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Supplementary Information

Spin-orbit Coupling Dependent Energy Transfer in Luminescent Nonanuclear Yb-Gd / Yb-Lu Clusters

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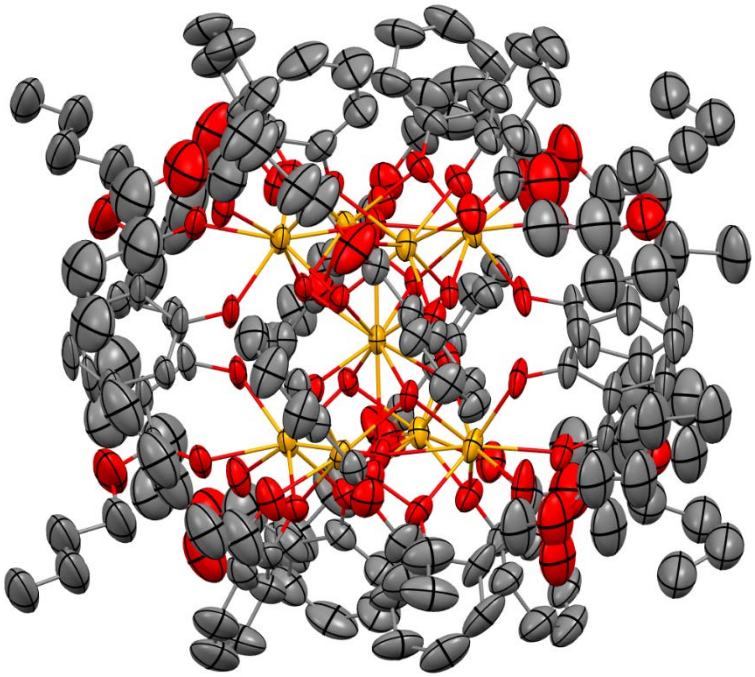
Crystallography

Colorless single crystal of Yb_9 and Lu_9 clusters obtained from solutions in methanol were mounted on a glass fiber by using epoxy resin glue. All measurements were made using a Rigaku RAXIS RAPID imaging plate area detector with graphite-monochromated MoKα radiation. Corrections for decay and Lorentz-polarization effects were made using a spherical absorption correction, solved by direct methods, and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically except for disordered atoms. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters. All calculations were performed using a CrystalStructure crystallographic software package. We confirmed the CIF data by using the checkCIF/PLATON service. CCDC-1578015 (Yb_9 cluster) and CCDC-1578016 (Lu_9 cluster) contains the crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Structure of Lu_9 Cluster

a)



b)

