Large mixed metal nitride clusters encapsulated in a small cage: the confinement of the C_{68}-based clusterfullerenes†

Shangfeng Yang,*[ab] Alexey A. Popov[ac] and Lothar Dunsch*[a]

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Three novel C_{68}-based mixed metal nitride clusterfullerenes, which comprise of a small non-IPR C_{68} cage encapsulating large nitride clusters including $DySc_2N$, $LuSc_2N$, and Lu_2ScN, have been synthesized and isolated, resulting in overpassing the confinement of the C_{68} cage.

Endohedral fullerenes as fullerenes with atoms, ions, or clusters trapped in their inner space exhibit a variety of cage size spaning from C_{66} to C_{100} with C_2 stepping.[1–6] Among them, those with cages smaller than C_{70} have been limited to $Sc_2@C_{66}$,[3] $Sc_3N@C_{68}$,[7] $Sc_2C_2@C_{68}$,[8] and $Sc_3N@C_{70}$.[9] One of the common features of these endohedral fullerenes with small cages is that their cages violate the isolated pentagon rule (IPR), resulting in the so-called non-IPR cages.[1,6–9] Recently the non-IPR endohedral fullerene family has been revealed to be largely expanded within the family of the metal nitride clusterfullerenes (NCFs).[1,9] This includes $Sc_3N@C_{68}$,[7,10] $Sc_3N@C_{70}$,[9] $M_3N@C_{84}$ (M = Tb, Tm, Gd),[11] $Dy_3N@C_{78}$ (II),[12] $Tm_3N@C_{78}$,[12] and $DySc_2N@C_{76}$.[13] In particular, as the first member of this line the C_{68} cage (D_3: 6140) within $Sc_3N@C_{68}$ appears quite unique not only due to its non-IPR nature as well as the interesting electrochemical behavior,[1,7,10,14] but also because this is the smallest cage isolated for NCFs so far. This is understood by the confinement of the limited inner space within such a small cage so that no homogeneous M_3N cluster larger than Sc_3N can be encapsulated. In this communication we precisely determine the maximum cluster size by which the confinement of the C_{68} cage has been overpassed and report the first synthesis and characterization of C_{68}-based mixed NCFs encapsulating different large nitride clusters ($DySc_2N$, $LuSc_2N$, and Lu_2ScN).

The synthesis of $DySc_2N@C_{68}$ (**1**), $LuSc_2N@C_{68}$ (**2**), and $Lu_2ScN@C_{68}$ (**3**) by the "reactive gas atmosphere" method[15] and isolation by two-step HPLC as well as their identification by mass spectroscopic (MS) analysis are summarized in detail in the Electronic Supplementary Information (ESI) S1.† Briefly, a mixture of Dy_2O_3 (or Lu_2O_3) and Sc_2O_3 and graphite powder with a molar ratio of Dy : Sc : C (or Lu : Sc : C) = 1 : 1 : 15 was subjected for DC-arc discharging by a modified Krätschmer-Huffman DC-arc discharging method with the addition of NH_3 (20 mbar).[1,9,10,13,15] The generated soot was pre-extracted by acetone and further Soxhlet-extracted by CS_2 for 20 h. The isolation of **1–3** from the as-prepared fullerene mixture was accomplished by a two-step HPLC (see ESI-S1†). The overall yield of the C_{68}-based NCFs among the fullerene mixture (including empty fullerenes C_{60} and C_{70}) is *ca.* 1.9% and the relative yield of **1** : $Sc_3N@C_{68}$ and **3** : **2** : $Sc_3N@C_{68}$ is estimated to be 1 : 2 and 1 : 6 : 12, respectively (see ESI-S1†). Fig. 1 presents the typical HPLC chromatograms of a $Lu_xSc_{3-x}N@C_{2n}$ fullerene extract (a) and the second-step HPLC isolation of C_{68}-based products (fraction A) by recycling HPLC (b) as well as their identification by MS (c). It has been shown recently that the formation of the mixed metal NCFs is an efficient way to boost the yield of NCFs, and the use of the mixed lanthanide–scandium protocol and variation of the lanthanide metal within this protocol enable the fine-tuning of the cluster size and hence the study of the more subtle effects of the interplay between the cluster and the cage sizes is possible.[1,13,16] In our previous study of the Gd–Sc

