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Multi-emissive lanthanide-based coordination polymers for potential application as luminescent bar-codes.

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ABSTRACT.

Isostructural lanthanide-based coordination polymers that are obtained by reactions in water of a lanthanide chloride and the sodium salt of 5-methoxyisophthalate (mip^{2-}), have general chemical formula $[Ln_2(mip)_3(H_2O)_8 \cdot 4H_2O]_\infty$ with Ln = Nd-Er except Pm plus Y (symbolized by $[Ln_2(mip)_3]_\infty$). Some of these homo-lanthanide compounds present very high luminescence brightness. The weak inter-metallic energy transfer between lanthanide ions observed in these compounds allows the design of hetero-lanthanide coordination polymers with tunable luminescence properties. A molecular alloy that involve six different lanthanide ions (Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}) has been prepared and its luminescent properties have been studied. This compound, under a unique irradiation wavelength (λ_{exc} = 325 nm), exhibits almost twenty emission peaks in both the visible and the NIR regions at room temperature. This unprecedented richness of the emission spectrum could be of great interest as far as luminescent bar-codes are targeted.

INTRODUCTION.

Because of lanthanide ions unique chemical and physical properties, lanthanide-based coordination polymers[1-3] arouse a growing interest for more than a decade.[4-9] Indeed, these compounds, that present fascinating molecular structures,[10-11] exhibit interesting and original magnetic[12] and optical[13-19] properties. They could find their application in various technological fields such as light and display,[20-24] chemical sensing,[25-28] thermometric sensing[29-32] and fight against counterfeiting,[33-35] for instance.

Targeting some of these technological applications requires the use of hetero-lanthanide coordination polymers.[36-37] It has been demonstrated that, because of their similar chemical behaviors,[38-39] it is possible to design series of hetero-lanthanide coordination polymers in which lanthanide ions are randomly distributed over the metallic sites of the crystal structure.[40-46] Consequently, it is possible to tune the intensity and the color of the emission of these systems (sometimes called "molecular alloys"[47]) by varying the relative contents of the different lanthanide ions. Indeed, inter-metallic energy transfers efficiency drastically decreases with the inter-metallic distance and it is commonly admitted that they become negligible when lanthanide ions are more than 10 Å far from each other.[48-49] Therefore, it is possible to control inter-metallic energy transfers and thus to modulate the intensity and the color of the emission by diluting optically active lanthanide ions by optically non-active ones.[40] Thanks to this strategy, it is possible to design taggants that can be introduced in a host material. However, as far as potential applications are targeted, this strategy presents a serious drawback because diluting optically active lanthanide ions may result in a decreasing of the overall luminescence intensity. Therefore, the search for systems, that would exhibit intense luminescence and in which control of the inter-metallic transfers would not require a too important dilution, constitutes a continuous concern. Another technological request is the design of multi-emissive materials that would emit in a broad

wavelength range and therefore act as sort of luminescent bar-codes. Several examples of luminescent bar code have been reported so far[50-54] but examples of systems that fulfill these requirements are scarce.[54]

Recently a series of lanthanide-based coordination polymers with 5-methoxyisophthalate (hereafter symbolized by mip^{2-}) as ligand has been reported.[55] Compounds that constitute this family have general chemical formula $[Ln_2(mip)_3(H_2O)_8 \cdot 4H_2O]_\infty$ with Ln = Nd-Er except Pm plus Y (hereafter symbolized by $[Ln_2(mip)_3]_\infty$). They are all iso-structural to the Y-derivatives (Figure S1). Crystal structure is 1D and can be described as the juxtaposition of wrapped ladder-like molecular double-chains that spread along the *a* axis (Figure 1).

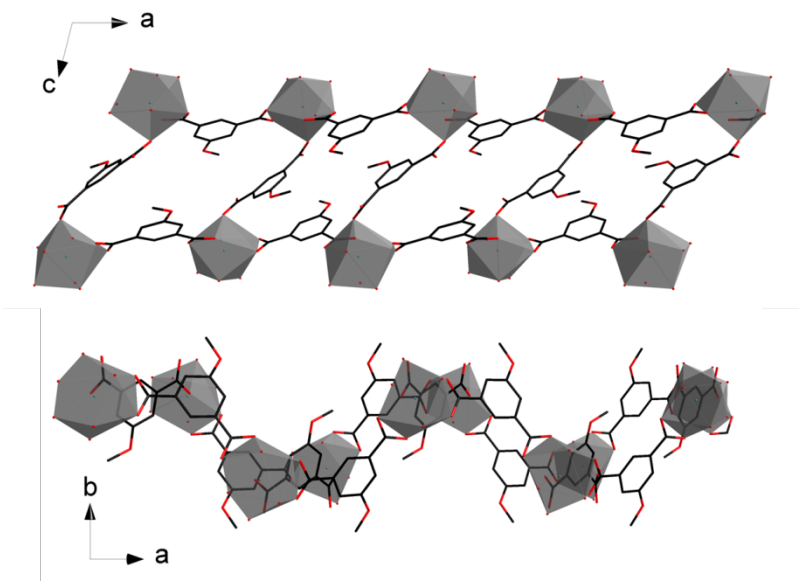


Figure 1. Projection views along the *b* (top) and *c* (bottom) axes of $[Y_2(mip)_3]_\infty$. It crystallizes in the monoclinic system, space group $P2_1/n$ (n°14) with the following cell parameters: a = 17.4214(11) Å, b = 10.7884(8) Å, c = 20.3688(15) Å, β = 104.136(2)°, V = 3712.4(5) Å^3 and Z = 4. Redrawn from reference [55].

In this crystal structure, lanthanide ions that belong to the same molecular motif are quite far from each other ($d_{Ln\text{-}Ln}$ > 9.8 Å) and the shortest intermetallic distances are observed between lanthanide ions that belong to adjacent ladder-like molecular motifs (≈ 6 Å). From a global point of view, mean intermetallic distance is about 9.6 Å which induces an unusually weak inter-metallic energy transfer[55] that could allow original luminescent properties.

In this paper we would like to report a luminescence study of some hetero-lanthanide coordination polymers that belong to this family of isostructural compounds. A hexa-lanthanide molecular alloy, $[Nd_{0.4}Sm_{0.4}Eu_{0.3}Gd_{0.20}Tb_{0.1}Dy_{0.6}(mip)_3]_\infty$, with unprecedented multi-emissive properties is particularly described.

EXPERIMENTAL SECTION.

Synthesis of the microcrystalline powders.

Lanthanide oxides (4N) were purchased from AMPERE and used without further purification. Corresponding chlorides have been prepared according to established procedures.[56] 5-methoxyisophthalic acid (> 98%) was purchased from TCI and used without further purification. Its di-sodium salt was prepared as previously described.[55]

Reactions in water of a lanthanide chloride and the di-sodium salt of 5-methoxyisophthalic acid lead to a series of iso-structural homo-lanthanide coordination polymers $[Ln_2(mip)_3(H_2O)_8\cdot 4H_2O]_\infty$ with Ln = Nd-Er except Pm plus Y (hereafter symbolized by $[Ln_2(mip)_3]_\infty$).[55] These compounds have been assumed to be iso-structural to $[Y_2(mip)_3]_\infty$ on the basis of their powder X-ray powder diffraction diagrams (Figure S1).

Hetero-lanthanide coordination polymers that belong to this series are prepared according a similar procedure in which the aqueous lanthanide chloride solution is replaced by an aqueous solution of the appropriate mixture of lanthanide chlorides. Iso-structurality of these compounds with $[Y_2(mip)_3]_\infty$ is assumed on the basis of their X-ray powder diagrams (Figures S2 to S8) and relative contents of the different lanthanide ions measured by EDS are listed in Table S1. Random distribution of the different lanthanide ions over the different metallic sites of the crystal structure has been assumed on the basis of studies on similar compounds that have been previously reported.[16, 18, 40-41]

X-ray powder diffraction.

Experimental X-ray powder diffraction diagrams have been recorded using a Panalytical X-Pert Pro diffractometer equipped with an X'Celerator detector. Typical measurements conditions were 45 kV, 40 mA for Cu K_α radiation (λ = 1.542 Å) in θ/θ mode. Simulated diagram was produced using Powdercell and WinPLOTR programs[57-59] on the basis of $[Y_2(mip)_3]_\infty$ crystal structure (CCDC-1501130).

^{1}H, ^{13}C and ^{89}Y solid state NMR spectroscopy

^{1}H MAS NMR spectra were acquired at 14 T using a 2.5 mm probe-head and a spinning rate of 30 kHz. Proton direct observation and RFDR experiments are reported in supporting information (Figures S9 and S10).

^{13}C MAS NMR spectra were acquired at 14 T using cross polarization (CP) from ^{1}H using a contact pulse duration of 2 ms (ramped 50−100% for ^{1}H), and SPINAL64 ^{1}H decoupling during acquisition with a rf field strength of ~ 35 kHz and a recycle interval of 3 s. Samples were packed into 4-mm outer diameter rotors and rotated at a spinning rate of 12 kHz using a commercial probe-head. Chemical shift scales are shown relative to TMS.

^{89}Y CPMAS experiments were recorded at 14 T, using a low-gamma two channels 7 mm probe (^{89}Y Larmor frequency 29.4 MHz). Spectrum recorded at a MAS rate of 5.5 KHz. ^{89}Y MAS NMR spectra were acquired using cross polarization (CP) from ^{1}H using a contact time of 4 ms (ramped for ^{1}H), SPINAL64 ^{1}H decoupling during acquisition with a rf field strength of ~ 60 kHz and recycle interval of 3 s. Chemical shift scales are shown relative to YCl_3 in aqueous solution.

Solid state NMR experiments were carried on a diamagnetic end-member of the solid solution $[Y_2(mip)_3(H_2O)_8{\cdot}4H_2O]_\infty$ in order to complement the description of the local environment of the lanthanide ions observed by X-ray diffraction. All the experiments were

carried out using a 14 T NMR spectrometer. The ^{89}Y NMR experiments can be challenging in terms of sensitivity due to the low gyromagnetic ratio of ^{89}Y (29.4 MHz at 14 T) and in many cases to low T_1 relaxation times. The use of proton to yttrium CPMAS experiments and a specially designed 7 mm MAS probe allowed us to record ^{89}Y MAS experiments with good signal to noise ratios.

Electronic microscopy and Energy Dispersive Spectroscopy (EDS).

EDS measurements have been performed with a Hitachi TM-1000, Tabletop Microscope version 02.11 (Hitachi High-Technologies, Corporation Tokyo Japan) with EDS analysis system (SwiftED-TM, Oxford Instruments Link INCA). Samples were assembled on carbon discs, stuck on an aluminium stub fixed at 7 mm from EDX beam, with an angle of measurement of 22°. Reproducibility of the elemental analyses has been checked by repeating the measurements several times. These experiments support the homogeneity of the samples.