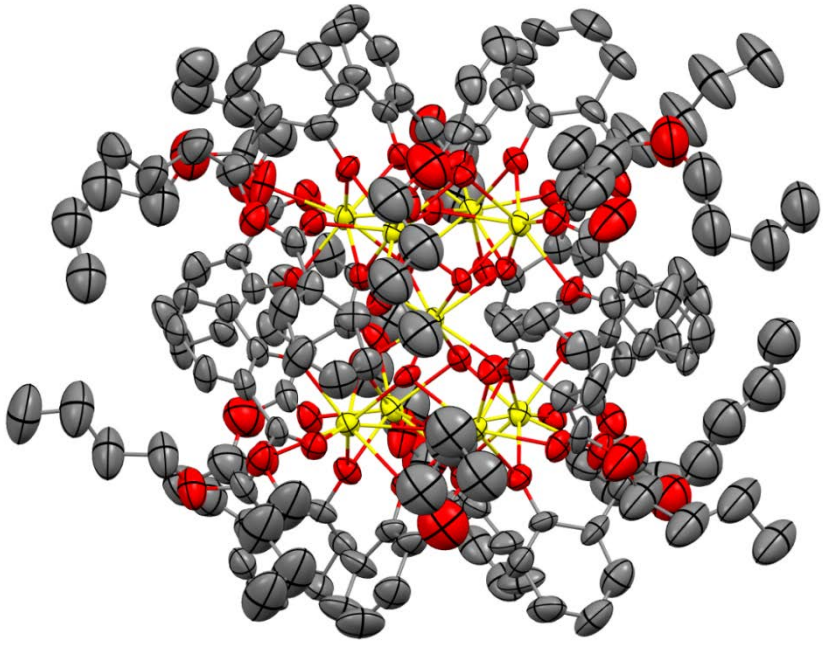


Fig. S1 ORTEP image of a) Yb_9 and b) Lu_9 clusters (thermal ellipsoids at 50% probability). Orange: Yb atoms, yellow: Lu atoms, red: oxygen atoms, and grey: carbon atoms. Hydrogen atoms as well as the random disorder of the butyl chains are omitted for clarity.

Crystallographic information of Yb_9 and Lu_9 clusters

Table S1 Crystallographic information of Yb_9 and Lu_9 clusters.

	Yb_9 cluster	Lu_9 cluster
Chemical formula	$C_{176}H_{208}O_{58}Yb_9$	$C_{176}H_{208}O_{58}Lu_9$
Formula weight	4808.90	4826.24
Crystal system	Tetragonal	Tetragonal
Space group	$P4_2/n$ (#86)	$P4_2/n$ (#86)
a / Å	23.5449(3)	23.857(3)
b / Å	23.5449(3)	23.857(3)
c / Å	36.1157(7)	36.2570(10)
α / deg	90	90
β / deg	90	90
γ / deg	90	90
V / Å^3	20021.2(5)	20636(4)
Z	4	4
D_{calcd} / g cm^{-3}	1.595	1.553
T / K	93.15	173.15
μ ($Mo_{K\alpha}$) / cm^{-1}	42.345	43.357
Max 2θ / deg	56.6	50.7
No. of measured reflections	74859	120501
No. of unique reflections	22456	18839
R [a]	0.0696	0.1265
wR_2 [b]	0.1726	0.2115

[a] $R = \Sigma||F_0| - |F_c|| / \Sigma|F_0|$

[b] $wR_2 = [\Sigma w(F_0^2 - F_c^2)^2 / \Sigma w(F_0^2)^2]^{1/2}$

Continuous Shape Measure

Continuous shape measure (CShM) calculates the deviation of the vertices of an actual structure to the vertices of a specified ideal structure. The CShM value S_{CShM} is given by the following equation:[1]

$$S_{\mathrm{CShM}} = \min \frac{\sum_k^N |\boldsymbol{Q}_k - \boldsymbol{P}_k|^2}{\sum_k^N |\boldsymbol{Q}_k - \boldsymbol{Q}_0|^2} \times 100 \quad \text{(S1)}$$

where $\boldsymbol{Q}_k$ is the vertices of an actual structure, $\boldsymbol{Q}_0$ is the center of mass of an actual structure, $\boldsymbol{P}_k$ is the vertices of an ideal structure, and N is the number of vertices. CShM calculation takes into account the deviation of the metal atom from the center of mass. Small S_{CShM} means that the actual structure is close to the ideal structure that the CShM calculated for.

