Supporting Information (SI) for:

Structural and spectroscopic studies of crystalline Eu(III)-aliphatic dicarboxylates formed spontaneously at room temperature

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Sample preparation Solid compounds were prepared under oversaturation conditions with various concentrations and stoichiometries of Ox, Mal, and Suc versus Eu. In attempt to probe solid structures under conditions as close as possible to those of aqueous complexes, test samples were prepared from lower bound concentrations of the reagents. In Table S1, samples prepared for this study are listed with the concentrations of the reagents, ratio of the organic ligand concentration to the Eu concentration ([Ox, Mal, Suc]/[Eu]) and pH. Whether precipitation formed or not was determined by bare eyes after one or two weeks. 'Yes' in the 'Precipitation' column indicates that sufficient amount of solid was collected for powder xrd and TRLFS measurements, 'little' indicates that solid grains were showed up, but not sufficient amount for further tests. Powder xrd patterns from the tested samples were identical for the same organic ligands. The highlighted samples in gray were chosen for detailed examination. These samples were prepared with similar stoichiometries (1.5–1.7) of the ligands to Eu(III) and provided good diffraction patterns.

FTIR spectroscopy IR spectra were obtained using a Nicolet 5 FTIR spectrometer (Fisher Sci.) and single-reflection diamond ATR (PIKE Technol.). The spectrometer was purged with N_2 gas before and during data collection. Spectra were collected by averaging 64 scans with a resolution of 2 cm^{-1}.

Raman spectroscopy Raman spectra were collected using a micro-Raman spectrometer system equipped with optical microscope (BX43, Olympus), a spectrograph (SR-500, Andor Technol.), and a CCD detector (DV401ABV, Andor Technol.). An argon laser (Innova 70, Coherent) of 514.5 nm was used as the light source. Raman signals were accumulated for 10 s and averaged over 10 measurements.

Table S1. List of sample preparation conditions and results

[Eu] (mM)	[Ox] (mM)	[Ox]/[Eu]	pH	Precipitation	Xrd pattern	N(H_2O) per an Eu (TRLFS)
2	6	3.0	5.5	Yes	yes	
2	3	1.5	5.5	Yes	yes	3
0.5	5	10.0	5.1	little		
0.2	5	25.0	5.3	little		
0.2	1	5.0	5.9	little		
0.1	1	10.0	5.4	No		

Eu (mM)	Mal (mM)	[Mal]/[Eu]	pH	Precipitation	Xrd pattern	N(H_2O) per an Eu (TRLFS)
30	50	1.7	5.7	Yes	yes	3
10	50	5.0	5.7	little	yes	3
3	10	3.3	5.7	No		

Eu (mM)	Suc (mM)	[Suc[/[Eu]	pH	Precipitation	Xrd pattern	N(H_2O) per an Eu (TRLFS)
10	50	5.0	5.8	Yes	yes	1
5	7.5	1.5	5.5	Yes	yes	1
3	5	1.7	5.7	little		
2	5	2.5	5.7	little		
1.5	5	3.3	5.7	little		
1	5	5.0	5.7	little		
0.5	5	10.0	5.7	no		

Highlighted in gray are the samples described in detail in main text.

