Electronic Supplementary Material (ESI) for Chemical Communications

A non-covalent strategy to prepare electron donor-acceptor rotaxanes

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Synthesis and Characterisation

Rotaxane **1** was synthesized following a previously reported procedure.[1] Commercial compounds were used as received. 5,10,15,20-Tetraphenyl-21H,23H-porphine zinc (ZnTPP) and 5,10,15,20-Tetraphenyl-21H,23H-porphine ruthenium(II) carbonyl (dye content ~80 %) (Ru(CO)TPP) were purchased from Aldrich.

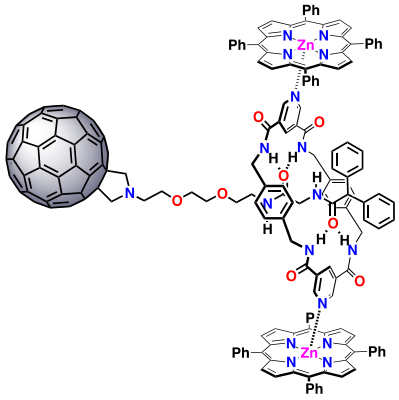
NMR spectra were recorded on a Varian Gemini (300 MHz), on a Bruker Avance DRX 500 (500MHz). Chemical shifts reported in ppm are referred to TMS. NMR signals of compounds **1**, **2**, and **3** were assigned by COSY experiments.

Mass Spectroscopy: Electrospray Ionization (ESI) was performed on a Thermo LCQ Advantage and Electron Impact (EI) on a Thermo TSQ700, at the Organische Chemie MS service (Freiburg im Breisgau).

UV-Vis spectra and **Emission** studies were performed with a Perkin-Elmer *Lambda 950* spectrometer, and a *LS55* Perkin-Elmer Fluorescence spectrometer.

Infrared spectra were recorded on a FT-IR Spectrometer Perkin-Elmer *Spectrum 1000*.

Ensemble 2



ZnTPP (1 mg, 1.47 µmol) was added to a solution of rotaxane **1** (1.3 mg, 0.75 µmol) in $CDCl_3$ (0.75 mL) and the mixture was protected from light. The low solubility of ensemble **2** did not allow recording ^{13}C NMR.

^1H NMR (500 MHz, $CDCl_3$): 8.92 (bs, $H\beta_{ZnTPP}$), 8.71 (bs, 1H, H_B), 8.61-8.57 (m, 2H, H_b), 8.37 (bs, 4H, H_c), 8.22 (bs, $H\alpha_{ZnTPP}$), 8.04-7.94 (m, 4H, H_a), 7.57 (bs, $H\alpha_{ZnTPP}$), 7.02-6.67 (m, 18H, $H_A + H_d$), 5.17-5.03 (m, 3H, $H_C + H_E$), 4.61-4.46 (m, 4H, $H_E + H_L$), 4.51 (s, 1H, H_D), 4.39-4.35 (m, 4H, H_e), 4.19-4.16 (m, 4H, H_e), 3.85 (m, 2H, H_I), 3.78 (m, 2H, H_I), 3.72 (bs, 2H, H_F), 3.55 (t, 2H, J = 3.5 Hz, H_J), 3.01 (bs, 2H, H_K), 2.82 (bs, 2H, H_G).

