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A Hydrogen-Bonded Ravel Assembled by Anion Coordination

Xiaotong Zhao, Heng Wang, Boyang Li, Wenyao Zhang, Xiaopeng Li, Wei Zhao,
Christoph Janiak, Andrew W. Heard, Xiao-Juan Yang, and Biao Wu*

Abstract: Anion-coordination-driven assembly (ACDA) is showing increasing power in the construction of anionic supramolecular architectures. Herein, by expanding the anion centers from oxoanion (phosphate or sulfate) to organic tris-carboxylates, an Archimedean solid (truncated tetrahedron) and a highly entangled, double-walled tetrahedron featuring a ravel topology have been assembled with tris-bis(urea) ligands. The results demonstrate the promising ability of tris-carboxylates as new anion coordination centers in constructing novel topologies with increasing complexity and diversity compared to phosphate or sulfate ions on account of the modifiable size and easy functionalization character of these organic anions.

Introduction

Knots, as a common phenomenon occurring in complicated structures, play important roles in many fields.^[1] In biology, knotted DNA, RNA, and protein molecules have been discovered with specific functions.^[2] To chemists, the construction of various molecular knots is one of the major interests.^[3] To date, only very few relatively simple knot topologies (out of more than six billion prime knots defined mathematically) have been synthesized from small-molecule building blocks.^[1a,b] The first trefoil knot was synthesized by metal-ion templation in late 1980s by Sauvage et al.,^[4] while several more complex knots (pentafoil 5₁,^[5] Figure-of-eight

4₁,^[6] septafoil 7₁,^[7] nonafoil 9₁,^[8] 8₁₉,^[9] and a molecular endless 7₄ knot^[10]) have only been obtained very recently.

On the other hand, the ravel terminology, which is a generalization of knots allowing three or more strands to fuse at a given point (junction), was introduced in 2008 to illustrate sophisticated entanglement modes that cannot be described by the knot theory.^[11] In 2011, the first universal 3-ravel motif, which may be considered as a branched knot, was observed in a 20-component, metal-coordination-based [Fe₈L₁₂] complex (L is a bis-β-diketone derivative).^[12] Recently, several [M₃L₂]_n metallo-supramolecular assemblies showing ravel structures have been reported, wherein the ligands containing pyridyl and alkyne groups (for π-coordination to metal ions) assembled with Cu¹ and Ag¹, respectively.^[13] Undoubtedly, the construction of ravels at the molecular level is essential to the understanding of their topologies and functions. As the complexity increases, however, synthetic access to these systems becomes more challenging.

In the pursuit of assemblies with high precision, increasing complexity and desired functions, anion-coordination-driven assembly (ACDA) is emerging as a new strategy to construct supramolecular architectures in parallel with metal-coordination-driven assembly. To date, various discrete anionic supramolecular structures have been successfully assembled, in which the anions serve as the connecting centers like metals.^[14] Compared to metallo-supramolecular systems, such anion-based assemblies with multiple weak interactions, typically dozens of hydrogen bonds, are prone to display adaptive conformational changes upon guest binding, and it is challenging to control the assembly process with predictable outcome.^[14d,e] Moreover, the anion in previous systems mainly focused on the high electron-density, inorganic phosphate (PO₄³⁻) or sulfate (SO₄²⁻) ion. To further define the scope of anions for ACDA and enrich the resulted supramolecular structures, we aim to expand the anion center to organic tris-carboxylates. The C₃-symmetric, triply deprotonated trianions (A³⁻) of tris-carboxylic acids (H₃A) can also potentially form 12 hydrogen bonds in total with three bis(urea) units, thus may lead to (tetrahedral) cages with significantly enlarged cavities. It is known that polycarboxylates are excellent building blocks for hydrogen-bonded frameworks.^[15] More importantly, since the shape, size, and substituents of these tris-carboxylates can be easily altered and modified, the structural diversity of assemblies could be significantly increased.

