JOC The Journal of Organic Chemistry
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Electroreductive Transformation of [60]Fullerosultones into Fullerosulfonic Acids

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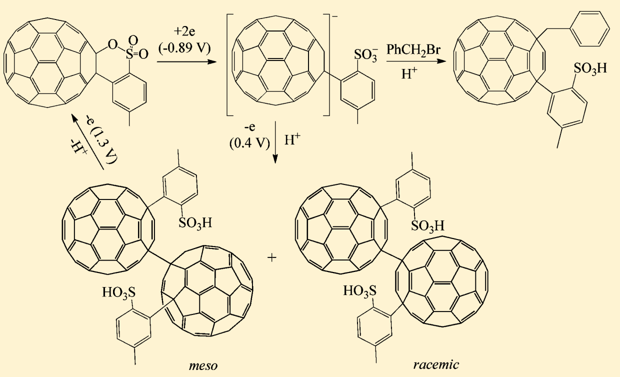
Ⓢ *Supporting Information*

ABSTRACT: Novel C_{60} derivatives of a singly bonded dimer and a 1,4-adduct bearing a sulfonic acid functionality have been prepared via the electroreductive transformation of a [60]fullerosultone. It has been shown that the reaction of the in situ formed dianion with benzyl bromide is initiated by a ring-opening of the [60]fullerosultone via the C_{60}–O bond cleavage upon receiving one electron. The [60]fullerosultone dianion is electrooxidized at 0.40 V to afford the singly bonded dimer species, which can be further electrooxidized at 1.30 V to restore the starting material [60]fullerosultone. The reaction mechanism is studied with the cyclic voltammetry and vis–NIR spectroscopy.



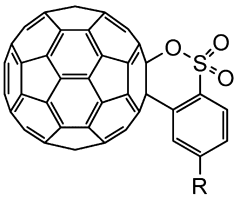
■ INTRODUCTION

Organic sulfonic acids are an important class of compounds, which can be used as acid catalysts,[1] detergents and surfactants,[2] dyes,[3] drugs,[4] and also for self-assemblies.[5] However, to the best of our knowledge, no work on the preparation of structurally well-defined fullerosulfonic acids has appeared so far, even though the chemistry of fullerenes has experienced a rapid development during the past two decades.[6]

We have recently reported the synthesis of C_{60}-fused sultones.[7] Cyclic voltammetry study of these compounds reveals that the first two reductive processes are irreversible, suggesting that the C_{60}-fused sultones may undergo an anion-induced ring-opening reaction, which can be employed for transformation of the sultones to other functionalities. Herein, we report the electrochemical study of C_{60}-fused sultones, and the transformation of a C_{60}-fused sultone into fullerosulfonic acids, that is, singly bonded dimer and 1,4-adduct.

■ RESULTS AND DISCUSSION

Three C_{60}-fused sultones (**1a**, **1b**, and **1c**) are used for the current work, and their structures are shown in Figure 1.



1a: R = CH_3; **1b**: R = H; **1c**: R = Cl

Figure 1. Structures of **1a**–**1c**.

The cyclic voltammograms (CVs) were measured with a platinum disk electrode as the working electrode, a platinum wire electrode as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. Figure 2 shows the CVs of compound **1a** in different potential windows recorded in *o*-dichlorobenzene (ODCB). As seen in Figure 2, the first two redox processes of the compound are irreversible with E_{pc} at −0.30 V (A) and −0.67 V (B), indicating that the compound undergoes a chemical reaction process after receiving one or two electrons. Notably, the E_{pc} of −0.30 V is unusually positive compared with the reduction potentials of C_{60} derivatives,[8] suggesting that this reduction probably occurs at the sultone group, rather than at the C_{60} cage. Further reductions result in two quasi-reversible redox processes with $E_{1/2}$ at −1.00 V (C and F) and −1.44 V (D and E), respectively, whose separation (440 mV) is relatively small compared with those of C_{60} derivatives (for example, 560 mV for 1,2-$PhCH_2(H)C_{60}$,[9] 530 mV for 1,2-$(PhCH_2)_2C_{60}$,[10] 510 mV for 1,4-$(PhCH_2)_2C_{60}$[11]), but resembles the separation between the redox processes of $RC_{60}^-/RC_{60}^{2-\bullet}$ and $RC_{60}^{2-\bullet}/RC_{60}^{3-}$ (420 mV for R = CH_2Ph,[9] 440 mV for R = $CH_2PO(OEt)_2$[12]), implying that a singly bonded anionic species is likely formed via a ring-opening

Received: May 2, 2013
Published: June 24, 2013

dx.doi.org/10.1021/jo400920f | *J. Org. Chem.* 2013, 78, 7093−7099

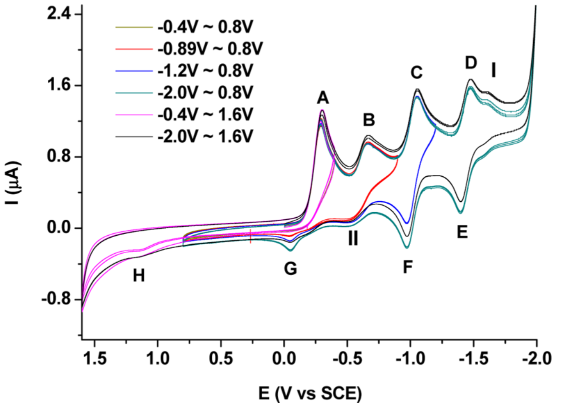


Figure 2. Cyclic voltammograms of compound **1a** (2×10^{-4} M) shown within different potential windows. The CVs were recorded in ODCB containing 0.1 M TBAP (tetra-*n*-butylammonium perchlorate) starting from 0.0 V toward the negative potential with a scan rate of 50 mV/s.

