

## Supporting Information

### Fused Core-Modified *meso*-Aryl Expanded Porphyrins

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## 1. General Information :

NMR spectra were recorded with Bruker 300 MHz or 500 MHz ADVANCE –II spectrometer in CDCl<sub>3</sub> or CD<sub>2</sub>Cl<sub>2</sub> using tetramethylsilane (TMS) as internal standard. Chemical shifts are expressed in parts per million (ppm) relative to TMS. FAB mass spectra were obtained on a JEOL SX-120/DA6000 spectrometer using argon (6 KV, 10 mA) as the FAB gas. ESI mass spectra were recorded on a MICRO MASS QUATTRO II triple quadrupole mass spectrometer. Electronic spectra were recorded with Perkin Elmer – Lambda 25 UV-Visible spectrophotometer and data analyses were done using the UV-winlab software package. CHN analyses were done on a Heraeus Calro Elba 1108 elemental analyzer.

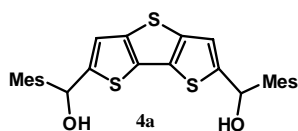
X-ray quality crystals for the compounds were grown by the slow diffusion of hexane over CH<sub>2</sub>Cl<sub>2</sub> / CHCl<sub>3</sub> solution. Single-crystal X-ray diffraction data were collected on a Bruker SMART Apex CCD diffractometer with MoK<sub>α</sub> radiation (0.71073 Å). Semi-empirical absorption correction was applied using SADABS and the program SAINT was used for integration of the diffraction profiles.<sup>1a</sup> The structures were solved by direct methods using the SHELXS program of the SHELXTL package.<sup>1b</sup> Missing atoms were located in subsequent difference Fourier maps and included in the refinement. The structures of all the compounds were refined by full-matrix least squares refinement on  $F^2$  (SHELXL-97). Hydrogen atoms were placed geometrically and refined using a riding model, including free rotation about C-C bonds for methyl groups with  $U_{iso}$  constrained at 1.2 for non-methyl groups, and 1.5 for methyl groups times  $U_{eq}$  of the carrier carbon atom. All non hydrogen atoms were refined anisotropically unless specified.

1. (a) SAINT, Bruker AXS: Madison, WI, 1998; (b) SHELXTL-PC Package, Bruker Analytical X-ray Systems, Madison, WI, 1998.

## 2. Synthetic method and characterization data of compounds:

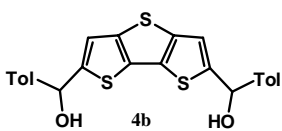
### 5,5'-Bis-(mesitylhydroxymethyl)-dithienothiophene - DTT diol (**4a**) :

To a solution of DTT (0.7 g, 3.5 mmol) in 50 ml THF n-BuLi (5 ml 1.6 M, 7.8 mmol) was added slowly at room temperature under argon atmosphere. It was allowed to stir for 1hr. Mesitaldehyde (1.154 g, 7.8 mmol) in 30ml of THF was added dropwise at 273K. The mixture was allowed to warm to room temperature and stirred further for one hour. To the reaction mixture 75 ml of saturated ammonium chloride solution was added and extracted with diethyl ether. The organic layers were combined, washed with brine and dried over sodium-sulphate. After evaporation, the crude was subjected to silica gel chromatography (1:5, Ethylacetate / Hexane) yielded 1.1g of diol **4a** .Yield:63%.



**4a**:  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ , 298K)  $\delta$ (ppm): 6.88(s, 4H), 6.78(s, 2H), 6.51(s, 2H), 2.35(s, 12H), 2.29(s, 6H); FAB-MS: m/z: 492.36 (60%) $[\text{M}]^+$ , Calcd for  $\text{C}_{28}\text{H}_{28}\text{O}_2\text{S}_3$  : 492.13

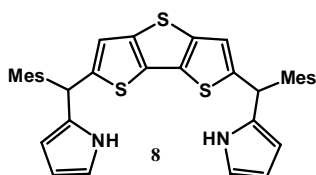
By a similar procedure diol **4b** was prepared by using tolualdehyde instead of mesitaldehyde.



**4b**:  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ , 298K)  $\delta$ (ppm) : 7.3(d, 4H), 7.22(d, 2H), 6.51(s, 2H), 2.32 (s, 6H); FAB-MS:m/z: 436.24 (54%) $[\text{M}]^+$ , Calcd for  $\text{C}_{24}\text{H}_{20}\text{O}_2\text{S}_3$  : 436.16

### 5,14-Dimesityl-20,21-dithienothiophenetetrapyrane (**8**):

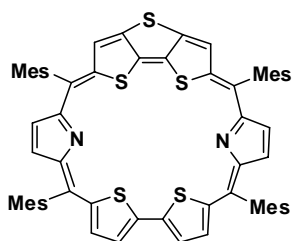
A mixture of DTT -diol **4a** (0.54 g, 1 mmol) and pyrrole (3 ml, 43 mmol) was degassed by bubbling nitrogen gas. TFA (0.008 ml, 0.1 mmol) was added to this solution and the mixture was stirred for about 30 minutes at room temperature. The completion of the reaction was followed with TLC. Dichloromethane (100 mL) was added and the reaction mixture was neutralized with 40% NaOH solution. The organic layer was separated and washed two times with water (50 ml) before drying over sodium sulfate. The excess pyrrole was removed at room temperature by vacuum (0.03 mm of Hg). Chromatography on silicagel with ethyl acetate and petroleum ether (5:95) gave the desired tetrapyrane **8** as light brown solid. Yield: 0.45 g



