

## $C_{120}O_n$ from $C_{60}Br_{24}$

M.R. Resmi<sup>a</sup>, Shuguang Ma<sup>b</sup>, R. Caprioli<sup>a</sup>, T. Pradeep<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry and Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Chennai 600 036, India

<sup>b</sup> Mass spectrometry Research Center, 802 A MRB I, Vanderbilt University, Nashville, TN 37232-0146, USA

Received 1 November 2000; in final form 1 December 2000

### Abstract

Microcrystalline mixture of fullerene dimer oxides ( $C_{120}O_n$ ,  $n = 1, 2, 3, \dots$ ) was extracted from decomposed  $C_{60}Br_{24}$ . Low-temperature FTIR studies of the product showed the absence of orientational ordering transitions indicating freezing of  $C_{60}$  rotations due to inter-cage bonding and epoxidation. Characteristic features due to inter-cage vibrations are seen in the far IR spectrum. Bond cleavages in MS/MS leave all the oxygen atoms of the dimer oxide with one fullerene molecule. We propose that dimers are formed by [3 + 2] cycloaddition of  $C_{60}$  with its oxides,  $C_{60}O_n$  rather than cycloaddition of the monomeric oxides. Results are discussed based on the possible reaction sequences. © 2001 Elsevier Science B.V. All rights reserved.

### 1. Introduction

Fullerenes can be manipulated in a variety of ways to yield new materials and chemical reactivity of  $C_{60}$  is an area of intense research [1]. Fullerene oxides were first identified in the carbon soot generated by the resistive heating of graphite during the bulk preparation of fullerenes [2]. Oxidation of  $C_{60}$  by photochemical [3] and electrochemical [4] methods and with strong oxidising agents such as ozone [5], *m*-chloroperoxybenzoic acid [6], etc. results in  $C_{60}$  epoxides in which up to six oxygen atoms can be bridged to the  $C_{60}$  sphere. Recently fullerene dimer oxides [7] have caught the attention, being the precursors for odd numbered all carbon fullerene dimers such as  $C_{119}$  [8,9].  $C_{120}O$  is formed in thermal conditions by the [3 + 2] cycloaddition of  $C_{60}$  with  $C_{60}O$  [10,11].

Gromov et al. [12] proposed structures for two isomers of the dimeric fullerene  $C_{120}O_2$ , one with fullerene cages bis-linked by furanoid rings and one with a single furanoid bridge. Deng et al. [13] have prepared V-shaped fullerene trimer oxides,  $C_{180}O_n$ , along with dimer oxides  $C_{120}O_n$  by simple heating of a mixture of  $C_{60}$  and  $C_{60}$  oxides and characterised them by electrospray ionisation mass spectrometry (ESI-MS). There are reports on the matrix-assisted laser-induced aggregation of  $C_{60}$  [14] and  $C_{70}$  [15] oxides giving rise to dimeric species. Fullerene dimer oxides have been extracted from fullerene soot by a special method called 'hydrothermally initiated dynamic extraction' or HIDE technique by Takahashi et al. [16].  $C_{120}O$  undergoes thermal reactions with sulphur forming  $C_{120}OS$  [17]. The electrochemical and EPR studies on  $C_{120}O$  throw more light into the electronic structures of fullerene dimer oxides [18]. Theoretical calculations on the structure and energetics of fullerene dimer oxides also exist in the literature [19,20].  $C_{120}O$  upon decarbonylation

\*Corresponding author. Fax: +91-44-235-0509 and 2545.

