First-principles Study on the Electronic Structure of Novel Titanium Yttrium Mixed-metal Nitride Clusterfullerene

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We present a first-principles study on the geometric, vibrational and electronic properties of a novel Y-based non-scandium mixed-metal nitride clusterfullerene (TiY$_2$N@C$_{80}$). Theoretical results indicate that the fundamental electronic properties of TiY$_2$N@C$_{80}$ are similar to that of TiSc$_2$N@C$_{80}$, but dramatically different from that of Sc$_3$N@C$_{82}$ and Y$_3$N@C$_{80}$ molecules. We find that the magnetism of TiY$_2$N@C$_{80}$ is quenched by carrier doping. The rotation energy barrier of the TiY$_2$N cluster in C$_{80}$ cage was obviously increased by exohedral chemical modification with pyrrolidine monoadduct.

Key words: TiY$_2$N@C$_{80}$, Electronic structure, Doping, Chemical modification, First-principles calculation

I. INTRODUCTION

In recent years, endohedral metallofullerenes have attracted a wide interest for their unique structures, novel electronic properties and potential applications in variety of fields, including electronic, optical, and biomedical applications [1, 2]. The trimetal nitride endohedral fullerences (clusterfullerenes), a new kind of endohedral metallofullerenes encaged with trimetallic nitride cluster, are the most abundant metallofullerenes with formal electronic configuration labeled with M$^{x+}$N@C$_{2n}$. Because of its feasibility of varying the trapped metal atoms and various isomeric structures, this kind of clusterfullerenes has stimulated many experimental and theoretical interests [2]. In particular, the mixed-metal nitride clusterfullerenes (MMNCFs) containing two different metals are recognized as minor members of the clusterfulleren family.

Until now, a few MMNCFs reported include M$_2$Sc$_{1−x}$N@C$_{68}$ (x=0–2; M=TM, Er, Gd, Ho, La), Lu$_x$Y$_{1−x}$N@C$_{80}$, and M$_x$Sc$_{3−x}$N@C$_{82}$ (M=Y, Ce, Nd, Gd, Tb, Dy, Er, Lu), where the metals usually are group III (Sc, Y, and lanthanide) metals [3−11]. Recently, via the DC-arc discharging method, a non-group-III metal, Ti, was encapsulated in a TiSc$_2$N@C$_{80}$ molecule [11]. The corresponding experimental measurements indicate that the encapsulation of Ti significantly affects the electronic properties of the C$_{80}$ cage, and the electronic-chemical property of TiSc$_2$N@C$_{80}$ is dramatically different from that of Sc$_3$N@C$_{82}$ in term of the reversible redox behavior [11, 12].

In this work, we investigated the geometric, electronic, vibrational, and magnetic properties of TiY$_2$N@C$_{80}$ molecule using first-principles method. We find that electronic and magnetic properties of TiY$_2$N@C$_{80}$ molecule are different from that of Sc$_3$N@C$_{82}$ and Y$_3$N@C$_{80}$ molecules, but similar to TiSc$_2$N@C$_{80}$ molecule. Moreover, the molecular magnetism and rotation energy barrier of TiY$_2$N cluster in C$_{80}$ cage can be effectively altered through carrier doping and exohedral chemical modification, respectively.

II. COMPUTATIONAL DETAILS

Our calculations are performed using the density functional theory (DFT) as implemented in the DMol$^3$ package [13, 14] based on the linear combination of atomic orbital-molecular orbital. The atomic orbitals are represented by a double-numeric quality basis set with polarization functions, which are comparable to Gaussian 6-31G** sets. The exchange correlation interactions are described by the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation [15]. All atomic positions are fully relaxed at the GGA level without symmetry restriction until the atomic forces are smaller than 10$^{-6}$ a.u. (1 a.u.=27.21 eV). The electronic structure is obtained by solving the Kohn-Sham equations self-consistently in the spin-polarized scheme, and the self-consistent field procedure is carried out with a convergence criterion of 10$^{-6}$ a.u. on the energy and electron density.

