

very few examples of *intermolecular* C—H...O hydrogen bonds with similar geometry are observed.

(9) In β -cyclodextrin (β -CD) inclusion complexes, numerous host/guest C—H...O hydrogen bonds with $d_{\text{H}\cdots\text{O}}$ as short as 2.39 Å are observed. These can be donated not only by CH groups of the inner cavity lining of β -CD to hydrophilic guest molecules but also from a guest to a glycosidic O atom of the cavity wall. Although they are weak, we consider the C—H...O bonds as a third, direct cohesive host/guest interaction besides van der Waals contacts and O—H...O hydrogen bonds; in concert, they will contribute to the overall stability and structure of the inclusion complexes of the cyclodextrins.

(10) If water molecules in a "hydrophobic" surrounding cannot arrange in the preferred tetrahedral or trigonal O—H...O hydrogen-bond coordination geometry, the "free" acceptor potential is often partially satisfied by C—H...O hydrogen bonds.

(11) C—H...O hydrogen bonds are not strong enough to significantly reduce the thermal vibrations of the engaged H atom.

(12) Any lengthening of the covalent C—H bond in the C—H...O hydrogen bond would supply *direct* experimental evidence for the strength of the interaction. The observed lengthening of d_{CH} by ~ 0.004 Å for the shortest distances $d_{\text{H}\cdots\text{O}} < 2.4$ Å, however, is at the very limit of experimental accuracy. It is desirable to verify this observation by other means or by an extended data set.

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Registry No. Sucrose, 57-50-1; β -cyclodextrin, 7585-39-9; methyl β -D-xylopyranoside, 612-05-5; 3-amino-1,6-anhydro-3-deoxy- β -D-glucopyranose, 57649-09-9; β -cyclodextrin ethanol octahydrate, 138858-69-2.

Versatile Nitronium Chemistry for C₆₀ Fullerene Functionalization

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Abstract: We have demonstrated the high reactivity of fullerene molecules toward the electrophilic attack of the nitronium ion in the presence of nucleophilic reagents, such as aromatic carboxylic acids, under mild reaction conditions. The observed nucleophilicity of fullerenes in terms of their vulnerability to electrophilic additions in solution compensates for difficulties that have been encountered in achieving the electronic oxidation of C₆₀ molecules for further functionalization. It also represents a versatile synthetic methodology for introducing multiple polar functionalities, especially hydroxyl and functionalized carboxylic ester groups, onto fullerene molecules, leading to an enormous variation of novel fullerene derivatives. The structure of these new fullerene derivatives was characterized as consisting of a chemical composition of an average of 13–15 hydroxyl substituents and 4–5 *p*-bromobenzoate moieties per C₆₀ molecule. Hydrolysis of these derivatives in alkaline aqueous solution affords the corresponding water-soluble fullerols consisting of 18–20 hydroxyl groups per C₆₀ molecule on average.

Introduction

The electron affinity of C₆₀ fullerene molecules has been investigated extensively by cyclic voltammetry.^{1,2} Six reversible consecutive electronic reductions can be achieved in solution to generate a stable hexaanionic fullerene (C₆₀⁶⁻).² Nevertheless, no reversible oxidation waves were detected in the cyclic voltammetry study, indicating its inherent inactivity to the multiple electronic oxidations. The observed high electron affinity of C₆₀ fullerene over its electron-donating ability leads to the prediction that this class of materials is more susceptible to nucleophilic additions³ than to electrophilic additions. In fact, certain nucleophiles, such as organoamines⁴ and organolithium or Grignard

reagents,^{3,5} were found to be effective for nucleophilic addition reactions on fullerenes. Recently, we have demonstrated that the reactivity of electrophilic additions on fullerenes can be significantly enhanced using aqueous acid chemistry.⁶ The acid chemistry transforms the instability of cationic fullerenes into highly reactive intermediates suitable for derivatization. In the presence of water molecules, these intermediates can be converted directly into polyhydroxylated fullerene derivatives (fullerols) with a high solubility in acidic water. Here we describe the synthesis and characterization of new polyhydroxyorganocarboxylated fullerene derivatives through the electrophilic addition of nitronium tetrafluoroborate onto fullerenes in the presence of arenecarboxylic acid in a nonaqueous medium. Hydrolysis of the ester moieties of polyhydroxyorganocarboxylated fullerene derivatives provides an alternative efficient route for the preparation of water-soluble fullerols.