process after two electrons are transferred to **1a**, in agreement with the previous work that the C_{60}−O bond in fullerene derivatives tends to be cleaved upon chemical or electrochemical reduction.[13]

Two irreversible anodic processes are also shown in Figure 2. The broad anodic wave with E_{pa} at −0.06 V (G) resembles the one reported for the formation of singly bonded C_{60} dimers from RC_{60}^{-},[9,12] whose E_{pa} is within the same range, suggesting that a dimer species is likely formed via this oxidation process, and it would probably be coupled with the reduction process of B. Further oxidation reveals another anodic wave with E_{pa} at 1.13 V (H). Since typically no oxidation wave has appeared for fullerene derivatives at such a positive potential,[8] it implies that this wave is probably related to the oxidation of the sulfonic functionality, and corresponds to the reduction process of A. In addition, weak humps labeled with I (−1.64 V) and II (−0.54 V) appear after peaks D and F in Figure 2. The hump I is likely due to an unknown material generated in situ after compound **1a** was reduced, whereas the hump II is likely caused by the diffusion of **1a** from the bulk solution to the electrode during the CV measurement due to a relatively slow scan rate (vide infra).

The electrochemical properties of compounds **1b** and **1c** have also been examined, and the results show that they exhibit similar voltammetric behaviors (Figures S1 and S2, Supporting Information) as **1a**. The cathodic and anodic wave potentials of **1a**−**1c** are listed in Table 1. Although the potentials for the fullerene-based redox steps are nearly unaffected, a slightly positive shift for the first cathodic potentials (from −0.30 to −0.26 V) and anodic potentials (from 1.13 to 1.20 V) from **1a** to **1c** is observed probably due to the increasing electron-deficient nature of the aryl moiety attached to the sultone group.

Controlled potential bulk electrolysis (CPE) was carried out using **1a** as a representative to obtain a better understanding of the electroreductive behaviors of C_{60}-fused sultones. A potential of −0.45 V was applied to transfer one electron to **1a**, and the obtained singly reduced species was then oxidized with a potential of 0.40 V for comparison. The anionic species obtained with CPE at different potentials have been characterized with the visible−near-infrared (vis−NIR) spectroscopy and is compared with the spectrum of **1a**, as shown in Figure 3.

A significant difference is shown for the visible spectrum of **1a** compared with that of the anionic species obtained at −0.45 V. Compound **1a** exhibits the characteristic absorption peak for C_{60} 1,2-isomers at 422 nm,[13a,14] consistent with the 1,2-configuration of [60]fullerosultones. However, the singly reduced species (CPE at −0.45 V) exhibits a strong absorption at 449 nm, which is the characteristic absorption band for the C_{60} 1,4-adducts,[7,9,11,12] suggesting that an anionic species with a 1,4-configuration is formed once **1a** receives one electron. Considering that the first electron is likely added to the sultone functionality, as indicated by the unusually positive reduction potential, it is quite probable that a ring-opening process would occur via the cleavage of the C_{60}−O bond once one electron is transferred to **1a**, and results in a ${}^{\bullet}C_{60}$−$Ph(CH_3)SO_3^{-}$ (**1a**$^{-\bullet}$) monoanion radical intermediate, which subsequently forms the singly bonded $^{-}O_3S(CH_3)PhC_{60}$−$C_{60}Ph(CH_3)SO_3^{-}$ dimer with the 1,4-addition pattern due to the bulky size of the addend. Because the negative charge is located on the resulting sulfonate functionality rather than on the carbon cage due to the electronegativity difference, no absorption bands appear in the range around 1000 nm (not shown) in the spectrum, which are characteristic for organofullerene monoanions.[10,11,15] In fact, the resulting dimeric species should consist of both the meso and the racemic regioisomers, similar to the unique configuration of the singly bonded C_{60} dimers with a 1,4-configuration.[7,9,12,16]

The assumption that the first negative charge is located on the sulfonate group rather than on the C_{60} cage is further supported by the spectrum (Figure 3c) of the product obtained via CPE at 0.40 V of the singly reduced species of **1a**. It is interesting to note that the vis−NIR spectrum of the product obtained by electrolysis at 0.40 V of the singly reduced species is essentially identical to the one of the singly reduced species itself, confirming that the negative charge for the dimeric anionic species is indeed located on the sulfonate group and not on the C_{60} cage, since the potential of 0.40 V vs SCE would be positive enough to remove any negative charge from the C_{60} cage.[8] The results, therefore, indicate that the products obtained by electrolysis both at −0.45 V and followed by oxidation at 0.40 V are the same anionic singly bonded $^{-}O_3S(CH_3)PhC_{60}$−$C_{60}Ph(CH_3)SO_3^{-}$ dimer.

