Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

for

Core-modified 48π and 42π Decaphyrins: Syntheses, properties and structure

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General Information:

The solvents required for the synthesis, such as Tetrahydrofuran, Dichloromethane, n-Hexane were purified by using standard procedure. Deuterated NMR solvent (CD_2Cl_2) was used as received. All NMR spectra were recorded with Bruker 400 MHz spectrometer in solvent CD_2Cl_2 using tetramethylsilane (TMS) as an internal standard. Chemical shifts are expressed in parts per million (ppm) units relative to TMS. Electron spray ionization (ESI) mass spectra were recorded on Bruker, micrOTOF-QII mass spectrometer. Electronic spectra were recorded with Perkin Elmer – Lambda 750 UV – winlab software package. X-ray quality crystals for the compounds were grown by the slow diffusion of acetonitrile over $CHCl_3$ solution and $CHCl_3$ over hexane. Single crystal X-ray diffraction data were collected on a Rigaku Oxford Diffraction, 2018, four-circle diffractometer and SuperNova, Dual, Cu at home/near.

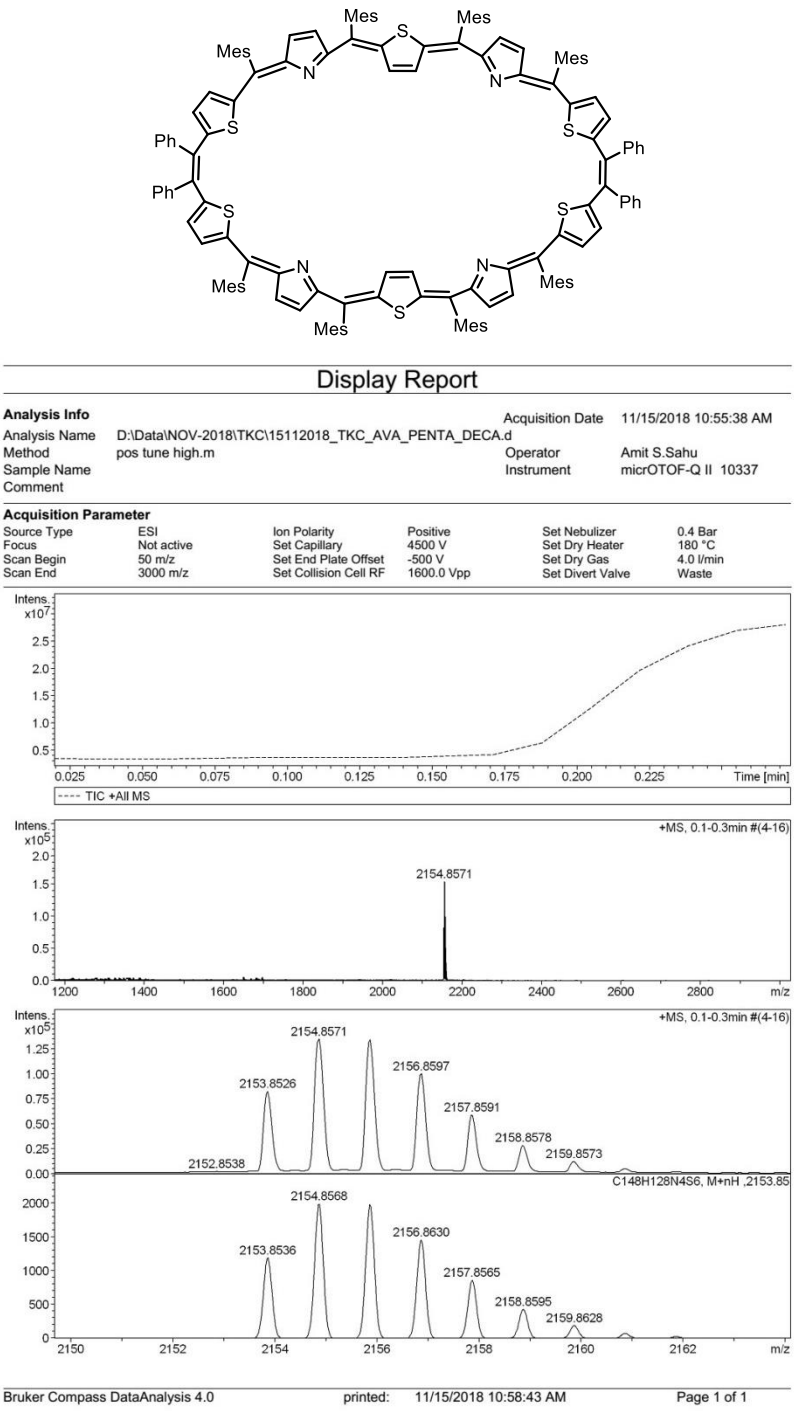


Figure S1: HRMS spectrum of **10**

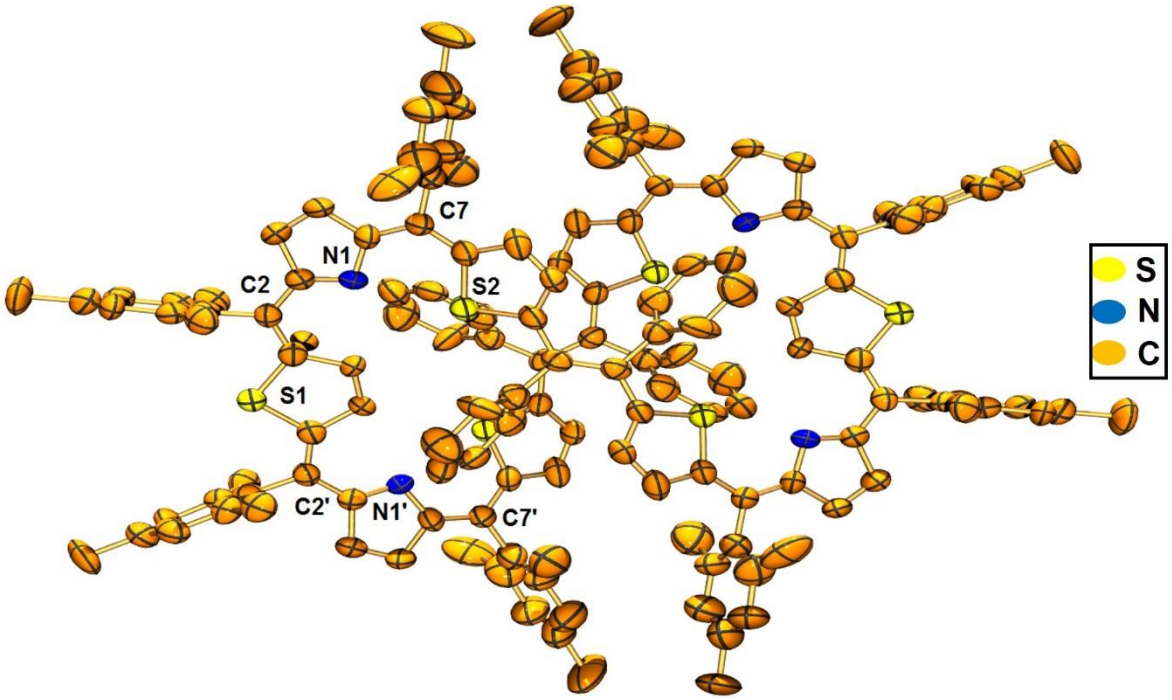


Figure S2: Crystal structure of **10** (Hydrogen atoms are omitted for clarity).Thermal ellipsoids are drawn at 50% probability.

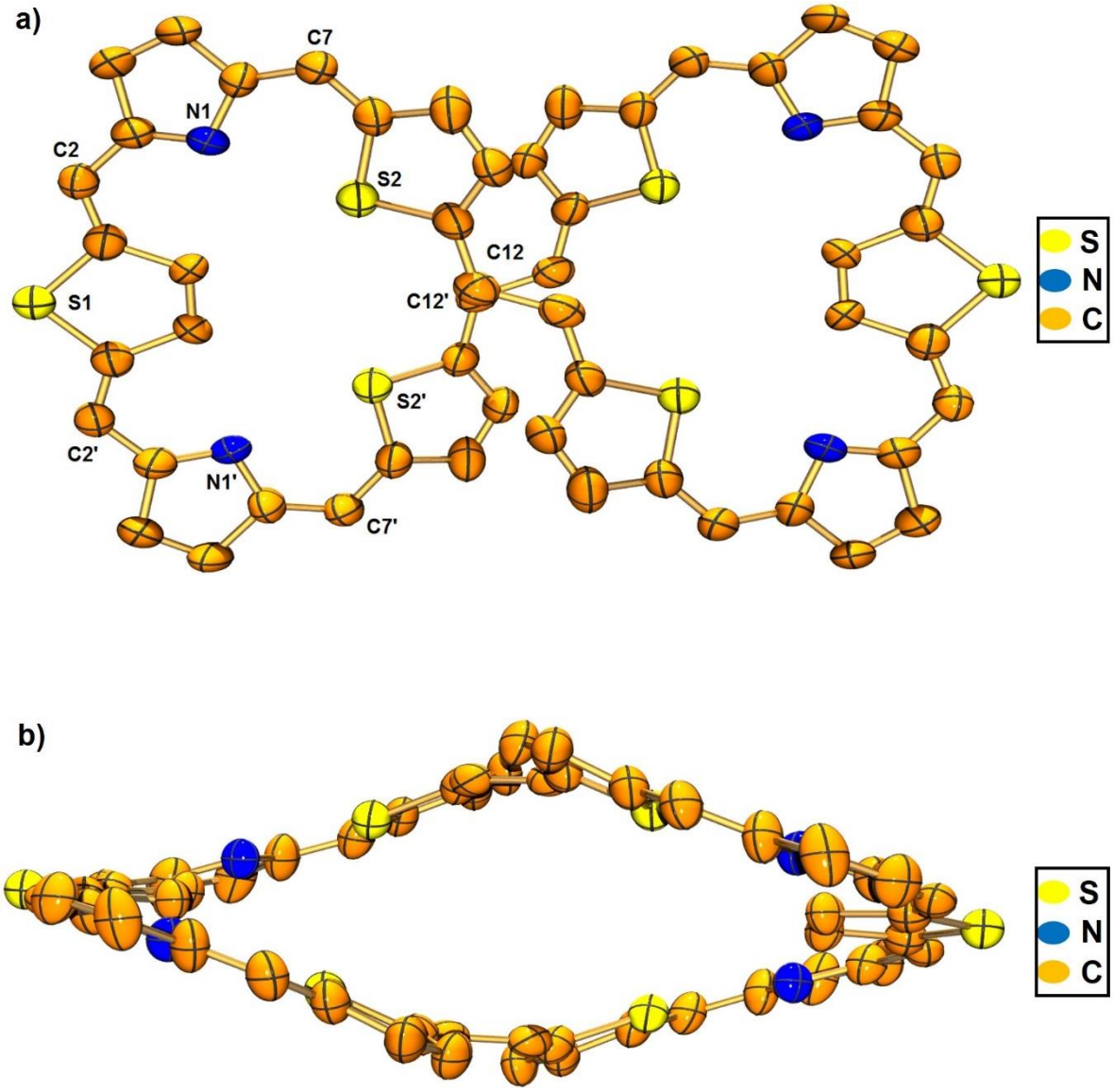


Figure S3: Crystal structure of **10** (a) Top view and (b) side view (*Meso* substituents and hydrogen atoms are omitted for clarity)

