

Lanthanide Energy Transfer

Lanthanide-to-Lanthanide Energy-Transfer Processes Operating in Discrete Polynuclear Complexes: Can Trivalent Europium Be Used as a Local Structural Probe?

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Abstract: This work, based on the synthesis and analysis of chemical compounds, describes a kinetic approach for identifying intramolecular intermetallic energy-transfer processes operating in discrete polynuclear lanthanide complexes, with a special emphasis on europium-containing entities. When all coordination sites are identical in a (supra)molecular complex, only heterometallic communications are experimentally accessible and a Tb \rightarrow Eu energy transfer could be evidenced in [TbEu(L5)(hfac)₆] (hfac=hexafluoroacetylacetonate), in which the intermetallic separation amounts to 12.6 Å. In the presence of different coordination sites, as found in the trinuclear complex [Eu₃(L2)(hfac)₉], homometallic communication can be induced by selective laser excita-

Introduction

The understanding of energy processes occurring between lanthanide cations in chemical compounds (including downshifting, up-conversion and down-conversion) is important for the design of more efficient solar energy conversion and optical telecommunication devices, lasers or reagents for bioanalytical applications with improved performances.^[1,2] Trivalent europium, Eu^{III}, plays a crucial role in this context since its [Xe]4f⁶ electronic configuration is associated with a non-degenerate Eu(⁷F₀) ground state, which can be excited by visible photons into the non-degenerate Eu(⁵D₀) excited level.^[3] Each type of metallic Eu^{III} site in a chemical compound therefore possesses a unique electronic Eu(⁵D₀ \leftrightarrow ⁷F₀) transition that appears as a specific narrow band in its absorption and/or emission spec-

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	Supporting information for this article is available on the WWW under
	http://dx.doi.org/10.1002/chem.201403206.

tion and monitored with the help of high-resolution emission spectroscopy. The narrow and non-degenerated character of the $Eu({}^{5}D_{0}\leftrightarrow {}^{7}F_{0})$ transition excludes significant spectral overlap between donor and acceptor europium cations. Intramolecular energy-transfer processes in discrete polynuclear europium complexes are therefore limited to short distances, in agreement with the Fermi golden rule and with the kinetic data collected for $[Eu_{3}(L2)(hfac)_{9}]$ in the solid state and in solution. Consequently, trivalent europium can be considered as a valuable local structural probe in discrete polynuclear complexes displaying intermetallic separation in the sub-nanometric domain, a useful property for probing lanthanido-polymers.

tra, a property that has been extensively exploited during the last few decades for probing the local composition and geometry of the donor atoms around the metallic centre in coordination complexes, in hybrid materials and in macromolecules.^[4] When several europium cations are located at close distances. as found in polynuclear complexes or in doped solids, the operation of intermetallic $4f \rightarrow 4f$ energy-transfer processes may severely limit the use of Eu^{III} as a local structural probe because site assignments and distributions may become debatable.^[5] In a test, alumina garnets were statistically doped with $\operatorname{Eu}^{\scriptscriptstyle I\hspace{-1pt}I}$ and their various environments were addressed by using high-resolution emission spectroscopy upon selective excitation of the $Eu({}^{5}D_{0}{\leftarrow}^{7}F_{0})$ transitions. ${}^{[6]}$ The intermetallic $Eu{\rightarrow}Eu$ energy transfers were analysed within the frame of the Inokuti-Hirayama equation,^[7] which led to critical distances for 50% energytransfer efficiency larger than 15 Å for multipolar intermetallic communications occurring between $\operatorname{Eu}^{\scriptscriptstyle I\!I}$ lying in identical sites. These values dropped to 4 Å when the two metals occupied different sites (arbitrarily referred to as A and B),^[6] a result that is in line with the highly limited spectral overlap integral expected between the narrow $Eu_A({}^5D_0 \rightarrow {}^7F_0)$ emission and $Eu_{B}({}^{5}D_{0} \leftarrow {}^{7}F_{0})$ absorption bands.^[8] The lack of significant intermetallic communication occurring between different Eu^{III} on the sub-nanometric scale was taken for granted in coordination chemistry, and Eu^{III} was exploited as a structural probe for investigating polynuclear lanthanide complexes such as helicates,^[9] wheels,^[10] arrays^[11] and polygons.^[12] However, rational

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investigations of Eu \rightarrow Eu energy transfers operating in discrete homometallic polynuclear complexes remain scarce, and no deep root exists that justifies the systematic neglect of intermetallic migration when using Eu^{III} as a structural probe. With this fact in mind, we were recently alerted by the pioneer work of Platas-Iglesias and Charbonnière, who addressed this challenge for the neutral dinuclear complex [Eu₂(L1-6H)(H₂O)₂] in solution.^[13] Taking advantage of the different europium environments present in the latter complex in solution, time-correlated single-photon counting experiments obtained upon an initial ligand-centred ultraviolet excitation pulse suggested that a reversible Eu^A \leftrightarrow Eu^B intermetallic energy-transfer (EnT) process was taking place (first-order rate constants: $k_{EnT}^{Eu^A \rightarrow Eu^B} = k_{EnT}^{Eu^A \rightarrow Eu^B} = 980 \text{ s}^{-1}$ and critical distances for 50% energy-transfer efficiencies: $R_0^{Eu^A \rightarrow Eu^B} \approx 7-8 \text{ Å}$, Figure 1).^[13]



Figure 1. Chemical structure of the dinuclear complex $[Eu_2(L1-6H)(H_2O)_2]$ highlighting the first-order rate constants $k_{Ent}^{Eut^{A} \rightarrow Eut^{B}}$ and the critical distances for 50% efficiencies $R_{0}^{Eut^{A} \rightarrow Eut^{B}}$ characterising the intramolecular intermetallic energy-transfer processes (293 K, 0.01 M Tris-HCl at pH 7.4).^[13]

Though remarkable by its novelty, this study has the limitation of not being rigorously site selective due to the presence of several competitive energy pathways for the indirect excitation of both sites in $[Eu_2(L1-6H)(H_2O)_2]$. It is therefore difficult to ascertain the ultimate directions and mechanisms of intermetallic energy transfers in a case for which the $Eu({}^5D_0)$ levels are populated through higher-energy levels, such as $Eu({}^5D_1)$ and $Eu({}^5D_2)$.^[6]

To 1) push forward the understanding, modelling and predictable design of directional homometallic $4f \rightarrow 4f$ energytransfer processes occurring in discrete complexes and 2) establish unambiguous experimental conditions for using Eu^{III} as a pertinent structural probe in discrete polynuclear complexes, we report herein on the monitoring and interpretation of the Eu-centred photophysical behaviour exhibited by the C_{2v} -symmetrical trinuclear complex $[Eu_3(L2)(hfac)_9]$ (hfac = hexafluoroacetylacetonate) under selective excitations of the various $Eu({}^5D_0 \leftarrow {}^7F_0)$ transitions (Scheme 1). A particular effort has been focused on the derivation of a simple kinetic protocol for identifying and quantifying intermetallic $4f \rightarrow 4f$ communications.



Scheme 1. Chemical structures of the complexes $[Eu_3(L2)(hfac)_9]$, $[Eu(L3)-(hfac)_3]$, $[Eu(L4)(hfac)_3]$ and $[Eu_2(L5)(hfac)_6]$ studied in this work (hfac = hexa-fluoroacetylacetonate).