**8:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.86 (brs, NH, 2H), 6.91 (d,  $J = 4\text{Hz}$ , 2H), 6.86 (s, 4H), 6.71 (d,  $J = 3.6\text{Hz}$ , 2H), 6.66 (d,  $J = 3.6\text{Hz}$ , 2H), 6.17 (m, 2H), 6.08 (brs, 2H), 6.01 (s, 2H), 2.2 (s, 12H), 2.13 (s, 6H). FAB-MS: 590 (58%) [ $\text{M}^+$ ],  
Calcd for  $\text{C}_{36}\text{H}_{34}\text{N}_2\text{S}_3$  : 590.19

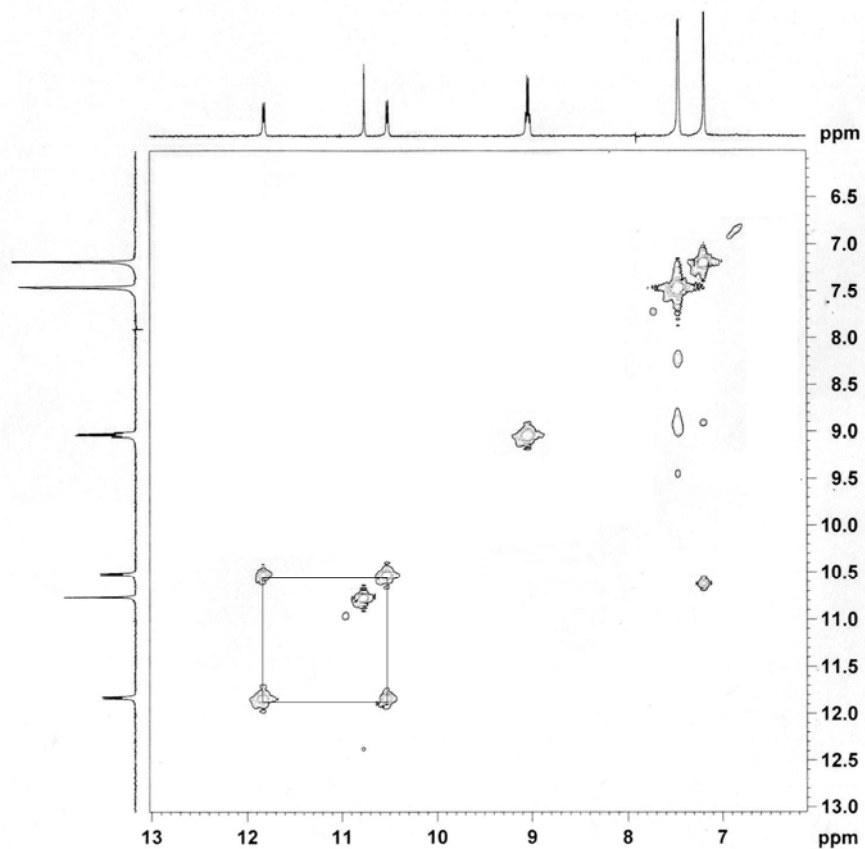
#### Rubyrin **6a**:

To a solution of **4a** (0.17 g, 0.35 mmol) and **5a** (0.2 g, 0.35 mmol) in 200 ml of dry  $\text{CH}_2\text{Cl}_2$  in argon atmosphere TFA (0.03 ml, 0.35 mmol) was added. The mixture was allowed to stir for 1 hr. *p*-Chloranil (0.13 g, 0.53 mmol) was added and the vessel was opened to air. The mixture was refluxed for 1 hr. The solvent was removed under reduced pressure. The crude was subjected to column chromatography (basic alumina). A pink color band eluted at 30:70  $\text{CH}_2\text{Cl}_2$ /Hexane was identified as **6a**. On further purification by column chromatography **6a** was obtained in 20% yield.



**6a:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  (ppm): 11.82 (d, 2H,  $J = 5.1\text{Hz}$ ), 10.76 (s, 2H), 10.52 (d, 2H,  $J = 5.1\text{ Hz}$ ), 9.05 (d, 2H,  $J=4.41\text{ Hz}$ ), 9.02 (d, 2 H,  $J=4.41\text{ Hz}$ ), 7.46 (d, 8H,  $J=3.21\text{ Hz}$ ), 2.73 (s, 12H), and 2.03 (s, 12 H), 1.97 (s, 12H); FAB-MS: 1010.66 [ $\text{M}$ ] $^+$  ; Elemental analysis Calcd. (%) for  $\text{C}_{64}\text{H}_{54}\text{N}_2\text{S}_5$  : C 76.00, H 5.38, N 2.77 - found C 75.60, H 5.88, N 2.57.

a)



b)

