Electronic supplementary information

Incorporating polyoxometalates and organic ligands to pursue 3d-4f heterometallic clusters: a series of $\{Cr_4Ln_4\}$ clusters stabilized by phthalic acid and $[SiW_{12}O_{40}]^{4-}$

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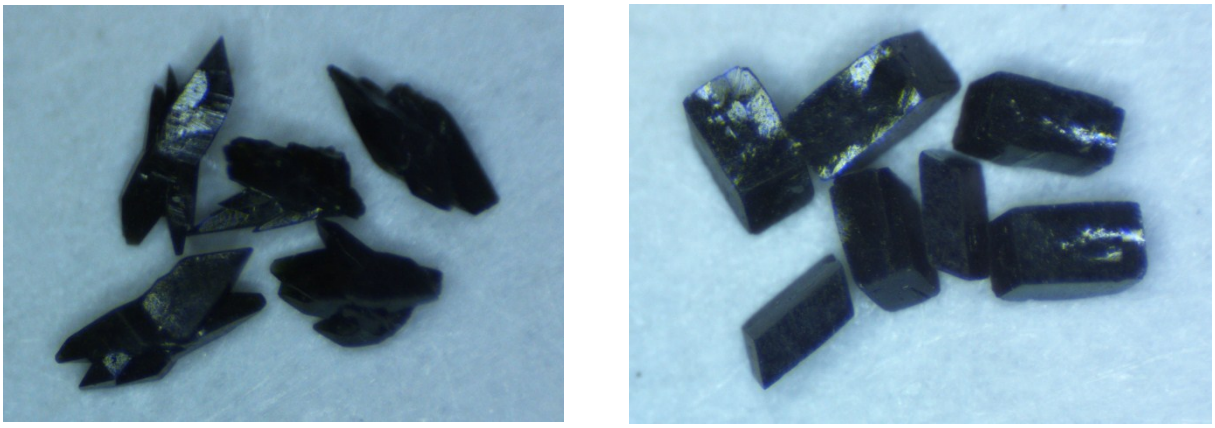

Figure S1 black block crystals of **1-Ce** (left) and **2-Tb** (right).

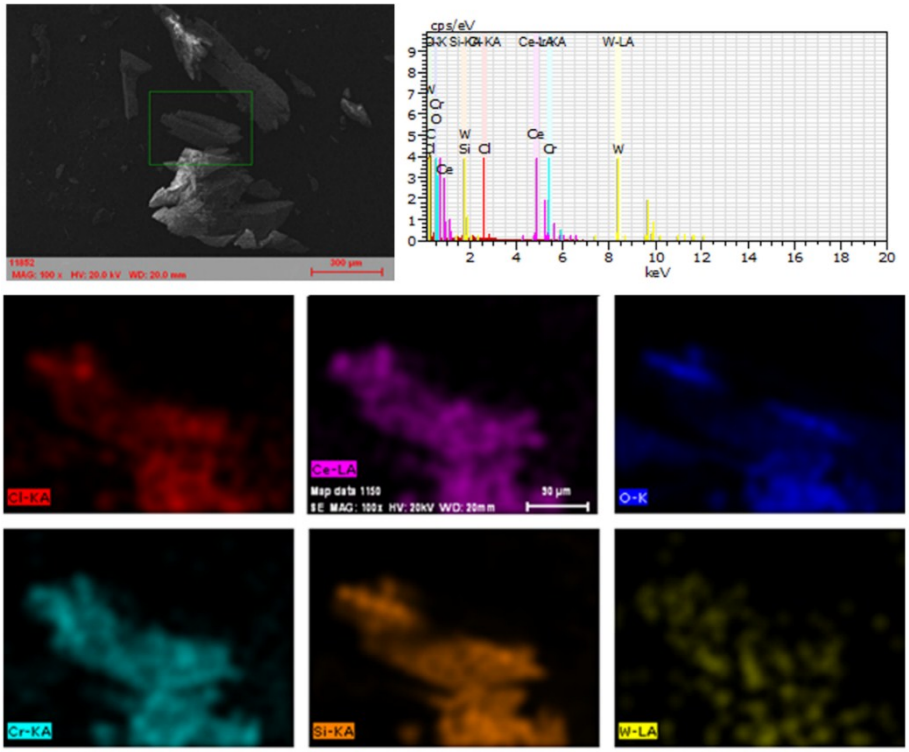

Figure S2 The EDS elemental mapping of Cl, Ce, O, Cr, Si, and W for **1-Ce**.