Results and Discussion

Theoretical background

For an isolated optically active centre S (S stands for sensitiser) excited at time t = 0, the probability $\varphi(t)$ of finding it in the excited state at time t follows a first-order kinetics and declines exponentially, namely, $\varphi(t) = \exp(-k_0^{s}t)$, in which k_0^{s} is the sum of the rate constants for radiative and non-radiative deactivation pathways affecting the centre **S**. Macroscopically, $\varphi(t)$ is proportional to the luminescence intensity I arising from the excited centres **S**^{*}, and $I(t) = I_0 \exp(-k_0^{S}t)$.^[7] When activator centres A are present in the vicinity of the sensitiser S, competitive resonant energy-transfer processes characterised by their probabilities $W_{S,A}$ obeying the Fermi's golden rule [Eq. (1)]^[8] contribute to the deactivation of the excited states S^* (H is the perturbation Hamiltonian modelling the interaction mechanism inducing $\mathbf{S}{\rightarrow}\mathbf{A}$ energy transfers and \varOmega_{SA} is the spectral overlap integral between the absorption spectrum of the activator A and the emission spectrum of the sensitiser S, which ensures the conservation of the energy).^[8]

$$W_{\mathsf{S},\mathsf{A}} = \frac{2\pi}{\hbar} |\langle \mathsf{S}\mathsf{A}^* | \mathsf{H} | \mathsf{S}^* \mathsf{A} \rangle|^2 \Omega_{\mathsf{S},\mathsf{A}} \tag{1}$$

We consider that $k_{EnT}^{S\to A}(R_k)$ is the rate constant for the energy transfer from the sensitiser **S** to an activator **A**_k located at a distance R_k . This rate constant $k_{EnT}^{S\to A}(R_k)$ is proportional to $W_{S,Ar}$ and the global probability $\varphi(t)$ declines more rapidly in the presence of *N* accessible activators. It can be described with the following mathematical expression [Eq. (2)]:^[7]

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$$\varphi(t) = \exp(-k_0^{\mathsf{S}} \cdot t) \prod_{k=1}^{N} \exp\left(-k_{\mathsf{EnT}}^{\mathsf{S} \to \mathsf{A}}(R_k) \cdot T\right)$$
$$= \exp\left[-\left(k_0^{\mathsf{S}} + \sum_{k=1}^{N} k_{\mathsf{EnT}}^{\mathsf{S} \to \mathsf{A}}(R_k)\right) \cdot t\right]$$
(2)

In other words, the analysis of the exponential decays of the **S**-centred luminescence profiles in the absence of activator, that is, when $\sum_{k=1}^{N} k_{EnT}^{S \to A}(R_k) = 0$, provides the characteristic life-time of **S**^{*} ($\tau_0^{S} = (k_0^{S})^{-1}$), whereas the same measurement performed in presence of the *N* activators yields $\tau_A^{S} = \left(k_0^{S} + \sum_{k=1}^{N} k_{EnT}^{S \to A}(R_k)\right)^{-1}$, from which the rate constants

[Eq. (3), left-hand side] and efficiencies [Eq. (4), left-hand side] for the ${\bm S} {\rightarrow} {\bm A}$ energy-transfer processes can be deduced: $^{[7]}$

$$\sum_{k=1}^{N} k_{EnT}^{S \to A}(R_k) = (\tau_A^S)^{-1} - (\tau_0^S)^{-1} = \sum_{k=1}^{N} k_0^S (R_{0,k}/R_k)^p$$
(3)

$$\eta_{\text{EnT}}^{S \to A} = \frac{\sum_{k=1}^{N} k_{\text{EnT}}^{S \to A}(R_k)}{k_0^{S} + \sum_{k=1}^{N} k_{\text{EnT}}^{S \to A}(R_k)} = \frac{\sum_{k=1}^{N} (R_{0,k}/R_k)^p}{1 + \sum_{k=1}^{N} (R_{0,k}/R_k)^p}$$
(4)

The interaction mechanism governing the $S \rightarrow A$ energytransfer process operating between a sensitiser and an activator separated by a distance R_k may be either 1) of multipolar electrostatic or magnetic origin $(k_{EnT}^{S \to A}(R_k) = k_0^S (R_{0,k}/R_k)^p$, in which p is the order of the multipolar interactions and $R_{0,k}$ is the critical distance for a 50% efficiency of energy transfer),^[14] or 2) of exchange coupling oriain $(k_{EnT}^{S \to A}(R_k) = \frac{2\pi}{\hbar} K^2 \Omega_{S,A} \exp(1 - R_k/R_{0,k})$, in which K is a constant with the dimension of energy).^[15] If we now focus on **S** and **A** being trivalent lanthanides displaying narrow electronic emission and absorption spectra resulting from the inner-sphere character of their [Xe]4fⁿ (n = 1-13) electronic configurations, the occurrence of large spectral overlap integrals Ω_{SA} is rare^[16] and noticeable intermetallic 4f-4f energy-transfer processes^[17] are limited to a few favourable S-A pairs such as Tb- $\mathsf{Eu},^{[18]} \ \mathsf{Tb}-\mathsf{Yb},^{[19]} \ \mathsf{Eu}-\mathsf{Nd},^{[20]} \ \mathsf{Yb}-\mathsf{Ho},^{[21]} \ \mathsf{Yb}-\mathsf{Tm}^{[22]} \ \text{and} \ \mathsf{Yb}-\mathsf{Er}.^{[2,23]}$ Moreover, the low expansion of the 4f orbitals restricts intermetallic 4f-4f energy-transfer processes to through-space interactions mediated by electrostatic multipolar mechanisms operative over long distances, as modelled on the right-hand side of Equations (3) and (4) (p=6 for dipole-dipole, p=8 for dipole-quadrupole and p = 10 for quadrupole-quadrupole interactions).^[14] Experimental critical distances for 50% heterometallic 4f \rightarrow 4f energy transfers typically lie in the 5 \leq R_0 \leq 15 Å range. On the other hand, the operation of resonant (i.e., $\Omega_{\rm SA}\!
eq$ 0) processes seems more probable between identical lanthanide cations, which are known to display minor crystalfield effects and negligible Stokes shifts. For these reasons, homometallic 4f-4f energy migration processes are thought to be efficient in crystals and in polynuclear complexes.^[6]

Synthesis and structural characterisation of [Eu₃(L2)(hfac)₉]

The series of tridentate binding units found in the segmental ligand **L2** was programmed for the design of C_2 -symmetrical trinuclear complexes, in which the two terminal coordination sites differ from the central one.^[9] Stoichiometric reaction of **L2** (1.0 equiv) with [Eu(diglyme)(hfac)₃] (3.0 equiv) yielded 80% of [Eu₃(**L2**)(hfac)₉], the crystal structure of which showed each europium being nine-coordinated by one meridional tridentate unit (N₃ for the central site, N₂O for the terminal sites) and by the six oxygen atoms of three bidentate hfac⁻ anions (Figure 2a).^[24] Beyond some minor changes affecting the geometry



Figure 2. a) Perspective view of the molecular structure of $[Eu_3(L2)(hfac)_3]$ in the solid state. Colours of atoms: grey = C, dark blue = N, red = O, pale blue = F, orange = Eu. Hydrogen atoms are omitted for clarity. b) Superimposition of the molecular structures of $[Eu_3(L2)(hfac)_3]$ (red) and $[Eu(L4)(hfac)_3]$ (twice, blue) and $[Eu(L3)(hfac)_3]$ (green). Hydrogen and fluorine atoms and isopropyl residues are omitted for clarity.

of the coordination spheres around the central Eu1 site (EuN₃O₆) and the terminal Eu2 and Eu3 sites (EuN₂O₇),^[24] Figure 2b shows that the coordination spheres in the molecular structure of [Eu₃(**L2**)(hfac)₉] are fully superimposable with those found in the mononuclear model complexes [Eu(**L3**)(hfac)₃] (central EuN₃O₆ site, Scheme 1)^[24] and [Eu(**L4**)(hfac)₃] (terminal EuN₂O₇ sites, Scheme 1).^[25]

The arrangement of the $[Eu_3(L2)(hfac)_9]$ molecules in the crystal structure is stabilised by weak offset intermolecular π -stacking interactions involving pairs of parallel aromatic benzimidazole rings belonging to neighbouring complexes related by inversion centres (Figure S1 in the Supporting Information). A dense packing is present in the crystals, which results in a complicated network of intermolecular Eu-Eu distances within the 10.8–20.0 Å range, comparable in length with distances of 9.593(1), 12.806(1) and 19.051(1) Å measured for the intramolecular Eu-Eu separations in $[Eu_3(L2)(hfac)_9]$ (Figure 2a

