Supramolecular Chemistry

Deutsche Ausgabe: DOI: 10.1002/ange.201411857
Internationale Ausgabe: DOI: 10.1002/anie.201411857

Unexpected Self-Sorting Self-Assembly Formation of a [4:4] Sulfate:Ligand Cage from a Preorganized Tripodal Urea Ligand**

Komala Pandurangan, Jonathan A. Kitchen, Salvador Blasco, Elaine M. Boyle, Bella Fitzpatrick, Martin Feeney, Paul E. Kruger, and Thorfinnur Gunnlaugsson**

Dedicated to Prof. John M. Kelly on the occasion of his 70th birthday

Abstract: *The design and synthesis of tripodal ligands **1–3** based upon the N-methyl-1,3,5-benzenetricarboxamide platform appended with three aryl urea arms is reported. This ligand platform gives rise to highly preorganized structures and is ideally suited for binding SO_4^{2-} and $H_2PO_4^-$ ions through multiple hydrogen-bonding interactions. The solid-state crystal structures of **1–3** with SO_4^{2-} show the encapsulation of a single anion within a cage structure, whereas the crystal structure of **1** with $H_2PO_4^-$ showed that two anions are encapsulated. We further demonstrate that ligand **4**, based on the same platform but consisting of two bis-urea moieties and a single ammonium moiety, also recognizes SO_4^{2-} to form a self-assembled capsule with [4:4] SO_4^{2-}:**4** stoichiometry in which the anions are clustered within a cavity formed by the four ligands. This is the first example of a self-sorting self-assembled capsule where four tetrahedrally arranged SO_4^{2-} ions are embedded within a hydrophobic cavity.*

Oxyanions play a major role in biology and in the environment and the development of synthetic receptors for such species is well established.[1,2] The tetrahedral sulfate anion SO_4^{2-} is heavily solvated in competitive media and remains extremely challenging to bind selectively.[3] In nature, SO_4^{2-} binding and transport is accomplished by specific sulfate-binding proteins using multiple well-organized and directional hydrogen-bonding arrays.[4] Consequently, great interest currently exists within the chemical community in designing ligands that can recognize, complex, or even transport SO_4^{2-}, as well as exploring the SO_4^{2-} anion as a platform for forming anion-directed self-assemblies, such as SO_4^{2-} templated capsules, through multiple-contact/binding interactions.[5] From these studies, urea- and thiourea-derived C_{3v}-symmetric tripodal receptors have emerged as good candidates for achieving SO_4^{2-} recognition.[6] The majority of these receptors have been based on "flexible" structures although structurally more rigid and preorganized examples, such as resorcinarene, pinwheel-based compounds, or more commonly metallocages, have also been developed, the latter giving rise to strong binding of SO_4^{2-} through electrostatic interactions.[7] Inspired by these results and the need to develop more structurally preorganized charge-neutral receptors, we recently reported[8] the synthesis of several C_3-symmetric urea-based anion receptors built on the 1,3,5-benzenetricarboxamide[9] platform. Our previous study showed that these structures recognized and bound anions, such as SO_4^{2-}, $H_2PO_4^-$ and Cl^-, in a 1:1 stoichiometry. However, as one of our main objectives was also to develop ligands that give rise to the formation of self-assembled anion capsules, these first-generation ligands failed this objective. The results indicated that the secondary amides prevented the formation of the desired preorganized cavity, instead giving rise to the formation of more open or bowl-shaped structures. With the goal of improving the design, molecular modelling of related structures having *N*-methyl tertiary amides indicated that such a minor structural change dramatically altered the preorganization of the ligand and resulted in the formation of a highly organized structure, where the urea arms are close to being orthogonal to the central benzene platform.[10] With this in mind we designed and prepared receptors **1–3**, possessing electron-withdrawing or lipophilic electron-donating substituents (Figure 1 a), and studied their ability to bind anions with the view of generating novel self-assembled anion capsules.[11] Herein we show that this design strategy works, **1–3** all have highly preorganized and "barrel"-shaped structures and have cavities that require minimal conformational changes to achieve strong interaction with tetrahedral anions through hydrogen bonding. We demonstrate that this preorganization results in the formation of self-assembled anion capsules with SO_4^{2-} in a 2:1 **L**:SO_4^{2-} stoichiometry in solution, or by using $H_2PO_4^-$ in 2:2 stoichiometry (**L**:$H_2PO_4^-$). Through X-ray crystallography we demonstrate that the SO_4^{2-} ion is hydrogen bonded through multiple hydrogen-bonding interactions,