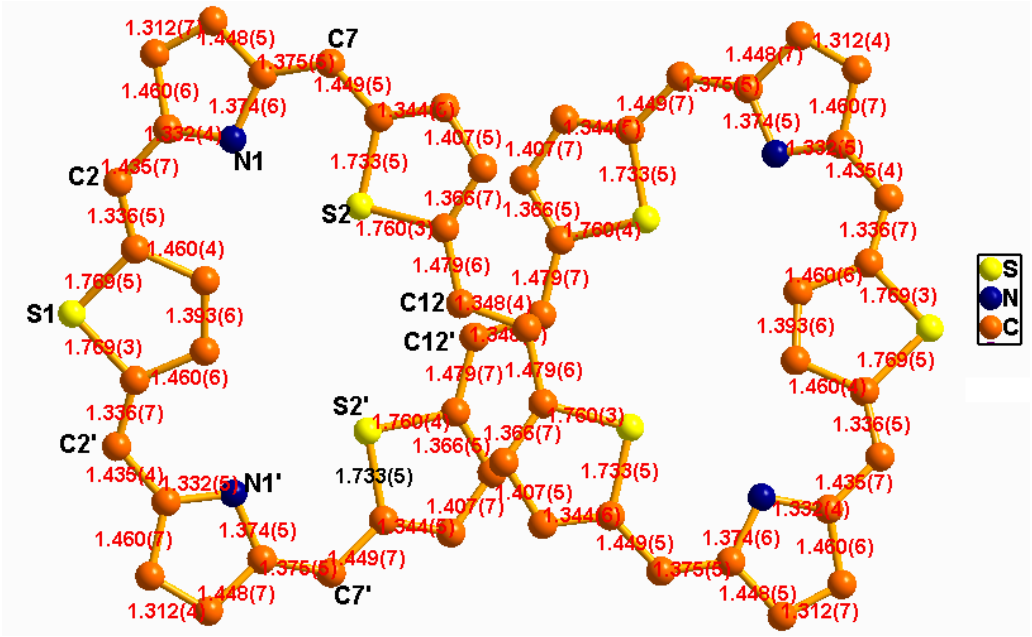


Figure S4: Bond length of **10**

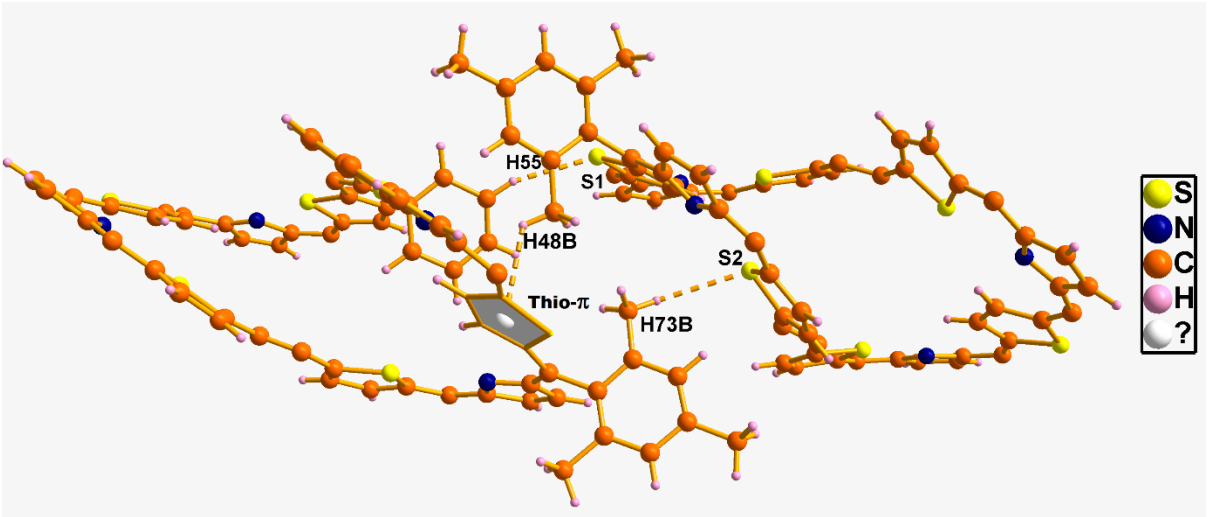


Figure S5: Self-assembled dimer of **10** (a) The CH….π interaction generated between thiophene π electron cloud and C48-H48 (b) Intermolecular molecular hydrogen bonding between (i) S2…H73-C73 and (ii) S1…H55-C55.

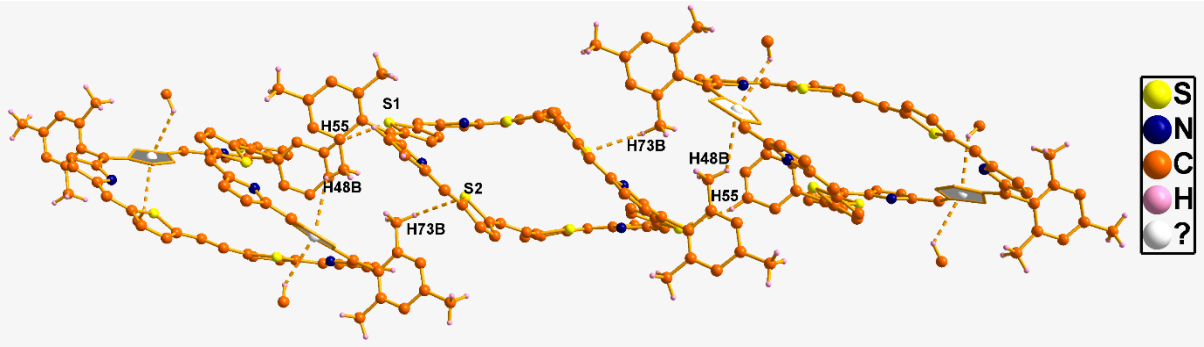


Figure S6: One dimensional array structure of **10**

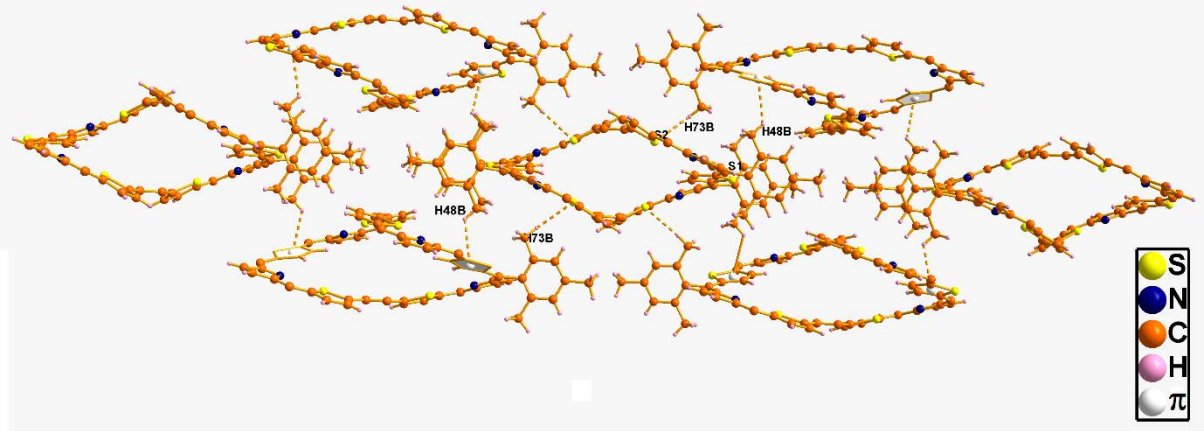


Figure S7: two dimensional arrays of **10**.

Table S1: Crystal data for **10**

Table 1. Crystal data and structure refinement for tkc_Decaphyrin_Final.	
Identification code	tkc_Decaphyrin_Final
Empirical formula	$C_{44.4}H_{38.4}N_{1.2}S_{1.8}$
Formula weight	646.47
Temperature/K	100.0
Crystal system	hexagonal
Space group	$P6_222$
a/Å	28.8585(6)
b/Å	28.8585(6)
c/Å	37.6170(4)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	27130.8(12)
Z	20
ρ_{calc}g/cm^3	0.791
μ/mm^{-1}	0.971
F(000)	6840.0
Crystal size/mm^3	0.2 × 0.15 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.88 to 154.814
Index ranges	$-31 \leq h \leq 31$, $-17 \leq k \leq 18$, $-46 \leq l \leq 46$
Reflections collected	18453
Independent reflections	18452 [R_{int} = 0.0000, R_{sigma} = 0.0636]
Data/restraints/parameters	18452/0/725
Goodness-of-fit on F^2	0.911
Final R indexes [I>=2σ (I)]	R_1 = 0.0421, wR_2 = 0.0947
Final R indexes [all data]	R_1 = 0.0697, wR_2 = 0.1041
Largest diff. peak/hole / e Å^{-3}	0.18/-0.15
Flack parameter	0.037(8)

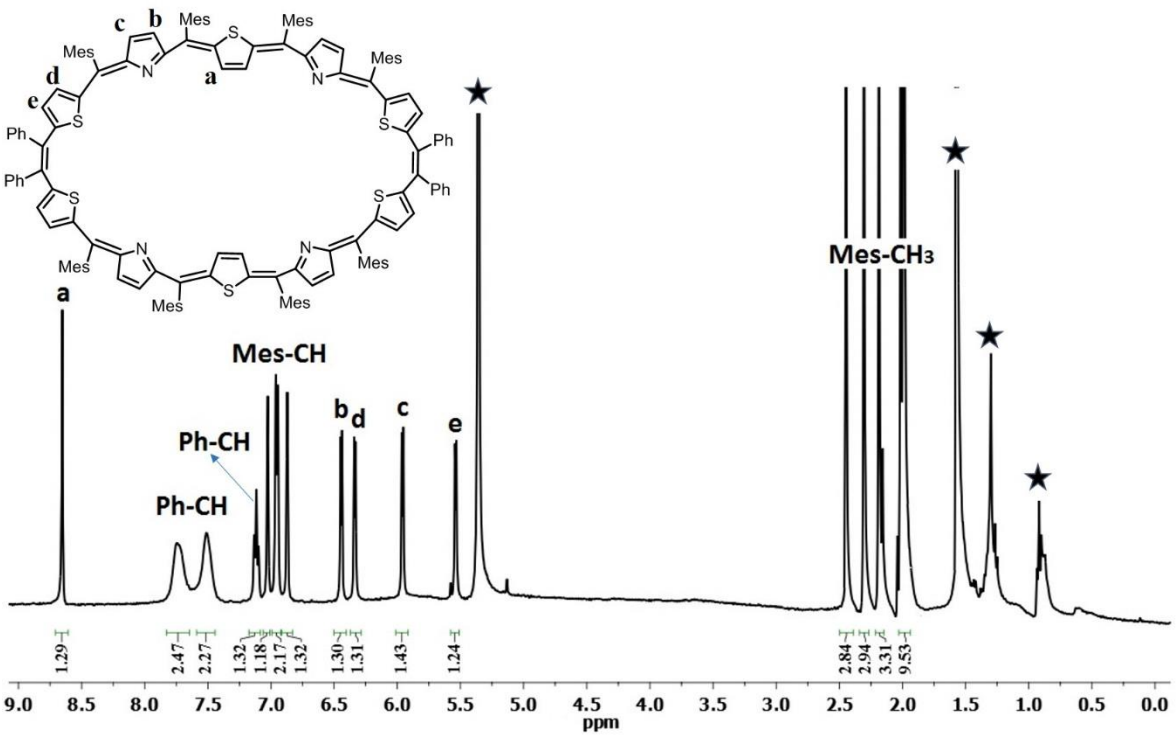


Figure S8: ^{1}H NMR spectrum of **10 i**n CD_2Cl_2

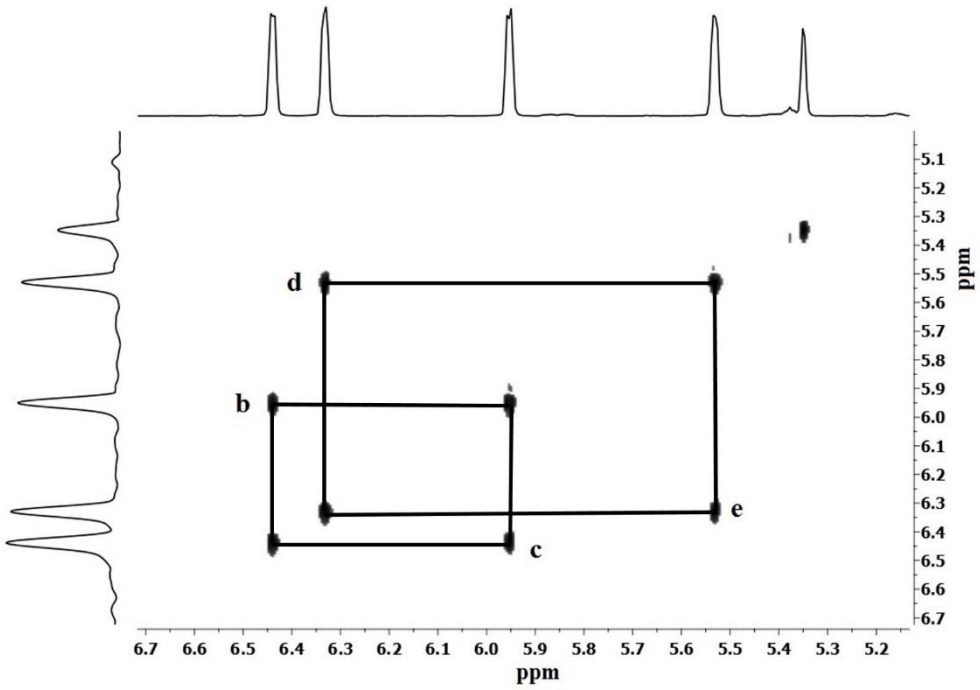


Figure S9: ^{1}H-^{1}H COSY spectrum of **10** with correlation in pyrrole and thiophene rings as part of the ethene bridge.

