Supporting Information

Synthesis of crown ether-capped highly symmetrical fluoride-centered lanthanide clusters $[Ln_6F_{13}(12\text{-crown-}4)_6]I_3F_2$ (Ln = Ho, Er)

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I. **Experimental Procedures**

General information

All the reactions were carried out using modified Schlenk-line and Ar-atmosphere glove box (<1 ppm O_2/H_2O) techniques. CH_3CN and Et_2O dried and degassed through a Vigor solvent purification system as well as CD_3CN were stored over 4 Å sieves for 24 h under argon atmosphere before use. Elemental analyses (C, H, N) were performed on a Vario EL III elemental analyser. The powder X-ray diffraction patterns were collected on a Rigaku Synergy R (Cu Kα) diffractometer at 180 K. The powder wrapped in inert oil was cooled under a cold stream of nitrogen, and CrysAlisPro software was used for data collection and integration. All NMR spectra were recorded on a Zhongke-Niujin Quantum-I Plus 400 spectrometer (Zhongke-Niujin, Wuhan, China). ^{19}F NMR spectra were referenced to external $CFCl_3$ (δ = 0). Due to the paramagnetic nature of trivalent holmium and erbium, conclusive ^{1}H and ^{13}C NMR data of complexes **1-3** could not be obtained. The X-ray photoelectron spectra (XPS) were recorded on a ThermoFisher Scientific ESCALAB Xi^{+} spectrometer. The charging effect and corresponding binding energy shift for all the elements have been calibrated by the carbon 1s peak at 284.8 eV. High-resolution mass spectra were collected using a Bruker Daltonics (Bremen, Germany) SolariX XR 7.0 T Fourier transform ion cyclotron resonance mass spectrometer (FTICR-MS) equipped with an ESI ionization source. HoI_3, ErI_3,12-crown-4 and $AgBF_4$ were used as purchased.

Synthesis of $[Ho_6(\mu_2\text{-}F)_{12}(\mu_6\text{-}F)(12\text{-crown-}4)_6]I_3F_2$ (1)

12-crown-4 (16.2 μL, 0.10 mmol) was added to a suspension of HoI_3 (27.8 mg, 0.05 mmol) in CH_3CN (1 mL) and stirred for 10 min at room temperature. Then $AgBF_4$ (10.2 mg, 0.05 mmol) was added and the reaction was continued for 10 min at room temperature. White precipitate was observed over the course of the reaction. The mixture was centrifuged and the resulting yellow supernatant is subjected to vapor diffusion with ether to give the yellow solids in 10.2 mg yield (45.1% based on Ho). The yellow crystals suitable for X-ray diffraction were grown from the slow evaporation of CH_3CN solution. ^{19}F NMR (CD_3CN, 376.1 MHz, 295.8 K): δ 148.66, -150.36, -151.97. Elemental analysis: Calcd. (%) for $C_{48}H_{96}Ho_6F_{15}O_{24}I_3$: C, 21.25; H,3.57. Found: C, 21.33; H, 3.52. m/z calcd. for $[Ho_6(\mu_2\text{-}F)_{12}(\mu_6\text{-}F)(12\text{-crown-}4)_6]^{5+}$: 458.63587. Found: 458.63753 (FTICR-MS).

Synthesis of $[Ho(12\text{-crown-}4)_2(CH_3CN)](BF_4)_3$ (2)

12-crown-4 (64.8 μL, 0.40 mmol) was added to a suspension of HoI_3 (108.8 mg, 0.20 mmol) in CH_3CN (4.5 mL) and stirred for 10 min at room temperature. Then $AgBF_4$ (116.6 mg, 0.60 mmol) was added and the reaction was continued for 10 min at room temperature. A yellow precipitate was observed. The mixture was centrifuged and the resulting pale orange supernatant was evaporated to give the colorless crystals in 72 mg yield (44.0% based on Ho). ^{1}H NMR (CD_3CN, 399.8 MHz, 293.8 K): δ 3.68 (s, 12H, CH_2). Elemental analysis: Calcd. (%) for $C_{18}H_{35}B_3F_{12}HoNO_8$: C, 26.40; H, 4.31; N, 1.71. Found: C, 26.24; H, 4.38; N, 1.51.

