

Structural and electrochemical studies of $\text{Sm}@D_{3h}\text{-C}_{74}$ reveal a weak metal–cage interaction and a small band gap species†

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Received 5th July 2013

Accepted 19th August 2013

DOI: 10.1039/c3nr03447j

www.rsc.org/nanoscale

A metallofullerene $\text{Sm}@D_{3h}\text{-C}_{74}$ that contains a divalent rare-earth metal has been studied structurally and electrochemically. The crystallographic analysis revealed that the endohedral Sm atom is more or less motional rather than being localized at a site where the pyracylene motif is nearby. This suggests a weaker metal–pyracylene interaction in $\text{Sm}@D_{3h}\text{-C}_{74}$ relative to that in $\text{M}^{\text{II}}@C_{74}$ ($M = \text{Group II metal}$), thus confirming the importance of the metal variety. The electrochemical studies showed a major difference between the redox properties of $\text{Sm}@D_{3h}\text{-C}_{74}$ and other Sm-fullerenes and indicated a small band gap for the title compound.

Introduction

Since the discovery of endohedral metallofullerenes (EMFs), these species have been of great interest to researchers from various disciplines due to their unique structures as well as their unprecedented physical and chemical properties.^{1–5} In recent years, some of abundantly produced EMFs have been well studied, and their potential applications in the fields of biomedicine,^{6–8} material science,⁹ and photovoltaics/photosynthesis^{10–12} have been anticipated. On the other hand, to date, studies concerning the structural and electronic features of various less-known EMFs are still going on,^{13–16} which aim to better understand the EMF family and therefore to advance this field.

Particularly, C_{74} EMFs are less-known species. Despite several previously performed studies, only very few C_{74} -EMFs have been unambiguously characterized. This might be due to their low solubility or low availability. For instance, the $\text{La}@C_{74}$ with a trivalent metal is almost insoluble in most common organic solvents. This feature is similar to that of pristine C_{74} and has been attributed to the ultra-small band gap of the pristine cage as suggested by the related theoretical calculations.¹⁷ Upon exohedral chemical modification, the resulting derivative, that is, $\text{La}@C_{74}(\text{C}_6\text{H}_3\text{Cl}_2)$,¹⁸ has a much wider band

gap and therefore much better solubility relative to $\text{La}@C_{74}$. Thus, the structural and electrochemical characterizations of $\text{La}@C_{74}(\text{C}_6\text{H}_3\text{Cl}_2)$ were well performed. On the other hand, the C_{74} species that contain a divalent metal, namely $\text{M}^{\text{II}}@C_{74}$ (where $M = \text{Ca},^{19} \text{Ba},^{20} \text{Sr},^{21} \text{Eu},^{22} \text{Sm}^{23,24}$ or $\text{Yb}^{25,26}$), are more soluble than empty C_{74} and $\text{La}@C_{74}$. Specifically, $\text{Ba}@C_{74}$ and $\text{Ca}@C_{74}$, which contain a Group II metal, have been studied by means of single-crystal X-ray diffraction or NMR spectroscopy. They were revealed to have the same cage of $D_{3h}\text{-C}_{74}$ and both endohedral Group II metals exhibited jumps between the three symmetry-equivalent pyracylene units of the cage, reflecting a featured metal–cage interaction. However, $\text{M}@C_{74}$ that contains a divalent rare-earth metal has been never characterized for clarity. Considering the different electronic features of Group II metal ions and rare-earth metal ions, we therefore guess that encapsulating a rare-earth metal instead of a Group II metal may render some difference to the endohedral structure of EMF.

In the early studies, we have detected the presence of a moderate amount of $\text{Sm}@C_{74}$ (ref. 23 and 24) and $\text{Yb}@C_{74}$ (ref. 25 and 26) in the soot produced by direct current arc discharge of M–Ni alloy/C composite rods under a He atmosphere. However, because of the lack of further characterization, these species are still little known. Herein, we investigate the title compound by employing a combined study of single-crystal X-ray diffraction, DFT calculations and electrochemistry. The following discussions will focus on its structural features as well as the metal–cage interaction and the size of band gap.

