Supplementary Material

Guest-controlled Self-Sorting in Assemblies driven by the Hydrophobic Effect

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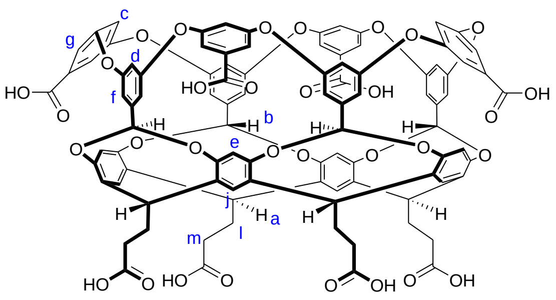
Experimental section

General

All reagents were purchased from Aldrich Chemical Company and used as received without further purification. Host **1** and **2** were synthesized as previously reported.[1,2] NMR spectra were recorded on a Varian Inova 500 MHz spectrometer. Chemical shifts are reported relative to D_2O (4.80 ppm).



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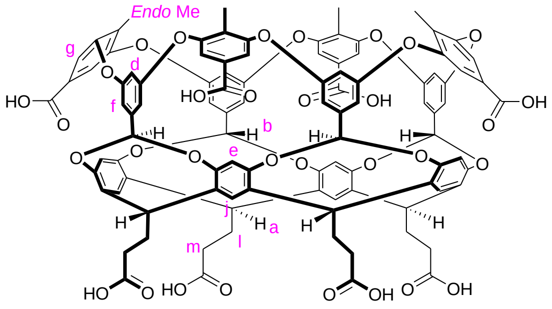

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^{1}H-NMR spectra of host 1, 2 and mixture of hosts in the absence of guests

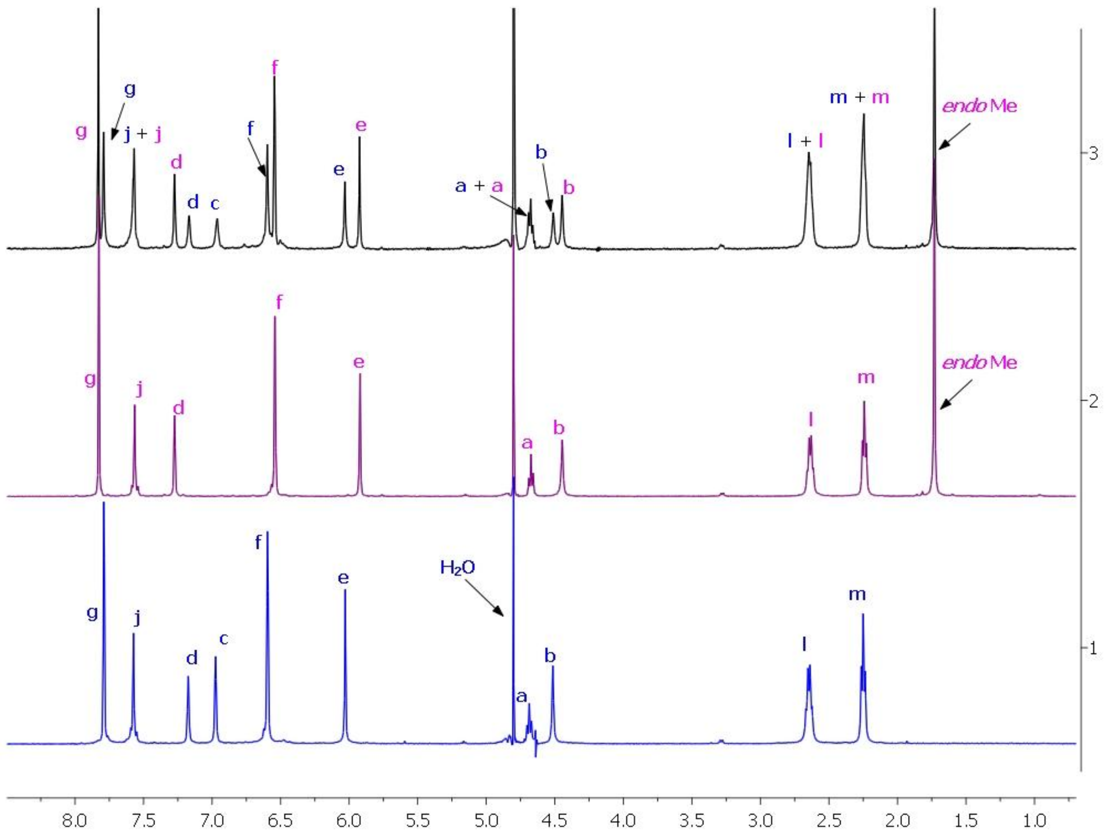

Figure S1: ^{1}H NMR spectra of: 1) 1 mM of **1**; 2) 1 mM of **2**; 3) 0.5 mM of both **1** and **2** (all 10 mM sodium tetraborate solution).

