

Facile Catch and Release of Fullerenes Using a Photoresponsive Molecular Tube

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S Supporting Information

ABSTRACT: A novel M_2L_2 molecular tube capable of binding fullerene C_{60} was synthesized from bispyridine ligands with embedded anthracene panels and $Ag(I)$ hinges. Unlike previous molecular cages and capsules, this open-ended tubular host can accommodate a single molecule of various C_{60} derivatives with large substituents. The fullerene guest can then be released by using the ideal, noninvasive external stimulus, light.

The selective recognition and binding of target analytes are essential properties if one wishes to design stable host–guest complexes as systems to engender unusual intermolecular interactions or examine new chemical reactions.¹ On the other hand, the facile release of encapsulated guest molecules (or reaction products) from the host molecule is necessary for the subsequent delivery or utilization of the captured guest molecules after sequestration.² Previous examples of guest release from molecular host–guest complexes typically utilize the addition of secondary guests in a guest-exchange process. Treatment with acid or base or the addition of ancillary metal ions (or ligands) also prompts complexes to release the guest as a result of structural rearrangement.³ For practical applications such as drug delivery systems, however, the development of noninvasive, external-stimuli-responsive guest-release systems for large molecules are of high priority.^{1,2} Although several photo- and redox-triggered systems for small-molecule and metal ion “guest” release have been reported,^{4–8} the catch and release of nanometer-sized functional molecules remains elusive.

Fullerenes are appealing nanosized molecules (~1 nm in diameter) with applications in a wide range of fields from material science to pharmacy.⁹ Accordingly, many molecular hosts for fullerenes have been reported.^{10–14} However, to the best of our knowledge, a host capable of capturing a fullerene and subsequently releasing the encapsulated fullerene in response to noninvasive stimuli at ambient temperature has never been described. We expected a suitably sized tubular structure composed of curved ligands with large aromatic panels and metal ions would present a molecular host suitable for binding fullerenes through aromatic–aromatic interactions (Figure 1). Judicious choice of metal hinges that respond to light stimulus should provide a mechanism to release the bound

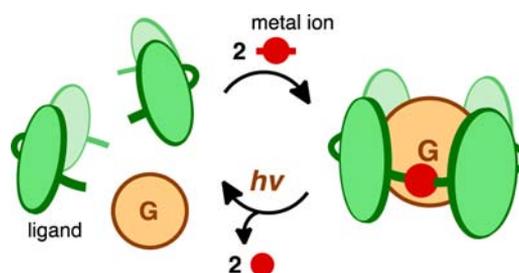


Figure 1. Catch and release of a large guest molecule (e.g., fullerene C_{60}) by using a tubular host composed of two curved ligands and two metal ions. Guest catch and release are triggered by the addition of metal hinges and the removal of the hinges upon photoirradiation, respectively.

large guests without the addition of supplementary reagents or solvents.

We have demonstrated that bispyridine **1** is a useful curved bidentate ligand for the formation of M_2L_4 molecular capsules with extended aromatic anthracene panels^{14,15} and that the capsule with square-planar Pd(II) hinges irreversibly binds fullerene C_{60} through π -stacking interactions.¹⁴ Here we used Ag(I) ions as metal hinges¹⁶ to generate novel M_2L_2 molecular tube **2** (Figure 2), which binds fullerene C_{60} at room temperature and subsequently releases the captured C_{60} upon UV–vis irradiation. Unlike palladium ions, silver ions form stable complexes from two ligands in a linear geometry but release the ligands upon photoexcitation. The tube– C_{60} host–guest complex spontaneously formed when ligands **1** and Ag(I) ions were mixed in the presence of C_{60} . More importantly, in contrast to the previous Pd(II) capsule, which only binds C_{60} , molecular tube **2** can catch and release a variety of C_{60} derivatives **3a–c** with large functional groups as a result of its open-ended tubular structure.

