Supporting Information for

Stabilizing non-IPR C_2(13333)-C_{74} cage with Lu_2C_2/Lu_2O: the importance of encaged non-metal elements

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Experimental

Preparation

The core-drilled graphite rods filled with a homogeneous mixture of graphite powder and Lu_2O_3 (molar ratio of M/C = 1:17) were annealed in a tube furnace at 1000 °C for 12 hours under argon atmosphere. The rods were then vaporized in a Krätschmer-Huffman-type fullerene generator with an arc current of 100 A under a mixture of 270 Torr helium and 15 Torr CO_2 atmospheres. The as-produced fullerene soot was collected and sonicated in carbon disulfide for 1h. After filtration, CS_2 was removed using a rotary evaporator. The solid residue was dissolved in toluene and filtered.

High-performance Liquid Chromatography (HPLC) Separation Processes

$Lu_2C_2@C_2(13333)$-C_{74} and $Lu_2O@C_2(13333)$-C_{74} were isolated by a multiple-stage HPLC process using toluene as eluent. The first stage was performed on a Buckyprep column (20 mm × 250 mm, Cosmosil Nacalai Tesque), and a fraction named as Fr5 was collected (Fig. S1a). Then, Fr5 was injected into a Buckyprep-M column (20 mm × 250 mm, Cosmosil Nacalai Tesque) for the second stage separation, and a fraction named as Fr5-2 was obtained (Fig. S1b). Fr5-2 was injected into a Buckyprep column (20 mm × 250 mm, Cosmosil Nacalai Tesque), and a fraction named as Fr5-2-3 was collected (Fig. S1c). As for Fr5-2-3, a 5PYE column (20 mm × 250 mm, Cosmosil Nacalai Tesque) was used for the separation, and a fraction named as Fr5-2-3-1 was obtained (Fig. S1d). After that, Fr5-2-3-1 was injected a Buckyprep-M column (10 mm × 250 mm, Cosmosil Nacalai Tesque), and a fraction named as Fr5-2-3-1-1 was collected along with pure $Lu_2C_2@C_2(13333)$-C_{74} (Fr5-2-3-1-3) was obtained (Fig. S1e). As for Fr5-2-3-1-1, a Buckyprep column (20 mm × 250 mm, Cosmosil Nacalai Tesque) was used for the last stage separation, and pure $Lu_2O@C_2(13333)$-C_{74} was finally obtained (Fig. S1f).

Spectroscopic and electrochemical studies

LDI-TOF mass spectrometry was conducted on a BIFLEX III spectrometer (Bruker Daltonics Inc., Germany). Vis-NIR spectra were measured on a Lambda 35 spectrophotometer (PerkinElmer, USA) in CS_2. CV curves were obtained in *o*-

dichlorobenzene with 0.05 M $TBAPF_6$ as electrolyte using a CHI-660E instrument.

Crystallographic characterizations

Crystalline blocks of $Lu_2C_2@C_2(13333)$-C_{74} and $Lu_2O@C_2(13333)$-C_{74} were obtained by layering a benzene solution of Ni^{II}(OEP) over a carbon disulfide solution of the endohedral in a glass tube, respectively. Single-crystal XRD measurements were performed at 100 K using synchrotron radiation (λ= 0.71073 Å) with a MarCCD detector at beamline BL17B station of Shanghai Synchrotron Radiation Facility. The multiscan method was used for absorption corrections. The structures were solved by direct method and were refined with SHELXL-2014. Hydrogen atoms were inserted at calculated positions and constrained with isotropic thermal parameters. Details of crystal data are listed in ESI. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre with CCDC Nos. 2268031 and 2268032.

Computational studies

The optimizations of $Lu_2C_2@C_2(13333)$-C_{74} and $Lu_2O@C_2(13333)$-C_{74} were carried out on the PBE0/6-31G(d)~SDD level without any imaginary frequency, where 6-31G(d) was for carbon and oxygen atoms and SDD with pseudopotential was for lutetium atoms. All of the above calculations were performed with Gaussian 16 software except for the specific illustration.

