Crystallographic characterization of \( \text{Lu}_2\text{C}_{2n} \) (2\( n = 76–90 \)): cluster selection by cage size†

Wangqiang Shen, Lipiao Bao, Shuaifeng Hu, Le Yang, Peng Jin, Yunpeng Xie, Takeshi Akasaka and Xing Lu

The successful isolation and unambiguous crystallographic assignment of a series of lutetium-containing endohedral metallofullerenes (EMFs), \( \text{Lu}_2\text{C}_{2n} \) (2\( n = 76, 78, 80, 84, 86, 88, 90 \)), reveal an unrecognized decisive effect of the cage size on the configuration of the encapsulated clusters. The molecular structures of these compounds are unambiguously assigned as \( \text{Lu}_2@\text{T}_{2}\text{(2)-C}_{76} \), \( \text{Lu}_2@\text{D}_{2}\text{(5)-C}_{76} \), Lu2@C2v(5)-C80, Lu2@C2v(7)-C84, Lu2@C1v(8)-C86, Lu2@C1v(15)-C86, Lu2@C1v(26)-C88, Lu2@C2v(9)-C86, Lu2C2@C1v(32)-C88 and Lu2C2@D2v(35)-C88. Specifically, when the cage is relatively small, \( \text{Lu}_2@\text{C}_{2n} \) (2\( n = 76–86 \)) are all dimetallofullerenes (di-EMFs) and a Lu–Lu single bond could be formed between the two lutetium ions inside the cages. However, when the cage expands further, the valence electrons forming the possible Lu–Lu bond donate to a readily inserted C2-unit, resulting in the formation of carbide EMFs, \( \text{Lu}_2\text{C}_2@\text{C}_{2n} \) (2\( n = 86, 88 \)). Consistently, our theoretical results reveal that all these EMFs are thermodynamically favorable isomers. Thus the comprehensive characterization of the series of \( \text{Lu}_2\text{C}_{76–90} \) isomers and the overall agreement between the experimental and theoretical results reveal for the first time that the exact configuration of the internal metallic cluster is determined by the cage size, taking a solid step towards the controlled synthesis of novel hybrid molecules which may have potential applications as building blocks of single molecule devices.

Introduction

Putting metal atoms or metallic clusters into fullerenes has generated a new class of novel hybrid molecules, defined as endohedral metallofullerenes (EMFs), possessing novel structures and fascinating properties which are different from those of empty fullerenes.1–4 During the last three decades, EMFs containing various metallic clusters, including metal nitride (M,N),5–10 metal carbide (M2C2/M2C2/M4C4),7–9 metal sulfide (M,S),10,11 metal oxide (M2O/M4O2/M4O3)12–14 and metal cyanide (M3CN/MCN)15–17 clusters, have been structurally characterized in addition to the conventional EMFs containing only metal atoms (M/M2/M3).3,18–20 EMFs exhibit a variety of electronic and physicochemical properties which markedly depend on the nature of the encapsulated species.21,22 One of the most brilliant features of EMFs is the charge transfer from the internal metallic species to the surrounding cage which is revealed to play an important role in determining the stability of the formed molecules.21,23,24 For example, the \( \text{C}_{2n}(9)-\text{C}_{82} \) cage is the most stable one after accepting three electrons, and the corresponding M@\( \text{C}_{2n}(9)-\text{C}_{82} \) isomers have the highest production yield among all reported mono-EMFs for a variety of lanthanide elements regardless of the metal type.24,25 As for cluster EMFs, theoretical and experimental results have suggested that the hexa-anionic \( \text{I}_{6}(7)-\text{C}_{80} \) cage is the most suitable candidate for encapsulating an M3N (M = Sc, Y, Gd, Lu, etc.) cluster.26,27

