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An Unprecedented Family of Lanthanide-Containing Coordination Polymers with Highly Tunable Emission Properties

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Reactions in water between mixtures of rare earth ions (Ln =Y, La−Tm, except Pm) and the sodium salt of terephthalic acid lead to an infinite family of isostructural heteropolynuclear coordination polymers. The monophasic character of the synthesized powders as well as the isostructurality of the heteropolynuclear compounds with the previously described mononuclear $[Tb_2(C_8H_4O_4)_3(H_2O)_4]_\infty$ are ascertained on the basis of the X-ray powder diffraction diagrams. One family of heterodinuclear compounds has been studied in detail, that is, $[(La_{2-x}Y_x)(C_8H_4O_4)_3(H_2O)_4]_\infty$ with $0 \le x \le 2$. This study demonstrates the random character of the spatial distribution of the metallic ions. In order to demonstrate the high modularity of the physical properties, the solid-state luminescent properties of the compounds of general formula $[(Eu_{2-x}Tb_x)(C_8H_4O_4)_3(H_2O)_4]_\infty$ with $0 \le x \le 2$ have been studied and compared to those of the corresponding mixtures of $[(Eu_2)(C_8H_4O_4)_3(H_2O)_4]_\infty$ and $[(Tb_2)(C_8H_4O_4)_3(H_2O)_4]_\infty$. In order to confirm the general character of these studies, the compound containing in equal proportions all 13 rare earth ions between La and Tm (except Pm) plus Y has been synthesized and characterized. At last, the solid-state luminescent properties of compounds belonging to the ternary system $[(Ce_{2-x-y}Eu_xTb_y)(C_8H_4O_4)_3(H_2O)_4]_\infty$ with $x + y \le 2$ are briefly described.

Introduction

Recently, remarkable progress has been made in the area of molecular inorganic−organic hybrid compounds. The synthesis and characterization of infinite networks has been an area of rapid growth.[1] Actually, the design of nanoporous open frameworks is the main factor of this revival[2−6] because these compounds are anticipated to exhibit good efficiency as far as size-selective separation, catalysis, and gas storage are concerned.[7,8]

Currently, there is also an increasing interest in luminescent systems. Lanthanide-containing systems often exhibit intense luminescence and are potentially interesting for the design of luminescent materials and devices.[9−18]

For a decade, our group has been interested in the synthesis at room temperature and ambient pressure of lanthanide-containing coordination polymers involving rigid benzene−polycarboxylate ligands.[19−23] The key point in this chemistry

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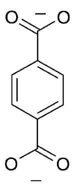
Scheme 1. 1,4-Benzene-Dicarboxylate or Terephthalate Ligand (bdc^{2-})



is the inner character of the 4f valence orbitals of the lanthanide ions, which are efficiently shielded by the 5s and 5p outer orbitals. These ions can therefore be described as typical Pearson's hard acids.[24,25] This induces a great homogeneity of the lanthanide ions' chemical properties. That is why lanthanide-containing materials are often claimed to exhibit tunable physical properties, because it is possible to design isostructural compounds involving different lanthanide ions. However, their coordination geometry is mainly governed by sterical considerations.[19] From lanthanum to lutetium, the 4f orbitals gradually filled, entailing a decrease of the ionic radii and one or more structure changes along the lanthanide series. This implies that, despite the great homogeneity of the lanthanide ions' chemical properties, there are very few examples of extended families of isostructural compounds,[26] and actually there are very few lanthanide-containing coordination polymer families exhibiting really tunable physical properties.

In the frame of our studies, we have recently reported a family of coordination polymers with the general formula $[Ln_2(C_8H_4O_4)_3(H_2O)_4]_\infty$ with Ln = La−Tm or Y[27] (except Pm) and where $(C_8H_4O_4)^{2-}$ stands for 1,4-benzene-dicarboxylate or terephthalate and is hereafter designated by bdc^{2-} (Scheme 1).

These 13 compounds are all isostructural to the previously described[27,28] $[Tb_2(bdc)_3(H_2O)_4]_\infty$ compound (see Figure 1). $[[Tb_2(bdc)_3(H_2O)_4]_\infty$ crystallizes in the triclinic system, space group $P\bar{1}$ (no. 2); its 8-fold coordination polyhedron can be described as a distorted dodecahedron.]

