

# Electrochemistry of *tert*-Butylcalix[8]arene–C<sub>60</sub> Films Using a Scanning Electrochemical Microscope–Quartz Crystal Microbalance

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The electrochemical reduction of *tert*-butylcalix[8]arene–C<sub>60</sub> 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<sub>60</sub> film. The QCM indicates a mass loss during reduction of the film. Even in electrolytes where C<sub>60</sub> 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  $\pi$  electron sharing of the complex is decreased by the additional electron density added to the fullerene by reduction to C<sub>60</sub><sup>−</sup>.

Buckminsterfullerene, C<sub>60</sub>, dissolved, e.g., in benzene, shows up to six nernstian, chemically reversible reduction waves,<sup>1</sup> but the electrochemistry of C<sub>60</sub> films in MeCN is more complex.<sup>2</sup> The reduction of C<sub>60</sub> films is complicated by C<sub>60</sub> 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.<sup>2</sup> By entrapping and diluting C<sub>60</sub> within a polymeric matrix of poly(pyrroledodecyl) (tri-*n*-butyl) ammonium fluoroborate, thermodynamically reversible, surface-confined reductions and reoxidations were found in MeCN.<sup>3</sup> Thus, the key to reversible electrochemistry of surface-immobilized C<sub>60</sub> is to isolate the C<sub>60</sub> molecules and provide space within the solid for charge balance.

C<sub>60</sub> forms a 1:1 complex with *p*-*tert*-butylcalix[8]arene (Figure 1). Throughout this paper, we represent this complex as C<sub>60</sub>L. This complexation has been used as a purification route from

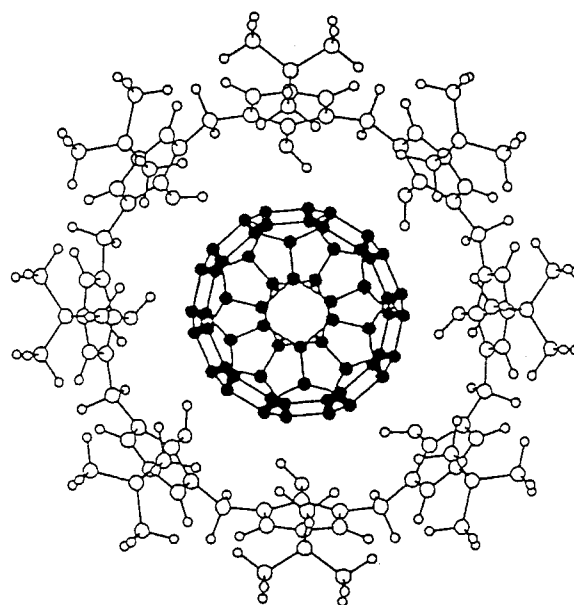


Figure 1. Representation of the *p*-*tert*-butylcalix[8]arene–C<sub>60</sub> complex, showing interaction of the components (not intended to imply detailed structural information).

carbon soot.<sup>4,5</sup> C<sub>60</sub>L forms as an insoluble precipitate when benzene or toluene solutions of C<sub>60</sub> and the calixarene are mixed and allows separation in dichloromethane, 1,2-dichloroethane, or chloroform, with the black C<sub>60</sub> precipitating and the calixarene remaining in solution. A special interest in C<sub>60</sub>L arises from its insolubility in any solvent, because a large number of other calixarene–C<sub>60</sub> complexes are soluble in benzene or toluene. Characterization of C<sub>60</sub>L has been carried out by <sup>13</sup>C NMR,<sup>4,6</sup> vibrational,<sup>4,5,7</sup> and UV–visible spectroscopies,<sup>4,5</sup> and in Langmuir–Blodgett films.<sup>8</sup> C<sub>60</sub>L is believed to contain the C<sub>60</sub> above the

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slightly enlarged center basket of the calixarene. Previous research suggests a small change in the calixarene configuration on C<sub>60</sub> association, the partial breaking up of the intramolecular hydrogen bonding of the native calixarene, the isolation of C<sub>60</sub> molecules from each other, and a weak  $\pi$  electron interaction between the C<sub>60</sub> and calixarene basket. The insolubility of C<sub>60</sub>L arises from intermolecular hydrogen bonding of the displaced OH groups<sup>9</sup> but has also been attributed to an encapsulation of C<sub>60</sub> to form a trimer aggregate by three calixarenes.<sup>10</sup> An electrochemical study looked at the reductions of C<sub>60</sub> in MeCN–toluene (1:4) solution upon addition of three different sized calixarenes to form complexes.<sup>11</sup> 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;<sup>11</sup> this is consistent with a complex, slow rate of intermolecular bonding being responsible for the insolubility of the complex.