Optical and colorimetric measurements.

Solid state emission and excitation spectra have been measured on a Horiba Jobin-Yvon Fluorolog III fluorescence spectrometer equipped with a Xe lamp 450 W and a UV-Vis photomultiplier (Hamamatsu R928, sensitivity 190-860 nm) and an IR-photodiode cooled by liquid nitrogen (InGaAs, sensitivity 800-1600 nm). Most of the luminescence spectra were recorded at room temperature. Quantum yields were measured using an integrating sphere from Jobin-Yvon company thanks to the following formula : $\Phi = (E_c-E_a)/(L_a-L_c)$ (E_c and L_c are the integrated emission spectrum and the absorption at the excitation wavelength of the sample, while E_a and L_a are the integrated "blank" emission spectrum and "blank" absorption, respectively). Quantum yield recordings and emission/excitation spectra recordings were realized on powder samples introduced in

cylindrical quartz cells of 0.7 cm diameter and 2.4 cm height, which were placed directly inside the integrating sphere, or on powder samples introduced in quartz capillary tubes or on powder samples pasted on copper plates with silver glue. Luminescence at variable temperature has been measured with an optical cryostat coupled to a liquid nitrogen bath able to reach temperatures down to 77 K under nitrogen atmosphere. Longest luminescence decays ($\tau > 10$ μs) have also been measured at room temperature using this apparatus with a Xenon flash lamp (phosphorescence mode). Shortest luminescence decays ($\tau < 10$ μs) were measured directly with the fluorescence spectrometer coupled with an additional TCSPC module (Time-Correlated-Single-Photon-Counting) and a 320 nm pulsed Delta-Diode. Lifetimes and quantum yields are averages of two or three independent determinations. Appropriate filters were used to remove the residual excitation laser light, the Rayleigh scattered light and associated harmonics from spectra. All spectra were corrected for the instrumental response function.

Luminescence intensities of the samples expressed in $Cd.m^{-2}$ have been measured with a Gigahertz-Optik X1-1 optometer with an integration time of 200 ms on 1.5 cm^2 pellets under UV irradiation (λ_{exc} = 312 nm). The intensity of the UV flux at sample location, 0.68(1) $mW.cm^{-2}$, has been measured with a VilberLourmat VLX-3W radiometer. $[Tb_2(bdc)_3 \cdot 4H_2O]_\infty$ where bdc^{2-} stands for terephthalate was used as a standard. Its luminance is 99(1) $Cd.m^{-2}$ under these operating conditions (λ_{exc} = 312 nm; flux = 0.68(1) $mW.cm^{-2}$).[40]

The CIE (Commission Internationale de l'Eclairage) (x, y) emission color coordinates[60-61] were obtained using a MSU-003 colorimeter (Majantys) with the PhotonProbe 1.6.0 Software (Majantys). Color measurements: 2°, CIE 1931, step 5 nm, under 312 nm UV light. $X = k \times \int_{380nm}^{780nm} I_\lambda \times x_\lambda$, $Y = k \times \int_{380nm}^{780nm} I_\lambda \times y_\lambda$ and $Z = k \times \int_{380nm}^{780nm} I_\lambda \times z_\lambda$ with k constant for the measurement system, I_λ sample spectrum intensity wavelength depending, x_λ, y_λ, z_λ trichromatic values x = X/(X+Y+Z), y = Y/(X+Y+Z) and

z = Z/(X+Y+Z). Mean xyz values are given for each sample, which act as light sources (luminescent samples). Standards from Phosphor Technology used, calibrated at 312 nm: red phosphor Gd_2O_2S:Eu (x = 0.667, y = 0.330) and green phosphor Gd_2O_2S:Tb (x = 0.328, y = 0.537).

RESULTS AND DISCUSSION.

Homo-lanthanide coordination polymers $[Ln_2(mip)_3]_\infty$ with Ln = Nd-Er except Pm plus Y.

In order to firmly establish the basis of our study of molecular alloys, solid state NMR spectra of $[Y(mip)_3]_\infty$ were recorded. ^{89}Y CPMAS NMR spectroscopy (Figure 2), allows one to clearly distinguish the two inequivalent yttrium ions in the unit cell, separated by 4.4 ppm. ^{89}Y isotropic chemical shifts appear to be very sensitive to local environments since these two yttrium atoms are both located on general 4e Wyckoff positions (no symmetry elements on the positions) and are equally surrounded by nine oxygen atoms (average distance respectively 2.416 Å and 2.417 Å, standard deviations 0.069 Å and 0.073 Å, respectively). Yttrium NMR will probably form an interesting tool in future studies dealing with the local ordering of diamagnetic Y-Lu or Y-La solid solutions.

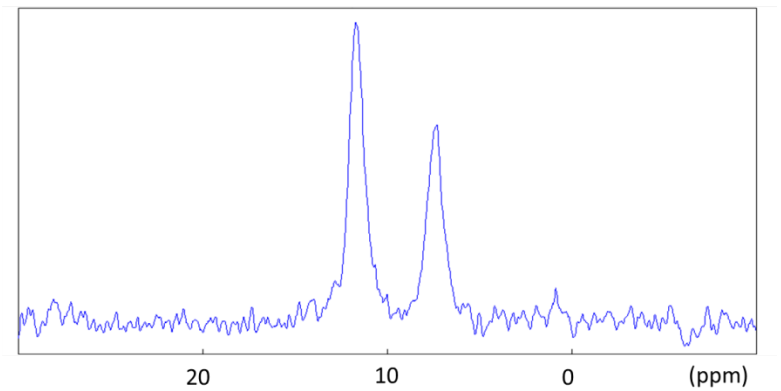


Figure 2. ^{89}Y CPMAS NMR of $[Y_2(mip)_3]_\infty$. 7 mm MAS probe-head, MAS rate 5.5 kHz.

^{13}C NMR (Figure 3) can also provide valuable information: one can easily distinguish the isotropic ^{13}C NMR signals of the methyl carbons (55 ppm), the aromatic carbons (between 125 and 170 ppm) and the carboxylate groups. It is worth noticing that two different carboxylates groups can be identified (174 and 178 ppm). These two different ^{13}C isotropic chemical shifts are presumably related to the presence in the structure of mono-dentate and bi-dentate carboxylate groups.

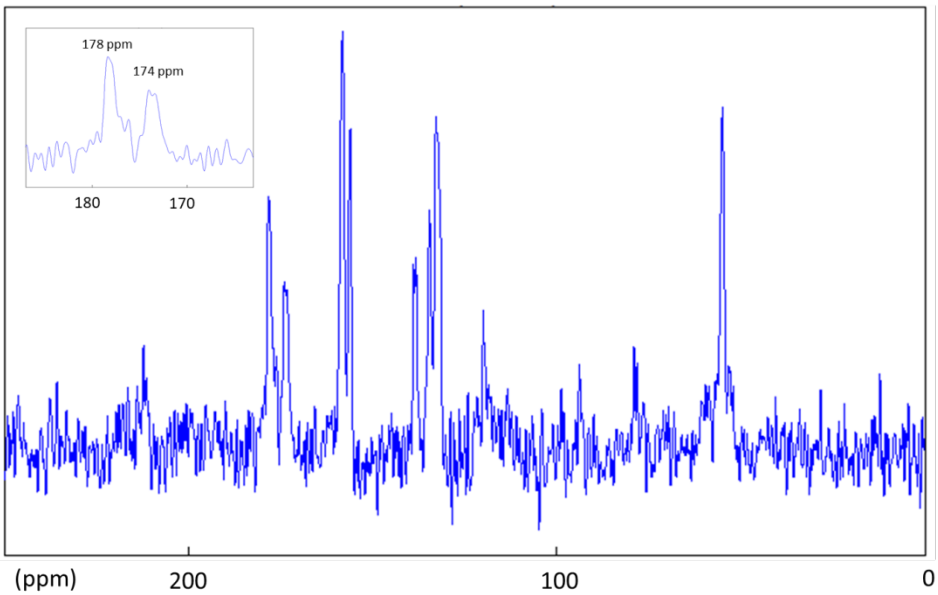
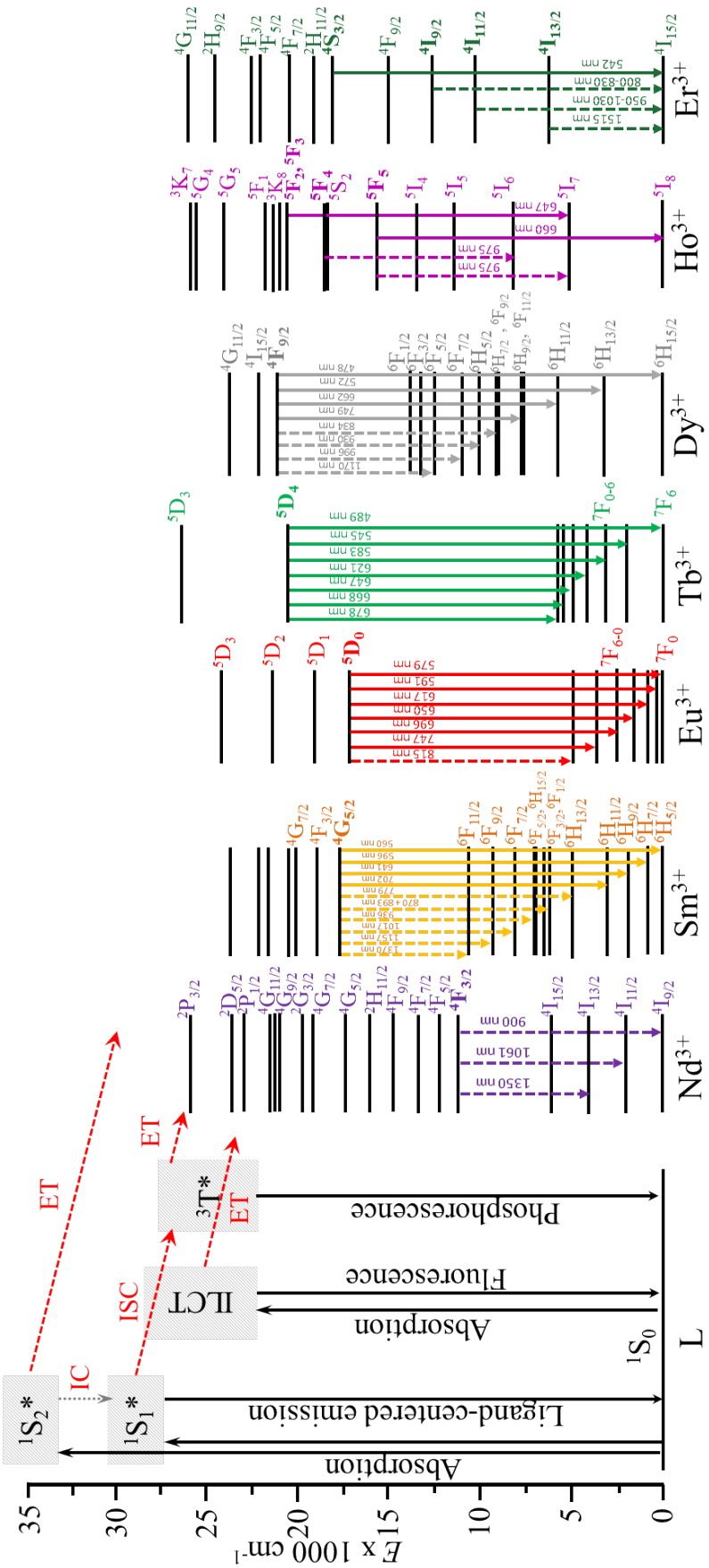


Figure 3. ^{13}C CPMAS NMR of $[Y_2(mip)_3]_\infty$. 4 mm MAS probe-head, MAS rate 12 kHz.

