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Noncovalent Immobilization of C_{60} on Gold Surfaces by SAMs of Cyclotriveratrylene Derivatives

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Two cyclotriveratrylene (CTV) derivatives, one containing a thioctic ester (**1**) and the other with thioether groups (**2**), were synthesized. UV−vis titration of C_{60} with these two CTV derivatives confirmed the host−guest interaction between C_{60} and the CTV derivatives. Self-assembled monolayers (SAMs) of **1** and **2** were formed on gold surfaces and were characterized by CV blocking experiments, impedance spectroscopy, and electrochemical reductive desorption. Noncovalent immobilization of C_{60} on gold surfaces was obtained with SAMs of the two CTV derivatives. SAMs of **1** can bind C_{60} after they are formed or during formation. However, SAMs of **2** can only incorporate C_{60} if they are formed from a solution containing both **2** and C_{60}.

Introduction

Fullerene[60] possesses many attractive and potentially useful physical and chemical properties.[1] Langmuir−Blodgett (LB) films and especially self-assembled monolayers (SAMs) have demonstrated obvious advantages to form definable and highly ordered fullerene arrays on surfaces. Thin films of fullerene-based materials exhibit interesting characteristics such as photovoltaic responses, superconductivity, nonlinear optical properties, and biological activity. Many reports have been published describing how to covalently construct densely packed C_{60} monolayers.[2] Covalent attachment of C_{60} on surfaces, however, partially destroys the π-delocalization due to introduction of the adduct. In addition, C_{60} has a high aggregation tendency, which affects its molecular electronic properties.[3] In 1996, we successfully assembled a fullerene-crown ether derivative on gold surfaces through the host−guest interaction between surface-attached ammonium groups and the crown-ether moiety appended to C_{60}.[4] Noncovalent incorporation of C_{60} onto surfaces has been accomplished by Shinkai et al. The cationic complex between C_{60} and a homooxacalix[3]arene derivative was attached as the second layer onto negatively charged indium/tin oxide electrodes through electrostatic interactions.[5] A third layer containing porphyrins was also introduced, and such a system exhibits a very high quantum yield (21%) upon irradiation. As far as we know, these are the only reports involving the noncovalent incorporation of C_{60} into the surfaces.

Since the pioneering researches done by Atwood et al. and Shinkai et al. to purify C_{60} by the selective complexation with *p-tert*-butylcalix[8]arene,[6] interest in constructing supramolecular architectures involving fullerenes has increased. Many supramolecules between fullerenes and γ-cyclodextrin,[7] calix[*n*]arenes,[8] cyclotriveratrylene (CTV),[9] and crown-ethers[10] have been developed. Most supramolecular complexes of C_{60} in solution exist only in aqueous systems. In

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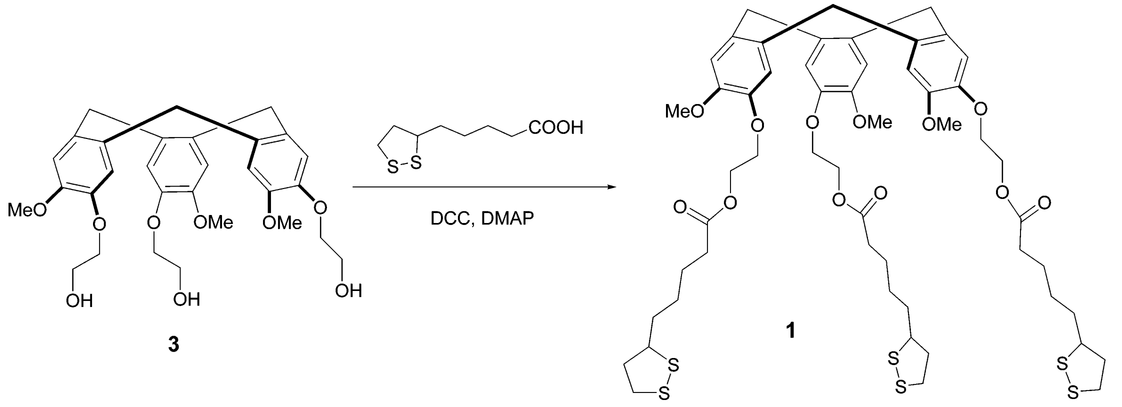
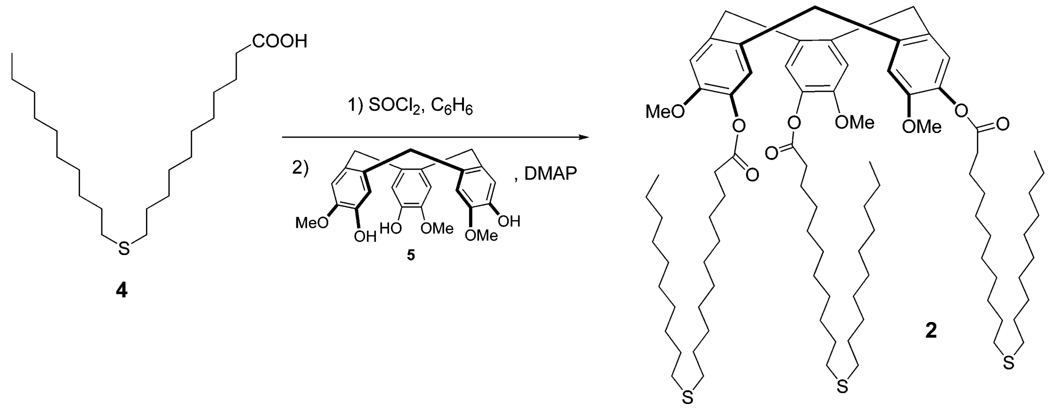
Scheme 1. Synthesis of CTV Thioctic Ester Derivative 1



