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Efficient Synthesis of Polyhydroxylated Fullerene Derivatives *via* Hydrolysis of Polycyclosulfated Precursors

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Novel cyclosulfation chemistry for the functionalization of C_{60} and its analogs is described. The cyclosulfation of C_{60} is accomplished in neat fuming sulfuric acid at 55−60 °C under N_2 to afford polycyclosulfated fullerene derivatives. Hydrolysis of these derivatives, either in the presence of water at 85−90 °C or in aqueous NaOH solution at ambient temperature, gives the corresponding polyhydroxylated fullerenes (fullerenols) in high yield. The functional characteristics and number of sulfate moieties per C_{60} molecule in the polycyclosulfated fullerene precursors, and the structure of fullerenols, were determined primarily by the analysis of the TGA−mass spectrum and the sulfur (S_{2p}) and carbon (C_{1s}) absorption bands in the XPS spectrum. We resolved an average of 10 to 12 hydroxyl addends in the chemical structure of fullerenols that can be correlated to the structure of polycyclosulfated fullerene precursors containing 5 to 6 cyclosulfate units. The cyclosulfation chemistry is, presumably, initiated by a one-electron oxidation of C_{60}, followed by the attack of anionic sulfate species on the resulting cationic C_{60} radical intermediates, to form the corresponding hydrogen sulfated C_{60} radicals. Further oxidation and intramolecular cyclization of this hydrogen-sulfated C_{60} yields the polycyclosulfated C_{60} products.

Introduction

The high electron-ionization threshold (>7.61 V)[1] of neutral C_{60} molecules has hindered attempts to generate a higher oxidation state of C_{60}. Even the first electronic oxidation of C_{60} is not reversible in neutral solution, owing to the low chemical stability of the resulting cationic radical. The stability of the C_{60} radical cation is significantly enhanced in strongly acidic medium. A respectable intensity of spins, attributed to the C_{60} cationic radical, was detected in EPR spectroscopic studies of C_{60} molecules dissolved in fuming sulfuric acid ($H_2SO_4-SO_3$)[2-4] and magic acid (FSO_3H-SbF_5).[4] Despite the resistance of C_{60} to electronic oxidations in organic solvents, the conjugated fullerenic structure is susceptible to attack by certain electrophilic reagents. This enables the use of the olefinic moieties of the C_{60} cage molecule as reactive electron-rich sites for reactions. This chemistry certainly enriches the scope of synthetic methodology for fullerene derivatization and provides practical routes for the preparation of C_{60} derivatives with multiple polar functional groups. Early examples of electrophilic approaches are represented by the halogenation reaction of C_{60} molecules, yielding highly fluorinated,[5] brominated,[6] and chlorinated[7] derivatives, and the arene addition of benzene and toluene in the presence of aluminum chloride,[8] as summarized in recent reviews by Taylor[9] and Miller.[10]

Recently, we have demonstrated versatile electrophilic additions that functionalize C_{60} fullerene molecules. Our techniques involve aqueous acid chemistry[11] and nitronium chemistry,[12] in the presence of either a mixture of sulfuric acid and nitric acid or nitronium tetrafluoroborate, respectively. Both methods are suitable for the synthesis of water-soluble polyhydroxylated fullerene derivatives (fullerenols, **1**). Nitronium tetrafluoroborate was used in the latter case as an electrophilic reagent to activate olefinic bonds of fullerene prior to the in situ nucleophilic addition of mild nucleophiles. The chemical structure of fullerenol prepared from these two procedures was determined to consist of several hemiketal carbons (**2**), each linked as an enol−ether and incorporated as a part of the expanded fullerene cage skeleton.[13] These particular functional moieties can be viewed as hydroxylated fullerene oxides.[14] Fullerenols containing hemiketal groups were found to be rather sensitive to acid, leading to the reversible interconversion between

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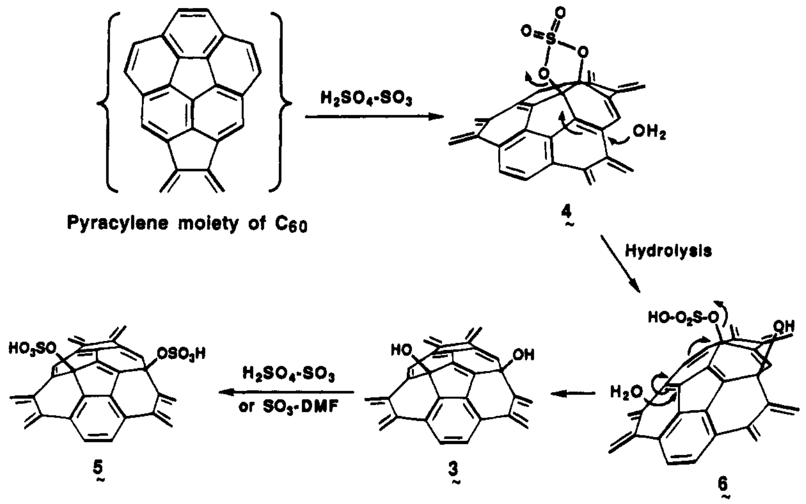
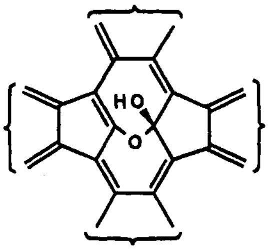
Scheme 1



the hemiketal and the corresponding hydroxyl ketone, upon variation of the pH of the solution.

In the present paper, we report that the hydrolysis of polycyclosulfated or hydrosulfated fullerene precursors[15] with water at 85 °C affords the second type of fullerenol **3**, which contains no hemiketal and enol−ether structures, as shown in Scheme 1. Fullerenols **3**, with a simple chemical structure of 60 carbons and multiple hydroxyl groups, exhibit enhanced stability in acidic media at ambient temperature and remarkable solubility in organic solvents such as dimethylformamide, dimethyl sulfoxide, and tetrahydrofuran.



