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Supramolecular Assemblies of Sulfonatocalixarenes with Phenanthroline: Factors Governing Capsule Formation versus Bilayer Arrangements

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Abstract: Four crystalline complexes were prepared by the inclusion complexation of the 1,10-phenanthrolinium ion (Phen) with *p*-sulfonatothiacalix[4]-arene (TCAS) (**2** from a solution at pH 1–2 and **4** from 1 M HCl) and with *p*-sulfonatocalix[5]arene (C5AS) (**3** from a solution at pH 1–2 and **5** from 1 M HCl) upon varying the acidity of the solution. By combining the results obtained for complexes **2**–**5** with those for our previously reported complex (**1**), *p*-sulfonatocalix[4]arene (C4AS) complexed to Phen, it was revealed that *p*-sulfonatocalixarenes (CASs) form "bis-molecular" capsules (**1**, **2**, and **3**) around Phen at pH 1–2, whereas complexes **4** and **5** display distinct host–guest inclusion behavior at higher acid concentrations. The degree of compactness of the capsules increases with the enlargement of the calixarene cavity, which is affected significantly by both the penetration depth of Phen and the structure of the Phen dimer. Furthermore, the complexation behavior of TCAS/C5AS with Phen in 1 M DCl was investigated by using NMR spectroscopy, and was discussed in comparison with the previously reported results obtained from solutions at pH 2.0.

Keywords: calixarenes · capsules · host–guest systems · supramolecular chemistry · X-ray diffraction

Introduction

Molecular capsules[1] have attracted extensive attention in recent years owing to their potential applications in binding, separation, and sensing of small molecules and ions;[2] stabilization of reactive intermediates; and catalysis.[3,4] Among them, a system of current interest is the molecular assembly formed by calixarenes as a result of their intrinsic bowl shape, which makes them versatile building blocks for forming capsules.[5] To date, most of the molecular capsules reported, mainly by the groups of Rebek and Böhmer, were dimeric in nature and assembled by hydrogen bonds.[6,7] Strong metal-coordination bonds represent another widely employed tool in the construction of predefined molecular capsules.[8] Most biological processes take place in an aqueous environment, therefore the synthesis of supramolecular containers in aqueous solution for biochemical applications has become increasingly significant. As a result, the groups of Schrader and Reinhoudt simultaneously reported the preparation of molecular capsules based on ionic interactions between oppositely charged calixarenes in polar solutions.[9,10]

In the pursuit of water-soluble capsules, highly charged *p*-sulfonatocalixarene (CAS) molecules have been exploited by using a combination of supramolecular interactions between the molecular subunits, namely, coordination, hydrogen-bonding, electrostatic, and van der Waals interactions. Seminal work in this area by Raston and co-workers opened the field towards the development of solid-state capsules based on two *p*-sulfonatocalix[4,5]arenes; many of these capsules that are capable of encapsulating other molecules such as crown ethers, tetraprotonated cyclam, diprotonated [2,2,2]cryptand, amino acids, H_2SO_4, and so forth have been established.[11,12,13] Recently, two new compact molecular capsules of *p*-sulfonatothiacalix[4]arene (TCAS) have been synthesized by using suitable guest molecule templates, namely, 1,2-bis(imidazol-1′-yl)ethane or 2,2′-bipyridine.[14] From the aforementioned results it can be deduced that, for CAS molecules, formation of a molecular capsule is dependent on guest size and/or shape to a large extent. In other words, we can design fascinating supramolecular architectures of CAS by subtly altering guest molecules or other factors, which is an area that has increasingly attracted our attention over recent years.[15] Herein, we wish to report re-

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sults of our investigations into the guest-induced formation of capsules of CAS, by using the 1,10-phenanthrolinium ion (Phen) as the guest molecule, and their disassembly. Phen was selected as a suitable guest because the inclusion complexation of Phen within CAS molecules is likely to result in the formation of a π-stacked motif, and offers the possibility of building novel aggregations.[16] A total of five solid-state complexes were synthesized: capsule complexes **1**–**3** are formed at pH 1–2, whereas the remaining complexes (**4** and **5**) are formed by the disassembly of the capsules that occurs in a more acidic mother liquor of 1 M HCl. Furthermore, a host–guest solution study was performed by using NMR spectroscopy for comparison with previous results.[17] Careful analysis into the manner of the host–guest binding, and a subtle comparison of the properties of the mother liquor, will help us to understand the key factors for constructing molecular capsules based on CAS.