On the basis of the relatively high number of mononuclear compounds belonging to the structural family as well as their rather high thermal and chemical stabilities, we have decided to synthesize heteropolynuclear systems. Actually, to date, there are only few reported mixed-lanthanide-containing coordination polymers.[29−32] Indeed, most of the syntheses lead either to poly phased mixtures of mononuclear compounds or in compounds in which a segregation of the metal ions is observed. Furthermore, to the best of our knowledge, among the rare already described heteropolynuclear lanthanide-containing coordination polymers, there is only one columinescent compound.[32]

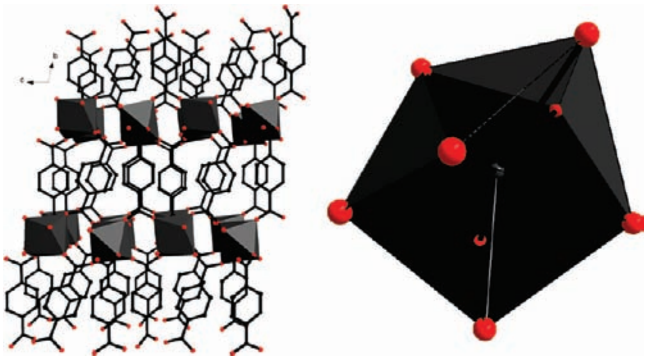


Figure 1. Left: Perspective view along the $\vec{a}$ axis of $[Tb_2(bdc)_3(H_2O)_4]_\infty$. Right: Terbium coordination polyhedron.

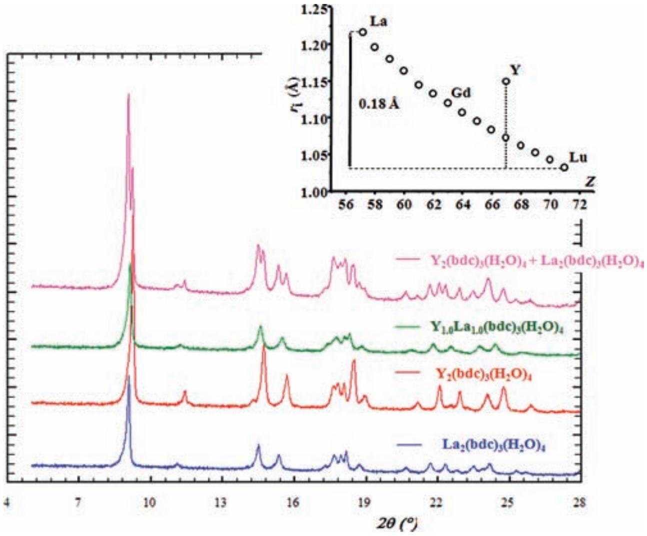


Figure 2. X-ray diffraction diagrams of microcrystalline powders. In the inset, the ionic radii of the various lanthanide ions in 8-fold coordination versus their atomic number (Y^{3+} is superimposed).

We describe here a family of isostructural heteropolynuclear lanthanide-containing coordination polymers with the general formula $[(\sum_{i=1}^{13}Ln^{i}_{x_i})(C_8H_4O_4)_3(H_2O)_4]_\infty$ with $\sum_{i=1}^{13} x_i = 2$ and where Ln^i symbolizes one of the lanthanide ions between La and Tm (except Pm) or Y.[3] All of these compounds are isostructural with $[Tb_2(C_8H_4O_4)_3(H_2O)_4]_\infty$. In order to demonstrate the tunable character of the physical properties of the compounds belonging to this family, we have measured their luminescence because lanthanide ions are well-known for their original luminescent properties.[9]

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Table 1. SEM Microanalysis Results for $[La_{2-x}Y_x(bdc)_3(H_2O)_4]_\infty$ and $[Eu_{2-x}Tb_x(bdc)_3(H_2O)_4]_\infty$ with $0 \le x \le 2$

theoretical atomic percent		experimental atomic percent		theoretical atomic percent		experimental atomic percent	
Y(III)	La(III)	Y(III)	La(III)	Eu(III)	Tb(III)	Eu(III)	Tb(III)
90	10	91(2)	9(2)	90	10	91(2)	9(2)
80	20	84(2)	16(2)	80	20	80(2)	20(2)
70	30	70(2)	30(2)	70	30	70(2)	30(2)
60	40	58(2)	42(2)	60	40	60(2)	40(2)
50	50	51(2)	49(2)	50	50	50(2)	50(2)
40	60	42(2)	58(2)	40	60	41(2)	59(2)
30	70	27(2)	73(2)	30	70	31(2)	69(2)
20	80	18(2)	82(2)	20	80	19(2)	81(2)
10	90	9(2)	91(2)	15	85	17(2)	83(2)
				10	90	8(2)	92(2)
				5	95	4(2)	96(2)

This study reveals strong intermetallic optical interactions in these compounds.

Experimental Section

Synthesis of the Microcrystalline Powders. Terephthalic acid was purchased from Acros Organics and used without further purification. Disodium terephthalate salt is prepared by addition of 2 equiv of sodium hydroxide to a suspension of terephthalic acid in deionized water. The obtained solution is then evaporated to dryness. The resulting solid is put in suspension in ethanol, and the mixture is stirred and refluxed for 1 h. After filtration and drying, a white powder of disodium 1,4-benzenedicarboxylate is collected in 90% yield.

Elem anal. calcd (found) for $C_8H_4O_4Na_2$ (MW = 210 g mol^{-1}): C, 45.7% (45.5%); H, 1.9% (2.0%); O, 30.5% (30.5%); Na, 21.9% (22.0%).

Hydrated lanthanide chlorides were prepared from the corresponding oxides according to literature methods.[33] Lanthanide oxides were purchased from STREM Chemicals and used without further purification.

