Buchwald-Hartwig Coupling at Naphthalenediimide-core: Access to Dendritic, Panchromatic NIR Absorbers with Exceptionally Low-Band Gap

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Supporting Information

Contents

Experimental Section

General: Chemicals were sourced either from Sigma-Aldrich, Spectrochem India, Loba-chemie, or Thomas-Baker-India and were used as received. Thin layer chromatography (TLC) was carried out on aluminium plates coated with silica gel mixed with fluorescent indicator and was sourced from Merck, Germany. NMR (^{1}H, ^{13}C, DEPT 135 and APT) spectra were recorded on a Bruker 500 MHz spectrometer in $CDCl_3$ with TMS as a standard. Spin multiplicities are reported as a singlet (s), doublet (d), and triplet (t) with coupling constants (*J*) given in Hz, or multiplet (m). MALDI-TOF mass spectral data were obtained using a Bruker made Auto flex TOF/TOF instrument with laser repetition rate of 50 psec. α-Cyano-4-hydroxycinnamic acid and 1,8,9-Anthracenetriol were used as the matrix for MALDI-TOF mass spectrometry. The control compound NDI-C_6[1] and the starting material 2,3-dibromonaphthalene-1,4,5,8-tetracarboxylic acid bisimide (NDI-Br_2)[2] and different derivatives of para-substituted diphenyl amines[3] (**A**[3a], B[3b] and **C**[3c]**, Chart S2, SI**) were synthesized by following the earlier reported procedures.

UV-vis-NIR and IR Spectroscopy: UV-vis-NIR spectra were recorded on a JASCO V-670UV-vis-NIR Spectrophotometer. All the spectroscopic experiments were carried out in UV Grade $CHCl_3$ and MeCN which was sourced from Spectrochem, India. Infrared spectra were recorded in KBr pellet using a Varian 3100 FT-IR instrument.

Cyclic and Differential Pulse Voltammetry (CV/DPV): CV and DPV were carried out using a computer controlled potentiostat (CHI 650C) and a standard three electrode arrangement that consisted of both platinum working and auxiliary electrodes and saturated calomel (SCE) as reference electrode. All electrochemical measurements were carried out in argon-purged DCM with n-Bu_4NPF_6 as the supporting electrolyte. CV studies of the all molecules (0.5 mM) were performed in degassed DMF under argon atmosphere and the scan rate for the measurements was typically 100 mV/s. DPV was carried out keeping peak amplitude 50 mV, pulse width 0.01 sec, pulse period 0.05 sec and increment E at 10 mV.

Theoretical calculations: The ground-state geometry optimization was carried out applying the density functional theory (DFT) with the Becke three-parameter[4] hybrid exchange functional in concurrence with the Lee-Yang-Parr gradient-corrected correlation function (B3LYP functional)[5]

with the 6-31G(d,p) basis set as implemented in Gaussian 09W.[6] All the geometries were optimized without any constrain.

X-ray Crystallography: Crystals of compound **7** were grown in mixture of solvent using Hexane and $CHCl_3$ solution by slow evaporation method at room temperature. The crystals were adequately stable under ambient conditions, losing the crystalline nature for long exposure to air. The reported data set was collected by mounting the crystal with paratone oil in a loop. X-ray reflections were collected on Bruker D8 Quest diffractometer with CMOS detector using Mo-Kα radiation, generated from the micro-focus sealed tube. Data collection was performed using φ and ω-scans of 0.5° steps at 100 K. Cell determination, data collection and data reduction were performed with the help of Bruker APEX2 (version: 2014.3-0) software. The structure were solved by intrinsic phasing method (SHELXS-97) and refined by full-matrix least squares refinement method based on F^2, using, SHELXL-2014. A total of 97555 reflections were measured out of which 13067 were independent and 8998 were observed [I > 2\s(I)] for theta 28.36°. All non-hydrogen atoms were refined anisotropically. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were fixed geometrically with their U_{iso} values 1.2 times of the phenylene and methylene carbons and 1.5 times of the methyl carbon using a riding model. A final refinement of 619 parameters has given R1 = 0.0649, wR2 = 0.1769 for the observed data. The ORTEP diagram is given in **Figure S1** of the manuscript. The crystal structure data are deposited to Cambridge Structural Database with CCDC number **1871901**.

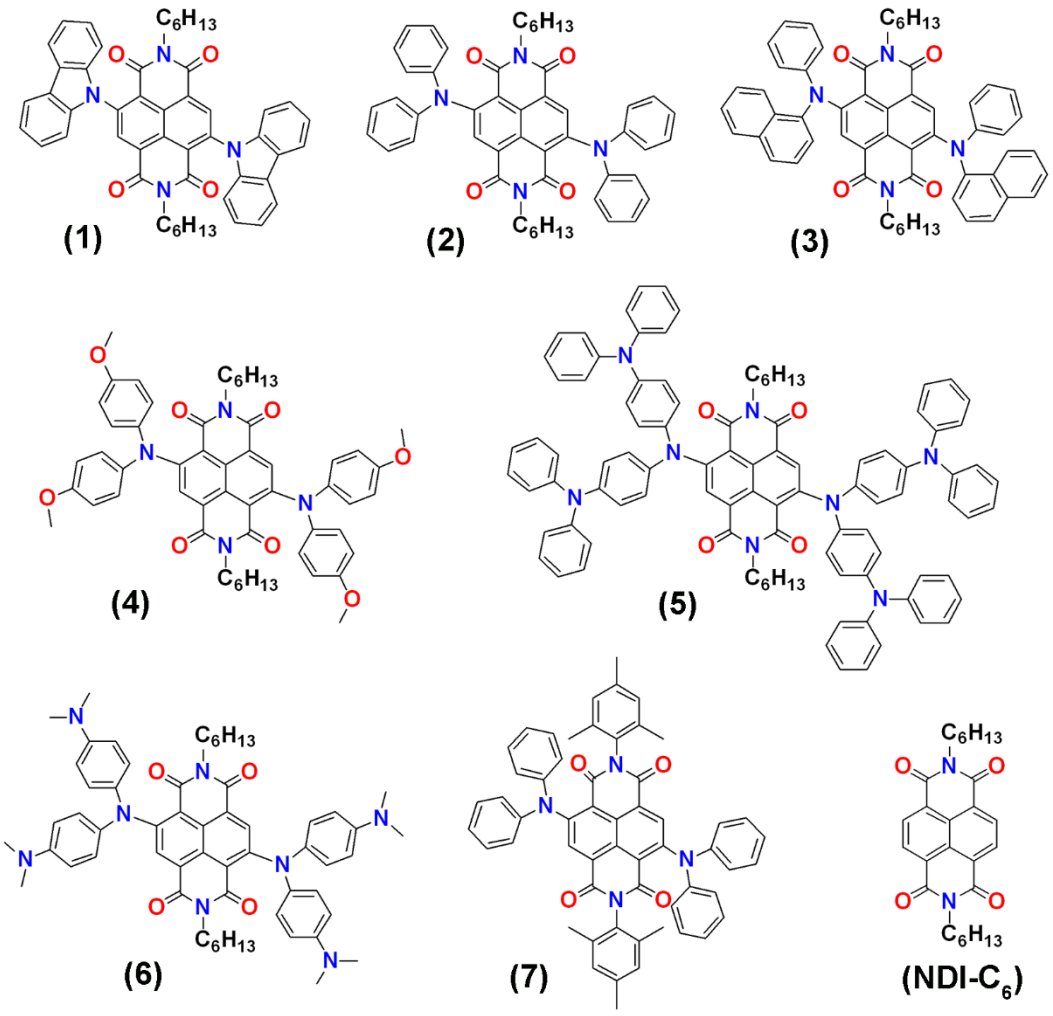


Chart S1: The molecular structures of secondary aryl-amines coupled *c*NDIs having donor-acceptor-donor conjugation (**1** to **7**) and **NDI-C$_6$** as the model compound.

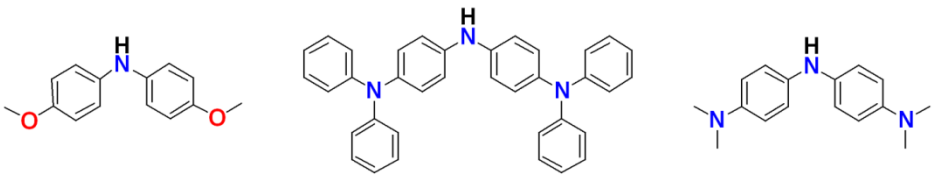
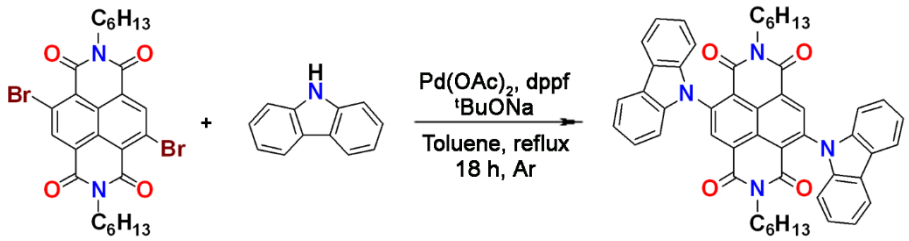


Chart S2: Molecular structure of donor amines synthesized by following reported procedure.

General Synthetic Procedure for 1 to 6:

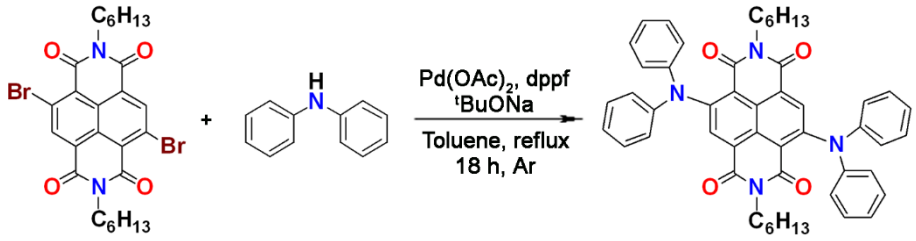
In a 100 ml three necked round bottomed (RB) flask containing 10 ml degassed toluene (freshly dried and degassed with freeze through), arylamine (1.28 mmol), sodium *tert*-butoxide (1.12 mmol), $Pd(OAc)_2$ (0.019 mmol), DPPF (0.038 mmol), and N,N'-dihexyl-2,3-dibromonaphthalene-1,4,5,8-tetracarboxylic acid bisimide (200 mg, 0.32 mmol) were added under N_2 atmosphere in glove box. The RB flask was completely closed and taken out from the glove box and the reaction mixture was refluxed for around 18 h under N_2 atmosphere. The reaction progress has been monitored with the TLC analysis. The reaction mixture gradually brought to room temperature and then precipitated with excess of hexane to obtain a blue/green solid product. This solid was again dissolved in minimum amount of $CHCl_3$ and further precipitated with help of MeOH and filtered, same have been procedure repeated for three more time. The obtained compound was again precipitated with the help of $CHCl_3$ and hexane to yield analytically pure compound in moderate yield from 35 to 50 % yield.

Synthesis of 1:



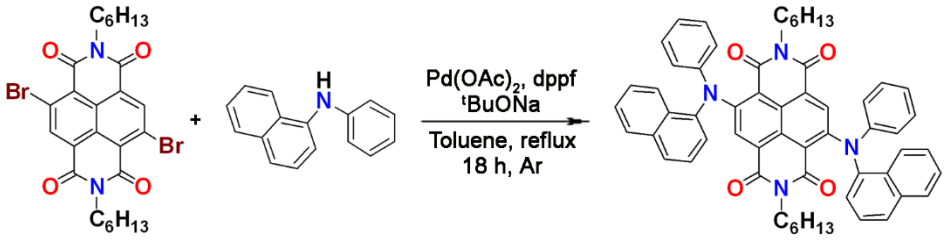
Compound **1** has been synthesized by utilizing carbazole as arylamine and dark blue colour product (105 mg) was isolated in moderate yield of 40%. Melting point: 332 °C. MS (MALDI-TOF, matrix-1,8,9-anthracenetriol): Calculated exact mass for $[C_{50}H_{44}N_4O_4+H^+]$, 765.34, found 765.36 (m/z). ^1H NMR (500 MHz, $CDCl_3$, 300 K): δ = 8.96 (s, 2H), 8.15 (d, *J* = 7 Hz, 4H), 7.35-7.29 (m, 8H), 7.11 (d, *J* = 7.5 Hz, 4H), 3.94 (t, *J* = 7.5 Hz, 4H), 1.48 (m, 4H), 1.18-1.15 (m, 12H), 0.75 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): 161.57, 159.83, 140.48, 139.92, 134.26, 127.95, 127.83, 126.37, 124.66, 121.51, 121.04, 120.97, 109.62, 41.03, 31.43, 27.91, 26.54, 22.46, 13.98. FTIR (KBr, cm^{-1}): 2929, 2836, 1705, 1665, 1450, 1324, 1229, 1190. Anal Calcd. for $C_{50}H_{44}N_4O_4$: C, 78.51; H, 5.80; N, 7.32; Found: C 78.64, H 5.88, N 7.81.

Synthesis of 2:



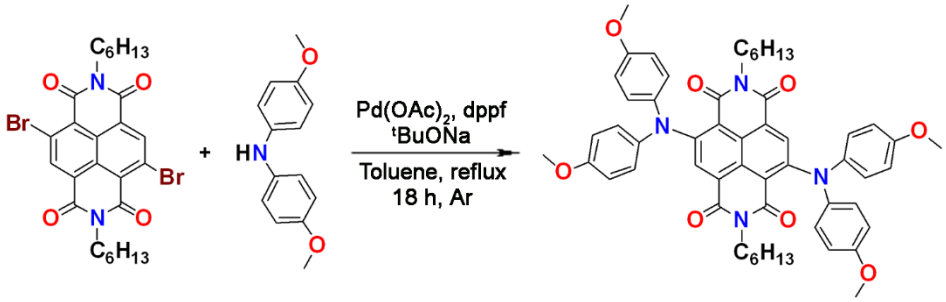
Compound **2** has been synthesized by utilizing diphenylamine as arylamine and royal blue colour product (130 mg) was isolated in moderate yield of 50%. Melting point: 320 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 8.40 (s, 2H), 7.27-7.24 (m, 8H), 7.07-7.05 (m, 12H), 3.86 (t, *J* = 7.5 Hz, 4H), 1.24-1.11 (m, 16H), 0.84 (t, *J*= 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): 162.52, 160.08, 148.83, 147.15, 133.54, 129.46, 126.26, 126.14, 124.49, 123.84, 116.51, 40.43, 31.39, 27.43, 26.39, 22.41, 14.07. MS (MALDI-TOF, matrix-1,8,9-anthracenetriol): Calculated exact mass for [$C_{50}H_{48}N_4O_4$+H], 768.38, found 769.31 (m/z). FTIR (KBr, cm^{-1}): 2931, 1692, 1658, 1562, 1493, 1449, 1194. Anal Calcd. for $C_{50}H_{48}N_4O_4$: C, 78.10; H, 6.29; N, 7.29; Found: C 78.21, H 6.41, N 7.33.

Synthesis of 3:



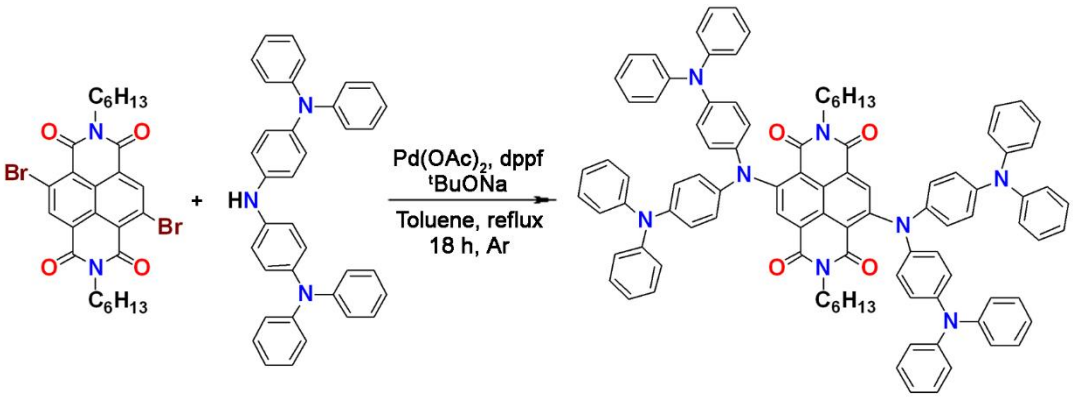
Compound **3** has been synthesized by utilizing N-Phenyl-1-naphthylamine as arylamine and royal blue colour product (112 mg) was isolated in moderate yield of 38%. Melting point: 330 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 8.37 (s, 2H), 7.69 (t, *J* = 6.5 Hz , 4H), 7.51 (d, *J* = 6.5 Hz, 2H), 7.36 (s, 2H), 7.32 (m, 4H), 7.22 (t, *J* = 8Hz, 4H), 7.17 (d, 2H), 7.04 (d, *J* = 7.5 Hz, 6H), 3.74 (t, *J* = 7.5 Hz, 4H), 1.02-1.00 (m, 8H), 0.91-0.90 (m, 8H), 0.71 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (125MHz, CDCl3, 298K): δ= 162.48, 160.11, 148.80, 147.03, 144.72, 134.19, 133.69, 130.93, 129.57, 129.36, 127.70, 127.25, 126.53, 126.38, 126.27, 125.27, 124.72, 124.00, 123.54, 120.78, 116.59, 40.38, 31.23, 27.38, 26.30, 22.32, 14.05. MS (MALDI-TOF, matrix- α-cyano-4-hydroxycinnamic acid): Calculated exact mass for [$C_{58}H_{52}N_4O_4$+H], 869.41, found 869.51(m/z). FTIR: 2926, 1691, 1657, 1593, 1564, 1490, 1444, 1319, 1272, 1190. Anal Calcd. for $C_{58}H_{52}N_4O_4$: C, 80.16; H, 6.03; N, 6.45; Found: C 80.23, H 6.16, N 6.57.