Our interest in films of C<sub>60</sub>L was to investigate whether the C<sub>60</sub> 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 C<sub>60</sub> reversibly in water by inclusion within a cyclodextrin.<sup>12</sup> Our studies of the electrochemical behavior of C<sub>60</sub>L films were performed in MeCN, consistent with most previous electrochemical studies of C<sub>60</sub> films, because the C<sub>60</sub>L, C<sub>60</sub>, and calixarene are all insoluble in this solvent. The role of the cation of the electrolyte, important in the behavior of C<sub>60</sub> films,<sup>2</sup> was also considered for the films of C<sub>60</sub>L.

To investigate the effects of ion and solvent transfer as well as dissolution processes that might occur during reduction of C<sub>60</sub>L, generation/collection experiments using a scanning electrochemical microscope (SECM)<sup>13</sup> coupled to a quartz crystal microbalance (QCM) were conducted.<sup>14</sup> While the use of each technique alone has been established for studying the reduction mechanism of C<sub>60</sub> films, the use of both techniques simultaneously provides a powerful tool for determining the effects of reduction upon the particulate films of C<sub>60</sub>L. 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.

## EXPERIMENTAL SECTION

The SECM coupled to the QCM has been described elsewhere.<sup>14</sup> A 5-MHz quartz crystal with gold electrodes (Maxtek, Torrance CA) was used in all QCM experiments. The sealed cell was assembled in a drybox and was constructed to allow for a microelectrode tip to move within the cell while maintaining a seal against oxygen leakage. Cyclic voltammograms (CV) were recorded on a BAS-100B electrochemical analyzer (Bioanalytical Systems, West Lafayette, IN) or with the bipotentiostat that was part of the SECM.

The *p*-*tert*-butylcalix[8]arene–C<sub>60</sub> complex was prepared as described previously<sup>4</sup> and was also synthesized immediately before casting the film by mixing benzene solutions of each component according to previous literature methods.<sup>4</sup> The C<sub>60</sub>L was not very soluble in benzene or in any other solvent we tried, but small particles of C<sub>60</sub>L could be suspended in benzene. Evaporation of the benzene from a drop of this suspension on an electrode resulted in a film of the C<sub>60</sub>L. The particle size in these pale green films, as determined by optical microscopy, was 3–5  $\mu$ m, comparable to the size of black C<sub>60</sub> crystals formed from evaporation of a benzene–C<sub>60</sub> solution.<sup>2</sup> The films were cast onto a gold electrode of a QCM with an area of 0.3 cm<sup>2</sup> or onto a gold disk electrode with an area of 2 cm<sup>2</sup>. MeCN (Burdick & Jackson, Muskegon, MI), KClO<sub>4</sub> (J.T. Baker, Phillipsburg, NJ), and KCF<sub>3</sub>SO<sub>3</sub> (Johnson Matthey) were transferred directly into the drybox and were used as received. Tetrabutylammonium tetrafluoroborate<sup>15</sup> ((TBA)BF<sub>4</sub>, SACHEM, Austin, TX) and Zn(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub><sup>16</sup> (where bpy is 2,2'-bipyridene) were prepared as described previously. Ferrocene (Fc) was recrystallized from hot ethanol and dried in a vacuum oven. All potentials were referenced to the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) couple, with Fc added as an internal standard. This potential was not affected by partial coating of the electrode by the complex.

