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# Hemicarceplexes Modify the Solubility and Reduction Potentials of $C_{60}$

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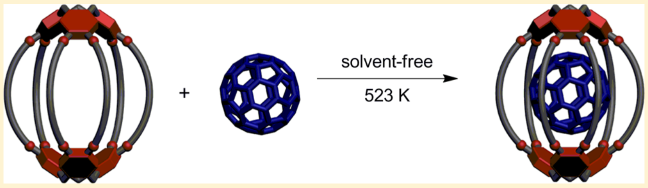
Supporting Information

**ABSTRACT:** A highly stable $C_{60}$-incarcerated hemicarceplex, which retains its molecular integrity after heating at 523 K in air for at least 3 h, significantly increases the solubility of $C_{60}$ in nonpolar solvents and increases the reduction potentials of the entrapped fullerene. Modification with $[(\eta^5\text{-}C_5Me_5)Ru^{II}]^+$ dramatically increases the solubility of this hemicarceplex in polar, protic solvents (e.g., MeOH).



## INTRODUCTION

Because of their versatile configurations and attractive properties, spherical and spheroidal fullerenes have found widespread applications in many fields, including materials science, chemistry, and biology.[1] Nevertheless, the limited solubility of fullerenes in common organic solvents remains bothersome, complicating their supply and chemical modification. One possible strategy to increase the solubility of fullerenes in organic solvents without disrupting their novel $\pi$-conjugated aromatic systems is to use macrocyclic hosts as phase-transfer agents, forming corresponding host/guest complexes.[2] In the past two decades, several macrocyclic hosts—prepared from cyclodextrins,[3] porphyrins,[4] cyclotriveratrylenes (CTVs),[5] and others[6]—have been employed to complex the highly symmetrical and spherical fullerene $C_{60}$, thereby increasing its solubility in various solvents and facilitating its purification and chemical modification. Because $C_{60}$ and its heteroatom-doped analogues $C_{59}N$ and $C_{59}B$ are valuable materials for the construction of molecular electronics (e.g., molecular junctions and rectifiers),[7] having them available in the form of more-soluble host/guest complexes might facilitate the fabrication of such devices and, in theory, allow tuning of the redox potentials of the complexed fullerenes and/or stabilization of the reduced species through the presence of the protective host shell. Most fullerene host/guest complexes prepared to date have, however, lacked sufficient stability for practical use, complicating their isolation, characterization, and operation.

A hemicarceplex is a room temperature-isolatable host/guest complex that can release its sequestrated guest(s) at elevated temperature.[8] Previously, we demonstrated that the CTV-based molecular cage **1** (Figure 1) can form a hemicarceplex with $C_{70}$, selectively over $C_{60}$, thereby allowing the direct isolation of $C_{70}$ in high purity from crude fullerene extracts.[9] We suspected that such supramolecular fullerene complexes might have potential for further modification into highly stable hemicarceplexes if we were to decrease the sizes of the host openings, thereby elevating the temperature required to release their guest fullerenes. Herein, we report the synthesis of a highly stable $C_{60}$-incarcerated hemicarceplex, the significant increase in the reductive potentials of its entrapped $C_{60}$ unit, and the improved solubility of this hemicarceplex in polar, protic solvents (e.g., MeOH) after modifying its host component with $[(\eta^5\text{-}C_5Me_5)Ru^{II}]^+$.

## RESULTS AND DISCUSSION

Previously, we reported that $C_{60}$ can freely enter and exit the cavity of the molecular cage **1** comprising two CTV units linked by six dodecamethylene units, but not the smaller molecular cage **2** featuring six decamethylene units, in $CDCl_2CDCl_2$ at 323 K.[9] We suspected that the formation of the hemicarceplex $C_{60}$@**2** would also be a thermodynamically favorable process, but it would be hampered by the high activation energy required for $C_{60}$ to pass through the openings and enter into the internal cavity of the molecular cage **2**, thereby making the complexation event extremely slow under the applied conditions. According to the principle of microscopic reversibility, if the squeezing of a $C_{60}$ unit through the openings of the molecular cage **2** could be achieved, the resulting hemicarceplex $C_{60}$@**2** should be an extremely stable complex—as desired—because its dissociation would require an even higher activation energy. When we heated a $CDCl_2CDCl_2$ solution containing the molecular cage **2** and an excess of $C_{60}$ at 373 K for 30 days, however, we did not observe any signals belonging to the corresponding hemicarceplex when monitoring using $^1$H NMR spectroscopy. The

