Supporting Information

meso-Aryl Core-Modified Fused Sapphyrins: Syntheses and Structural diversity

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1. General Information:

All the dried solvents used for synthesis and characterization such as Dichloromethane, Tetrahydrofuran and *n*-Hexane were purified by standard distillation procedures. NMR solvents were used as received. The NMR spectra were recorded with Bruker 400 MHz spectrometer in $CDCl_3$ or CD_2Cl_2 using tetramethylsilane (TMS) as internal standard. Chemical shifts are expressed in parts per million (ppm) relative to TMS. Electron spray ionization- mass spectra of the compounds were recorded on Bruker, micrOTOF-QII mass spectrometer. Electronic absorption spectra were recorded with Perkin Elmer – Lambda 750 UV-Visible spectrophotometer and data analyses were done using the UV-winlab software package. Uv titration was carried out with TFA or MSA in Dichloromethane solvent.

2. Experimental Section

2.1 Synthesis of **3**

5,5'-bis-(mesitylhydroxylmethyl)dithienothiophene (DTT-Mes-diol) **7** (1.0 g, 1 equiv, 2.03mmol) and Thiophene-tripyrrane **8** (0.97g, 1 equiv, 2.03mmol) were dissolved in 200 mL of CH_2Cl_2 and stirred in an inert atmosphere for 10 min. The acid catalyst *p*-Toluenesulfonic acid (0.172g, 0.5 equiv, 1.0 mmol) was added to this solution and continued stirring for another 90 min in ambient temperature. Chloroanil (0.691g, 1.5 equiv, 3.04mmol) was added to the above solution and the solution was opened to air, and then heated to reflux for 2 hrs. The solvent was evaporated by reduced pressure in rotary evaporator. The crude product was purified by first basic alumina column. The brownish green color band eluted by CH_2Cl_2: hexane (10:90) was identified as sapphyrin in 10% yield.

3: mp 217-219 °C (decomposition); ESI-MS: *m/z* calcd for $C_{60}H_{52}N_2S_4+H^+$: 929.3013; found: 929.3014; elemental analysis: Calcd for $C_{60}H_{52}N_4S_4$: C, 77.54; H, 5.64; N, 3.01. Found: C,

77.52; H, 5.63; N, 3.05. Uv/Vis (CH_2Cl_2): λ_{max}[nm] (ε [$10^5M^{-1}cm^{-1}$]): 495 (0.58), 662 (0.12); **3.2H**$^+$: λ_{max}[nm] (ε [$10^5M^{-1}cm^{-1}$]): 525 (0.81), 759 (0.18);

3:^{1}H NMR (400MHz, CD_2Cl_2, 25^{o}C, TMS) δ[ppm]: 8.49 (s, 2H), 8.10 (d, 2H), 7.81 (d, 2H), 7.19 (s, 4H), 7.09 (d, 4H), 2.54 (s, 6H), 2.47 (s, 6H), 2.15 (s, 2H), 1.09 (s, 24H).

3.2H$^+$: 9.76 (d, 2H), 9.49 (s, 2H), 9.28 (d, 2H), 7.81 (s, 4H), 7.72 (d, 4H), 7.15 (s, 4H), 6.77 (s, 4H), 3.27 (s, 6H), 3.23 (s, 6H), 2.40 (s, 6H), 2.32 (s, 6H), 2.06 (s, 6H), 1.15 (s, 6H), 0.62 (s, 2H), -2.70 (brs, 2H).

2.2 Synthesis of **4**

DTT-diol, **7** (1.0 g, 1 equiv, 2.03mmol) and Selenophene-tripyrrane **9** (1.06g, 1 equiv, 2.03mmol) were dissolved in 200 mL of dichloromethane and stirred in an inert atmosphere for 10 min. The acid catalyst *p*-Toluenesulfonic acid (0.172g, 0.5 equiv, 1.0 mmol) was added to this solution and continued stirring for another 90 min in ambient temperature. Chloroanil (0.691g, 1.5 equiv, 3.04mmol) was added to the above solution and the solution was opened to air, and then heated to reflux for 2 hrs. The solvent was evaporated by reduced pressure in rotary evaporator. The crude product was purified by first basic alumina column. The brownish green colour band eluted by dichloromethane: hexane (14:86) was identified as sapphyrin in 08% yield.

4: mp 224-227 °C (decomposition); ESI-MS: *m/z* calcd for $C_{60}H_{52}N_2S_3Se$: 976.2458; found: 976.2456; elemental analysis: Calcd for $C_{60}H_{52}N_2S_3Se$: C, 73.82; H, 5.37; N, 2.87. Found: C, 73.81; H, 5.38; N 2.86; Uv/Vis (CH_2Cl_2): λ_{max}[nm] (ε [$10^5M^{-1}cm^{-1}$]): 502 (0.59), 616 (0.15), 653 (0.08); **4.2H**$^+$: λ_{max}[nm] (ε [$10^5M^{-1}cm^{-1}$]): 532 (0.83), 692 (0.11), 759 (0.121);

4: SE-1: 8.94 (s, 2H), 8.51 (s, 2H), 8.05 (d, 2H), 7.67 (d, 2H), 7.16 (s, 4H), 7.15 (s, 4H), 2.9-2.4 (36H); SE-2: 8.25 (s, 2H), 7.87 (d, 2H), 7.51 (s, 2H), 7.11(s, 4H), 6.99 (s, 4H), 2.21 (s, 2H), 2.9-2.4 (36H).

