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Quantum-Chemical Studies on Lanthanide Encapsulated Metallofullerenes Towards Designing Functional Materials

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[Abstract] Encapsulation of the atoms/cluster inside the fullerene cage results in the hybrid class of molecules known as endohedral metallofullerenes (EMFs).^[1-2] In this work, an extensive study of the structural and electronic properties on a series of neutral and anionic species of homonuclear dimetallofullerenes (di-EMFs) $M_2@C_{80}$ ($M = \text{Sc, Y, La, Gd, Lu}$) and heteronuclear di-EMFs such as $\text{LaM}@C_{80}$ ($M = \text{Ce, Pr, Sm, Eu}$) and $\text{GdM}@C_{80}$ ($M = \text{Sc, Y, Gd, Lu}$) has been performed using DFT and ab-initio computational calculations. We considered different configurations of homo/heteronuclear di-EMFs followed by examining their ground state. The di-EMFs with a higher spin ground state was found to be kinetically unstable due to the unpaired spin distribution over the C_{80} cage. Thus, in search of a stable di-EMF, we have further analysed the anions of the di-EMFs and also have introduced some feasible exohedral functional group on the cage. Then, we succeeded in the confinement of the unpaired electron inside the carbon cage and obtaining the stability for anions as well as the exohedral derivatives of di-EMFs. Finally, we were able to design systems, which could be promising toward designing functional materials.

[Introduction] I_h-C_{60} is the most stable and abundant fullerene, which has been reported so far.^[3] It is expected that the high symmetry of these structures reduces the surface tension and increases the stability.^[3] However, I_h-C_{80} is extremely unstable. This difference arises due to the open-shell electronic structure of I_h-C_{80} , which has a four-fold degenerate HOMO occupied by only two electrons. Hence, it is anticipated that once the degenerate HOMO accepts six electrons, it forms a closed shell electronic structure similar to I_h-C_{60} with comparable stability. The stabilization of I_h-C_{80} is possible by reduction through the encapsulation of the metals. Therefore, I_h-C_{80} is an ideal candidate for the study of endohedral fullerenes where two metal encapsulated species are frequently found and is stabilized by forming $M_2@C_{80}$.^[4] This study theoretically investigated the electronic states of $M_2@C_{80}$ derivatives in terms of the kinetic instability.

[Methods] All the geometry optimization has been performed using Gaussian 09 programme

using unrestricted B3LYP functional. The quasi-relativistic effective core potential by Stuttgart-Cologne group in combination with the corresponding optimized valence basis sets was used to describe Sc, Y, La, Ce, Pr, Sm, Eu, Gd and Lu and 6-31G* and 6-31+G(d) basis sets for C atom were employed for the neutral and anionic species respectively. All the ab initio calculations have been performed using MOLCAS 8.0 code.

[Results and Discussion] Studies on the homonuclear di-EMFs such as $M_2@C_{80}$ ($M = \text{Sc, Y, La, Gd, Lu}$) revealed that except $\text{La}_2@I_h\text{-C}_{80}$, all other di-EMFs prefer to exist in the higher spin state as a ground state. Further, analysis on the heteronuclear di-EMFs showed that $\text{LaCe}@C_{80}$ and $\text{LaPr}@C_{80}$ are kinetically stable and all other di-EMFs were found to be unstable due to the unpaired spin distribution over the C_{80} cage. Any di-EMF, having an unpaired spin on the cage, remains unstable with respect to an attack by the external reactive species. Also, we found that the energy level of the metal-based orbital plays a profound role in determining the stability of the di-EMFs.

Toward the observation and isolation of stable di-EMFs, we theoretically explored two approaches: anionization or the introduction of an exohedral functional group to the $I_h\text{-C}_{80}$ cage (Fig. 1) so as to achieve the disappearance of an unpaired electron on the cage and confinement of the unpaired spin inside the cage. Anionization and exterior functionalization in fact lead to stable di-EMFs although the functional group for exterior functionalization should be carefully chosen. Experimentally, the isolation of anionic species of $M_2@C_{80}$ ($M = \text{Y, Gd}$)^[5] and the exohedral derivatives such as $M_2@C_{80}\text{-(CF}_3\text{)}$ ($M = \text{Y, Gd}$) was actually reported.^[6] Eventually, we succeeded in designing possible candidates toward functional materials.

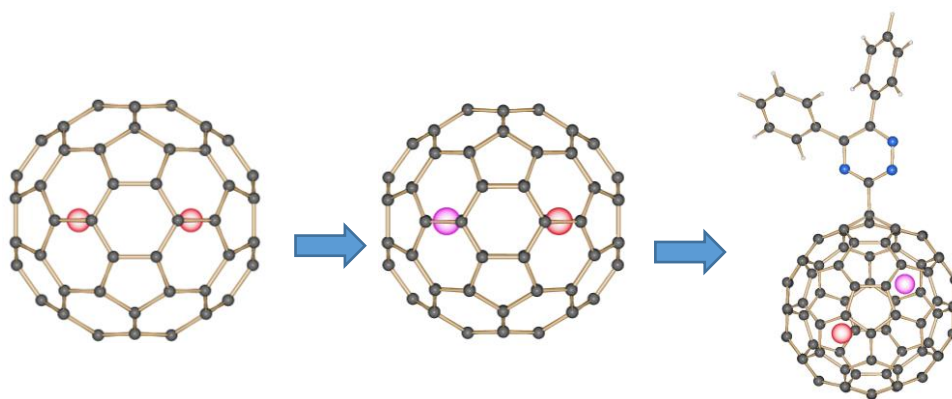


Fig 1. Representation of homo/heteronuclear di-EMFs and the exohedral derivative

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