

## ELECTRONIC SUPPLEMENTARY INFORMATION

for

### Fused Core-Modified Planar Antiaromatic $32\pi$ Heptaphyrins: Unusual Synthesis and Structural Diversity

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## 1. General Information:

All solvents 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<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. TMS, residual solvent, grease impurity and water peaks are marked in asterisks. ESI mass spectra were recorded on Bruker, micrOTOF-QII mass spectrometer. Electronic spectra were recorded with Perkin Elmer – Lambda 750 UV-Visible spectrophotometer and data analyses were done using the UV-winlab software package. X-ray quality crystals for the compounds were grown by the slow diffusion of hexane over CH<sub>2</sub>Cl<sub>2</sub> solution. Single-crystal X-ray diffraction data were collected on a Bruker KAPPA APEX-II, four angle rotation system, MoK $\alpha$  radiation (0.71073 Å). Quantum mechanical calculations were carried out using the Gaussian09 program suite.<sup>1-2</sup> All calculations were performed using density functional theory (DFT) with the Becke's three parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP), employing a basis set of 6-31G(d,p) for all atoms.<sup>3</sup>

1. Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford CT, 2009, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, Jr. J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople.
2. Frisch et al. Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford CT, 2009.
3. Y. Zhao, D. G. Truhlar, *J. Chem. Phys.* 2006, **125**, 194101.

## 2. Experimental Section:

### Synthesis of 3

DTT-diol **5** (1.0g, 1 equiv, 0.002 mol) and thia-tripyrane **6** (0.971g, 1 equiv, 0.002 mol) were dissolved in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (200 mL) and stirred in an inert atmosphere for 10 min. The acid catalyst TFA (0.153 mL, 1 equiv, 0.002 mol) was added to this solution and continued stirring for further 90 min at ambient temperature. *p*-Chloroanil (0.735g, 1.5 equiv, 0.003mol) 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 under rotary evaporator. The residue was purified by first basic alumina column followed by neutral alumina column, the greenish brown color band eluted by CH<sub>2</sub>Cl<sub>2</sub>: hexane (10:90) was identified as sapphyrin **8** in 4% yield and the second blue band (CH<sub>2</sub>Cl<sub>2</sub>: hexane, 15:85) was identified as fused heptaphyrin **3** in 06 % yield.

**3**: mp 212-214 °C (decomposition); elemental analysis: C<sub>88</sub>H<sub>79</sub>N<sub>3</sub>S<sub>5</sub>: C, 78.94; H, 5.95; N, 3.14. Found: C, 78.91; H, 5.96; N 3.12; ESI-MS: *m/z* calcd for C<sub>88</sub>H<sub>79</sub>N<sub>3</sub>S<sub>5</sub>+H<sup>+</sup>: 1338.4878; found: 1338.4881.

**3**: Uv/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub>[nm] (ε [10<sup>4</sup>M<sup>-1</sup>cm<sup>-1</sup>]): 502 (0.805), 597 (0.427);

**3**: <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>, 25°C, TMS) δ[ppm]: 15.68 (s, 2H), 12.86 (s, 2H), 7.52 (d, <sup>3</sup>J=4 Hz, 2H), 7.13 (d, <sup>3</sup>J=4 Hz, 2H), 6.68 (s, 4H), 6.65 (s, 4H), 6.35 (s, 4H), 5.24 (d, <sup>3</sup>J=4 Hz, 2H), 4.79 (d, <sup>3</sup>J=4 Hz, 2H), 4.47 (br, s, 1H), 2.16 (s, 12H), 2.12 (s, 6H), 2.01 (s, 12H), 1.89 (s, 6H), 1.43 (s, 12H), 1.37 (s, 6H)

**3.2H<sup>+</sup>**: Uv/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub>[nm] (ε [10<sup>4</sup>M<sup>-1</sup>cm<sup>-1</sup>]): 556 (1.09);

**3.2H<sup>+</sup>**: <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>, 25°C, TMS) δ[ppm]: 13.12 (s, br, 2H), 7.42 (s, 2H), 7.40 (s, 2H), 7.37 (d, <sup>3</sup>J=4 Hz, 2H), 7.34 (d, <sup>3</sup>J=4 Hz, 2H), 7.14 (d, <sup>3</sup>J=4 Hz, 2H), 7.12 (d, <sup>3</sup>J=4 Hz, 2H), 6.17 (s, 4H), 6.15 (s, 4H), 5.66 (s, 4H), 2.17 (s, 12H), 1.75 (s, 6H), 1.45 (s, 12H), 1.40 (s, 6H), 1.30 (s, 6H), 1.27 (s, 12H), -0.81 (s, br, 2H).

### Synthesis of 4

DTT-diol **5** (1.0g, 1 equiv, 0.002 mol) and seleno-tripyrane **7** (0.971g, 1 equiv, 0.002 mol) were dissolved in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (200 mL) and stirred in an inert atmosphere for 10 min. The acid catalyst TFA (0.153 mL, 1 equiv, 0.002 mol) was added to this solution and continued stirring for further 90 min at ambient temperature. *p*-Chloroanil (0.735g, 1.5 equiv, 0.003mol) 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 under rotary evaporator. The residue was purified by first basic alumina column followed by neutral alumina column, the greenish brown color band eluted by CH<sub>2</sub>Cl<sub>2</sub>: hexane (14:86) was identified as sapphyrin **9** in 3% yield and the second blue band (CH<sub>2</sub>Cl<sub>2</sub>: hexane, 18:82) was identified as fused heptaphyrin **4** in 4 % yield.

