Cooperative loading of multisite receptors with lanthanide containers: an approach for organized luminescent metallopolymers

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Supporting Information

(44 pages)

Appendix 1: Experimental section

Chemicals were purchased from Strem, Acros, Fluka AG, and Aldrich, and used without further purification unless otherwise stated. The hexafluoroacetylacetonate salts [Ln(hfa)$_3$dig] were prepared from the corresponding oxide (Aldrich, 99.99%).[A1-1] Dichloromethane and DMF were distilled over calcium hydride. Silica gel plates Merck 60 F$_{254}$ were used for thin layer chromatography (TLC) and Fluka silica gel 60 (0.04-0.063 mm) or Acros neutral activated alumina (0.050-0.200 mm) was used for preparative column chromatography. Ligands **L1**[A1-2] and **L2**-**L4**[A1-3] were synthesised according to published literature procedures.

NMR and analytic measurements: ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded at 298 K on a Bruker Avance 400 MHz and Bruker DRX-300 MHz spectrometers. Chemical shifts are given in ppm with respect to tetramethylsilane Si(CH$_3$)$_4$ (TMS) for ^{1}H NMR and with C$_6$F$_6$ for ^{19}F NMR. Spectral assignment was assisted by 2D NMR experiments (COSY, NOESY, HSQC and HMBC) where appropriate. Pneumatically-assisted electrospray (ESI) mass spectra were recorded from 10^{-4} M solutions on an API 150EX (AB/MDS Sciex) equipped with a Turbo Ionspray source®. High resolution (ESI-HRMS) was performed at the same concentration on a QSTAR pulsar *i* (AB/MDS Sciex) equipped with a Turbo Ionspray source®. Elemental analyses were performed by K. L. Buchwalder from the Microchemical Laboratory of the University of Geneva.

Photophysical measurements: Electronic absorption spectra in the UV-Vis were recorded at 20 °C from solutions in CH$_2$Cl$_2$ with a Perkin-Elmer Lambda 900 spectrometer and Perkin-Elmer Lambda 1050 spectrometer using quartz cells of 10 or 1 mm path length. Emission spectra were measured using a Jobin Yvon–Horiba Fluorolog-3 spectrofluorimeter. Spectra were corrected for both excitation and emission responses (excitation lamp, detector and both excitation and emission monochromator responses). Quartz tube sample holders were employed. The quantum yields Φ in solution were determined through the relative method with respect to quinine sulfate 6.42 10^{-6} M in 0.05 M H$_2$SO$_4$ (refractive index 1.338 and quantum yield 0.546)[A1-4] and to europium-tris(dipicolinate) 6.87 10^{-5} M in aq. tris-buffer (quantum yield 0.24(2)),[A1-5] and using the equation

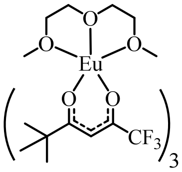
$$\frac{\Phi_x}{\Phi_r} = \frac{A_r\left(\bar{\upsilon}\right) I_x\left(\bar{\upsilon}\right) n_x^2 D_x}{A_x\left(\bar{\upsilon}\right) I_r\left(\bar{\upsilon}\right) n_r^2 D_r}$$

where *x* refers to the sample and *r* to the reference; *A* is the absorbance corrected for partial dissociation in solution (see Appendix 2), *v* the excitation wavenumber used, *I* the intensity of the excitation light at this energy, *n* the refractive index and *D* the integrated emitted intensity. Quantum yield measurements of solid state samples were measured on quartz tubes with the help an integration sphere[A1-6] developed by Frédéric Gumy and Jean-Claude G. Bünzli (Laboratory of Lanthanide Supramolecular Chemistry, École Polytechnique Féderale de Lausanne (EPFL), BCH 1402, CH- 1015 Lausanne, Switzerland) commercialized by GMP S.A. (Renens, Switzerland).

X-Ray Crystallography. Crystals were mounted on a capton loop with protection oil. Cell dimensions and intensities were measured at 180 K on an Agilent Supernova diffractometer with mirror monochromated CuKα (λ= 1.54184Å) and MoKα (λ= 0.71073Å) radiations and an Atlas CCD camera. Data were corrected for Lorentz and polarization effects and for absorption. The structure was solved by direct methods (SIR97[A1-7]) or charge flipping (superflip[A1-8], Olex2 solve[A1-9]), all other calculations were performed with SHELXL,[A1-10] OLEX2,[A1-9] and ORTEP[A1-11] programs. CCDC 1551909-1551912 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Summary of crystal data, intensity measurements, structure refinements, bond distances and bond angle, interplanar angles and bond valences[A1-13] for [Eu(tta)$_3$dig] (**1**), [Y(tta)$_3$dig] (**2**), [Eu(pbta)$_3$dig] (**3**) and [Eu(pbta)$_3$**L1**]·CH_2Cl_2 (**4**) were collected in Tables S1-S13 and S18-S22. The three heterocycles of the thenoyl groups in [Eu(tta)3dig] were disordered by a 2-fold rotation along the axis passing through the carbon atom in position 2 of the thiophen ring and the middle of the carbon-carbon bond between the carbon atoms in position 4 and 5 of the ring. They were refined with two different set of positions (occupancy factor 0.7-0.8). Restraints were applied on distances (DFIX DANG) and on anisotropic displacement parameters (RIGU) as well as constraints on displacement parameters for close atoms (EADP). Diglyme was also slightly disordered in [Eu(tta)3dig] and was refined using two positions for the four central carbon atoms (occupancy factor 0.7). Restraints on distances and anisotropic displacement parameters were also used. Two thenoyl groups in [Y(tta)3dig] showed the same 2-fold rotation disorder as observed in compound 1 and were also refined with two different sets of positions (occupancy factor 0.8-0.9). Restraints were applied on distances (DFIX DANG) and on anisotropic displacement parameters (RIGU) as well as constraints on displacement parameters for close atoms (EADP). The third thenoyl group might also be slightly disordered but this small disorder was not modelled. The crystal structure of **4** included solvent accessible voids (V ~ 630Å^3), but the absence of features in the electron density map did not enable us to locate solvent molecules (dichloromethane) in [Eu(pbta)$_3$**L10**]·CH_2Cl_2 structure. We used the Squeeze bypass program (Platon,[A1-12]) and 150 electrons per cell were counted. It represented ~1 dichloromethane molecule per formula unit which was included in molecular formula, in the calculated density, molecular weight and *F*(000).

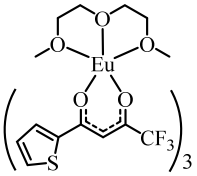
Computational Details. The geometry of mononuclear complexes [YX$_3$dig] (X= hfa, tta, pbta) and [YX$_3$**L1**] (X= hfa, tta, pbta) were optimized at the DFT/B97-D/def2-TZVP level of theory, using the pseudopotential def2-ecp for metal centers.[A1-14] Single point calculations for energy and dipole moments were carried out at the DFT/B97-D/def2-TZVP/def2-ecp level of theory. All calculations were carried out using the Turbomole v6.6 package program.[A1-15]

Preparation of [Eu(pta)$_3$dig].



Europium oxide Eu_2O_3 (500 mg, 1.42 mmol) was first suspended in toluene (20 mL) and diglyme (505 µL, 1.0 eq.) was added. Hpta (1.48 mL, 3.0 eq.) was added after 10 min under vigorous stirring and the mixture was refluxed for 4h. The solvent was removed under vacuum and the resulting solid was sublimed to yield light yellow crystals of [Eu(pta)$_3$dig] (181 mg, 9%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.24-12.19 (m, 14H), 1.29 (s, 28H), 0.15 (br, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -82.69 (s, 3CF$_3$). Elemental analyses: calcd for $C_{30}H_{44}EuF_9O_9$, C 41.34, H 5.09; found C 41.35, H 5.05. ESI-MS (positive mode/CH_3OH) : *m/z* 543.5 ([M-pta-dig]$^+$), 677.5 ([M-pta]$^+$), 739.5 ([M-dig+H]$^+$).

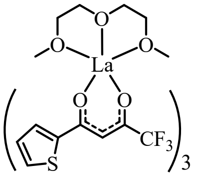
Preparation of [Eu(tta)$_3$dig].



Europium oxide Eu_2O_3 (0.17 g, 0.48 mmol) was first suspended in hydrochloric acid (0.3 mL). The mixture was heated until complete evaporation to obtain a white powder of $EuCl_3 \cdot xH_2O$. Htta (1.30 g, 3.0 eq.) and sodium hydroxide (233 mg, 3.0 eq.) in EtOH (10 mL) were heated at 60°C for 2h. A solution of $EuCl_3 \cdot xH_2O$ (1.0 eq.) in EtOH (10 mL) was slowly added to the mixture. The resulting precipitate was filtered off (1.49 g) and re-dissolved in dichloromethane (10 mL). Diglyme (124 µL, 1.0 eq.) was added and the mixture was refluxed for 2h. The solvent was removed under vacuum and the resulting solid was crystallised in a hot mixture of CH_2Cl_2/hexane to yield orange crystals of [Eu(tta)$_3$dig] (708 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 16.75 (br, 6H), 12.50 (br, 4H), 10.23 (br, 4H), 7.27 (d, J = 5.2 Hz, 3H), 6.52 (t, J = 4.4 Hz, 3H), 6.03 (br, 3H), 0.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.66 (3 CH), 126.16

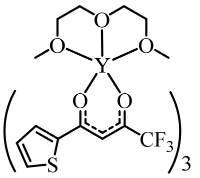
(3 CH), 123.67 (3 CH), 98.97 (2 CH_2), 95.84 (2 CH_2), 94.51 (2 CH_3), 50.21 (3 CH). ^{19}F NMR (376 MHz, $CDCl_3$) δ -82.39 (s, $3CF_3$). Elemental analyses: calcd for $C_{30}H_{26}EuF_9O_9S_3$, C 37.94, H 2.76; found C 37.89, H 2.80. ESI-MS (positive mode/CH_3OH) : *m/z* 595.5 ([M-tta-dig]$^+$), 729.8 ([M-tta]$^+$), 817.5 ([M-dig+H]$^+$).

Preparation of [La(tta)$_3$dig].



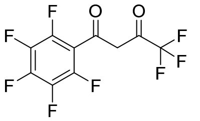
Lanthanum oxide La_2O_3 (0.25 g, 0.77 mmol) was first suspended in water (1 mL) and hydrochloric acid (0.4 mL). The mixture was heated until complete evaporation to obtain a white powder of $LaCl_3 \cdot xH_2O$. Diglyme (218 µL, 1.0 eq.) and sodium hydroxide (184 mg, 3.0 eq.) were added to a suspension of this powder (1.0 eq.) in hexane (10 mL). Htta (1.0 g, 3.0 eq.) was added after 10 min under vigorous stirring and the mixture was refluxed for 4h. The solvent was removed under vacuum and the resulting solid was crystallised in a hot mixture of CH_2Cl_2/hexane to yield white crystals of [La(tta)$_3$dig] (1.31 g, 92%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.65 (d, *J* = 3.7 Hz, 3H), 7.53 (d, *J* = 4.7 Hz, 3H), 7.07 (dd, *J* = 4.8, 3.9 Hz, 3H), 6.26 (s, 3H), 3.99-3.85 (m, 4H), 3.85-3.74 (m, 4H), 3.51 (s, 6H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 180.90 (3 C_{quat}), 169.91 (3 C_{quat}), 145.82 (3 C_{quat}), 131.90 (3 CH), 129.63 (3 CH), 127.95 (3 CH), 120.71 (3 C_{quat}), 91.87 (3 CH), 71.47 (2 CH_2), 70.69 (2 CH_2), 60.05 (2 CH_3). ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.02 (s, $3CF_3$). Elemental analyses: calcd for $C_{30}H_{26}F_9LaO_9S_3$, C 38.47, H 2.80; found C 38.39, H 2.76.

Preparation of [Y(tta)$_3$dig].



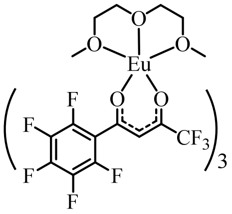
Yttrium hydroxide $Y(OH)_3 \cdot xH_2O$ (72 mg, 0.52 mmol) was first suspended in toluene (2 mL) and diglyme was added (81 µL, 1.0 eq.). Htta (377 mg, 3.0 eq.) was added after 10 min under vigorous stirring and the mixture was refluxed for 4h. The solvent was removed under vacuum and the resulting solid was crystallised in a hot mixture of CH_2Cl_2/hexane to yield white crystals of [Y(tta)$_3$dig] (242 mg, 53%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.65 (d, *J* = 3.6 Hz, 3H), 7.52 (d, *J* = 4.8 Hz, 3H), 7.05 (t, *J* = 4.4 Hz, 3H), 6.27 (s, 3H), 4.14-4.05 (m, 4H), 3.78-3.68 (m, 4H), 3.48 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.87 (s, $3CF_3$). Elemental analyses: calcd for $C_{30}H_{26}F_9O_9S_3Y \cdot 0.5703\ H_2O$, C 40.17, H 3.05; found C 40.15, H 2.93.

Preparation of 4,4,4-trifluoro-1-(perfluorophenyl)butane-1,3-dione (Hpbta).



