Facile Synthesis of an Extensive Family of Sc₂O@C_{2n} (n = 35–47) and Chemical Insight into the Smallest Member of Sc₂O@C_2(7892)–C_{70}

Meirong Zhang,†,⊥ Yajuan Hao,† Xiaohong Li,‡ Lai Feng,*,† Ting Yang,‡ Yingbo Wan,‡ Ning Chen,*,‡ Zdeněk Slanina,*§ Filip Uhlík,‖ and Hailin Cong,*†

†College of Physics, Optoelectronics and Energy & Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou 215006, China
‡College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215163, China
§Life Science Center of Tsukuba Advanced Research Alliance, University of Tsukuba, Tsukuba 305-8577, Japan
‖Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University in Prague, Albertov 6, 128 43 Praha 2, Czech Republic
⊥Lab for New Fiber Materials and Modern Textile-Growing Base for State Key Laboratory, College of Chemical and Environmental Engineering, Qingdao University, Qingdao 266071, China

Supporting Information

ABSTRACT: An extensive family of oxide cluster fullerenes (OCFs) Sc₂O@C_{2n} (n = 35–47) has been facilely produced for the first time by introducing CO₂ as the oxygen source. Among this family, Sc₂O@C_{70} was identified as the smallest OCF and therefore isolated and characterized by mass spectrometry, ⁴⁵Sc nuclear magnetic resonance, UV–vis–near-infrared absorption spectroscopy, cyclic voltammetry, and density functional theory calculations. The combined experimental and computational studies reveal a non-isolated pentagon rule isomer Sc₂O@C_{72}(7892)–C_{70} with reversible oxidative behavior and lower bandgap relative to that of Sc₂S@C_{72}(7892)–C_{70}, demonstrating a typical example of unexplored OCF and underlining its cluster-dependent electronic properties.

1. INTRODUCTION

Since the discovery of fullerenes, their three-dimensional structures and unique properties have attracted great interests.¹,² In particular, inside fullerene cage there is a nanometer-sized space that is big enough to accommodate a cluster of heteroatoms or even a small molecule. On the basis of this knowledge, in the past decade, many efforts have been devoted to the science of endohedral fullerenes.³–⁹ It has been well demonstrated that a variety of metal, nonmetal atoms, or even small molecules can be encapsulated into a fullerene cage using physical or chemical methods, resulting in stable endohedrals such as H₂@C₆₀,¹⁰,¹¹ N₂@C₆₀,¹²–¹⁴ Gd₃N@C₂₅,¹⁵ and H₂O@C₆₀.¹⁶ These endohedrals are potentially useful in the fields of molecular electronics, hydrogen storage, and medical and material sciences.¹⁷–²³

Particularly, it has been approved that most group 2–3 elements and lanthanides can be trapped inside a fullerene cage in the form of Mₓ (x = 1–3)²⁴–²⁷ or a cluster of metal carbide MₓCₓ (x = 2–4),²⁸–³² metal nitride MₓNₓ³³–³⁵ metal sulfide MₓSₓ³⁶–³⁸ metal cyanide MₓNC (x = 1,3),³⁹–⁴¹ or even metal oxide Sc₂O/Sc₄O₂/Sc₄O₃⁴²–⁴⁴ giving rise to the formation of endohedral metallofullerenes (EMFs). For bulk preparations of EMFs, the Krätschmer–Huffman generator has been widely used since 1991,⁴⁵ in which a graphite anode containing metal oxide or metallic alloy is evaporated in an electric arc under a low-pressure helium atmosphere. Noteworthy is that, as for the production of nitride, cyanide, or sulfide cluster fullerenes, additional nitrogen and sulfur sources are very essential, which may be provided by either reactive gases (i.e., N₂, NH₃, SO₂) or solid compounds containing nitrogen or sulfur element (i.e., guanidium thiocyanate).⁴⁶ As demonstrated by previous experiments, the gaseous additives usually give rise to better productions than the solid additives probably due to their significant stabilities and homogeneities.

