

Supporting Information for

Luminescent Sensing and Slow Magnetic Relaxation Properties in Two Isostructural Ln-MOFs

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Materials and General Methods All the reagents and solvents were purchased from commercial sources and used directly without further purification.

Elemental analyses (C, H, and N) were performed on a PerkinElmer 2400C elemental analyzer. The powder X-ray diffraction (PXRD) was collected by using a Bruker D8 ADVANCE X-ray powder diffractometer (Cu $K\alpha$, $\lambda = 1.5418 \text{ \AA}$) with 2θ (5-50°). A luminescent spectrum was measured on an Edinburgh FLS55 luminescence spectrometer. Magnetic measurements were measured by using a Quantum Design MPMSXL-7 SQUID magnetometer on polycrystalline samples.

Experimental procedure of luminescence and PXRD for sensing ions: Crystalline samples of **1-Eu** were immersed in the individual aqueous solutions of different salt solutions, and the suspensions were obtained by being sonicated for 30 minutes. Then the luminescence spectra of the obtained dispersions were recorded. When the crystalline samples settled down after one day, the precipitates were used to do PXRD measurements.

Synthesis of H₂L. The ligand of 5-((pyridin-4-ylthio)methyl)isophthalic acid was prepared by mixing 4-mercaptopyridine and 5-(bromomethyl)isophthalic acid in water at refluxing temperature for 24 hours. After cooling down to room temperature, the white solid of H₂L was collected by filtration with a yield of 85%. IR/cm⁻¹ (KBr): 3438 (m), 3084 (m), 2972 (w), 2790 (w), 2517 (m), 2148 (w), 2031 (w), 1865 (w), 1672 (s), 1620 (s), 1475 (s), 1348 (m), 1265 (s), 1209 (s), 1105 (s), 974 (m), 912 (m), 860 (w), 812 (s), 771 (s), 687 (s), 611 (m), 484 (w), 426 (m). ¹H NMR (400 MHz, DMSO): δ : 4.55 (s, 2H), 7.32–7.34 (m, 2H), 8.25 (d, $J = 1.5 \text{ Hz}$, 2H), 8.34–8.37 (m, 3H), 13.34 (s, 2H).

Synthesis of [Ln(HL)L]·H₂O (Ln = Eu, Dy) A mixture of Ln(NO₃)₂·6H₂O (0.1mmol), H₂L(0.05mmol, 0.0145g), DMA-H₂O (2:2, 4 mL) was sealed in a 25 mL Teflon-lined stainless steel vessel, which was then heated at 120°C for 72 h. After cooling down to room temperature at a rate of 5°C min⁻¹, colorless needle shaped crystals were obtained.

[Eu(HL)L]·H₂O (1-Eu): Yield. 58% (based on H₂L). Calcd for C₂₈H₂₁EuN₂O₉S₂(%): C, 45.11; H, 2.84; N, 3.76. Found: C,44.55; H, 2.30; N, 3.90. IR/cm⁻¹ (KBr): 3410 (w), 3219 (w), 3053 (w), 2925 (w), 1629 (s), 1564 (s), 1452 (s), 1373 (s), 1250 (w), 1201 (w), 1107 (m), 928 (w), 787 (m), 715 (m), 593 (w), 489 (w), 433 (w).

[Dy(HL)L]·H₂O (1-Dy): Yield. 60% (based on H₂L). Calcd for C₂₈H₂₁DyN₂O₉S₂(%): C, 44.48; H, 2.80; N, 3.71. Found: C,44.42. H, 2.30. N, 3.70. IR/cm⁻¹ (KBr): 3410 (W), 3219 (w), 3055 (w), 2927 (w), 1624 (s), 1562 (s), 1452 (s), 1373 (s), 1250 (w), 1205 (w), 1107 (m), 928 (w), 787 (m), 715 (m), 592 (w), 488 (w), 434 (w).

X-ray Data Collection and Structure Determination

Single-crystal X-ray diffraction measurements of **1-Eu** and **1-Dy** were performed on Bruker Apex-II CCD. The structures were solved by the direct methods and refined by full-matrix least-squares refinements based on F^2 with the SHELXTL program. Anisotropic thermal parameters were applied to non-hydrogen atoms, and all hydrogen atoms from the organic ligands were calculated and added at idealized positions. Other details of relevant crystallographic data are given in Table S1, and the selected bond lengths and angles

were listed in Tables S2 and S3.

