

Lighting-Up Two-Dimensional Lanthanide Phosphonates: Tunable Structure-Property Relationships towards Visible and Near-Infrared Emitters

Adam R. Patterson, Wolfgang Schmitt* and Rachel C. Evans*

School of Chemistry and CRANN, The University of Dublin, Trinity College, Dublin 2, Ireland.

* Corresponding authors: Tel: +353 1 896 1602, E-mail: schmittw@tcd.ie; Tel: +353 1 896 3495, E-mail: raevans@tcd.ie; Tel: +353 1 896 4215

SUPPORTING INFORMATION

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S1. Experimental Details

S1.1 Materials

Tert-butyl phosphonic acid (98%), 4-bromo biphenyl ($\geq 90\%$) and triethyl phosphite (98%), lanthanide chloride hexahydrate salts ($\text{Ln} = \text{Eu(III)}, \text{Tb(III)}, \text{Yb(III)}, \text{Nd(III)}, \geq 99\%$), nickel(II) bromide (98%) and 1,3-diisopropylbenzene (96%) were purchased from Sigma Aldrich and used without further purification. 1-bromonaphthalene ($\geq 95\%$) was obtained from Fluka and used as received. Acetonitrile and ethanol were of HPLC grade from Sigma Aldrich.

S1.2 Ligand Synthesis

Synthesis of 1-naphthalene phosphonic acid (L1-Naph). The ligand was prepared using a modified Arbusov reaction as outlined in previous syntheses of other aromatic phosphonic acids.¹ A 250 mL round bottom flask was charged with 1,3-diisopropyl benzene (50 mL), NiBr_2 (0.500 g) and 1-bromo naphthalene (3.380 mL, 20 mmol) and heated to 185 °C. Triethyl phosphite (5 mL, 29 mmol) was slowly added over six hours and the reaction mixture was left to reflux for twenty four hours. Additional NiBr_2 (0.250 g) and triethyl phosphite (2.5 mL, 14.5 mmol) were subsequently added over three hours followed by a further twenty four hour reflux. The resulting black solution was distilled under vacuum to remove solvent, unreacted triethyl phosphite and side-products, leaving a viscous black oil. The black oil was dissolved in dichloromethane (DCM) and passed through a celite plug to remove any remaining nickel, yielding a yellow filtrate. The DCM washings were concentrated to give a golden yellow oil, which was identified as the phosphate ester through ^1H and ^{31}P nuclear magnetic resonance (NMR) spectroscopy. Hydrolysis of the ester was achieved through reflux of the oil in HCl (50 mL, 37%) overnight. Upon cooling, the desired product, **L1**, precipitated from solution, and was subsequently filtered and washed with DCM to give a white powder. Yield: 2.997 g (72%); m.p: 203-205 °C. ^1H NMR (400 MHz, d_6 -DMSO) δ_{H} : 8.58 (d, 1H, H^5), 7.54-7.63 (m, 3H), 7.98-8.09 (m, 3H). ^{31}P NMR (162 MHz,

d_6 -DMSO) δ_P : 13.10 ppm. FTIR ν_{\max} (cm^{-1}): 3044 (w), 2284 (br), 1956 (w), 1726 (w), 1621 (w), 1593 (w), 1573 (w), 1508 (m), 1459 (w), 1338 (w), 1433 (w), 1224, 1189 (s), 1065 (s), 1028 (s), 996 (s), 913 (s), 861 (m), 797 (s), 770 (s), 671(s). HRMS (m/z -ES): Found: 207.0211 (M^- -H. $\text{C}_{10}\text{H}_8\text{O}_3\text{P}$; *calc.*: 207.0211). CHN analysis for $\text{C}_{10}\text{H}_9\text{PO}_3$: Expected: C 57.70%; H 4.36%. Found: C 54.91%; H 4.40%.

Synthesis of 4-biphenyl phosphonic acid (L2-Biphen). A similar procedure to **L1** was adopted, where 1-bromonaphthalene was substituted for 4-bromobiphenyl (4.684 g, 20 mmol) and reacted with triethyl phosphite under the conditions described above. Yield: 1.306 g (56%); m.p: 237-240 °C. ^1H NMR (400 MHz, d_6 -DMSO) δ_H : 7.42 (t, 1H, H^5), 7.50 (t, 2H, H^4), 7.71 (d, 2H, H^3), 7.77 (t, 4H, $\text{H}^{4,5}$). ^{31}P NMR (162 MHz, d_6 -DMSO) δ_P : 13.81 ppm. FTIR ν_{\max} (cm^{-1}): 2736 (br), 2271 (br) 1678 (w), 1602 (m), 1553 (m), 1484 (m), 1448 (w), 1391 (m), 1143 (m), 1017 (s), 1000 (s), 977 (s), 942 (s), 835 (m), 759 (s), 721 (m), 689 (m), 665 (s). HRMS (m/z -ES): Found: 233.0368 (M^- -H. $\text{C}_{12}\text{H}_{10}\text{O}_3\text{P}$ *calc.*: 233.0368).

