

Supporting Information

Unsolvated Buckycatcher and its First Dianion

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Synthesis of 2. All manipulations were carried out using break-and-seal¹ and glove-box techniques under an atmosphere of argon. THF (2.0 mL, dried over Na/benzophenone) was added to the freshly-sublimed C₆₀H₂₈ (2.0 mg, 0.0027 mmol, prepared according to literature²), 18-crown-6 ether (2.1 mg, 0.0080 mmol) and Rb metal (0.6 mg, ca. 2.5 eq.). The color of the mixture immediately turned green. The reaction mixture was stirred for 10 hours (resulting in a deep green color) and filtered. The filtrate was layered with hexanes (0.7 mL) and kept at 10 °C. Dark green crystals (needles) were deposited after 65 hours. Yield: 2.1 mg, 47%. UV-vis (*in situ*, THF, nm): $\lambda_{\text{max}} = 411$ ($\epsilon = 9300 \text{ M}^{-1} \cdot \text{cm}^{-1}$), 462 ($\epsilon = 7700 \text{ M}^{-1} \cdot \text{cm}^{-1}$), 638 ($\epsilon = 7400 \text{ M}^{-1} \cdot \text{cm}^{-1}$), 908.

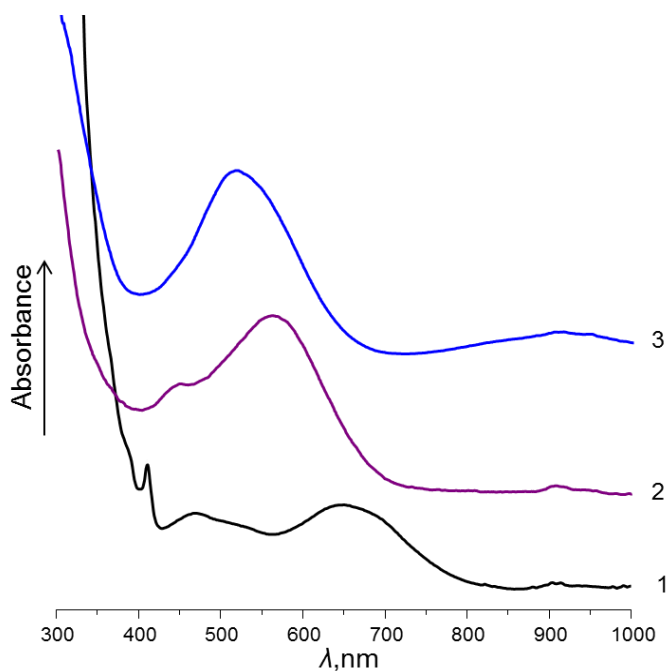
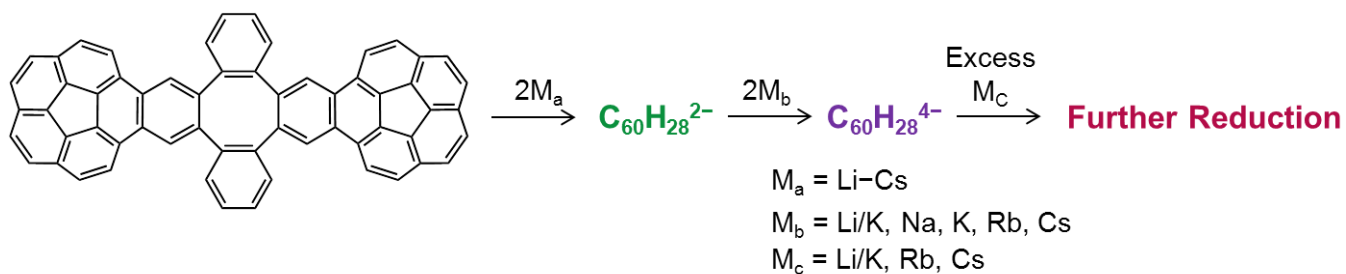


Fig. S1 UV-vis spectra of the *in situ* generated reduction products of C₆₀H₂₈.