Electrolysis of **1a** with a more negative potential at −0.89 V was carried out to generate the doubly reduced species of **1a**.

Table 1. Cathodic and Anodic Wave Potentials of 1a−1c[a]

compound	E_{pc1}	E_{pa1}	E_{pc2}	E_{pa2}	E_{pc3}	E_{pa3}	E_{pc4}	E_{pa4}
1a	−0.30	1.13	−0.67	−0.06	−1.05	−0.95	−1.48	−1.40
1b	−0.28	1.15	−0.65	−0.06	−1.05	−0.95	−1.48	−1.39
1c	−0.26	1.20	−0.64	−0.05	−1.05	−0.95	−1.47	−1.37

[a] V versus SCE. Conditions: 0.2 mM **1a**−**1c** and 0.1 M TBAP in anhydrous ODCB; working electrode: 2 mm diameter platinum disk; auxiliary electrode: platinum wire; reference electrode: saturated calomel electrode.

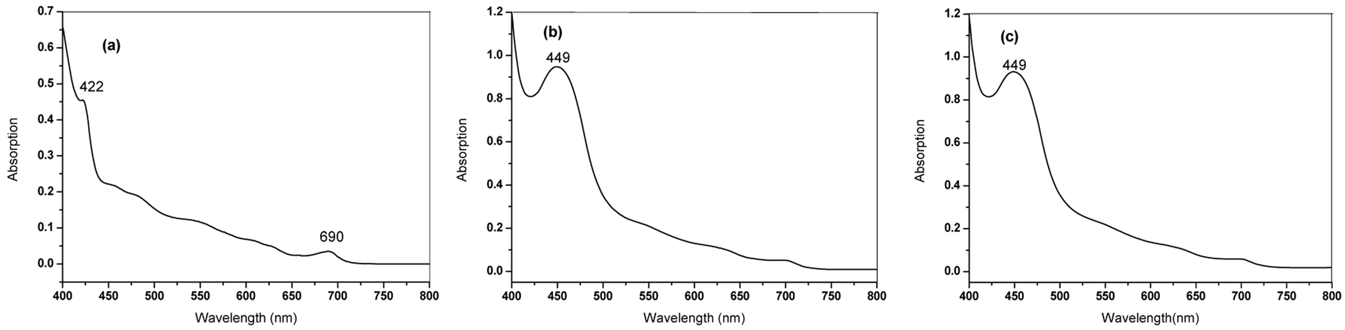


Figure 3. Vis−NIR spectra of (a) neutral compound **1a**, (b) the singly reduced species obtained via CPE of **1a** at −0.45 V, and (c) the species obtained via CPE at 0.40 V of the singly reduced species of **1a**. The measurements were performed in ODCB containing 0.1 M TBAP using a 1 mm quartz cuvette; $c = 1.6 \times 10^{-3}$ mol/L.

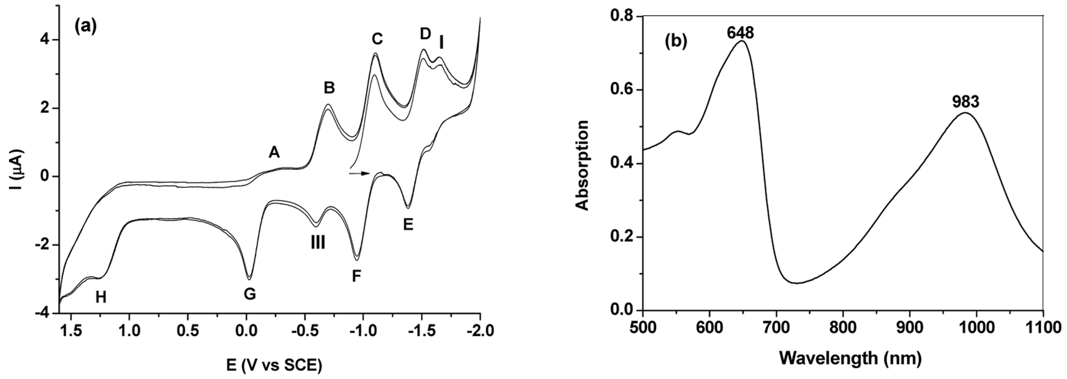


Figure 4. (a) In situ cyclic voltammograms of the doubly reduced species of **1a** ($c = 1.7 \times 10^{-3}$ mol/L) recorded in ODCB containing 0.1 M TBAP with a scan rate of 50 mV/s. (b) Vis−NIR spectrum of the doubly reduced species of **1a** ($c = 1.7 \times 10^{-3}$ mol/L).

