Electronic Supplementary Material (ESI) for ChemComm.
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Electronic Supporting Information (ESI)

Synthesis of Highly-soluble Push-pull Perylenemonoimide Derivatives by Regioselective Peri-functionalization for Switchable Memory Application

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Experimental section:

(A) General procedure

Unless otherwise mentioned, reactions were performed in oven-dried glassware under a nitrogen atmosphere and stirred with Teflon-coated magnetic stirring bars. Tetrahydrofuran was distilled over sodium/benzophenone ketyl. All other solvents and reagents were used as received unless otherwise stated. Reaction temperatures above room temperature (25 °C) refer to oil bath temperature. Thin layer chromatography was performed using Merck Silica gel 60 F-254 pre-coated plates and visualized using UV irradiation (λ = 254/365 nm). Silica gel from Merck (particle size 100-200 mesh) was used for column chromatography. If not otherwise noted, the material was dissolved in a minimum quantity of CH_2Cl_2 and the solution obtained poured on top of the silica gel column. The compositions of solvent mixtures are given in volume ratios. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 500 MHz spectrometers with operating frequencies of 126 MHz for ^{13}C. Chemical shifts (δ) are reported in ppm relative to the residual solvent signal (δ = 7.26 for ^{1}H NMR and δ = 77.0 for ^{13}C NMR). Atmospheric pressure chemical ionization (APCI) data were recorded on MicroTOF-Q-II mass spectrometer using chloroform as a solvent.

(B) Instrumentation

(a) Steady-state absorption and fluorescence measurement:

Steady-state absorption measurements were performed using Cary 5000 Spectrophotometer from Agilent Technologies using 1 cm path length quartz cuvette. Steady-state fluorescence measurements were carried out using HORIBA Jobin Yvon Fluorolog fluorimeter using Origin 8 software provided with the instrument. Fluorescence and excitation spectra were recorded using 1 cm path length quartz cuvette and keeping both excitation and emission slit at 3/3 nm using very dilute dye solution (OD< 0.05) to avoid the effect of aggregation. All the experiments were carried out at ambient temperature (25 ºC) otherwise stated.

(b) Time-resolved measurement:

Time-resolved fluorescence measurements were performed using a Hamamatsu MCP photomultiplier (R-3809U-50). The time-correlated single photon counting (TCSPC)

setup consists of an Ortec 9327 pico-timing amplifier and using pulse Diode laser (λ_{ex} =509 nm and 635 nm) with fwhm ~140 ps and 80 ps respectively with a setup target 10,000 counts. The instrument response function (IRF) was measured before fluorescence lifetime measurement using a dilute suspension of Ludox (purchased from Sigma-Aldrich). The emission polarizer was positioned at magic angle (54.7 º) with respect to excitation polarizer. Single or bi-exponential (only in case of **3c**) fitting function was employed by iterative deconvolution method using supplied software DAS v6.2. The quality of the fitted data was evaluted from the reduced chi-squared value (χ^2), calculated using the software provided with the instrument. All the measurements were carried out at an ambient temperature (25 ºC).

(c) **Electrochemical measurements**

Electrochemical measurements were carried out using a CHI 6205 electrochemical analyzer using $[Bu_4N][PF_6]$ as the supporting electrolyte (0.1 M) and the concentration of PMI derivatives was *ca.* 10^{-3} M. For a typical electrochemical measurement a Pt disk was used as working electrode, Pt wire as counter electrode and aqueous saturated Ag/AgCl as reference electrode. The half-wave potential $\Delta E^0_{o\square\square}$ ΔE^0_r was set equal to 0.5 (E_{pa} + E_{pc}), where E_{pa} and E_{pc} are anodic and cathodic cyclic voltammetric peak potentials, respectively. In this cell, Fc/Fc^+ couple had an $E_{1/2}$ value of 0.39 V and all the voltammogram were measured at 100 mV/s scan rate in CH_2Cl_2. The dye solution in CH_2Cl_2 was purged with dry nitrogen for 15 min to remove dissolved oxygen. Every time before measurement the electrode was polished on a felt pad with alumina and washed thoroughly. All the measurements were repeated at least three times for reproducibility.

(d) **Device fabrication**

Step 1. The compound has been dissolved in chloroform at 4 mg/ml and stirred for 4 hr in closed vials.

Step 2. Transparent conducting substrates, ITOs, were cleaned very carefully by ultrasonication with distilled H_2O, acetone, and isopropanol and then UV treated for half an hour.

Step 3. Dissolved material has been deposited on ITO by using spin coating method at 1500 rpm for 60 s and then the thin films were annealed in vacuum at 90 °C for an hour in order to evaporate the solvent.

Step 4. Finally, aluminium was deposited on the thin organic films by thermal evaporation method.

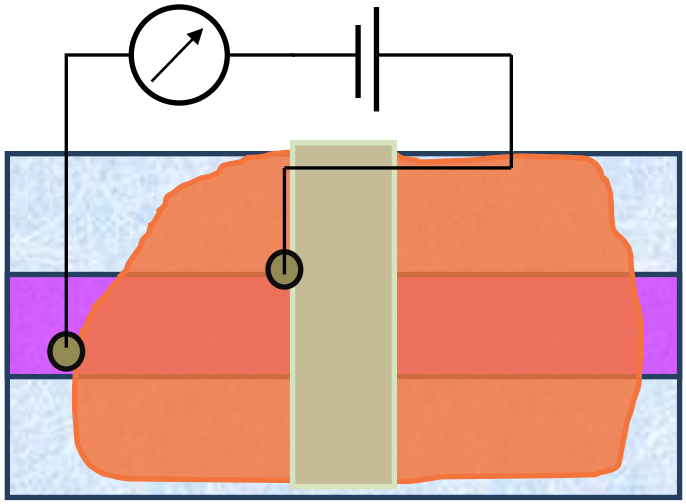
Deposition rate = 1 Å/s

Thickness of Al = 180 nm

The cell area of the devices was 3×3 mm^2.

Step 5. The ITO electrode was used as ground while the top Al electrode is used biasing electrode. The two probe current-voltage (I-V) characterizations were carried out with Keithley 2450 source-measurement unit. An Abet 1000 Solar Simulator has been used as light source wherever it required. The intensity of light source was fixed at 1 W/cm^2.

Schematic of memory device:



(e) **Theoretical calculation**

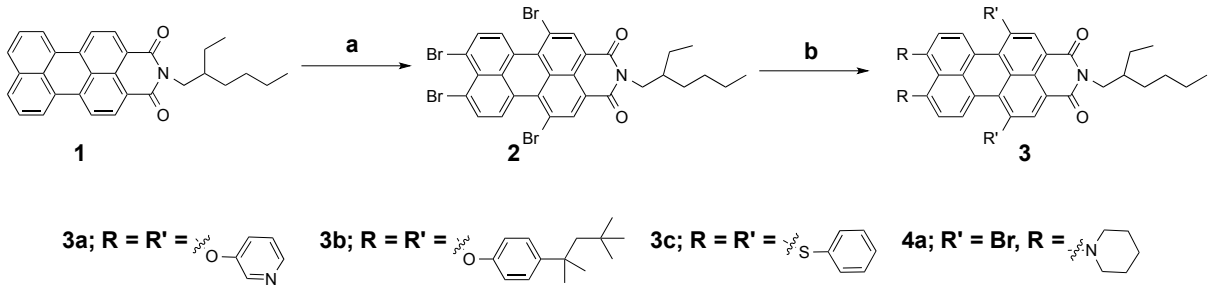
Density functional theory calculations were performed on PMI derivatives using Gaussian 09 suite of quantum chemical programs.[1] Ground-state geometry optimizations were performed with Becke three-parameter exchange functional in conjunction with Lee−Yang−Parr correlation functional (B3LYP)[2-4] using 6-311G as a basis set.

(C) **Synthesis and characterization**

The PMI **1** was synthesized as the reported procedure.[5, 6] Piperidine, were purchased from Alfa Aesar. 3-Hydroxyphenol, N-Methyl-2-pyrrolidone, Copper(I) iodide, 4-*tert*-

Octylphenol were purchased from Sigma Aldrich. Caesium carbonate, Thiophenol, Tetrahydrofuran (THF), Toluene, Triethyl ammine, DBU, sodium sulfate were purchased from Spectrochem (India), sulfur powder, selenium powder were purchased from Otto Chemie (India), Bromine ampoule from Merck.

Scheme S1 Synthesis of tetra-subsituted PMI derivatives



(a) Br_2 , $CHCl_3$, Reflux, 12 h, 46.0 %; (b) for **3a:** anhyrous K_2CO_3, NMP, 3-hydroxypyridine, 80 ºC, 4 h, 82.0 %; for **3b:** 4-*tert*-Octylphenol, CuI, Cs_2CO_3, toluene, EtOAc, reflux, 16 h, 57.0 %; for **3c:** Thiophenol, CuI, Cs_2CO_3, toluene, EtOAc, reflux, 16 h, 86.0 %; for **4a:** Piperidine, 60 ºC, 36 h, 88.0 %

***N*-(2-Ethylhexyl)-1,6,9,10-tetrabromo-perylene-3,4-dicabodimide (2):** To a solution of PMI **1** (200.0 mg, 0.46 mmol) in chloroform (21.0 ml) Br_2 (4.7 ml, 92.3 mmol) was added slowly. The reaction mixture was refluxed at 70 °C. After cooling down the reaction mixture to room temperature excess bromine was removed by flow of nitrogen. The reaction mixture was washed with saturated sodium thiosulfite solution (3x100 ml) followed by water (2x100 ml). The organic phase was dried over $MgSO_4$ and the solvent was evaporated on a rotary evaporator until free flowing precipitates come out and filtered. The obtained solids were dried in high vacuum to obtain desired compound **2** (158 mg, 46.0%).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.92 (d, *J* = 8.2 Hz, 2H), 8.84 (s, 2H), 8.10 (d, *J* = 8.3 Hz, 2H), 4.12 (dd, *J* = 12.6, 7.3 Hz, 2H), 1.93 (s, 1H), 1.38-1.31 (m, 8H), 0.94 (t, *J* = 7.3 Hz, 3H), 0.89 (t, *J* = 7.1 Hz, 3H).

Chemical formula-$C_{30}H_{23}Br_4NO_2$ **Calculated mass**-744.4482 and **obtained mass**-*m/z* 745.8526 $[M+H]^+$

***N*-(2-Ethylhexyl)-1,6,9,10-tetra(pyridin-3-yloxy)-perylene-3,4-dicarboximide (3a):** To a mixture of compound **2** (100.0 mg, 0.13 mmol), 3-Hydroxypyridine (75.0 mg,

0.801 mmol) and dry K_2CO_3 (110.0 mg, 0.80 mmol) in 25.0 ml round bottom flask under nitrogen atmosphere anhydrous NMP (6.0 ml) was added. The reaction mixture was stirred at a bath temperature of 80 ºC for overnight. The reaction mixture was cooled to room temperature and then poured into a mixture of water and HCl (4:1). The resulting precipitates were filtered out and washed with sufficient amount of water until the pH of the filtrate is neutral and dried. The crude product was purified by column chromatography using silica gel and a mixture of DCM and methanol (v/v, 20:0.5) to afford the desired compound **3a** (90.0 mg, 82.0 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.22 (d, *J* = 8.8 Hz, 2H), 8.50 (d, *J* = 2.8 Hz, 2H), 8.47 (dd, *J* = 4.6, 1.3 Hz, 2H), 8.32 (dd, *J* = 4.7, 1.2 Hz, 2H), 8.25 (s, 2H), 8.17 (d, *J* = 2.8 Hz, 2H), 7.41 (dd, *J* = 2.8, 1.4 Hz, 1H), 7.40 (dd, *J* = 2.8, 1.4 Hz, 1H), 7.35 (d, *J* = 4.6 Hz, 1H), 7.33 (d, *J* = 5.0 Hz, 1H), 7.21 (d, *J* = 4.7 Hz, 1H), 7.19 (d, *J* = 4.7 Hz, 1H), 7.13 (d, *J* = 8.8 Hz, 2H), 7.10 (dd, *J* = 2.9, 1.3 Hz, 1H), 7.08 (dd, *J* = 2.9, 1.3 Hz, 1H), 4.07 (ddd, *J* = 19.5, 12.9, 7.3 Hz, 2H), 1.88 (dd, *J* = 12.5, 6.9 Hz, 1H), 1.41 – 1.24 (m, 8H), 0.91 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 163.28, 154.08, 153.13, 152.59, 152.21, 145.79, 144.66, 141.30, 140.55, 133.73, 131.19, 130.66, 127.11, 125.80, 124.89, 124.78, 124.50, 124.32, 124.25, 123.42, 121.88, 120.12, 117.83, 44.52, 38.10, 30.91, 28.86, 24.21, 23.17, 14.24, 10.73.

Chemical formula-$C_{50}H_{39}N_5O_6$ **Calculated mass**-805.2900 and **obtained mass**- *m/z* 806.2973 $[M+H]^+$

***N*-(2-Ethylhexyl)-1,6,9,10-tetra(4-*tert*-octylphenoxy)-perylene-2,3-dicarboximide (3b):** To a mixture of compound **2** (48.0 mg, 0.06 mmol), 4-*tert*-octylphenol (128.0 mg, 0.62 mmol) dry toluene (3.0 ml) was added under nitrogen followed by addition of CuI (3.6 mg, 0.019 mmol), Cs_2CO_3 (230.0 mg, 0.706 mmol) and three drops of EtOAc. The mixture was heated to reflux for 16 hours under nitrogen atmosphere. The reaction mixture was diluted with chloroform after cooling down to room temperature and washed three times with water (3x100 ml). The crude product was dried via rotary evaporation and purified by column chromatography using a solvent mixture of DCM and n-hexane (v/v, 2:3) to afford the desired compound **3b** (46.0 mg, 57.0 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.26 (d, *J* = 8.9 Hz, 2H), 8.25 (s, 2H), 7.37 (d, *J* = 8.7 Hz, 4H), 7.22 (d, *J* = 8.7 Hz, 4H), 7.02-7.00 (2d, J_1 = 6.0 Hz, J_2 = 6.1 Hz, 6H), 6.70 (d, *J* = 8.6 Hz, 4H), 4.12 – 3.98 (m, 2H), 1.93 – 1.86 (m, 1H), 1.73 (s, 4H), 1.69 (s, 4H), 1.39-1.29 (2s, 12H each and m, 8H), 0.90 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 6.8 Hz, 3H), 0.76 (s, 18H), 0.73 (s, 18H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 163.87, 155.08, 155.04, 153.53, 152.82, 146.40, 145.07, 133.74, 131.16, 130.68, 128.02, 127.34, 127.22, 124.15, 123.37, 122.68, 120.67, 119.85, 57.27, 57.12, 44.34, 38.49, 38.31, 38.07, 32.57, 32.51, 31.98, 31.76, 31.61, 30.91, 28.87, 24.24, 23.21, 14.26, 10.78.

Chemical formula-$C_{86}H_{107}NO_6$ **Calculated mass**-1249.8098 and **obtained mass**- *m/z* 1250.8173 $[M+H]^+$

***N*-(2-Ethylhexyl)-1,6,9,10-tetrakis(phenylthio)-perylene-2,3-dicarboximide (3c):** To a mixture of tetrabromo PMI **2** (40.0 mg, 0.0534 mmol), thiophenol (57.0 mg, 0.517 mmol) and dry toluene (5.0 ml) was added under nitrogen followed by addition of CuI (3.0 mg, 0.016 mmol), Cs_2CO_3 (190.6 mg, 0.59 mmol) and three drops of EtOAc. The mixture was heated to reflux for 16 hours under nitrogen atmosphere. The reaction mixture was diluted with chloroform after cooling down to room temperature and washed three times with water (3x100 ml). The crude product was dried *via* rotary evaporation and purified by column chromatography using a solvent mixture of $CHCl_3$ and n-hexane (v/v, 2:1) to afford the desired compound **3c** (39.8 mg, 86.0 %).

^{1}H NMR (500 MHz, $CDCl_3$): ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.38 (s, 2H), 8.28 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 7.4 Hz, 4H), 7.42 – 7.29 (m, 16H), 3.98 (t, *J* = 6.6 Hz, 2H), 1.84 (s, 1H), 1.33 – 1.19 (m, 10H), 0.86 (t, *J* = 7.5 Hz, 3H), 0.82 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 163.85, 139.88, 136.25, 135.23, 135.12, 134.51, 134.40, 132.90, 132.25, 131.44, 130.31, 129.90, 129.85, 129.45, 128.84, 128.65,

128.23, 126.80, 124.48, 119.96, 44.40, 37.92, 31.07, 30.76, 28.71, 24.14, 23.21, 14.19, 10.75.

Chemical formula-$C_{54}H_{43}NO_2S_4$ **Calculated mass**-865.2177 and **obtained mass**-866.2265 *m/z* $[M+H]^+$

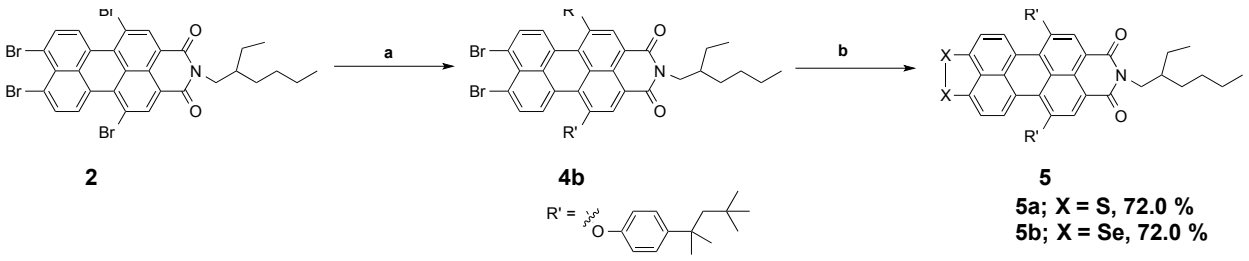
***N*-(2-Ethylhexyl)-1,6-dibromo-9,10-di(piperidin-1-yl)-perylene-2,3-dicarboximide (4a):** A solution of compound **2** (29.0 mg, 0.04 mmol) in 3.0 ml piperidine was stirred and heated at 60 ˚C for 36 hours. After cooling down to room temperature, piperidine was evaporated by rotary evaporator. The crude product was purified by silica gel column chromatography using chloroform as eluent to afford the desired compound **4a** (25.8 mg, 88.0 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.09 (d, *J* = 8.6 Hz, 2H), 8.74 (s, 2H), 7.05 (d, *J* = 8.7 Hz, 2H), 4.12 (ddd, *J* = 19.6, 12.8, 7.3 Hz, 2H), 3.52 (broad s, 4H), 3.13 (broad s, 4H), 2.01 – 1.88 (m, 1H), 1.85 – 1.62 (m, 12H), 1.45 – 1.26 (m, 8H), 0.94 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 9.0, 5.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 163.51, 154.56, 137.85, 136.67, 135.88, 131.10, 129.48, 126.96, 119.87, 117.76, 116.20, 114.44, 112.05, 54.00, 44.34, 38.04, 30.93, 28.93, 26.03, 24.72, 24.23, 23.23, 14.28, 10.81.

Chemical formula-$C_{40}H_{43}Br_2N_3O_2$ **Calculated mass**-755.1722 and **obtained mass**-756.1795 *m/z* $[M+H]^+$

Scheme S2 Synthesis of di-sulfur and di-selenium PMI derivatives



(a) Anhyrous K_2CO_3, NMP, 4-*tert*-Octylphenol, 80 ^oC, 4 h, 30.0 %; (b) Se or S, NMP, 190 ^oC, 5 h

***N*-(2-Ethylhexyl)-1,6,-dibromo-9,10-bis(4-*tetr*-octylphenoxy)-perylene-2,3-dicarboximide (4b):** To a mixture of compound **2** (100.0 mg, 0.13 mmol), 4-*tert*-octylphenol (60.0 mg, 0.29 mmol) and dry K_2CO_3 (18.4 mg, 0.29 mmol) in 25.0 ml round bottom flask under nitrogen atmosphere anhydrous NMP (10.0 ml) was added. The reaction mixture was heated at 80 ºC for 4 h. After cooling down the reaction mixture to room temperature it was poured into a mixture of water and HCl (4:1). The resulting precipitates were filtered out and washed with sufficient amount of water until the filtrate shows a neutral pH and dried. The crude product was purified by column chromatography using silica gel and a mixture of DCM and n-hexane (v/v, 1:3) to afford the desired compound **4b** (40.4 mg, 30.0 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.97 (d, *J* = 8.6 Hz, 2H), 8.22 (s, 2H), 8.01 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.7 Hz, 4H), 6.99 (d, *J* = 8.7 Hz, 4H), 4.03 (ddd, *J* = 19.7, 12.9, 7.3 Hz, 2H), 1.93 – 1.83 (m, 1H), 1.74 (s, 4H), 1.39 (s, 12H), 1.36 – 1.25 (m, 8H), 0.89 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 6.9 Hz, 3H), 0.76 (s, 18H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 163.61, 153.96, 153.12, 146.88, 135.79, 133.97, 130.66, 129.68, 128.61, 128.17, 128.09, 125.51, 123.64, 122.07, 122.03, 121.79, 118.53, 57.28, 44.43, 38.54, 38.09, 32.57, 31.98, 31.62, 30.90, 28.84, 24.23, 23.19, 14.24, 10.76.

Chemical formula-$C_{58}H_{65}Br_2NO_4$ **Calculated mass**- 997.3280 and **obtained mass**-*m/z* 998.3346 $[M+H]^+$

***N*-(2-Ethylhexyl)-1,6-bis(4-*tert*-octylphenoxy)-[9,10]dithiolo-perylene-2,3-dicarboximide (5a):** A mixture of compound **4b** (15.0 mg, 0.015 mmol) and sulfur (9.6 mg, 0.150 mmol) were taken in a sealed microwave vial (5.0 ml capacity) under nitrogen atmosphere and then 1.5 ml of anhydrous NMP (1.5 ml) was added. The reaction mixture was stirred and heated at 190 ºC for 5 h. After cooling down to room temperature the reaction mixture was poured into ice cold water. The resulting precipitates were filtered and washed with water and dried. The Crude compound was purified by column chromatography using neutral alumina as stationary phase and a

mixture of $CHCl_3$ and n-hexane (v/v, 2:1) as eluent to afford the desired compound **5a** (9.7 mg, 72.0 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.25 (d, *J* = 8.7 Hz, 2H), 8.24 (s, 2H), 7.38 – 7.36 (m, 2H), 7.35 (d, *J* = 8.7 Hz, 2H), 7.02 – 6.98 (m, 2H), 4.05 (ddd, *J* = 19.6, 12.9, 7.3 Hz, 2H), 1.92 – 1.86 (m, 1H), 1.74 (s, 4H), 1.39 (s, 12H), 1.36 – 1.24 (m, 8H), 0.90 (t, *J* = 7.4 Hz, 3H), 0.85 (t, *J* = 7.1 Hz, 3H), 0.77 (s, 18H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 163.78, 153.39, 152.29, 147.24, 146.42, 134.36, 131.93, 131.58, 130.56, 128.03, 126.81, 124.09, 123.54, 120.17, 118.21, 117.50, 57.29, 44.39, 38.51, 38.07, 32.58, 31.99, 31.60, 30.95, 28.89, 24.28, 23.23, 14.26, 10.78.

