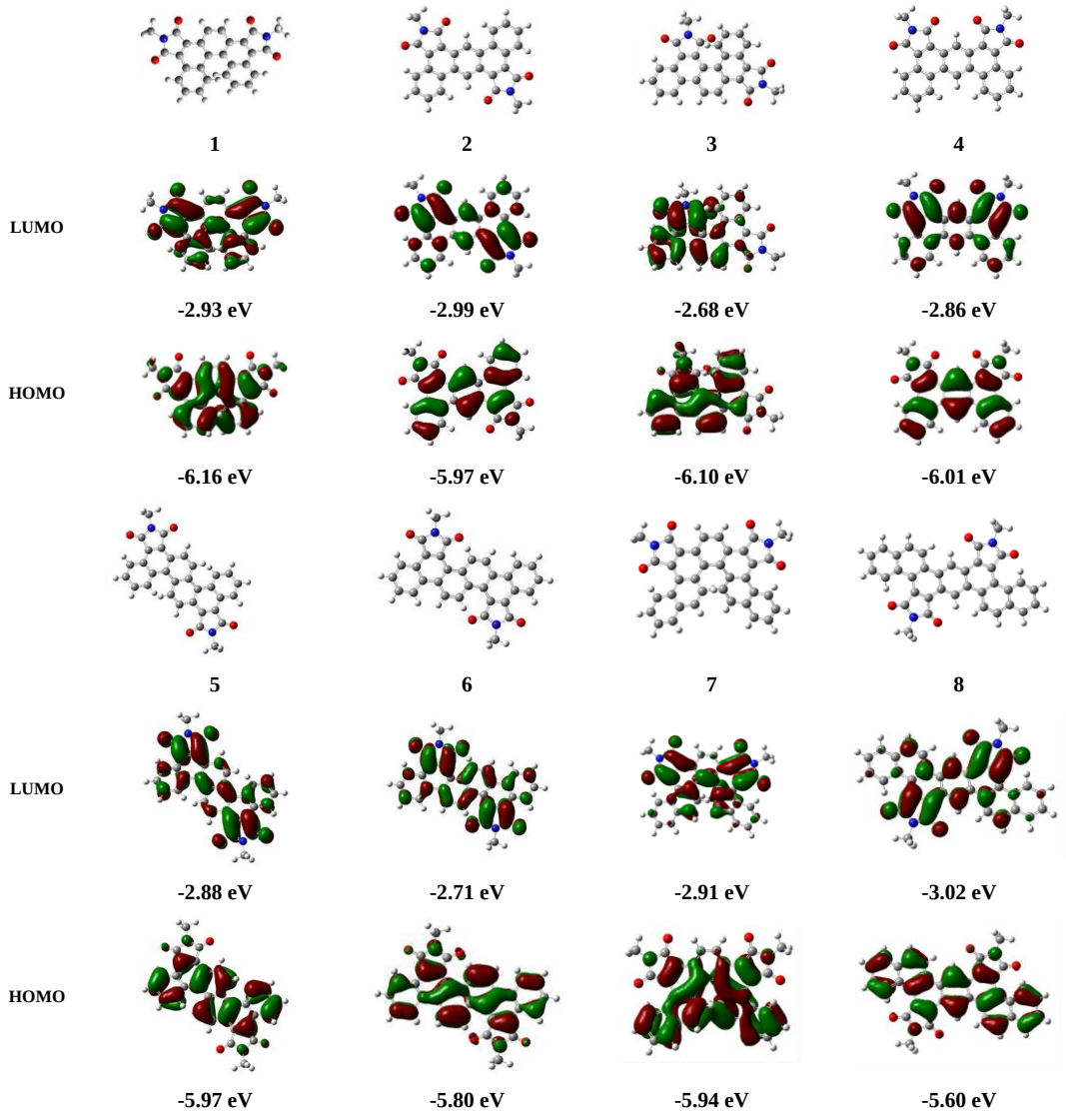


Fig. S1 DFT calculated frontier orbitals of **1**-**8**.

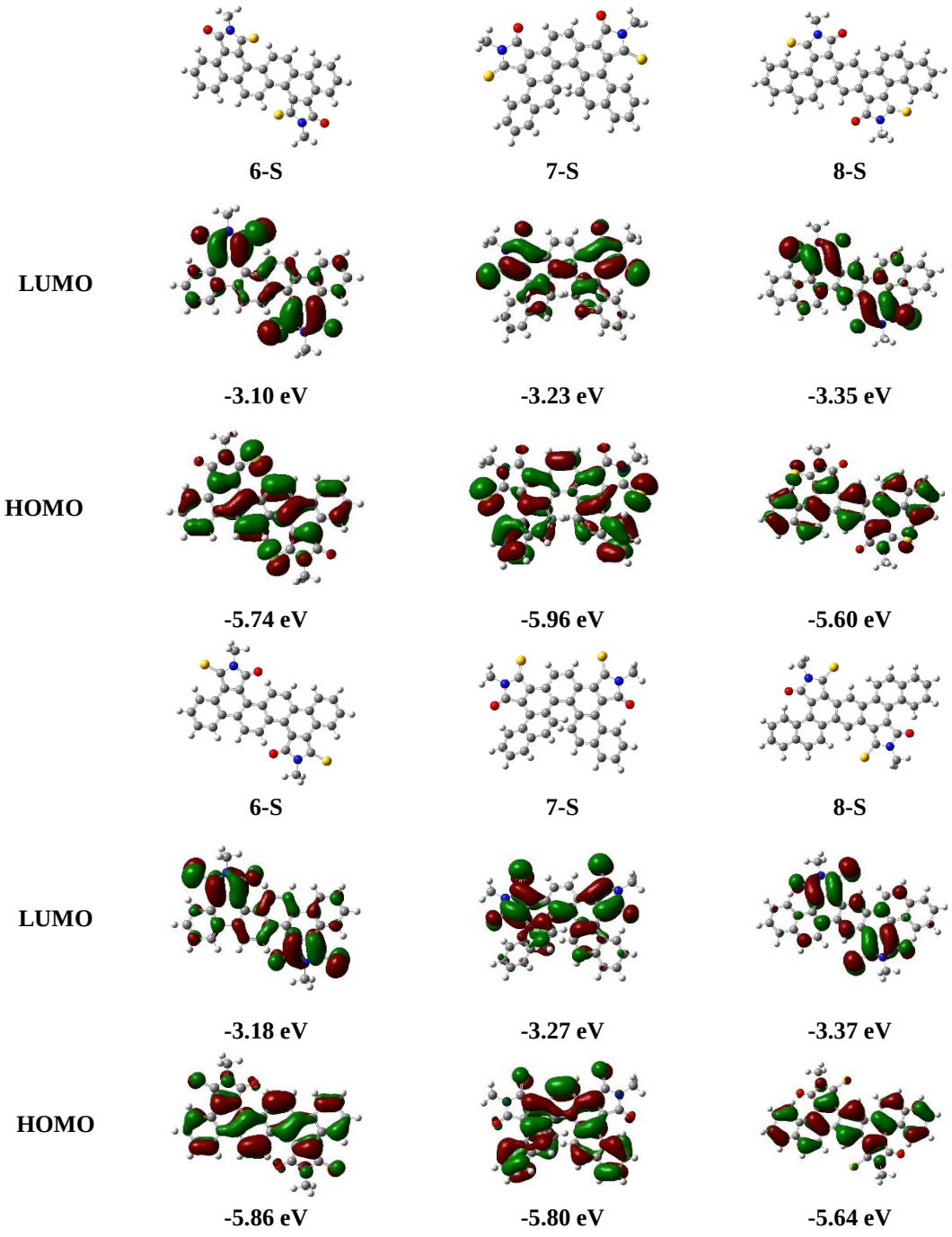


Fig. S2 DFT calculated frontier orbitals of **6-S**, **7-S** and **8-S**.

III. AFM and XRD Characterizations

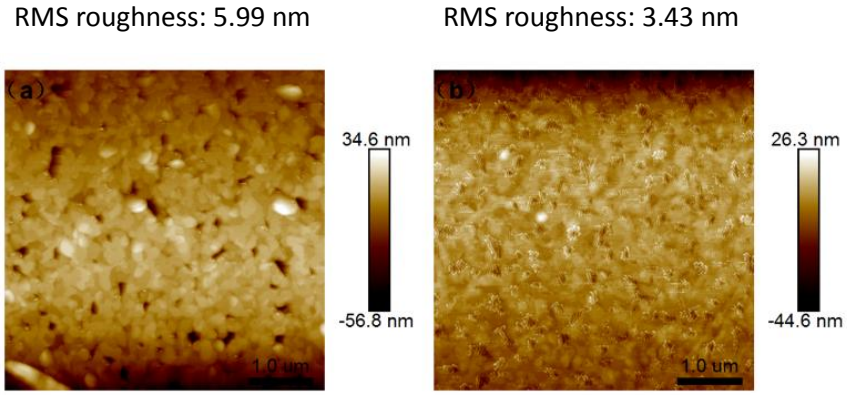


Fig. S3 AFM topography images (5 × 5 μm^2) of annealed thin films of **2** (a) and **8** (b) on n^{++}-Si/SiO_2 substrates.

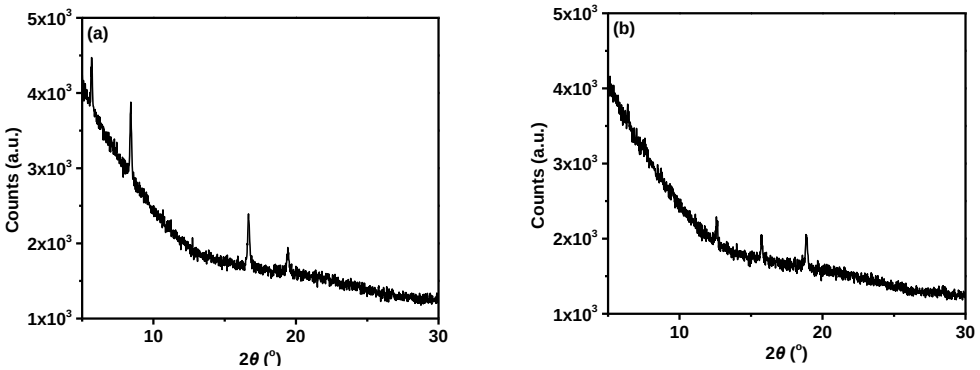


Fig. S4 XRD profiles of thin films of PAI **2** (a) and **8** (b) on n^{++}-Si/SiO_2 substrates.

IV. References

1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A. Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, Revision C.02; Gaussian Inc.: Wallingford CT, 2004**.**

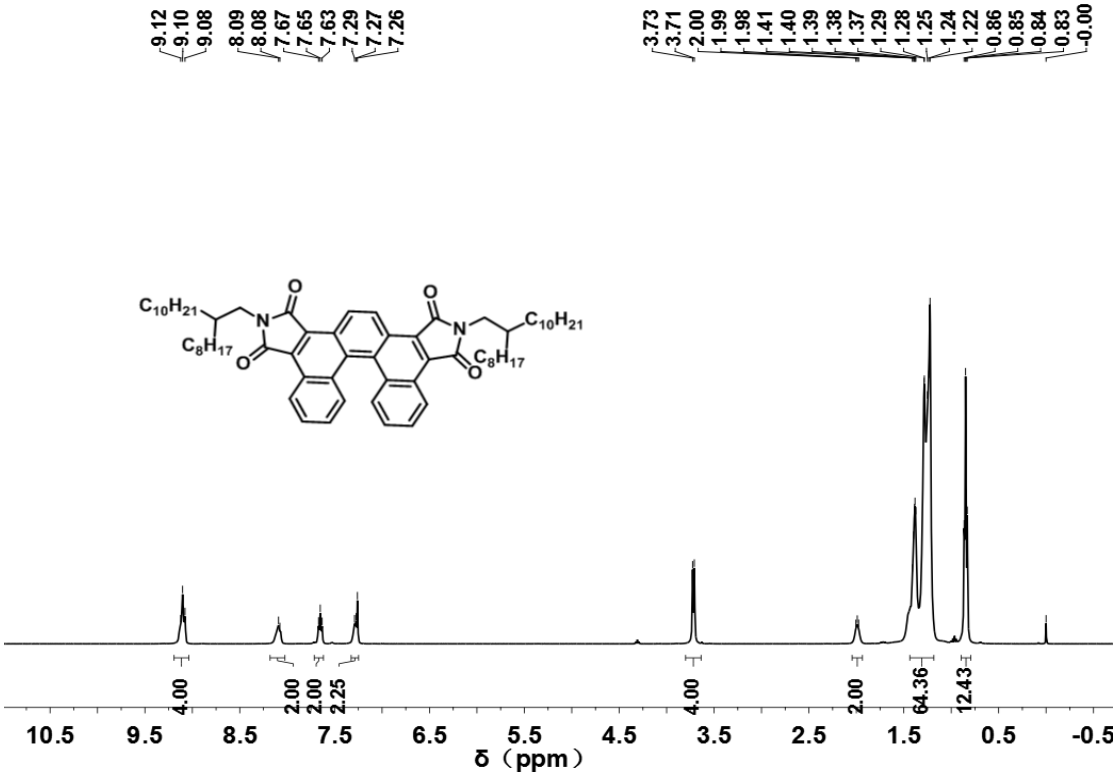
2. Dennington, R., II; Keith, T.; Millam, J.; Eppinnett, K.; Hovell, W. L.; Gilliland, R. GaussView, Version 3.09; Semichem, Inc.: Shawnee Mission, KS, 2003.

