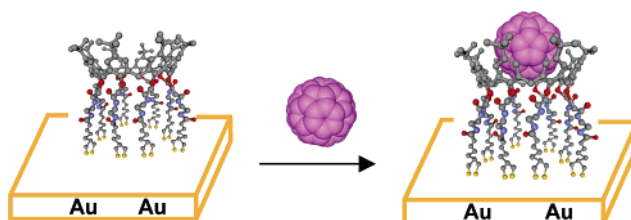# Supramolecular Incorporation of Fullerenes on Gold Surfaces: Comparison of C_{60} Incorporation by Self-Assembled Monolayers of Different Calix[*n*]arene (*n* = 4, 6, 8) Derivatives

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Two new calix[6]arene derivatives **3** and **4** in a 1,4-anti conformation and one calix[8]arene derivative **5** were synthesized. SAMs of calix[*n*]arene (*n* = 4, 6, 8) derivatives **1**−**5** were formed on gold bead electrodes. Cyclic voltammetry with $Ru(NH_3)_6^{3+/2+}$ as a redox probe, together with impedance spectroscopy and reductive desorption, indicates that SAMs of **5** have a higher coverage than those of **3** and **4** due to the presence of hydrogen bonding and possibly its conformation. Noncovalent immobilization of C_{60} on gold surfaces was achieved with SAMs of calix[8]arene derivative **5** but not with those of **1**−**4**.

Introduction

The construction of supramolecular architectures including fullerenes has been ongoing since the first reported inclusion complex of C_{60} by γ-cyclodextrin.[1] Supramolecular aggregates and polymers have recently been obtained from gold nanoparticles modified by β-cyclodextrins.[2] The addition of cyclotriveratrylene (CTV) to a toluene solution of C_{60} resulted in black crystals of CTV−C_{60} complexes.[3] The X-ray structure showed that C_{60} stands well above the cavity of the CTV compound. Very recently, supramolecular stacks of highly reduced geodesic π-systems have been prepared by the reduction of fullerene derivatives and corannulene with lithium metal.[4] In 2004, Oda et al. reported complexes of cyclic-[6]paraphenyleneacetylene with [60]- and [70]fullerene derivatives.[5] More interestingly, they have also constructed onion-type fullerene supramolecules based on carbon nanorings.[6]

Among the various hosts for fullerenes, calixarenes have received considerable attention since the time when pioneering work was performed by Atwood et al. and Shinkai et al. to purify C_{60} from carbon soot by the selective complexation with *p-tert*-butylcalix[8]arene.[7] The host−guest complex of fullerene with *p-tert*-butylcalix-[8]arene is unstable in most organic solvents, and no crystallographic data have been reported. Recently, well-ordered arrays of complexes of C_{60} with a calix[8]arene derivative have been constructed on a Au (111) surface, and the configuration has been clearly established using scanning tunneling microscopy.[8] In the calixarene family, host molecules including calix[3]-, calix[4]-, calix[5]-, calix[6]-, and calix[8]arenes have been found to form complexes with C_{60} and/or C_{70}.[8−10] Evaporation of a solution mixture of C_{60} and C_{70} in the presence of calix-

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SCHEME 1. Calix[*n*]arene Thioctic Ester Derivatives 1−5

[6]arene afforded complexes of calix[6]arene with C_{60} and C_{70}.[9a] Fukazawa et al. reported that the complexation of a calix[5]arene dimer with C_{60} shows a very large binding constant with C_{60} in organic solvents.[10a] This year, they reported supramolecular polymeric nano networks formed by molecular-recognition-directed self-assembly of a calix-[5]arene dimer and a dumbbell-shaped C_{60} dimer.[10b] In addition, C_{60} complexation with azacalix[*m*]arene[n]py-ridines has been investigated.[11] However, Shinkai et al. found that not all calixarenes can form ball-and-socket structures with fullerenes in a detailed study of C_{60} complexation with calix[*n*]arenes.[9b]

The power of host−guest chemistry lies in the fact that it can provide supramolecular structures that cannot be obtained by conventional synthetic methods. Fullerene-containing inclusion supramolecules possess specific advantages over derived fullerenes for specific applica-tions, because they inhibit self-aggregation and retain the fullerene's electronic properties unmodified. It has been known that the electronic properties of fullerene derivatives are related to the electronegativity of the attached groups. In contrast to fullerene derivatives, both the structure and electronic properties of fullerene mol-ecules are preserved within supramolecular complexes. This is very important for the application of fullerenes in materials science, as indicated by the enhancement of light-energy conversion efficiency by multi-porphyrin arrays of porphyrin-peptide oligomers with fullerene clusters.[12]