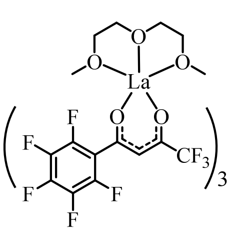
Dry sodium methoxide NaOMe (2.8 g, 51.4 mmol, 1.2 eq.) was suspended in dry ether (50 mL) under nitrogen. A solution of ethyl trifluoroacetate (5.1 mL, 42.8 mmol) in dry Et_2O (15 mL) was added dropwise to the suspension followed by the dropwise addition of a solution of pentafluoroacetophenone (6.1 mL, 42.8 mmol) in dry Et_2O (15 mL). The reaction mixture was stirred at RT for 12h and then quenched with aqueous H_2SO_4 (50 mL, 10%). The organic phase was separated, washed with water (50 mL), dried with Na_2SO_4, filtered and evaporated to dryness. The resulting mixture (13 g) was distilled using a Vigreux apparatus at 160°C under reduced pressure (5 mbar) to obtain 4,4,4-trifluoro-1-(perfluorophenyl)butane-1,3-dione (Hpbta, head of column 74°C, 9.38 g, 56%) as a colorless oil. A small impurity (ratio 1:0.03 compared to the desired product) characterized by ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.26 (d, 1H), 4.02 (d, 2H)) forced us to further purify a small portion of this oil (3 g) using a micro-distillation apparatus (Kugelrohr) to yield 1.52 g of pure Hpbta. ^{1}H NMR (400 MHz, $CDCl_3$, enol ratio 1 : 2) δ 13.77 (br, 1H), 6.33 (t, J = 1.4 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.28 (s, CF_3), -138.06 (m, 2CF), -146.24 (tt, J = 21.0, 5.2 Hz, CF), -159.24 (m, 2CF). ESI-MS (negative mode/CH_3OH) : *m/z* 285.05 ($[M-F]^-$), 305.25 ($[M-H]^-$).

Preparation of [Eu(pbta)$_3$dig].



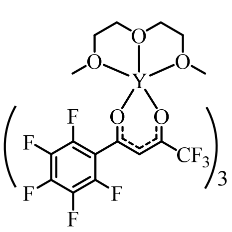
Europium oxide Eu_2O_3 (105 mg, 0.30 mmol) was suspended in toluene (5 mL) and diglyme (94 µL, 1.0 eq.) was added. Hpbta (551 mg, 3.0 eq.) was added after 10 min under vigorous stirring and the mixture was refluxed for 4h. The solvent was removed under vacuum and the resulting solid was crystallised in a hot mixture of CH_2Cl_2/hexane to yield light orange crystals of [Eu(pbta)$_3$dig] (675 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 22.85 (br, 6H), 11.97 (br, 4H), 5.40 (br, 4H), -0.49 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -82.38 (s, $3CF_3$), -142.13 (dd, J = 16.8, 7.2 Hz, 6CF), -153.26 (t, J = 21.8 Hz, 3CF), -162.73 (m, 6CF). Elemental analyses: calcd for $C_{36}H_{17}EuF_{24}O_9$, C 35.99, H 1.43; found C 36.04, H 1.57.

Preparation of [La(pbta)$_3$dig].



Lanthanum oxide La$_2$O$_3$ (98 mg, 0.30 mmol) was suspended in toluene (5 mL) and diglyme (94 µL, 1.0 eq.) was added. Hpbta (551 mg, 3.0 eq.) was added after 10 min under vigorous stirring and the mixture was refluxed for 4h. The solvent was removed under vacuum and the resulting solid was crystallised in a hot mixture of CH$_2$Cl$_2$/hexane to yield white crystals of [La(pbta)3dig] (497 mg, 70%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.92 (s, 3H), 3.96-3.87 (m, 4H), 3.87-3.78 (m, 4H), 3.51 (s, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 178.72 (3 C$_{quat}$), 172.74 (q, J = 33 Hz, 3 C$_{quat}$), 145.7-135.9 (m, 15 C$_{quat}$), 122.7-114.0 (m, 3 C$_{quat}$), 98.74 (3 CH), 71.46 (2 CH$_2$), 70.87 (2 CH$_2$), 60.31 (2 CH$_3$). ^{19}F NMR (376 MHz, CDCl$_3$) δ -76.45 (s, 3CF$_3$), -141.28 (dd, J = 22.5, 7.1 Hz, 6CF), -152.43 (t, J = 22.2 Hz, 3CF), -161.41 (m, 6CF). Elemental analyses: calcd for C$_{36}$H$_{17}$F$_{24}$LaO$_9$, C 36.38, H 1.44; found C 36.51, H 1.58.

Preparation of [Y(pbta)$_3$dig].



Yttrium hydroxide Y(OH)$_3\cdot x$H$_2$O (72 mg, 0.52 mmol) was suspended in toluene (2 mL) and diglyme was added (81 µL, 1.0 eq.). Hpbta (520 mg, 3.0 eq.) was added after 10 min under vigorous stirring and the mixture was refluxed for 4h. The solvent was removed under vacuum and the resulting solid was crystallised in a hot mixture of CH$_2$Cl$_2$/hexane to yield white crystals of [Y(pbta)$_3$dig] (171 mg, 56%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.01 (s, 3H), 4.05-3.84 (m, 4H), 3.78-3.67 (m, 4H), 3.44 (s, 6H). ^{19}F NMR (376 MHz, CDCl$_3$) δ -76.44 (s, 3CF$_3$), -140.87 (dd, J = 16.8, 7.6 Hz, 6CF), -152.43 (t, J = 22.0 Hz, 3CF), -161.08 (m, 6CF). Elemental analyses: calcd for C$_{36}$H$_{17}$F$_{24}$O$_9$Y, C 37.98, H 1.50; found C 38.00, H 1.62.

Preparation of the X-ray quality prims of [LnX$_3$dig] (Ln = Eu, Y and X= tta, pbta). Slow evaporation of hexane solutions yielded crystals of [Y(tta)$_3$dig] (**1**), [Eu(tta)$_3$dig] (**2**) and [Eu(pbta)$_3$dig] (**3**) suitable for X-Ray diffraction.

Preparation of the X-ray quality prims of [Eu(pbta)$_3$L1]. In a typical procedure, **L1** (0.012 mmol) and [Eu(pbta)$_3$dig] (0.013 mmol) were dissolved and stirred in chloroforme/acetonitrile mixtures (ca 1-2 ml). Slow diffusion of volatile ethers (diisopropylether) yielded crystals of [Eu(pbta)$_3$**L10**]$\cdot$CH$_2$Cl$_2$ suitable for X-Ray diffraction.

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Appendix 2: Correction of the absorption spectra for the partial dissociation of [Eu(X)$_3$L1] (X= hfa, tta or pbta).

For the monomeric complex, dissociation in solution can be written as

$$[\mathrm{LnX_3}\mathbf{L1}] \rightleftharpoons [\mathrm{LnX_3}] + \mathbf{L1} \qquad 1/\beta_{1,1,\mathrm{cond}}^{\mathrm{Ln},\mathbf{L1}} \tag{A2-1}$$

Once the conditional formation constant $\beta_{1,1,\mathrm{cond}}^{\mathrm{Ln},\mathbf{L1}}$ is at hand (eq. A2-1), the speciation in solution is easily obtained from the mass balances given in eqs (A2-2) and (A2-3) and the law of mass action (A2-4).

$$[\mathbf{L1}]_{\mathrm{tot}} = [\mathbf{L1}] + [\mathrm{LnX_3}\mathbf{L1}] \Rightarrow [\mathrm{LnX_3}\mathbf{L1}] = [\mathbf{L1}]_{\mathrm{tot}} - [\mathbf{L1}] \tag{A2-2}$$

$$[\mathrm{Ln}]_{\mathrm{tot}} = [\mathrm{LnX_3}] + [\mathrm{LnX_3}\mathbf{L1}] \Rightarrow [\mathrm{LnX_3}] = [\mathrm{Ln}]_{\mathrm{tot}} - [\mathrm{LnX_3}\mathbf{L1}] \tag{A2-3}$$

$$\beta_{1,1,\mathrm{cond}}^{\mathrm{LnX_3},\mathbf{L1}} = \frac{[\mathrm{LnX_3}\mathbf{L1}]}{[\mathbf{L1}][\mathrm{LnX_3}]} = \frac{[\mathrm{Ln}]_{\mathrm{tot}} - [\mathrm{LnX_3}]}{[\mathrm{LnX_3}]^2} \tag{A2-4}$$

Straightforward algebraic transformations lead to

$$\beta_{1,1,\mathrm{cond}}^{\mathrm{LnX_3},\mathbf{L1}} [\mathrm{LnX_3}]^2 + [\mathrm{LnX_3}] - [\mathrm{Ln}]_{\mathrm{tot}} = 0 \tag{A2-5}$$

For any total concentration of metal $[\mathrm{Ln}]_{\mathrm{tot}}$, the quadratic eq. (A2-6) provides the concentration of the free metal [LnX$_3$], from which those of the complex $[\mathrm{LnX_3}\mathbf{L1}]$ (eq. A2-3) and free ligand $[\mathbf{L1}]$ (eq. A2-2) are deduced. The total absorbance $A_{\mathrm{tot}}^{\lambda}$ at a wavelength λ is given by the Lambert-Beer relationship (eq. A2-6), where $\varepsilon_{\mathrm{Ln}}^{\lambda}$, $\varepsilon_{\mathrm{L}}^{\lambda}$ and $\varepsilon_{\mathrm{LnL}}^{\lambda}$ are the molar extinction coefficients of LnX$_3$, **L1** and [LnX$_3$**L1**], respectively, and l is the pathlength of the cell. According that the absorption spectra of [LnX$_3$dig] and **L1** can be recorded independently (Figures 12 and S13), the absorption of the pure complex at a given wavelength corrected for dissociation is obtained by using eq. (A2-7).

$$A_{\mathrm{tot}}^{\lambda} = l \sum_n \varepsilon_n^{\lambda} [n] \tag{A2-6}$$

$$\varepsilon_{\mathrm{LnL}}^{\lambda} = \frac{\left(A_{\mathrm{tot}}^{\lambda} / l\right) - \varepsilon_{\mathrm{Ln}}^{\lambda} [\mathrm{LnX_3}] - \varepsilon_{\mathrm{L}}^{\lambda} [\mathbf{L1}]}{[\mathrm{LnX_3}\mathbf{L1}]} \tag{A2-7}$$

Table S1 Summary of Crystal Data, Intensity Measurements and Structure Refinements for [Eu(tta)$_3$dig] (**1**).

Empirical formula	$C_{30}H_{26}EuF_9O_9S_3$	
Formula weight	949.65	
Temperature	183(7) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 11.81000(16) Å	α= 90°
	b = 16.5659(2) Å	β= 92.9627(13)°
	c = 18.3880(2) Å	γ= 90°
Volume	3592.68(8) Å^3	
Z	4	
Density (calculated)	1.756 Mg/m^3	
Absorption coefficient	2.017 mm^{-1}	
F(000)	1880	
Crystal size	0.5013 x 0.2665 x 0.1021 mm^3	
Theta range for data collection	4.436 to 59.026°.	
Index ranges	$-16<=h<=15$, $-22<=k<=22$, $-25<=l<=25$	
Reflections collected	39183	
Independent reflections	8971 [R(int) = 0.0369]	
Completeness to theta = 52°	99.9 %	
Absorption correction	Analytical	
Max. and min. transmission	0.824 and 0.488	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8971 / 321 / 611	
Goodness-of-fit on F^2	1.075	
Final R indices [I>2sigma(I)]	$R1$ = 0.0251, w$R2$ = 0.0512	
R indices (all data)	$R1$ = 0.0362, w$R2$ = 0.0573	
Largest diff. peak and hole	0.61 and -0.90 e·Å^{-3}	

Table S2 Selected Bond Distances (Å) and Bond Angles (°) in [Eu(tta)$_3$dig] (**1**).

Bond distances /Å

Atoms 1-2	Distance	Atoms 1-2	Distance	Atoms 1-2	Distance
Eu-O1	2.574(2)	Eu-O4	2.416(2)	Eu-O7	2.395(2)
Eu-O2	2.585(2)	Eu-O5	2.373(2)	Eu-O8	2.387(2)
Eu-O11	2.578(2)	Eu-O6	2.384(2)	Eu-O9	2.367(2)

Chelate angles /°

Atoms 1-2-3	Angle	Atoms 1-2-3	Angle	Atoms 1-2-3	Angle
O1-Eu-O2	63.35(5)	O1-Eu-O11	126.26(6)	O2-Eu-O11	63.16(6)
O4-Eu-O5	72.81(5)	O6-Eu-O7	70.65(5)	O8-Eu-O9	71.71(6)

O-Eu-O angles /°

Atoms 1-2-3	Angle	Atoms 1-2-3	Angle	Atoms 1-2-3	Angle
O1-Eu-O4	84.31(5)	O1-Eu-O6	84.80(5)	O1-Eu-O8	141.40(6)
O1-Eu-O5	140.86(5)	O1-Eu-O7	71.04(5)	O1-Eu-O9	72.66(6)
O2-Eu-O4	67.92(5)	O2-Eu-O6	133.87(5)	O2-Eu-O8	113.66(6)
O2-Eu-O5	130.14(5)	O2-Eu-O7	122.07(6)	O2-Eu-O9	66.48(6)
O11-Eu-O4	71.61(6)	O11-Eu-O6	139.35(6)	O11-Eu-O8	68.59(6)
O11-Eu-O5	76.30(6)	O11-Eu-O7	138.80(6)	O11-Eu-O9	90.77(6)

Table S3 Selected Least-Squares Planes Data in [Eu(tta)$_3$dig] (**1**).

