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Dual Emission from Luminescent Nonalanthanide Clusters

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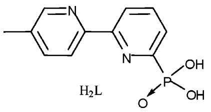
Clusters containing nine lanthanide and six sodium ions are crystallized with the help of a tridentate ligand bearing a phosphonic acid group; the structure of the Eu^{III} compound reveals a host–guest assembly $Eu{\subset}Na_6Eu_8L_{16}$ with a substantial quantum yield (32%). A similar Eu^{III}–Yb^{III} structure displays dual luminescence in the visible (Eu^{III}) and NIR (Yb^{III}) ranges.

The designs of bimetallic 4f−4f edifices for dual probes, of 3d−4f complexes in which the luminescence of the 4f ion is steered by the d transition-metal ion, or of similar bimetallic molecules for the study of magnetic interactions are stunning examples of the degree of control chemists can achieve on the electronic and, henceforth, physicochemical properties of these molecules.[1,2] In parallel, potential applications in telecommunications and light-emitting diodes have stirred the development of lanthanide-containing coordination polymers, nanoparticles, and extended inorganic clusters featuring luminescent centers. On the other hand, exploration of discrete polymetallic molecular frameworks with high nuclearity is less advanced,[1,2] except in the cases of dendrimeric structures for magnetic resonance imaging contrast agents[3] and of metallacrowns.[4] Such molecules have, however, a large potential interest as precursors for doped materials or for the study of (and implementation of) metal−metal interactions, e.g., energy transfers or magnetic interactions.[5] Research on these clusters has usually focused in obtaining wheel- or cage-like edifices, some of them acting as supramolecular receptors for anions or cations. They can be assembled using different synthetic strategies, with the key being to avoid the extension of the structure into a coordination polymer and, possibly, to control the nuclearity (i.e., the number of metal ions in the core, m) or the global complexity $m + n$ of $[Ln_mL_n]$.[6] This can be achieved with simple polydentate ligands leaving some coordination vacancies around the metal ion, as demonstrated by the following examples: (i) the reaction of La^{III} ions with a tris(bidentate) pyrazolonate led to the isolation of octametallic clusters La_8L_8 with a three-dimensional ring structure;[7] (ii) the self-assembly of a tetradentate terpyridine fitted with a carboxylic acid function with Eu^{III} ions resulted in a cyclic structure containing a hexametallic ring hosting a seventh metal ion in its center $[Eu{\subset}(EuL_2)_6]^{9+}$;[8] (iii) a decametallic wheel structure with nonplanar skeleton was isolated with seven-coordinate Dy^{III} ions;[9] (iv) octameric ellipsoid complexes of La^{III} and Ce^{III} have been obtained, which display nonlinear optical properties;[10] (v) polymetallic oxo/hydroxo clusters have been crystallized with the help of amino acids as ancillary ligands and of templating halide ions.[11] Alternatively, a d transition-metal complex with functionalized ligands can serve as the templating agent to assemble star-like polymetallic Gd^{III} compounds.[12]



H_2L

In this work, we make use of 5′-methyl-2,2′-bipyridyl-6-phosphonic acid, H_2L, to produce discrete polymetallic clusters. Previously, we have shown that this ligand reacts in water with lanthanide perchlorates to successively form

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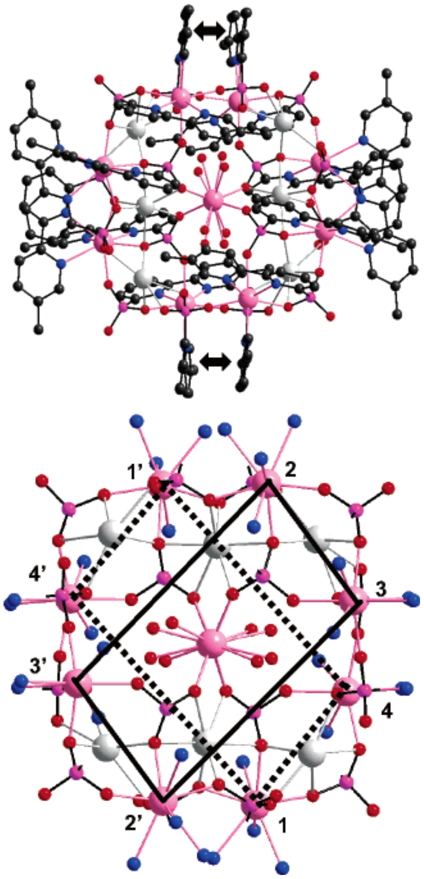

