



**From Corannulene to Larger Carbon Bowls:
Are They Better for Multiple Metal Encapsulation?**

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Frontier

**From Corannulene to Larger Carbon Bowls:
Are They Better for Multiple Metal Encapsulation?**

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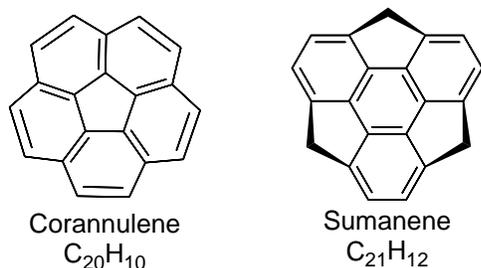
Carbon bowls having two distinctly different faces, convex and concave, represent a unique class of non-planar π -ligands with defined molecular compositions and structures. The smallest π -bowl called corannulene is known to exhibit the record alkali metal ion binding abilities upon multi-electron acquisition. In contrast, the potential of larger carbon bowls with extended π -surfaces in self-assembly with multiple metal ions is yet to be revealed. This Frontier article opens a discussion of the effect of size, charge and symmetry of the bowl-shaped π -ligands on their supramolecular assembly and metal ion intercalation trends.

Suggested TOC



1. Introduction

Bowl-shaped polycyclic aromatic hydrocarbons (often known as fullerene fragments, buckybowl, carbon or π -bowls¹) attract significant attention as symmetric scaffolds for controlled functionalization² and as curved building blocks in synthesis of novel organic and metal-organic functional materials.³ In addition, carbon bowls represent a unique class of π -ligands since they can provide two distinctly different faces, concave (*exo*) and convex (*endo*), for metal coordination.⁴ Furthermore, π -bowls can readily accept multiple electrons in stepwise reduction reactions to form sets of consequently reduced carbanions.⁵ The resulting highly-negatively charged bowl-shaped ligands can be stabilized through the formation of novel supramolecular architectures with multiple alkali metal ions inside and out, as revealed for triply- and tetra-reduced forms of corannulene ($C_{20}H_{10}$, Scheme 1).^{6,7} Based on its unique intercalation with lithium ions, corannulene was shown to be an advanced anode material in energy storage devices.⁸ The recent discovery of a remarkable family of heterometallic supramolecular assemblies formed by $C_{20}H_{10}^{4-}$ has demonstrated its record ability to encapsulate unprecedented high-nuclearity mixed alkali metal units.⁹ These advancements of corannulene chemistry stimulated a broad new investigation of reaction pathways and outcomes of negatively charged π -bowls with increasing surface sizes and diverse structural topologies.¹⁰ The nanocarbon bowls exhibit very rich redox chemistry and, therefore, are expected to show new reactivity and to participate in new chemical transformations. Their deeply reduced carbanions having high negative charge density are especially intriguing as they can be stabilized through the formation of unique and yet unknown metal-rich self-assemblies.



Scheme 1

Herein, the types of supramolecular assemblies formed by the tetrareduced corannulene are briefly reviewed with the focus on its remarkable ability to intercalate previously unseen alkali metal units. The bowl-shaped sumanene, $C_{21}H_{12}$ (Scheme 1), is considered next, followed by an overview of the multi-electron acquisition abilities of larger carbon bowls ranging from $C_{22}H_{10}$ to $C_{30}H_{12}$. This Frontier article opens the first discussion of the effects of surface size, curvature and symmetry on the resulting supramolecular architectures that can be formed by the multi-charged nanocarbon bowls.

2. Supramolecular Architectures Formed by Tetrareduced Corannulene

Corannulene ($C_{20}H_{10}$, Scheme 1) first discovered by Barth and Lawton¹¹ is the smallest C_{5v} symmetric bowl-shaped polyarene which can be considered as a one-third of the C_{60} -fullerene. Owing to its doubly degenerate low-lying unoccupied molecular orbitals, corannulene can accept up to four electrons in stepwise reduction reactions.¹² In its tetrareduced form, corannulene self-assembles with multiple Li^+ ions to afford the sandwich-type aggregates, as predicted by Scott and Rabinovitz with co-workers in 1994 by *in situ* NMR spectroscopy investigations.¹³ In 2011, we revealed a unique structure of this supramolecular product having five Li^+ ions encapsulated

between the convex faces of two $C_{20}H_{10}^{4-}$ decks (Figure 1) using X-ray crystallography augmented by NMR spectroscopy and DFT calculations.¹⁴

