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Stabilizing a three-center single-electron metal-metal bond in a fullerene cage
Stabilizing a three-center single-electron metal–metal bond in a fullerene cage†

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Trimetallic carbide clusterfullerenes (TCCFs) encapsulating a quinary M3C2 cluster represent a special family of endohedral fullerenes with an open-shell electronic configuration. Herein, a novel TCCF based on a medium-sized rare earth metal, dysprosium (Dy), is synthesized for the first time. The molecular structure of Dy3C2@Ih(7)-C80 determined by single crystal X-ray diffraction shows that the encapsulated Dy3C2 cluster adopts a bat ray configuration, in which the acetylide unit C2 is elevated above the Dy3 plane by ~1.66 Å, while Dy–Dy distances are ~3.4 Å. DFT computational analysis of the electronic structure reveals that the endohedral cluster has an unusual formal charge distribution of (Dy3)8+(C2)2−@C80 and features an unprecedented three-center single-electron Dy–Dy–Dy bond, which has never been reported for lanthanide compounds. Moreover, this electronic structure is different from that of the analogous Sc3C2@Ih(7)-C80 with a (Sc3)9+(C2)3−@C80 charge distribution and no metal–metal bonding.

Introduction

Endohedral clusterfullerenes featuring encapsulation of an unstable metallic cluster within a fullerene cage have been attracting considerable interest over the past two decades due to the versatility of the types of encapsulated cluster and its charge transfer to the outer fullerene cage.‡a Soon after the discovery of Sc3N@C80 as the first endohedral clusterfullerene encapsulating a trimetallic nitride cluster in 1999,a the first metal carbide clusterfullerene (CCF), Sc3C2@C84, was identified by Shinohara and coworkers in 2001.10 The identification that a C2 moiety can be encapsulated in the form of a metal carbide cluster revealed a competition between CCFs M2C2@C2n−2 and genuine dimesoferfullerenes (di-EMFs) M2C2n in the hot carbon vapor during the fullerene formation. Importantly, CCFs and di-EMFs have different electronic structures and metal valence states. For Sc, Y, and heavy lanthanides, di-EMFs feature a (M2)n+(C2)n− charge distribution with M–M bonding and formally divalent metal M2+,2,12–14 while the charge distribution in dimetallic CCFs is [M2]6+(C2)2−@C2n with the more traditional M3+ state of rare-earth metals.8,15–16 Thus, by accumulating a certain negative charge, the C2 group has a paramount influence on the valence state of endohedral metal atoms.

The C2 group in CCFs has a variable formal charge state adapting to the metal cluster composition, from [C2]2− in M2C2@C2n to [C2]6− in ScC2@C80.17 In ScC2@C80, the first trimetallic CCF (TCCF) and the only TCCF characterized by single-crystal X-ray diffraction (SC-XRD),19 the acetylide unit has a formal [C2]3− charge state.20 A similar charge distribution is also proposed for Lu3C2@C88.21 In mixed-metal M2TiC2@C80 TCCFs (M = Sc, Lu, Dy), the acetylide unit adopts a [C2]4− state to balance the tetravalent Ti4+.22,23 In these five TCCFs, rare-earth metals are present in their 3+ oxidation state and thus do not form metal–metal bonding interactions. Interestingly, three-center M–M bonding was predicted in Y3@C80 and Er3@C74 trimetallofullerenes (tri-EMFs) based on computational analysis, but structural characterization of such tri-EMFs is still lacking.24,25

In this work, we aim at filling the gap in the knowledge about rare-earth TCCFs and synthesized a novel TCCF based on a medium-sized rare-earth metal, dysprosium (Dy) – Dy3C2@C80. Astonishingly, SC-XRD and computational analysis of Dy3C2@C80 revealed that, dramatically different from the analogous Sc3C2@C80 based on the small-sized metal Sc, Dy3C2@C80 exhibits an unusual (Dy3)8+(C2)2−@C80 formal charge distribution and features a unique three-center single-electron Dy–Dy–Dy bond, which has never been reported in molecular lanthanide chemistry.26–28

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Results and discussion

Synthesis, isolation and molecular structure of Dy₃C₂@I₈(7)-C₈₀

Dy₃C₂@C₈₀ was synthesized by a modified Kratschmer–Huffman DC arc discharge method using a mixture of Dy₂O₃ and graphite (molar ratio of Dy : Ti : C = 1 : 1 : 15) as the raw material under 200 mbar He and 10 mbar N₂ gas. Isolation of Dy₃C₂@C₈₀ was fulfilled by three-step HPLC (see ESI S1† for details). The purity of the isolated Dy₃C₂@C₈₀ was confirmed by laser desorption time-of-flight (LD-TOF) mass spectroscopic (MS) and HPLC analyses (Fig. 1a and b). The LD-TOF MS spectrum shows a dominant mass peak at m/z = 1471.5 with the isotopic distribution resembling the calculated one for Dy₃C₈₂.