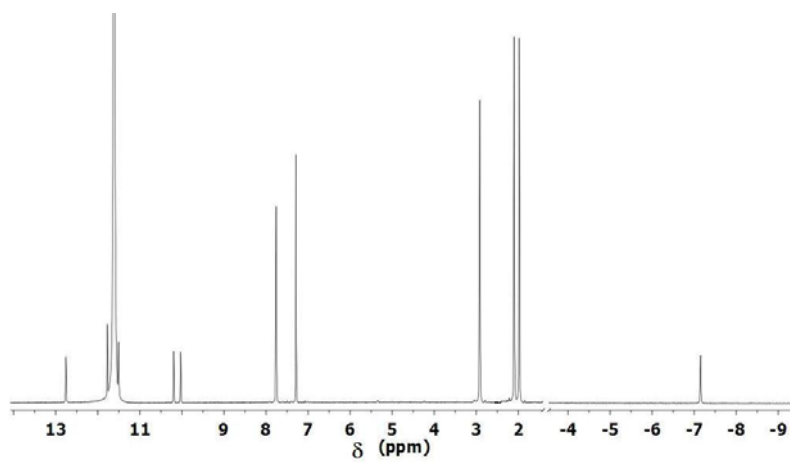


Figure S1: a)  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **6a** b)  $^1\text{H}$  NMR of of **6a**.TFA in  $\text{CDCl}_3$  at 233K  
RUBYRIN **6b**:

Synthesized as above using **4b** and **5b**.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  (ppm): 11.90 (d, 2H,  $J = 5$  Hz), 11.14 (s, 2H), 10.73 (d, 2H,  $J = 5$  Hz), 9.33 (d, 2H,  $J = 4.5$  Hz), 9.25 (d, 2H,  $J = 4.5$  Hz), 8.57 (d, 4H,  $J = 7.8$  Hz), 8.48 (d, 4H,  $J = 7.8$  Hz), 7.85 (d, 4H,  $J = 7.8$  Hz), 7.8 (d, 4H,  $J = 7.8$  Hz), 2.88 (s, 12H), 2.16 (s, 24H); FAB-MS: 898.56  $[\text{M}]^+$ ; Elemental analysis Calcd. for  $\text{C}_{56}\text{H}_{38}\text{N}_2\text{S}_5$  (%) - C 74.80, H 4.26, N 3.12 found C 74.54, H 4.32, N 3.32; UV-Vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  nm ( $\epsilon \times 10^{-5}$ ): 519 (3.2), 537 (1.6), 615 (0.05), 663 (0.12), 720 (0.6), 820 (0.03) and 929 (0.03); **6b**.TFA: 542 (2.55), 570 (1.4) and 900 (0.81)

