

## **Supporting Information**

### **The Self-assembly of Resorcin[4]arene in the Presence of Small Alkylammonium Guests in Solution**

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## Experimental Section

*General:* NMR diffusion measurements were performed on a 400 MHz Avance Bruker NMR spectrometer equipped with a Great1 gradient system capable of producing magnetic field pulse gradients in the z-direction of about 50 G cm<sup>-1</sup>. All experiments were carried out using a 5mm inverse probe. All measurements were performed at least three times and the reported diffusion coefficients are the mean  $\pm$  standard deviation of three experiments. Only data where the correlation coefficients of  $\ln(I/I_0)$  versus  $\gamma^2 \delta^2 g^2 (\Delta - \delta/3)$  were higher than 0.999 are reported. The measurements were all performed at 298.0 K. All diffusion measurements were performed in a 4 mm NMR tube inserted in a 5 mm NMR tube.

*Materials:* All starting materials, guest molecules, reagents and CDCl<sub>3</sub> were purchased from Aldrich (USA) and were used as supplied, without further purification. Compounds **1a** and **1b** were prepared according to the procedure previously published (Tunstad, L. M.; Tucker, J. A.; Dalcanale, E.; Weiser, J.; Bryant, J. A.; Sherman, J. C.; Helgeson, R. C.; Knobler, C. B.; Cram, D. J. *J. Org. Chem.* **1989**, *54*, 1305-1312.). See also Avram L.; Cohen Y. *J. Am Chem. Soc.* **2004**, *126*, 11556-11563. Compounds **1a** and **1b** were obtained as yellowish solids and the yields were typically between 70 to 80%.

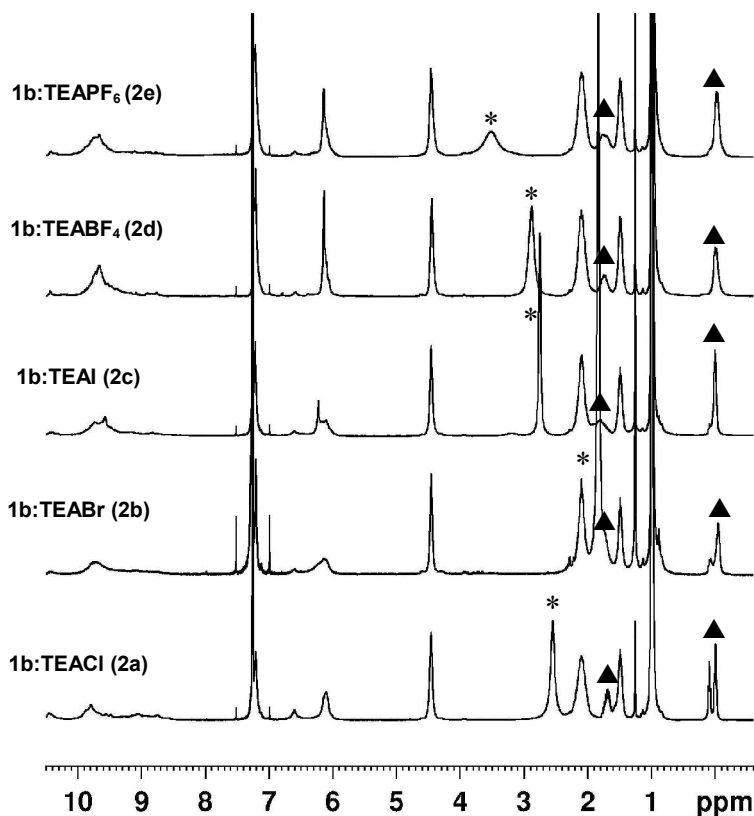
The <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic parameters of the obtained hexameric capsules in CDCl<sub>3</sub> solutions are given below.

<sup>1</sup>H-NMR of [(**1a**)<sub>6</sub>(H<sub>2</sub>O)<sub>8</sub>] (400 MHz, CDCl<sub>3</sub>, 25°C, 65 mM):  $\delta$ = 9.52 (OH, broad, 48H), 7.21 (s, 24H), 6.12 (s, 24H), 4.30 (t, J=7.0Hz, 24H), 2.22 (broad, 48H), 1.27 (m, 432H), 0.88 (t, J=6.7Hz, 72H).