In this work, we establish a library of assemblies with four C₃-symmetric, planar tris-bis(urea) ligands (L¹–L⁴) and four tris-carboxylate anions (A¹–A⁴), from which three new types of anionic supramolecular structures were obtained

* X. Zhao, B. Li, W. Zhang, Prof. B. Wu
College of Chemistry and Materials Science
Northwest University, Xi'an 710069 (China)

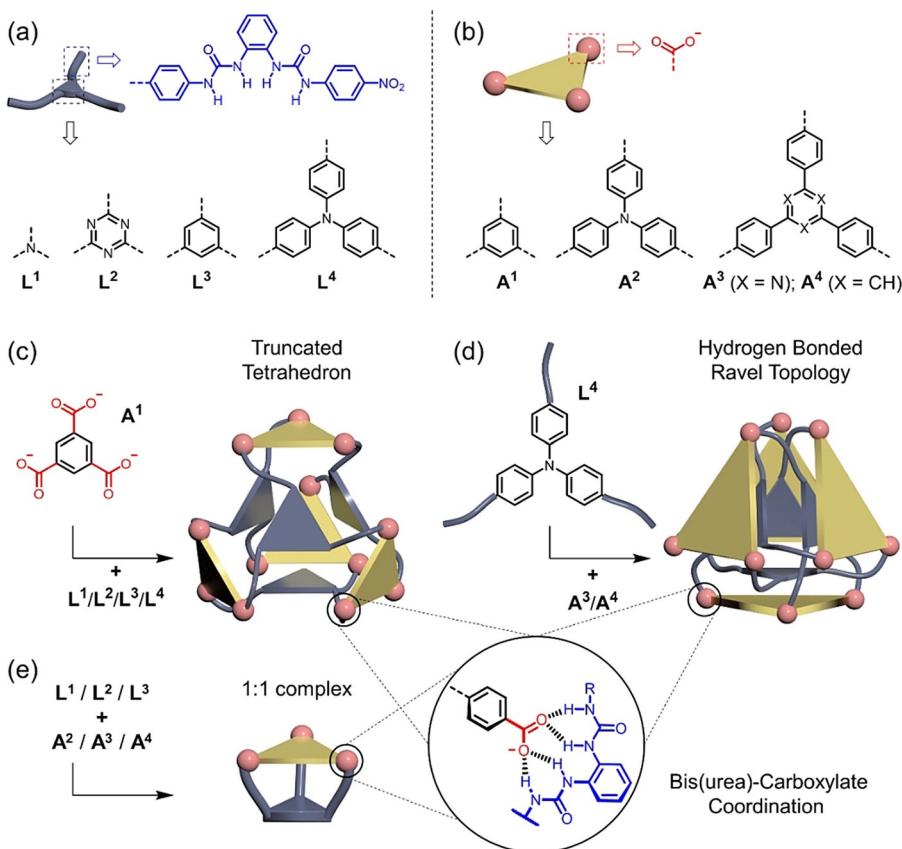
Dr. H. Wang, Prof. X. Li
College of Chemistry and Environmental Engineering
Shenzhen University, Shenzhen 518055 (China)

W. Zhao, Prof. X.-J. Yang, Prof. B. Wu
Key Laboratory of Medical Molecule Science and Pharmaceutics
Engineering, Ministry of Industry and Information Technology,
School of Chemistry and Chemical Engineering
Beijing Institute of Technology, Beijing 102488 (China)
E-mail: wubiao@bit.edu.cn

Prof. C. Janiak
Institut für Anorganische Chemie und Strukturchemie
Heinrich-Heine-Universität Düsseldorf
40204 Düsseldorf (Germany)

Dr. A. W. Heard
Department of Chemistry, University of Cambridge
Cambridge (UK)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
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Scheme 1. Representatives for anion-coordination-driven assembly by carboxylates. a),b) Chemical structures for the C_3 -symmetric tris-bis(urea) ligands and tris-carboxylate anions; c)–e) The assembly of three types of architectures: truncated tetrahedra, double-walled ravelled tetrahedra, and simple 1:1 chelating complexes, respectively.

(Scheme 1, S1; Table S1). It is found that the size (length) of the anion and ligand has a profound effect on the assembled structure. The smallest trianion \mathbf{A}^1 favors the Archimedean-type, truncated tetrahedron with each of the \mathbf{L}^1 – \mathbf{L}^4 ligands. Strikingly, the medium-sized anions (\mathbf{A}^3 and \mathbf{A}^4) assemble with the larger ligands (\mathbf{L}^4) to form a unique double-walled tetrahedron that features a highly entangled, ravel structure, but with the smaller ligands (\mathbf{L}^1 , \mathbf{L}^2 and \mathbf{L}^3), a simple 1:1 assembly is obtained (Scheme 1).

