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Article

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$Lu_2@C_{2n}$ ($2n$ = 82, 84, 86): Crystallographic Evidence of Direct Lu-Lu Bonding between Two Divalent Lutetium Ions inside Fullerene Cages

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ABSTRACT:

Although most of the M_2C_{2n}-type metallofullerenes (EMFs) tend to form carbide cluster EMFs, we report herein that Lu-containing EMFs Lu_2C_{2n} ($2n$ = 82, 84, 86) are actually dimetallofullerenes (di-EMFs), namely, $Lu_2@C_s(6)\text{-}C_{82}$, $Lu_2@C_{3v}(8)\text{-}C_{82}$, $Lu_2@D_{2d}(23)\text{-}C_{84}$ and $Lu_2@C_{2v}(9)\text{-}C_{86}$, respectively. Unambiguous X-ray results demonstrate the formation of a Lu-Lu single bond between two lutetium ions which transfer four electrons in total to the fullerene cages, thus resulting in a formal divalent state for each Lu ion. Population analysis indicate that each Lu atom formally donates a 5d electron and a 6s electron to the cage with the remaining 6s electron shared with the other Lu atom to form a Lu-Lu single bond, so that only four electrons are transferred to the fullerene cages with the formal divalent valence for each lutetium ion. Accordingly, we have confirmed both experimentally and theoretically that the dominating formation of di-EMFs are thermodynamically very favorable for Lu_2C_{2n} isomers.

INTRODUCTION

Endohedral metallofullerenes (EMFs) are a class of novel hybrid molecules resulting from the endohedral doping of fullerenes with metallic species.[1–3] EMFs have attracted great attention because of their fascinating properties and broad applications in materials science, photovoltaics, electronics, and biomedicine.[2,4] In addition to such conventional EMFs containing only metal atoms, novel EMFs encapsulating a variety of metallic compounds, including metal carbide ($M_2C_2/M_3C_2/M_4C_2$),[5–7] metal nitride (M_3N),[8,9] metal oxide ($M_2O/M_4O_2/M_4O_3$),[10–12] metal sulfide (M_2S),[13] and metal cyanide (M_3CN/MCN)[14,15] clusters have been obtained and structurally confirmed in recent years.

M_2C_{2n}-type EMFs may exist as dimetallofullerenes (di-EMFs), $M_2@C_{2n}$, or as carbide cluster metallofullerenes (CCMFs), $M_2C_2@C_{2n-2}$.[16–18] Surprisingly, most of the M_2C_{2n}-type EMFs that have been crystallographically characterized prefer to take the carbide form. For instance, almost all the Sc_2C_{2n}-type EMFs are CCMFs, most probably because of the strong coordinating ability and the small ionic radius of scandium that facilitate the formation of carbide clusters suitable for encapsulation inside common fullerene cages.[5,18–22] Recently, more and more M_2C_{2n}-type compounds are confirmed as CCMFs, instead of di-EMFs, such as $Tm_2C_2@C_s(6)\text{-}C_{82}$,[23] $M_2C_2@C_1(51383)\text{-}C_{84}$ (M = Y, Gd),[24] $Gd_2C_2@D_3(85)\text{-}C_{92}$[25] and $Tb_2C_2@C_s(6)\text{-}C_{82}$.[26] Furthermore, it is found that the even larger La^{3+} ions also prefer the carbide structure to form some giant cages,[27–29] which are rationalized by considering a synergistic effect of inserting a C_2-unit on the stabilization of CCMFs both electronically and geometrically.

Since lutetium possesses a similar ionic radius to scandium, it has been proposed that Lu-containing EMFs should also take the cluster structures as Sc-containing EMFs do. Indeed, $Lu_3N@I_h(7)\text{-}C_{80}$ was synthesized with a comparable yield to that of $Sc_3N@I_h(7)\text{-}C_{80}$ and was revealed to possess nearly the same chemical properties.[30] However, the unambiguous structural characterization of other Lu-containing EMFs has rarely been reported. For instance, $Lu_2@C_{76}$ was reported to have the T_d-symmetric cage according to NMR results,[31] and recently $Lu_2C_2@C_{72}$, $Lu_2C_2@C_{74}$(I), $Lu_2C_2@C_{80}$, and $Lu_2C_2@C_{82}$(III) are reported to exist but no further experimental evidence was available.[32] In addition, Zhao *et al*. proposed theoretically that $Lu_2C_2@C_2(157)\text{-}C_{96}$