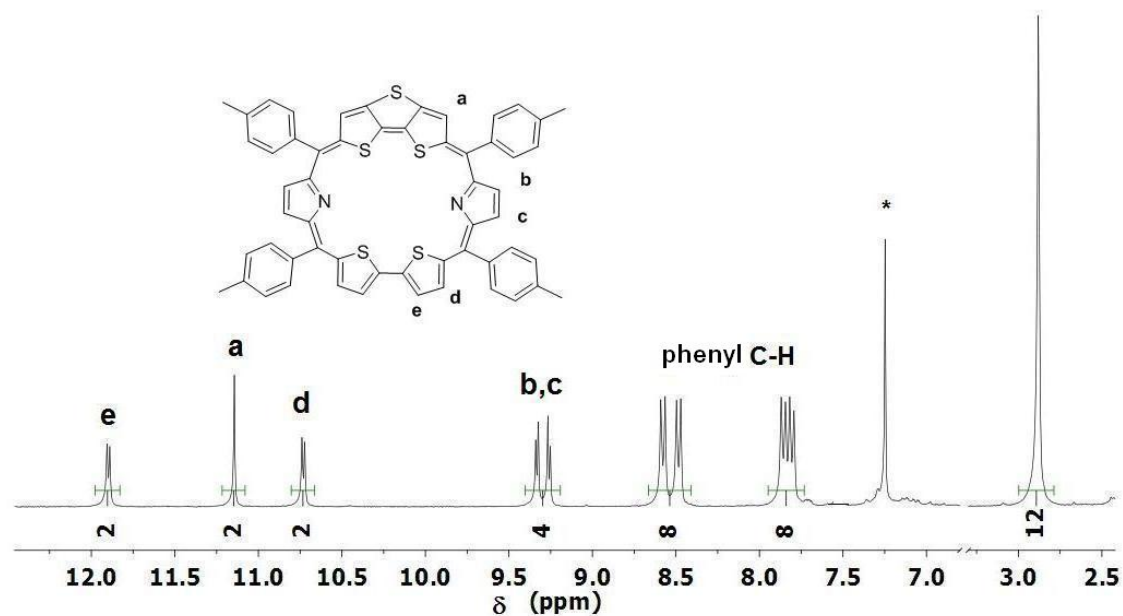


Figure S2:  $^1\text{H}$  NMR spectrum of **6b** in  $\text{CDCl}_3$

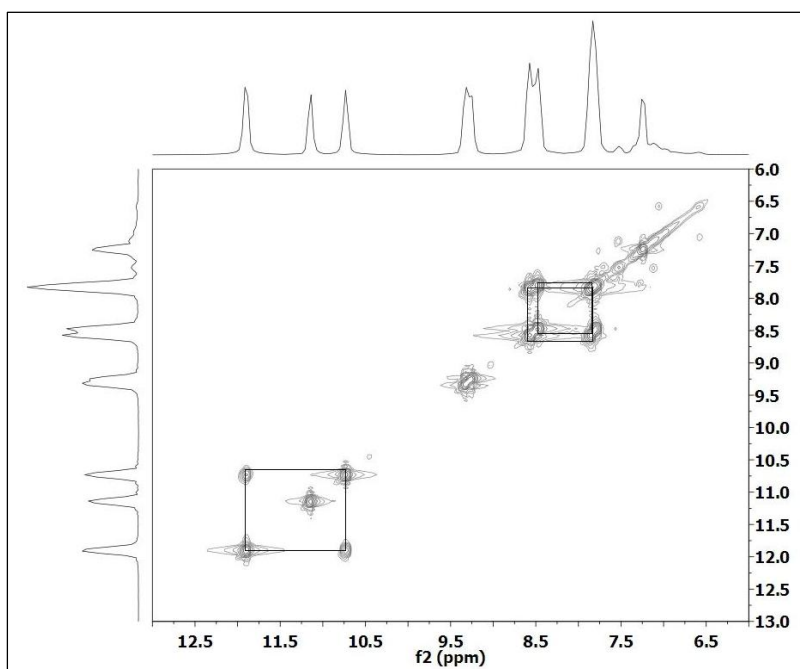


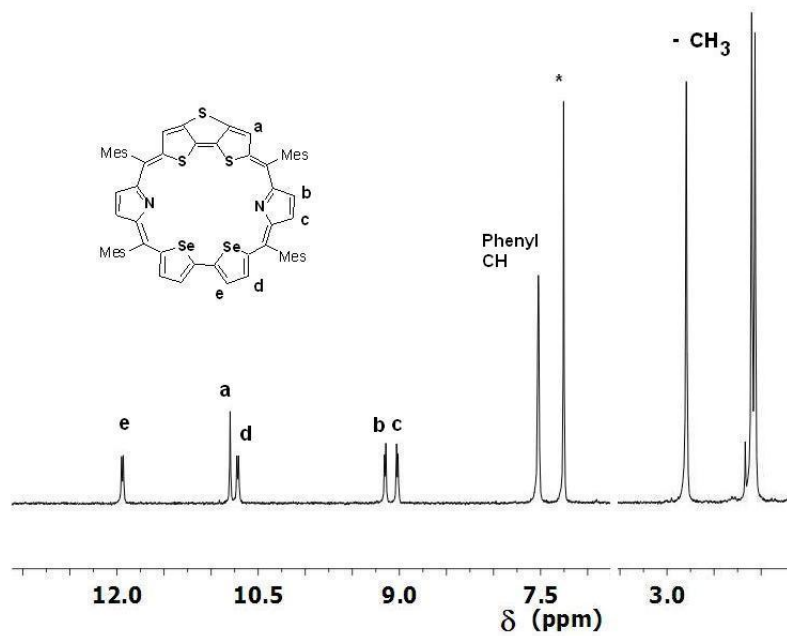
Figure S3:  $^1\text{H}$ - $^1\text{H}$  COSY Spectrum of **6b**

Rubyrin **6c**:

Synthesized as above using 4a and 5c

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  (ppm): 11.94 (d, 2H,  $J = 5.4$  Hz), 10.8 (s, 2H), 10.72 (d, 2H,  $J = 5.4$  Hz), 9.15 (d, 2H,  $J = 4.4$  Hz), 9.02 (d, 2H,  $J = 4.4$  Hz), 7.5 (s, 8H), 7.25 (s, 8H), 2.8 (s, 12H), 2.17 (s, 12H), 2.10 (s, 12H); MALDI-TOF: 1107.31  $[\text{M}+\text{H}]^+$ ; Elemental analysis Calcd. for  $\text{C}_{64}\text{H}_{55}\text{N}_2\text{S}_3\text{Se}_2$  (%) - C 69.55, H 4.92, N 2.53 found C 69.85, H 4.95, N 2.23; UV-Vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  nm ( $\epsilon \times 10^{-5}$ ): 527 (9.9), 542 (6.2), 608 (0.27), 657 (0.7), 710 (1.42), 822 (0.11); **6c**.TFA: 552 (7.3), 562 (5.4), 793 (0.36), 839 (1.1)

a)



b)