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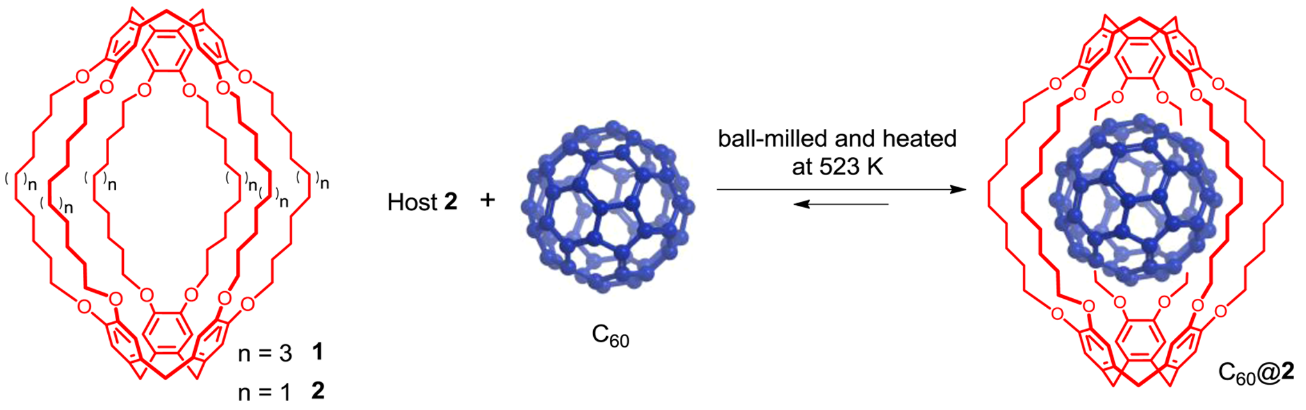


**Figure 1.** Chemical structures of the molecular cages **1** and **2** and the formation of the highly stable hemicarceplex $C_{60}$@**2**.

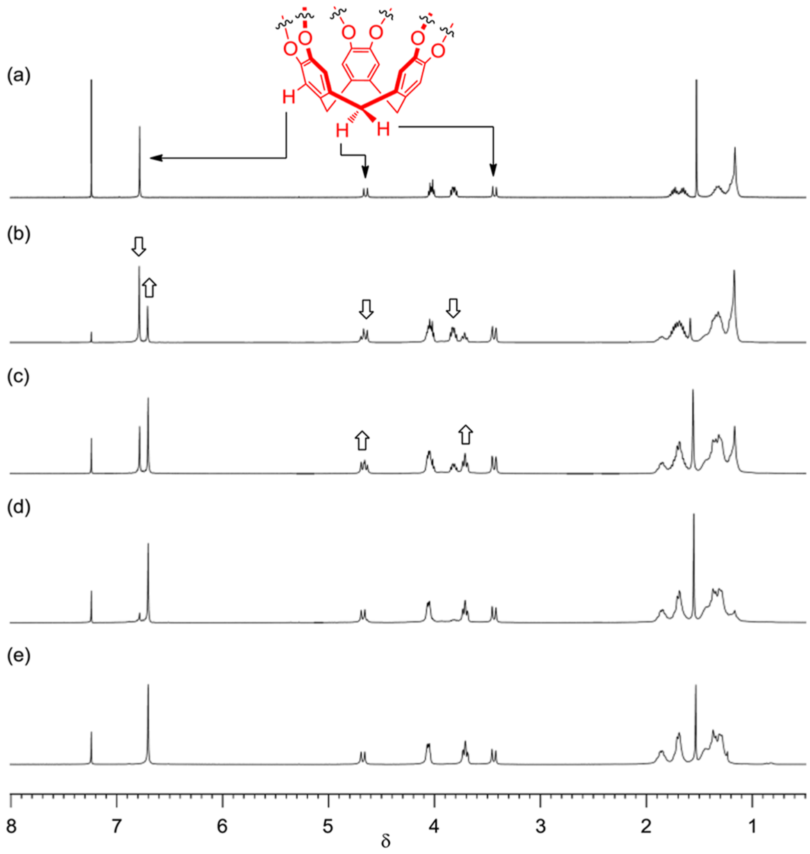


**Figure 2.** $^1$H NMR spectra (400 MHz, 298 K, $CDCl_2CDCl_2$) of (a) the molecular cage **2**; (b–d) the crude mixtures obtained after heating a mixture of $C_{60}$ and **2** at 523 K for (b) 3, (c) 9, and (d) 15 h; and (e) the purified hemicarceplex $C_{60}$@**2**.