Results and Discussion

Solid-state structures: Throughout our ongoing investigation of inclusion phenomena and the assembly behavior of different CAS derivatives with Phen as a guest, five complexes were obtained in their monocrystalline forms by slow evaporation of the solvent. Complexes **1**–**3** (Figure 1) were obtained from a solution at pH 1–2, whereas a 1 M HCl solution yielded complexes **4** and **5**. Their molecular structures have been determined by means of single-crystal X-ray diffraction analyses. Complex **1** was briefly introduced in our previous solution study,[17] and the other complexes (**2**–**5**) all crystallize in the same triclinic space group $P\bar{1}$. For capsule **1**, the asymmetric unit in the crystal structure contains one crystallographically distinct *p*-sulfonatocalix[4]arene (C4AS), four Phen, and 9.5 water molecules. Alternatively, in capsule **2** the asymmetric unit contains one TCAS, four Phen, and 14 water molecules, whereas that of capsule **3** contains one *p*-sulfonatocalix[5]arene (C5AS), five Phen, and 8.5 water molecules. Some sulfonate groups of CAS may be protonated in complexes **4** and **5** as a result of increasing the solution acidity from pH 1–2 to that of 1 M HCl, which alters the asymmetric unit. Therefore, the asymmetric unit contains one TCAS, 2.5 Phen, and 10 water molecules in complex **4**, and one C5AS, one Phen, and 8.5 water molecules in complex **5**. Unfortunately, it was not possible to obtain the crystal structure of C4AS complexed to Phen in 1 M HCl. Several attempts at crystallization failed (using both the methods of hydrothermal synthesis and solvent evaporation), and only a yellow precipitate of the complex was obtained. Analysis of the X-ray diffraction data shows the fascinating structures of the different guest-induced "bis-molecular" capsules (**1**–**3**), whereas in complexes **4** and **5** capsule formation was not possible as a consequence of the increased acidity. Furthermore, there are also obvious differences in the extended structures of the complexes between those formed at pH 1–2 and at 1 M HCl concentrations.

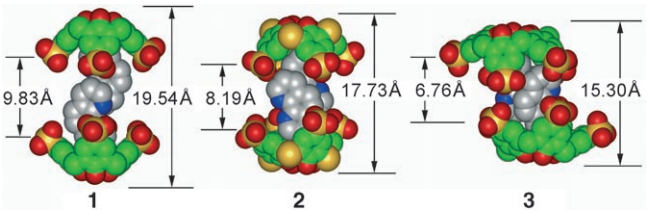

Figure 1. Bis-molecular capsules formed by using Phen as a guest template with *p*-sulfonatocalixarenes C4AS (**1**), TCAS (**2**), and C5AS (**3**) at pH 1–2.

In capsules **1**–**3**, one Phen guest is bound in each CAS cavity in the same vertical orientation (Figure 1), while the others act as counterions in the crystal lattice. However, the penetration depths[18] of Phen and the host–guest interactions differ from **1** to **3**. In **1**, Phen penetrates into the C4AS cavity to a depth of 4.268 Å and is stabilized by three noncovalent interactions, including two edge-to-face π-stacking interactions (C–H···aromatic ring: 2.719 Å, 154.2°; 2.708 Å, 150.4°) and one nonconventional hydrogen bond (C···O, 3.378 Å). In **2**, Phen penetrates into the TCAS cavity to a depth of 4.542 Å and is also stabilized by two edge-to-face π-stacking interactions (C–H···aromatic ring: 2.991 Å, 145.6°; 3.293 Å, 126.1°) and one nonconventional hydrogen bond (3.462 Å). In **3**, Phen is deeply bound in the C5AS cavity (3.923 Å), but stabilized by only two π-stacking interactions (π aromatic ring···π aromatic ring: 3.917 Å; C–H···aromatic ring: 3.239 Å, 152.6°).