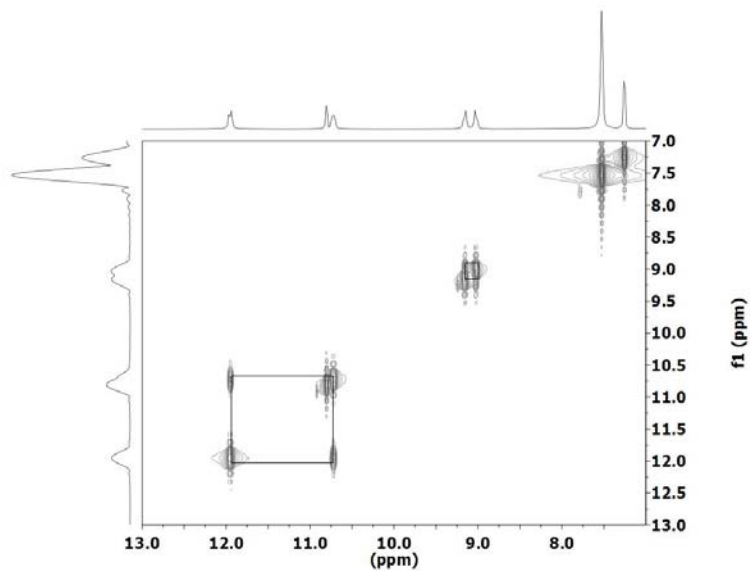


Figure S4: a)  $^1\text{H}$  NMR b)  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **6c** in  $\text{CDCl}_3$



Doubly Fused Rubyrin **7a** by [4+2] condensation:

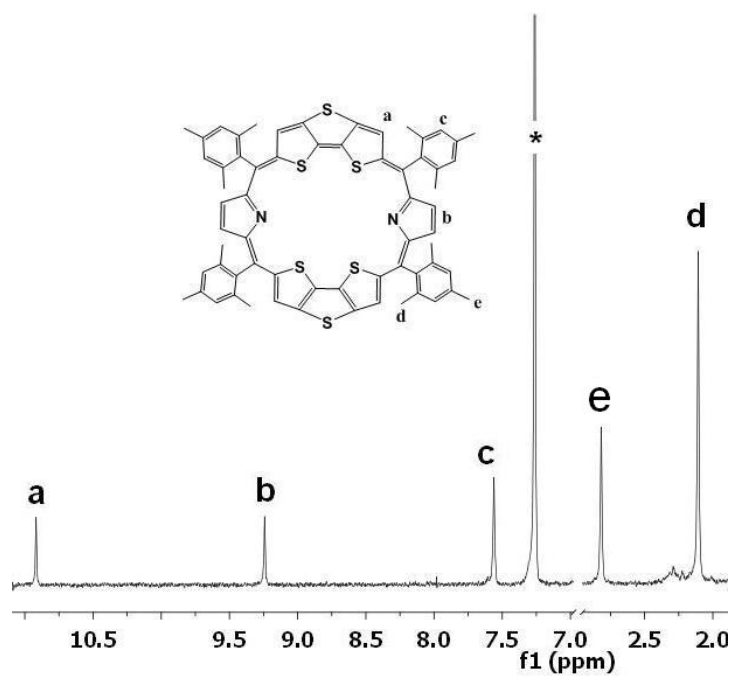
To a solution of diol **4a** (0.17g, 0.35mmol) and tetrapyrane **8** (0.21 g, 0.35 mmol) in 200 ml of dry CH<sub>2</sub>Cl<sub>2</sub>, TFA (0.03mL, 0.35 mmol) was added under argon atmosphere. The mixture was allowed to stir for 1 hr. Chloranil (0.13g, 0.53 mmol) was added and the vessel was opened to air. The mixture was refluxed for 1h. The solvent was removed under reduced pressure. The crude was subjected to column chromatography (basic alumina). A pink color band eluted at 35:65 CH<sub>2</sub>Cl<sub>2</sub>/Hexane was identified as **7a**. On further purification by column chromatography yielded **7a** in 18% yield.

By Lindsey's modified procedure:

To a solution of **4a** (0.17g, 0.35mmol) and pyrrole (0.047 g, 0.70 mmol) in 200 ml in dry CH<sub>2</sub>Cl<sub>2</sub>, TFA (0.03mL, 0.35 mmol) was added under argon atmosphere. The mixture was allowed to stir for 1 hr. Chloranil (0.13g, 0.53 mmol) was added and the vessel was opened to air. The mixture was refluxed for 1h. The solvent was removed under reduced pressure. The crude was subjected to column chromatography (basic alumina). A pink color band eluted at 35:65 CH<sub>2</sub>Cl<sub>2</sub>/Hexane was identified as **7a**. On further purification by column chromatography yielded **7a** in 15% yield

**7a**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K) δ (ppm): 10.92 (s, 4H), 9.24 (s, 4H), 7.56 (s, 8H), 2.82 (s, 12H), 2.23 (s, 24H); FAB-MS: 1040 [M]<sup>+</sup>, Elemental analysis Calcd. for C<sub>64</sub>H<sub>52</sub>N<sub>2</sub>S<sub>6</sub> (%) - C 73.81, H 5.03, N 2.69 found C 74.11, H 4.75, N 2.47.

a)



b)