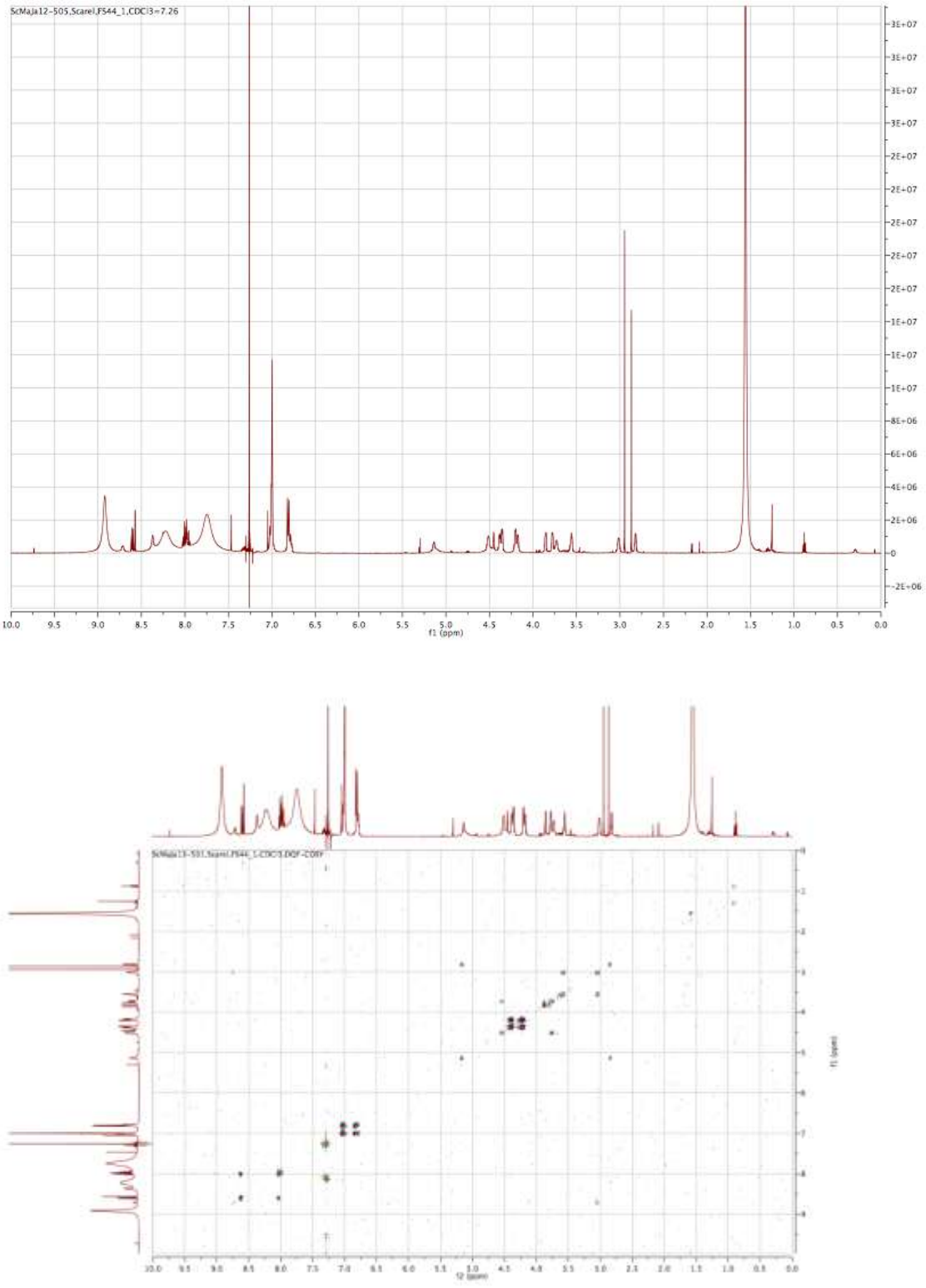
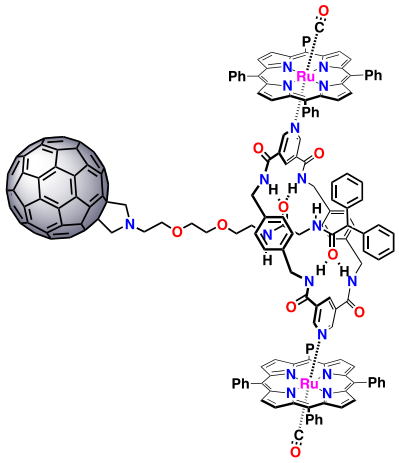


Figure S1. ^{1}H NMR (top) and COSY (bottom) spectra of ensemble **2** in $CDCl_3$.

Ensemble 3



RuTPP (1.4 mg, 1.5 µmol) was added to a solution of rotaxane **1** (1.3 mg, 0.77 µmol) in $CDCl_3$ (0.75 mL) and the mixture was protected from light. The low solubility of ensemble **3** did not allow recording the ^{13}C NMR spectrum.

^1H NMR (500 MHz, $CDCl_3$): 8.69 (s, $H\beta_{RuTPP}$), 8.66 (s, $H\beta_{RuTPP}$), 8.56 (s, $H\beta_{RuTPP}$), 8.20-8.11 (m, H_B + $H\alpha_{RuTPP}$), 7.73-7.59 (m, H_c + $H\alpha_{RuTPP}$), 6.89 (s, 2H, H_b), 6.53 (s, 4H, H_d), 6.17-5.90 (m, 10H, H_A), 4.96 (d, 2H, J = 4.7 Hz, H_E), 4.50 (d, 2H, J = 4.7 Hz, H_E), 4.17 (bs, 2H, H_L), 4.09-4.08 (m, 4H, H_e), 4.06-4.05 (m, 4H, H_e), 3.95 (bs, 1H, H_C), 3.63-3.55 (m, 5H, H_F + H_D + H_I), 3.48 (s, 2H, H_I), 3.04 (s, 2H, H_J), 2.51 (s, 2H, H_K), 2.22 (s, 4H, H_a), 1.97(s, 2H, H_G).