Synthesis of 4:



Compound **4** has been synthesized by utilizing 4,4'-dimethoxy diphenylamine as arylamine and greenish blue colour product (126 mg) was isolated in moderate yield of 42%. Melting Point = >340°C. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 8.25 (s, 2H), 6.91 (d, *J* = 8.5 Hz, 8H), 6.72 (m, 8H), 3.80 (t, *J* = 7 Hz, 4H), 3.71 (s, 12H), 1.18-1.06 (m, 16H), 0.79 (t, *J*= 6.5 Hz, 6H). ^{13}C NMR (125MHz, CDCl3, 298K): δ= 162.78, 160.04, 156.63, 148.68, 140.85, 132.51, 125.71, 125.20, 114.72, 114.44, 55.45, 40.35, 31.42, 27.55, 26.51, 22.45, 14.09. MS (MALDI-TOF, matrix-1,8,9-anthracenetriol): Calculated exact mass for [$C_{54}H_{56}N_4O_8$], 888.41, found 888.46 (m/z) FTIR (KBr, cm^{-1}): 2955, 2930, 2856, 1692, 1656, 1559, 1509, 1447, 1244, 1028. Anal Calcd. for $C_{54}H_{56}N_4O_8$: C, 72.95; H, 6.35; N, 6.30; Found: C, 73.11; H, 6.44; N, 6.22.

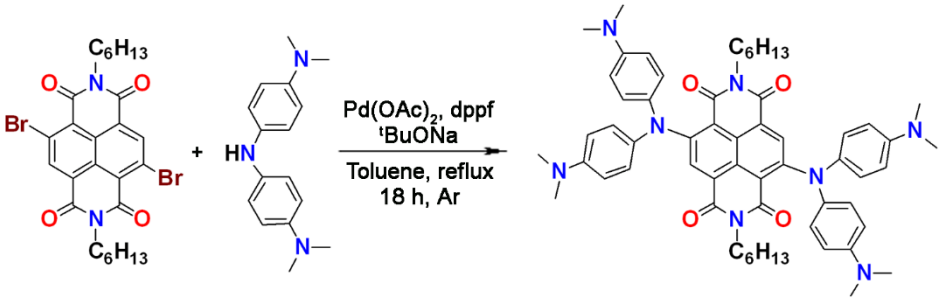
Synthesis of 5:



Compound **5** has been synthesized by utilizing G1 Dendrimeric of diphenylamine as arylamine and blackish green colour product (170 mg) was isolated in moderate yield of 35%. Melting Point = >350 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 8.42 (s, 2H), 7.18 (m, 16H), 7.02 (d, *J* = 8 Hz, 16H), 6.93 (t, *J* = 7 Hz, 8H), 6.88 (d, *J* = 9.5 Hz 16 H), 3.89 (t, *J* = 7.5 Hz, 4H), 1.41 (m, 4H), 1.22 (m, 12H), 0.77 (t, *J* = 6.5 Hz, 6H, *CH_3*). ^{13}CNMR (125MHz, $CDCl_3$, 298K): δ= 162.72, 160.03, 148.18, 147.56, 144.17, 141.69, 133.88, 129.25, 126.37, 125.95, 124.56, 124.35, 124.17, 122.81, 115.78,

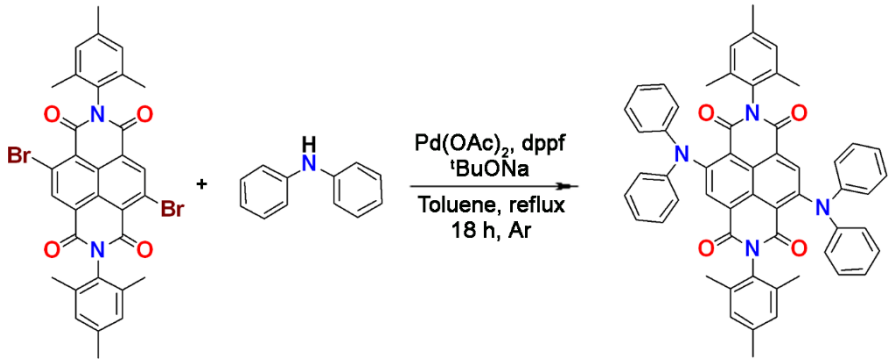
40.67, 31.42, 27.77, 26.82, 22.62, 14.09. MS (MALDI-TOF, matrix- α-cyano-4-hydroxycinnamic acid): Calculated exact mass for [$C_{98}H_{84}N_8O_4$], 1437.66, found 1437.70 (m/z). FTIR (KBr, cm^{-1}): 2931, 2673, 1694, 1660, 1586, 1497, 1273, 1191. Anal Calcd. for $C_{98}H_{84}N_8O_4$: C, 81.87; H, 5.89; N, 7.79; Found: C, 81.98; H, 5.96; N, 7.87.

Synthesis of 6:



Compound **6** has been synthesized by utilizing N1-(4-(Dimethylamino)phenyl)-N_4,N_4-dimethylbenzene-1,4-Diamine as arylamine and dark green colour product (112 mg) was isolated in moderate yield of 35%. Melting Point = >350 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 8.22 (s, 2H), 6.87 (d, *J* = 8.5 Hz, 8H), 6.53 (d, *J* = 8.5 Hz, 8H), 3.79 (t, *J* = 8 Hz, 4H), 2.85 (s, 24H), 1.14 (m, 8H), 1.08 (m, 8H), 0.77 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 163.16, 159.97, 148.29, 147.77, 137.72, 132.26, 125.55, 125.09, 125.01, 113.30, 113.15, 40.81, 40.19, 31.50, 29.72, 27.53, 26.61, 22.52, 14.13. MS (MALDI-TOF, matrix- α-cyano-4-hydroxycinnamic acid): Calculated exact mass for [$C_{58}H_{68}N_8O_4$], 940.54, found 940.59 (m/z). FTIR (KBr, cm^{-1}): 2931, 2856, 1689, 1653, 1516, 1447, 1318, 1193, 950. Anal Calcd. for $C_{58}H_{68}N_8O_4$: C, 74.01; H, 7.28; N, 11.91; Found: C, 74.14; H, 7.35; N, 11.84.

Synthesis of 7:

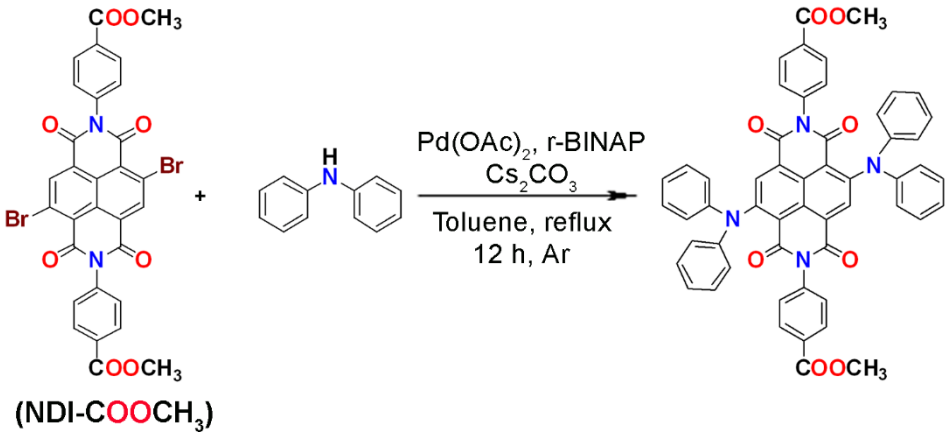


In a 100 ml three necked round bottomed (RB) flask containing 10 ml degassed toluene (freshly dried and degassed with freeze through), arylamine (1.21 mmol), sodium *tert*-butoxide (1.02 mmol), $Pd(OAc)_2$ (0.017 mmol), DPPF (0.034 mmol), and N,N'-mesityl-2,3-dibromonaphthalene-1,4,5,8-tetracarboxylic acid bisimide (200 mg, 0.30 mmol) were added under N_2 atmosphere in glove box. The RB flask was completely closed and taken out from the glove box and the reaction mixture was refluxed for around 18 h under N_2 atmosphere. The reaction progress has been monitored with the TLC analysis. The reaction mixture gradually brought to room temperature and then precipitated with excess of hexane to obtain a blue/green solid product. This solid was again dissolved in minimum amount of $CHCl_3$ and further precipitated with help of MeOH and filtered, same have been procedure repeated for three more time. The obtained compound was again precipitated with the help of $CHCl_3$ and hexane to yield 120 mg of analytically pure blue colour compound in 47 %. Melting Point = >350 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 8.49 (s, 2H), 7.22 (t, *J* = 7.5 Hz, 8H), 7.07-7.06 (m, 12H), 6.86 (s, 4H), 2.26 (s, 6H), 1.72 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 161.98, 159.25, 149.51, 147.16, 138.30, 134.83, 134.18, 130.72, 129.46, 129.18, 127.24, 126.51, 124.56, 124.20, 117.71, 21.09, 17.47. MS (MALDI-TOF, matrix-1,8,9-Anthracenetriol): Calculated exact mass for [$C_{56}H_{44}N_4O_4$+ H^+], 837.34, found 837.13 (m/z). FTIR (KBr, cm^{-1}): 2918, 1708, 1667, 1559, 1491, 1212, 1103. Anal Calcd. for $C_{56}H_{44}N_4O_4$: C, 80.36; H, 5.30; N, 6.69; Found: C, 80.45; H, 5.44; N, 6.76.

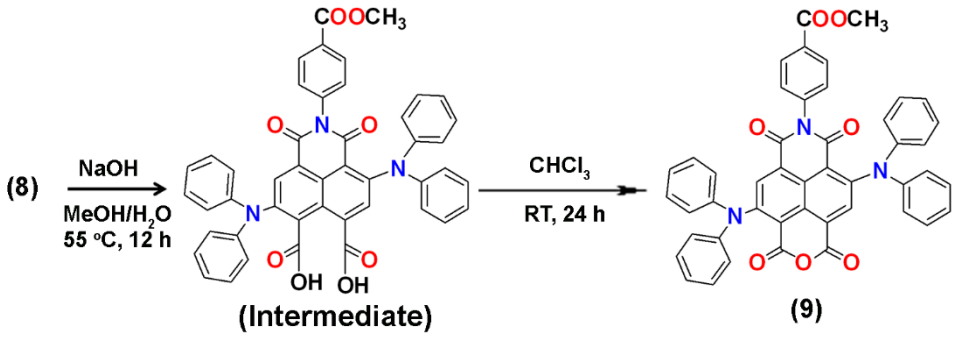
Synthesis of 8:

In a 100 mL three necked round bottom (RB) flask containing 8 ml degassed toluene, diphenylamine (1.26 mmol), cesium carbonate (1.26 mmol) were added under N_2 atmosphere in glove box. $Pd(OAc)_2$ (0.02 mmol), r-BINAP (0.04 mmol), NDI-$COOCH_3$ (250 mg, 0.36 mmol) were added. The mixture was refluxed for 12 h under N_2 atmosphere. The reaction progress has been monitored with the TLC

analysis. The reaction mixture gradually brought to room temperature and then precipitated with excess of hexane to obtain a greenish blue solid product. This solid was again dissolved in minimum amount of $CHCl_3$ and further precipitated with help of MeOH and filtered, same procedure have been repeated for three more time. The obtained compound was again precipitated with the help of $CHCl_3$ and hexane to yield 194 mg of analytically pure blue compound in quite good of 62%. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 8.39 (s, 2H), 7.96 (d, *J* = 8.5 Hz, 4H), 7.22-7.16 (m, 8H), 7.06 (t, *J* = 7.5 Hz, 4H), 7.00 (d, *J* = 8.0 Hz, 8H), 6.79 (d, *J* = 8.0 Hz, 4H), 3.84 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 166.32, 162.26, 160.42, 149.34, 147.01, 139.31, 133.55, 130.58, 130.47, 130.16, 129.64, 128.46, 126.38, 126.28, 124.96, 124.18, 116.06, 52.32. MS (ESI-HRMS): calculated exact mass for [$C_{54}H_{36}N_4O_8$+H^+], 869.26, found 869.05 (m/z). FTIR (KBr, cm^{-1}): 3071, 2956, 1715, 1674, 1564, 1435, 1284, 1212. Anal Calcd. for $C_{54}H_{36}N_4O_8$: C, 74.64; H, 4.18; N, 6.45; Found: C, 74.76; H, 4.26; N, 6.53.



Synthesis of 9:



The ester based compound **8** (80 mg) was transferred to a 50 mL RB containing 10 mL MeOH and 5 ml H_2O. The 2 equimolar ratio of NaOH (dissolved in H_2O) was added to it. The reaction mixture

was allowed to heat at 55 °C for 12 h to yield a deep red colour solution. The reaction progress has been monitored by the TLC. After completion the reaction mixture was cooled to RT. The acid work-up with HCl converts the red colour solution to purple colour, which was washed with water and dried with dry $MgSO_4$. The solvent was removed by rotary evaporator to get a purple colour solid of Intermediate compound. The solid compound was dissolved in $CHCl_3$ and stored in a close vessel for 24 h to get 47 mg of blue colour monoanhydride product **9** in a good yield of 70%. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 8.35 (s, 2H), 7.95 (d, *J* = 8.5 Hz, 2H), 7.25-7.17 (m, 8H), 7.09 (t, *J* = 7.5 Hz, 4H), 7.00 (t, *J* = 8.5 Hz, 8H), 6.76 (d, *J* = 8.5 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 161.86, 160.07, 159.57, 154.89, 150.27, 149.25, 146.83, 146.77, 139.08, 134.94, 133.36, 130.47, 130.29, 129.79, 129.75, 128.36, 128.15, 127.04, 126.19, 125.57, 125.28, 124.38, 124.21, 122.56, 122.28, 116.56, 111.84, 52.29. MS (ESI-HRMS): calculated exact mass for [$C_{46}H_{29}N_3O_7$ + H^+], 736.21, found 736.20 (m/z). FTIR (KBr, cm^{-1}): 2960, 2918, 1715, 2862, 1734, 1719, 1702, 1687, 1672, 1599, 1459, 1409, 1259, 1100, 1017, 804. Anal Calcd. for $C_{46}H_{29}N_3O_7$: C, 75.09; H, 3.97; N, 5.71; Found: C, 75.19; H, 3.89; N, 5.84.

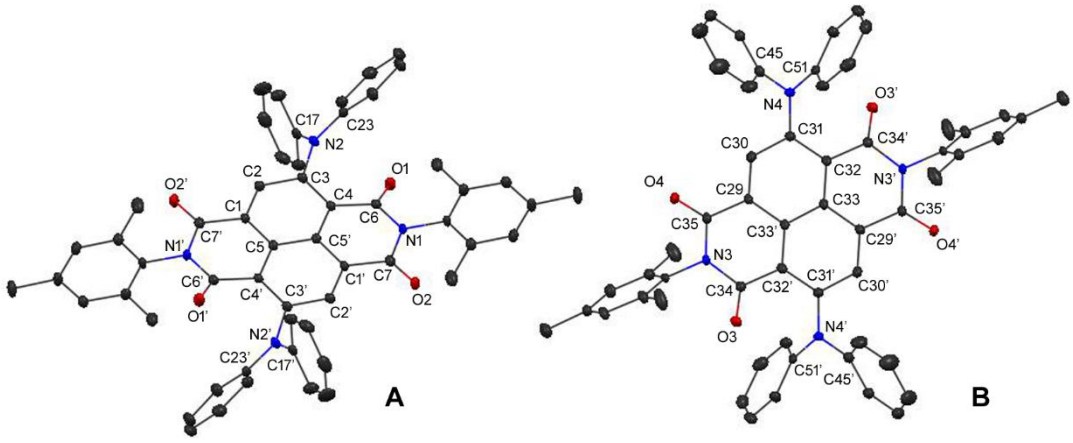


Figure S1: X-ray crystal structure of compound **7** with atom numbering scheme having two asymmetric units.