**4:** mp 206-209 °C (decomposition); elemental analysis: Calcd for C<sub>88</sub>H<sub>79</sub>N<sub>3</sub>S<sub>3</sub>Se<sub>2</sub>: C, 73.77; H, 5.56; N, 2.93. Found: C, 73.75; H, 5.53; N 2.94; ESI-MS: *m/z* calcd for C<sub>88</sub>H<sub>79</sub>N<sub>3</sub>S<sub>3</sub>Se<sub>2</sub>+H<sup>+</sup>: 1434.3767; found: 1434.3769.

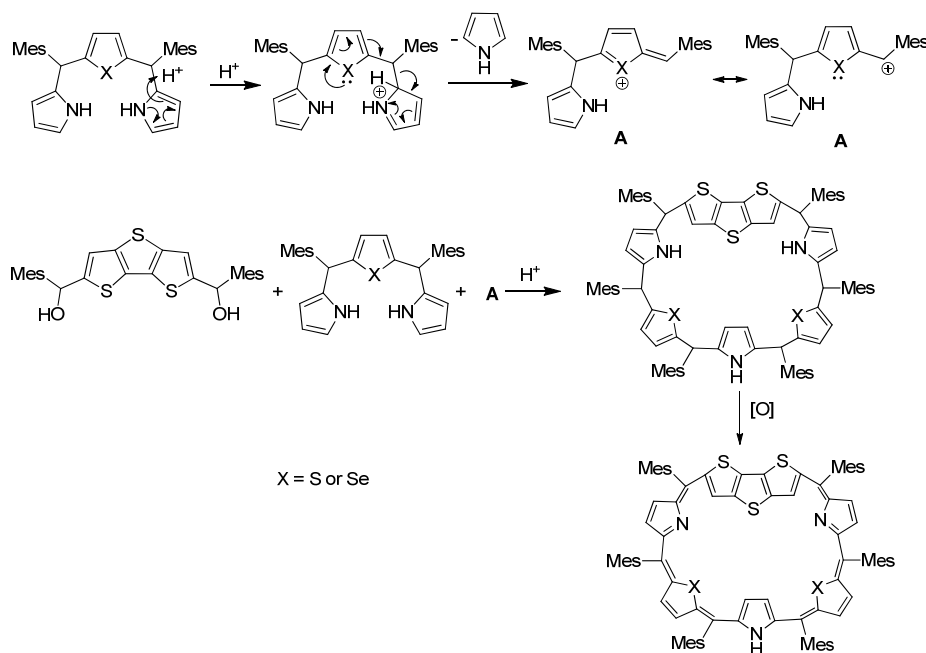
**4:** Uv/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub>[nm] (ε [10<sup>4</sup>M<sup>-1</sup>cm<sup>-1</sup>]): 524(0.905);

**4:** <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>, 25°C, TMS) δ[ppm]: 16.69 (s, 2H), 15.26 (s, 2H), 8.28 (d, <sup>3</sup>J=4 Hz, 2H), 7.83(d, <sup>3</sup>J=4 Hz, 2H), 6.78 (s, 4H), 6.76 (s, 4H), 6.61 (s, 4H), 5.98 (d, <sup>3</sup>J=8 Hz, 2H), 4.59 (d, <sup>3</sup>J=8 Hz, 2H), 3.86 (br, s, 1H), 2.19(s, 12H), 2.10 (s, 12H), 1.94 (s, 6H), 1.83 (s, 12H), 1.74 (s, 6H), 1.63(s, 6H)

**4.2H<sup>+</sup>:** Uv/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub>[nm] (ε [10<sup>4</sup>M<sup>-1</sup>cm<sup>-1</sup>]): 612 (1.15);

**4.2H<sup>+</sup>:** <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>, 25°C, TMS) δ[ppm]: 9.78 (s, br, 1H), 8.35 (s, 2H), 7.82 (s, 2H), 7.41 (d, <sup>3</sup>J=4 Hz, 2H), 7.34 (d, <sup>3</sup>J=4 Hz, 2H), 7.15 (d, <sup>3</sup>J=8 Hz, 2H), 6.87 (d, <sup>3</sup>J=8 Hz, 2H), 6.17 (s, 4H), 6.15 (s, 4H), 5.66 (s, 4H), 1.75 (s, 12H), 1.45 (s, 12H), 1.40 (s, 6H), 1.30 (s, 6H), 1.27 (s, 12H), 1.24 (s, 6H), -1.64 (s, br, 2H)

### 3. Plausible mechanism:



Scheme S1. Plausible mechanism for the heptaphyrin synthesis

Table S1. Effect of acid and its concentration

S. No	Acid	Equivalent of acid	Isolated yield of <b>8</b> (%)	Isolated yield of <b>3</b> (%)
1	TFA	0.5	8	3
2	TFA	1.0	4	6
3	TFA	1.5	1	2
4*	<i>p</i> -TSA	0.5	10	0
5	<i>p</i> -TSA	1.0	8	4
6	<i>p</i> -TSA	1.5	2	2
7	MSA	0.5	9	0
8	MSA	1.0	8	4
9	MSA	1.5	2	2

\* G. Karthik, A. Srinivasan and T. K. Chandrashekar, *Org. Lett.*, 2014, **16**, 3472.