Tubular capsule **2** was formed only in the presence of all three components, ligand **1**, AgNO₃, and guest C_{60} (Figure 3). No tubular structures or interactions were observed by ¹H NMR analysis when only ligand **1** and AgNO₃, or only ligand **1** and C_{60} were combined in CD₃CN (Figure 3b). However, when C_{60} powder (17 μ mol) was suspended in a solution of **1** (11 μ mol) and AgNO₃ (13 μ mol) in CD₃CN (0.5 mL) at room

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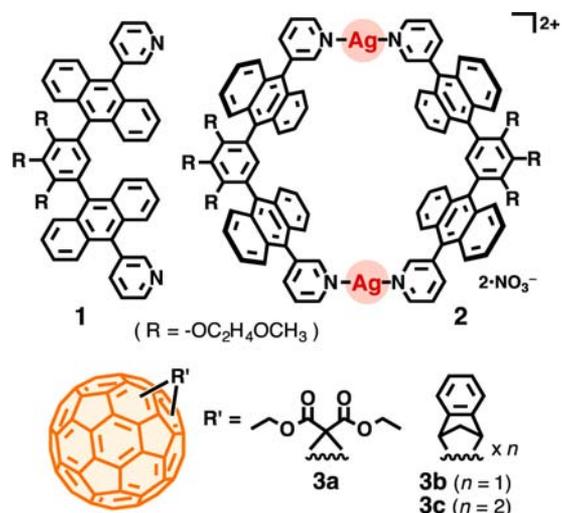


Figure 2. Chemical structures of curved bispyridine ligand **1**, Ag(I)-linked molecular tube **2**, and C_{60} derivatives **3a–c**.

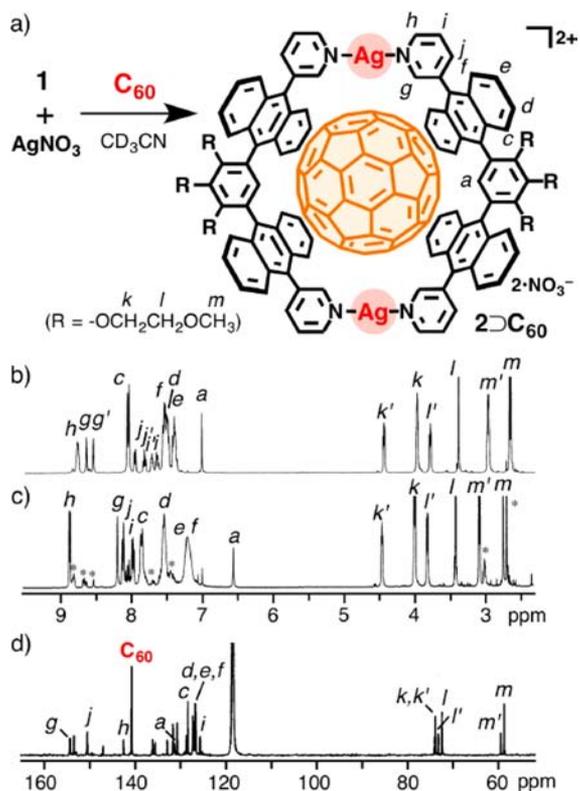


Figure 3. (a) Schematic representation of the selective formation of the $2C_{60}$ complex upon mixing of ligand **1** and $AgNO_3$ in the presence of C_{60} in CD_3CN at room temperature. (b, c) 1H NMR spectra (400 MHz, CD_3CN , rt) of (b) a mixture of **1** and $AgNO_3$ and (c) the $2C_{60}$ complex (* = free ligand). (d) ^{13}C NMR spectrum (100 MHz, CD_3CN , rt) of the $2C_{60}$ complex.

temperature for 1 h in the dark, the color of the solution dramatically changed from pale yellow to red-purple. After the removal of the suspended free C_{60} by filtration, NMR and electrospray ionization time of flight mass spectrometry (ESI-TOF MS) analyses of the resultant clear solution revealed the formation of the 1:1 host–guest complex $2C_{60}$ in 88% yield.¹⁷ In the 1H NMR spectrum (Figure 3c), nine proton signals were observed for the anthracene ($H_{c,d,e,f}$), pyridine ($H_{g,h,i,j}$), and m -

phenylene (H_a) rings in the aromatic region. The large upfield shifts of the two inner protons H_a and H_g ($\Delta\delta = -0.51$ and -0.48 ppm, respectively) would be expected to result from the enhanced shielding by the bound C_{60} . Although C_{60} is effectively insoluble in acetonitrile,¹⁸ the single carbon signal of C_{60} was prominently observed at 140.5 ppm in the ^{13}C NMR spectrum (Figure 3d). Diffusion-ordered NMR spectroscopy (DOSY) revealed the formation of a single host assembly, as all of the proton signals showed the same diffusion coefficient of $8.83 \times 10^{-10} m^2 s^{-1}$, indicating a diameter of 1.4 nm. ESI-TOF MS analysis confirmed the $1_2 \cdot (Ag)_2 \cdot C_{60}$ composition of the product with a signal at m/z 1274.7 ($[2C_{60} - 2NO_3]^{2+}$; Figure S18 in the Supporting Information). The UV–vis spectrum of $2C_{60}$ showed an apparent absorption band at $\lambda_{max} = 510$ nm corresponding to C_{60} enclathrated in the cavity of tube **2** (see Figure 5b). The absorption band is sharper than that of free C_{60} in usual organic solvents (e.g., $CHCl_3$ and *o*-dichlorobenzene; Figure S32).¹⁷ The prominent spectral narrowing originates from symmetrically selective perturbation of the electronically excited states of encapsulated C_{60} by the tubular framework of **2** (Figure S33).^{17,19}