3. Spectral Characterization

3.1 Mass spectra:

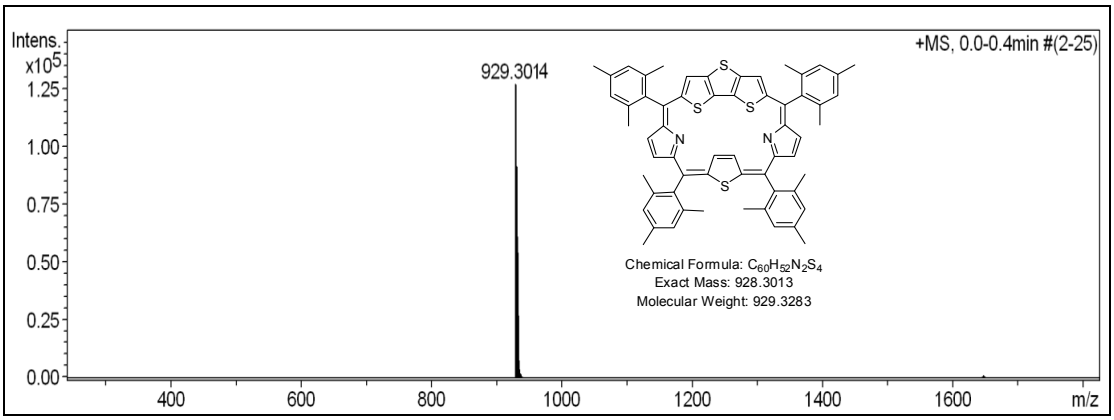


Figure S1. ESI-Mass spectrum of **3**

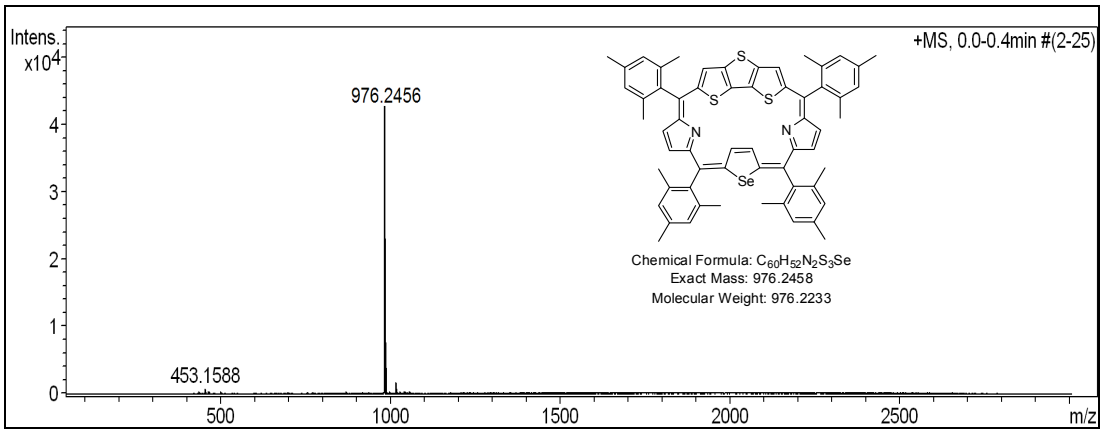


Figure S2. ESI-Mass spectrum of **4**

3.2 NMR spectral analysis

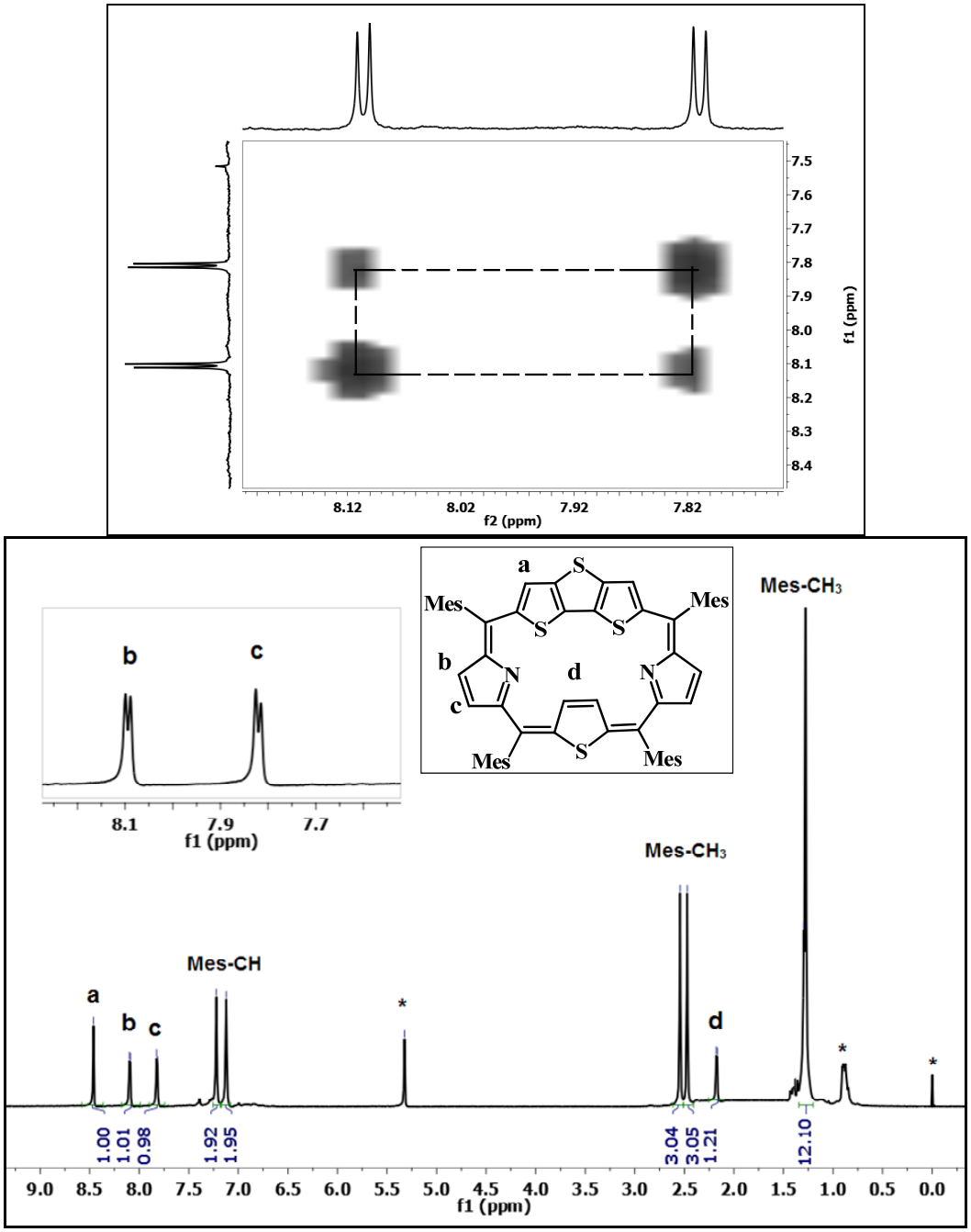


Figure S3. ^{1}H NMR spectrum of **3** in CD_2Cl_2 at 298K. (Inset: COSY spectrum of pyrrole protons b & C) (*Residual solvent, impurity grease and TMS peaks)

