

# Electrochemistry of Fullerenes and Their Derivatives

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## Introduction

The serendipitous discovery of  $C_{60}$  and of the general class of carbon compounds called the fullerenes has provided the chemist with a plethora of novel and versatile architectures with which to work, expanding beyond the two-dimensional chemistry of benzene to an almost infinite array of possibilities in three dimensions. Since  $C_{60}$  was detected in 1985,<sup>1</sup> the increasing interest and significance of the work in the fullerene field led to the award of the 1996 Nobel Prize in Chemistry to the founders, Smalley, Curl, and Kroto.<sup>2</sup>

Soon after the appearance of the proposed structure of  $C_{60}$ , **1**,<sup>1</sup> theoretical predictions indicated that the lowest unoccupied molecular orbital (LUMO) of  $C_{60}$  was ener-



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getically low lying and triply degenerate, and thus capable of accepting at least 6 electrons upon reduction.<sup>3</sup> In

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Lourdes E. Echegoyen was born in Caracas, Venezuela, in 1958. She attended the University of Miami where she received a B.S. in chemistry in 1982. She returned to the University of Miami in 1984 where she obtained a Ph.D. in chemistry in 1990 with Professor George Gokel. She worked as a teacher for Belen Jesuit Preparatory School in Miami, and she is currently accompanying her husband, Professor Luis Echegoyen, while on sabbatical at the ETH in Zürich, Switzerland.

addition, X-ray and NMR studies determined that  $C_{60}$ , along with the family of higher fullerenes, was fully conjugated, with no possible electron delocalization because of distinct and different single and double bond lengths.<sup>4</sup> Consequently, electroanalytical techniques such as cyclic voltammetry (CV), Osteryoung square wave voltammetry (OSWV), and differential pulse voltammetry (DPV) quickly became the methods of choice to investigate the rich electronic properties of the fullerenes and their derivatives in solution. The role of electrochemistry in the field of fullerenes has not stopped at the analytical end, however. Synthesis and detection of new materials, from derivatives to thin films and polymers, have been achieved with the aid of electrochemical techniques.

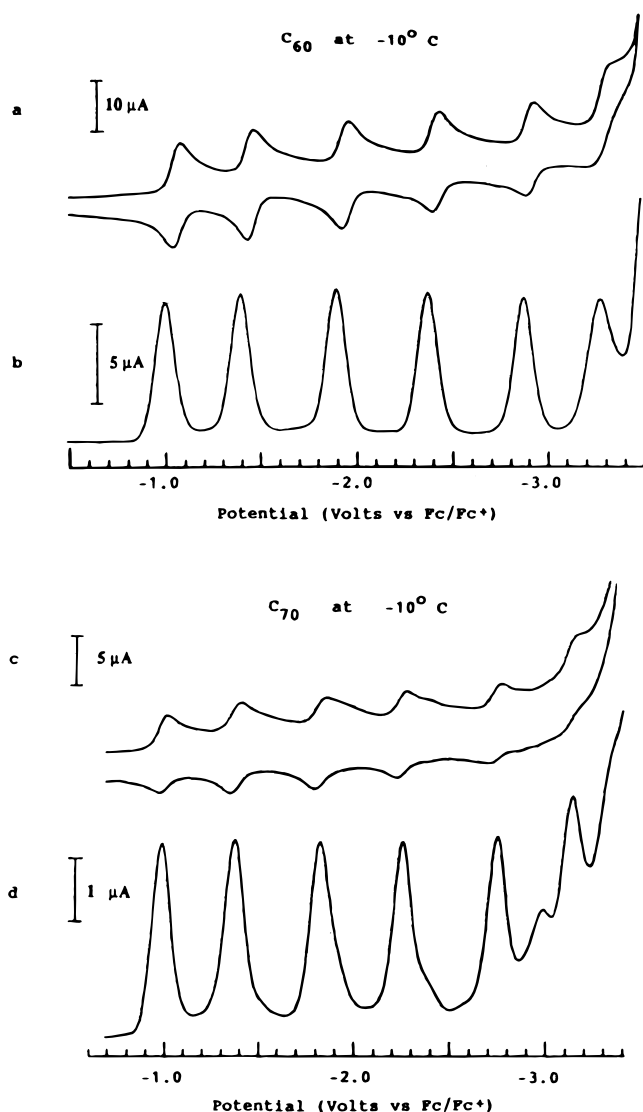
This Account will focus on electrochemical studies of  $C_{60}$ , of some of its electrochemically significant derivatives, and of the higher fullerenes ( $C_{70}$ ,  $C_{76}$ ,  $C_{78}$ ,  $C_{84}$ ). In addition, electrochemical methods for detecting the formation of fullerene-based films are reviewed.

## Electrochemistry of the Pristine Fullerenes $C_{60}$ and $C_{70}$

The systematic electrochemical proof of the triple degeneracy of the LUMO of  $C_{60}$  came in several steps with the detection of  $C_{60}^{2-}$ ,<sup>5</sup>  $C_{60}^{3-}$ ,<sup>6</sup>  $C_{60}^{4-}$ ,<sup>7</sup> and  $C_{60}^{5-}$ .<sup>8a</sup> The hexaanion species,  $C_{60}^{6-}$ , eluded detection until 1992, mainly due to limitations in the potential “window” available with the solvents used. In 1992, our group managed to generate and detect stable  $C_{60}^{n-}$  ( $n = 1-6$ ) using CV and DPV.<sup>9</sup> The voltammetric experiments were carried out under vacuum, using the mixed solvent system acetonitrile–toluene (1:5), and at low temperature ( $-10$  °C). The potentials measured ( $E_{1/2}$ ) were  $-0.98$ ,  $-1.37$ ,  $-1.87$ ,  $-2.35$ ,  $-2.85$ , and  $-3.26$  V vs Fc/Fc<sup>+</sup>. The separation between any two successive reductions under these conditions was relatively constant at ca.  $450 \pm 50$  mV. It is important to emphasize that the penta- and hexaanions are stable and exhibit reversible behavior on the voltammetric time scale. However, when produced by controlled potential coulometry, only the anions up to and including the tetraanion are stable.

The electrochemical characterization of  $C_{70}$  followed a simultaneous, similar historical path. Its LUMO was predicted to be only doubly degenerate, but the calculated energy difference between the LUMO and the LUMO + 1 was small enough that six 1-electron reductions were anticipated for  $C_{70}$ .<sup>3</sup> Kadish and co-workers could unambiguously detect up to four electron reductions due to solvent limitations.<sup>7</sup> Using the same mixed solvent system described above, our group was able to generate and detect  $C_{70}^{n-}$  ( $n = 1-6$ ).<sup>9</sup> Figure 1 shows the six reversible reduction waves observed for both  $C_{60}$  and  $C_{70}$ .

