Quantifying Enhanced Photoluminescence in Mixed-Lanthanide Carboxylate Polymers: Sensitization versus Reduction of Self-quenching

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Supplementary Information

Experimental

Synthesis: All polymer types were synthesized by either hydrothermal or ambient solvent diffusion methods. **1-Ln**: 0.5mmol $Ln(OAc)_3.xH_2O$: 0.75mmol 2,2'-biphenic acid : 0.5mmol KOH in 2mL H_2O, heated at T=160°C, 2 days. Large granular crystals filtered off, isolated yields varied from 68-78%. Crystalline powder products filtered off, isolated yields varied from 85-93%.

Phase identification and purity of phase types **1** was by powder X-ray diffraction, carried out on a Panalytical diffractometer operating with Xpert-pro strip-detector. The diffractograms were compared to simulated patterns from individual single crystal structure determinations and revealed no additional peaks or broad baseline maxima. Examples are given in the Supplementary data. The polymer types were chosen due to the isostructurality across the lanthanide series enabling formation of solid solutions. Hetero-lanthanide polymers of different metal ratios were prepared either stoichiometrically by direct weighing of appropriate molar ratios of lanthanide acetates (e.g. for 50:50 or 25:75 samples) or through addition of standard solutions for more accurate doping of smaller amounts below 10%. Preferential incorporation of metals into the solid samples was found to be minimal by checking metal ratios by X-ray fluorescence spectroscopy. Values from hetero-polymers agreed within 5% to XRF standards made from mixing the appropriate ratios of homo-polymers, thus indicating formation of random solid solutions.

Photo-luminescence: PL measurements were made based on crystalline powder samples of compounds. All samples were prepared in ca. 200mg quantity and used to fill a 1cm width spectrophotometric quartz sample cuvette. Excitation wavelength at 267 nm was generated from 3rd harmonics output of the femtosecond Ti: sapphire laser amplifier at 1kHz repetition rate. The laser pulse width was approximate 200 fs and the excitation power varied between 0.025 to 1mW from run to run dependent on the strength of the PL response of the samples.

Similarly integration times for the emission spectrum were varied from 5ms to 500ms. To check the effect of the exciting wavelength a near-uv CW He-Cd source operating at 325nm was also used. The experimental set-up is shown in the supplementary material; the laser focus would pass through the sample with a path length of ca 2mm. The photoluminescence (PL) is collected orthogonal to the incident beam by a collimating and focusing lens system and detected by a fiber coupled spectrometer/CCD system (Ocean Optics USB 2000) with spectral resolution about 2nm. Removal of residual 800nm line from the Ti sapphire source was carried out and in general the PL was measured and plotted between 300 and 700nm. Values for PL in the Tables are semi-quantitative and a variability of ca. 5% is found for sample based on multiple measurements. The effect of sample particle size was found to be minimal based on comparisons of PL from coarse granular powder of **1-Ln** compared to samples that had been finely ground. Quantum yield data were based on summation from all emission lines and obtained using an integrating sphere to collect the PL light, with the methodology adapted from that of Friend et al.[16]