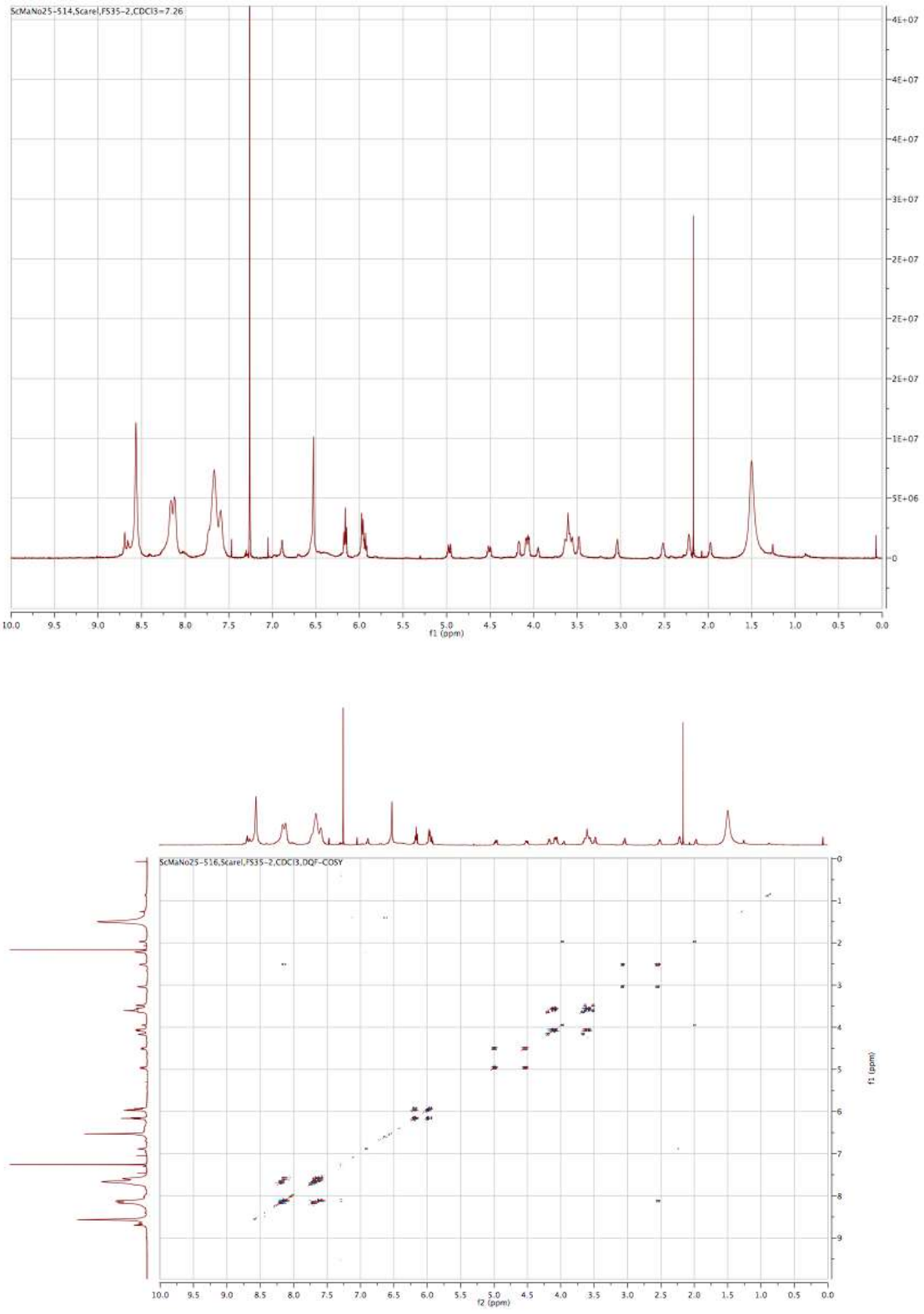
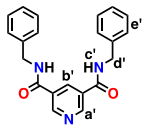


Figure S2. ^{1}H NMR (top) and COSY (bottom) spectra of ensemble **3** in $CDCl_3$.

Dibenzyl 3,5-pyridinedicarboxylate 4



4

NEt_3 (1 ml, 7.2 mmol) was added to a solution of benzylamine (290 μL, 2.64 mmol) and pyridine-3,5-dicarbonyl dichloride (244 mg, 1.2 mmol) in dichloromethane (10 ml) under Argon. The solution was than stirred under Argon over night at room temperature. The reaction mixture was taken up with dichloromethane (50 ml) and than filtered off. The organic layer was washed with HCl (3.6%, x5), $NaHCO_3$ (50%, x4) and BRINE, then dried and the solvent removed, to obtain **5** as a white solid (41 mg, 98%).

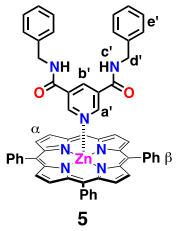
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.11 (d, J = 2.1 Hz, 2H, H_a), 8.49 (t, J = 2.1 Hz, 1H, H_b), 7.37-7.31 (m, 10H, H_d), 6.59 (bs, 1H, H_c), 4.66 (d, J = 5.6 Hz, 2H, H_e).

^{13}C NMR (500 MHz, $CDCl_3$) δ 164.6 (C=O), 150.6 (Ar), 137.4 (Ar), 133.6 (Ar), 129.8 (Ar), 129.0 (Ar), 128.16 (Ar), 128.10 (Ar), 44.53 (CH_2).

MS (EI): 106.1 (39%), 212.1 (28%), 345.2 (100%, M^+)

FT-IR (NaCl): 3263, 3020, 2922, 1636, 1541, 1215.

Complex 5



5

ZnTPP (2 mg, 2.94 µmol) was added to a solution of **4** (0.6 mg, 1.73 µmol) in $CDCl_3$ (0.75 mL) and the mixture was protected from light.

