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Identifying Tm@C₈₂ isomers with density functional theory calculations

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Abstract

Density functional theory calculations have been performed to study the geometrical and electronic properties of endohedral metallofullerene Tm@C₈₂ isomers. Three energetically favorable isomers (with C_s, C₂ and C_{2v} symmetry, respectively) are identified which are consistent with the nuclear magnetic resonance (NMR) observations. The simulated ultraviolet photoelectron spectra (UPS) based on the three structures agree well with the measurements. Particularly, the parent cage of the experimentally observed Tm@C₈₂ isomer with C_s symmetry is newly assigned, which matches the experiments better than early assignments. In addition, strong interaction between an endohedral Tm atom and the C₈₂ cage is discussed and is thought to be responsible for the dramatic change in the relative stability of C₈₂ isomers when Tm is encapsulated.

1. Introduction

Endohedral metallofullerenes have a unique structure in which one or more metal atoms are encapsulated inside the carbon cage. Since the first successful extraction of La@C₈₂ in 1991 [1], many different metallofullerenes have been purified and successfully isolated in macroscopic quantities [2–11], among which lanthanum-containing metallofullerenes, M@C₈₂ (M is a lanthanide metal atom), have attracted special interest because of their solubility in organic solvents and unique stability at room temperature, as well as their potential applications in the field of nanomaterials and biomedical science.

Tm@C₈₂ was first isolated and characterized by Kirbach and Dunsch in 1996 [4]. Three Tm@C₈₂ isomers with C_s, C_{3v} and C_{2v} symmetry were identified with nuclear magnetic resonance (NMR) spectroscopy. The endohedral Tm atom was found in the Tm²⁺ valence state with an electronic

configuration of 4f¹³ in the ground state [4, 12, 13]. In another NMR measurement, Kodama *et al* also identified three isomers but with C_s, C₂ and C_{2v} symmetry, respectively [14]. Correspondingly, the cage structure of C₈₂ was explored in several studies [15–17]. Nine C₈₂ isomers were generated from the isolated pentagon rule (IPR), three of which, C₈₂(1), C₈₂(3) and C₈₂(5) are in C₂ symmetry, the next three in C_s (C₈₂(2), C₈₂(4) and C₈₂(6)), two in C_{3v} (C₈₂(7), C₈₂(8)) and another one in C_{2v} (C₈₂(9)) [18]. A problem then arises: how do we assign the nine C₈₂ structures to the three experimentally observed Tm@C₈₂ isomers? Since only one C_{2v} structure exists for C₈₂, it is uniquely assigned to the Tm@C₈₂ with the same symmetry by Kodama *et al* [14]. By comparison with the measured and simulated ultraviolet photoelectron spectra (UPS), the C₈₂(5) and C₈₂(4) structures were previously assigned to the parent cages of the experimentally observed Tm@C₈₂ isomers with C₂ and C_s symmetries, respectively [19, 20]. In these assignments, the endohedral metallofullerenes were approximately described as the empty anionic carbon cages with the amount of charge

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equal to the oxidation numbers of the encapsulated metal atoms, without specific inclusion of the metal atom. And this approximate treatment not only overestimates the charge transfer but also ignores the hybridization between the metal atom and the cage [19–24]. Accordingly, the assignment of the cage structures in Tm@C_{82} complexes remains questionable and is worthy of further investigation.

In this work, density functional theoretical (DFT) calculations have been carried out to study the geometrical and electronic properties of C_{82} cages and Tm@C_{82} complexes, and to identify the structures of Tm@C_{82} isomers observed in experiments. The influence of Tm encapsulation on the relative stability of C_{82} isomers is addressed. Since UPS spectra of Tm@C_{82} isomers have been found to be isomer dependent [20], we simulated the UPS spectra of some isomers to help with the assignments. We will show below an assignment different from early studies [20] for the observed C_s isomer of Tm@C_{82} .