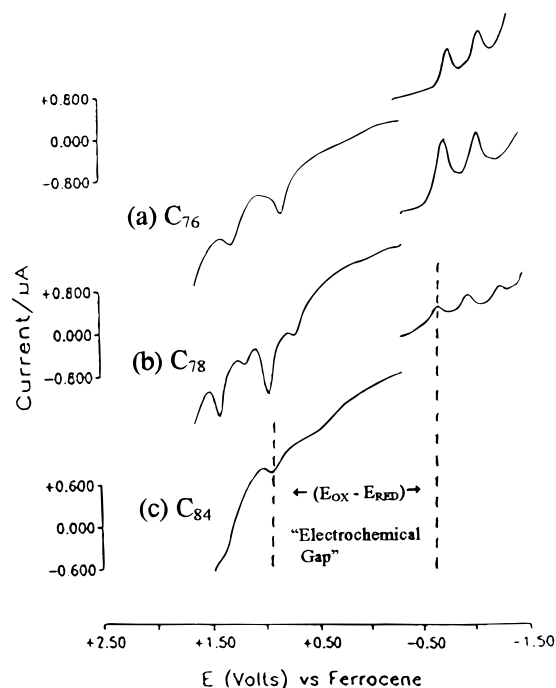
It was also predicted theoretically that oxidation of  $C_{60}$  would be difficult.<sup>3</sup> The gas-phase ionization potential of  $C_{60}$  was measured to be ca. 7.6 eV.<sup>10</sup> The first chemically reversible and electrochemically quasireversible oxidation of  $C_{60}$  and  $C_{70}$  was reported by our group in



**FIGURE 1.** Reduction of  $C_{60}$  and  $C_{70}$  in acetonitrile–toluene with  $TBAPF_6$  as supporting electrolyte at  $-10^\circ\text{C}$  using (a and c) CV at a  $100\text{ mV/s}$  scan rate and (b and d) DPV at a  $25\text{ mV/s}$  scan rate,  $50\text{ mV}$  pulse,  $50\text{ ms}$  pulse width, and  $300\text{ ms}$  period. Reprinted from ref 9. Copyright 1992 American Chemical Society.

1993, after several other reports described the process as irreversible.<sup>8</sup> Voltammetric studies showed that the first 1-electron oxidation of  $C_{60}$  in 1,1,2,2-tetrachloroethane (TCE) indeed occurs at a very positive potential,  $+1.26\text{ V}$  vs  $Fc/Fc^+$ , confirming the theoretical prediction. For  $C_{70}$ , the same process occurs at a potential  $60\text{ mV}$  more negative than that of  $C_{60}$ , at  $+1.20\text{ V}$ .<sup>11</sup> The difference between the first oxidation and the first reduction of  $C_{60}$  (at room temperature), a measure of the HOMO–LUMO gap in solution, is then calculated to be  $2.32\text{ V}$ . For  $C_{70}$ , this gap is somewhat smaller at  $2.22\text{ V}$ . These results showed the rich redox chemistry of  $C_{60}$  and  $C_{70}$ , with eight and nine accessible oxidation states, respectively.

Later studies have demonstrated that the choice of solvent and supporting electrolyte has a profound effect on the potentials at which the different anions are generated.<sup>12</sup> Furthermore, the solubility of the electro-generated species is also affected by these parameters,



**FIGURE 2.** OSW in TCE for (a)  $C_{76}$ , (b)  $C_{78}$ , and (c)  $C_{84}$  recorded at  $60\text{ mV/s}$ . Reprinted from ref 15. Copyright 1995 American Chemical Society.

making it possible to fine-tune the conditions for electro-synthesis of  $C_{60}$  adducts<sup>13,43,44</sup> (vide infra) and for electrodeposition of  $C_{60}$  films in various oxidation states with different cations.<sup>14</sup>

### Electrochemistry of the Higher Fullerenes ( $>C_{70}$ )

More recently, reductive and oxidative electrochemistry of the higher fullerenes  $C_{76}$ ,  $C_{78}$ ,  $C_{82}$ , and  $C_{84}$  has been reported.<sup>15–17</sup> These larger cages possess the added complication of isomerism.<sup>18</sup> Depending on their symmetry, the presence of simultaneous isomers in solution may result in the observation of multiple redox waves.

$C_{76}$  has been shown to consist of only two enantiomers of  $D_2$  symmetry,<sup>18</sup> the electrochemistry of which cannot be separately identified, (see Figure 2a).<sup>15</sup>  $C_{78}$ , on the other hand, has three known isomers of  $C_{2v}$ ,  $C_{2v}$ , and  $D_3$  symmetry.<sup>18</sup> The  $C_{2v}$  and  $C_{2v}$  isomers should not be electrochemically different from each other, but they should be different from the  $D_3$  isomer. Theoretical studies of  $C_{78}$  predicted comparable LUMO and different HOMO energies for the two isomers, with the lower abundance  $D_3$  isomer being easier to oxidize.<sup>19</sup> This would translate electrochemically into both isomers reducing at nearly the same potential, while oxidations should occur at different potentials. Once again, electrochemistry has played an important role in providing experimental confirmation of these theoretical predictions. The reductive OSW and the CV of  $C_{78}$  show, indeed, no isomeric (separate waves) effects in tetrachloroethane. Two cathodic waves are observed within the solvent “potential window”, each corresponding to a 1-electron reduction to form  $C_{78}^-$  and  $C_{78}^{2-}$ . Using the same

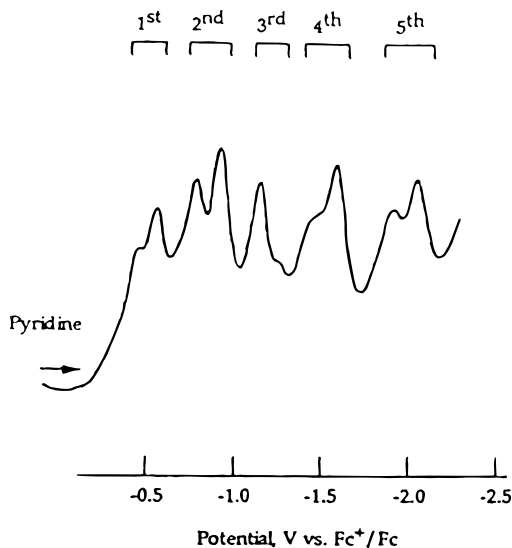


FIGURE 3. DPV of a saturated solution of  $C_{84}$  in 0.1 M TBAP-pyridine (scan rate 2 mV/s; pulse amplitude 40 mV). Reprinted from ref 16b. Copyright 1996 American Chemical Society.

techniques, four oxidation waves are clearly visible (see Figure 2b).<sup>15</sup> These consist of two pairs of consecutive small and large waves. The current intensity ratio (1:5) of these “double waves” is in excellent agreement with the reported isomeric ratio of  $C_{78}$  ( $D_3/C_{2v}$ ),<sup>18</sup> a fact that supports the idea that the small and large waves correspond to the  $D_3$  and  $C_{2v}$  isomers, respectively.

The best example of how complicated the issue of isomerism is for electrochemical studies of the larger fullerenes is represented by studies of  $C_{84}$ . Although 24 isomers of  $C_{84}$  are known to satisfy the “isolated pentagon rule”,<sup>18</sup> only two have been experimentally observed, the  $D_2$  and the  $D_{2d}$  isomers.<sup>20</sup> Their separation by HPLC was not reported until very recently.<sup>20c</sup> In TCE, it is not possible to resolve separate reduction or oxidation waves for these  $C_{84}$  isomers (Figure 2c).<sup>15</sup> However, Kadish et al. have been able to observe 10 redox waves in pyridine (see Figure 3).<sup>16b</sup> Supported by ESR evidence, the first six waves are assigned to the first, second, and third 1-electron reductions of each of the two isomers,  $D_{2d}$  and  $D_2$ , with the  $D_{2d}$  isomer being the easiest to reduce. The last four waves cannot be unequivocally assigned to either isomer. They are thought to be the result of a chemical process occurring upon addition of a fourth electron to both isomers. Kadish has attributed the ability to observe separate waves for the two isomers to a solvent effect.

