Supporting Information for:

Covalently Linked Perylenetetracarboxylic Diimide Dimers and Trimers with Rigid "J-type" Aggregation Structure

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Contents

1. Synthesis and characterization of these compounds.

1.1 Materials:

1,7-Di(4-tert-butyl)phenoxyl-perylene-9,10-(N-hexyl)-dicarboxylic imide-3,4-dicarboxylic anhydride (**7**),[S1] 1,7-di(p-tert-butylphenoxy)perylene-3,4:9,10-tetracarboxylic dianhydride (**10**),[S2] 4-Bromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene (**1**),[S3] 4-ethynylaniline, [S4] **4** and **6**[S5-S6] were prepared following the literature methods and fully characterized by ^{1}H NMR and MALDI-TOF or ESI mass spectra. All other chemicals were purchased from commercial source. Solvents were analytical grades.

Compound 2: Method A: To a suspension of **1**[S3] (401 mg, 1 mmol) in acetic acid (50 mL) was added dropwise a mixture of fuming nitric acid (50 ml) and acetic acid (50 mL) over 1 h. The resulted reaction mixture was stirred continuously for 42 h at room temperature. Then the reaction mixture was poured into lots of water. Precipitates were collected by filtration. After washed with water for several times, the solid was dried at room temperature in vacuum. The solid was purified by column chromatography on silica gel (petroleum ether/chloroform=1.7:1) to give **2** as a orange solid (210 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$, 25℃, TMS): 7.80 (d, 1H), 7.66 (d, 1H), 7.51 (d, 1H), 7.36 (d, 1H), 1.68 (s, 6H), 1.38 (s, 9H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): 148.1, 146.1, 144.3, 141.8, 138.4, 132.6, 130.4, 128.9, 127.3, 121.5, 120.5, 110.5, 35.5, 34.8, 34.7, 32.1, 31.9, 31.5, 31.4, 31.2, 30.9; MS (ESI): m/z： calcd: 445.13; found: 446.13 [M+H$^+$]; Elemental analysis (%), calculated for $C_{23}H_{28}BrNO_3$: C 61.89, H 6.32, N 3.14; found: C 61.74, H 6.28, N 3.10.

Method B: Compound **2** was also synthesized by the nitration of **1** with $SiO_2 \cdot HNO_3$ according to a literature procedure.[S5a] Over a stirred suspension of HNO_3 (1.03 g, 0.5 mmol, 25% on SiO_2) in 40 ml of CH_2Cl_2, **1** (401 mg, 1

mmol) in 10 ml of CH_2Cl_2 was rapidly added. The resulting solution was stirred at room temperature for 15 min, and then SiO_2 was separated from the solution by filtration and washed for several times with CH_2Cl_2. The combined solution was evaporated to dry under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/chloroform=1.7:1) to give **2** as orange solid (165 mg, 37%).

Compound 3: Under the protection of nitrogen, a mixture of **2** (446 mg, 1 mmol), 4-aminophenylboric acid (164 mg, 1.2 mmol), sodium tert-butoxide (192 mg, 2 mmol), tetrakis(triphenylphosphine) palladium (5.78 mg, 0.005 mmol), and DMF (50 ml) was heated to 90°C for 10 h. Upon cooling, 200 mL water was added. The mixture was extracted with dichloromethane for three times (3×50 mL) and organic phase were combined and dried over $MgSO_4$ for over night. After removing the solvents under reduced pressure, the crude solid was purified by column chromatography on silica gel (petroleum ether/chloroform=1.5:1) to give **3** as a yellow solid (320 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$, 25℃, TMS): 7.66 (d, 1H), 7.63 (d, 1H), 7.40 (m, 2H), 7.35 (d, 1H), 7.28 (d, 1H), 6.80 (d, 2H), 1.70 (s, 6H), 1.35 (d, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): 146.6, 145.5, 145.3, 144.3, 142.2, 138.5, 132.9, 130.9, 129.7, 129.0, 127.7, 127.1, 126.4, 120.7, 120.1, 114.8, 35.1, 34.7, 34.6, 32.2, 31.5, 31.2. MS (ESI): m/z： calcd: 458.59; found: 459.26 [M+H$^+$], 481.24 [M+Na$^+$]; Elemental analysis (%), calculated for $C_{29}H_{34}N_2O_3$: C 75.95, H 7.47, N 6.11; found: C 75.81, H 7.38, N 6.02.

Compound 5: [S7] Following the Sonogashira coupling protocol, **2** (446.0 mg, 1.0 mmol), 4-ethynylaniline (140.0 mg, 1.2 mmol), $PdCl_2(PPh_3)_2$ (35.5 mg, 0.05 mmol), and CuI (19.1 mg, 0.1 mmol) were dissolved in triethylamine (100 ml). The solution was bubbled with N_2 for 10 min, then the resulting solution

was heated to 80°C and stirred at this temperature for overnight. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (CH_2Cl_2). **5** is collected as a yellow solid (246 mg, 51%). ^{1}H NMR (300 MHz, $CDCl_3$, 25℃, TMS): 7.80 (d, 1H), 7.64 (d, 1H), 7.55 (m, 2H), 7.42 (d, 1H), 7.32(d, 1H), 6.68 (m, 2H), 1.66 (s, 6H), 1.36 (s, 9H), 1.33 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): 147.4, 146.7, 146.5, 145.6, 142.0, 138.3, 133.4, 132.7, 128.7, 128.2, 127.4, 121.8, 120.5, 114.8, 112.9, 112.4, 95.1, 82.7, 34.9, 34.7, 34.5, 32.1, 31.4, 31.2; MS (ESI): m/z： calcd: 482.61; found: 483.26 [M+H$^+$], 505.24 [M+Na$^+$]; Elemental analysis (%), calculated for $C_{31}H_{34}N_2O_3$: C 77.15, H 7.10, N 5.80; found: C 77.21, H 7.18, N 5.71.

Compound 8: A mixture of **7** (77.2 mg, 0.1 mmol), **3** (45.8 mg, 0.1 mmol), and imidazole (0.5 g, 7.4 mmol) in toluene (50 ml) was refluxed under N_2 for 12 h. After the solvent was evaporated under reduced pressure, the residue was dissolved in chloroform and washed with water for several times to remove imidazole. The chloroform was then removed under reduced pressure. The residue was purified by column chromatography on silica gel using CH_2Cl_2 as the eluent. **8** was collected as a red solid (97.0 mg, 80%). M.p. > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25℃, TMS): 9.60 (d, 2H), 8.64 (d, 1H), 8.56 (d, 1H), 8.40 (s, 1H), 8.34 (s, 1H), 7.76 (d, 2H), 7.67 (d, 1H), 7.64 (d, 1H), 7.49-7.44 (m, 7H), 7.39 (d, 1H), 7.14-7.10 (m, 4H), 4.15 (t, 2H), 1.73 (s, 6H), 1.67 (m, 2H), 1.45-1.30 (m, 42H), 0.88 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 163.5, 163.3, 163.0, 155.7, 155.5, 152.6, 152.5, 148.3, 148.2, 146.8, 145.5, 144.3, 141.9, 138.5, 137.8, 134.0, 133.7, 133.6, 132.7, 130.9, 130.4, 130.1, 129.4, 129.3, 129.2, 128.9, 128.1, 127.5, 127.4, 127.1, 126.9, 125.3, 125.0, 124.1, 124.0, 123.9, 123.8, 123.7, 122.5, 122.2, 121.9, 120.2, 119.3, 119.1, 40.9, 35.1,

34.7, 34.6, 34.5, 32.3, 31.5, 31.4, 31.2, 28.0, 26.8, 22.5, 14.0; MS (MALDI-TOF): *m/z*: calcd: 1211.57; found: 1212.58 [M+H$^+$], 1234.56 [M+Na$^+$]; Elemental analysis (%). calculated for $C_{79}H_{77}N_3O_9$: C 78.26, H 6.40, N 3.47; found: C 78.15, H 6.28, N 3.54.

Compound 9: Method C:[S5-S6] Compound **8** (121.2 mg, 0.10 mmol), $NH_2NH_2{\cdot}H_2O$ (5.0 mg, 0.067 mmol), and graphite (excess) were heated in refluxing EtOH (50 ml) for 24 h under N_2 atmosphere. The cooled mixture was diluted with CH_2Cl_2 (50 ml). Graphite was filtered and washed for several times with CH_2Cl_2. The solution was concentrated in a rotary evaporator. The residue was purified by column chromatography on silica gel using CH_2Cl_2 as the eluent. **9** was collected as a violet solid (106.4 mg, 90%). M.p. > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25℃, TMS): 9.56 (m, 2H), 8.61 (d, 1H), 8.53 (d, 1H), 8.35 (s, 1H), 8.30 (s, 1H), 7.81 (d, 2H), 7.49-7.41 (m, 7H), 7.30 (d, 1H), 7.12-7.07 (m, 4H), 6.79 (s, 1H), 6.60 (s, 1H), 4.14 (t, 2H), 1.73 (m, 2H), 1.64 (s, 6H), 1.37-1.25 (m, 42H), 0.88 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 163.5, 163.2, 163.1, 162.9, 155.6, 152.5, 152.4, 148.4, 148.3, 145.8, 145.3, 145.2, 139.5, 133.8, 133.3, 130.6, 130.4, 130.0, 129.5, 129.3, 129.2, 128.9, 128.8, 128.3, 128.0, 127.5, 125.7, 125.3, 124.9, 123.9, 123.8, 123.7, 123.6, 122.4, 122.3, 122.2, 119.3, 119.1, 40.7, 34.9, 34.5, 34.4, 31.8, 31.6, 31.5, 28.0, 26.8, 22.5, 14.0; MS (MALDI-TOF): *m/z*: calcd: 1183.60; found: 1184.20 [M+H$^+$]; Elemental analysis (%), calculated for $C_{79}H_{79}N_3O_7$: C 80.24, H 6.73, N 3.55; found: C 80.34, H 6.61, N 3.64.

Method D: To a solution of **8** (121.2 mg, 0.10 mmol) in ethanol (10 mL) was added a mixture of HCl (36%, 0.3 ml) and $SnCl_2{\cdot}2H_2O$ (102 mg, 0.45 mmol) in ethanol (10 mL) at room temperature in 1 h.[14C] After refluxing for 24 h, the solvent was evaporated under reduced pressure, the residue was dissolved in

chloroform and extracted with chloroform for several times. And the chloroform phase was washed with diluted NaOH aqueous solution until pH ≥11 was reached. The chloroform was then removed under reduced pressure. The residue was purified by column chromatography on silica gel using CH_2Cl_2 as the eluent. **9** was collected as a violet solid (99.4 mg, 84%).

Compound 11: By using a similar procedure to that for preparing compound **8**, with **5** (42.8 mg, 0.1 mmol) instead of **3** as starting material, compound **11** was synthesized. The product was purified by column chromatography on silica gel using dichloromethane as the eluent. **11** was collected as a red solid (98.8 mg, 80%). M.p. > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25℃, TMS): 9.61 (m, 2H), 8.63 (d, 1H), 8.56 (d, 1H), 8.38 (s, 1H), 8.34 (s, 1H), 7.90 (d, 2H), 7.79 (d, 1H), 7.65 (d, 1H), 7.49-7.46 (m, 5H), 7.40 (d, 1H), 7.36 (d, 2H), 7.11 (m, 4H), 4.14 (t, 2H), 1.68 (m, 8H), 1.41-1.25 (m, 42H), 0.88 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 163.4, 163.3, 163.0, 155.6, 155.5, 152.6, 152.5, 148.3, 148.2, 147.8, 146.6, 145,7 141.8, 138.4, 134.6, 133.8, 133.4, 132.9, 132.5, 130.5, 130.1, 129.4, 129.3, 129.0, 128.9, 128.7, 127.5, 127.3, 125.4, 124.9, 124.2, 124.0, 123.8, 123.7, 122.9, 122.2, 120.5, 119.3, 119.1, 111.6, 85.5, 93.5, 41.0, 35.0, 34.8, 34.6, 32.2, 31.5, 31.4, 31.2, 29.7, 28.0, 26.8, 22.5, 14.0; MS (MALDI-TOF): *m/z*: calcd: 1236.49; found: 1237.80 [M+H$^+$]; Elemental analysis (%), calculated for $C_{81}H_{77}N_3O_9$**:** C 78.68, H 6.28, N 3.40; found: C 78.60, H 6.19, N 3.57**.**

Compound 12: was synthesized according to the above method C from compound **11** (123.6 mg, 0.10 mmol). The product was purified by column chromatography on silica gel using dichloromethane as the eluent. **12** was collected as a violet solid (108.5 mg, 90%). M.p. > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25℃, TMS): 9.58 (m, 2H), 8.56 (d, 2H), 8.32 (d, 2H), 7.74 (d,

2H), 7.49-7.46 (m, 4H), 7.41 (m, 2H), 7.33 (d, 2H), 7.10 (m, 4H), 6.85 (s, 1H), 6.80 (s, 1H), 4.14 (t, 2H), 1.72 (m, 2H), 1.63 (s, 6H), 1.45-1.29 (m, 42H), 0.88 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 163.4, 163.3, 163.0, 162.9, 155.6, 155.5, 152.5, 152.4, 148.9, 148.4, 148.3, 146.1, 145.2, 134.6, 133.9, 133,3, 132.5, 130.5, 130.0, 129.4, 129.2, 129.0, 128.8, 127.7, 127.5, 125.3, 124.9, 124.4, 124.1, 124.0, 123.9, 123.8, 123.6, 123.5, 122.3, 122.0, 119.2, 119.1, 92.5, 87.0, 41.0, 34.8, 34.6, 34.5, 31.9, 31.5, 31.4, 28.0, 26.8, 22.5, 14.0; MS (MALDI-TOF): *m/z*: calcd: 1207.60; found: 1208.49 [M+H$^+$]; Elemental analysis (%), calculated for $C_{31}H_{34}N_2O_3$: C 80.63, H 6.60, N 3.48; found: C 80.77, H 6.72, N 3.40.

This compound was also synthesized according to method D from compound **11** (123.6 mg, 0.10 mmol). After purification, Compound **12** was collected as a violet solid (103.8 mg, 86%).

D_1: A mixture of **7** (155 mg, 0.2 mmol), **4** (42.8 mg, 0.1 mmol), and imidazole (0.5 g, 7.4 mmol) in toluene (50 mL) was refluxed under N_2 for 12 h. After the solvent was evaporated under reduced pressure, the residue was dissolved in chloroform and washed with water for several times to remove imidazole. The chloroform was then removed under reduced pressure. The residue was purified by column chromatography on silica gel using $CHCl_3$ as the eluent. After recrystallization from chloroform and methanol, **D_1** was collected as a red solid (34.8mg, 18%). M.p. > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25℃, TMS): 9.55 (d, 1H; perylene), 9.30 (m, 3H; perylene), 8.60 (m, 2H; perylene), 8.35 (s, 1H; perylene), 8.25 (d, 2H; perylene), 8.16 (d, 1H; perylene), 8.04 (s, 1H; perylene), 7.84 (s, 1H; perylene), 7.59 (d, 2H; phenyl), 7.56 (s, 2H; xanthene), 7.54-7.32 (m, 12H; phenoxyl), 7.14 (s, 2H; xanthene), 7.09-7.01 (m, 4H; phenoxyl), 6.22 (d, 2H; phenyl), 4.16 (t, 2H; NCH_2), 2.87

(m, 1H; NCH_2), 2.73 (m, 1H; NCH_2), 1.75 (m, 8H; xanthene(CH_3)+CH_2), 1.43-1.32 (m, 60H; xanthene(t-butyl)+phenyl(t-butyl)+CH_2), 1.21-1.05 (m, 8H; CH_2), 0.90 (t, 3H; CH_3), 0.80 (t, 3H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): 163.2, 163.1, 163.0, 162.9, 162.2, 161.8, 161.6, 156.7, 156.5, 154.8, 154.3, 152.6, 152.4, 152.1, 148.7, 148.1, 145.6, 144.2, 143.6, 138.4, 133.5, 133.4, 133.0, 132.7, 132.2, 130.3, 130.2, 129.9, 129.8, 129.7, 129.2, 129.0, 128.6, 128.4, 128.1, 128.0, 127.7, 127.6, 127.4, 127.3, 127.1, 125.3, 124.7, 124.6, 124.3, 124.1, 123.7, 123.5, 123.0, 122.8, 122.6, 122.3, 122.2, 122.1, 121.6, 121.1, 121.0, 120.5, 120.3, 119.0, 118.9, 40.7, 39.3, 34.8, 34.7, 34.6, 34.5, 33.8, 32.7, 31.6, 31.5, 31.2, 28.2, 27.3, 26.9, 26.5, 22.6, 22.4, 14.0, 13.9; MS (MALDI-TOF): *m/z*: calcd: 1937.37; found: 1938.97 [M+H^+]; Elemental analysis (%), calculated for $C_{129}H_{122}N_4O_{13}$: C 80.01, H 6.35, N 2.89; found: C 79.89, H 6.29, N 2.81.

D_2: By using a similar procedure to that for preparing **D_1**, with **6** (45.2 mg, 0.1 mmol) instead of **4** as starting material, JD_2 was synthesized. The product was purified by column chromatography on silica gel using chloroform as the eluent. After recrystallization from chloroform and methanol, **D_2** was collected as a red solid (39.2mg, 20%). M.p. > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25℃, TMS): 9.67 (d, 1H; perylene), 9.45 (m, 3H; perylene), 8.62 (q, 2H; perylene), 8.39 (s, 1H; perylene), 8.31 (s, 1H; perylene), 8.10 (q, 2H; perylene), 7.96 (s, 1H; perylene), 7.92 (s, 1H; perylene), 7.53 (m, 3H; phenoxyl+xanthene), 7.48-7.42 (m, 6H), 7.29 (m, 3H; phenoxyl+xanthene), 7.17-7.10 (m, 7H; phenoxyl+xanthene), 7.01 (d, 1H; xanthene),6.68 (d, 2H; phenyl), 6.48 (d, 2H; phenyl), 4.16 (t, 2H; NCH_2), 2.94 (t, 2H; NCH_2), 1.70 (m, 8H; xanthene(CH_3)+CH_2), 1.40-1.31 (m, 60H; xanthene(t-butyl)+phenyl(t-butyl)+CH_2), 1.10(m, 3H; CH_3), 0.90 (m, 8H CH_2), 0.73 (t, 3H; CH_3); ^{13}C

NMR (75 MHz, CDCl3): 163.3, 163.0, 162.9, 162.8, 162.2, 162.0, 161.9, 156.3, 156.2, 155.3, 155.1, 152.7, 152.6, 152.5, 148.4, 148.3, 148.2, 148.1, 145.7, 145.4, 144.5, 142.2, 133.6, 133.5, 131.5, 131.1, 130.2, 130.1, 129.9, 129.7, 129.5, 129.4, 129.3, 129.2, 129.0, 128.9, 128.7, 128.0, 127.8, 127.6, 127.5, 127.4, 125.3, 124.8, 124.5, 124.4, 124.2, 124.0, 123.9, 123.8, 123.7, 123.6, 123.5, 123.4, 123.3, 123.0, 122.9, 122.4, 122.3, 121.7, 121.3, 121.2, 120.5, 120.0, 119.8, 119.1, 40.7, 39.5, 35.7, 34.9, 34.6, 34.5, 32.6, 32.0, 31.9, 31.6, 31.5, 30.88, 29.7，28.0, 27.2, 26.8, 26.4, 22.5, 22.3, 14.1, 13.9; MS (MALDI-TOF): m/z: calcd: 1960.39; found: 1961.24 [M+H^+]; Elemental analysis (%), calculated for $C_{131}H_{122}N_4O_{13}$: C 80.26, H 6.27, N 2.86; found: C 80.13, H 6.18, N 2.94.