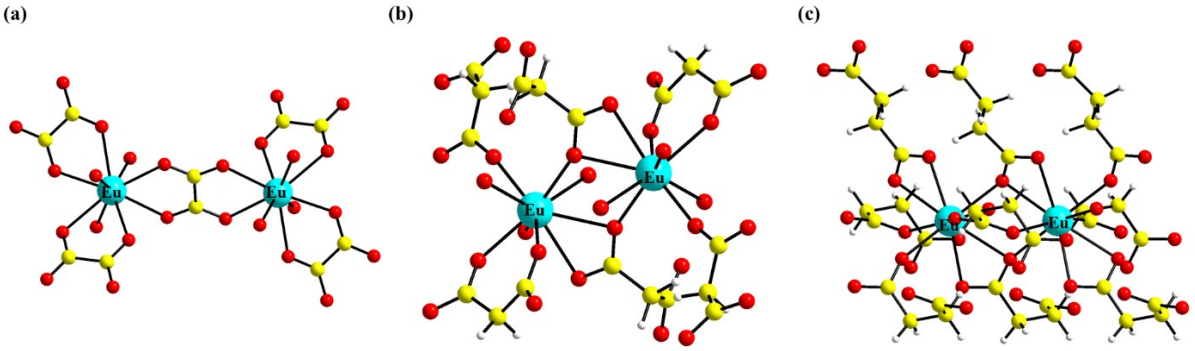

Figure S1. Ball-and-stick representations of (a) $Eu_2(Ox)_3(H_2O)_6$, (b)[$Eu_2(Mal)_3(H_2O)_6$, and (c) $Eu_2(Suc)_3(H_2O)_2$ frameworks (cyan, Eu; yellow, C; red, O; white, H).[1-3]

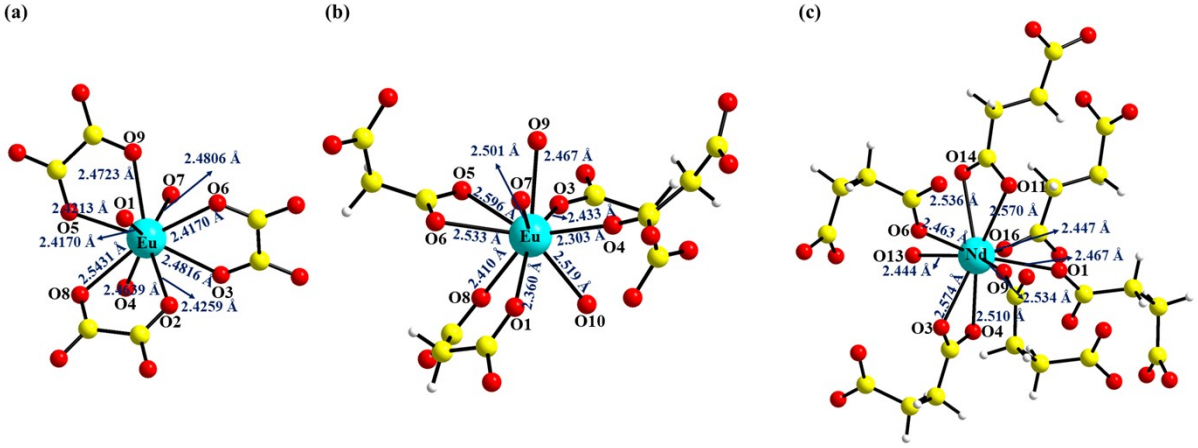

Figure S2. Ball-and-stick representations and bond distances of (a) $Eu_2(Ox)_3(H_2O)_6$, (b) $Eu_2(Mal)_3(H_2O)_6$, and (c) $Nd_2(Suc)_3(H_2O)_2$ frameworks (cyan, Eu or Nd; yellow, C; red, O; white, H).

Table S2. Average bond lengths (Å) of binding modes for [$Eu_2(Ox)_3(H_2O)_6$], [$Eu_2(Mal)_3(H_2O)_6$], and [$Nd_2(Suc)_3(H_2O)_2$].[1-3]

Compound	Binding mode	average M−O_{lig} bond length (Å)
$Eu_2(Ox)_3(H_2O)_6$[1]	H_2O	2.548
	side-on Ox	2.460
$Eu_2(Mal)_3(H_2O)_6$[2]	H_2O	2.496
	side-on Mal	2.376
	end-on Mal	2.564
$Nd_2(Suc)_3(H_2O)_2$[3]	H_2O	2.444
	Mono Suc	2.478
	end-on Suc	2.548