Powder XRD

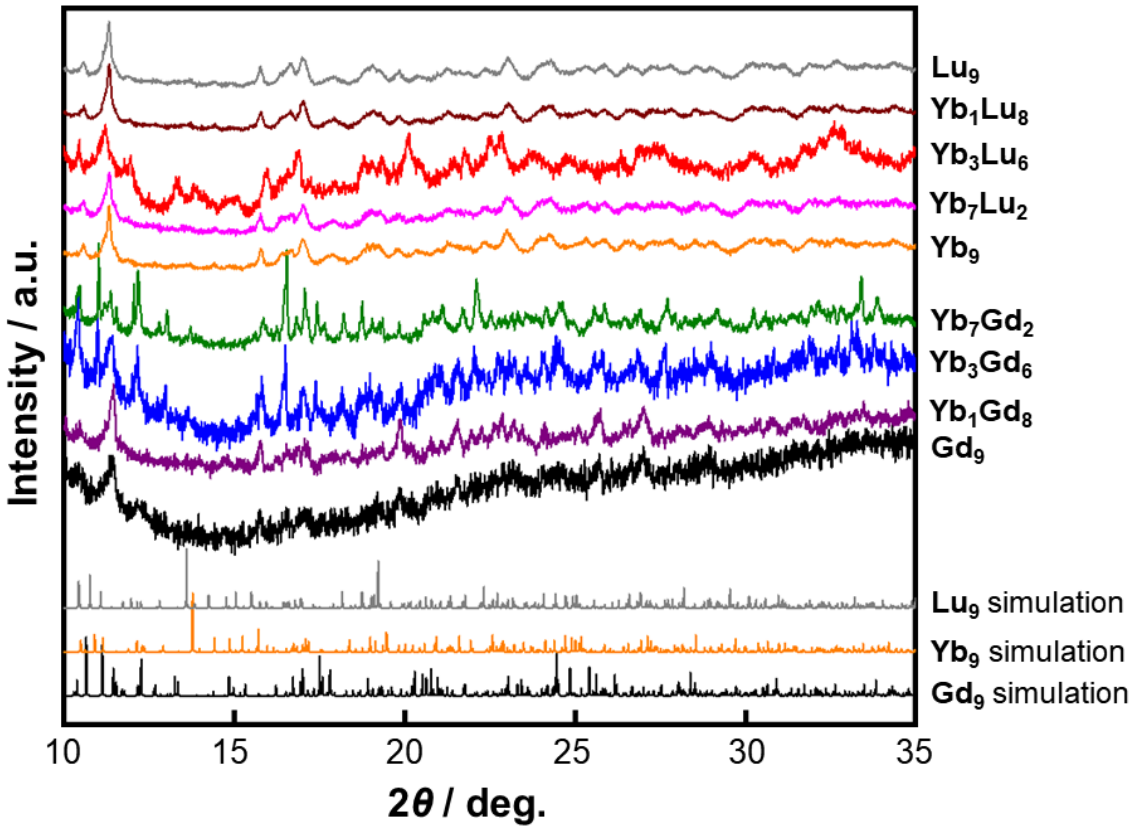


Fig. S2 Powder XRD of the clusters.

