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Dimeric Capsules with a Nanoscale Cavity for [60]Fullerene Encapsulation

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Abstract: The acid-assisted and guest-induced formation of superstructures was achieved by the addition of haloacetic acids to a toluene solution of the resorcin[4]arene derivatives **1** and [60]fullerenes. The formation of dimeric superstructures that encapsulated a nanosized guest molecule was observed when appropriate acids, such as haloacetic acids, and suitable guest molecules, such as [60]fullerenes, were co-added to a toluene solution of cavitand **1** that has four pyridine units, whereas a complicated equilibrium between several species was detected without [60]fullerenes, and the formation of discrete superstructures was not monitored in the absence of haloacetic acids. The spectroscopic data indicate that the formed [60]fullerene-encapsulated complexes have the structure of **2**. These complexes are self-assembled through pyridinium–anion–pyridinium interactions and by π–π and van der Waals interactions. The rate of decomplexation of **2** is estimated to be 3.1 s^{-1} from a 2D exchange NMR spectrum. The [60]fullerene encapsulation process can be controlled by modifying the amounts of acids used, changing the temperature of the system, altering the ratio of acid/base, and even through varying the solvent polarity. Moreover, the fluorescence spectra show band-narrowing spectral changes and a retardation of the relaxation characteristics of isolated and isotropic [60]fullerenes, which indicates that the environmental change around [60]fullerene is induced upon its encapsulation.

Keywords: cavitands · fullerenes · hydrogen bonds · self-assembly · supramolecular chemistry

Introduction

Supramolecular complexation involving nanosized, electron-deficient fullerenes has generated a great deal of interest in the field of host–guest chemistry and construction of novel nanostructures. To date, studies on such complex formation have been mainly based on inclusion phenomena with dish- or cup-shaped hosts, such as azacrown ethers,[1] cyclodextrins,[2] cyclotriveratrylenes,[3] calix[*n*]arenes,[4] and homooxacalix[3]arenes.[5] Porphyrins and metalloporphyrins have also been studied and some outstanding examples have been reported.[6] There are, however, only a few examples that show the encapsulation phenomena of [60]fullerene within the cavity of the capsulelike host. This is mainly due to the fact that with covalently linked macromolecules it is very difficult to encapsulate such a large guest without any strong driving forces for inclusion, since the hosts must have a window large enough for a guest to enter but which can also serve as an exit door. This limitation, however, can be overcome if noncovalently linked macromolecules are employed, which are usually formed by making use of hydrogen bonds and/or metal–ligand interactions. The construction of self-assembled cage molecules utilizing these interactions has attracted widespread interest and considerable progress has been achieved. Recently, Claessens and Torres reported [60]fullerene encapsulation phenomena in an M_3L_2 subphthalocyanine cage.[7,8] Shinkai and co-workers showed the

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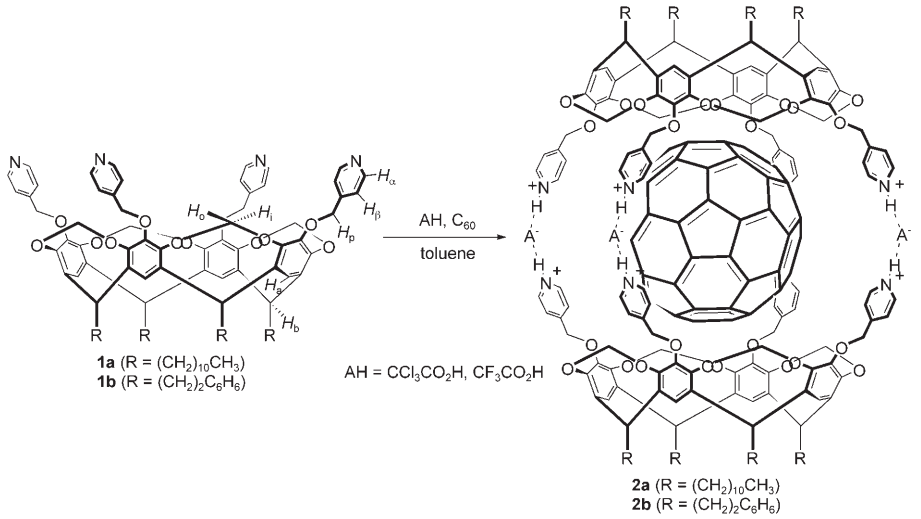
same phenomena in a homooxacalix[3]arene-based dimeric capsule constructed by Pd^{II}–pyridine interactions.[7,8]

