Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

I. Materials and Methods

All manipulations were carried out using break-and-seal and glove-box techniques under an atmosphere of argon. THF and hexanes, purchased from Pharmco-Aaper, were dried over Na/benzophenone and distilled prior to use. THF-d_8 was purchased from Sigma Aldrich, dried over NaK_2 alloy and vacuum-transferred. Sodium and potassium were purchased from Strem Chemicals and used as received. Crown ether, 18-crown-6 (99%), was purchased from Sigma Aldrich and dried over P_2O_5 *in vacuo* for 24 hours. [6]CPP (**1**) was prepared as described previously[1] and sublimed at *ca.* 235 °C prior to use. The UV-vis spectra were recorded on a PerkinElmer Lambda 35 spectrometer. The ^1H NMR spectra were measured on a Bruker AC-400 spectrometer at 400 MHz. Mass spectra were acquired using a DART-SVP ion source (IonSense, Saugus, MA, USA) coupled to a JEOL AccuTOF time-offlight mass spectrometer (JEOL USA, Peabody, MA, USA) in positive ion mode. Spectra were recorded with a gas heater temperature of 300 °C. The extreme air- and moisture sensitivity of the isolated crystals **2** and **3** (*below*), coupled with the presence of interstitial THF molecules, prevented obtaining of elemental analysis data.

Crystallization of 1. [6]CPP (5 mg, 0.01 mmol) was loaded in a small glass ampoule (*ca*. 5 cm length, 1 cm OD). The ampule was sealed under vacuum and placed into an electric oven having a small temperature gradient along the lenth of the tube. The temperature was set at 220 °C. Yellow blocks of **1** were deposited in the cold zone of the ampule after 3.5 weeks. Yield: *ca*. 50%.

Preparation of [{Na^+(18-crown-6)$(THF)_2$}{([6]CPP^-)•2THF}] (2)

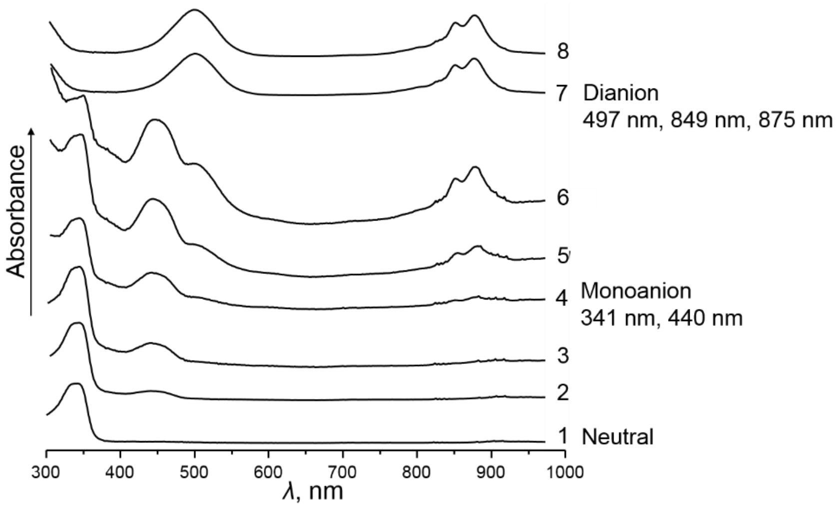
THF (3.0 mL) was added to a flask containing excess Na metal (0.6 mg, 0.026 mmol, 6 eq.), 18-crown-6 (4.6 mg, 0.018 mmol, 4 eq.), and [6]CPP (2 mg, 0.004 mmol). The initial color of the suspension was very pale orange-yellow. After one hour of stirring at room temperature, the reaction color began to darken. The swirls coming off the Na metal were red-brown. The mixture was allowed to stir for an additional 1.5 hours at room temperature to afford a red-brown suspension. The rection mixture was filtered; the red-brown filtrate was layered with hexanes (2.0 mL) and placed at 10 °C. Dark block-shaped crystals were present in moderate yield after 4 days. Yield: 2.5 mg, 50%.