S1.3 Synthesis of Lanthanide Phosphonates

In a typical synthesis, a mixture of ligand (0.4 mmol), $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ (0.02 mmol, $\text{Ln}^{\text{III}} = \text{Nd}^{\text{III}}$, Eu^{III} , Tb^{III} and Yb^{III}) and an appropriate solvent (5 mL) were placed in a 20 mL Teflon liner and stirred for 30 minutes to give a white cloudy suspension. The pH was adjusted to 2 using 1 M NaOH aqueous solution. The Teflon liner was inserted into a steel autoclave and placed in an oven at 100 °C for 48 hours. Following cooling to room temperature, the resulting material was filtered and washed with water and ethanol before drying at 80 °C.

Synthesis of lanthanide *tert*-butyl phosphonates (Ln-Bu^t). The ligand used is *tert*-butyl phosphonic acid (0.055 g, 0.4 mmol) and the solvent acetonitrile. For **Eu-Bu^t** small plate crystals suitable for single X-ray diffraction were found to form in solution. Yield: 0.078 g (67%). FTIR ν_{\max} (cm^{-1}): 2976 (m), 2952 (m), 2908 (m), 2870 (m), 1640 (m), 1475 (m), 1397 (m), 1361 (m), 1122 (s), 1051 (s), 945 (s), 888 (s), 869 (s), 832 (s), 774 (m), 658 (s). **Nd-Bu^t**:

Yield 65 mg (53%). FTIR ν_{\max} (cm^{-1}): 2973 (m), 2950 (m), 2904 (m), 2868 (m), 1626 (m), 1481 (m), 1393 (m), 1364 (m), 1119 (s), 1063 (s), 1028 (s), 972 (s), 898 (s), 834 (s). **Tb-Bu^f**: Yield 69 mg (56%). FTIR ν_{\max} (cm^{-1}): 2952 (m), 2906 (m), 2869 (m), 1649 (m), 1479 (m), 1394 (m), 1362 (m), 1127 (s), 1061 (s), 1034 (s), 1004 (m), 966 (s), 893 (s), 836 (s), 661 (s). **Yb-Bu^f**: Yield 74 mg (64%). FTIR ν_{\max} (cm^{-1}): 2973 (m), 2907 (m), 2871 (m), 1640 (m), 1480 (m), 1396 (m), 1363 (m), 1237 (m), 1115 (s), 1071 (s), 1039 (s), 981 (s), 943 (s), 914 (s), 878 (s), 834 (s), 656 (s). CHN analysis for $\text{EuC}_{12}\text{H}_{32}\text{P}_3\text{O}_{10}$: Expected: C 11.35%; H 7.62%. Found: C 11.09%; H 6.97%.

Synthesis of lanthanide naphthalene phosphonates (Ln-Naph). The ligand was naphthalene phosphonic acid (0.083 g, 0.4 mmol) and deionised water was used for solvent.

Nd-Naph: Yield 0.068 g (59%). FTIR ν_{\max} (cm^{-1}): 3057 (w), 3041 (w), 1591 (w), 1574 (w), 1507 (m), 1460 (w), 1335 (m), 1211 (m), 1134 (s), 1043 (s), 1014 (s), 966 (s), 797 (s), 770 (s), 677 (s). **Eu-Naph:** Yield 0.077 g (67%). FTIR ν_{\max} (cm^{-1}): 3057 (w), 1591 (w), 1506 (m), 1460 (w), 1334 (w), 1211 (m), 1140 (s), 1080 (s), 1034 (s), 1016 (s), 968 (s), 856 (m), 830 (m), 796 (s), 770 (s), 727 (m), 677 (s). **Tb-Naph:** Yield 73 mg (65%). FTIR ν_{\max} (cm^{-1}): 3058 (w), 3043 (w), 1592 (w), 1507 (m), 1460 (w), 1335 (w), 1212 (m), 1142 (s), 1077 (s), 1046 (s), 1016 (s), 968 (s), 857 (m), 830 (m), 797 (s), 770 (s), 728 (m), 678 (s). **Yb-Naph:** 0.074 g (61%). FTIR ν_{\max} (cm^{-1}): 3048 (w), 3009 (w), 1622 (w), 1593 (w), 1574 (w), 1507 (m), 1460 (w), 1337 (w), 1221 (m), 1135 (s), 1094 (s), 1061 (s), 991 (m), 896 (s), 797 (s), 770 (s), 675 (s). CHN analysis for $\text{EuC}_{20}\text{H}_{18}\text{P}_2\text{O}_8$: Expected: C 40.02%; H 3.02%. Found: C 39.66%; H 2.61%.

Synthesis of lanthanide biphenyl phosphonates (Ln-Biphen). Biphenyl phosphonic acid (0.094 g, 0.4 mmol) was used following the general method in deionised water as the solvent.

Nd-Biphen: Yield 0.108 g (85%). FTIR ν_{\max} (cm^{-1}): 3054 (w), 3031 (w), 1678 (w), 1603 (m), 1554 (m), 1485 (m), 1446 (m), 1391 (m), 1185 (w), 1116 (s), 1054 (s), 1025 (m), 973 (s), 933

