ON THE WAY TO Fe–C$_{60}$ COMPOUNDS

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Abstract

Iron: fullerides were prepared by chemical methodes in the solution using nitric acid as activation agent. Experimental results of thermal analyses, X-ray diffraction and Mössbauer spectroscopy of the products are presented. To interpret these results, standard quantum chemistry calculations were used to determine the geometry and charge distribution in Fe:C$_{60}$ complexes, which might be formed in the reaction.

Keywords: ferrocene, fullerenes, Mössbauer spectroscopy, quantum chemistry calculation

Introduction

Transition metals (Fe, Ni, Co) with partially occupied 3d-orbitals are interesting dopants to fullerites because of possible magnetic and conducting properties of these materials. The endohedral Fe@C$_{60}$ and exohedral FeC$_{60}$ complexes were detected in a gas phase by mass spectroscopy [1], and ion beam scattering technique [2]. In other experiments it was shown that iron might be introduced into the fullerite matrix by electrochemical method [3], metal vapor deposition [4], or Fe ion implantation [5]. However the properties of those materials did not result from the interaction between Fe and C$_{60}$, also in a host-guest C$_{60}$(ferrocene)$_2$ compound [6–8] iron does not directly interact with fullerenes. In our experiments [9–12] we used ferrocene (Fn=Fecp$_2$, cp=C$_5$H$_5$) as a source of the metal activating either Fn or C$_{60}$ in anticipation that ferrocene adducts to C$_{60}$ would be formed. To predict direction of the reactions, to determine possible reaction products and to estimate their stability we used semiempirical quantum chemistry model ZINDO 1 [13], which well reproduces geometry of C$_{60}$ giving the bonds lengths d_{66}=0.1398 nm and d_{56}=0.1451 nm.

Experimental results and discussion

Nitration of fullerenes

The reaction was carried out in toluene solution, to which mixture of nitric acid and acetate acid was added. Nitration of fullerenes [14] occurred during annealing of the solution to 95°C what led to change of its color to yellow without any characteristic absorption bands in the UV/VIS region. The addition of Fn to this solution at

C$_{60}$:Fe=1:2 molar proportion caused formation of an amorphous precipitate containing fullerenes and Fn derivatives, which was insoluble in standard organic solvents.

The samples were analyzed by DSC and TG methods by using Du Pont 910 and 951 instruments. It exhibited an exothermic peak at 150–250°C and mass loss extending up to 450°C (Fig. 1a). The exothermic effect resulted probably from polymerization of fullerenes and cyclopentadiens induced by the nitric groups, the evaporation of which was observed as the mass loss. It showed that the volatile hydrocarbon impurities may be removed from the samples by annealing in vacuum to 380–450°C. The concentration of iron 2Fe/60C in the annealed samples was determined by X-ray fluorescence.
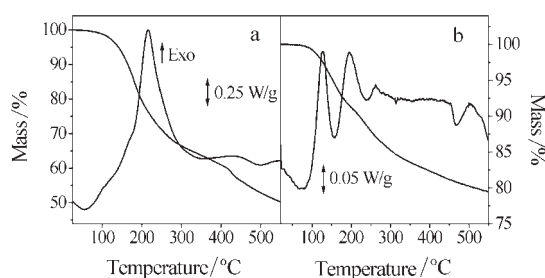
Fig. 1 The DSC and TG plots of Fn:C$_{60}$ adducts prepared by nitrofullerenes (a) and ferricenium ions (b)

A diffuse scattering by objects of the size of 1 nm observed by the X-ray diffraction and electron diffraction pattern characteristic for amorphous fullerite proved that fullerenes did not degrade in the reaction.

Reaction with ferricenium ion

Nitric acid can be used to ionize ferrocene to Fn^{1+} state where Fe binding is weaker. These reactions were performed in toluene solution heated to 70°C for 2 h, at the proportion of active components HNO$_3$/Fn/C$_{60}$ in the range of (8–2)/2/1. Proportion of the components was chosen to minimize polymerization of fullerenes. The dried products of the reaction exhibited weak exothermic peaks (Fig. 1b) which we ascribe to polymerization of cp groups and solvent molecules induced by NO$_3^-$. Mass spectroscopy in fresh samples, with electron impact ionization, revealed a sequence of peaks in the low mass range, which might be ascribed to fragmentation of C$_{11}$H$_{10}$ suggesting, that polymerization of C$_5$H$_5$ occurred already in the toluene solution. It was verified by using molecular modeling that in the complexes that might be formed Fe bonding was weaker than in ferrocene. The HOMO in those complexes is localized at Fe site, what indicates that this fragment is chemically the most active one. The X-ray diffraction pattern measured on the powder comprised several broad reflections that indicated the beginning of the crystallization of the product. The diffraction pattern resembled that of C$_{60}$:C$_7$H$_8$ solvates, yet the pattern was insufficient to identify the crystalline structure of the samples. Fullerene adducts and polymerized cp's were re-

moved by annealing of the samples above 400°C in vacuum. The samples after heating remained partially soluble in toluene. This part contained iron at a concentration 0.5–1Fe/C$_{60}$. After annealing in vacuum to 250°C, the powder still containing Fe adopted a mixture of the fcc and hcp lattices. Iron in the fullerene based lattice might occupy interstitial sites (even these in the (111) planes) without distorting the structure much.

