Core-Modified Naphthalene-diimides Generate Persistent Radical Anion and Cation: New Panchromatic, NIR Probes

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Supporting Information

Contents

Experimental Details:

General: All the starting materials were obtained from Sigma Aldrich or Spectrochem India and were used as received. All the cations were used as their hydrated perchlorate or anhydrous perchlorate except Ag^+ which was used as nitrate salt and anions were used as their tetrabutylammonium (TBA) salts. 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 spectra were recorded in $CDCl_3$ on a Bruker spectrometer operating at 500 MHz for ^1H and 125 MHz for ^{13}C, DEPT-135 and APT with TMS as an internal standard. Coupling constants (*J* values) are given in terms of Hz whereas chemical shifts are reported in parts per million (ppm). Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), sext (sextet), b (broad) and m (multiplets). Protons at NDI core are designated as Ar and protons at axial position to NDI-core are termed as Ax. MALDI-TOF mass spectral data were obtained using a Bruker made Autoflex TOF/TOF instrument and α-Cyano-4-hydroxycinnamic acid as the matrix. Infra Red spectra were recorded in KBr pellets using a Varian 7000 FT-IR instrument. The UV-vis-NIR absorption spectra were taken using a JASCO V-670 model spectrometer. The steady state fluorescence spectra were measured using a Varian Cary Eclipse Fluorescence Spectrometer. All UV-vis-NIR spectroscopic experiments were performed in a quartz cuvette with 1.0 mm optical pathlength and fluorescence studies were carried out in a 1.0 cm quartz cuvette.

Electrochemistry: The electrochemical properties were studied using a computer-controlled potentiostat (CHI 650C) and a standard three electrode arrangement that consisted of both platinum working and auxiliary electrodes and a saturated calomel reference electrode. All electrochemical measurements were carried out in Ar-purged dry MeCN/$CHCl_3$ (1:1 v/v) with 0.1 M Bu_4NClO_4 as the supporting electrolyte. The scan rate for cyclic voltametry (CV) experiments was typically 200-300 mV/s. Differential Pulse Voltametry (DPV) was carried out keeping peak amplitude 50 mV, peak width 0.01 sec, pulse period 0.05 sec and increment E at 20 mV.

Quantum Yield: Quantum yields were calculated using cresyl violate perchlorate in MeOH (excited at 575 nm) as reference (ø = 0.54) following the relation:

$$\phi = \phi_R \left(\frac{A_R}{F_R}\frac{F}{A}\right)\left(\frac{\eta}{\eta_R}\right)^2$$

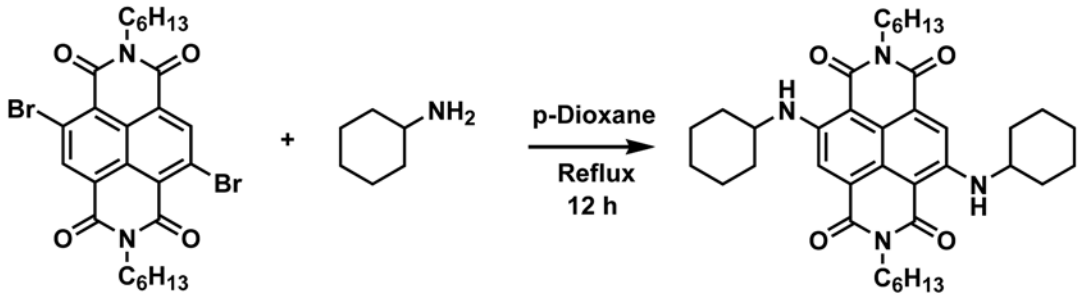
where, Ø is the quantum yield of reference compound, A is absorbance at excitation wavelength, F is the area under fluorescence peak, η is refractive index of solvent and subscripts 'R' stand for the reference.[1]

EPR: Electron Paramagnetic Resonance (EPR) spectra were recorded using Bruker EMX 1444 EPR spectrometer operating at 9.455 GHz. Diphenylpicrylhydrazyl, DPPH (g = 2.0037), was used for the calibration of EPR spectrometer.

Theoretical calculations: All theoretical calculations were done using Density Functional or Hartree–Fock Theory (DFT or HF) with the Gaussian 09 quantum chemistry program package. Molecule **1a** and its radical ions were optimized at HF/6-31+G(d,p) and submitted

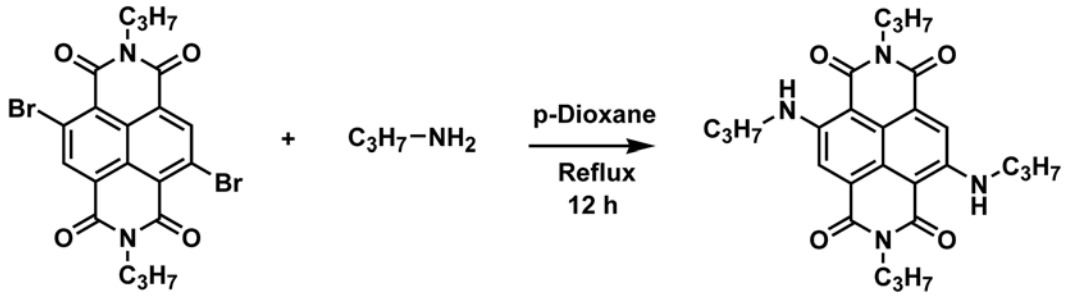
for TD-DFT calculations using B3LYP/6-31++G(d,p). In TD-DFT calculations, bulk solvent (MeCN) effects were approximated using a polarizable continuum model (PCM), specifically the integral equation formalism model (IEF-PCM). Molecule **1b, 1e** and their radical ions were optimized at the DFT/B3LYP/6-31+G(d,p) level of theory. Average logP values were calculated using a freely available online program VCCLAB 2007[2].

Compound 1a



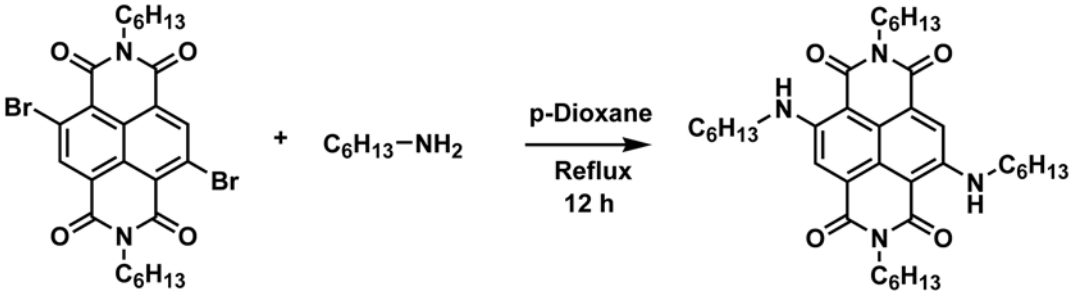
Synthesis of 1a: In a 50 mL round bottomed (RB) flask containing 8 mL dry p-dioxane, N, N'-dihexyl-2,3-dibromonaphthalene-1,4,5,8-tetracarboxylic acid bisimide (200 mg, 0.34 mmol) and cyclohexyl amine (1.0 mL, 8.79 mmol) were added. The mixture was refluxed for 12 h under N_2 atmosphere. Reaction mixture was gradually brought to room temperature and dried under reduced pressure. The blue colored solid was thoroughly washed with excess of MeOH (100 mL) and finally purified by silica column chromatography (230-400 mesh) with $CHCl_3$ as the eluent. Yield = 20%. R_f = 0.68 (8:2 $CHCl_3$/n-hexane). Melting Point: 220 °C. Average logP = 8.27. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 9.43 (d, *J* = 7.5 Hz, 2H, *NH*), 8.14 (s, 2H, Ar*H*), 4.15 (t, *J* = 7.5 Hz, 4H, AxC*H*$_2$), 3.76 (b, 2H, NHC*H*), 2.13 (b, 4H, AxCH$_2$C*H*$_2$), 1.84 (m, 4H, AxCH$_2$CH$_2$*CH*$_2$), 1.68 (m, 8H, NHCH*(CH*$_2$*)*$_2$), 1.50-1.35 (m, 20H, *CH*$_2$), 0.91 (m, 6H, *CH*$_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 166.20, 163.21, 148.28, 125.76, 121.19, 118.59, 101.69, 51.15, 40.50, 33.27, 31.59, 28.10, 26.91, 25.64, 24.72, 22.63, 14.10. MS (MALDI-TOF, matrix- α-cyano-4-hydroxycinnamic acid): 629.43 (m/z). FTIR (KBr, cm^{-1}): 3276, 2921, 2855, 1685, 1633, 1582, 1484, 1315. Anal. Calcd. for $C_{38}H_{52}N_4O_4$: C, 72.58; H, 8.33; N, 8.91; O, 10.18. Anal. Found C, 72.47; H, 8.50; N, 8.83.

