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High-Yield Synthesis of Endohedral Metallofullerenes $Y@C_{2n}$ and $Y_2@C_{2n}$

Yong Fu LIAN, Zu Jin SHI, Xi Huang ZHOU, Xiao Ran HE, Zhen Nan GU*

Department of Chemistry, Peking University, Beijing 100871

Abstract: A series of yttrium metallofullerenes, some of them are first reported, have been synthesized by the DC arc discharge method at high helium pressure. Mass spectra results show that the contents of metallofullerenes are very high both in primary soot and in CS_2 or DMF extract, and $Y@C_{82}$ with *ca.* 85% purity is obtained through column chromatographic isolation.

Keywords: Metallofullerene, yttrium, DC arc discharge, catalyst, mass spectra.

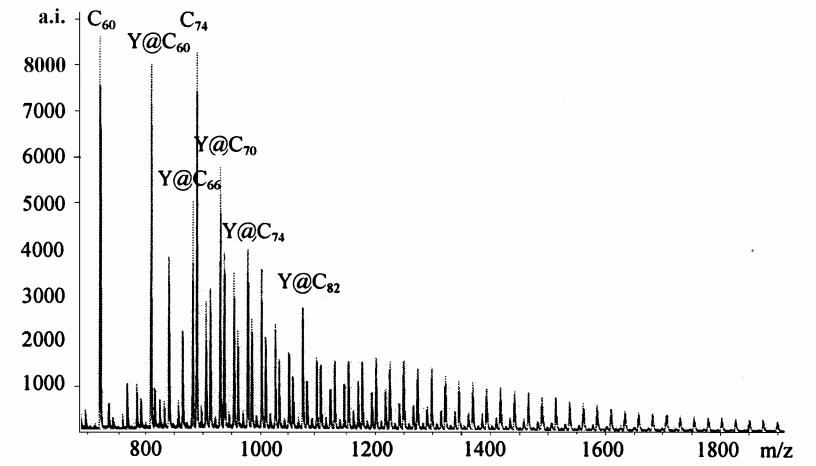
Because of their unusual structure and many expected novel optic, electric and magnetic properties, endohedral metallofullerenes (EMFs) have intensely attracted the interest of both chemists and material scientists. The original yttrium EMFs were synthesized by laser ablation[1] and arc burning method[2]. Up to now, only $Y@C_{82}$ was isolated and purified by HPLC[3] in milligram quantities and some spectroscopic and structural analyses including XPS[1,] EXAFS[4], STM[5], ESR[6], XRD[7] and Raman technique[8] have been used to characterize it. However, further investigations are strongly hampered by its generally low-yield production and difficult separation. In this letter, some new synthesis conditions, extraction and isolation methods including Y-Ni alloy, high helium pressure, successive Soxhlet-extraction with CS_2 and DMF, and column chromatographic separation are used. Mass spectra demonstrate that yttrium EMFs, some of them are first reported, are successfully synthesized in high yield and $Y@C_{82}$ with *ca.* 85% purity is obtained in milligrams.

The soot was produced by DC arc discharge method. A ϕ6×150 mm graphite rod (specpure), drilled a ϕ4×100 mm hole and filled with a powder mixture of Y-Ni alloy and graphite in (Y+Ni)/C atomic ratio of 3:10, was used as anode. An arc was generated between the anode and a ϕ10 mm graphite cathode (the gap distance remained *ca.* 10 mm) at 60A in a helium (5×10^4 Pa) static atmosphere. The produced soot was successively Soxhlet-extracted by CS_2 and DMF. The DMF extract was processed through column chromatography on silica gel with xylene and DMF as eluents. The DMF eluate, along with the primary soot, CS_2 extract and DMF extract, was analyzed by laser desorption mass-spectrometry (MALDI-TOF, SIFLEX III).