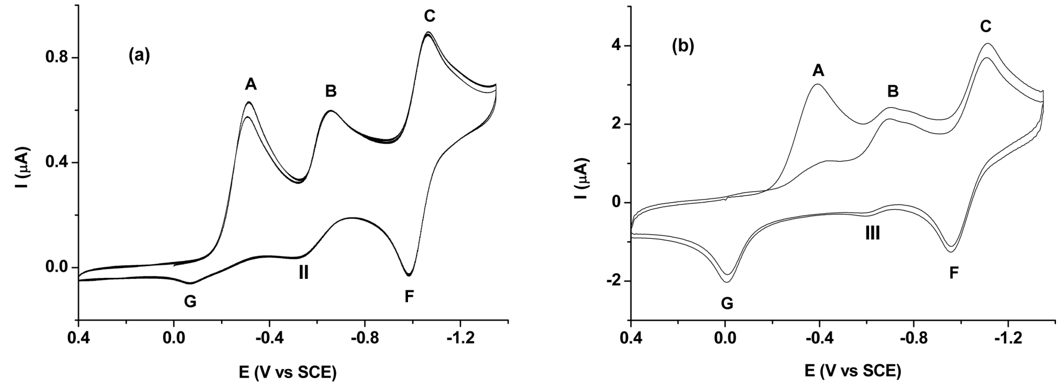


Figure 5. Cyclic voltammograms of compound **1a** (2×10^{-4} M) recorded in ODCB containing 0.1 M TBAP with a scan rate of (a) 20 and (b) 500 mV/s.

Further addition of electrons is expected to occur at each C_{60} cage of $^{-}O_3S(CH_3)PhC_{60}{-}C_{60}Ph(CH_3)SO_3^{-}$ at this potential, which may subsequently result in the cleavage of the dimeric species due to the repulsion between the two closely positioned negatively charged C_{60} cages.[9,12] Details of the electrolysis are described in the Experimental Section. The in situ cyclic voltammetry and vis−NIR spectroscopy were performed and are shown in Figure 4 to assess the obtained anionic species.

Figure 4a shows the in situ CV of the doubly reduced species produced after compound **1a** receives two electrons. The CV is essentially identical to that for the neutral **1a** by displaying the redox processes of B, C, D, E, F, G, and H, as shown in Figure 2, indicating that the doubly reduced species are stable on the time scale of electrolysis. However, the cathodic wave with E_{pc} at −0.30 V (A), which arises from the one-electron transfer to **1a** and is rather prominent in the CV of neutral **1a** (Figure 2), disappears in Figure 4a, suggesting that **1a** is completely consumed, in agreement with the formation of a C_{60} sulfonate derivative via a charge-induced ring-opening process. It is noteworthy that there also appear additional waves (labeled with I and III in Figure 4a) after peaks D and F, and become more prominent relative to peaks D and F when the electrolysis is carried out with a longer time (Figure S3, Supporting Information). The wave I (−1.65 V) is essentially identical to the hump after peak D shown in the cyclic voltammograms of **1a** (Figure 2), confirming that hump I is indeed caused by an unidentified species generated in situ after compound **1a** is reduced. As for the wave III (−0.59 V), it is also likely due to an unidentified species generated in situ after compound **1a** is reduced, since the potential difference is quite significant with respect to that of wave II (−0.54 V) observed in Figure 2, suggesting different origins for the oxidative waves II and III.

Figure 4b displays the vis−NIR spectrum of the doubly reduced species of **1a**. The spectrum shows strong absorption bands at 983 and 648 nm and is very similar to that of the dianion of a C_{60} oxazoline derivative (963 and 645 nm),[17] which also has a ring-opened structure with one electron located on the hetero addend and the other one on the C_{60} cage.[13b] This result, therefore, indicates that the electron is added at the C_{60} cage of the $^{-}O_3S(CH_3)PhC_{60}-C_{60}Ph(CH_3)SO_3^{-}$ dimer during further reduction, which subsequently leads to $^{-}O_3S(CH_3)PhC_{60}^{-}$ via the cleavage of the pivotal bond linking two C_{60} cages.

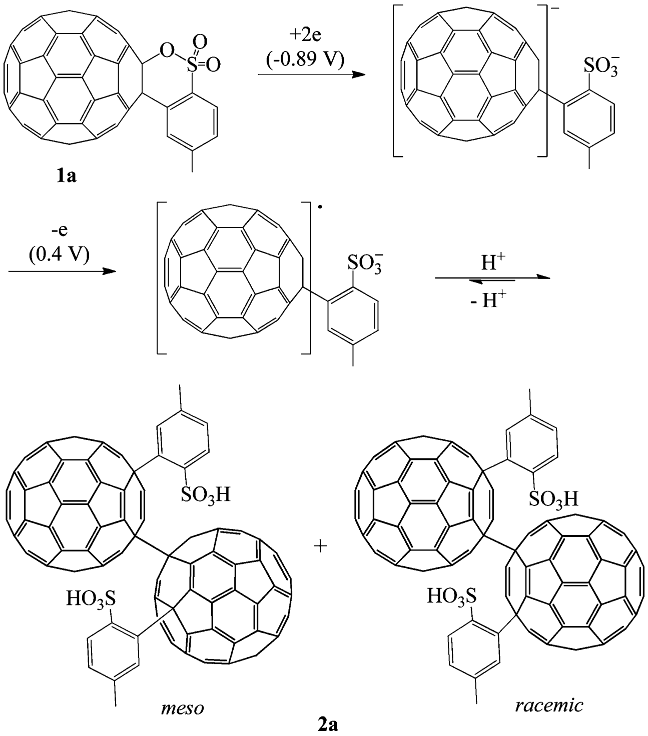
To gain more information on the irreversible redox processes, the CVs of **1a** in the range of 0.4 to −1.35 V at different scan rates were recorded, and two typical ones are shown in Figure 5. Compared to the CV at a slow scan rate (20 mV/s), peak A nearly disappears at the second cycle and peak G becomes much stronger at a much faster scan rate (500 mV/s), while the reversible redox couple of C/F remains almost unaffected. Such a result confirms that compound **1a** likely undergoes an irreversible chemical process after receiving one electron (A), and a new species, which cannot be reduced as **1a** with the potential at peak A, is formed via the oxidation of the resulting anionic species with the potential around 0.0 V, consistent with the conclusion that **1a** undergoes ring-opening after receiving one electron and forms dimeric species with the electron located at the sulfonate functionality rather than on the C_{60} cage, as drawn from the results of CPE and vis−NIR methods. In addition, a difference is shown between the CVs with different scan rates for the oxidative waves labeled with II and III. For the CVs with a scan rate of 20 mV/s, an oxidative wave appears at −0.54 V, which is identical to the one shown in Figure 2, but with a stronger intensity, confirming that peak II is caused by the diffused **1a** during the measurement due to a relatively slow scan rate. As for the CVs with a scan rate of 500 mV/s, where the diffusion process is eliminated, a very weak oxidative wave is exhibited with the peak potential of −0.59 V and resembles the wave observed after **1a** is bulk electrolyzed with a potential of −0.89 V, as shown in Figure 4a, confirming that peak III originates from an unknown anionic species after **1a** is reduced.

