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The influence of phenylated by-products on the MALDI analysis of chlorinated fullerenes

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Dedicated to Professor Helmut Schwarz, on the occasion of his 60th birthday

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Abstract

Chlorinated [60]fullerenes which have been prepared by a variety of different synthetic methods have been studied by means of direct laser desorption/ionisation (LDI), matrix-assisted laser desorption/ionisation (MALDI) and desorption electron ionisation (DEI) mass spectrometry. The aim of this investigation has been the elucidation of the unusual signal sequence observed in earlier positive-ion MALDI experiments, which featured a spacing of 77 Da between the signals of fullerene-containing ions. Circumstantial evidence has been provided, which strongly indicates that the 77 Da correspond to a C_6H_5 (phenyl) ligand. The findings reveal that phenylated by-products that result from the use of benzene during synthesis may be of strong influence on the physico-chemical characterisation of chlorinated C_{60}.

Keywords: LDI; MALDI; Chlorinated fullerenes

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1. Introduction

Schwarz and co-workers were the first to observe by routine electron ionisation the intact molecular ion of CCl_4, which had been a long-standing example of a molecule that would dissociate completely upon ionisation [1]. The challenge to obtain intact molecular ions of molecules like CCl_4, representing the smallest molecule that is entirely composed of chlorine and carbon, extends to the larger relatives, the chlorinated fullerenes. In addition to ion-fragmentation, chlorine release upon excitation may occur during evaporation of the solid chlorofullerene which further complicates the situation. Chlorofullerenes are potentially useful synthons in fullerene chemistry [2,3], however, all efforts to obtain meaningful positive-ion mass spectra of this compound class remained so far unsuccessful. While two reports have been concerned with the generation of positive-ions of chlorofullerenes using in situ chlorination of C_{60} in the Knudsen cell [4,5], experiments with chlorofullerenes as starting material

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have been focused on negative-ion mass spectrometry. The analysis by negative-ion fast atom bombardment (FAB) mass spectrometry has been described [6], followed by recent success for the application of matrix-assisted laser desorption/ionisation (MALDI) to the analysis of highly chlorinated fullerenes in the negative-ion mode. Following an initial report on the use of dihydroxy benzoic acid (DHB) as the matrix material for MALDI of chlorofullerenes [7], Boltalina and co-workers revealed that highly chlorinated fullerenes would produce chlorine-containing C_{60} ions even under harsh laser desorption/ionisation (LDI) conditions and established the use of sulphur as the appropriate matrix to obtain a more accurate indication of the actual chlorine content of the neutral compound [8].

For the present study, several groups with research interest into the mass spectrometry of chlorofullerenes have joined forces to investigate an unusual observation that was made in earlier positive-ion MALDI experiments [9]. Rogner et al. developed a two component matrix composed of 5-methoxysalicylic acid and $NaBF_4$ [9]. The development of this matrix is based on a concept whereby the well-established matrix properties of 5-methoxysalicylic acid would be enhanced through the release of decomposition products of $NaBF_4$, which would promote the desorption process by cooling. When applied to the analysis of hydrofullerenes, the quasi molecular ion of $C_{60}H_{36}$ could be obtained for the first time without further dissociation [9], a finding which also paved the way to the re-establishment of $C_{60}H_{36}$ as the major product of the Birch reduction of C_{60} [10]. The analysis of chlorofullerenes was less encouraging, leading to several signals beyond $C_{60}{}^{+}$ which were spaced by 77 Da. Considering the elemental composition of those compounds involved in this experiment, the 77 mass units were tentatively assigned as (NaClF) ligand [9]. Recent investigations into metal attachment to derivatised fullerenes cast doubt on the feasibility of such a ligand attachment to C_{60} during MALDI [11]. Therefore, this unusual finding is examined here in more detail by making use of differently prepared chlorofullerene samples.

2. Experimental

LDI and MALDI have been performed using a nitrogen laser at an ultraviolet wavelength of 337 nm with a pulse width of 3 ns and frequency 1.5 Hz. The resulting ions were accelerated by a continuous acceleration voltage of 20 kV into a reflectron time-of-flight (ToF) mass spectrometer (Kompact MALDI IV, Kratos Inc., Manchester, UK). The instrumental set-up has been described in more detail elsewhere [12]. All positive-ion mass spectra were recorded in reflectron mode. Two hundred single laser shot events were accumulated for each individual mass spectrum and viewed in electronically processed form. To ensure activation of a pristine target area, the sample holder was moved prior to each individual laser shot. The mass assignment has been achieved using external calibration. For LDI analysis, the chlorofullerenes were dissolved in toluene and applied to a stainless steel sample holder. Targets were dried by use of compressed air from an airbrush. For MALDI, sulphur was used as the matrix material, which was also dissolved in toluene and combined with the chlorofullerene solution prior to deposition onto the sample holder to result in a molar analyte-to-matrix ratio of 1:40 (for S_8) or 1:320 (per S atom).

