Synthesis, Optical and Redox Attributes of Core-/Bay-Substituted Thionated NDIs, PDIs and their Diverse Radical Anions

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Supporting Information

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General

Chemicals were sourced either from Fluka, Sigma−Aldrich, Spectrochem India 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 having particle size of 25 μm and was sourced from Sigma−Aldrich. 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. The elemental analysis was performed using a Perkin-Elmer 2400 CHN elemental analyser. MALDI−TOF mass spectral data were obtained using a Bruker Autoflex TOF/TOF instrument with laser repetition rate of 50 ps. α−Cyano−4−hydroxycinnamic acid and

1,8,9−Anthracenetriol were used as the matrix for MALDI−TOF mass spectrometry. IR spectra were recorded using a Varian 7000 FT−IR instrument.

DFT calculations were performed at B3LYP/6−311++G(d,p)/CPCM in DCM to optimize the molecular geometries of all the molecules in Gaussian 09 program package. To reduce computational time, axial groups have changed by methyl group. The HOMO, LUMO, ESP and spin densities were calculated by using the optimized geometries.

UV−Vis−NIR and FT−IR Spectroscopy: UV−Vis−NIR spectra were recorded on a JASCO V−670 Spectrophotometer having path length of 10 mm were used. Wavelength reported in nanometer (nm). UV−Grade solvents were used for the spectroscopic experiments. Fourier transform infrared (FT−IR) spectra were recorded on a Varian 7000 FT−IR spectrometer. Samples were analyzed in powder form. A background scan of air was collected prior to analysis while FT−IR in neat were taken using Bruker Tensor 37 FT−IR Spectrometer.

CV and DPV: CV and DPV were carried out using a computer controlled potentiostat (CHI 650C) and a standard three electrode arrangement that consisted of Pt as working and auxiliary electrodes and SCE as reference electrode. All the electrochemical measurements were carried out in Ar−purged solvents containing *n*−Bu_4NPF_6 (0.1 M) as the supporting electrolyte. The scan rate for CV experiments was typically 200−300 mV/s. DPV was carried out keeping peak amplitude 50 mV, peak width 0.01 s, pulse period 0.05 s and increment E at 20 mV.

Experimental Section

Molecule 1: Yield = 9 %. R_f= 0.70 $CHCl_3$/n-hexane (3:7), Melting Point: 210 °C, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 8.95 (s, 2H, *Ar-H*), 8.84 (d, *J* = 7.0 Hz, 1H, *Ar-H*), 8.63 (d, *J* = 6.5 Hz, 1H, *Ar-H*), 6.98], *J* = 6.5 Hz, 4H, Mes*Bz-H*), 2.32 (s, 6H, Mes-*pCH₃*), 1.98 (s, 12H, Mes-*oCH₃*), ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 192.56, 188.01, 187.98, 160.46, 140.63, 138.91, 138.71, 136.64, 136.02, 135.40, 135.33, 134.28, 133.67, 131.41, 131.24, 130.64, 129.72, 129.68, 128.51, 126.32, 125.50, 122.65, 29.73, 21.37, 21.33, 17.67, 17.64. MS (MALDI-TOF, matrix- α-cyano-4-hydroxycinnamic acid): Calculated: Exact Mass: 550.120, Found: 550.076 (m/z). FT−IR (cm^{-1}): 2919, 1738, 1680, 1439, 1206. Anal.Calcd for $C_{32}H_{26}N_2OS_3$: C, 69.78; H, 4.76; N, 5.09; Found: C, 68.91; H, 4.36; N, 4.92.

Molecule 2: Yield = 15 %. R_f= 0.65 $CHCl_3$/ n-hexane (1:1), Melting Point: 255 °C, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 9.08 (d, *J* = 8.0 Hz, 2H, *Ar-H*), 8.67 (d, *J* = 8.0 Hz, 2H, *Ar-H*), 6.99 (s, 4H, Mes*Bz-H*), 2.31 (s, 6H, Mes-*pCH₃*), 1.98 (s, 12H, Mes-*oCH₃*), ^{13}C

NMR (125 MHz, $CDCl_3$, 300 K): δ = 192.37, 160.08, 138.94, 135.83, 135.32, 134.26, 131.21, 129.92, 129.68, 126.20, 126.01, 31.95, 29.72, 29.39, 22.72, 21.32, 17.64, 14.16. MS (MALDI-TOF, matrix- α-cyano-4-hydroxycinnamic acid): Calculated Exact Mass: 534.143, Found 534.207 (m/z). FT-IR (cm^{-1}): 2911, 1738, 1688, 1439, 1214. Anal. Calcd for $C_{32}H_{26}N_2O_2S_4$: C, 71.88; H, 4.90; N, 5.24; Found: C, 71.61; H, 4.82; N, 5.42.

Molecule 3: Yield = 8 %. R_f= 0.45 (7:3) , Melting Point: 285 °C, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 9.09 (d, *J* = 7.5 Hz, 1H, *Ar-H*), 8.78 (d, *J* = 8 Hz, 2H, *Ar-H*), 8.69 (d, *J* = 8 Hz, 1H, *Ar-H*), 6.99 (s, 4H, Mes*Bz-H*), 2.31 (s, 6H, Mes-*pCH₃*), 2.0 (s, 12H, Mes-*oCH₃*), ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 192.17, 170.53, 170.41, 162.60, 162.56, 162.30, 159.74, 139.14, 138.97, 135.77, 135.27, 134.96, 134.27, 131.73, 131.52, 131.49, 131.08, 130.41, 130.35, 129.70, 129.60, 127.83, 127.62, 127.18, 126.95, 126.61, 125.98, 125.73, 21.33, 21.25, 21.18, 21.06, 17.80, 17.65,14.17. MS (MALDI-TOF, matrix- α-cyano-4-hydroxycinnamic acid): Calculated Exact Mass: 518.166, found 518.080 (m/z). FT-IR (cm^{-1}): 2919, 1730, 1683, 1439, 1339, 1223. Anal. Calcd for $C_{32}H_{26}N_2O_3S$: C, 74.11; H, 5.05; N, 5.40; Found: C, 73.91; H, 4.92; N, 5.46.

Molecule 4 [Reference 1]: Yield: 20 %, R_f=0.56 ($CHCl_3$/n-hexane 6:4), Melting Point: >300°C, ^{1}HNMR (500 MHz, $CDCl_3$, 298 K): δ = 9.34 (s, 2H, *Ar-H*), 6.99 (s, 4H, Mes*Bz-H*), 2.31 (s, 6H, Mes-*pCH₃*), 1.99 (s, 12H, Mes-*oCH₃*), ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 189.30, 158.08, 143.68, 139.15, 135.38, 134.06, 129.77, 128.33, 128.27, 127.17, 123.54, 21.29, 17.72, 17.67. MS (MALDI-TOF, matrix- α-cyano-4-hydroxycinnamic acid): Calculated Exact Mass: 689.964, found 689.959 (m/z). FT-IR (cm^{-1}): 2911, 1688, 1414, 1331, 1214. Anal. Calcd for $C_{32}H_{24}Br_2N_2O_2S_2$: C, 55.50; H, 3.49; Br, 23.08; N, 4.05; Found: C, 55.10; H, 3.59; N, 4.25.

Molecule 5: Yield = 15 %. R_f= 0.35 ($CHCl_3$/n-hexane 6:4), Melting Point: >300°C, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 9.34 (s, 1H, *Ar-H*), 9.01 (s, 1H, *Ar-H*), 6.99 (s, 4H, Mes*Bz-H*), 2.30 (s, 6H, Mes-*pCH₃*), 1.99 (s, 12H, Mes-*oCH₃*); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 189.12, 170.49, 170.37, 160.50, 160.42, 157.75, 143.69, 139.44, 139.31, 139.14, 135.35, 134.81, 134.07, 130.27, 129.76, 129.65, 129.03, 128.82, 128.53, 128.35, 126.94, 125.49, 124.76, 123.23, 114.07, 39.24, 37.11, 34.41, 33.83, 31.94, 31.45, 30.21, 30.05, 29.71, 29.67, 29.52, 29.37, 29.17, 28.97, 22.70, 21.26, 21.02. TOF-MS-ES: calculated Exact Mass (M+H): 674.995, found 674.990 (m/z). FT-IR (cm^{-1}): 2919, 1721,

1671, 1356, 1223. Anal. Calcd for $C_{32}H_{24}Br_2N_2O_3S$: C, 56.82; H, 3.58; Br, 23.63; N, 4.14. Found: C, 56.41; H, 3.59; N, 4.24.

Molecule 6: Yield = 11 %. R_f= 0.30 ($CHCl_3$/n-hexane 9:1), Melting Point: >300°C, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 8.96 (s, 1H, *Ar-H*), 8.73 (s, 1H, *Ar-H*), 4.20 (t, *J* = 7.5 Hz, 2H), 4.15 (t, *J* = 7.5 Hz, 2H) 1.75-1.67 (m, 4H), 1.42-1.36 (m, 4H), 1.34-1.25 (m, 8H), 0.91 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 201.98, 160.82, 160.25, 147.22, 135.35, 133.27, 128.28, 127.18, 126.64, 126.29, 116.19, 114.47, 41.88, 41.62, 41.56, 31.42, 27.87, 26.73, 26.66, 22.54, 22.51, 14.00. MS (MALDI-TOF, matrix- α-cyano-4-hydroxycinnamic acid): Calculated Exact Mass: 516.165, Found 516.075 (m/z). FT−IR (cm^{-1}): 2927, 2853, 1713, 1646, 1455, 1322, 1255. Anal. Calcd for $C_{28}H_{28}N_4O_2S_2$: C, 65.09; H, 5.46; N, 10.84; O, 6.19; Found: C, 69.62; H, 4.26; N, 9.76.

Molecule 7: Yield = 24 %. R_f= 0.48 ($CHCl_3$/n-hexane 6:4), Melting Point: >300°C, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 8.82 (s, 2H, *Ar-H*), 7.42 (d, *J* = 7 Hz, 4H, Ph*H*), 7.25 (t, 2H, Ph*H*), 7.12 (t, 4H, Ph*H*), 6.97 (d, 4H, Mes*Bz-H*), 2.32 (t, 6H, Mes-*pCH₃*), 2.03 (t, 12H, Mes-*oCH₃*), ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 190.51, 158.37, 157.64, 138.59, 135.58, 134.14, 131.34, 130.30, 129.57, 129.52, 124.97, 124.76, 119.14, 114.03, 21.19, 17.65. TOF-MS-ES: Calculated Exact Mass for (M+H): 719.204, found 719.151. FT−IR (cm^{-1}): 2919, 1688, 1480, 1372, 1223. Anal. Calcd for $C_{44}H_{34}N_2O_4S_2$: C, 73.51; H, 4.77; N, 3.90; Found: C, 73.41; H, 4.97; N, 3.92.

Molecule 8: Yield = 11 %. R_f= 0.55 ($CHCl_3$/n-hexane 7:3), Melting Point:>300°C, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 8.48 (s, 2H, *Ar-H*), 7.59 (d, 4H, Ph*H*), 7.48-7.01 (6H, Ph*H*), 6.96 (s, 4H, Mes*Bz-H*), 2.32 (t, 6H, Mes-*pCH₃*), 2.04 (t, 12H, Mes-*oCH₃*), ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 190.95, 150.03, 138.68, 136.26, 136.02, 134.92, 134.19, 130.46, 130.34, 129.68, 129.55, 127.65, 124.92, 42.27, 29.70, 26.76, 21.22, 17.72, 17.67, 17.53. MS (MALDI-TOF, matrix- α-cyano-4-hydroxycinnamic acid): Calculated Exact Mass (M+H): 750.150, Found 750.123 (m/z). Anal. Calcd for $C_{44}H_{34}N_2O_2S_4$: C, 70.37; H, 4.56; N, 3.73; Found: C, 70.23; H, 4.76; N, 3.91.

Molecule 9: Yield = 9 %. R_f= 0.60 ($CHCl_3$/n-hexane 7:3), Melting Point: >300°C, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 8.23 (s, 2H, *Ar-H*), 7.68 (d, 4H, Ph*H*), 7.43-7.35 (6H, Ph*H*), 6.94 (t, 4H, Mes*Bz-H*), 2.28 (t, 6H, Mes-*pCH₃*), 1.94 (t, 12H, Mes-*oCH₃*), MS (MALDI-TOF, matrix- α-cyano-4-hydroxycinnamic acid): Calculated Exact Mass:

846.039, Found 846.038 (m/z). FT-IR (cm^{-1}): 2927, 2853, 1663, 1455, 1239. Anal.Calcd for $C_{44}H_{34}N_2O_2S_2Se_2$: C, 62.56; H, 4.06; N, 3.32; Found: C, 62.56; H, 4.06; N, 3.32.

Molecule Br_2PDICy: Yield = 40 %. R_f= 0.65 ($CHCl_3$/n-hexane 7:3), Melting Point: >300°C, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 9.38 (s, 2H, *Ar-H*), 8.79 (s, 2H, *Ar-H*), 8.58 (d, 2H, *J* = 8Hz, *Ar-H*), 4.97-4.91 (m, 2H), 2.50-2.42 (m, 4H), 1.86-1.26 (16H), ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 163.32, 162.77, 137.95, 132.82, 132.67, 129.96, 129.25, 128.45, 127.04, 123.73, 123.33, 120.70, 54.28, 29.11, 26.51, 25.39. FT-IR (cm^{-1}): 2919, 2844, 1738, 1646, 1572, 1389, 1231. Anal.Calcd for $C_{36}H_{28}Br_2N_2O_4$: C, 60.69; H, 3.96; N, 3.93; Found: C, 60.33; H, 4.12; N, 4.03.