^{1}H-NMR spectra of the complexes of 1•2 and hydrocarbons *n*-pentane through *n*-heptadecane

In all cases an excess of guest was added to the mixture of host **1** and **2**. To a mixture of 0.275 mL of 1 mM host **1** and 0.275 mL of 1 mM host **2** (both in 10 mM sodium tetraborate), 10 μL of the guest was added and the NMR spectra recorded. The samples were then briefly sonicated to ensure maximal dissolution of the guest. The ^{1}H NMR spectra for all the guests investigated are shown in Figure S2. Integration of the host peaks versus the bound guest methyl peaks gave ratio of host to guest. The, “island” of kinetic instability for the complexes formed by the guests, *n*-hexane to *n*-nonane is apparent in the high field, bound guest, region of the relevant spectra. For clarity, the ^{1}H NMR spectra of the complexes formed by *n*-pentane, *n*-octane, *n*-decane are reproduced in Figure S3 along with the assignments for the ‘d’, endo-methyl, and bound guest signals. These examples emphasize how small *n*-pentane and large *n*-decane form kinetically stable complexes, but that intermediate sized *n*-octane forms a less stable complex.

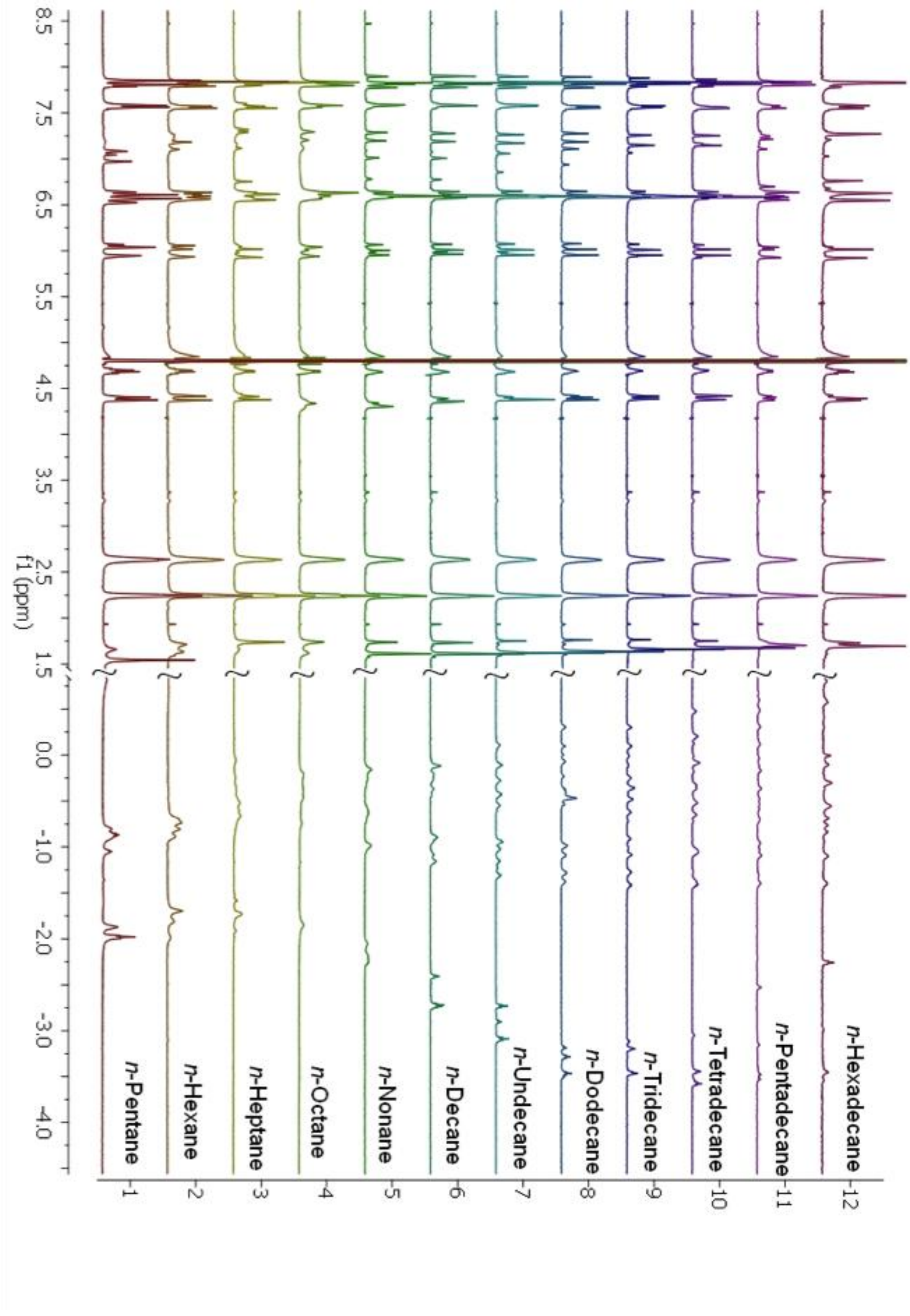

Figure S2. Partial ^{1}H NMR spectra of the **1.2** hetero-capsules and hydrocarbons pentane through *n*-hexadecane.

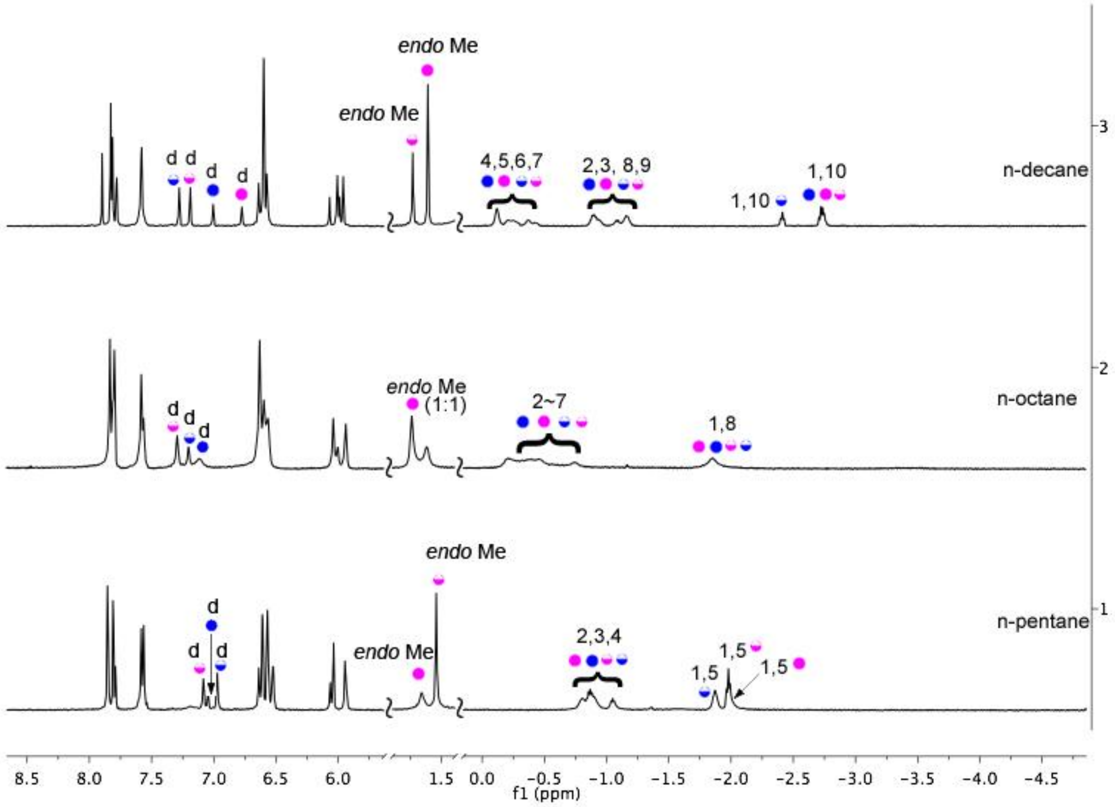

Figure S3. Partial ^{1}H NMR spectra of the complexes formed between hosts **1** and **2** and: a) *n*-pentane; b) *n*-octane; c) *n*-decane. Designations are: $\mathbf{1}_2$ homo-capsule (③), $\mathbf{2}_2$ homo-capsule (③), host **1** of hetero-capsule (◒), host **2** of hetero-capsule (◒). In each spectrum the total host concentration is 1 mM, each guest was added to the solution as an excess, and the buffer was 10 mM sodium tetraborate.

