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Cavitand Gelators

Exploiting Cavities in Supramolecular Gels

*Jonathan A. Foster and Jonathan W. Steed**

calixarenes · cavitands · gels · host–guest systems · supramolecular chemistry

Endowing supramolecular gelators with cavities opens up a number of opportunities not possible with other gel systems. The well-established host–guest chemistry of cavitands can be utilized to build up and break down gel structures, introduce responsive functionalities, or enhance selectivity in applications such as catalysis and extraction. Cavity-containing gelators provide an excellent case study for how different aspects of supramolecular chemistry can be used intelligently to create responsive materials.

1. Introduction

Supramolecular gels have received considerable recent attention both as an intriguing case of self-assembly and phase separation, and as a means of creating "smart" materials.[1–3] The gel state is characterized by its solidlike properties despite being largely liquid in composition.[4,5] Conventional polymeric gels are formed by cross-linked covalent polymers which are able to swell and trap many times their own weight in solvent.[6] In contrast, supramolecular gels are generally formed from low-molecular-weight organic compounds which utilize noncovalent interactions to self-assemble into supramolecular networks capable of trapping solvent. Because such gels are held together by multiple weak and therefore reversible interactions, supramolecular gels are a particularly responsive and tuneable form of soft matter. The dramatic changes in viscosity brought about by gelation can be triggered by a wide range of stimuli such as changes in temperature, sonication[7] and oxidation,[8] and changes in pH,[9] addition of anions,[10,11] and irradiation with light.[12] A wide variety of chemical species have been shown to exhibit gelation including surfactants,[13] sugars,[14] fatty acids,[15] and amino acids,[16] amongst many others.[4,5,17]

Their diversity and remarkable properties make supramolecular gels of interest for a number of high-tech applications.[2,3,18] For example, incorporating drug functionality into a gelator which forms a stable gel under physiological conditions but which breaks up in the presence of a particular physiological stimulus (change in pH, presence of a particular ion or enzyme) would allow for the targeted delivery of a drug to a diseased site.[19] This would reduce the dosage of drug required and potentially reduce any adverse side effects. Other applications envisaged for supramolecular gels include use in light harvesting,[20] sensing,[21] and catalysis,[22] and as templates for the synthesis of nanoporous organic[23] and inorganic materials.[24]

Cavitands are molecules that have a permanent or intrinsic guest-binding cavity.[25] The formation of such a cavity necessarily requires curvature of the host in at least two dimensions, and the receptor must be relatively rigid to prevent collapse of the internal space. Aromatic rings are a good way of introducing this depth and rigidity into a molecule, and a wide variety of cyclophane-type cavitands are readily synthesized,[26] most importantly calixarenes,[27] resorcarenes,[9] and cyclotriveratrylenes.[28] Other classes of cavitands, such as cucurbit[*n*]urils[29] and particularly cyclodextrins,[30] are also commercially important and of academic interest. The basic units of these families of molecules can be extensively derivatized to increase the depth or modify the chemical nature of the binding site, whilst varying the number of units in each macrocycle changes the diameter of the cavity. The strength and selectivity of the binding of the guest to the host cavity may be determined by specific intermolecular bonding within the cavity or by solvophobic and entropic effects alongside steric considerations.

Cavitands have found application as part of a diverse range of complexing systems, for example, in analytical, drug-delivery, and stabilizing applications. For example, owing to the low cost, biocompatibility, and water solubility of cyclodextrins, 1500 tons are produced annually for use in the food, pharmaceutical, and fragrance industries.[31] The specificity of the host site allows for the selective encapsulation,[32] sensing,[33] and catalysis of molecular guests.[34] Cavitands threaded onto polymers to form rotaxanes[35] can be used to

[*] J. A. Foster, Prof. J. W. Steed
Department of Chemistry, Durham University
South Road, Durham, DH13LE (UK)
Fax: (+44) 191-384-4737
E-mail: jon.steed@durham.ac.uk

create molecular motors, shuttles, and machines.[36,37] Rotaxanes have also been utilized to form slide-ring gels,[38] and organogels incorporating switchable rotaxanes have also been reported.[39] Cavitands trapped in silica gels have been used for environmental monitoring[40] and chromatography.[41]