The HPLC profile with a single peak at a retention time of 53.5 min confirms the high purity of the isolated Dy₃C₂@C₈₀. Based on the integrated area of the corresponding HPLC peaks, the yield of Dy₃C₂@C₈₀ relative to Dy₃N@I₈(7)-C₈₀ is estimated to be 1 : 320 (see ESI Table S1†).

The molecular structure of Dy₃C₂@C₈₀ was established by SC-XRD using co-crystallization with a recently developed decap-yrrylcorannulene (DPC) host. Mixing a CS₂ solution of fullerene with a toluene solution of DPC afforded co-cryocrystal Dy₃C₂@I₈(7)-C₈₀-2[DPC]-3[C₄H₆], and its SC-XRD analysis confirmed unambiguously that the isolated Dy₃C₂@C₈₀ is Dy₃C₂@I₈(7)-C₈₀ TCCF. The cocystal falls into the monoclinic P2₁/a space group, its asymmetric unit cell is composed of four complete Dy₃C₂@I₈-2C₈₀ fullerene molecules and four pairs of 2DPC. Fig. 1c illustrates the relative orientations of the Dy₃C₂@I₈(7)-C₈₀ and the DPC molecules in the cocystal, in which only one orientation of the fullerene cage together with the major site of the Dy₃C₂ cluster is shown for clarity. The nearest DPC-cage distances are 3.322(11) and 3.341(12) Å, respectively, which are comparable to those of the cocystals of DPC with other endohedral fullerenes. It is noteworthy that so far only two TCCFs with a homometallic M₃C₂ cluster have been reported, Sc₃C₂@I₈(7)-C₈₀ (ref. 19 and 34–38) and Lu₃C₂@I₈(35)-C₈₈, both with rare-earth metals of relatively small ionic radius (R⁹⁺ is 0.75 Å for Sc and 0.86 Å for Lu⁹⁺), and only Sc₃C₂@I₈(7)-C₈₀ has been structurally determined by SC-XRD. Therefore, Dy₃C₂@I₈(7)-C₈₀ represents the first TCCF based on a medium-sized rare-earth metal (R(Dy⁹⁺) = 0.91 Å) with the molecular structure determined unambiguously by SC-XRD.

While the I₈(7)-C₈₀ cage is fully ordered in the crystal, Dy atoms are disordered over 14 positions, whose site occupancies range from 0.051(2) to 0.501(2) (see ESI Fig. S2b†). The further structural analysis is based on the major Dy₁-Dy₃ sites with the largest occupancies of 0.482(2), 0.501(2) and 0.429(3), respectively. Dy atoms are located near the junctions of one pentagon and two hexagons as shown in Fig. 2a, with the shortest Dy-C(cage) distances of 2.202(16), 2.253(12), and 2.254(9) Å, suggesting a strong metal–cage interaction. The Dy-Dy distances are 3.381(1), 3.361(2), and 3.389(1) Å, respectively, which are all shorter than Sc-Sc distances inSc₃C₂@I₈(7)-C₈₀ (3.407(3), 3.712(3), and 3.989(3) Å)ⁱ⁹ or Dy-Dy distances in Dy₃N@I₈(7)-C₈₀ (3.476(3), 3.541(3), and 3.564(3) Å).⁴⁰

In view of a considerable disorder of heavy Dy atoms, positions of endohedral carbons are not very well defined. The best refinement results were obtained for a bat ray configuration of the Dy₃C₂ cluster shown in Fig. 2. The center of the C₂ unit is elevated above the Dy₁-Dy₂-Dy₃ plane by ~1.66 Å. The bat ray configuration was also found in the SC-XRD study of Sc₃C₂@I₈(7)-C₈₀, but the elevation of the C₂ unit above the Sc₁ plane is considerably smaller (0.44 Å). Besides, the C-C distance within the Dy₃C₂ cluster is determined to be 1.134(32) Å, which is smaller than that within Sc₃C₂ (1.29(3) Å (ref. 19)). Overall, these results reveal the strong influence of the metal size on the geometry of the encapsulated M₃C₂ cluster within the TCCF. The rare earth metals with larger size push the C₂ unit further above the M₁ plane and at the same time afford shorter M⋯M distances.