Compared to the extensive studies of fullerene su-pramolecular complexes in solution and in the solid state, the investigation of fullerene complexes at solid−liquid interfaces and on solid substrates remains largely unex-plored. Langmuir studies of the complex of *p-tert*-butylcalix[8]arene with C_{60} indicate that the pleated-loop conformation adopted by calix[8]arene is retained upon C_{60} complexation.[13] It was also found that C_{60} encapsu-lated in anionic calix[8]arenes can be readily deposited by electrochemical oxidative polymerization of ethylene-dioxythiophene.[14] The resultant electrode generates a photocurrent upon visible light irradiation. Electrochemi-cal studies of a C_{60}−*p-tert*-butylcalix[8]arene inclusion complex film in mixed acetonitrile and water exhibit a pair of stable reduction/reoxidation peaks.[15] C_{60} embed-ded in a gel-like membrane formed from tetraoctylphos-phonium bromide on an electrode in an aqueous system

also gives stable reductive responses.[16] Shinkai et al. accomplished the noncovalent immobilization of C_{60} by complexation with homooxacalix[3]arene on surfaces combining eletrostatic and *π*-stacking.[17] A very high quantum yield (21%) was obtained for the ITO electrodes modified by the homooxacalix[3]arene−C_{60} complexes. Photovoltaic cells were also constructed by using su-pramolecular nanoclusters of porphyrins and fullerenes with gold nanoparticles. The composite cluster electrode exhibits an incident photon-to-photocurrent efficiency (IPCE) as high as 54%.[18] Along these lines, we recently reported noncovalent immobilization of C_{60} on gold surfaces by SAMs of CTV and porphyrin derivatives.[19,20] We report herein the use of the noncovalent interaction between calixarene receptors and fullerenes to immobi-lize C_{60} on surfaces. One calix[4]arene derivative (**1**), three calix[6]arene derivatives (**2−4**), and one calix[8]-arene derivative (**5**) with surface anchoring groups were synthesized (Scheme 1). All compounds were fully char-acterized by ^{1}H and ^{13}C NMR and MS spectroscopies.

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SCHEME 2. Syntheses of Calix[6]arene Thioctic Ester Derivatives 3 and 4

Self-assembled monolayers (SAMs) of these calixarene compounds were formed on gold surfaces and characterized by cyclic voltammetric (CV) blocking experiments, impedance spectroscopy, and reductive desorption. Stable SAMs of these compounds were used to immobilize C_{60} on gold surfaces noncovalently.

Results and Discussion

Synthesis. The syntheses of cone-calix[4]arenecrown-6 derivative **1** and calix[6]crown-4 thioctic ester **2** have been reported previously, which adopt cone and 1,4-bridged cone conformations, respectively.[21,22] The synthetic methods used for the preparation of calix[6]arene thioctic ester derivatives (**3**, **4**) and calix[8]arene derivative **5** are shown in Schemes 2 and 3. Reaction of *p-tert*-butylcalix[6]arene with triethylene glycol monotosylate in refluxed acetonitrile using K_2CO_3 as base afforded calix[6]arene hexa-alcohol derivative **7**. Calix[6]arene hexa-alcohol **6** was prepared according to a published procedure.[23] Calix[6]arene thioctic ester derivatives **3** and **4** were prepared in 52 and 47% yields, respectively, by direct coupling between the corresponding hexa-alcohols and thioctic acid in CH_2Cl_2 in the presence of DCC and DMAP. *p-tert*-Butylcalix[8]arene octa-amine compound **8** was obtained by refluxing *p-tert*-butylcalix[8]arene octa-ethylester **9** in ethylenediamine for 4 days. Coupling compound **8** with thioctic acid in the presence of HATU and triethylamine afforded *p-tert*-butylcalix[8]arene thioctic ester derivative **5**.[24]

All the target compounds were characterized by ^{1}H NMR, ^{13}C NMR, mass spectroscopy, and elemental

analysis. The ^{1}H NMR spectral pattern at room temperature suggests that compound **3** has a high degree of symmetry in solution. All the peaks are relatively sharp, compared to the ^{1}H NMR spectra of its corresponding precursors, calix[6]arene hexa-methylester and calix[6]arene hexa-alcohol **6**. This indicates that the conformational interconversion through oxygen and through the annulus is somehow frozen. The methylene protons on the annulus of **3** showed a very complicated signal pattern in the ^{1}H NMR spectrum. There is one singlet and two pairs of doublets in the region of 3.1–4.7 ppm, corresponding to bridging methylene protons, as shown in Figure 1. However, the conformation of **3** can be assigned according to the ^{1}H NMR spectrum, especially the signal pattern of the *p-tert*-butyl groups. The signals of the *p-tert*-butyl groups observed at 0.98 and 1.34 ppm have an intensity of 2:1. This ratio suggests a 1,4-anti or 1,2,3-alternate conformation.[25] Proton signals of four *p-tert*-butyl groups show at higher field, whereas those of two *p-tert*-butyl groups appear at lower field, indicating an aromatic ring-current effect. These observations indicate that compound **3** exists in the 1,4-anti conformation. This conformational assignment was further supported by the ^{1}H NMR pattern of the protons on the benzene rings by observing one singlet and two doublets. The singlet at 7.17 ppm can be assigned to protons of two benzene rings placed on the "down" side of the rim in the 1,4-anti conformation. The two doublets at 7.43 and 6.62 ppm correspond to protons of four benzene rings on the "up" side of the rim. The doublet is due to the spin–spin interaction among protons within the aromatic rings. Such 1,4-anti conformation was observed when the bulky groups were attached to the low rim of calix[6]arenes.[25] ^{1}H NMR of compound **4** exhibits three singlets for aromatic protons, two singlets in a ratio of 1:2 for the *p-tert*-butyl groups, and a complicated signal pattern for