In the early 1990s, Shinkai and co-workers[42,43] discovered that calixarenes functionalized with long aliphatic chains formed gels in a number of organic solvents whilst Rango et al. observed the formation gels in β-cyclodextrin–pyridine/water systems.[44] However, despite the rapidly growing body of literature on gels, there are relatively few examples of cavity-containing molecules shown to form supramolecular gels. Those that exist demonstrate how the principles of macrocyclic chemistry can be incorporated into gel design and highlight the opportunities this offers. This Minireview is split into three parts: In the first we consider how the host–guest chemistry of cavitands can be used at different levels of gel structure to control gel formation; in the second part we discuss ways in which the cavity can be enhanced and exploited once the gel is formed; and in the final section we consider other remarkable examples of cavity-containing gelators that distinguish them from other gels.

2. Controlling Gel Formation

Integral to gel formation by low-molecular-weight gelators (LMWGs) is their ability to stack preferentially in one dimension to give elongated, fibrillar structures that then aggregate into cross-linked fibers to give a sample-spanning network. Fibril formation is normally achieved through the use of complementary groups which form linear hydrogen-bonding motifs or which are brought together through hydrophobic or aromatic interactions. Cavitands offer the additional possibility of exploiting well-defined interactions between the host cavity and a guest to build the fibers required for gel formation. Work by Harada and co-workers[45–47] demonstrates a variety of possible host–guest motifs for the construction of such supramolecular polymers (Figure 1).

One such system, based on a β-cyclodextrin (β-CD) unit functionalized with a trinitrophenyl group, was found to form gels at concentrations of less than 2.9 wt%, when a hot aqueous solution was cooled below 50 °C.[48] The trinitrophenyl group is a known guest of β-CD, and 2D ROESY NMR spectroscopy confirmed intermolecular interactions

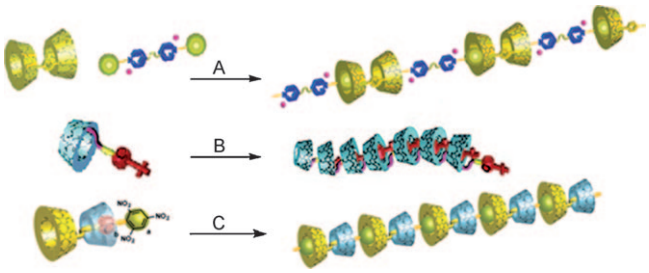

Figure 1. Formation of supramolecular polymers using A) covalently linked α-CD dimers with a ditopic guest,[45] B) α-CD functionalized with a guest,[46] C) [2]rotaxane formed by α-CD threaded between a β-CD and a stopper unit that acts as a guest for another β-CD.[47] Adapted with permission from the American Chemical Society and the Royal Society of Chemistry.

between the inner protons of the β-CD and those of the trinitrophenyl substituent with correlations between other protons indicating a tail-to-head, rather than tail-to-tail polymeric structure (type B in Figure 1). The immediate advantage of using the host properties of the cyclodextrin for gel-fiber formation is that it possible to reverse gel formation and fine-tune the gels by the addition of a competitive guest. In this case, the addition of adamantane carboxylic acid (AdCA), a strong competitive guest for binding to β-CD, results in ejection of trinitrophenyl moieties from the CD cavities and hence the breakup of the supramolecular fibers.

Cavitands are necessarily rigid molecules to prevent collapse of their internal cavity. In the right system, this rigidity can be useful for providing a preorganized scaffold with well-defined stereochemistry to aid the complementary interactions necessary for gel formation. Hannon and co-workers[49] have shown that compound **1** assembles around sodium ions to give one-dimensional fibers, with the acetal functions on the outside, capable of trapping a range of organic solvents and giving rise to robust gels. It was anticipated that grafting **1** onto the C_3-symmetrical cyclotriveratrylene (CTV) derivative **2** would have a similar organisational effect as the sodium ions and allow gelation (Figure 2). Gelator **3** was found to form robust, opaque gels in a range of solvents, although compound **2** was also found to gel a number of solvents.[50] Freeze-fracture electron microscopy images of dichloromethane gels of this material revealed long flat stiff ribbonlike structures with 4–5 nm striations and 9 nm fiberlike flexible strands. Dreiding stereomodels predict

Jonathan Foster obtained his M.Chem. degree from Durham University in 2008. He is currently a PhD student under the supervision of Prof. Jonathan Steed working on the development of cavitand-based gelators and seeking to exploit their host–guest properties to develop responsive materials.