Table S1: Selected bond length and torsion angle in the crystal of compound **7**.

Atoms	Selected Bond length [Å] Crystal Data
C6 − O1, C6’ – O1’	1.207 Å
C7 − O2, C7’ – O2’	1.214 Å
C6 − N1, C6’ –N1’	1.412 Å
C7 − N1, C7’ – N1’	1.389 Å
C1 − C2, C1’ – C2’	1.366 Å
C2 − C3, C2’ – C3’	1.412 Å
C3 − C4, C3’ – C4’	1.403 Å

C4 − C5', C4' – C5	1.414 Å
C1 − C5, C1' – C5	1.416 Å
C5 − C5'	1.417 Å
C4 − C6, C4' − C6'	1.481 Å
C1 − C7', C1' − C7	1.486 Å
C3 − N2, C3' − N2'	1.402 Å
N2 − C17, N2' − C17'	1.426 Å
N2 − C23, N2' − C23'	1.419 Å
C34 − O3, C34' – O3'	1.209 Å
C35 − O4, C35' – O4'	1.214 Å
C34 − N3, C34' –N3'	1.411 Å
C35 − N3, C35' – N3'	1.390 Å
C29 − C30, C29' – C30'	1.372 Å
C30 − C31, C30' – C31'	1.413 Å
C31 − C32, C31' – C32'	1.406 Å
C32 − C33, C32' – C33'	1.410 Å
C29 − C33', C29' – C33	1.418 Å
C33 − C33'	1.419 Å
C29 − C35, C29' − C35'	1.479 Å
C32 − C34', C32' − C34	1.487 Å
C31 − N4, C31' − N4'	1.403 Å
N4 − C45, N4' − C45'	1.417 Å
N4 − C51, N4' − C51'	1.426 Å

Atom	**Selected torsion angle (Degree)**
C2 − C3 − N2 − C17, C2' − C3' − N2' − C17'	52.93°
C4 − C3 − N2 − C23, C4' − C3' − N2' − C23'	47.82°
C2 − C3 − N2 − C23, C2' − C3' − N2' − C23'	129.61°
C4 − C3 − N2 − C17, C4' − C3' − N2' − C17'	129.64°
C6 – C4 – C3 – N2, C6' – C4' – C3' – N2'	14.66°
C30 − C31 − N4 − C45, C30' − C31' − N4' − C45'	43.56°
C32 − C31 − N4 − C51, C32' − C31' − N4' − C51'	49.75°
C30 − C31 − N4 − C51, C30' − C31' − N4' − C51'	127.00°
C32 − C31 − N4 − C45, C32' − C31' − N4' − C51'	139.69°
C34 – C32 – C31 – N4, C34' – C32' – C31' – N4'	14.39°

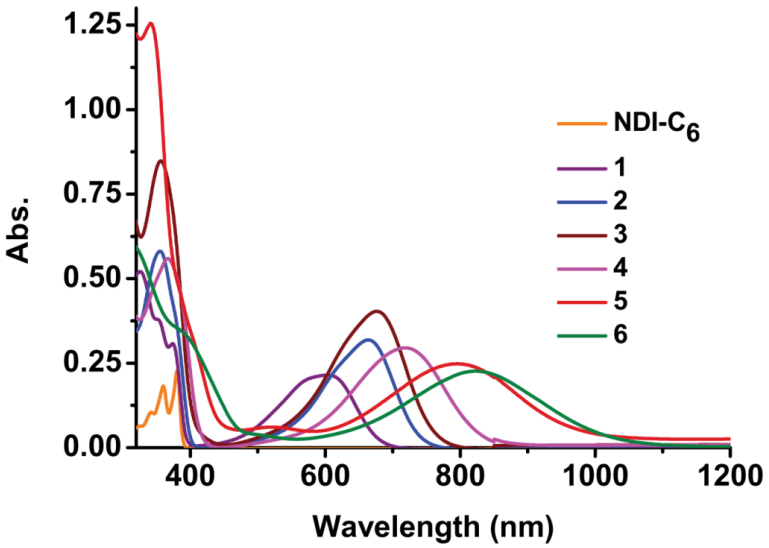


Figure S2a. UV-vis-NIR absorption spectra of compound **NDI-C$_6$**, **1**, **2, 3**, **4**, **5** and **6** in $CHCl_3$ (0.2 mM).

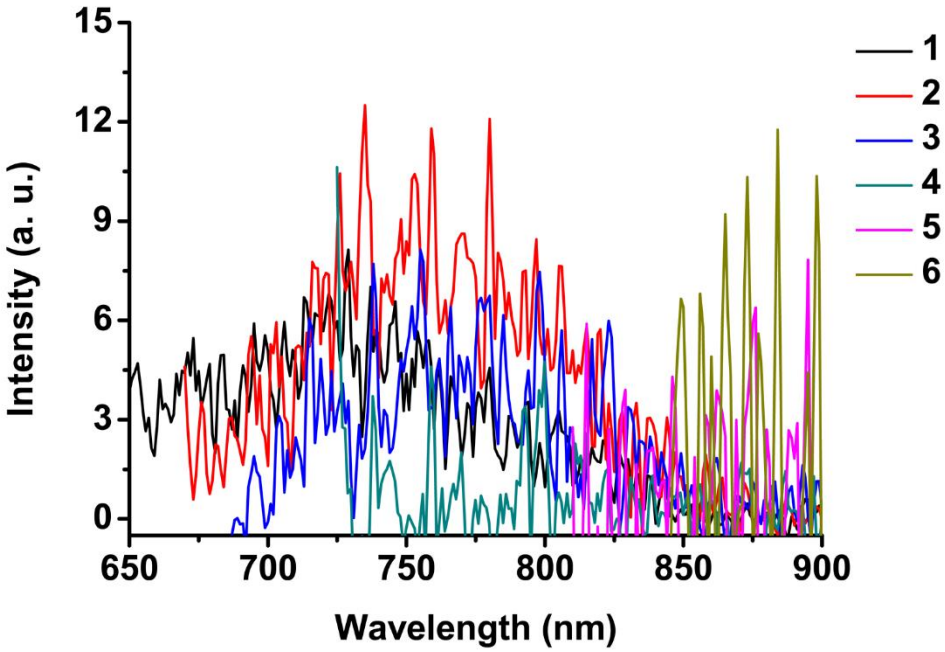


Figure S2b. Emission spectra of compound **1**, **2, 3**, **4**, **5** and **6** in $CHCl_3$ (0.05 mM), with excitation wavelength of 630 nm, 663 nm, 677 nm, 719 nm, 800 nm and 830 nm, respectively.

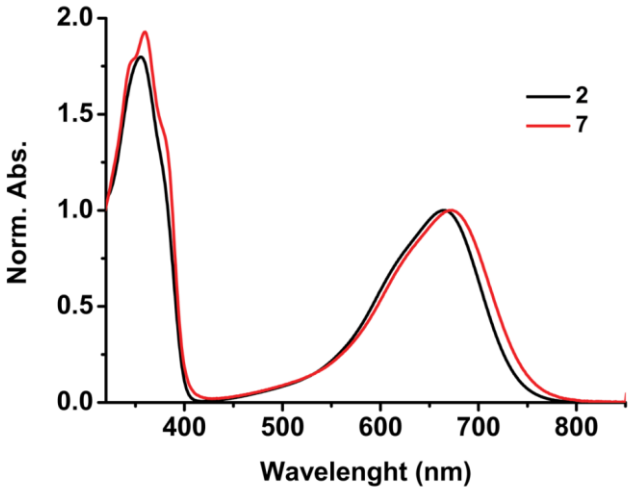


Figure S3. UV-vis-NIR absorption spectra of compound **2** and **7** in $CHCl_3$ (0.02 mM).

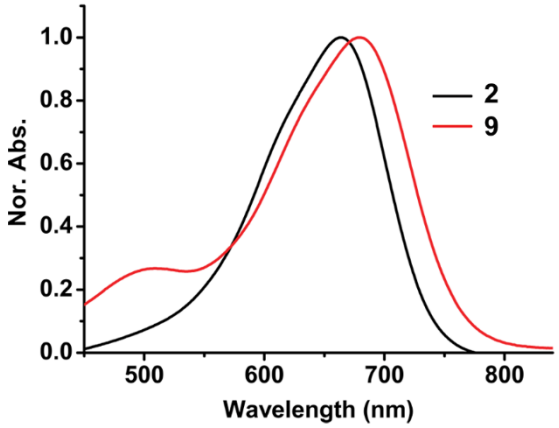
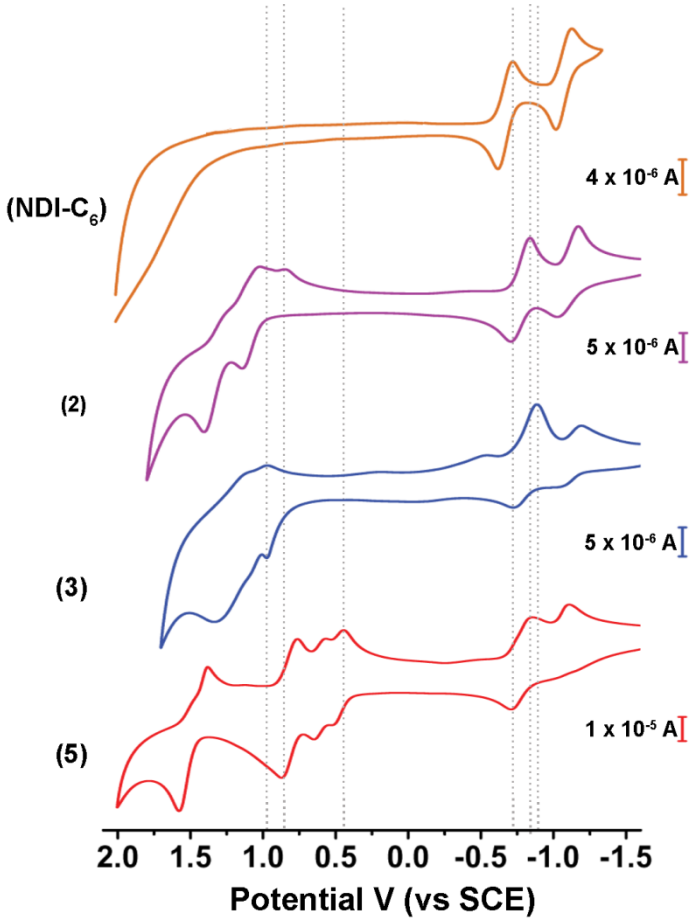


Figure S4. UV-vis-NIR absorption spectra of compound **2** and **9** in $CHCl_3$ (0.02 mM).

a)



b)

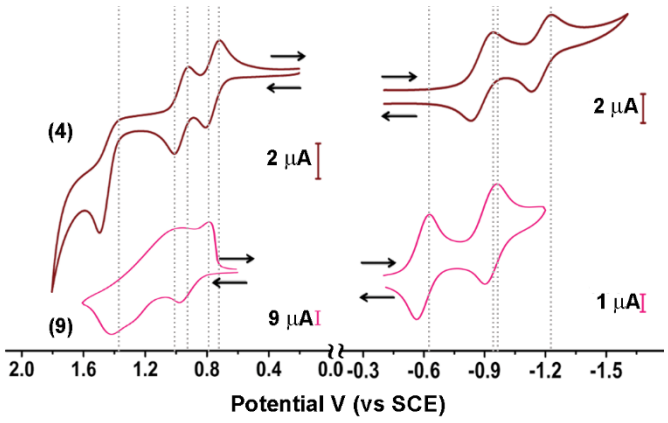


Figure S5: Cyclic Voltammogram results of compound **NDI-C$_6$**, **2**, **3**, **5** (a) and **4, 9** (b) (0.5 mM) in degassed DCM with 0.1M TBAPF$_6$ at room temperature.

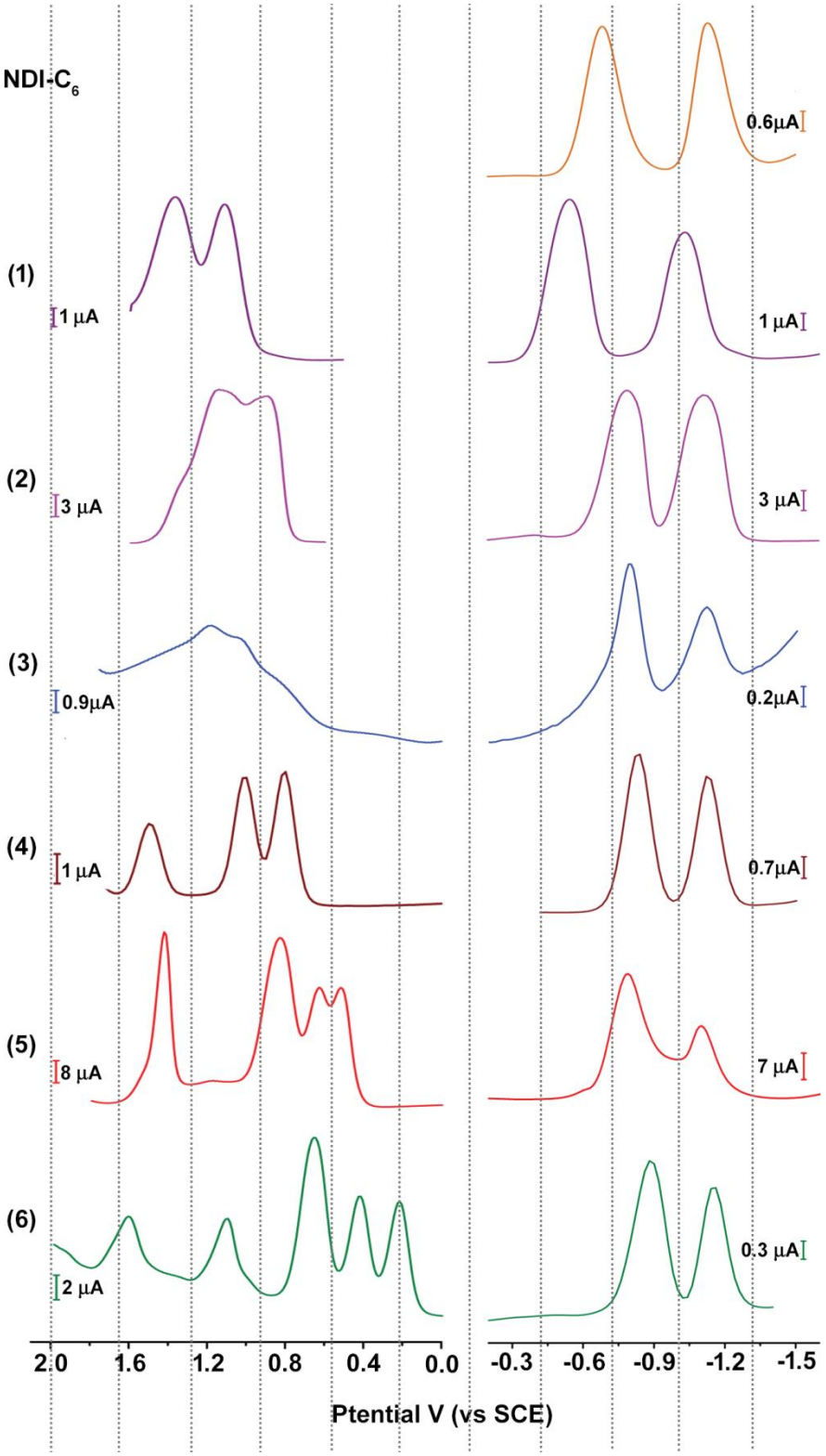
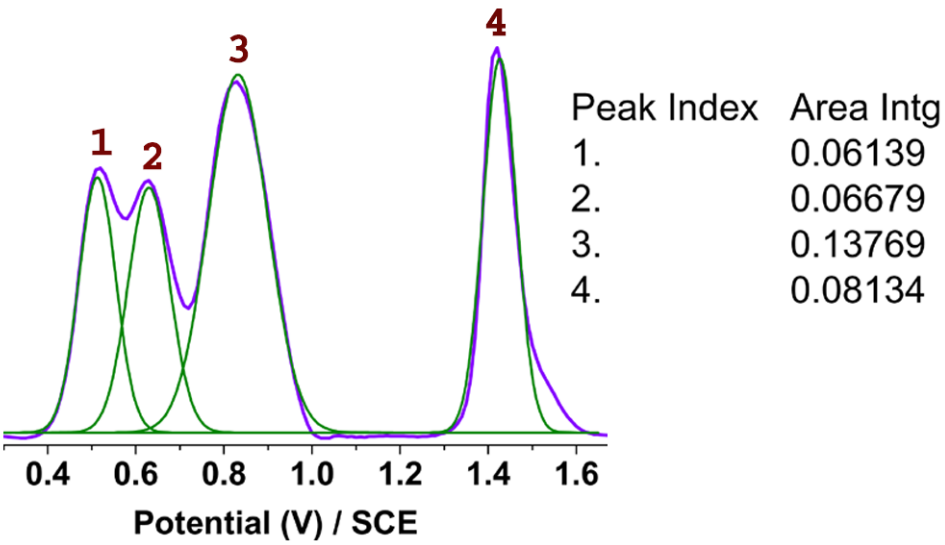


Figure S6: DPV results in degassed DCM (0.5 mM) at 298 K.

a)



b)

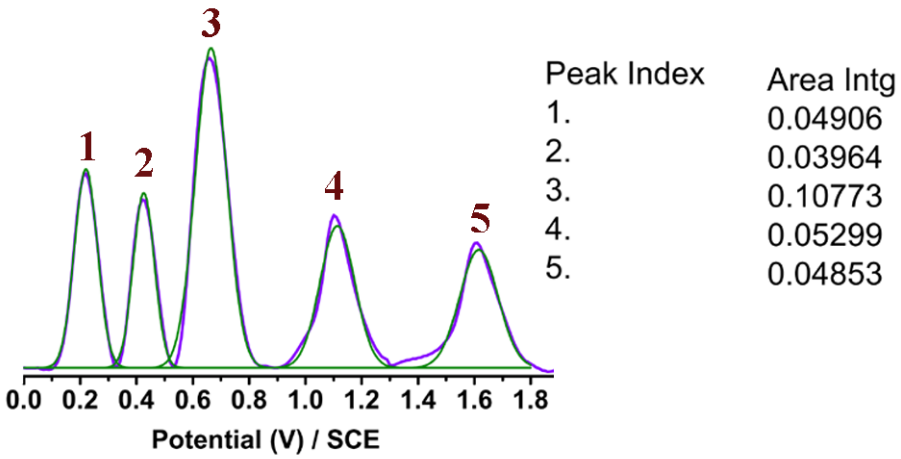


Figure S7: Peak fitting analysis for the number of electrons involving during oxidation of **5** (a) and **6** (b), respectively.