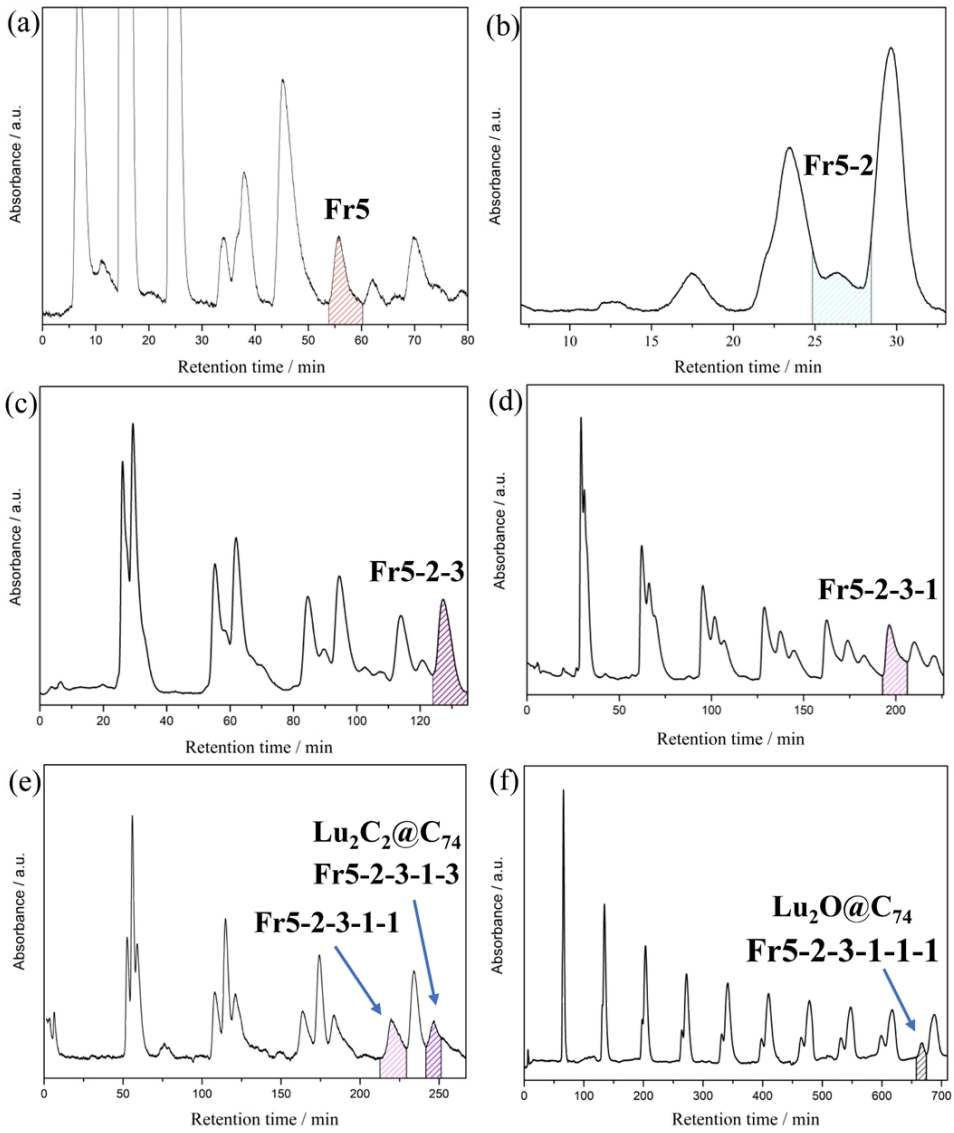

Figure S1. Isolation schemes of $Lu_2C_2@C_2$(13333)-C_{74} and $Lu_2O@C_2$(13333)-C_{74}. (a) HPLC profile of soot extract containing Lu-based metallofullerene on a Buckyprep column. Conditions: 20 mL injection volume; 10 mL/min toluene flow. (b) HPLC chromatogram of Fr5 on a Buckyprep-M column. Conditions: 20 mL injection volume; 10 mL/min toluene flow. (c) Recycling HPLC profile of Fr5-2 on a Buckyprep column. Conditions: 15 mL injection volume; 10 mL/min toluene flow. (d) Recycling HPLC profile of Fr5-2-3 on a 5PYE column. Conditions: 10 mL injection volume; 10 mL/min toluene flow. (e) Recycling HPLC profile of Fr5-2-3-1 on a Buckyprep-M column. Conditions: 10 mL injection volume; 10 mL/min toluene flow. (f) Recycling HPLC profile of Fr5-2-3-1-1 on a Buckyprep column. Conditions: 10 mL injection volume; 10 mL/min toluene flow. (All of the detection wavelengths are 330 nm.)