Experimental

Synthesis and isolation

The synthesis of Sm-metallofullerenes was described in earlier studies.²⁷

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3nr03447j



Single-crystal X-ray diffraction analysis

Black co-crystals of $\text{Sm}@D_{3h}\text{-C}_{74}/\text{Ni}^{\text{II}}(\text{OEP})$ were obtained by allowing a benzene solution of fullerene and a chloroform solution of $\text{Ni}^{\text{II}}(\text{OEP})$ to diffuse together. X-ray data were collected at 90 K using a diffractometer (APEX II; Bruker Analytik GmbH) equipped with a CCD collector. The multi-scan method was used for absorption correction. The structure was resolved using direct methods (SHELXS97) and refined on F^2 using full-matrix least squares using SHELXL97.²⁸ The intact cage was modeled *via* the crystallographic mirror plane in refinement. Hydrogen atoms were added geometrically and refined with a riding model.

Electrochemistry

Differential pulse voltammetry (DPV) and cyclic voltammetry (CV) were carried out in *o*-dichlorobenzene (*o*-DCB) using a BAS CW-50 instrument. A conventional three-electrode cell consisting of a platinum working electrode, a platinum counter-electrode, and a saturated calomel reference electrode (SCE) was used for both measurements. 0.05 M (*n*-Bu)₄NPF₆ was used as the supporting electrolyte. All potentials were recorded against a SCE reference electrode and corrected against Fc/Fc^+ . DPV and CV were measured at a scan rate of 20 and 100 mV s^{-1} , respectively.

Computational method

All calculations were carried out using the Gaussian 09 program package.²⁹ Geometry optimizations and Mulliken population analysis were performed using the density functional theory with the recently introduced M06-2X functional,³⁰ 3-21G basis set³¹ for the C atom, and the SDD basis set³² (with the SDD effective core potential) for Ni and Sm atoms (the M06-2X/3-21G~SDD level). The orbital energies were also calculated at a higher level (the M06-2X/6-31G~SDD level).

Results and discussion

The purity and the composition of the $\text{Sm}@C_{74}$ sample were confirmed by HPLC and MALDI-TOF mass, respectively (see Fig. S1†). The absorption spectrum of $\text{Sm}@C_{74}$ is almost identical to that reported previously,²³ as well as those of analogous species $\text{M}@C_{74}$ ($\text{M} = \text{Eu}, \text{Sr}, \text{Ba}$ and Ca)^{19–26} (See Fig. S2†). The absolute structure of $\text{Sm}@D_{3h}\text{-C}_{74}$ was identified *via* a single-crystal X-ray diffraction (XRD) study. Co-crystals of $\text{Sm}@D_{3h}\text{-C}_{74}/[\text{Ni}^{\text{II}}(\text{OEP})]$ suitable for X-ray analysis were obtained by slow diffusion of a benzene solution of EMF into a chloroform solution of $[\text{Ni}^{\text{II}}(\text{OEP})]$. The molecular structure was resolved and refined in a monoclinic space group C_2 (no. 5).³³ Fig. 1 shows the X-ray structure of $\text{Sm}@D_{3h}\text{-C}_{74}$ together with an adjacent $[\text{Ni}^{\text{II}}(\text{OEP})]$ moiety. Note that the $D_{3h}\text{-C}_{74}$ cage has been crystallographically identified in two orientations with fractional occupancies of 0.67 and 0.33. Only the major cage is depicted in Fig. 1. The porphyrin moiety is approaching a flat region of the $D_{3h}\text{-C}_{74}$ cage with the shortest nickel-to-cage carbon distance ranging from 2.606 to 2.867 Å, indicating their strong π - π stacking interaction.