Microcrystalline powders of the coordination polymers were obtained by mixing stoichiometric amounts of mixtures of lanthanide chlorides in water with the disodium salt of terephthalic acid. Precipitations immediately occurred. The white precipitates were filtered and dried in the air. The yields of the reactions are close to 100%. FT-IR spectra show the expected strong characteristic absorptions for the symmetric and asymmetric vibrations of benzene−dicarboxylate ligands (1650−1550 cm^{-1} and 1420−1335 cm^{-1}) and the coordinated water molecules (3460 cm^{-1}). They show no absorption band of any protonated ligand (1715−1680 cm^{-1}).

The obtained microcrystalline powders have all been assumed to be isostructural to the previously described compound $[Tb_2(bdc)_3(H_2O)_4]_\infty$,[28] on the basis of their X-ray powder diffraction diagram.

The granulometry of the microcrystalline powders has been measured using a CILAS Laser Sizer 1180. All of the measured powders display similar size distributions: 25% of the particles have a size < 0.3 μm, 50% have a size between 0.3 and 1.4 μm, and the size of the remaining 25% ranges between 1.4 and 9.0 μm. There is also a great amount of particles around 50 nm which can be related to the size of the elemental crystallites that constitute the particles. This is in perfect agreement with what had been observed for the related mononuclear compounds.[27]

The global chemical compositions of the powders were checked by inductively coupled plasma−atomic emission spectrometry (ICP-AES) measurements using a Perkin-Elmer Optima 3000 apparatus. In all cases, these measurements revealed that the relative weight of each lanthanide ion was in perfect agreement with what had been anticipated during the synthesis.

The homogeneity of the powders has been checked using scanning electron microscopy (SEM) measurements. From each synthesized powder, five samples have been taken, and five measurements have been done on each sample. The results were in good agreement with each other as well as with the results of ICP measurements. In Table 1, the results for two families of binuclear compounds, namely, $[La_{2-x}Y_x(bdc)_3(H_2O)_4]_\infty$ and $[Eu_{2-x}Tb_x(bdc)_3(H_2O)_4]_\infty$ with $0 \le x \le 2$, are reported. These results confirm that all of the particles forming the microcrystalline powders have the same chemical formula that the powders themselves have.

X-Ray Powder Diffraction. The diagrams have been collected using a Panalytical X'Pert Pro diffractometer with an X'celerator detector. The typical recording conditions were 40 kV and 40 mA for Cu Kα (λ = 1.542Å); the diagrams were recorded in θ/θ mode for 60 min between 5° and 75° (8378 measurements) with a step size of 0.0084° and a scan time of 50 s. The calculated patterns were produced using the Powdercell and WinPLOTR software programs.[34−37]

The patterns have been taken as experimental data in the REFLEX module of the MS Modeling software.[38] Then, were refined using Rietveld refinement[39,40] with a pseudo-Voigt profile to compute refined cell parameters for each compound. These experimental data have been compared with the cell parameters of $[Tb_2(bdc)_3\cdot(H_2O)_4]_\infty$.

Scanning Electron Microscopy−Energy-Dispersive Spectrometry (SEM-EDS) Analysis. The powder measurements of the heteropolymetallic coordination polymers were done using SEM. All observations and measurements were carried out with a JEOL JSM 6400 scanning electron microscope (JEOL Ltd., Tokyo, Japan) with an EDS analysis system (OXFORD Link INCA). The voltage was kept at 9 kV, and the samples were mounted on carbon stubs and coated for 5 min with a gold/palladium alloy using a sputter coater (Jeol JFC 1100).

Solid-State Luminescence Measurements. Solid-state emission spectra were measured on a Perkin-Elmer LS-55 fluorescence spectrometer with a pulse Xe lamp. Slit widths were 5 nm for excitation and 5 nm for emission. The excitation wavelength has