Scheme 2. Synthesis of CTV Thioether Derivative 2



organic solvents, such complexes are prone to dissociation. Shinkai et al. have investigated many different calix[*n*]arenes to screen suitable receptors for C_{60} and discovered that most of them do not interact with C_{60} in solution.[11] On the other hand, Atwood et al. found that excess CTV and C_{60} in toluene result in micelle-like aggregates, and the CTV−C_{60} interaction does persist even in toluene solution.[9] Here, we explore the use of noncovalent interactions between CTV receptors and C_{60} to trap fullerenes on surfaces. In this way, underivatized C_{60} could adhere to surfaces and aggregation of C_{60} could be inhibited by the encapsulation within the CTV receptors.

Results and Discussion

Synthesis of Cyclotriveratrylene Derivatives 1 and 2. Two novel CTV derivatives containing thioctic ester (**1**) and thioether (**2**) residues were designed for the immobilization studies. Previous evaluations of molecular models suggested that the spacers introduced on the CTV matrix provide an appropriate distance to the electrode surface for C_{60} complexation.

Compound **1** was obtained in 73% yield by coupling the CTV tris-alcohol derivative **3**[12] with thioctic acid in the presence of DCC and DMAP (Scheme 1). On the other hand, treatment of 11-thiodecyl-undecanoic acid (**4**)[13] with $SOCl_2$ afforded the corresponding acyl chloride, which was reacted with triphenol **5**[14] in dry benzene in the presence of DMAP to give CTV thioether derivative **2** in 63% yield (Scheme 2).

UV Titration of C_{60} with CTV Derivatives. The complexation of **1** and **2** with C_{60} was first studied in solution by observing the changes of the absorption spectrum of C_{60} in toluene upon addition of increasing concentrations of the receptors (Figure 1). As can be seen, the spectral changes are more pronounced for receptor **1**, indicating a stronger interaction than with **2**. Data treatment for a 1:1 complex according to the method proposed by Rose and Drago[15] afforded a binding constant of 120 ± 30 M^{-1}. This value is in good agreement (10^2 M^{-1}) with the binding reported by Nierengarten et al. for dendrimers based on the CTV scaffold.[16]

In contrast, the spectra of C_{60} in the presence of **2** showed no appreciable changes in the absorbance even after the addition of 40 equiv, indicative of weak binding, so no binding constant could be determined. This could be due to the presence of the long alkyl chains directly attached to the