Compound 1b



Synthesis of 1b: In a 50 mL round bottomed (RB) flask containing 15 mL dry p-dioxane, N, N'-dihexyl-2,3-dibromonaphthalene-1,4,5,8-tetracarboxylic acid bisimide (610 mg, 1.20 mmol) and *n*-propyl amine (3.0 mL, 36.50 mmol) were added. The mixture was refluxed for 12 h under N_2 atmosphere. Reaction mixture was gradually brought to room temperature and dried under reduced pressure. The blue colored solid was thoroughly washed with excess of MeOH (100 mL) and finally purified by silica column chromatography (100-200 mesh) with $CHCl_3$/n-hexane (7:3) as the eluent. Yield = 21.5%. R_f = 0.17 (8:2 $CHCl_3$/n-hexane). Melting Point: 280 °C. Average log P = 3.61. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 9.35 (t, *J* = 5.5 Hz, 2H, *NH*), 8.09 (s, 2H, Ar*H*), 4.13 (t, *J* = 8.0 Hz, 4H, Ax*CH*$_2$), 3.46 (q, J = 7.0 Hz, 4H, NH*CH*$_2$), 1.84 (sext, J = 7.5 Hz, 4H, AxCH$_2$*CH*$_2$), 1.75 (sext, *J* = 7.5 Hz, 4H, NHCH$_2$*CH*$_2$), 1.11 (t, *J* = 7.5 Hz, 3H, Ax*CH*$_3$), 1.03 (t, *J* = 7.5 Hz, 3H, NHCH$_2$*CH*$_2$*CH*$_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 166.23, 163.11, 149.20, 125.73, 121.08, 118.28, 101.75, 44.91, 41.90, 31.60, 29.72, 22.69, 21.39, 14.15, 11.73, 11.59. MS (MALDI-TOF, matrix- α-cyano-4-hydroxycinnamic acid): 464.12 (m/z). FTIR (KBr, cm^{-1}): 3284, 2965, 2936, 2877, 1685, 1633, 1589, 1490, 1317. Anal. Calcd. for $C_{26}H_{32}N_4O_4$: C, 67.22; H, 6.94; N, 12.06; O, 13.78. Anal. Found C, 67.47; H, 6.75; N, 12.25.

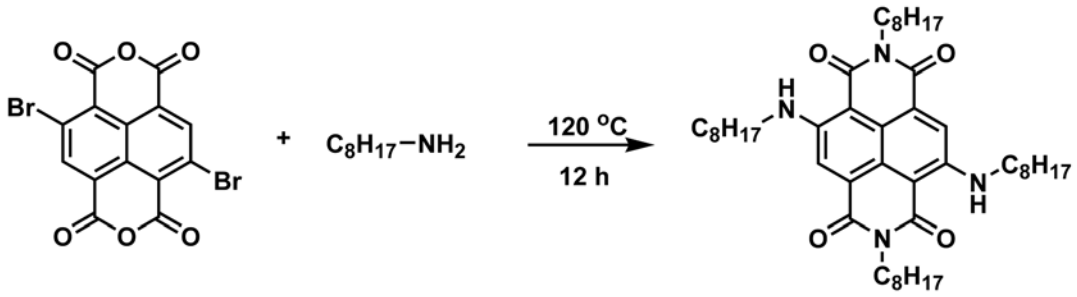
Compound 1c



Synthesis of 1c: In a 50 mL round bottomed (RB) flask containing 10 mL dry p-dioxane, N, N'-dihexyl-2,3-dibromonaphthalene-1,4,5,8-tetracarboxylic acid bisimide (500 mg, 0.84 mmol) and *n*-hexyl amine (1 mL, 7.59 mmol) were added. The mixture was refluxed for 12 h

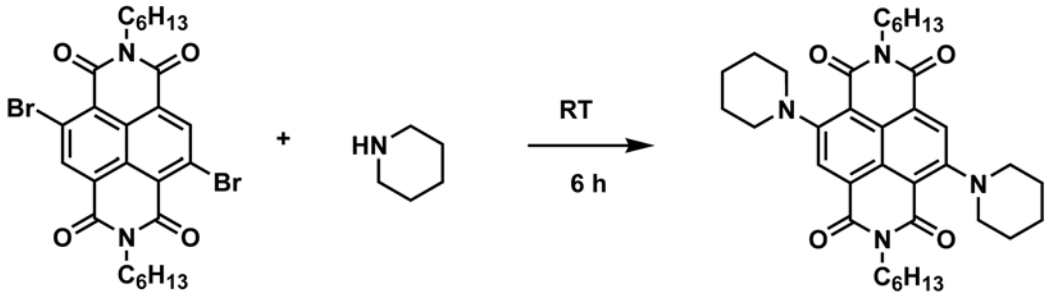
under N_2 atmosphere. Reaction mixture was gradually brought to room temperature and dried under reduced pressure. The blue colored solid was thoroughly washed with excess of MeOH (100 mL) and finally purified by silica column chromatography (100-200 mesh) with $CHCl_3$/n-hexane (7:3) as the eluent. Yield = 20%. R_f = 0.82 (8:2 $CHCl_3$/n-hexane).Melting Point: 230 °C. Average logP = 8.39. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 9.31 (t, *J* = 7.5, 2H, *NH*),8.07 (s, 2H, Ar*H*), 4.15 (t, *J* = 7.5 Hz, 4H, Ax*CH*$_2$), 3.47 (q, *J* = 8.0 Hz, 4H, NH*CH*$_2$), 1.80 (p, *J* = 8.0 Hz, 4H, AxCH$_2$*CH*$_2$), 1.71 (p, *J* = 8.0 Hz, 4H, AxCH$_2$*CH*$_2$), 1.52-1.42 (m, 24H, *CH*$_2$), 0.92 (m, 6H, C*H*$_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 166.14, 163.04, 149.12, 125.69, 121.02, 118.21, 101.70, 43.22, 40.44, 31.58, 31.53, 29.39, 28.07, 26.87, 26.84, 22.59, 14.08, 14.04. MS (MALDI-TOF, matrix- α-cyano-4-hydroxycinnamic acid): 633.43 (m/z). FTIR (KBr, cm^{-1}): 3275, 2959, 2925, 2855, 1677, 1625, 1587, 1491, 1330. Anal. Calcd. For $C_{38}H_{56}N_4O_4$: C, 72.12; H, 8.92; N, 8.85; O, 10.11. Anal. Found C, 72.35; H, 9.15; N, 8.72.

Compound 1d



Synthesis of 1d: In a 50 mL round bottomed (RB) flask 2,3-dibromonaphthalene-1,4,5,8-tetracarboxylic acid anhydride (400 mg, 0.94 mmol) and *n*-octyl amine (10 mL, 60.50 mmol) were added. The mixture was refluxed for 12 h under N_2 atmosphere. Reaction mixture was gradually brought to room temperature and dried under reduced pressure. The blue colored solid was thoroughly washed with excess of MeOH (100 mL) and finally purified by silica column chromatography (100-200 mesh) using $CHCl_3$/n-hexane (7:3) as eluent. Yield = 10%. R_f = 0.89 (8:2 $CHCl_3$/n-hexane). Melting Point: 180 °C. Average logP = 11.79.^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 9.33 (t, *J* = 6.0 Hz, 2H, *NH*), 8.11 (s, 2H, Ar*H*), 4.16 (t, *J* = 7.5 Hz, 4H, CoCH$_2$), 3.48 (q, *J* = 8.0 Hz, 4H, NH*CH*$_2$), 1.80 (p, *J* = 8.0 Hz, 4H, AxCH$_2$*CH*$_2$), 1.71 (p, *J* = 7.5 Hz, 4H, NHCH$_2$*CH*$_2$), 1.53-1.25 (m, 40H, *CH*$_2$), 0.89 (m, 6H, CH$_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 166.21, 163.12, 149.18, 125.77, 121.10, 118.31, 101.78, 43.22, 40.46, 31.84, 31.83, 29.42, 29.38, 29.31, 29.26, 29.21, 18.14, 27.23, 27.15, 22.67, 14.12. MS (MALDI-TOF, matrix- α-cyano-4-hydroxycinnamic acid): 745.48 (m/z). FTIR (KBr, cm^{-1}): 3274, 2956, 2923, 2850, 1679, 1627, 1589, 1495, 1332. Anal. Calcd. For $C_{46}H_{72}N_4O_4$: C, 74.15; H, 9.74; N, 7.52; O, 8.59. Anal. Found C, 74.37; H, 9.90; N, 7.43.

Compound 1e



Synthesis of 1e: In a 50 mL round bottomed (RB) flask, N, N'-dihexyl-2,3-dibromonaphthalene-1,4,5,8-tetracarboxylic acid bisimide (200 mg, 0.34 mmol) and piperidine (4 mL, 40.56 mmol) were added. The mixture was stirred at room temperature under N_2 atmosphere. After 6 h, the reaction mixture was mixed with 50 mL MeOH. The blue colored solid was filtered out and thoroughly washed with excess of MeOH (100 mL). Further purification was performed by silica column chromatography (100-400 mesh) using $CHCl_3$/n-hexane (7:3) as eluent. Yield =15%. R_f = 0.84 (98:2 $CHCl_3$/MeOH). Melting Point: 170 °C. Average logP = 7.33. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 8.44 (s, 2H, ArH), 4.17 (t, *J* = 7.5 Hz, 4H, , Ax*CH*$_2$), 3.38 (b, 8H, N*(CH*$_2$*)*$_2$), 1.84 (m, 4H, AxCH$_2$*CH*$_2$), 1.74-1.69 (m, 12H, *CH*$_2$), 1.42-1.33 (m, 12H, *CH*$_2$), 0.89 (t, *J* = 6.5 Hz, 6H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 163.30, 162.01, 152.25, 125.50, 125.34, 124.37, 53.69, 40.87, 31.59, 28.19, 26.85, 26.25, 24.02, 22.062, 14.10. MS (MALDI-TOF, matrix- α-cyano-4-hydroxycinnamic acid): 602.32 (m/z). FTIR (KBr, cm^{-1}): 2952, 2932, 2852, 1690, 1655, 1573, 1450, 1313. Anal. Calcd. for $C_{36}H_{48}N_4O_4$: C, 71.97; H, 8.05; N, 9.33; O, 10.65. Anal. Found C, 71.67; H, 8.35; N, 9.43.

