

Supporting Information

Lanthanoid containing phosphotungstates: Syntheses, crystal structure, electrochemistry, photoluminescence and magnetic properties

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Table S1. Crystallographic table of polyanions $K_{11}[Ln(PW_{11}O_{39})_2].xH_2O$ ($Ln = Pr^{3+}$ (**1a**), Nd^{3+} (**2a**), Eu^{3+} (**3a**), Tb^{3+} (**5a**), Dy^{3+} (**6a**), Er^{3+} (**8a**), and Tm^{3+} (**9a**)) crystallized in the monoclinic system.

Polyanion	Pr-1a	Nd-2a	Eu-3a	Tb-5a	Dy-6a	Er-8a	Tm-9a
Emperical Formula	$K_{10}O_{109.50}PrP_2W_{22}$	$K_{10}NdO_{109.50}P_2W_{22}$	$K_{10}EuO_{109.50}P_2W_{22}$	$Cs_{0.50}K_9TbO_{109.50}P_2W_{22}$	$Cs_{0.50}DyK_{8.50}O_{108.50}P_2W_{22}$	$K_{10}ErO_{107.50}P_2W_{22}$	$K_{10}TmO_{110.50}P_2W_{22}$
Formula weight	6390.55	6393.88	6401.60	6435.92	6403.95	6384.90	6434.57
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a [Å]	18.7470(6)	18.7109(7)	18.5849(8)	18.8569(15)	18.6874(6)	18.6999(9)	18.9058(6)
b [Å]	37.8100(12)	37.6178(11)	37.4594(9)	37.794(2)	37.5496(10)	37.2860(10)	37.4737(8)
c [Å]	14.1269(4)	14.1038(5)	14.0613(4)	14.0876(7)	14.0978(3)	14.0901(3)	14.1131(3)
α [°]	90	90	90	90	90	90	90
β [°]	92.533(3)	92.572(4)	92.838(3)	92.352(5)	92.233(2)	92.577(3)	92.384(2)
γ [°]	90	90	90	90	90	90	90
V [Å ³]	10003.7(5)	9917.1(6)	9777.2(6)	10031.4(11)	9885.0(5)	9814.3(6)	9990.1(4)
Z	4	4	4	4	4	4	4
ρ_{calcd} [g cm ⁻³]	4.243	4.282	4.349	4.261	4.303	4.321	4.294
μ [mm ⁻¹]	26.229	26.491	26.943	26.4513	26.924	27.092	26.667
Refelction collected	91066	62641	79788	74640	88342	79036	88565
Unique (Rint)	16343	12477	15018	14003	17140	16201	16706
Observed[$I > 2\sigma(I)$]							
Parameters	746	746	747	746	742	738	754
Gof	1.014	1.113	1.085	1.077	1.259	1.093	1.202
$R[I > 2\sigma(I)]^{[a]}$	0.0575	0.0989	0.0673	0.0939	0.0743	0.0716	0.0779
$Rw(\text{ all data})^{[b]}$	0.11825	0.2313	0.1308	0.1908	0.1323	0.1462	0.1422

[a] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. [b] $R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$

Table S2. Bond lengths of Ln-O (Å) for polyanions $K_{11}[Ln(PW_{11}O_{39})_2] \cdot xH_2O$ (Ln = Pr³⁺ (**1a**), Nd³⁺ (**2a**), Eu³⁺ (**3a**), Gd³⁺ (**4a**), Tb³⁺ (**5a**), Dy³⁺ (**6a**), Ho³⁺ (**7a**), Er³⁺ (**8a**), and Tm³⁺ (**9a**)).

Ln ³⁺ =	Pr	Nd	Eu	Gd	Tb	Dy	Ho	Er	Tm
Ln-O36	2.445(12)	2.46(2)	2.394(13)	2.377(12)	2.35 (2)	2.376(15)	2.343(12)	2.347(14)	2.324(16)
Ln-O37	2.436(13)	2.38(3)	2.390(15)	2.407(10)	2.35(2)	2.354(15)	2.381(11)	2.345(16)	2.340(17)
Ln-O38	2.470(12)	2.49(3)	2.414(16)	2.342(12)	2.41(2)	2.397(15)	2.321(12)	2.375(16)	2.368(16)
Ln-O39	2.467(11)	2.47(2)	2.416(14)	2.443(12)	2.40(2)	2.378(14)	2.385(11)	2.342(14)	2.351(16)
Ln-O40	2.450(13)	2.46(3)	2.407(14)	2.372(12)	2.36(2)	2.345(15)	2.337(11)	2.331(14)	2.305(16)
Ln-O41	2.446(12)	2.44(3)	2.411(16)	2.372(11)	2.37(2)	2.367(14)	2.358(11)	2.338(14)	2.338(16)
Ln-O42	2.433(12)	2.40(3)	2.406 (14)	2.406(11)	2.373(19)	2.355(15)	2.376(12)	2.316(15)	2.341(16)
Ln-O43	2.441(12)	2.39(2)	2.372(14)	2.411(11)	2.335(19)	2.340(15)	2.390(11)	2.340(13)	2.316(15)
Average	2.45	2.44	2.40	2.39	2.38	2.36	2.36	2.34	2.33