Results and Discussion

The C_3 -symmetric tris-bis(urea) ligands \mathbf{L}^1 (with the central triphenylamine node),^[14b] \mathbf{L}^2 (with 2,4,6-triphenyl-1,3,5-triazine),^[14c] \mathbf{L}^3 (with 1,3,5-triphenylbenzene),^[14d] and \mathbf{L}^4 (with the largest tris(biphenyl)amine node; Scheme 1)^[16] were prepared as described before. The combination of these ligands with the four tris-carboxylates, 1,3,5-trimesate (\mathbf{A}^1), 4,4',4"-nitrilotribenzoate (\mathbf{A}^2), 1,3,5-triazine-2,4,6-tris(4-benzoate) (\mathbf{A}^3), and benzene-1,3,5-tris(4-benzoate) (\mathbf{A}^4 ; Scheme 1) possessing different sizes and/or electronic effects gave 16 complexes that can be classified as three different structure types (Table S1).

Treating the smallest trianion $\text{TPA}_3\mathbf{A}^1$ (TPA = tetrapropyl ammonium; generated *in situ* by mixing $(\text{TPA})\text{OH}$ and

trimesic acid $\text{H}_3\mathbf{A}^1$) with ligand \mathbf{L}^1 in a 1:1 stoichiometry in acetone afforded the complex $(\text{TPA})_{12}\cdot[(\mathbf{A}^1)_4(\mathbf{L}^1)_4]$ (**1**) (Scheme 1). Single-crystal X-ray diffraction^[17] revealed the formation of a truncated tetrahedron (Figure 1), where the flat tris-carboxylate anion is the truncating face. The COO^- groups adopt the typical binding mode with bis(urea) unit through four N–H···O hydrogen bonds, where each O atom is chelated by two NH donors of a urea (Figure 1b).^[17] In this way each tris-carboxylate trianion acquires 12 N–H···O bonds. As such, there are a total of 48 H-bonds in the entire system, the same as in the phosphate tetrahedral cage, the complex exists as a racemic mixture of the all- Λ or all- Δ configurations. The N···O distances range from 2.663(3) to 3.122(9) Å, av. 2.842(3) Å, and N–H···O angles from 140 to 173°, av. 154° (Figure 1c and Table S1). It is worth noting that Gale et al. reported the first crystallographically characterized complex of mono-carboxylate (benzoate) and bis(urea), via four hydrogen bonds in the range 2.740(4)–2.939(4) Å, which result in down-field shifts of urea NH proton signals ($\Delta\delta = 1.10$ ppm) in the NMR spectrum.^[18a]

There are several approaches for building a truncated tetrahedron. In the metal-coordination-driven assembly, a general way is that the metal ions serve as the 12 vertices, while the ligands span the 4 hexagons (C_3 -ligands) or 18 edges (linear ligands).^[13c,19] Besides these entities, wherein the three metal ions within a truncating face (equilateral triangles) are separated, the three metals could also be interconnected by other ligands or groups.^[20] For example, metal-carboxylate clusters, such as the sulfate-capped, oxygen-centered iron-carboxylate trimer, $\text{Fe}_3\text{O}(\text{COO})_3(\text{SO}_4)_3$, can serve as rigid nodes (triangles) that are linked by linear or trigonal linkers.^[21] Tris(Zn^{II} -cyclen) can also function as the triangles to construct a truncated cage.^[22] This architecture has also been obtained through dynamic covalent chemistry, by which, Cooper et al. reported a trigonal prismatic imine cage that can rearrange to a truncated tetrahedron in 2018.^[23] As such, the current compound **1** represents the first anion-coordination-based, Archimedean-type polyhedron.

Moreover, when the larger ligands \mathbf{L}^2 , \mathbf{L}^3 , or \mathbf{L}^4 (Scheme 1) were assembled with $\text{TBA}_3\mathbf{A}^1$ in acetonitrile, similar truncated tetrahedra $(\text{TBA})_{12}[(\mathbf{A}^1)_4(\mathbf{L}^2)_4]$ (**2**), $(\text{TBA})_{12}[(\mathbf{A}^1)_4(\mathbf{L}^3)_4]$ (**3**), and $(\text{TBA})_{12}[(\mathbf{A}^1)_4(\mathbf{L}^4)_4]$ (**4**) were isolated. Interestingly, combination of the largest ligand \mathbf{L}^4 with the medium-sized \mathbf{A}^2 anion also led to a truncated