and $Lu_2C_2@D_{2d}(163)\text{-}C_{96}$ are perfectly stable.[33] However, we herein report that Lu-containing EMFs prefer to form di-EMFs, instead of the common carbide structures. Single-crystal X-ray crystallographic results of these four new compounds show that they are $Lu_2@C_s(6)\text{-}C_{82}$, $Lu_2@C_{3v}(8)\text{-}C_{82}$, $Lu_2@D_{2d}(23)\text{-}C_{84}$ and $Lu_2@C_{2v}(9)\text{-}C_{86}$, respectively. More meaningfully, theoretical results show that the encapsulated Lu_2 cluster transfers four electrons to the cage with a formal divalent valence for each lutetium ion. Thus, the dominating formation of di-EMFs instead of CCMFs for Lu_2C_{2n} ($2n$ = 82, 84, 86) are thermodynamically very favorable, by forming a Lu-Lu single bond in these $Lu_2@C_{82\text{-}86}$ isomers.

RESULTS AND DISCUSSION

Carbon soot containing lutetium-EMFs was synthesized using a direct current arc discharge method. Briefly, a core-drilled graphite rod filled with graphite/Lu_2O_3 (molar ratio: Lu/C=1:17) was burned under 250 Torr helium and 50 Torr nitrogen atmosphere with a power of 100 A × 20 V. Multistage HPLC separations gave pure isomers of $Lu_2@C_{82\text{-}86}$ (Figures S1-S6, Supporting Information). Figure 1 shows their HPLC chromatograms and the laser-desorption ionization time-of-flight (LDI-TOF) mass spectra to confirm their purity as 99%.

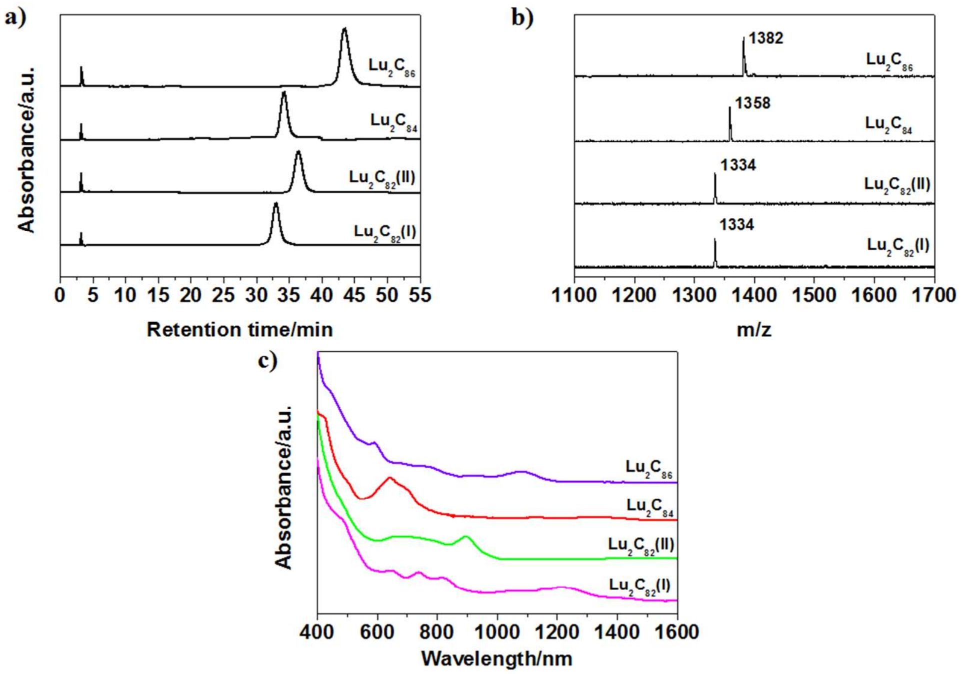


Figure 1. (a) HPLC chromatograms, (b) LDI-TOF mass spectra and (c) Vis-NIR absorption spectra of purified $Lu_2C_{82\text{-}86}$ isomers. (HPLC conditions: eluent = toluene, flow rate = 1.0 mL min^{-1}, detection wavelength = 330 nm, room temperature).