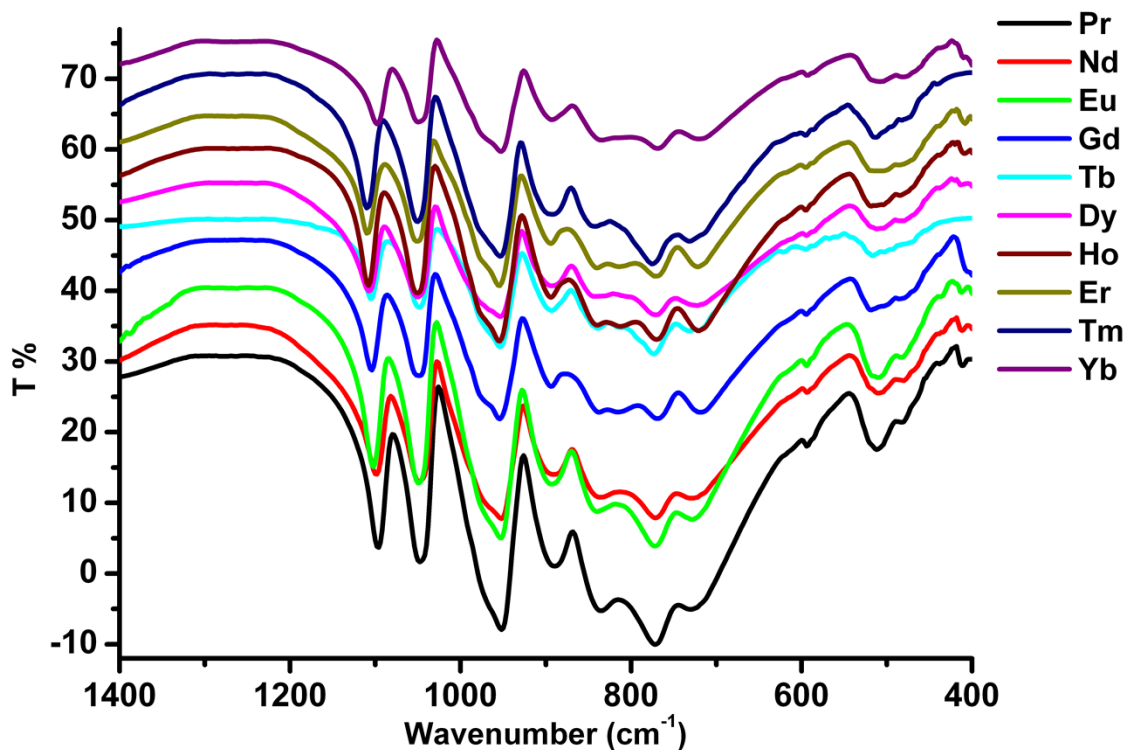


Figure S3. FT-IR spectra of molecular cluster **Pr(1a) – Yb(10a)** (recorded in KBr pellet, only the “*fingerprint*” signature of polyoxophosphotungstate is displayed).

Table S4. Vibrational frequencies of P-O and W-O bands of molecular cluster **Pr(1a) – Yb(10a)**

Sl. No.	ν_{as} (P-O)	$\nu_{as}(W-O_i)$ (W=O)	ν_{as} (W-O _b -W) (Corner sharing)	ν_{as} (W-O _c -W) (Edge sharing)
Pr³⁺(1a)	1096,1048	951	887	836, 772, 727
Nd³⁺(2a)	1100, 1048	957	891	840, 772, 724
Eu³⁺(3a)	1104, 1048	953	891	838, 772, 727
Gd³⁺(4a)	1104, 1050	955	891	842, 770, 729
Tb³⁺(5a)	1106, 1050	951	897	838, 774, 729
Dy³⁺(6a)	1106, 1052	953	891	845, 770, 719
Ho³⁺(7a)	1110, 1050	955	893	842, 770, 721
Er³⁺(8a)	1110, 1050	955	895	842, 772, 724
Tm³⁺(9a)	1110, 1050	951	893	842, 774, 729
Yb³⁺(10a)	1197, 1049	951	893	835, 768, 718