Experimental Section

Nitronium tetrafluoroborate was purchased from Aldrich Chemicals and used as received. Methylene chloride was distilled over CaH₂ prior to use. ¹H NMR and ¹³C NMR spectra were measured with either a Bruker 360 spectrometer or a JEOL FX-100 Fourier transform spectrometer. The infrared spectra were recorded on a Perkin-Elmer 680 series spectrometer as KBr pellets. Mass spectroscopic studies of all

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samples 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. The X-ray photoelectron spectroscopic measurement (XPS) was carried out on a Perkin-Elmer 5600 XPS spectrometer using Al K α radiation at 1486.6 eV.

General Procedure for the Synthesis of Polyhydroxyorganocarboxylated Fullerene Derivatives 3. In a 50-mL screw-capped vial sealed with a Teflon-faced silicone septum liner were placed either a mixture of C₆₀ (84%) and C₇₀ (16%) fullerenes or pure C₆₀ (148 mg, 0.2 mmol based on C₆₀/C₇₀ mixtures), nitronium tetrafluoroborate (8.0 mL, 4.0 mmol, 0.5 M in sulfolane), areneorganocarboxylic acid (4.0 mmol), and methylene chloride (20 mL). The mixture was stirred at ambient temperature for 48 h under N₂. At the end of reaction, methylene chloride was evaporated in the rotary evaporator to give a thick sulfolane solution. The solution was added dropwise into ice-water (40 mL), and the mixture was stirred at 5 °C to ambient temperature for 3 h to afford a suspension of yellow to orange solids. These solids were collected by the centrifuge technique, washed repeatedly with cool water, and dried in vacuo at a temperature lower than 40 °C. The dried solids were dissolved in a minimum amount of tetrahydrofuran (about 5 mL), and a trace amount of insoluble particles was removed by centrifuge. The clear tetrahydrofuran solution was transferred dropwise into a mixture of 1:1 diethyl ether and hexane (v/v) with vigorous stirring to cause a precipitation of products. These products were collected and washed with a mixture of 1:1 diethyl ether and hexane (v/v) to yield yellowish-orange solids of compound 3 (260 mg for 3a and 340 mg for 3b).

The physical data of compound 3a prepared from pure C₆₀ are as follows: IR ν_{\max} (KBr) 3440 (br, OH), 2920, 2850 (C-H), 1730 (s, C=O), 1573, 1536, 1440, 1350, 1315, 1270 (s), 1180, 1090 (s), 1065, 1025, 990, 798 (w), 710 (s), 568, 530; ¹H NMR (THF-d₆) δ 2.58 (OH), 7.40–7.80 (br, C-H); MS (LSIMS, positive ion, mass of the highest ion peak in the fragmentation group), m/z 661, 672, 685, 697, 713, 721 (C₆₀H⁺, 100% relative intensity), 737, 753, 769, 781, 797, 813, 829, 841, 859, 875, 887, 891, 901, 907, 917, 935, 951, 963, 979, 997, 1013, 1029, 1039, 1057, 1071. Elemental analysis: C, 76.45; H, 2.34; O, 18.55; N, 0.5. XPS (atomic %): C, 84.0; O, 15.2; N, 0.8.

The physical data of compound 3b prepared from pure C₆₀ are as follows: IR ν_{\max} (KBr) 3427 (br, OH), 2933, 2864, 1728 (s, C=O), 1587, 1566, 1539, 1481, 1396, 1351, 1271 (s), 1174, 1095 (s), 1074, 1011, 843, 753, 681 (w), 526 (br), 470; ¹H NMR (THF-d₆) δ 3.20 (OH), 7.72 (br, C-H), 8.10 (br, C-H); ¹³C NMR (THF-d₆) δ 82.0 (C-O), 129.5, 133.0, 149.5, 166.0 (C=O); MS (LSIMS, positive ion, mass of the highest ion peak in the fragmentation group), m/z 661, 672, 686, 689, 696, 713, 720 (C₆₀⁺, 100% relative intensity), 729, 736, 753, 769, 785, 803, 820, 837, 853, 889, 907, 925, 971, 987, 1005, 1021, 1039, 1073, 1091, 1123, 1143, 1157, 1173, 1189, 1204, 1222, 1239, 1257, 1287, 1311, 1339, 1357, 1373, 1389, 1407, 1423, 1441, 1457, 1473. Elemental analysis: C, 57.63; H, 1.85; O, 18.81; Br, 19.27. XPS (atomic %): C, 77.5; O, 17.9; Br, 3.67; N, 0.92.

