

# FULLERENIUM SALTS: NEW C<sub>60</sub> CATION BASED MATERIALS

Mauro Riccò<sup>1</sup>, Daniele Pontiroli<sup>1</sup>, Marcello Mazzani<sup>1</sup>, Giorgia Zandomeneghi<sup>2</sup>, Beat H. Meier<sup>2</sup> and Toni Shiroka<sup>3</sup>

<sup>1</sup>Dipartimento di Fisica, Università di Parma, Via G.Usberti 7/a, 43100 Parma, Italy.

<sup>2</sup>Physical Chemistry Laboratory, ETH-Zurich, Wolfgang-Pauli-Strasse 10, CH-8093 Zurich, Switzerland.

<sup>3</sup>Laboratorium für Festkörperphysik, ETH-Zurich, Schafmattstrasse 16, CH-8093 Zurich, Switzerland.

## Introduction

The large variety of compounds referred to as fullerides are intensively investigated due to their exciting electronic and transport properties, such as high-T<sub>c</sub> superconductivity, molecular magnetism, and ionic conductivity[1-4]. These C<sub>60</sub> charge-transfer salts invariably contain C<sub>60</sub> in its anionic form. In fact, the observation of six reversible reduction states[5] confirms that C<sub>60</sub> is an exceptionally good electron acceptor, but, consequently, also a bad electron donor. However, the interest in producing a fullerene salt, namely a solid in which the fullerenes are in the oxidized state, is kept rather high, prompted by the noticeable electronic properties expected in a “hole-doped” C<sub>60</sub> compound[6, 7].

Although the oxidation of C<sub>60</sub> has already been reported in the gas phase[8] and in solution[9], the preparation of an ionic solid containing C<sub>60</sub> as a cation has proved to be quite a challenging task, due to the extreme reactivity of the C<sub>60</sub><sup>n+</sup> species. Here, we report the synthesis and the extensive characterization of the compound C<sub>60</sub>(AsF<sub>6</sub>)<sub>2</sub>, where fullerenes are in the 2+ oxidized state. We show that in this system the extremely reactive C<sub>60</sub><sup>2+</sup> cations, among the most reactive molecular ions in nature, organize themselves to form a novel 1D polymer architecture. Either Nuclear Magnetic Resonance (NMR), SQUID magnetometry and DC conductivity show that this polymer is a diamagnetic semiconductor. These results establish a new class of C<sub>60</sub> based materials, with still unexplored physical and chemical properties.

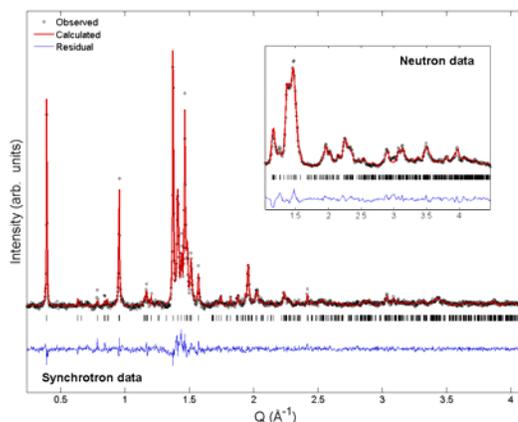
## Experimental

The fullerene salt C<sub>60</sub>(AsF<sub>6</sub>)<sub>2</sub> was prepared starting from C<sub>60</sub> powder (purity 99.9%, MER Corporation) and gaseous AsF<sub>5</sub> (purity 99.9%, ABCR GmbH), in ratio 1:3; the two compounds were made to react using SO<sub>2</sub> as a solvent (purity 99.9+%, Aldrich) [10]. After having dispersed C<sub>60</sub> in liquid SO<sub>2</sub> (previously dried in CaH<sub>2</sub>), the stoichiometric amount of AsF<sub>5</sub> was condensed on this mixture at 77 K in a high-pressure reactor. The system was slowly heated up to 323 K and the mixture was left under continuous stirring for 16 hours at a pressure of 8.5 bar. The precise control of the AsF<sub>5</sub> stoichiometry and reaction temperature proved essential for obtaining a pure and properly crystallized product. This was not followed in other similar preparations described in the literature[11], which gave compounds sensibly different from the one reported here, probably consisting in a mixture of different phases. Both the solvent and the volatile reaction products were successively