[*] Dr. K. Pandurangan, Dr. J. A. Kitchen,[+] Dr. S. Blasco, Dr. E. M. Boyle, B. Fitzpatrick, Dr. M. Feeney, Prof. T. Gunnlaugsson
School of Chemistry and Trinity Biomedical Sciences Institute (TBSI), University of Dublin, Trinity College Dublin
Dublin 2 (Ireland)
E-mail: gunnlaut@tcd.ie
Prof. P. E. Kruger
MacDiarmid Institute for Advanced Materials and Nanotechnology
Department of Chemistry, University of Canterbury
Private Bag 4800, Christchurch 8041 (New Zealand)
E-mail: paul.kruger@canterbury.ac.nz
[+] Current address: Chemistry, Faculty of Natural and Environmental Sciences, University of Southampton
Highfield, Southampton, SO17 1BJ (UK)

[**] Financial support from Science Foundation Ireland (SFI RFP 2008 and SFI PI 2010 and 2013 grants awarded to T.G.) and IRCSET Postdoctoral Fellowship (J.A.K.) is acknowledged. S.B. thanks R.E.A. for an IEF Marie Curie Fellowship.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201411857.

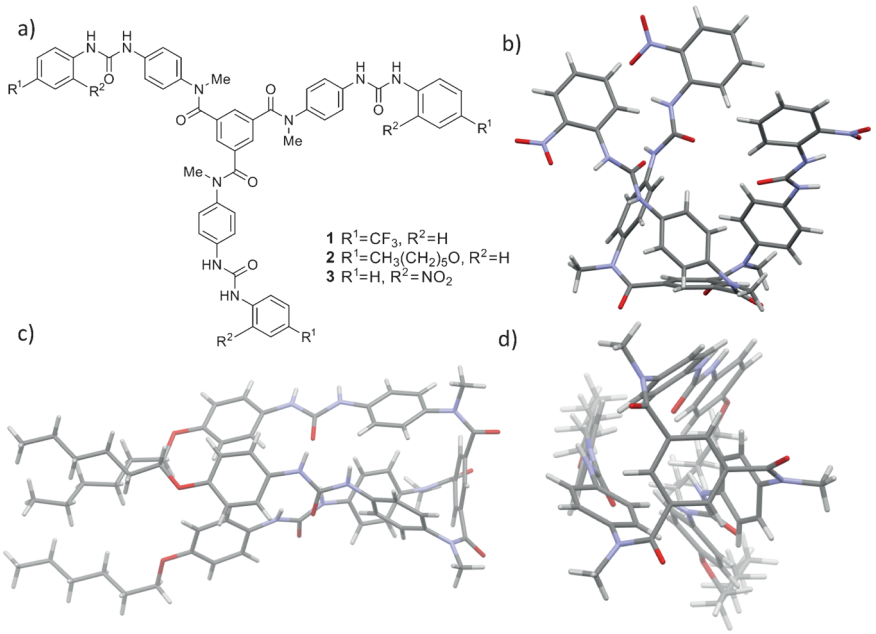

Figure 1. a) The tripodal receptors **1**–**3** developed in this study. b) Crystal structure of **3**, showing the preorganization induced by the *N*,*N*,*N*-trimethyl-1,3,5-benzenetricarboxamide platform. c) Side view of the crystal structure of **2**. d) The structure of **2** when viewed down the C_3 axis. Solvent molecules omitted for clarity. Atom colors: C = gray; N = blue; O = red; H = white.

while the $H_2PO_4^-$ ions are bridged by a single water molecule. More importantly we show that **4**, an analogous structure of **2** but having only two urea moieties and a free single amine moiety, gives rise to a highly organized self-assembled structure upon recognition of the SO_4^{2-} ion. This self-assembly process occurs through a self-sorting mechanism from a mixture of both **2** and **4**. The resulting structure was characterized by X-ray crystallography and consists of 4 units of ligand **4** which closely engulf 4 SO_4^{2-} ions through 36 hydrogen-bonding interactions within a tetrahedron arrangement.

