Supplementary Information for

Enhancing the Quantum Yield of Lanthanide Clusters via Single-Site Ligand Modulation

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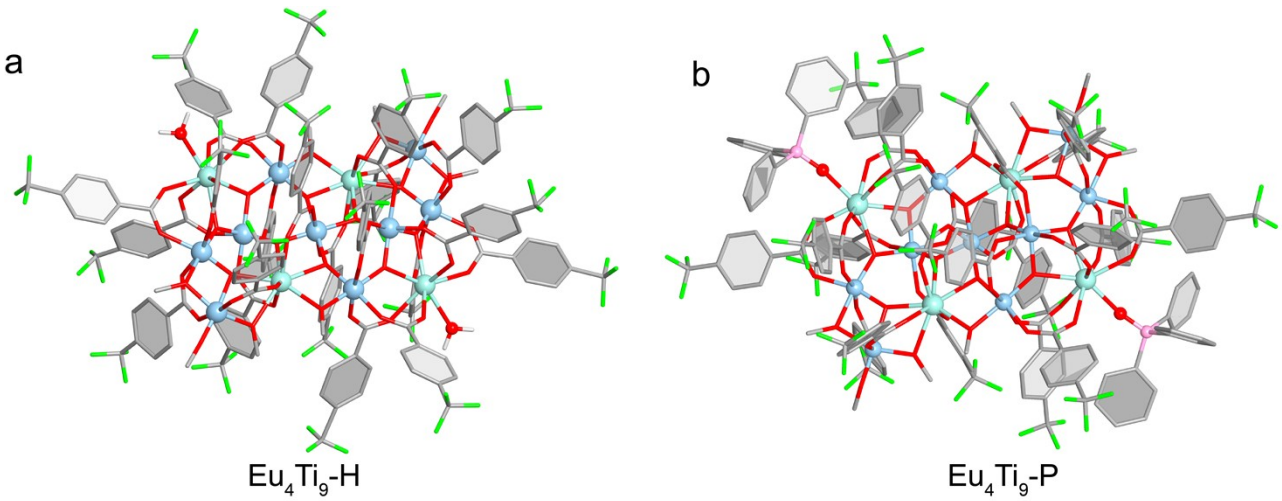


Fig. S1. (a) The structure of **Eu_4Ti_9-H**; (b) The structure of **Eu_4Ti_9-P.**

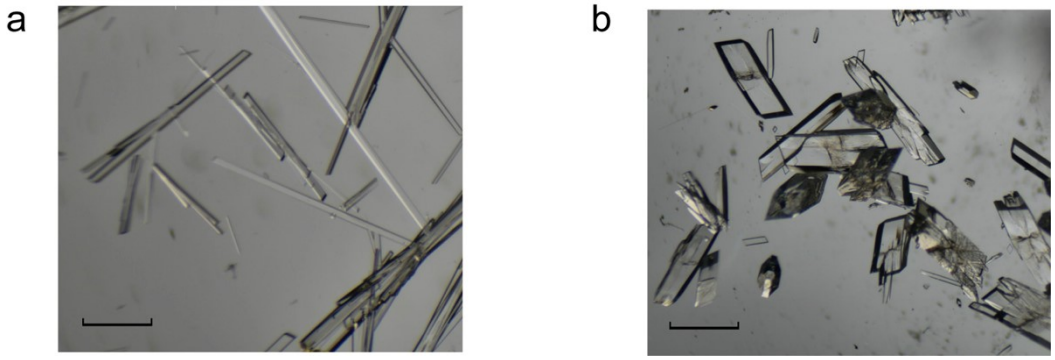


Fig. S2. Photographs of the **Eu_4Ti_9-H** (a) and **Eu_4Ti_9-P** (b). Typical optical image of as-grown large-scale clusters achieved. The size of the crystal can be well controlled by the growth time. Scale bar: 50 μm