(m), 826 (s), 755 (s), 720 (s), 687 (s), 678 (s), 661 (s). **Eu-Biphen:** Yield 0.106 g (84%). IR FTIR ν_{max} (cm^{-1}): 3054 (w), 3034 (w), 1678 (w), 1602 (m), 1555 (m), 1484 (m), 1447 (m), 1392 (m), 1185 (w), 1145 (s), 1060 (s), 1025(m), 980 (s), 933 (m), 909 (m), 833 (s), 756 (s), 719 (m), 688 (s), 673 (s). **Tb-Biphen:** Yield 0.103 g (82%). FTIR ν_{max} (cm^{-1}): 3054 (w), 3033 (w), 1678 (w), 1602 (m), 1555 (m), 1484 (m), 1447 (m), 1392 (m), 1146 (s), 1062 (s), 981 (s), 910 (s), 833 (s), 757 (s), 720 (s), 689(s), 671 (s). **Yb-Biphen:** Yield 0.102 g (82%). FTIR ν_{max} (cm^{-1}): 3056 (w), 3031 (w), 1603 (m), 1554 (m), 1484 (m), 1446 (m), 1427 (m), 1392 (m), 1241 (m), 1146 (s), 1075 (s), 1006 (m), 985 (s), 911 (s), 833 (s), 757 (s), 723 (s), 691 (s), 670 (s). CHN analysis for $\text{EuC}_{24}\text{H}_{18}\text{P}_2\text{O}_6$: Expected: C 46.77%; H 2.94%. Found: C 46.47%; H 2.54%.

S2. Supporting Data

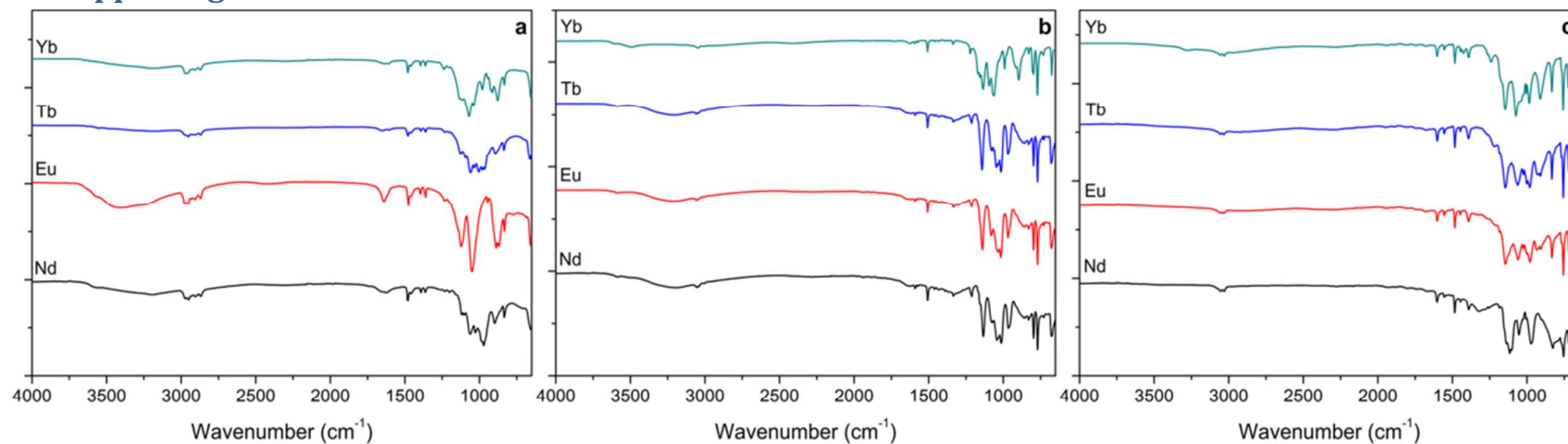


Figure S1: FTIR spectra of (a) Ln-Bu' (b) Ln-Naph and (c) Ln-Biphen.

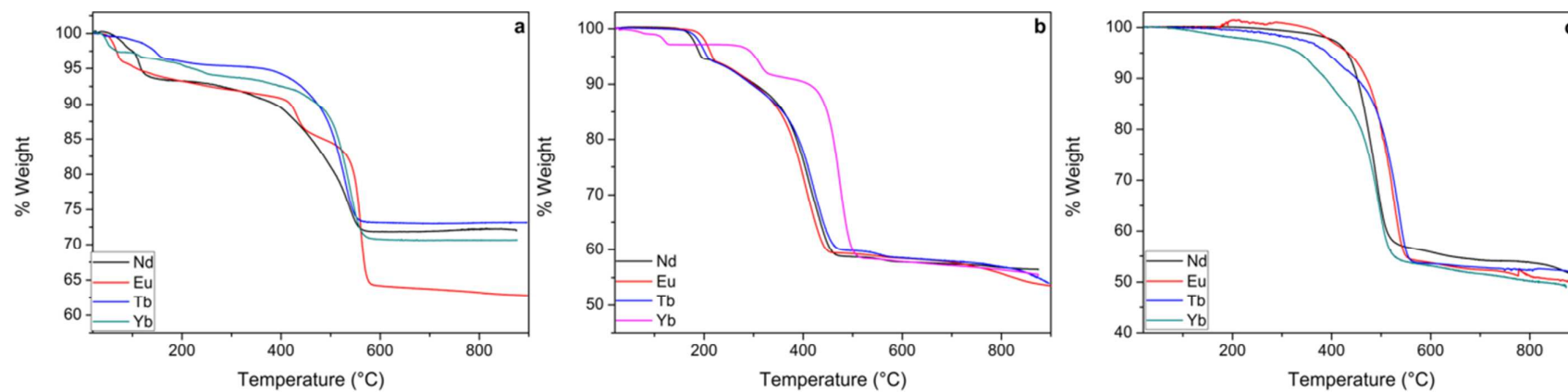


Figure S2: TGA curves of (a) Ln-Bu' (b) Ln-Naph and (c) Ln-Biphen.