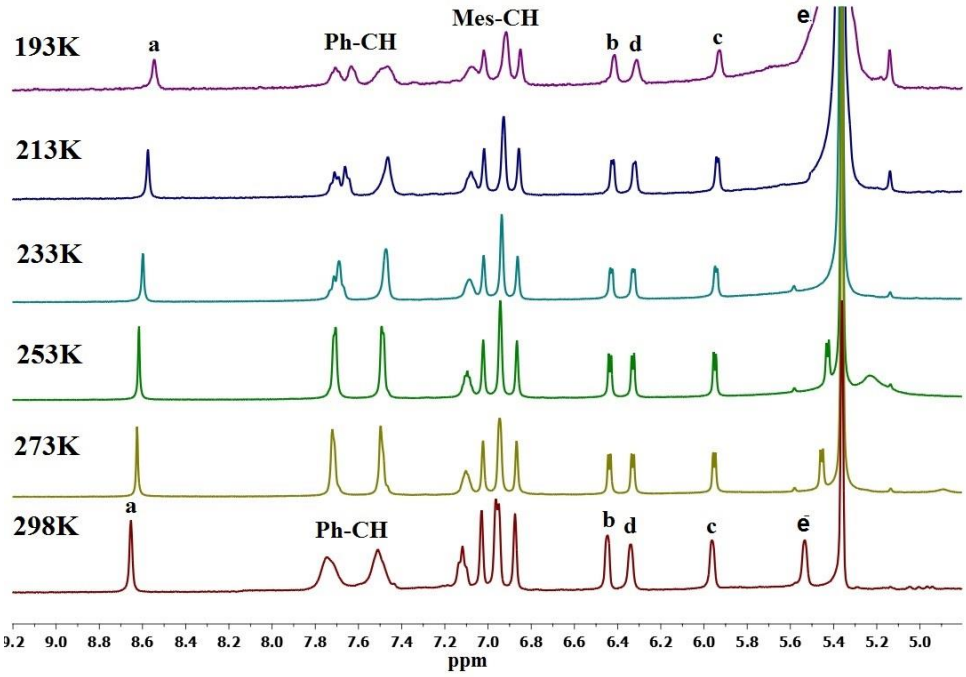


Figure S10: Low temperature ^{1}H NMR spectrum of **10** in CD_2Cl_2 (Aromatic region)

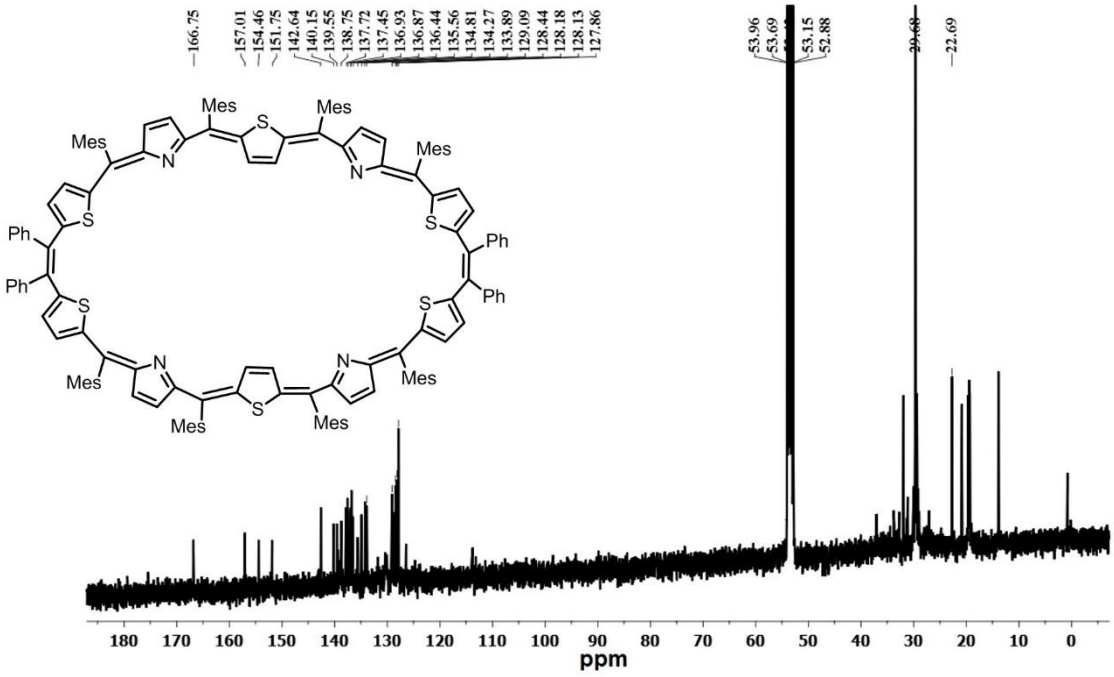


Figure S11: ^{13}C NMR spectrum of **10 i**n CD_2Cl_2

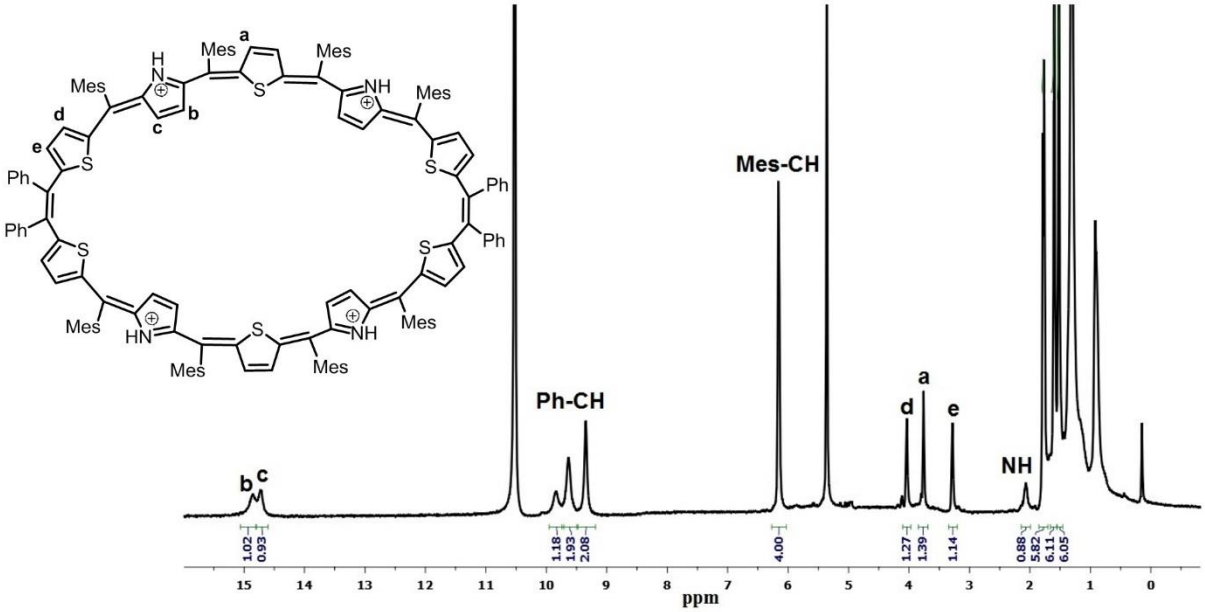


Figure S12: ^{1}H NMR spectrum of **10.4H**$^{+}$in CD_2Cl_2

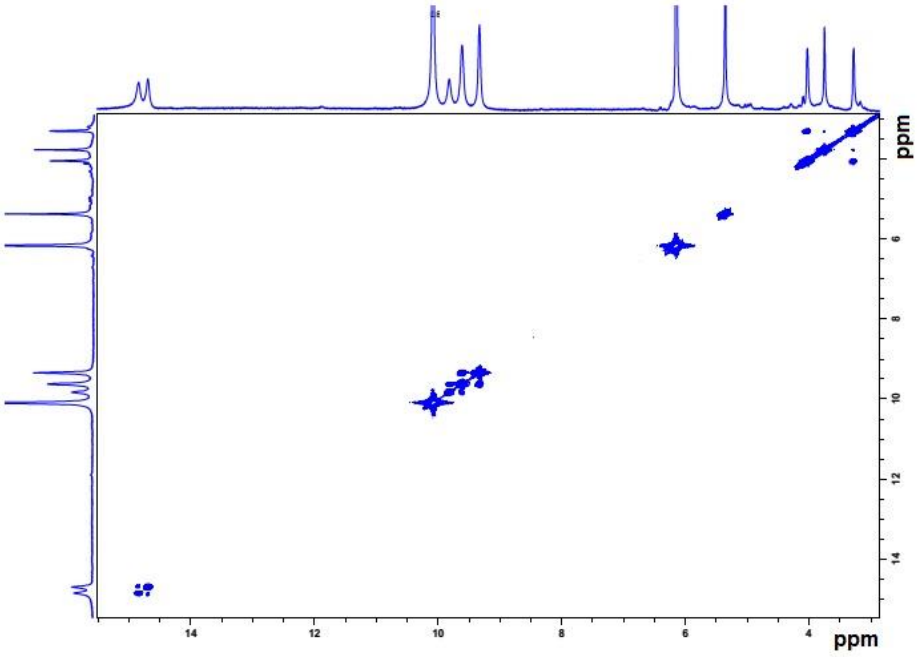


Figure S13: ^{1}H-^{1}H COSY spectrum of **10**.4H^{+} with correlation in pyrrole and thiophene rings as part of the ethene bridge

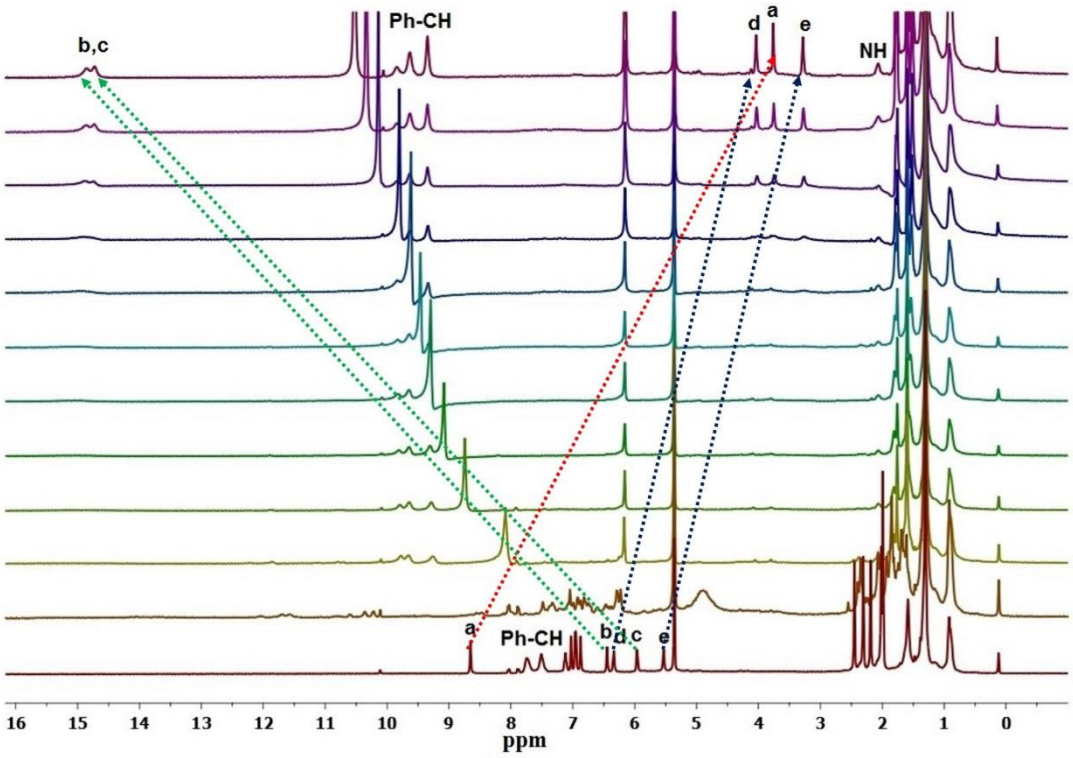


Figure S14: ^{1}H NMR titration experiment of **10** with dilute solution of TFA in CD_2Cl_2

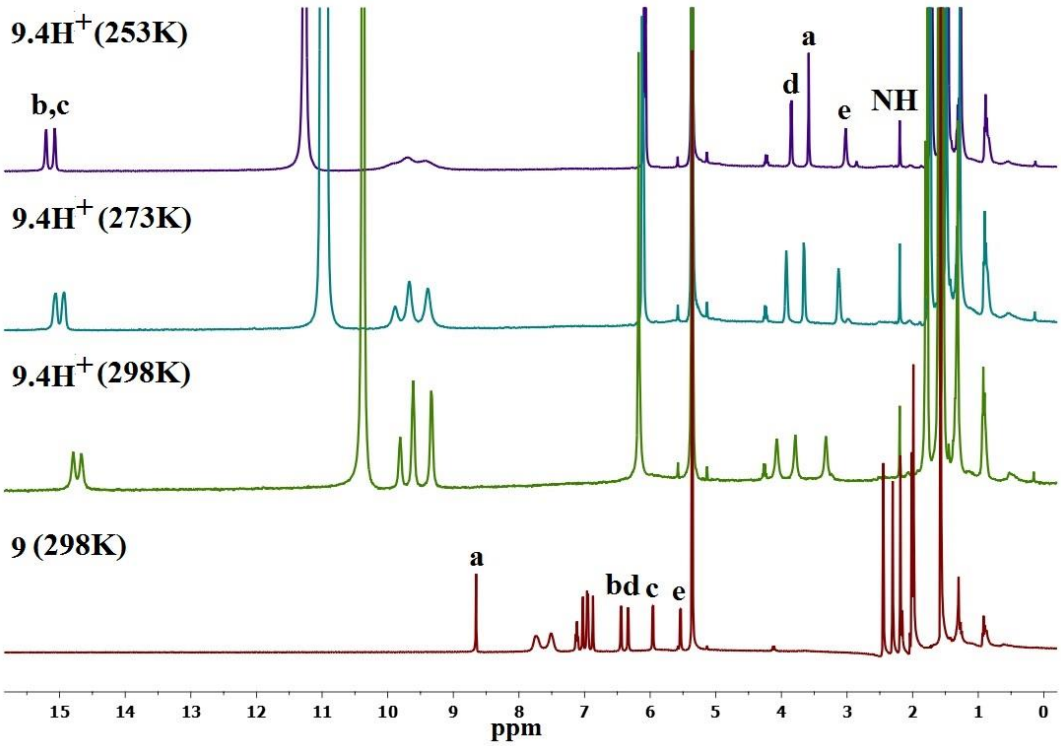


Figure S15: Low temperature ^{1}H NMR spectrum of **10**.4H^{+} in CD_2Cl_2 (Full)

a)

b)

