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Charged Nanobelts

Tightening of the Nanobelt upon Multielectron Reduction**

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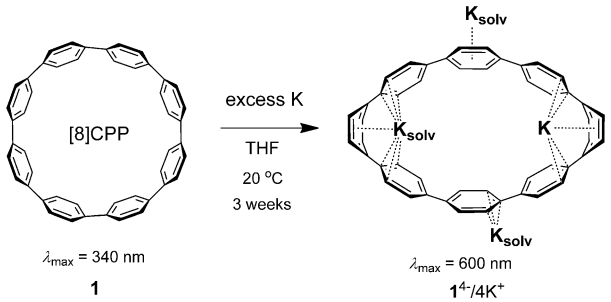
Curved polyaromatic hydrocarbons (PAHs) and their charged products are of special fundamental interest owing to their unique balance of strain and conjugation, which sheds new light on the concepts of aromaticity, optoelectronics, conductivity, and magnetism.[1] In particular, anions of buckybowls—nonplanar PAHs that can be mapped onto the surface of fullerenes[2]—have been studied extensively, and unique electronic structures have been discovered.[3] Negatively charged curved polyarenes are also known to form a great variety of aggregates with metal counterions both in solution and in the solid state; these aggregates range from discrete units to various supramolecular assemblies.[4] Furthermore, owing to their high symmetry and the presence of degenerate lowest unoccupied molecular orbitals (LUMOs), buckybowls have the capacity to be supercharged.[4g,j] This property has been exploited for applications in high-performance batteries and ultracapacitors.[5]

Recently, cycloparaphenylenes—the shortest possible fragments of armchair carbon nanotubes—have burst onto the scene as new nonplanar PAHs.[6] These structures had long been sought since their early conceptualization in 1934[7] and the pioneering synthetic efforts of Vögtle and co-workers in the 1990s.[8] Following the first preparation of [*n*]cycloparaphenylenes ([*n*]CPPs) in 2008,[9] scalable[10] and selective syntheses of [*n*]CPPs of a variety of sizes[11] and studies examining their size-dependent optoelectronic properties,[9,11d,12] unique crystal stacking,[10,11f] and supramolecular behavior[10b,13] have all been reported. To date, however, the charging of these unique curved PAHs with additional electrons has not been investigated.[14] Herein, we report the first synthesis and characterization of a multireduced cycloparaphenylene, namely, the tetraanion [8]CPP^{4-} ($\mathbf{1}^{4-}$; Scheme 1).



Scheme 1. Preparation of $\mathbf{1}^{4-}$/4 K$^+$.

The direct reduction of [8]CPP with potassium metal in THF in the presence of [18]crown-6 ether led to the precipitation of the dark-blue potassium salt of the nanobelt tetraanion: $\mathbf{1}^{4-}$/4 K$^+$ (Scheme 1).[15] The resulting air- and moisture-sensitive product is sparingly soluble in common organic solvents. The absorbance maximum corresponding to the π–π* transition in the UV/Vis spectrum for $\mathbf{1}^{4-}$/4 K$^+$ (THF) was observed at $\lambda_{max} = 600$ nm. A significant bathochromic shift from the absorbance maximum of the neutral ligand ($\lambda_{max} = 340$ nm) was observed upon reduction.[11c] This shift indicates substantial alteration of the electron structure of $\mathbf{1}^{4-}$ with respect to $\mathbf{1}^0$.

Crystals of $\mathbf{1}^{4-}$/4 K$^+$ suitable for an X-ray diffraction study were obtained by allowing a solution of **1** and [18]crown-6 in THF to stand for a prolonged period (3 weeks) over potassium metal. X-ray crystal-structure elucidation[16] revealed that the overall composition of the crystallized product is [{K(THF)([18]crown-6)$^+$}{K$^+$(K(THF)$_2^+$)($\mathbf{1}^{4-}$)}-{K([18]crown-6)$^+$}] (Figure 1 a).

A remarkable distortion of the [8]CPP structure relative to that of the neutral ligand upon the acquisition of four electrons was revealed by X-ray crystallography (Figure 1 b,c). The presence of four additional electrons and the coordination of alkali-metal ions changed the dimensions of the nanobelt core from 10.3 × 11.6 Å^2 in **1**[10b] to 8.7 × 13.4 Å^2 in $\mathbf{1}^{4-}$. The C2–C3 and C6–C7 bonds connecting the benzene rings in $\mathbf{1}^{4-}$ are shortened (av. 1.437(8) Å) relative to those in the neutral ligand (1.486(2) Å), whereas the C1–C2, C3–C4, and C5–C6 bonds are slightly elongated (to 1.419(8) from 1.401(2) Å). The rim C1–C1′ and C4–C5 bond distances in $\mathbf{1}^{4-}$ (av. 1.370(8) Å) are shorter than other C–C bonds within benzene rings and are almost identical in length to those measured in **1** (av. 1.383(2) Å). The benzene rings involved in interior η^6 metal coordination show a boat conformation with a notable deviation of the C7 atoms (av. 0.317(9) Å) from the bottom of the "boat". The related average deviations for the remaining C_6 rings are much smaller (0.091(9) Å). This