Desorption electron ionisation (DEI) experiments [13] have been performed with a triple-sector mass spectrometer (Autospec, Micromass, Altringham, UK) of EBE configuration ($E = $ electric sector, $B = $ magnet). Chlorofullerenes were loaded onto a platinum wire from toluene solution and dried before introduction into the EI source. Thermally desorbed species through heating the wire were ionised by interaction with 70 eV electrons.

3. Results and discussion

The direct LDI and MALDI mass spectrum of a chlorinated [60]fullerene are displayed in Fig. 1a and b, respectively. In both experiments the $[C_{60} + 77]^{+}$ signal is clearly detected. The MALDI experiment leads to an enhancement of this peak and a succession of $[C_{60} + (77)_n]^+$ signals is observed, which extended up to $n = 3$ for some of the samples under study. However, the elemental composition of those materials involved with both the LDI experiment and the MALDI analysis would not allow the generation of a ligand composed of [NaClF], as tentatively assigned earlier and plausibly based on the material composition of the ablated target [9].

Though the sodium ion is omnipresent and frequently observed in MALDI without being actually added to the target, the presence of fluorine in amounts that would account for the generation of such ligands has to be discounted for the present experiments. Unfortunately, mass accuracy and resolution of the set-up used here were insufficient to establish the elemental composition of the ligand through accurate mass