TFA = Trifluoroacetic acid

*p*-TSA = *p*-Toluenesulphonic acid

MSA = Methanesulphonic acid

#### 4. Spectral Characterization

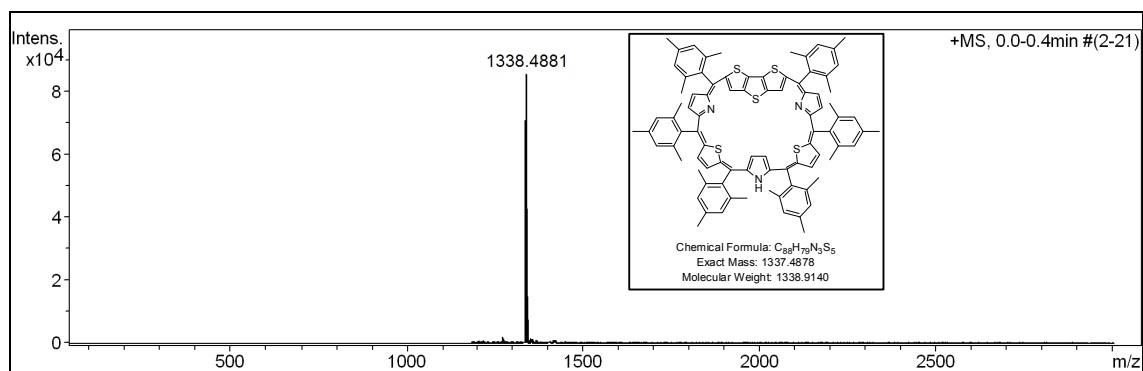


Figure S1. ESI-Mass spectrum of **3**

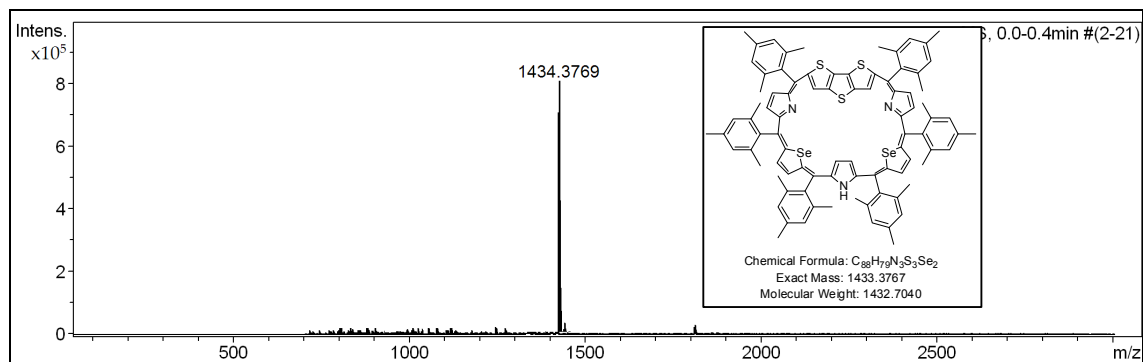


Figure S2. ESI-Mass spectrum of **4**

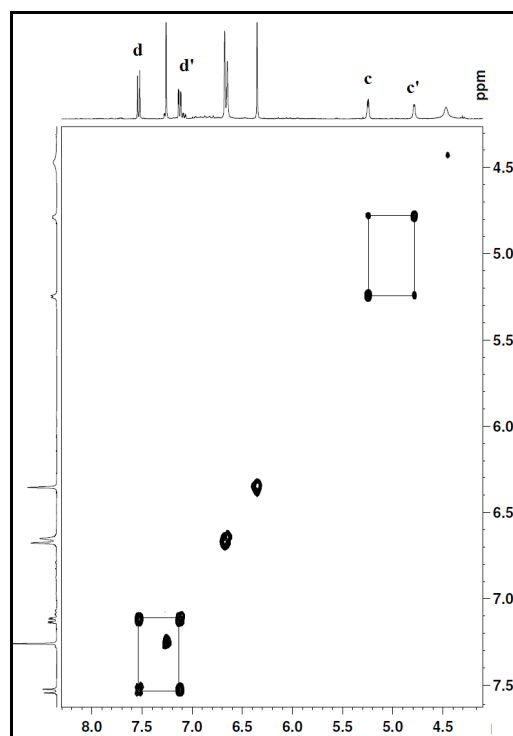
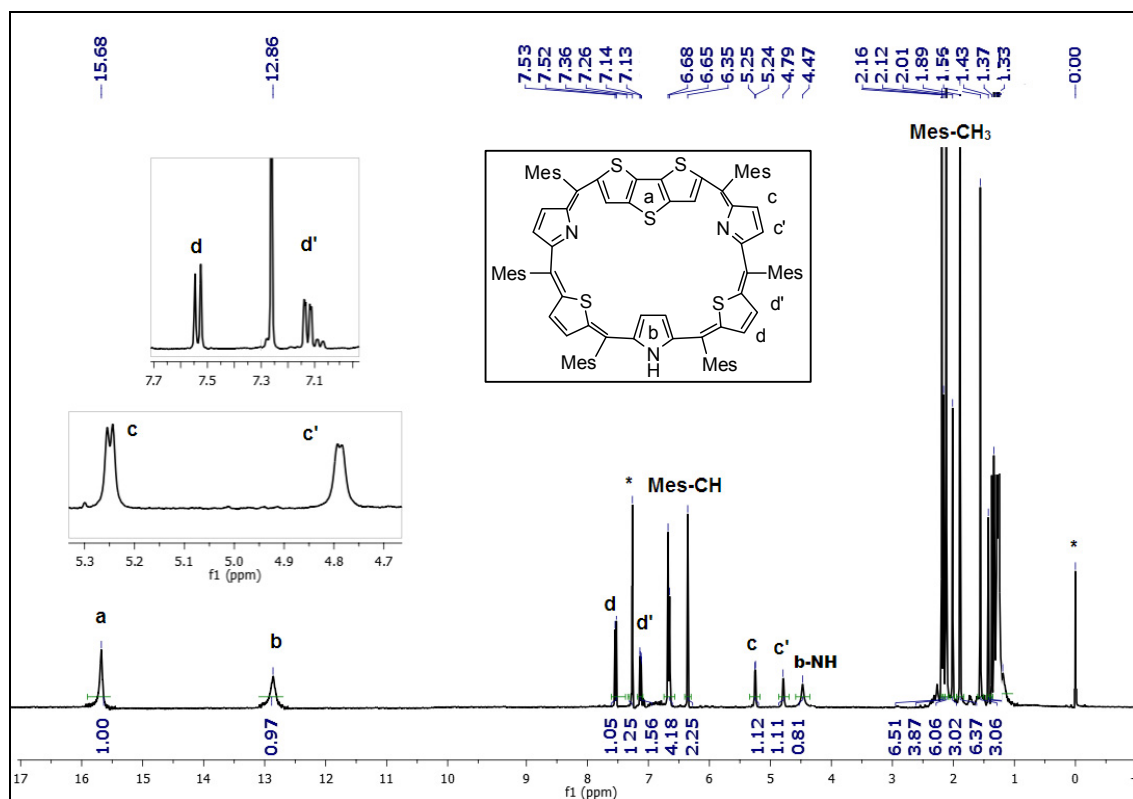