The electrochemistry of  $C_{82}$  has also been studied in detail, but with a primary interest to compare its redox properties to those of its fascinating endohedral structures.<sup>17</sup> Since this topic is beyond the scope of this Account, the reader is referred to a recent review,<sup>17a</sup> and to other reports<sup>17b-d</sup> in the area of electrochemistry of endohedral metallofullerenes.

## Electrochemistry of $C_{60}$ Derivatives

Driven by visions of interesting new materials such as three-dimensional electroactive polymers, molecular wires,

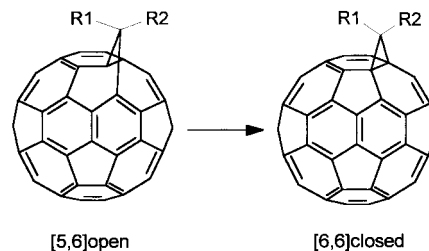
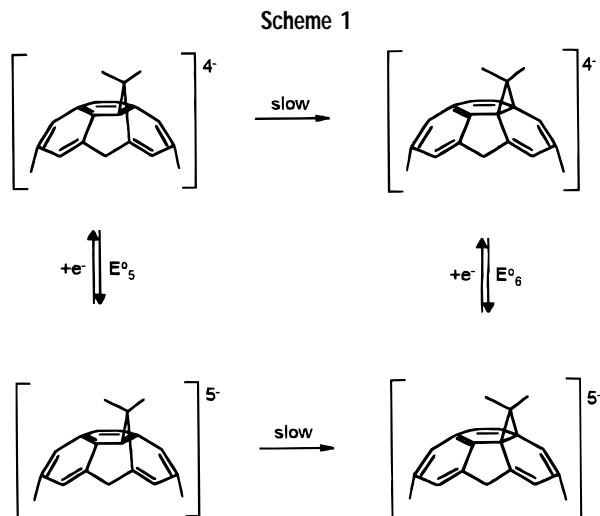


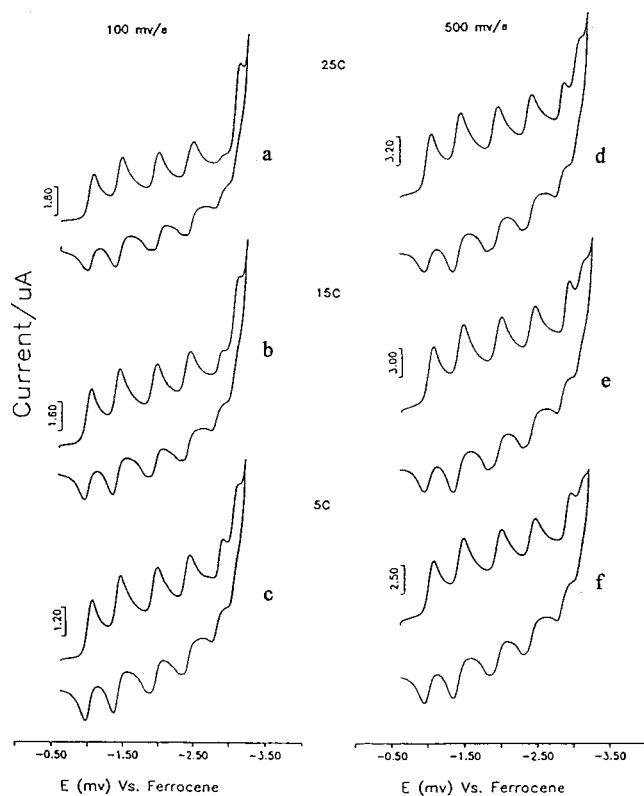
FIGURE 4. Fulleroid-methanofullerene isomerization.



surface coatings, and electrooptic devices, investigators in the fullerene area have been derivatizing  $C_{60}$  with adducts that promise to tune the sphere’s electronic properties. It has thus become of real interest to investigate how the nature, geometry, structure, and number of addends influence the electrochemical behavior of this fullerene.

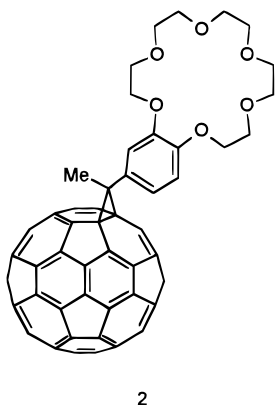
**Electrochemically Induced Isomerization.** One attractive aspect of the three-membered ring bridged family of  $C_{60}$  derivatives (Figure 4) is that, depending on whether the bridge head carbon atoms are bonded or not, four different structures are possible. Of the four, only two are stable synthetically: the [5,6]open, also called a fulleroid (the kinetic product),<sup>21</sup> and the [6,6]closed, also called a methanofullerene (the thermodynamic product after thermalization).<sup>22</sup> The reason these two are the only observed isomers is partly due to the preservation of the [5]radialene structure of  $C_{60}$ .<sup>23</sup> Formation of the [6,6]closed methanofullerene results in a partial loss of conjugation of the  $C_{60}$  sphere, from the  $60\pi$  electron to a  $58\pi$  electron configuration. In contrast, formation of fulleroids ([5,6]-open) does not result in loss of conjugation. They are the only derivatives that retain the  $60\pi$  electron configuration of  $C_{60}$ .<sup>24</sup>

The fulleroid to fullerene rearrangement can also be induced electrochemically, and the effect of the  $\pi$  electron count on the electron affinity of the two isomers has been investigated by our group<sup>25</sup> as well as by the groups of Wudl<sup>26</sup> and Roffia.<sup>27</sup> Interestingly, the three studies have shown that there is essentially no difference in the reduction potentials of the two isomers until the third,<sup>26,27</sup> fourth (below 5 C),<sup>27</sup> or fifth<sup>25</sup> electron reductions. Also,



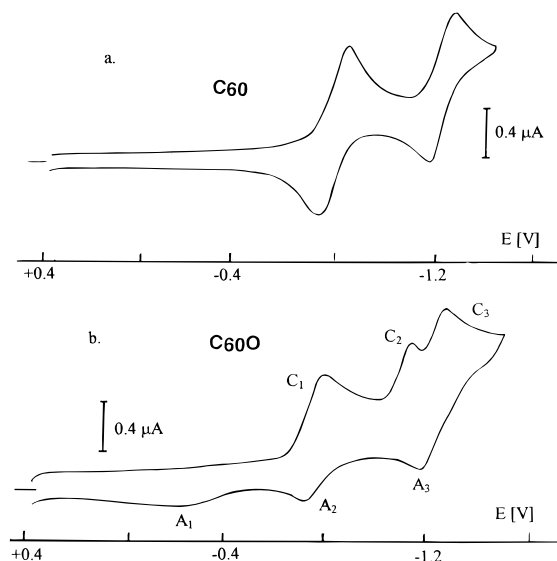
**FIGURE 5.** CVs for compound **2** in 0.1 M TBAPF<sub>6</sub> acetonitrile–toluene (1:5) as a function of variable temperature and variable scan rate: at 100 mV/s and (a) 25, (b) 15, and (c) 5 °C and at 500 mV/s and (d) 25, (e) 15, and (f) 5 °C. Reprinted from ref 25b. Copyright 1994 American Chemical Society.

the fulleroid to fullerene rearrangement is clearly observed during the corresponding third,<sup>26,27</sup> fourth (below 5 °C),<sup>27</sup> or fifth electron reduction.<sup>25</sup> Figure 5 shows the variable scan CV sequence that clearly demonstrates the isomerization process presented in Scheme 1 for compound **2**



during the fifth electron reduction.<sup>25</sup> The fact that the same results are obtained in all three studies at different reduction steps may indicate a solvent and/or substituent effect. It should be emphasized, however, that the reduction potentials of the two corresponding isomers are identical or nearly so until at least three electrons have been added to the C<sub>60</sub> moiety.

