Supplementary Material (ESI) for Chemical Communications

Encapsulation of Oligoethylene Glycols and Perfluoro-*n*-alkanes in a Cylindrical Host Molecules

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Supplementary Information

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I. Experimental Procedures

General Methods

Cylindrical capsule half **1** was synthesized as previously reported by our group. Mesitylene-d_{12} was purchased from Cambridge Isotope Laboratories, Andover, MA and used without further purification. Triethylene glycol, triethylene glycol monomethyl ether, and pentaethylene glycol were purchased from Aldrich, St. Louis, MO and used without further purification. Triethylene glycol dimethyl ether, tetraethylene glycol, tetraethylene glycol monomethyl ether, and tetraethylene glycol dimethyl ether were purchased from Acros, Fairlawn, NJ and used without further purification. All perfluoro-*n*-alkanes were purchased from Lancaster, Windham, NH and used without further purification except perfluorodecyl iodide which was purchased from Daikin, Orangeburg, NY and used without further purification. All *n*-alkanes were purchased from Aldrich and used without further purification.

^{1}H NMR spectra were recorded using a Bruker DRX-600 at 600 MHz at 300 K. ^{19}F spectra were recorded on the same instrument at 565 MHz at 300 K.

NMR Sample Preparation

NMR samples were prepared at 1.1 mM in dimeric capsule $\mathbf{1}_2$ in mesitylene-d_{12}. Guest molecules were typically at a concentration of 22 mM in the same solution. Competitive binding experiments were carried out using two different guests at relative concentrations which were experimentally determined to give a ratio of encapsulated species that could be accurately measured by integration of the NMR spectrum. Samples were maintained at room temperature or at 50 °C and spectra were taken periodically to ensure equilibrium was reached. The two temperatures did not result in equilibria that were significantly different.