Table S1: Oxidation and reduction potentials E^1_{ox}, E^2_{ox} and E^1_{red} obtained from CV/DPV measurements in MeCN/$CHCl_3$ (1:1). The experimental HOMO and LUMO levels were calculated using following equations: $E_{HOMO/LUMO}$ = -(4.4 + $E^1_{ox/red}$) eV.[3]

	E^1_{ox}(V)	E^2_{ox}(V)	E^1_{red}(V)	HOMO(eV)	LUMO(eV)
1a	+0.987/+0.965	+1.343/+1.322	-0.890/-0.875	-5.387	-3.510
1b	+0.983/+0.958	+1.334/+1.317	-0.895/-0.875	-5.383	-3.505
1c	+0.975/+0.955	+1.325/+1.305	-0.898/-0.879	-5.375	-3.502
1d	+0.982/+0.961	+1.340/+1.319	-0.927/-0.911	-5.382	-3.473
1e	+0.921/+0.896	+1.172/+1.152	-0.860/-0.845	-5.321	-3.540

Table S2: Comparison of the experimental UV-vis-NIR absorptions of **1a**, **1a**$^{\cdot+}$ and **1a**$^{-}$ with TD-DFT/B3LYP/6-31++G(d,p) predicted values. The optimized geometries at HF/6-31+G(d,p) level of calculation were used for TD-DFT single point energy calculations with 10-24 states. Bulk solvent (MeCN) effects were approximated using a polarizable continuum model (PCM), specifically the integral equation formalism model (IEF-PCM).[4]

	λ_{exp} nm (ε M^{-1} cm^{-1})	λ_{theo} nm (osc. strength)
1a	345 (9150)	331 (0.0222)
	361 (11000)	377 (0.2217)
	570 (15000)	495 (0.0127)
	613 (20612)	618 (0.2268)
1a$^{\cdot+}$	464 (2500)	500 (0.0001)
	669 (16800)	596 (0.2287)
	768 (9700)	662 (0.0000)
	874 (26906)	747 (0.1896)
1a^{-}	455 (10200)	445 (0.1204)
	494 (14990)	480 (0.1350)
	678 (7950)	648 (0.1920)
	778 (1700)	768 (0.0023)

Table S3: Comparison of the geometric parameters of **1b** and **1e** and their radical ions in gas phase using DFT/B3LYP/6-31G+(d,p) level of theory.

	1b	**1b**$^{\cdot+}$	**1b**$^{-}$	**1e**	**1e**$^{\cdot+}$	**1e**$^{-}$
N-H	1.018 Å	1.027 Å	1.019 Å	-	-	-
C=O	1.241 Å	1.236 Å	1.259 Å	1.228 Å	1.224 Å	1.243 Å
C=C	1.426 Å	1.444 Å	1.440 Å	1.424 Å	1.438 Å	1.463 Å
C-C	1.463 Å	1.484 Å	1.444 Å	1.483 Å	1.494 Å	1.440 Å
N-H···O	1.845 Å	1.790 Å	1.816 Å	-	-	-
N···O	2.659 Å	2.635 Å	2.652 Å	2.814 Å	2.870 Å	2.790 Å
∠N-H···O	134^{o}	137 ^{o}	137 ^{o}	-	-	-

Table S4. Mulliken atomic charges distributions obtained by DFT calculations at B3LYP/6-31+ G (d, p).

atom	atomic charges		
	(**1b**)	(**1b**$^{+}$)	(**1b**$^{-}$)
C1, C5	-0.259	-0.304	-0.289
C2, C6	+0.372	+0.425	+0.445
C3, C7	-0.392	-0.515	-0.443
C4, C8	+0.085	+0.236	-0.018
C9, C10	-0.123	-0.106	-0.095
O11, O16	-0.474	-0.421	-0.551
C12, C17	+0.379	+0.397	+0.349
N13, N18	-0.135	-0.136	-0.126
C14, C19	+0.464	+0.471	+0.438
O15, O20	-0.514	-0.462	-0.588
N21, N22	-0.399	-0.341	-0.412

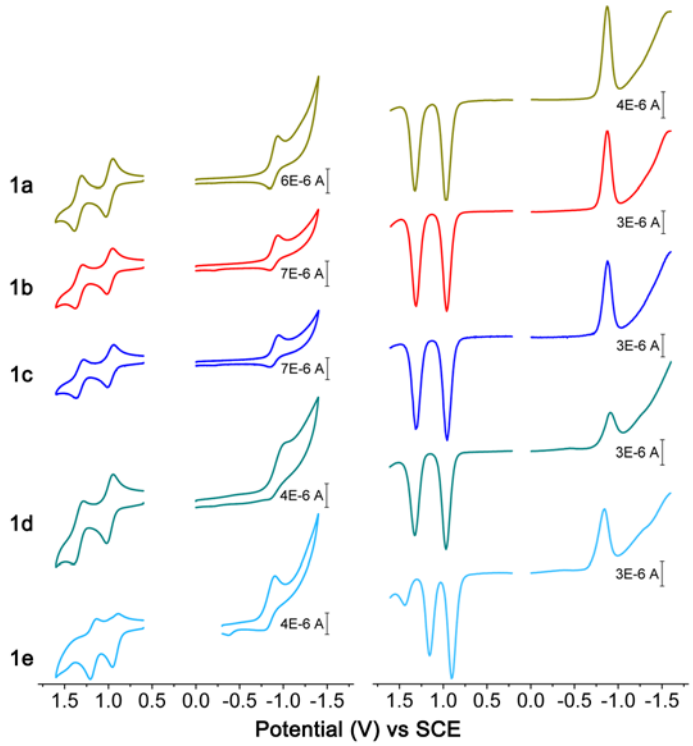


Figure S1: Cyclic Voltammogram (left panel) and Differential Pulse Voltammetry (right panel) results of **1a**-**1e** (0.5 mM) in degassed MeCN/$CHCl_3$ (1:1).

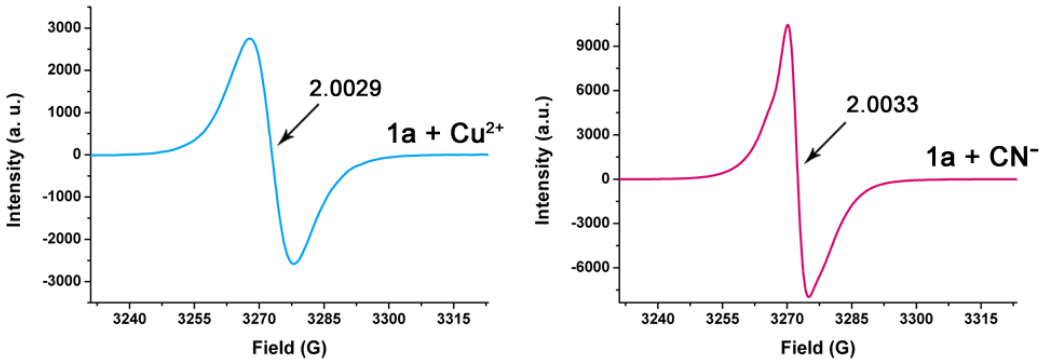


Figure S2: EPR spectrum of **1a** (5×10^{-4} M) with 1.0 equiv. of Cu^{2+} (blue) in MeCN/$CHCl_3$ (8:2) and **1a** with 3.0 equiv. (purple) of CN^- in THF.

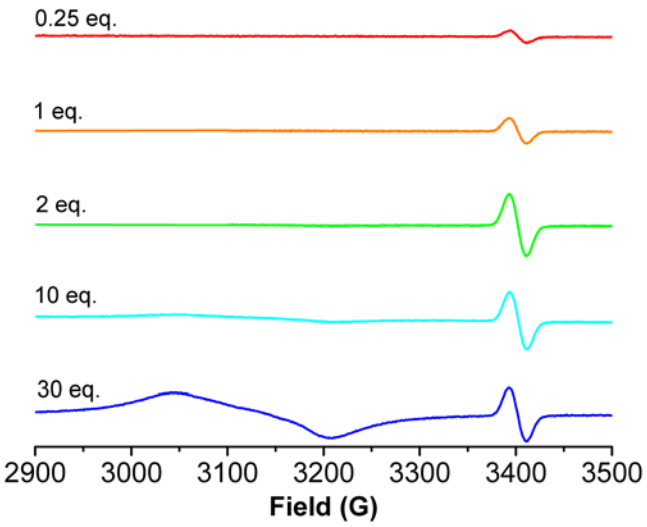


Figure S3: EPR spectrum of **1a** (5×10^{-4} M) with different equiv. of Cu^{2+} in MeCN/$CHCl_3$ (8:2).