Compared to those well-studied cluster fullerenes, oxide cluster fullerenes (OCFs) are relatively less-explored. Up to now, only a few OCFs including Sc₂O₂₋ₓ@C₆₀ and Sc₂O@C₆₂ have been reported.⁴² According to the authors, the introduction of a small amount of air might provide the oxygen source for the OCF synthesis. However, such method resulted in, besides empty fullerenes, mainly nitride cluster fullerenes along with limited varieties of OCFs.⁴³ Herein, we...
demonstrate that an extensive family of scandium OCFs with cage size ranging from C_{70} to C_{84} can be synthesized in macroscopic quantities by introducing CO_{2} as the oxygen source. In addition, Sc_{2}O@C_{78}, the smallest OCF identified by means of mass spectroscopy, has been isolated and characterized for the first time.

2. EXPERIMENTAL SECTION

2.1. Synthesis and Isolation. A new family of scandium OCFs Sc_{2}O@C_{2n} was synthesized in a typical Krätschmer–Huffman arc reactor. The details are briefly described as follows. The graphite anode was filled with a mixture of Sc_{2}O_{3} and graphite powder with a molar ratio of 1:1 and was annealed at 1000 °C for 10 h under Ar atmosphere before use. The DC-arc discharging was carried out under 3 × 10^{4} pa He/CO_{2} atmosphere (the ratio of He/CO_{2} is 9/1 in volume) and current of 100 A. After DC-arc discharging, the generated soot was collected under ambient conditions, and the mixture was Soxhlet extracted by chlorobenzene for 18 h. The resulting dark brown solution was evaporated to remove chlorobenzene, immediately redissolved in toluene, and subsequently passed through a 0.45 μm Teflon filter for HPLC separation. The separation of Sc_{2}O@C_{2n} was performed by a multistep HPLC procedure using columns including Buckyprep M column (25 mm × 250 mm, Nacalai Tesque, Japan), Buckyprep column (10 mm × 250 mm, Nacalai Tesque, Japan), and SPBB column (10 mm × 250 mm, Nacalai Tesque, Japan).

The mass characterization was done by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry using the Biflex III spectrometer (Bruker, Germany) with positive- and negative-ion modes, respectively. UV–vis–near-infrared (NIR) spectrum of the purified OCF sample was measured in toluene solution with an UV 3600 spectrometer (Shimadzu, Japan) using a quartz cell of 1 mm layer thickness and 1 nm resolution. The ^{45}Sc nuclear magnetic resonance (NMR) spectroscopic study was performed at 145 MHz with an Agilent 600 MHz NMR spectrometer at 25 °C in CS_{2} solution with D_{2}O as the lock and a 0.4 M Sc(NO_{3})_{3} solution in D_{2}O as the reference.

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were carried out in o-dichlorobenzene (o-DCB) using a CHI-660E 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)_{3}NPF_{6} (0.05 M) was used as the supporting electrolyte. All potentials were recorded against a SCE reference electrode and corrected against FeC/Fe^+. CV and DPV were measured at a scan rate of 100 and 20 mV s^−1, respectively.

2.2. Computational Method. All calculations were carried out using the Gaussian 09 program package. Geometry optimizations and population analysis were performed using the density functional theory with the recently introduced M06-2X functional, 3-21G basis set for the C and O atoms, and the SDD basis set (with the SDD effective core potential) for Sc atom (the M06-2X/3-21G~SDD level). The orbital energies and distributions were calculated at a higher level (the M06-2X/6-311G*~SDD level). Time dependant (TD) DFT calculations were performed at the B3LYP/6-311G~SDD level.