2. Computational methods

In the present study, all of the electronic structure calculations were carried out with spin-polarized DFT at the B3LYP level [25–27], which has been successfully used in the theoretical investigations of fullerenes and endohedral metallofullerenes [15–17, 28]. The standard 6-31G(d) and the relativistic effective core potential CEP-121G basis sets [29], as implemented in the Gaussian03 program [30], were employed for C and Tm atoms, respectively. Several studies have used the B3LYP/6-31G(d) method to investigate the structure of fullerenes (C_{60} , C_{80} and C_{82}) and produced results in good agreement with experiments [15, 16, 31, 32]. To validate the computational method, the first and second ionization potentials (IPs) of Tm atom were calculated. The calculated values, 5.88 eV and 11.99 eV, agree well with the observed ones, 6.18 eV [33] and 12.05 eV [34], respectively. Therefore, we used this computational strategy to study the Tm@C_{82} systems.

To compare with experiments, the UPS spectra of Tm@C_{82} isomers were obtained by broadening the calculated IPs of Tm@C_{82} isomers with a Lorentzian function of 0.25 eV full width at half maximum (FWHM) [20]. The partial density of states (PDOS) of Tm and C atoms in Tm@C_{82} were obtained by Lorentzian extension of energy levels of molecular orbitals. The broadening width parameter was chosen to be 0.15 eV and the Fermi level (E_F) was taken as zero [35].

3. Results and discussion

3.1. Geometry and energetics

The optimized structures of the nine $\text{Tm@C}_{82}(i)$ ($i = 1, 2, \dots, 9$) isomers are displayed in figure 1. The shortest, longest and averaged C–C and Tm–C bond lengths of these isomers are listed in table 1. The corresponding bond lengths of their parent C_{82} cages are also given for comparison. Our calculated bond lengths of C_{82} are consistent with other works [15–17]. The incorporation of the Tm atom slightly

Table 1. The statistics of C–C and Tm–C bond lengths (in angstrom) of C_{82} and Tm@C_{82} isomers.

	Shortest R_{CC}^a	Longest R_{CC}^a	Average R_{CC}^a	$N_{\text{Tm}-\text{C}}$	Average $R_{\text{Tm}-\text{C}}$
1	1.383 (1.365) [1.363]	1.484 (1.470) [1.470]	1.435 (1.433) [1.433]	6	2.629
2	1.370 (1.363) [1.363]	1.473 (1.472) [1.472]	1.435 (1.433) [1.433]	5	2.642
3	1.373 (1.371) [1.371]	1.479 (1.470) [1.470]	1.435 (1.433) [1.433]	6	2.625
4	1.366 (1.369) [1.369]	1.472 (1.472) [1.472]	1.435 (1.433) [1.433]	4	2.607
5	1.367 (1.366) [1.366]	1.474 (1.471) [1.471]	1.435 (1.433) [1.433]	6	2.610
6	1.367 (1.367) [1.367]	1.474 (1.473) [1.473]	1.435 (1.433) [1.433]	3	2.564
7	1.366 (1.359) [1.362]	1.483 (1.474) [1.473]	1.435 (1.433) [1.433]	6	2.702
8	1.363 (1.365) [1.365]	1.470 (1.469) [1.469]	1.435 (1.433) [1.433]	4	2.582
9	1.373 (1.367) [1.367]	1.475 (1.476) [1.476]	1.435 (1.432) [1.433]	6	2.606

^a The first values correspond to the results of Tm@C_{82} obtained in this work, whereas the values in parentheses are obtained in this work for C_{82} and the values in square brackets are from [17] at the B3LYP/6-31G(d, p) level for C_{82} .

elongates the corresponding C–C bonds, except for the shortest R_{CC} of $\text{C}_{82}(8)$ and the longest R_{CC} of $\text{C}_{82}(9)$. Like the case of empty C_{82} cages, the nine Tm@C_{82} isomers almost have the same average R_{CC} . The symmetry of C_{82} could be changed upon encapsulation of the Tm atom. For example, the stationary structure of $\text{Tm@C}_{82}(7)$ is in C_1 symmetry, while its parent cage C_{82} has C_{3v} symmetry.