The *n*-pentane complex showed an unexpected property, namely a ‘disappearing’ guest methyl signal (Figure S4). ^{1}H NMR spectra recorded at two different host concentrations are shown in Figure S4. In the mixture of the hosts at a total concentration of 1 mM, the signal for the methyl groups of the bound guest in the $\mathbf{1}_2$ homo complex are barely visible at ca. 1.75 ppm. However, at 2 mM host complexation this same signal is readily apparent. This phenomenon suggests that at low host concentration the exchanging rate of the methyl groups in this complex is on the NMR time scale.

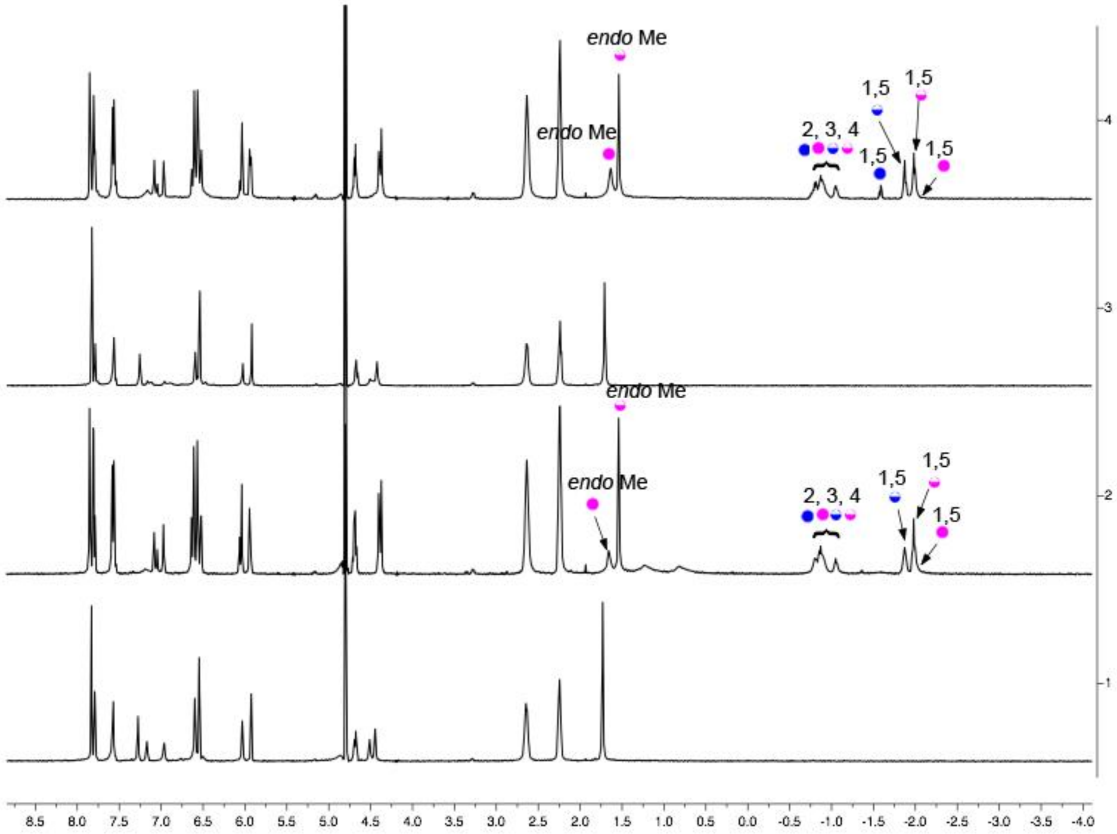

Figure S4. ^{1}H NMR spectra of 1:1 mixtures of hosts **1** and **2** in the absence/presence of *n*-pentane: Spectra 1) and 2), [host] = 1 mM, [$Na_2B_4O_7$] = 10 mM, excess *n*-pentane present in the latter.
Spectra 3) and 4), [host] = 2 mM, [$Na_2B_4O_7$] = 20 mM, excess *n*-pentane present in the latter.

