Theoretical Insights into the Metal–Nonmetal Interaction Inside $\text{M}_2\text{O}@\text{C}_{2v}(31922)-\text{C}_{80}$ ($\text{M} = \text{Sc or Gd}$)

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ABSTRACT: The metal–nonmetal interaction is complicated but significant in organometallic chemistry and metallic catalysis and is susceptible to the coordination surroundings. Endohedral metallofullerenes is considered to be an excellent model for studying metal–nonmetal interactions with the shielding effect of fullerenes. Herein, with the detection of ScGdO@C$_{80}$ in a previous mass spectrum, we studied the effects of metal atoms (Sc and Gd) on the metal–nonmetal interactions of the thermodynamically stable molecules $\text{M}_n\text{O}@\text{C}_{2v}(31922)-\text{C}_{80}$ ($\text{M} = \text{Sc and Gd}$), where metal atoms M can be the same or different, using density functional theory calculations. The inner metal atom and the fullerene cage show mainly ionic interactions with some covalent character. The Sc atom with higher electronegativity plays a greater important role in the metal–nonmetal interactions than the Gd atom. This study would be useful for the further study of the metal–nonmetal interaction.

INTRODUCTION

Endohedral metallofullerene (EMF) is a unique carbon nanomaterial in which metal ions, metal atoms, or metal clusters are embedded in fullerene carbon cages. Since the discovery of LaC$_{80}$, the prototype of EMFs, in 1985, EMFs have attracted much attention because of their unique core–shell structure and promising applications in biomedicine, solar cells, and materials science.

Additionally, more and more EMFs have been reported, such as Sc$_2$N@C$_{2v}$ (2n = 68–70 and 78–82),$^{8,10}$ Sc$_2$C$_@$C$_{2v}$ (2n = 68, 72–74, and 80–84),$^{17–22}$ Sc$_2$S@C$_{2v}$ (2n = 70 and 82),$^{23–25}$ YCN@C$_{82}$,$^{26}$ Sc$_2$CH@C$_{80}$, Sc$_n$NC@C$_{2v}$ (2n = 78–80),$^{28,29}$ and Sc$_n$O@C$_{2v}$ (n = 35–47).$^{30–40}$ According to the types of inner clusters, clusterfullerenes can be classified into nitride clusterfullerenes, carbide clusterfullerenes, sulfide clusterfullerenes, cyanide clusterfullerenes, metal hydrocarbon clusterfullerenes, metal carbonitride clusterfullerenes, and oxide clusterfullerenes (OCFs).$^{41–46}$ OCFs, including Sc$_2$O@C$_{2v}$,$^{47}$ Ho$_2$O@C$_{74}$,$^{48}$ Ho$_3$O@C$_{84}$,$^{49}$ Dy$_2$O@C$_{80}$,$^{50}$ etc., have been widely studied. In particular, Sc$_2$O@C$_{2v}$ has attracted much attention since 2010 due to their successful preparation and characterization. The molecular orbital energy levels and internal cluster dynamics of OCFs rely on both the cluster and the carbon cages.$^{51}$ In general, with the increase in the size of the carbon cage, the angle of Sc–O–Sc clusters gradually increases and the M$_n$O clusters become more disordered. This may be attributed to the strong metal–carbon interaction and the spatial limitation of fullerene cages.$^{52}$

Clusterfullerene is an ideal model for studying the interaction between metals and nonmetals (C, N, and O atoms), which is of great significance for the reasonable design of metal–organic frameworks and metal catalysts that show promising and excellent applications in dealing with global warming and the energy crisis. In addition, the study of the metal–nonmetal interaction in EMFs is very important to reveal the reaction selectivity and predict the molecular structure and reactivity of EMFs.$^{42,43}$ To date, there have been many studies on the metal–nonmetal interaction in the model of clusterfullerenes, but only a few studies on the effect of different metals on the metal–nonmetal interaction in the same fullerene cage. Luckily, Chen et al. isolated a mixed metal oxide cluster fullerene (MMOCF), ScGdO@C$_{80}$, for the first time in 2018.$^{43}$ The mass spectra showed the existence of ScGdO@C$_{80}$ and Sc$_2$O@C$_{80}$ was prepared previously. Clearly, ScGdO@C$_{80}$ is an excellent prototype to understand the effect of Gd and Sc on the metal–nonmetal interaction. Here, a theoretical study was first carried out on the thermodynamic stability, geometry, and electronic structure of ScGdO@C$_{80}$. Then, the metal–nonmetal interaction in M$_n$O@C$_{2v}$ (31922)-C$_{80}$ ($\text{M} = \text{Sc and Gd}$), where metal atoms M can be the same or different, was studied and compared in detail using density functional theory (DFT) calculations and wave functional analyses. Note that the name of the fullerene cage in references has not been changed with respect to the...
original authors, and in this work we use the spiral number to name the fullerene cages.

