

RESEARCH ARTICLE

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Cite this: *Inorg. Chem. Front.*, 2022, **9**, 5688Decisive role of non-rare earth metals in high-regioselectivity addition of μ_3 -carbido clusterfullerene[†]Muqing Chen,^{†,a,b} Yaoxiao Zhao,^{†,c,f} Fei Jin,^b Mengyang Li,^c Runnan Guan,^b Jinpeng Xin,^b Yang-Rong Yao,^b Xiang Zhao,^c Guan-Wu Wang,^d Qianyan Zhang,^e Su-Yuan Xie^e and Shangfeng Yang^e

Endohedral clusterfullerenes featuring encapsulation of metal clusters which transfer electrons to the outer fullerene cages show intriguing chemical properties different from empty fullerenes. Despite the extensive studies on the chemical properties of empty fullerenes, especially C_{60} , chemical functionalization of endohedral clusterfullerenes has been less explored, and previous reports are primarily limited to the well-known metal nitride and carbide clusterfullerenes. Herein, we report the first chemical functionalization of an emerging endohedral clusterfullerene μ_3 -carbido clusterfullerene (abbreviated as μ_3 -CCF) bearing central μ_3 -C and Ti(IV) atoms forming a Ti=C double bond. A μ_3 -CCF $Dy_2TiC@I_h-C_{80}$ is synthesized, and its molecular structure is unambiguously determined by single-crystal X-ray diffraction for the first time. A photochemical cycloaddition reaction of $Dy_2TiC@I_h-C_{80}$ with 2-adamantane-2,3-[3H]-diazirine (abbreviated as AdN₂) is then carried out and only one monoadduct $Dy_2TiC@I_h-C_{80}$ -Ad is obtained, indicating its high regioselectivity. According to the X-ray single-crystal structure of $Dy_2TiC@I_h-C_{80}$ -Ad, the Ad moiety selectively attacks the [6,6]-bond (conjunction of two fused hexagons), which is adjacent to the Ti⁴⁺ ion instead of the two Dy³⁺ ions, affording a [6,6]-open addition pattern. Theoretical calculations unveil that the Ti(IV) ion plays a decisive role in high regioselectivity, and the formation of [6,6]-open $Dy_2TiC@I_h-C_{80}$ -Ad is thermodynamically preferred. Contrarily, a similar reaction of a Ti(III)-containing nitride clusterfullerene $Y_2TiN@C_{80}$ with AdN₂ is predicted to generate a different type of adduct with the addition sites adjacent to the Y³⁺ ion instead of the Ti³⁺ ion. This reveals the peculiarity of the chemical property of μ_3 -CCF resulting from the existence of the non-rare earth metal Ti with a high oxidation state.

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Introduction

Chemical functionalization of fullerenes offers an opportunity to expand the properties and functionalities of the pristine fullerenes and is essential for applications of fullerene materials in versatile fields such as organic photovoltaic, biomedicine, and catalysis.^{1–3} During the past three decades, extensive studies on the chemical properties of empty fullerenes, especially C_{60} , have been reported.^{4,5} Upon encapsulating metal clusters into fullerene cages, endohedral clusterfullerenes form and exhibit intriguing chemical properties different from empty fullerenes owing to electron transfer from the encapsulated metal cluster to the outer fullerene cage.⁶ Among the known clusterfullerenes, metal nitride and carbide clusterfullerenes were discovered first, and thus their chemical properties have been widely studied.^{7–9} Up to now, several different types of chemical reactions, including [2 + 2]-cycloadditions,^{10,11} 1,3-dipolar cycloaddition reactions,^{12–14} disilylations,¹⁵ Bingel-Hirsch reaction,^{16,17} azide addition reac-

tions,¹⁸ Lewis acid–base addition reactions,^{19–21} carbene addition,^{22–25} and radical reactions,^{26,27} have been applied in functionalizing metal nitride and carbide clusterfullerenes. However, chemical functionalization of other types of endohedral clusterfullerenes has been less explored due mainly to their relatively low yield compared to the metal nitride clusterfullerenes (NCFs) such as $\text{Sc}_3\text{N@C}_{80}$.