Synthesis of Water-Soluble Fullerols 5. To a reaction flask (25 mL) charged with polyhydroxyorganocarboxylated fullerene derivatives 3 (50 mg) and water (10 mL) was added sodium hydroxide (150 mg). The mixture was heated at 60–70 °C overnight with stirring. At the end of reaction, the clear aqueous solution was concentrated to a volume of 3 mL and added slowly to methanol (20 mL) to cause the precipitation of fullerols 5 (30–40 mg).

The physical data of fullerols 5 prepared from pure C₆₀ are as follows: IR ν_{\max} (KBr) 3432 (br, OH), 1590 (br), 1380 (br), 1045 (br), 462 (br); MS (LSIMS, positive ion, mass of the highest ion peak in the fragmentation group), m/z 661, 675, 693, 721 (C₆₀H⁺, 100% relative intensity), 737, 753, 765, 785, 799, 813, 829, 845, 859, 875, 889, 907, 919, 939, 951, 965, 981, 999, 1011, 1027, 1041, 1057, 1071, 1089, 1103. Elemental analysis: C, 65.98; H, 1.88; O, 28.54. XPS (atomic %): C, 72.3; O, 27.7.

Results and Discussion

The high electrophilicity of the nitronium ion enables its use as a versatile reagent for fullerene functionalization. Both pure C₆₀ and a mixture of C₆₀ (84%) and C₇₀ (16%) were used in the study. In a typical reaction, C₆₀ fullerenes partially dissolved in methylene chloride (distilled under CaH₂ and stored over molecular sieves) were allowed to react with an excess of nitronium tetrafluoroborate (20 equiv) in the presence of either an aromatic or an aliphatic organocarboxylic acid (20 equiv) at ambient temperature under an atmospheric pressure of N₂. Quick change of the brown suspension to a clear yellow or reddish solution, depending upon different acids used, within 30 min of reaction indicated a fast addition of organocarboxylic acid to fullerenes

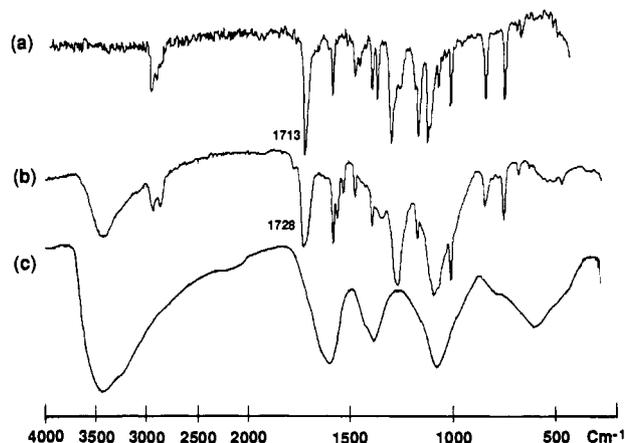
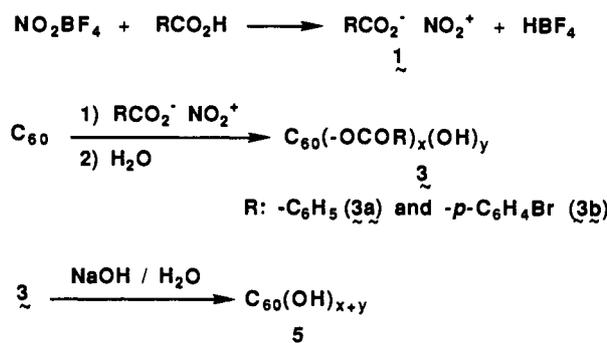


Figure 1. Infrared spectra of (a) *tert*-butyl *p*-bromobenzoate, (b) the products 3b from the reaction of C₆₀ with *p*-bromobenzoic acid and nitronium tetrafluoroborate, and (c) fullerols prepared from the hydrolysis of 3b.