Figure 1. (Top) Molecular structure of the $Na_6Eu_9L_{16}$ cluster (H atoms and Na−O bonds are not shown for the sake of clarity). Bold double arrows denote $\pi-\pi$ interactions. (Bottom) Detailed view of the metal ion cluster, along with the numbering scheme of the Eu atoms.

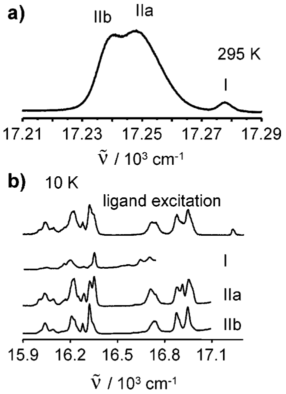

Figure 2. (a) $^5D_0 \leftarrow {}^7F_0$ excitation spectrum of a polycrystalline sample of the $Na_6Eu_9L_{16}$ cluster ($\tilde{\nu}_{an}$ = 16 234 cm^{-1}; band-pass 500 cm^{-1}). (b) $^5D_0 \rightarrow {}^7F_J$ (J = 1 and 2) transitions ($\tilde{\nu}_{ex}$ = 28 170 cm^{-1}, top, and on the specific $^5D_0 \leftarrow {}^7F_0$ transition) of the $Na_6Eu_9L_{16}$ cluster (for site I, the spectrum is too noisy above 16 700 cm^{-1} to be informative).

1:1, 1:2, and 1:3 complexes with log β_3 in the range of 18−20 at pH 7.4.[13] Here we report that slow diffusion of acetone into aqueous solutions with a 1:3 $Ln-H_2L$ stoichiometric ratio and adjusted to pH 7.4 yields monoclinic crystals of $Na_6Ln_9L_{16}$ clusters, with the lanthanide ions lying in the middle of the series (Eu, Gd, Tb, and Er), as well as of the heterospecies $Na_6Eu_xYb_{9-x}L_{16}$. The crystallization process is strictly controlled because any change in the $Ln-H_2L$ proportion, in the nature of the base, or in the crystallization pH results in a failure to isolate the polymetallic edifices.

The molecular structure of C_2-symmetrical $[Na_6Eu_9L_{16}]$-$(OH)\cdot 51H_2O$[14] is shown in Figure 1. Eight eight-coordinate peripheral Eu_p^{III} ions are arranged on the corners of two parallel parallelepipeds (Eu1, Eu4, Eu1′, and Eu4′, angles 80.6 and 99.2°; Eu2, Eu3, Eu2′, and Eu3′, angles 79.6 and 100°) twisted by approximately 90°, 4.33 Å apart, and perpendicular to the C_2 axis. The ninth Eu_c^{III} ion is disordered and occupies two positions (Eu5A−Eu5B = 0.78 Å; occupancy factor = 0.5) around the baricenter of the peripheral Eu atoms. The centroid of these positions lies in the middle of the plane defined by the six sodium ions, but slightly below (−0.101 Å). Each peripheral Eu_p^{III} is three-coordinated by two ligand strands and its coordination sphere is completed by two O atoms from the phosphonate groups of two other ligand strands. The central Eu_c^{III} ion is linked to four water molecules and four O atoms from four different phosphonate groups. The latter present a rare coordination outfit, with one O atom being monodentate, another one bridging between a Eu_c^{III} ion and a Na^I ion, and the third O implying a trifurcated binding to two Na^I ions and a peripheral Eu_p^{III} ion. The mean Eu−O and Eu−N distances are standard for the eight-coordinate peripheral Eu_p^{III} ions,[14] while they are slightly longer for the central ion (closer to nine-coordinate values). In fact, the Na_6Eu_9 cluster is held together by an intricate network of bridging phosphonate groups. In addition, sizable $\pi-\pi$ interactions occur between one pyridine of pairs of parallel ligand strands, with a mean distance of 3.42 Å. The asymmetric unit contains 36 water molecules; 26 surround the cluster, and 6 of them show disorder.