2 (The representative hemiketal moiety of Fullerenols 1)

Results and Discussion

Oleum ($H_2SO_4-SO_3$ (28%)) is one of the most widely used sulfonating or sulfating agents for unsaturated hydrocarbons. The high reactivity of sulfur trioxide with olefins often results in sulfonation across carbon−carbon double bonds, which converts an olefin into a mixture of sultones and alkane sulfonic acids.[16] In the presence of concentrated sulfuric acid, the direct sulfation of an alkene, catalyzed by the electrophilic proton, to form a $C-OSO_3H$ moiety, is also possible. It is, then, reasonable to predict that the reaction of C_{60} with oleum may proceed to result in either the sulfonation or the sulfation of fullerenic C=C bonds. The reaction of C_{60} with oleum was carried out at 65 °C under an inert atmosphere. Upon exposure of C_{60} to fuming sulfuric acid, a partially suspended green solution was immediately obtained, indicating the existence of organic radicals. Detection of these radicals in the EPR spectrum[2-4] provided clear evidence of a reaction mechanism involving the electronic oxidation of C_{60} to initially form its cationic radical. Within 5 h, visible change from a dark green to a brown suspension was observed, which revealed the limited stability of C_{60} cationic radicals in this reaction medium. This instability enhances the reactivity of the C_{60} radical cation toward the addition of sulfuric acid. The acid suspension was added dropwise to anhydrous diethyl ether, resulting in the precipitation of solid orange products **4**. Hydrolysis of **4**, either in water at 85 °C or in aqueous alkaline solution at ambient temperature, afforded fullerenols **3** in an overall yield of roughly 80% from C_{60}.

Characterization of Cyclosulfatic Structure in 4. The infrared spectrum of **3** (Figure 1e) displayed a strong hydroxyl absorption band at 3317 cm^{-1} and three additional bands at 1623, 1381, and 1049 cm^{-1}, in a pattern similar to that of **1**. Interestingly, both the elemental analysis and the X-ray photoelectron spectroscopic (XPS) measurements of fullerenol **3** gave a low sulfur content, less than 0.3% by weight and 0.1% by atomic ratio, respectively. In addition, no absorption in the C−S region (e.g., 500−700 cm^{-1}) of the Raman spectrum of **4** was observed. These results clearly exclude direct sulfur bonding on fullerenic carbons, such as sulfonyl or sulfonic acid functional groups with $C-SO_2-$ linkages, from the structure of **4**. Thus the possible polar functional moieties in **4** are sulfate ($C-OSO_2-O-$) or sulfinate ($C-OSO-O-$) groups. Compound **4** exhibited relatively weak, broad alkanolic hydroxyl and hydrogen sulfatic hydroxyl absorptions, centered at 2920 and 2400 cm^{-1}, respectively, in its infrared spectrum, as shown in Figure 1c. The spectrum showed two strong absorptions centered at 1426 and 1233 cm^{-1}, corresponding to assymmetric $RO-SO_2-OR$ stretch and symmetric $RO-SO_2-OR$ stretch bands, respectively. Both the absorption intensities and the peak positions of these two bands were found to be in good agreement with those of $-SO_2-$ absorptions (1386 and 1195 cm^{-1}) in the spectrum of diethyl sulfate, indicating prominent sulfate entities in the structure of **4**, presumbly a polycyclosulfated C_{60} derivative. The close resemblance of the overall spectrum of **4** (Figure 1c) to that of diethyl sulfate (Figure 1b) in the region of 500−1500 cm^{-1}, and its deviance from the spectrum of

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(14) Without the stabilization of hemiketal function, fullerene oxide preferentially equilibrates in the epoxide form. Creegan, K. M.; Robbins, J. L.; Robbins, W. K.; Millar, J. M.; Sherwood, R. D.; Tindall, P. J.; Cox, D. M.; Smith, A. B.; McCauley, J. P.; Jones, D. R.; Gallagher, R. T. *J. Am. Chem. Soc.* **1992**, *114*, 1103.

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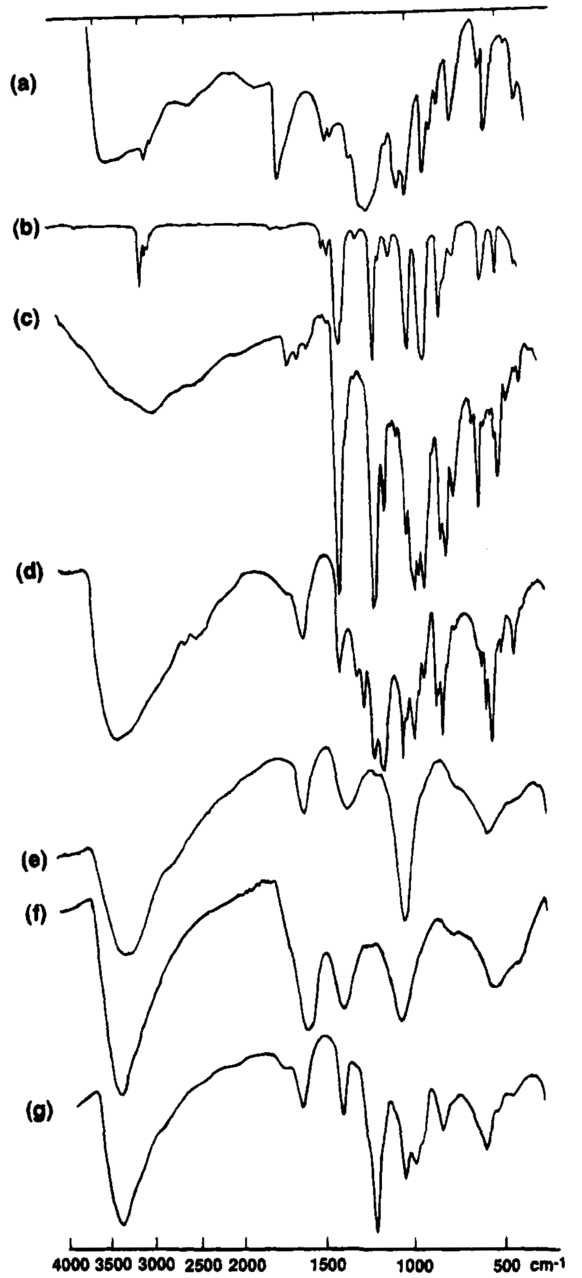

Figure 1. Infrared spectra of (a) 2-hydroxyethyl hydrogen sulfate, (b) diethyl sulfate, (c) polycyclosulfated C_{60} derivatives **4**, (d) partially hydrolyzed polycyclosulfated C_{60} derivatives **6**, (e) fullerenols **3** prepared by the reaction of **4** or **6** in H_2O at 85 °C, (f) fullerenols prepared by the reaction of **4** or **6** in NaOH/H_2O at 85 °C, and (g) compound **5** prepared from the reaction of **3** with $H_2SO_4-SO_3$.