E-mail address: pradeep@iitm.ac.in (T. Pradeep).

produces  $C_{119}$ , which has been isolated and characterised [8]. Infrared spectroscopic studies by Taylor et al. [21] confirm CO and  $CO_2$  losses from fullerene dimer oxides by thermal means. Because fullerene oxides can easily liberate attached oxygen atoms as CO and  $CO_2$ , the established techniques for their mass spectrometric studies are laser desorption mass spectrometry (LD-MS) and electrospray techniques (ESI-MS), often in the negative ion mode [13]. During matrix-assisted laser desorption ionisation (MALDI), laser-induced aggregation of  $C_{60}$  [14] and  $C_{70}$  oxides [15] occurs giving dimeric species. Recently, it was shown that the narrow line-width signal appearing in the electron paramagnetic resonance (EPR) spectrum of  $C_{60}O^-$  is due to  $C_{120}O^-$  formed from the unavoidable  $C_{120}O$  impurity in air exposed  $C_{60}$  [22].

Halogen compounds are well known as important synthetic intermediates due to their reactivity towards various nucleophiles. Chlorinated [23] and fluorinated [24] fullerenes have been used in the preparation of various derivatives.

In this Letter we show that  $C_{60}$  formed by the solid state thermal decomposition of  $C_{60}Br_{24}$  readily undergoes oxidation reactions with atmospheric oxygen which otherwise happens only with strong oxidising agents like ozone or by using photochemical or electrochemical methods. The fullerene epoxides thus formed undergo dimerisation reactions forming fullerene dimer oxides. Based on the observations and the available literature reports, possible reaction sequences during fullerene bromide decomposition have been proposed.

## 2. Experimental

$C_{60}Br_{24}$  was prepared by adding excess bromine to about 5 mg of  $C_{60}$  and the reaction was allowed to proceed overnight. After pumping away excess bromine, the product was separated as a yellow powder [25]. Purity of the product was checked with the FTIR spectroscopy. For thermal decomposition, the  $C_{60}Br_{24}$  sample was kept in air at 200°C for 12 h in an alumina boat. It was then taken out and  $C_{60}$  along with monomeric fullerene

oxides was removed by repeated washing with toluene. The dimer oxides were extracted with *o*-dichlorobenzene (ODCB) and evaporation of the solvent gave a microcrystalline powder. Yield was about 20% (in weight) of the parent  $C_{60}$ .

FTIR studies were performed with a Perkin Elmer Spectrum RXI FTIR spectrometer. A 10% (by weight) pellet of the sample was made by mixing it with pure KBr powder. A Leybold commercial cryostat was used for low-temperature FTIR measurements. The UV/VIS absorption spectra were taken with a VARIAN CARY-05 spectrophotometer.  $^{13}C$  NMR measurements were done in  $CS_2$  solutions with  $Cr(acac)_3$  as the relaxation agent using a 400 MHz GEOL NMR spectrometer.

Mass spectrometry was performed on a Finnigan LCQ ion trap mass spectrometer (Finnigan MAT, San Jose, CA, USA) with a nano-ESI ion source (Protana A/S, Odense, Denmark). A sample of 1–2  $\mu$ l solution of the oxides in 1,2-dichlorobenzene was loaded into the metal-coated glass capillary. The capillary was positioned about 1 mm away from the heated capillary. Electrospray was performed in the negative ion mode and the spray voltage was set at 800 V. The heated capillary was kept at 150°C. In the MS/MS mode, the precursor ion was isolated and fragmented at 40% collision energy.

## 3. Results and discussion

The negative ion electrospray mass spectrum of the products extracted from the reaction mixture using ODCB (Fig. 1) showed peaks corresponding to various fullerene dimer oxides,  $C_{120}O$ ,  $C_{120}O_2$ ,  $C_{120}O_3$ ,  $C_{120}O_4$ ,  $C_{120}O_5$ ,  $C_{120}O_6$ ,  $C_{120}O_7$  etc. as well as to the monomeric epoxides of  $C_{60}$ , such as  $C_{60}O$ ,  $C_{60}O_2$ ,  $C_{60}O_3$ ,  $C_{60}O_4$ ,  $C_{60}O_5$  etc. The MS/MS spectrum of  $C_{120}O$  (inset of Fig. 1) showed peaks corresponding to  $C_{60}$  and  $C_{60}O$  indicating the presence of one furanoid ring system bridging the cages which ruptures on fragmentation in agreement with the literature reports [10,11].

