# Making Fluorofullerenes:an Unusual Behavior of the C60-CeF4 System

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For the preparation of the specific fluorofullerenes, the method of the solid state fluorination with binary and complex fluorides as fluororeagents was developed by our group. This work has resulted in the successful synthesis of $C_{60}F_{18}$ (in reaction with potassium hexafluoroplatinate) and $C_{60}F_{36}$ - by using manganese trifluoride.

In the system $C_{60}$ - $CeF_4$ we predicted formation of $C_{60}F_{36}$, because of the comparable fluorinating activity of cerium tetrafluoride and $MnF_3$, thus the stoichiometric mass ratio 1:10.8 was applied for100% $C_{60}F_{36}$ formation.

However, a very peculiar behavior of the C60-CeFx system was observed. For our syntheses we used samples of $CeF_x$, which had the coefficient X in the range between 3.60 and 3.71 (as followed from the elemental analysis), whereas X-ray diffraction showed similar phase composition with varying fraction of the amorphous phase. All samples with CeFx≥3.7 gave the same product (T=380$^o$C, P=10$^{-2}$ Torr) – C60F36, showing virtually no impurities of the molecules with lower fluorine content, which are normally observed with other fluorinating reagents, except for the trace amounts of $C_{60}F_{34}O$ and $C_{60}F_{36}O$. Thus, the best known selectivity for the C60F36 formation was achieved in these reactions, with the yields being75-80%.

Samples of CeFx (x<3.7) did not form C60F36 as a main product but yielded fluorofullerenes of the lower F content – 30<n(F)<34, with $n_{max}$ decreasing in accordance with the stoichiometric coefficient x in CeFx. Thus for the first time we found the group of reagents which can be used for the preparation of the fluorofullerenes with uncommon F content.

Chemical and X-ray diffraction analyses have shown that thermal decomposition of $CeF_4$ occurs to $CeF_3$. The temperature of the complete l decomposition is 400$^o$C. In the process of pyrolysis the solid soloution of CeF3 in $CeF_4$ is formed. As the temperature of the synthesis of $CeF_4$ lies approximately in the same range so the process of formation of $CeF_4$ may take place simultaneously with its destruction.

Thus, we decided to examine the possibility of using CeF3 as reducing agent in defluorination reactions of highly fluorinated fullerenes.

Indeed, as shown in our report, for the first time selective defluorination of C60Fx took place in these reactions, and the most stable fluorofullerenes were made.

The reactions between $C_{60}$ and the series of complex salts $M_3CeF_7$ (M=Li, Na, K, Rb) were studied. Strength of the fluorinating reagents of which degree of fluorination of fullerenes can serve as qualitative measure, decreased with the increse of number of alkali metal in the observed series.