

Supporting Information

A double-cavity-containing porphyrin host as a highly stable epoxidation catalyst

Paul J. Thomassen, Shaji Varghese, Edward J. A. Bijsterveld, Johannes A. A. W. Elemans,* Alan E. Rowan,* and Roeland J. M. Nolte^{[a]*}

1) Determination of association constants by UV-vis titrations

UV titrations were carried out using a Varian Cary 50 UV-Vis spectrometer. The binding constants were determined according to a reported procedure.^[1] CHCl₃ and CH₃CN were distilled before use. To a weighed amount of approximately 2.0 mL of a 1.0-2.0 μM stock solution of the porphyrin host in CHCl₃ / CH₃CN (1:1 v/v) were added small amount (25-100 μL, microsyringe) of a stock solution containing the porphyrin host **ZnDC** in the same concentration and approximately 60 μM of guest, so that at the end approximately 10-20 equiv. of guest were present. For each titration, at least 25 data points were collected. Typically four wavelengths were monitored at the same time, two around the absorption maxima for the host and two around the absorption maxima for the complex formed. This gave four data sets from which the binding constants were obtained using a custom written global nonlinear regression analysis program within the Matlab 5.3 package utilizing the Simplex algorithm. For the UV titrations a simple 1:1 complexation (assuming only one binding site per molecule of porphyrin) was used according to equation S-1.^[2-4]

$$A_{\text{obs}} = A_0 - \frac{\Delta\varepsilon}{2} \left\{ [H]_0 + [L]_0 + 1/K - \sqrt{([H]_0 + [L]_0 + 1/K)^2 - 4[H]_0[L]_0} \right\} \quad (\text{S-1})$$

In the case of 1:2 complexation, the data were fitted according to the equations (S-2) and (S-3).^[2,3] and the binding constants K₁ and K₂ were calculated.^[4]

$$\Delta A = \frac{[H_{\text{tot}}](\Delta\varepsilon_{11}K_1[L] + \Delta\varepsilon_{12}K_1K_2[L]^2)}{1 + K_1[L] + K_1K_2[L]^2} \quad \text{and} \quad (\text{S-2})$$

$$K_1K_2[L]^3 + \{K_1(2K_2[H]_0 - K_2[L]_0 + 1)\}[L]^2 - \{K_1([H]_0 - [L]_0) + 1\}[L] + [L]_0 = 0 \quad (\text{S-3})$$

[1] P. Thordarson, R. G. E. Coumans, J. A. A. W. Elemans, P. J. Thomassen, J. Visser, A. E. Rowan, R. J. M. Nolte, *Angew. Chem. Int. Ed.*, **2004**, *43*, 4755-4759.

[2] H. Tsukube, H. Furuta, Y. Takeda, Y. Kudo, Y. Inoue, Y. Liu, H. Sakamoto, D.D. Kimura, F. Vogtle, J. A. Ripmeester, J. M. Lehn, Elsevier Science Ltd., Pergamon, **1996**, Vol. 8, 425.

[3] K. A. Connors, A. Paulson, D. J. Toledo-Velasquez, *J. Org. Chem.*, **1988**, *53*, 2023.

[4] Matlab version 5.3.0.620a (R11) ed.; The Mathworks, Inc.: Natick, M.A, **1999**.

2) UV-vis Studies.

A UV cuvette containing 1.5 mL of a solution of **MnDC**, **MnMC** or **MnOMP** in CH_2Cl_2 ($1.0 \times 10^{-5} \text{ M}^{-1}$) was vigorously mixed with 1.5 mL of an aqueous NaOCl solution (0.6 M). The organic layer and the water layer were separated and a UV-vis spectrum of the organic phase was recorded. This procedure was repeated every 12 sec. over a period of 30 min.