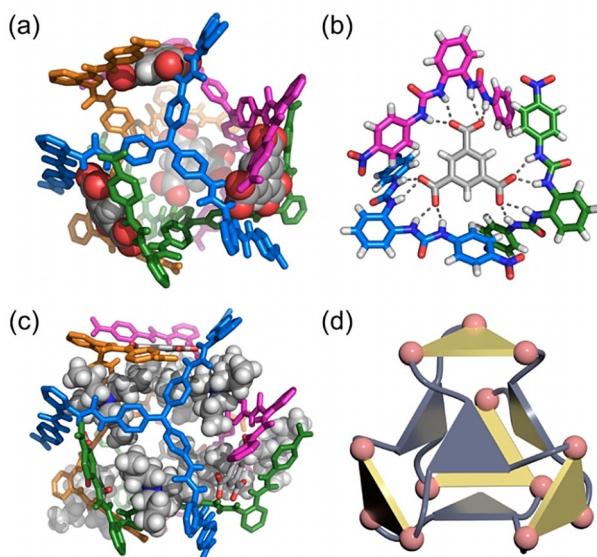


Figure 1. Crystal structure of the truncated tetrahedron, $(TPA)_{12}[(A^3)_4(L^1)]$ (**1**). a) Front view, with tris-carboxylate anions (as the truncating faces) shown in CPK model and ligands in sticks. b) Representation of the hydrogen bonding geometry (12 hydrogen bonds) between one 1,3,5-trimesate anion and three bis(urea) groups. c) View of the binding of seven peripheral tetrapropylammonium (TPA^+) cations around the truncated cage in **1**, showing the insertion of two propyl arms of TPA^+ into the truncated cage and the clathration of propyl groups within the grooves formed by neighboring ligand arms. Excess counter-cations, hydrogen atoms, and solvent molecules were omitted for clarity. d) Cartoon representation of the truncated tetrahedron geometry.

tetrahedron $(TBA)_{12}[(A^2)_4(L^4)]$ (**5**) (Table S1). The formation of such a structure in **2–5** was supported by 1H NMR, DOSY, ESI-MS, and theoretical structural optimization results (Figures S14–S30 and S65–S66).

Along this design principle, the medium-size tris-carboxylate anion **A²** and the larger **A³** and **A⁴** were also used in the ACDA with the tris-bis(urea) ligands in the hope of constructing larger truncated tetrahedra. Unexpectedly, treatment of either **A²**, **A³** or **A⁴** (as TEA^+ or TBA^+ salts; $TEA =$ tetraethyl ammonium) with **L¹**, **L²** or **L³** yielded nine 1 + 1 (but not 4 + 4) constructs, $(TEA)_3[(A^{2/3/4})_3(L^{1/2/3})]$ (**6–14**) (Scheme 1). Although attempts to grow crystals of these complexes were yet unsuccessful, ESI-MS and 1H NMR studies provided sufficient support for the 1 + 1 composition of these assemblies (Figures S31–S50). DOSY experiments of **7** and **8** gave diffusion constants of $D = 8.29 \times 10^{-11} \text{ m}^2 \text{s}^{-1}$ and $8.37 \times 10^{-11} \text{ m}^2 \text{s}^{-1}$, with solvodynamic radii (r) of about 13.2 Å and 13.1 Å, respectively (Figures S34, S37). In addition, theoretical modeling of these complexes suggested that they adopt an almost parallel face-to-face arrangement with the ligand showing a bowl-like conformation to embrace the anion by binding the three COO^- groups with the three bis(urea) arms (Figures S63 and S64).

We then switched to the combination of larger anions (**A³** and **A⁴**) with the largest ligand (**L⁴**). When **L⁴** (Scheme 1) was treated with TEA_3A^3 in acetonitrile, the complex $(TEA)_{12}[(A^3)_4(L^4)]$ (**15**) was isolated. The 1H NMR spectrum of complex **15** in $[D_6]DMSO$ shows one set of dominant signals,

indicating the formation of a single, well-defined complex (Figure S51). The ESI-MS studies indicated that the $(A^3)_4(L^4)_4$ assembly was formed with a series of peaks containing different numbers of counter-cations (Figure 2). The appear-

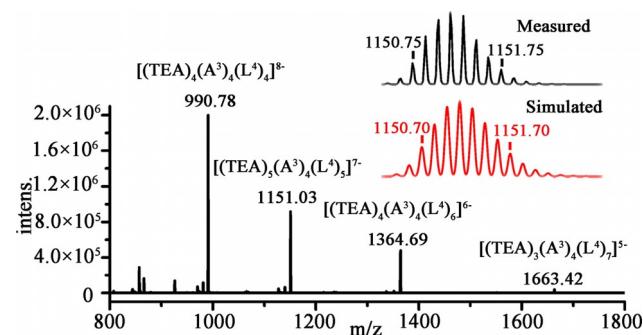


Figure 2. ESI-MS spectrum of the complex $(TEA)_{12}[(A^3)_4(L^4)_4]$ (**15**).

ance of continuous charge states implies the formation of a rather robust assembly with enhanced stability, which could be attributed to the entanglement in the system as shown by the crystal structure described below. Moreover, the other anion, **A⁴**, can also assemble with **L⁴** to form a similar double-walled tetrahedral complex, $(TEA)_{12}[(A^4)_4(L^4)_4]$ (**16**).

