Available online at www.sciencedirect.com

International Journal of Mass Spectrometry 229 (2003) 3–10

www.elsevier.com/locate/ijms

MALDI mass spectrometric determination of molecular site-specific charge localisation, and laser-induced coalescence reactivity of fullerenodendrimers

Dorina Fati [a], Yury V. Vasil'ev [a], Norbert K. Wachter [b], Roger Taylor [b], Thomas Drewello [a,*]

[a] Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK
[b] School of Chemistry, Physics and Environmental Sciences, Sussex University, Brighton BN1 9QJ, UK

Received 28 November 2002; accepted 28 February 2003

Abstract

Fullerenodendrimers have been studied by matrix-assisted laser desorption/ionization (MALDI) time-of-flight (ToF) mass spectrometry. The compounds under investigation included the first-, second- and slightly modified second-generation phenylacetylene dendritic C_{60} monoligands. The bimodal structure of these fullerenodendrimers is reflected in the charge localisation and ion formation during MALDI mass spectrometry. While metal ion (Ag^+) attachment occurs through interaction with the dentritic ligand, electron-transfer ionization seems to involve predominately the fullerene moiety. The latter conclusion is particularly evident for the formation of the negatively charged molecular ions. In direct laser ablation experiments, the coalescence reactivity has been compared with methano[60]fullerene derivatives featuring smaller ligands that display enhanced formation of larger carbon clusters. However, the presence of the dendritic phenylacetylene ligand hindered reactive interactions between the fullerene entities, thereby completely preventing coalescence.

Keywords: Fullerenes; Dendrimers; MALDI; Coalescence; Laser desorption/ionization; Charge localisation

1. Introduction

The chemistry of fullerenes offers interesting possibilities for designing molecular properties through the combined tailoring of geometrical and physico-chemical features [1,2]. Fullerene-based dendrimers are particularly intriguing examples of this kind of molecular architecture [3]. While the rigid fullerene core provides a template for the shape, further physical and chemical properties can be altered through the nature and amount of the dendritic ligands. The material properties of these fullerenodendrimers feature uses in timely areas connected with nano-science and technology, such as for instance host/guest chemistry, membrane and micelle production, liquid crystal formation, as well as photovoltaic and pharmacology [3].

Closely related to the research into properties and applications of these dendrimers is the establishment of homogeneity, monodispersity and stability of these materials. Mass spectrometry plays a particular important role to obtain this information. The dendrimer as a macromolecular, monodisperse polymeric entity can be expected to show characteristics regarding gas-phase transfer and ion formation similar to those of related polymers. It is therefore not surprising that the mass spectrometry of polymers, which has advanced tremendously in recent years [4], and dendrimers is similar. In particular, the use of matrix-assisted laser desorption/ionization (MALDI) mass spectrometry features prominently with investigations into dendrimers [5–7]. The ion formation in MALDI of these compounds is achieved almost entirely through the attachment of appropriate metal cations [5–7].

The present study details the MALDI investigation of three fullerenodendrimers, the structures of which are depicted in Fig. 1. These methano[60]fullerenes are the result of the monoaddition of a first-, second- and slightly modified second-generation phenylacetylene dendrimer to C_{60}. The synthesis [8], electrochemical behaviour [8] and photophysical properties [9] of these dendrimers have been published earlier. In solution, both electrochemistry and photophysical behaviour of these molecules indicate that

---

[*] Corresponding author. Tel.: +44-2476-524934;
fax: +44-2476-524112.
E-mail address: T.Drewello@warwick.ac.uk (T. Drewello).

1387-3806/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S1387-3806(03)00249-5

