

Measurement of Supramolecular Effective Molarities for Intramolecular H-bonds in Zinc Porphyrin-Imidazole Complexes

Michael A. Jinks, Hongmei Sun and Christopher A. Hunter*

Supplementary Information

Partially Bound State Populations

The population of fully bound state, P_1 , where the intramolecular H-bond is made, is given by Equation S1.

$$P_1 = \frac{4K_AEM}{1+4K_AEM} \quad (\text{S1})$$

The population of partially bound state, P_2 , where the intramolecular H-bond is not made, is given by Equation S2.

$$P_2 = \frac{1}{1+4K_AEM} \quad (\text{S2})$$

Table S1 – Occupancy of the fully bound H-bonded state (P_1) in toluene (%).

porphyrin	ligand			
	1	2	3	4
P1a	<i>nb</i>	72	<i>nb</i>	87
P2a	58	<i>nb</i>	<i>nb</i>	54
P3a	<i>nb</i>	72	<i>nb</i>	73
P4a	<i>nb</i>	<i>nb</i>	<i>nb</i>	<i>nb</i>

nb indicates complexes that do not form an intramolecular hydrogen bond.

Table S2 – Occupancy of the fully bound H-bonded state (P_1) in TCE (%).

porphyrin	ligand			
	1	2	3	4
P1a	<i>nb</i>	52	65	74
P2a	<i>nb</i>	72	<i>nb</i>	<i>nb</i>
P3a	<i>nb</i>	78	51	79
P4a	<i>nb</i>	<i>nb</i>	<i>nb</i>	<i>nb</i>

nb indicates complexes that do not form an intramolecular hydrogen bond.

Statistically-corrected equilibrium constants for formation of intramolecular H-bonds

Table S3 – K_{ref} EM values measured in toluene.^a

porphyrin	ligand			
	1	2	3	4
P1a	<i>nb</i>	0.6	<i>nb</i>	1.7
P2a	<i>nb</i>	<i>nb</i>	<i>nb</i>	0.3
P3a	<i>nb</i>	0.6	<i>nb</i>	0.7
P4a	<i>nb</i>	<i>nb</i>	<i>nb</i>	<i>nb</i>

^a Errors are $\pm 50\%$. *nb* indicates complexes that do not make detectable H-bonds.

Table S4 – K_{ref} EM values measured in TCE.^a

porphyrin	ligand			
	1	2	3	4
P1a	<i>nb</i>	0.3	0.5	0.7
P2a	<i>nb</i>	0.6	<i>nb</i>	<i>nb</i>
P3a	<i>nb</i>	0.9	0.3	0.9
P4a	<i>nb</i>	<i>nb</i>	<i>nb</i>	<i>nb</i>

^a Errors are $\pm 50\%$. *nb* indicates complexes that do not make detectable H-bonds.