In addition to the electronic interactions, the geometry of the cluster, especially the cluster size, also has a significant effect on the cage structure and symmetry. For instance, Dunsch and co-workers proposed theoretically that the small Sc,N cluster presents a planar geometry inside the \( \text{D}_{3h}(5)-\text{C}_{78} \) cage, whereas the larger M3N (M = Y, Lu, Dy, Tm) clusters prefer the \( \text{C}_{2}(22 010)-\text{C}_{78} \) cage that violates the isolated pentagon rule (IPR) to keep their planarity.28 And a subsequent experimental report confirmed that the large Gd,N unit prefers to adopt the planar geometry in the \( \text{C}_{2}(22 010)-\text{C}_{78} \) cage.29 Another example demonstrated that M3N clusters containing metals with a relatively small radius (e.g. Sc, Y and Gd) are preferentially encapsulated inside a \( \text{C}_{80} \) cage. In contrast, larger metals like La and Nd prefer to template \( \text{C}_{88} \) or \( \text{C}_{90} \).30,31 Accordingly, it seems that the size, shape, and charge of the encapsulated cluster play important roles in the selection of the complementary carbon cages. However, there is still a lack of experimental evidence to

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confirm whether the cage size has any influence on the cluster configuration or not. For example, Dunsch et al. proposed that the number of Sc atoms in the internal GdSc3N clusters decreases along with the cage expansion (C78 to C88), as demonstrated by absorption and vibrational spectroscopy, electrochemical studies and density functional theory (DFT) computations.22 Popov et al. reported a systematic computational study on the analysis of the distortions in three classes of EMFs with nitride, sulfide, and carbide clusters, indicating that the preferable shapes of the internal clusters can be altered by the cage size.33 Moreover, an interesting report from Dorn and co-workers theoretically revealed that the fullerene cage may compress the internal Y3C2 cluster to adopt different shapes, from butterfly-like configurations in small cages to nearly linear structures in large cages.34 Nonetheless, there are no crystallographic results showing that the composition of the metallic species is controllable by the cage size.

We herein confirm for the first time that the exact composition of the internal metallic cluster is determined by the cage size based on the concrete single-crystal X-ray crystallographic results of ten lutetium-containing endohedrals, namely, Lu2@Td(2)-C78, Lu2@D3h(5)-C78, Lu2@D5h(5)-C78, Lu2@C2v(9)-C86, Lu2@C2h(8)-C86, Lu2@C2h(15)-C86, Lu2@C2v(5)-C88, Lu2@C2v(9)-C88, Lu2@C2h(32)-C88 and Lu2@C2v(35)-C88. It is revealed that the Lu−Lu distance increases along with the cage expansion as a direct result of the preferential coordination of the Lu atoms with the cage carbon atoms. Accordingly, the small cages can only accommodate a Lu3 cluster because of the limited inner space, accompanied by the possible formation of a Lu−Lu bond. However, when the cage expands further, a C2-unit is inserted between the two Lu atoms, which takes over partially the absorption spectra of Lu2@C76 and Lu2@C78, respectively, taking advantage of the high-quality of the co-crystals of Lu2@C76/NiII(OEP) [OEP = 2,3,7,8,12,13,17,18-octaeethylporphyrin dianion]. Although Lu2@Td(2)-C76 was first isolated and confirmed to have a T6-symmetric cage according to 1H NMR spectroscopic studies in combination with scanning tunneling microscopy results,15 and D3h(5)-C78, D5h(5)-C86, C2v(9)-C86 and D35-C88 cages were obtained and crystallographically characterized for EMFs possessing the same cage symmetry, such as Sc2O@D3h(5)-C78, Sc2O@C2v(5)-C80, Sc2@C2h(9)-C86 and Lu2@C2v(35)-C88, it is noteworthy that the cages of C2v(7)-C84, C2v(8)-C86, C15(15)-C86, C26(26)-C88 and C32(32)-C88 have never been experimentally reported before in spite of the fact that Sc2O@C2v(7)-C84 was theoretically predicted without further experimental evidence.16