Molecule 10: Yield = 15 %. R_f= 0.58 ($CHCl_3$/n-hexane 6:4), Melting Point: >300°C, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 9.31 (d, 2H, *J* = 8.5 Hz*, Ar-H*), 8.99 (d, 2H, *J* = 8.5 Hz*, Ar-H*), 8.79 (s, 2H, *Ar-H*), 5.92 (s, 2H), 2.53 (d, 4H), 1.86-1.30 (16H), ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 194.40, 159.95, 138.95, 135.85, 132.69, 132.03, 129.06, 128.39, 127.94, 125.06, 124.12, 120.83, 62.73, 28.66, 26.52, 25.46. MS (MALDI-TOF, matrix- α-cyano-4-hydroxycinnamic acid): Calculated Exact Mass: 741.995, Found 741.950 (m/z). FT-IR (cm^{-1}): 2927, 2853, 1671, 1580, 1314, 1206. Anal. Calcd for $C_{36}H_{28}Br_2N_2O_2S_2$: C, 58.07; H, 3.79; N, 3.76; Found: C, 57.93; H, 3.81; N, 3.96.

Molecule 11: Yield = 11 %. R_f= 0.56 ($CHCl_3$/n-hexane 6:4), Melting Point: >300°C, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 9.35 (d, 1H, *Ar-H*), 9.30 (d, 1H, *Ar-H*), 9.25 (s, 1H, *Ar-H*), 9.18 (d, 1H, *Ar-H*), 8.75 (s, 1H, *Ar-H*), 8.55 (m, 1H, *Ar-H*), 5.91 (m, 2H), 2.57-2.49 (m, 4H), 1.86-1.25 (16H), ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 194.33, 193.28, 160.46, 159.85, 143.63, 138.02, 137.98, 135.88, 132.68, 132.46, 132.07, 131.97, 130.07, 129.98, 128.71, 128.46, 128.31, 128.04, 127.23, 125.01, 124.46, 124.14, 120.94, 120.82, 120.67, 62.90, 62.73, 29.71, 28.70, 28.66, 26.53, 25.46. MS (MALDI-TOF, matrix- α-cyano-4-hydroxycinnamic acid): Calculated Exact Mass: 741.995, Found 741.593 (m/z). FT-IR (cm^{-1}): 2919, 2853, 1680, 1580, 1305, 1206. Anal. Calcd for $C_{36}H_{28}Br_2N_2O_2S_2$: C, 58.07; H, 3.79; N, 3.76; Found: C, 57.97; H, 3.83; N, 3.94.

Molecule 12: Yield = 13 %. R_f= 0.48 ($CHCl_3$/n-hexane 6:4), Melting Point: >300°C, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ= 9.41 (d, 1H, *Ar-H*), 9.31 (d, 1H, *Ar-H*), 9.00 (d, 1H, *Ar-H*), 8.80 (s, 2H, *Ar-H*), 8.60 (d, 1H, *Ar-H*), 5.92 (s, 1H, *Ar-H*), 4.95 (s, 1H, *Ar-H*), 2.53-2.44 (m, 4H), 1.83-1.19 (16H), ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 194.45, 163.37, 159.93, 138.02, 135.93, 132.95, 132.83, 132.61, 131.91, 129.95, 129.30, 129.05, 128.67,

128.23, 127.99, 127.01, 125.10, 124.17, 123.69, 120.88, 120.68, 62.72, 54.23, 29.09, 28.65, 26.50, 25.45, 25.39. MS (MALDI-TOF, matrix- α-cyano-4-hydroxycinnamic acid): Calculated Exact Mass: 726.018, Found 726.097 (m/z). FT-IR (cm^{-1}): 2927, 2853, 1655, 1580, 1314, 1214. Anal. Calcd for $C_{36}H_{28}Br_2N_2O_3S$: C, 59.35; H, Br, 21.94; 3.87; N, 3.85; Found:C, 59.15; H, 3.93; N, 3.95.

Molecule 13: Yield = 9 %. R_f=0.46 ($CHCl_3$/n-hexane 6:4), Melting Point: >300°C, ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 9.41 (t, 2H, *Ar-H*), 9.23 (s, 1H, *Ar-H*), 8.80 (s, 1H, *Ar-H*), 8.59 (m, 2H, *Ar-H*), 5.90 (s, 1H, *Ar-H*), 4.95 (s, 1H, *Ar-H*), 2.55-2.46 (m, 4H), 1.86-1.1 (16H), ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 143.64 137.97, 130.10, 130.04, 128.60, 128.42, 54.23,29.09, 28.69, 26.50, 25.45, 25.38. MS (MALDI-TOF, matrix- α-cyano-4-hydroxycinnamic acid): Calculated Exact Mass: 726.018, Found 726.070 (m/z). Anal. Calcd for $C_{36}H_{28}Br_2N_2O_3S$:C, 59.35; H, 3.87; Br, 21.94; N, 3.85; Found: C, 58.93; H, 3.93; N, 3.98.

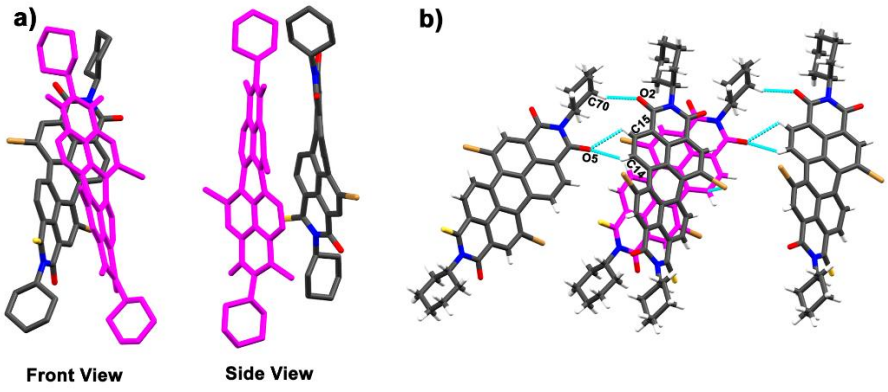


Figure S1: Showing monomeric pair and supramolecular interactions in molecule **12**.

The carbonyl imide (C=O) and thionyl imide (C=S) bond distances in the PDI crystal structure were reported to be 1.220(7)−1.307(8) and 1.621(6), respectively. The annular bond distances for C11−C12 and C47−C48 were determined to be 1.410(8) and 1.429(8) respectively. The molecule was obtained as a monomeric *M*···*M* combination. The enantiomers are linked by infinite supramolecular contacts with the shortest π-π contacts of 3.54 Å and also linked by weak C=O···H-C bonding interactions.

UV-Vis-NIR studies

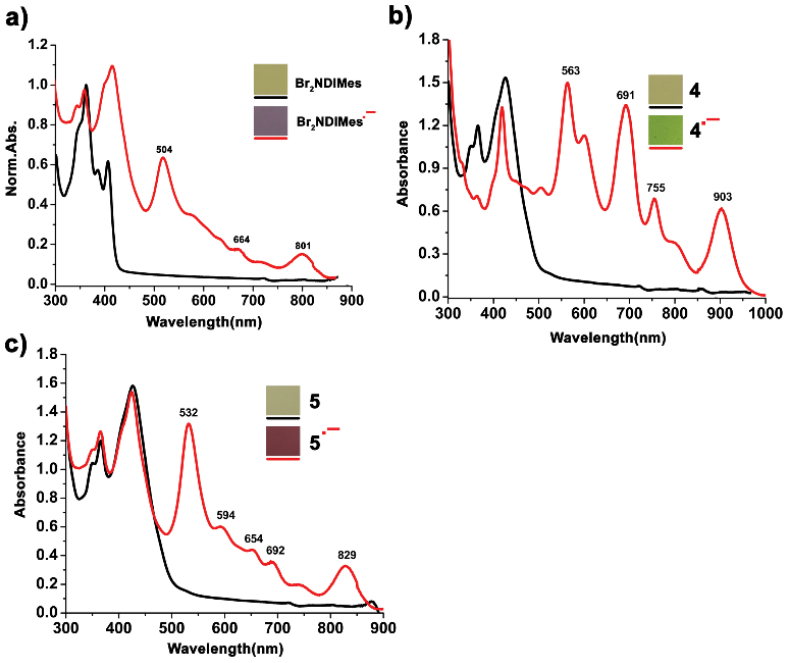


Figure S2: UV−Vis−NIR spectra of Br_2NDIMes, **4**, **5** and their corresponding radical anion peaks on addition of cobaltocene in degassed DCM.

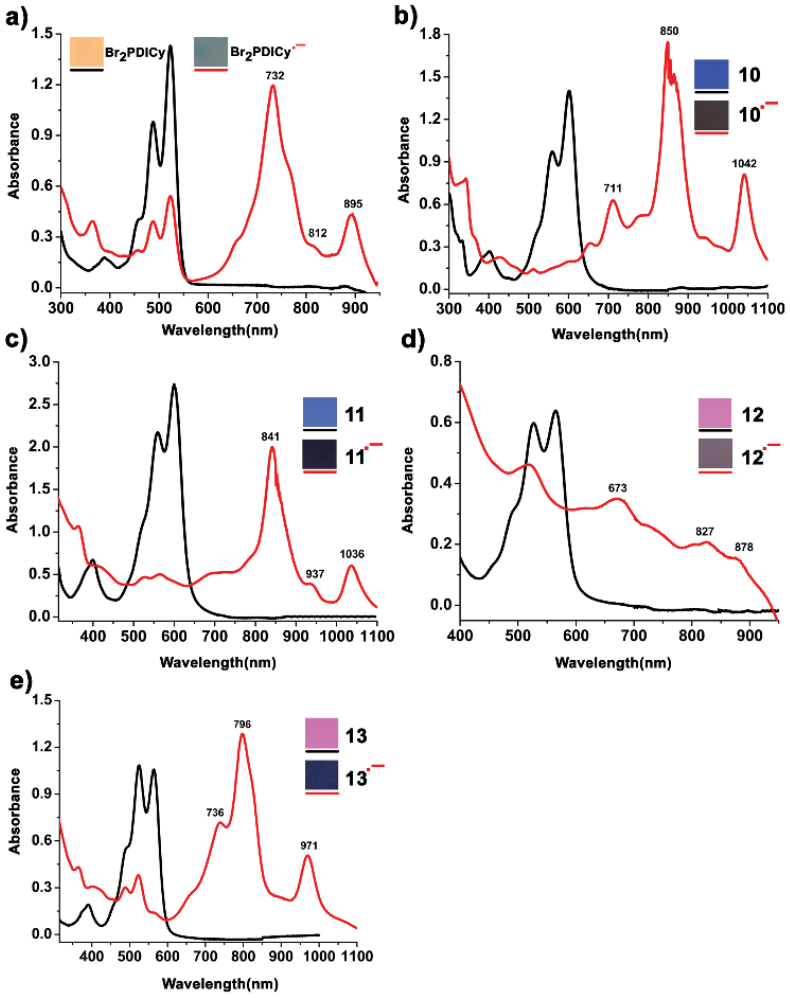


Figure S3: UV−Vis−NIR spectra of Br_2PDICy, **10, 11, 12, 13** and their corresponding radical anion peak on addition of cobaltocene in degassed DCM.

Theoretical Studies

To investigate the frontier molecular orbitals, DFT calculation was performed at B3LYP/6311++G(d,p)/CPCM/DCM in Gaussian 09 by altering the axially-substituted long alkyl/mesityl groups by the methyl groups to save computational time. Next, we performed electrostatic potential (ESP) calculation for all the molecules and their respective radical anion. ESP plots clearly demonstrate that the neutral molecules have electron deficient central region (blue) and the radical anions have an electron rich region (orange).

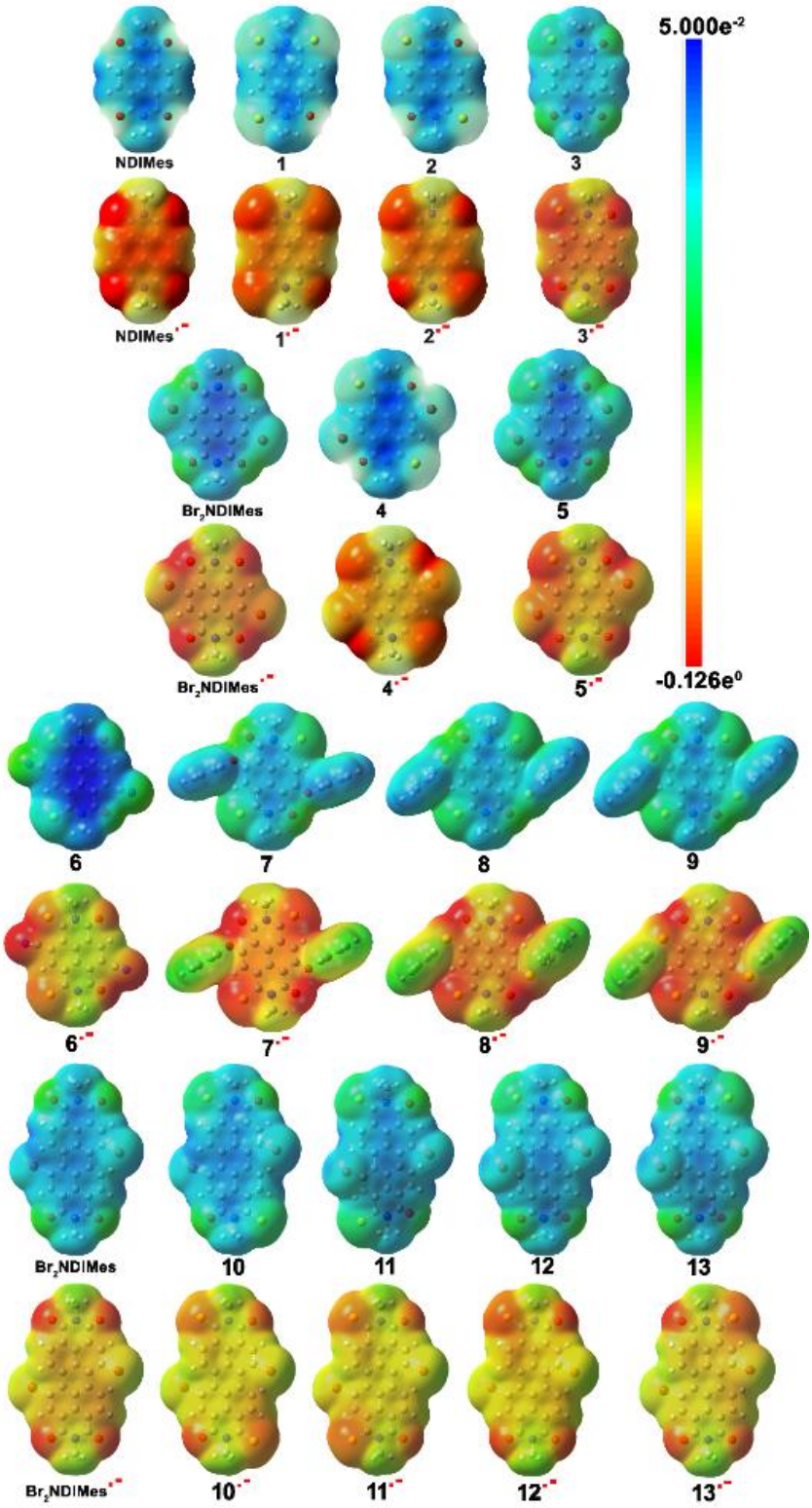


Figure S4: ESP diagrams of all molecules in the neutral and radical states.