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and Figure S2 and Tables S1–S3 in the Supporting Information). $\ensuremath{^{[24]}}$

Photophysical properties of [Eu₃(L2)(hfac)₉]

Ligand-centred excitation ($\tilde{\nu}_{exc} = 28570-27030 \text{ cm}^{-1}$ or $\lambda_{exc} = 350-370 \text{ nm}$) of crystalline samples of $[\text{Eu}_3(\text{L2})(\text{hfac})_9]$ induces typical Eu-centred sharp emission bands resulting from the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ (J=0-6) transitions. This phenomenon is known as the antenna effect, in which ligand-centred light harvesting is followed by energy migration within the complex ($\eta_{\text{sens}}^{\text{L2,Eu}} = 48(9)$ %, solid state 293 K) and metal-centred emission (intrinsic quantum yield $\Phi_{\text{Eu}}^{\text{Eu}} = 51(6)$ %, solid state 293 K).^[24] The high-resolution monitoring of the Eu(${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$) emission bands shows the presence of two main components centred at 17250.2 cm⁻¹ (site A) and 17239.9 cm⁻¹ (site B) at 293 K (Figure 3a and Figure S3a in the Supporting Information), the sep-



Figure 3. High-resolution emission spectra recorded for $[Eu_3(L2)(hfac)_9]$ ($\tilde{\nu}_{exc} = 27\,030 \text{ cm}^{-1}$, full trace), $[Eu(L3)(hfac)_3]$ ($\tilde{\nu}_{exc} = 27\,400 \text{ cm}^{-1}$, dashed trace) and $[Eu(L4)(hfac)_3]$ ($\tilde{\nu}_{exc} = 28\,570 \text{ cm}^{-1}$, dotted trace) in the solid state at a) 293 and b) 10 K.

aration of which (10.3 cm⁻¹) is comparable with the 13 cm⁻¹ reported for the two different sites in $[Eu_2(L1-6H)(H_2O)_2]$.^[13] The usual low-energy drift of 1 cm⁻¹ per 24 K for the $Eu({}^5D_0 \rightarrow {}^7F_0)$ transition is observed on cooling,^[26] and this shifts the two main components towards 17 239.9 cm⁻¹ (site A) and 17 226.4 cm⁻¹ (site B1) at 10 K. A minor additional component at 17 232.3⁻¹ (site B2) is revealed by improved resolution at low

temperature (Figure 3b and Figure S3b in the Supporting Information). The energy tuning of the non-degenerate $Eu(^{5}D_{0} \rightarrow$ ⁷F₀) transitions can be mainly assigned to the specific charge borne by the europium centre.^[27] Frey and Horrocks^[28] proposed an empirical linear relationship [Eq. (5)] correlating the energy of this transition in a given complex $ilde{
u}_{ ext{calcd}}^{0 o 0}$ with its energy in the free ion $\tilde{\nu}_{\text{free}}^{0\to0} = 17374 \text{ cm}^{-1}$ and with the sum of the nephelauxetic effects δ_i produced by each set of n_i atoms of type *i* bound to Eu^{III} in its coordination sphere (CN is the coordination number). Equation (5) was parameterised at 295 K by using an empirical coefficient C_{CN} depending on the coordination number of the Eu^{III} cation in the complex ($C_{CN} = 1.0$ for CN = 9 found in $[Eu_3(L2)(hfac)_9])^{[28]}$ combined with specific nephelauxetic parameters $\delta_{\text{O-amide}} = -15.7 \text{ cm}^{-1}$, $\delta_{\text{O-betadiketo-}}$ $_{\rm nate} = -13.9 \ {\rm cm}^{-1}$, $\delta_{\rm N-pyridine} = -25.3 \ {\rm cm}^{-1}$ and $\delta_{\rm N-benzimidazole} = -25.3 \ {\rm cm}^{-1}$ -8.0 cm^{-1} :^[29]

$$\tilde{\nu}_{calcd}^{0\to0} = \tilde{\nu}_{free}^{0\to0} + C_{CN} \sum_{i=1}^{CN} n_i \delta_i$$
(5)

The introduction of these parameters into Equation (5) allows one to predict a value of $\tilde{\nu}_{calcd}^{0\to0} = 17249 \text{ cm}^{-1}$ for the central EuN₃O₆ site and $\tilde{\nu}_{calcd}^{0\to0} = 17242 \text{ cm}^{-1}$ for the terminal EuN₂O₇ sites in [Eu₃(L2)(hfac)₉] at 295 K. These two values are in good agreement with the experimental energies found in the high-resolution Eu(${}^{5}D_{0} \rightarrow {}^{7}F_{0}$) luminescence spectrum recorded at 293 K (Figure 3a).⁽³⁰⁾ The high-energy site A is thus assigned to the central EuN₃O₆ site, and the low-energy site B to the terminal EuN₂O₇ sites, a feature further confirmed by the emission energies of the related Eu(${}^{5}D_{0} \rightarrow {}^{7}F_{0}$) transitions recorded for the mononuclear model complexes [Eu(L3)(hfac)₃] (EuN₃O₆ site, dashed trace in Figure 3) and [Eu(L4)(hfac)₃] (EuN₂O₇ site, dotted trace in Figure 3).

The laser-selective excitations of the Eu(${}^{5}D_{0} \leftarrow {}^{7}F_{0}$) transitions corresponding to sites A and B in $[Eu_{3}(L2)(hfac)_{9}]$ result in the generation of two independent emission spectra, each being characterised by the occurrence of five specific components for the Eu(${}^{5}D_{0} \rightarrow {}^{7}F_{2}$) transition (Figure 4b), which are reminiscent of those recorded upon related selective excitations of the mononuclear model complexes $[Eu(L3)(hfac)_{3}]$ (Figure 4a) and $[Eu(L4)(hfac)_{3}]$ (Figure 4c).

Selective excitations of the high-energy central EuN₃O₆ site (site A) in [Eu₃(L2)(hfac)₉] or in [Eu(L3)(hfac)₃] produce monoexponential decays for the Eu(${}^{5}D_{0} \rightarrow {}^{7}F_{2}$) emission profile with $\tau_{\text{siteA}}^{\text{Eu,L2}}({}^{5}\text{D}_{0}) = 0.93(3) \text{ ms}$ characteristic lifetimes of and $\tau_{siteA}^{Eu,L3}({}^{5}D_{0}) = 0.92(2)$ ms at 10 K (Table 1 and Table S4 and Figure S4 in the Supporting Information). A similar behaviour is observed upon selective excitation of the low-energy terminal EuN₂O₇ sites (site B) in [Eu₃(L2)(hfac)₉] or in [Eu(L4)(hfac)₃] for which the mono-exponential decays give slightly shorter lifetimes of $\tau_{siteB}^{Eu,L2}({}^5D_0)\!=\!0.82$ (2) ms and $\tau_{siteB}^{Eu,L4}({}^5D_0)\!=\!0.81$ (1) ms at 10 K (Table 1 and Table S4 and Figure S4 in the Supporting Information). Related kinetic data collected at 77 and 293 K did not show major variations (Table S4 in the Supporting Information). In summary, the selective excitation of the Eu(${}^{5}D_{0} \leftarrow {}^{7}F_{0}$) transitions assigned to each coordination site in [Eu₃(L2)(hfac)₉]





Figure 4. High-resolution $Eu({}^{5}D_{0} \rightarrow {}^{7}F_{2})$ emission spectra recorded upon laserselective excitation in the solid state at 10 K of the $Eu({}^{5}D_{0} \leftarrow {}^{7}F_{0})$ transitions for a) [Eu(L3)(hfac)_{3}] ($\tilde{\nu}_{exc} = 17244 \text{ cm}^{-1}$, site $A = EuN_{3}O_{6^{r}}$ dotted trace), b) [Eu₃(L2)(hfac)_{3}] ($\tilde{\nu}_{exc} = 17243 \text{ cm}^{-1}$, site $A = EuN_{3}O_{6^{r}}$ dotted trace and $\tilde{\nu}_{exc} = 17224 \text{ cm}^{-1}$, site $B = EuN_{2}O_{7^{r}}$ full trace) and c) [Eu(L4)(hfac)_{3}] ($\tilde{\nu}_{exc} = 17227 \text{ cm}^{-1}$, site $B = EuN_{2}O_{7^{r}}$ full trace).