Single crystals of **15** were obtained by slow evaporation of a diethyl ether/acetonitrile solution.^[17] X-ray diffraction analysis revealed a double-walled tetrahedral geometry (space group $P\bar{1}$). The C_3 -symmetric **L⁴** ligands are located at the four inner triangular faces, while the 1,3,5-triazine-

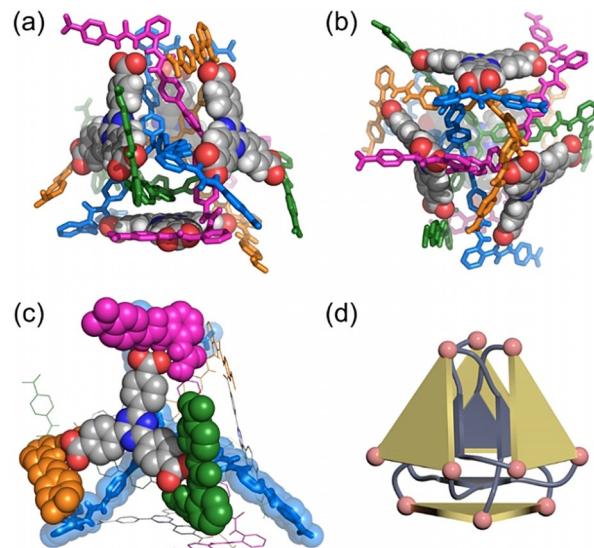


Figure 3. Crystal structure of the double-walled tetrahedron, $[(A^3)_4(L^4)_4]^{12-}$ (**15**). a) Front view and b) top view of the tetrahedron structure, with tris-carboxylate anions (as outer walls) shown in CPK model and the three-arm ligands (as inner walls) in sticks. c) Representation for the bonding geometry between tris-carboxylate anions and ligands. Counter-cations, hydrogens, and solvent molecules were omitted for clarity. d) Cartoon representation of the double-walled ravel structure.

2,4,6-tris(4-benzoate) (**A**³) anions span the four outer faces of the tetrahedron (Figure 3a). This positioning of the large, nearly planar anions is different from that in the truncated tetrahedra **1–4** with **A**¹ and **5** with **A**² which are small enough to be placed on the vertices. Nevertheless, such an arrangement allows the bis(urea) arms of ligand **L**⁴ and the carboxylate termina of **A**³ to meet at the four virtual vertices of a tetrahedron, forming comprehensive hydrogen bonds. Since the three carboxylate arms of an anion **A**³ are bound by bis(urea) groups from three different ligands, a fully entangled structure is assembled. Each COO[−] group accepts four N–H···O hydrogen bonds from a bis(urea), and there are 48 H-bonds altogether (N···O distances range from 2.709(6) to 3.296(9) Å, av. 2.128 Å; N–H···O angles from 116° to 177°, av. 151°; Table S3). Note that one of the urea groups is not involved in the binding of anion; instead, it forms two N–H···O hydrogen bonds with a carbonyl O atom of the ligand (Figure S61). Like the truncated tetrahedra and previous phosphate tetrahedral cages, the complex is also racemic with both $\Delta\Delta\Delta\Delta$ and $\Delta\Delta\Delta\Delta$ configurations (Figure S72).

On each double-walled face, the two kinds of C_3 -symmetric backbones, that is, the inner ligand and outer tris-carboxylate anion, are overlapped with both centroids (amine N atom of ligand and center of the triazine of **A**³, respectively) falling on the center of the triangular face (Figure 3a). However, the three arms of the two layers are arranged in a staggered manner, with an angle of ca. 33° (Figure S73b). The rigid **A**³ moiety is planar, while the tris(biphenyl)amine fragment of ligand **L**⁴ is not flat, forming CH···π interactions between the aryl CH groups of **L**⁴ and the benzene rings of **A**³ (Figure S73c). The formation of such a double-walled structure could be attributed to the multiple hydrogen bonds on the vertices and the favorable CH···π interactions on the faces of tetrahedra.