Jonathan Steed obtained his PhD at University College London, working with Derek Tocher. From 1993 to 1995 he was a NATO postdoctoral fellow with Jerry Atwood at the University of Missouri – Columbia. He is currently Professor of Inorganic Chemistry at Durham University (UK). Prof. Steed is coauthor of a number of books on supramolecular chemistry and is the winner of the 2010 Corday–Morgan Prize. His research interests are in anion sensing, supramolecular gels, and crystal engineering.

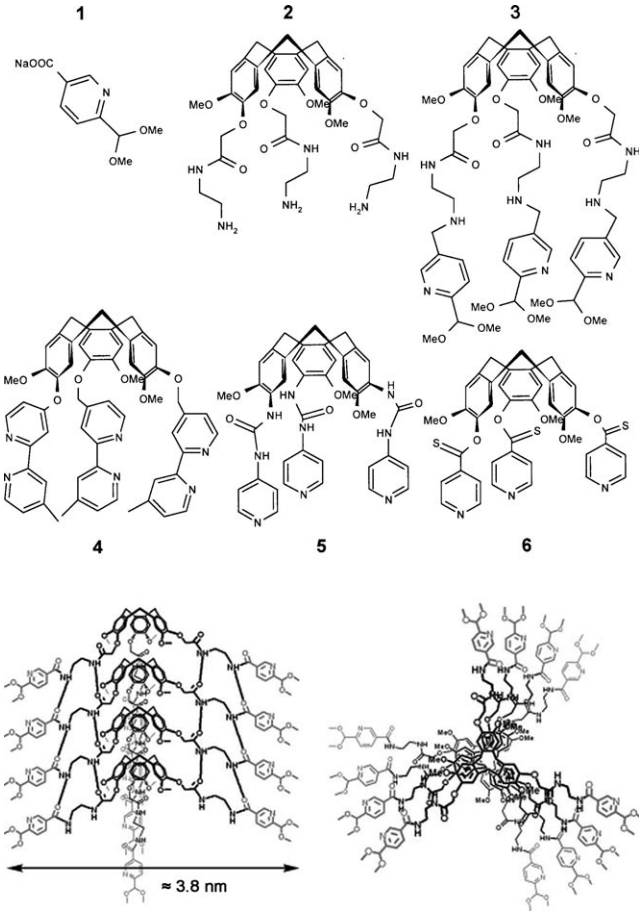

Figure 2. Top: CTV-derived gelators **2**–**6**. Compound **1** was grafted onto the C_3-symmetric scaffold **2** to give gelator **3.** Bottom: A molecular model of CTV derivative **3** shows stacking by self-inclusion. Adapted from Ref. [49] with permission from the Royal Society of Chemistry.

the lateral dimensions of CTV in a flat conformation to be approximately 3.8 nm. Along with X-ray powder diffractograms showing small-angle reflections consistent with columnar stacks, this implies columnar packing of individual CTV molecules into chains in the ribbons and twisting of two chains together in the fibers.

This columnar packing of CTV derivatives, as seen in the crystal structure of CTV itself,[51] highlights another feature of cavitands that can be exploited to encourage fiber formation, namely self-inclusion. The shallow bowls of CTV derivatives mean one molecule readily slots inside the bowl of another to form one-dimensional stacks held together by offset π–π interactions. Hardie and co-workers have prepared a number of metallo-CTV- (based on complexes of **4** and **5**) and organo-CTV-based gelators (**6**) that gel solvents such as DMF, acetonitrile, and 2,2,2-trifluoroethanol, depending on the gelator.[52] This work shows that with the exception of **6**, which has strongly hydrogen-bonding thiourea groups, the principal supramolecular interaction between gelator molecules is likely to be π–π stacking interactions.

