The electrochemical reduction of tert-butylcalix[8]arene—C$_{60}$ particle films was studied using the scanning electrochemical microscope combined with a quartz crystal microbalance (QCM) for several electrolytes in MeCN. Complexation of the fullerene within the film results in a negative shift of the peak potential of the first cathodic wave by about 400 mV compared to the reduction of a pure C$_{60}$ film. The QCM indicates a mass loss during reduction of the film. Even in electrolytes where C$_{60}$ anions normally remain in the surface film, a loss of fullerene electrochemical activity occurs. The complex breaks apart upon reduction of the fullerene center, with the fullerene escaping from the calixarene basket into the MeCN solution, leaving the calixarene as an insoluble film on the electrode surface. These results show that the electron sharing of the complex is decreased by the additional electron density added to the fullerene by reduction to C$_{60}^-$. Buckminsterfullerene, C$_{60}$, dissolved, e.g., in benzene, shows up to six nernstian, chemically reversible reduction waves, but the electrochemistry of C$_{60}$ films in MeCN is more complex. The reduction of C$_{60}$ films is complicated by C$_{60}$ anion dissolution from the film, cation and anion incorporation into the film with film reorganization, and solvent transfer resulting in decreased electrochemical response upon cycling and large potential splittings between the reduction and reoxidation of the films. Entrapment and diluting C$_{60}$ within a polymeric matrix of poly(pyrrole-dodecyl)(tri-n-butyl)ammonium fluoroborate, thermodynamically reversible, surface-confined reductions and reoxidations were found in MeCN. Thus, the key to reversible electrochemistry of surface-immobilized C$_{60}$ is to isolate the C$_{60}$ molecules and provide space within the solid for charge balance.

C$_{60}$ forms a 1:1 complex with p-tert-butylcalix[8]arene (Figure 1). Throughout this paper, we represent this complex as C$_{60}$L. This complexation has been used as a purification route from carbon soot. C$_{60}$L forms as an insoluble precipitate when benzene or toluene solutions of C$_{60}$ and the calixarene are mixed and allows separation in dichloromethane, 1,2-dichloroethane, or chloroform, with the black C$_{60}$ precipitating and the calixarene remaining in solution. A special interest in C$_{60}$L arises from its insolubility in any solvent, because a large number of other calixarene—C$_{60}$ complexes are soluble in benzene or toluene. Characterization of C$_{60}$L has been carried out by $^{13}$C NMR, vibrational, and UV—visible spectroscopies, and in Langmuir—Blodgett films. C$_{60}$L is believed to contain the C$_{60}$ above the

![Figure 1. Representation of the p-tert-butylcalix[8]arene—C$_{60}$ complex, showing interaction of the components (not intended to imply detailed structural information).](image-url)
slightly enlarged center basket of the calixarene. Previous research suggests a small change in the calixarene configuration on C₆₀ association, the partial breaking up of the intramolecular hydrogen bonding of the native calixarene, the isolation of C₆₀ molecules from each other, and a weak π electron interaction between the C₆₀ and calixarene basket. The insolubility of C₆₀L arises from intermolecular hydrogen bonding of the displaced OH groups but has also been attributed to an encapsulation of C₆₀ to form a trimer aggregate by three calixarenes. An electrochemical study looked at the reductions of C₆₀ in MeCN—toluene (1:4) solution upon addition of three different sized calixarenes to form complexes. The results showed that additional reduction waves, attributed to the reduction of the complexes, appeared about 200 mV more negative than the second, third, and fourth reductions of the original fullerene, but none appeared after the first reduction. The incomplete complexation or precipitation with the p-tert-butylcalix[8]arene over a period of a few minutes was also reported; this is consistent with a complex, slow rate of intermolecular bonding being responsible for the insolubility of the complex.

Our interest in films of C₆₀L was to investigate whether the C₆₀ trapped and isolated within a solid formed with calixarene would have sufficient space for cations to provide charge balance during reduction without major structural changes in the film. An analogous approach had demonstrated the ability to reduce C₆₀ reversibly in water by inclusion within a cyclodextrin. Our studies of the electrochemical behavior of C₆₀L films were performed in MeCN, consistent with most previous electrochemical studies of C₆₀ films, because the C₆₀L, C₆₀, and calixarene are all insoluble in this solvent. The role of the cation of the electrolyte, important in the behavior of C₆₀ films, was also considered for the films of C₆₀L.