Compound **1a** was employed as the representative fullerosultone to demonstrate the electroreductive transformation. The generated doubly reduced species of **1a** can be used for further functionalization since fullerenyl anions readily react with electrophiles to provide various fullerene derivatives[7,10,11,13] or oxidized to afford fullerene dimers.[9,12,16]

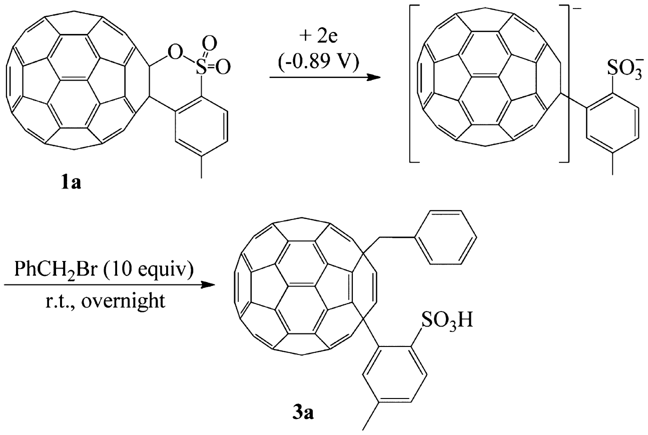
Electrooxidation of the doubly reduced species of **1a** at 0.40 V, followed by subsequent protonation during the workup process, provided the highly polar dimer $HO_3S(CH_3)PhC_{60}-C_{60}Ph(CH_3)SO_3H$ (**2a**) as a mixture of racemic and meso isomers in 86% yield (Scheme 1). The same dimer could be also obtained by the direct CPE of **1a** at −0.45 V, followed by a usual workup.

To trap the dianion of **1a**, 5 equiv of benzyl bromide was added, and the reaction mixture was stirred overnight at room temperature. After purification on a silica gel column, a highly polar 1,4-adduct **3a** was obtained in 88% yield (Scheme 2).[18]

Scheme 1. Synthesis of 2a via Controlled Potential Electrolysis of the Dianion Species of 1a



Scheme 2. Synthesis of 3a from the Reaction of the in Situ Generated Dianion of 1a with Benzyl Bromide



The HRMS (ESI) of **2a** gave a peak at *m*/*z* 890.0035, corresponding to the half molecular ion due to facile cleavage of the weak pivot bond[16a,b] and loss of H^+ from SO_3H ($C_{67}H_6SO_3^{-}$, calcd 890.0043), whereas **3a** showed the molecular ion of $[M - H]^{-}$ at *m*/*z* 981.0595 due to the easy loss of a proton from the sulfonic acid group ($C_{74}H_{13}SO_3$, calcd 981.0591). Both products **2a** and **3a** bear the highly polar sulfonic acid group and have very low solubility in carbon disulfide, a common solvent for fullerene derivatives, yet can be slightly dissolved in polar solvents, such as dimethyl sulfoxide (DMSO) and ethanol.