Table 1. Characteristic Eu(${}^{5}D_{0}$) luminescence lifetimes $\tau({}^{5}D_{0})$ deduced from the analysis of three components of the Eu(${}^{5}D_{0} \rightarrow {}^{7}F_{2}$) transitions (λ_{em} or $\tilde{\nu}_{em}$) upon selective excitation of the Eu(${}^{5}D_{0} \leftarrow {}^{7}F_{0}$) transition (λ_{exc} or $\tilde{\nu}_{exc}$) in [Eu₃(L2)(hfac)₉] at 10 K in the solid state.

Site	λ _{exc} [nm]	$ ilde{ u}_{ m exc}$ [cm ⁻¹]	λ _{em} [nm]	$ ilde{ u}_{em}$ [cm ⁻¹]	$\tau({}^{5}D_{0})$ [ms]
EuN ₃ O ₆ EuN ₂ O ₇	579.95 580.60	17 243 17 224	614.4 616.4 620.5 614.4 616.4 620.5	16276 16223 16116 16276 16223 16116	0.962(4) 0.910(6) 0.903(2) 0.836(5) 0.809(2) 0.808(1)

produces 1) its own emission spectrum and 2) its own excitedstate lifetime value. This behaviour is compatible with the lack of detectable intramolecular intermetallic europium-to-europium energy transfer in the 10–293 K temperature range.

In search of intermetallic Eu \rightarrow Eu energy-transfer processes operating in [Eu₃(L2)(hfac)₉]

To establish a model of the intermetallic Eu \rightarrow Eu energy transfer detected in [Eu₂(L1-6H)(H₂O)₂], Platas-Iglesias and Charbonnière applied a simplified kinetic treatment that neglected 1) possible successive excitations of the sensitisers and 2) the depletion of the population density of the ground state, even for large incident pump intensities. Based on the experimental observation of an initial rising of the intensity of the Eu(⁵D₀)centred emission profile assigned to site B in [Eu₂(L1-6H)(H₂O)₂] upon ligand excitation, the authors concluded that a reversible intermetallic energy transfer occurred in their dinuclear complex with $k_{EnT}^{Eu^A \rightarrow Eu^B} = k_{EnT}^{Eu^A \rightarrow Eu^A} = 980 \text{ s}^{-1}$ (Figure 1).^[13] Following this reasoning, the systematic detection of mono-exponential emission decays upon selective excitation of each Eu site in [Eu₃(**L**2)(hfac)₉] suggests that no significant intermetallic communication occurs between the site A (EuN₃O₆, $\tilde{\nu}_{A}^{0\rightarrow0} =$ 17250 cm⁻¹) and the site B (EuN₂O₇, $\tilde{\nu}_{B}^{0\rightarrow0} =$ 17240 cm⁻¹), and this despite the facts that 1) the intermetallic distances between the europium cations are comparable in [Eu₃(**L**2)(hfac)₉] (10 Å) and in [Eu₂(**L**1-6H)(H₂O)₂] (7 Å)^[13] and 2) the Eu(⁷F₀-⁵D₀) energy gaps are similar ($\tilde{\nu}_{A}^{0\rightarrow0} - \tilde{\nu}_{B}^{0\rightarrow0} =$ 13 cm⁻¹ for [Eu₂(**L**1-6H)(H₂O)₂] and 10 cm⁻¹ for [Eu₃(**L**2)(hfac)₉]).

A global kinetic scheme for the trinuclear europium complex $[Eu_3(L2)(hfac)_9]$ possessing two different metallic sites in idealised C_{2v} symmetry (referred to as BAB for characterising the europium sites) is shown in Figure 5, and Equations (6) and (7) collect the pertinent set of first-order differential equations obeying the mass conservation given in Equation (8) (in which $N^{|i|}$ is the normalised population density in state i.^[31] The pumping rate constant $k_A^{\text{exc}(0\to1)}$ is given by Equation (9), in which λ_P is the pump wavelength, P is the incident pump intensity, $\sigma_A^{0\to1}$ is the absorption cross section of the sensitisercentred $0\to1$ transition, h is the Planck constant and c is the speed of light in vacuum.^[32]

$$\left[\frac{\mathrm{d}N^{|i\rangle}}{\mathrm{d}t}\right] = \mathbf{M} \times \left[N^{|i\rangle}\right] \tag{6}$$

$$\mathbf{M} = \begin{bmatrix} -k_{A}^{\text{exc}(0\to1)} & k_{A}^{1\to0} & k_{B}^{1\to0} & 0 \\ k_{A}^{\text{exc}(0\to1)} & -\binom{k_{A}^{1\to0}+}{2k_{\text{EnT}}^{\text{Eu}^{A}\to\text{Eu}^{B}}} & k_{\text{EnT}}^{\text{Eu}^{B}\to\text{Eu}^{A}} & k_{B}^{1\to0} \\ 0 & 2k_{\text{EnT}}^{\text{Eu}^{A}\to\text{Eu}^{B}} & -\binom{k_{A}^{\text{exc}(0\to1)}}{+k_{\text{EnT}}^{B}} & k_{A}^{1\to0} \\ 0 & 0 & k_{A}^{\text{exc}(0\to1)} & -\binom{k_{A}^{1\to0}}{+k_{B}^{\text{Eu}^{A}\to\text{Eu}^{A}}} \end{bmatrix}$$

$$\sum_{i=0}^{4} N^{|i\rangle} = N_{\text{tot}} = 1$$
(8)

$$k_{A}^{\exp(0\to1)} = \frac{\lambda_{P}}{hc} P \sigma_{A}^{0\to1} = f P \sigma_{A}^{0\to1}$$
(9)

normalised steady-state population The densities $\left(\left[dN^{|i\rangle}/dt\right] = [0]\right)$ induced by the selective continuous-wave irradiation of the high-energy EuN₃O₆ site (site A) in [Eu₃(L2)- $(hfac)_{9}$ are obtained by the combination of Equations (6)–(8), followed by a matrix symmetrisation and an inversion (Figure 6; see Appendix 1 in the Supporting Information). As expected, the normalised population densities of the Eu-centred excited states, hence their associated emission intensities, depend on the regime of energy-transfer processes, and three different model situations are considered in Figure 6. These models correspond to 1) absence of communication with $k_{EnT}^{Eu^A \rightarrow Eu^B} = k_{EnT}^{Eu^B \rightarrow Eu^A} = 0 \text{ s}^{-1}$ (full traces), 2) irreversible communication with $k_{EnT}^{Eu^A \rightarrow Eu^B} = 980 \text{ s}^{-1}$ and $k_{EnT}^{Eu^A \rightarrow Eu^A} = 0 \text{ s}^{-1}$ (dashed traces)





Figure 5. Kinetic scheme depicting the modelling of the intermetallic energy-transfer processes taking place in $[Eu_3(L2)(hfac)_9]$ considered as an idealised C_{2v} -symmetrical BAB complex. $k_A^{1-\circ}$ stands for the global (i.e., the sum of radiative and non-radiative) decay rate constant of the A* excited state and $k_B^{Eu^{3}-Eu^{3}}$ similarly applies for the B* excited state. $k_{Eu}^{Lu^{4}-Eu^{3}}$ and $k_{Eu}^{Eu^{4}-Eu^{3}}$ are the rate constants for intramolecular intermetallic energy transfers and $k_A^{exc(0-1)}$ is the pumping rate constant [Eq. (9)].