T_1: A mixture of **9** (236 mg, 0.2 mmol), **10** (68.8 mg, 0.1 mmol), and imidazole (1.0 g, 14.8 mmol) in toluene (50 mL) was refluxed under N_2 for 12 h. After the solvent was evaporated under reduced pressure, the residue was dissolved in chloroform and washed with water for several times to remove imidazole. The chloroform was then removed under reduced pressure. The residue was purified by column chromatography on silica gel using $CHCl_3$ as the eluent. After recrystallization from chloroform and methanol, **T_1** was collected as a red solid (42.2 mg, 14%). M.p. > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25℃, TMS): 9.41(d, 2H; perylene), 9.36(d, 2H; perylene), 9.15(d, 2H; perylene), 8.32(d, 2H; perylene), 8.30(s, 2H; perylene), 8.22(dd, 4H; perylene), 7.82(s, 2H; perylene), 7.50(s, 2H; xanthene), 7.48(s, 2H; perylene), 7.45(d, 4H; phenyl), 7.36(s, 2H; xanthene), 7.31(t, 8H; phenoxyl), 7.22-7.14 (m, 8H; phenoxyl), 7.04 (s, 2H; xanthene), 6.96 (s, 2H; xanthene), 6.90 (t, 8H; phenoxyl), 6.12 (d, 4H; phenyl), 4.08 (t, 4H; NCH_2), 1.73-1.64 (m, 16H; xanthene(CH_3)+CH_2), 1.35-1.22 (m, 102H; xanthene(t-butyl)+phenyl(t-

butyl)+CH_2), 0.89 (t, 6H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): 163.1, 162.9, 162.5, 162.4, 162.1, 161.6, 155.8, 155.6, 154.2, 152.9, 152.7, 152.6, 148.2 147.9, 147.7, 145.5, 145.1, 144.4, 143.8, 138.5, 135.5, 133.9, 133.2, 132.7, 132.3, 130.3, 130.2, 129.6, 129.5, 129.3, 129.0, 128.2, 127.7, 127.5, 127.4, 127.3, 127.0, 126.3, 125.2, 125.1, 125.0, 124.9, 124.7, 124.4, 124.1, 123.8, 123.6, 123.4, 123.3, 123.1, 122.9, 122.5, 122.4, 122.2, 121.5, 121.4, 119.4, 119.3, 118.1, 40.5, 34.8, 34.6, 34.4, 33.1, 32.3, 31.5, 31.4, 28.0, 26.8, 22.5, 14.0; MALDI-TOF: *m/z*: calcd: 3017.67 ; found: 3058.72 [M+K^+]; Elemental analysis (%), calculated for $C_{202}H_{186}N_6O_{20}$: C 80.40, H 6.21, N 2.78; found: C 80.51, H 6.38, N 2.65.

T_2: By using a similar procedure to that for preparing **T_1**, with **12** (241 mg, 0.2 mmol) instead of **9** as starting material, **T_2** was synthesized. The product was purified by column chromatography on silica gel using chloroform as the eluent. After recrystallization from chloroform and methanol, **T_2** was collected as a red solid (39.8 mg, 13%). M.p. > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25℃, TMS): 9.61(d, 1H; perylene), 9.58(d, 1H; perylene), 9.54(d, 2H; perylene), 9.50(d, 1H; perylene), 9.38 (d, 1H; perylene), 8.51 (d, 1H; perylene), 8.40(d, 2H; perylene), 8.37(d, 2H; perylene), 8.33(s, 1H; perylene), 8.21(s, 2H; perylene), 8.17(d, 1H; perylene), 8.16(s, 1H; perylene), 8.11(s, 1H; perylene), 7.50(s, 1H; perylene), 7.40(dd, 4H; xanthene), 7.35-7.28(m, 13H; phenoxyl+xanthene), 7.08-6.98(m, 10H; phenoxyl+xanthene), 6.92(d, 2H; phenyl), 6.82(d, 2H; phenyl), 6.74(s, 1H; xanthene), 6.62-6.58(m, 6H; phenoxyl+phenyl), 6.43(d, 2H; phenyl), 4.13 (m, 4H; NCH_2), 1.69-1.61 (m, 16H; xanthene(CH_3)+CH_2), 1.35-1.14 (m, 102H; xanthene(t-butyl)+phenyl(t-butyl)+CH_2), 0.89 (t, 6H; CH_3); ^{13}C NMR (75 MHz, $CDCl_3$):163.4, 163.0, 162.7, 162.5, 162.4, 156.0, 155.8, 155.3, 155.1, 153.0, 152.7, 152.5, 152.3,

148.2, 148.1, 148.0, 147.9, 147.8, 147.5, 147.4, 145.7, 145.4, 145.2, 133.7, 133.4, 131.2, 130.6, 130.3, 130.0, 129.8, 129.7, 129.6, 129.3, 129.0, 128.8, 128.3, 127.9, 127.4, 127.2, 127.1, 125.3, 125.2, 124.9, 124.8, 124.5, 123.9, 123.8, 123.6, 123.5, 123.4, 123.3, 122.9, 122.1, 121.9, 121.7, 119.9, 119.4, 119.1, 118.6, 118.5, 110.6, 92.0, 91.8, 87.1, 40.6, 34.8, 34.5, 34.4, 34.2, 31.5, 31.4, 31.2, 31.1, 29.7, 28.0, 26.8, 26.7, 22.6, 14.1; MS (MALDI-TOF): *m/z*: calcd: 3065.71; found: 3065.17 $[M]^+$; Elemental analysis (%), calculated for $C_{206}H_{186}N_6O_{20}$: C 80.71, H 6.12, N 2.74; found: C 80.59, H 6.24, N 2.65.

2. Copies of the ^{1}H NMR spectra, ^{13}C NMR spectra and MALDI-TOF or ESI-MS spectra of the new compounds.

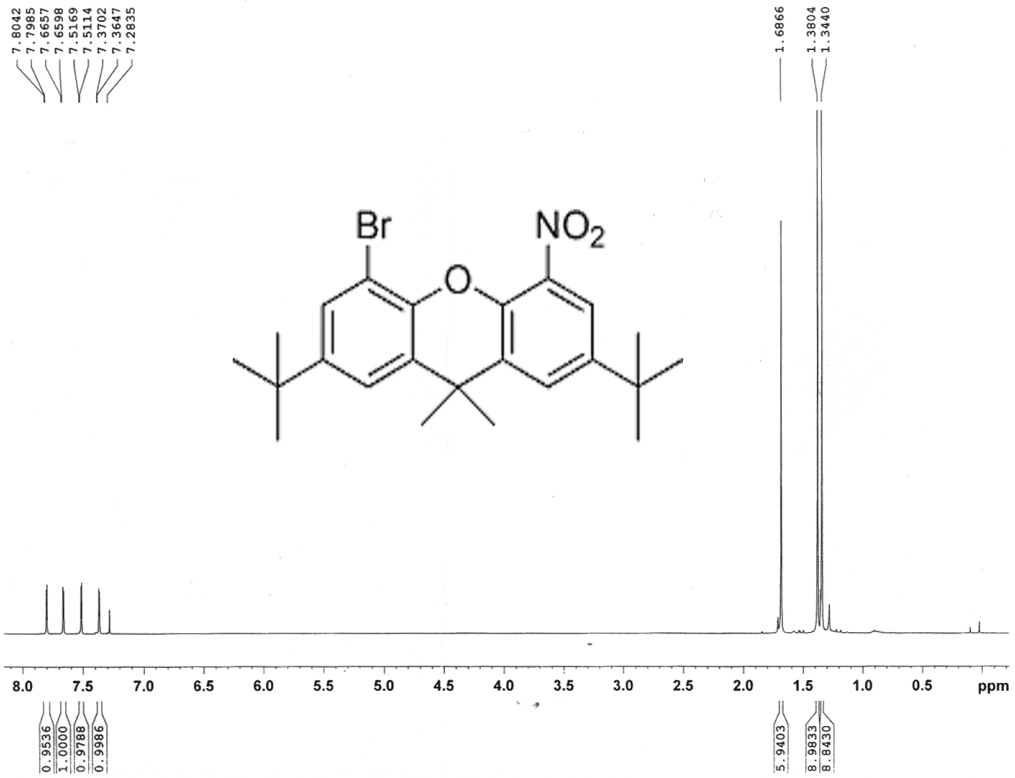

Figure S1. ^{1}H NMR spectrum of compound **2** in $CDCl_3$

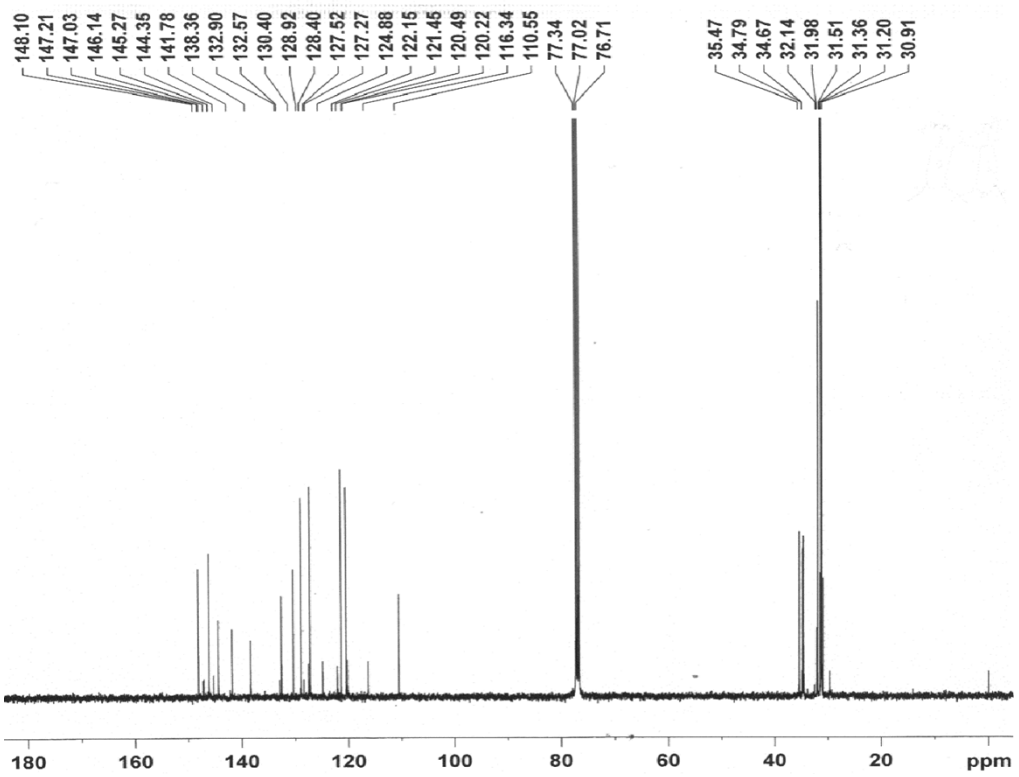

Figure S2. ^{13}C NMR spectrum of compound **2** in $CDCl_3$

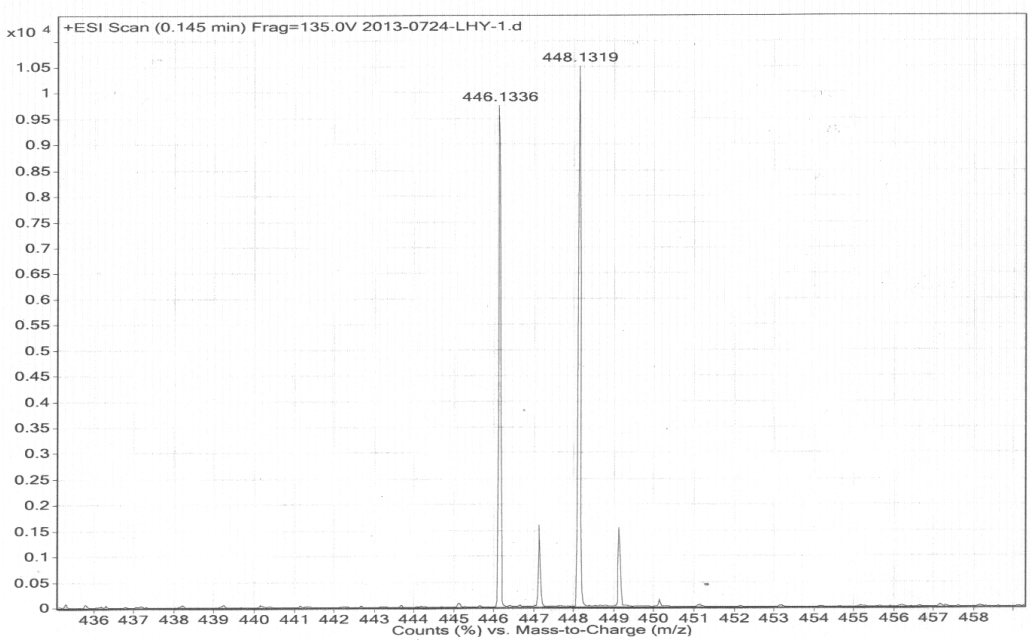

Figure S3. ESI-MS spectra of Compound **2**.

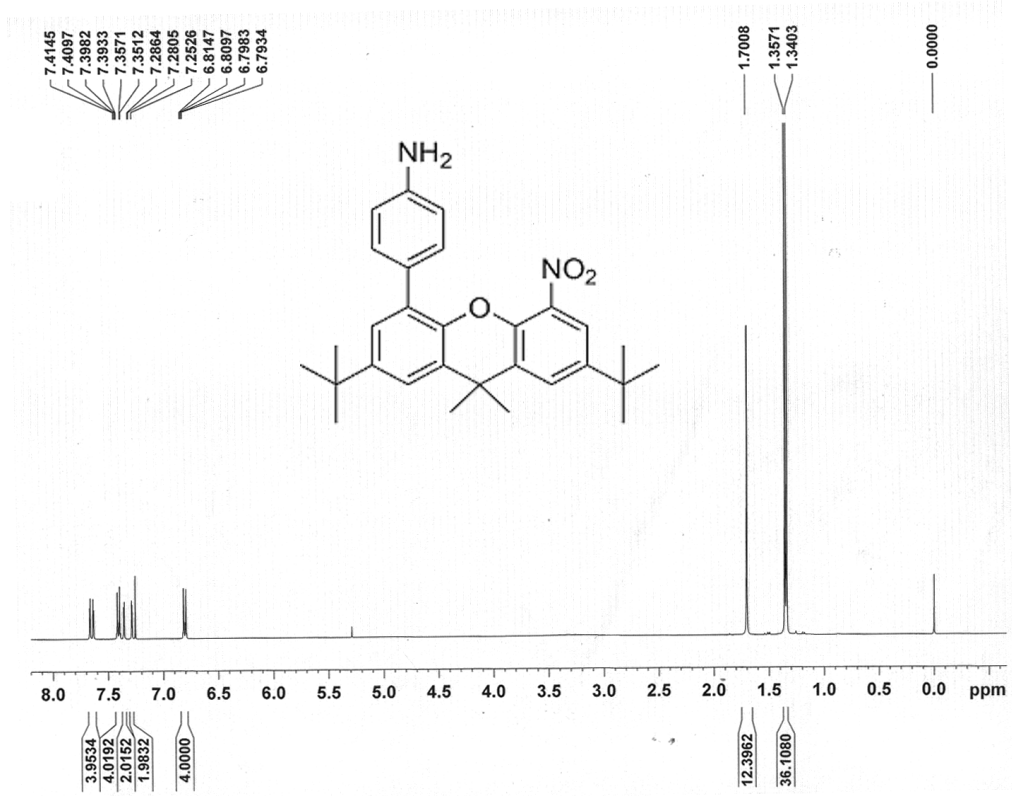

Figure S4. ^{1}H NMR spectrum of compound **3** in $CDCl_3$

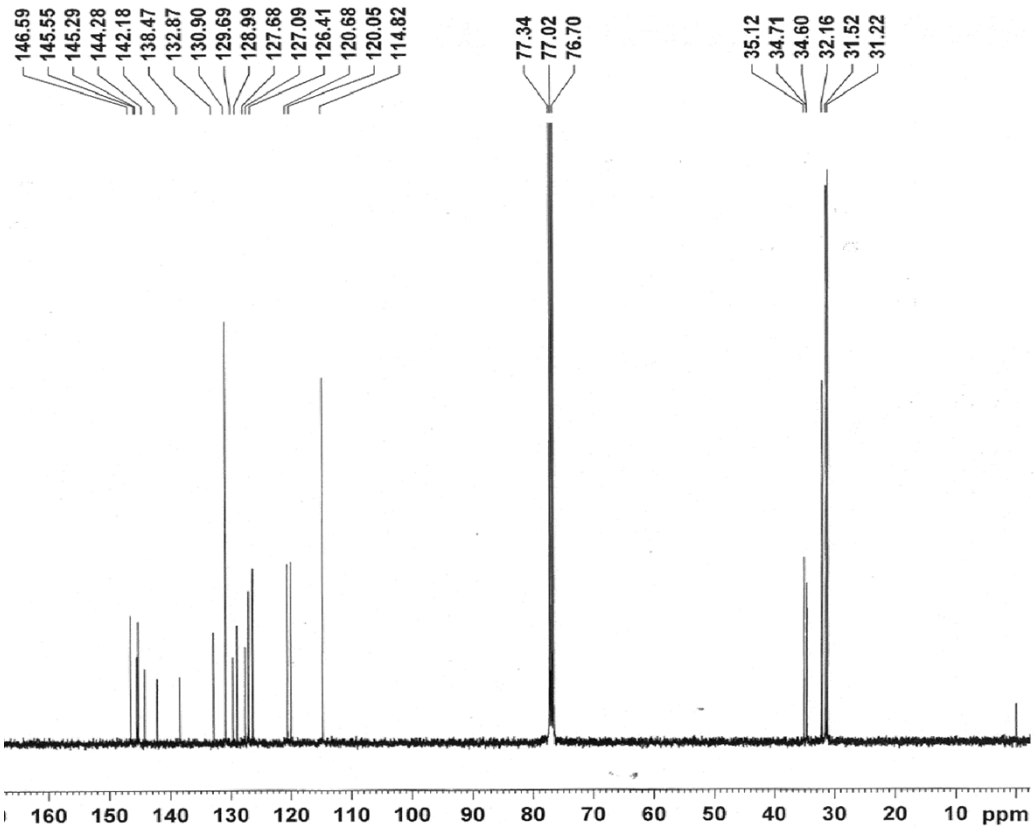

Figure S5. ^{13}C NMR spectrum of compound **3** in $CDCl_3$

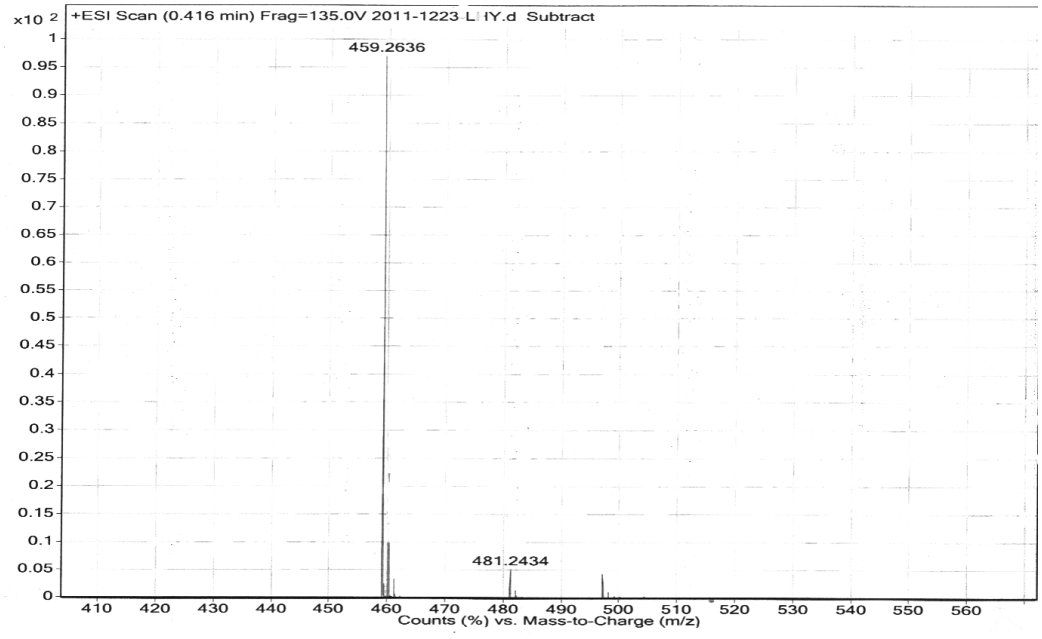

Figure S6. ESI-MS spectra of Compound **3**.