Chemical formula-$C_{58}H_{65}NO_4S_2$ **Calculated mass**-903.4355 and **obtained mass**- *m/z* 904.4432 $[M+H]^+$

***N*-(2-Ethylhexyl)-1,6-bis(4-*tert*-octylphenoxy)-[9,10]diselenolo-perylene-2,3-dicarboximide (5b):** A mixture of compound **4b** (20.0 mg, 0.02 mmol) and selenium (20.0 mg, 0.253 mmol) were taken in a sealed microwave vial (5.0 ml capacity) under nitrogen atmosphere and then anhydrous NMP (1.5 ml) was added. The reaction mixture was stirred and heated at 190 ºC for 5 h. After cooling down to room temperature the reaction mixture was poured into ice cold water. The resulting precipitates were filtered and washed with water and dried. The Crude compound was purified by column chromatography using neutral alumina as stationary phase and a mixture of $CHCl_3$ and n-hexane (v/v, 2:1) as eluent to afford the desired compound **5b** (14.4 mg, 72.0 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.15 (d, *J* = 8.6 Hz, 2H), 8.23 (s, 2H), 7.52 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 4H), 6.99 (d, *J* = 8.7 Hz, 4H), 4.05 (ddd, *J* = 19.6, 12.9, 7.3 Hz, 2H), 1.89 (d, *J* = 3.9 Hz, 1H), 1.73 (s, 4H), 1.39 (s, 12H), 1.37 – 1.24 (m, 8H), 0.89 (t, *J* = 7.4 Hz, 3H), 0.85 (t, *J* = 7.0 Hz, 3H), 0.77 (s, 18H).
Chemical formula-$C_{58}H_{65}NO_4Se_2$ **Calculated mass**-999.3244 and **obtained mass**-*m/z* 1000.3359 $[M+H]^+$

Detailed characterization and analysis using optical spectroscopy, ^{1}H- NMR, ^{13}C NMR spectra and mass spectra of synthesized compounds

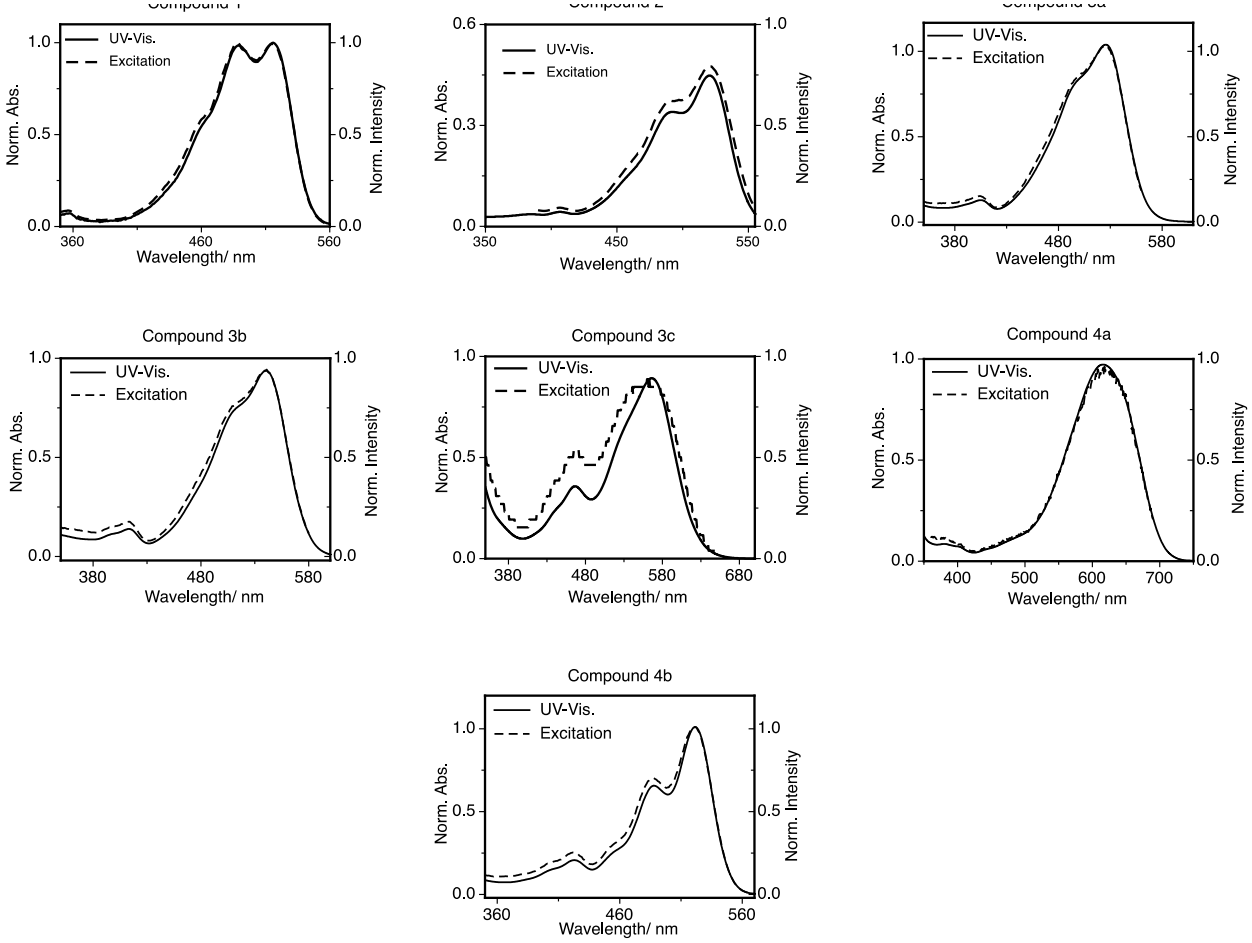


Fig. S1: Testing the optical purity of **1**, **2**, **3a**, **3b**, **3c**, **4a** and **4b** in toluene by comparing their UV-Vis. and excitation spectra.

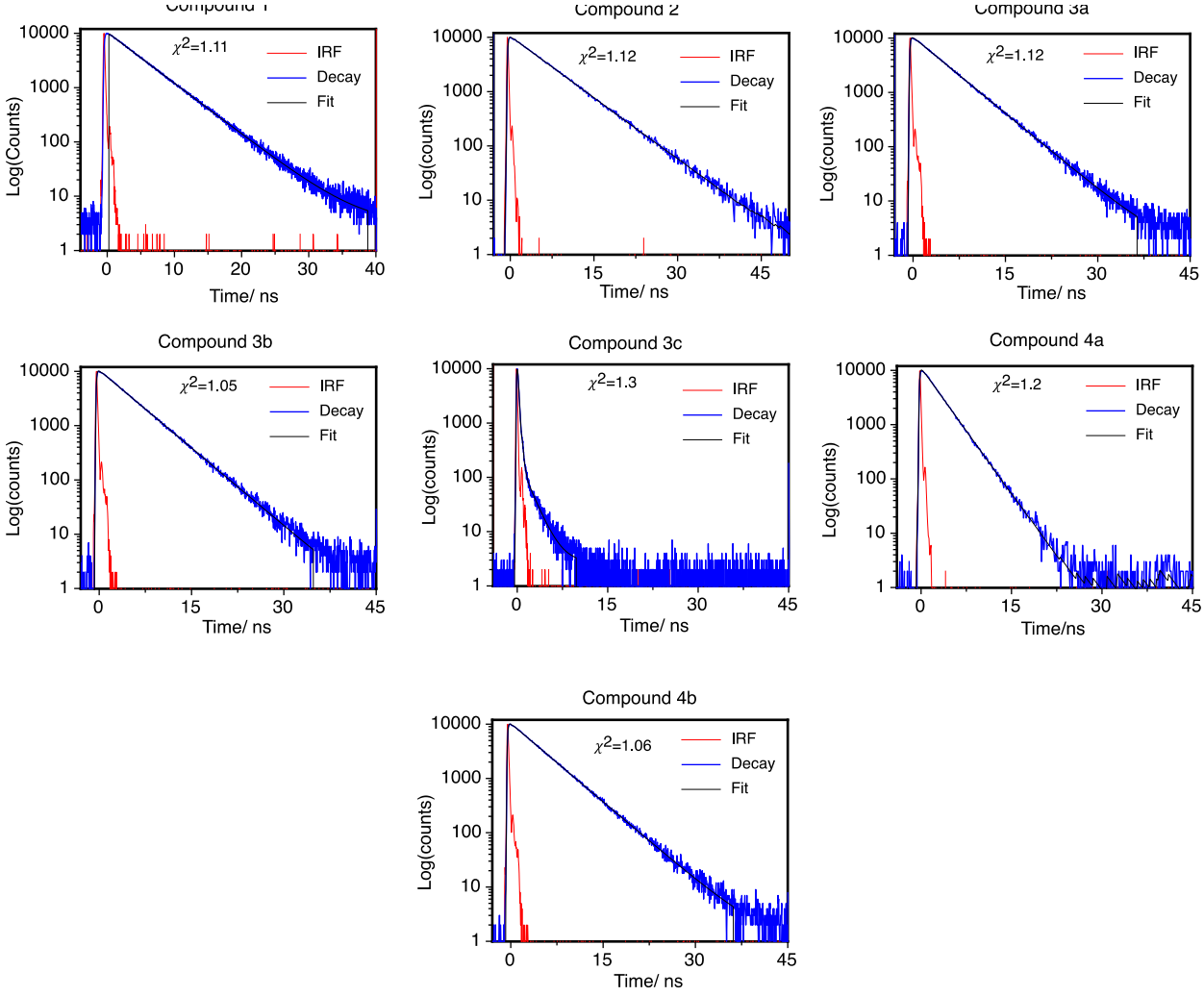


Fig. S2: Fluorescence lifetime decay of **1**, **2**, **3a**, **3b**, **3c**, **4a** and **4b** in toluene. Fluorescence lifetime values are provided in Table 1. Single exponential fitting function was used for the fitting except for **3c** where bi-exponential fitting was used.

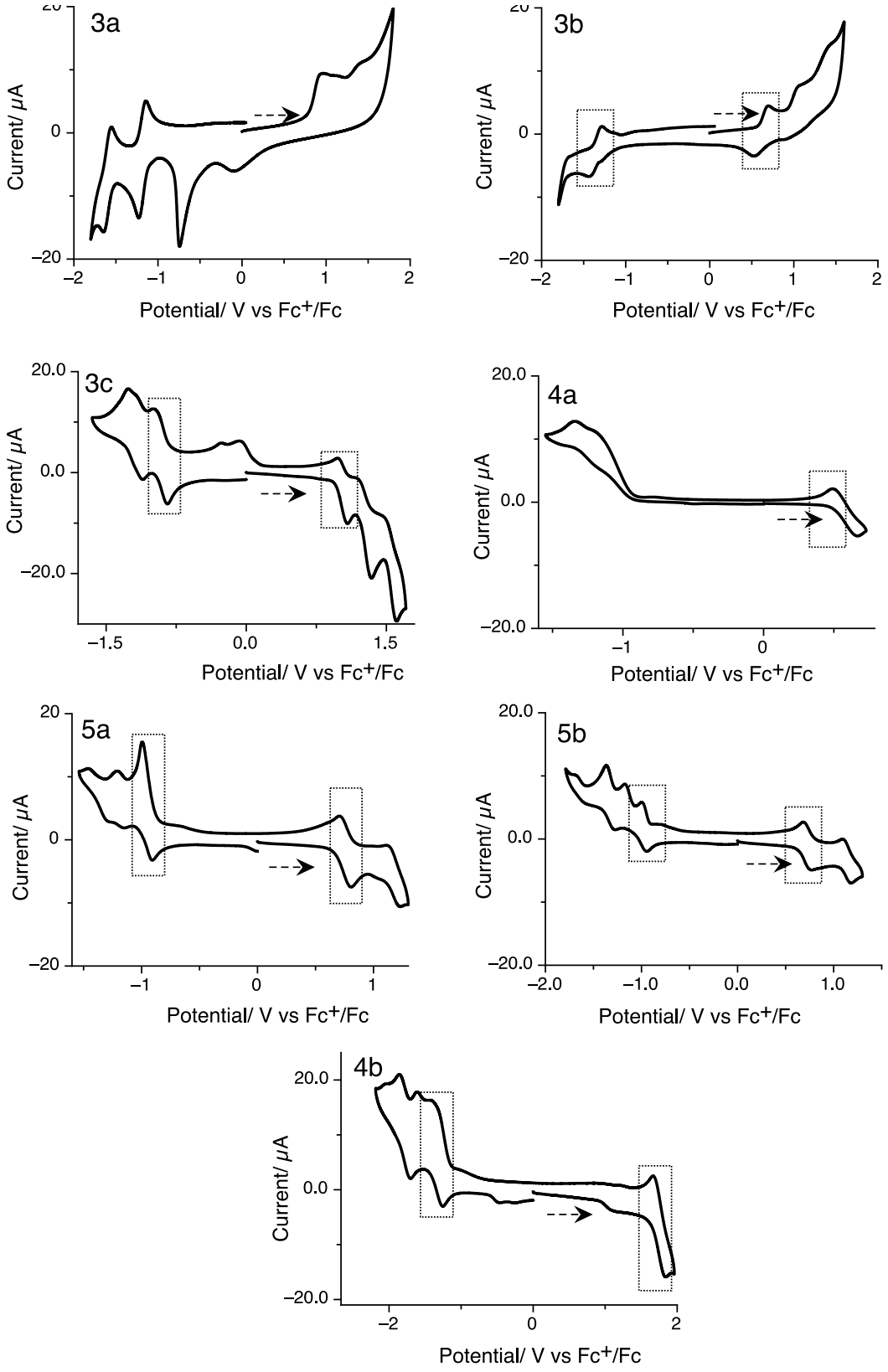


Fig. S3: Cyclic voltamogram of **3a-c**, **4a-b** and **5a-b** versus Fc^+/Fc in 0.1 M Bu_4NPF_6 in dry DCM, with a platinum disk as the working electrode with a scan rate of 100 mV/s.

Table S1: Electrochemical properties of PMI derivatived measured in dichloromethane

PMI	Oxidation Potential (ΔE_o°) / V[a]		Reduction Potential (ΔE_r°) / V[a]		E_{HOMO}/ eV	E_{LUMO}/ eV	E_g/ eV
	ΔE_o° (1)	ΔE_o° (2)	ΔE_r° (1)	ΔE_r° (2)			
1	_	1.08[b]	-1.20[b]	_	-5.78	-3.50	2.28
3a	1.00[c]	-	-1.15[c]	-1.55	-[d]	-[d]	-[d]
3b	0.60[b]	1.00[b]	-1.35[b]	-	-5.30	-3.35	1.95
3c	1.05[b]	1.29	-0.90[b]	-1.18	-5.75	-3.80	1.95
4a	0.60[b]	-	-1.30[c]	-	-5.30	-[d]	-[d]
4b	1.35[b]	-	-0.95[b]	-1.35	-6.05	-3.75	2.30
5a	0.75[b]	1.15	-0.95[b]	-1.15	-5.45	-3.75	1.70
5b	0.70[b]	1.15	-0.95[b]	-1.21	-5.40	-3.75	1.65

[a] versus Fc^+/Fc in 0.1 M Bu_4NPF_6 in dry DCM, with a platinum disk as the working electrode with a scan rate of 100 mV/s. [b] reversible oxidation/reduction potential, [c] quasi-reversible potential, [d] E_g not determined due quasi-reversible oxidation and reduction potential

Table S2: Theoretically calculated properties of PMI derivatives

PMI	E_{HOMO}/ eV	E_{LUMO}/ eV	E_g/ eV	Dipole moment/ Debye	Dihedral angle/ Degree[a]
1	-5.794	-3.167	2.627	9.9108	0.63
3a	-5.754	-3.258	2.496	10.0701	15.29
3b	-5.537	-3.105	2.432	6.7509	14.37
3c	-5.735	-3.294	2.441	4.1782	26.64
4a	-5.008	-2.846	2.162	27.0944	17.67
4b	-6.05	-3.75	2.30	–	–
5a	-5.399	-3.149	2.25	2.8259	10.53
5b	-5.40	-3.75	1.65	–	–

[a] between lower and upper napthalene rings

Symbolic Z-matrix for the optimized configuration of **1:**

Charge = 0 Multiplicity = 1

C	4.33911	2.74138	0.247
C	3.76601	1.47839	0.08972
C	4.6184	0.32583	0.11753
C	6.03093	0.50279	0.30648
C	6.55842	1.81256	0.45987
C	5.72385	2.90954	0.43016
H	3.72168	3.62612	0.23173
C	4.09374	-0.99947	-0.03811
C	6.88146	-0.63427	0.33763
H	6.12568	3.90596	0.54757
C	6.35929	-1.90145	0.18802
C	4.97635	-2.08003	0.00169
H	7.00664	-2.76655	0.21266
H	4.60908	-3.08831	-0.1104
C	2.6467	-1.18125	-0.23264
C	2.3183	1.29702	-0.10123
C	1.79326	-0.02893	-0.25309
C	1.42809	2.37725	-0.14171
C	2.06807	-2.44555	-0.40024
C	-0.15628	-1.50737	-0.59712
C	0.38352	-0.20601	-0.43675
C	-0.47893	0.91899	-0.46463
C	0.05605	2.19343	-0.32145
H	-0.60793	3.04471	-0.34915
C	0.6935	-2.60682	-0.58077
H	0.27335	-3.59357	-0.70751

C	-1.92429	0.74907	-0.65073
C	-1.59783	-1.70127	-0.78305
N	-2.4223	-0.5623	-0.73028
O	-2.70782	1.72856	-0.73619
O	-2.10013	-2.83795	-0.97608
C	-3.88841	-0.75578	-0.92609
H	-4.23382	0.09103	-1.51245
H	-3.98659	-1.65691	-1.5246
C	-4.77012	-0.90773	0.34321
H	-5.73463	-1.21732	-0.0783
C	-5.01846	0.40761	1.12039
H	-5.51864	0.15212	2.06241
H	-4.06225	0.85738	1.39431
C	-5.87367	1.46455	0.39175
H	-5.83718	2.39203	0.97518
H	-5.42264	1.70442	-0.57482
C	-7.35059	1.07657	0.19476
H	-7.42364	0.17123	-0.4157
H	-7.78794	0.82678	1.1681
C	-8.17612	2.19244	-0.46476
H	-7.77852	2.44311	-1.45179
H	-9.21947	1.89513	-0.59145
H	-8.1594	3.10287	0.14025
C	-4.35025	-2.07023	1.28653
H	-4.07247	-2.93137	0.67543
H	-5.24155	-2.36379	1.85148
C	-3.22577	-1.77894	2.29706

H	-2.29546	-1.48162	1.81432
H	-3.50583	-0.98444	2.99059
H	-3.01677	-2.6721	2.89053
H	2.68277	-3.33133	-0.39306
H	1.79131	3.38659	-0.03316
H	7.62426	1.93365	0.60013
H	7.94376	-0.48844	0.48111

Table S3: Calculated energies of Kohn-Sham molecular orbitals (MO) of **1** using DFT the B3LYP/6-311G as basis set.

MO's	Energy/Hartree	Energy/ eV
LUMO+4	-0.02146	-0.58395
LUMO+3	-0.04167	-1.13389
LUMO+2	-0.05083	-1.38315
LUMO+1	-0.05379	-1.46370
LUMO	-0.11640	-3.16740
HOMO	-0.21296	-5.79493
HOMO-1	-0.26833	-7.30163
HOMO-2	-0.27138	-7.38462
HOMO-3	-0.27405	-7.45727
HOMO-4	-0.27724	-7.54408

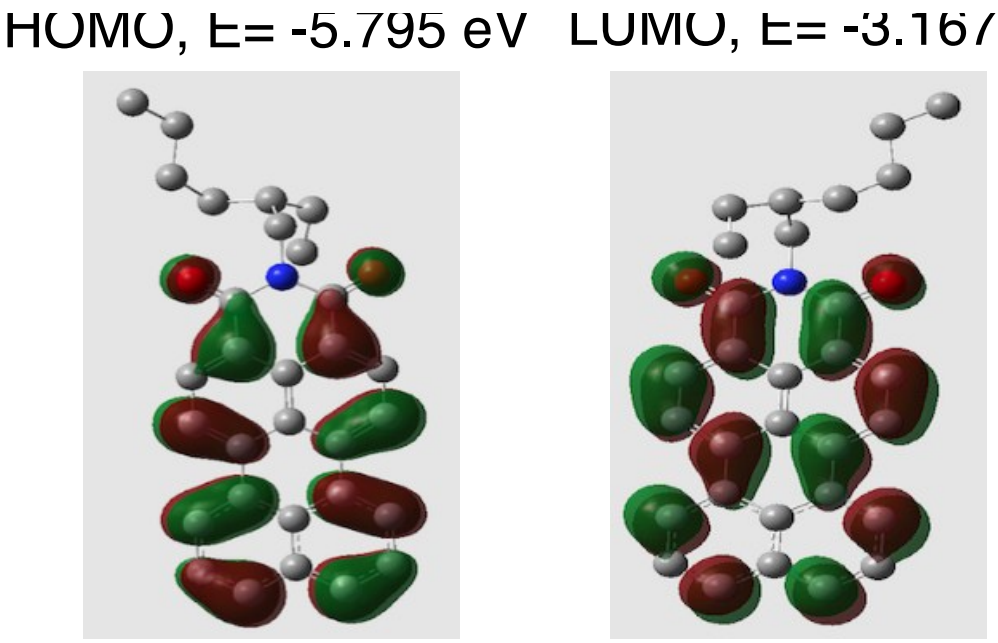


Fig. S4: Energy optimized Kuhn-Sham HOMO and LUMO of compound **1**

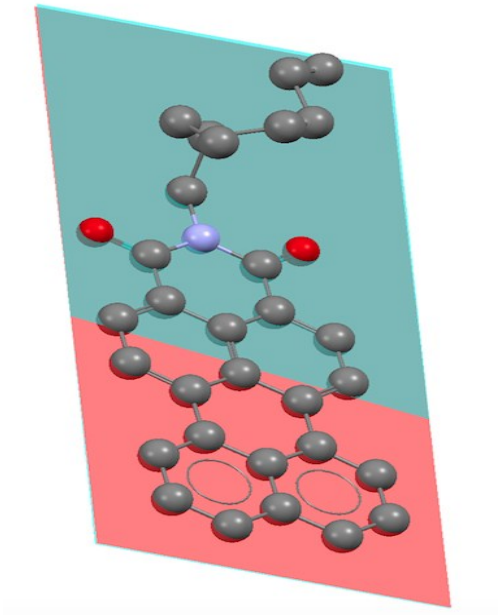


Fig. S5: Shows the twisting of perylene core (0.63 º) from the energy-optimized structure of **1** calculated by DFT at the B3LYP/6-311G level

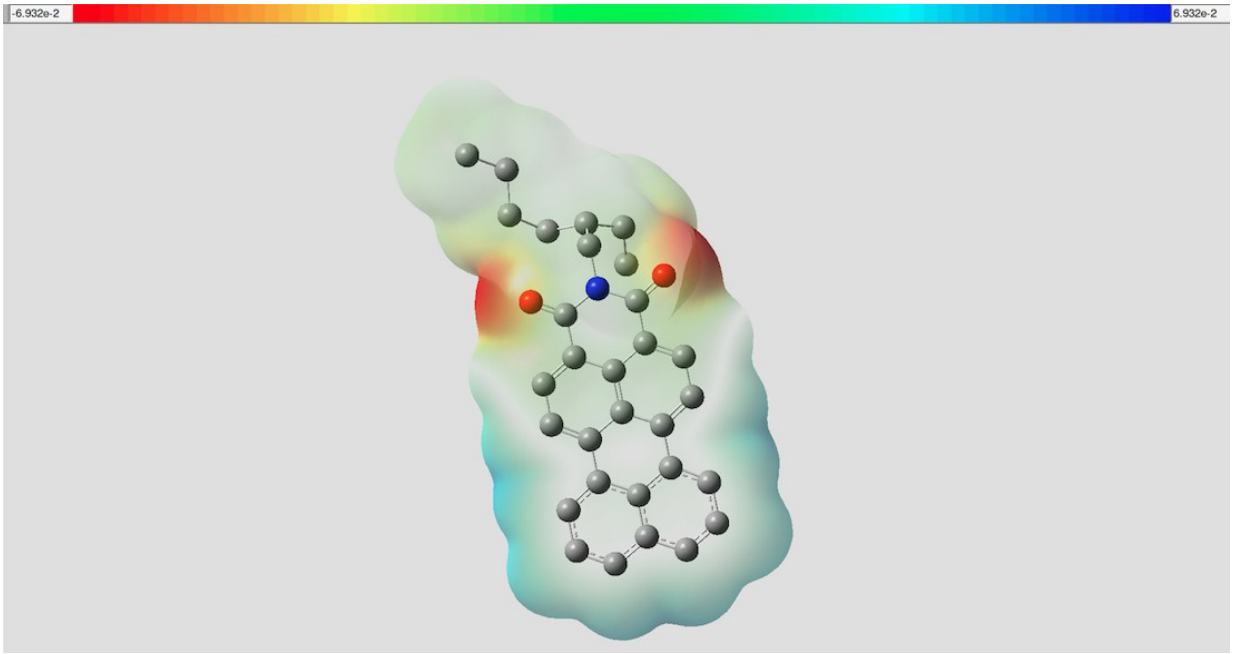


Fig. S6: Computed electrostatic potentials map **1**; red color indicates more negative charge.