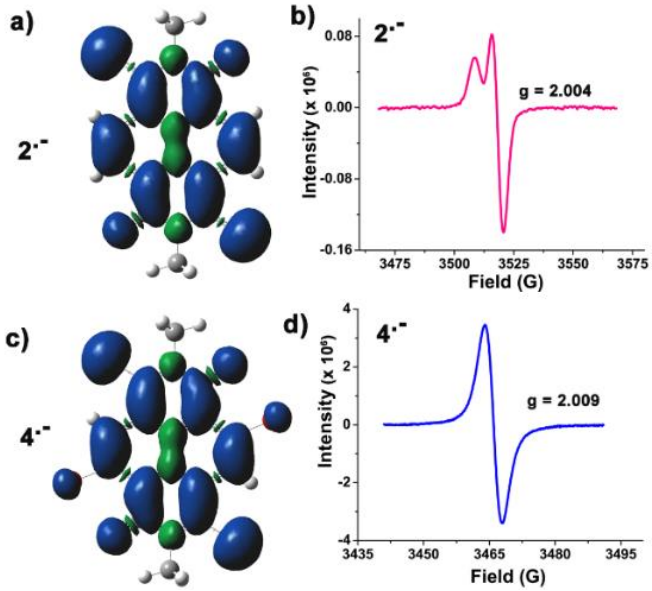


Figure S5. Spin density distribution (DFT/B3LYP/6−311++G (d,p)/CPCM/DCM) and EPR spectra of $\mathbf{2}^{\bullet-}$ and $\mathbf{4}^{\bullet-}$.

NMR studies

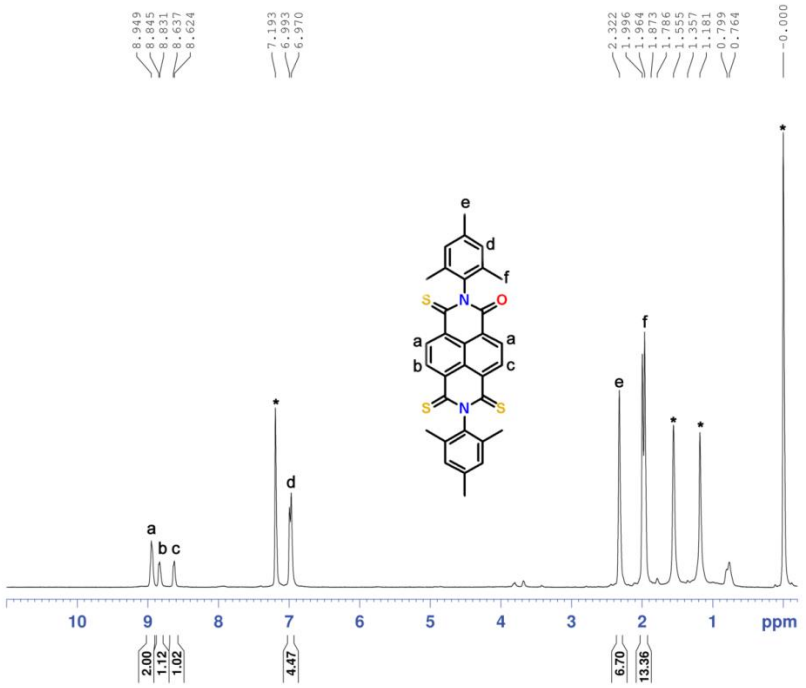


Figure S6: 500 MHz ^{1}H NMR spectrum of **1** in $CDCl_3$ at RT.

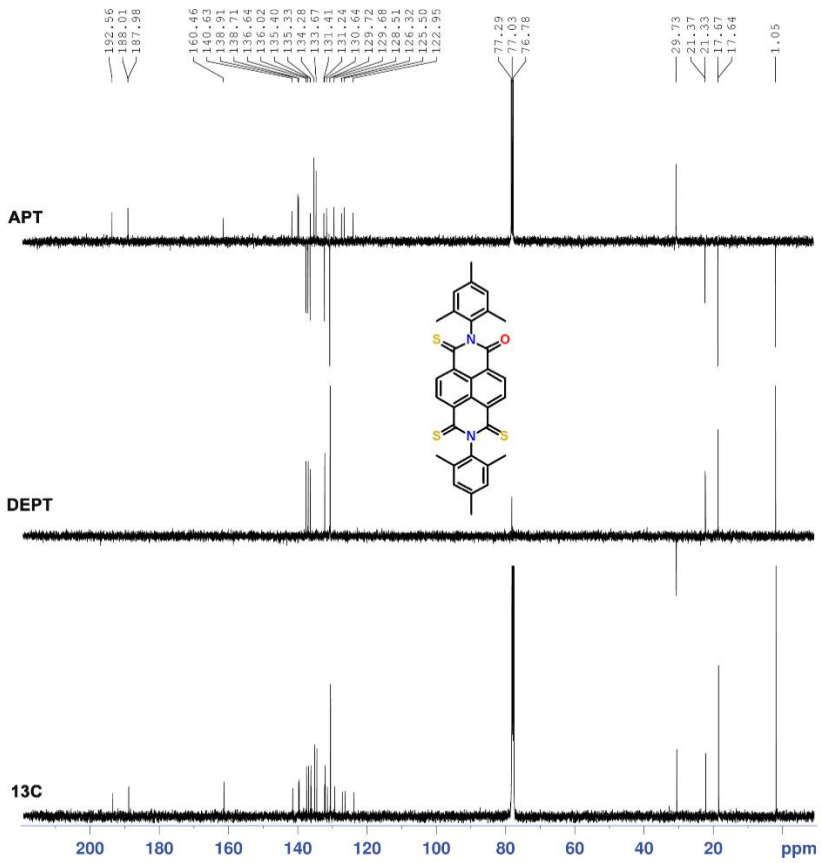


Figure S7: 125 MHz ^{13}C NMR, APT, DEPT-135 spectra of **1** in $CDCl_3$ at RT.

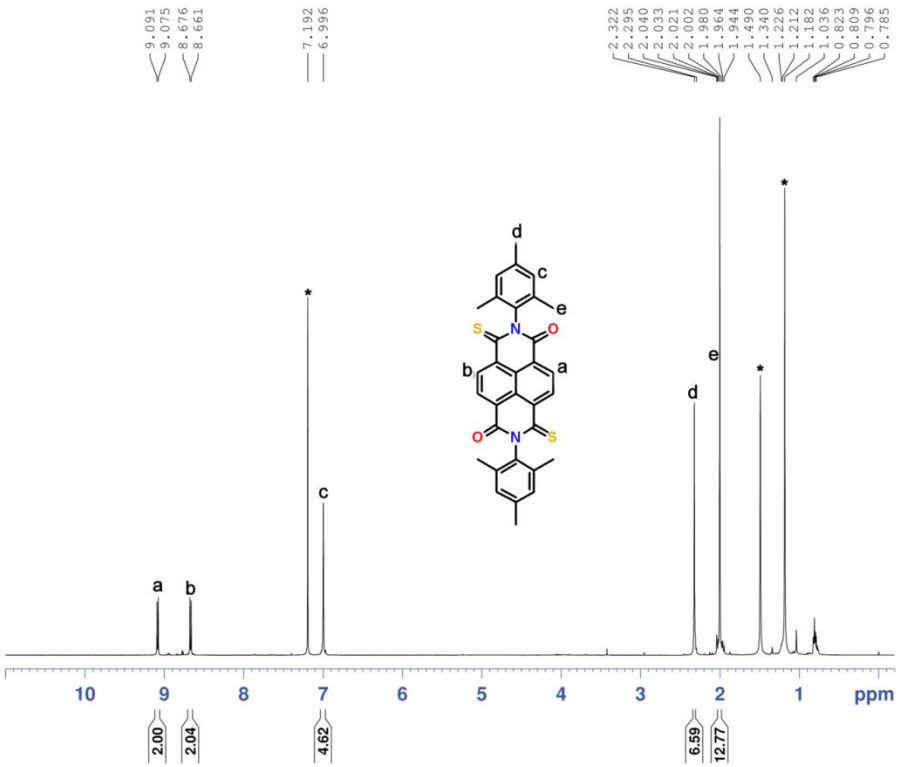


Figure S8: 500 MHz ^{1}H NMR spectrum of **2** in $CDCl_3$ at RT.

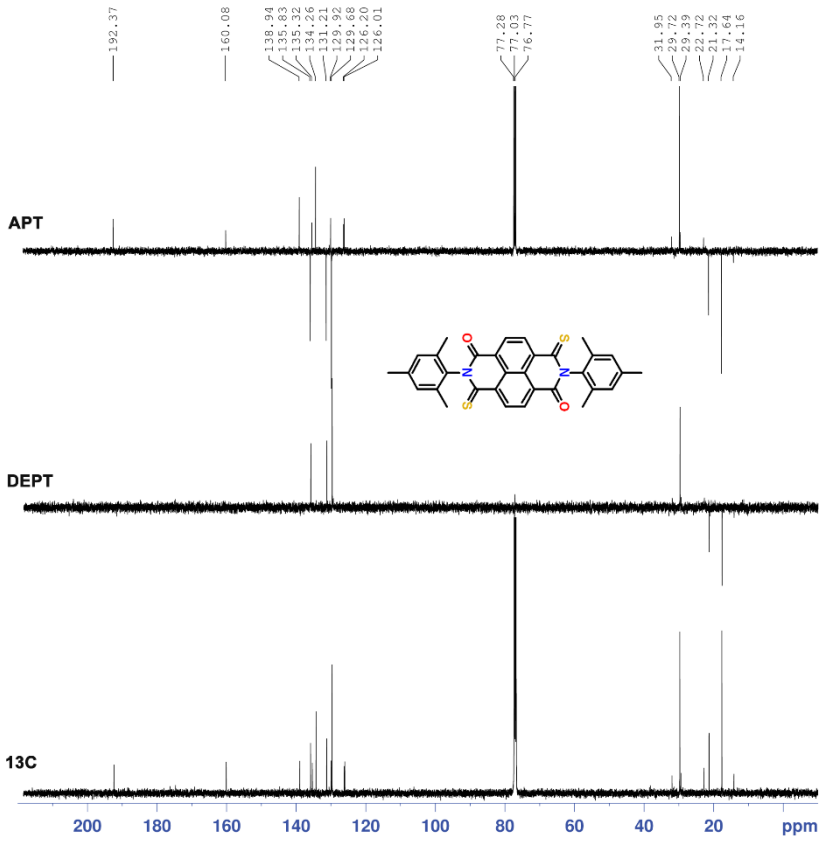


Figure S9: 125 MHz ^{13}C NMR, APT, DEPT-135 spectra of **2** in $CDCl_3$ at RT

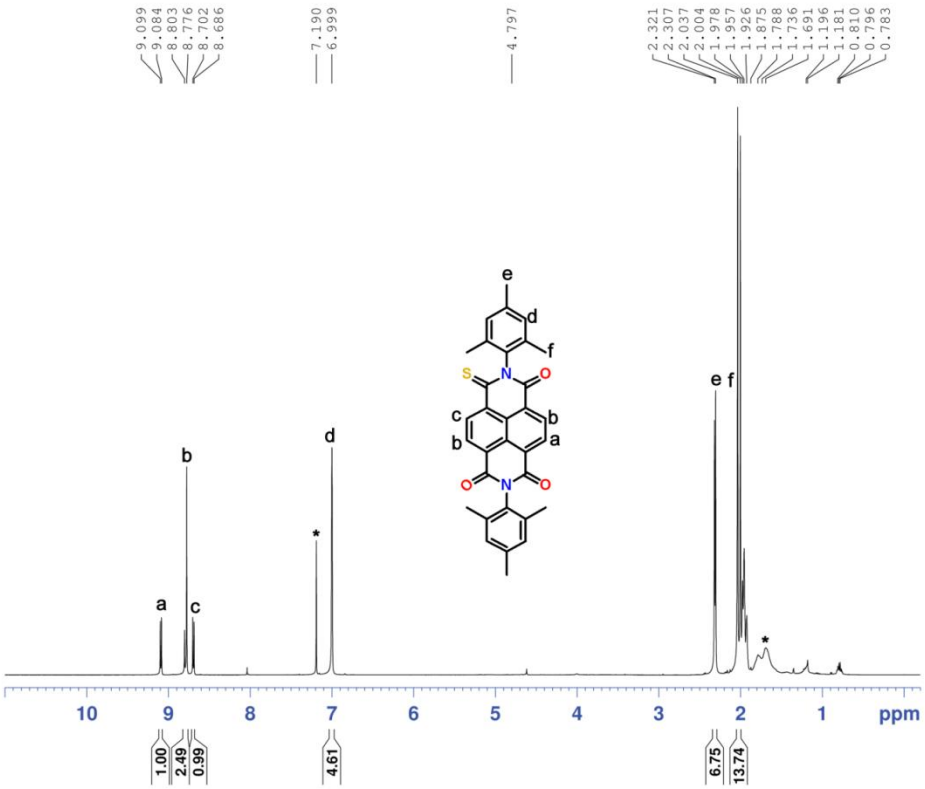


Figure S10: 500 MHz ^{1}H NMR spectrum of **3** in $CDCl_3$ at RT.