2-hydroxyethyl hydrogen sulfate[17] (Figure 1a), provides additional support for this structure. In Figure 1a, a weak assymmetric band and a strong, broad symmetric C—O*SO*$_2$OH absorption band of 2-hydroxyethyl hydrogen sulfate were centered at 1454 and 1227 cm^{-1}, respectively. The ^{1}H NMR spectrum of **4** in DMF-d_7 showed a weak, broad peak centered at roughly δ 14.5, corresponding to acidic protons. This suggested the presence of a small number of hydrogen sulfate O—SO$_2$—OH groups in the structure of **4**. The ^{13}C NMR spectrum of **4** in DMF-d_7 (Figure 2c) exhibited a broad peak centered at δ 148.0 and weak, broad peaks between δ 70.0 and 80.0, corresponding to olefinic carbons and monooxygenated carbons, respectively. The spectrum was nearly identical to that of fullerenol **3** in the same solvent, showing only a slight shift of hydroxylated carbon peaks to δ 70–85 (Figure 2d). The lack of carbon peaks in the δ 160–175 region, which would correspond to the chemical shift of vinyl ether carbons, in spectra 2c and 2d pointed to the absence of hemiketal functional moieties **2** in fullerenol **3**., This differentiates the chemical structure of **3** from fullerenol **1**, which has been synthesized from by the aqueous acid[11] or the nitronium reaction of C_{60}.[12] Unlike fullerenol **1**, the treatment of **3** with dilute HCl (2 N) at ambient temperature gave products showing a nearly identical infrared spectrum to that of the starting fullerenol **3**, with no carbonyl absorptions.[13] As expected, the simple polyhydroxylated fullerene structure of **3** showed a single strong peak centered at δ 4.85, corresponding to hydroxyl protons in the ^{1}H NMR spectrum (Figure 2a). These protons were further substantiated by deuterium exchange, as shown in Figure 2b. A clear disappearance of the hydroxyl proton (C—O*H*) peaks was observed, along with the appearance of a new, sharp peak due to water protons, at δ 4.0. We found that polycyclosulfated C_{60} derivatives **4** readily undergo partial hydrolysis in wet diethyl ether solution, in the presence of residual acids, to afford the corresponding hydroxyl hydrogen sulfated derivative **6**. To minimize the hydrolysis of fullerenic cyclosulfate, the complete removal of residual acids and the use of vigorously dried solvent in the isolation and purification procedure, under an inert atmosphere, are

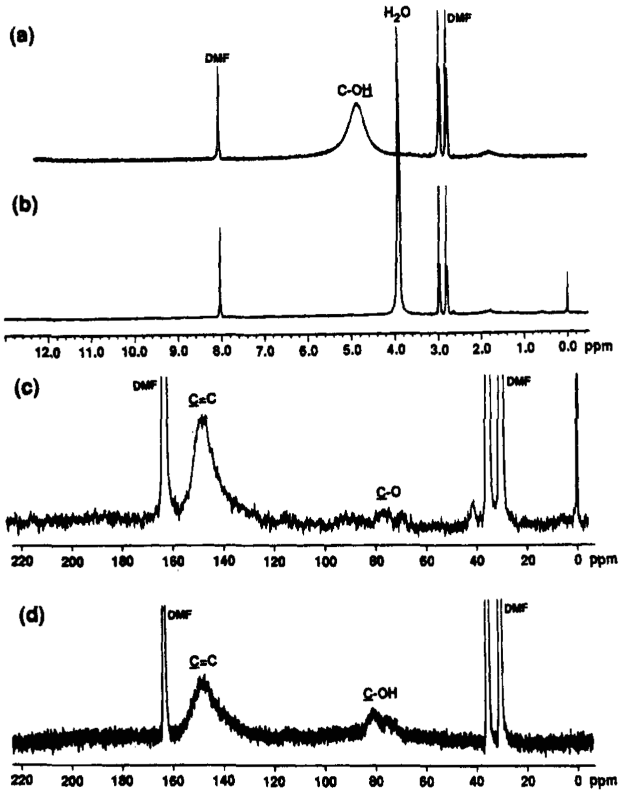

Figure 2. ^{1}H NMR spectra of (a) fullerenols **3**, derived from the hydrolysis of polycyclosulfated C_{60}, in DMF-d_7, (b) the solution (a) treated with D_2O, showing disappearance of a peak centered at δ 4.85 due to the deuterium exchange of hydroxyl protons, and the ^{13}C NMR spectra of (c) polysulfated C_{60} derivatives **4** and (d) fullerenols **3**.

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[17] 2-Hydroxyethyl hydrogen sulfate was synthesized from the reaction of sulfur trioxide–DMF complex with an excess of ethylene glycol in CH_3CN at 65 °C. Infrared spectrum of 2-hydroxyethyl hydrogen sulfate: v_{max} (KBr) 3320 (br, -OH), 2947, 1706 (s), 1454, 1227 (s), 1060, 1014, 917, 776, and 585 cm^{-1}.