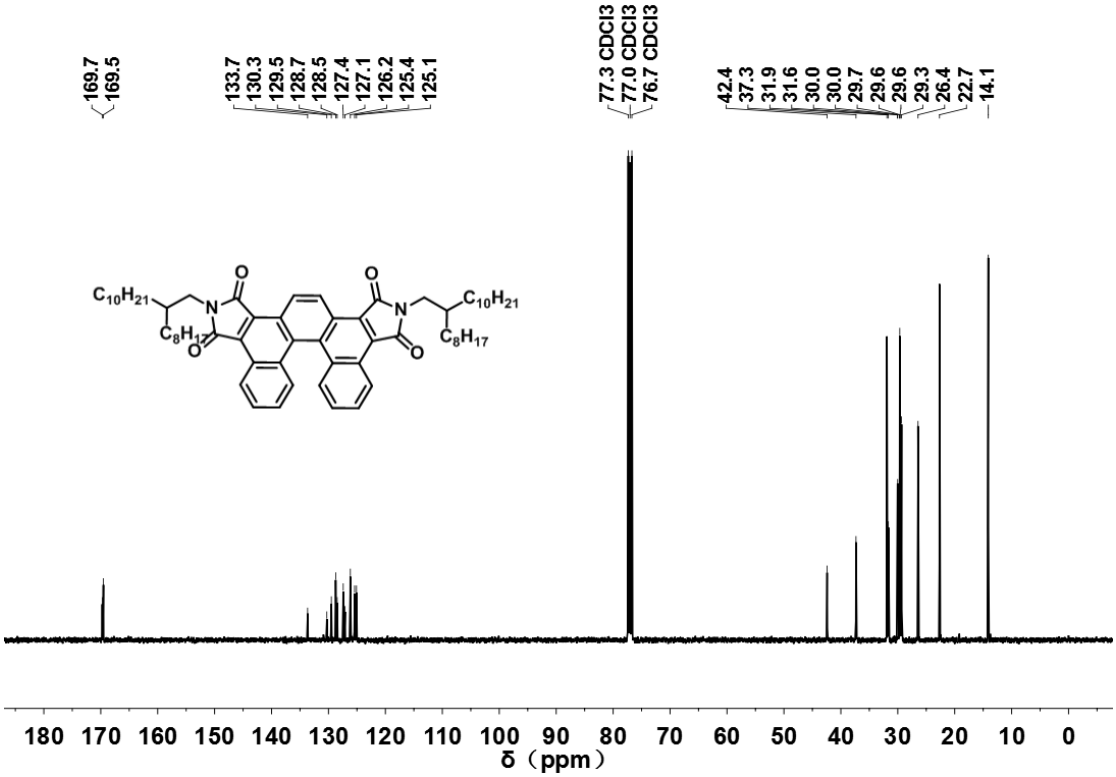
3. Becke, A. D. *Phys. Rev. A* 1988, **38**, 3098.

4. Lee, C.; Yang, W.; Parr, G. G. *Phys. Rev. B* 1988, **37**, 785.

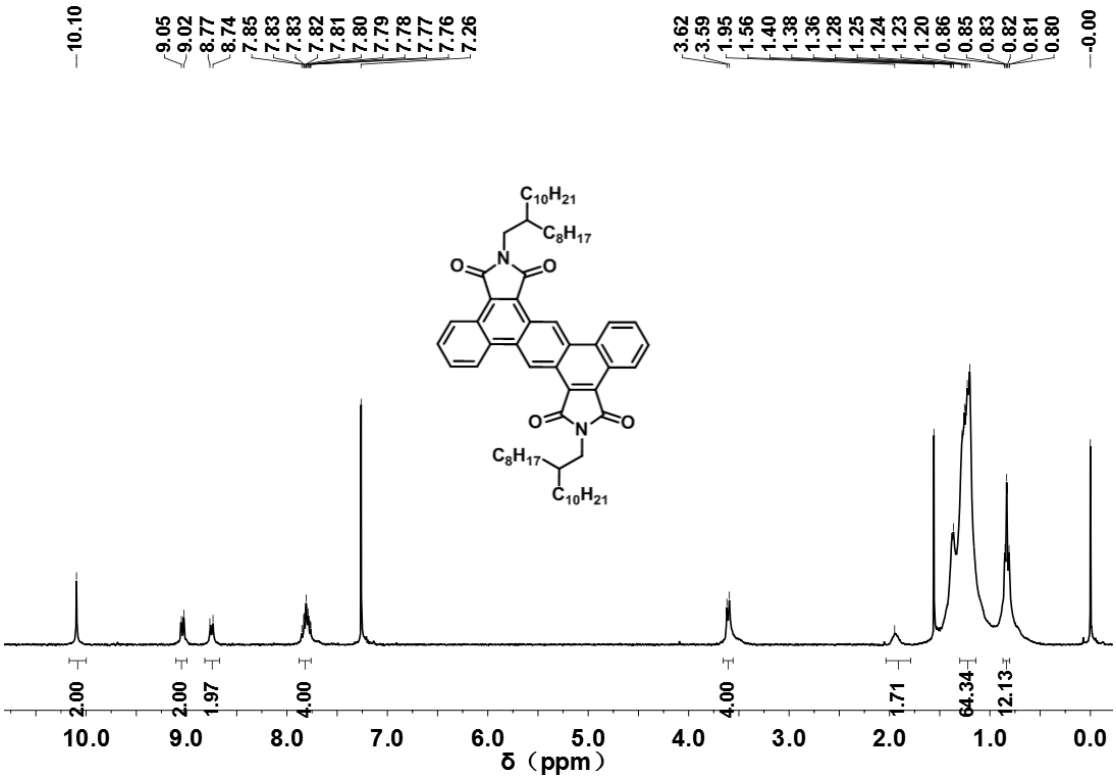
Copies of ^{1}H and ^{13}C NMR Spectra

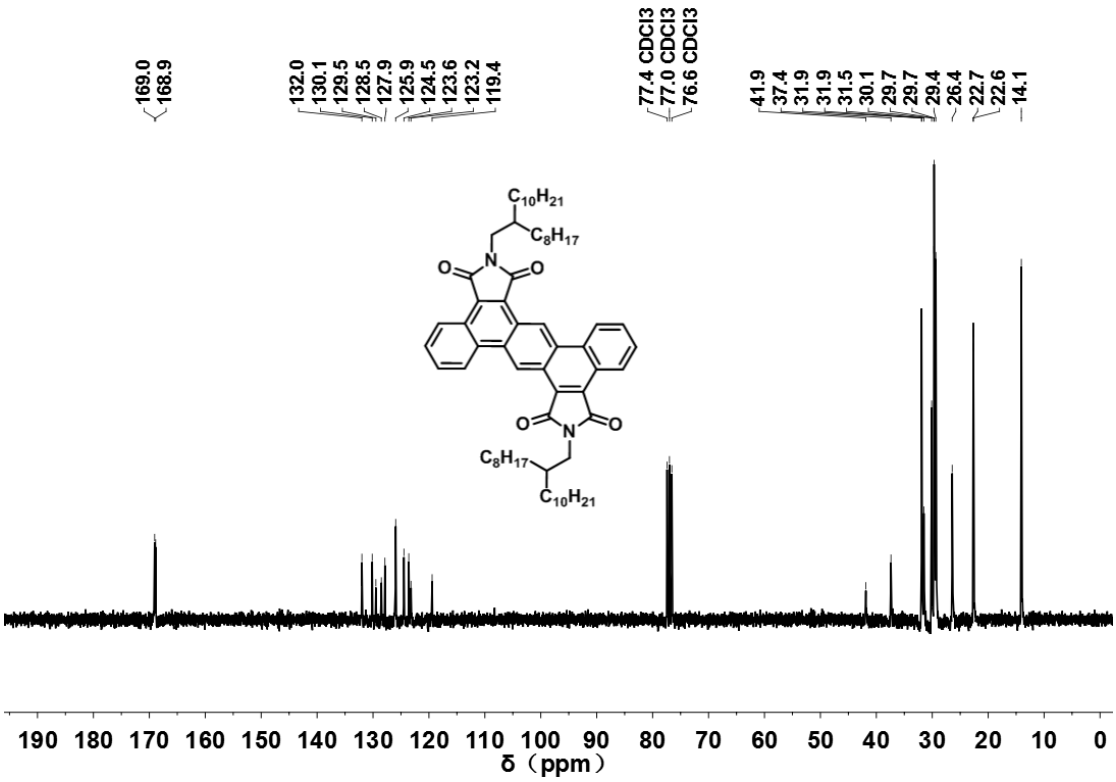
1:



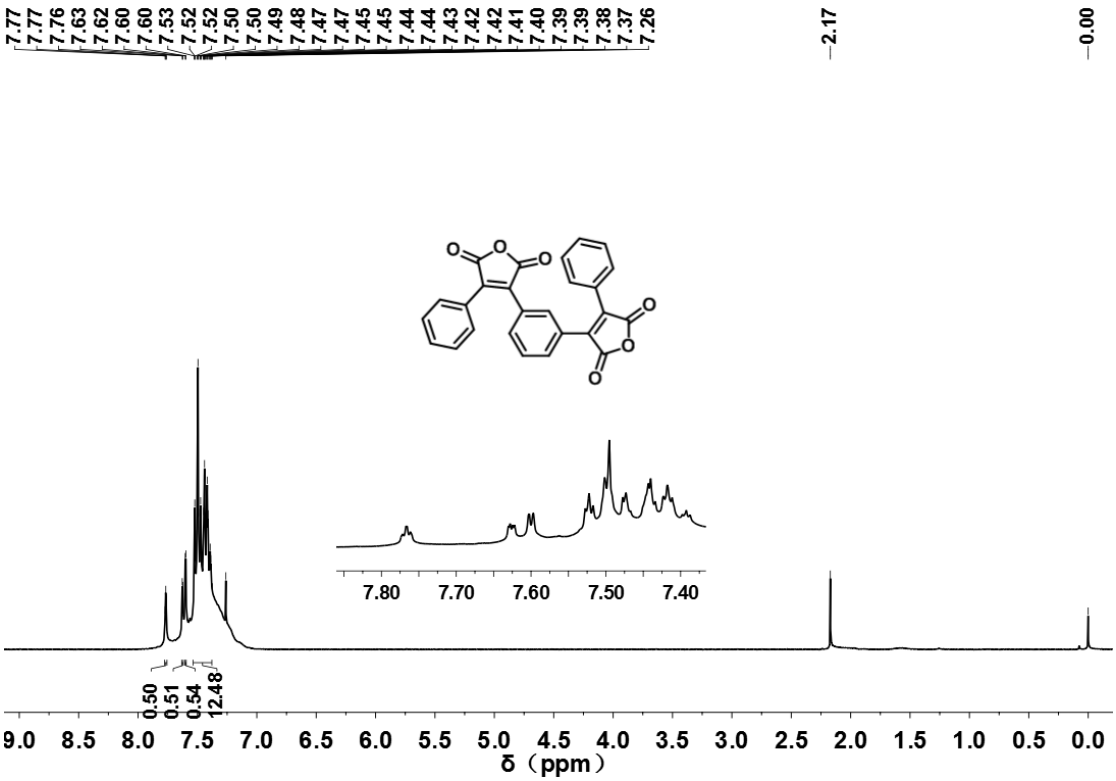


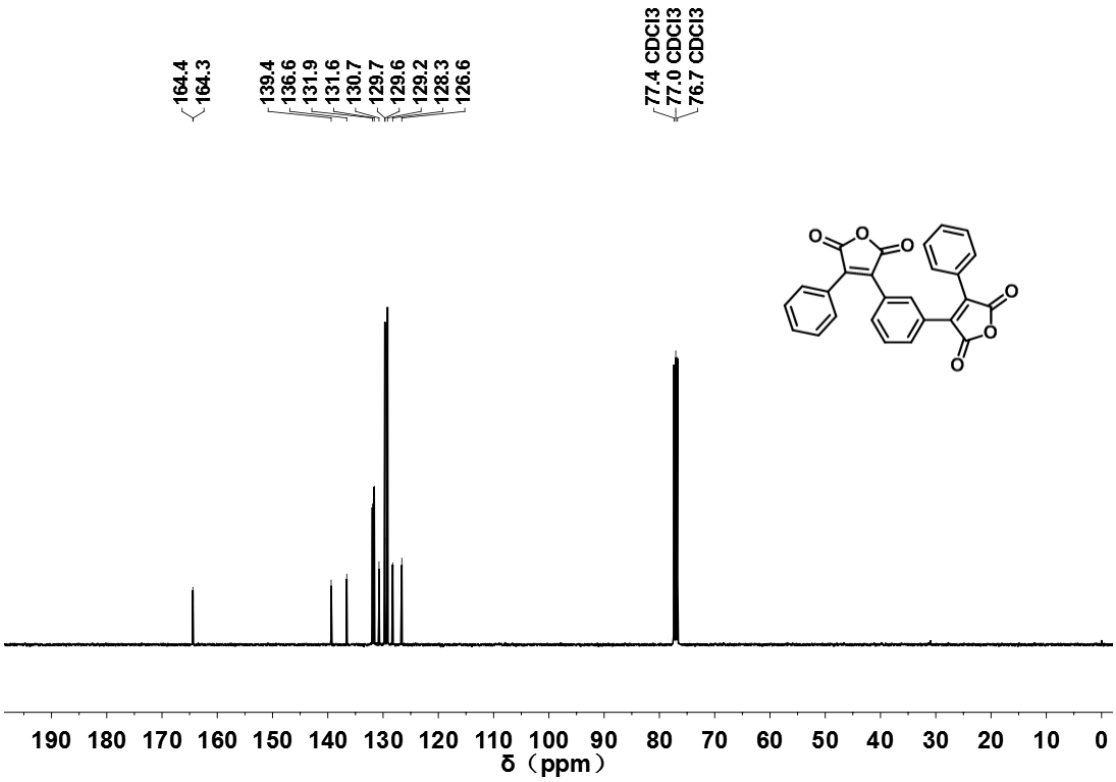
2:


10.10
9.05
9.02
8.77
8.74
7.85
7.83
7.83
7.82
7.81
7.80
7.79
7.78
7.77
7.76
7.26
3.62
3.59
1.95
1.56
1.40
1.38
1.36
1.28
1.25
1.24
1.23
1.20
0.86
0.85
0.83
0.82
0.81
0.80
0.00
2.00
2.00
1.97
4.00
4.00
1.71
64.34
12.13
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ（ppm）