Figure S3: <sup>1</sup>H NMR and <sup>1</sup>H-<sup>1</sup>H COSY spectrum of **3** in CDCl<sub>3</sub> (\* TMS and residual solvent)

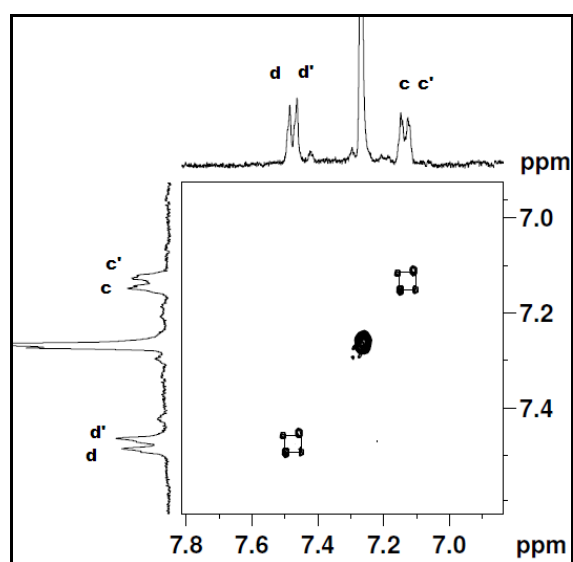
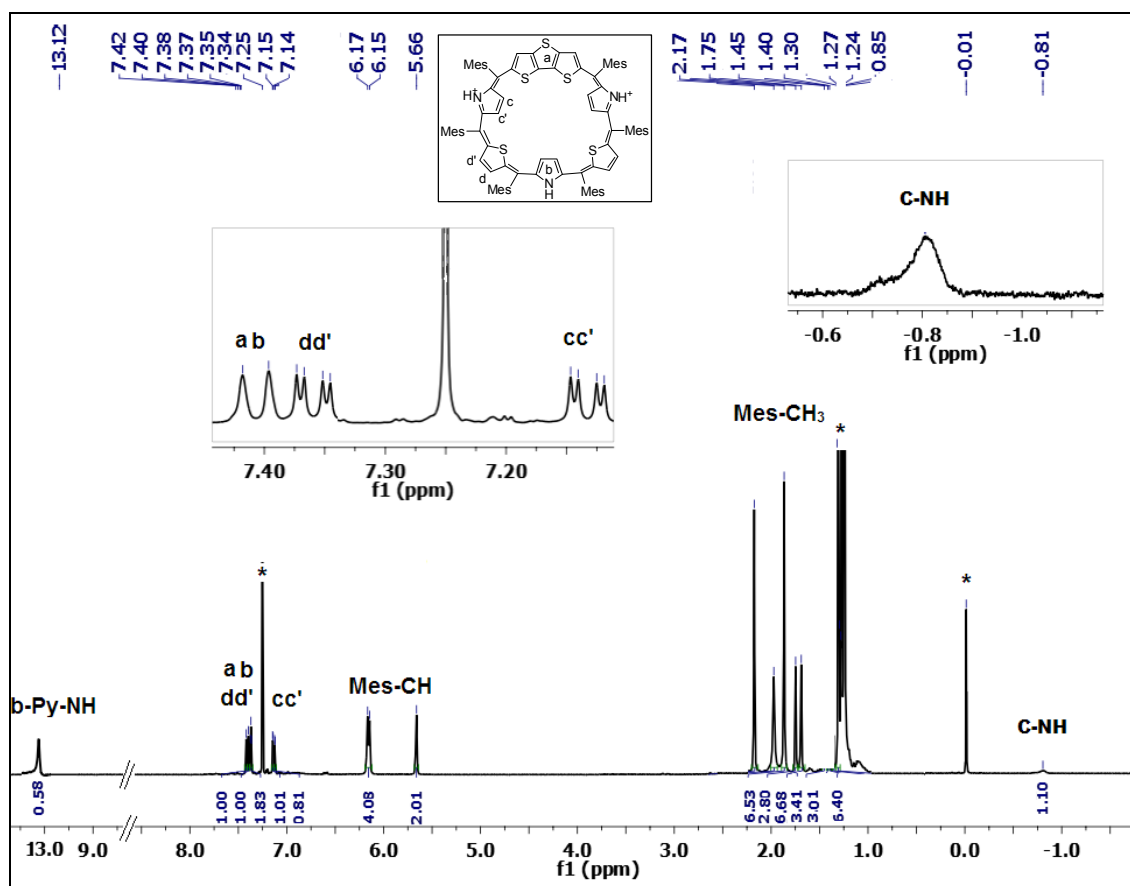


Figure S4:  $^1H$  NMR spectrum of  $3.2H^+$  in CDCl<sub>3</sub> (\* TMS, residual solvent and water peaks)