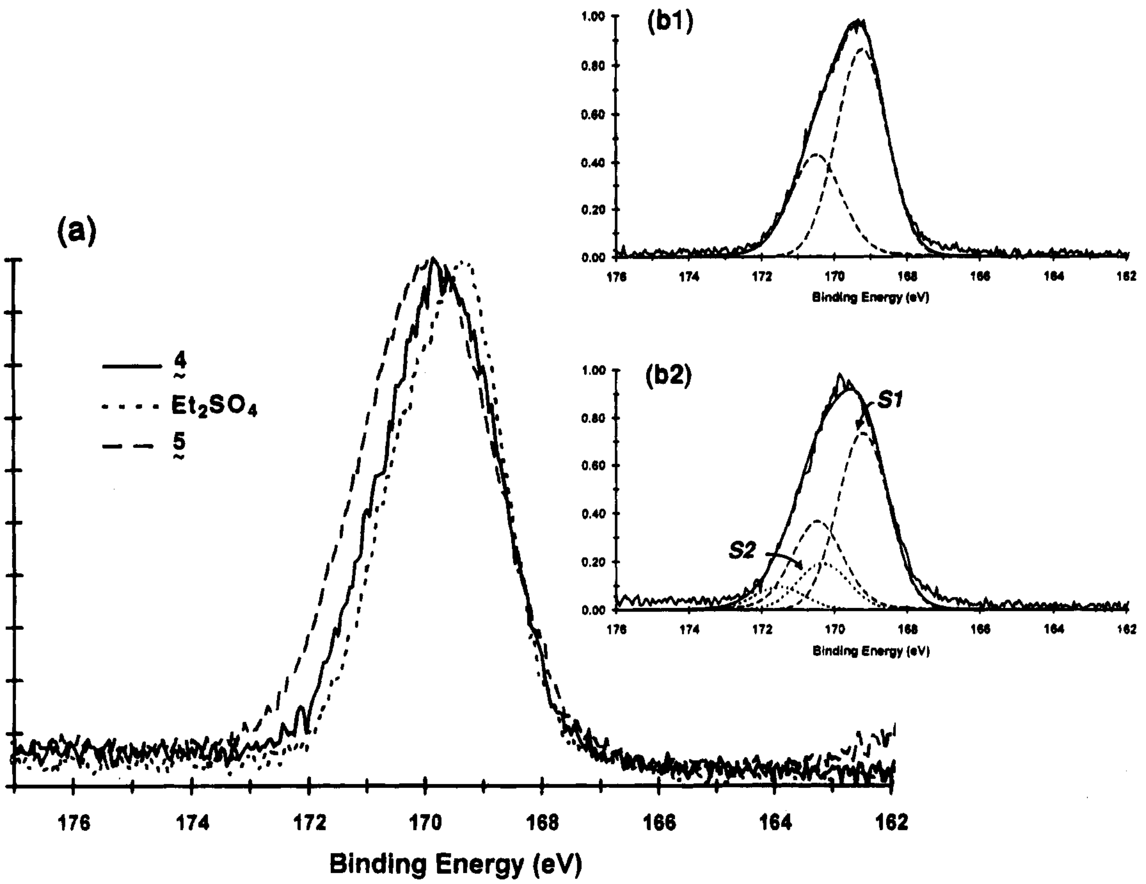

Figure 3. X-ray photoelectron (XPS) spectra of the S_{2p} binding energy of (a) polycyclosulfated fullerene derivatives **4**, Et_2SO_4, and partially hydrogensulfated fullerenol derivatives **5**, (b1) Et_2SO_4, and (b2) polycyclosulfated fullerene derivatives **4**. In Figures b1 and b2, the curve-fitting analysis (dotted lines) is indicated inside the experimental curves (solid lines). The binding energy in the spectra is not calibrated.

necessary. Predictably, the infrared spectrum of partially hydrolyzed derivatives **6** (Figure 1d) showed a sharp decrease in the RO—SO_2—OR absorption bands at 1426 cm^{-1}. To further substantiate and differentiate the characteristic IR absorptions of the fullerenic hydroxyl hydrogen sulfate from those of the fullerenic dialkyl sulfate, fullerenol **3** was allowed to react with H_2SO_4–SO_3 or SO_3–DMF complex at ambient temperature to afford polyhydroxy hydrogen sulfated fullerene derivatives **5**, as shown in Scheme 1. Compound **5** displays an infrared spectrum (Figure 1g) with absorption bands similar to those of **6**, with a strong symmetric O—SO_2—OH absorption at 1225 cm^{-1} and a weak assymmetric O—SO_2—OH absorption at 1413 cm^{-1}. This confirms the presence of hydrogen sulfate moieties in the structure of **6**.

We found that sulfur (S_{2p}) peaks with a maximum absorption centered at the binding energy of 169.8 and 169.9 eV in the XPS spectrum of **4** and **5**, respectively, were similar to peaks of the sulfur function in diethyl sulfate (169.4 eV). These data further proved that the sulfur atoms in molecules **4** and **5** are in the same oxidation state as that of sulfur in diethyl sulfate. By utilizing the resolved two S_{2p} peaks of diethyl sulfate (Figure 3b1) obtained from the curve-fitting analysis as a reference, we are able to fit two sets of sulfur peaks (S1 and S2) into the experimental S_{2p} absorption band of compound **4** as depicted in Figure 3b2.[18] These two sets of sulfur peaks, S1 and S2, corresponding to the absorptions of different sulfur atoms in dialkyl sulfate and the hydrogen sulfate function, respectively, showed an intensity ratio of roughly 4:1. The ratio revealed a much higher content of cyclosulfate moieties than hydrogen sulfate moieties in the structure of **4**, consistent with the infrared data. The FAB mass spectroscopic studies were carried out using the liquid secondary ion mass spectrometry (LSIMS) technique. The positive ion (Figure 4) and the negative ion (Figure 5) FAB mass spectra of polyhydroxy hydrogen sulfated C_{60} derivatives, cast from DMF solution, showed maximum relative intensities at peaks of *m/z* 721 and 720, respectively, corresponding to the C_{60} ion fragmentation. Interestingly, the spectra were comprised of groups of peaks due to consecutive weight increases of 16, 18, or 32 mass units, corresponding to the gain of an oxygen atom, a water molecule, or a sulfur atom, respectively, to the preceding ion fragment. This observation agrees well with the structure of partially hydrolyzed polycyclosulfated C_{60} derivatives. The highest detectable masses in the fragmentation groups were found to be *m/z* 1129 and 1056 in the positive and negative ion FAB mass spectra, respectively.

Determination of Hydroxyl Quantity in Structure of Fullerenol 3. The presence of carbon–oxygen covalent bonds on the fullerene derivatives was easily

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[18] The sulfur binding energy of diethyl sulfate was found to center at 169.3 eV (66.6% and FWHM = 1.65 eV) and 170.5 eV (33.3% and FWHM = 1.65 eV) in a ratio of 2:1, whereas the curve-fitting analysis of the sulfur peak in the XPS spectrum of **4** gave four peaks (two sets) with a binding energy centered at 169.2 eV (52.9% and FWHM = 1.65 eV) and 170.3 eV (26.5% and FWHM = 1.65 eV) as the first set and at 170.5 eV (13.7% and FWHM = 1.65 eV) and 171.5 eV (6.8% and FWHM = 1.65 eV) as the second set.