## RESULTS

**Reduction of Calix[8]arene–C<sub>60</sub> 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.<sup>2</sup> For example, C<sub>60</sub> film reduction in K<sup>+</sup> electrolyte in MeCN leads to dissolution of C<sub>60</sub> anions into solution.<sup>17</sup> We were interested in seeing whether immobilizing the C<sub>60</sub> within the calixarene would keep the C<sub>60</sub> anions trapped in the film, since K<sup>+</sup> might fit within the space of the C<sub>60</sub>L 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 C<sub>60</sub>L. 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 C<sub>60</sub> within the film on the basis of the two reverse processes and comparison with C<sub>60</sub> films. The two reverse oxidations correspond to the oxidation of the dianion to monoanion (II), followed by the oxidation of the monoanion to neutral C<sub>60</sub> (III). If we compare the reduction of the complex in

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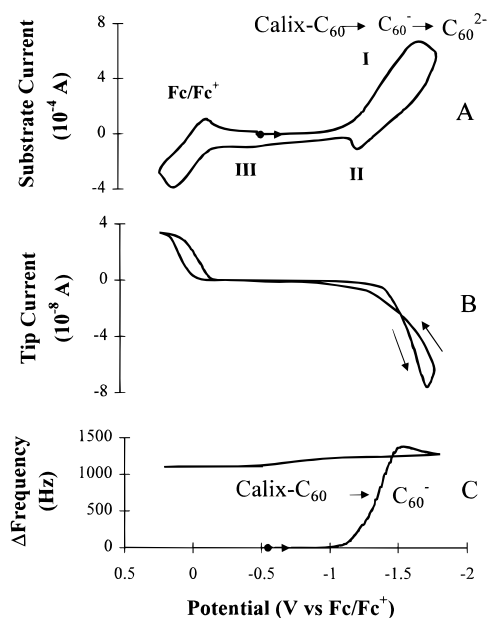


Figure 2. Reduction of calixarene- $C_{60}$  film in 0.03 M  $KCF_3SO_3/MeCN$ . (A) Substrate cyclic voltammogram on a Au QCM electrode at 50 mV/s scan rate. (B) Collection current at a 50- $\mu m$ -diameter Pt tip held at a potential of  $-0.5$  V vs Fc at a distance of 160  $\mu m$  from the substrate. (C) QCM frequency change during the scan.

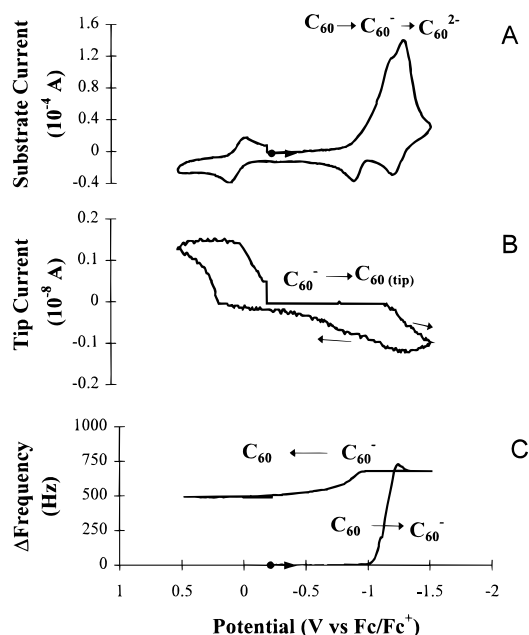


Figure 3. SECM-QCM substrate generation/tip collection experiment for a  $C_{60}$  evaporated film in 0.03 M  $KCF_3SO_3/MeCN$ . (A) Substrate cyclic voltammogram at 50 mV/s. (B) Current at a 50- $\mu m$ -diameter Pt tip electrode held at  $-0.25$  V vs Fc/Fc $^+$  about 60  $\mu m$  away, showing the collection of dissolved  $C_{60}$  anions. The solution contained 5 mM ferrocene as a potential standard and mediator to allow positioning of the tip. (C) QCM response. Reprinted from ref 14.

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 ( $C_{60}^{2-}$

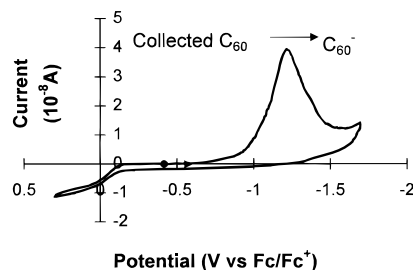


Figure 4. Cyclic voltammogram of  $C_{60}$  on the surface of the 50- $\mu m$ -diameter Pt microelectrode collected during previous reductions of the calixarene- $C_{60}$  film on the substrate, 50 mV/s scan rate.

