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General Experimental Information

Solution state NMR spectra were recorded on Bruker DRX-400 (400 MHz for $^1$H), Bruker Avance 500 (500 MHz for $^1$H), Bruker Avance 500 Cryo (125 MHz for $^{13}$C) and Bruker Avance QNP (400 MHz for $^{19}$F) spectrometers. Where high resolution was required $^1$H NMR spectra were acquired as 32 K FIDs and zero filled to 64 K points (accuracy to within the third decimal place). Unless otherwise stated, NMR spectra were recorded in deuterated chloroform (CDCl$_3$) at 298 K ± 3 K. In preparing freebase porphyrin samples for NMR spectroscopy acid titration studies the $d$-chloroform was filtered through alumina to remove traces of acid and reduce the water content.

Two dimensional spectra were acquired using standard Burker pulse programs. Gradient double quantum filtered COSY spectra were typically recorded with 640 slices in $F_1$ and 2048 points in $F_2$. NOESY spectra (1.2 seconds mixing time) were typically recorded with 800 slices in $F_1$ and 2048 points in $F_2$.

In the solution state, porphyrin $^1$H and $^{13}$C NMR assignments were made by comparison with previously assigned similarly substituted porphyrin species and were labelled according to the systems shown. Chemical shifts ($\delta$) were quoted in ppm, the downfield direction being positive, and were referenced to the solvent resonances. Coupling constants ($J$) were given in Hz and uncertainties quoted as ± 0.05 Hz. For convenience, the following abbreviations were used: s, singlet; d, doublet; t, triplet; dd, doublet of doublets; dt, doublet of triplets, m, multiplet; br, broad, etc.

Column chromatography was performed on either 60 mesh silica gel (Breckland Scientific) or alumina ($\text{Al}_2\text{O}_3$), basic grade (Aldrich). Thin layer chromatography was performed on Kiesel silica gel 60 PF$_{254}$ (Merck) 0.2 mm glass plates.

With the exception of chloroform, freshly distilled solvents were used in all preparations. Dry solvents were obtained from solvent stills in accordance with literature procedures.

UV-Vis spectra were measured on a Perkin Elmer Lambda UV/Vis/NIR spectrometer (25°C) using a 1 cm path length quartz cell versus a pure solvent reference. For MALDI-TOF-MS analysis the samples were deposited directly onto the MADI target plate.

The Matrix-assisted laser desorption/ionization time of flying (MALDI-TOF) mass spectra were recorded on 4700 Proteomics analyser (Applied Biosystems) with TOF/TOF optics. The spectra acquired in reflector mode and 2500 laser shots were average together. HR-MS were recorded using LTQ Orbitrap analyser.
**Synthetic Experimental Procedures**

The schemes below outline the methodology applied for the preparation of the key building blocks. Most of the compounds presented were synthesised based on literature precedent (see references below), however slight modifications outlined below either led to improved yields, simplified syntheses or new compounds.

**Synthesis of the components 3 and M-5 (where M=Ru or Zn)**

![Synthetic route diagram for compounds 3 and M-5]

Synthetic route for the preparation of ligand 3. The syntheses for S1-S5 followed literature precedent.[1]
Synthetic route for the preparation of ligand Ru-5. The syntheses of S7-S9 and porphyrin S10 have been described previously in the literature. The analogous Zn-5 was prepared using the same methodology.
2-[2-[2-[2-Nicotinoyloxy-ethoxy]-ethoxy]-ethoxy]-ethyl, 7-[2-[2-[2-Tosyl-ethoxy]ethoxy]-ethoxy]-ethyl] -1,4,5,8-naphthalenedicarboxiimide (S6)

