

Sm@C_{2v}(19138)-C₇₆: A Non-IPR Cage Stabilized by a Divalent Metal Ion

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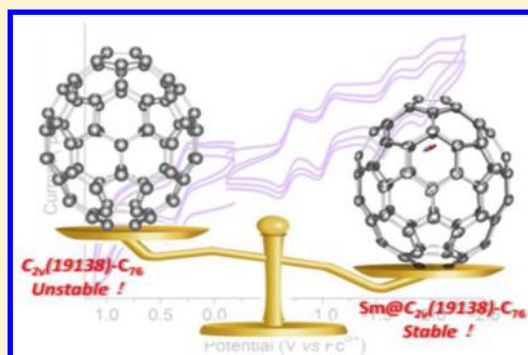
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Supporting Information

ABSTRACT: Although a non-IPR fullerene cage is common for endohedral cluster fullerenes, it is very rare for conventional endofullerenes M@C_{2n}, probably because of the minimum geometry fit effect of the endohedral single metal ion. In this work, we report on a new non-IPR endofullerene Sm@C_{2v}(19138)-C₇₆, including its structural and electrochemical features. A combined study of single-crystal X-ray diffraction and DFT calculations not only elucidates the non-IPR cage structure of C_{2v}(19138)-C₇₆ but also suggests that the endohedral Sm²⁺ ion prefers to reside along the C₂ cage axis and close to the fused pentagon unit in the cage framework, indicative of a significant metal–cage interaction, which alone can stabilize the non-IPR cage. Furthermore, electrochemical studies reveal the fully reversible redox behaviors and small electrochemical gap of Sm@C_{2v}(19138)-C₇₆, which are comparable to those of IPR species Sm@D_{3h}-C₇₄.



INTRODUCTION

Fullerene is a spherical carbon cage C_{2n} composed of 12 pentagons and a number of hexagons (i.e., (2n - 20)/2), which increases with the cage size.¹ The most typical fullerene C₆₀ was discovered as early as 1985,² and the followed studies unambiguously revealed its I_h symmetry as well as the significant stability in air.³ Noteworthy is that among the numerous C₆₀ isomers only the I_h isomer can be obtained under ambient conditions. Structural characterization revealed that in the framework of I_h-C₆₀ all 12 pentagons are isolated by hexagons. Later, such a topological feature has been approved to be common for all stable fullerenes and widely accepted as the isolated pentagon rule (IPR) for determining the stabilities of fullerene isomers.⁴ In contrast, the non-IPR fullerenes that violate the IPR rule were proposed to have reduced stabilities relative to those of IPR isomers due to the enhanced local strain on the fused pentagons.⁵ It was long believed that the non-IPR fullerenes had the least stabilities and could not survive in air.

However, in recent years, a number of non-IPR fullerenes have been emerging in the forms of fullerene derivatives (i.e., C_{2n}Cl_x, C₆₄H₄),⁶ endohedrals,⁷ or combinations.⁸ For instance, in 2000 the first non-IPR fullerene Sc₃N@D₃(6140)-C₆₈ was unambiguously characterized,^{7a} demonstrating the improved

stability of the non-IPR cage in the presence of endohedral metallic cluster. In fact, a huge number of non-IPR fullerenes are found to be available in topology, which challenges researchers to search for those that can survive in air. To date, more than 20 non-IPR endohedral metallofullerenes (EMFs) have been isolated and characterized by means of NMR, single-crystal XRD, or a combination.⁹ In most cases, the non-IPR cage is stabilized by a metallic cluster (i.e., M₃N, M₂, Sc₂S; M = group 2 and 3 elements and most lanthanides). Echegoyen et al. recently proposed that not only the electron transfer between the cluster and the cage but also the geometry fit effect of the endohedral cluster contributes to the stabilization of the non-IPR cage.¹⁰ However, as for conventional EMF M@C_{2n}, a non-IPR cage is very rare, probably because of the minimum geometry fit effect of the endohedral single metal ion. In particular, a non-IPR isomer La@C₇₂ was identified in the form of La@C₂(10612)-C₇₂(C₆H₃Cl₂).⁸ It appears that both the endohedral La³⁺ ion and the exohedral derivatization contribute to the cage stabilization. Besides, other non-IPR M@C_{2n}, including Ca@C₂(10612)-C₇₂¹¹ and M@C₇₆

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($C_{2v}(19138)$ and $C_1(17459)$, $M = \text{Yb, Ca, Sr, Ba}$),¹² were obtained only at the theoretical level. It is still unconfirmed whether a non-IPR cage can be stabilized by a single metal ion alone, and further experimental studies are very necessary. Herein, we report a non-IPR isomer of $\text{Sm}@C_{76}$, including structural characterization and electrochemical surveys. These studies experimentally demonstrate for the first time that the non-IPR cage can be stabilized by an endohedral divalent metal ion.