To investigate the effects of ion and solvent transfer as well as dissolution processes that might occur during reduction of C₆₀L, generation/collection experiments using a scanning electrochemical microscope (SECM) coupled to a quartz crystal microbalance (QCM) were conducted. While the use of each technique alone has been established for studying the reduction mechanism of C₆₀ films, the use of both techniques simultaneously provides a powerful tool for determining the effects of reduction upon the particulate films of C₆₀L. The generation/collection mode of the SECM uses a microelectrode to monitor the solution conditions near the substrate and thus gives information about the flux of electrochemically active species in and out of the particle film. The QCM measures small changes in the mass of the substrate resulting from ion incorporation or dissolution processes within the film. Together, these two techniques provide useful insight into the dynamic processes occurring during the reduction of a surface-immobilized layer.

**RESULTS**

**Reduction of Calix[8]arene–C₆₀ Films with Potassium Cation Electrolyte.** In previous studies of fullerene films, the cation present in the electrolyte was shown to play a large role in determining the processes that occur upon film reduction. For example, C₆₀ film reduction in K⁺ electrolyte in MeCN leads to dissolution of C₆₀ anions into solution. We were interested in seeing whether immobilizing the C₆₀ within the calixarene would keep the C₆₀ anions trapped in the film, since K⁺ might fit within the space of the C₆₀L without the need for significant structural changes in the film. Figure 2 depicts the results of an SECM—QCM experiment on the reduction of a particle film of C₆₀L. The substrate CV (Figure 2A) shows a single, broad reduction wave (I) at −1.65 V vs Fc. Upon scan reversal, two much smaller oxidation waves (II, III) are seen. We attribute the broad reduction wave I to an unresolved combination of the first and second reductions of the C₆₀ within the film on the basis of the two reverse processes and comparison with C₆₀ films. The two reverse oxidations correspond to the oxidation of the dianion to monoanion (II), followed by the oxidation of the monoanion to neutral C₆₀ (III). If we compare the reduction of the complex in

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Figure 2 to the reduction of fullerene in Figure 3 under similar conditions, we see a negative shift in $E_{pc}$ for C$_{60}$L by about 0.4 V and a large positive shift in wave III. The change in wave III probably results from the formation of a layer of insulating calixarene on the surface because, as shown in the QCM results discussed below, wave II is caused by a solution process (C$_{60}^2$ $\rightarrow$ C$_{60}^-$), and wave III involves deposition of C$_{60}^-$. Evidence for the production of soluble electroactive species was obtained by SECM. In this experiment, a 50-$\mu$m-diameter Pt collection tip was held at a potential ($E_T$) of $-0.5$ V vs Fc at a distance of 160 $\mu$m from the substrate. The tip current ($i_T$) is recorded as a function of substrate potential ($E_S$) during a CV experiment. An anodic $i_T$ is observed when $E_S$ attains values in the region of wave I. The onset of $i_T$ is delayed by the time required for product to diffuse from the film to the tip (Figure 2B). This oxidation tip current could result from dissolution of the anionic form of the complex or from free C$_{60}$ anions liberated from C$_{60}$L. Additional information about the loss of mass from the substrate can distinguish between the two cases. Figure 2C shows a scan of the QCM frequency during the CV. The QCM frequency indicates a large mass loss during the scan through the broad reduction wave I. The loss occurs during the first part of the wave, indicating that the first reduction event results in dissolution. This is directly comparable with the QCM results in Figure 3C for C$_{60}$ films, which also show a large mass loss during the first reduction wave. Kadish and co-workers$^{17}$ explored the nature of this first reduction process and its effect on the QCM frequency and suggested that a square scheme rearrangement of C$_{60}$ and K$^+$C$_{60}$ occurred within the film; our C$_{60}$ QCM results are in accord with their findings. The C$_{60}$L films have the same QCM behavior as C$_{60}$ films, implying that the complicated reduction mechanism is also present.