Scheme I



under these conditions. After the completion of reaction, methylene chloride was evaporated, and the resulting mixtures were stirred in water for 3 h to afford yellow to orange solids, which were then repeatedly washed with both water and a mixture of diethyl ether and hexane to remove unreacted reagents. Most of the reaction products exhibited good solubility in THF, acetone, and many organic solvents.

Upon the treatment of nitronium tetrafluoroborate with organocarboxylic acid, the corresponding nitronium carboxylate salt **1** was immediately formed, as shown in Scheme I. The initial electrophilic attack of nitronium ion on fullerenes gave presumably intermediates of C₆₀(NO₂⁺)_x adducts **2**. The subsequent nucleophilic 1,3- or 1,5-substitution of organocarboxylates on adduct **2**, followed by treatment with water, afforded the corresponding polyhydroxyorganocarboxylate derivatives of fullerene **3**. Even though there is evidence that C₆₀ fullerene can form an adduct with multiple nitronium ions, the mechanism of most addition and substitution reactions is stepwise. Surprisingly, both the elemental analysis and the X-ray photoelectron (XPS) spectroscopic measurement of derivatives **3** indicated consistently a chemical composition of less than one nitrogen atom per C₆₀ molecule. The result revealed that most nitro groups in derivatives **3** have been replaced. It is understandable that the tertiary nitro group, behaving as a good leaving group, can be easily substituted by nucleophiles in acidic medium.

Infrared spectra of polyhydroxyorganocarboxylate fullerene derivatives 3a or 3b (Figure 1b), which were synthesized from benzoic acid or *p*-bromobenzoic acid, respectively, showed a disappearance of characteristic C₆₀ fullerene peaks with a strong, broad absorption band centered at 3430–3440 cm⁻¹, corresponding to hydroxyl moieties of **3**. A carbonyl absorption band at 1725–1730 cm⁻¹ in the spectra of 3a and 3b is clearly indicative of the incorporation of benzoate esters on fullerene molecules. To correlate peaks in Figure 1b to the characteristic absorption bands of benzoate moieties of 3b, we synthesized a model compound of *tert*-butyl *p*-bromobenzoate from the reaction of *p*-bromobenzoyl

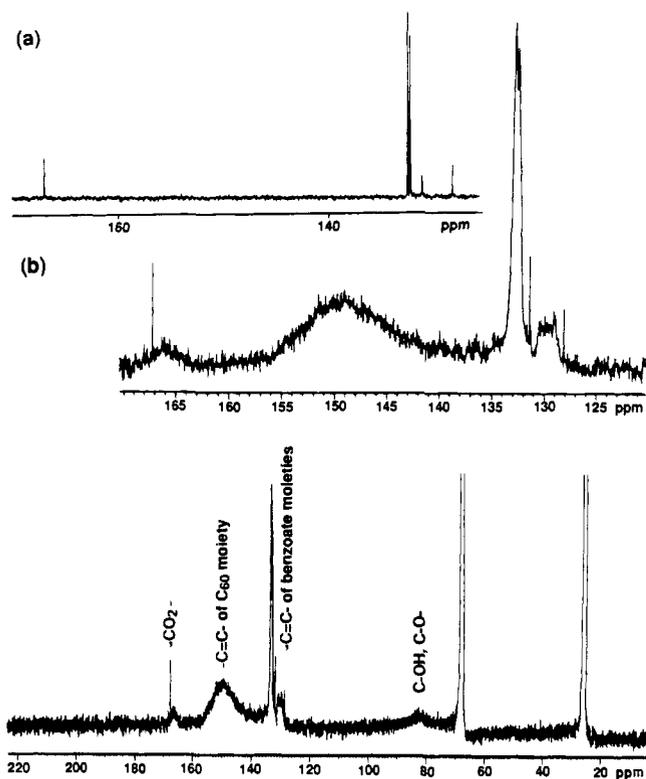


Figure 2. ^{13}C NMR spectra of (a) *p*-bromobenzoic acid and (b) the fullerene derivative **3b** in $\text{THF-}d_8$ showing both hydroxylated and *p*-bromobenzoate carbon peaks.