Table S1. Crystal Data and Structure Refinement of **1-Ln**.

Compound reference	1-Eu	1-Dy
Chemical formula	C ₂₈ H ₂₁ EuN ₂ O ₉ S ₂	C ₂₈ H ₂₁ DyN ₂ O ₉ S ₂
Formula Mass	745.55	756.09
Crystal system	Monoclinic	Monoclinic
<i>a</i> /Å	14.249(4)	14.2186(19)
<i>b</i> /Å	12.490(4)	12.5012(16)
<i>c</i> /Å	15.997(4)	15.946(2)
<i>a</i> /°	90	90
<i>b</i> /°	109.471(8)	109.894(2)
<i>g</i> /°	90	90
Unit cell volume/Å ³	2684.1(14)	2665.3(6)
Temperature/K	296.15	296.15
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
No. of formula units per unit cell, <i>Z</i>	4	4
<i>r</i> _{calc} /g cm ⁻³	1.845	1.894
Absorption coefficient, μ/mm ⁻¹	2.553	3.037
F(000)	1480.0	1492.0
Crystal size/mm ³	0.15 × 0.12 × 0.1	0.12 × 0.1 × 0.08
2θ range for data collection/°	4.654 to 50.678	3.326 to 51.996
No. of reflections measured	48232	14028
No. of independent reflections	4889	5175
<i>R</i> _{int}	0.0438	0.0468
Final <i>R</i> ₁ ^a values (<i>I</i> > 2σ(<i>I</i>))	0.0215	0.0368
Final <i>wR</i> ₂ (<i>F</i> ²) values (<i>I</i> > 2σ(<i>I</i>))	0.0508	0.1065
Final <i>R</i> ₁ values (all data)	0.0255	0.0524
Final <i>wR</i> ₂ (<i>F</i> ²) values (all data)	0.0530	0.1421
Goodness of fit on <i>F</i> ²	1.059	1.057
CCDC number	1862728	1862729

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, ^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$

Table S2. Selected bonds lengths [Å] and angles [°] for **1-Eu**.

Eu1-O1	2.373(2)	O2#1-Eu1-O8#3	82.91(8)
Eu1-O2#1	2.345(2)	O3#2-Eu1-O7#3	80.76(7)
Eu1-O3#2	2.487(2)	O4#2-Eu1-O3#3	53.13(7)
Eu1-O4#2	2.435(2)	O4#2-Eu1-O7#3	72.87(8)
Eu1-O5	2.3699(19)	O4#2- Eu1-O8#3	107.62(7)
Eu1-O6#1	2.369(2)	O5-Eu1-O1	74.28(7)
Eu1-O7#3	2.566(2)	O5-Eu1-O3#2	98.31(7)
Eu1-O8#3	2.484(2)	O5-Eu1-O4#2	147.85(7)
O1-Eu1-O3#2	78.87(7)	O5-Eu1-O7#3	121.56(7)
O1-Eu1-O4#2	84.66(8)	O5-Eu1-O8#3	71.93(7)
O1-Eu1-O7#3	155.94(7)	O6#1-Eu1-O1	78.53(7)
O1-Eu1-O8#3	132.09(7)	O6#2-Eu1-O3#2	123.61(7)
O2#1-Eu1-O1	124.59(7)	O6#2-Eu1-O4#2	73.85(7)
O2#1-Eu1-O3#2	154.98(7)	O6#2-Eu1-O5	123.52(7)
O2#1- Eu1-O4#2	130.07(7)	O6#2- Eu1-O7#3	102.64(7)
O2#1-Eu1-O5	82.08(7)	O6#2-Eu1-O8#3	149.22(7)
O2#1-Eu1-O6#1	74.25(7)	O8#3-Eu1-O3#2	73.59(8)
O2#1-Eu1-O7#3	77.90(7)	O8#3-Eu1-O7#3	51.56(6)

Symmetry transformations used to generate equivalent atoms: #1: 1-x, 1-y, 1-z; #2: -1/2+x, 1/2-y, -1/2+z; #3: -1/2+x, 3/2-y, -1/2+z.

Table S3. Selected bonds lengths [Å] and angles [°] for **1-Dy**.