Additional scans of the substrate potential show a much smaller reduction current at potentials of wave I; this current is about the magnitude of wave III in the original scan and is attributed to reoxidation of C$_{60}$ deposited on the substrate. After scanning the substrate a few times, the tip electrode held at $-0.5$ V should collect C$_{60}$ on its surface. The CV of the tip following substrate reduction is shown in Figure 4. In this voltammogram, the large reduction wave is attributed to a C$_{60}$ film. Given a moderately slow scan rate and fast diffusional transport of C$_{60}^-$ away from the microelectrode in this electrolyte, the reduced C$_{60}$ anions are not reoxidized at the tip. The $E_{pc}$ for the C$_{60}$ film in Figure 4 is $-1.21$ V vs Fc, which is 440 mV less negative than the $E_{pc}$ for the C$_{60}$L in Figure 2A and is at the same potential as a film of C$_{60}$ cast from a benzene solution (Figure 3A). This difference of $-440$ mV in $E_{pc}$ for the complex is similar to the shift in the second, third, and fourth reduction peak potentials for the series of calixarene–C$_{60}$ complexes previously studied in solution.$^{11}$ After 1–2 tip reduction scans, the C$_{60}$ film was completely removed from the tip surface. Thus, the process in K$^+$ electrolyte can be represented as...
The SECM approach curve with a bare tip was used to determine the tip-to-substrate separation, \( d \). This is accomplished using the \( \text{Fc/Fc}^+ \) couple as a redox mediator and an uncoated tip. The approach curve was used to establish that \( d = 160 \, \mu \text{m} \) when the tip was monitoring the solution conditions near the substrate in the C60 experiments. The nature of the approach curve depended upon the location on the electrode surface. The approach curve was characterized by positive feedback from the conductive Au substrate, but, at locations where the electrode was covered with an insulating calixarene film, the approach curve showed negative feedback effects. Typical approach curves at two different locations, shown in Figure 5, indicate that the substrate is a mixture of conducting and insulating zones, as expected for a conductive substrate (Au QCM electrode) with insulating particles (calixarene). This negative feedback behavior indicates the presence of a nonconductive film remaining on the substrate, probably the p-tert-butylcalix[8]arene left behind when the C60 anions dissolved out of the film. From these results, we conclude that the reduction of the C60 film results in the dissolution of fullerene anions, leaving the calixarene behind on the surface; the anions are oxidized at the tip and form a pure C60 film, as illustrated schematically in Figure 6. We were not able to characterize the calixarene structure after the experiment except to note under an optical microscope that small particles similar to the initial complex were present, but their color was not the original pale green color of the complex.

**Reduction of p-tert-Butylcalix[8]arene–C60 Films in TBA⁺ Electrolyte.** The behavior of C60 films in MeCN is different with TBA⁺ because TBA⁺C60⁻ is fairly insoluble (as compared to the more soluble K⁺C60⁻). Thus, the first reduction of C60 films in TBA⁺ electrolyte results in only a small amount of dissolution of C60⁻ and a significant cation incorporation within the film. Note that the nernstian waves of polymer-entrapped C60 used a TBA⁺ electrolyte. Moreover, other calixarene–C60 complex studies suggest a slight interaction between tert-butyl groups of the calixarene and the C60 rings.

The CV of C60L in a TBA⁺ electrolyte, Figure 7A, showed a broad, unresolved double peak characteristic of the first two reductions of the fullerene. The reverse oxidations were much better defined in TBA⁺ electrolyte compared to K⁺. The QCM data in Figure 7B show a large mass loss from the film during the first part of the reduction wave, followed by a complicated series of gain–loss–gain, which characterizes the competition between dissolution and TBA⁺ incorporation, with the added possibility of some calixarene reorganization as the bound L is released. Comparison of the charge passed to mass lost and SECM tip collection again indicates that only C60 is lost and the calixarene remains behind, as with the K⁺ electrolyte. For example, the amount of charge passed in the reduction wave to a potential of –1.3 V (Figure 7) is 1.3 mC, which would be equivalent to a mass change of 8.6 \( \mu \text{g} \), assuming only C60 dissolves. The QCM frequency change of 1100 Hz is equivalent to 8.3 \( \mu \text{g} \).

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**Figure 5.** Two SECM approach curves for a 50-\( \mu \text{m} \)-diameter Pt microelectrode tip using Fc/Fc⁺ as a redox mediator as it moved toward the calixarene particles remaining on the gold substrate. The top smooth line is the theoretical line for a purely conductive substrate, and the bottom smooth line is the theoretical line for a purely insulating substrate.

**Figure 6.** Diagram of calix[8]arene–C60 reduction processes in the SECM–QCM experiment.

\[
\text{(substrate)} \quad \text{C}_6\text{O}_L + e^- \rightarrow \text{L} + \text{C}_6\text{O}^- \quad (1)
\]

\[
\text{(tip)} \quad \text{C}_6\text{O}^- \rightarrow \text{C}_6\text{O} + e^- \quad (2)
\]