We have extensively investigated resorcin[4]arene derivatives **1** (Scheme 1) that have four pyridine units as pendent groups for the construction of metal-induced superstructures by using *cis*-protected square-planar M^{II} ions (M = Pd, Pt). We have demonstrated how metal-induced self-assembly can be tuned by subtle changes in the solvent system: an interclipped supramolecular capsule (composed of two units of cavitand **1** and four metal ions) is formed as a sole adduct in chloroform/methanol,[9a] an intraclipped supramolecular bowl (composed of one cavitand **1** and two metal ions) is formed exclusively in an aqueous phase,[9b] and a capsule and a bowl coexist in a dynamic manner in nitromethane.[9c]

Herein, we describe the utilization of the pendent pyridine units of cavitand **1** as bases instead of ligands and the formation of [60]fullerene-encapsulated superstructures, which take advantage of the cooperative function of a suitable guest and appropriate acids (Scheme 1). To the best of knowledge, this is the first example in which hydrogen-bonded cage molecules encapsulate a fullerene and appropriately designed macromolecules with basic pendent moieties lead to supramolecular nanocavities by the simple addition of acids.



Scheme 1. Formation of [60]fullerene-encapsulated superstructures.

Results and Discussion

Design strategy and ^{1}H NMR spectroscopy: Resorcin[4]arene derivatives **1** prepared from the corresponding tetrol cavitand[10] were first utilized as ligands for the construction of metal-induced dimeric capsules.[9] Due to the availability of the pyridine units of cavitand **1** as bases, acid-assisted formation of dimeric capsules would be possible by charged hydrogen-bonding interactions, such as pyridine–pyridinium and pyridinium–anion–pyridinium interactions. The acid-assisted formation of capsules by the simple addition of acids was investigated by ^{1}H NMR spectroscopy. The ^{1}H NMR titration spectra, however, show the existence of a complicated equilibrium between several species when trifluoroacetic acid (TFA) is added to a [D_8]toluene solution of **1a**.[11,12] It was anticipated that suitable guest(s) might induce the formation of guest-encapsulated superstructures. From CPK and computer-aided modeling it was expected that large and spherical guests, such as [60]fullerene, would be suitable for the cavity of a dimeric supramolecular capsule formed through pyridine–pyridinium or pyridinium–anion–pyridinium interactions (Figure 1).[13]

The interaction between cavitand **1** and [60]fullerene without additional acids was investigated by UV/Vis titration in toluene. No significant change in the absorption spectrum was observed (see Figure S2 in the Supporting Information), which indicates that without acid assistance there is little interaction of cavitand **1** with [60]fullerene.[14]

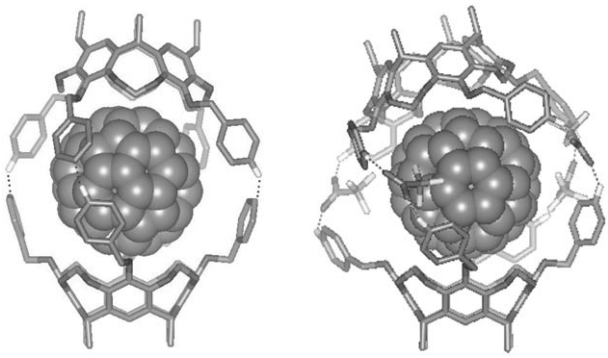


Figure 1. Computer-aided models of the [60]fullerene-encapsulated complexes based on pyridine–pyridinium interactions (left) and pyridinium–anion–pyridinium interactions (right) (MacroModel 7.0).

The concept of acid-assisted and guest-induced formation of a superstructure was first validated by ^{1}H NMR spectroscopy (Figure 2). When **1a** and two equivalents of [60]fullerene were dissolved in [D_8]toluene, no evidence of any interaction between **1a** and [60]fullerene was observed (Figure 2b), which is consistent with the UV/Vis measurements. However, as an increasing amount of TFA was added, a new set of peaks appeared which became the sole product when four equivalents of TFA were added (Figure 2e).[15]

Similar results were observed with trichloroacetic acid but not with acetic acid. Presumably this is due to the small ΔpK_a value between pyridine and acetic acid, since the