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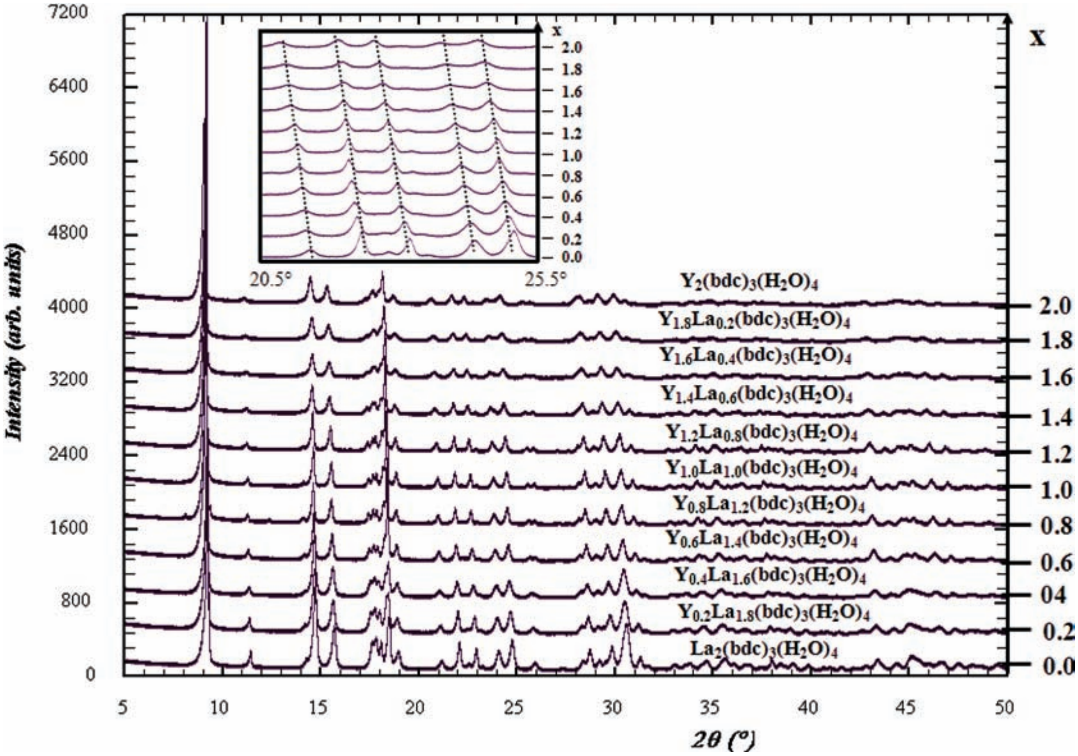

Figure 3. X-ray powder diffraction diagrams of several compounds with general formula $[La_{2-x}Y_x(bdc)_3(H_2O)_4]_\infty$ with $0 \leq x \leq 2$.

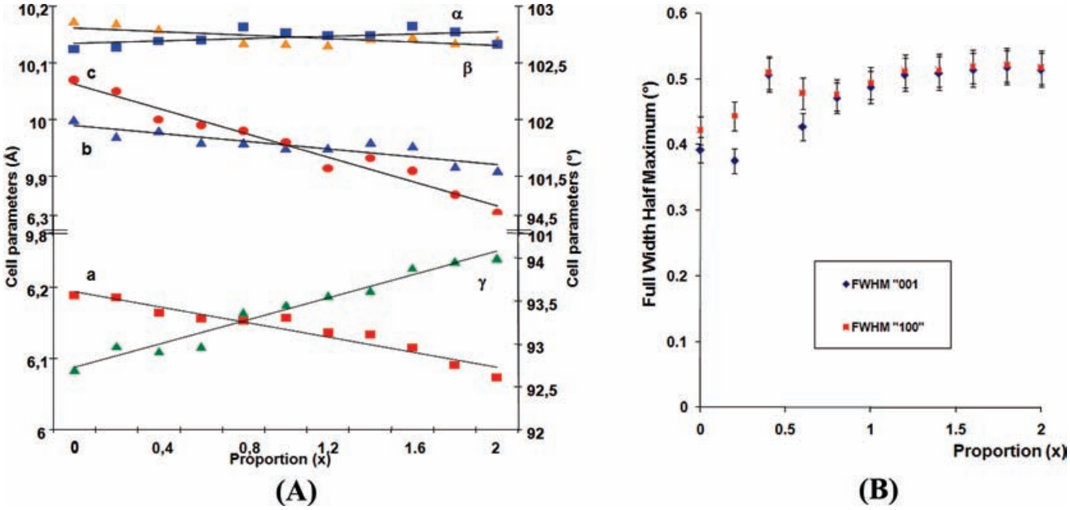

Figure 4. Left (A): Cell parameters versus x for compounds with the general formula $[La_{2-x}Y_x(bdc)_3(H_2O)_4]_\infty$ with $0 \leq x \leq 2$. Right (B): Full-width half-maximum for diffraction peaks [001] or [010] and diffraction peaks [100] for compounds with the general formula $[La_{2-x}Y_x(bdc)_3(H_2O)_4]_\infty$ with $0 \leq x \leq 2$.

been fixed at 312 nm because it corresponds to a maximum of absorption of the terephthalate ligand.[41] Spectra were all recorded at room temperature between 400 and 800 nm in identical operating conditions without turning the lamp off, to ensure a valid comparison between the emission spectra. Reproducibility of the measurements has been carefully checked using reproduction several times. The data were collected, at 100 nm min^{-1}, in phosphorescence mode with a 0.3 ms delay time between the excitation pulse and the emission measurement.