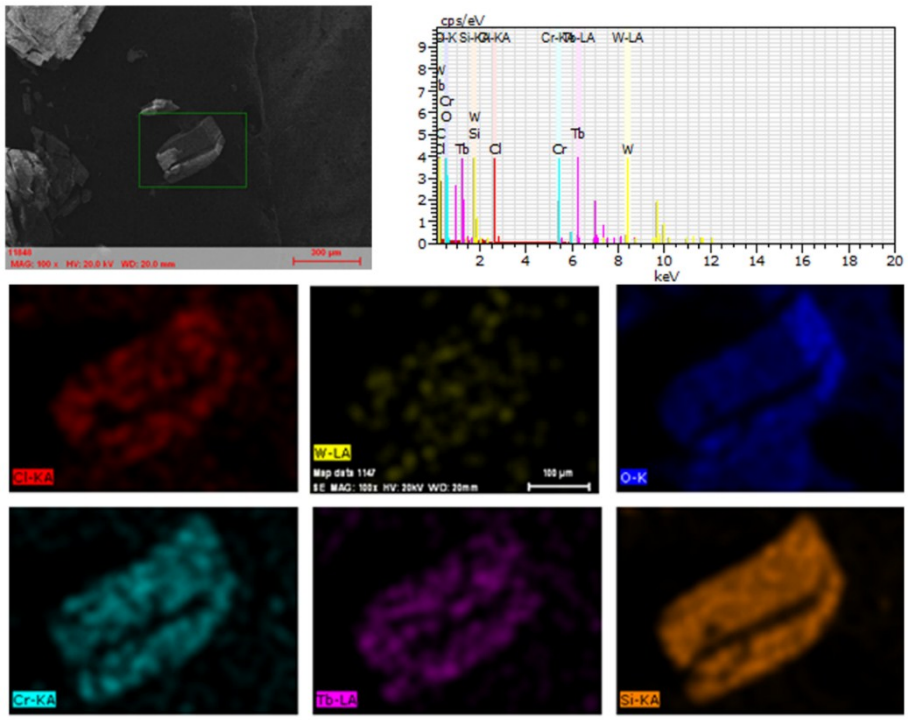

Figure S3 The EDS elemental mapping of Cl, W, O, Cr, Tb and Si for **2-Tb**.