It is worth mentioning that in these three cases (**1**–**3**) a face-to-face dimer is formed by the π···π stacking interaction of one bound Phen with another bound Phen molecule, which results in the formation of the 2:2 bis-molecular capsule (Figure 1). Upon enlargement of the cavity of CAS (C4AS→TCAS→C5AS), the capsules become more and more compact. As a result, the capsule based on C5AS presents the highest degree of compactness, which is considered to be reasonable from the aforementioned penetration depths of Phen. However, the fact that the capsule based on TCAS (**2**) is more compact than the capsule based on C4AS (**1**) cannot be explained from their penetration depths alone. Careful examination of the crystal structures of capsules **1** and **2** confirm differences between the Phen dimers in **1** and **2**. Figure 2 shows that the two Phen molecules in **1** stack through one π···π interaction between the nonprotonated heterocycles (3.427 Å), whereas the two Phen molecules in **2** form a face-to-face dimer through two π···π interactions between the central ring and the nonprotonated heterocycle (3.698 Å). In the same way, the Phen dimer in **3** is also reinforced through two π···π interactions between the central ring and the nonprotonated heterocycle (3.598 Å). Therefore, the Phen dimer in **1** acts like a pillar that holds the C4AS molecules further apart than the TCAS molecules in **2** and the C5AS molecules in **3**, which results in **1** being the least compact capsule.

During capsule formation, aside from the interactions between host and guest, the stability of the capsule is also rein-

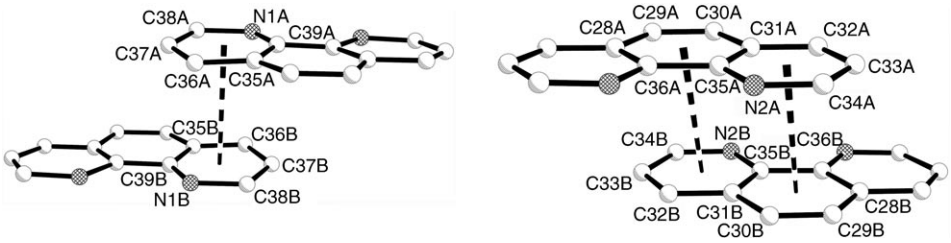

Figure 2. Views of the Phen dimers in **1** (left) and **2** (right). The dashed lines represent the intermolecular π···π interactions.

forced by several noncovalent interactions from water molecules. By using the most compact capsule (**3**) as an example, it can be seen from Figure 3 that a total of 12 hydrogen

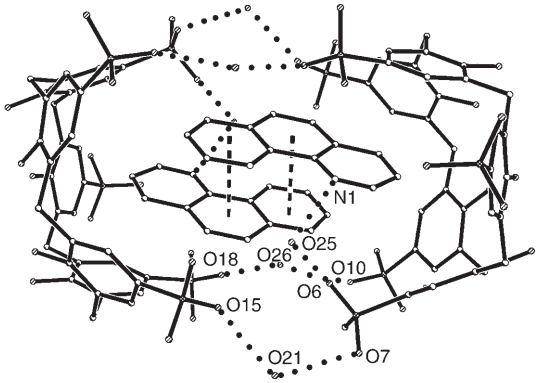

Figure 3. A view of the 12 hydrogen bonds (•••••) that participate in closing capsule **3**, and the two π···π interactions (-----) between Phen groups. For clarity, only one set of hydrogen bonds have been labeled.

bonds participate in closing the capsule. These hydrogen bonds are generated by two equivalent sets of three water molecules that are observed in the crystal structure. Each set of water molecules has six crystallographically distinct hydrogen bonds. For example, one set labeled O21, O25, and O26 (Figure 3) has the following hydrogen-bond distances: N1···O25, 2.916 Å; O25···O6, 2.839 Å; O21···O7, 2.960 Å; O21···O15, 2.820 Å; O26···O10, 2.831 Å; O26···O18, 3.107 Å.