**Derivatization and Electron Affinity.** Several cases have been reported in which derivatization, regardless of



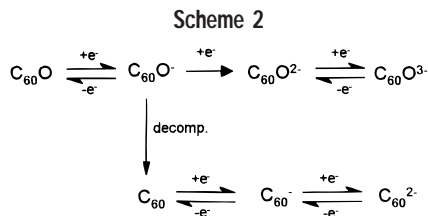
**FIGURE 6.** CV of (a) C<sub>60</sub> and (b) **3** in 0.1 M TBAP/4:1 toluene–acetonitrile (scan rate 100 mV/s). Reprinted from ref 32a. Copyright 1995 American Chemical Society.

the nature or the number of addends, decreases the electron affinity of the C<sub>60</sub> sphere, as observed by electrochemical reduction. Typically, cathodically (more negative) shifted waves, with shifts ranging from 30 to 350 mV per adduct with respect to those of pure C<sub>60</sub>, have been observed by CV, OSWV, and/or DPV.<sup>28–38</sup> Reduction of some of these functionalized derivatives has (disappointingly) resulted in the release of the attached fragment(s) and recovery of pure C<sub>60</sub>. Examples of these are the dihydrofullerene, C<sub>60</sub>H<sub>2</sub>,<sup>28,29</sup> a few metal (M) derivatives (M = Ni, Pd, Pt), where the metal constitutes the bridging atom,<sup>30</sup> and the epoxyfullerene, C<sub>60</sub>O, (**3**).<sup>31,32</sup> The con-



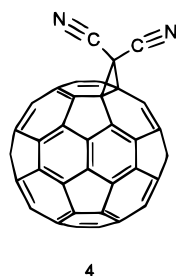
version of C<sub>60</sub>H<sub>2</sub> to C<sub>60</sub> does not occur until after the third reduction, and it is solvent and temperature dependent.<sup>29</sup> In contrast, the metal derivatives as well as C<sub>60</sub>O decompose to the parent C<sub>60</sub> upon addition of the first electron.<sup>31,32</sup> Interestingly, C<sub>60</sub>O shows an irreversible reduction potential, which is 50 mV more positive than that of pure C<sub>60</sub> in *o*-dichlorobenzene.<sup>31</sup>

More recently, in a more extensive investigation, Balch and Fawcett have determined that **3** undergoes an electropolymerization process as a result of electroreduction.<sup>32</sup> Of the three 1-electron reduction waves observed by CV (Figure 6), wave one corresponds to formation of C<sub>60</sub>O<sup>•-</sup> with a solvent and sweep-rate-dependent decomposition to the parent C<sub>60</sub> as represented in Scheme 2. Wave two corresponds to the irreversible formation of the radical dianion C<sub>60</sub>O<sup>2•-</sup>. The authors believe that the latter species

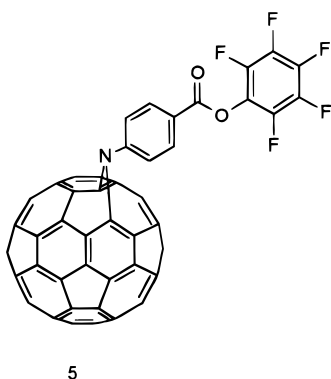


is the polymer initiator. The proposed structure for the polymer film is  $(-C_{60}O-C_{60}O-)$ .<sup>32</sup>

Attempts at increasing the electron affinity of the  $C_{60}$  sphere via derivatization with electron-withdrawing groups (EWG) have resulted in the preparation of organo-fullerenes,<sup>31</sup> spiromethanofullerenes,<sup>33</sup> iminofullerenes,<sup>34</sup> and fluorinated fullerenes,<sup>35</sup> among others.<sup>36</sup> Of these, the most electronegative monofunctionalized fullerene prepared so far appears to be a dicyano derivative, **4**,



whose first (quasireversible) reduction potential at  $-72$  °C is 156 mV more positive than that of  $C_{60}$ .<sup>33c</sup> This same reduction is, however, irreversible at room temperature. The enhanced effect of the EWG has been attributed to an orbital through-space interaction phenomenon called "periconjugation".<sup>33</sup> Another notable example of increased electronegativity is the iminofullerene **5**. At room



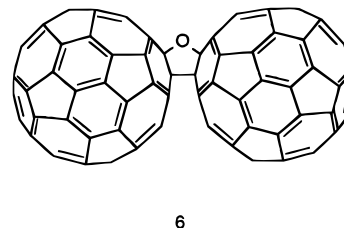
temperature, **5** undergoes its first reversible reduction 48 mV more positive than its parent,  $C_{60}$ .<sup>34</sup> It is not surprising, however, that due to the high electronegativity of fluorine, multifluorinated derivatives of  $C_{60}$  and  $C_{70}$  exhibit the highest electron affinities reported for fullerene derivatives, with reduction potentials ranging from 1.35 to 1.57 V more positive than the corresponding parent compounds  $C_{60}$  and  $C_{70}$ .<sup>35</sup>

Efforts to determine changes in the redox properties of  $C_{60}$  derivatives as a function of the number of addends have shown that as the fullerene cage becomes increasingly functionalized, reductions become increasingly more

difficult and irreversible. This has been explained in terms of a stepwise loss of conjugation, which causes the LUMO to become increasingly higher in energy.<sup>36</sup>

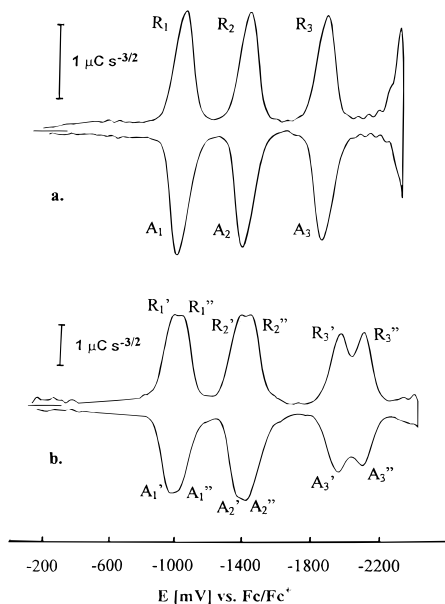
**Derivatization and Electronic Communication.** Another type of fullerene derivative has been designed to combine the fullerene properties with those of other electroactive compounds, such as ferrocene,<sup>37</sup> tetrathiafulvalene (TTF),<sup>37b</sup> and various quinones.<sup>33b,38,39</sup> The immediate aim is to investigate which adducts are best at establishing electronic "communication" with the fullerene moiety, but the final target is the design and preparation of new fullerene-based materials whose redox properties can be modified and controlled. Electrochemistry results reported to date for all these compounds, particularly the ferrocenes, show features that are not observed for other  $C_{60}$  derivatives, such as 1-electron reductions in sets of two consecutive waves.<sup>37</sup> However, it has not been demonstrated conclusively that there is electronic coupling between the covalently linked electroactive moieties. Further investigation is still pending.

