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Interplay of *p*-Sulfonatocalix[4]arene and Crown Ethers En Route to Molecular Capsules and "Russian Dolls"

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Abstract: Diffusion-ordered ^{1}H NMR spectroscopy techniques have been used to determine the binding strength of *p*-sulfonatocalix[4]arene (SO_3[4]) towards a number of charged crown ether species in aqueous conditions. For several (doubly) charged (di)azacrown ethers, all were bound by SO_3[4] either well or very well with binding constants between 5.1×10^2–9.9×10^5 M^{-1}. These results correlate with, and thus explain the phenomenon of rapid capture of azacrown ethers in molecular capsules based on *p*-sulfonatocalix[4]arene and lanthanide metals. Similarly, the formation of "Russian doll" superanions in the solution phase is also elucidated. These superanions have been shown to selectively crystallise particular polynuclear aquated metal ions from mixtures in the aqueous phase. Neutral [18]crown-6 is not bound by *p*-sulfonatocalix[4]arene and displays a binding constant of 0 M^{-1}. When sodium [18]crown-6 is examined in a similar fashion, binding by SO_3[4] is observed in solution with $K_a\sim3.1\times10^3$ M^{-1}.

Keywords: calixarenes · crown compounds · host–guest systems · NMR spectroscopy · supramolecular chemistry

Introduction

Calixarenes are a fascinating family of macrocyclic molecules that feature extensively in the field of supramolecular chemistry.[1] This relates to their synthetic availability and ease of modification, coupled with the presence of cavities/clefts that are capable of binding a variety of species.

Water soluble calixarenes are readily accessible by functionalising either the upper or lower rim of the polyphenol macrocycle.[2] We, amongst others, have been exploring the supramolecular chemistry of one such class of calixarene, the *p*-sulfonatocalix[*n*]arenes (in which $n=4,5,6,8$). These molecules display a range of biological activities that include enzyme inhibition, ion-channel blocking and anti-viral properties.[3] The smallest molecule in this class, *p*-sulfonatocalix[4]arene (SO_3[4]), usually crystallises with a truncated cone conformation, a shape that lends itself to the formation of self-assembled "up–down" antiparallel bilayer arrays.[4,5] These extended solid-state arrays can be built up of supermolecules based on molecular capsules, "Russian dolls" or ferris wheels, and can incorporate two- and three-dimensional coordination polymers, as well as other structural features.[5] The series of "Russian doll" structures feature a superanionic capsule (in which two *p*-sulfonatocalix[4]arenes shroud a sodium [18]crown-6 complex) that is capable of selectively crystallising polynuclear aquated metal cations from solution.[5]

In particular, *p*-sulfonatocalix[4]arene has been shown to assemble into spectacular nanospheroids of varied geometries, or nanotubules depending on the guest molecules and metal ions present in solution.[6] Exchanging [18]crown-6 for pyridine *N*-oxide in a ternary lanthanide/SO_3[4]/guest system results in an icosahedral to cuboctahedral geometric change in a nanospheroid composed of twelve *p*-sulfonatocalix[4]arenes, with a concomitant increase of ~30% in the internal spheroid volume.[6] In addition, the formation of pores in the outer "shell" of the spheroid associated with this change allows the tentative analogy to viral mimicry of the cowpea chloritic mottle virus that has been shown to

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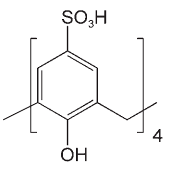
behave in a similar manner under particular pH control.[7] The icosahedral to cuboctahedral change in geometry is ascribed to the two *p*-sulfonatocalix[4]arenes being forced to assemble in a head-to-head manner around a lanthanide [18]crown-6 complex as a "Russian doll" (cuboctahedral geometry), rather than in a flexible C-shaped calixarene dimer tecton with pyridine *N*-oxide (icosahedral geometry) as a guest in the aforementioned system.[6]

Recent structural studies have focused on the rapid capture and crystallisation of (di)cationic cyclic (aza)crown ethers in molecular capsules based on two *p*-sulfonatocalix[4]arenes with lanthanide metal cations providing charge balance at the exterior periphery of the capsules.[8] Capsule formation can be pH dependent for the capture of some monocationic crown ethers, but under the correct conditions millimetre-sized single crystals form rapidly, over several minutes.[8c] It is therefore likely that some level of crown ether/*p*-sulfonatocalix[4]arene pre-association may occur in solution. This is the focus of the present study along with solution studies directed at elucidating the formation of "Russian doll" superanions in the aqueous phase, prior to their crystallising with polynuclear aquated metal cations.