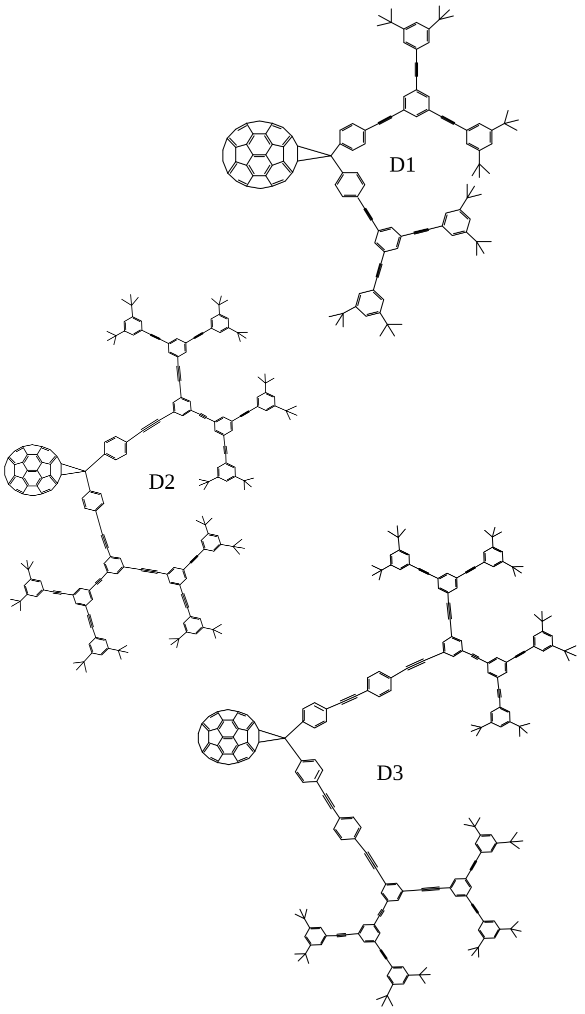

Fig. 1. The structure of the fullerenodendrimers D1, D2 and D3.

there is no significant electronic communication between dendrimeric addend and fullerene core, essentially preserving their identity as isolated units [8,9]. This investigation is concerned with the question as to whether this behaviour is retained during gas-phase ionization. Therefore, the ion formation of these compounds during the MALDI process has been of special attention. The dendrimer addend may host particular metal ions, while complexation with the fullerene core can be discounted for the conditions applied [10]. Conversely, ionization through electron transfer is rarely observed in MALDI of dendrimers and would thus indicate the involvement of the fullerene core. In further experiments, the laser-induced coalescence reactivity of the fullerenodendrimers has been evaluated by direct laser ablation. Methanofullerenes with small malonate branches display enhanced coalescence reactivity, whereby the methano-carbon atom is retained with the fullerene core and presumably facilitates the aggregation [11]. To reveal the effect of the dendritic ligand, comparison is made with the coalescence of the di-isopropyl malonate adduct to C_{60}.

2. Experimental

2.1. Instrumentation

All MALDI experiments were performed with an instrumental set-up described in more detail elsewhere [12], and applied recently to the formation [13] and analysis [10] of fullerene-related compounds, as well as to elucidate their gas-phase behaviour [14]. In brief, the mass spectrometer is composed of a linear flight tube and a quadratic-field reflectron (Kompact MALDI IV, Kratos Inc., Manchester, UK). Target activation was achieved using a nitrogen laser at an ultraviolet wavelength of 337 nm with a pulse width of 3 ns and frequency 1.5 Hz. MALDI-generated ions were accelerated by a continuous acceleration voltage of 20 kV into the time-of-flight (ToF) mass spectrometer for analysis. All positive- and negative-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 was achieved by external calibration.

The mass resolution remained below 1000 and was therefore insufficient to resolve signals isotopically in the mass range studied. In fact, the low resolving power also affected the mass accuracy so that mass assignments had to be made with an uncertainty of ±2 mass units. However, earlier experiments established for the analysis of closely related derivatised fullerenes using the same matrix materials, that ionization occurs through electron transfer [15] and that metal attachment does not involve hydrogen transfer [10]. This in turn allows assignment of the analyte ions observed here as either the radical cation or anion, or metal cation complex of the intact fullerenodendrimer. However, the assignment of the observed metal cation-complexed ion of the released dendrimer addend is less certain and may be affected by up-take or loss of hydrogen.

2.2. Materials and target preparation

The fullerenodendrimers were synthesized as described earlier [8]. Unless otherwise stated, all solutions applied to the sample holder were freshly prepared prior to each experiment. 9-Nitroanthracene, nor-harmane and DCTB (2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylpropyl-2-enylidene]malononitrile) were used as the matrix materials, respectively [10,15]. Acetone was used as solvent for nor-harmane, whereas all other matrix materials and analytes were dissolved in toluene. Analyte and matrix solutions were combined to give a molar matrix-to-analyte ratio of 1000:1. The solutions were then deposited onto the stainless steel sample holder using a 10-μl syringe. The sample holder was dried in a cold air stream, leaving a thin film of solid material behind. Metal cation attachment was tested using NaCl, KSCN and CF_3CO_2Ag, respectively. A solid layer was prepared from aqueous solutions of these salts and covered with a matrix/analyte top layer.

3. Results and discussion

In contrast to the recent successful cationisation of amphiphilic fullerene derivatives with alkali metal cations [10], all efforts to achieve attachment of Na^+ and K^+ to the fullerenodendrimers under investigation remained unsuccessful. However, use of CF_3CO_2Ag as the bottom layer led to efficient complexation with Ag^+ as shown in Fig. 2. These findings indicate that metal attachment occurs through interaction of the metal cation with the fullerene ligand. Alkali metal cationisation occurs with fullerene ligands that incorporate heteroatoms such as oxygen and fails with unsaturated hydrocarbon ligands, in which case silver cationisation is effective. In fact, Ag^+ complexation is the method of choice for the ion formation of non-polar, hydrocarbonic π-systems in MALDI. Binding results from π electron donation into the empty 5s orbital of Ag^+ and back donation of d electrons from Ag^+ into the antibonding π orbital. Particular intriguing examples of tagging carbon centred π-bonds with Ag^+ include the complexation of supramolecular assemblies [16] and its use in coordination-ionspray as a means to cationise unsaturated hydrocarbons [17].