Note: The first reduction step is accompanied by a formation of green solution (1), which endures higher reduction and transforms to a deep purple solution (2). Finally, the furthest reduction stage of C₆₀H₂₈, with Rb metal, can be detected by the appearance of a red-purple solution (3). Notably, the red-purple color is only observed after an extended period of time, up to two weeks. Each distinctive stage of C₆₀H₂₈ reduction, with rubidium metal, has been followed by optical spectroscopy and the results are summarized in Table S1 (along with our tentative assignment).

Scheme S1. Controlled reduction of $C_{60}H_{28}$ with Group 1 metals.



Scheme S2. Reduction of $C_{60}H_{28}$ with rubidium metal.

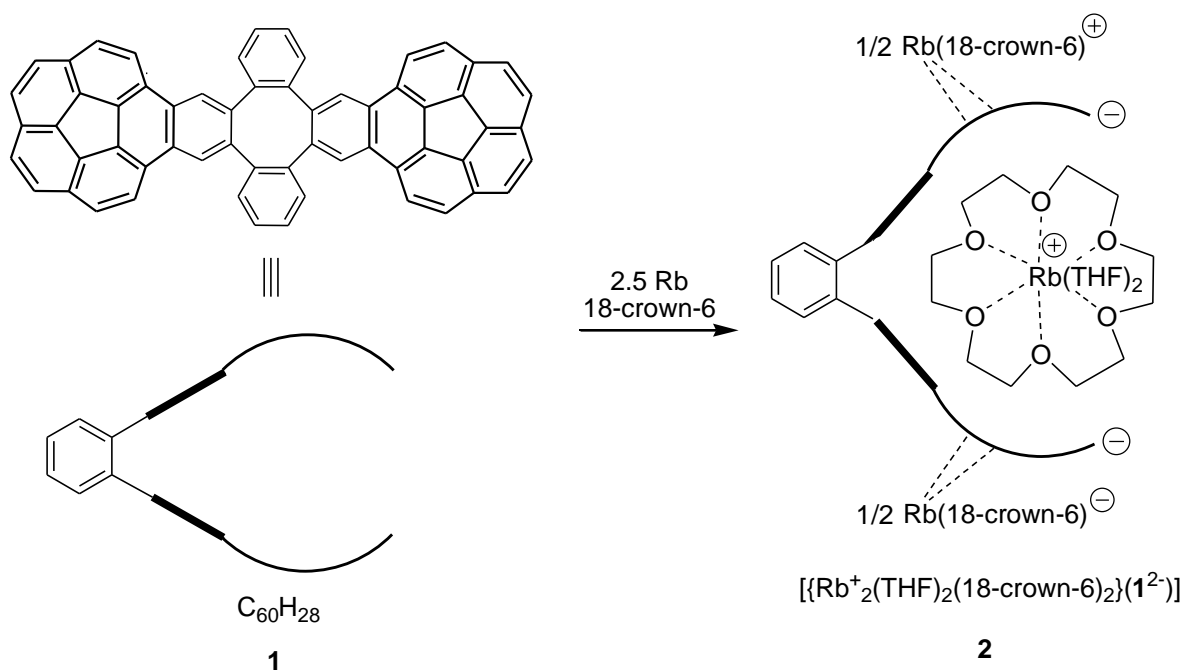


Table S1 Optical absorption data in THF (Rb-reduction)

Reduction Stage	λ
$C_{60}H_{28}^{2-}$	410, 468, 647, 907
$C_{60}H_{28}^{4-}$	440, 560, 907
Further Reduction	515, 914