Example COSY and NOESY NMR data (for the *n*-undecane hetero-complex)

As an example of the typical COSY and NOESY NMR obtained for peak assignments, Figures S5 shows the COSY NMR for the mixture of hosts **1** and **2** in the presence of *n*-undecane (bound guest region shown). Figure S6 shows the NOESY NMR for the mixture of hosts **1** and **2** in the presence of *n*-undecane. Figure S7 shows the bound hosts **1** and **2** aromatic region in the presence of *n*-undecane.

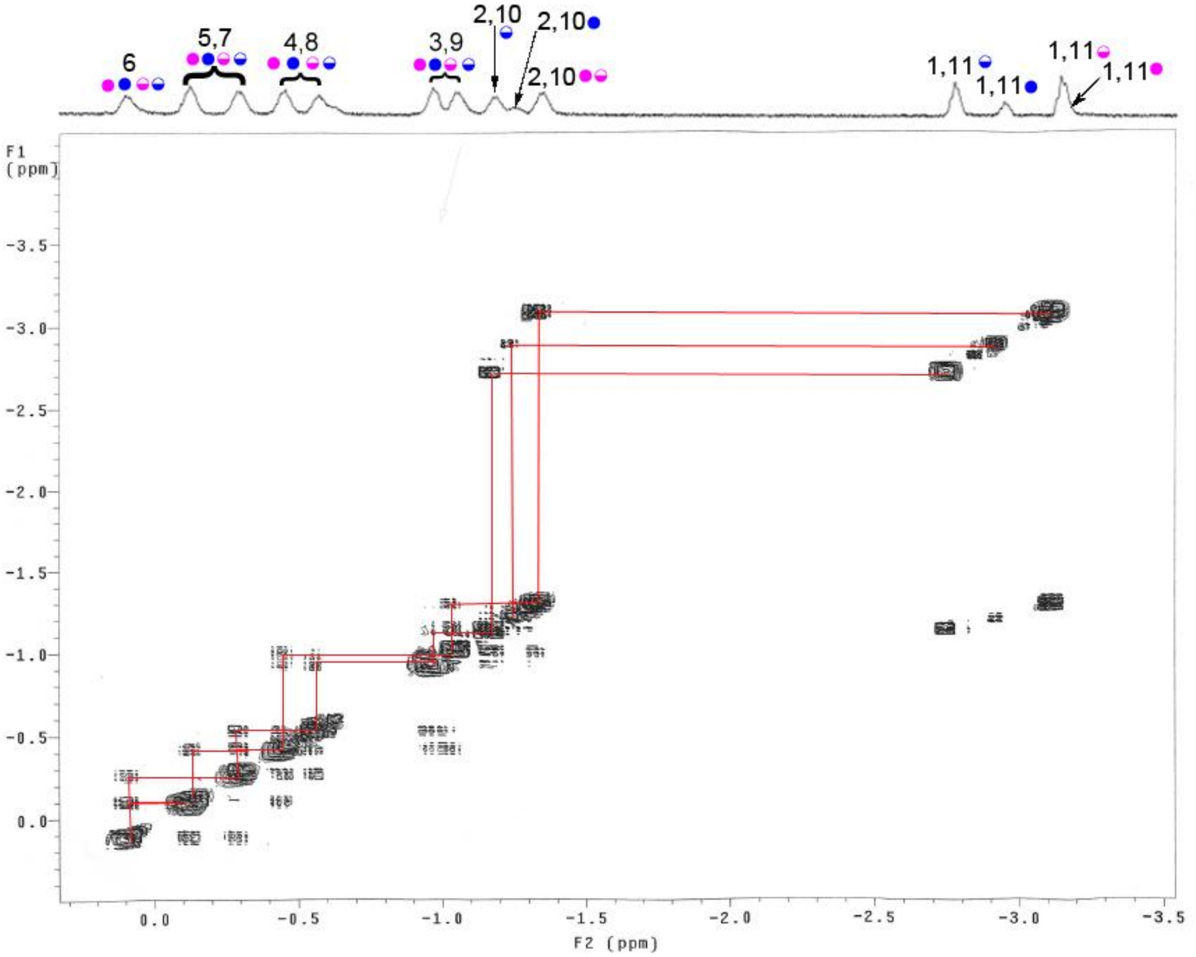

Figure S5. Bound guest region of the COSY NMR spectra of the mixture of hosts **1** and **2** in the presence of *n*-undecane ([total host] = 1 mM, [$Na_2B_4O_7$] = 10 mM).