RESULTS AND DISCUSSION

The major isomer of $\text{Sm}@C_{76}$ (i.e., $\text{Sm}@C_{76}(\text{I})$) was prepared and isolated according to the previously reported procedure.¹³ The sample purity was estimated to be higher than 95% based on chromatographic analysis (see Figure S1, Supporting Information). The composition of $\text{Sm}C_{76}$ was confirmed by MALDI-TOF mass (see Figure S2, Supporting Information). The UV-vis-NIR absorption spectrum of the sample is shown in Figure 1, which is consistent with the previous report.¹³

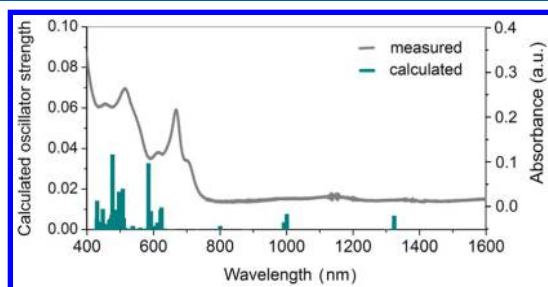


Figure 1. Measured and calculated UV-vis-NIR absorption spectra of $\text{Sm}@C_{2v}(19138)-C_{76}$.

Besides, the minor isomer of $\text{Sm}@C_{76}$ (i.e., $\text{Sm}@C_{76}(\text{II})$) was also observed, as suggested by the literature.¹³ However, this isomer was not subjected to further characterization because of its lower yield.

A cocrystal of $\text{Sm}@C_{76}/[\text{Ni}^{\text{II}}(\text{OEP})]$ suitable for X-ray analysis was obtained by slow diffusion of a benzene solution of EMF into a CHCl_3 solution of $[\text{Ni}^{\text{II}}(\text{OEP})]$. The molecular structure was resolved and refined in a monoclinic space group C_2 . In the cocrystal, both the fullerene cage and the endohedral metal were found to be disordered. Specifically, two cage orientations have been identified with a ratio of 0.671:0.329. Figure 2 shows the major cage orientation, the major samarium site ($\text{Sm}1$, 0.376 occupancy), along with an adjacent $[\text{Ni}^{\text{II}}(\text{OEP})]$ moiety. The X-ray structure clearly shows a non-IPR cage of $C_{2v}(19138)-C_{76}$ that is one of 19 151 possible non-IPR isomers for C_{76} . As can be seen clearly in Figure S3, Supporting Information, the C_2 axes of the two disordered cage orientations are similarly aligned relative to the porphyrin plane. Generally, the adjacent $[\text{Ni}^{\text{II}}(\text{OEP})]$ moiety is approaching the flat region of the $C_{2v}(19138)-C_{76}$ cage, giving rise to the largest π - π stacking between fullerene and the porphyrin moiety. The distances between the nickel ion in $[\text{Ni}^{\text{II}}(\text{OEP})]$ and the closest carbon ion in the major and minor cage orientations are 2.776 and 2.88 Å, respectively, similar to the values of 2.812 Å found in $\text{Sm}@C_{2v}(3)-C_{80}/[\text{Ni}^{\text{II}}(\text{OEP})]$ ¹⁴ and 2.606 Å in $\text{Sm}@C_{3h}-C_{74}/[\text{Ni}^{\text{II}}(\text{OEP})]$,¹⁵ suggesting similar interactions between Sm -fullerene and $[\text{Ni}^{\text{II}}(\text{OEP})]$.