Another approach to the same theme has been the study of fullerene dimers, in which two fullerene spheres are connected via a molecular bridge. Studies with phenylene and acetylene spacers separating two fullerene cores have not detected electronic communication between the two. Only unresolved multielectronic processes have been observed at potentials that correspond to individual  $C_{60}$  components.<sup>36a,40</sup> Remarkably, the dimer  $C_{120}O$ , **6**, reported by Balch, appears to be the first



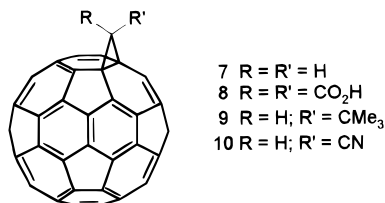
molecule consisting of two covalently linked fullerene units in which the two moieties appear to be interacting.<sup>41</sup> The cathodic CV and DPV in *o*-dichlorobenzene show two reversible asymmetric peaks,  $R_1$  and  $R_2$ , along with a resolved set of two reversible peaks,  $R_3$  and  $R_3'$ . Deconvolution of each of the two asymmetric peaks indicates that each one corresponds to two closely spaced waves, resulting from the superposition of two processes with very close reduction potentials (see Figure 7). The fact that each of the 1-electron processes is resolved to some degree is a good indicator that the two  $C_{60}$  moieties are communicating. This conclusion is supported by the observation of a triplet feature in the ESR of  $C_{120}O^{2-}$ .<sup>41</sup>

**Electrochemistry as a Synthetic Tool.** Electrochemical studies of the protonation of  $C_{60}^-$  and  $C_{60}^{2-}$  indicate that  $C_{60}^-$  is a very weak base. The dianion,  $C_{60}^{2-}$ , is, however, a relatively strong base with an estimated  $pK_{a,2}$  value of 10 in *o*-dichlorobenzene and 16 in DMSO.<sup>42</sup> Furthermore, the fact that the coulometrically stable mono- to tetraanions of  $C_{60}$  can be progressively generated at modestly negative potentials allows for their versatile use in organic



**FIGURE 7.** Deconvoluted CV of (a) 0.35 mM  $C_{60}$  and (b) 0.19 mM  $C_{120}O$  in 0.1 M TBAP-*o*-dichlorobenzene (sweep rate 100mM/s). Reprinted from ref 41. Copyright 1996 American Chemical Society.

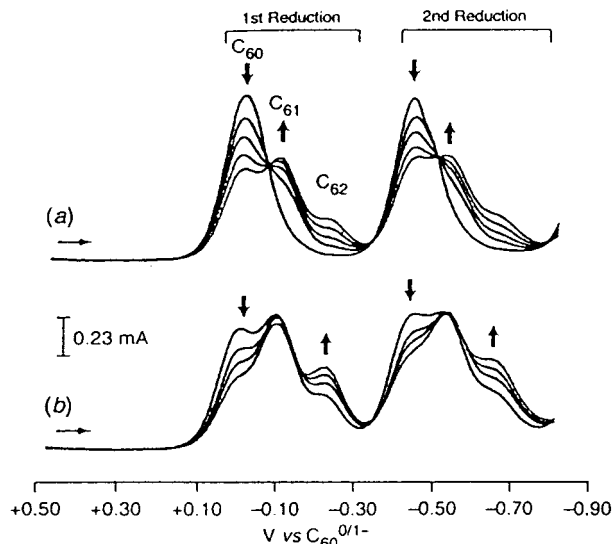
electrosynthesis, particularly in the area of fullerene derivatization. This is an area, however, that has not been exploited extensively. Only a few  $C_{60}$ -derived compounds resulting from electrosynthesis have been reported, mainly by Kadish<sup>43</sup> and Mangold.<sup>44</sup> Our group has also reported the electrosynthesis of compounds **7–10**.<sup>13</sup> The general



method involves the use of controlled potential bulk electrolysis to generate  $C_{60}^{2-}$  in the absence of oxygen. The reduction potential depends on the solvent and supporting electrolyte chosen,<sup>12</sup> and it is maintained until the current drops to a baseline value. At this point, the desired electrophile is added and allowed to react while the reaction progress is monitored by measuring the rest potential of the solution. The reaction is complete when no change in the rest potential is detected. An alternative way to monitor the extent of reaction is by observing the growth of the voltammetric peaks of the products at the expense of those of the reactants in a “pseudospectroscopic” way (see Figure 8). In this respect, electrochemistry is truly powerful and useful, since it is used as the effector of the chemical transformation, as well as the detector in situ of the reaction progress.

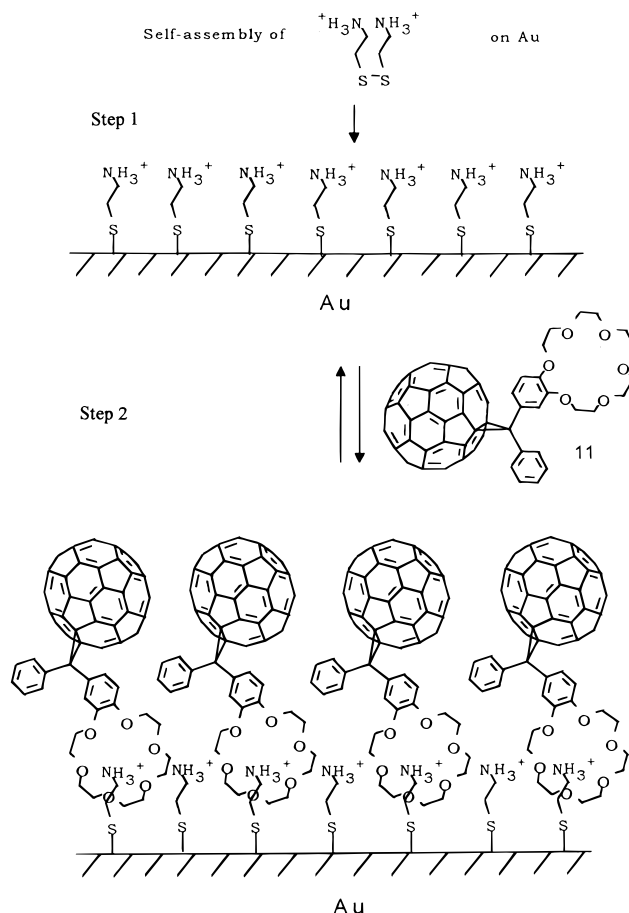
## Electrochemistry of Fullerene-Based Thin Films

Because of its unique properties and potential applications as a ferromagnet, as a superconductor, and in electrooptic devices and polymers,<sup>45</sup>  $C_{60}$  is being incorporated into yet