To achieve these goals, a series of diffusion-ordered (DOSY) ^{1}H NMR spectroscopy measurements were performed in D_2O on a variety of host–guest systems, composed of hosts **1** and **2** and guests **3**–**8**. The *p*-sulfonic acid calix[4]arene (**1**) was examined in the presence of all the crown ether guests **3**–**8** for ascertaining the nature of the "rapid capture in acidic aqueous media", whilst the sodium salt of $SO_3[4]$ (**2**) was only examined with [18]crown-6 (**8**) for direct comparison with the **1·8** system. These last experiments were performed with a view to explore differences in [18]crown-6/$SO_3[4]$ pre-organisation in solution, both in the absence or presence of sodium ions (which would form a well-known sodium [18]crown-6 species and thus complex when present). Binding of a sodium [18]crown-6 complex to *p*-sulfonatocalix[4]arene would confirm the presence of a partial "Russian doll" superanion in the solution phase.[5]



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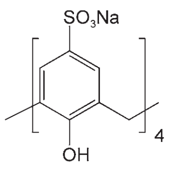

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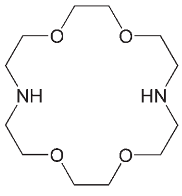

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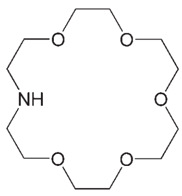

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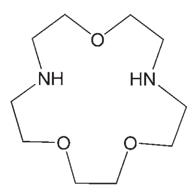

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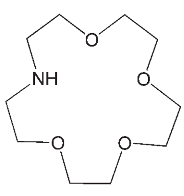

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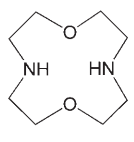

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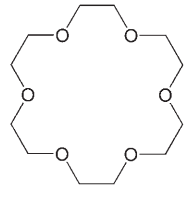

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DOSY NMR spectroscopy is a powerful technique for probing intermolecular interaction or complex formation in supramolecular chemistry.[9] This phenomenon is achieved through the use of pulse field gradients that allow the measurement of diffusion in solution, a parameter that is directly related to molecular weight.[10] One advantage of this technique over the traditional NMR titration for studying host–guest interactions is that fewer experimental runs are required in order to measure or observe complex formation. The NMR titration method and chemical shift changes have been used to some effect by others on host–guest systems incorporating $SO_3[4]$ in order to determine various phenomena, such as cone conformation or binding constants.[11] These studies have typically focused on the inclusion of small, charged, aromatic species although complexation of various amino acids and dye molecules have also been investigated.[12] Despite this, it is surprising that the DOSY NMR technique has to our knowledge not yet been employed as an analytical tool in studying $SO_3[n]$ host–guest systems ($n=4,5,6,8$). In addition to the above, DOSY NMR spectroscopy can also be used to good effect as a supporting tool in identifying large multicomponent molecular species present in solution.[13] Most importantly, in the context of the results presented here, the technique can be used to calculate binding constants and "approximate molecular weights" in order to gain insight into host–guest behaviour in the solution phase including complex size/stoichiometry.[10]

Results and Discussion

Experiments were run at host/guest ratios shown in Table 1. Additional runs were recorded for system **1·4**, which displayed complex behaviour; more than one species seems to be present in solution, at least one of which displays diffusion behaviour that would be consistent with a 2:1 complex of host **1** and guest **4**. However, more evidence is required to confirm this and hence this system is not described in

Table 1. Diffusion rates for the host and guest in system **1·3** at particular [H]/[G] ratios.