^1H NMR (500 MHz, $CDCl_3$): 8.88 (bs, $H\beta_{ZnTPP}$), 8.61-8.56 (m, 1H, H_b), 8.19 (bs, $H\alpha_{ZnTPP}$), 8.01-7.95 (m, 2H, H_a), 7.74 (bs, $H\alpha_{ZnTPP}$), 7.30-7.14 (m, 10H, H_d), 5.61 (bs, 2H, H_c), 4.34 (bs, 4H, H_e).

^{13}C NMR (125 MHz, $CDCl_3$): 162.61 (C=O), 150.07 (Ar), 145.91 (Ar), 142.92 (Ar), 137.79 (Ar), 134.50 (Ar), 133.47 (Ar), 131.88 (Ar), 128.87 (Ar), 128.55 (Ar), 127.94 (Ar), 127.91 (Ar), 127.38 (Ar), 126.47 (Ar), 120.96 (Ar), 44.09 (CH_2).

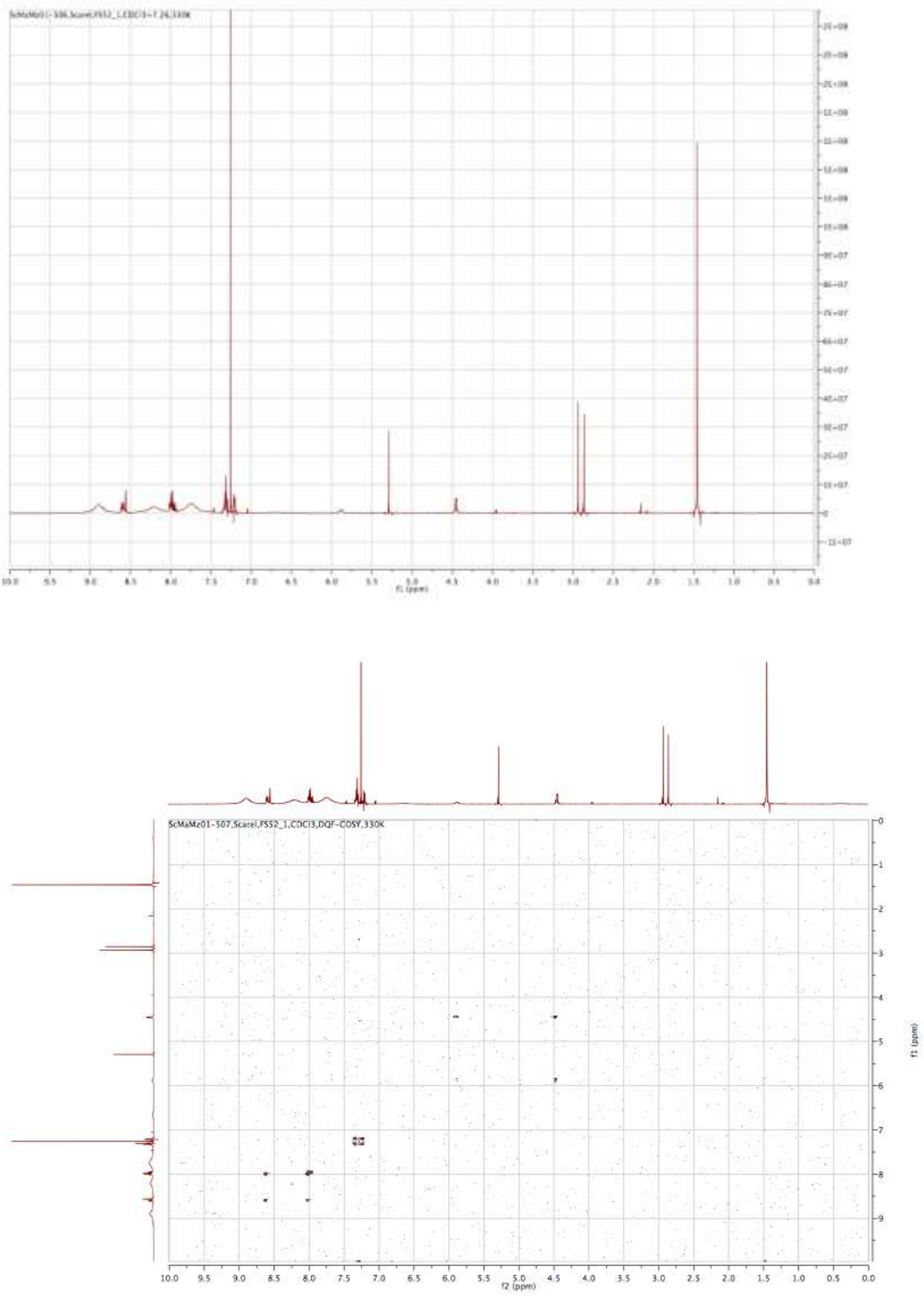


Figure S3. ^{1}H NMR and COSY spectra of complex **5** in $CDCl_3$.

Model studies to corroborate the formation of ensemble 2.

To corroborate our assignment, we synthesised benzyl dinicotinamide **4** and studied its complexation with an excess of ZnTPP. The chemical shifts and the fine structure of the signals of protons a' and b' of complex **5** correspond with those observed for the signals of protons a and b in ensemble **2**, thus confirming our assignment (Figure S4).