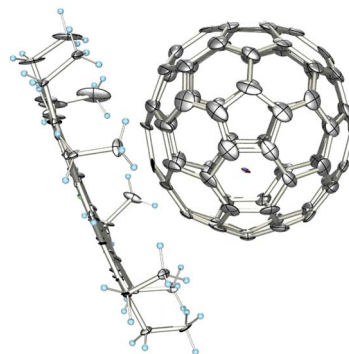


Fig. 1 Ortep drawing of $\text{Sm}@D_{3h}\text{-C}_{74}\text{-Ni}^{\text{II}}(\text{OEP})$ with 25% thermal ellipsoids, showing the intermolecular interaction. The major Sm site with fractional occupancy of 0.311 and the major cage position with fractional occupancy of 0.673 are depicted. The solvent molecules are omitted for clarity.

Inside the cage of $D_{3h}\text{-C}_{74}$, the Sm atom is highly disordered and several metal-sites have been refined with fractional occupancies ranging from 0.311 to 0.024, reflecting a motional behavior of the endohedral Sm atom. This feature is unlike that of previously reported $\text{Ba}@C_{74}$, in which only two different Ba positions were identified, corresponding well to the disordered cage, which is aligned in two orientations. Summarizing all the crystallographically characterized Sm-fullerenes that have different cage sizes and structures, it is noteworthy that such a dynamic endohedral feature is common for Sm-fullerenes,^{34,35} indicating their weaker metal-cage interactions relative to those of other mono-metallofullerenes.^{3,36} Considering the occupancies of cage and metal, we initially assigned the major Sm-site (*i.e.*, Sm01) to the major cage, as shown in Fig. 1, while another Sm-site with the second highest occupancy (*i.e.*, Sm02) was assigned to the minor cage, as shown in Fig. S3.† Such assignments give rise to a pair of identical conformers of $\text{Sm}@C_{74}$, in which the metal is localized off-center, being close to one of the three symmetry-equivalent pyracylene units at the horizontal mirror plane with a distance of 2.417 Å between the Sm and the central 6 : 6 bond of that pyracylene motif. Such a metal-cage alignment is very similar to that of $\text{Ba}@C_{74}$, confirming the previous assumption that there is a significant interaction between the pyracylene motif and the endohedral divalent metal. Nevertheless, this Sm-pyracylene motif interaction might be weaker than that in $\text{Ba}@C_{74}$, as reflected by the fact that the Sm atom can jump to other sites where the pyracylene unit is far from.

In addition, a series of computational studies were performed at the levels of M06-2X/3-21G~SDD and M06-2X/6-31G*~SDD to investigate the electronic features of $\text{Sm}@C_{74}$. As shown in Fig. 2, the DFT-optimized pristine $\text{Sm}@D_{3h}\text{-C}_{74}$ is in good agreement with the X-ray structure of $\text{Sm}@D_{3h}\text{-C}_{74}$. Particularly, the optimized Sm site is approaching the central 6 : 6 bond of a pyracylene unit with a distance of 2.533 Å, very close to that detected in the X-ray structure. Note that there are three equivalent pyracylene units on the cage of $D_{3h}\text{-C}_{74}$. However, if considering the influence of the adjacent



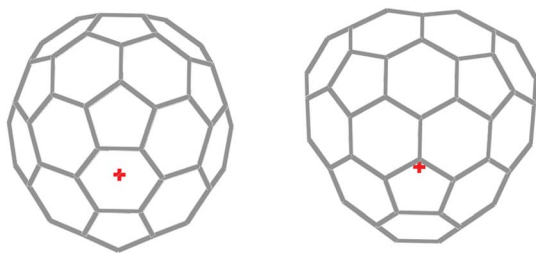


Fig. 2 Two views of DFT-optimized pristine $\text{Sm}@D_{3h}\text{-C}_{74}$ at M06-2X/6-31G*~SDD level.