$\rightarrow C_{60}^-$ ), 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<sup>17</sup> 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.<sup>11</sup> 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

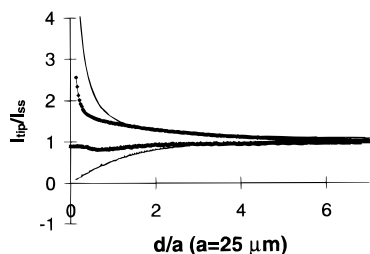


Figure 5. Two SECM approach curves for a 50- $\mu\text{m}$ -diameter Pt microelectrode tip using  $\text{Fc}/\text{Fc}^+$  as a redox mediator as it moved toward the calixarene particles remaining on the gold substrate. The top smooth line is the theoretical line for a purely conductive substrate, and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

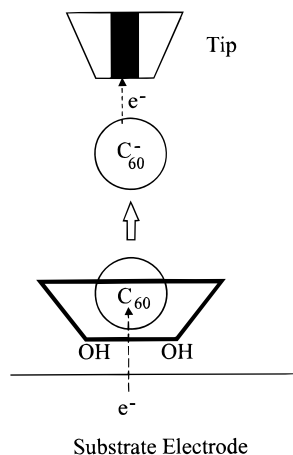
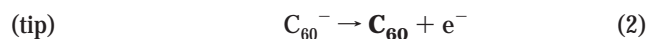
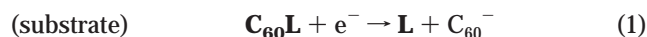


Figure 6. Diagram of calix[8]arene- $\text{C}_{60}$  reduction processes in the SECM-QCM experiment.



The SECM approach curve with a bare tip was used to determine the tip-to-substrate separation,  $d$ . This is accomplished using the  $\text{Fc}/\text{Fc}^+$  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  $\text{C}_{60}$  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  $\text{C}_{60}$  anions dissolved out of the film. From these results, we conclude that the reduction of the  $\text{C}_{60}\text{L}$  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  $\text{C}_{60}$  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

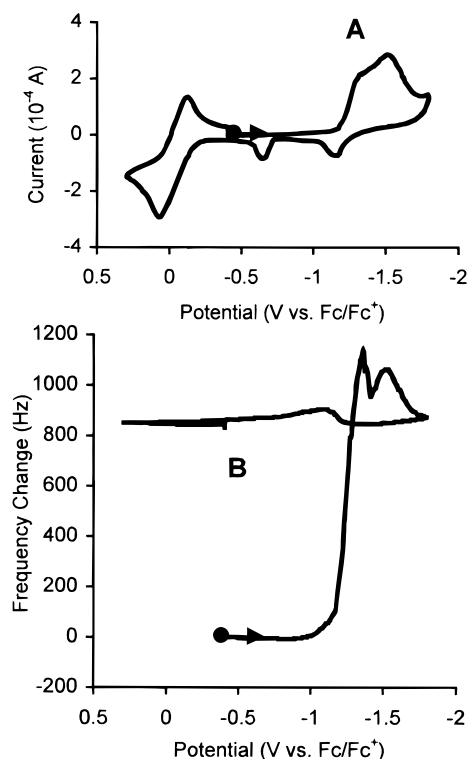


Figure 7. (A) Substrate cyclic voltammogram of a calixarene- $\text{C}_{60}$  film on a Au QCM electrode in 0.10 M  $(\text{TBA})\text{BF}_4/\text{MeCN}$  at 50 mV/s. (B) QCM frequency change during the cyclic voltammogram.