Note: Complex **2** can also be synthesized by adding one equivalent of $AgBF_4$ to the solution of complex **1** in CH_3CN.

Synthesis of [Er$_6$(μ$_2$-F)$_{12}$(μ$_6$-F)(12-crown-4)$_6$]I$_3$F$_2$ (3)

12-crown-4 (16.2 μL, 0.10 mmol) was added to a suspension of ErI_3 (27.5 mg, 0.05 mmol) in CH_3CN (5 mL) and stirred for 10 min at room temperature. Then $AgBF_4$ (10.4 mg, 0.05 mmol) was added and the reaction was continued for 10 min at room temperature. White precipitate was observed over the course of the reaction. The mixture was centrifuged and the resulting yellow supernatant is subjected to vapor diffusion with ether to give the yellow solids in 9.2 mg yield (40.5% based on Er). The yellow crystals suitable for X-ray diffraction were grown from the slow evaporation of CH_3CN solution. ^{19}F NMR (CD_3CN, 376.1 MHz, 295.4 K): δ -149.82, -150.45, -152.53. Elemental analysis: Calcd. (%) for $C_{48}H_{96}Er_6F_{15}O_{24}I_3$: C, 21.14; H,3.55. Found: C, 21.09; H, 3.58. m/z calcd. for $[Er_6(\mu_2\text{-}F)_{12}(\mu_6\text{-}F)(12\text{-crown-}4)_6]^{5+}$: 461.43883. Found: 461.43977 (FTICR-MS).

II. Supporting figures

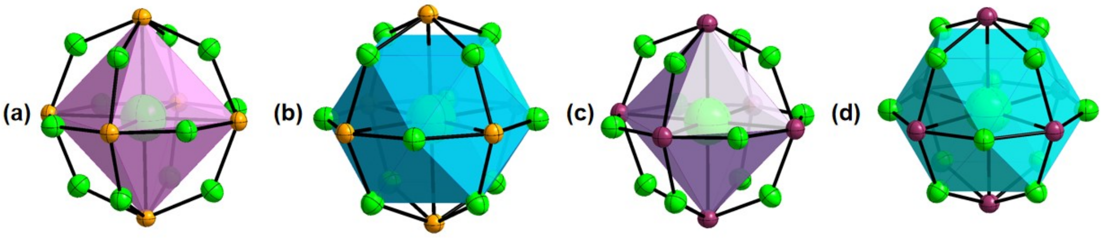

Figure S1. Polyhedral representation of Ho^{3+} ions of **1** (a), μ$_2$-F$^-$ ions of **1** (b), Er^{3+} ions of **3** (c) and μ$_2$-F$^-$ ions of **3** (d).

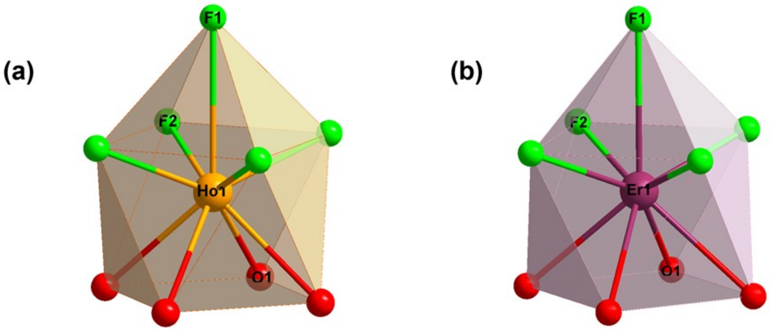

Figure S2. Polyhedral coordination environment of Ho^{3+} ion in **1** (a) and Er^{3+} ion in **3** (b).