Fig. 2 reveals further clues as to the complexing site of the molecules. The spectra are dominated by the silver cationised fullerene derivative, which is accompanied by signals corresponding to the Ag^+ complexation of the free ligand. Post-source decay experiments were conducted with the Ag^+ complexed fullerenodendrimers (referred to as D-Ag^+ ions in Fig. 2) to establish the Ag^+ complexed dendritic ligand (L-Ag^+ ions, Fig. 2) as possible fragment ions. However, the parent ion abundances were too low to provide meaningful data. The silver attached ligands may therefore be derived through either fragmentation of the neutral analyte followed by complexation, or through direct fragmention of the Ag^+/analyte complex. In either case, complexation of the free ligand is evident, while complexation of C_{60} is not observed, providing a further clear indication for metal ion complexation of the ligand. The only other signal that appears in all three spectra corresponds to the $C_{60}^{\bullet +}$ radical cation the abundance of which increases with

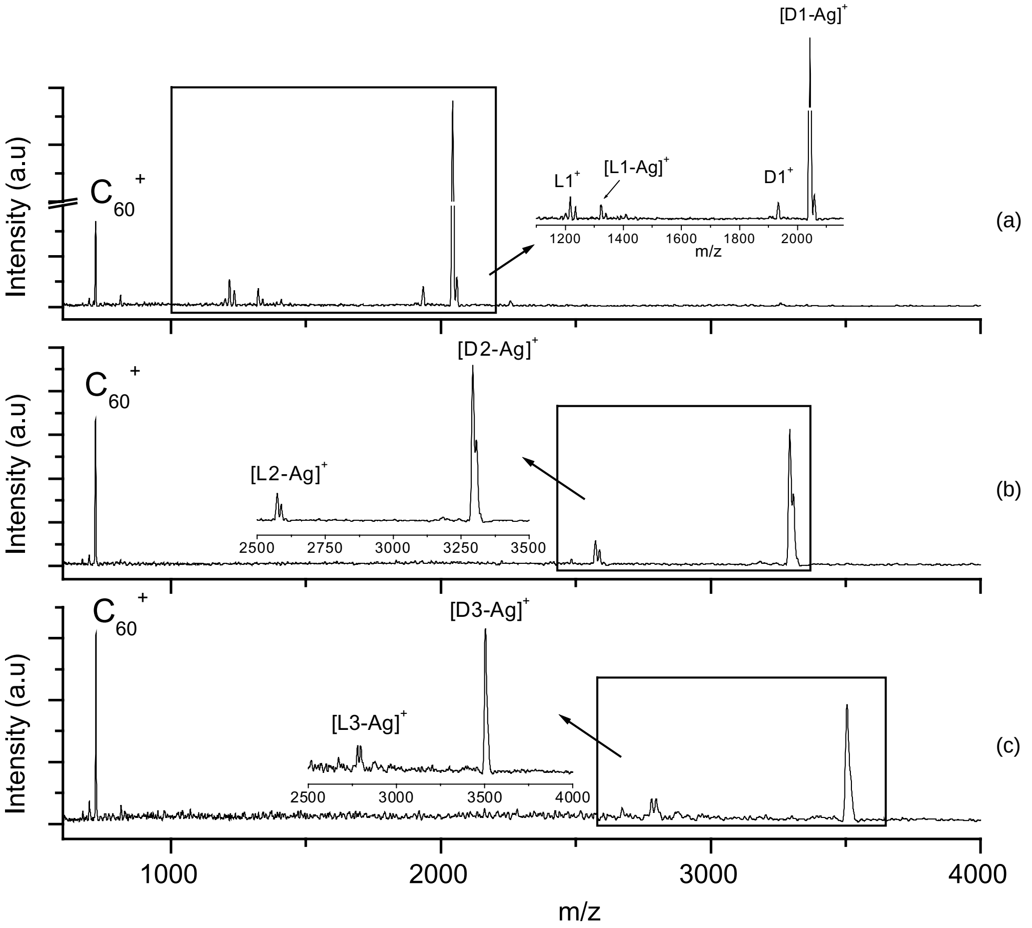

Fig. 2. The positive-ion MALDI mass spectra of (a) D1, (b) D2 and (c) D3, using 9-NA as the matrix and a silver salt layer to promote Ag^+ attachment. The laser fluence for (a) and (b) was approximately 150 mJ/cm^2 and for (c) approximately 180 mJ/cm^2.