Fiber formation alone is insufficient to ensure the creation of a stable gel. The fibers must either entangle or cross-link so as to prevent sedimentation and ensure the formation of a sample-spanning network. Harada and co-workers[53] created a multicomponent supramolecular hydrogel composed of single-walled carbon nanotubes (SWNTs) cross-linked to a polymer through host–guest interactions to create a reversible hydrogel (Figure 3). β-CDs were functionalized with pyrene

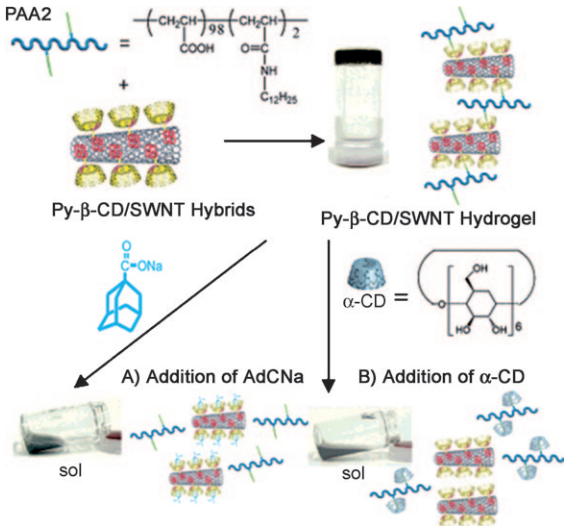

Figure 3. Py-β-CD/SWNT hydrogel with PAA2. Gel-to-sol transition upon addition of A) the competitive guest AdCNa and B) the competitive host α-CD. Adapted from Ref. [53] with permission from the American Chemical Society.

(Py), which is able to bind strongly to the SWNTs through π–π interactions. Sonication of SWNTs with Py-β-CD leads to stable solutions of the SWNTs because of the formation of a Py-β-CD/SWNT hybrid. The cavity of the CDs can be used to host dodecyl chains. Mixing poly(acrylic acid) (M_w = 250000 Da) carrying 2 mol% dodexyl groups (PAA2) with the Py-β-CD/SWNT hybrid in aqueous solution results in the formation of a hydrogel. Again, the addition of a competitive guest for β-CDs, in this case AdCNa, results in a gel–sol transition. The same effect was achieved by adding α-CD, a competitive host for the dodecyl chains. There is potential for these Py-β-CD/SWNT hybrids to bring other guest species in close contact with SWNTs for applications in solar energy conversion and photo-oxidation, and as fluorescence labels in biomedicine.[53] Very recently, Hennink and co-workers utilized clusters of β-CDs to cross-link cholesterol-derivatized poly(ethylene glycol) through host–guest interactions to form physical gels.[54]

Gel formation can be thought of as a type of arrested crystallization, with molecules stacking preferentially in one dimension to form the long fibers necessary for gel formation. Yang et al.[55] found that the addition of small amounts of cucurbit[6]uril (CB[6]) to hot acidic aqueous solutions of 1-aminium 4-methylbenzenesulfonate (BAMB) resulted in the formation of hydrogels upon cooling. In the absence of CB[6], BAMB crystallizes as large blocklike aggregates, as shown in Figure 4 A. However, in the presence of CB[6] long, thick rodlike fibers form which extend over several micrometers

(Figure 4B). NMR spectroscopic studies show that the presence of CB[6] results in an upfield shift for some of the protons on the butyl chains of BAMB, indicating the formation of a [2]pseudorotaxane. It appears that the