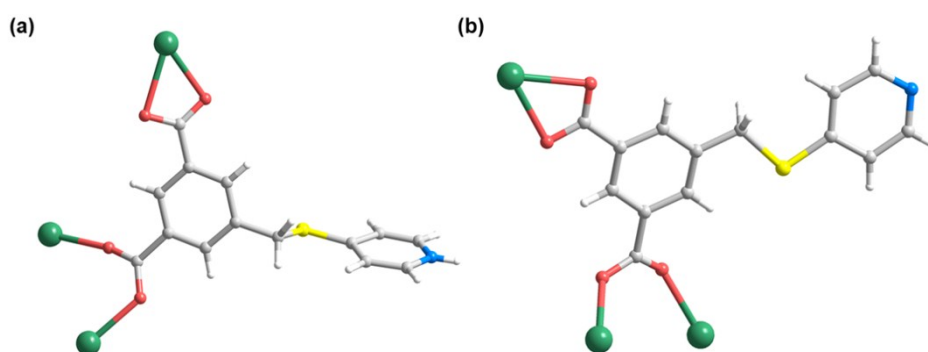
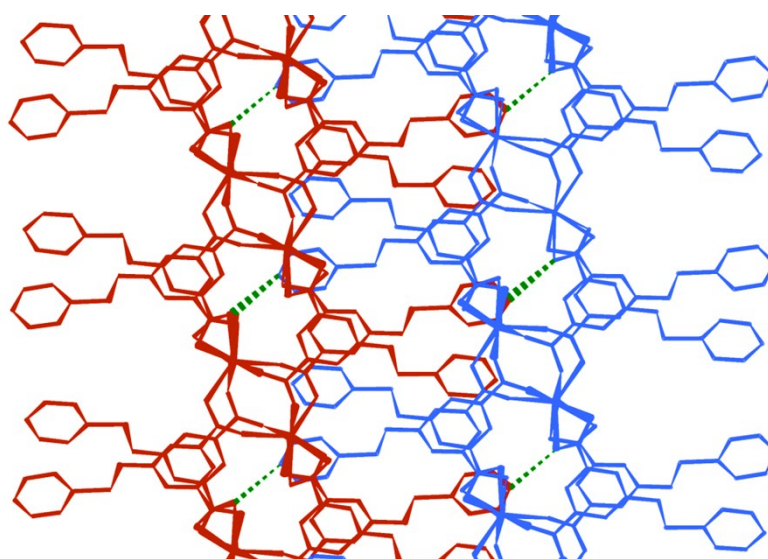
Dy1-O1	2.324(4)	O2#1-Dy1-O8#3	82.76(15)
Dy1-O2#1	2.299(4)	O3#2- Dy1-O7#3	81.50(15)
Dy1-O3#2	2.456(4)	O4#2- Dy1-O3#3	54.06(15)
Dy1-O4#2	2.396(5)	O4#2- Dy1-O7#3	72.62(17)
Dy1-O5	2.320(4)	O4#2- Dy1-O8#3	107.88(16)
Dy1-O6#1	2.320(4)	O5- Dy1-O1	74.30(15)
Dy1-O7#3	2.536(4)	O5-Dy1-O3#2	97.53(15)
Dy1-O8#3	2.446(4)	O5-Dy1-O4#2	148.06(16)
O1-Dy1-O3#2	78.62(15)	O5-Dy1-O7#3	121.95(15)
O1-Dy1-O4#2	84.77(17)	O5-Dy1-O8#3	71.55(14)
O1-Dy1-O7#3	155.97(16)	O6#1-Dy1-O1	78.67(16)
O1-Dy1-O8#3	131.74(15)	O6#2-Dy1-O3#2	124.20(16)
O2#1-Dy1-O1	124.62(15)	O6#2-Dy1-O4#2	73.65(15)
O2#1-Dy1-O3#2	154.78(15)	O6#2-Dy1-O5	123.65(15)
O2#1-Dy1-O4#2	130.17(16)	O6#2-Dy1-O7#3	101.94(16)
O2#1-Dy1-O5	81.77(15)	O6#2-Dy1-O8#3	149.41(16)
O2#1-Dy1-O6#1	74.54(15)	O8#3-Dy1-O3#2	73.25(16)
O2#1-Dy1-O7#3	77.71(15)	O8#3-Dy1-O7#3	52.46(14)

Symmetry transformations used to generate equivalent atoms: #1: 1-x, 1-y, 1-z; #2: -1/2+x, 1/2-y, -1/2+z; #3: -1/2+x, 3/2-y, -1/2+z.