There are only very few examples of metal-based, double-walled tetrahedra in the literature. Oppel et al. reported the first tetrahedron-shaped, double-walled complex that contains two different C_3 -symmetric ligands based on the slight mismatch of metal ion and ligand.^[24] A thorium-based MOF featuring a double-walled tetrahedral cage structure was synthesized by Xing and Bai,^[25] while an M₁₂L₈ (M=Pd) double-walled, knotted cage was constructed by Fujita et al.^[26] Very recently, a molecular-strain-engineered double-walled tetrahedron was also reported.^[27] In all of these examples, the ligands (same or different) serve as the double walls of the tetrahedron, while the metal ions are either located within the faces or at the vertices. In a sharp contrast, in the current work, the anion itself serves as one (outer) of the walls, thus representing a different assembling mode.

To get deeper insight into the entanglement mode in this double-walled tetrahedral structure, topological analysis was performed. The two C_3 -symmetric, three-armed components (ligand and anion) with the three isolated anion coordination sites can be viewed as three-connecting points (junctions), while the linkage between each COO[−] arm and a bis(urea) unit (typically four N–H···O hydrogen bonds, see Figure 1 and Figure S68) can be extracted as a line. In this way, there are a total of 8 points and 12 lines in the simplified geometry (Figure S68). As mentioned in above structural discussion,

the three carboxylate arms of an anion **A**³ are bonded by three bis(urea) groups from three different ligands in complex **15**. Such a binding between inner-wall ligands and outer-wall anions results in a fully entangled structure, which can be viewed as a hydrogen-bonded ravel. If we choose two of the three-connecting centers (points A and B from the ligand and anion, respectively, see Figure S70), we can see that the three strands (colored in red, orange, and cyan) between vertices A and B weave with each other, thus forming a 3-ravel topology. However, it should be noted that in the interwoven system, three short lines (colored in gray in Figure S70), which link other anion and ligand units, are not involved in the raveling strands. Nevertheless, these free lines do not interfere with the main ravel structure. Overall this is an unprecedented motif for anion-coordination-based assemblies and may expand the ACDA strategy to the realm of complicated ravel systems.

Moreover, if we look further into the structure, we can see six closed loops (Figure S68), and two of them form a Solomon link (Figure 4), a well-known interlocked mode of two loops.

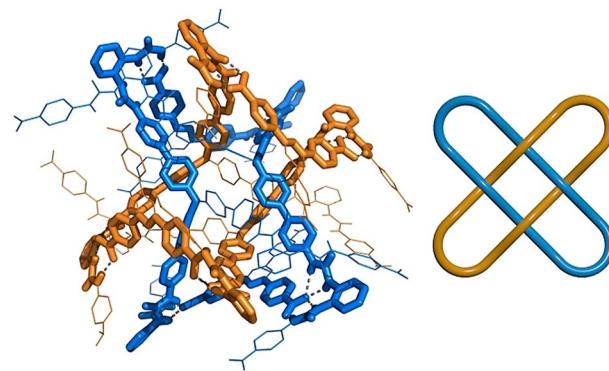


Figure 4. Representation of one of the Solomon links in the double-walled tetrahedron $[(A^3)_4(L^4)_4]^{12-}$.

The first successful synthesis of a molecular Solomon link was achieved by using metal templation to create a helical arrangement of molecular fragments which could then be cyclized to form the required doubly interlocked link.^[28] Then, several other methods have been developed, such as all-in-one syntheses using template-directed self-assembly.^[1d,29] Up to now, reported Solomon links are limited to metal-ion-templated assemblies,^[30] and most of them contain only a single Solomon link.^[6a] In the current case, there are three such links, the same number as in Fujita's work.^[13c]

From another point of view, on each of the double-walled faces, the entanglement of the H-bonded strands results in a trefoil knot, and thus there are four trefoil knots in the structure (Figure 5). As the simplest knot topology, trefoil knots have been extensively studied. The first synthetic molecular trefoil knot was prepared in 1989 by Sauvage and co-workers, where the three crossings were generated by twisting a linear helicate around two copper(I) ions.^[4] Since then many trefoil knots have been synthesized in different ways, including both single and composite trefoil motifs.^[31] Moreover, multiple trefoil knot topologies have also been obtained.^[13c] In our structure, it can be viewed as that four

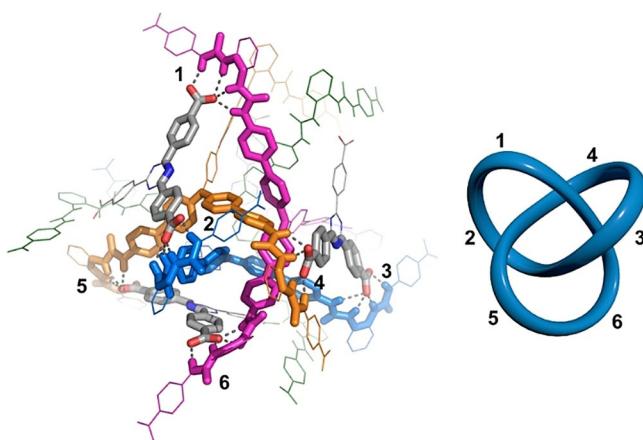


Figure 5. Representation of one of the four trefoil knots in the double-walled tetrahedron structure.