The synthesis of the receptors **1**–**3** was straightforward and was achieved in a few steps, starting from 1,3,5-benzenetricarbonyl trichloride and *N*-methyl-4-nitroaniline (see the Supporting Information). The first intermediate (**A**; Scheme S1 in the Supporting Information) yielded crystals from a dimethylsulfoxide (DMSO) solution that were suitable for X-ray crystal structure analysis.[14] The crystal structure confirmed the effect that the *N*-methyl group has on directing the three aryl amides in the same direction, in a manner predicted above (see the Supporting Information). Reduction of **A** (using Pd/C and hydrazine hydrate) under microwave conditions gave the corresponding amine (**B**; Scheme S1) which was reacted with the appropriate isocyanates in 1:3.3 ratio, giving receptors **1**–**3** in circa 90% yields after workup. All three ligands were characterized using conventional methods. Moreover, we were able to grow single crystals of ligands **2** and **3** suitable for X-ray crystal structure analysis by slow evaporation of CH_3CN and CH_3CN:DMF solutions, respectively (Figure 1; DMF = dimethylformamide).[14] Both structures clearly show that the three urea arms are highly preorganized and generate an extended "cavity" within the molecules. This can be seen clearly in Figure 1 d for **2** when viewed down the C_3 axis and from the back side. Both ligands self-assemble further into extended hydrogen-bonding polymeric networks (see the packing diagrams in the Supporting Information). As can be seen in Figure 1 b and c, the carboxamide oxygen atoms are all orientated below the plane of the benzene platform, resembling that seen in the crystal structure of intermediate **A**. In the solid-state structure of **2**, two of the urea groups have their N–H hydrogen atoms oriented away from the cavity, whereas for **3** they all are oriented away from the cavity. Moreover, in **3** the (distal) N–H urea hydrogen atoms interact with the 2-nitro substituent through hydrogen bonding to form a six-membered ring system.

We envisaged that **1**–**3** would self-assemble around tetrahedral anions such as SO_4^{2-} and $H_2PO_4^-$ through hydrogen bonding to form supramolecular capsules. Initially we studied their formation by tracking changes within their ^{1}H NMR and UV/Vis absorption spectra following titration with the tetrabutylammonium (TBA) salts of SO_4^{2-} and $H_2PO_4^-$, as well as Cl^- and AcO^-. Unfortunately, the changes in the absorption spectra in DMSO (optical density = 1.0) solution were minor upon titration with SO_4^{2-}, where a small red shift for the λ_{max} value was detected upon binding of SO_4^{2-} to **1**–**3** (see the Supporting Information for details). Consequently, ^{1}H NMR spectroscopy (400 MHz, [D$_6$]DMSO) titrations were conducted to probe the formation of the anion-templated capsules in solution. In each case, the titration of **1**–**3** with SO_4^{2-} showed a downfield shift and broadening of the resonance signals attributable to the N–H urea hydrogen atoms consistent with fast exchange (see the Supporting Information for full titrations). Fitting the ^{1}H NMR titration data for SO_4^{2-} showed that two binding stoichiometries exist for **1**–**3** (the binding isotherms and fits, determined using the program NMRTit HGG, are given in the Supporting Information). In the case of **1**, this included the initial formation of a self-assembly with the desired 2:1 stoichiometry ($\log K_{1:2} = 3.01$, where K is the binding constant), which was followed by a formation of a 1:1 stoichiometry ($\log K_{1:1} = 1.76$). Similarly for **2** and **3**, two species were identified in solution, with $\log K_{1:2} = 3.02$ and $\log K_{1:1} = 1.96$, respectively, for **3**. Titrations using $H_2PO_4^-$, Cl^-, and AcO^- were also conducted (see the Supporting Information). Of these, the titrations with $H_2PO_4^-$ gave dissimilar behavior; the anion binding was in slow exchange for **1** and **2**, whereas in the case of **3** the changes were in fast exchange (see the Supporting Information). The formation of these self-assembled SO_4^{2-} structures was also investigated using both MALDI-TOF and ESI mass spectrometry. In each case, the results showed the formation of the predicted anion-tem-

plated capsule species when recorded in negative mode (see the Supporting Information). Moreover, the detected isotopic distribution patterns matched perfectly that of the calculated species for all three receptors. In the case of $H_2PO_4^-$, the mass spectrum also showed the formation of a self-assembled structure but only the 1:1 stoichiometry was observed.