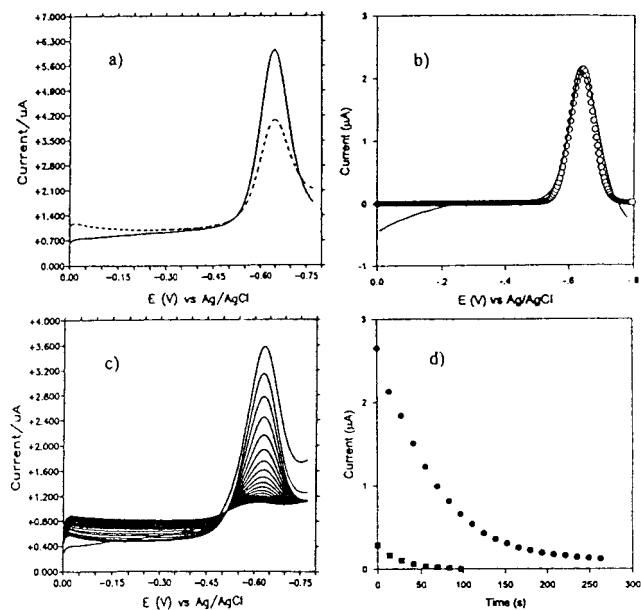


**FIGURE 8.** OSWV of a solution of  $C_{60}$  in a 0.1 M solution of TBAPF<sub>6</sub> in acetonitrile-toluene (1:2) containing  $I_2CHCMe_3$ .  $C_{61}$  and  $C_{62}$  represent  $C_{61}HCMe_3$  and  $C_{62}H_2(CMe_3)_2$ , respectively. Voltammograms recorded (a) during the first 80 min and (b) during the last 60 min. Sweep width 25 mV; frequency 15 Hz; potential step 4 mV. Reprinted with permission from ref 13. Copyright 1996 The Electrochemical Society.

### Scheme 3



another type of material, thin films. Two excellent and quite comprehensive reviews appeared recently on the preparation of thin film fullerene-based materials<sup>46,47</sup> and

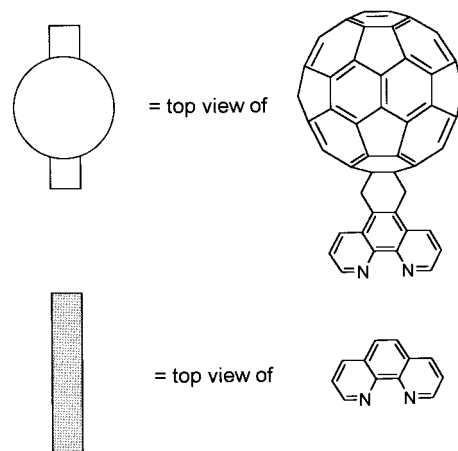
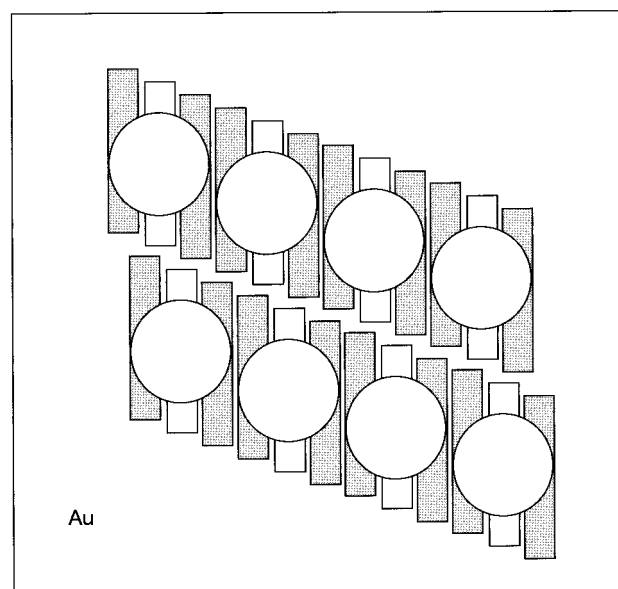


**FIGURE 9.** (a) OSWV for a 0.13 mM solution of **11** in  $\text{CH}_2\text{Cl}_2$  in the presence of a  $-\text{S}(\text{CH}_2)_2\text{NH}_3^+$  monolayer on the gold surface (continuous line) and after removal of the monolayer (discontinuous line). (b) Difference OSWV by subtraction of the two OSWVs in (a). The circles represent a digital simulation. (c) Successive OSWV responses of the fully treated electrode (secondary SAM of **11** complexed to the first thiolated SAM) immersed in pure solvent containing only the supporting electrolyte. (d) Time dependence of the peak current in (c) (circles), and when the same experiment was performed with pure  $\text{C}_{60}$  under identical conditions (squares). Reprinted from ref 49. Copyright 1996 American Chemical Society.

their electrochemical behavior.<sup>47</sup> Consequently, we will focus here on the role of electrochemistry as a detector of self-assembled monolayer (SAM) film formation and as a diagnostic tool of the properties of the films. The emphasis will be on work performed in our laboratories.

SAMs are monomolecular films formed from the chemical adsorption of molecules onto specific surfaces. A typical approach used involves the modification of a gold electrode using a thiolated molecule. The strong Au–S interaction immobilizes the molecules on the Au surface, and electrochemical analysis can be performed if the compound is electroactive. Prior to our work, Mirkin and co-workers reported two elegant methods of preparing SAMs of  $\text{C}_{60}$ , both of which involved a covalent linkage between the fullerene and thiolated moieties.<sup>48</sup> Others have reported similar approaches.<sup>46</sup>

The work performed in our laboratories involves a simple two-step process. Instead of modifying the electrode with a thiol-derivatized fullerene, molecular recognition principles are used. Scheme 3 shows a graphic illustration of the concepts used. Step one involves the modification of a gold electrode with a thiolated SAM terminated in ammonium groups. In step two, a secondary SAM is formed as the crown ether arm of **11** forms a complex with the ammonium groups of the first monolayer. OSWV has been used in this case because of its greater sensitivity compared to CV. The advantage of using electrochemistry as the analytical tool is based on several facts: (1) A quantitative analysis of surface cover-



**FIGURE 10.** Schematic representation of the phen/phen–fullerene mixed monolayer self-assembled on Au. The model for the molecular packing is idealized, but it is based on an STM image.<sup>50</sup> The phenanthrolyl group of the phen–fullerene molecule intercalates and forms  $\pi$ -stacks with other phenanthroline molecules in a 1:2 ratio. The diameter of the  $\text{C}_{60}$  moiety corresponds roughly to three phen molecules along a chain.

age can be obtained. Following current measurement of the electrode modified as shown in Scheme 3, step 2, the gold surface is completely desorbed, cleaned, and immersed in a solution of **11**. Since the current measured in this case is that of free **11** in solution, subtraction of this current from that of the complexed form results in a quantitative measure of surface confinement (see Figure 9a,b). (2) Desorption of compound **11** from the ammonium-terminated SAM can be easily analyzed by immersing the fully treated surface (after step two) in the pure solvent. This process leads to decomplexation but leaves the first layer intact. Following the current as a function of time leads to the description of the desorption process (see Figure 9c,d).<sup>49</sup>

The molecular recognition process described above provides reversible control of film formation because (1) the film can be desorbed easily and perhaps induced via pH changes or cation addition because there are no

covalent bonds involved, (2) the film properties can be easily analyzed by voltammetric methods, (3) multilayer films can be envisioned by bis-functionalizing C<sub>60</sub> with different “complementary” arms, and (4) bearing the appropriate functionality, polymerization could yield a more stable, removable, easier to manipulate material, analogous to an LB film.