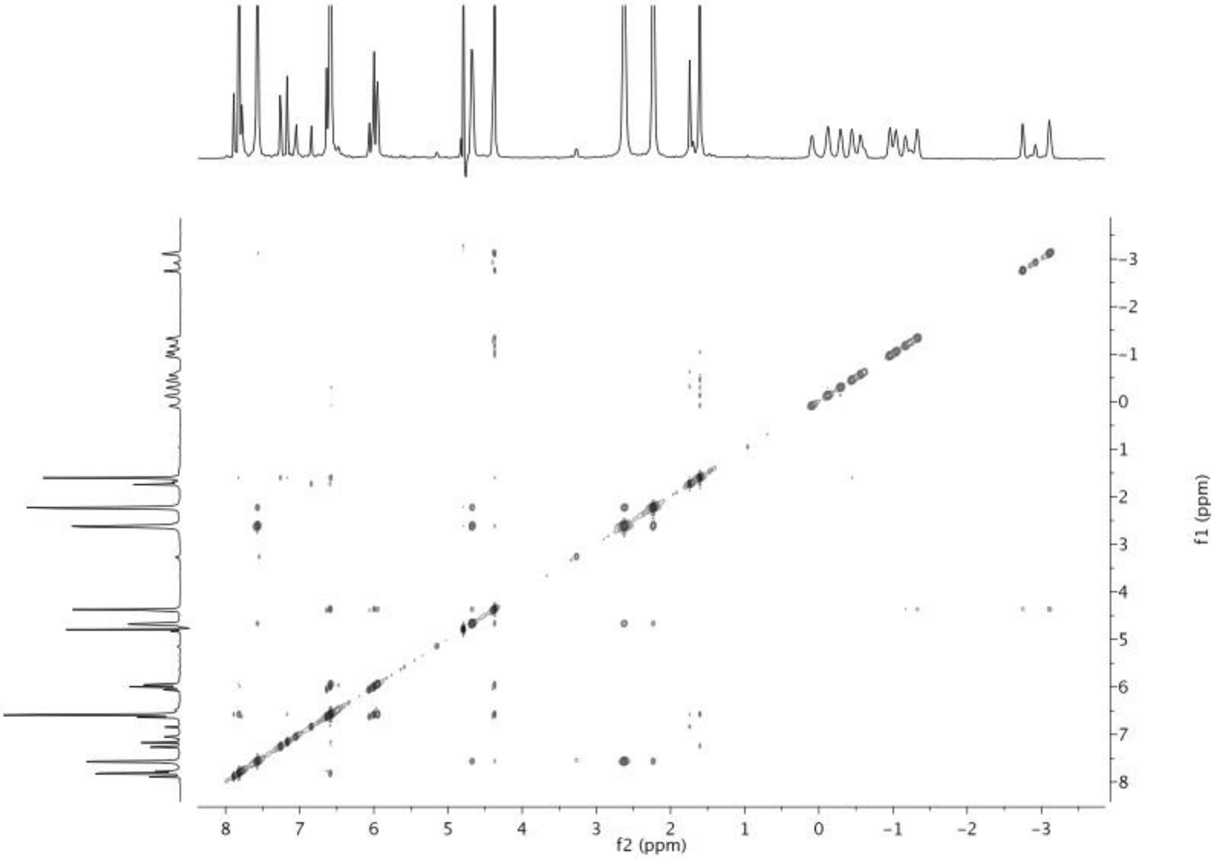

Figure S6. NOESY NMR spectra of the mixture of host **1** and **2** in the presence of *n*-undecane (C11). The total host concentration is 5 mM, in the presence of an excess of guest. The buffer was 50 mM $Na_2B_4O_7$.