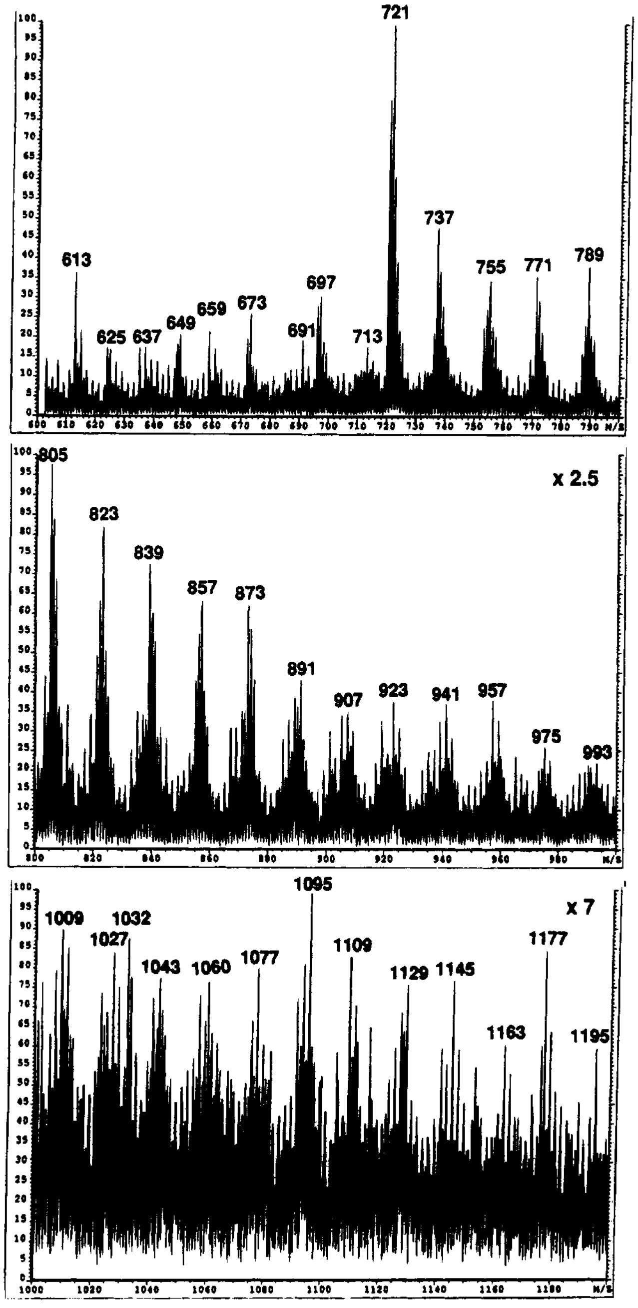

Figure 4. Positive ion FAB mass spectra of polysulfated fullerene derivatives prepared from pure C_{60}, using the LSIMS technique.

validated by the X-ray photoelectron spectroscopic measurements. Compound **4** and fullerenol **3** showed similar peak profiles of carbon absorptions. Absorptions with a binding energy higher than 285.5 eV, corresponding to oxygenated carbons, are distinct from those of nonoxygenated carbons, permitting the reasonably accurate curve-fitting analysis of the carbon peaks shown in Figure 6. Since the reaction involved no hydrocarbon-containing reagents or solvents other than fullerene molecules, the carbon peaks in the spectrum should correspond solely to the absorption of carbon elements in fullerene derivatives. Therefore, the analysis of carbon peaks makes a fair determination of the average number of hydroxyl addends in each fullerene molecule. In the analysis, we assumed that the first-fitted carbon peak matches the lower binding energy region of the experimental curve and then inserted the second carbon peak to fit the rest of the absorptions in the higher binding energy region. The spectrum of **4**, shown in Figure 6a, was in good agreement, with a strong absorption band of C_{1s} binding energy, corresponding to nonoxygenated carbons (*C*—C), centered at 284.2 eV (76.6%) with a full width at half maximum (FWHM) of 1.6 eV, and the second absorption band, corresponding to monooxygenated carbons (*C*—O), centered at 286.3 eV (19.4%) with a FWHM of 2.0 eV. The separation between these two bands is in the range of 2.1 eV. Given that **4** was a solid in a heterogeneous mixture, a slightly larger FWHM of 1.6–2.0 eV for each fitted peak was expected. The atomic ratio between nonoxygenated carbons and monooxygenated carbons was found to be 48:12, indicating the presence of 12 oxygen-bearing carbons in the polysulfated C_{60} derivative **4**. The spectrum of fullerenols, shown in Figure 6b, displayed a nonoxygenated carbon band and a monooxygenated carbon band, centered at 284.2 (74.6%) and 286.1 eV (20.2%), with FWHM of 1.6 and 1.9 eV, respectively. The atomic ratio between nonoxygenated carbons and monooxygenated carbons of **3** was found to be 47:13, in close resemblance to that of **4**. Further esterification of **3**, using trifluoroacetic anhydride as a reagent, afforded fullerenol trifluoroacetylates **7**. The XPS data of **7** (Figure 6c) showed a clear four-band spectrum with three maximum binding energies centered at 284.2 (68.7%, FWHM of 1.7 eV), 286.3 (19.9%, FWHM of 1.9 eV) and 288.8 eV (7.7%, FWHM of 2.4 eV). The latter corresponds to the binding energy of ester carbons. The binding energy of fluorinated carbons was found to be 292.0 eV (3.7%, FWHM of 1.7 eV), which can be distinguished easily from the other carbon peaks. The atomic ratio of nonoxygenated carbons to monooxygenated carbons to fluorinated carbons of **7** was found to be 47:13:2.5, which agrees reasonably well with a partially esterified fullerenol structure containing 9 hydroxyl and 3 trifluoroacetoxy groups, on average.[19] These results consistently support an average structure of fullerenols **3** that is a fullerene derivative with a maximum of 12 hydroxyl addends. In combination with elemental analysis data and the spectroscopic measurements, we concluded that the chemical structure of compound **4** can be assigned as a polysulfated fullerene derivative containing a maximum of 5–6 cyclosulfate units. Partial hydrolysis of **4** readily occurred during the workup procedure, as revealed by chemical evidence of hydroxyl and hydrogen sulfate functions.

Since the partially hydrolyzed compound **6** contains acidic protons in hydrogen sulfate moieties, we carried out the complexation reaction of **6** with an excess of 4-(dimethylamino)pyridine (DMAP) in DMF solution and precipitated the resulting **6**–DMAP adduct. Elemental analysis of this adduct revealed a C:S:N ratio of 39:1:2 corresponding to 1.9 DMAP units per C_{60} molecule. The ^{1}H NMR spectrum of the **6**–DMAP adduct in DMSO-d_6-DMF-d_7 solution (dried over molecular sieves) showed distinguishable peaks at δ 8.13, 6.62, and 2.98, corresponding to the aromatic α protons, β protons, and methyl protons in the DMAP moieties in addition to the hydroxyl proton peak at δ 3.34. The latter peak can be clearly identified by deuterium exchange with D_2O. From the integration ratio between the aromatic protons and hydroxyl protons, we estimated the presence of more than 10 hydroxyl groups in the adduct of **6**–DMAP.

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[19] About 2.7 atomic % of carbons with an oxidation state higher than that of the monooxygenated carbons may be contributed from impurities. XPS (atomic %) of **5**: C, 74.2; O, 16.0; F, 9.8