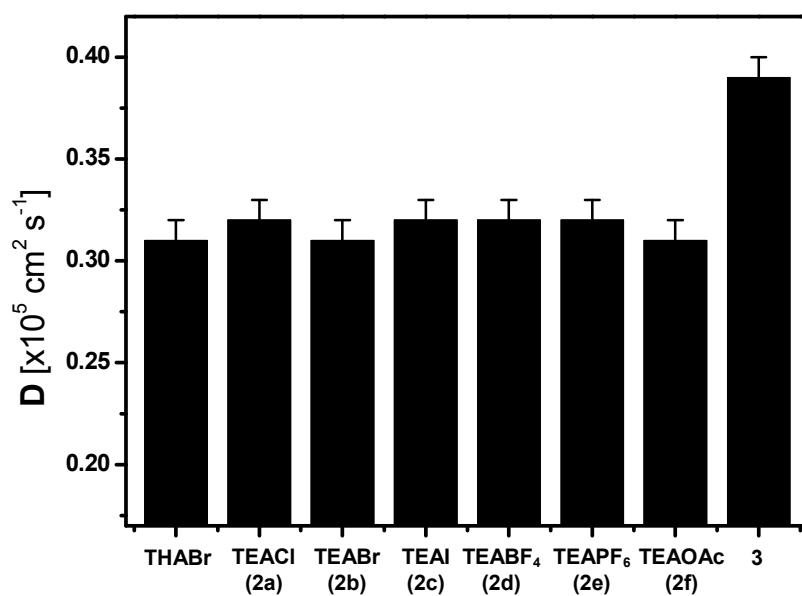
<sup>13</sup>C {<sup>1</sup>H}-NMR of [(**1a**)<sub>6</sub>(H<sub>2</sub>O)<sub>8</sub>] (100 MHz, CDCl<sub>3</sub>, 25°C, 65 mM):  $\delta$ =151.3, 151.0, 125.5, 124.5, 103.5, 103.3, 34.0, 33.8, 32.6, 30.5, 30.4, 30.4, 30.4, 30.3, 30.1, 28.8, 23.4, 14.8 ppm.

<sup>1</sup>H-NMR of [(**1b**)<sub>6</sub>(H<sub>2</sub>O)<sub>8</sub>] (400 MHz, CDCl<sub>3</sub>, 25°C, 20 mM):  $\delta$ = 9.52 (OH, broad, 48H), 7.20 (s, 24H), 6.14 (s, 24H), 4.44 (t, J=7.4Hz, 24H), 2.09 (m, 48H), 1.49 (m, 24H), 0.98 (t, J=6.2Hz, 144H).

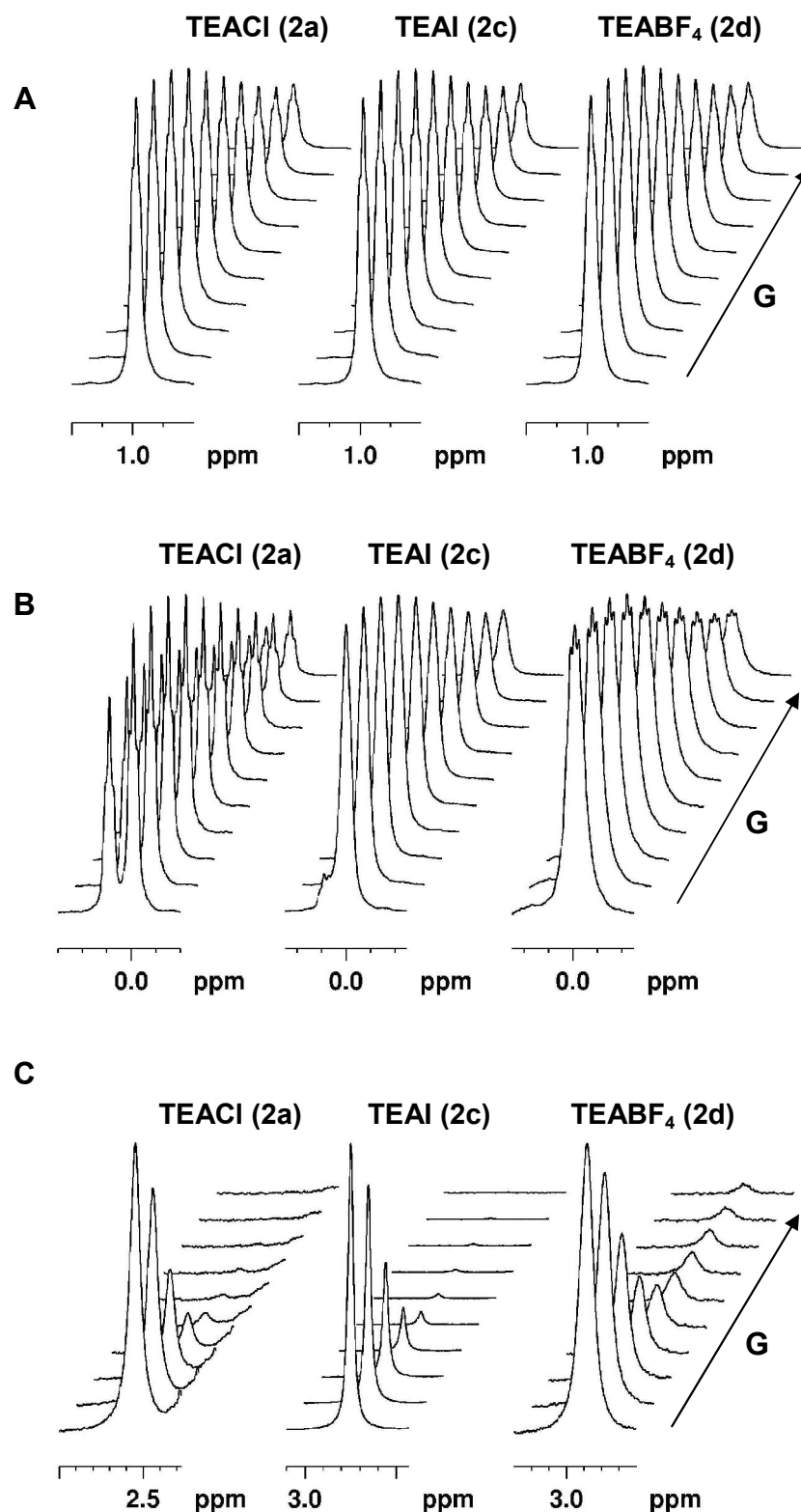
$^{13}\text{C}$   $\{^1\text{H}\}$ -NMR of  $[(\mathbf{1b})_6(\text{H}_2\text{O})_8]$  (100 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ , 20 mM):  $\delta=151.3, 151.0, 125.60, 125.5, 124.9, 103.6, 42.8, 31.6, 26.8, 23.6, 23.4$  ppm.