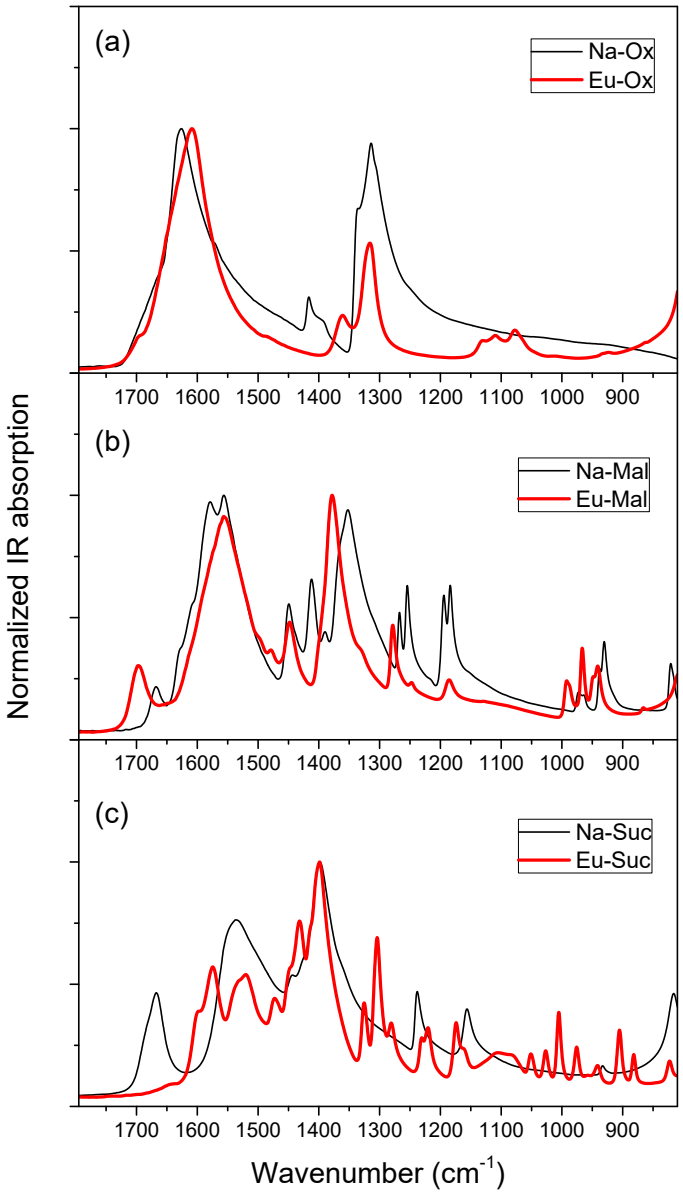

Figure S3. FTIR spectra of the Eu-Ox, Mal, Suc solid compounds (red). FTIR spectrum of disodium form of each organic ligand (black) was co-plotted for comparisons. Two major vibrational modes of the ν_{as}(COO) asymmetric and ν_{s}(COO) symmetric motions are expected at 1620-1520 and 1400-1310 cm^{-1} regions, respectively.[4-6] Eu compounds induce shifts of the IR peak positions as well as developing new peaks in comparisons to those of disodium forms of the ligands.[4-6] Another noticeable feature is peak splittings, especially in Mal and Suc compounds. Presence of the different binding modes of the carboxyl groups as well as combination of two and more of vibrational motions must have resulted in the observed splitted peak patterns.