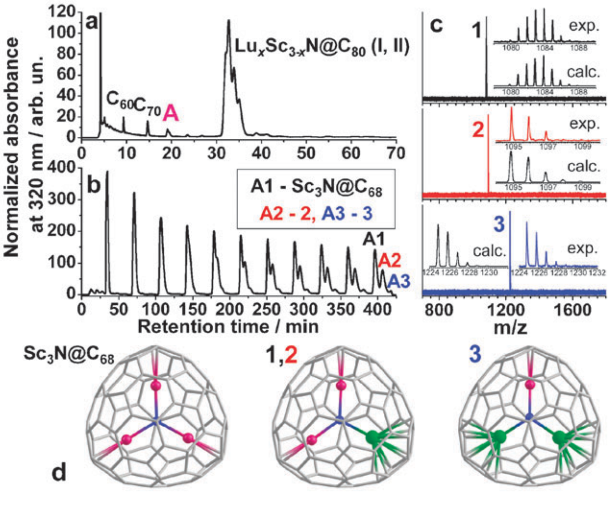

Fig. 1 (a) The HPLC chromatogram of the $Lu_xSc_{3-x}N@C_{2n}$ fullerene extract mixture; (b) HPLC chromatogram of the isolated fraction A by the second-step recycling HPLC; (c) Positive-ion laser desorption time-of-flight (LD-TOF) mass spectra (MS) of $DySc_2N@C_{68}$ (**1**), $LuSc_2N@C_{68}$ (**2**), and $Lu_2ScN@C_{68}$ (**3**). The insets show the measured and calculated isotope distributions of **1–3**; (d) DFT-optimized structures of $Sc_3N@C_{68}$ (left), **1** and **2** (middle), and **3** (right), for which the C_{68} cages are all based on D_3:6140 symmetry. Sc violet, N blue, Dy and Lu green.

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[a] *Group of Electrochemistry and Conducting Polymers, Leibniz-Institute for Solid State and Materials Research (IFW) Dresden, D-01171 Dresden, Germany. E-mail: l.dunsch@ifw-dresden.de; Fax: +49(351)4659 811; Tel: +49(351)4659 660*
[b] *Hefei National Laboratory for Physical Sciences at Microscale & Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, 230026, China. E-mail: sfyang@ustc.edu.cn; Fax: +86(551)3601 750; Tel: +86(551)3601 750*
[c] *Department of Chemistry, Moscow State University, Leninskiye Gory, 119992 Moscow, Russia*

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mixed NCFs we did not find any detectable amounts of C_{68}-based clusterfullerenes with Gd-containing clusters.[16] In this work we have studied two lanthanide–Sc mixed NCFs including Dy–Sc and Lu–Sc. Dy was chosen because its ionic radius (0.91 Å) is only slightly smaller than that of Gd^{3+} (0.94 Å) and also because it is known to provide the largest distribution of the cage sizes,[14] while Lu is the smallest metal among the lanthanide although its ionic radius (0.85 Å) is still significantly larger than Sc^{3+} (0.75 Å).[17] For the C_{68}-based homogenous NCFs ($M_3N@C_{68}$), the limited inner space of the small C_{68} cage permits only the accommodation of Sc_3N cluster but the larger Dy_3N and Lu_3N clusters could not be hosted. When one or two of these ions within the M_3N (M = Dy, Lu) cluster are replaced by Sc ions, the smaller clusters ($DySc_2N$, $LuSc_2N$, and Lu_2ScN) become suitable for being accommodated by the C_{68} cage, and the respective clusterfullerenes are formed in sufficient amounts to be separated by HPLC (Fig. 1). Therefore we succeeded in obtaining *ca.* 2 mg **1** and **2** and 0.5 mg **3** in high purity of ≥ 99% (as confirmed from MS measurements) for the further spectroscopic study below. However, further enlargement of the cluster size to Dy_2ScN, $GdSc_2N$ or Gd_2ScN makes their encapsulation in C_{68} cage impossible as confirmed by MS analysis. This indicates that the inner space of the C_{68} cage is very sensitive to the size of the encaged cluster. As a result, the small Sc_3N has been found to be the threshold for the homogenous NCFs which can be accommodated by the C_{68} cage, while for the mixed NCFs, Lu_2ScN appears to be the uplimit based on the confinement of the small C_{68} cage.