3. RESULTS AND DISCUSSION

A series of scandium OCFs Sc_{2}O@C_{2n} (n = 35–47) were synthesized in a typical Krätschmer–Huffman arc reactor under a He/CO_{2} atmosphere. The as-prepared soot was Soxhlet extracted with chlorobenzene. As shown in Figure 1, which demonstrates the high-performance liquid chromatography (HPLC) profile of the extracted fullerene mixture, the empty fullerenes C_{60} and C_{70} are seen as the major products and eluted before 13 min on a Buckyprep-M column. The fractions with retention time longer than 13 min were collected and analyzed by mass spectroscopy. As shown in Figure 1, a series of scandium OCFs Sc_{2}O@C_{2n} with cage size ranging from C_{70} to C_{84} can be identified in the mass spectrum, most of which have never been reported before. Besides, typical nitride cluster fullerenes and carbide cluster fullerenes, for example, Sc_{3}N@C_{80} and Sc_{2}C_{2}@C_{82}, are also detectable in the mass spectrum. Nevertheless, their contents are found to be lower than that of the most abundantly yielded OCF Sc_{2}O@C_{78}, according to a combined analysis of HPLC and mass spectrum, indicating a selective synthesis of OCFs under our employed conditions. In contrast, in a control experiment, where a He/air atmosphere was utilized, besides empty fullerenes, mainly nitride cluster fullerenes were obtained, while only a trace of Sc_{2}O@C_{82} was detected (see Figure S1, Supporting Information), which agrees well with the previous report. Thus, this comparative study suggests that CO_{2} is a better oxygen source than air for the
production of OCFs. Moreover, in another control experiment, where pure He atmosphere was employed, the most abundantly produced metallofullerene was found to be Sc\textsubscript{2}C\textsubscript{2}@C\textsubscript{82} rather than Sc\textsubscript{2}O@C\textsubscript{82} (see Figure S2, Supporting Information). It appears that the introduction of CO\textsubscript{2} causes a significant increase of the relative yields of OCFs and suppresses the generation of carbide cluster fullerenes, which are otherwise abundantly yielded under pure helium atmosphere.

As the mass spectrum (Figure 1) shows, in this OCF family, the smallest fullerene that can be identified by far is Sc\textsubscript{2}O@C\textsubscript{70}. A combined analysis of HPLC and mass spectroscopy suggests that the Sc\textsubscript{2}O@C\textsubscript{70} fraction overlaps with those of C\textsubscript{76} and C\textsubscript{78} and is eluted with a retention time of around 15 min on a Buckyprep-M column (see Figure S3, Supporting Information). Sc\textsubscript{2}O@C\textsubscript{70} was further separated using a Buckyprep column and a SPBB column, which resulted in the isolation of a pure sample of Sc\textsubscript{2}O@C\textsubscript{70} (see Figures S4–S5, Supporting Information). Compared to other OCFs, the yield of Sc\textsubscript{2}O@C\textsubscript{70} is relatively lower. By consuming 90 packed graphite rods, only ca. 2 mg of Sc\textsubscript{2}O@C\textsubscript{70} was obtained after HPLC purification.

The composition of Sc\textsubscript{2}O@C\textsubscript{70} was confirmed by MALDI-TOF mass spectroscopy. As shown in Figure 2, the purified sample of Sc\textsubscript{2}O@C\textsubscript{70} shows a predominant signal at 946 m/z, and its observed isotopic distribution agrees very well with the calculated values. Moreover, the \(^{45}\text{Sc}\) NMR spectrum of Sc\textsubscript{2}O@C\textsubscript{70} was measured at room temperature. As shown in Figure 2, a \(^{45}\text{Sc}\) NMR signal at 32.4 ppm is clearly seen, suggesting that the two Sc ions are either equivalent or undergo fast rotation inside the cage. However, because of the small amount of the sample, the \(^{13}\text{C}\) NMR data is not available.

The purified sample of Sc\textsubscript{2}O@C\textsubscript{70} shows a brown color in toluene solution and its UV–vis–NIR spectrum exhibits (see Figure 3) a broad and strong absorption centered around 1188 nm along with other relatively weaker absorptions at 393, 459, 497, 706, and 1015 nm. Such absorption feature is different from that of previously reported Sc\textsubscript{2}N@C\textsubscript{82} (7854), C\textsubscript{70} higher stability (DFT) based population analysis on the optimized Sc\textsubscript{2}O@C\textsubscript{70} isomers reveals that there is a formal transfer of four electrons between the cluster and the cage, and the electronic structure can be described as (Sc\textsubscript{2}O\textsuperscript{4−}@C\textsubscript{70}).\(^{46}\) (ii) A tetraionic cluster may possibly fit well in a cage satisfying isolated pentagon rule (IPR) or a non-IPR cage with two or less adjacent pentagon pairs (APPs).\(^{8}\) (iii) According to the previous work, the tetraanions of these IPR or non-IPR C\textsubscript{70} cages show lower relative energies with respect to the others.\(^{48}\) Therefore, our computations involving only the OCFs corresponding to the lowest-energy tetraionic cages shall be reasonable and more extensive computations are not very necessary.\(^{48}\) The relative energies of these optimized isomeric Sc\textsubscript{2}O@C\textsubscript{70} structures are listed in Table 1. Among them, Sc\textsubscript{2}O@C\textsubscript{70} (7892)–C\textsubscript{70} is found to be the lowest-energy isomer at the M06-2X/3-21G–SDD level of theory,\(^{50–52}\) at least 20 kcal mol\(^{-1}\) lower than the others, despite the fact that the tetraion of the empty IPR cage D\textsubscript{1h} (8149)–C\textsubscript{70} exhibits the lowest energy. This situation is very similar to the case of Sc\textsubscript{2}S@C\textsubscript{70} in which Sc\textsubscript{2}S@C\textsubscript{70} (7892)–C\textsubscript{70} is 18 kcal mol\(^{-1}\) more stable than others at the BP86/TZP level.\(^{48}\) Thus, it appears that the encapsulation of either a Sc\textsubscript{2}O cluster or a Sc\textsubscript{2}S cluster, which are valence isoelectronic (i.e., (Sc\textsubscript{2}X\textsuperscript{4+}, X = O or S), renders the non-IPR cage of C\textsubscript{70} higher stability with respect to the other isomers.