Inside the fullerene cage, apart from the major Sm sites, four minor Sm sites with fractional occupancies ranging from 0.25 to 0.03 were detected. Figure 3 shows the major cage with all

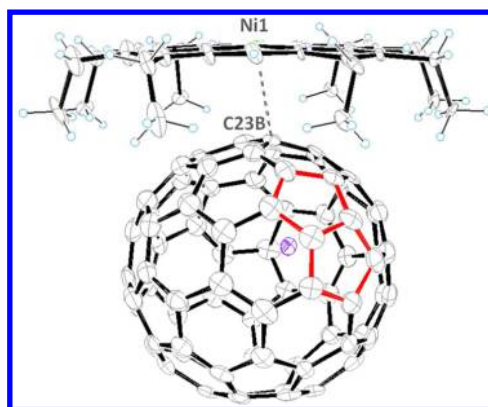


Figure 2. Ortep drawing of $\text{Sm}@C_{2v}(19138)-C_{76}\cdot[\text{Ni}^{\text{II}}(\text{OEP})]$ with 25% thermal ellipsoids, showing the relationship between the fullerene cage and $[\text{Ni}^{\text{II}}(\text{OEP})]$. Only the major cage orientation with 0.671 occupancy and the major Sm site ($\text{Sm}1$ with 0.376 occupancy) are shown, and the fused pentagons in the cage framework are highlighted in red. For clarity, the solvent molecules, minor cage orientation, and minor metal sites are omitted.

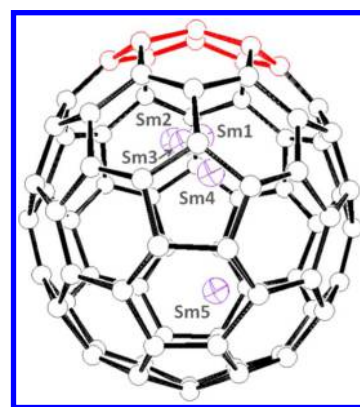


Figure 3. Drawing of $\text{Sm}@C_{2v}(19138)-C_{76}$, showing all of the samarium sites in the major cage orientation with 0.671 occupancy. Fused pentagons in the cage framework are highlighted by red. Occupancies of identified samarium sites are as follows: $\text{Sm}1$, 0.376(6); $\text{Sm}2$, 0.253(3); $\text{Sm}3$, 0.223(6); $\text{Sm}4$, 0.114(4); and $\text{Sm}5$, 0.034(3).

identified metal sites. Considering the major occupancy of the $\text{Sm}1$ site (0.376 occupancy), it is reasonable to assign the $\text{Sm}1$ site to the major cage orientation (0.671 occupancy). A closer look reveals that the $\text{Sm}1$ site resides slightly off the C_2 axis but is very close to the fused pentagons in the framework of $C_{2v}(19138)-C_{76}$. The shortest Sm - C distances in the major cage were determined in the range of 2.559–2.573 Å (see Table S1, Supporting Information). As for the minor metal sites $\text{Sm}2$ and $\text{Sm}3$ (0.253 and 0.223 occupancy), it is hard to determine which of the two sites corresponds to the minor cage orientation (0.325 occupancy). Nevertheless, either the $\text{Sm}2$ or the $\text{Sm}3$ site was found to be close to the fused pentagons in the framework of the minor cage. The shortest distances between cage carbons and $\text{Sm}2$ or $\text{Sm}3$ are similar to those between the major cage and $\text{Sm}1$ (see Table S1, Supporting Information). Therefore, the crystallographic data suggests that the samarium ion prefers to reside under the fused pentagons of $C_{2v}(19138)-C_{76}$, and the shortest Sm - C distances are comparable to those in $\text{Sm}@C_2(5)-C_{82}$ ¹⁶ but shorter than the normal Sm - C bonding length (i.e., 2.8–3.0 Å) in some typical Sm complexes,¹⁷ indicating the significant coordination

interaction between the Sm^{2+} ion and the fused pentagons of $\text{C}_{2v}(19138)\text{-C}_{76}$. It has been found that such a feature is common for most non-IPR endohedral fullerenes.

To further shed light onto the structural and electronic feature of $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$, DFT calculations were performed at the M06-2X/3-21G-SDD level¹⁸ using the Gaussian 09 package.¹⁹ The DFT-optimized $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$ structure is shown in Figure S4, Supporting Information. Inside the cage, the Sm^{2+} ion is residing along the C_2 axis and close to the fused pentagons, which is consistent with the XRD result. The shortest Sm–C distances in the optimized $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$ was revealed as 2.685 Å, slightly longer than that determined by X-ray analysis. Moreover, natural population analysis revealed that the Mulliken charge on the endohedral Sm atom is +2.037 e. This result may be interpreted as samarium donating two electrons to the fullerene cage, suggesting a formal electronic structure of $\text{Sm}^{2+}@\text{C}_{76}^{2-}$. The Mulliken charges on cage carbons are plotted in Figure S4, Supporting Information. High charge densities are found for the fused pentagons and nearby carbons, indicative of strong ionic interactions between the endohedral metal and the fused pentagons.

