Supporting Information

Construction of high-nuclear 4p-4f heterometallic $\{Ln_{11}Ge_{12}\}$ cluster-organic frameworks with high-sensitivity luminescent sensing of Fe³⁺ in aqueous solution

Leilei Li, ^{*}a Bin Cai,^b Donghui Pang,^a Xinxin Du,^a Xingliang Yin,^a Huaiwei Wang,^a Jie Yang,^a Dacheng Li,^a Jianmin Dou^{*}a

^{*a*} Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, College of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng, 252059, P. R. China.

^b School of Chemistry and Chemical Engineering, Zhoukou Normal University, Zhoukou 466001, P. R. China.

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Figure S1. The FT-IR spectra of L1 before and after treated with Fe³⁺ aqueous, and L2.



Figure S2. Coordination environments and geometries of Pr^{3+} ions in L1.





Figure S4. The distorted square window in L1 with the dimensions of 9.820×8.747 Å².



Figure S5. The PXRD patterns of original L1 and metal-ion-treated L1.



Figure S6. The TGA curves of L1 and L2.



Figure S7. The UV-Vis-NIR absorption spectra of solid H₂E₂Ge₂O₃, L2, and L1 before and after treated with Fe³⁺.



Figure S8. The colours of L1 and Fe³⁺-treated L1.



Figure S9. Plots of Kubelka-Munk function of H₂E₂Ge₂O₃, **L1** and **L2** band gaps.



Figure S10. The solid-state excitation ($\lambda_{em} = 434 \text{ nm}$) and emission spectra ($\lambda_{ex} = 307 \text{ nm}$) of H₂E₂Ge₂O₃.



Figure S11. The excitation spectra of L1 (a) and L2 (b) (λ_{em} : 420 nm for L1; 1063 nm for L2).



Figure S12. The excitation (a) and emission (b) spectra of L1 dispersed in aqueous solutions containing different metal ions ($\lambda_{ex} = 368 \text{ nm}$, $\lambda_{em} = 420 \text{ nm}$).



Figure S13. High resolution XPS spectra of Bi 4f and O 1s in Bi³⁺-treated L1.



Figure S14. UV-Vis absorption spectra of metal ions in aqueous solutions and excitation and emission spectra of L1 in water.



Figure S15. UV-Vis absorption spectra of Fe^{3+} aqueous solution before and after the addition of L1.



Figure S16. Emission decay curves of L1 in the absence (a) /presence (b) of Fe^{3+} .



Figure S17. High resolution XPS spectra of Fe 2p (a) and O 1s (b) in L1 treated with Fe^{3+} aqueous solution.

	L1	L2
formula	$C_{76}H_{111}N_{16}O_{84}Ge_{12}Pr_{11}$	C ₇₆ H ₁₁₁ N ₁₆ O ₈₄ Ge ₁₂ Nd ₁₁
fw	5013.89	4999.47
crystal system	monoclinic	monoclinic
space group	Cc	Cc
<i>a</i> , Å	27.515(7)	27.547(5)
b, Å	19.112(5)	19.086(4)
<i>c</i> , Å	27.087(7)	27.056(5)
α , deg	90	90
β , deg	102.745(3)	103.120(2)
γ, deg	90	90
<i>V</i> , Å ³	13893(6)	13854(5)
Ζ	4	4
$D_{\rm c}$, g cm ⁻³	2.397	2.421
<i>F</i> (000)	9536	9580
μ , mm ⁻¹	6.433	6.706
Reflections collected/unique	13429/16622	15131/20934
R_{int}	0.0634	0.0501
GOF on F^2	1.007	0.999
$R_1, wR_2 (I > 2\sigma(I))^a$	0.0503, 0.1263	0.0680, 0.1691
R_1 , wR_2 (all data)	0.0715, 0.1416	0.1029, 0.1946

 Table S1. Crystallographic data and structure refinements for L1 and L2.

 Table S2. Standard deviation for L1.

Blank Readings	Luminescence Intensity (a.u.)	
1	947	
2	948	
3	938	
4	938	
5	943	
6	939	
Standard Deviation (S_b)	4.54	