A three-dimensional model of the $2' \cdot C_{60}$ complex ($R = -OCH_3$) was generated using force-field and density functional theory (DFT) calculations (see the Supporting Information for computational details)^{17,19} based on the metal–ligand ratios observed by MS and NMR analyses. The C_{60} molecule fits snugly within the aromatic panels of tubular host $2'$, and the closest distance between the enclathrated C_{60} and the anthracene aromatic panels is only 3.4 Å (Figure 4). The

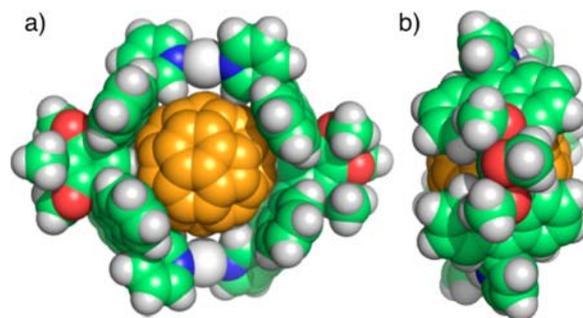


Figure 4. Optimized structure of the $2' \cdot C_{60}$ complex ($R = -OCH_3$) by force-field and DFT calculations without counterions: (a) front view; (b) side view.

predicted aromatic–aromatic interactions found in the optimized structure are in accordance with the large upfield shifts of protons H_a and H_g in the 1H NMR spectrum of $2C_{60}$ (Figure 3c). The beltlike structure also reveals the open nature of tube **2** wherein two surfaces of C_{60} remain exposed to the exterior. We therefore expected tube **2** to readily accommodate various functionalized C_{60} derivatives.

The captured C_{60} guest can then be released as the host disassembles upon external stimulation with UV–vis light (Figure 5). UV–vis irradiation of the red-purple solution of $2C_{60}$ in MeCN at room temperature for 1.5 h using a 36 W incandescent light bulb produced a pale-yellow solution with a powdery suspension of solids, indicating the release of C_{60} from the tube. The broad UV–vis absorption band of C_{60} encapsulated in **2** (400–700 nm) disappeared (Figure 5b). The suspension of C_{60} and $Ag(0)$ was collected by filtration and the C_{60} was extracted with toluene and isolated as a brown solid in

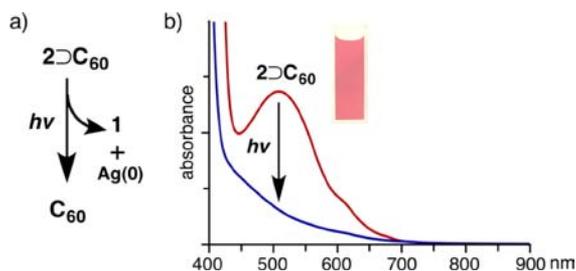


Figure 5. (a) Guest release from 2C_{60} complex by photoirradiation. (b) UV-vis spectra (MeCN, rt, 10.6 mM) before and after photoirradiation of an MeCN solution of 2C_{60} at rt for 1.5 h using a 36 W incandescent light bulb.

68% recovery based on 2C_{60} . After the UV-vis irradiation of 2C_{60} in MeCN, the 2C_{60} complex was regenerated in $\sim 60\%$ yield from the suspended mixture of **1** and C_{60} by the addition of AgNO_3 at room temperature. The tube could selectively bind C_{60} from a mixture of C_{60} and C_{70} . Therefore, it should be noted that starting with commercially available fullerene soot containing only 5% C_{60} , the present catch-and-release procedure provided pure C_{60} in 63% yield based on **2**.