3) $^1\text{H-NMR}$ spectra of porphyrin isomers

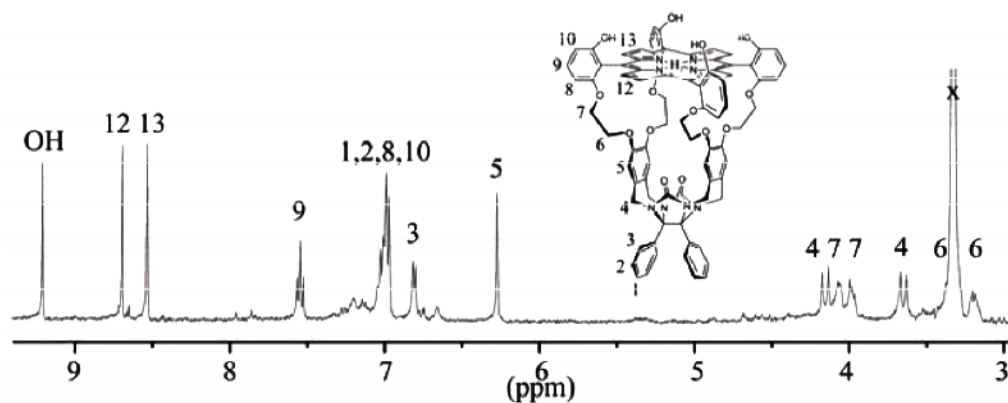


Figure S1a) Downfield region of the $^1\text{H-NMR}$ spectrum (400.18 MHz, 298K, DMSO-d_6) of tetra-hydroxy mono-cavity porphyrin isomer I.

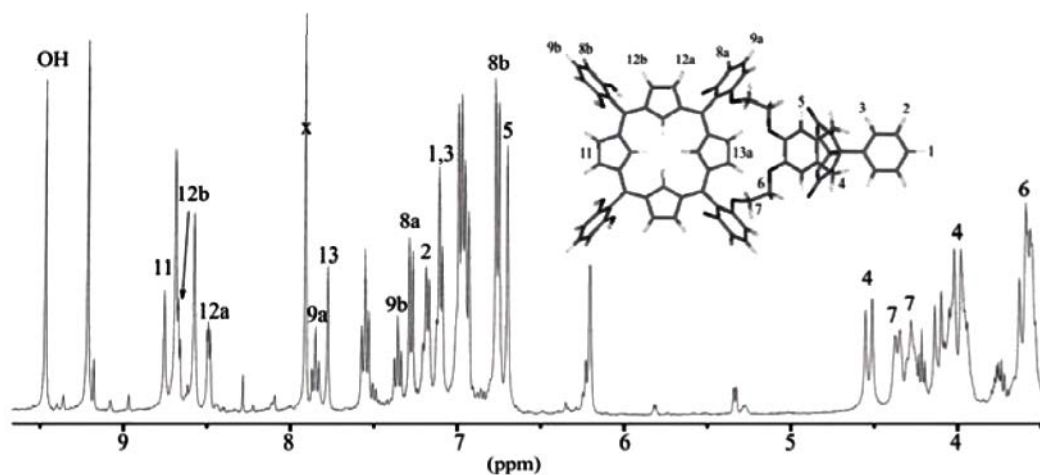


Figure S1b) *Idem*, of a mixture of tetra-hydroxy mono-cavity porphyrin isomers **I** and **II** with proton assignments for isomer **II**.

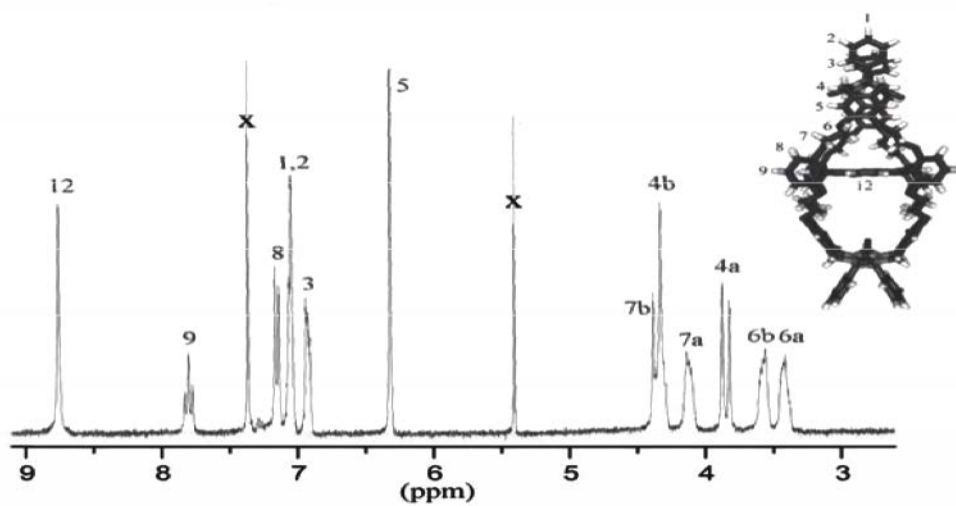


Figure S1c) *Downfield region of the $^1\text{H-NMR}$ spectrum (400.18 MHz, 298K, CDCl_3) of DC.*