Figure S1. Schematic setup for measurement of powder sample photo-luminescence

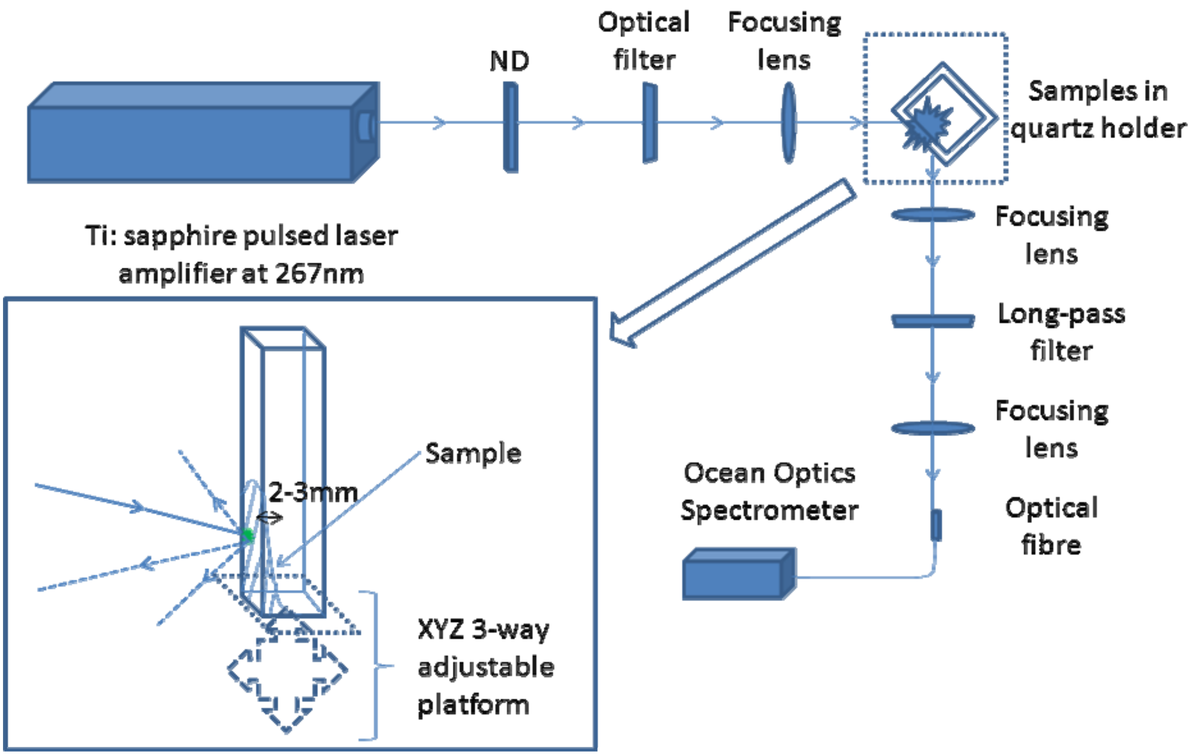


Figure S2. Schematic setup for quantum efficiency measurement (after Friend et al)

