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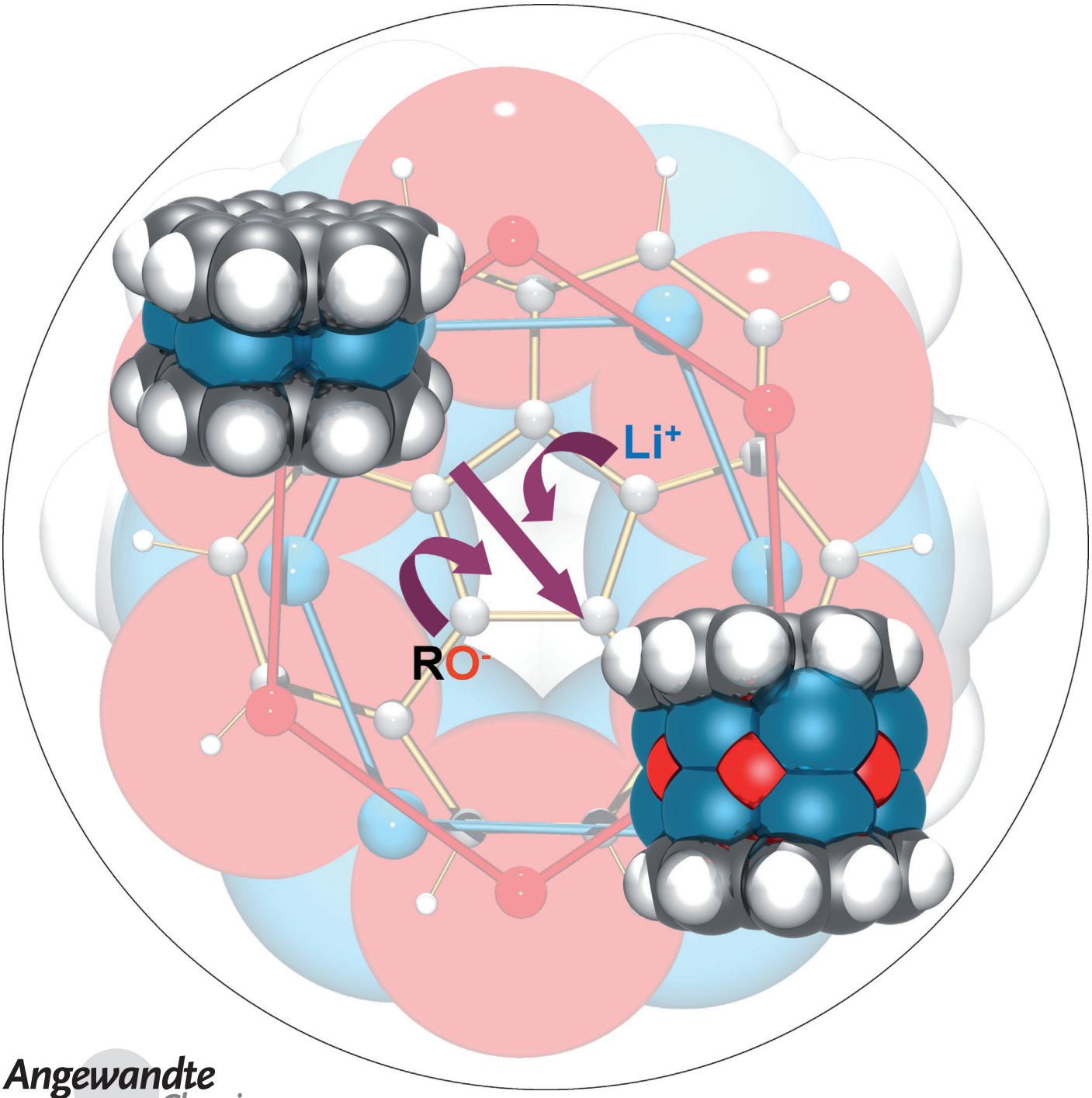
# Pentadecker Supramolecules with a Lithium Alkoxo Nanobelt Sandwiched between Two Highly Charged Buckybowl Surfaces**