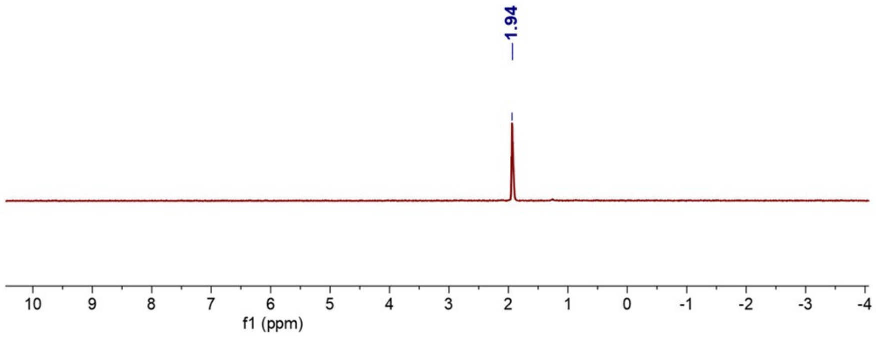

Figure S3. ^{1}H NMR spectrum of complex **1** at 295.9 K in CD_3CN.

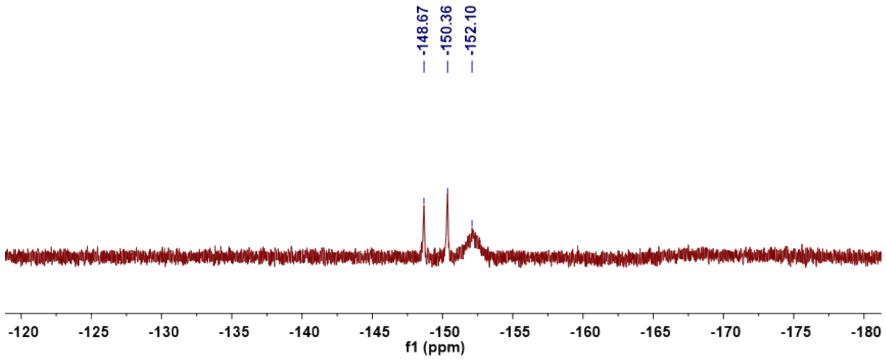

Figure S4. ^{19}F NMR spectrum of complex **1** at 295.8 K in CD_3CN.

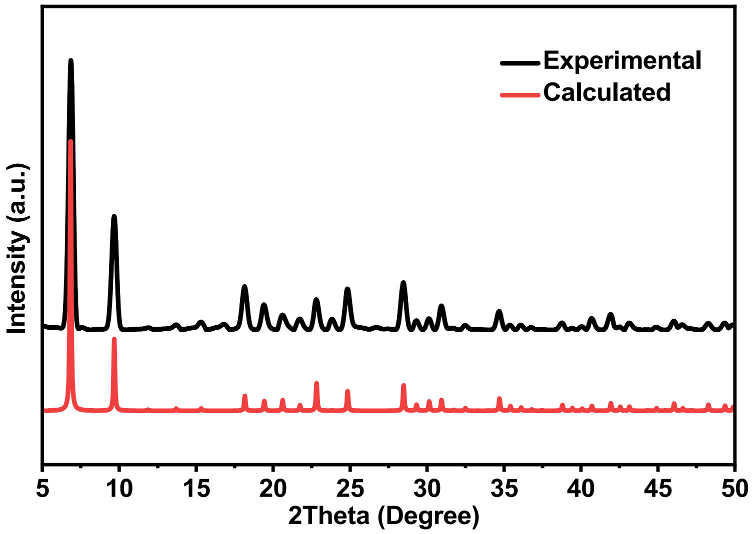

Figure S5. Experimental and calculated PXRD patterns for $[Ho_6(\mu_2\text{-}F)_{12}(\mu_6\text{-}F)(12\text{-crown-}4)_6]I_3F_2$.