2-[2-[2-[2-Nicotinoyloxy-ethoxy]-ethoxy]-ethoxy]-ethyl, 7-[2-[2-[2-Tosylate-ethoxy]ethoxy]-ethoxy]-ethyl]benzo[lmn]-[3,8]phenanthroline,1,3,6,8-tetratetraone, S5, (1.0 g, 1.4 mmol)\(^{[1]}\) was dissolved in dry, freshly distilled CH\(_2\)Cl\(_2\) (50 mL). Ag\(_2\)O (1.5 equiv., 490 mg, 2.1 mmol) was added and the solution stirred at 0 °C for one hour. p-Toluenesulfonyl chloride (1.1 equiv.) and KI (0.2 equiv.) were added at 0 °C and stirred for a further hour and the mixture then allowed to warm to room temperature and stirred overnight. The resulting suspension was filtered into a plug of Celite and washed with dry CH\(_2\)Cl\(_2\). The solvent was removed under reduced pressure and the resulting yellow viscous liquid was washed with water, the product was extracted into chloroform, the organic phase was dried (over MgSO\(_4\)), and the solvent was removed under reduced pressure. Finally, the resulting oil was purified by flash column chromatography (beginning with CH\(_2\)Cl\(_2\) and then increasing the polarity to 5% CH\(_3\)OH) giving the product as a yellow-orange viscous oil (860 mg, 70%) which can be stored at 0 °C for several months. \(^1\)H NMR (CDCl\(_3\), 400 MHz): 9.18 (s, 1H), 8.73 (dd, 1H), 8.70 (s, 4H), 8.28 (d, 1H), 7.88 (d, 2H), 7.37 (dd, 1H), 7.29 (d, 2H), 4.44-4.38 (m, 6H), 4.17 (t, 2H), 3.82-3.85 (m, 24H), 2.46 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 400 MHz): 165.61, 163.27, 153.87, 151.40, 145.16, 137.53, 133.34, 131.73, 130.20, 128.36, 127.16, 127.03, 126.41, 123.66, 71.12, 71.08, 71.05, 71.04, 70.94, 70.52, 69.62, 69.44, 69.08, 68.21, 64.90, 53.82, 40.00, 22.03. ES-MS. 879.12 [S6 + H\(^+\)].
2-[2-{2-[2-Nicotinoyloxy-ethoxy]-ethoxy}-ethoxy]-ethyl]-7-[2-{2-[2-[2,2’:6’,2”-terpyridine]-ethoxy]ethoxy}-ethoxy]-ethyl]-1,4,5,8-naphthalenedicarboxiimide (3)

K₂CO₃ was added to a solution of HO-terpy (1.1 equiv., 157 mg, 0.63 mmol) in dry DMF (50 mL) and the resulting suspension was heated to 70°C for one hour. The tosyl protected S₆ (500 mg, 0.57 mmol) was added to the reaction mixture and this was stirred at 70 °C for three days, after which the solvent was removed under reduced pressure and residue was washed with water. The crude product was extracted with CHCl₃ and the organic phase was dried (over MgSO₄) giving an orange solid which was purified by Al₂O₃ column chromatography to give the product as a viscous yellow oil (331 mg, 61%).

^1H NMR (CDCl₃, 400 MHz): 9.19 (d, 1H), 8.73 (dd, 1H), 8.63 (complex m, 2H), 8.62 (s, 4H), 8.49 (d, 2H), 8.28 (dt, 1H), 7.91 (s, 2H), 7.79 (t, 2H), 7.36 (dd, 1H), 7.28 (dd, 2H), 5.28-4.3 (m, 8H), 3.90-3.61 (m, 24H).

^13C NMR (CDCl₃, 400 MHz): 167.12, 165.47, 163.02, 157.15, 156.11, 153.72, 151.24, 149.27, 137.37, 136.96, 131.07, 126.80, 126.69, 126.24, 124.07, 123.50, 121.43, 107.51, 71.28, 70.98, 70.93, 70.92, 70.88, 70.46, 70.36, 69.65, 69.28, 68.04, 68.02, 64.74, 39.91, 39.77, 31.48, 29.94. ES-MS: 977.71 [3 + Na⁺].