Preparation of $[\{K^+(18\text{-crown-}6)(THF)\}_2([6]CPP^{2-})\cdot 2THF]$ (3)

THF (3.5 mL) was added to a flask containing excess K metal (1.0 mg, 0.026 mmol, *ca*. 6 eq.), 18-crown-6 (4.6 mg, 0.018 mmol, 4 eq.), and [6]CPP (2 mg, 0.004 mmol). The initial color of the suspension was very pale orange-yellow. After one hour of stirring at room temperature, the reaction color began to darken to red-brown. After stirring the reaction mixture at room temperature for 17 hours, the color of the suspension appeared blue. The mixture was filtered to remove the blue precipitate and to give a purplish-red filtrate. The filtrate was layered with hexanes (2.7 mL) and placed at 10 °C. After 6 days, dark plate-shaped crystals were present in moderate yield. Yield: 3.3 mg, 55 %.

UV-Vis Spectroscopy Study

THF (2.8 mL) was added to a small glass ampule containing [6]CPP (1 mg, 0.002 mmol) and excess (> 10 eq.) alkali metal, Na or K. The ampule was sealed. Due to the low concentration of the resulting solution, sonication was used to initiate the reduction. The sample was closely monitored and UV-Vis spectra were recorded accordingly (Figures S1–S4).



Label	Time (minutes)
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2	45
3	90
4	135
5	180
6	225
7	270
8	315

Figure S1. UV-Vis spectra of the kinetic monitoring of the *in-situ* reduction of [6]CPP/ with Na (excess) in THF.

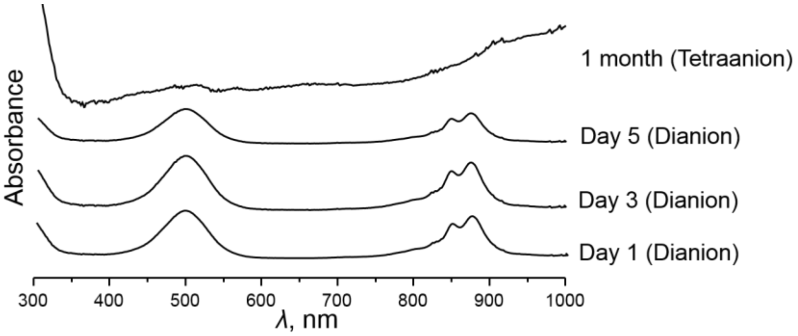
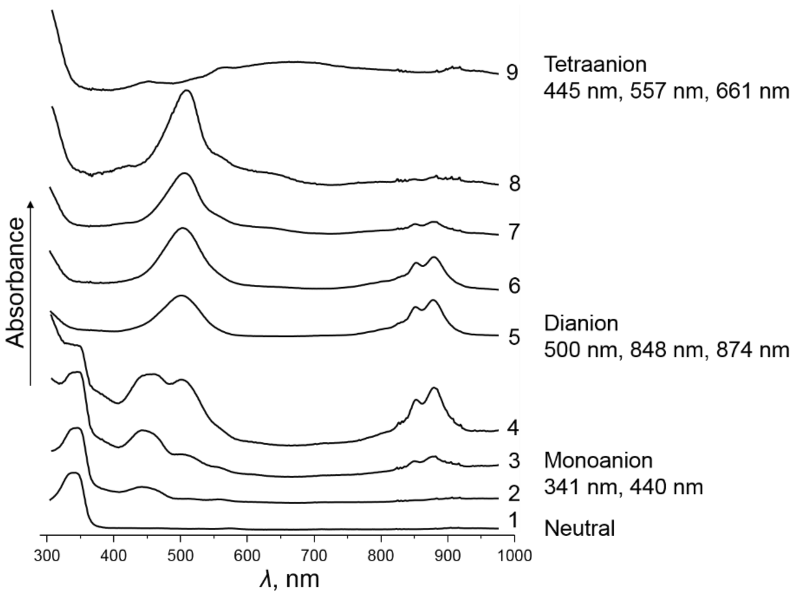


Figure S2. UV-Vis spectra of [6]CPP/Na in THF.



Label	**Time (minutes)**
1	0
2	4
3	8
4	12
5	16
6	20
7	24
8	28
9	32

Figure S3. UV-Vis spectra of the kinetic monitoring of the *in-situ* reduction of [6]CPP with K (excess) in THF.