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SCHEME 3. Synthesis of Calix[8]arene Thioctic Ester Derivative 5
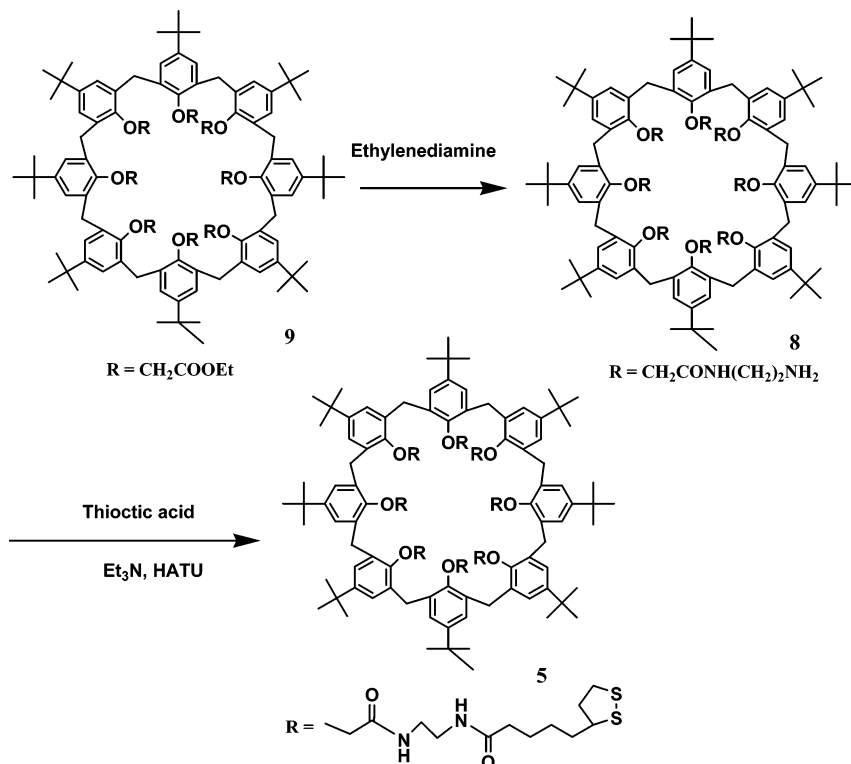
the methylene bridging protons. These observations reveal that compound **4** possesses a 1,4-anti conformation as well. Well-resolved and sharp proton signals were observed in the ¹H NMR spectrum of compound **5** because of the reduced conformational mobility of the *p-tert*-butylcalix[8]arene caused by the introduction of eight thioctic ester legs. The ¹H NMR of compound **5** shows six singlets for protons on the benzene rings, a multiplet for the bridging methylene protons, and four singlets for the *p-tert*-butyl groups. The conformation of compound **5** is, however, not assigned from its NMR data. Calix[8]-arene can adopt 16 possible "up−down" conformations and numerous other conformations caused by projection "out" of one or more aryl rings, which makes the assignment of the conformation of **5** difficult.

