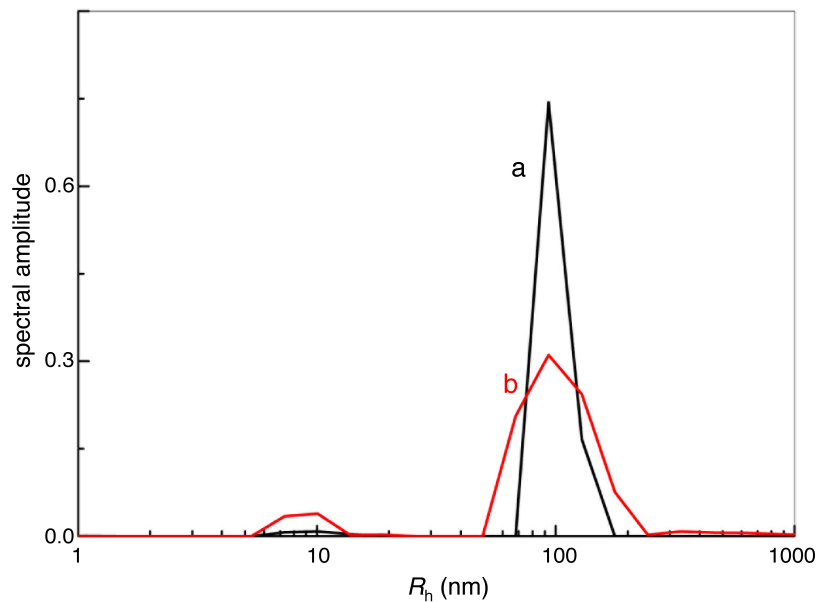# Electronic Supplementary Information

Tuning the Aggregation of an Amphiphilic Anionic Calix[5]arene by Selective Host-guest Interactions with Bola-type Dications

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Figure S1. DLS size distribution of the aggregates present in aqueous solutions of: (a) [**1**] = 0.1 mM; (b) [**1**] = 0.1 mM and [**NC₈N**] = 0.05 mM. The spectral amplitude represents the intensity-related contribution of each scatterer.
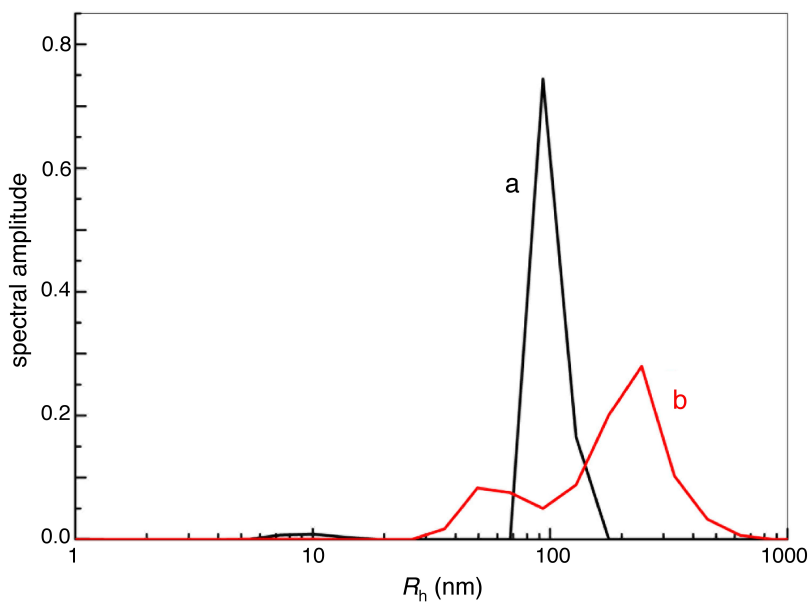