The FTIR spectrum of the mixture of fullerene dimer oxides is shown in Fig. 2 (top trace). The four IR peaks in the  $C_{60}$  spectrum at 1430, 1183,

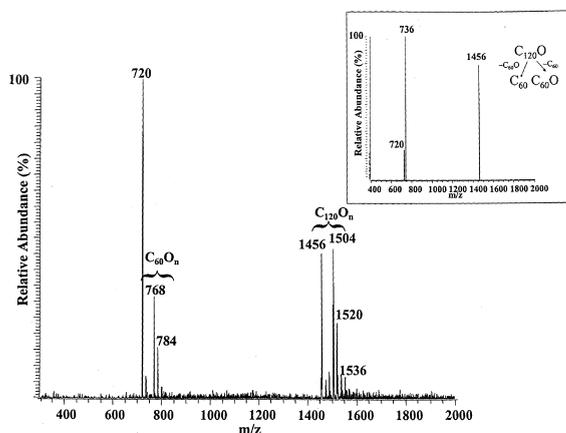


Fig. 1. The negative ion electrospray mass spectrum of the products extracted from the reaction mixture using ODCB. MS/MS data and fragmentation processes of  $C_{120}O^-$  are shown in the inset.

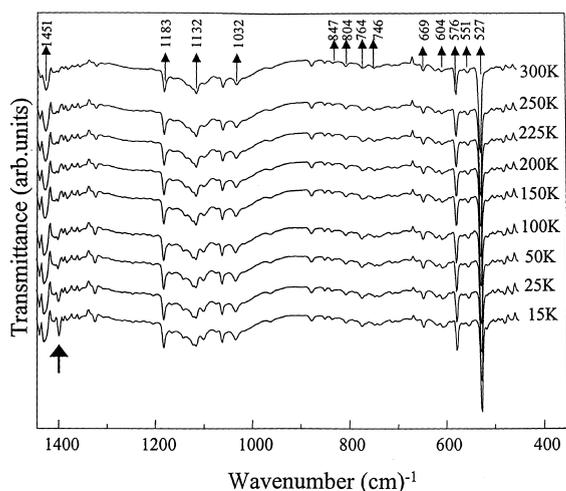


Fig. 2. Variable temperature IR spectra of the mixture of the fullerene dimer oxides in the  $1440\text{--}1450\text{ cm}^{-1}$  region, in the temperature range  $300\text{--}315\text{ K}$ . The temperatures are marked. The top trace gives the room temperature data. Some of the important peaks are labelled. The thick arrow shows the emergence of a band near  $1400\text{ cm}^{-1}$  around  $50\text{ K}$  indicating a phase transition. Note that no changes in the spectra are observed around the orientational ordering temperature of  $C_{60}$ .

$576$  and  $527\text{ cm}^{-1}$  (the  $F_{1u}$  modes) are shown up almost at the same positions for the dimer oxides, indicating that the fullerene cages are intact in these dimers. The presence of the  $527\text{ cm}^{-1}$  band, although at reduced intensity, seems to suggest

that complete  $C_{60}$  removal has not been achieved. However, the weakening of this signal and persistence of the other  $F_{1u}$  modes suggest that 1,2-functionalisation has occurred. The peak at  $1032\text{ cm}^{-1}$  can be attributed to the C–O stretching of the epoxide moieties. Several additional bands are observed in the spectrum, all of which can be attributed to the various intra-cage vibrations arising due to the removal of the  $I_h$  symmetry of the  $C_{60}$  cage due to epoxidation and dimerisation. A detailed study on the vibrational properties of  $C_{120}O$  and  $C_{120}O_2$  is reported by Krause et al. [20]. Our IR spectrum is consistent with the reported spectra of  $C_{120}O$  and  $C_{120}O_2$  and based on this, tentative assignments of the bands are given in Table 1. The far IR spectrum of the  $C_{120}O_n$  mixture shows several vibrations in the  $300\text{--}100\text{ cm}^{-1}$  region which correspond to the various inter-cage vibrations of the fullerene dimer oxides. Because the spectrum was taken for the mixture of compounds, a complete and clear assignment of the vibrational bands is difficult. Raman spectroscopic investigations on the cage–cage vibrations of fullerene dimer oxides have been reported by Eisler et al. [26].