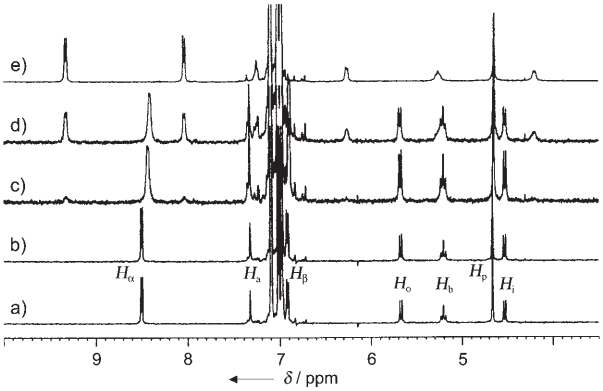


Figure 2. Portion of the ^{1}H NMR spectra with gradual addition of TFA to a [D_8]toluene solution of **1a**·2C_{60} (300 MHz, 300 K). a) **1a**; b) **1a**·2C_{60}; c) **1a**·2C_{60}+1 equiv TFA; d) **1a**·2C_{60}+2 equiv TFA; e) **1a**·2C_{60}+4 equiv TFA.

degree of proton transfer is a function of $\Delta pK_{a.}$[16] The pyridinium proton of the complex is observed at $\delta = 19.77$ ppm (see Figure S5 in the Supporting Information) and the peak-intensity ratio of the pyridinium proton of the complex to the pyridine's α proton is about 1:2, which indicates that all pyridines are protonated. It is also noteworthy that H_β undergoes a more downfield shift than H_α ($\delta = 1.1$ and 0.8 ppm for H_β and H_α, respectively) when the complex is formed. This means that H_β is closer to the encapsulated electron-deficient [60]fullerene than H_α.

^{1}H and ^{13}C NMR spectroscopy with ^{13}C-enriched [60]fullerene: The cooperation of acid and guest for the construction of the supramolecular capsule was also confirmed by ^{13}C NMR spectroscopy (Figure 3). In the ^{13}C NMR spectra

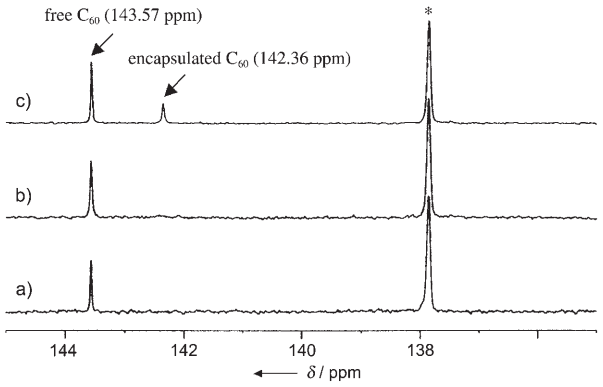


Figure 3. Portion of the ^{13}C NMR spectra with gradual addition of TFA (125 MHz, [D_8]toluene, 300 K). a) C_{60}; b) **1a**·2C_{60}; c) **1a**·2C_{60}+4 equiv TFA. A signal at $\delta = 137.7$ ppm from C_7D_8 is marked with an asterisk.

with ^{13}C-enriched [60]fullerene, a new peak appeared at a higher magnetic field ($\delta = 142.36$ ppm) than the peak for free [60]fullerene ($\delta = 143.57$ ppm) only when TFA was added to the [D_8]toluene solution of **1a** and [60]fullerene.[17] This peak can be assigned to the encapsulated [60]fullerene, and the peak-intensity ratio of free to encapsulated [60]fullerene is about 3:1, which means that all [60]fullerenes are encapsulated in the dimeric capsule considering that four equivalents of [60]fullerene are added to each dimeric capsule. The 2:1 stoichiometry between **1a** and [60]fullerene is also observed by ^{13}C and ^{1}H NMR spectroscopy carried out with the gradual addition of **1a**·4TFA (the latter number refers to the number of equivalents used) to the [D_8]toluene solution of ^{13}C-enriched [60]fullerene (Figure 4). When two equivalents of **1a**·4TFA were added,

