In the case of 1:2 complexation, the data were fitted according to the equations (S-2) and (S-3), and the binding constants $K_1$ and $K_2$ were calculated.

\[
\frac{\Delta A}{2} = \left[ \frac{[H][L][K_1][L] + \Delta \varepsilon_{11} K_1 K_2 [L]^2}{1 + K_1[L] - K_1 K_2 [L]^2} \right] \]

(S-2)

\[
K_1 K_2 [L]^3 + \{K_1(2K_2[H][L] - K_2[L][L] + 1)[L] + \{K_1([H][L] + [L][L]) + 1)[L] + [L][L][L] = 0 \]

(S-3)

2) UV-vis Studies.

A UV cuvette containing 1.5 mL of a solution of MnDC, MnMC or MnOMP in CH$_2$Cl$_2$ (1.0 × 10$^{-5}$ 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) $^1$H-NMR spectra of porphyrin isomers

Figure S1a) Downfield region of the $^1$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 $^1$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, CDCl$_3$/CD$_3$CN 9:1 (v/v) 298 K) of the ZnDC:V: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, CDCl₃/CD₃CN 9:1 (v/v) 298 K) of ZnDC:V:py complex.