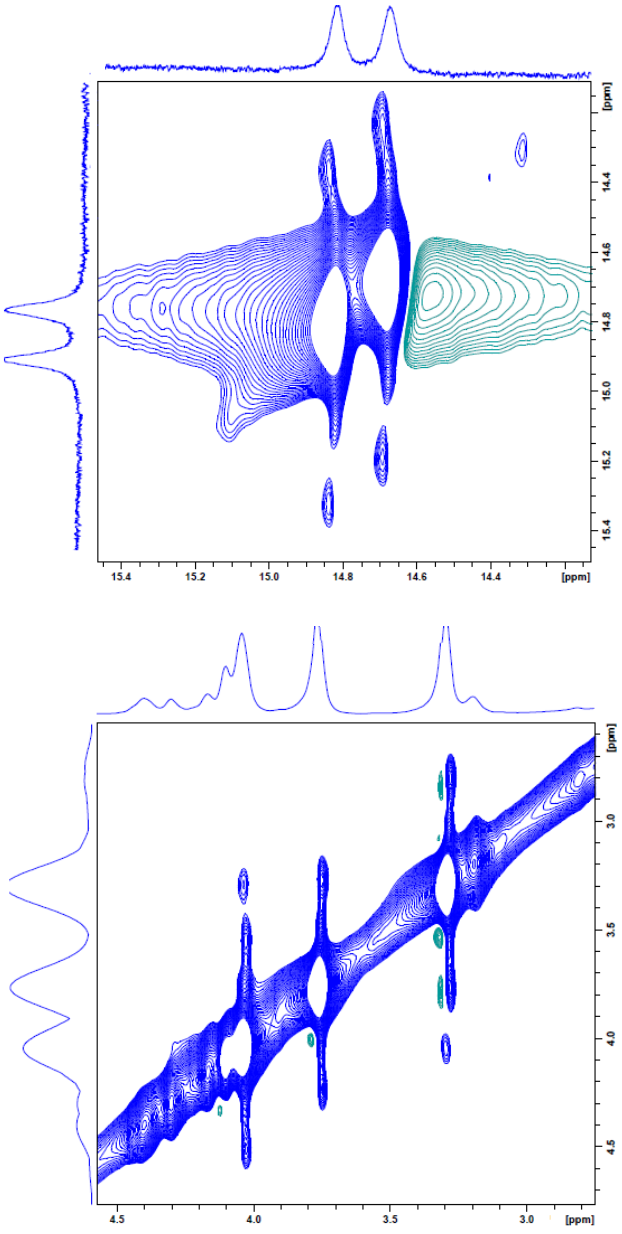


Figure S16: 2D NMR NOESY spectrum of **10**.4H$^+$ in CD_2Cl_2

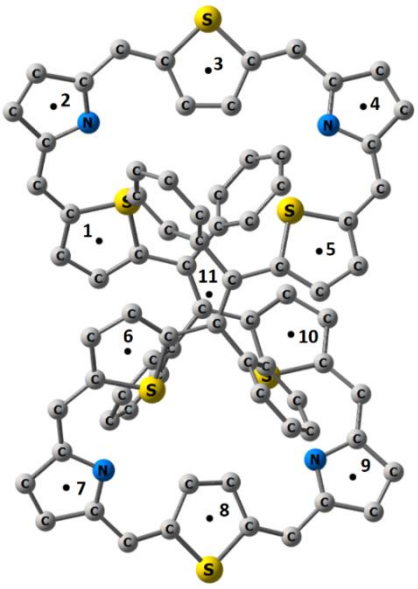


***Figure S17*:** Optimized structure of **10** without meso groups at M062X/6-31G** level of DFT

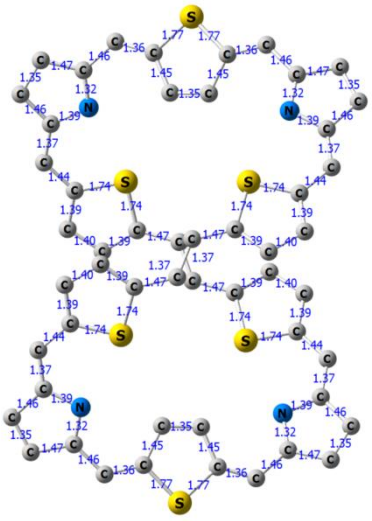
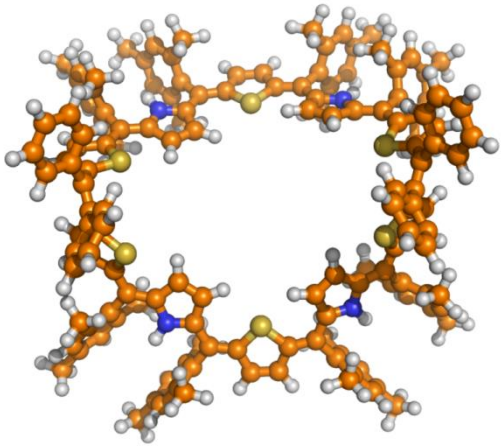


Figure S18: Bond length parameters in Å for **10** at M062X/6-31G** level of DFT. Mesityl groups and Hydrogen atoms are omitted for clarity.

a)



b)

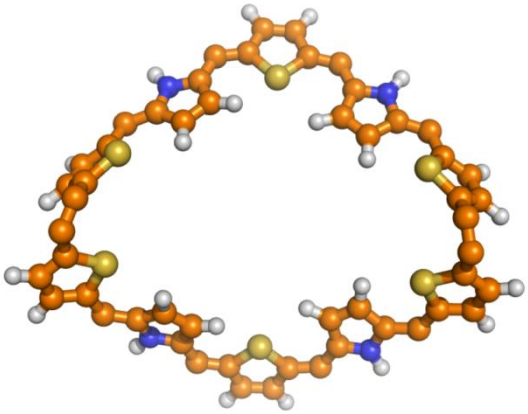
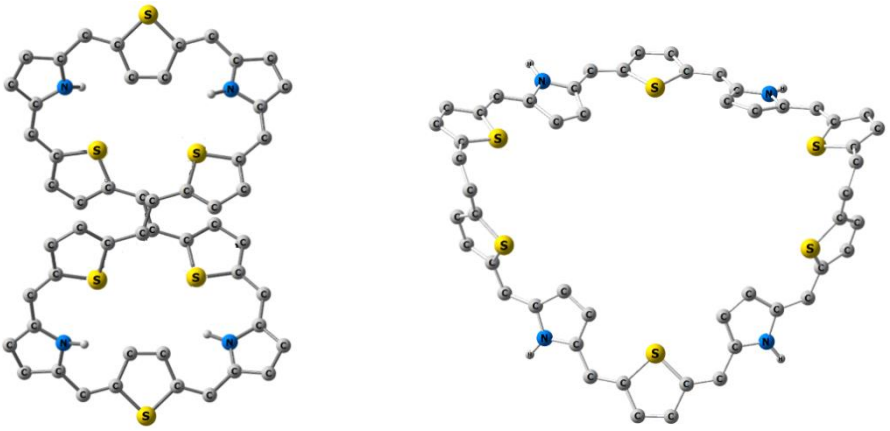


Figure S19: Optimized structure of **10.4H**$^{+}$ (a) with meso groups (b) without meso groups at M062X/6-31G** level of DFT



A **B**

E = -8323.828790 a.u. **E = -8323.855464 a.u.**

Relative E = 16.7 kcal/mol **0.0 kcal/mol**

***Figure S20*:** Energy and relative energy of the two configurations of **10**.4H$^+$ at M062X/6-31G** level of DFT. Mesityl groups, phenyl groups and the H atoms are omitted for clarity.

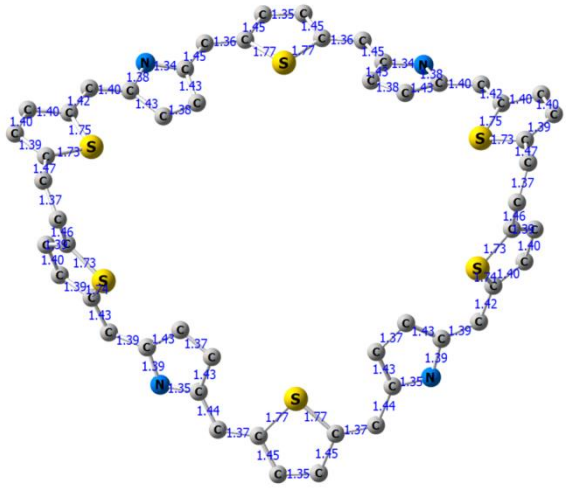
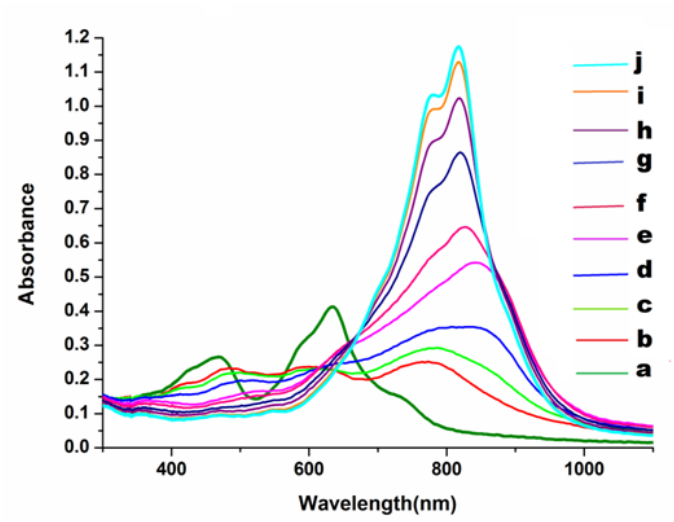


Figure S21: Bond length parameters in Å for **10.4H**$^+$ at M062X/6-31G** level of DFT. Mesityl groups and Hydrogen atoms are omitted for clarity.



	λmax (nm)	Shift (nm)
10	478, 634, 736	
10.H⁺	773	139
10.2H⁺	773, 840	139, 206
10.3H⁺	774, 819	140, 185
10.4H⁺	777, 813	143, 179

Figure S22: Titration with dilute solution of TFA in CH_2Cl_2 on decaphyrin **10** with concentration 1.39 x 10^{-5} M. The concentration of TFA used are a) 0 M, b) 6.5 x 10^{-6} M, c) 1.3 x 10^{-5} M, c) 2.6 x 10^{-5} M, e) 3.9 x 10^{-5} M, f) 5.2 x 10^{-5} M, g) 7.8 x 10^{-5} M, h) 1.04 x 10^{-4}M, i) 1.3 x 10^{-4} M and j) 1.56 x 10^{-4} M

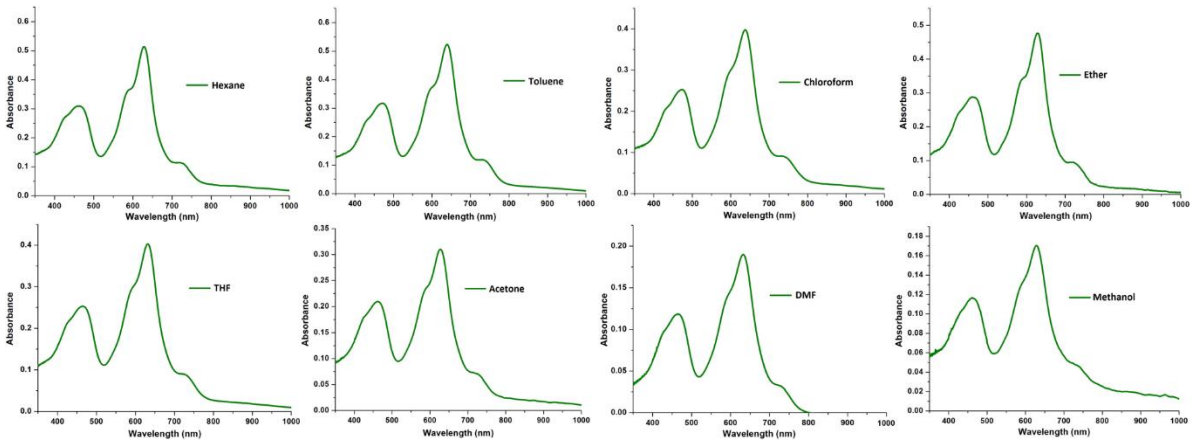


Figure S23: Electronic absorption spectra of **10** in various solvents.