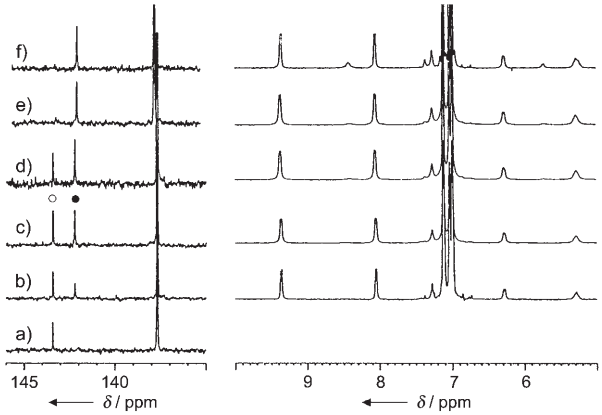


Figure 4. Portion of the ^{13}C and ^{1}H NMR spectra with gradual addition of **1a**·4TFA to a [D_8]toluene solution of ^{13}C-enriched [60]fullerene (300 MHz, 300 K): a) 0, b) 0.5, c) 1.0, d) 1.5, e) 2, and f) 2.5 equiv. The peak from the encapsulated [60]fullerene is indicated by ● and that from the free [60]fullerene by ○.

the ^{13}C resonance from free [60]fullerene disappeared without the appearance of any additional peak in the ^{1}H NMR spectra (Figure 4e). Further augmentation of **1a**·4TFA, however, caused the appearance of ^{1}H NMR spectroscopic peaks from nonencapsulated material (Figure 4f). These findings mean that [60]fullerene is strongly wrapped in the supramolecular capsule composed of two **1a** molecules.

We can obtain more information from the ^{13}C NMR spectra (Figures 3 and 4); the observed peak separation implies that the complexation–decomplexation exchange rate is slower than the timescale of the ^{13}C NMR spectroscopic measurements. According to Cram's studies on molecular containers, the rate of guest liberation from a hemicarcerand is known to be related not only to the size of the guest molecules but also to their rigidity and shape.[18] As might be expected from the rigidity, spherical shape, and complementary size of [60]fullerene, the exchange rate was observed to be slower than the ^{13}C NMR timescale. Notably, the [60]fullerene within complex **2a** gives a single ^{13}C signal. This means that [60]fullerene within the supramolecular cavity still rotates at a speed faster than the ^{13}C NMR spectroscopic timescale.

Structure elucidation: The guest-induced and acid-assisted formation of the dimeric capsule complex might utilize charged hydrogen bonds, such as pyridine–pyridinium and pyridinium–anion–pyridinium interactions (Figure 1). A

great deal of effort has been made to determine which interactions are the sources of the supramolecular structure. Countless trials to obtain a suitable crystal for X-ray crystallography were in vain. The crystals obtained from slow diffusion of a toluene solution of **1b**·C_{60}·4TFA were too unstable to handle because they were too brittle and decomposed rapidly when exposed to air. Mass spectrometers equipped with soft-ionization apparatus are broadly used for the characterization of supramolecular structures. Mass spectrometric evidence for the [60]fullerene-encapsulated superstructures, however, has not been obtained even from soft-ionization methods, such as matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) and cold-spray ionization mass spectrometry (CSI-MS).[19] In the case of MALDI-MS, the addition of a somewhat polar matrix might cause the destruction of the supramolecular complex, and in CSI-MS the solvent, toluene, does not have sufficient ionization ability; the addition of polar solvent to promote ionization resulted in decomplexation.

^{13}C and ^{1}H NMR spectroscopic studies revealed evidence for the formation of the [60]fullerene-encapsulated complex through pyridinium–anion–pyridinium interactions: 1) four equivalents of acid are required for the formation of the dimeric capsule structure, 2) all the pyridine moieties of **1** are protonated, and 3) the 2:1 stoichiometry between **1a** and [60]fullerene is observed. Therefore, the above data suggest that the [60]fullerene-encapsulated complex would be formed not through pyridine–pyridinium interactions but through pyridinium–anion–pyridinium interactions.[20,21]

^{1}H–^{1}H exchange spectroscopy (EXSY) and the rate of guest release: The transfer of spin polarization from the [60]fullerene-encapsulated complex **2a** to its debris was observed in a ^{1}H–^{1}H EXSY experiment (Figure 5).[22] Intense exchange cross-peaks between the pyridine α protons of the complexed and dissociated material are obtained. The rate constant, estimated on the basis of the integration of the cross-peaks, was 3.1 s^{-1}. The free energy of activation ($\Delta G^{\neq}$) was calculated by the Eyring equation to be 16.8 kcal mol^{-1}.