a b

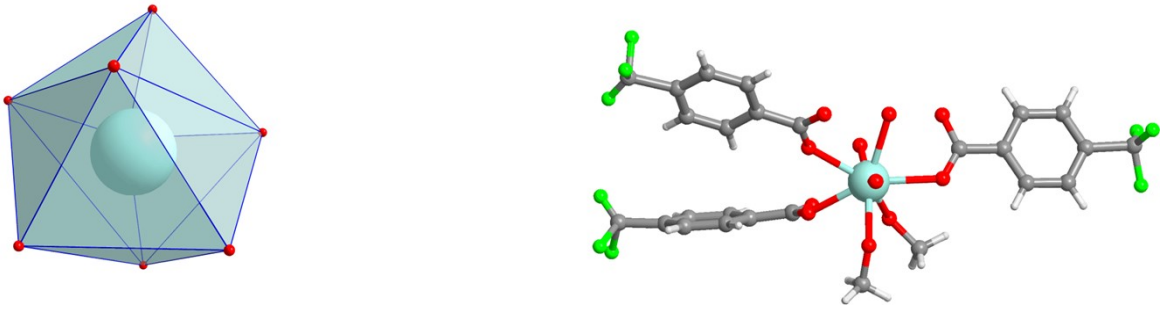


Fig. S3. The coordination geometry (a) and coordination environment (b) of Eu1 ion for the **Eu_4Ti_9-H**.

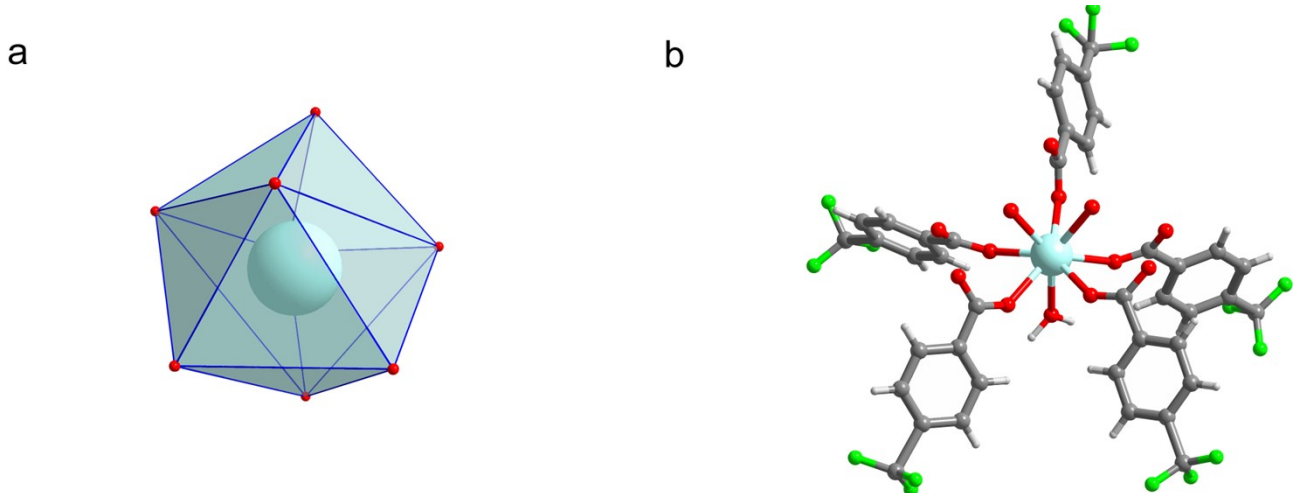


Fig. S4. The coordination geometry (a) and coordination environment (b) of Eu2 for the **Eu_4Ti_9-H**.

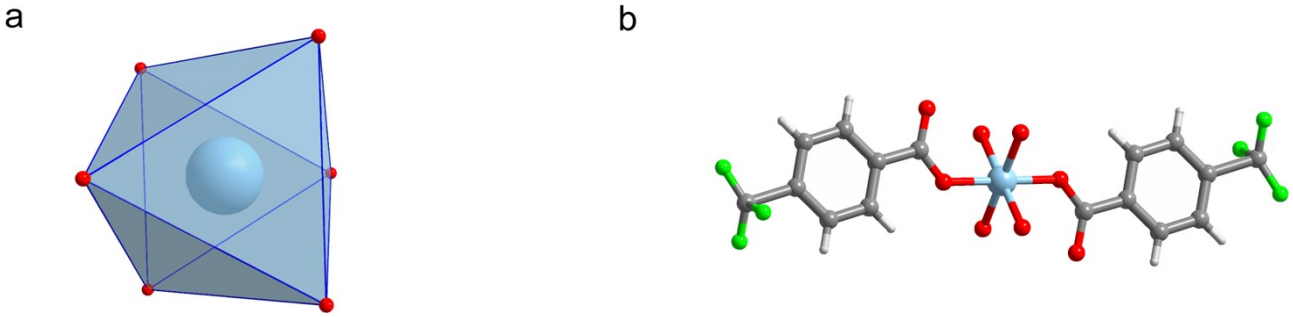


Fig. S5. The coordination geometry and coordination environment of Ti1 for the **Eu_4Ti_9-H**.