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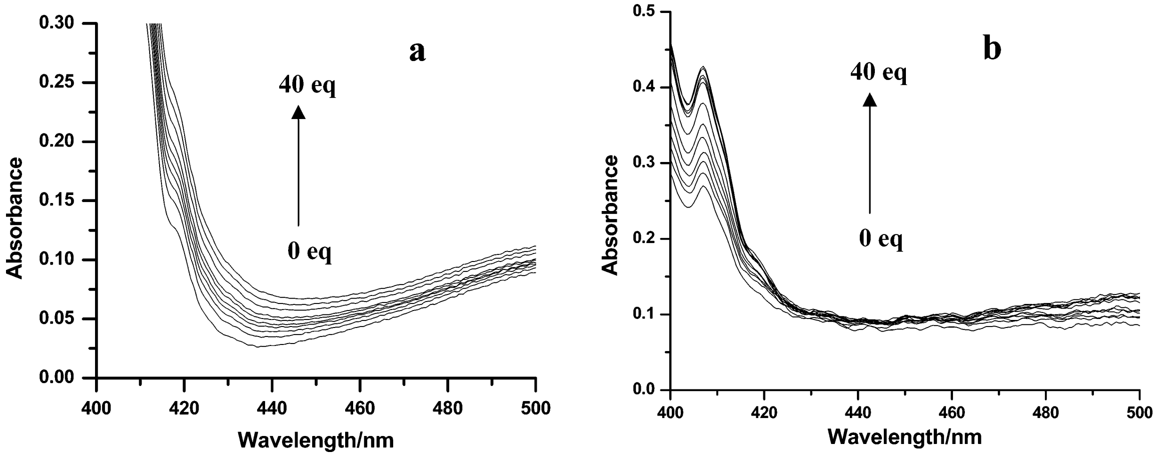

Figure 1. UV−visible spectra of titrations of C_{60} (0.101 mM) with compounds **1** (a) and **2** (b) in toluene.

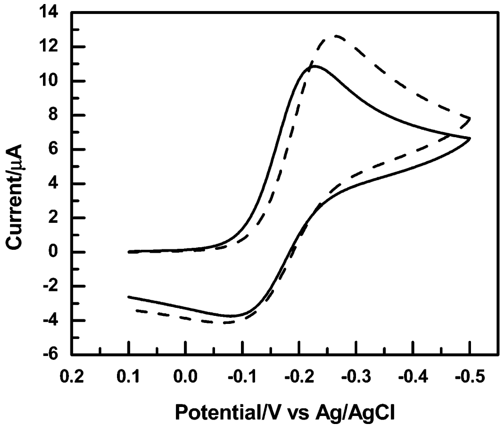

Figure 2. CV of 1 mM $Ru(NH_3)_6^{3+/2+}$ in 0.1 M aqueous NEt_4NCl at SAM modified electrodes with **1** (−) and **2** (- - - -). Scan rate: 0.1 V/s.

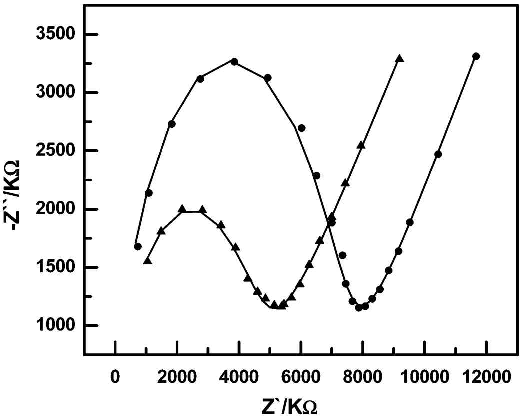

Figure 3. Impedance responses of 1 mM $Ru(NH_3)_6^{3+/2+}$ at the monolayer modified gold electrodes with **1** (●) and **2** (▲). The solid lines represent the fits of the experimental points.

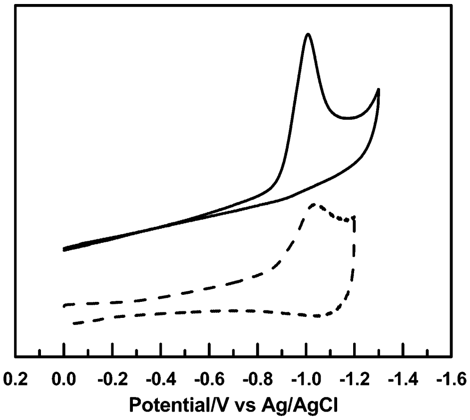

Figure 4. Electrochemical desorption of SAMs of **1** (−) and **2** (- - - -) on Au in 0.5 M KOH.

CTV phenol groups, pointing outside the cavity, that are not expected to interact with the guest and thus reduce its binding ability.