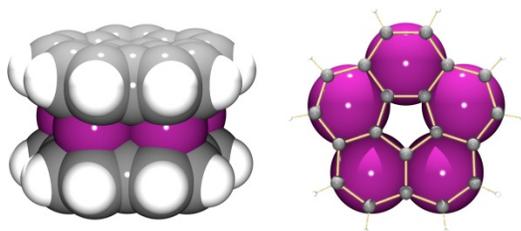


Fig. 1 Sandwich core formed by corannulene tetraanions with five Li^+ ions, $[(C_{20}H_{10}^{4-})//5Li^+//(C_{20}H_{10}^{4-})]^{3-}$ (left) and the pentanuclear lithium belt overlaid with a corannulene framework (right).

We have also demonstrated that the coordination limits of the electron-rich $C_{20}H_{10}^{4-}$ anion (0.2 electrons per C-atom) can be further extended by using two alkali metals in chemical reduction reactions. The use of binary combinations of Li with K, Rb or Cs metals resulted in the discovery of a new class of heterobimetallic supramolecules formed by tetrareduced corannulene, which is able to sandwich the highly-charged hexanuclear units of the $(Li_3M_3)^{6+}$ ($M = K, Rb, Cs$; Figure 2) and $(LiM_5)^{6+}$ ($M = K$ and Rb) compositions.⁷ All the above products have been isolated as bulk crystalline solids and crystallographically characterized, showing the similarities of reaction pathways for K, Rb, and Cs metals. The formation of the cesium-based analogue with the $(LiCs_5)^{6+}$ core has been confirmed by 7Li NMR spectroscopy.

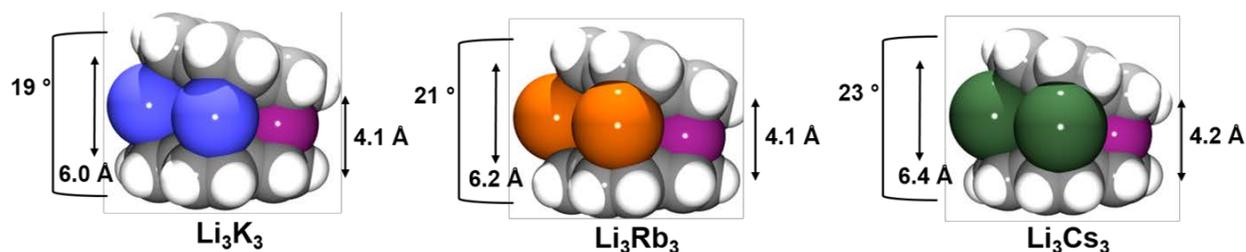


Fig. 2 Space-filling depiction of the Li_3M_3 -core sandwiches ($\text{M} = \text{K}, \text{Rb}, \text{and Cs}$) with the $\text{C}_{20}\text{H}_{10}^{4-}$ bowls bound in the convex-convex fashion, along with selected geometric parameters.

The isolation of these remarkable sandwich-type supramolecules formed by the $\text{C}_{20}\text{H}_{10}^{4-}$ bowls has raised many interesting questions. Is corannulene unique as having the right set of properties for self-assembly with multiple metal ions? Can other carbon bowls behave in a similar fashion? What combination of charge, surface size and bowl depth are optimal for the formation of metal-rich self-assemblies? Can these parameters be effectively used in order to tune the intercalated metal ion content? The overview and analysis of unique self-assembly patterns of nanocarbon bowls can reveal the general trends and open a broad new area of supramolecular chemistry for investigation.