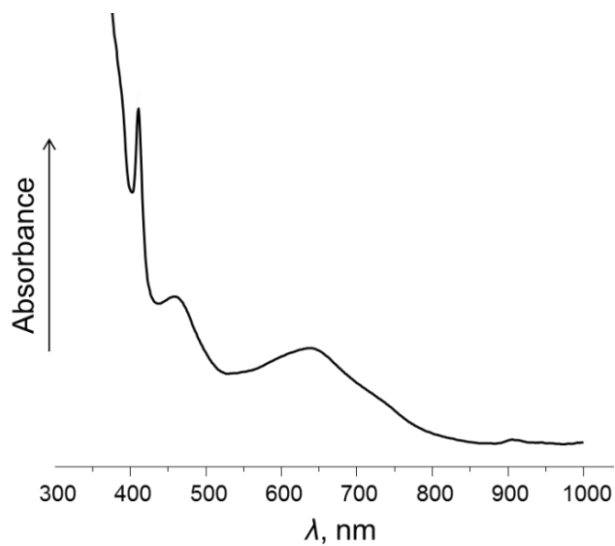


Fig. S2 Uv-vis spectrum of **2** (in THF).

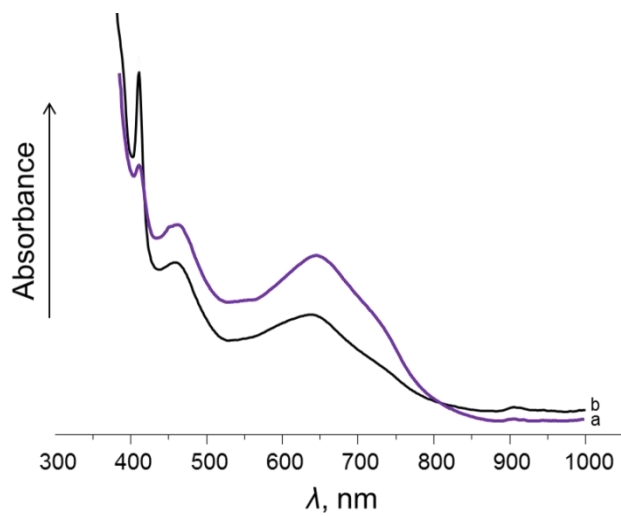


Fig. S3 Uv-vis spectra of *in situ* generated $C_{60}H_{28}^{2-}$ with Rb in the presence of 18-crown-6 ether (a) and re-dissolved crystals of **2** in THF (b).

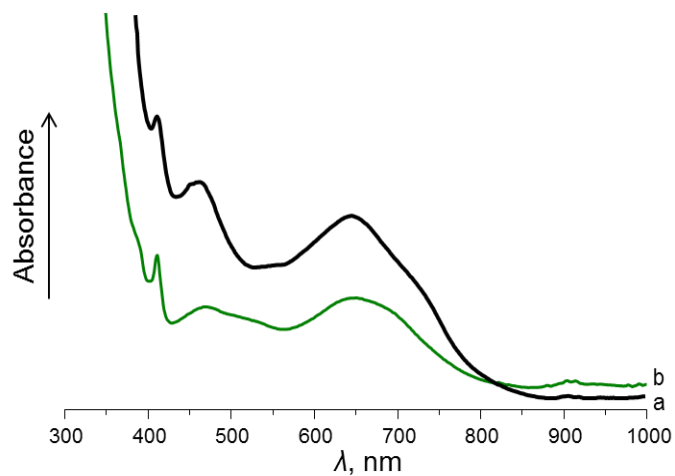


Fig. S4 Uv-vis spectra of **2** (a) and *in situ* generated $C_{60}H_{28}^{2-}$ with Rb in THF (b).