Table S4. Continuous Shape Measures calculation for **1-Dy**

complex	OP-8 (D_{8h})	HPY-8 (C_{7v})	HBPY-8 (D_{6h})	CU-8 (O_h)	SAPR-8 (D_{4d})	TDD-8 (D_{2d})	JGBF-8 (D_{2d})	JETBPY-8 (D_{3h})
	33.365	22.367	11.330	5.407	4.471	2.613	13.253	25.630
1-Dy	JBTPR-8 (C_{2v})	BTPR-8 (C_{2v})	JSD-8 (D_{2d})	TT-8 (T_d)	ETBPY-8 (D_{3h})			
	4.154	3.060	6.516	6.105	19.957			

OP-8 = Octagon; HPY-8 = Heptagonal pyramid; HBPY-8 = Hexagonal bipyramid; CU-8 = Cube; SAPR-8 = Square antiprism; TDD-8 = Triangular dodecahedron; JGBF-8 = Johnson gyrobifastigium J26; JETBPY-8 = Johnson elongated triangular bipyramid J14; JBTPR-8 = Biaugmented trigonal prism J50; BTPR-8 = Biaugmented trigonal prism; JSD-8 = Snub diphenoid J84; TT-8 = Triakis tetrahedron; ETBPY-8 = Elongated trigonal bipyramid.

**Figure S1.** Coordination models of the ligand in **1-Ln**. Colour schemes for the structure: Dy, green; N, blue; C, light grey, H, white.**Figure S2.** Hydrogen bonds (green dash lines) between adjacent 2D networks.

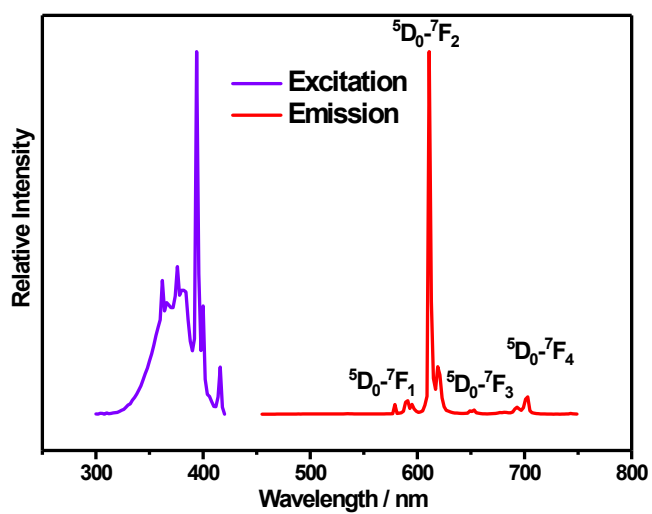


Figure S3. The solid-state luminescent properties of 1-Eu.

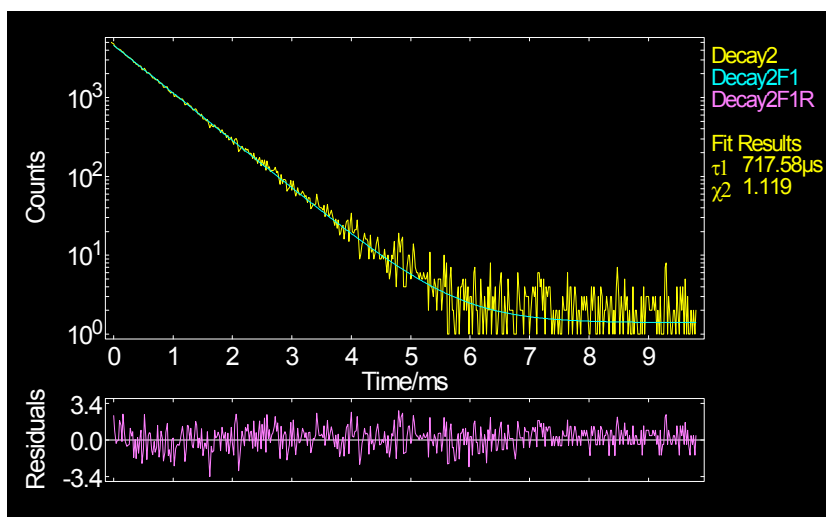


Figure S4. Luminescence decay of 1-Eu measured at the excitation/emission maxima.