Having analyzed the anion-templated self-assembly formation in solution, we next synthesized the anion capsules by reacting **1**–**3** with SO_4^{2-} in various stoichiometries and solvent conditions. From these experiments, we were able to obtain crystals of all three complexes suitable for single-crystal X-ray diffraction analysis.[14] The structures of **2** and **3** are shown in Figure 2 a and b, respectively. Crystals were obtained by slow evaporation of CH_3CN:DMF solutions of the products, both of which crystallized within the triclinic space group $P\bar{1}$. Both structures, $(SO_4^{2-})\cdot\mathbf{2}_2$ and $(SO_4^{2-})\cdot\mathbf{3}_2$ clearly demonstrate that the anion is fully encapsulated within a cavity formed from two interdigitated ligands, through an extended hydrogen-bonding network involving all of the twelve urea N–H hydrogen atoms. The complexes are packed with two TBA cations per complex with the packing driven through hydrophobic and electrostatic interactions. Although the packing demonstrates highly hydrophobic structures, within these channels there are also some hydrophilic pockets containing solvent molecules, including a hydrogen-bonded water molecule that bridges two neighboring capsules through one of the carboxamide oxygen atoms of each of the 1,3,5-benzenetricarboxamide units. There are also two DMF solvent molecules within these channels per asymmetric unit. However, the encapsulated nature of the SO_4^{2-} ion means it is not accessible to these solvent molecules. In the case of $(SO_4^{2-})\cdot\mathbf{2}_2$ the anion was strongly bound through the twelve hydrogen bonds, with N–H···O(S) bond lengths ranging from 1.95–2.41 Å, with an average N–H···O bond length of 2.22 Å (Table S2). By comparing the X-ray crystal structure of **3** with that of $(SO_4^{2-})\cdot\mathbf{3}_2$ it is clear that the preorganization observed in **3** is maintained to a great extent in the self-assembled SO_4^{2-} capsule. The capsule forms through reciprocal intramolecular hydrogen bonding between three urea arms of one tripod and the nitro group of each of the urea arms of the other tripod, with twelve intermolecular hydrogen-bond interactions between SO_4^{2-} and the two tripodal receptors. The X-ray structure of **1** showed the same SO_4^{2-} capsule formation. The structure $(SO_4^{2-})\cdot\mathbf{1}_2$ was obtained within the triclinic system with space group $P\bar{1}$ but full refinement could not be achieved (Supporting Information). Although the atom connectivity of the capsule itself was clear and the SO_4^{2-} ion was shown to be hydrogen bonded to all six urea groups, the high *R* indices were attributed to disorder in the TBA cations, solvent molecules, and the CF_3 groups of the ligands. Ligands **1**–**3** were also treated $H_2PO_4^-$; however, in each case the anion complexes were isolated as oils or oily precipitates, except for **1**. This combination gave rise to the formation of crystals suitable for X-ray crystal structure analysis. Similar to that detected for $(SO_4^{2-})\cdot\mathbf{1}_2$, full atom connectivity could be established and the structures showed that **1** also formed a capsule with $H_2PO_4^-$ ions through an extensive array of hydrogen-bond interactions. However, unlike that seen above, in this case the stoichiometry was in the form of 2+2 (see the Supporting Information), where the two $H_2PO_4^-$ ions were bridged by a water molecule within the cage. This result clearly demonstrates the ability of $H_2PO_4^-$ to also act as a template for the formation of self-assembled supramolecular capsules from such highly preorganized tripodal platforms.