1H NMR spectrum (400 MHz, CD₂Cl₂, 298 K) of 3.
4’-{2-[2-(2-Hydroxyethoxy)ethoxy]ethoxy}-2,2’,6’,2”-terpyridine (S8)

4’-Hydroxy-2,2’:6’,2’’-terpyridine (1.0 g, 4.0 mmol, 249 gmol\(^{-1}\)) and K\(_2\)CO\(_3\) (2.0 g) were added to dry DMF (40 mL) at room temperature. The mixture was heated to 70 °C and stirred for one hour. Then 1.2 equiv. (1.67 g, 4.8 mmol, 348 gmol\(^{-1}\)) of tetra (ethylene glycol) mono tosylate\(^{[3]}\) were added to the reaction flask. The suspension was stirred at 70 °C for three days, and subsequently the flask was cooled to room temperature and the liquid was removed under reduced pressure. The product was extracted from water with CH\(_2\)Cl\(_2\) and the organic phase was dried (over MgSO\(_4\)). The resulting viscous liquid was subjected to column chromatography Al\(_2\)O\(_3\) (beginning with pure CH\(_2\)Cl\(_2\) and then gradually increasing polarity to 5% CH\(_3\)OH; RF= 0.1, CD\(_2\)Cl\(_2\)-2% CH\(_3\)OH). The product was obtained as a colourless viscous liquid (1.48 g, 75%). \(^1\)H NMR (CDCl\(_3\), 400 MHz): 8.59 (d, 2H), 8.58 (d, 2H), 8.03 (s, 2H), 7.83 (t, 2H), 7.76 (d, 2H), 7.31 (dd, 2H), 4.40 (t, 2H), 4.25 (t, 1H, OH), 3.92 (t, 2H), 3.77-3.61 (m, 12H). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz): 166.97, 157.07, 156.024, 149.01, 136.83, 123.85, 121.36, 107.44, 72.97, 72.48, 70.61, 70.53, 69.94, 69.43, 67.78, 61.57. \textbf{ES-MS}: 520.73 [S8 + Na\(^+\)].

\(^1\)H NMR spectrum (400 MHz, CDCl\(_3\), 298 K) of S8.
4’-{2-[2-[tosylate-2-ethoxy]ethoxy]ethoxy}ethoxy)-2,2’:6’,2”-terpyridine (S9)

Compound S8 (1.2 g, 2.4 mmol, 497 gmol) was dissolved in dry CH$_2$Cl$_2$ (50 mL) then Ag$_2$O was added (1.5 equiv., 835 mg, 3.6 mmol, 232 gmol$^{-1}$). The reaction mixture was stirred at 0 °C for 30 minutes then TsCl (1.1 equiv., 500 mg, 2.64 mmol) and KI (0.2 equiv., 77 mg, 0.48 mmol) were added. The solution was stirred for one hour at 0 °C then for 24 hours at room temperature. The suspension was filtered through a plug of Celite and washed extensively with dry CH$_2$Cl$_2$ (200 mL), after which the solvent was removed under reduced pressure. The crude product of the reaction was washed with water, the product was extracted with CH$_2$Cl$_2$, and the organic phase dried (over MgSO$_4$). The resulting viscous liquid was purified by column chromatography Al$_2$O$_3$ (CH$_2$Cl$_2$ first then increasing polarity to 3% CH$_3$OH; RF= 0.12, CD$_2$Cl$_2$-2% CH$_3$OH) to give a colourless viscous liquid (1.15 g, 85%).

$^1$H NMR (CDCl$_3$, 400 MHZ): 8.66 (d, 2H), 8.59 (d, 2H), 8.00 (s, 2H), 7.83 (t, 2H), 7.76 (d, 2H), 7.32-7.28 (m, 4H), 4.37 (t, 2H), 4.13 (t, 2H), 3.9 (t, 2H), 3.63 (t, 2H), 3.61-3.64 (m, 8H).

$^{13}$C NMR (CDCl$_3$, 125 MHZ): 166.97, 157.11, 156.03, 149.04, 144.75, 136.80, 132.97, 129.79, 123.84, 121.32, 107.42, 70.97, 70.74, 70.69, 70.57, 69.44, 69.24, 68.65, 67.77, 21.62. ES-MS: 611.16 [7 + Na$^+$].

$^1$H NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298 K) of S7.