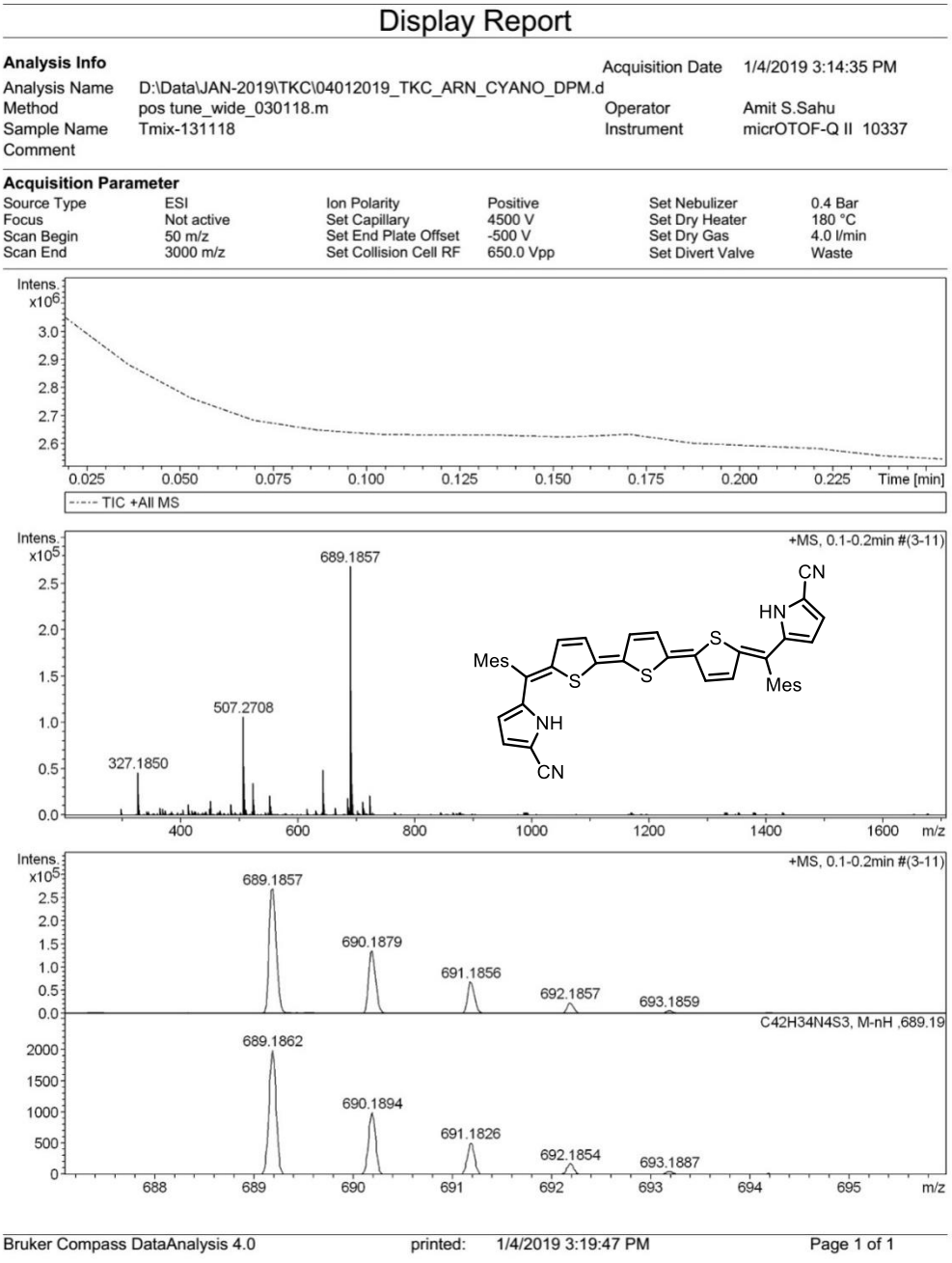


Figure S24: HRMS spectrum of **13.**

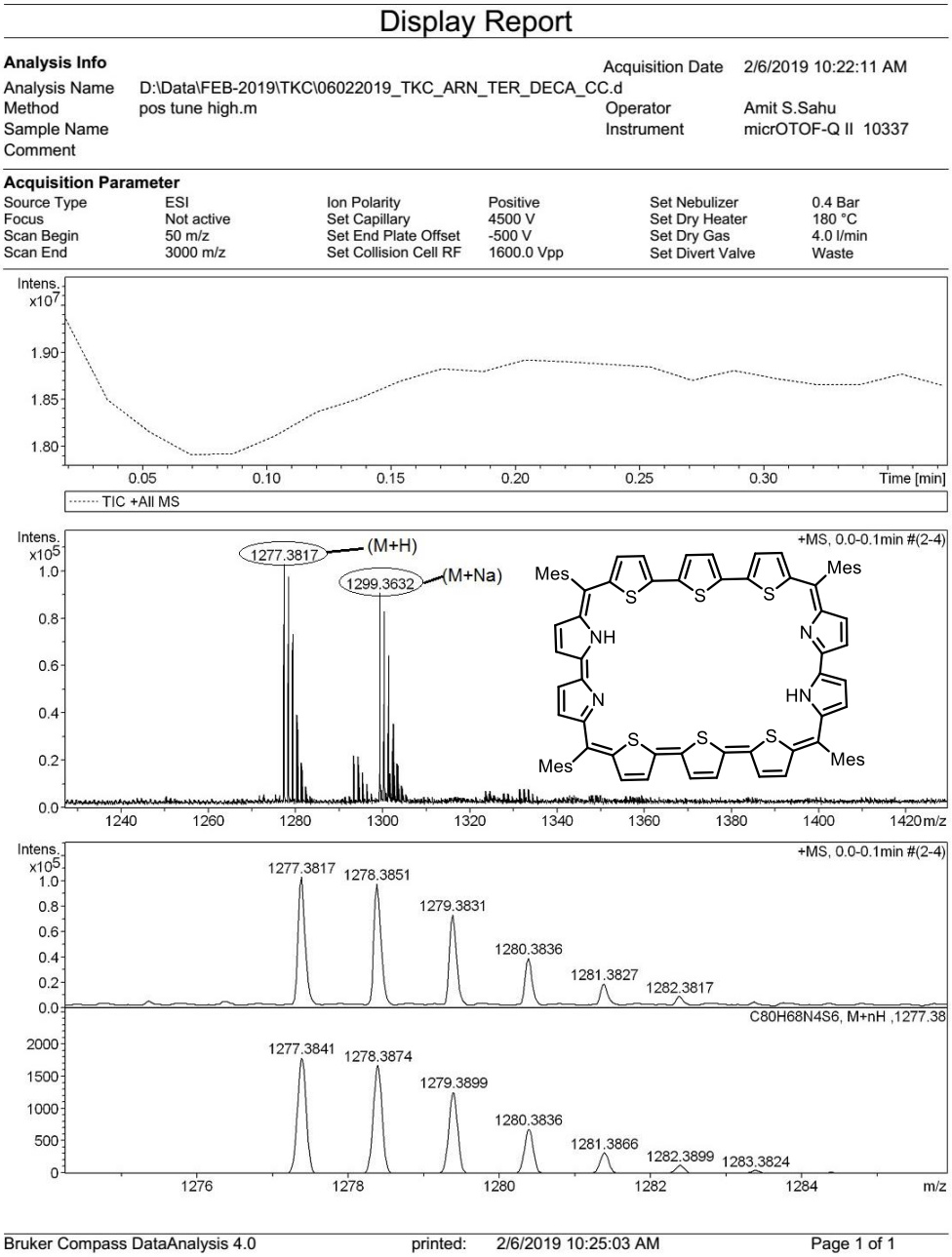


Figure S25: HRMS spectrum of **12**.

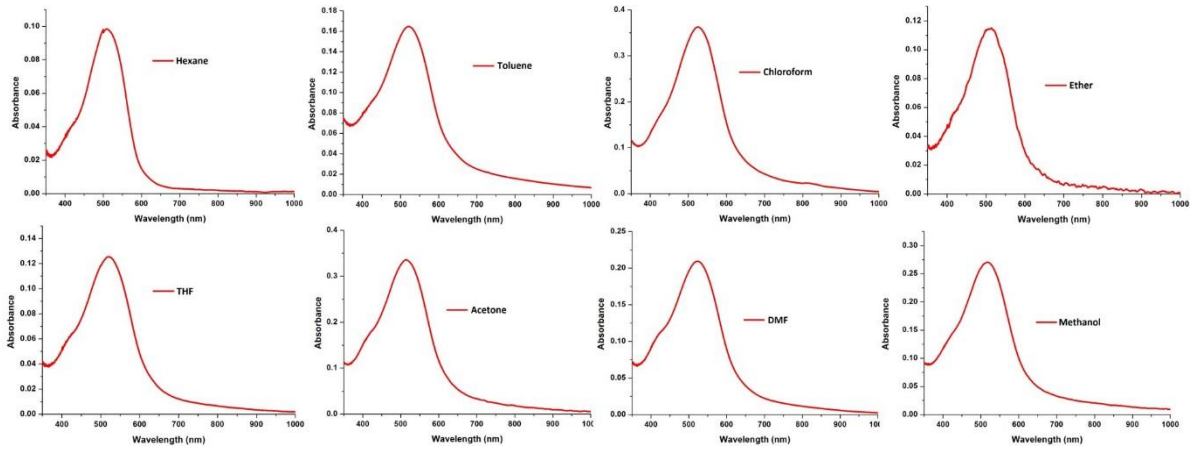
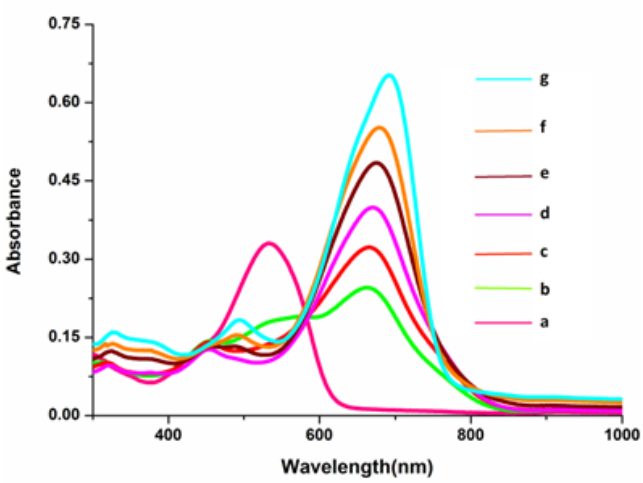


Figure S26: Electronic absorption spectra of **12** in various solvents.



	λmax (nm)	Shift (nm)
12	535	
12.H⁺	661	126
12.2H⁺	703	168

Figure S27: Titration with dilute solution of TFA in CH_2Cl_2 on decaphyrin **12** with concentration 7.83 x 10^{-7} M. The concentration of TFA used are a) 0 M, b) 1.3 x 10^{-7} M, c) 3.9 x 10^{-7} M, d) 7.8 x 10^{-7} M, e) 1.1 x 10^{-6} M, f) 1.5 x 10^{-6} and g) 1.9 x 10^{-6}M.