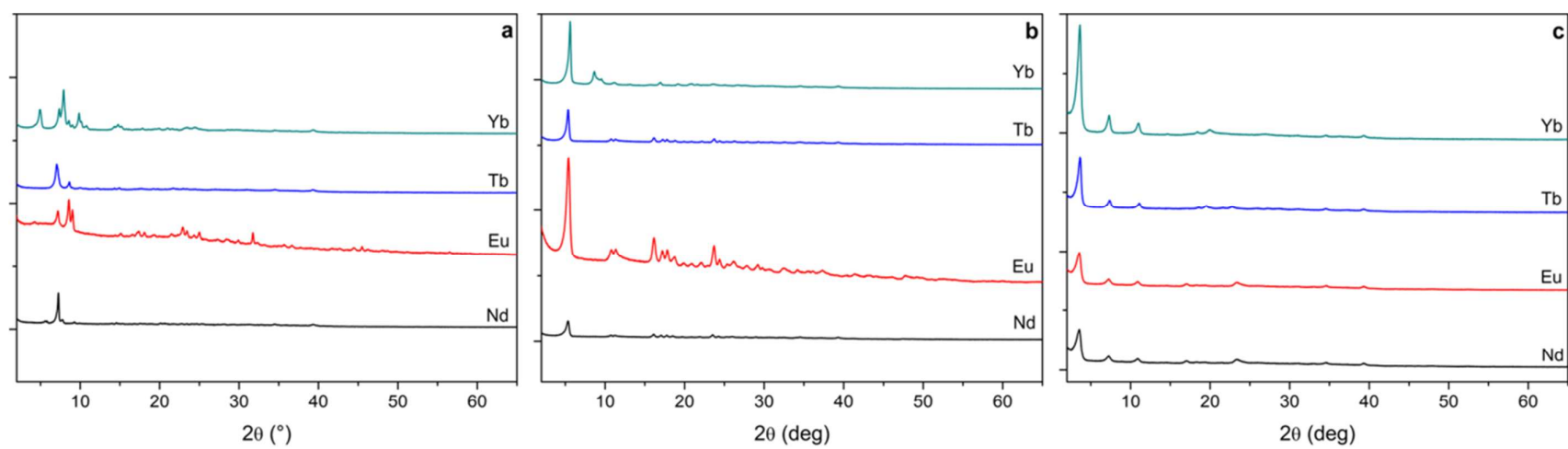


Figure S3: Powder X-ray diffraction patterns of the three isostructural Ln-phosphonate series (a) Ln-Bu' (b) Ln-Naph and (c) Ln-Biphen.