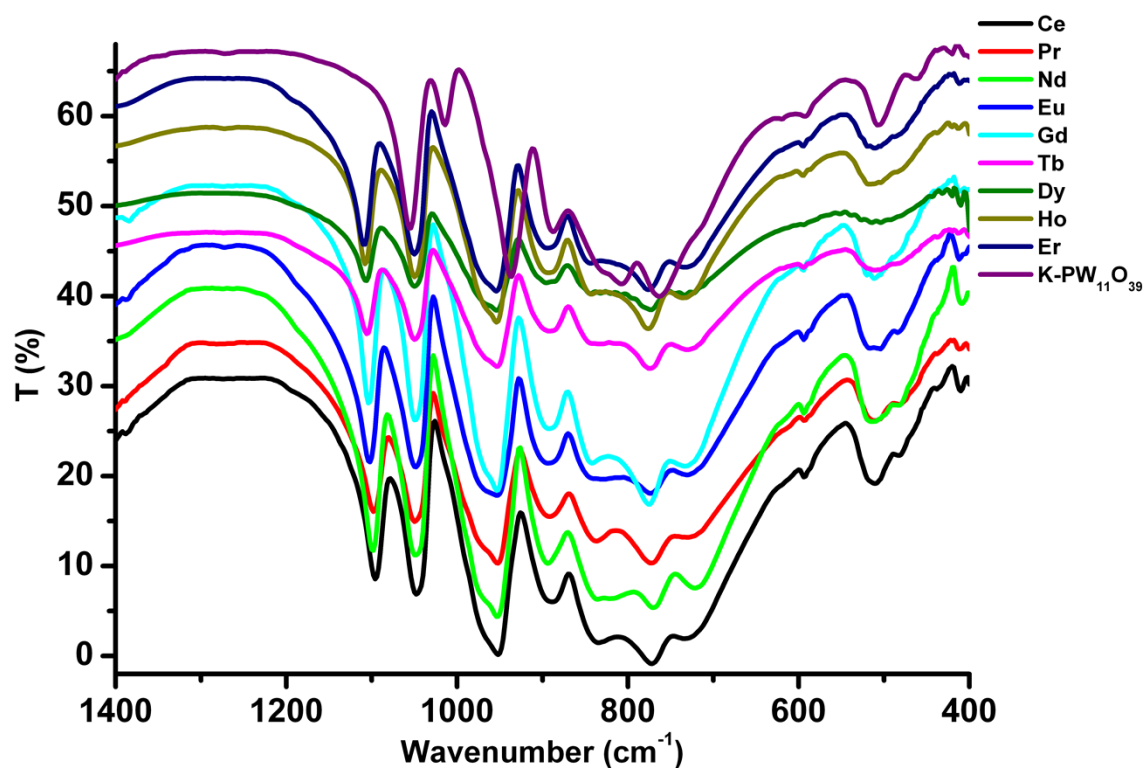


Figure S5. FT-IR spectra of Ce – Er complexes obtained from reaction of $[\alpha\text{-PW}_{11}\text{O}_{39}]^{7-}$ with lanthanoid metal salts (recorded in KBr pellet, only the “*fingerprnt*” signature of polyoxophosphotungstate is displayed).

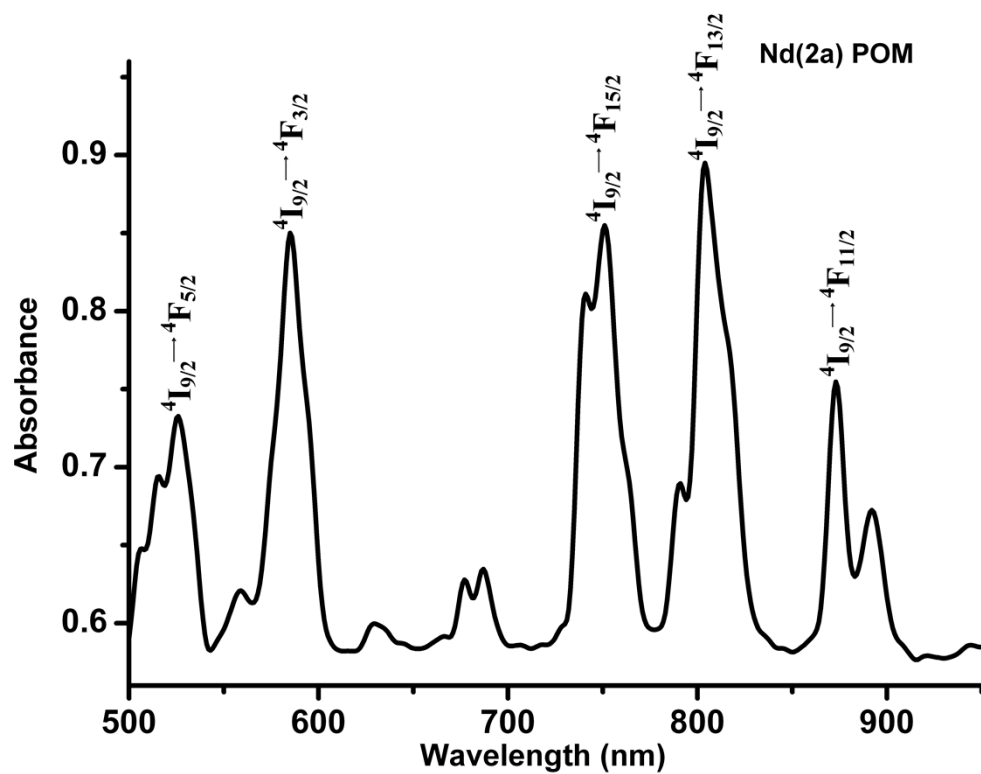


Figure S6. Solid state UV/vis spectrum of molecular cluster **Nd(2a)**.