chloride and *tert*-butyl alcohol. The infrared spectrum of *tert*-butyl *p*-bromobenzoate⁷ (depicted in Figure 1a) evidently supports the structural characterization of **3b**. Addition of hydroxyl and ester functional groups onto fullerene carbons was also substantiated by the ^{13}C NMR spectrum of **3b** in $\text{THF-}d_8$ solution, as depicted in Figure 2b (δ relative to TMS). Due to the heterogeneous molecular distribution of **3b**, the spectrum shows a weak, broad band centered at δ 82.0 and a broad peak centered at δ 149.5, corresponding to hydroxylated (C–OH) or carboxylated (C–OCO) carbons and unreacted olefinic carbons of fullerenes, respectively. The spectrum also exhibits three groups of carbon peaks centered at δ 129.5, 133.0, and 166.0, corresponding to carbons of *p*-bromobenzoate moieties in **3b**. The chemical shifts of these benzoate carbons were compared with those of carbons in *p*-bromobenzoic acid (**4**, Figure 2a).⁸ The distinct peaks at δ 128.0, 131.2, 132.2, 132.4, and 167.3 in Figure 2b are apparently derived from the residual *p*-bromobenzoic acid physically absorbed in **3b**. These sharp peaks were utilized as internal standards for the spectral comparison. In the expanded spectrum of Figure 2b, the chemical shifts of ester carbons (OCO) centered at δ 166.0 and non-hydrogenated carbons (C_1 and C_4 of the benzene ring in *p*-bromobenzoate ester moieties) at δ 128.5–131 represent only about 1.0-ppm upfield or downfield shift from those of the corresponding carbons in **4**. In addition, the chemical shifts of hydrogenated carbons (C_2 , C_3 , C_5 , and C_6 of the benzene ring in *p*-bromobenzoate ester moieties) at δ 132.2 and 132.4 are identical to those of the corresponding carbons in **4**. The spectrum provides direct evidence of additions of *p*-bromobenzoate on fullerenes.

The ^1H NMR spectrum of **3b** in $\text{THF-}d_8$, after the complete removal of residual **4** (Figure 3a, δ relative to TMS) shows evidently a broad proton peak centered at δ 3.20 and two broad peaks centered at δ 7.72 and 8.10, corresponding to hydroxy protons and two adjacent protons in *p*-bromobenzoate moieties of **3b**, re-

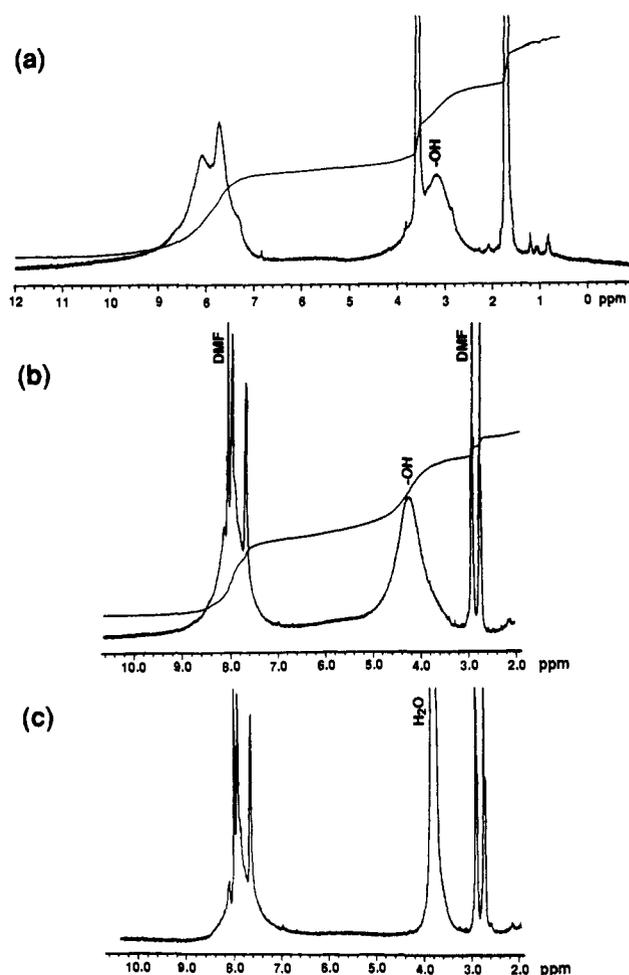


Figure 3. ^1H NMR spectra of the fullerene derivative **3b** in (a) $\text{THF-}d_8$, (b) $\text{DMF-}d_7$, and (c) $\text{DMF-}d_7\text{-D}_2\text{O}$.