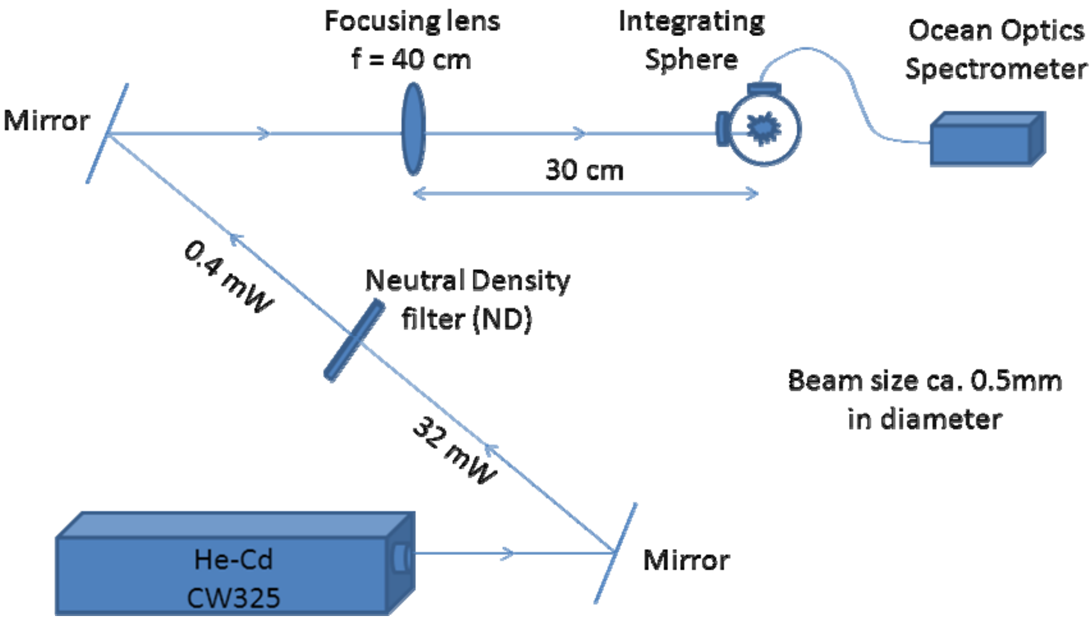


Figure S3. Emission Spectra for **1-Ln** Homopolymers excited by 325 nm

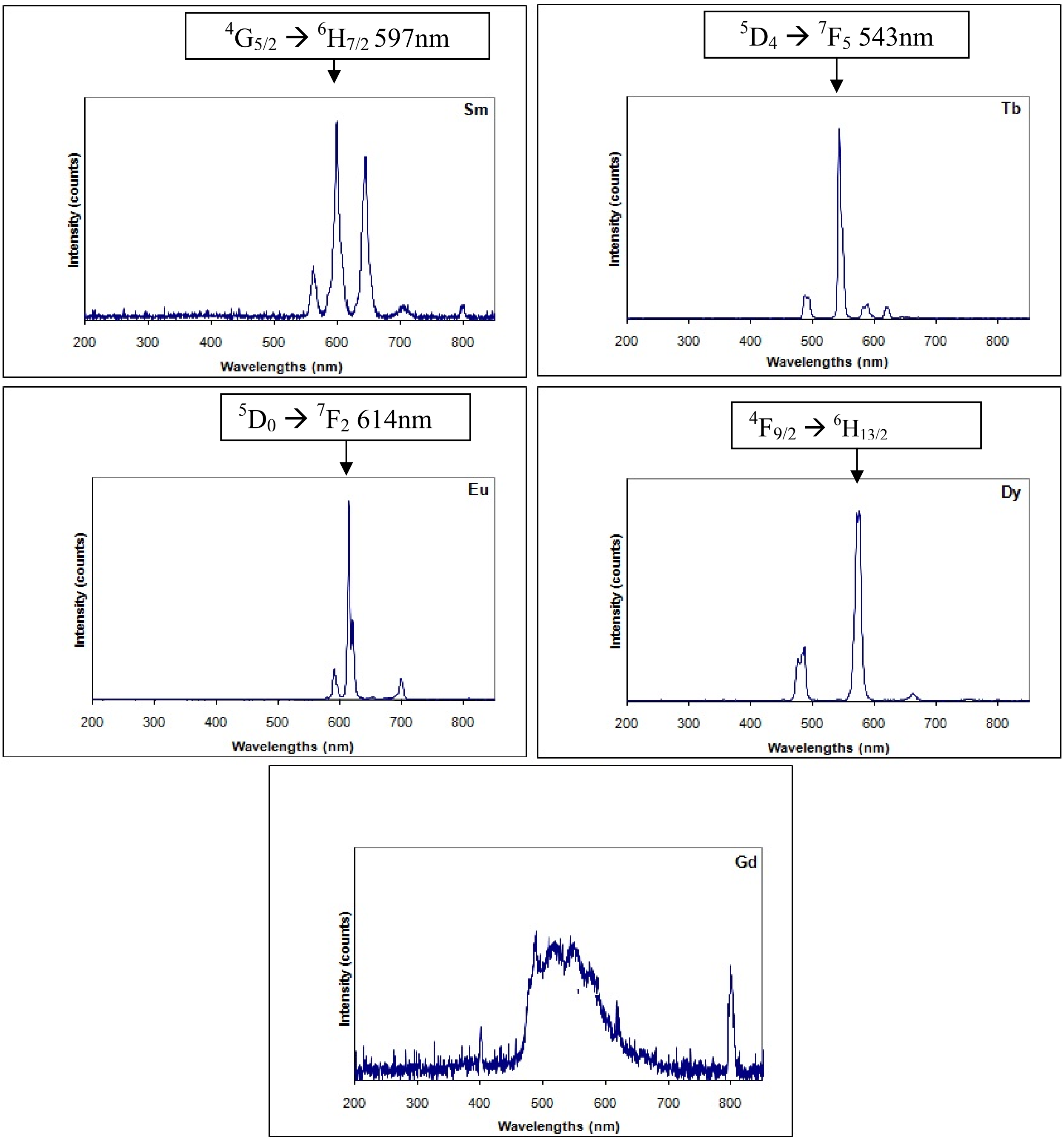


Figure S4. Photoluminescent Energy Transfer Cascade proposed for **1-Ln (Tb-Eu)**