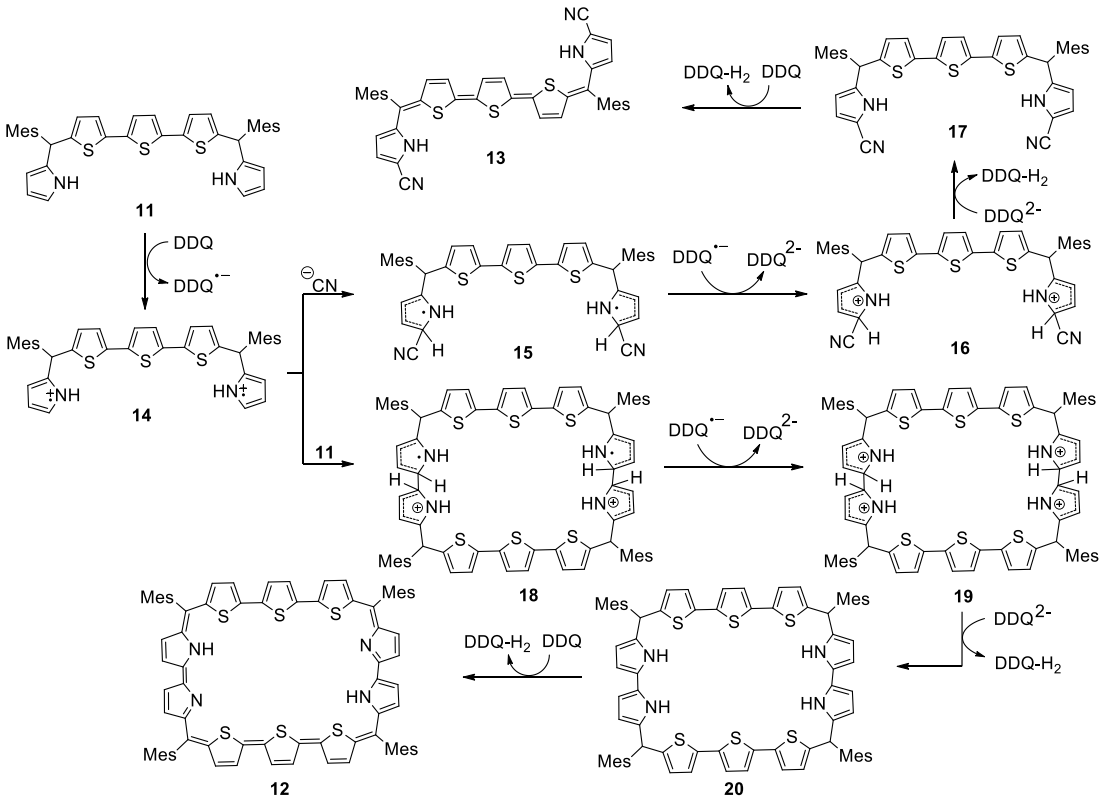


Figure S28: A possible mechanism for the formation of products **13** and **12.**

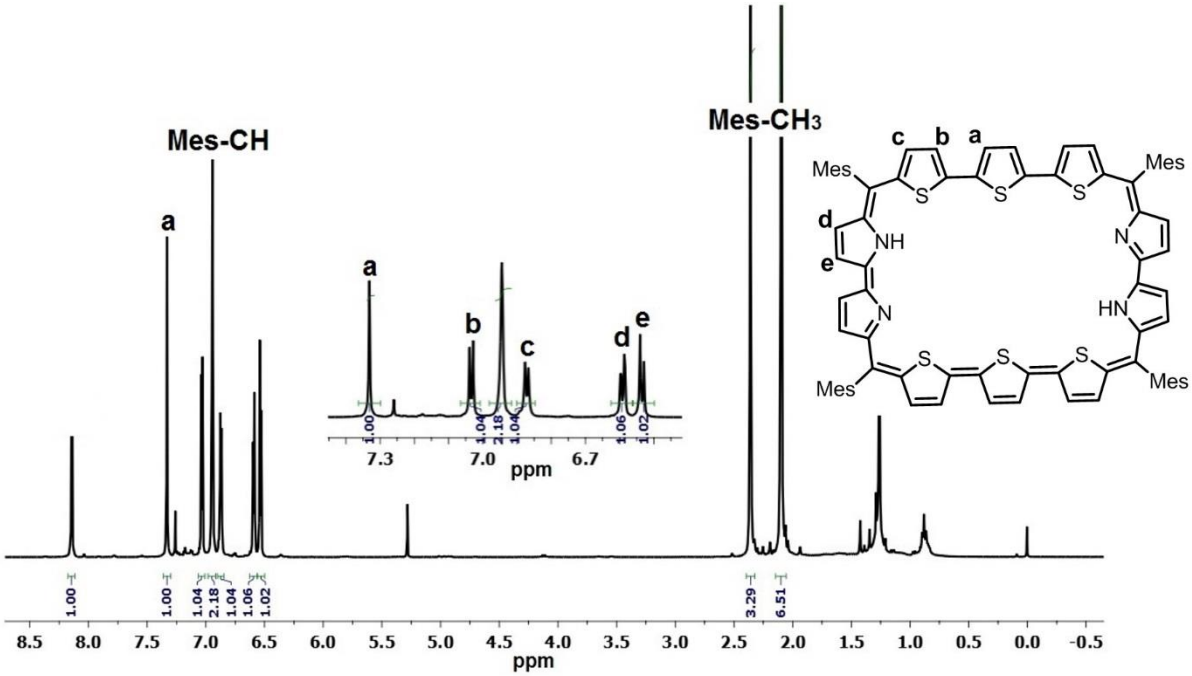


Figure S29: ^{1}H NMR spectrum of **12 i**n CD_2Cl_2

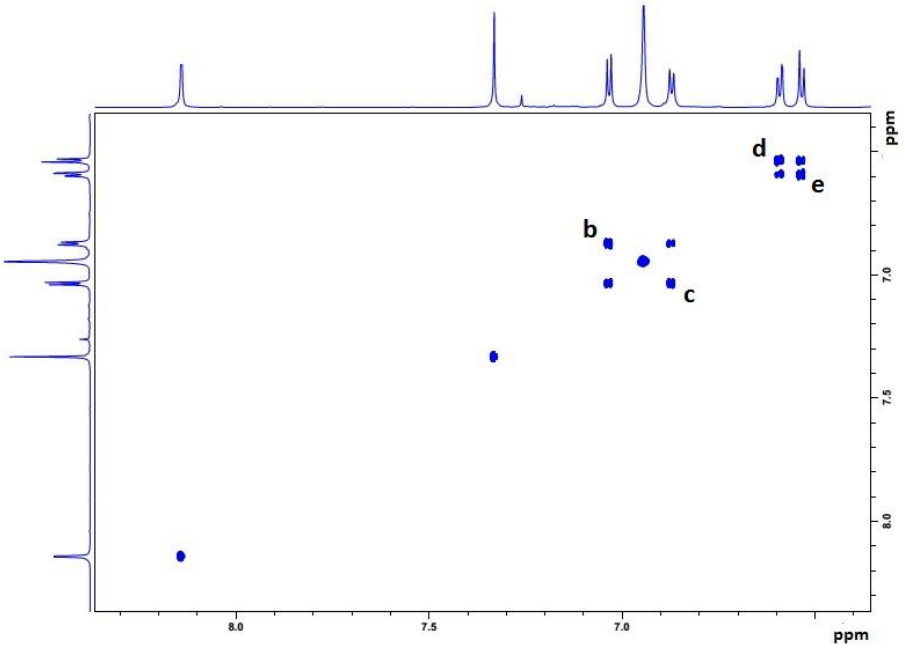


Figure S30: ^{1}H-^{1}H COSY spectrum of **12** with correlation in pyrrole and thiophene rings

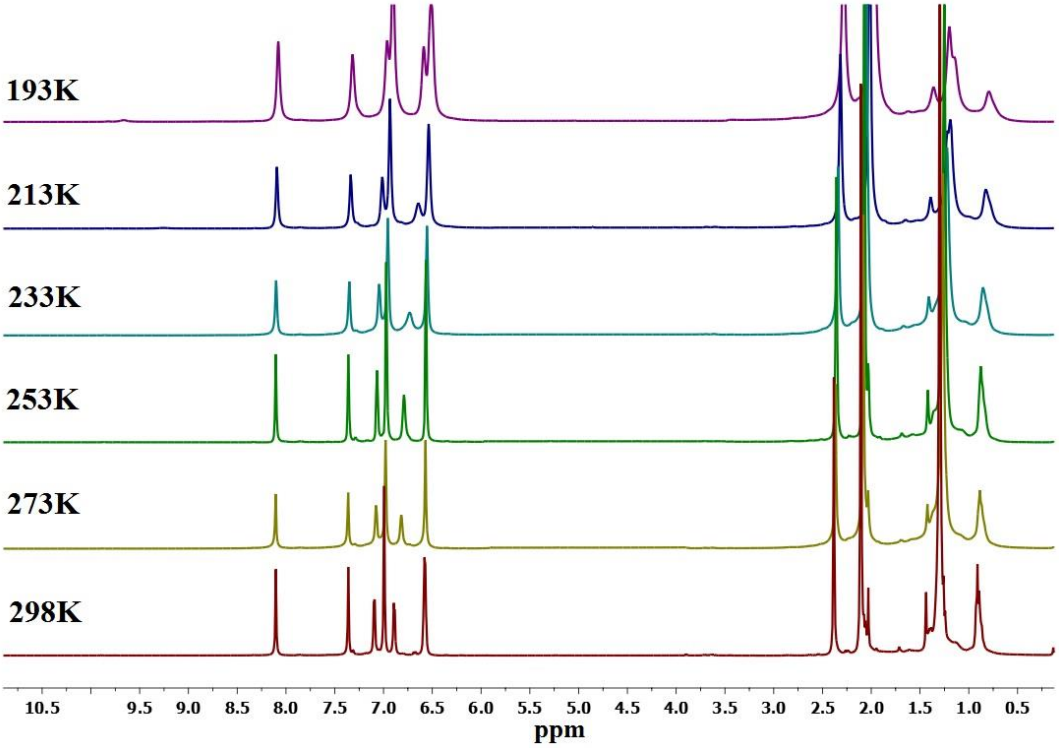


Figure S31: Low temperature ^{1}H NMR spectrum of **12** in CD_2Cl_2 (Full)

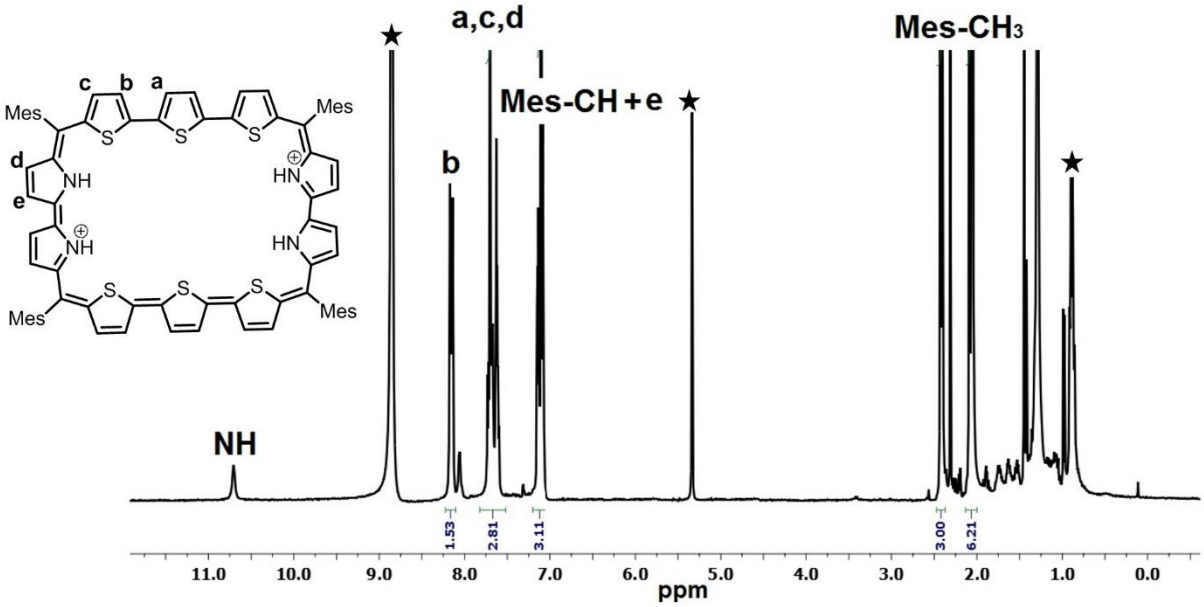


Figure S32: ^{1}H NMR spectrum of **12**.2H^{+}in CD_2Cl_2

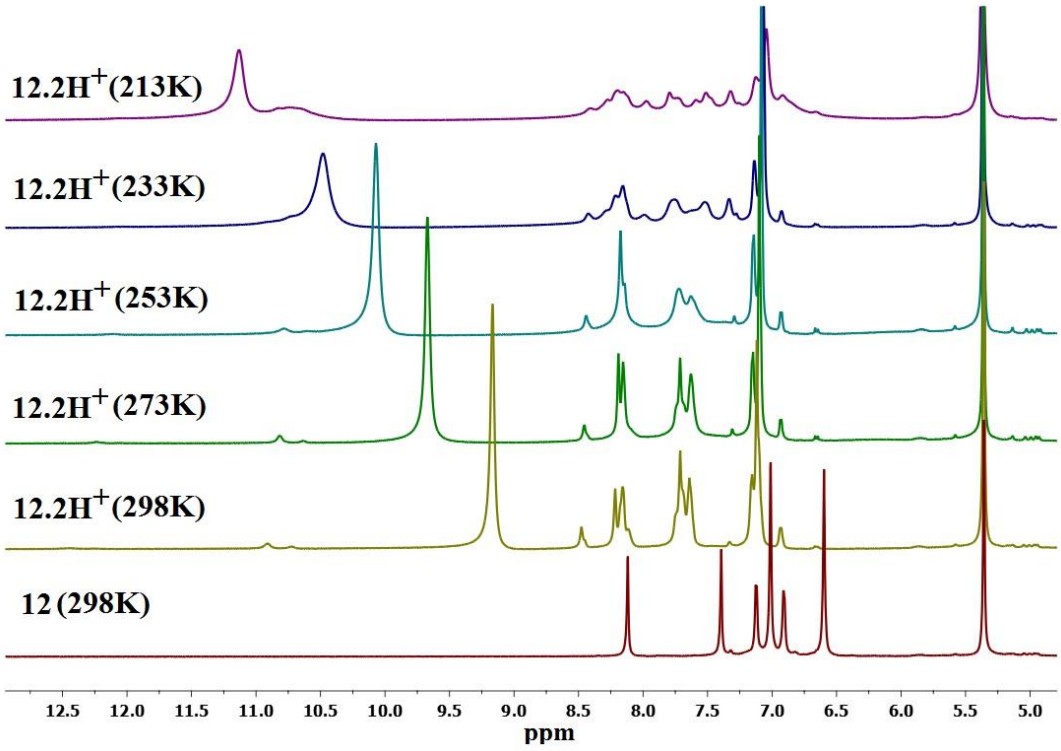


Figure S33: Low temperature ^{1}H NMR spectrum of **12**.2H^{+} in CD_2Cl_2 (Full)