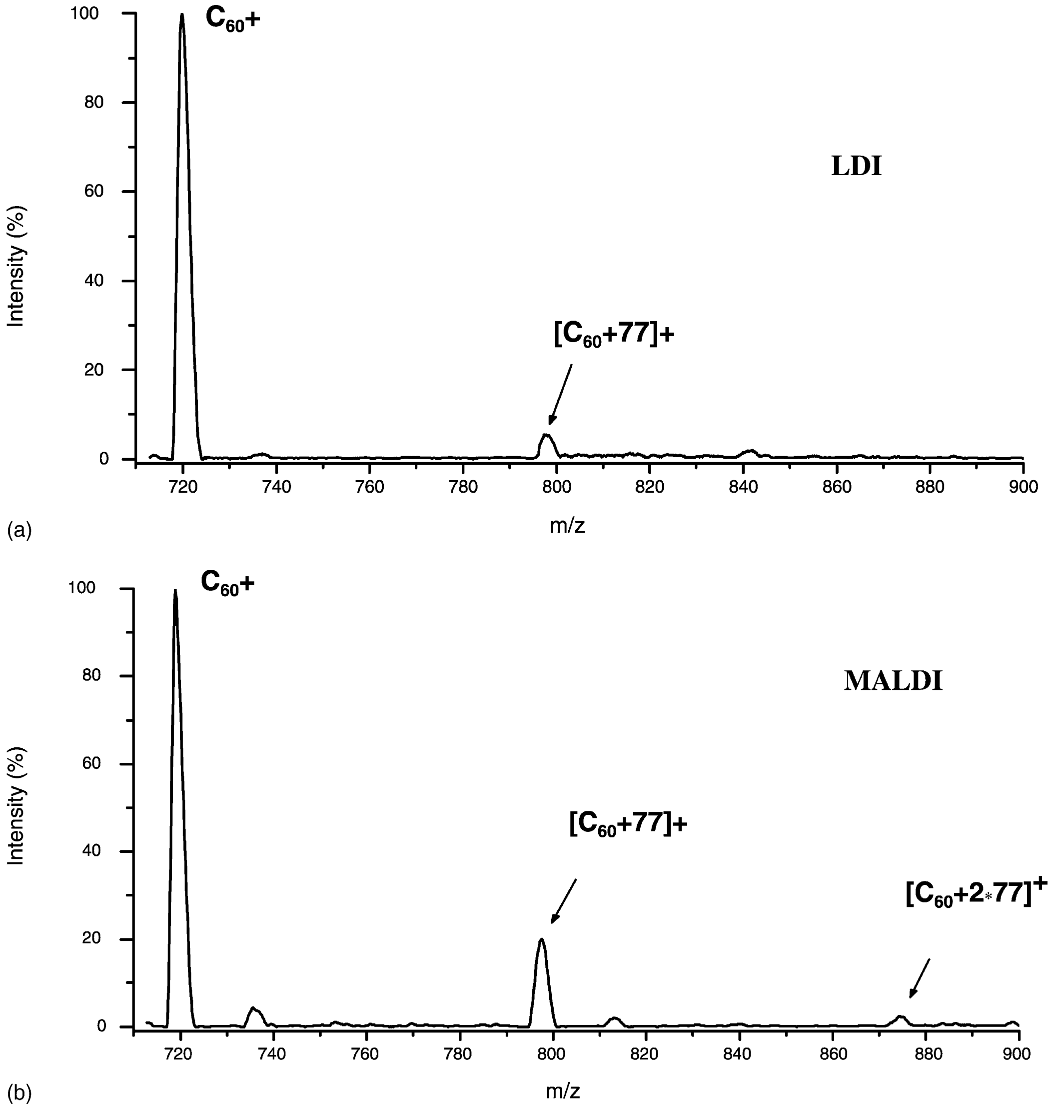

Fig. 1. (a) Direct laser desorption/ionisation of $C_{60}Cl_{12}$ (average Cl content), derived from stepwise synthesis that employed benzene as solvent, (b) MALDI of the same sample, and (c) MALDI of $C_{60}Cl_6$, using a benzene-free synthesis. Sulphur was used as the matrix.

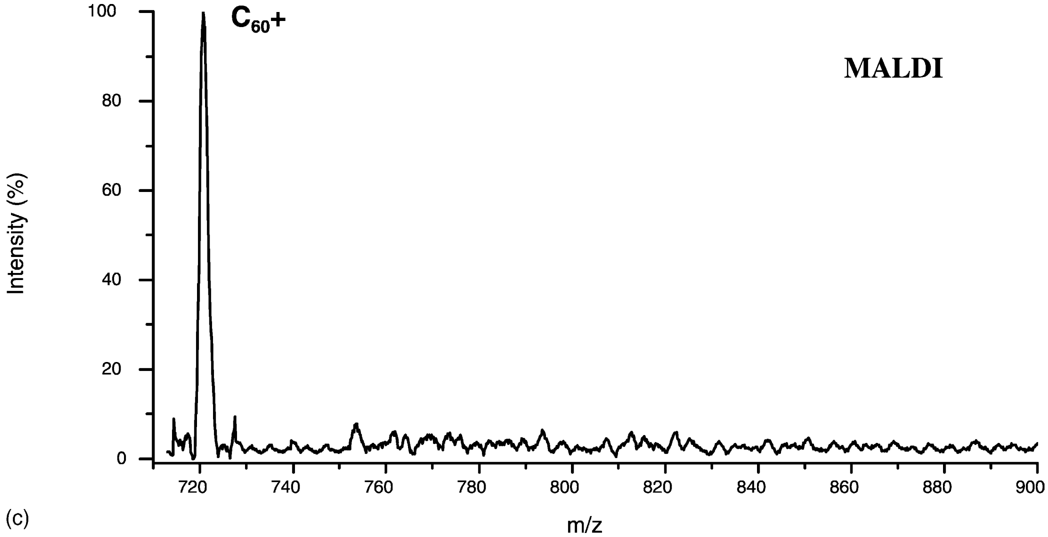

Fig. 1. (*Continued*).

measurement or analysis of the isotopic pattern. Therefore, several chlorofullerene samples of different synthetic origin were analysed in the hope that their distinct pedigree would provide clues for the identification of the ligand. Interestingly, $[C_{60} + (77)_n]^+$ signals are entirely absent in the MALDI mass spectrum shown in Fig. 1c. The sample studied for Fig. 1a and b had according to elemental analysis the composition $C_{60}Cl_{12}$ (average Cl content) and resulted from the reaction of a $C_{60}Cl_6$ sample with ICl in CH_2Cl_2. The $C_{60}Cl_6$ starting material showed a similar pattern and had been obtained by treatment of C_{60} with ICl in benzene. The infrared analysis of the sample studied for Fig. 1c showed characteristics of $C_{60}Cl_6$. Separate MALDI experiments including this and other chlorinated fullerene samples will be discussed in a forthcoming publication [14]. The sample has been prepared by reaction of C_{60} with ICl in CH_2Cl_2. The obvious difference in the history of both these samples is thus the use of benzene as solvent in the synthesis of the material that shows the $[C_{60} + (77)_n]^+$ pattern. Note that also the initial $C_{60}Cl_6$ MALDI sample [9] was obtained by the use of benzene. This in turn thus strongly suggests that phenylation might have taken place and that C_6H_5 may account for the composition of the ligand.