Figure 6. Normalised steady-state population densities computed for the ground state ($|0\rangle = BAB$) and excited levels ($|1\rangle = BA^*B$, $|2\rangle = B^*AB$ and $|3\rangle = B^*A^*B$) upon selective irradiation^[33] of the high-energy EuN₃O₆ site (site A) at increasing incident pump intensity for $[Eu_3(L2)(hfac)_3]$ ($\lambda_P = 579.7$ nm (site A) absorption cross sections $\sigma_A^{0-1} = 3.8 \times 10^{-25} \text{ m}^2$, $k_A^{1-0} = (\tau_{\text{siteA}}^{\text{EuA}})^{-1} = (920 \ \mu\text{s})^{-1}$, $k_B^{1-0} = (\tau_{\text{siteB}}^{\text{EuA}})^{-1} = (805 \ \mu\text{s})^{-1}$). The full traces correspond to $k_{\text{EuA}}^{\text{EuA}^{-\text{EuB}^{0}}} = k_{\text{EuA}}^{\text{EuA}^{0}} = 0 \text{ s}^{-1}$ (absence of communication), the dashed traces refer to $k_{\text{EuA}}^{\text{EuA}^{0}-\text{EuB}^{0}} = 980 \text{ s}^{-1}$ and $k_{\text{EuA}}^{\text{EuA}^{0}-\text{EuB}^{0}} = k_{\text{EnT}}^{\text{EuA}^{0}-\text{EuB}^{0}} = 980 \text{ s}^{-1}$ (reversible $A \leftrightarrow B$ communication) and the dotted traces hold for $k_{\text{EnT}}^{\text{EuA}^{0}-\text{EuB}^{0}} = 980 \text{ s}^{-1}$ (reversible $A \leftrightarrow B$ communication).

and 3) reversible communication with $k_{EnT}^{Eu^{A} \rightarrow Eu^{B}} = k_{EnT}^{Eu^{B} \rightarrow Eu^{A}} =$ 980 s⁻¹ (dotted traces).^[34]

We note that, under reasonable pump intensities ($P < 20 \text{ Wmm}^{-2}$), the normalised population densities of the singly excited levels BA*B ($|1\rangle$) and B*AB ($|2\rangle$) remain marginal ($\leq 2\%$), whereas that of the doubly excited level B*A*B ($|3\rangle$) is negligible ($\leq 0.1\%$). This situation leads to a minor depletion of the ground-state population density under standard pump-

ing intensities, for which the approximation $N^{[0]} \approx N_{tot}$ holds. With this hypothesis in mind, Equations (6) and (7), which are strictly limited to the consideration of intramolecular energytransfer processes operating in a discrete complex, can be easily extended for the modelling of the sum of intra- and intermolecular Eu \rightarrow Eu energy-transfer processes occurring in a crystal of [Eu₃(L2)(hfac)₉] as measured in this study (see Appendix 2 in the Supporting Information).^[35]

$$\left[\boldsymbol{N}^{[i]}\right] = \sum_{i=0}^{3} \left\{ \boldsymbol{e}^{\lambda_{i}t} \prod_{\substack{j=0\\j\neq i}}^{3} \left\{ \mathbf{M} - \lambda_{j}\mathbf{I} \right\} / \prod_{\substack{j=0\\j\neq i}}^{3} \left(\lambda_{i} - \lambda_{j}\right) \times \left[\boldsymbol{N}_{0}^{[i]}\right] \right\}$$
(10)

The time-dependent relaxation of the population densities of the different Eu-centred excited states, and hence of their emission intensities, following a pulsed excitation can be modelled by solving Equations (6) and (7) with the help of projection operators using the Lagrange-Sylvester formula to give Equation (10), in which λ_i are the eigenvalues of the square kinetic matrix ${\bf M}$ and ${\bf I}$ is the identity matrix (see Appendix 3 in the Supporting Information).^[31] Using an arbitrarily normalised population density of $N_0^{(1)} = 0.1$ in the BA*B excited state produced by the initial pulsed excitation of site A, Equation (10) allows the prediction of strict mono-exponential relaxations for the A-centred excited state as long as no reverse $\mathsf{EuA}\!\leftarrow\!\mathsf{EuB}$ energy transfer occurs ($k_{Ent}^{Eu^{B} \rightarrow Eu^{A}} = 0$, Equations (A3-4) and (A3-5) in the Supporting Information). The rates of the A-centred exponential decays correspond to $k_{decay}(BA^*B) = k_A^{1 \to 0} = 1087 \text{ s}^{-1}$ in the absence of $Eu^A \to Eu^B$ energy transfer $(k_{EnT}^{Eu^A \to Eu^B} = 0, \text{ full})$ trace in Figure 7a, Equation (A3-4) in the Supporting Informa-tion), and to $k_{\text{decay}}(BA^*B) = k_A^{1 \rightarrow 0} + 2k_{\text{EnT}}^{Eu^A \rightarrow Eu^B} = 3047 \text{ s}^{-1}$ when $k_{EnT}^{Eu^A \rightarrow Eu^B} = 980 \text{ s}^{-1}$ (dashed trace in Figure 7a, Equation (A3-5) in the Supporting Information). The implementation of a reversible $Eu^{A} \rightleftharpoons Eu^{B}$ energy-transfer process $(k_{EnT}^{Eu^{B} \rightarrow Eu^{A}} = k_{EnT}^{Eu^{A} \rightarrow Eu^{B}} =$ 980 s⁻¹) results in a bi-exponential decay describing the relaxation of A* with two different characteristic rate constants of $k_{\text{decay}}(BA^*B) = 4080 \text{ s}^{-1}$ (64%) and $k_{\text{decay}}^2(BA^*B) = 1190 \text{ s}^{-1}$ (36%) (dotted trace in Figure 7a, Equation (A3-6) in the Supporting Information).

The discrimination between the different regimes of energy transfer is much simpler when the luminescence profile of the B centre is monitored upon a pulsed excitation of the A centre. Firstly, the emission from the B centre only occurs when $k_{EnT}^{Eu^A \rightarrow Eu^B} \neq 0$ (full trace in Figure 7 b illustrates the situation for $k_{EnT}^{Eu^A \rightarrow Eu^B} = 0$). This situation can be used as a criterion revealing an $Eu^A \rightarrow Eu^B$ energy transfer following a selective A-centred excitation. Secondly, the time-dependent intensity profile arising from the B centre systematically shows a bi-exponential feature with a rising time strongly correlated with the decay rate of the donor BA*B level and a relaxation time corresponding to the deactivation of the B*AB excited state (dashed and dotted traces in Figure 7 b). The accurate differentiation between irreversible and reversible intermetallic energy transfer further requires an exact fit of the bi-exponential experimental curves (Equations A3-5 and A3-6 in the Supporting Information).^[13] Let us stress here that the arbitrary choice of $k_{EnT}^{Eu^A \rightarrow Eu^B} = 980 \text{ s}^{-1}$,^[34] taken in the same range as $k_{decay}(BA^*B) = k_A^{1 \rightarrow 0} = 1087 \text{ s}^{-1}$ and

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Figure 7. Time evolution of the various normalised population densities computed with Equation (10) for $[Eu_3(L2)(hfac)_9]$ at 10 K following an initial selective laser pulse producing a normalised population density of $N_0^{(1)} = 0.1$ in the BA*B excited state and showing the profiles for a) the BA*B excited state ($|1\rangle$ in Figure 5) and b) the B*AB excited state ($|2\rangle$ in Figure 5). The full traces correspond to $k_{EnT}^{Eu^A - Eu^B} = k_{EnT}^{Eu^A - Eu^B} = 980 \text{ s}^{-1}$ (absence of communication), the dashed traces refer to $k_{EnT}^{Eu^A - Eu^B} = 980 \text{ s}^{-1}$ and $k_{EnT}^{Eu^A - Eu^B} = 980 \text{ s}^{-1}$ (irreversible A \rightarrow B communication) and the dotted traces hold for $k_{EnT}^{Eu^A - Eu^B} = 980 \text{ s}^{-1}$ (reversible A \leftrightarrow B communication).

