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Application of sulfur as a matrix for laser desorption/ionization in the characterization of halogenated fullerenes

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The application of sulfur as a matrix for matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOFMS) analysis of highly chlorinated and fluorinated fullerenes is reported. Control over fluorofullerene fragmentation which resulted in the domination of the molecular peak $C_{60}F_{36}^-$ was achieved, with the optimal matrix-to-analyte ratio found to be 1000:1. We suggest the possible mechanism of the molecular ion formation according to the charge transfer between the sulfur anions and $C_{60}F_{36}$. For the first time the LDI and MALDI mass spectra of the highly chlorinated fullerene $C_{60}Cl_x$ ($x_{\max} \approx 32$) are presented. The formation of odd chlorine ions (positive and negative) is observed. We conclude that use of sulfur as a matrix leads to a significant decrease in fragmentation of the halogenated fullerenes. Copyright © 2001 John Wiley & Sons, Ltd.

Due to the high thermal stability of fluorinated fullerenes, mass spectrometry is the most applicable method for their analysis. It can be characterized by electron impact (positive ions) and electron capture (negative ions) mass spectrometry with the minimal fragmentation to generate mass spectra and the high intensity of the signal according to the molecular peak.¹

Laser desorption/ionization mass spectrometry (LDI-MS) is known as an efficient, facile and sensitive method for the characterization of higher fullerenes and endohedral metallofullerenes.^{2,3} Negative ion LDI-MS can be used as an analytical tool to approximately establish the degree of fluorination in fluorofullerenes, which are regarded as the most thermally stable exohedral fullerene derivatives. On the other hand, the drastic change in ionization energy of C_{60} upon multiple addition of F atoms (7.65 eV for C_{60} ⁴ vs. 12 eV for $C_{60}F_{48}$ ⁵) makes it impossible to observe positively charged fluorofullerenes in LDI mass spectra – only cations of parent fullerenes. However, this approach has suffered a marked limitation. It is very difficult (if not possible) to estimate accurately the composition of such materials from the MS data because of the observed loss of fluorines from the fluorine-doped fullerenes. Nevertheless, this method was claimed to be useful in estimating the highest degree of fluorination.⁶

Success in the MALDI-TOFMS experiments depends on the choice of matrix. Previously, application of MALDI-MS analysis for the organic derivatives of fullerenes was reported.⁷ Rogner *et al.*⁸ reported on 'cooled' MALDI with 5-methoxysalicylic acid as matrix and $NaBF_4$ as co-matrix for

investigation of chlorinated fullerene $C_{60}Cl_6$. In the positive ion MALDI mass spectrum only relatively stable carbocations generated from $NaBF_4$, such as $C_{60}(ClFNa)^+$, $C_{60}(ClFNa)_2^+$ and $C_{60}(ClFNa)_3^+$, were presented. On the other, application of this matrix appeared successful for analysis of $C_{60}H_{36}$; in the positive ion mass spectrum, $C_{60}H_{36}$ can be detected as the $C_{60}H_{35}^+$ ion. It was also reported that the number of the attached chlorine atoms was determined with the help of MALDI-MS of negative ions (with 2,5-dihydroxybenzoic acid as matrix).⁹ However, the determined degree of chlorination was essentially underestimated in comparison with other analytical methods of chlorine detection.

In our study, the MALDI mass spectra of chloro- and fluorofullerenes using sulfur as matrix are reported for the first time, and the influence of matrix-to-analyte ratio on mass spectra is discussed. We have found the optimum conditions for mass analysis of $C_{60}F_{36}$, in which we were able to observe the molecular ion. The negative ion mass spectrum of the chlorinated fullerene sample with the highest known degree of chlorination is presented.

