ENDOHEDRAL METALLOFULLERENES: SYNTHESIS, ISOLATION, REACTIVITY AND POSSIBLE APPLICATION

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Endometallofullerenes (EMF) were firstly reported by R.E. Smalley et al [1] even in 1985 immediately after they had discovered fullerenes. However, structure and properties of EMF were initiated to be studied in the 90ies only when electric arc method was used to prepare EMF in which graphite rods compounded by different metals or metal oxides were used. Nevertheless, physical and especially chemical properties of EMF have not been studied in detail so far mainly because of limited accessibility of EMF to researchers, which originates from the problem [2] of their synthesis and isolation as individual compounds. Since the content of EMF in soot is not higher than 1%, they are prepared as individual compounds by a laborious method of high-performance preparative liquid chromatography. Thus, pure EMF are still accessible in milligrams only. In contrast to fullerenes C_{60}, C_{70} and even higher fullerenes and nanotubes, EMF are still commercial products.

In spite of the problem of synthesis of EMF, about 50 EMF have now been isolated and characterized by various methods [2]. It was found that stable EMF are formed mainly from higher fullerenes C_{82}, C_{80}, C_{84} with metals from the 2nd and the 3rd group (Ca, Sr, Ba, Sc, Y, La) and all lanthanides. EMF involving these fullerenes were prepared and characterized which contained 1 and/or 2 metals atoms. For Sc there were even 3 and 4 metal atoms inside the fullerene cage. The EMF molecules can be considered as superatoms (Fig.1) which involve positively charged metal a negatively charged fullerene cage. Due to unique structure and unusual properties, EMF are of great interest as molecular conductors, magnets and ferroelectrics.

In the early 90ies EMF were assumed to exhibit superconducting properties. These suggestions were based on illusory similarity between exocomplexes of K_3C_{60} type and EMF since in both complexes 3 electrons are transferred from metal to the fullerene cage. As a result, a paramagnetic molecule is formed. However, recent direct conductivity measurements performed on the EMF Dy, La, Ce films allowed one to conclude on that EMF are semiconductors with low

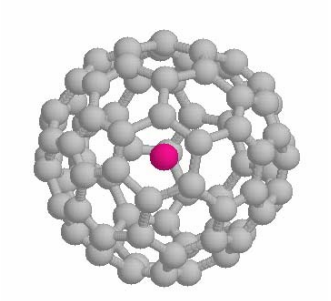

Fig.1. Structure of EMF $La^{3+}@C_{82}{}^{3}$.

conductivity activation energy, namely, from 0.2 to 0.4 eV depending on inserted metal that is essentially lower than for C_{60}, which is 1.8-2.2 eV. Room-temperature conductivity of EMF is 10^{-2} - 10^{-3} $Ohm^{-1}cm^{-1}$ that is 6 orders of magnitude higher than that of C_{60}.

In 1999 one more class of EMF was discovered [3], which are fullerene endotrimetalnitrides, $M_3N@C_{2n}$, M=Sc, Er, Lu; C_{2n}= 80, 78, which were prepared by arc evaporation of graphite electrodes in helium atmosphere with small admixture of nitrogen (Fig.2). It should be noted that progress in understanding structures and properties of such compounds is much faster than that for EMF first of all due to their higher solubility. For this reason, they are more easily isolated from soot and their reactivity can be studied. Single crystals of $Sc_3N@C_{80}$ and $Lu_3N@C_{80}$ solvates with o-xylene

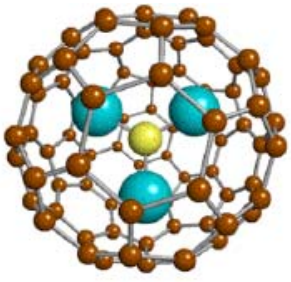

Fig. 2. Trimetal nitrides endohedral metallofulerene $Sc_3N@C_{80}$.

have already been prepared and their crystal structures have been determined. The M_3N fragment is planar, nitrogen is located in the center of the fullerene cage, and the M-N-M angle is 120°.

Successful functionalization of "empty" fullerenes allows one to conclude on that commercial application of EMF should be sought as in case of "empty" fullerenes through preparing EMF derivatives which show higher solubility, and unique physical-chemical and biological properties. However, now chemistry of EMF derivatives has weakly been studied in contrast to well-known exohedral modifications of fullerene C_{60}.

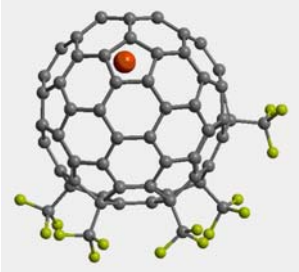

Fig.3. Trifluoromethyl derivative of EMF $Y@C_{82}(CF_3)_5$.

In contrast to fullerenes, the task of synthesis of EMF in preparative quantities has not been solved yet. As a result, there are very few publications on functionalization of EMF. Nevertheless, there are publications on trifluoromethylation of EMF in which the tasks of synthesis of derivatives were solved using anionic forms rather than individual EMF, particularly, as N,N-dimethylformamide extracts [4], which can be prepared in preparative quantities.

The most important and high efficient applications of EMF were found to be those in magnetic resonance imaging and radio therapy. Commercially available amine complexes based on Gd^{3+} with S=7/2 are conventionally used as contrast agents in NMR tomography to enhance water protons relaxation rates. It was found that EMF $Gd@C_{82}$ functionalized by OH groups to enhance water solubility is 20 times more efficient than these complexes [5]. The development of this field can result in new more efficient and lower toxic contrast agents in NMR tomography. This result gives impetus to the development of new approaches to the isolation of EMF and the synthesis of new water soluble compounds based on EMF.

Conclusions

EMF and their derivatives are promising engineering structural materials in nanotechnologies of XXI century.

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