Electronic structures of $Lu_2@C_{82\text{-}86}$ were characterized with absorption spectroscopy. (Figure 1c and Table S1). Lu_2C_{82}(I) exhibits distinct absorptions at 481, 646, 740, 813 and 1213 nm with an onset at 1440 nm, corresponding to a small optical bandgap (0.86 eV). The spectrum of Lu_2C_{82}(II) has two distinct peaks at 705 and 895 nm with an onset at 1024 nm, corresponding to a relatively large optical bandgap (1.21 eV). Lu_2C_{84} and Lu_2C_{86} exhibit absorption onsets at 1513 and 1261 nm, respectively, thus suggesting their small bandgaps (0.82 eV for Lu_2C_{84} and 0.98 eV for Lu_2C_{86}). Furthermore, Lu_2C_{84} shows distinct absorption bands at 422, 643, 686, 1115 and 1318 nm, and Lu_2C_{86} shows characteristic bands at 429, 590, 679, 782, 950 and 1080 nm. Interestingly, the spectra of the four compounds under study are similar to the respective curves of the corresponding Sc-containing CCMFs ($Sc_2C_2@C_s(6)\text{-}C_{82}$, $Sc_2C_2@C_{3v}(8)\text{-}C_{82}$, $Sc_2C_2@D_{2d}(23)\text{-}C_{84}$ and $Sc_2C_2@C_{2v}(9)\text{-}C_{86}$),[5,19–21] which have been widely accepted to have the $(Sc_2C_2)^{4+}@(C_{82\text{-}86})^{4-}$ configuration. In addition, the absorption spectra of the two $Lu_2@C_{82}$ isomers are also similar to the respective curves of the corresponding $Er_2@C_{82}$ isomers.[34] Accordingly, it infers that $Lu_2C_{82\text{-}86}$ isomers may be di-EMFs instead of CCMFs, and the Lu_2 cluster transfers four electrons to the cages with a formal divalent valence for each lutetium ion.

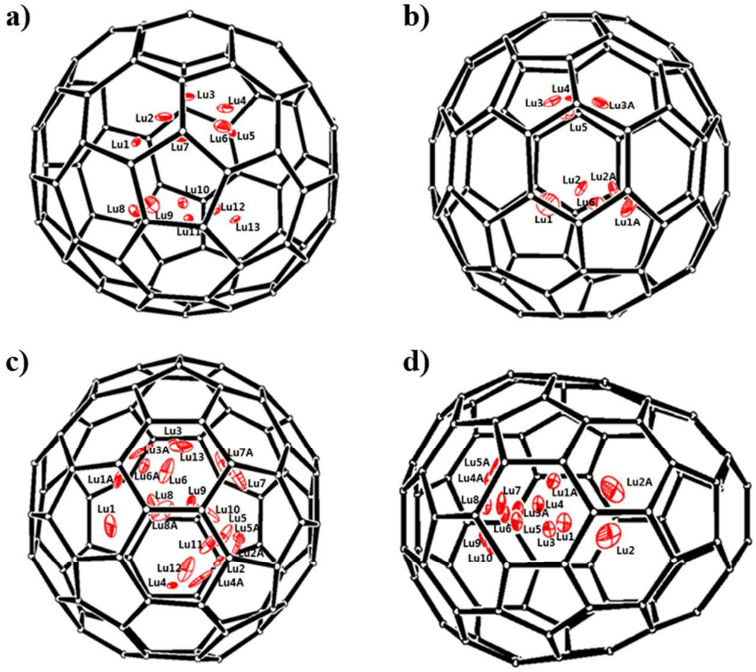


Figure 2. Positions of the disordered lutetium sites in (a) $Lu_2@C_s(6)\text{-}C_{82}$, (b) $Lu_2@C_{3v}(8)\text{-}C_{82}$, (c) $Lu_2@D_{2d}(23)\text{-}C_{84}$ and (d) $Lu_2@C_{2v}(9)\text{-}C_{86}$ relative to a cage orientation. Those Lu atoms labeled with “A” are generated by crystallographic operation.