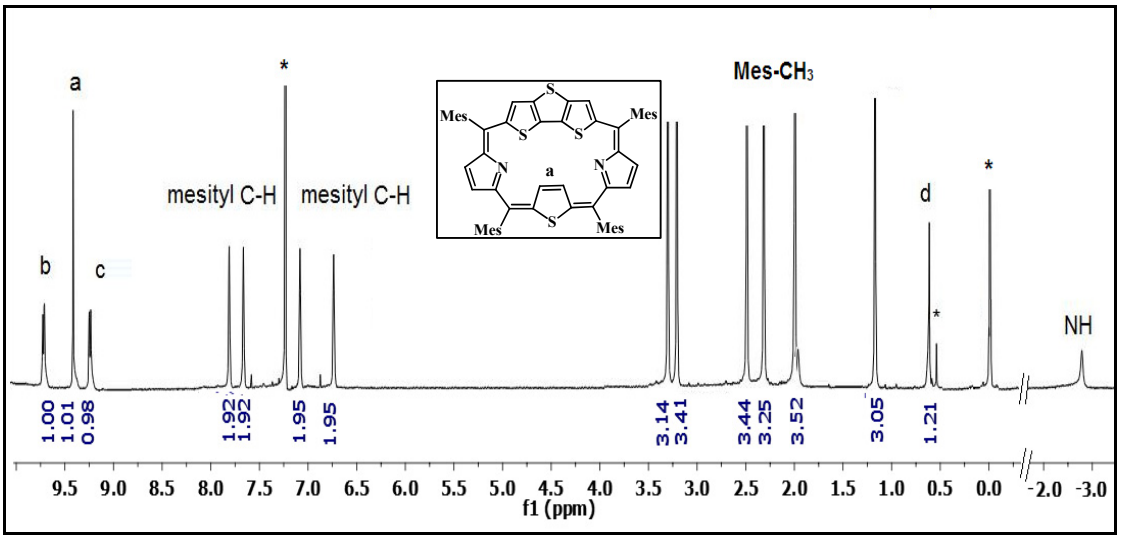


Figure S4. ^{1}H NMR spectrum of **3.2H**$^{+}$ in dilute solution of TFA in $CDCl_3$ at 298K (*Residual solvent, impurity grease and TMS peaks)

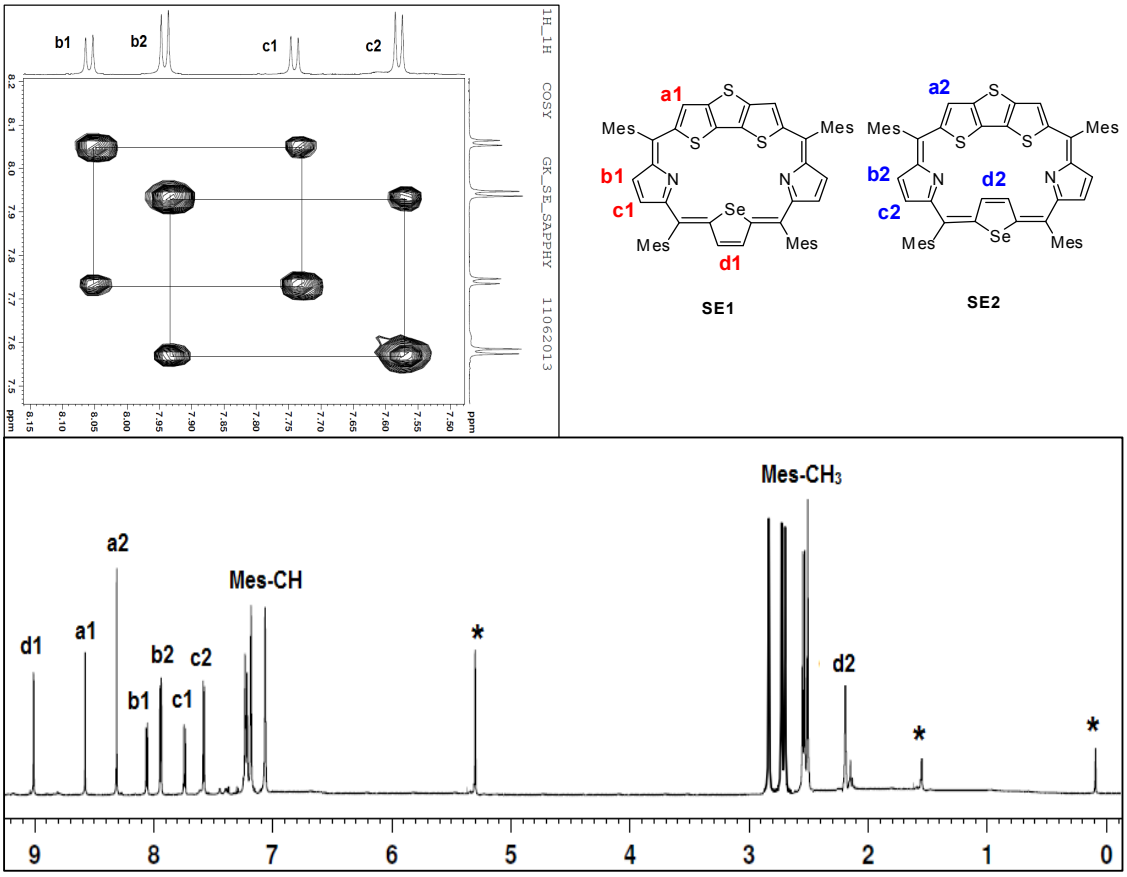
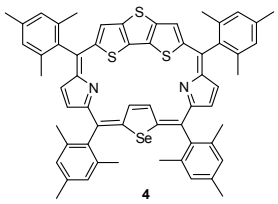


Figure S5. ^{1}H NMR spectrum of **4** in CD_2Cl_2 at 298K (*Residual solvent, water and TMS peaks)