^{1}H NMR spectroscopy with varying temperatures, solvent polarities, and TEA/TFA ratios: It is well-known that intermolecular non-bonding interactions are so labile that external stimuli affect the formation of non-bonded complexes. To validate this concept in our system, temperature-dependent ^{1}H NMR spectroscopy was carried out with a [D_8]toluene solution of **1a**·2C_{60}·2TFA from 300 to 333 K (Figure 6). As the temperature increases, the intensity of the peaks assigned to **2a** decreases. Moreover, these peaks completely disappear at 333 K. When the temperature returns to 300 K, the original peaks are restored. This phenomenon implies that the [60]fullerene-encapsulated complex **2a** is disassembled with increasing temperature owing to attenuation of the assembling forces, such as triple-ion interactions, π–π interactions, and van der Waals interactions, and that the encapsulation of [60]fullerene is a reversible process since reassembly occurs with decreasing temperature.

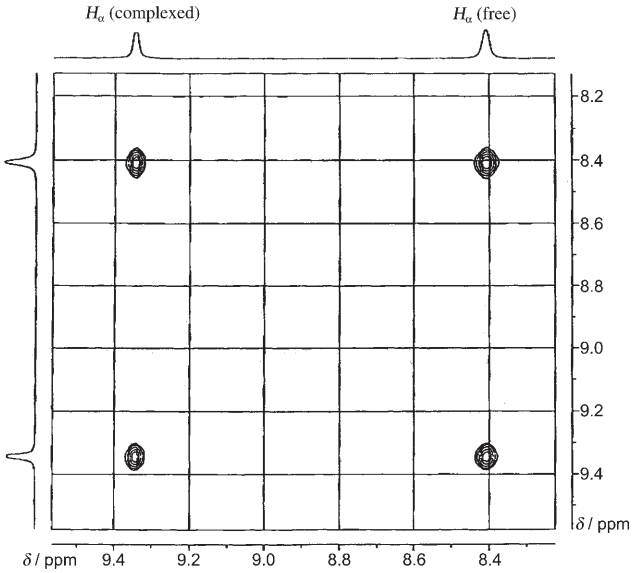


Figure 5. Downfield region of the ^{1}H–^{1}H EXSY spectrum (600 MHz, 298 K, **1a**·C_{60}·2TFA concentration = 2.0 mM, [D_8]toluene, mixing time 0.6 s).

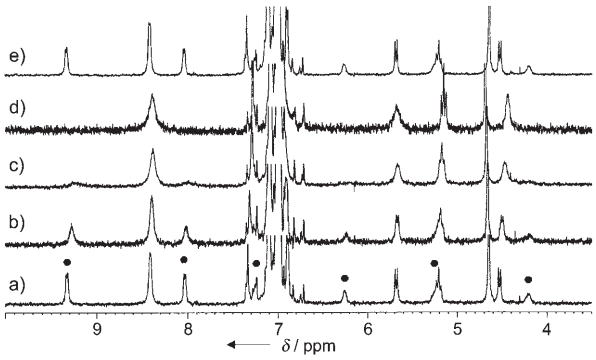


Figure 6. Portion of temperature-dependent ^{1}H NMR spectra of a [D_8]toluene solution of **1a**·2C_{60}·2TFA. a) 300, b) 313, c) 323, d) 333 K, and e) return to 300 K. The peaks from the fullerene-encapsulated capsules are indicated by ●.

Decomplexation phenomena were also observed by the addition of relatively polar solvents, such as [D]chloroform, [D_2]dichloromethane, and [D_3]acetonitrile. This may be partially due to a decrease in the solubility of the complex or [60]fullerene and partially to diminution of pyridinium–anion–pyridinium interactions.[23] Moreover, the [60]fullerene encapsulation process can be controlled through the addition of a base (Figure 7). The addition of triethylamine (TEA) to a [D_8]toluene solution of **1a**·2C_{60}·4TFA destroyed the acid-assisted formation of the [60]fullerene-encapsulated superstructure; the gradual addition of TEA caused the destruction of **2a** and complete destruction was achieved when four equivalents of TEA were added. Subsequent addition of four equivalents of TFA restored the original complex.