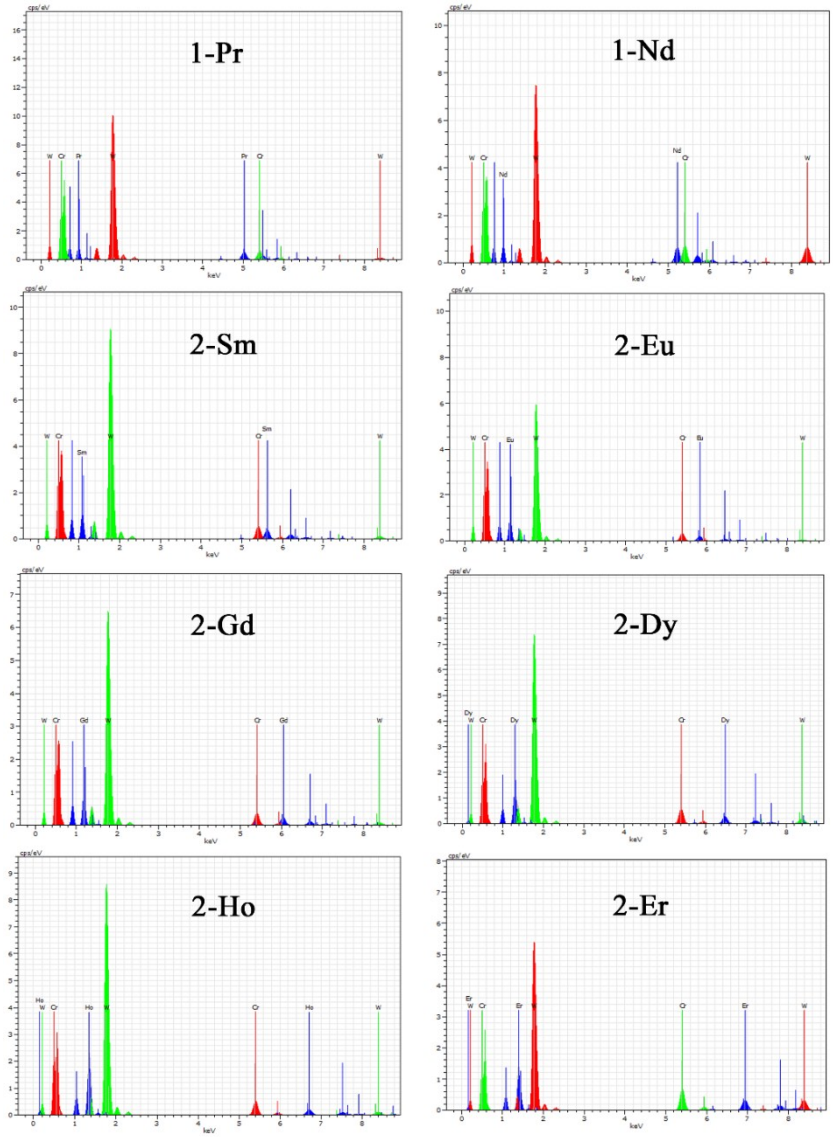

Figure S4 The EDS spectra of **1-Ln** (Ln = Pr^{3+}, Nd^{3+}) and **2-Ln** (Sm^{3+}, Er^{3+}, Gd^{3+}, Tb^{3+}, Ho^{3+}, Er^{3+})

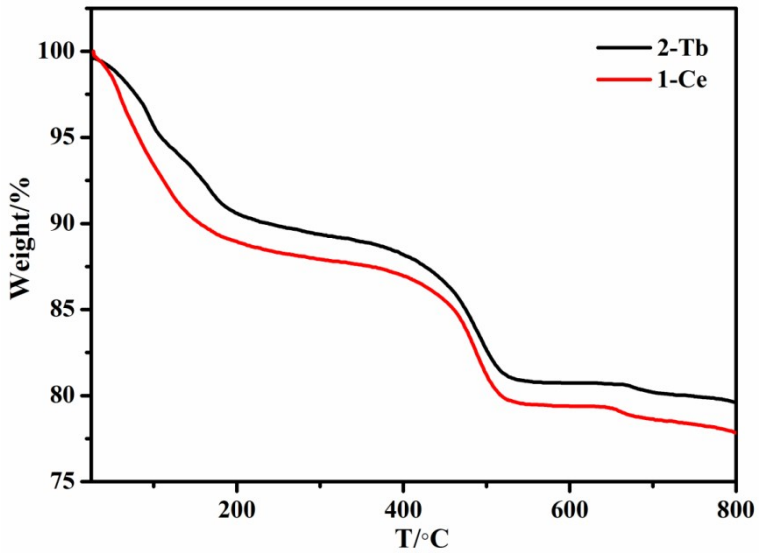

Figure S5 The TG curves of **1-Ce** and **2-Tb**.