Excitation and emission spectra of all the homo-lanthanide coordination polymers have also been recorded in both the visible and the infra-red regions. These measurements complete and confirm results that have been published previously for Eu^{3+}- and Tb^{3+}-derivatives. They are reported in Figures S11 to S17. These figures evidence that mip^{2-} acts as an antenna[62] toward all these homo-lanthanide coordination polymers (λ_{exc} = 325 nm). This is quite rare because of the different energies of the acceptor levels of the lanthanide ions (Scheme 1). Some overall quantum yields (Q_{Ln}^{Ligand}) and observed luminescent lifetimes (τ_{obs}) have been measured. They are listed in Table 1.



Scheme 1. Simplified Jablonsky and Dieke diagrams for lanthanide ions.[63] S = singlet, T = triplet, ILCT = intra-ligand charge transfer, ISC = intersystem crossing, ET = energy-transfer.

Table 1. Overall quantum yields (Q_{Ln}^{Ligand}), observed luminescent lifetimes (τ_{obs}) and transitions that are observed for $[Ln_2(mip)_3]_\infty$ with Ln = Nd, Sm, Eu, Tb, Dy, Ho and Er.

Compound	Q_{Ln}^{Ligand} (%)	τ_{obs}	Observed transitions
$[Nd_2(mip)_3]_\infty$	n/a	n/a	$^4F_{3/2}\rightarrow{}^4I_{9/2\text{-}13/2}$
$[Sm_2(mip)_3]_\infty$	0.18(5)	0.25(1) µs	$^4G_{5/2}\rightarrow{}^6H_{5/2\text{-}13/2}$ and $^4G_{5/2}\rightarrow{}^6F_{1/2\text{-}11/2}$
$[Eu_2(mip)_3]_\infty$	3.6(1)	0.21(1) ms	$^5D_0\rightarrow{}^7F_{0\text{-}6}$
$[Tb_2(mip)_3]_\infty$	47.5(9)	0.70(2) ms	$^5D_4\rightarrow{}^7F_{6\text{-}0}$
$[Dy_2(mip)_3]_\infty$	0.68(8)	1.47(1) µs	$^4F_{9/2}\rightarrow{}^6H_{15/2\text{-}5/2}$ and $^4F_{9/2}\rightarrow{}^6F_{9/2\text{-}5/2}$
$[Ho_2(mip)_3]_\infty$	n/a	n/a	$^5F_3\rightarrow{}^5I_7$, $^5F_5\rightarrow{}^5I_8$ and $^5F_5\rightarrow{}^5I_7$, $^5F_4\rightarrow{}^5I_6$
$[Er_2(mip)_3]_\infty$	n/a	n/a	$^2H_{9/2}$, $^2G_{9/2}$, $^4F_{9/2}\rightarrow{}^4I_{13/2}$

Figures S13 and S14 confirm that Eu- and Tb-based compounds present a significant luminescence in agreement with Latva's[64] and Reinhouldt's[65] empirical rules. Discrepancy that is observed between overall quantum yields of this two derivatives can be related to a photon induced electron transfer (PET)[66-69] that may occur for the Eu-based compound because of the presence of the methoxy group on the ligand. This has already been observed previously for similar lanthanide-based coordination polymer.[17-18]

Figures S16 shows that Ho^{3+}-derivative exhibits weak luminescence in the IR region. On the contrary (Figure S17), Er^{3+}-derivative presents no emission in the IR region but all the characteristic emission transitions are observed via re-absorption bands (DIP)[70-71] from the internal Er(III)-centered reabsorption of the broad residual ligand centered $^1\pi^* \rightarrow {}^1\pi$ emission ($^2H_{11/2}$, $^4F_{7/2}$, $^4F_{5/2}$, $^4F_{3/2} \leftrightarrow {}^4I_{15/2}$ at 521, 486 and 450 nm, respectively), except for the low green emission with a maximum at 557 nm, that can attributed to transitions $^2H_{9/2}$, $^2G_{9/2}$, $^4F_{9/2} \rightarrow {}^4I_{13/2}$. At 77 K, characteristic infrared emission of Er(III) centered at approximately 1500 nm (transition $^4I_{13/2} \rightarrow {}^4I_{15/2}$) is also observed.

Sm- and Dy-based compounds present unusually intense luminescence in both visible and IR regions (Figures S12 and S15). Transitions $^4G_{5/2} \rightarrow {}^6H_{5/2\text{-}13/2}$ and $^4G_{5/2} \rightarrow {}^6F_{1/2\text{-}11/2}$ are observed for $[Sm_2(mip)_3]_\infty$ and $^4F_{9/2} \rightarrow {}^6H_{15/2\text{-}5/2}$ and $^4F_{9/2} \rightarrow {}^6F_{9/2\text{-}5/2}$, for $[Dy_2(mip)_3]_\infty$. Last, quite intense $^4F_{3/2} \rightarrow {}^4I_{9/2\text{-}13/2}$ transitions are observed in the IR region for $[Nd_2(mip)_3]_\infty$ (Figure S11).

These unusually strong emissions encouraged us to prepare hetero-lanthanide molecular alloys.

Emission in the visible region: Hetero-lanthanide coordination polymers $[EuTb(mip)_3]_\infty$, $[Gd_{0.2}Eu_{0.9}Tb_{0.9}(mip)_3]_\infty$, $[Gd_{0.2}Eu_{2x}Tb_{1.8-2x}(mip)_3]_\infty$, $[Gd_{0.2}Dy_{2x}Tb_{1.8-2x}(mip)_3]_\infty$ and $[Gd_{0.2}Dy_{2x}Eu_{1.8-2x}(mip)_3]_\infty$ with $0 \leq x \leq 0.9$.

Because it has been previously established[55] that, in this system, dilution by 10% of optically active lanthanide by an optically non-active one leads to optimized luminescent intensity, we have prepared and compared two molecular alloys: $[EuTb(mip)_3]_\infty$ and $[Gd_{0.2}Eu_{0.9}Tb_{0.9}(mip)_3]_\infty$ (Figure 4). Overall quantum yields and luminescent lifetimes are reported in Table 2.

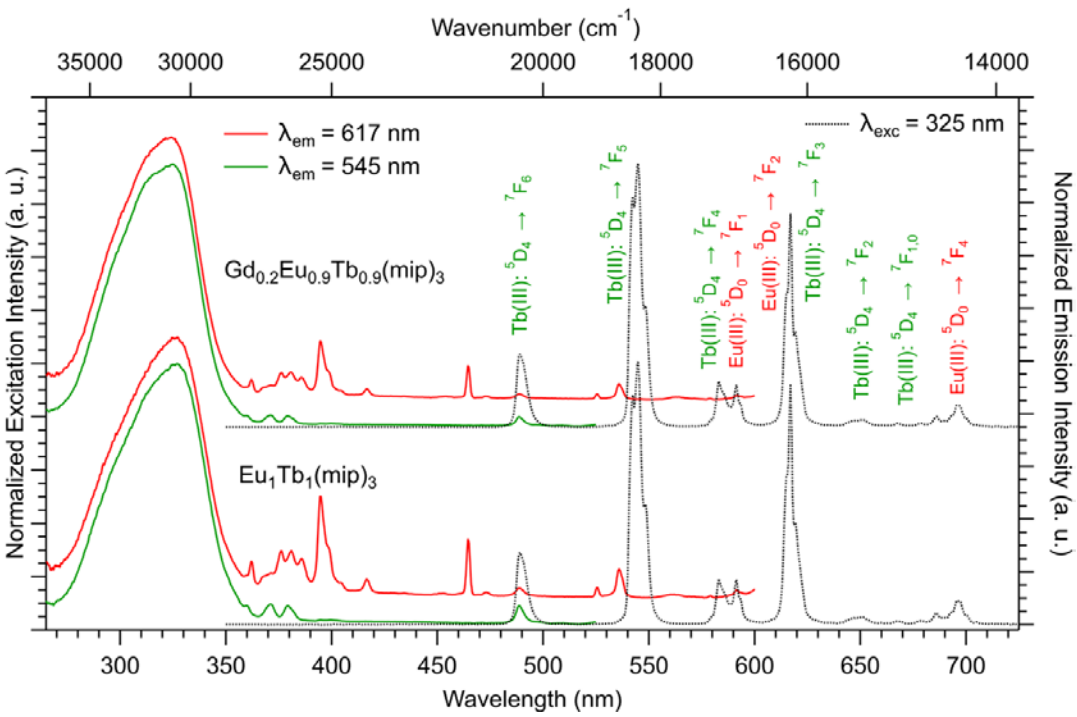


Figure 4. Room temperature solid state excitation (λ_{em} = 545 nm and λ_{em} = 617 nm) and emission (λ_{exc} = 325 nm) spectra of $[Gd_{0.2}Eu_{0.9}Tb_{0.9}(mip)_3]_\infty$ (top) and $[EuTb(mip)_3]_\infty$ (bottom). Maximum intensities ratios I_{Tb}/I_{Eu} are 1.24(1) for $[Gd_{0.2}Eu_{0.9}Tb_{0.9}(mip)_3]_\infty$ and 1.10(1) for $[EuTb(mip)_3]_\infty$.

Table 2. Overall quantum yields (Q_{Ln}^{Ligand}), observed luminescent lifetimes (τ_{obs}) for $[Gd_{0.2}Eu_{0.9}Tb_{0.9}(mip)_3]_\infty$ and $[EuTb(mip)_3]_\infty$.

