Electronic supplementary information (ESI)

**meso-Dichloropyrimidinyl substituted expanded porphyrins**

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1. Experimental procedures and data

* **Expanded porphyrins 1-3**


The reaction mixture was separated by column chromatography (silica, eluent CH$_2$Cl$_2$-petroleum ether 1-1 $\rightarrow$ CH$_2$Cl$_2$) to afford porphyrin 1 (purple solid, 10 %), pentaphyrin 2 (brown-black solid, 11 %) and hexaphyrin 3 (gold-coloured solid, 11 %) and a mixture of the higher homologues.

- **Porphyrin 1**

UV/VIS (DMF): $\lambda_{max}$ (log $\varepsilon$) = 281.3 (4.841), 291.8 (4.861), 424.8 (5.374), 517.4 (4.120), 546.9 (3.362), 593.0 (3.634), 655.0 (3.093).

MS (ESI): m/z = 1203.0 [M+H]$^+$.  

- **Pentaphyrin 2**

$^1$H-NMR (300 MHz, CDCl$_3$) $\delta$ (ppm) = 9.08 (d, $^3J$ = 5.1 Hz, 1H, H$_{\beta}$-pyr), 8.98 (d, $^3J$ = 5.1 Hz, 1H, H$_{\beta}$-pyr), 8.80-8.30 (m, 14H), 7.75-7.50 (m, 15H), 3.51 (s, 1H), -1.87 (s, 1H); some signal assignments remain unclear due to solvent impurities and overlapping signals.

UV/VIS (CH$_2$Cl$_2$): $\lambda_{max}$ (log $\varepsilon$) = 278.1 (4.971), 482.0 (4.677), 533.2 (4.662), 800.0 (3.869).

MS (ESI): m/z = 1502.0 [M+H]$^+$.  

- **Hexaphyrin 3**

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) = 9.43 (d, $^3J$ = 4.8 Hz, 4H, H$_{\beta}$-pyr), 9.14 (d, $^3J$ = 4.8 Hz, 4H, H$_{\beta}$-pyr), 8.82 (d, $^3J$ = 7.2 Hz, 4H), 8.49 (d, $^3J$ = 7.2 Hz, 8H), 7.70 (m, 6H), 7.54 (t, $^3J$ = 7.6 Hz, 4H), 7.41 (t, $^3J$ = 7.6 Hz, 8H), -2.09 (sbr, 2H, NH), -2.50 (s, 4H, H$_{\beta}$-pyr).

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) = 166.0, 164.9, 163.8, 162.9, 155.3, 149.1, 134.9, 134.7, 134.7, 134.3, 134.3, 132.9, 132.0, 131.9, 129.6, 129.4, 129.1, 128.9, 128.7, 125.1, 122.8, 113.8.

MS (ESI): m/z = 1803.8 [M+H]$^+$.  

UV/VIS (CH$_2$Cl$_2$): $\lambda_{max}$ (log $\varepsilon$) = 271.0 (5.039), 575.2 (5.380), 606.9 (4.961), 722.6 (4.424), 782.9 (4.009), 899.1 (3.749), 1035.1 (4.103).

Crystals could be grown from THF.

* **Octasubstitution on porphyrin 1**

Octafunctional porphyrin 1 (25 mg, 20.8 $\mu$mol) and 4-t-butylphenol (38 mg, 253 $\mu$mol) were dissolved together in DMF (5 mL). K$_2$CO$_3$ (55 mg, 400 $\mu$mol) was added and the mixture was heated at 70 °C during 24h. DMF was evaporated, the residue was dissolved in CH$_2$Cl$_2$ (25 mL), washed with water (3 x 25 mL) and the organic fraction was dried over MgSO$_4$. The octasubstituted porphyrin was, after purification by column chromatography (silica, eluent CH$_2$Cl$_2$-petroleumether 1-1), obtained in 64 % yield (28 mg).