Figure S2. DLS size distribution of the aggregates present in aqueous solutions of: (a) [**1**] = 0.1 mM; (b) [1] = 0.1 mM and [**NC₁₆N**] = 0.05 mM. The spectral amplitude represents the intensity-related contribution of each scatterer.
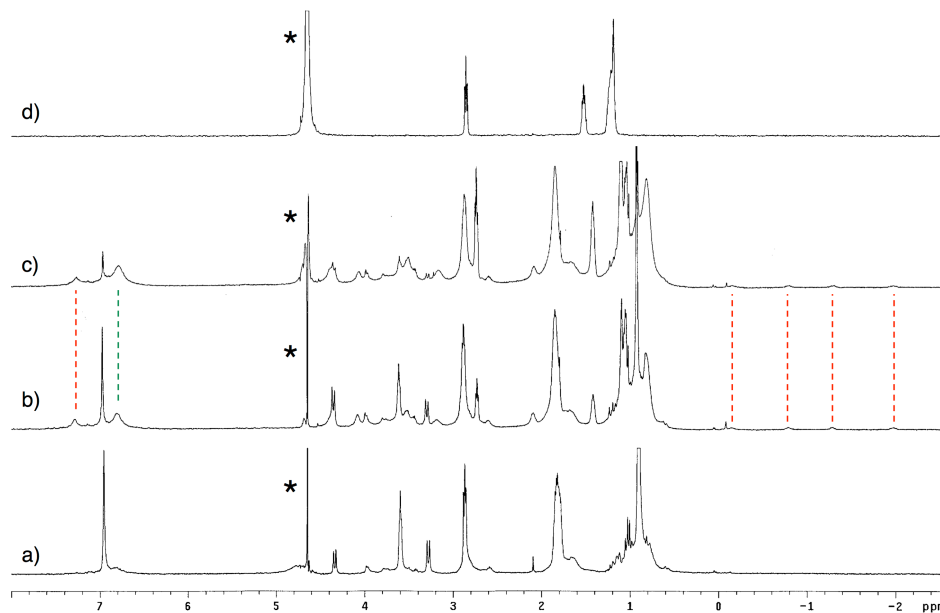
Figure S3. ¹H NMR spectra (D$_2$O, 500 MHz, 298 K) of: (a) [**1**] = 0.4 mM; (b) [**1**] = 0.4 mM and [**NC$_8$N**] = 0.2 mM; (c) [**1**] = [**NC$_8$N**] = 0.4 mM; (d) [**NC$_8$N**] = 0.4 mM. Red and green dashed lines refer to selected resonances of the type-I aggregate and the catanionic aggregate respectively. The suppressed HDO resonance is marked with an asterisk.
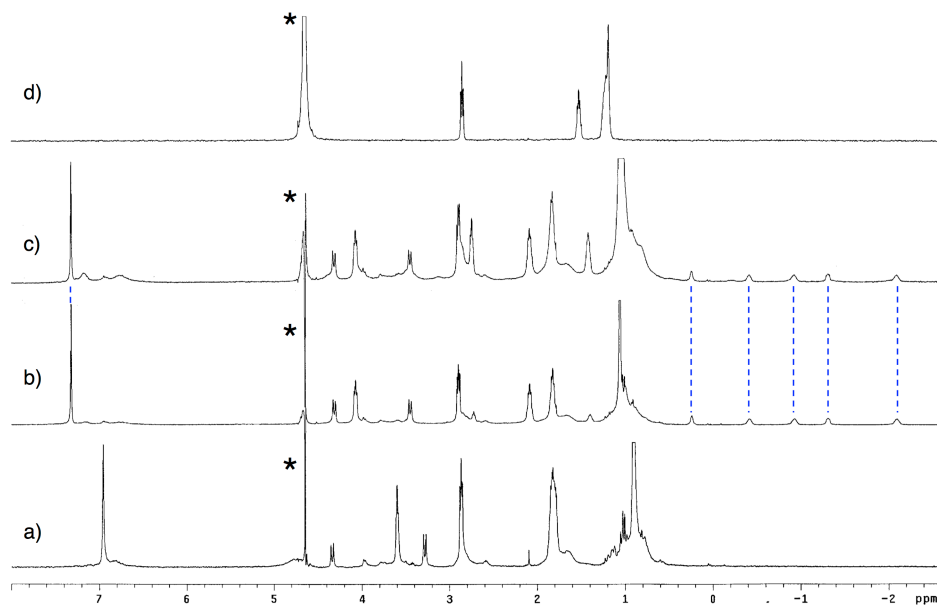
Figure S4. ¹H NMR spectra (D$_2$O, 500 MHz, 298 K) of: (a) [**1**] = 0.4 mM; (b) [**1**] = 0.4 mM and [**NC$_{10}$N**] = 0.2 mM; (c) [**1**] = [**NC$_{10}$N**] = 0.4 mM; (d) [**NC$_{10}$N**] = 0.4 mM. Blue dashed lines refer to selected resonances of the type-II complex. The suppressed HDO resonance is marked with an asterisk.