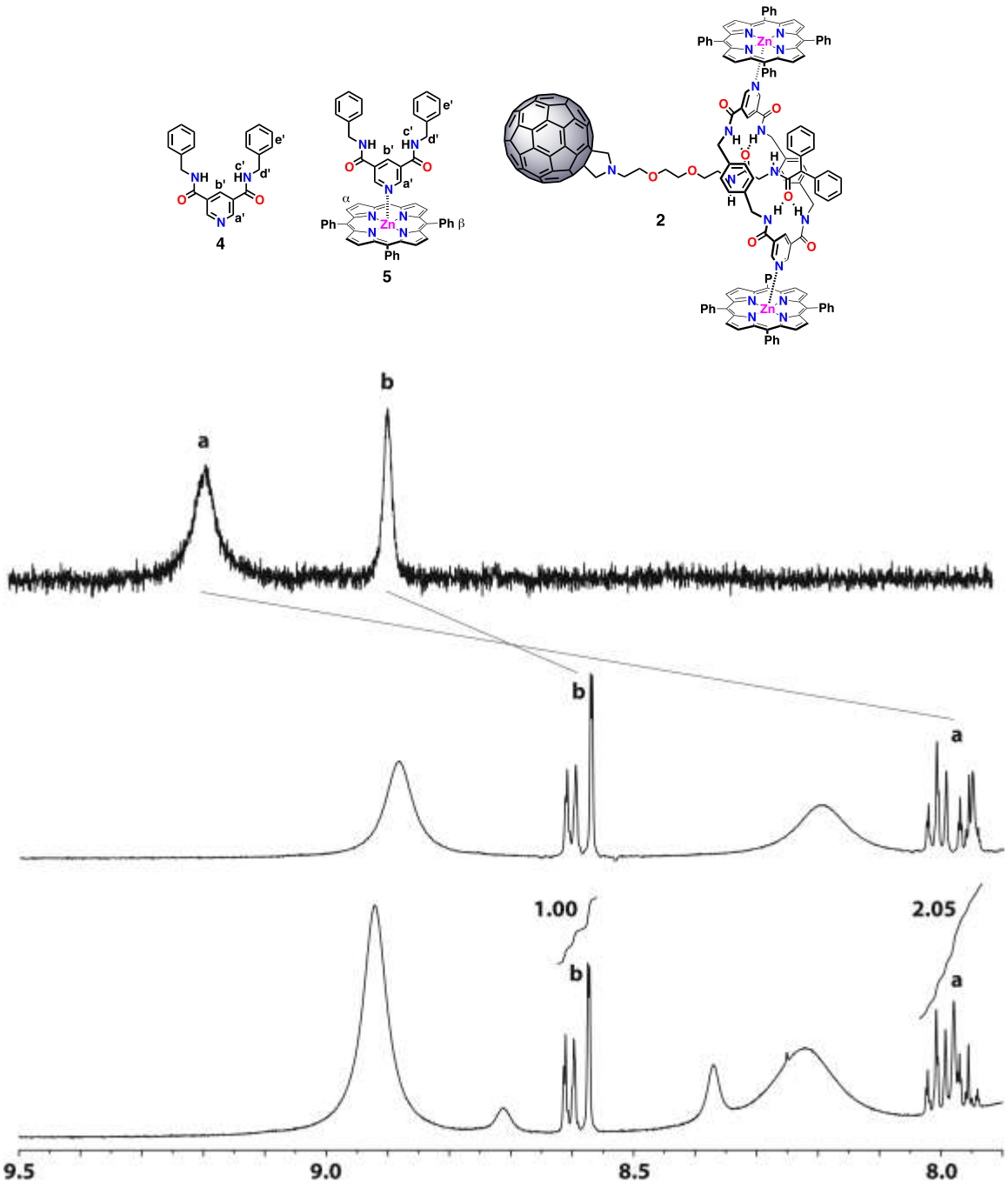


Figure S4. Partial ^{1}H NMR of **4** (top), **5** (middle), **2** (bottom).

Titration studies

UV-Vis titrations were performed at room temperature on a *Lambda 950* Perkin-Elmer Spectrometer and on a *LS55* Perkin-Elmer Fluorescence Spectrometer in $CHCl_3$ (stabilized with amylenes). The HOST (ZnTPP) concentration was kept constant at 4.4×10^{-6} M and a solution of GUEST (rotaxane) at 1.13×10^{-4}M was added in increments of 30 μL by syringe into the cuvette. After each addition, the cuvette was shaken for 30 seconds and after a UV-Vis spectrum was collected. The low solubility of rotaxane **1** and the corresponding complex in solution, which makes difficult carrying out the studies at higher concentration regimes

The solution of HOST was prepared by dissolving 0.6 mg of ZnTPP in a 200 ml of $CHCl_3$ (stabilized with amylenes) using a volumetric flask. 10 ml of this solution was used to dissolve the GUEST sample, in order to keep the concentration of ZnTPP constant throughout the titration.

