Conformational Analysis and Binding Properties of a Cavity Containing Porphyrin Catalyst Provided with Urea Functions

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Supporting Information

1. Determination of association constants by UV/vis and fluorescence titrations

All UV/vis and fluorescence titrations were carried out in duplo. The solvents used were freshly distilled before use. To exactly 2 ml of a 1.0–2.0 μl stock solution of the porphyrin (and the co-ligand when applied) under investigation in a 1:1 (v/v) mixture of $CHCl_3$ and CH_3CN were added small amounts (25-100 μl using a micro syringe) of a stock solution containing 1.0–2.0 μl of the porphyrin (and the co-ligand, when applicable) under investigation and approximately 60 μl of guest, so that at the end at least 10–20 equivalents 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 the following equations.

The data were fitted to a simple 1:1 binding model (assuming only one binding site per molecule of porphyrin). For the UV/vis titrations, Eq. 1 was applied:

$$A = A_o - \frac{\Delta\varepsilon}{2}\left([H]_o + [G]_o + \frac{1}{K_a} - \sqrt{\left([H]_o + [G]_o + \frac{1}{K_a} \right)^2 - 4([H]_o[G]_o)} \right) \quad \textit{Eq. 1}$$

in which A is the observed absorption, A_0 is the absorption in the absence of guest and $\Delta\varepsilon$ is the difference between the two molar absorption coefficients of the two species. $[H]_0$ and $[G]_0$ are the total concentrations of the host and guest, respectively.

For the fluorescence titration experiments, Eq. 2 was used:

$$F = F_0 - \frac{\Delta F}{2[H]_o}\left([H]_o + [G]_o + \frac{1}{K_a} - \sqrt{\left([H]_o + [G]_o + \frac{1}{K_a} \right)^2 - 4([H]_o[G]_o)} \right) \quad \textit{Eq. 2}$$

in which F is the observed fluorescence, F_0 is the fluorescence in the absence of guest and $\Delta F = F_0 - F_{HG}$.

For NMR titrations, the data were fitted to Eq. 3:

$$\delta_{obs} = \delta_H - \frac{\Delta\delta}{2[H]_o}\left([H]_o + [G]_o + \frac{1}{K_a} - \sqrt{\left([H]_o + [G]_o + \frac{1}{K_a} \right)^2 - 4([H]_o[G]_o)} \right) \quad \textit{Eq. 3}$$

where δ_{obs} is the observed chemical shift of the signal under observation, δ_H is the chemical shift of the host in the absence of a ligand, and $\Delta\delta$ is the complexation induced shift of the complex relative to the host, i. e., $\delta_{HG} - \delta_H$.

In NMR experiments where the substrate V was present, most of the signals under observation had moved from the fast to the slow exchange regime. This allowed the direct determination of the concentrations of different species by integration of the signals.

2. FT-IR data for H_2UPC and ZnUPC

Table S1. *Selected FT-IR data for* ***H_2UPC*** *and* ***ZnUPC*** *both in the solid state and in solution. The values found for model compound* ***1*** *are shown as the reference.*

	Absorption (cm^{-1})					
Compound	**NH-stretch**		**Amide-I (CO-stretch)**		**Amide-II (NH-bending)**	
	dilute	*H-bonding*	*dilute*	*H-bonding*	*dilute*	*H-bonding*
ZnUPC[a]	3400	3343	– [d]	1639	– [d]	1564
H_2UPC[a]	3326	3308	– [d]	1641	– [d]	1558
1[a]	3390[c]	3304	1678[c]	1640	1542[e]	1564
ZnUPC[b]	3400	3330[e]	– [d]	1658	– [d]	1564
H_2UPC[b]	3404	3330	– [d]	1658	– [d]	1563
1[b]	3429	–	1674	–	1527	–

[a] Solid state FT-IR. [b] Solution FT-IR ($CHCl_3$, c = 1 mM). [c] Weak absorption. [d] Values not found or overlapping with absorption bands of the mono-cavity porphyrin scaffold. [e] Appearing as a shoulder.

3. UV/vis spectra

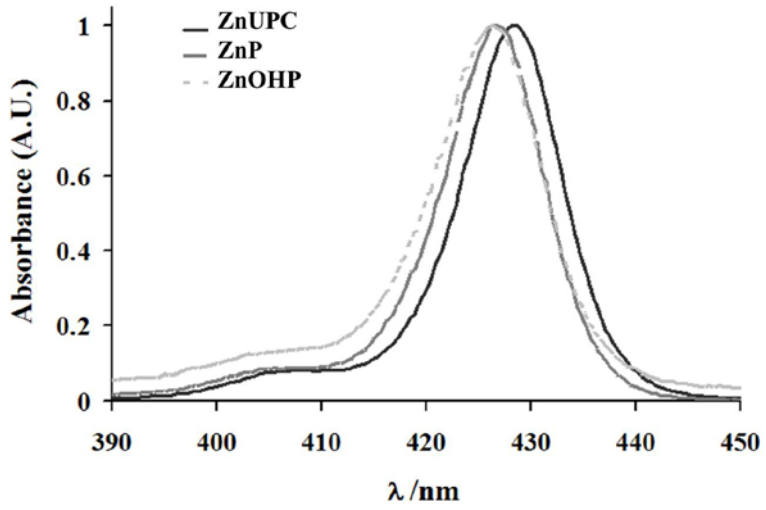

Figure S1. *Soret bands in the UV/vis absorption spectra ($CHCl_3$/CH_3CN, 1:1 v/v) of* ***ZnUPC*** *(λ_{max} at 428.5 nm),* ***ZnP****(λ_{max} at 427.5 nm), and* ***ZnOHP*** *(λ_{max} at 427.0 nm).*