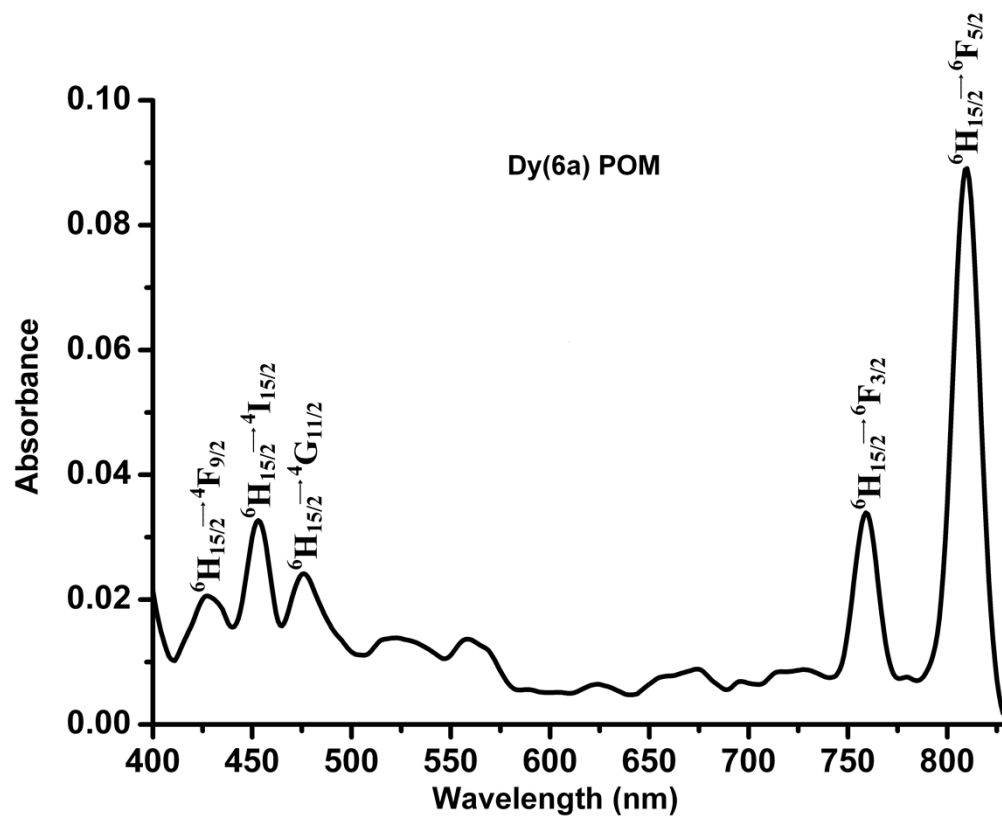


Figure S7. Solid state UV/vis spectrum of molecular cluster **Dy(6a)**.

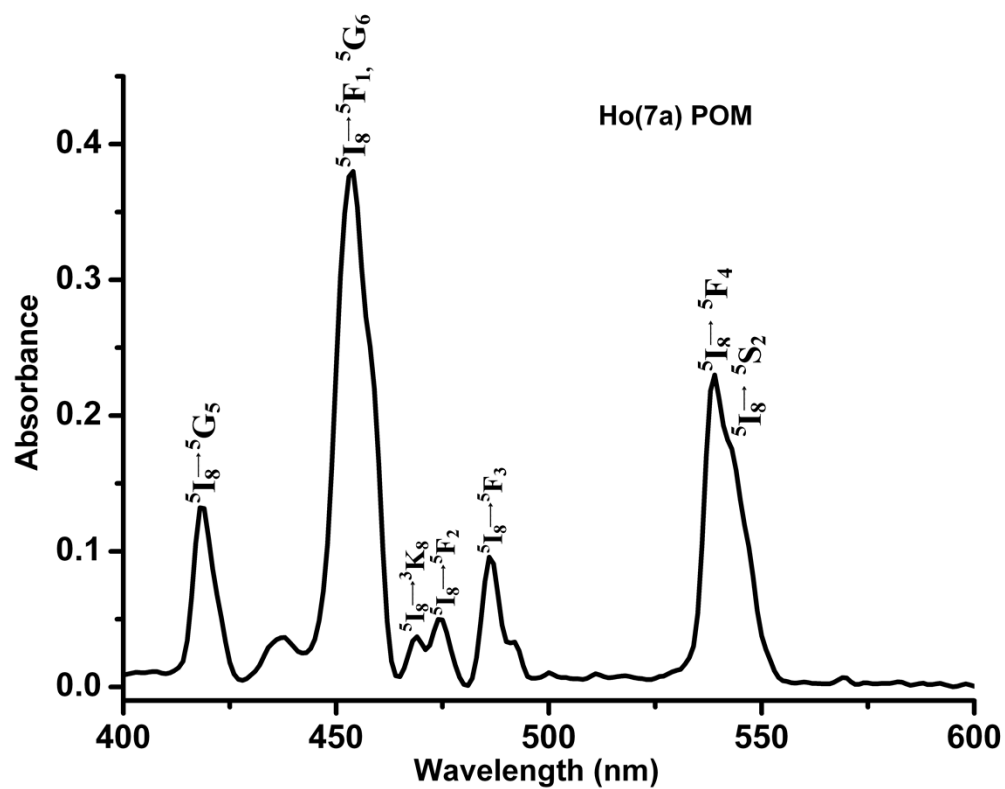


Figure S8. Solid state UV/vis spectrum of molecular cluster **Ho(7a)**.