Symbolic Z-matrix for the optimized configuration of **3a:**

Charge = 0 Multiplicity = 1

C	-2.00498	-2.06922	-0.71836
C	-1.289	-0.96908	-0.23909
C	-2.02455	0.12879	0.32566
C	-3.45225	0.00804	0.52973
C	-4.10489	-1.16437	0.03622
C	-3.39441	-2.15966	-0.59863
H	-1.484	-2.87761	-1.19397
C	-1.35572	1.34607	0.69205
C	-4.11588	1.05737	1.22938
H	-3.90385	-3.02229	-0.99812
C	-3.43145	2.16465	1.67443
C	-2.07042	2.31879	1.39614
H	-3.96408	2.91704	2.23656
H	-1.57483	3.21019	1.72979
C	0.05981	1.51858	0.3385
C	0.17473	-0.89655	-0.30042
C	0.8218	0.37004	-0.07514
C	1.01535	-1.99534	-0.57094
C	0.74087	2.75065	0.37995
C	2.86987	1.74903	-0.14423
C	2.23445	0.49133	-0.2713
C	3.01229	-0.64326	-0.60038
C	2.3956	-1.87271	-0.73281
H	2.99078	-2.73998	-0.97511
C	2.11338	2.8654	0.15553

H	2.59504	3.82812	0.23413
C	4.46235	-0.53372	-0.80615
C	4.32066	1.88689	-0.33173
O	5.1606	-1.51626	-1.15694
O	4.8953	3.00143	-0.26333
C	6.53037	0.85242	-0.78798
H	6.79681	0.15662	-1.57858
H	6.68501	1.86507	-1.149
C	7.44572	0.61996	0.44419
H	8.42414	0.94996	0.0733
C	7.59771	-0.86166	0.86653
H	8.13828	-0.88429	1.82038
H	6.61267	-1.28892	1.06381
C	8.34313	-1.76902	-0.13346
H	8.23523	-2.80674	0.20295
H	7.85526	-1.72238	-1.11071
C	9.84457	-1.46468	-0.28639
H	9.98634	-0.44197	-0.64919
H	10.3212	-1.50921	0.69944
C	10.55465	-2.43708	-1.24126
H	10.11926	-2.39108	-2.24301
H	11.61822	-2.20449	-1.32913
H	10.4663	-3.4681	-0.88857
C	7.14128	1.54118	1.6597
H	6.92957	2.54708	1.29109
H	8.06351	1.6133	2.246
C	6.01262	1.09776	2.60782

H	5.04942	1.01684	2.10521
H	6.22812	0.13064	3.06495
H	5.89904	1.82318	3.4168
O	0.04629	3.92813	0.73455
C	0.1775	5.09619	-0.0413
C	0.27972	5.08121	-1.43169
C	0.33278	6.30948	-2.09424
H	0.31045	4.15062	-1.97852
C	0.27534	7.48935	-1.3515
H	0.40983	6.34685	-3.1708
C	1.02754	-4.41147	-0.16107
C	1.04533	-5.59257	-0.89914
C	1.54166	-6.74294	-0.28456
H	0.67955	-5.59948	-1.91495
C	2.00177	-6.66536	1.03123
H	1.57473	-7.68088	-0.81871
O	0.45265	-3.2763	-0.76655
O	-5.49068	-1.23295	0.19228
O	-5.47424	0.96833	1.59713
C	-6.20813	-2.39727	-0.16422
C	-6.88188	-2.44727	-1.38071
C	-7.65684	-3.57767	-1.65117
H	-6.80646	-1.62821	-2.08024
C	-7.722	-4.59771	-0.7011
H	-8.20111	-3.66275	-2.57987
C	-6.48858	1.42632	0.7474
C	-6.26649	2.04095	-0.48306

C	-7.38049	2.46543	-1.2135
H	-5.26653	2.18709	-0.86273
C	-8.65838	2.26165	-0.69515
H	-7.2519	2.94738	-2.1717
H	-9.54099	2.57649	-1.23203
H	-8.31115	-5.48613	-0.87444
H	2.39453	-7.53317	1.5401
H	0.31319	8.45621	-1.83111
C	-7.79501	1.24959	1.21012
C	1.49347	-4.39935	1.15481
C	-6.31852	-3.44512	0.74791
N	5.05733	0.7187	-0.58793
N	0.16985	7.49418	-0.00079
N	1.97943	-5.51406	1.74344
N	-7.06734	-4.5379	0.48361
N	-8.866	1.66051	0.50277
C	0.12653	6.30971	0.64465
H	0.04305	6.32569	1.72149
H	-7.97233	0.77116	2.16234
H	-5.81105	-3.40625	1.70099
H	1.47871	-3.49697	1.74846

Table S4: Calculated energies of Kohn-Sham molecular orbitals (MO) of **3a** using DFT B3LYP as a basis set.

MO's	Energy/ Hartree	Energy/ eV
LUMO+4	-0.04790	-1.30342
LUMO+3	-0.05196	-1.41390
LUMO+2	-0.05840	-1.58914
LUMO+1	-0.06156	-1.67513
LUMO	-0.11973	-3.25801
HOMO	-0.21148	-5.75466
HOMO-1	-0.25189	-6.85427
HOMO-2	-0.25407	-6.91359
HOMO-3	-0.26452	-7.19795
HOMO-4	-0.26700	-7.26543

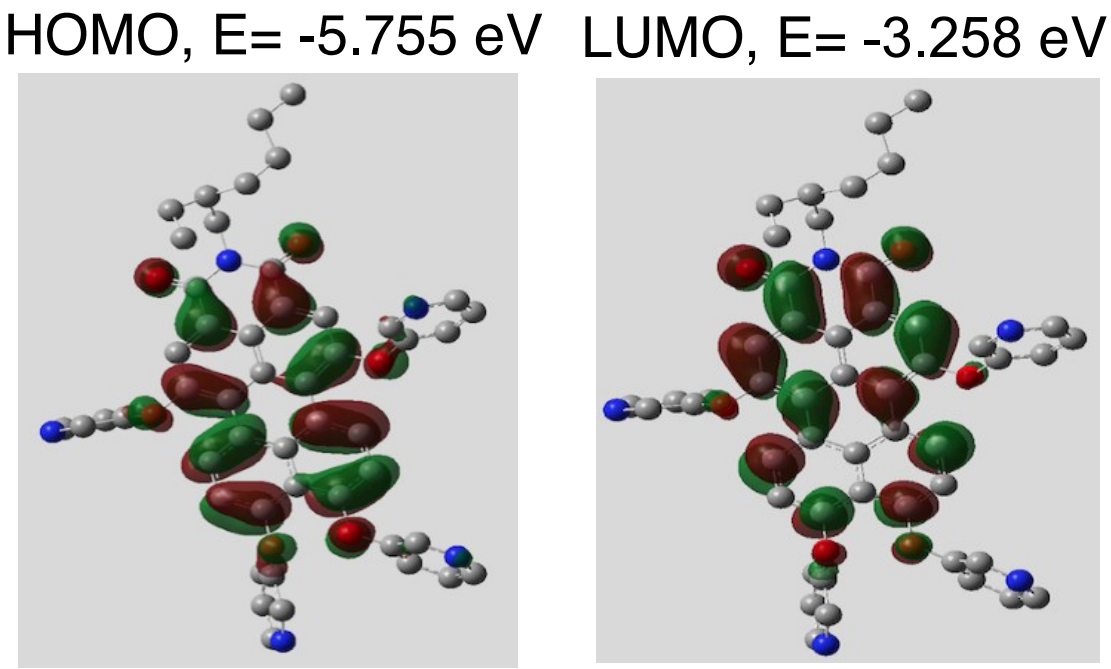


Fig. S7: Energy optimized Kuhn-Sham HOMO and LUMO of compound **3a**

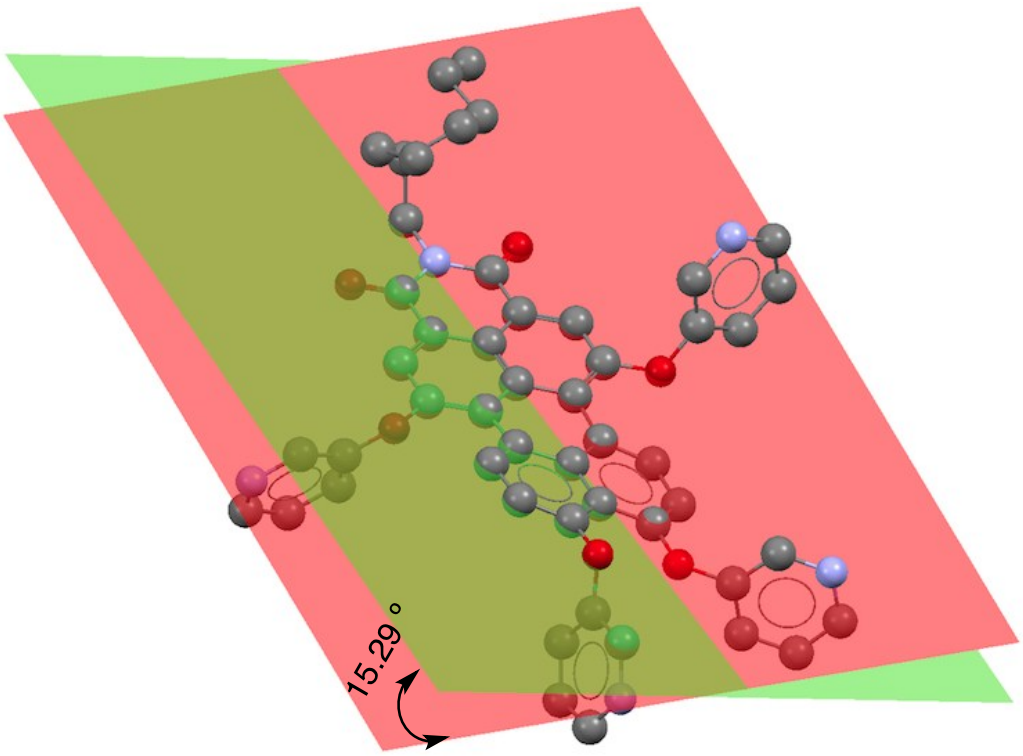


Fig. S8: Shows the twisting of perylene core from the energy-optimized structure of **3a** calculated by DFT at the B3LYP/6-311G level

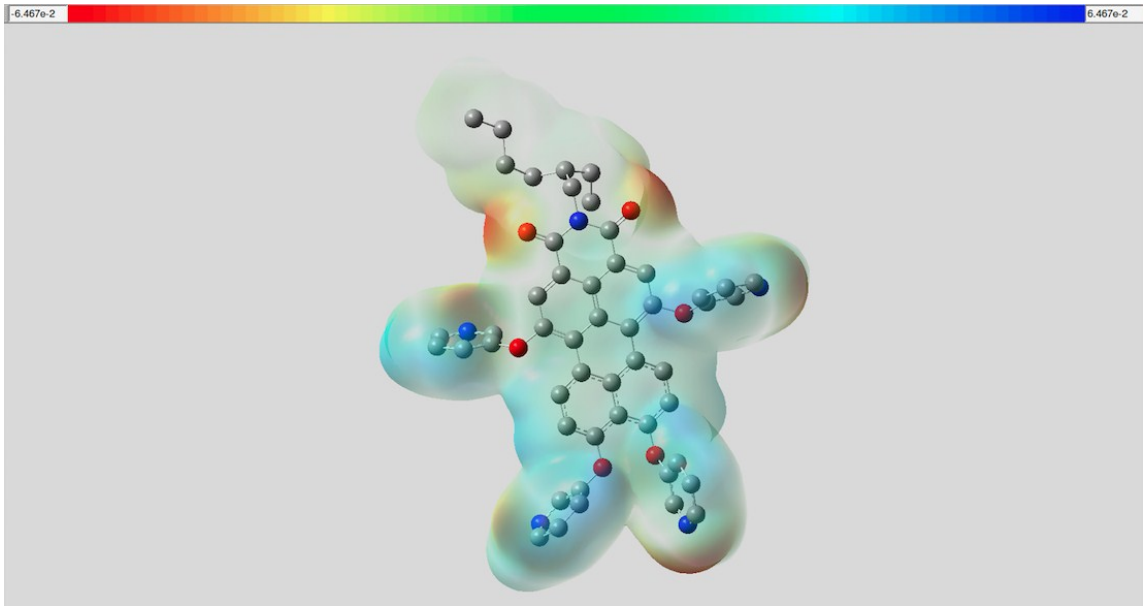


Fig. S9: Computed electrostatic potentials map **3a**; red color indicates more negative charge.

Symbolic Z-matrix for the optimized configuration of **3b:**

Charge = 0 Multiplicity = 1

C	1.2231	-1.78592	0.2462
C	0.38154	-0.76911	-0.21409
C	0.98163	0.37621	-0.84375
C	2.40518	0.38873	-1.10848
C	3.19326	-0.69964	-0.61815
C	2.60747	-1.74533	0.06329
H	0.80046	-2.63071	0.75453
C	0.1805	1.50928	-1.21755
C	2.93879	1.47258	-1.86639
H	3.21917	-2.54531	0.45049
C	2.12666	2.49193	-2.31023
C	0.77022	2.52304	-1.97868
H	2.56268	3.27047	-2.91874
H	0.17444	3.35061	-2.31208
C	-1.23007	1.55708	-0.8096
C	-1.07787	-0.83124	-0.07114
C	-1.85401	0.35885	-0.31079
C	-1.79334	-1.99279	0.29661
C	-2.03205	2.71689	-0.87145
C	-4.02061	1.53993	-0.18087
C	-3.26074	0.35509	-0.04057
C	-3.90656	-0.83181	0.37521
C	-3.17051	-1.99056	0.5257
H	-3.67558	-2.89228	0.83642
C	-3.39688	2.70706	-0.57378

H	-3.98208	3.60985	-0.65984
C	-5.34914	-0.85475	0.65883
C	-5.46478	1.55616	0.10128
N	-6.06904	0.33418	0.4514
O	-5.92927	-1.8866	1.06826
O	-6.1424	2.60724	0.03557
C	-7.52512	0.34523	0.76881
H	-7.66217	-0.34813	1.59479
H	-7.73929	1.35395	1.11269
C	-8.51503	-0.00467	-0.37374
H	-9.48714	0.23312	0.07772
C	-8.55417	-1.50055	-0.76791
H	-9.19875	-1.59316	-1.65111
H	-7.55909	-1.82312	-1.08049
C	-9.06578	-2.47595	0.31161
H	-8.94996	-3.49457	-0.0767
H	-8.4189	-2.42429	1.18998
C	-10.53652	-2.27968	0.72235
H	-10.67278	-1.29435	1.17934
H	-11.1675	-2.28995	-0.17418
C	-11.02689	-3.35549	1.70424
H	-10.426	-3.35541	2.61726
H	-12.06857	-3.19234	1.98976
H	-10.95428	-4.35258	1.262
C	-8.41238	0.92308	-1.61822
H	-8.26012	1.94904	-1.27743
H	-9.38712	0.90093	-2.11803

C	-7.33806	0.57324	-2.66401
H	-6.33159	0.57748	-2.24684
H	-7.50913	-0.41015	-3.10571
H	-7.35644	1.30448	-3.47529
O	-1.4605	3.92935	-1.30501
C	-1.91074	5.16337	-0.77271
C	-1.955	5.38754	0.60282
C	-2.23289	6.17555	-1.667
C	-2.34747	6.63891	1.07315
H	-1.6841	4.59902	1.29062
C	-2.61519	7.42862	-1.17669
H	-2.18442	5.98144	-2.72889
C	-2.69779	7.68741	0.20032
H	-2.37587	6.79583	2.14229
H	-2.86228	8.19906	-1.89083
C	-1.71087	-4.44664	0.27246
C	-1.6925	-5.38204	1.29843
C	-2.25038	-4.76633	-0.97297
C	-2.22992	-6.65433	1.07737
H	-1.26325	-5.11484	2.25344
C	-2.78989	-6.03557	-1.17229
H	-2.24294	-4.037	-1.77072
C	-2.80288	-7.00877	-0.15386
H	-2.20452	-7.36344	1.89029
H	-3.20265	-6.26734	-2.14406
O	-1.08871	-3.19488	0.50499
C	-3.09707	9.06656	0.77092

C	-4.25105	8.95577	1.8307
H	-4.27301	9.91339	2.36407
H	-3.92535	8.21936	2.57092
C	-1.85869	9.63174	1.53348
H	-1.5902	9.00476	2.38492
H	-0.99434	9.68747	0.8692
H	-2.07119	10.63601	1.90687
C	-3.43358	10.08308	-0.34178
H	-4.23103	9.74211	-1.00019
H	-3.74991	11.02649	0.10544
H	-2.55437	10.2884	-0.95652
C	-5.73782	8.61391	1.47113
C	-5.8804	7.41047	0.51442
H	-6.93757	7.17	0.37653
H	-5.45674	7.61714	-0.46835
H	-5.38796	6.52044	0.90866
C	-6.43028	8.25307	2.81269
H	-7.49306	8.05585	2.65518
H	-5.98434	7.35967	3.25597
H	-6.3418	9.07056	3.53326
C	-6.48833	9.83249	0.87918
H	-7.55337	9.60418	0.78945
H	-6.38892	10.7066	1.5282
H	-6.12834	10.10368	-0.11155
C	-3.3779	-8.41554	-0.43444
C	-4.83329	-8.35543	-1.02231
H	-5.04245	-9.35104	-1.4308

H	-4.79295	-7.69014	-1.88949
C	-2.4893	-9.06814	-1.53856
H	-2.81822	-10.09161	-1.73216
H	-2.54267	-8.51278	-2.4759
H	-1.44529	-9.09619	-1.22118
C	-3.29767	-9.33556	0.80319
H	-2.25797	-9.51722	1.08431
H	-3.81322	-8.92306	1.66894
H	-3.75008	-10.3013	0.57362
C	-6.09438	-7.94263	-0.18893
C	-5.88265	-6.67116	0.66121
H	-6.82199	-6.38561	1.14143
H	-5.14207	-6.82247	1.44679
H	-5.55353	-5.82796	0.0524
C	-6.59026	-9.09237	0.72344
H	-7.551	-8.82388	1.16989
H	-6.73481	-10.01185	0.14992
H	-5.89984	-9.3057	1.53749
C	-7.2162	-7.65535	-1.22235
H	-8.1527	-7.41251	-0.71532
H	-6.95107	-6.81073	-1.86258
H	-7.394	-8.52387	-1.86221
O	4.56815	-0.63097	-0.82251
O	4.2735	1.50093	-2.29653
C	5.41241	-1.71715	-0.48466
C	6.1609	-1.65288	0.6831
C	5.55204	-2.78834	-1.36397

C	7.05855	-2.6844	0.97921
H	6.05206	-0.80127	1.33912
C	6.45028	-3.8087	-1.05444
H	4.97573	-2.81005	-2.27801
C	7.22452	-3.78469	0.12255
H	7.63197	-2.61199	1.89038
H	6.54967	-4.63043	-1.74924
C	5.28778	2.0849	-1.51541
C	5.06118	2.7034	-0.28729
C	6.57196	2.03084	-2.04795
C	6.13689	3.2756	0.39555
H	4.06718	2.74018	0.13446
C	7.63322	2.61085	-1.35234
H	6.72401	1.53408	-2.99503
C	7.44537	3.25629	-0.11764
H	5.93722	3.74731	1.34816
H	8.61746	2.55288	-1.79171
C	8.19559	-4.95272	0.43818
C	8.61091	3.87266	0.68964
C	8.3171	5.35153	1.12956
H	7.35475	5.3373	1.64951
H	9.05799	5.59964	1.899
C	7.27444	-6.20132	0.72129
H	6.78098	-6.4311	-0.22834
H	6.4767	-5.85949	1.38921
C	8.28135	6.56636	0.14112
C	9.702	7.029	-0.26721

H	10.20871	6.30598	-0.90348
H	9.64203	7.96916	-0.82158
H	10.32537	7.20163	0.61416
C	7.44517	6.29855	-1.12867
H	7.88374	5.51757	-1.74913
H	6.42893	5.98942	-0.87992
H	7.38354	7.20983	-1.73017
C	7.62154	7.73545	0.92042
H	7.60862	8.64345	0.31286
H	6.59034	7.4938	1.18875
H	8.16911	7.95367	1.84119
C	8.7535	3.05032	2.00758
H	9.605	3.40884	2.59107
H	7.85927	3.1329	2.62699
H	8.91129	1.99461	1.77961
C	9.95973	3.75438	-0.05505
H	10.74593	4.24441	0.52147
H	10.24346	2.70648	-0.17539
H	9.93671	4.20977	-1.04393
C	9.11027	-5.16847	-0.80021
H	9.58528	-4.22619	-1.08056
H	9.89673	-5.89029	-0.59106
H	8.55024	-5.52919	-1.66373
C	9.10437	-4.60622	1.63728
H	9.8511	-5.38484	1.78448
H	9.64071	-3.6724	1.45517
H	8.5438	-4.50239	2.56702

C	7.77516	-7.56556	1.312
C	6.60457	-8.56551	1.10655
H	6.84577	-9.53429	1.55021
H	5.68793	-8.19835	1.57446
H	6.40292	-8.72082	0.04403
C	8.04665	-7.48094	2.83432
H	8.91266	-6.86615	3.071
H	7.18306	-7.06768	3.3614
H	8.23327	-8.48057	3.23531
C	9.02024	-8.14084	0.60087
H	8.87562	-8.18997	-0.4804
H	9.91564	-7.55096	0.79884
H	9.21298	-9.15617	0.95705

Table S5: Calculated energies of Kohn-Sham molecular orbitals (MO) of **3b** using DFT B3LYP as a basis set.

MO's	**Energy/ Hartree**	**Energy/ eV**
LUMO+4	-0.02989	-0.81335
LUMO+3	-0.03998	-1.08791
LUMO+2	-0.05190	-1.41227
LUMO+1	-0.05619	-1.52901
LUMO	-0.11413	-3.10564
HOMO	-0.20349	-5.5372
HOMO-1	-0.22879	-6.22569
HOMO-2	-0.23719	-6.45427
HOMO-3	-0.24503	-6.66761
HOMO-4	-0.25081	-6.82489

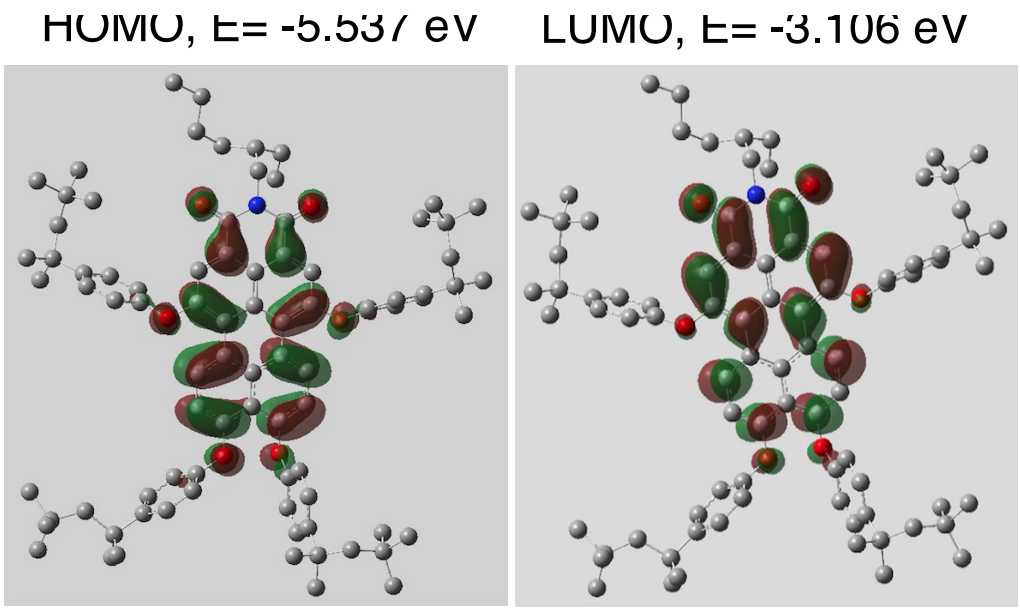


Fig. S10: Energy optimized Kuhn-Sham HOMO and LUMO of compound **3b** .