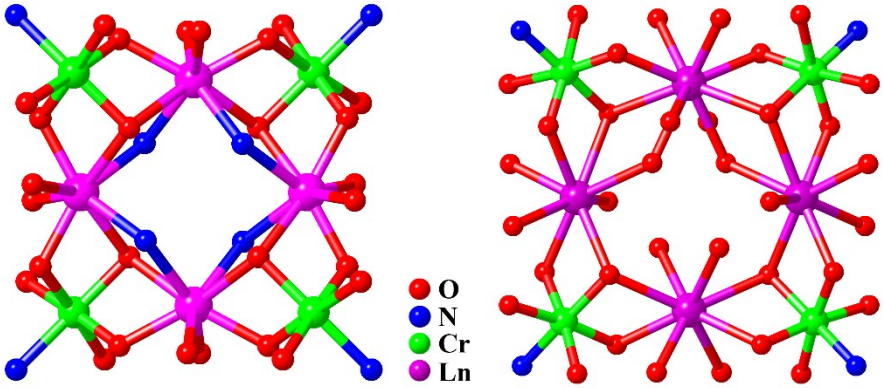

Figure S6 The planar square-like [Cr4Ln4] clusters in Powell's work.

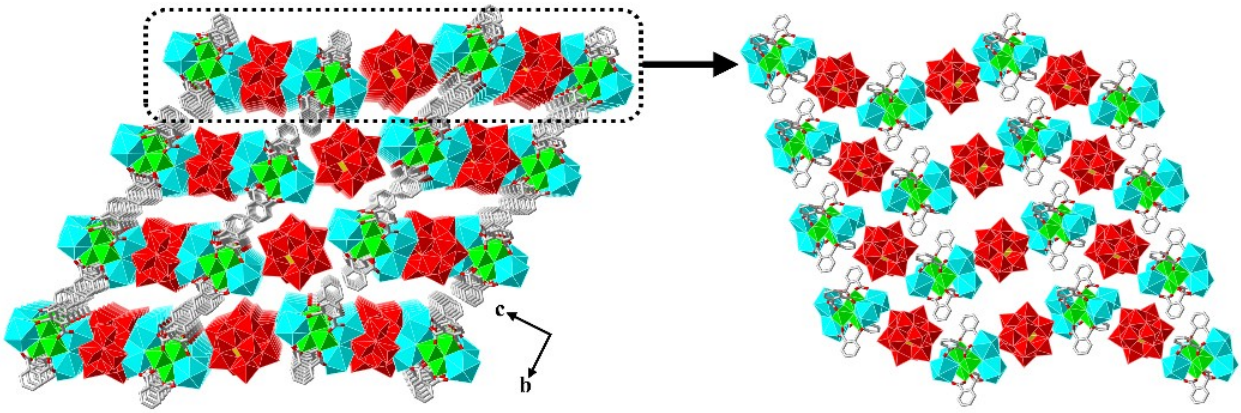

Figure S7 View of the stacking style of 1-D chains in **1-Ce**.

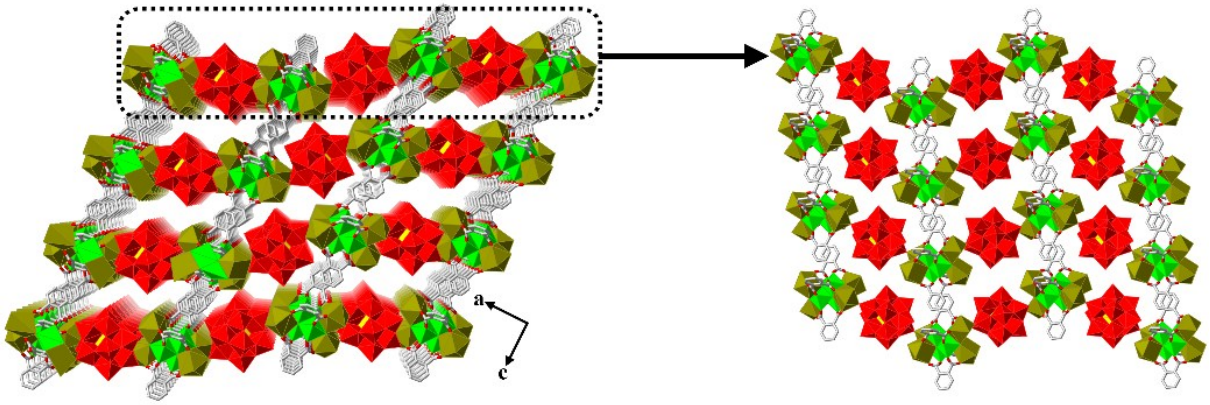

Figure S8 View of the stacking style of 1-D chains in **2-Tb**.