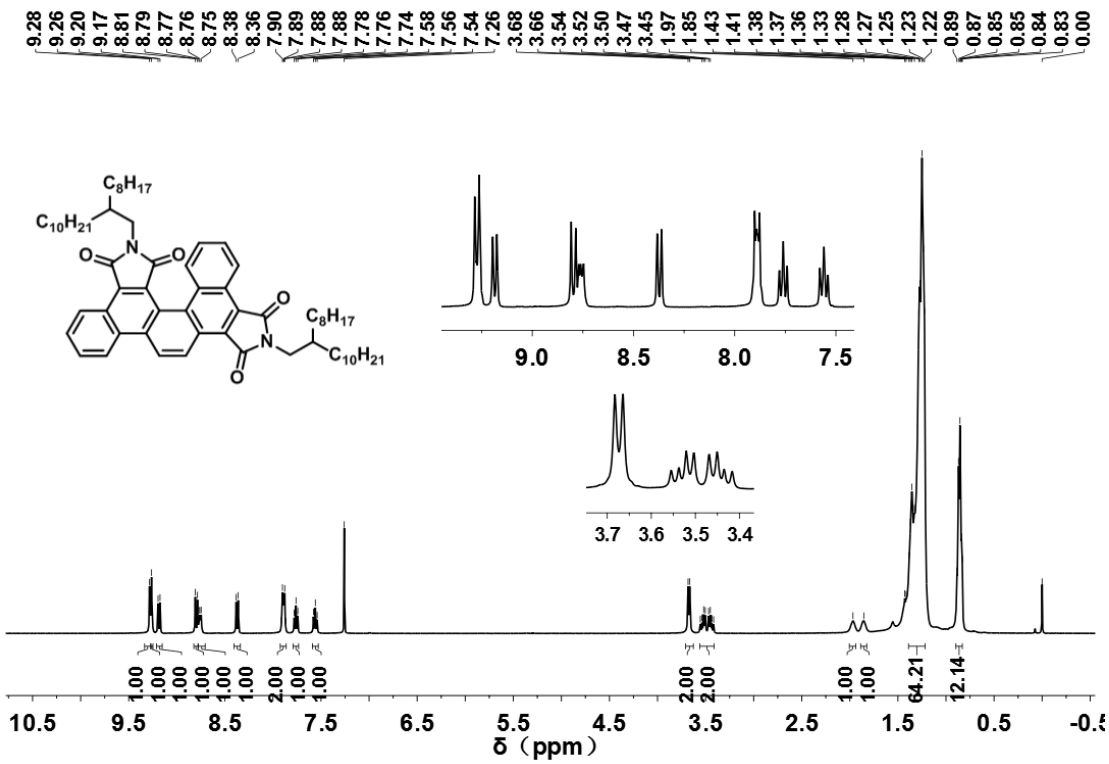

169.0
168.9
132.0
130.1
129.5
128.5
127.9
125.9
124.5
123.6
123.2
119.4
77.4 CDCl3
77.0 CDCl3
76.6 CDCl3
41.9
37.4
31.9
31.9
31.5
30.1
29.7
29.7
29.4
26.4
22.7
22.6
14.1
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ（ppm）

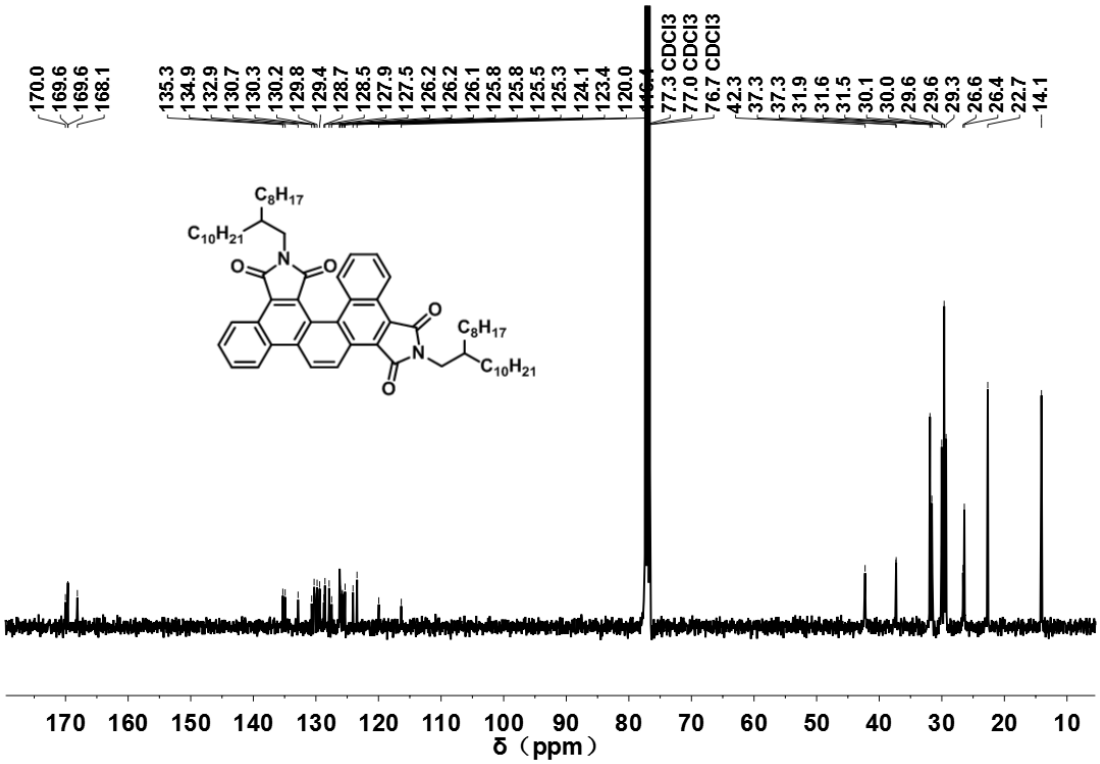
10:


7.77
7.77
7.76
7.63
7.62
7.60
7.60
7.53
7.52
7.52
7.50
7.50
7.49
7.48
7.47
7.47
7.45
7.45
7.44
7.44
7.43
7.42
7.42
7.41
7.40
7.39
7.39
7.38
7.37
7.26
2.17
0.00
7.80
7.70
7.60
7.50
7.40
0.50
0.51
0.54
12.48
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ（ppm）

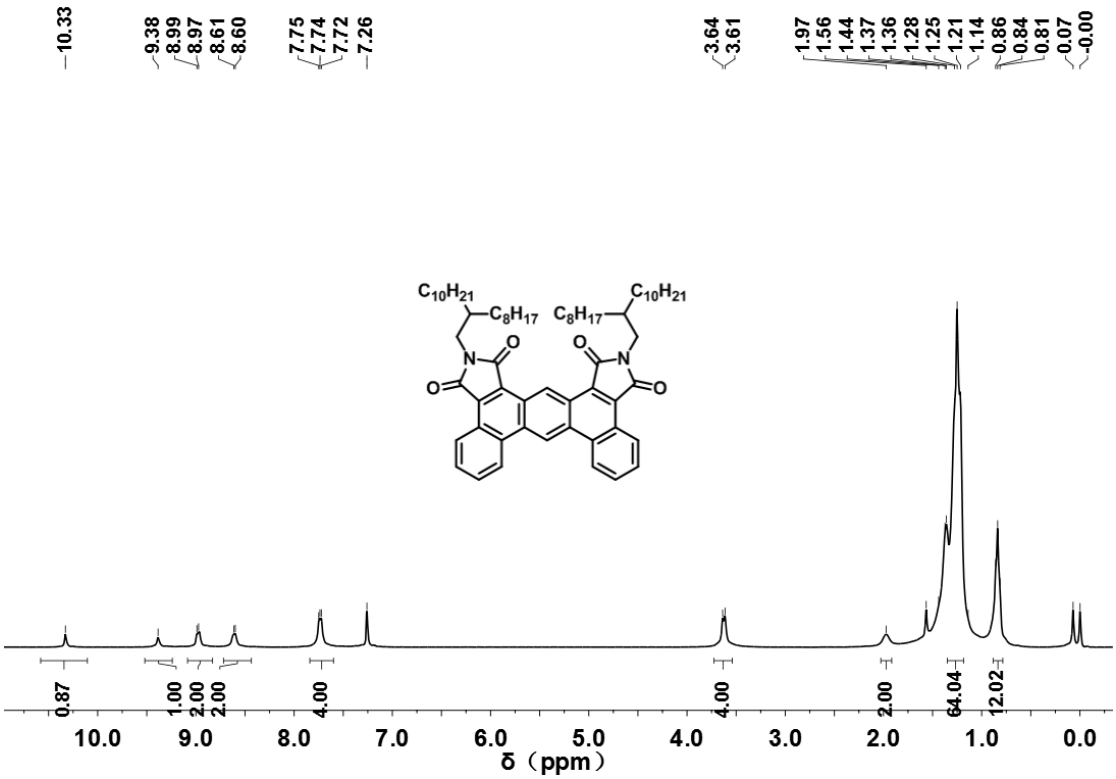

164.4
164.3
139.4
136.6
131.9
131.6
130.7
129.7
129.6
129.2
128.3
126.6
77.4 CDCl3
77.0 CDCl3
76.7 CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ（ppm）

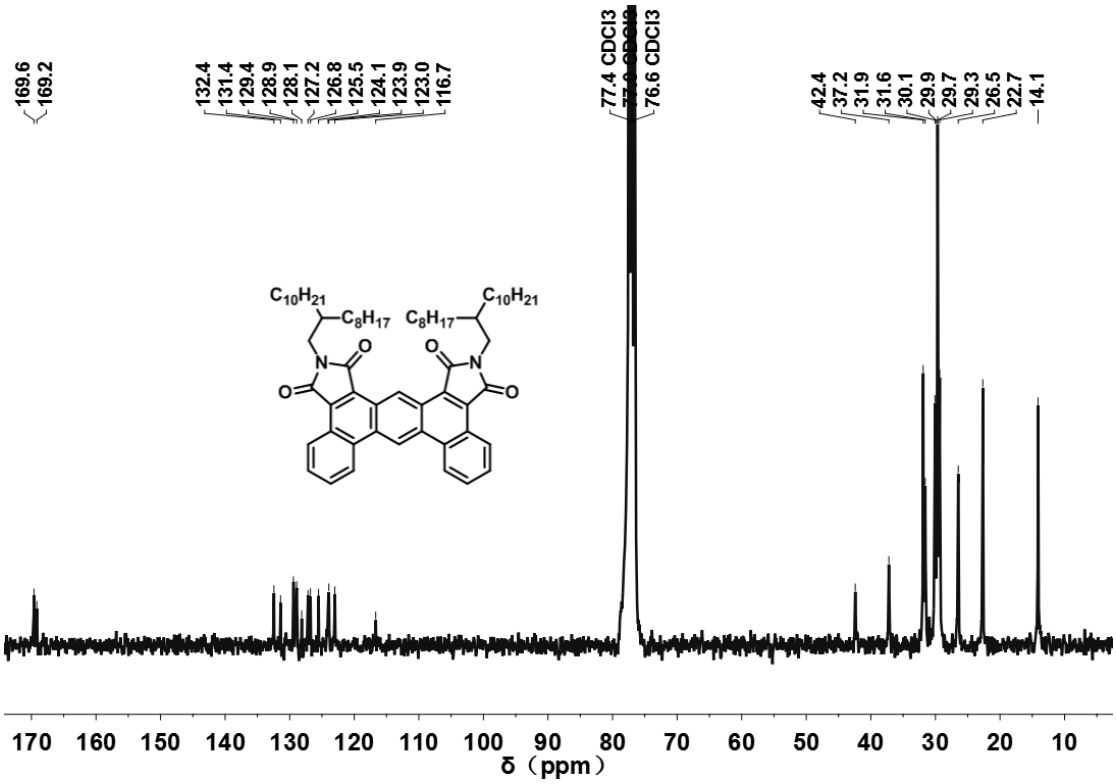
3:


9.28 9.26 9.20 9.17 8.81 8.79 8.77 8.76 8.75 8.38 8.36 7.90 7.89 7.88 7.88 7.78 7.76 7.74 7.58 7.56 7.54 7.26 3.68 3.66 3.54 3.52 3.50 3.47 3.45 1.97 1.85 1.43 1.41 1.38 1.37 1.36 1.33 1.28 1.27 1.25 1.23 1.22 0.89 0.87 0.85 0.85 0.84 0.83 0.00
C8H17
C10H21
9.0 8.5 8.0 7.5
3.7 3.6 3.5 3.4
1.00 1.00 1.00 1.00 1.00 2.00 1.00 1.00 2.00 2.00 1.00 1.00 64.21 12.14
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
δ（ppm）

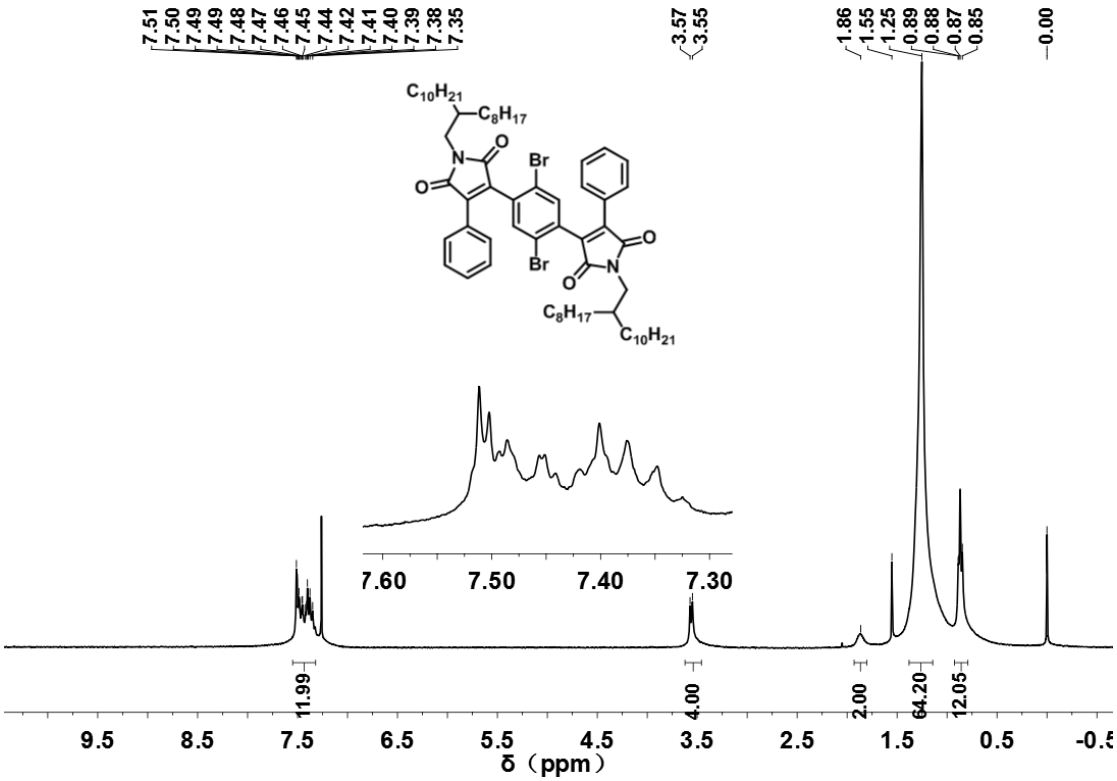

170.0 169.6 169.6 168.1 135.3 134.9 132.9 130.7 130.3 130.2 129.8 129.4 128.7 128.5 127.9 127.5 126.2 126.2 126.1 125.8 125.8 125.5 125.3 124.1 123.4 120.0 77.3 CDCl3 77.0 CDCl3 76.7 CDCl3 42.3 37.3 37.3 31.9 31.6 31.5 30.1 30.0 29.6 29.6 29.3 26.6 26.4 22.7 14.1
C8H17
C10H21
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
δ（ppm）