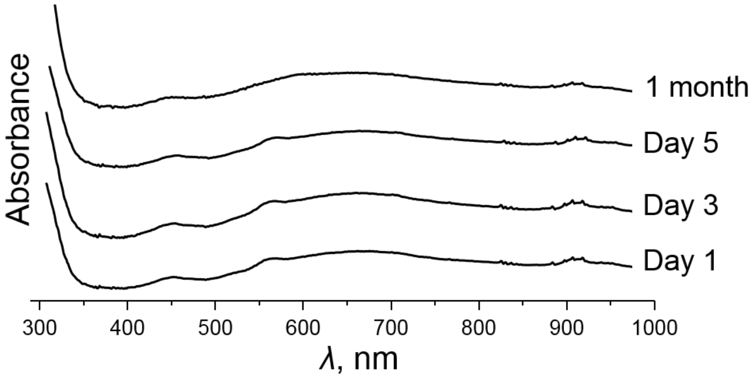


Figure S4. UV-Vis spectra of [6]CPP/K in THF.

NMR and DART Study

THF-d_8 (0.6 mL) was added to a NMR probe containing excess K metal (1.0 mg, 0.026 mmol, 6 eq.), 18-crown-6 (4.6 mg, 0.018 mmol, 4 eq.), and [6]CPP (2 mg, 0.004 mmol). Due to the lack of vigorous stirring, sonication was used to initiate the reduction. The sample was closely monitored until the formation of [6]CPP^{4-} was observed (which is indicative by the blue color of the suspension).

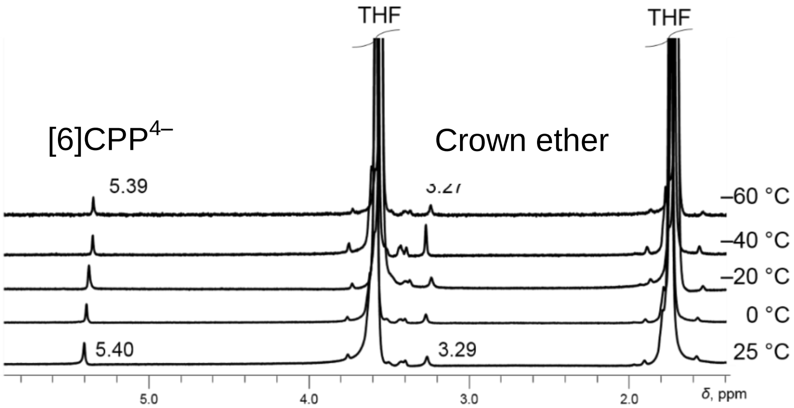


Figure S5. Variable-temperature 1H NMR spectra of *in situ* generated [6]CPP^{4-} with K, in THF-d_8. Neutral [6]CPP: δ: 7.64 ppm. Free 18-crown-6: δ: 3.57 ppm.

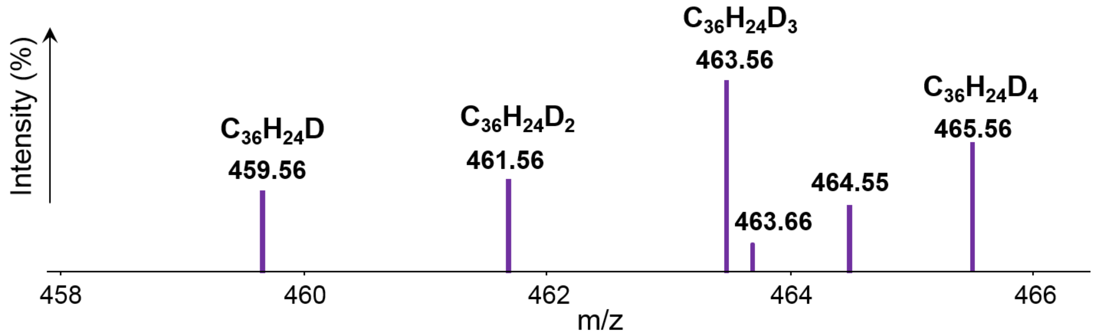


Figure S6. DART spectrum of [K_4[6]CPP^{4-}] quenched with D_2O. Positive mode: 300 °C

II. Crystal Structure Solution and Refinement

Data collection of three structures was performed on a Bruker D8 VENTURE X-ray diffractometer with PHOTON 100 CMOS shutterless detector equipped with a Cu-target X-ray tube (λ = 1.54178 Å) at T = 100(2) K. Data reduction and integration were performed with the