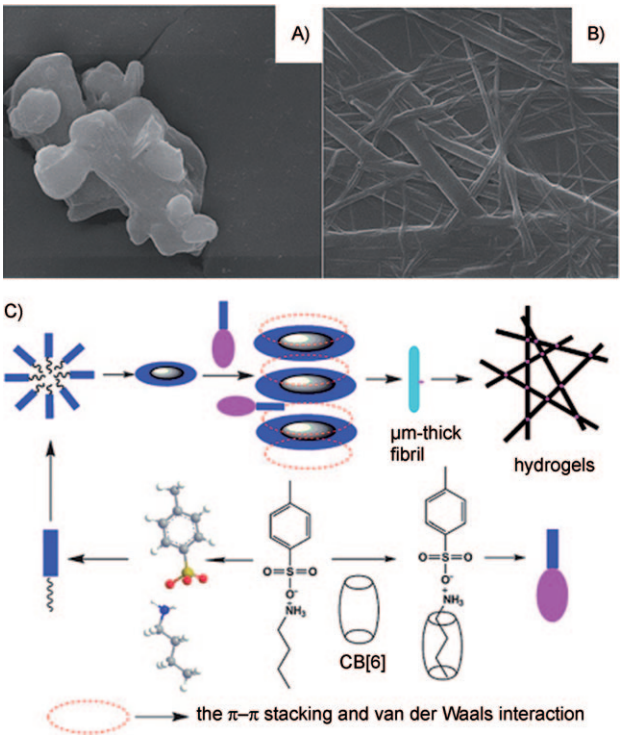

Figure 4. SEM images of A) pure BAMB and B) the xerogel of BAMB hydrogel formed in presence of CB[6]. C) Schematic showing proposed hierarchical assembly of hydrogels. Reproduced with permission from the Royal Society of Chemistry.[55]

CB[6]–BAMB pseudorotaxane acts as an additive, disrupting the crystallization process and resulting in gel formation. The authors put forward a speculative mechanism for the hierarchical assembly of the hydrogels which is shown in Figure 4C. It would be interesting to see the effect of a competitive guest for CB[6] on the gel structure.

3. Enhancement and Applications

Kim and co-workers[56] have utilized the guest-binding properties of curcurbit[7]uril to introduce stimuli-responsive functionality to a gel. Cucurbit[*n*]urils are a family of cavitands with a hydrophilic cavity accessible through two identical hydrophilic portals; as a result their host–guest chemistry is considerably different from that of other macrocyclic cavitands. Cucurbit[7]uril, but none of the other cucurbiturils, dissolves in warm solutions of dilute mineral acids and forms gels upon cooling (Figure 5). A combination of AFM, IR, SAXS, and single-crystal data indicate gel fibrils are formed by CB[7] packed in a herringbone motif and held together by extensive C–H···O and water/oxonium ion mediated hydrogen bonding. The gels are sensitive to pH,

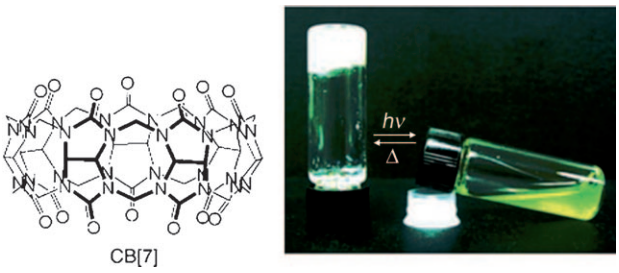

Figure 5. Left: Structure of CB[7]. Right: Guest-induced stimuli-responsive behavior of CB[7] gel; photographs of CB[7] (5 wt%) gel containing 0.1 equivalent of *trans*-4,4′-diaminostilbene dihydrochloride before (left) and after (right) UV irradiation (365 nm) for 2 h.[56]

with optimum gel formation between pH 0 and 2. The system forms sols upon addition of alkali-metal ions. This is thought to highlight the importance of complexation of oxonium ions with the CB[7] portals to gel formation.

Both the *cis* and *trans* forms of 4,4′-diaminostilbene dihydrochloride are known to form stable inclusion complexes with CB[7]. CB[7] forms a white gel in the presence of small amounts of the *trans* isomer; however, irradiation of the gel with UV light results in the formation of a yellow sol. Heating for 2 h followed by slow cooling regenerates a pale yellow gel, which again forms a sol on irradiation. The breakup of the gels through disruption of the hydrogen-bonding network is thought to be greater with the *cis* isomer than with the *trans*. The presence of a host cavity allows for the introduction of novel functionalities by the inclusion of guests. This sidesteps the incorporation of functionalities into the gelator molecules themselves which could potentially disrupt or alter the gel structure, as observed in other examples of stimuli-responsive gels.