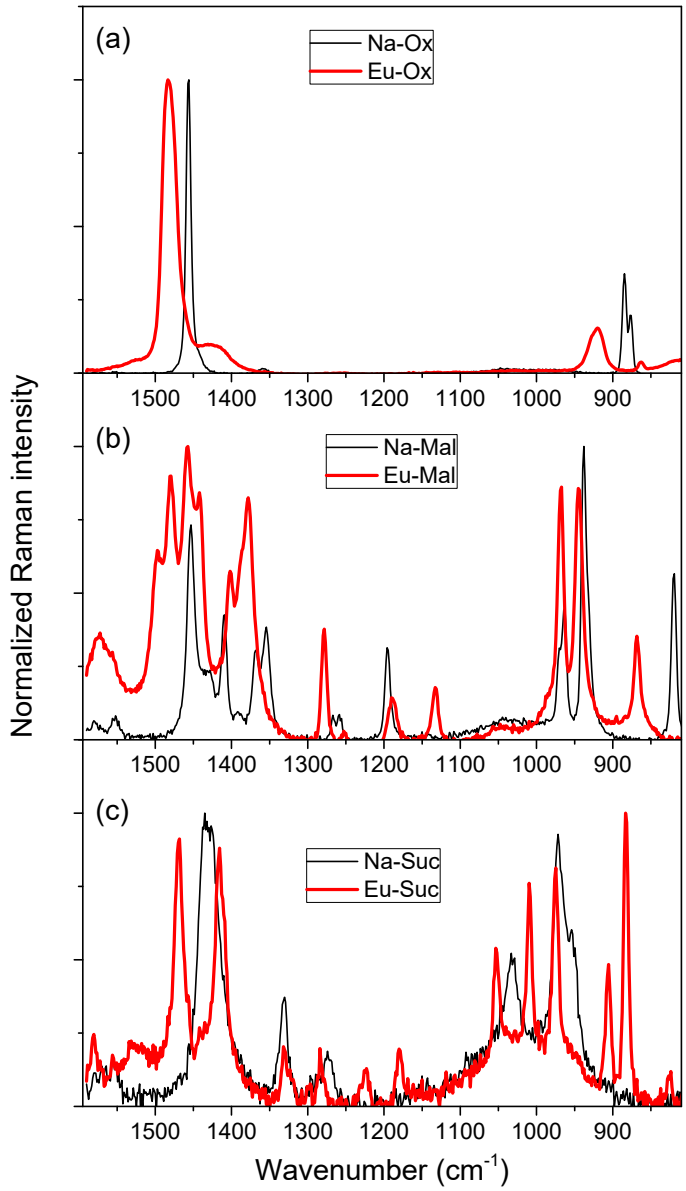

Figure S4. Raman spectra of Eu-Ox, Mal, Suc compounds (red) by using an argon laser (514.5 nm). Raman spectra were collected from samples prepared with 30 mM Eu + 50 mM Ox, 10 mM Eu + 50 mM Mal, and 2 mM Eu + 5 mM Suc, whose powder XRD patterns are the same as those in Fig. 1. Some of the strong peaks in the two major regions of around 1500-1400 cm^{-1} and 1000-900 cm^{-1} are attributed to symmetric stretching of carboxyl groups ν_s(COO) and C-C stretching motions (ν_s(CC)), respectively.[7] Similarly, Raman spectra showed peak splittings on the Mal and Suc compounds likely due to the non-equivalent bindings of the ligands within the structures.