The four compounds under study were cocrystallized with Ni^{II}(OEP) (OEP = 2,3,7,8,12,13,17,18-octaethylporphin dianion) to obtain good crystals suitable for X-ray measurements. Their molecular structures are unambiguously determined with single-crystal X-ray diffraction (XRD) crystallography. The results confirm that all these compounds are actually di-EMFs instead of CCMFs, namely $Lu_2@C_s(6)\text{-}C_{82}$, $Lu_2@C_{3v}(8)\text{-}C_{82}$, $Lu_2@D_{2d}(23)\text{-}C_{84}$ and $Lu_2@C_{2v}(9)\text{-}C_{86}$, respectively. Inside the fullerene cages, the Lu ions show some degree of disorder. Details of the disorder are given in Figure 2 and Table S2. The crystal system of

$Lu_2@C_s(6)\text{-}C_{82}$•$Ni^{II}$(OEP) falls into the monoclinic space group $P2_1/c$. Up to thirteen Lu sites are distinguished (Figure 2a). In comparison, the crystal systems of the other three EMFs belong to the monoclinic space group C2/*m* where the asymmetric unit contains two halves of the carbon cage. Accordingly, taking $Lu_2@C_{3v}(8)\text{-}C_{82}$ as an example, six disordered Lu sites are found in the cage. Because some disordered Lu sites do not reside at the symmetric plane, three additional Lu sites are generated by symmetric operation (Figure 2b and Table S2). Similarly, twenty-one Lu sites and fifteen Lu sites are distinguished in the cages of $Lu_2@D_{2d}(23)\text{-}C_{84}$ and $Lu_2@C_{2v}(9)\text{-}C_{86}$ (Figure 2c, 2d and Table S2), respectively. In other midsized dimetallic EMFs that have been crystallographically characterized, such as $La_2@I_h(7)\text{-}C_{80}$, $Er_2@C_s(6)\text{-}C_{82}$ and $Er_2@C_{3v}(8)\text{-}C_{82}$, the disordered metal sites are found to be along a band of 10 contiguous hexagons,[34–36] but this phenomenon does not happen here in these $Lu_2@C_{82\text{-}86}$ isomers.

Figures 3a-3d portray the molecular structures of these EMFs showing the major components together with the cocrystallized Ni^{II}(OEP) molecule. The shortest distances between Ni and a cage carbon range from 2.851 Å to 3.045 Å, suggesting substantial $\pi-\pi$ interactions between the fullerene cage and Ni^{II}(OEP). Furthermore, the geometries of $Lu_2@C_s(6)\text{-}C_{82}$, $Lu_2@C_{3v}(8)\text{-}C_{82}$ and $Lu_2@D_{2d}(23)\text{-}C_{84}$ allow only one of the two Lu ions to be positioned near the planar porphyrin, whereas both Lu ions in $Lu_2@C_{2v}(9)\text{-}C_{86}$ reside near the planar porphyrin because of the unique pyramidal shape of the cage. The Lu···Lu distances between any two opposite Lu sites with similar occupancy values are in the range of 3.35-3.67 Å, 3.21-3.57 Å, 3.24-3.75 Å and 3.43-3.72 Å, for $Lu_2@C_s(6)\text{-}C_{82}$, $Lu_2@C_{3v}(8)\text{-}C_{82}$, $Lu_2@D_{2d}(23)\text{-}C_{84}$ and $Lu_2@C_{2v}(9)\text{-}C_{86}$, respectively (Table S4). These values are all comparable to a Lu-Lu single bond length (3.28-3.81 Å),[37,38] confirming crystallographically the direct Lu-Lu bonding to result in a divalent state for each lutetium ion in these cages.