Preparation and Characterization of SAMs of 1 and 2. SAMs were formed by immersion of bare gold electrodes in freshly prepared solutions of the receptors. They were initially characterized by observing their blocking effect on the cyclic voltammetric (CV) response of the $Ru(NH_3)_6^{3+/2+}$ redox couple (Figure 2). As compared to the reversible redox behavior on a bare gold electrode, a pronounced attenuation of the anodic current reveals that the monolayers block the redox process reasonably well. SAMs of **1** exhibit a better blocking effect than those of **2**. Obviously, the blocking effect of both SAMs is not perfect, because large cathodic currents were still observed. This can be attributed to a loosely packed SAM, to good electron permeability through the monolayers, or to a combination of both.

Further characterization of the SAMs was performed by electrochemical impedance spectroscopy (Figure 3). Fitting of the experimental data using the commercially available program EQUIVALENT CIRCUIT,[17] charge-transfer resistance (R_{ct}) values of 8.1 and 5.2 kΩ were obtained for SAMs of **1** and **2**, respectively. The charge-transfer resistance is caused by the blocking of electron transfer by the monolayers formed on the electrodes. In contrast, the Nyqyist plot obtained on bare gold electrodes is simple straight lines (the Warburg impedance), because the redox reactions are very fast on bare gold surfaces. These observations are consistent with the CV blocking experiments.

To characterize the SAMs quantitatively, reductive desorption experiments were conducted by dipping the SAM modified gold beads into thoroughly deoxygenated 0.5 M KOH. 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. The cyclic voltammograms in Figure 4 were recorded on gold electrodes covered with SAMs of **1** or **2**

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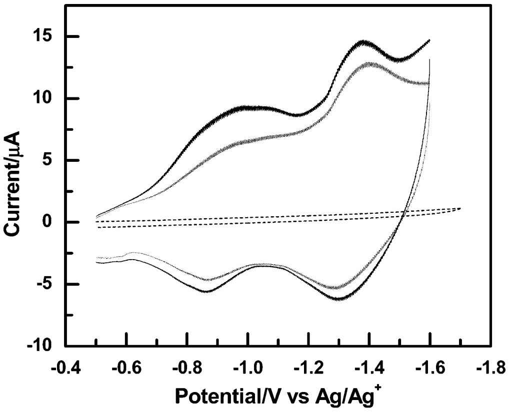

Figure 5. CV recorded in CH_3CN of SAMs of **1** before (- - - -) and after dipping into a solution of C_{60} (—, second scan; · · · ·, sixth scan). Supporting electrolyte: 0.1 M Bu_4NPF_6. Scan rate: 0.1 V/s.

and show desorption waves at −1.0 V vs Ag/AgCl, which is due to the reductive desorption of the surface attached thiolates. The shape and position of the desorption peaks are similar to those reported before for SAMs of thioctic acid.[18] By integrating the current under the cathodic wave, estimated surface coverages of 4.47×10^{-10} and 3.26×10^{-10} mol/cm^2 were obtained for SAMs of **1** and **2**, respectively. The data obtained by CV, impedance, and desorption indicate that SAMs of **1** are more compact than those of **2**. This result is expected considering that the dithiolane moiety of thioctic acid interacts stronger with the surface than thioether groups.

C_{60} Trapping by CTV Derivative 1. The voltammetric response of SAMs of **1** was recorded before and after interaction with C_{60} (Figure 5). The dashed line is the CV in the absence of C_{60}, which, as expected, showed no response. When the modified gold beads were immersed into 1,2-dichlorobenzene solutions of C_{60} for 10 h, a clear redox response of the fullerene was observed. Two well-resolved reversible redox waves at $E_{1/2} = -0.93$ and −1.34 V versus Ag/Ag$^+$ were observed, which correspond to the first and second reduction processes of C_{60}, respectively, confirming the incorporation of C_{60} on gold surfaces. The peaks are relatively broad, suggesting the presence of different interaction modes of C_{60}. This interaction can take place either through encapsulation of C_{60} in the cavity of **1** or by introduction into the space between the attached CTV molecules. After conversion of the potentials vs Ag/Ag$^+$ to those vs Fc/Fc$^+$,[19] the values are −0.97 and −1.38 V for the first and second reduction of C_{60}, respectively, which are essentially the same as those of free C_{60} in solution. There have been numerous reports of reduction potentials for immobilized C_{60} on surfaces, both covalently and supramolecularly.[2,5a,20−22] The values are inconsistent, some reporting significant cathodic shifts and others reporting the opposite, relative to the values in solution. A cathodic potential shift of about 200 mV was observed when C_{60} was immobilized on cysteamine modified gold surfaces.[2a] On the other hand, when C_{60} was incorporated on electrode surfaces via electropolymerization of pyrrole, the reduction waves for C_{60} shift anodically by more than 200 mV.[22] Other covalently immobilized C_{60}'s displayed relatively smaller potential shifts (10−50 mV) as compared to their values in solution.[2c,f,21] Our observation of no apparent redox potential difference from surface-confined C_{60} to its solution values is surprising, and perhaps it is the net result due to immobilization and donor−acceptor interactions. Further experiments are needed to clarify these observations.