The open-ended, tubular cavity of **2** readily accommodated functionalized C_{60} molecules **3a–c**. When a mixture of ligand **1**, AgNO_3 , and diethyl malonate-derivatized C_{60} (**3a**) in CHCl_3 was stirred at room temperature for 1 h, host-guest complex $2\text{C}3\text{a}$ was obtained as an orange solution in almost quantitative yield. The formation of the host-guest complex was confirmed by NMR and MS analyses. In the ^1H NMR spectrum, all of the observed proton signals were assigned to the tubular framework and the diethyl malonate substituent ($\text{H}_{\text{A,B}}$) of the encapsulated **3a** (Figure 6a). The ESI-TOF MS spectrum clearly showed the signals corresponding to the composition of $2\text{C}3\text{a}$ (e.g., $[2\text{C}3\text{a} + m\text{CH}_3\text{OH} - 2\text{NO}_3]^{2+}$, $m = 0-4$; Figure 6b). Host-guest complexes $2\text{C}3\text{b}$ and $2\text{C}3\text{c}$ were obtained in a similar fashion from C_{60} derivatives **3b** and **3c** functionalized with one and two indene groups, respectively (Figures S25–S31).¹⁷ The host–

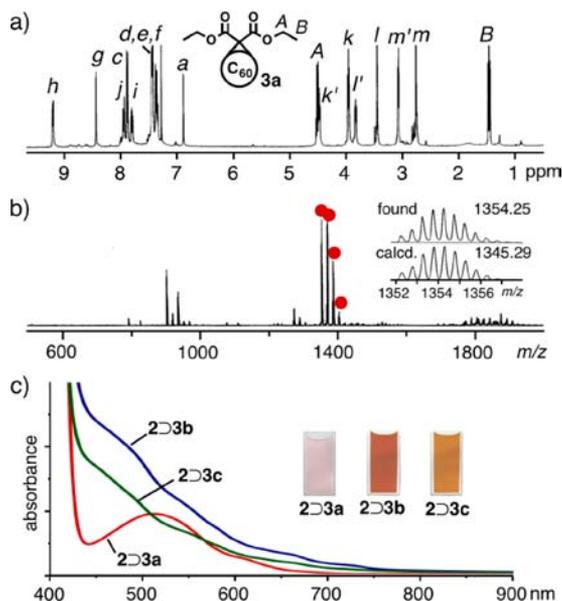


Figure 6. (a) ^1H NMR (400 MHz, CDCl_3 , rt) and (b) ESI-TOF MS spectra of the $2\text{C}3\text{a}$ complex. (c) UV-vis spectra (MeCN, rt) of $2\text{C}3\text{a}$, $2\text{C}3\text{b}$, and $2\text{C}3\text{c}$ with pictures of the solutions.

guest complexes exhibited broadened UV-vis absorption bands in the range of 450–700 nm in MeCN solution (Figure 6c). Similar to C_{60} , the diethyl malonate derivative **3a** was recovered in 75% yield after triggered release from complex $2\text{C}3\text{a}$ upon UV-vis irradiation at room temperature for 2 h.

In summary, we have prepared a photoresponsive molecular tube that can catch and release large fullerene guests. Unlike previous fullerene molecular hosts, the bound guest is readily released using noninvasive UV-vis irradiation. Light-responsive guest release is superior to release triggered by chemical, electrochemical, or heat stimuli: not only can the intensity of the light stimuli can be regulated, but also, the excitation wavelength is tunable and the area of the effect can be spatially localized using laser excitation. We anticipate that further modification of the organic framework of tubular host **2**, including improvement of its solubility and stability and the incorporation of specific recognition motifs, will provide a practical platform for the development of novel photoresponsive molecular hosts in chemical and biological systems.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and physical properties. 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.

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(19) The entire structures of C₆₀ and the 2'⊃C₆₀ complex were optimized at the LC-BOP+LRD/6-31G* level in the gas phase, where the molecular-mechanics-optimized structure was employed as the initial structure for 2'⊃C₆₀. The ECP28MDF pseudopotential was used for silver atoms throughout the present study. Excitation energies and oscillator strengths of the optimized structures were calculated by time-dependent DFT using the LC-BOP functional. The same basis set as in the geometry optimization was used for C₆₀. For 2'⊃C₆₀, the 6-31G basis set was used for atoms other than Ag. No symmetry was imposed in the calculations. The numbers of excited states calculated were 50 and 24 for C₆₀ and 2'⊃C₆₀, respectively. The GAMESS program package was used for all of these quantum-chemical calculations.