Upon increasing the acidity of the mother liquor through the use of 1 M HCl solutions, the crystalline complexes of Phen with TCAS (**4**) and C5AS (**5**) are also obtained. Under these conditions, the binding geometry of Phen within CAS changes dramatically. The Phen molecules in **4** and **5** are included into the calixarene cavity horizontally, as shown in Figure 4. The Phen molecule in **4** is bound at an angle whereas the Phen molecule in **5** is bound in the cavity entirely horizontally. The host–guest interactions in complexes **4** and **5** also differ from those observed in capsules **1**–**3**. In complex **4**, a total of four noncovalent interactions contribute to the complexation of TCAS with Phen, including two C–H···π interactions (2.750 Å, 142.6°; 2.811 Å, 143.8°) and two nonconventional hydrogen bonds (3.414, 3.349 Å). In complex **5**, there is one π···π (3.813 Å) and two C–H···π (2.637 Å, 149.7°; 2.623 Å, 137.4°) interactions between C5AS and Phen. The slight difference in binding modes between **4** and **5** may arise from the size of the cavity. The cavity of TCAS is not large enough to accommodate Phen in a fully horizontal mode, whereas the

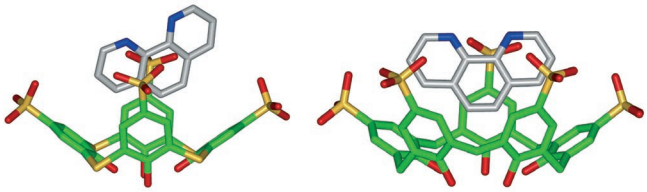

Figure 4. The molecule structures of complexes **4** (left) and **5** (right) in 1 M HCl. The other Phen counterions, water molecules and hydrogen atoms have been omitted for clarity.

larger cavity of C5AS is capable of horizontal complexation. There is an implication that the crystal complex of C4AS with Phen in a 1 M HCl solution is difficult to prepare as a result of the limited cavity of C4AS. On the other hand, guest-induced conformational perturbations of calixarenes are also different between the compounds formed in pH 1–2 and 1 M HCl solutions. In capsule **2**, the TCAS cone structure is pinched to give C_{2v} symmetry with sulfur distances of 11.899 and 9.671 Å for oppositely oriented sulfonate groups. For complex **4**, TCAS has a cone conformation of C_{2v} symmetry that is pinched to a greater extent (S···S: 13.062 and 8.217 Å). This pinched symmetry can also be observed in C5AS, as shown by the actual φ (in **3**: 125.6, 51.1, 92.8, 109.1, 41.8°; in **5**: 106.9, 72.9, 89.8, 83.4, 60.9°) and χ (in **3**: −84.2, −94.4, −83.9, −86.0, 91.0°; in **5**: −74.8, −104.3, −56.5, −88.3, 89.4°) torsion angle values of C5AS according to the Ugozzoli–Andreetti convention[19] .

The most significant observation for these complexes concerns the fact that **1** to **3** form as bis-molecular capsules, whereas **4** and **5** merely form as inclusion complexes of Phen within CAS. The orientations of the Phen guests in complexes **4** and **5** do not lead to the formation of π···π dimers, so we can conclude that these Phen–Phen π···π interactions are key factors in stabilizing the capsule structures in the solid state. A reasonable explanation for the different binding interactions is that all the sulfonate groups of CAS are ionized at pH 1–2, and the electrostatic interactions between SO_3^- and positively charged NH^+ play as important a role in complexation as π-stacking interactions. An alternative explanation is that some of the sulfonate groups are protonated in the 1 M HCl solution, thus weakening the largely electrostatic interactions, and as a result, the π-stacking interactions between CAS and Phen become the dominating forces for complexation. The change of guest orienta-

tion from vertical to horizontal reflects the change in the host–guest interactions, for which the center of positive charge in the Phen guest moves away from the cavity and the aromatic portion moves to be more in line with the cavity to form stronger π-stacking interactions.