SAM Preparation and Characterization. SAMs of **1**−**5** were prepared by immersion of bare gold bead electrodes, which were made from gold wire as described previously,[19−24] in freshly prepared dichloromethane solutions of the compounds for 2 days. After being rinsed with copious CH_2Cl_2 and dried under a stream of Ar, SAM-modified gold beads were characterized by observing their blocking effect on the electrochemical response of the $Ru(NH_3)_6^{3+/2+}$ redox probe, as shown in Figure 2. Reversible redox behavior with $E_{1/2} = -0.16$ V vs Ag/AgCl was observed on bare gold electrodes (solid line). As compared to the reversible redox process on a bare gold
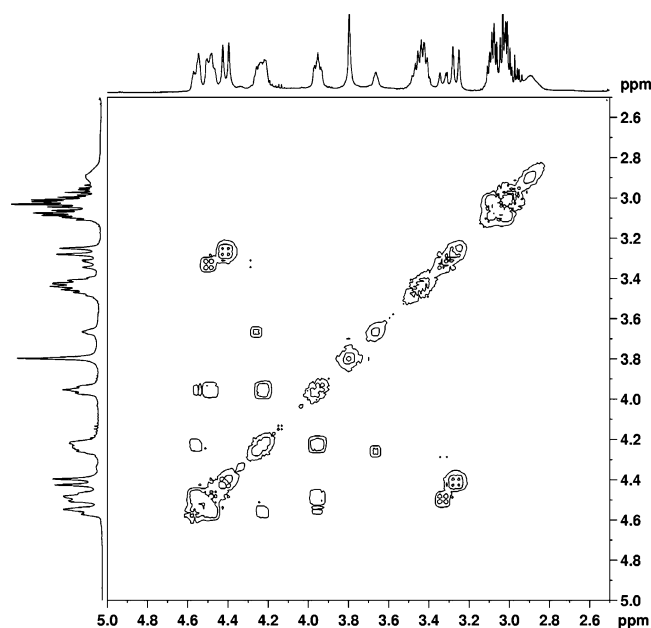
FIGURE 1. Partial COSY NMR spectrum of compound **3**.
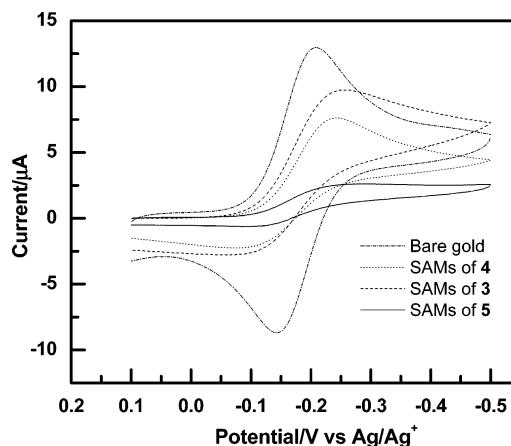
FIGURE 2. CVs of $Ru(NH_3)_6^{3+/2+}$ at bare gold electrodes and gold electrodes modified by SAMs of **3**−**5**.
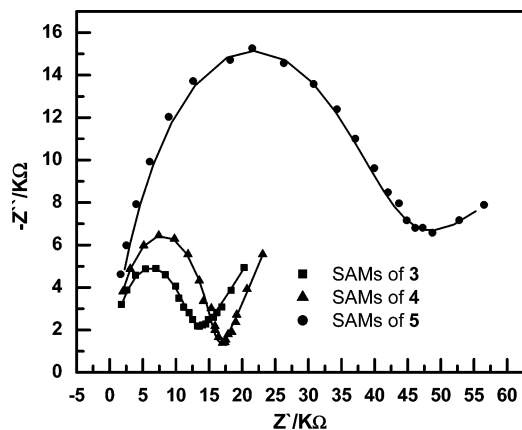
FIGURE 3. Impedance response of $Ru(NH_3)_6^{3+/2+}$ at monolayer-modified gold electrodes by **3**−**5**.
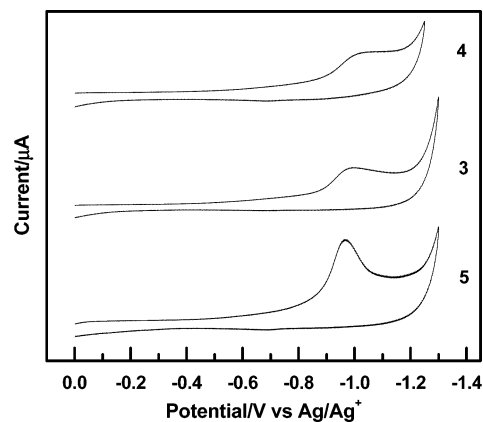

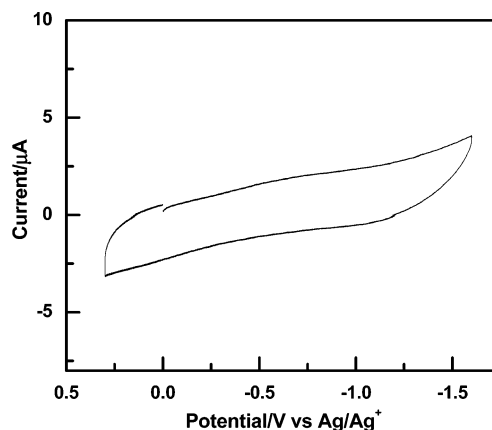**FIGURE 4.** Electrochemical desorption of SAMs of **3**−**5** on gold in 0.5 M KOH.

FIGURE 5. CV recorded in CH_3CN of SAMs of **1** after dipping into a solution of C_{60}. Supporting electrolyte: 0.1 M Bu_4NPF_6.

electrode, obvious attenuation of the current, especially the anodic current, reveals that SAMs of **3**−**5** were formed on the electrode surfaces, which partially block the redox process of $Ru(NH_3)_6^{3+/2+}$. Compared to SAMs of **3** and **4**, those of **5** exhibit a better blocking effect. The difference in blocking effect may be related to the packing modes of the SAMs and/or electron permeability through the monolayers. Compounds **3** and **4** adopt a 1,4-anti conformation, which probably explains why large cathodic currents were still observed for electrodes modified by SAMs of **3** and **4**. Calix[8]arene derivative **5** may have a conformation favorable for SAM formation because of the use of all eight of its thioctic ester legs. In addition, hydrogen bonds that formed among amide groups in **5** could also contribute to the better CV blocking effect of its corresponding SAMs.

SAMs of **3**, **4**, and **5** were also characterized by electrochemical impedance spectroscopy. The impedance spectra at gold electrodes modified with **3**, **4**, and **5** in the presence of 1 mM $Ru(NH_3)_6^{3+/2+}$ exhibit sigmoidal voltammograms with a semicircle and a straight line (Figure 3). Fitting of the experimental data using the commercially available program EQUIVALENT CIRCUIT yielded charge-transfer resistance (R_{ct}) values of 14.1, 17.6, and 51.8 kΩ for SAMs of **3**, **4**, and **5**, respectively. This indicates the degree of inhibition of redox reactions by these SAMs on the electrode surfaces. In contrast, the Nyquist plot obtained on bare gold bead electrodes displays mainly the Warburg impedance (a straight line), because the redox reactions are very fast on bare gold surfaces and the processes are diffusion-controlled. These observations are consistent with the CV blocking experiments. Characterization of SAMs of **1** and **2** by CV blocking experiments and impedance spectroscopy have been reported previously.[21,22]