Compound	Q_{Tb}^{Ligand} (%)	τ_{obs}(Tb) (ms)	Q_{Eu}^{Ligand} (%)	τ_{obs}(Eu) (ms)
$[Gd_{0.2}Eu_{0.9}Tb_{0.9}(mip)_3]_\infty$	8.9(2)	0.51(1)	5.0(1)	0.37(1)
$[Eu_1Tb_1(mip)_3]_\infty$	6.1(2)	0.46(1)	3.7(2)	0.35(1)

Figure 4 shows that dilution by 10% of Gd^{3+} ions reduces the Tb-to-Eu energy transfer by about 12%. Increasing the dilution rate to 20% does not bring significant improvement. On this basis, some compounds of the series of molecular alloys $[Gd_{0.2}Eu_{2x}Tb_{1.8-2x}(mip)_3]_\infty$ with $0 \leq x \leq 0.9$ have been prepared and their luminescence properties have been studied (Figure 5).

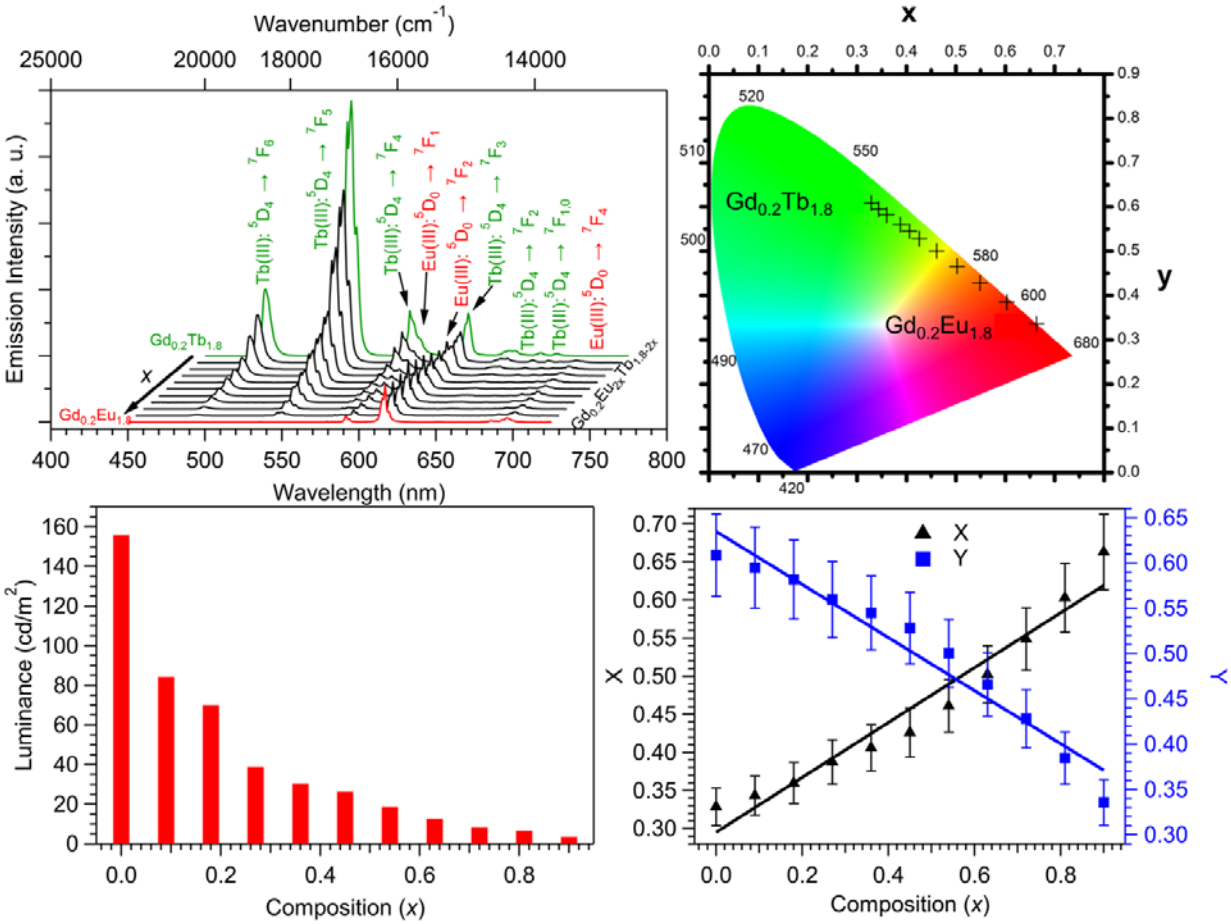


Figure 5. Solid state emission spectra (top left), colorimetric coordinates (top right), luminance (bottom left) and colorimetric coordinates *versus x* (bottom right) of $[Gd_{0.2}Eu_{2x}Tb_{1.8-2x}(mip)_3]_\infty$with $0 \leq x \leq 0.9$ under UV irradiation (λ_{exc} =325 nm). Measurements have been performed at room temperature.

Figure 5 evidences that in this series inter-metallic energy transfers are so weak that it is possible to control the emission color by a simple colors addition strategy as highlighted by the curves that represent colorimetric coordinates *versus x*. To the best of our knowledge, this behavior is unprecedented and very different from what is usually observed.[40]

Of course, the doping rate that is necessary for achieving such an almost linear variation of the colorimetric coordinates *versus x*, depends on the overall quantum yields and luminance of the two optically active lanthanide ions as well as on the nature of the inter-metallic energy transfer mechanisms that are involved. This is exemplified by the luminescence properties of the two series of molecular alloys $[Gd_{0.2}Dy_{2x}Tb_{1.8-2x}(mip)_3]_\infty$ and $[Gd_{0.2}Dy_{2x}Eu_{1.8-2x}(mip)_3]_\infty$ with $0 \leq x \leq 0.9$ (Figure 6).

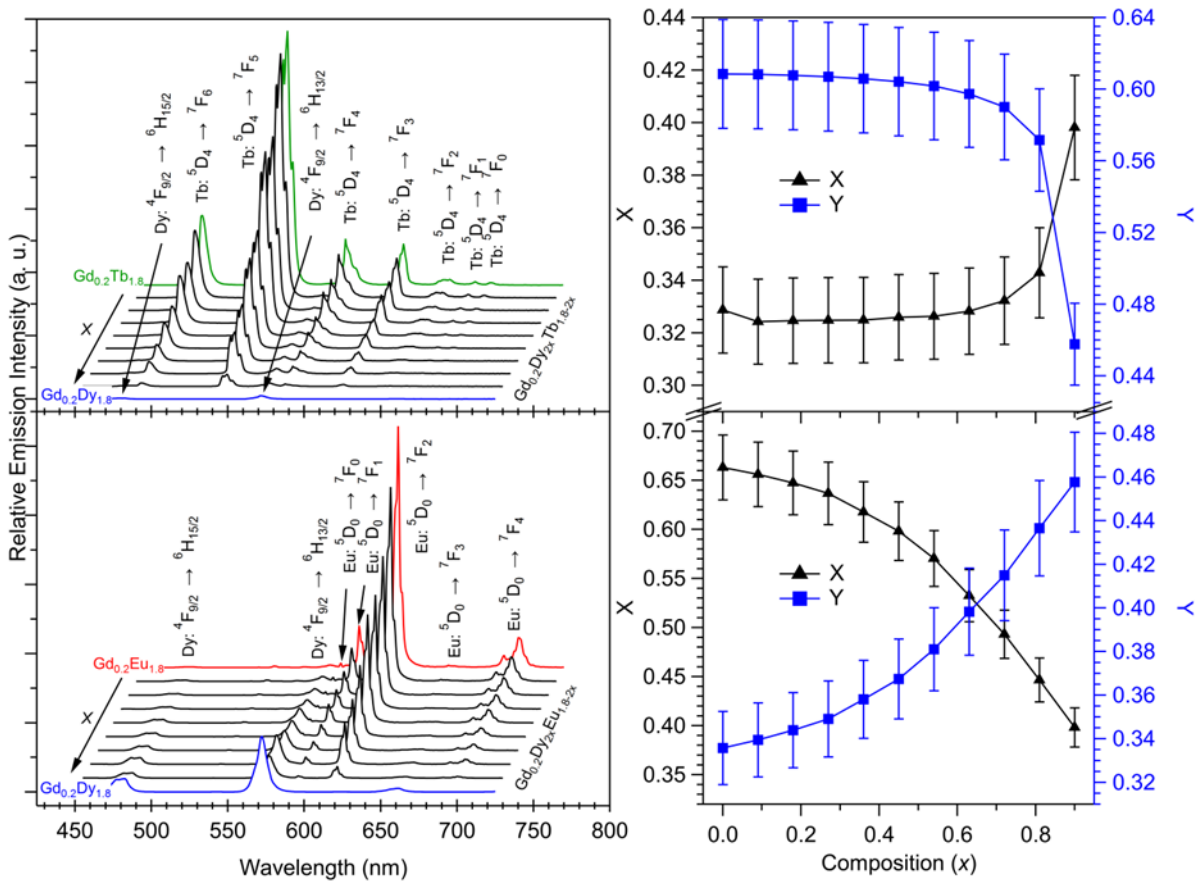


Figure 6. Room temperature solid state emission spectra (left) and colorimetric coordinates (right) of $[Gd_{0.2}Dy_{2x}Tb_{1.8-2x}(mip)_3]_\infty$ (top) and $[Gd_{0.2}Dy_{2x}Eu_{1.8-2x}(mip)_3]_\infty$ (bottom) with $0 \leq x \leq 0.9$ *versus x* under UV irradiation (λ_{exc} = 325 nm).

On the basis of Figure 6, it clearly appears that a dilution by 10% with Gd^{3+} ions does not allow a linear variation of the colorimetric coordinates *versus* *x* for $[Gd_{0.2}Dy_{2x}Tb_{1.8-2x}(mip)_3]_\infty$ and $[Gd_{0.2}Dy_{2x}Eu_{1.8-2x}(mip)_3]_\infty$ series. Therefore, if one wants to mix several optically active lanthanide ions in the same molecular alloy, he will have to find a dilution rate (by optically inactive lanthanide ions) that is relevant for all optically active lanthanide ions that are involved. This may lead to a strong dilution that could induce very low overall luminescence intensity.

Emission in both visible and Infra-Red regions. Hetero-lanthanide coordination polymers $[Nd_{0.9}Gd_{0.2}Tb_{0.9}(mip)_3]_\infty$, $[Nd_{0.2}Gd_{0.2}Tb_{1.6}(mip)_3]_\infty$ and $[Nd_{0.2}Sm_{1.2}Dy_{0.6}(mip)_3]_\infty$.

Commonly, the presence of a lanthanide ion that emits in the IR region (Nd^{3+} for instance) causes the quenching of the emission in the visible region of Tb^{3+} or Eu^{3+} ions, because of inter-metallic energy transfers.[40, 72] In this system in which inter-metallic energy transfers are intrinsically weak, and even reduced by Gd^{3+} dilution, it is possible to observe significant emission in both spectral regions as exemplified in figure 7.

