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

The intramolecular interactions produced by the loading of
neighbouring binding sites with neutral lanthanide complexes can
be judiciously exploited for the selective organization of optically
active metals in organic polymers. As in a group of climbers, the
nature of the intersite correlation (i.e. the rope) decides which
thermodynamic trajectory (i.e. the trace) can be followed to
reach the summit of cooperativity, a situation illustrated in the
associated cover picture for unsymmetrical lanthanide containers.

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

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Metal-containing (bio)organic polymers are materials of continuously increasing importance for applications in energy storage and conversion, drug delivery, shape-memory items, supported catalysts, organic conductors and smart photonic devices. The embodiment of luminescent components provides a revolution in lighting and signaling with the ever-increasing development of polymeric light-emitting devices. Despite the unique properties expected from the introduction of optically and magnetically active lanthanides into organic polymers, the deficient control of the metal loading currently limits their design to empirical and poorly reproducible materials. We show here that the synthetic efforts required for producing soluble multi-site host systems **Lk** are largely overcome by the virtue of reversible thermodynamics for mastering the metal loading with the help of only two parameters: (1) the affinity of the luminescent lanthanide container for a single binding site and (2) the cooperative effect which modulates the successive fixation of metallic units to adjacent sites. When unsymmetrical perfluorobenzene-trifluoroacetylacetonate co-ligands (pbta[−]) are selected for balancing the charge of the trivalent lanthanide cations, Ln³⁺, in six-coordinate [Ln(pbta)₃] containers, the explored anti-cooperative complexation processes induce nearest-neighbor intermetallic interactions $\Delta E_{\text{Lk}}^{\text{Ln(pbta)}_3, \text{Ln(pbta)}_3}$ twice as large as thermal energy at room temperature ($RT = 2.5 \text{ kJ mol}^{-1}$). These values have no precedent when using standard symmetrical containers and they pave the way for programming metal alternation in luminescent lanthanidopolymers.

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Introduction

Metal-containing (bio)organic polymers are of the utmost importance in actual daily life and have found a wealth of applications in tailor-made materials for energy storage and energy conversion,¹ drug delivery,² shape-memory systems,³ supported catalysts and organic conductors,⁴ smart photonic devices,⁵ and modern light-emitting diodes.⁶ In the absence of metal, rationalization of the organization of (bio)organic (co) polymers relies on micro-segregation events described by the Huggins–Flory theory of phase demixing,⁷ a model which has been recently extended for the programming of thermotropic liquid crystals.⁸ The introduction of open-shell transition metals within the polymeric backbone results in novel optical and magnetic properties that are not available in pure organic

polymers.^{1–5} However, the multifaceted (supra)molecular interactions operating between the polymeric backbone and the metal are at the origin of major difficulties in mastering the formation of metallopolymer with respect to stability, organization, processability and reproducibility. These limitations are even amplified for lanthanidopolymers (*i.e.* lanthanide-containing polymers) because of the versatile coordination behavior of these metallic centers.⁵ In order to avoid this pitfall, coordination chemists have restricted the concept of metallopolymer to infinite crystalline assemblies made of anionic ligand strands and cationic nodes forming extended 3D-networks, originally referred to as Wolf-type III metallopolymer⁴ or coordination polymers,⁹ and nowadays often named metal–organic frameworks (MOFs).¹⁰ These infinite assemblies resemble ionic solids in their essence and lead to robust and inert scaffolds possessing variable porosities. When trivalent emissive lanthanides occupy some nodes of the network, the associated luminescence can be tuned by metal doping¹¹ or by external stimuli such as temperature jumps or mechanical stress.¹² However, the production of solvent-resistant lanthanidopolymers compatible with partial metal occupancy, specific organization, flexible shaping and adaptable sensing properties is not yet available. Current efforts exploit the empirical mixing of polymeric organic receptors with metallic salts, from which non-soluble adducts are isolated. Their

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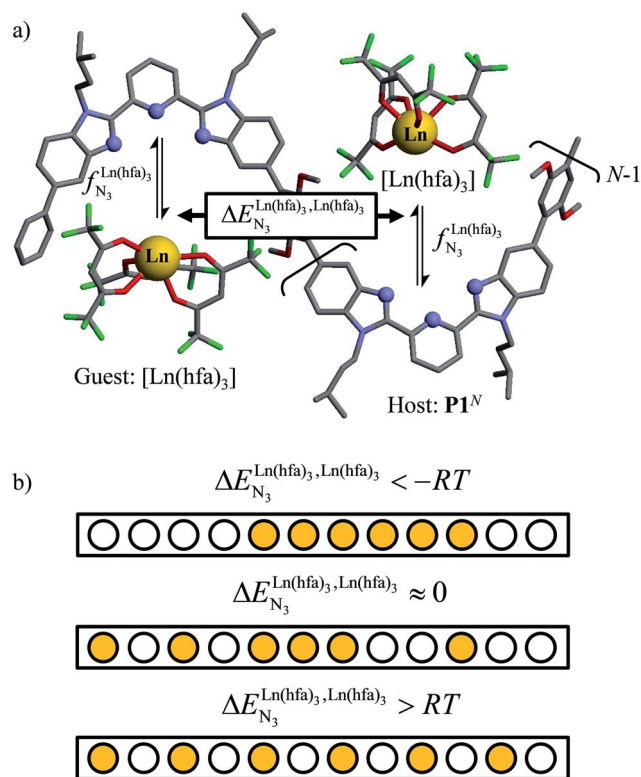


Fig. 1 (a) Thermodynamic model showing successive intermolecular connections of $[\text{Ln}(\text{hfa})_3]$ to one-dimensional multi-terdentate receptors P1^N ($N = 10\text{--}30$).¹⁵ $\Delta G_{N_3}^{\text{Ln}(\text{hfa})_3} = -RT \ln(f_{N_3}^{\text{Ln}(\text{hfa})_3})$ is the intrinsic intermolecular affinity and $\Delta E_{N_3}^{\text{Ln}(\text{hfa})_3, \text{Ln}(\text{hfa})_3}$ is the nearest-neighbor interaction (color code: C = grey, N = blue, O = red, F = green, Ln = orange). (b) Pictorial representation of the effect of intermetallic interactions on the microstates of a half-filled metalopolymer (orange disc = occupied site, white disc = empty site).

limited reproducibility and difficult characterization¹³ severely restrict pertinent developments along this line. An alternative approach proposes to take advantage of the powerful toolkit of reversible thermodynamics that has been developed to unravel multiple protonations in linear polyelectrolytes,¹⁴ for the in-depth deciphering of the loading of linear polymeric multi-terdentate receptors P1^N with neutral luminescent $[\text{Ln}(\text{hfa})_3]$ complexes (Ln = trivalent lanthanide, hfa = hexafluoroacetylacetonate) in dichloromethane (Fig. 1a).¹⁵ In solution, lanthanide tris-betadiketone complexes exist as Lewis base adducts $[\text{Ln}(\text{hfa})_3 \cdot \text{X}]$ where X is a solvent molecule or an additional donor atom borne by co-ligands. Upon reaction with the target binding site of a polymer, for instance P1^N , only the core $[\text{Ln}(\text{hfa})_3]$ is transferred (Fig. 1a). In order to use a single concept for the source $[\text{Ln}(\text{hfa})_3 \cdot \text{X}]$ and the transferable core $[\text{Ln}(\text{hfa})_3]$, we use the term 'neutral lanthanide container' for describing these beta-diketone coordination complexes. Using the site-binding model,^{14,16} complexation processes can be modeled using two simple parameters: (1) the free energy of the intermolecular affinity of the entering metal for one terdentate N_3 site $\Delta G_{N_3}^{\text{Ln}(\text{hfa})_3} = -RT \ln(f_{N_3}^{\text{Ln}(\text{hfa})_3})$, which is the unique parameter to be considered for a monomeric unit and (2) the inter-site interaction energy $\Delta E_{N_3}^{\text{Ln}(\text{hfa})_3, \text{Ln}(\text{hfa})_3}$ which accounts for modulations of the intrinsic affinity when multiple binding events operate in binuclear (or higher-order) linear receptors (*i.e.* cooperativity).¹⁷ Whereas major attention is usually focused on the maximization of host-guest affinities (*i.e.* minimizing $\Delta G_{N_3}^{\text{Ln}(\text{hfa})_3}$), an instructed programming of $\Delta E_{N_3}^{\text{Ln}(\text{hfa})_3, \text{Ln}(\text{hfa})_3}$ is more tricky since both negative (cooperative) or positive (anti-cooperative) issues are attractive for specific applications.