Furthermore, the calculated molecular orbital diagrams are presented in Figure 4. As compared with those of empty

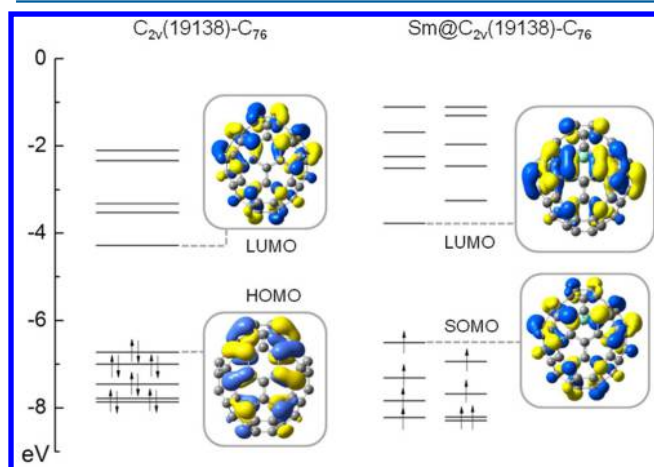


Figure 4. Molecular orbital diagrams for $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$ and $\text{C}_{2v}(19138)\text{-C}_{76}$. The empty fullerene $\text{C}_{2v}(19138)\text{-C}_{76}$ was calculated with the geometry that it has in the endohedral fullerene. (Note: As an unrestricted M06-2X description is used for $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$, just the alpha orbitals are shown. As for the beta orbitals, they are not shown for simplicity; their energy levels are not exactly the same as the alpha levels; however, they are close to them.) Insets show the SOMO (HOMO) and LUMO distributions of $\text{C}_{2v}(19138)\text{-C}_{76}$ and $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$ at the DFT-M06-2X/3-21G~SDD level.

fullerene $\text{C}_{2v}(19138)\text{-C}_{76}$, the frontier orbitals (SOMO and LUMO) of $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$ are slightly shifted to higher energy levels, giving rise to a wider band gap of 2.74 eV relative to that of $\text{C}_{2v}(19138)\text{-C}_{76}$ (2.45 eV). Calculations also reveal that both the SOMO and the LUMO of $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$ are mostly the cage orbitals with negligible contribution from the endohedral Sm^{2+} ion, which resemble those of most monometallofullerenes and indicate that the redox reactions take place mainly on the cage. In addition, it is also noteworthy that the SOMO distribution of $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$ is almost identical with the LUMO distribution of empty $\text{C}_{2v}(19138)\text{-C}_{76}$. Such a similarity might be accounted for by the proposal

that the SOMO formation of $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$ is a direct result of filling the LUMO of $\text{C}_{2v}(19138)\text{-C}_{76}$ by electron transfer from the endohedral Sm^{2+} ion. This proposal also facilitates understanding why there is no localization on the metal in the computed SOMO of $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$.

The electronic spectrum of $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$ was calculated by means of time-dependent (TD) DFT at the B3LYP/3-21G~SDD level. As shown in Figure 1, the calculated absorption bands are presented mainly in the regions of 455–536 and 570–640 nm, composed of several sharp peaks. Such spectral features roughly resemble those of the measured spectrum of $\text{Sm}@C_{76}(\text{I})$ as well as the calculated results of $\text{Yb}@C_{2v}(19138)\text{-C}_{76}$,^{12a} despite the minor wavelength difference (i.e., ~100 nm). Considering these similarities, it is reasonable to conclude that $\text{Sm}@C_{76}(\text{I})$ possesses a cage of $\text{C}_{2v}(19138)\text{-C}_{76}$, which is consistent with our X-ray crystallographic result.