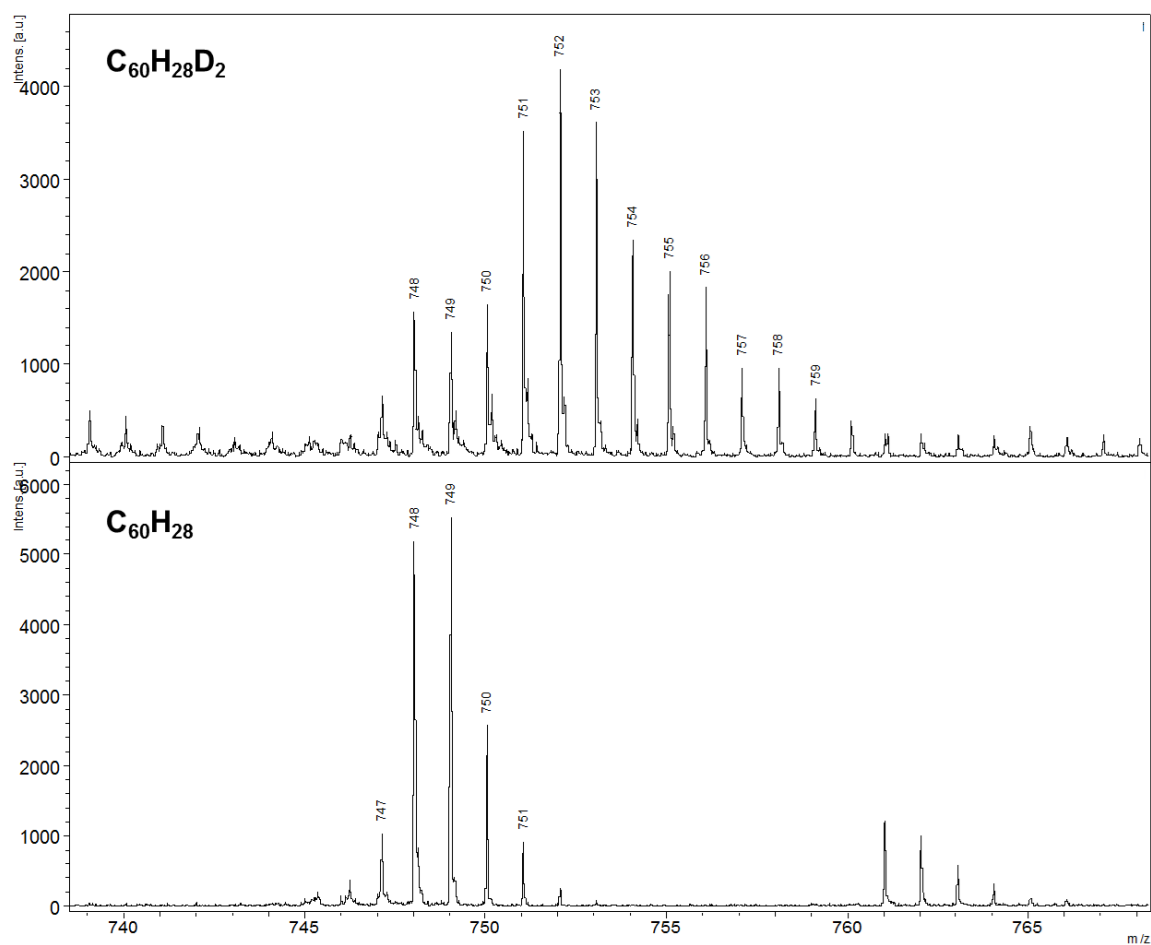


Fig. S5 MALDI (no matrix) spectra of **1** (bottom) and the product of the reaction of **2** with D_2O (top).