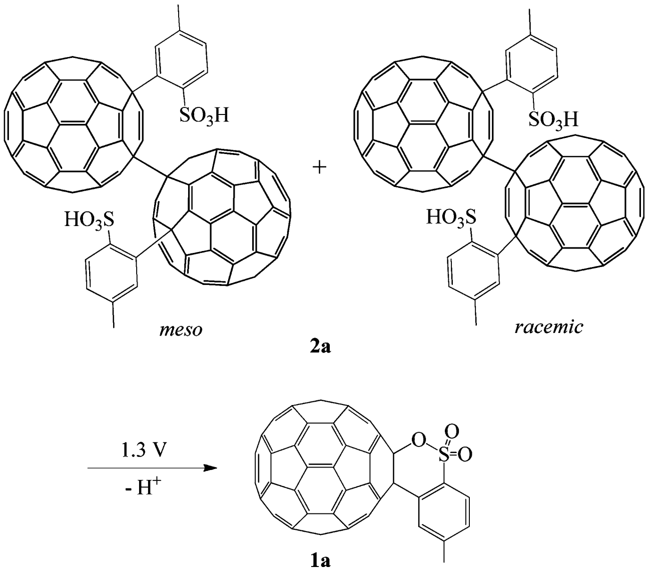
The ^1H NMR spectrum of **2a** in DMSO-d_6 shows a complex pattern due to the existence of the racemic and meso isomers. A similar phenomenon was observed in our previously reported dimer bearing sulfonate ester groups.[7] Unfortunately, a ^{13}C NMR spectrum of **2a** with a good signal/noise ratio could not be obtained because of the existence of the racemic and meso isomers and very limited solubility. The ^1H NMR spectrum of

3a in DMSO-d_6 displays the expected signals for the aromatic protons, and a singlet at 2.56 ppm for the methyl group. In addition, one AB doublet centered at 4.19 ppm (AB_q, $\Delta\nu$ = 52 Hz, J_{AB} = 12.8 Hz, 2H) is observed, consistent with the unsymmetrical 1,4-addition mode of the product. The ^{13}C NMR spectrum of **3a** in DMSO-d_6 exhibits 52 peaks, including some overlapping ones for the 58 sp^2-carbons of the fullerene skeleton, in agreement with its C_1 symmetry.

The formation and isolation of the singly bonded dimer **2a** and 1,4-adduct **3a** further confirm the sultone ring-opening via the C_{60}−O bond cleavage during the electroreductive process. It should be emphasized that the C_{60}−O bond cleavage of the oxazoline heterocycle[13b] or the C_{60}−H bond[9] usually occurs after two electrons are transferred to fullerene derivatives, whereas fullerosultones undergo the C_{60}−O bond cleavage once they receive only one electron, reflecting the higher stability of the sulfonate anion and the strong electronegativity of the sultone group.

Notably, the isolated neutral dimer **2a** can be converted back to the starting material **1a**, but an extremely positive oxidation potential of 1.30 V is demanded (Scheme 3). In addition, the anionic singly bonded dimer species generated by the CPE at −0.45 V can also be electrooxidized at 1.30 V to give **1a**. The identity of the recovered material is confirmed by the ^1H NMR spectrum (Figure S7, Supporting Information).

Scheme 3. Conversion to 1a from 2a via Controlled Potential Electrolysis



A plausible mechanism leading to various intermediates and products for the electrochemical processes, using **1a** as an example, is shown in Scheme 4. The first reduction occurs on the sultone group, which immediately undergoes ring-opening via the C_{60}−O bond rupture, and forms the anionic dimer **2a** via radical coupling reaction of $\mathbf{1a}^{-\bullet}$. Further reduction results in an electron transfer to the C_{60} cage of anionic **2a**, and subsequently leads to the pivotal bond cleavage of anionic **2a** and forms $\mathbf{1a}^{2-}$. 1,4-Adduct **3a** is obtained via the nucleophilic attack of the fullerenyl anion $\mathbf{1a}^{2-}$ to benzyl bromide. Further reductions of $\mathbf{1a}^{2-}$ result in the trianion radical $\mathbf{1a}^{3-\bullet}$ and tetraanion $\mathbf{1a}^{4-}$ still with the ring-opened structure. For the anodic processes, $\mathbf{1a}^{4-}$ affords $\mathbf{1a}^{3-\bullet}$ and then $\mathbf{1a}^{2-}$ by successively yielding an electron. Further oxidation of $\mathbf{1a}^{2-}$ with a potential at 0.40 V results in $\mathbf{1a}^{-\bullet}$, which quickly undergoes dimerization and generates the dianonic dimer species. Finally, by applying a potential that is positive enough to remove the negative charge on the sulfonate group, compound **1a** can be recovered. Therefore, the anodic peak at 1.13 V in the CV of **1a** (Figure 2) should be ascribed to the eletrooxidation of the SO_3^- group.

■ CONCLUSION

In summary, the charge-induced transformation reaction of [60]fullerosultones to [60]fullerosulfonic acids has been studied with the electrochemical method and vis−NIR spectroscopy. Ring-opening of the sultone moiety occurs upon electroreduction and results in a singly bonded C_{60} dimer with sulfonic functionalities. Further reduction decomposes the dimer species and affords the dianion intermediate of $^-O_3SArC_{60}{}^-$, which can react with an electrophile, such as benzyl bromide, to afford a 1,4-adduct containing the sulfonic group. In addition, the neutral and anionic singly bonded dimers can be converted back to the starting material [60]fullerosultone by removing the electron from the sulfonate group with an extremely positive potential. A possible pathway is proposed to explain the CV behaviors and product formation. The obtained fullerosulfonic acids may have potential applications in areas such as self-assembly and catalysis.