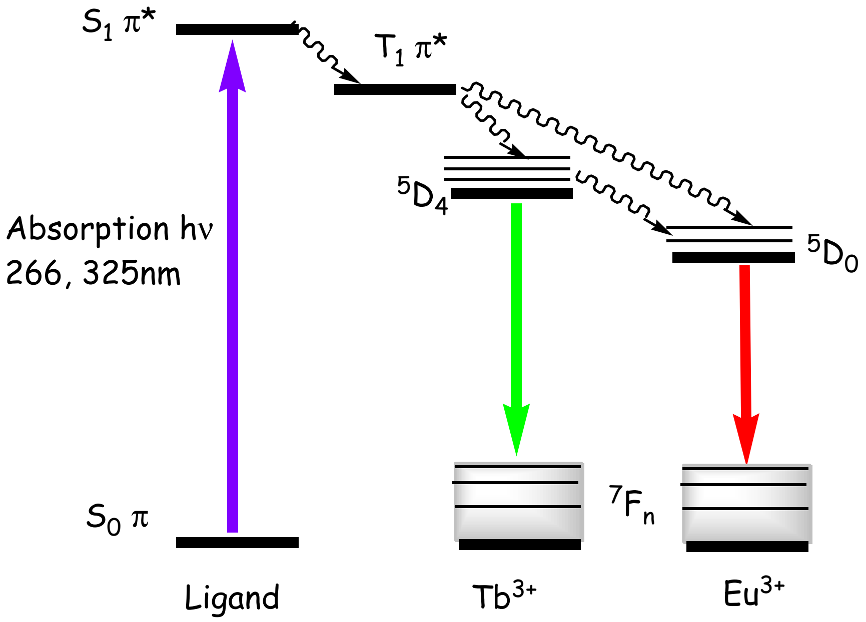


Figure S5. Photoluminescence for polymer types **1-Ln** and **[Ln(135-BTC)]** using 325 and 266 nm excitation for Ln = Eu and Ln = $Eu_{0.02}$:$Tb_{0.98}$.
Note In all cases stronger signals seen at 2% Eu doping.