Bruker software package SAINT (version 8.37A).[2] Data were corrected for absorption effects, using the empirical methods as implemented in SADABS (version 2016/2).[3] The structures were solved by SHELXT (version 2014/5)[4] and refined by full-matrix least-squares procedures using the Bruker SHELXTL (version 2017/1)[5] software package. All non-hydrogen atoms, including those in disordered molecules, were refined anisotropically. The H-atoms were included at calculated positions and refined as riders, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2\ U_{\mathrm{eq}}(\mathrm{C})$. In **2**, the THF molecule coordinated with sodium atom was found to be disordered and was modelled with two orientations with relative occupancies of 0.85:0.15 for the two parts. The geometries of the disordered parts were restrained to be similar. The anisotropic displacement parameters of the solvent THF molecule in the direction of the bonds were restrained to be equal with a standard uncertainty of 0.005 Å^2. They were also restrained to have the same U_{ij} components, with a standard uncertainty of 0.01 Å^2. In both **2** and **3**, interstitial THF molecules were fully refined. Selected crystallographic data for **1**–**3** are shown in Table S1. Selected C–C distances are presented in Table S2.

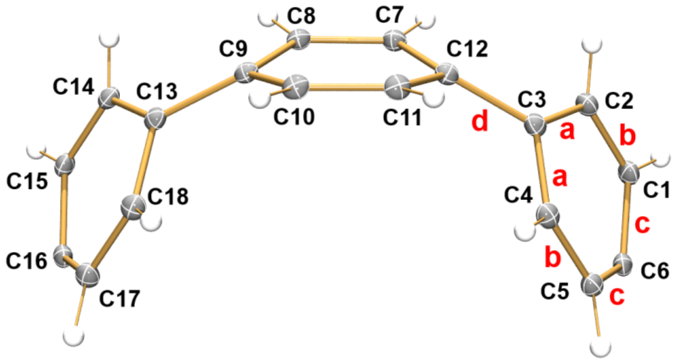
Table S1. Crystallographic data of **1**, **2**, and **3**.

	1	**2**	**3**
Empirical formula	$C_{36}H_{24}$	$C_{64}H_{80}O_{10}Na$	$C_{76}H_{104}O_{16}K_2$
Formula weight	456.55	1032.27	1351.79
Temperature (K)	100(2)	100(2)	100(2)
Wavelength (Å)	1.54178	1.54178	1.54178
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a (Å)	11.1772(5)	10.1288(4)	10.1496(2)
b (Å)	10.3120(4)	17.2370(6)	23.2584(6)
c (Å)	11.2725(5)	16.0129(6)	15.4171(4)
α (°)	90.00	90.00	90.00
β (°)	106.3290(10)	102.514(2)	98.7840(10)
γ (°)	90.00	90.00	90.00
V (Å^3)	1246.85(9)	2729.28(18)	3596.73(15)
Z	2	2	2
ρ_{calcd} (g·cm^{-3})	1.216	1.256	1.248
μ (mm^{-1})	0.522	0.732	1.700
F(000)	480	1110	1452
Crystal size (mm)	0.22×0.17×0.16	0.19×0.16×0.06	0.30×0.07×0.04
θ range for data collection (°)	4.12-72.09	4.47-73.53	3.47-74.51

Reflections collected	10681	72274	63334
Independent reflections	2409 [R_{int} = 0.0255]	5438 [R_{int} = 0.0616]	6892 [R_{int} = 0.0654]
Transmission factors (min/max)	0.9326/1	0.8051/1	0.8587/1
Data/restraints/params.	2409/0/163	5438/180/386	6892/0/424
$R1$,[a] $wR2$[b] ($I > 2\sigma(I)$)	0.0414, 0.1058	0.0537, 0.1464	0.0406, 0.0909
$R1$,[a] $wR2$[b] (all data)	0.0433, 0.1076	0.0624, 0.1544	0.0558, 0.0983
Quality-of-fit[c]	1.030	1.025	1.014

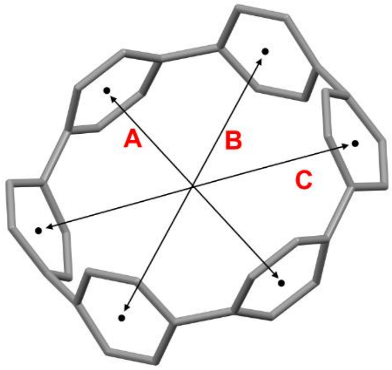
[a] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]$.