The low-temperature FTIR study of the fullerene dimer oxides (Fig. 2) shows the absence of orientational ordering transitions in these materials, found in pristine  $C_{60}$  around  $247\text{ K}$  which manifest in the IR spectra as a splitting of the  $1429\text{ cm}^{-1}$  band and a substantial narrowing of the other bands. None of these changes are observed in the spectrum of the dimeric oxides down to  $50\text{ K}$ . Below  $50\text{ K}$  a new peak is found to emerge in the  $1400\text{ cm}^{-1}$  region, indicating a phase transition. But this cannot be compared with the orientational ordering transition of  $C_{60}$  found at  $247\text{ K}$  [27]. From the low-temperature FTIR study, it is evident that the  $C_{60}$  balls in these dimers are not free to rotate unlike the case of pristine  $C_{60}$  and  $C_{60}$  derivatives such as  $C_{60}O$  [28] and  $C_{60}Br_{24}$  [29] which also show the orientational ordering transition. Thus, it can be concluded that at least two C atoms from each fullerene ball are involved in inter-cage bonding restricting the free rotation.

Fig. 3 shows the comparison of the UV–visible absorption spectra of fullerene dimer oxides with pure  $C_{60}$  in ODCB. The  $C_{60}$  bands at  $338$  and  $404$

Table 1  
Infrared frequencies and their assignments for the fullerene dimer oxides<sup>a</sup>

Frequency (cm <sup>-1</sup> )	Assignments
527	F <sub>1u</sub> (1)
551, 576, 604	F <sub>1u</sub> (2)
644, 669, 690, 727, 746, 764, 804, 847	H <sub>g</sub> (3) and H <sub>g</sub> (4)
1032	Furanoid ring vibration
1100	H <sub>g</sub> (5)
1183	F <sub>1u</sub> (3)
1384, 1430, 1451	F <sub>1u</sub> (4)

<sup>a</sup> The notations F<sub>1u</sub>(1), F<sub>1u</sub>(2), F<sub>1u</sub>(3) and F<sub>1u</sub>(4) represent the vibrational modes derived from the F<sub>1u</sub> modes and H<sub>g</sub>(2), H<sub>g</sub>(3), H<sub>g</sub>(4) and H<sub>g</sub>(5) represent the vibrational modes derived from the H<sub>g</sub> modes of C<sub>60</sub>.

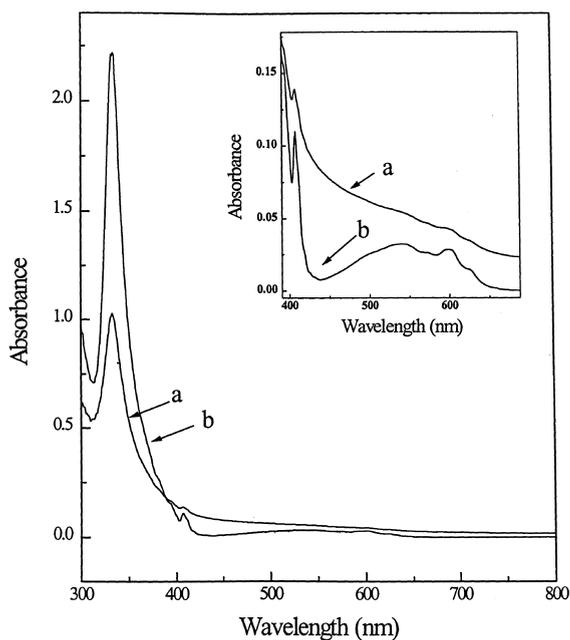


Fig. 3. A comparison of the UV-visible absorption spectra of fullerene dimer oxides (a) with pure C<sub>60</sub>, (b) both in ODCB.