Least-Squares Planes

Least squares planes description	Abbreviation	Max. deviation/Å	Atom
Thenoyltrifluoroacetylacetonate O4, C13, C14, C15, O5	tta1	0.019	C15
Thenoyltrifluoroacetylacetonate O6, C20, C21, C22, O7	tta2	0.022	C22
Thenoyltrifluoroacetylacetonate O8, C27, C28, C29, O9	tta3	0.010	C28

Interplanar angles /° [a]

	tta1	tta2	tta3
tta1		60.98	24.87
tta2			70.46

[a] Typical uncertainties: 0.5°

Table S4 Bond Distances ($\delta_{\mathrm{Ln},j}$), Bond Valences ($\nu_{\mathrm{Ln},j}$)[a] and Total Atom Valence (V_{Ln})[b] in the Crystal Structure of [Eu(tta)$_3$dig] (**1**).

Atom [c]	Donor type	$\delta_{\mathrm{Ln},j}$ / Å	$\nu_{\mathrm{Ln},j}$	
O2	dig (central)	2.585	0.228	
O1	dig (distal)	2.574	0.235	Average O-dig
O11	dig (distal)	2.578	0.232	0.232(3)
O4	tta	2.416	0.360	
O5	tta	2.373	0.404	
O6	tta	2.384	0.393	Average O-tta
O7	tta	2.395	0.381	0.39(2)
O8	tta	2.387	0.389	
O9	tta	2.367	0.411	
		V_{Ln}	3.034	

[a] $\nu_{\mathrm{Ln},j} = e^{\left[\left(R_{\mathrm{Ln}j}-\delta_{\mathrm{Ln},j}\right)/b\right]}$, whereby $\delta_{\mathrm{Ln},j}$ is the Ln-donor atom j distance. The valence bond parameters $R_{\mathrm{Ln,O}}$ are taken from ref. A1-13f and b = 0.37Å. [b] $V_{\mathrm{Ln}} = \sum_{j} \nu_{\mathrm{Ln},j}$.[A1-13] [c] Numbering taken from Figure S4.

Table S5 Summary of Crystal Data, Intensity Measurements and Structure Refinements for [Y(tta)$_3$dig] (**2**).

Empirical formula	$C_{30}H_{26}F_9O_9S_3Y$	
Formula weight	886.60	
Temperature	180.0(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 10.5124(3) Å	α= 90°.
	b = 18.3614(5) Å	β= 98.264(2)°.
	c = 18.9788(5) Å	γ= 90°.
Volume	3625.30(16) Å^3	
Z	4	
Density (calculated)	1.624 Mg/m^3	
Absorption coefficient	1.877 mm^{-1}	
F(000)	1784	
Crystal size	0.3761 x 0.2202 x 0.1982 mm^3	
Theta range for data collection	4.5 to 58.836°.	
Index ranges	$-14<=h<=14$, $-19<=k<=24$, $-25<=l<=25$	
Reflections collected	21728	
Independent reflections	8819 [R(int) = 0.0293]	
Completeness to theta = 52°	99.9 %	
Absorption correction	Analytical	
Max. and min. transmission	0.946 and 0.917	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8819 / 140 / 542	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2sigma(I)]	$R1$ = 0.0441, w$R2$ = 0.0943	
R indices (all data)	$R1$ = 0.0750, w$R2$ = 0.1078	
Largest diff. peak and hole	0.55 and -0.75 e·Å^{-3}	

Table S6 Selected Bond Distances (Å) and Bond Angles (°) in [Y(tta)$_3$dig] (**2**).

Bond distances /Å

Atoms 1-2	Distance	Atoms 1-2	Distance	Atoms 1-2	Distance
Y-O1	2.490(2)	Y-O4	2.344(2)	Y-O7	2.336(2)
Y-O2	2.407(2)	Y-O5	2.290(2)	Y-O8	2.295(2)
Y-O3	4.926(3)	Y-O6	2.278(2)	Y-O9	2.311(2)

Chelate angles /°

Atoms 1-2-3	Angle	Atoms 1-2-3	Angle
O1-Y-O2	66.18(7)	O6-Y-O7	72.90(6)
O4-Y-O5	72.91(7)	O8-Y-O9	73.43(6)

O-Y-O angles /°

Atoms 1-2-3	Angle	Atoms 1-2-3	Angle	Atoms 1-2-3	Angle
O1-Y-O4	116.19(7)	O1-Y-O6	77.78(7)	O1-Y-O8	140.35(7)
O1-Y-O5	72.36(7)	O1-Y-O7	75.25(7)	O1-Y-O9	144.16(7)
O2-Y-O4	73.76(7)	O2-Y-O6	138.28(7)	O2-Y-O8	149.54(7)
O2-Y-O5	105.14(7)	O2-Y-O7	78.03(7)	O2-Y-O9	86.75(7)

Table S7 Selected Least-Squares Planes Data in [Y(tta)$_3$dig] (**2**).

Least-Squares Planes

Least squares planes description	Abbreviation	Max. deviation/Å	Atom
Thenoyltrifluoroacetylacetonate O4, C16, C22, C23, O5	tta1	0.025	C16
Thenoyltrifluoroacetylacetonate O6, C28, C34, C35, O7	tta2	0.027	C35
Thenoyltrifluoroacetylacetonate O8, C40, C46, C47, O9	tta3	0.042	C40

Interplanar angles /° [a]

	tta1	tta2	tta3
tta1		30.48	44.95
tta2			62.29

[a] Typical uncertainties: 0.5°

Table S8 Bond Distances ($\delta_{\mathrm{Ln},j}$), Bond Valences ($\nu_{\mathrm{Ln},j}$)[a] and Total Atom Valence (V_{Ln})[b] in the Crystal Structure of [Y(tta)$_3$dig] (**2**).

Atom [c]	Donor type	$\delta_{\mathrm{Ln},j}$ / Å	$\nu_{\mathrm{Ln},j}$	
O2	dig (central)	2.407	0.346	Average O-dig
O1	dig (distal)	2.490	0.276	0.31(5)
O4	tta	2.344	0.410	
O5	tta	2.290	0.474	
O6	tta	2.278	0.490	Average O-tta
O7	tta	2.336	0.419	0.45(3)
O8	tta	2.295	0.468	
O9	tta	2.311	0.448	
		V_{Ln}	3.331	

[a] $\nu_{\mathrm{Ln},j} = e^{\left[\left(R_{\mathrm{Ln}j}-\delta_{\mathrm{Ln},j}\right)/b\right]}$, whereby $\delta_{\mathrm{Ln},j}$ is the Ln-donor atom j distance. The valence bond parameters $R_{\mathrm{Ln,O}}$ are taken from ref. A1-13f and b = 0.37Å. [b] $V_{\mathrm{Ln}} = \sum_{j} \nu_{\mathrm{Ln},j}$ .A1-13 [c] Numbering taken from Figure S5.

Table S9 Summary of Crystal Data, Intensity Measurements and Structure Refinements for [Eu(pbta)$_3$dig] (**3**).

Empirical formula	$C_{36}H_{17}EuF_{24}O_9$	
Formula weight	1201.45	
Temperature	180(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 8.38538(15) Å	α= 90°
	b = 27.3868(4) Å	β= 102.2707(17)°
	c = 18.8875(3) Å	γ= 90°
Volume	4238.38(12) Å^3	
Z	4	
Density (calculated)	1.883 Mg/m^3	
Absorption coefficient	12.074 mm^{-1}	
F(000)	2336	
Crystal size	0.2511 x 0.1933 x 0.1062 mm^3	
Theta range for data collection	3.23 to 73.37°.	
Index ranges	$-7<=h<=10$, $-22<=k<=33$, $-23<=l<=22$	
Reflections collected	15468	
Independent reflections	8286 [R(int) = 0.0461]	
Completeness to theta = 67.50°	99.9 %	
Absorption correction	Analytical	
Max. and min. transmission	0.434 and 0.132	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8286 / 0 / 633	
Goodness-of-fit on F^2	1.022	
Final R indices [I>2sigma(I)]	$R1$ = 0.0607, w$R2$ = 0.1575	
R indices (all data)	$R1$ = 0.0700, w$R2$ = 0.1689	
Largest diff. peak and hole	1.379 and -2.293 e·Å^{-3}	

Table S10 Selected Bond Distances (Å) and Bond Angles (°) in [Eu(pbta)$_3$dig] (**3**).

Bond Distances /Å

Atoms 1-2	Distance	Atoms 1-2	Distance	Atoms 1-2	Distance
Eu-O1	2.420(4)	Eu-O4	2.390(4)	Eu-O7	2.519(4)
Eu-O2	2.377(4)	Eu-O5	2.391(4)	Eu-O8	2.543(4)
Eu-O3	2.424(4)	Eu-O6	2.420(4)	Eu-O9	2.550(4)

Chelate Angles /°

Atoms 1-2-3	Angle	Atoms 1-2-3	Angle	Atoms 1-2-3	Angle
O1-Eu-O2	73.10(12)	O3-Eu-O4	69.06(13)	O5-Eu-O6	71.58(14)
O7-Eu-O8	64.08(14)	O7-Eu-O9	126.84(15)	O8-Eu-O9	62.88(14)

O-Eu-O Angles /°

Atoms 1-2-3	Angle	Atoms 1-2-3	Angle	Atoms 1-2-3	Angle
O7-Eu-O1	78.42(13)	O7-Eu-O3	76.16(15)	O7-Eu-O5	74.71(14)
O7-Eu-O2	141.64(14)	O7-Eu-O4	79.38(15)	O7-Eu-O6	139.84(14)
O8-Eu-O1	67.94(13)	O8-Eu-O3	127.86(14)	O8-Eu-O5	65.73(14)
O8-Eu-O2	124.39(13)	O8-Eu-O4	129.27(15)	O8-Eu-O6	118.18(14)
O9-Eu-O1	79.03(13)	O9-Eu-O3	138.42(13)	O9-Eu-O5	87.11(14)
O9-Eu-O2	72.12(14)	O9-Eu-O4	141.10(14)	O9-Eu-O6	72.65(14)

Table S11 Selected Least-Squares Planes Data in [Eu(pbta)$_3$dig] (**3**).

Least-Squares Planes

Least squares planes description	Abbreviation	Max. deviation/Å	Atom
Trifluoroperfluorophenylacetylacetonate O1, C7, C8, C9, O2	pbta1	0.016	C9
Trifluoroperfluorophenylacetylacetonate O3, C17, C18, C19, O4	pbta2	0.015	C17
Trifluoroperfluorophenylacetylacetonate O5, C27, C28, C29, O6	pbta3	0.015	C27

Interplanar angles /° [a]

	pbta1	pbta2	pbta3
pbta1		73.71	16.28
pbta2			77.04

[a] Typical uncertainties: 0.5°

Table S12 Bond Distances ($\delta_{\mathrm{Ln},j}$), Bond Valences ($\nu_{\mathrm{Ln},j}$)[a] and Total Atom Valence (V_{Ln})[b] in the Crystal Structure of [Eu(pbta)$_3$dig] (**3**).

Atom [c]	Donor type	$\delta_{\mathrm{Ln},j}$ / Å	$\nu_{\mathrm{Ln},j}$	
O8	dig (central)	2.543	0.255	
O7	dig (distal)	2.519	0.273	Average O-dig
O9	dig (distal)	2.550	0.251	0.26(1)
O1	pbta	2.420	0.356	
O2	pbta	2.377	0.400	
O3	pbta	2.424	0.352	Average O-pbta
O4	pbta	2.390	0.386	0.37(2)
O5	pbta	2.391	0.385	
O6	pbta	2.420	0.356	
		V_{Ln}	3.015	

[a] $\nu_{\mathrm{Ln},j} = e^{\left[\left(R_{\mathrm{Ln}j}-\delta_{\mathrm{Ln},j}\right)/b\right]}$, whereby $\delta_{\mathrm{Ln},j}$ is the Ln-donor atom j distance. The valence bond parameters $R_{\mathrm{Ln,O}}$ are taken from ref. A1-13f and b = 0.37Å. [b] $V_{\mathrm{Ln}} = \sum_j \nu_{\mathrm{Ln},j}$.[A1-13] [c] Numbering taken from Figure S6.

Table S13 Average Bond Distances (Ln-O_{dig} and Ln-$O_{diketone}$), Average Bond Valences ($\nu_{Ln,Odig}$ and $\nu_{Ln,Odiketone}$)[a] and Total Atom Valence (V_{Ln})[b] in the Molecular Structures of [LnX_3dig] (X= hfa, tta, pbta).