As a result of the different binding modes and number of counterions in complexes **1**–**3** and those of **4** and **5**, the extended structures of the complexes are also different. For example, the packing structure of **3** has a contorted bilayer arrangement as a result of the dominating forces of π···π interactions (3.582 Å; 3.786 Å) and nonconventional hydrogen bonds (2.587, 3.256 Å), as shown in Figure 5a. One of the

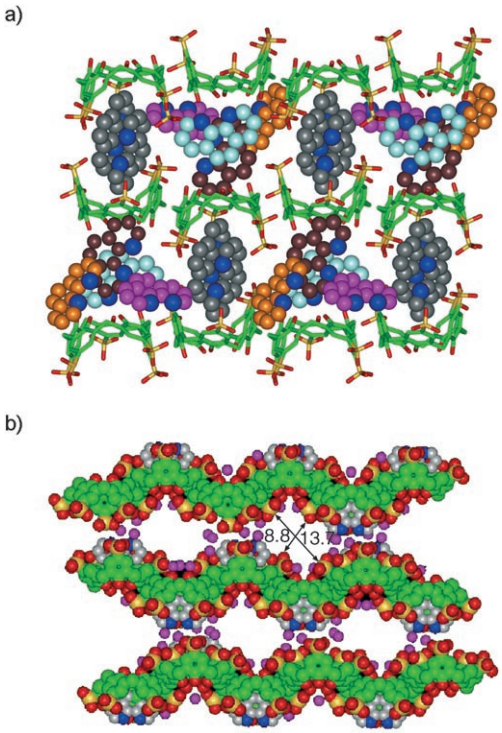

Figure 5. a) The extended structure of crystal **3**. A conventional bilayer array was formed. The water molecules and hydrogen atoms have been omitted for clarity. b) The extended bilayer structure of crystal **5**, which possessed microporous channels.

five Phen guests encapsulated within the cavity of C5AS and the other Phen counterions were restricted to either the hydrophilic or the hydrophobic layer. From this position they were able to contribute to the stabilization of the bilayer structure of C5AS. In the extended structure of **5**, C5AS molecules arranged themselves in a typical up-down fashion to form a "zig-zag" bilayer arrangement through two π···π interactions (3.738 Å, 3.682 Å) and one additional hydrogen-bond interaction (2.915 Å). However, it was not anticipated that the packing structure would contain many ordered nanopores when viewed from the crystallographic $a \times b$ plane. However, these pores (8.6×13.7 Å^2) extended infinitely along the crystallographic c direction to form one-dimensional nanotubes (Figure 5b). The solvated water molecules lie around the walls of the channels forming "water pipes" within the nanotubes. Careful examination of the structure of **5** showed that each pore was formed by a close hydrogen-bonding system assisted by water molecules (2.915, 2.609, 2.606, 2.679, 2.711, 2.753, 2.728 Å).

Solution investigations: To further investigate the complexation behavior of TCAS/C5AS with Phen in a 1 M HCl solution, ^{1}H NMR experiments were performed in 1 M DCl/D_2O solutions. The ^{1}H,^{1}H 2D ROESY NMR spectrum of C5AS with Phen shown in Figure 6 exhibits three clear cross peaks (circled A, B, and C) between a proton of Phen and the aromatic calixarene protons (Ar–H). Peak A represents the cross peak involving H2 of Phen, peak B represents that involving H3, and peak C represents that involving H4. This ROESY NMR result (in 1 M DCl) is distinctly different from that of C5AS with Phen at pH 2.0.[17] The cross peak between H1 and Ar–H in **5** has disappeared, which indicates that the H1 portion of Phen is remote from the cavity of C5AS in the 1 M DCl solution. In addition, the correlation of H4 is much stronger than those of H2 and H3, and therefore, we rationally deduce that Phen is bound horizontally within the C5AS cavity in the 1 M DCl solution with the same binding interactions as in the crystal structure.