As Lu is the only lanthanide capable of producing dilanthanide-scandium nitride cluster within the C_{68} cage in isolable amounts, it is instructive to analyze the confinement effect of the small C_{68} cage on the $Lu_xSc_{3-x}N$ clusters geometry. Fig. 1d shows the DFT optimized structures of **1–3**. The changes in the structure with the variation of the cluster composition are similar to those observed in the C_{80}-based mixed NCFs (M = Y, Gd, Er).[16,18] Subsequent substitution of Sc by Lu in the cluster results in the displacement of the nitrogen atom from its position on the C_3-axis in $Sc_3N@C_{68}$ toward Sc atom(s) with considerable shortening of the Sc–N bonds. Thus, Sc–N bond shortens from 1.993 Å in $Sc_3N@C_{68}$ to 1.948 Å in **2** and further to 1.899 Å in **3**.[16,19] Lu–N bonds also shorten with the increase of the number of Lu atoms in the cluster: 2.092 Å in **2**, 2.052 Å in **3**, and 2.032 Å in $Lu_3N@C_{68}$. Note that the cluster is planar in **2**, but becomes pyramidal when more Lu atoms are present. The pyramid height is 0.185 Å in **3** and 0.490 Å in hypothetical $Lu_3N@C_{68}$. Obviously, the Lu_3N cluster is too large for the C_{68} cage, and hence $Lu_3N@C_{68}$ is not formed in detectable amounts.

The structures of the carbon cage for **1–3** can be unambiguously confirmed by the spectroscopic UV-vis-NIR (Fig. 2) and FTIR (Fig. 3) analysis. UV-vis-NIR absorption spectra of **1–3** are virtually congruent in terms of the optical bandgap (*ca.* 1200 nm), the number of observed bands and their energies (see Fig. 2). As a result, the colors of **1–3** dissolved in toluene (purple, Fig. S3†) are completely the same to that of $Sc_3N@C_{68}$ (see ESI-S2†). This result is in perfect agreement with the DFT calculations, which show that MO levels in $Sc_3N@C_{68}$, $LuSc_2N@C_{68}$ (**2**) and $Lu_2ScN@C_{68}$ (**3**) are almost identical in spite of the reduced molecular symmetry of the mixed clusterfullerenes (Fig. 2, inset). Significantly, this is different to the case of $M_xSc_{3-x}N@C_{80}$ (**I**) (M = Y, Gd, Er) NCFs,[16,18] indicating considerable variations in their absorption spectra with the change of the encaged cluster, including an increase of the bandgap and the development of a more resolved absorption pattern with the increase of the number of lanthanide atoms in the cluster.[16,18]

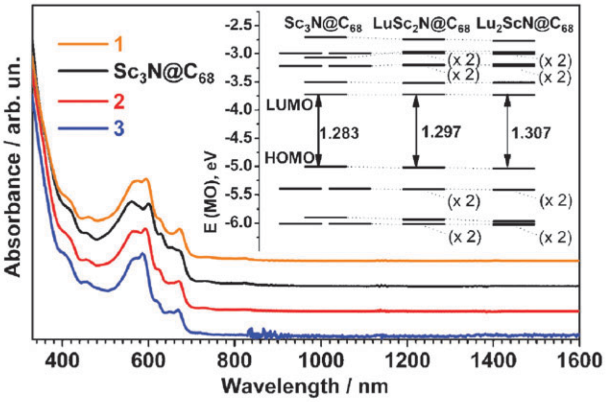

Fig. 2 UV-vis-NIR spectra of **1–3** dissolved in toluene in comparison with that of $Sc_3N@C_{68}$. The inset shows MO levels in $Lu_xSc_{3-x}N@C_{68}$ (x = 0–2) computed at the PBE/TZ2P level.