Xing et al.[57] have developed a particularly stable DMSO metallogel based on calix[4]arene **7** and $[Pd(en)(H_2O)_2]^{2+}$ (en = ethylenediamine) which has been used to extract neutral organic molecules from aqueous solution (Figure 6). At a concentration of 2 wt% gelator a highly stable gel was formed which did not redissolve or leach Pd^{II} upon heating or sonication, over a range of pH, or in the presence of a wide range of solvents. The uptake of toluene by the gel from an aqueous solution was measured using UV absorbance. The results showed first-order kinetics and gave a partition coefficient of toluene between the gel and aqueous phase of approximately 47.0 ± 2.0. This corresponds to a $\Delta G_{298} =$

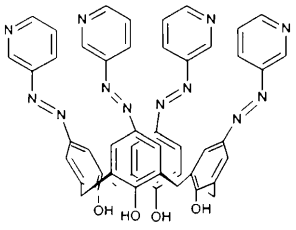

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Figure 6. Azocalix[4]arene gelator **7** forms stable metallogel with palladium complexes $[Pd(en)(H_2O)_2]^{2+}$ or $[Pd(OAc)_2]$ in DMSO.

-2.3 ± 0.4 kcal mol^{-1}, which is comparable with commonly used absorbents such as active carbon. Similar experiments have been carried out using other, non-cavity-containing gelators using a range of substances.[58,59] However, the specificity of cavitands potentially offers additional control over the selective uptake, storage, and release of molecular guests.

Xing et al.[60] were also able to utilize the Pd^{II} moieties of this gel as catalytic centers for the oxidation of benzyl alcohol to benzaldehyde. When $[Pd(en)(H_2O)_2]^{2+}$ served as the metal-containing unit, the catalytic turnover of this gel was twice that of free $[Pd(OAc)_2]$ and three times that of the corresponding dry gel. This increase was attributed to the superior stability of the catalyst in the gel, which unlike the free catalyst did not form Pd black. The rate of the catalytic reaction was found to be controlled by diffusion of the substrate from the surrounding solution to the catalytic sites in the gel. A leveling off of the rate was attributed to saturation of the gel with benzaldehyde. It proved possible to reuse the gels, albeit with reduced turnover which was attributed to the retention of benzaldehyde. Furthermore, because pyridine moieties form part of the gel structure, molecular pyridine was not required for the oxidation reaction, greatly simplifying the subsequent purification procedure.

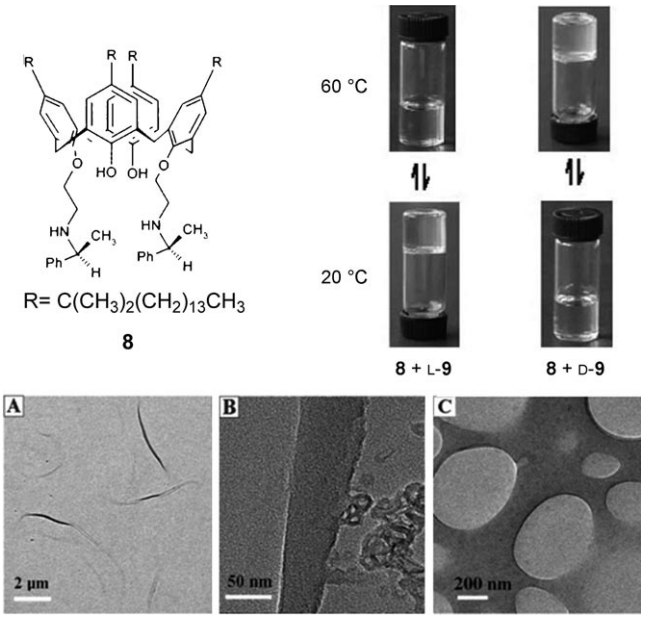

Figure 7. Top: Structure of **8** and photographs showing phase changes for gels of **8** with the D and L enantiomers of 2,3-dibenzoyltartaric acid. Bottom: TEM images showing **8** and D-**9** at 60 °C (A and B) and 20 °C. Reproduced with permission from the Royal Society of Chemistry.[61]