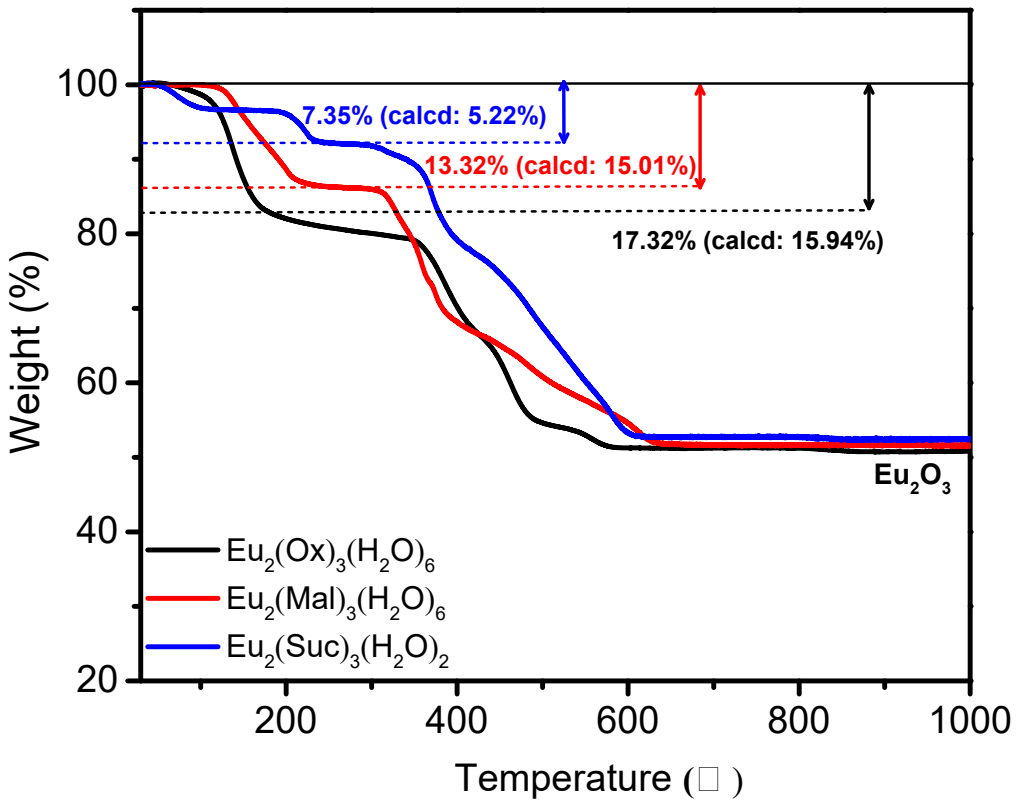

Figure S5. Thermogravimetric analysis diagrams for Eu-compounds

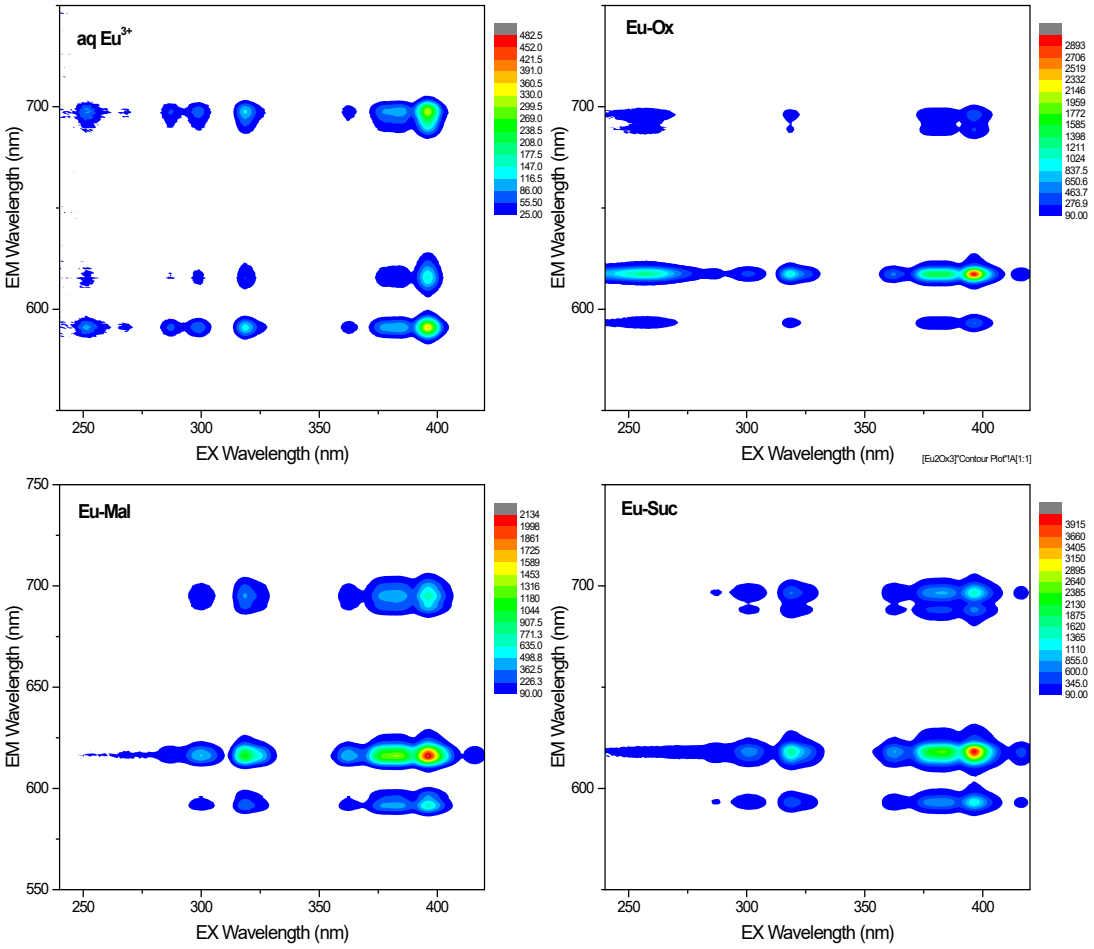

Figure S6. Excitation and emission map of Eu-Ox, Eu-Mal, and Eu-Suc compounds. The intensities are color coded from deep blue (low intensity) to red (high intensity)