II. NMR Spectra – Oligoethylene Glycol Encapsulation

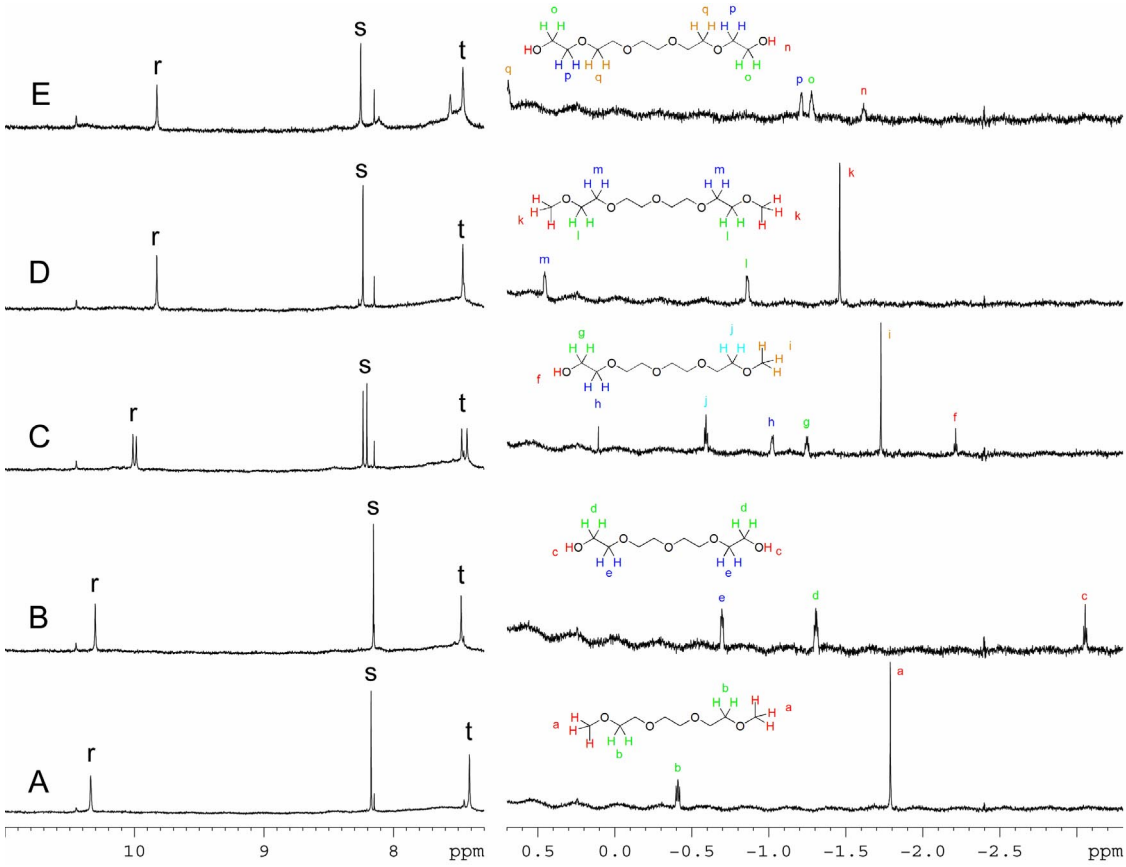

Figure S1. ^{1}H NMR spectra of oligoethylene glycols encapsulated in cylindrical capsule $\mathbf{1}_2$. (A) triethylene glycol dimethyl ether; (B) tetraethylene glycol; (C) tetraethylene glycol monomethyl ether; (D) tetraethylene glycol dimethyl ether; (E) pentaethylene glycol. Assigned chemical shifts of encapsulated oligoethylene glycols are shown in the upfield region of the spectrum. Unassigned hydrogens of oligoethylene glycol guests are buried in the 0.7 to 2.7 ppm window (not shown) which contains the signals of the undecyl R groups of **1** (Figure 1). The remaining signals correspond to (r) imide N*H* of **1**; (s) and (t) aryl C*H*'s of **1**. The signals of $\mathbf{1}_2$ are split in (C) because encapsulation of this guest makes the capsule asymmetrical.

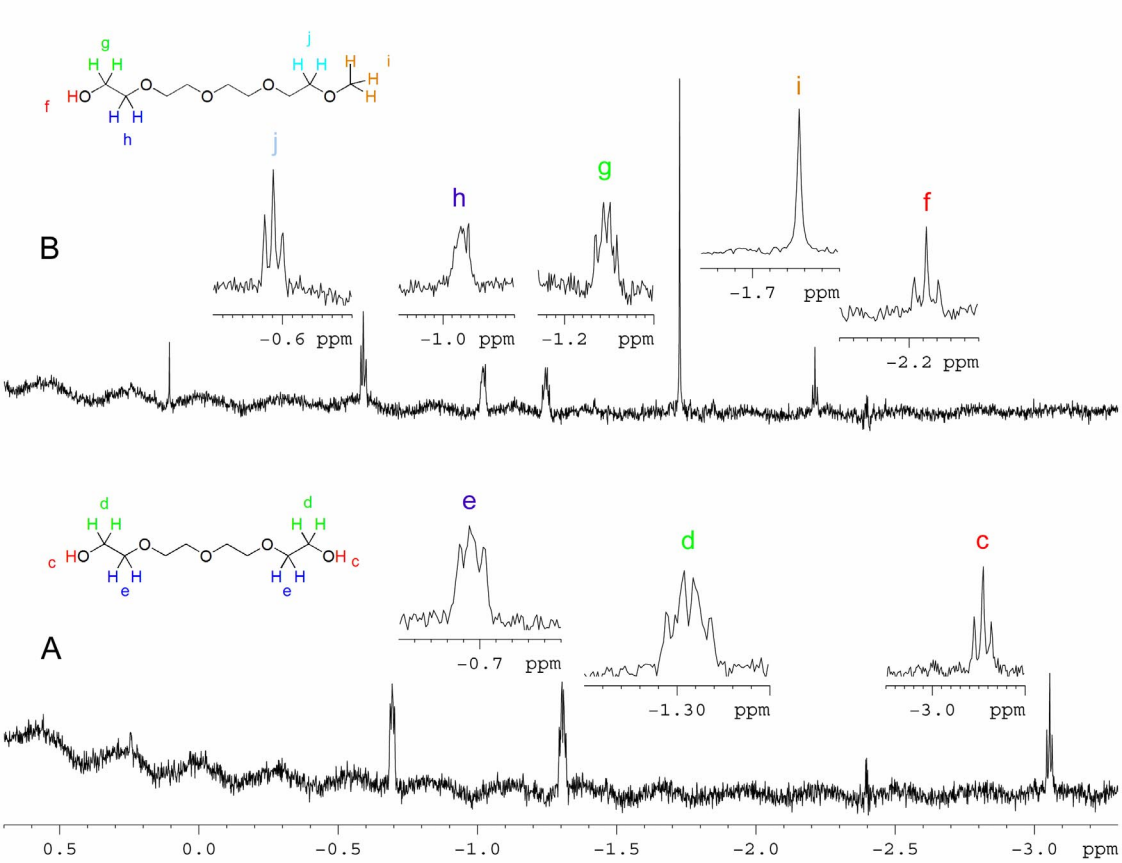

Figure S2. Upfield window of ^{1}H NMR spectra of (A) tetraethylene glycol and (B) tetraethylene glycol monomethyl ether encapsulated in cylindrical capsule $\mathbf{1}_2$. Hydroxyl hydrogens c and f show strong coupling to adjacent methylene hydrogens d and g respectively ($^{3}J_{c\text{-}d}$ = 6 Hz; $^{3}J_{f\text{-}g}$ = 5 Hz).