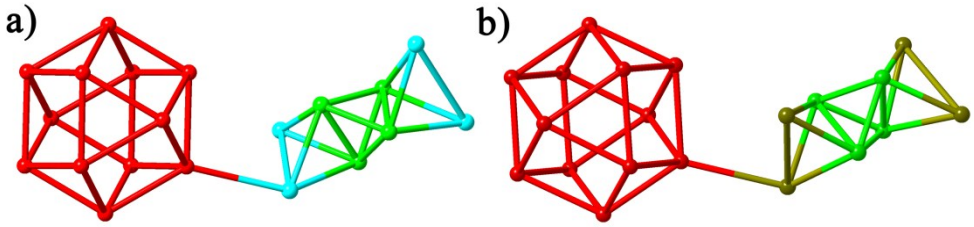

Figure S9 The decorated motif of compounds **1-Ce** and **2-Tb** with symbol of 3,4,4,5,5M20-1. Color code: W (red balls), Ce (cyan balls), Tb (olive balls), Cr (green balls).

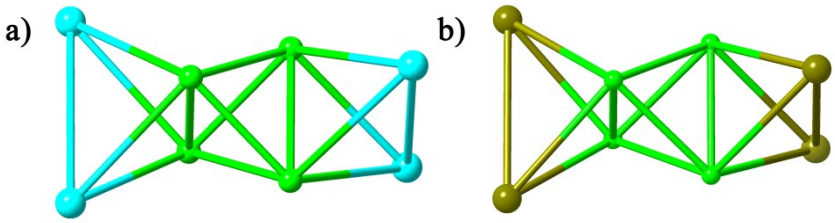

Figure S10 The decorated motif 3,5M8-1 of Cr_4Ce_4 and Cr_4Tb_4 core. Color code: W (red balls), Ce (cyan balls), Tb (olive balls), Cr (green balls).

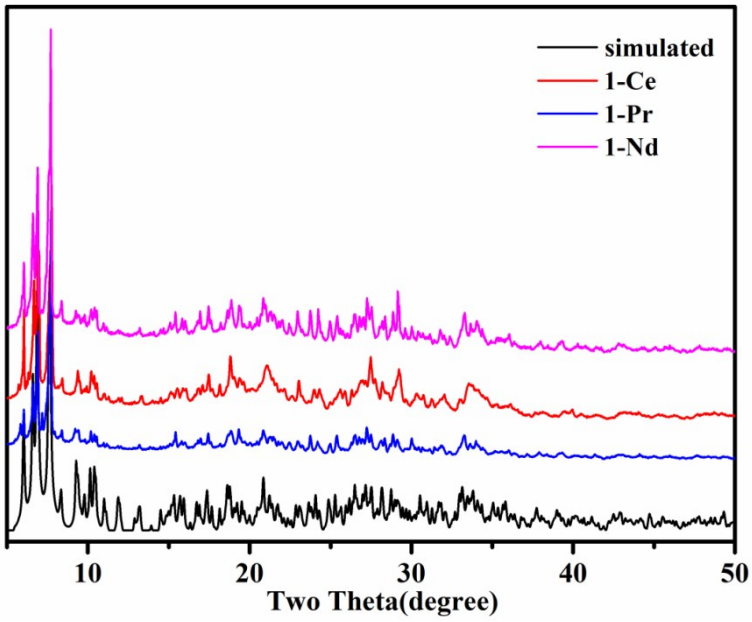

Figure S11 The simulated and experimental PXRD patterns of **1-Ln** (Ln = Ce, Pr, Nd).