the size of the analyte. The low ionization potential of silver makes it unlikely that $C_{60}^{\bullet+}$ originated as a charge-retaining fragment from the metal complexed analyte. More likely, $C_{60}^{\bullet+}$ results from decomposition of the neutral analyte followed by charge transfer ionization with matrix-derived cations or from direct photoionization of C_{60}. Likewise, the ions corresponding to the metal ion-free analyte radical cation and the ligand, which are most clearly observed in Fig. 2a, are not likely to result from fragmentation of the D-Ag^+ ions. The analyte radical cation is most likely to be also formed by charge transfer with matrix-derived ions.

The tagging with Ag^+ ions has been thus established as an appropriate means to generate gas-phase ions from the fullerenodendrimers using the dendrimer addend as the charge-carrying site. The observation of the radical cation of dendrimer D1 in Fig. 2a, however, indicates that ion formation may also be achieved through other mechanisms. Further experiments focussed, therefore, on the selective formation of the molecular anions and cations of the analytes promoting electron-transfer pathways for the formation of ions. The negative-ion MALDI mass spectra of compounds D1 to D3 are depicted in Fig. 3a–c, respectively. Owing to its excellent performance regarding the negative-ion formation of organic ligand-bearing fullerene derivatives, nor-harmane has been used as the matrix material in these experiments [15]. The efficient formation of negatively charged molecular ions is evident for all three fullerenodendrimers. The negative-ion mass spectra confirm that the C_{60} ion abundance increases relative to the analyte ion when the size of the dedrimer ligand increases. This observation applies for all different sets of MALDI experiments in this study and although ion dissociation into C_{60} ions have to be considered, this finding may also reflect an increasing instability of the neutral dendrimer, whereby upon laser desorption the release of bulkier ligands from the fullerene surface is facilitated.

The spectra in Fig. 3 also reveal that the dendrimer signals, especially those for D2 and D3, are accompanied by two small satellite peaks which are spaced by approximately 14–16 mass units. These satellites are also evident with metal complexed analytes and dendrimer addends in Fig. 2. Their occurrence is matrix independent, which strongly suggests the presence of a synthetic by-product. Sample oxidation can be discounted on the basis that no oxygen-containing C_{60} fragments could be found, although the fullerene core would certainly represent the main target for this degradation. As a result, it seems reasonable to assume that a minor methyl group-addition to the dendrimer addend had occurred during the synthesis.

The generation of the molecular anions of the fullerenodendrimers raises the issue of charge localisation, as