III. NMR Spectra – Perfluoro-*n*-alkane Encapsulation

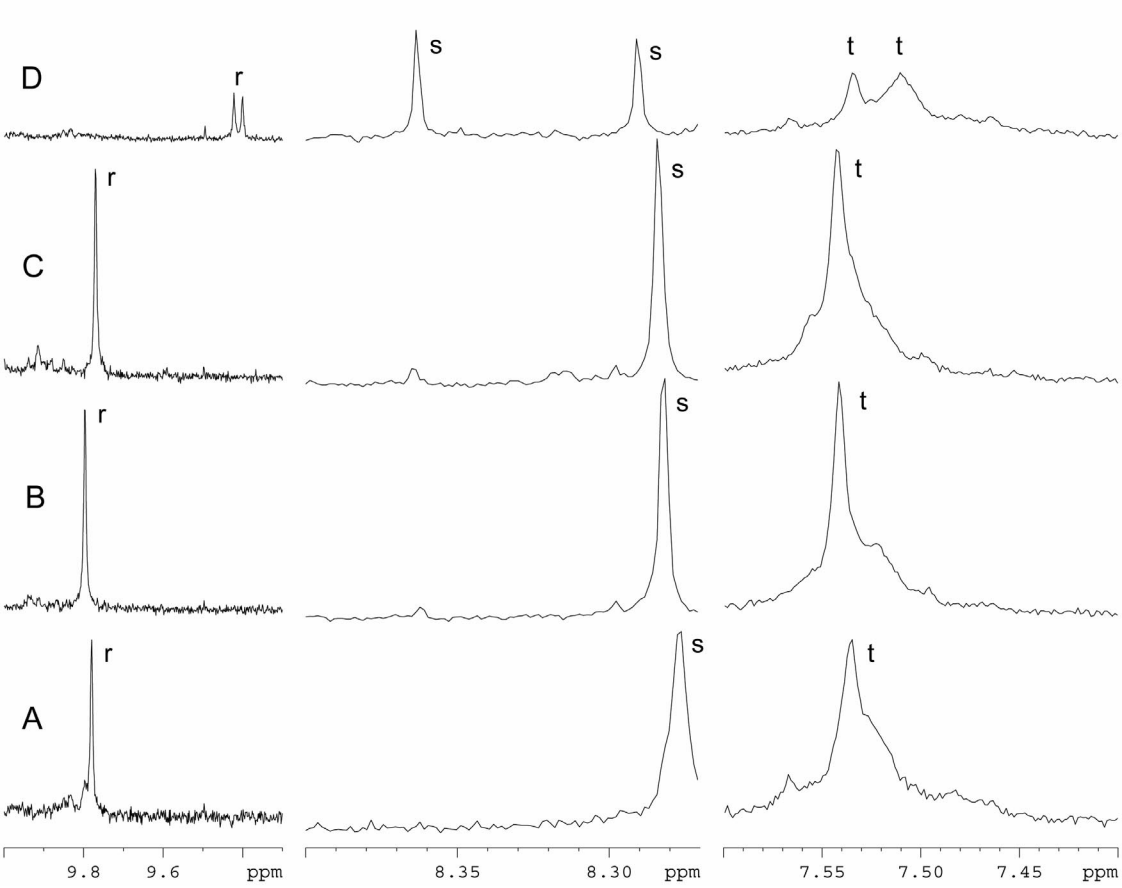

Figure S3. Upfield windows of the ^{1}H NMR spectra of perfluoro-*n*-alkanes encapsulated in cylindrical capsule $\mathbf{1}_2$. (A) perfluoro-*n*-heptane; (B) perfluoro-*n*-octane; (C) perfluoro-*n*-nonane; (D) perfluorodecyl iodide. Peak labels r, s, and t are the same as in Figure S1. Spectra (A), (B), and (C) are nearly identical with only small chemical shift differences observed. The peaks are, however, sufficiently resolved in competitive binding experiments to integrate separately and thus determine the ratio of host-guest complexes present. Spectrum (D) shows an asymmetrical capsule; c.f. spectrum (C) in Figure S1.