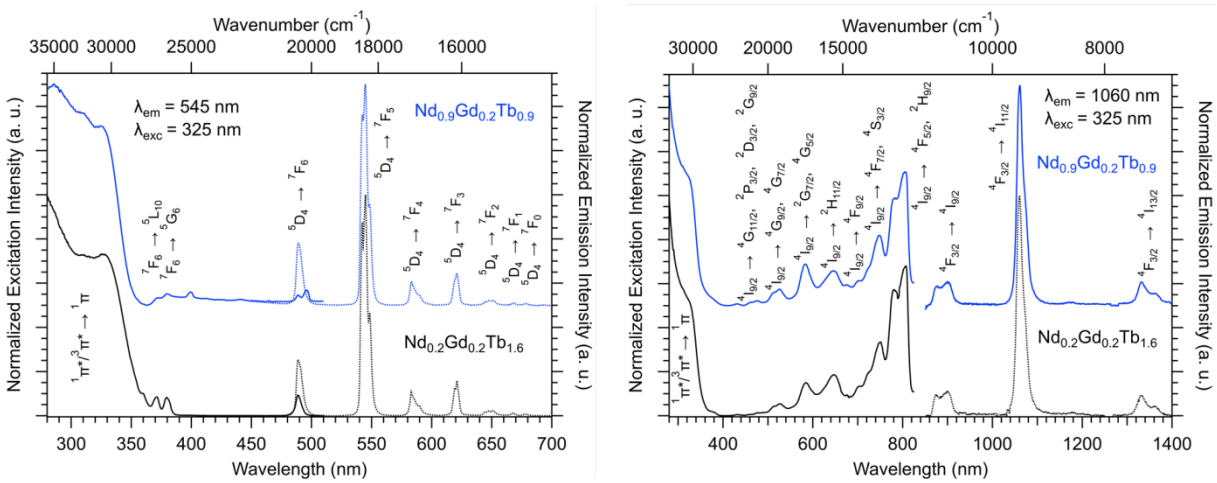


Figure 7. Solid state excitation and emission spectra recorded at room temperature of $[Nd_{0.9}Gd_{0.2}Tb_{0.9}(mip)_3]_\infty$ and $[Nd_{0.2}Gd_{0.2}Tb_{1.6}(mip)_3]_\infty$ in visible (left) and IR (right) region. Observed luminescent lifetimes for Tb^{3+} are 0.27(1) ms for $[Nd_{0.2}Gd_{0.2}Tb_{1.6}(mip)_3]_\infty$ and 0.19(3) ms for $[Nd_{0.9}Gd_{0.2}Tb_{0.9}(mip)_3]_\infty$.

Figure 7 shows that, even when Nd^{3+} content is important, inter-metallic energy transfer remains moderate. It is also noticeable that Nd^{3+} emission intensity is not enhanced a lot by an increasing of Nd^{3+} ion content while, on the contrary, Tb^{3+} emission is drastically reduced. This suggests that, as far as multi-emissive compound is targeted, a quite small Nd^{3+} content (≈ 10%) is sufficient for insuring significant Nd^{3+} luminescence.

On the basis of this observation we have prepared a molecular alloy ($[Nd_{0.2}Sm_{1.2}Dy_{0.6}(mip)_3]_\infty$) that contains the three lanthanide ions whose homo-metallic coordination polymers exhibit significant emission in the visible (Sm^{3+} and Dy^{3+}) and in the IR region (Sm^{3+}, Dy^{3+} and Nd^{3+}). Its luminescent properties have been recorded (Figures 8 and S18).

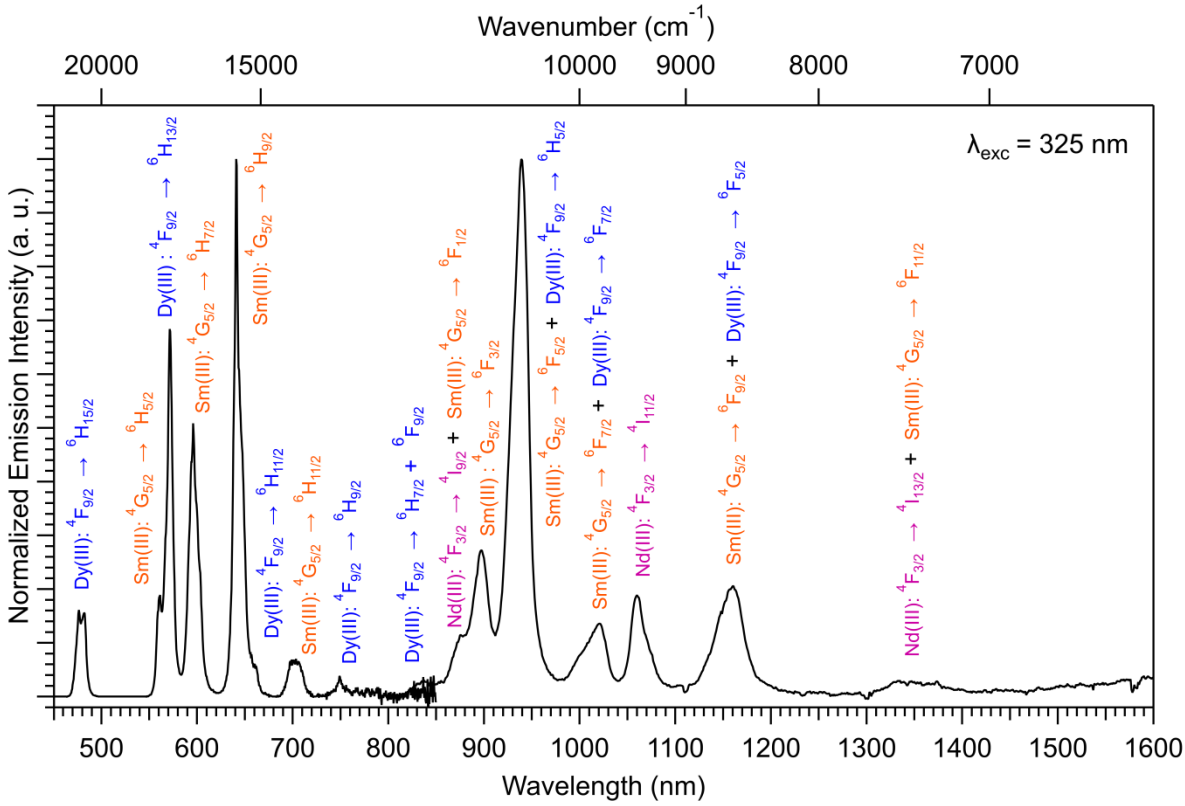


Figure 8. Solid state emission spectrum recorded at room temperature of $[Nd_{0.2}Sm_{1.2}Dy_{0.6}(mip)_3]_\infty$. Spectra normalized on the most intense peak of the visible (450-850) and NIR regions (850-1600 nm), respectively.

Figure 8 shows that this molecular alloy exhibits numerous characteristic emission peaks, with sizeable intensities, from the three involved lanthanide ions. Once more it looks like as if inter-metallic energy transfers have almost vanished. On the basis of this observation and trying to get a compound that would exhibit as numerous as possible significant emission peaks we have prepared the hexa-nuclear molecular alloy: $[Nd_{0.4}Sm_{0.4}Eu_{0.3}Gd_{0.2}Tb_{0.1}Dy_{0.6}(mip)_3]_\infty$.

Multi-emissive molecular alloy: $[Nd_{0.4}Sm_{0.4}Eu_{0.3}Gd_{0.2}Tb_{0.1}Dy_{0.6}(mip)_3]_\infty$.

In $[Nd_{0.4}Sm_{0.4}Eu_{0.3}Gd_{0.2}Tb_{0.1}Dy_{0.6}(mip)_3]_\infty$ composition is not rigorously optimized. It has been set on the basis of two main ideas: First, intermetallic energy transfers can be neglected, and second, lanthanide ions relative contents can be estimated on the basis of the relative intensities of the corresponding homo-lanthanide coordination polymers. Its luminescent properties have been recorded (Figures 9 and S19). As for $[Nd_{0.2}Sm_{1.2}Dy_{0.6}(mip)_3]_\infty$, excitation spectra for Nd^{3+} and Sm^{3+} in $[Nd_{0.4}Sm_{0.4}Eu_{0.3}Gd_{0.2}Tb_{0.1}Dy_{0.6}(mip)_3]_\infty$ are clearly measured (Figure S19). Indeed, the absorption band of the ligand, with a maximum around 325 nm, is observed, which reveals a good antenna effect, and the characteristic f-f transitions for the Nd(III) and Sm(III) are observed as well.