More recently, we reported the formation of well-ordered SAMs based on the strong adsorption of phenanthroline (phen) nitrogens on gold surfaces. A novel 1,10-phenanthroline–fullerene derivative was incorporated into these monolayers (see Figure 10). The result was a very stable monolayer that owes its stability to three factors: the phenanthroline–Au interactions, the  $\pi$ – $\pi$  interactions between phenanthrolines, and the fullerene–fullerene interactions.<sup>50</sup> Electrochemical studies of these monolayers are currently underway.

## Concluding Remarks

The versatility of electrochemical techniques has not only permitted the experimental demonstration of the predicted electronic structures for many members of the fullerene family, but also allowed investigators to reach into the realm of discovery and creation. It is evident that although the electronic properties of the fullerenes have been established, the many intricacies that constitute the delicate nature of these properties are only beginning to surface as new derivatives are prepared and studied.

The generality of the decomposition of fullerene derivatives (in some cases back to C<sub>60</sub>) upon electrochemical reduction is an area under intense exploration at the present time by the authors in collaboration with the research group of Professor F. Diederich. Most studies have investigated the voltammetric behavior of the derivatives, not their coulometric or ESR behavior. It appears, on the basis of our own experience and on a few reported results, that fullerene derivative anions are, generally, very unstable. Current research is exploring this fundamentally important area. Indirectly related to this is the fact that isomeric product analysis has not been done in detail for electrosynthesis. Ongoing research seems to indicate that some regioisomers that are not accessible kinetically or thermodynamically by chemical synthesis may be electrosynthesized.

The design of technologically important fullerene-based materials is only limited by the imagination and the laws of physics. Undoubtedly, electrochemistry will continue to play a leading role in this venture.

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## References

- (1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature (London)* **1985**, *318*, 162–163.
- (2) Curl, R. F. *Angew. Chem., Int. Ed. Eng.* **1997**, *36*, 1566–1576. (b) Kroto, H. *Angew. Chem., Int. Ed. Eng.* **1997**, *36*, 1578–1593. (c) Smalley, R. E. *Angew. Chem., Int. Ed. Eng.* **1997**, *36*, 1594–1601.
- (3) Haddon, R. C.; Brus, L. E.; Raghavachari, K. *Chem. Phys. Lett.* **1986**, *125*, 459–464.
- (4) (a) Haddon, R. C. *Acc. Chem. Res.* **1992**, *25*, 127–133. (b) Johnson, R. D.; Bethune, D. S.; Yannoni, C. S. *Acc. Chem. Res.* **1992**, *25*, 169–175.
- (5) Haufler, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* **1990**, *94*, 8634–8636.
- (6) Allemand, P.-M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 1050–1051.
- (7) Dubois, D.; Kadish, K. M.; Flanagan, S.; Haufler, R. E.; Chibante, L. P. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4364–4366.
- (8) (a) Dubois, D.; Kadish, K. M.; Flanagan, S.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 7773–7774. (b) Jeboulet, C.; Bard, A. J.; Wudl, F. *J. Am. Chem. Soc.* **1991**, *113*, 5456–5457.
- (9) Xie, Q.; Perez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978–3980.
- (10) (a) Zimmerman, J. A.; Eyster, J. R.; Bach, S. B. H.; McElvany, S. W. *J. Chem. Phys.* **1991**, *94*, 3556–3562. (b) Lichtenberger, D. L.; Nebesny, K. W.; Ray, C. D.; Huffman, L.; Lamb, D. *Chem. Phys. Lett.* **1991**, *176*, 203–208. (c) Cox, D. M.; Trevor, D. J.; Reichmann, K. C.; Kaldor, A. *J. Am. Chem. Soc.* **1986**, *108*, 2457–2458.
- (11) Xie, Q.; Arias, F.; Echegoyen, L. *J. Am. Chem. Soc.* **1993**, *115*, 9818–9819.
- (12) Dubois, D.; Moninot, G.; Kutner, W.; Jones, M. T.; Kadish, K. M. *J. Phys. Chem.* **1992**, *96*, 7173–7145.
- (13) (a) Boulas, P. L.; Zuo, Y.; Echegoyen, L. *Chem. Commun.* **1996**, 1547–1548. (b) Arias, F.; Boulas, P.; Zuo, Y.; Dominguez, O.; Gomez-Kaifer, M.; Echegoyen, L. In *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society, Inc.: Pennington, NJ, 1996; Vol. 3, pp 165–176.
- (14) Koh, W.; Dubois, D.; Kutner, W.; Jones, M. T.; Kadish, K. M. *J. Phys. Chem.* **1993**, *97*, 6871–6879.
- (15) Yang, Y.; Arias, F.; Echegoyen, L.; Chibante, L. P. F.; Flanagan, S.; Robertson, A.; Wilson, L. J. *J. Am. Chem. Soc.* **1995**, *117*, 7801–7804.
- (16) (a) Meier, M. S.; Guarr, T. F.; Selegue, J. P.; Vance, V. K. *J. Chem. Soc., Chem. Commun.* **1993**, 63–65. (b) Boulas, P. L.; Jones, M. T.; Ruoff, R. S.; Lorents, D. C.; Malhotra, R.; Tse, D. S.; Kadish, K. M. *J. Phys. Chem.* **1996**, *100*, 7573–7579. (c) Li, Q.; Wudl, F.; Thilgen, C.; Whetten, R. L.; Diederich, F. *J. Am. Chem. Soc.* **1992**, *114*, 3994–3996.
- (17) (a) Suzuki, T.; Kikuchi, K.; Oguri, F.; Nakao, Y.; Suzuki, S.; Achiba, Y.; Yamamoto, K.; Funasaka, H.; Takahashi, T. *Tetrahedron* **1996**, *52*, 4973–4982. (b) Burbank, P. M.; Gibson, J. R.; Dorn, H. C.; Anderson, M. R. *J. Electroanal. Chem.* **1996**, *417*, 1–4. (c)