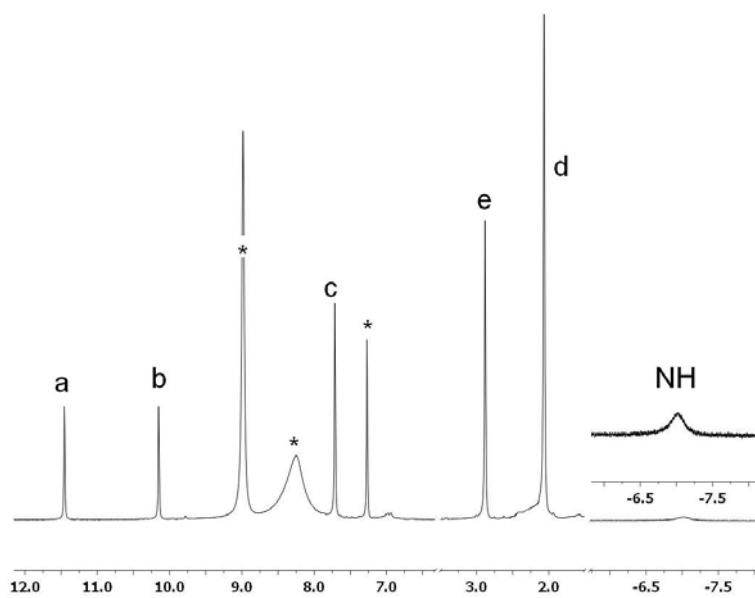


Figure S5: <sup>1</sup>H NMR of a) **7a** b) **7a**. TFA (at 233K) in CDCl<sub>3</sub>

**7b** was synthesized by similar procedure using diol **4b**

**7b**:  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  (ppm): 11.21 (s, 4H), 9.49 (s, 4H), 8.64 (d, 8H,  $J = 7.5$  Hz), 7.9 (d, 8H,  $J = 7.5$  Hz), 2.91 (s, 12H); FAB-MS: 929  $[\text{M}]^+$ , Elemental analysis calcd. For  $\text{C}_{56}\text{H}_{36}\text{N}_2\text{S}_6$  (%) - C 72.38, H 3.90, N 3.01 found C 72.65, H 3.72, N 2.76 ; UV-Vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  nm ( $\epsilon \times 10^{-5}$ ): 516 (2.9), 543 (1.6), 674 (0.12), 730 (0.66), 800 (0.05), 903 (0.03); **7b.TFA**: 535 (2.14), 577 (1.2), 903 (1)

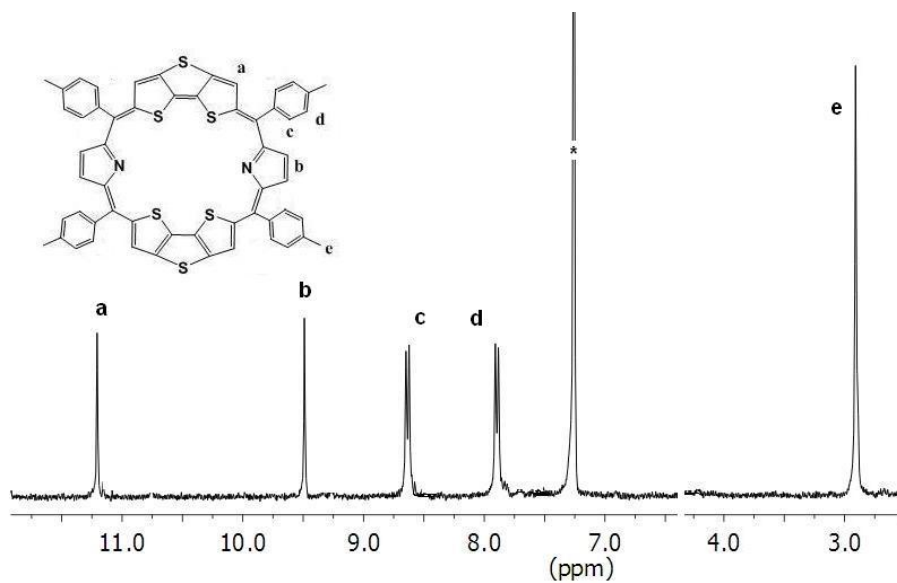
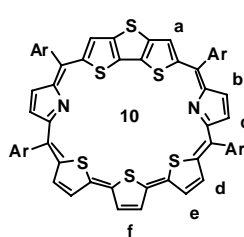


Figure S6:  $^1\text{H NMR}$  of **7b** in  $\text{CDCl}_3$

### Fused Heptaphyrin **10**:

To a solution of tetrapyrane **8** (0.21g, 0.35mmol) and diol **9** (0.194 g, 0.35 mmol) in 200 ml of dry CH<sub>2</sub>Cl<sub>2</sub>, TFA (0.03mL, 0.35 mmol) was added under argon atmosphere. The mixture was allowed to stir for 1 hr. Chloranil (0.13g, 0.53 mmol) was added and the vessel was opened to air. The mixture was refluxed for 1h. The solvent was removed under reduced pressure. The crude was subjected to column chromatography (basic alumina). A violet color band eluted at 30:70 CH<sub>2</sub>Cl<sub>2</sub>/Hexane was identified as **10**. On further purification by column chromatography yielded **10** in 23% yield.



**10**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K) δ (ppm): 11.42 (s, 2H), 11.23 (d, 2H, 4.5 Hz), 10.59 (s, 2H), 10.17 (d, 2H, 4.5 Hz), 8.87 (d, 2H, 4.5 Hz), 8.7 (d, 2H, 4.5 Hz), 7.53 (s, 4H), 7.47 (s, 2H), 2.80 (s, 6H), 2.7 (s, 6H), 2.12 (s, 12H), 2.10 (s, 12H); FAB-MS : 1093.28 [M+1]<sup>+</sup>; Elemental analysis calcd. for C<sub>68</sub>H<sub>56</sub>N<sub>2</sub>S<sub>6</sub> (%) -

C 74.68, H 5.16, N 2.56 found C 74.94, H 4.98, N 2.33.