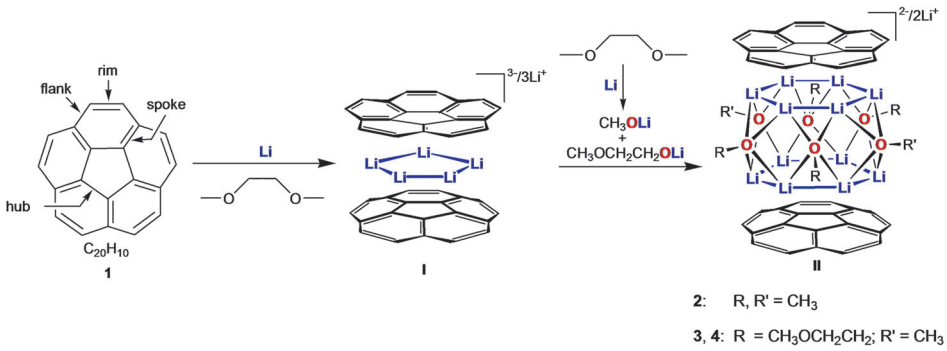
*Alexander V. Zabula, Sarah N. Spisak, Alexander S. Filatov, and Marina A. Petrukhina**




Angewandte Chemie

The knowledge and fundamental understanding of charge/discharge processes in Li-ion batteries and side-reactions leading to their aging are critical for the design and fabrication of highly efficient rechargeable cells.[1] Decomposition of most common electrolytes such as organic carbonates upon manifold charge/discharge cycles in graphite-based Li-ion batteries leads to power fade and reduces battery performance and durability.[2] The decomposition products formed upon the first charging of graphitic anodes are known to include lithium carbonate, dicarbonates, alkoxides, and other fragmentation species.[3] These compounds form a solid–electrolyte interphase (SEI) on the graphite surface that provides the transportation of lithium ions to the negative graphitic electrode. Numerous experimental and theoretical investigations are now focused on the modeling and study of the SEI structure and the mechanism of its formation.[4]




***Scheme 1.*** Preparation of multilayered sandwiches **2**–**4**.

It has been demonstrated that carbon allotropes with curved π-surfaces can substitute graphite and serve as prospective anode materials for the fabrication of Li-ion batteries.[5] In this regard, bowl-shaped carbon-rich polyaromatic hydrocarbons have been widely used as useful and effective models for investigation of fullerenes and nanotubes[6] and their alkali metal intercalated products.[7] Recently, we accomplished the first structural characterization of a supramolecular aggregate formed by the highly reduced 1/3 structural subunit of $C_{60}$-fullerene, the corannulene tetraanion ($C_{20}H_{10}^{4-}$, $\mathbf{1}^{4-}$), with lithium ions.[8] The resulting product formed in tetrahydrofuran (THF; **I**, Scheme 1) exhibits high lithium encapsulation capacity having five lithium ions sandwiched between two tetrareduced corannulene decks. Notably, the triple-decker structure is retained upon recrystallization of **I** from THF in the presence of such strong O-donors as crown ethers and diglyme.[8a,9] At the same time, the use of neat diglyme for reduction of $C_{20}H_{10}$ with lithium metal has prevented the high-order self-assembly of $\mathbf{1}^{4-}$ with $Li^+$ ions, according to our recent NMR investigations.[9] Supramolecular assembly processes of highly charged corannulene and other π-bowls have not been explored in other solvent media, which is important and pertinent to the Li-induced electrolyte decomposition and Li–graphite intercalation processes. In this work, we investigate the reduction of corannulene with lithium metal in dimethoxyethane (DME) and report the formation of multilayered supramolecular aggregates of a new type, namely $[\mathbf{1}^{4-}/Li_6/(OR)_6/Li_6/\mathbf{1}^{4-}]^{2-}$ (**II**, Scheme 1).