### COMPUTATIONAL DETAILS

The previous study showed the relative stability of anion \( C^{-} \) wherein seven lowest-energy tetra-anionic cages (less than \( \sim 40 \text{ kcal/mol}^{-1} \)) were selected to encase ScGdO. Then, the optimizations of ScGdO@C\(_{80}\) were performed at the BP86/6-31G(d)−CEP-4G level of theory, where the basis set 6-31G(d) was used for C and O atoms and CEP-4G, including the pseudopotential function, was used for Sc and Gd atoms. The BP86 function has been used to study many EMFs theoretically with negligible spin contamination. The core electron of the heavy metal atom will not affect the electronic features of metal-based complexes, and the CEP-4G basis function including a pseudopotential can accurately describe the electronic features of Gd. The vibration frequency analysis was carried out at the same theoretical level to confirm that all the stationary points were minimums and free from an imaginary frequency. Furthermore, the results of the single-point calculations at the MP2/6-31G(d)−CEP-4G level of theory confirm the optimization results at the BP86/6-31G(d)−CEP-4G level of theory, indicating the rationality of the theoretical levels in the present work. Based on the structure and vibration data, the relative concentration of ScGdO@C\(_{80}\) and the enthalpy−entropy effect were calculated, which is a reliable method of evaluating the thermodynamic stability of EMFs in the fullerene-formation temperature region. The interaction energies of ScGdO@C\(_{80}\), Sc\(_{2}\)O@C\(_{80}\), and Gd\(_{2}\)O@C\(_{80}\) were also calculated to elucidate their relative stabilities. Their electronic structures were studied by natural population analysis, and infrared (IR) spectra were also simulated to give more information to help characterize the structures experimentally. All the above DFT calculations in this work were performed with the Gaussian 16 program. The Mayer bond order analysis, the DOS, and the BCP analysis were based on the results of the geometric optimization and frequency calculation at the BP86/6-31G(d)−CEP-4G level of theory and were carried out with the Multiwfyn program to study the interactions between metal and nonmetal atoms.

### RESULTS AND DISCUSSION

According to the ionic model of EMFs, the seven low-lying \( C^{-} \)−ions were selected to encage ScGdO cluster. After the encapsulations, IPR ScGdO@C\(_{80}\) (31922)−C\(_{80}\) possesses the lowest potential energy, followed by IPR ScGdO@I\(_{8}\) (31924)−C\(_{80}\) and ScGdO@D\(_{8}\) (31923)−C\(_{80}\) with higher relative energies of 2.4 and 6.0 kcal mol\(^{-1}\), respectively, as shown in Table S1. Additionally, because of the electron transfer, the energy gaps between the singly occupied molecular orbital (SOMO) and the lowest unoccupied molecular orbital (LUMO) of the ScGdO@C\(_{80}\) isomers (Figure S1) decreased after the encapsulation compared with those of the \( C^{-} \)−ions. The energies of the single-point calculations at the MP2/6-31G(d)−level of theory also indicate that ScGdO@C\(_{80}\) (31922)−C\(_{80}\) has the lowest relative energy (Table S1). As shown in Figure 1, the statistical thermodynamic analysis of ScGdO@C\(_{80}\) isomers, including the enthalpy−entropy effects, confirmed the highest concentration of ScGdO@I\(_{8}\) (31922)−C\(_{80}\) in the whole temperature region, followed by ScGdO@I\(_{8}\) (31924)−C\(_{80}\) and ScGdO@D\(_{8}\) (31923)−C\(_{80}\) with highest concentrations of no more than 24.1% and 10%, respectively, below about 2500 K. This showed that ScGdO@C\(_{80}\) (31922)−C\(_{80}\) had the highest thermodynamic stability. The accuracy of this theoretical method has been confirmed in many experiments, such as those for Sc\(_{2}\)O@T\(_{2}\) (1915)−C\(_{80}\), Sc\(_{2}\)O@C\(_{8}\) (5)−C\(_{80}\), Sc\(_{2}\)O@C\(_{8}\) (6)−C\(_{80}\), and Sc\(_{2}\)O@C\(_{8}\) (8)−C\(_{82}\).