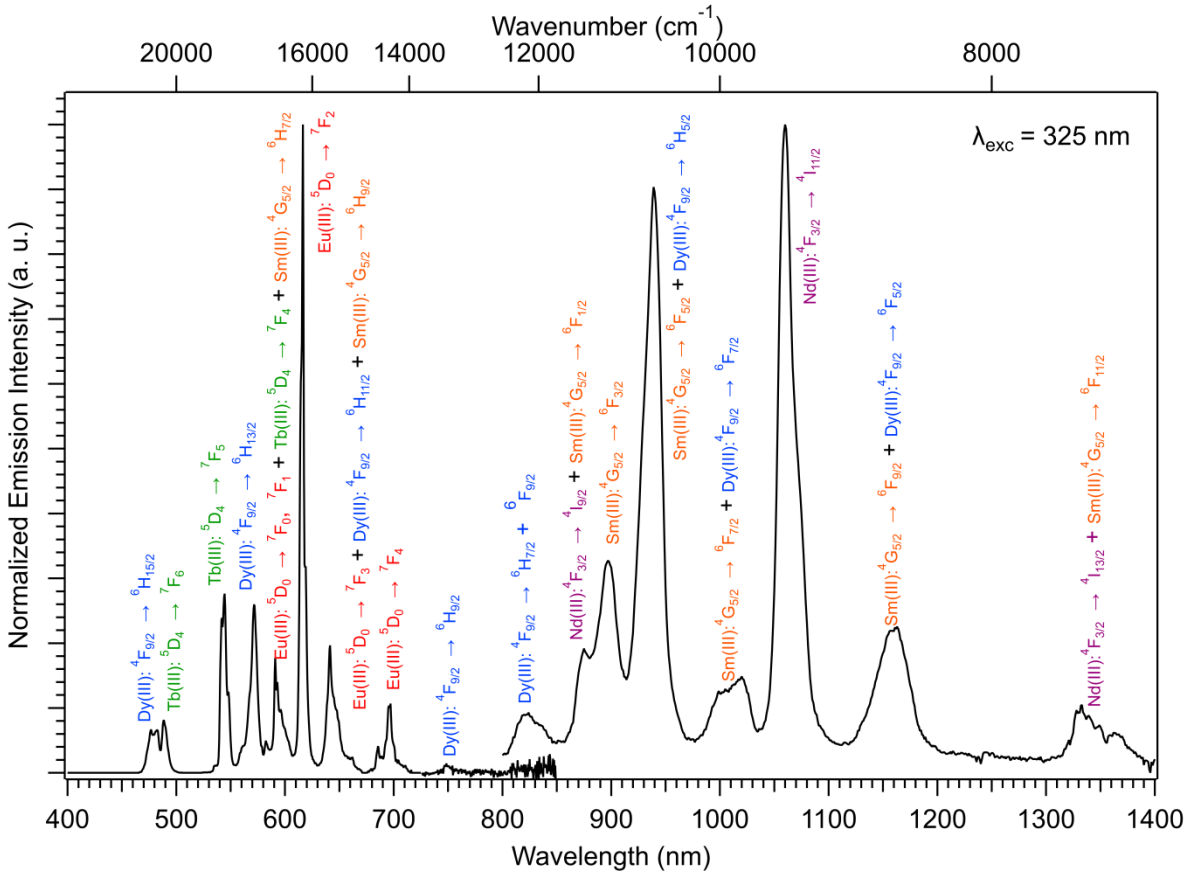


Figure 9. Emission spectrum, recorded at room temperature under UV irradiation (λ_{exc} = 325 nm), in the visible and IR regions, of $[Nd_{0.4}Sm_{0.4}Eu_{0.3}Gd_{0.2}Tb_{0.1}Dy_{0.6}(mip)_3]_\infty$. τ_{obs}(Tb) = 0.08(1) ms and τ_{obs}(Eu) = 0.12(1) ms. Spectra normalized on the most intense peak of the visible (450-850) and NIR regions (850-1600 nm), respectively.

This compound exhibits more than seventeen sizeable emission peaks under unique irradiation wavelength. To the best of our knowledge such a richness of the emission spectrum of a lanthanide-based coordination polymer is unprecedented. Hence, it is possible to design other molecular alloys with unique and very complex optical signatures which can be of great interest as far as luminescent bar-codes are targeted.

Moreover, as shown on Figure 10, it is possible to modulate the emission spectrum by varying excitation wavelength. This is of particular interest in the field of security taggants. Indeed, thanks to this property, it is possible to get different optical signatures for a single taggant which makes its counterfeiting almost impossible.

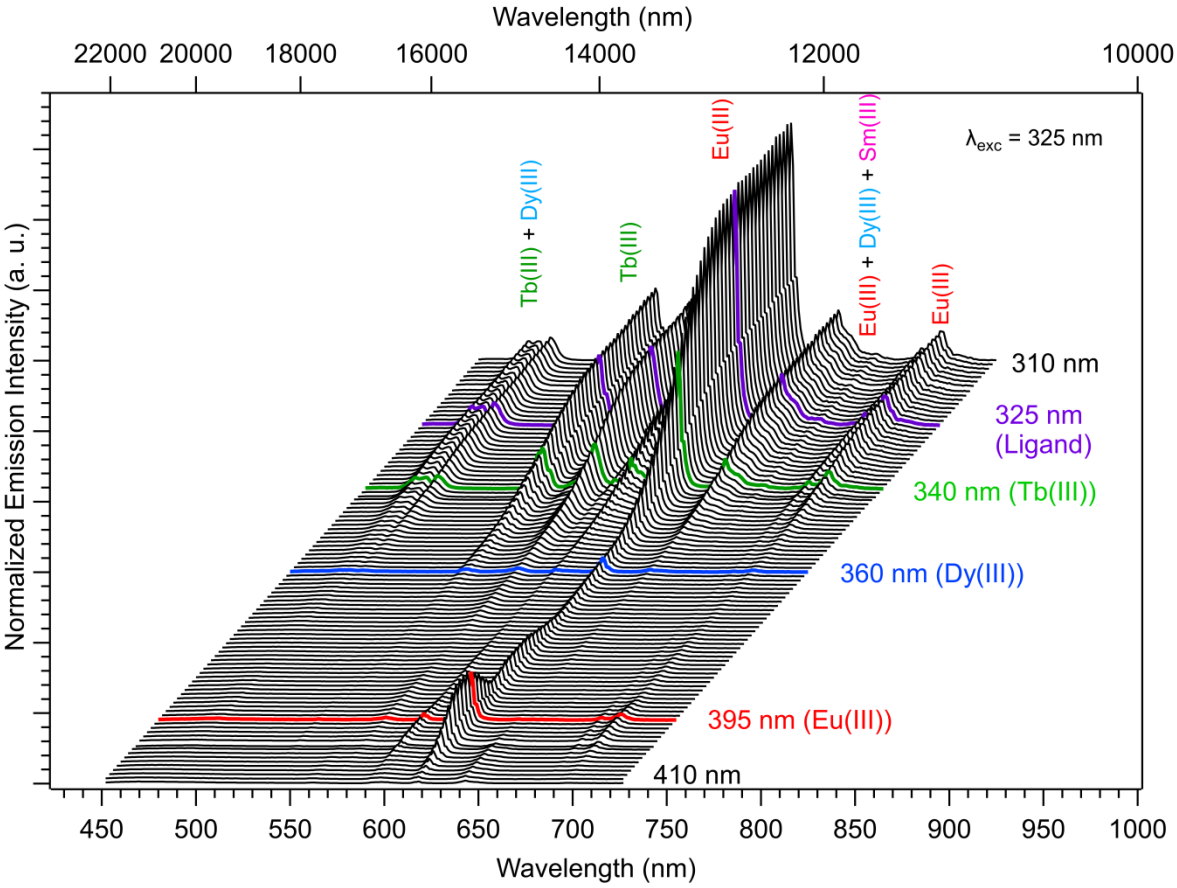


Figure 10. Emission spectra *vs* excitation wavelength of $[Nd_{0.4}Sm_{0.4}Eu_{0.3}Gd_{0.2}Tb_{0.1}Dy_{0.6}(mip)_3]_\infty$ at room temperature in the visible region. Referenced excitation wavelengths correspond to excitation from ligand at 325 nm, and from direct f-f irradiation of Tb(III) at 340 nm, Dy(III) at 360 nm and Eu(III) at 395 nm.

Spectra reported on Figure 10 have been integrated and corresponding colorimetric coordinates have been calculated (Figure S20). These calculations show that color emission variation *versus* excitation wavelength is sizeable. This is an asset as far as easy and fast detection is needed. This figure also shows that the red Eu^{3+} component is important in most of the spectra.

Emission spectra *versus* excitation wavelength have also been recorded at 77 K (Figure S21) and colorimetric coordinates have been calculated (Figure S22).

Figures S21 and S22 are clearly different from Figures 10 and S20. The major difference is that the red component of the emission spectrum is enhanced at low temperature (Figure S23). This was expected because a PET mechanism, which is observed for the

Eu-based homo-lanthanide coordination polymer is highly temperature dependent[66] and it has been shown that inter-metallic energy transfer are strongly temperature dependent.[63]

CONCLUSION AND OUTLOOKS.

In this series of lanthanide-based coordination polymers inter-metallic energy transfers are intrinsically weak because of the crystal structure. They can be even weakened by dilution by an optically non-active lanthanide ion. Thanks to this strategy, for the first time, it has been possible to prepare a series of molecular alloys whose emission color varies linearly with composition. This strategy also allows the preparation of hexa-metallic molecular alloys that exhibit unprecedented multi emission under a unique excitation wavelength. Moreover, their very rich emission spectra are highly dependent on temperature or excitation wavelength.

These original optical properties make this family of molecular alloys of great interest for potential applications such as materials tagging or thermometric measurements.

Of course, inter-metallic energy transfer is not fully controlled as evidences by the different luminescent lifetimes that are measured for all these compounds. Mechanisms that govern these transfers are, to date, not fully understood. However, this series of molecular alloys evidences that to prevent these transfers is possible.

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SUPPORTING INFORMATION.

Experimental powder X-ray diffraction diagrams of $[Ln_2(mip)_3]_\infty$ with Ln = Nd-Er except Pm plus Y ; Experimental powder X-ray diffraction diagrams of

$[Gd_{0.2}Dy_{2x}Tb_{1.8-2x}(mip)_3]_\infty$, $[Gd_{0.2}Eu_{2x}Tb_{1.8-2x}(mip)_3]_\infty$ and $[Gd_{0.2}Dy_{2x}Tb_{1.8-2x}(mip)_3]_\infty$ with $0 \leq x \leq 0.9$; Experimental powder X-ray diffraction diagrams of $[EuTb(mip)_3]_\infty$, $[Nd_{0.9}Gd_{0.2}Tb_{0.9}(mip)_3]_\infty$, $[Nd_{0.2}Gd_{0.2}Tb_{1.6}(mip)_3]_\infty$, $[Nd_{0.2}Sm_{1.2}Dy_{0.6}(mip)_3]_\infty$ and $[Nd_{0.4}Sm_{0.4}Eu_{0.3}Gd_{0.2}Tb_{0.1}Dy_{0.6}(mip)_3]_\infty$; Relative metallic contents measured by EDS ; ^1H MAS NMR and ^1H MAS NMR RFDR of $[Y_2(mip)_3]_\infty$; Excitation and emission spectra at room temperature of $[Nd_2(mip)_3]_\infty$, $[Sm_2(mip)_3]_\infty$, $[Eu_2(mip)_3]_\infty$, $[Tb_2(mip)_3]_\infty$, $[Dy_2(mip)_3]_\infty$ and $[Ho_2(mip)_3]_\infty$; Excitation and emission spectra at77 K and room temperature of $[Er_2(mip)_3]_\infty$; Solid state excitation and emission spectra of $[Nd_{0.2}Sm_{1.2}Dy_{0.6}(mip)_3]_\infty$ and of $[Nd_{0.4}Sm_{0.4}Eu_{0.3}Gd_{0.2}Tb_{0.1}Dy_{0.60}(mip)_3]_\infty$in the visible and IR regions ; Calculated colorimetric coordinates of $[Nd_{0.4}Sm_{0.4}Eu_{0.3}Gd_{0.2}Tb_{0.1}Dy_{0.60}(mip)_3]_\infty$ versus excitation wavelength at room temperature and 77K ; Solid state emission spectra of $[Nd_{0.4}Sm_{0.4}Eu_{0.3}Gd_{0.2}Tb_{0.1}Dy_{0.60}(mip)_3]_\infty$ in the visible under different excitation wavelength (from ligand at 325 nm, and from direct f-f irradiation of Tb(III) at 340 nm, Dy(III) at 360 nm and Eu(III) at 395 nm) at room-temperature (curves) and 77 K (dotted curves).

REFERENCES.