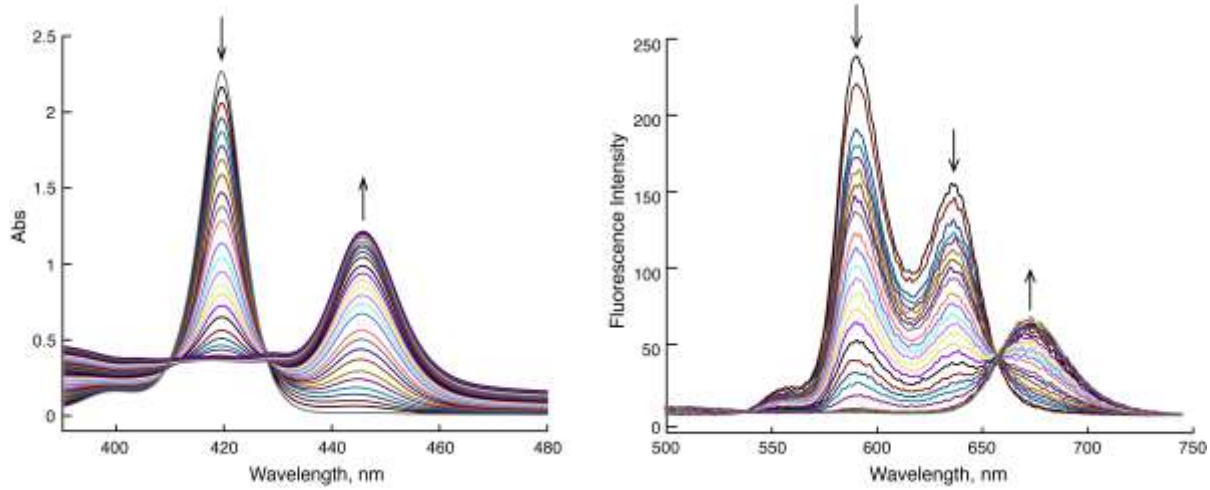


Figure S5. Titration of rotaxane **1** with ZnTPP.

Job Plot analysis

Two stock solutions in $CHCl_3$ (stabilized with amylenes) at the same concentration ($4.4x10^{-6}$M) were prepared in two 200 ml volumetric flasks: solution of HOST containing 0.6 mg of ZnTPP and a solution of GUEST containing 1.5 mg of rotaxane **1**. Then the cuvette was filled eleven times with the two solutions in the following volume ratios (maximum volume 2 ml): 2:0, 1.8:0.2, 1.6:0.4, 1.4:0.6, 1.2:0.8, 1.0:1.0, 0.8:1.2, 0.6:1.4, 0.4:1.6, 0.2:1.8 and 0:2.0 ml, and a UV-Vis spectrum was collected for each mixture.

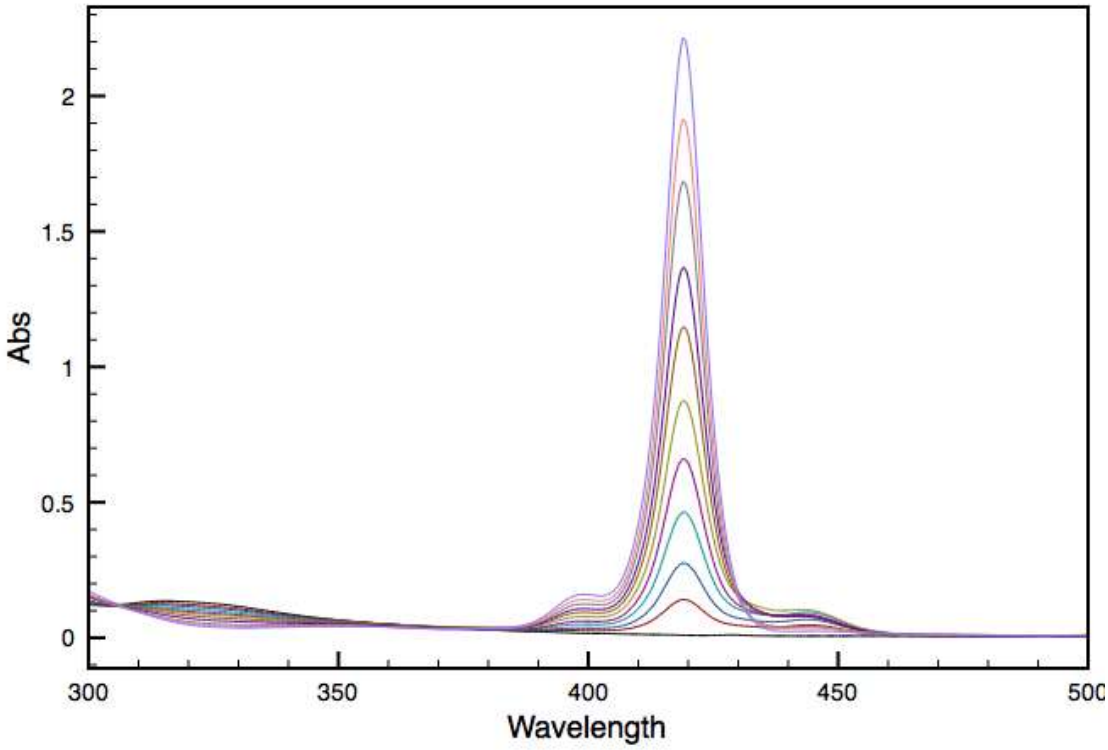


Figure S6. UV-Vis spectra collected from the Job Plot analysis of the ensemble **2** in $CHCl_3$.