UV/Vis–fluorescence spectroscopy: The symmetrically forbidden lowest-absorption band at 540 nm of [60]fullerene appears weakly in solution due to a reduction in local sym-

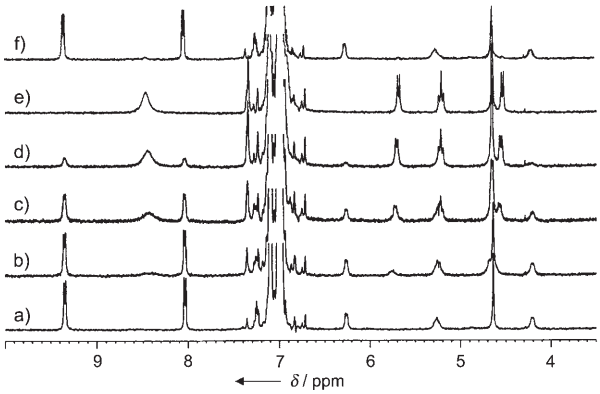


Figure 7. Portion of the ^{1}H NMR spectra with gradual addition of TEA to a [D_8]toluene solution of **1a**·2C_{60}·4TFA (300 MHz, 296 K). a) 0, b) 1, c) 2, d) 3, and e) 4 equiv TEA; f) 4 equiv TEA then 4 equiv TFA.

metry resulting from solute–solvent interactions. Addition of **1a**·4TFA) to the toluene solution of [60]fullerene led to an increase in the absorption band at 440 nm and a decrease at 540 nm, characteristic of complexation (see Figure S7 in the Supporting Information). The decrease of the forbidden transition band at 540 nm can be attributed to suppressed solute–solvent interactions, which implies that the guest, [60]fullerene, is encapsulated by the host complex and partially isolated from solvent molecules.

The [60]fullerene encapsulation phenomenon was also clearly seen in the fluorescence spectra (Figure 8a). Bare [60]fullerene in toluene showed a typical fluorescence spectrum around 700 nm, which matched very well with reported cases.[24] However, the addition of 2**1a**·8TFA led to a band-narrowing spectral change. The change of the environment, mainly polarity, around [60]fullerene upon its encapsulation is presumed to cause the spectral change. Of note is that such a phenomenon was observed only with the co-addition of **1a** and TFA; the addition of **1a** or TFA alone did not affect the fluorescence spectrum of [60]fullerene.

Retardation of the relaxation of [60]fullerene at the lowest excited singlet state (S_1) was also observed (Figure 8b). The lifetime of [60]fullerene at S_1 was measured to be (1.19 ± 0.02) ns in a toluene solution, and was hardly affected by the variation of the solvent.[25] When [60]fullerene forms the complex **2a**, a 6% elongation of the lifetime ((1.26 ± 0.02) ns) was observed. Although it shows a small elongation of the lifetime at S_1, this finding clearly indicates the great reduction of nonradiative relaxation channels, other than the very efficient intersystem crossing to the triplet state ($\Phi_T\approx0.96$),[26] by solute–solvent interactions to the ground state.

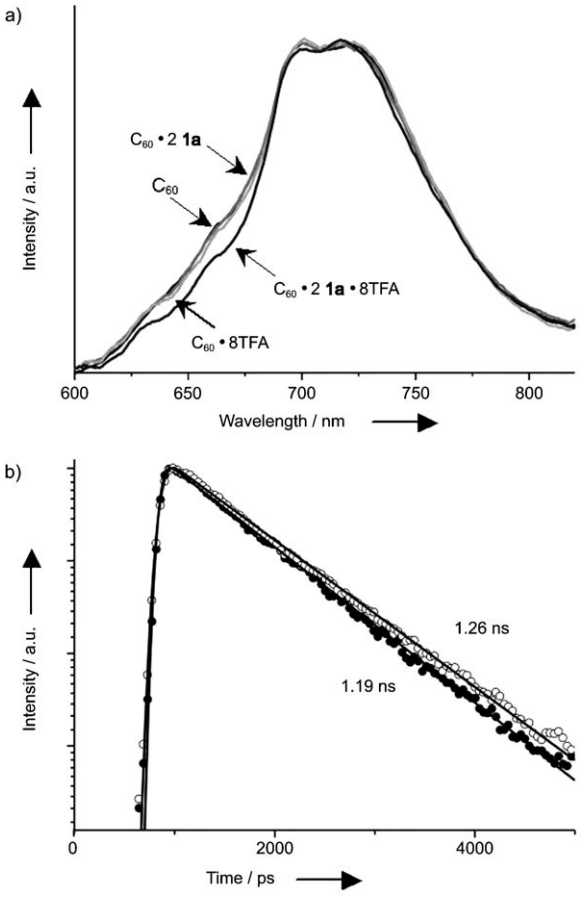


Figure 8. a) Fluorescence spectra of [60]fullerene, C_{60}·2**1a**, C_{60}·8TFA, and C_{60}·2**1a**·8TFA in toluene. Samples were excited at 330 nm. b) Fluorescence kinetic profiles of [60]fullerene (●) and C_{60}·2**1a**·8TFA (○), excited at 532 nm and monitored above 660 nm, in toluene. Fitted curves (——) are also shown.