Further direct evidence for SAM formation on gold electrode surfaces comes from electrochemical reductive desorption. Desorption experiments were performed by immersing the SAM-modified gold beads into thoroughly deoxygenated 0.5 M KOH by high-purity Ar. The scans were initiated at a potential of 0 V and swept cathodically to a potential of −1.35 V at a scan rate of 0.1 V/s. As shown in Figure 4, gold electrodes modified by SAMs of **3**, **4**, and **5** exhibit cyclic voltammetric responses with irreversible cathodic waves at ca. −1.0 V, which correspond to the reductive desorption of the surface-

attached thiolates. By integrating the current under the cathodic wave, we find that the estimated surface coverages for **3**, **4**, and **5** are 7.82×10^{-11}, 8.51×10^{-11}, and 1.28×10^{-10} mol/cm^2, respectively. The shape and potential position of the desorption peak for SAMs of **5** are similar to those previously reported for SAMs of thioctic acid.[26] Compared to the sharp desorption peak of SAMs of **5**, those observed for SAMs of **3** and **4** are relatively broad. The CV blocking experiments, impedance spectroscopy, and reductive desorption experiments consistently suggest that SAMs of **5** are more compact than those of **3** and **4**. This may be attributed to the different conformation and the presence of hydrogen bonding in calix[8]arene derivative **5**.

Attempts To Trap C_{60} by Calix[n]arene Derivatives (n = 4, 6). After immersing the modified gold beads with **1** into 1,2-dichlorobenzene solutions of C_{60} overnight, we recorded the voltammetric responses of the corresponding gold electrodes. As shown in Figure 5, no redox response of the fullerene was observed, indicating that SAMs of calix[4]crown-6 derivative **1** cannot incorporate C_{60} on the surfaces. The cavity of cone-isomer **1** is probably too small to exhibit an effective supramolecular interaction between the calix[4]crown-6 derivative and C_{60}. SAMs of calix[6]arene thioctic ester derivatives were

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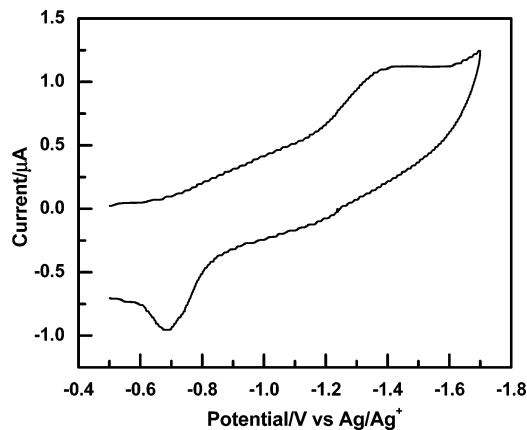
FIGURE 6. CV recorded in CH_3CN of SAMs of **3** (last scan) after dipping into a solution of C_{60}. Supporting electrolyte: 0.1 M Bu_4NPF_6.

FIGURE 7. CV recorded in CH_3CN of SAMs of **5** after dipping into a solution of C_{60}. Supporting electrolyte: 0.1 M Bu_4NPF_6. Scan rate: 1 V/s. Inset: plot of peak intensity versus scan rates.

thus prepared and used in an attempt to trap C_{60} on electrode surfaces. After the incubation of SAMs of **3** in 1,2-dichlorobenzene solutions of C_{60}, the typical electrochemical behavior for physically adsorbed C_{60} was observed.[27] This may be due to the direct physical adsorption of C_{60} on the gold electrodes because of the loosely packed calix[6]arene SAMs. It could also be ascribed to the physical adsorption of C_{60} onto monolayer-coated electrodes, as no physically adsorbed C_{60} was observed in the case of SAMs of **1**. After repeated washing of the surface with toluene and subsequent reductive scans, electrochemical responses changed significantly; finally, one pair of irreversible reduction/reoxidation waves was obtained, as shown in Figure 6. SAMs of **2** and **4** exhibit similar electrochemical behavior. It is well-known that the electrochemical behavior of C_{60} drop-coated films is rather complicated,[27] as compared to the well-defined and reversible redox behaviors of C_{60} in solutions and SAMs of fullerene derivatives.[28,29] In the case of C_{60} drop-coated films, significant differences were observed between the first and subsequent scans.[27] Film reductions are influenced by transportation of electrolyte ions into the films, and by structural rearrangements and dissolution. SAMs of **2**−**4** after the incubation in C_{60} solutions behave like electrodes modified by C_{60} drop-coated films. In addition, the presence of calix[6]arene derivatives on electrode surfaces may also affect the electrochemical behavior of the physically adsorbed C_{60}.