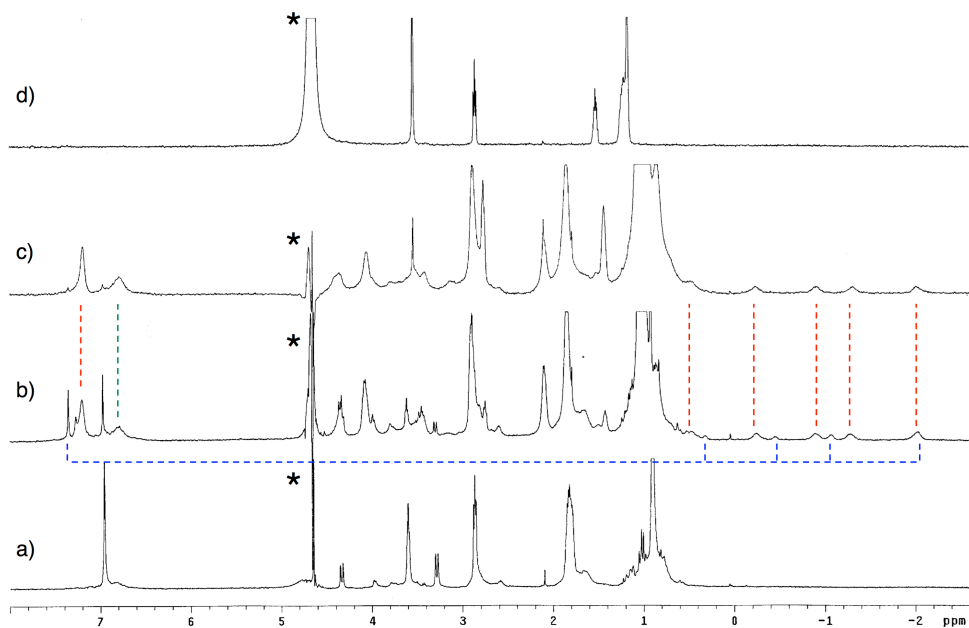
Figure S5. ^{1}H NMR spectra (D$_2$O, 500 MHz, 298 K) of: (a) [**1**] = 0.4 mM; (b) [**1**] = 0.4 mM and [**NC$_{12}$N**] = 0.2 mM; (c) [**1**] = [**NC$_{12}$N**] = 0.4 mM; (d) [**NC$_{12}$N**] = 0.4 mM. Red, blue and green dashed lines indicate selected resonances of the type-I aggregate, the type-II complex and the catanionic aggregate, respectively. The suppressed HDO resonance is marked with an asterisk.
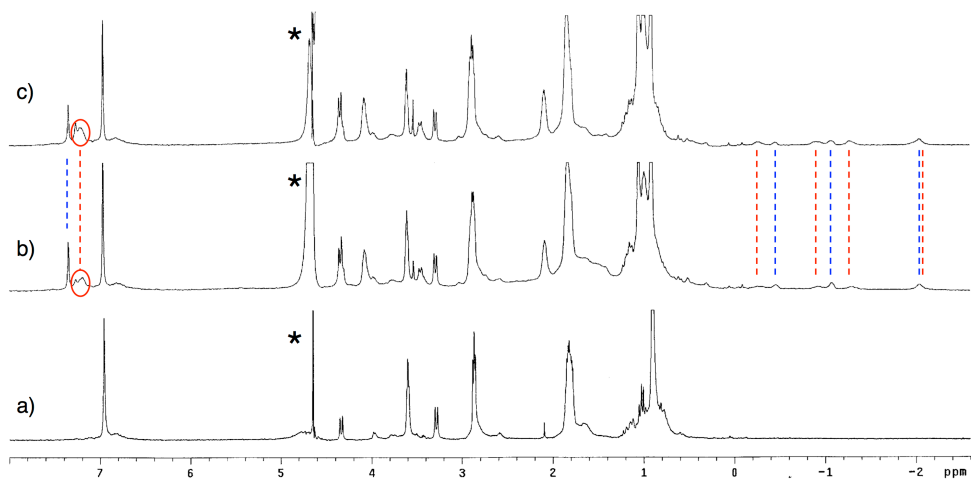
Figure S6. ^{1}H NMR spectra (D$_2$O, 500 MHz, 298 K) of: (a) [**1**] = 0.4 mM; (b) [**1**] = 0.2 mM and [**NC$_{12}$N**] = 0.05 mM; (c) [**1**] = 0.4 mM and [**NC$_{12}$N**] = 0.1 mM. Red and blue dashed lines refer to selected resonances of the type-I aggregate and the type-II complex respectively. The suppressed HDO resonance is marked with an asterisk.