nm are found almost at the same positions. The visible region (inset) shows featureless absorption around 450 nm, where C<sub>60</sub> does not absorb, consistent with the absorption spectra of fullerene epoxides [3] and fullerene dimer oxide [30].

In order to get a better understanding of the structure of the dimer oxides, an MS/MS study of

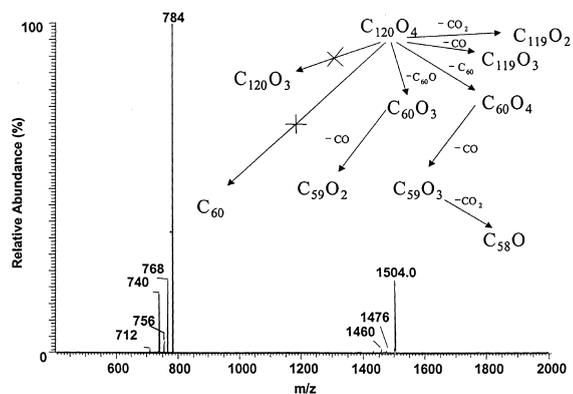


Fig. 4. The MS/MS data and fragmentation processes of C<sub>120</sub>O<sub>4</sub><sup>-</sup>. Unobserved channels are marked.

other species was undertaken. The most intense peak in the MS/MS spectrum of C<sub>120</sub>O<sub>4</sub><sup>-</sup> (Fig. 4) is the one corresponding to C<sub>60</sub>O<sub>4</sub><sup>-</sup>. This observation is apparently quite interesting which means that the dimer can fragment in such a way that all the oxygen atoms are on the same fullerene cage leaving the other fullerene monomers without any oxygen. The peak at *m/z* 768 corresponds to C<sub>60</sub>O<sub>3</sub><sup>-</sup>, which can come from the C<sub>120</sub>O<sub>4</sub><sup>-</sup> by a loss of C<sub>60</sub>O. The formation of C<sub>60</sub>O<sub>3</sub><sup>-</sup> by O loss from C<sub>60</sub>O<sub>4</sub><sup>-</sup> is ruled out by the MS/MS/MS study of C<sub>60</sub>O<sub>4</sub><sup>-</sup> (data not shown) which does not show any peak at *m/z* 768. The peaks at *m/z* 756, 740 and 712 correspond to C<sub>59</sub>O<sub>3</sub><sup>-</sup>, C<sub>59</sub>O<sub>2</sub><sup>-</sup> and C<sub>58</sub>O<sup>-</sup>, respectively. The MS/MS/MS studies of C<sub>60</sub>O<sub>4</sub><sup>-</sup> and C<sub>60</sub>O<sub>3</sub><sup>-</sup> show fragment ions of C<sub>59</sub>O<sub>3</sub><sup>-</sup>, C<sub>59</sub>O<sub>2</sub><sup>-</sup> and C<sub>58</sub>O<sup>-</sup> by sequential elimination of CO and CO<sub>2</sub>. There are two small peaks corresponding to C<sub>119</sub>O<sub>3</sub><sup>-</sup> and C<sub>119</sub>O<sub>2</sub><sup>-</sup> arising from CO and CO<sub>2</sub> losses of C<sub>120</sub>O<sub>4</sub><sup>-</sup>. C<sub>119</sub>, the 'non-classical' fullerene with odd numbered carbon atoms, formed from the decarbonylation of the C<sub>120</sub>O, is found to be not a transient species produced during mass spectrometric conditions, but a stable molecule which has been isolated and characterized [8]. The possible decomposition channels are depicted in the figure.