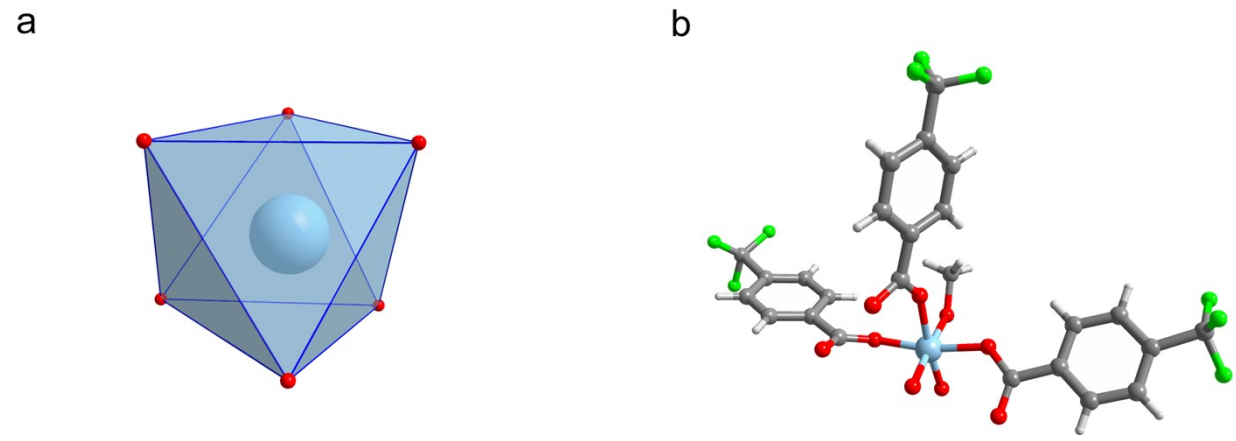


Fig. S6. The coordination geometry and coordination environment of Ti2 for the **Eu_4Ti_9-H**.

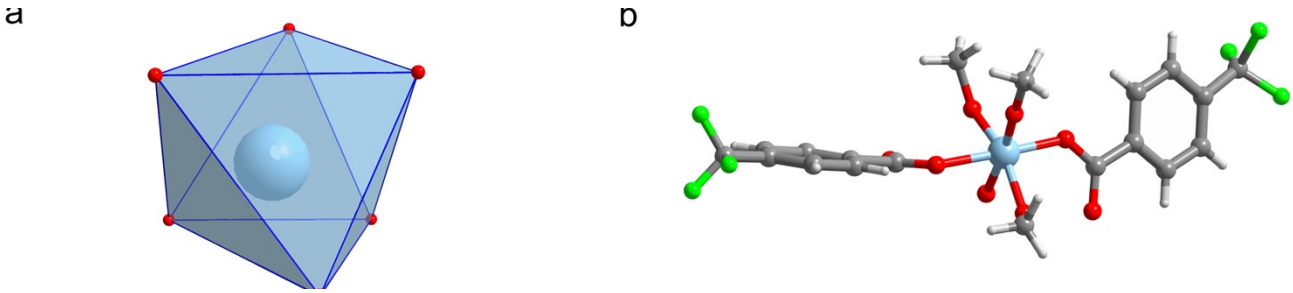
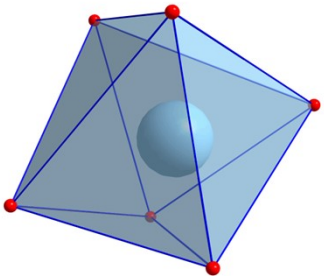


Fig. S7. The coordination geometry and coordination environment of Ti3 for the **Eu_4Ti_9-H**.

a



b

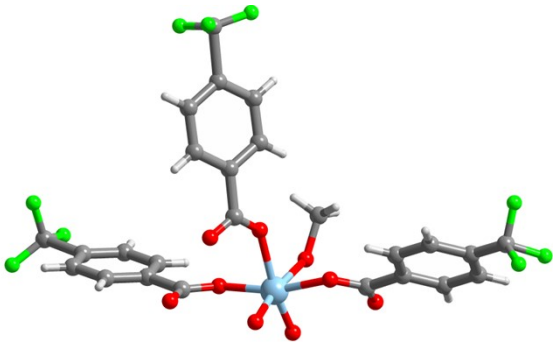


Fig. S8. The coordination geometry and coordination environment of Ti4 for the **Eu_4Ti_9-H**.