DFT computational studies of M₃C₂@I₈(7)-C₈₀ (M = Dy, Sc)

The different shapes of the Dy₃C₂ and Sc₃C₂ clusters motivated us to conduct a DFT computational study (Pirioda and Orca codes⁴¹,⁴²) of the molecular and electronic structure of
$\text{M}_3\text{C}_2\text{@C}_{80}$ ($\text{M} = \text{Dy, Sc}$) molecules. In $\text{Sc}_3\text{C}_2\text{@C}_{80}$, earlier computations and SC-XRD studies revealed two quasi-isoenergetic structures of the $\text{Sc}_3\text{C}_2$ unit.$^{19,20}$ In the lower-energy bat ray configuration, the C$_2$ unit is almost parallel to the Sc$_3$ plane and is elevated above it (Fig. 3a). The trifoliate structure has a trigonal bipyramidal shape with the Sc$_3$ triangle in the base and two C atoms in the apexes. Using these structures as starting configurations for optimization of $\text{Dy}_3\text{C}_2\text{@C}_{80}$ showed that $\text{Dy}_3\text{C}_2$ also has a minimum for a trifoliate configuration albeit with high relative energy, but the bat ray configuration changed considerably during optimization by elevating the C$_2$ unit by 1.620 Å above the Dy$_3$ plane and giving a structure quite similar to that found by SC-XRD. Analogous results were obtained in computations of $\text{Y}_3\text{C}_2\text{@C}_{80}$ (see the ESI†). Thus, the larger ionic radii of Dy$^{3+}$ and Y$^{3+}$ do not affect the trifoliate conformation of $\text{Dy}_3\text{C}_2\text{@C}_{80}$ and $\text{Sc}_3\text{C}_2\text{@C}_{80}$ (top) and $\text{Sc}_3\text{C}_2$ (bottom) clusters in $\text{M}_3\text{C}_2\text{@C}_{80}$ and their relative energies. The Dy distances of 3.440, 3.382, and 3.408 Å agree well with the SC-XRD results, while the trifoliate configuration has longer Dy−Dy distances of 3.637, 3.651, and 3.939 Å. The transition state connecting these two cluster configurations is found at a relative energy of 140 kJ mol$^{-1}$. The bat ray structure with an elevated C$_2$ unit similar to the $\text{Dy}_3\text{C}_2$ cluster is also found to be an energy minimum for $\text{Sc}_3\text{C}_2\text{@C}_{80}$, but this configuration is 65 kJ mol$^{-1}$ less stable than the trifoliate and flattened bat-ray configurations. Thus, in agreement with the experimental results, our calculations confirm that the lowest energy configuration of the Dy$_3$C$_2$ cluster has relatively short Dy⋯Dy distances and a significantly elevated position of the C$_2$ unit, which is different from the optimal geometry of the Sc$_3$C$_2$ cluster.

Confinement of the Dy$_3$C$_2$ cluster within the I$_p$-C$_{80}$ cage not only changes the molecular structure in comparison to the Sc congener, but also results in a completely new bonding situation. Previous studies showed that the electronic configuration of $\text{Sc}_3\text{C}_2\text{@C}_{80}$ is best described as $\text{(Sc}_3)^{16}(\text{C}_2)^3\text{@C}_{80}$ with the spin density mainly localized on the C$_2$ unit and Sc atoms featuring their typical Sc$^{3+}$ oxidation state.$^{20}$ Surprisingly, in the Dy analog the charge distribution changes to $\text{(Dy}_3)^{18}(\text{C}_2)^3\text{@C}_{80}$ (see ESI S† for the analysis of the canonical and Pipek–Mezey localized orbitals of the cluster). Acetylide unit C$_2$ in $\text{Dy}_3\text{C}_2\text{@C}_{80}$ has negligible spin population, while the main part of spin density is shared between three Dy ions (Fig. 3b). This spin distribution reflects the shape of the SOMO, which has Dy−Dy−Dy bonding character and corresponds to the three-center single-electron bonding of all three Dy atoms (Fig. 3c) with main contributions from the 6s, 6p, and 5d atomic orbitals of Dy. The presence of the M−M bonding in medium-size rare-earth $\text{M}_3\text{C}_2\text{@C}_{80}$ TCCFs is further corroborated by topological analysis of the electron density as described in the ESI.† Dimetallofullerenes were already shown to stabilize unique single-electron lanthanide−lanthanide bonds.$^{47-50}$ $\text{Dy}_3\text{C}_2\text{@C}_{80}$ described in this work is the first example of the new lanthanide bonding motif, i.e., three-center single-electron Dy−Dy−Dy bond. Three-center metal–metal bonding was earlier predicted in trimetallofullerenes Y$_3\text{@C}_{80}$, but in this molecule the Y⋯Y bonding MO is occupied by two electrons.$^{22,23}$ Interestingly, $\text{Dy}_3\text{C}_2\text{@C}_{80}$ with a trifoliate cluster configuration has a more traditional $\text{(Dy}_3)^{16}(\text{C}_2)^3\text{@C}_{80}$ electron distribution without metal–metal bonding (see the ESI† for further analysis). Thus, variation of the C$_2$ unit position within the M$_3$C$_2$ cluster has a strong influence on the valence state of metal atoms.