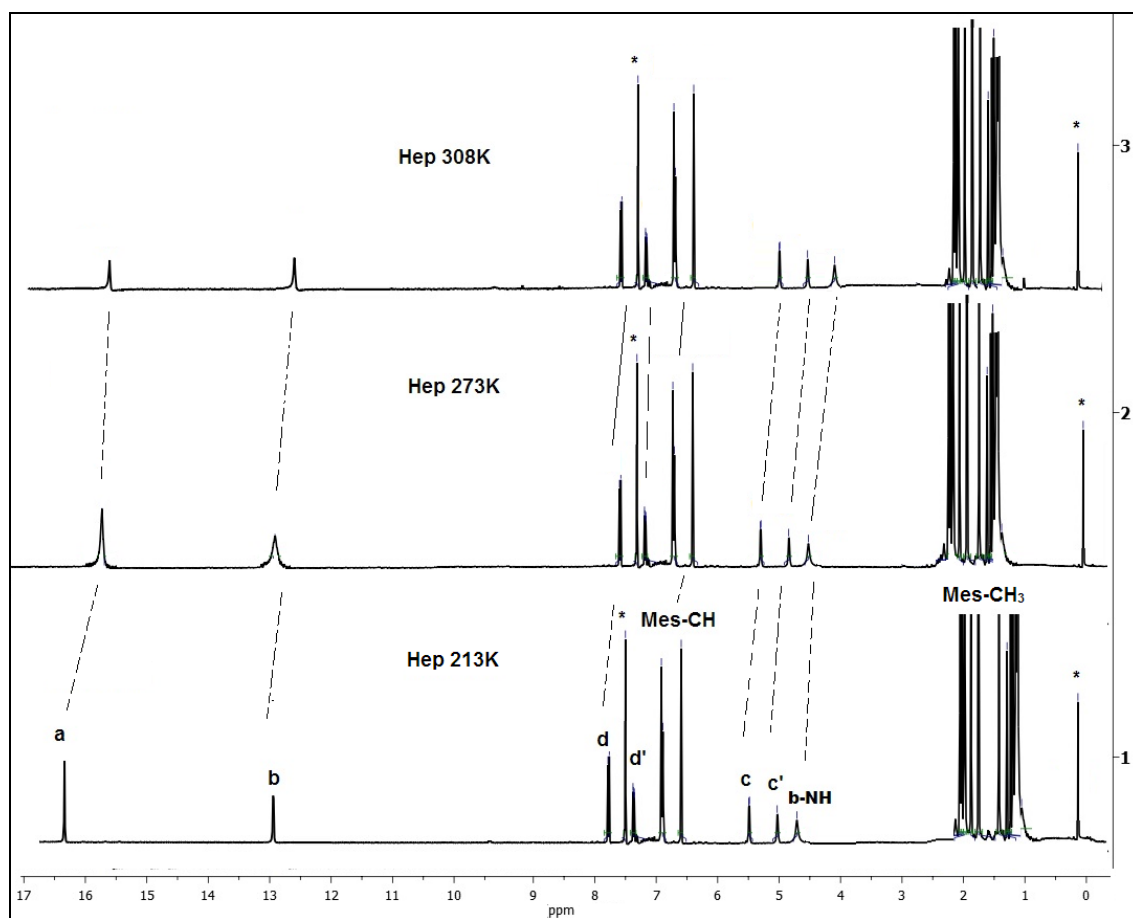
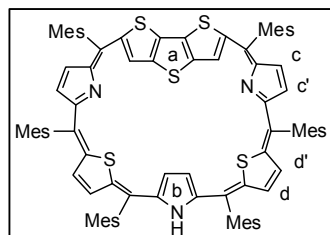


Figure S5: Variable temperature  $^1\text{H}$  NMR spectrum of **3** in  $\text{CD}_2\text{Cl}_2$  (\* TMS and residual solvent peak)