*K₂CO₃* was added to a solution of ruthenium(II) carbonyl 5-[m-hydroxy phenyl]10,15,20-tris-[p-tolyl]porphyrin, **S₁₀**, (200 mg, 0.25 mmol, 800 gmol⁻¹) in dry DMF (40 mL). The resulting suspension was heated to 70 °C for one hour, and then 4'(2{2[tosylate-2-ethoxy]ethoxy]ethoxy]ethoxy)-2,2':6',2''-terpyridine **S₇** (1.1 equiv., 162 mg, 0.28 mmol) was added to the reaction mixture. The reaction mixture was stirred at 70 °C for three days, after which the solvent was removed under reduced pressure and the mixture washed with water. The product was extracted with CHCl₃ and the organic phase was dried (over MgSO₄), giving an orange solid which was subjected to Al₂O₃ column chromatography (beginning with CH₂Cl₂ then gradually increasing the polarity with CH₃OH). Two orange bands were identified. The first orange band collected was the 4'-[2-[2-[2-(Ruthenium(II)carbonyl5-[m-hydroxyphenyl]10,15,20-tris-[p-tolyl]porphyrin (**S₁₀**) and the second band collected was the product (Ru-5) which was re-crystallized from chloroform layered with methanol to give the product as red/orange powder (120 mg, 40%).

**¹H NMR:** (CD₂Cl₂, 400 MHz): 8.65-8.59 (s, 8H), 8.08-7.46 (m), 7.26-7.25 (m), 4.26 (s, 2H), 3.87 (m, 2H), 3.64-3.16 (m), 2.68 (s, 12H).

**¹³C NMR** (CD₂Cl₂, 125 MHz): 181.45, 167.28, 167.00, 157.45, 157.32, 156.93, 156.11, 155.83, 149.16, 148.83, 144.34, 144.10, 139.79, 139.76, 137.39, 137.34, 134.52, 134.49, 134.11, 134.10, 131.88, 131.82, 131.77, 131.70, 127.77, 127.65, 127.57, 127.41, 124.21, 124.19, 122.26, 122.17, 121.65, 121.31, 120.51, 113.51, 107.54, 71.08, 71.01, 70.97, 70.82, 69.54, 69.42, 67.98, 67.75, 21.41.

**MALDI-TOF:** 1179.46.

**¹H NMR spectrum (400 MHz, CD₂Cl₂, 298 K) of Ru-5.**

$K_2CO_3$ was added to a solution of Zn(II) 5-[m-hydroxy phenyl] 10,15,20-tris-[p-tolyl]porphyrin (500 mg, 0.68 mmol, 736 gmol$^{13}$) in dry DMF (70 mL). The resulting suspension was heated to 70 °C for one hour, and then $4'-[2-[2-(tosylate-2-ethoxy)ethoxy]ethoxy]ethoxy)-2,2',6',2''-terpyridine, S7, (1.1 equiv., 430 mg, 0.75 mmol) was added to the reaction mixture which was stirred at 70 °C for three days. Subsequently the solvent was removed under reduced pressure and mixture was washed with water. The product was extracted with CHCl$_3$ and the organic phase was dried (over MgSO$_4$) giving a purple solid which was subjected to Al$_2$O$_3$ column chromatography (beginning with CH$_2$Cl$_2$ then gradually increasing the polarity with CH$_3$OH). The second coloured band was identified as the purple product Zn-5 (430 mg, 56%). $^1$H NMR (CDCl$_3$, 400 MHz): 8.80 (s, 8H), 8.46 (d, 2H), 8.44 (d, 2H), 8.10-8.07 (m, 6H), 7.80-7.70 (m, 4H), 7.68 (t, 2H), 7.55 (t, 1H), 7.52 (d, 6H), 7.25 (s, 1H), 7.16 (dd, 2H), 4.21 (b, 2H), 3.94 (b, 2H), 3.79 (b, 2H), 3.46 (b, 2H), 3.27 (b, 4H), 3.27 (b, 4H), 2.69 (s, 9H). $^{13}$C NMR (CDCl$_3$, 100 MHz) 167.10, 157.47, 157.26, 156.27, 150.66, 150.68, 150.36, 149.27, 144.75, 140.47, 137.34, 136.98, 134.86, 132.34, 132.24, 132.18, 128.13, 127.64, 124.03, 121.57, 121.54, 121.47, 121.40, 120.84, 114.51, 107.66, 71.13, 70.93, 70.71, 70.26, 69.43, 68.15, 67.83, 53.85, 21.94. MALDI-TOF: 1141.42.