After immersing the modified gold beads into 1,2-dichlorobenzene solutions of C_{60} for 10 h, the charging current is several times larger than that obtained for the monolayer of **1**, as shown in Figure 5. To prove that this effect is not due to a possible desorption caused by the incubation of SAMs into 1,2-dichlorobenzene, a control experiment was performed by dipping a monolayer of **1** in 1,2-dichlorobenzene and measuring the background electrochemical response of the corresponding SAMs. Essentially no change was observed for the CV responses of SAMs of **1** before and after the incubation in 1,2-dichlorobenzene, indicating that no desorption occurred during the incubation period.

Most remarkably, the color of the gold bead electrodes changed significantly, after several scans, from an original copper color to dark red. This observation might be due to the rearrangement of the monolayer structure and to charge-transfer processes associated with complexation. A similar observation was reported earlier during electrochemical scans of films of C_{60}−*p*-*tert*-butylcalix[8]arene complex on glassy carbon electrodes. In that case, the color change of the C_{60}−*p*-*tert*-butylcalix[8]arene film was from brownish to dark red.[23]

Based on the apparent structural rearrangements observed electrochemically for SAMs of **1** in the presence of C_{60}, we decided to grow SAMs from mixed solutions containing both **1** and C_{60}. The gold beads were immersed into 1,2-dichlorobenzene solutions containing 1 mM of **1** and 6 mM of C_{60} for 2 days. Interestingly, no differences in electrochemical behavior were observed as compared to those of SAMs of **1** to which C_{60} was added later. The CV shows two pairs of reversible broad peaks corresponding to the first and second redox processes of C_{60}. Also, the SAM modified gold beads turned to dark red after several scans.

C_{60} Trapping by CTV Derivative 2. A CTV derivative having long alkyl chains with thioether groups (**2**) was also evaluated for C_{60} immobilization. Initially, we tried to bind C_{60} after forming the SAMs of **2**. However, the SAMs of **2**, unlike those of **1**, cannot incorporate C_{60}, as judged by the lack of an electrochemical response for the fullerene. Instead, the CV exhibits a typical electrochemical response of physically adsorbed C_{60}.[24] The long alkyl side chains are probably blocking the insertion of C_{60} in the CTV cavity.

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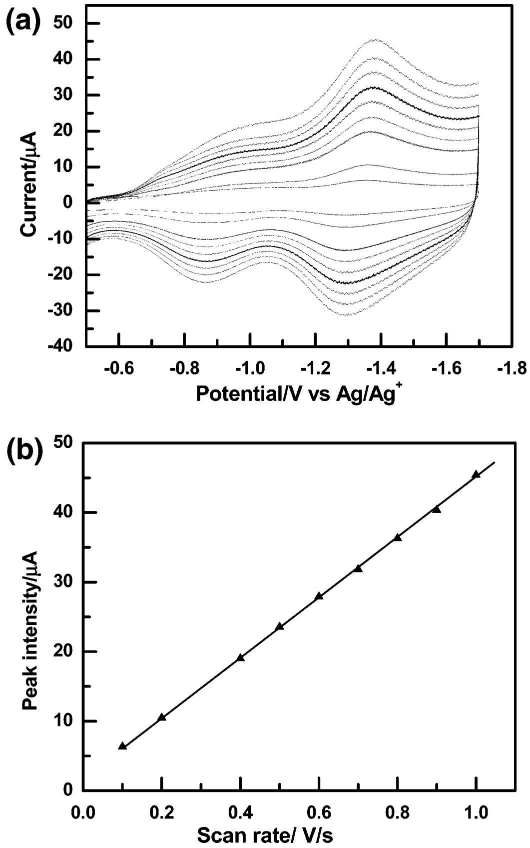

Figure 6. (a) CV recorded in CH_3CN of SAMs grown from a mixture of C_{60} and **2** at variable scan rates (0.1, 0.2, 0.4−1.0 V/s). Supporting electrolyte: 0.1 M Bu_4NPF_6. (b) Plot of peak intensity versus scan rates for SAMs grown from a mixture of C_{60} and **2**.