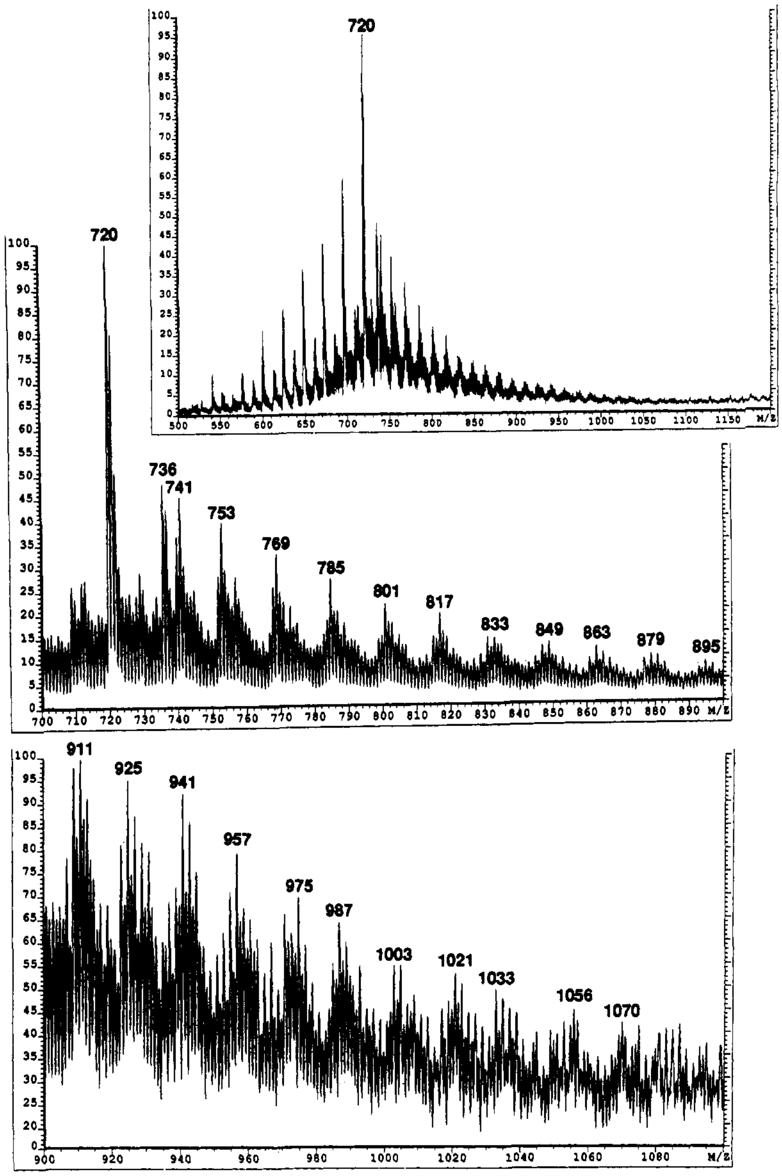


Figure 5. Negative ion FAB mass spectra of polysulfated fullerene derivatives prepared from pure C_{60}.

These results also support the above structural assignment of fullerenol **3**.

Thermal Analysis of Polycyclosulfated Derivatives 4. The chemical characteristics and number of sulfate moieties per C_{60} molecule were further confirmed by a thermogravimetric analysis (TGA)–mass spectroscopic study. In the TGA–MS spectrum of polycyclosulfated derivatives **4** (Figure 7), a clear desorption of the physically absorbed water molecules at temperatures below 180 °C, with a total weight loss of 4%, was detected. It was then followed by a strong, sharp, thermal evolution of SO_2 molecules at an onset temperature of 187 °C that reached a maximum at 245 °C. The observed SO_2 evolution from compound **4** confirmed the presence of cyclic sulfate $-O-SO_2-O-$ entities in **4**. The thermal reaction obviously caused the cleavage of S—O bonds. Other gases evolved in this temperature range, including CO_2 and CO. The detection of CO_2 molecules may reveal the occurrence of a structural rearrangement of radical intermediates, in conjunction with the SO_2 elimination. Since the intensity of CO_2 was significantly lower than that of SO_2, and the intensity of CO was negligible, most of the material weight loss (28%) at temperatures between 190 and 310 °C can be correlated to the quantity of SO_2 molecules eliminated. This allowed an estimation of slightly less than 6 cyclosulfate units per C_{60} molecule in the chemical structure of **4**, consistent with the XPS data.

Consideration of Reaction Mechanism. Concerning the reaction mechanism, one plausible reaction pathway predicts the attack of sulfur trioxide on the hexagon moiety of C_{60}, forming the 1,2 (α) or 1,4 (δ) sultone derivative **8**, as do unsaturated hydrocarbons normally in their reaction with SO_3, illustrated in Scheme 2. Hydrolysis of compound **8** should give fullerenic hydroxy sulfonic acid **9**, which contains an obvious covalent C—S bond. Therefore, the absence of detectable sulfur atoms, according to both the elemental analysis and the XPS measurement of the hydrolyzed products, allowed us to conclude that the treatment of C_{60} with $H_2SO_4-SO_3$ did not lead to the formation of sultone **8**. Instead, we propose that the primary function of sulfur trioxide in this case is to promote the one-electron oxidation of fullerene molecules, forming a cationic C_{60} radical as depicted in Scheme 3. Trapping of the C_{60} cation **10** by anionic HSO_4^- or $HS_2O_7^-$ (a combination of HSO_4^- and SO_3) species affords the corresponding hydrogen sulfated C_{60} radical **11**. Since the open allylic

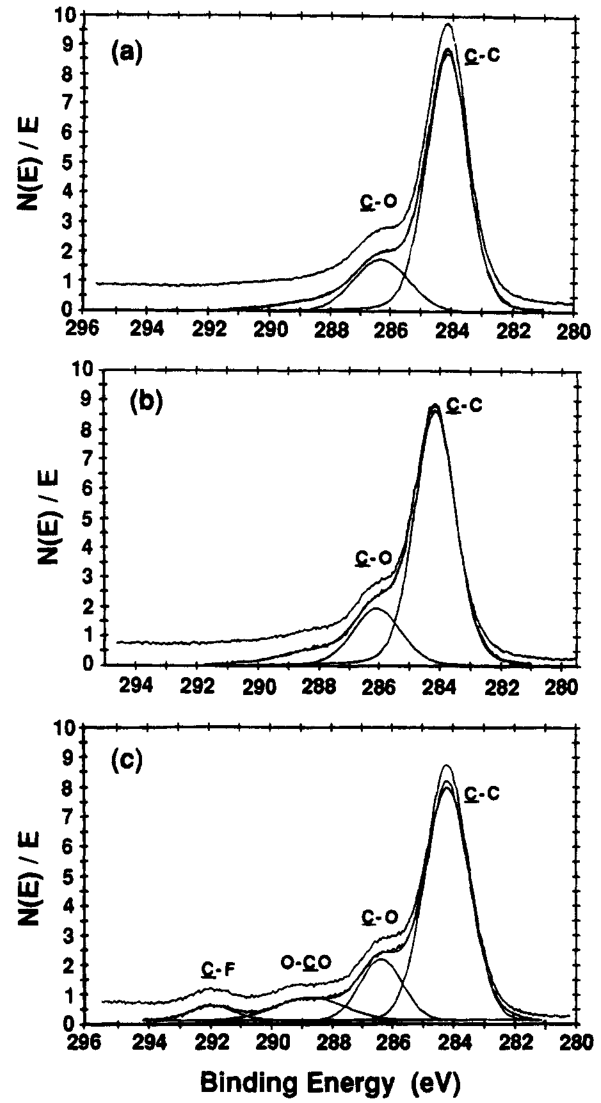


Figure 6. X-ray photoelectron (XPS) spectra of the C_{1s} binding energy of (a) polycyclosulfated fullerene derivatives **4**, (b) fullerenols **3**, and (c) partially esterified trifluoroacetylfullerenol derivatives **7**. The curve-fitting analysis is indicated inside the experimental curves. The binding energy in the spectra is not calibrated.