To clarify whether the shape of the $\text{Dy}_3\text{C}_2$ cluster in $\text{Dy}_3\text{C}_2\text{@C}_{80}$ results from the templating effect of the fullerene cage or has a universal character for rare-earth TCCFs, we performed optimization of the molecule with a larger fullerene cage, $\text{Y}_3\text{C}_2\text{@C}_{88}$ (Y$^{3+}$ has a comparable ionic radius (0.90 Å) to Dy$^{3+}$). Three different shapes of the cluster were used in the starting configurations: trifoliate, planar bat ray, and bat ray with an elevated C$_2$ unit like in $\text{Dy}_3\text{C}_2\text{@C}_{80}$. In all cases, optimization converged to the structure with a flattened bat ray configuration, and re-optimization of the latter with Dy instead of Y also left the shape intact (see ESI Fig. S4†). This result agrees with the earlier study of Lu$_3\text{C}_2\text{@C}_{85}$, which predicted a planar shape of the Lu$_3$C$_2$ cluster, with the C$_2$ unit lying in the triangle plane of three metals.$^{31}$ Finally, an earlier computational study of $\text{Y}_3\text{C}_2\text{@C}_{96}$ also favoured the flattened shape of the cluster.$^{24}$ Based on these results, we conclude that the unique structure of the $\text{Dy}_3\text{C}_2$ cluster supporting the Dy−Dy−Dy bonding in $\text{Dy}_3\text{C}_2\text{@C}_{80}$ is a result of the favourable

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**Fig. 3** DFT computational study on the electronic structure of $\text{M}_3\text{C}_2\text{@C}_{80}$ ($\text{M} = \text{Dy, Sc}$). (a) DFT-optimized configurations of the $\text{Dy}_3\text{C}_2$ (top) and $\text{Sc}_3\text{C}_2$ (bottom) clusters in $\text{M}_3\text{C}_2\text{@C}_{80}$ and their relative energies. Dy is depicted in green, Sc is shown in magenta, and ‘TS’ means transition state. (b) DFT- computed valence spin density distribution in $\text{Dy}_3\text{C}_2\text{@C}_{80}$. (c) Singly occupied MO (SOMO) in $\text{Dy}_3\text{C}_2\text{@C}_{80}$; (d) Kohn–Sham MO energy levels in the lowest energy configurations of $\text{Dy}_3\text{C}_2\text{@C}_{80}$ and $\text{Sc}_3\text{C}_2\text{@C}_{80}$ (red and pale blue lines denote the occupied and unoccupied components of the singly occupied MO, and dashed arrows highlight the gap between the SOMO components). Computations are performed with the PBE functional, def2-TZVPP basis set for C and Sc, and 4f-in-core ECP55MWB-II basis set of Dolg and coworkers for Dy.$^{45-46}$
matching between the fullerene cage size and metal size. When the metal is smaller like Sc or the fullerene cage has a larger inner space (say, C_{88} or C_{90}), the M_{3}C_{2} cluster tends to adopt a flattened bat ray shape, which does not lead to direct metal–metal bonding.