EXPERIMENTAL

Materials

A sample of $C_{60}F_{36}$ was prepared by the selective fluorination of C_{60} with MnF_3 as described elsewhere¹⁰ and characterized by ¹⁹F NMR, IR and HPLC; the latter two methods indicated a purity >95%. $C_{60}Cl_x$ was prepared using an original technique by direct chlorination of C_{60} under UV irradiation. 31.6 mg (0.044 mmol) of C_{60} were placed into a spherical thick-wall quartz ampoule, then about 4 mL (92 mmol) of pure chlorine were condensed into it, frozen and the ampoule was sealed. After 20 h UV

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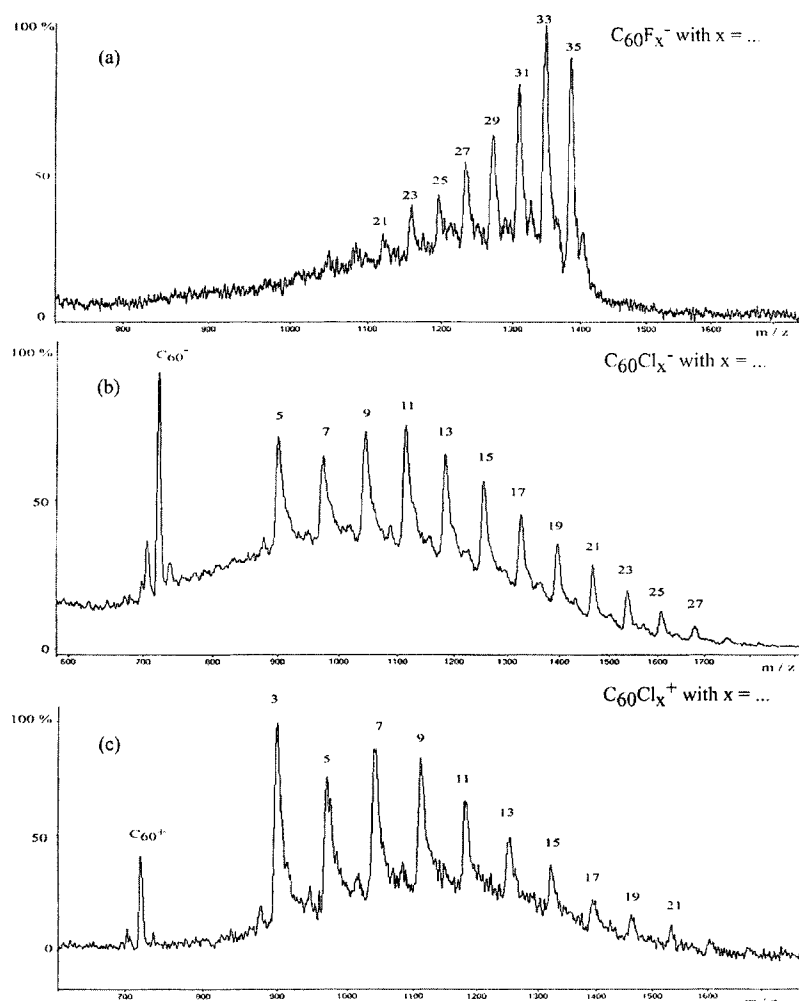


Figure 1. (a) LDI-MS negative ion spectra of $C_{60}F_{36}$; negative (b) and positive (c) (16) ion LDI mass spectra of $C_{60}Cl_x$.

irradiation with a 1 kW Hg super high pressure lamp, a yellow-orange precipitate of the pure product was formed. IR spectra showed no traces of unreacted C_{60} , only intensive bands in the C-Cl stretching were seen at 887, 866, 787, 764, 640, 436 cm^{-1} . Thermogravimetric data indicated an approximate composition $C_{60}Cl_x = 30 \pm 2$.

MALDI-TOFMS measurements

Experiments were performed using a Vision 2000 MALDI-TOF (Finnigan, USA) instrument with a UV laser (337 nm, 3 ns laser pulse). All the measurements were carried out in the reflectron mode. Analyte solutions in toluene were prepared at concentrations from 1 to 20 mM. The sulfur solution in toluene had a concentration of 1000 mM. Calibration of the mass spectrometer was performed using a mixture of fullerenes (C_{60} , C_{70} and higher fullerenes). We used a sandwich technique for the matrix preparation when the fullerene sample was deposited (volume 0.2–0.4 μL) between the two matrix layers and was dried at room temperature before introduction into the ion source. Mass spectra are presented as sums of 100–150 single laser shots.

Laser power was chosen as minimum for the ionization threshold.