Figure S7. ^{1}H NMR spectra (D$_2$O, 500 MHz, 298 K) of: (a) [**1**] = 0.4 mM; (b) [**1**] = 0.4 mM and [**NC$_{16}$N**] = 0.2 mM; (c) [**1**] = [**NC$_{16}$N**] = 0.4 mM; (d) [**NC$_{16}$N**] = 0.4 mM. Red and green dashed lines refer to selected resonances of the type-I aggregate and the catanionic aggregate respectively. The suppressed HDO resonance is marked with an asterisk.
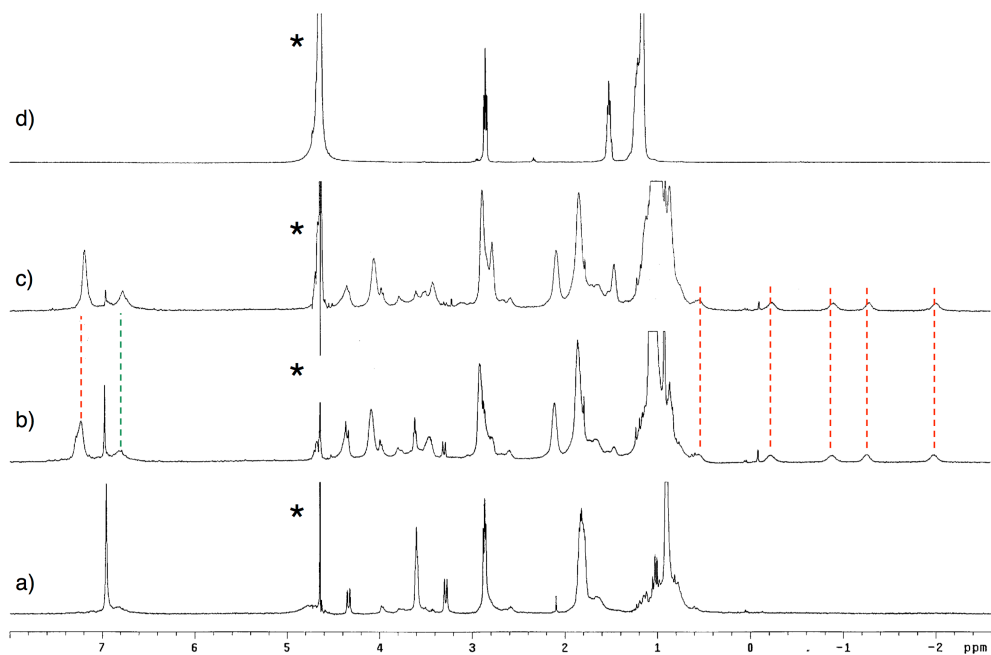
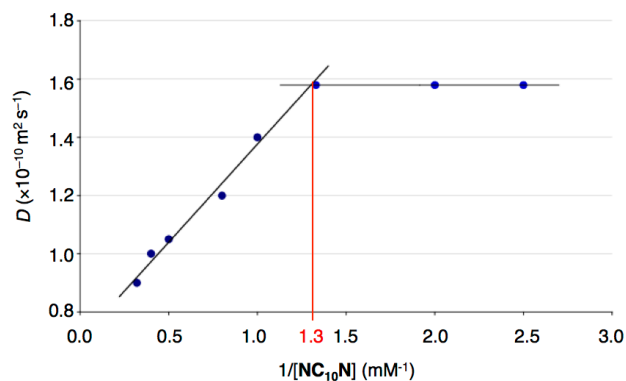**Cac determination of $NC_{10}N$/type-II bola-amphiphile.**