Low Temperature Emission Spectra

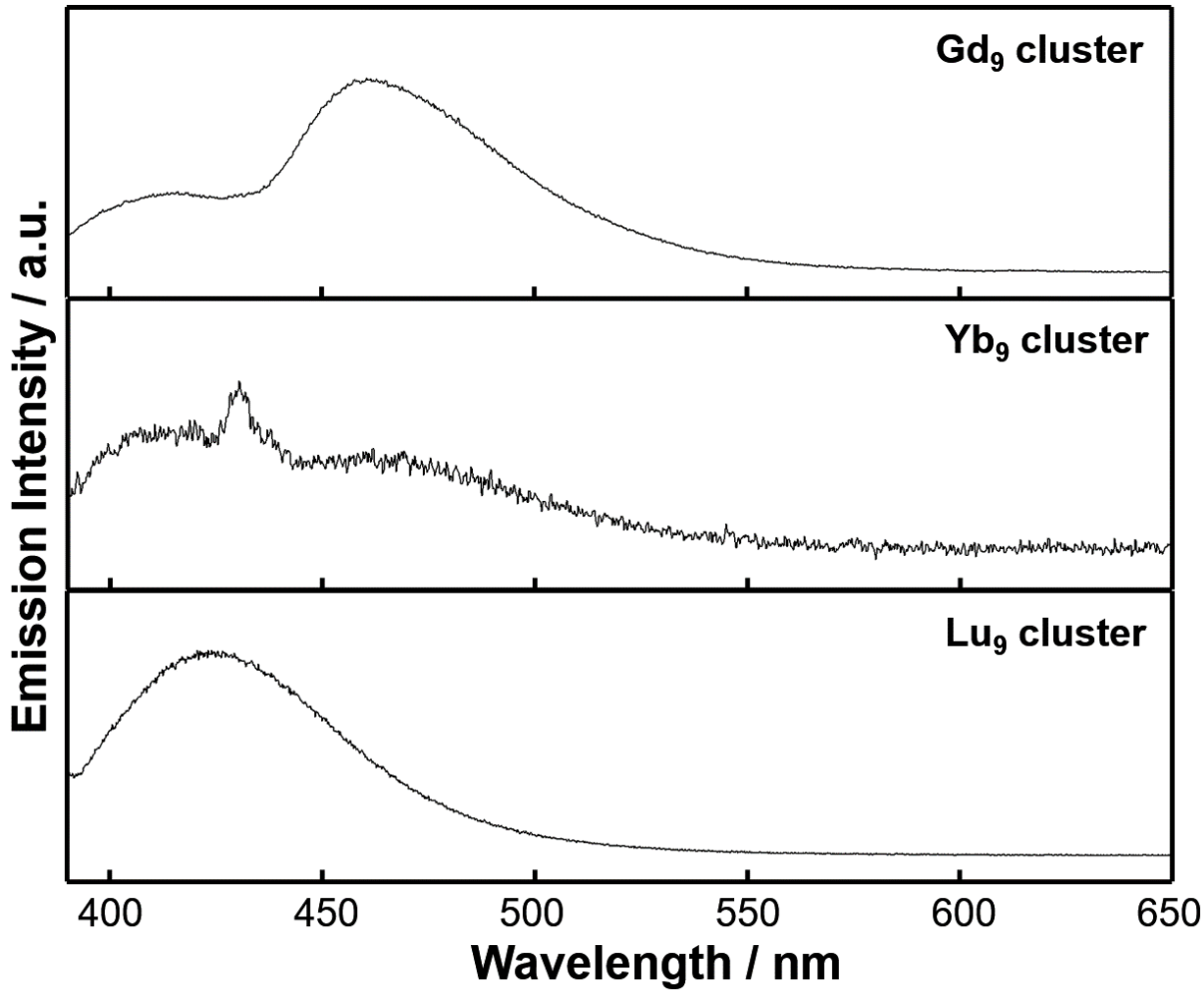
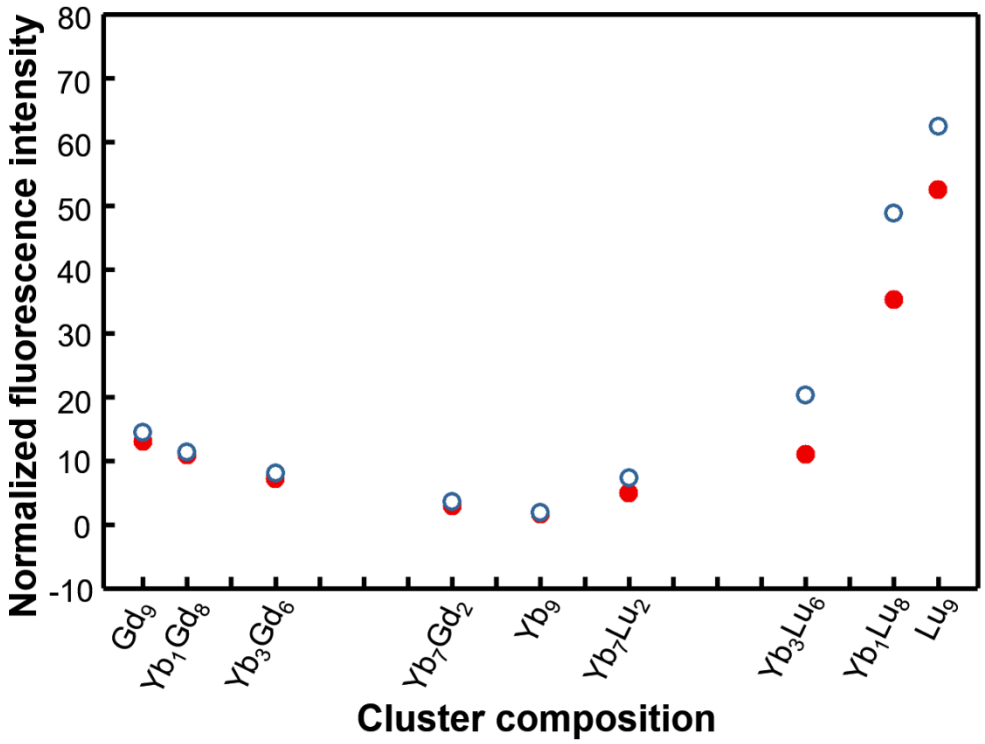