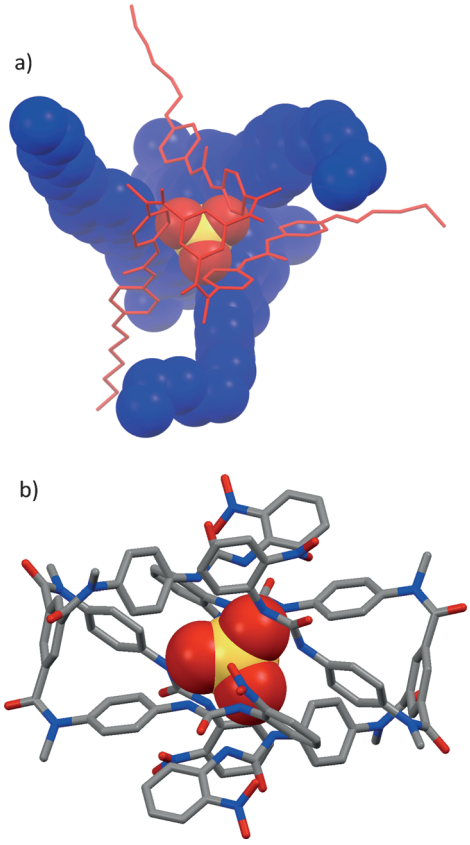

Figure 2. a) Receptor **2** with SO_4^{2-} capsule formation in a 2:1 stoichiometry as shown through a mixed space-filling and stick representation highlighting both the C_3 symmetry and the SO_4^{2-} template within the cavity. b) The 2:1 complex of **3** with SO_4^{2-} showing the encapsulation of the anion through hydrogen bonding of all twelve N-H urea hydrogen atoms. TBA and solvent molecules omitted for clarity. Atom colors in (b): C = gray; S = yellow; N = blue; O = red.

It was noted during the synthesis of ligand **2** that the ^{1}H NMR spectrum of the crude material showed the presence of an additional minor side product which we characterized as being the dipodal ligand, **4**, where only two of the amine groups had reacted with the isocyanate (Supporting Information). Although the desired tripodal ligand, **2**, could be isolated as a pure compound from this minor product, we were unable to isolate **4** in high yield (see the Supporting Information for characterization of **4**). Given that it would be expected to maintain the preorganized structure and interact with anions, we treated the mixture of **2** and **4** with SO_4^{2-} in CH_3CN in the hope that this would allow for self-sorting to occur, where either the [2+1] capsule would be formed or an alternative SO_4^{2-} self-assembled structure employing ligand **4** would form. This gave rise to a crystalline material consisting of a mixture of two types. The result showed that **4** in the presence of SO_4^{2-} ions gave rise to the formation of a more

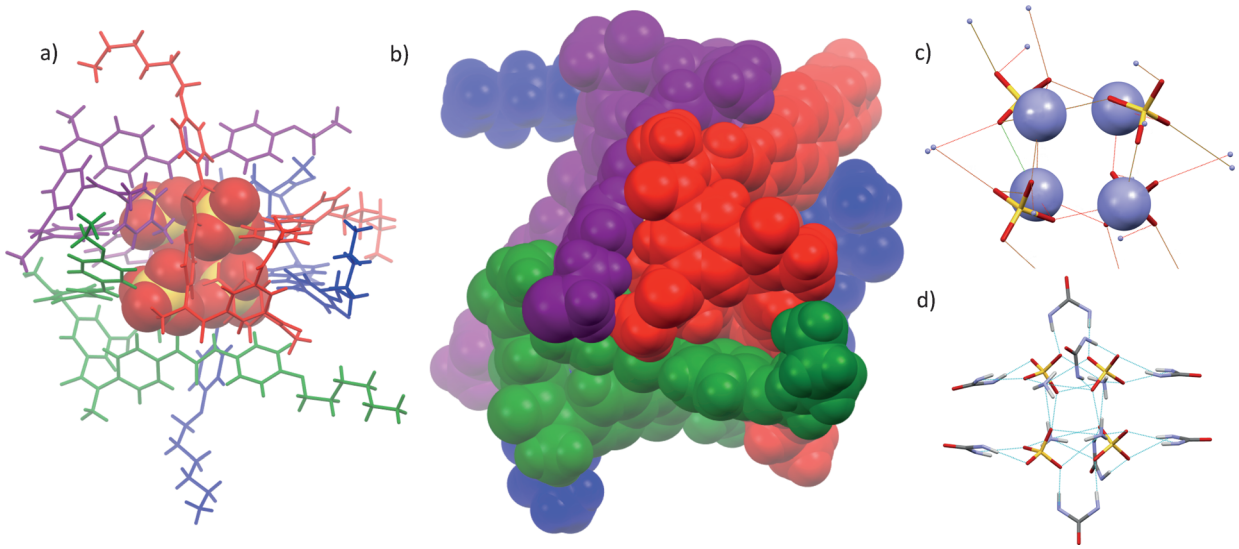

Figure 3. a) Representation of the complex $[(SO_4^{2-})_4{\cdot}H\mathbf{4}_4]^{4-}$ showing the encapsulation of the four sulfate anions (given in space-filling representation) inside the capsule formed by four molecules of $H\mathbf{4}^+$ (stick representation; a different color is used per unit of $H\mathbf{4}^+$). b) Space-filling representation of the complex $[(SO_4^{2-})_4{\cdot}H\mathbf{4}_4]^{4-}$ when viewed down the c^* crystallographic axis showing the arrangement and packing of the $\mathbf{4}_4$ self-assembled structure. c) and d) The hydrogen-bonding network within the cavity. The blue spheres in (c) represent protonated amino moieties.

complex supramolecular anion capsule (Figure 3). An important point to highlight is that in this system the free amine groups are protonated to give each ligand a +1 charge.