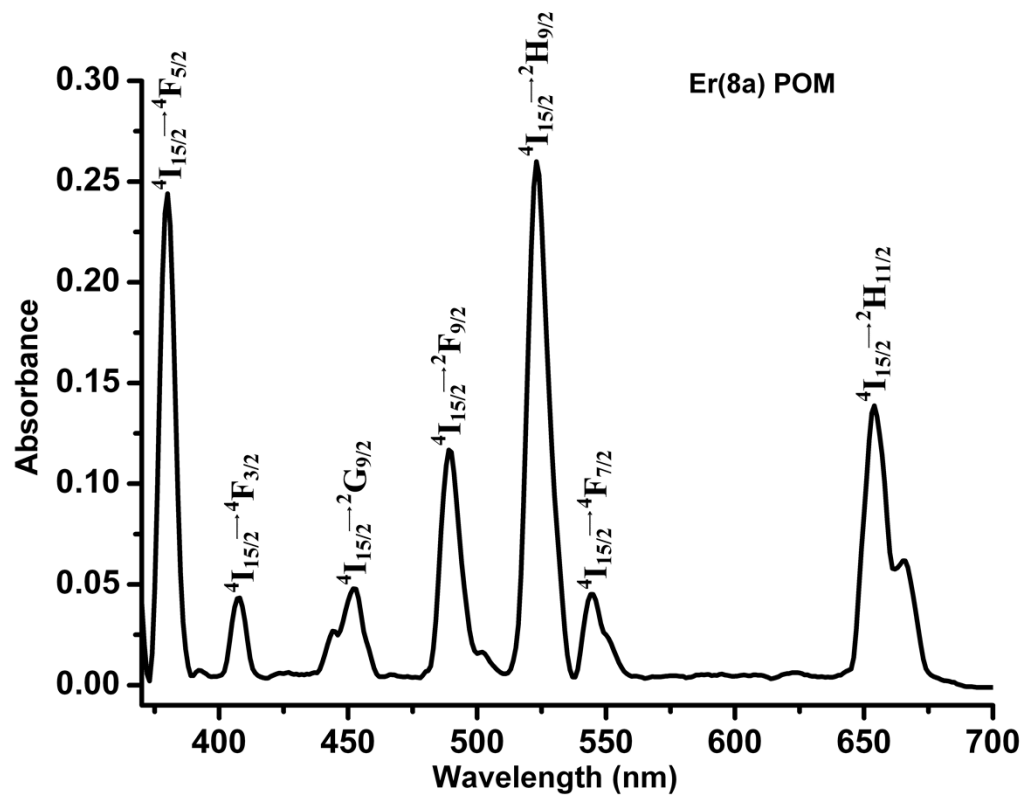


Figure S9. Solid state UV/vis spectrum of molecular cluster **Er(8a)**.

Table S10. Cathodic (E_{pc}) peak potentials, peak potential differences ($\Delta E_p = E_{pa} - E_{pc}$), formal redox potentials ($E^0 = 1/2(E_{pa} + E_{pc})$) and cathodic peak potential differences with respect to the first reduction wave of **{PW11}** (ΔE_{pc1}) for the electron transfer processes discussed in the text. The values are taken from voltammograms recorded at 10 mV.s^{-1} . All values are in V vs. SCE. Concentrations were $2 \times 10^{-4} \text{ M}$ unless otherwise stated.

pH	Species	E_{pc}	ΔE_p	E^0	ΔE_{pc1}
3.0	Tm(9a)	-0.716	0.064	-0.684	
		-0.840	0.086	-0.797	
4.0	PW ₁₁ $4 \times 10^{-4} \text{ M}$	-0.714	0.076	-0.676	0.000
		-0.842	0.056	-0.814	
	Eu(3a)	$\approx$ -0.834	0.200	-0.734	-0.120
		-0.934	0.128	-0.870	
	Gd(4a)	-0.842	0.200	-0.742	-0.128
		-0.928	0.138	-0.859	
	Tb(5a)	-0.836	0.186	-0.743	-0.122
		-0.926	0.084	-0.884	
	Dy(6a)	-0.846	0.196	-0.748	-0.132
		-0.926	0.130	-0.861	
	Ho(7a)	-0.834	0.184	-0.742	-0.120
		-0.916	0.126	-0.853	
	Er(8a)	-0.846	0.210	-0.741	-0.132
		-0.922	0.134	-0.855	
	Tm(9a)	-0.794	0.102	-0.743	-0.080
		-0.920	0.102	-0.869	
	Eu ³⁺ $8 \times 10^{-4} \text{ M}$	-0.950	0.392	-0.754	
5.0	PW ₁₁ $4 \times 10^{-4} \text{ M}$	-0.826	0.116	-0.768	0.000
		-0.906	0.046	-0.883	
	Eu(3a)	-0.918	0.252	-0.792	-0.092
		-1.006	0.122	-0.945	
	Tm(9a)	-0.840	0.110	-0.785	-0.014
		-0.974	0.108	-0.920	