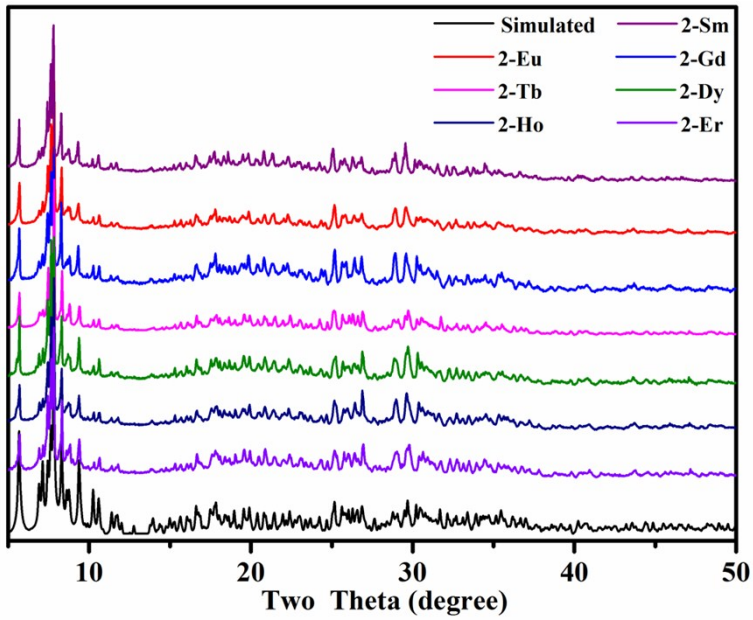

Figure S12 The simulated and experimental PXRD patterns of **2-Ln** (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er).

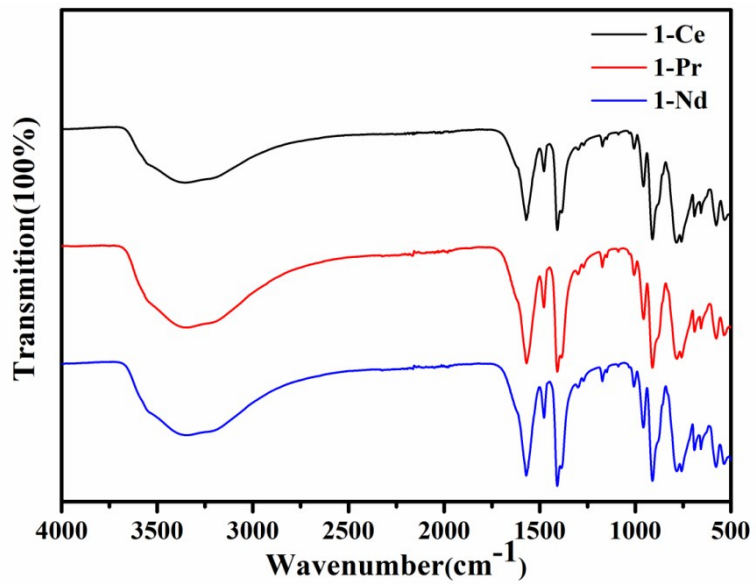

Figure S13 The IR spectra of **1-Ln** (Ln = Ce, Pr, Nd).

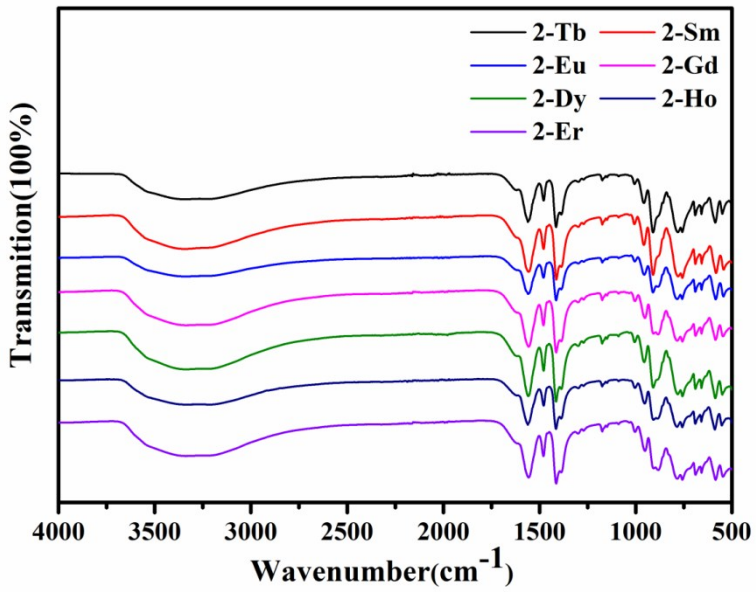

Figure S14 The IR spectra of **2-Ln** (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er).