As shown in Figure 3, this self-assembled [4+4] structure consists of 4 closely packed SO_4^{2-} ions fully embedded and bound through 36 hydrogen-bond interactions within a tetrahedral arrangement.[14] Additionally, the structure contains four units of ligand **4** which together with the anions form a supramolecule with stoichiometry $[(SO_4^{2-})_4{:}(H\mathbf{4}^+)_4]$ with a total charge of −4 (where charge balance is achieved with four TBA cations). In addition to the large number of hydrogen bonds seen in $[(SO_4^{2-})_4{\cdot}(H\mathbf{4}^+)_4]$, the capsule is further stabilized by electrostatic interactions. This result is complementary to that seen by Steed et al. who developed pinwheel-based compound using both urea and pyridinium ions for the binding of Cl^- or Br^- ions.[7g] Although examples of the use of metal complexes as platforms to self-assemble anions within cages are known, to our knowledge $[(SO_4^{2-})_4{\cdot}(H\mathbf{4}^+)_4]$ is the first example of such a highly ordered encapsulated SO_4^{2-} cluster arrangement using hydrogen-bonding interactions as the primary bonding motif, formed without the need of bridging solvent molecules or the need of metal coordinating binding sites, as discussed below. The closest example to $[(SO_4^{2-})_4{\cdot}(H\mathbf{4}^+)_4]$ in the literature is a [2+2] "rugby-ball"-shaped adduct where two sulfates are encapsulated along with three water molecules.[12]

Further details of the [4+4] stoichiometric capsule can be seen in Figure 3, demonstrating the close packing in this structure. It can be seen that most of the hydrophilic groups (all urea NH and Ar-NH_3^+ groups) are directed towards the inside of the cavity, where the sulfate anions reside, while the hydrophobic moieties can be found in the outer shell. In this capsule, hydrogen bonding is the dominant interaction that holds the self-assembled structure together. These interactions consist of both urea N–H···O(S) hydrogen bonds, with average bond lengths of 2.22 Å (Table S2) and hydrogen-bonding interactions between SO_4^{2-} and the protonated anilines, Ar-NH_3^+···O(S). For each of the four ligands, the ammonium moiety is directly bound to three different SO_4^{2-} ions through four hydrogen bonds, while the N–H urea hydrogen atoms are hydrogen bonded to one or two SO_4^{2-} ions (Figure 3d). Among the total of eight urea moieties, six of them are doubly hydrogen bonded to a single SO_4^{2-} ion and two of them are singly bonded to two different SO_4^{2-} ions (Scheme S2). The anionic nature of the capsule is charge balanced by TBA^+ molecules that interact both electrostatically and hydrophobically with the $[(SO_4^{2-})_4{\cdot}(H\mathbf{4})_4]^{4-}$ complex.[13] As was the case in the SO_4^{2-} complexes of **1**–**3**, the carboxamide oxygen atoms of **4** are oriented away from the cavity in the same manner to that seen for **2** (Figure 1), demonstrating that the 1,3,5-benzenetricarboxamide central platform remains the foundation for the preorganization of both molecules. Some of the carboxamide oxygen atoms also interact with a total of three water molecules in the asymmetric unit, as well as a single CH_3CN molecule.

The results presented herein clearly demonstrate the power of using highly preorganized receptors for the anion-directed self-assembly synthesis of supramolecular capsules. We show that minor structural modifications (as in the case of **2** versus **4**) can lead to the formation of unexpected and novel self-sorted supramolecular structures, which as in the case of the $[(SO_4^{2-})_4{\cdot}(H\mathbf{4})_4]^{4-}$ complex have not been demonstrated before. We are in the process of further exploring the use of highly preorganized receptors in the design of novel anion-containing supramolecular architectures.

