ELECTRONIC SUPPLEMENTARY INFORMATION

for

Fused Core-Modified Planar Antiaromatic 32π 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 CDCl₃ or CD₂Cl₂ 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 CH₂Cl₂ solution. Single-crystal X-ray diffraction data were collected on a Bruker KAPPA APEX-II, four angle rotation system, MoKα radiation (0.71073 Å). Quantum mechanical calculations were carried out using the Gaussian09 program suite.¹⁻² 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.³


2. Experimental Section:

Synthesis of 3

DTT-diol 5 (1.0g, 1 equiv, 0.002 mol) and thia-tripyrrane 6 (0.971g, 1 equiv, 0.002 mol) were dissolved in anhydrous CH₂Cl₂ (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 CH₂Cl₂: hexane (10:90) was identified as sapphyrin 8 in 4% yield and the second blue band (CH₂Cl₂: hexane, 15:85) was identified as fused heptaphyrin 3 in 06 % yield.

3: mp 212-214 °C (decomposition); elemental analysis: C₈₈H₇₉N₃S₅: 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 C₈₈H₇₉N₃S₅+: 1338.4878; found: 1338.4881.

3: Uv/Vis (CH₂Cl₂): λ_max[nm] (ε [10⁴M⁻¹cm⁻¹]): 502 (0.805), 597 (0.427);
3: ¹H NMR (400MHz, CDCl3, 25°C, TMS) δ[ppm]: 15.68 ( s, 2H), 12.86 (s, 2H), 7.52 (d, 3J=4 Hz, 2H), 7.13 (d, 3J=4 Hz, 2H), 6.68 (s, 4H), 6.65 (s, 4H), 6.35 (s, 4H), 5.24 (d, 3J=4 Hz, 2H), 4.79 (d, 3J=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⁺: Uv/Vis (CH₂Cl₂): λ_max[nm] (ε [10⁴M⁻¹cm⁻¹]): 556 (1.09);
3.2H⁺: ¹H NMR (400MHz, CDCl3, 25°C, TMS) δ[ppm]: 13.12 ( s, br, 2H), 7.42 (s, 2H), 7.40 (s, 2H), 7.37 (d, 3J=4 Hz, 2H), 7.34 (d, 3J=4 Hz, 2H), 7.14 (d, 3J=4 Hz, 2H), 7.12 (d, 3J=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 selena-tripyrrane 7 (0.971g, 1 equiv, 0.002 mol) were dissolved in anhydrous CH₂Cl₂ (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 CH₂Cl₂: hexane (14:86) was identified as sapphyrin 9 in 3% yield and the second blue band (CH₂Cl₂: hexane, 18:82) was identified as fused heptaphyrin 4 in 4 % yield.
4: mp 206-209 °C (decomposition); elemental analysis: Calcd for C_{88}H_{79}N_{3}S_{3}Se_{2}: 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_{88}H_{79}N_{3}S_{3}Se_{2}+H^{+}: 1434.3767; found: 1434.3769.

4: Uv/Vis (CH_{2}Cl_{2}): \lambda_{\text{max}}[\text{nm}] (\varepsilon [10^{4} \text{M}^{-1} \text{cm}^{-1}]): 524 (0.905);

4: ^1H NMR (400MHz, CDCl_{3}, 25°C, TMS) \delta[ppm]: 16.69 (s, 2H), 15.26 (s, 2H), 8.28 (d, ^3J=4 Hz, 2H), 7.83(d, ^3J=4 Hz, 2H), 6.78 (s, 4H), 6.76 (s, 4H), 6.61 (s, 4H), 5.98 (d, ^3J=8 Hz, 2H), 4.59 (d, ^3J=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+: Uv/Vis (CH_{2}Cl_{2}): \lambda_{\text{max}}[\text{nm}] (\varepsilon [10^{4} \text{M}^{-1} \text{cm}^{-1}]): 612 (1.15);