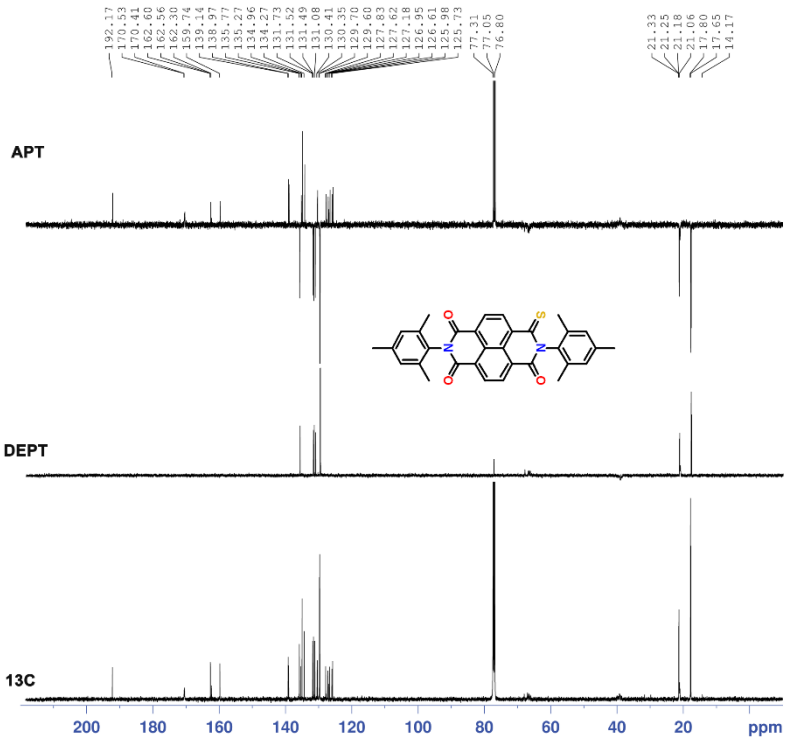


Figure S11: 125 MHz ^{13}C NMR, APT, DEPT-135 spectra of **3** in $CDCl_3$ at RT

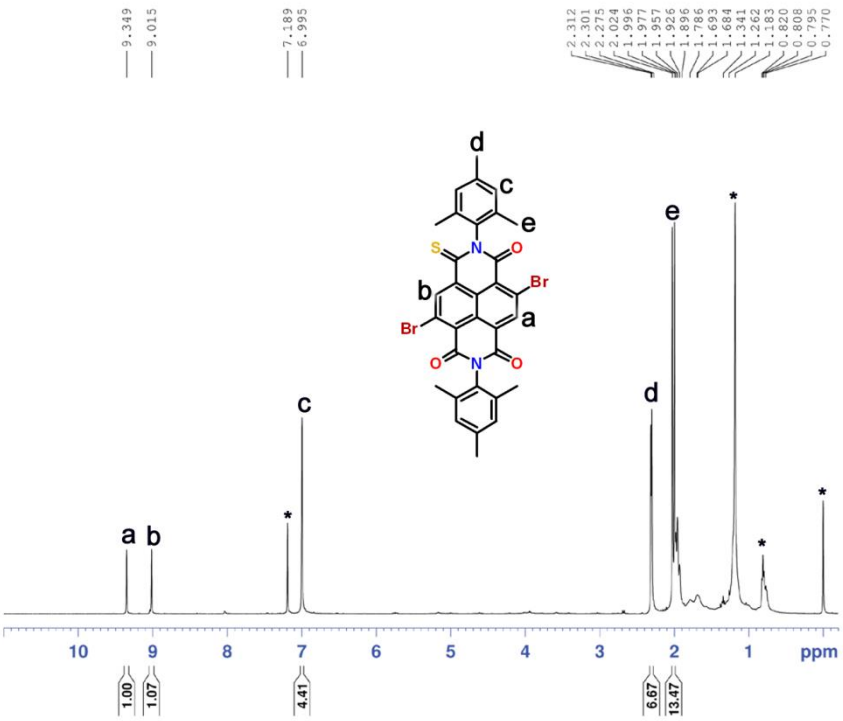


Figure S12: 500 MHz ^{1}H NMR spectrum of **5** in $CDCl_3$ at RT.

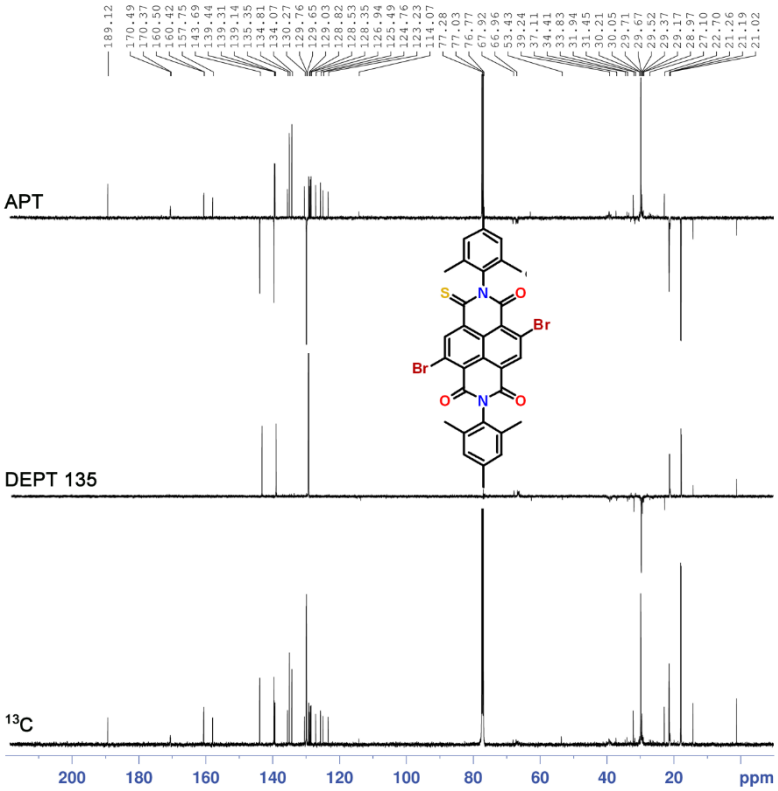


Figure S13: 125 MHz ^{13}C NMR, APT, DEPT-135 spectra of **5** in $CDCl_3$ at RT

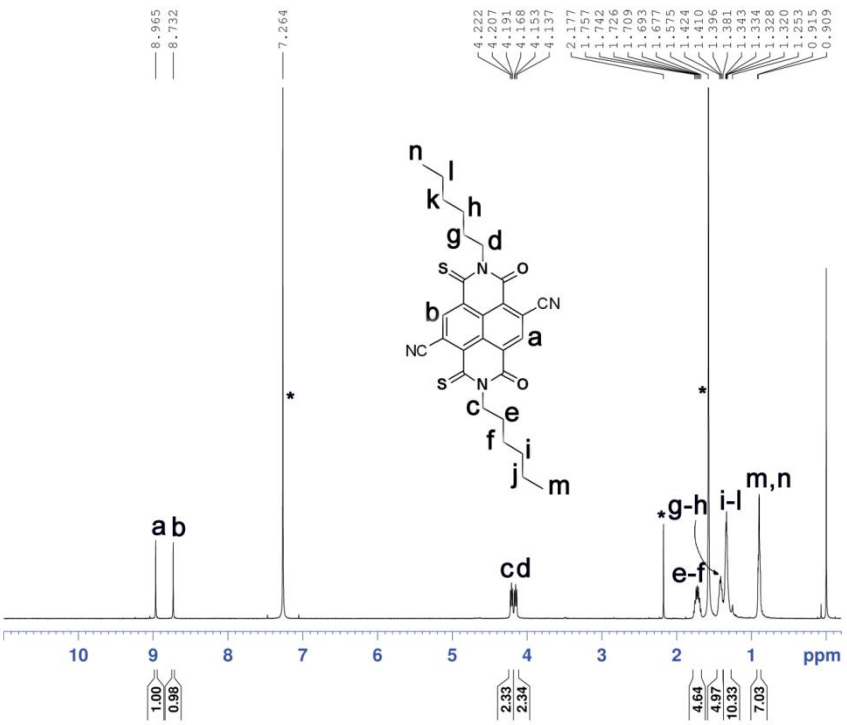


Figure S14: 500 MHz ^{1}H NMR spectrum of **6** in $CDCl_3$ at RT.

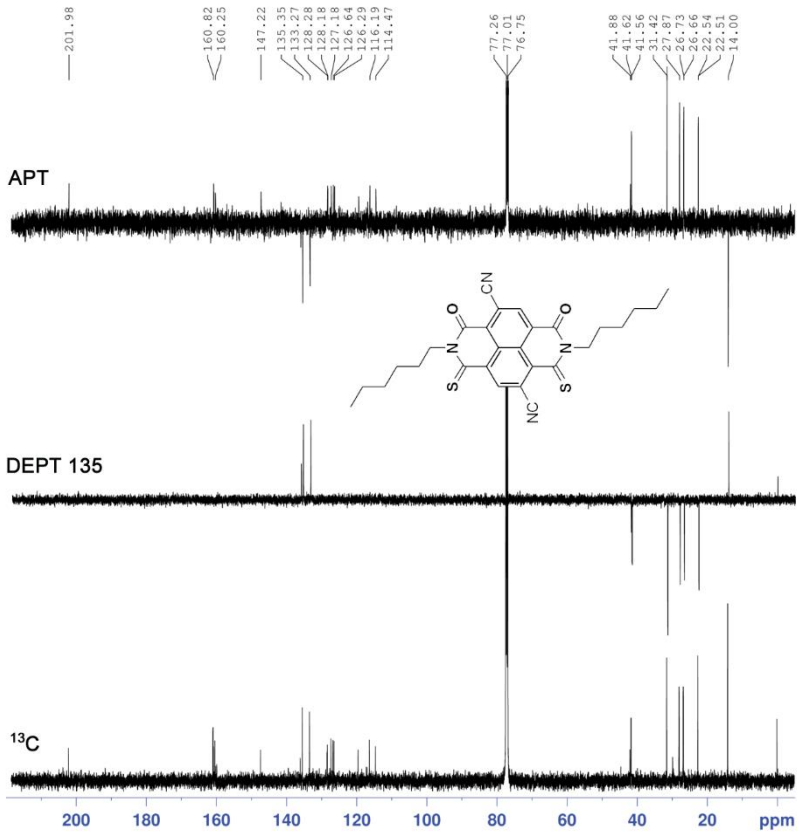


Figure S15: 125 MHz ^{13}C NMR, APT, DEPT-135 spectra of **6** in $CDCl_3$ at RT

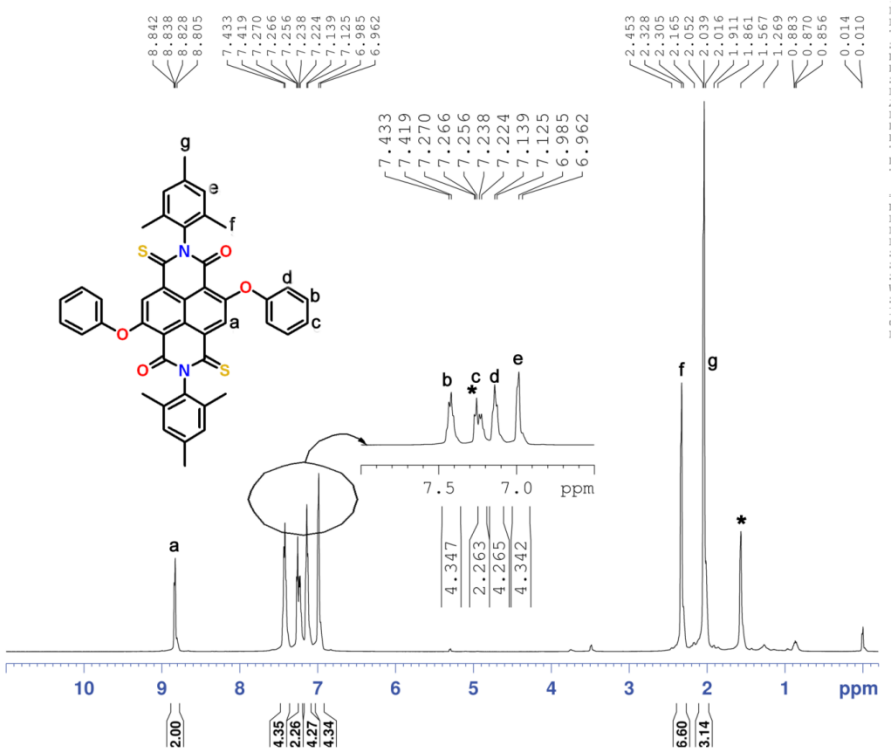


Figure S16: 500 MHz ^{1}H NMR spectrum of **7** in $CDCl_3$ at RT.