3. From Corannulene to Larger Carbon Bowls

From corannulene we moved to sumanene (Scheme 1), a larger and deeper carbon bowl with different symmetry, properties and unique chemistry.¹⁵ The formation of carbanions for the C_{3v} symmetric sumanene, $\text{C}_{21}\text{H}_{12}$, proceeds through stepwise deprotonation of the five-membered rings, as reported by Hirao and co-workers.¹⁶ We have recently completed a theoretical investigation of these processes evaluating the charge distribution and aromaticity changes of sumanene upon deprotonation.¹⁷ While the sumanenyl mono- and dianions, $\text{C}_{21}\text{H}_{11}^-$

and $C_{21}H_{10}^{2-}$, exhibit the localization of negative charge in the five-membered rings,¹⁸ the $C_{21}H_9^{3-}$ anion has its charge delocalized over the bowl surface. This delocalization makes it a perfect highly-charged π -ligand for sandwich formation, as it was demonstrated in the structurally characterized assembly with multiple potassium ions.¹⁹ In the main building unit, two $C_{21}H_9^{3-}$ bowls trap a belt of six potassium ions in between, utilizing all binding sites except the central six-membered ring of sumanenyl trianion. As a result, a triple-decker neutral sandwich is formed, which upon filling the open concave cavities of the bowls with two external metal ions becomes dicationic (Figure 3), thus requiring co-crystallization with sumanenyl dianions for balancing the overall charge. This results in the formation of a complex 2D network in the crystal structure of the only supramolecular product reported for $C_{21}H_9^{3-}$ so far.¹⁹ However, this X-ray structural characterization and analysis of building blocks in the sumanenyl-potassium self-assembly showed the need to search for the carbon bowls that can accommodate higher negative charge than $C_{21}H_9^{3-}$.

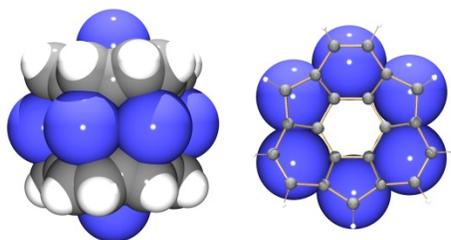
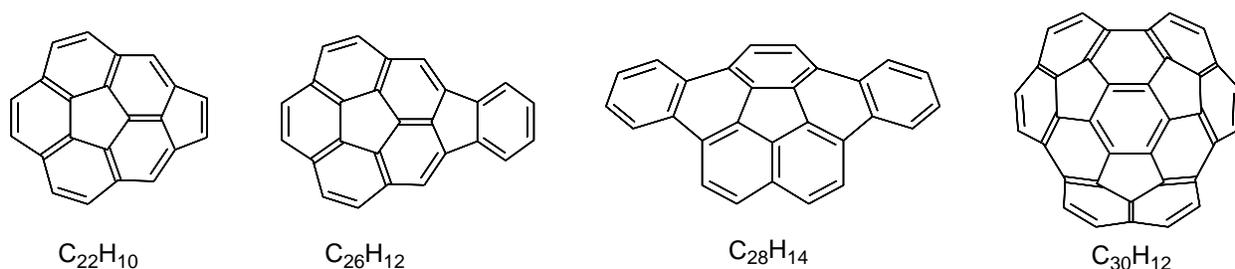


Fig. 3. Sandwich core formed by sumanenyl trianions with multiple K^+ ions, $\{K^+{}_2[(C_{21}H_9^{3-})//6K^+//(C_{21}H_9^{3-})]\}^{2+}$ (left) and the hexanuclear potassium belt overlaid with a sumanene framework (right).

The stepwise chemical reduction of several bowl-shaped polycyclic aromatic hydrocarbons (PAHs) with larger surfaces than corannulene has been carefully investigated by

Scott and Rabinovitz with co-workers using spectroscopic methods. They demonstrated that corannulene derivatives, such as cyclopenta[*b,c*]corannulene ($C_{22}H_{10}$) and indenocorannulene ($C_{26}H_{12}$) (Scheme 2), can form tetraanions in solution upon *in situ* reduction with alkali metals.²⁰ The analysis of reaction outcomes demonstrated a great variation and complexity of the aggregation pathways for the highly-charged carbon bowls with extended π -surfaces.