$\text{Ni}^{\text{II}}(\text{OEP})$ moiety, these pyracylene units are chemically non-equivalent. Therefore, we further optimize the unit of $\text{Sm}@D_{3h}\text{-C}_{74}/[\text{Ni}^{\text{II}}(\text{OEP})]$ to investigate the most preferred Sm-site relative to the adjacent $\text{Ni}^{\text{II}}(\text{OEP})$ moiety. Two DFT-optimized configurations of $\text{Sm}@D_{3h}\text{-C}_{74}/[\text{Ni}^{\text{II}}(\text{OEP})]$ are shown in Fig. 3 and S4† in different views. Particularly, in each configuration, the Sm site is close to one of the pyracylene units but differently aligned relative to the adjacent $\text{Ni}^{\text{II}}(\text{OEP})$ moiety. Calculations further revealed that the configuration shown in the left panel, which is fully consistent with the X-ray structure of $\text{Sm}@D_{3h}\text{-C}_{74}/[\text{Ni}^{\text{II}}(\text{OEP})]$ (see Fig. 1), is 0.079 kcal mol⁻¹ more stable than that in the right panel. Although such a difference between the relative energies of these two configurations is very small, it is detectable at the present DFT level, suggesting a weak but salient influence of the porphyrin moiety on the location of endohedral metal.

HOMO and LUMO distributions of $\text{Sm}@D_{3h}\text{-C}_{74}$ were calculated at a M06-2X/3-21G~SDD level, as shown in Fig. 4. Specifically, the HOMO is uniformly delocalized on the $D_{3h}\text{-C}_{74}$ framework, while the LUMO is mostly localized on the cage area where the Sm is close to. The calculated Mulliken charge on the endohedral Sm atom is 2.04, indicative of a formal two-electron transfer from the metal to the cage. Thus, an ionic model of $\text{Sm}^{2+}@D_{3h}\text{-C}_{74}^{2-}$ has been verified, which well describes the electronic feature of $\text{Sm}@D_{3h}\text{-C}_{74}$. Also, because of the off-center position of the endohedral divalent metal, the metal-donated charges are mainly

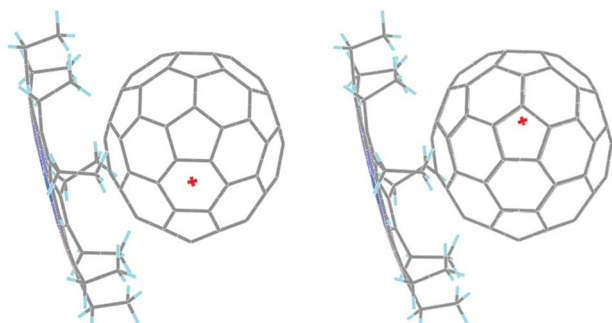


Fig. 3 Two DFT-optimized units of $\text{Sm}@D_{3h}\text{-C}_{74}/[\text{Ni}^{\text{II}}(\text{OEP})]$ at M06-2X/3-21G~SDD level.

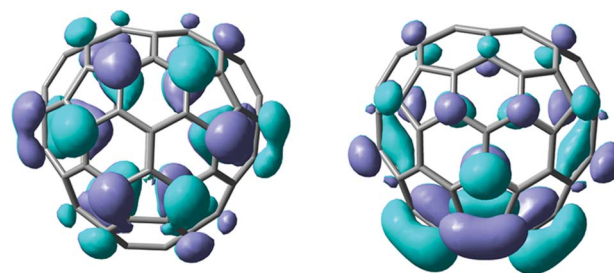


Fig. 4 HOMO (left) and LUMO (right) distributions of $\text{Sm}@D_{3h}\text{-C}_{74}$ DFT-calculated at M06-2X/6-31G*~SDD level.

delocalized on the pyracylene motif and the nearby area, as suggested by the Mulliken population analysis. In particular, the carbons on the central 6 : 6 bond of that pyracylene motif are much more negatively charged than others (see Fig. S3 and Table S1†), indicating their higher nucleophilic affinity.