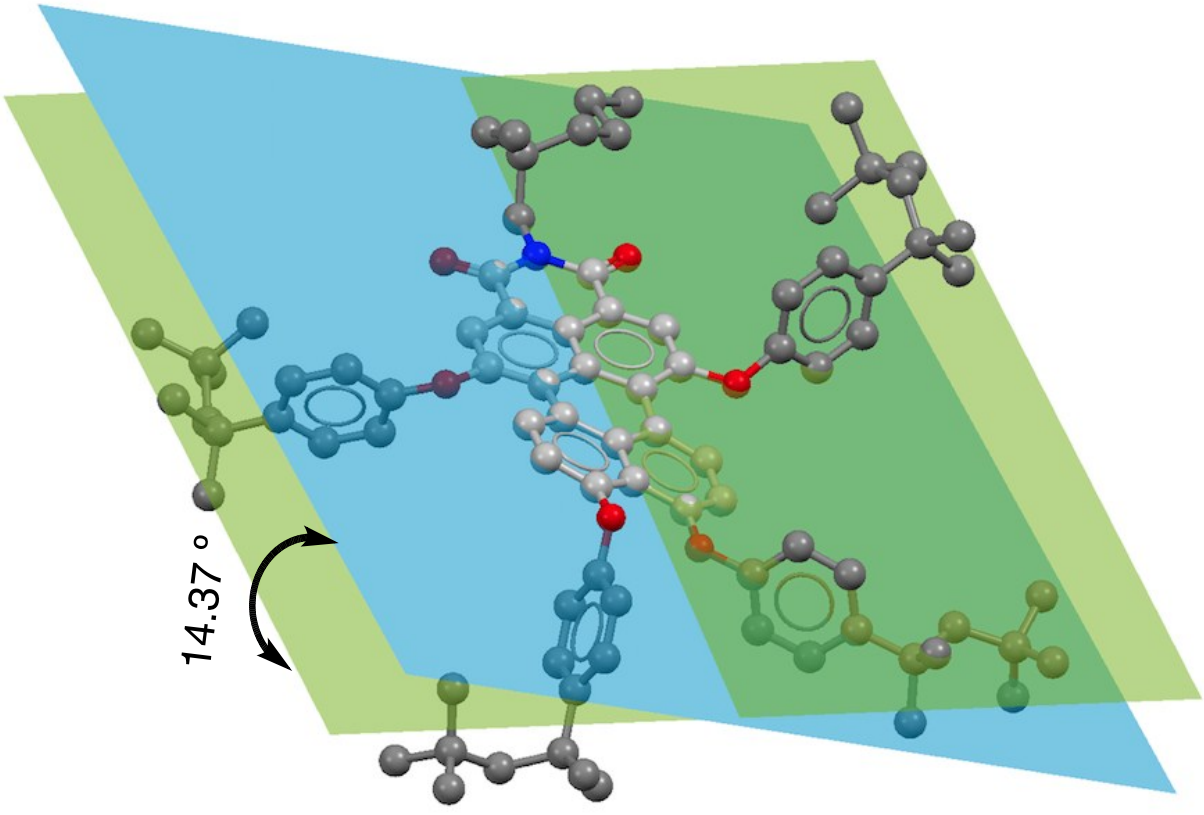


Fig. S11: Shows the twisting of perylene core from the energy-optimized structure of **3b** calculated by DFT at the B3LYP/6-311G level

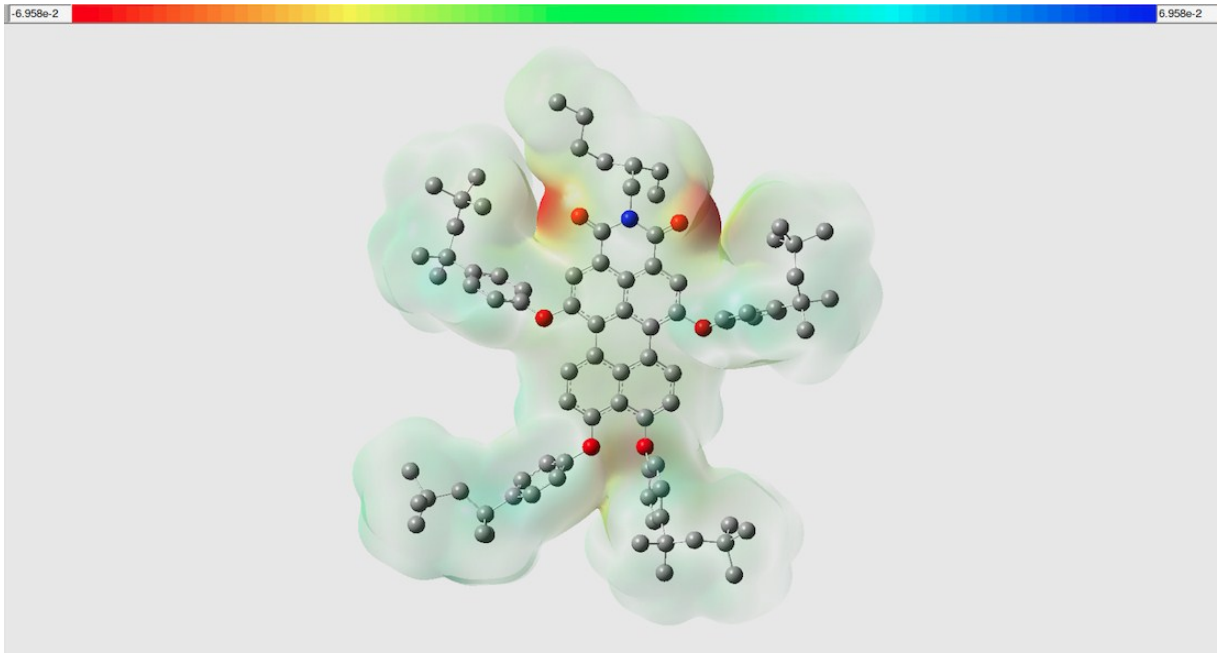


Fig. S12: Computed electrostatic potentials map **3b**; red color indicates more negative charge.

Symbolic Z-matrix for the optimized configuration of **3c**:

Charge = 0 Multiplicity = 1

C	1.2231	-1.78592	0.2462
C	0.38154	-0.76911	-0.21409
C	0.98163	0.37621	-0.84375
C	2.40518	0.38873	-1.10848
C	3.19326	-0.69964	-0.61815
C	2.60747	-1.74533	0.06329
H	0.80046	-2.63071	0.75453
C	0.1805	1.50928	-1.21755
C	2.93879	1.47258	-1.86639
H	3.21917	-2.54531	0.45049
C	2.12666	2.49193	-2.31023
C	0.77022	2.52304	-1.97868
H	2.56268	3.27047	-2.91874
H	0.17444	3.35061	-2.31208
C	-1.23007	1.55708	-0.8096
C	-1.07787	-0.83124	-0.07114
C	-1.85401	0.35885	-0.31079
C	-1.79334	-1.99279	0.29661
C	-2.03205	2.71689	-0.87145
C	-4.02061	1.53993	-0.18087
C	-3.26074	0.35509	-0.04057
C	-3.90656	-0.83181	0.37521
C	-3.17051	-1.99056	0.5257
H	-3.67558	-2.89228	0.83642
C	-3.39688	2.70706	-0.57378
H	-3.98208	3.60985	-0.65984
C	-5.34914	-0.85475	0.65883
C	-5.46478	1.55616	0.10128
N	-6.06904	0.33418	0.4514
O	-5.92928	-1.8866	1.06826
O	-6.14241	2.60724	0.03557
C	-7.52512	0.34523	0.76881

H	-7.66217	-0.34813	1.59479
H	-7.73929	1.35395	1.11269
C	-8.51503	-0.00467	-0.37374
H	-9.48714	0.23312	0.07772
C	-8.55417	-1.50055	-0.76791
H	-9.19875	-1.59316	-1.65111
H	-7.55909	-1.82312	-1.08049
C	-9.06578	-2.47595	0.31161
H	-8.94996	-3.49457	-0.0767
H	-8.4189	-2.42429	1.18998
C	-10.53652	-2.27968	0.72235
H	-10.67278	-1.29435	1.17934
H	-11.1675	-2.28995	-0.17418
C	-11.02689	-3.35549	1.70424
H	-10.42601	-3.35541	2.61726
H	-12.06858	-3.19234	1.98976
H	-10.95428	-4.35258	1.262
C	-8.41238	0.92308	-1.61822
H	-8.26012	1.94904	-1.27744
H	-9.38712	0.90093	-2.11803
C	-7.33806	0.57324	-2.66401
H	-6.33159	0.57748	-2.24684
H	-7.50913	-0.41015	-3.10571
H	-7.35644	1.30448	-3.47529
C	-1.91074	5.16337	-0.77271
C	-1.955	5.38754	0.60282
C	-2.23289	6.17555	-1.667
C	-2.34747	6.63891	1.07315
H	-1.6841	4.59902	1.29062
C	-2.61519	7.42862	-1.17669
H	-2.18442	5.98144	-2.72889
H	-2.37587	6.79583	2.14229
H	-2.86228	8.19906	-1.89083
C	-1.71087	-4.44664	0.27246

C	-1.6925	-5.38204	1.29843
C	-2.25038	-4.76633	-0.97297
C	-2.22992	-6.65433	1.07737
H	-1.26325	-5.11484	2.25344
C	-2.78989	-6.03557	-1.17229
H	-2.24294	-4.037	-1.77072
C	-2.80289	-7.00877	-0.15386
H	-2.20452	-7.36344	1.89029
H	-3.20265	-6.26734	-2.14406
C	5.41241	-1.71715	-0.48466
C	6.1609	-1.65288	0.6831
C	5.55204	-2.78834	-1.36397
C	7.05855	-2.6844	0.97921
H	6.05206	-0.80127	1.33912
C	6.45028	-3.8087	-1.05444
H	4.97573	-2.81005	-2.27801
H	7.63197	-2.61199	1.89038
H	6.54967	-4.63043	-1.74924
C	5.28778	2.0849	-1.51541
C	5.06118	2.7034	-0.28729
C	6.57197	2.03084	-2.04795
C	6.13689	3.2756	0.39555
H	4.06718	2.74018	0.13446
C	7.63322	2.61085	-1.35234
H	6.72401	1.53408	-2.99503
C	7.44537	3.25629	-0.11764
H	5.93722	3.74731	1.34816
H	8.61746	2.55288	-1.79171
S	-1.08871	-3.19488	0.50499
S	-1.4605	3.92935	-1.30501
S	4.56816	-0.63097	-0.82251
S	4.2735	1.50093	-2.29653
C	-2.69779	7.68741	0.20032
H	-3.07244	8.61897	0.57008

H	-3.201	-7.98277	-0.34812
H	8.25206	3.68289	0.44109
C	7.22452	-3.78469	0.12255
H	7.86412	-4.60145	0.38468

Table S6: Calculated energies of Kohn-Sham molecular orbitals (MO) of **3c** using DFT B3LYP as a basis set.

MO's	Energy/ Hartree	Energy/ eV
LUMO+4	-0.03736	-1.01662
LUMO+3	-0.04413	-1.20084
LUMO+2	-0.04635	-1.26125
LUMO+1	-0.05966	-1.62344
LUMO	-0.12106	-3.29421
HOMO	-0.21077	-5.73534
HOMO-1	-0.23845	-6.48855
HOMO-2	-0.24015	-6.53481
HOMO-3	-0.24937	-6.78570
HOMO-4	-0.25890	-7.04503

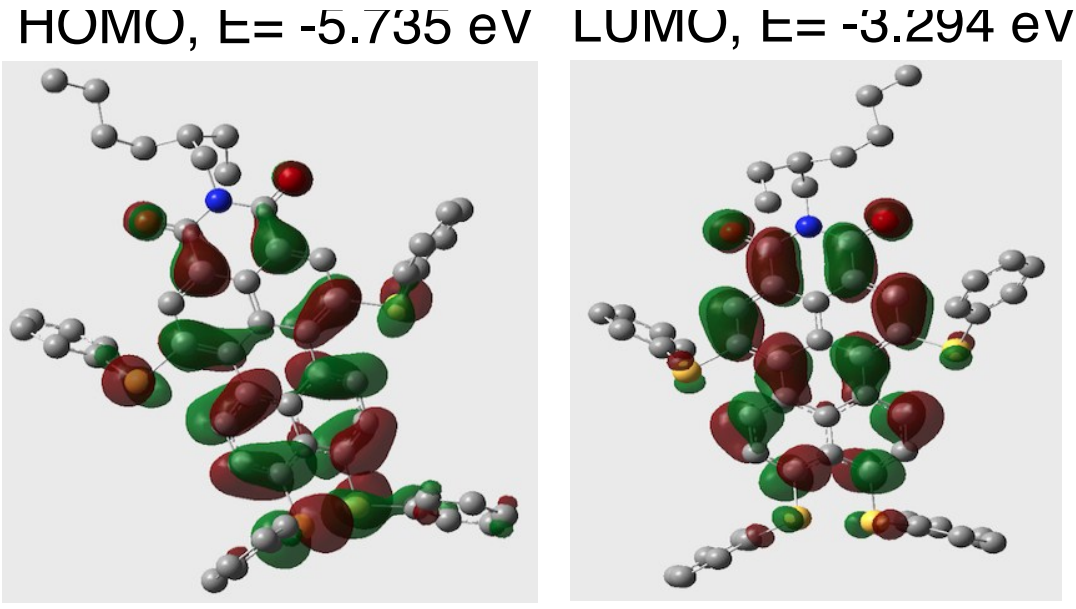


Fig. S13: Energy optimized Kuhn-Sham HOMO and LUMO of compound **3c**

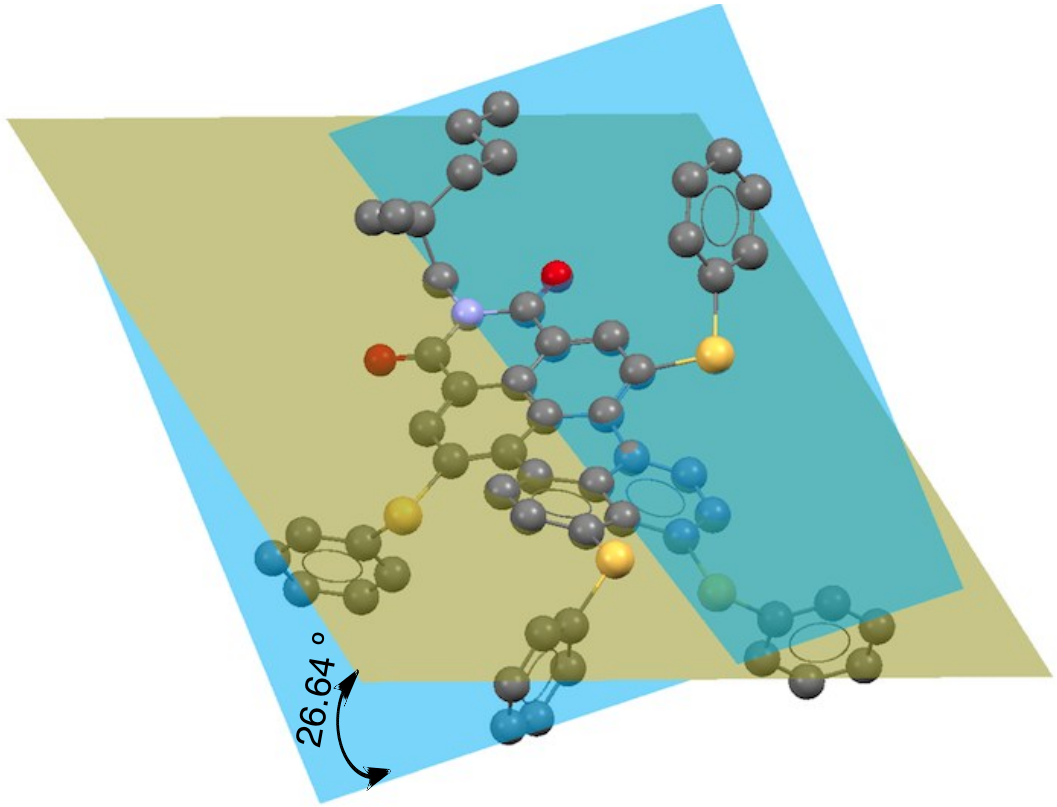


Fig. S14: Shows the twisting of perylene core from the energy-optimized structure of **3c** calculated by DFT at the B3LYP/6-311G level

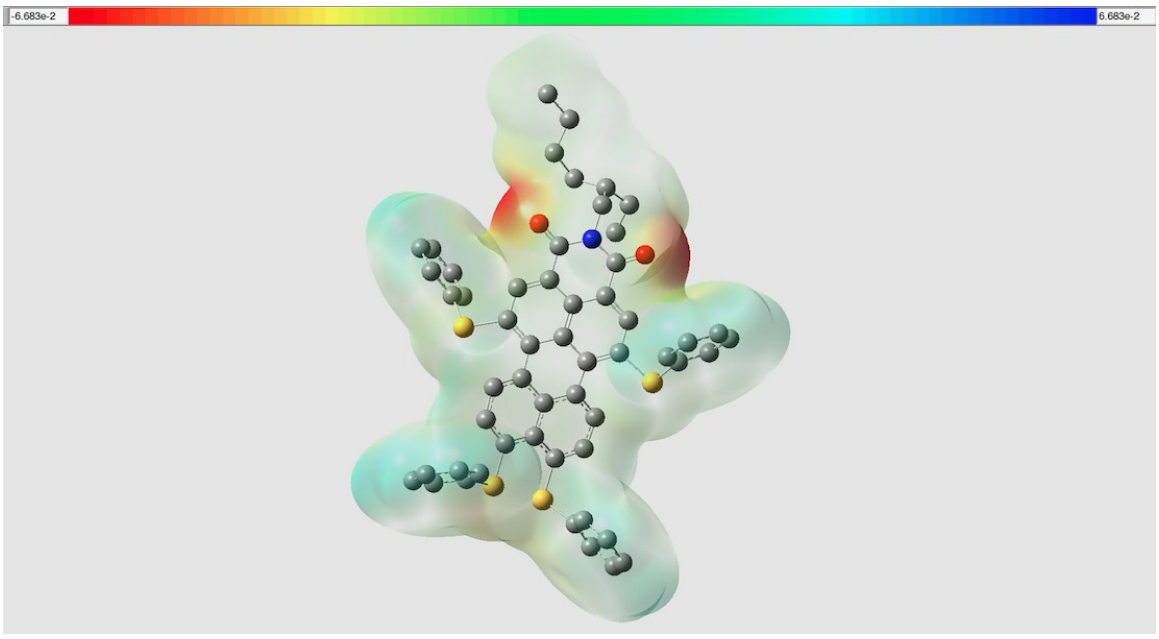


Fig. S15: Computed electrostatic potentials map **3c**; red color indicates more negative charge.

Symbolic Z-matrix for the optimized configuration of **4a:**

Charge = 0 Multiplicity = 1

C	-1.97075	-2.1937	-1.19603
C	-1.27974	-1.11691	-0.59492
C	-2.07568	-0.04579	-0.07836
C	-3.50767	-0.20187	0.04861
C	-4.07672	-1.5121	-0.1983
C	-3.32254	-2.39127	-1.02264
H	-1.43165	-2.91283	-1.78665
C	-1.45071	1.18112	0.30871
C	-4.29579	0.95758	0.40835
H	-3.77274	-3.28017	-1.43154
C	-3.61778	2.01048	1.07967
C	-2.24691	2.11034	1.0174
H	-4.17176	2.80633	1.5494
H	-1.78461	2.95145	1.50233
C	-0.05754	1.40619	-0.00251
C	0.16135	-1.0431	-0.51296
C	0.76571	0.25569	-0.30742
C	1.05801	-2.14509	-0.60518
C	0.59303	2.67206	-0.04636
C	2.78075	1.68472	-0.31464
C	2.18669	0.40483	-0.41016
C	3.01144	-0.7248	-0.6159
C	2.42977	-1.98998	-0.67344
H	3.07723	-2.84862	-0.75734
C	1.96182	2.80499	-0.18167

H	2.42124	3.78069	-0.19624
C	4.45819	-0.59174	-0.72448
C	4.2236	1.85547	-0.41047
O	5.21432	-1.57459	-0.96142
O	4.77699	2.99053	-0.37415
C	6.48189	0.85361	-0.65282
H	6.82006	0.11991	-1.37951
H	6.63749	1.84829	-1.06074
C	7.31944	0.71984	0.648
H	8.31256	1.05534	0.3231
C	7.47955	-0.72843	1.17021
H	7.95484	-0.67908	2.15757
H	6.49408	-1.17088	1.32522
C	8.31417	-1.67184	0.2802
H	8.20549	-2.69139	0.66853
H	7.89589	-1.69335	-0.72948
C	9.81574	-1.33741	0.21715
H	9.96058	-0.33333	-0.19351
H	10.21974	-1.31322	1.23568
C	10.61531	-2.34305	-0.62597
H	10.25237	-2.36599	-1.65695
H	11.67692	-2.08726	-0.65194
H	10.52533	-3.35432	-0.22041
C	6.91195	1.70211	1.7829
H	6.70237	2.67771	1.33969
H	7.78967	1.83272	2.42521
C	5.72965	1.28571	2.67641

H	4.80744	1.15064	2.11265
H	5.93396	0.35298	3.20489
H	5.54328	2.05412	3.43062
N	5.00485	0.6913	-0.54503
Br	0.50368	-4.03997	-0.47185
Br	-0.35766	4.40693	-0.09733
C	-6.47828	2.15152	0.64397
H	-6.11814	2.43935	1.62635
H	-8.14135	1.40526	-1.48693
H	-5.76704	4.05641	-0.14624
C	-6.21649	0.4393	-1.12217
C	-7.12379	1.43487	-1.88437
C	-6.57268	2.8677	-1.79023
C	-6.58543	3.35528	-0.31854
N	-5.62081	1.08414	0.07662
H	-6.77825	-0.45398	-0.84373
H	-5.3975	0.12244	-1.76636
H	-7.18641	1.10708	-2.92339
H	-5.54953	2.87951	-2.17604
H	-7.15332	3.54345	-2.41968
H	-7.51397	3.88731	-0.09764
H	-7.46352	1.70861	0.79581
C	-5.75791	-1.40538	1.65463
H	-4.96936	-0.80761	2.10408
C	-7.28667	-3.36978	0.4707
C	-7.28084	-3.42644	2.01512
H	-7.90299	-2.53624	0.1257

H	-7.16187	-4.45822	2.35231
C	-5.87571	-3.21111	-0.104
C	-6.13655	-2.55991	2.59346
H	-5.25176	-4.06338	0.18646
H	-5.92265	-3.1929	-1.19251
H	-7.72915	-4.2751	0.05267
H	-8.24577	-3.08225	2.3926
H	-5.2469	-3.17074	2.76387
H	-6.41866	-2.1396	3.56032
H	-6.61384	-0.74738	1.49146
N	-5.25124	-1.94045	0.36336

Table S7: Calculated energies of Kohn-Sham molecular orbitals (MO) of **4a** using DFT B3LYP as a basis set.