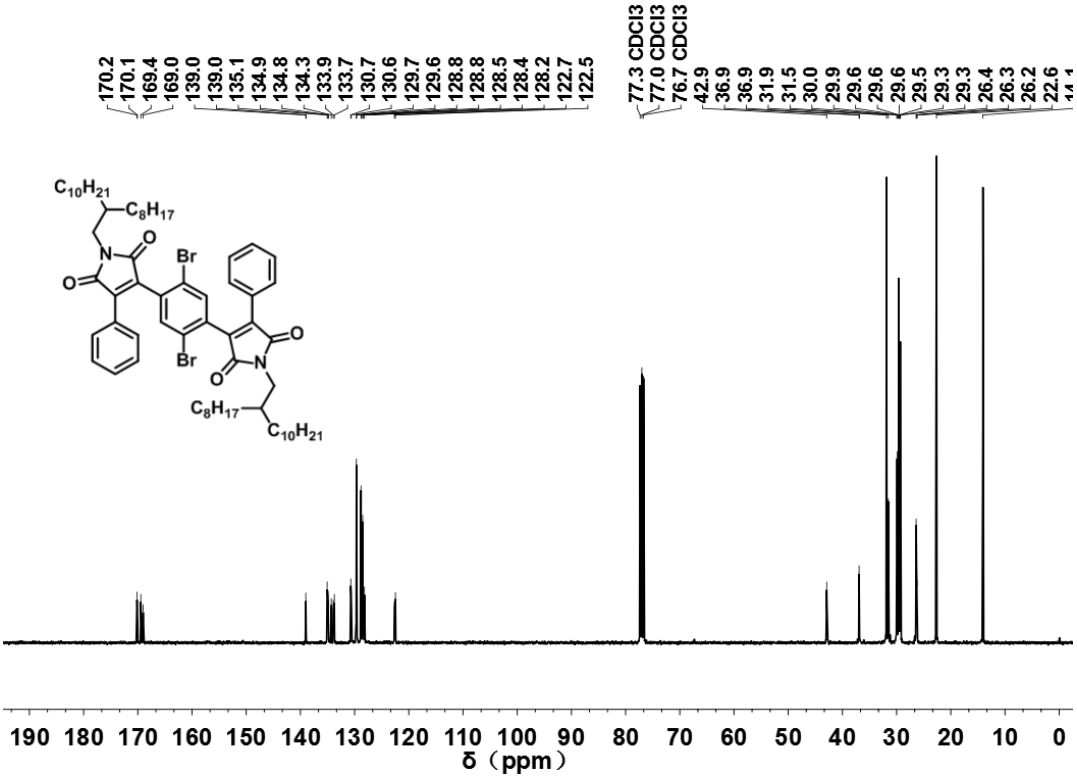
4:


10.33
9.38
8.99
8.97
8.61
8.60
7.75
7.74
7.72
7.26
3.64
3.61
1.97
1.56
1.44
1.37
1.36
1.28
1.25
1.21
1.14
0.86
0.84
0.81
0.07
-0.00
0.87
1.00
2.00
2.00
4.00
4.00
2.00
64.04
12.02
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ（ppm）

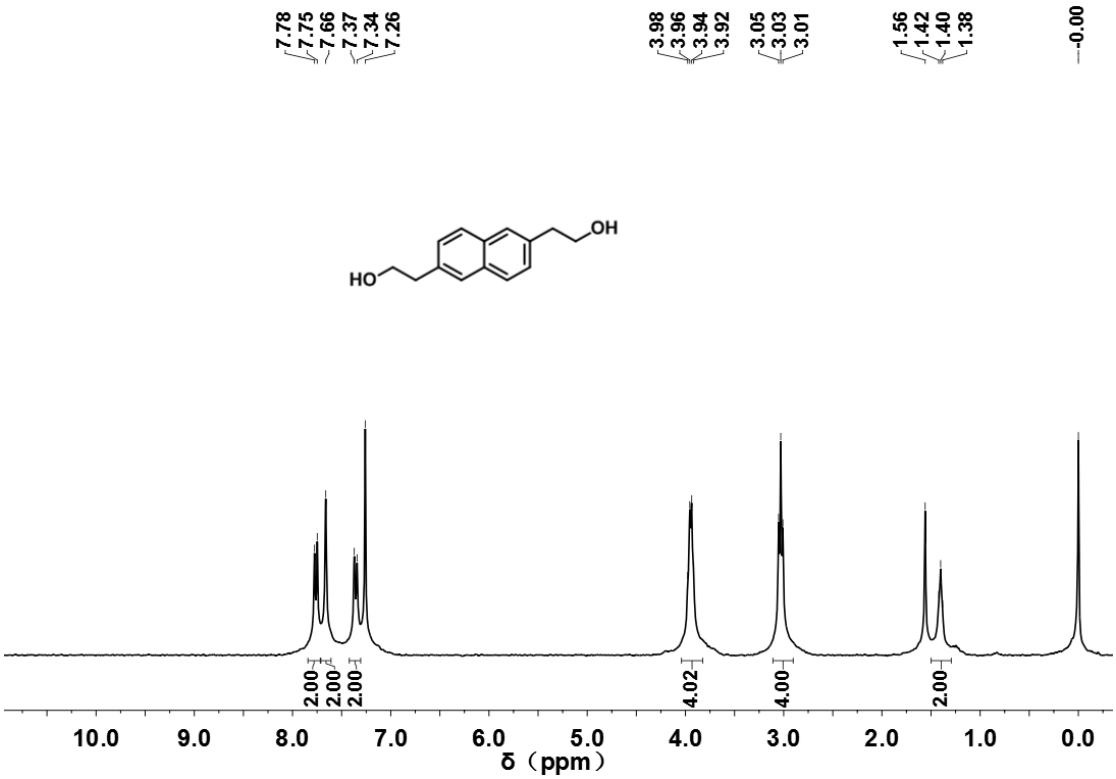

169.6
169.2
132.4
131.4
129.4
128.9
128.1
127.2
126.8
125.5
124.1
123.9
123.0
116.7
77.4 CDCl3
76.6 CDCl3
42.4
37.2
31.9
31.6
30.1
29.9
29.7
29.3
26.5
22.7
14.1
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
δ（ppm）

11:

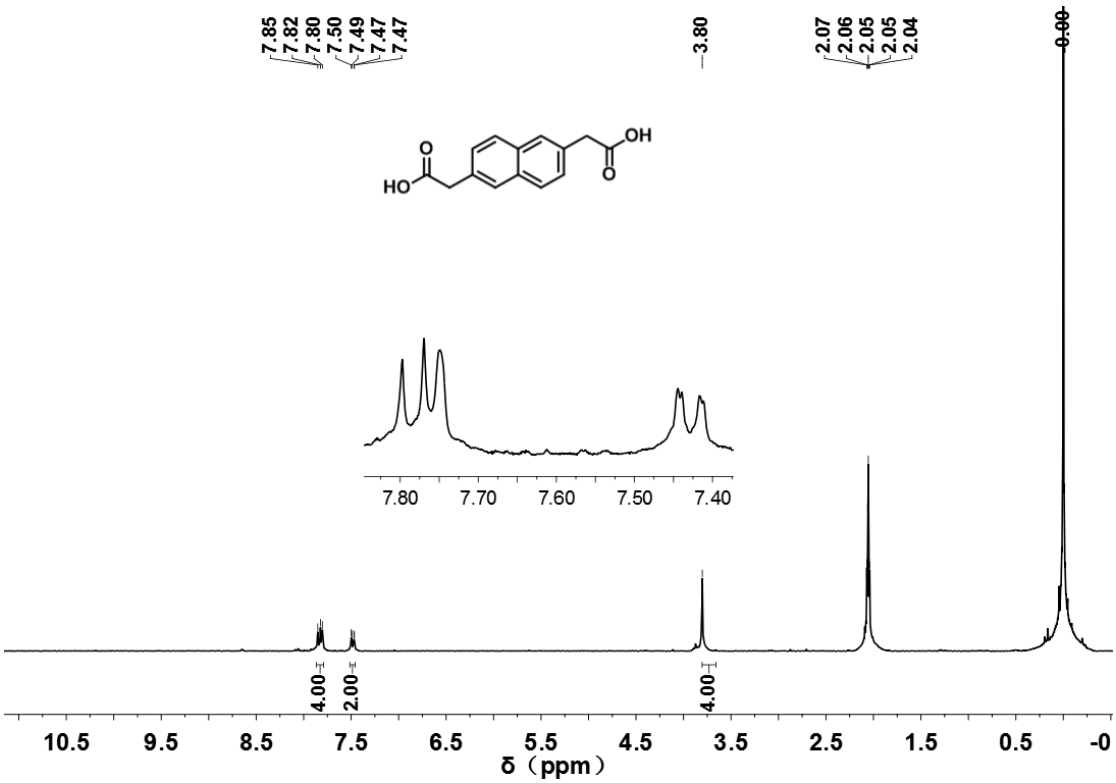

7.51
7.50
7.49
7.49
7.48
7.47
7.46
7.45
7.44
7.42
7.41
7.40
7.39
7.38
7.35
3.57
3.55
1.86
1.55
1.25
0.89
0.88
0.87
0.85
0.00
11.99
4.00
2.00
64.20
12.05
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
δ（ppm）


170.2
170.1
169.4
169.0
139.0
139.0
135.1
134.9
134.8
134.3
133.9
133.7
130.7
130.6
129.7
129.6
128.8
128.8
128.5
128.4
128.2
122.7
122.5
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
42.9
36.9
36.9
31.9
31.5
30.0
29.9
29.6
29.6
29.6
29.5
29.3
29.3
26.4
26.3
26.2
22.6
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ（ppm）

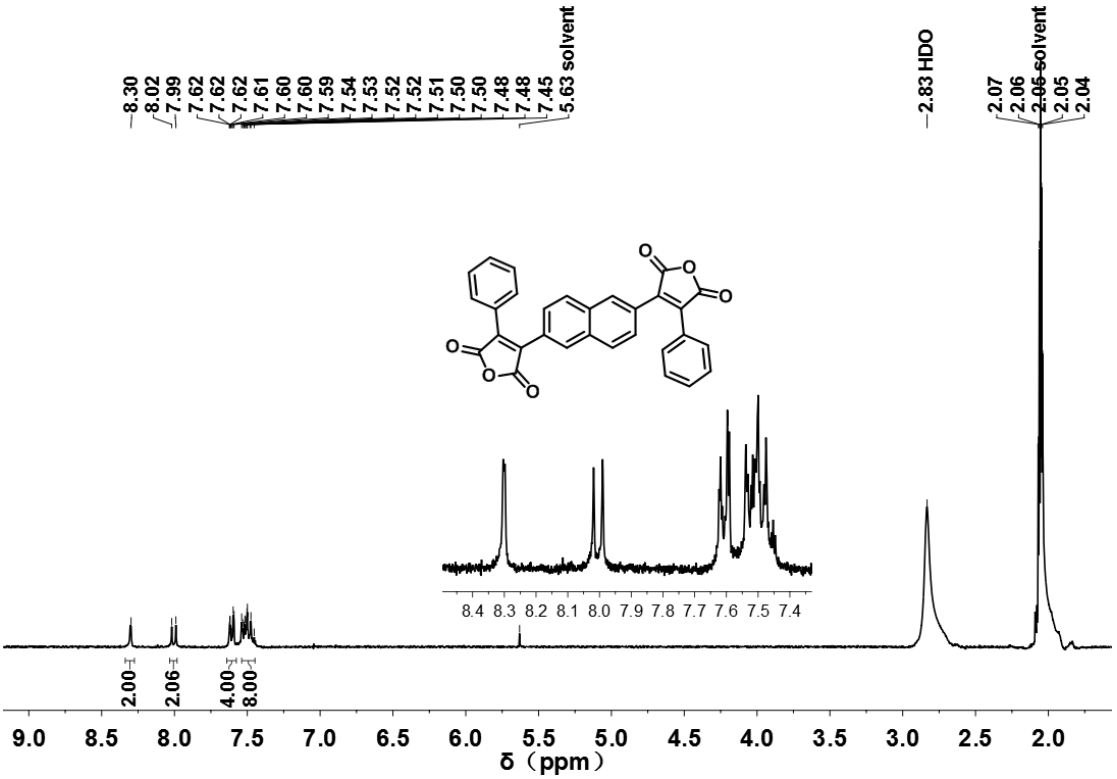
2,2'-(naphthalene-2,6-diyl)diethanol:



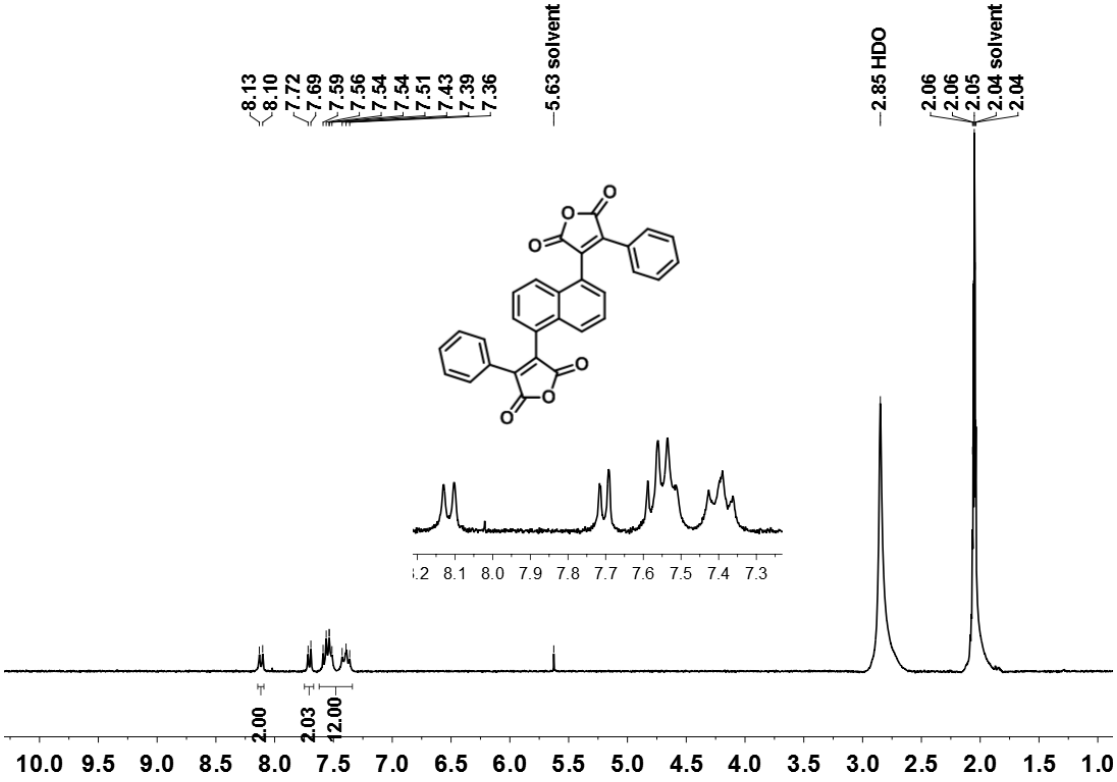
2,2'-(naphthalene-2, 6-diyl)diacetic acid:



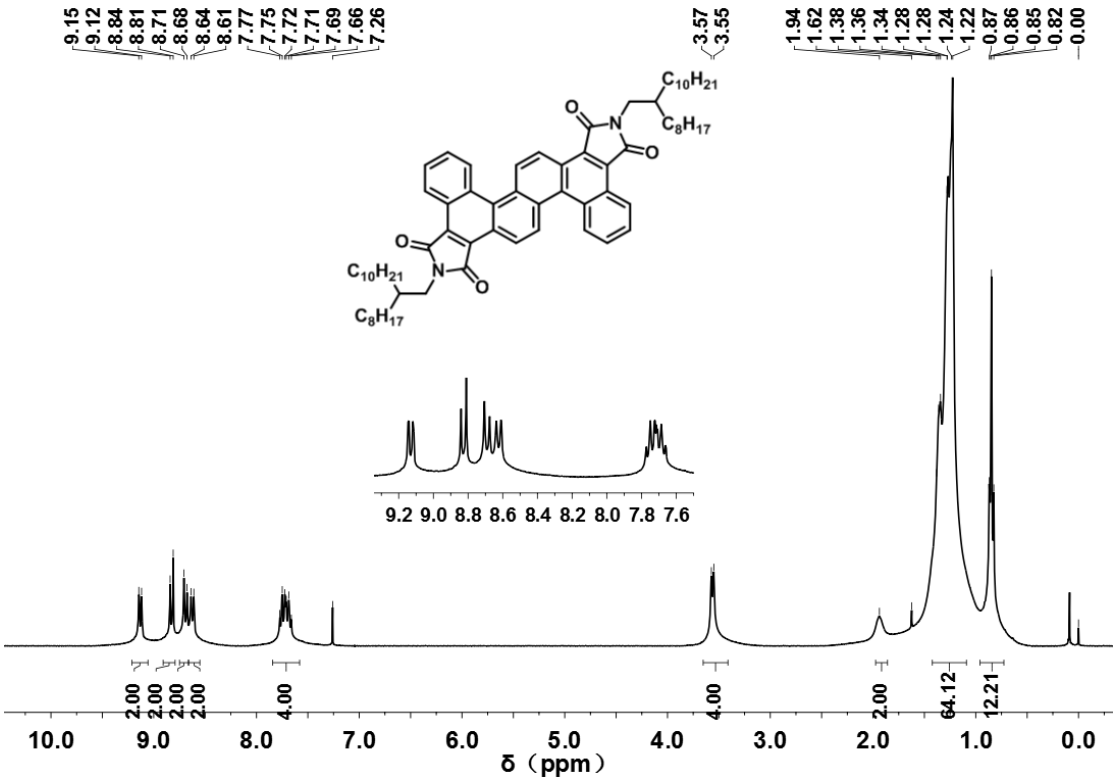
12:

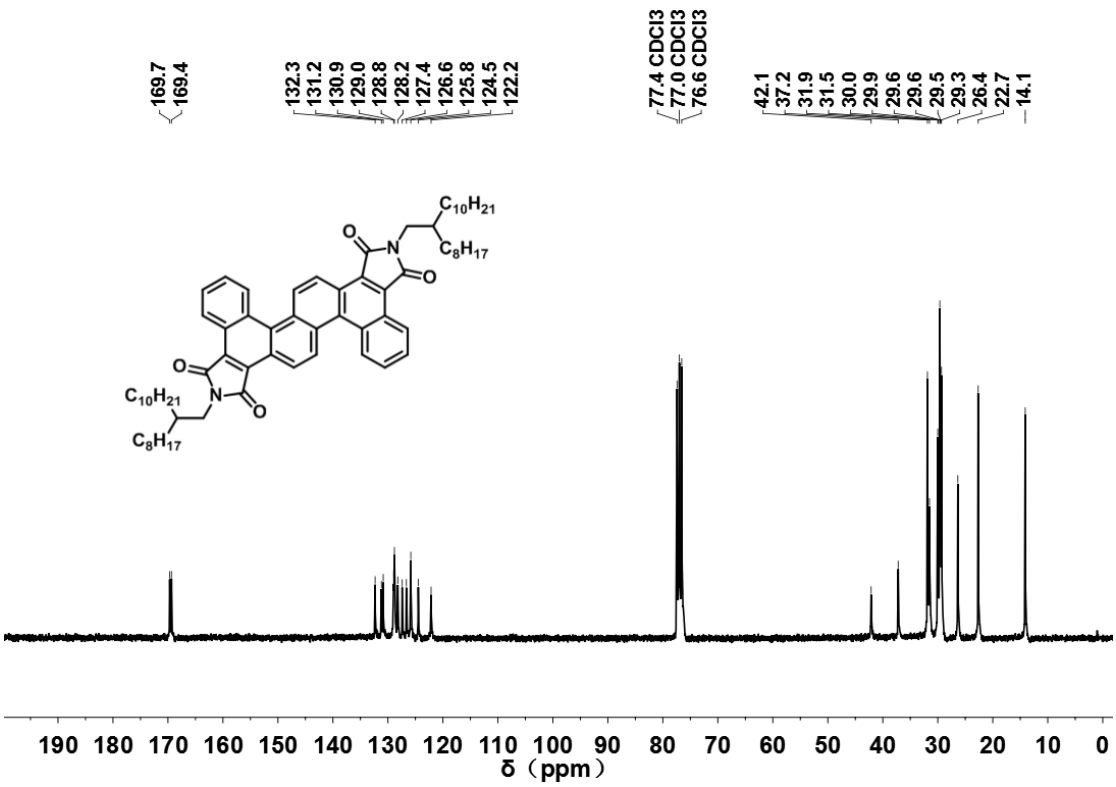

8.30
8.02
7.99
7.62
7.62
7.62
7.61
7.60
7.60
7.59
7.54
7.53
7.52
7.52
7.51
7.50
7.50
7.48
7.45
5.63 solvent
2.83 HDO
2.07
2.06
2.05 solvent
2.05
2.04
2.00
2.06
4.00
8.00
δ（ppm）

13:

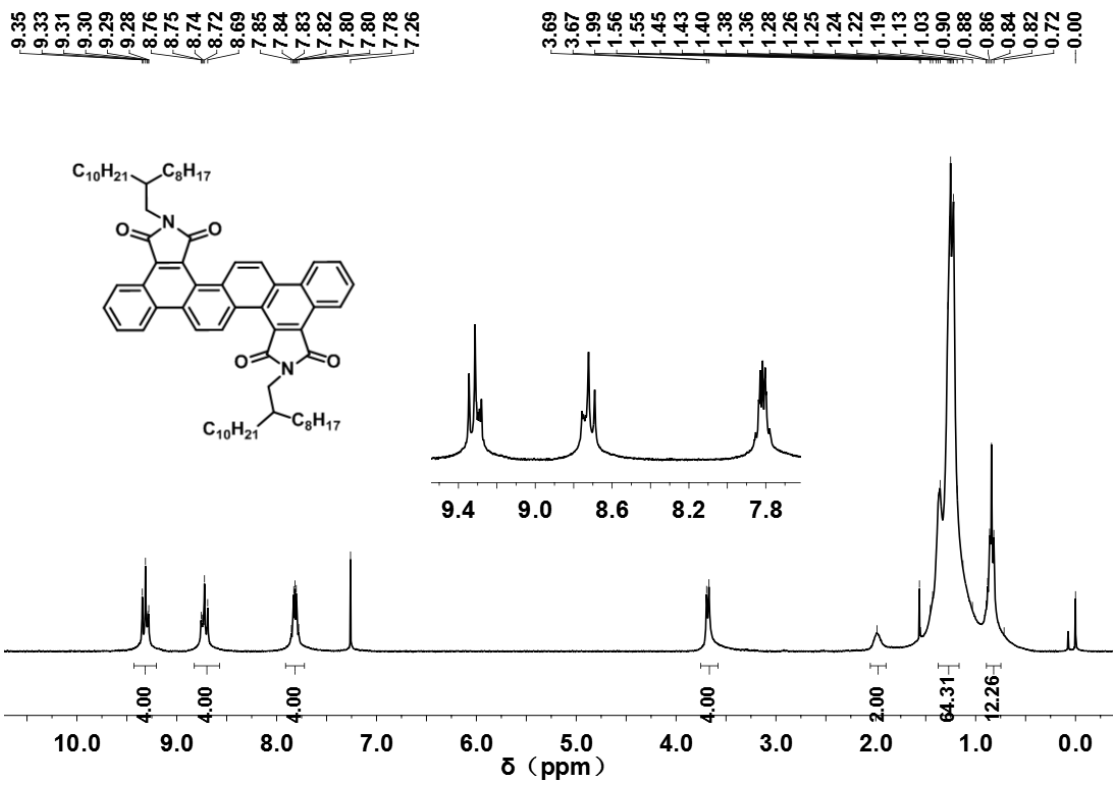

8.13
8.10
7.72
7.69
7.59
7.56
7.54
7.54
7.51
7.43
7.39
7.36
5.63 solvent
2.85 HDO
2.06
2.06
2.05
2.04 solvent
2.04
2.00
2.03
12.00

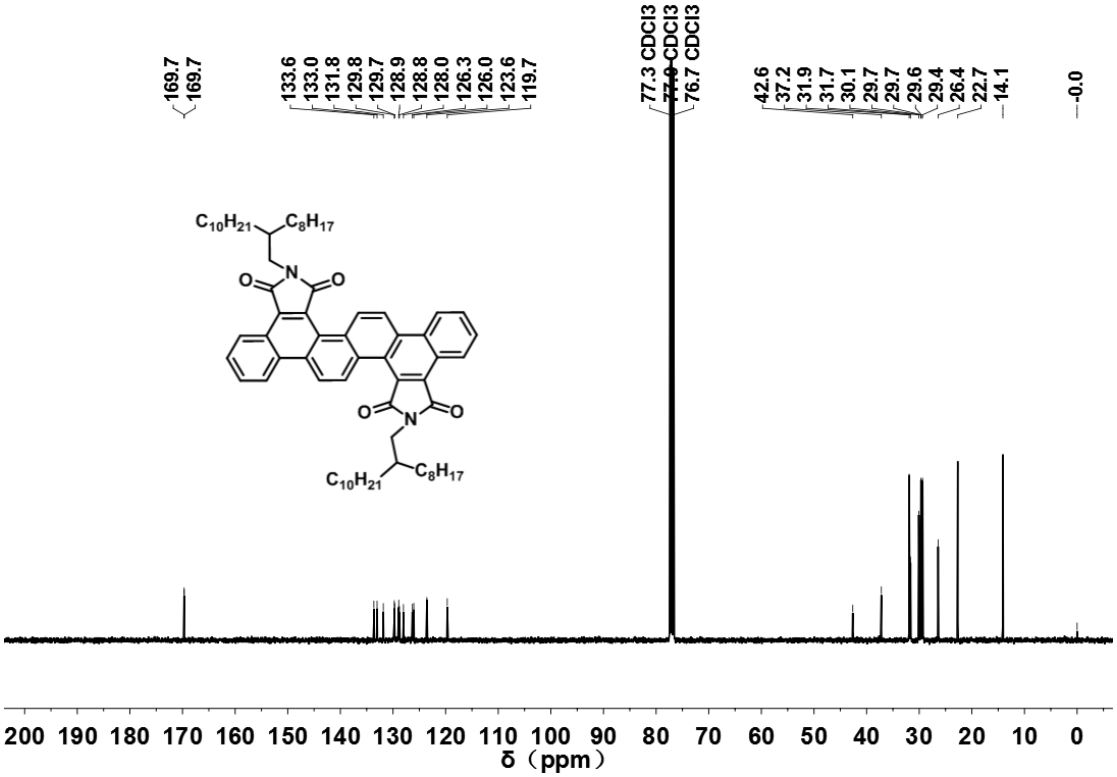
5:


9.15
9.12
8.84
8.81
8.71
8.68
8.64
8.61
7.77
7.75
7.72
7.71
7.69
7.66
7.26
3.57
3.55
1.94
1.62
1.38
1.36
1.34
1.28
1.28
1.24
1.22
0.87
0.86
0.85
0.82
0.00
2.00
2.00
2.00
2.00
4.00
4.00
2.00
64.12
12.21
δ（ppm）

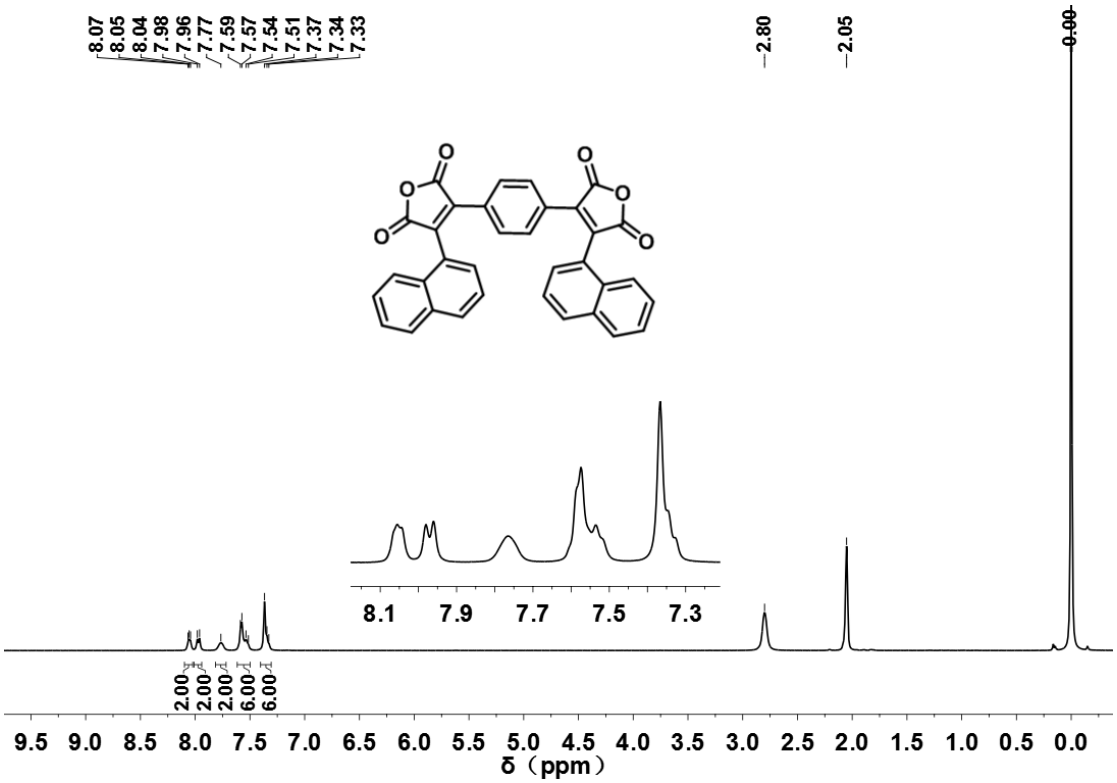

169.7
169.4
132.3
131.2
130.9
129.0
128.8
128.2
127.4
126.6
125.8
124.5
122.2
77.4 CDCl3
77.0 CDCl3
76.6 CDCl3
42.1
37.2
31.9
31.5
30.0
29.9
29.6
29.6
29.5
29.3
26.4
22.7
14.1
δ（ppm）