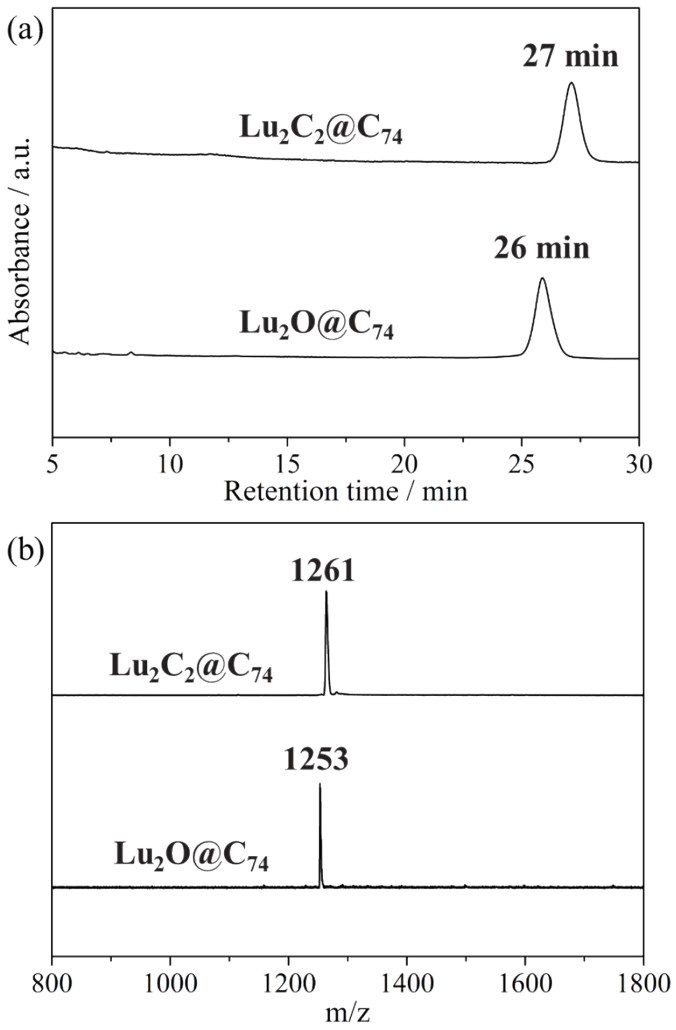

Figure S2. (a) HPLC chromatograms and (b) LDI-TOF mass spectra of $Lu_2C_2@C_{74}$ and $Lu_2O@C_{74}$. HPLC conditions: Buckyprep column (Ø = 4.6 × 250 mm); 20 μL injection volume; 1 mL min^{-1} toluene flow; 330 nm detection wavelength; 40 °C.

Table S1. Crystallographic data of $Lu_2C_2@C_2(13333)$-C_{74}·Ni^{II}(OEP)·2(C_6H_6)·CS_2 and $Lu_2O@C_2(13333)$-C_{74}·Ni^{II}(OEP)·2(C_6H_6)·CS_2.

	$Lu_2C_2@C_2(13333)$-C_{74}·Ni^{II}(OEP)·2(C_6H_6)·CS_2	**$Lu_2O@C_2(13333)$-C_{74}·Ni^{II}(OEP)·2(C_6H_6)·CS_2**
***T*, K**	100(2)	100(2)
***λ*, Å**	0.71073	0.71073
color/habit	black/block	black/block
cryst size, mm	0.08×0.06×0.04	0.08×0.06×0.06
empirical formula	$C_{244}H_{106}Lu_4N_8S_4Ni_2$	$C_{240}H_{106}Lu_4N_8S_4Ni_2O_2$
fw	4094.90	4078.79
cryst system	monoclinic	monoclinic
space group	*C*2/*m*	*C*2/*m*
***a*, Å**	25.898(3)	25.811(3)
***b*, Å**	16.702(2)	16.724(2)
***c*, Å**	17.940(2)	17.817(2)
***α*, deg**	90	90
***β*, deg**	106.615(4)	106.529(4)
***γ*, deg**	90	90
***V*, Å^3**	7435.7(17)	7734.3(4)
Z	2	2
***ρ*, g/cm^3**	1.829	1.837
***μ*, mm^{-1}**	3.010	3.036
***R*$_1$ [I > 2\σ(I)]**	0.0724(5410)	0.0830(5268)
***wR*$_2$ (all data)**	0.2404(6963)	0.2775(6953)

