Electronic Supplementary Material (ESI) for ChemComm.

Crystallographic and spectroscopic characterization of a mixed actinide-lanthanide carbide cluster stabilized inside an $I_h(7)$-C_{80} fullerene cage

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Experimental Details

Synthesis of $Sc_2UC@I_h(7)$-C_{80}. A modified Krätschmer-Huffman DC arc-discharge method was applied for the synthesis of $Sc_2UC@I_h(7)$-C_{80}. In a typical process, 1.27 g of U_3O_8 powder, 0.61g of Sc_2O_3 powder, and 1.62g of graphite powder (molar ratio of U/Sc/C = 1:2:30) were packed in each drilled carbon rod. The filled rods were vaporized under a He atmosphere of 200 Torr and 1 Torr NH_3. Totally, 50 rods were vaporized and ca. 2.0 g crude fullerene extract was obtained(ca. 40mg per rod), out of which ca. 0.5 mg $Sc_2UC@I_h(7)$-C_{80} was finally isolated. Besides $Sc_2UC@I_h(7)$-C_{80}, uranium-based EMFs $U@C_{2n}$ and $Sc_3N@C_{2n}$ are also formed along with empty fullerenes during the arcing process.

High-performance liquid chromatography (HPLC) separation process of $Sc_2UC@I_h(7)$-C_{80}. The first stage was performed on a Buckyprep-M column (25 mm × 250 mm, Cosmosil Nacalai Tesque) with toluene as mobile phase. After that, as shown in Figure S1, fraction from 37 to 42 min (marked in red) was re-injected into a Buckyprep column (10 mm × 250 mm, Cosmosil Nacalai Tesque) for the second stage separation using toluene as the eluent. The fraction marked in blue was collected. The third stage of separation was conducted on a Buckyprep-D column (10 mm × 250 mm, Cosmosil Nacalai Tesque) using toluene as the eluent. The fraction marked in green was collected. The final stage of separation was conducted on a Buckyprep column with toluene as mobile phase and pure $Sc_2UC@I_h(7)$-C_{80} was got. The purity of the isolated $Sc_2UC@I_h(7)$-C_{80} was then re-confirmed by chromatography on a Buckyprep column (10mm × 250mm, Cosmosil Nacalai Tesque) with toluene at a flow rate of 4.0 mL/min, along with the MALDI-TOF mass spectrometry in a positively charged mode (Figure 1).