Fig. S3 Emission spectra of Gd_9, Yb_9, and Lu_9 clusters in 1.0×10^{-4} M methanol solution (EX: 380 nm) at 180 K. Raman peak is observed for Yb_9 cluster at around 440 nm.

Emission Intensity and Oxygen Purging

a)



b)

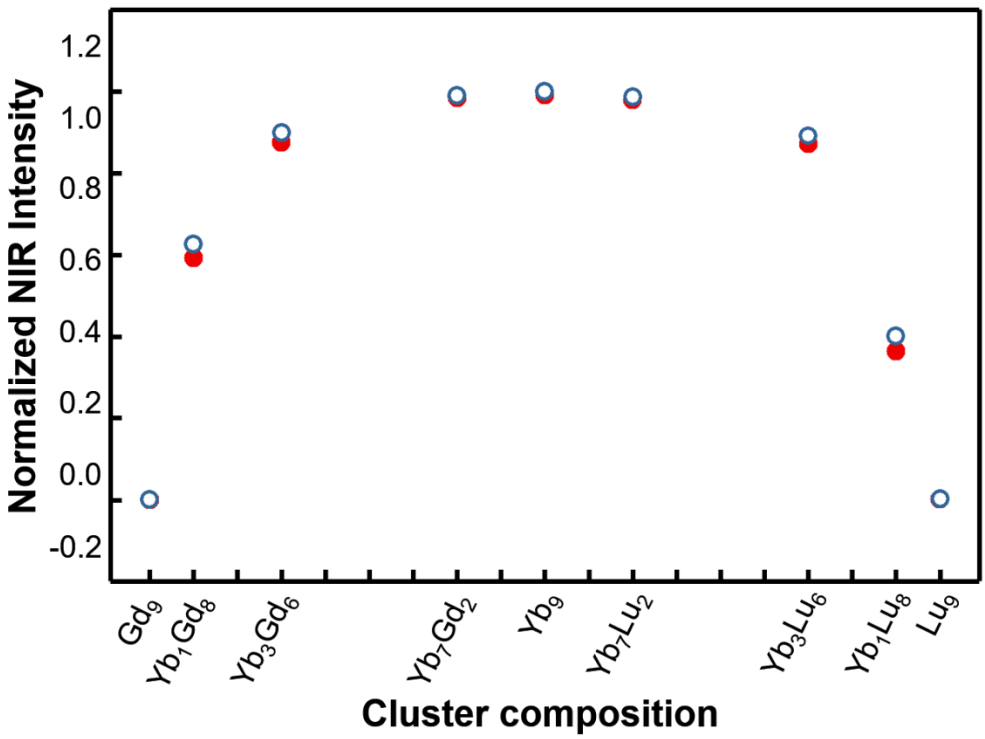


Fig. S4 Plot of emission intensity of Fig.3 for a) fluorescence from the ligands, b) emission from Yb(III) ions. Filled red circles: before oxygen purge, open blue circles: after oxygen purge.