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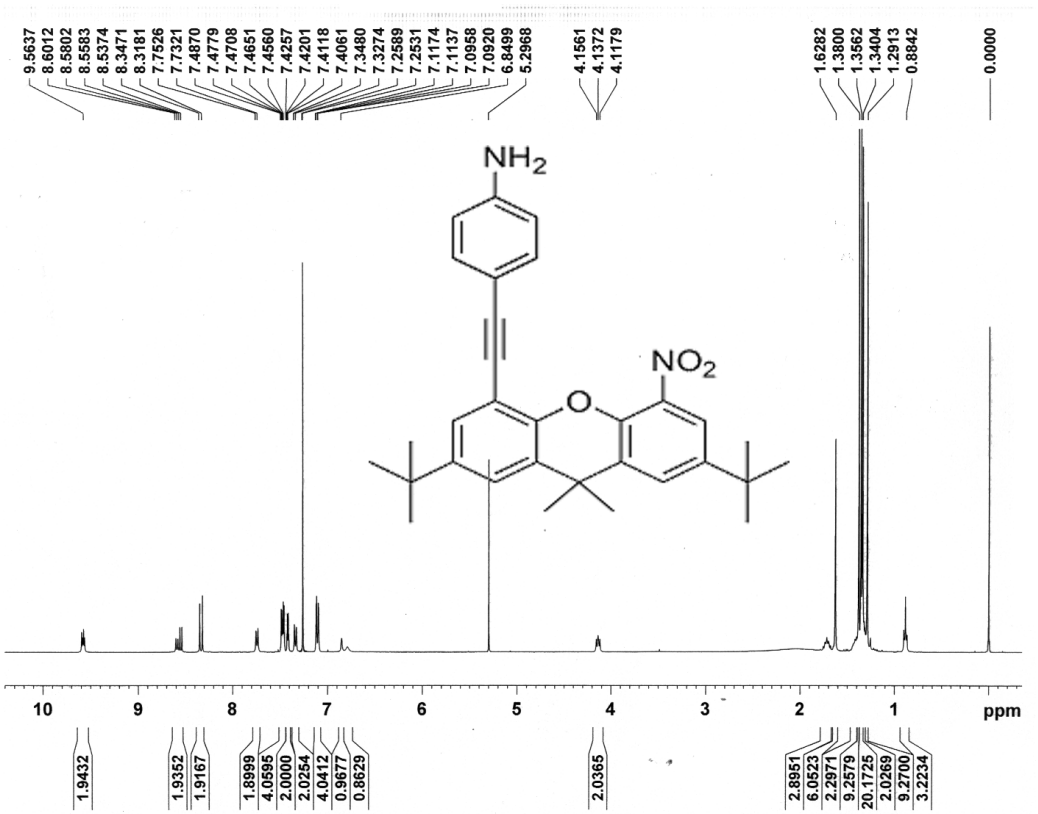


Figure S7. ^{1}H NMR spectrum of compound **5** in $CDCl_3$

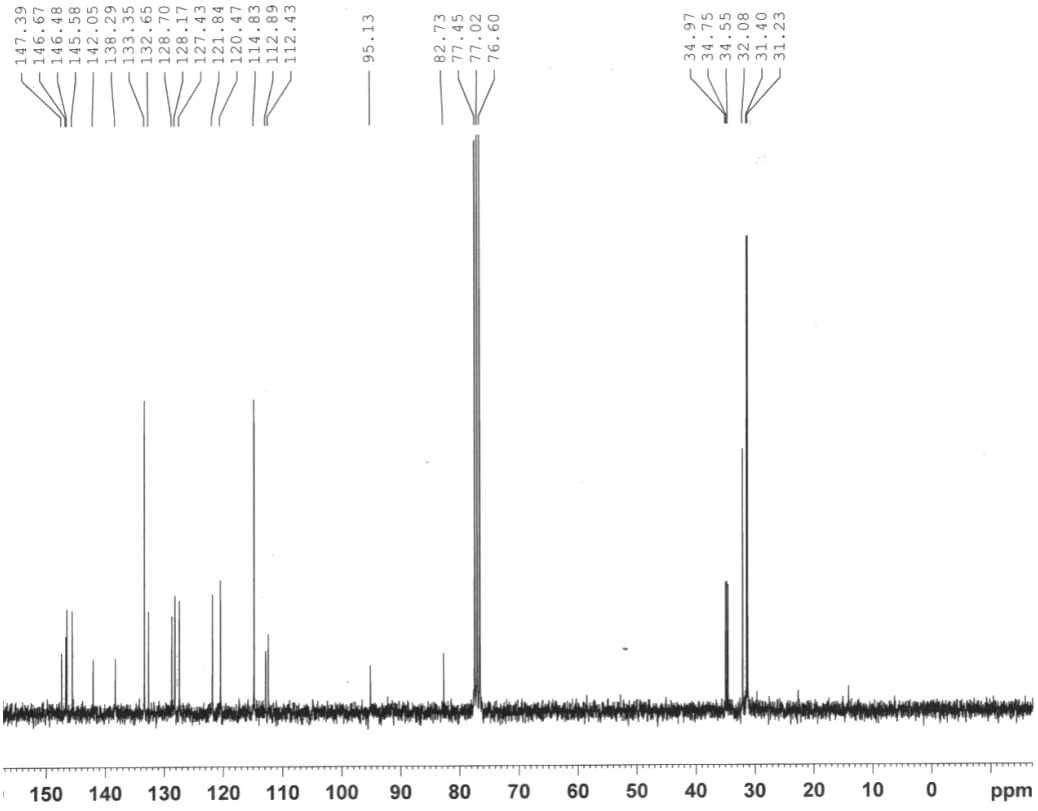


Figure S8. ^{13}C NMR spectrum of compound **5** in $CDCl_3$

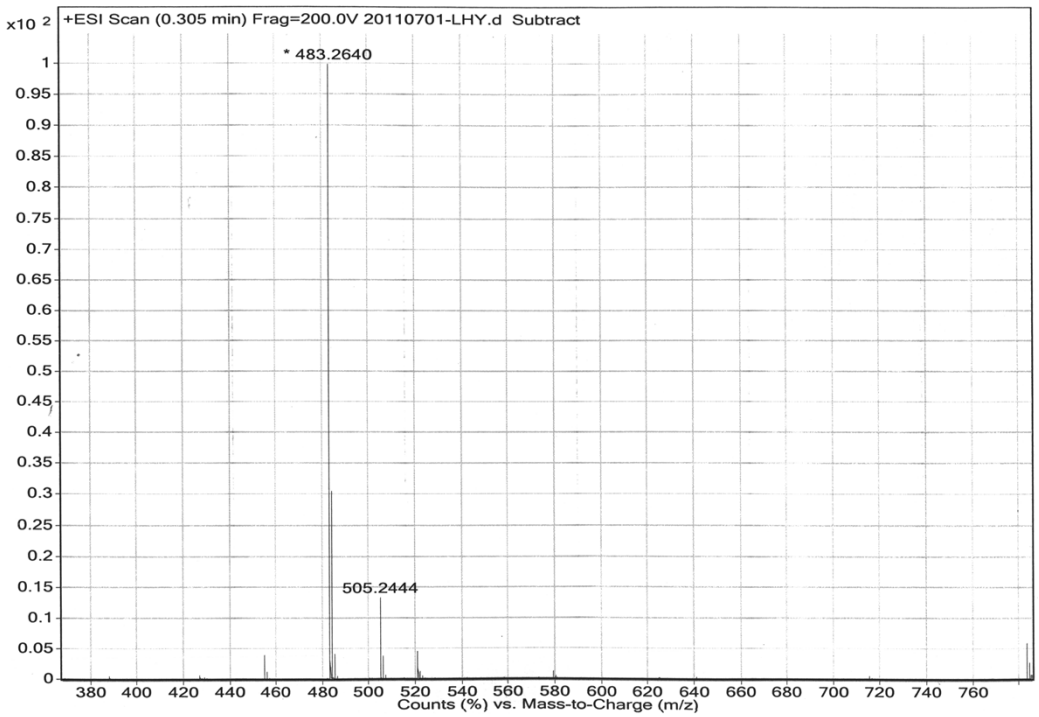


Figure S9. ESI-MS spectra of Compound **5**.

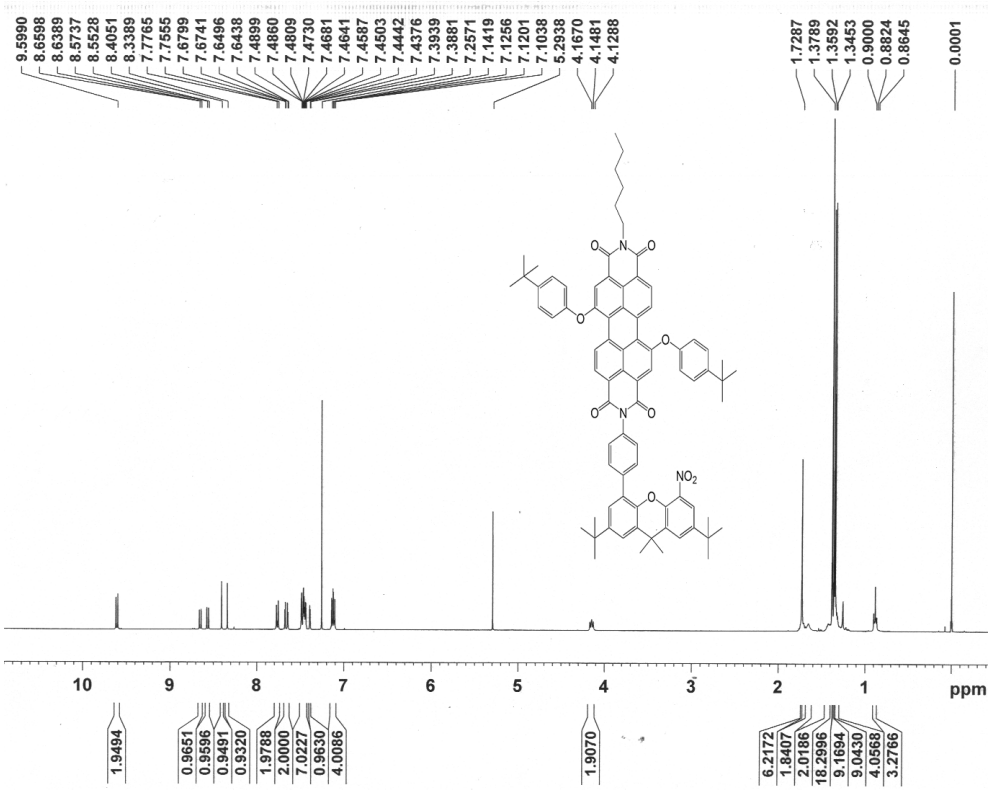


Figure S10. ^{1}H NMR spectrum of compound **8** in $CDCl_3$

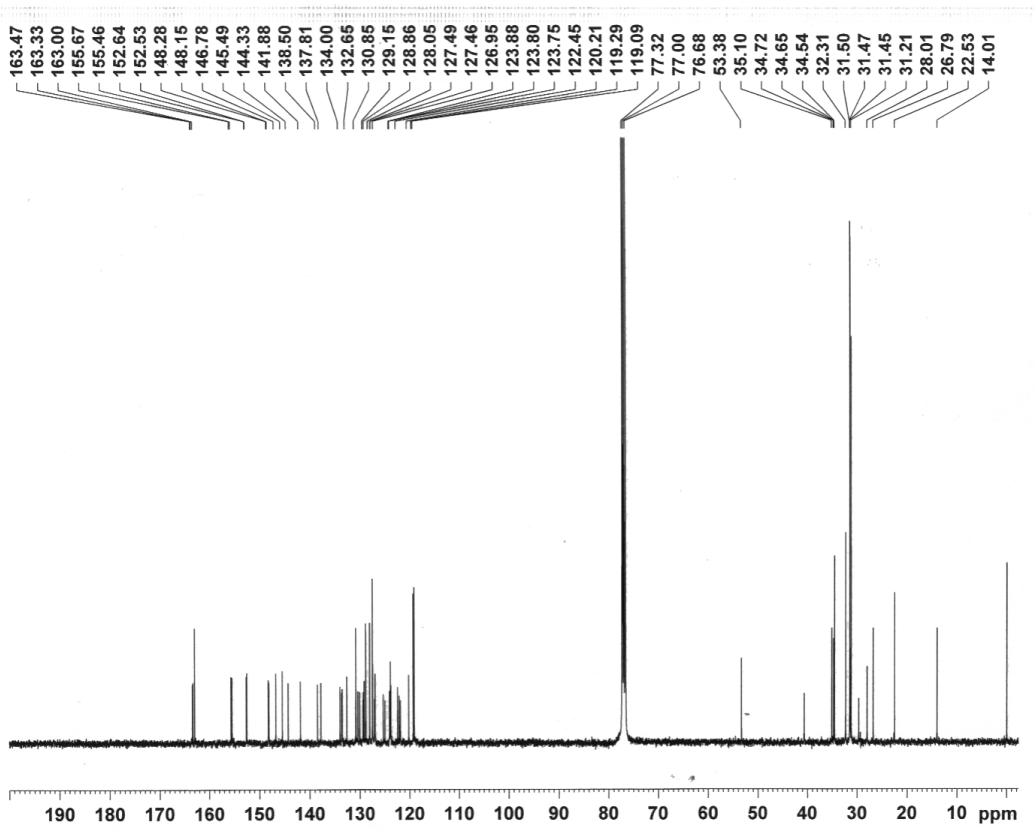


Figure S11. ^{13}C NMR spectrum of compound **8** in $CDCl_3$

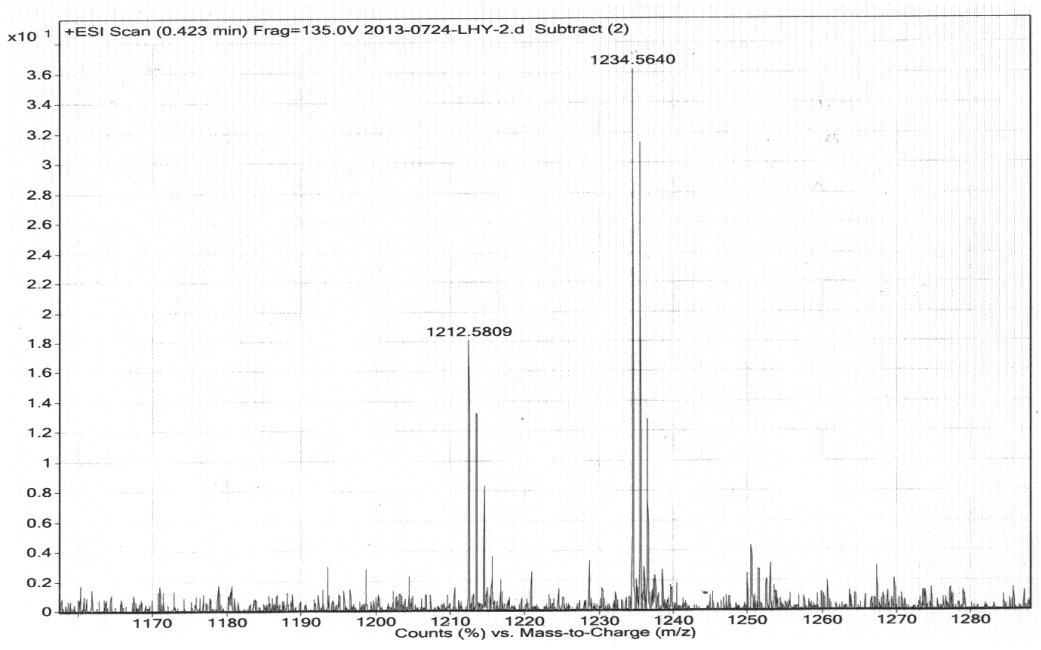


Figure S12. ESI-MS spectra of Compound **8**.

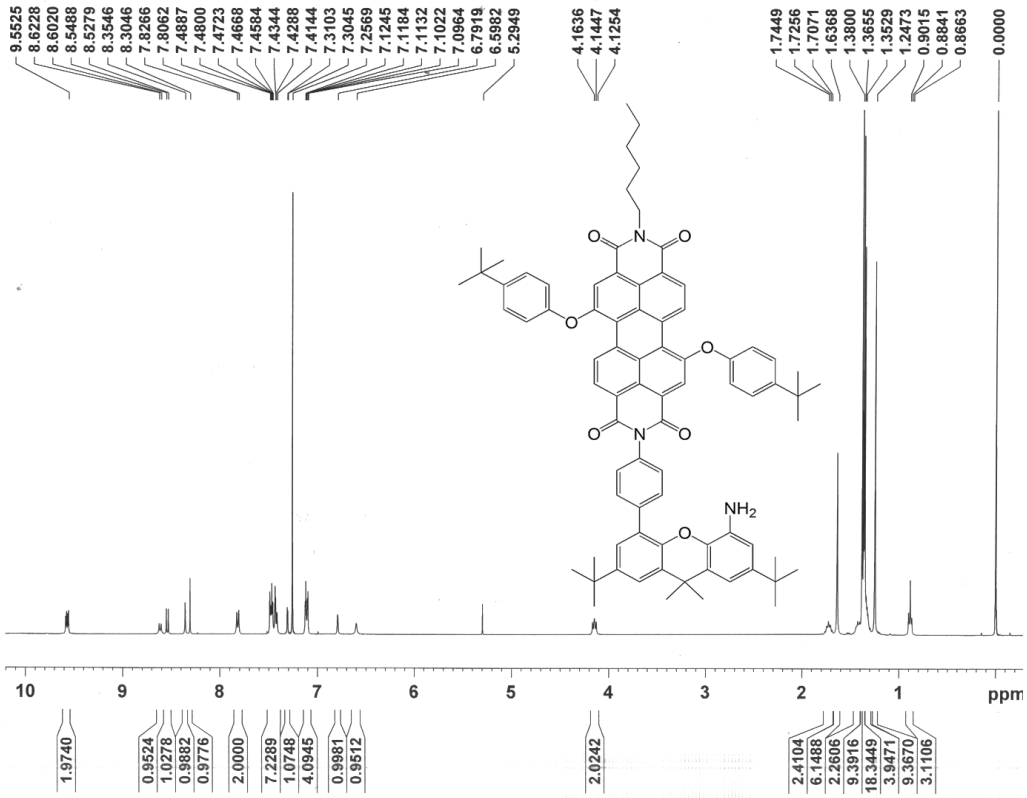


Figure S13. ^{1}H NMR spectrum of compound **9** in $CDCl_3$

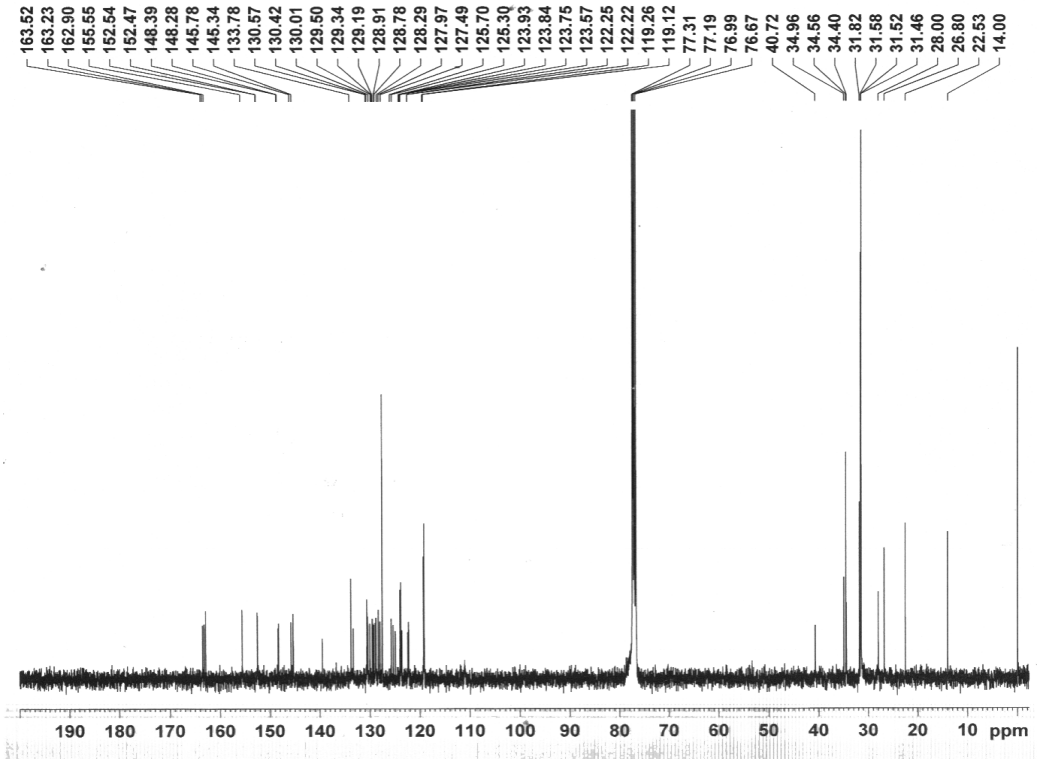


Figure S14. ^{13}C NMR spectrum of compound **9** in $CDCl_3$

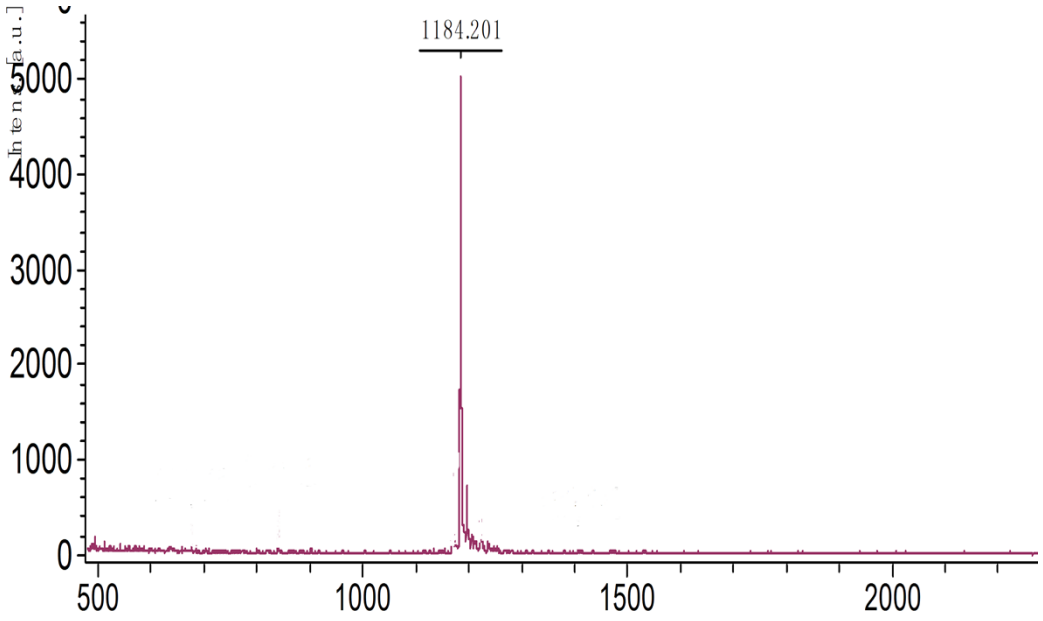


Figure S15. MALDI-TOF spectra of Compound **9**.