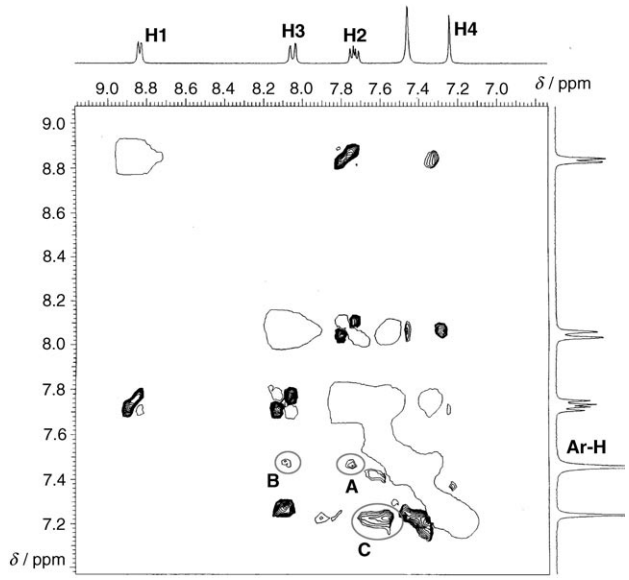

Figure 6. The 2D ROESY NMR spectrum of C5AS with Phen with a mixing time of 300 ms at 25 °C. The concentrations of both host and guest are about 10 mM.

The thermodynamic parameters and binding ability of TCAS/C5AS with Phen in a 1 M HCl solution cannot be measured by using isothermal titration calorimetry (ITC) owing to limitations of the apparatus, thus an NMR spectroscopic titration experiment was performed to study the complexation phenomena of TCAS/C5AS with Phen. The obtained complex stability constant values (K_S) and Gibbs energies are listed in Table 1 together with our previous ITC

Table 1. Complex stability constants (K_S) and Gibbs energies ($\Delta G°$) for the 1:1 intermolecular complexation of Phen with either TCAS or C5AS at 25 °C.

Condition	Host	K_S [M^{-1}]	$-\Delta G°$ [kJ mol^{-1}]
pH 2.0[a]	TCAS	4981	21.1
	C5AS	2281	19.2
1 M DCl	TCAS	323	14.3
	C5AS	249	13.7

[a] Results taken from ref. [17].

results recorded at pH 2.0. In fact, the complexation of calixarenes with Phen retains 1:1 stoichiometry at both pH 2.0 and in a 1 M DCl solution, which is consistent with the recent solution studies reported by Raston et al.[20] Therefore, 1:1 solution complexes act as precursors to solid-state capsules.

The K_S values obtained for the complexation of TCAS/C5AS with Phen in 1 M DCl, shown in Table 1, are much lower than those obtained at pH 2.0. Through collating previous results and the information from the crystal structures of **4** and **5** it seems that the unusual differences in K_S between 1 M DCl and pH 2.0 should be attributed to the protonation of the sulfonate groups of CAS in 1 M DCl. The partial dehydration of NH^+ in the guest and SO_3^- in the host upon interaction plays a crucial role in controlling the binding ability and selectivity of CAS.[17] The desolvation effect during the course of complexation in the 1 M DCl solution is not as significant as at pH 2.0 because some of the sulfonate groups are protonated. On the other hand, the horizontal complexation modes of TCAS/C5AS with Phen in 1 M HCl solutions make the loss of conformational degrees of freedom more obvious than those at pH 2.0 with vertical complexation modes, which also contributes to a reduction of complex stability. Therefore, the complex stability constants of CAS with Phen in 1 M HCl solutions are much smaller than those at pH 2.0, although there are more π-stacking or hydrogen bonding interactions between TCAS/C5AS and Phen in 1 M HCl than at pH 2.0 (cf. crystal structures).