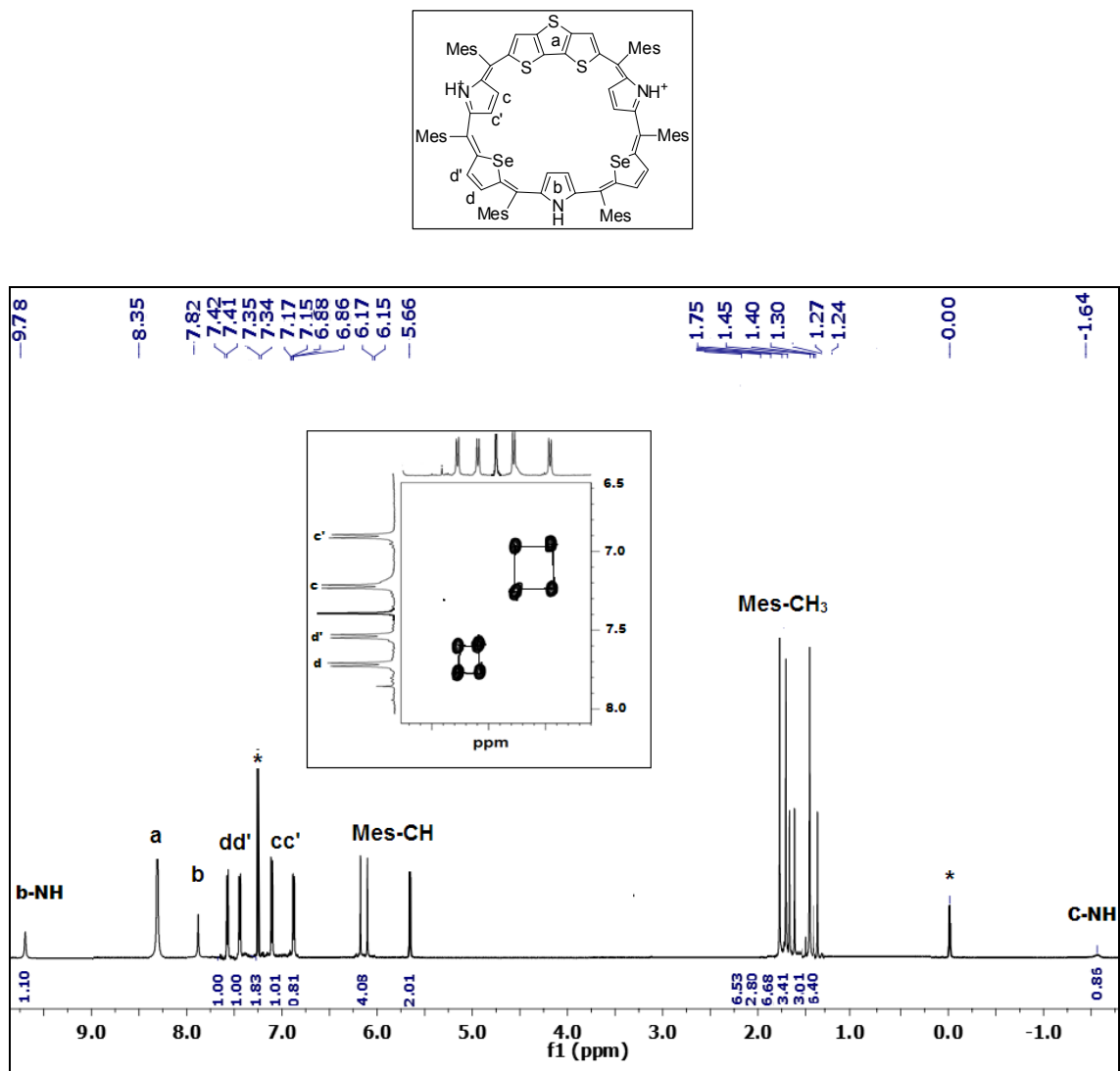


Figure S7:  $^1H$  NMR spectrum of  $4.2H^+$  in  $CDCl_3$  (\* TMS and residual solvent)

## 5. Voltammetry analysis:

Electrochemical analysis was carried out in the three electrode cell system; Glassy carbon working electrode, platinum wire counter electrode and Ag/Ag<sup>+</sup> reference electrode containing 0.1M TBAPF<sub>6</sub> (tetra-*n*-butylammoniumhexafluorophosphate) as supporting electrolyte in anhydrous CH<sub>2</sub>Cl<sub>2</sub> solution.

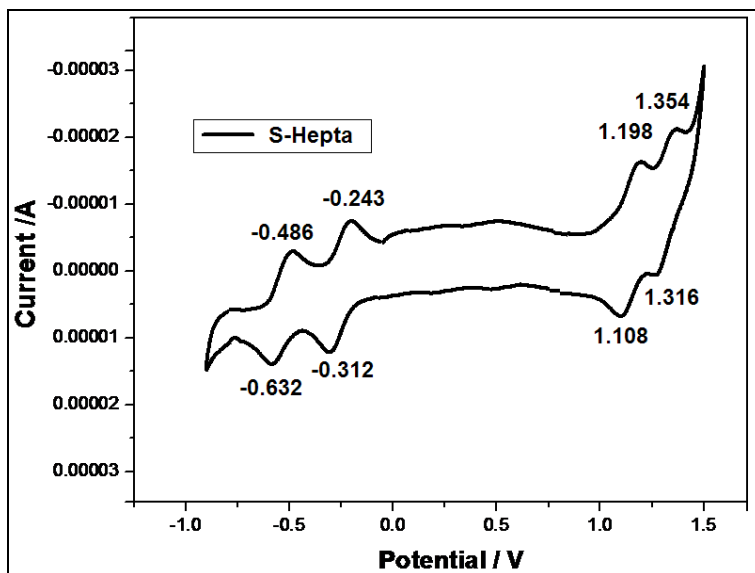


Figure S8: Cyclic Voltammogram of **3** in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAPF<sub>6</sub> with scan rate of 50 mV/s

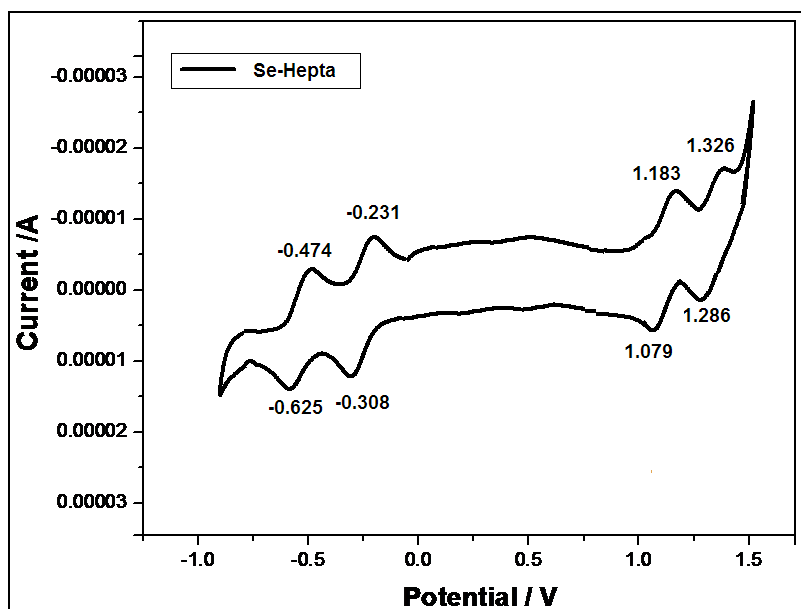


Figure S9: Cyclic Voltammogram of **4** in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAPF<sub>6</sub> with scan rate of 50 mV/s