Conclusion

We have shown the formation of [60]fullerene-encapsulated superstructures **2** by the addition of an appropriate acid to a toluene solution of the resorcin[4]arene derivatives **1**, which have four pyridine units, and [60]fullerenes. The formation of the superstructures was demonstrated by ^{1}H NMR, ^{13}C NMR, and UV/Vis–fluorescence spectroscopies. The [60]fullerene encapsulation process can be controlled through changing the temperature, adding an acid/base, and even through varying the solvent polarity. Moreover, the fluorescence spectra of the encapsulated [60]fullerenes show band-narrowing spectral changes and a retardation of the relaxation characteristics of isolated and isotropic [60]fullerenes. This study proposes a new strategy by which the simple addition of acids to appropriately designed macromolecules with basic pendent moieties leads to supramolecular nanocavities capable of encapsulating large molecules, such as [60]fullerene.

Experimental Section

General: All chemicals were of reagent grade and were used without further purification. [60]Fullerene (99.5%) was obtained from Southern Chemical Group (USA) and ^{13}C-enriched [60]fullerene (^{13}C content: 10–

15%) was purchased from MER Corporation (USA). NMR spectra were recorded on either a Bruker Avance DPX-300 or a Bruker Avance 600 spectrometer. Chemical shifts are given in parts per million by using the residual resonances of deuterated solvents ($\delta = 7.27$ ppm for chloroform; $\delta = 7.00$ ppm for toluene) as an internal reference. The rates of chemical exchange were measured by using EXSY by integrating the peaks of 2D NOESY. Molecular modeling was performed on a Silicon Graphics O2 machine with a MacroModel 7.0 program. Fast atom bombardment mass spectrometry (FAB-MS) data were obtained on a JEOL JMS-AX505WA mass spectrometer with *m*-nitrobenzyl alcohol as matrix. CSI-MS data were obtained on a four-sector (BE/BE) tandem mass spectrometer (JEOL, JMS-700T) equipped with a CSI source. UV/Vis spectra were recorded on a Beckman DU650 spectrophotometer. Fluorescence spectra were obtained by using a homemade fluorimeter composed of a 75 W Xe lamp (Acton Research, XS 432), 0.15 and 0.30 m monochromators (Acton Research, Spectrapro 150 and 300), and a photomultiplier tube (Acton Research, PD438). Fluorescence spectra were not corrected for the spectral sensitivity of the fluorimeter. Pulses (532 nm) of 25 ps duration from an actively and passively mode-locked Nd:YAG laser (Quantel, YG 701) were employed to excite the samples. The fluorescence wavelength was selected by using an appropriate combination of filters. Fluorescence kinetic profiles were detected with a 10 ps streak camera (Hamamatsu, C2830) attached to a CCD (Princeton Instruments, RTE-128-H). Fluorescence kinetic constants were extracted by fitting a measured kinetic profile to a computer-simulated kinetic curve convoluted with the temporal response function (≈ 50 ps) iteratively. Unless specified otherwise, all the fluorescence measurements were carried out with a [60]fullerene concentration of 1 mM in toluene with/without two equivalents of **1a** and/or eight equivalents of TFA at room temperature.