RESULTS AND DISCUSSION

Prior to the MALDI experiments we obtained LDI mass spectra of the samples of $C_{60}F_{36}$ and highly chlorinated fullerene $C_{60}Cl_x$ without a matrix. Anions with the odd fluorine number are present in the mass spectrum of the former with fragmentation through F_2 loss down to $C_{60}F_{15}^-$ (Fig. 1(a)). Maximal intensity corresponds to $C_{60}F_{33}^-$, the heaviest ion is $C_{60}F_{35}^-$. This result agrees qualitatively with the previously published data on LDI analysis of this compound.⁶

The negative ion LDI mass spectrum of the chlorinated fullerene sample is given in Fig. 1(b). Besides C_{60}^- , peaks due to the chlorofullerene anions with an odd number of chlorine atoms ($C_{60}Cl_{5-29}^-$) were identified. Comparison of the mass spectrum of fluorofullerene with that of chlorofullerene revealed similar processes of dissociation due to loss of two halogen atoms.

In contrast to the positive ion mass spectrum of fluoro-

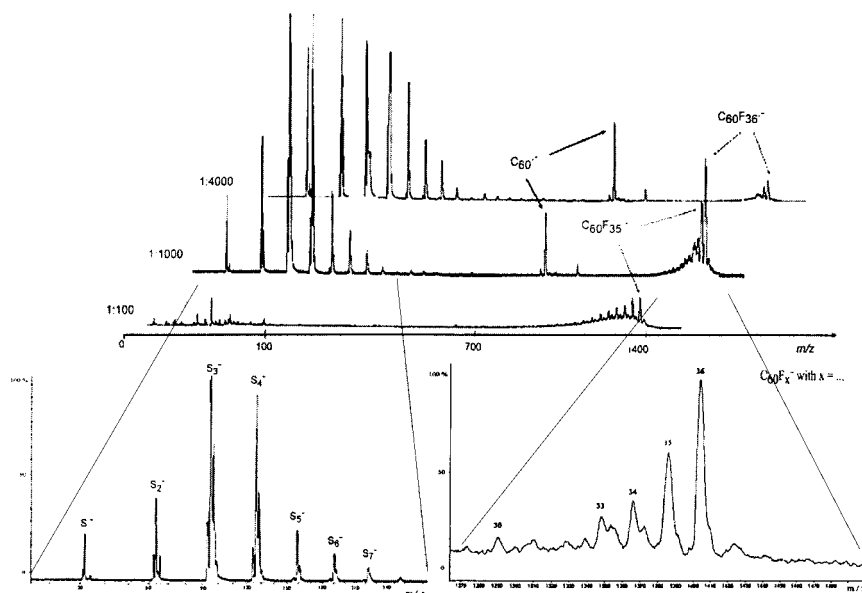


Figure 2. MALDI negative ion mass spectra of $C_{60}F_{36}$. The matrix used was sulfur in the ratio-to-analyte as 1:100, 1:1000 and 1:4000.

fullerene with only a C_{60}^+ peak,⁶ in the case of $C_{60}Cl_x$ we could see (Fig. 1(c)) cations from $C_{60}Cl_3^+$ to $C_{60}Cl_{23}^+$. It is interesting that the distribution of ions in the negative and positive modes is very similar for chlorofullerene; fragmentation readily occurs down to the relatively bare C_{60} due to the weak C-Cl bond.

In the MALDI mass spectrum of $C_{60}F_{36}$ (Fig. 2) recorded for the probes with different matrix-to-analyte ratio we were able to avoid a substantial fragmentation of analyte, with

appearance of the molecular anion of $C_{60}F_{36}^-$, maximum intensity for which was achieved for the ratio 1000:1. In the case when we used a 100:1 ratio, the mass spectrum of $C_{60}F_{36}$ is similar to that of that obtained by LDI.

As seen in Fig. 2, in the low mass range, sulfur anions up to S_7^- are formed. It is known that the vertical electron affinity (EA) of the polyatomic sulfur molecule lies in the range 1.57–3.87 eV,¹¹ whereas the EA of $C_{60}F_{36}$ is estimated as 3.48 eV.¹² Thus, we suggest that a charge-transfer ionization process