Besides, Sc\(_{2}\)O@C\(_{8}\) (5)−C\(_{80}\) has been isolated with the same carbon cage as optimal ScGdO@C\(_{8}\) (31922)−C\(_{80}\). To elucidate the effect of inner metal atoms on M\(_{2}\)O@C\(_{8}\) (M = Sc and Gd), including the metal−nonmetal interactions, crystallized Sc\(_{2}\)O@C\(_{8}\) (31922)−C\(_{80}\) and the Gd\(_{2}\)O@C\(_{8}\) (31922)−C\(_{80}\) model were optimized at the same theoretical level used for the optimization of ScGdO@C\(_{8}\) (31922)−C\(_{80}\). The interaction energies (\( E \)) in ScGdO@C\(_{8}\) (31922)−C\(_{80}\), Sc\(_{2}\)O@C\(_{8}\) (31922)−C\(_{80}\), and Gd\(_{2}\)O@C\(_{8}\) (31922)−C\(_{80}\) between inner metal oxides...
and $\text{C}_2v(31922)-\text{C}_{80}$ are $-167.9$, $-172.3$, and $-178.2$ kcal mol$^{-1}$, respectively, indicating the thermodynamically maintained present configurations; the interaction energy was calculated using $E = E_{\text{EMF}} - E_{\text{carbon cage}} - E_{\text{cluster}}$. The energies of EMFs ($E_{\text{EMF}}$) were obtained by the optimization of EMFs, and the energies of the singlet-ground-state carbon cage ($E_{\text{carbon cage}}$) and the inner cluster ($E_{\text{cluster}}$ octet-ground state ScGdO, singlet-ground-state Sc$_2$O, and 15-et-ground-state Gd$_2$O) were obtained from the single-point calculations of the carbon cage and the inner cluster from the corresponding optimized EMFs, respectively. ScGdO@C$_2v(31922)-\text{C}_{80}$ has the largest interaction energy, indicating its lower thermodynamically stability; thus, it is a bit difficult to isolate and crystallize ScGdO@C$_2v(31922)-\text{C}_{80}$, likely because of its asymmetric geometry.

As shown in Figures 2 and S2, the Sc–O bond length in ScGdO@C$_2v(31922)-\text{C}_{80}$ is 1.889 Å, which is shorter than the length of the Gd–O bond (2.113 Å). The greater electronegativity of Sc possibly leads to this result. Surprisingly, both distances are slightly larger than those (1.859 and 2.056 Å for Sc–O and Gd–O bonds, respectively) in ScGdO@C$_2v(8)$-C$_{82}^{(3)}$ with larger fullerene cages, which is derived from the

Figure 3. TDOS and PDOS of ScGdO@C$_2v(31922)-\text{C}_{80}$, Sc$_2$O@C$_2v(31922)-\text{C}_{80}$ and Gd$_2$O@C$_2v(31922)-\text{C}_{80}$.

Figure 4. BCPs in ScGdO@C$_2v(31922)-\text{C}_{80}$, Sc$_2$O@C$_2v(31922)-\text{C}_{80}$ and Gd$_2$O@C$_2v(31922)-\text{C}_{80}$. BCPs are represented as brown sticks. BCPs between metal atoms and the carbon cage are highlighted in red, and those between metal atoms and O atoms are circled in blue.
orientation of the inner ScGdO cluster along the short axis of C$_{2v}$(31922)-C$_{80}$.

Additionally, the Sc–O and Gd–O bond lengths are 1.924 and 2.053 Å in Sc$_2$O$_2$C$_{2v}$(31922)-C$_{80}$ and 1.960 and 2.067 Å in Gd$_2$O$_2$C$_{2v}$(31922)-C$_{80}$, respectively. The Sc–O–Gd angle (163.0°) is larger than the Sc–O–Sc angle (161.7°) and the Gd–O–Gd angle (139.9°) in Sc$_2$O$_2$C$_{2v}$(31922)-C$_{80}$ and Gd$_2$O$_2$C$_{2v}$(31922)-C$_{80}$, respectively. These results show the more serious effect of the Sc metal atom on the geometries of metal oxide fullerenes compared to the Gd metal atom, which further illustrates the influence of the electronegativity of the Sc atom.