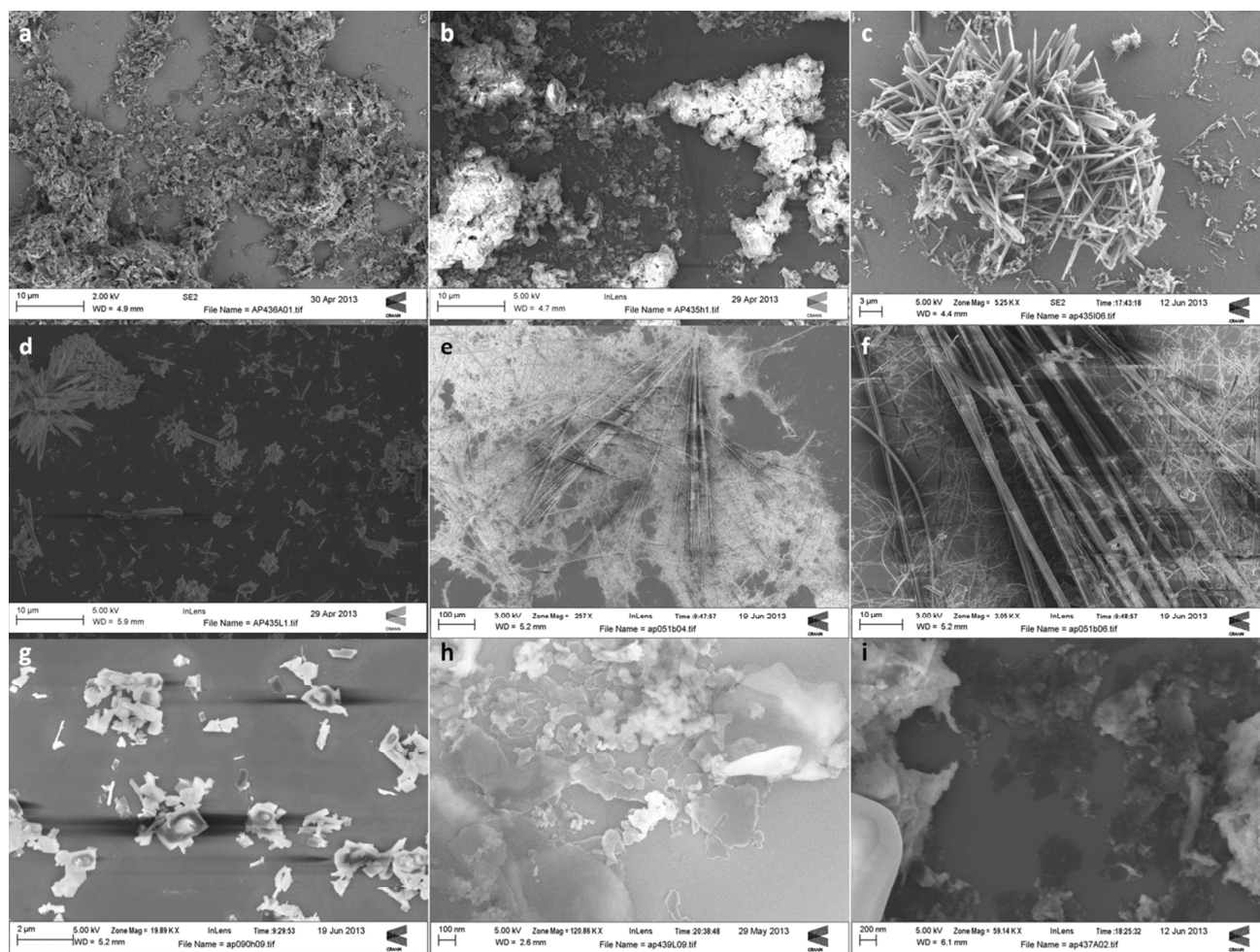


Figure S4. SEM images showing overview of plates formed for (a,b) **Nd-Naph** and **Eu-Naph** (without STS), (c) rods of **Yb-Naph** surrounded by nanoparticles (without STS), (d) monodisperse rods of **Yb-Naph** (with STS), (e,f) overviews of the rod structures of **Yb-Bu'**, (g) rod structures of **Nd-Bu'** and (h,i) films of **Yb-Biphen** and **Nd-Biphen**, respectively, with some amorphous nature.

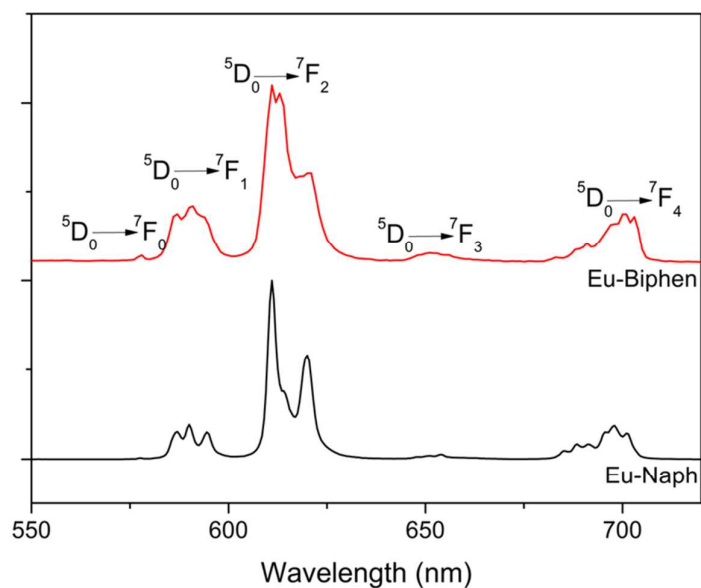


Figure S5. Room-temperature (RT) photoluminescence (PL) spectra for **Eu-Naph** and **Eu-Biphen** obtained upon direct excitation at 393 nm ($^5L_6 \leftarrow ^7F_0$).