MO's	Energy/ Hartree	Energy/ eV
LUMO+4	-0.031616	-0.86032
LUMO+3	-0.03653	-0.99403
LUMO+2	-0.04802	-1.30669
LUMO+1	-0.05320	-1.44765
LUMO	-0.10458	-2.84577
HOMO	-0.18407	-5.00880
HOMO-1	-0.22144	-6.02569
HOMO-2	-0.24798	-6.74788
HOMO-3	-0.25832	-7.02925
HOMO-4	-0.26377	-7.17755

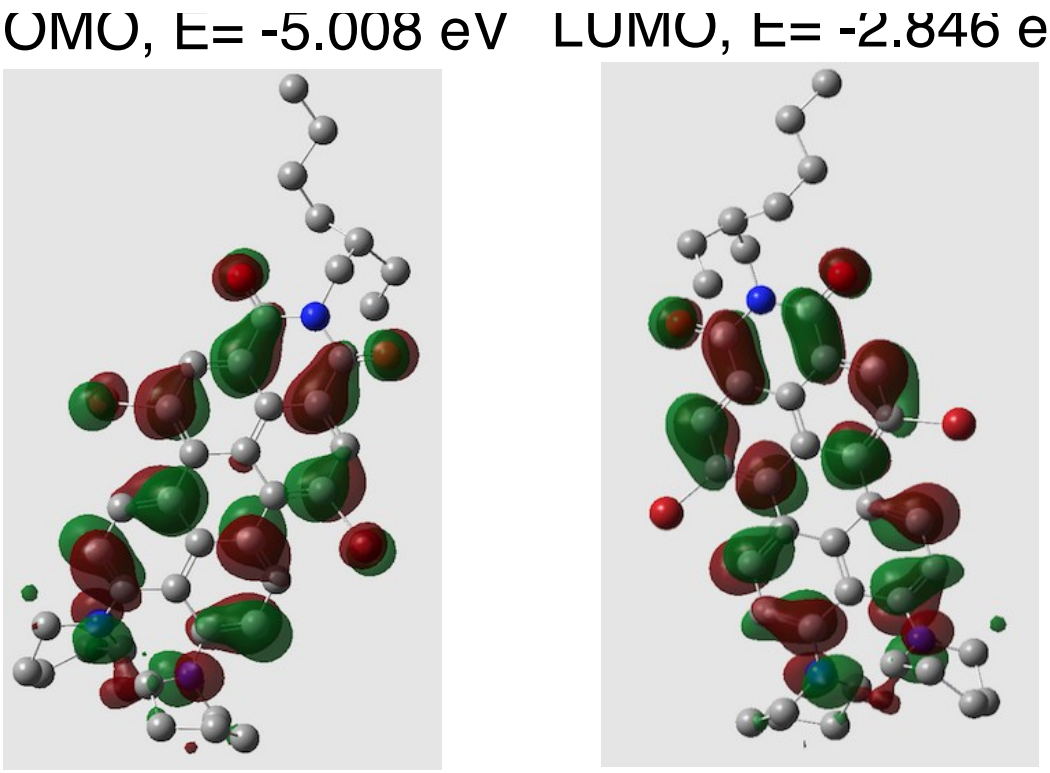


Fig. S16: Energy optimized Kuhn-Sham HOMO and LUMO of compound **4a**

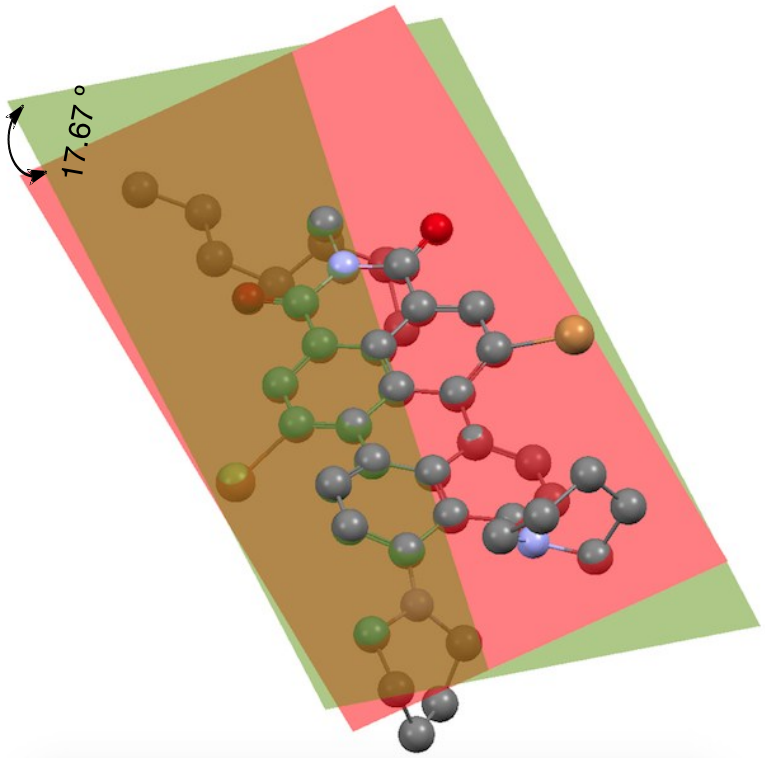


Fig. S17: Shows the twisting of perylene core from the energy-optimized structure of **4a** calculated by DFT at the B3LYP/6-311G level

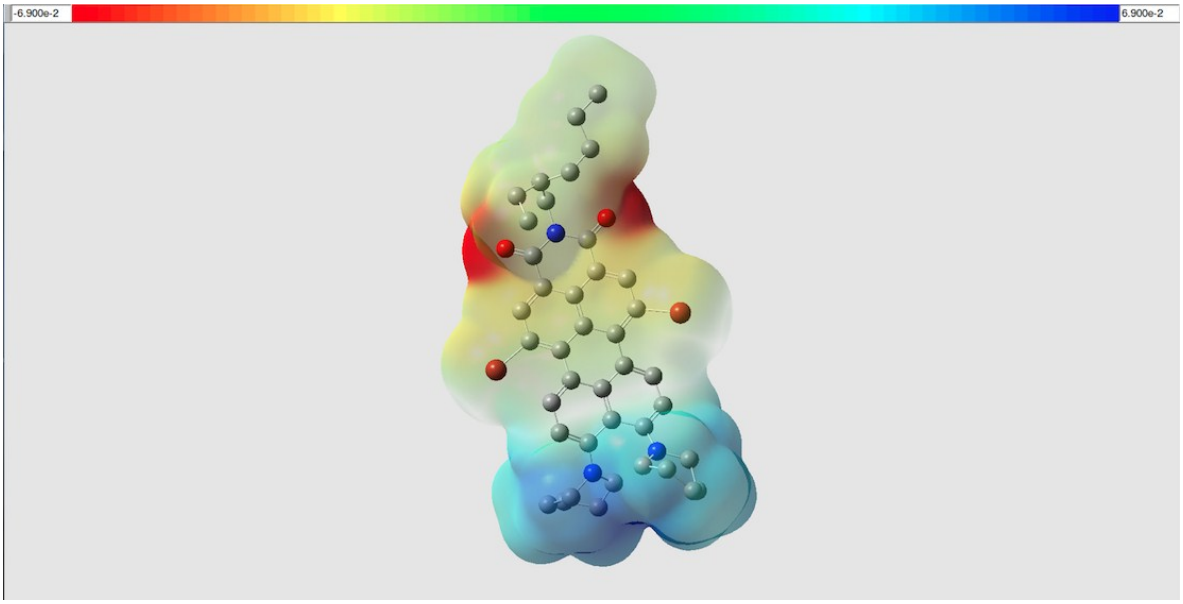


Fig. S18: Computed electrostatic potentials map **4a**; red color indicates more negative charge.

Symbolic Z-matrix for the optimized configuration of **5a**:

Charge = 0 Multiplicity = 1

C	-1.61907	4.54168	-0.92763
C	-0.64526	3.65597	-0.43815
C	0.5783	4.20807	0.06891
C	0.7065	5.63346	0.15896
C	-0.32956	6.47021	-0.32039
C	-1.46924	5.93478	-0.88035
H	-2.52237	4.14761	-1.35093
C	1.67872	3.38861	0.48885
C	1.8693	6.20614	0.72729
H	-2.25275	6.56658	-1.27131
C	2.8908	5.4112	1.20046
C	2.79074	4.01896	1.07054
H	3.77025	5.83979	1.6574
H	3.60667	3.42138	1.42786
C	1.58355	1.93788	0.29713
C	-0.81465	2.19916	-0.42311
C	0.31892	1.36525	-0.09966
C	-2.03629	1.54299	-0.70024
C	2.6662	1.04538	0.47338
C	1.29938	-0.89952	0.06779
C	0.18773	-0.06106	-0.17956
C	-1.05391	-0.6513	-0.51025
C	-2.14913	0.15456	-0.75581
H	-3.09478	-0.30293	-0.99943
C	2.5249	-0.33756	0.37081

H	3.37142	-0.98334	0.54188
C	-1.20147	-2.10907	-0.60238
C	1.17927	-2.36059	0.0018
N	-0.09058	-2.8979	-0.26798
O	-2.27875	-2.64953	-0.95906
O	2.16601	-3.11923	0.18236
C	-0.21847	-4.38205	-0.34975
H	-0.90376	-4.58667	-1.16775
H	0.76836	-4.744	-0.62324
C	-0.68525	-5.13466	0.92562
H	-0.50546	-6.1832	0.65719
C	-2.19534	-5.00148	1.23956
H	-2.37345	-5.44479	2.22675
H	-2.45989	-3.94613	1.3255
C	-3.14835	-5.67242	0.22919
H	-4.17147	-5.35602	0.46341
H	-2.94552	-5.297	-0.77739
C	-3.10771	-7.21156	0.22711
H	-2.10248	-7.56129	-0.02774
H	-3.31193	-7.576	1.24025
C	-4.11651	-7.83177	-0.75231
H	-3.91633	-7.50929	-1.77758
H	-4.07362	-8.92298	-0.73175
H	-5.13853	-7.5329	-0.50455
C	0.19405	-4.88246	2.18329
H	1.24347	-4.87954	1.88104
H	0.06413	-5.74682	2.8433

C	-0.10501	-3.61417	3.00263
H	0.0277	-2.7	2.42515
H	-1.1262	-3.61653	3.38711
H	0.56742	-3.55824	3.86193
O	3.92791	1.56607	0.80999
C	5.11118	0.83079	0.52217
C	5.51388	0.63516	-0.79806
C	5.8929	0.38916	1.58117
C	6.71397	-0.02899	-1.04787
H	4.90442	1.00144	-1.6122
C	7.09727	-0.27189	1.31158
H	5.5673	0.55915	2.59746
C	7.53014	-0.50828	-0.00334
H	7.01389	-0.1688	-2.07655
H	7.68828	-0.60838	2.14905
C	-4.47954	1.79392	-0.7536
C	-5.32926	1.64422	-1.84139
C	-4.91809	1.52455	0.54207
C	-6.64194	1.2064	-1.62781
H	-4.97284	1.86806	-2.83666
C	-6.22686	1.08448	0.73556
H	-4.25198	1.66434	1.38183
C	-7.11813	0.90417	-0.3416
H	-7.28468	1.09617	-2.48734
H	-6.5522	0.88489	1.74655
O	-3.17619	2.3175	-0.97793
C	8.87066	-1.20514	-0.32685

C	8.69643	-2.3784	-1.35637
H	9.70198	-2.62192	-1.717
H	8.17164	-1.9613	-2.2205
C	9.78439	-0.14994	-1.0252
H	9.36265	0.17844	-1.97619
H	9.91115	0.72668	-0.38702
H	10.77008	-0.57764	-1.22067
C	9.61192	-1.66266	0.94837
H	9.01581	-2.33089	1.5678
H	10.5274	-2.18779	0.67258
H	9.8961	-0.80348	1.55981
C	8.00482	-3.74301	-1.01802
C	6.65502	-3.58372	-0.28481
H	6.18189	-4.56229	-0.1659
H	6.77984	-3.15134	0.70817
H	5.96936	-2.94501	-0.8445
C	7.73874	-4.43702	-2.38084
H	7.3044	-5.42792	-2.22853
H	7.04499	-3.85138	-2.98873
H	8.66653	-4.55796	-2.94632
C	8.92671	-4.67753	-0.19627
H	8.47421	-5.66968	-0.11857
H	9.89908	-4.79034	-0.68244
H	9.09408	-4.31303	0.81546
C	-8.57147	0.45199	-0.07557
C	-8.63707	-0.84666	0.80518
H	-9.67206	-0.92671	1.15625

H	-8.04145	-0.6486	1.70068
C	-9.26071	1.57601	0.75948
H	-10.31127	1.32873	0.92618
H	-8.78347	1.70188	1.73221
H	-9.21209	2.52927	0.22959
C	-9.38357	0.30333	-1.38065
H	-9.49052	1.26736	-1.88258
H	-8.92791	-0.39143	-2.08441
H	-10.38548	-0.06104	-1.15018
C	-8.2318	-2.27044	0.29234
C	-6.88316	-2.29442	-0.45997
H	-6.6147	-3.32646	-0.70206
H	-6.92673	-1.73465	-1.3946
H	-6.08	-1.87181	0.14632
C	-9.32749	-2.90238	-0.60138
H	-9.07822	-3.94587	-0.81161
H	-10.29748	-2.88498	-0.09791
H	-9.43247	-2.39115	-1.55645
C	-8.09724	-3.15996	1.55731
H	-7.86944	-4.19149	1.27828
H	-7.29594	-2.79842	2.20625
H	-9.02584	-3.16302	2.13417
S	-0.08211	8.28387	-0.16899
S	1.94925	8.03909	0.80836

Table S8: Calculated energies of Kohn-Sham molecular orbitals (MO) of **5a** using DFT B3LYP as a basis set.

MO's	Energy/ Hartree	Energy/ eV
LUMO+4	-0.03938	-1.07158
LUMO+3	-0.05491	-1.49417
LUMO+2	-0.05871	-1.59758
LUMO+1	-0.10801	-2.93910
LUMO	-0.11576	-3.14999
HOMO	-0.19843	-5.39955
HOMO-1	-0.24160	-6.57427
HOMO-2	-0.24765	-6.73890
HOMO-3	-0.25282	-6.87958
HOMO-4	-0.25948	-7.06081

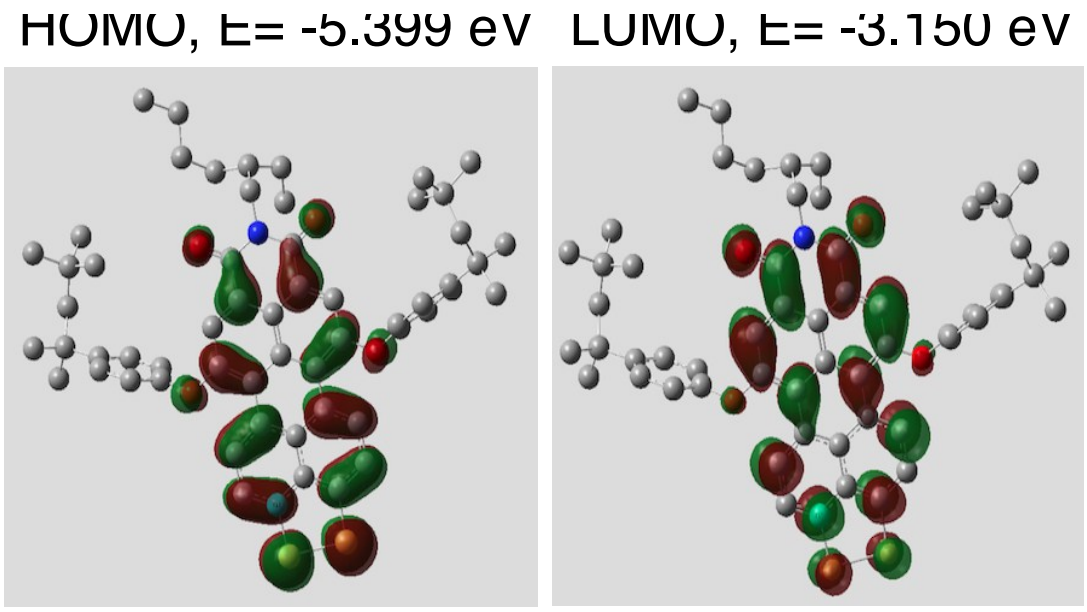


Fig. S19: Energy optimized Kuhn-Sham HOMO and LUMO of compound **5a**

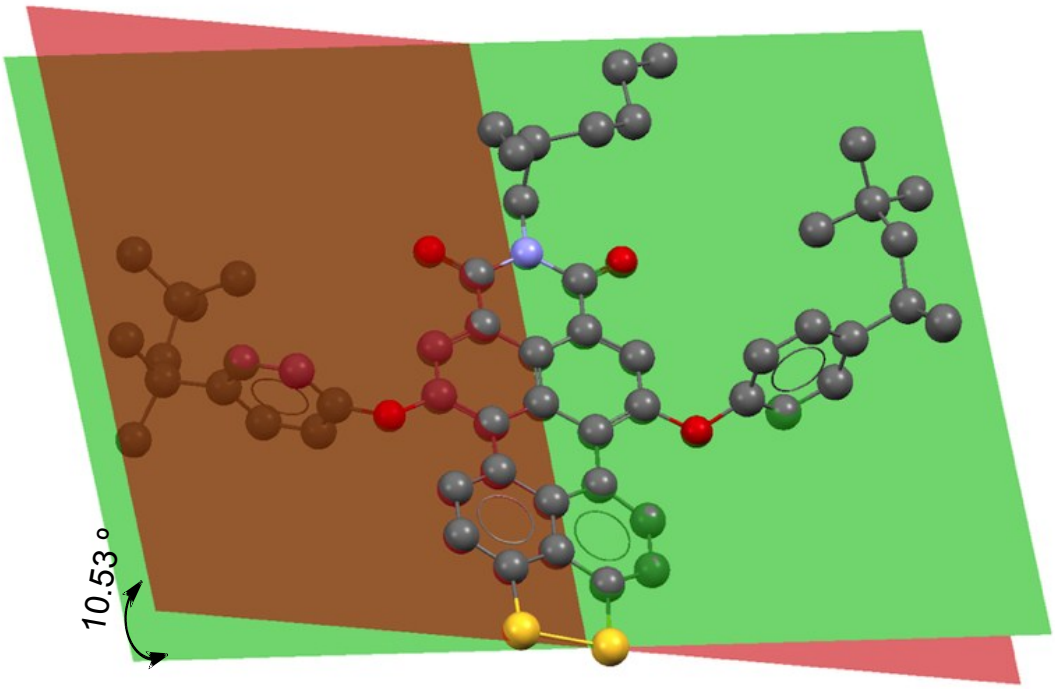


Fig. S20: Twisting of perylene core from the energy-optimized structure of **5a** calculated by DFT at the B3LYP/6-311G level

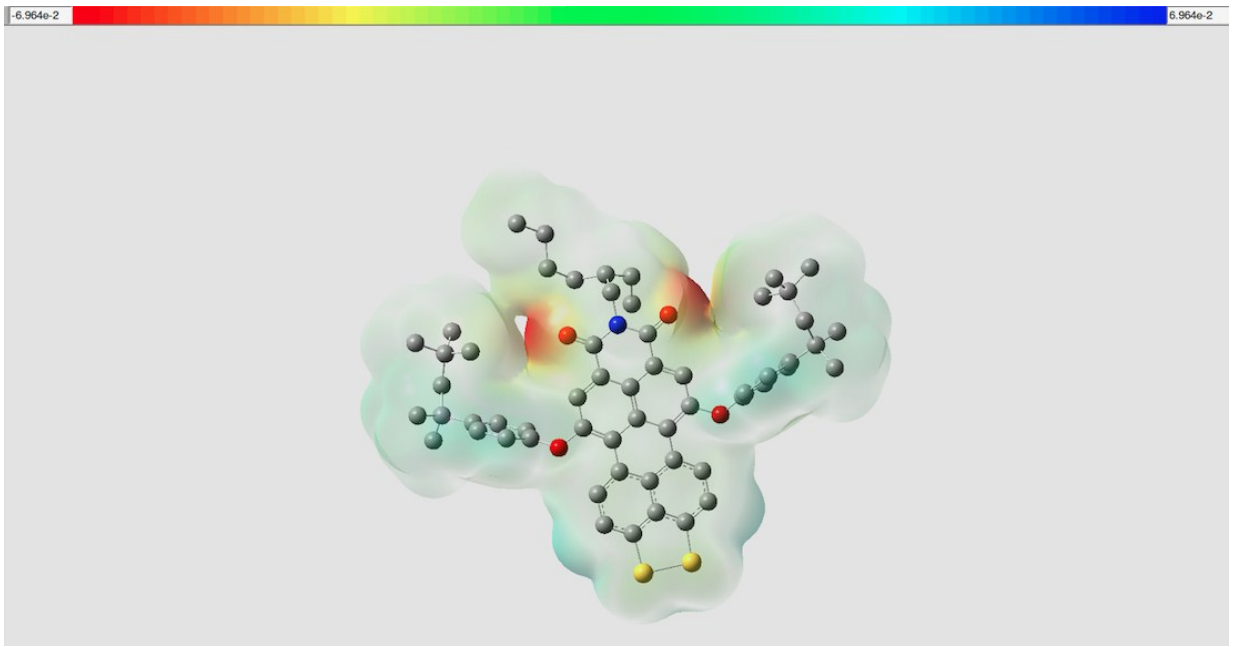


Fig. S21: Computed electrostatic potentials map **5a**; red color indicates more negative charge.

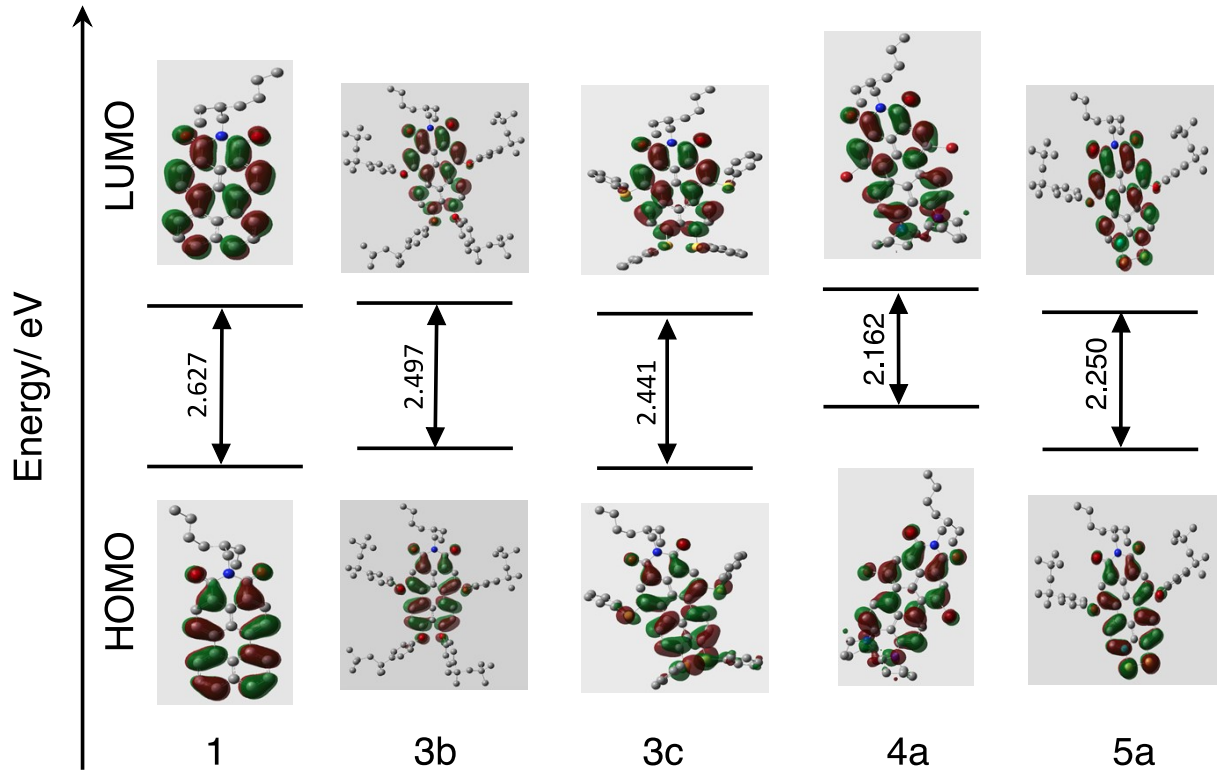


Fig. S22. Comparison of frontiers orbitals energy levels of PMI derivatives

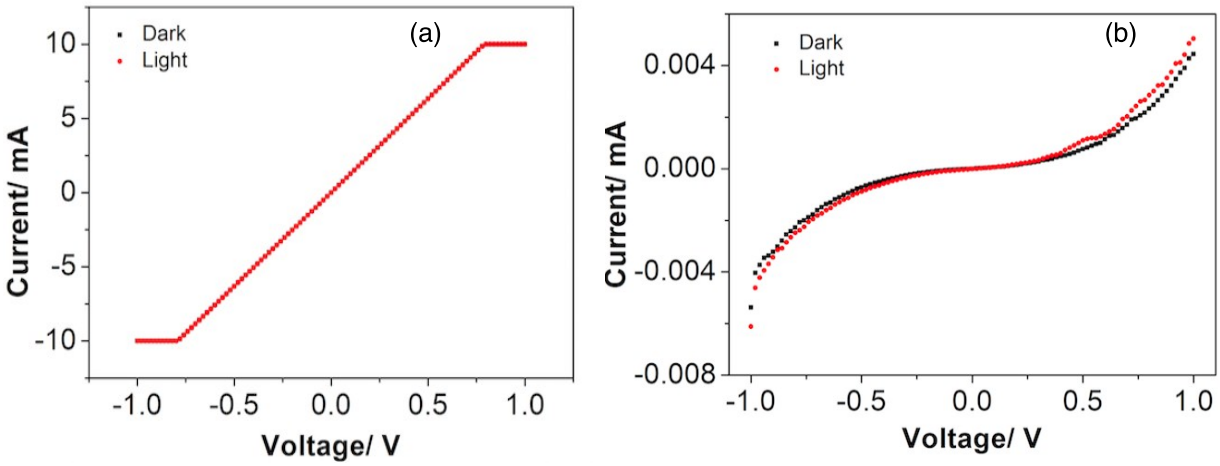


Fig. S23: Dark and light I-V characteristics of samples (a) **3a** and (b) **4a**