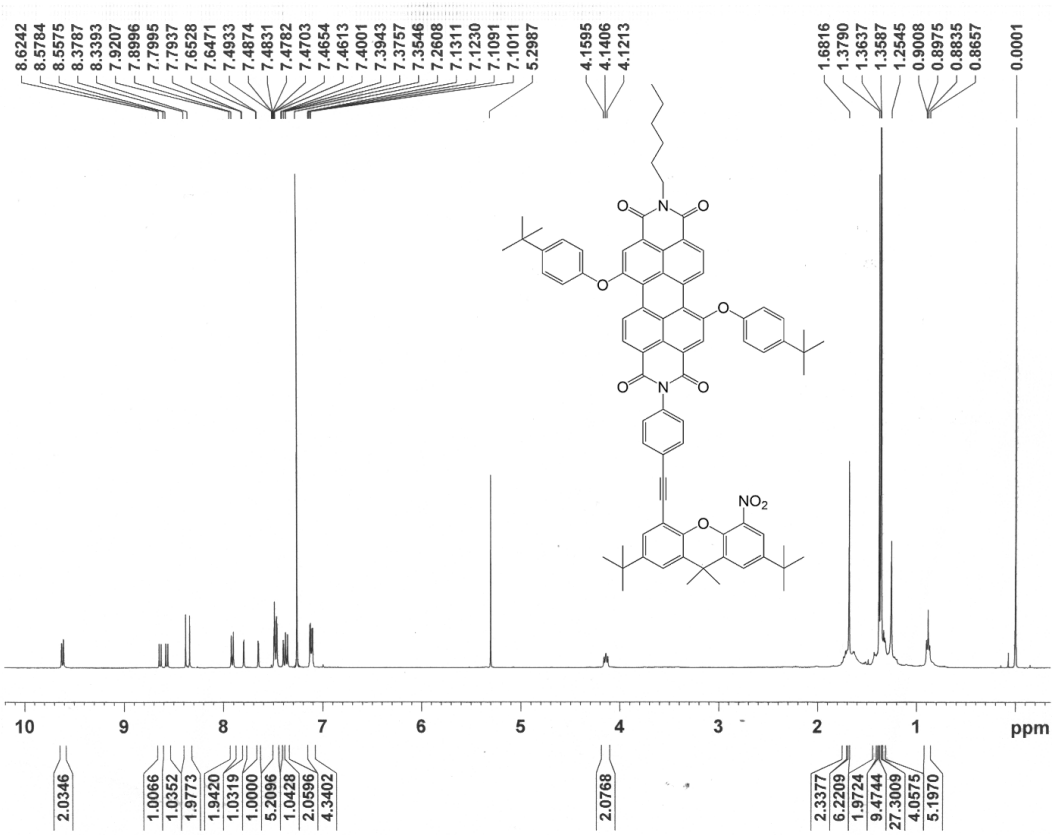


Figure S16. ^{1}H NMR spectrum of compound **11** in $CDCl_3$

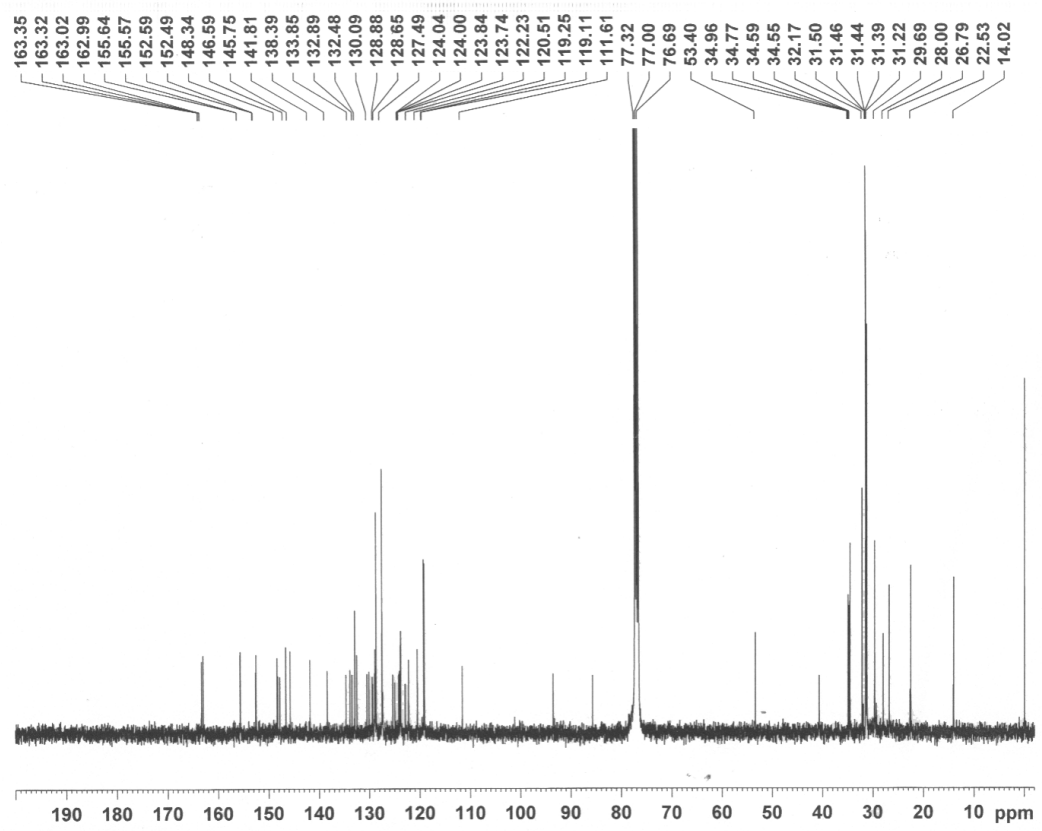


Figure S17. ^{13}C NMR spectrum of compound **11** in $CDCl_3$

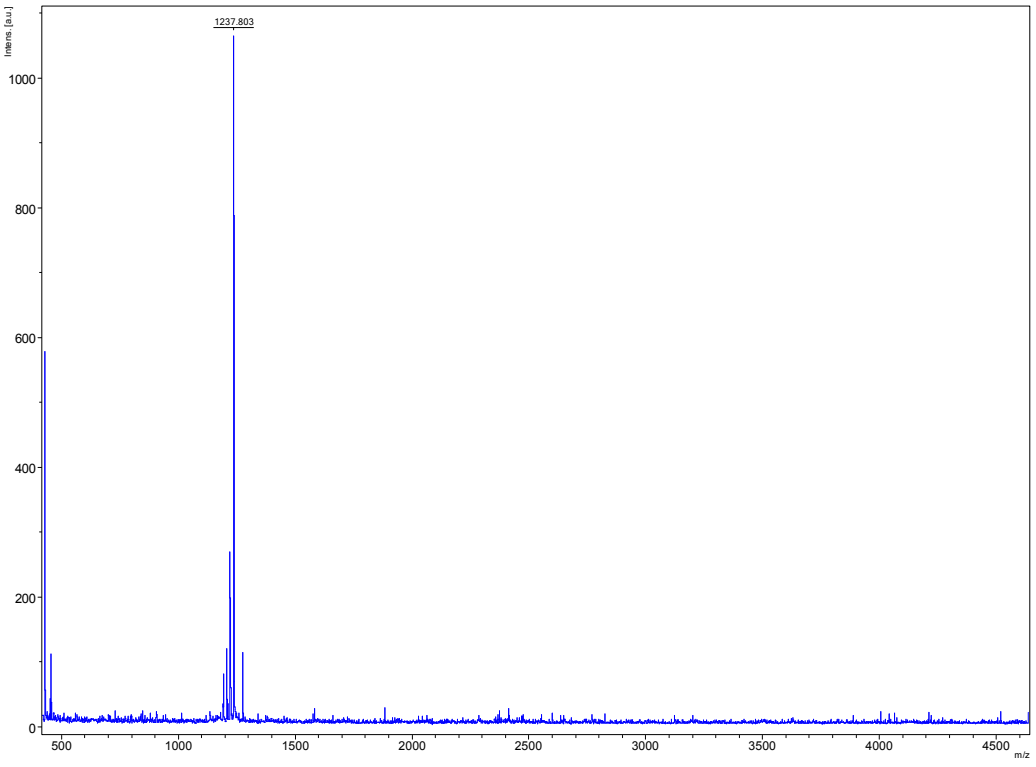


Figure S18. MALDI-TOF spectra of Compound **11**.

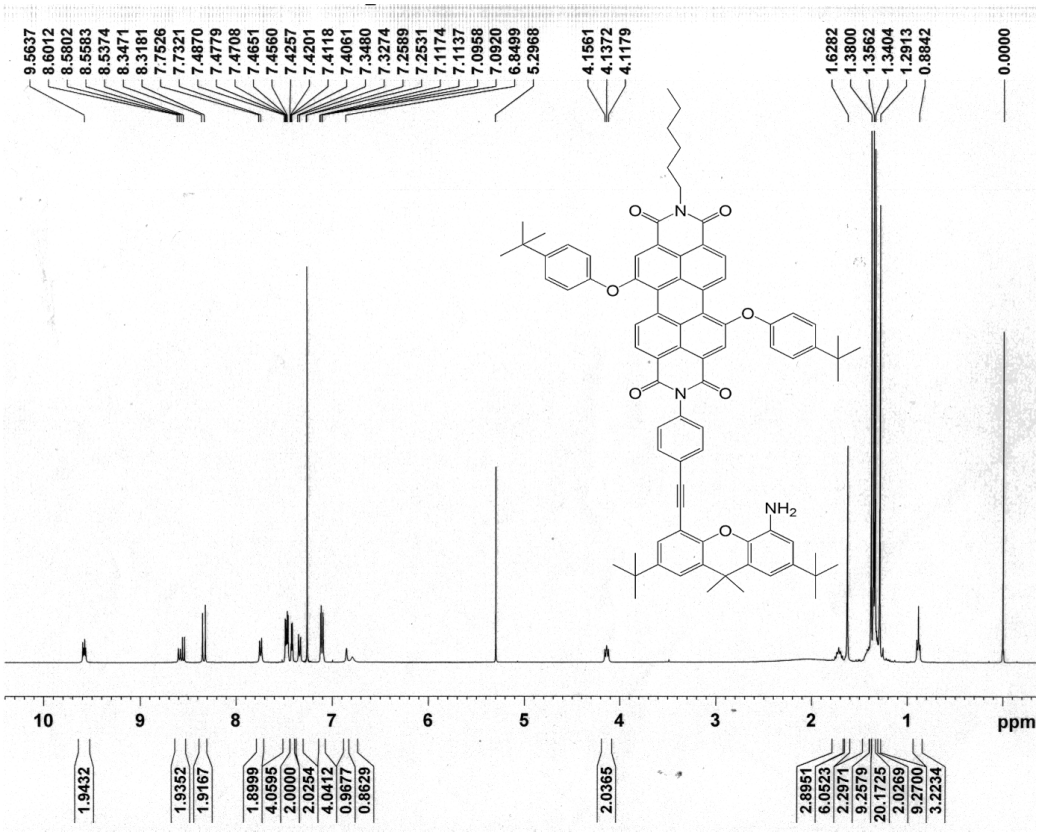


Figure S19. ^{1}H NMR spectrum of compound **12** in $CDCl_3$

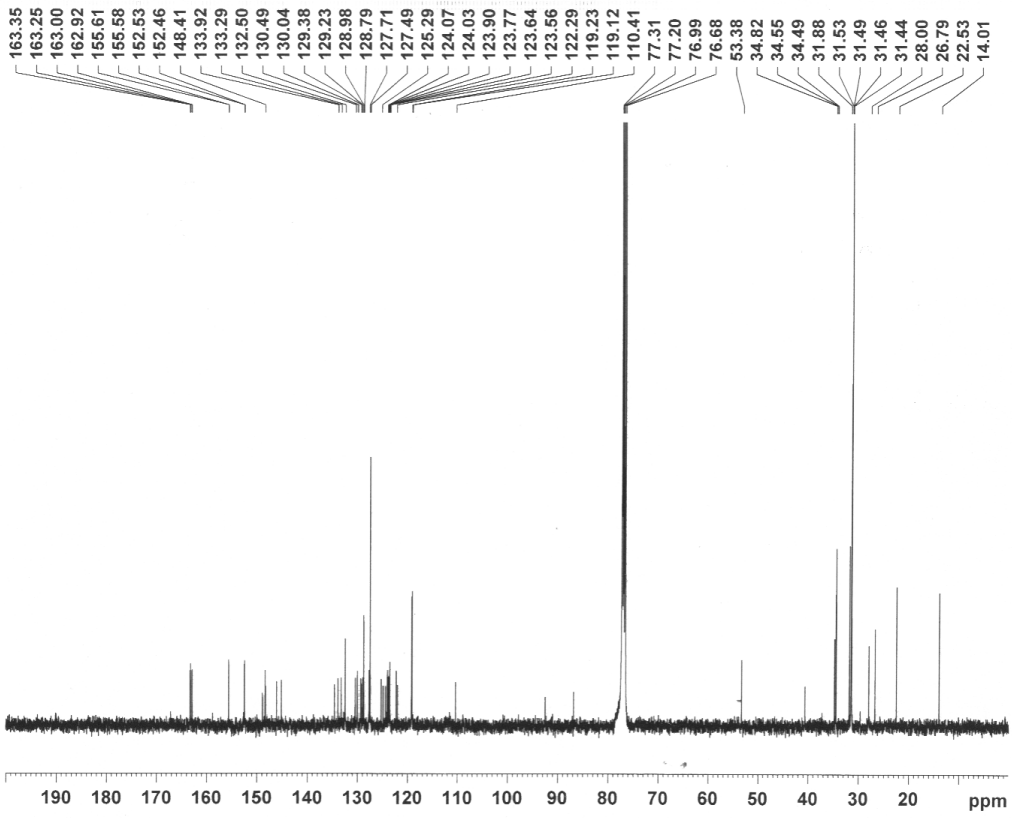


Figure S20. ^{13}C NMR spectrum of compound **12** in $CDCl_3$

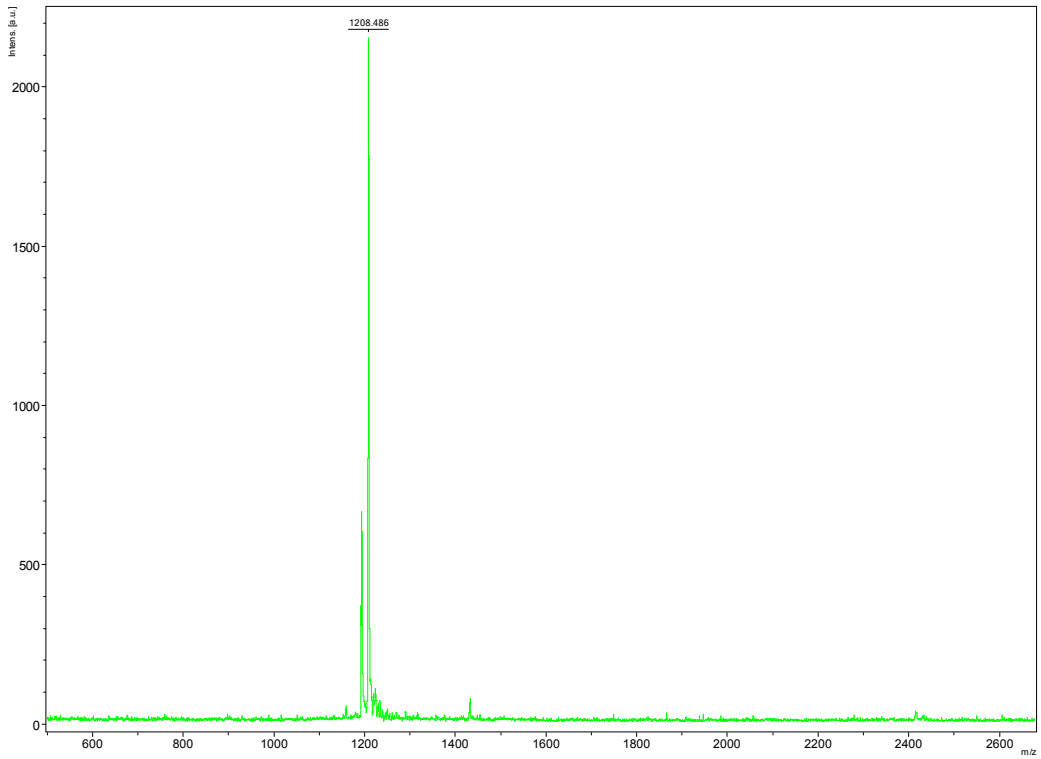


Figure S21. MALDI-TOF spectra of Compound **12**.