For instance, metal clustering compatible with efficient short-range intermetallic communication and energy migration¹⁸

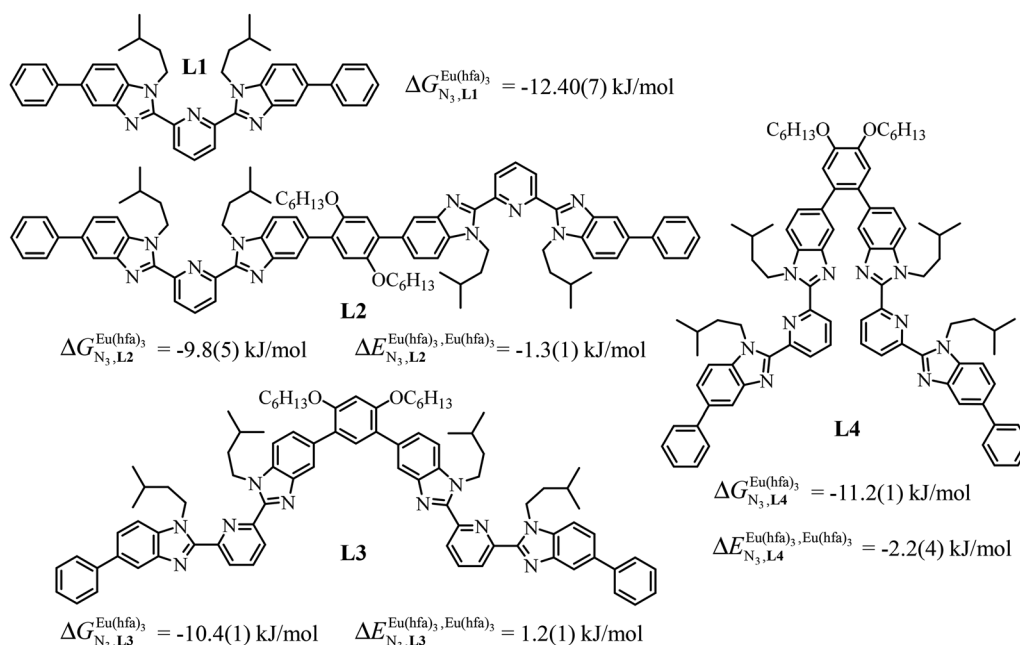


Fig. 2 Chemical structures of ligands L1–L4 gathering the thermodynamic intermolecular affinities $\Delta G_{N_3}^{\text{Eu}(\text{hfa})_3}$ and nearest-neighbor interactions $\Delta E_{N_3}^{\text{Eu}(\text{hfa})_3, \text{Eu}(\text{hfa})_3}$ for their loading with $[\text{Eu}(\text{hfa})_3]$ (CD_2Cl_2 , 298 K).



Synthesis and characterization of unsymmetrical neutral lanthanide containers [Ln(tfa)₃dig], [Ln(pta)₃dig], [Ln(tta)₃dig] and [Ln(pbta)₃dig]

The ^1H and ^{19}F -NMR spectra confirm the formation of pseudo- C_3 species in solution, which are dynamic on the NMR time scale (Fig. 4 and S1–S4 in the ESI†).²⁴ Elemental analyses of the microcrystalline powders point to the formation of unsolvated $[\text{Ln}(\beta\text{-diketonate})_3\text{dig}]$ adducts (Appendix 1), a trend confirmed by the X-ray crystal structures solved for $[\text{Eu}(\text{tta})_3\text{dig}]$ (1), $[\text{Y}(\text{tta})_3\text{dig}]$ (2) and $[\text{Eu}(\text{pbta})_3\text{dig}]$ (3) (Fig. 5, S4–S6 and Tables

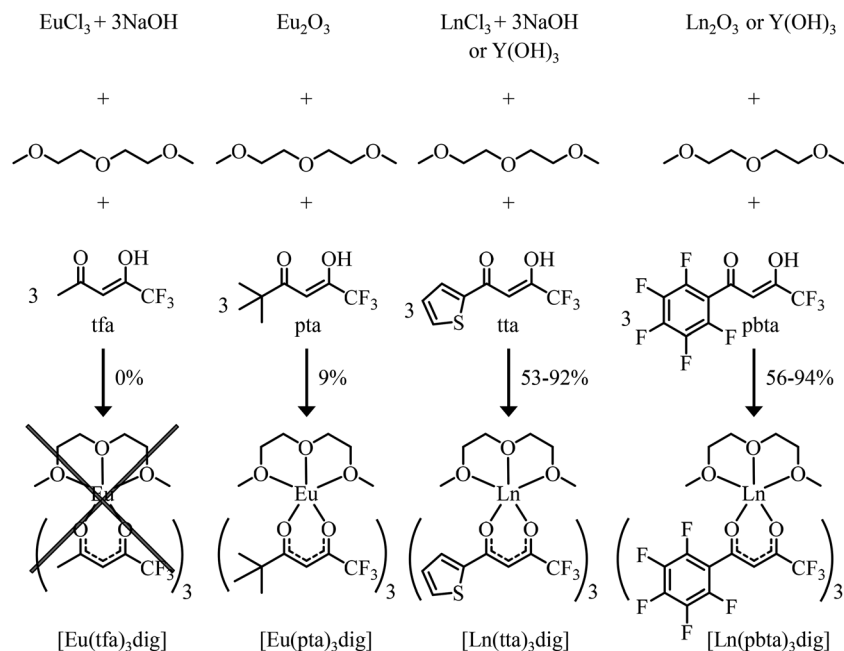


Fig. 3 Reaction pathways for the syntheses of unsymmetrical lanthanide containers.

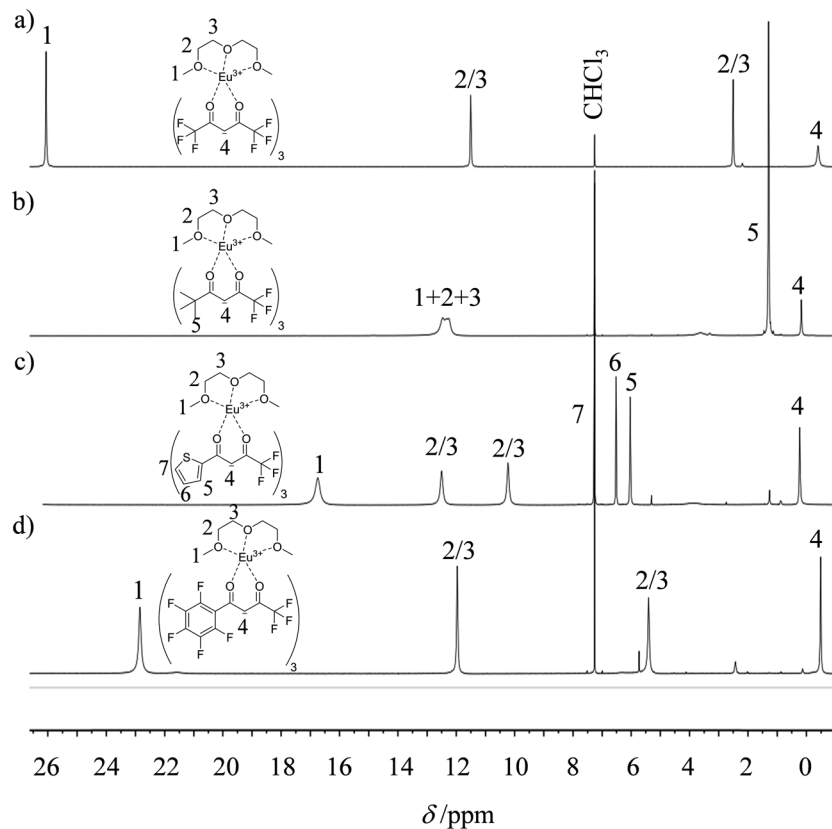


Fig. 4 ^1H NMR spectra of europium-containing lanthanide containers (a) $[\text{Eu}(\text{hfa})_3]\text{dig}$, (b) $[\text{Eu}(\text{ppta})_3]\text{dig}$, (c) $[\text{Eu}(\text{tta})_3]\text{dig}$ and (d) $[\text{Eu}(\text{ppta})_3]\text{dig}$ with numbering scheme (CDCl_3 , 298 K).