To further understand the effect of the metal atom on electronic structures, natural bond orbital (NBO) calculations were performed (Table 1). Based on the ground-state electronic configurations of the Sc (3d$^1$4s$^2$) and Gd (4f$^7$5d$^1$6s$^2$) atoms and the spin electronic population of ScGdO@C$_{2v}$(31922)-C$_{80}$ in the octet ground state (Figure S3 and Table S2), the formal oxidation states of inner Sc and Gd atoms are III. In the similar way, the formal oxidation states of Sc and Gd in singlet-ground-state Sc$_2$O@C$_{2v}$(31922)-C$_{80}$ and 15-et-ground-state Gd$_2$O@C$_{2v}$(31922)-C$_{80}$ are also III. The spin ground state of Sc$_2$O@C$_{2v}$(31922)-C$_{80}$ was calculated previously, and we inferred the spin state of Gd$_2$O@C$_{2v}$(31922)-C$_{80}$ from the other two isomers. The NBO charge is negative for the O atom and positive for the metal atom, which shows there is electron transfer from metal atoms to the O atom. In ScGdO@C$_{2v}$(31922)-C$_{80}$, the NBO charge of the O atom is less negative and the two metals are quite different. Because of the f orbital, the Gd atoms seem to lose electrons more easily. The partial charge in outer s, p, and d orbitals is derived from back-donation from the O atom and the fullerene cage, indicating the covalent features between metal and nonmetal atoms; these features were also confirmed by the density of states (Figure 3). The large difference in atomic charge between Sc and Gd is attributed to their electronegativity. According to the eight-electron rule of the O atom, the formal four-electron transfer occurs from the inner cluster (ScGdO, Sc$_2$O, and Gd$_2$O) to C$_{2v}$(31922)-C$_{80}$.

Bonding critical point (BCP) indicators based on the quantum theory of atoms in molecules (QTAIM, a mature quantum theory for analyzing the topology of the electron density) were studied (Figure 4) to further determine the metal–nonmetal interactions. As shown in Table 2, the BCP
indicators between Sc(Gd) and carbon atoms have similar values. The density of electrons ($\rho_{BCP}$) is small, and the Laplacian of electron density ($\nabla^2 \rho_{BCP}$) is positive, in line with the previous results on EMFs. $\nabla^2 \rho_{BCP}$ is positive, so $\rho_{BCP}$ values are positive. $\nabla^2 \rho_{BCP}$ values, energy density ($E_{BCP}^{\rho}$) close to zero, and low Mayer bond orders (MBOs) show the ionic interaction between metal and nonmetal atoms. The larger than 1 ratio between the absolute value of the potential energy density and the kinetic energy density ($|V_{BCP}|/G_{BCP}$) indicates the interaction consists of an ionic interaction and a covalent interaction, and the negative $H_{BCP}$ value is the symbol of the covalent interaction. Therefore, the metal–nonmetal interaction inside $M_2O@C_5$ (31922)-C$_{80}$ ($M = \text{Sc or Gd}$) is mainly an ionic interaction with some covalent character. Because of larger $\rho_{BCP}$ more negative $H_{BCP}$ larger $\nabla^2 \rho_{BCP}$ larger MBO, and shorter atom distance, the Sc–O and Sc–C interactions are stronger than the Gd–O and Gd–C interactions in ScGdO@C$_5$ (31922)-C$_{80}$, which may be attributed to the higher electronegativity of the Sc atom. Compared with Sc$_2O@C_5$ (31922)-C$_{80}$, Table 2 shows that the Sc–O interaction in ScGdO@C$_5$ (31922)-C$_{80}$ is stronger according to the BCP indicators. In contrast, the Gd–O interaction in ScGdO@C$_5$ (31922)-C$_{80}$ is weaker than that in Gd$_2O@C_5$ (31922)-C$_{80}$. This phenomenon is likely related to (1) the difference in electronegativity determining the electron-withdrawing ability, (2) the atomic orbital energy level determining the degree of effective overlap between bonding atoms, and (3) the size of the atomic radius. Additionally, close to zero bond ellipticity values between Sc or Gd and O atoms indicate single bonds, confirming the four-electron transfer phenomenon. Replacing the Sc atom with the Gd atom in Sc$_2O@C_5$ (31922)-C$_{80}$ makes the Sc–C interaction (Sc82–C51 and Sc82–C52) stronger; interestingly, however, substituting the Sc atom for the Gd atom in Gd$_2O@C_5$ (31922)-C$_{80}$ makes the Gd–C (Gd82–C71 and Gd82–C72) interaction weaker.