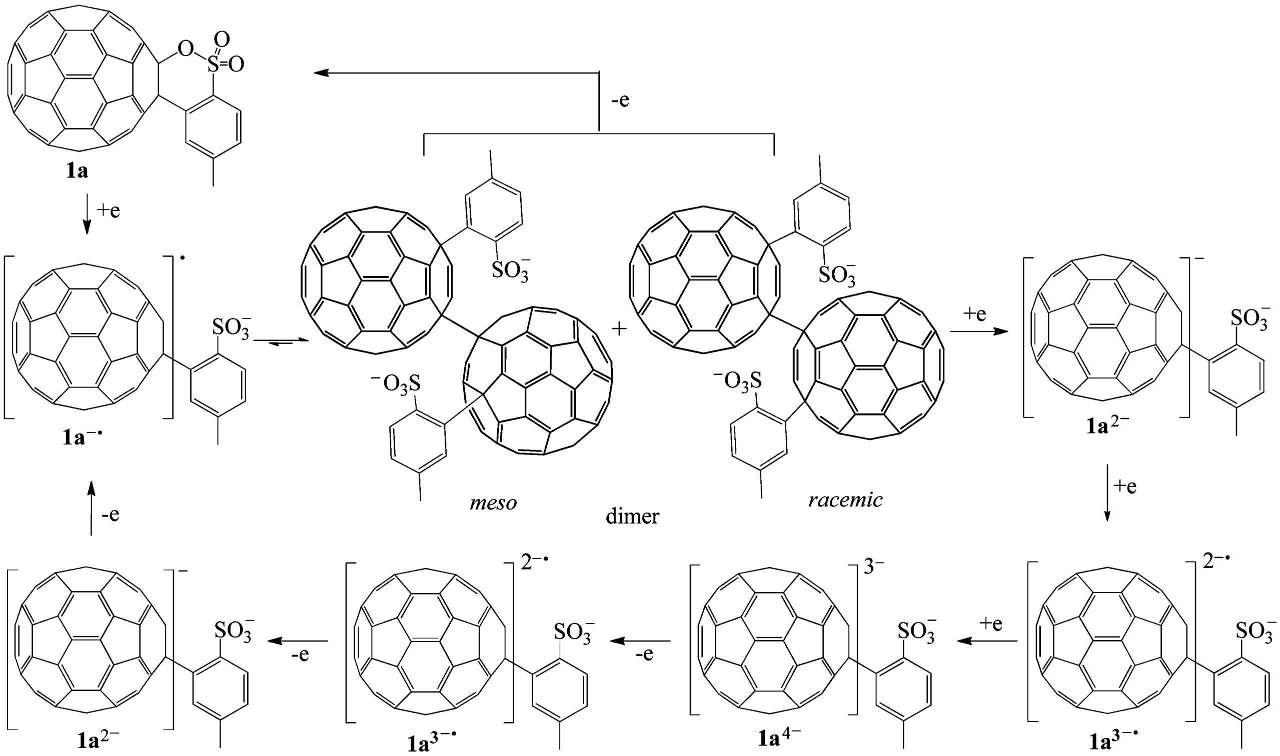
■ EXPERIMENTAL SECTION

General Methods. Compounds **1a**−**1c** were synthesized according to our previously reported procedure.[7] All CVs and electrochemical reactions were performed under an argon atmosphere. TBAP was recrystallized from absolute ethanol and dried in a vacuum at 313 K prior to use. Controlled-potential bulk electrolysis was carried out on a potentiostat/galvanostat using an "H"-type cell, which consisted of two platinum gauze electrodes (working and counter electrodes) separated by a sintered glass frit. A conventional three-electrode cell was used for CV measurements and consisted of a 2 mm diameter platinum disc working electrode, a platinum counter electrode, and a saturated calomel reference electrode (SCE). The SCE was separated from the bulk of the solution by a fritted-glass bridge of low porosity, which contained the solvent/supporting electrolyte mixture.

Cyclic Voltammetry of 1a−1c. [60]Fullerosultone (**1a**, **1b**, or **1c**) dissolved in anhydrous ODCB ($c = 2 \times 10^{-4}$ M) containing 0.1 M TBAP was added into an electrochemical cell under an argon atmosphere. CV measurements were then undertaken.

Vis−NIR Spectral Measurements of the Singly and Doubly Reduced Species of 1a. For the singly reduced species: 11.3 mg (12.7 μmol) of **1a** was electroreduced at −0.45 V vs SCE in 8 mL of anhydrous ODCB solution containing 0.1 M TBAP under argon. The electrolysis was stopped when the theoretical number of coulombs required for a full transfer of electrons was reached. A brownish red solution was obtained after the electrolysis, indicating that no negative charge is located on the C_{60} cage. The solution containing the singly reduced species of **1a** was transferred to a 1 mm quartz cuvette under argon and sealed with a rubber septum and Parafilm for the vis−NIR measurement. For the doubly reduced species: 12.2 mg (13.7 μmol) of **1a** was electroreduced at −0.89 V vs SCE in 8 mL of anhydrous ODCB solution containing 0.1 M TBAP. The electrolysis was stopped when the theoretical number of coulombs required for a full transfer of electrons was reached. A green-colored solution was obtained after the electrolysis, which is the typical color for C_{60} anionic species bonded with only one addend.[17,19] The resulting solution was transferred to a 1 mm quartz cuvette under argon and sealed with a rubber septum and Parafilm for the vis−NIR measurement. For the in situ CV, the platinum gauze working electrode was replaced with a platinum disk electrode, and the CV was then recorded immediately.