S1–S13[†]). All bond lengths in the europium complexes $[\text{Eu}(\text{tta})_3]\text{dig}$ (1) and $[\text{Eu}(\text{ppta})_3]\text{dig}$ (3) are within the standard range and are comparable to those reported for symmetrical $[\text{Eu}(\text{hfa})_3]\text{dig}$ (Table S13[†]),²⁵ a trend in line with similar affinities displayed by any of the fluorinated β -diketonate ligands (hfa^- , tta^- and ppta^-) for the central trivalent cation.

Subject to SHAPE²⁶ analysis, the EuO_9 coordination spheres correspond best to monocapped square antiprisms with the central oxygen donor of the diglyme ligand occupying the capping position (Fig. S7a[†]). The smaller size of trivalent yttrium leads to eight-coordination in $[\text{Y}(\text{tta})_3]\text{dig}$ (2) where the diglyme acts as a bidentate ligand (Fig. 5b). The eight bound oxygen atoms occupy the vertices of an approximate square antiprism,²⁶ a trend in line with quantum chemical calculations performed on $[\text{Y}(\text{tta})_3(\text{H}_2\text{O})_x]$ in the gas-phase.²⁷ Compared with $[\text{Eu}(\text{tta})_3]\text{dig}$

(Fig. 5a), two tta diketonate ligands are significantly twisted in $[\text{Y}(\text{tta})_3]\text{dig}$ (Fig. S8[†]). All bond valences significantly increase as a result of the larger residual charge carried by the eight-coordinate Y^{III} (Table S13[†]). The electric dipole moments computed for the gas-phase optimised geometries (Fig. S7b[†]) roughly point along the $\text{Ln}-\text{O}_{\text{central}}(\text{diglyme})$ bond direction and decrease in the order hfa (7.7 D) > ppta (6.7 D) > tta (4.6 D), a tendency which contrasts with pioneer calculations performed for six-coordinate $[\text{Ln}(\beta\text{-diketonate})_3]$ systems²⁸ and with chemical intuition, which naively associates larger dipole moments with unsymmetrical β -diketonate ligands. We conclude that the magnitudes of the dipole moments in $[\text{LnX}_3]\text{dig}$ are indeed controlled by the residual positive charge borne by the trivalent lanthanide, which increases with the electron-withdrawing effect of the bound β -diketonate ligands ($\text{hfa} > \text{ppta} \gg \text{tta}$).

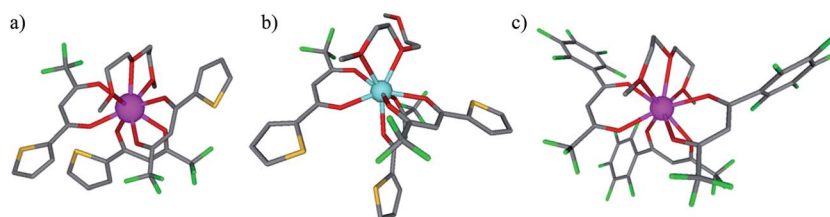


Fig. 5 Molecular structures of (a) $[\text{Eu}(\text{tta})_3]\text{dig}$ (1), (b) $[\text{Y}(\text{tta})_3]\text{dig}$ (2) and (c) $[\text{Eu}(\text{ppta})_3]\text{dig}$ (3) as observed in their crystal structures. Color codes: C = grey, O = red, S = yellow, F = green, Eu = magenta, and Y = light blue. The hydrogen atoms have been omitted for clarity.



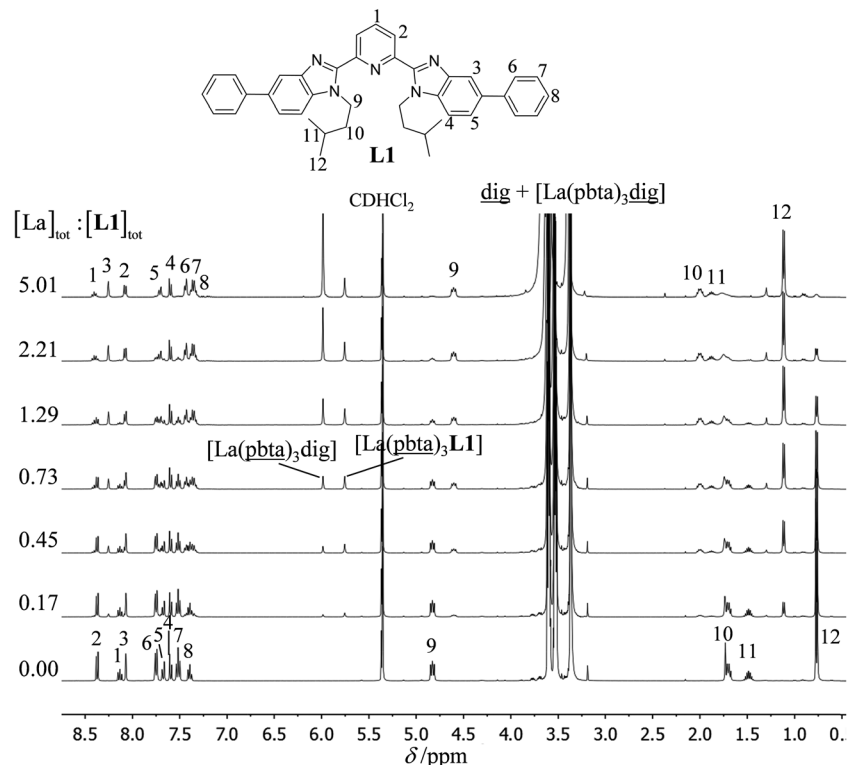
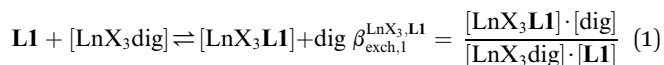


Fig. 6 ^1H NMR titration of **L1** (10 mM) with $[\text{La}(\text{ppta})_3\text{dig}]$ in CD_2Cl_2 + 0.14 m diglyme at 298 K.

Thermodynamic loading of the terdentate ligand **L1** with the unsymmetrical neutral lanthanide containers $[\text{Ln}(\text{pta})_3\text{dig}]$, $[\text{Ln}(\text{tta})_3\text{dig}]$ and $[\text{Ln}(\text{pbta})_3\text{dig}]$: a strategy for addressing intrinsic intermolecular affinities

The ^1H NMR titrations of 10 mM of the monomeric terdentate ligand **L1** with $[\text{LnX}_3\text{dig}]$ ($\text{Ln} = \text{La}, \text{Eu}, \text{ and } \text{Y}$; $\text{X} = \text{pta}, \text{tta}$ and pbta ; $\text{dig} = \text{diglyme}$) conducted in dichloromethane containing an excess of diglyme ($[\text{dig}]_{\text{tot}} = 0.14 \text{ m}$) show the formation of a single adduct $[\text{LnX}_3\text{L1}]$ complex according to eqn (1) (Fig. 6 and Tables S14 and S15†).^{15a}



Since the total concentration of diglyme does not significantly vary, the stability constant $\beta_{\text{exch},1}^{\text{LnX}_3,\text{L1}}$ associated with the ligand exchange process depicted in eqn (1) reduces to the conditional association constant $\beta_{\text{cond},1,1}^{\text{LnX}_3,\text{L1}}$ summarized in eqn (2), where $f_{\text{L1,cond}}^{\text{LnX}_3}$ is the conditional affinity factor of a terdentate site for a $[\text{LnX}_3]$ container (Fig. 1a).^{15a}

$$\beta_{\text{cond},1,1}^{\text{LnX}_3,\text{L1}} = \frac{\beta_{\text{exch},1}^{\text{LnX}_3,\text{L1}}}{[\text{dig}]_{\text{tot}}} = \frac{[\text{LnX}_3\text{L1}]}{[\text{LnX}_3\text{dig}] \cdot [\text{L1}]} = f_{\text{L1,cond}}^{\text{LnX}_3} \quad (2)$$