In particular, the Sc–O–Sc angle in the optimized Sc\textsubscript{2}O@C\textsubscript{70} (7892)–C\textsubscript{70} was measured at 139.23°, much larger than that for Sc\textsubscript{2}S@C\textsubscript{70} (98.96°), which was optimized at the same computational level (see Figure 4). Despite the uncertainty of the DFT Optimized structures, noteworthy is that such a Sc–O–Sc (X = O or S) angle difference (Δθ ≈ 40°) is very comparable to that found between Sc\textsubscript{2}S@C\textsubscript{6}(6)–C\textsubscript{62} and

![Figure 2. MALDI-TOF mass spectrum of the purified sample Sc\textsubscript{2}O@C\textsubscript{70} in a positive-ion reflection mode. The insets show the observed and calculated isotopic distributions of Sc\textsubscript{2}O@C\textsubscript{70}.](image)
Sc$_2$O@C$_6$(6)–C$_{32}$, which have a Sc–S–Sc angle of 113.8° and a Sc–O–Sc angle of 156.6°, respectively, according to the X-ray analysis.\textsuperscript{38,45} It appears that in the small or middle-sized fullerene cage the Sc$_2$O cluster is more linearly aligned, as compared to the Sc$_2$S cluster, probably due to the shorter Sc–O distance (i.e., 1.896 Å for Sc$_2$O@C$_7$(7892)–C$_{70}$ with respect to the Sc–S distance (i.e., 2.365 Å for Sc$_2$O@C$_7$(7892)–C$_{70}$). Moreover, the Mulliken atomic charges on Sc and O in the Sc$_2$O cluster are calculated to be +2.082 e and +0.539 e, respectively, while the values for Sc$_2$S cluster are +1.805 e for Sc and +0.026 e for S. Such Mulliken charge difference can be explained by the higher electronegativity of O relative to that of S (i.e., 3.610 for O and 2.589 for S)\textsuperscript{53} and suggests different electronic configuration of these enclosed clusters. Nevertheless, in the optimized Sc$_2$O@C$_7$(7892)–C$_{70}$ each scandium ion of the cluster is equally approaching a pentagonal motif, which resembles that of Sc$_2$S@C$_7$(7892)–C$_{70}$ suggesting their similar cluster–cage interactions. Such a cluster–cage contact has also been found in most cluster fullerenes with non-IPR cages, for example, Sc$_2$N@D$_6$(6140)–C$_6$\textsuperscript{54} Gd$_3$N@C$_{(39663)}$–C$_{82}$\textsuperscript{55} and Sc$_2$S@C$_{(10528)}$–C$_{72}$\textsuperscript{56} which results in localized electron transfer between the cluster and the pentagonal motif. Therefore, despite some geometric and electronic differences, Sc$_2$O and Sc$_2$S clusters apparently play similar roles on the selection of cage isomer, along with the electronic stabilization resulting from the similar cluster–cage interactions.