4

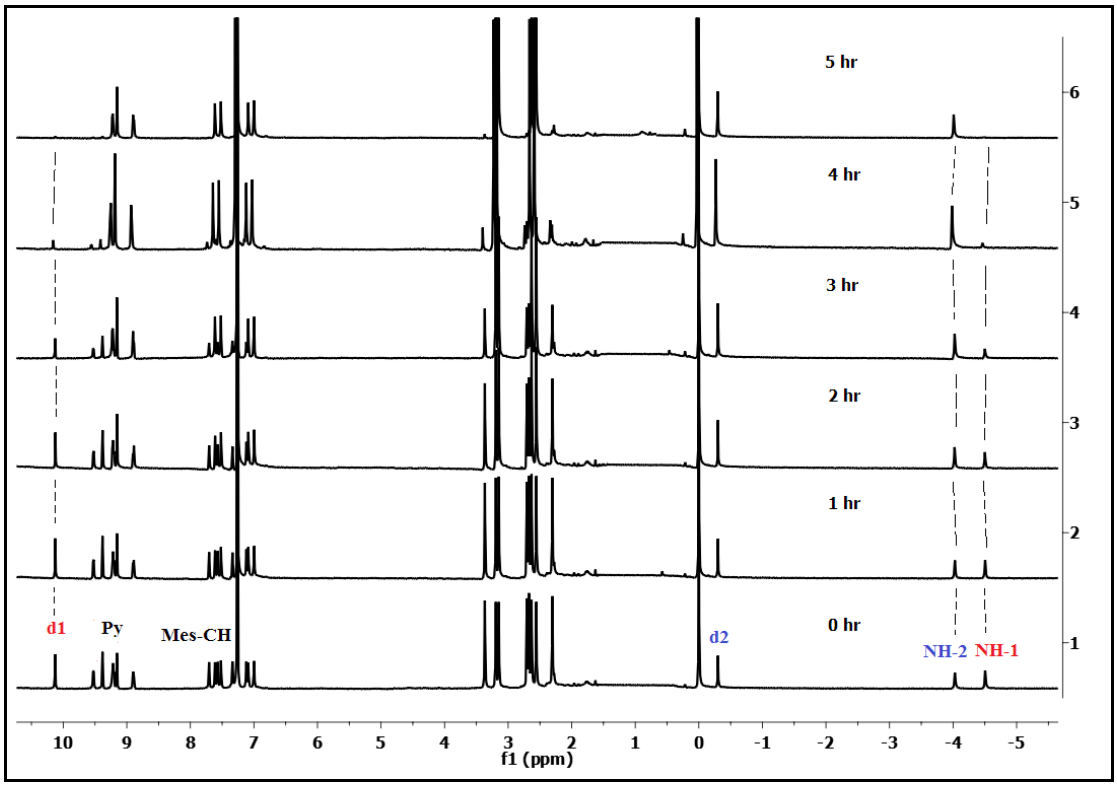


Figure S6. ^{1}H NMR spectrum of **4.2H**$^{+}$ in dilute solution of TFA in $CDCl_3$ at different time intervals

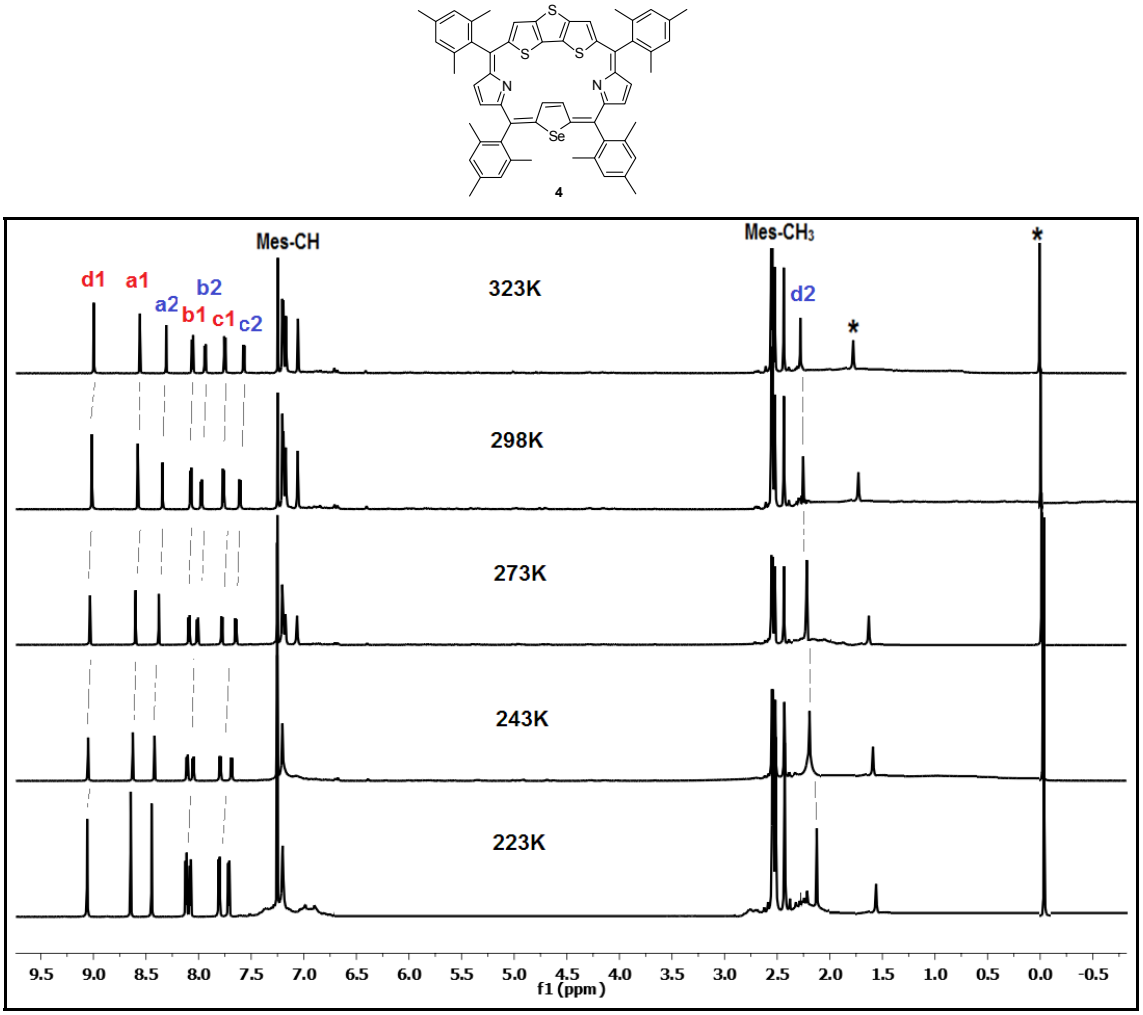


Figure S7. ^{1}H NMR spectrum of **4** in $CDCl_3$ at variable temperature (*Residual water and TMS peaks)