As an emerging endohedral clusterfullerene, the μ_3 -carbido clusterfullerene (abbreviated as μ_3 -CCF) discovered in 2014 appears quite special since a non-rare earth (RE) metal such as titanium (Ti) is needed, which bonds with a central μ_3 -C atom *via* a $\text{Ti}=\text{C}$ double bond along with two RE metals.²⁸ So far, a few Ti-based μ_3 -CCFs have been isolated, including $\text{TiM}_2\text{C@C}_{80}$ ($\text{M} = \text{Sc}, \text{Y}, \text{Nd}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Er}, \text{and Lu}$)^{29–33} and $\text{TiSc}_2\text{C@C}_{78}$,²⁹ featuring the electronic configurations of $[\text{Ti}^{4+}(\text{M}^{3+})_2\text{C}^{4-}]^6+$ involving a Ti^{4+} cation. Noteworthily, this is distinctly different from the conventional metal nitride clusterfullerenes (NCFs) $\text{M}_3\text{N@C}_{2n}$ in which the encapsulated RE and non-RE metals take formal oxidation states of 3+, affording electronic configurations of $[(\text{M}^{3+})_3\text{N}^{3-}]^6+\text{C}_{2n}^{6-}$.^{34–36} Thus, an open question arises: given that μ_3 -CCFs have similar trimetallic cluster compositions and the same charge state of the outer fullerene cage (C_{2n}^{6-}) with NCFs, whether are their chemical properties similar to those of NCFs? However, to the best of our knowledge, the chemical functionalization of μ_3 -CCFs has never been reported yet, and hence their chemical properties, specifically, the impact of the encapsulated Ti^{4+} cation, remain unknown.

Herein, we report the first chemical functionalization of μ_3 -CCF by a cycloaddition reaction of $\text{Dy}_2\text{TiC@I}_h\text{-C}_{80}$ with 2-adamantane-2,3-[3H]-diazirine (abbreviated as AdN_2). $\text{Dy}_2\text{TiC@I}_h\text{-C}_{80}$ is synthesized and its molecular structure is unambiguously determined by single-crystal X-ray diffraction for the first time. After a photochemical reaction of $\text{Dy}_2\text{TiC@I}_h\text{-C}_{80}$ with

AdN_2 , only one monoadduct $\text{Dy}_2\text{TiC@I}_h\text{-C}_{80}\text{-Ad}$ is obtained, indicating its high regioselectivity. On the basis of the X-ray single-crystal structure of $\text{Dy}_2\text{TiC@I}_h\text{-C}_{80}\text{-Ad}$, a [6,6]-open addition pattern is identified. Theoretical calculations are carried out to unveil the role of the Ti^{4+} ion within $\text{Dy}_2\text{TiC@I}_h\text{-C}_{80}$ μ_3 -CCF in its high regioselectivity.

Results and discussion

Synthesis, isolation and X-ray crystallographic structure of $\text{Dy}_2\text{TiC@I}_h\text{-C}_{80}$

The synthesis procedure of $\text{Dy}_2\text{TiC@C}_{80}$ by a modified Krätschmer–Huffman DC-arc discharge method is similar to that of $\text{Tb}_2\text{TiC@C}_{80}$ we reported previously.³² Isolation of $\text{Dy}_2\text{TiC@I}_h\text{-C}_{80}$ was fulfilled by a three-step high performance liquid chromatography (HPLC) procedure, and its high purity was confirmed by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectroscopy and HPLC (see ESI Fig. S1†).

Although $\text{Dy}_2\text{TiC@C}_{80}$ was reported by Popov *et al.* before,³³ its molecule structure has not been determined unambiguously yet. In this work, we succeeded in determining the molecular structure of $\text{Dy}_2\text{TiC@C}_{80}$ unambiguously by single-crystal X-ray diffraction for the first time on the basis of growing high-quality cocrystals with decapyrrylcorannulene (DPC) as the host. The relative orientation of $\text{Dy}_2\text{TiC@I}_h\text{-C}_{80}$ and two DPC molecules within a $2\text{DPC}\cdot\{\text{Dy}_2\text{TiC@I}_h\text{-C}_{80}\}$ cocrystal is shown in Fig. 1a, which includes only one orientation of the fullerene cage together with the major site of the Dy_2TiC cluster for clarity (see ESI Table S1† for detailed crystallographic data). Similar to other reported clusterfullerene-DPC cocrystals,^{37–39} the asymmetric crystal unit cell consists of one pair of fully ordered DPC molecules and one $\text{Dy}_2\text{TiC@I}_h\text{-C}_{80}$ molecule.

