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Supporting Information for

Crystallographic Determination of Lu@C2v(9)-C82: Electronic Configuration and Encapsulation Energy-Driven Formation Preference

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Experimental

Preparation of Lu@C_{82}

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

High-performance Liquid Chromatography (HPLC) Separation Processes

Lu@C_{82} was isolated through a multi-stage HPLC procedure using toluene as eluent. The first stage was performed with a Buckyprep column (20 mm × 250 mm, Cosmosil Nacalai Tesque), affording a fraction named Fr6 (Fig. S1-1). Then, Fr6 was injected into a Buckyprep column (20 mm × 250 mm, Cosmosil Nacalai Tesque) for the second stage separation, and a fraction named as Fr6-4 was obtained (Fig. S1-2a). Finally, purification using a 5PBB column (20 mm × 250 mm, Cosmosil Nacalai Tesque) afforded pure Lu@C_{82} (Fig. S1-2b).

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

Crystallographic characterizations

Single crystal of Lu@C_{2v}(9)-C_{82} was obtained by layering a benzene solution of Ni^{II}(OEP) over a carbon CS_2 of the endohedral compound. X-ray diffraction data was collected at 100 K using synchrotron radiation (λ= 0.71073 Å) with a MarCCD detector at beamline BL17B station of Shanghai Synchrotron Radiation Facility. The multi-scan method was used for absorption corrections. The structure was solved by direct method and was refined with SHELXL-2014. Hydrogen atoms were inserted at calculated positions and constrained with isotropic thermal

parameters. Details of crystal data are listed in Table S1, and CIF files are available from The Cambridge Crystallographic Data Centre with CCDC Nos

Computational studies

Geometry optimization of Lu@C_{2v}(9)-C_{82} was carried out on the PBE0/6-31G(d)~SDD level without any imaginary frequency. The 6 31G(d) basis set was used for C and O atoms, while the SDD basis set with pseudopotentials was applied for Lu. All of the above calculations were performed with Gaussian 16 software except for the specific illustration.

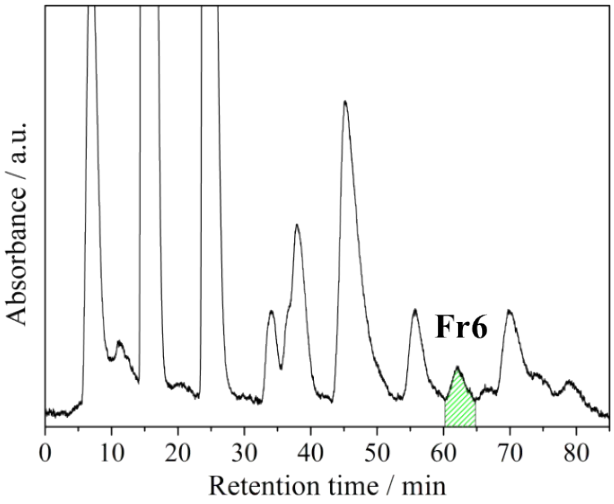

Figure S1. Isolation scheme of fullerene extract on a Buckyprep column. Conditions: inject volume of 20 mL; toluene flow of 10 mL/min; detection wavelength of 330 nm