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III. RESULTS AND DISCUSSION

A. Geometric structure

To obtain the most stable isomer of TiY$_2$N@C$_{80}$ molecule, we examine the TiY$_2$N cluster encapsulated in C$_{80}$ cage with two different symmetries (C$_{80}$-D$_{5h}$ and C$_{80}$-I$_h$). We find that all conformers of TiY$_2$N@C$_{80}$-D$_{5h}$ are less stable than those of TiY$_2$N@C$_{80}$-I$_h$ with several hundreds of meV. Thus, we only discuss C$_{80}$-I$_h$ carbon cage and its symmetry designation will be omitted. During the geometric optimization of TiY$_2$N@C$_{80}$ molecule without symmetry restriction, the initial locations of TiY$_2$N cluster within the cage are referred to these predicted lowest energy conformers of Sc$_3$N@C$_{80}$ and TiSc$_2$N@C$_{80}$ molecules [8, 10, 11]. Figure 1 shows several optimized molecular structures of TiY$_2$N@C$_{80}$ molecule. In all optimized conformers, TiY$_2$N cluster in the cage has a slightly pyramidal structure (the torsion angle is about 179.34$^\circ$). TiY$_2$N@C$_{80}$ molecule with a C$_1$ symmetry is found to be more stable, while the preferred conformer of TiSc$_2$N@C$_{80}$ has a C$_s$ symmetry [12]. The relative energies between different conformers of TiY$_2$N@C$_{80}$ molecule are rather small within several tens of meV, as shown in Fig.1 (a)–(c) as examples. The most stable conformer is shown in Fig.1(a), where the N atom is displaced from the center of the TiY$_2$N@C$_{80}$ molecule toward the Ti atom. The Y atom is bound to a hexagonal ring of C$_{80}$ with a little displacement toward the edge between hexagonal and pentagonal rings. The Ti–N distance is about 1.85 Å, which is shorter than that in TiSc$_2$N@C$_{80}$ (d$_{Ti-N}$=1.92 Å), whereas the Y–N distances are 2.14 and 2.15 Å, respectively, which are longer than Sc–N distance in TiSc$_2$N@C$_{80}$ molecule (d$_{Sc-N}$=2.08 Å) [12]. These difference can be understood with the radius of Ti, Sc, and Y cations ($r_{Ti}$=0.67 Å, $r_{Sc}$=0.75 Å, and $r_{Y}$=0.90 Å) [3].

Since the vibrational spectra have the high structural sensitivity, the infrared spectroscopy (IR) of TiY$_2$N@C$_{80}$ is simulated to elucidate TiY$_2$N@C$_{80}$ molecular structure. We find that the calculated tangential and radial cage vibrational modes of TiY$_2$N@C$_{80}$ (1383, 1461, 1516 cm$^{-1}$) are virtually identical to those of Y$_2$N@C$_{80}$ molecule (1376, 1461, 1516 cm$^{-1}$) [11]. This result enables us to assign the same cage isomer, that is, C$_{80}$ cage has I$_h$ symmetry. The anti-symmetric M–N stretching vibrational modes appear in 600–800 cm$^{-1}$, which displays the characteristic for the encapsulated TiY$_2$N cluster. For example, the Ti–N stretching vibrational frequency is about 731 cm$^{-1}$, which is obviously higher than the Ti–N vibrational frequency (606 cm$^{-1}$) of TiSc$_2$N@C$_{80}$. This originates from the different Ti–N distance in two MMNCFs. The predicted Ti–N distances in TiY$_2$N@C$_{80}$ and TiSc$_2$N@C$_{80}$ are 1.85 and 1.92 Å, respectively.

B. Electronic structure

Figure 2 shows the calculated spin-polarized density of states (DOS) of TiY$_2$N@C$_{80}$ molecule. Here, the Fermi level shifts to the center of the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), and the vertical lines stand for the energy levels. Figure 2(a) shows the total DOS of TiY$_2$N@C$_{80}$ molecule. The partial DOS of Ti, Y, N atoms in the encapsulated TiY$_2$N cluster, and C$_{80}$ cage are shown in Fig.2 (b)–(e), respectively. It is clear that the total DOS of spin-up and spin-down channels are not exact symmetric, which indicates that TiY$_2$N@C$_{80}$ molecule displays magnetic (the calculated magnetic moment (MM) is about 0.86 $\mu_B$), similar to that of TiSc$_2$N@C$_{80}$ [12]. As shown in Fig.2 (b)–(e), the spin-up and spin-down partial DOS of Y and N atoms are nearly symmetric, while the partial DOS of Ti atom is obvious asymmetric and the spin-up states are filled more than the spin-down states. These observations imply that the MM of TiY$_2$N@C$_{80}$ is mainly contributed by Ti atom. It should be pointed out that there is a small peak locating at $-0.4$ eV in the partial DOS of C$_{80}$ cage, which manifests that C$_{80}$ cage also give a little contribution to the molecular magnetic moment. The calculated magnetic moment of carbon cage is about 0.12 $\mu_B$.

To clearly explore the magnetic property of TiY$_2$N@C$_{80}$ molecule, the spin density is plotted in Fig.3(a). The spin density locates inside of the C$_{80}$ cage, which mainly localizes around the Ti atom and the con-
FIG. 2 (a) The calculated total DOS of TiY\(_2\)N@C\(_{80}\), and the arrows present the energy levels. For clarity, the Fermi level shifted to zero. (b)–(e) The partial DOS of Ti, Y, N, and C\(_{80}\) cage, respectively.