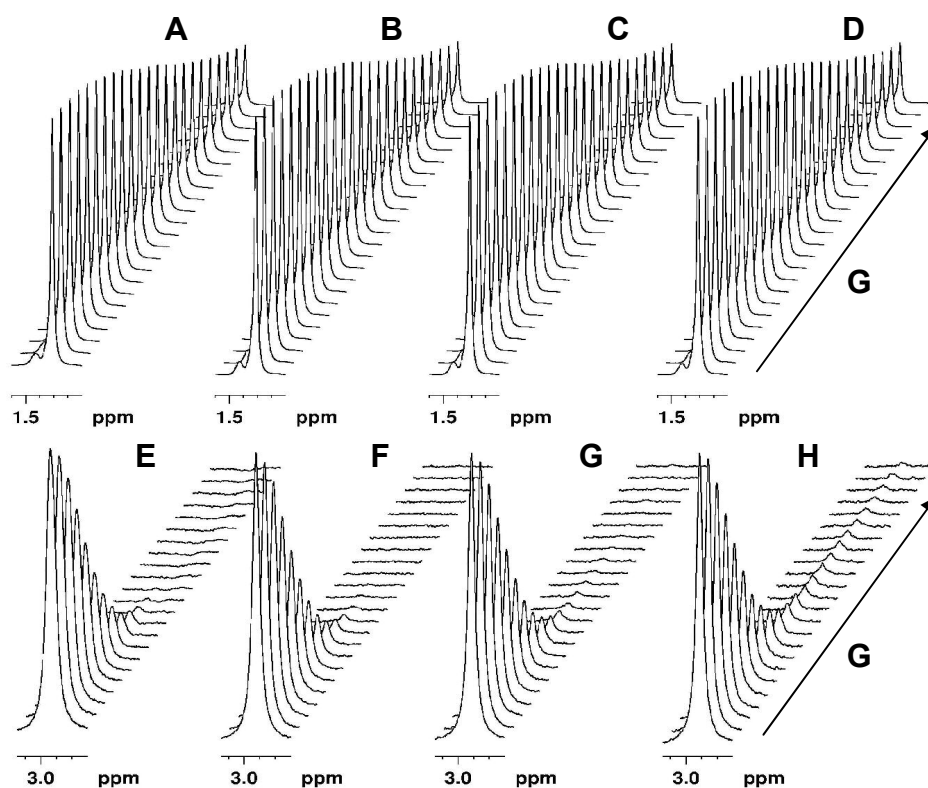
**Figure S-1:**  $^1\text{H}$  NMR spectra (400 MHz, 298 K) of  $\mathbf{1b}$  in  $\text{CDCl}_3$  in the presence of different tetraethylammonium salts ( $\mathbf{2a-e}$ ). The \* symbol indicates the water peak and  $\blacktriangle$  indicates the peaks of the encapsulated salts.