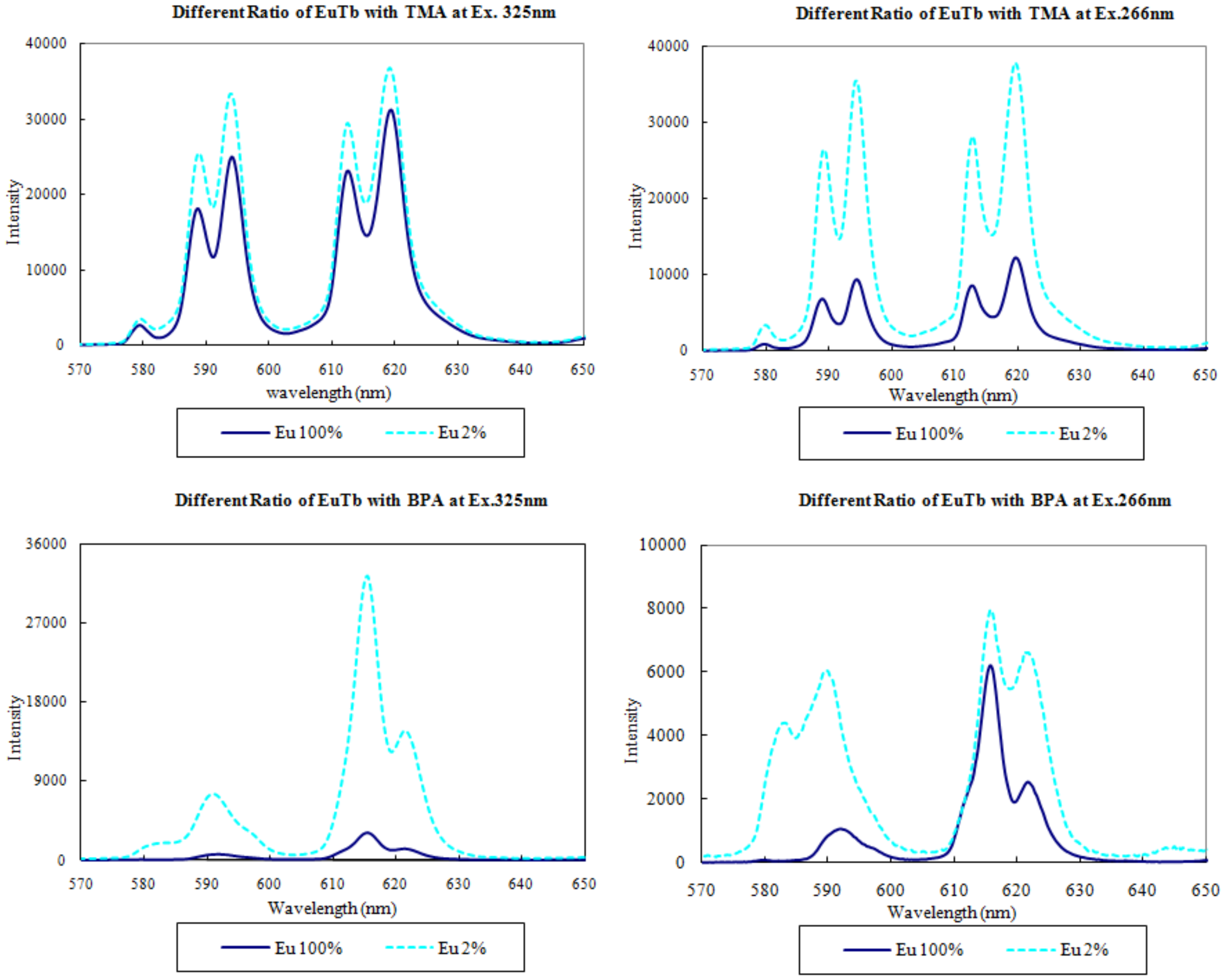
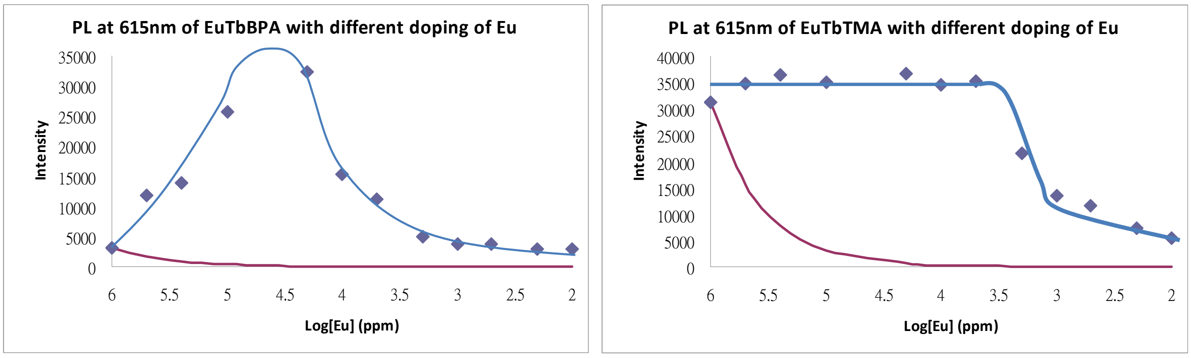