Self-diffusion coefficients of the type-II bola-amphiphile were determined in 2:1 **1/$NC_{10}N$** D_2O solutions with concentrations of **1** ranging from 0.4 to 6.2 mM. The weighted average of the diffusion coefficients of the monomer and the aggregates was conveniently extracted from the resonances of thiomethylene groups (δ = 2.83 ppm) that were found to be isochronous over the entire concentration range under investigation. A cac value of 0.77 mM was estimated from the intersection point of the two lines best fitting the experimental data points obtained by plotting the D_{obs} *vs* the inverse of the type-II complex concentration. The concentration of the complex is based on that of **$NC_{10}N$**, assuming that all the guest was consumed to afford the supramolecular capsule.
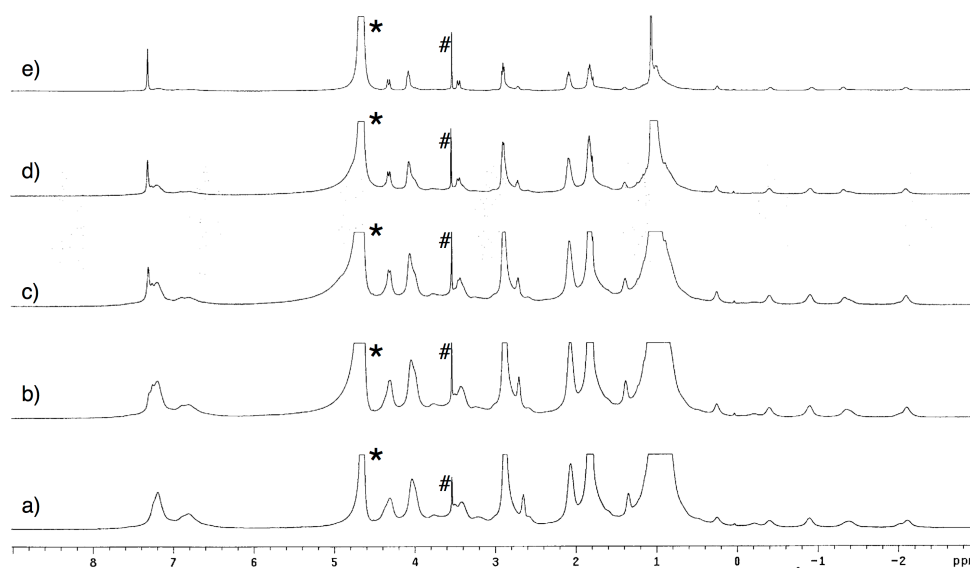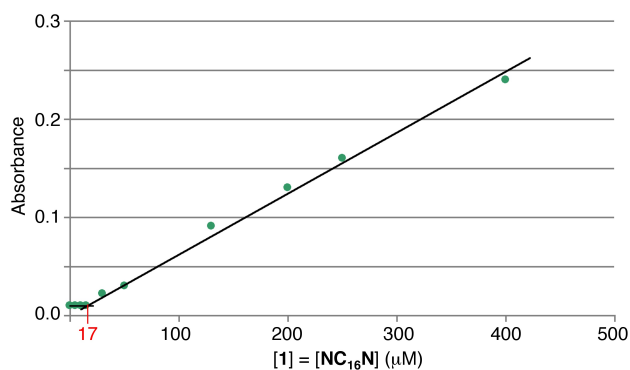