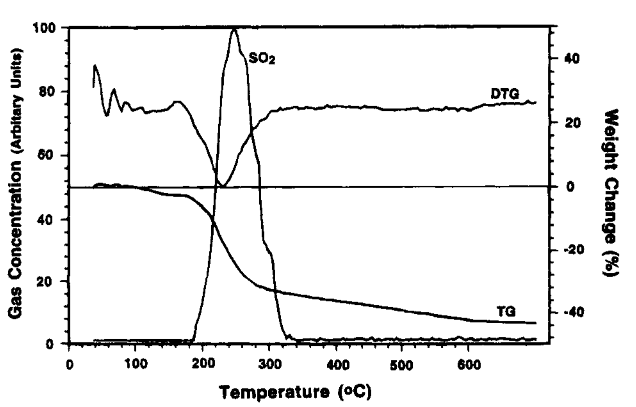
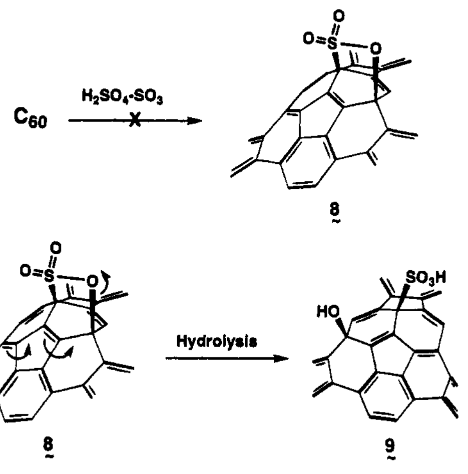


Figure 7. TGA–mass spectroscopic data of polycyclosulfated fullerene derivatives **4** showing the percent weight change (TG), differential weight change (DTG), and the intensity of SO_2 gas evolved upon the thermal treatment at a rate of 6 °C/min.

Scheme 2



carbocationic C_{60} radicals **10** are prone to rearrange, the formation of various isomeric products is feasible. Further electron oxidation of the radical intermediate **11** yields the corresponding cationic hydrogen sulfated C_{60} **12**. Intramolecular cyclization of intermediate **12**, via the elimination of one proton, produces the 1,2- or 1,4-cyclosulfated C_{60} derivatives **4**. Unlike the organic sulfonates, which exhibit remarkable hydrolytic stability even after prolonged heating, cyclosulfated C_{60} derivatives **4**, which have a $-C-OSO_2-$ linkage, are readily susceptible to acid hydrolysis. The hydrolysis rate of cyclic sulfates can be 20 times as fast as that of open-chain dialkyl sulfates.[20] Hydrolysis proceeds mainly by a C–O bond cleavage, resulting from the attack of a water molecule at the conjugated β carbon, as depicted in Scheme 1, to yield the final product—fullerenols **3**.

Conclusion

We have demonstrated a novel cyclosulfation method for the functionalization of fullerene molecules that results in DMF-soluble polycyclosulfated fullerene derivatives **4**. The cyclosulfation of C_{60} is accomplished in neat fuming sulfuric acid at 55–60 °C under N_2. Hydrolysis of **4**, either in the presence of water at 85–90 °C or in aqueous NaOH solution at ambient temperature, gives, in high yield, the corresponding polyhydroxylated fullerenes **3** (fullerenols) which contain no hemiketal structure. The facile hydrolysis of cyclosulfated C_{60} **4** or hydrogen sulfated C_{60} during purification often prohibits the accurate quantification of its sulfur atoms. The functional characteristics and number of sulfate moieties per C_{60} molecule in polycyclosulfated fullerene precursors **4**, and the structure of fullerenols **3**, were determined primarily by analysis of the TGA–mass spectrum and by the two absorption bands, corresponding to the binding energy of sulfur (S_{2p}) and carbon (C_{1s}), in the XPS spectrum. The XPS spectrum was used to determine the oxidation state of sulfur and the number of carbons possessing a higher oxidation state than unreacted fullerenic carbon. We resolved an average of 10 to 12 hydroxyl addends in the chemical structure of fullerenol **3**, which can be correlated to the structure of polycyclosulfated fullerene **4**, which contains 5 to 6 cyclosulfate units. Mechanistically, we assume that the cyclosulfation chemistry is initiated by a one-electron oxidation of C_{60}, followed by the attack of anionic sulfate species on the resulting cationic C_{60} radical intermediates, to form the

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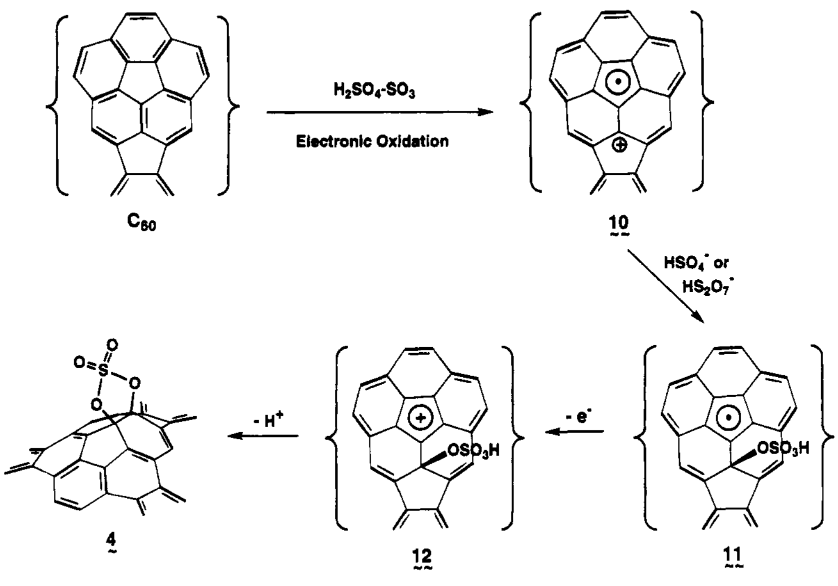
(20) Deacon, T.; Steltner, A.; Williams, A. *J. Chem. Soc., Perkin Trans. II* **1975**, 1778.