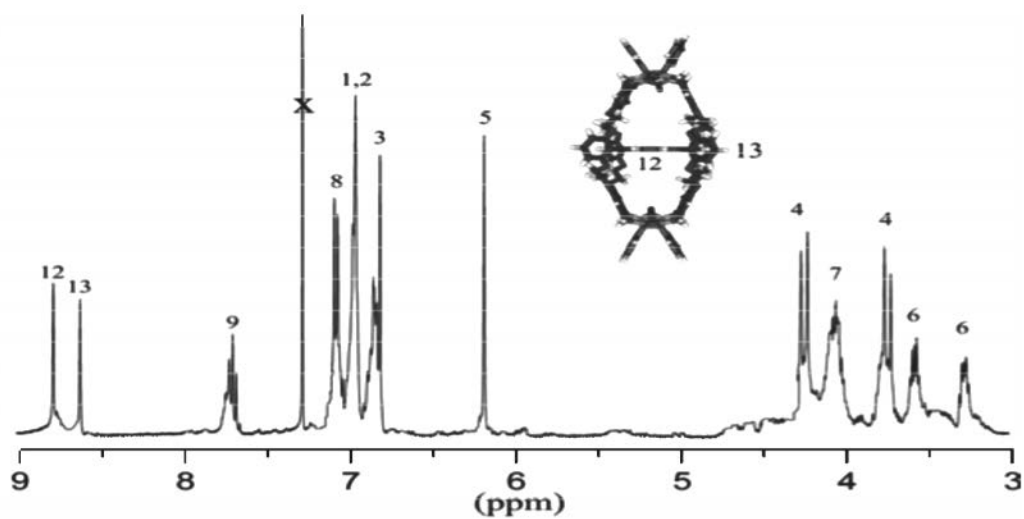


Figure S1d) *Idem*, of double-cavity porphyrin isomer **IV**. The β -pyrrole protons are designated 12 and 13.

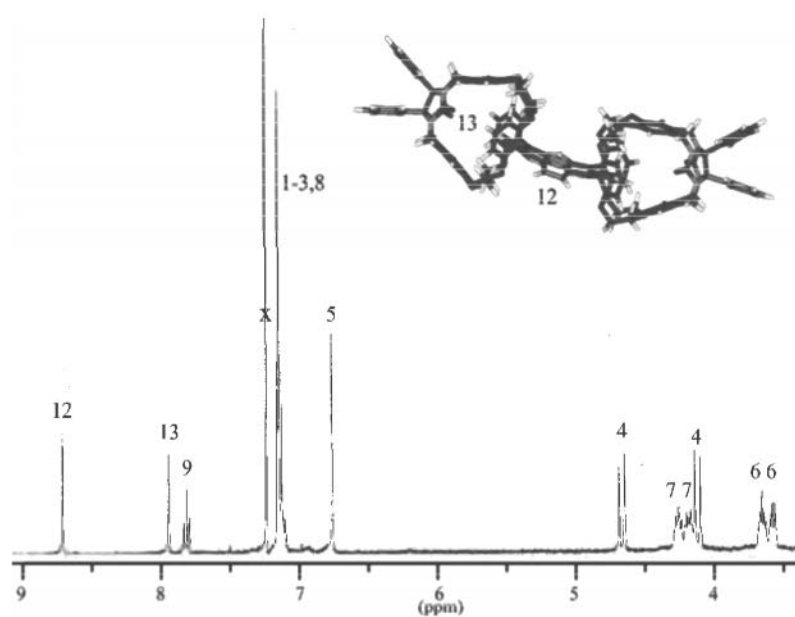


Figure S1e) *Idem*, of double-cavity porphyrin isomer **V**. The β -pyrrole protons are designated 12 and 13.