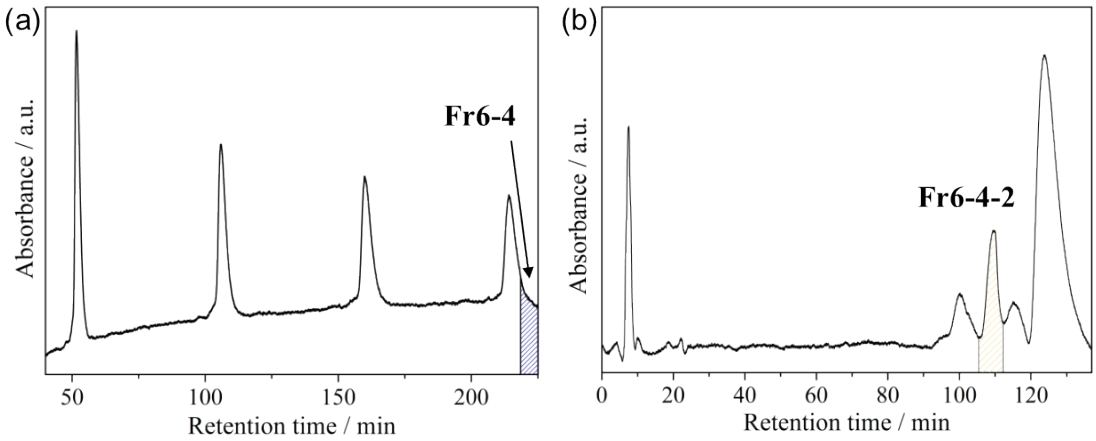

Figure S2. (a) HPLC chromatogram of Fr6 in Buckyprep column. Parameters: operating volume of 15 mL; toluene flow rate of 10 mL/min; (b) Isolation scheme of Fr6-4 in 5PBB column. Parameters: operating volume of 10 mL; toluene flow of 10 mL/min. All detection wavelengths are 330 nm

Table S1. Crystallographic data of Lu@C_{2v}(9)-C_{82}·Ni^{II}(OEP)

	Lu@C_{2v}(9)-C_{82}•Ni^{II}(OEP)·1.5(C_6H_6)
***T*, K**	100(2)
***λ*, Å**	0.61250
color / habit	black / block
crystal size, mm	0.08×0.06×0.04
empirical formula	$C_{130}H_{56}LuN_4Ni$
fw	1907.46
crystal system	monoclinic
space group	*C*2/*m*
***a*, Å**	25.2393(18)
***b*, Å**	15.1444(11)
***c*, Å**	19.8378(14)
***α*, deg**	90
***β*, deg**	94.756(2)
***γ*, deg**	90
***V*, Å^3**	7544.8(7)
Z	4
***ρ*, g/cm^3**	1.677
***μ*, mm^{-1}**	1.102
***R*$_1$ [I > 2\σ(I)]**	0.0862
***wR*$_2$ (all data)**	0.2458

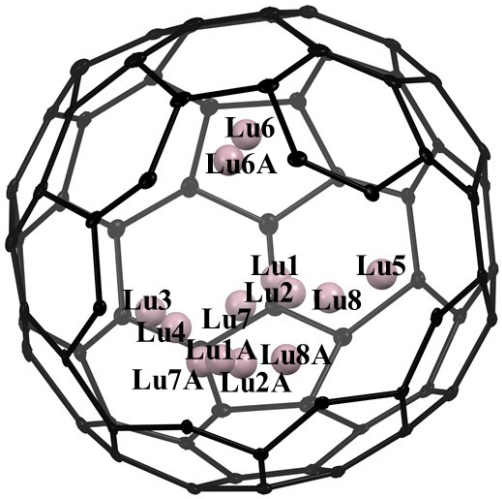

Figure S3. Disordered positions of the Lu atoms within Lu@C_{2v}(9)-C_{82} relative to a cage orientation. Position labeled with "A" of Lu atoms are obtained by crystallographic symmetry operation; some atoms on the cage are omitted for clarity

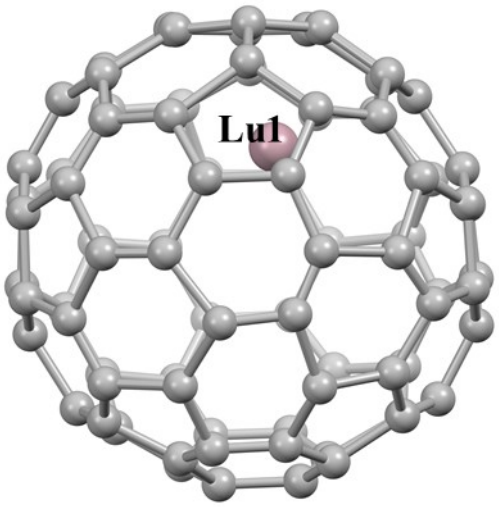

Figure S4. Location of Lu metal inside Lu@C_{2v}(9)-C_{82}

Table S2. Occupancies of all disordered Lu metal sites in Lu@C_{2v}(9)-C_{82}

EMFs	Occupancies of all disordered Lu metal sites			
	Lu1/Lu1A	Lu2/Lu2A	Lu3	Lu4
Lu@C_{2v}(9)-C_{82}	0.16	0.14	0.10	0.06
	Lu5	Lu6/Lu6A	Lu7/Lu7A	Lu8/Lu8A
	0.06	0.04	0.03	0.02