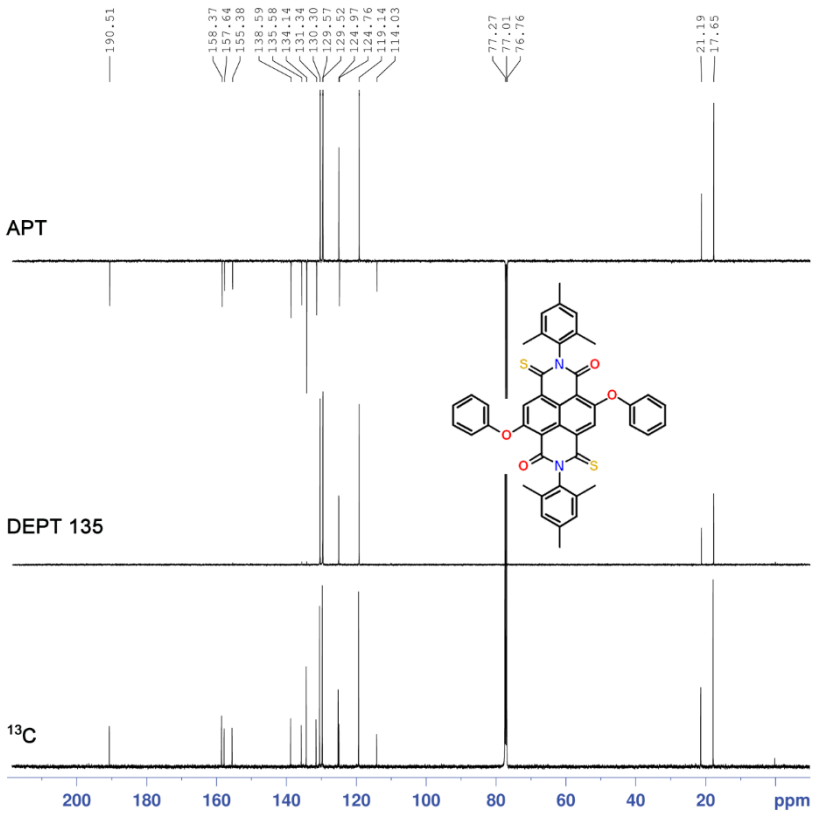


Figure S17: 125 MHz ^{13}C NMR, APT, DEPT-135 spectra of **7** in $CDCl_3$ at RT

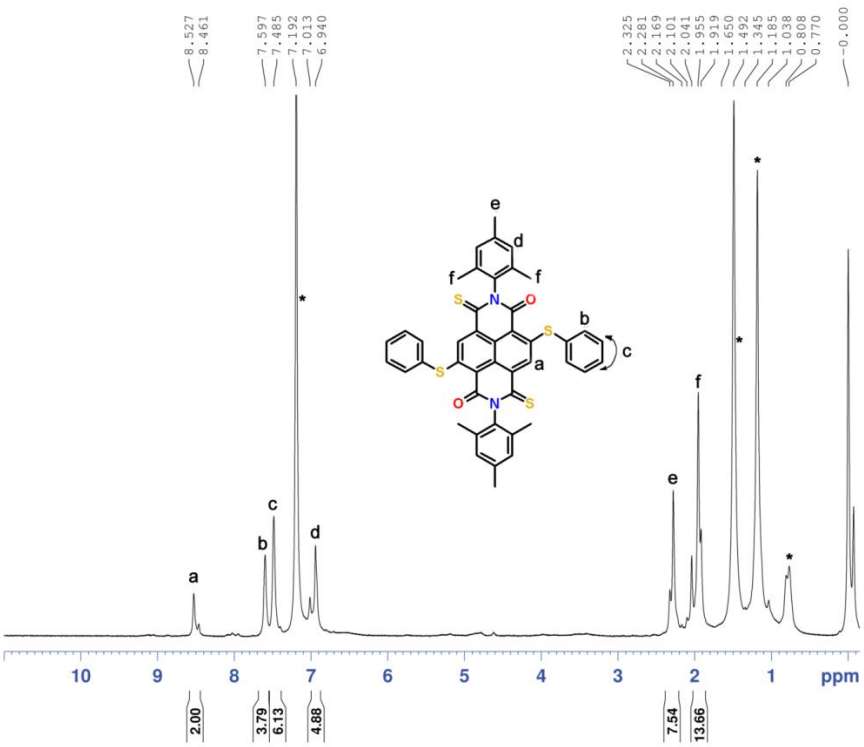


Figure S18: 500 MHz ^{1}H NMR spectrum of **8** in $CDCl_3$ at RT.

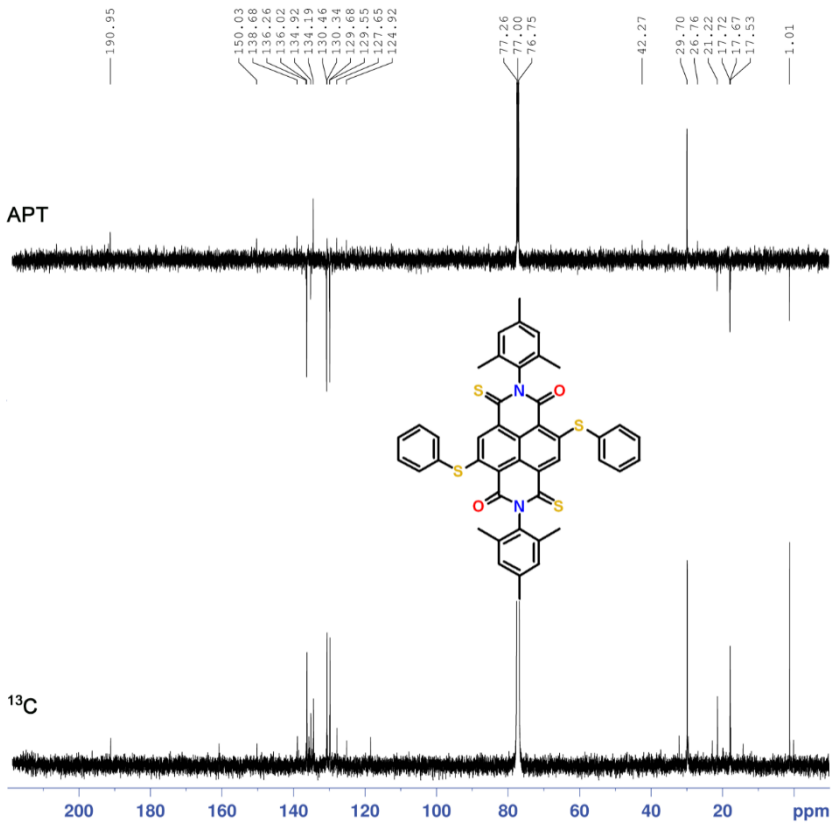


Figure S19: 125 MHz ^{13}C NMR, APT, DEPT-135 spectra of **8** in $CDCl_3$ at RT

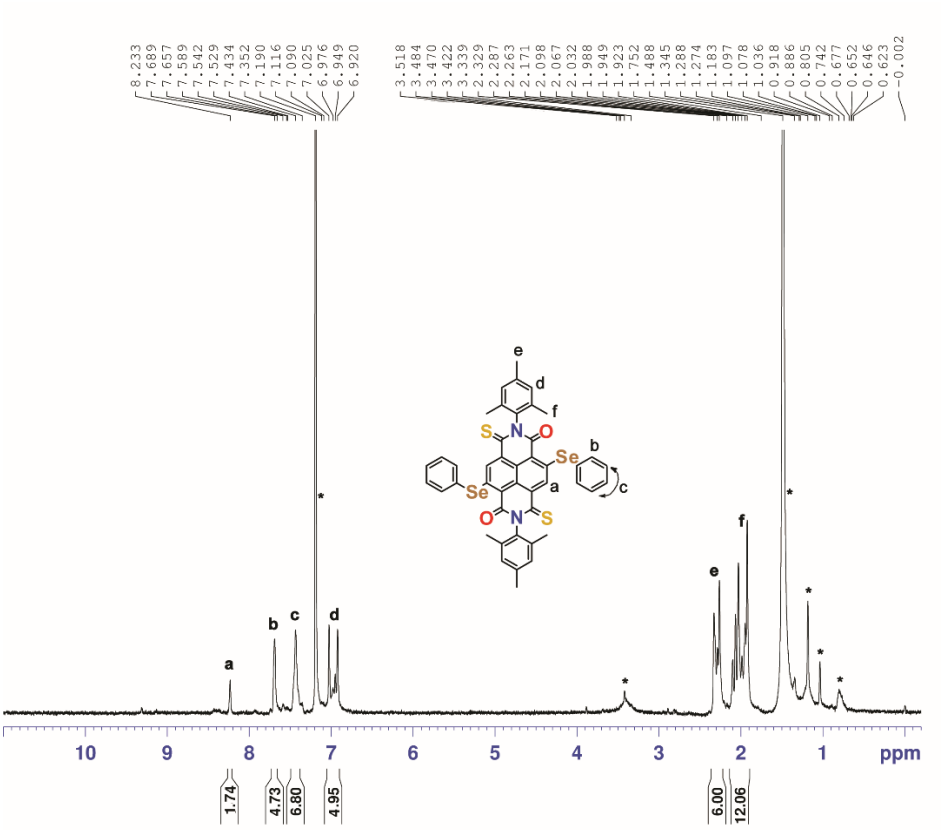


Figure S20: 500 MHz ^{1}H NMR spectrum of **9** in $CDCl_3$ at RT.

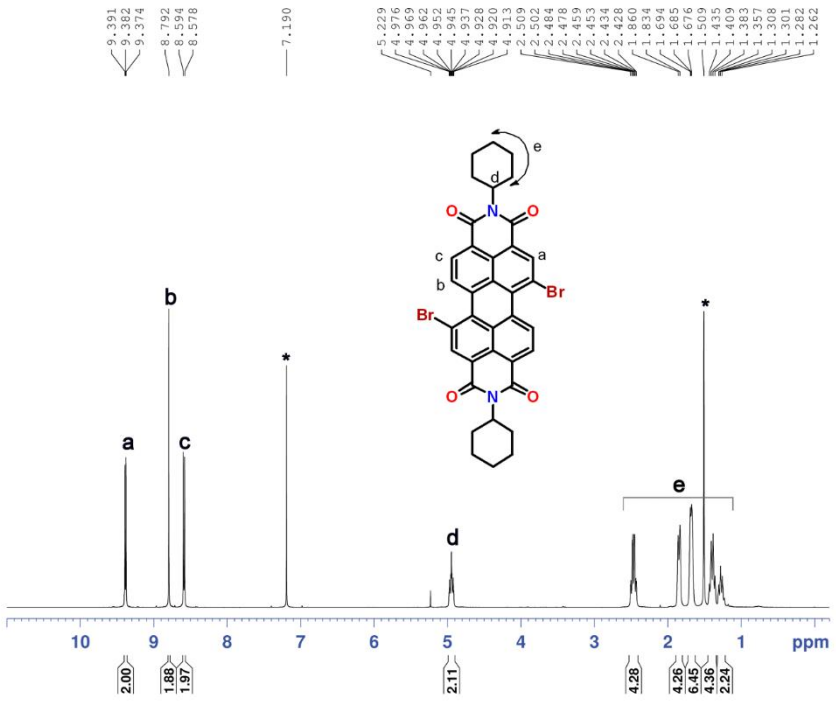


Figure S21: 500 MHz ^{1}H NMR spectrum of **Br_2PDICy** in $CDCl_3$ at RT.

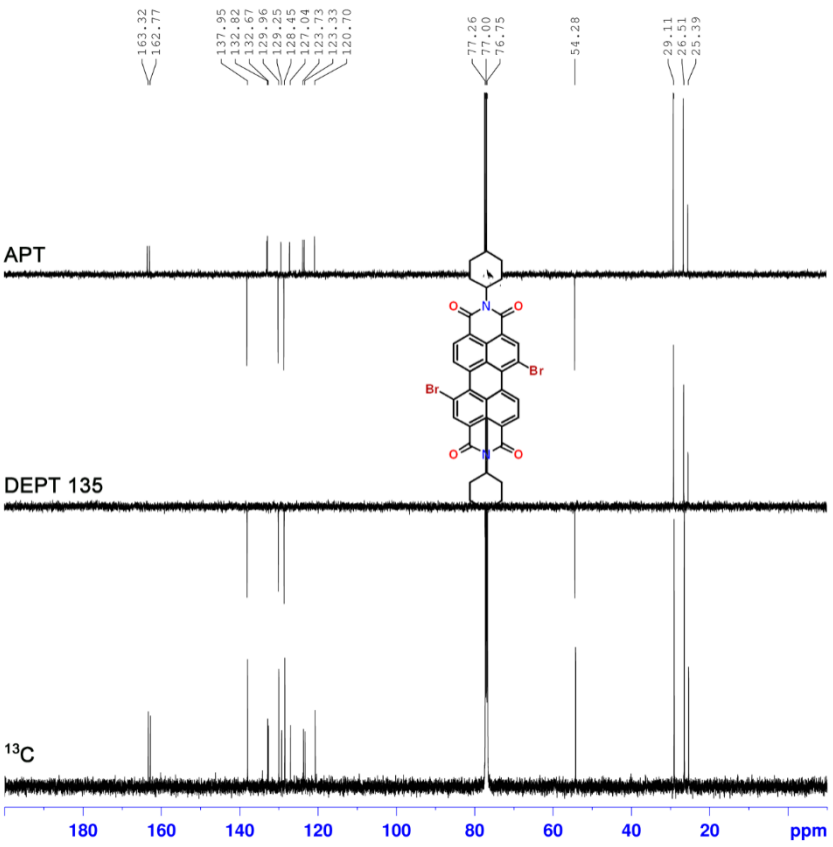


Figure S22: 125 MHz ^{13}C NMR, APT, DEPT-135 spectra of **Br_2PDICy** in $CDCl_3$ at RT