This assumption is further corroborated by Table 1, which lists the different chlorofullerene samples under investigation. Table 1 also refers to the synthetic method of their production and indicates as to whether or not the $[C_{60} + (77)_n]^+$ pattern could be observed by MALDI. It is evident from Table 1 that the $[C_{60} + (77)_n]^+$ signals appear only for those samples which were in contact with benzene at some point during the

Table 1
Correlation of the use of benzene during synthesis and observation of $[C_{60} + (77)_n]^+$ ions

Sample	Synthesis	Benzene contact	$[C_{60} + (77)_n]^+$
$C_{60}Cl_6$	C_{60} + ICl in C_6H_6	+	+
$C_{60}Cl_{12}$	$C_{60}Cl_6$ (above synthesis) + ICl in CH_2Cl_2	+	+
$C_{60}Cl_6$	C_{60} + ICl in CH_2Cl_2	−	−
$C_{60}Cl_{x<32}$	C_{60} + Cl_2 ($h\nu$)	−	−

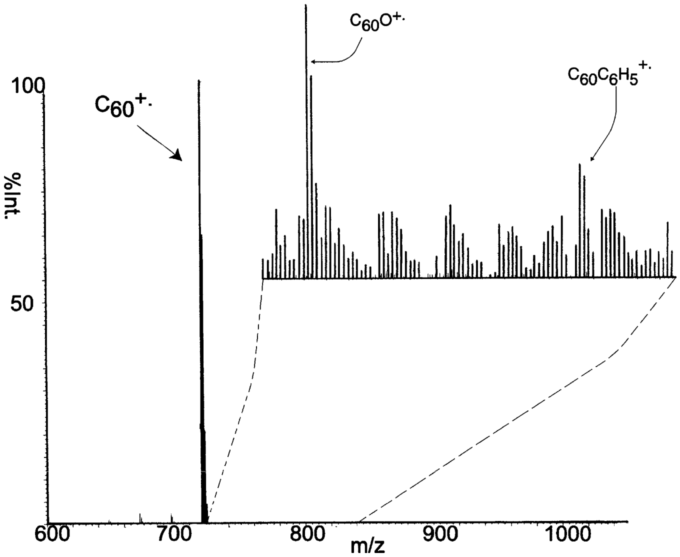

Fig. 2. DEI of the same $C_{60}Cl_{12}$ sample used for Fig. 1a and b.

synthesis, providing further support for the C_6H_5 assignment.

Fig. 2 displays the DEI mass spectrum of the $C_{60}Cl_{12}$ sample that showed the $[C_{60} + 77]^+$ peak in LDI and MALDI (Fig. 1a and b). The low abundance of the $[C_{60} + 77]^+$ peak prevents the accurate analysis of the isotopic pattern. However, the observed pattern is clearly more in line with phenylated C_{60} than with a chlorinated ion for which the $[C_{60} + 79]^+$ peak should be considerably more abundant due to the presence of the ^{37}Cl isotope. The detection of $[C_{60} + 77]^+$ ions applying DEI allows two additional conclusions to be drawn. Firstly, while aggregation reactions are in principle common in LDI and MALDI [15,16], association of C_{60} with a free ligand is unlikely to occur under DEI conditions. As a result, it is clear from the DEI experiment that the ligand had been linked to the fullerene prior to the analysis. The second conclusions refers to the extent to which phenylation may have occurred during the synthesis. Fig. 2 reveals that the $[C_{60} + 77]^+$ signal is of very low abundance. In earlier DEI experiments under similar conditions it has been possible to obtain an abundant molecular ion signal for $C_{60}(C_6H_5)_5Cl$ [17]. Although the present experiments would not allow accurate quantification, the low abundance of the $[C_{60} + 77]^+$ peak (Fig. 2) might suggest that the phenylated impurities are only a minor component in the sample. The fact that only the phenylated by-products could be detected by MALDI is a consequence of the low efficiency whereby intact chlorinated ions were generated under the applied conditions.

The phenyl attachment to C_{60} occurred most probably through substitution of chlorine atoms that were already attached to the carbon sphere. Phenylation of chlorinated [60]fullerenes is facile and in fact has been used to establish mass spectrometrically the chlorine content by analysis of the more stable phenylated products [18]. In line with the considerations outlined here, in recent methylation experiments with $C_{60}Cl_6$ derived from chlorination of C_{60} by ICl in benzene traces of $C_{60}PhCl_5$ could be found [19].

In summary, the unusual $[C_{60} + (77)_n]^+$ pattern previously observed during MALDI analysis of chlorinated C_{60} has been assigned to phenylated by-products which were generated through the use of benzene in the synthesis.

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