Figure 1 is a mass spectrum of the primary soot dispersed in toluene. All of the MS peaks can be ascribed to C_{2n} (2n = 44 - 290), $Y@C_{2n}$ (2n = 48 - 144) and $Y_2@C_{2n}$ (2n

= 48 - 120). Besides $Y@C_{2n}$ and $Y_2@C_{2n}$ having been reported in literature[2,9,10], the soot contains many new EMFs, such as $Y@C_{2n}$(2n = 48 -54, 108 -144) and $Y_2@C_{2n}$ (2n = 48 -58). Furthermore, the prominent peaks of $Y@C_{2n}$ (2n = 60, 66 - 84) reveal that the abundance of yttrium EMFs in the soot is very high.

Figure 1 The positive-ion MALDI-TOF mass-spectrum of primary soot.



As **Figure 2** shows, there are many soluble $Y@C_{2n}$ (2n= 70 - 134) and $Y_2@C_{2n}$ (2n = 70 -134) in the CS_2 extract and the peak of $Y@C_{82}$ or $Y_2@C_{82}$ is higher than that of any empty fullerenes. It is clear that high-yield yttrium EMFs have been extracted by CS_2. However, no peak of $Y@C_{60}$ and $Y@C_{66}$, which are two main EMFs in the primary soot, is found in **Figure 2**. It means that they are unable to be extracted by CS_2. This conclusion is in agreement with what have been reported previously[11].

Figure 2 The positive-ion MALDI-TOF mass-spectrum of CS_2 extract

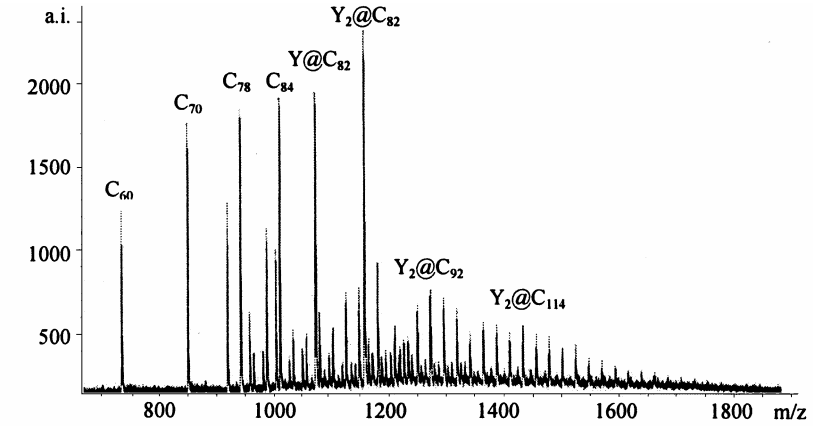


Figure 3, the mass spectrum of DMF extract from the residues after CS_2 extraction, exhibits high peaks of $Y@C_{82}$, $Y_2@C_{80}$, $Y@C_{80}$, $Y@C_{74}$ and $Y@C_{84}$ and low peaks of empty fullerenes. It suggests that a mixture of yttrium EMFs with a trace of empty fullerenes has been extracted by DMF. Comparing **Figure 3** with **Figure 2**, it can be seen that bimetallofullerenes are main components in apolar solvent while mono-metallofullerenes are main components in polar solution. This phenomenon can be explained by the dipole-dipole interaction[12] between EMFs and solvents.