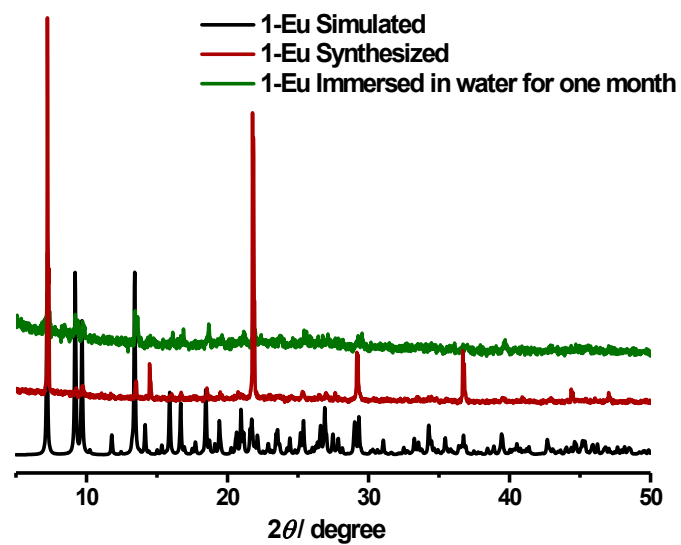


Figure S5. PXRD patterns of 1-Eu.

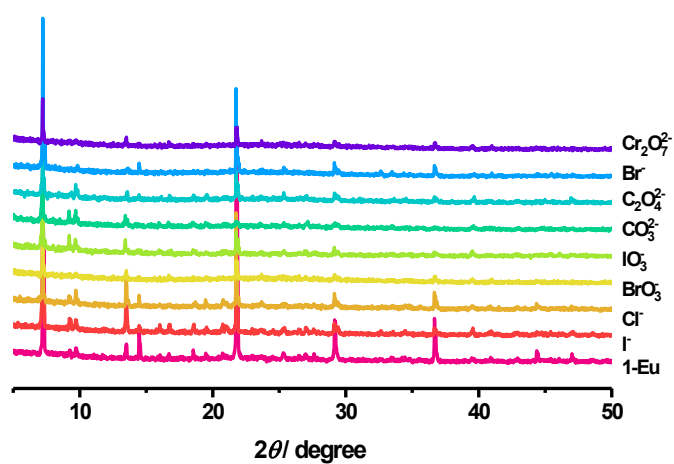


Figure S6. PXRD patterns of 1-Eu treated by different anion water solutions.

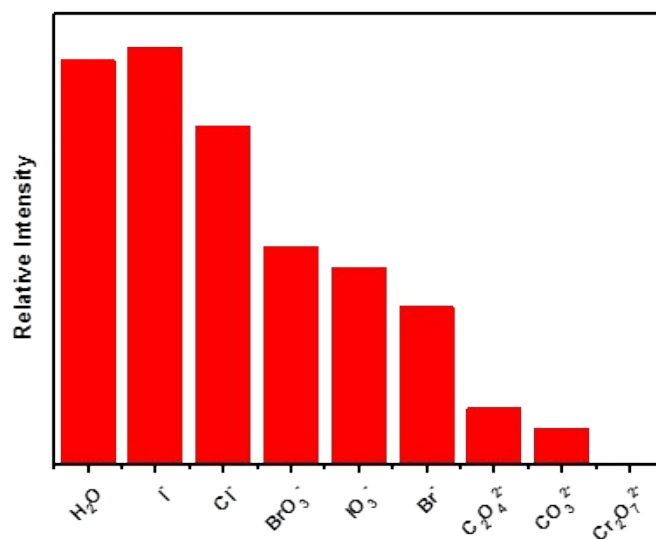


Figure S7. The luminescent intensity at 611 nm of 1-Eu in various anion solutions when excited at 394 nm.