[c] Quality-of-fit = $[\Sigma[w(F_o^2-F_c^2)^2]/(N_{\text{obs}}-N_{\text{params}})]^{½}$, based on all data



	Solvent-Free	Solution
a (Å)	1.4042(18)	1.404(2)
b (Å)	1.3856(18)	1.387(2)
c (Å)	1.4036(18)	1.403(2)
d (Å)	1.4897(18)	1.490(2)

Figure S7. ORTEP drawing of the asymmetric unit of **1** with thermal ellipsoids shown at the 40% probability level (left). Table of average C–C bond lenght distances in **1** (solvent-free) compared with the previously reported structure (solution).[1]



	Solid state	Solution
A (Å)	8.049	8.088
B (Å)	8.050	8.088
C (Å)	8.117	8.088
deformation parameter[a]	1.008	1.000

[a]deformation parameter = the maximum diameter value/ the minimum diameter value.

Figure S8. Estimated diameters of [6]CPP in two crystal structures.

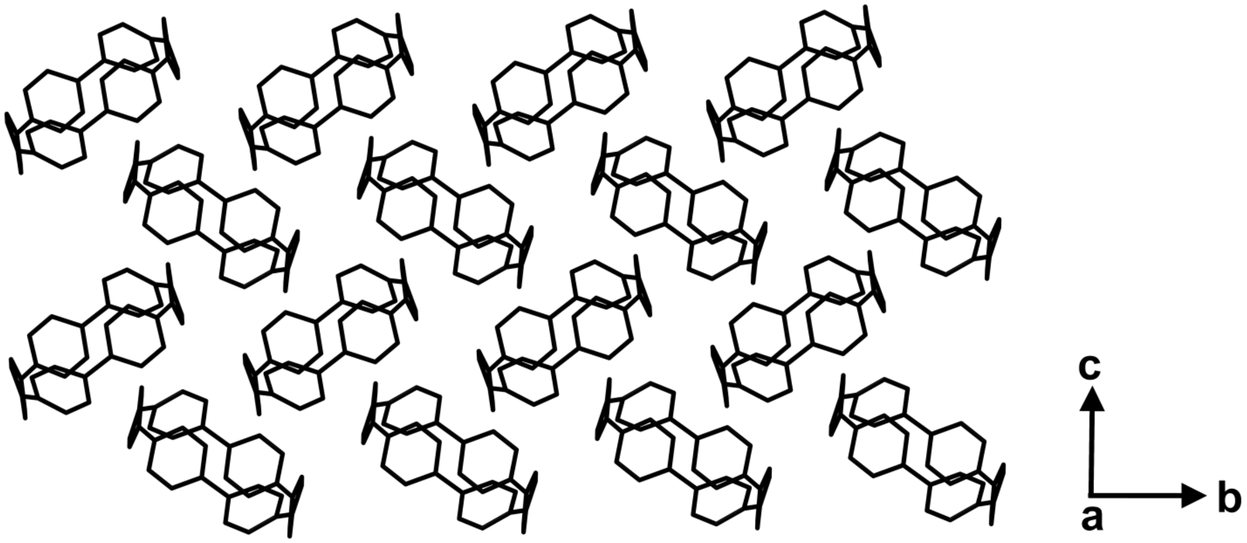


Figure S9. Solid-state packing in **1** (capped-stick model, only C-atoms are shown).