Conclusion

In summary, three "bis-molecular" capsules possessing different degrees of compactness were constructed by the complexation of C4AS, TCAS, and C5AS with Phen at pH 1–2. Increasing the acidity of the mother liquor by using 1 M HCl as the solvent changed the complexation orientation of Phen within CAS from the original vertical mode to a horizontal mode, which prevented the dimerization of 1,10-phenanthrolinium guests required for capsule formation. The 2D ROESY NMR experiment showed that there is consistency between the binding interactions in solution and in the solid-state crystal structures. The experiment also showed that the binding ability of CAS with Phen in 1 M HCl is lower than that in solution at pH 1–2, which is mainly a result of the protonation of the sulfonate groups in CAS. These observations demonstrate unambiguously that pH value is as important a factor for the manipulation and design of supramolecular architectures based on CAS as the choice of guest molecule.

Experimental Section

Materials: The three *p*-sulfonatocalixarenes, namely, tetrasodium *p*-sulfonatocalix[4]arene (C4AS),[21] tetrasodium *p*-sulfonatothiacalix[4]arene (TCAS),[22] and tetrasodium *p*-sulfonatocalix[5]arene (C5AS),[23] were synthesized and purified according to literature procedures. Guest molecule 1,10-phenanthroline was commercially available and used without further purification. In 1 M HCl, 1,10-phenanthroline is monoprotonated to give the 1,10-phenanthrolinium ion (Phen) according to its pK_a value of 4.84 at 25 °C.[24]

Measurements: ^{1}H and ^{1}H,^{1}H 2D ROESY (rotating frame Overhauser effect spectroscopy) NMR spectra were recorded in 1 M DCl solutions (D_2O) on a Varian Mercury VX300 spectrometer. Chemical shifts (δ in ppm) in water were externally referenced to 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) in order to avoid any possible interaction with CAS or the guest molecule. ^{1}H NMR spectroscopic titrations were carried out by keeping the guest concentration fixed (1×10^{-3} mol dm^{-3}) and varying the host concentrations to obtain the desired host/guest ratio. Chemical shifts for each titration were refined to obtain the final K_S values.

Synthesis: The synthesis of $[C4AS^{4-}][Phen^+]_4\cdot9.5H_2O$ (**1**) has been reported in our previous work.[17] Crystals of $[TCAS^{4-}][Phen^+]_4\cdot14H_2O$ (**2**), $[C5AS^{5-}][Phen^+]_5\cdot8.5H_2O$ (**3**), $[TCAS^{4-}+1.5H^+][Phen^+]_{2.5}\cdot10H_2O$ (**4**), and $[C5AS^{5-}+4H^+][Phen^+]\cdot8.5H_2O$ (**5**) were prepared by using the method of slow evaporation of the solution.

Preparation of complex ***2***: Phen (4 equiv) was added to an aqueous solution of TCAS (0.05 mmol, 20 mL). The solution was stirred and adjusted to pH 1–2 by adding 1 M HCl dropwise. After filtration, the filtrate was left to evaporate for about five days. The colorless crystal that formed was collected along with its mother liquor for X-ray crystallographic analyses.

Preparation of complex ***3***: Phen (5 equiv) was added to an aqueous solution of C5AS (0.10 mmol, 50 mL). The solution was stirred and adjusted to pH ≈ 2 by adding 1 M HCl dropwise. After filtration, the filtrate was left to evaporate for about two days. The colorless crystal that formed was collected along with its mother liquor for X-ray crystallographic analyses.

Preparation of complex ***4***: TCAS (0.05 mmol) was dissolved in 1 M HCl (15 mL) and Phen (4 equiv) was added. The solution was stirred briefly before it was filtered. The filtrate was then collected and left to evaporate slowly for about two days. The colorless crystal that formed was collected along with its mother liquor for X-ray crystallographic analyses.