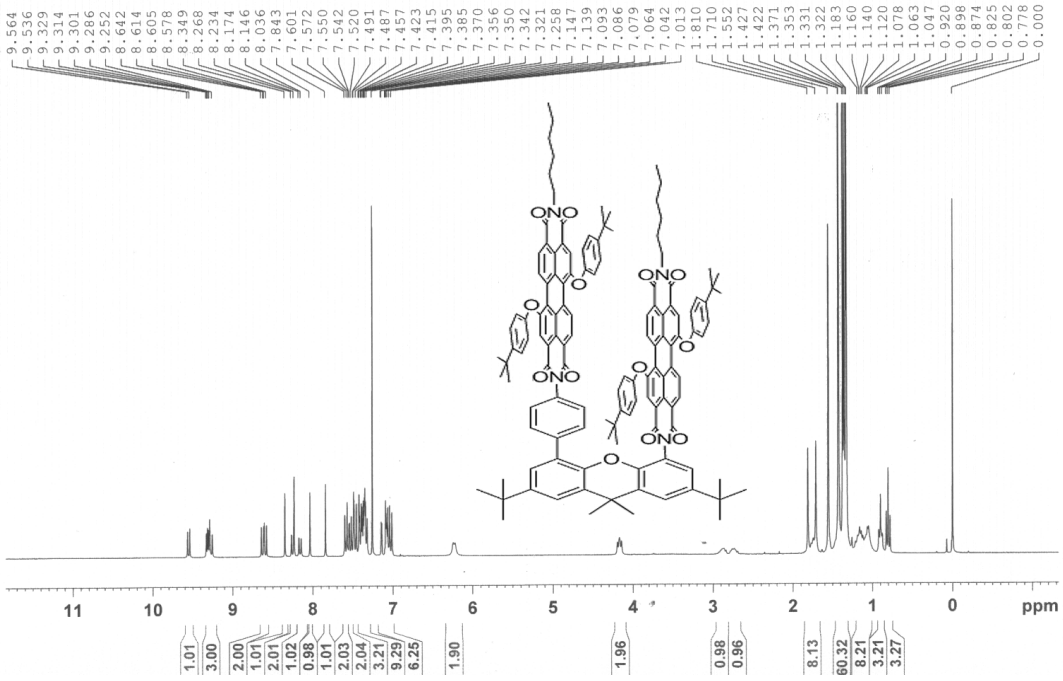


Figure S22. ^{1}H NMR spectrum of compound $\mathbf{D_1}$ in $CDCl_3$. (The four singlet peaks in the region of 7.8-8.4 ppm can be assigned to the protons at 2' positions of PDI ring, which show clearly that the compound is a pure compound, not a mixture of isomers).

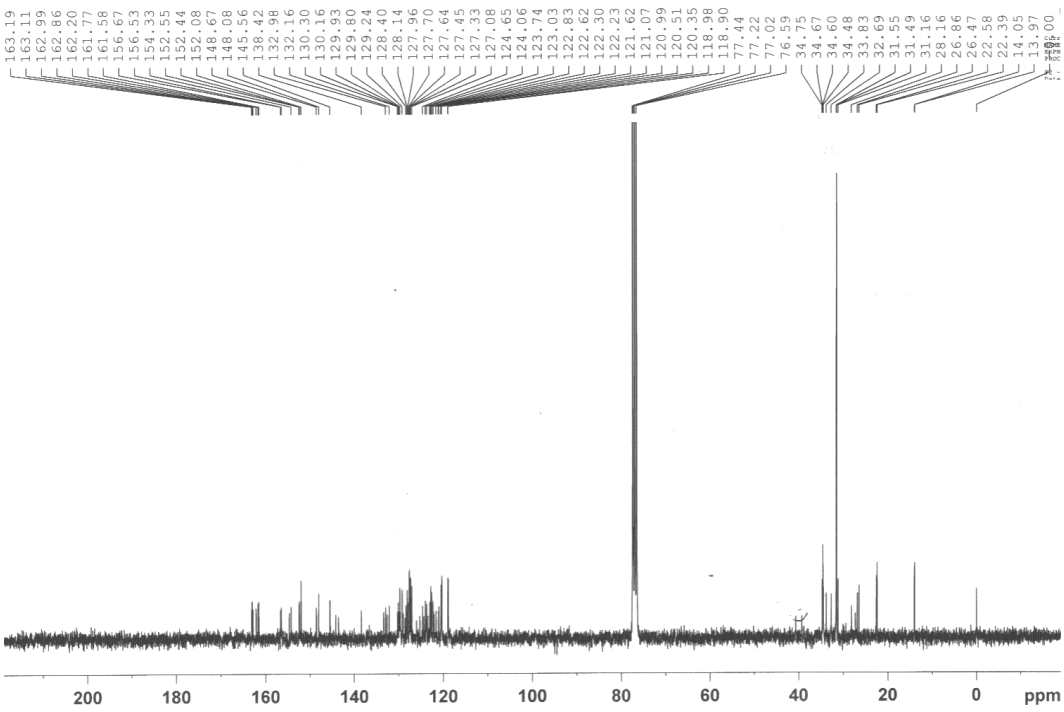


Figure S23. ^{13}C NMR spectrum of compound $\mathbf{D_1}$ in $CDCl_3$

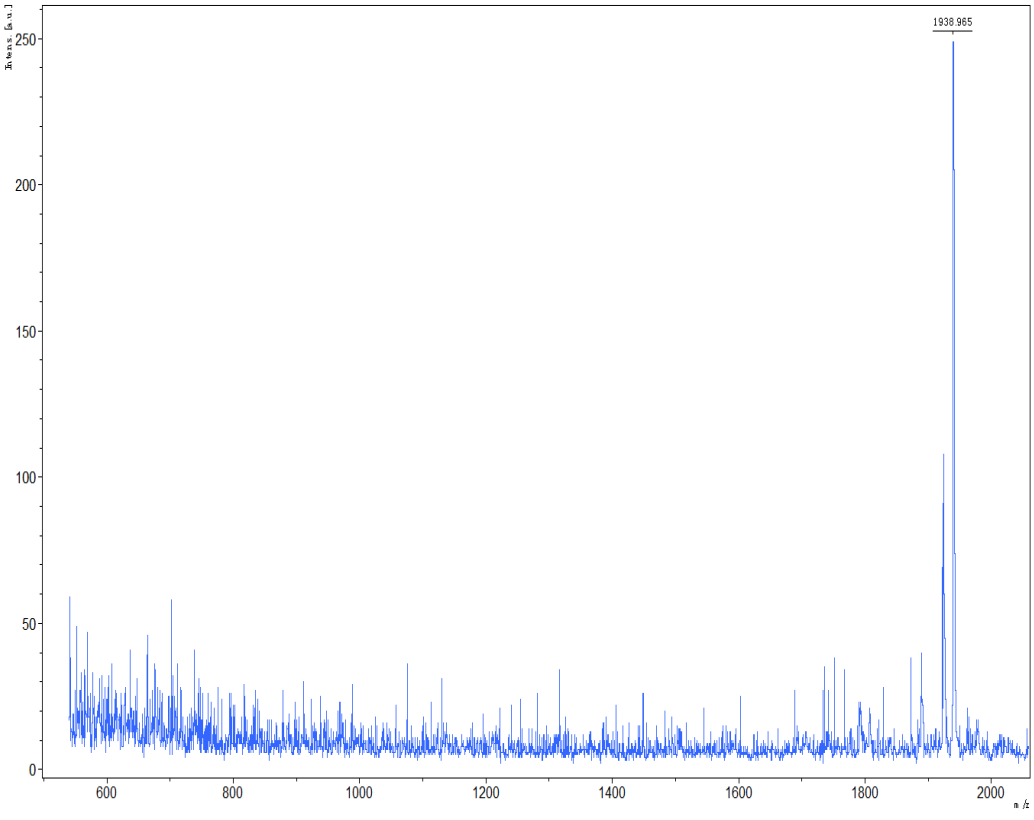


Figure S24. ^{1}H NMR, ^{13}C NMR and MALDI-TOF spectra of $\mathbf{D_1}$.

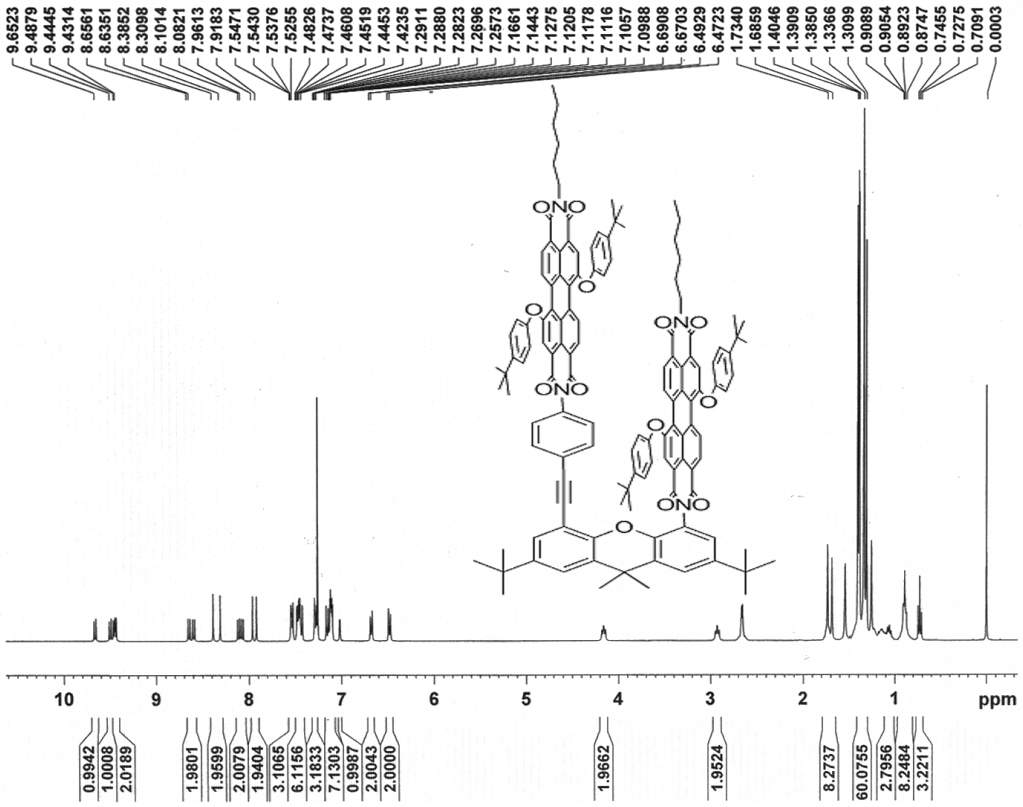


Figure S25. ^{1}H NMR spectrum of compound **D_2** in $CDCl_3$

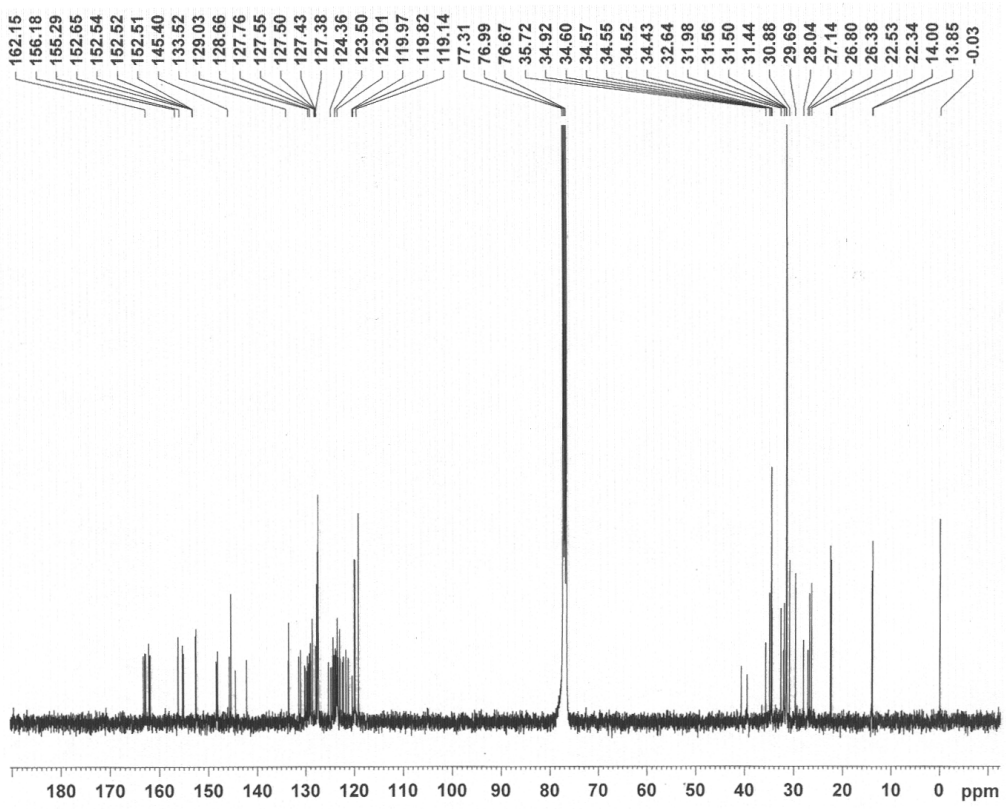


Figure S26. ^{13}C NMR spectrum of compound **D_2** in $CDCl_3$

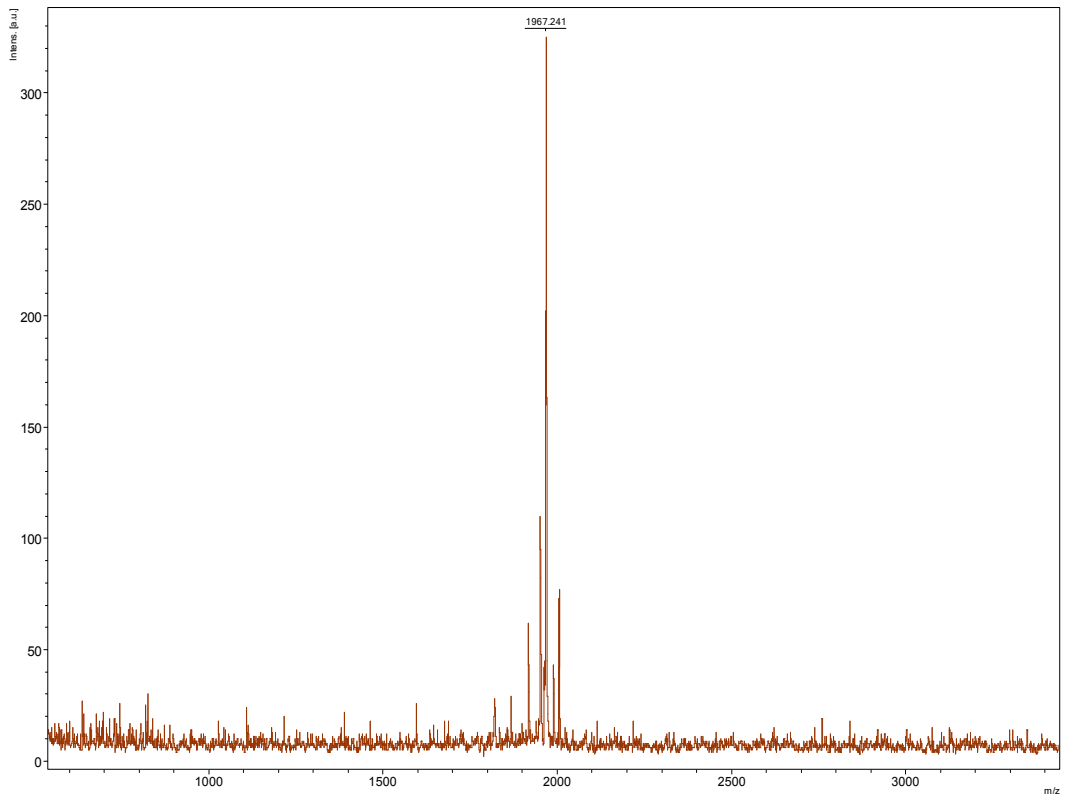


Figure S27. MALDI-TOF spectra of $\mathbf{D_2}$.

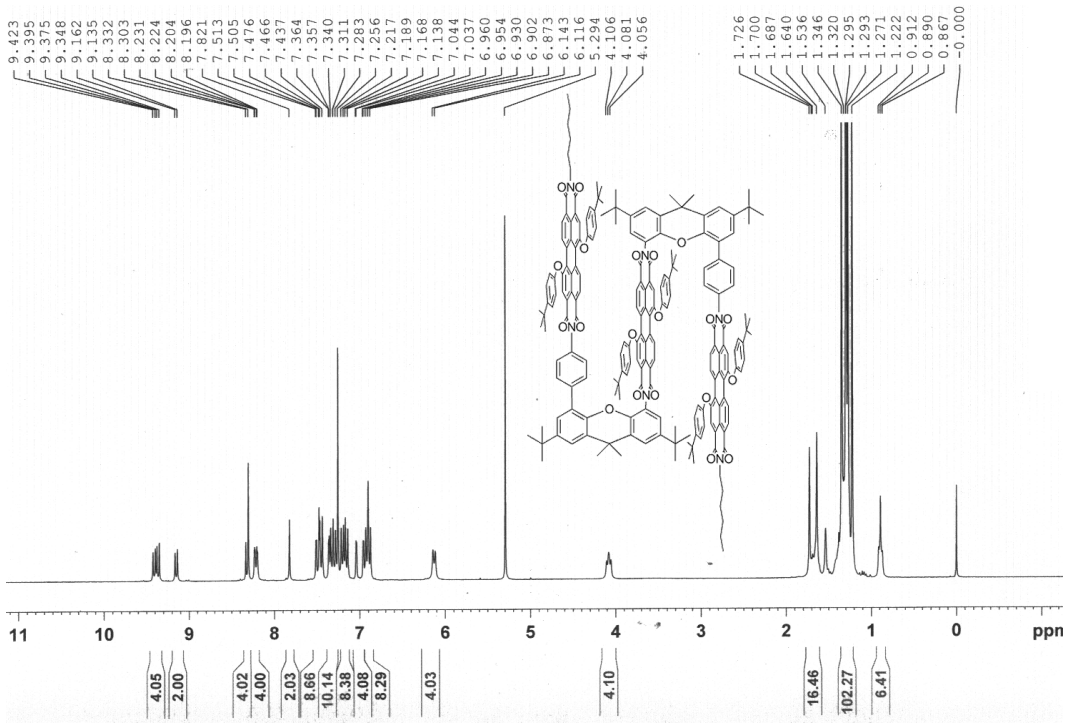


Figure S28. ^{1}H NMR spectrum of $\mathbf{T_1}$ in $CDCl_3$

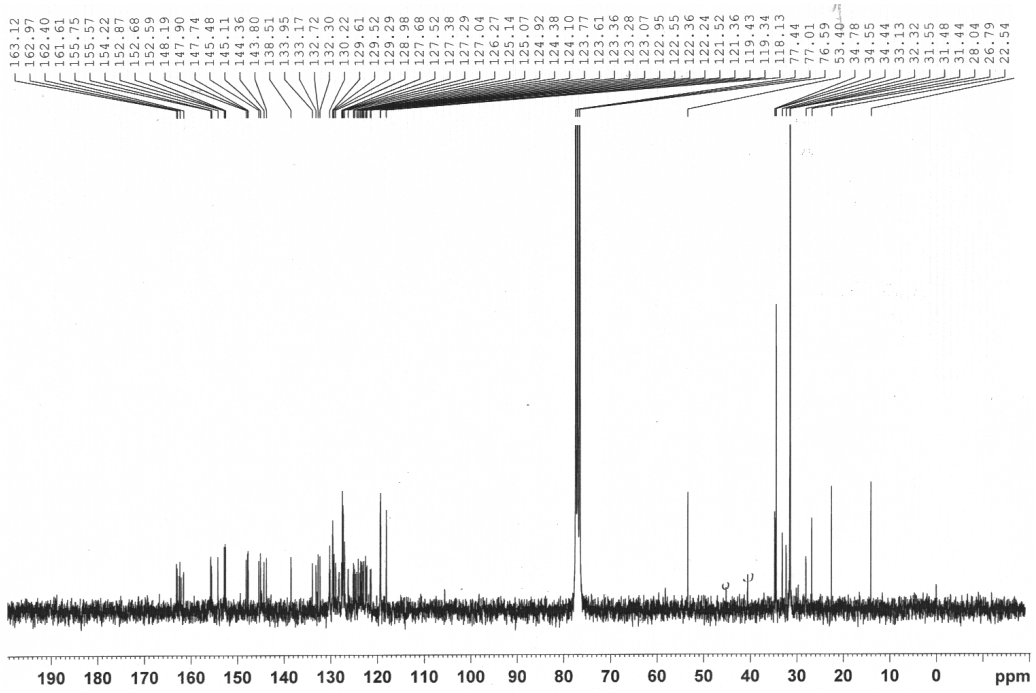


Figure S29. ^{13}C NMR spectrum of compound $\mathbf{T_1}$ in $CDCl_3$

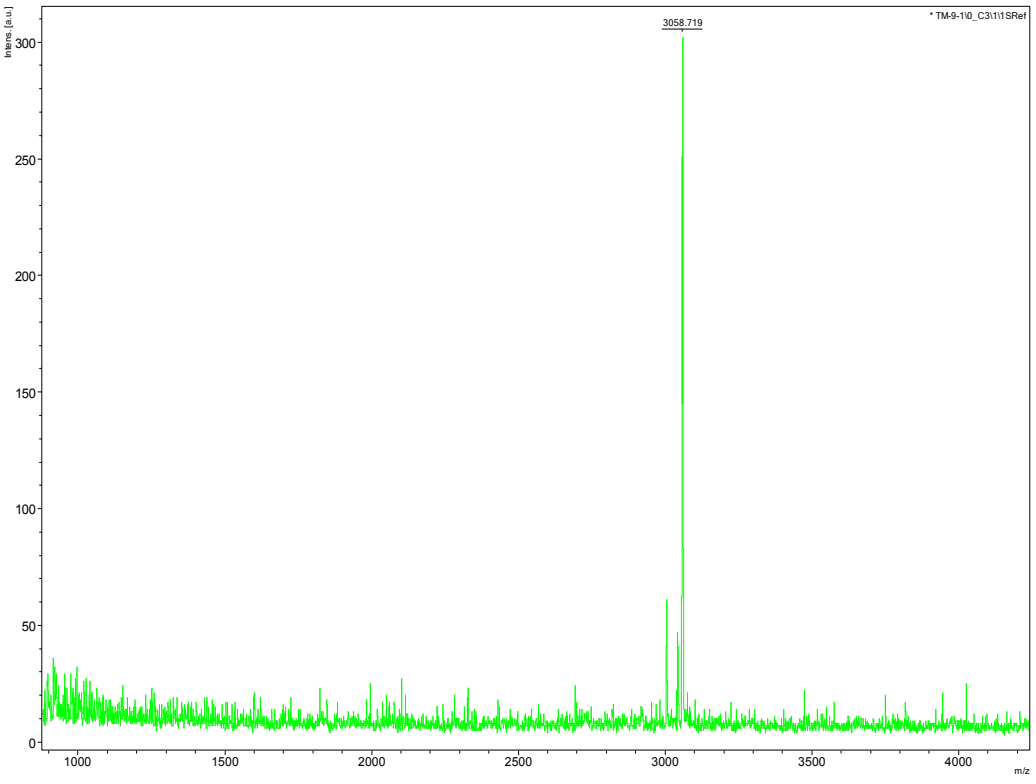


Figure S30. MALDI-TOF spectra of $\mathbf{T_1}$.