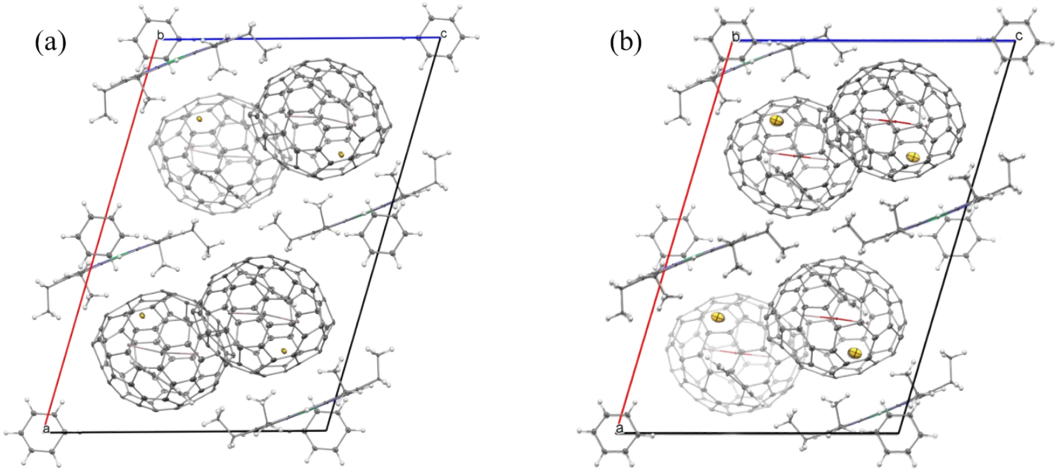

Figure S3. Packing structures of (a) $Lu_2C_2@C_2(13333)$-C_{74}·Ni^{II}(OEP)·2(C_6H_6)·CS_2 and (b) $Lu_2O@C_2(13333)$-C_{74}·Ni^{II}(OEP)·2(C_6H_6)·CS_2.

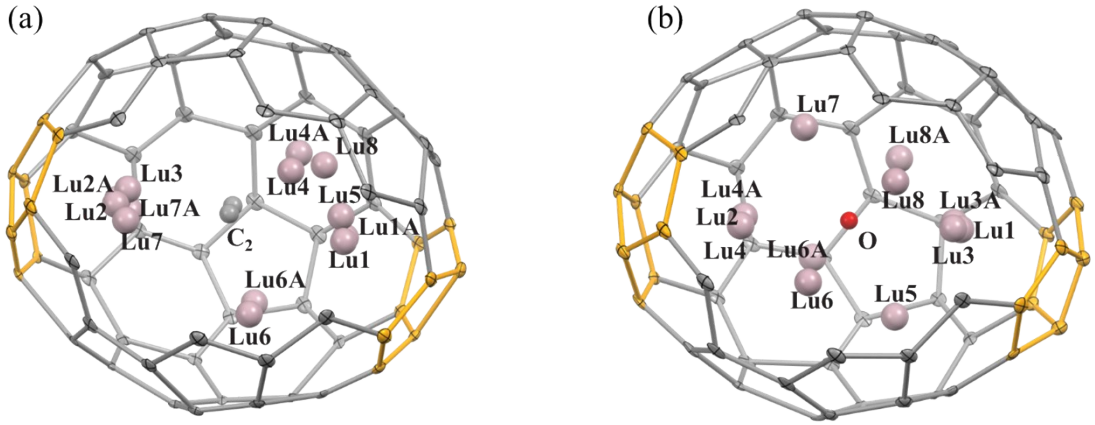

Figure S4. Positions of the disordered metal sites in (a) $Lu_2O@C_s(6)$-C_{82} and (b) $Er_2O@C_s(6)$-C_{82} relative to the cage orientation. The metal sites labeled with "A" are generated by crystallographic operation and a part of the cages are omitted for clarity.

Table S2. The fractional occupancies of the metal positions in $Lu_2O@C_s(6)$-C_{82} and $Er_2O@C_s(6)$-C_{82}.

Compounds	**Fractional occupancy of the metal positions**							
$Lu_2C_2@C_2(13333)$-C_{74}	Lu1/Lu1A	Lu2/Lu2A	Lu3	Lu4/Lu4A	Lu5	Lu6/Lu6A	Lu7/Lu7A	Lu8
	0.35	0.33	0.11	0.08	0.08	0.08	0.05	0.02
$Lu_2O@C_2(13333)$-C_{74}	Lu1	Lu2	Lu3/Lu3A	Lu4/Lu4A	Lu5	Lu6/Lu6A	Lu7	Lu8/Lu8A
	0.31	0.50	0.22	0.12	0.09	0.07	0.05	0.10