The relative stability of C_{82} isomers changes considerably when they encapsulate Tm atoms, as in other well studied metallofullerenes M@C_{82} ($\text{M} = \text{Ca}, \text{La}, \text{Y}, \text{Sc}, \text{Ce}$) [21, 22, 36, 37]. As seen in table 2, the stability order of nine Tm@C_{82} isomers is $9 > 6 > 5 > 8 > 4 > 1 > 3 > 2 > 7$, but different order, $3 > 4 > 2 > 1 > 5 > 6 > 9 > 7 > 8$, is found for their parent C_{82} isomers. $\text{Tm@C}_{82}(9)$ is predicted to be the most stable one, followed by $\text{Tm@C}_{82}(6)$ and $\text{Tm@C}_{82}(5)$, while their parent C_{82} lies above the most stable isomer $\text{C}_{82}(3)$ by 0.790, 0.525 and 0.351 eV, respectively. In contrast, $\text{Tm@C}_{82}(3)$, which corresponds to the most stable C_{82} cage, is less stable than $\text{Tm@C}_{82}(9)$ by 1.096 eV. It is worth noting that the three most stable isomers, $\text{Tm@C}_{82}(9, 6, 5)$, have C_{2v} , C_s and C_2 symmetry, respectively, which is in good agreement with Kodama's measurement [14]. The three isomers are therefore supposed to be observed in experiment. Table 2 also compares the gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of C_{82} and Tm@C_{82} isomers. It is obvious that the order of HOMO–LUMO gaps of carbon cages is also altered by the encapsulation of Tm atoms.

The location of metal atoms in carbon cages is of interest in the study on metallofullerenes. Tm atoms are located in different positions in the nine Tm@C_{82} isomers. Here we focus on the three most stable ones, $\text{Tm@C}_{82}(i)$ ($i = 5, 6, 9$).

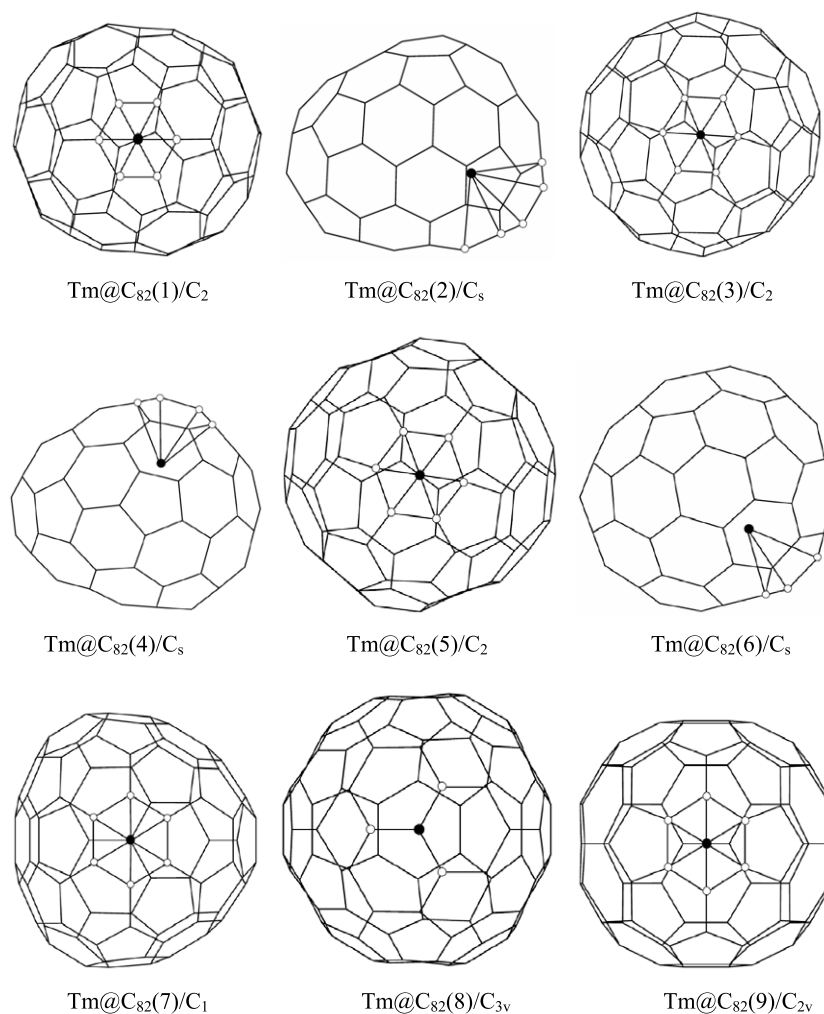


Figure 1. Nine Tm@C_{82} isomers optimized with B3LYP/6-31G(d). Solid and open circles stand for the bonded Tm and C atoms, respectively.