spectively. Hydroxyl protons in the spectrum were substantiated by deuterium exchange with D_2O as shown in Figures 3b and 3c. In this case, deuterated DMF is a better solvent for the experiment. We detected a downfield shift (about 1.0 ppm) of hydroxyl proton peak position compared to that in Figure 3a, due to the solvent effect. Interestingly, in $\text{DMF-}d_7$ the chemical shifts of two aromatic proton peaks (doublets at 7.62 and 7.93 ppm) are well resolved, with less than 0.1-ppm downfield shift from the corresponding protons (two sharp doublets at 7.56 and 7.83 ppm) in *tert*-butyl *p*-bromobenzoate. Upon treatment with D_2O , a clear disappearance of a broad peak of hydroxyl protons (C–OH) centered at δ 4.25 was observed in Figure 3c, with a new sharp peak of water protons at δ 3.90. From the proton integration in Figures 3a and 3b, we determined the ratio between the number of hydroxyl protons and the total number of aromatic *p*-bromobenzoate protons to be 0.65 and 0.78, respectively. Elemental analysis of compound **3b** indicated a carbon vs bromine ratio of 20, which corresponds to a chemical composition of **3b** with 4–5 *p*-bromobenzoate substituents per C_{60} molecule on average. Therefore, we calculate an average of 13–15 hydroxy substituents per C_{60} molecule in the structure of **3b**, in addition to five *p*-bromobenzoate functional moieties. On the basis of this process of structural analysis, the hydrolysis of **3b** in alkaline aqueous solution should give the corresponding water-soluble fullerols **5**, containing 18–20 hydroxyl groups per C_{60} molecule on average. The infrared spectrum of fullerols **5** (Figure 1c) showed a strong and broad hydroxyl absorption band centered at 3432 cm^{-1} and three broad absorption bands centered at 1590, 1380, and 1045 cm^{-1} , in close resemblance to those in the infrared spectrum of fullerols prepared from aqueous acid chemistry.⁶

Mass spectroscopic study of **3b** was performed using the fast cesium ion bombardment (or liquid secondary ion mass spec-

(7) Infrared spectrum of *tert*-butyl *p*-bromobenzoate: ν_{max} (KBr) 2973, 2917, 1713 (s, C=O), 1586, 1476, 1454, 1393, 1367, 1293, 1163, 1118, 1070, 1011, 848, 758.

(8) ^{13}C NMR spectrum of *p*-bromobenzoic acid: ($\text{THF-}d_8$) δ 128.12, 131.01, 132.20, 132.41, 167.10 (CO–O).