## 6. Single crystal X-ray analysis

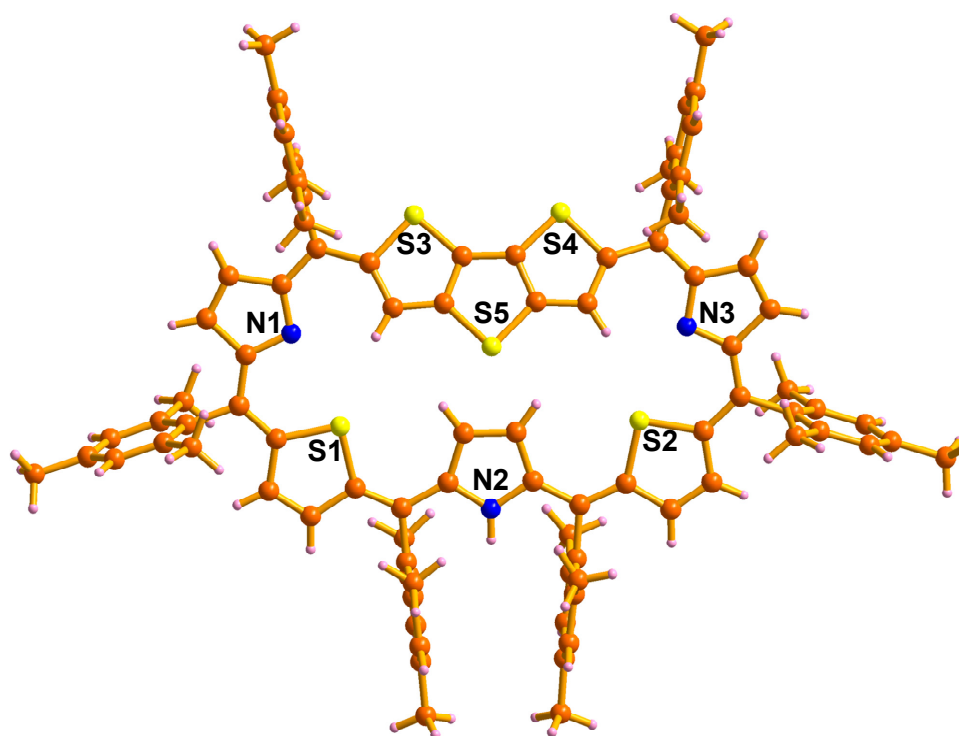


Figure S10. Single crystal X-ray structure of **3**

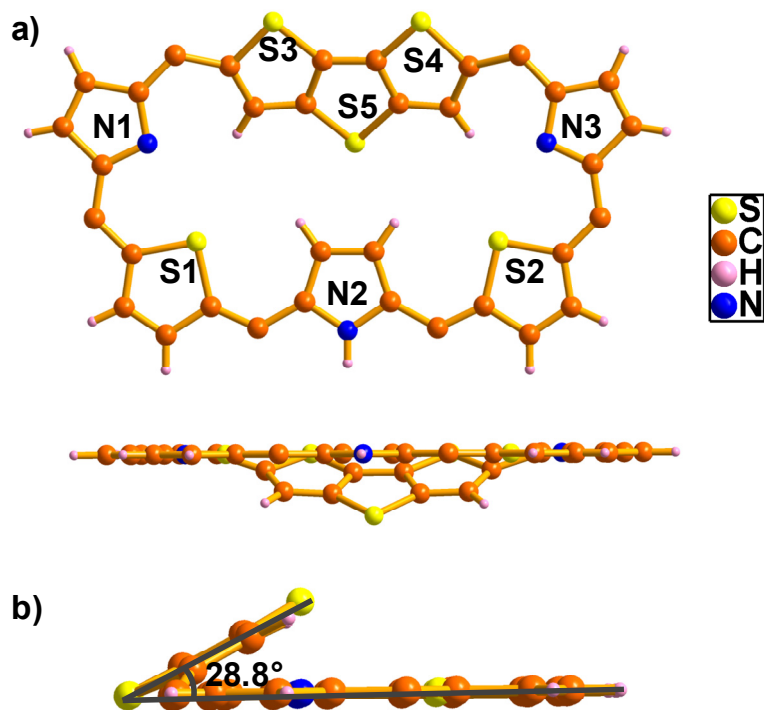


Figure S11. Single crystal X-ray structure of **3** a) Top view b) side view (*meso*-aryl groups are omitted for clarity)