relatively low boiling points of common organic solvents and the low solubility of $C_{60}$ in them presumably resulted in slow kinetics of complexation by limiting the amount of available applied thermal energy and the molar concentration of $C_{60}$, respectively.

To avoid these problems, we turned our attention to solvent-free reactions.[10] Thus, we first ball-milled (ground) a mixture of $C_{60}$ and the molecular cage **2** (2.15:1) for 30 min and then heated the solid mixture under vacuum at 523 K for 15 h. The $^1$H NMR spectrum of the crude product (Figure 2) displayed a weak set of signals for the original free molecular cage **2** and a new, predominant set featuring upfield shifts of the signals for the aromatic protons ($\delta$ 6.70) of the CTV units in the molecular cage **2** and its oxygen atom-adjacent methylene protons ($\delta$ 3.67–3.75), suggesting the formation of the hemicarceplex $C_{60}$@**2** because these particular protons would presumably be shielded by the incarcerated $C_{60}$ unit. Gratifyingly, chromatographic purification afforded the desired hemicarceplex $C_{60}$@**2** in 38% yield.[11] The signals for most of the aromatic nuclei of the molecular cage **2** in the $^{13}$C NMR spectrum of the hemicarceplex $C_{60}$@**2** in $CDCl_3$ (Figure 3, spectrum b) were shifted slightly upfield relative to those of the free host (Figure 3, spectrum a), again suggesting shielding induced by the encapsulated $C_{60}$ unit. Because the solubility of uncomplexed $C_{60}$ in $CDCl_3$ is low, we used a mixture of $CDCl_3$ and $CS_2$ (9:1) to compare the $^{13}$C NMR spectrum of $C_{60}$ with that of the hemicarceplex $C_{60}$@**2**. The presence of a single signal shifted slightly upfield for the incarcerated $C_{60}$ suggested

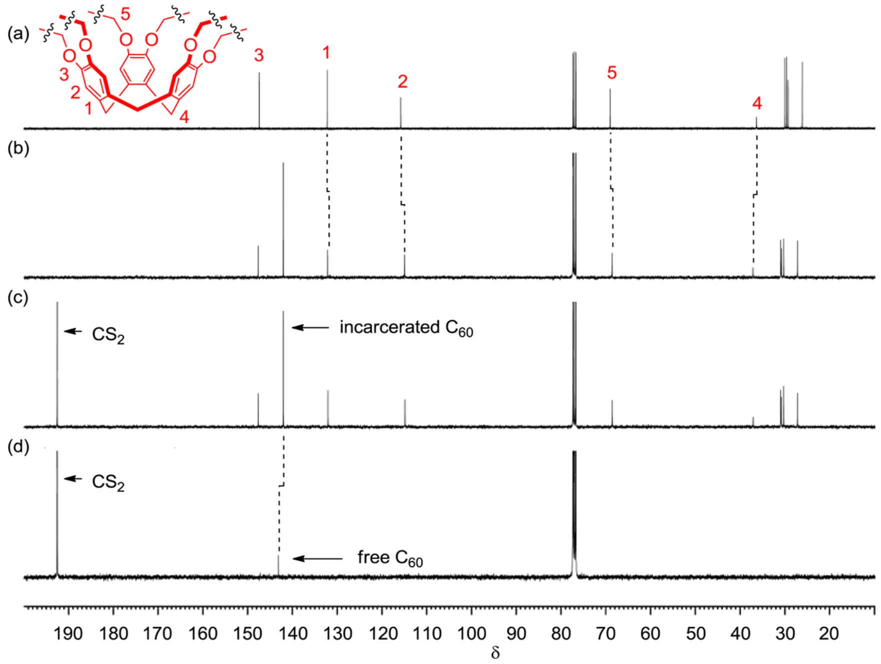


**Figure 3.** $^{13}$C NMR spectra (100 MHz, 298 K) of (a) the molecular cage **2** and (b) the hemicarceplex $C_{60}$@**2** in $CDCl_3$ and of (c) the hemicarceplex $C_{60}$@**2** and (d) free $C_{60}$ in $CDCl_3/CS_2$ (9:1).