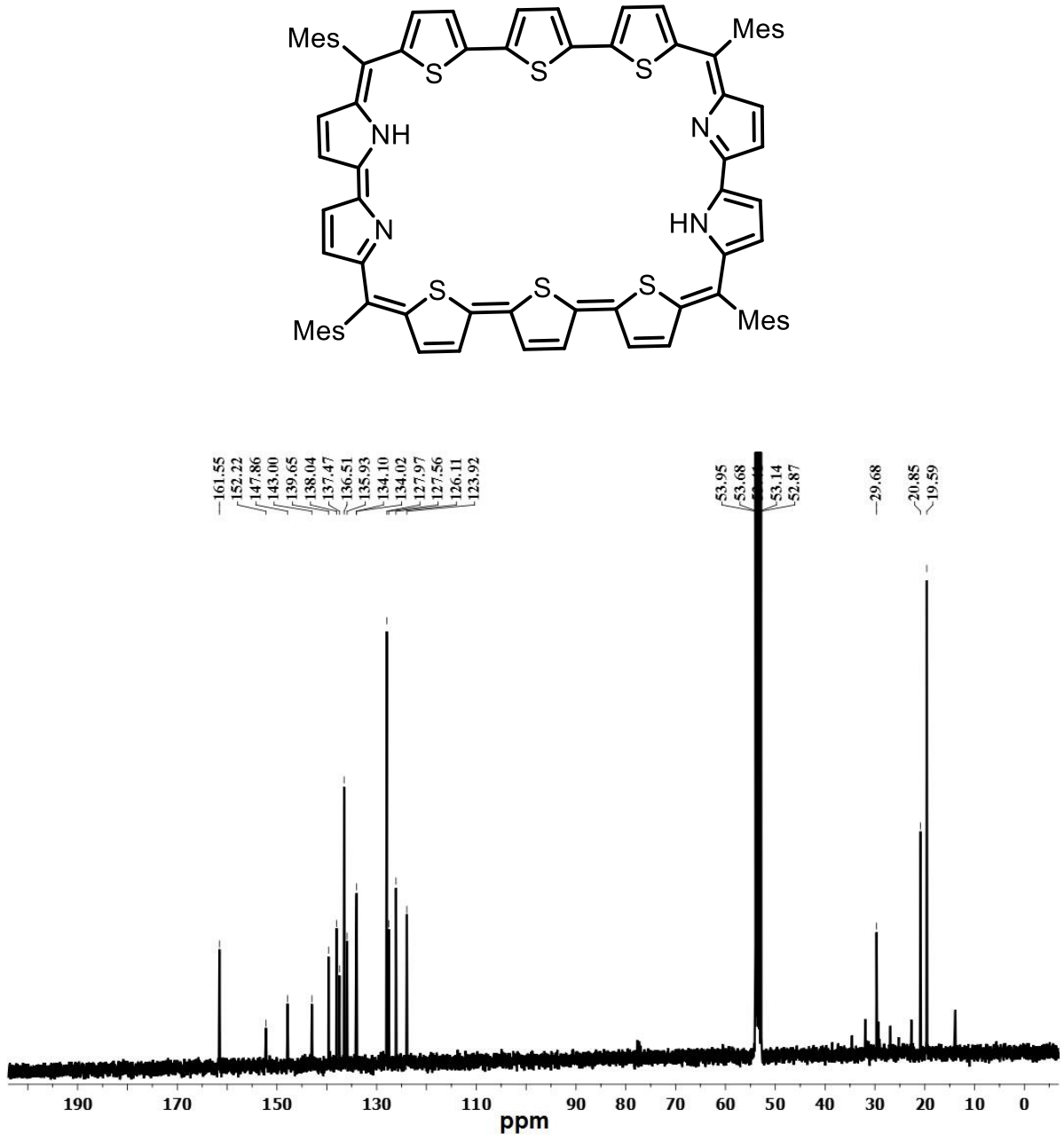
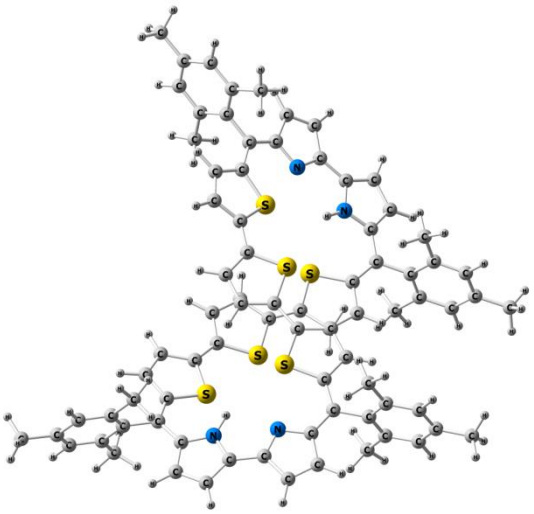


Figure S34: Proton decoupled ^{13}C NMR spectrum of **12** in CD_2Cl_2

a)



b)

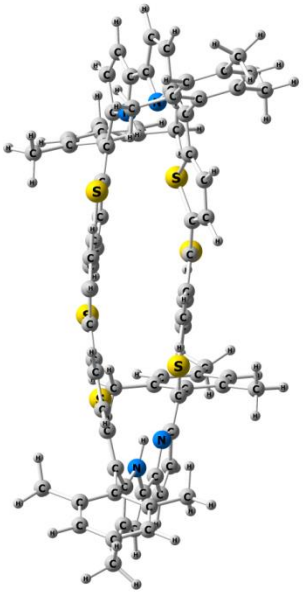


Figure S35: (a) Front view (b) side view of the optimized structure of **12** in figure-eight configuration at M062X/6-31G** level of DFT.

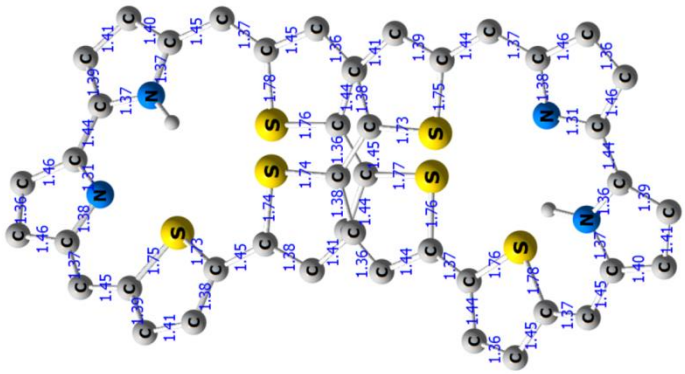


Figure S36: Bond length parameters in Å for **12** at M062X/6-31G** level of DFT. Mesityl groups and Hydrogen atoms are omitted for clarity.

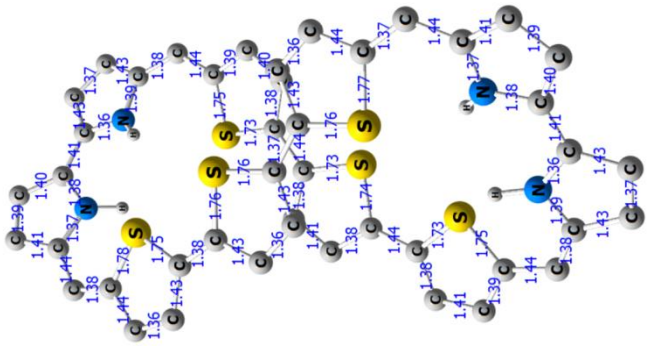


Figure S37: Optimized structure of **12.2H**$^{+}$at M062X/6-31G** level of DFT. Bond lengths in Å. Mesityl groups and Hydrogen atoms are omitted for clarity.

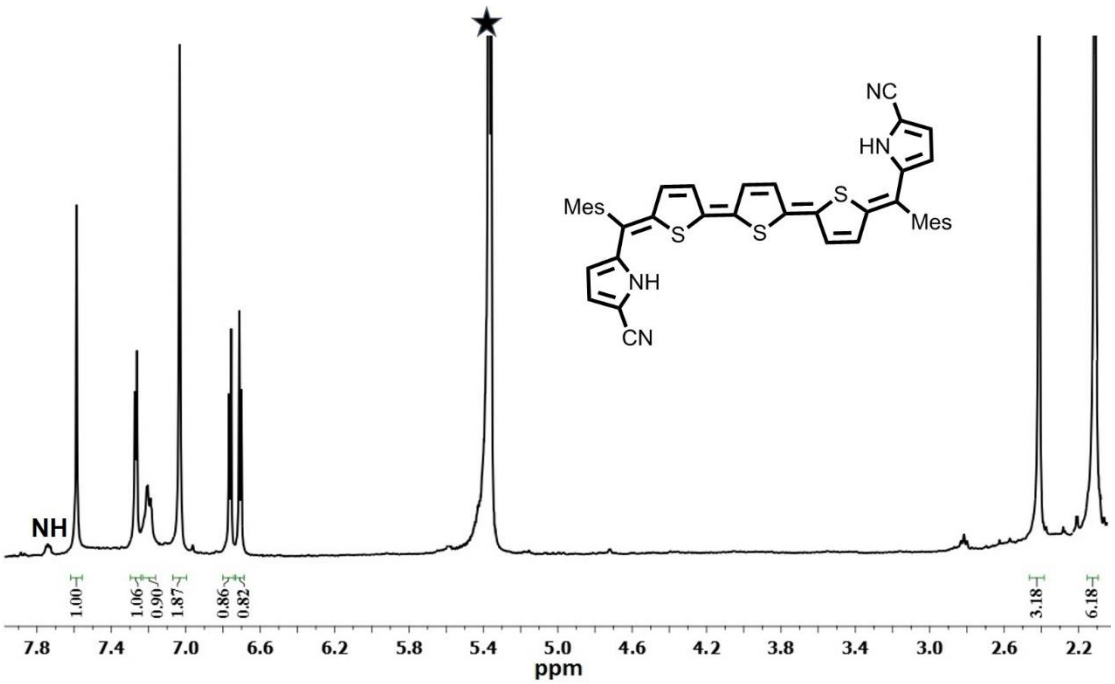


Figure 38: ^{1}H NMR spectrum of **13 i**n CD_2Cl_2

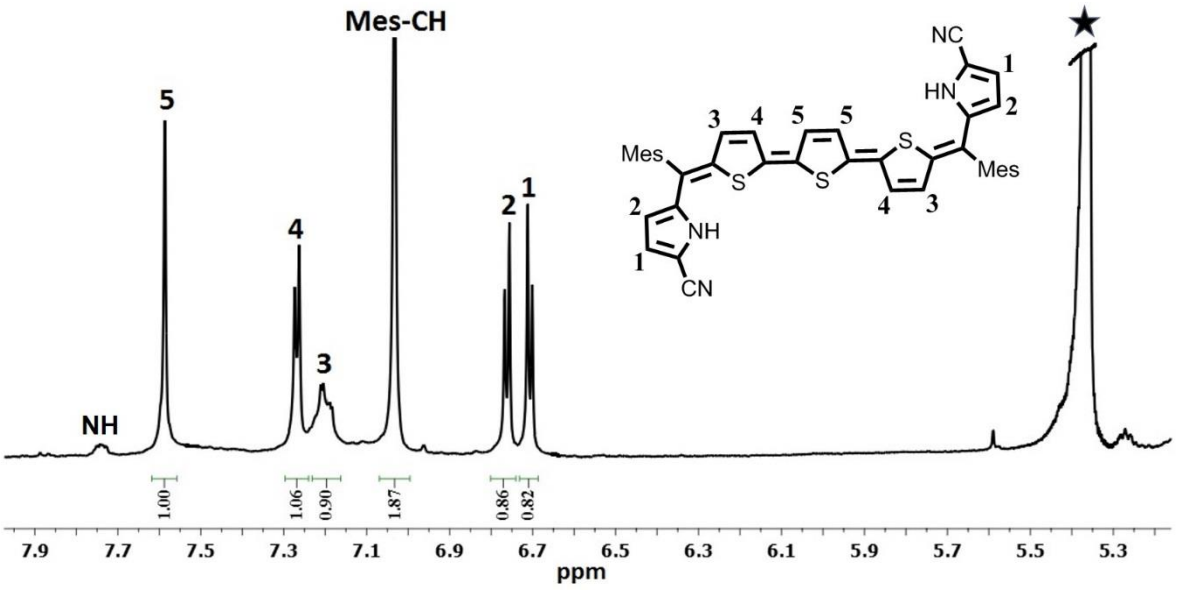


Figure S39: ^{1}H NMR spectrum of **13 i**n CD_2Cl_2 (Aromatic region)