Results and Discussion

In order to check the monophasic character of the microcrystalline powders, we have first studied the compounds with general chemical formula $[La_{2-x}Y_x(bdc)_3(H_2O)_4]_\infty$ with $0 \leq x \leq 2$. These two metallic ions have been chosen because of their very different ionic radii. In Figure 2 are reported the X-ray diffraction diagrams of four microcrystalline powders: (i) the powder of the mononuclear compound with chemical formula $[La_2(bdc)_3(H_2O)_4]_\infty$, (ii) the powder of the mononuclear compound with chemical formula $[Y_2(bdc)_3(H_2O)_4]_\infty$, (iii) the powder obtained by mixing equal amounts of the two previous powders, and (iv) the powder of the heterobinuclear compound with chemical formula $[LaY(bdc)_3(H_2O)_4]_\infty$. As one can notice in this figure, the ionic radii of Y^{3+} and La^{3+} ions are rather different, and

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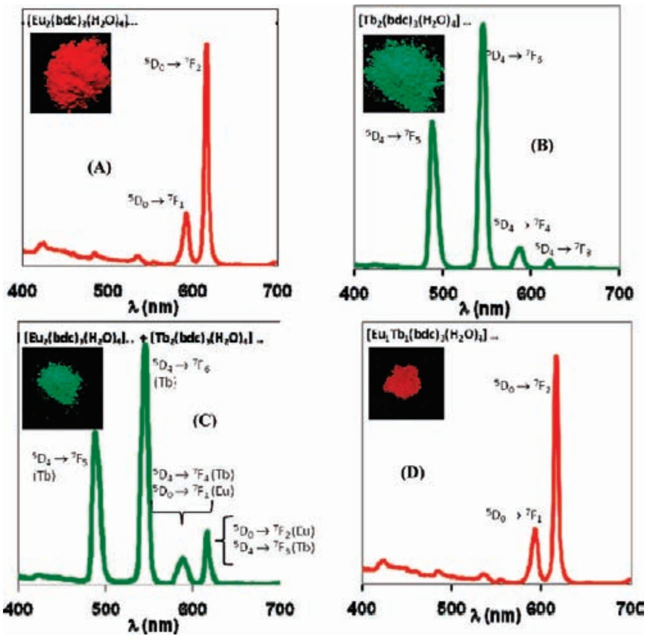


Figure 5. Photographs under UV irradiation (312 nm) and luminescent spectra (λ_{exc} = 312 nm) of four microcrystalline powders. Top left (A): $[Eu_2(bdc)_3(H_2O)_4]_\infty$. Top right (B): $[Tb_2(bdc)_3(H_2O)_4]_\infty$. Bottom left (C): Mixture of $[Tb_2(bdc)_3(H_2O)_4]_\infty$ and $[Eu_2(bdc)_3(H_2O)_4]_\infty$, 50% each. Bottom right (D): $[EuTb(bdc)_3(H_2O)_4]_\infty$.

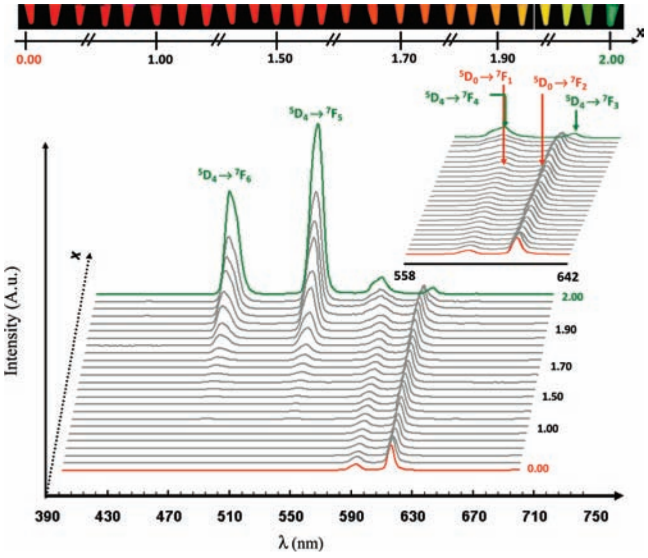
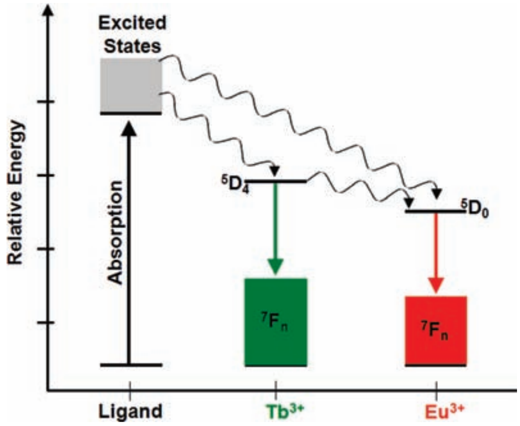


Figure 6. Luminescence spectra of compounds $[Eu_{2-x}Tb_x(bdc)_3(H_2O)_4]_\infty$ with $0 \leq x \leq 2$ versus x. The x axis is not linear, for clarity. On the top, photographs of the compounds under UV radiations are reported (λ_{exc} = 312 nm).

the diffraction diagrams of both corresponding mononuclear compounds cannot be confused with each other. Consequently, as expected, on the diffraction diagram of the mixture, the diffractions peaks are split in two. On the other hand, the diffraction peaks on the diffraction diagram of the heterobinuclear compound show no splitting. Furthermore, there is neither an additional peak (characteristic of a superstructure) nor a broadening of the peaks (characteristic of disorder). This indicates that, in this heterobinuclear compound, there is no order or segregation. In this compound, the metallic ions are randomly distributed on the metallic sites.

