SUPPLEMENTARY MATERIALS

Self-assembly of Discrete Porphyrin/Calix[4]tube Complexes Promoted by Potassium Ion Encapsulation

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Figure S1. Absorbance variation (at 271 nm) vs pH of a 20 μ M water solution (pH = 3.0) of octa-amino calix[4]tube C4T.



Figure S2. UV/vis absorption spectra of **CuTPPS** in aqueous solution at pH = 3.0 ([**CuTPPS**] ranged from 0.25 to 1 μ M).



Figure S3. UV/vis absorption spectra recorded over the course of the titration of a 2 μ M aqueous solution of **C4T** at pH 3.0 with successive aliquots of an aqueous solution of **CuTPPS** ([**CuTPPS**] ranged from 0.25 to 3.0 μ M).



Figure S4. UV/vis absorption spectra recorded over the course of the titration of a 2 μ M aqueous solution of C4T@K⁺ at pH = 3 with successive aliquots of an aqueous solution of CuTPPS ([CuTPPS] ranged from 0.25 to 4.5 μ M).



Figure S5. UV/vis absorption spectra ($\lambda_{max} = 412 \text{ nm}$) recorded over the course of the titration of a 2 µM aqueous solution of **C4T**@K⁺ at pH = 3 with: *i*) successive aliquots of an aqueous solution of **CuTPPS** ([**CuTPPS**] ranged from 0.25 to 2.5 µM) (black traces) and *ii*) successive aliquots of **CuTPPS** ([**CuTPPS**] ranged from 2.5 to 8.5 µM) after increasing the concentration of **C4T**@K⁺ to 8 µM. The inset shows the spectra of the 5:4-(**CuTPPS/C4T**@K⁺) and the 5:16-(**CuTPPS/C4T**@K⁺) assemblies (black and red traces respectively).



Figure S6.¹H NMR (DMF-*d*⁷, 298 K) of octa-nitro calix[4]tube **2**. The hashtag and the asterisks indicate the H₂O and the residual solvent peaks respectively.



Figure S7.13C NMR (DMF-d7, 298 K) of octa nitro calix[4]tube 2. Asterisks indicate the residual solvent peaks.



Figure S8.¹H NMR (DMF-*d*⁷, 298 K) of octa-amino calix[4]tube **C4T**. The hashtag and the asterisks indicate the H₂O and the residual solvent peaks respectively.



Figure S9.¹³C NMR (DMF-*d*₇, 298 K) of octa-amino calix[4]tube **C4T**. Asterisks indicate the residual solvent peaks.



Figure S10. HMQC NMR (DMF-dz, 298 K) of octa-amino calix[4]tube C4T.



Figure S11. ESI(+)-MS spectrum of the potassium complex of octa-ammonium calix[4]tube C4T@K⁺.