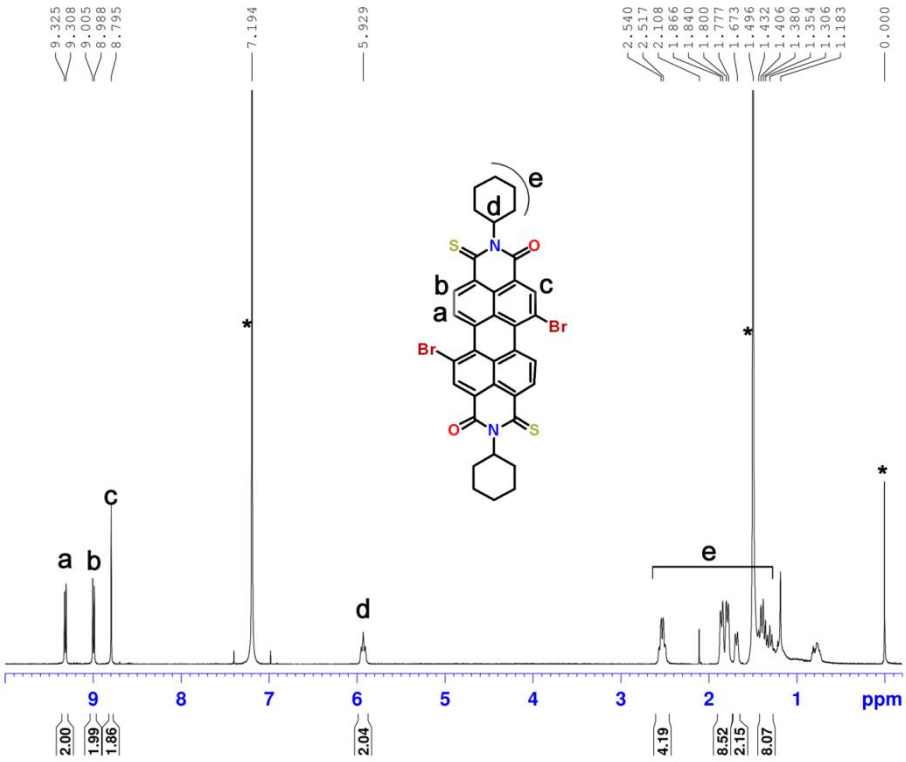


Figure S23: 500 MHz ^{1}H NMR spectrum of **10** in $CDCl_3$ at RT

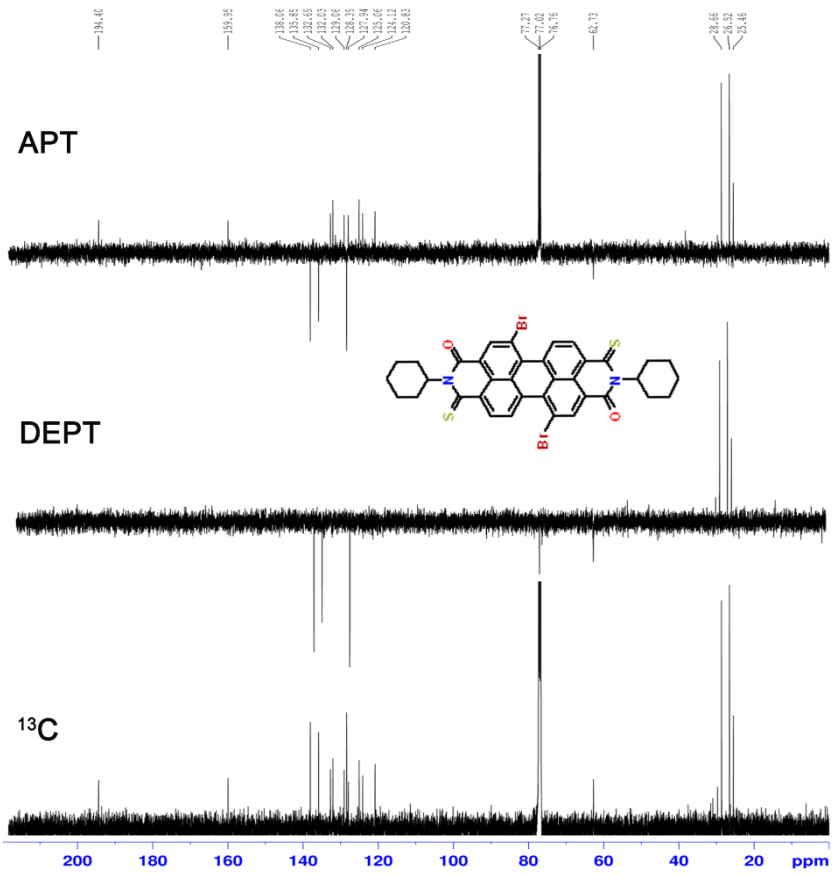


Figure S24: 125 MHz ^{13}C NMR, APT, DEPT-135 spectra of **10** in $CDCl_3$ at RT

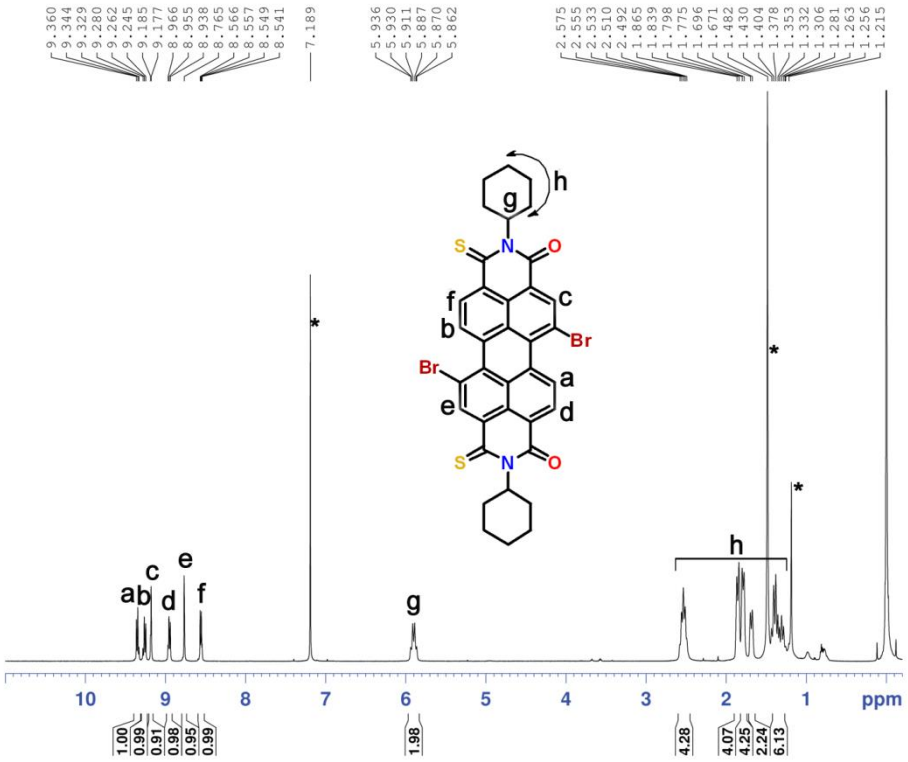


Figure S25: 500 MHz ^{1}H NMR spectrum of **11** in $CDCl_3$ at RT

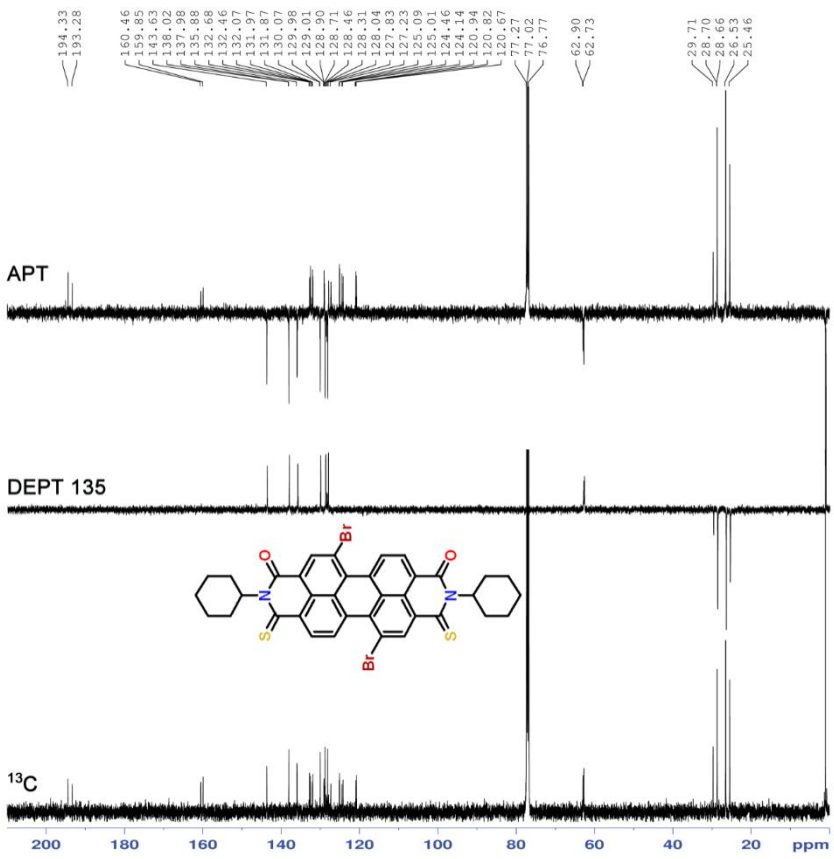


Figure S26: 125 MHz ^{13}C NMR, APT, DEPT-135 spectra of **11** in $CDCl_3$ at RT

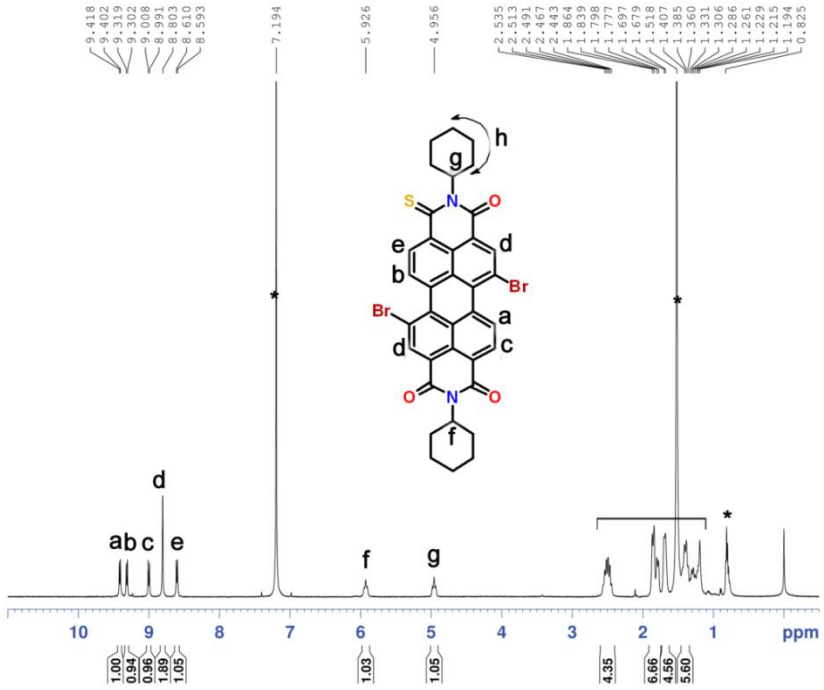


Figure S27: 500 MHz ^{1}H NMR spectrum of **12** in $CDCl_3$ at RT.

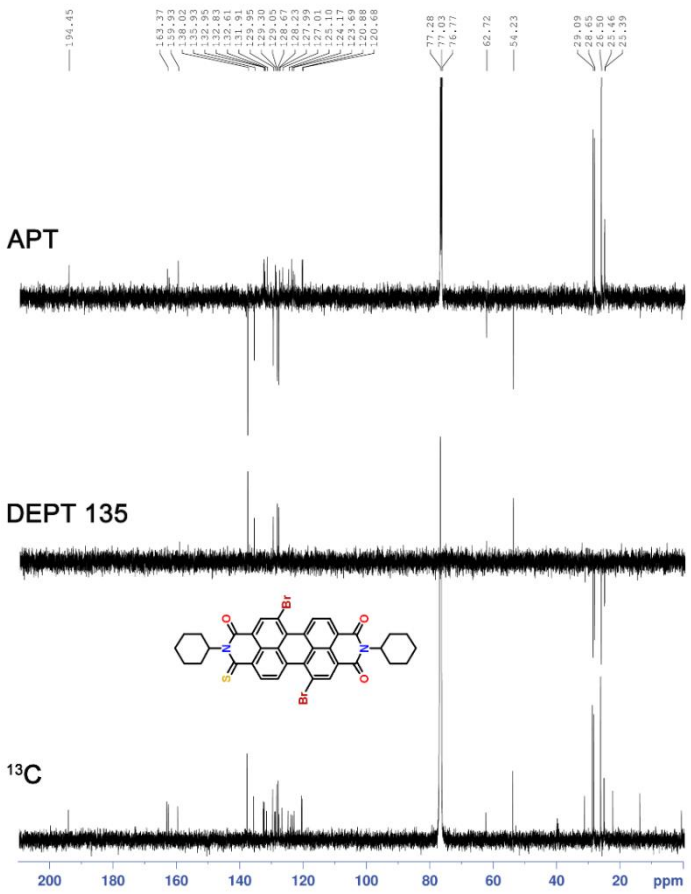


Figure S28: 125 MHz ^{13}C NMR, APT, DEPT-135 spectra of **12** in $CDCl_3$ at RT.