Electronic properties of Dy_{3}C_{2}@I_{h}(7)-C_{80}

We next characterized the electronic properties of Dy_{3}C_{2}@I_{h}(7)-C_{80} by UV-vis-NIR spectroscopy and electrochemistry (Fig. 4). The electronic absorption spectrum of yellow Dy_{3}C_{2}@I_{h}(7)-C_{80} solution in toluene looks featureless without discernible absorption peaks and is similar to the spectrum of Sc_{3}C_{2}@I_{h}(7)-C_{80}. Both compounds have their absorption onset at around 850–900 nm (Fig. 4a). Electrochemical characterization by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) gives more distinct characteristics of the compound (Fig. 4b). Dy_{3}C_{2}@I_{h}(7)-C_{80} exhibits one reversible oxidation step at +0.19 V, one reversible reduction step at E_{1/2} = −0.99 V, and one irreversible reduction with a peak potential of −1.65 V. The electrochemical gap ΔE_{EC} of Dy_{3}C_{2}@I_{h}(7)-C_{80} is thus 1.18 V. It is remarkable that the ΔE_{EC} gap of Sc_{3}C_{2}@I_{h}(7)-C_{80} is only 0.47 V, as its first oxidation and reduction potentials are found at −0.03 V and −0.50 V, respectively (see ESI Fig. S10 and Table S6†). Both TCCFs have their SOMO localized on the M_{3}C_{2} cluster, but their different electronic configurations result in a considerable difference of the frontier MO energies (Fig. 3d).

The Dy–Dy–Dy-bonding nature of the SOMO in (Dy_{3})^{9+} indicates that reduction and oxidation should substantially change the Dy–Dy bonding situation in Dy_{3}C_{2}@I_{h}(7)-C_{80}. Indeed, DFT calculations show that Dy–Dy bond lengths in the anion shorten to 3.363/3.366/3.320 Å as a result of the stronger Dy–Dy bonding provided by the population of the Dy–Dy bonding MO by the second electron in the (Dy_{3})^{7+} fragment. In the Dy_{3}C_{2}@C_{80} fragment, the Dy–Dy distances increase to 3.668/3.473/3.542 Å as the metal–metal bonding is diminished when the Dy_{3}-bonding MO is completely depopulated in [Dy_{3}]^{0}. The electrochemical gap of 1.10 V estimated by DFT with the polarized continuum model of the solvent agrees well with the experimental value, confirming the reliable interpretation of the redox process by theory.

Conclusions

In summary, for the first time we synthesized and isolated a novel TCCF based on a medium-sized rare-earth metal, dysprosium (Dy) – Dy_{3}C_{2}@I_{h}(7)-C_{80}. Its molecular structure elucidated by SC-XRD reveals Dy_{3}C_{2} with a bat ray configuration similar to Sc_{3}C_{2}@C_{80}. But the larger size of Dy pushes the acetylide unit above the Dy_{3} plane and at the same time results in shorter Dy–Dy distances than Sc–Sc distances in Sc_{3}C_{2}@C_{80}. The electronic configuration of Dy_{3}C_{2}@C_{80} is described as (Dy_{3})^{8+}(C_{3})^{2}−@C_{80}^{6−} and features a unique three-center single-electron Dy–Dy–Dy bond, which represents the first example of such bonding motif in molecular lanthanide chemistry. Furthermore, the population of the Dy–Dy–Dy-bonding SOMO can be changed electrochemically, providing access to ionic species with either strengthened or weakened Dy–Dy bonds. Our finding on the unprecedented three-center single-electron metal–metal bond offers new insight into the bonding theory of lanthanide coordination compounds.

Author contributions

S. F. Y. conceived and designed this research. F. J. and J. P. X. synthesized, isolated the samples and conducted characterizations. R. N. G. helped with sample separation and characterizations. M. Q. C. helped with X-ray crystallographic measurements. A. A. P. did the DFT calculations. X. M. X., Q. Y. Z. and S. Y. X. afforded decapryrylcorannulene. F. J., J. P. X., A. A. P. and S. F. Y. co-wrote the paper, and all the authors commented on it.

Conflicts of interest

There are no conflicts to declare.

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Fig. 4 Electronic properties of Dy_{3}C_{2}@I_{h}(7)-C_{80}. (a) UV-vis-NIR absorption spectra of Dy_{3}C_{2}@I_{h}(7)-C_{80} and Sc_{3}C_{2}@I_{h}(7)-C_{80} dissolved in toluene. Inset: the photograph of Dy_{3}C_{2}@I_{h}(7)-C_{80} solution in toluene. (b) Cyclic voltammogram (top) and differential pulse voltammogram (bottom) of Dy_{3}C_{2}@I_{h}(7)-C_{80} measured in o-DCB solution with TBAPF_{6} as the supporting electrolyte (scan rate: 100 mV s^{-1}); ferrocene Fe(Cp)_{2} was added as the internal standard. Each redox step of Dy_{3}C_{2}@C_{80} is marked with a solid dot; the asterisk denotes the oxidation peak of ferrocene. Variation of the formal charge of the Dy_{3} fragment in different potential ranges is indicated.
Notes and references