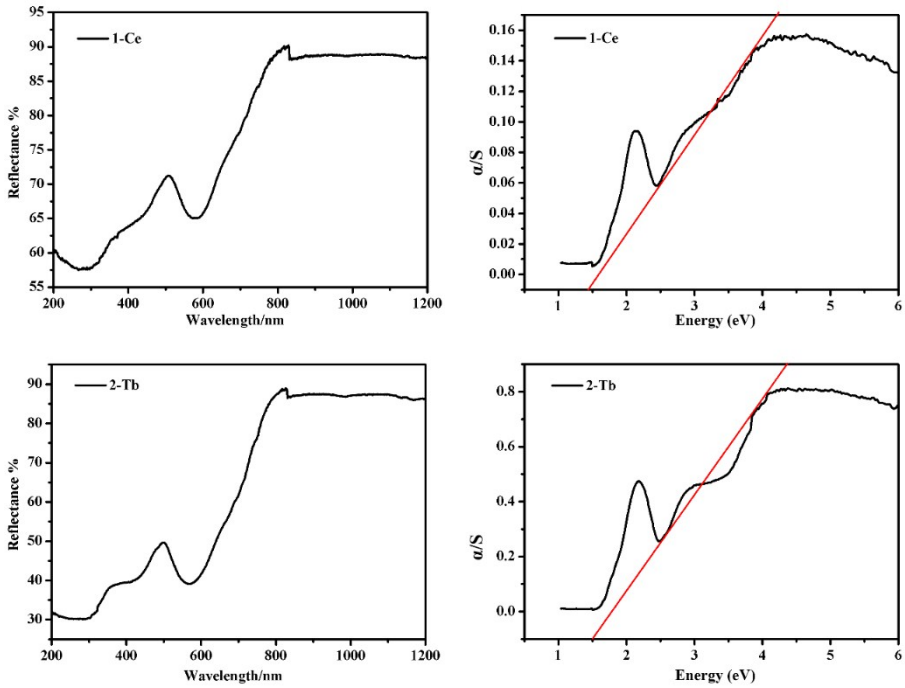

Figure S15 The UV-Vis diffuse reflectance spectra and Kubelka-Munk Function *vs*. energy curves of **1-Ce** and **2-Tb.**

Table S1 Selected bond lengths (Å) and bond valence calculations (Σs) for **1-Ce** and **2-Tb**.

1-Ce			
Bond	Bond lengths (Å)	Bond valence	Sum of Bond valence
Cr1-O9	1.971	0.470	Σs = 2.702
Cr1-O7	1.971	0.470	
Cr1-O6	1.984	0.451	
Cr1-O18	1.983	0.452	
Cr1-O14	1.99	0.442	
Cr1-O2	2.008	0.418	
Cr2-O18	1.959	0.485	Σs = 2.723
Cr2-O1	1.963	0.482	
Cr2-O8	1.976	0.462	
Cr2-O7	1.996	0.434	
Cr2-O5	1.995	0.435	
Cr2-O17	2.003	0.422	
Cr3-O7	1.973	0.467	Σs = 2.643
Cr3-O13	1.981	0.455	
Cr3-O4	1.994	0.437	
Cr3-O6	1.994	0.437	
Cr3-O1	2.003	0.424	
Cr3-O16	2.004	0.423	
Cr4-O1	1.962	0.483	Σs = 2.738
Cr4-O10	1.962	0.483	
Cr4-O18	1.981	0.455	
Cr4-O3	1.983	0.452	
Cr4-O6	1.994	0.437	
Cr4-O15	2.001	0.427	
Bond	Bond lengths (Å)	Bond valence	Sum of Bond valence
Ce1-O7	2.484	0.407	Σs = 3.130
Ce1-O7w	2.496	0.393	
Ce1-O38	2.512	0.3742	
Ce1-O12	2.514	0.372	
Ce1-O13	2.523	0.362	
Ce1-O4w	2.532	0.353	
Ce1-O9	2.538	0.347	
Ce1-O6w	2.588	0.299	
Ce1-O17w	2.688	0.222	
Ce2-O1	2.495	0.394	Σs = 3.190
Ce2-O1w	2.496	0.393	
Ce2-O8w	2.511	0.376	
Ce2-O10	2.513	0.373	
Ce2-O25	2.513	0.373	