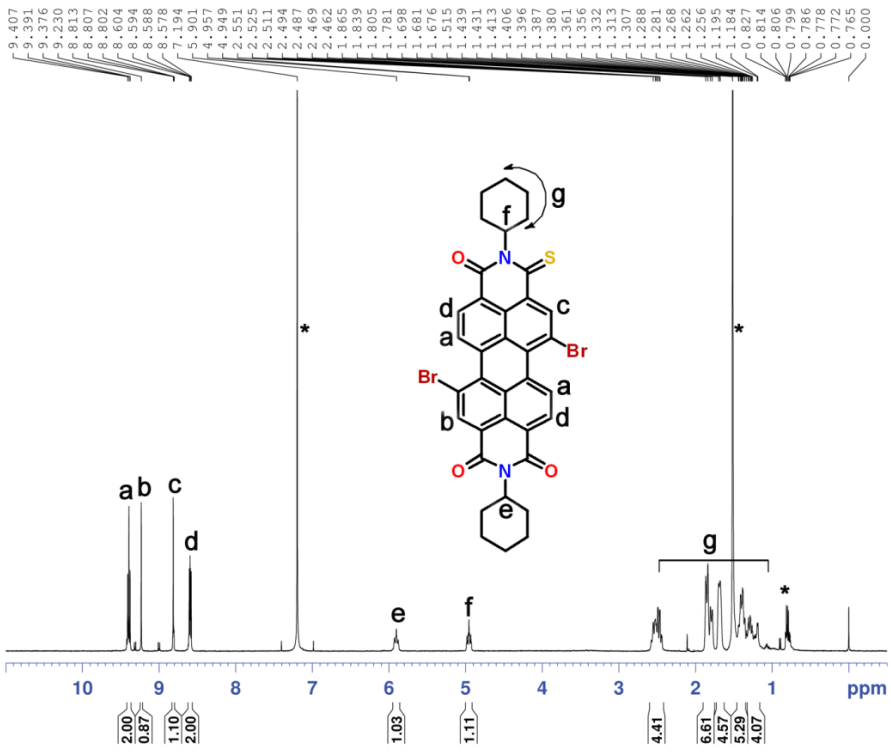


Figure S29: 500 MHz ^{1}H NMR spectrum of **13** in $CDCl_3$ at RT

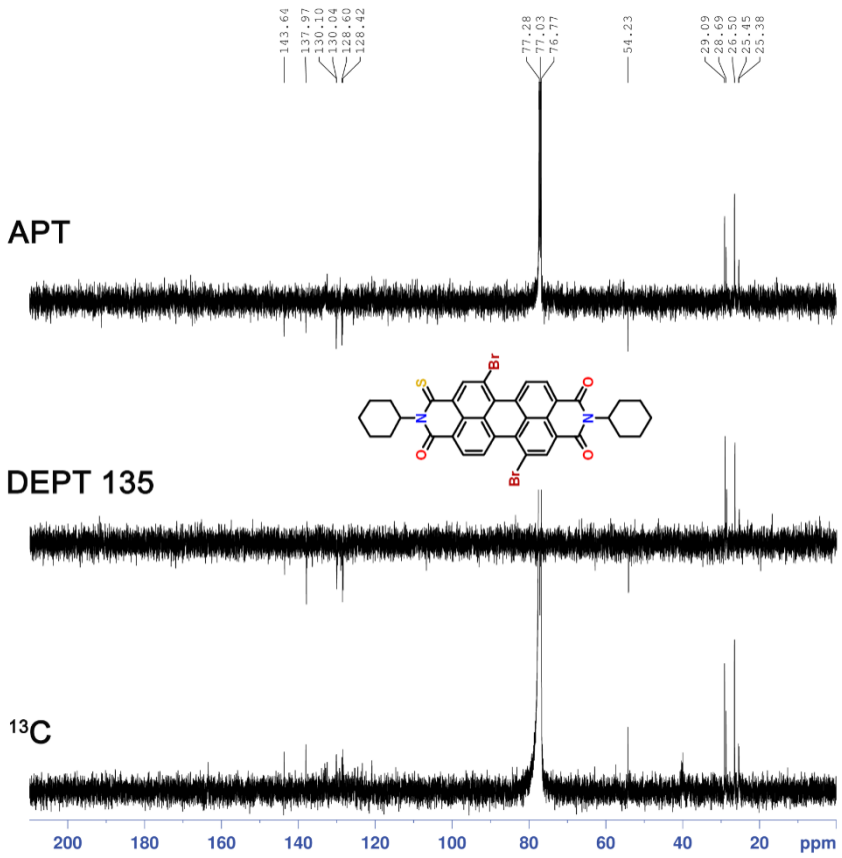


Figure S30: 125 MHz ^{13}C NMR, APT, DEPT-135 spectra of **13** in $CDCl_3$ at RT.

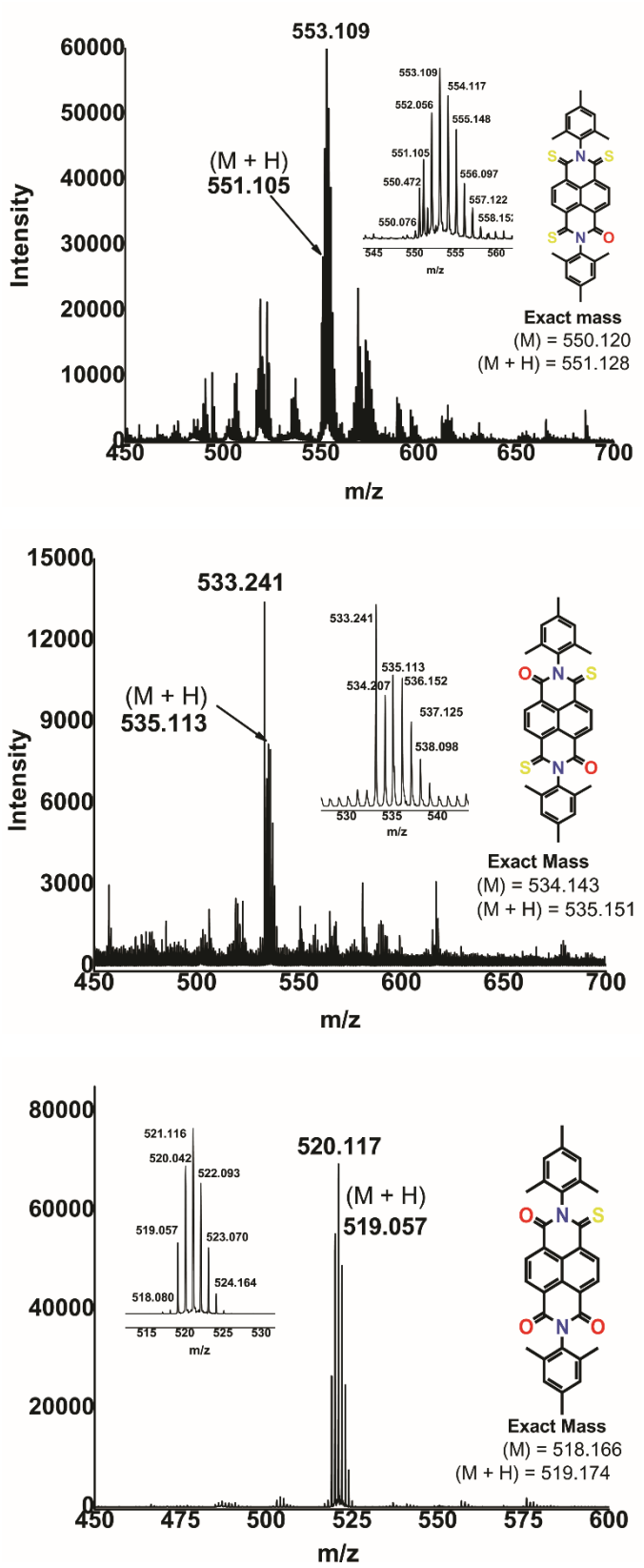


Figure S31: Mass Spectrometry of **1, 2** and **3**.

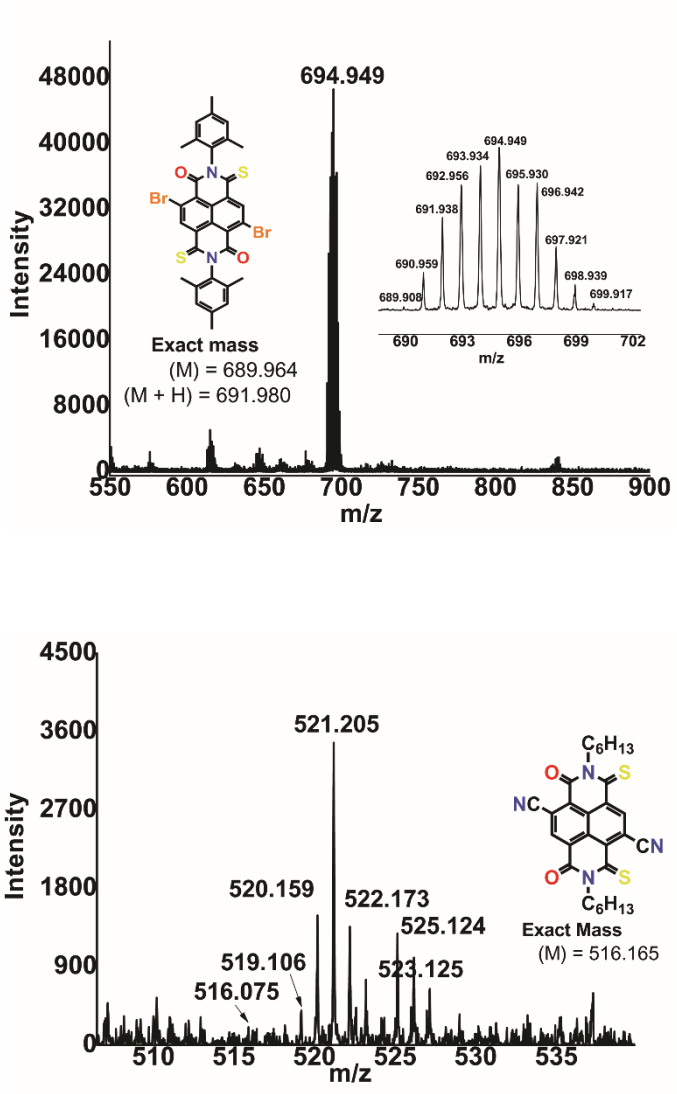
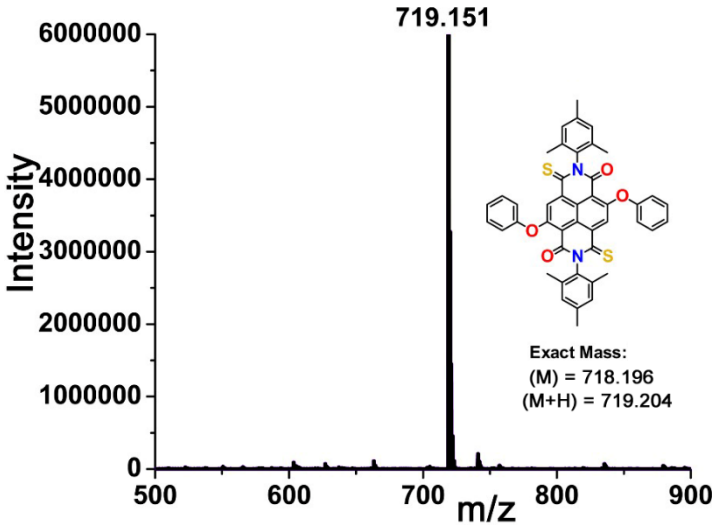


Figure S32: Mass Spectrometry of **5** and **6**.



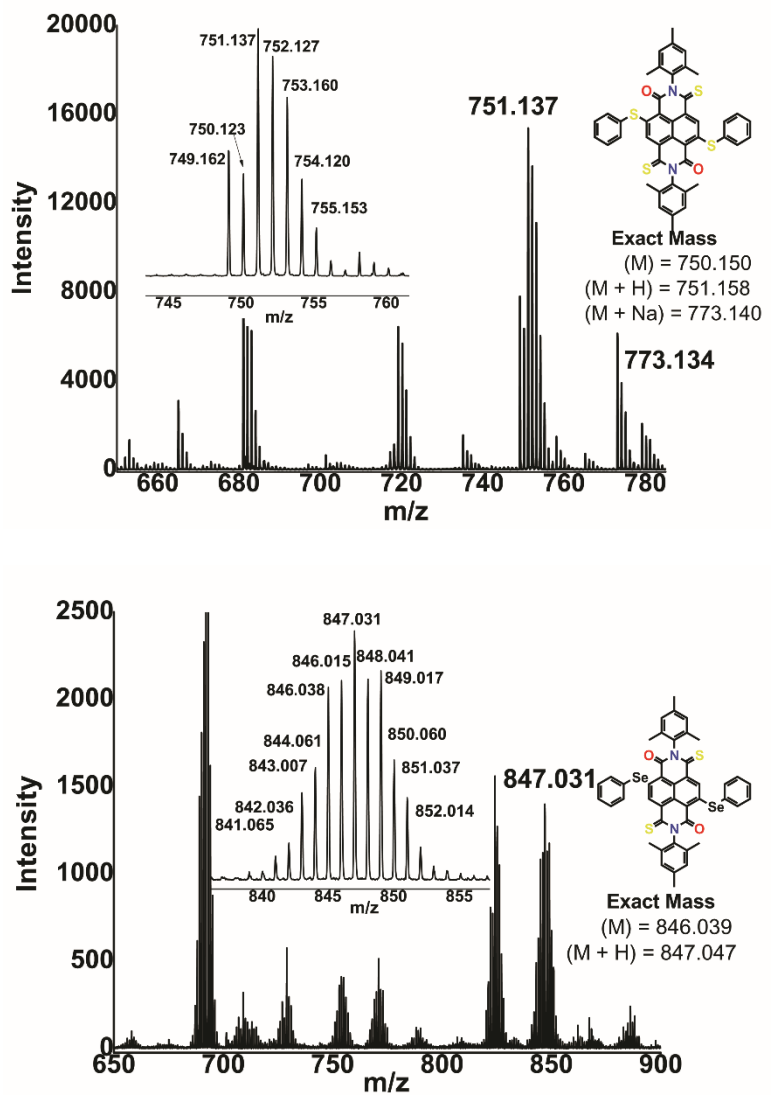
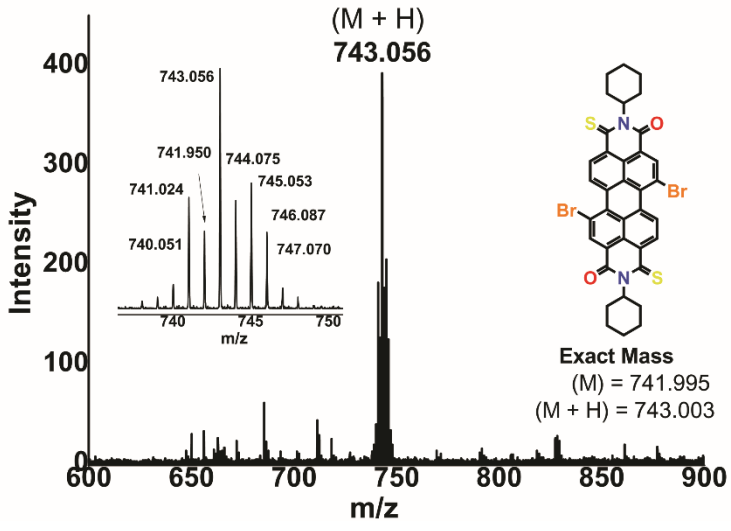


Figure S33: Mass Spectrometry of **7**, **8** and **9**.