Experimentally, the integrations of the ^1H NMR signals recorded for a given proton connected either to the free ligand **L1** (I_{L1}^{H}) or to the coordinate ligand in $[\text{LnX}_3\text{L1}]$ ($I_{\text{LnX}_3\text{L1}}^{\text{H}}$) can be combined to determine the occupancy factor $\theta_{\text{Ln}}^{\text{L1}}$ (left part of

eqn (3)), which is related to the association constant $\beta_{\text{cond},1,1}^{\text{LnX}_3,\text{L1}}$ via the Langmuir binding isotherm (right part of eqn (3)).^{15a}

$$\begin{aligned} \theta_{\text{Ln}}^{\text{L1}} &= \frac{[\text{Ln}]_{\text{bound}}}{[\text{L1}]_{\text{tot}}} = \frac{I_{\text{LnX}_3\text{L1}}^{\text{H}}}{I_{\text{L1}}^{\text{H}} + I_{\text{LnX}_3\text{L1}}^{\text{H}}} = \frac{[\text{Ln}]_{\text{tot}} - [\text{LnX}_3\text{dig}]}{[\text{L1}]_{\text{tot}}} \\ &= \frac{\beta_{\text{cond},1,1}^{\text{LnX}_3,\text{L1}} [\text{LnX}_3\text{dig}]}{1 + \beta_{\text{cond},1,1}^{\text{LnX}_3,\text{L1}} [\text{LnX}_3\text{dig}]} \quad (3) \end{aligned}$$

Repeating this procedure for different $[\text{L1}]_{\text{tot}}:[\text{Ln}]_{\text{tot}}$ ratios (Fig. 6) yields occupancy factors $\theta_{\text{Ln}}^{\text{L1}}$ (eqn (3), left) for various free concentrations of the lanthanide container $[\text{LnX}_3\text{dig}]$ (eqn (3), middle). Plots of $\theta_{\text{Ln}}^{\text{L1}}$ related to $\log([\text{LnX}_3\text{dig}])$ (Fig. 7), often referred to as binding isotherms, are fit to eqn (3) (right part) using non-linear least-square techniques to give the conditional association constant $\beta_{\text{cond},1,1}^{\text{LnX}_3,\text{L1}} = f_{\text{L1,cond}}^{\text{LnX}_3}$ collected in Table S16† and the intrinsic exchange affinities $\Delta G_{\text{N}_3,\text{L1}}^{\text{LnX}_3} = -RT \ln(f_{\text{L1,cond}}^{\text{LnX}_3} \cdot [\text{dig}]_{\text{tot}}) = -RT \ln(f_{\text{L1}}^{\text{LnX}_3})$ depicted in Fig. 8.

For the unsymmetrical perfluorobenzene-trifluoroacetylacetonate lanthanide containers $[\text{Ln}(\text{pbta})_3\text{dig}]$ ($\text{Ln} = \text{La}, \text{Eu}, \text{ and } \text{Y}$, the blue traces in Fig. 7 and 8), the intrinsic exchange affinities $\Delta G_{\text{N}_3,\text{L1}}^{\text{LnX}_3}$ (eqn (1)) increase by 8–14% with respect to those found for the famous symmetrical $[\text{Ln}(\text{hfa})_3\text{dig}]$ analogues (red traces in Fig. 7 and 8). For the unsymmetrical, but less electron-deficient thienyl-trifluoroacetylacetonate lanthanide containers $[\text{Ln}(\text{tta})_3\text{dig}]$ ($\text{Ln} = \text{La}, \text{Eu}, \text{ and } \text{Y}$, the green traces in Fig. 7 and 8), the affinity for **L1** is still detectable, but low enough when $\text{Ln} = \text{Y}$ for providing fast exchange on the NMR scale. In these conditions, the monitoring of a single



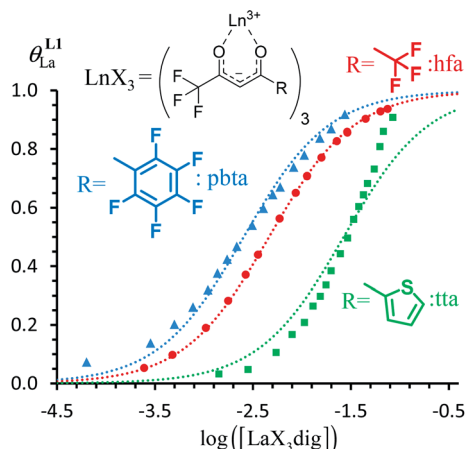


Fig. 7 Binding isotherms built from ^1H NMR titrations of **L1** with $[\text{LaX}_3\text{dig}]$ ($\text{X} = \text{hfa}$ (red), tta (green) or pbta (blue)) in CD_2Cl_2 + 0.14 M dig at 293 K. The dotted traces correspond to the fitted curves computed with eqn (3) and using $\beta_{\text{cond},1,1}^{\text{LnX}_3,\text{L1}}$ collected in Table S16.†

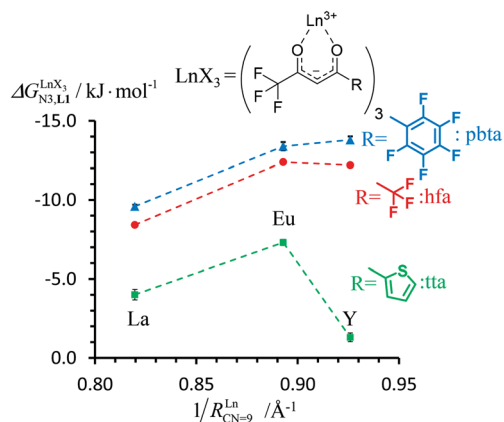


Fig. 8 Intrinsic exchange affinities $\Delta G_{\text{N}_3,\text{L1}}^{\text{LnX}_3} = -RT \ln(f_{\text{L1,cond}}^{\text{LnX}_3} [\text{dig}]_{\text{tot}}) = -RT \ln(f_{\text{L1}}^{\text{LnX}_3})$ for the loading of monomeric ligand **L1** with $[\text{Ln}(\text{hfa})_3\text{dig}]$ (red), $[\text{Ln}(\text{tta})_3\text{dig}]$ (green) and $[\text{Ln}(\text{pbta})_3\text{dig}]$ (blue) in CD_2Cl_2 at 298 K. $1/R_{\text{CN}=9}^{\text{Ln}}$ is the inverse of the nine-coordinate lanthanide radius. The dotted trend lines are provided as guides.

broadened ^1H NMR signal $\delta_{\text{obs}}^{\text{H}}$ for each proton in solution during the titration prevents the use of eqn (3), which is replaced by eqn (4) for estimating the occupancy factor θ_Y^{L1} ($\delta_{\text{L1}}^{\text{H}}$ and $\delta_{\text{Y}(\text{tta})_3\text{L1}}^{\text{H}}$ stand for the chemical shifts of the same proton in pure **L1** and $[\text{Y}(\text{tta})_3\text{L1}]$, respectively).

$$\theta_Y^{\text{L1}} = \frac{[\text{Y}]_{\text{bound}}}{[\text{L1}]_{\text{tot}}} = \frac{[\text{Y}(\text{tta})_3\text{L1}]}{[\text{L1}]_{\text{tot}}} = \frac{\delta_{\text{obs}}^{\text{H}} - \delta_{\text{L1}}^{\text{H}}}{\delta_{\text{Y}(\text{tta})_3\text{L1}}^{\text{H}} - \delta_{\text{L1}}^{\text{H}}} = \frac{\beta_{\text{cond},1,1}^{\text{Y}(\text{tta})_3,\text{L1}} [\text{Y}(\text{tta})_3\text{dig}]}{1 + \beta_{\text{cond},1,1}^{\text{Y}(\text{tta})_3,\text{L1}} [\text{Y}(\text{tta})_3\text{dig}]} \quad (4)$$

For these $[\text{Ln}(\text{tta})_3]$ containers, occupancy factors larger than 20% are only obtained in a large excess of $[\text{Ln}(\text{tta})_3\text{dig}]$,

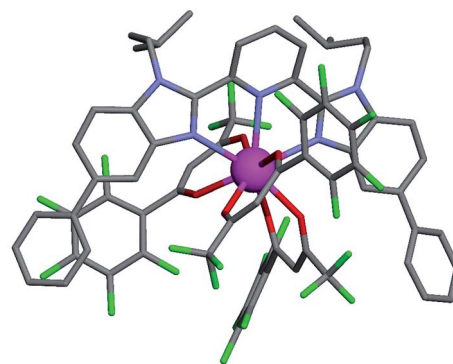


Fig. 9 Molecular structure of $[\text{Eu}(\text{pbta})_3\text{L1}]$ found in the crystal structure of $[\text{Eu}(\text{pbta})_3\text{L1}] \cdot \text{CH}_2\text{Cl}_2$ (**4**). Color codes: C = grey, O = red, F = green, and Eu = magenta. The hydrogen atoms have been omitted for clarity.