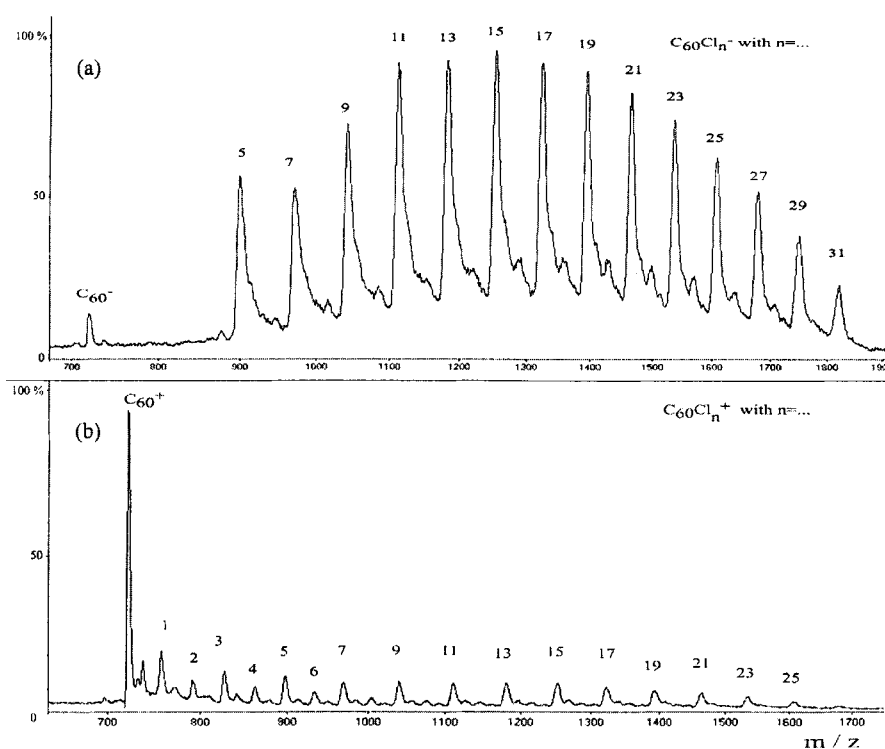
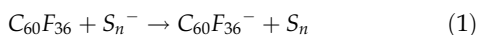


Figure 3. MALDI negative (a) and positive (b) ion mass spectra of $C_{60}Cl_x$ with matrix sulfur.

occurs in MALDI which can be presented as reaction (1):



This means that the EA of the $\text{C}_{60}\text{F}_{36}$ may exceed the EA of some of the sulfur species generated under laser vaporization. Hence the process is thermodynamically feasible and the radical molecular anion of $\text{C}_{60}\text{F}_{36}^-$ is detected.

In contrast to the LDI experiments, MALDI-MS of chlorinated fullerenes provided a remarkable decrease in fragmentation (Figs 3 (a) and 3 (b)). The heaviest negative ion corresponding to $\text{C}_{60}\text{Cl}_{31}^-$ was detected, and in the positive mode – $\text{C}_{60}\text{Cl}_{27}^+$.

Our preliminary results allow us to conclude that sulfur is applicable as a matrix for MALDI analysis of the chlorinated and fluorinated derivatives of fullerenes. At present we do not have a satisfactory explanation of why positive ion mass spectra of chloro- and fluorofullerenes are so different. It is known that the ionization potential of fluorofullerene goes from C_{60} (7.6 eV)³ through $\text{C}_{60}\text{F}_{18}$ (near by 7–10 eV)¹³ up to $\text{C}_{60}\text{F}_{48}$ (12 eV),⁴ thus absence of the fluorofullerene cations can be understood energetically. It is also known from the literature that ion distribution in hydrogenated fullerenes is dependant on the ionic properties: in the negative ion mode ionization of $\text{C}_{60}\text{H}_{36}$ only species up to $\text{C}_{60}\text{H}_x^-$ ($x = 1-9$) were detected by FTICRMS,¹⁴ while, in the positive mode, series of ions up to $\text{C}_{60}\text{H}_{35}^+$ were formed. Such behavior was explained by change in the ionization energies, IE: $\text{C}_{60}\text{H}_{36}$ has lower IE than C_{60} , while EA decreases from 2.65 eV (C_{60})¹⁵ to negative values in case of $\text{C}_{60}\text{H}_{36}$. One would expect similar trends in the case of other electronegative addends; however, observation of the rich positive ion mass spectra for the chlorofullerene with almost the same distribution of ions as in the negative ion mode provides evidence that the energetics of ion formation is different from fluoro derivatives. The IEs of chlorofullerenes may appear lower than those of fluorofullerenes, as observed for the chlorinated and fluorinated benzene derivatives,⁶ the latter having on average 0.5–1.0 eV higher IE than the former.

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