4.2H+: ^1H NMR (400MHz, CDCl_{3}, 25°C, TMS) \delta[ppm]: 9.78 (s, br, 1H), 8.35 (s, 2H), 7.82 (s, 2H), 7.41 (d, ^3J=4 Hz, 2H), 7.34 (d, ^3J=4 Hz, 2H), 7.15 (d, ^3J=8 Hz, 2H), 6.87 (d, ^3J=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:

\[ \text{Scheme S1. Plausible mechanism for the heptaphyrin synthesis} \]
Table S1. Effect of acid and its concentration

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


TFA = Trifluoroacetic acid  
*p*-TSA = *p*-Toluenesulphonic acid  
MSA = Methanesulphonic acid

### 4. Spectral Characterization

![Figure S1. ESI-Mass spectrum of 3](image)

![Figure S2. ESI-Mass spectrum of 4](image)
Figure S3: $^1$H NMR and $^1$H-$^1$H COSY spectrum of 3 in CDCl$_3$ (* TMS and residual solvent)
Figure S4: $^1$H NMR spectrum of 3.2H$^+$ in CDCl$_3$ (* TMS, residual solvent and water peaks)
Figure S5: Variable temperature $^1$H NMR spectrum of 3 in CD$_2$Cl$_2$ (* TMS and residual solvent peak)
Figure S6: $^1$H NMR spectrum of 4 in CDCl$_3$ (* TMS and residual solvent)
Figure S7: $^1$H NMR spectrum of $4.2\text{H}^+$ 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+ reference electrode containing 0.1M TBAPF$_6$ (tetra-$n$-butylammoniumhexafluorophosphate) as supporting electrolyte in anhydrous CH$_2$Cl$_2$ solution.

![Figure S8: Cyclic Voltammogram of 3 in CH$_2$Cl$_2$ containing 0.1 M TBAPF$_6$ with scan rate of 50 mV/s](image1)

Figure S8: Cyclic Voltammogram of 3 in CH$_2$Cl$_2$ containing 0.1 M TBAPF$_6$ with scan rate of 50 mV/s

![Figure S9: Cyclic Voltammogram of 4 in CH$_2$Cl$_2$ containing 0.1 M TBAPF$_6$ with scan rate of 50 mV/s](image2)

Figure S9: Cyclic Voltammogram of 4 in CH$_2$Cl$_2$ containing 0.1 M TBAPF$_6$ 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 CHCl₃/hexane): C₈₈H₇₈N₃S₅, \(M_w = 1337.83\), Triclinic, \(a = 8.9864(12)\), \(b = 14.484(2)\), \(c = 14.484(2)\) Å, \(\alpha = 90.144(10)\), \(\beta = 90.062(7)\), \(\gamma = 107.934(7)^{\circ}\), \(V = 4963.2(12)\) Å³, \(T = 296\) K, space group P-1, \(Z = 2\), \(D_c = 0.895\) mg/m³, \(\mu(\text{Mo-K} \alpha) = 0.152\) mm⁻¹, 45404 reflections collected, 18408 unique \((R_{int} = 0.0383), R_1 = 0.0718, wR_2 = 0.2274, GOF = 0.948 \{I>2\sigma(I)\}\). 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.

Crystal data for 4 (from CHCl₃/hexane): C₈₈H₇₈N₃S₃Se₂, \(M_w = 1431.63\), Triclinic, \(a = 8.9330(2)\), \(b = 14.5081(4)\), \(c = 40.1827(9)\) Å, \(\alpha = 90.036(10)\), \(\beta = 89.997(10)\), \(\gamma = 107.971(10)^{\circ}\), \(V = 4953.6(2)\) Å³, \(T = 296(2)\) K, space group P-1, \(Z = 2\), \(D_c = 0.960\) mg/m³, \(\mu(\text{Mo-K} \alpha) = 0.845\) mm⁻¹, 61768 reflections collected, 18868 unique \((R_{int} = 0.0508), R_1 = 0.0508, wR_2 = 0.1458, GOF = 0.863 \{I>2\sigma(I)\}\). 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.