Furthermore, a comparison study between $D_{3h}\text{-C}_{74}$, $(D_{3h}\text{-C}_{74})^{2-}$ and $\text{Sm}@D_{3h}\text{-C}_{74}$ was performed to estimate the role of the endohedral Sm atom in stabilizing the otherwise unstable $D_{3h}\text{-C}_{74}$ cage. The DFT-calculated HOMO/LUMO energy levels of $D_{3h}\text{-C}_{74}$, $(D_{3h}\text{-C}_{74})^{2-}$ and $\text{Sm}@D_{3h}\text{-C}_{74}$ are summarized in Fig. 5. The ultra-small band gap of $D_{3h}\text{-C}_{74}$ (*i.e.*, 1.65 eV) and the high HOMO/LUMO energy levels of $(D_{3h}\text{-C}_{74})^{2-}$ shall account for their low stabilities. In contrast, $\text{Sm}@D_{3h}\text{-C}_{74}$ shows a band gap (*i.e.*, 2.76 eV) larger than that of $D_{3h}\text{-C}_{74}$ but smaller than that of $(D_{3h}\text{-C}_{74})^{2-}$. Besides, the lower-lying HOMO/LUMO of $\text{Sm}@D_{3h}\text{-C}_{74}$ as compared with those of $(D_{3h}\text{-C}_{74})^{2-}$ is in line with its higher stability relative to the other. Thus, our computational studies show that the encapsulation of a divalent rare-earth metal can definitely improve the stability of a $D_{3h}\text{-C}_{74}$ cage by rationalizing the size of band gap as well as the HOMO/LUMO energy levels.

The electrochemical properties of $\text{Sm}@D_{3h}\text{-C}_{74}$ were investigated by means of cyclic voltammetry (CV) and differential pulse voltammetry (DPV). As shown in Fig. 6, both CV and DPV profiles suggest four reversible one-electron reductive steps on

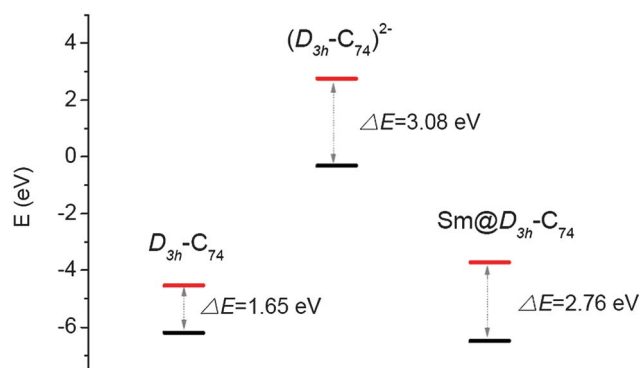


Fig. 5 MO diagram for $D_{3h}\text{-C}_{74}$, $(D_{3h}\text{-C}_{74})^{2-}$ and $\text{Sm}@D_{3h}\text{-C}_{74}$. At M06-2X/3-21G~SDD level (their HOMO–LUMO gaps at M06-2X/6-31G*~SDD level are 1.72, 3.01 and 2.74 eV, respectively).



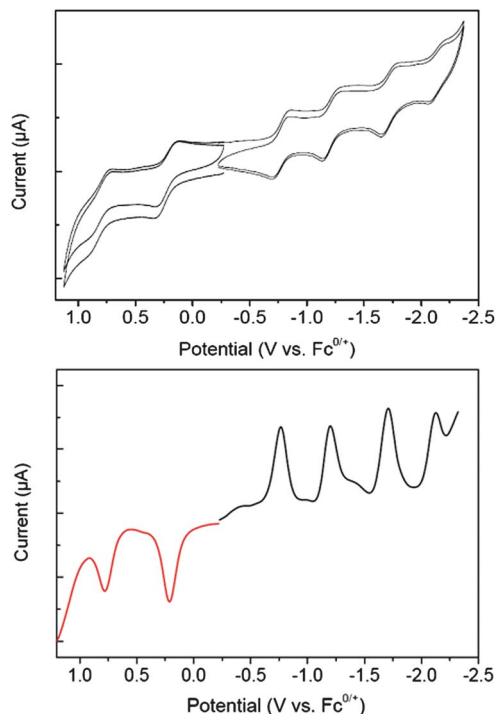


Fig. 6 Cyclic voltammograms (top) and differential pulse voltammogram (bottom) of Sm@D_{3h}-C₇₄ in o-DCB (0.05 M (n-Bu)₄NPF₆; scan rate: 100 mV s⁻¹ and 20 mV s⁻¹ for CV and DPV, respectively).