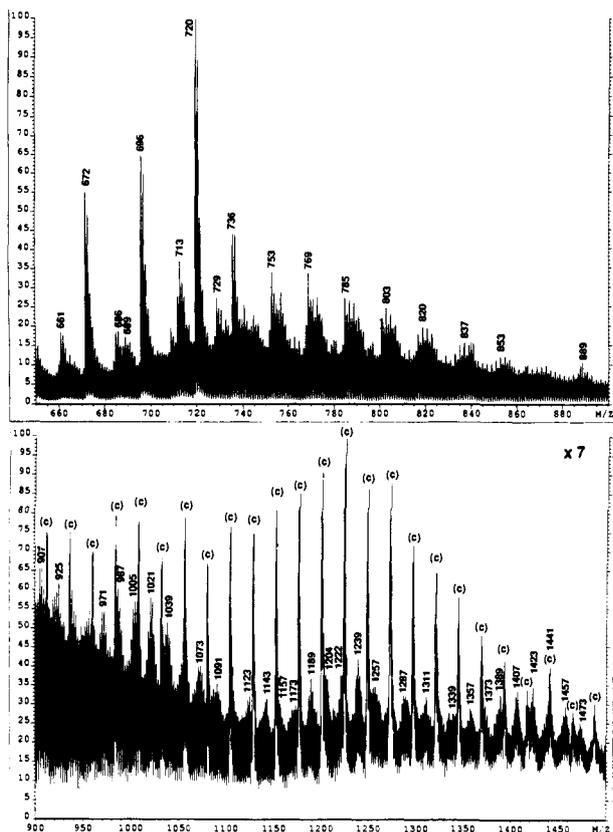


Figure 4. Mass spectrum of the fullerene derivative **3b**, prepared from pure C₆₀, using the positive ion FAB/LSIMS technique. Mass of the highest ion peak in the fragmentation group was indicated in the spectrum. Ion clusters of higher fullerenes, presumably generated by the carbon recombination of fragments under the MS experimental conditions, with 24 mass units (C₂) apart are marked by (c).

trometry (LSIMS)) technique. A VG ZAB-T four-sector instrument was used for the positive ion LSIMS experiments. Prior to the FAB/LSIMS analysis, fullerene derivatives **3b**, prepared from pure C₆₀, were filtered through Celite followed by deposition on a matrix of (3:1) dithiothreitol and dithioerythritol. The matrix was bombarded by a Cs⁺ ion beam (35 keV). The positive ion FAB/LSIMS spectrum of **3b** is shown in Figure 4. The most abundant ions in this mass spectrum are centered at *m/z* 720. There are many ion clusters above *m/z* 720 clearly separated by multiples of 16 (O), 17 (OH), or 18 (OH₂) mass units, providing evidence of oxygen entities in the molecule. Ion clusters of higher fullerenes, presumably generated by the carbon recombination

of fragments under the MS experimental conditions, were observed above *m/z* 900. The much lower intensity of ion fragments above *m/z* 1500 indicates the fast cleavage of *p*-bromobenzoate moieties upon the cesium ion bombardment. However, we detected two groups of ion fragments with the highest-peak mass unit as high as *m/z* 1457 or 1473, in good agreement with the mass of an ion of a C₆₀ derivative with two *p*-bromobenzoate and 20 hydroxyl substituents (*m/z* 1458) or 21 hydroxyl substituents (*m/z* 1475), respectively. A consecutive weight loss or separation of 17 mass units from an ion at *m/z* 1458 (A⁺) was clearly observed and gave groups of ion fragmentations centered at *m/z* 1441 (A⁺ - OH), 1424 (A⁺ - 2OH), 1407 (A⁺ - 3OH), 1390 (A⁺ - 4OH), 1373 (A⁺ - 5OH), and 1356 (A⁺ - 6OH). Interestingly, the spectrum also showed a distinct band with the mass of the highest ion peak at *m/z* 1239 as a fragment derived from the dehydration of ion at *m/z* 1257, which corresponds to the mass of an ion of C₆₀ derivative with one *p*-bromobenzoate, 18 hydroxyl, and two oxide (dehydration of the adjacent diol gave the corresponding oxide) substituents. Further sequential weight loss or separation of 17 mass units from an ion at *m/z* 1239 (B⁺) was detected and gave groups of ion fragmentations centered at *m/z* 1222 (B⁺ - OH), 1205 (B⁺ - 2OH), and 1188 (B⁺ - 3OH). These results provide strong evidence supporting the characterized chemical composition of **3b**.

Conclusion

We have observed the high reactivity of fullerene molecules toward the electrophilic attack of the nitronium ion in the presence of nucleophilic reagents under mild reaction conditions. Results demonstrated that electrophilic addition on C₆₀ fullerenes can be achieved by solution chemistry. The method exemplifies an alternative versatile synthetic methodology for introducing multiple polar functionalities, especially hydroxyl and functionalized carboxylic ester groups, onto fullerene molecules. The structure of these new fullerene derivatives was characterized as consisting of a chemical composition of an average of 13–15 hydroxyl substituents and 4–5 *p*-bromobenzoate moieties per C₆₀ molecule. Hydrolysis of these derivatives in alkaline aqueous solution affords the corresponding water-soluble fullerols consisting of 18–20 hydroxyl groups per C₆₀ molecule on average. In principle, fullerol can serve as a basic building block for the design of various polymer networks. Further chemical transformations of fullerol derivatives may also allow one to study their potential role in the catalysis area.

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