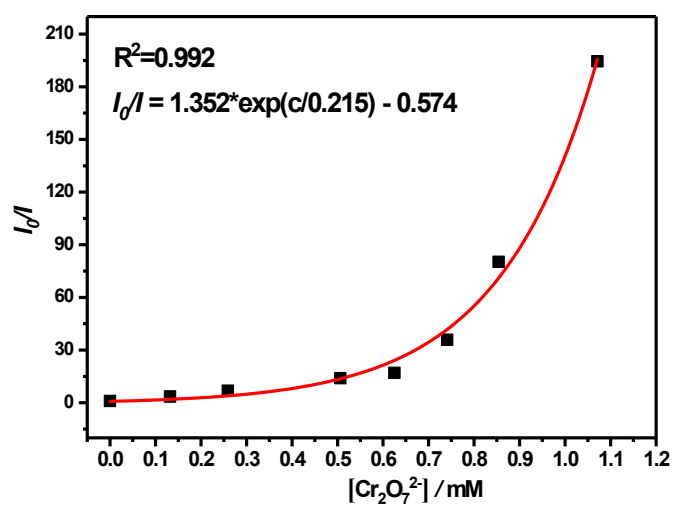


Figure S8. The plot of luminescent intensity vs Cr₂O₇²⁻ concentration.

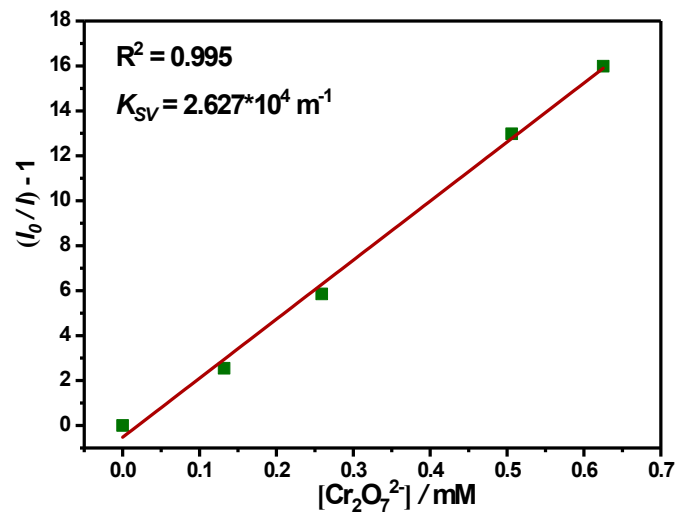


Figure S9. The linear correlation for the plot of $(I_0/I)-1$ vs concentration of $\text{Cr}_2\text{O}_7^{2-}$ in low concentration range.

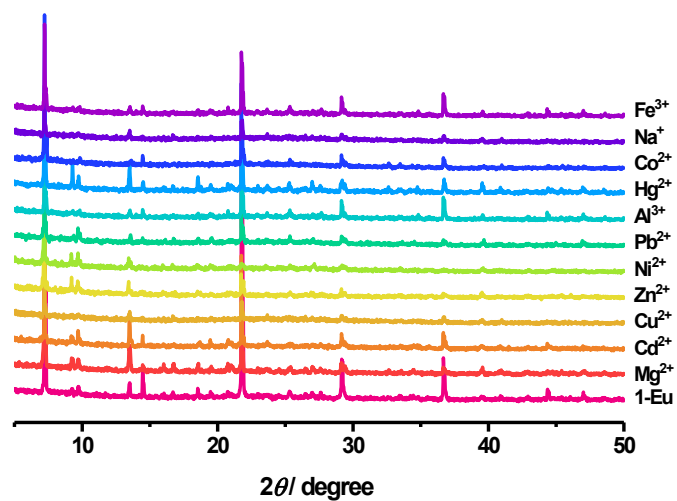


Figure S10. The PXRD patterns of **1-Eu** treated by different $\text{M}(\text{NO}_3)_x$ ($\text{M} = \text{Fe}^{3+}, \text{Na}^+, \text{Co}^{2+}, \text{Hg}^{2+}, \text{Al}^{3+}, \text{Pb}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}, \text{Cu}^{2+}, \text{Cd}^{2+}$ and Mg^{2+}) aqueous solutions.

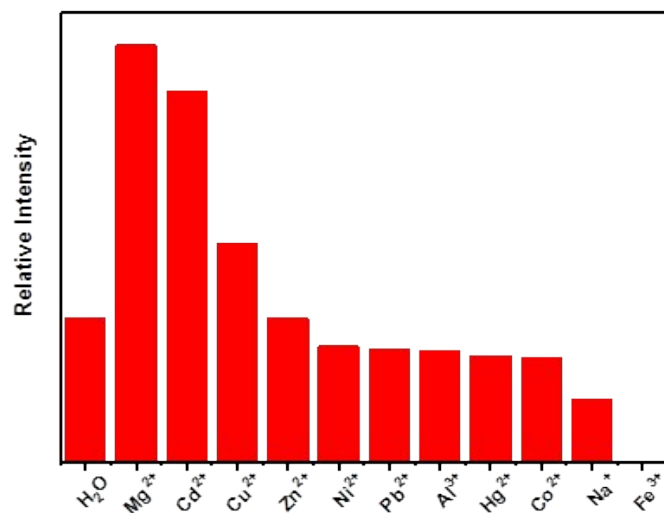


Figure S11. The luminescent intensity at 611 nm of 1-Eu in various cation solutions when excited at 394 nm.