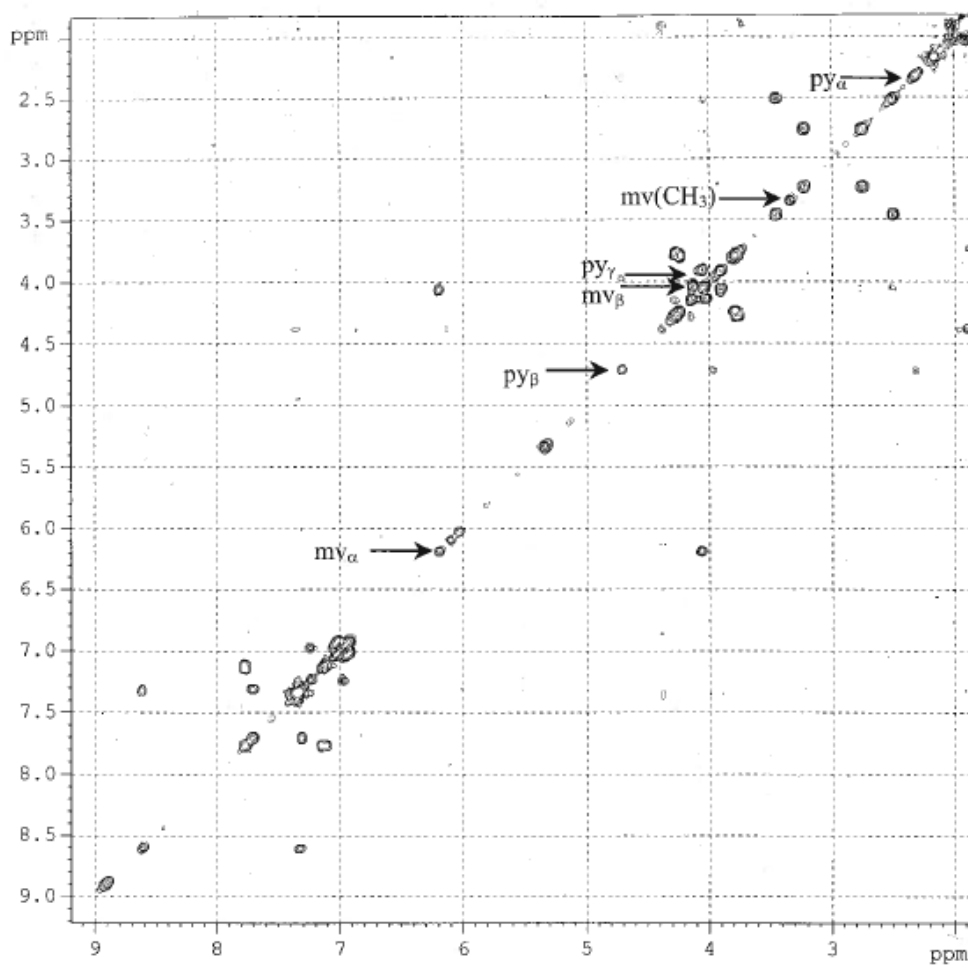


Figure S1f) COSY NMR spectrum (500 MHz, $\text{CDCl}_3/\text{CD}_3\text{CN}$ 9:1 (v/v) 298 K) of the $\text{ZnDC}:\text{V}:\text{py}$ complex.