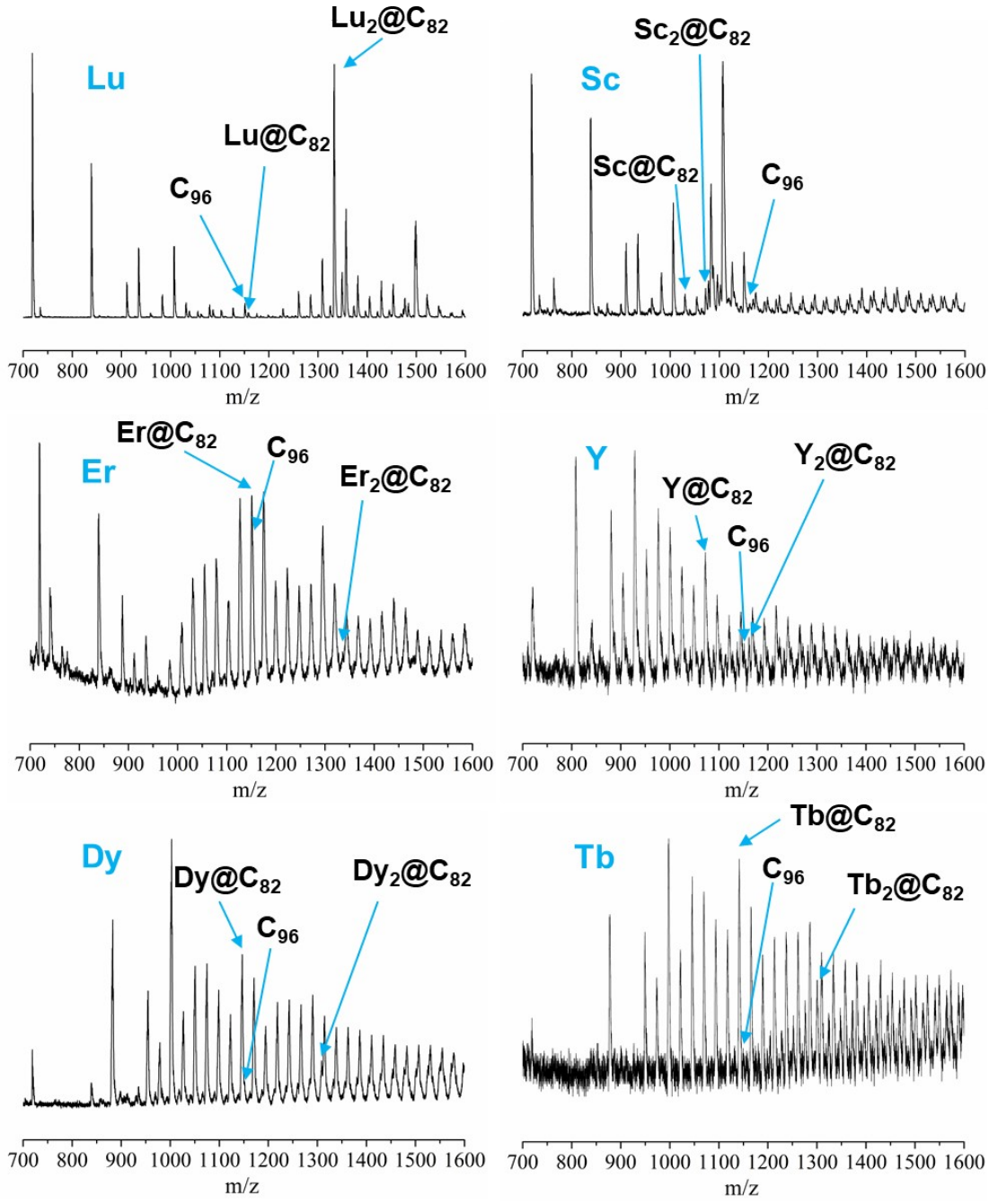

Figure S5. LDI-TOF mass spectra of fullerene raw soot containing different rare earth metal