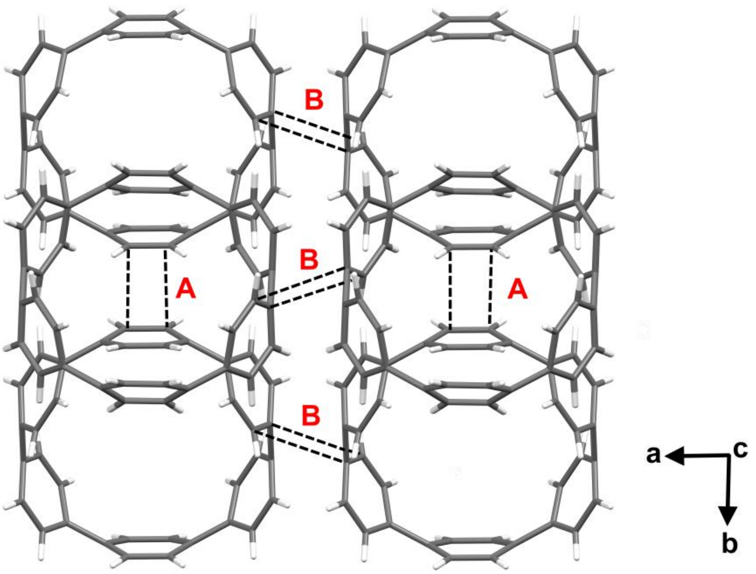


Figure S10. Solid-state packing in **1** showing two types of π-π intermolecular interactions at 3.335(2) Å (**A**) and 3.374(2) Å (**B**).

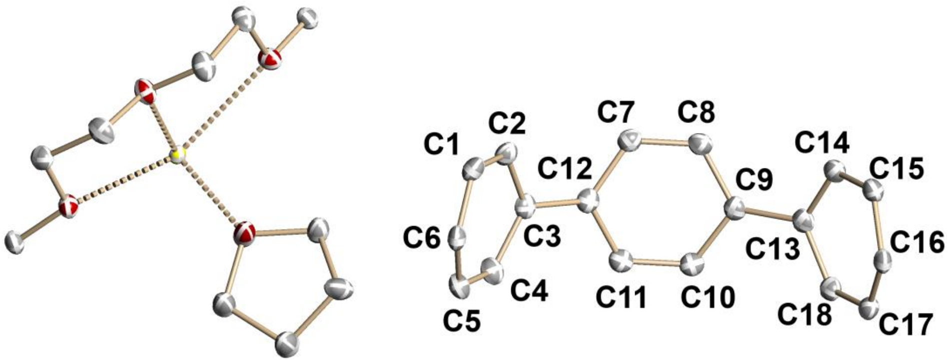


Figure S11. ORTEP drawing of the asymmetric unit of **2** with thermal ellipsoids shown at the 40% probability level. All hydrogen atoms and interstitial THF molecules have been removed for clarity.

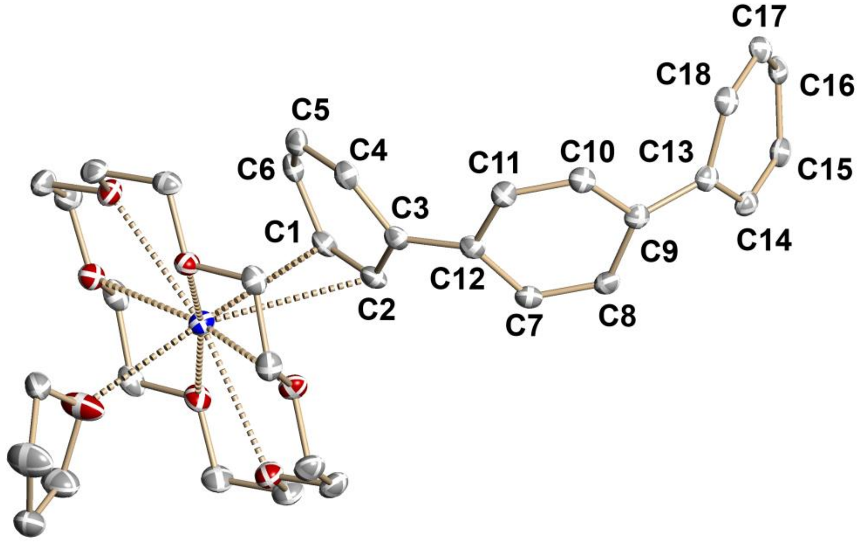


Figure S12. ORTEP drawing of the asymmetric unit of **3** with thermal ellipsoids shown at the 40% probability level. All hydrogen atoms and interstitial THF molecules have been removed for clarity.