Scheme 2. Energy Transfer Diagram



In order to confirm this observation, we have studied several other compounds of the family involving both Y^{3+} and La^{3+} in various ratios. These compounds have general chemical formula $[La_{2-x}Y_x(bdc)_3(H_2O)_4]_\infty$ with $0 \leq x \leq 2$, and their diffraction diagrams are reported in Figure 3.

These diagrams have been indexed and their cell parameters fitted. From these calculations, it appears that the cell

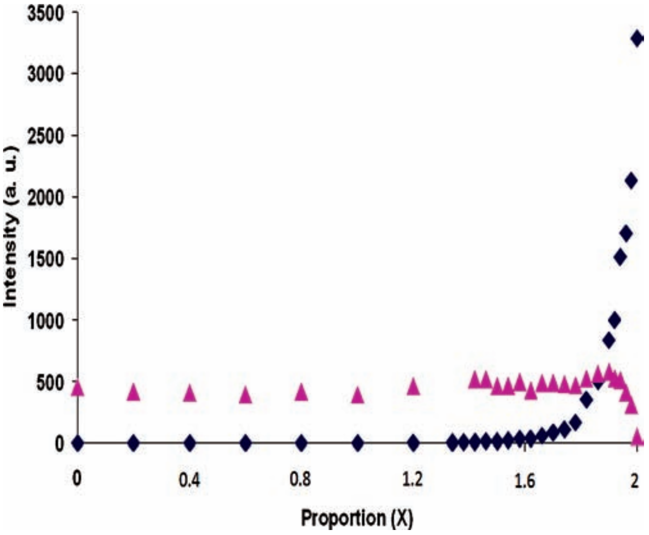


Figure 7. Integrated intensities of the peaks that can be attributed to Eu(III) luminescence (▲) and Tb(III) luminescence (♦) in the emission spectra of several $[Eu_{2-x}Tb_x(bdc)_3(H_2O)_4]_\infty$ compounds versus x.

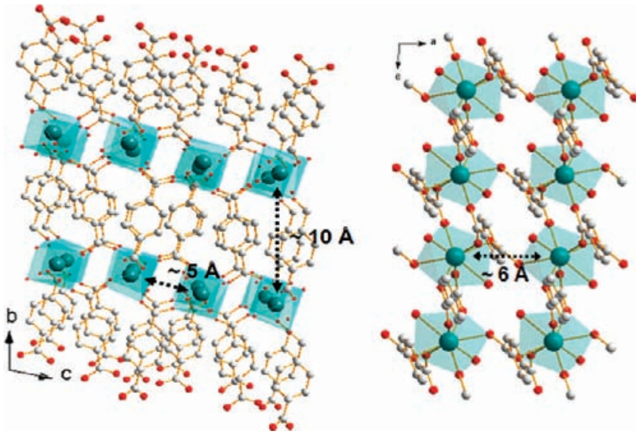
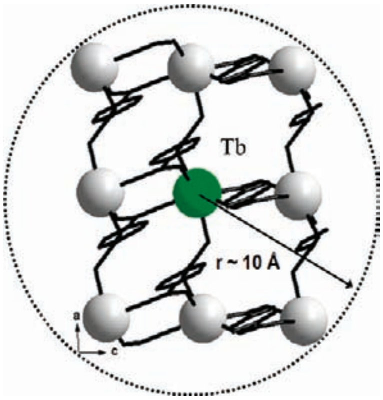


Figure 8. Views of the crystal structure of $[Tb_2(bdc)_3(H_2O)_4]_\infty$ along the $\vec{a}$ axis (left) and the $\vec{b}$ axis (right).

Scheme 3. Schematic Representation of the Metallic Surrounding of One Considered Metallic Center in $[Eu_{2-x}Tb_x(bdc)_3(H_2O)_4]_\infty$



parameters vary almost linearly with x and, so, with the weighted average of the metallic ions' ionic radii (see Figure 4). The full widths at half maximum of the diffraction peaks have also been measured for both [001] or [010] diffraction peaks and [100] diffraction peaks, and no variation was observed whatever the value of x was.

In order to verify the general character of the random metallic distribution in the compounds, we have decided to study another heterobinuclear system. Because of their well-known interesting optical properties, we have chosen the Eu^{3+} and Tb^{3+} ions. The compounds with general chemical formula $[Eu_{2-x}Tb_x(bdc)_3(H_2O)_4]_\infty$ with $0 \leq x \leq 2$ have thus been synthesized, and their X-ray diffraction diagrams have been recorded. A study using powder X-ray diffraction similar to the one described above has been carried out and led to similar conclusions. However, the ionic radii of the Eu^{3+} and the Tb^{3+} ions are very close to each other, and the variations of the cell parameters are very small. We have so decided to confirm these results by studying the luminescent properties of the compounds belonging to this family. These luminescent properties have been studied both by optical microscopy under UV radiation ($\lambda = 312$ nm) and by fluorimetry. In these compounds, upon excitation of the conjugated organic ligand, intersystem crossing and energy transfer occur, leading to lanthanide ions' luminescence. This phenomenon is well-known and is often referred to as the "antenna effect".[30,42,43]