The low-temperature $^7$Li NMR spectrum of tetrareduced corannulene in DME, measured after the formation of a brown solution characteristic of $\mathbf{1}^{4-}$ (3 h, 20 °C), shows the sharp resonance of $[\mathbf{1}^{4-}/Li_5/\mathbf{1}^{4-}]^{3-}$ at $\delta = -11.3$ ppm and the broad signal of solvated $Li^+$ ions at $\delta = -1.3$ ppm (Figure 1). The $^7$Li signal of the type **I** sandwich in DME is shifted slightly up-field compared to that observed in THF ($\delta = -11.7$ ppm).[8] The prolonged reaction time leads to a decrease of the resonance intensity of **I**. This process is accompanied by the appearance of the $^7$Li NMR signals in the range from $\delta = -6.0$ to $\delta = -11.0$ ppm (Figure 1), illustrating the formation of new contact ion pairs and sandwiched lithium ions. At ambient conditions, the $^7$Li NMR resonance signal of sandwich **I** completely disappears in eight days.

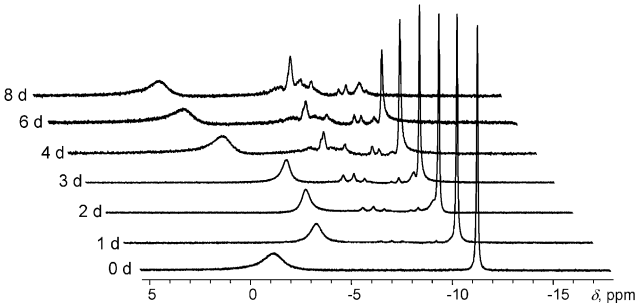



***Figure 1.*** Time-evolution of the $^7$Li NMR spectra (−40 °C) of the $[\mathbf{1}^{4-}/Li_5/\mathbf{1}^{4-}]^{3-}$ sandwich in DME in the presence of Li metal.

Investigation by $^1$H NMR spectroscopy also demonstrates the disappearance of the singlet at $\delta = 6.95$ ppm of **I** and the appearance of multiple new resonances of aromatic protons in the range of $\delta_H = 7.25$–$7.15$ ppm. Moreover, the time-dependent $^1$H NMR spectra show the formation of $H_2C{=}CHOCH_3$ and $H_2C{=}CH_2$ in the reaction mixture. It should be emphasized that sandwich **I** is stable in THF solution in the presence of lithium metal. The NMR study of **I**

[*] Dr. A. V. Zabula, S. N. Spisak, Dr. A. S. Filatov, Prof. Dr. M. A. Petrukhina
Department of Chemistry, University at Albany
State University of New York, Albany, NY 12222 (USA)
E-mail: mpetrukhina@albany.edu

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does not show any noticeable changes for the probe kept at ambient conditions for two months. However, the Li- and K-induced cleavage of DME with the formation of $CH_3OCH_2CH_2O^-$ alkoxide species has been previously detected by West and co-workers.[10]

Various crystallization techniques have been applied and lead to the successful isolation of several new supramolecular aggregates of tetrareduced corannulene with lithium ions (**2**–**4**). Based on the above NMR observations, we can speculate that products **2**–**4** are formed upon reaction of the initially produced sandwich **I** with the reactive ionic species resulting from the DME cleavage (Scheme 1). Compound **2** has been crystallized from a DME/THF mixture (v/v 20:1) as black blocks with an overall formula of $[Li_2(dme)_3][\mathbf{1}^{4-}/Li_6(thf)/(OCH_3)_6/Li_6(thf)/\mathbf{1}^{4-}]$. Its X-ray diffraction study[11] revealed the formation of a unique $Li_6/(OCH_3)_6/Li_6$ cluster core stabilized by two corannulene tetraanions to form a remarkable supramolecular aggregate (Figure 2a). The layered lithium alkoxo belt with the overall dimensions of $6.5 \times 5.5 \times 2.5$ Å consists of an $O_6$-ring bridging two essentially planar $Li_6$-hexagons. The Li–O distances within the cluster are in the range of 1.942(5)–1.994(5) Å and comparable to those measured in lithium methoxide (1.94(3) Å).[12]

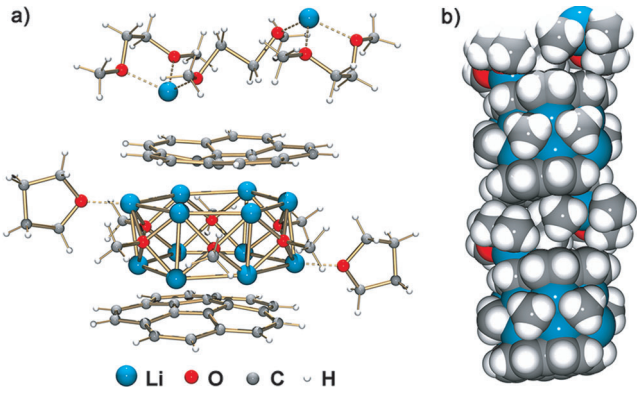



***Figure 2.*** The building unit (a) and the space-filling model of a fragment of a 1D polymeric chain of **2** (b, THF molecules are omitted for clarity).