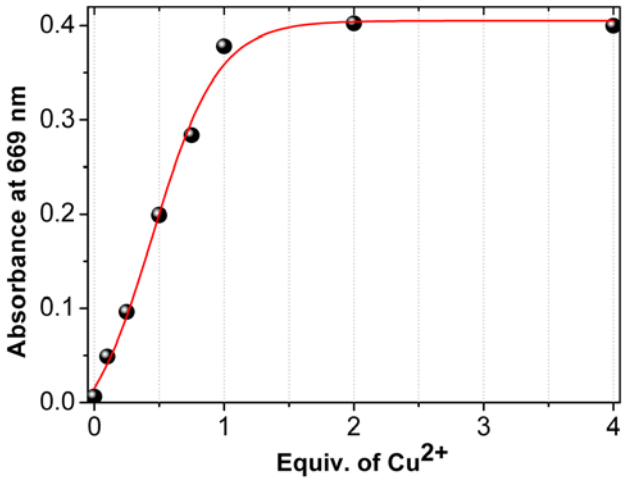


Figure S4: Plot shows the formation of **1a**$^{\bullet+}$ with the successive addition of different equiv. of Cu^{2+} in MeCN/$CHCl_3$ (8:2). [**1a** (2×10^{-4} M)].

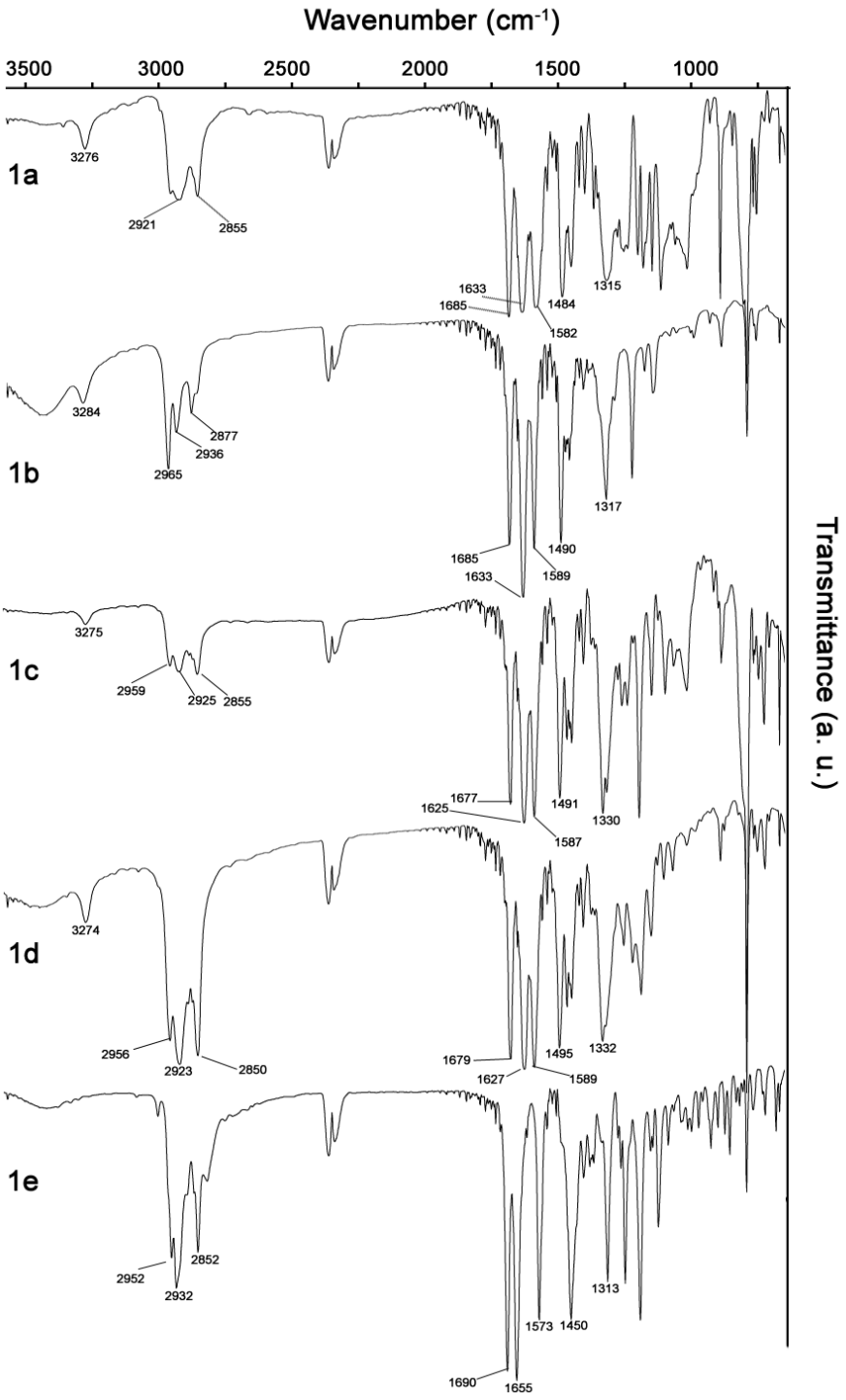


Figure S5: FT-IR spectra of **1a-1e.**

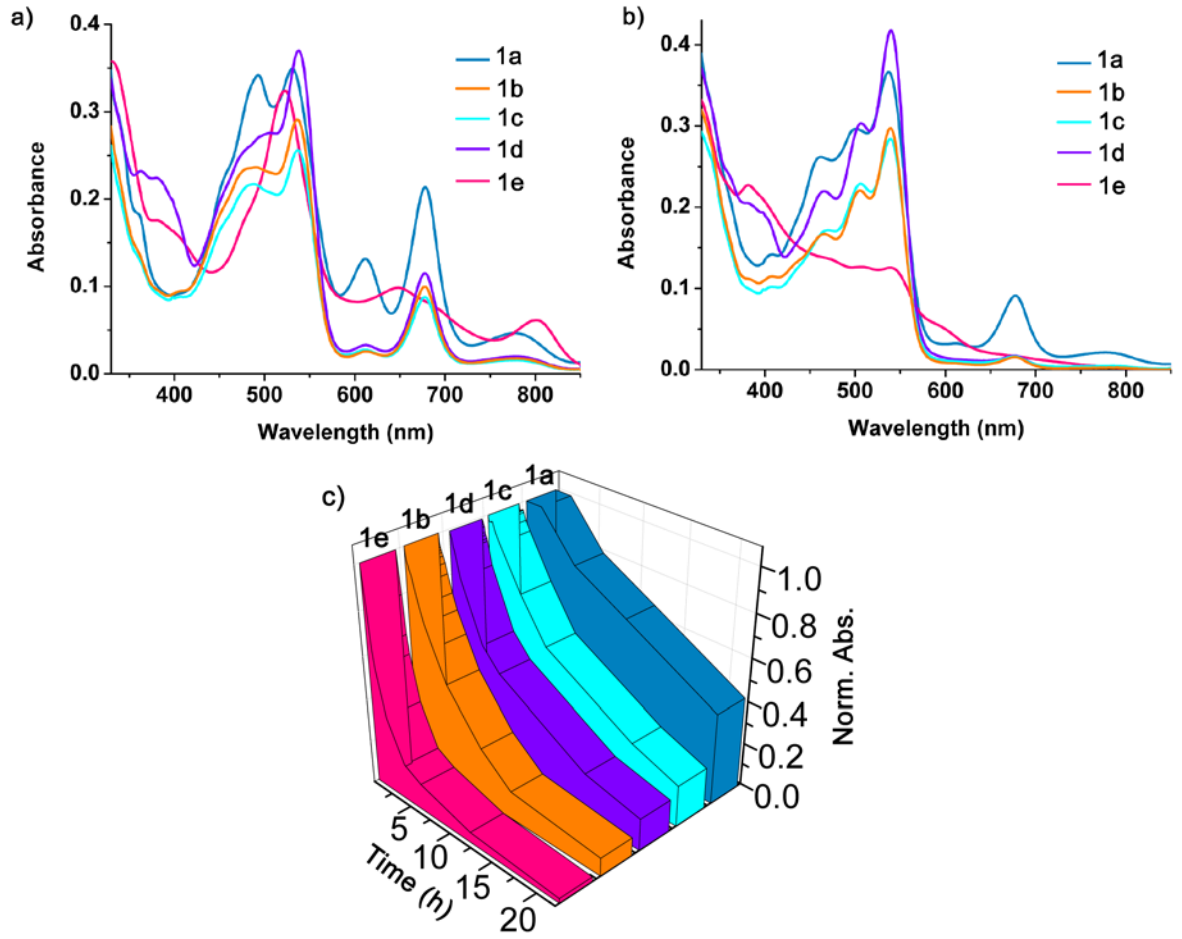


Figure S6: UV-vis-NIR spectra of **1a-e** (2×10^{-4} M) with 3 equiv. of CN^- in THF at (a) 30 min and (b) 20 h and (c) decay profile of **1a**$^{\cdot-}$**, 1b**$^{\cdot-}$**, 1c**$^{\cdot-}$**, 1d**$^{\cdot-}$ and **1e**$^{\cdot-}$ (>778 nm).