Absorption Spectra

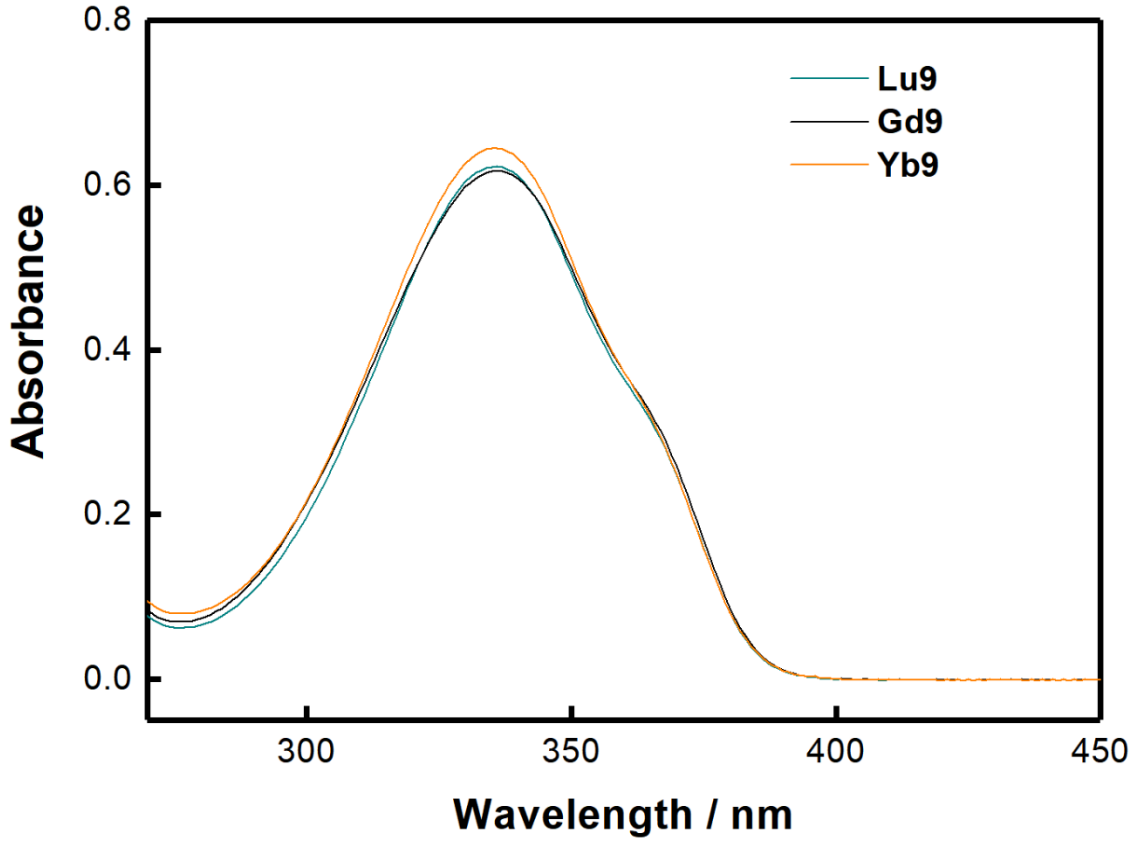


Fig. S5 Absorption spectra of Yb_nGd_{9-n} / Yb_nLu_{9-n} clusters in 1.0×10^{-4} M methanol solution.