FIG. 3 The spin density of TiY\(_2\)N@C\(_{80}\). (a) Neutral TiY\(_2\)N@C\(_{80}\), (b) TiY\(_2\)N@C\(_{80}\)^+\(^{+}\), (c) TiY\(_2\)N@C\(_{80}\)^−\(^{−}\). The isovalue is set to be 0.01 a.u./Å\(^3\). Pink and yellow stands for spin-up and spin-down channels, respectively. For interpretation of the color in this figure legend, the reader can refer to the web version of this article.

FIG. 4 The spatial distribution of three types of TiY\(_2\)N@C\(_{80}\) molecular orbitals (labeled in Fig.2(a)). (a) Type I, cage-dominated orbital, (b) type II, encapsulated TiY\(_2\)N cluster-dominated orbital, (c) type III, the cluster-cage hybrid orbital. The isovalue is set to be 0.02 a.u./Å\(^3\).

distribution from Y atoms is very small. This observation verifies again that one unpaired electron in TiY\(_2\)N@C\(_{80}\) molecule is largely contributed by Ti atom. According to the analysis of the Mulliken charges, the chemical valence state of Ti can be formally described as Ti\(^{3+}\), similar to that of TiSc\(_2\)N@C\(_{80}\) molecule [12].

The molecular orbital population analysis shows that TiY\(_2\)N@C\(_{80}\) molecular orbitals (MOs) can be divided into three types, type I: C\(_{80}\) cage-dominated orbital, type II: TiY\(_2\)N cluster-dominated orbital, and type III: metal-cage hybrid orbital. To clearly display the feature of three types MOs, the spatial distribution of types I–III MOs are shown in Fig.4, which locate at −1.4, −0.4, and 2.6 eV, respectively. Generally speaking, type I and II MOs show no direct information on the relative position of encapsulated TiY\(_2\)N cluster, since the cage-dominated MO (type I) are irrelevant to the TiY\(_2\)N cluster, and type II MO belongs to the cluster, but localized in the cage. Note that, using the Tersoff-Hamann formula [16], the TiY\(_2\)N cluster-C\(_{80}\) cage hybrid MOs (type III) can be used to simulate the dI/dV mappings of the scanning tunneling microscopy. Then, the relative position of the encapsulated TiY\(_2\)N cluster can be referred by comparing the experimental results with theoretical simulations [17].

C. Carrier-doping effect

Carrier doping is a common method to tune the electronic structures and magnetic properties of molecules and materials. Here, we examine the geometric and electronic structures of the carrier doped TiY\(_2\)N@C\(_{80}\) molecule including TiY\(_2\)N@C\(_{80}\)^+\(^{+}\) (cation) and TiY\(_2\)N@C\(_{80}\)^−\(^{−}\) (anion). The optimized structures of the carrier doped molecules are close to that of the neutral TiY\(_2\)N@C\(_{80}\) molecule. The net Mulliken charge
(about +2.07 e) of Ti$\text{Y}_2\text{N}$ cluster changes very slightly within 0.1 e when Ti$\text{Y}_2\text{N}@\text{C}_{80}$ molecule is charged with an electron or hole. However, the magnetism of Ti$\text{Y}_2\text{N}@\text{C}_{80}$ molecule is quenched by carrier doping, according to the spin density of Ti$\text{Y}_2\text{N}@\text{C}_{80}$ and Ti$\text{Y}_2\text{N}@\text{C}_{80}$, as shown in Fig.3 (b) and (c), respectively. Theoretical results indicate a spatial charge separation in Ti$\text{Y}_2\text{N}@\text{C}_{80}$ molecule, where the spin changes localize on the encapsulated Ti$\text{Y}_2\text{N}$ cluster and the charge change mainly happens on the C$_{80}$ cage. This behavior has also been reported in other endohedral fullerenes, such as Sc$_3$N@C$_{80}$ and TiSc$_2$N@C$_{80}$ molecules [8, 12].

Moreover, we calculated the adiabatic ionization potential (AIP) and adiabatic electron affinity (AEA) of Ti$\text{Y}_2\text{N}@\text{C}_{80}$ molecule. The corresponding predicted values are about 6.48 and 3.19 eV, respectively, which are similar to those of TiSc$_2$N@C$_{80}$ (6.62 and 3.20 eV at the same calculation level), but smaller than those of Y$_3$N@C$_{80}$ (7.14 and 2.89 eV). The AIP and AEA of Y$_3$N@C$_{80}$ and TiSc$_2$N@C$_{80}$ are close to the previously reported values [12]. Our calculation suggests that Ti$\text{Y}_2\text{N}@\text{C}_{80}$ is more easy to be oxidized and reduced compared to Y$_3$N@C$_{80}$ molecule. These AIP and AEA differences originate from the properties of the frontier MOs (including HOMO and LUMO) of three different molecules.