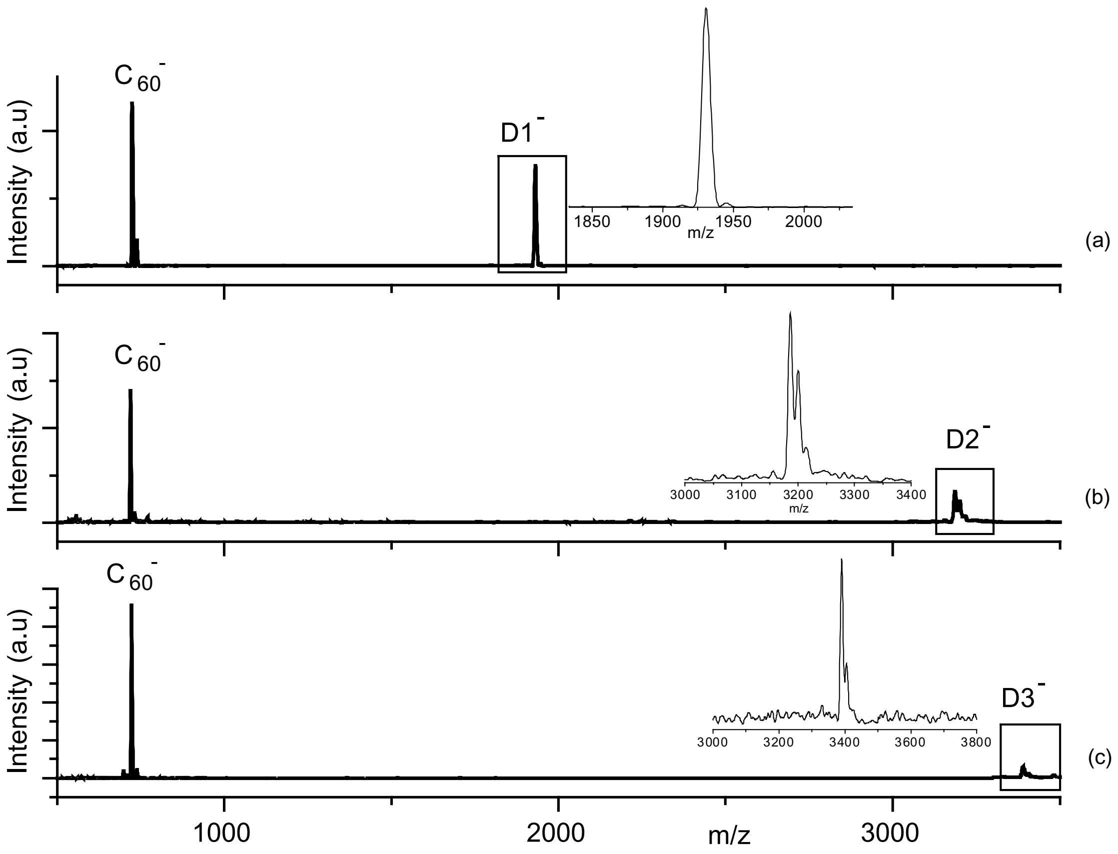

Fig. 3. The negative-ion MALDI mass spectra of (a) D1, (b) D2 and (c) D3, using nor-harmane as the matrix. The laser fluence for (a) and (b) was approximately 130 mJ/cm^2 and for (c) approximately 70 mJ/cm^2.

negative-ion MALDI is rather uncommon for the analysis of dendrimers without fullerene core. The negative-ion mass spectra in Fig. 3 provide already important clues regarding the location of the extra electron, in that none of the derivatives shows signals that can be associated with the free dendrimer addend or fragments thereof. Therefore, neither a scenario whereby decomposition of the neutral analyte was followed by electron attachment, nor a potentially occurring direct ion-dissociation of the molecular anion, would produce negative ions that can be assigned to the dendrimer addend. This in turn makes the charge localisation on the dendrimer branch of the fullerenodendrimer rather implausible.

To confirm that negative ligand ions remain absent even under relatively harsh activation conditions, the negative-ion MALDI mass spectra of D1 were recorded with the activating laser fluence varied from the threshold value of ion formation up to settings for which extensive fragmentation is induced. The result of these experiments is given in Fig. 4. The abundance of the molecular analyte anion shows an envelope-like behaviour as the laser fluence is varied. Initially the molecular anion is increasingly formed, followed by its decline through fragmentation at higher laser fluences. While, the C_{60}^- abundance increases continually throughout, there is no evidence of anionic species derived from the dendritic ligand. The extra electron is thus established to reside exclusively on the fullerene core.

Attempts have been made also to generate selectively the positively charged molecular ions, for which minor co-formation was observed in the Ag^+ complexation experiments (Fig. 2a). A recent MALDI investigation of amphiphilic fullerene derivatives revealed that metal attachment occurs at lower laser fluences than the electron-transfer ionization into the analyte radical cation [10]. This in turn identifies the ion formation through metal cation complexation as the overall softer approach. Since the use of both nor-harmane and 9-NA resulted in positive-ion mass spectra for the fullerenodendrimers of only poor quality, DCTB was used as the matrix material. With this matrix, the ion formation of other organic fullerene derivatives has been observed at markedly reduced laser fluences, which is probably achieved through a much more efficient desorption process. For these experiments only, the dendrimer D2 was available in pristine form as a solid (Fig. 5b). D1 (Fig. 5a) and D3 (Fig. 5c) were kept in toluene for several weeks prior to the analysis, so that some insight into possible degradation processes could be obtained. Under these conditions, the molecular radical cation of the pristine dendrimer D2 (Fig. 5b) is only accompanied by $C_{60}^{\bullet+}$. Comparison with the D1 and D3 samples that were aged in solution reveals that degradation has in fact taken place. The study of dendrimer degradation by MALDI has been of some controversy [18]. Although a detailed assignment cannot be provided with the present set-up, the data give clear evidence of degradation through both further addition to the dendrimer and decay of the attached ligand. However, the abundant signals for the dendritic addends (Fig. 5a and c) indicate that the separation of fullerene core and dendritic ligand has been the dominant decomposition reaction over time.