	[Eu(hfa)$_3$dig]	[Eu(tta)$_3$dig]	[Y(tta)$_3$dig]	[Eu(pbta)$_3$dig]
Ln-O_{dig} /Å[c]	2.55(2)	2.579(6)	2.45(6)	2.54(2)
Ln-$O_{diketone}$/Å[d]	2.40(3)	2.39(2)	2.31(3)	2.40(2)
$\nu_{Ln,Odig}$[c]	0.25(1)	0.232(3)	0.31(5)	0.26(1)
$\nu_{Ln,Odiketone}$[d]	0.37(3)	0.39(2)	0.45(3)	0.37(2)
V_{Ln}	2.986	3.034	3.331	3.015

[a] $\nu_{Ln,j} = e^{\left[\left(R_{Ln,j}-\delta_{Ln,j}\right)/b\right]}$, whereby $\delta_{Ln,j}$ is the Ln-donor atom j distance. The valence bond parameters $R_{Ln,O}$ are taken from ref. A1-13f and b = 0.37 Å. [b] $V_{Ln} = \sum_j \nu_{Ln,j}$.[A1-13] [c,d] Each value corresponds to the average of three[c] or six[d] bond distances. The numbers between brackets are the estimated standard deviations associated with the averaging process.

Table S14 ^{1}H NMR Aromatic Chemical Shifts for Complexes (CD_2Cl_2 + 0.14 M dig at 298 K).[a]

	H1	H2	H2'	H3	H3'	H4	H4'	H5	H5'	H6	H7	H8	H13	H14	H-X7[b]	H-X6[b]	H-X5[b]
[Y(pbta)$_3$**L1**]	8.35	-	8.08	-	8.23	-	7.54	-	7.62	7.30	7.30	7.30	-	-	-	-	-
[La(tta)$_3$**L1**]	8.34	-	8.02	-	8.31	-	7.53	-	7.61	7.38	7.26	7.25	-	-	7.38	7.25	6.85
[La(pbta)$_3$**L1**]	8.37	-	8.04	-	8.22	-	7.57	-	7.68	7.41	7.34	7.32	-	-	-	-	-
[Eu(tta)$_3$**L1**]	8.89	-	8.91	-	24.37	-	8.81	-	9.79	10.00	8.36	8.07	-	-	6.86	6.34	6.12
[Eu(pbta)$_3$**L1**]	7.74	-	7.42	-	25.39	-	9.10	-	10.26	10.21	8.38	8.06	-	-	-	-	-
[Eu$_2$(pbta)$_6$**L2**]	8.52	8.39	7.62	24.42	21.32	9.02	8.54	10.42	9.84	10.22	8.50	8.16	10.10	-	-	-	-
[Eu$_2$(pbta)$_6$**L3**]	8.28	8.21	7.04	20.32	25.62	8.98	8.73	10.09	9.76	10.48	8.62	8.24	10.72	7.76	-	-	-
[Eu$_2$(pbta)$_6$**L4**]	7.60	7.28	7.28	24.76	24.76	9.19	9.05	12.67	10.24	10.24	8.45	8.12	10.74	-	-	-	-

[a] Numbering in Figure 6. [b] Hydrogen atoms on the thienyl group.

Table S15 ^{1}H NMR Aliphatic Chemical Shifts for Complexes (CD_2Cl_2 + 0.14 M dig at 298 K).[a]

	H9	H9'	H10	H10'	H11	H11'	H12	H12'	H15	H16	H17	H18	H19	H20	H-X4[b]
[Y(pbta)$_3$**L1**]	-	4.61	-	1.96	-	1.86	-	1.10	-	-	-	-	-	-	5.73
[La(tta)$_3$**L1**]	-	4.54	-	2.01	-	1.88	-	1.09	-	-	-	-	-	-	6.02
[La(pbta)$_3$**L1**]	-	4.57	-	1.97	-	1.85	-	1.08	-	-	-	-	-	-	5.72
[Eu(tta)$_3$**L1**]	-	6.45	-	3.45	-	2.66	-	1.59	-	-	-	-	-	-	1.65
[Eu(pbta)$_3$**L1**]	-	6.11	-	3.11	-	2.35	-	1.35	-	-	-	-	-	-	n.d.
[Eu$_2$(pbta)$_6$**L2**]	6.67	5.79	2.86	2.27	2.75	2.27	1.65	1.32	5.15	2.27	1.87	1.44	1.32	0.80	n.d.
[Eu$_2$(pbta)$_6$**L3**]	6.68	5.43	3.66	2.52	2.71	2.02	1.57	1.13	4.88	2.30	1.93	1.51	1.45	0.96	n.d.
[Eu$_2$(pbta)$_6$**L4**]	6.15	5.93	3.22	3.04	2.28	1.99	1.36	0.89	5.10	2.28	1.73	1.49	1.32	0.84	n.d.

[a] Numbering in Figure 6. [b] Hydrogen atoms on the *β*-diketonate ligand (n.d. = not detected).

Table S16 Conditional Intrinsic Affinity $f_{\mathbf{L1},\mathrm{cond}}^{\mathrm{LnX}_3}$ and Exchange Affinity $f_{\mathbf{L1}}^{\mathrm{LnX}_3} = f_{\mathbf{L1},\mathrm{cond}}^{\mathrm{LnX}_3} \cdot [\mathrm{dig}]_{\mathrm{tot}}$ for the Monomeric Ligand **L1** with [Ln(hfa)$_3$dig], [Ln(tta)$_3$dig] and [Ln(pbta)$_3$dig] (Ln=Y, La, Eu) in CD_2Cl_2 + 0.14 M dig at 298 K.

Metal	*β*-diketonate	$f_{\mathbf{L1},\mathrm{cond}}^{\mathrm{LnX}_3}$	$f_{\mathbf{L1}}^{\mathrm{LnX}_3}$	$\Delta G_{\mathrm{N3},\mathbf{L1}}^{\mathrm{LnX}_3}$ [a] /kJ·mol^{-1}	*AF* [b]	Reference
Y	hfa	981(6)	137.3(8)	-12.2(1)	0.006	15
Y	tta	12(1)	1.7(2)	-1.3(3)	0.112	this work
Y	pbta	1871(160)	262(22)	-13.8(2)	0.086	this work
La	hfa	213(1)	29.9(2)	-8.4(1)	0.006	15
La	tta	36(5)	5.0(7)	-4.0(3)	0.133	this work
La	pbta	343(14)	48(2)	-9.6(1)	0.039	this work
Eu	hfa	1060(9)	149(1)	-12.4(1)	0.008	15
Eu	tta	136(11)	19(2)	-7.3(2)	0.079	this work
Eu	pbta	1589(167)	222(23)	-13.4(3)	0.105	this work

[a] $\Delta G_{\mathrm{N3},\mathbf{L1}}^{\mathrm{LnX}_3} = -RT\ln\left(f_{\mathbf{L1},\mathrm{cond}}^{\mathrm{LnX}_3} \cdot [\mathrm{dig}]_{\mathrm{tot}}\right) = -RT\ln\left(f_{\mathbf{L1}}^{\mathrm{LnX}_3}\right)$.

[b] Agreement factor $AF = \sqrt{\dfrac{\sum\left(\theta_{\mathrm{Ln}}^{\mathrm{exp}} - \theta_{\mathrm{Ln}}^{\mathrm{calcd}}\right)^2}{\sum\left(\theta_{\mathrm{Ln}}^{\mathrm{exp}}\right)^2}}$.

Table S17 Elemental Analyses for [LnX$_3$(**L1**)] Complexes (X= tta, pbta, Ln= La, Eu, Y).

Compound	Formula	%C	%H	%N	%C	%H	%N
			Found			Calculated	
[La(tta)$_3$**L1**]	$C_{65}H_{53}F_9LaN_5O_6S_3$	55.29	3.72	4.79	55.52	3.80	4.98
[La(pbta)$_3$**L1**]	$C_{71}H_{44}F_{24}LaN_5O_6$	51.11	2.59	4.07	51.43	2.67	4.22
[Eu(tta)$_3$**L1**]·0.6 H_2O [a]	$C_{65}H_{54.2}EuF_9N_5O_{6.6}S_3$	54.60	3.81	4.86	54.60	3.82	4.90
[Eu(pbta)$_3$**L1**]	$C_{71}H_{44}EuF_{24}N_5O_6$	50.85	2.76	4.13	51.03	2.65	4.19
[Y(pbta)$_3$**L1**]·2.9 H_2O [a]	$C_{71}H_{49.8}F_{24}N_5O_{8.9}Y$	53.42	3.01	4.04	53.40	2.90	4.04

[a] Presence of water confirmed in proton NMR spectra.

Table S18 Summary of Crystal Data, Intensity Measurements and Structure Refinements for [Eu(pbta)$_3$**L1**]·CH$_2$Cl$_2$ (**4**).

Empirical formula	$C_{72}H_{46}Cl_2EuF_{24}N_5O_6$	
Formula weight	1756.00	
Temperature	180(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 13.7492(4) Å	α= 90°
	b = 20.1925(3) Å	β= 90.402(2)°
	c = 25.8290(6) Å	γ= 90°
Volume	7170.8(3) Å^3	
Z	4	
Density (calculated)	1.627 Mg/m^3	
Absorption coefficient	8.012 mm^{-1}	
F(000)	3496	
Crystal size	0.3581 x 0.0478 x 0.0164 mm^3	
Theta range for data collection	3.422 to 73.664°.	
Index ranges	$-16<=h<=16$, $-24<=k<=14$, $-31<=l<=30$	
Reflections collected	26328	
Independent reflections	14104 [R(int) = 0.0581]	
Completeness to theta = 67.50°	99.9 %	
Absorption correction	Analytical	
Max. and min. transmission	0.885 and 0.307	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14104 / 0 / 966	
Goodness-of-fit on F^2	0.990	
Final R indices [I>2sigma(I)]	$R1$ = 0.0605, w$R2$ = 0.11418	
R indices (all data)	$R1$ = 0.1028, w$R2$ = 0.1576	
Largest diff. peak and hole	1.527 and -1.003 e·Å^{-3}	

Table S19 Selected Bond Distances (Å) and Bond Angles (°) in [Eu(pbta)$_3$**L1**]·CH$_2$Cl$_2$ (**4**).

Bond distances /Å

Atoms 1-2	Distance	Atoms 1-2	Distance	Atoms 1-2	Distance
Eu-O1	2.400(4)	Eu-O4	2.449(4)	Eu-N1	2.567(5)
Eu-O2	2.397(4)	Eu-O5	2.435(4)	Eu-N3	2.642(5)
Eu-O3	2.417(4)	Eu-O6	2.413(4)	Eu-N4	2.611(5)

Chelate angles /°

Atoms 1-2-3	Angle	Atoms 1-2-3	Angle	Atoms 1-2-3	Angle
N1-Eu-N3	63.28(16)	N1-Eu-N4	126.38(17)	N3-Eu-N4	63.12(17)
O1-Eu-O2	71.99(14)	O3-Eu-O4	68.53(14)	O5-Eu-O6	73.04(14)

N-Eu-O angles /°

Atoms 1-2-3	Angle	Atoms 1-2-3	Angle	Atoms 1-2-3	Angle
N3-Eu-O1	119.28(16)	N3-Eu-O2	70.77(13)	N3-Eu-O3	137.30(15)
N3-Eu-O4	124.57(15)	N3-Eu-O5	66.79(14)	N3-Eu-O6	124.19(15)
N1-Eu-O1	142.48(14)	N1-Eu-O2	74.76(15)	N1-Eu-O3	85.96(16)
N1-Eu-O4	75.56(16)	N1-Eu-O5	77.62(14)	N1-Eu-O6	140.77(15)
N4-Eu-O1	70.17(15)	N4-Eu-O2	89.11(15)	N4-Eu-O3	137.97(15)
N4-Eu-O4	138.43(15)	N4-Eu-O5	80.82(15)	N4-Eu-O6	73.81(16)

Table S20 Selected Least-Squares Planes Data in [Eu(pbta)$_3$**L1**]·CH$_2$Cl$_2$ (**4**).

Least-squares planes

Least squares planes description	Abbreviation	Max. deviation/Å	Atom
Pyridine N3, C19, C20, C21, C22, C23	py	0.021	N3
Benzimidazole C24, N5, C30, C31, C32, C33, C34, C35, N4	bz1	0.021	C33
Benzimidazole C13, N2, C10, C9, C8, C7, C12, C11, N1	bz2	0.035	C8
Trifluoroperfluorophenylacetylacetonate O1, C42, C43, C44, O2	pbta1	0.033	C42
Trifluoroperfluorophenylacetylacetonate O3, C52, C53, C54, O4	pbta2	0.003	C52/C53
Trifluoroperfluorophenylacetylacetonate O5, C62, C63, C64, O6	pbta3	0.020	C64

Interplanar angles /° [a]

	bz2	py	pbta1	pbta2	pbta3
bz1	19.59	29.97	76.13	69.31	79.90
bz2		26.14	89.39	87.83	83.44
py			75.22	76.61	73.77
pbta1				60.57	11.62
pbta2					51.18

[a] Typical uncertainties: 0.5°

Table S21 Bond Distances ($\delta_{\mathrm{Ln},j}$), Bond Valences ($\nu_{\mathrm{Ln},j}$)[a] and Total Atom Valence (V_{Ln})[b] in the Crystal Structure of [Eu(pbta)$_3$**L1**]·CH_2Cl_2 (**4**).