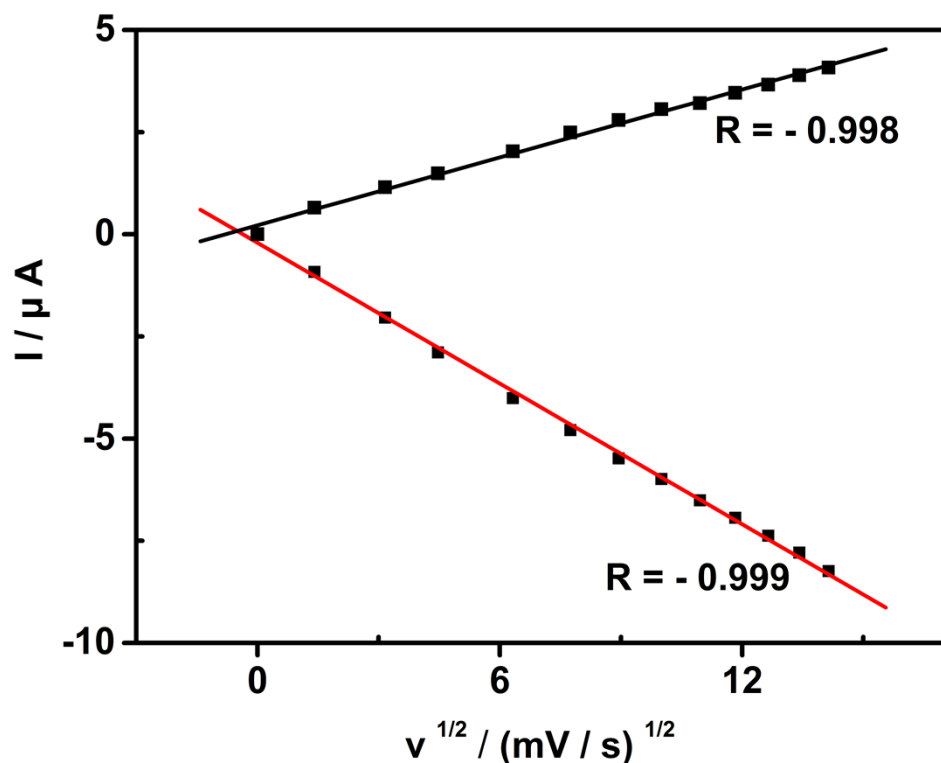


Figure S11: Dependence of the peak current on the square root of the scan rate for the most positive redox couple of a 0.2 mM **Tm(9a)** solution in 1 M $\text{CH}_3\text{COOLi} + \text{CH}_3\text{COOH}$, pH = 5 ($v = 2 ; 10 ; 20 ; 40 ; 60 ; 80 ; 100 ; 120 ; 140 ; 160 ; 180 ; 200 \text{ mV.s}^{-1}$).

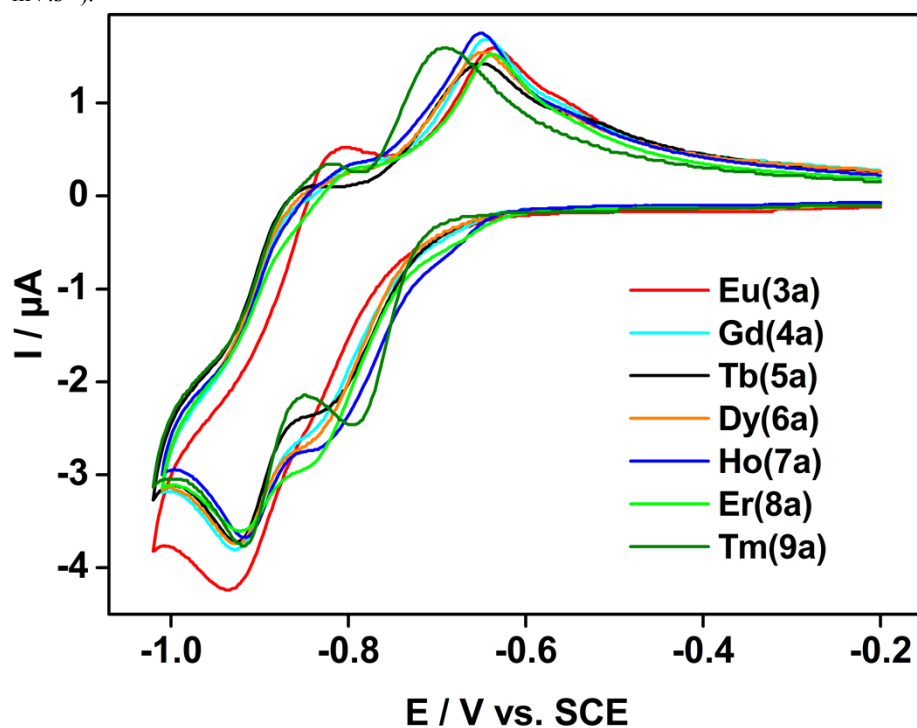


Figure S12. Comparison of the cyclic voltammograms obtained from solutions of conc. $2 \times 10^{-4} \text{ M}$ for **Eu(3a)** -**Tm(9a)** in 1 M $\text{LiCH}_3\text{COO}/\text{CH}_3\text{COOH}$, pH = 4.0, at 10 mV.s^{-1} .