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- $\text{C}_{60}$  Films in  $\text{TBA}^+$  Electrolyte.** The behavior of  $\text{C}_{60}$  films in MeCN is different with  $\text{TBA}^+$  because  $\text{TBA}^+\text{C}_{60}^-$  is fairly insoluble (as compared to the more soluble  $\text{K}^+\text{C}_{60}^-$ ). Thus, the first reduction of  $\text{C}_{60}$  films in  $\text{TBA}^+$  electrolyte results in only a small amount of dissolution of  $\text{C}_{60}^-$  and a significant cation incorporation within the film.<sup>18</sup> Note that the Nernstian waves of polymer-entrapped  $\text{C}_{60}$  used a  $\text{TBA}^+$  electrolyte.<sup>3</sup> Moreover, other calixarene- $\text{C}_{60}$  complex studies suggest a slight interaction between *tert*-butyl groups of the calixarene and the  $\text{C}_{60}$  rings.<sup>4,7</sup>

The CV of  $\text{C}_{60}\text{L}$  in a  $\text{TBA}^+$  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  $\text{TBA}^+$  electrolyte compared to  $\text{K}^+$ . 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  $\text{TBA}^+$  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  $\text{C}_{60}$  is lost and the calixarene remains behind, as with the  $\text{K}^+$  electrolyte. For example, the amount of charge passed in the reduction wave to a potential of  $-1.3 \text{ V}$  (Figure 7) is 1.3 mC, which would be equivalent to a mass change of  $8.6 \mu\text{g}$ , assuming only  $\text{C}_{60}$  dissolves. The QCM frequency change of 1100 Hz is equivalent to  $8.3 \mu\text{g}$ .

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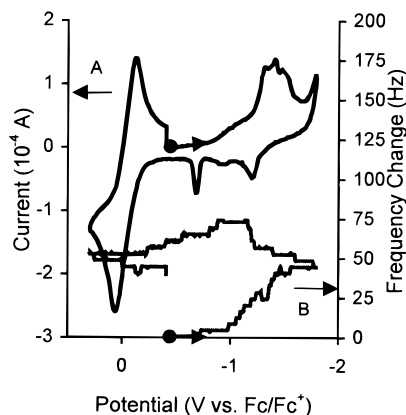
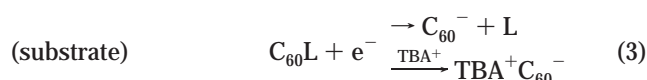


Figure 8. Second cyclic voltammogram of the film in Figure 7. (A) Cyclic voltammogram at 50 mV/s. (B) QCM frequency change.

In general, coulometrically calculated weight changes were within  $\pm 20\%$  of those obtained by QCM. The reverse oxidation shows a mass loss from the film, indicating the loss of  $\text{TBA}^+$  incorporated into the film during the reduction. This mass loss is followed by a slower increase in mass as  $\text{C}_{60}^-$  and  $\text{C}_{60}$  form on the substrate. During the reduction of a  $\text{C}_{60}\text{L}$  film, an SECM tip (25  $\mu\text{m}$ , diameter) held 25  $\mu\text{m}$  from the surface showed an anodic current for  $\text{C}_{60}^-$  oxidation about 25% of that seen with a  $\text{K}^+$  electrolyte. The second scan of the film looked more like a  $\text{C}_{60}$  film and showed a smaller, broad reduction wave with more distinct peak shapes superimposed (Figure 8). The reduction started at a potential about 400 mV more positive than the first scan of the  $\text{C}_{60}\text{L}$ , as expected for a  $\text{C}_{60}$  film. Again, the QCM shows that the dominant process during reduction is dissolution of  $\text{C}_{60}$  from the film. Thus, the dissolution of the  $\text{C}_{60}$  anions was greater from films of  $\text{C}_{60}\text{L}$  than from pure  $\text{C}_{60}$  films in  $\text{TBA}^+$  electrolyte. We saw no evidence that  $\text{TBA}^+\text{C}_{60}^-$ , on oxidation, caused any reincorporation of  $\text{C}_{60}$  into the calixarene cavity; indeed, the growth of a pure  $\text{C}_{60}$  peak indicates that this does not happen. Thus, the process in  $\text{TBA}^+$  electrolyte can be represented as



The scan rate,  $\nu$ , dependence of the voltammograms for the first scan of similarly cast films of the  $\text{C}_{60}\text{L}$  showed a negative shift in  $E_{\text{pc}}$ . The reverse oxidation wave from  $\text{C}_{60}^{2-}$  to  $\text{C}_{60}^-$  had a shape and  $\nu$  dependence between that expected for a solution process and that of a surface process, while the  $\text{C}_{60}^-$  to  $\text{C}_{60}$  wave was Gaussian in shape and had a peak current proportional to  $\nu$ , indicating a surface-confined process.