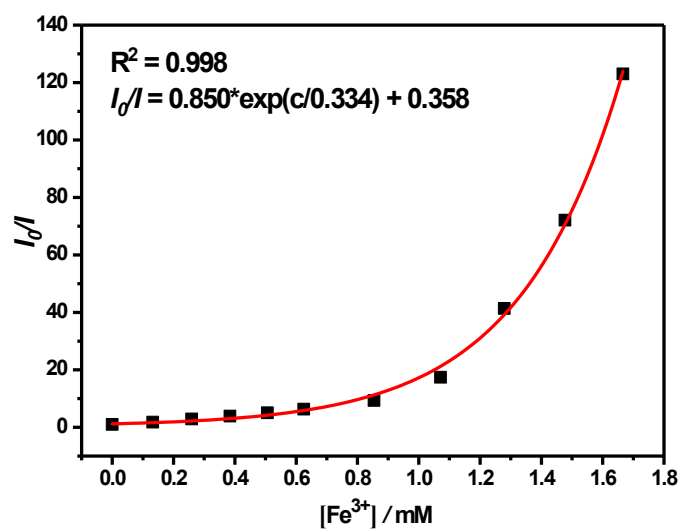


Figure S12. The plot of luminescent intensity vs Fe³⁺ concentration.

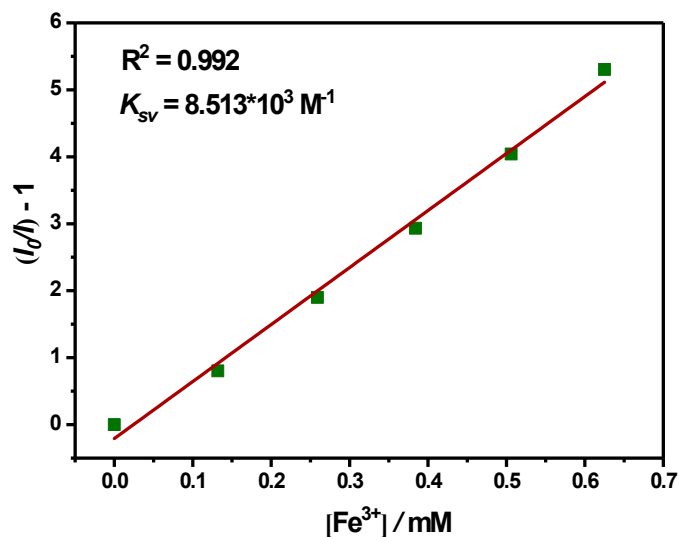


Figure S13. The linear correlation for the plot of $(I_0/I) - 1$ vs concentration of Fe^{3+} in low concentration range.

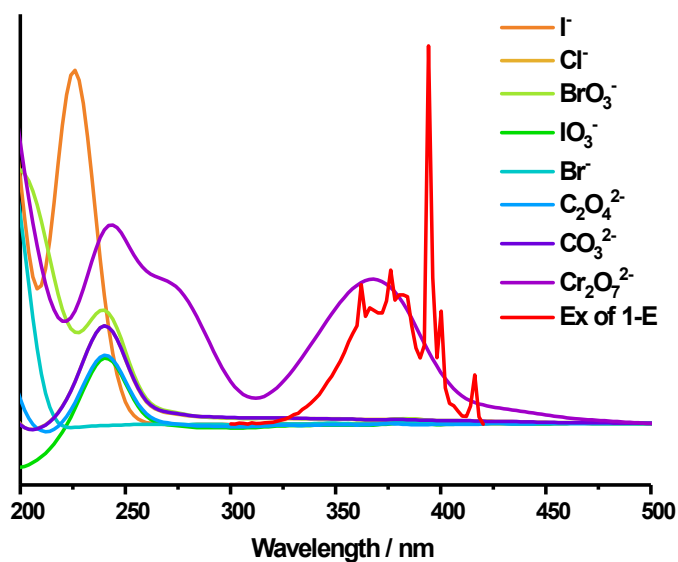


Figure S14. UV-Vis adsorption spectra of anion aqueous solutions and the excitation spectrum of **1-Eu**.

