TRIFLUOROMETHYLATION OF ENDOHEDRAL METALLOFULLERENES M@C_{82} (M = Y, CE): SYNTHESIS, ISOLATION AND STRUCTURE

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Introduction

In contrast to the well-developed exohedral modification of empty fullerenes, the development of regioselective reactions for endohedral metallofullerenes (EMF) is still in its infancy. This is due to their limited availability to most synthetic chemists, the difficulty in their purification to homogeneity from fullerene soots, the difficulty in characterizing EMF (many EMF are paramagnetic, precluding routine NMR characterization), and the paucity of theoretical studies on hypothetical chemically-modified EMF that would guide synthetic chemists to investigate productive but non-obvious reaction schemes.

The first chemical modification of an EMF, cycloaddition of disilacyclopropane to La@C_{82}, was reported in 1995 [1]. Several other groups also reported cycloadducts of EMF [2,3], but unambiguous structural characterization has only been achieved in one study [4]. More recently, water-soluble EMF, such as the cycloadduct Gd@C_{60}(C(COOH)$_2$)$_{10}$ reported by Bolskar et al. [5], have been prepared to explore their potential use as MRI contrast agents [5,6], and Shinohara et al. used fluorous biphase techniques to prepare La@C_{82}(C_8F_{17})$_2$ [7]. Until this work, however, La@C_{82}(C_8F_{17})$_2$ was the only reported exohedral derivative of an EMF with atomic substituents such as H, F, Cl, or Br, or with organic substituents R having only R–C_{EMF} single bonds.

In this work, we applied our recent proven synthetic strategy for the chemical derivatization of the rare stable EMF. The chemical reaction of interest, the first trifluoromethylation of an EMF, was carried out on crude EMF material, followed by exhaustive chromatographic separation and characterization of the isolated purified products. This approach gives the synthetic chemist the advantage of not wasting mg or even sub-mg quantities of precious EMF samples trying to purify the starting material, especially at the preliminary stage of exploring various sets of reaction conditions. In addition, many underivatized EMF have low solubilities and tend to oxidize and/or polymerize in air during their separation and purification from crude EMF-containing fullerene soots. Therefore, a derivatized EMF may not only be more soluble than the parent EMF, it may also be more stable, further aiding the laborious but necessary purification by chromatography.

Results and discussion

We have now extended our trifluoromethylation work to more intriguing and much less available fullerenes – endohedral metallofullerenes. The preparation of the metallofullerene-containing soot and extraction methods were previously described in works [8]. Several metallofullerenes were reacted with fluoromethylating agents, yielding a number of compounds, in some cases with remarkable domination of a single product. Crude reaction products were separated and isolated fractions were purified with the use of the HPLC technique. Complete spectroscopic characterization in combination with computational methods resulted in the structural elucidation for several new isolated derivatives of endometallofullerenes. Effect of the nature of the entrapped metal on the isomerism of the the fluoromethylated derivatives of endometallofullerenes is discussed.

Figure 1 shows the MALDI mass spectrum of the main products Y@C_{82}(CF_3)$_5$ (a) and Ce@C_{82}(CF_3)$_5$ (b). The addition of an odd number of CF_3 groups to paramagnetic Y@C_{82} rendered the two compound of Y@C_{82}(CF_3)$_5$ and Ce@C_{82}(CF_3)$_5$ diamagnetic, allowing 1D and 2D ^{19}F NMR spectroscopy to be used for structure elucidation. Previously reported EMF cyclo-addition products retained the paramagnetic nature of the parent EMF, and routine NMR characterization was not possible. Both isomers of Y@C_{82}(CF_3)$_5$ exhibited a ^{19}F NMR spectrum with

five resonances having a 1:1:1:1:1 intensity pattern (**Figure 2**).

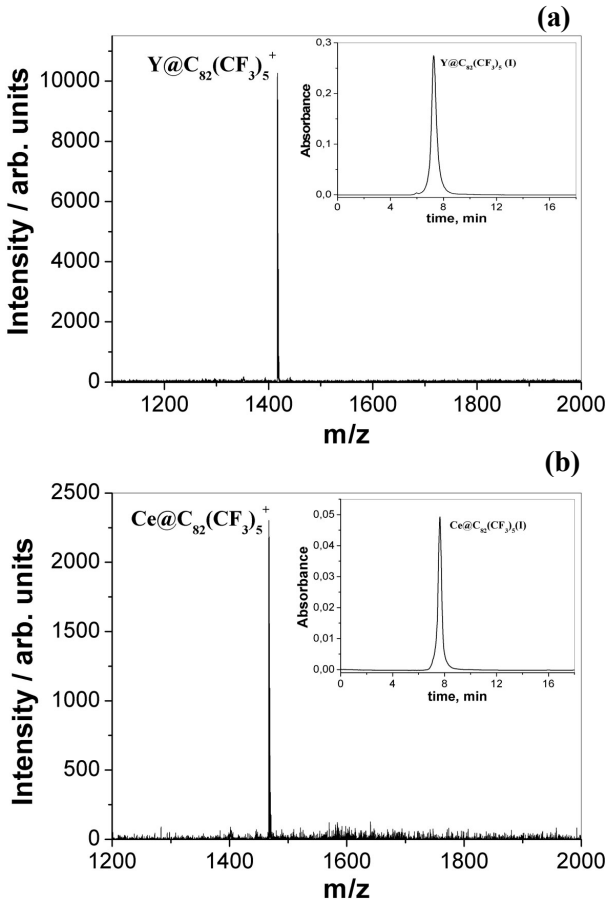

Fig. 1. MALDI mass spectrum of the main products $Y@C_{82}(CF_3)_5$ (a) and $Ce@C_{82}(CF_3)_5$ (b). The inset shows the HPLC trace purified sample of $Y@C_{82}(CF_3)_5$ isomer **I** (a) and $Ce@C_{82}(CF_3)_5$ isomer **I** (b).

Conclusions

In summary, we have demonstrated an efficient method for the exohedral derivatization of the EMF $Y@C_{82}$ and $Ce@C_{82}$ isolated and characterized two diamagnetic stable compound of $Y@C_{82}(CF_3)_5$ and $Ce@C_{82}(CF_3)_5$. Used a combination of 2D ^{19}F NMR spectroscopy and DFT calculations to elucidate the most probable type of CF_3 addition pattern of these products.

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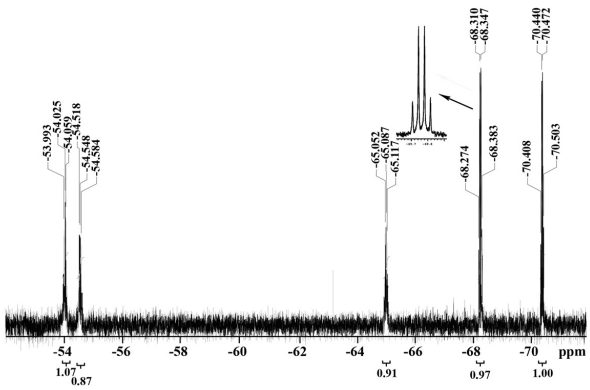

Fig. 2. ^{19}F NMR spectra of $Y@C_{82}(CF_3)_5$ isomer **I** in benzene-d_6.

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