Scheme 4. Possible Intermediates and Products for the Electrochemical Processes of 1a



Synthesis of Singly Bonded C_{60} Dimer 2a. **1a** (19.8 mg, 22.2 μmol) dissolved in 40 mL of anhydrous ODCB containing 0.1 M TBAP was electroreduced at −0.89 V (vs SCE) under an argon atmosphere. The potentiostat was switched off after the electrolysis of **1a** was completed (4 h). The potential was then set at +0.40 V for electrooxidation until completion (4 h). The mixture was stirred overnight at room temperature (9 h). The solvent was removed with a rotary evaporator under vacuum. The residue was purified on a short silica gel column with $CS_2/CH_2Cl_2 = 5/1$ to remove the small amount of unreacted **1a**, and then eluted with CS_2/EtOH = 10/1. After solvent removal of the second fraction, and subsequent washing with acetone and petroleum ether separately for three times, it provided **2a** (17.1 mg, 86%) as an amorphous brown solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.56–7.05 (m, 6 H), 2.50–2.18 (m, 6 H); FT-IR ν/cm^{-1} (KBr) 2957, 2925, 2867, 1459, 1432, 1382, 1225, 1188, 1083, 1021, 822, 678, 566, 528; UV−vis λ_{max}/nm (log ε) ($CHCl_3$) 264 (4.36), 326 (3.95), 446 (3.57), 696 (3.23); HRMS (ESI-ion trap MS): m/z [M/2 − H]$^-$ calcd for $C_{67}H_6SO_3^-$, 890.0043; found, 890.0035.

Synthesis of 1,4-Bisadduct 3a. **1a** (20.8 mg, 23.4 μmol) dissolved in 40 mL of anhydrous ODCB containing 0.1 M TBAP was electroreduced at −0.89 V (vs SCE) under an argon atmosphere. The potentiostat was switched off after electrolysis of **1a** was completed (4 h). $PhCH_2Br$ (14 μL, 118 μmol) was then added into the solution, and the reaction mixture was stirred overnight (9 h) at room temperature. The same workup procedure as for **2a** afforded **3a** (20.3 mg, 88%) as an amorphous brown solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.70 (s, 1H), 8.30 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 7.4 Hz, 2H), 7.39 (d, J = 8.0 Hz, 1H), 7.32 (t, J = 7.4 Hz, 2H), 7.23 (t, J = 7.4 Hz, 1H), 4.25 (d, J = 12.8 Hz, 1H), 4.12 (d, J = 12.8 Hz, 1H), 2.56 (s, 3H); ^{1}H NMR (75 MHz, DMSO-d_6, all 1C unless indicated) δ 158.23, 157.05, 152.00, 151.69, 151.19, 149.08, 148.56, 148.47, 148.43, 148.28, 147.05 (2C), 146.92 (2C), 146.87, 146.84, 146.79, 146.67, 146.55, 145.45, 145.32, 145.18 (2C), 145.04, 144.90, 144.59, 144.53, 144.48, 144.28, 144.22, 144.12, 144.08, 143.88, 143.85, 143.79, 143.59, 143.43, 143.03, 142.94 (3C), 142.77, 142.72 (2C), 142.50, 142.44, 142.27, 142.22, 141.55, 140.48, 140.45, 140.12, 139.50, 139.04, 138.96, 138.71, 138.07, 136.79, 136.72, 136.28, 132.36 (aryl C), 131.32 (2C, aryl C), 131.21 (aryl C), 130.97 (aryl C), 128.80 (aryl C), 128.46 (2C, aryl C), 127.50 (aryl C), 60.81 (sp^3-C of C_{60}), 55.02 (sp^3-C of C_{60}), 46.47 (CH_2), 21.56 (CH_3); FT-IR ν/cm^{-1} (KBr) 2956, 2923, 2856, 1452, 1430, 1383, 1217, 1186, 1159, 1083, 1018, 819, 685, 566, 527; UV−vis λmax/nm (log ε) (CHCl3) 256 (4.07), 327 (3.90), 447 (3.63), 696 (2.78); HRMS (ESI-ion trap MS): m/z [M − H]$^-$ calcd for $C_{74}H_{13}SO_3^-$, 981.0591; found, 981.0595.

Conversion to [60]Fullerosultone 1a from the Singly Bonded C_{60} Dimer 2a. A 10.0 mg (5.6 μmol) portion of **2a** was electrooxidated at 1.30 V vs SCE in 8 mL of anhydrous ODCB solution containing 0.1 M TBAP under an argon atmosphere for 15 h. The same workup procedure as for **2a** afforded **1a** (1.7 mg, 17%) along with unreacted **2a** (6.9 mg, 69%).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CVs of **1b**, **1c**, and **1a**$^{2-}$, and NMR spectra of **2a**, **3a**, and restored **1a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful for the financial support from the National Natural Science Foundation of China (21132007, 20972145 for G.-W.W., and 21172212, 20972150 for X.G.) and the National Basic Research Program of China (2011CB921402).

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