The orbital energy levels as well as the orbital distributions of Sc$_2$O@C$_7$(7892)–C$_{70}$ have been further calculated at the M06-2X/3-21G~SDD level. As shown in Figure 5, both the HOMO and LUMO are mainly contributed by the cage orbitals with small but salient contributions from the metal cluster. Substantial orbital overlap between the cage and cluster can be clearly identified, indicating both the covalent and ionic interactions between the cluster and fullerene cage. Thus, the computational results suggest two equivalent Sc ions in a rotationally hindered Sc$_2$O cluster for Sc$_2$O@C$_7$(7892)–C$_{70}$ which agrees well with the experimentally observed single $^{45}$Sc NMR signal. However, the HOMO energy level of Sc$_2$O@C$_7$(7892)–C$_{70}$ is calculated as −6.07 eV at the M06-2X/6-311G~SDD level, 0.07 eV higher than that of Sc$_2$S@C$_7$(7892)–C$_{70}$ (i.e., −6.14 eV calculated at the same level), while the LUMO is −2.99 eV, 0.07 eV lower than that of Sc$_2$S@C$_7$(7892)–C$_{70}$ (i.e., −2.92 eV calculated at the same level). Thus, the bandgap of Sc$_2$O@C$_7$(7892)–C$_{70}$ is determined as 3.08 eV, 0.14 eV smaller than that of Sc$_2$S@C$_7$(7892)–C$_{70}$ (i.e., 3.22 eV). These results agree very well with their spectral comparison, which indicates a smaller bandgap of Sc$_2$O@C$_7$(7892)–C$_{70}$ compared to that of Sc$_2$S@C$_7$(7892)–C$_{70}$. It appears that, despite the identical cage symmetry as well as the similar cluster–cage interactions, slightly varying the endohedral composition from Sc$_2$S to Sc$_2$O indeed gives rise to a fine modulation on the MO energy levels as well as on the bandgaps of cluster fullerenes.

The electronic spectra of Sc$_2$O@C$_7$(7892)–C$_{70}$ and Sc$_2$S@C$_7$(7892)–C$_{70}$ were also computed using time-dependent (TD)-DFT at the B3LYP/6-311G~SDD level. Their most intense lowest-energy excitations are listed in Table 2. Particularly, the lowest excitation energy of Sc$_2$O@C$_7$(7892)–C$_{70}$ (corresponding to the HOMO–LUMO transition) is calculated as 1.237 eV or a λ of 1002 nm, while a λ of 920 nm is calculated for Sc$_2$S@C$_7$(7892)–C$_{70}$. Compared to the experimental values (i.e., 1188 nm for Sc$_2$O@C$_7$(7892)–C$_{70}$ and 1102 nm for Sc$_2$S@C$_7$(7892)–C$_{70}$), all the computed excitation energies are apparently overestimated to a similar extent at our computational level. Nevertheless, the computed energy difference (i.e., 0.11 eV) between the singlet-excited Sc$_2$O@C$_7$(7892)–C$_{70}$ and Sc$_2$S@C$_7$(7892)–C$_{70}$ can compare reasonably well with the experimentally estimated difference (i.e., 0.08 eV). These results further underline the influence of internal clusters Sc$_2$X (X = O or S) on the MO levels of cluster fullerenes and suggest that the Sc$_2$O@C$_{70}$ and the previously reported Sc$_2$S@C$_{70}$ share the same cage of C$_7$(7892)–C$_{70}$.

The electrochemical properties of Sc$_2$O@C$_{70}$ were studied by means of cyclic voltammogram (CV) and differential pulse
voltammogram (DPV), as shown in Figure 6. CV and DPV were recorded in o-dichlorobenzene (o-DCB) and tetra-(n-butyl)-ammonium hexafluorophosphate (n-Bu4NPF6; 0.05 M) respectively. Such an oxidative behavior is different from that of Sc2S@C70, which exhibits a reversible first oxidation at 0.14 V and an irreversible second oxidation at 0.65 V. In conclusion, by introducing CO2 as the oxygen source, facile production of an extensive OCF family of Sc2O@Cn (n = 35−47) has been demonstrated for the first time. Compared with the control experiments, in which the productions were performed under a pure He or He/air atmosphere, utilizing the He/CO2 atmosphere apparently gives rise to a more selective generation of OCFs. Moreover, the Sc2O@C70 identified by far as the smallest OCF has been found to be available only by using the present method. The experimental and computational studies reveal that the Sc2O can be constrained inside a small non-IPR cage of C2(7892)−C70, giving rise to a novel OCF with fully reversible oxidative behavior and lower bandgap relative to that of Sc2S@C2(7892)−C70. To this end, these studies might open a new way to explore an extensive OCF family and underline the unique electronic and electrochemical properties of cluster fullerenes, which are internal-cluster-dependent.