Because the SAMs were unable to bind C_{60}, experiments were conducted to incorporate C_{60} during SAM formation. The SAMs were grown from 1,2-dichlorobenzene solutions containing 1 mM of **2** and 6 mM of C_{60}. Immersion of the gold beads into a freshly prepared solution allowed SAMs of **2** to be formed, as indicated by the blocking effect of the of the $Ru(NH_3)_6^{3+/2+}$ redox couple, although no faradaic response for C_{60} was observed. This indicates that the monolayers cannot incorporate the fullerene, a result that is consistent with the UV titration experiments. The binding appears to be thermodynamically and/or kinetically unfavorable. Interestingly, if the mixture of **2** and C_{60} is kept for 2 weeks and SAMs are then grown from the resulting solution, they do show evidence of C_{60} incorporation (Figure 6a), indicating that complexation between C_{60} and **2** is a very slow process. The cyclic voltammetric response recorded in CH_3CN exhibits two broad waves at $E_{1/2} = -0.92$ and -1.32 V vs Ag/Ag^+, which correspond to the first two reduction processes of C_{60}. As can be seen, the shape and potential positions are very similar to those obtained by trapping C_{60} by SAMs of **1**. The peak intensities increased linearly with the scan rate in the range of 0.1−1.0 V/s (Figure 6b), indicative of surface-confined behavior. The second reduction wave looks sharper and larger as compared to the first one, as in the case of **1**.

Conclusions

Two new CTV derivatives with gold surface anchoring groups were prepared. Their supramolecular interactions with C_{60} were investigated via UV−vis titration experiments. Taking advantage of the host−guest interaction between C_{60} and the CTV derivatives, this work shows the noncovalent immobilization of C_{60} on gold surfaces by observing its electrochemical responses. Further investigation will include the study of the photoelectrochemical properties of these fullerene-trapped monolayers.

Experimental Section

Monolayer Preparation. Gold bead electrodes were prepared by heating a gold wire in a natural gas/O_2 flame followed by cooling in deionized water. A glass capillary was inserted from the opposite side of the gold beads and melted onto the wire, insulating the gold electrodes. The gold beads were electrochemically cleaned as reported previously.[25] Monolayers on gold were prepared by chemisorption, that is, by immersion of freshly prepared gold beads in 1 mM solutions of compounds **1** (in CH_2Cl_2) or **2** (in toluene), or mixtures of the CTV derivative (1 mM) and C_{60} (6 mM) in 1,2-dichlorobenzene, for 48 h. After removal, the gold beads were thoroughly washed with the appropriate solvent and dried in a stream of argon.

Electrochemical Measurements. Cyclic voltammetry (CV) and impedance measurements were conducted with a CHI-660 electrochemical workstation by using a three-electrode cell. A gold bead was used as the working electrode, in combination with Ag/AgCl or Ag/Ag^+ as references. A Pt wire served as the counter electrode. 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 to 0.1 Hz with an ac-amplitude of 5 mV. The electrochemical desorption experiments were performed in a 0.5 M KOH solution thoroughly purged by argon.

UV−Vis Titrations. CTV hosts **1** and **2** were added to a toluene solution of C_{60} (0.101 mM). Additions were made between 0 and 40 equiv. The absorbance was recorded at 430 nm. The concentration of C_{60} was kept constant throughout the experiment so that the change in absorbance is due to both free CTV host and the complex. The data obtained were then treated according to the method described by Rose and Drago, which is based on the original Hildebrand−Benesi equation.[26] The only assumption for the method employed here is that the species present obey Beer's law in the concentration range employed.