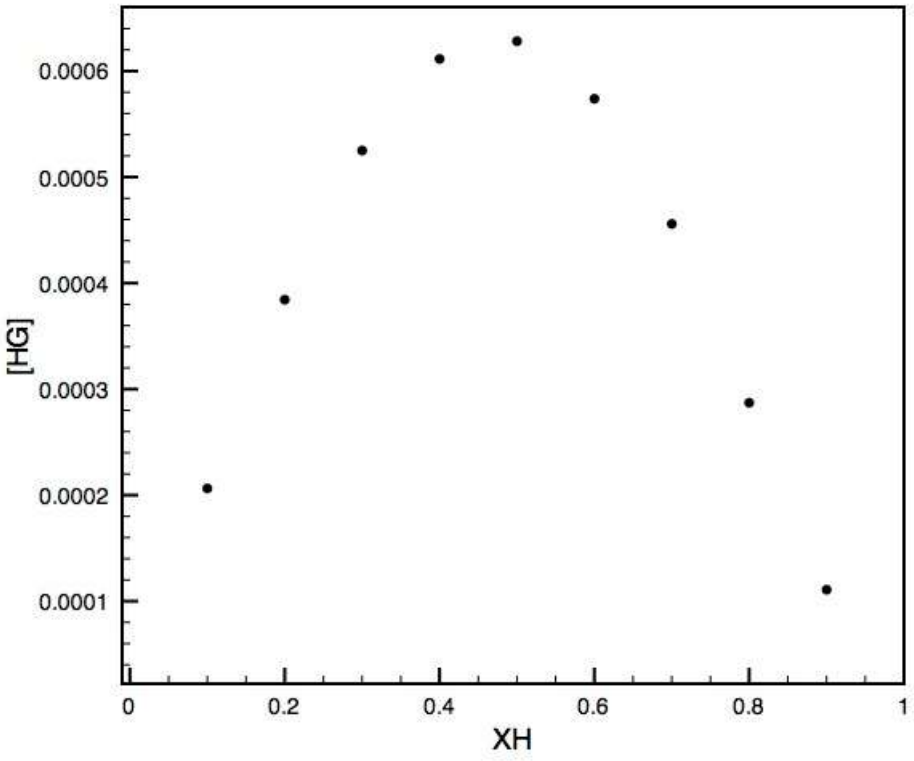


Figure S7. Job Plot analysis. The ensemble **2** concentration [HG] is plot against the HOST molar fraction X_H.

Electrochemistry

Tetrabutylammonium perchlorate ($TBAClO_4$ from Fluka), as supporting electrolyte, was used as received. *o*-Dichlorobenzene was employed as solvent for electrochemical measurements. The solvent was used in an electrochemical cell containing the supporting electrolyte and the species under examination. Electrochemical experiments were carried out in a single-compartment cell by using platinum as working and counter electrodes, and silver as a quasi-reference electrode.
All the $E_{1/2}$ potentials have been directly obtained from CV curves as averages of the cathodic and anodic peak potentials for one-electron. The $E_{1/2}$ values are referred vs SCE to the ferrocene standard ($E_{1/2}$ Fc^+/Fc = +0.48V) and have been determined by adding, at the end of each experiment, ferrocene as an internal standard. Voltammograms were recorded with a PARSTAT 2273 potentiostat.

Compound	I_{ox}	II_{ox}	I_{red}	II_{red}
ZnTPP	+0.42	+0.77	-1.77	-2.08
Ensemble 2	+0.42	+0.83	-1.53	-1.81
Ru(CO)TPP	+0.49	+0.97	-1.79	-
Ensemble 3	+0.79	-	-1.63	-

Table S1. Half-wave potentials of the oxidations and reductions waves of the different porphyrins alone and when complexed with rotaxane **1**.

Photophysics

Steady-state absorption spectroscopy. The spectra were measured with a Perkin Elmer Lambda 959 ultraviolet, visible and near-infrared spectrometer.

Steady-state emission spectroscopy. The spectra were recorded on a Perkin Elmer LS-55 (visible detection) The measurements were carried out at room temperature.

Time-resolved absorption spectroscopy. Femtosecond transient-absorption studies were performed with 420 nm nm laser pulses (1 kHz, 150-femtosecond pulse width) from an amplified titanium–sapphire laser system (Clark-MXR, CPA 2101); the laser energy was 200 nJ.