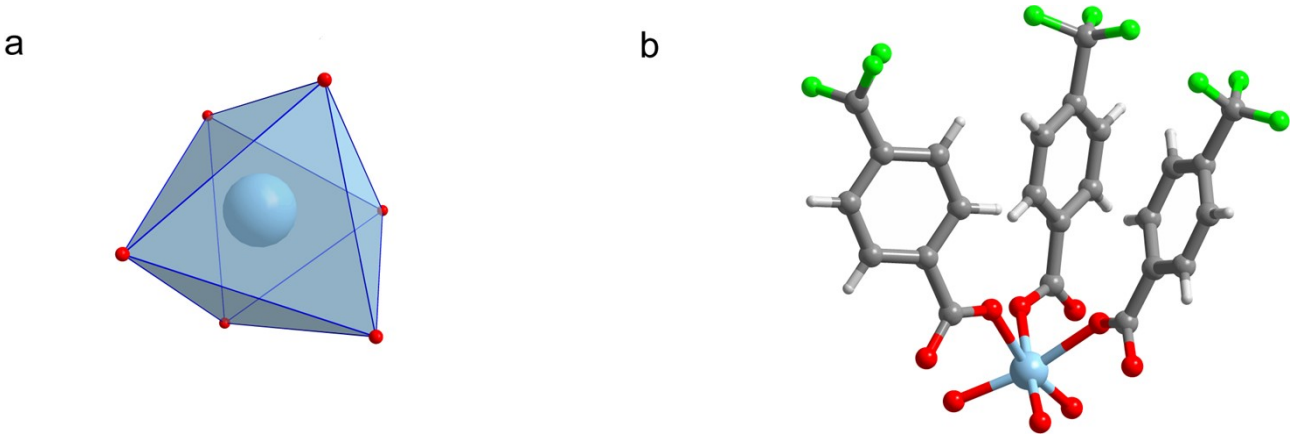


Fig. S9. The coordination geometry and coordination environment of Ti5 for the **Eu_4Ti_9-H**

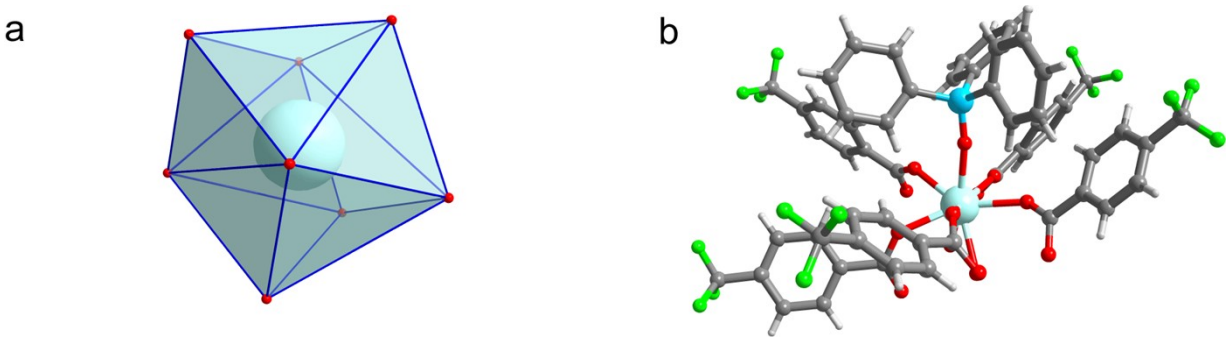


Fig. S10. The coordination geometry (a) and coordination environment (b) of Eu2 for the **Eu_4Ti_9-P**.