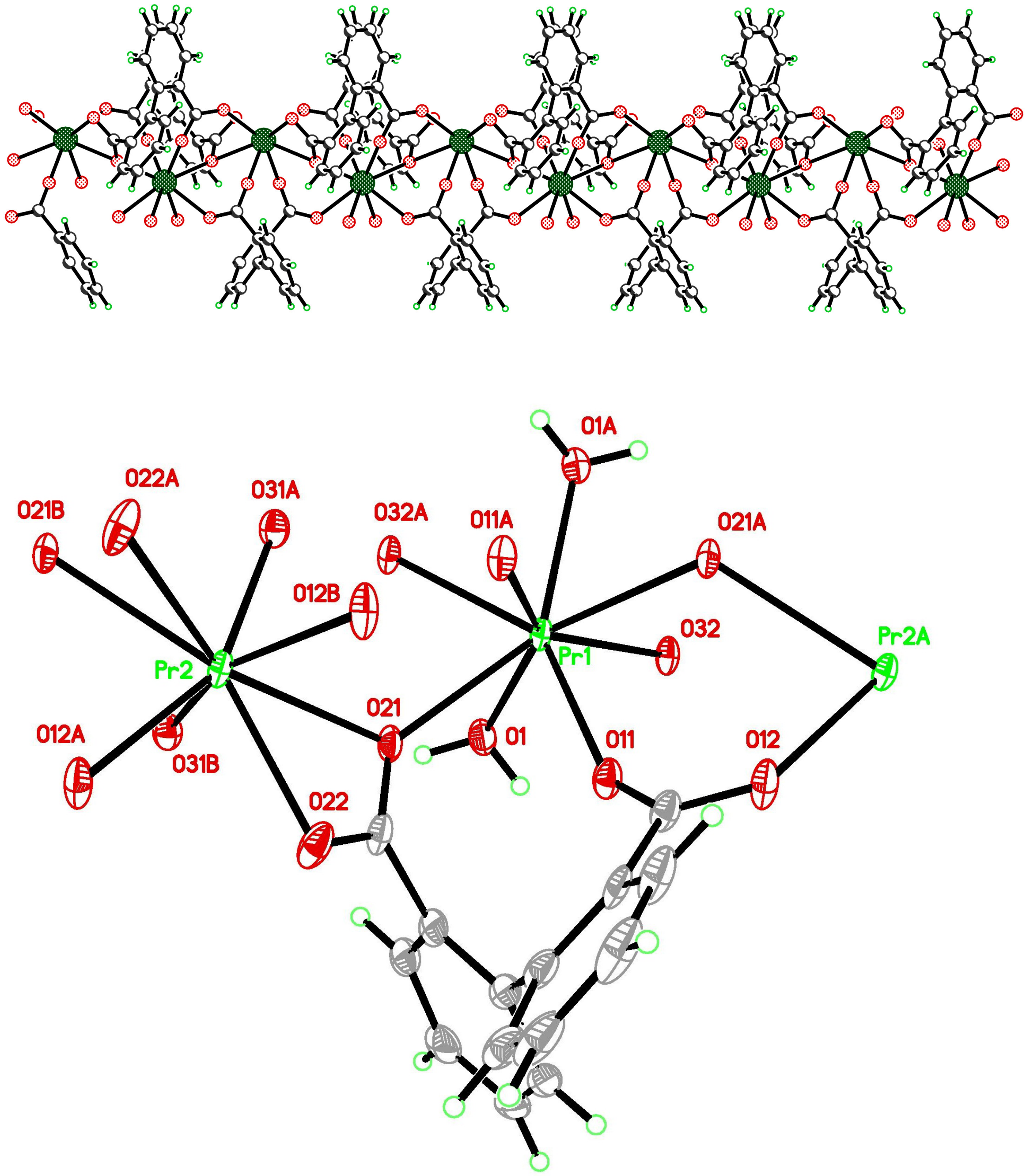