the total concentrations of which may reach 0.1 M in solution. The express requisite for using an invariant total concentration of diglyme in eqn (2) is no more obeyed and deviations from simple Langmuir isotherms are observed (green trace in Fig. 7). The conditional association constants reported for $[\text{Ln}(\text{tta})_3\text{L1}]$ complexes are therefore only mere estimations. Finally, the pyvaloyl-trifluoroacetylacetone europium container $[\text{Eu}(\text{pta})_3\text{dig}]$, which bears the lowest residual positive charge on the metal,²⁹ displayed no measurable affinity for **L1** in CD_2Cl_2 at millimolar concentrations, a result in line with the lack (to the best of our knowledge) of crystal structures reporting a nine-coordinate $[\text{Ln}(\text{pta})_3\text{L}]$ adduct, where **L** is a terdentate chelate nitrogen donor ligand.³⁰ Leaving pta-based complexes aside, pure $[\text{Ln}(\text{pbta})_3\text{L1}]$ ($\text{Ln} = \text{La}$, Eu , and Y) and $[\text{Ln}(\text{tta})_3\text{L1}]$ ($\text{Ln} = \text{La}$ and Eu) complexes could be isolated as crystalline materials from concentrated solutions in 41–92% yield (Appendix 1, Tables S13, S14 and S17†). The crystal structure of $[\text{Eu}(\text{pbta})_3\text{L1}] \cdot \text{CH}_2\text{Cl}_2$ (**4**) confirms nine-coordinate around the europium cation by the three nitrogen atoms of the bound aromatic ligand and the six oxygen atoms of the three bidentate pbta anions (Fig. 9, Tables S18–S21 and Fig. S9†). The $[\text{EuN}_3\text{O}_6]$ chromophore adopts a distorted monocapped square antiprism geometry,²⁶ very similar to that previously described for $[\text{La}(\text{hfa})_3\text{L1}]$ (Table S22 and Fig. S10†).^{15a}

In conclusion, two strong electron-withdrawing groups per β -diketonate in hfa (two CF_3 groups) or in pbta (CF_3 and C_6F_5) are required in order to get intrinsic affinities $\Delta G_{\text{N}_3,\text{L1}}^{\text{LnX}_3}$ large enough to form significant amounts of $[\text{LnX}_3\text{L1}]$ at millimolar concentrations (Fig. 8, X represents the β -diketonate anion). The connections of less electron-withdrawing thenoyl ($\text{X} = \text{tta}$) or pivaloyl groups ($\text{X} = \text{pta}$) are detrimental in terms of the global stabilities of the adducts. This trend is correlated with the dipole moments computed for the gas-phase optimized $[\text{YX}_3\text{L1}]$ complexes, which reveal that the global asymmetry of the charge distribution increases along the series $[\text{Y}(\text{pbta})_3\text{L1}]$ ($\mu = 13.1 \text{ D}$) $\approx [\text{Y}(\text{hfa})_3\text{L1}]$ ($\mu = 13.8 \text{ D}$) $< [\text{Y}(\text{tta})_3\text{L1}]$ ($\mu = 14.9 \text{ D}$, Fig. S11†).



Thermodynamic loading of multi-terdentate ligands L2–L4 with unsymmetrical neutral lanthanide containers [Eu(tta)₃dig] and [Eu(pbta)₃dig]: a strategy for addressing nearest-neighbor interactions

A reliable analysis of the inter-site interactions $\Delta E_{\text{Lk}}^{\text{LnX}_3, \text{LnX}_3}$, which control the successive binding of two adjacent [LnX₃] containers in linear multi-site receptors, requires the investigation of the dimeric receptors L2–L4 (eqn (5) and (6)), for which the cumulative conditional association constants $\beta_{\text{cond}, m, 1}^{\text{LnX}_3, \text{Lk}}$ are given in eqn (7) and (8).

$$\text{Lk} + [\text{LnX}_3\text{dig}] \rightleftharpoons [\text{LnX}_3\text{Lk}] + \text{dig} \quad \beta_{\text{exch}, 1}^{\text{LnX}_3, \text{Lk}} = \frac{[\text{LnX}_3\text{Lk}] \cdot [\text{dig}]}{[\text{LnX}_3\text{dig}] \cdot [\text{Lk}]} \quad (5)$$

$$\text{Lk} + 2[\text{LnX}_3\text{dig}] \rightleftharpoons [\text{Ln}_2\text{X}_6\text{Lk}] + 2\text{dig} \quad \beta_{\text{exch}, 2}^{\text{LnX}_3, \text{Lk}} = \frac{[\text{Ln}_2\text{X}_6\text{Lk}] \cdot [\text{dig}]^2}{[\text{LnX}_3\text{dig}]^2 \cdot [\text{Lk}]} \quad (6)$$

$$\beta_{\text{cond}, 1, 1}^{\text{LnX}_3, \text{Lk}} = \frac{\beta_{\text{exch}, 1}^{\text{LnX}_3, \text{Lk}}}{[\text{dig}]_{\text{tot}}} = \frac{[\text{LnX}_3\text{Lk}]}{[\text{LnX}_3\text{dig}] \cdot [\text{Lk}]} = 2f_{\text{Lk}, \text{cond}}^{\text{LnX}_3} \quad (7)$$

$$\beta_{\text{cond}, 2, 1}^{\text{LnX}_3, \text{Lk}} = \frac{\beta_{\text{exch}, 2}^{\text{LnX}_3, \text{Lk}}}{([\text{dig}]_{\text{tot}})^2} = \frac{[\text{Ln}_2\text{X}_6\text{Lk}]}{[\text{LnX}_3\text{dig}]^2 \cdot [\text{Lk}]} = (f_{\text{Lk}, \text{cond}}^{\text{LnX}_3})^2 e^{-\left(\frac{\Delta E_{\text{Lk}}^{\text{LnX}_3, \text{LnX}_3}}{RT}\right)} = (f_{\text{Lk}, \text{cond}}^{\text{LnX}_3})^2 u_{\text{Lk}}^{\text{LnX}_3, \text{LnX}_3} \quad (8)$$

According to the site binding model,¹⁶ $\beta_{\text{cond}, 1, 1}^{\text{LnX}_3, \text{Lk}}$ (eqn (7)) reflects the intrinsic binding affinity of the lanthanide container for a single terdentate site, but modulated by a statistical factor of 2 in a dimer. With this in mind, $\beta_{\text{cond}, 2, 1}^{\text{LnX}_3, \text{Lk}}$ (eqn (8)) easily provides an estimation of the inter-site interactions measured as their Boltzmann factors $u_{\text{Lk}}^{\text{LnX}_3, \text{LnX}_3} = \exp(-\Delta E_{\text{Lk}}^{\text{LnX}_3, \text{LnX}_3} / RT) = 4\beta_{\text{cond}, 2, 1}^{\text{LnX}_3, \text{Lk}} / (\beta_{\text{cond}, 1, 1}^{\text{LnX}_3, \text{Lk}})^2$, a parameter often referred to as the allosteric cooperativity factor.³¹ As the intrinsic affinity of [Ln(tta)₃dig] for the terdentate binding unit is too weak to produce significant quantities of the binuclear [Ln₂(tta)₆Lk] complexes at millimolar concentrations, the thermodynamic studies performed on the symmetrical [Eu₂(hfa)₆Lk] dimers¹⁷ are completed here with the recording of ¹H and ¹⁹F NMR spectra for the complexation of L2–L4 (5 mm) with [Eu(pbta)₃dig] in CD₂Cl₂ + 0.14 m diglyme (Fig. S12†). The integrations of the various signals (¹H and ¹⁹F) gave occupancy factors (eqn (9) and Fig. 10), which could be fitted to eqn (10) to get the intrinsic affinities $f_{\text{Lk}, \text{cond}}^{\text{EuX}_3}$ and cooperativity factors $u_{\text{N}_3}^{\text{EuX}_3, \text{EuX}_3}$ collected in Fig. 11 (Table S23†).