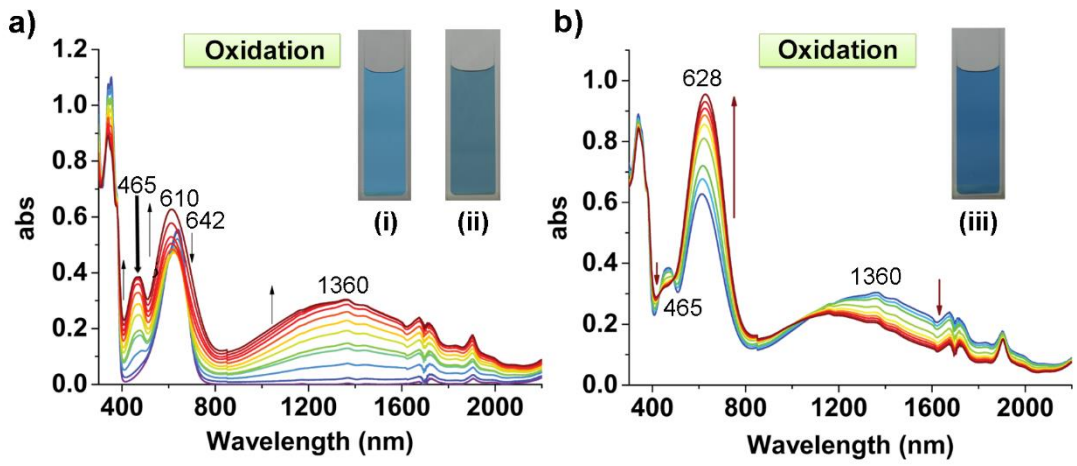


Figure S8: UV-vis-NIR spectra showing the spectral response of compound **2** (0.2 mM) in MeCN:$CHCl_3$ solution (8:2 ratio) with the gradual addition of $Cu(ClO_4)_2$ from 0 to 2.2 equivalent (a) and 2.2 to 6 equivalent (b) and their corresponding coloured solution picture with zero equiv. (i), 2.2 equiv. (ii) and 6 equiv. (iii) of $Cu(ClO_4)_2$.

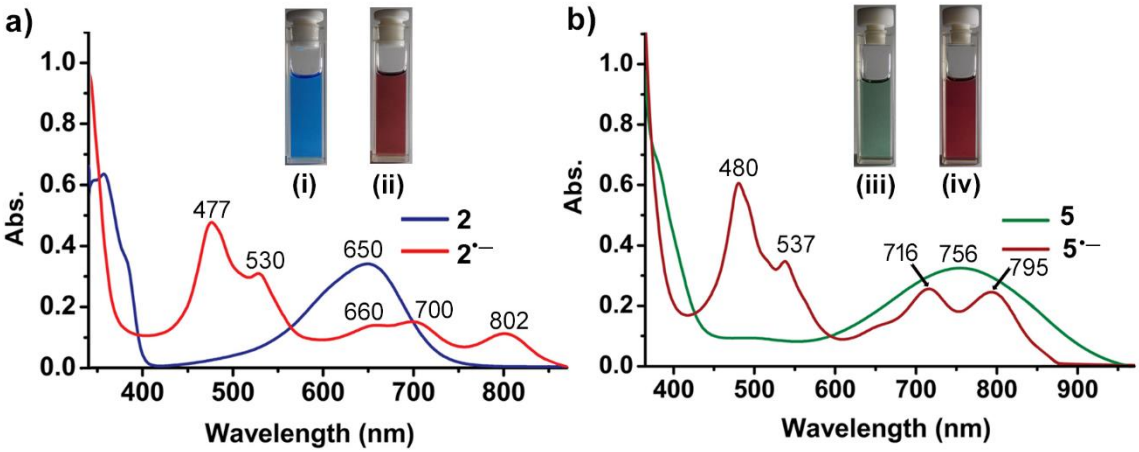


Figure S9: : UV-vis-NIR spectra showing the spectral response of compound **2** (a) and **5** (b) in 0.03 mM DMSO solution with the addition of Na_2S to generate their resultant radical anion, and their corresponding coloured solution pictures for **2** (i), $\mathbf{2}^{\bullet-}$ (ii) and **5** (iii) and $\mathbf{5}^{\bullet-}$ (iv) species**.**

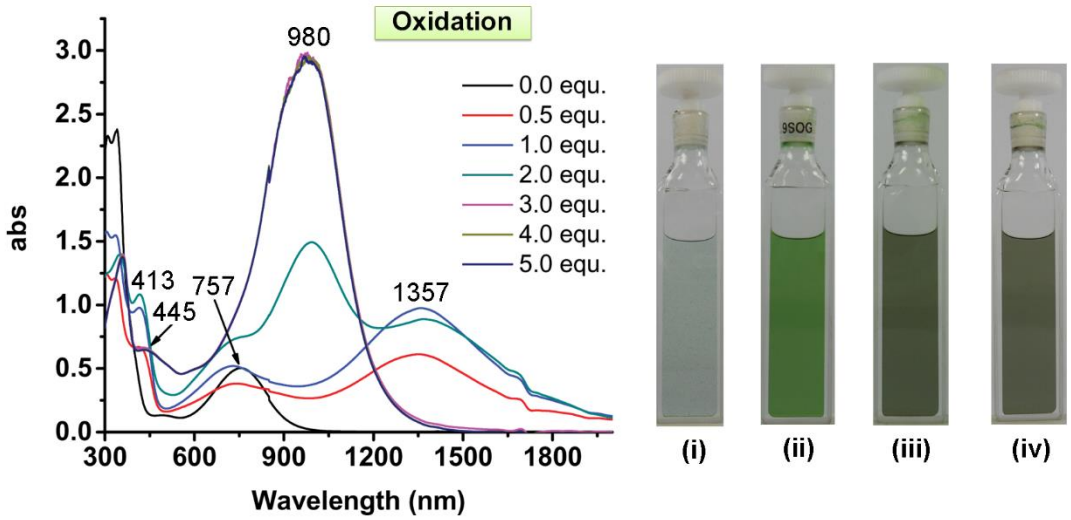


Figure S10: UV-vis-NIR spectra showing the spectral response of compound **5** (0.04 mM) in MeCN:$CHCl_3$ solution (8:2 ratio) with the gradual addition of $Cu(ClO_4)_2 \cdot xH_2O$ from 0 to 5 equivalent and their corresponding coloured solution picture with zero equiv. (i), 1 equiv. (ii) 2 equiv.(ii) and 3 equiv. (iii) of $Cu(ClO_4)_2 \cdot xH_2O$.

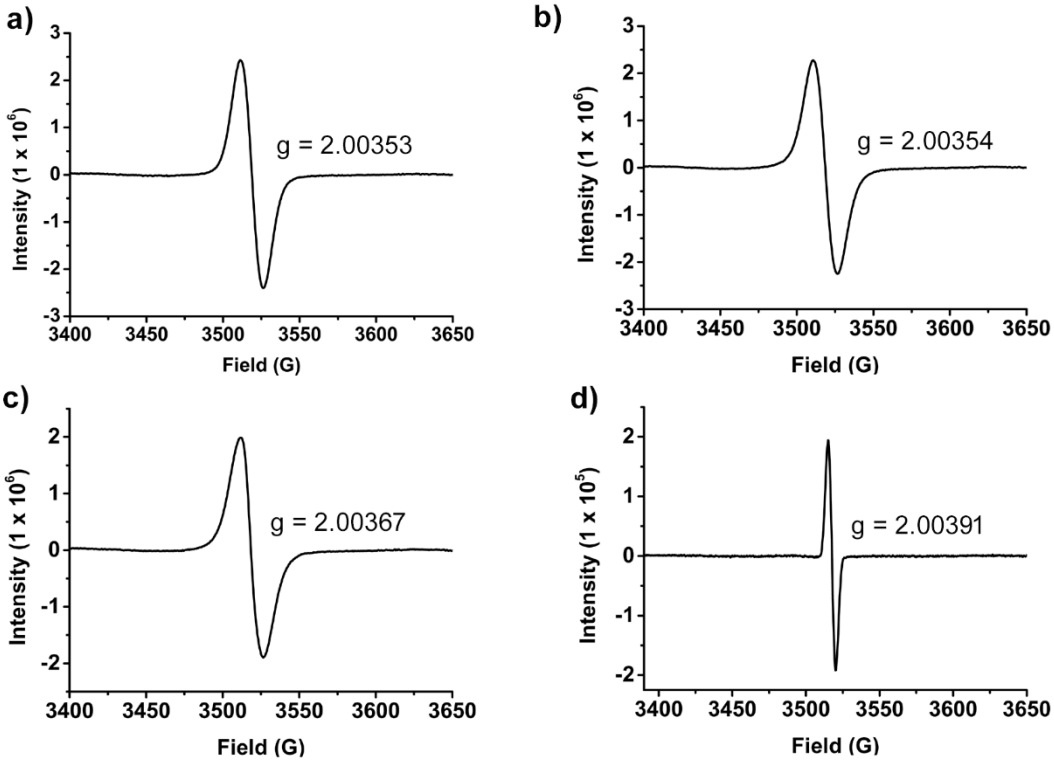


Figure S11: ESR spectrum of oxidized species of **6** with1 equiv. (a) 2 equiv. (b) and 3 equiv. (c) of Cu(II) (a)**,** in 1 mM MeCN:$CHCl_3$ (8:2) solution at 298 K. The ESR signal of $\mathbf{6}^{\bullet-}$, generated by the reduction with Na_2S in 1 mM DMSO solution (d). The existence of ESR signal confirmed the high-spin nature of the di-oxidized and tri- oxidized redox species.[4] The hyperfine splitting pattern was not observed probably due to the presence of residual oxygen in the capillary, since all the experiments have been carried out under ambient condition.

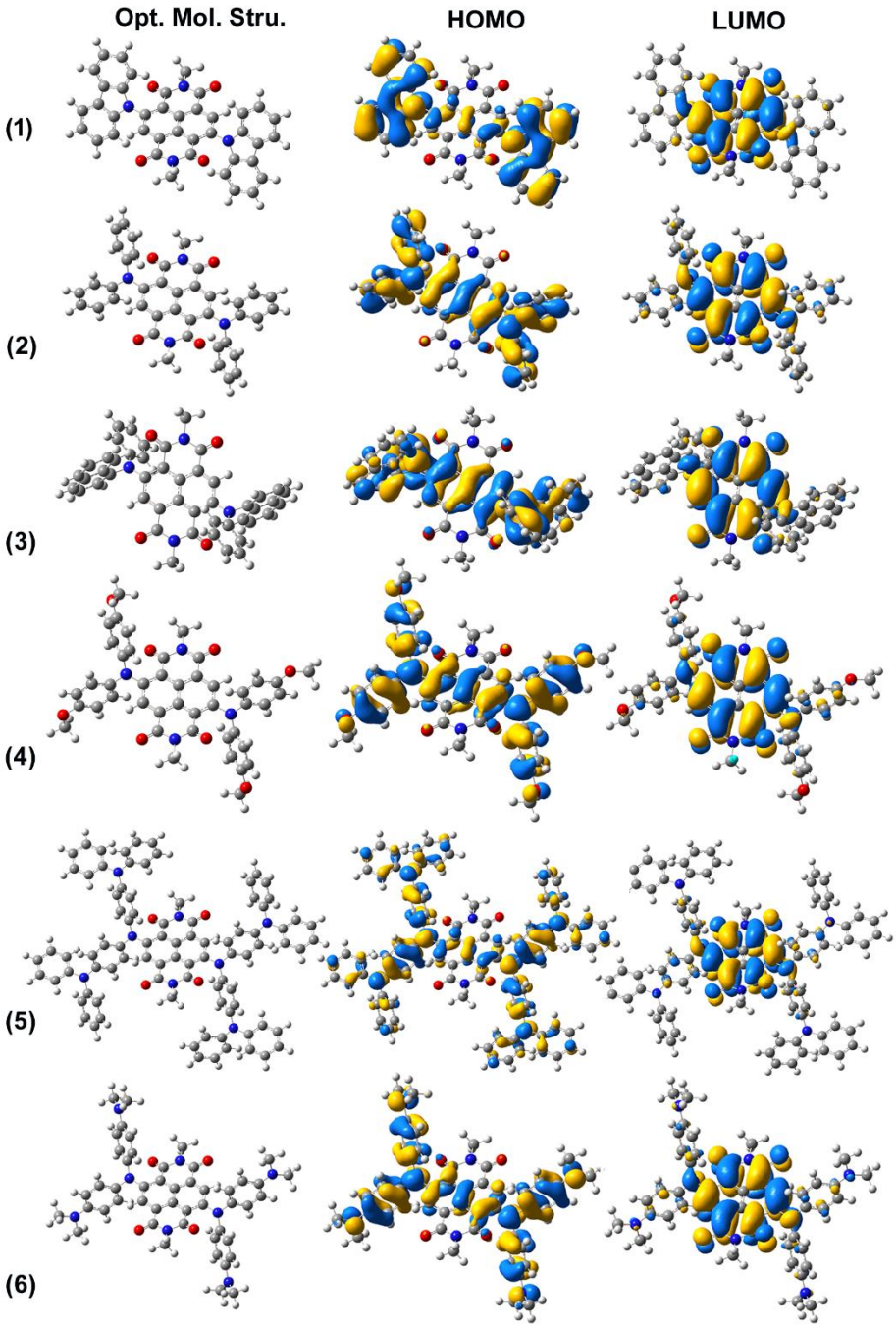


Figure S12: Optimized molecular structures of compounds **1—6** and their corresponding HOMO and LUMO orbital diagrams with the DFT calculation on B3LYP/631g (dp) basis set. In all the compounds the LUMO surface is localized over the acceptor NDI motif with partial contribution of nitrogen atoms of the donor. These LUMO orbitals are extended along the long molecular axis and exhibited the classical quinoidal character. On the other hand, the HOMO of all the compounds are delocalized over the whole molecular system with major contribution at the donor nitrogen atoms and polarized perpendicular to the long molecular axis. These features of the HOMO surfaces confirmed the strong interaction between arylamine and naphthalene π-conjugated core.