TableS2. C–C bond length distances of the [6]CPP core in **1**, **2** and **3**

	1	**2**	**3**
C1—C2	1.3838 (19)	1.382(3)	1.372(3)
C2—C3	1.4097 (18)	1.411(3)	1.431(2)

C3—C4	1.4040 (18)	1.420(3)	1.421(3)
C4—C5	1.3867 (19)	1.377(3)	1.371(3)
C5—C6	1.3992 (19)	1.415(3)	1.429(3)
C7—C8	1.3844 (18)	1.374(3)	1.369(3)
C8—C9	1.4011 (18)	1.420(3)	1.424(2)
C9—C10	1.4064 (18)	1.411(3)	1.423(3)
C10—C11	1.3850 (19)	1.376(3)	1.373(3)
C11—C12	1.4059 (18)	1.415(3)	1.426(2)
C13—C14	1.4073 (18)	1.415(3)	1.429(3)
C14—C15	1.3880 (19)	1.379(3)	1.369(3)
C15—C16	1.4079 (19)	1.417(3)	1.422(3)
C16—C17	1.3959 (19)	1.415(3)	1.425(3)
C17—C18	1.3869 (19)	1.379(3)	1.373(3)
C1—C6	1.4094 (18)	1.412(3)	1.422(3)
C3—C12*	1.4873 (18)	1.463(3)	1.434(2)
C7—C12	1.4039 (18)	1.414(3)	1.423(3)
C9—C13*	1.4904 (18)	1.464(3)	1.442(3)
C13—C18	1.3959 (18)	1.419(3)	1.425(3)
C6—C16(A)*	1.4913 (18)	1.462(3)	1.443(3)

*ring-ring connection

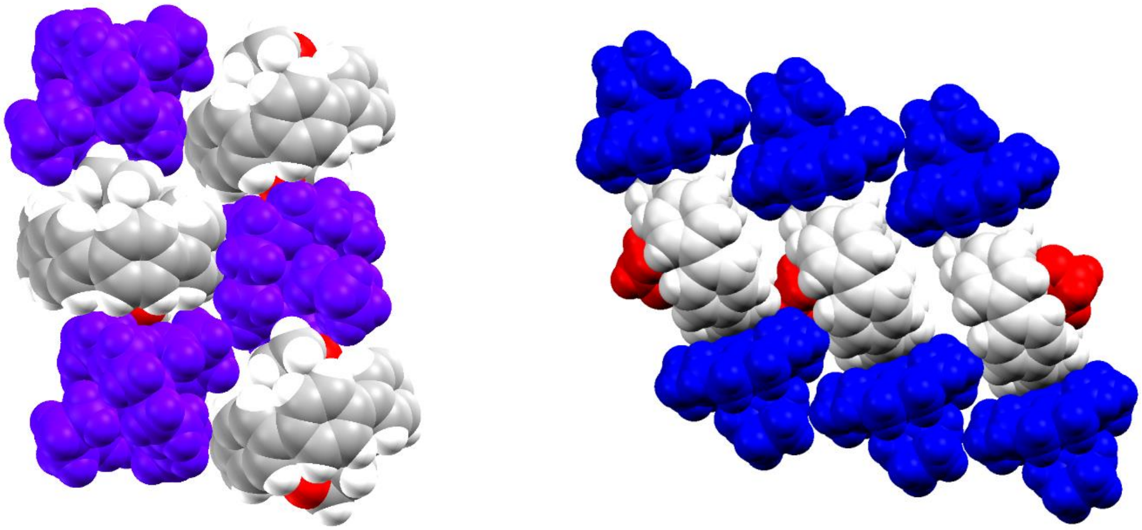


Figure S13. Solid-state packing in **2** (left) and **3** (right), space-filling models. In **2**, the [{Na$^+$(18-crown-6)(THF)$_2$}] cation is shown in purple. In **3**, the [{K$^+$(18-crown-6)(THF)}] cation is shown in blue (right). THF molecules are shown in red.

III. References

1. E. R. Darzi, B. M. White, L. K. Loventhal, L. N. Zakharov and R. Jasti, *J. Am. Chem. Soc.*, 2017, **139**, 3106.

2. SAINT; part of Bruker APEX3 software package (version 2016.9-0): Bruker AXS, 2016.

3. SADABS; part of Bruker APEX3 software package (version 2016.9-0): Bruker AXS, 2016.

4. G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3-8.

5. G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.