Atom [c]	Donor type	$\delta_{\mathrm{Ln},j}$ / Å	$\nu_{\mathrm{Ln},j}$	
O1	pbta	2.400	0.376	
O2	pbta	2.397	0.379	
O3	pbta	2.417	0.359	
O4	pbta	2.449	0.329	
O5	pbta	2.435	0.342	Average O-hfa
O6	pbta	2.413	0.363	0.36(2)
N3	py (central)	2.642	0.273	
N1	bzim (distal)	2.567	0.334	Average N-heterocyclic
N4	bzim (distal)	2.611	0.296	0.30(3)
		V_{Ln}	3.051	

[a] $\nu_{\mathrm{Ln},j} = e^{\left[\left(R_{\mathrm{Ln}j} - \delta_{\mathrm{Ln},j}\right)/b\right]}$, whereby $\delta_{\mathrm{Ln},j}$ is the Ln-donor atom j distance. The valence bond parameters $R_{\mathrm{Ln,O}}$ are taken from ref. A1-13f and b = 0.37Å. [b] $V_{\mathrm{Ln}} = \sum_j \nu_{\mathrm{Ln},j}$.[A1-13] [c] Numbering taken from Figure S9.

Table S22 Average Bond Distances with Nitrogen Donor Atoms (Ln-N$_{bzim}$ and Ln-N$_{py}$) and Oxygen Donor Atoms (Ln-O), Average Bond Valences ($\nu_{Ln,N(bzim)}$, $\nu_{Ln,N(py)}$ and $\nu_{Ln,O}$)[a] and Total Atom Valence (V_{Ln})[b] in the Molecular Structures of [Ln(X)$_3$**L1**].

	[La(hfa)$_3$**L1**]	[Eu(pbta)$_3$**L1**]
Ln-N$_{bzim}$ /Å[c]	2.670(6)	2.59(3)
Ln-N$_{py}$ /Å	2.767	2.642
Ln-O /Å[d]	2.51(3)	2.42(2)
$\nu_{Ln,N(bzim)}$[c]	0.331(5)	0.32(3)
$\nu_{Ln,N(py)}$	0.255	0.273
$\nu_{Ln,O}$[d]	0.38(3)	0.36(2)
V_{Ln}	3.18	3.05

[a] $\nu_{Ln,j} = e^{\left[\left(R_{Ln,j}-\delta_{Ln,j}\right)/b\right]}$, whereby $\delta_{Ln,j}$ is the Ln-donor atom j distance. The valence bond parameters $R_{Ln,O}$ are taken from ref. A1-13f and b = 0.37 Å. [b] $V_{Ln} = \sum_j \nu_{Ln,j}$.[A1-13] [c,d] Each value corresponds to the average of two[c] or six[d] bond distances. The numbers between brackets are the estimated standard deviations associated with the averaging process.

Table S23 Conditional Intrinsic Affinity $f_{\mathbf{L}\boldsymbol{k},\mathrm{cond}}^{\mathrm{EuX_3}}$, Exchange Affinity $f_{\mathbf{L}\boldsymbol{k}}^{\mathrm{EuX_3}} = f_{\mathbf{L}\boldsymbol{k},\mathrm{cond}}^{\mathrm{EuX_3}} \cdot \left[\mathrm{dig}\right]_{\mathrm{tot}}$ and Cooperativity Factors $u_{1-2}^{\mathrm{EuX_3,EuX_3}}$ for the Ligands **L2-L4** with [Eu(hfa)$_3$dig] and [Eu(pbta)$_3$dig] in CD_2Cl_2 + 0.14 M dig at 298 K.

L*k*	X	$f_{\mathbf{L}\boldsymbol{k},\mathrm{cond}}^{\mathrm{EuX_3}}$	$f_{\mathbf{L}\boldsymbol{k}}^{\mathrm{EuX_3}}$	$\Delta G_{\mathrm{N3},\mathbf{L}\boldsymbol{k}}^{\mathrm{EuX_3}}$ /kJ·mol^{-1} [a]	$u_{1-2}^{\mathrm{EuX_3,EuX_3}}$	$\Delta E_{\mathbf{L}\boldsymbol{k}}^{\mathrm{EuX_3,EuX_3}}$ /kJ·mol^{-1} [b]	AF [c]	Ref
L2	hfa	373(7)	52(1)	-9.80(5)	1.7(1)	-1.3(1)	0.020	17
L2	pbta	433(8)	61(1)	-10.17(5)	1.14(6)	-0.3(1)	0.019	This work
L3	hfa	470(10)	66(1)	-10.37(5)	0.61(4)	1.2(2)	0.020	17
L3	pbta	943(28)	132(4)	-12.10(7)	0.17(1)	4.4(2)	0.029	This work
L4	hfa	659(33)	92(5)	-11.2(1)	2.40(36)	-2.2(4)	0.050	17
L4	pbta	1363(83)	191(12)	-13.0(2)	2.06(38)	-1.8(5)	0.061	This work

[a] $\Delta G_{\mathrm{N3},\mathbf{L}\boldsymbol{k}}^{\mathrm{EuX_3}} = -RT\ln\left(f_{\mathbf{L}\boldsymbol{k},\mathrm{cond}}^{\mathrm{EuX_3}} \cdot \left[\mathrm{dig}\right]_{\mathrm{tot}}\right) = -RT\ln\left(f_{\mathbf{L1}}^{\mathrm{EuX_3}}\right)$. [b] $\Delta E_{\mathbf{L}\boldsymbol{k}}^{\mathrm{EuX_3,EuX_3}} = -RT\ln\left(u_{\mathbf{L}\boldsymbol{k}}^{\mathrm{EuX_3,EuX_3}}\right)$.

[c] Agreement factor $AF = \sqrt{\dfrac{\sum\left(\theta_{\mathrm{Ln}}^{\mathrm{exp}} - \theta_{\mathrm{Ln}}^{\mathrm{calcd}}\right)^2}{\sum\left(\theta_{\mathrm{Ln}}^{\mathrm{exp}}\right)^2}}$.

Table S24 Europium-Centered Emission Lifetimes $\tau_{\text{exp}}^{\text{Eu}}$ and Global Quantum Yields $\Phi_{\text{Eu}}^{\text{L}}$ Recorded for Mononuclear [EuX$_3$dig], [EuX$_3$**L1**] (X= hfa, tta, tfpfac) and Dimeric [Eu$_2$(hfa)$_6$**L*k***] (**L*k*** = **L2**-**L4**) Complexes in Solution (CH$_2$Cl$_2$ + 10^{-6} M dig) and in the Solid State at 293 K.

Compounds		$\tilde{\nu}_{\text{exc}}$ /cm^{-1}	$\varepsilon\left(\tilde{\nu}_{\text{exc}}\right)$ /M^{-1}cm^{-1}	$\tau_{\text{exp}}^{\text{Eu}}$ /ms [a]	$\Phi_{\text{Eu}}^{\text{L}}$ /%
[Eu(hfa)$_3$dig]	Solution	29850	$1.15\cdot10^4$	n.d.	5(1)
[Eu(tta)$_3$dig]	Solution	28570	$5.47\cdot10^4$	n.d.	4(2)
[Eu(pbta)$_3$dig]	Solution	29850	$3.12\cdot10^4$	n.d.	3(1)
[Eu(hfa)$_3$**L1**]	Solution	25840	$1.70\cdot10^4$	n.d.	45(1) [b]
[Eu(tta)$_3$**L1**]	Solution	25000	$1.65\cdot10^3$	n.d.	22(5) [b]
[Eu(pbta)$_3$**L1**]	Solution	25970	$1.77\cdot10^4$	n.d.	35(6) [b]
[Eu(hfa)$_3$dig]	Solid	29850	-	0.927(5)	7.5(2)
[Eu(tta)$_3$dig]	Solid	28570	-	0.341(3)	4.5(1)
[Eu(pbta)$_3$dig]	Solid	29850	-	0.645(2)	9.4(3)
[Eu(hfa)$_3$**L1**]	Solid	29850	-	0.878(1)	30.5(9)
	Solid	25970	-	n.d.	30.5(7)
[Eu(tta)$_3$**L1**]	Solid	28570	-	0.531(6)	24.5(7)
	Solid	25970	-	n.d.	41(1)
[Eu(pbta)$_3$**L1**]	Solid	29850	-	0.67(2)	12.4(1)
		25970	-	n.d.	23.2(7)
[Eu$_2$(hfa)$_6$**L2**]	Solid	29850	-	0.79(1)	3.2(1)
		25970	-	n.d.	2.5(1)
[Eu$_2$(hfa)$_6$**L3**]	Solid	29850	-	0.79(1)	4.7(1)
		25970	-	n.d.	4.58(6)
[Eu$_2$(hfa)$_6$**L4**]	Solid	29850	-	0.65(2)	2.1(1)
		25970	-		1.48(6)

[a] The lifetimes are mainly mono-exponential. A second faster decay component, the contributions of which never exceeds 8% of the total measured intensity can be obtained by bi-exponential analysis and has been considered to be negligible. [b] Using $\tilde{\nu}_{\text{exc}} < 26000$ cm^{-1}, any contribution from [EuX$_3$dig] to the emission spectrum is considered as negligible and the quantum yield was only corrected for changes in absorption resulting from partial dissociation of the complexes (see Appendix 2).

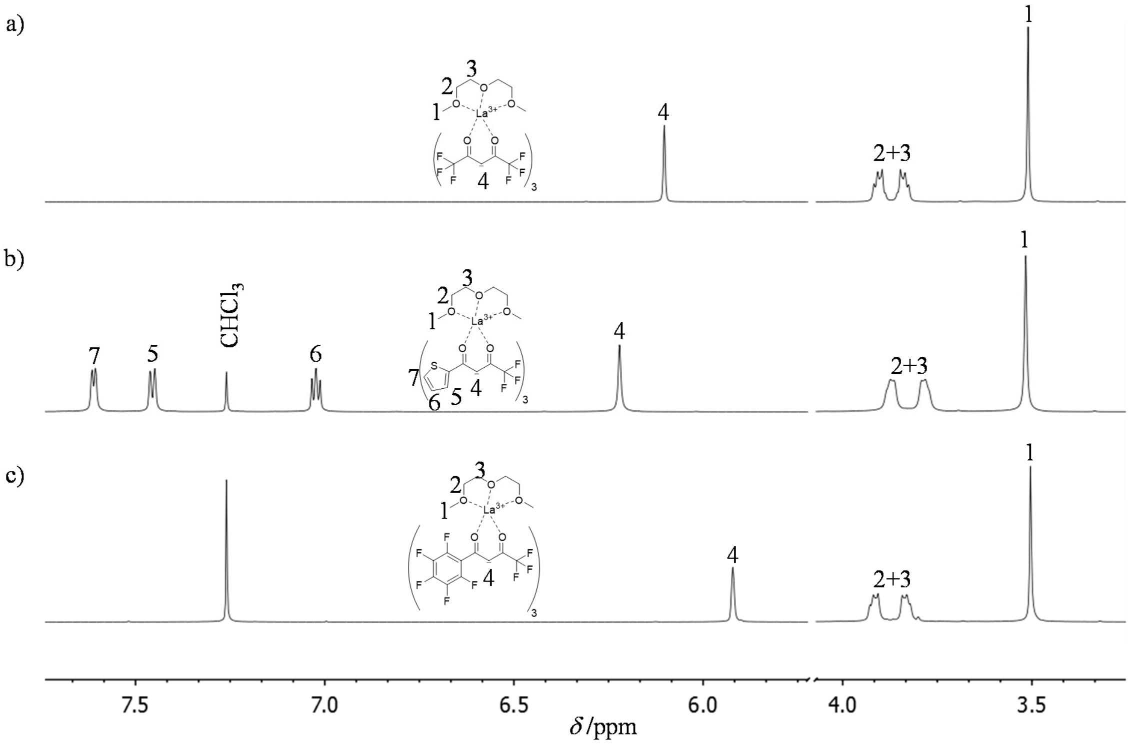

Fig. S1 ^{1}H NMR spectra of lanthanum containers a) [La(hfa)$_3$dig], b) [La(tta)$_3$dig], c) [La(pbta)$_3$dig] with numbering scheme (CDCl$_3$, 298K).