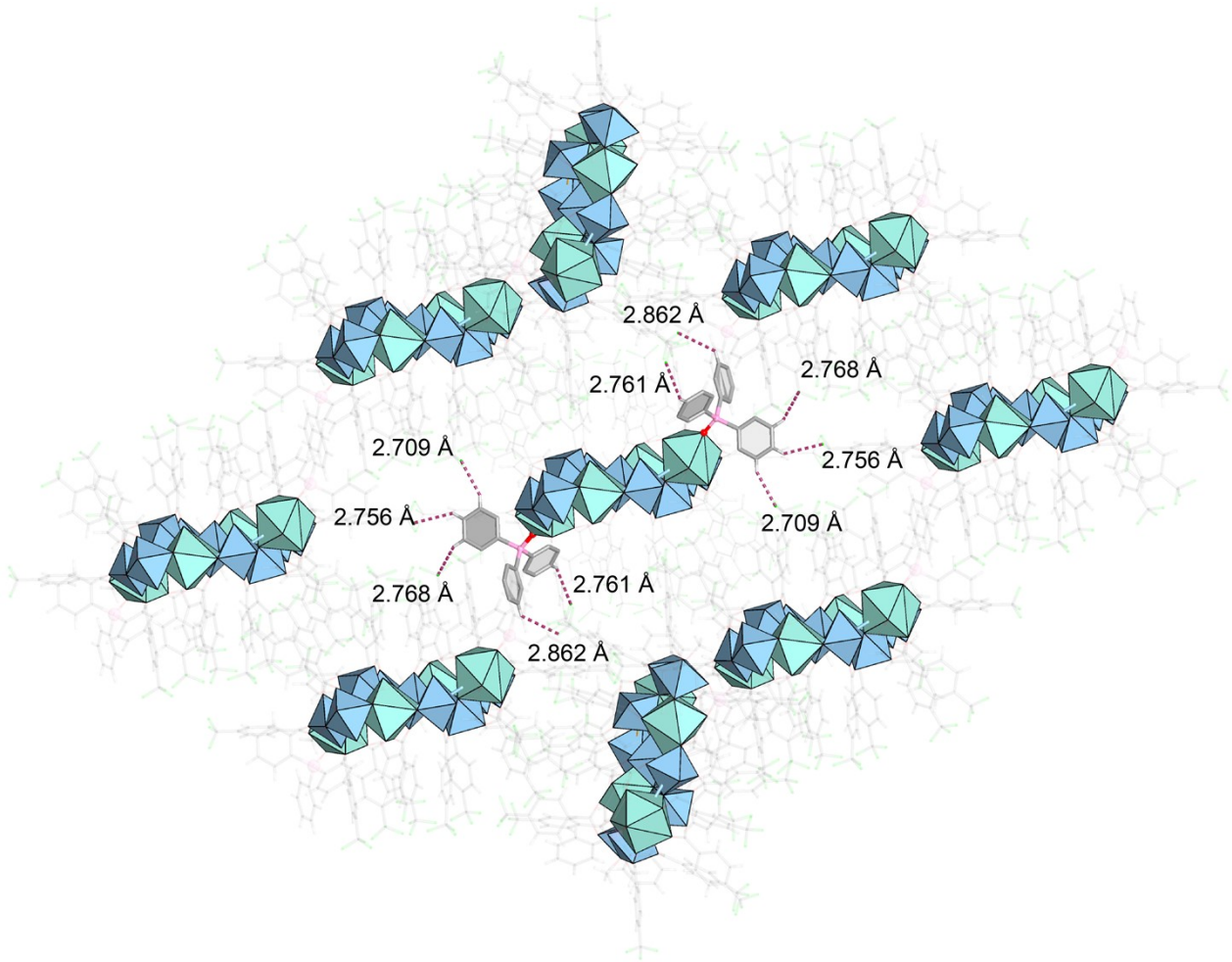


Fig. S11. Schematic representation of the C–H···F interactions between adjacent **Eu_4Ti_9-P** clusters.