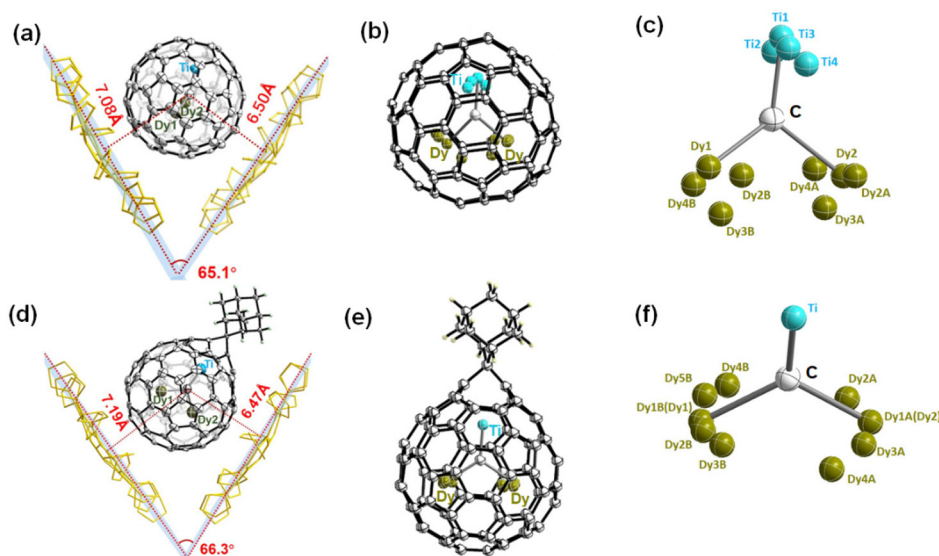


Fig. 1 Crystal structures of (a) $2\text{DPC}\cdot\{\text{Dy}_2\text{TiC@I}_h\text{-C}_{80}\}$ and (d) $2\text{DPC}\cdot\{\text{Dy}_2\text{TiC@I}_h\text{-C}_{80}\text{-Ad}\}$. Geometric configurations of (b) $\text{Dy}_2\text{TiC@I}_h\text{-C}_{80}$ and (e) $\text{Dy}_2\text{TiC@I}_h\text{-C}_{80}\text{-Ad}$ along with the metal positional disorder of the Dy_2TiC cluster within (c) $\text{Dy}_2\text{TiC@I}_h\text{-C}_{80}$ and (f) $\text{Dy}_2\text{TiC@I}_h\text{-C}_{80}\text{-Ad}$.

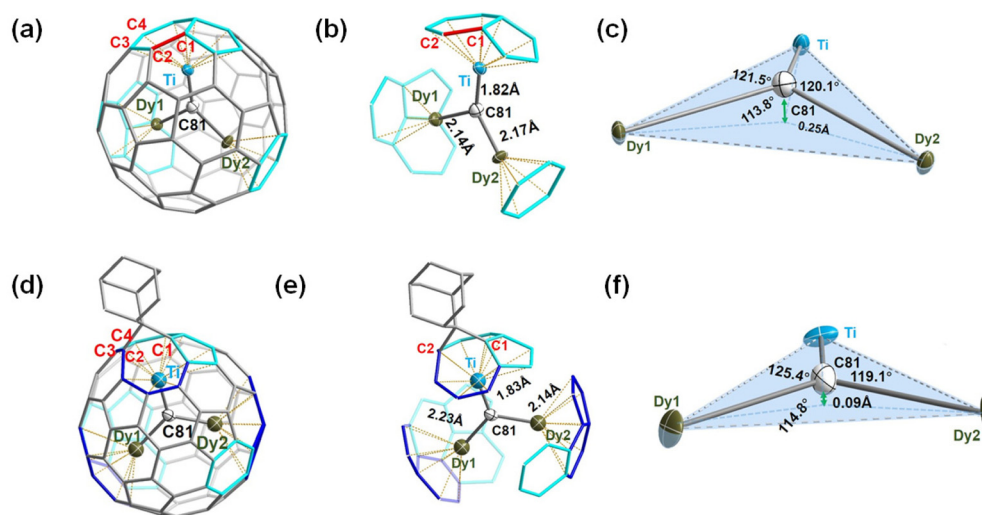


Fig. 2 The crystallographic orientation of the encapsulated Dy_2TiC cluster inside (a and b) $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}$ and (d and e) $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\text{-Ad}$, as well as (c and f) the configurations of the Dy_2TiC cluster inside both fullerene cages, are also shown. The blue and cyan regions indicate the coordination interactions between the encapsulated metals and the fullerene cage, and the C1–C2 bond is highlighted in red to show the difference before and after the Ad addition.

Meanwhile, two DPC molecules within $2\text{DPC}\cdot\{\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\}$ exhibit a V-shape geometry with a dihedral angle of 65.1° , and the nearest DPC- C_{80} cage center distances are 7.08 Å/6.50 Å, which is evidently different from that of $2\text{DPC}\cdot\{\text{Sc}_3\text{N}@I_h\text{-C}_{80}\}$ with a dihedral angle of 1.4° and a DPC- C_{80} cage center distance of 6.77/6.77 Å,³⁹ predicting the distinct electronic configuration of $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}$, although they share the same I_h -symmetry C_{80} cage.