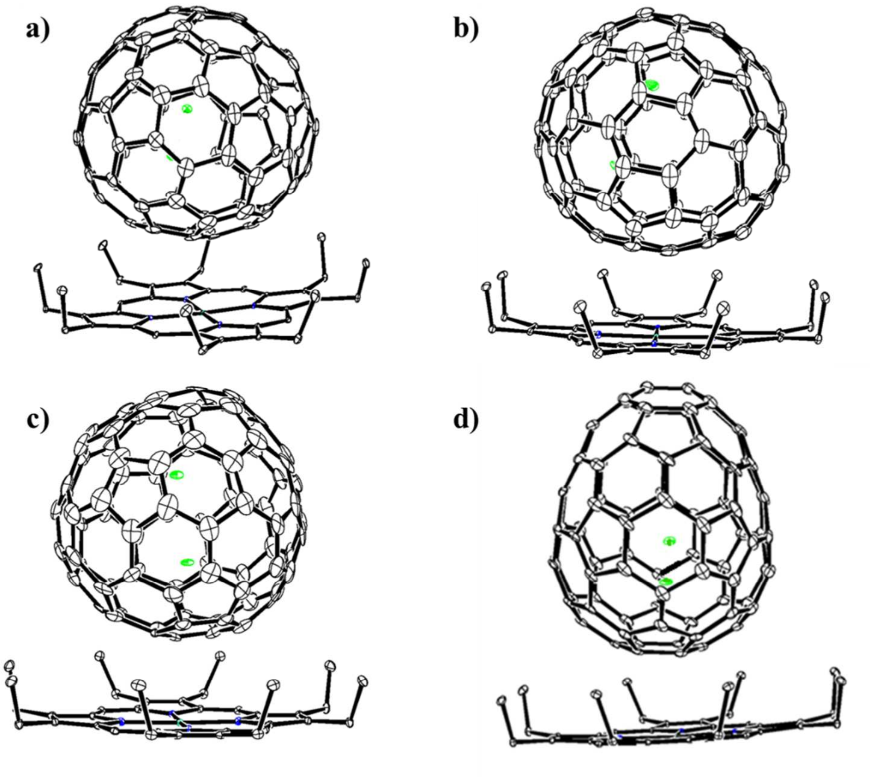


Figure 3. ORTEP drawings of (a) $Lu_2@C_s(6)\text{-}C_{82}$•$Ni^{II}$(OEP), (b) $Lu_2@C_{3v}(8)\text{-}C_{82}$•$Ni^{II}$(OEP), (c) $Lu_2@D_{2d}(23)\text{-}C_{84}$•$Ni^{II}$(OEP) and (d) $Lu_2@C_{2v}(9)\text{-}C_{86}$•$Ni^{II}$(OEP). Thermal contours are drawn at the 10% probability level. Only one fullerene cage and the predominant metal sites are shown, whereas minor sites and solvent molecules are omitted for clarity.

Theoretical calculations were conducted to rationalize the formation of the Lu—Lu bond in these compounds. The geometries of the four molecules optimized at the M06-2X/6-31G*~SDD level agree perfectly with their X-ray structures (Figure S8). They all bear a singlet ground state (^1A) with other spin states much higher in energy (Table S6).