Fig. 1 and 2 portray the molecular structures of Lu2@C2n (2n = 76, 78, 80, 84, 86, 88, 90) isomers co-crystallized with the NiII(OEP) molecules. For Lu2@C2h(8)-C86 and Lu2@C2v(35)-C88, each fullerene cage is surrounded by two NiII(OEP) molecules in a sandwich-like arrangement, and the ethyl groups of one of the NiII(OEP) molecules are arranged in such a way that they can embrace the fullerene cage from both sides whereas the other endohedrals adopt the normal one-EMF-one-Ni(OEP) fashion. The shortest Ni-cage distances in all the systems fall in the range of 2.631 Å−3.050 Å, suggesting substantial π−π interactions between the fullerene cage and the NiII(OEP) molecule(s).47−49 Inside these cages, the Lu atoms show severe disorder in all EMFs (Fig. 3, Tables S2 and S3, ESI†), indicating a motional behavior of the two Lu ions which may account for the strong Lu−cage interactions by fulfilling the coordination requirements of the Lu ions as much as possible. In detail, 19, 16 and 27 Lu positions are found for the two Lu atoms inside the Lu2@C2v(7)-C84, Lu2@C2v(5)-C78 and Lu2@C2v(5)-C80 cages, respectively, whereas 26, 13 and 20 Lu sites are positioned for the two Lu atoms in the respective Lu2@C2h(8)-C86, Lu2@C2v(35)-C88, Lu2@C2h(15)-C86 cage. In Lu2@C2v(26)-C88, 27 Lu sites are positioned for the two Lu atoms. Moreover, 13, 24 and 16 Lu sites are found for the two Lu atoms in Lu2@C2h(9)-C86, Lu2@C2h(32)-C88 and Lu2@C2v(35)-C88, respectively.

Furthermore, the representative structural data of Lu2@C76−90 isomers, such as the cage length/width ratio (L/W ratio), major Lu−Lu distance, Lu−Lu distance range and Lu−cage distance, are summarized in Table 1. The Lu−Lu distances between any two opposite Lu sites with comparable occupancy values are in the range of 3.31−3.53 Å, 3.27−3.67 Å, 3.22−3.73 Å, 3.33−3.84 Å, 3.49−3.73 Å, 3.34−3.84 Å and 3.57−3.62 Å for Lu2@Td(2)-C76, Lu2@D3h(5)-C78, Lu2@C2v(9)-C86, Lu2@C2h(15)-C86, Lu2@C2v(35)-C88 and Lu2@C2h(32)-C88 cages are quite different from those of the corresponding EMFs possessing C84, C86 and C88 cages reported before,13,15,16 indicating their different structures.

Finally, the molecular structures of Lu2@C2n (2n = 76, 78, 80, 84, 86, 88, 90) isomers were unambiguously determined by single-crystal X-ray diffraction (XRD) crystallography to be Lu2@Td(2)-C76, Lu2@D3h(5)-C78, Lu2@C2h(8)-C86, Lu2@C2v(9)-C86, Lu2@C2h(15)-C86, Lu2@C2v(35)-C88, Lu2@C2h(32)-C88, Lu2@C2v(35)-C88, Lu2@C2h(15)-C86 and Lu2@C2v(26)-C88, respectively, taking advantage of the high-quality of the co-crystals of Lu2@C76/NiII(OEP) [OEP = 2,3,7,8,12,13,17,18-octaeethylporphyrin dianion]. Although Lu2@Td(2)-C76 was first isolated and confirmed to have a T6-symmetric cage according to 1H NMR spectroscopic studies in combination with scanning tunneling microscopy results,15 and D3h(5)-C78, D5h(5)-C86, C2v(9)-C86 and D35-C88 cages were obtained and crystallographically characterized for EMFs possessing the same cage symmetry, such as Sc2O@D3h(5)-C78, Sc2O@C2v(5)-C80, Sc2@C2h(9)-C86 and Lu2@C2v(35)-C88, it is noteworthy that the cages of C2v(7)-C84, C2v(8)-C86, C15(15)-C86, C26(26)-C88 and C32(32)-C88 have never been experimentally reported before in spite of the fact that Sc2O@C2v(7)-C84 was theoretically predicted without further experimental evidence.16