To further verify the superior availability of $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$ relative to other isomers (i.e., $C_1(17459)$ and $T_d(19151)$ isomers), relative energies of these isomers were calculated, though not at the same levels owing to convergence difficulties. In particular, $\text{C}_{2v}(19138)\text{-C}_{76}$, $C_1(17459)\text{-C}_{76}$, and $T_d(19151)\text{-C}_{76}$ have been previously proposed to be the best hosts for Yb^{2+} and $(\text{Lu}_2)^{4+}$.^{12a,20} Our calculation results reveal that the IPR species $\text{Sm}@T_d(19151)\text{-C}_{76}$ is located 11.61 kcal mol⁻¹ above $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$ at the M06-2X/3-21G~SDD level. The non-IPR isomer $\text{Sm}@C_1(17459)\text{-C}_{76}$ comes 1.54 kcal mol⁻¹ higher than $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$ at the B3LYP/6-311+G*~SDD level. Also, the SOMO–LUMO gap of the $\text{C}_{2v}(19138)$ isomer was determined as 2.72 eV at the M06-2X/3-21G~SDD level, larger than 2.17 eV for the $T_d(19151)$ isomer. At the B3LYP/6-311+G*~SDD level, though, the band gap of the $\text{C}_{2v}(19138)$ isomer (i.e., 1.39 eV) is lower than 1.65 eV for $C_1(17459)$. Overall, theoretical calculations predict the higher stability of $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$ relative to others, which is consistent with the higher production yield of $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$. Note that these calculated relative stabilities of $\text{Sm}@C_{76}$ isomers are very close to those reported for $\text{Yb}@C_{76}$ isomers,^{12a} suggesting the similar role of divalent metal ions in cage formation. The current studies also infer that the non-IPR $\text{M}@C_{2n}$ can be more stable than the IPR analogue due to the strong metal–cage interactions.

Moreover, to better understand the superior stability of $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$, a comparison study was performed between the non-IPR cage of $\text{C}_{2v}(19138)\text{-C}_{76}$ and the well-known IPR cage of $D_{3h}\text{-C}_{74}$,¹⁴ because both are of similar size and can be stabilized by a Sm^{2+} ion in the form of $\text{Sm}@C_{2n}$ ($n = 37$ or 38). The DFT-optimized $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$ and $\text{Sm}@D_{3h}\text{-C}_{74}$ are presented in Figure 5. It is clearly seen that the two cages show very close geometrical similarity despite their different symmetries. The different cage motif is found at the pole of either cage, where a [5,5] bond is observed for $\text{C}_{2v}(19138)\text{-C}_{76}$ but not for $D_{3h}\text{-C}_{74}$. Thus, as illustrated in Scheme 1, the cage of $D_{3h}\text{-C}_{74}$ can be converted to $\text{C}_{2v}(19138)\text{-C}_{76}$ by inserting a C_2 unit along the symmetric plane and the C_2 axis of the C_{74} cage, suggesting an unexpected structural correlation between the IPR and the non-IPR cages. It is also rational to propose that the similar cage structures of $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$ and $\text{Sm}@D_{3h}\text{-C}_{74}$ are highly relevant to their superior stabilities relative to other isomers.

The electrochemical properties of $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$ were investigated by means of cyclic voltammogram (CV) and differential pulse voltammogram (DPV) studies. CV and DPV

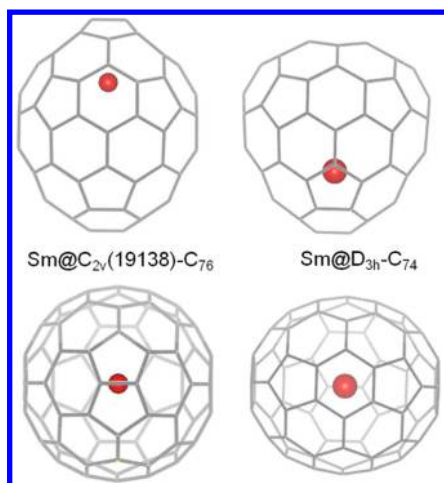
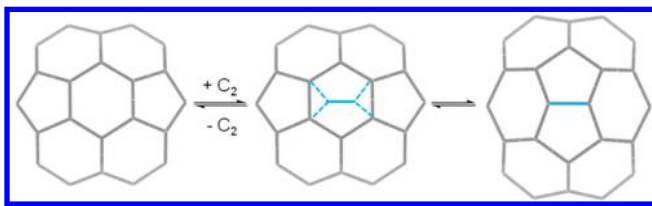


Figure 5. DFT-optimized structures of $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$ and $\text{Sm}@D_{3h}\text{-C}_{74}$: side views (up) and top views (down).