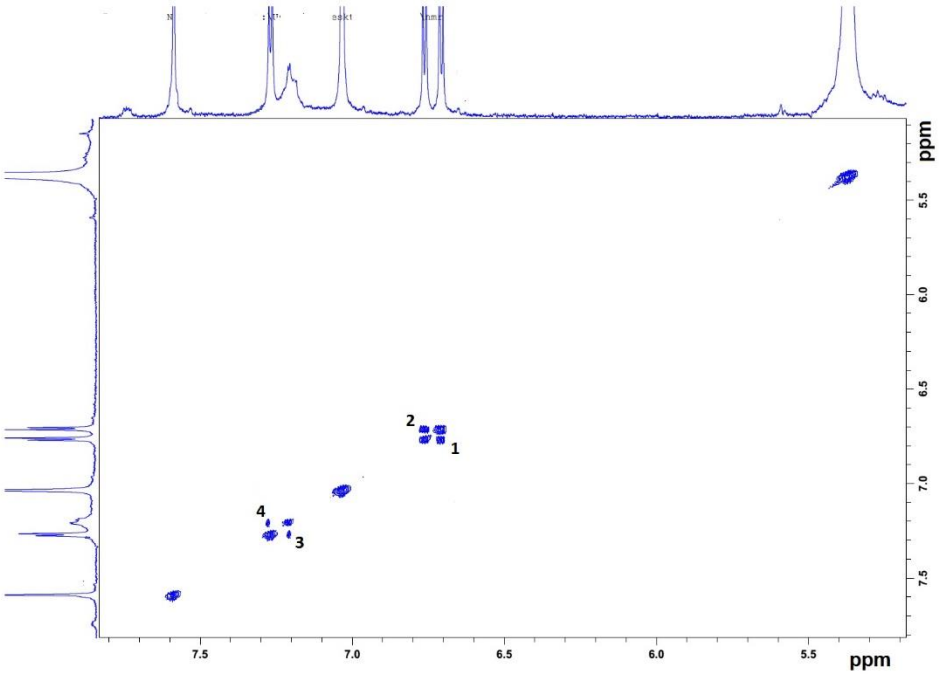


Figure S40: ^{1}H-^{1}H COSY spectrum of **13** with correlation in pyrrole and thiophene rings

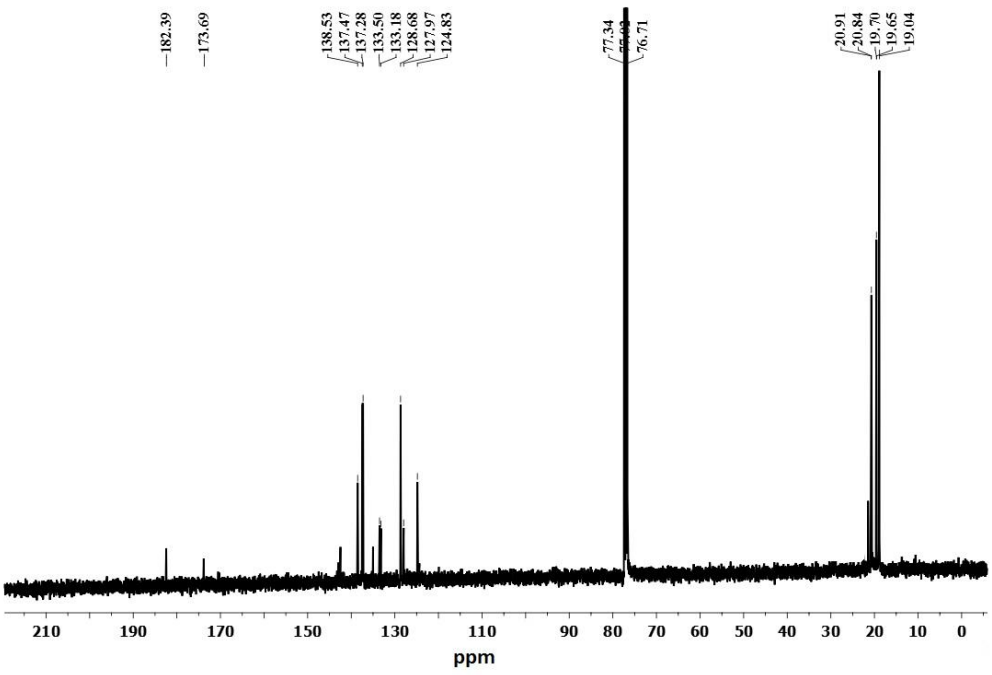


Figure S41: Proton decoupled ^{13}C NMR spectrum of **13 i**n $CDCl_3$

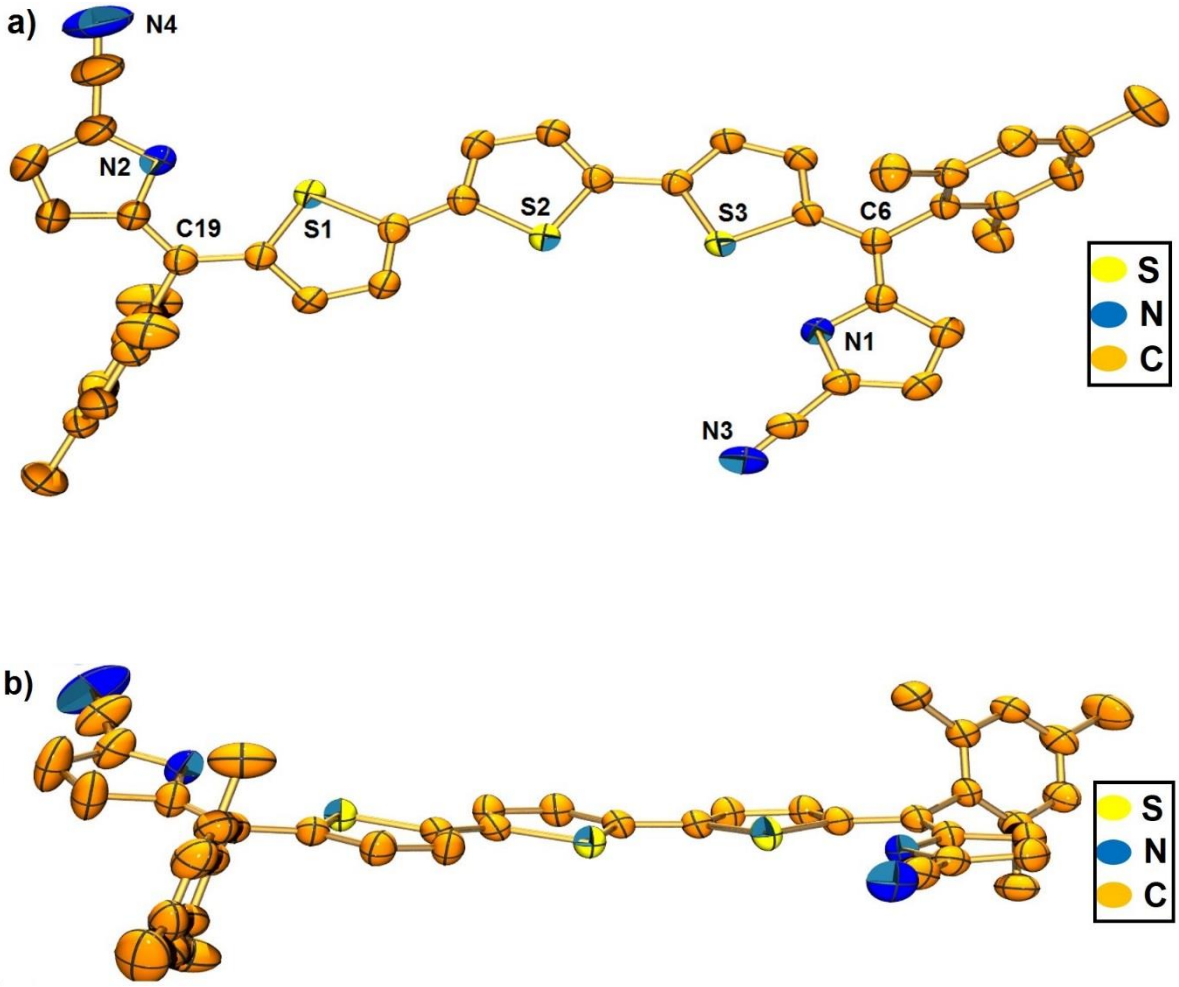


Figure S42: Crystal structure of **13** (a) Top view and (b) side view(Hydrogen atoms are omitted for clarity).Thermal ellipsoids are drawn at 50% probability.

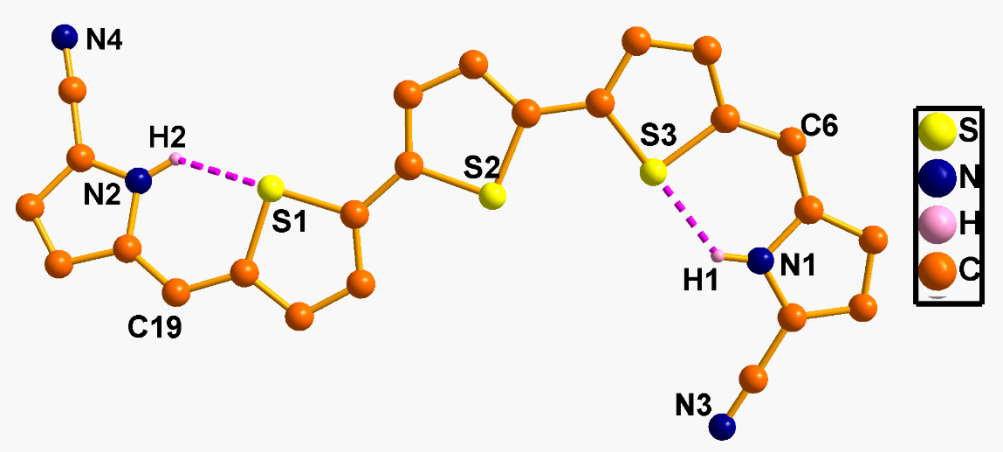


Figure S43: Self assembled dimer through intermolecular hydrogen bonding of **13** (C40-H40…N3 with a distance 2.71Å and angle 149.41º)

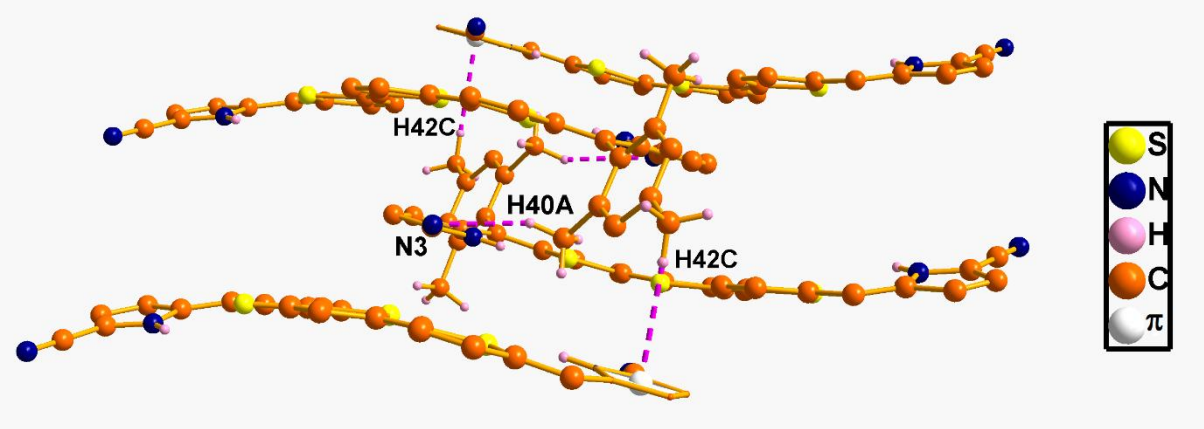


Figure S44: Two dimensional array of **13** (a) Intermolecular hydrogen bonding (C40-H40…N3 with a distance 2.71Å and angle 149.41º) (b) π…H interaction between Py(π)…C42-H42C

Table S2: Crystal data for 13

Table 2. Crystal data and structure refinement for TKC_CYANO_TPM.	
Identification code	TKC_CYANO_TPM
Empirical formula	$C_{28}H_{22.67}N_{2.67}S_2$
Formula weight	460.61
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.69725(17)
b/Å	10.9283(2)
c/Å	20.5323(5)
α/°	84.0758(17)
β/°	88.6243(18)
γ/°	67.6514(18)
Volume/Å^3	1795.05(7)
Z	3
ρ_{calc}g/cm^3	1.278
μ/mm^{-1}	2.162
F(000)	724.0
Crystal size/mm^3	0.18 × 0.16 × 0.14
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.66 to 136.49
Index ranges	$-10 \leq h \leq 10$, $-10 \leq k \leq 13$, $-24 \leq l \leq 24$
Reflections collected	25727
Independent reflections	6570 [R_{int} = 0.0934, R_{sigma} = 0.0607]
Data/restraints/parameters	6570/0/448
Goodness-of-fit on F^2	1.092
Final R indexes [I>=2σ (I)]	R_1 = 0.0779, wR_2 = 0.2323
Final R indexes [all data]	R_1 = 0.0852, wR_2 = 0.2367
Largest diff. peak/hole / e Å^{-3}	0.59/-0.53