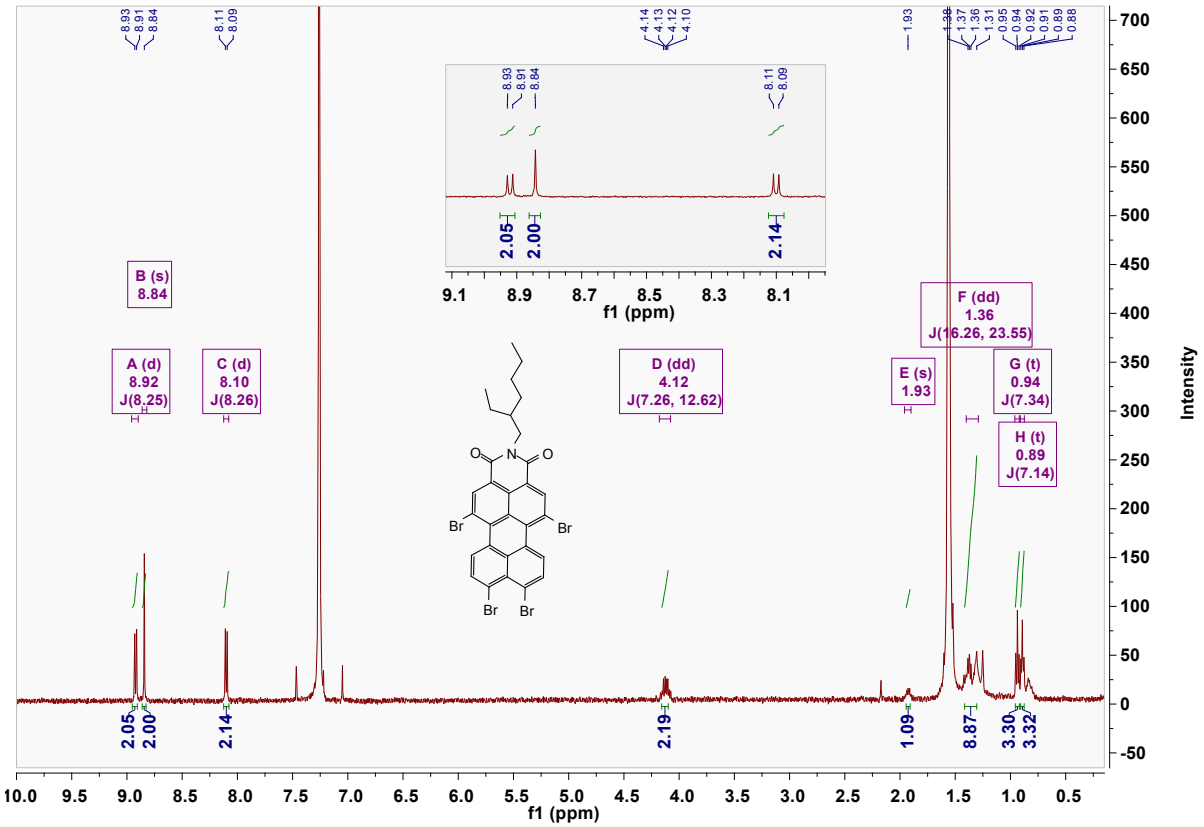


Fig. S24: ^{1}H NMR spectrum of compound **2**

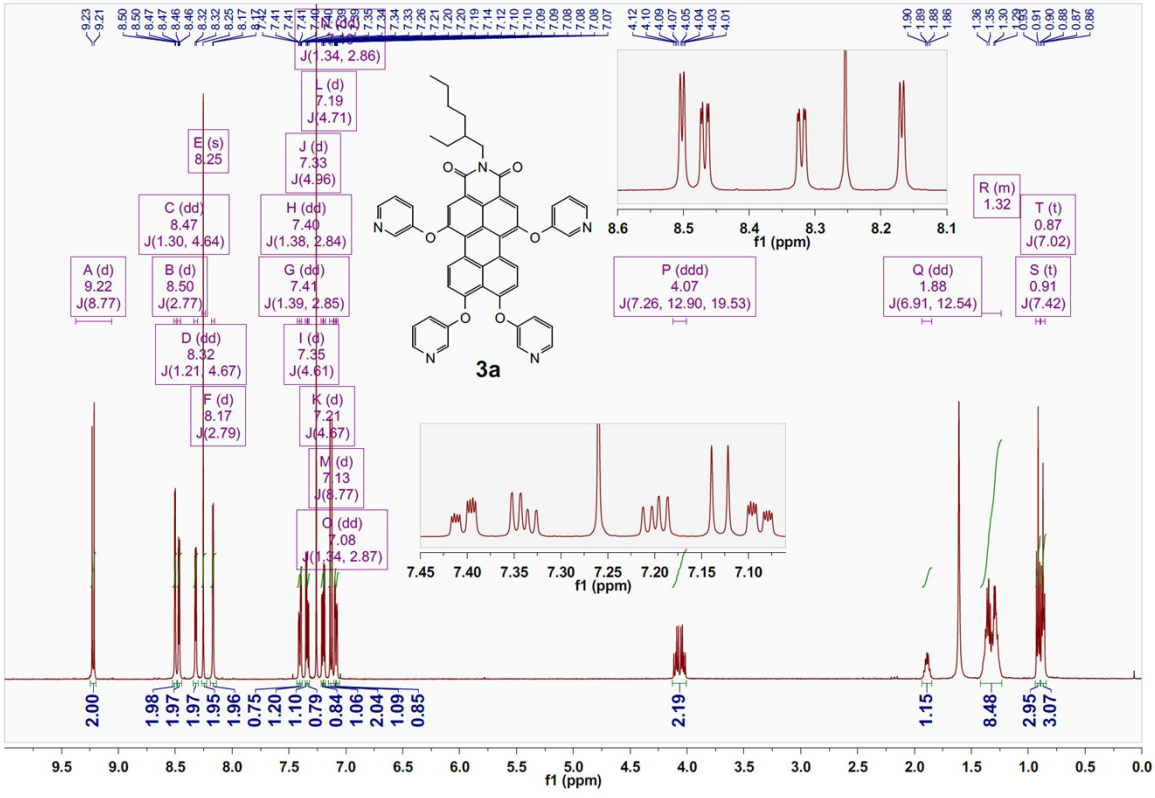


Fig. S25: ^{1}H NMR spectrum of compound **3a**

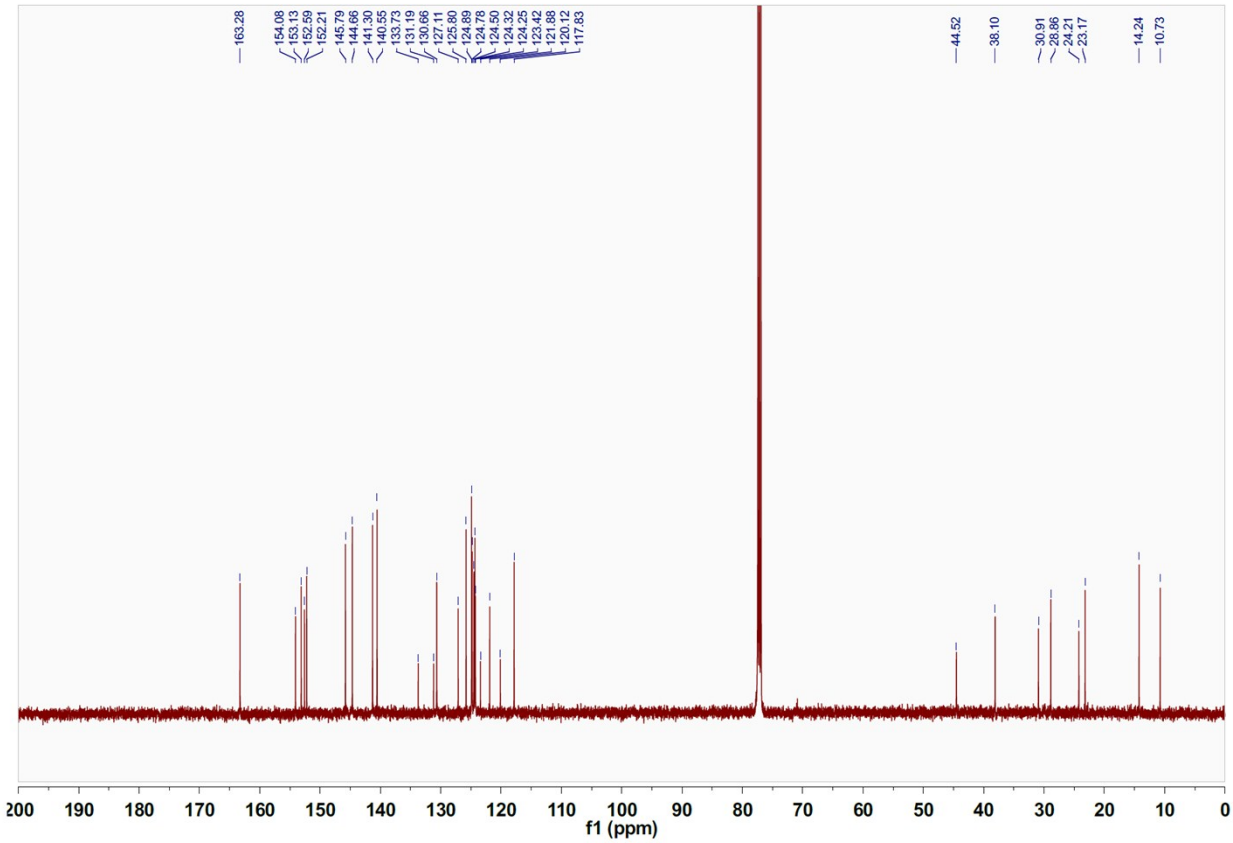


Fig. S26: ^{13}C NMR spectrum of compound **3a**

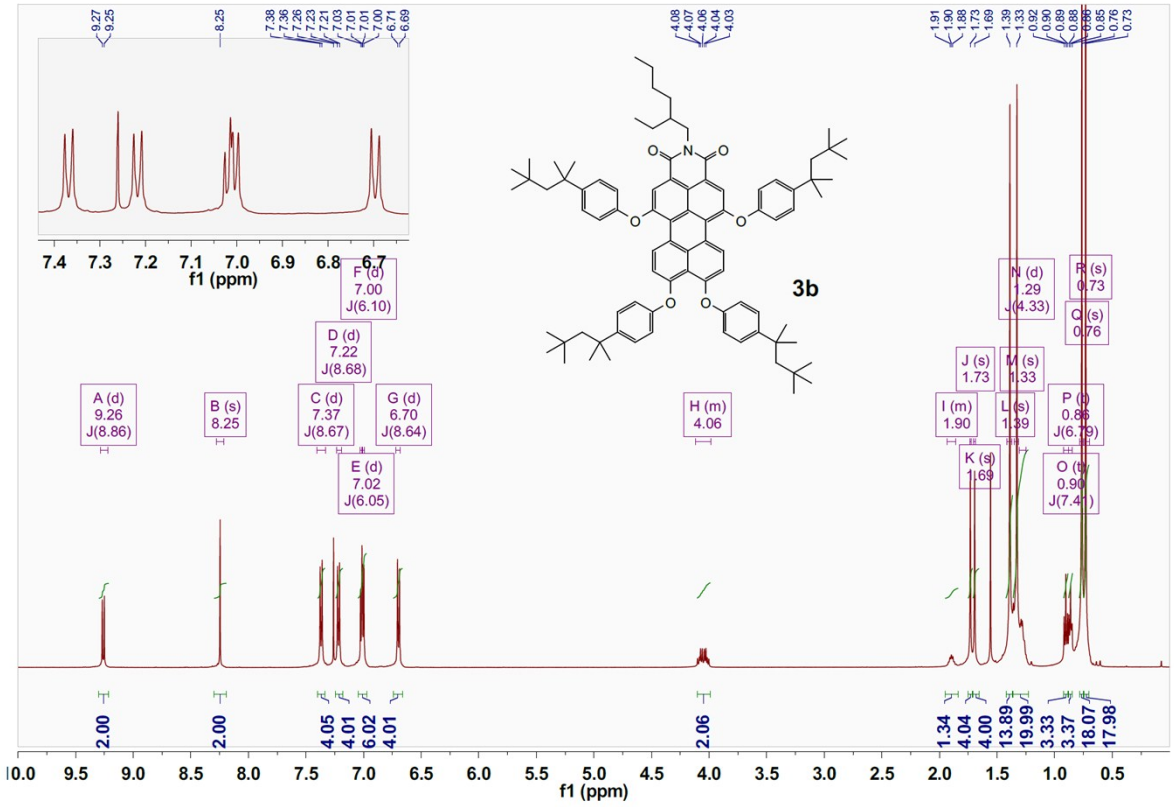


Fig. S27: ^{1}H NMR spectrum of compound **3b**

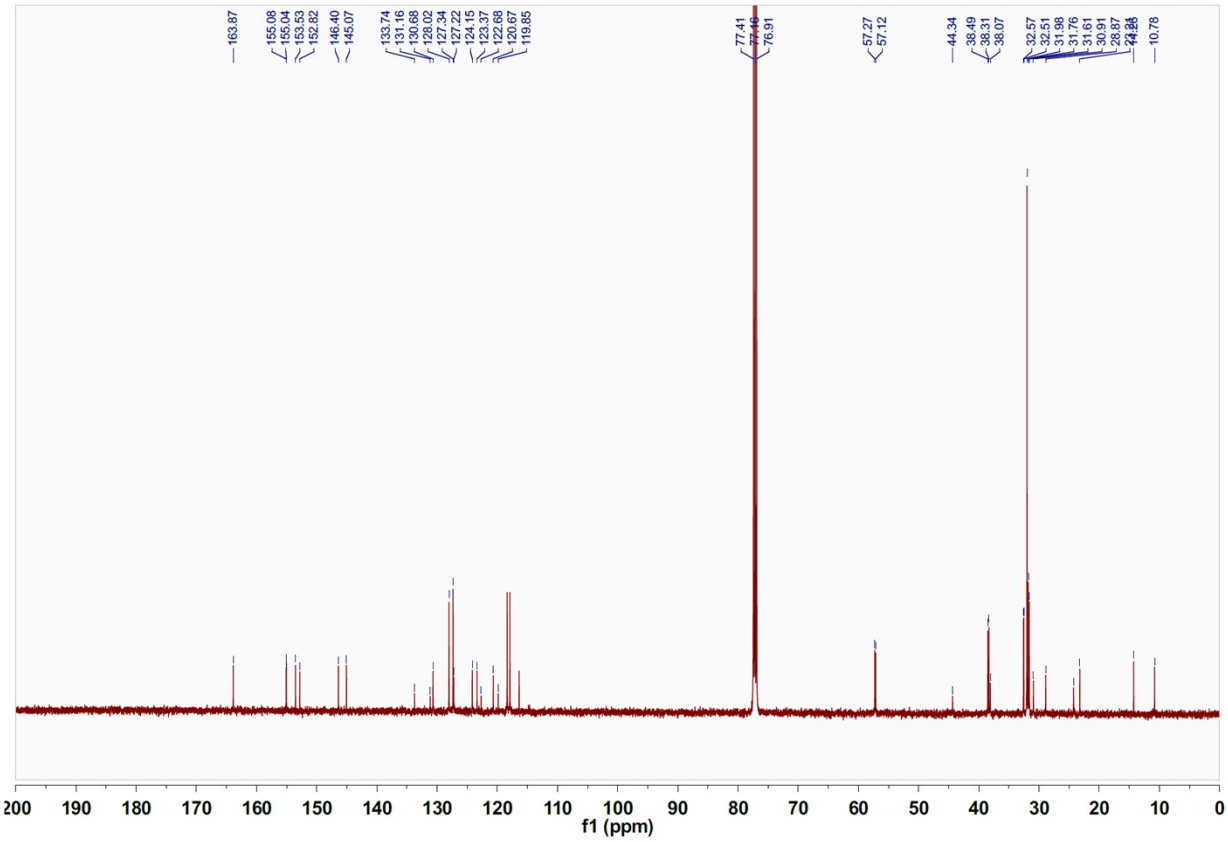


Fig. S28: ^{13}C NMR spectrum of compound **3b**

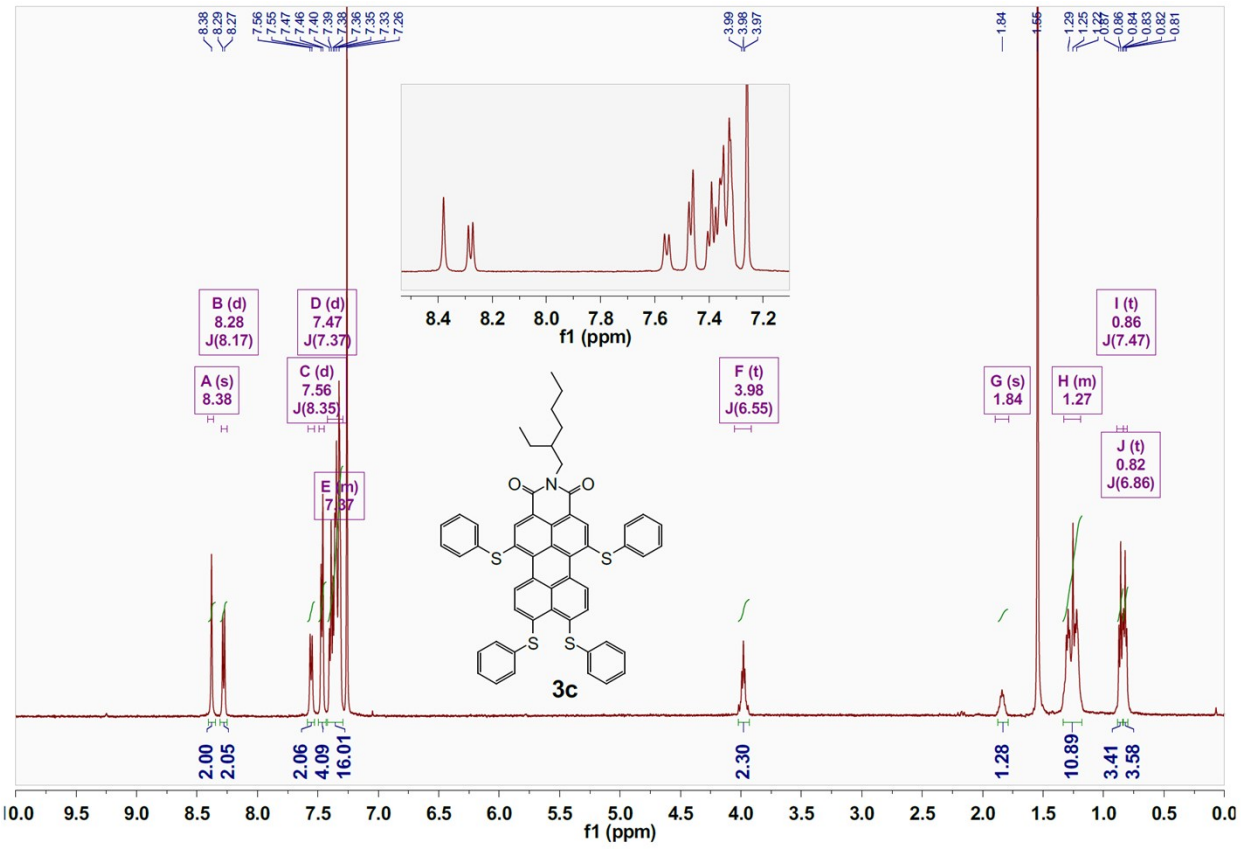


Fig. S29: ^{1}H NMR spectrum of compound **3c**

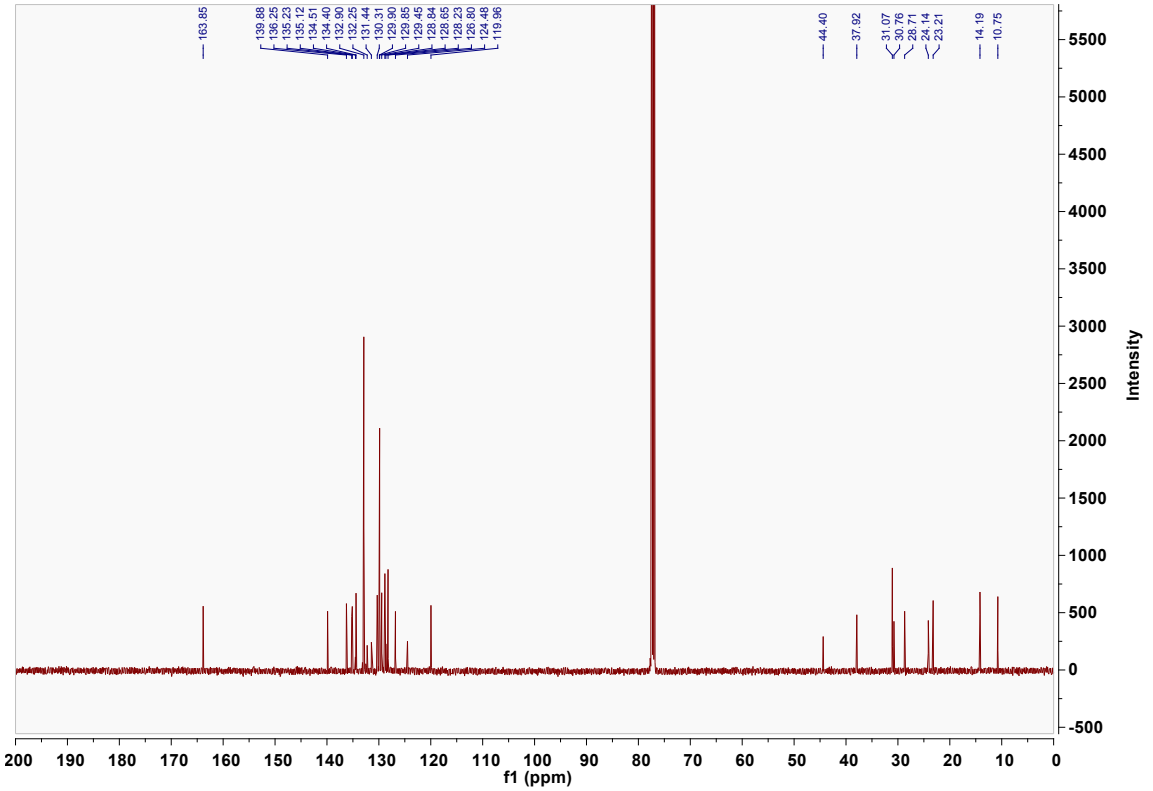


Fig. S30: ^{13}C NMR spectrum of compound **3c**

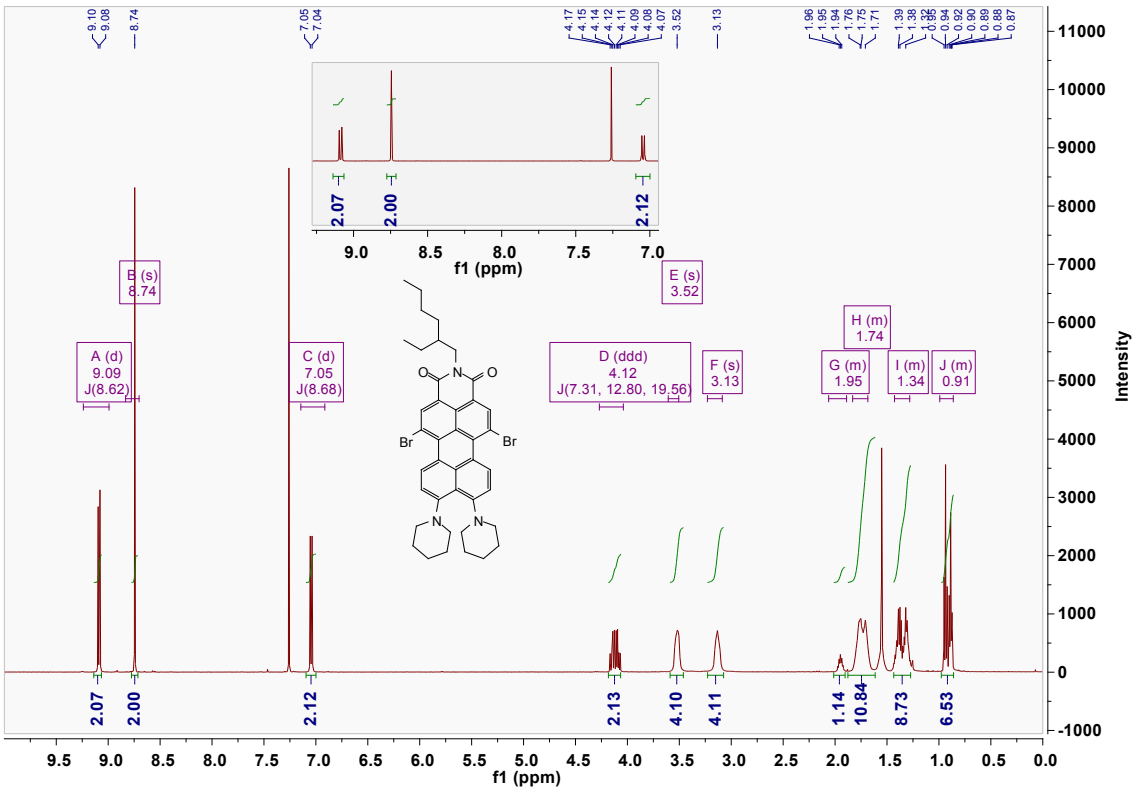


Fig. S31: ^{1}H NMR spectrum of compound **4a**