The ordered $I_h\text{-C}_{80}$ cage and the major Dy/Ti sites with the largest occupancies (0.82, 0.91, and 0.80 for Dy1, Dy2, and Ti1, respectively) were extracted from the cocrystal for clarity (ESI Table S2†), showing that the Ti atom is located beneath a [5,6] bond, while the two Dy atoms are positioned beneath a hexagon and a [5,5,6] junction, respectively. Meanwhile, the shortest distances of the encapsulated metals and the outer cage carbons are 2.399 (9) Å, 2.344 (7) Å, and 2.132 (6) Å for Dy1–C75, Dy2–C11, and Ti–C42, respectively (ESI Table S3†), indicating strong metal–cage interactions which were verified by the high occupancy of two Dy atom and one Ti atom disorders. Furthermore, the bond length of Ti–C81 (1.824 (6) Å) is much shorter than those of Dy1–C81 (2.144(6) Å) and Dy2–C81 (2.175(6) Å) (Fig. 2b), indicating the existence of a Ti=C double bond as the characteristic of $\mu_3\text{-CCF}$.^{28,33} It is intriguing to investigate whether the encapsulated Dy_2TiC cluster takes a planar or pyramidal configuration. We find that the sum value of $\angle\text{Dy1-C81-Ti}$, $\angle\text{Dy2-C81-Ti}$, and $\angle\text{Dy1-C81-Dy2}$ is 355.4° (Fig. 2c), indicating that the encapsulated Dy_2TiC cluster is pyramidal, in which the C81 atom is 0.25 Å deviated from the plane composed of the TiDy_2 unit. This is similar to the case of $\text{Tb}_2\text{TiC}@C_{80}$ but different from the planar cluster found in $\text{Lu}_2\text{TiC}@C_{80}$, in which the central carbon is 0.07 Å deviated from the trimetallic plane,²⁸ revealing the influence of the size of RE metal on the geometry of the M_2TiC cluster.

Photochemical reactions of $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}$ with AdN_2

Among the chemical functionalization methods developed for metal nitride and carbide clusterfullerenes, a cycloaddition reaction using AdN_2 as a reagent has been demonstrated to exhibit high reactivity and regioselectivity.^{22,24,25,40–43} Hence, in our present work we managed to investigate the cycloaddition reaction of $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}$ $\mu_3\text{-CCF}$ with AdN_2 . The photochemical reaction of $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}$ with AdN_2 is shown in Fig. 3a. A mixture solution of $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}$ and excess AdN_2 in toluene was irradiated with a high-pressure mercury lamp, and the reaction process was monitored by analytical HPLC (Fig. 3b). Before the reaction, the HPLC profile of the pristine mixture solution showed two peaks at 3.6 and 39.8 min which were assigned to the AdN_2 /solvent peak and the pristine $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}$, respectively. After light irradiation

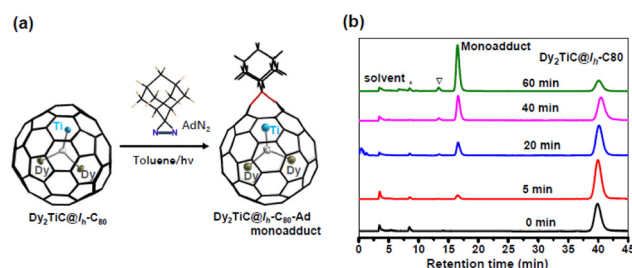


Fig. 3 (a) Synthetic route of $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\text{-Ad}$ through the photochemical reaction of $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}$ with AdN_2 ; (b) HPLC profiles of the reaction mixtures during the photochemical reaction process of $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}$ with AdN_2 with different reaction times. Conditions: Buckyprep column (\varnothing 4.6 mm \times 250 mm), 20 μL injection volume, 1.0 mL min^{-1} toluene flow. The inverted triangle and asterisk present the bisadduct and impurity, respectively.

for 5 min, a new peak appeared at 16.5 min, indicating the generation of the monoadduct $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\text{-Ad}$ as confirmed by MALDI-TOF mass spectroscopic characterization. After prolonging the reaction time up to 60 min, the peak at 16.5 min continued to increase along with a decrease of the peak corresponding to the pristine $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}$, indicating the promoted conversion of $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}$ to the monoadduct $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\text{-Ad}$. Finally, the reaction was stopped when an obvious peak of bisadduct at 13.3 min appears. Noteworthily, only one monoadduct $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\text{-Ad}$ was obtained even after the reaction proceeded for 60 min, indicating its high regioselectivity. The resultant solution was then subjected to preparative HPLC separation, and the purity of $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\text{-Ad}$ was verified by analytical HPLC (ESI Fig. S2a†). The purified $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\text{-Ad}$ product was characterized by MALDI-TOF mass spectroscopy, showing an intense mass peak at $m/z = 1479.8$ (ESI Fig. S2b†).