The final section of this investigation has been devoted to direct laser desorption/ionization of the fullerenodendrimers. An interesting phenomenon observed in connection with laser ablation of fullerene-based compounds is their ability to undergo aggregation and coalescence reactions. In these reactions, larger entities are formed through reac-

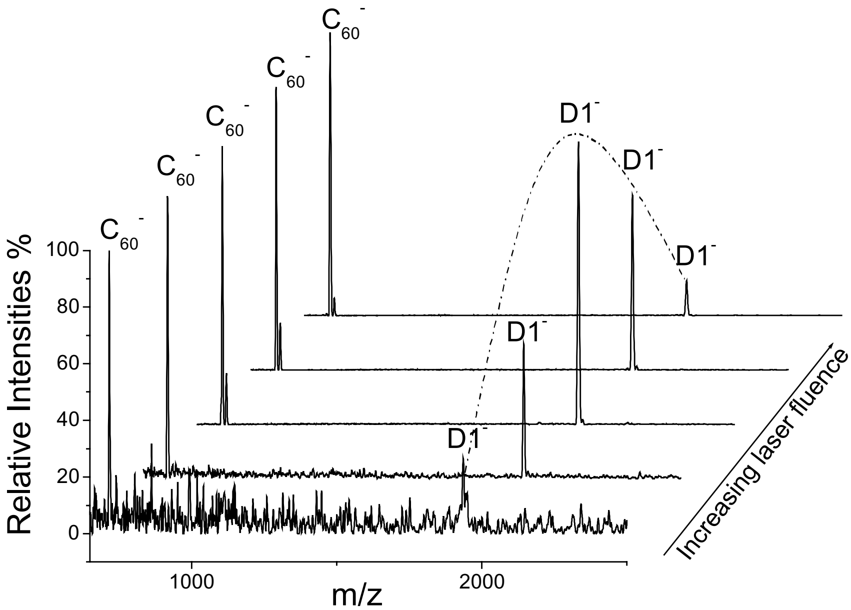

Fig. 4. The negative-ion MALDI mass spectrum of D1 as function of the laser fluence which was gradually increased from approximately 40 to 180 mJ/cm^2.

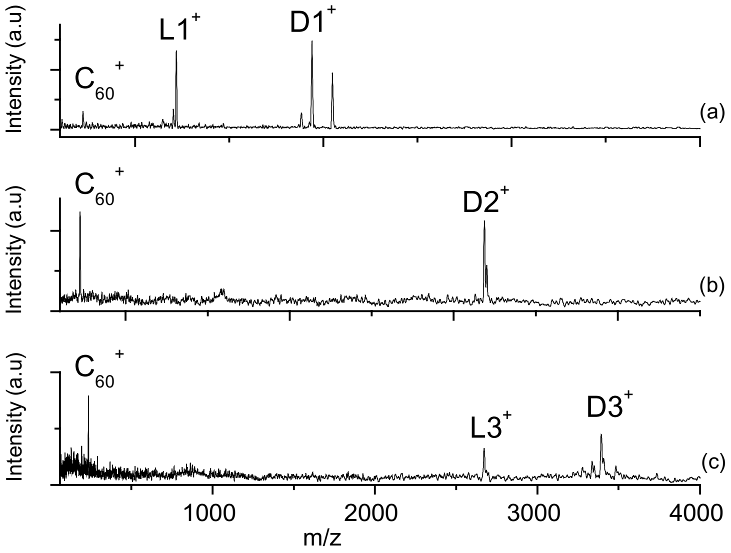

Fig. 5. The positive-ion MALDI mass spectra of (a) a degraded D1 sample, (b) a pristine D2 sample and (c) a degraded D3 sample, at a laser fluence of approximately 50 mJ/cm^2 using DCTB as the matrix.