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In general, coulometrically calculated weight changes were within ±20% of those obtained by QCM. The reverse oxidation shows a mass loss from the film, indicating the loss of TBA+ incorporated into the film during the reduction. This mass loss is followed by a slower increase in mass as C602- and C60 form on the substrate. During the reduction of a C60L film, an SECM tip (25 μm, diameter) held 25 μm from the surface showed an anodic current for C60− oxidation about 25% of that seen with a K+ electrolyte. The second scan of the film looked more like a C60 film and showed a smaller, broad reduction wave with more distinct peak shapes superimposed (Figure B). The reduction started at a potential about 400 mV more positive than the first scan of the C60L, as expected for a C60 film. Again, the QCM shows that the dominant process during reduction is dissolution of C60 from the film. Thus, the dissolution of the C60 anions was greater from films of C60L than from pure C60 films in TBA+ electrolyte. We saw no evidence that TBA+C60−, on oxidation, caused any reincorporation of C60 into the calixarene cavity; indeed, the growth of a pure C60 peak indicates that this does not happen. Thus, the process in TBA+ electrolyte can be represented as

\[(\text{substrate}) \xrightarrow{\text{C}_{60} \text{L} + e^- \rightarrow C_{60}^+ + L} \text{TBA}^+ C_{60}^- \quad (3)\]

\[(\text{substrate reversal}) \xrightarrow{TBA^- C_{60}^- \rightarrow TBA^- + C_{60}} \quad (4)\]

The scan rate, ν, dependence of the voltammograms for the first scan of similarly cast films of the C60L showed a negative shift in Epc. The reverse oxidation wave from C602− to C60− had a shape and ν dependence between that expected for a solution process and that of a surface process, while the C60− to C60 wave was Gaussian in shape and had a peak current proportional to ν, indicating a surface-confined process.

Reduction of C60L with M(bpy)32− Electrolyte. Previous studies on the reduction of C60 films in MeCN showed that metal bipyridyl complex cations as electrolytes produced insoluble C60− films and stable electrochemistry, although there were large potential splittings between the reduction and reverse oxidation peaks corresponding to structural changes in the film to accommodate the bulky cation. In Figure 9, the CV of C60L in Zn(bpy)32− (PF6)2 electrolyte showed only a very small reverse oxidation. The QCM evidence indicated a large loss of mass from the surface during reduction (Figure 9B) as the C60− left the calixarene and dissolved into the MeCN. Results were similar for a Cd(bpy)32− (PF6)2 electrolyte. This result with C60L is completely different than that of pure C60 films in the same solvent, where a mass gain is observed upon reduction from cation incorporation. These results, along with those in TBA+ electrolyte, suggest that the production of C60− from C60L results in a smaller amount of precipitation of the C60− salt than when C60− is produced from a C60 film. Perhaps the TBA+C60− or M(bpy)32−C60− adheres less well to the remaining calixarene layer than to a metal substrate. The calixarene may also interact with either of these cations after the C60 leaves.

Results in Alcohol Solvents. We also attempted to find a solvent capable of dissolving the C60L without dissociating it. The solid C60L dissolved in butanol, hexanol, and dodecanol but dissociated with C60 remaining in solution and the calixarene largely precipitating as a white solid. This is different than other solvents, like toluene-MeCN, where, on dissociation, the C60 largely precipitated and the calixarene remained in solution.5,6 Figure 10 compares the UV−visible spectra of the C60L, C60, and pure calixarene left overnight in dodecanol with an excess of each solid. The color of the solution of the C60L changed from its original green to purple, reminiscent of C60 in solution. The UV−visible spectrum shows both C60 and the calixarene peaks. The C60 peaks from the C60L were larger than those from the pure C60, suggesting that the pure C60 dissolved more slowly than the C60L. After a few days, the C60 spectrum did grow to a similar concentration as from the C60L. The UV−visible spectra show that all three dissolve in alcohols to differing concentrations but show no evidence of complexation, i.e., a shift in the peak wavelength. In Figure 11, the cyclic voltammogram of the
complex in hexanol with 0.1 M (TBA)BF₄ electrolyte shows two reduction processes. The first process is a reversible solution couple, probably C₆₀ to C₆₀⁻. The second is an electrodeposition and stripping process and is likely C₆₀⁻ reduction to (TBA⁺)₂C₆₀²⁻. Even though both C₆₀ and calixarene are present in this solution, no electrochemical evidence was found for a C₆₀⁻–calixarene interaction in this solvent.

CONCLUSIONS

The electrochemical reduction of a tert-butylcalix[8]arene–C₆₀ film results in the liberation of the fullerene anion out of the calixarene ring and into the surrounding MeCN solution for K⁺, TBA⁺, and M(bpy)₃²⁺ electrolytes. The calixarene remains as a particle film on the Au substrate. This indicates that the calixarene–C₆₀⁻ interaction is weak and that the π electron sharing of the host–guest complex is weakened by the addition of an electron into the electron-poor fullerene structure. Reoxidation of the fullerene does not result in the fullerene returning into the calixarene, but with TBA⁺ and M(bpy)₃²⁺ it forms C₆₀⁻ films. Complexation of the fullerene in the film results in a negative potential shift of the cathodic peak compared to a pure fullerene film.

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