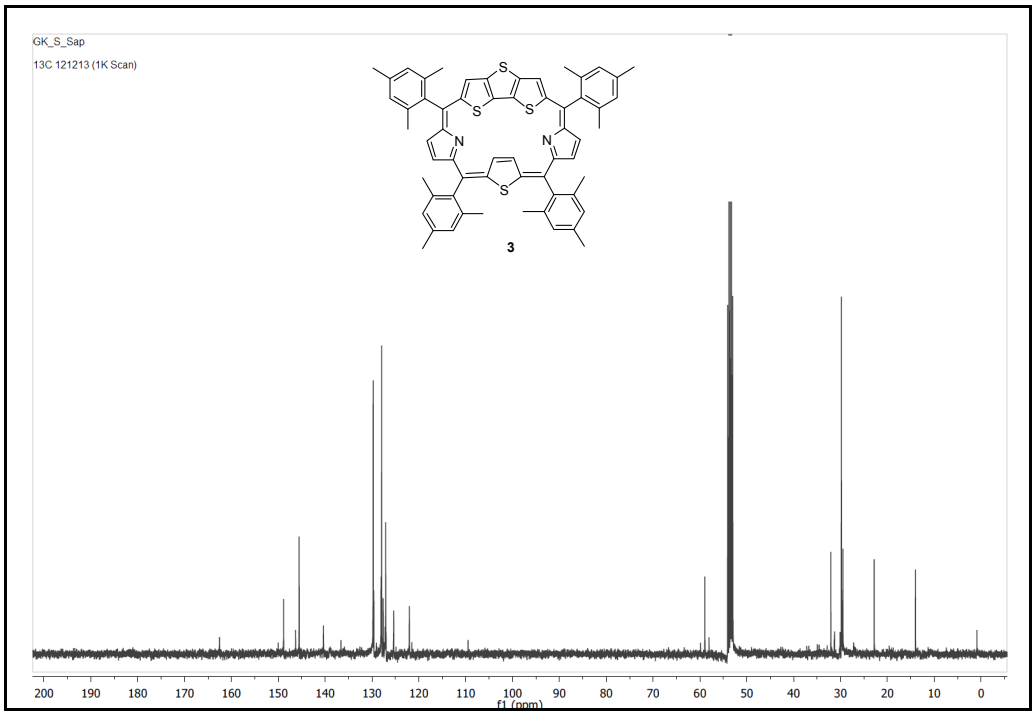


Figure S8. ^{13}C NMR spectrum of **3** in CD_2Cl_2 at 298K

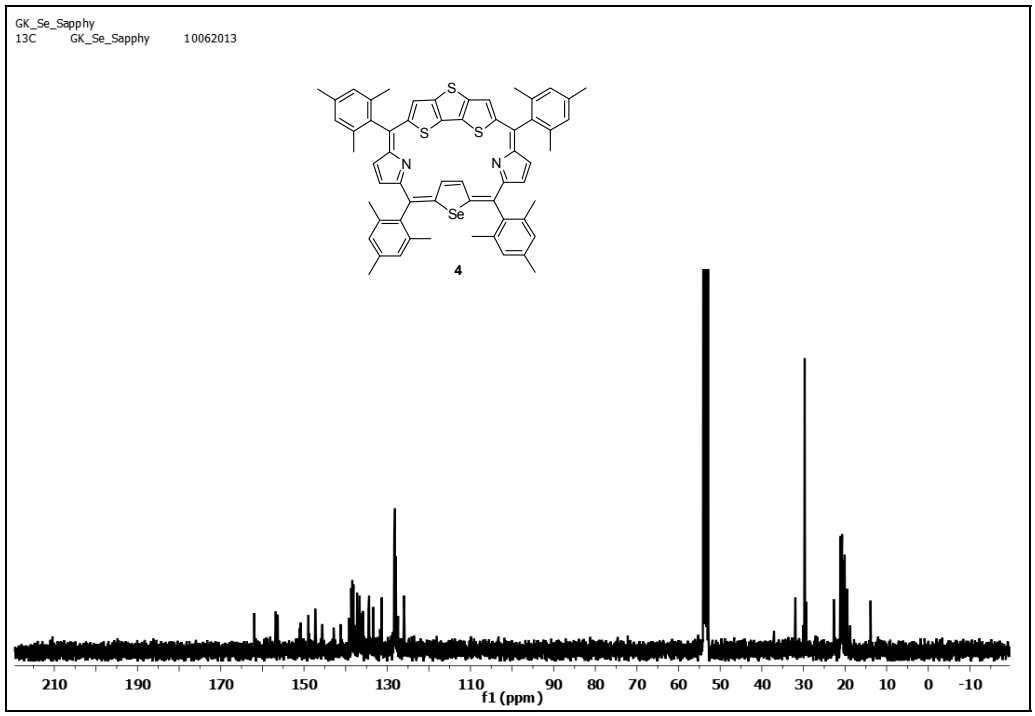
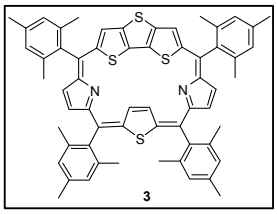