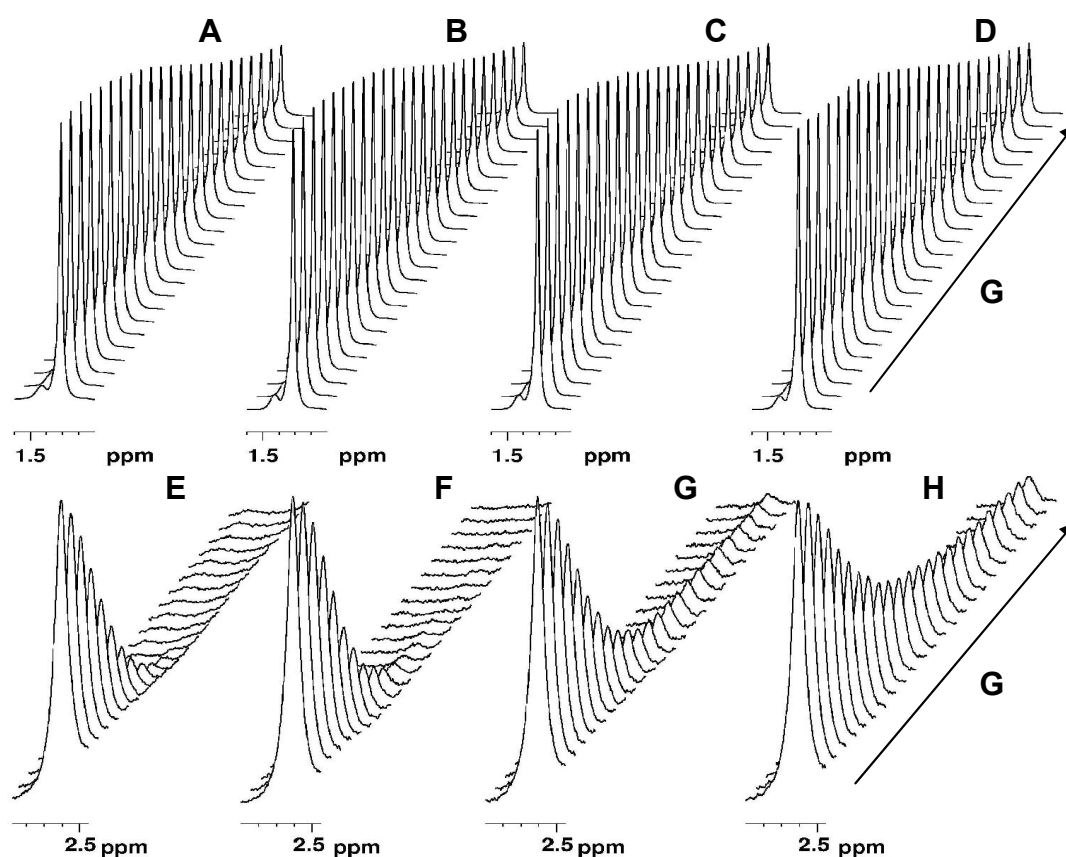
**Figure S-2:** The diffusion coefficients of the peaks of different encapsulated ammonium salts encapsulated in **1b** and biscalix[5]arene (**3**). Compound **3** has a molecular weight of  $2398 \text{ g mol}^{-1}$ , which is much higher than the molecular weight of the dimer of **1b** ( $1424 \text{ g mol}^{-1}$ ).



**Figure S-3:**  $^1\text{H}$  NMR signal decay as a function of the gradient strength ( $G$ ) (400 MHz, 298 K) of one of the peaks of **1b** (A), encapsulated salt (B) and water (C) in a  $\text{CDCl}_3$  solution with the following salts: TEACl (**2a**), TEAI (**2c**) and TEABF<sub>4</sub> (**2d**), as extracted from the LED sequence with a  $t_e$  of 50 ms.



**Figure S-4:**  $^1\text{H}$  NMR signal decay as a function of the gradient strength ( $G$ ) (400 MHz, 298 K) of one of the peaks of **1a** (A-D) and of water (E-H) in a  $\text{CDCl}_3$  solution of **1a** with TEACl (**2a**) as extracted from the (A and E) PGSTE diffusion sequence and the LED sequence with the following  $t_e$ s: (B and F) 5 ms, (C and G) 50 ms, and (D and H) 150 ms.



**Figure S-5:**  $^1\text{H}$  NMR signal decay as a function of the gradient strength ( $G$ ) (400 MHz, 298 K) of one of the peaks of **1a** (A-D) and of water (E-H) in a  $\text{CDCl}_3$  solution of **1a** with  $\text{TEABF}_4$  (**2d**) as extracted from the (A and E) PGSTE diffusion sequence and the LED sequence with the following  $t_e$ s: (B and F) 5 ms, (C and G) 50 ms, and (D and H) 150 ms.