C_{60} Immobilization by Calix[8]arene Derivative 5. Compared to calix[n]arene derivatives ($n = 4$, 6), calix[8]arene derivatives offer a better size fit for complexation of C_{60}. In their so-called pleated-loop-complexation conformation, they provide a cavity with internal and external diameters of 0.7−0.8 and 1.4 nm, respectively. SAMs of **5** were immersed into 1,2-dichlorobenzene solutions of C_{60}. After washing the gold beads with
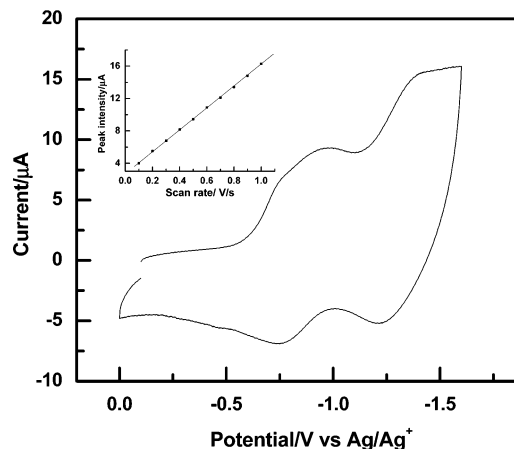
copious 1,2-dichlorobenzene, toluene, and CH_2Cl_2, and drying them under a stream of Ar, we investigated them by cyclic voltammetry. Figure 7 shows two reversible redox waves at $E_{1/2} = -0.84$ and -1.31 V vs Ag/Ag$^+$, which correspond to the first and second reduction processes, respectively, of surface-immobilized C_{60}. The electrochemical behavior is very similar to that for the noncovalent surface fullerene immobilization by CTV derivatives.[19] The peaks are broad, and the first reduction process consists of two overlapped peaks, suggesting the presence of different interaction modes of C_{60}. The peak intensities increased linearly with the scan rate, indicative of surface-confined behavior.

The electrochemical behavior of the C_{60}−calix[8]arene complex film has been investigated.[13−16] For the [60]-fullerene−calix[8]arene complex deposited on the electrode surfaces through electrochemical oxidative polymerization of ethylenedioxythiophene, a redox peak was observed at -0.73 V vs Ag/AgCl, corresponding to the first fullerene reduction process.[14] The CV of C_{60}−calix[8]arene complex drop-coating film in a TBA$^+$ electrolyte exhibited a broad, unresolved double peak that is due to the first two reductions of the fullerene. The QCM experiment indicated C_{60} dissolution upon reduction.[30] In another report, one pair of stable reduction/reoxidation peaks was obtained for the C_{60}−calix[8]arene inclusion complex in a mixed acetonitrile and water solution.[15] The peak currents of SAM-modified electrodes with **5** after incubation in the C_{60} solution were reduced gradually upon successive scans, indicating the dissolution of C_{60} and/or the desorption of the monolayers. The electrochemical behavior of the C_{60}−calix[8]arene complex-modified electrodes is dependent on the film preparation method. As reported, significant electrochemical responses were detected for C_{60} films obtained via drop coating, Langmuir−Blodgett, electrochemical deposition, and self-assembled monolayers.[27]

SAMs were also grown from mixed solutions containing both **5** and C_{60}. The gold beads were immersed in mixed CH_2Cl_2/1,2-dichlorobenzene (1:2) solutions containing 1 mM **5** and 5 mM C_{60} for 2 days. The CV shows two pairs

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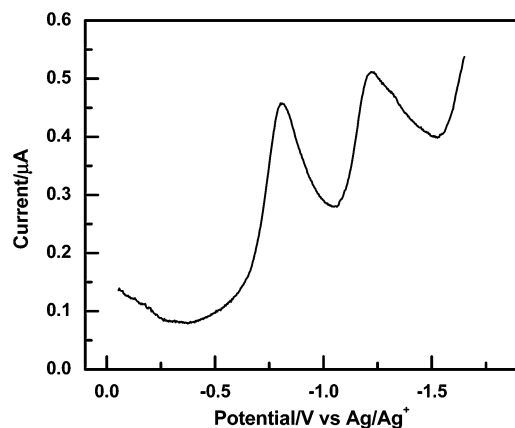(30) Cliffel, D. E.; Bard, A. J. *Anal. Chem.* **1998**, *70*, 4146.

FIGURE 8. DPV recorded in CH_3CN of SAMs grown from a mixture of **5** and C_{60}.

of broad peaks corresponding to the first two redox processes of C_{60}. The peak currents are weaker than those of the SAMs of **5** in which C_{60} was later incorporated. DPV of the corresponding SAMs exhibits the first two C_{60} reduction peaks at -0.81 and -1.24 V vs Ag/Ag$^+$, as shown in Figure 8. This observation further confirms that SAMs of calix[8]arene derivative **5** can immobilize C_{60} on gold surfaces through host−guest interactions.

In summary, several new calix[*n*]arene derivatives with thioctic ester groups were prepared. SAMs of these compounds were formed on gold surfaces, and characterized by CV blocking experiments, impedance spectroscopy, and reductive desorption. Only the calix[8]arene derivative was effective for trapping C_{60} on gold surfaces, as judged by the observation of its first two reduction responses. The SAMs of the smaller analogues, calix[*n*]-arene derivatives **1**−**4** ($n = 4, 6$), did not exhibit any ability to bind C_{60} on the gold surfaces. The photoelectrochemical properties of such supramolecular monolayers are currently under investigation.