Half-life of **1a**$^{\cdot-}$**:** 18h; **1b**$^{\cdot-}$**:** 4.1 h; **1c**$^{\cdot-}$**:** 7.6 h; **1d**$^{\cdot-}$**:** 5.2 h and **1e**$^{\cdot-}$**:** 1.3 h

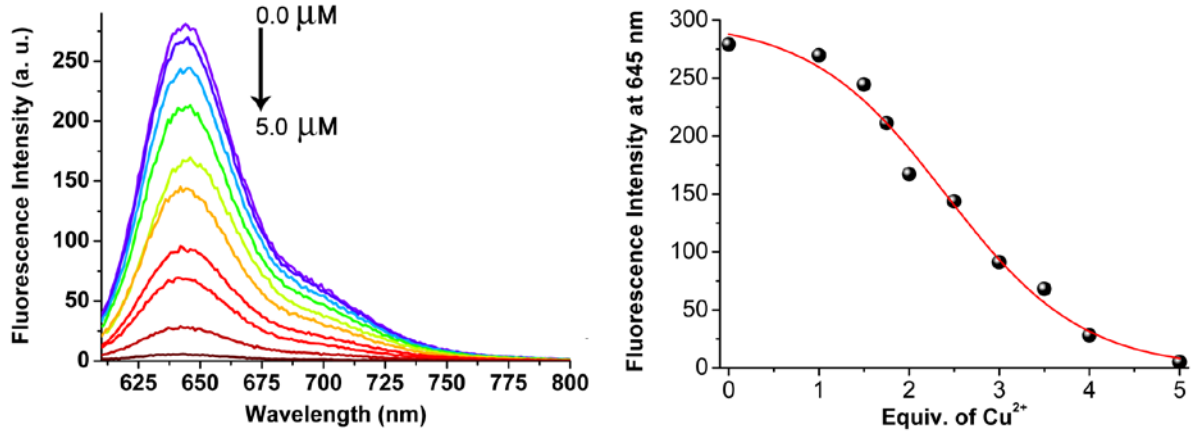


Figure S7: Fluorescence spectra of **1a** (1×10^{-6} M) with varying equiv. of Cu^{2+} in MeCN/$CHCl_3$ (8:2) [λ_{ex} = 598 nm]. φ of **1a** was found to be 0.34.

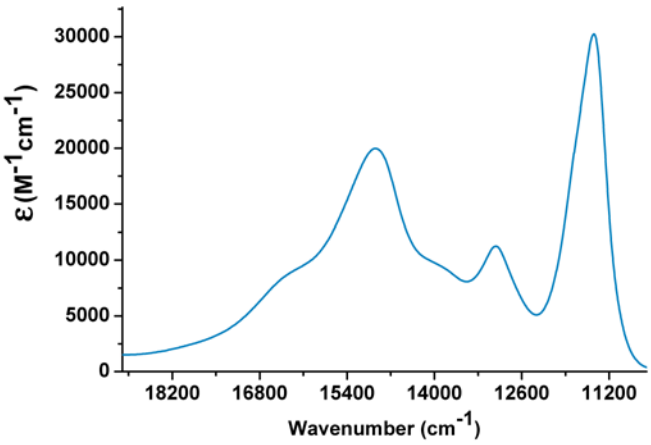


Figure S8: UV-vis-NIR spectra of **1a**$^{\cdot+}$ in MeCN/$CHCl_3$ (8:2 v/v) showing the narrow half-width of 652 cm^{-1} of the intense NIR band at 11,447 cm^{-1} (874 nm).

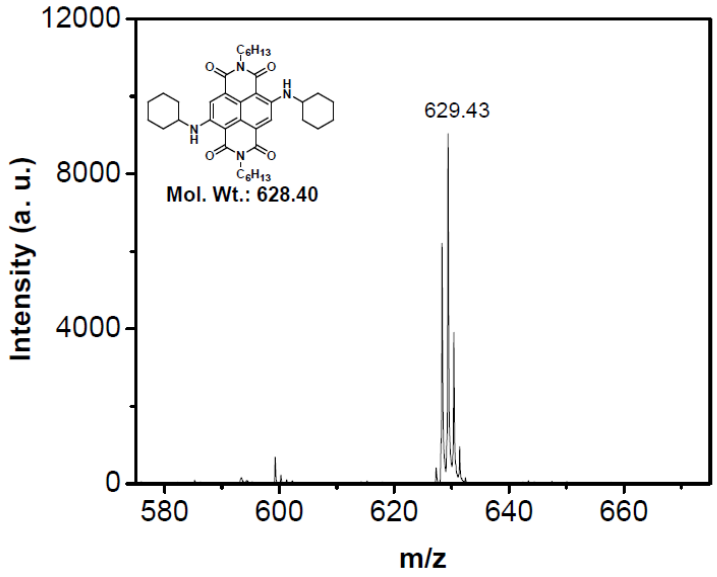


Figure S9: MALDI-TOF mass spectrum of **1a**.

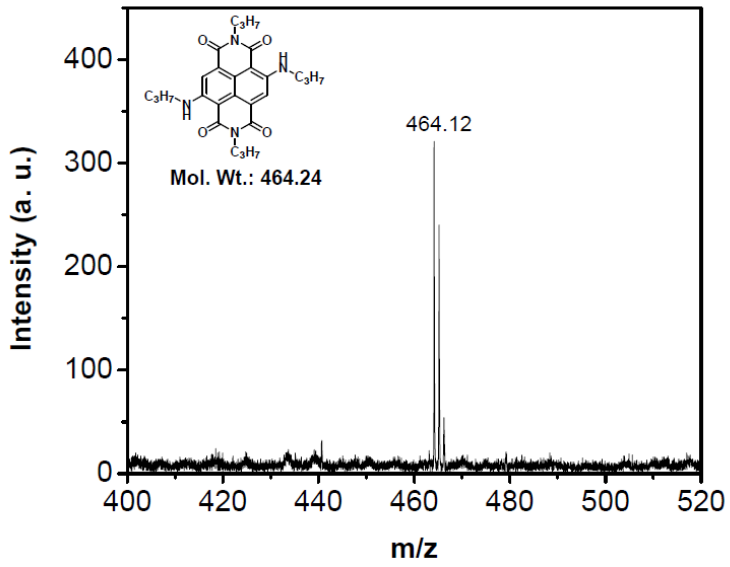


Figure S10: MALDI-TOF mass spectrum of **1b**.

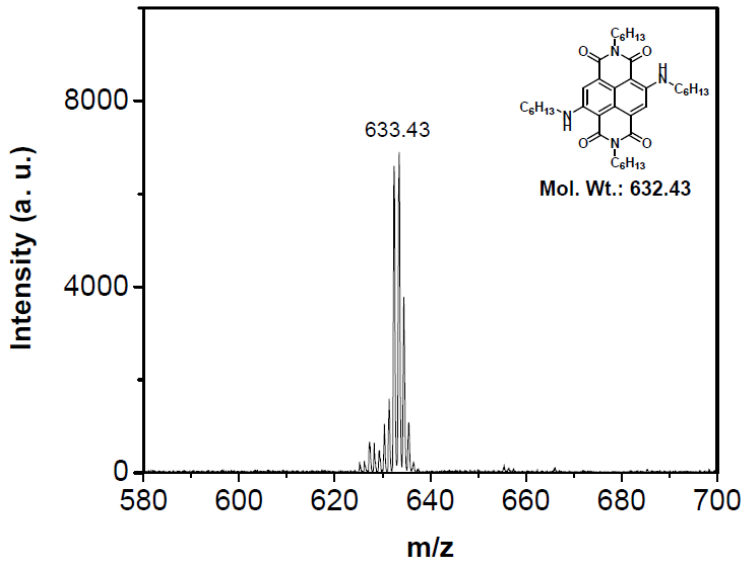


Figure S11: MALDI-TOF mass spectrum of **1c**.

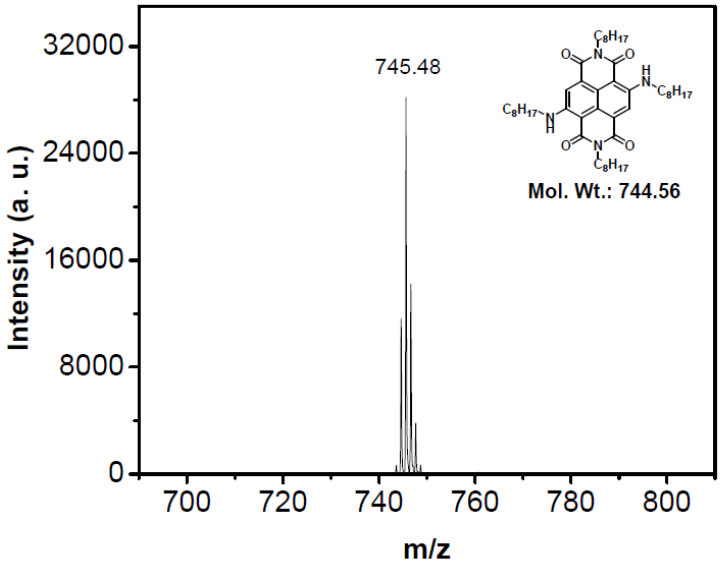


Figure S12: MALDI-TOF mass spectrum of **1d**.