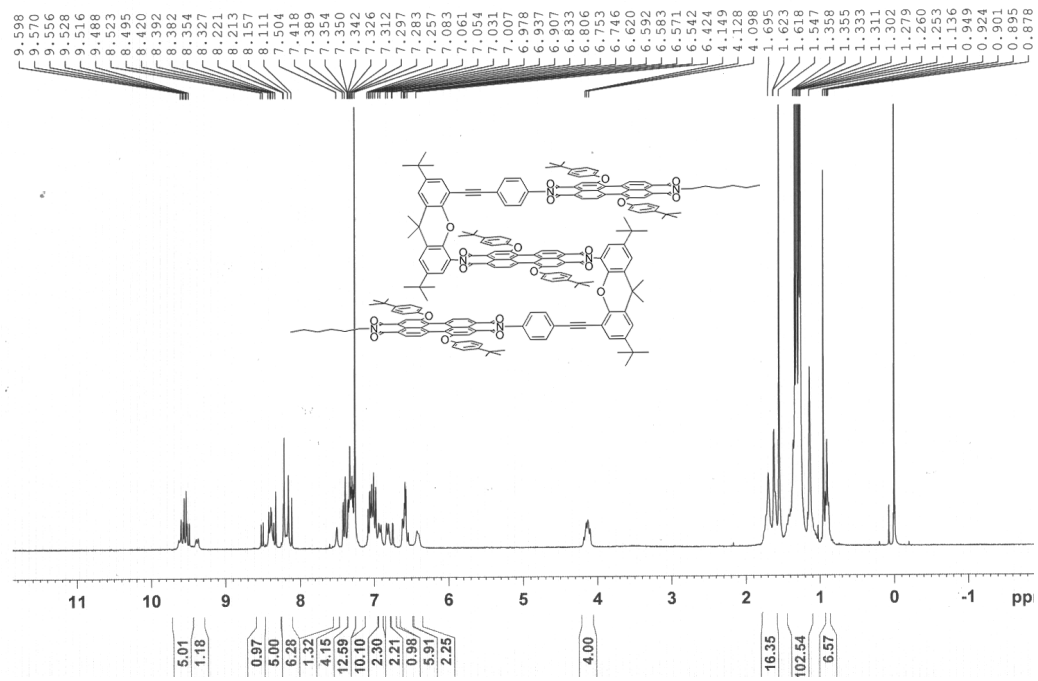


Figure S31. ^{1}H NMR spectrum of compound $\mathbf{T_2}$ in $CDCl_3$

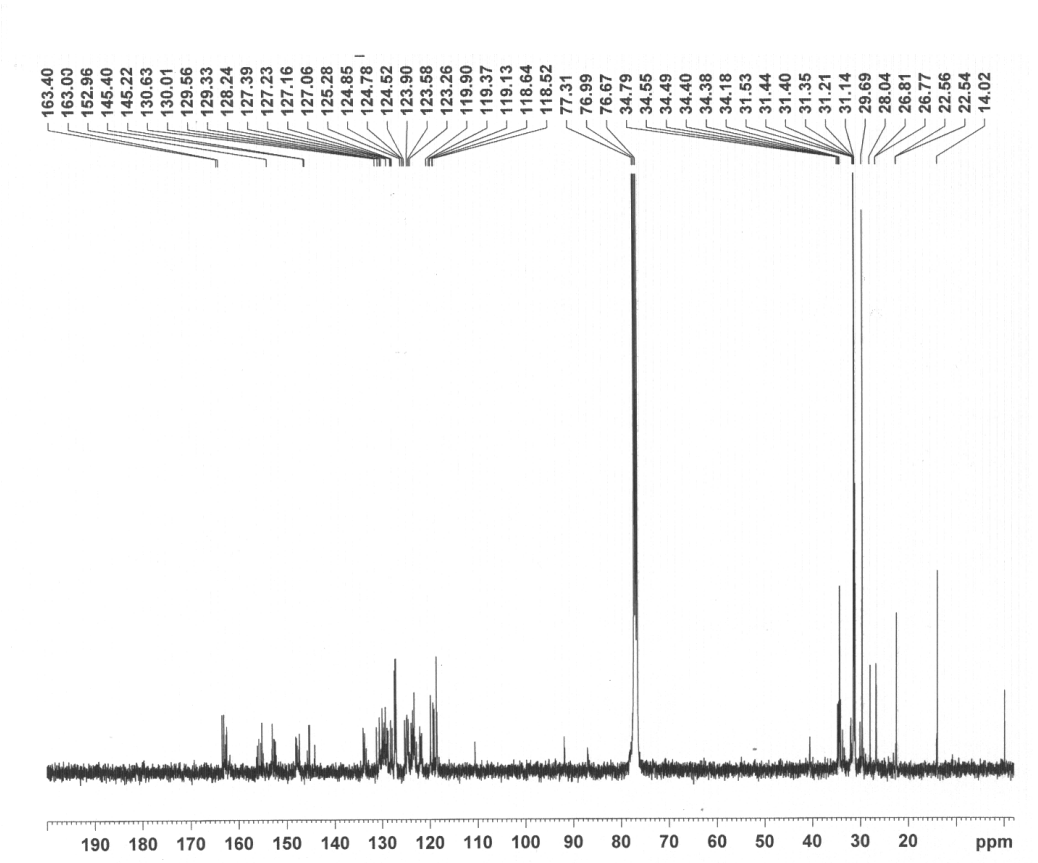


Figure S32. ^{13}C NMR spectrum of compound $\mathbf{T_2}$ in $CDCl_3$

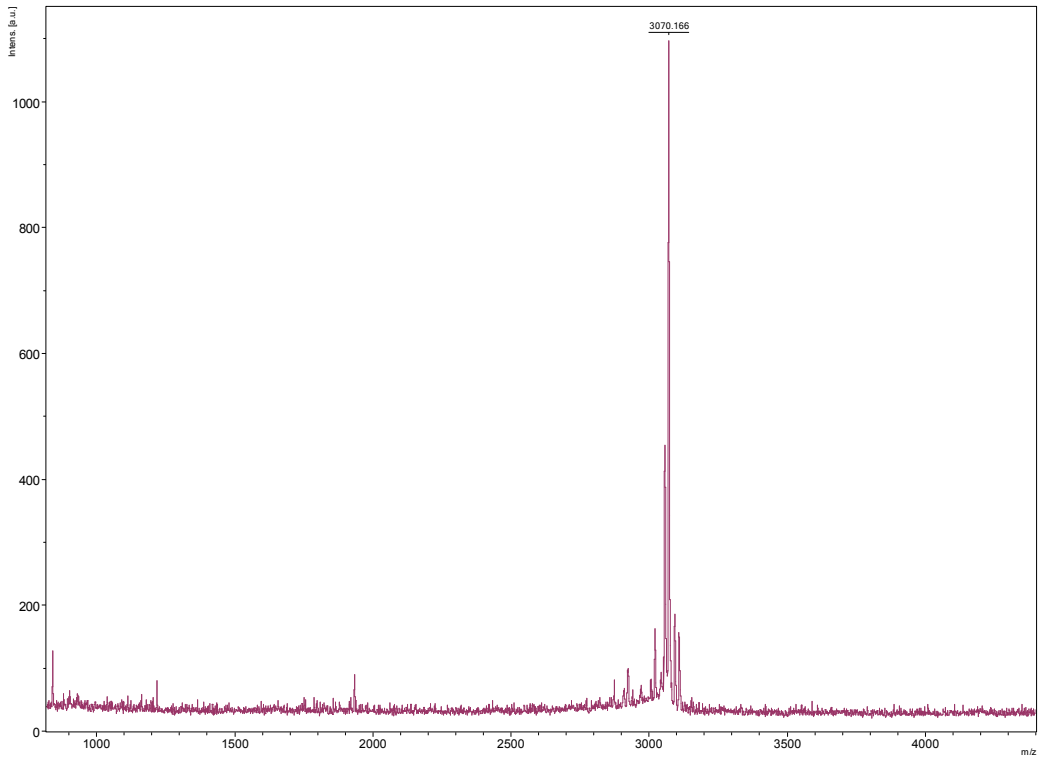


Figure S33. MALDI-TOF spectra of $\mathbf{T_2}$.

3. Copies of the ^{1}H NMR spectra of the two isomers of H-aggregates.

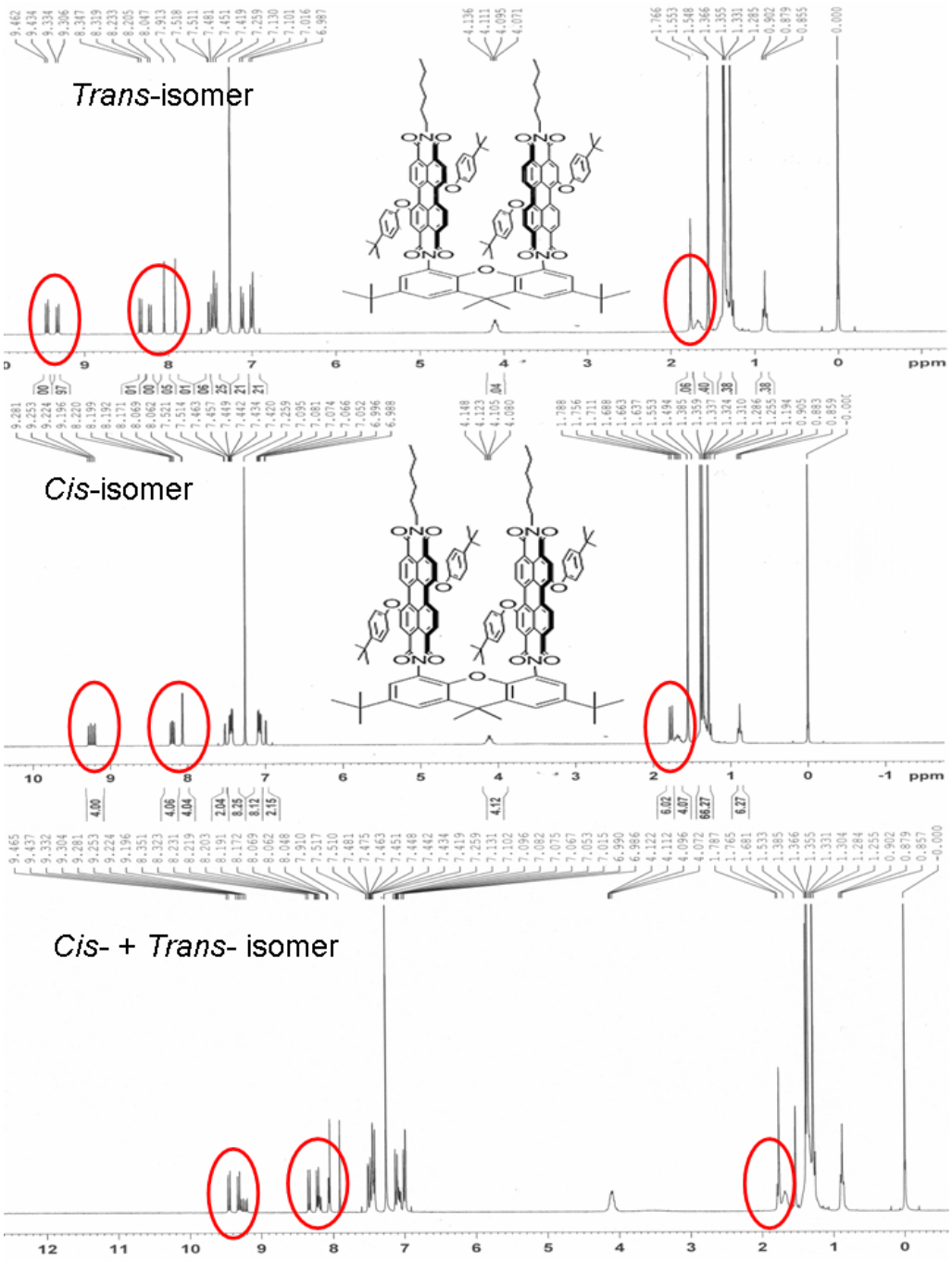
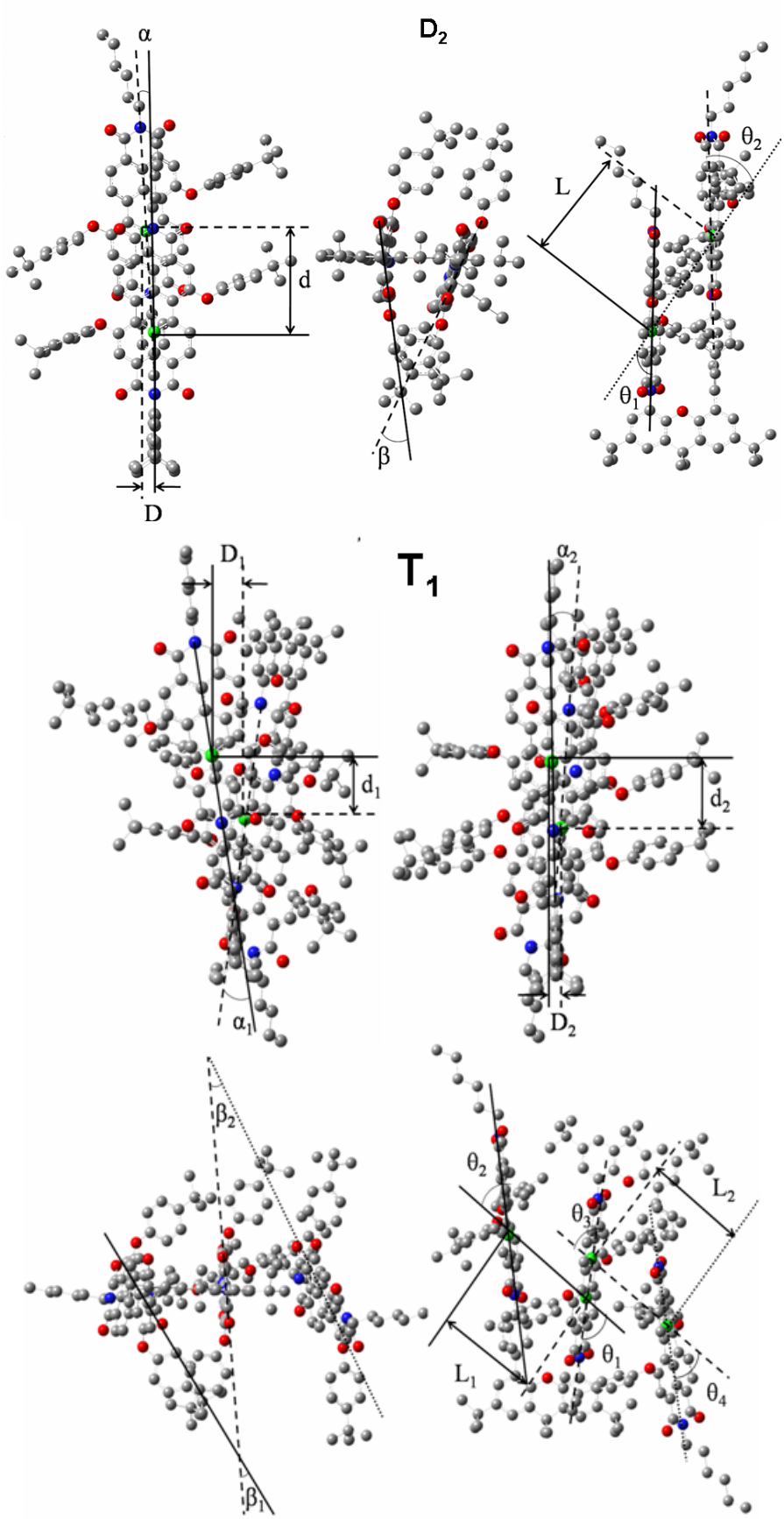


Figure S34. Comparison of ^{1}H NMR spectra of the cis- and trans-isomers and their mixture of H-type PDI dimer in $CDCl_3$. Significant difference (in the region of red circles) between these two isomers can be identified at 1.8, 8.0-8.4, and 9.0-9.5 ppm. With this figure as reference, we can imagine that if all the new dimers (D_1 and D_2) and trimers (T_1 and T_2) are mixture of different isomers, the ^{1}H NMR spectra will be much complicated than they are presented in Figure S22 and S25.