Table 2. Relative energy (RE, in eV), HOMO–LUMO gaps (ϵ , in electronvolt), net charge on Tm atom (q , in atomic unit) and electron configurations of Tm in Tm@C_{82} complexes.

	Relative E^a	ϵ (HOMO–LUMO) ^a	q	Electron configuration
1	−0.14 (0.33)	1.58 (1.26)	1.78	$6s^{0.10}4f^{12.97}5d^{0.12}6p^{0.01}7s^{0.02}$
2	0.01 (0.29)	1.12 (1.64)	1.75	$6s^{0.15}4f^{12.97}5d^{0.11}6p^{0.01}7s^{0.01}$
3	0.00 (0.00)	1.20 (1.63)	1.79	$6s^{0.10}4f^{12.98}5d^{0.12}6p^{0.01}7s^{0.02}$
4	−0.39 (0.17)	1.28 (1.56)	1.79	$6s^{0.10}4f^{12.97}5d^{0.12}6p^{0.01}7s^{0.01}$
5	−0.76 (0.35)	1.64 (1.28)	1.78	$6s^{0.11}4f^{12.97}5d^{0.12}6p^{0.01}7s^{0.01}$
6	−0.93 (0.53)	1.45 (1.11)	1.78	$6s^{0.11}4f^{12.97}5d^{0.12}6p^{0.01}7s^{0.01}$
7	0.94 (1.10)	1.48 (0.86)	1.83	$6s^{0.07}4f^{12.98}5d^{0.10}6p^{0.01}7s^{0.01}$
8	−0.58 (1.32)	1.06 (0.75)	1.87	$6s^{0.03}4f^{12.97}5d^{0.12}6p^{0.01}7s^{0.01}$
9	−1.10 (0.79)	1.44 (0.75)	1.78	$6s^{0.11}4f^{12.97}5d^{0.12}6p^{0.01}7s^{0.01}$

^a Values in parentheses are for C_{82} .

As shown in figure 1, the Tm atom is off-center and situated adjacent to the hexagonal ring along the C_2 axis of the cages for $i = 5$ and 9, like the cases of other metallofullerenes such as M@C_{82} ($M = \text{Ce}, \text{Gd}, \text{Y}, \text{La}$ and Eu) [24, 28, 37–40]. The distances between the Tm atom and its nearest neighbor carbon atoms are 2.589 Å and 2.595 Å for $\text{Tm@C}_{82}(5)$ and $\text{Tm@C}_{82}(9)$, respectively. Some correlation between stability and Tm–C distances can be noted in tables 1 and 2. Among

the five isomers with six Tm–C bonds, $\text{Tm@C}_{82}(9)$ and $\text{Tm@C}_{82}(5)$ have the shortest Tm–C distances and are more stable than the other three. Although $\text{Tm@C}_{82}(6)$ have only three Tm–C bonds, the averaged bond length is shorter than in other isomers. These three isomers, 9, 5 and 6 are the three most stable isomers predicted in this study. For comparison, the metal–C distances are 2.466 Å for Ce@C_{82} [24], 2.610 Å for Eu@C_{82} [39] and 2.496 Å for Gd@C_{82} [40], respectively.