removed by slow evaporation by letting them gurgle into a 1 M NaOH solution. The reaction vessel was then evacuated to a pressure of 10<sup>-2</sup> mbar for 5 minutes at 273 K. Finally the sample was removed from the vessel in an Ar glove box (<1 ppm O<sub>2</sub> and H<sub>2</sub>O). All successive manipulations were done under pure Ar.

The diffraction experiments were performed at ambient temperature, respectively on the ID31 beamline ( $\lambda = 0.9337 \text{ \AA}$ ) at the European Synchrotron Radiation Facility (ESRF), and at the SuperD2B diffractometer ( $\lambda = 1.59432 \text{ \AA}$ ) at the Institut Laue Langevin (ILL), Grenoble. Gas picnometry was performed using a home-built picnometer operating in an Ar glove box.

MAS-NMR spectra were recorded with a Varian Infinity+300 spectrometer operating at a <sup>13</sup>C frequency of 75.23 MHz in a Chemagnetics 4 mm double resonance MAS probe. 4 mm Chemagnetics rotors were used, whose PTFE inserts were glued to avoid exposure to air.

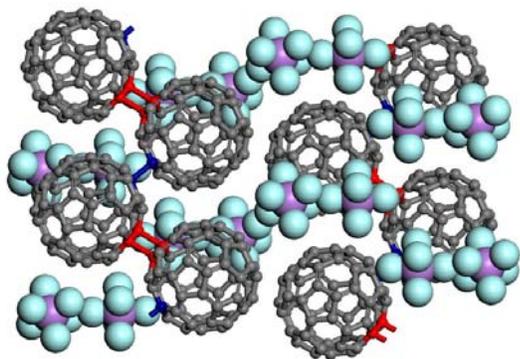


**Fig. 1** Observed (o) and calculated (solid red line) powder diffraction pattern of C<sub>60</sub>(AsF<sub>6</sub>)<sub>2</sub> at 300 K, from synchrotron and neutron diffraction data.

## Results and Discussion

Due to the complex structure of the compound, the combination of high-resolution synchrotron and neutron powder diffraction proved necessary to achieve a definitive structural identification of this material. At room temperature both techniques show the presence of a single phase, which we indexed with an orthorhombic cell ( $a = 10.450(3) \text{ \AA}$ ,  $b = 9.993(6) \text{ \AA}$ ,  $c = 32.07(1) \text{ \AA}$ ), although by studying the molecular configuration we proved that the true symmetry is monoclinic (space group I2/m) with  $\beta \approx 90^\circ$ . These data and the density of the compound, 2.2(2) gr/cm<sup>3</sup> as determined by gas picnometry, suggest that the correct stoichiometry is C<sub>60</sub>(AsF<sub>6</sub>)<sub>2</sub>. We then achieved the rough structural model of the fullerene salt through the use of a simulated annealing algorithm, after the extraction of the structural factors by whole pattern decomposition (Pawley method). The best agreement between the observed and calculated data was reached with the C<sub>60</sub> centers of mass at the special position 4i ( $x, 0, z$ ), with  $x = 0.751(1)$  and  $z = 0.1140(8)$ , while the two AsF<sub>6</sub><sup>-</sup> molecular ions naturally occupy the available empty voids, allowed by the sterical hindrance of the fullerenes, centered at the position 4i with  $x = 0.76(2)$ ,  $0.75(2)$  and  $z = 0.700(3)$ ,  $0.558(2)$ . With such an arrangement, the

minimum centre-to-centre distance of two neighboring  $C_{60}$  units is approximately 9 Å, a value compatible with the polymerisation of the molecules. The closest contacts for each fullerene are obtained along two different vectors of the  $ac$  plane, which are not mutually orthogonal. This generates a “zigzag” disposition of  $C_{60}$ s, which propagate along the a crystallographic direction (see Figure 2). Rietveld refinement was performed at the same time on both synchrotron and neutron data: while the former allowed to localise the various components of the cell, the latter permitted the determination of the precise molecular orientation.