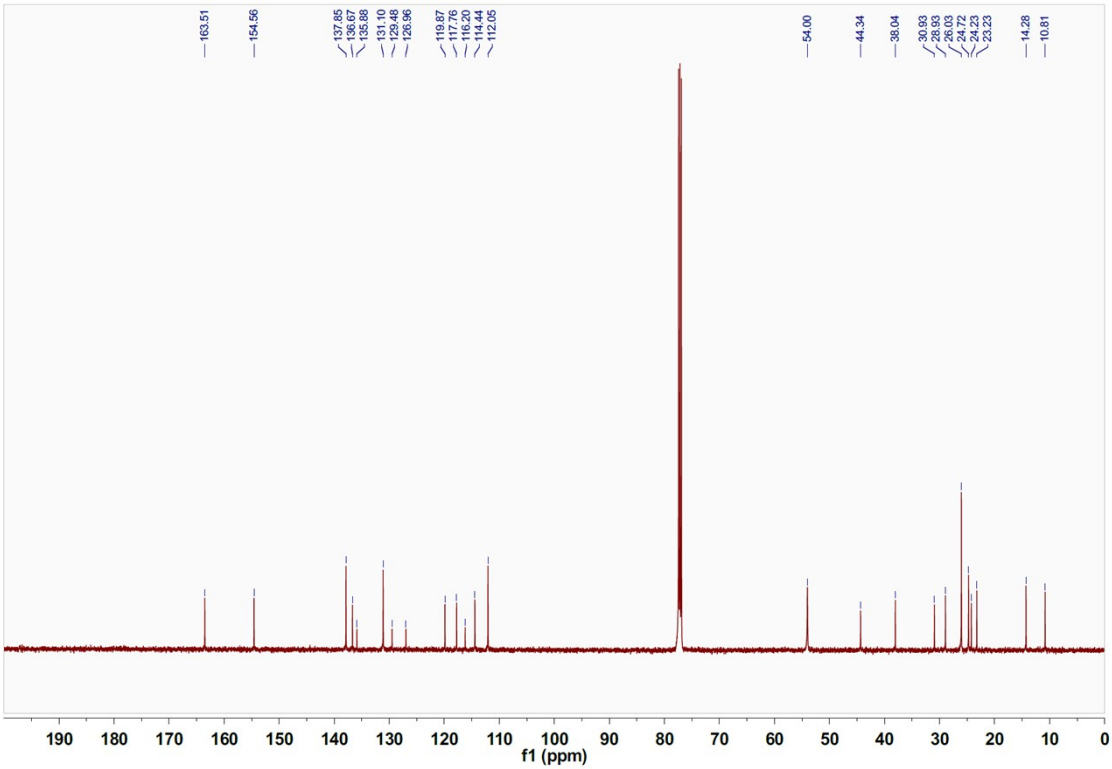


Fig. S32: ^{13}C NMR spectrum of compound **4a**

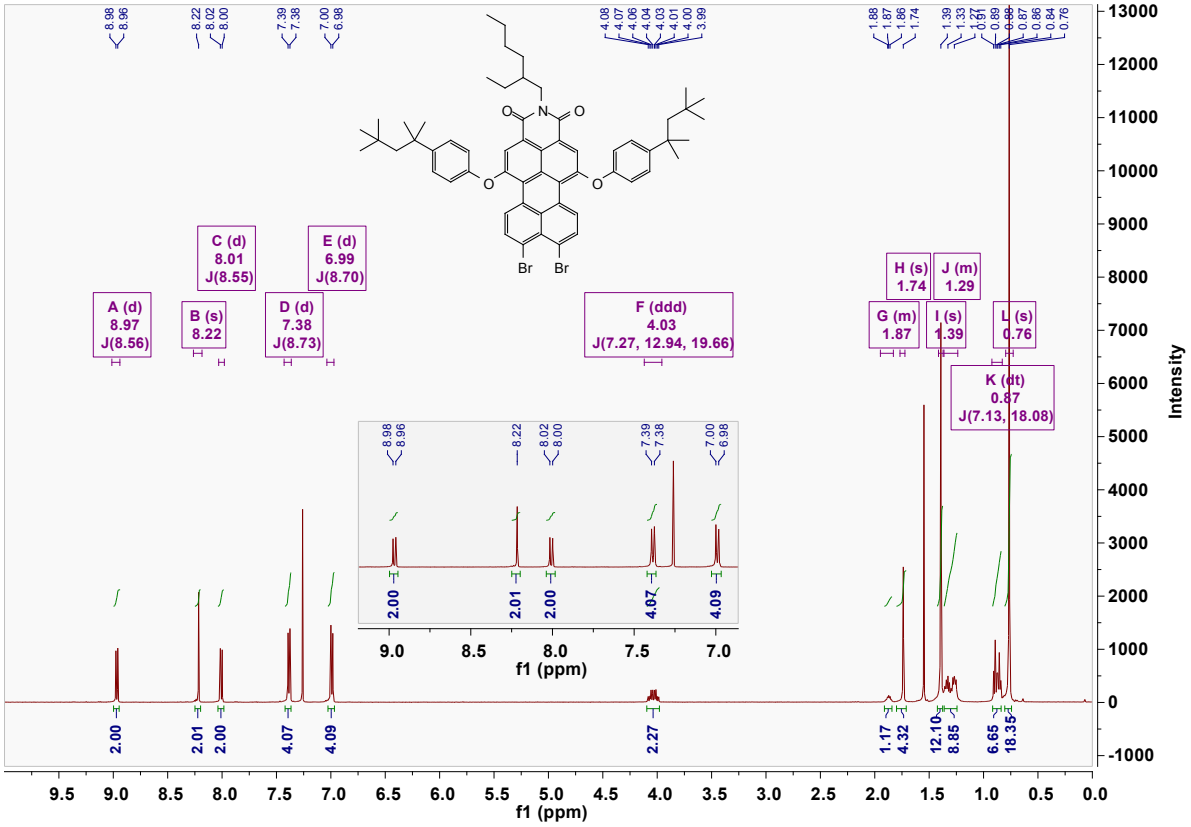


Fig. S33: ^{1}H NMR spectrum of compound **4b**

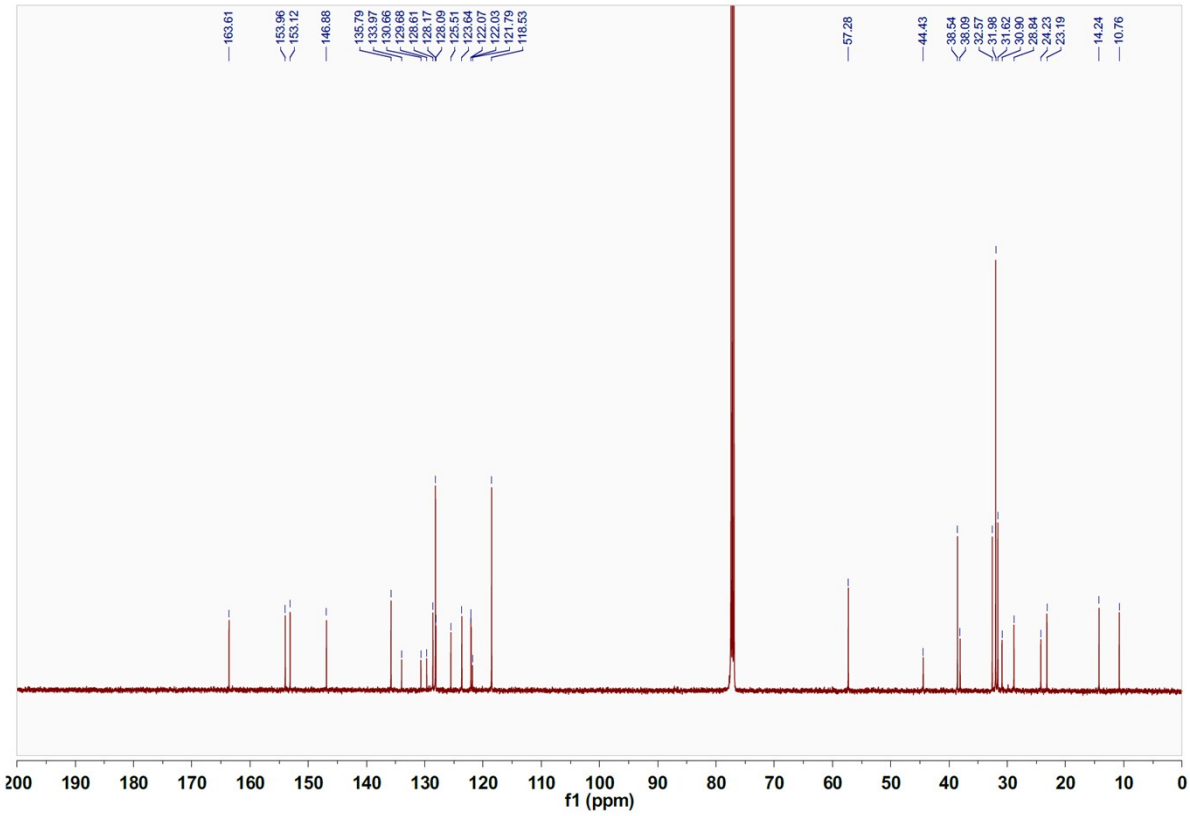


Fig. S34: ^{13}C NMR spectrum of compound **4b**

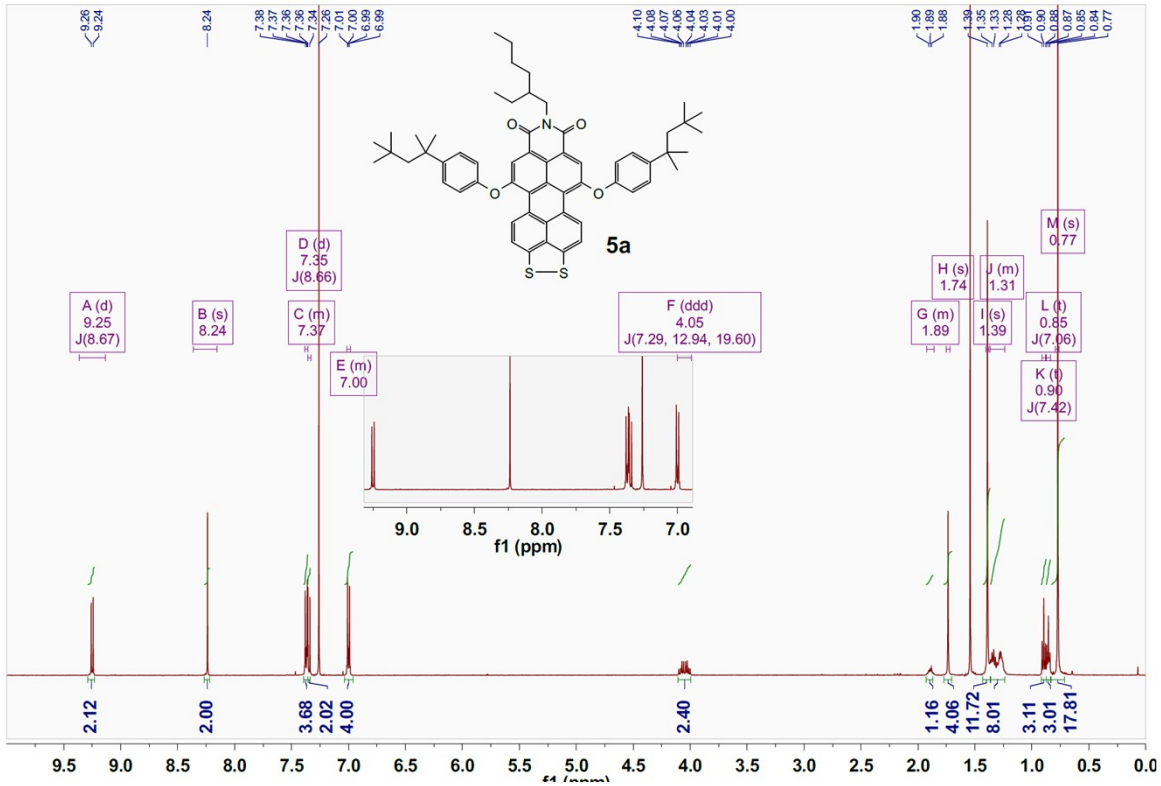


Fig. S35: ^{1}H NMR spectrum of compound **5a**

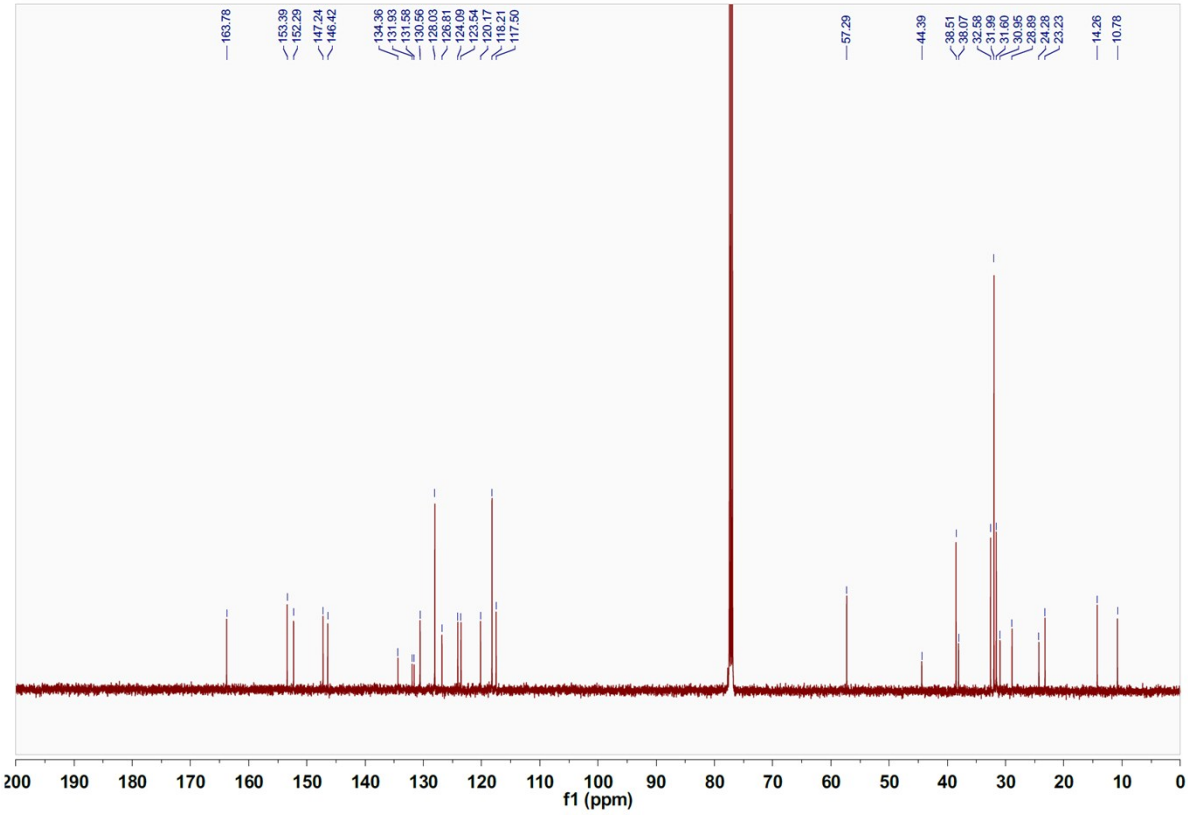


Fig. S36: ^{13}C NMR spectrum of compound **5a**

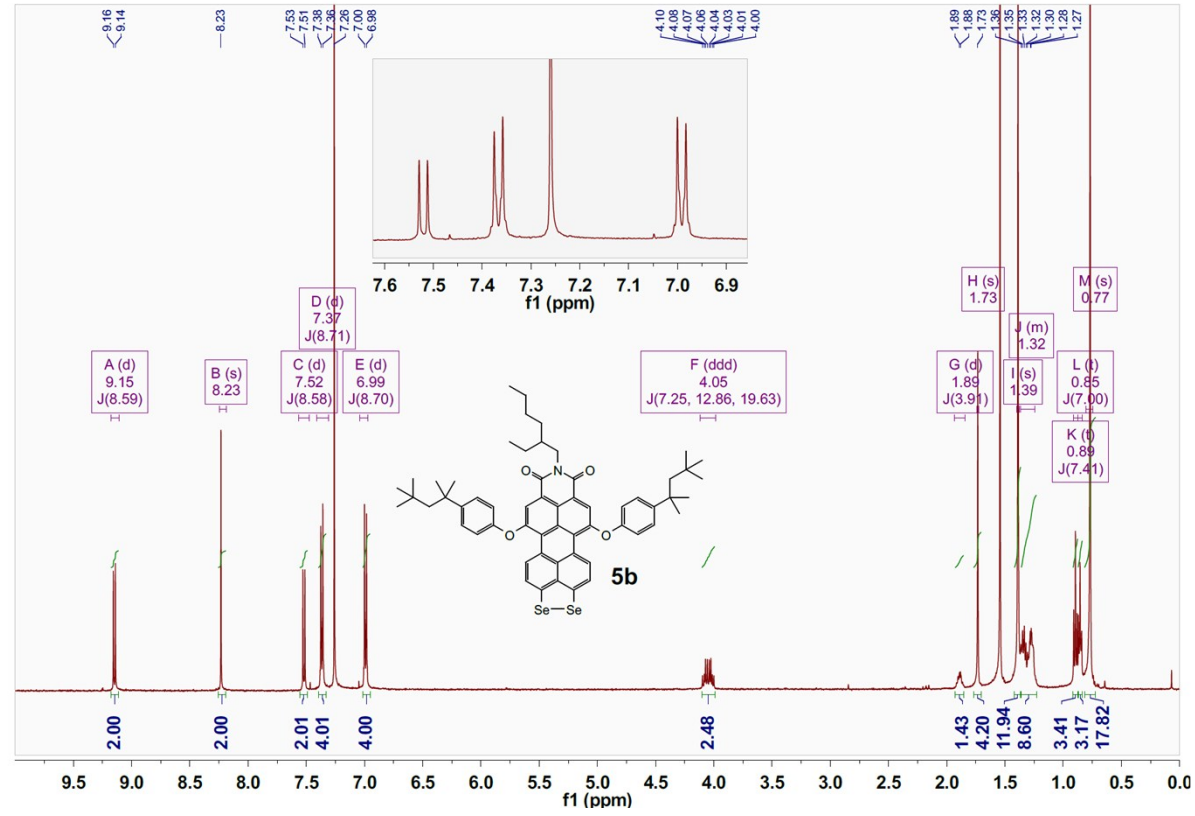


Fig. S37: ^{1}H NMR spectrum of compound **5b**

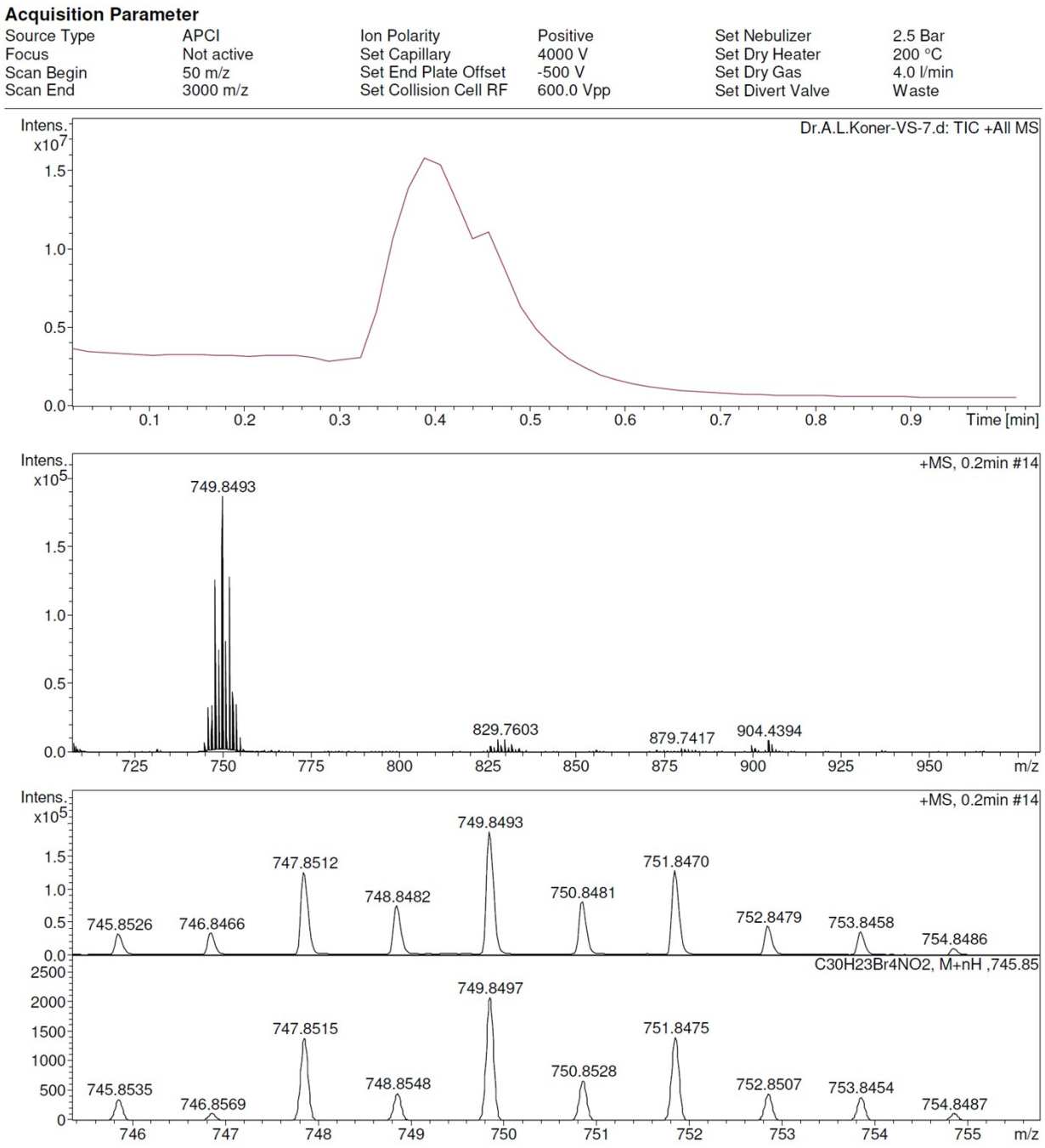


Fig. S38: APCI mass spectrum of compound **2**

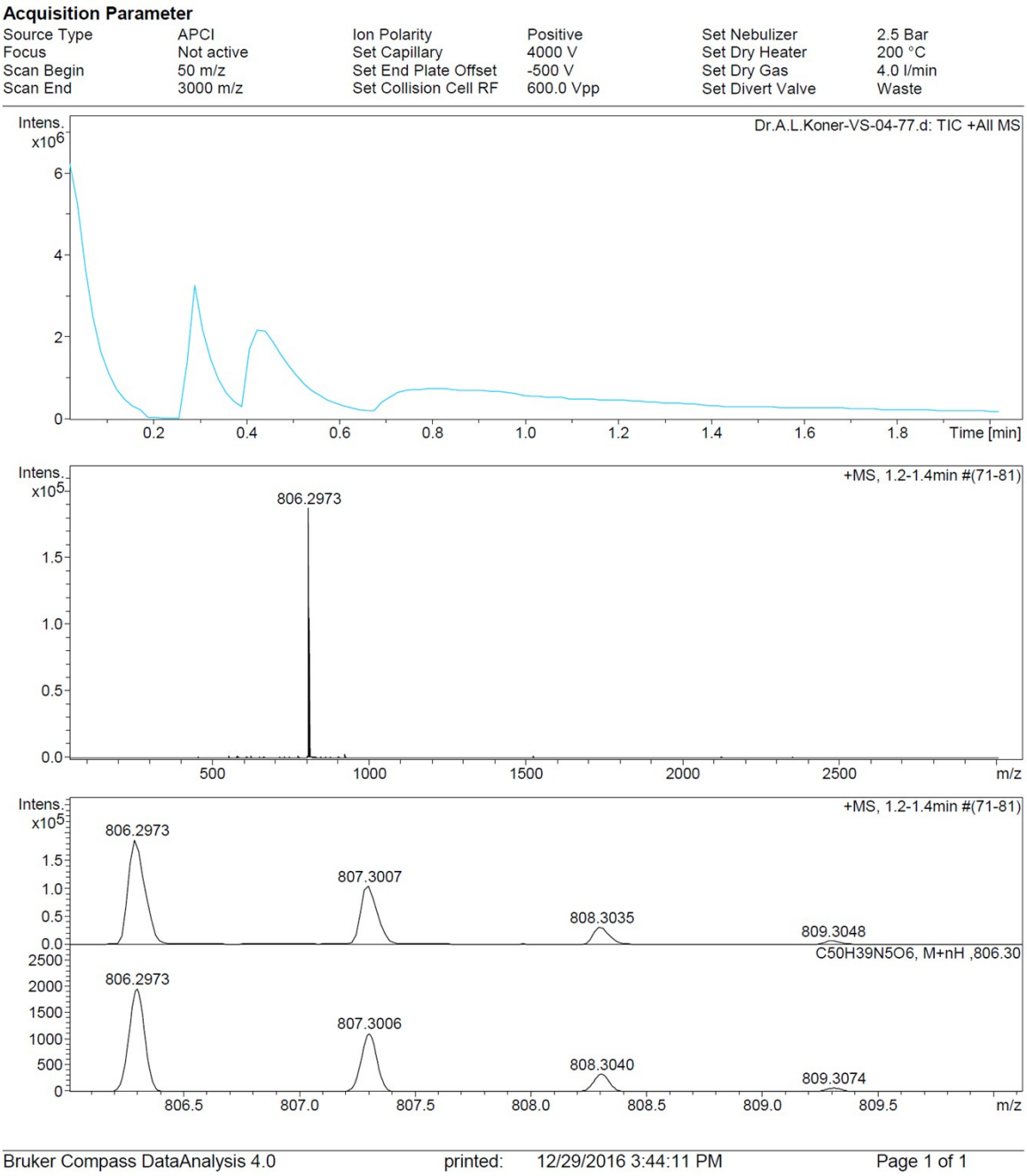


Fig. S39: APCI mass spectrum of compound **3a**