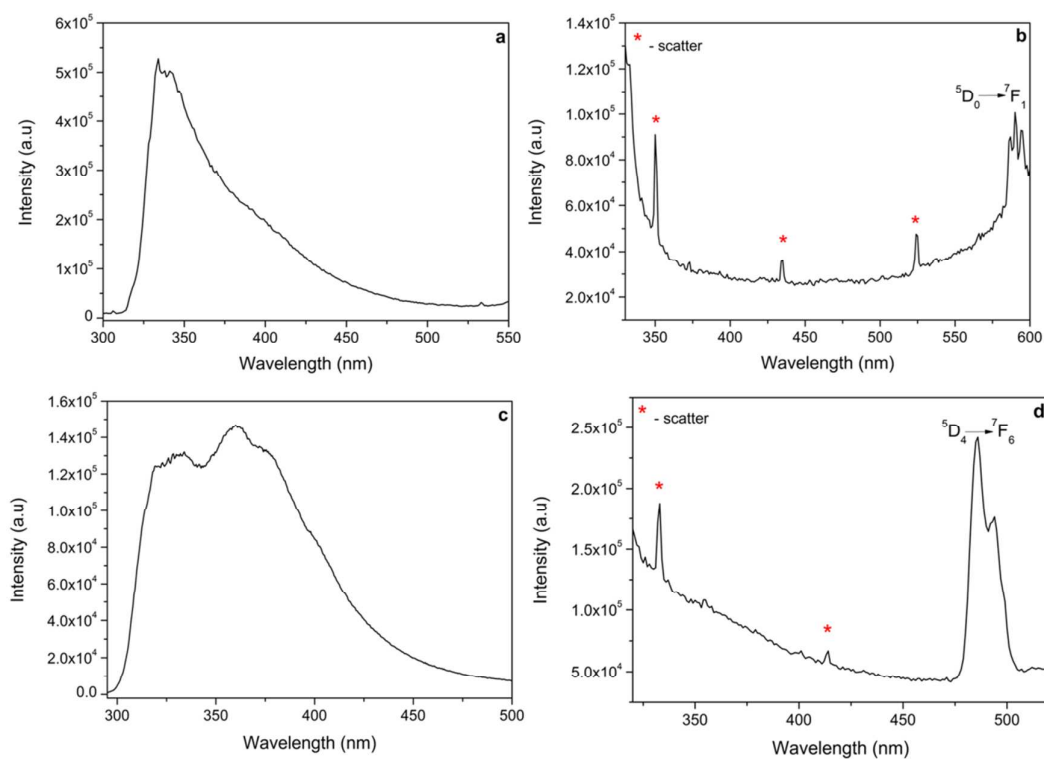


Figure S6. Solid state PL spectra for (a) naphthalene phosphonic acid, (b) **Eu-Naph**, (c) biphenyl phosphonic acid and (d) **Tb-Biphen**. Note the absence of ligand emission in the Ln-phosphonate hybrids indicating efficient sensitization from the ligand to Ln^{III} center.

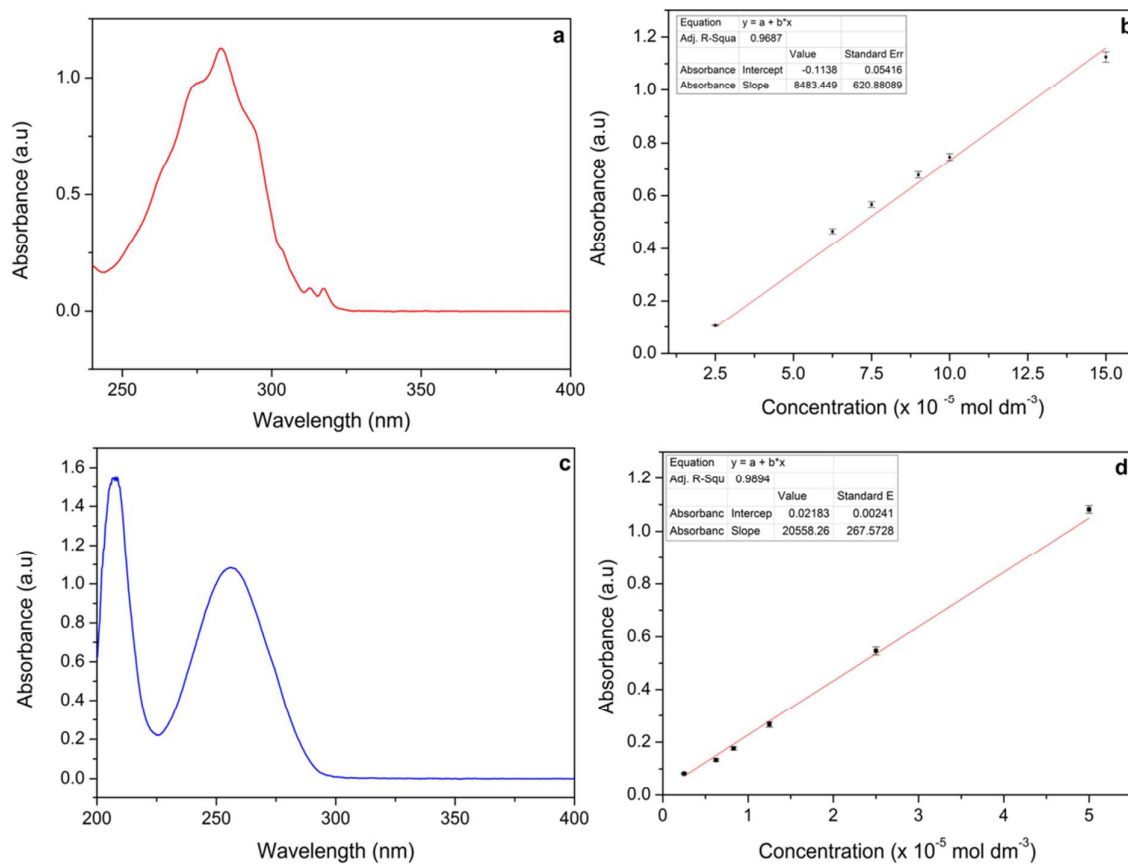


Figure S7. UV/Vis absorption spectra and corresponding Beer-Lambert plots plot for (a, b) naphthalene phosphonic and (c, d) biphenyl phosphonic acid in ethanol, respectively.