 $k_{\text{decay}}(B^*AB) = k_B^{1 \rightarrow 0} = 1242 \text{ s}^{-1}$ for the simulations of the europium-centred luminescence decays occurring in [Eu₃(L2)(hfac)₉] (Figure 7), is not critical for establishing the occurrence of intermetallic energy-transfer processes, and the use of $k_{EnT}^{Eu^A \rightarrow Eu^B} \ll$ $k_{A,B}^{1\to0}$ or $k_{EnT}^{Eu^A \to Eu^B} \gg k_{A,B}^{1\to0}$ (Figures S5 and S6 in the Supporting Information) or of variable characteristic lifetimes for the A* and B* excited states (Figure S7 in the Supporting Information) lead to similar conclusions. According to the first criterion, the experimental mono-exponential decay traces observed upon monitoring the emission that corresponds to the $Eu({}^{5}D_{0} \rightarrow {}^{7}F_{2})$ transition arising from the EuN_3O_6 site in $[Eu(L3)(hfac)_3]$ or in [Eu₃(L2)(hfac)₉] following a short pulsed laser excitation on the same site (in the order of 7 ns) excludes the operation of an intermetallic backward Eu^B→Eu^A energy-transfer process. Following the second criterion, the absence of a signal showing a rising time for the $Eu({}^{5}D_{0} \rightarrow {}^{7}F_{2})$ emission originating from the terminal EuN₂O₇ sites in [Eu₃(L2)(hfac)₉] upon pulsed laser excitation of the EuN₃O₆ site unambiguously confirms the lack of any significant forward $Eu^A \rightarrow Eu^B$ energy transfer occurring in the trinuclear complex $[Eu_3(L2)(hfac)_9]$. Taking into account 1) the non-negligible 10 cm⁻¹ energy gap between the Eu(${}^{5}D_{0}$) excited states of the sensitiser and of the activator (Figure 3), 2) the small full width at half-height of the Eu(${}^{5}D_{0} \leftrightarrow {}^{7}F_{0}$) transitions (Figure 3) and 3) the minute oscillator strengths of the latter transitions, the lack of any detectable intermetallic energy-transfer process between the different europium sites in the trinuclear complex indeed obeys the Fermi golden rule [Eq. (1)]. This situation is substantiated by the gathering of closely related, but broadened spectroscopic and kinetic data recorded for $[Eu_3(L2)(hfac)_9]$ in acetonitrile solution, in which the energy transfers are strictly limited to intramolecular processes (Table S5 and Figures S8–S10 in the Supporting Information).

Intermetallic Tb \rightarrow Eu energy-transfer processes operating in [TbEu(L5)(hfac)₆]

To get rid of the limitations brought by the faint spectral overlap integral between the absorption and emission spectra of Eu[™] centres in a discrete complex, we extend our investigation to the parent dinuclear complex [Ln₂(L5)(hfac)₆], the structure of which possesses two trivalent lanthanide cations in similar LnN₂O₇ sites separated by 12.594(1) Å (Figure S11 in the Supporting Information).^[24] The pseudo-equivalence of the sites in L5 makes the homodinuclear complexes of no use for investigating intramolecular intermetallic energy-transfer processes, but it offers the advantage of limiting the number of different species produced upon statistical reaction with mixtures of different lanthanide cations.^[36] With this fact in mind, the reaction of the di-tridentate ligand L5 with a 1:1 ratio of Tb(hfac)₃ and Eu(hfac)₃ produces a mixture of only three well-defined species, $[Tb_2(L5)(hfac)_6]$, $[TbEu(L5)(hfac)_6]$ and $[Eu_2(L5)(hfac)_6]$, termed {TbEu(L5)(hfac)₆} for the remaining part of the discussion, and for which one expects a 1:2:1 statistical ratio. As expected for the Tb/Eu pair,[18] the considerable spectral overlap between the $Tb({}^{5}D_{4} \rightarrow {}^{7}F_{4})$ transition in the emission spectrum of $[Tb_2(L5)(hfac)_6]$ and the $Eu({}^5D_0 \leftarrow {}^7F_0)$ transition in the excitation spectrum of $[Eu_2(L5)(hfac)_6]$ ensures efficient $Tb \rightarrow Eu$ energy-transfer processes (Figure 8a). Consequently, the selective laser excitation of the $Tb({}^{5}D_{4} \leftarrow {}^{7}F_{6})$ transition in {TbEu(L5)-(hfac)₆} (λ_{exc} = 491 nm or $\tilde{\nu}_{exc}$ = 20367 cm⁻¹) shows Tb(⁵D₄)-centred emission arising from [Tb₂(L5)(hfac)₆], but also Eu(⁵D₀)-centred emission originating from the population of the Eu(⁵D₀) excited state fed by the Tb \rightarrow Eu energy-transfer processes occurring in [TbEu(L5)(hfac)₆] (Figure 8b). The associated luminescence profile displays a mono-exponential decay for the Tb(⁵D₄) excited state with $k_{\text{Tb}}^{\{\text{EuTb}\},\text{L5}} = (\tau_{\text{Tb}}^{\{\text{EuTb}\},\text{L5}})^{-1} = (695 \text{ } \mu\text{s})^{-1}$ at 10 K (Table 2, entry 6), which can be assigned to the luminescence of the homometallic [Tb₂(L5)(hfac)₆] complex contained in ${TbEu(L5)(hfac)_6},$ in agreement with $k_{\text{Tb}}^{1\rightarrow0} = (\tau_{\text{Tb}}^{\text{TbTb,L5}})^{-1} = (691(6) \text{ }\mu\text{s})^{-1}$ measured in pure samples at 10 K (Table 2, entry 2). Because of the thermal activation of Tb(${}^{5}D_{4}$) \rightarrow L5(${}^{3}\pi^{*}$) back-transfers,^[18] the Tb(${}^{5}D_{4}$) excited-state lifetimes dropped to a few microseconds when placed at room temperature (Table 2, entries 4 and 8). Attempts to fit these decay profiles with multi-exponential functions systematically failed, which suggests that either no intermetallic transfer occurs (criterion 1) or that the residual $Tb(^{5}D_{4})$ -centred emission originating from the heterodinuclear [TbEu(L5)(hfac)₆]





Figure 8. a) Normalised Tb(${}^{5}D_{4} \rightarrow {}^{7}F_{4}$) emission of [Tb2(**L5**)(hfac)₆] ($\tilde{\nu}_{exc} = 28\,170 \text{ cm}^{-1}$, full trace) highlighting the spectral overlap with the Eu(${}^{5}D_{0} \leftarrow {}^{7}F_{0}$) excitation spectrum recorded for [Eu₂(**L5**)(hfac)₆] ($\tilde{\nu}_{exc} = 16\,260 \text{ cm}^{-1}$, dashed trace, solid state at 77 K). b) Emission spectrum of {TbEu(**L5**)(hfac)₆} recorded upon laser-selective excitation of the Tb(${}^{5}D_{4} \leftarrow {}^{7}F_{6}$) transition ($\tilde{\nu}_{exc} = 20\,367 \text{ cm}^{-1}$) at 10 K.

complex is too faint to be detected in the presence of the intense Tb-centred emission produced by $[Tb_2(L5)(hfac)_6]$.