Results and discussion

Lu-EMFs were synthesized by a direct-current arc discharge method and pure isomers of Lu2@C2n (2n = 76, 78, 80, 84, 86, 88, 90) were obtained by multistage HPLC separation (see ESI, Fig. S1−S4 for details†). The analytical HPLC chromatograms (Fig. S5†) and the laser-desorption/ionization time-of-flight (LDI-TOF) mass spectra (Fig. S6†) of Lu2@C2n (2n = 76, 78, 80, 84, 86, 88, 90) isomers confirm their high purity. Fig. S7 and Table S1† show the visible-near-infrared (Vis-NIR) absorption spectra and the detailed characteristic bands of Lu2@C76−90 isomers dissolved in carbon disulfide (CS2), respectively. The absorption spectra of Lu2@C2v(7)-C84, Lu2@C2h(8)-C86, Lu2@C2h(15)-C86, Lu2@C2v(35)-C88 and Lu2@C2h(32)-C88 cages are quite different from those of the corresponding EMFs possessing C84, C86 and C88 cages reported before,13,15,16 indicating their different structures.
requirement of the Lu ions by taking partially the charges from the metal ions. The shortest Lu-cage distances are consistently 2.108 Å, 2.263 Å, 2.065 Å, 2.106 Å, 2.086 Å, 2.103 Å, 2.291 Å, 2.269 Å, 2.319 Å and 2.166 Å for Lu₂@C₁₇₆(5)-C₇₈, Lu₂@D₁₃₁(5)-C₇₈, Lu₂@C₂₅(5)-C₈₀, Lu₂@C₂₅(7)-C₈₄, Lu₂@C₈₂(8)-C₈₆, Lu₂@C₁₅₁(15)-C₈₈, Lu₂@C₁₇₆(26)-C₈₈, Lu₂@C₂₅₄(9)-C₈₆, Lu₂@C₂₅₄(32)-C₈₈ and Lu₂@D₁₃₅(35)-C₈₈, respectively, which are all shorter than the calculated values for Lu₂@T₉₋₆-C₇₆ (2.37–2.42 Å), suggesting strong Lu-cage interactions.

It is interesting to find that the small cages (C₇₆–₈₆) prefer to accommodate a Lu₂ dimer to form di-EMFs whereas carbide cluster metallofullerenes (CCMFs) are formed for Lu₂C₈₈ or Lu₂C₉₀, which possess relatively large cages. We speculate that this phenomenon is caused by the different cage structure parameters, particularly the cage length and width. As clearly shown in Table 1, the cage length and L/W ratio increase in accordance with cage expansion, resulting in a substantial increase of the Lu–Lu distance. In particular, C₈₆-based lutetium-containing EMFs have two different compositions: C₈₆(8)-C₈₆ (L/W = 1.16) and C₈₆(15)-C₈₆ (L/W = 1.16) possess relatively round cages and they choose to encapsulate a Lu₂ dimer instead of a Lu₂C₂ cluster because of the limited inner space, whereas the elongated C₈₆(9)-C₈₆ (L/W = 1.20) causes the increased Lu–Lu distance because of strong Lu-cage interactions and easy C₂ insertion, resulting in the formation of the CCMF Lu₂C₂@C₂₅₄(9)-C₈₆. As a matter of fact, the cages smaller than C₈₆ can only accommodate a Lu₂ dimer and the larger ones always prefer the Lu₂C₂ composition to make the resultant EMFs more stable.