**ASSOCIATED CONTENT**

**Supporting Information**
Detailed experimental data including HPLC profiles and mass spectra; coordination of the optimized Sc2O@C2(7892)−C70 and Sc2S@C2(7892)−C70 complete references. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

E-mail: fenglai@suda.edu.cn.
E-mail: chenning@suda.edu.cn.
E-mail: fromzdenek@yahoo.com.
E-mail: hailincong@yahoo.com.

Table 3. Redox Potentials (V vs Fc0/+b) of Sc2O@C2(7892)−C70 and Sc2S@C2(7892)−C70

<table>
<thead>
<tr>
<th></th>
<th>Sc2O@C2(7892)−C70</th>
<th>Sc2S@C2(7892)−C70</th>
</tr>
</thead>
<tbody>
<tr>
<td>E (eV)</td>
<td>λ (nm)</td>
<td>fσ</td>
</tr>
<tr>
<td>1.2371</td>
<td>1002.20</td>
<td>0.0120</td>
</tr>
<tr>
<td>1.4018</td>
<td>884.49</td>
<td>0.0063</td>
</tr>
<tr>
<td>1.9866</td>
<td>624.09</td>
<td>0.0086</td>
</tr>
<tr>
<td>2.191</td>
<td>585.05</td>
<td>0.0101</td>
</tr>
</tbody>
</table>

aHalf-wave potentials. bPeak potentials. cDPV values. dX = C2(7892)−C70

**Table 2. TD-DFT Calculations for the Most Intense Lowest-Energy Excitations in the Absorption Spectra of Sc2O@C2(7892)−C70 and Sc2S@C2(7892)−C70**

<table>
<thead>
<tr>
<th>Excitation</th>
<th>eV</th>
<th>λ (nm)</th>
<th>fσ</th>
<th>Leading Configurations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.2191</td>
<td>789.2</td>
<td>0.0101</td>
<td>HOMO → LUMO + 1</td>
</tr>
<tr>
<td>2</td>
<td>1.9866</td>
<td>624.09</td>
<td>0.0086</td>
<td>HOMO → LUMO + 3</td>
</tr>
</tbody>
</table>

"TD B3LYP/6-311G*~SDD calculations; only excitations with fσ (oscillator strength) > 0.001 are listed.

**Figure 6.** Cyclic voltammograms (up) and differential pulse voltammogram (down) of Sc2O@C2(7892)−C70 in o-dichlorobenzene (o-DCB) and tetra-(n-butyl)-ammonium hexafluorophosphate (n-Bu4NPF6; 0.05 M) scan rate 100 and 20 mV s−1 for CV and DPV, respectively.

**Table 3. TD-DFT Calculations for the Most Intense Lowest-Energy Excitations in the Absorption Spectra of Sc2O@C2(7892)−C70 and Sc2S@C2(7892)−C70**

<table>
<thead>
<tr>
<th>Excitation</th>
<th>eV</th>
<th>λ (nm)</th>
<th>fσ</th>
<th>Leading Configurations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.2191</td>
<td>789.2</td>
<td>0.0101</td>
<td>HOMO → LUMO + 1</td>
</tr>
<tr>
<td>2</td>
<td>1.9866</td>
<td>624.09</td>
<td>0.0086</td>
<td>HOMO → LUMO + 3</td>
</tr>
</tbody>
</table>

"TD B3LYP/6-311G*~SDD calculations; only excitations with fσ (oscillator strength) > 0.001 are listed.
Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is the supported in part by the NSFC (21241004, 51372158, 21305098, and 51302178), SRFPD (20123201120014), the NSF of Jiangsu Province (BK2012611 and BK20130295), Jiangsu Specialy Appointed Professor Program (SR10800113), the Project for Jiangsu Scientific and Technological Innovation Team (2013), and the Czech Science Foundation/GACR (P208/10/1724).

REFERENCES


dx.doi.org/10.1021/jp509975w | J. Phys. Chem. C 2014, 118, 28883–28889


(47) Yang, S.; Popov, A. A.; Dunsch, L. Violating the Isolated Pentagon Rule (IPR): the Endohedral Non-IPR C70 Cage of Sc4N@Cs2. Angew. Chem., Int. Ed. 2007, 46, 1256–1259.