4. **Minimized structure of compound D_2, T_1 and T_2 (hydrogen atoms are omitted for clarity).**



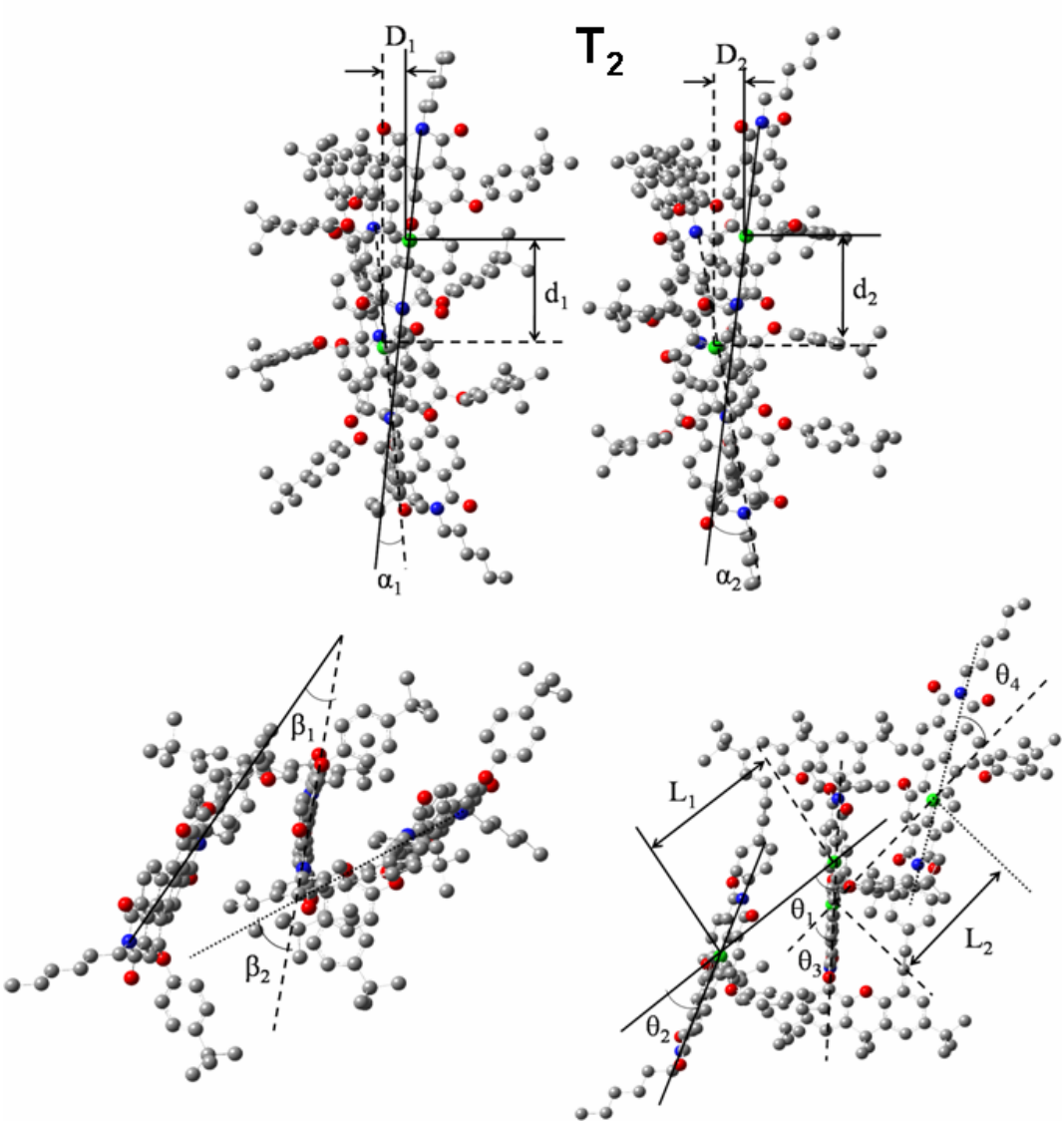


Figure S35. Minimized structures of compounds $\mathbf{D_2}$, $\mathbf{T_1}$ and $\mathbf{T_2}$ (hydrogens are omitted for clarity).

5. The excitation spectra of D_1, D_2, T_1 and T_2

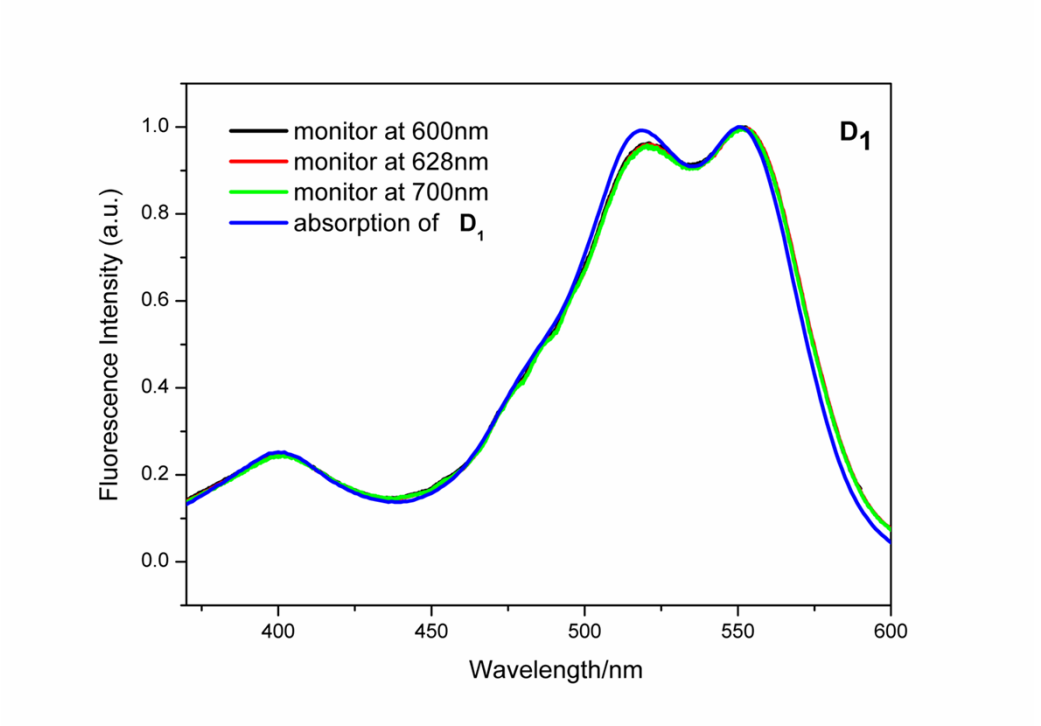


Figure S36. The excitation spectra of $\mathbf{D_1}$ in toluene.

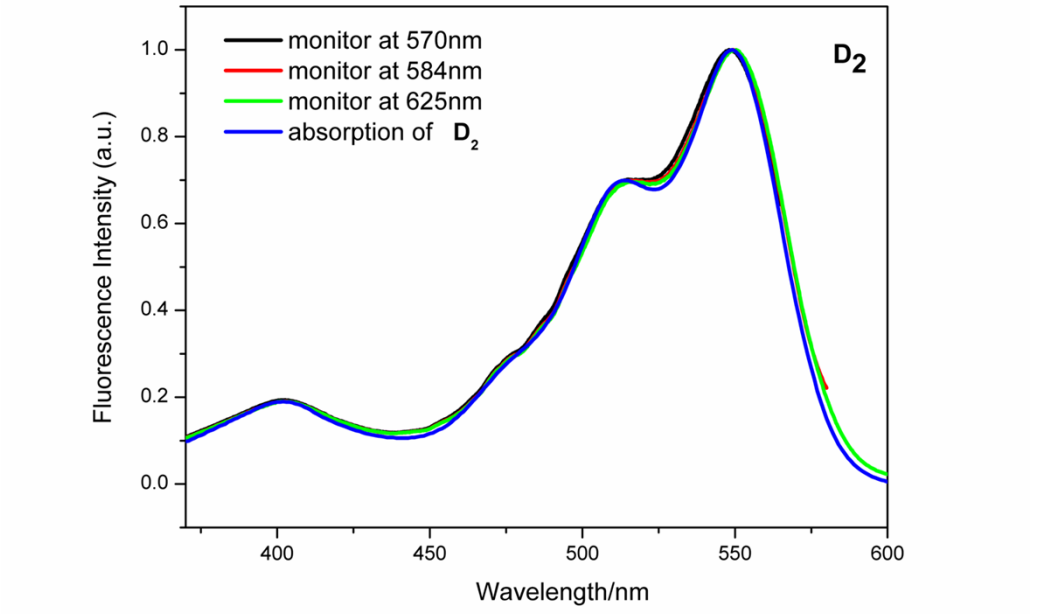


Figure S37. The excitation spectra of $\mathbf{D_2}$ in toluene

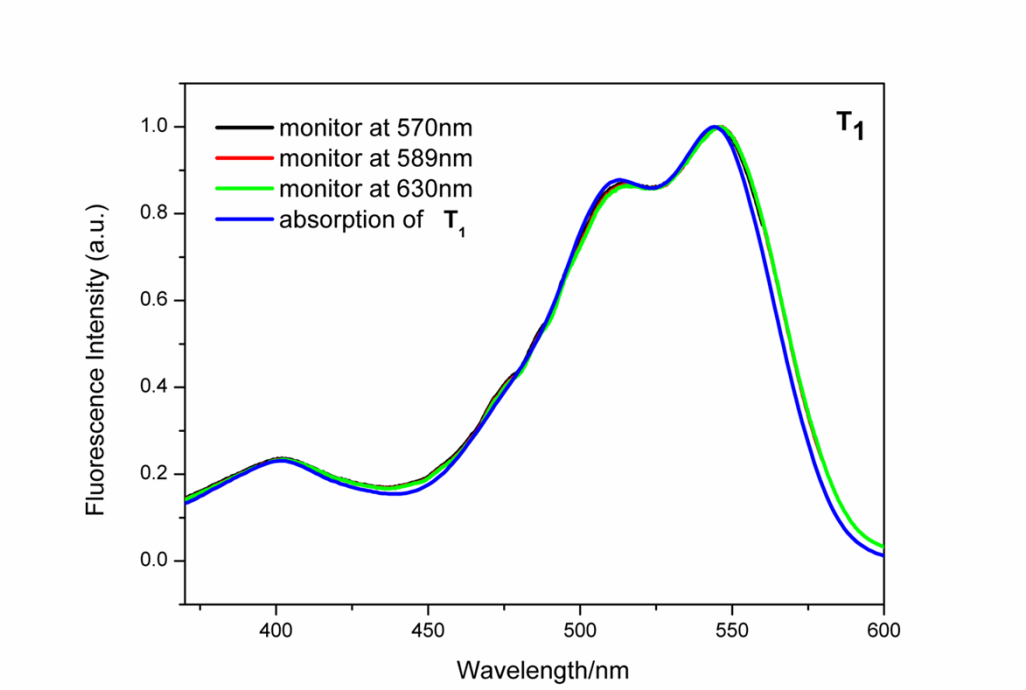


Figure S38. The excitation spectra of $\mathbf{T_1}$ in toluene

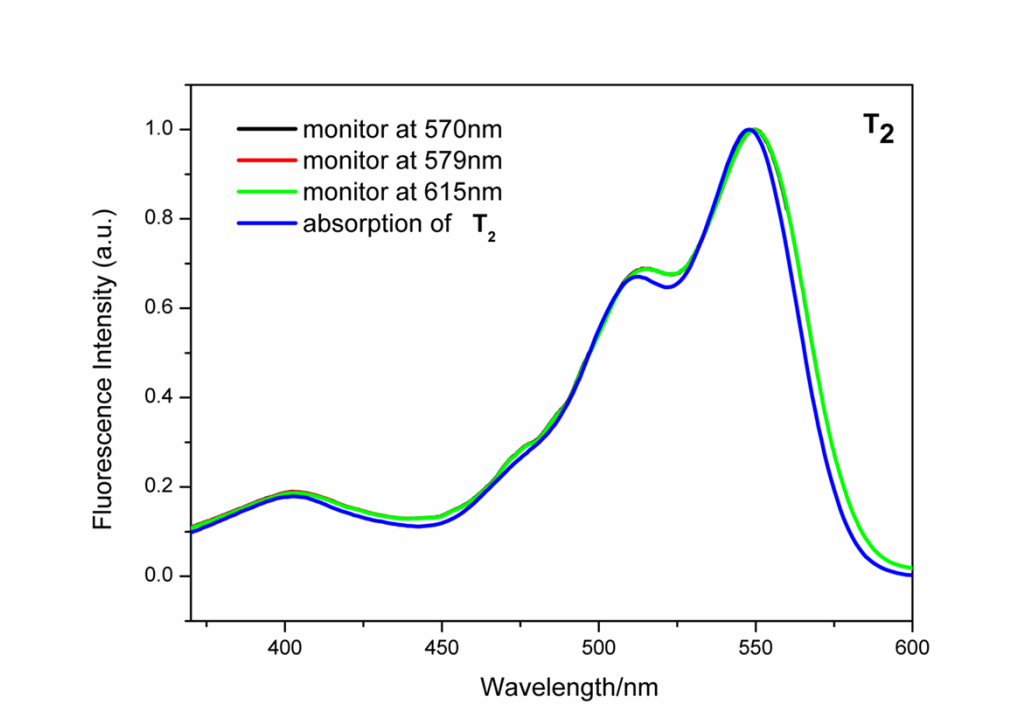


Figure S39. The excitation spectra of $\mathbf{T_2}$ in toluene

The excitation spectra of these compounds are found to be identical with their absorption respectively. This means there is no other emissive impurities in the samples and all these compounds are pure compounds, not a mixture of isomers.

6. The split transient fluorescence spectra of D_2 and T_1

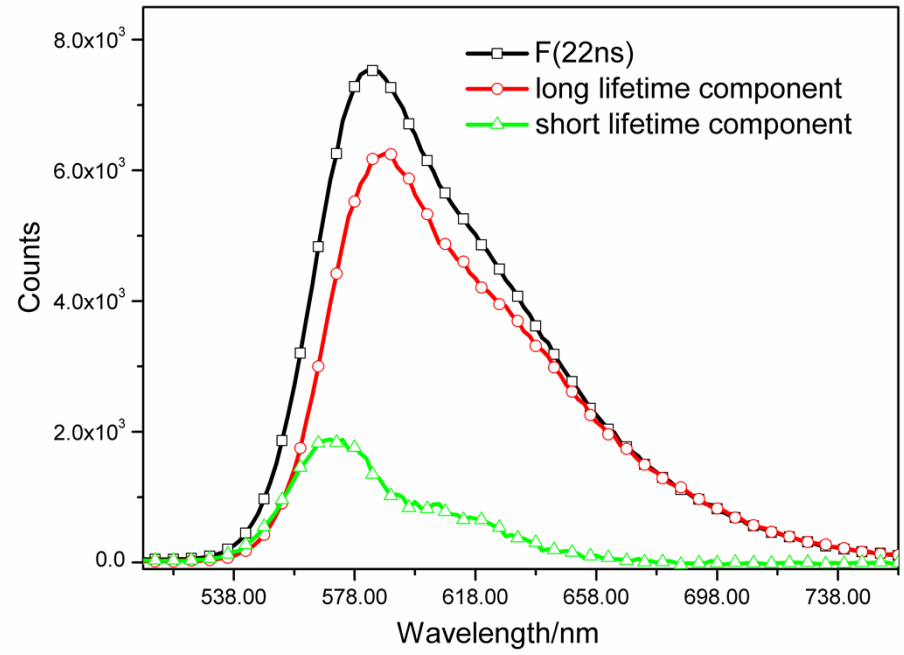


Figure S40. The split transient fluorescence spectra of $\mathbf{D_2}$. (red, component with long lifetime; green, component with short lifetime).

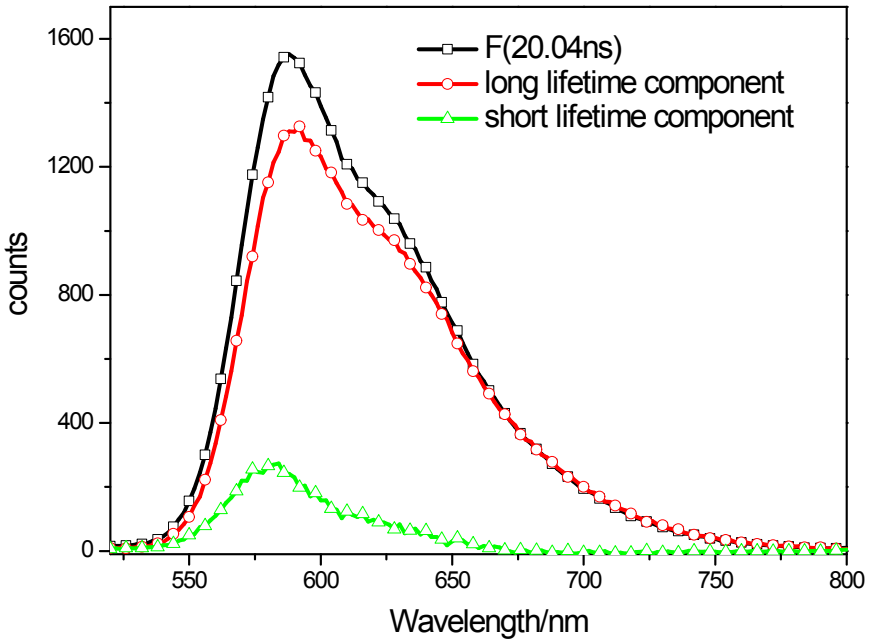


Figure S41. The split transient fluorescence spectra of $\mathbf{T_1}$. (red, component with long lifetime; green, component with short lifetime).

7. The absorption and fluorescence spectra of D_1, D_2, T_1 and T_2 in CH_2Cl_2.

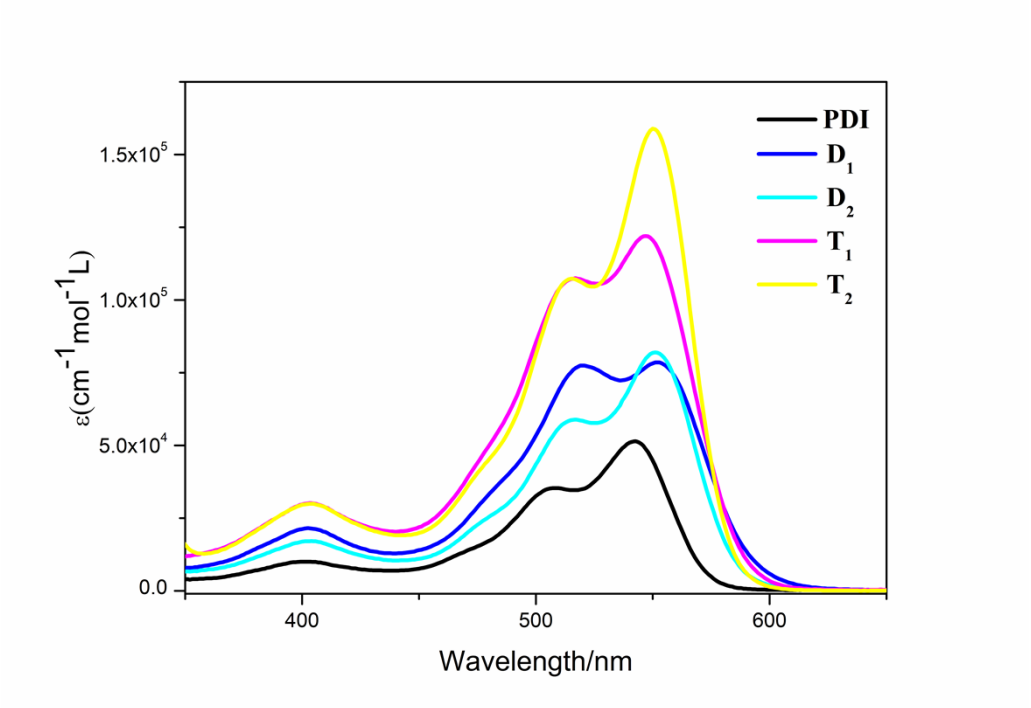


Figure S42. The absorption spectra of $\mathbf{D_1}$, $\mathbf{D_2}$, $\mathbf{T_1}$ and $\mathbf{T_2}$ in CH_2Cl_2.

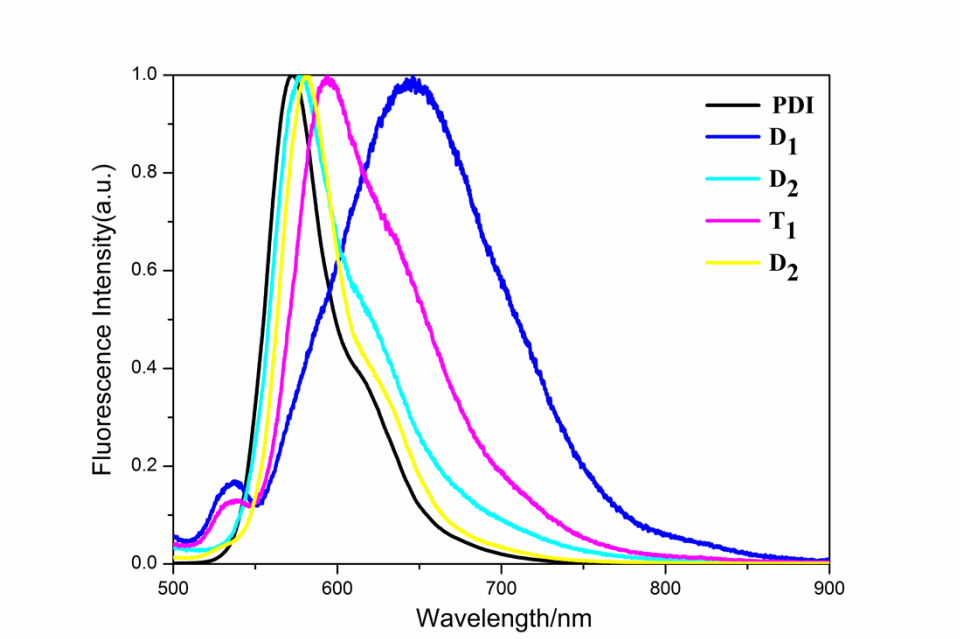


Figure S43. The fluorescence spectra of $\mathbf{D_1}$, $\mathbf{D_2}$, $\mathbf{T_1}$ and $\mathbf{T_2}$ in CH_2Cl_2.