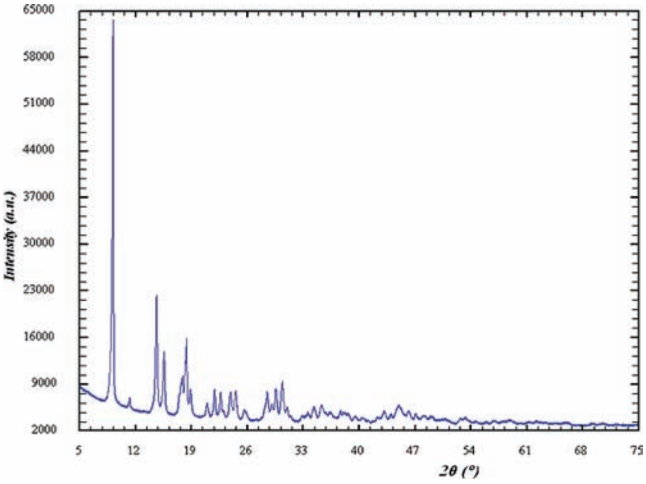


Figure 9. X-ray diffraction diagram of $[(\sum_{i=1}^{13} Ln^i_{2/13})(C_8H_4O_4)_3(H_2O)_4]_\infty$.

Both experiments indicate that the mixture of the microcrystalline powders of the two mononuclear compounds exhibits different luminescent properties than the heterobinuclear compound does (see Figure 5). Indeed, all of the particles of the microcrystalline powder of the binuclear compound exhibit the same color of luminescence, confirming the homogeneity of the powder. On the other hand, the mixture of the two microcrystalline powders of the mononuclear compounds shows, as expected, two types of luminescent particles: one emitting in the red ($[Eu_2(bdc)_3(H_2O)_4]_\infty$) and the another one in the green ($[Tb_2(bdc)_3(H_2O)_4]_\infty$). Furthermore, neither the observed emission color nor the emission spectrum of the heterobinuclear compound corresponds to a simple superimposition of the emission colors or spectra of the mononuclear pure compounds. Indeed, its spectrum is very similar to the spectrum of the pure europium-containing mononuclear compound (it emits in the red). This is despite the fact that the quantum yield of the pure terbium-containing mononuclear compound is much greater than that of the pure europium-containing one.[27] These observations strongly suggest that there are complex intermetallic interactions in the binuclear compound. In order to verify this assumption, we have recorded the luminescent spectra of several compounds with the general chemical formula $[Eu_{2-x}Tb_x(bdc)_3(H_2O)_4]_\infty$ with $0 \leq x \leq 2$ (see Figure 6).

Figure 6 suggests that an energy transfer is occurring in the heterobinuclear compounds presented here. This phenomenon is also commonly encountered for mixed 4f−3d systems where lanthanide ion emission is sensitized via the ligand-to-metal charge transfer state of the transition metal ion.[44] In the present case, upon UV irradiation, the energy is transferred from the excited states of the benzene dicarboxylate ligand to the excited states of both Eu^{3+} and Tb^{3+} ions. However, most of the energy in the $^5D_4$ level of the Tb^{3+} ion is transferred to the $^5D_0$ level of the Eu^{3+} ion (see Scheme 2).

Actually, the transitions $^5D_0 \rightarrow {}^7F_n$ arising from the Eu^{3+} ion surpass the transition $^5D_4 \rightarrow {}^7F_n$ arising from the Tb^{3+} ion, and their intensities remain fairly constant for all compounds where x is between 0 and 1.8 (see Figure 7).

This type of intermetallic energy transfer mechanism has already been reported.[14,30,32,45] For compounds with x greater than 1.8, the intensities of the transitions attributable to the Eu^{3+} ions decrease rapidly while the intensities of the transitions attributable to the Tb^{3+} ion increase abruptly. This behavior can be related to the crystal structure of the compounds.

Actually, it is commonly accepted that intermetallic optical interactions become inefficient when the involved metallic centers are more than 10 Å from each other. As can be seen from Figure 8, the crystal structure can be described as planes spreading parallel to the $(\vec{a}, \vec{c})$ plane and more than 10 Å