trefoil knots are interconnected by the branches of the three-connecting components (anions and ligands). Notably, the formation of these Solomon links and trefoil knots is observed for the first time in anion-coordination-based systems, which demonstrates the intriguing future development of ACDA.

In the truncated tetrahedral structures (**1–5**), also noticeable is the binding of the peripheral counter-cations. In our previous work, the phosphate cage with the same ligand **L¹** was too small to encapsulate a counter-cation, not even the small tetramethyl ammonium, TMA⁺.^[14b] Here, upon replacing phosphate by **A¹**, the cavity volume increased remarkably (764 Å³), which should be suitable for large quaternary ammonium ions as predicted by calculations (Figure S60). Surprisingly, the crystal structure revealed some acetonitrile molecules rather than TPA⁺ ion (volume 311 Å³) sit in the central cavity of complex **1**. In contrast, seven TPA⁺ cations are located in close proximity to the truncated cage, being trapped in the peripheral aromatic grooves (Figure 1c), while the other five counter-cations are found in the crystal lattice. Indeed, two of the propyl arms of each TPA⁺ ion already insert into the central cavity and form CH···π interactions with a benzene ring of a neighboring **A¹** tri-anion (Figure S71). Thus, it appears that such peripheral binding of multiple guests is more favorable than the complete encapsulation of one single guest within the inner cavity. In fact, the binding of peripheral guests has increasingly been found to be critical in stabilizing supramolecular assemblies, and sometimes their templating effect can even surpass the inner guest.^[32] Our previous work also demonstrated that in anion-coordination-based systems, the peripheral guests could either determine the outcome of the assembled structure^[33] or induce chirality to the ultimate assemblies with chiral guest.^[34]

Herein, the binding of these peripheral guests implies that the size of guest is no more a critical factor as that for the internal cavity, and thus a wider variety of guests might be bound in the outside grooves. This is clearly observed in the case of the larger TBA⁺ ion (TBA = tetrabutyl ammonium), which can also template the formation of a truncated tetrahedron and shows similar binding profiles to TPA⁺ as confirmed by ¹H NMR results (Figures S6–S9). More inter-

estingly, the phosphonium cation with a long alkyl chain, tributyltetradecylphosphonium chloride (**TPPC**), which is widely used in industrial cleaning water systems, killing of sea water mollusks, and inhibition of microbial reproduction and biological fouling treatment, etc.,^[35] was tested and proved to be able to fit into the peripheral grooves of the cage. The formation of the peripheral inclusion complex (**TPP**)₁₂[**(A¹)₄(L¹)₄**] was confirmed by ¹H NMR, NOESY, and ESI-MS (Figures S11–S13). This further proves the excellent guest binding ability of the cage, though in the peripheral grooves, toward industrially important quaternary ammonium/phosphonium cations.

The ¹H NMR spectrum of (**TPA**)₁₂[**(A¹)₄(L¹)₄**] (**1**) in [D₆]DMSO indicates the formation of a highly symmetric product in solution (Figure S1). Downfield shifts of all urea NH proton signals ($\Delta\delta=0.98\text{--}1.88$ ppm) are observed upon hydrogen bonding to the trianion **A¹**, which are considerably smaller than those ($\Delta\delta=2.75\text{--}3.58$ ppm) with PO₄³⁻, thus indicating weaker hydrogen bonds to the carboxylate than phosphate. The signals of protons in the aromatic region, H4 and H5, shift to upfield due to the shielding effect of the closely packed anion complex, while H3 and H6 suffer downfield shifts caused by the anion-urea bonding. The TPA⁺ protons Hα/β/γ give rise to slightly upfield peaks ($\Delta\delta=-0.16\text{--}-0.17$ ppm), supporting the existence and fast exchange of groove-bound and free TPA⁺ ions as found in the crystal structure. The HR ESI-MS spectrum exhibits intense peaks for the species [**(TPA)**_x**(A¹)₄(L¹)₄**]^{y-} at *m/z* = 1764.92 (*x* = 8, *y* = 4, calc. 1764.80), 1374.67 (*x* = 7, *y* = 5, calc. 1374.60), thus confirming the **A₄L₄** composition of complex **1** (Figure S5). In the NOESY spectrum (Figure S4), cross-peaks are observed between all adjacent H¹/H1, H¹/H2, H¹/H7, H¹/H8 protons, indicating the spatial proximity of the ligand and trianion as shown in the crystal structure. Meanwhile, the Hα/β/γ atoms of the peripheral TPA⁺ ions show the expected through-space interactions with the H1/2/7/8/9 protons on the ligand (Figure 6a). DOSY experiment gives a diffusion constant of $D=6.00\times10^{-11}$ m²s⁻¹ with a solvodynamic radius (*r*) of about 18.3 Å, which is comparable to that measured in the crystal structure (15.5 Å) (Figure S2).