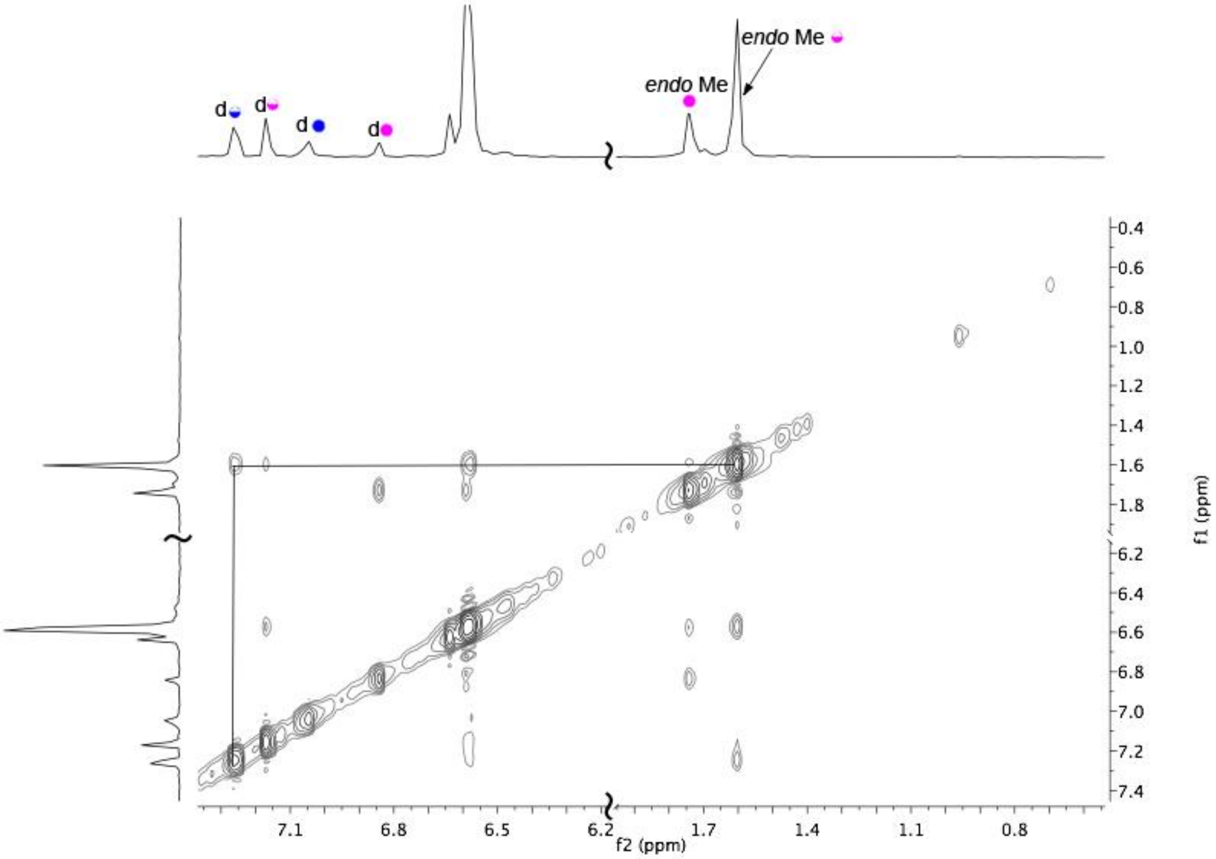

Figure S7. Bound host region of the NOESY NMR spectra of the mixture of host **1** and **2** in the presence of *n*-undecane (C11). Designations are: **1.1** homo-capsule (③), **2.2** homo-capsule (③), host **1** of hetero-capsule (◒), host **2** of hetero-capsule (◒). The total host concentration is 5 mM, in the presence of an excess of guest. The buffer was 50 mM $Na_2B_4O_7$.

Pulse-gradient stimulated spin-echo NMR studies

Diffusion measurements were performed on an INOVA 500 MHz (Varian Inc.) instrument equipped with a Performa II pulsed field gradient (PFG) module capable of producing pulses up to 52 gauss/cm. The experiments were carried out on a 5 mm PFG indirect detection probe. The STE (stimulated echo) diffusion experiment using the Varian pulse sequence “pge” (stimulated option on) were performed with pulse gradients of 2 ms in duration separated by 155 ms. Calibration utilized D_2O samples with a diffusion constant of 1.88×10^{-5} cm^2/s. The data was analyzed using the optional Varian diffusion software. Figure S8 and Figure S9 show a typical plot of the ln(amplitude) versus the square of the gradient strength applied that was obtained. The experiments were run at 25°C, at a total host concentration of 1 mM in 10 mM sodium tetraborate.