To identify the addition pattern of $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\text{-Ad}$, we grew high-quality cocrystals using DPC as the host similar to the case of the pristine $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}$, and successfully determined the molecular structure of $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\text{-Ad}$ unambiguously by single-crystal X-ray diffraction. As illustrated in Fig. 1d, the asymmetric crystal unit cell of the $4\text{DPC} \cdot 2\{\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\text{-Ad}\}$ cocrystal contains two pairs of fully ordered DPC molecules and two $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\text{-Ad}$ molecules. DPC molecules within $2\text{DPC} \cdot \{\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\text{-Ad}\}$ exhibit a V-shape geometry with a dihedral angle of 66.3° similar to the pristine $2\text{DPC} \cdot \{\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\}$ cocrystal and the nearest DPC- C_{80} cage center distances ($7.19 \text{ \AA}/6.47 \text{ \AA}$) exhibit only minor changes. However, different from the case of the pristine $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}$ with multiple position disorders of Dy and Ti atoms, the encapsulated Ti atom within $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\text{-Ad}$ exhibits no positional disorders while the two Dy atoms still show several disorders (Fig. 1f, Table S2†). This indicates that the attachment of the Ad group between the C1–C2 bond which is fractured effectively traps the underneath Ti atom as a result of the strengthened Ti-cage interaction as discussed in detail below. Furthermore, the main occupancies of the endohedral two Dy atom disorder are 0.42 and 0.43 for $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\text{-Ad}$, which are obviously less than those (0.82 and 0.91) of pristine $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}$, suggesting the weakened interaction of Dy atoms and the $I_h\text{-C}_{80}$ cage after carbene addition.

According to a close analysis of the single crystal structure of $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\text{-Ad}$, the Ad moiety selectively attacks the [6,6]-bond (conjunction of two fused hexagons, C1–C2) which is adjacent to the Ti^{4+} ion instead of the two Dy^{3+} ions shown in Fig. 2d and e. Intriguingly, the distance ($2.216(2) \text{ \AA}$) of the addition sites (C1, C2) is much longer than that of the conventional C–C single bond (1.54 \AA), indicating an open-cage addition pattern.^{22,41} Hence, a [6,6]-open addition pattern of the Ad moiety can be deduced, which is similar to the cases of photochemical cycloaddition reactions of Ad with metal nitride and carbide clusterfullerenes.^{22,24,25,40} Based on the largest occupancy, Dy1, Dy2, and Ti atoms within $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\text{-Ad}$ locate underneath a [5,6] bond, a [5,6]-bond, and a fractured [6,6]-bond, respectively (Fig. 2d and e). It is obvious that

Ad addition leads to rotation of the Dy_2TiC cluster from the coordinated blue region to the cyan region (see Fig. 2ab, d and e) due to the self-adaptive interaction between the endohedral cluster and the outer cage. For the encapsulated Dy_2TiC cluster within $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\text{-Ad}$, the bond lengths of Dy1–C81 ($2.242(5) \text{ \AA}$), Dy2–C81 ($2.140(5) \text{ \AA}$), and Ti–C81 ($1.829(5) \text{ \AA}$) are close to those within the pristine $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}$ as discussed above (ESI Table S3†). These results indicate that the μ_3 -carbido nature of the encapsulated Dy_2TiC cluster remains unchanged after grafting the Ad moiety. Moreover, the sum value of $\angle\text{Dy1-C81-Ti}$, $\angle\text{Dy2-C81-Ti}$ and $\angle\text{Dy1-C81-Dy2}$ becomes 359.3° (Fig. 2f), which is larger than that observed for the pristine $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}$ (355.4°), indicating that the cycloaddition of the Ad moiety to μ_3 -CCF induces an obvious geometric change of the encapsulated μ_3 -carbido cluster. A plausible explanation is that the grafted Ad moiety results in the deformation of the $I_h\text{-C}_{80}$ cage with an enlargement of the confined internal space, and thus the strain of the Dy_2TiC cluster is reduced.^{22,24,25,40}

Theoretical calculation of $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\text{-Ad}$

To understand the high regioselectivity of Ad addition to $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80} \mu_3\text{-CCF}$ and unveil the role of the non-RE metal Ti within the μ_3 -carbido cluster, we performed comprehensive theoretical studies. Density functional theory (DFT) computations on the pristine $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80} \mu_3\text{-CCF}$ with $S = 5$ spin ground state (spin multiple state $2S + 1 = 11$) were carried out, verifying that the encapsulated Dy_2TiC cluster takes a μ_3 -carbido structure bearing a Ti^{4+} ion and $\text{Ti}=\text{C}$ double bond (1.79 \AA) (ESI Tables S4–S5, Fig. S3–S4†). Besides, the electronic configuration of $[(\text{Dy}^{3+})_2\text{Ti}^{4+}\text{C}^{4-}]^{6+}@[I_h(31924)\text{-C}_{80}]^{6-}$ is confirmed similar to the case of the first $\mu_3\text{-CCF}$ $\text{Lu}_2\text{TiC}@I_h\text{-C}_{80}$.²⁸

The high regioselectivity of Ad addition around Ti instead of Dy can be understood by further analyzing the geometric and electronic configuration of $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}$. First, the shorter Ti–C (cage) distances than those of Dy–C (cage) suggest much stronger interactions between Ti^{4+} with the $I_h\text{-C}_{80}$ cage (ESI Table S6†), which is also confirmed by the larger Mayer bond order (MBO), density of electrons, and the Laplacian of the electron density between the Ti^{4+} ion and the $I_h\text{-C}_{80}$ cage than those of Dy^{3+} ions with the $I_h\text{-C}_{80}$ cage (ESI Tables S6 and S7†). Besides, the Ti^{4+} ion and its adjacent cage carbons with much more negative charges also contribute to the stronger interactions of $\text{Ti}^{4+}\text{-C}$ (cage) than that of $\text{Dy}^{3+}\text{-C}$ (cage) (ESI Fig. S4d†).