$[H]_o$ [mM]	$[G]_o$ [mM]	D_H [10^{-6} cm^{2}s^{-1}]	D_G [10^{-6} cm^{2}s^{-1}]
1.0	0	3.27 (+/−0.01)	–
1.0	0.5	3.11 (+/−0.02)	3.08 (+/−0.04)
1.0	1.0	3.08 (+/−0.01)	3.32 (+/−0.02)
1.0	2.0	2.90 (+/−0.01)	3.67 (+/−0.02)
0	1.0	–	3.85 (+/−0.05)

greater detail here. Buffers were not used to regulate pH in the current experiments, as we believe their components are likely to interfere with the host–guest interactions of the crown ether and calixarene. System **1·3** displays rapid crystal growth in under thirty minutes when a lanthanide(III) chloride salt is added to a pre-prepared solution containing **1** and **3** at low pH (<3) with $SO_3H[4]$ as the proton source. For system **1·3**, the sample of $SO_3H[4]$ in the absence of guest gave the two expected singlets at $\delta = 7.63$ and 4.08 ppm in the DOSY spectrum at ambient temperature (Figure 4a in the Supporting Information). Diaza[18]crown-6 in the absence of host (calixarene) gave the expected multiplet and triplet at approximately $\delta = 3.7$ and 2.9 ppm, respectively (relative ratio 4:2, Figure 4b in the Supporting Information). When host and guest are combined at a 1:0.5 ratio, the calixarene methylene signals broaden and three distinct signals are observed for the guest (sharp lines, Figure 5a in the Supporting Information). There is a concomitant reduction in the diffusion coefficients for both components (as shown in Table 1), thus indicating that the [diaza[18]crown-6+2 H]$^{2+}$ species is complexed by the calixarene. At a 1:1 ratio, the calixarene methylene signals broaden to the baseline and the signals for the guest begin to broaden (Figure 5b in the Supporting Information). At a 1:2 ratio, two clean doublets can be seen for the calixarene methylene protons and the guest signals begin to be resolved again (Figure 6 in the Supporting Information). The presence of doublets for the calixarene methylene protons is indicative of the molecule adopting a cone conformation in solution at ambient temperature, that is, complexed all of the time. The diffusion coefficients for the host and guest in system **1·3** (Table 1) show a clear reduction in the diffusion rates of both molecules at around a 1:1 ratio, relative to uncomplexed values. When the crown ether is in excess, the calixarene is clearly under a conformational restriction from the typically fluxional solution behaviour normally observed in the absence of guest at ambient temperature.

As a full discussion relating to the spectra of system **1·3** has been given, tabulated data and related comments for the remaining systems are given in the Supporting Information. Similar trends were observed for the diffusion coefficients of all the remaining aza-functionalised crown ether systems (**1·4**–**1·7**), but to varied extents. Assuming that a 1:1 complex were formed in **1·3**, a complex fraction (X_{HG}) can be calculated and this value is used to determine the binding constant as $6.1(5)\times10^3\,\text{M}^{-1}$. This value for K_a was determined by using a "single-point" calculation. The results of such calculations need to be treated with caution when the diffusion coefficient of the host and guest are quite similar. In such situations it is useful to also estimate K_a following a curve fitting procedure in which the diffusion coefficients and K_a are varied to fit diffusion data collected for different host/guest ratios. Such a procedure has been conducted for **1·3** by using an Excel spreadsheet.[14] The K_a determined by using this approach was essentially identical ($6.37\times10^3\,\text{M}^{-1}$) to that determined by the single-point method (Table 1 in the Supporting Information). Although the binding is not *very* strong, it is indicative of some degree of calixarene/crown ether pre-association in solution and explains the relatively rapid crystal growth (~30 min) of molecular capsules upon addition of lanthanide(III) chloride salt.[8b] This hypothesis is on the basis that fewer molecular components are required to organise around a central node in order to achieve a stable species for crystallisation (Figure 1). Table 2 lists all the binding constants calculated for systems **1·3**–**1·7**. From the K_a values of the remaining charged aza-functionalised crown ether guest species, it is clear that all the charged guest species, except for 1-aza[15]crown-5, are strongly bound. This observation is consistent with exclusion of 1-aza[15]crown-5 (in a neutral or charged state) from any of our *p*-sulfonatocalix[*n*]arene structural motifs to date.[8] 1-Aza[18]crown-6 forms millimetre-sized single crystals of a lanthanide $SO_3[4]$ complex based on molecular capsules in under 15 minutes.[8c] This *very* rapid crystallisation can thus be explained by the excellent binding of [1-aza[18]crown-6+H]$^+$, as indicated by the K_a value in Table 2. Although this species presents a smaller electro-positive charge for interaction with calixarene SO_3^- groups than [diaza[18]crown-6+2 H]$^{2+}$, we believe that the guest may not only be "of a good fit", but that it may also be able to orient itself deeper into the calixarene cavity, possibly by maximising NH_2^+/SO_3^- and hydrophobic cavity interactions.

