**An Anomalous Endohedral Structure of Eu@C\textsubscript{82}**

**Metallofullerenes**

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S1: The relative yields of the three isomers

The relative yields of isomers of divalent metallofullerenes are not so different with each other as in the case of trivalent metallofullerenes. Three or four isomers, such as Eu@C\textsubscript{82}(I, II, III),\textsuperscript{[2c]} Tm@C\textsubscript{82}(I, II, III),\textsuperscript{[2a]} Sm@C\textsubscript{82}(I, II, III),\textsuperscript{[12a]} and Ca@C\textsubscript{82}(I, II, III,?)\textsuperscript{[12b,12c]} have been isolated in similar amounts, whereas one isomer (C\textsubscript{2v}) tends to be more abundant than other isomers in trivalent metallofullerenes. In this study, three isomers of Eu@C\textsubscript{82} have been isolated, in which Eu@C\textsubscript{82} with C\textsubscript{2v} symmetry (i.e., Eu@C\textsubscript{82}(III)) is the most abundant isomer as in the case of the trivalent C\textsubscript{82}-caged mono-metallofullerenes. The second most abundant isomer for Eu metallofullerenes, Eu@C\textsubscript{82}(I), has been determined to possess C\textsubscript{s}(No.6) symmetry. Eu@C\textsubscript{82}(II), which is considered to have C\textsubscript{2} symmetry,\textsuperscript{[2c]} is the least abundant among the three isomers. The XRD structure determination of this isomer has not yet been successful.

S2: Experimental section

Eu@C\textsubscript{82}(I, III) were synthesized and isolated by the methods described before.\textsuperscript{[2c]} In brief, the soot containing Eu-metallofullerenes was produced by the DC arc discharge method at 400 A under a 10 l/min He flow using Eu/Ni/C composite rods (15×15×
300mm, 0.8/1.6 at.% Eu/Ni/C, 1200°C annealed, Toyo Tanso Co. Ltd.) as the anodes. The raw soot was extracted by the high-temperature DMF method. The isolation of Eu@C$_{82}$(I, III) was achieved by the multi-step HPLC separation (LC-908-C60, Japan Analytical Industry) using a 5PYE column (20×250mm, Nakalai Tesque), a Buckyprep column (20×250 mm, Nakalai Tesque) and a Buckyclutcher column (21×500 mm, Regis Chemical). Toluene was used as the mobile phase with a 312nm UV detection. The purity was determined to be higher than 99.9% by both positive and negative LD-TOF mass spectrometry (Shimadzu Kratos MALDI-4).

Eu@C$_{82}$(isomers I and III) powders were grown from toluene solution and were then sealed in silica glass capillaries (0.3mm inner diameter). The synchrotron X-ray powder diffraction experiment at room temperature (300K) was performed at SPring-8 BL02B2 using an imaging plate (IP) as the detector. The exposure time on the IP for isomers I and III of Eu@C$_{82}$ was 100min and 180min, respectively. The wavelength of the incident X-ray was 1.00084(5) Å. The X-ray powder patterns of Eu@C$_{82}$ (I, III) were collected with a 0.01°step up to 2θ =36.6°for isomer I and 34.3°for isomer III, which correspond to 1.594 Å and 1.695 Å resolution in the d-spacing, respectively.