Scheme 2

Cyclopenta[*b,c*]corannulene was shown to undergo an unusual aggregation process at the highest reduction stage to form a new type of coordinative dimer with entrapped lithium ions.²⁰ Based on NMR spectroscopy data, the dimer was predicted to consist of two $C_{22}H_{10}^{4-}$ anions bound together in a convex-convex fashion through the formation of the C–Li–C bonds between two rehybridized carbon atoms from each bowl. Up to date, the crystallographic characterization of the $(C_{22}H_{10}^{4-})_2/8Li^+$ aggregate, revealing its unique internal and external binding with multiple lithium ions (Figure 4), is still lacking. In contrast to the Li-induced reduction of $C_{22}H_{10}$, its reaction with potassium stops at the formation of a very reactive trianion-radical, clearly showing the effect of metal on the degree of reduction. The use of other metals or their dual combinations has not been investigated and may unravel new reaction pathways for this bowl.

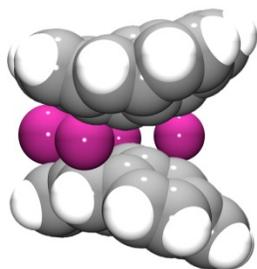


Fig. 4 Proposed self-assembly of two $C_{22}H_{10}^{4-}$ bowls with four intercalated Li^+ ions.²⁰ External lithium ions are not shown.

The chemical reduction of indenocorannulene follows a different path and also shows a great influence of alkali metals on the reaction outcome. The reaction of $C_{26}H_{12}$ with potassium, by successive one-electron transfers, proceeds through four reduction steps that include alternating dimerization/bond-cleavage processes.²¹ At the final stage, the $C_{26}H_{12}^{4-}$ tetraanion (*ca.* 0.15 electrons per C-atom) is formed; however, its aggregation pattern with potassium ions is yet to be revealed. The solution investigations showed a persistent trend that larger bowls in their highly-reduced forms require larger alkali metal ions for stabilization, in contrast to corannulene and cyclopenta[*b,c*]corannulene.

This trend has also been seen upon reduction of dibenzo[*a,g*]corannulene, containing a central corannulene core fused by benzene rings on two sides (Scheme 2).²² Interestingly, chemical reduction of $C_{28}H_{14}$ with excess lithium metal stops at the formation of trianion-radicals and could not proceed beyond this stage.²³ This contrasts the lithium-induced reduction of parent corannulene known to afford the tetraanions. However, when potassium metal is used for chemical reduction of $C_{28}H_{14}$, the formation of tetrareduced dibenzocorannulene has been observed, contrary to unsubstituted corannulene which can only be reduced to the trianion stage under these conditions. The observed differences clearly reflect on the effect of framework

topology, surface size and charge distribution upon electron acquisition for bowl-shaped PAHs. It is expected that the larger π -system of $C_{28}H_{14}$ allows for better delocalization of four negative charges and can be stabilized by potassium counteranions without the need to form sandwich-type dimers observed for the tetrareduced corannulene with lithium ions. As the charge density in the $C_{28}H_{14}^{4-}$ anion is smaller than that in $C_{20}H_{10}^{4-}$ that may lead to less tight binding of lithium counteranions, thus disfavoring sandwich assembly. However, these predictions remain to be proven, as no crystalline products of dibenzocorannulene anions have been isolated yet.

The effect of metal has also been seen upon supercharging of the larger and deeper hemifullerene bowl, $C_{30}H_{12}$ (Scheme 2).²⁴ It was found that stepwise reduction of $C_{30}H_{12}$ with lithium gives no new diamagnetic species, while reacting it with potassium metal affords the stable hexaanion, $C_{30}H_{12}^{6-}$.²⁵ The latter highly-reduced species bears one negative charge per five carbon atoms (or 0.2 electrons per C-atom), precisely as in the $C_{20}H_{10}^{4-}$ anion discussed above. Nevertheless, $C_{30}H_{12}^{6-}$ does carry a very high absolute charge over a relatively small and curved carbon skeleton and is the smallest polyaromatic hexaanion so far detected. Based on NMR investigation, it was concluded that the $C_{30}H_{12}^{6-}$ anion is strongly perturbed by its close environment, and the observed species cannot be simply monomeric. Experimental evidence from NMR spectroscopy and DFT calculations together were best explained by the formation of a remarkable tetrameric structure self-assembled in solution, $(C_{30}H_{12}^{6-})_4/24K^+$ (Figure 5). Furthermore, it was predicted that six potassium ions are covalently bound (or have strong contact-ion character) with the tetramer, while additional eighteen K^+ ions remain solvent-separated from this large assembly.²⁵ The overall network of intra- and intermolecular interactions in the crystal structure of this spectacular product can be more complex and remains

to be uncovered. Notably, the higher order superstructures, such as an octamer or 20-mer, were not ruled out, thus presenting a very intriguing example waiting for X-ray structural elucidation.