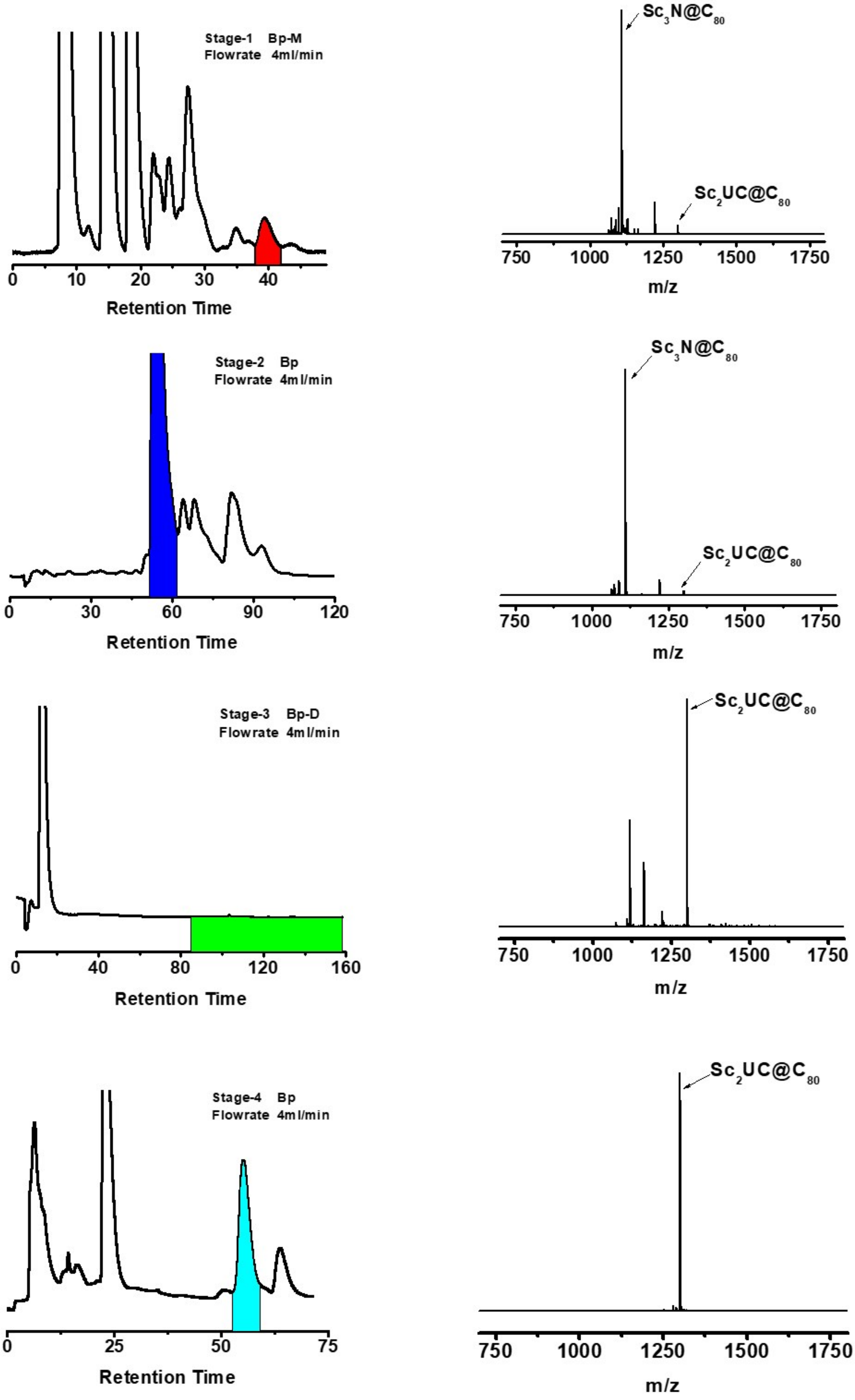

Figure S1. HPLC profiles showing the separation procedures of $Sc_2UC@I_h(7)$-C_{80}(left) and the corresponding MALDI-TOF mass spectra (right).

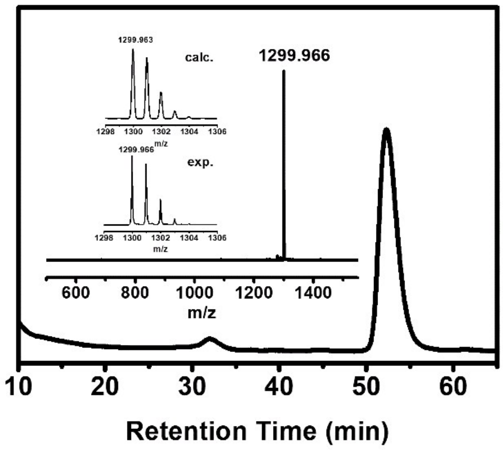

Figure S2. HPLC chromatogram of purified Sc$_2$UC@I_h(7)-C$_{80}$ on a Buckyprep column with toluene as the eluent. (HPLC condition: λ = 310 nm, flow rate: 4 mL/min. The insets show the positive-ion mode MALDI-TOF mass spectra and expansions of the corresponding experimental isotopic distributions of Sc$_2$UC@I_h(7)-C$_{80}$ in comparison with the theoretical ones.).

Spectroscopic and Electrochemical Studies. The positive-ion mode matrix-assisted laser desorption/ionization time-of-flight (Bruker, Germany) was employed for the mass characterization. The UV-vis-NIR spectra of the purified Sc$_2$UC@I_h(7)-C$_{80}$ were measured in CS$_2$ solution with a Cary 5000 UV-vis-NIR spectrophotometer (Agilent, USA). The Raman spectra were obtained using a Horiba Lab RAM HR Evolution Raman spectrometer using a laser at 633 nm. The Micro Fourier transform infrared spectra were recorded at room temperature by a Vertex 70 spectrometer (Bruker, Germany) with a resolution of 4 cm^{-1}. For the IR and Raman measurements, the samples were drop-coated on aluminized paper and a quartz plate, respectively. The residual CS$_2$ was removed in a drying chamber in vacuum at 40℃. Cyclic voltammetry (CV) was obtained in o-dichlorobenzene using a CHI-660E instrument. A conventional three-electrode cell consisting of a platinum counter-electrode, a glassy carbon working electrode, and a silver reference electrode was used for the measurement. (n-Bu)$_4$NPF$_6$ (0.05 M) was used as the supporting electrolyte. The CV was measured at a scan rate of 100 mV/s.