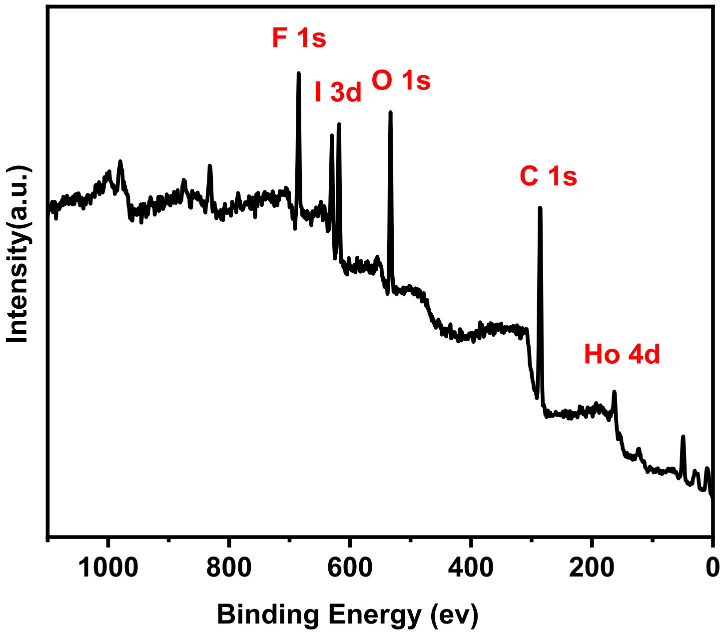

Figure S6. XPS survey spectrum of **1**.

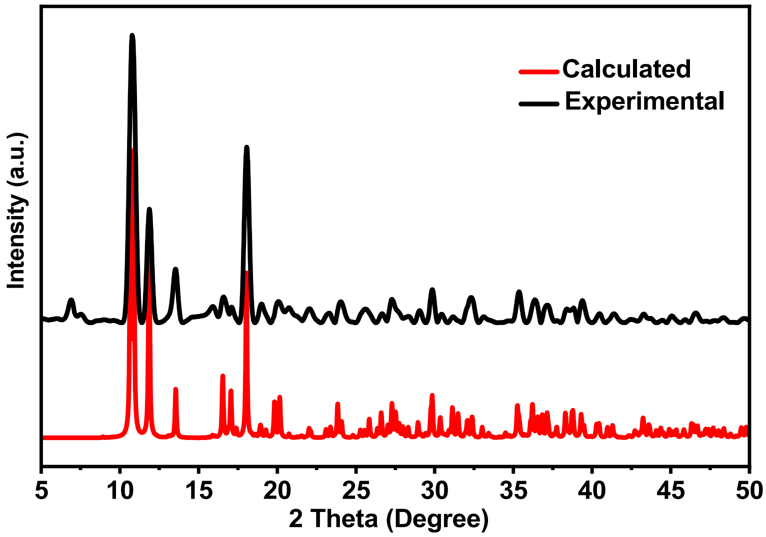

Figure S7. Experimental and calculated PXRD patterns for [Ho(12-crown-4)$_2$(CH$_3$CN)](BF$_4$)$_3$.