The Li···Li distances between the two $Li_6$-rings in **2** (2.500(6)–2.538(6) Å) are very short. They are shorter than those found in $[CH_3Li]_4$ (2.591(9) Å).[13] The Li···Li interatomic separations within the $Li_6$-rings (2.751(7)–2.767(7) Å) are longer than the above but still remain significantly shorter than those in the type **I** sandwich (3.053(5)–3.104(5) Å)[8a] and in lithium metal (3.04 Å).[14] Notably, the formation of lithium alkoxo nanobelts may represent possible structural motifs of Li–O deposits on a carbon composite electrode in Li-ion cells.[15]

Two additional lithium ions are bound to the sandwich exteriors in an $\eta^2$-binding mode (2.256(5)–2.308(5) Å) in **2**. In **I**, the exterior coordination of lithium ions to the concave face of $C_{20}H_{10}^{4-}$ was of the $\eta^3$-type.[8a] The coordination of the extraneous $Li^+$ ions is completed by a chelating dme molecule. One additional dme molecule bridges two neighboring $Li(dme)^+$ cations to form $[Li_2(dme)_3]^{2+}$ units that link the sandwiches **II** into a 1D polymer in the crystal lattice of **2** (Figure 2b).

A few crystals of **3** were deposited from the reaction mixture of corannulene with excess lithium metal in DME layered with hexanes and kept at 13 °C for three weeks. An X-ray diffraction study of **3** revealed the presence of the same pentadecker $[\mathbf{1}^{4-}/Li_6/(OR)_6/Li_6/\mathbf{1}^{4-}]^{2-}$ supramolecular aggregate. In contrast to **2**, both methoxide ($CH_3O$-) and 2-methoxyethoxide ($CH_3OCH_2CH_2O$-) groups participate in the formation of the lithium alkoxo nanobelt to afford $[Li_2(dme)_2][\mathbf{1}^{4-}/Li_6/(OCH_3)_2(OCH_2CH_2OCH_3)_4/Li_6/\mathbf{1}^{4-}]$ (**3**, Figure 3a). The Li–O bond lengths within the belt in **3** span a broader range (1.87(3)–2.07(2) Å) than in **2**. The extraneous

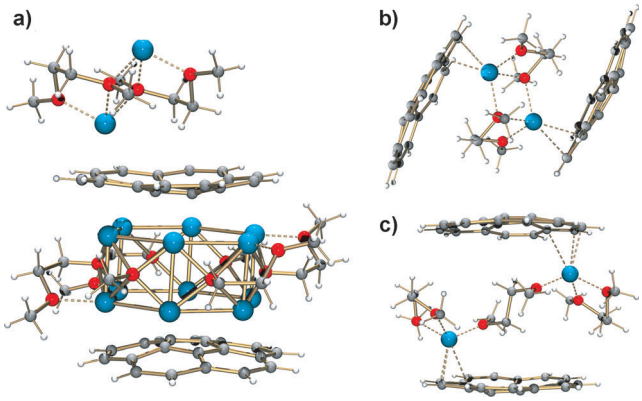


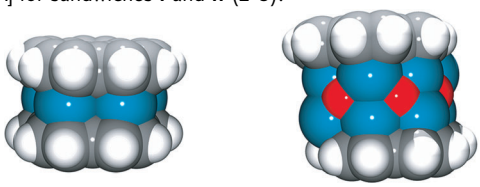

***Figure 3.*** The building unit (a) of a 1D polymeric chain of **3**; the $[Li_2(dme)_2]^{2+}$ of **3** (b) and $[Li_2(dme)_3]^{2+}$ of **2** and **4** (c) that hold the two corannulene tetraanions of neighboring sandwiches **II** together.