(1) Berg, E. W.; Alam, A., Studies on coordination polymers. Part I : Coordination polymers of 8,8'-dihydroxy-5,5'-biquinolyl. *Anal. Chim. Acta* **1962,** *27*, 454-459.

(2) Knobloch, F. W.; Rausher, W. H., Coordination polymers of copper(II) prepared at liquid-liquid interfaces. *J. Polym. Sci.* **1959,** *38* (133), 261-262.

(3) Zhou, D.; Huang, C.; Wang, K.; Xu, G., Synthesis, characterization, crystal structure and luminescent property studies on a novel heteronuclear lanthanide complex $\{H[EuLa_2(DPA)_5.8H_2O].8H_2O\}_n$ (H_2DPA=pyridine-2,6-dicarboxylic acid). *Polyhedron* **1994,** *13* (67), 987-991.

(4) Janiak, C., Engineering coordination polymers toward applications. *Dalton Trans.* **2003**, 2781-2804.

(5) Janiak, C.; Vieth, J. K., MOFs, MILs and more : cocepts, properties and application for porous coordination networks (PCNs). *New J. Chem.* **2010,** *34* (11), 2366-2388.

(6) Feng, J.; Zhang, H. J., Hybrid materials based on lanthanide organic complexes : a review. *Chem. Soc. Rev.* **2013,** *42*, 387-410.

(7) Cui, Y.; Li, B.; He, H.; Zhou, W.; Chen, B.; Qian, G., Metal-organic frameworks as platforms for functionnal materials. *Accounts Chem. Res.* **2016,** *49*, 483-493.

(8) Foo, M. L.; Matsuda, R.; Kitagawa, S., Functional Hybrid Porous Coordination Polymers. *Chem. Mater.* **2014,** *26*, 310-322.

(9) Li, B.; Wen, H.-M.; Cui, Y.; Qian, G.; Chen, B., Multifunctionnal lanthanide coordination polymers. *Prog. Polym. Sci.* **2015,** *48*, 40-84.

(10) Alezi, D.; Peedikakkal, A. M. P.; Weselinski, L.; Guillerm, V.; Belmabkhout, Y.; Cairns, A. J.; Chen, Z.; Wojtas, L.; Eddaoudi, M., Quest for highly connected metal-organic framework platforms : rara earth polynuclear clusters versatility meets net topology needs. *J. Am. Chem. Soc.* **2015,** *137*, 5421-5430.

(11) Calvez, G.; Le Natur, F.; Daiguebonne, C.; Bernot, K.; Suffren, Y.; Guillou, O., Lanthanide-based hexanuclear complexes and their use as molecular precursors. *Coord. Chem. Rev.* **2017,** *340*, 134-153.

(12) Lorusso, G.; Sharples, J. W.; Palacios, E.; Roubeau, O.; Brechin, E. K.; Sessoli, R.; Rossin, A.; Tuna, F.; Mc Innes, E. J. L.; Collison, D.; Evangelisti, M., A Dense Metal–Organic Framework for Enhanced Magnetic Refrigeration. *Adv. Mater.* **2013,** *25*, 4653-5656.

(13) Gai, S.; Li, C.; Yang, P.; Lin, J. D., Recent progress in rare earth micro/nanocrystals : Soft chemical synthesis, luminescent properties and biomedical applications. *Chem. Rev.* **2014,** *114*, 2243-2389.

(14) Bünzli, J. C. G., Rising stars in science and technology : Luminescent lanthanide materials. *Eur. J. Inorg. Chem.* **2017**, 5058-5063.

(15) Bünzli, J. C. G., On the design of highly luminescent lanthanide complexes. *Coord. Chem. Rev.* **2015,** *293-294*, 19-47.

(16) Fan, X.; Freslon, S.; Daiguebonne, C.; Le Polles, L.; Calvez, G.; Bernot, K.; Guillou, O., A family of lanthanide based coordination polymers with boronic acid as ligand. *Inorg. Chem.* **2015,** *54*, 5534-5546.

(17) Freslon, S.; Luo, Y.; Calvez, G.; Daiguebonne, C.; Guillou, O.; Bernot, K.; Michel, V.; Fan, X., Influence of photo-induced electron transfer on lanthanide-based coordination polymers luminescence : A comparison between two pseudo-isoreticular molecular networks. *Inorg. Chem.* **2014,** *53*, 1217-1228.

(18) Fan, X.; Freslon, S.; Daiguebonne, C.; Calvez, G.; Le Polles, L.; Bernot, K.; Guillou, O., Heteronuclear lanthanide-based coordination polymers exhibiting tunable multiple emission spectra. *J. Mater. Chem. C* **2014**, 5510-5525.

(19) Luo, Y.; Zheng, Y.; Calvez, G.; Freslon, S.; Bernot, K.; Daiguebonne, C.; Roisnel, T.; Guillou, O., Synthesis, Crystal Structure and Luminescent Properties of New Lanthanide-Containing Coordination Polymers Involving 4,4'-oxy-bis-benzoate as Ligand. *Cryst. Eng. Comm.* **2013,** *15*, 706-720.

(20) da Luz, L. L.; Viana, B. F. L.; da Silva, G. C. O.; Gatto, C. C.; Fontes, A. M.; Malta, M.; Weber, I. T.; Rodrigues, M. O.; Junio, S. A., Controlling the energy transfer in lanthanide-organic frameworks for the production of white-light emitting materials. *Cryst. Eng. Comm.* **2014,** *16*, 6914-6918.
(21) Lekshmi, S. S.; Ramya, A. R.; Reddy, M. L. P.; Varughese, S., Lanthanide complex-derived white-light emitting solids: A survey on design strategies. *J. Photochem. Photobiol. C* **2017,** *33*, 109-131.
(22) Reddy, M. L. P.; Sivakumar, S., Lanthanide benzoates: a versatile building block for the construction of efficient light emitting materials. *Dalton Trans.* **2013,** *42*, 2663-2678.
(23) Yang, Q.-Y.; Wu, K.; Jiang, J.-J.; Hsu, C.-W.; Pan, M.; Lehn, J.-M.; Su, C. Y., Pure white light and yellow to blue emission tuning in single crystals of Dy(III) metal-organic frameworks. *Chem. Comm.* **2014,** *50*, 7702-7704.
(24) Jüstel, T.; Nikol, H.; Ronda, C., New Developments in the Field of Luminescent Materials for Lighting and Displays. *Angew. Chem. Int. Ed.* **1998,** *37*, 3084-3103.
(25) Zhang, X.; Wang, W.; Hu, Z.; Wang, G.; Uvdal, K., Coordination polymers for energy transfer: Preparations, properties, sensing applications, and perspectives. *Coord. Chem. Rev.* **2015,** *284*, 206-235.
(26) Serwy, I. B.; Wanderlay, K. A.; Lucena, M. A. M.; Maldaner, A. O.; Talhavini, M.; Rodrigues, M. O.; Weber, I. T., $[Ln_2(BDC)_3(H_2O)_4]_n$: A low cost alternative for GSR luminescent marking. *J. Lumin.* **2018,** *200*, 24-29.
(27) Weber, I. T.; A.J.G, d. M.; de melo Lucena, M. A.; Rodrigues, M. O.; Alves Junior, S., High Photoluminescent MetalOrganic Frameworks as Optical Markers for the Identification of Gunshot Residues. *Anal. Chem.* **2011,** *83*, 4720-4723.
(28) De Lill, D. T.; De Bettancourt-Dias, A.; Cahill, C. L., Exploring lanthanide luminescence in metal-organic framework : synthesis, structure, and guest-sensitized luminescence of a mixed europium/terbium-adipate framework and a terbium-adipate framework. *Inorg. Chem.* **2007,** *46* (10), 3960-3965.
(29) Miyata, K.; Konno, Y.; Nakanishi, T.; Kobayashi, A.; Kato, M.; Fushimi, K.; Hasegawa, Y., Chameleon Luminophore for Sensing Temperatures: Control of Metal-to-Metal and Energy Back Transfer in Lanthanide Coordination Polymers. *Angew. Chem. Int. Ed.* **2013,** *52*, 6413-6416.
(30) Rocha, J.; Brites, D. S. C.; Carlos, L. D., Lanthanide organic framework luminescent thermometers. *Chem. - Eur. J.* **2016,** *22*, 14782-14795.
(31) Cadiau, A.; Brites, D. S. C.; Costa, P. M. F. J.; Ferreira, R. A. S.; Rocha, J.; Carlos, L. D., Ratiometric nanothermometer based on an emissive Ln^{3+} organic framework. *ACS Nano* **2013,** *7* (8), 7213-7218.
(32) Brites, D. S. C.; Lima, P. P.; Silva, N. J. O.; Millan, A.; Amaral, V. S.; Palacio, F.; Carlos, L. D., Lanthanide-based luminescent molecular thermometers. *New J. Chem.* **2011,** *35*, 1177-1183.
(33) Gooch, J.; Daniel, B.; Abbate, V.; Frascione, N., Taggant materials in forensic science. *Trends Anal. Chem.* **2016,** *83*, 49-54.
(34) Qi, Q.; Li, C.; Liu, X.; Jiang, S.; Xu, Z.; Lee, R.; Zhu, M.; Xu, B.; Tian, W., Solid-state photoinduced luminescence swithfor advanced anticounterfeiting and super-resolution imaging. *J. Am. Chem. Soc.* **2017,** *139*, 16036-16039.
(35) Guillou, O.; Daiguebonne, C.; Calvez, G.; Bernot, K., A long journey in lanthanide chemistry : from fundamental crystallogenesis studies to commercial anti-counterfeiting taggants. *Accounts Chem. Res.* **2016,** *49*, 844-856.
(36) do Nascimento, J. F. S.; de Araujo, A. M. U.; de Farias Montero, A. F.; Junior, S. A.; Barros, B. S., Solid-state tunable photoluminescence in gadolinium-organic frameworks : effects of the Eu3+ content and co-doping with Tb3+. *New J. Chem.* **2018,** *42*, 5514-5522.
(37) Freslon, S.; Luo, Y.; Daiguebonne, C.; Calvez, G.; Bernot, K.; Guillou, O., Brightness and color tuning in a series of lanthanide-based coordination polymers with benzene 1,2,4,5-tetracarboxylic acid as ligand. *Inorg. Chem.* **2016,** *55*, 794-802.
(38) Karraker, D. G., Coordination of trivalent lanthanide ions. *J. Chem. Educ.* **1970,** *47* (6), 424-430.