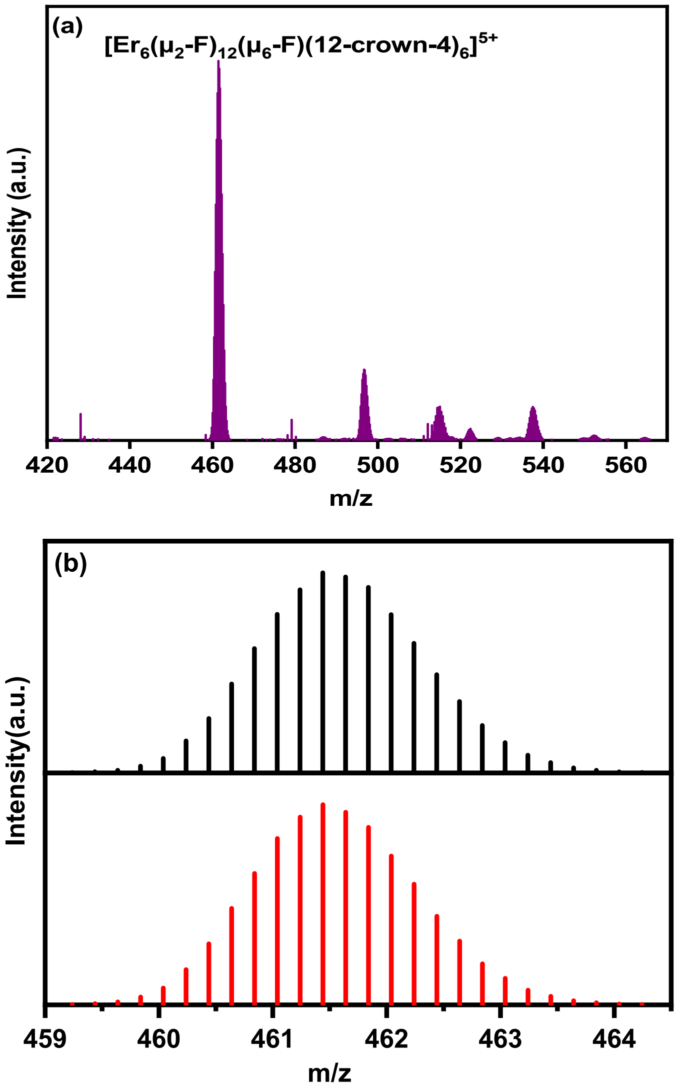

Figure S8. (a) Mass spectra of **3** in CH_3CN, (b) Experimental (black) and simulated (red) mass spectra showing the isotopic pattern of the $[Er_6(\mu_2\text{-}F)_{12}(\mu_6\text{-}F)(12\text{-crown-}4)_6]^{5+}$ ion.

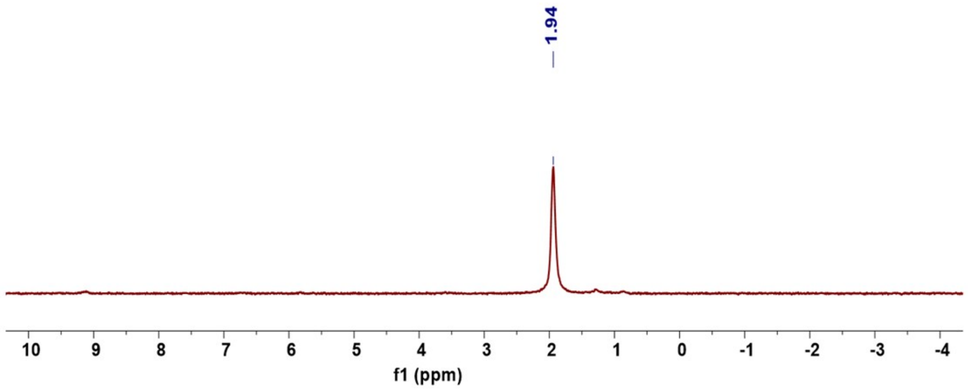

Figure S9. ^1H NMR spectrum of complex **3** at 295.6 K in CD_3CN.

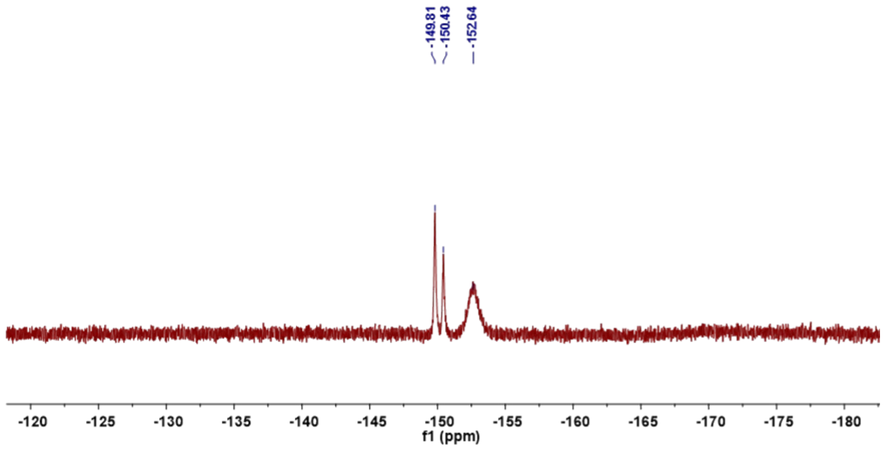

Figure S10. ^{19}F NMR spectrum of complex **3** at 295.4 K in CD_3CN.