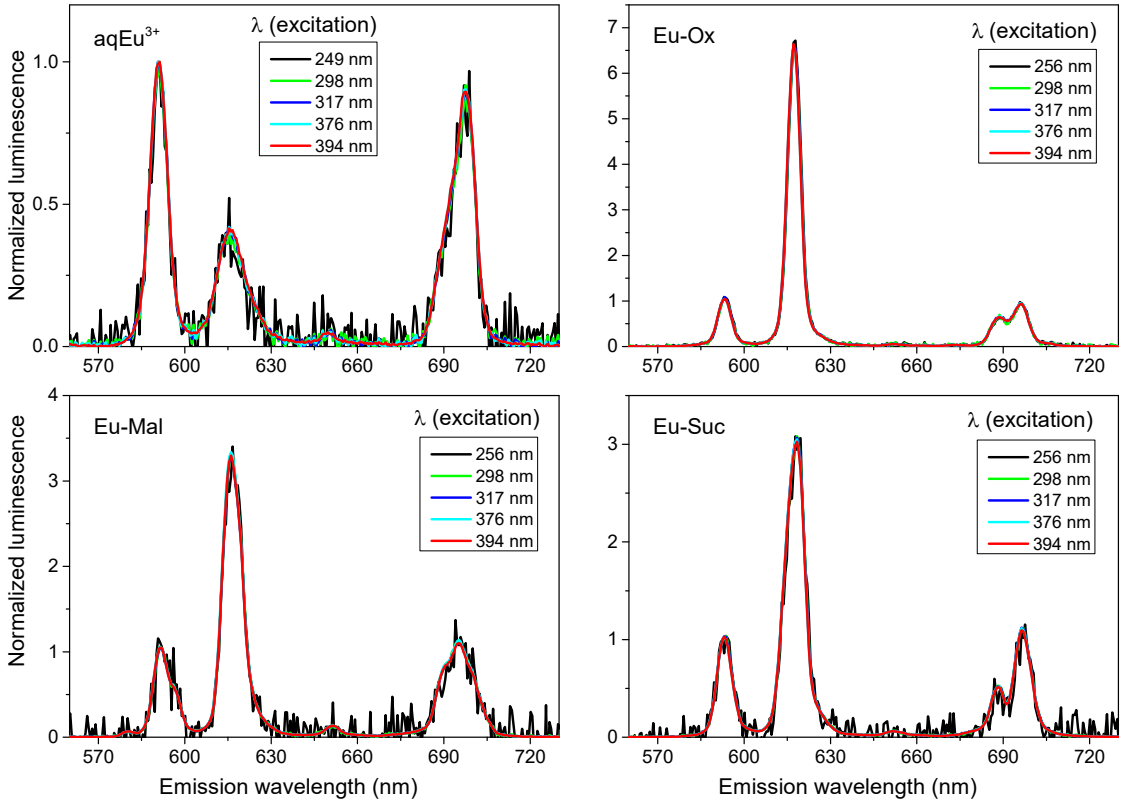

Figure S7. Luminescence spectra of Eu(III) excited by different wavelengths. The spectra were extracted from EEM data set and the intensities were normalized to the J=1 peak.

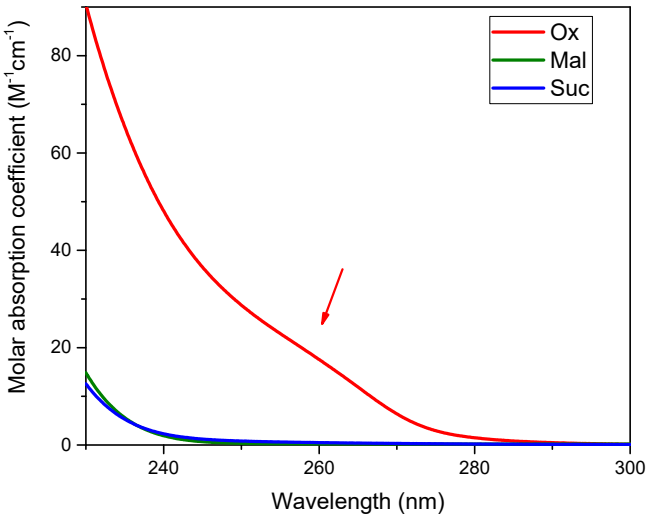

Figure S8. Molar absorption coefficients of aqueous Ox, Mal, and Suc ligands. Samples are 10 mM disodium ligands prepared in water (pH > 7).

References

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