Focusing on the second criterion, we can indeed observe a bi-exponential luminescence intensity profile with a short



Figure 9. Luminescence intensity profile of Eu(${}^{5}D_{0} \rightarrow {}^{7}F_{2}$) in {TbEu(L5)(hfac)₆} recorded upon selective excitation of the Tb(${}^{5}D_{4} \leftarrow {}^{7}F_{6}$) transition ($\tilde{\nu}_{exc} = 20.367 \text{ cm}^{-1}$) at 298 K. The dotted black trace corresponds to the biexponential fit computed by using $k_{EnT}^{Tb-Eu} = (1.24(1) \text{ }\mu\text{s})^{-1} = 8.07(7) \times 10^{5} \text{ s}^{-1}$ and $k_{Eu}^{1-0} = (\tau_{Eu}^{EuTb,L5})^{-1} = (738(6) \text{ }\mu\text{s})^{-1} = 1.36(1) \times 10^{3} \text{ s}^{-1}$ (Table 2, entry 8). The inset shows the profile during the first 50 μs .

rising time within the microsecond range, followed by a much longer decay lifetime within the millisecond range for the $Eu({}^{5}D_{0} \rightarrow {}^{7}F_{2})$ emission signal recorded upon Tb-sensitisation of {TbEu(L5)(hfac)₆} ($\lambda_{em} = 618 \text{ nm}$ or $\tilde{\nu}_{em} = 16180 \text{ cm}^{-1}$) (Table 2, entries 5-8, Figure 9, and Figure S12 in the Supporting Information). Taking into account that the long decay rate mirrors the value measured for the pure homometallic [Eu₂(L5)(hfac)₆] complex $k_{\text{Tb}}^{1 \to 0} = (\tau_{\text{Tb}}^{\text{EuEu,L5}})^{-1} = (800(10) \, \mu \text{s})^{-1} \, (24)$ we conclude that the observed rising time is an acceptable estimation for the rate of the intermetallic $Tb \rightarrow Eu$ energy-transfer processes $(k_{EnT}^{Tb \rightarrow Eu} \simeq (\tau_{Eu,rising}^{TbEu,L5})^{-1}$ operating in {TbEu(**L5**)(hfac)₆} ້≫ $k_{\text{Tb}}^{1 \to 0} = (r_{\text{Tb}}^{\text{TbTb,L5}})^{-1}$, Table 2, column 9). The experimental energy-transfer rate constants fall within the $0.6 \times 10^5 \text{ s}^{-1} <$ $k_{\text{EnT}}^{\text{Tb}\rightarrow\text{Eu}}\!<\!1.1\!\times\!10^6~\text{s}^{-1}$ range, but the timescale limit of our setup (\approx 0.1–0.5 $\mu s)$ prevents a deeper analysis of these data (see Table 2 and Figure S12 in the Supporting Information). Finally, if we assume that the Tb-Eu energy-transfer process evi-

Table 2. Characteristic Tb(${}^{5}D_{4}$) and Eu(${}^{5}D_{0}$) luminescence lifetimes (τ) obtained upon ligand-centred (λ_{exc} =355 nm) or Tb(${}^{5}D_{4}$ $\leftarrow^{7}F_{6}$)-centred (λ_{exc} =491 nm) excitation for [Tb₂(L5)(hfac)_{6}] and {TbEu(L5)(hfac)_{6}} in the solid state.

Entry	Compound	Т	λ_{exc}	$\tilde{\nu}_{exc}$	λ_{em}	${ ilde u}_{ m em}$	τ	k ^{tb→Eu} FnT	$\eta_{ extsf{Ent}}^{ extsf{Tb} ightarrow extsf{Eu}[b]}$	$R_0^{\text{Tb} \rightarrow \text{Eu}}$
		[K]	[nm]	[cm ⁻¹]	[nm]	[cm ⁻¹]	[µs]	[s ⁻¹] ^[a]		[Å] ^[b]
1	$[Tb_2(L5)(hfac)_6]$	10	355	28170	542	18450	725(6) Tb(⁵ D ₄)	_	-	-
2		10	491	20430	542	18450	691(6) Tb(⁵D₄)	-	-	-
3		298	355	28170	545	18350	42(1) Tb(⁵ D ₄)	-	-	-
4		298	491	20430	545	18350	33(1) Tb(⁵D₄)	-	-	-
5	{TbEu(L5)(hfac) ₆ }	10	355	28170	542	18450	745(3) Tb(⁵ D ₄)	-	-	-
					618	16180	1.59(1) Eu(⁵D₀) rising	6.29(4)×10 ⁵	0.99(1)	\geq 30
							728(6) Eu(⁵ D ₀) decay	-	-	-
6		10	491	20430	542	18450	695(6) Tb(⁵ D ₄)	-	-	-
					618	16180	0.9(2) Eu(⁵ D ₀) rising	$1.1(3) \times 10^{6}$	0.9(2)	\geq 35
							807(5) Eu(⁵ D ₀) decay	-	-	-
7		298	355	28170	542	18450	1.1(1) Tb(⁵ D ₄)	-	-	-
					618	16180	1.02(1) Eu(⁵D₀) rising	9.8(1)×10 ⁵	0.98(1)	23(2)
							792(8) Eu(⁵ D ₀) decay	-	-	-
8		298	491	20430	542	18450	0.66(3) Tb(⁵ D ₄)	-	-	-
					618	16180	1.24(1) Eu(⁵ D ₀) rising	8.07(7)×10 ⁵	0.96(1)	22(1)
							738(6) Eu(⁵ D ₀) decay	-	-	-

[a] Estimated from the rising time of $Eu(^{5}D_{0})$ -centred emission (see text). The uncertainties are those obtained during the bi-exponential fitting process. [b] Computed by using Equation (4) for an isolated molecule within the frame of the dipole–dipole mechanism.



denced in {TbEu(**L5**)(hfac)₆} relies exclusively on intramolecular intermetallic communications, the use of Equation (4) within the frame of a dipole–dipole mechanism (p = 6) allows the estimation of close to quantitative efficiencies ($\eta_{EnT}^{Tb \rightarrow Eu} \ge 90\%$) and distances for the 50% Tb–Eu energy transfer in the nanometric range ($R_0 \ge 20$ Å, Table 2, columns 10 and 11).