$Li^+$ ions are bound to the sandwich **II** in an $\eta^3$-mode (2.250(6)–2.478(6) Å). They also have one dme molecule coordinated in a chelating fashion with additional Li···O contacts (2.143(6) Å) that hold two neighboring $Li(dme)^+$ moieties together. As a result, the slightly different cationic building units, $[Li_2(dme)_2]^{2+}$, hold the anionic sandwiches together in **3** (Figure 3b), but the overall 1D polymeric chains in **2** and **3** are quite similar.

Crystals of **4**, $[Li_2(dme)_3][\mathbf{1}^{4-}/Li_6/(OCH_3)_2(OCH_2CH_2OCH_3)_4/Li_6/\mathbf{1}^{4-}]$, were deposited from the reaction mixture in DME kept at 20 °C for seven days. Their X-ray diffraction investigation shows the formation of the type **II** sandwich, identical to that observed in **3**, with four $CH_3OCH_2CH_2O$- and two $CH_3O$- equatorial groups around the nanobelt interior (Figure S1). At the same time, the cationic building block in **4**, $[Li_2(dme)_3]^{2+}$, is the same as that in **2** (Figure 3c). Importantly, all three new products **2**–**4** contain the same type of lithium alkoxo nanobelt showing its stability and wide occurrence under different experimental settings.

The C–C bond distances of $C_{20}H_{10}^{4-}$ in **2** and **3** (sandwich **II**) are almost equidistant to those measured for sandwich **I** (Table 1). Similarly, the C–C bond length perturbations of the corannulene core upon the acquisition of four electrons are indicative of the formation of the central aromatic cyclopentadienyl $6e^-/5C$ ring surrounded by an aromatic $18e^-/15C$ annulenyl cycle.[16]

***Table 1:*** Key distances [Å] for sandwiches **I** and **II** (**2**–**3**).



**I** **II**

| | $[\mathbf{1}^{4-}/Li_5/\mathbf{1}^{4-}]^{3-}$ (sandwich **I**)[a] | $[\mathbf{1}^{4-}/Li_6/(OR)_6/Li_6/\mathbf{1}^{4-}]^{2-}$ (sandwich **II**) | |
|---|---|---|---|
| | | **2** | **3** |
| hub | 1.390(3)–1.400(2) | 1.394(4)–1.406(4) | 1.390(4)–1.404(4) |
| spoke | 1.421(2)–1.433(2) | 1.421(4)–1.436(4) | 1.426(4)–1.436(4) |
| flank | 1.429(3)–1.445(2) | 1.431(4)–1.444(4) | 1.421(4)–1.439(4) |
| rim | 1.449(3)–1.490(2) | 1.445(4)–1.484(4) | 1.443(4)–1.474(4) |
| bowl depth | 0.241(2)–0.355(2) | 0.354(4) | 0.433(4) |
| $Li_{sandwcd}\cdots C$ | $\eta^6$: 2.204(4)–2.690(4) | $\eta^6$: 2.337(5)–2.600(5)<br>$\eta^4$: 2.235(5)–2.528(5)<br>$\eta^3$: 2.344(5)–2.665(5) | $\eta^6$: 2.322(5)–2.688(6)<br>$\eta^2$: 2.301(6)–2.381(6) |
| $Li_{extraneous}\cdots C$ | $\eta^3$: 2.316(4)–2.776(4)<br>$\eta^6$: 2.208(4)–2.736(4) | $\eta^2$: 2.256(5)–2.308(5) | $\eta^3$: 2.250(6)–2.479(6) |
| Li···Li | 3.053(5)–3.104(5) | 2.751(7)–2.768(7)[b]<br>2.500(6)–2.539(6)[c] | 2.773(7)–2.898(8)[b]<br>2.481(7)–2.525(6)[c] |

[a] for the $[\{Li(thf)_2\}\{\mathbf{1}^{4-}/Li_5/\mathbf{1}^{4-}\}\{Li(thf)_3\}][Li(thf)_4]$ salt;[8a] [b] within the $Li_6$-ring; [c] between two $Li_6$-rings.