Besides the crystal structure, 1D and 2D (COSY, NOESY and DOSY) NMR results also provided evidence for the

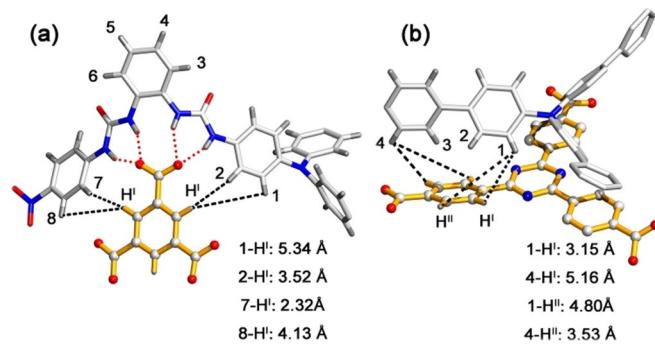


Figure 6. a) Part of the crystal structure of the truncated tetrahedron [**(A¹)₄(L¹)₄**]¹²⁻ (**1**) showing distances between **L¹** and **A¹**. b) Part of the crystal structure of the double-walled tetrahedron [**(A³)₄(L⁴)₄**]¹²⁻ (**15**) showing the through-space interactions between **L⁴** and **A³**.

formation of complex **15** (Figures S51–S54). All urea NH protons display large downfield shifts ($\Delta\delta = 0.60$ – 2.29 ppm) as in the above cases. Upon overlap of the ligand and anion backbones in each double-walled face, the H1 protons on the ligand give rise to upfield-shifted peaks ($\Delta\delta = -0.85$ ppm), while H2/3/4 protons also resonate at slightly upper field ($\Delta\delta = -0.05$ – 0.17 ppm) (Figure S51), as a result of interaction with the outer-wall anion. In the NOESY spectrum (Figure S54), cross-peaks are observed between all adjacent H(1/2/3/4)/H^I and H(1/2/3/4)/H^{II} protons, indicating the spatial proximity of the ligand and 1,3,5-triazine-2,4,6-tris(4-benzoate) as shown in the crystal structure (Figure 6b). The identity of (TEA)₁₂[**(A⁴)₄(L⁴)₄**] (**16**) was also proved by ¹H NMR, COSY, NOESY and DOSY spectra, and HR ESI-MS results (Figures S55–S59).

It can be seen from above results that the sizes of the anions and ligands play an important role in determining the outcome structure. With phosphate in previous work, the anions could only act as points (vertices). When switching to tris-carboxylates, the smallest anion **A**¹ (and in one case relatively small **A**² compared to the largest ligand **L**⁴) favors the truncated tetrahedral geometry because it can serve as the vertex. For the medium-sized anions and ligands, they prefer to form the 1 + 1 complex. Finally, with the largest ligand **L**⁴, which also shows larger degrees of freedom, the highly entangled ravel topology is formed. This structural diversity nicely proves the effect of the adjustable backbone and size and different degrees of freedom on the resulted assembly.

Conclusion

Anion-coordination-driven assembly (ACDA) has proven to be a powerful tool for constructing well-defined supramolecular architectures. Herein we expanded the scope of anion from phosphate or sulfate (zero-dimensional, point) to organic tris-carboxylates (two-dimensional, plane), which yielded novel topologies (truncated tetrahedron and a ravel architecture). Moreover, the three-armed anions and ligands enable the generation of suitable peripheral cavities (or grooves) that can efficiently bind guests, including the biologically and industrially important tetraalkyl-ammonium or-phosphonium cations with long alkyl chains. Because these tris-carboxylate anions can be readily modified and functionalized, the current results shed light to the ACDA strategy in both supramolecular assembly of sophisticated architectures and in related applications.

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Conflict of Interest

The authors declare no conflict of interest.

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