Experimental Section

General. *p-tert*-Butylcalix[6]arene, *p-tert*-butylcalix[8]arene octaethylester **9**, and thioctic acid were purchased and used as received. Compound **6** and triethylene glycol monotosylate were synthesized as described in the literature.[23,31] The syntheses of **1** and **2** have been reported before.[21,22] Gold wire (99.999%) was obtained commercially. NMR spectra were recorded on a Bruker Ac 300 or 500 spectrometer. UV−vis spectroscopy was conducted on a Shimadzu 2101PC spectrophotometer. Mass spectroscopy was recorded with an Omni Flex Maldi Tof spectrometer. Elemental analyses were performed using a Carlo Erba EA 1106. Deionized water was prepared with a Nanopure infinity ultrapure water system.

Electrochemical Measurements. Impedance measurements and cyclic voltammetry (CV) were conducted with a CHI-660 electrochemical workstation by using a three-electrode cell. A gold bead and a Pt wire were used as the working electrode and counter electrode, respectively, in combination with Ag/AgCl or Ag/Ag$^+$ as references. The electrochemical desorption experiments were performed in a 0.5 M KOH solution thoroughly purged by argon. Impedance measurements were performed in a solution containing equal concentrations (1 mM) of oxidized and reduced forms of the Ru(NH$_3$)$_6^{3+/2+}$ redox couple. The formal redox potential [$E_{1/2} = (E_p^c + E_p^a)/2$] was determined by cyclic voltammetry. The

frequency range utilized was 1 kHz−0.1 Hz with an ac amplitude of 5 mV.

Monolayer Preparation. Gold beads were prepared as reported before by heating the gold wire in a natural gas/O$_2$ flame, and were cleaned by electrolysis in 0.1 M HClO$_4$.[19−22] The gold beads were then washed with copious amounts of water and acetonitrile. Monolayers on gold were prepared by immersing freshly prepared gold beads in 1 mM solutions of compounds **1**−**5** in CH$_2$Cl$_2$ or acetonitrile for 48 h. After removal, the monolayer-modified gold beads were thoroughly washed with the appropriate solvent, and dried in a stream of argon.

Synthesis of 7. *p-tert*-Butylcalix[6]arene (0.3 g, 0.31 mmol), triethylene glycol monotosylate (0.94 g, 3.09 mmol), K$_2$CO$_3$ (0.47 g, 3.4 mmol), and acetone (15 mL) were refluxed under Ar for 48 h. After filtration and solvent removal, the brownish residue was dissolved with CH$_2$Cl$_2$. The crude residue was chromatographed on silica gel using 30% MeOH/ethyl acetate as eluent to afford a sticky pale yellow oil **7** (0.39 g, 71%). ^{1}H NMR (CDCl$_3$): δ 0.95 (s, broad, 54 H), 3.32−3.83 (m, 84 H), 4.57 (s, broad, 6 H), 6.92 (s, 12 H). ^{13}C NMR (CDCl$_3$): δ 30.5, 31.2, 33.9, 61.2, 70.1, 72.0, 72.4, 72.5, 125.9, 132.6, 145.3, 152.5. MS (MALDI): $m/z = 1789$ [M$^+$ + Na].

Synthesis of 8. *p-tert*-Butylcalix[8]arene octaethylester **9** (0.8 g, 0.40 mmol) was added to 70 mL of ethylenediamine, and the mixture was refluxed under Ar for 3 days. After being cooled to room temperature, the resulting mixture was poured into 200 mL of ice−water and stored at 4 °C overnight. The precipitate was collected by suction filtration, and recrystallization from hot ethanol afforded 0.64 g of white solid **8** (76%). ^{1}H NMR (CDCl$_3$): δ 0.85−1.26 (s, broad, 72 H), 3.49 (s, broad, 90 H), 6.51−6.72 (m, 8 H), 7.89−7.93 (s, 16 H). MS (MALDI): $m/z = 2098$ [M$^+$].

Synthesis of 3. *p-tert*-Butylcalix[6]arene hexa-alcohol **6** (0.12 g, 0.10 mmol) and thioctic acid (0.27 g, 1.3 mmol) were dissolved in CH$_2$Cl$_2$ (10 mL). The mixture was stirred for 30 min at 0 °C under Ar. DCC (0.27 g, 1.3 mmol) and DMAP (0.05 g, 0.41 mmol) were then added, and the mixture was stirred for another 30 min at 0 °C. The cooling bath was then removed, and the solution was allowed to warm to room temperature. After being stirred for 3 days at room temperature, the reaction mixture was filtered. The filtrate was washed with water, and dried over Na$_2$SO$_4$. The mixture was purified by column chromatography (SiO$_2$, 4% EtOAc/CH$_2$Cl$_2$) to give a pale yellow sticky oil **3** (0.12 g, 52%). ^{1}H NMR (CDCl$_3$): δ 0.97 (s, 36 H), 1.34 (s, 18 H), 1.38−1.60 (m, 36 H), 1.74−1.82 (m, 6 H), 2.27−2.36 (m, 18 H), 3.02−3.10 (m, 12 H), 3.25−3.28 (d, $J = 15$ Hz, 3 H), 3.31−3.34 (d, $J = 15$ Hz, 1 H), 3.41−3.46 (m, 6 H), 3.80 (s, 4 H), 3.95 (m, 8 H), 4.22 (m, 8 H), 4.40−4.43 (d, $J = 15$ Hz, 3 H), 4.48 (m, 5 H), 4.55 (m, 4 H), 6.61−6.62 (d, $J = 2$ Hz, 4 H), 7.17 (s, 4 H), 7.43 (d, $J = 2$ Hz, 4 H). ^{13}C NMR (CDCl$_3$): δ 24.6, 24.8, 28.8, 29.2, 31.3, 31.6, 34.1, 34.6, 38.4, 40.2, 56.2, 62.3, 64.8, 65.2, 70.4, 71.2, 123.4, 124.5, 125.7, 127.9, 133.1, 133.6, 134.7, 146.1, 146.6, 152.1, 153.2, 172.3, 174.5. MS (MALDI): $m/z = 2367.7$ [M$^+$ + 1], 2389.3 [M$^+$ + Na]. Anal. Calcd for C$_{126}$H$_{180}$O$_{18}$S$_{12}$: C, 63.92; H, 7.66. Found: C, 64.31; H, 7.25.