Fig. S8† shows the location of the major Lu₂/Lu₂C₂ cluster relative to the cage orientation in the ten EMFs under study. In Lu₂@C₂₅(5)-C₈₀, Lu₂@C₂₅(7)-C₈₄, Lu₂@C₂₅(8)-C₈₆, Lu₂@C₂₅(32)-C₈₈ and Lu₂@D₁₃₅(35)-C₈₈, one major Lu site is situated over a [5,6]-bond, whereas the other one is close to a hexagonal ring. In the other five endohedrals, each prominent Lu position is located over a [5,6]-bond. Moreover, the configurations of the Lu₂C₂ clusters inside the carbon cages are all shaped like a butterfly with two tightly bonded carbon atoms in the respective cage centers. The Lu–C–Lu dihedral angles are 132.13°, 145.46° and 142.83° in the C₂₅(9)-C₈₆, C₂₅(32)-C₈₈ and D₁₃₅(35)-C₈₈ cages, respectively. Furthermore, the C–C bond lengths of the C₅ unit in Lu₂@C₂₅(9)-C₈₆, Lu₂@C₂₅(32)-C₈₈ and Lu₂@D₁₃₅(35)-C₈₈ are 1.11 Å, 1.20 Å and 1.00 Å, respectively, which represent typical C–C triple bonds (Fig. S8†).
processes, either reduction or oxidation, are found for processes than the di-EMFs. For instance, several irreversible appears that the CCMFs show better reversibility of the redox of Lu₂C₂ oxidation steps together with four reduction steps within the Lu₂C₂@ (1.19 eV (d) 26 in Lu₂@ | and S₁₀ 19 in Lu₂@ and Lu₂@ Perspecti...
considered isomers. Moreover, Lu$_2@$T$_d$(7)-C$_{76}$ is 6.6 kcal mol$^{-1}$ lower in energy than Lu$_2@$C$_{2v}$(5)-C$_{80}$ when it has a triple ground state. Therefore, it is highly possible that Lu$_2@$T$_d$(7)-C$_{76}$ is generated together with Lu$_2@$C$_{2v}$(5)-C$_{80}$ during the arc-discharge process, but it may form insoluble products in the raw soot due to its radical character and thus is absent in the usual solvent extract (Table 2). As for Lu$_2$C$_8$, a previous report has revealed that Lu$_2@$C$_{2v}$(6)-C$_{82}$ and Lu$_2@$C$_{3v}$(8)-C$_{82}$ are both lower in energy than any of the Lu$_2$C$_2@$C$_{80}$ isomers (Table 2). Accordingly, for a composition of Lu$_2$C$_{76}$-$x$C$_{82}$, Lu$_2@$C$_{2v}$ is always more stable than the corresponding carbide form Lu$_2$C$_2@$C$_{2v}$. indicating that the formation of di-EMFs is energetically favorable within this cage size range. However, Lu$_2$C$_{64}$-$x$C$_{80}$, Lu$_2@$C$_{2v}$(7)-C$_{84}$, Lu$_2@$C$_{2v}$(8)-C$_{86}$ and Lu$_2@$C$_{2v}$(15)-C$_{88}$ and their respective Lu$_2$C$_2@$C$_{2v}$- isomers are mixed in energy, with the recently reported Lu$_2@$D$_{2d}$(23)-C$_{84}$ and Lu$_2@$C$_{2v}$(9)-C$_{86}$ being the most stable ones (Table 2). These results imply that the formation of CCMFs is gradually favored with increasing cage size. Indeed, as shown in Fig. S16 and S17, Lu$_2@$C$_2@$C$_{2v}$(9)-C$_{86}$ Lu$_2@$C$_2@$D$_{3d}$(35)-C$_{88}$ and Lu$_2@$C$_2@$C$_{3v}$(32)-C$_{88}$ are the lowest-energy Lu$_2$C$_{88}$ and Lu$_2@$C$_{90}$ isomers, respectively. Therefore, as the cage size increases to C$_{88}$ and C$_{90}$, the CCMFs are energetically more stable than the corresponding di-EMFs. Overall, our experimental and theoretical results have unambiguously confirmed that the exact composition of the internal cluster is changed from Lu$_2$ to Lu$_2$C$_2$ along with the cage expansion, which is a synergetic result of C2 insertion and the strong Lu-cage coordination of the Lu ions with the cage carbon atoms.

### Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cage length (Å)</th>
<th>Cage width (Å)</th>
<th>L/W ratio</th>
<th>Major Lu-Lu distance (Å)$^a$</th>
<th>Calculated Lu-Lu distance (Å)</th>
<th>Lu-Lu distance range (Å)$^b$</th>
<th>Shortest Lu-cage distance$^c$</th>
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<tr>
<td>Lu$_2@$T$<em>d$(2)-C$</em>{76}$</td>
<td>7.126</td>
<td>7.110</td>
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<td>3.44</td>
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<td>8.338</td>
<td>7.548</td>
<td>1.10</td>
<td>3.27</td>
<td>3.41</td>
<td>3.27–3.67</td>
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<td>Lu$<em>2@$C$</em>{2v}$(5)-C$_{80}$</td>
<td>8.245</td>
<td>7.896</td>
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<td>3.60</td>
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<td>8.315</td>
<td>1.01</td>
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<td>8.199</td>
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<td>4.64</td>
<td>4.14–4.41</td>
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</table>

$^a$ Lu-Lu distance between the major Lu sites. $^b$ Lu-Lu distance between any two opposite Lu sites with comparable occupancy. $^c$ The shortest Lu-cage distance between the major Lu sites and the cage carbon atoms.
namely La$_2@D_2$($1061$)-C$_{72}$, $^{64}$ La$_2@C_6$($17490$)-C$_{76}$, $^{62}$ La$_2@D_3h(5)$-C$_{78}$, $^{64}$ La$_2@I_h(7)$-C$_{80}$, $^{64}$ and La$_2@D_3$($450$)-C$_{100}$ $^{65}$ have been confirmed by single crystal XRD crystallography, the La$^{3+}$ ions are also more inclined to form carbide structures with some giant cages such as C$_{90}$-104, which are rationalized by considering the synergistic effect of inserting a C$_2$-unit on the stabilization of CCMFs both electronically and geometrically.$^{47-49}$

## Conclusions

In summary, a series of lutetium-containing EMFs, namely Lu$_2@T_d$-C$_{76}$, Lu$_2@D_3h(5)$-C$_{78}$, Lu$_2@C_5$-C$_{80}$, Lu$_2@C_7$-C$_{84}$, Lu$_2@C_8$-C$_{86}$, Lu$_2@C_9$-C$_{88}$, Lu$_2@C_{10}$-C$_{88}$, Lu$_2@C_{94}$-Lu$_2@C_{96}$ and Lu$_2@D_3$($35$)-C$_{88}$ have been isolated and structurally determined. Based on our experimental and theoretical results, a clear correlation between the cage size and the configuration of the internal metallic cluster is revealed. Moreover, we also propose that the C$_{86}$ cage is the threshold for Lu$_2$C$_{2n}$-type EMFs transforming from di-EMFs to CCMFs. Specifically, the relatively small cages, i.e. C$_{76}$-C$_{86}$, choose to encapsulate a Lu$_2$ cluster with the possible formation of a Lu–Lu bond because of the limited inner space. However, further cage expansion elongates the Lu–Lu distance due to the strong Lu-cage interactions and the insertion of a C$_2$-unit, resulting in the formation of CCMFs, Lu$_2$C$_2@C_{2n}$ ($2n = 86$, 88). Accordingly, we confirm for the first time that the preferential formation of the Lu$_2@C_{2n}$/Lu$_2@C_{2n+2}$ composition is determined by the cage size, presenting a practical strategy for the templated synthesis of EMFs possessing desired internal clusters, which may facilitate the application of EMFs as building blocks for molecular devices/machines.

## Experimental

### Synthesis and isolation of Lu$_2$C$_{2n}$ ($2n = 76$, 78, 80, 84, 86, 88, 90)

Soot containing Lu-EMFs was synthesized by a direct-current arc discharge method and was extracted using carbon disulfide (CS$_2$). After the removal of CS$_2$, the residue was dissolved in toluene and the solution was subjected to a multi-stage high-performance liquid chromatography (HPLC) separation. The experimental details are given in the ESI.$^\dagger$