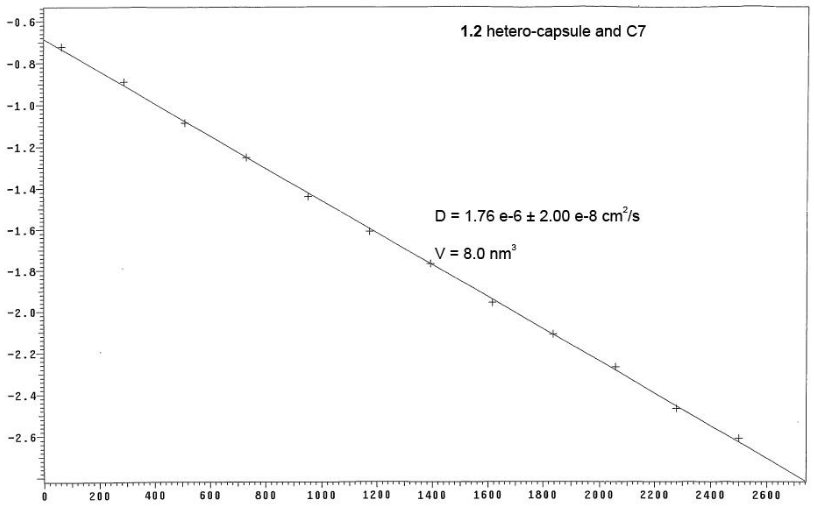

Figure S8. Plot of the ln(amplitude) versus the square of the gradient strength applied that was obtained (in this case for *endo* methyl proton of 1:1 complexes of **2** and *n*-heptane in the formation of **1.2** hetero-complex).

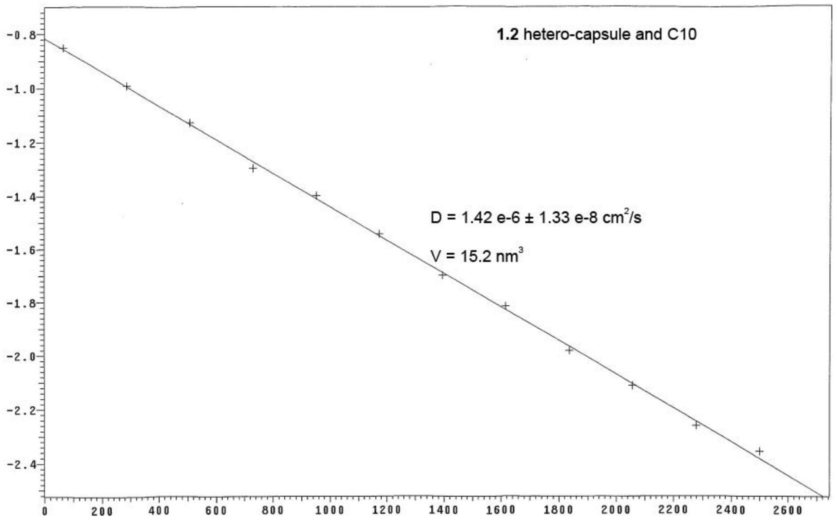

Figure S9. Plot of the ln(amplitude) versus the square of the gradient strength applied that was obtained (in this case for "d" proton of hemisphere comprised of **2** in **1.2** hetero-complex and *n*-decane)

The obtained diffusion constants were the converted into corresponding hydrodynamic volumes using the Stokes Einstein Equation ($R_H = k_B T/6\pi\eta D$, where R_H is the hydrodynamic radius, k_B is the Boltzmann constant, η is the viscosity, and D is the diffusion coefficient), and the assumption that the shapes of the different complexes approximate to spheres ($V = 4/3\pi R_H^3$).

Table of Percentage of Hetero-complex Formation

The percentage of hetero-complex formation is calculated from the integration of homo and hetero *endo* Me signals (for guest *n*-pentane, *n*-heptane through *n*-heptadecane) and integration of the signals from the "e" protons of the hosts (for guest *n*-hexane) applying the iNMR® deconvolution program. The given percentage of each hetero-complex is shown in Table S1. Calculations based on using the host aromatic region "d" protons gave similar values differing less than ±5%.

Table S1. Percentage of hetero-complex formation in the presence of guest *n*-pentane through *n*-hexadecane.

Guest	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15	C16
%Hetero-capsule	61	55*	24	38	65	63	69	68	74	74	46	44

*Calculation is based on "e" peak.

References

(1) Liu, S.; Whisenhunt-Ioup, S. E.; Gibb, C. L. D.; Gibb, B. C. *Supramolecular Chemistry* **2011**, *24*, 480.

(2) Gan, H.; Benjamin, C. J.; Gibb, B. C. *J. Am. Chem. Soc.* **2011**, *133*, 4770.