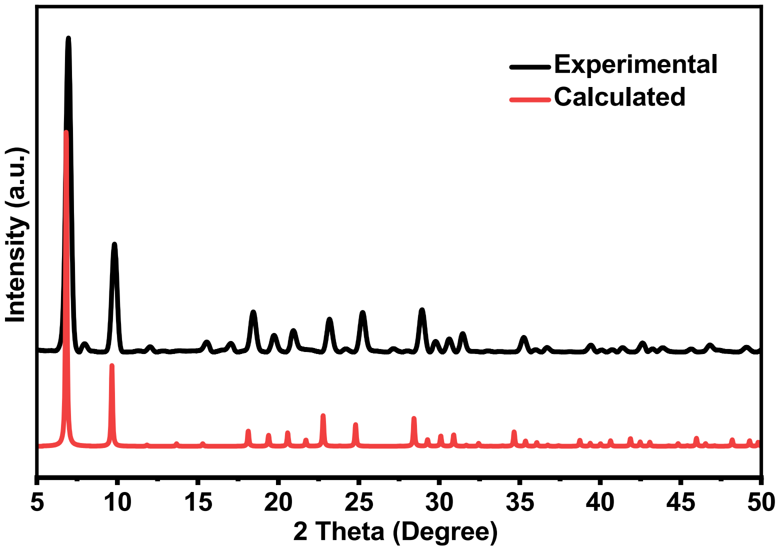

Figure S11. Experimental and calculated PXRD patterns for $[Er_6(\mu_2\text{-}F)_{12}(\mu_6\text{-}F)(12\text{-crown-}4)_6]I_3F_2$.