### General characterization

High-performance liquid chromatography (HPLC) was conducted on an LC-9130 NEXT machine (Japan Analytical Industry Co., Ltd.) with toluene as the mobile phase. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a BIFLEX III spectrometer (Bruker Daltonics Inc., Germany). Vis-NIR spectra were obtained on a PE Lambda 750S spectrophotometer in CS$_2$. Cyclic voltammograms (CV) were measured in 1,2-dichlorobenzene with 0.05 $\text{M}$ n-Bu$_4$NPF$_6$ as the supporting electrolyte at a Pt working electrode with a CHI660E workstation.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Relative energies of the selected low-lying isomers</th>
<th>Relative energies of the selected low-lying isomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lu$<em>2@C</em>{76}$</td>
<td>$-0.0$ (2.98)</td>
<td>$-0.0$ (2.98)</td>
</tr>
<tr>
<td>Lu$<em>2@C</em>{80}$</td>
<td>$-0.0$ (2.98)</td>
<td>$-0.0$ (2.98)</td>
</tr>
<tr>
<td>Lu$<em>2@C</em>{84}$</td>
<td>$-0.0$ (2.98)</td>
<td>$-0.0$ (2.98)</td>
</tr>
<tr>
<td>Lu$<em>2@C</em>{86}$</td>
<td>$-0.0$ (2.98)</td>
<td>$-0.0$ (2.98)</td>
</tr>
<tr>
<td>Lu$<em>2@C</em>{88}$</td>
<td>$-0.0$ (2.98)</td>
<td>$-0.0$ (2.98)</td>
</tr>
<tr>
<td>Lu$<em>2@C</em>{90}$</td>
<td>$-0.0$ (2.98)</td>
<td>$-0.0$ (2.98)</td>
</tr>
</tbody>
</table>
Single crystal XRD measurements of Lu₂C_{2n} (2n = 76, 78, 80, 84, 86, 88, 90)

The crystallographic data are shown in Tables S4 and S5.† Crystalline blocks of Lu₂C_{2n} (2n = 76, 78, 80, 84, 86, 88, 90) isomers were obtained by layering a benzene solution of Ni^{II}OEP (OEP) over a CS₂ solution of the corresponding metallofullerenes at room temperature. Over a 20-day period, the two solutions diffused together, and black crystals formed. Single-crystal XRD measurement of Lu₂@C_{68} Lu₃@C_{68}(15)-C_{68} and Lu₂C₂@C_{96}(9)-C_{96} was performed at 173 K on a Bruker D8 QUEST machine equipped with a CMOS camera (Bruker AXS Inc., Germany). Crystallographic characterization of Lu₂@T_{d}(2)-C_{76}, Lu₂@D_{3h}(5)-C_{78}, Lu₂@D_{2h}(5)-C_{80}, Lu₂@C_{2h}(7)-C_{84}, Lu₂@C_{1h}(26)-C_{88}, Lu₂C₂@C_{32}(32)-C_{88} and Lu₂C₂@D_{3h}(35)-C_{88} was performed at 100 K at BL17B station of the Shanghai Synchrotron Radiation Facility. The multi-scan method was used for absorption corrections. The structures were solved by the direct method and were refined with SHELXL-2014/7.66, CCDC-1582214 (Lu₂@T_{d}(2)-C_{76}), CCDC-1582215 (Lu₂@D_{3h}(5)-C_{78}), CCDC-1582216 (Lu₂@C_{2h}(5)-C_{80}), CCDC-1582217 (Lu₂@C_{2h}(7)-C_{84}), CCDC-1582218 (Lu₂@C_{1h}(8)-C_{84}), CCDC-1582219 (Lu₂@C_{1h}(15)-C_{86}), CCDC-1836827 (Lu₂@C_{1h}(26)-C_{88}), CCDC-1836828 (Lu₂C₂@C_{2h}(9)-C_{86}), CCDC-1836829 (Lu₂C₂@C_{32}(32)-C_{88}) and CCDC-1836830 (Lu₂C₂@D_{3h}(35)-C_{88}) contain the supplementary crystallographic data for this paper.†

Computational details

Density functional theory calculations were carried out by using the M06-2X functional in conjunction with the 6-31G*-SDD basis set and corresponding effective core potential for Lu^9+ (denoted as 6-31G*-SDD), as implemented in the Gaussian 09 software package.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references