Figure S6. Enhancement of Eu^{3+} Photoluminescence by Tb^{3+}. Intensity at 615nm versus Eu conc from 10^6 ppm to 100 ppm Eu at the Ln sites in **1-EuTb** and **[(EuTb)TMA)]** respectively

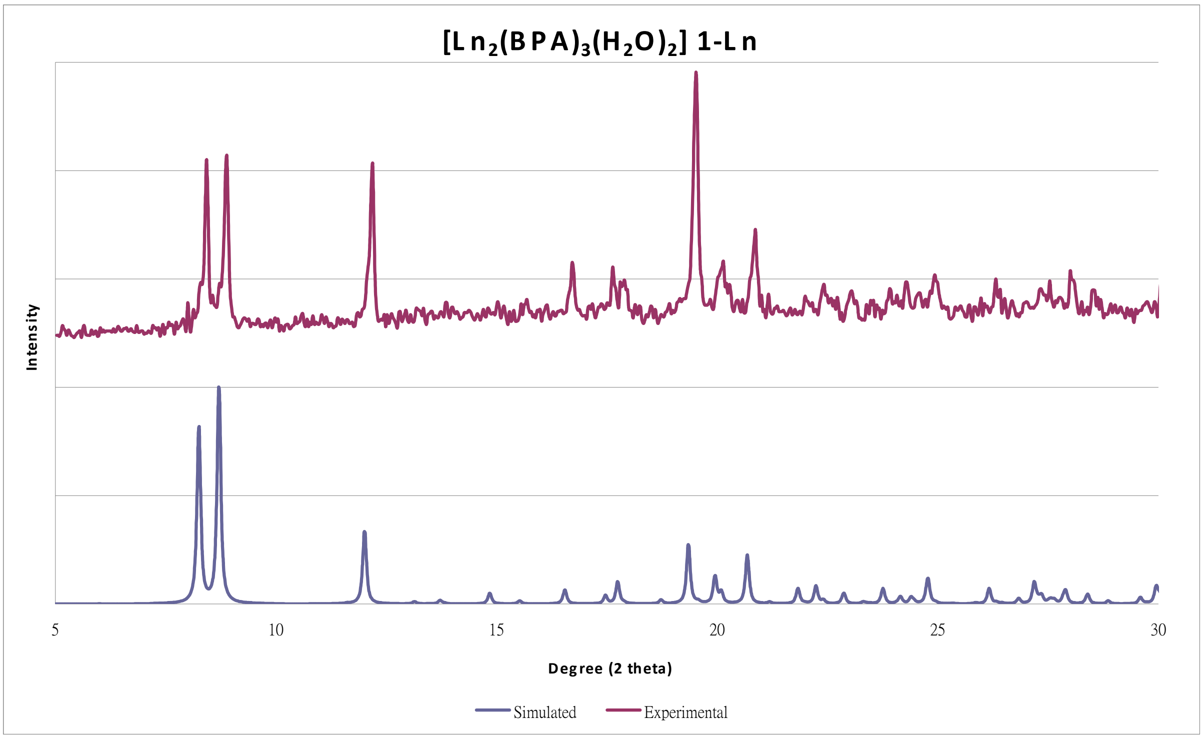


The 2,2-biphenate (BPA) polymer **1-Ln** shows clear enhancement with a well-defined peak, whilst the trimesate (TMA) polymer exhibits a 'plateau' we have found in many systems.