Considering the simultaneously appeared [5,6]-adduct and [6,6]-adduct isomers in the reaction of $\text{M}_3\text{N}@I_h\text{-C}_{80}$ ($\text{M} = \text{Sc}, \text{Lu}$) with carbene Ad: under light irradiation,²² it is interesting that our experimental finding shows that only [6,6]-adduct around the Ti^{4+} ion obtained with C1 and C2 as the addition sites instead of C2 and C3 ([5,6]-adduct isomer). The theoretical calculations indicate that the [6,6]-adduct has $3.3 \text{ kcal mol}^{-1}$ potential energy (Fig. 4) lower than the [5,6]-adduct. Furthermore, statistical thermodynamic analysis considering the entropy–enthalpy effect shows that [6,6]-open $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\text{-Ad}$ (C1, C2) has the 99.97% distribution relative to that

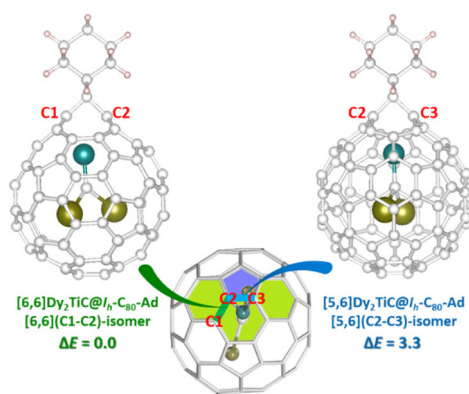


Fig. 4 Relative energies (ΔE , in kcal mol⁻¹) of [5,6]-Dy₂TiC@I_h-C₈₀-Ad (in blue) and [6,6]-Dy₂TiC@I_h-C₈₀-Ad (in green). The cyan, brown, and light gray balls represent the titanium, dysprosium and carbon atoms, respectively.

(0.03%) of [5,6]-open Dy₂TiC@I_h-C₈₀-Ad (C2-C3) at 298.15 K. Thus, the [6,6]-open Dy₂TiC@I_h-C₈₀-Ad obtained in experiment is the thermodynamic product, which is the same as the reactions of AdN₂ with several endohedral metallofullerenes previously reported.^{23,43}

In order to consolidate the universal role of the Ti(IV) within the μ_3 -carbido cluster in determining the regioselectivity and reaction mechanism of μ_3 -CCF, we further computed similar cycloaddition products of the analogously reported μ_3 -CCF Y₂TiC@I_h-C₈₀³³ and nitride clusterfullerene Y₂TiN@C₈₀ bearing Ti(III)^{44,45} with AdN₂, in which replacing Dy³⁺ with Y³⁺ is to ensure the validity of μ_3 -CCF clusterfullerenes. Fig. 5 shows that without the presence of Ti(IV), the Ad moiety of Ti(III)-based [6,6]-Y₂TiN@I_h-C₈₀-Ad with the lowest potential energy is located nearly around the Y atom. However, similar to Dy₂TiC@I_h-C₈₀-Ad, the Ad moiety selectively attacks the [6,6]-bond of I_h-C₈₀ adjacent to the Ti(IV) instead of the Y atom to form a Y₂TiC@I_h-C₈₀-Ad adduct with energy superiority. Further frontier molecular orbital (FMO) computations in Fig. S6† show that in the presence of Ti(IV), the FMO occupancy of Dy₂TiC@I_h-C₈₀ and Y₂TiC@I_h-C₈₀ are similar to each other (ESI Fig. S5†), but different to that of Y₂TiN@I_h-C₈₀ bearing Ti(III). This reveals the decisive role of the Ti⁴⁺ ion with a high formal oxidation state (IV) in the electronic configuration of μ_3 -CCF M₂TiC@I_h-C₈₀, which directly affects the reactivity. Thus, the cycloaddition reaction of Y₂TiC@I_h-C₈₀ with AdN₂ is expected to exhibit similar regioselectivity and addition pattern to that of Dy₂TiC@I_h-C₈₀.