$$\theta_{\text{Ln}}^{\text{exp}} = \frac{\langle m \rangle}{N} = \frac{1}{2} \frac{|\text{Ln}|_{\text{bound}}}{|\text{Lk}|_{\text{tot}}} = \frac{1}{2} \frac{I_{\text{LnLk}}^{\text{H}} + 2(I_{\text{Ln}_2\text{Lk}}^{\text{H}})}{I_{\text{Lk}}^{\text{H}} + I_{\text{LnLk}}^{\text{H}} + I_{\text{Ln}_2\text{Lk}}^{\text{H}}} = \frac{I_{\text{LnLk}}^{\text{F}} + I_{\text{Ln}_2\text{Lk}}^{\text{F}}}{I_{\text{Ln}}^{\text{F}} + I_{\text{LnLk}}^{\text{F}} + I_{\text{Ln}_2\text{Lk}}^{\text{F}}} \cdot \frac{[\text{Ln}]_{\text{tot}}}{2[\text{Lk}]_{\text{tot}}} \quad (9)$$

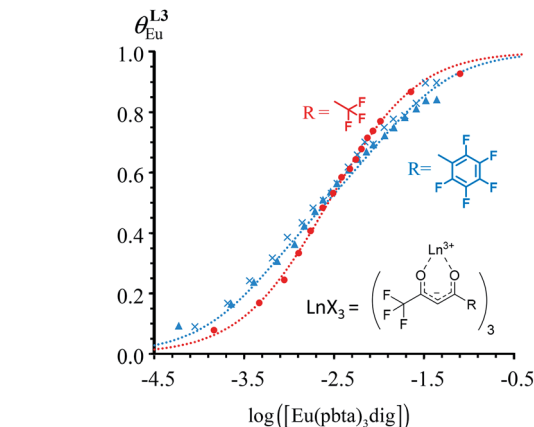


Fig. 10 Occupancy factors and binding isotherms built from NMR titrations of L3 with [Eu(hfa)₃dig] (red disks, ¹H NMR)¹⁷ and [Eu(pbta)₃dig] (blue triangles for ¹H NMR, blue crosses for ¹⁹F NMR) in CD₂Cl₂ + 0.14 m dig at 298 K. The dotted traces correspond to the fitted curves computed with eqn 10 and using $f_{\text{Lk}, \text{cond}}^{\text{EuX}_3}$ and $u_{1-2}^{\text{EuX}_3, \text{EuX}_3}$ collected in Table S23.†

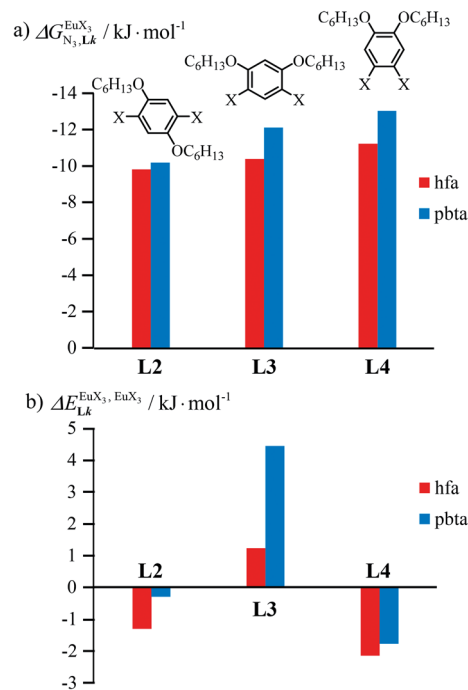


Fig. 11 (a) Intrinsic exchange affinities $\Delta G_{\text{N}_3, \text{Lk}}^{\text{EuX}_3} = -RT \ln(f_{\text{Lk}}^{\text{EuX}_3})$ and (b) intermetallic interactions $\Delta E_{\text{Lk}}^{\text{EuX}_3, \text{EuX}_3} = -RT \ln(u_{\text{Lk}}^{\text{EuX}_3, \text{EuX}_3})$ for the loading of dimeric ligands L2–L4 (geometries of the spacers are highlighted) with [Eu(hfa)₃dig] (red) and [Eu(pbta)₃dig] (blue) (CD₂Cl₂, 298 K).

$$\theta_{\text{Ln}}^{\text{calcd}} = \frac{1}{2} \frac{|\text{Ln}|_{\text{bound}}}{|\text{Lk}|_{\text{tot}}} = \frac{[\text{LnX}_3\text{Lk}] + 2[\text{Ln}_2\text{X}_6\text{Lk}]}{2[\text{Lk}]_{\text{tot}}} = \frac{1}{2} \left(\frac{2f_{\text{Lk}, \text{cond}}^{\text{LnX}_3} [\text{Ln}] + 2(f_{\text{Lk}, \text{cond}}^{\text{LnX}_3})^2 u_{1-2}^{\text{LnX}_3, \text{LnX}_3} [\text{Ln}]^2}{1 + 2f_{\text{Lk}, \text{cond}}^{\text{LnX}_3} [\text{Ln}] + (f_{\text{Lk}, \text{cond}}^{\text{LnX}_3})^2 u_{1-2}^{\text{LnX}_3, \text{LnX}_3} [\text{Ln}]^2} \right) \quad (10)$$

In line with the trend observed for the monomeric ligand **L1** (Fig. 8), the intrinsic affinities of a terdentate unit in the dimeric ligands **L2–L4** are roughly 10% larger for $[\text{Eu}(\text{pbta})_3\text{dig}]$ than for $[\text{Eu}(\text{hfa})_3\text{dig}]$ (Fig. 11a). The observed intermetallic interactions $\Delta E_{\text{Lk}}^{\text{EuX}_3, \text{EuX}_3}$ are systematically shifted toward more anti-cooperative processes for $[\text{Eu}_2(\text{pbta})_6\text{Lk}]$ complexes (Fig. 11b).

This drift culminates for $[\text{Eu}_2(\text{pbta})_6\text{L3}]$, in which the anti-cooperative interaction between the two unsymmetrical $[\text{Eu}(\text{pbta})_3]$ containers amounts to almost $+5 \text{ kJ mol}^{-1}$, a value which should prevent a statistical redistribution due to thermal energy in half-filled linear polymers integrating this bis-terdentate structural motif. Considering that (i) the intermetallic distances are similar in the structures of $[\text{Eu}_2(\text{hfa})_3\text{L3}]$ ($\text{Eu}\cdots\text{Eu} = 12.61 \text{ \AA}$ in its crystal structure)¹⁷ and $[\text{Eu}_2(\text{pbta})_3\text{L3}]$ and (ii) the dipole moment calculated for $[\text{Y}(\text{pbta})_3\text{L1}]$ is only slightly smaller than that found for $[\text{Eu}(\text{hfa})_3\text{L1}]$ (Fig. S11[†]), we assign the gain in intermetallic repulsion by a factor of 3.7(6), going from $[\text{Eu}_2(\text{hfa})_3\text{L3}]$ (symmetrical β -diketonate) to $[\text{Eu}_2(\text{pbta})_3\text{L3}]$ (unsymmetrical β -diketonate), to specific solvation effects which are known to largely dominate over the minor contributions produced by intramolecular dipole-dipole interactions.¹⁷

Photophysical properties and luminescence quantum yields of the europium containers $[\text{EuX}_3(\text{dig})]$ ($\text{X} = \text{hfa}, \text{tta}, \text{pbta}$) and of their mononuclear $[\text{EuX}_3\text{L1}]$ and binuclear $[\text{Eu}_2(\text{hfa})_6\text{Lk}]$ complexes ($\text{Lk} = \text{L2–L4}$)