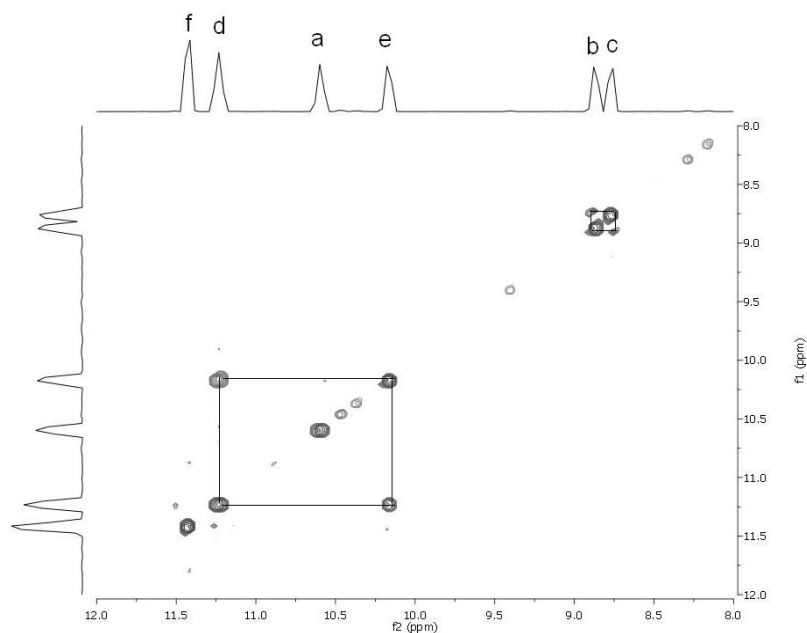


Figure S7: <sup>1</sup>H-<sup>1</sup>H COSY spectrum of **10** in CDCl<sub>3</sub>

### 3. X-ray Crystallographic data

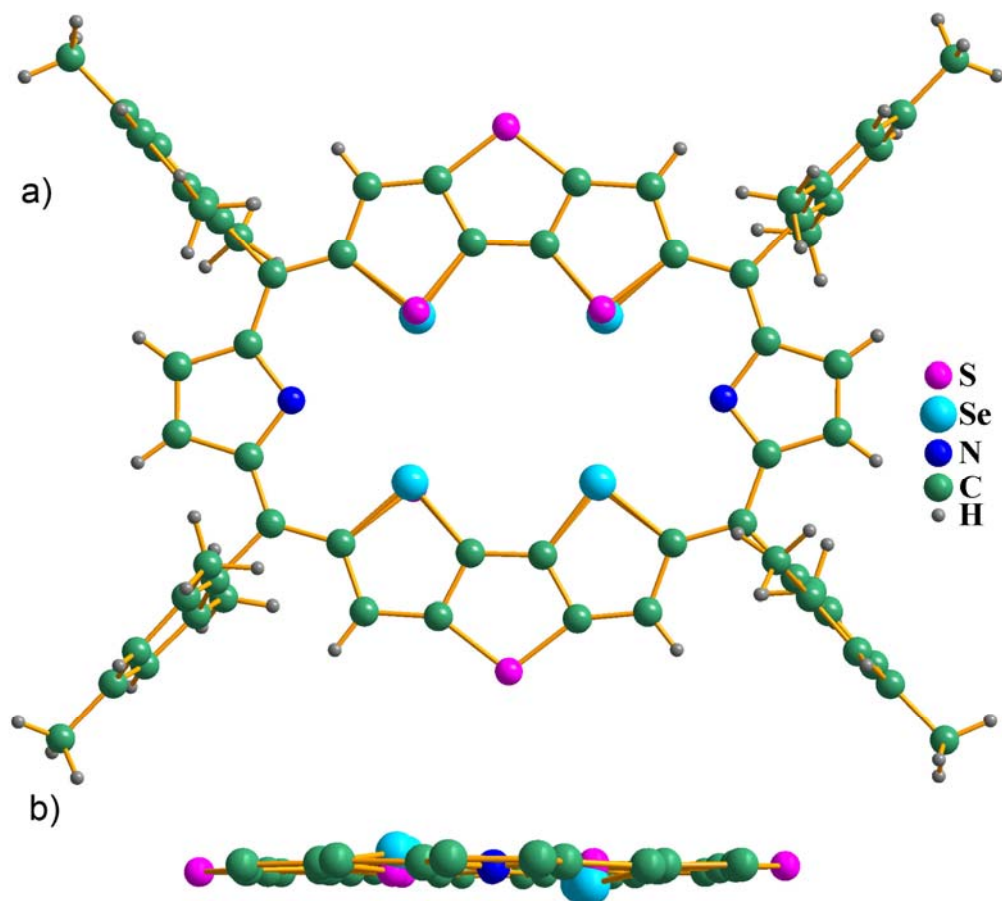


Figure S8: Preliminary X-ray crystal structure of **6c** a) Top view b) Side view