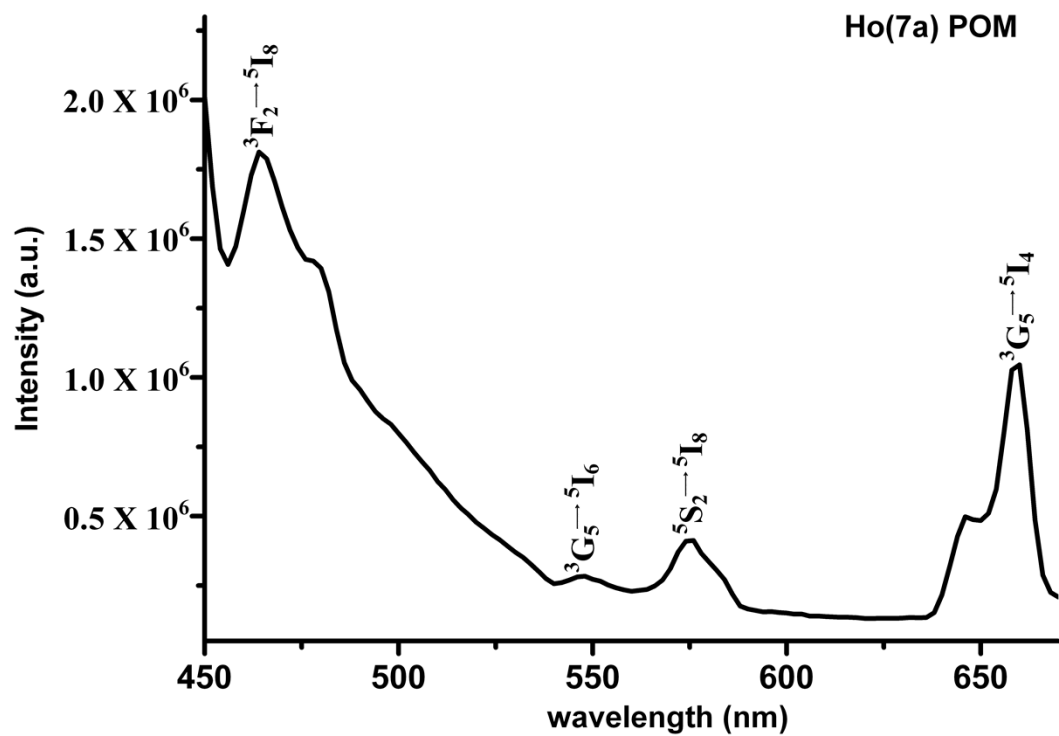


Figure S13. Photoluminescence spectrum of molecular cluster **Ho(7a)** POMs.

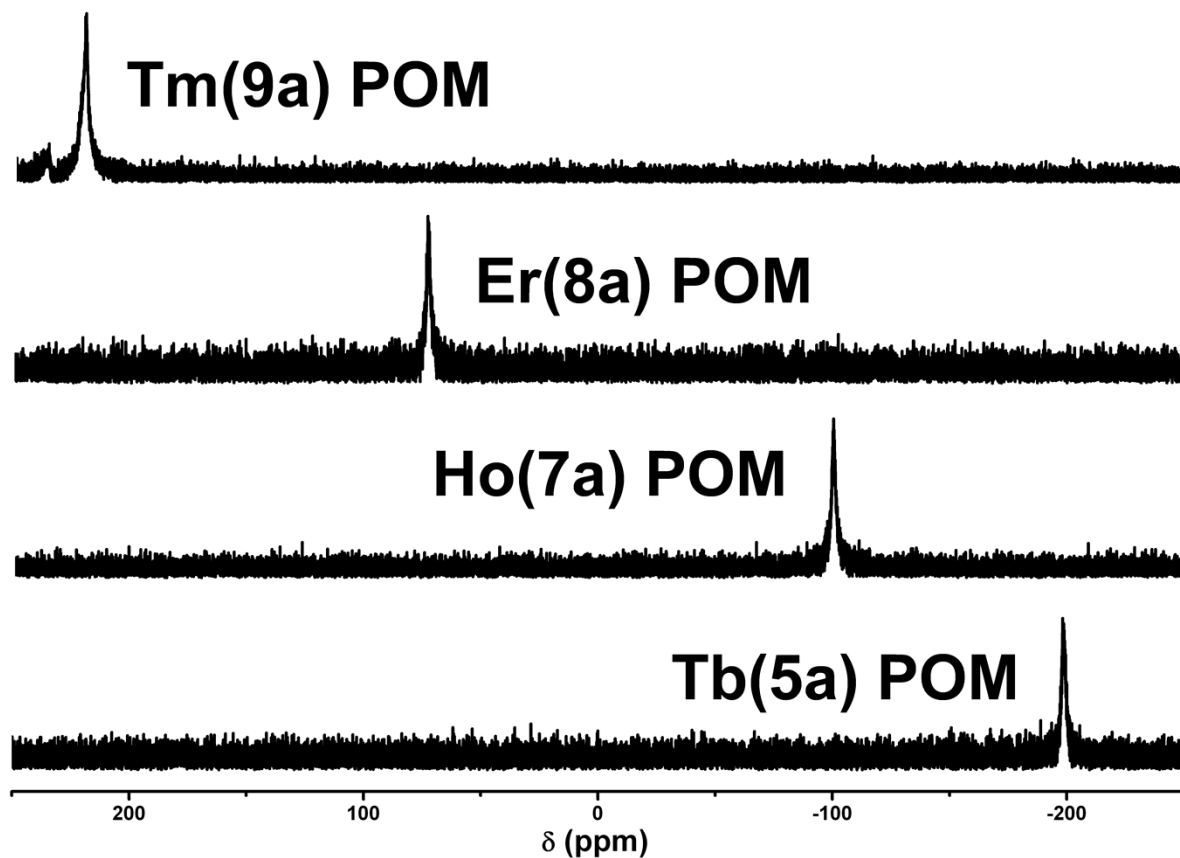


Figure S14. ^{31}P NMR spectra of Ln-POM (Ln = Tb(5a) top, Ho(7a), Er(8a), Tm(9a)) redissolved in D_2O solvent.