Figure S8. ^{1}H NMR spectra (D_2O, 500 MHz, 298 K) of: (a) [**1**] = 6.2 mM and [**$NC_{10}N$**] = 3.1 mM; (b) [**1**] = 4.0 mM and [**$NC_{10}N$**] = 2.0 mM; (c) [**1**] = 2.5 mM and [**$NC_{10}N$**] = 1.75 mM; (d) [**1**] = 1.0 mM and [**$NC_{10}N$**] = 0.5 mM; e) [**1**] = 0.4 mM and [**$NC_{10}N$**] = 0.2 mM. Asterisks and hashtags indicate residual solvent peaks.

Figure S9. Plot of the self-diffusion coefficients (*D*) *vs* the inverse of **NC$_{10}$N** concentration.

**Cac determination of NC$_{16}$N/type-I bola-amphiphile by dye solubilisation experiments.**

The dye solubilisation experiments were carried out by adding an excess of Sudan I (as a solid) to equimolar solutions of **1** and **NC$_{16}$N** of different concentrations ([**1**] = [**NC$_{16}$N**] = 0–400 µM). Solutions were left to equilibrate for 24 h at room temperature, filtered through a 0.4 µm Millipore filter, to remove excess undissolved dye, and their absorbance measured at λ = 485 nm. The cac of the **NC$_{16}$N/**type-I bola-amphiphile was derived from the intersection between the two lines best fitting the experimental data points of the dye Abs$_{485}$ *vs* [**1**] = [**NC$_{16}$N**] plot. The formation of **1/NC$_{16}$N** type-I aggregates was seen to start at a concentration of [**1**] = [**NC$_{16}$N**] = 17 µM.
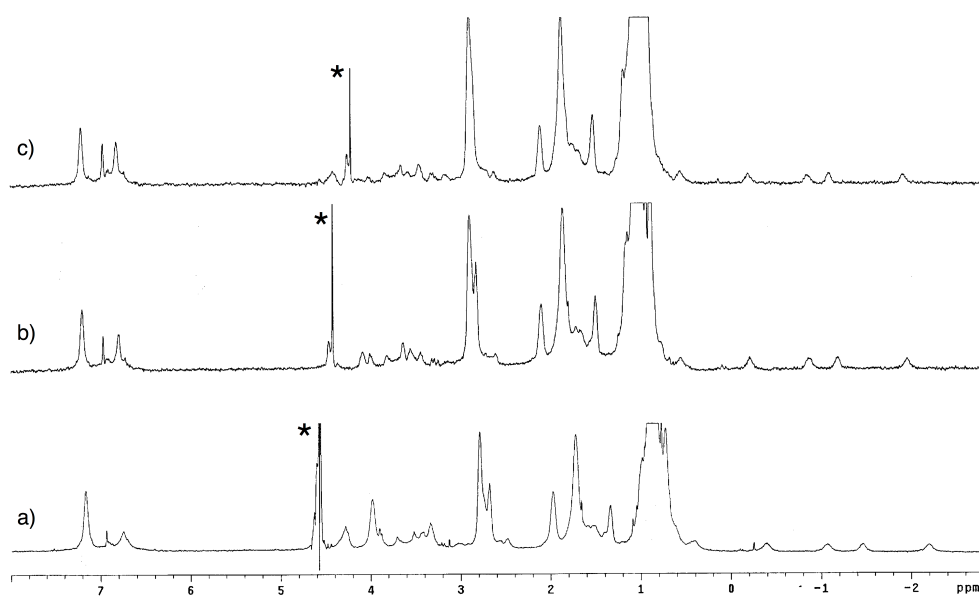

Figure S10. Sudan I absorbance variations (at 485 nm) for increasing concentrations of type-I bola-amphiphile (reported as [**1**] = [**NC$_{16}$N**]).

S8
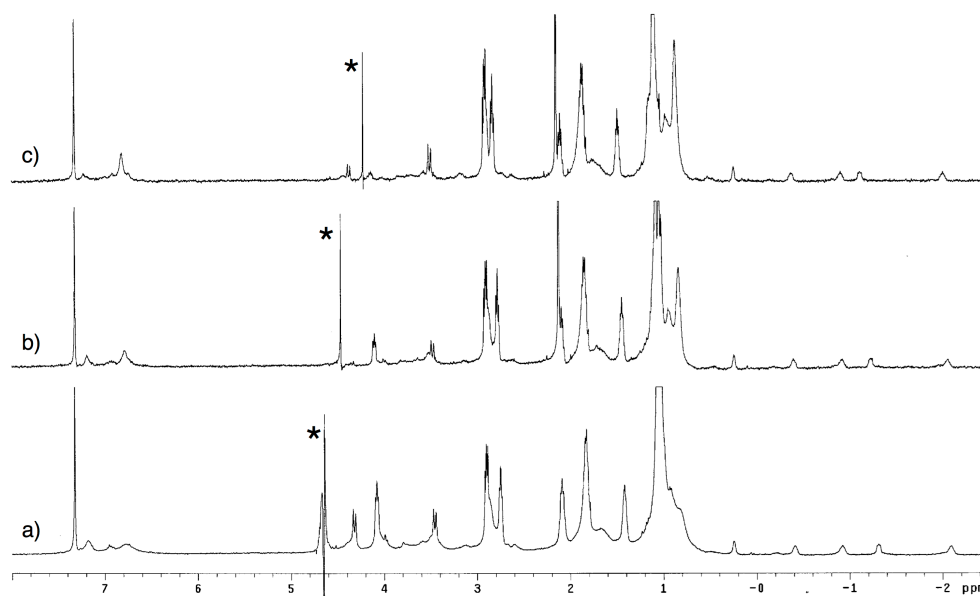
Figure S11. ^{1}H NMR spectra (D$_2$O, 500 MHz) of [**1**] = [**NC$_{10}$N**] = 0.4 mM at: (a) T = 298 K, (b) T = 318 K and (c) T = 348 K. The suppressed HDO resonance is marked with an asterisk.