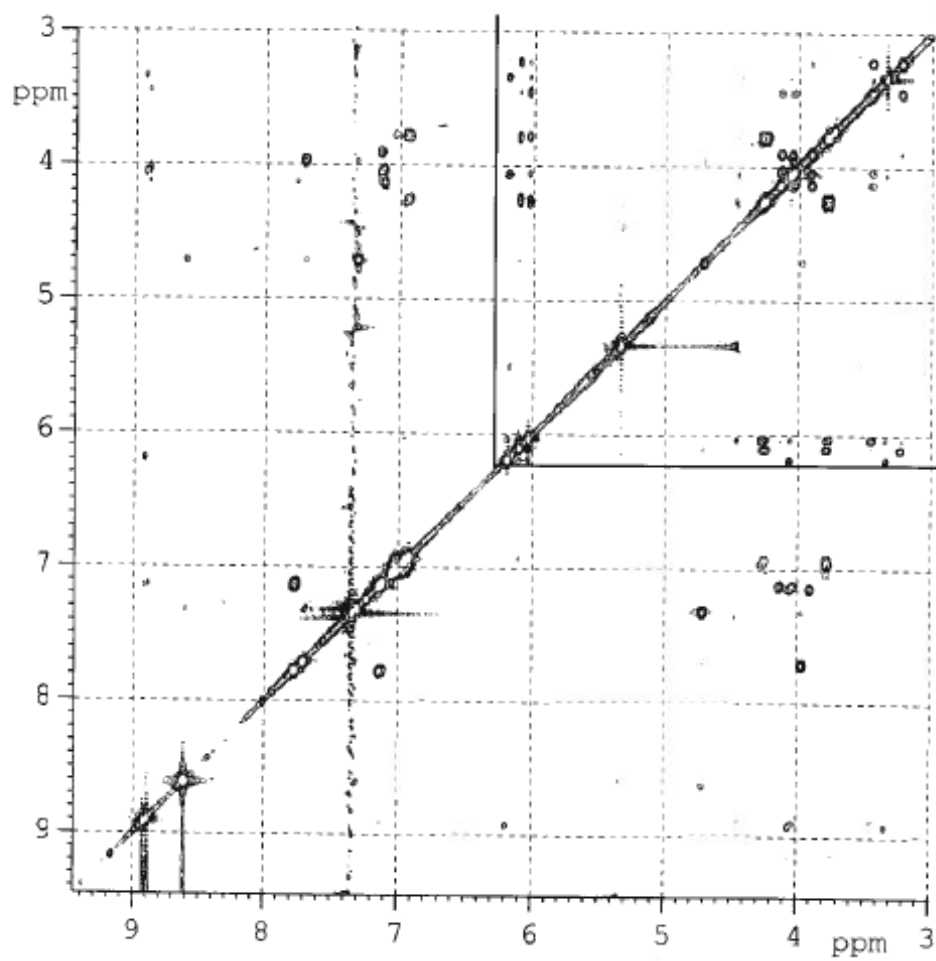


Figure S1g) 2D-NOESY NMR spectrum (500 MHz, CDCl₃/CD₃CN 9:1 (v/v) 298 K) of the ZnDC:V:py complex.

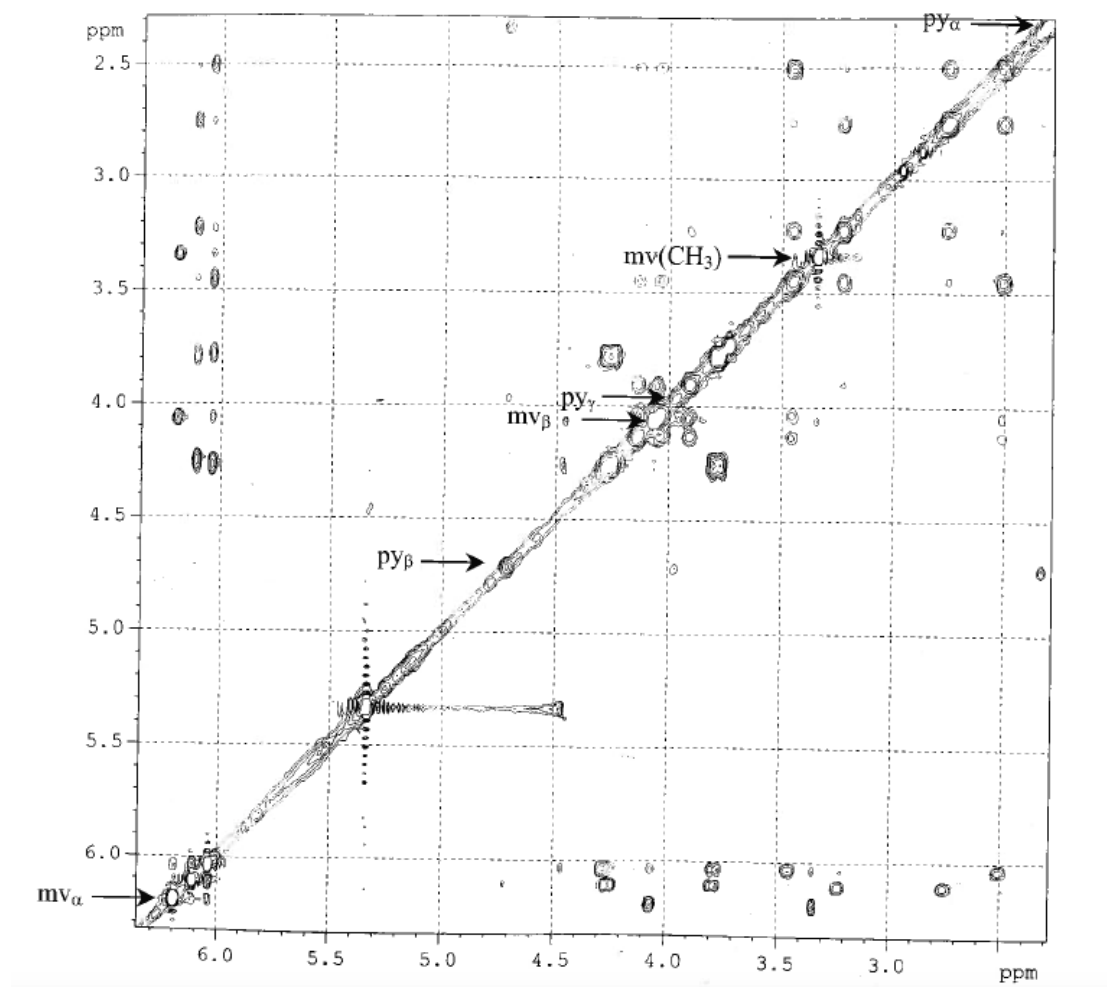


Figure S1h) COSY NMR spectrum (500 MHz, $\text{CDCl}_3/\text{CD}_3\text{CN}$ 9:1 (v/v) 298 K) of $\text{ZnDC}:\text{V}:\text{py}$ complex.