In the MS/MS spectrum of C<sub>120</sub>O<sub>5</sub><sup>-</sup> (Fig. 5), the major peaks at *m/z* 800 and 784 correspond to C<sub>60</sub>O<sub>5</sub><sup>-</sup> and C<sub>60</sub>O<sub>4</sub><sup>-</sup>. A small peak at *m/z* 768 corresponding to C<sub>60</sub>O<sub>3</sub><sup>-</sup> is also found in the spectrum. The C<sub>59</sub>O<sub>3</sub><sup>-</sup> peak is found to be a very



appears that halogenation and its subsequent elimination may be made use of in several solid state synthetic routes involving fullerenes. Our results on the formation of polymeric fullerene oxides are consistent with the recent literature reports which show that inter-cage linkages in fullerenes are achieved more easily using less stable fullerene oxides rather than with pure fullerenes which require extreme conditions like high pressure, specific photochemical conditions or mechano-chemical methods. From the detailed mass spectrometric studies of fullerene dimer oxides, it is evident that for the dimerisation via [3 + 2] cycloaddition reactions, the fullerene epoxides show a clear preference for pure C<sub>60</sub> rather than other C<sub>60</sub> epoxides. This manifests in the MS/MS spectra of the dimers as specific cleavages leaving all the oxygen atoms on one fullerene monomer. The reason for such a preference is not clear and an understanding requires further investigations. Although the sequential decarbonylations can distort the fullerene cages and completely alter their symmetry, like in C<sub>119</sub>, these molecules can possibly be stable so as to be isolated in preparative amounts. Such a possibility can open up research on an entirely new class of fullerene-based materials with new physical and chemical properties and potential applications.

### Acknowledgements

MRR thanks the CSIR, New Delhi for a research fellowship.