Effect of Ad addition on the electronic properties of Dy₂TiC@I_h-C₈₀

In order to unveil the effect of Ad addition on the electronic properties of Dy₂TiC@I_h-C₈₀, we carried out UV-vis-NIR spectroscopic characterization and electrochemical studies (Fig. 6). Their characteristic absorption data and redox potentials along with those of other analogous clusterfullerenes are sum-

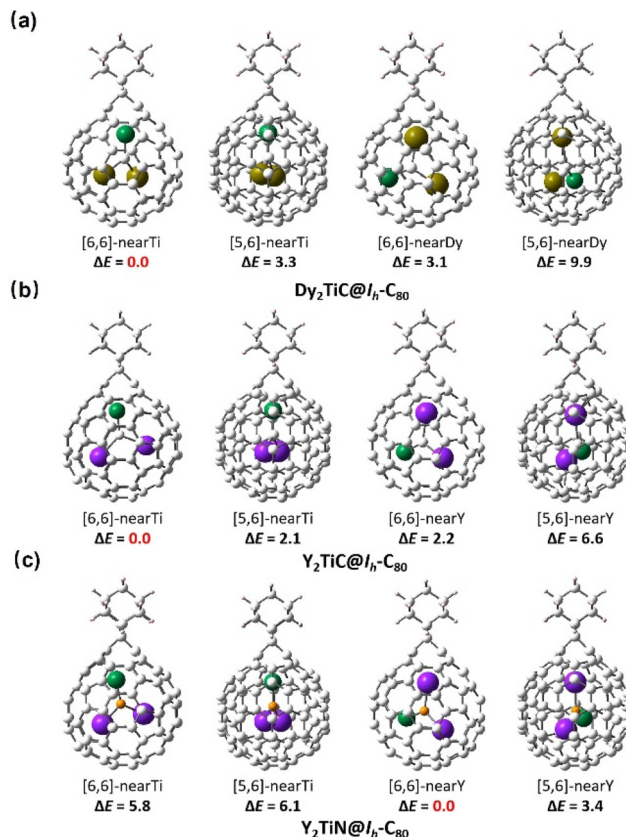


Fig. 5 Relative energies (ΔE , in kcal mol⁻¹) of Dy₂TiC@I_h-C₈₀ (a), Y₂TiC@I_h-C₈₀ (b) and Y₂TiN@I_h-C₈₀ (c) with different addition sites of Ad. The green, brown, purple and light gray balls represent the titanium, dysprosium, yttrium and carbon atoms, respectively.

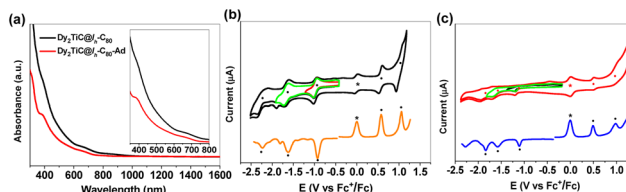


Fig. 6 (a) UV-vis-NIR spectra of Dy₂TiC@I_h-C₈₀ and Dy₂TiC@I_h-C₈₀-Ad dissolved in toluene. Inset: Enlarged spectral region of 350–800 nm. Cyclic voltammograms of (b) Dy₂TiC@I_h-C₈₀ and (c) Dy₂TiC@I_h-C₈₀-Ad in 1,2-dichlorobenzene solution with ferrocene (Fc) as the internal standard under a nitrogen atmosphere. Scan rate: 100 mV s⁻¹, tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte. Each redox step is marked with a solid dot to aid comparison; the asterisk denotes the oxidation peak of ferrocene.

marized (ESI Table S8†). The absorption spectrum of Dy₂TiC@I_h-C₈₀ in the range of 300–1600 nm is featureless, with two broad shoulder peaks at 390 and 676 nm. After grafting an Ad moiety, the shoulder peak at 390 nm becomes more apparent in the absorption spectrum of Dy₂TiC@I_h-C₈₀-Ad (Fig. 6a) and the shoulder peak at 676 nm exhibits a negligible change. These results indicate that Ad addition induces little influence on the optical absorption of Dy₂TiC@I_h-C₈₀.

Cyclic voltammometry (CV) and differential pulse voltammetry (DPV) of the pristine $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}$ and $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\text{-Ad}$ are then compared as illustrated in Fig. 6b and c. The pristine $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}$ exhibits two reversible reduction steps, one irreversible reduction step and two reversible oxidation steps which are similar to those reported by Popov *et al.*³³ After Ad addition, all three reduction steps become irreversible, and the first reduction potential shifts negatively from -0.93 V (half-wave potential) to -1.10 V (peak potential), whereas the second and third reduction potentials exhibit a negligible cathodical shift. Only one reversible oxidation step and one irreversible oxidation peak are observed for $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\text{-Ad}$, with the first oxidation potential cathodically shifting from 0.57 V to 0.49 V relative to that of the pristine $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}$ (ESI Table S8†). This cathodical shift of redox potentials in $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}$ after carbene functionalization is similar to those of Ad adducts of $\text{M}_3\text{N}@C_{80}$ ($\text{M} = \text{Sc}, \text{Lu}$) reported previously.²²