We have recently reported the rapid formation and structural elucidation of a molecular capsule containing [diaza[15]crown-5+2 H]$^{2+}$ and an alternative bilayer structure incorporating [diaza[12]crown-4+2H]$^{2+}$, both of which formed in the presence of lanthanide metal cations.[8d] Both crown ethers are found herein to bind moderately or very strongly with $SO_3[4]$ in the acidic aqueous media, respectively, as indicated in Table 2. Clearly the presence of an additional NH_2^+ group in a [15]crown-5 molecule results in stronger binding through increased electrostatic/hydrogen-bonding interactions relative to [1-aza[15]crown-5+H]$^+$. The [diaza[12]crown-4 + 2H]$^{2+}$ species is found to reside deep in the molecular cavity of the calixarene in the solid state, a possible reason for the increase in guest binding in these solution studies relative to [1-aza[15]crown-5+H]$^+$.[8d]

With respect to elucidating the presence of "Russian doll" superanions in the solution phase, we note that system **1·8** showed no interaction between $SO_3H[4]$ and [18]crown-6, which is not unsurprising given that the potential guest is a neutral species (Table 3). However, when the sodium salt of $SO_3[4]$ is employed, a change in diffusion coefficient for both host and guest is observed and it is indicative of complex formation. This is likely to occur through the binding of a [sodium–[18]crown-6]$^+$ complex to $SO_3[4]$; a binding constant of $3.1\times10^3\,\text{M}^{-1}$ was obtained, confirming the presence of a partial "Russian doll" superanion in the solution phase (Table 3, Figure 2). Given that other related supramolecular architectures are formed with lanthanide–[18]crown-6 complexes, one would expect the binding to be significantly stronger.

The Stokes–Einstein relationship can be used to calculate "approximate molecular weights" (the diffusion coefficient/