Scheme 1. Cage Motif Conversion via a C_2 Insertion (the C_2 unit is colored in blue)



were recorded in *o*-dichlorobenzene (*o*-DCB) containing 0.05 M tetra(*n*-butyl)ammonium hexafluorophosphate ($(n\text{-Bu})_4\text{NPF}_6$) as supporting electrolyte. All obtained redox potentials are summarized in Table 1 and compared with those of previously reported Sm–fullerenes. As shown in the CV profile (see Figure 6), $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$ exhibits four reversible one-electron reduction steps in the cathodic region but two reversible oxidation steps in the anodic region. In this respect, $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$ is very similar to most conventional endofullerenes and empty fullerenes, which usually show fully reversible redox behaviors.²¹ Nevertheless, $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$ and other Sm–fullerenes show a major difference between their redox potentials. Specifically, the first oxidation potential of $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$ is 120 mV higher than that of $\text{Sm}@D_{3h}\text{-C}_{74}$ but ca. 100 mV lower than those of middle-sized Sm–fullerenes (i.e., $\text{Sm}@C_{3v}\text{-C}_{80}$ and $\text{Sm}@C_2(5)\text{-C}_{82}$),^{14,15,16a} indicative of a moderate electron-donating ability. The first reduction potential of $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$ is 80–160 mV lower than those of previously reported Sm–fullerenes, suggesting a strong electron-accepting ability. All redox steps are also visible in the DPV profile (see Figure S5, Supporting Information), and their potential values are fully consistent with those obtained from CV. The electrochemical gap of $\text{Sm}@$

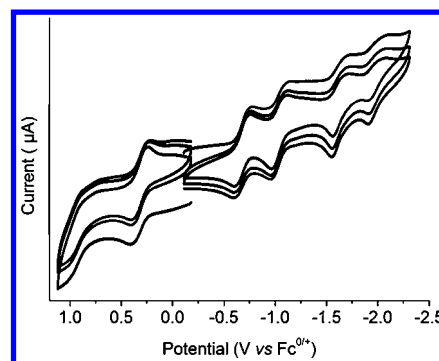


Figure 6. Cyclic voltammogram of $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$ in *o*-dichlorobenzene containing 0.05 M $(n\text{-Bu})_4\text{NPF}_6$ (scan rate 100 mV s^{-1}).

$C_{2v}(19138)\text{-C}_{76}$ is determined as 1.01 eV, similar to that of $\text{Sm}@D_{3h}\text{-C}_{74}$ (0.97 eV)¹⁴ but substantially smaller than those of middle-sized Sm–fullerenes (i.e., 1.28 eV for $\text{Sm}@C_{2v}(3)\text{-C}_{80}$ and 1.26 eV for $\text{Sm}@C_2(5)\text{-C}_{82}$).^{15,16} Therefore, the band gap of divalent $\text{M}@C_{2n}$ might be mainly dependent on the cage size and cage structure rather than the IPR or non-IPR cage configuration.

CONCLUSIONS

In summary, a new non-IPR fullerene $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$ has been structurally characterized by a combined study of single-crystal XRD and DFT calculations. It was revealed that the endohedral Sm^{2+} ion prefers to reside along the C_2 cage axis and close to the fused pentagons in the framework of $C_{2v}(19138)\text{-C}_{76}$, suggesting significant metal–cage interaction, which alone can stabilize this non-IPR cage. Further investigations also suggested an unexpected structural correlation between the IPR and the non-IPR cages (i.e., $D_{3h}\text{-C}_{74}$ and $C_{2v}(19138)\text{-C}_{76}$) as well as the larger band gap of $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$ relative to its IPR isomer (i.e., $\text{Sm}@T_d(19151)\text{-C}_{76}$). In addition, electrochemical investigations demonstrated the fully reversible redox behaviors of $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$, which are similar to those of most IPR fullerenes.

EXPERIMENTAL SECTION

Synthesis and Isolation. The synthesis of Sm–metallofullerenes was described in earlier studies.¹³ Briefly, Sm–metallofullerenes were produced using a modified arc-discharge method. Specifically, the anode graphite rod was filled with SmNi_2 /graphite powder (1:10 atomic ratio), while a pure graphite rod was employed as the cathode. The arc discharge was carried out at 70 A with an electrode gap of ca. 1 cm under 400 Torr helium static atmosphere. Fullerene species were extracted from soot using *o*-xylene at high temperature under nitrogen atmosphere. The pure sample of $\text{Sm}@C_{76}(\text{I})$ was isolated and purified via a multistage HPLC procedure.