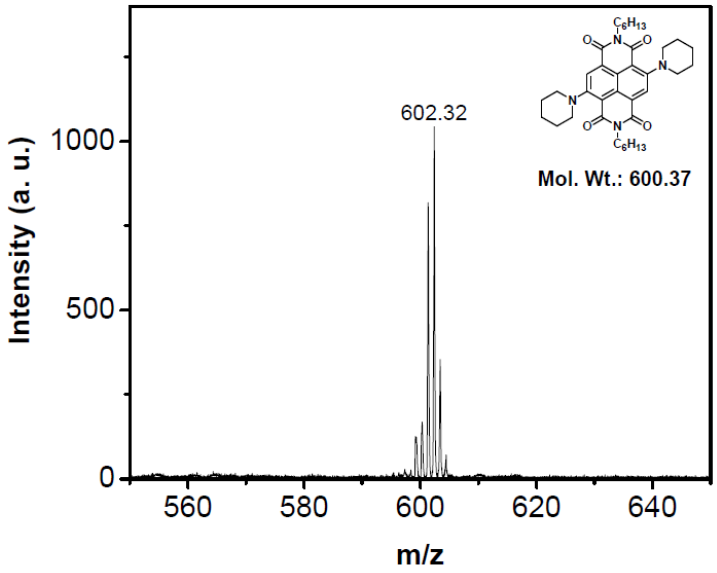


Figure S13: MALDI-TOF mass spectrum of **1e**.

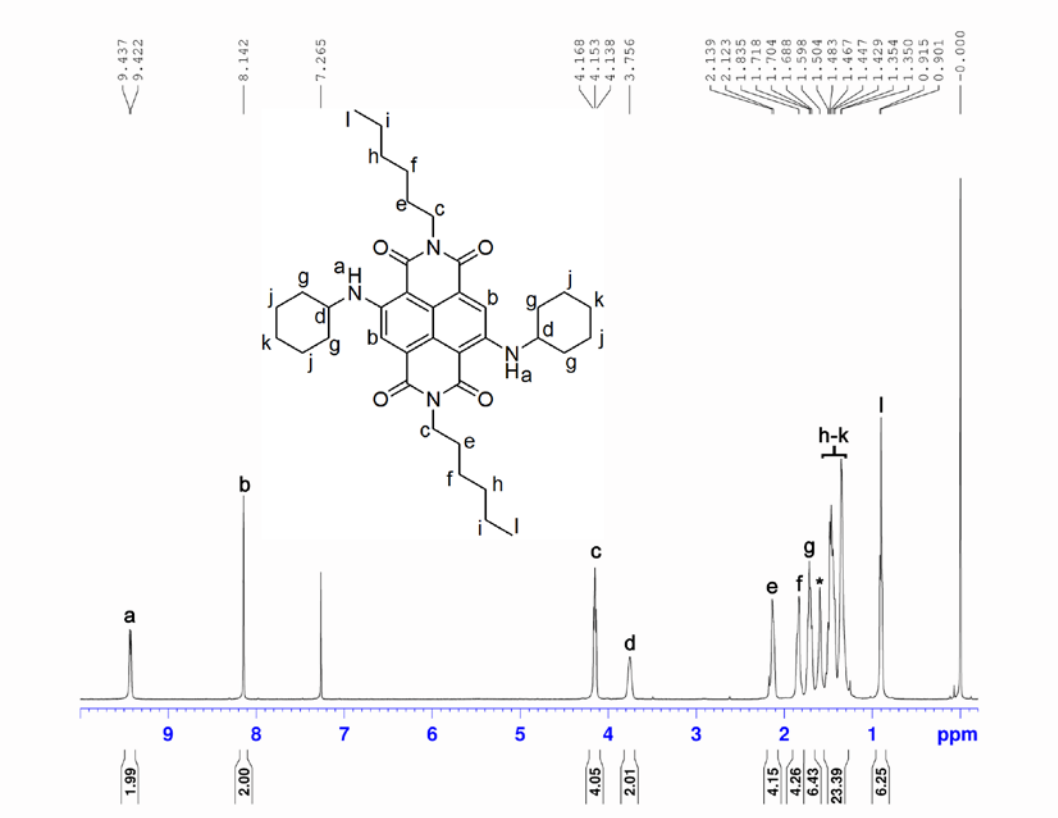


Figure S14: 500 MHz ^{1}H NMR spectrum of **1a** in $CDCl_3$ at room temperature.

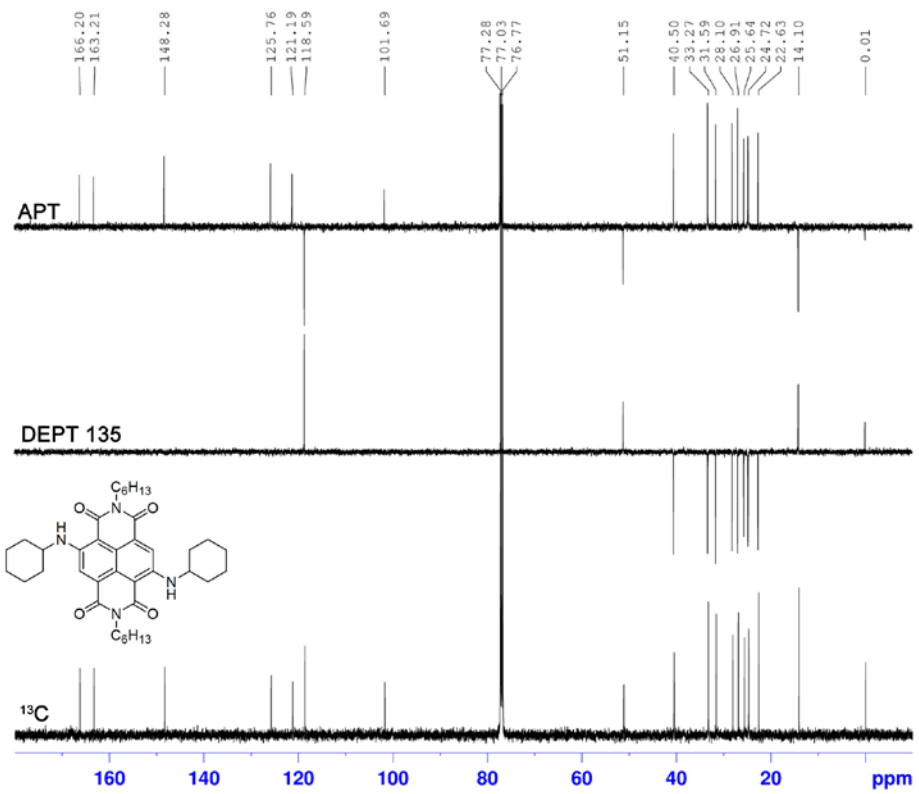


Figure S15: 125 MHz ^{13}C, DEPT-135 and APT spectra of **1a** in $CDCl_3$ at room temperature.

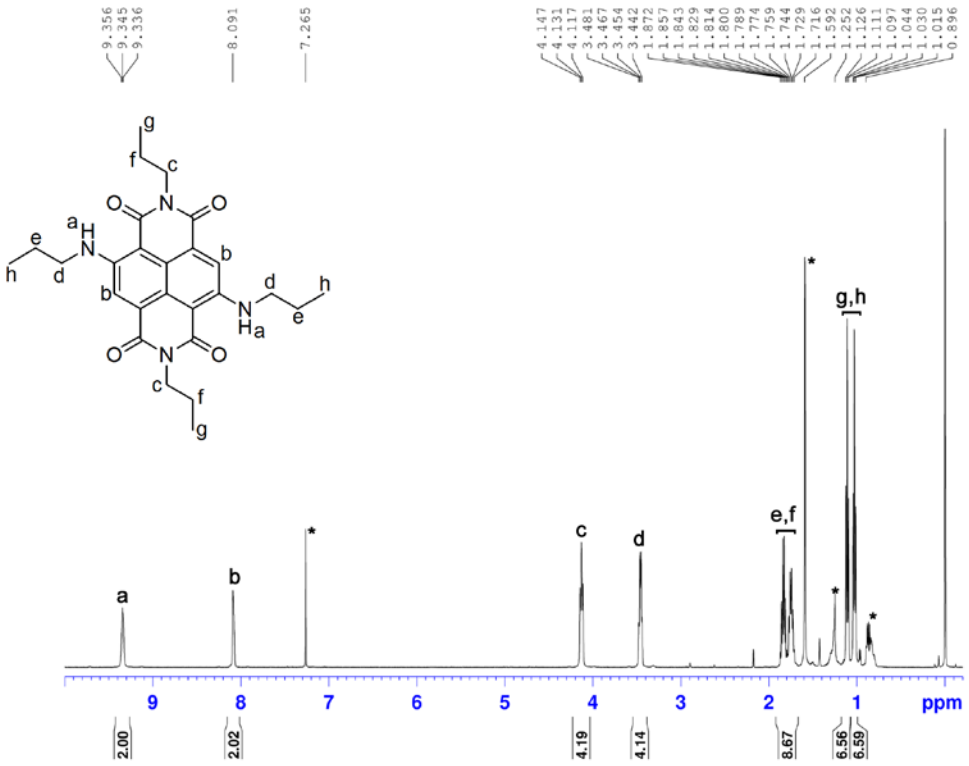


Figure S16: 500 MHz ^{1}H NMR spectrum of **1b** in $CDCl_3$ at room temperature.