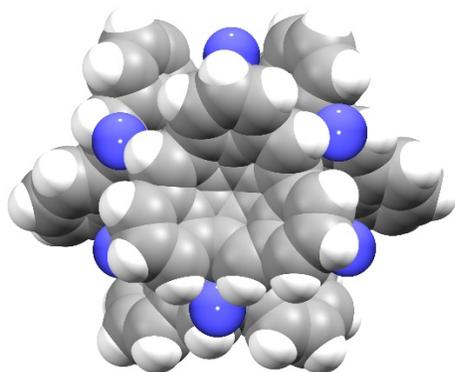


Fig. 5 Proposed tetrameric self-assembly of four $C_{30}H_{12}^{6-}$ bowls with six intercalated K^+ ions.²⁵ The 18 solvent-separated potassium ions are not shown.

Overall, the unique class of carbon bowls with different symmetries, bowl depth and surface size provides a great variation of structural parameters for further investigation that is ongoing in our group. The symmetry reduction coupled with π -surface enlargement alters the negative charge and spin distribution and that could induce new coupling pathways,²⁶ which these non-planar PAHs can undergo. Incorporation of specific heteroatom donor sites into bowl-shaped carbon frameworks²⁷ can be additionally used in the programmable ligand design strategies.²⁸ Several large carbon bowls have potential to serve as multi-electron reservoirs and in their highly-negatively charged forms are expected to show novel supramolecular and organometallic chemistry. This chemistry is very challenging as the deeply-reduced carbanions exhibit high reactivity and extreme sensitivity to air and moisture, requiring special care during all experiment steps and handling of the products. Full characterization of the resulting

crystalline materials provides additional set of challenges and requires special techniques to be developed.

4. Conclusions

The discovery and structural characterization of remarkable supramolecular aggregates formed by tetra-reduced corannulene has revealed the unique ability of bowl-shaped carbanions to encapsulate unprecedented high-nuclearity homo- and heterometallic units ranging from five to six alkali metals.⁹ The direct comparison of the lithium-only product to self-assemblies having heavy alkali metal ions has demonstrated unmatched flexibility of corannulene framework to adapt to different internal and external coordination environments. This has opened a new research direction in supramolecular chemistry of highly-charged non-planar PAHs that can be stabilized through the formation of unique supramolecular aggregates. Several possible aggregation and coupling pathways have been predicted based on the *in situ* solution spectroscopic investigations of larger π -bowls.^{20,21,23,25} However, only for the highly-charged corannulene the self-assembly patterns with Group 1 metals have been crystallographically confirmed so far.^{5,9} Notably, the ability of bowl-shaped carbon systems to undergo reversible multi-electron reduction processes and to store high amount of charge is very attractive for the development and advancement of new rechargeable batteries and other energy storage devices, further stimulating research interest in these systems.

The journey of investigating the size and symmetry effects of nonplanar π -ligands on the resulting supramolecular architectures and metal binding patterns has just started. Can the expansion of carbon bowl surface coupled with the high negative charge of their carbanions be

used in order to tune and increase the encapsulated alkali metal content? Does symmetry of the bowl play an important role? How the depth of the bowls would affect the resulting self-assembly patterns? Can this unique chemistry be expanded beyond the Group 1 metals? This all remains to be discovered.

Acknowledgements

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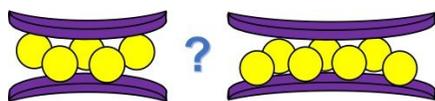
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Suggested TOC



A discussion of the effect of size, charge and symmetry of carbon π -bowls on their supramolecular assembly and metal ion intercalation trends is provided.