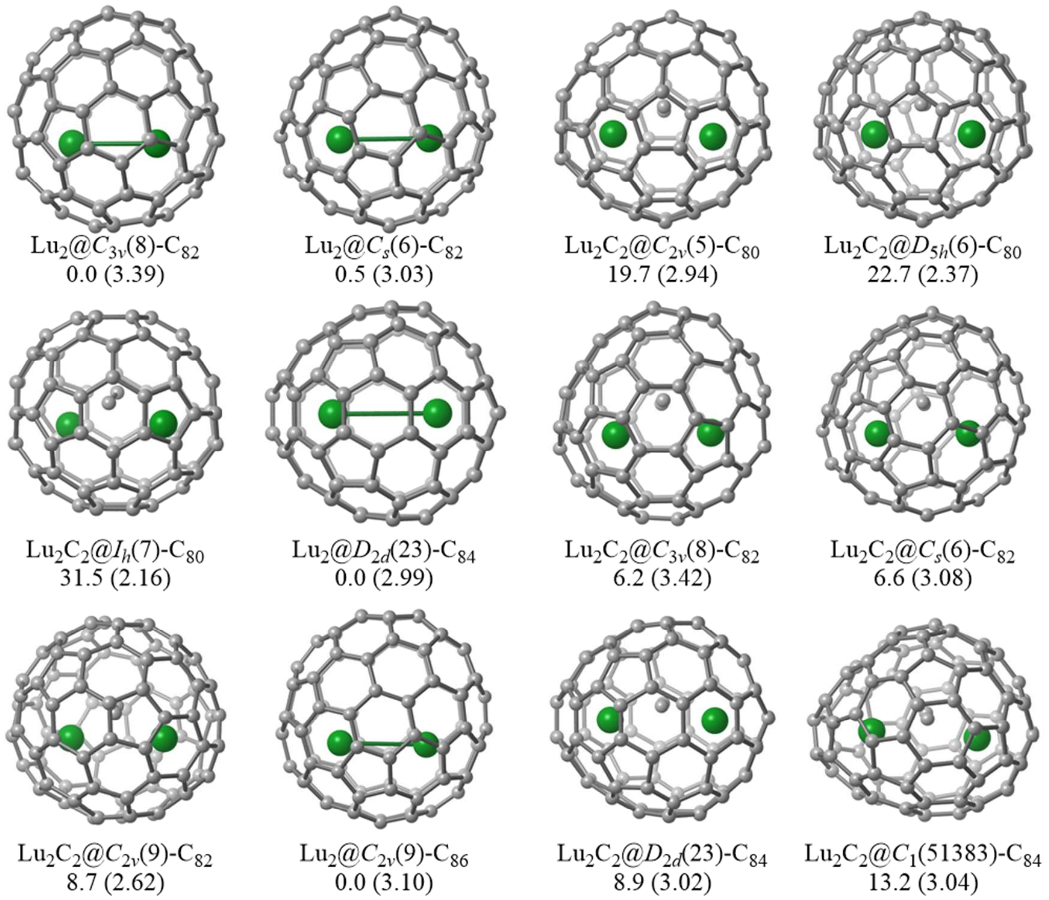
As for Lu element, which has a $[Xe]4f^{14}6s^25d^1$ electronic configuration and may keep its 6s electrons due to the relativistic contraction and excellent stabilization of the 6s atomic orbital.[39] The Lu_2 dimer has a triplet $(6s)\sigma_g^2(6s)\sigma_u^2(5d)\pi_u^2$ electronic structure with the σ_g^2 orbital much lower in energy than the σ_u^2 and π_u^2 molecular orbitals.[40] Natural bond order (NBO) analyses on the $Lu_2@C_{82\text{-}86}$ isomers demonstrate that the Lu atoms form a Lu-Lu single bond with electron occupancy of 1.97-1.98 *e*, which is supported by the calculated Wiberg bond orders (WBOs) ranging from 0.92 to 0.97 (Table 1). Consistent with the low-lying Lu_2 σ_g^2 molecular orbital, the hybrid compositions of Lu-Lu bonds reveal that the largest contribution to the metal bonding - molecular orbitals stems from the Lu-6s orbitals, and each Lu atom formally donates one 5d electron and one 6s electron to the cage with the 4f electrons remaining intact. It is also noteworthy that C_s(6)-C_{82}, C_{3v}(8)-C_{82} and D_{2d}(23)-C_{84} are all the lowest-lying isomers of the corresponding charged C_{2n}^{4-} cage, and they are thus suitable to encapsulate tetravalent metal species to form EMFs.[5,21] The C_{2v}(9)-C_{86} cage has large (LUMO+2)-(LUMO+1) gap energies and is very favorable to formally accept four electrons.[41] Accordingly, the above results strongly suggest that each $Lu_2@C_{82-86}$ isomer bears a $(Lu^{2+})_2@(C_{82-86})^{4-}$ electronic state, resulting in a formal divalent state for each Lu ion. On the other hand, the unoccupied Lu atomic orbitals (6p, 6d and 7p) have considerable electron populations, which are ascribed to their participation in the metal-metal bonding and/or the substantial electron back-donation from the occupied cage π orbitals (Table 1). Actually, our results are perfectly consistent with those from Zhao *et al*. and Popov *et al*. who independently proposed that a metal-metal bond may exist in dimetallofullerenes between two metal atoms with low valence states, [40,42,43] and our crystallographic results confirm unambiguously the presence of direct Lu-Lu bonding in $Lu_2@C_{82-86}$ isomers.

Table 1 Bond lengths ($R_{\text{Lu-Lu}}$, Å), Wiberg bond orders (WBOs), electron occupancies (Occ., *e*), natural population analysis (NPA) charges and natural electron configuration populations of the Lu-Lu single bonds in $Lu_2@C_{82-86}$ isomers. The Lu atoms are numbered from left to right in Figure S8.