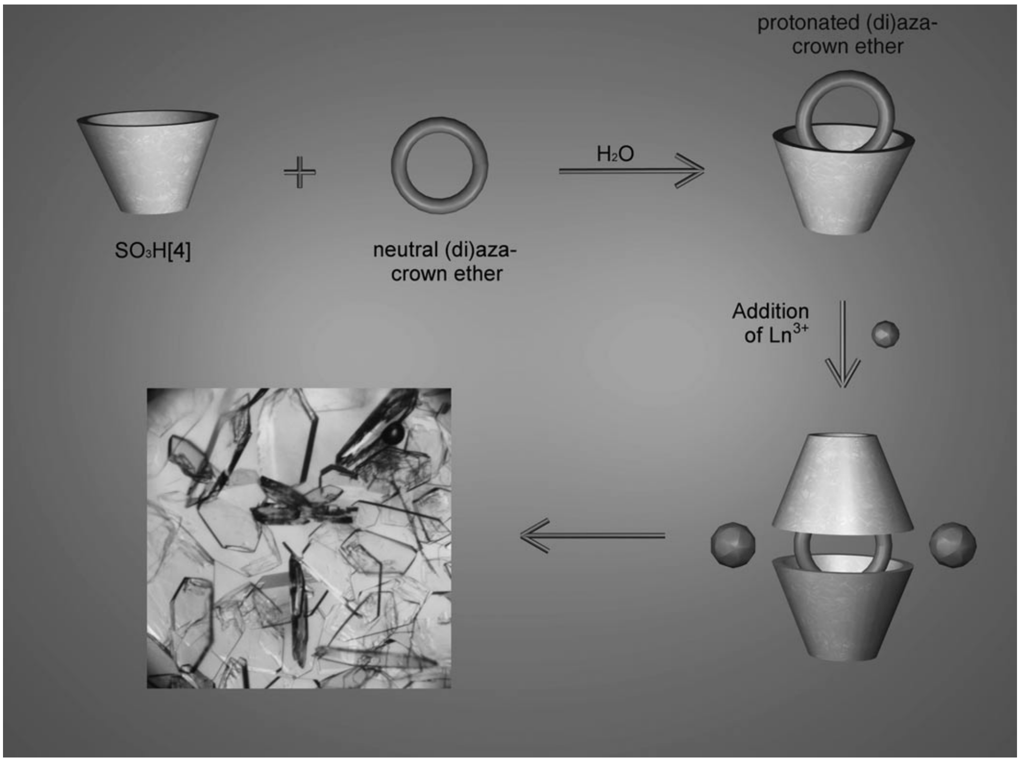

Figure 1. Schematic showing the protonation of a neutral azacrown ether and concomitant complexation in solution by *p*-sulfonatocalix[4]arene. X-ray diffraction quality crystals of lanthanide-based molecular capsules containing mono-protonated 1-aza[18]crown-6 (actual crystals shown), di-protonated 4,13-diaza[18]crown-6, and di-protonated 1,7-diaza[15]crown-5, all grow in under thirty minutes upon addition of a particular lanthanide(III) chloride salt.

Table 2. Complex fractions and binding constants calculated for the 1:1 [H]/[G] samples from systems **1·3**–**1·7**.

System	Fraction of complex (X_{HG})	K_a [M^{-1}]
1·3	0.67	$6.1(5)\times10^3$
1·4	0.99, 0.66, 0.11	9.9×10^5–1.4×10^2[a]
1·5	0.73	2.5×10^4
1·6	0.27	5.1×10^2
1·7	0.92	1.4×10^5

[a] For system **1·4**, the fraction of the 1:0.5 [H]/[G] complex is 0.66 and K_a is $4.8\times10^3\,M^{-1}$.

Table 3. Complex fractions and binding constants calculated for the 1:1 [H]/[G] samples from systems **1·8** and **2·8**.

System	Fraction of complex (X_{HG})	K_a [M^{-1}]
1·8	~0	0
2·8	0.2	3.1×10^3

molecular weight calibration curve presented in reference [10c] was used for the estimates presented here) and in doing so herein a general trend is observed (Table 4). All systems, except **1·8** (which showed no complexation), have average molecular weights that suggest a 1:1 calixarene/crown ether stoichiometry. It should be noted that whilst these values are approximate, they can be used as an indicative tool for relative molecular component stoichiometries.

To conclude, we have successfully implemented DOSY NMR techniques to show that *p*-sulfonatocalix[4]arene binds a series of (di-)protonated (di-)aza-functionalised crown ether molecules in the cavity of the host with varied strengths in the solution phase. All but 1-aza[15]crown-5 bind either well or very well, and for 1-aza[18]crown-6 the binding is remarkably strong with a $K_a > 9\times10^5\,M^{-1}$. These results both correlate with and explain the rapid molecular capsule or bilayer crystallisation phenomenon described in our related structural studies with these systems and lanthanide metal cations.[8] The studies involving [18]crown-6 or sodium–[18]crown-6 guest species with $SO_3[4]$ show that the presence of a sodium ion bound to the crown ether slows the rate of diffusion of both host and guest; that is, complex formation through the generation of a charged guest species results. Although the diffusion coefficient for **2** is less than that of **1**, this difference is due to the increased molecular weight of the monomer and not aggregation (Table 4). These results confirm the presence of partial "Russian doll" superanions based on *p*-sulfonatocalixarene and sodium–[18]crown-6 complexes in the solution phase. Work continues on the elucidation of the assembly process in nanometre-scale spheroids based on *p*-sulfonatocalix[4]arene in lanthanide-based systems.