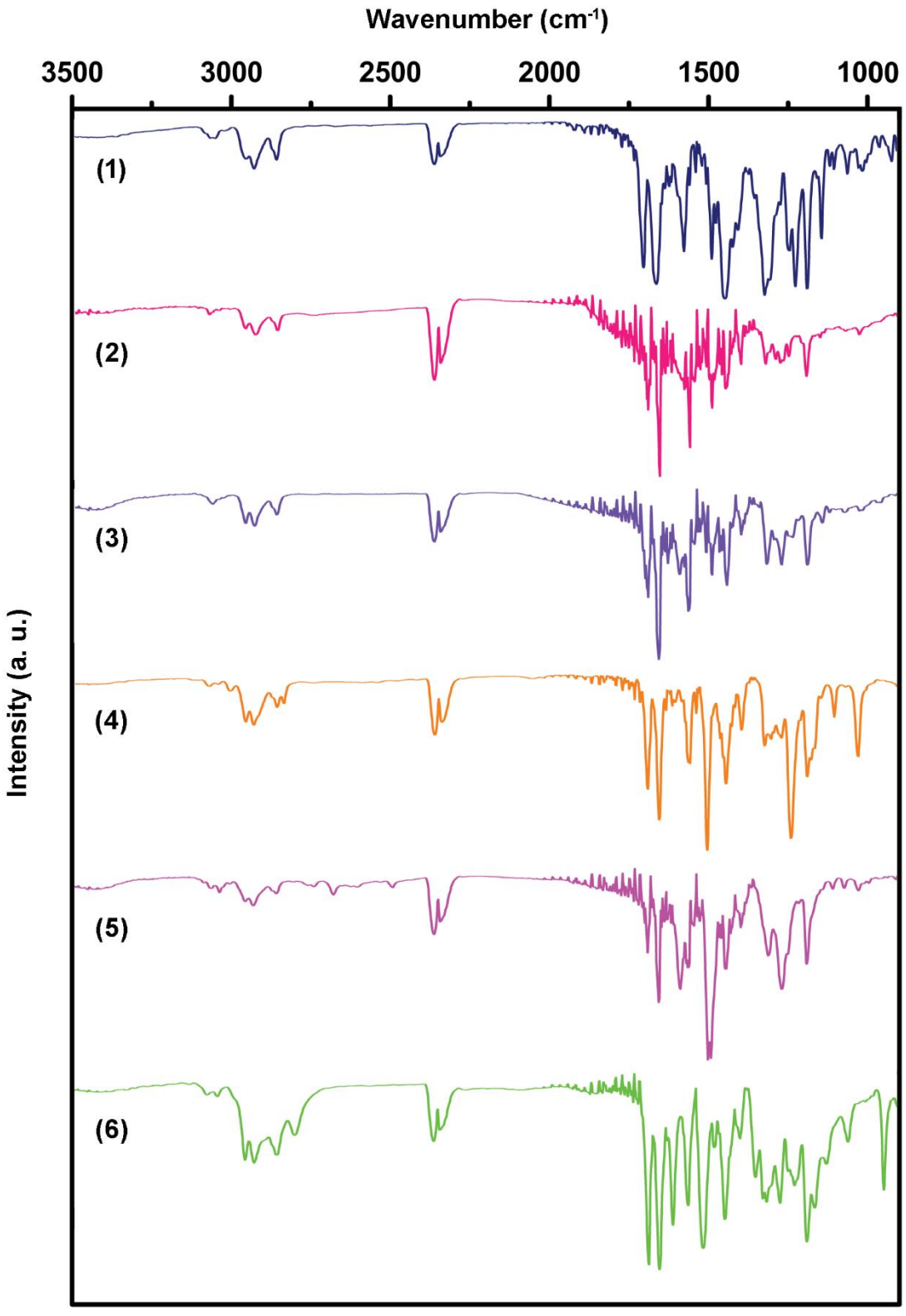


Figure S13: FTIR spectra of compound **1-6.**

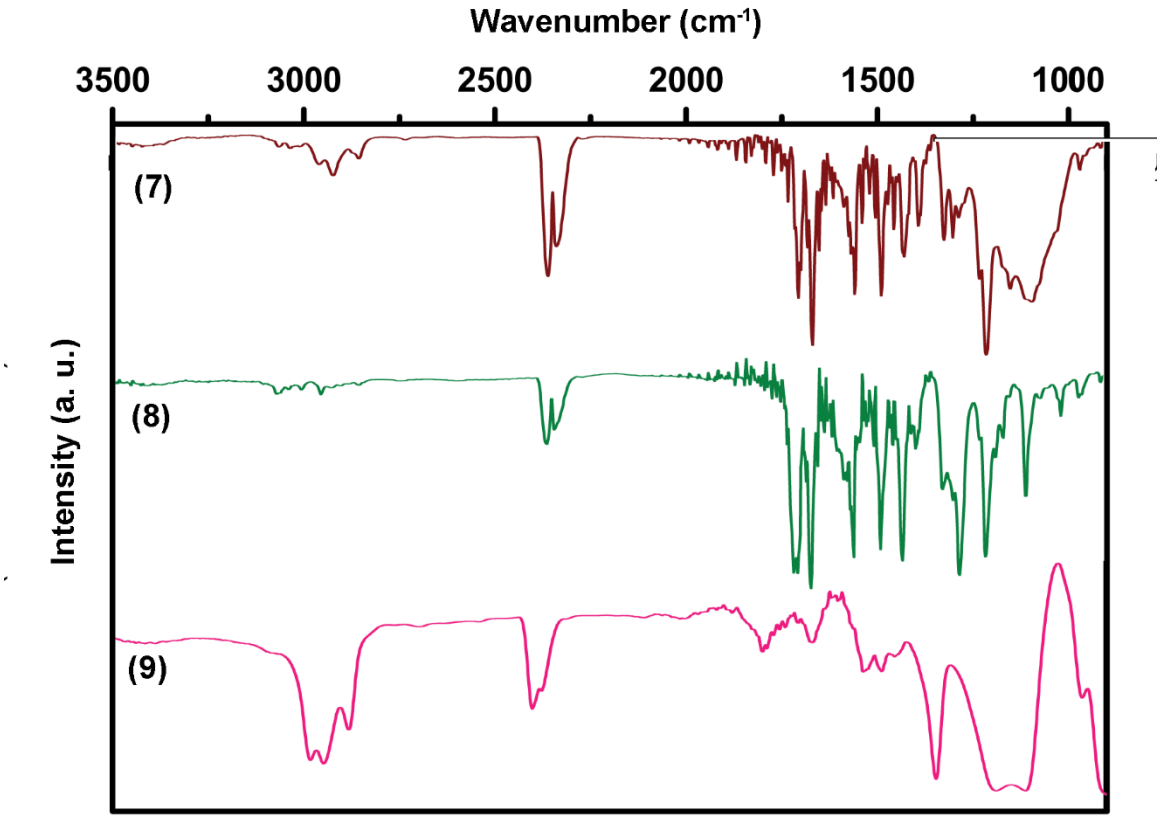


Figure S14: FTIR spectra of compound **7—9.**

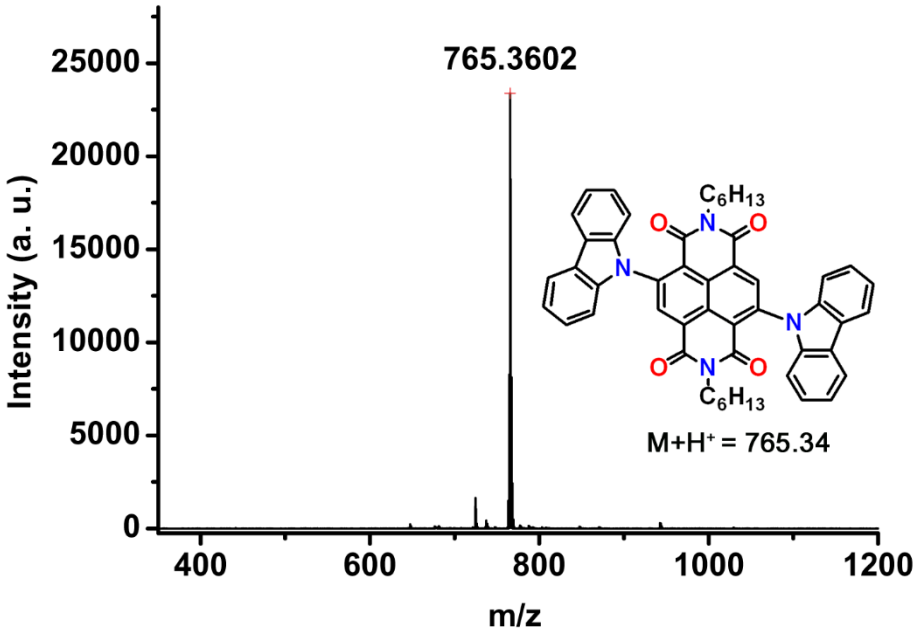


Figure S15: MALDI-TOF mass spectrum of **1**.

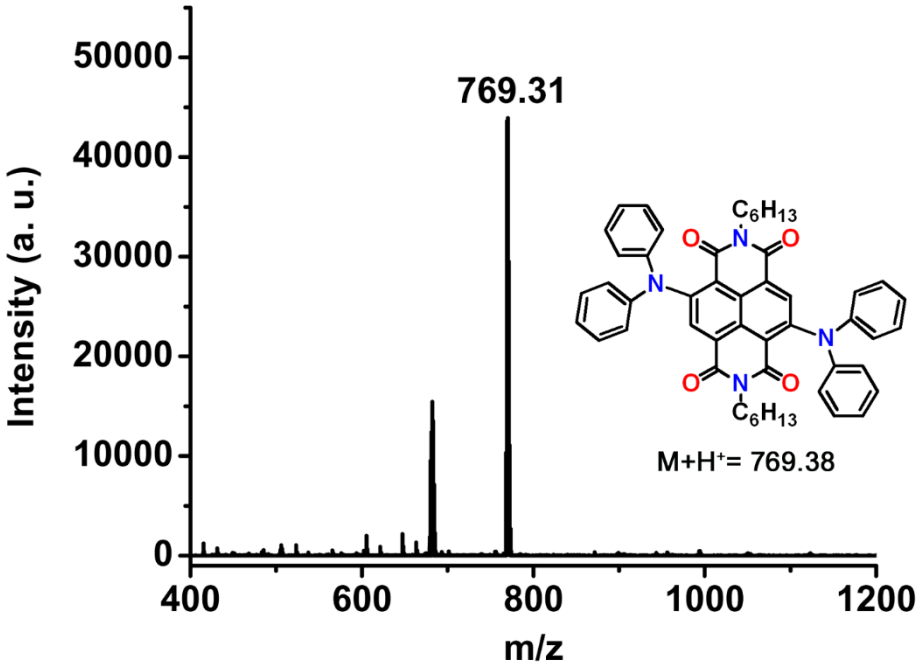


Figure S16: MALDI-TOF mass spectrum of **2**.

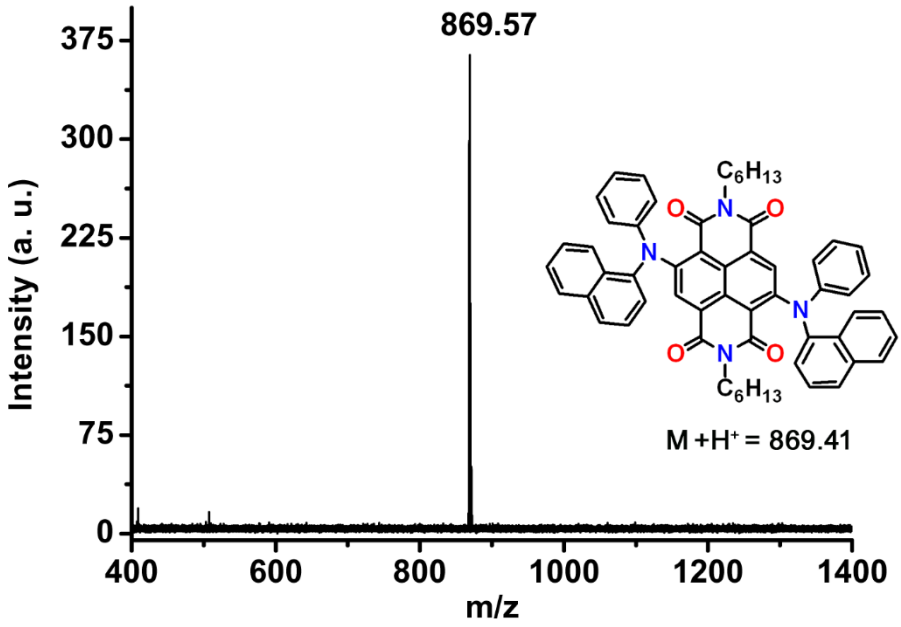


Figure S17: MALDI-TOF mass spectrum of **3**.

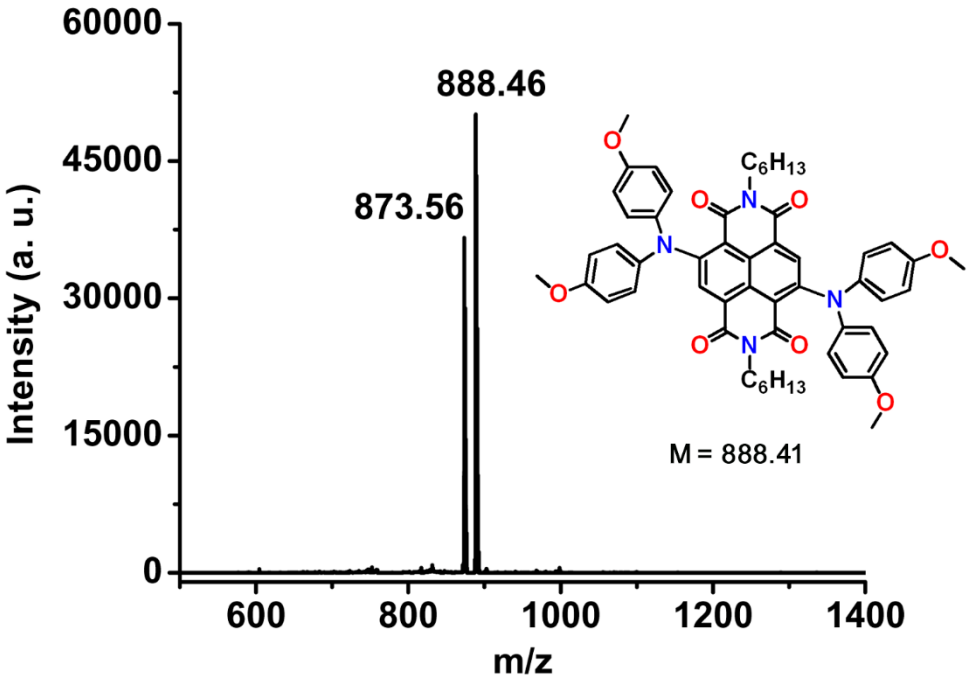


Figure S18: MALDI-TOF mass spectrum of **4**.