**Fig. 2.** View of the crystal structure along the (110) crystalline direction.

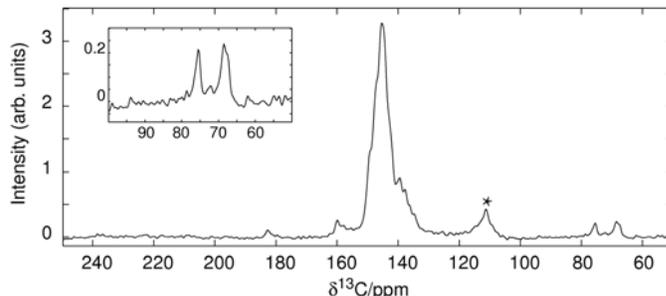
Such an unusual polymer texture was further confirmed by  $^{13}\text{C}$  MAS NMR (Figure 3). The  $^{13}\text{C}$  NMR spectrum of  $C_{60}(\text{AsF}_6)_2$  consists of a multiplet at about 140-150 ppm due to  $sp^2$  carbons and two well resolved peaks in the  $sp^3$  hybridized carbon region, at 68 and 75 ppm. The ratio of the integrals of the peaks at 68 and 75 ppm is about 1:2. This is consistent with the presence of two  $sp^3$  carbons involved in the single and double intermolecular bonds. The broad structure of the  $sp^2$  component is, on the other hand, indicative of the deformation of the  $C_{60}$  units upon polymerization.  $^{19}\text{F}$ -decoupling did not produce any difference in the  $^{13}\text{C}$  spectrum, thus proving that the  $sp^3$  carbon are not bonded to fluorine.

The electronic properties of the compound can be inferred from the NMR spectra (both static and MAS) which, in the case of metallic behaviour, would be heavily affected by the Knight shift interaction, contrary to what is observed here. In fact, the  $^{13}\text{C}$  static spectrum can be fitted by a shift tensor characterized by an isotropic shift of 145 ppm and an anisotropy of -107 ppm. These values are close to the parameters of the chemical shift tensor of pristine  $C_{60}$ .  $^{13}\text{C}$  NMR spin-lattice relaxation and DC conductivity further confirm this result by showing an Arrhenius behavior with an activation energy  $E_a^{\text{NMR}} = 65$  meV in the case of NMR relaxation and  $E_a^{\text{DC}} = 78.5$  meV for DC conductivity.

## Conclusions

We have successfully synthesized the fullerene salt  $C_{60}(\text{AsF}_6)_2$  where  $C_{60}$  is present in its dication form. Its solid-state structure studied by combined synchrotron radiation x-ray diffraction and neutron diffraction, evidences the polymerization of the  $C_{60}$  units with an unusual zig-zag bonding motif. Although the low nucleophilic propensity of  $\text{AsF}_6^-$  allows the stabilization of  $C_{60}^{2+}$  in the solid state, the extremely high reactivity of the

dication is certainly at the origin of the observed polymerization. This effect put doubts on the possibility that a monomer fullerene salt with enhanced superconducting and/or magnetic properties (as theoretically predicted in several studies[6, 7] and in few cases also claimed[12, 13]) could be successfully produced. The synthesized material is, on the other hand, a small gap semiconductor which shows a weak molecular diamagnetism.



**Fig. 3.**  $^{13}\text{C}$  MAS NMR spectrum of the fullerene salt  $C_{60}(\text{AsF}_6)_2$  collected at room temperature, with spinning frequency of 10 kHz. The peak marked with an asterisk is due to PTFE inserts of the rotor.

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