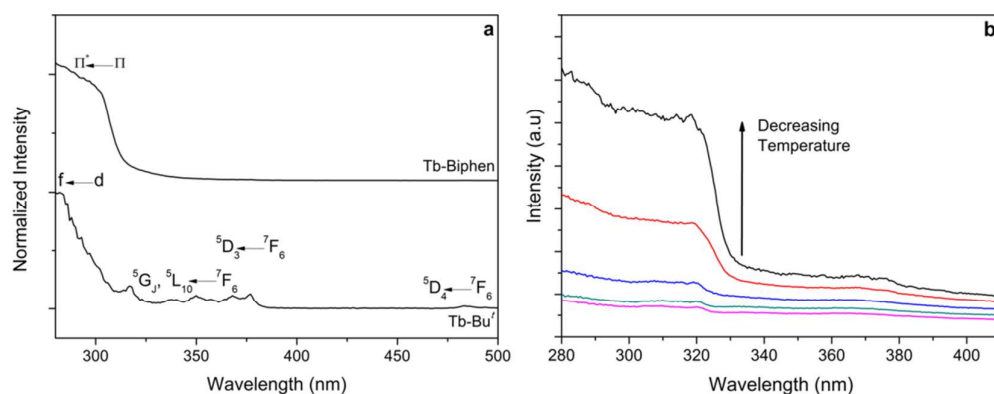


Figure S8. (a) RT photoluminescence excitation spectra for **Tb-Bu'** and **Tb-Biphen** ($\lambda_{em} = 540$ nm, $^5D_4 \rightarrow ^7F_5$). (b) Variable low temperature photoluminescence excitation spectra of Tb-Naph ($T = 77$ -250K).

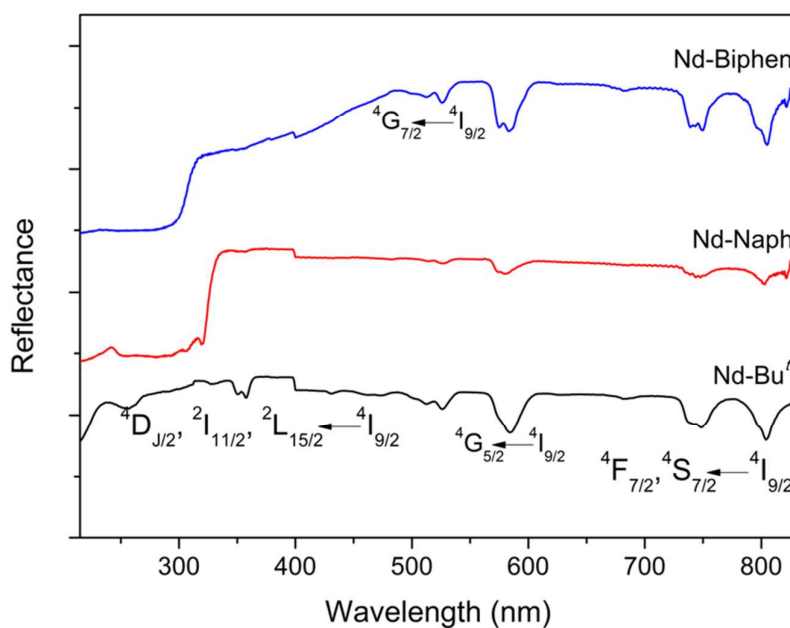


Figure S9. RT UV/Vis diffuse reflectance spectra for **Nd-Bu'**, **Nd-Naph** and **Nd-Biphen**.

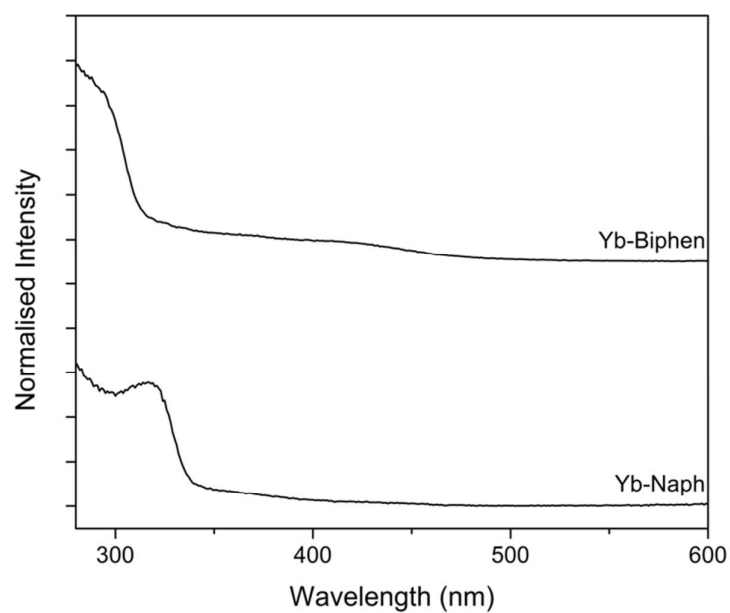


Figure S10. RT excitation spectra for **Yb-Naph** and **Yb-Biphen** ($\lambda_{\text{em}} = 977\text{-}978\text{ nm}$, $^5\text{F}_{5/2} \rightarrow ^4\text{F}_{7/2}$).