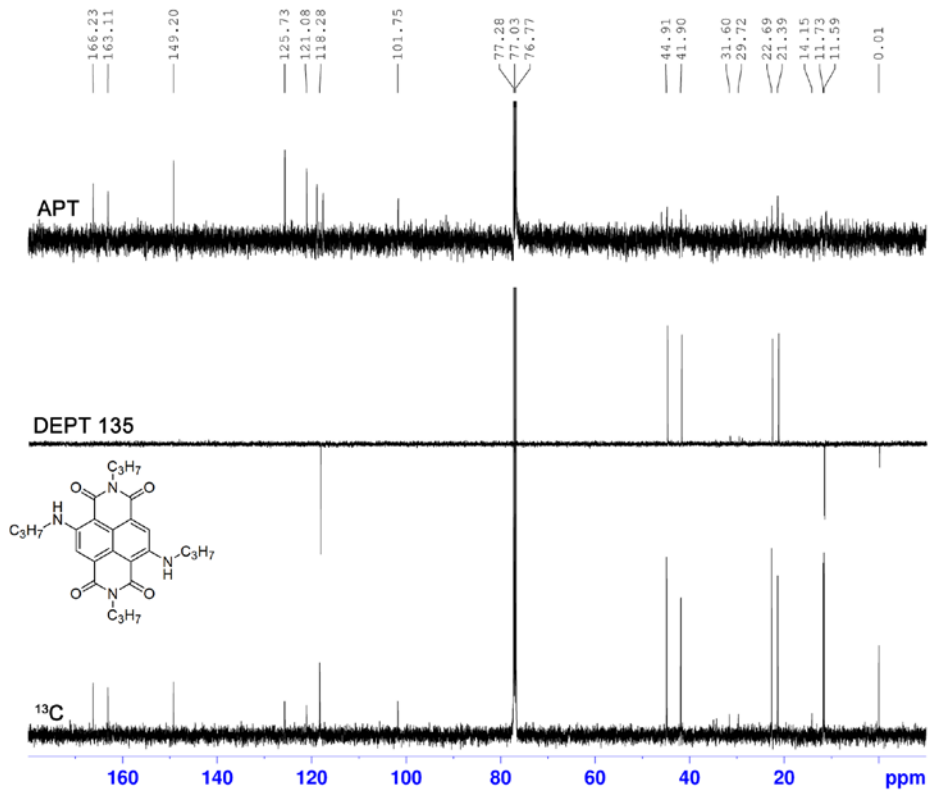


Figure S17: 125 MHz ^{13}C, DEPT-135 and APT spectra of **1b** in $CDCl_3$ at room temperature.

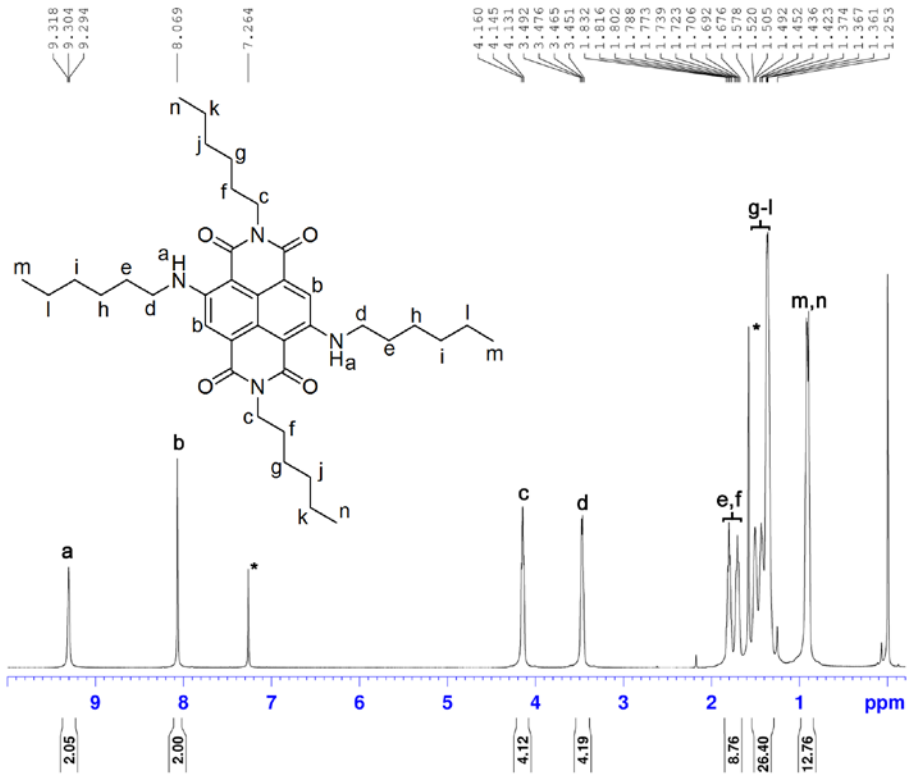


Figure S18: 500 MHz ^{1}H NMR spectrum of **1c** in $CDCl_3$ at room temperature.

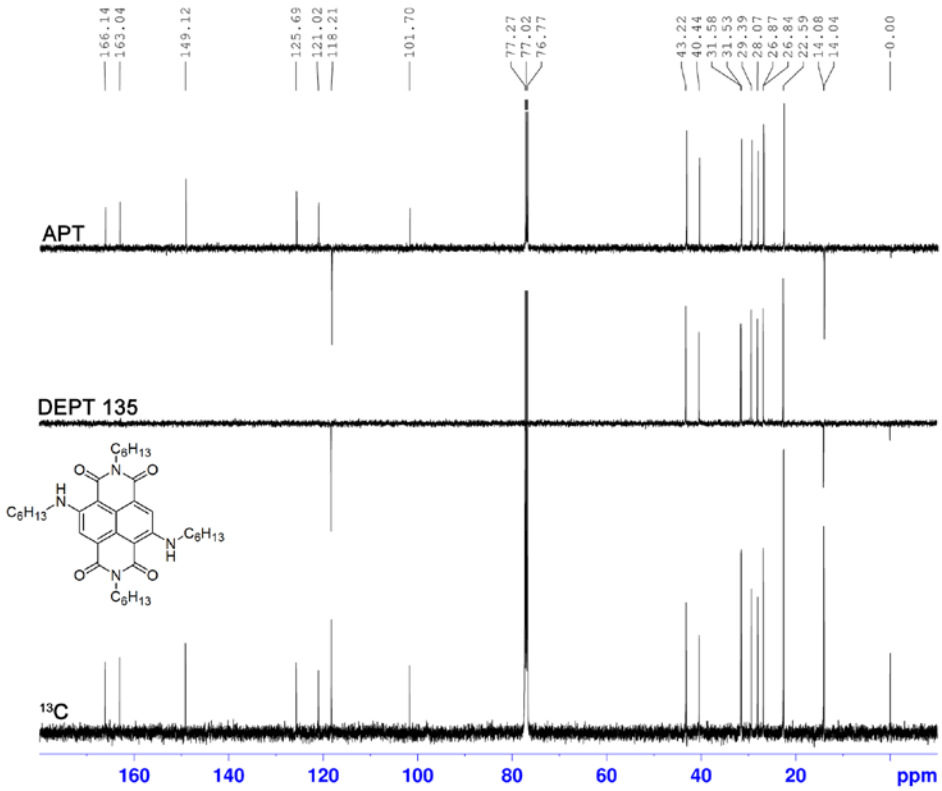


Figure S19: 125 MHz ^{13}C, DEPT-135 and APT spectra of **1c** in $CDCl_3$ at room temperature.

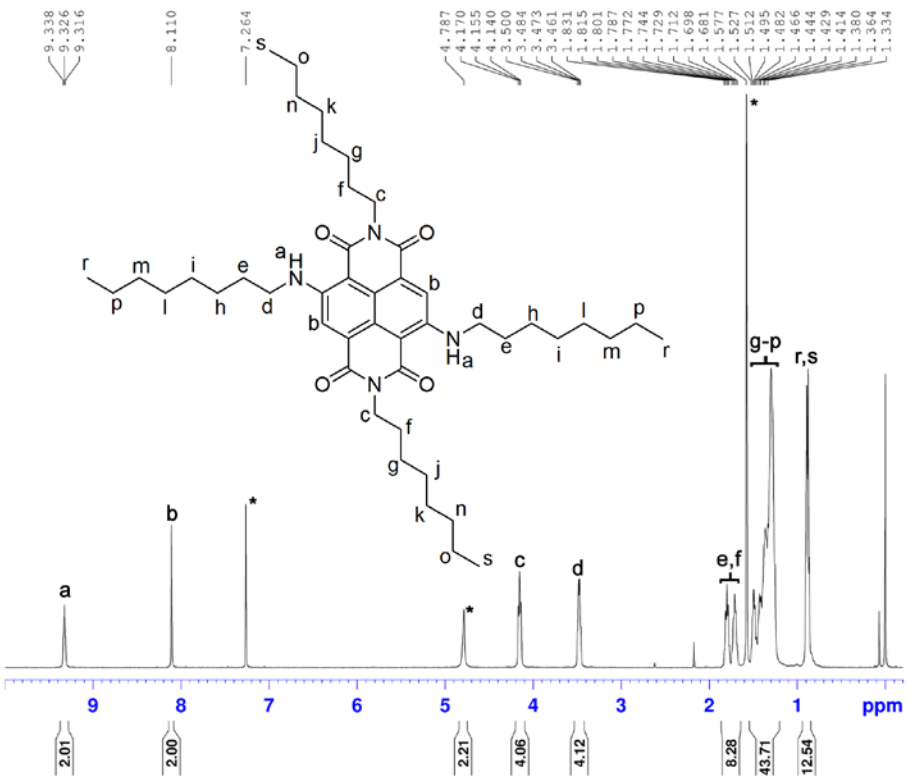


Figure S20: 500 MHz ^{1}H NMR spectrum of **1d** in $CDCl_3$ at room temperature.