(±)-2,7,12-Tris{2-[(±)-1,2-dithiolane-3-pentanoyl]ethoxy}-3,-8,13-trimethoxy-10,15-dihydro-*H*-tribenzo[*a*,*d*,*g*]cyclononene (1). CTV alcohol **3**[12] (0.1 g, 0.185 mmol) and thioctic acid (0.23 g, 1.11 mmol) were dissolved in anhydrous DMF (5 mL) and stirred at 0 °C for 30 min under Ar. DCC (0.23 g, 1.11 mmol) and DMAP (20 mg, 0.17 mmol) were then added, and the mixture was stirred at 0 °C for another 30 min. The cooling bath was then removed, and the reaction mixture was stirred at room temperature for 48 h. The insoluble urea byproduct was removed by filtration through a fine glass frit. The solvent was removed, and the residue was dissolved in CH_2Cl_2, washed with water, and dried over $MgSO_4$. Column chromatography (SiO_2, 6−10% ether/CH_2Cl_2) of the crude residue afforded a pale yellow glassy solid **1** (0.15 g, 73%). ^{1}H

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NMR (300 MHz, $CDCl_3$): δ 6.91 (s, 3H), 6.86 (s, 3H), 4.77−4.73 (d, 3H, $J = 13.6$ Hz), 4.42−4.36 (m, 6H), 4.20−4.15 (m, 6H), 3.83 (s, 9H), 3.78−3.73 (m, 3H), 3.56−3.52 (d, 3H, $J = 13.6$ Hz), 3.13−3.00 (m, 6H), 2.42−2.32 (m, 9H), 1.88−1.21 (m, 21H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.3, 148.5, 146.5, 133.1, 131.7, 116.5, 114.0, 67.5, 62.5, 56.2, 40.0, 38.3, 36.3, 34.4, 33.8, 28.6, 24.5. MALDI-TOF MS: *m*/*z* 1128 $[(M + Na)^+]$. IR (KBr): ν 3354, 2928, 2852, 1737, 1509, 1442, 1261, 1144, 1089, 1050, 845. Anal. Calcd for $C_{54}H_{72}O_{12}S_6$: C, 58.68; H, 6.57. Found: C, 58.75; H, 6.62.

(±)-2,7,12-Tris[11-(decylthio)undecanoyl]-3,8,13-trimethoxy-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (2). A solution of **4**[13] (1.56 g, 4.2 mmol) in dry benzene (40 mL) was treated with $SOCl_2$ (1 mL) under argon for 2 h at room temperature, and then concentrated to dryness at a temperature not exceeding 45 °C. The resulting oil was redissolved in dry benzene (10 mL) and added dropwise under argon to a vigorously stirred mixture of compound **5**[14] (0.30 g, 0.74 mmol) and DMAP (0.68 g, 2.8 mmol) in dry benzene (50 mL). Stirring was continued overnight at room temperature, and then the reaction mixture was diluted with $CHCl_3$ (100 mL), washed with 0.1 M HCl and brine, dried with Na_2SO_4, and concentrated to dryness. The residue is a mixture of the desired product with **4** as revealed by TLC. Column chromatography (SiO_2, CH_2Cl_2/cyclohexane 95:5) of the crude residue afforded **2** (eluted first) as a colorless oil (0.66 g, 63%), which was dried overnight under high vacuum at 50 °C to give a paraffin-like solid. Mp: 49−50 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.03 (s, 3H), 6.89 (s, 3H), 4.75−4.72 (d, 3H, $J = 13$ Hz), 3.81 (s, 9H), 3.61−3.58 (d, 3H, $J = 13$ Hz), 2.59−2.55 (m, 6H), 2.53 (t, 12H, $J = 7.4$ Hz), 1.77 (qt, 6H, $J = 7.3$ Hz), 1.62 (qt, 12H, $J = 7.3$ Hz), 1.50−1.25 (m, 78H), 0.91 (t, 9H, $J = 7.1$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.8, 149.7, 138.5, 137.7, 131.4, 123.9, 114.1, 56.1, 36.4, 34.0, 32.2, 31.9, 29.8, 29.60, 29.57, 29.52, 29.48, 29.4, 29.3, 29.1, 29.0, 27.0, 25.0, 22.7, 14.2. MALDI-TOF MS: *m*/*z* 1429.9 $[(M + H)^+]$. Anal. Calcd for $C_{87}H_{144}O_9S_3$: C, 73.06; H, 10.15. Found: C, 73.30; H, 10.00.

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