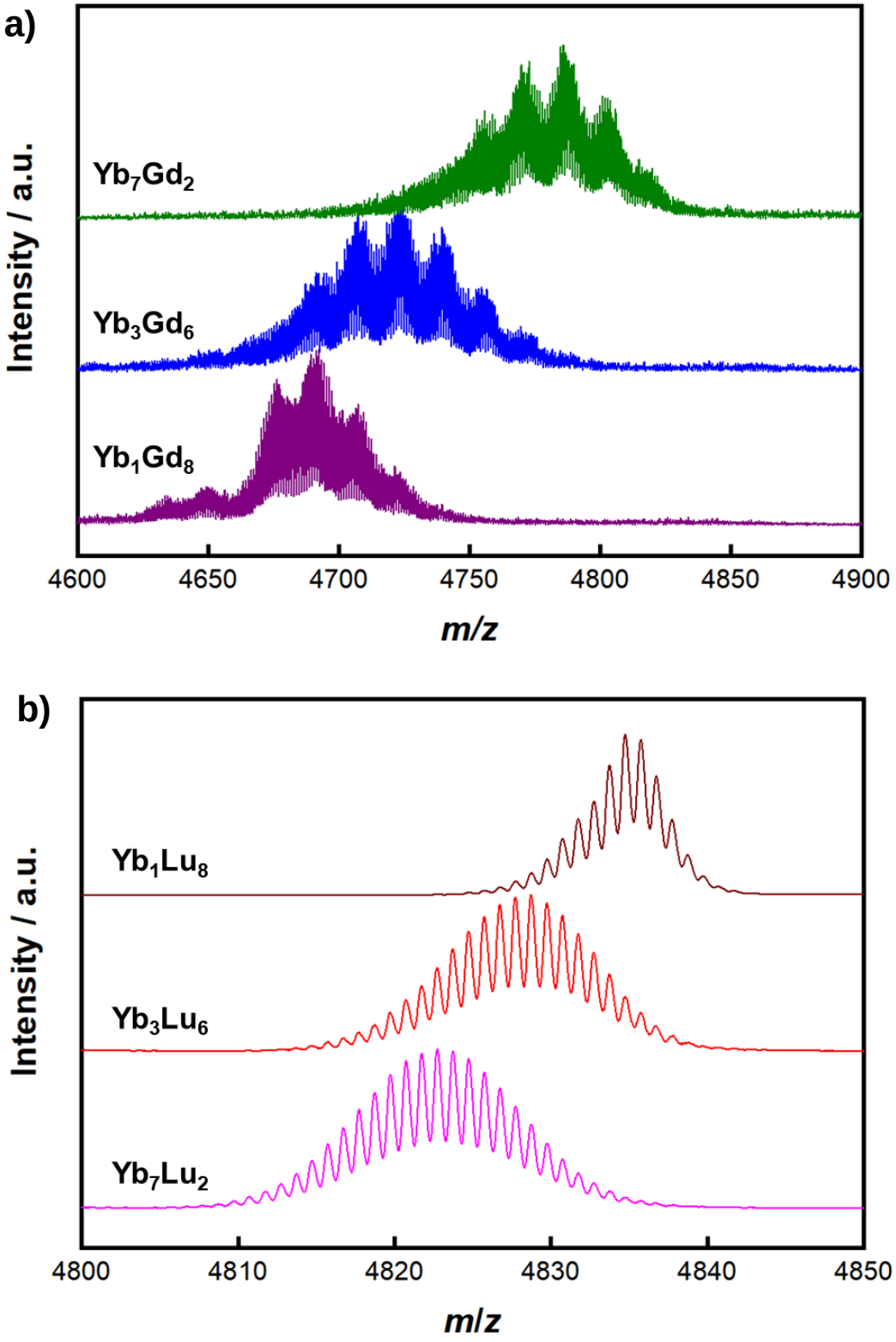


Fig. S6 a) FAB-MS of Yb_1Gd_8, Yb_3Gd_6, Yb_7Gd_2. b) ESI-MS of Yb_1Lu_8, Yb_3Lu_6, Yb_7Lu_2.

References

[1] M. Pinsky, D. Avnir, Continuous Symmetry Measures. 5. The Classical Polyhedra, Inorg. Chem. 37 (1998) 5575–5582. doi:10.1021/ic9804925.