Crystal Structure Determination and Refinement

The X-ray quality crystals were coated with paratone oil and mounted onto a MiTeGen MicroMount fiber. Complete and redundant data were collected on a single flash-cooled crystal ($T = 100$ K with an Oxford Cryostream LT device) using a Bruker X8 Prospector Ultra X-ray diffractometer system with a three-circle goniometer and an APEX II CCD area detector mounted on D8-platform and equipped with a Cu-I μ S ($\lambda = 1.54178$ Å) microfocus X-ray source operated at 30 W. The frames were collected with a scan width of 0.5° in ω and an exposure time of 10 s/frame. The intensity datasets consisted of ϕ and ω scans at a crystal to detector distance of 4.00 cm. The APEX II³ and SAINT⁴ software packages were used for data collection and data integration. The data were corrected for absorption effects using the SADABS empirical method.⁵ The structures were solved and refined by the full matrix least squares techniques based on F^2 (SHELXL-97).⁶ The asymmetric unit of **1** contains one neutral buckycatcher molecule, C₆₀H₂₈. The asymmetric unit of **2** contains the dianion, C₆₀H₂₈²⁻, two cationic [Rb(18-crown-6)]⁺ moieties, two THF molecules strongly bound to one cationic [Rb(18-crown-6)]⁺ unit, and severely disordered solvent, which based on the electron count by PLATON and crystallization conditions was assigned as a 1.5 molecule of THF. The disordered solvent could not be modeled appropriately and the routine SQUEEZE⁷ was applied to the data for **2**, which dramatically improved the agreement indices. The cationic [Rb(18-crown-6)]⁺ unit with two bound molecules of THF, above and below the plane of the 18-crown-6 ether, was disordered, and disorder was modeled over two orientations with the related occupancies of 0.61:0.39. Additionally, both bound THF molecules were disordered, and each disorder was modeled over two orientations with the related occupancies of 0.62:0.38 for the O8-bound THF molecule and 0.58:0.42 for the O7-bound THF molecule. In both structures, all of the non-hydrogen atoms were refined with anisotropic thermal parameters, while all H-atoms were included at geometrically idealized positions. For further crystallographic information see Table S2.

Table S2 Crystallographic details for **1** and **2**.

compound	1 (CCDC 973696)	2 (CCDC 973695)
empirical formula	C ₆₀ H ₂₈	C ₉₈ H ₁₀₄ O _{15.5} Rb ₂
Fw	748.82	1700.75
crystal size (mm ³)	0.14 × 0.07 × 0.03	0.18 × 0.04 × 0.02
crystal system	triclinic	triclinic
space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	9.8507(3)	9.3921(2)
<i>b</i> (Å)	14.1479(4)	16.1731(3)
<i>c</i> (Å)	15.1646(4)	28.6015(5)
α (deg)	105.607(1)	80.358(1)
β (deg)	102.809(1)	89.767(1)
γ (deg)	110.367(1)	80.008(1)
<i>V</i> (Å ³)	1788.10(9)	4216.81(14)
<i>Z</i>	2	2
<i>T</i> (K)	100(2)	100(2)
λ (Å)	1.54178	1.54178
<i>d</i> _{calc} (g·cm ⁻³)	1.391	1.339
μ (mm ⁻¹)	0.605	2.048
θ_{\max} (deg)	69.93	66.49
unique data	26110	56730
observed data [<i>I</i> > 2 σ (<i>I</i>)]	5763	10031
Parameters	541	1150
GOF ^a on <i>F</i> ²	1.024	1.045
<i>R</i> ₁ ^b , <i>wR</i> ₂ ^c [<i>I</i> > 2 σ (<i>I</i>)]	0.0374, 0.0930	0.0655, 0.1740
<i>R</i> ₁ ^b , <i>wR</i> ₂ ^c (all data)	0.0424, 0.0971	0.0916, 0.1892
$\Delta\rho_{\max,\min}$ (e·Å ⁻³)	0.215, -0.203	1.531, -0.670
<i>T</i> _{min} / <i>T</i> _{max}	0.70/0.75	0.65/0.75

^aGOF = $[\sum[w(F_o^2 - F_c^2)^2]/(N_{\text{obs}} - N_{\text{params}})]^{1/2}$. ^b*R*₁ = $\sum||F_o| - |F_c||/\sum|F_o|$. ^c*wR*₂ = $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)]]^{1/2}$.