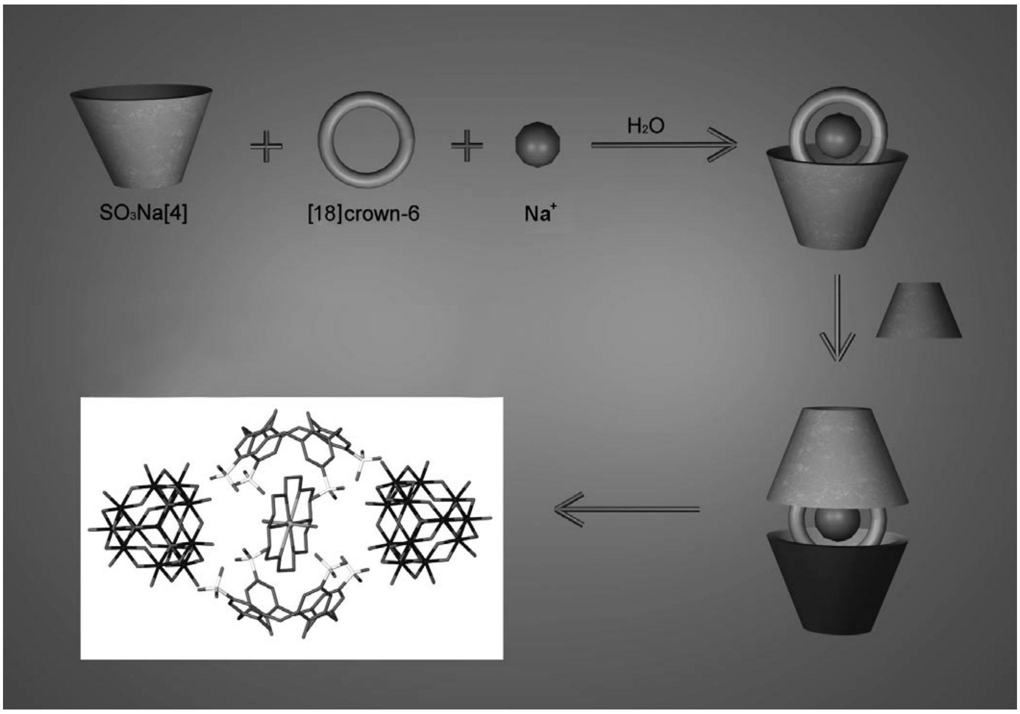

Figure 2. The formation of a partial "Russian doll" superanion via the binding of a sodium [18]crown-6 complex in the solution phase. Once formed, the entire superanion is capable of selectively crystallising polynuclear aquated metal cations from mixtures (an aluminium Keggin ion is shown as an example).

Table 4. List of calculated and averaged molecular weights for the complexes in systems **1·3**–**2·8**.

	D_H (1:1) [10^{-6} cm^{2}s^{-1}]	MW D_H (1:1)	D_G (1:1) [10^{-6} cm^{2}s^{-1}]	MW D_G (1:1)	Average MW (1:1)	Expected MW (1:1)[a]
1·3	3.08	1279	3.32	1056	1167	1009.1
1·4[b]	2.89	1502	2.8, 3.2, 3.7	1625, 1161, 799	1271	1009.1
1·5	3.10	1258	3.3	1072	1165	965.1
1·6	3.00	1367	3.6	857	1112	965.0
1·7	3.16	1198	3.3	1072	1135	921.0
1·8	3.11	1248	4.25	555	901	1009.0
2·8	2.85	1555	3.7	799	1177	1068.1

[a] Unsolvated. [b] Three molecular weights were calculated in complex **1·4**, as a complex spectrum is observed for this system (consistent with slow exchange behaviour, including the formation of a 2:1 host–guest complex, as detected in the normal one-dimensional spectrum).

Experimental Section

The *p*-sulfonatocalix[4]arene sulfonic acid and sodium salts were purchased from Acros and used as supplied without further purification. Similarly, all guest molecules were purchased from Aldrich and used as supplied.

All samples were prepared by a general procedure such that the concentrations were 1 mM with respect to host, except those which were of 0:1 [H]/[G] ratio and were made to be 1 mM with respect to guest, all at a constant volume of 600 μL (D_2O). As an example, a 1:1 [H]/[G] solution was prepared by addition of a 2 mM guest solution (300 μL) to a 2 mM host solution (300 μL). All NMR experiments were carried out on a Varian Unity Inova 500 spectrometer equipped with a single axis field gradient unit and a 5 mm ^{1}H/^{19}F/^{13}C triple-resonance *z*-gradient probe. ^{1}H NMR spectra were recorded at 25 °C and typically with 128 scans, spectral width of 4000 Hz in 8k complex points and zero filled to 32k complex points. NMR diffusion coefficients were measured from DOSY spectra by using the Dbppste pulse sequence with a 50 ms delay and 1.5 ms bipolar gradient pulses. Between 10–15 gradient field-strength increments were recorded. The spectra were deconvoluted using the "fiddle" macro on the spectrometer prior to production of the 2-D DOSY spectrum.

Acknowledgements

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