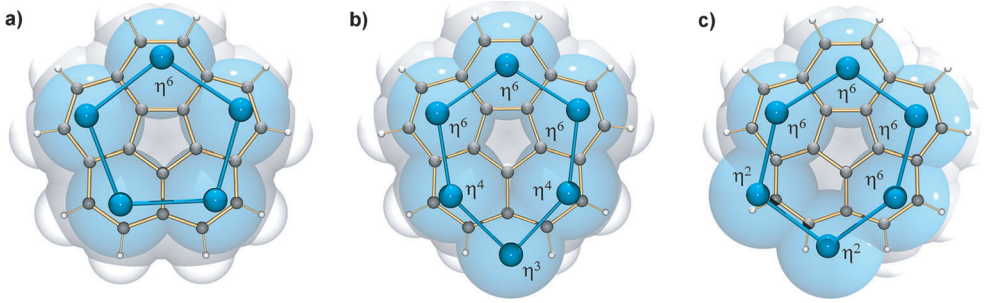



***Figure 4.*** Coordination of the interior $Li^+$ ions (blue spheres) to a corannulene tetraanion in sandwiches of the type **I** (a) and **II** (**2** (b), **3** and **4** (c)) superimposed with the space-filling models.

The presence of the quadruple negative charge along with the binding of multiple $Li^+$ ions to the corannulene surface lead to a significant flattening of the bowl depth (0.354(4)–0.433(4) Å) compared to the neutral ligand (0.875(2) Å).[17] Notably, relatively large bowl-depth variations are observed for tetrareduced corannulene in different coordination environments. For example, an approximately 0.2 Å difference is revealed for $C_{20}H_{10}^{4-}$ in **I** and **II**. Thus, the highly reduced corannulene bowl shows sufficient core flexibility which allows it to readily adjust for the geometry and electrostatic forces of the encapsulated positively charged Li-based clusters.

Coordination of internal lithium ions to the tetrareduced surface of corannulene in **I** and **II** is shown in Figure 4. All sandwiched $Li^+$ ions in **I** exhibit an asymmetric $\eta^6$-binding to five six-membered rings of the anionic surface (Figure 4a); whereas variations in coordination are observed for **II** in **2**–**4**. Overall, the Li···C interatomic distances are shorter in **I** than those in **II** (Table 1). Three different $Li_{sandwcd}\cdots C$ binding modes, namely $\eta^3$-, $\eta^4$-, and $\eta^6$-, are observed for the sandwiched lithium ions in **2** (Figure 4b). Notably, strong binding of the solvated thf molecule ($Li{-}O_{thf}$ 1.933(5) Å) completes the coordination of the $\eta^3$-bound lithium ion. For **3** and **4**, four internal $Li^+$ ions are coordinated to the π-surface of $\mathbf{1}^{4-}$ in the $\eta^6$-fashion, while two others exhibit $\eta^2$-binding (Figure 4c). Additional intermolecular Li···O interactions with the donor functionalities of the equatorial alkoxo groups (1.971(6) and 2.011(8) Å for **3**) can be identified for these $\eta^2$-coordinated lithium ions.

In conclusion, the self-assembly of tetrareduced corannulene with the products of Li-induced DME decomposition constitutes a new facet in supramolecular chemistry of highly charged bowl-shaped polyarenes. In addition to a better understanding of possible solvent/electrolyte cleavage processes in the presence of carbonaceous materials and excess lithium, a novel type of high-order multilayered sandwiches, $[C_{20}H_{10}/Li_6(OR)_6Li_6/C_{20}H_{10}]^{2-}$, has been reproducibly obtained under different crystallization conditions. The above pentadecker supramolecular aggregates show only slight variations of coordination environment at the exterior and perimeter, according to the X-ray diffraction studies of **2**–**4**. But in all cases, the formation of a unique lithium alkoxo cluster with nanosize dimensions sandwiched between two tetrareduced corannulene decks has been revealed, expanding the organometallic chemistry of lithium(I) and coordination limits of $C_{20}H_{10}^{4-}$.

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[11] CCDC 895016 (**2**), 895018 (**3**), and 895017 (**4**) 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.

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