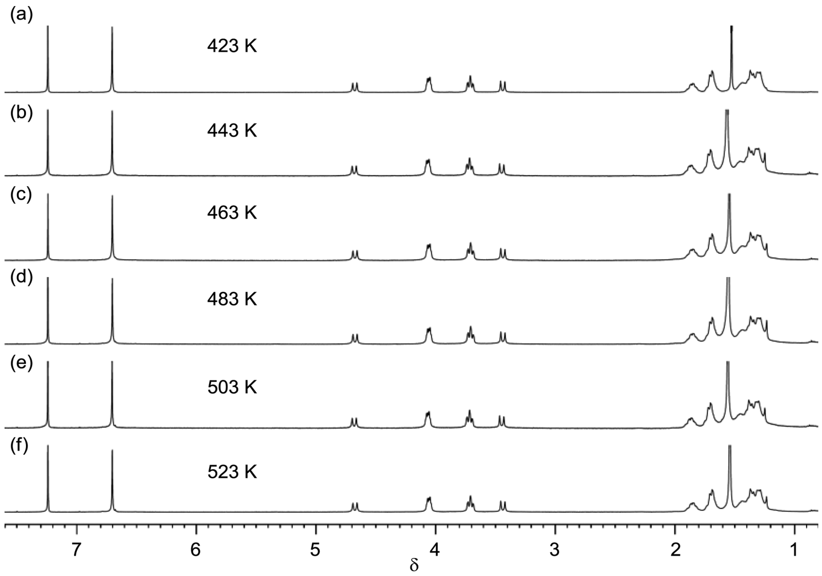


**Figure 4.** $^1$H NMR spectra (400 MHz, $CDCl_3$, 298 K) recorded after heating the solid hemicarceplex $C_{60}$@**2** in air at a constant temperature for 3 h at intervals of 20 K from 423 to 523 K.

shielding of the spherical guest component by the CTV units of the molecular cage **2** as well as rapid rotation kinetics of the $C_{60}$ unit within the host component under these conditions (Figure 3, spectra c and d). In previous studies, the complexation of CTV and $C_{60}$ has been observed primarily in the solid state, rather than in solution, except when $\pi$-electron-rich substituents have been attached to the catechol rings to enlarge the cavity and the area of the $\pi$ cloud available for guest contact;[12] therefore, we suspect that less-than-perfect structural complementarity exists between the CTV units of the molecular cage **2** and the spherical $C_{60}$ guest component, leading to the relatively minor shifts of their aromatic signals in the $^{13}$C NMR spectrum. Electrospray ionization (ESI) mass spectrometry revealed an intense peak at $m/z$ 2281.1, matching the ion $[C_{60}@\mathbf{2}]^+$ and supporting the successful synthesis and isolation of the hemicarceplex $C_{60}$@**2**.

In a previous study, we isolated high-purity $C_{70}$ by heating the hemicarceplex $C_{70}$@**1** in $d_8$-toluene at 313 K for several hours.[9] The stability of our new hemicarceplex $C_{60}$@**2** is much greater than that of $C_{70}$@**1**; indeed, we did not observe any signals for the free molecular cage **2** in the $^1$H NMR spectrum recorded after heating $C_{60}$@**2** in $d_8$-toluene (1.5 mM) at 353 K for at least 30 days. In device settings, we suspect that the hemicarceplex $C_{60}$@**2** might be subjected to heating in the absence of any surrounding solvent molecules; therefore, we heated $C_{60}$@**2** open to the air at 423 K for 3 h and then dissolved the sample in $CDCl_3$ and used $^1$H NMR spectroscopy to check for any signals belonging to the free molecular cage **2**.