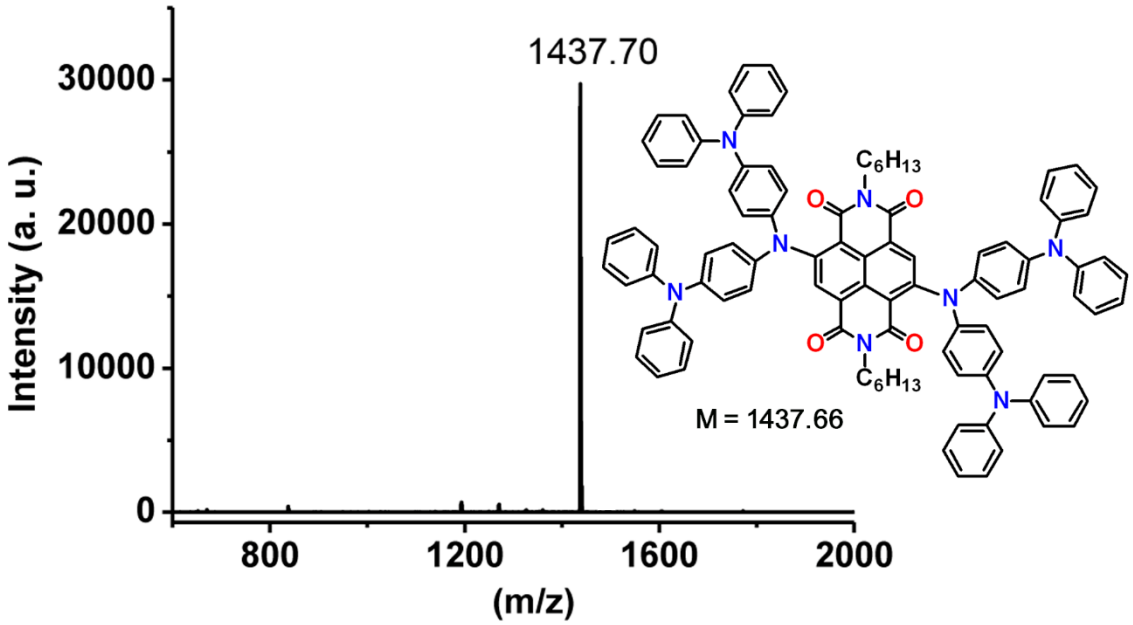


Figure S19: MALDI-TOF mass spectrum of **5.**

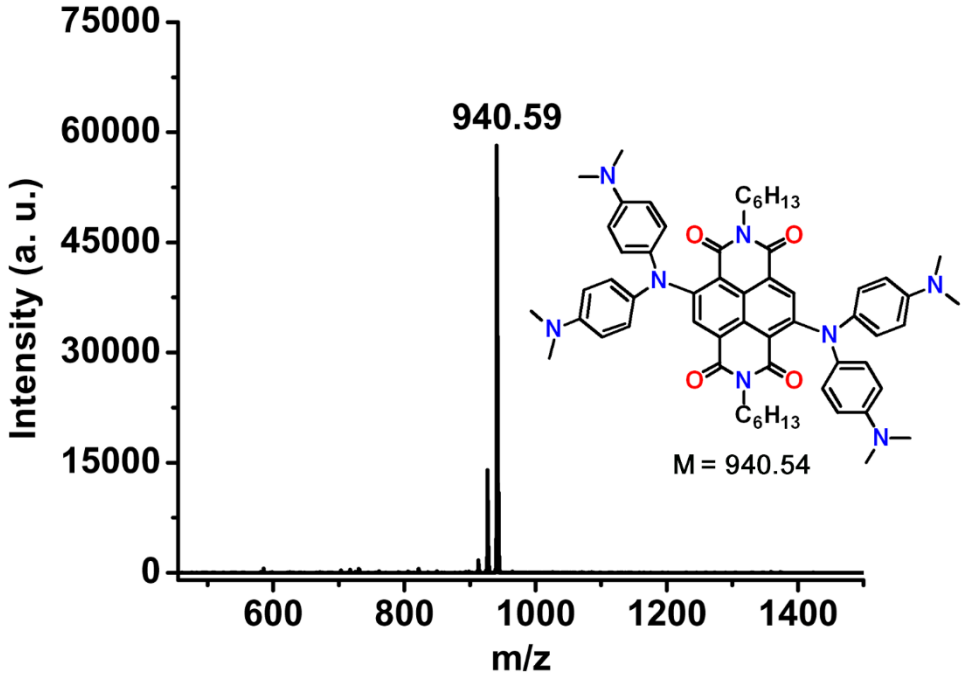


Figure S20: MALDI-TOF mass spectrum of **6.**

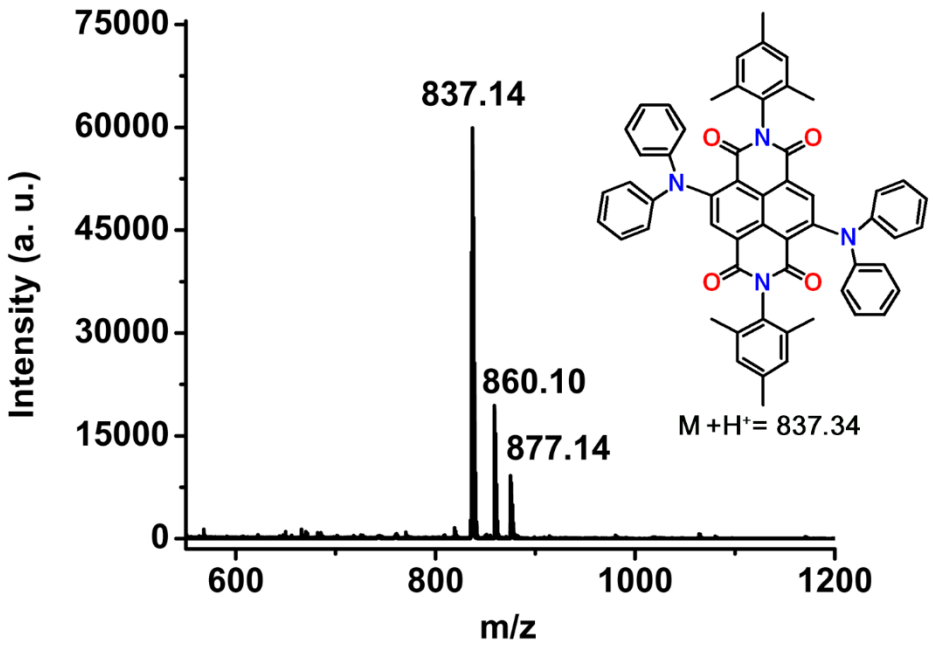


Figure S21: MALDI-TOF mass spectrum of **7.**

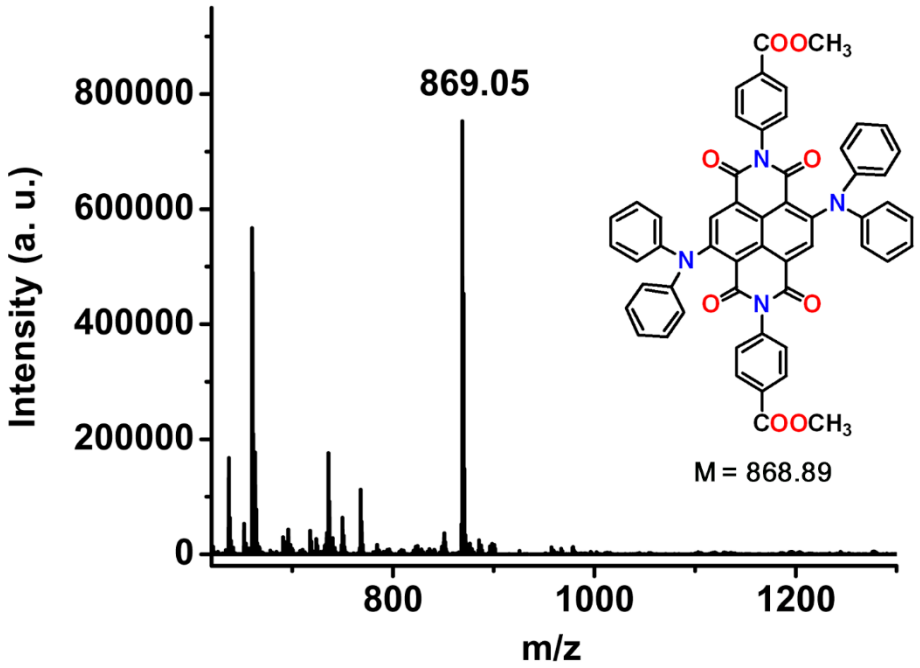


Figure S22: ESI mass spectrum of **8.**

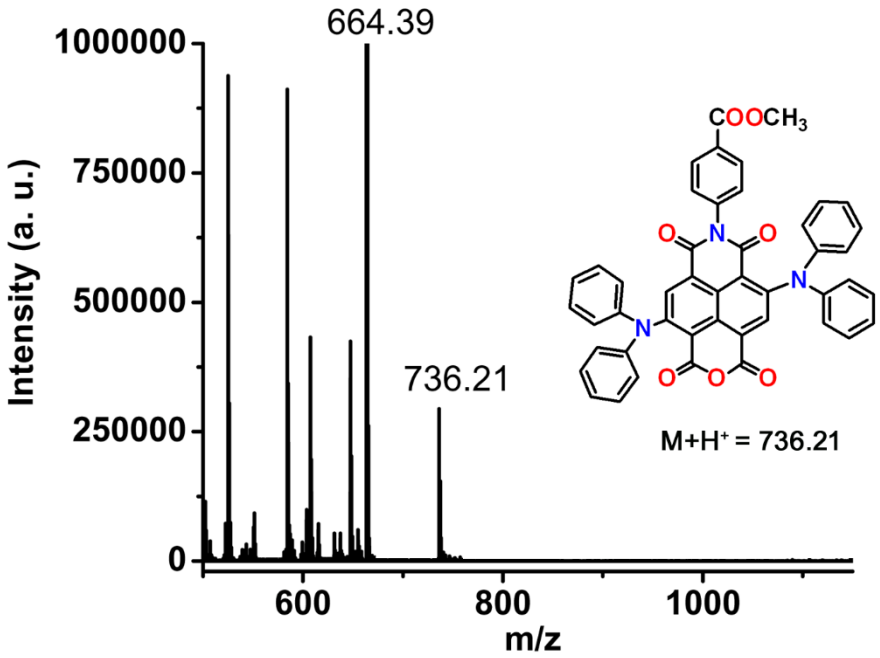


Figure S23: ESI mass spectrum of **9.**

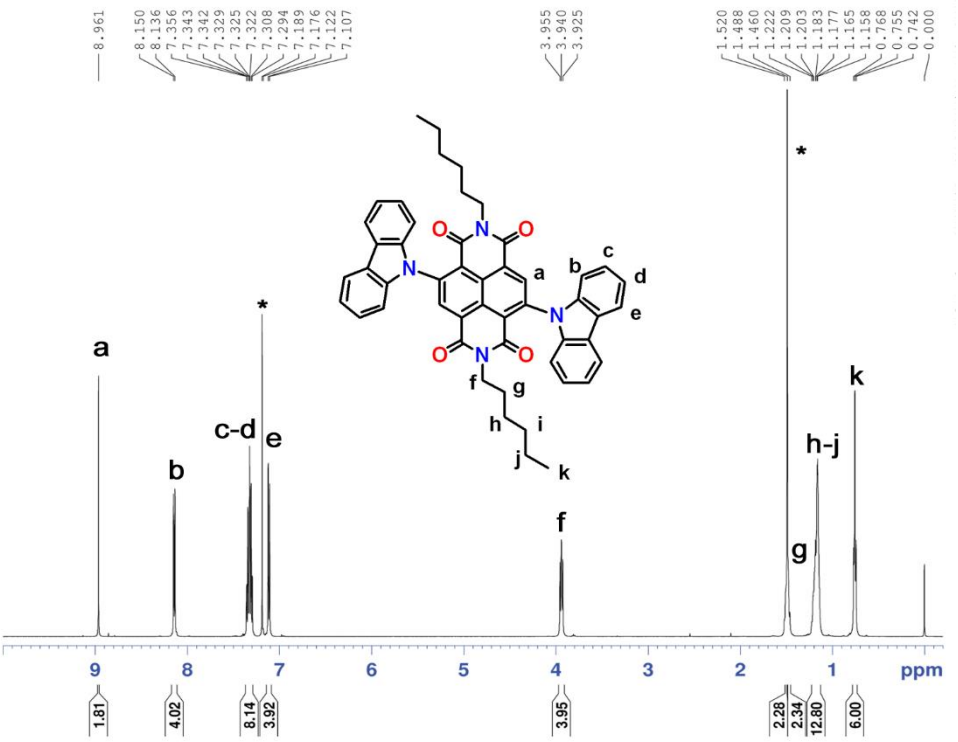


Figure S24: 500 MHz ^{1}H NMR spectrum of **1** in $CDCl_3$ at RT.

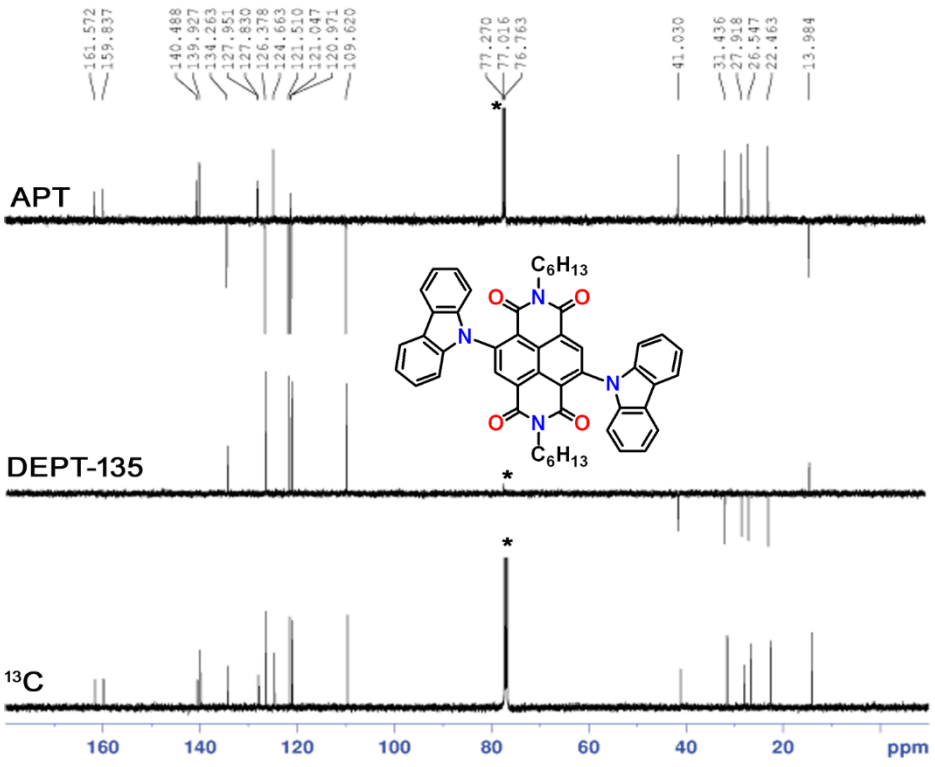


Figure S25: 125 MHz ^{13}C NMR spectrum of **1** in $CDCl_3$ at RT.

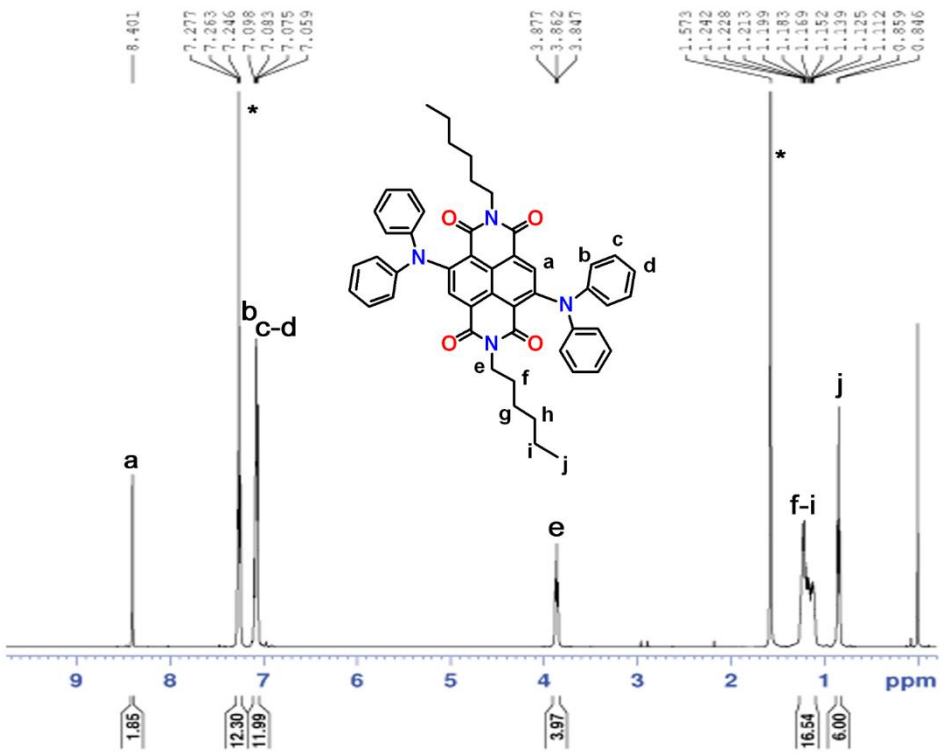


Figure S26: 500 MHz ^{1}H NMR spectrum of **2**in $CDCl_3$ at RT.

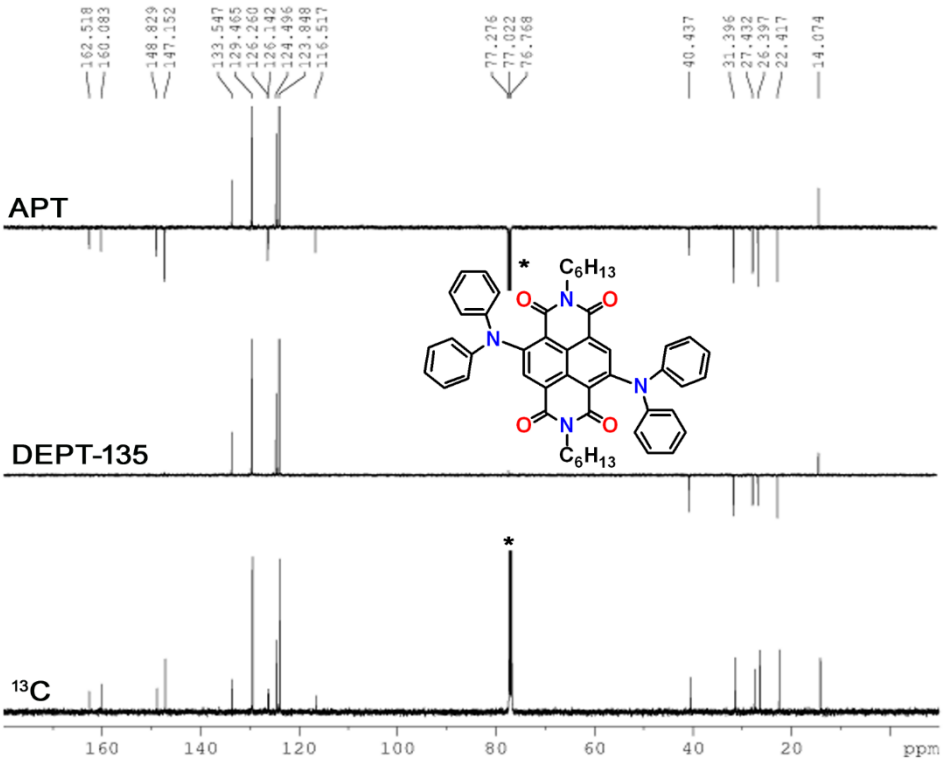


Figure S27: 125 MHz ^{13}C NMR spectrum of **2** in $CDCl_3$ at RT.