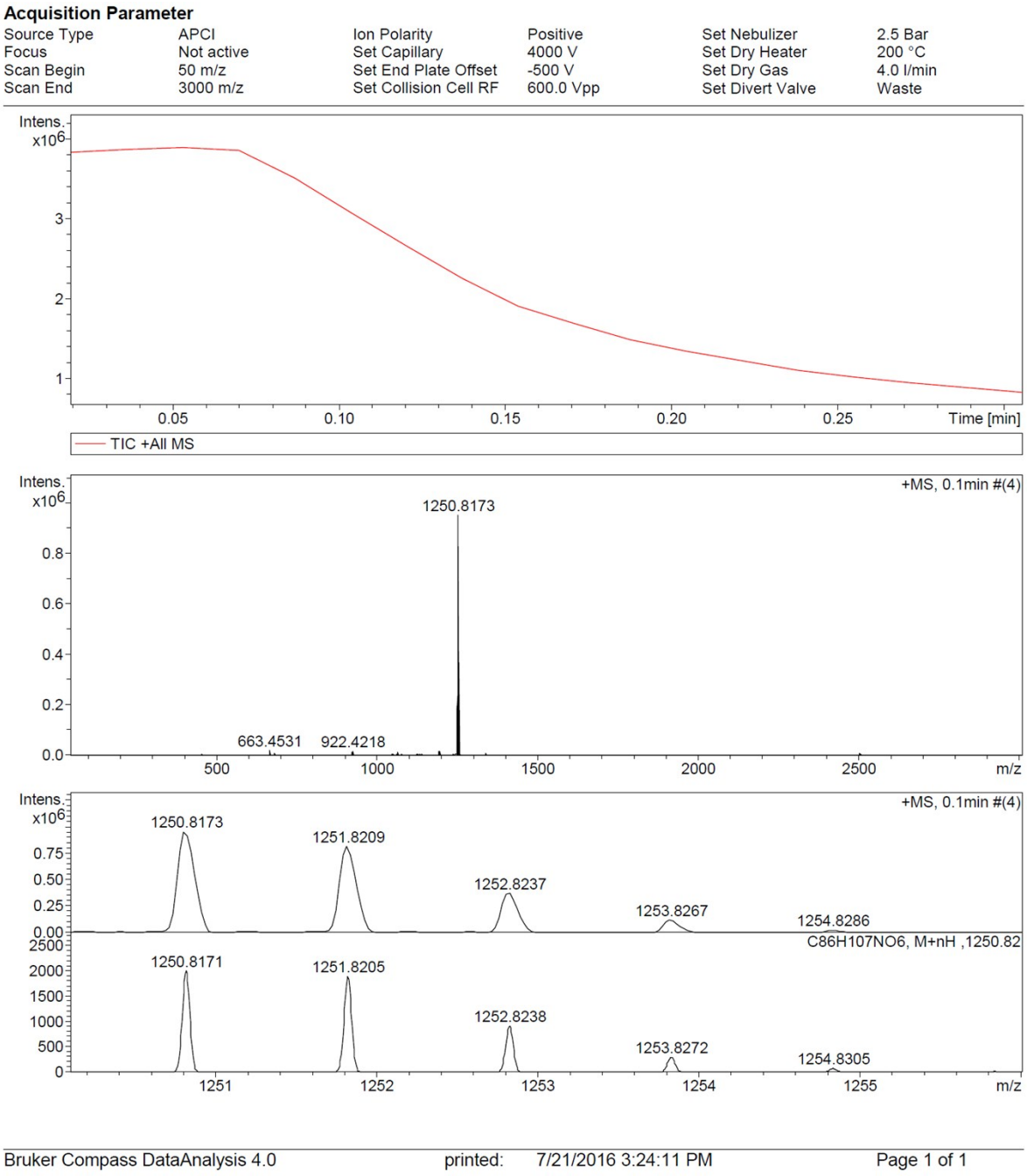


Fig. S40: APCI mass spectrum of compound **3b**

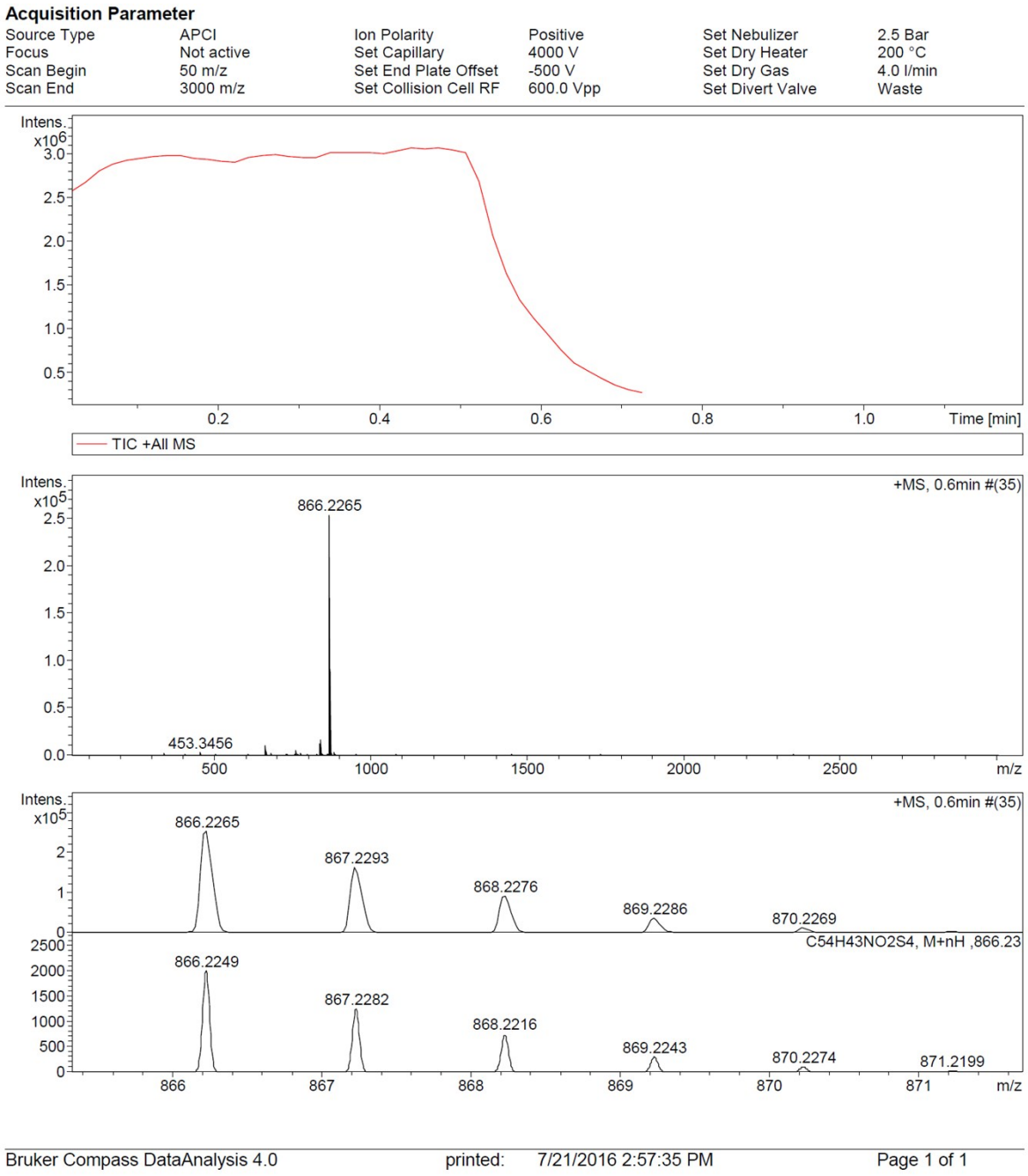
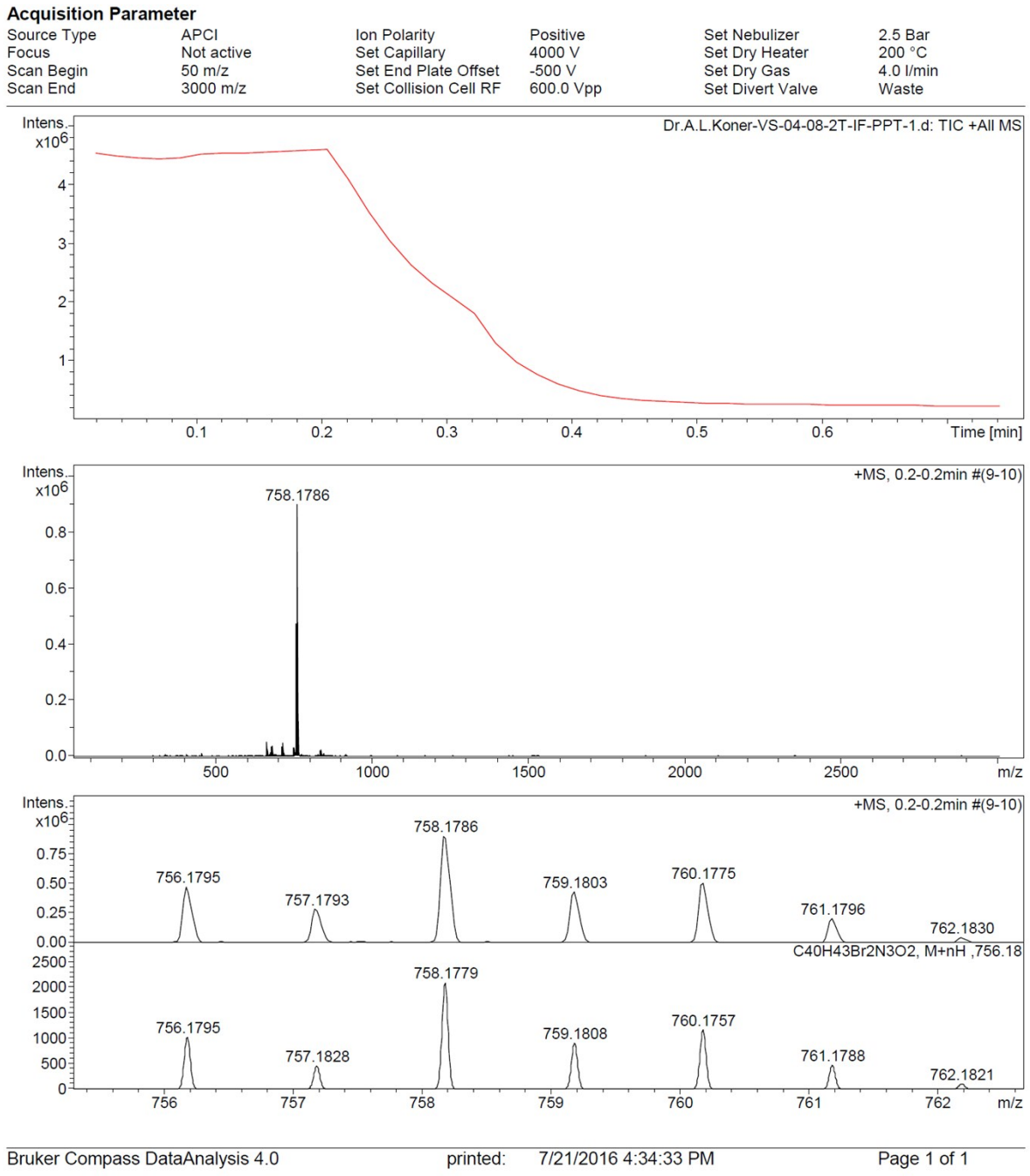


Fig. S41: APCI mass spectrum of compound **3c**



Fi

g. S42: APCI mass spectrum of compound **4a**

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	2.5 Bar
Focus	Not active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Waste

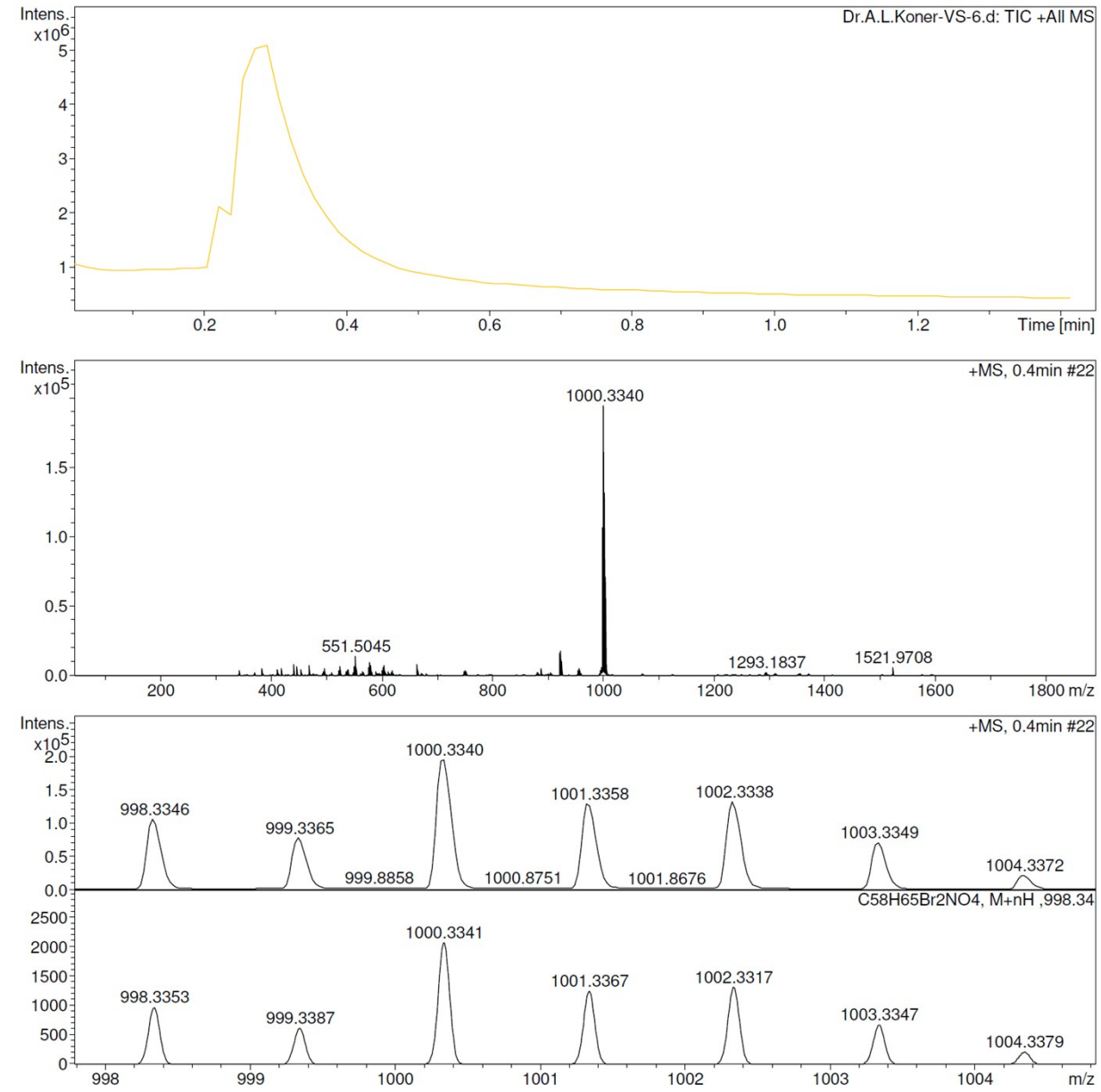


Fig. S43: APCI mass spectrum of compound **4b**

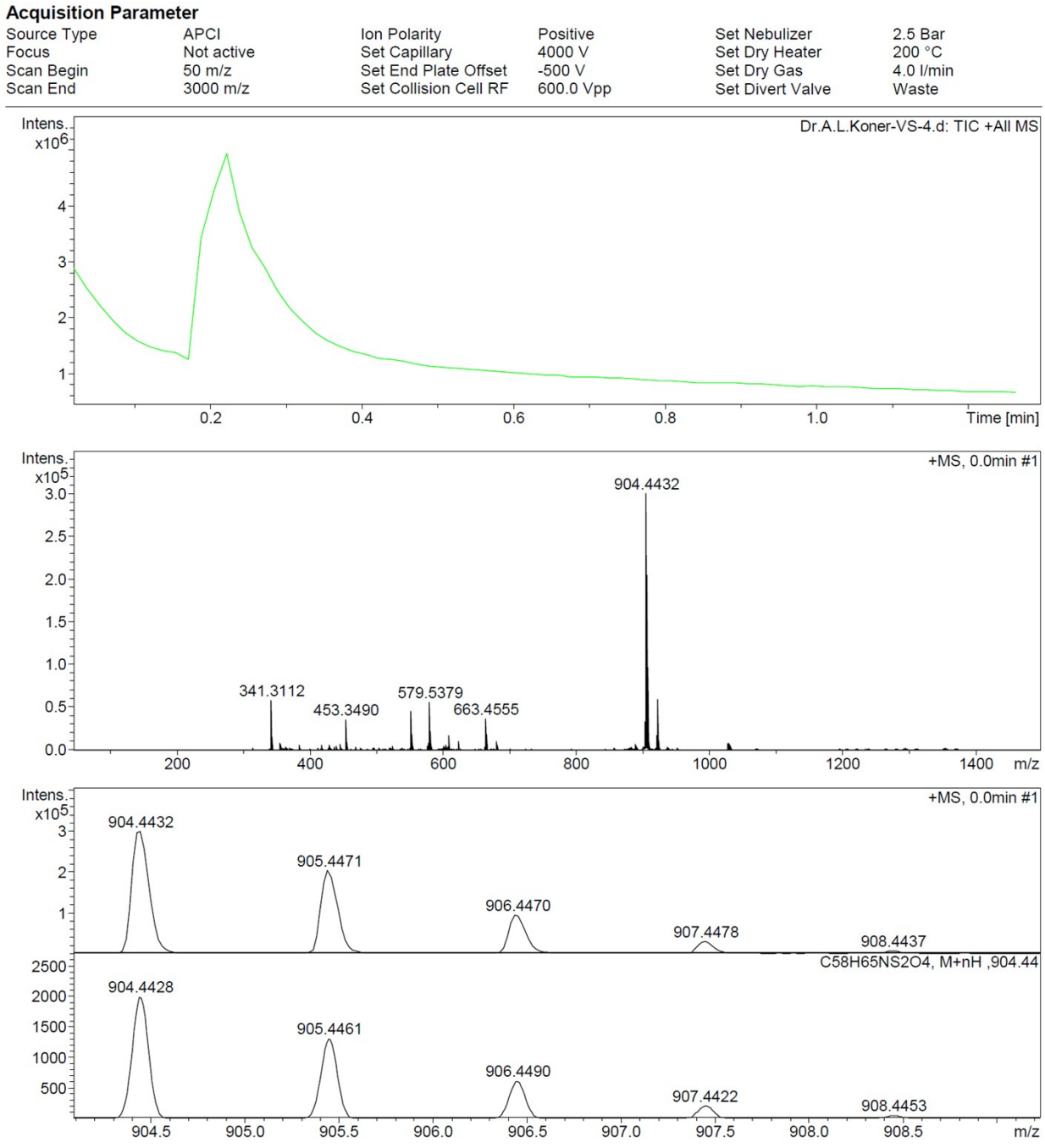


Fig. S44: APCI mass spectrum of compound **5a**

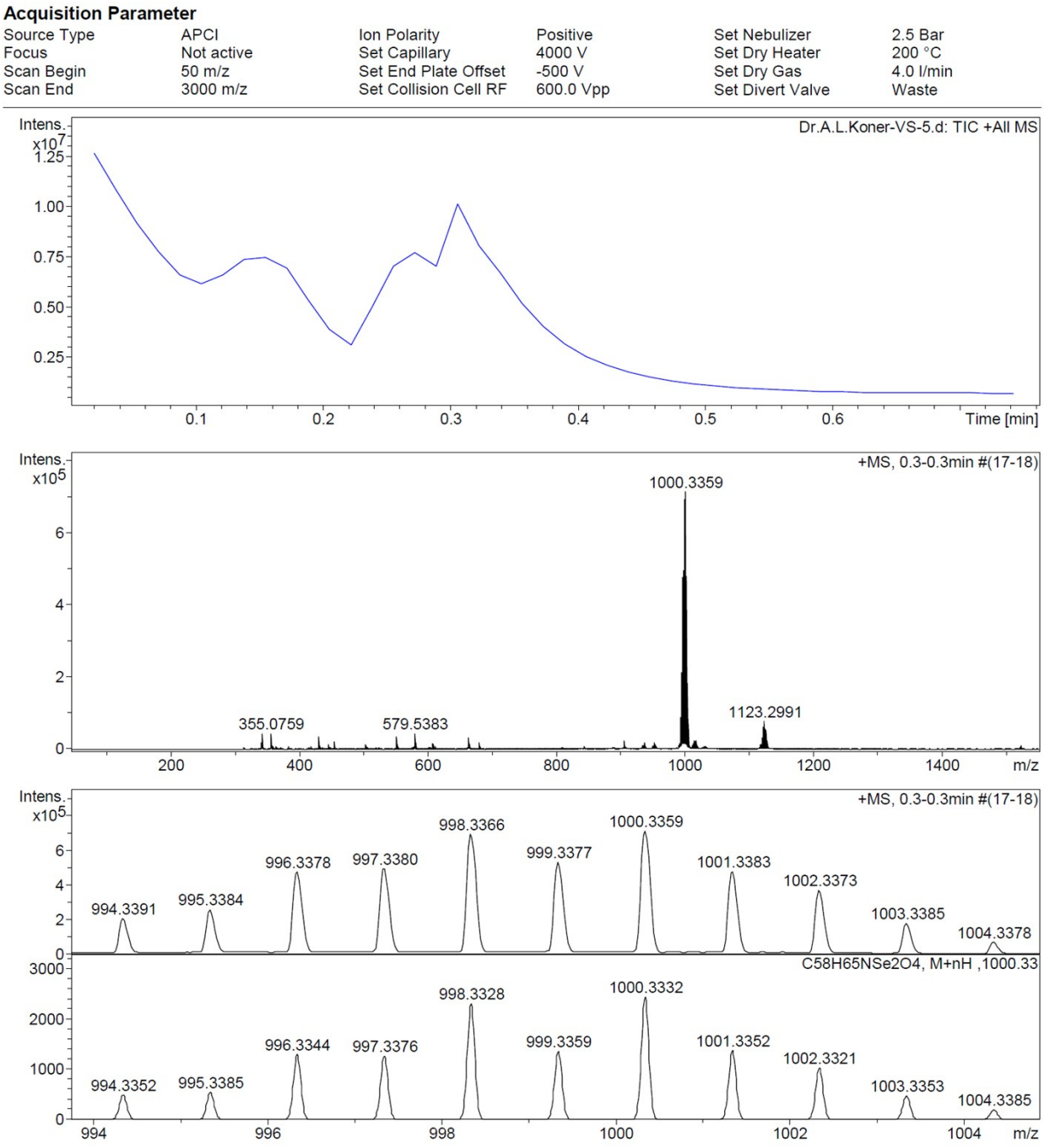


Fig. S45: APCI mass spectrum of compound **5b**

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