Gratifyingly, the $^1$H NMR spectrum of the resulting solid displayed only one set of signals belonging to $C_{60}$@**2**, indicating that this hemicarceplex is sufficiently stable to retain its molecular integrity under these conditions. We then heated the solid for 3 h at intervals of 20 K from 423 to 523 K (Figure 4), but again observed no dissociation of the hemicarceplex, confirming that $C_{60}$@**2** is an extremely stable complex and that the release of its incarcerated $C_{60}$ unit should not occur under normal material or device operational conditions.

Because $C_{60}$ is used frequently as an electron-receiving material, we wished to compare its reduction potentials when incarcerated within the molecular cage **2** with those in its free state. Figure 5 presents the cyclic voltammogram of the hemicarceplex $C_{60}$@**2** in toluene/$CH_3CN$ (5:1, 0.5 mM). We observe four consecutive cathodic steps at peak potentials of −1.48, −2.10, −2.75, and −3.45 V, respectively, versus Fc/Fc$^+$; they are all more negative—by approximately 0.44, 0.65, 0.80, and 0.99 V, respectively—than the first four reduction potentials measured for free $C_{60}$ under the same conditions.[13] This result suggests the existence of stabilizing interactions between the two electron-rich CTV caps of the molecular cage **2** and the electron-deficient $C_{60}$ component in the hemicarceplex $C_{60}$@**2**, such that the presence of the host inhibits reduction of the encapsulated spherical guest. The phenomenon of greater differences in the reduction potentials upon increasing the number of electrons injected into the incarcerated $C_{60}$ unit is consistent with negatively charged entrapped guests interacting unfavorably with the electron-rich CTV units of the molecular cage **2**. The absence of any notable signals belonging to the free molecular cage **2** in the $^1$H NMR spectrum of the solid obtained upon concentrating the solution from the cell after performing cyclic voltammetry over 20 potential sweeps from −0.3 to −3.5 V at a rate of 100 mV s$^{-1}$ suggested that, even when the reduced forms of $C_{60}$ were repelled electronically by the molecular cage **2**, the hemicarceplex $C_{60}$@**2** did not dissociate to any significant degree during any stage of the electrochemical reduction process. Therefore, the very high energy barrier for $C_{60}$ entering the internal cavity of the molecular cage **2**—requiring a temperature of 523 K to proceed—also inhibited the dissociation of the reduced $C_{60}$ guest species from the hemicarceplex $C_{60}$@**2**. Taken together, our results confirm that $C_{60}$@**2** is a highly stable material capable of tolerating the high temperatures and redox conditions that it might encounter during the operation of a device.

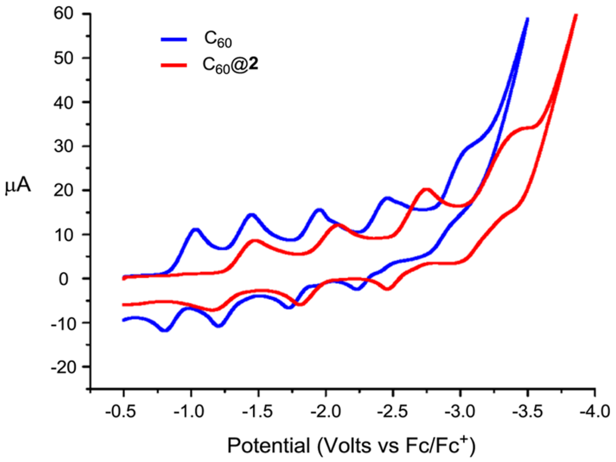
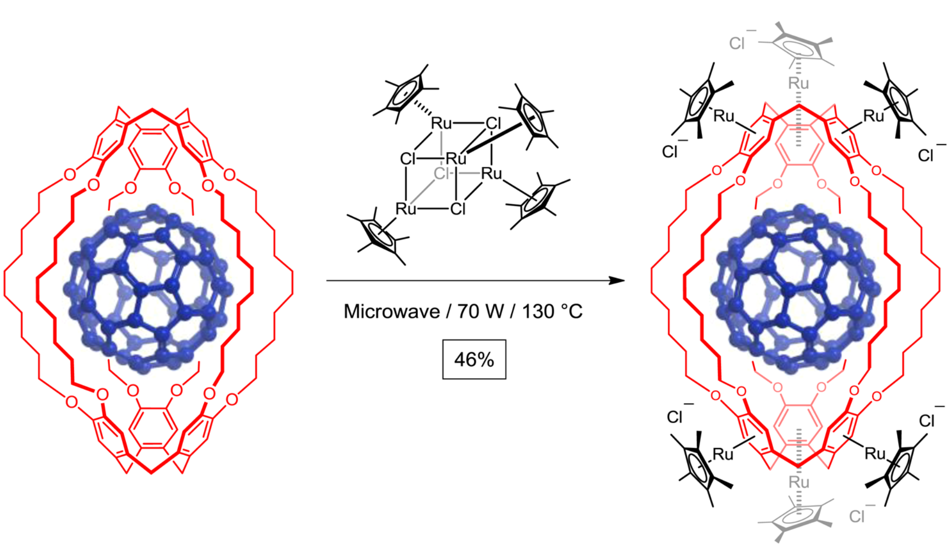