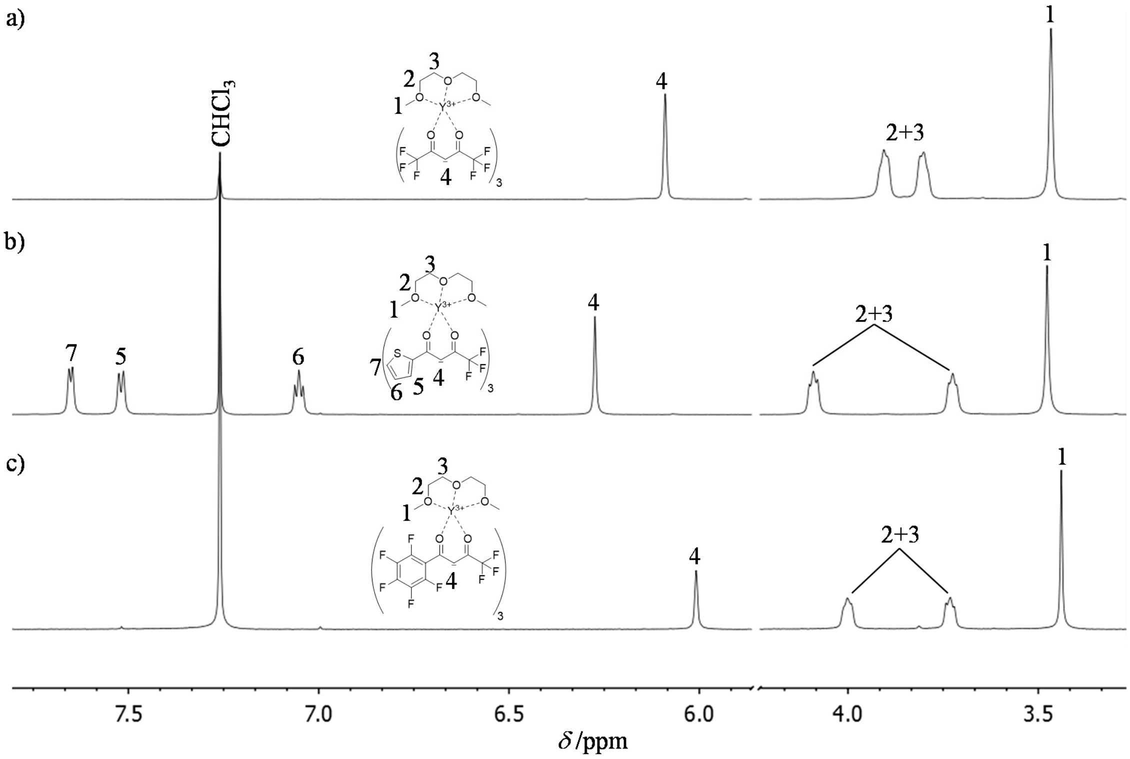

Fig. S2 ^{1}H NMR spectra of yttrium containers a) [Y(hfa)$_3$dig], b) [Y(tta)$_3$dig], c) [Y(pbta)$_3$dig] with numbering scheme (CDCl$_3$, 298K).

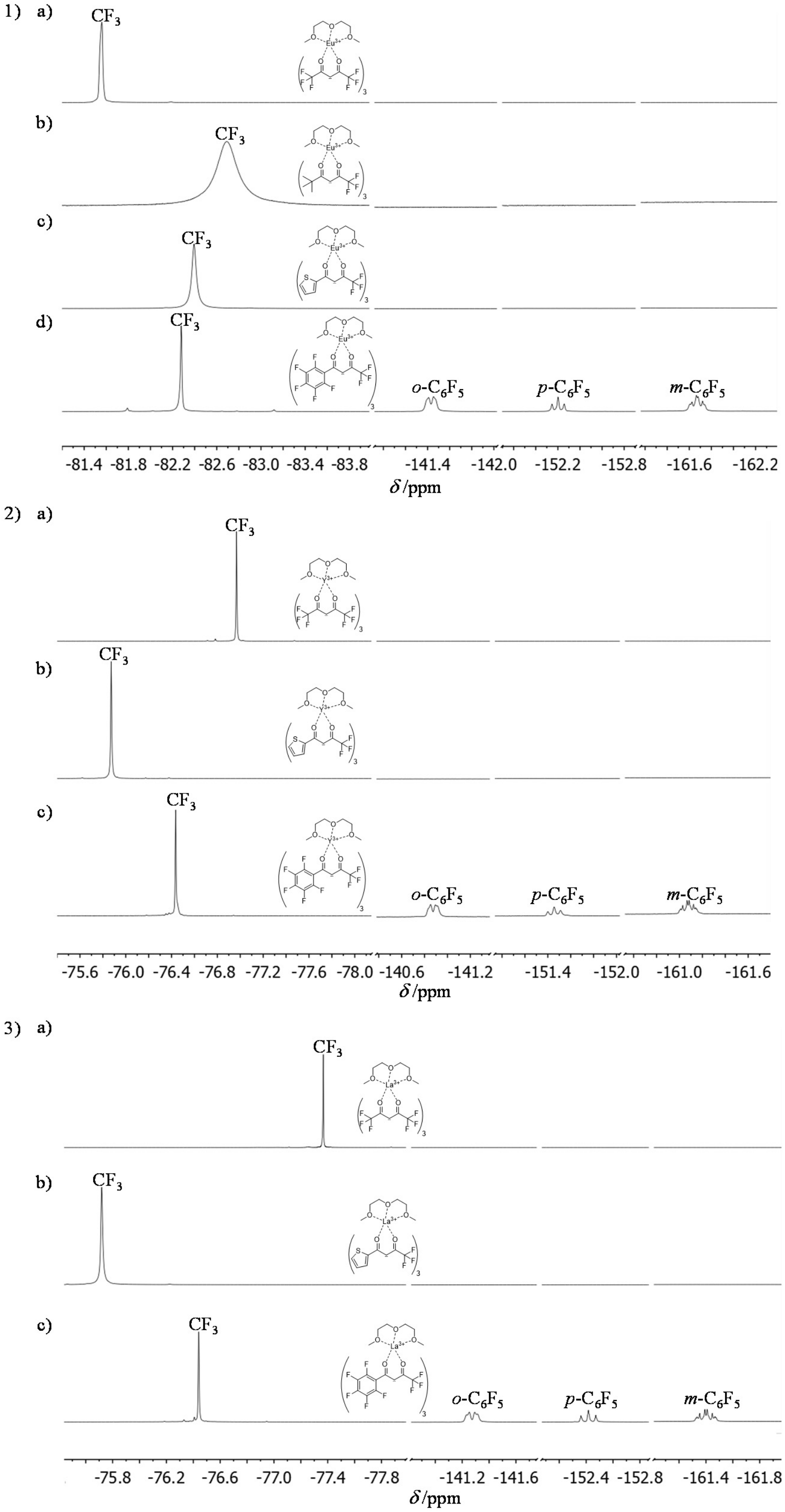

Fig. S3 ^{19}F NMR spectra of 1) europium containers a) [Eu(hfa)$_3$dig], b) [Eu(pta)$_3$dig], c) [Eu(tta)$_3$dig] and d) [Eu(pbta)$_3$dig], of 2) yttrium containers a) [Y(hfa)$_3$dig], b) [Y(tta)$_3$dig], c) [Y(pbta)$_3$dig] and of 3) lanthanum containers a) [La(hfa)$_3$dig], b) [La(tta)$_3$dig], c) [La(pbta)$_3$dig] (CDCl$_3$, 298K).

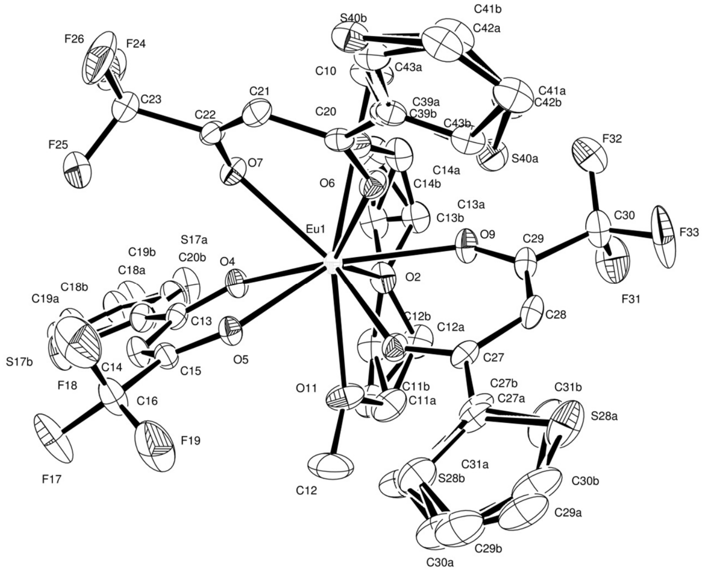

Fig. S4 ORTEP molecular view of [Eu(tta)$_3$dig] in the crystal structure of **1** and numbering scheme (thermal ellipsoids are drawn at 40% probability level). Hydrogen atoms are omitted for clarity.

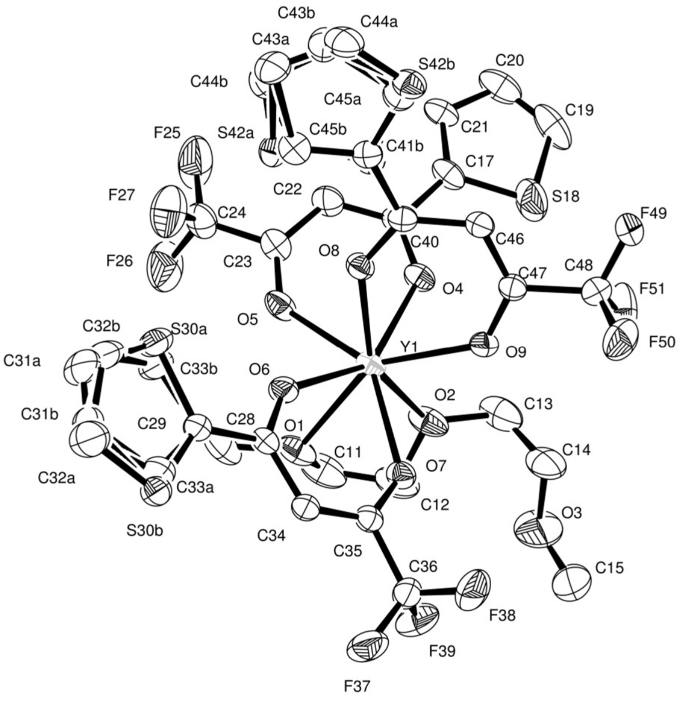

Fig. S5 ORTEP molecular view of [Y(tta)$_3$dig] in the crystal structure of **2** and numbering scheme (thermal ellipsoids are drawn at 40% probability level). Hydrogen atoms are omitted for clarity.

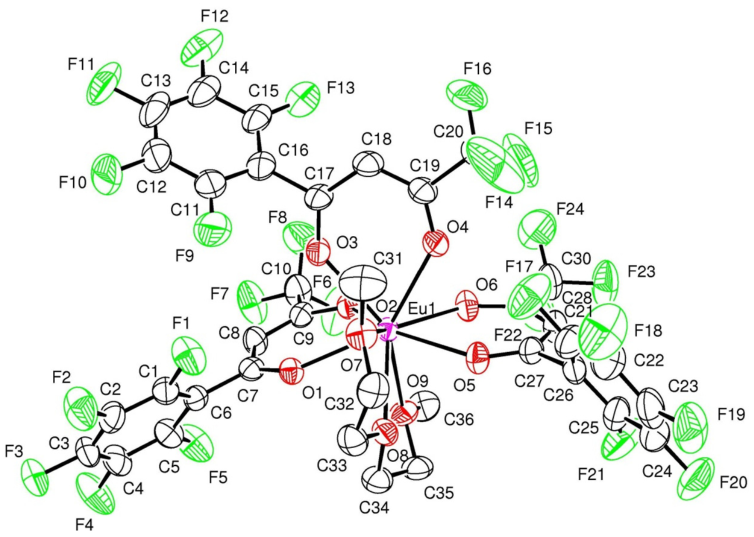

Fig. S6 ORTEP molecular view of [Eu(pbta)$_3$dig] in the crystal structure of **3** and numbering scheme (thermal ellipsoids are drawn at 30% probability level). Hydrogen atoms are omitted for clarity.

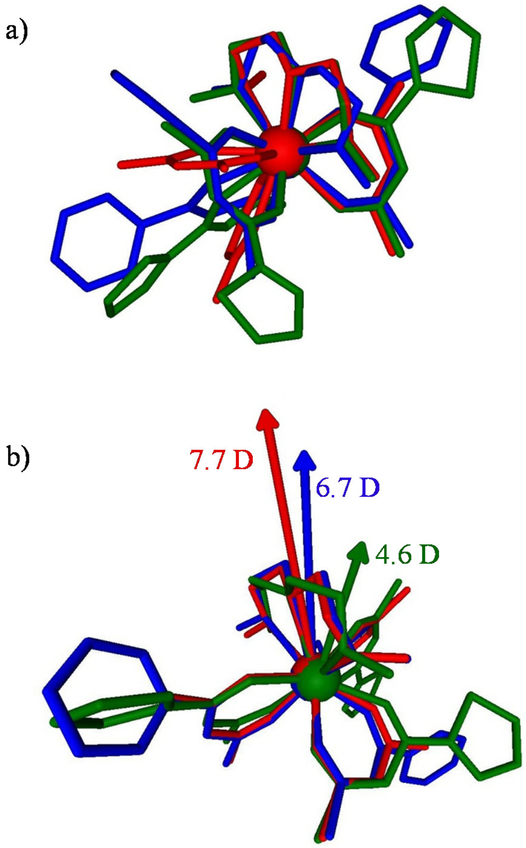

Fig. S7 Superimposition of the molecular structures of [Eu(hfa)$_3$dig] (red),[25] [Eu(pbta)$_3$dig] (blue) and [Eu(tta)$_3$dig] (green) (a) in their X-ray crystal structures and (b) in their DFT-optimised gas-phase structures with associated dipole moments in Debyes (1 D = 3.335 64×10^{-30} C·m). The hydrogen and fluorine atoms are omitted for clarity. Dipole moments were computed with DFT/B-97D/def2-TZVP using Turbomole v6.6.