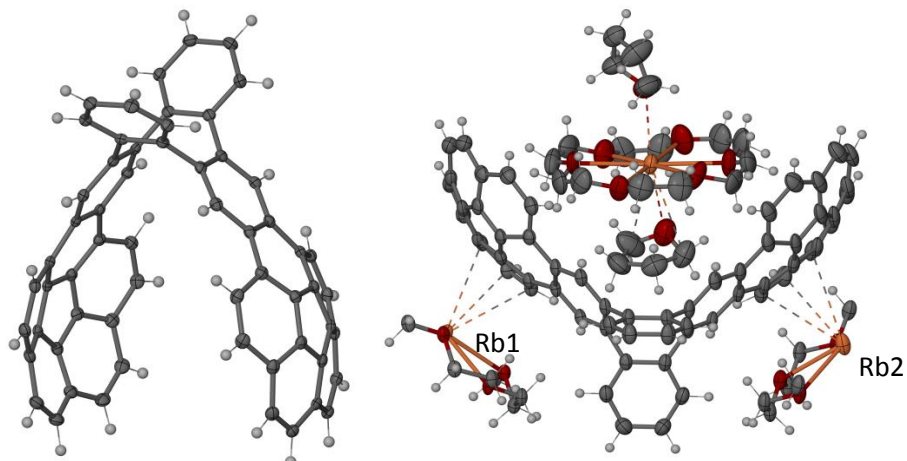


Fig. S6 Perspective drawings of **1** (left) and **2** (right, Rb1 and Rb2 has occupancies of 0.5 in the asymmetric unit, minor disorder components are not shown) with atoms represented by thermal ellipsoids at the 50% probability level.

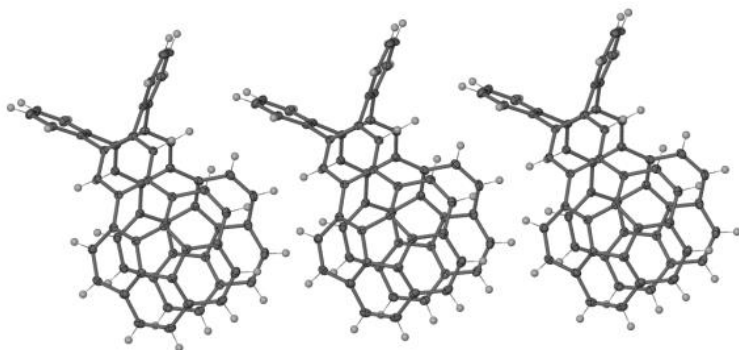


Fig. S7 Packing diagrams of **1** (*a* direction).

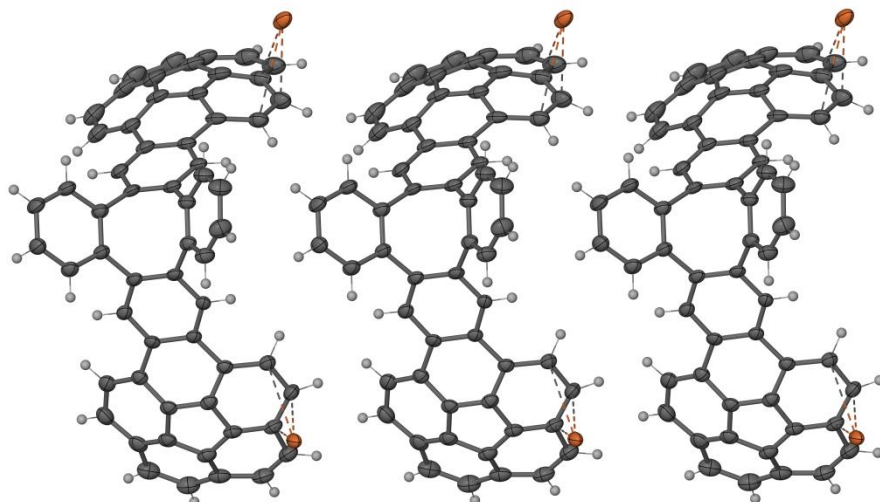


Fig. S8 A view along the *a* direction in the crystal structure of **2** ([Rb(18-crown-6)(THF)₂]⁺ and crown ether moieties are not shown).

References

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