**Figure 5.** Cyclic voltammograms of $C_{60}$ (0.5 mM) and the hemicarceplex $C_{60}$@**2** (0.5 mM) in toluene/$CH_3CN$ (5:1). Supporting electrolyte: $Bu_4PF_6$ (0.1 M); scan rate: 300 mV s$^{-1}$.

Although the hemicarceplex $C_{60}$@**2** is highly soluble in less-polar solvents (e.g., $CHCl_3$, $CH_2Cl_2$, toluene), its solubility in more-polar solvents (e.g., $CH_3CN$, MeOH, water) remains limited. To enhance the solubility of $C_{60}$@**2** in polar solvents, without modifying the structure of $C_{60}$, we coordinated cationic $[(\eta^5\text{-}C_5Me_5)Ru^{II}]^+$ moieties[14] to the aromatic rings of the CTV units of the hemicarceplex; this approach has been applied previously to generate a water-soluble cryptophane host for further trapping of Xe atoms.[15] Although the harsh reaction conditions (microwave heating at 403 K for 2 h) would not be tolerated by most host/guest complexes (i.e., they would dissociate into their individual components), the highly stable hemicarceplex $C_{60}$@**2** allowed the synthesis of the desired complex $C_{60}$@[**3**]$Cl_6$, which we isolated in reasonable yield (46%) after column chromatography (Scheme 1). Although, gratifyingly, the complex $C_{60}$@[**3**]$Cl_6$ is soluble in MeOH,

**Scheme 1. Synthesis of the Complex $C_{60}$@[3]$Cl_6$**



EtOH, and their aqueous blends, it is not soluble in pure water, presumably because the equatorial regions of the hemicarceplex $C_{60}$@**2** remain too hydrophobic.

We grew single crystals suitable for X-ray crystallography through liquid diffusion of hexane into a $CH_2Cl_2$ solution of the complex $C_{60}$@[**3**]$Cl_6$. The solid-state structure of $C_{60}$@[**3**]$^{6+}$ reveals[16] (Figure 6) a geometry in which the spherical $C_{60}$ component is located within the cavity of the molecular cage **3**.