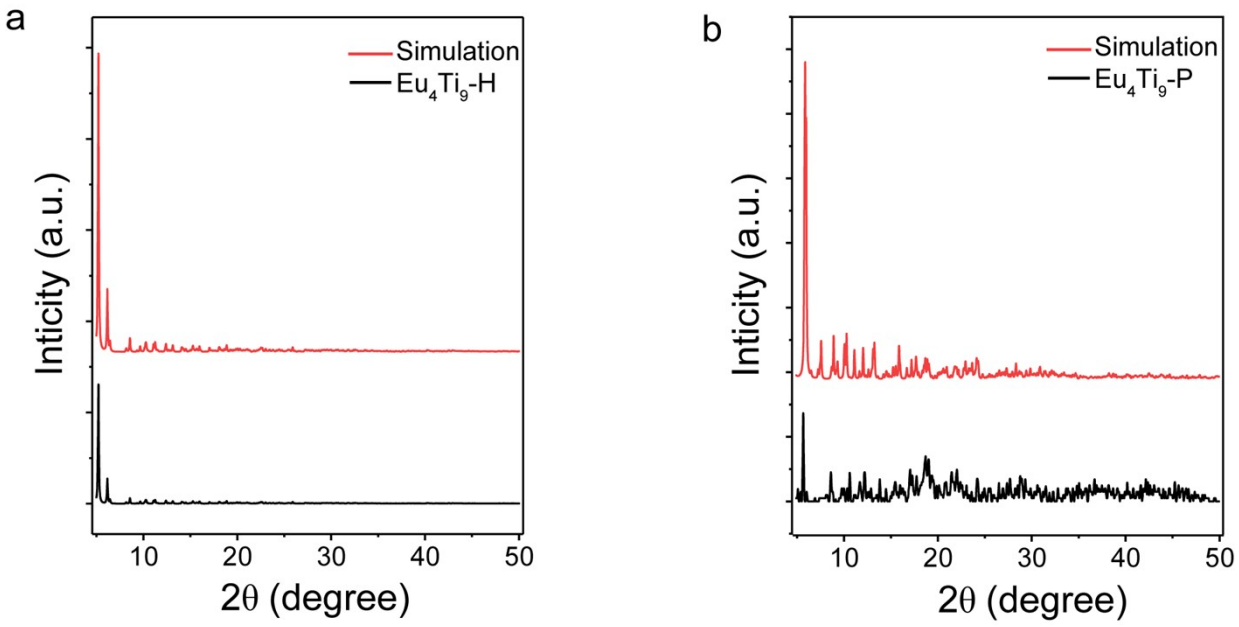


Fig. S12. The XRD of the **Eu_4Ti_9-H** (a) and **Eu_4Ti_9-P** (b). The diffraction peaks of all the cluster crystal powder samples are in good agreement with the simulated diffraction patterns, indicating that the crystal structures of these clusters do not change significantly and have a high degree of similarity.

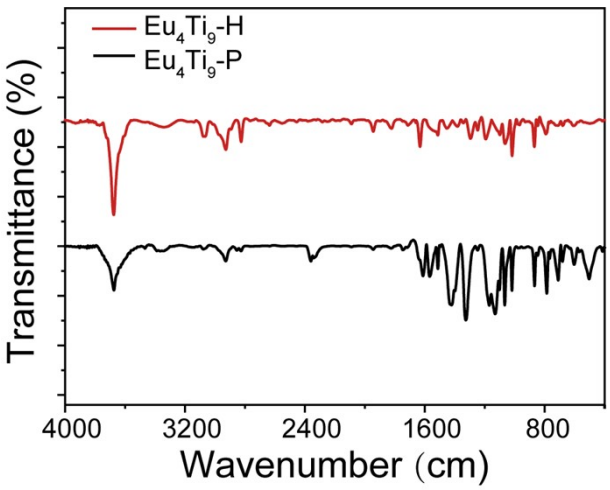


Fig. S13. IR spectra of the **Eu_4Ti_9-H** and **Eu_4Ti_9-P**. The strong absorption bands from1630 cm^{-1} to1060 cm^{-1} were caused by the C=O and C-O stretching vibration of 4-TFMBA;