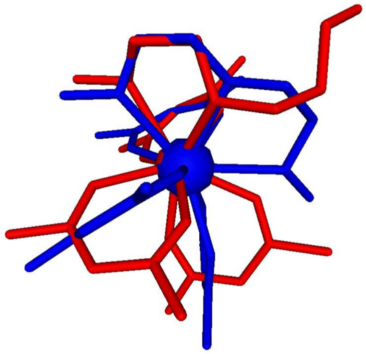

Fig. S8 Superimposition of the molecular structures of [Eu(tta)$_3$dig] (blue) and [Y(tta)$_3$dig] (red) in their X-ray crystal structures. The hydrogen atoms and substituents groups on the *β*-diketonates are omitted for clarity.

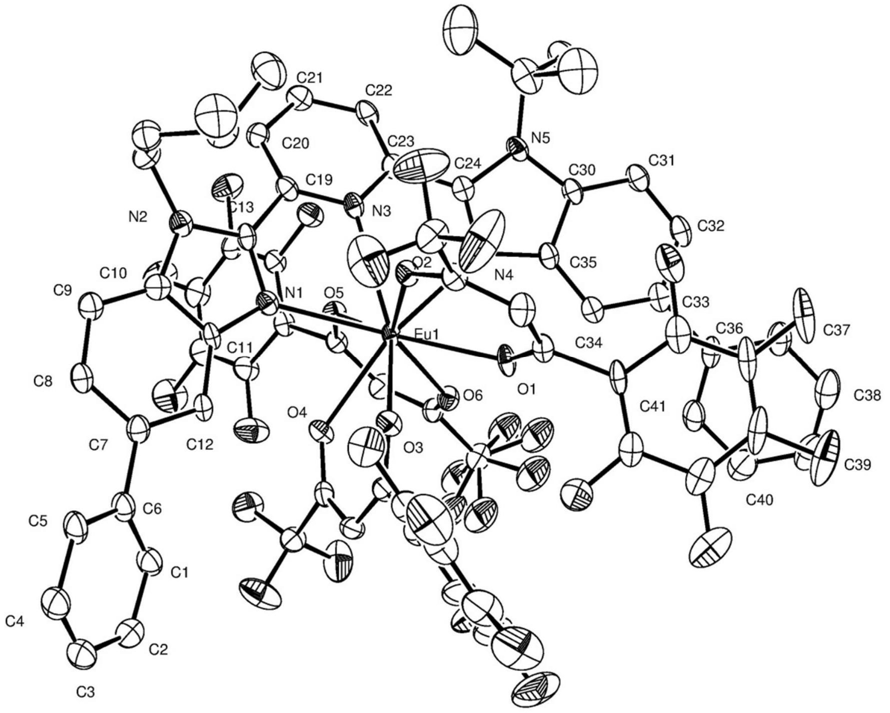

Fig. S9 ORTEP molecular view of [Eu(pbta)$_3$**L1**] in the crystal structure and numbering scheme (thermal ellipsoids are drawn at 30% probability level). Hydrogen atoms are omitted for clarity.

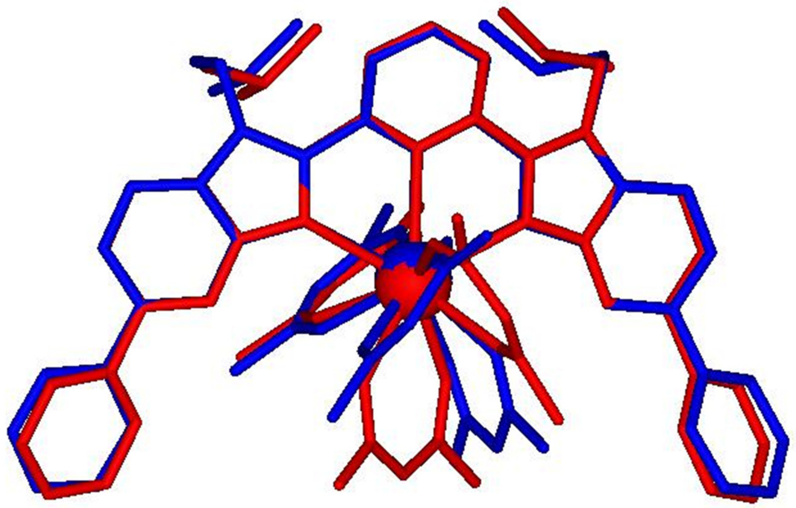

Fig. S10 Superimposition of the molecular structures of [La(hfa)$_3$**L1**] (red)[15a] and [Eu(pbta)$_3$**L1**] (blue). Fluorine (hfa + pbta) and perfluorobenzene (pbta) have been omitted for clarity.

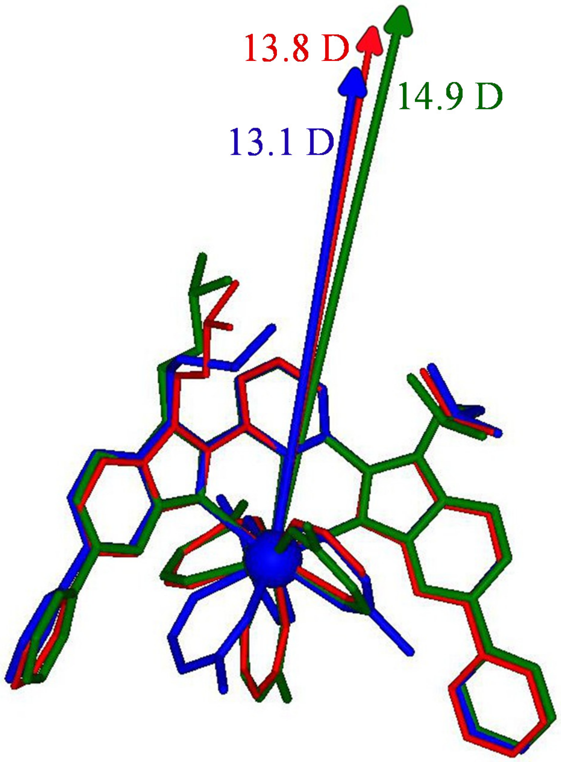

Fig. S11 Superimposition of the molecular structures of [Y(hfa)$_3$**L1**] (red), [Y(pbta)$_3$**L1**] (blue) and [Y(tta)$_3$**L1**] (green) in the DFT-optimised gas-phase structures with associated dipole moments. The hydrogen and fluorine atoms are omitted for clarity. Dipole moments were computed with DFT/B-97D/def2-TZVP using Turbomole v6.6.

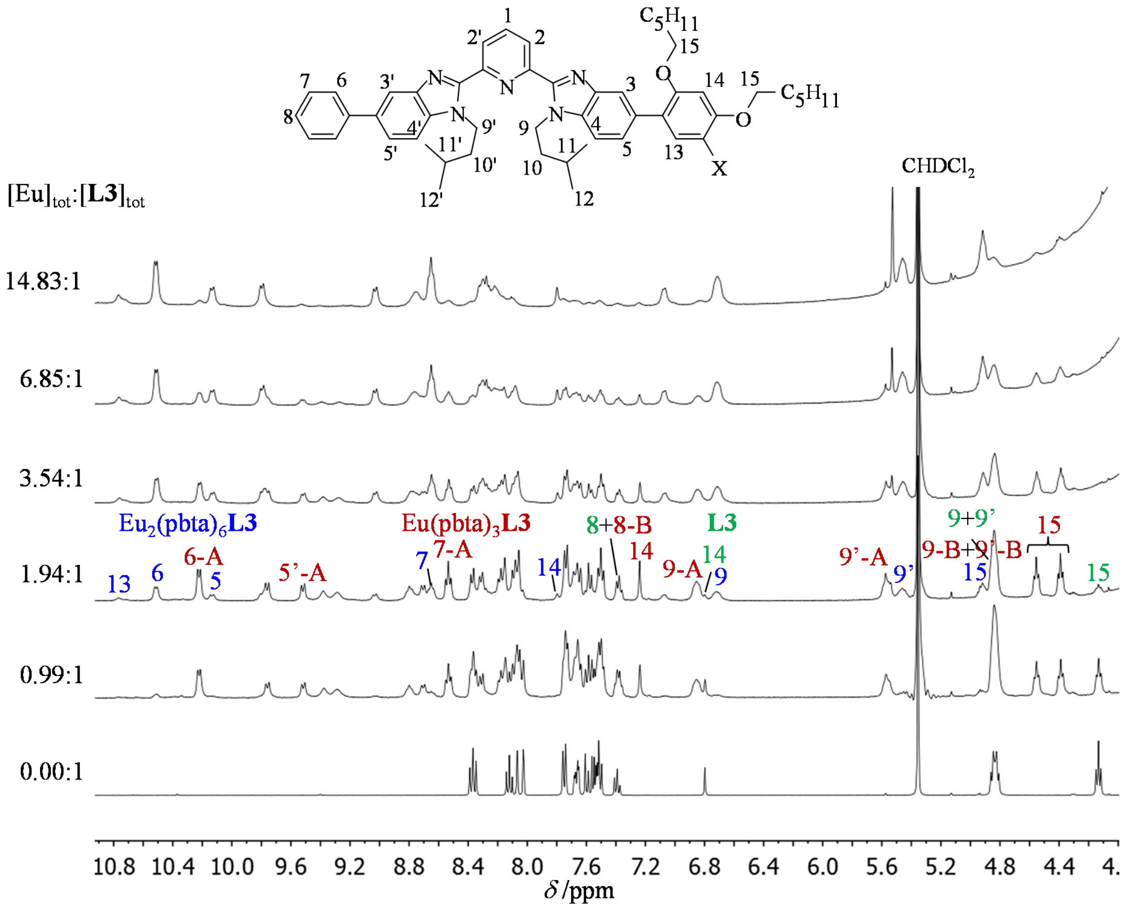

Fig. S12 ^{1}H NMR titration of **L3** (5 mM) with [Eu(pbta)$_3$dig] in CD$_2$Cl$_2$ + 0.14 M diglyme at 298 K. Partial assignment for the free ligand (**L3**, green), for the mononuclear complex [Eu(pbta)$_3$**L3**] (red: A stands for the occupied tridentate binding unit and B for the free site) and for the dinuclear complex [Eu$_2$(pbta)$_6$**L3**] (blue).

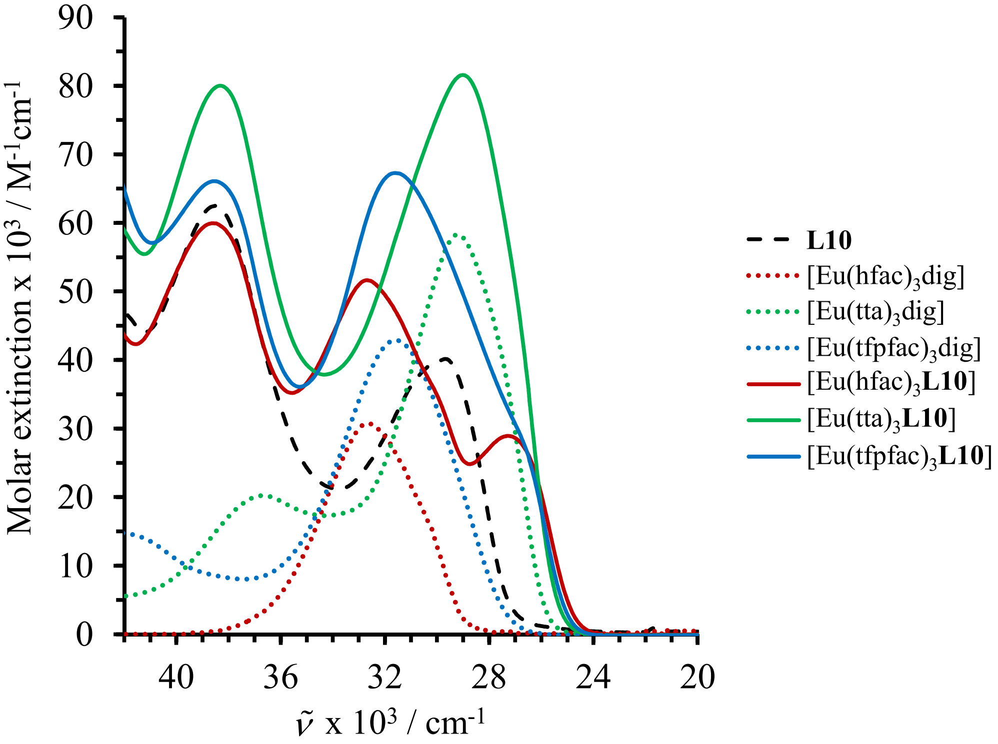

Fig. S13 Electronic absorption spectra recorded for [EuX$_3$dig] (dotted traces), [EuX$_3$**L1**] (full traces) complexes and free ligand **L1** (dashed trace) with X= hfa (red), X = tta (green) and X = pbta (blue) in CH_2Cl_2 + 10^{-6} M diglyme at 293 K. The absorption spectra were recorded for $[Eu]_{tot}$ = 10^{-5} M and corrected for partial dissociation in solution (Appendix 2).