Figure S9. ^{13}C NMR spectrum of **4** in CD_2Cl_2 at 298K

3.3 Electronic absorption spectra



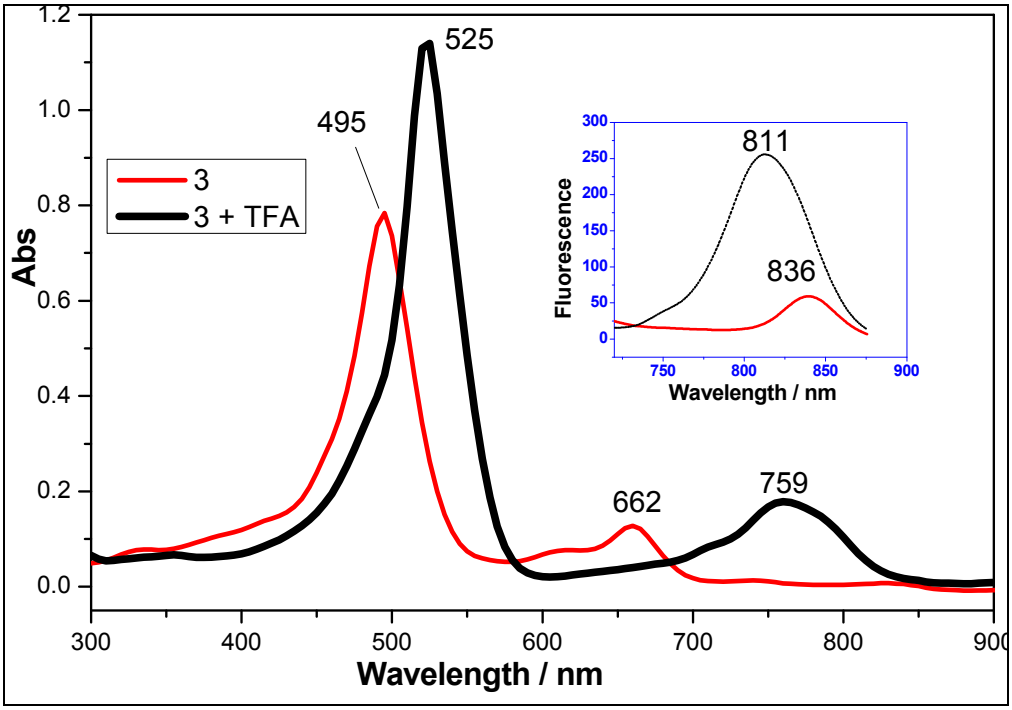
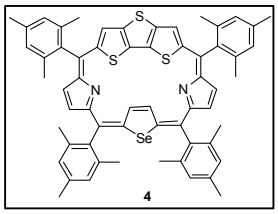


Figure S10. Electronic absorption and emission (inset) spectrum of **3** and **3.2H**$^+$ in CH_2Cl_2.



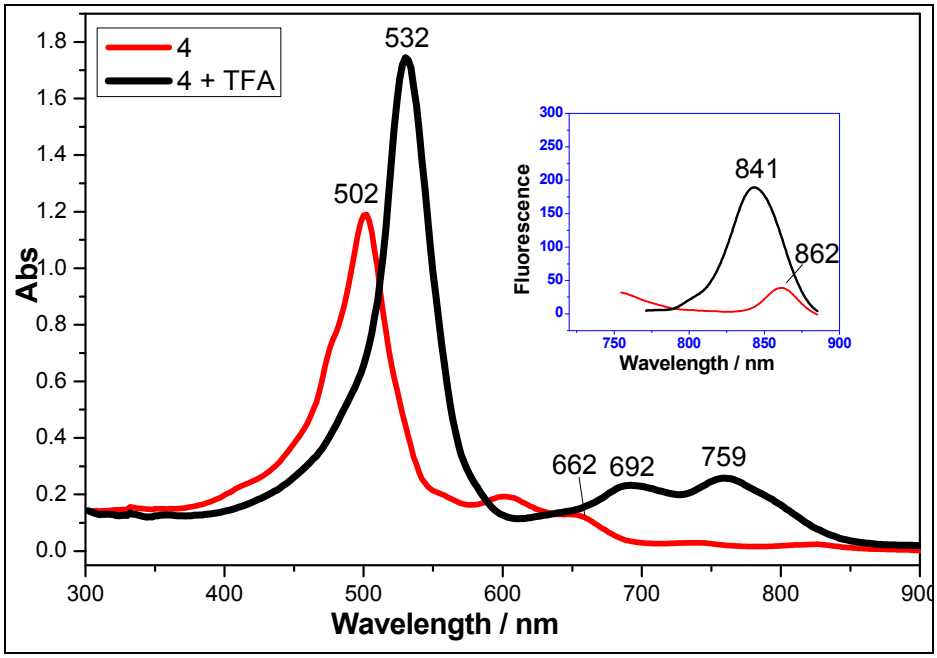


Figure S11. Electronic absorption and emission (inset) spectrum of **4** and **4.2H**$^{+}$ in CH_2Cl_2.

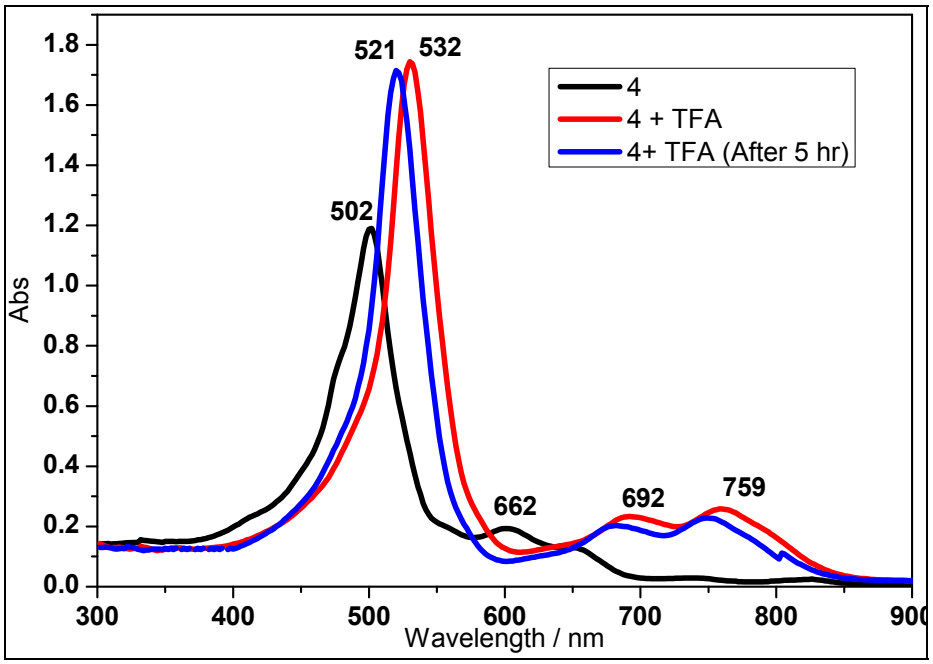


Figure S12. Electronic absorption spectrum of **4** and **4.2H**$^{+}$ in CH_2Cl_2.

3.4 Cyclic voltammetry:

Electrochemical analysis of **3** and **4** were studied by cyclic voltammetry and differential pulse voltammetry and was carried out in three electrode cell system; Glassy carbon working electrode, platinum wire counter electrode and Ag/Ag^{+} reference electrode containing 0.1M $TBAPF_6$ (tetra-n-butylammoniumhexafluorophosphate) as supporting electrolyte in CH_2Cl_2 in the potential region 1.0 to -1.5 V vs Ag/Ag^{+} reference electrode.