Mössbauer spectroscopy

The Mössbauer spectroscopy was used to identify the binding between Fe and C$_{60}$. The Mössbauer spectra (in the temperature range of 78–300 K) were measured at various stages of annealing to observe evolution of iron state in the compound. Here we present the measurements performed on samples prepared by method 'a' because in both methods HNO$_3$ was utilized as the activating agent therefore at some stage ferricenium ions were formed and Mössbauer spectra were similar.

The values of Quadrupole Splitting – QS=1.22 mm s^{-1} and Isomer Shift - IS=0.44 mm s^{-1} observed in the fresh samples are very close to those in ferricenium ions and are usually ascribed to iron Fe^{3+}, which proves that in the amorphous sediment ferrocene was oxidized to ferricenium ion by nitrofullerenes. A second doublet with QS=2.37 mm s^{-1} and IS=0.52 mm s^{-1} emerged in samples heated in vacuum beside the main component (Figs 2a, b). This doublet, very close to that found in pure ferrocene, is usually ascribed to Fe^{2+}. The effect may result from the reduction of Fn^{1+} to Fn due to decreasing concentration of the nitric groups. However, further annealing lowered its intensity, the intensity of the first doublet increased. These changes indicated that Fn was bound to C$_{60}$ by an unidentified molecular bridge because if there was a direct chemical bonding between fullerene and cyclopentadiene then, according to our molecular modeling results, charge distribution around Fe should differ from that in Fn, therefore, should exhibit other Mössbauer spectra. On the other hand, if there were only van der Waals interaction between C$_{60}$ and Fn, as in C$_{60}$Fn$_2$ crystals, Fn would evaporate below 200°C [15].
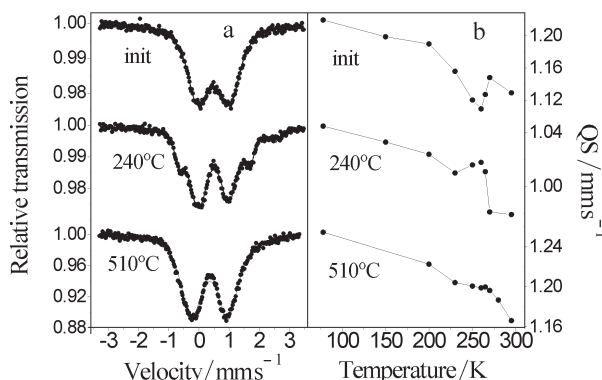
Fig. 2 Mössbauer spectra measured at 78 K (a) and QS temperature dependence (b) in the samples prepared by method 'a'

Trying to explain the observations we calculated the charge distribution in the vicinity of Fe in FeC$_{60}$ complexes using the ZINDO 1 method. The charge distribution resembling that in Fn was found in FeC$_{60}$h (total spin S=2) where Fe is outside the cage and close to hexagon, C$_{60}$FeC$_{60}$ in linear conformation (S=0, 2) with Fe between hexagons. In several other: exohedral FeC$_{60}$p (S=0) with Fe above a pentagon, exohedral FeC$_{60}$h (S=0) with Fe opposite a hexagon, endohedral Fe@C$_{60}$ (S=0 or 2) with Fe localized in the center of C$_{60}$ or shifted towards one of the hexagons, and C$_{60}$FeC$_{60}$ in nonlinear conformation (S=0 or 2) with Fe between pentagons (Fig. 3), the charge distribution resembles octahedrally distorted sphere, where neither the spherical nor the octahedral part contribute to the QS, hence it ought to be small. The doublet with low QS observed in the high temperature annealed samples might originate from iron in any of those states.

The QS of the main component exhibits strong fluctuation around 260 K (Fig. 2b), this effect was not observed in the pure Fn and in the van der Waals C$_{60}$Fn$_2$ crystals. The fluctuation may be ascribed to the influence of fullerenes on the charge distribution around Fe ion.
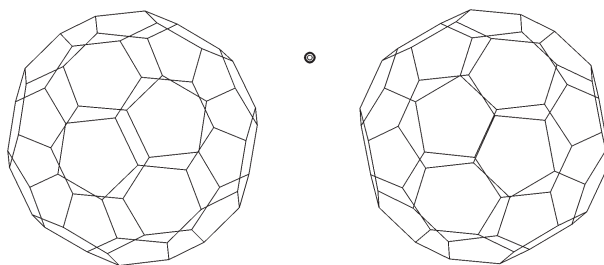

Fig. 3 One of the possible structure of Fe:C$_{60}$ complex with charge distribution around Fe similar to that in Fn[1+]

Conclusions

We have presented two reactions binding complexes containing iron to fullerenes under mild conditions excluding formation of clusters of iron, iron oxides or carbides. The samples exhibited two Mössbauer doublets, intensities of which varied with thermal treatment. We are inclined to suppose that iron may exist in two different states in the fullerite lattice and thermal treatment can change iron position. These results are consistent with Mössbauer spectroscopy measurements. Our calculations based on quantum chemical methods presented here also indicate that iron can bind fullerene in a few different configurations.

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