Crystal data for **6c**:  $C_{64} H_{52} N_2 S_{4.60} Se_{0.40}$ , monoclinic, space group  $P2(1)/n$ ,  $a = 15.0818(30) \text{ \AA}$ ,  $b = 15.1228(30) \text{ \AA}$ ,  $c = 16.1830(32) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 114.696(30)^\circ$ ,  $\gamma = 90.00^\circ$ ,  $V = 3353.4(14) \text{ \AA}^3$ ,  $T = 293(2) \text{ K}$ ,  $Z = 2$ ,  $\mu(\text{MoK}\alpha) = 0.411 \text{ mm}^{-1}$ ,  $F(000) = 1074.4$ . 31858 reflections were measured, of which 6366 were unique ( $R_{\text{int}} = 0.0512$ , Final  $R_1 (I > 2\sigma(I)) = 0.1251$ ,  $wR_2 = 0.3594$ ,  $\text{GOF on } F^2 = 1.503$ . CCDC-694221 contains the supplementary crystallographic data for this crystal.

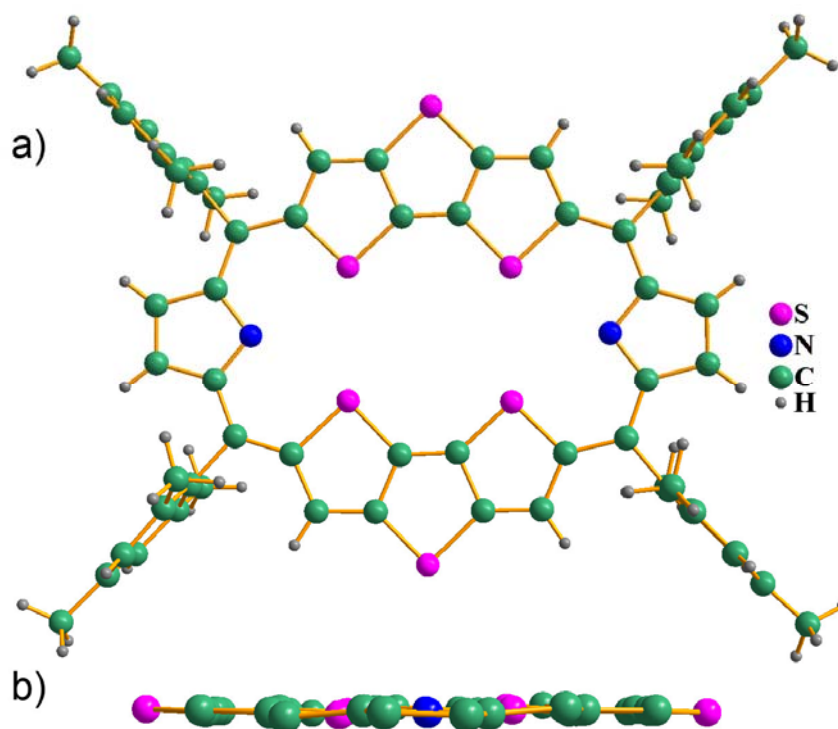


Figure S9: Preliminary X-ray crystal structure of **7a** a) Top view b) Side view

Crystal data for **7a**:  $C_{64}H_{52}N_2S_6$ , monoclinic, space group  $P2(1)/c$ ,  $a = 14.784(3) \text{ \AA}$ ,  $b = 15.083(3) \text{ \AA}$ ,  $c = 16.781(7) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 117.69(2)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 3313.4(17) \text{ \AA}^3$ ,  $T = 293(2) \text{ K}$ ,  $Z = 2$ ,  $\mu(Mo_{k\alpha}) = 0.052 \text{ mm}^{-1}$ ,  $F(000) = 856$ , 35033 reflections were measured, of which 3902 were unique ( $R_{int} = 0.4827$ , Final  $R_1(I > 2\sigma(I)) = 0.2268$ ,  $wR_2 = 0.5036$ , GOF on  $F^2 = 1.755$ . CCDC-694220 contains the supplementary crystallographic data for this crystal.

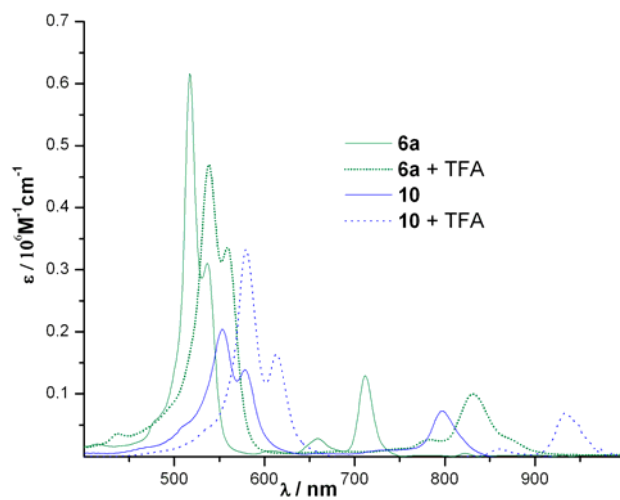


Figure S10: UV-Visible spectra of **6a**, **10** and their protonated forms in  $\text{CH}_2\text{Cl}_2$