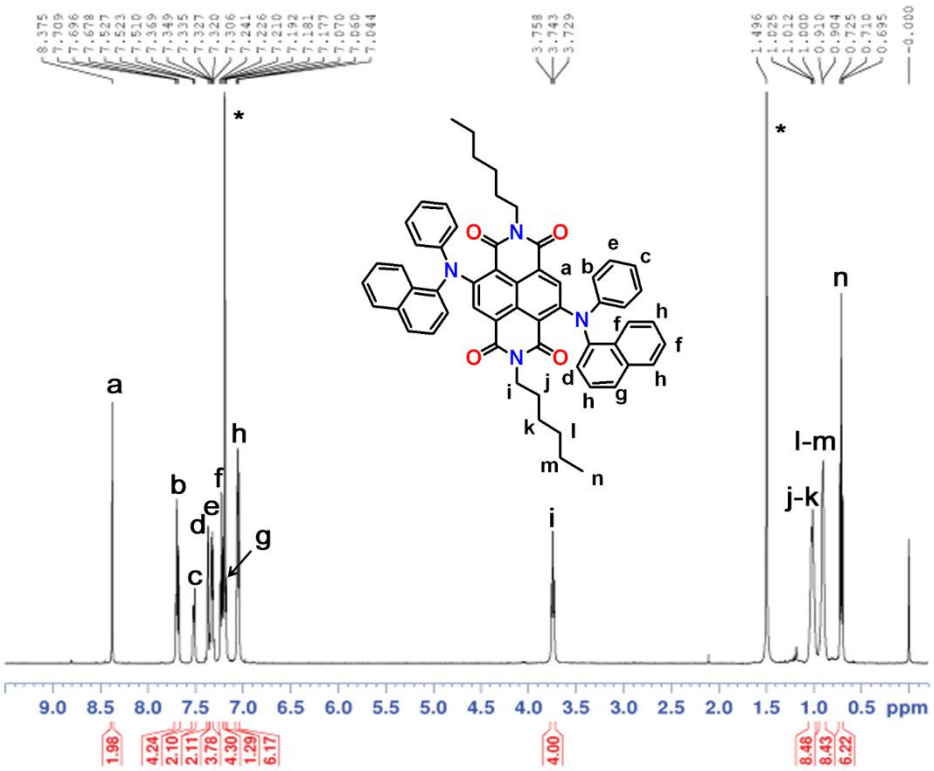


Figure S28: 500 MHz ^{1}H NMR spectrum of **3** in $CDCl_3$ at RT.

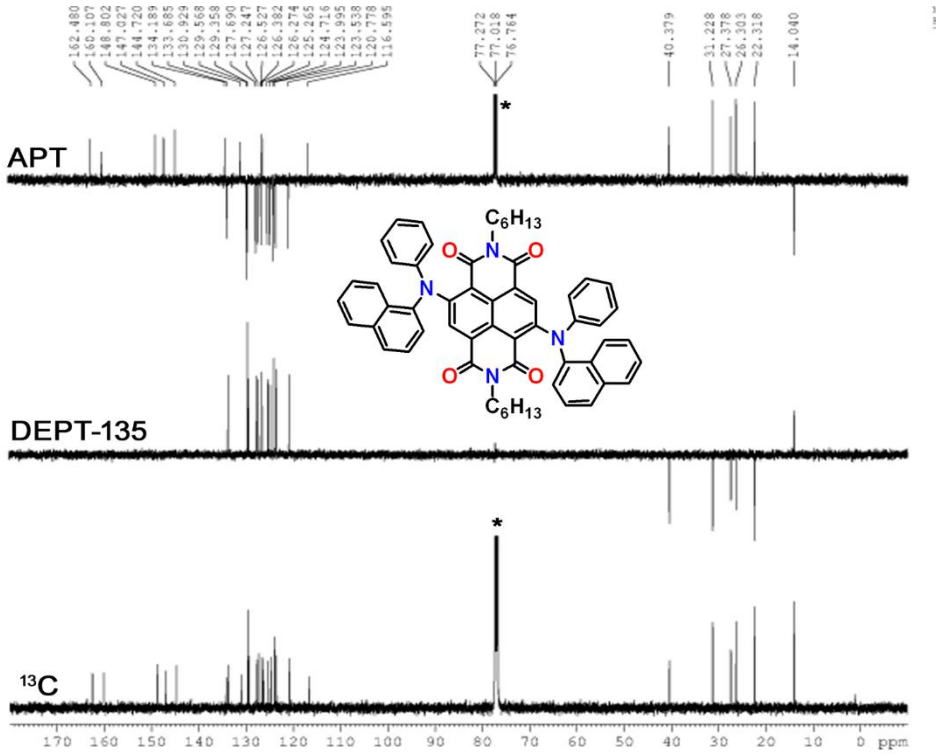


Figure S29: 125 MHz ^{13}C NMR spectrum of **3** in $CDCl_3$ at RT.

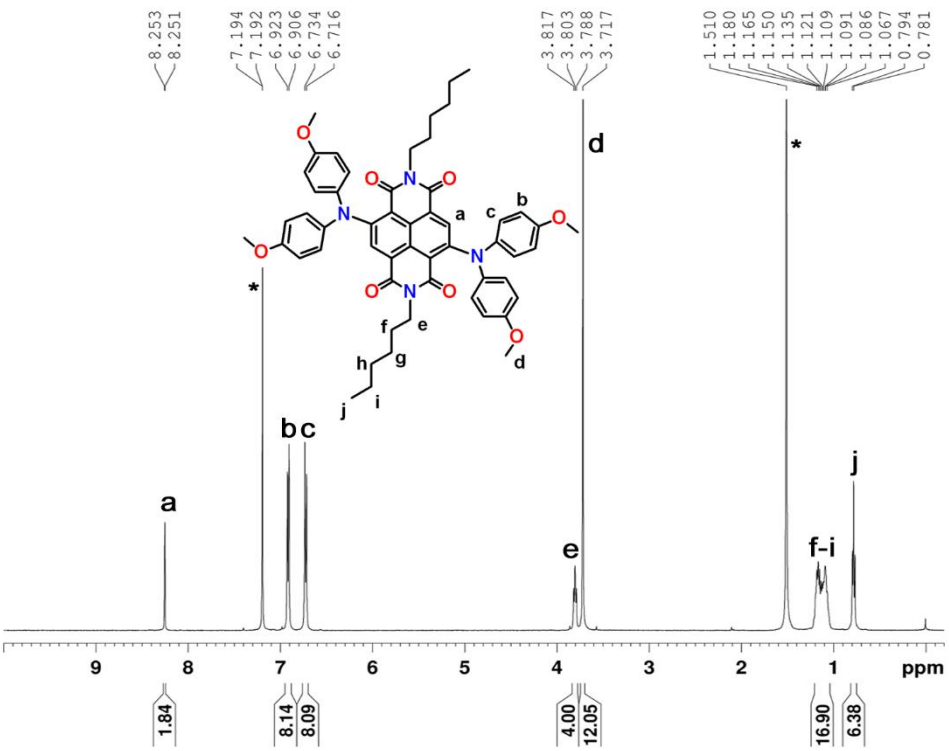


Figure S30: 500 MHz ^{1}H NMR spectrum of **4** in $CDCl_3$ at RT.

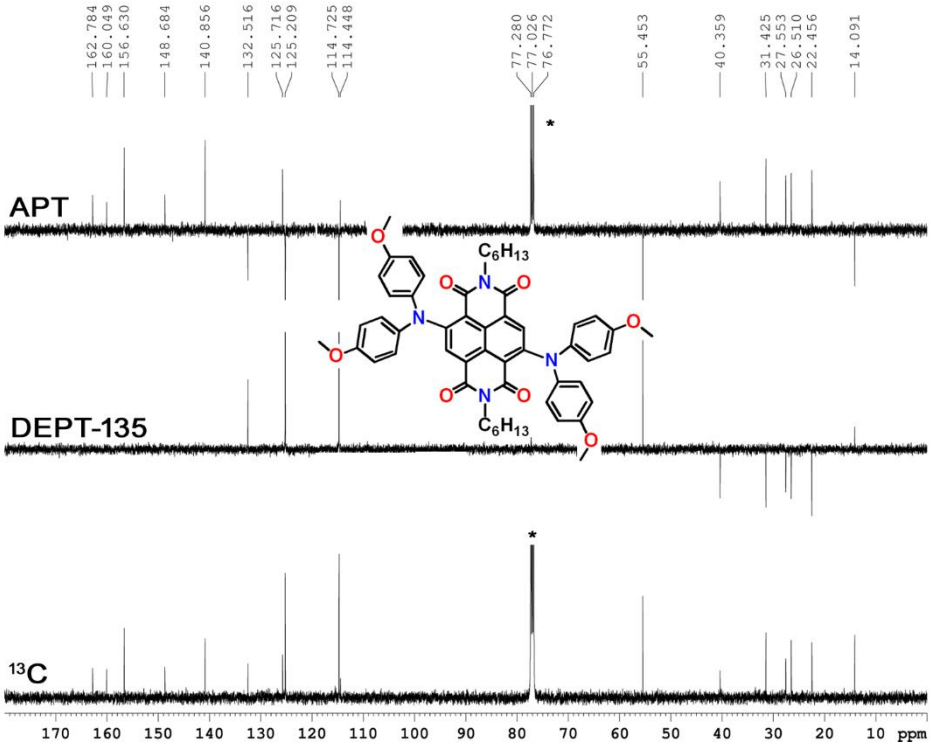


Figure S31: 125 MHz ^{13}C NMR spectrum of **4** in $CDCl_3$ at RT.

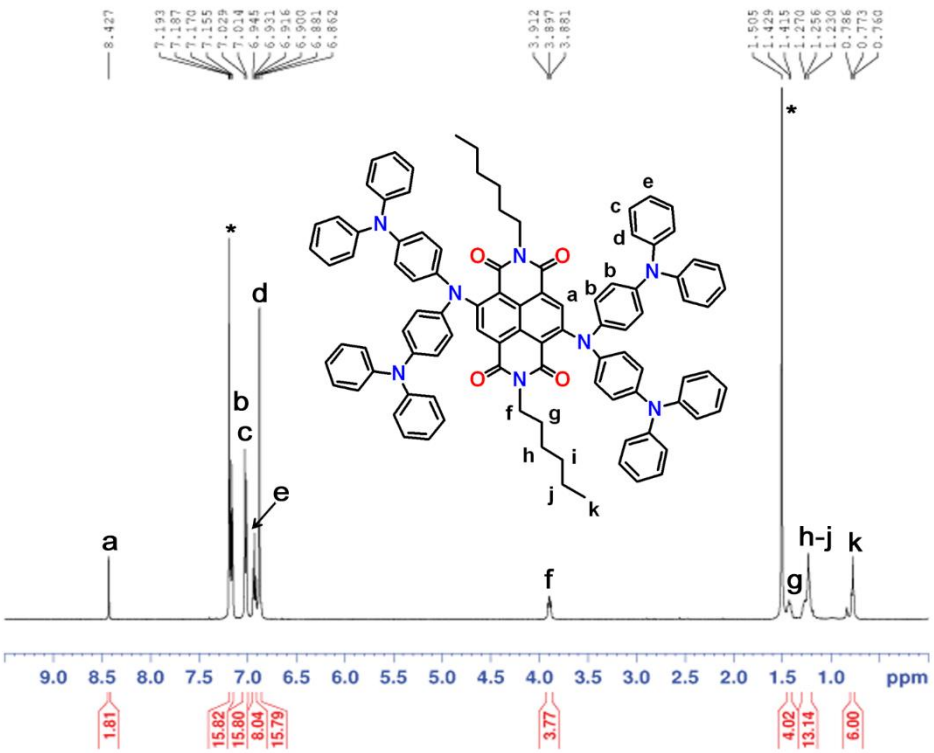


Figure S32: 500 MHz ^{1}H NMR spectrum of **5** in $CDCl_3$ at RT.

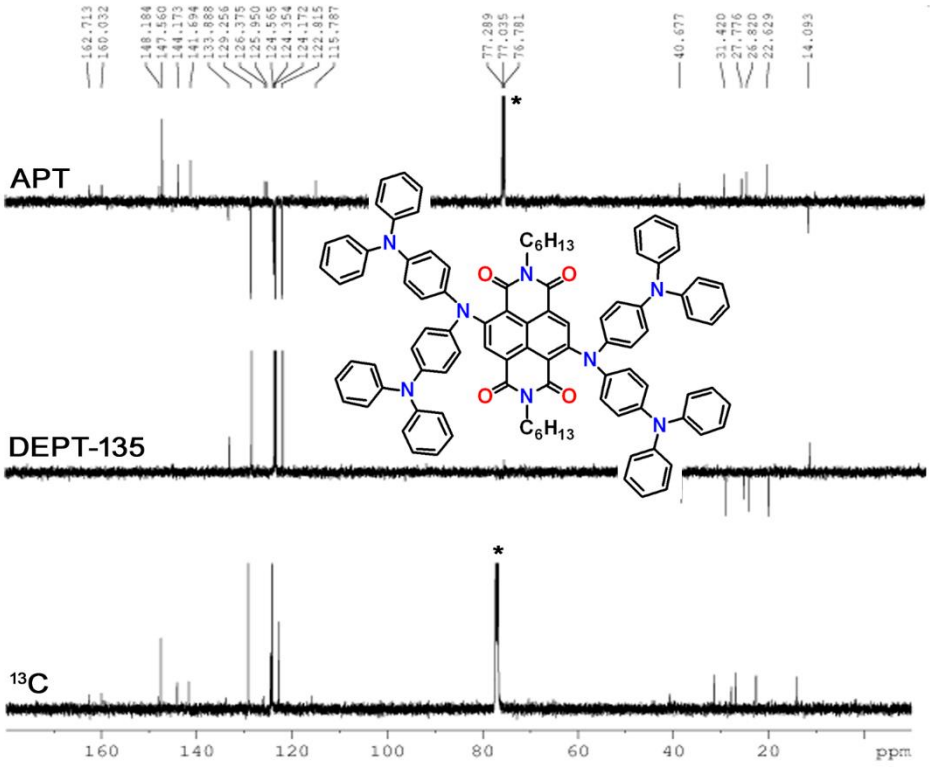


Figure S33: 125 MHz ^{13}C NMR spectrum of **5** in $CDCl_3$ at RT.

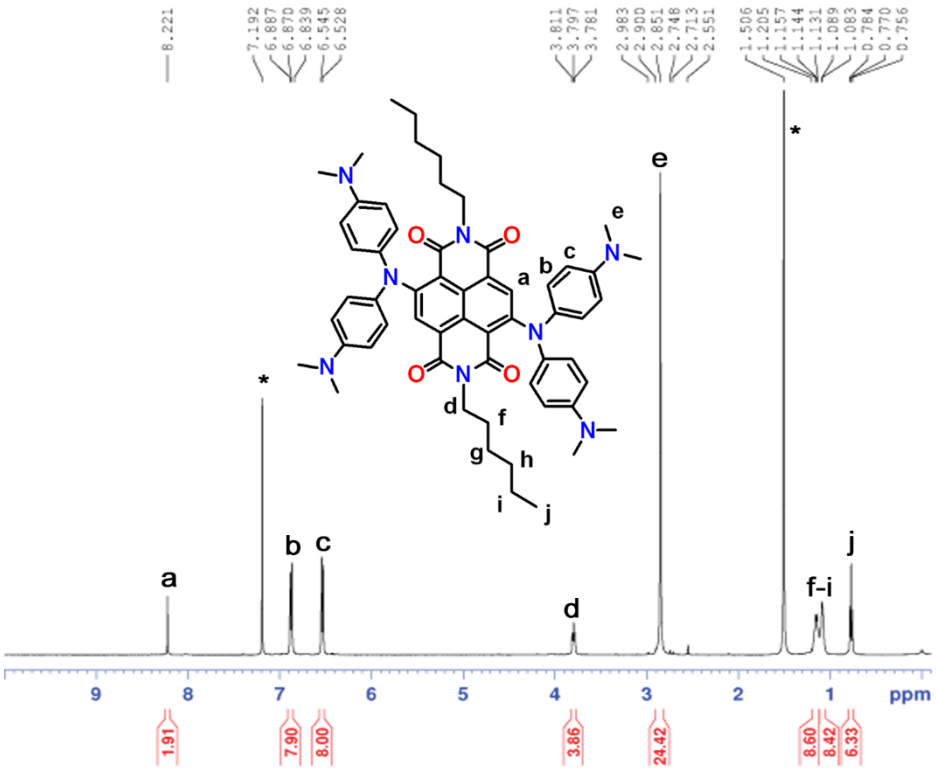


Figure S34: 500 MHz ^{1}H NMR spectrum of **6** in $CDCl_3$ at RT.