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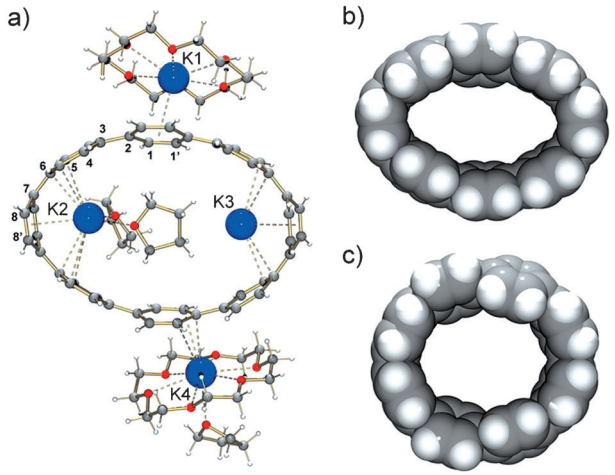

Figure 1. a) Molecular structure of $\mathbf{1}^{4-}/4\,K^+$; b) space-filling model of $\mathbf{1}^{4-}$; c) space-filling model of the neutral [8]CPP molecule (C gray, H white, O red, K blue). This color scheme is used in all figures.

observation indicates significant sp^3 character of the C7 atoms. The rim C8–C8′ bonds within the distorted C_6 rings are much shorter (1.345(9) Å) than the four adjacent C–C bonds (1.455(9) Å). The interatomic C6–C7 distances between the equatorial and neighboring C_6 rings (av. 1.410(9) Å) are shortened relative to the C2–C3 bonds (av. 1.464(9) Å). The above-mentioned geometrical perturbations reflect the essential *para*-quinone type of π-electron delocalization for the equatorial benzene rings in the highly reduced nanobelt.

The tetrareduced nanobelt functions as a versatile multisite π ligand for the binding of alkali-metal ions. Both its *exo* and its *endo* surfaces are engaged in coordination of the potassium centers in $\mathbf{1}^{4-}/4\,K^+$ (Figure 1a). The exterior K1 and K4 ions are additionally associated with one [18]crown-6 ether molecule each. The K1 ion is asymmetrically η^6-coordinated to the benzene ring with K···C distances of 3.196(6)–3.643(6) Å (K···$C_{centroid}$ 3.059(6) Å). The exterior K4 ion is η^3-bound to the antipodal benzene ring with two short and one elongated K···C contact (3.204(6)/3.293(6) and 3.567(6) Å). The coordination environment of K4 is completed by one THF molecule with a K4···O contact of 2.758(6) Å.

The two cations K2 and K3 are encapsulated inside the large open cavity of $\mathbf{1}^{4-}$. The K2 ion shows strong η^6 coordination to the equatorial benzene ring (K···C 2.942(6)–3.248(6), K···$C_{centroid}$ 2.792(6) Å) as well as η^3 binding of the adjacent C_6 rings (2.903(6)–3.704(6) Å). Two THF molecules are coordinated to this encapsulated K2 cation with K···O contacts (2.644(5) and 2.683(5) Å) that are significantly shorter than those for K4···O_{THF} and K···O_{crown} (2.758(6)–2.955(4) Å). The K3 ion is attached to one benzene ring with four short (2.984(6)–3.086(6) Å) and two long (3.618(12)/3.635(12) Å) K···C contacts. It is also η^2-bound to two adjacent C_6 rings with K···C distances of 3.097(7)–3.165(6) Å. Overall, the K···C contacts in $\mathbf{1}^{4-}/4\,K^+$ are comparable to those measured in the known π adducts of planar[17] and nonplanar polyarene anions.[4k] Notably, our DFT calculations (B3LYP/6-31g(d,p)) showed the effect of cations on the circular carbon core of [8]CPP upon reduction. Whereas the effect of lithium is minimal, an elliptical distortion becomes noticeable for the dianion and even more pronounced for the tetraanion of [8]CPP with potassium counterions (see the Supporting Information). With potassium counterions, up to 30% tightening of the nanobelt is accompanied by approximately 15% elongation of the perpendicular dimension on going from **1** to $\mathbf{1}^{4-}$.

The cavity of the charged nanobelt filled with two interior potassium ions additionally hosts one THF molecule, owing to their perfect steric complementarity (Figure 2a). The excellent ability of charged nonplanar polyarenes to encapsulate guests has been observed previously for both cations and anions of buckybowls.[4k,18]

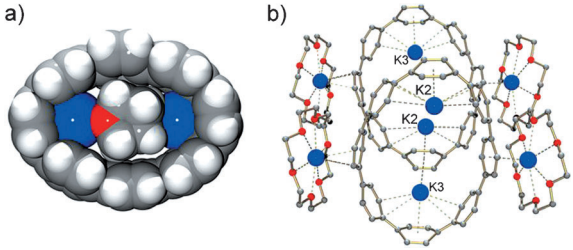

Figure 2. a) Space-filling model showing the encapsulation of a THF molecule and two K^+ ions inside $\mathbf{1}^{4-}$; b) structure of two units of $\mathbf{1}^{4-}/4\,K^+$ (THF molecules and hydrogen atoms are not shown).