The FTIR spectra of **1–3** exhibit remarkable similarity with that of $Sc_3N@C_{68}$ (Fig. 3) in the range of the cage vibrations (400–500 and 800–1600 cm^{-1}),[10] confirming that they have the same formal cage symmetry (D_3), even though the molecular symmetry of the mixed clusterfullerenes is lower than D_3 and hence the splitting of the two-fold degenerated vibrations of $Sc_3N@C_{68}$ could be expected (but not observed). Such a splitting is indeed observed for the metal–nitrogen stretching mode in the mixed clusters (in $Sc_3N@C_{68}$ this mode is two-fold degenerated[10]). Shortening of Sc–N bonds results in the increase of the frequencies of the vibrations associated with this bond. For instance, the cluster vibrations with prevailing Sc–N stretching contribution are observed at 731 cm^{-1} (**2**) and 782 cm^{-1} (**3**) as compared to 661 cm^{-1} in $Sc_3N@C_{68}$.[10] In **1**, Sc–N stretching vibration is assigned to the band at 758 cm^{-1}, which is higher than in **2** (731 cm^{-1}). This is a reasonable

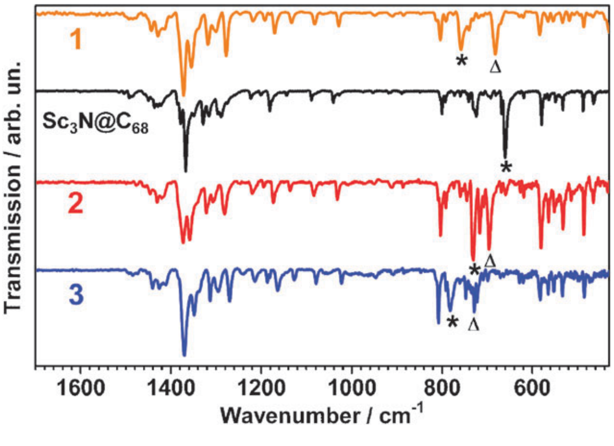

Fig. 3 FTIR spectra of **1–3** in comparison with that of $Sc_3N@C_{68}$. The asterisks and triangles label the antisymmetric Sc–N and Dy–N (Lu–N) stretching vibrational modes, respectively.

consequence of the larger radius of Dy^{3+} as compared to Lu^{3+} which results in the shorter Sc–N bonds in $DySc_2N$ cluster than in $LuSc_2N$. Vibrations with a prevailing Lu–N contribution are found at 696 cm^{-1} in **2** and at 729 cm^{-1} in **3** as compared to 715 cm^{-1} in $Lu_3N@C_{80}$.[17a] Thus, the order of Lu–N stretching frequencies in the experimentally available Lu-based clusterfullerenes correlates sensibly with Lu–N bondlengths. The detailed studies on the vibrational structures of **1–3** including the charge transfer from the large cluster to the C_{68} cage are currently underway.

In conclusion, we have synthesized and isolated three new C_{68}-based mixed metal NCFs with large nitride clusters $DySc_2N$, $LuSc_2N$, and Lu_2ScN (**1–3**). Lu_2ScN is found to be the largest cluster which can be accommodated within the small C_{68} cage (D_3) and be isolated in appreciable yield. The identity of the carbon cage structures is confirmed by UV-vis-NIR and FTIR spectroscopy in combination with the DFT computations. The changes of the metal–nitrogen vibrations in $DySc_2N$ and $Lu_xSc_{3-x}N$ clusters are analyzed by FTIR and related to the DFT-predicted structures. In addition to unveiling the confinement of the C_{68} cage, this study provides a new avenue for entrapping the large species into small fullerene cages.

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19. Note that the Sc–N bond within **3** is the shortest Sc–N bond found in the experimentally isolated clusterfullerenes so far.