Preparation of complex ***5***: C5AS (0.10 mmol) was dissolved in 1 M HCl solution (30 mL) and Phen (5 equiv) was added. The solution was stirred briefly before it was filtered. The filtrate was then left to evaporate for about three weeks. The yellow crystal that formed was collected along with its mother liquor for X-ray crystallographic analyses.

X-ray crystal structure analysis: The X-ray intensity data for **2**–**5** were collected on a standard Bruker SMART-1000 CCD Area Detector System equipped with a normal-focus molybdenum-target X-ray tube ($\lambda = 0.71073$ Å) operated at 2.0 kW (50 kV, 40 mA) and a graphite monochromator at $T = 293(2)$ K. The structures were solved by using direct methods and were refined by employing full-matrix least-squares cycles on F^2 (Bruker, SHELXTL-97[25]). Summaries of crystal data and structure refinements are given in Table 2. CCDC-606937, -606938, -606939, and -606940 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Three sulfonate groups of C5AS in **5** are disordered and were refined in two positions with equal occupancies. In addition, the data of **5** is very weak (only 45 % observed), which leads to the high R values for this structure.

Table 2. Crystal structure data and details of structure refinements for complexes **2**–**5**.

	2	**3**	**4**	**5**
CCDC no.	CCDC-606937	CCDC-606938	CCDC-606939	CCDC-606940
formula	$C_{72}H_{76}N_8O_{30}S_8$	$C_{95}H_{87}N_{10}O_{28.5}S_5$	$C_{54}H_{56}N_5O_{26}S_8$	$C_{47}H_{55}N_2O_{28.5}S_5$
M_r [g mol^{-1}]	1789.89	1985.05	1447.52	1264.23
crystal system	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	14.247(4)	16.725(2)	13.8138(10)	11.1409(13)
b [Å]	17.113(5)	16.967(2)	15.0545(12)	17.431(2)
c [Å]	18.109(5)	17.348(2)	16.5097(13)	20.135(2)
α [°]	68.997(4)	68.604(2)	74.8050(10)	115.410(2)
β [°]	72.254(5)	82.553(2)	69.0100(10)	91.426(2)
γ [°]	82.636(5)	84.779(2)	83.4810(10)	92.933(2)
V [Å^3]	3924.9(19)	4539.9(10)	3092.7(4)	3522.5(7)
Z	2	2	2	2
ρ_{calcd} [g cm^{-3}]	1.515	1.452	1.554	1.192
μ [mm^{-1}]	0.319	0.217	0.379	0.238
$F(000)$	1864	2070	1502	1318
crystal size [mm^3]	0.20×0.18×0.16	0.14×0.12×0.10	0.28×0.24×0.22	0.40×0.36×0.28
θ range [°]	1.25–26.46	1.23–25.01	1.40–25.01	1.83–25.01
reflns collected/unique	32721/15971 (R_{int} = 0.0502)	22244/15742 (R_{int} = 0.0401)	15803/10818 (R_{int} = 0.0170)	17821/12198 (R_{int} = 0.0331)
GOF	1.028	1.017	1.053	1.128
final R indices [$I>2\sigma(I)$]	$R1$ = 0.0666, $wR2$ = 0.1724	$R1$ = 0.0699, $wR2$ = 0.1747	$R1$ = 0.0469, $wR2$ = 0.1261	$R1$ = 0.1129, $wR2$ = 0.2914
R indices (all data)	$R1$ = 0.1368, $wR2$ = 0.2145	$R1$ = 0.1506, $wR2$ = 0.2264	$R1$ = 0.0614, $wR2$ = 0.1425	$R1$ = 0.2058, $wR2$ = 0.3741

To balance the charges, TCAS in **4** should possess 1.5 protonated sulfonate groups and C5AS in **5** should possess 4 protonated sulfonate groups, which are acceptable given the pH of the reaction solution. Unfortunately, it was not possible to locate all hydrogen atoms from the Fourier difference map for this to be clarified.[13c]

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