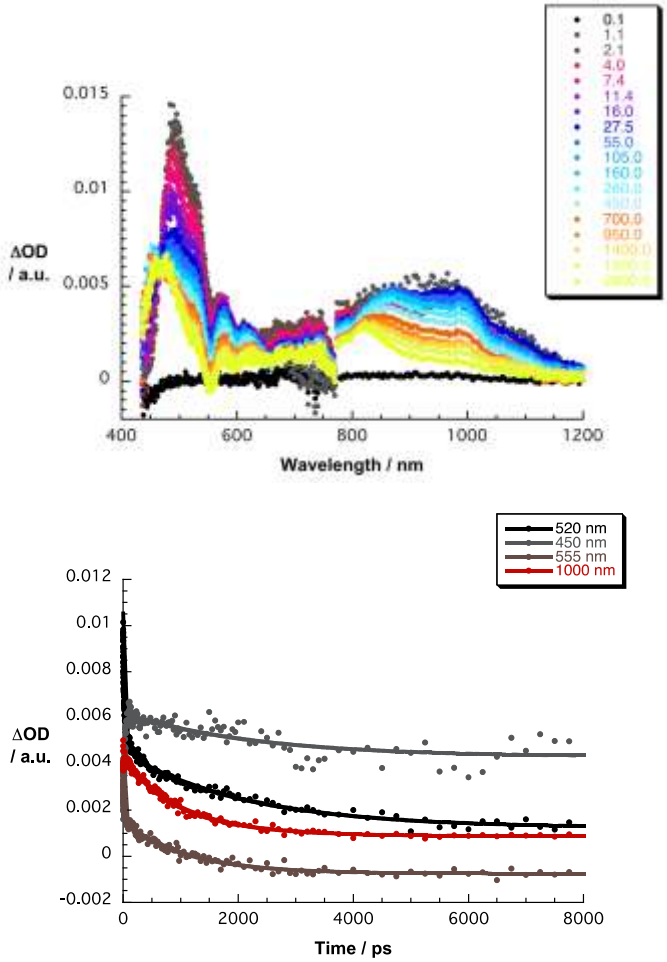


Figure S8. Top: Differential absorption spectra (vis and near-infrared) obtained upon femtosecond pump probe experiments (420 nm) of ensemble **2** in $CHCl_3$ with several time delays (0.1-2800 ps) at room temperature. The best results have been observed by mixing solutions of approx. $8x10^{-5}$ M ZnTPP and $4x10^{-5}$ M **1**. Bottom: Time absorption profiles of the spectra at different wavelengths of ensemble **2** monitoring the excited state decay.

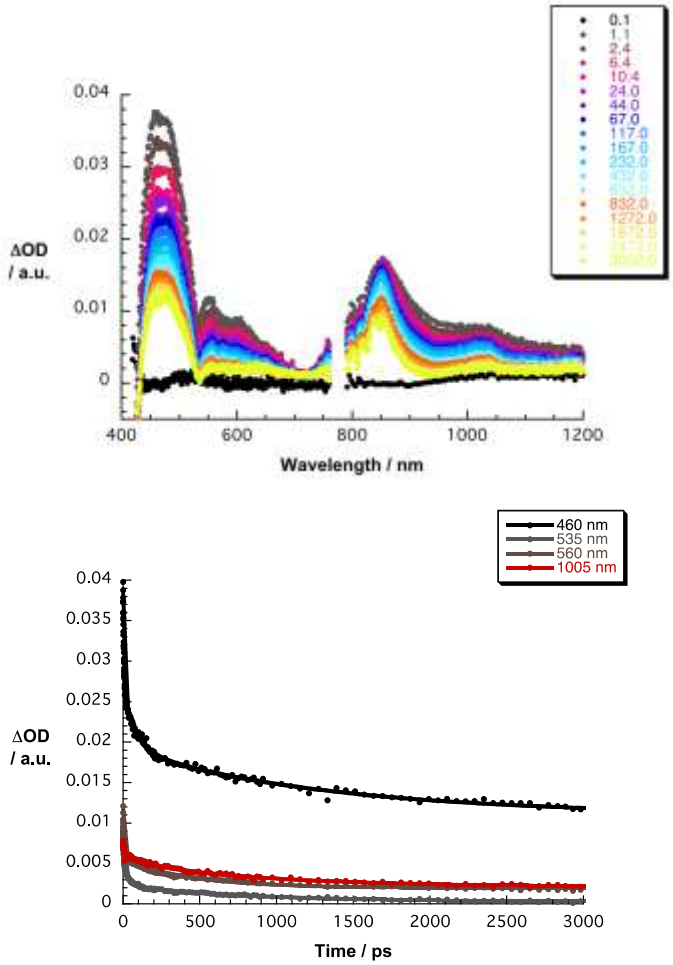


Figure S9. Top: Differential absorption spectra (vis and near-infrared) obtained upon femtosecond pump probe experiments (420 nm) of ensemble **3** in $CHCl_3$ with several time delays (0.1-3032 ps) at room temperature. The best results have been observed by mixing solutions of approx. $8x10^{-5}$ M Ru(CO)TPP and $4x10^{-5}$ M **1**. Bottom: Time absorption profiles of the spectra at different wavelengths of ensemble **2** monitoring the excited state decay.

References

1. F. Scarel, G. Valenti, S. Gaikwad, M. Marcaccio, F. Paolucci and A. Mateo-Alonso, *Chem. Eur. J.*, 2012, **18**, 14063-14068.