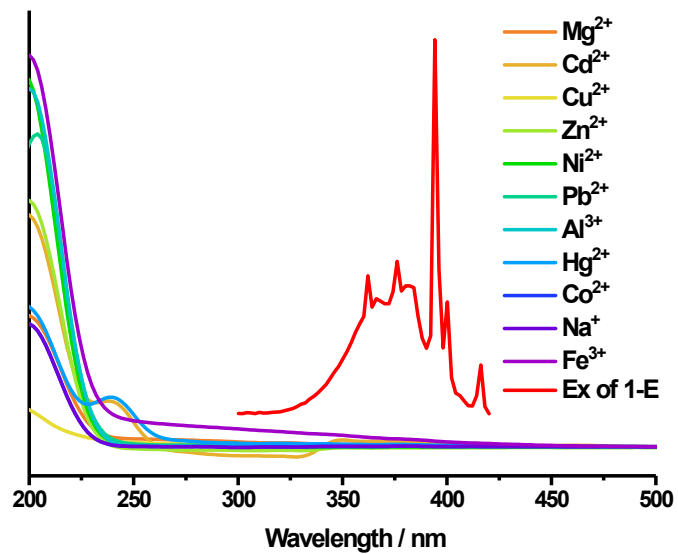


Figure S15. UV-Vis adsorption spectra of $M(\text{NO}_3)_x$ aqueous solutions and the excitation spectrum of **1-Eu**.

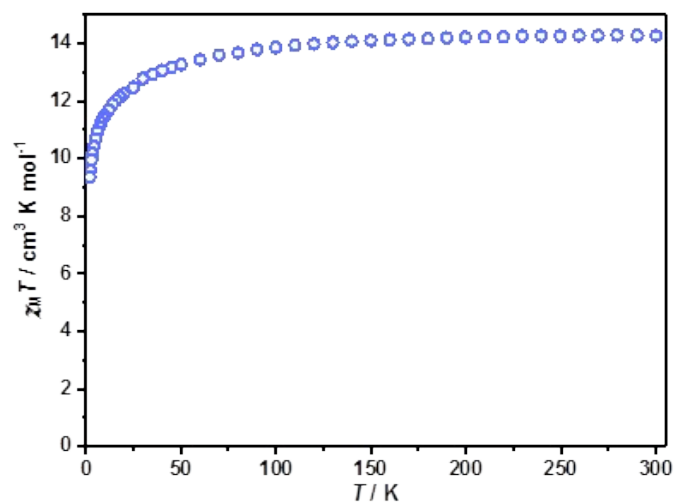


Figure S16. Plot of the $\chi_M T$ versus temperature for **1-Dy** in an applied magnetic field of 1 kOe.

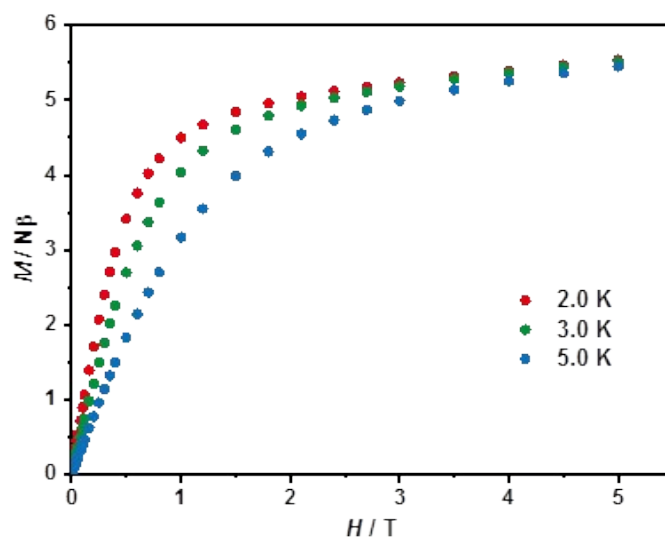


Figure S17. Field dependence of the magnetization, M , at 2, 3 and 5 K for **1-Dy** plotted as M vs. H .