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) = 9.21 (s, 8H, H$_{\beta}$-pyr), 8.36 (dd, $^3J$ = 8.2 Hz, $^4J$ = 1.6 Hz, 8H), 7.47 (m, 12H), 7.13 (d, $^3J$ = 8.8 Hz, 16H), 7.02 (d, $^3J$ = 8.8 Hz, 16 H), 1.12 (s, 72H, t-Bu), -2.38 (sbr, 2H, NH).
* Doubly N-fused hexaphyrins 6 and 7

To a solution of [26]hexaphyrin 3 (50 mg, 27.7 µmol) in DMF (10 mL) were added K₂CO₃ (192 mg, 1.39 mmol) and 4-t-butylphenol (104 mg, 693 µmol) and the mixture was heated at 90 °C under Ar atmosphere. After 48h, DMF was evaporated and the residue was dissolved in Et₂O (25 mL) and washed with water (3 x 25 mL). The organic phase was dried over MgSO₄ and evaporated to dryness. The crude product was subjected to column chromatographic purification (silica, eluent CH₂Cl₂-petroleumether 1-1) and the syn- and anti-doubly N-fused hexaphyrins 6 and 7 were obtained in 13 mg (16 %) and 39 mg (49 %) yield.

- syn-Doubly N-fused hexaphyrin 6

1H-NMR (400 MHz, CDCl₃) δ (ppm) = ~16 (s br, 2H, NH), 10.86 (d, 2J = 5.7 Hz, 2H, H₆-pyr), 9.90 (d, 2J = 5.6 Hz, 2H, H₆-pyr), 8.03 (d, 2J = 8.6 Hz, 4H), 7.38-7.10 (m, 38H), 7.09 (d, 3J = 8.5 Hz, 2H), 6.87 (m, 6H, m/p-Ph), 6.39 (d, 3J = 4.4 Hz, 2H, H₆-pyr), 6.28 (d, 3J = 4.3 Hz, 2H, H₆-pyr), 6.20 (d, 3J = 4.2 Hz, 2H, H₆-pyr), 5.74 (d, 2J = 4.4 Hz, 2H, H₆-pyr), 1.42 (s, 18H, t-Bu), 1.36 (s, 18H, t-Bu), 1.33 (s, 18H, t-Bu).

13C-NMR (100 MHz, CDCl₃) δ (ppm) = 169.0, 168.7, 162.6, 161.8, 161.7, 157.7 (Cα-pyr), 157.6, 155.0, 151.1 (Cα-pyr), 150.9, 150.7, 150.5, 150.4, 150.3, 148.1, 147.8, 147.5, 147.4, 145.9 (Cα-pyr), 145.4 (Cα-pyr), 141.3 (Cα-pyr), 130.7, 130.6, 136.5 (CHβ), 136.4, 131.0 (CH), 130.4 (CH), 129.4 (CH), 128.4 (CH₂), 128.3 (CH), 128.25 (CH), 128.20 (CH), 127.68 (CH), 127.6 (CH), 127.5 (CH), 126.3, 126.1 (CH), 125.9 (CH), 125.8 (CH), 125.7 (CH), 125.0 (CH), 121.6 (CH₆), 121.5 (CH), 121.2 (CH), 121.0 (CH), 120.6 (CH), 120.1 (CH₂), 116.0, 113.9, 108.1, 107.8, 104.2, 100.7, 34.6, 34.5, 34.4, 34.3, 34.2.

MS (ESI): m/z = 2869.9 [M+H]+, 1434.9 [M+H]²⁺.

UV/VIS (CH₂Cl₂): λmax (log ε) = 264.0 (5.106), 547.0 (4.872).

- anti-Doubly N-fused hexaphyrin 7

1H-NMR (400 MHz, CDCl₃) δ (ppm) = ~16 (s, 2H, NH), 10.82 (d, 2J = 5.6 Hz, 2H, H₆-pyr), 10.37 (d, 2J = 5.6 Hz, 2H, H₆-pyr), 7.75 (d, 2J = 7.5 Hz, 4H, o-Ph), 7.62 (m, 4H, o-Ph), 7.46-7.08 (m, 42H), 6.30 (d, 2J = 4.7 Hz, 2H, H₆-pyr), 6.25 (d, 2J = 4.0 Hz, 2H, H₆-pyr), 5.70 (d, 2J = 3.8 Hz, 2H, H₆-pyr), 1.39 (s, 36H, t-Bu), 1.34 (s, 18H, t-Bu), 1.25 (s, 36H, t-Bu).
2. Spectra

* Hexaphyrin 3

- ESI-MS
- $^1$H NMR
- $^{13}$C NMR
HMBC
- $^1$H NMR
- $^{13}$C NMR
anti-Doubly N-fused hexaphyrin 7
- $^1$H NMR
$^{13}$C NMR