### References

- [1] R. Taylor (Ed.), *The Chemistry of Fullerenes*, World Scientific, Singapore, 1996, and references therein.
- [2] F. Diederich, R. Etil, Y. Rubin, R.L. Whetten, R. Beck, M. Alvarez, S. Anz, D. Sensharma, F. Wudl, K.C. Khemaniand, A. Koch, *Science* 252 (1991) 548.
- [3] K.M. Creegan, J.L. Robbins, W.K. Robbins, J.M. Millar, R.D. Sherwood, P.J. Tindall, D.M. Cox, *J. Am. Chem. Soc.* 114 (1992) 1103.
- [4] W.A. Kalsbeck, T.H. Horp, *J. Electroanal. Chem.* 314 (1991) 363.
- [5] R. Malhotra, S. Kumar, A. Satyam, *J. Chem. Soc. Chem. Commun.* (1994) 1339.
- [6] A.L. Balch, D.A. Costa, B.C. Noll, M.M. Olmstead, *J. Am. Chem. Soc.* 117 (1995) 8926.
- [7] J.L. Segura, N. Martin, *Chem. Soc. Rev.* 29 (2000) 13.
- [8] A. Gromov, A. Ballenweg, S. Giesa, S. Lebedkin, W.E. Hull, W. Kratschmer, *Chem. Phys. Lett.* 267 (1997) 460.
- [9] R. Taylor, *J. Chem. Soc. Chem. Commun.* (1994) 1629.
- [10] A. Gromov, S. Lebedkin, W.E. Hull, W. Kratschmer, *J. Phys. Chem. A* 102 (1998) 4997.
- [11] S. Lebedkin, A. Ballenweg, J. Gross, R. Taylor, W. Kratschmer, *Tetrahedron Lett.* 36 (1995) 4971.
- [12] A. Gromov, S. Lebedkin, A. Ballenweg, A.G. Avent, R. Taylor, W. Kratschmer, *J. Chem. Soc. Chem. Commun.* (1997) 209.
- [13] J.P. Deng, C.Y. Mou, C.C. Han, *Chem. Phys. Lett.* 256 (1996) 96.
- [14] M.P. Barrow, N.J. Tower, R. Taylor, T. Drewello, *Chem. Phys. Lett.* 293 (1998) 302.
- [15] M.S.A. Jafari, M.P. Barrow, N.J. Tower, R. Taylor, T. Drewello, *Int. J. Mass. Spectrom.* 184 (1999) L1.
- [16] H. Takahashi, K. Tohji, I. Matsuoka, B. Jeyadevan, A. Kasuya, S. Ito, Y. Nishina, T. Nirasawa, *J. Phys. Chem. B* 102 (1998) 5438.
- [17] S. Giesa, J.H. Gross, W.E. Hull, S. Lebedkin, A. Gromov, R. Gleiter, W. Kratschmer, *J. Chem. Soc. Chem. Commun.* (1999) 465.
- [18] S.P. Solodovnikov, B.L. Tumanskii, V.V. Bashilov, S.F. Lebedkin, W. Kratschmer, *Chem. Phys. Lett.* 303 (1999) 390.
- [19] P.W. Fowler, D. Mitchell, R. Taylor, G. Seifert, *J. Chem. Soc. Perkin Trans. 2* (1997) 1901.
- [20] M. Krause, L. Dunsch, G. Seifert, P.W. Fowler, A. Gromov, W. Kratschmer, R. Gutierrez, D. Porezag, T. Fraueheim, *J. Chem. Soc. Faraday. Trans.* 94 (1998) 2287.
- [21] R. Taylor, A. Penicaud, N.J. Tower, *Chem. Phys. Lett.* 295 (1998) 481.
- [22] P. Paul, R.D. Bolskar, A.M. Clark, C.A. Reed, *J. Chem. Soc. Chem. Commun.* (2000) 1229.
- [23] Y. Yoshida, A. Otsuka, O.O. Drozdova, G. Saito, *J. Am. Chem. Soc.* 122 (2000) 7244 and references cited therein.
- [24] E.T. Mickelson, R.H. Hauge, J.L. Margrave, *J. Fluorine Chem.* 92 (1998) 59.
- [25] P.R. Birkett, P.B. Hitchcock, H.W. Kroto, R. Taylor, D.R.M. Walton, *Nature* 357 (1992) 479.
- [26] H.J. Eisler, F.H. Hennrich, E. Werner, A. Hertwig, C. Stoermer, M.M. Kappes, *J. Phys. Chem. A* 102 (1998) 3889.
- [27] P.A. Heiney, J.E. Fisher, A.R. McGhie, W.J. Romanow, A.M. Denenstein, J.P. McCauley Jr., A.B. Smith III, D.E. Cox, *Phys. Rev. Lett.* 67 (1991) 1467.
- [28] G.B.M. Vaughan, P.A. Heiney, D.E. Cox, A.R. McGhie, D.R. Jones, R.M. Strongin, M.A. Cichy, A.B. Smith III, *Chem. Phys.* 168 (1992) 185.
- [29] M.R. Resmi, L. George, S. Singh, U. Shankar, T. Pradeep, *J. Mol. Struct.* 435 (1997) 11.

- [30] A.B. Smith III, H. Tokuyama, R.M. Strongin, G.T. Furst, W.J. Romanow, *J. Am. Chem. Soc.* 117 (1995) 9359.
- [31] M.R. Resmi, K. Smitha, T. Pradeep, *Proc. Indian Acad. Sci. (Chem. Sci.)* 109 (1997) 221.
- [32] P. Scheier, R. Robl, B. Schiestl, T.D. Mark, *Chem. Phys. Lett.* 220 (1994) 141.
- [33] P.M. Ajayan, T.W. Ebbesen, T. Ichihashi, S. Iijima, K. Tanigaki, H. Hiura, *Nature* 362 (1993) 522.