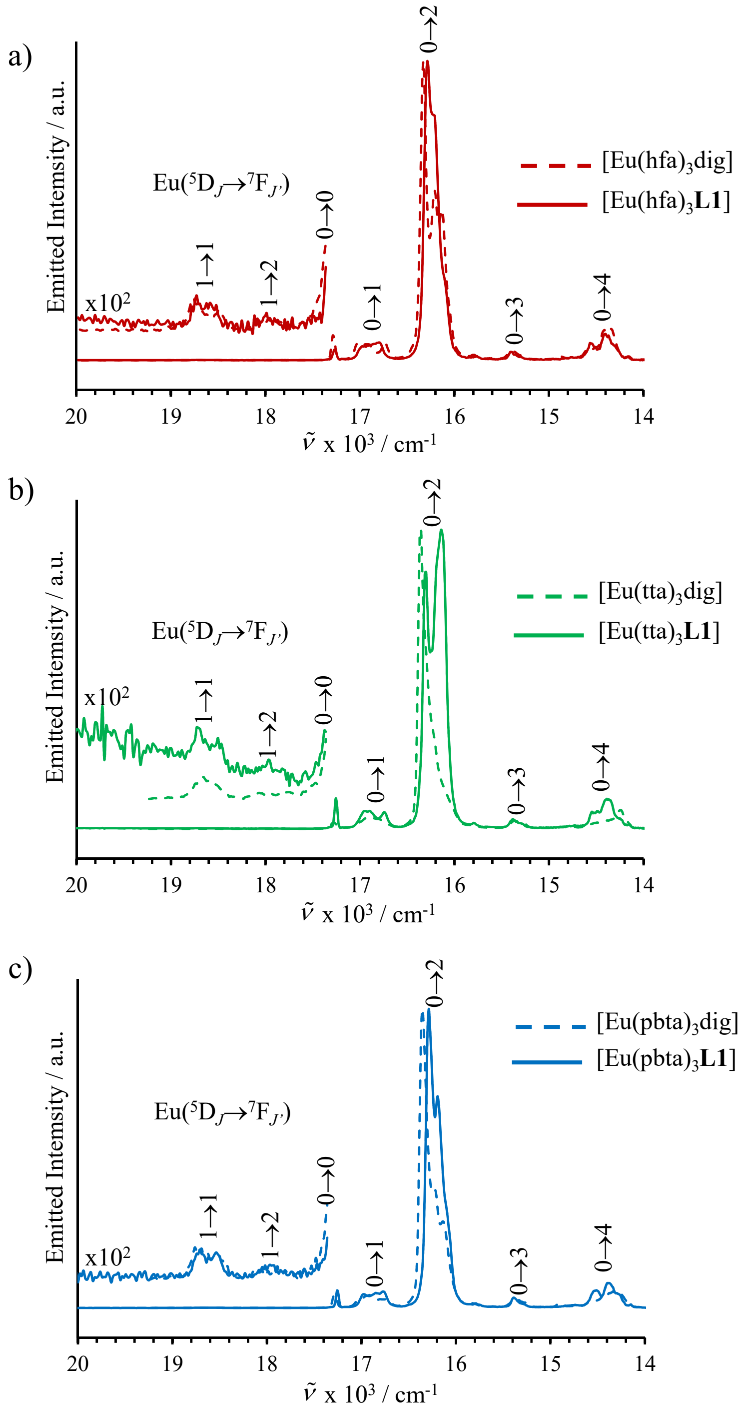

Fig. S14 Emission spectra recorded for a) [Eu(hfa)$_3$dig] ($\tilde{\nu}_{\mathrm{exc}}$ = 29850 cm^{-1}, [Eu]$_{\mathrm{tot}}$ = 8.6·10^{-5} M, dashed trace) and [Eu(hfa)$_3$**L1**] ($\tilde{\nu}_{\mathrm{exc}}$ = 25840 cm^{-1}, [Eu]$_{\mathrm{tot}}$ = 4.0·10^{-5} M, full trace),[15a] b) for [Eu(tta)$_3$dig] ($\tilde{\nu}_{\mathrm{exc}}$ = 28570 cm^{-1}, [Eu]$_{\mathrm{tot}}$ = 1.8·10^{-5} M, dashed trace) and [Eu(tta)$_3$**L1**] ($\tilde{\nu}_{\mathrm{exc}}$ = 25000 cm^{-1}, [Eu]$_{\mathrm{tot}}$ = 5.5·10^{-4} M, full trace) and c) for [Eu(pbta)$_3$dig] ($\tilde{\nu}_{\mathrm{exc}}$ = 29850 cm^{-1}, [Eu]$_{\mathrm{tot}}$ = 3.3·10^{-5} M, dashed trace) and [Eu(pbta)$_3$**L1**] ($\tilde{\nu}_{\mathrm{exc}}$ = 25970 cm^{-1}, [Eu]$_{\mathrm{tot}}$ = 6.1·10^{-5} M, full trace) in CH_2Cl_2 + 10^{-6} M diglyme at 293 K.

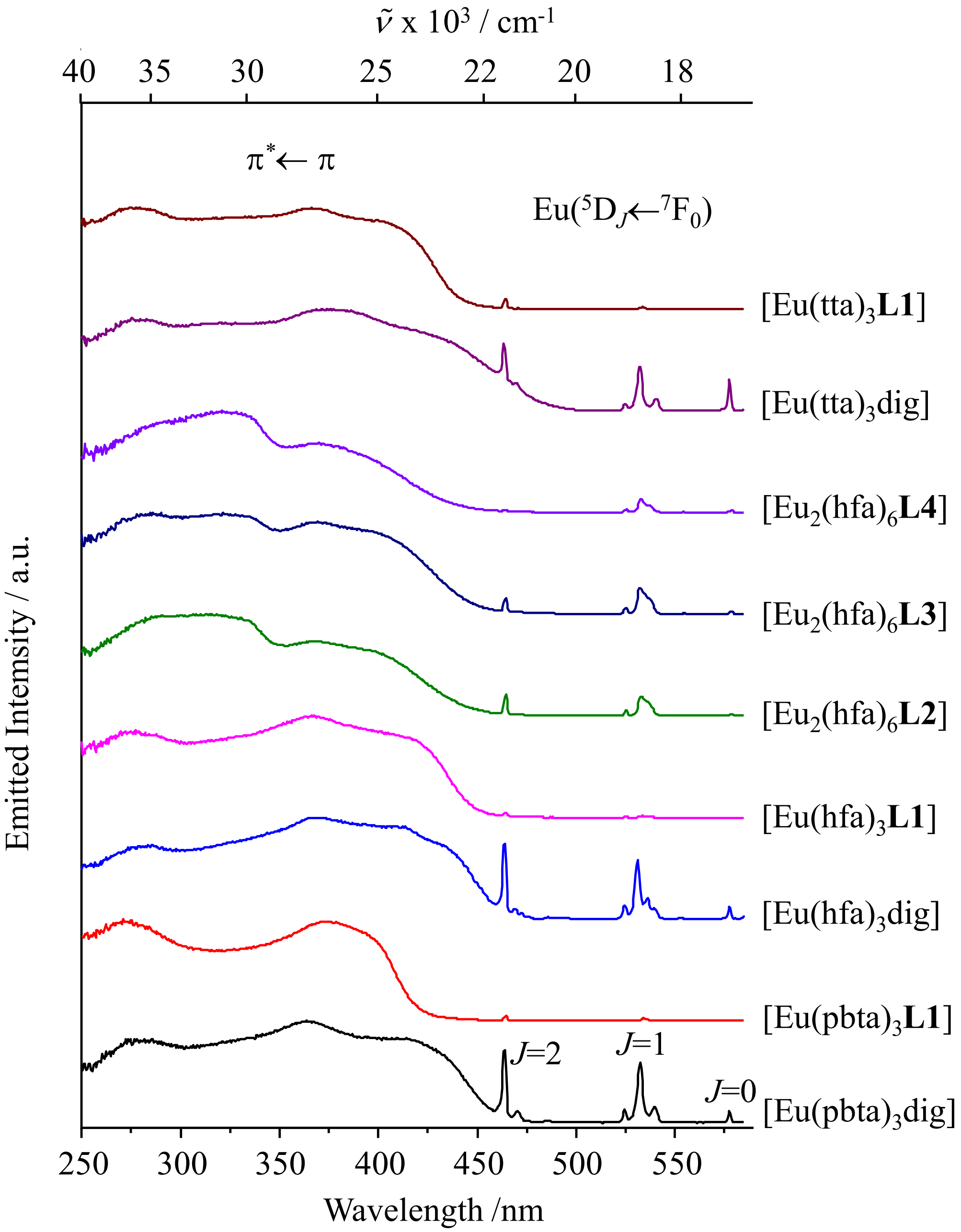

Fig. S15 Excitation spectra recorded for [EuX$_3$dig] and [EuX$_3$**L1**] in the solid state (X= hfa, tta, pbta) using λ_{an} = 613-620 nm ($^5D_0 \rightarrow ^7F_2$) at 293 K.

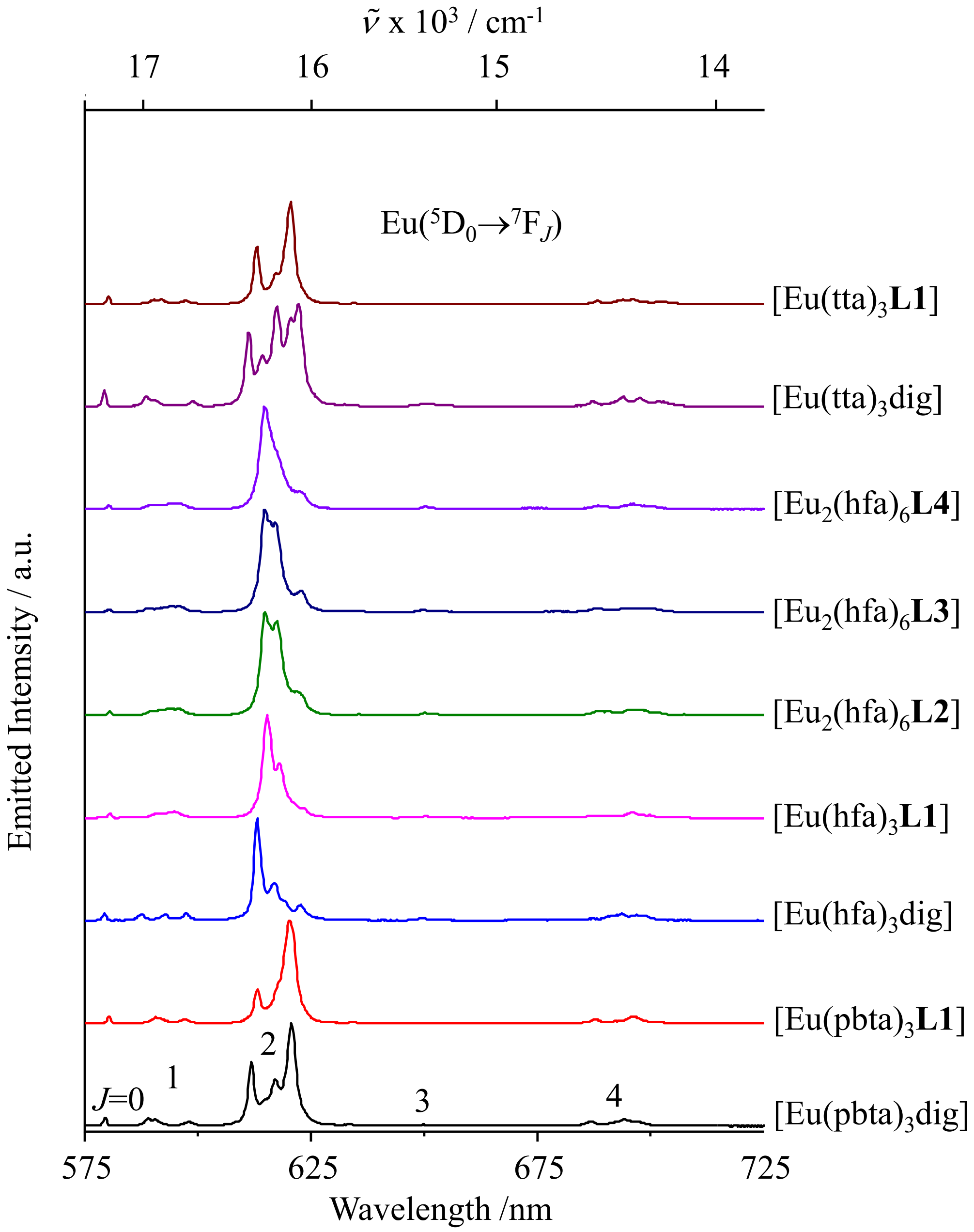

Fig. S16 Emission spectra recorded for [EuX$_3$dig] and [EuX$_3$**L1**] in the solid state using λ_{exc} = 335 nm for X= hfa, pbta and λ_{exc} = 350 nm for X = tta (293 K).