Figure 3 The positive-ion MALDI-TOF mass-spectrum of DMF extract

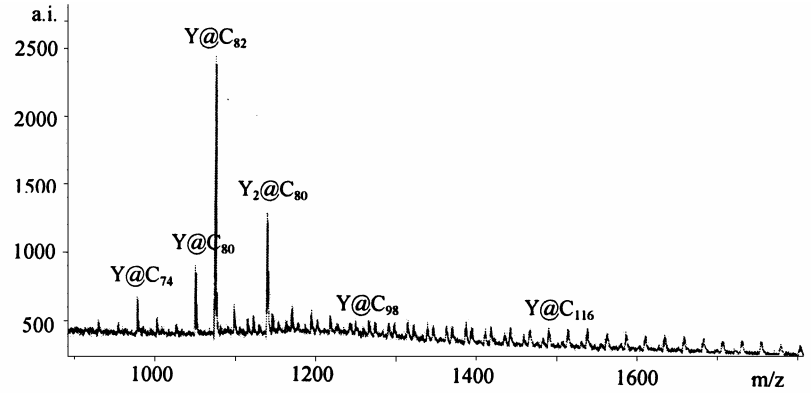
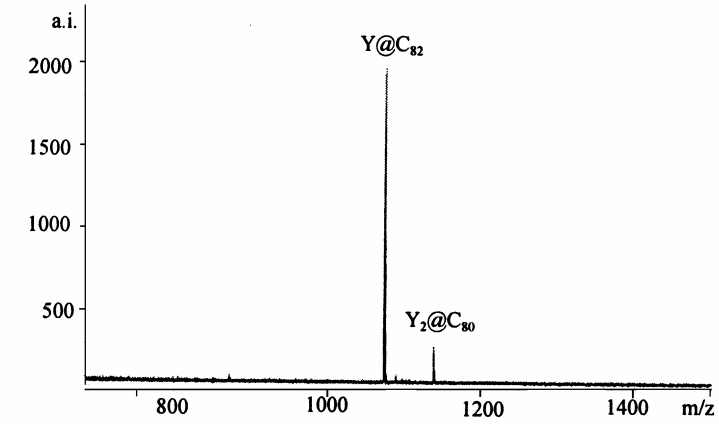


Figure 4 presents the mass spectrum of the DMF extract separated by column chromatography on silica gel with DMF as eluent. It is estimated that $Y@C_{82}$ with a purity of *ca*. 85% is obtained and the main impurity is $Y_2@C_{80}$.

Figure 4 The positive-ion MALDI-TOF mass-spectrum of DMF eluate



Our successful synthesis of yttrium EMFs in high yield lies in two aspects. On one hand, because nickel EMFs is not found in the primary soot and extracts, it is conjectured that nickel only plays the role of a catalyst during the formation of yttrium

EMFs. On the other hand, our synthesis conditions (high helium pressure, low electric current, wide gap of electrodes and high atomic ratio of Y/C) are beneficial for carbon ions and yttrium atoms to impact each other and form a wide range of EMFs. The content of $Y@C_{82}$ in DMF extract is especially high, so that it can be partly isolated from other yttrium EMFs and empty fullerenes through column chromatographic separation.

In summary, high yield yttrium EMFs, some of them are first reported, have been synthesized by the DC arc discharge method under our synthesis conditions and successively extracted with CS_2 and DMF, and $Y@C_{82}$ with a purity of *ca.* 85% was obtained.

Acknowledgments

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References

1. J. H. Weaver, Y.Chai, R.E. Smalley. *et al. Chem. Phys. Lett.* **1992**, *190* (5), 460.
2. H. Shinohara, H. Saito, Y. Saito. *et al. J. Phys. Chem.*, **1992**, *96* (9), 3571.
3. H. Shinohara. *et al. J. Phys. Chem.*, **1993**, *97* (17), 4259.
4. Y. Tomioka, H. Kajiyama, M. Ishibashi, *et al. Mol. Cryst. Liq.Cryst. Sci. Tech.* A, **1995**, *267*, 347.
5. Y. Hasegawa, Y. Ling, H. Shinohara. *et al. Phys. Rev.* B, **1997,** *56* (11), 6470.
6. G. Seifert, A. Bartl, L. Dunsch. *et al. Appl. Phys.* A, **1998**, *66* (3), 265.
7. M. Takata, B. Umeda, H. Shinohara. *et al. Nature*,**1995,** *377* (6544), 46.
8. S. Lebedkin, B. Renker, R.Heid, *et al. Appl. Phys.* A, **1998**, *66* (3), 273.
9. S. W. McElvany. *J. Phys. Chem.*, **1992**, *96* (12), 4935.
10. L. Soderholm, P. Wurz, K. R. Lykke. *et al. J. Phys. Chem.*, **1992**, *96* (18), 7153.
11. Y. Kubozono, H. Maeda, Y. Takabayashi. *et al. J. Am. Chem. Soc.* **1996**, *118* (29), 6998.
12. D. Fuchs, H. Rietschel, R. H. Michel, e*t al. J. Phys. Chem.*, **1996**, *100* (2), 725.

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