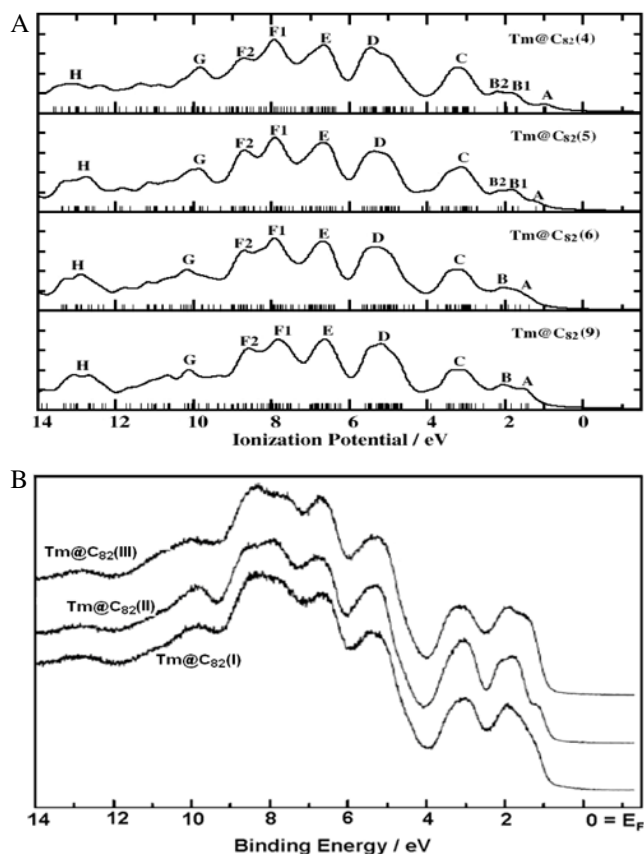


Figure 2. (A) Calculated UPS spectra of $\text{Tm@C}_{82}(4, 5, 6, 9)$ isomers. Shifts of 0.8, 0.8, 0.8 and 0.62 eV are applied for isomers $\text{Tm@C}_{82}(4, 5, 6, 9)$, respectively. (B) Experimental UPS spectra of three Tm@C_{82} isomers obtained with 40 eV photon energy (reproduced from [20] with permission from Elsevier).

3.2. UPS spectra

The UPS technique has already been used to reveal the electronic structures of fullerenes and to distinguish their isomers [19, 20, 41]. In Hino's UPS experiment [20], the Tm@C_{82} isomer with C_s symmetry was assigned to with $C_{82}(4)$ parent cage, inconsistent with our calculated result that $\text{Tm@C}_{82}(6)$ is more stable than $\text{Tm@C}_{82}(4)$, although both of them are in C_s symmetry. We then compare our calculations with the experimental UPS spectra for $\text{Tm@C}_{82}(i)$ ($i = 4, 5, 6, 9$) isomers (figure 2). Our simulated UPS spectra well reproduce most characteristics of the experimental curves in the energy region from 0 to 14 eV for the three most stable isomers.

Following the measured UPS spectra [20], we label the main band structures in the simulated spectra as A–H, as shown in figure 2. It is clear that the isomers have different profiles, especially for the lower bands A, B and C. The features of these UPS profiles are consistent with the experimental findings [20]. For $\text{Tm@C}_{82}(5)$, the locations of bands A and B (which has two subbands, B_1 and B_2), are in good agreement with the measurement of the isomer with C_2 symmetry. Similarly, the calculated band structures of $\text{Tm@C}_{82}(9)$ are consistent with the measured UPS spectra of the C_{2v} isomer. However, for $\text{Tm@C}_{82}(4)$ which was previously assigned to the observed

isomer with C_s symmetry [20], the two-peak feature of band B (named B_1 and B_2) in simulated UPS spectrum was not observed in experiment. Instead, the simulated spectrum of $\text{Tm@C}_{82}(6)$, with band A at 1.3 eV and B at 2.0 eV, reproduces the main features of the measured spectra of the C_s Tm@C_{82} . Combining this with the results of the energy calculation that $\text{Tm@C}_{82}(6)$ is more stable than $\text{Tm@C}_{82}(4)$, we could conclude that $\text{Tm@C}_{82}(6)$, but not $\text{Tm@C}_{82}(4)$, should be assigned to the C_s isomer detected in the NMR measurement [14].

The upper bands in the UPS spectra for these isomers are quite similar to each other and in agreement with the measurements. So only the lower bands are isomer dependent and can be used to distinguish the isomer structures. It is also worth mentioning that the simulated UPS spectra obtained from C_{82}^{2-} show a correspondence in the lower band region (0–5 eV) [20], but wrong patterns in the upper bands in comparison with the experiments, indicating that the cage structure of $\text{Tm@C}_{82}(6)$ cannot be simply described by C_{82}^{2-} .