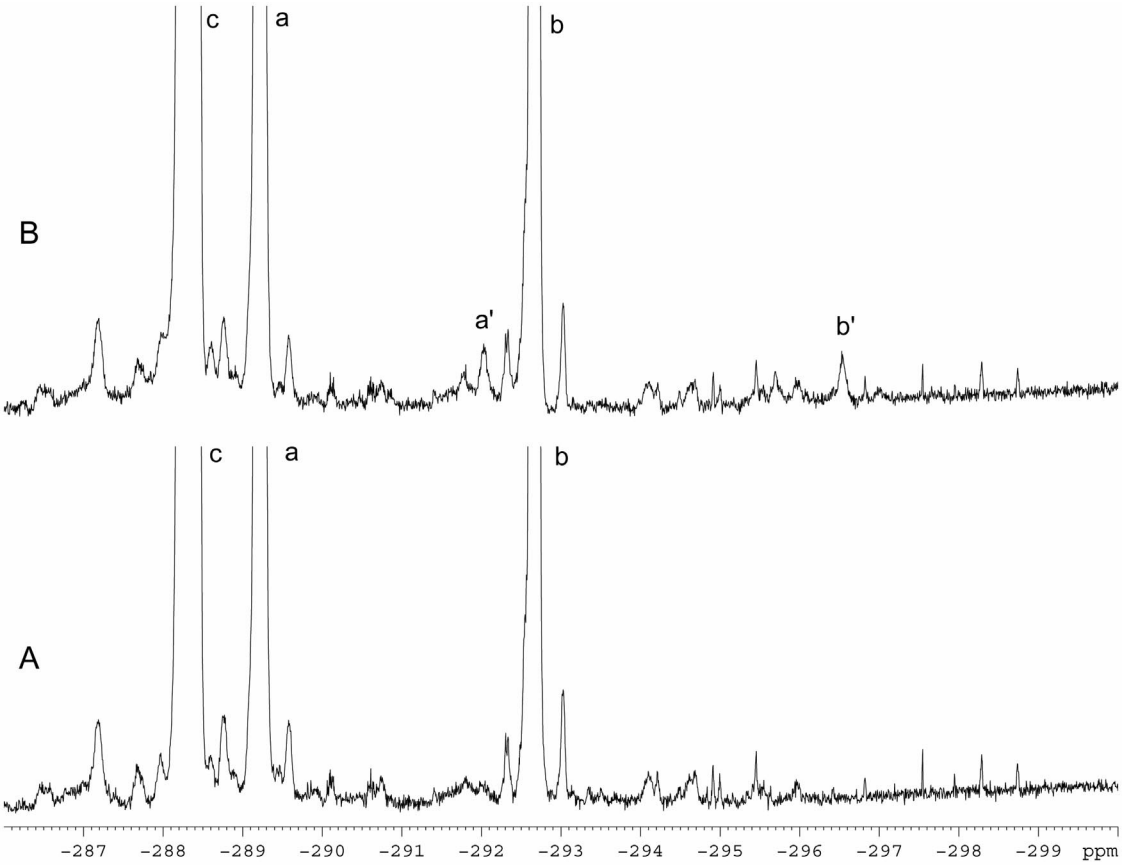

Figure S4. (A) A window of the ^{19}F spectrum of a saturated solution of perfluoro-*n*-nonane in mesitylene-d_{12} (approximately 20 mM). (B) Identical sample plus 1 mM cylindrical capsule $\mathbf{1}_2$. New signals **a′** and **b′** likely corresponding to encapsulated perfluoro-*n*-nonane. The many minor impurities are branched isomers of the perfluoro-*n*-alkane.

IV. Competitive Binding Experiments

Competitive binding experiments were carried out to measure the equilibrium constant of reactions of the form

$$\mathrm{A}\cdot\mathbf{1}_2 \;+\; \mathrm{B} \;\overset{K_{\mathrm{rel}}}{\rightleftharpoons}\; \mathrm{B}\cdot\mathbf{1}_2 \;+\; \mathrm{A} \qquad (1)$$

where A and B represent guest molecules which compete to occupy host $\mathbf{1}_2$ and $\mathrm{A}\cdot\mathbf{1}_2$ and $\mathrm{B}\cdot\mathbf{1}_2$ represent the respective host-guest complexes. Samples were prepared as described in Experimental Procedures. In typical results, the total concentration of encapsulated species was small compared to the concentration of free guest molecules and the equilibrium constant K_{rel} could be expressed in simplified form:

$$K_{\mathrm{rel}} = \frac{\int \mathrm{B}\cdot 1_2}{\int \mathrm{A}\cdot 1_2} \bullet \frac{[\mathrm{A}]_{\mathrm{init.}}}{[\mathrm{B}]_{\mathrm{init.}}} \qquad (2)$$

where $\frac{\int \mathrm{B}\cdot 1_2}{\int \mathrm{A}\cdot 1_2}$ represents the integral ratio of $\mathrm{B}\cdot\mathbf{1}_2$ to $\mathrm{A}\cdot\mathbf{1}_2$ as determined from the ^{1}H spectrum.