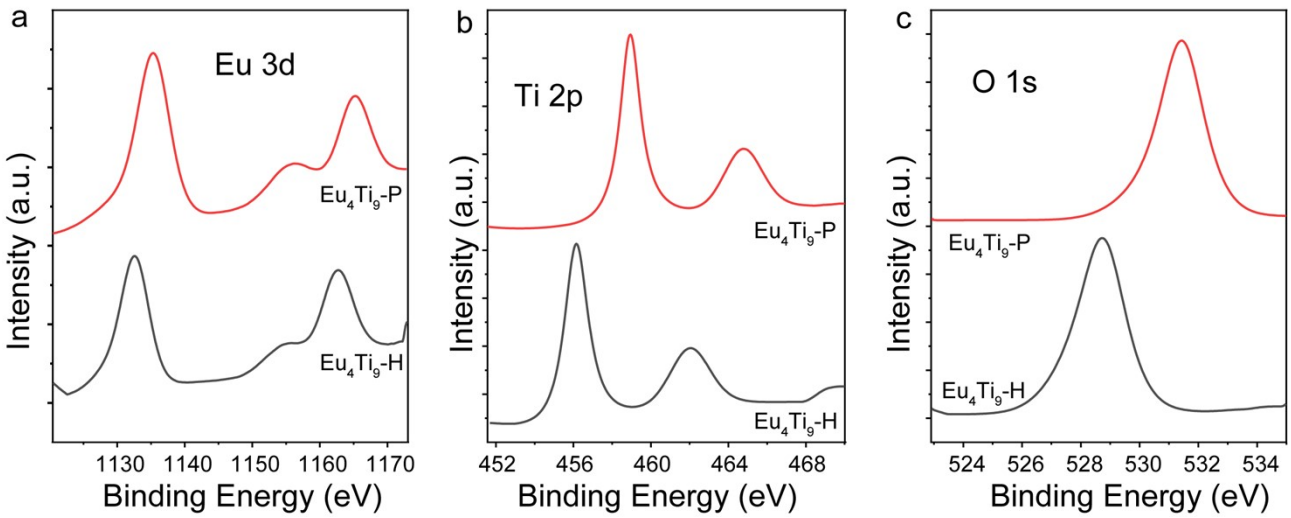


Fig. S14. The XPS of the **Eu_4Ti_9-H** and **Eu_4Ti_9-P**. The binding energy peaks in the range of 1130-1170 eV correspond to Eu 3d (a), 452-468 eV correspond to Ti 2p (b), and 524-534 eV correspond to O 1s (c), respectively.

Table S1. Crystallographic data for the **Eu_4Ti_9-H** and **Eu_4Ti_9-P**.

Complex	**Eu_4Ti_9-H**	**Eu_4Ti_9-P**
formula	$C_{177}H_{144}Eu_4F_{60}O_{69}Ti_9$	$C_{214}H_{154}Eu_4F_{60}N_4O_{62}P_2Ti_9$
Formula weight	5553.85	6014.28
Crystal system	monoclinic	monoclinic
Space group	*C*2/*c*	$P2_1/n$
a/Å	29.4514(10)	19.3775(18)
b/Å	22.7927(7)	21.280(2)
c/Å	36.9556(10)	28.197(2)
α/°	90	90
β/°	111.077(3)	90.647(3)
γ/°	90	90
Volume/Å^3	23147.7(13)	11626.3(18)
Z	4	2
ρ_{calc}g/cm^3	1.594	1.718
μ/mm^{-1}	11.232	1.495
F(000)	10992	5964
Crystal size/mm^3	0.2 × 0.1 × 0.1	0.13 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.038 to 152.232	5.074 to 55.036
Index ranges	-36 ≤ h ≤ 34, -28 ≤ k ≤ 28, -46 ≤ l ≤ 44	-25 ≤ h ≤ 25, -27 ≤ k ≤ 27, -36 ≤ l ≤ 35
Reflections collected	108528	473631
Independent reflections	22470 [R_{int} = 0.1094, R_{sigma} = 0.1219]	26726 [R_{int} = 0.0577, R_{sigma} = 0.0190]
Data/restraints/parameters	22470/883/1571	26726/760/1840
Goodness-of-fit on F^2	1.063	1.122
Final R indexes [I>=2σ (I)]	R_1 = 0.0918, wR_2 = 0.2536	R_1 = 0.0329, wR_2 = 0.0769
Largest diff. peak/hole / e Å^{-3}	0.79/-1.39	0.80/-0.89

Table S2. Best-fitting parameters for the thermometric parameter (Δ)

	Eu_4Ti_9-H	Eu_4Ti_9-P
A_1	1.900	2.231
A_2	1.490	0.984
X_0	67.180	139.465
R^2	0.843	0.991