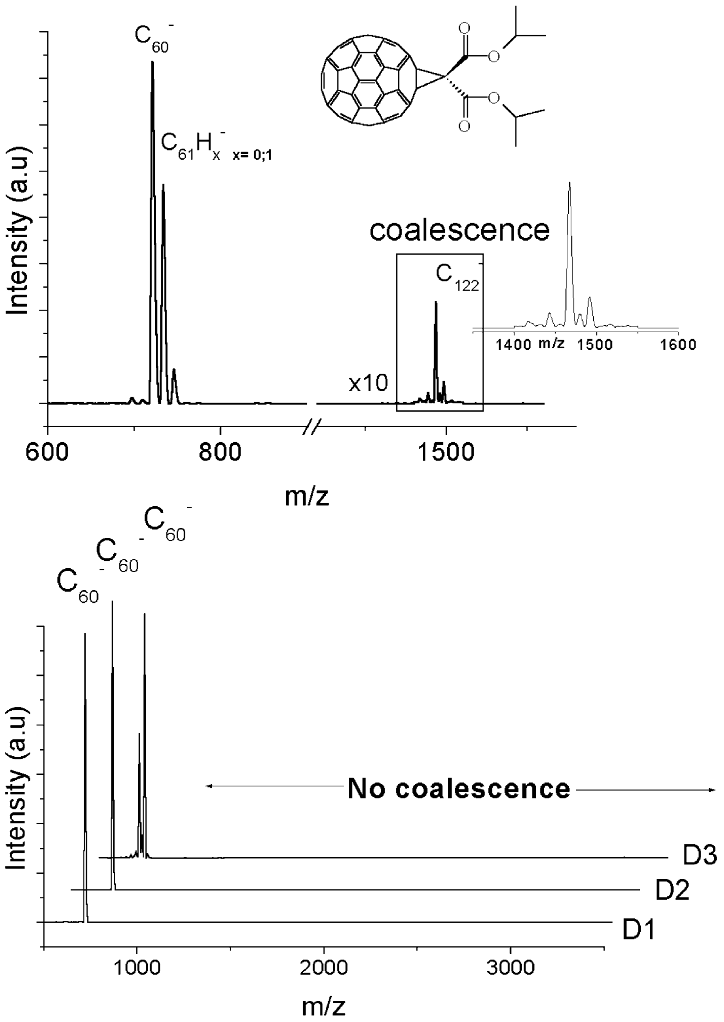

Fig. 6. Direct laser ablation in the negative-ion mode, comparing the coalescence reactivity of $C_{60}C(CO_2CH(CH_3)_2)_2$ with D1, D2 and D3 at a laser fluence of approximately 330 mJ/cm^2.

tive collisions occurring in the expanding material plume following activation of the target materials. The analysis of the resulting product distribution provides important insight into mechanistic aspects, covering, for instance, the identification of reactive intermediates and structural features of the products. The laser-induced reactivity is clearly dependent on structure and type of derivatisation of the fullerene compounds, as well as on the extent by which the target is energetically activated. Fullerene oxides, for example, show under “hard” LDI conditions coalescence into giant, closed-cage carbon clusters at higher rates than pure fullerenes [19]. The application of MALDI, however, leads to “soft” aggregation, whereby dumbbell-shaped $(C_n)_2O_m$ dimers ($n = 60, 70$, $m = 1, 2, \ldots$) have been formed [20,21]. Laser ablation of methanofullerenes of the type $C_{60}[C(CO_2Et)_2]_n$ where $n = 1–3$ has been also detailed and the coalescence reactivity observed of these target materials is in fact remarkable [11]. It has been found that the mono-, bis- and tris-methylene adducts would preferably coalesce into C_{122}, C_{124} and C_{126}, respectively. These observations have been explained in terms of loss of the CO_2Et units, retaining the methano-carbon atoms at the C_{60} sphere followed by dimerisation of the resulting C_{61}, C_{62} and C_{63} clusters [11]. Since the linkage of C_{60} and dendritic ligand in the present case shows the same structural motif, it is interesting to reveal possible effects induced through the dendritic ligand on this type of reaction.

Fig. 6 compares the negative-ion LDI mass spectrum of $C_{60}C[CO_2CH(CH_3)_2]_2$, as a representative of the coalescence reactivity described above, with the spectra obtained for the dendrimer compounds D1 to D3. While $C_{60}C[CO_2CH(CH_3)_2]_2$ shows the expected formation of C_{122}, the dendritic derivatives show no sign of coalescence. The experimental conditions were carefully adjusted to allow coalescence in principle to occur. The fact that C_{122} is not formed during the laser ablation of the fullerenodendrimers is certainly connected with the observation that a fragment containing 61 carbon atoms, which would subsequently dimerise, is also almost entirely absent. In contrast to the reference $C_{60}C[CO_2CH(CH_3)_2]_2$ compound, the derivatives D1 to D3 decompose obviously via loss of the entire dendrimer ligand. Since C_{60}^- is thus the most abundantly observed ion, it is interesting to note also that the well-known coalescence pattern that would derive from a pure C_{60} target is absent [22]. As a result, the presence of the dendrimer ligands prevents coalescence entirely under the present conditions. In the light of the size and the structure of the dendritic ligand, it seems reasonable to assume that the particle composition of the laser-generated material plume may hinder the efficient interaction between individual C_{60} units. Furthermore, release and decomposition of the dendrimer ligand may serve as an efficient energy release channel, leading to relatively “cold” C_{60} fragments that are not sufficiently excited to undergo further reactions.

4. Conclusion

Fullerenodendrimers composed of a first-, second- and slightly modified second-generation phenylacetylene dendrimer to C_{60} have been studied by MALDI mass spectrometry. Of particular interest has been the identification of the charge-carrying site in these molecules. It has been found that Ag^+ ion attachment occurs exclusively with the dendritic ligand. For negative ions, the findings seem to indicate that the additional electron resides on the fullerene moiety. For positive molecular ions the situation is less clear. However, the lack of signals due to the ionised ligand using pristine sample material, may indicate that the C_{60} moiety possesses the lower ionization energy and would therefore represent the preferred charge-carrying site. The fact that electron-transfer ionization is not commonly observed for polyaryl dendrimers may indicate that in the present case the fullerene moiety facilitates the ion formation through electron transfer. In direct laser ablation experiments using the fullerenodendrimers as target, the dentritic ligand prevents coalescence occurring. The interaction between individual fullerene units is either spatially hindered through the co-expanding, released ligands and fragments thereof, or the energy content of the fullerene moieties may be insufficient to drive coalescence reactions.