$^1$H NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298 K) of Zn-5.
Synthesis of the heteroleptic complexes 1, 2, and 6.

Complex 6

Porphyrin 5 (1.3 mg, 1.1 μmol) and NDI 3 (1.0 equiv., 1.03 mg, 1.1 μmol) were mixed in CD$_2$Cl$_2$ (0.4 mL) and then 1 equiv. of Fe(BF$_4$)$_2$.4H$_2$O (dissolved in CD$_3$OD) was added. The formation of complex 6 was supported by $^1$H NMR analysis and mass spectrometry.

Complex 1 and 2

NDI 3 (2.0 mg, 2.1 μmol) and approximately 10.0 equiv. of crown ether 4 were mixed together in CD$_2$Cl$_2$ (0.4 mL). To this solution 1.0 equiv. of porphyrin 5 (2.4mg, 2.1 μmol) in CD$_2$Cl$_2$ was added, and the reaction mixture was cooled to -78 °C for five minutes. One equiv. of Fe(BF$_4$)$_2$ (dissolved in CD$_3$OD) was added and the reaction mixture was allowed to warm to room temperature. The formation of the complex 2 was supported by $^1$H NMR analysis and mass spectrometry. Complex 1 was obtained using a similar protocol but using only one equivalent of the crown ether 4.
Figure S1. a) The electron deficient π aromatic system of the NDI 3 (pale yellow, in the NMR tube) and the electron rich π system of the crown ether 4 (colourless, in the volumetric flask); b) the charge transfer complex formed between the two components gives rise to a change in colour from pale yellow to pale red; c) the intensity of the colour increases when the mixture is cooled down to 195 K; d) the UV-Vis spectrum of the charge transfer complex formed when molecule 4 is added to a solution of 3 (CH₂Cl₂, 298K). 'y' axis; absorbance, 'x' axis; λ(nm).
Figure S2. HR-MS of the heteroleptic complex formed (Zn-5·3) when one equivalent of Zn(II) is added to an equimolar mixture of Zn-5 and 3.
Figure S3. $^1$H-$^1$H COSY NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298 K) of complex Ru-5·3.
Figure S4. $^1$H NMR spectrum (400 MHz, CD$_2$Cl$_2$-CD$_3$OD/9:1, 298 K) of the heteroleptic dimer (6).
Figure S5. $^1$H-$^3$H COSY NMR spectrum (400 MHz, CD$_2$Cl$_2$-CD$_3$OD/9:1, 298 K) of 6. The ruthenium bound aromatic pyridyl resonances are more complex than expected due to the possibility of a number of atropisomers.
Figure S6. $^1$H-$^1$H COSY NMR spectrum (400 MHz, CD$_2$Cl$_2$-CD$_3$OD/9:1, 298 K) of 2. As in Figure S5, the bound aromatic pyridyl resonances are more complex than expected due to the possibility of a number of atropisomers.
Figure S7. DOSY NMR spectrum (CD$_2$Cl$_2$-CD$_3$OD/ 9:1) of the multicomponent [2] and [3]catenanes, 1 and 2 respectively.
Figure S8. Isotopic distribution pattern for 2 (expansion of spectrum shown in Figure 3).

Figure S9. Isotopic distribution pattern for 1 (expansion of spectrum shown in Figure 3).
**Figure S10.** Isotopic distribution pattern for 6 (expansion of spectrum shown in Figure 3).

**Figure S11.** Isotopic distribution pattern for 4 (expansion of spectrum shown in Figure 3).
Figure S12. HR-MS of complex 1 acquired under the same conditions as for Figure 3. In this case only one equivalent of 4 was added to a mixture of Ru-5 and 3 prior to ring closure – no peak can be identified for the formation of 2.

References