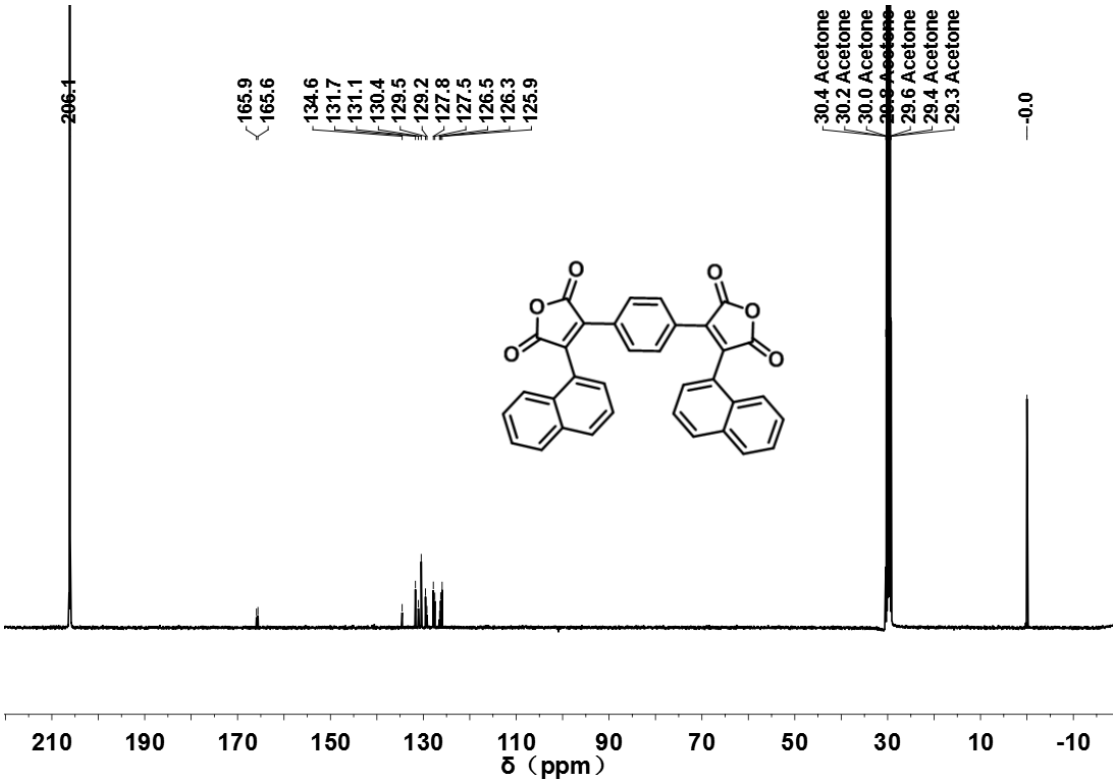
6:


9.35 9.33 9.31 9.30 9.29 9.28 8.76 8.75 8.74 8.72 8.69 7.85 7.84 7.83 7.82 7.80 7.80 7.78 7.26
3.69 3.67 1.99 1.56 1.55 1.45 1.43 1.40 1.38 1.36 1.28 1.26 1.25 1.24 1.22 1.19 1.13 1.03 0.90 0.88 0.86 0.84 0.82 0.72 0.00
C10H21 C8H17
N
O
C10H21 C8H17
9.4 9.0 8.6 8.2 7.8
4.00 4.00 4.00 4.00 2.00 64.31 12.26
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
δ（ppm）

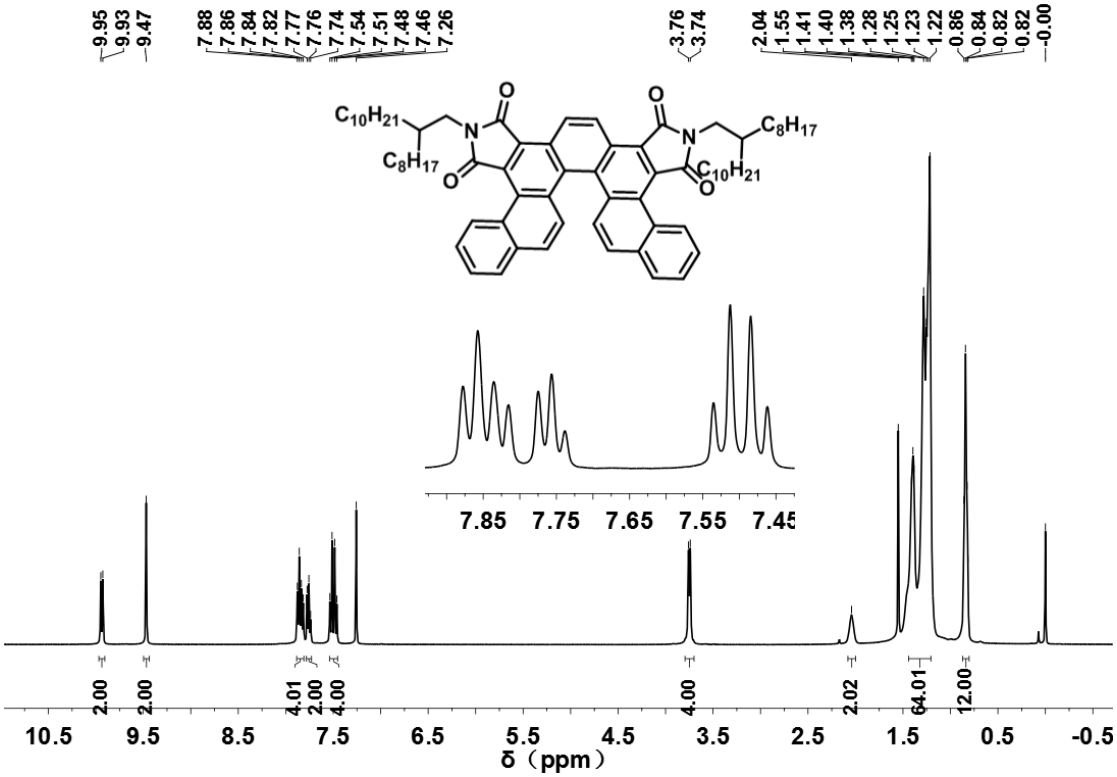

169.7 169.7
133.6 133.0 131.8 129.8 129.7 128.9 128.8 128.0 126.3 126.0 123.6 119.7
77.3 CDCl3 77.0 CDCl3 76.7 CDCl3
42.6 37.2 31.9 31.7 30.1 29.7 29.7 29.6 29.4 26.4 22.7 14.1
-0.0
C10H21 C8H17
N
O
C10H21 C8H17
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ（ppm）

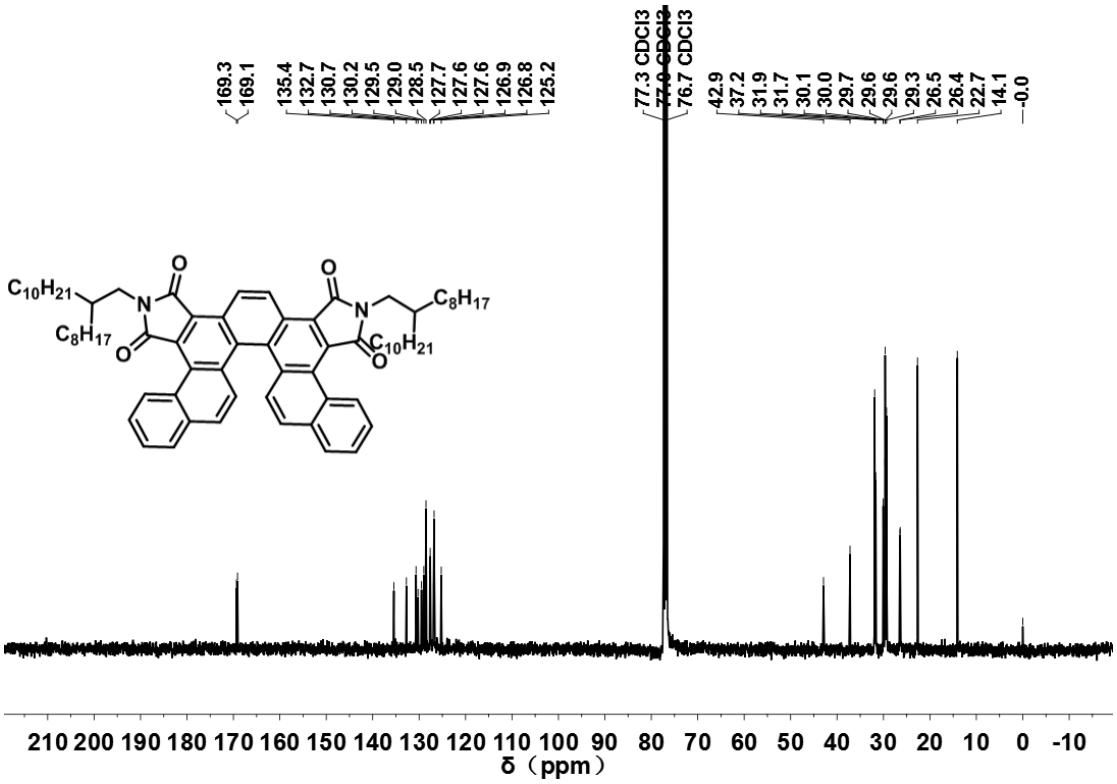
14:


8.07
8.05
8.04
7.98
7.96
7.77
7.59
7.57
7.54
7.51
7.37
7.34
7.33
2.80
2.05
0.00
2.00
2.00
2.00
6.00
6.00
8.1
7.9
7.7
7.5
7.3
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ（ppm）

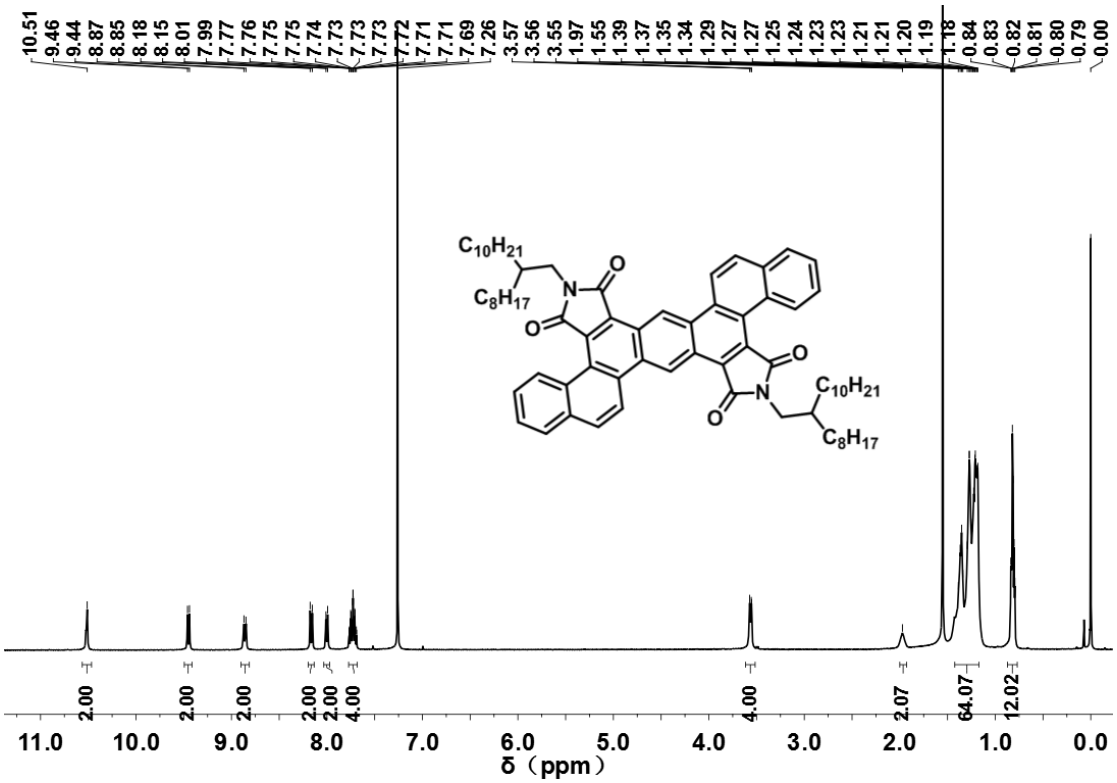

206.1
165.9
165.6
134.6
131.7
131.1
130.4
129.5
129.2
127.8
127.5
126.5
126.3
125.9
30.4 Acetone
30.2 Acetone
30.0 Acetone
29.6 Acetone
29.4 Acetone
29.3 Acetone
-0.0
210 190 170 150 130 110 90 70 50 30 10 -10
δ（ppm）