To give some useful structural information to distinguish similar molecules of ScGdO@C$_5$ (31922)-C$_{80}$, Sc$_2O@C_5$ (31922)-C$_{80}$, and Gd$_2O@C_5$ (31922)-C$_{80}$ in future experiments, their infrared spectra were simulated, as shown in Figure 5. These three kinds of EMFs have very similar absorption peaks. The absorption peak between 200 and 800 cm$^{-1}$ is the vibration of the fullerene frame. The absorption peaks above 1000 cm$^{-1}$ come from the stretching vibration of the C–C bond. For higher numbers of Gd atoms, the strongest absorption peak is slightly red shifted, which is meaningful for their experimental characterization.

**CONCLUSION**

Using density functional theory and statistical thermodynamic analysis, ScGdO@C$_5$ (31922)-C$_{80}$ was found to be the most likely isomer isolated in the experiment. The comparative study on Sc$_2O@C_5$ (31922)-C$_{80}$ and Gd$_2O@C_5$ (31922)-C$_{80}$ shows that ScGdO@C$_5$ (31922)-C$_{80}$ has the largest bond angle because of its stronger interaction between metal and carbon atoms, and the Sc atom with higher electronegativity plays a much more important role in the metal–nonmetal interactions than the Gd atom. The interactions of Sc–O and Sc–C are larger than those of Gd–C and Gd–O, which is likely related to the higher electronegativity of the Sc atoms and the much closer orbital energy levels. Finally, IR spectra of three isomers were simulated to help future experimental research.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c04978.

Relative energies, single-point energies, relative concentrations, spin density maps, structures for BCPs, BCP parameters, TDOS and PDOS, SOMO- and HOMO–LUMO gaps and maps, and Cartesian coordinates of M$_2O@C_5$ ($M = \text{Sc or Gd}$) (PDF)

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

1. Heath, J. R.; O’Brien, S. C.; Zhang, Q.; Liu, Y.; Curl, R. F.; Tittel, F. K.; Smalley, R. E. Lanthanum Complexes of Spherical Carbon Shells. J. Am. Chem. Soc. 1985, 107, 7779–7780.
2. Popov, A. A.; Yang, S. F.; Dunsch, L. Endohedral Fullerenes. Chem. Rev. 2013, 113, 5989–6113.
3. Lu, X.; Bao, L. P.; Akasaka, T.; Nagase, S. Recent Progress in the Chemistry of Endohedral Metallofullerenes. Chem. Commun. 2014, 50, 14701–14715.
4. Liu, Y.; Jiao, F.; Qiu, Y.; Li, W.; Lao, F.; Zhou, G. Q.; Sun, B. Y.; Xing, G. M.; Dong, J. Q.; Zhao, Y. L.; Chai, Z. F.; Chen, C. Y. The
Effect of Gd[6@C_{20}(OH)_{2}] Nanoparticles on the Release of Th1/Th2 Cytokines and Induction of TNF-A Mediated Cellular Immunity. *Biomaterials* 2009, 30, 3934–3945.

(5) Wang, J.; Hu, Z. B.; Xu, J. J.; Zhao, Y. L. Therapeutic Applications of Low-Toxicity Spherical Nanocarbon Materials. *NPG Asia Mater.* 2014, 6, e84.

(6) Li, J.; Zhao, F. W.; Wang, T. S.; Nie, M. Z.; Li, J. J.; Wei, Z. X.; Jiang, L.; Wang, C. R. Ethylenediamine Functionalized Fullerene Nanoparticles as Independent Electron Transport Layers for High- Efficiency Inverted Polymer Solar Cells. *J. Mater. Chem.A* 2017, 5, 947–951.