The electronic absorption spectra of the europium containers $[\text{EuX}_3(\text{dig})]$ ($\text{X} = \text{hfa}, \text{tta}, \text{and pbta}$) are dominated by β -diketonate-centred $\pi^* \leftarrow \pi$ transitions occurring in the near-UV range (dotted traces in Fig. 12 and S13[†]). The maximum of the absorption envelope is shifted stepwise toward lower energy upon the replacement of the trifluoromethyl substituents found in $[\text{Eu}(\text{hfa})_3\text{dig}]$ ($33\,100 \text{ cm}^{-1}$, Fig. S13[†]) with aromatic groups in $[\text{Eu}(\text{pbta})_3\text{dig}]$ ($32\,000 \text{ cm}^{-1}$ for one pentafluorobenzene unit, Fig. 12b) and $[\text{Eu}(\text{tta})_3\text{dig}]$ ($30\,000 \text{ cm}^{-1}$ for one thenoyl unit, Fig. 12a). Exchanging the saturated diglyme ligand with the aromatic terdentate ligand **L1** in $[\text{EuX}_3\text{L1}]$ provides absorption spectra (full traces in Fig. 12) which combine the contributions of each individual chromophore, *i.e.* the β -diketonate-centred $\pi^* \leftarrow \pi$ transitions (dotted traces in Fig. 12) together with **L1**-centred ${}^1\pi_{\text{L1}}^* \leftarrow {}^1\pi_{\text{L1}}$ and ${}^1\pi_{\text{L1}}^* \leftarrow {}^1\pi_{2,\text{L1}}$ transitions (dashed traces in Fig. 12).³² Room-temperature excitations ($\tilde{\nu}_{\text{exc}} = 26\,000\text{--}30\,000 \text{ cm}^{-1}$) of the $[\text{EuX}_3\text{dig}]$ or $[\text{EuX}_3\text{L1}]$ complexes ($\text{X} = \text{hfa}, \text{tta}, \text{and pbta}$) in solution (Fig. 13 and S14[†]) or in the solid state (Fig. S15 and S16[†]) produce typical europium-centred red luminescence, which results from indirect sensitization according to the antenna mechanism.³⁴ The initial ligand-centred ${}^1\pi^* \leftarrow {}^1\pi$ excitation is followed by a (probable)³⁵ intersystem crossing process, then $\text{L1} \rightarrow \text{Eu}$ and/or $\text{X} \rightarrow \text{Eu}$ energy transfers occur, thus leading to $\text{Eu}({}^5\text{D}_1)$ and $\text{Eu}({}^5\text{D}_0)$ -centred emissions.^{34,35} The europium-centred emission bands recorded for $[\text{EuX}_3\text{dig}]$ and $[\text{EuX}_3\text{L1}]$ are diagnostic for the existence of low-symmetry tris- β -diketonates $\text{Eu}(\text{III})$ complexes with (i) $\text{Eu}({}^5\text{D}_1 \rightarrow {}^7\text{F}_j)$ emissions being far less intense than for $\text{Eu}({}^5\text{D}_0 \rightarrow {}^7\text{F}_j)$ ^{15a,33} and (ii) $\text{Eu}({}^5\text{D}_0 \rightarrow {}^7\text{F}_j)$ emissions being

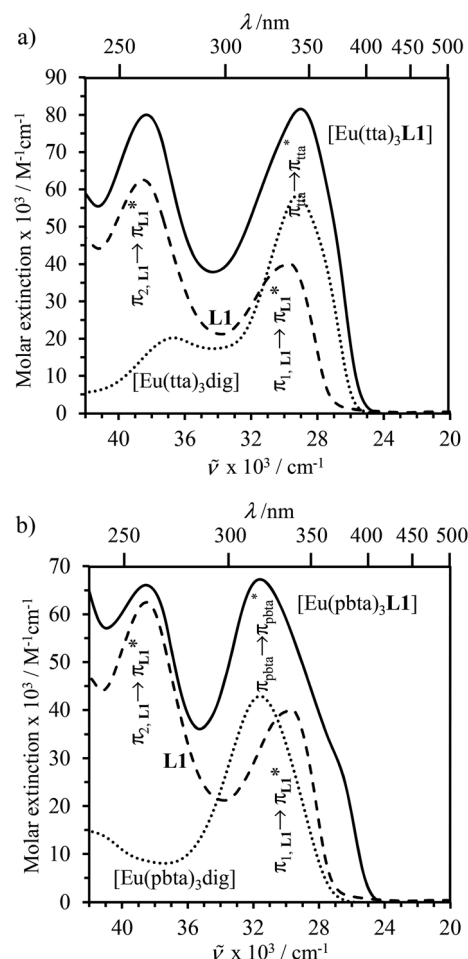


Fig. 12 Electronic absorption spectra recorded for (a) **L1** (dashed trace), $[\text{Eu}(\text{tta})_3\text{dig}]$ (dotted trace) and $[\text{Eu}(\text{tta})_3\text{L1}]$ (full trace), and (b) **L1** (dashed trace), $[\text{Eu}(\text{pbta})_3\text{dig}]$ (dotted trace) and $[\text{Eu}(\text{pbta})_3\text{L1}]$ (full trace) in $\text{CH}_2\text{Cl}_2 + 10^{-6} \text{ m}$ diglyme at 293 K. The absorption spectra were recorded for $[\text{Eu}]_{\text{tot}} = 10^{-5} \text{ m}$ and corrected for partial dissociation in solution (Appendix 2).

dominated by the $2J + 1 = 5$ split components of the hypersensitive forced electric dipolar ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition monitored around $16\,320 \text{ cm}^{-1}$ (Fig. 13 and S14[†]).³⁶ Only minor changes can be detected in terms of the relative intensities, splitting and energies for the $\text{Eu}({}^5\text{D}_0 \rightarrow {}^7\text{F}_j)$ transitions when the diglyme in $[\text{EuX}_3\text{dig}]$ is replaced with **L1** in $[\text{EuX}_3\text{L1}]$. However, the global quantum yields $\Phi_{\text{Eu}}^{\text{L}}$, recorded upon UV-irradiation of the ligands while measuring the Eu-centered emission, rise by factors of 2 to 10 going from $[\text{EuX}_3\text{dig}]$ ($3\% \leq \Phi_{\text{Eu}}^{\text{L}} \leq 10\%$) to $[\text{EuX}_3\text{L1}]$ ($22\% \leq \Phi_{\text{Eu}}^{\text{L}} \leq 45\%$, Table S24[†]). These considerable global quantum yields are typical among tris- β -diketonate complexes, for which a systematic optimization may lead to 40–70% quantum yield values.^{24,37}

More precisely, we note that the quantum yield $\Phi_{\text{Eu}}^{\text{L}} = 5(1)\%$ obtained here for $[\text{Eu}(\text{hfa})_3\text{dig}]$ in dichloromethane is much lower than $\Phi_{\text{Eu}}^{\text{L}} = 35\%$ reported for the same complex in ether : isopentane : ethanol (5 : 5 : 2).³⁸ In contrast, those obtained for $[\text{EuX}_3\text{L1}]$ in the solid state (15–40%) are in line with $\Phi_{\text{Eu}}^{\text{L}} = 20\text{--}30\%$ previously reported for closely related $[\text{Eu}(\text{hfa})_3\text{L}]$



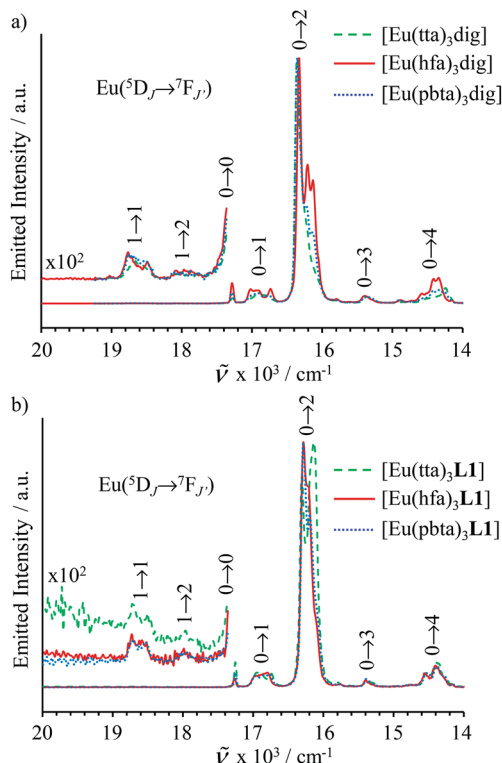


Fig. 13 Emission spectra recorded for (a) $[\text{EuX}_3\text{dig}]$ with $\text{X} = \text{hfa}$ ($\bar{\nu}_{\text{exc}} = 29\,850\text{ cm}^{-1}$, $[\text{Eu}]_{\text{tot}} = 8.6 \times 10^{-5}\text{ m}$, red full trace), $\text{X} = \text{tta}$ ($\bar{\nu}_{\text{exc}} = 28\,570\text{ cm}^{-1}$, $[\text{Eu}]_{\text{tot}} = 1.8 \times 10^{-5}\text{ m}$, green dashed trace) and $\text{X} = \text{pbta}$ ($\bar{\nu}_{\text{exc}} = 29\,850\text{ cm}^{-1}$, $[\text{Eu}]_{\text{tot}} = 3.3 \times 10^{-5}\text{ m}$, blue dotted trace) and for (b) $[\text{EuX}_3\text{L1}]$ with $\text{X} = \text{hfa}$ ($\bar{\nu}_{\text{exc}} = 25\,840\text{ cm}^{-1}$, $[\text{Eu}]_{\text{tot}} = 4.0 \times 10^{-5}\text{ m}$, red full trace), $\text{X} = \text{tta}$ ($\bar{\nu}_{\text{exc}} = 25\,000\text{ cm}^{-1}$, $[\text{Eu}]_{\text{tot}} = 5.5 \times 10^{-4}\text{ m}$, green dashed trace) and $\text{X} = \text{pbta}$ ($\bar{\nu}_{\text{exc}} = 25\,970\text{ cm}^{-1}$, $[\text{Eu}]_{\text{tot}} = 6.1 \times 10^{-5}\text{ m}$, blue dotted trace) in $\text{CH}_2\text{Cl}_2 + 10^{-6}\text{ m}$ diglyme at 293 K.

