Synthesis and Functionalizations of Trimetallic Nitride Template Endohedral Metallofullerenes

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ABSTRACT

This thesis addresses the synthesis of a new mix-metal trimetallic nitride template endohedral metallofullerene (TNT-EMF) and the functionalizations of $M_3N@C_{80}$ (M = Sc, Gd, Ho) under the high-speed vibration milling (HSVM) condition. In addition, this thesis discusses the internal motion of the cluster, Sc_3N inside three different carbon cages, C_{68}, C_{78} and C_{80}.

Water-soluble derivatives of endohedral metallofullerenes possess a unique potential for medical applications, such as magnetic resonance imaging (MRI) contrast agents, X-ray contrast agents and nuclear medicine. The TNT-EMFs have inherent advantages over other endohedral metallofullerenes, such as $M@C_{60}$ and $M@C_{82}$, due to the encapsulation of up to three metal atoms inside the carbon cages. $M_3N@C_{80}(OH)_m(O)_n$ (M = Sc, Gd, Ho) were synthesized under the HSVM condition and characterized by FT-IR, MALDI-TOF and XPS. The relaxivity studies on these water-soluble derivatives have shown that Gd-based metallofullerols have significantly higher relaxivities than commercially used MRI contrast agents (e.g. Omniscan^{TM}) and can be the next generation MRI contrast agent. The Ho containing species has a high R_2/R_1 ratio compared to other samples showing the potential to be a T_2 agent.

In contrast to homonuclear M_3N clusters, there is a paucity of mixed-metal cluster cases of TNT-EMFs reported to date because the mixed-metal metallofullerenes are difficult to be separated and purified. In this thesis, $CeSc_2N@C_{80}$ was synthesized, separated in pure form and fully characterized. Single-crystal X-ray diffraction shows that $CeSc_2N@C_{80}$ consists of a four atom asymmetric top ($CeSc_2N$) inside a C_{80} (I_h) carbon cage and the nitride ion is not located at the center of the carbon cage but is offset by 0.36 Å. The NMR studies, together with the XPS results, show that $CeSc_2N@C_{80}$ is a

weakly paramagnetic system with a single buried f electron spin. A new cage isomer of the $Sc_3N@C_{80}$ (D_{5h}) metallofullerene was also isolated from the Ce-Sc mixture and the cage symmetry was confirmed by single-crystal X-ray diffraction.

The internal motion of the metal-nitride cluster, Sc_3N within the carbon cages (C_{68}, C_{78} and C_{80}) was studied at various temperatures using ^{45}Sc NMR spectroscopy. The reorientation barriers (presumably dominated by motion internal to the cage) were calculated for these three TNT-EMFs. The preliminary results show that the quadrupole coupling constant of $Sc_3N@C_{80}$ (I_h) is quite close to that of $Sc_3N@C_{68}$.

Dedicated to my mother, Fengzhen He

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