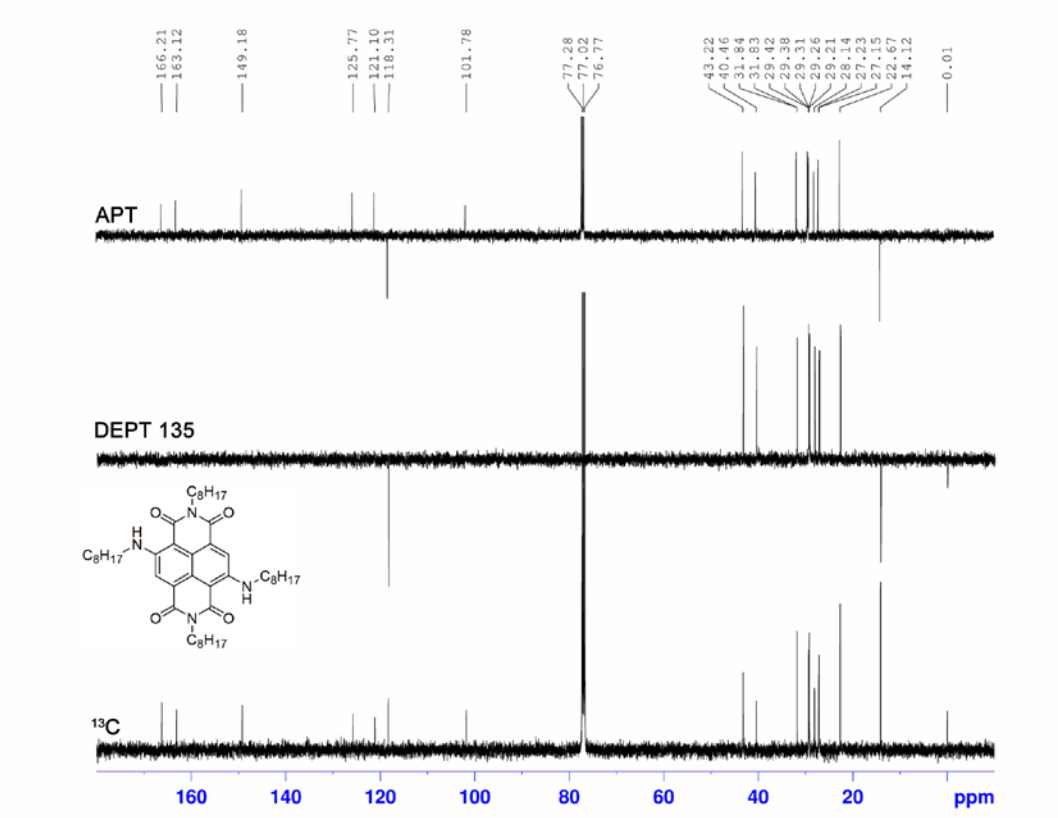


Figure S21: 125 MHz ^{13}C, DEPT-135 and APT spectra of **1d** in $CDCl_3$ at room temperature.

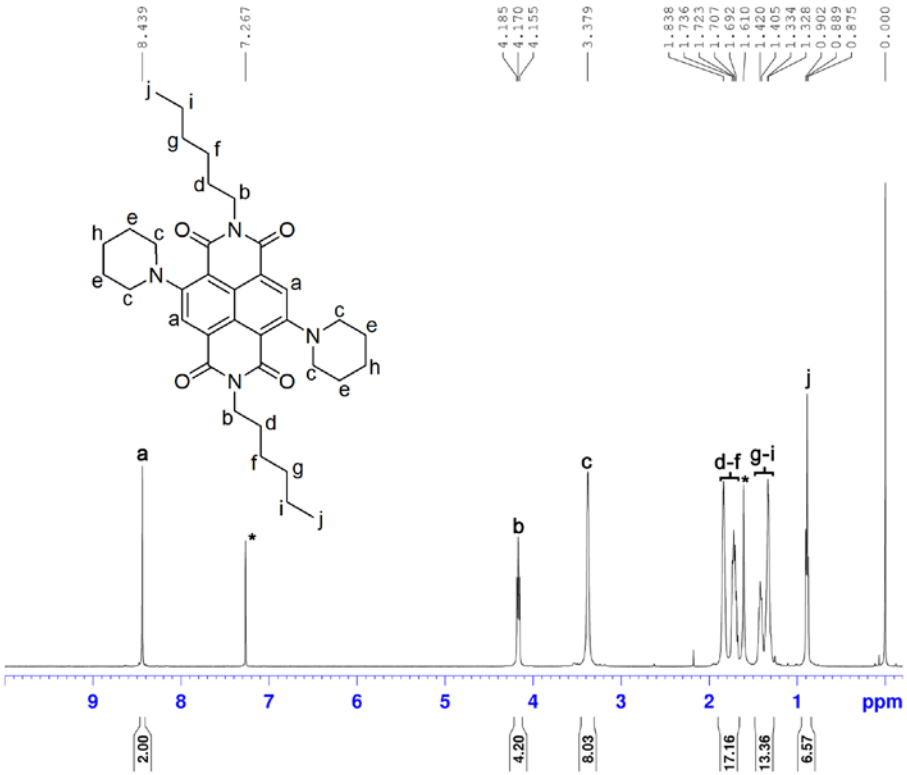


Figure S22: 500 MHz ^{1}H NMR spectrum of **1e** in $CDCl_3$ at room temperature.

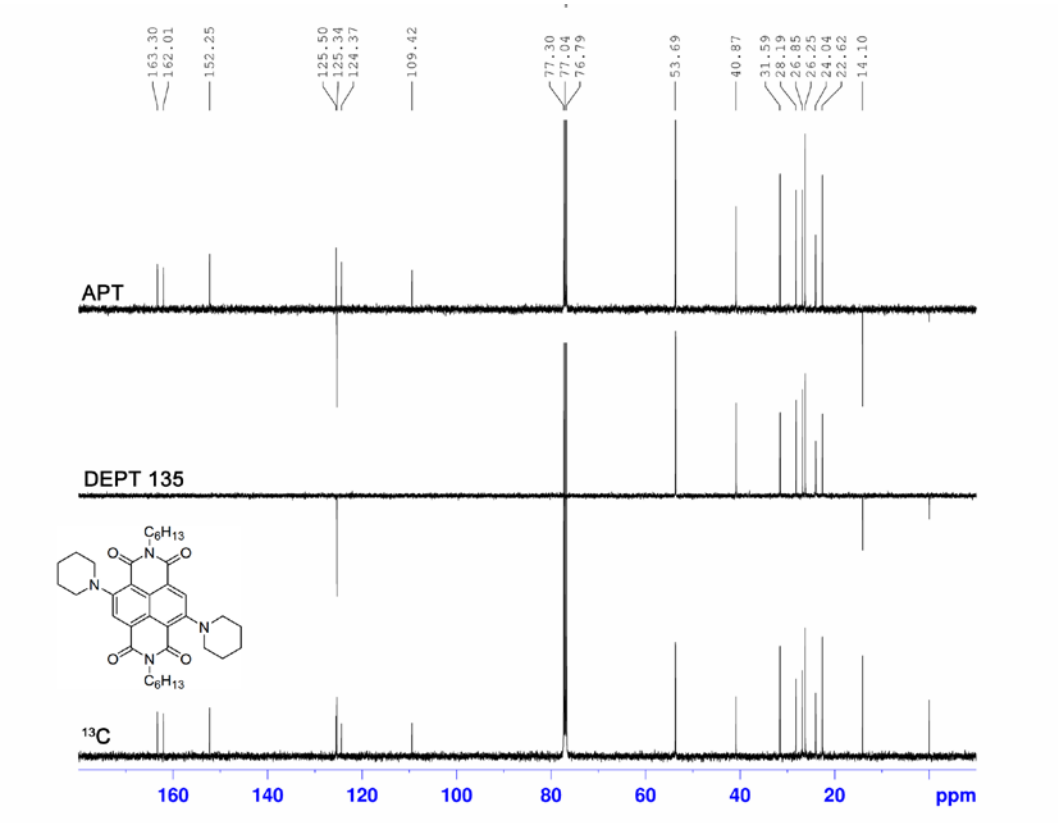


Figure S23: 125 MHz ^{13}C, DEPT-135 and APT spectra of **1e** in $CDCl_3$ at room temperature.

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