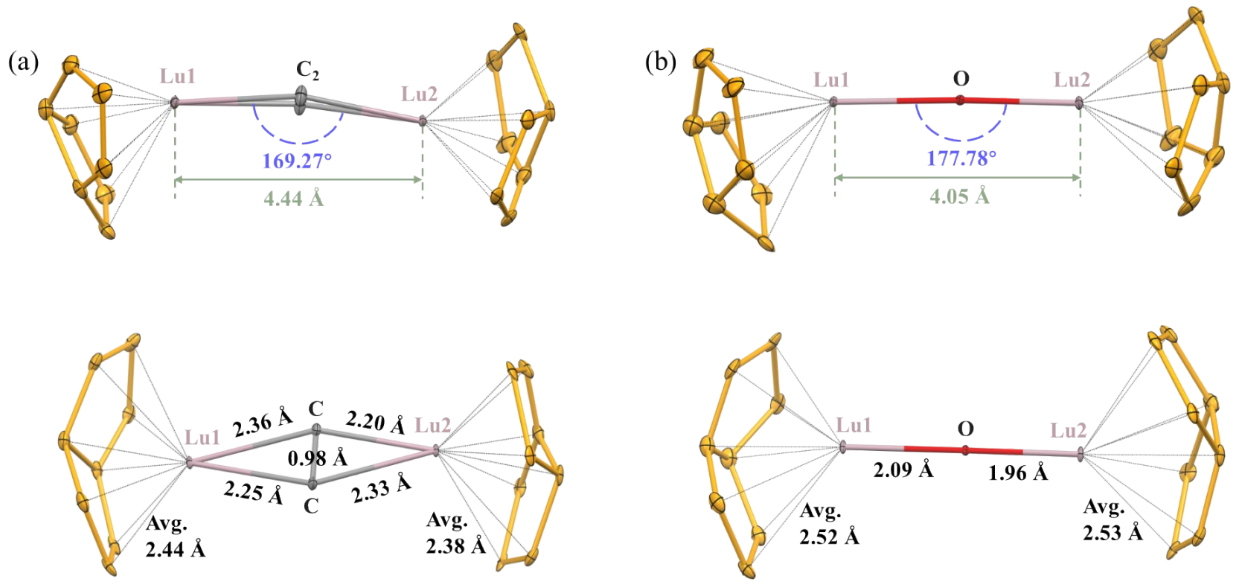

Figure S5. Structures of the major Lu metal sites with respect to the neighboring fused pentagons in (a) $Lu_2C_2@C_2(13333)$-C_{74} and (b) $Lu_2O@C_2(13333)$-C_{74}.

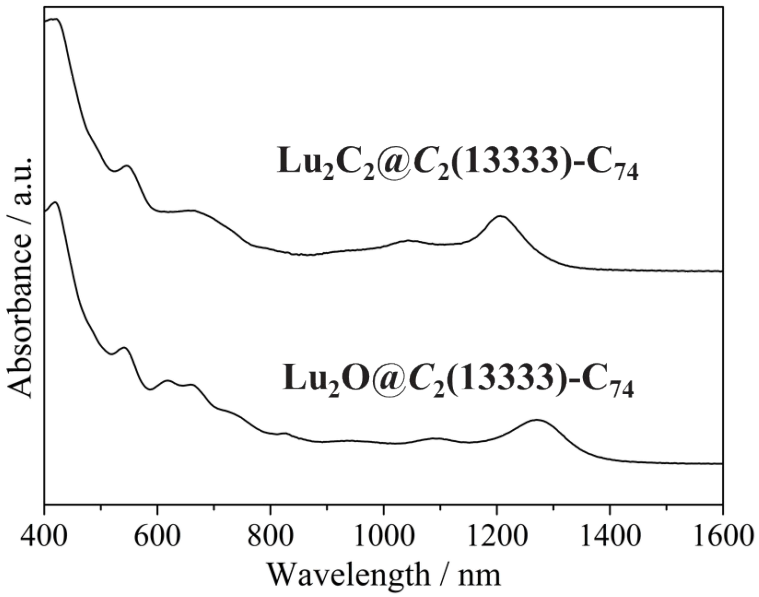

Figure S6. Vis-NIR absorption spectra of $Lu_2C_2@C_2(13333)\text{-}C_{74}$ and $Lu_2O@C_2(13333)\text{-}C_{74}$ dissolved in CS_2 at room temperature.

Table S3. Characteristic absorption data of $Lu_2C_2@C_2(13333)\text{-}C_{74}$ and $Lu_2O@C_2(13333)\text{-}C_{74}$.

Componds	Absorption peaks (nm)	Absorption onset (λ_{onset}, nm)	$\Delta E_{gap,\ optical}$ / eV[a]
$Lu_2C_2@C_2(13333)\text{-}C_{74}$	546, 667, 1042	1324	0.94
$Lu_2O@C_2(13333)\text{-}C_{74}$	542, 618, 663, 1089	1380	0.90

[a]$\Delta E_{gap,\ optical} = 1240/\lambda_{onset}$