D. Exohedral chemical modification

To improve the solubility and processability of metallofullerenes for expanding their practical applications [18–20], or to control the position of encapsulated atoms and corresponding properties, one possible effective method is exohedral chemical functionalization [21]. Here, we consider the the exohedral functional of pyrrolidine addition (C$_5$NH$_5$) on C$_{80}$ cage. The electrostatic potentials (EP) of Ti$\text{Y}_2\text{N}@\text{C}_{80}$ molecule is plotted in Fig.5(a). The region of positive EP appears around Ti atoms. Because the negative counterelectron prefers to occupy the electronegative region, favorable binding site of pyrrolidine addition to Ti$\text{Y}_2\text{N}@\text{C}_{80}$ is far away from the Ti atom. Figure 5(b) presents the optimized structure of fulleropyrrolidine monoadduct (Ti$\text{Y}_2\text{N}@\text{C}_{80}$-C$_5$NH$_5$), where pyrrolidine connects to the carbon-carbon bond between hexagonal and pentagonal rings of carbon cage.

In general, the encapsulated atom or cluster is able to rotate inside the fullerene cage [12]. Ti$\text{Y}_2\text{N}$ cluster can rotate around the Ti–N axis in Ti$\text{Y}_2\text{N}@\text{C}_{80}$ molecule, which originates from the relatively strong Ti–C$_{80}$ interaction. The calculated rotational barriers of encapsulated Ti$\text{Y}_2\text{N}$ cluster in Ti$\text{Y}_2\text{N}@\text{C}_{80}$ with and without pyrrolidine addition are about 4.0 and 2.8 eV, respectively, as shown in Fig.6. It suggests that the rotation of Ti$\text{Y}_2\text{N}$ cluster becomes more difficult due to the exohedral chemical modification with pyrrolidine addition.

FIG. 5 (a) Electrostatic potential maps of Ti$\text{Y}_2\text{N}@\text{C}_{80}$ molecule. (b) Optimized structure of fulleropyrrolidine monoadduct (Ti$\text{Y}_2\text{N}@\text{C}_{80}$-C$_5$NH$_5$). (c) Spin density of fulleropyrrolidine monoadduct, here, the isovalue is set to be 0.01 a.u./Å$^3$, pink and yellow colors stand for spin-up and spin-down channels, respectively. For interpretation of the color in this figure legend, the reader can refer to the web version of this article.

FIG. 6 The calculated energy barriers of Ti$\text{Y}_2\text{N}$ cluster rotating around the Ti–N axis for Ti$\text{Y}_2\text{N}@\text{C}_{80}$ and the fulleropyrrolidine monoadduct (Ti$\text{Y}_2\text{N}@\text{C}_{80}$-C$_5$NH$_5$).

Importantly, the restricted movement of the cluster enhances anisotropic properties in terms of the molecular electronic conductance and magnetic moments, suggesting that controlling the movement of the cluster in the cage would be applicable for molecular electronic devices [21].

Moreover, the magnetism of Ti$\text{Y}_2\text{N}@\text{C}_{80}$ does not obviously change due to the presence of pyrrolidine addition. The calculated spin density of Ti$\text{Y}_2\text{N}@\text{C}_{80}$-C$_5$NH$_5$ is shown in Fig.5(c), which is very similar to that of Ti$\text{Y}_2\text{N}@\text{C}_{80}$ without exohedral chemical modification (Fig.3(a)). However, the predicted AIP and AEA of Ti$\text{Y}_2\text{N}@\text{C}_{80}$-C$_5$NH$_5$ is 6.16 and 2.96 eV, respectively,

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implying the change of redox property in fulleropyrro-

didine monoadduct.

**IV. CONCLUSION**

We perform a DFT investigation on the geomet-

ic, vibrational, magnetic and electronic properties of

\[ \text{TiY}_2 \text{N@C}_{80} \]

We find that the properties of \( \text{TiY}_2 \text{N@C}_{80} \) are dramatically different from that of \( \text{Sc}_3 \text{N@C}_{80} \) and \( \text{Y}_3 \text{N@C}_{80} \) molecules, but similar to that of \( \text{TiSc}_2 \text{N@C}_{80} \). We also observe the spin-charge sepa-

ration in this MMNCF, the spin change localizes at Ti

atom of \( \text{TiY}_2 \text{N} \) cluster while the charge change occurs

at carbon cage. Carrier doping is an effective method
to control the magnetism of \( \text{TiY}_2 \text{N@C}_{80} \). Exohedral

chemical modification can be used to increase the rota-

tion energy barriers of the \( \text{TiY}_2 \text{N} \) cluster in \( \text{C}_{80} \) cage

with pyrrolidine addition.

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