Figure S7. Structure of Polymer Chains in **1-Ln**, with atomic labelling below
Ln (Pr) = dark green, O = red, C = black, H = pale green

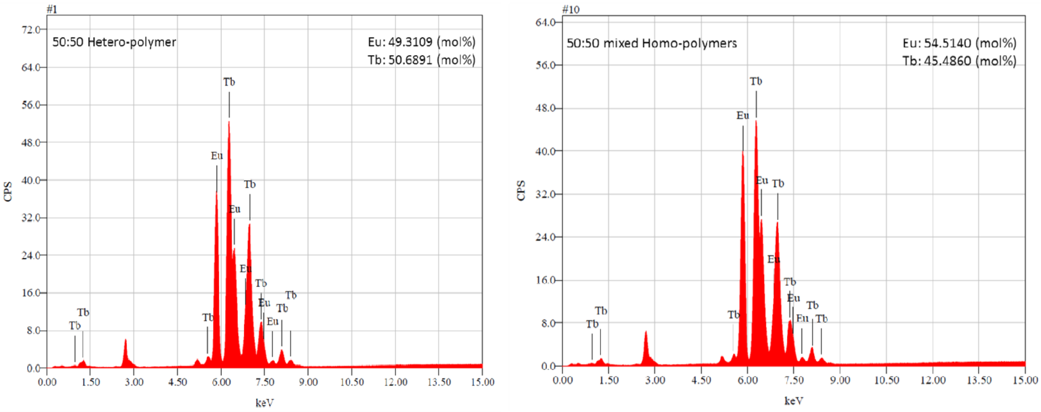


Experimental and Simulated Powder Diffractograms:
1-Ln [$Ln_2(BPA)_3(H_2O)_2$] BPA = 2,2-biphenate, $C_{14}H_8O_4$;



Above patterns based on Ln =Eu; an isostructural series found for all Ln.

X-ray Fluorescence Data:



Comparison of XRF results with 50:50 Hetero-polymer and

50:50 mixed Homo-polymer of [$(Eu:Tb)_2(BPA)_3(H_2O)_2$]

Additional Photo-luminescent Data:

Table S1. Photoluminescent Intensities from **1-Ln** [Ln(BPA)(H_2O)$_2$] Homo-polymers and 50:50 Hetero-polymers using exciting wavelength of 325nm.

1-Ln-@ 325nm	Sm	Eu	Gd	Tb	Dy
Sm (597nm)	**25**	0	540	420	9
Eu (614nm)	900	**3200**	12000	12000	110
Gd (none)	0	0	**0**	0	0
Tb (543nm)	1000	2000	200000	**340000**	33000
Dy (580nm)	27	30	7500	1500*	**300**

Notes: Absolute values cannot be compared with 267nm excitation wavelength, since different laser powers and flux apply. General trends are very similar.

Table S2. Estimated Quantum Efficiencies

The quantum efficiencies for various biphenate and trimesate polymers were estimated by the method of Friend et al. (reference 16) and using the experimental set up shown in Figure S2 and excitation wavelength of 325nm.

	La	Lc	Abs%	QE%
1-Tb	73123	28570	61	18.0
1-$Tb_{0.5}Gd_{0.5}$	73123	19382	73	9.2
1-Eu	73123	19364	74	0.09
Tb(TMA)	17830	8265	54	14.0
Eu(TMA)	17830	7983	55	5.3
$Eu_{0.5}Tb_{0.5}$(TMA)	17830	10673	40	9.9

Table S3. Europium and Terbium Emissions[a] in Eu-Tb(ss) Polymers

Biphenate 1-Ln @325nm			
Eu%	Tb%	Eu signal	Tb signal
100	0	3200	0
1	99	15400	44400
0.5	99.5	10000	59700
0.2	99.8	4000	56700
0.1	99.9	2500	75500
0.05	99.95	1900	97800
0.02	99.98	800*	113000
0.01	99.99	500*	114000
0	100	0	340000

[a] PL intensities listed at 614nm (Eu) first and 543nm (Tb) second.

* Numbers becoming uncertain due to tailing from a Tb signal at 619nm.