4. Other Cavity-Containing Gelators

The majority of supramolecular gels are prepared by dissolving the LMWG in a suitable (hot) solvent and allowing the solution to cool, usually to room temperature. Zheng and co-workers[61] were able to form a two-component gel from a hexane solution of the chiral calix[4]arene **8** and L-2,3-dibenzoyltartaric acid (L-**9**) in this manner (Figure 7). However, the same conditions but using the other enantiomer, D-**9**, led to a clear solution. Surprisingly, whilst heating **8** and L-**9** to 60 °C led to the formation of a clear solution, heating **8** and D-**9** led to the formation of a gel. This type of heat-set gel is very rare for low-molecular-weight gelators. Detailed microscopic studies showed that both gels consist of ribbonlike fibers but the heat-set gel also contains some of the egglike vesicles found in the solution at 20 °C. It is thought that because of the mismatched interactions between the chiral centers of **8** and D-**9**, the fibrous lamellar structures that give rise to the gels at 60 °C are not favored at 20 °C. Unmatched interactions will be more significant at lower temperatures where intermolecular distances are shorter. When the flat lamellae are curved into vesicles, the unfavorable interactions between the chiral centers of **8** and D-**9** can be reduced.

Many examples of metallogelators are known[62] where metal ions become incorporated into the gel structure triggering or enhancing gelation. In contrast, anions have often been reported to inhibit gel formation by disrupting bonding motifs such as urea tapes. Much more unusual is the case where gelation is triggered by the presence of specific anions, as reported by Ogden and co-workers.[63] Whilst studying the interactions of the proline-functionalized calix[4]arene **10** with metal ions, they noticed that **10** formed aqueous gels in the presence of various salts (Figure 8). Investigating the phenomena further, Ogden's group showed that gel formation is critically dependent on the choice of anion, with cations having a noticeable but less significant effect. Their observations were found to correlate well with the Hofmeister series (Figure 8), which classifies ions in order of their ability to order water, an effect that is much stronger for anions than cations.[31] More hydrated salts (termed kosmotropic) have the effect of strengthening the hydrophobic effect and decreasing the solubility of nonpolar molecules. Less hydrated salts (termed chaotropic) have the opposite effect, increasing the solubility of nonpolar molecules. The origins of the effect remain an area of active investigation. In the presence of kosmotropic anions, such as SO_4^{2-}, **10** remained in solution whilst more chaotropic anions, such as nitrate, bromide, and chloride, induce gel formation. With strongly chaotropic anions, such as ClO_4^- and I^-, a gel initially forms before **10** crystallizes out of solution. The

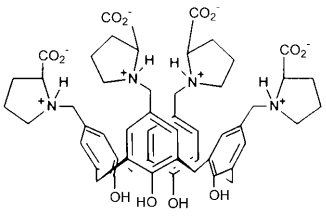

Figure 8. Calixarene-based pH-triggered gelator **10** and the Hofmeister series of anions in order left to right from most chaotropic to most kosmotropic.

conclusion reached is that the choice of electrolyte determines the extent of agglomeration of these aggregates, with gel formation occurring within a particular regime.

5. Conclusion

The presence of a molecular cavity brings an additional dimension to supramolecular gels. Host–guest interactions can be used in a variety of ways to form the supramolecular polymers and cross-linking interactions required for gel formation. The presence of such interactions at different levels of self-assembly of the gel structure means that the addition of competitive guests can be used to disrupt or adapt the gel-formation process and create responsive materials. Cavitands can themselves be used as additives to modify crystal growth resulting in gel formation. Self-inclusion by cavitands can be used to drive gel formation or cavitands can simply provide a useful, preorganized scaffold onto which gel-forming functional groups can be appended. Where the host cavity is not essential to gel formation, it can be used to introduce novel functional groups to the gel system without the need to build them in synthetically. Combining the physical properties of gels with the selectivity of cavitands offers great potential for extracting, storing, and releasing compounds such as pharmaceuticals. Cavitand-based metallogels combine the high surface area associated with homogeneous catalysis with the ease of separation afforded by a heterogeneous process. Cavity-containing gels have also been shown to display some rare gel properties such as gelation triggered by heating or the addition of anions. We hope this Minireview illustrates how broader principles of supramolecular chemistry and an understanding of gel structure can be intelligently utilised in the design of "smart" materials.

Addendum

In the period between the acceptance and publication of this manuscript a number of high-profile papers on this topic have been released, for example, on photoresponsive pseudopolyrotaxane hydrogels based on competing host–guest interactions,[64] hydrogels composed of organic amphiphiles and α-cyclodextrin,[65] and light-controlled protein release from a supramoleculare hydrogel.[66]

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