complexes where **L** is a terdentate N-donor ligand.³³ Although no detailed separation of radiative and non-radiative contributions to the various rate constants implied by the antenna mechanism are currently available, the observed mono-exponential millisecond range $\text{Eu}(\text{III})$ lifetimes (Table S24†) reveal a reasonable protection of the $\text{Eu}(\text{III})$ emissive center against the harmonics of high-energy oscillators in these unsymmetrical complexes. Finally, the introduction of bis(hexyloxy)phenyl spacers in the binuclear complexes $[\text{Eu}_2(\text{hfa})_6\text{Lk}]$ (**Lk** = **L2–L4**) has a deleterious effect on the global quantum yields, which are reduced by one order of magnitude ($2\% \leq \Phi_{\text{Eu}}^{\text{L}} \leq 5\%$) regarding those collected for the mononuclear analogues $[\text{Eu}(\text{hfa})_3\text{Lk}]$. This specific effect was previously documented for related binuclear europium complexes^{35a} and unambiguously assigned to a drastic reduction of the **Lk** → $\text{Eu}(\text{III})$ energy transfer rate constants when electron-donor groups are connected to the phenyl spacers. Our overview of the luminescence properties of $[\text{EuX}_3\text{dig}]$, $[\text{Eu}(\text{hfa})_3\text{L1}]$ and $[\text{Eu}_2(\text{hfa})_6\text{Lk}]$ confirms that the replacement of symmetrical $\text{X} = \text{hfa}$ ligands with unsymmetrical β -diketonate analogues ($\text{X} = \text{tta}$ and pbta) does not dramatically impact the global photo-physical properties of these complexes, which remain highly luminescent and therefore compatible with the preparation of

strong red emissive lanthanidopolymers assuming that the thermodynamic metal loading is under control.

Conclusion

In line with theoretical predictions,¹⁷ the replacement of symmetrical $\text{X} = \text{hfa}$ with unsymmetrical $\text{X} = \text{tta}$ or $\text{X} = \text{pbta}$ β -diketonates in nine-coordinate neutral $[\text{LnX}_3\text{dig}]$ lanthanide containers induces major changes in the thermodynamic loading of terdentate N_3 binding units. For both monomeric $[\text{LnX}_3\text{L1}]$ and dimeric $[\text{Eu}_2\text{X}_6\text{Lk}]$ complexes (**Lk** = **L2–L4**), the intrinsic affinity $f_{\text{N}_3, \text{cond}}^{\text{LnX}_3}$ depends on the residual positive charge borne by the metal. It increases in the order $f_{\text{N}_3, \text{cond}}^{\text{Ln}(\text{tta})_3} \ll f_{\text{N}_3, \text{cond}}^{\text{Ln}(\text{hfa})_3} \leq f_{\text{N}_3, \text{cond}}^{\text{Ln}(\text{pbta})_3}$, which matches the electron-withdrawing character of the substituent groups located in the β -diketonate ligand (Fig. 8 and 11a). The supplementary inter-site repulsion operating in the dinuclear $[\text{Eu}_2\text{X}_6\text{Lk}]$ complexes (**Lk** = **L2–L4**) is greatest for $[\text{Eu}_2(\text{pbta})_6\text{L3}]$ (Fig. 11b) with a remarkable anti-cooperative factor of $u_{\text{L3}}^{\text{Eu}(\text{pbta})_3, \text{Eu}(\text{pbta})_3} = 0.17(1)$, which translates into a repulsive free energy of $\Delta E_{\text{L3}}^{\text{Eu}(\text{pbta})_3, \text{Eu}(\text{pbta})_3} = 4.4(2)\text{ kJ mol}^{-1}$. The latter value is almost twice as large as the room temperature thermal energy.

Assuming a thought experiment in which (i) a linear infinite polymer P2^N ($N \rightarrow \infty$) based on the meta-substituted phenyl spacers, as found in **L3**, is at hand (Fig. 14 top), and (ii) the anti-cooperative factors $u_{\text{L3}}^{\text{Eu}(\text{hfa})_3, \text{Eu}(\text{hfa})_3} = 0.61(4)$ and $u_{\text{L3}}^{\text{Eu}(\text{pbta})_3, \text{Eu}(\text{pbta})_3} = 0.17(1)$ found for **L3** similarly operate in P2^N , the cluster expansion techniques¹⁴ predict the appearance of an unprecedented identifiable ‘plateau’ in the binding isotherm of

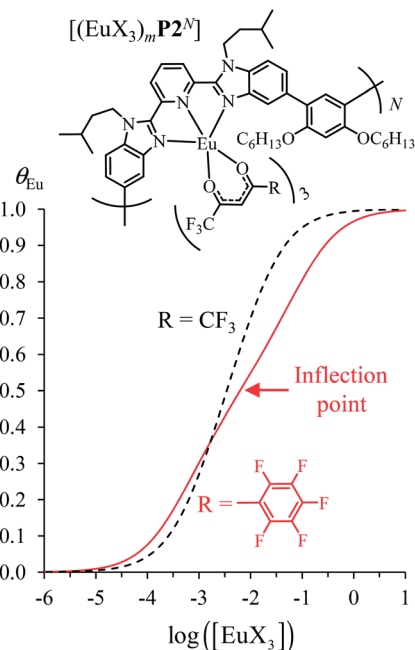


Fig. 14 Occupancy factors and binding isotherms computed for the loading of polymer P2^N ($N \rightarrow \infty$) in $\text{CH}_2\text{Cl}_2 + 0.14\text{ m}$ diglyme at 293 K with $[\text{Eu}(\text{hfa})_3\text{dig}]$ (dotted black trace, $\Delta E_{\text{L3}}^{\text{Eu}(\text{hfa})_3, \text{Eu}(\text{hfa})_3} = 1.2\text{ kJ mol}^{-1}$, Table S23†) and $[\text{Eu}(\text{pbta})_3\text{dig}]$ (full red trace, $\Delta E_{\text{L3}}^{\text{Eu}(\text{pbta})_3, \text{Eu}(\text{pbta})_3} = \Delta E_{\text{L3}}^{\text{Eu}(\text{pbta})_3, \text{Eu}(\text{pbta})_3} = 4.4\text{ kJ mol}^{-1}$, Table S23†).

the potential unsymmetrical linear $\{[\text{Eu}(\text{pbta})_3]_m \text{P2}^N\}$ lanthanidopolymer ($N \rightarrow \infty$, full red trace in Fig. 14), while its symmetrical analogue $\{[\text{Eu}(\text{hfa})_3]_m \text{P2}^N\}$ would exhibit only the standard stochastic distributions of metal ions (dashed black trace in Fig. 14). In other words, a predictable $[\text{P2}^N]_{\text{tot}}/[\text{Eu}(\text{pbta})_3]_{\text{tot}}$ stoichiometric ratio should provide an inflection point at $\theta_{\text{Eu}} = 0.5$, where the half-filled polymer $\{[\text{Eu}(\text{pbta})_3]_{N/2} \text{P2}^N\}$ is dominated by the formation of a micro-species, in which metal-occupied sites and metal-free sites strictly alternate (Fig. 1b bottom). The exact physical origin of this beneficial anti-cooperative effect remains elusive in the absence of quantitative access to solvation energies³⁹ and Born-Haber cycles,^{17,22,40} but computational efforts are underway for unravelling the conditions required for exploiting this unprecedented effect for the preparation of highly organized metallopolymer.

Conflicts of interest

There are no conflicts to declare.

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