3.3. Electronic structures

It has been shown that electron transfer from an interior metal atom to the carbon cage plays a crucial role in stabilizing endohedral metallofullerenes. Hereby, we inspect the charge flow between the Tm atom and the cage for the Tm@C_{82} isomers. Natural bond orbital (NBO) analysis [42] was applied to evaluate the atomic net charges in the nine isomers. As seen in table 2, the transferred charges are in the range from 1.75 to 1.87 electrons for the nine Tm@C_{82} isomers, indicating that these isomers possess strong ionic character. Such character has also been noted in previous experimental studies [12, 13]. Thus, the electronic structure is often described approximately as $\text{Tm}^{2+}@C_{82}^{2-}$ to highlight its ionic nature, similar to other endohedral metallofullerenes. For example, in $\text{Eu}^{2+}@C_{82}^{2-}$, two valence 6s electrons on an Eu atom are transferred to the C_{82} cage [39, 40]. For $\text{Gd}^{3+}@C_{82}^{3-}$, one 5d and two 6s electrons on a Gd atom are donated to the carbon cage [28, 40]. The stabilization of electron flow from metal atom to carbon cage has been used to rationalize the stability of metallofullerenes of $M@C_{82}$ ($M = \text{Ca}, \text{Sc}, \text{Eu}, \text{Y}$ etc) complexes [21, 22, 40].

A more specific picture of the charge transfer between Tm and C_{82} can be addressed with the electronic configurations of Tm atoms, as listed in table 2. For example, the calculated electronic configuration of the Tm atom in $\text{Tm@C}_{82}(9)$ is $6s^{0.11}6p^{0.01}5d^{0.12}4f^{12.97}$. Compared to the configuration ($6s^{2.00}4f^{13.00}$) of an isolated Tm atom, we can find that 1.89 6s electrons are donated to C_{82} , while 0.12 feedback electrons are compensated to 5d, suggesting strong hybridization between the 5d orbital of the Tm atom and the π orbital of the carbon cage, as found in some other metallofullerenes such as La@C_{82} , Sc@C_{82} etc [36]. The hybridization can also be seen from the PDOS of Tm and C_{82} in Tm@C_{82} , shown in figure 3. In the PDOS of the Tm atom, two main bands are found below the Fermi level with one assigned to 4f and the other to 5p, which are consistent with XPS experiments [12]. The contribution from 6s is rather small, whereas that from 5d spreads over a wide energy region and is clearly noted.

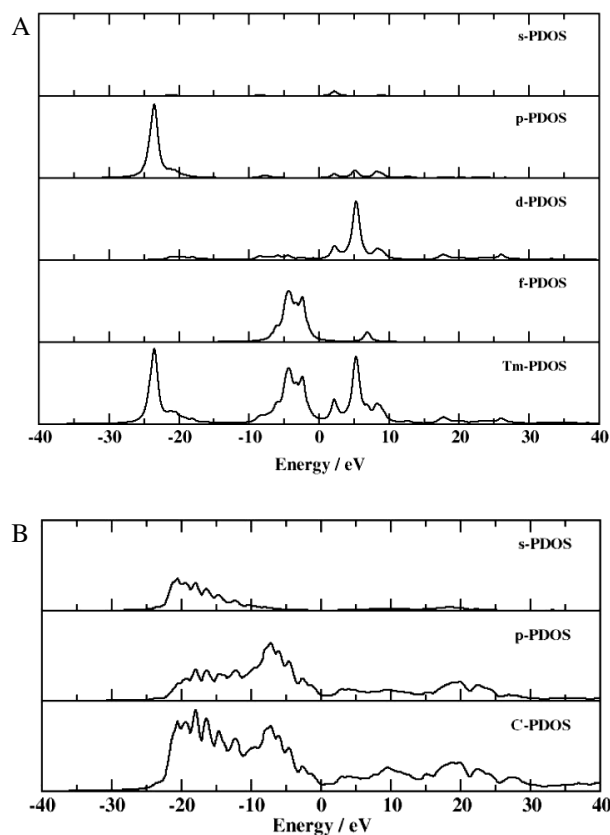


Figure 3. PDOS of Tm (A) and C_{82} (B) in $Tm@C_{82}(9)$.

In the PDOS of the C_{82} moiety, the bands below the Fermi level are assigned to 2p, followed by the 2s bands. Spin-orbit coupling in $Tm@C_{82}$ mainly arises from the one unpaired f electron in Tm. Since the f electrons are not involved in the bonding between Tm and C_{82} , as indicated by the electronic configurations of Tm atoms, the spin-orbit coupling is expected to have little effect on the energy order of the $Tm@C_{82}$ isomers.