Conclusion

In summary, the first chemical functionalization of $\mu_3\text{-CCF}$ exemplified by $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}$ is studied, revealing the decisive role of the non-rare earth metal Ti(IV) in high-regioselectivity addition. The molecular structure of the pristine $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}$ is unambiguously determined by single-crystal X-ray diffraction for the first time, revealing the feature of the $\text{Ti}=\text{C}$ double bond and the influence of the size of rare earth metals on the geometry of the M_2TiC cluster. A photochemical cycloaddition reaction of $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}$ with I_2 affords only one monoadduct $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\text{-Ad}$, indicating its high regioselectivity. On the basis of the X-ray single crystal structure of $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\text{-Ad}$, the Ad moiety selectively attacks the [6,6]-bond which is adjacent to the Ti^{4+} ion instead of the two Dy^{3+} ions, and the presence of a [6,6]-open addition pattern is confirmed. According to theoretical calculations, $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\text{-Ad}$ is thermodynamically preferred, and the Ti(IV) ion plays a decisive role in high regioselectivity. In contrast, a similar reaction of a Ti(III)-containing nitride clusterfullerene $\text{Y}_2\text{TiN}@C_{80}$ with AdN_2 is predicted theoretically to generate a different type of adduct with the addition site adjacent to the Y^{3+} ion instead of the Ti^{3+} ion. Hence, the peculiarity of the chemical properties of $\mu_3\text{-CCF}$ resulting from the existence of the non-rare earth metal Ti with a high oxidation state is unveiled. As the first chemical functionalization of $\mu_3\text{-carbido}$ clusterfullerene with high regioselectivity, our finding on the decisive role of non-rare earth metal titanium in the regioselectivity fulfills an in-depth understanding of the fascinating chemical properties of endohedral fullerenes.

Experimental

Detailed experimental process

A toluene solution (25 mL) containing approximately 5 mg of $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}$ and excessive AdN_2 was first degassed for

about 15 minutes and later was irradiated with a high-pressure mercury-arc lamp (cutoff <350 nm) at room temperature. The reaction process was monitored by analytical HPLC. The detailed separation procedure of monoadduct $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\text{-Ad}$ using preparative HPLC is presented in the ESI† (LC-908 instrument, Japan Analytical Industry Co., Ltd, toluene as the mobile phase). MALDI-TOF MS was performed on a BIFLEX III (Bruker, Germany) with 1,1,4,4-tetraphenyl-1,3-butadiene (TPB) as the matrix.

Spectroscopic and electrochemical studies

UV-Vis-NIR spectra were recorded on a UV 3150 (Shimadzu, Japan) in toluene. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were obtained in 1,2-dichlorobenzene with 0.1 M ($n\text{-Bu}$)₄NPF₆ as the supporting electrolyte using a CHI660E workstation. Pt disc, Pt wire and silver wire were used as the working electrode, reference electrode and auxiliary electrode, respectively. The scan rate for CV was 20 mV s⁻¹. Conditions for DPV: pulse amplitude, 50 mV; scan rate, 20 mV s⁻¹.

X-ray crystallographic study

Crystal blocks of $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}$ and $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\text{-Ad}$ were obtained by slow volatilization of a toluene solution of DPC and $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}/\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\text{-Ad}$ in a glass tube. After two weeks, black block crystals suitable for crystal measurements were formed. Single-crystal XRD measurements of $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}$ and $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\text{-Ad}$ crystals were conducted at 100 K at the BL17B station of Shanghai Synchrotron Radiation Facility. The crystal structures were solved with the ShelXT structure solution program using the Intrinsic Phasing method, later refined with the ShelXL⁴⁶ refinement package embedded within OLEX2.⁴⁷ CCDC 2036864 and 2036865† contain the supplementary crystallographic data for $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}$ and $\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}\text{-Ad}$, respectively.

Author contributions

M. C. and Y. Z. contributed equally to this work. M. C. performed the chemical reaction of $\text{Dy}_2\text{TiC}@C_{80}$ with AdN_2 and confirmed the crystal structures of $\text{Dy}_2\text{TiC}@C_{80}$ and $\text{Dy}_2\text{TiC}@C_{80}\text{-Ad}$ by the crystal growth, crystal measurements and resolution. Meanwhile, M. C. wrote the original draft. Y. Z., M. L. and X. Z. carried out the theoretical calculation and analysis of $\text{Dy}_2\text{TiC}@C_{80}$ and $\text{Dy}_2\text{TiC}@C_{80}\text{-Ad}$. F. J., J. X. and R. G. synthesized and separated $\text{Dy}_2\text{TiC}@C_{80}$ for crystal growth and further chemical functionalization. Q. Z. provided decapyrrylcorannulene (DPC) which was used as the host to obtain high-quality single crystals of $\text{Dy}_2\text{TiC}@C_{80}$ and $\text{Dy}_2\text{TiC}@C_{80}\text{-Ad}$. S. X., G. W. and S. Y. provided the discussion and article revision.

Conflicts of interest

The authors declare no competing financial interest.

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