8. The fitting of the fluorescence decay curves of D_1, D_2, T_1 and T_2 in toluene.

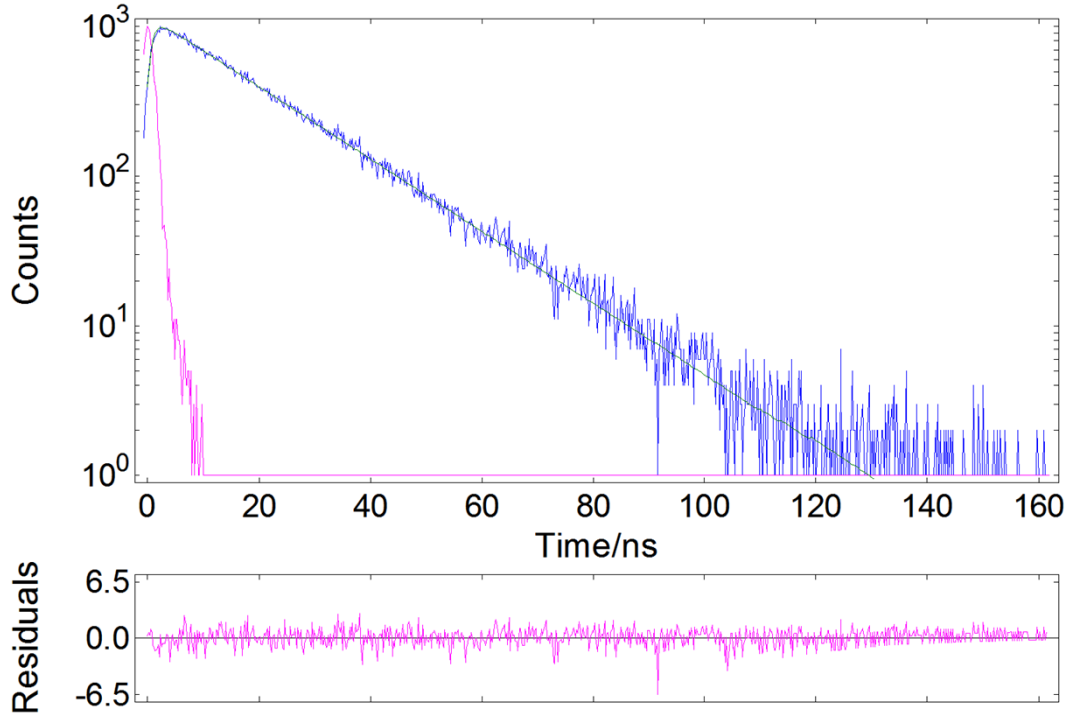


Figure S44. The kinetic of emission decays of $\mathbf{D_1}$.

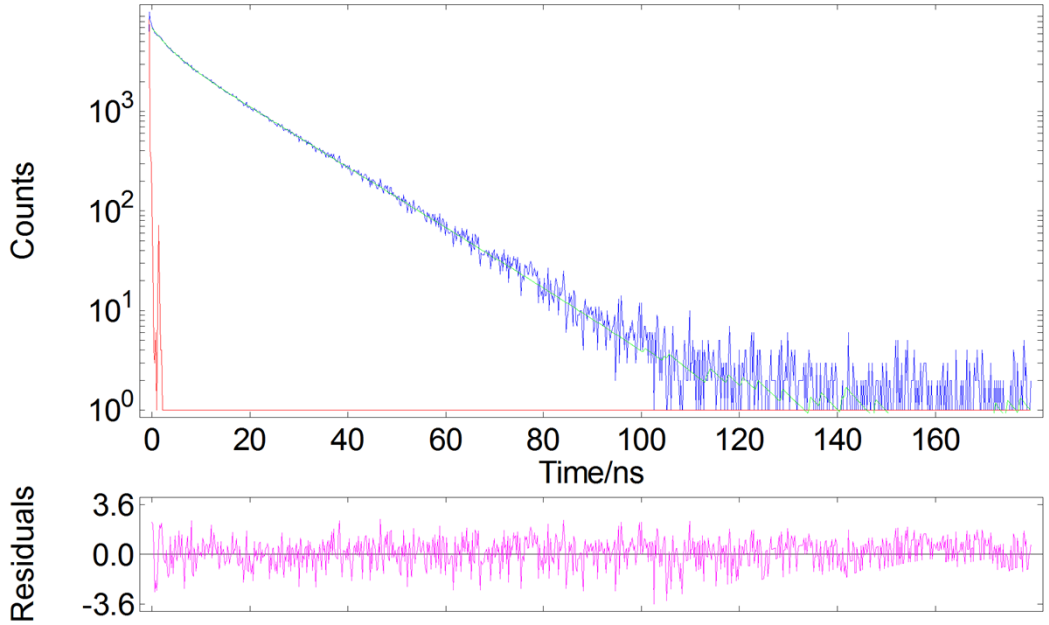


Figure S45. The kinetic of emission decays of $\mathbf{D_2}$.

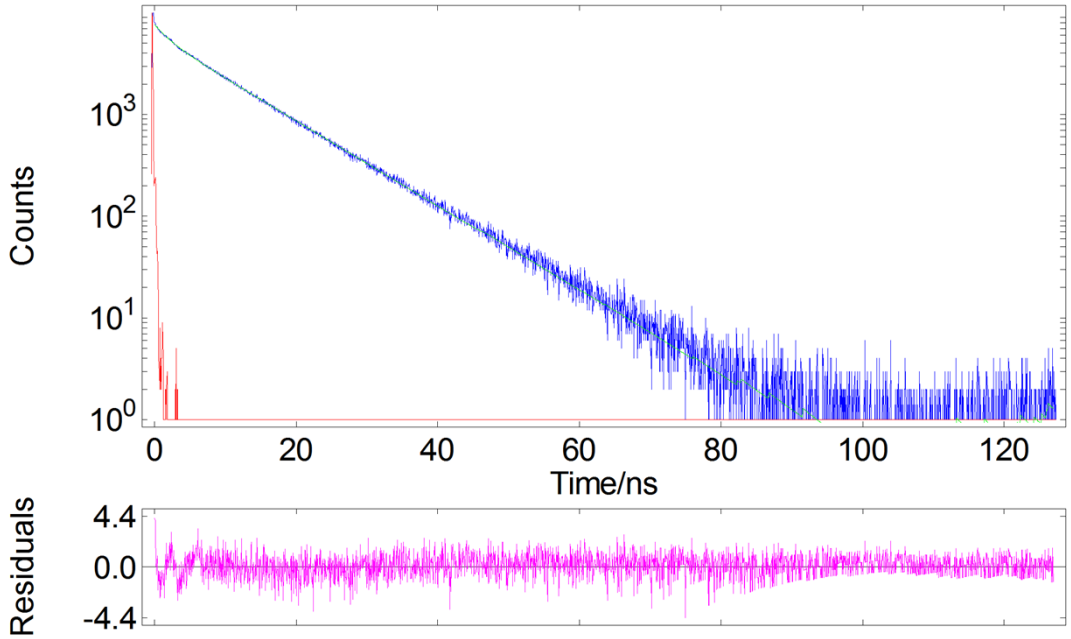


Figure S46. The kinetic of emission decays of $\mathbf{T_1}$.

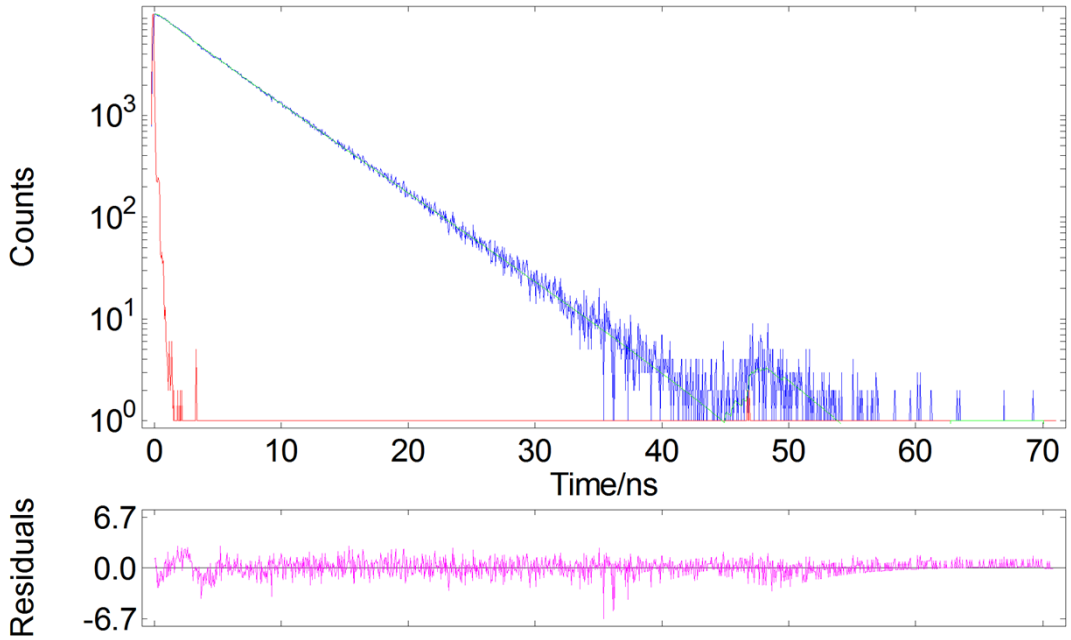


Figure S47. The kinetic of emission decays of $\mathbf{T_2}$.

9. HPLC analysis of D_1, D_2, T_1 and T_2.

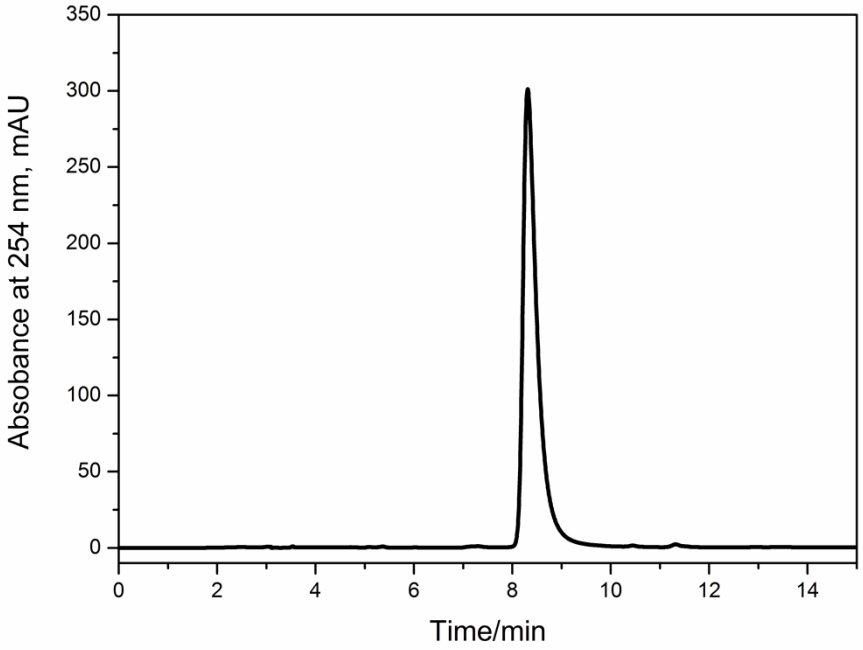


Figure S48. HPLC chromatogram of $\mathbf{D_1}$.

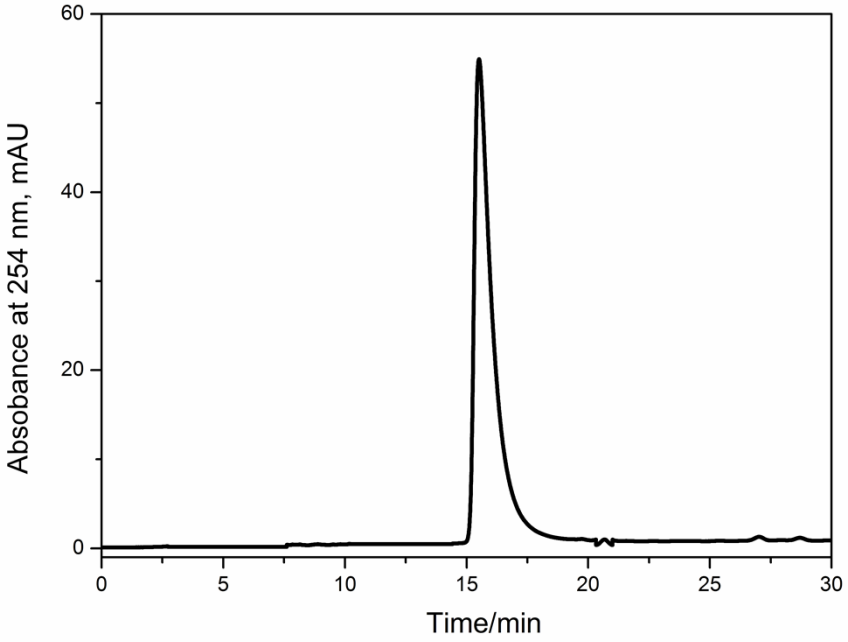


Figure S49. HPLC chromatogram of $\mathbf{D_2}$.

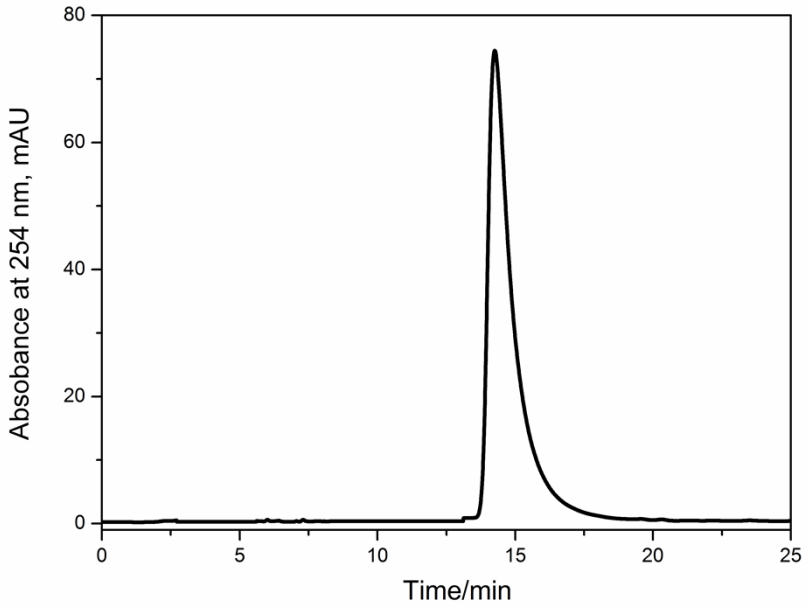


Figure S50. HPLC chromatogram of $\mathbf{T_1}$.

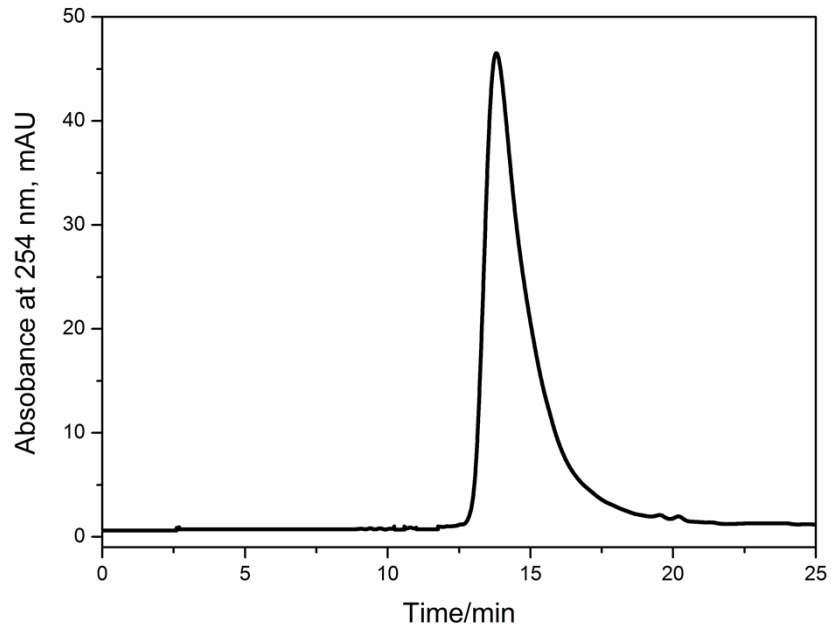


Figure S51. HPLC chromatogram of $\mathbf{T_2}$.

10. The ^{1}H NMR spectra of N,N'-di(cyclohexyl)perylene-3,4:9,10-tetracarboxylic diimide (pure 1,7-isomer).

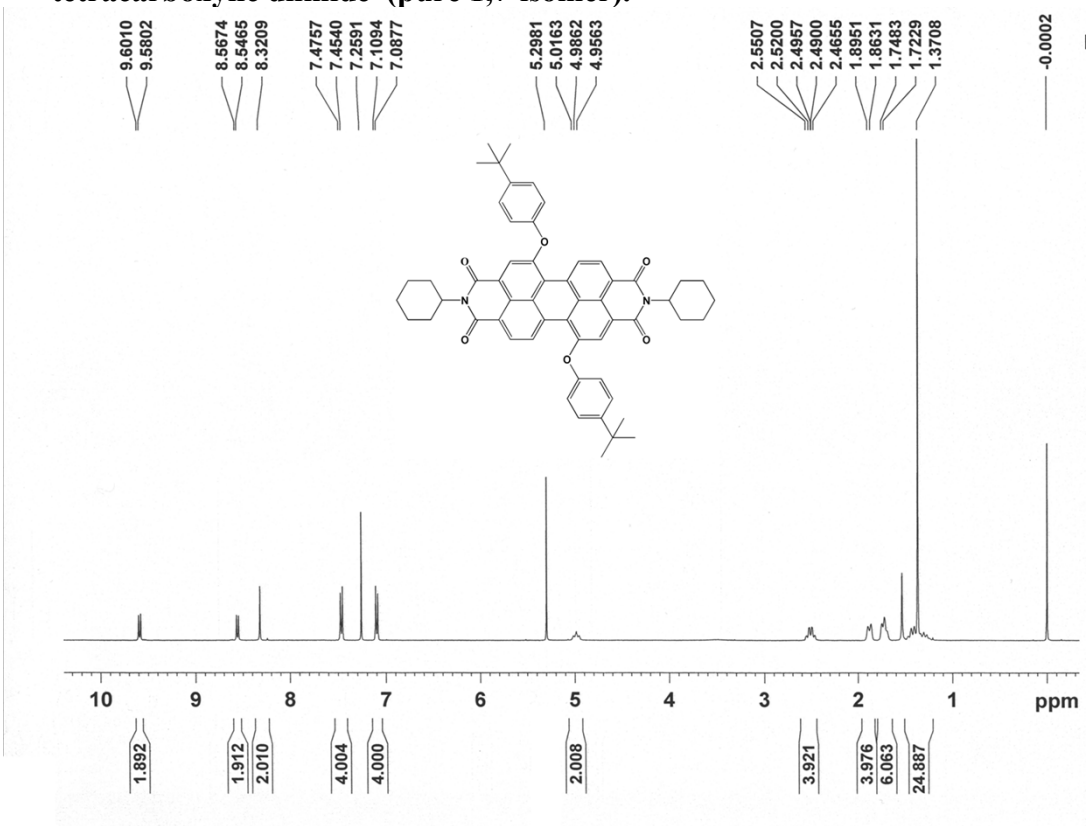


Figure S52. The ^{1}H NMR spectra of N,N'-di(cyclohexyl)perylene-3,4:9,10-tetracarboxylic diimide (pure 1,7-isomer). The crude material is pure 1,7-isomer, so the dimers and trimers have no 1,6-isomers.

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