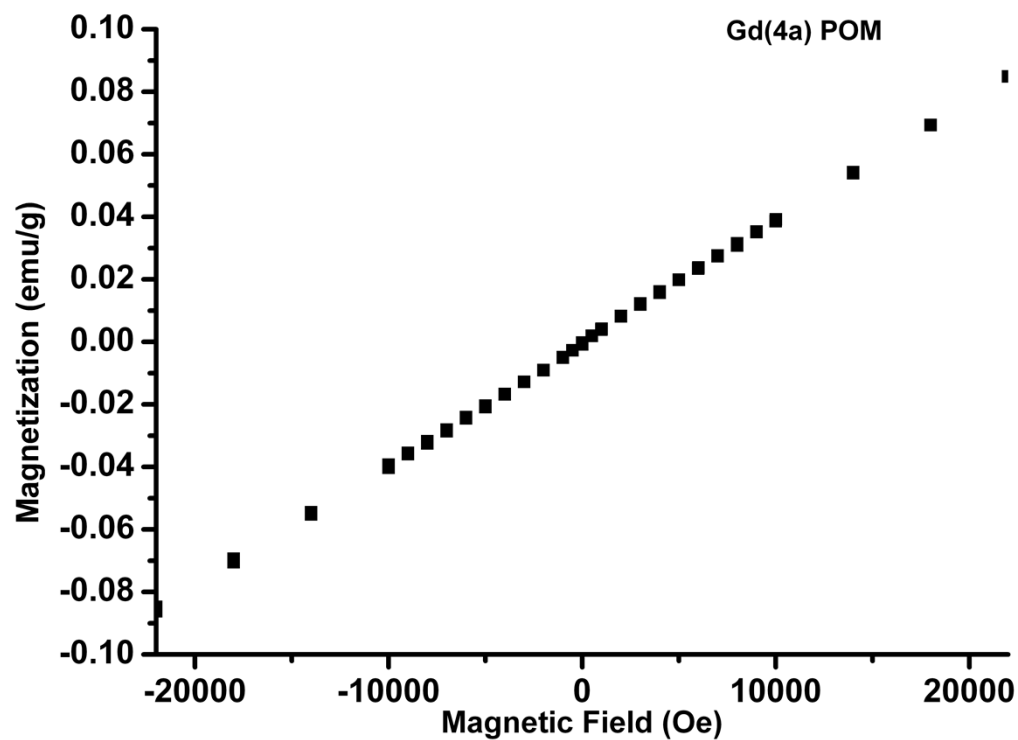


Figure S15. Plot of magnetization (M) vs magnetic field (H) for **Gd(4a)** POM at room temperature.

$$\mu_{\text{eff}} = 2.828(\chi_m T)^{1/2} \dots\dots\dots(\text{Eq.1})$$

Where, χ_m is magnetic susceptibility and T = temperature

$$\chi_m = M/H \times \text{Molecular weight} \dots\dots\dots(\text{Eq.2})$$

$\chi_m = 0.02515$, substitute the value of χ_m in (Eq.1)

$$\mu_{\text{eff}} = 7.75 \mu_B$$

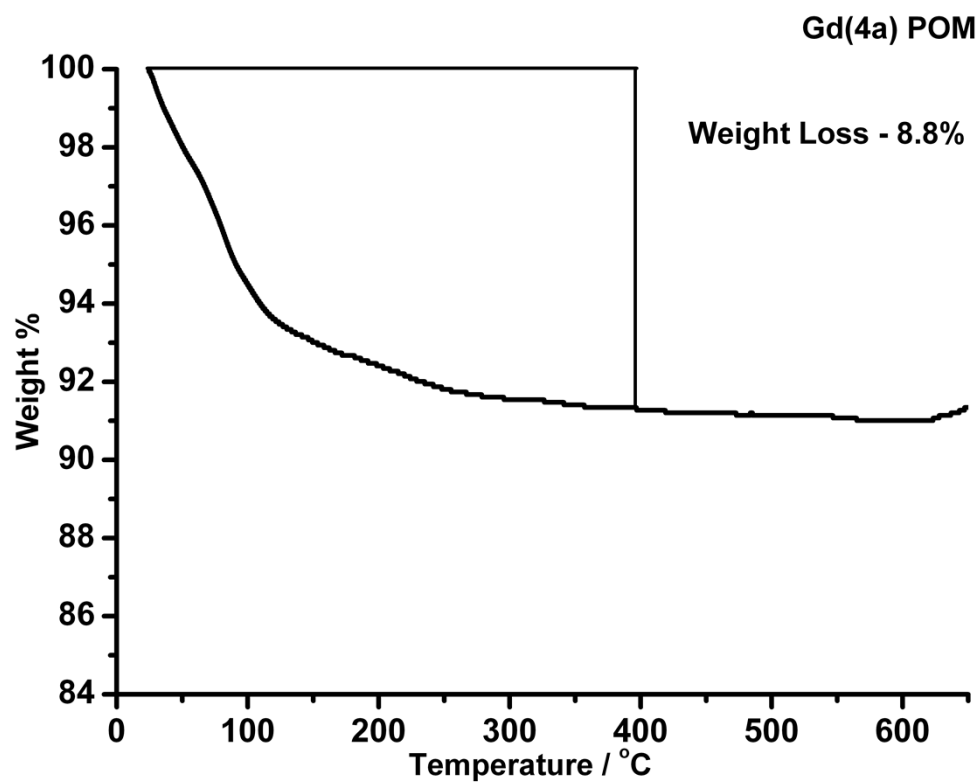


Figure S16. Thermogravimetric analysis of **Gd(4a)** POM displaying the weight loss corresponding to crystal water molecules. (Pr^{3+} (**1a**) = 5.9 %, Nd^{3+} (**2a**) = 6.9 %, Eu^{3+} (**3a**) = 7.2 %, Tb^{3+} (**5a**) = 5.9 %, Dy^{3+} (**6a**) = 7.0 %, Ho^{3+} (**7a**) = 6.8 %, Er^{3+} (**8a**) = 8.6 %, Tm^{3+} (**9a**) = 6.8 %, and Yb^{3+} (**10a**) = 7.8%.