Synthesis of 4. 4 was prepared from **7** by following the same procedure as **3**, and was purified by column chromatography (SiO$_2$, 30% EtOAc/CH$_2$Cl$_2$) to afford a pale yellow sticky oil **4** (47%). ^{1}H NMR (CDCl$_3$): δ 1.01 (s, 36 H), 1.37 (s, 18 H), 1.52−1.65 (m, 36 H), 1.82−1.87 (m, 6 H), 2.23−2.28 (m, 12 H), 2.36−2.42 (m, 6 H), 3.09−3.13 (m, 12 H), 3.21−4.15 (m, 86 H), 4.33−4.36 (d, $J = 15$ Hz, 3 H), 4.46−4.49 (d, $J = 15$ Hz, 1 H), 6.66 (s, broad, 4 H), 7.18 (s, 4 H), 7.35 (s, broad, 4 H). ^{13}C NMR (CDCl$_3$): δ 24.4, 28.5, 31.3, 33.7, 34.4, 38.3, 40.0, 56.1, 63.3, 68.8, 69.0, 70.4, 70.8, 71.5, 124.1, 126.7, 127.8, 132.2, 132.6, 133.3, 145.1, 145.5, 152.2, 152.9, 173.2. MS (MALDI): $m/z = 2918.6$ [M$^+$ + Na]. Anal. Calcd for C$_{150}$H$_{228}$O$_{30}$S$_{12}$·H$_2$O: C, 61.82; H, 7.96. Found: C, 62.13; H, 7.81.

Synthesis of 5. Thioctic acid (0.16 g, 0.78 mmol) was dissolved in anhydrous DMF (5 mL) and cooled to 0 °C under

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argon. Triethylamine (0.18 g, 1.78 mmol) and HATU (0.30 g, 0.78 mmol) were added, and the mixture was allowed to stir at room temperature for 10 min, and was cooled to 0 °C again. Compound **8** (0.10 g, 0.05 mmol) in 6 mL of DMF was added, and the mixture was stirred for another 50 min at 0 °C. The cooling bath was then removed, and the mixed solution was stirred for 3 days at room temperature. After removing the solvent, we dissolved the residue in CH_2Cl_2, washed it with 10% HCl and water, and dried it over Na_2SO_4. The solvent was removed, and the residue was subjected to column chromatography (SiO_2, 5% $MeOH/CH_2Cl_2$) to give a pale yellow solid **5** (106 mg, 62%). ^{1}H NMR (CDCl$_3$): δ 0.79 (s, 27 H), 0.90 (s, 9 H), 1.28 (s, 18 H), 1.30 (s, 18 H), 1.40−1.82 (m, 56 H), 1.84−2.04 (m, 24 H), 2.87−2.90 (d, J = 15 Hz, 2 H), 3.07−3.85 (m, 72 H), 4.04−4.07 (d, J = 15 Hz, 2 H), 4.13−4.54 (m, 12 H), 6.43 (s, 2 H), 6.56 (s, 4 H), 6.63 (s, 2 H), 6.76 (s, 2 H), 6.98 (s, 2 H), 7.09 (s, 2 H), 7.14 (s, 2 H), 7.24 (s, 2 H), 7.40 (s, 4 H), 7.55 (s, 4 H), 7.63 (s, 4 H), 8.63 (s, 2 H). ^{13}C NMR (CDCl$_3$): δ 25.3, 25.4, 25.6, 28.8, 28.9, 29.1, 29.4, 29.7, 31.2, 31.4, 31.6, 34.2, 34.4, 34.6, 34.7, 35.9, 36.1, 36.2, 38.5, 40.3, 40.4, 56.5, 70.6, 70.8, 71.6, 72.0, 123.3, 123.6, 123.9, 128.1, 128.6, 128.8, 128.9, 130.5, 130.9, 131.6, 131.9, 132.3, 132.5, 132.6, 132.7, 146.9, 147.3, 147.5, 150.9, 151.2, 151.9, 125.3, 169.1, 169.3, 169.5, 174.0, 174.6. MS (MALDI): m/z = 3627.6 [M$^+$ + Na]. Anal. Calcd for $C_{184}H_{272}O_{24}S_{16}N_{16}$·$H_2O$: C, 61.00; H, 7.62. Found: C, 61.48; H, 7.25.