- Kirbach, U.; Dunsch, L. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2380–2383. (d) Anderson, M. R.; Dorn, H. C.; Stevenson, S.; Burbank, P. M.; Gibson, J. R. *J. Am. Chem. Soc.* **1997**, *119*, 437–438.
- (18) Diederich, F.; Whetten, R. L. *Acc. Chem. Res.* **1992**, *25*, 119–126.
- (19) Colt, J. R.; Scuseria, G. E.; *Chem. Phys. Lett.* **1992**, *199*, 505–512.
- (20) (a) Kikuchi, K.; Nakahara, N.; Wakabayashi, T.; Susuki, S.; Shiromaru, H.; Miyake, Y.; Saito, K.; Ikemoto, I.; Kainosho, M.; Achiba, Y. *Nature* **1992**, *357*, 142–145. (b) Taylor, R.; Langley, G. J.; Avent, A. G.; Dennis, T. J. S.; Kroto, H. W.; Walton, D. R. M. *J. Chem. Soc., Perkin Trans. 2* **1993**, *2*, 1029–1036. (c) Dennis, T. J. S.; Kai, T.; Tomiyama, T.; Shinohara, H. *Chem. Commun.* **1998**, 619–620.
- (21) (a) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 7301–7302. (b) Isaacs, L.; Wehrsig, A.; Diederich, F. *Helv. Chim. Acta* **1993**, *76*, 1231–1250.
- (22) (a) Osterodt, J.; Nieger, M.; Windschief, P.-M.; Vögtle, F. *Chem. Ber.* **1993**, *126*, 2331–2336. (b) Smith, A. B., III; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J.; Owens, K. G.; King, R. C. *J. Am. Chem. Soc.* **1993**, *115*, 5829–5830.
- (23) (a) Isaacs, L.; Diederich, F. *Helv. Chim. Acta* **1993**, *76*, 2454. (b) Taylor, R. J. *J. Chem. Soc., Perkin Trans.* **1992**, 3–6.
- (24) Wudl, F. *Acc. Chem. Res.* **1992**, *25*, 157–161.
- (25) (a) Arias, F.; Echegoyen, L.; Wilson, S. R.; Lu, Q.; Lu, Q. *J. Am. Chem. Soc.* **1995**, *117*, 1422–1427. (b) Arias, F.; Xie, Q.; Wu, Y.; Lu, Q.; Wilson, S. R.; Echegoyen, L. *J. Am. Chem. Soc.* **1994**, *116*, 6388–6394.
- (26) Eiermann, M.; Wudl, F.; Prato, M.; Maggini, M. *J. Am. Chem. Soc.* **1994**, *116*, 8364–8365.
- (27) Paolucci, F.; Marcaccio, M.; Roffia, S.; Orlandi, G.; Zerbetto, F.; Prato, M.; Maggini, M.; Scorrano, G. *J. Am. Chem. Soc.* **1995**, *117*, 6572–6580.
- (28) Guarr, T. F.; Meier, M. S.; Vance, V. K.; Clayton, M. *J. Am. Chem. Soc.* **1993**, *115*, 9862–9863.
- (29) Boulas, P.; D'Souza, F.; Henderson, C. C.; Cahill, P. A.; Jones, M. T.; Kadish, K. M. *J. Phys. Chem.* **1993**, *97*, 13435–13437.
- (30) Lerke, S. A.; Parkinson, B. A.; Evans, D. H.; Fagan, P. J. *J. Am. Chem. Soc.* **1992**, *114*, 7807–7813.
- (31) Suzuki, T.; Maruyama, Y.; Akasaka, T.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1994**, *116*, 1359–1363.
- (32) (a) Winkler, K.; Costa, D. A.; Balch, A. L.; Fawcett, W. R. *J. Phys. Chem.* **1995**, *99*, 17431–17436. (b) Ferduco, M.; Costa, D. A.; Balch, A. L.; Fawcett, W. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 194–196.
- (33) (a) Eiermann, M.; Haddon, R. C.; Knight, B.; Li, Q. C.; Maggini, M.; Martin, N.; Ohno, T.; Prato, M.; Suzuki, T.; Wudl, F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1591–1594. (b) Ohno, T.; Martin, N.; Knight, B.; Wudl, F.; Suzuki, T.; Yu, H. *J. Org. Chem.* **1996**, *61*, 1306–1309. (c) Keshavarz-K, M.; Knight, B.; Haddon, R. C.; Wudl, F. *Tetrahedron* **1996**, 5149–5159.
- (34) Zhou, J.; Rieker, A.; Grösser, T.; Skiebe, A.; Hirsch, A. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1–5.
- (35) (a) Liu, N.; Touhara, H.; Morio, Y.; Komichi, D.; Okino, F.; Kawasaki, S. *J. Electrochem. Soc.* **1996**, *143*, L214–L217. (b) Zhou, F.; Van Berkel, G. J.; Donovan, B. T. *J. Am. Chem. Soc.* **1994**, *116*, 5485–5486.
- (36) (a) Boudon, C.; Gisselbrecht, J.-P.; Gross, M.; Isaacs, L.; Anderson, H. L.; Faust, R.; Diederich, F. *Helv. Chim. Acta* **1995**, *78*, 1334–1344. (b) Guldi, D. M.; Hungerböler, H.; Asmus, K.-D. *J. Phys. Chem.* **1995**, *99*, 9380–9385.
- (37) (a) Prato, M.; Maggini, M.; Giacometti, C.; Scorrano, G.; Sandona, G.; Farnia, G. *Tetrahedron* **1996**, *52*, 5221–5234. (b) Maggini, M.; Karlsson, A.; Scorrano, G.; Sandona, G.; Farnia, G. *J. Chem. Soc., Chem. Commun.* **1994**, 589–590.
- (38) Illescas, B.; Martin, N.; Seoane, C. *Tetrahedron Lett.* **1997**, *38*, 2015–2018.
- (39) Iyoda, M.; Sultana, F.; Sasaki, S.; Yoshida, M. *J. Chem. Soc., Chem. Commun.* **1994**, 1929–1939.
- (40) Susuki, T.; Li, Q.; Khemani, K.; Wudl, F.; Almarson, Ö. *J. Am. Chem. Soc.* **1992**, *114*, 7300–7301.
- (41) Balch, A. L.; Costa, D. A.; Fawcett, R.; Winkler, K. J. *J. Phys. Chem.* **1996**, *100*, 4823–4827.
- (42) (a) Cliffel, D. E.; Bard, A. J. *J. Phys. Chem.* **1994**, *98*, 8140–8143. (b) Niyazymbetov, M. E.; Evans, D. E.; Lerke, S. A.; Cahill, P. A.; Henderson, C. C. *J. Phys. Chem.* **1994**, *98*, 13093–13098. (c) Niyazymbetov, M. E.; Evans, D. H. *J. Electrochem. Soc.* **1995**, *142*, 2655–2658.
- (43) Caron, C.; Subramanian, R.; D'Souza, F.; Kim, J.; Kutner, W.; Jones, M. T.; Kadish, K. M. *J. Am. Chem. Soc.* **1993**, *115*, 8505–8506.
- (44) Mangold, K.-M.; Kutner, W.; Dunsch, L.; Fröhner, J. *Synth. Met.* **1996**, *77*, 73–76.
- (45) Prato, M. *J. Mater. Chem.* **1997**, *7*, 1097–1109 and references therein.
- (46) Mirkin, C. A.; Caldwell, W. B. *Tetrahedron* **1996**, *52*, 5113–5130.
- (47) Chlistunoff, J.; Cliffel, D.; Bard, A. J. *Thin Solid Films* **1995**, *257*, 166–184.
- (48) (a) Caldwell, W. B.; Chen, K.; Mirkin, C. A.; Babinec, S. J. *Langmuir* **1993**, *9*, 1945–1947. (b) Shi, X.; Caldwell, W. B.; Chen, K.; Mirkin, C. A. *J. Am. Chem. Soc.* **1994**, *116*, 11598–11599.
- (49) Arias, F.; Godínez, L. A.; Wilson, S. R.; Kaifer, A. E.; Echegoyen, L. *J. Am. Chem. Soc.* **1996**, *118*, 6086–6087.
- (50) Dominguez, O.; Echegoyen, L.; Cunha, F.; Tao, N. *Langmuir* **1998**, *14*, 821–824.

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