**Reduction of  $\text{C}_{60}\text{L}$  with  $\text{M}(\text{bpy})_3^{2+}$  Electrolyte.** Previous studies on the reduction of  $\text{C}_{60}$  films in MeCN showed that metal bipyridyl complex cations as electrolytes produced insoluble  $\text{C}_{60}^-$  films and stable electrochemistry,<sup>2</sup> 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  $\text{C}_{60}\text{L}$  in  $\text{Zn}(\text{bpy})_3(\text{PF}_6)_2$  electrolyte showed only a very small reverse oxidation. The

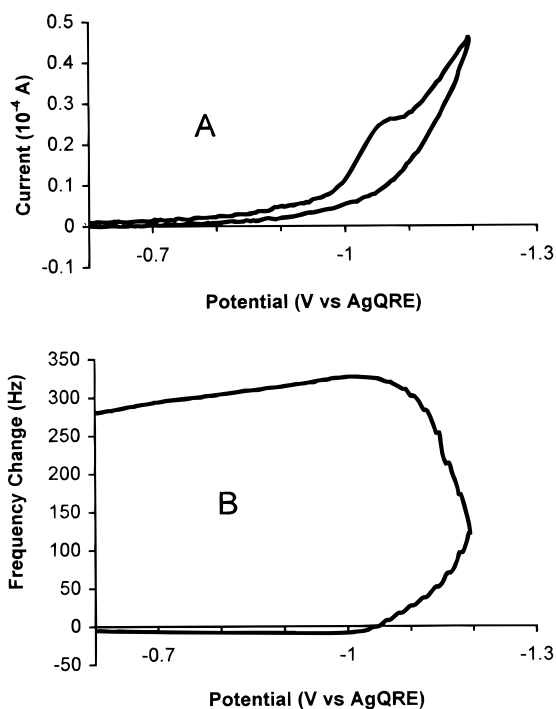


Figure 9. (A) Cyclic voltammogram of a 20- $\mu\text{g}$  calixarene- $\text{C}_{60}$  film in 40 mM  $\text{Zn}(\text{bpy})_3(\text{PF}_6)_2/\text{MeCN}$  at 25 mV/s on a Au QCM electrode. (B) QCM frequency change.

QCM evidence indicated a large loss of mass from the surface during reduction (Figure 9B) as the  $\text{C}_{60}^-$  left the calixarene and dissolved into the MeCN. Results were similar for a  $\text{Cd}(\text{bpy})_3(\text{PF}_6)_2$  electrolyte. This result with  $\text{C}_{60}\text{L}$  is completely different than that of pure  $\text{C}_{60}$  films in the same solvent, where a mass gain is observed upon reduction from cation incorporation. These results, along with those in  $\text{TBA}^+$  electrolyte, suggest that the production of  $\text{C}_{60}^-$  from  $\text{C}_{60}\text{L}$  results in a smaller amount of precipitation of the  $\text{C}_{60}^-$  salt than when  $\text{C}_{60}^-$  is produced from a  $\text{C}_{60}$  film. Perhaps the  $\text{TBA}^+\text{C}_{60}^-$  or  $\text{M}(\text{bpy})_3^{2+}\text{C}_{60}^-$  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  $\text{C}_{60}$  leaves.