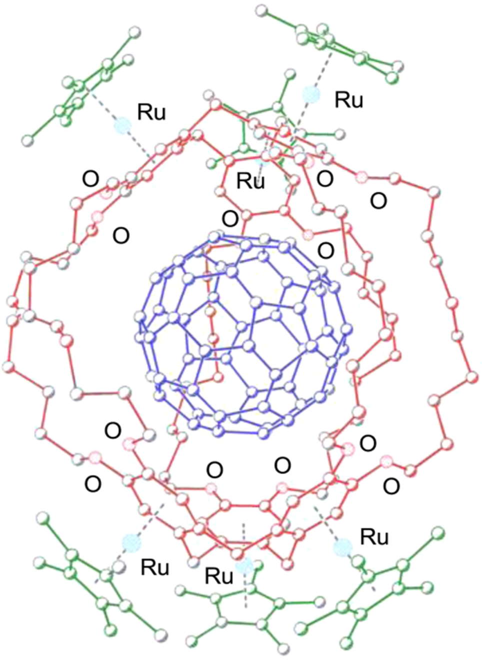


**Figure 6.** Ball-and-stick representation of the solid-state structure of the complex $C_{60}$@[**3**]$^{6+}$.

We have synthesized $C_{60}$@**2**, a highly stable $C_{60}$-incarcerated hemicarceplex that maintains its molecular integrity—that is, it does not release its guest moiety—even when heated as a solid at 523 K for at least 3 h in air. The first four reduction potentials of the entrapped $C_{60}$ unit of this hemicarceplex are more negative, relative to those of free $C_{60}$, by 0.45–0.99 V. Attaching six $[(\eta^5\text{-}C_5Me_5)Ru^{II}]^+$ units to the two CTV caps of the hemicarceplex $C_{60}$@**2** forms a new complex, $C_{60}$@[**3**]$Cl_6$, that is soluble in MeOH, EtOH, and their aqueous blends. Therefore, this pair of hemicarceplexes allows the spherical fullerene $C_{60}$ to be dissolved in solvents over a wide range of polarities for various applications. The increased solubility and more-negative reduction potentials of $C_{60}$ when incarcerated within these CTV-based molecular cages suggest that these highly stable hemicarceplexes could be applied as new types of fullerene derivatives for studies in both materials science and molecular electronics. We are currently investigating the applications of $C_{60}$@**2** and $C_{60}$@[**3**]$Cl_6$ as well as synthesizing other highly stable hemicarceplexes incorporating higher fullerenes.

## ■ EXPERIMENTAL SECTION

**General.** All glassware, stirrer bars, syringes, and needles were either oven- or flame-dried prior to use. All reagents, unless otherwise indicated, were obtained from commercial sources. Column chromatography was performed on silica gel (70–230 mesh) or LiChroprep RP-18 (40–61 μm). Melting points are uncorrected. For NMR spectroscopy, the deuterated solvent was used as the lock and the solvent's residual proton(s) or TMS was employed as the internal standard. Chemical shifts are reported in parts per million (ppm). Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), or br (broad). High-resolution electrospray ionization mass spectra were recorded using a time-of-flight (TOF) mass analyzer. Microwave irradiation of sealed reaction vessels was performed in a CEM-Discover Labmate microwave oven; the temperatures were recorded using an external infrared sensor. Ball-milling was performed using a swing-mill, containing two 5 mL stainless-steel cells and two stainless-steel balls (diameter: 7 mm); the mill was operated at a 20 Hz frequency at room temperature.

**Hemicarceplex $C_{60}$@2.** A solid mixture of the molecular cage **2** (40 mg, 26 μmol) and $C_{60}$ (40 mg, 56 μmol) was ball-milled at room temperature for 30 min, and then the resulting solid was washed into a round-bottom flask with $CHCl_3$ (20 mL). After evaporating the organic solvent under reduced pressure, the solid residue was heated under vacuum at 523 K for 15 h. The resulting solid was purified chromatographically ($SiO_2$; $CS_2$ then $CH_2Cl_2$/hexane, 4:1) to afford a brown solid (22 mg, 38%). mp > 300 °C; $^1H$ NMR (400 MHz, $CDCl_3$, 298 K) $\delta$ = 1.20–1.50 (m, 60H), 1.60–1.79 (m, 24H), 1.80–1.91 (m, 12H), 3.44 (d, $J$ = 13.6 Hz, 6H), 3.66–3.75 (m, 12H), 4.05–4.07 (m, 12H), 4.68 (d, $J$ = 13.6 Hz, 6H), 6.70 (s, 12H); $^{13}C$ NMR (100 MHz, $CDCl_3$, 298 K) $\delta$ = 27.2, 30.2, 30.8, 30.9, 37.1, 68.6, 114.9, 132.1, 142.0, 147.7; HR-MS (ESI) calcd for $C_{162}H_{144}O_{12}^+$ $[M]^+$, $m/z$ 2281.0658; found, $m/z$ 2281.0689.