In conclusion, we have designed and studied the complexation and self-assembly of ligands **1**–**3** with various anions (SO_4^{2-}, $H_2PO_4^-$, AcO^-, and Cl^-). Each of the ligands bind SO_4^{2-} in a 2:1 stoichiometry. Moreover, compound **4**, an

analogue of **2** but possessing two urea arms, was shown to give rise to a self-assembled structure consisting of a [4:4] stoichiometry between the ligand and SO_4^{2-} as demonstrated by X-ray crystallography. For each of these preorganized ligands, the encapsulation of the SO_4^{2-} ion was observed and in the case of $H_2PO_4^-$ and **1**, the X-ray crystal structure showed the formation of [2+2] structure. The asymmetric dipodal receptor **4** was also isolated and characterized, and through the use of a self-sorting process we were able to isolate a [4+4] self-assembled structure based on ligand **4**. In this structure, the anions are encapsulated in a closely packed arrangement that excludes any solvent molecules and is held together by both electrostatic and a total of 36 hydrogen-bonding interactions. To our knowledge, these are the first examples of such ordered anion-driven self-assemblies based on the use of SO_4^{2-} as a templating agent, demonstrating that minor structural changes can have a large effect on the ability of the ligands to self-sort and form highly ordered self-assemblies. We are currently investigating these and related systems in greater detail.

Keywords: anion recognition · self-assembly · self-sorting · supramolecular chemistry · tripodal ligands

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 4566–4570
Angew. Chem. **2015**, *127*, 4649–4653

[1] a) R. M. Duke, E. B. Veale, F. M. Pfeffer, P. E. Kruger, T. Gunnlaugsson, *Chem. Soc. Rev.* **2010**, *39*, 3936–3953; b) T. Gunnlaugsson, M. Glynn, G. M. Tocci, P. E. Kruger, F. M. Pfeffer, *Coord. Chem. Rev.* **2006**, *250*, 3094–3117; c) P. A. Gale, *Chem. Soc. Rev.* **2010**, *39*, 3746–3771; d) J. W. Steed, *Chem. Soc. Rev.* **2010**, *39*, 3686–3699; e) A.-F. Li, J.-H. Wang, F. Wang, Y.-B. Jiang, *Chem. Soc. Rev.* **2010**, *39*, 3729–3745.

[2] a) J. Cai, J. L. Sessler, *Chem. Soc. Rev.* **2014**, *43*, 6198–6213; b) P. A. Gale, C. Caltagirone, *Chem. Soc. Rev.* **2015**, DOI: 10.1039/C4CS00179F; c) R. B. P. Elmes, K. K. Y. Yuen, K. A. Jolliffe, *Chem. Eur. J.* **2014**, *20*, 7373–7380.

[3] a) N. Busschaert, L. E. Karagiannidis, M. Wenzel, C. J. E. Haynes, N. J. Wells, P. G. Young, D. Makuc, J. Plavec, K. A. Jolliffe, P. A. Gale, *Chem. Sci.* **2014**, *5*, 1118–1127; b) M. N. Piña, B. Soberats, C. Rotger, P. Ballester, P. M. Deyà, A. Costa, *New J. Chem.* **2008**, *32*, 1919–1923; c) B. A. Moyer, R. Custelcean, B. P. Hay, J. L. Sessler, K. Bowman-James, V. W. Day, S.-O. Kang, *Inorg. Chem.* **2013**, *52*, 3473–3490.

[4] a) J. L. Sessler, P. A. Gale, W.-S. Cho, *Anion Receptor Chemistry*, Royal Society of Chemistry, Cambridge, **2006**; b) J. W. Pflugrath, F. A. Quiocho, *J. Mol. Biol.* **1988**, *200*, 163–180.

[5] a) V. Amendola, L. Fabbrizzi, L. Mosca, *Chem. Soc. Rev.* **2010**, *39*, 3889–3915; b) M. Wenzel, J. R. Hiscock, P. A. Gale, *Chem. Soc. Rev.* **2012**, *41*, 480–520; c) S. Kubik, *Chem. Soc. Rev.* **2009**, *38*, 585–605; d) C. Jin, M. Zhang, L. Wu, Y. Guan, Y. Pan, J. Jiang, C. Lin, L. Wang, *Chem. Commun.* **2013**, *49*, 2025–2027; e) P. A. Gale, J. R. Hiscock, C. Z. Jie, M. B. Hursthouse, M. E. Light, *Chem. Sci.* **2010**, *1*, 215–220; f) C. R. Bondy, P. A. Gale, S. J. Loeb, *J. Am. Chem. Soc.* **2004**, *126*, 5030–5031.