**Results in Alcohol Solvents.** We also attempted to find a solvent capable of dissolving the  $\text{C}_{60}\text{L}$  without dissociating it. The solid  $\text{C}_{60}\text{L}$  dissolved in butanol, hexanol, and dodecanol but dissociated with  $\text{C}_{60}$  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  $\text{C}_{60}$  largely precipitated and the calixarene remained in solution.<sup>4,5</sup> Figure 10 compares the UV-visible spectra of the  $\text{C}_{60}\text{L}$ ,  $\text{C}_{60}$ , and pure calixarene left overnight in dodecanol with an excess of each solid. The color of the solution of the  $\text{C}_{60}\text{L}$  changed from its original green to purple, reminiscent of  $\text{C}_{60}$  in solution. The UV-visible spectrum shows both  $\text{C}_{60}$  and the calixarene peaks. The  $\text{C}_{60}$  peaks from the  $\text{C}_{60}\text{L}$  were larger than those from the pure  $\text{C}_{60}$ , suggesting that the pure  $\text{C}_{60}$  dissolved more slowly than the  $\text{C}_{60}\text{L}$ . After a few days, the  $\text{C}_{60}$  spectrum did grow to a similar concentration as from the  $\text{C}_{60}\text{L}$ . 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

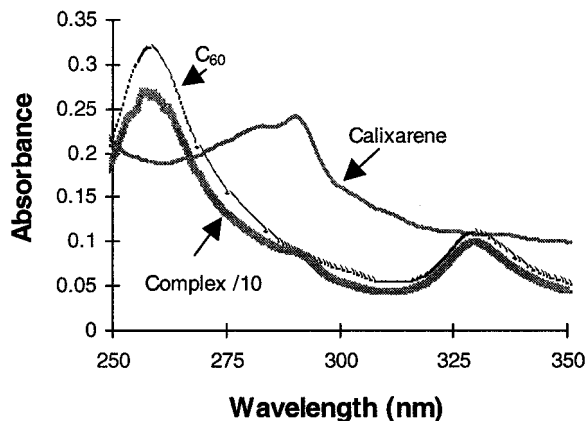


Figure 10. UV-visible spectra of dodecanol saturated overnight with the complex,  $C_{60}$ , and the calixarene. Note that the absorbance of the complex is divided by 10.

complex in hexanol with 0.1 M  $(TBA)BF_4$  electrolyte shows two reduction processes. The first process is a reversible solution couple, probably  $C_{60}$  to  $C_{60}^-$ . The second is an electrodeposition and stripping process and is likely  $C_{60}^-$  reduction to  $(TBA^+)_2C_{60}^{2-}$ . Even though both  $C_{60}$  and calixarene are present in this solution, no electrochemical evidence was found for a  $C_{60}^-$ -calixarene interaction in this solvent.

#### CONCLUSIONS

The electrochemical reduction of a *tert*-butylcalix[8]arene- $C_{60}$  film results in the liberation of the fullerene anion out of the calixarene ring and into the surrounding MeCN solution for  $K^+$ ,  $TBA^+$ , and  $M(bpy)_3^{2+}$  electrolytes. The calixarene remains as a particle film on the Au substrate. This indicates that the

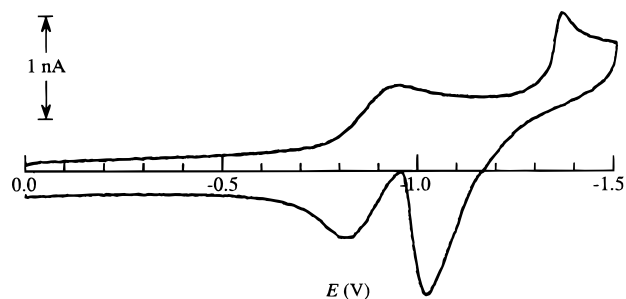


Figure 11. Cyclic voltammogram of the complex dissolved overnight in 0.1 M  $(TBA)BF_4$ /hexanol at a scan rate of 2 V/s. Some of the calixarene had settled out of solution.

calixarene- $C_{60}^-$  interaction is weak and that the  $\pi$  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  $M(bpy)_3^{2+}$  it forms  $C_{60}^-$  films. Complexation of the fullerene in the film results in a negative potential shift of the cathodic peak compared to a pure fullerene film.

#### ACKNOWLEDGMENT

The support of this work by the National Science Foundation (CHE-9508525) and the Robert A. Welch Foundation is gratefully acknowledged. This material is based upon work supported under a National Science Foundation Graduate Research Fellowship and an ACS Analytical Division Graduate Fellowship (D.E.C.).

Received for review February 17, 1998. Accepted July 7, 1998.

AC980183W