**$C_{60}$@[3]$Cl_6$.** $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ (63 mg, 79 μmol) and degassed water (4 mL) were added to a suspension of the hemicarceplex $C_{60}$@**2** (60 mg, 26 μmol) in THF (2 mL) in a 10 mL microwave reaction vessel, which was then sealed and heated at 130 °C under microwave irradiation for 2 h. The resulting red solution was concentrated, and the solid residue was purified (RP-C18; $H_2O$/MeOH, 3:7) to afford a brown solid (47 mg, 46%). mp > 300 °C; $^1H$ NMR (400 MHz, $CD_3OD$, 298 K) $\delta$ = 1.31–2.02 (m, 96H), 2.03 (s, 90H), 3.44 (d, $J$ = 14 Hz, 6H), 3.70 (d, $J$ = 14 Hz, 6H), 3.80–3.90 (m, 12H), 4.20–4.23 (m, 12H), 7.11 (s, 12H); $^{13}C$ NMR (100 MHz, $CD_3OD$, 298 K) $\delta$ = 11.0, 29.3, 31.3, 31.7, 32.3, 32.7, 73.2, 77.3, 96.2, 96.7, 125.3, 143.9; HR-MS (ESI) calcd for $C_{222}H_{234}O_{12}Ru_6Cl_4$ $\{C_{60}@[\mathbf{3}]Cl_4\}^{2+}$, $m/z$ 1921.5403, found $m/z$ 1921.5455; $C_{222}H_{234}O_{12}Ru_6Cl_3$ $\{C_{60}@[\mathbf{3}]Cl_3\}^{3+}$, $m/z$ 1269.3708, found $m/z$ 1269.3661; $C_{222}H_{234}O_{12}Ru_6Cl_2$ $\{C_{60}@[\mathbf{3}]Cl_2\}^{4+}$, $m/z$ 943.2861, found $m/z$ 943.2808.

**Electrochemistry.** CV was performed to determine the redox potentials of $C_{60}$ and the hemicarceplex $C_{60}$@**2** ($5 \times 10^{-4}$ M) (Table 1). The electrochemical instrumentation used consisted of a commercially available electrochemical analyzer and a conventional personal computer. A conventional three-electrode configuration was used, with a Pt disk (0.07 $cm^2$) as the working electrode, a platinum counter electrode, and Ag/AgCl as the reference electrode. The reference electrode was calibrated using $Fc/Fc^+$ before and after the experiments. Tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$, 0.1 M) was the supporting electrolyte. The measurements were performed for samples in anhydrous solvents under Ar; all samples were deoxygenated with Ar prior to measurement.

**Table 1. Redox Potentials (V vs $Fc/Fc^+$) of $C_{60}$ and $C_{60}$@2, Determined Using Cyclic Voltammetry**[a,b]

| compound | $E^1_{re}$ | $E^2_{re}$ | $E^3_{re}$ | $E^4_{re}$ | $E^5_{re}$ | $E^1_{ox}$ | $E^2_{ox}$ | $E^3_{ox}$ | $E^4_{ox}$ | $E^5_{ox}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $C_{60}$ | −1.04 | −1.45 | −1.95 | −2.46 | −3.01 | −2.74 | −2.23 | −1.73 | −1.20 | −0.80 |
| $C_{60}$@**2** | −1.48 | −2.10 | −2.75 | −3.45 |  | −3.04 | −2.46 | −1.81 | −1.15 |  |

[a] $E^n_{re}$: *n*th reduction peak potential of the neutral compound. [b] $E^n_{ox}$: *n*th oxidation peak potential of the highest reduced species.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

$^1$H and $^{13}$C NMR spectra of the hemicarceplexes and Crystal Information File (CIF) of $C_{60}$@[**3**]$Cl_6$. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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(16) Crystal data for $C_{60}$@[**3**]$Cl_6$: [$C_{222}H_{234}O_{12}Ru_6 \cdot 6Cl$]; $M_r$ = 3913.21; monoclinic; space group $C2/c$; $a$ = 24.3252(4) Å; $b$ = 37.1919(9) Å; $c$ = 24.5257(5) Å; $V$ = 22058.7(8) Å$^3$; $\rho_{calcd}$ = 1.178 g cm$^{-3}$; $\mu$(Mo K$\alpha$) = 0.526 mm$^{-1}$; $T$ = 100(2) K; brown cubic; 24 797 independent measured reflections; $F^2$ refinement; $R_1$ = 0.087; $wR_2$ = 0.247. The program PLATON/SQUEEZE was applied to account for the residual electron density. CCDC-978460 contains the supplementary crystallographic data for this study. Spek, A. L. *PLATON/SQUEEZE*; Utrecht University: Utrecht, The Netherlands.