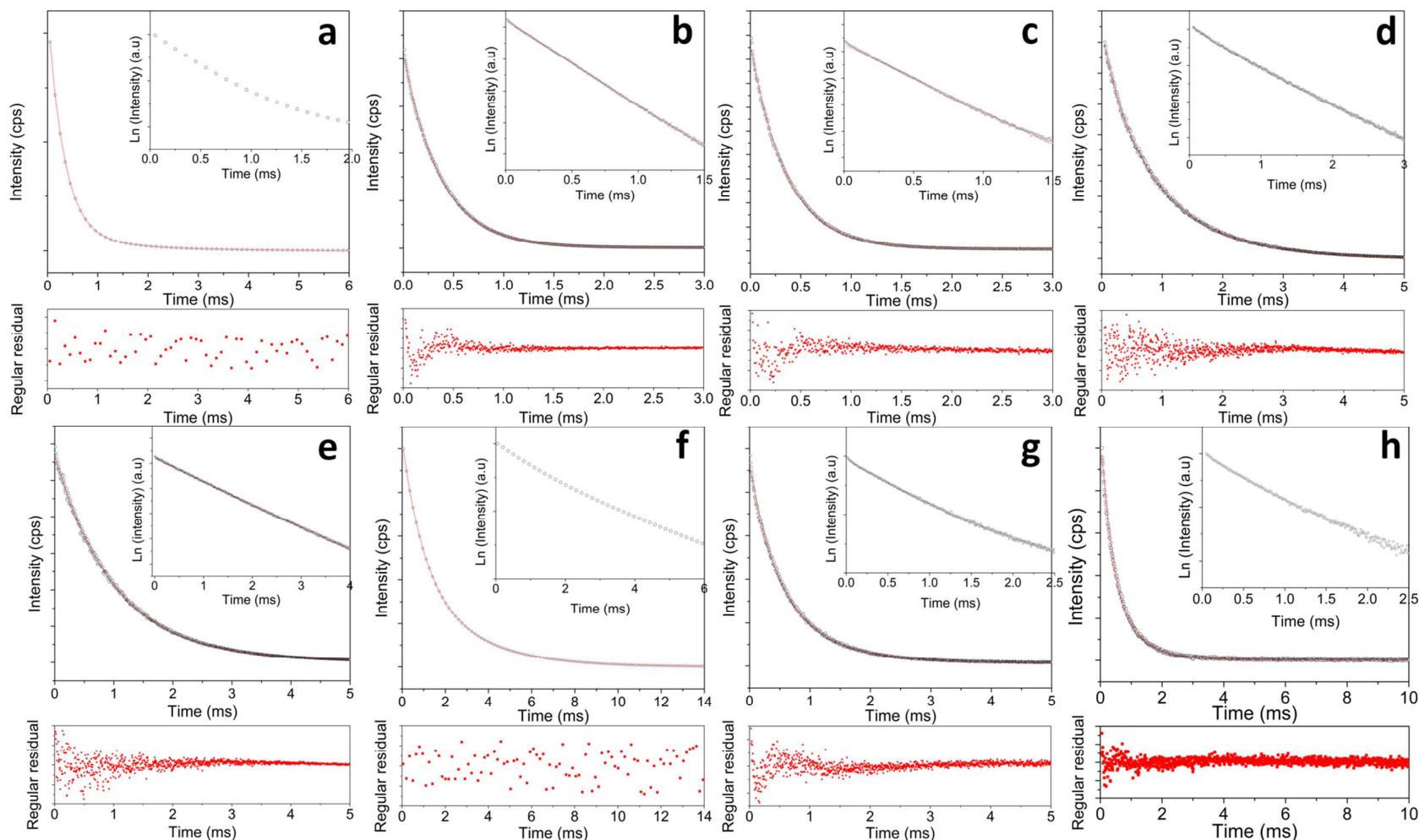


Figure S11. Emission decay curves (solid symbols), curve fits (solid lines) and residuals for (a) **Eu-Bu^f** ($\lambda_{\text{ex}} = 393$ nm, biexponential fit), (b,c) **Eu-Naph** ($\lambda_{\text{ex}} = 393$ nm and 330 nm, respectively, monoexponential fits), (d,e) **Eu-Biphen** ($\lambda_{\text{ex}} = 393$ nm and 305 nm, respectively, biexponential fits), (f) **Tb-Bu^f** ($\lambda_{\text{ex}} = 377$ nm, biexponential fit) and (g,h) **Tb-Biphen** ($\lambda_{\text{ex}} = 377$ nm and 305 nm, respectively, biexponential fits). We note that the sinusoidal appearance of the residuals for some curves fits suggests that the decay kinetics deviate from simple exponential behaviour. The insets show the decay curves on a ln-lin scale.

Table S1. Crystal data and structure refinement for **Eu-Bu^f**.

Identification code	Eu-Bu ^f	
Empirical formula	C ₁₂ H ₂₉ EuO ₁₀ P ₃	
Formula weight	578.22	
Temperature	108(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P (1)2 ₁ /c	
Unit cell dimensions	a = 13.037(3) Å	α = 90°.
	b = 17.836(4) Å	β = 108.24(3)°.
	c = 10.327(2) Å	γ = 90°.
Volume	2280.7(9) Å ³	
Z	4	
Density (calculated)	1.684 Mg/m ³	
Absorption coefficient	3.001 mm ⁻¹	
F(000)	1156	
Crystal size	0.2 x 0.2 x 0.2 mm ³	
Theta range for data collection	1.64 to 24.99°.	
Index ranges	-15<=h<=15, -21<=k<=21, -8<=l<=12	
Reflections collected	16414	
Independent reflections	3879 [R(int) = 0.0731]	
Completeness to theta = 24.99°	96.4 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3879 / 0 / 244	
Goodness-of-fit on F ²	1.319	
Final R indices [I>2sigma(I)]	R1 = 0.0803, wR2 = 0.2058	
R indices (all data)	R1 = 0.0849, wR2 = 0.2190	
Largest diff. peak and hole	1.736 and -1.968 e.Å ⁻³	

S3. References

- (1) Wang, Z. K.; Heising, J. M.; Clearfield, A. *Journal of the American Chemical Society* **2003**, *125*, 10375.