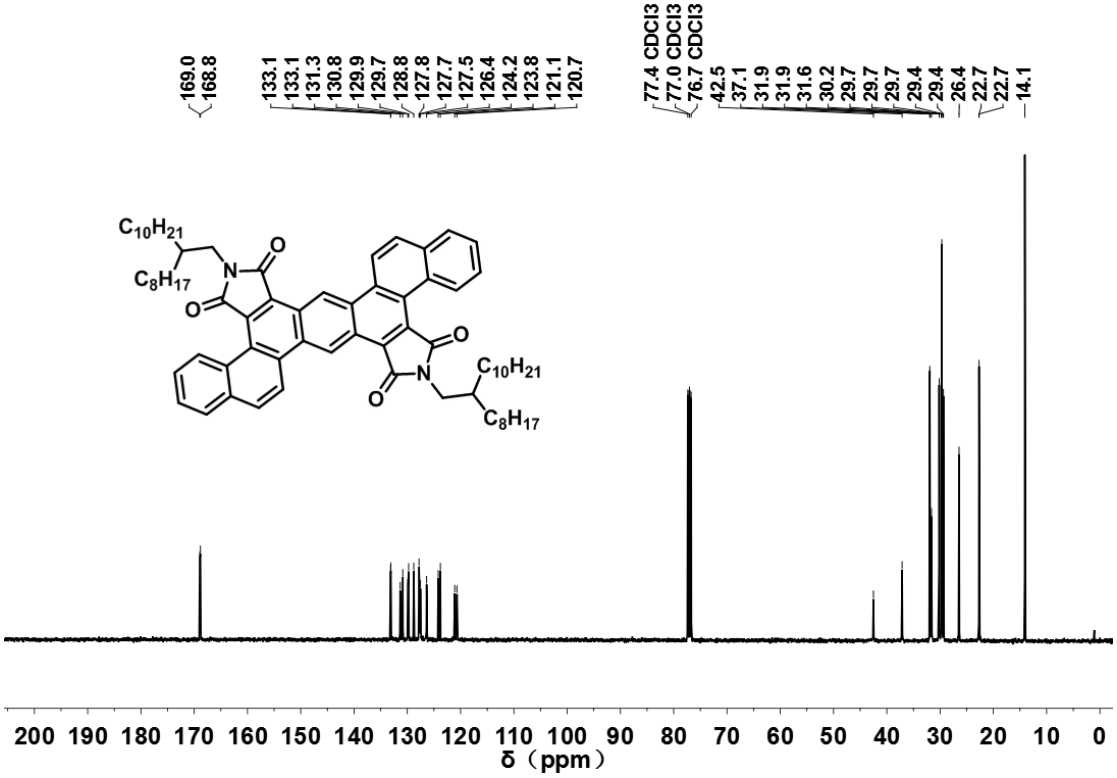
7:


9.95
9.93
9.47
7.88
7.86
7.84
7.82
7.77
7.76
7.74
7.54
7.51
7.48
7.46
7.26
3.76
3.74
2.04
1.55
1.41
1.40
1.38
1.28
1.25
1.23
1.22
0.86
0.84
0.82
-0.00
7.85 7.75 7.65 7.55 7.45
2.00 2.00 4.01 2.00 4.00 4.00 2.02 64.01 12.00
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5
δ（ppm）

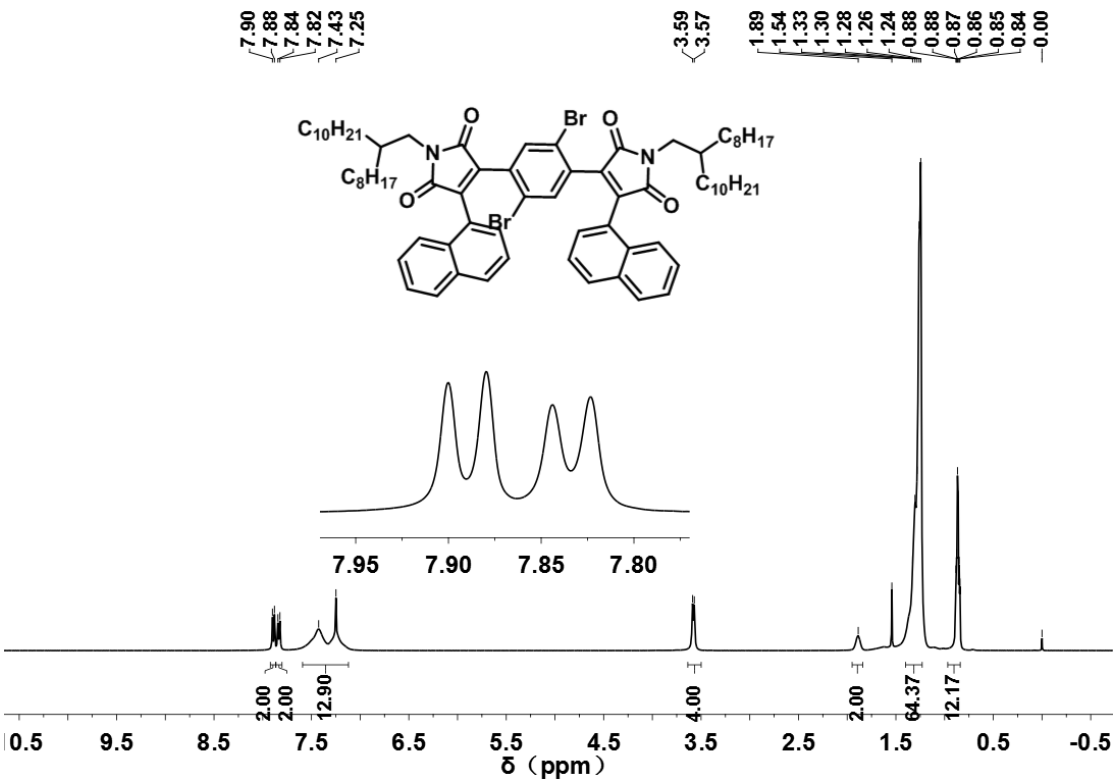

169.3
169.1
135.4
132.7
130.7
130.2
129.5
129.0
128.5
127.7
127.6
127.6
126.9
126.8
125.2
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
42.9
37.2
31.9
31.7
30.1
30.0
29.7
29.6
29.6
29.3
26.5
26.4
22.7
14.1
-0.0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ（ppm）

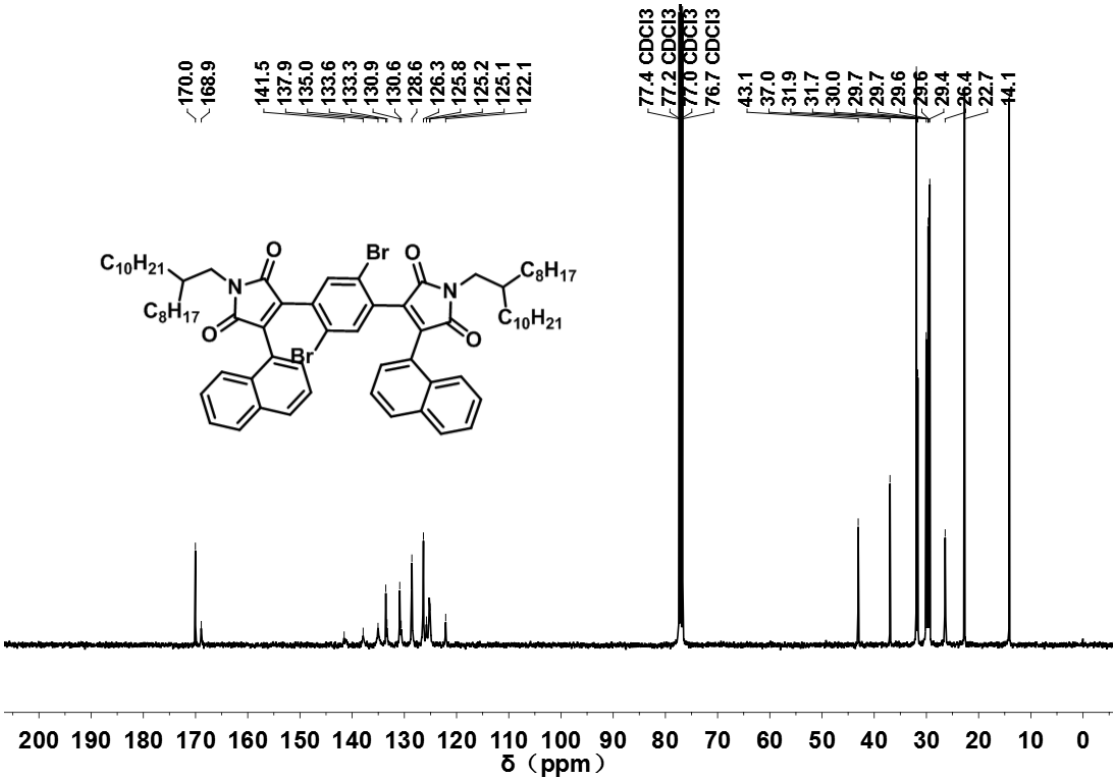
8:


10.51
9.46
9.44
8.87
8.85
8.18
8.15
8.01
7.99
7.77
7.76
7.75
7.75
7.74
7.73
7.73
7.72
7.71
7.71
7.69
7.26
3.57
3.56
3.55
1.97
1.55
1.39
1.37
1.35
1.34
1.29
1.27
1.27
1.25
1.24
1.23
1.23
1.21
1.21
1.20
1.19
1.18
0.84
0.83
0.82
0.81
0.80
0.79
0.00
C10H21
C8H17
O
N
O
O
N
C10H21
C8H17
2.00
2.00
2.00
2.00
2.00
4.00
4.00
2.07
64.07
12.02
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ（ppm）

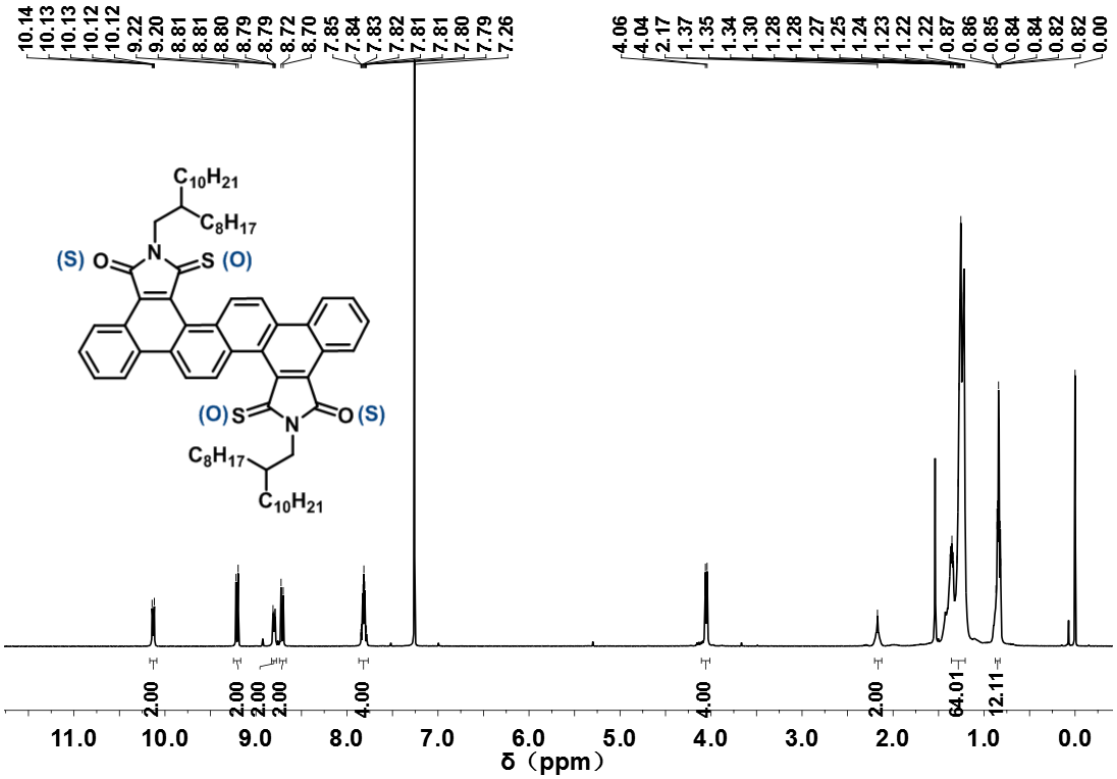

169.0
168.8
133.1
133.1
131.3
130.8
129.9
129.7
128.8
127.8
127.7
127.5
126.4
124.2
123.8
121.1
120.7
77.4 CDCl3
77.0 CDCl3
76.7 CDCl3
42.5
37.1
31.9
31.9
31.6
30.2
29.7
29.7
29.7
29.4
29.4
26.4
22.7
22.7
14.1
C10H21
C8H17
O
N
O
O
N
C10H21
C8H17
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ（ppm）

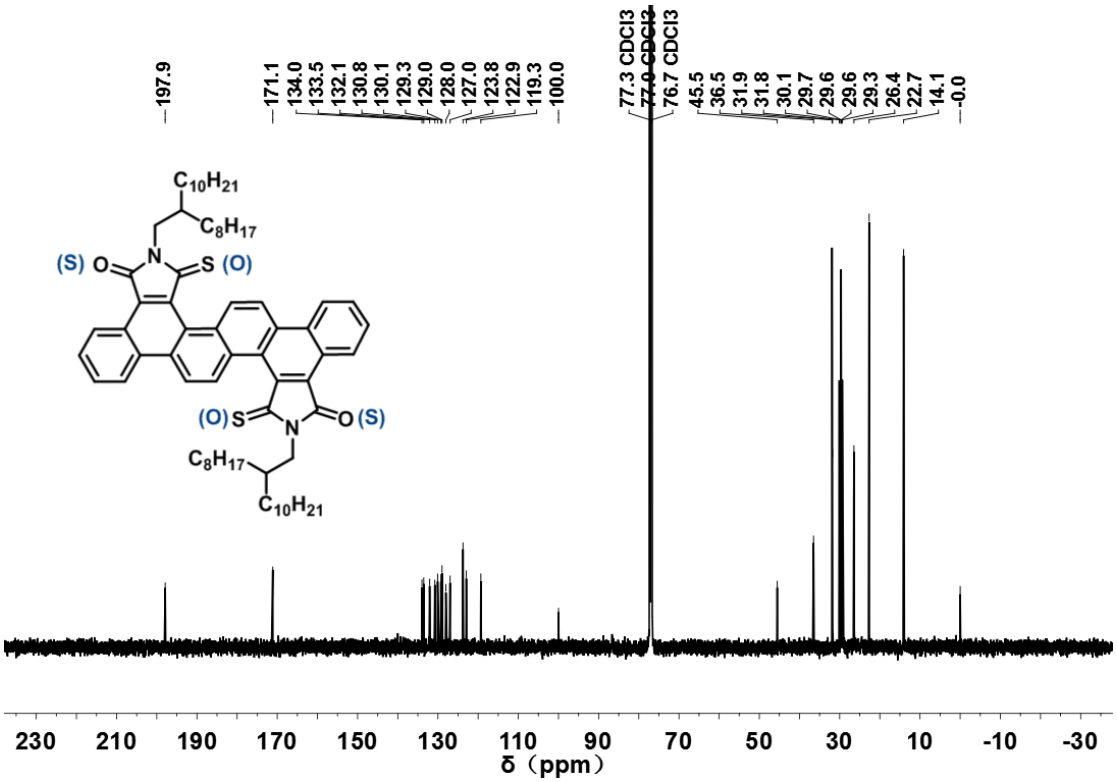
15:


7.90
7.88
7.84
7.82
7.43
7.25
3.59
3.57
1.89
1.54
1.33
1.30
1.28
1.26
1.24
0.88
0.88
0.87
0.86
0.85
0.84
0.00
Br
Br
7.95
7.90
7.85
7.80
2.00
2.00
12.90
4.00
2.00
64.37
12.17
0.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ（ppm）

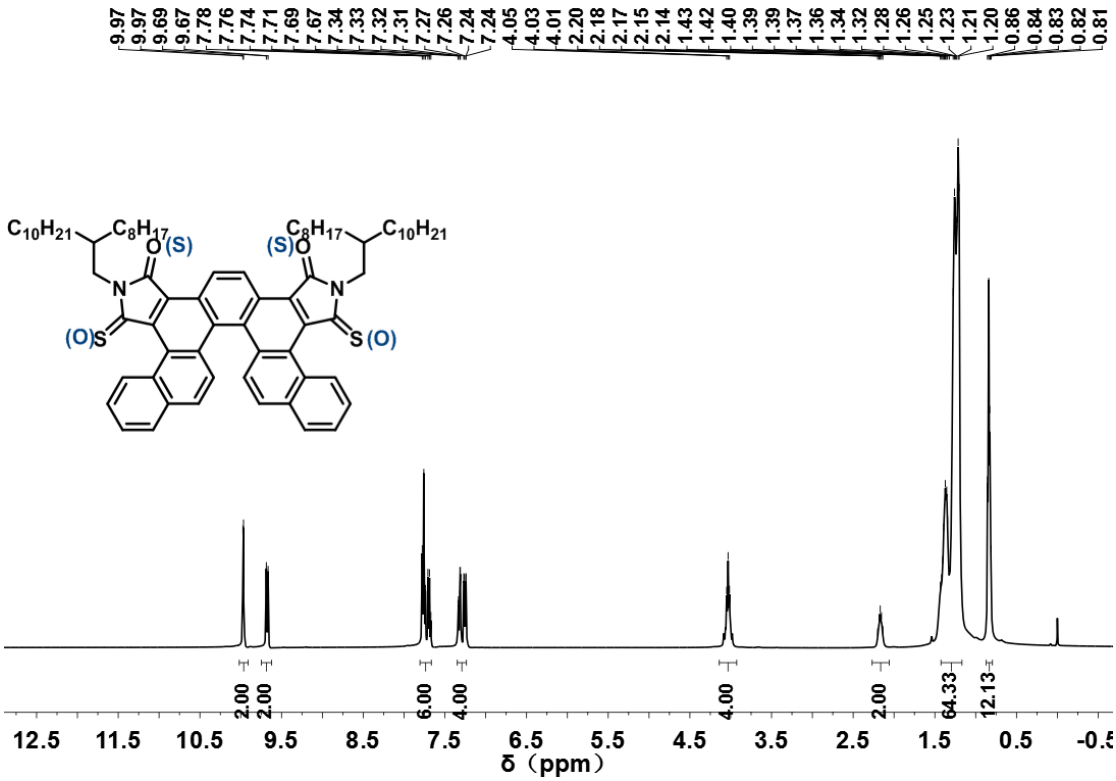

170.0
168.9
141.5
137.9
135.0
133.6
133.3
130.9
130.6
128.6
126.3
125.8
125.2
125.1
122.1
77.4 CDCl3
77.2 CDCl3
77.0 CDCl3
76.7 CDCl3
43.1
37.0
31.9
31.7
30.0
29.7
29.7
29.6
29.6
29.4
26.4
22.7
14.1
Br
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ（ppm）

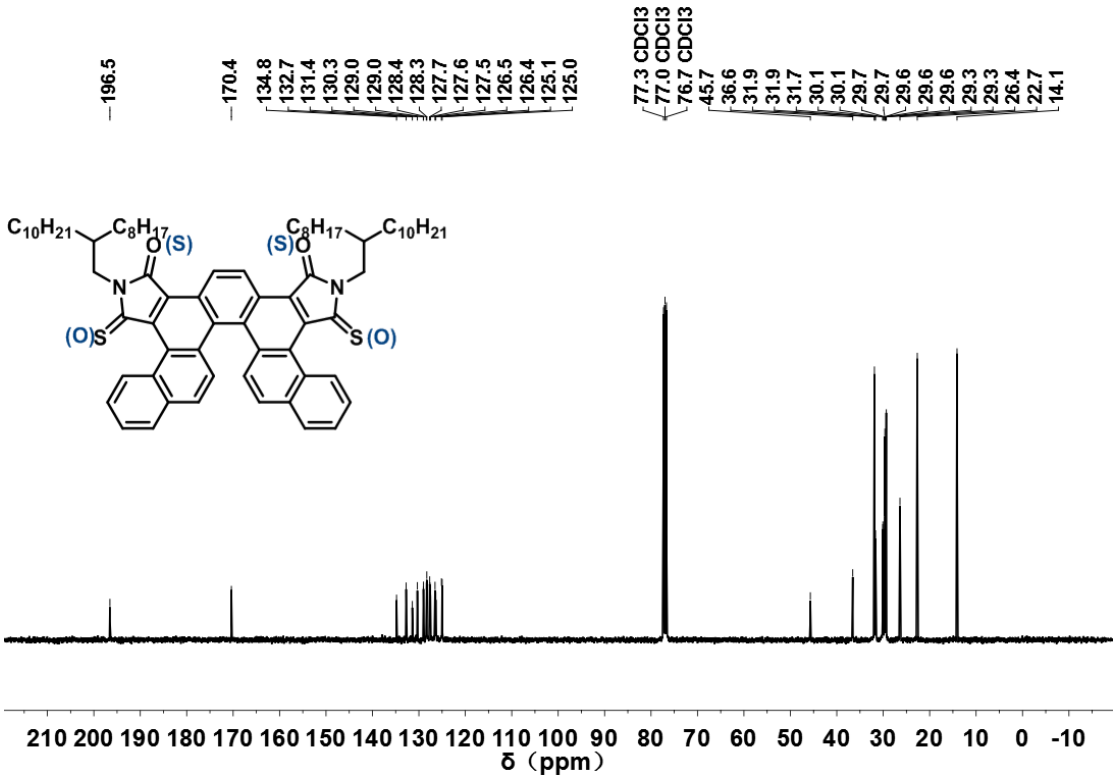
6-S:


10.14
10.13
10.13
10.12
10.12
9.22
9.20
8.81
8.81
8.80
8.79
8.79
8.72
8.70
7.85
7.84
7.83
7.82
7.81
7.81
7.80
7.79
7.26
4.06
4.04
2.17
1.37
1.35
1.34
1.30
1.28
1.28
1.27
1.25
1.24
1.23
1.22
1.22
0.87
0.86
0.85
0.84
0.84
0.82
0.82
0.00
2.00
2.00
2.00
2.00
4.00
4.00
2.00
64.01
12.11
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ（ppm）

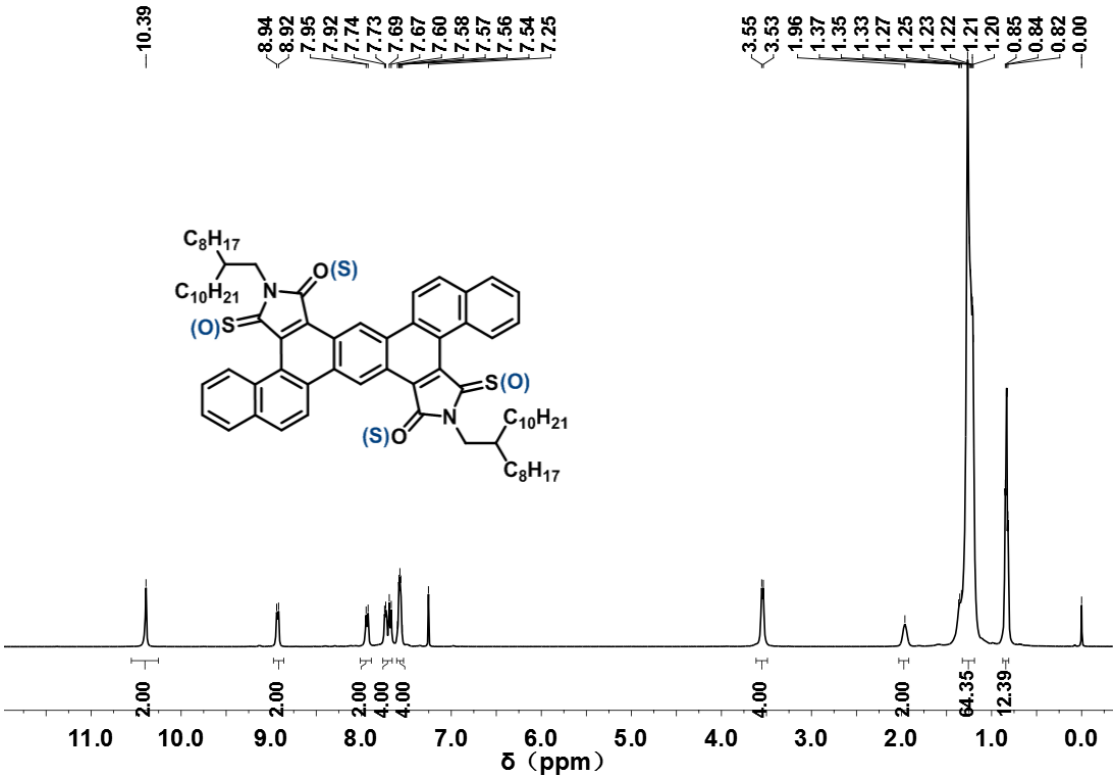

197.9
171.1
134.0
133.5
132.1
130.8
130.1
129.3
129.0
128.0
127.0
123.8
122.9
119.3
100.0
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
45.5
36.5
31.9
31.8
30.1
29.7
29.6
29.6
29.3
26.4
22.7
14.1
-0.0
230
210
190
170
150
130
110
90
70
50
30
10
-10
-30
δ（ppm）

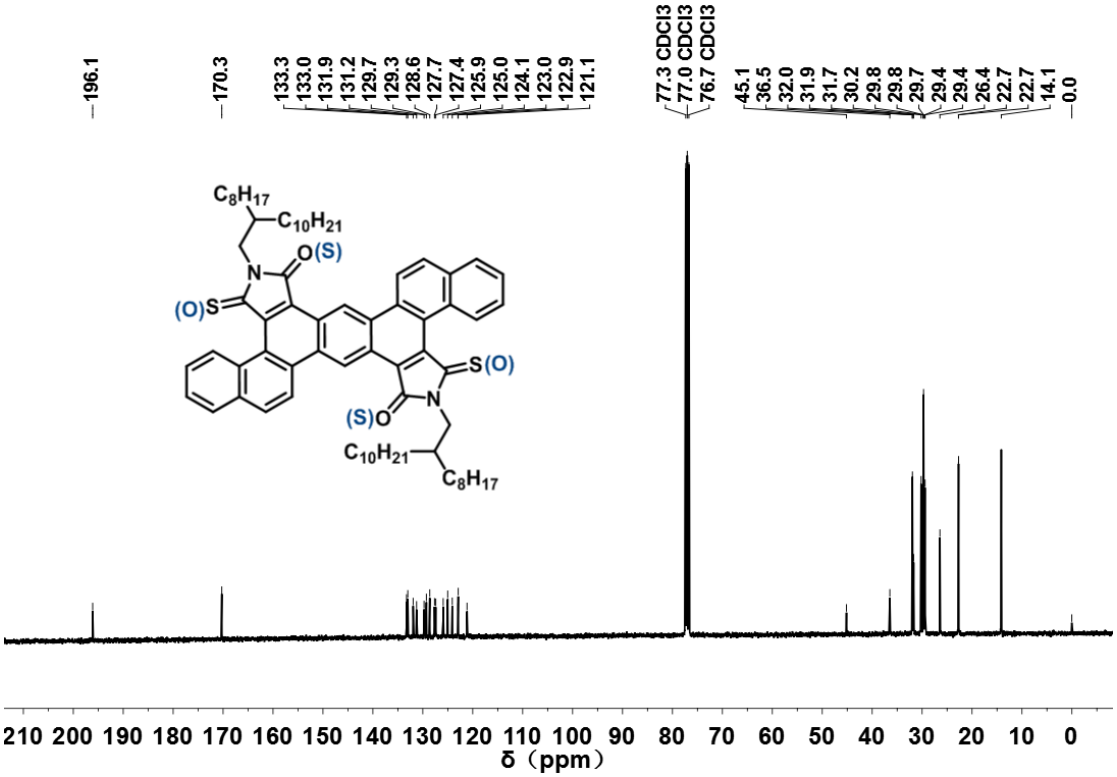
7-S:


9.97 9.97 9.69 9.67 7.78 7.76 7.74 7.71 7.69 7.67 7.34 7.33 7.32 7.31 7.27 7.26 7.24 7.24 4.05 4.03 4.01 2.20 2.18 2.17 2.15 2.14 1.43 1.42 1.40 1.39 1.39 1.37 1.36 1.34 1.32 1.28 1.26 1.25 1.23 1.21 1.20 0.86 0.84 0.83 0.82 0.81
C10H21 C8H17 O (S) (S) O C8H17 C10H21
N N
(O)S S (O)
2.00 2.00 6.00 4.00 4.00 2.00 64.33 12.13
12.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
δ（ppm）


196.5 170.4 134.8 132.7 131.4 130.3 129.0 129.0 128.4 128.3 127.7 127.6 127.5 126.5 126.4 125.1 125.0
77.3 CDCl3 77.0 CDCl3 76.7 CDCl3
45.7 36.6 31.9 31.9 31.7 30.1 30.1 29.7 29.7 29.6 29.6 29.6 29.3 29.3 26.4 22.7 14.1
C10H21 C8H17 O (S) (S) O C8H17 C10H21
N N
(O)S S (O)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ（ppm）

8-S:


10.39
8.94
8.92
7.95
7.92
7.74
7.73
7.69
7.67
7.60
7.58
7.57
7.56
7.54
7.25
3.55
3.53
1.96
1.37
1.35
1.33
1.27
1.25
1.23
1.22
1.21
1.20
0.85
0.84
0.82
0.00
C8H17
C10H21
O(S)
(O)S
S(O)
(S)O
2.00
2.00
2.00
4.00
4.00
4.00
2.00
64.35
12.39
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ（ppm）


196.1
170.3
133.3
133.0
131.9
131.2
129.7
129.3
128.6
127.7
127.4
125.9
125.0
124.1
123.0
122.9
121.1
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
45.1
36.5
32.0
31.9
31.7
30.2
29.8
29.8
29.7
29.4
29.4
26.4
22.7
22.7
14.1
0.0
C8H17
C10H21
O(S)
(O)S
S(O)
(S)O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ（ppm）