All observable resolved peaks were compared for the two species and an average integral ratio was calculated.

All experiments were done at least in duplicate and were reproducible. Data is summarized in Table 1. A sample spectrum is shown in Figure S5.

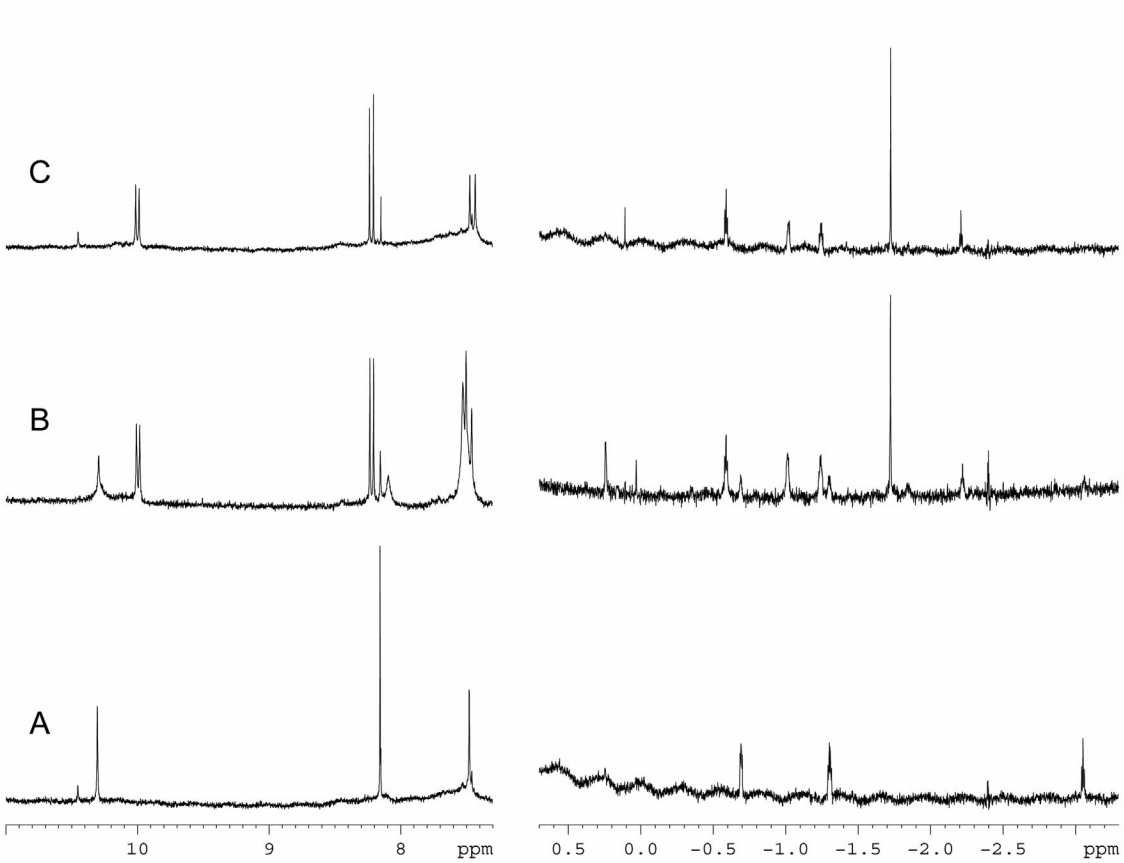

Figure S5. Sample competitive binding experiment spectra. (A) Tetraethylene glycol encapsulated in $\mathbf{1}_2$. (C) Tetraethylene glycol monomethyl ether encapsulated in $\mathbf{1}_2$. (B) Mixture of tetraethylene glycol (22 mM) and tetraethylene glycol monomethyl ether (22 mM) in competition to occupy $\mathbf{1}_2$. Tetraethylene glycol monomethyl ether is the better guest; $K_{rel} = 2.9$.

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V. References

1. T. Heinz, D. M. Rudkevich, J. Rebek, Jr. *Nature* **1998**, *394*, 764.