Compound	**$R_{\text{Lu-Lu}}$**	**WBO**	**Occ.**	**Atom**	**Charge**	**Population**	**Hybrid Composition**
$Lu_2@C_s(6)$-C_{82}	3.60	0.96	1.97	Lu1	1.06	$6s^{0.54}5d^{0.30}6p^{0.62}$ $6d^{0.51}7p^{0.01}$	s(48%)p(35%)d(17%)
				Lu2	1.10	$6s^{0.62}5d^{0.19}6p^{0.55}$ $6d^{0.56}7p^{0.01}$	s(55%)p(31%)d(14%)
	3.47	0.97	1.98	Lu1	1.09	$6s^{0.55}5d^{0.20}6p^{0.59}$ $6d^{0.59}7p^{0.01}$	s(49%)p(35%)d(16%)

$Lu_2@C_{3v}(8)$-C_{82}				Lu2	1.10	$6s^{0.60}5d^{0.27}6p^{0.57}$ $6d^{0.48}7p^{0.01}$	s(53%)p(33%)d(14%)
$Lu_2@D_{2d}(23)$-C_{84}	4.00	0.92	1.97	Lu1	1.09	$6s^{0.63}5d^{0.31}6p^{0.16}$ $7s^{0.01}6d^{0.43}7p^{0.40}$	s(57%)p(30%)d(13%)
				Lu2	1.09	$6s^{0.63}5d^{0.31}6p^{0.16}$ $7s^{0.01}6d^{0.43}7p^{0.40}$	s(57%)p(30%)d(13%)
$Lu_2@C_{2v}(9)$-C_{86}	3.70	0.94	1.97	Lu1	1.11	$6s^{0.59}5d^{0.19}6p^{0.54}$ $6d^{0.58}7p^{0.01}$	s(53%)p(31%)d(16%)
				Lu2	1.07	$6s^{0.57}5d^{0.19}6p^{0.56}$ $6d^{0.62}7p^{0.01}$	s(52%)p(31%)d(17%)

Moreover, as for Lu-containing EMFs, Shinohara *et al.* proposed recently the structural formulas of $Lu_2C_2@C_{72}$, $Lu_2C_2@C_{74}$(I), $Lu_2C_2@C_{80}$, and $Lu_2C_2@C_{82}$(III) according to a linear relationship between the effective volume of the cage and the atom number.[32] Meanwhile, Zhao and coworkers reported the excellent stability of $Lu_2C_2@C_2(157)$-C_{96} and $Lu_2C_2@D_{2d}(163)$-C_{96} by DFT calculations.[33] However, we did not obtain any Lu-based CCMFs in our experiment. Accordingly, we investigated a series of possible $Lu_2C_2@C_{2n-2}$ isomers based on the reported low-energy C_{2n-2}^{4-} cages, including $C_{2v}(5)$-C_{80}, $D_{5h}(6)$-C_{80}, $I_h(7)$-C_{80}, $C_s(6)$-C_{82}, $C_{3v}(8)$-C_{82}, $C_{2v}(9)$-C_{82}, $D_{2d}(23)$-C_{84} and $C_1(51383)$-C_{84}. Figure 4 depicts their optimized structures and relative energies. It is evident that the carbide cluster isomers are more than 6 kcal/mol higher in energy than the corresponding $Lu_2@C_{82\text{-}86}$ isomers, suggesting that the dominating formation of di-EMFs is thermodynamically very favorable.



$Lu_2@C_{3v}(8)$-C_{82} 0.0 (3.39)

$Lu_2@C_s(6)$-C_{82} 0.5 (3.03)

$Lu_2C_2@C_{2v}(5)$-C_{80} 19.7 (2.94)

$Lu_2C_2@D_{5h}(6)$-C_{80} 22.7 (2.37)

$Lu_2C_2@I_h(7)$-C_{80} 31.5 (2.16)

$Lu_2@D_{2d}(23)$-C_{84} 0.0 (2.99)

$Lu_2C_2@C_{3v}(8)$-C_{82} 6.2 (3.42)

$Lu_2C_2@C_s(6)$-C_{82} 6.6 (3.08)

$Lu_2C_2@C_{2v}(9)$-C_{82} 8.7 (2.62)

$Lu_2@C_{2v}(9)$-C_{86} 0.0 (3.10)

$Lu_2C_2@D_{2d}(23)$-C_{84} 8.9 (3.02)

$Lu_2C_2@C_1(51383)$-C_{84} 13.2 (3.04)

Figure 4. Optimized structures of $Lu_2@C_{82\text{-}86}$ isomers and their corresponding low-energy $Lu_2C_2@C_{80\text{-}84}$ isomers with relative energies (kcal/mol) and HOMO-LUMO gap energies (eV, in parenthesis).