[6] a) C. Jia, B. Wu, S. Li, X. Huang, Q. Zhao, Q.-S. Li, X.-J. Yang, *Angew. Chem. Int. Ed.* **2011**, *50*, 486–490; *Angew. Chem.* **2011**, *123*, 506–510; b) R. Custelcean, *Chem. Commun.* **2013**, *49*, 2173–2182; c) M. Li, Y. Hao, B. Wu, C. Jia, X. Huang, X.-J. Yang, *Org. Biomol. Chem.* **2011**, *9*, 5637–5640; d) I. Ravikumar, P. Ghosh, *Chem. Soc. Rev.* **2012**, *41*, 3077–3098; e) J. R. Hiscock, P. A. Gale, M. J. Hynes, *Supramol. Chem.* **2012**, *24*, 355–360; f) V. J. Dungan, H. T. Ngo, P. G. Young, K. A. Jolliffe, *Chem. Commun.* **2013**, *49*, 264–266; g) P. G. Young, K. A. Jolliffe, *Org. Biomol. Chem.* **2012**, *10*, 2664–2672; h) A. Basu, G. Das, *Dalton Trans.* **2012**, *41*, 10792–10802; i) A. Basu, G. Das, *J. Org. Chem.* **2014**, *79*, 2647–2656; j) J. L. Bolliger, T. K. Ronson, M. Ogawa, J. R. Nitschke, *J. Am. Chem. Soc.* **2014**, *136*, 14545–14553.

[7] a) See Ref. [6a]; b) R. Custelcean, P. Remy, P. V. Bonnesen, D. E. Jiang, B. A. Moyer, *Angew. Chem. Int. Ed.* **2008**, *47*, 1866–1870; *Angew. Chem.* **2008**, *120*, 1892–1896; c) R. Custelcean, P. V. Bonnesen, N. C. Duncan, X. Zhang, L. A. Watson, G. Van Berkel, W. B. Parson, B. P. Hay, *J. Am. Chem. Soc.* **2012**, *134*, 8525–8534; d) R. Custelcean, J. Bosano, P. V. Bonnesen, V. Kertesz, B. P. Hay, *Angew. Chem. Int. Ed.* **2009**, *48*, 4025–4029; *Angew. Chem.* **2009**, *121*, 4085–4089; e) S. Yi, V. Brega, B. Captain, A. E. Kaifer, *Chem. Commun.* **2012**, *48*, 10295–10297; f) A. L. Cresswell, M.-O. M. Piepenbrock, J. W. Steed, *Chem. Commun.* **2010**, *46*, 2787–2789; g) D. R. Turner, M. J. Paterson, J. W. Steed, *Chem. Commun.* **2008**, 1395–1397.

[8] C. M. G. dos Santos, E. M. Boyle, S. De Solis, P. E. Kruger, T. Gunnlaugsson, *Chem. Commun.* **2011**, *47*, 12176–12178.

[9] a) S. Cantekin, T. F. A. de Greef, A. R. A. Palmans, *Chem. Soc. Rev.* **2012**, *41*, 6125–6137; b) O. Kotova, R. Daly, C. M. G. dos Santos, M. Boese, P. E. Kruger, J. J. Boland, T. Gunnlaugsson, *Angew. Chem. Int. Ed.* **2012**, *51*, 7208–7212; *Angew. Chem.* **2012**, *124*, 7320–7324.

[10] F. D. Lewis, T. M. Long, C. L. Stern, W. Liu, *J. Phys. Chem. A* **2003**, *107*, 3254–3262.

[11] R. Dutta, P. Ghosh, *Chem. Commun.* **2014**, *50*, 10538–10554.

[12] D. A. Jose, D. K. Kumar, B. Ganguly, A. Das, *Inorg. Chem.* **2007**, *46*, 5817–5819.

[13] F. Zhuge, B. Wu, J. Liang, J. Yang, Y. Liu, C. Jia, C. Janiak, N. Tang, X.-J. Yang, *Inorg. Chem.* **2009**, *48*, 10249–10256.

[14] CCDC-1007393 (**A**), 1046452 (**1**(phosphate)), 1046453 (**1**-(sulfate)), 1007394 (**2**), 1007395 (**3**), 1046450 (**2**(sulfate)), 1007396 (**3**(sulfate)), and 1046451 (**4**(sulfate)) 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.

Received: December 9, 2014
Revised: January 19, 2015
Published online: February 18, 2015