Ce2-O8	2.528	0.357	
Ce2-O23	2.527	0.358	
Ce2-O32	2.543	0.342	
Ce2-O3w	2.685	0.224	
Ce3-O18	2.458	0.440	
Ce3-O11	2.492	0.397	
Ce3-O20	2.502	0.386	Σs = 3.005
Ce3-O2w	2.513	0.373	
Ce3-O8	2.505	0.382	
Ce3-O29	2.506	0.381	
Ce3-O10	2.513	0.373	
Ce3-O9w	2.62	0.272	
Ce4-O6	2.443	0.459	
Ce4-O9	2.488	0.402	
Ce4-O26	2.49	0.400	Σs = 3.134
Ce4-O13	2.496	0.393	
Ce4-O28	2.502	0.386	
Ce4-O19	2.508	0.379	
Ce4-O5w	2.519	0.367	
Ce4-O21	2.536	0.349	

2-Tb			
Bond	Bond lengths (Å)	Bond valence	Sum of Bond valence
Cr1-O14	1.954	0.496	
Cr1-O12	1.963	0.482	Σs = 2.783
Cr1-O18	1.97	0.471	
Cr1-O20	1.975	0.464	
Cr1-O33	1.988	0.445	
Cr1-O17	2.002	0.426	
Cr2-O3	1.958	0.490	
Cr2-O8	1.97	0.471	Σs = 2.723
Cr2-O18	1.983	0.452	
Cr2-O20	1.984	0.451	
Cr2-O19	1.985	0.449	
Cr2-O34	1.989	0.444	
Cr3-O10	1.978	0.460	
Cr3-O19	1.979	0.458	
Cr3-O20	1.979	0.457	Σs = 2.684
Cr3-O2	1.986	0.448	
Cr3-O17	1.99	0.442	
Cr3-O36	2.005	0.420	
Cr4-O17	1.964	0.480	

Cr4-O19	1.974	0.467	Σs = 2.730
Cr4-O6	1.98	0.457	
Cr4-O18	1.983	0.452	
Cr4-O15	1.989	0.444	
Cr4-O35	1.996	0.434	
Bond	Bond lengths (Å)	Bond valence	Sum of Bond valence
Tb1-O18	2.351	0.426	Σs = 2.990
Tb1-O13	2.368	0.405	
Tb1-O34	2.394	0.375	
Tb1-O9w	2.398	0.370	
Tb1-O31	2.405	0.362	
Tb1-O5	2.413	0.356	
Tb1-O10w	2.412	0.355	
Tb1-O33	2.425	0.341	
Tb2-O20	2.334	0.448	Σs = 3.086
Tb2-O4	2.355	0.421	
Tb2-O11	2.398	0.370	
Tb2-O7w	2.399	0.369	
Tb2-O8w	2.420	0.347	
Tb2-O6w	2.425	0.341	
Tb2-O33	2.422	0.344	
Tb2-O34	2.336	0.445	
Tb3-O17	2.323	0.463	Σs = 2.957
Tb3-O16	2.382	0.388	
Tb3-O9	2.384	0.386	
Tb3-O5w	2.397	0.371	
Tb3-O4w	2.412	0.356	
Tb3-O36	2.429	0.337	
Tb3-O35	2.436	0.330	
Tb3-O32	2.441	0.326	
Tb4-O19	2.332	0.451	Σs = 3.061
Tb4-O7	2.363	0.411	
Tb4-O1	2.366	0.408	
Tb4-O1w	2.392	0.378	
Tb4-O3w	2.392	0.377	
Tb4-O36	2.413	0.354	
Tb4-O35	2.424	0.342	
Tb4-O2w	2.427	0.340	