Synthesis of tetrapyridine-tethered cavitand (1a): A mixture of the corresponding tetrol cavitand (244 mg, 0.2 mmol),[10] K_2CO_3 (690 mg, 5.0 mmol), and 4-picolyl chloride hydrochloride (328 mg, 2.0 mmol) in dry DMF (5 mL) was stirred under a nitrogen atmosphere at 60 °C for 18 h. The solvent was evaporated under vacuum and the residue was dissolved in chloroform (50 mL). The solution was washed with water and brine, then dried ($MgSO_4$) and evaporated to dryness under vacuum. Silica-gel chromatography with CH_2Cl_2/CH_3OH (15:1) was used to obtain **1a** (yield 238 mg; 75%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.61$ (d, ^3J(H,H) = 5.89 Hz, 8H; PyH_α), 7.32 (d, ^3J(H,H) = 5.79 Hz, 8H; PyH_β), 6.88 (s, 4H; Ar*H*), 5.79 (d, ^2J(H,H) = 7.11 Hz, 4H; ArOCH_oH$_i$OAr), 5.01 (s, 8H; OCH_2Py), 4.75 (t, ^3J(H,H) = 7.92 Hz, 4H; C*H*CH$_2$), 4.49 (d, ^2J(H,H) = 7.12 Hz, 4H; ArOCH$_o$*H*$_i$OAr), 2.22 (br m, 8H; CHCH_2CH$_2$), 1.4–1.1 (br s, 72H; CH$_2$(CH_2)$_9$CH$_3$), 0.90 ppm (t, ^3J(H,H) = 6.58 Hz, 12H; CH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 149.69$, 147.97, 147.01, 144.09, 139.07, 121.39, 114.69, 99.45, 73.37, 36.91, 31.92, 29.83, 29.71, 29.40, 27.91, 22.68, 14.11 ppm; FAB-MS: *m/z*: calcd: 1581.9920; found: 1581.9962 $[M+H]^+$; elemental analysis calcd (%) for $C_{100}H_{132}N_4O_{12}$: C 75.91, H 8.41, N 3.54; found: C 76.04, H 8.66, N 3.38.

Synthesis of tetrapyridine-tethered cavitand (1b): Prepared by a similar method to **1a** in 70% yield. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.66$ (d, ^3J(H,H) = 3.34 Hz, 8H; PyH_α), 7.44 (d, ^3J(H,H) = 3.13 Hz, 8H; PyH_β), 7.24 (br m, 12H; Ph*H*), 7.18 (d, ^3J(H,H) = 2.60 Hz, 8H; Ph*H*), 6.94 (s, 4H; Ar*H*), 5.83 (d, ^2J(H,H) = 6.38 Hz, 4H; ArOCH_oH$_i$OAr), 5.08 (s, 8H; OCH_2Py), 4.86 (t, ^3J(H,H) = 7.46 Hz, 4H; C*H*CH$_2$), 4.53 (d, ^2J(H,H) = 6.12 Hz, 4H; ArOCH$_o$*H*$_i$OAr), 2.70 (br m, 8H; CH$_2$CH_2Ph), 2.53 ppm (br m, 8H; CH_2CH$_2$Ph); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 148.92$, 148.23, 147.99, 144.30, 141.50, 138.99, 128.63, 128.40, 126.16, 121.77, 114.66, 99.51, 73.43, 37.07, 34.44, 32.30 ppm; FAB-MS: *m/z*: calcd: 1381.5538; found: 1381.5527 $[M+H]^+$; elemental analysis calcd (%) for $C_{88}H_{76}N_4O_{12}$: C 76.50, H 5.54, N 4.06; found: C 75.12, H 5.79, N 3.82.

Preparation of [60]fullerene-encapsulated capsule (2): Diluted TFA (4 mmol) in toluene was added to a toluene solution of tetrapyridine-tethered cavitand **1** (1 mmol) and [60]fullerene (> 0.5 mmol) in a vial.

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[15] Addition of more than four equivalents of TFA caused decomplexation. Complete destruction of the capsule structure was observed when four more equivalents of TFA were added (see Figure S3 in the Supporting Information). This finding might be explained by considering that the 2:1 TFA–pyridine complex is the most stable species when two equivalents of haloacetic acids are added to a nonpolar solution containing pyridine derivatives (see ref. [12] and Figure S4 in the Supporting Information).

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[21] One referee suggested a new model for the complex, in which the two cavitands are staggered and each of the eight acetate anions bridges two pyridinium moieties to form a continuous seam around the equator, since our proposed model would have charges so would lead to precipitation from toluene. In fact, a cloudy solution was detected when the cavitand's R group was methyl and a slightly opaque solution was detected at high concentration even when R was CH_2CH_2Ph, which implies the formation of charged species. Moreover, it was found from computer-aided modeling (MacroModel 7.0) that the model suggested by the referee could not be formed to encapsulate [60]fullerene due to the short length of linkers (acetate) and severe strain. There might, however, be an equilibrium among several species including our proposed structures and the structure formed through quadrupole interactions (two acetate ions are between the two pyridinium moieties on the two cavitands: pyridinium–two anions–pyridinium interactions).

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