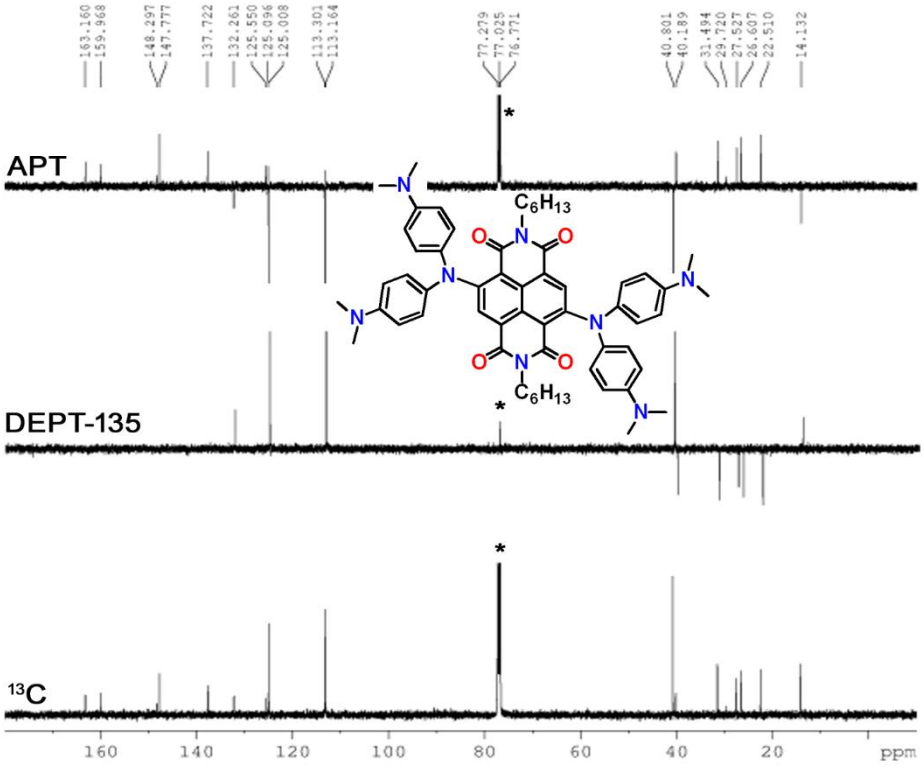


Figure S35: 125 MHz ^{13}C NMR spectrum of **6** in $CDCl_3$ at RT.

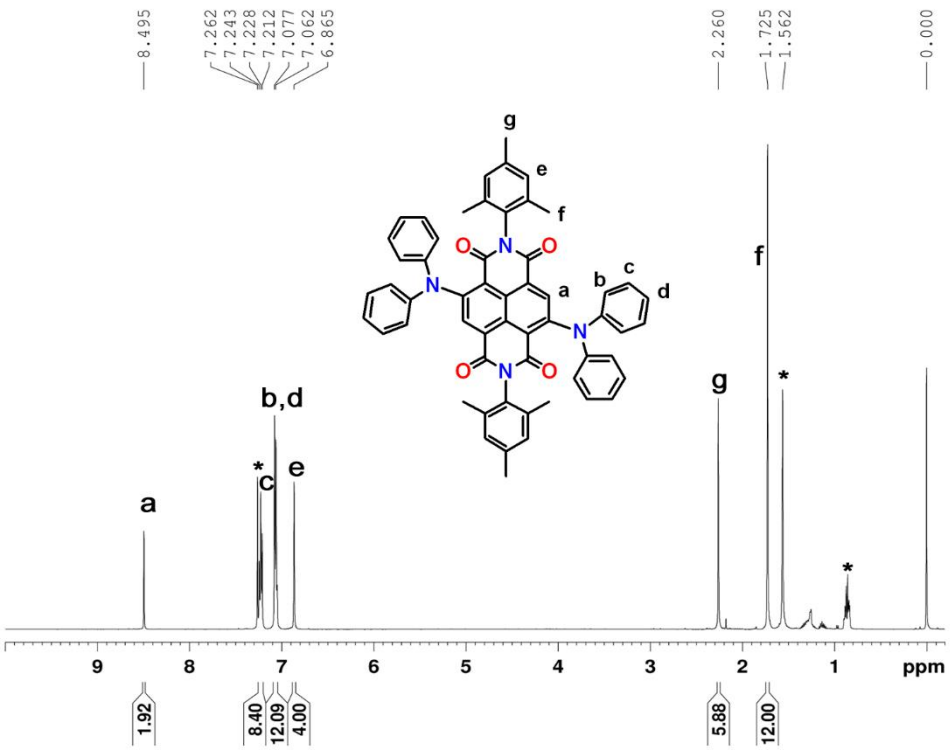


Figure S36: 500 MHz ^{1}H NMR spectrum of **7** in $CDCl_3$ at RT.

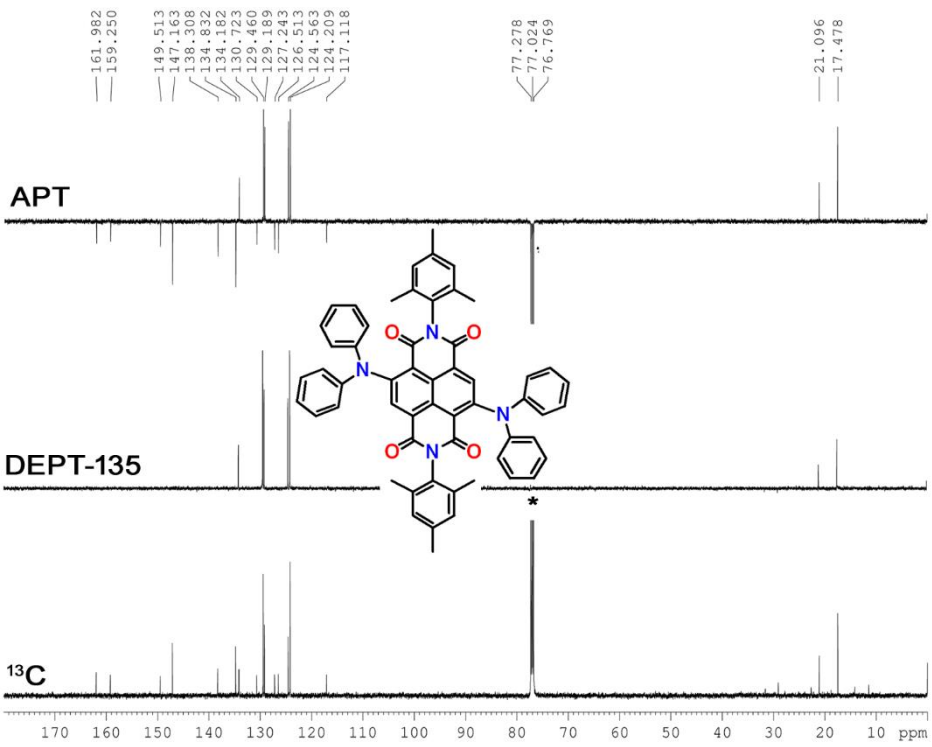


Figure S37: 125 MHz ^{13}C NMR spectrum of **7** in $CDCl_3$ at RT.

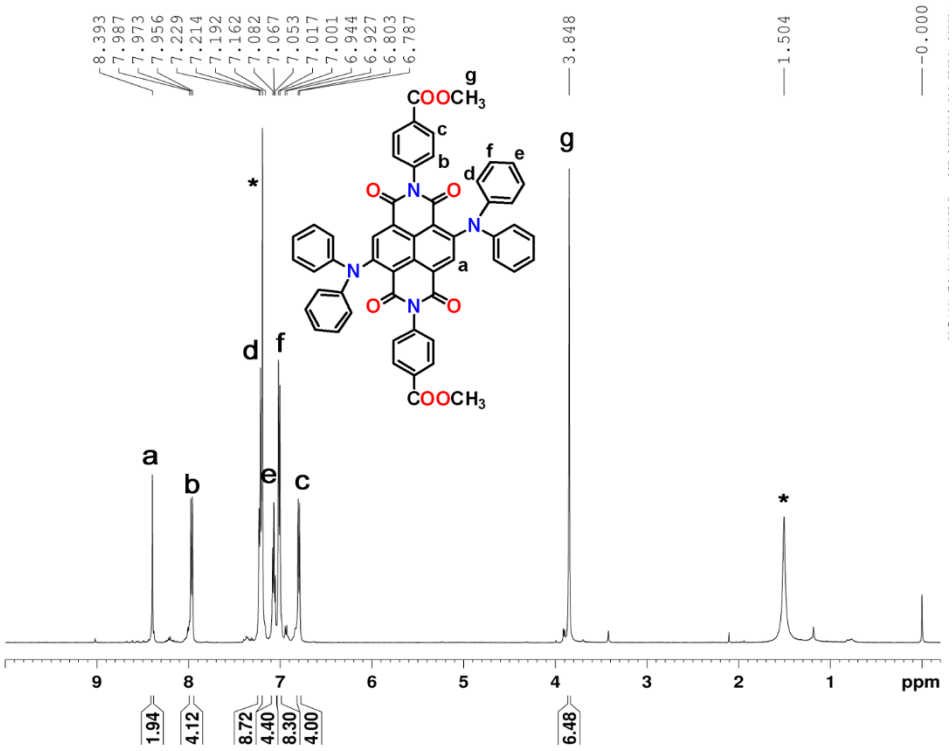


Figure S38: 500 MHz ^{1}H NMR spectrum of **8** in $CDCl_3$ at RT.

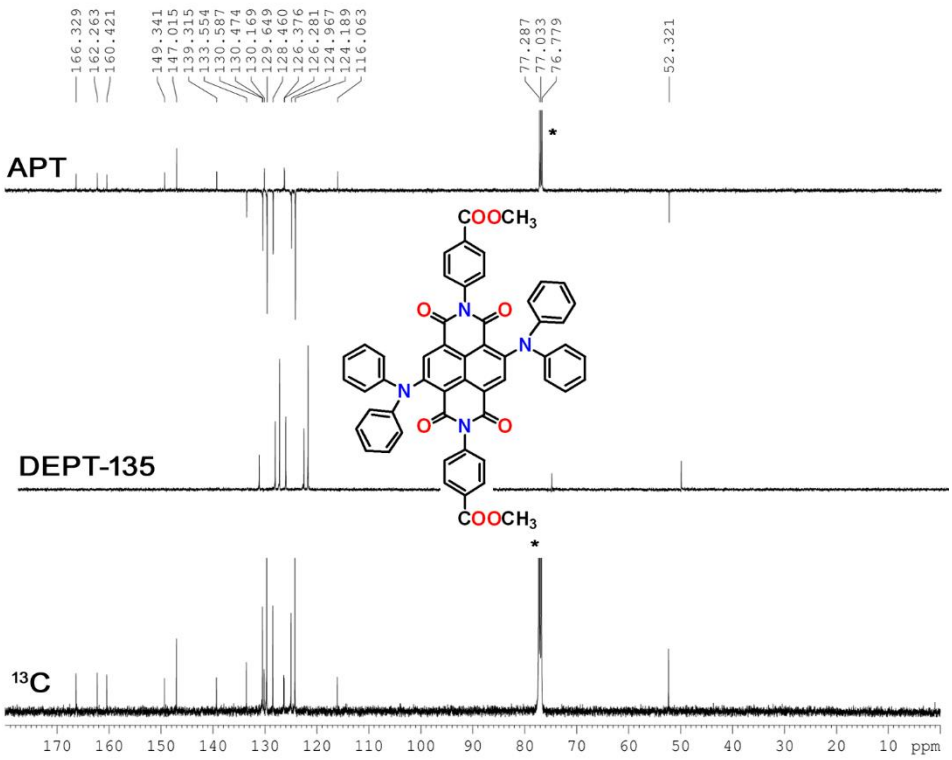


Figure S39: 125 MHz ^{13}C NMR spectrum of **8** in $CDCl_3$ at RT.

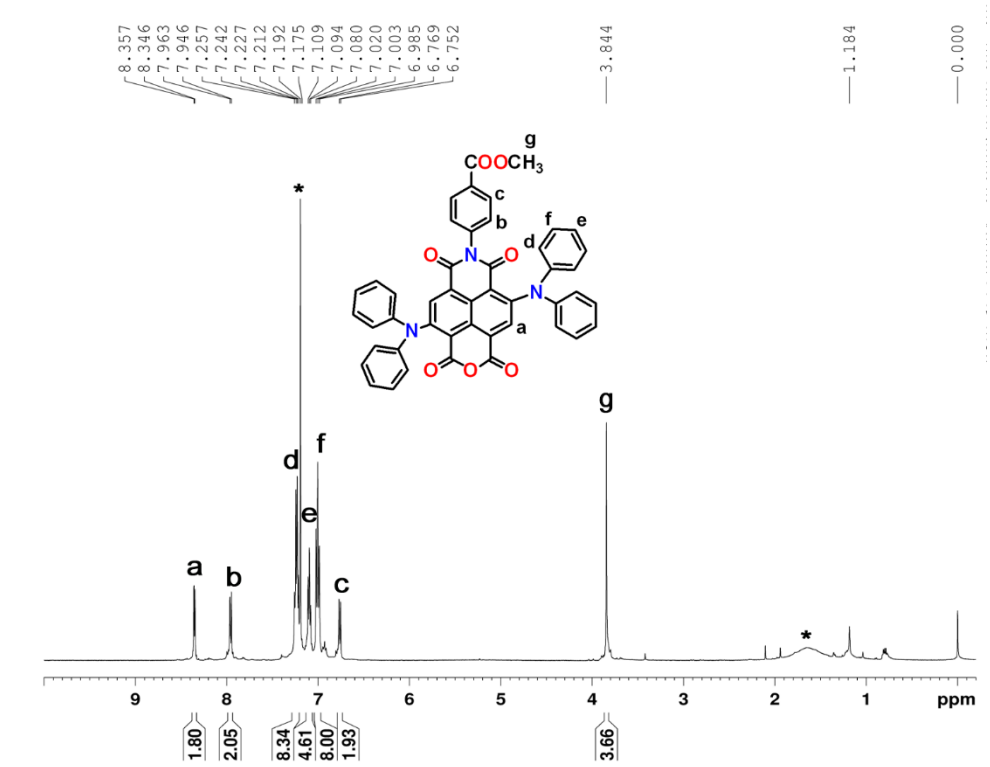


Figure S40: 500 MHz ^{1}H NMR spectrum of **9** in $CDCl_3$ at RT.

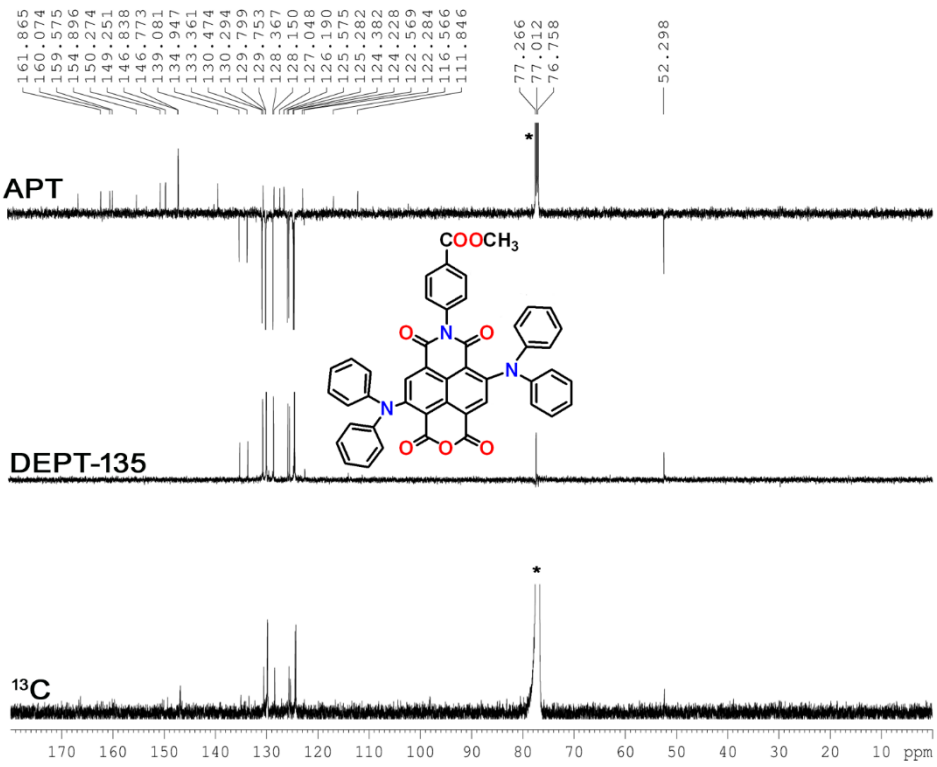


Figure S41: 125 MHz ^{13}C NMR spectrum of **9** in $CDCl_3$ at RT.

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