Conclusion

Because of the very difficult preparation of discrete and pure heterometallic f-f' complexes, the detailed understanding of intermetallic $4f \rightarrow 4f$ energy-transfer processes mainly relies on photophysical data collected in doped materials as exemplified in this work with the 90-99% efficiency estimated for the Tb \rightarrow Eu energy transfer operating in {TbEu(L5)(hfac)₆}, a solid sample containing a mixture of [Tb₂(L5)(hfac)₆], [TbEu(L5)-(hfac)₆] and [Eu₂(L5)(hfac)₆] complexes. Due to 1) the considerable spectral overlap observed between the Tb(${}^{5}D_{4} \rightarrow {}^{7}F_{4}$) emission and the Eu(${}^{5}D_{0} \leftarrow {}^{7}F_{0}$) absorption spectra and 2) the presence of an efficient through-space electric energy-transfer multipolar mechanism $[|\langle SA^*|H|S^*A\rangle|^2 > 0$ in Eq. (1)],^[19] the critical distance for 50% energy transfer for the Tb/Eu pair in [TbEu(L5)(hfac)₆] exceeds 20 Å and a quantitative directional intermetallic energy migration occurs. The situation is less documented for energy-transfer processes taking place between lanthanides of the same nature in polynuclear homometallic complexes. A major limitation is due to the strict equivalence of the lanthanide ions occupying identical sites in a discrete complex, a situation occurring in [Ln₂(L5)(hfac)₆]. A considerable spectral overlap integral is expected, but the luminescence intensity profile produced by the emissive metals is not affected by the intermetallic energy-transfer rate constants. Consequently, reliable data concerning the efficiency of $\mathsf{Eu}\!\rightarrow\!\mathsf{Eu}$ energy migration processes involving identical metallic sites could only be obtained for doped solids, for which statistical distribution makes identical sites different in terms of intermetallic communications. Under these conditions, detailed fits to the Inokuti–Hirayama equation^[7] give estimates of $R_0 \approx 15$ Å for the critical distances for 50% energy transfer between europium cations in identical environments.^[6] Polynuclear complexes possessing different metallic sites, as found in [Eu2(L1-6H)(H_2O_2],^[13] in [Eu₃(**L2**)₃]^{9+[9]} and in [Eu₃(**L2**)(hfac)₉], allow a simple monitoring of the luminescence intensity profile of one specific Eu^{III} site upon selective excitation of the other coordination site. With this setup, we demonstrated that the acquisition of a bowl-shaped luminescence profile is a good criterion indicating the occurrence of intermetallic $4f \rightarrow 4f$ energy-transfer processes, a situation detected experimentally for [Eu₂(L1-6H)(H₂O)₂] in solution upon non-selective ligandcentred excitation (Eu.-Eu = 7.05 Å, energy gap of 13 cm⁻¹, $R_0 \ge 7$ Å).^[13] Surprisingly, our thorough analysis of the luminescence arising from the $Eu({}^{5}D_{0})$ levels in $[Eu_{3}(L2)(hfac)_{9}]$ upon selective metal excitations suggests the absence of significant intermetallic $Eu \rightarrow Eu$ communication operating between the two different sites, which are separated by 1) a distance of circa 10 Å and 2) an energy gap of 10 cm⁻¹. In this context, it is worth reminding ourselves here that $Eu \rightarrow Eu$ energy-transfer processes taking place between different sites in Eu-doped alumina are limited to short distances with $R_0 = 4$ Å.^[6] As Eu^{III} has often been used as a structural probe in polynuclear complexes without any report of complications originating from intermetallic energy migration,^[9-12,20b] we can conclude that long-range Eu→Eu energy migration processes in polynuclear complexes are limited to communications between isoenergetic sites, whereas directional intramolecular energy transfers between different sites do not exceed a few hundreds of picometres upon selective excitation of specific Eu^{III} coordination sites. The large critical distance for 50% energy transfer reported for $[Eu_2(L1-6H)(H_2O)_2]$ could not be observed in $[Eu_3(L2)(hfac)_9]$ or in $[Eu_3(L2)_3]^{9+}$. We therefore suspect that additional Eu-centred excited states lying higher in energy than the Eu(⁵D₀) electronic level in $[Eu_2(L1-6H)(H_2O)_2]$ contribute to the global intermetallic energy transfer upon ligand-centred excitation.

Altogether, the lack of efficient intramolecular Eu \rightarrow Eu communication involving different Eu^{III} sites is detrimental to the implementation of directional energy-transfer processes operating in discrete polynuclear complexes upon selective excitation.^[37] On the positive side, the limited intramolecular Eu \rightarrow Eu communication ensures that a selective excitation remains focused on a single centre and different europium cations can be addressed individually in polynuclear complexes and polymers, thus allowing their use as local luminescent probes.^[38]

Experimental Section

Solvents and starting materials

These were purchased from Strem, Acros, Fluka AG and Aldrich and used without further purification unless otherwise stated. The ligand **L5** and the complexes $[Eu_3(L2)(hfac)_9]$, $[Eu(L3)(hfac)_3]$, $[Eu(L4)(hfac)_3]$ and $[Eu_2(L5)(hfac)_3]$ were prepared according to literature procedures.^[24] The hexafluoroacetylacetonate salts [Ln-(diglyme)(hfac)_3] were prepared from the corresponding oxide (Aldrich, 99.99%).^[39] Acetonitrile and dichloromethane were distilled over calcium hydride.

CCDC-909094 ($[Eu_3(L2)(hfac)_9]$ -5.5CH₃CN),^[24] CCDC-843157 ($[Eu(L3)-(hfac)_3]$),^[25] CCDC-909092 ($[Eu(L4)(hfac)_3]$)^[24] and CCDC-909093 ($[Eu_2(L5)(hfac)_6]$)^[24] contain 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.

Preparation of the complex {TbEu(L5)(hfac)₆}

Reaction of stoichiometric amounts of L5 (1 equiv), [Eu(diglyme)-(hfac)₃] (1.0 equiv) and [Tb(diglyme)(hfac)₃] (1.0 equiv) in dichloromethane/acetonitrile yielded 70–80% (based on ligand) of a microcrystalline white powder. Slow evaporation of concentrated acetonitrile solutions gave prisms that were used for photophysical investigations.

Spectroscopic measurements

High-resolution emission spectra were recorded upon either ligand excitation with a xenon lamp (Oriel) or selective lanthanide(III) excitation with a Quantel YG 980 laser equipped with a dye laser Quantel TDL +. The emitted light was analysed with a high-resolu-

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tion monochromator iHR-320 from Horiba-Jobin-Yvon (holographic gratings 2400 grooves mm⁻¹ blazed at 400 nm). Light intensity was detected by a photomultiplier tube (Hamamatsu R928). Appropriate filters were utilised to remove the contribution of the laser light, the Rayleigh scattered light and associated harmonics from the emission spectra. The emission spectra were corrected for the instrumental response functions. Lanthanide-centred luminescence lifetimes were measured upon excitation provided by a Nd:YAG Quantel YG 980 laser equipped with a frequency doubler, tripler or quadrupler (ligand excitation), and a dye laser Quantel TDL+ (selective lanthanide(III) excitation). Emission was collected at a right angle to the excitation beam and wavelengths were selected with an iHR320 monochromator (Horiba-Jobin-Yvon). The signal was monitored by a Hamamatsu R928 photomultiplier tube, and was collected on a 500 MHz band pass digital oscilloscope (Tektronix TDS 724C). For low-temperature measurements the samples were placed into a closed-cycle He cryostat (Sumitomo SHI-950/Janis Research CCS-500/204). Experimental luminescence decay curves were treated with Origin 8.0 software using exponential fitting models. Three decay curves were collected on each sample, and reported lifetimes are an average of at least two successful independent measurements. The mathematical analyses were performed by using Igor Pro (WaveMetrics Inc.) and Excel (Microsoft) software.

Acknowledgements

This work was supported through grants from the Swiss National Science Foundation, the University of Geneva (INNO-GAP), la Ligue contre le Cancer and the Institut National de la Santé et de la Recherche Médicale (INSERM). The work was carried out within the COST Actions TD1004 and CM1006.

Keywords: energy transfer · lanthanides · photophysics · polynuclear complexes · structural probes

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analysis of Eu(${}^5D_0 \rightarrow {}^7F_2$) emission) systematically match the related emission Eu(${}^5D_0 \rightarrow {}^7F_0$) spectra recorded under indirect ligand-centred sensitization.

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- [34] The experimental rate constants used in the simulation are given in the caption of Figure 6. The energy-transfer rate constant is arbitrarily fixed to $k_{\rm En}^{\rm Eu-Eu} = 980 \ {\rm s}^{-1}$ reported in ref. [13] and the absorption cross section $\sigma_{\rm A}^{\rm 0-1} = 3.8 \times 10^{-25} \ {\rm m}^2$ taken for the Eu(${}^5D_0 \leftarrow {}^7F_0$) transition corresponds to a (maximum) value of $\varepsilon = 1 \ {\rm M}^{-1} \ {\rm cm}^{-1}$ ($\sigma_{\rm A}^{\rm 0-1}$ in units of cm²).
- [35] The conclusions drawn for the isolated complexes also hold for crystal-

line samples when $k_{EnT}^{Eu^A \to Eu^B}$ is replaced with $k_{EnT}^{Eu^A \to Eu^B} + \sum_{j=1}^{n} W_{EnT,j}^{Eu^A \to Eu^B} \cdot N_j^{tot}$

and $k_{EnT}^{Eu^8 \rightarrow Eu^A}$ is replaced with $k_{EnT}^{Eu^8 \rightarrow Eu^A} + \sum_{j=1}^n W_{EnT,j}^{Eu^8 \rightarrow Eu_j^A} \cdot N_j^{tot}$; see Appendix 2 in the Supporting Information.

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Received: April 23, 2014 Published online on August 5, 2014