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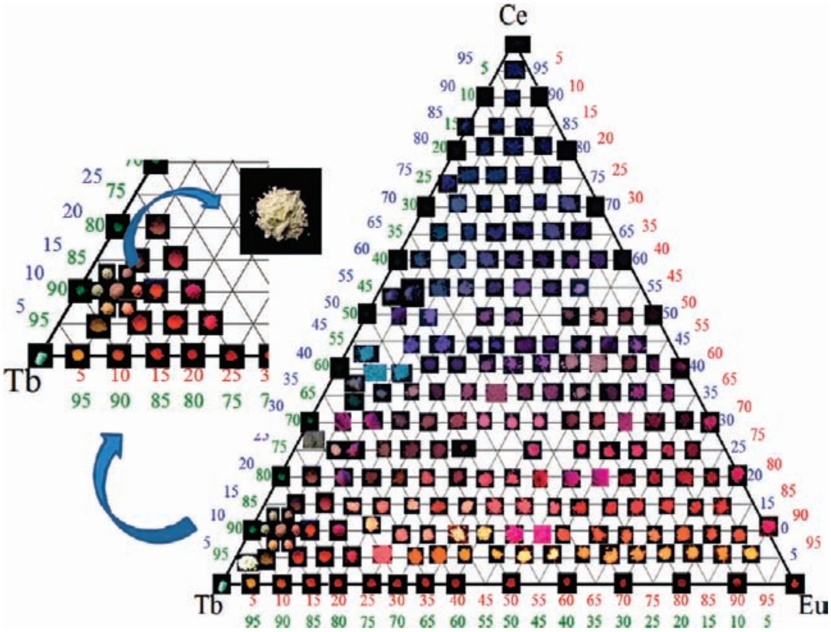
Scheme 4. Photographs of the Luminescence of the Compounds with General Formula $[(Ce_{2-x-y}Eu_xTb_y)(C_8H_4O_4)_3(H_2O)_4]_\infty$ with $x + y \leq 2$ under UV Irradiation[a]



[a] In the inset, a photograph of a compound belonging to this family and exhibiting almost white light.

from each other. An analysis of these planes reveals that there are only eight metallic centers nearer than 10 Å from a considered central metallic ion (see Scheme 3). So, let us consider a Tb^{3+} ion as a central metallic ion, with the assumption that the Eu^{3+} and the Tb^{3+} ions are actually randomly distributed in the crystal structure. This central Tb^{3+} ion is statistically isolated from Eu^{3+} ions when the ratio Tb^{3+}/Eu^{3+} is greater than 90%, that is, when x is greater than 1.8 in the general chemical formula $[Eu_{2-x}Tb_x(bdc)_3(H_2O)_4]_\infty$.

At this stage, we were convinced that the synthesis of a perfectly disordered heterobinuclear compound with general formula $[Ln_{2-x}Ln_x'(bdc)_3(H_2O)_4]_\infty$ is possible, whatever Ln and Ln′ are (Ln and Ln′ = La−Tm except Pm plus Y). We then studied different heterotrinuclear and heterotetranuclear compounds of this family, and in all cases, the results of our studies confirm the monophasic character of the compound as well as the random character of the metal ions' distributions. We have thus undertaken the synthesis and the characterization of a compound with chemical formula $[(\sum_{i=1}^{13}Ln^i_{2/13})(C_8H_4O_4)_3(H_2O)_4]_\infty$, that is, the compound containing, in equal proportions, all of the lanthanide ions between lanthanum and thulium (except promethium) plus yttrium. The homogeneity of the chemical composition was good, the content of each metallic ion being 7.7% ± 0.5% (SEM measurements). The X-ray diffraction pattern of the powder shows neither broadening nor twinning of the diffraction peaks, nor apparition of peaks attributable to superstructure (see Figure 9). It so confirms the monophasic character of the powder and the random distribution of the metal ions over the metallic sites of the structure.

This compound presents obviously very little interest in and of itself. However, it confirms the infinite number of isomorphous compounds that constitute this family.

Conclusion and Outlooks

In this paper, we have described and characterized a family of compounds containing an infinite number of isostructural compounds with general formula $[(\sum_{i=1}^{13}Ln^i_{x_i})(C_8H_4O_4)_3(H_2O)_4]_\infty$ with $\sum_{i=1}^{13} x_i = 2$ and where Ln^i symbolizes one of the lanthanide ions between La and Tm (except Pm) or Y. This family of lanthanide-based coordination polymers is, to the best of our knowledge, the most extended family ever reported in this class of materials. Thanks to the tunable chemical composition of its compounds, it is possible to tune the physical properties, such as optical properties, for instance, modifying neither the crystal structure nor the granulometry of the powder. We think that this system could be a good tool for theoretical investigations in physics. On the other hand, during the studies reported above, we investigated the family of compounds with chemical formula $[(Ce_{2-x-y}Eu_xTb_y)(C_8H_4O_4)_3(H_2O)_4]_\infty$ with $x + y \leq 2$. After a control using X-ray diffraction analysis in which all of the synthesized powders were monophasic and all of the metallic ions were randomly distributed over the metallic sites, we undertook the study of their solid-state luminescent properties. Preliminary results of this study are reported in Scheme 4.

In Scheme 4, it clearly appears that the combinations in various ratios of Ce^{3+} (whose luminescence occurs in the blue), Tb^{3+}, and Eu^{3+} ions lead to a great variety of luminescent properties. This study also confirms that there are complex intermetalic interactions. Finally, this study reveals that it is possible to obtain a white luminophore under UV radiation by mixing well-chosen rare earth ions in well-chosen relative ratios. We are currently pursuing this objective.

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