(7) Nagano, T.; Kuwahara, E.; Takayanagi, T.; Kubozono, Y.; Fujiwara, A. Fabrication and Characterization of Field-Effect Transistor Device with C_{60} Isomer of Pr@C_{60}. *Chem. Phys. Lett.* 2005, 409, 187–191.

(8) Hino, S.; Ogasawara, N.; Ohta, T.; Yagi, H.; Miyazaki, T.; Nishi, T.; Shinohara, H. Electronic Structure of ScN@C_{60}. *Chem. Phys.* 2013, 421, 39–43.

(9) Yang, S. F.; Popov, A. A.; Dunsch, L. Violating the Isolated Pentagon Rule (IPR): The Endohedral Non-IPR C_{70} Cage of ScN@C_{70}. *Angew. Chem., Int. Ed.* 2007, 46, 1256–1259.

(10) Campanera, J. M.; Bo, C.; Osmund, M. M.; Balch, A. L.; Poblet, J. M. Bonding within the Endohedral Fullerenes ScN@C_{70} and ScN@C_{80} as Determined by Density Functional Calculations and Reexamination of the Crystal Structure of {ScN@C_{70}}. Co(OEP)-1.5(CH_{3}OH)·0.3(CHCl). *J. Phys. Chem. A* 2002, 106, 12356–12364.

(11) Krause, M.; Popov, A.; Dunsch, L. Vibrational Structure of Endohedral Fullerene ScN@C_{70} (D_{3h}): Evidence for a Strong Coupling between the ScN Cluster and C_{70} Cage. *ChemPhysChem* 2006, 7, 1734–1740.

(12) Cai, T.; Xu, L.; Gibson, H. W.; Dorn, H. C.; Chancellor, C. J.; Osmund, M. M.; Balch, A. L. ScN@C_{60}: Encapsulated Cluster Regiocontrol of Adduct Docking on an Ellipsoidial Metallofullerene Sphere. *J. Am. Chem. Soc.* 2007, 129, 10795–10800.

(13) Stevenson, S.; Rice, G.; Glass, T.; Harich, K.; Cromer, F.; Jordan, M. R.; Craft, J.; Meijer, E.; Osmund, M. M.; Matra, K.; Fisher, A. J.; Balch, A. L.; Dorn, H. C. Small-Bandgap Endohedral Metallofullerenes in High Yield and Purity. *Nature* 1999, 402, 898–898.

(14) Stevenson, S.; Lee, H. M.; Osmund, M. M.; Kozikowski, C.; Stevenson, P.; Balch, A. L. Preparation and Crystallographic Characterization of a New Endohedral, LuN@C_{60}(S-oxyylene), and Comparison with ScN@C_{60}(S-oxyylene). *Chem. Eur. J.* 2002, 8, 4528–4535.

(15) Lee, H. M.; Osmund, M. M.; Iezzi, E.; Duchamp, J. C.; Dorn, H. C.; Balch, A. L. Crystallographic Characterization and Structural Analysis of the First Organic Functionalization Product of the Endohedral Fullerene ScN@C_{60}. *J. Am. Chem. Soc.* 2002, 124, 3494–3495.

(16) Wei, T.; Wang, S.; Liu, F. P.; Tan, Y. Z.; Zhu, X. J.; Xie, S. Y.; Yang, S. F. Capturing the Long-Sought Small-Bandgap Endohedral Fullerenes ScN@C_{60} with Low Kinetic Stability. *J. Am. Chem. Soc.* 2013, 135, 3119-3123.

(17) Shi, Z. Q.; Wu, X.; Wang, C. R.; Lu, X.; Shinohara, H. Isolation and Characterization of ScN@C_{60}: A Metal-Carboide Endohedral cage with a Non-IPR Carbon Cage. *Angew. Chem., Int. Ed.* 2006, 45, 2107–2111.

(18) Feng, Y. Q.; Wang, T. S.; Wu, J. J.; Feng, L.; Xiang, J. F.; Ma, Y. B.; Zhang, Z. X.; Jiang, L.; Shu, C. Y.; Wang, C. R. Structural and Electronic Studies of Metal Carbide Cluster fullerene ScC_{60}@C_{60}. *Nanoscale* 2013, 5, 6704–6707.

(19) Wang, Y. F.; Tang, Q.; Feng, L.; Chen, N. ScC_{60}@D_{3h}(14246)-C_{44}: A Missing Piece of the Clusterfullerene Puzzle. *Inorg. Chem.* 2017, 56, 1974–1980.