Scheme 3



corresponding hydrogen sulfated C_{60} radicals. Further oxidation and intramolecular cyclization of this hydrogen sulfated C_{60} yields the polycyclosulfated C_{60} products. Fullerenol 3 has a simple chemical composition of 60 carbons and multiple hydroxyl groups and is significantly different from fullerenols prepared by the aqueous acid method reported previously.[11] Interestingly, when the hydrolysis of 4 was carried out in aqueous NaOH solution at higher temperatures of 85–90 °C, the derived fullerenol products were found to exhibit an infrared spectrum (Figure 1f) closely resembling that of fullerenols prepared by the aqueous acid chemistry. A secondary reaction beyond simple hydrolysis probably occurs under alkaline conditions at elevated temperatures. Finally, fullerenols are of interest owing to their utilization as basic building blocks in the synthesis of star polymers and the highly cross-linked polymer networks.

Experimental Section

^{13}C NMR solution spectra were measured with either a Brucker 360 spectrometer or a JEOL FX-100 Fourier transform spectrometer. X-ray photoelectron spectroscopic measurements (XPS) were carried out on a Perkin-Elmer 5600 XPS spectrometer using Al Kα radiation at 1486.6 eV. All peak positions in the XPS measurement were calibrated using the binding energy of Si_{2p} at 102.2 eV as a reference. Infrared spectra were recorded on a Perkin-Elmer 680 spectrometer as KBr pellets. Mass spectroscopic studies of fullerenols were performed using the fast cesium ion bombardment (or liquid secondary ion mass spectrometry (LSIMS)) technique. A VG ZAB-T four-sector instrument at the Center of Advanced Food Technology of Rutgers University was used for the positive ion LSIMS experiments. TGA (thermogravimetric analysis)–mass spectroscopy data of fullerenol were collected on Mettler-TA2000C thermogravimetric analyzer interfaced with a Balzers QMG511 quadruple mass spectrometer at a heating rate of 6 °C per min. Fuming sulfuric acid was purchased from Aldrich Chemicals and used as received. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Synthesis of Polycyclosulfated Fullerene Derivatives 4. A reaction flask (50 mL) charged with a fullerene mixture of C_{60} (84%) and C_{70} (16%) (1.0 g) and fuming sulfuric acid (15 mL) was stirred at 55–60 °C under N_2 for 3 days to give a dark brown solution with orange suspensions. The resulting mixture was added dropwise into anhydrous diethyl ether (200 mL, distilled over CaH_2) with vigorous stirring in an ice bath to cause the precipitation of products. Precipitates were separated from solution by the centrifuge technique. They were then washed and centrifuged three times with anhydrous diethyl ether and twice with 2:1 anhydrous diethyl ether–CH_3CN and dried in vacuum at 40 °C to afford brown-orange solids of polycyclosulfated fullerene derivatives 4 (1.3 g).

The physical data of compound 4 are as follow: IR $\nu_{\max}$ (KBr, Figure 1c) 2920 (br), 2400 (br), 1706 (w), 1654 (w), 1598 (w), 1426 (s), 1233 (s), 1168, 1046, 1002 (s), 981, 953 (s), 855, 826 (s), 783, 641, 530, 485 (w), and 411 (w) cm^{-1}; ^{13}C NMR (DMF-d_7, peak center) δ 148.0, 77.0, 71.0; ^{1}H NMR (DMF-d_7, peak center) δ 14.6 (w, OSO_2–OH); MS (LSIMS, positive ion, mass of the highest ion peak in the fragmentation group), *m/z* 613, 625, 637, 649, 659, 673, 691, 697, 713, 721 (rel intensity 100), 737 755, 771, 789, 805, 823, 839, 857, 873, 891, 907, 923, 941, 957, 975, 993, 1009, 1027, 1043, 1060, 1077, 1095, 1109, 1129; MS (LSIMS, negative ion, mass of the highest ion peak in the fragmentation group), *m/z* 720 (rel intensity 100), 736, 741, 753, 769, 785, 801, 817, 833, 849, 863, 879, 895, 911, 925, 941, 957, 975, 987, 1003, 1021, 1033, 1056, 1070. Anal. of 4: C, 59.13; H, 0.93; O, 25.46; S, 12.02. XPS (atomic %): C, 67.7; O, 26.6; S, 4.8. Elemental analysis data are in good agreement with an average composition of 4 as $C_{60}(SO_4)_{5.0}(Et_2O)_{1.3}$. Partially hydrolyzed 4: IR $\nu_{\max}$ (KBr, Figure 1d) 3327 (br, OH), 2400 (br), 1627, 1423, 1287, 1228 (s), 1172 (s), 1067, 1004, 883, 852, 611, 582 (s), and 448 (w) cm^{-1}.

Synthesis of Polyhydroxylated Fullerene Derivatives 3. A reaction flask (50 mL) equipped with a condenser and an inert gas bubbler was charged with polycyclosulfated fullerene derivatives 4 (500 mg) and distilled water (10 mL). The mixture was stirred at 85 °C under N_2 for 10 h to give a dark brown suspension. The suspended solids were separated from aqueous solution by the centrifuge technique. They were washed and centrifuged twice with water and dried in vacuum at 40 °C to afford brown solids of polyhydroxylated fullerene derivatives 3 (fullerenols, 405 mg, 80% overall yield from C_{60}).

The physical data of compound 3 are as follow: IR $\nu_{\max}$ (KBr, Figure 1e) 3317 (br, s, OH), 1623, 1381, 1049 (s), and 607; ^{1}H NMR (DMF-d_7, peak center) δ 4.85 (OH); ^{13}C NMR (DMF-d_7, peak center) δ 148.0, 81.0, 76.0. Anal.: C, 69.07; H, 2.51; O, 23.82. XPS (atomic %): C, 79.9; O, 20.0; S, 0.09. Even though fullerenol 3 is not highly soluble in water, the product often contained one to several water molecules per fullerene derivative. Therefore, a slightly higher oxygen and hydrogen content in the elemental analysis was expected.

Synthesis of Polyhydroxy Hydrogen Sulfated Fullerene Derivatives 5 from 3. A reaction vial (10 mL) capped with a Teflon liner was charged with fullerenols 3 (50 mg) and fuming sulfuric acid (3 mL). The mixture was stirred at ambient temperature under N_2 for 3 days to give a dark brown suspension. The resulting mixture was added dropwise into anhydrous diethyl ether (40 mL, distilled over CaH_2) with vigorous stirring in an ice bath to cause the precipitation of products. The precipitates were separated from solution by the centrifuge technique. They were then washed and centrifuged three times with anhydrous diethyl ether and twice with 2:1 anhydrous diethyl ether−CH_3CN and dried in vacuum at 40 °C to afford brown solids of polyhydroxy hydrogen sulfated fullerene derivatives **5** (55 mg): IR v_{max} (KBr, Figure 1g) 3429 (br s, OH), 1627, 1413, 1225 (s), 1054, 992, 842, 598, and 534 (w) cm^{-1}. XPS (atomic %): C, 70.55; O, 26.28; S, 3.16.

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