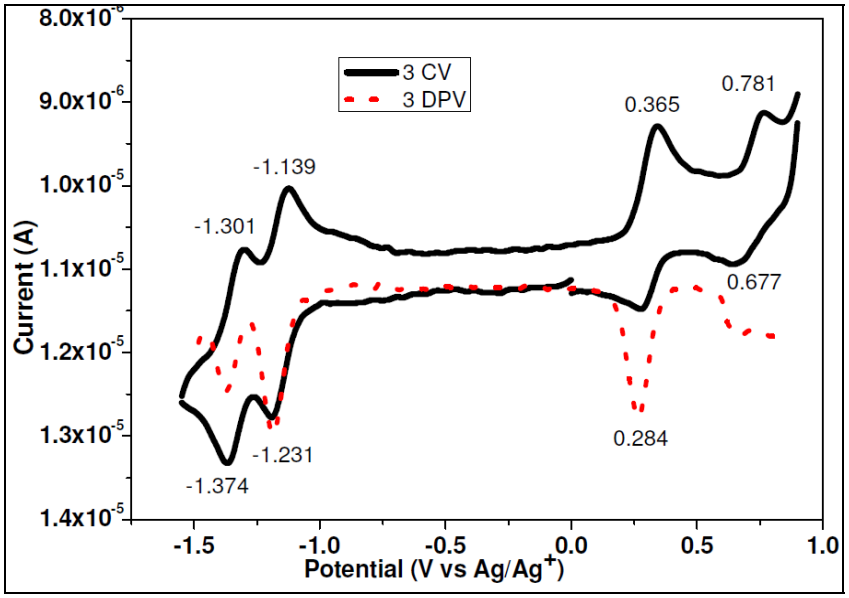


Figure S13. Cyclic voltammetry and Differential pulse voltammetry of **3** in CH_2Cl_2, containing 0.1 M $TBAPF_6$, Scan rate 50 mV/s.

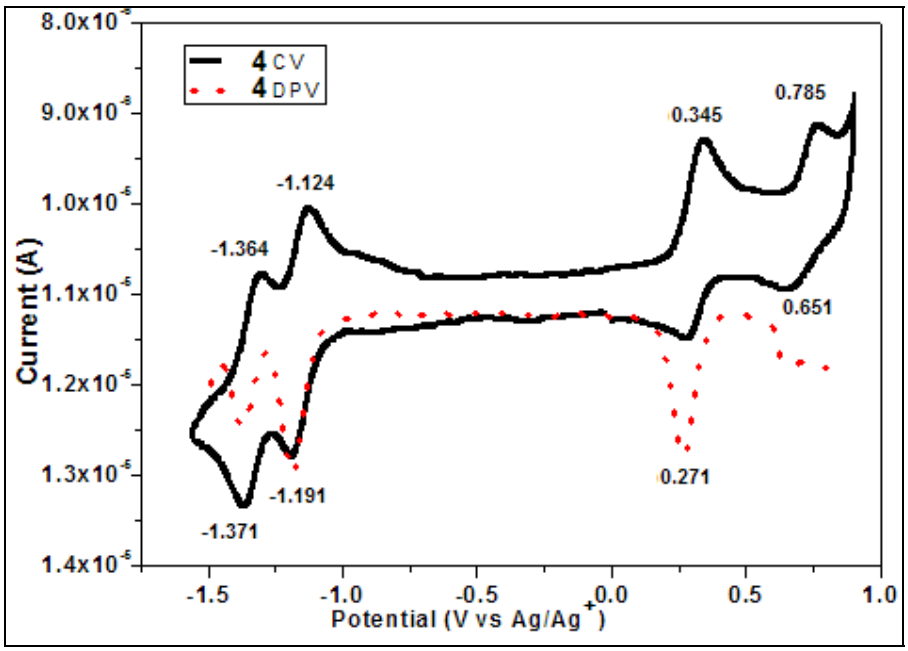


Figure S14. Cyclic voltammetry and Differential pulse voltammetry of **4** in CH_2Cl_2, containing 0.1 M $TBAPF_6$, Scan rate 50 mV/s.

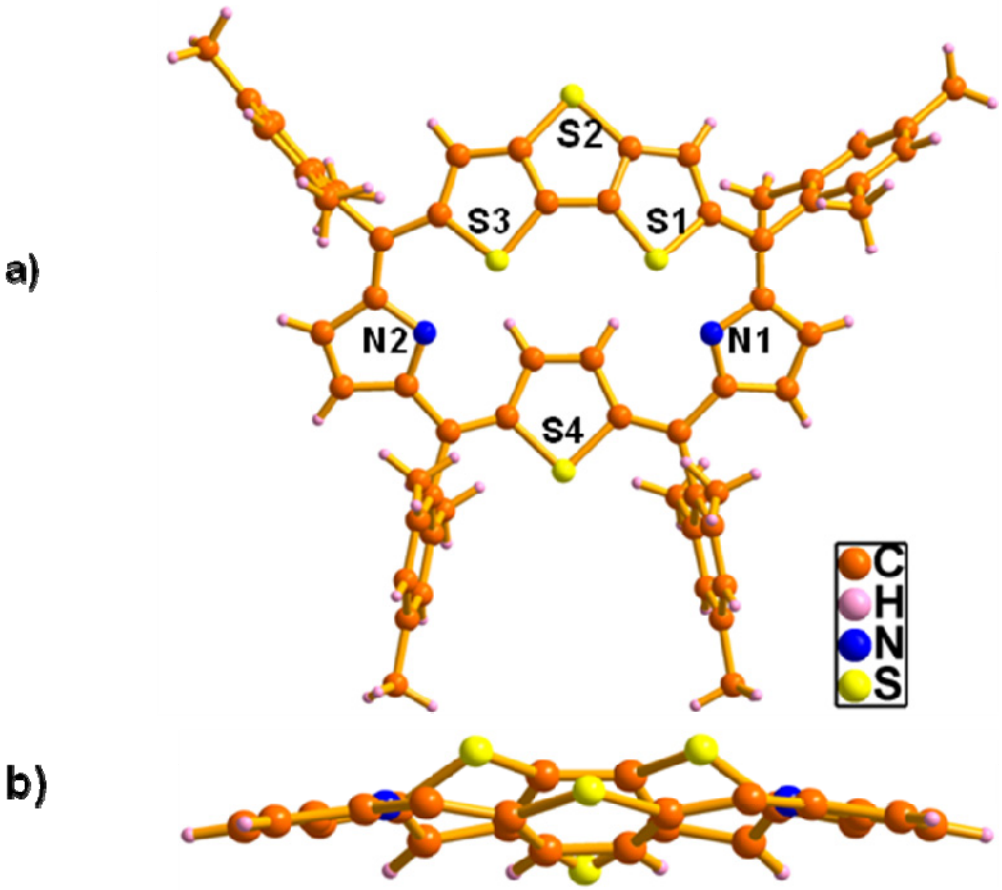


Figure S15. Single crystal X-ray structure of **3** a) Top view b) side view (meso-aryl groups are omitted for clarity)