(20) Kurihara, H.; Lu, X.; Iduka, Y.; Mizogori, N.; Slanina, Z.; Tsuchiya, T.; Akasaka, T.; Nagase, S. ScC_{60}@C_{60} Rather Than ScC_{60}: Templated Formation of Unexpected C_{5}(S)-C_{60} and Temper-
Cluster Expands within a Small Non-IPR Fullerene Cage of C_{2,13333}-C_{4,6}.

(38) Cong, H. L.; Liu, A.; Hao, Y. J.; Feng, L.; Slanina, Z.; Ullik, F.

(39) Velkos, G.; Yang, W.; Yao, Y. R.; Sudarkova, S. M.; Liu, F. P.;

(40) Osuna, S.; Swart, M.; Sola, M. The Reactivity of Endohedral Fullerenes. What Can Be Learnt from Computational Studies? Phys. Chem. Chem. Phys. 2011, 13, 3585–3603.

(41) Garcia-Borràs, M.; Osuna, S.; Luis, J. M.; Swart, M.; Sola, M. The Role of Aromaticity in Determining the Molecular Structure and Reactivity of (Endohedral Metallo)Fullerenes. Chem. Soc. Rev. 2014, 43, 5089–5105.

(42) Li, M. Y.; Zhao, R. S.; Dang, J. S.; Zhao, X. Theoretical Study on the Stabilities, Electronic Structures, and Reaction and Formation Mechanisms of Fullerenes and Endometallofullerenes. Coord. Chem. Rev. 2022, 471, 214762.

(43) Yang, W.; Abella, L.; Wang, Y. F.; Li, X. H.; Gu, J. L.; Poblet, J. M.; Rodriguez-Fortea, A.; Chen, N. Mixed Dimetallic Cluster Fullerences: ScGdO@C_{6,8}-C_{8,2} and ScGdC_{8,9}-C_{8,2}. Inorg. Chem. 2018, 57, 11597–11605.

(44) Zhao, Y. X.; Li, M. Y.; Zhao, P.; Ehara, M.; Zhao, X. New Insight into U@C_{68}: Missing U@D_{3h}(31921)-C_{68} and Nuanced Enantiomers of U@C_{12}(28324)-C_{68}. Inorg. Chem. 2019, 58, 14159–14166.

(45) Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic-Behavior. Phys. Rev. A 1988, 38, 3098–3100.

(46) Perdew, J. P. Density-Functional Approximation for the Correlation-Energy of the Inhomogeneous Electron-Gas. Phys. Rev. B 1986, 33, 8822–8824.

(47) Cundari, T. R.; Stevens, W. J. Effective Core Potential Methods for the Lanthanides. J. Chem. Phys. 1993, 98, 5555–5565.

(48) Rassolov, V. A.; Pople, J. A.; Ratner, M. A.; Windus, T. L. 6-31G* Basis Set for Atoms K through Zn.

(49) Zhang, X. X.; Wang, Y. F.; Morales-Martinez, R.; Zhong, J.; de Graaf, C.; Rodriguez-Fortea, A.; Poblet, J. M.; Echegoyen, L.; Feng, L.; Chen, N. U@{12}(5)-C_{8,2}: Crystallographic Characterization of a Long-Sought Dimetallic Actinide Endohedral Fullerene. J. Am. Chem. Soc. 2018, 140, 3907–3915.

(50) Zhao, P.; Yang, T.; Guo, Y. J.; Dang, J. S.; Zhao, X.; Nagase, S. Dimetallic Sulfide Endohedral Metallofullerene Sc_{2}S@C_{68}: Density Functional Theory Characterization. J. Comput. Chem. 2014, 35, 1657–1663.

(51) Zheng, H.; Zhao, X.; He, L.; Wang, W. W.; Nagase, S. Quantum Chemical Determination of Novel C_{68} Monometallofullerenes Involving a Heterogeneous Group. Inorg. Chem. 2014, 53, 12911–12917.

(52) Yang, T.; Zhao, X.; Nagase, S. Quantum Chemical Insight of the Dimetallic Sulfide Endohedral Fullerene Sc_{2}S@C_{68}: Does It Possess the Conventional D_{3h} Cage? Chem. Eur. J. 2013, 19, 2649–2654.

(53) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.;