CONCLUSIONS

In summary, four unprecedented EMFs containing lutetium atoms have been isolated and structurally determined to be di-EMFs, namely $Lu_2@C_s(6)$-C_{82}, $Lu_2@C_{3v}(8)$-C_{82}, $Lu_2@D_{2d}(23)$-C_{84} and $Lu_2@C_{2v}(9)$-C_{86} by single-crystal XRD crystallography. Our experimental and theoretical results reveal that a Lu-Lu single bond is formed between the two lutetium ions which transfer four electrons in total to the fullerene cages, thus resulting in a formal divalent state for each Lu ion. Moreover, our theoretical calculations unambiguously reveal that the dominating formation of di-EMFs are thermodynamically very favorable for Lu-containing EMFs because of the formation of a metal-metal bond. Our study has not only added four new members to the less-explored di-EMFs family, but also confirms that the metal−metal bonding can be achieved when the metals adopt low valence states inside fullerene cages, which may be a result from the strong reductive atmosphere of carbon plasma during the arc-discharging process.

EXPERIMENTAL SECTION

Synthesis and Isolation of $Lu_2C_{82\text{-}86}$. Soot containing Lu-EMFs was synthesized by a direct current arc discharge method and was extracted using carbon disulfide. After removal of CS_2, the residue was dissolved in toluene and the solution was subjected to a three-stage high-performance liquid chromatography (HPLC) separation. Further experimental details are described in Supporting Information.

Single-Crystal XRD Measurements of $Lu_2C_{82\text{-}86}$. Crystalline blocks of $Lu_2C_{82\text{-}86}$ were obtained by layering a benzene or a chloroform solution of Ni^{II}(OEP) over a nearly saturated solution of the respective endohedral in CS_2 in a glass tube. Over a 20-day period, the two solutions diffused together, and black crystals formed. XRD measurements were performed at 173 K on a Bruker D8 QUEST machine equipped with a CMOS camera (Bruker AXS Inc., Germany). The multiscan method was used for absorption corrections. The structures were solved by direct method and were refined with SHELXL-2014/7[44]. CCDC-1539295 ($Lu_2@C_s(6)\text{-}C_{82}$), CCDC-1539296 ($Lu_2@C_{3v}(8)\text{-}C_{82}$), CCDC-1539297 ($Lu_2@D_{2d}(23)\text{-}C_{84}$) and CCDC-1539298 ($Lu_2@C_{2v}(9)\text{-}C_{86}$) contain the supplementary crystallographic data for this paper. Details of the structural refinement can be found in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at http://pubs.acg.org.

Additional crystal data for $Lu_2@C_s(6)\text{-}C_{82}\bullet Ni^{II}(OEP)\bullet 2(C_6H_6)$

Additional crystal data for $Lu_2@C_{3v}(8)\text{-}C_{82}\bullet Ni^{II}(OEP)\bullet 0.84(CHCl_3)\bullet 1.16(CS_2)$

Additional crystal data for $Lu_2@D_{2d}(23)\text{-}C_{84}\bullet Ni^{II}(OEP)\bullet 2(CHCl_3)$

Additional crystal data for $Lu_2@C_{2v}(9)-C_{86}•Ni^{II}(OEP)•2(CHCl_3)$

Experimental details, HPLC retention time and details of the vis-NIR spectra of $Lu_2@C_{82–86}$, crystallographic solution of $Lu_2@C_{82–86}$, the X-ray results of $Lu_2@C_{82–86}$, redox potentials (V vs Fc/Fc^+) of $Lu_2@C_s(6)-C_{82}$ and $Lu_2@C_{2v}(9)-C_{86}$ and optimized geometries of Lu_2C_{82-86} isomers.

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Notes

The authors declare no competing financial interests.

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