The interior K3 ion is free of any interactions with O donors and instead η^6-bound to the *exo* surface of the adjacent nanobelt with measured K···C distances of 3.094(6)–3.535(6) Å (K···$C_{centroid}$ 2.967(6) Å; Figure 2b). These intermolecular K···C contacts lead to a zigzag 1D polymeric arrangement of the $\mathbf{1}^{4-}/4\,K^+$ entities in the crystal lattice (Figure 3a,b).

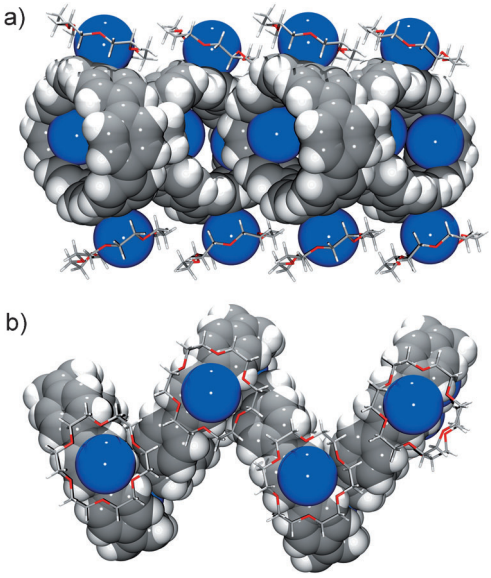

Figure 3. Space-filling depictions of the polymeric chain in $\mathbf{1}^{4-}/4\,K^+$: a) side view; b) top view (THF molecules are omitted).

In summary, the first X-ray structural characterization of the multiply charged anion of a fragment of an armchair carbon nanotube revealed a significant distortion of the carbon framework and C–C bond perturbation in comparison with the neutral ligand. The observation that the large cavity of [8]CPP was filled by two encapsulated alkali-metal ions along with one THF molecule points to the unique host abilities of the highly reduced nanobelt. The observed flexibility in changing the cavity size and shape through charging of the nanobelts with multiple electrons and metal binding may need to be accounted for during doping or intercalation processes involving carbon nanotubes. This phenomenon may also allow the use of charged [*n*]CPPs in host–guest separation processes through controlled manipulation of their shape during redox reactions. Importantly, the use of nanobelts as discrete fragments of carbon nanotubes enables the investigation of these processes at the molecular level and provides estimates of the expected structural perturbations.

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[15] Synthesis of $\mathbf{1}^{4-}/4\,K^+$: THF (3 mL, dried over NaK_2) was condensed into a glass tube containing [8]CPP (2.0 mg, 0.0035 mmol), potassium (5.0 mg, 0.128 mmol, excess), and [18]crown-6 (3.0 mg, 0.01 mmol). The tube was subsequently sealed under reduced pressure. A blue crystalline precipitate started forming on the metal surface at 25 °C within several days. Crystals of $\mathbf{1}^{4-}/4\,K^+$ (2.5 mg, 50 %) were separated manually from the metal surface after 3 weeks. UV/Vis (THF): $\lambda_{max} = 600$ nm. The very low solubility of $\mathbf{1}^{4-}/4\,K^+$ precluded the collection of satisfactory NMR spectroscopic data.

[16] X-ray crystal-structure determination of $\mathbf{1}^{4-}/4\,K^+$: $C_{84}H_{104}K_4O_{15}$, $M_r = 1510.07$, $0.29 \times 0.12 \times 0.10\ mm^3$, $a = 22.0146(19)$, $b = 23.057(2)$, $c = 15.4562(13)$ Å, $\beta = 94.5860(10)°$, $V =$

7820.3(12) Å^3, $\rho_{calcd} = 1.283\ g\,cm^{-3}$, $\mu = 0.292\ mm^{-1}$, 33001 measured intensities ($1.28° \le 2\theta \le 50.0°$, 99.6% completeness), $\lambda =$ 0.71073 Å, $T = 100(2)$ K, 13719 independent reflections, monoclinic, $P2_1/c$, $Z = 4$. The crystal was found to be a nonmerohedral twin. Subsequently, a TWINABS absorption correction was carried out ($0.9200 \le T \le 0.9713$), and the final refinement cycles were carried out against the HKLF 5 file with BASF 0.48824. $R_1 = 0.0944$, $wR_2 = 0.1640$ for $[I \ge 2\sigma(I)]$ and $R_1 = 0.1283$, $wR_2 =$ 0.1794 for all data. Goodness-of-fit on F^2: 1.098, largest diff. peak and hole: 0.566 and $-0.543\ e\,Å^3$. All atoms were refined with anisotropic thermal parameters; hydrogen atoms were refined by using a riding model. CCDC 923514 contains 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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