(39) Pearson, R. G., Hard and soft acids and bases - the evolution of a chemical concept. *Coord. Chem. Rev.* **1990,** *100*, 403-425.
(40) Haquin, V.; Etienne, M.; Daiguebonne, C.; Freslon, S.; Calvez, G.; Bernot, K.; Le Polles, L.; Ashbrook, S. E.; Mitchell, M. R.; Bünzli, J. C. G.; Guillou, O., Color and Brightness tuning in hetero-nuclear lanthanide teraphthalate coordination polymers. *Eur. J. Inorg. Chem.* **2013**, 3464-3476.
(41) Le Natur, F.; Calvez, G.; Daiguebonne, C.; Guillou, O.; Bernot, K.; Ledoux, J.; Le Polles, L.; Roiland, C., Coordination polymers based on hexanuclear rare earth complexes : Toward independant luminescence brightness and color emission. *Inorg. Chem.* **2013,** *52*, 6720-6730.
(42) Wu, J.; Zhang, H.; Du, S., Tunable luminescence and white light emission of mixed lanthanide–organic frameworks based on polycarboxylate ligands. *J. Mater. Chem. C* **2016,** *4*, 3364-3374.
(43) Huang, W.; Pan, F.; Liu, Y.; Huang, S.-C.; Li, Y.; Yong, J.; Li, Y.; Kirillov, A. M.; Wu, D., An Efficient Blue-Emissive Metal−Organic Framework (MOF) for Lanthanide-Encapsulated Multicolor and Stimuli-Responsive Luminescence. *Inorg. Chem.* **2017,** *56*, 6362-6370.
(44) Chorazy, S.; Kumar, K.; Nakabayashi, K.; Sieklucka, B.; Ohkoshi, S. I., Fine Tuning of Multicolored Photoluminescence in Crystalline Magnetic Materials Constructed of Trimetallic EuxTb1−x[Co(CN)6] Cyanido-Bridged Chains. *Inorg. Chem.* **2017,** *56*, 5239-5252.
(45) Roberts, R. J.; Le, D.; Leznoff, D. B., Color-Tunable and White-Light Luminescence in Lanthanide−Dicyanoaurate Coordination Polymers. *Inorg. Chem.* **2017,** *56*, 7948-7959.
(46) Gai, Y.; Guo, Q.; Xiong, K.; Jiang, F.; Li, C.; Li, X.; Chen, Y.; Zhu, C.; Huang, Q.; Yao, R.; Hong, M., Mixed-Lanthanide Metal−Organic Frameworks with Tunable Color and White Light Emission. *Cryst. Growth Des.* **2017,** *17*, 940-944.
(47) Dechambenoit, P.; Ferlay, S.; Kyritsakas, N.; Hosseini, M. W., Playing with isostructurality : from tectons to molecular alloys and composite crystals. *Chem. Comm.* **2009**, 1559-1561.
(48) Bünzli, J. C. G.; Eliseeva, S. V., Basics of lanthanide photophysics. In *Lanthanide Luminescence*, Hänninen, P.; Härmä, H., Eds. Springer Berlin Heidelberg: 2010; pp 1-45.
(49) Piguet, C.; Bünzli, J. C. G.; Bernardinelli, G.; Hopfgatner, G.; Williams, A. F., Self-assembly and photophysical properties of lanthanide dinuclear triple-helical complexes. *J. Am. Chem. Soc.* **1993,** *115* (18), 8197-8206.
(50) White, K. A.; Chengelis, D. A.; Gogick, K. A.; Stehman, J.; Rosi, N. L.; Petoud, S., Near infra-red luminescent lanthanide MOF barcodes. *J. Am. Chem. Soc.* **2009,** *131* (50), 18069-18071.
(51) Yang, Q. Y.; Pan, M.; Wei, S. C.; Li, K.; Du, B. B.; Su, C. Y., Linear dependance of photomuminescence in mixed Ln-MOFs for color tunability and barcode application. *Inorg. Chem.* **2015,** *54* (12), 5707-5716.
(52) Du, B.-B.; Zhu, Y.-X.; Pan, M.; Yue, M.-Q.; Hou, Y.-J.; Wu, K.; Zhang, L.-Y.; Chen, L.; Yin, S.-Y.; Fan, Y.-N.; Su, C. Y., Direct white light and dual-channel barcode module from Pr(III)-MOF crystals. *Chem. Comm.* **2015,** *51*, 12533-12536.
(53) Gao, M.-L.; Wang, W.-J.; Liu, L.; Han, Z.-B.; Wei, N.; Cao, X.-M.; Yuan, D.-Q., Microporous hexanuclear Ln(III) cluster-based metal-organic frameworks: color tunability for barcode applications ans selective removal of methylene blue. *Inorg. Chem.* **2017,** *56* (1), 511-517.
(54) Badiane, A. M.; Freslon, S.; Daiguebonne, C.; Suffren, Y.; Bernot, K.; Calvez, G.; Costuas, K.; Camara, M.; Guillou, O., Lanthanide based coordination polymers with a 4,5-dichlorophthalate ligand exhibiting highly tunable luminescence : Toward luminescent bar codes. *Inorg. Chem.* **2018,** *57*, 3399-3410.
(55) Badiane, I.; Freslon, S.; Suffren, Y.; Daiguebonne, C.; Calvez, G.; Bernot, K.; Camara, M.; Guillou, O., High britness and easy color modulation in lanthanide-based coordination polymers with 5-methoxyisophthalate as ligand: Toward emission colors additive strategy. *Cryst. Growth Des.* **2017,** *17* (3), 1224-1234.
(56) Desreux, J. F., In *Lanthanide Probes in Life, Chemical and Earth Sciences*, Choppin, G. R.; Bünzli, J. C. G., Eds. Elsevier: Amsterdam, 1989; Vol. Elsevier, p 43.

(57) Kraus, W.; Nolze, G., POWDER CELL - A program for the representation and manipulation of crystal structures and calculation of the resulting X-ray powder patterns. *J. Appl. Crystallogr.* **1996,** *29*, 301-303.
(58) Roisnel, T.; Rodriguez-Carjaval, J., A Window Tool for Powder Diffraction Patterns Analysis. *J. Mater. Sci. Forum* **2001,** *378* (3), 118-123.
(59) Roisnel, T.; Rodriguez-Carjaval, J., WinPLOTR : a windows tool for powder diffraction pattern analysis. *Materials Science Forum, Proceedings of the Seventh European Powder Diffraction Conference (EPDIC 7)* **2000**, 118-123.
(60) CIE, *International Commission on Illumination - Technical report*. CIE: 1995; Vol. 13-3, p 16.
(61) Wyszecki, G., Colorimetry. In *Handbook of Optics*, Driscoll, W. G.; Vaughan, W., Eds. Mac Graw-Hill Book Company: New-York, 1978; pp 1-15.
(62) Weissman, S. I., Intramolecular energy transfer - The fluorescence of complexes of europium. *J. Chem Phys* **1942,** *10* (4), 214-217.
(63) Abdallah, A.; Freslon, S.; Fan, X.; Rojo, A.; Daiguebonne, C.; Suffren, Y.; Bernot, K.; Calvez, G.; Roisnel, T.; Guillou, O., Lanthanide based coordination polymers with 1,4 carboxyphenylboronic ligand: multi emissive compounds for multi sensitive luminescent thermometric probes. *Inorg. Chem.* **2019,** *58*, 462-475.
(64) Latva, M.; Takalo, H.; Mukkala, V.-M.; Matachescu, C.; Rodriguez-Ubis, J. C.; Kankare, J., Correlation between the lowest triplet state energy level of the ligand and lanthanide luminescence quantum yields. *J. Lumin.* **1997,** *75*, 149-169.
(65) Steemers, F. J.; Verboom, W.; Reinhoudt, D. N.; Van der Tol, E. B.; Verhoeven, J. W., New sensitizer-modified calix[4]arenes enabling Near-UV Excitation of complexed luminescent lanthanide ions. *J. Am. Chem. Soc.* **1995,** *117* (37), 9408-9414.
(66) Prodi, L.; Maestri, M.; Ziessel, R.; Balzani, V., Luminescent Eu3+, Tb3+ and Gd3+ complexes of a branched triazacyclononane ligand containing three 2,2'bipyridine units. *Inorg. Chem.* **1991,** *30* (20), 3798-3802.
(67) Galaup, C.; Couchet, J.-M.; Bedel, S.; Tisnès, P.; Picard, C., Direct access to terpyridine-containing polyazamacrocycles as photosensitizing ligands for Eu(III) luminescence in aqueous media. *J. Org. Chem.* **2005,** *70* (6), 2274-2284.
(68) Bünzli, J.-C. G., Lanthanide luminescence for biomedical analyses and imaging. *Chem. Rev.* **2010,** *111*, 2729-2755.
(69) Ward, M. D., Transition metal sensitized near infrared luminescence from lanthanide in d-f heteronuclear arrays. *Coord. Chem. Rev.* **2007,** *251*, 1663-1677.
(70) Suffren, Y.; Golessorkhi, B.; Zare, D.; Guénée, L.; Nozary, H.; Eliseeva, S. V.; Petoud, S.; Hauser, A.; Piguet, C., Taming lanthanide centered upconversion at the molecular level. *Inorg. Chem.* **2016,** *55* (20), 9964-9972.
(71) Zare, D.; Suffren, Y.; Guénée, L.; Eliseeva, S. V.; Nozary, H.; Aboshyan-Sorgho, L.; Petoud, S.; Hauser, A.; Piguet, C., Smaller than a nanoparticle with the desgn of discrete polynuclear molecular complexes displaying near-infrared to visible upconversion. *Dalton Trans.* **2015,** *44*, 2529-2540.
(72) Kerbellec, N.; Kustaryono, D.; Haquin, V.; Etienne, M.; Daiguebonne, C.; Guillou, O., An Unprecedented Family of Lanthanide-Containing Coordination Polymers with Highly Tunable Emission Properties. *Inorg. Chem.* **2009,** *48* (7), 2837-2843.

TABLE OF CONTENT GRAPHIC

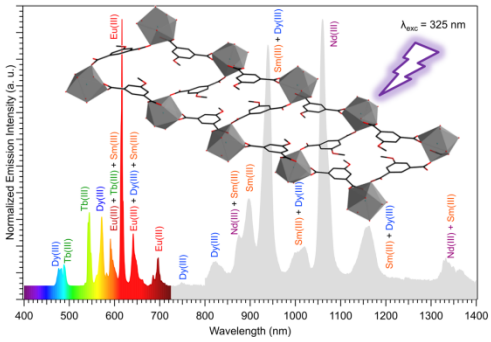

TABLE OF CONTENT TEXT

A molecular alloy, that contains six different lanthanide ions ($[Nd_{0.4}Sm_{0.4}Eu_{0.3}Gd_{0.2}Tb_{0.1}Dy_{0.6}(mip)_3(H_2O)_8 \cdot 4H_2O]_\infty$), under a unique irradiation wavelength, exhibits almost twenty emission peaks in both the visible and the NIR regions which could be of great interest as far as luminescent bar-codes are targeted.