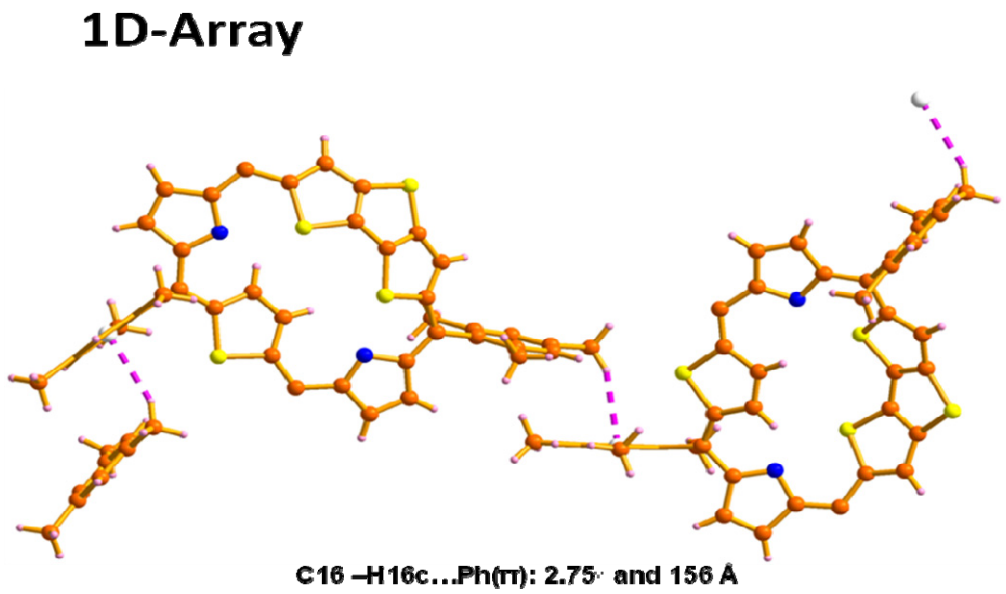


Figure S16. Single crystal X-ray structure of **3** in 1-D array

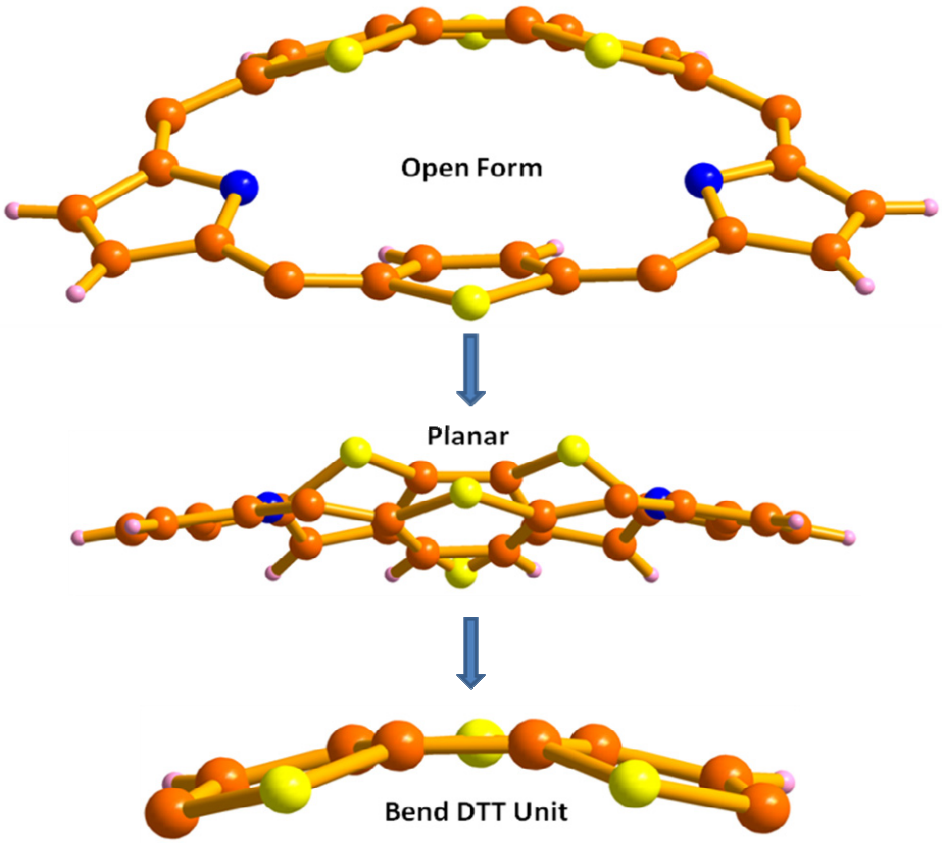


Figure S17. Single crystal X-ray structure of **3**

Crystal data for **3** (from $CHCl_3$/hexane): $C_{60}H_{52}N_2S_4$, M_w = 929.28, monoclinic, a = 12.860(6), b = 26.508(12), c = 15.338(7) Å, α = 90.00, β = 110.628, γ = 90.00°, V = 4893(3) $Å^3$, T = 100 K, space group P2(1)/c, Z = 4, D_c = 1.261 mg/m^3, μ(Mo-Kα) = 0.236 mm^{-1}, 49754 reflections collected, 9105 unique (R_{int} = 0.1014), R_1 = 0.0487, wR_2 = 0.1133, GOF = 1.029 {I>2σ(I)}. CCDC-1002207 contains the supplementary crystallographic data for **3**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.