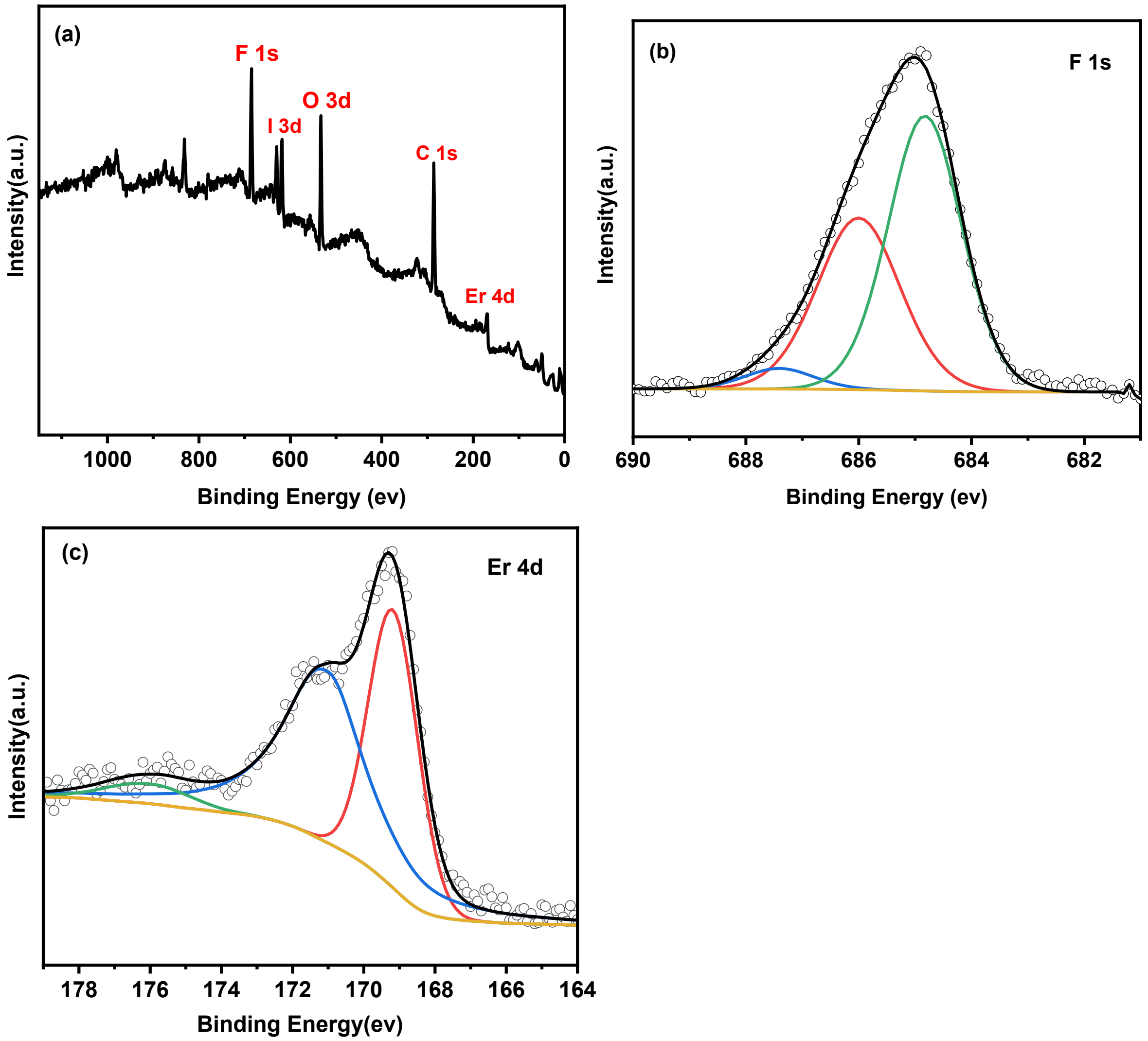

Figure S12. XPS spectra of **3**. (a) survey spectrum, (b) F 1s spectrum, (c) Er 4d spectrum.

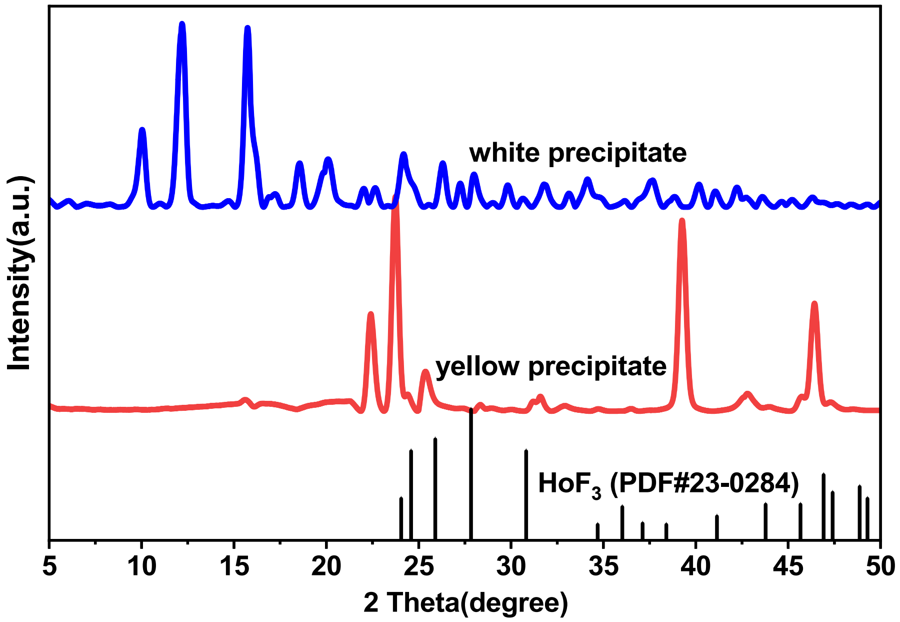

Figure S13. PXRD patterns of HoF$_3$ (PDF#23-0284) and the white and yellow precipitates generated along with the formation of complexes **1** and **2**, respectively. HoF$_3$ was not formed in these reactions.

III. X-ray Crystallographic Data

The intensity data were collected on a Rigaku Synergy R (Mo Kα) diffractometer at 180 K. Absorption corrections were applied by using the program CrysAlisPro (multi-scan). The crystal structures were solved by SHELXT structure solution program using Intrinsic Phasing, and nonhydrogen atoms were refined anisotropically by least-squares techniques on F^2 by SHELXL with the graphical user interfaces of Olex2.[1] Platon Squeeze[2] integrated into Olex2 interface was used in the refinement of the structures. For all structures, H-atom parameters were constrained. For complexes **1** and **3**, disordered solvent molecules were removed using the Olex2 solvent mask command. Appropriate distance and ADP restraints were implemented to assist convergence.