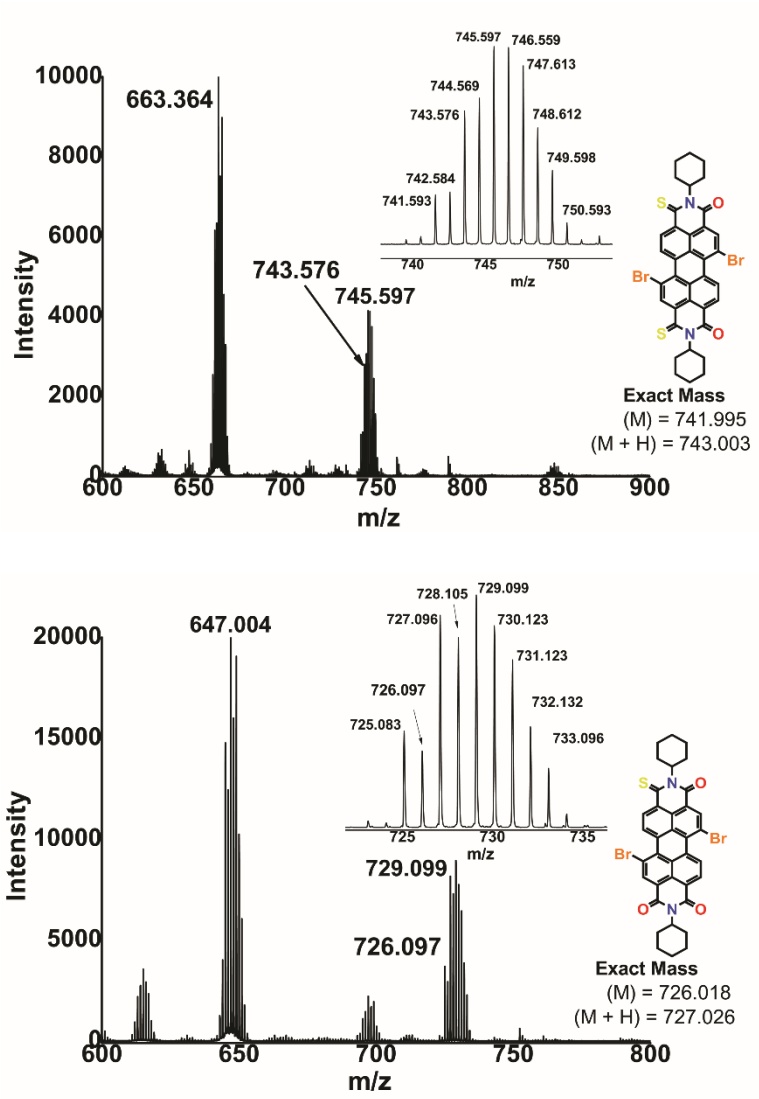


Figure S34: Mass Spectrometry of **10, 11**and **12**.

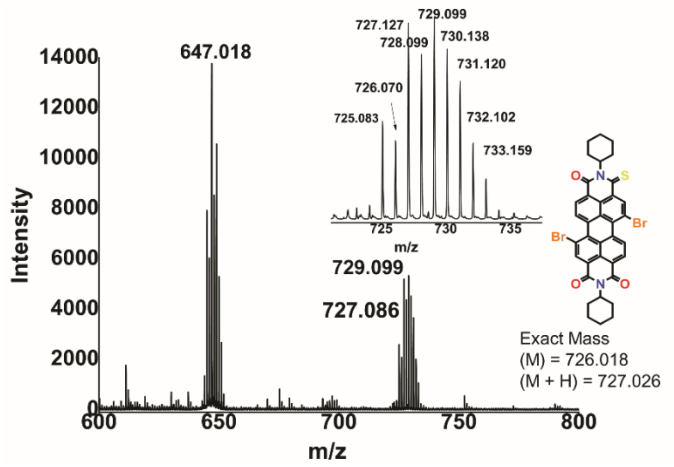


Figure 35: Mass Spectrometry of **13**.

IR Spectroscopy

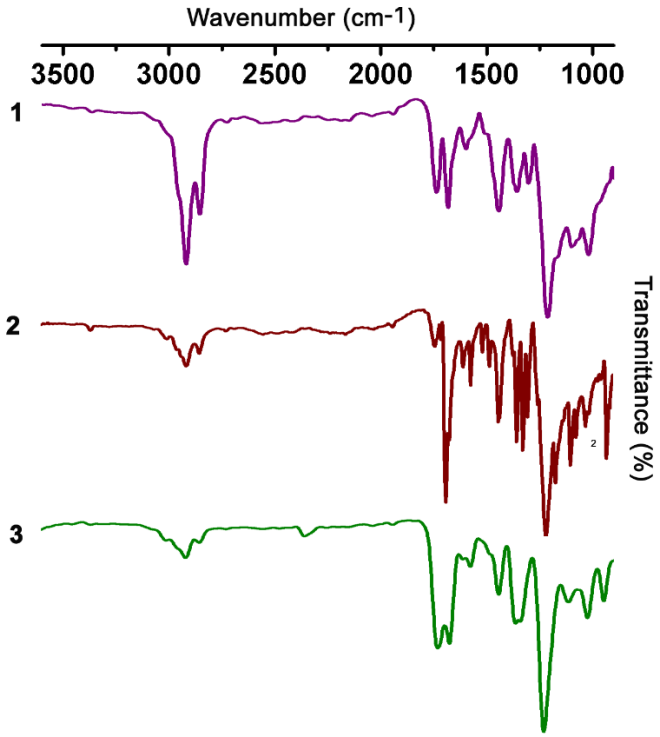


Figure S36: FT-IR spectra of class I molecules, **1**, **2**, and **3**.

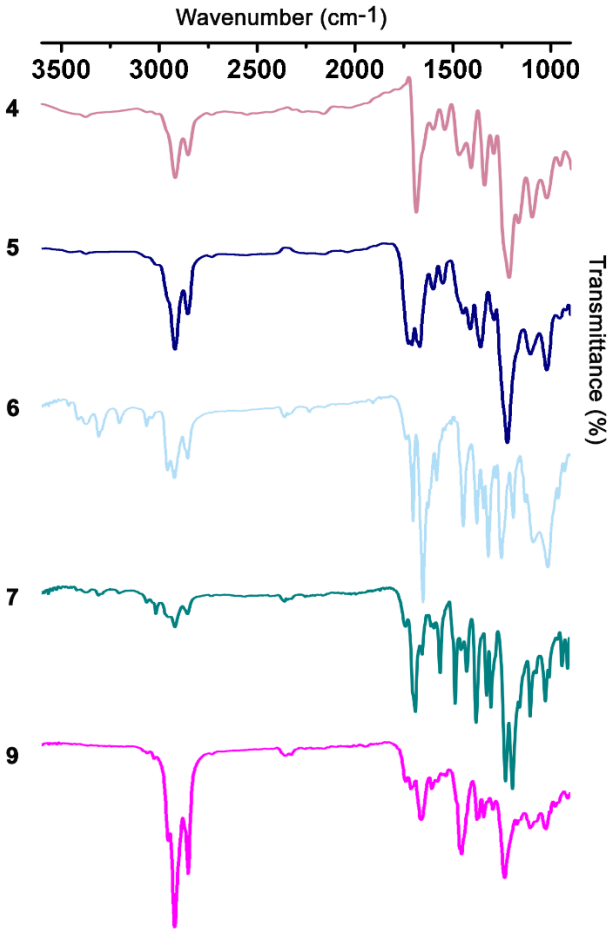


Figure S37: FT-IR spectra of **4**, **5**, **6**, **7** and **9**.

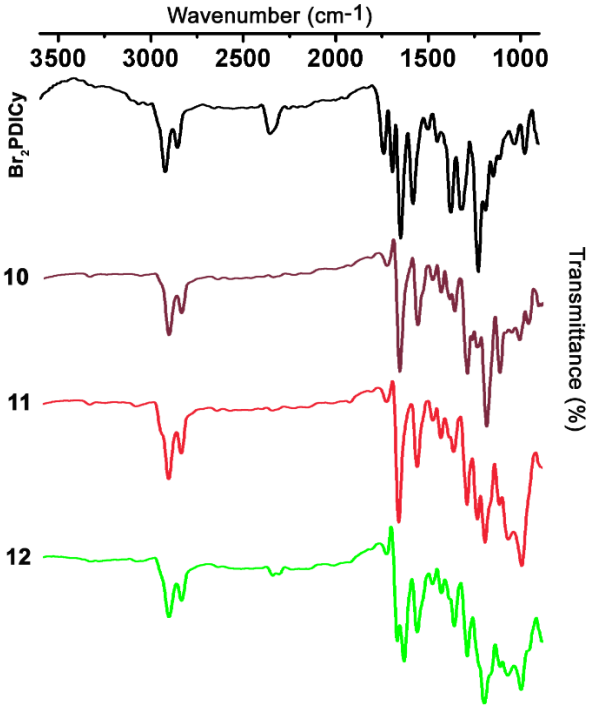


Figure S38: FT-IR spectra of class IV molecules, **Br$_2$PDICy**, **10**, **11**, **12** and **13**.

TableS1: Crystallographic information of molecule **12**.

Empirical formula	$C_{36}H_{28}N_2O_3SBr_2$
Formula weight	728.46
Temperature/K	276.46
Crystal system	triclinic
Space group	P-1
a/Å	11.6632(7)
b/Å	14.6944(8)
c/Å	18.9643(12)
α/°	91.705(3)
β/°	93.702(3)
γ/°	107.315(3)
Volume/Å^3	3092.3(3)
Z	4
ρ_{calc}g/cm^3	3.329
μ/mm^{-1}	13.707
F(000)	2920.0
Crystal size/mm^3	0.8 × 0.6 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.31 to 57.328
Reflections collected	153053
Independent reflections	15537 [R_{int} = 0.2611, R_{sigma} = 0.2107]
Data/restraints/parameters	15537/0/794
Goodness-of-fit on F^2	1.000
Final R indexes [I>=2σ (I)]	R_1 = 0.0892, wR_2 = 0.1308
Final R indexes [all data]	R_1 = 0.2462, wR_2 = 0.1720
CCDC No.	***2245050***

Table S2: Redox potentials (V *vs* Ag/AgCl), CV and DPV reported in DCM, [a]Calculated from the reduction potential: $E_{LUMO} = -(4.8 + E^1_{red})$. [b]Calculated from theoretical calculation.

Molecule	**$E^1_{1/2}$ (V)**	**$E^2_{1/2}$ (V)**	**ΔE^a (V)**	**LUMO[a] (eV)**	**LUMO[b] (eV)**	**HOMO[b] (eV)**
NDIMes	-0.346	-0.819	0.473	-4.454	-3.671	-7.231
1	+0.084	-0.239	0.323	-4.884	-4.171	-6.456
2	-0.051	-0.408	0.357	-4.749	-4.007	-6.599
3	-0.181	-0.602	0.421	-4.618	-3.955	-6.645
Br_2NDIMes	-0.257	-0.693	0.436	-4.143	-3.813	-7.258
4	-0.019	-0.368	0.349	-4.381	-4.106	-6.661
5	-0.099	-0.505	0.406	-4.301	-3.976	-6.681

6	-0.103	-0.536	0.433	-4.297	-4.486	-6.798
7	-0.049	-0.365	0.316	-4.750	-3.849	-6.499
8	-0.143	-0.468	0.325	-4.656	-3.866	-6.328
9	-0.081	-0.412	0.331	-4.719	-3.879	-6.197
Br_2PDICy	-0.288	-0.469	0.181	-4.512	-3.807	-6.294
10	-0.097	-0.207	0.110	-4.703	-4.036	-6.185
11	-0.094	-0.198	0.104	-4.705	-4.053	-6.219
12	-0.192	-0.354	0.162	-4.608	-3.949	-6.265
13	-0.173	-0.333	0.160	-4.627	-3.951	-6.271

Reference:

1. K. Mandal, D. Bansal, Y. Kumar, Rustam, J. Shukla and P. Mukhopadhyay, *Chem. Eur. J*. 2020, **26**, 10607-10619.