X-ray Crystallographic Study. The black block crystals of Sc$_2$UC@I_h(7)-C$_{80}$·[Ni^{II}-(OEP)] were obtained by slow diffusion of a carbon disulfide solution of Sc$_2$UC@I_h(7)-C$_{80}$ into a benzene solution of [Ni^{II}-(OEP)]. Single-crystal X-ray data of Sc$_2$UC@I_h(7)-C$_{80}$ were collected using synchrotron radiation (0.77491 Å) with a MX300-HE CCD detector at beamline BL17B at Shanghai Synchrotron Radiation Facility (SSRF). The multi-scan method was used for absorption correction. The structures were solved using intrinsic phasing method and refined by the full-matrix method based on F^2 using SHELXL-2018 software package within Olex2 software.[1, 2] All the non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were generated by riding model. The crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre (CCDC) with the deposition number 1965581.

Crystal data for Sc$_2$UC@I_h(7)-C$_{80}$.[Ni^{II}-(OEP)]·2C$_6$H$_6$: M_r = 2007.91, 0.15 mm × 0.12 mm × 0.1 mm, monoclinic, $C2/c$ (No. 15), a = 25.2486(5) Å, b = 15.0232(3) Å, c = 39.5120(8) Å, α = 90°, β = 95.3650(10)°, γ = 90°, V = 14921.8(5) Å^3, Z = 8, ρ_{calcd} = 1.788 g • cm^{-3}, μ = 1.549 mm^{-1}, θ = 1.722 − 28.573, T = 273(2) K, R_1/wR_2 = 0.0828/0.1994 for all data; R_1/wR_2 = 0.0724/0.1897 for 14620 reflections (I >= 2σ(I)) with 1327 parameters, Goodness-of-fit indicator = 1.038, Maximum residual electron density = 1.314 e·Å^{-3}.

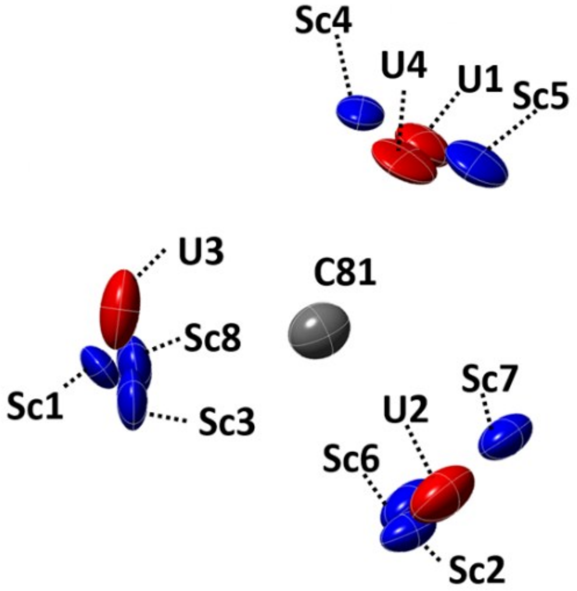

Figure S3. The perspective drawing showing the disorder of U and Sc in the Sc_2UC cluster.

Table S1. Occupancy of disordered U and Sc sites.

Atoms	U1, Sc1, Sc2	U2, Sc3, Sc4	U3, Sc5, Sc6	U4, Sc7, Sc8
Occupancy	0.588(2)	0.1419(15),	0.1102(14)	0.0368(12)

Table S2. Bond lengths and bond angles of the Sc_2UC cluster in the major orientation.

	U1-C81	Sc1-C81	Sc2-C81
Length (Å)	2.011(5)	2.053(6)	2.060(6)
	U1-C81-Sc1	U1-C81-Sc2	Sc1-C81-Sc2
Angle (°)	127.4(3)	127.5(3)	105.0(3)

References

[1] Sheldrick, G.M. *Acta Cryst. C* 2015, **71**, 3-8.

[2] Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. *J. Appl. Cryst.* 2009, **42**, 339-341.