Table S1. Crystal data and structure refinements for complexes **1**, **2** and **3**

Complex	1	2	3
CCDC No.	2400569	2463498	2400570
Empirical formula	$C_{48}H_{96}F_{15}Ho_6I_3O_{24}$	$C_{18}H_{35}B_3F_{12}HoNO_8$	$C_{48}H_{96}Er_6F_{15}I_3O_{24}$
Formula weight	2712.554	818.83	2726.50
Temperature/K	180.00(10)	180.00(10)	179.99(10)
Crystal system	cubic	orthorhombic	cubic
Space group	$Im\bar{3}m$	$P2_12_12_1$	$Im\bar{3}m$
a /Å	18.2616(3)	10.3911(3)	18.2915(4)
b/Å	18.2616(3)	10.7144(3)	18.2915(4)
c/Å	18.2616(3)	26.1234(7)	18.2915(4)
α/°	90	90	90
β/°	90	90	90
γ/°	90	90	90
Volume/Å^3	6089.99(17)	2908.43(14)	6120.0(4)
Z	2	4	2
ρ_{calc}g/cm^3	1.479	1.870	1.480
μ/mm^{-1}	4.675	2.840	4.887
F(000)	2545.2	1616.0	2556.0
2θ range/deg	4.46 to 50.7	4.108 to 52.736	4.454 to 50.608
Index ranges	$-19 \leq h \leq 28$	$-12 \leq h \leq 12$	$-10 \leq h \leq 20$
	$-19 \leq k \leq 16$	$-12 \leq k \leq 13$	$-21 \leq k \leq 19$
	$-10 \leq l \leq 29$	$-28 \leq l \leq 32$	$-14 \leq l \leq 22$
Reflections collected	5713	13042	4004

Independent reflections	586	5821	581
Completeness	99.8	99.9	99.0
Data/restraints/parameters	586/3/27	5821/6/404	581/9/27
Goodness-of-fit on F^2	0.977	1.091	1.149
Final R indexes [I>=2σ (I)]	$R_1 = 0.0489$	$R_1 = 0.0304$	$R_1 = 0.0603$
	$wR_2 = 0.1788$	$wR_2 = 0.0780$	$wR_2 = 0.1859$
Final R indexes [all data]	$R_1 = 0.0504$	$R_1 = 0.0334$	$R_1 = 0.0630$
	$wR_2 = 0.1811$	$wR_2 = 0.0794$	$wR_2 = 0.1882$
Largest diff. peak/hole / e Å^{-3}	1.82/-1.90	1.76/-1.61	1.89/-2.07

Note：Considering the slightly large ellipsoids of the central F^- in complexes **1** and **3**, attempts were made to model the central site as oxygen. However, a charge imbalance issue occurred when it was defined as O^{2-}. The incorporation of an OH^- group did not meet the requirement of a spherically symmetric atom at the center of the octahedron as indicated by the crystallographic data. Furthermore, the m/z values from the high-resolution mass spectra would completely differ from the m/z obtained for the cluster ion with a central F^- (see Table S2) if the central ion were replaced by O^{2-} or OH^-.

Table S2. The m/z values of different cluster ions

Cluster ion	m/z
$[\mathrm{Ho_6(\mu_2\text{-}F)_{12}(\mu_6\text{-}F)(12\text{-}crown\text{-}4)_6}]^{5+}$ (observed)	458.63587
$[\mathrm{Ho_6(\mu_2\text{-}F)_{12}(\mu_6\text{-}O)(12\text{-}crown\text{-}4)_6}]^{4+}$	572.54617
$[\mathrm{Ho_6(\mu_2\text{-}F)_{12}(\mu_6\text{-}OH)(12\text{-}crown\text{-}4)_6}]^{5+}$	458.23839

IV. References

1. (a) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339; (b) G. M. Sheldrick, *Acta Crystallogr. Section A*, 2015, **71**, 3; (c) G. M. Sheldrick, *Acta Crystallogr. Section C*, 2015, **71**, 3.
2. A. L. Spek, *Acta Crystallogr. Sect. C-Struct. Chem.*, 2015, **71**, 9.