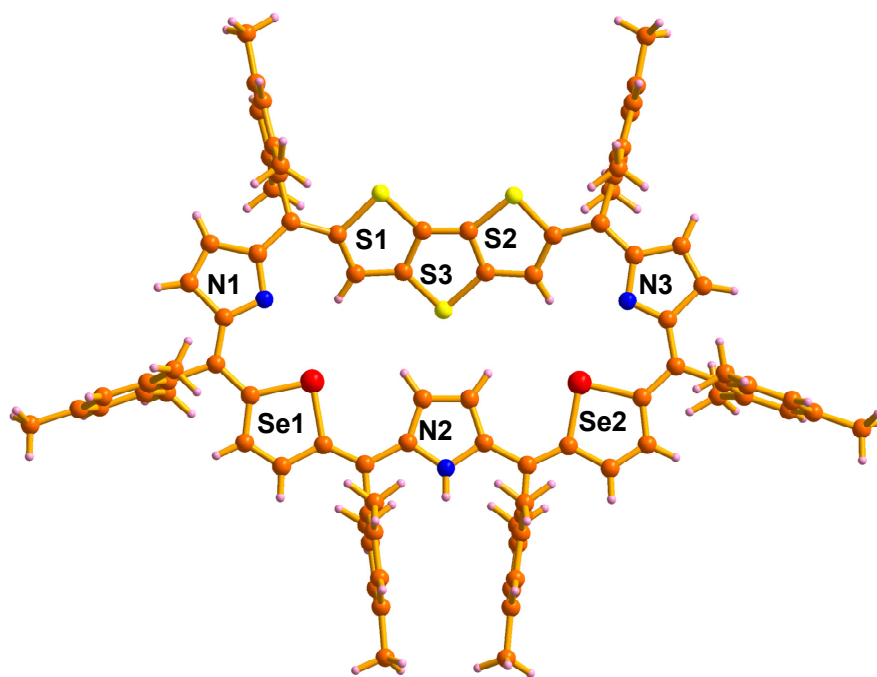


Figure S12. Single crystal X-ray structure of 4

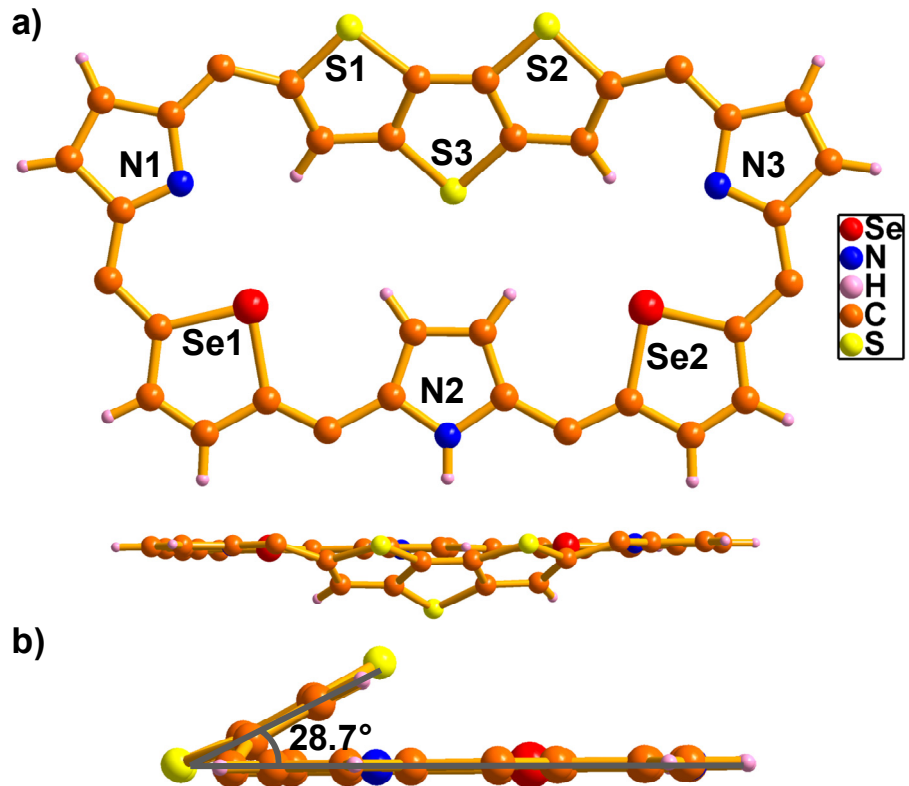


Figure S13. Single crystal X-ray structure of 4 a) Top view b) side view (*meso*-aryl groups are omitted for clarity)

## 7. Crystal data for **3** and **4**:

Crystal data for **3** (from CHCl<sub>3</sub>/hexane): C<sub>88</sub>H<sub>78</sub>N<sub>3</sub>S<sub>5</sub>,  $M_w = 1337.83$ , Triclinic,  $a = 8.9864(12)$ ,  $b = 14.484(2)$ ,  $c = 14.484(2)$  Å,  $\alpha = 90.144(10)$ ,  $\beta = 90.062(7)$ ,  $\gamma = 107.934(7)^\circ$ ,  $V = 4963.2(12)$  Å<sup>3</sup>,  $T = 296$  K, space group P-1,  $Z = 2$ ,  $D_c = 0.895$  mg/m<sup>3</sup>,  $\mu(\text{Mo-K } \alpha) = 0.152$  mm<sup>-1</sup>, 45404 reflections collected, 18408 unique ( $R_{\text{int}} = 0.0383$ ),  $R_1 = 0.0718$ ,  $wR_2 = 0.2274$ , GOF = 0.948  $\{I > 2\sigma(I)\}$ . CCDC-1013536 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](http://www.ccdc.cam.ac.uk/data_request/cif).

Crystal data for **4** (from CHCl<sub>3</sub>/hexane): C<sub>88</sub>H<sub>78</sub>N<sub>3</sub>S<sub>3</sub>Se<sub>2</sub>,  $M_w = 1431.63$ , Triclinic,  $a = 8.9330(2)$ ,  $b = 14.5081(4)$ ,  $c = 40.1827(9)$  Å,  $\alpha = 90.036(10)$ ,  $\beta = 89.997(10)$ ,  $\gamma = 107.971(10)^\circ$ ,  $V = 4953.6(2)$  Å<sup>3</sup>,  $T = 296(2)$  K, space group P-1,  $Z = 2$ ,  $D_c = 0.960$  mg/m<sup>3</sup>,  $\mu(\text{Mo-K } \alpha) = 0.845$  mm<sup>-1</sup>, 61768 reflections collected, 18868 unique ( $R_{\text{int}} = 0.0508$ ),  $R_1 = 0.0508$ ,  $wR_2 = 0.1458$ , GOF = 0.863  $\{I > 2\sigma(I)\}$ . CCDC-1013537 contains the supplementary crystallographic data for **4**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).