the cathodic side and two reversible one-electron oxidative steps on the anodic side. All the redox potentials obtained from CV are summarized in Table 1 and compared with those of other Sm-fullerenes such as Sm@C_{2v}(3)-C₈₀³⁴ and Sm@C₂(5)-C₈₂.³⁵ It is noteworthy that the first oxidation potential of Sm@D_{3h}-C₇₄ is 220–230 mV lower than those of middle-sized Sm-fullerenes, indicating a much stronger electron-donating ability. On the other hand, only a minor difference is found among the first reduction potentials of these Sm-fullerenes. Thus, the electrochemical potential gap of Sm@D_{3h}-C₇₄ is 0.97 eV, substantially smaller than those of other Sm-fullerenes (i.e., 1.28 eV for Sm@C_{2v}(3)-C₈₀ and 1.26 eV for Sm@C₂(5)-C₈₂), indicative of a smaller band gap relative to the others. This has been reflected by the fact that Sm@D_{3h}-C₇₄ shows lower solubility in common organic solvents. As a result, the resolution of the ¹³C NMR spectrum of Sm@D_{3h}-C₇₄ was too low to be acceptable even after long-time scans because of the insufficient solubility of Sm@D_{3h}-C₇₄ in CS₂.

Table 1 Redox potentials (V vs. Fc^{0/+})^a of Sm@D_{3h}-C₇₄ and other Sm-fullerenes

	oxE ₂	oxE ₁	redE ₁	redE ₂	redE ₃	redE ₄
Sm@D _{3h} -C ₇₄	0.76 ^b	0.20 ^b	-0.77 ^b	-1.21 ^b	-1.72 ^b	-2.14 ^b
Sm@C _{2v} (3)-C ₈₀ ^d	0.85 ^c	0.43 ^b	-0.85 ^b	-1.23 ^b	-1.76 ^b	-2.07 ^c
Sm@C ₂ (5)-C ₈₂ ^e		0.42 ^c	-0.84 ^b	-1.01 ^b	-1.51 ^b	-1.90 ^b

^a Half-cell potentials unless otherwise noted. ^b Reversible process.

^c DPV value. ^d ref. 34. ^e ref. 35.

Conclusions

In conclusion, we have studied a divalent metallofullerene Sm@D_{3h}-C₇₄ structurally and electrochemically. Specifically, single-crystal X-ray diffraction analysis revealed that the endohedral Sm atom mainly binds to one pyracylene motif on the cage, which has been confirmed by computational studies. Nevertheless, the Sm-cage interaction is weaker than that in Ba@C₇₄, as reflected by the fact that the Sm atom more or less jumps to an other site far from the pyracylene motif. Thus, this study has confirmed that the variety of endohedral metal indeed imposes a salient influence on the metal-cage interaction and therefore affects the endohedral behavior. In addition, electrochemical studies demonstrated a smaller electrochemical potential gap of Sm@D_{3h}-C₇₄ relative to those of other Sm-fullerenes, indicative of a small band gap species.

Acknowledgements

This work is supported in part by National Natural Science Foundation of China (21171013, 21241004), the Ministry of Science and Technology of China (no. 2013CB933402, no. 2011CB932601), NSF of Jiangsu province of China (no. BK2012611), and the Ministry of Education of the Czech Republic (MSM0021620857), including the access to the Meta-Centrum computing facilities (LM2010005), and the Czech Science Foundation/GACR (P208/10/0179). Also, we are grateful to Prof. T. Akasaka and Dr M. Suzuki at University of Tsukuba for their support in XRD measurement.

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