Acknowledgements

The authors are indebted to Prof. H. Hungerbühler for a sample of the di-isopropyl malonate adduct to C_{60} and to T. Brown and Dr. N.L. Clipston for their contributions to this investigation. Financial support for the work at Warwick through the EPSRC and the Leverhulme Trust is gratefully acknowledged. D.F. has been visiting Warwick as Ph.D. student from the University of Liège (B. Leyh’s group) and acknowledges financial support by the Direction de la Recherche Scientifique de la Communauté Française de Belgique through an Action de Recherche Concertée (A.R.C.).

References

[1] R. Taylor, Lecture Notes on Fullerene Chemistry: A Handbook for Chemists, Imperial College Press, London, 1998.
[2] A. Hirsch, The Chemistry of the Fullerenes, G. Thieme Verlag, Stuttgart, 1994.
[3] A. Hirsch, O. Vostrowsky, Top. Curr. Chem. 217 (2001) 51.
[4] G. Montaudo, R.P. Lattimer (Eds.), Mass Spectrometry of Polymers, CRC Press, Boca Raton, 2002.
[5] H.S. Sahota, P.M. Lloyd, S.G. Yeates, P.J. Derrick, P.C. Taylor, D.M. Haddleton, J. Chem. Soc., Chem. Commun. (1994) 2445.
[6] K.L. Walker, M.S. Kahr, C.L. Wilkins, Z.F. Xu, J.S. Moore, J. Am. Soc. Mass Spectrom. 5 (1994) 731.
[7] I.A. Mowat, R.J. Donovan, M. Bruce, W.J. Feast, N.M. Stainton, Eur. Mass Spectrom. 4 (1998) 451.
[8] A.G. Avent, P.R. Birkett, F. Paolucci, S. Roffia, R. Taylor, N.K. Wachter, J. Chem. Soc., Perkin Trans. 2 (2000) 1409.

[9] M. Schwell, N.K. Wachter, J.H. Rice, J.-P. Galaup, S. Leach, R. Taylor, R.V. Bensasson, Chem. Phys. Lett. 339 (2001) 29.

[10] D. Fati, V. Leeman, Y.V. Vasil'ev, B. Leyh, H. Hungerbühler, T. Drewello, J. Am. Soc. Mass Spectrom. 13 (2002) 1448.

[11] R.D. Beck, P. Weis, A. Hirsch, I. Lamparth, J. Phys. Chem. 98 (1994) 9683.

[12] M.P. Barrow, T. Drewello, Int. J. Mass Spectrom. 203 (2000) 111.

[13] M.M. Boorum, Y.V. Vasil'ev, T. Drewello, L.T. Scott, Science 294 (2001) 828.

[14] Y.V. Vasil'ev, R.R. Absalimov, S.K. Nasibullaev, A.S. Lobach, T. Drewello, J. Phys. Chem. A 105 (2001) 661.

[15] T. Brown, N.L. Clipston, N. Simjee, H. Luftmann, H. Hungerbühler, T. Drewello, Int. J. Mass Spectrom. 210 (2001) 249.

[16] P. Timmerman, K.A. Jolliffe, M.C. Calama, J.-L. Weidmann, L.J. Prins, F. Cardullo, B.H.M. Snellink-Ruel, R.H. Fokkens, N.M.M. Nibbering, S. Shinkai, D.N. Reinhoudt, Chem. Eur. J. 6 (2000) 4104.

[17] E. Bayer, P. Gfrörer, C. Rentel, Angew. Chem. Int. Ed. 38 (1999) 992.

[18] A.J. Clark, A.A. Coleshill, D.M. Haddleton, S.J. Isles, H.S. Sahota, P.C. Taylor, S.G. Yeates, Eur. Mass Spectrom. 5 (1999) 273.

[19] R.D. Beck, C. Stoermer, C. Schulz, R. Michel, P. Weis, G. Bräuchle, M.M. Kappes, J. Chem. Phys. 101 (1994) 3243.

[20] M.P. Barrow, N.J. Tower, R. Taylor, T. Drewello, Chem. Phys. Lett. 293 (1998) 302.

[21] M.S. Al-Jafari, M.P. Barrow, R. Taylor, T. Drewello, Int. J. Mass Spectrom. 184 (1998) L1.

[22] C. Yeretzian, K. Hansen, F. Diederich, R.L. Whetten, Nature 359 (1992) 44.