Figure S12. ^{1}H NMR spectra (D$_2$O, 500 MHz) of [**1**] = [**NC$_{16}$N**] = 0.4 mM at: (a) T = 298 K, (b) T = 318 K and (c) T = 348 K. The suppressed HDO resonance is marked with an asterisk.

**Tamoxifen solubilisation experiments.**

Solid tamoxifen (1 μmol) was added to a 0.4 mM solution of **1** and **NC$_{16}$N** (1:1) in ultrapure H$_2$O (1.0 mL). After equilibration for 24 h at room temperature in the dark, the solution was centrifugated (6000 rpm) for 10 minutes to remove undissolved solid. 900 μL of the supernatant were extracted with 900 μL of CHCl$_3$ in a screw-top vial for 12 h at 20 °C. The organic phase was diluited 10 times prior to UV analysis. The solubilization experiment was performed in triplicate and the amount of the extracted tamoxifen (140±3 μg) was determined from the absorbance value at λ = 275 nm.

200 μL of CDCl$_3$ were added to 300 μL of the tamoxifen chloroformic solution and the concentration of recovered tamoxifen was determined from the integral of selected peaks by using the quantitative qNMR Varian Vnmrj 3.2 software.
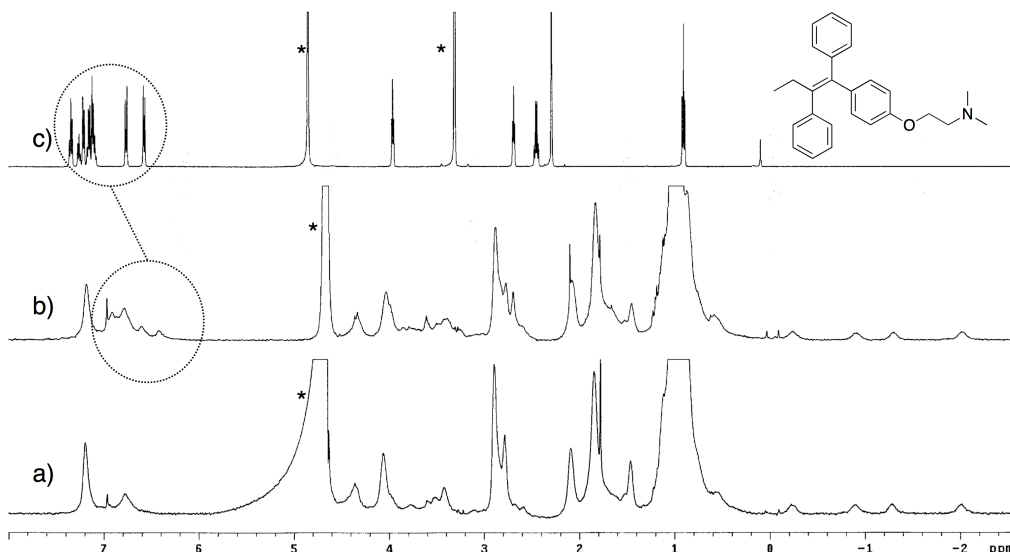
Figure S13. ^{1}H NMR spectra (500 MHz, 298 K) of a D$_2$O solution of [**1**] = [**NC$_{16}$N**] = 0.4 mM (a) prior to and (b) after exctraction of tamoxifen; (c) tamoxifen in CD$_3$OD.