Table 1. Redox Potentials^a (V vs $\text{Fc}^{0/+}$) of $\text{Sm}@C_{2v}(19138)\text{-C}_{76}$ and Other Sm–Fullerenes

	$\text{ox}E_2$	$\text{ox}E_1$	$\text{red}E_1$	$\text{red}E_2$	$\text{red}E_3$	$\text{red}E_4$	EC gap
$\text{Sm}@D_{3h}\text{-C}_{74}^c$	0.76	0.20	−0.77	−1.21	−1.72	−2.14	0.97
$\text{Sm}@C_{2v}(19138)\text{-C}_{76}$	0.95	0.32	−0.69	−1.04	−1.62	−1.97	1.01
$\text{Sm}@C_{2v}(3)\text{-C}_{80}^d$	0.85 ^b	0.43	−0.85	−1.23	−1.76	−2.07 ^b	1.28
$\text{Sm}@C_2(5)\text{-C}_{82}^e$		0.42 ^b	−0.84	−1.01	−1.51	−1.90	1.26

^aHalf-wave potentials unless otherwise stated. ^bDPV values. ^cData in ref 14. ^dData in ref 15. ^eData in ref 16a.

Single-Crystal X-ray Diffraction Analysis. Black cocrystals of $\text{Sm}@C_{76}/[\text{Ni}^{\text{II}}(\text{OEP})]$ were obtained by allowing the benzene solution of fullerene and the 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. Multiscan 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 SHELXL97.²² Hydrogen atoms were added geometrically and refined with a riding model.

A cocrystal of $\text{Sm}@C_{2v}(19138)-C_{76}\cdot[\text{Ni}^{\text{II}}(\text{OEP})]\cdot 0.86C_6H_6\cdot 0.14CHCl_3$ contains another severely disordered lattice of C_6H_6 and $CHCl_3$ molecules that could not be modeled properly. Therefore, the program SQUEEZE, a part of the PLATON package of crystallographic software,²³ was used to calculate the solvent disorder area and remove its contribution from the intensity data.

Crystal data for $\text{Sm}@C_{2v}(19138)-C_{76}\cdot[\text{Ni}^{\text{II}}(\text{OEP})]\cdot 0.86C_6H_6\cdot 0.14CHCl_3$: C, 114.75; H, 46.75; Cl, 2; N, 4; Ni; Sm. $M_r = 1761.27$, $0.28 \times 0.15 \times 0.12$ mm, monoclinic, C_2 (No.5), $a = 25.339(11)$ Å, $b = 14.944(6)$ Å, $c = 19.147(8)$ Å, $\beta = 93.844(5)^\circ$, $V = 7234(5)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.617$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 1.203$ mm⁻¹, $\theta = 4.11\text{--}29.570^\circ$, $T = 90$ K, $R_1 = 0.1326$, $wR_2 = 0.3076$ for all data; $R_1 = 0.1201$, $wR_2 = 0.2990$ for 16 996 reflections ($I > 2.0\sigma(I)$) with 1456 parameters. Goodness of fit indicator 1.034. Maximum residual electron density 1.181 e Å⁻³. More detailed crystal data are presented in Table S2, Supporting Information.

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. (*n*-Bu)₄NPF₆ (0.05 M) 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.¹⁹ Geometry optimizations and Mulliken population analysis were performed using density functional theory with the recently introduced M06-2X functional or B3LYP functional,^{18a} 3-21G basis set^{18b} for the C atom, and the SDD basis set^{18c} (with the SDD effective core potential) for the Sm atom (the M06-2X/3-21G~SDD level). The orbital energies were also calculated at a higher level (the M06-2X/6-311G*~SDD level).

■ ASSOCIATED CONTENT

Supporting Information

HPLC, mass, and DPV profile of $\text{Sm}@C_{2v}(19138)-C_{76}$; coordinates and Mulliken charges of the DFT-optimized $\text{Sm}@C_{2v}(19138)-C_{76}$; X-ray crystallographic file in CIF format for $\text{Sm}@C_{2v}(19138)-C_{76}\cdot[\text{Ni}^{\text{II}}(\text{OEP})]\cdot 0.86C_6H_6\cdot 0.14CHCl_3$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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