The encapsulation of the Tm atom changes drastically the order of the relative stability of the C_{82} cages. Taking

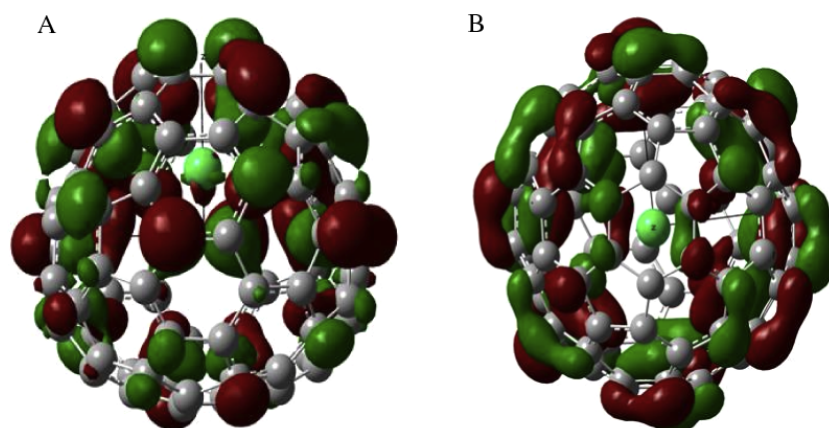


Figure 4. Wavefunctions of HOMO (A) and LUMO (B) of $Tm@C_{82}(9)$.

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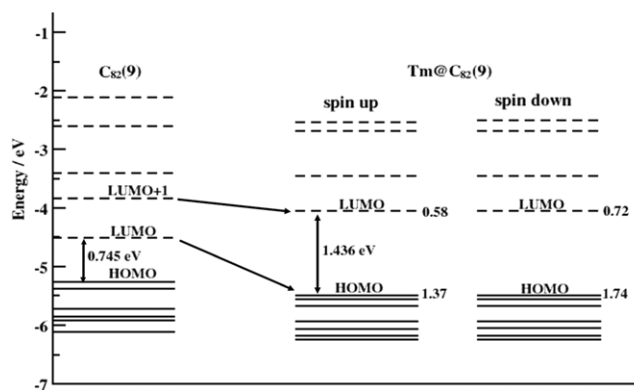


Figure 5. Energy levels of $C_{82}(9)$ and $Tm@C_{82}(9)$. Solid and dashed lines stand for the occupied and unoccupied orbitals, respectively.

$Tm@C_{82}(9)$ as an example, we analyze the formation of its molecular orbitals. Figure 4 displays the wavefunctions of the HOMO and LUMO of $Tm@C_{82}(9)$. Both are contributed mainly by the carbon cage. The Tm atom contributes only 0.58% and 1.37% to HOMO and LUMO, respectively, suggesting that both the HOMO and LUMO are carbon-like, a similar case was also found in $Si@C_{74}$ [35]. In addition, we perform the overlap integration between the molecular orbitals of $Tm@C_{82}(9)$ and $C_{82}(9)$ near their Fermi levels. The large value (0.99) of overlap integration indicates that the HOMO of $Tm@C_{82}(9)$ is almost the same as the LUMO of $C_{82}(9)$ and about two 6s electrons of Tm atom are transferred to the LUMO of $C_{82}(9)$. Figure 5 illustrates the formation of the frontier molecular orbitals of $Tm@C_{82}(9)$. It can also be seen that the HOMO–LUMO gap of $Tm@C_{82}(9)$, 1.44 eV, is nearly twice as wide as that of its parent C_{82} cage, 0.75 eV, indicating the enhanced stability of the encapsulated structure of $Tm@C_{82}(9)$.

4. Conclusions

In this work density functional theory calculations have been performed to study the relative stability and electronic

properties of nine endohedral Tm@C₈₂ isomers. Our results illustrate that the encapsulation of Tm atom alters considerably the stability order of C₈₂ cages. The three most stable isomers, which have similar UPS spectra with measurements, are identified as samples that have been observed in NMR experiments. In particular, the parent cage of the observed Tm@C₈₂ with C_s symmetry is identified to be C₈₂(6), rather than C₈₂(4). Strong interactions between Tm and C₈₂ in Tm@C₈₂ complexes are discussed by analyzing their electronic configurations and PDOS. Electron transfer from Tm atom to C₈₂ cage was noted in the Tm@C₈₂ isomers, which plays an important role in stabilizing the endohedral metallofullerenes. Our results show that quantum chemistry calculations combining with experimental measurements could provide reliable information for both the structure identifications and the electronic properties of the novel metallofullerene complexes.

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