To further characterize the cluster, we have resorted to high-resolution luminescence spectroscopy of the Eu^{III} ion on polycrystalline samples. At room temperature, the excitation spectrum mainly displays two broad bands at 29 700 and 35 900 cm^{-1} arising from the ligand states and pointing to energy transfer from the ligand to the metal ion, as observed for the monometallic tris complex;[13] a high-resolution scan in the spectral range of the $^5D_0 \leftarrow {}^7F_0$ transition evidences three components: a weak one at 17 278 cm^{-1}, labeled I, and two more intense ones of equal intensity at 17 248 (IIa) and 17 240 (IIb) cm^{-1}, corresponding to at least three different chemical environments for the Eu^{III} ions (Figure 2a). Excitation on these bands yields spectra that are very similar at room temperature but that reveal

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(14) Crystal data: M_t = 6610.33, monoclinic, space group $C2/c$ (No. 15), a = 29.602(4) Å, b = 31.335(5) Å, c = 27.502(3) Å; β = 91.265(10)°; V = 25504(6) $Å^3$; Z = 4; ρ_{calc} = 1.722 mg m^{-3}; $2.84° < \theta < 25.03°$; crystal dimensions (mm), 0.31 × 0.30 × 0.28; T = 140(2) K.; 21 712 unique of 78 415 reflections collected; 1548 parameters used for full-matrix-block least-squares refinement on F^2, R1 = 0.0839 and wR1 = 0.2274 [$I > 2\sigma(I)$]; CCDC 286125 contains the supplementary crystallographic data for this paper. These can be obtained free of charge via www.ccdc.cam.ac.uk/products/csd/request (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, U.K., fax (+44) 1223-336-033, or e-mail deposit@ccdc.cam.ac.uk). Peripheral Eu_p-Eu_p distances range between 5.48 and 5.80 Å (mean 5.63 ± 0.24 Å), while Eu_p-Eu_c distances are in the range 5.94−6.66 Å (mean 6.39 ± 0.74 Å); mean Eu−O distances are 2.32 ± 0.04 (2.24−2.37) and 2.44 ± 0.13 (2.25−2.54) Å for the peripheral and central ions, respectively; mean Eu−N distances are 2.63 ± 0.04 (2.56−2.69) Å.

significant differences at 10 K (Figure 2b). Because of excitation band overlap and, possibly, energy transfers between the various Eu^{III} environments, excitation on sites IIa and IIb results in the observation of a number of components larger than $2J + 1$ for each transition.

Taking this into account, the emission spectra arising from sites IIa and IIb are very similar, while the one originating from site I is clearly different. They all point to low symmetry. The luminescence decays obtained under selective excitation ($^5D_0 \leftarrow {}^7F_0$ transition, 10 K) are monoexponential, and the lifetime of the Eu($^5D_0$) excited level is the same for IIa and IIb with an average value of 2.37 ± 0.07 ms, while it is much shorter for I (0.24 ± 0.02 ms). This clearly points to the absence of coordinated water molecules in the inner sphere of the metal ions in IIa and IIb, while a rough estimate taking the lifetime of IIa as a reference[1] yields a hydration number $q \approx 3.8$ for site I. Therefore, the spectroscopic data are perfectly in line with the crystal structure determination, which reveals that sites IIa and IIb have a similar coordination environment although displaying substantially different mean Eu−O distances.[14] The quantum yield measured on polycrystalline samples upon ligand excitation at 30 300 cm^{-1}, using an integration sphere and an absolute method,[15] is 32 ± 5%. This is much larger than the quantum yield obtained in water for the monometallic tris complex (8.9%, with $q = 1.3$),[13] in line with the absence of coordinated water molecules on the peripheral Eu^{III} ions.

In view of these interesting photophysical properties, we have tried to produce heteropolymetallic clusters and succeeded in crystallizing a mixed Eu−Yb assembly from a solution containing a 4:5:27 Eu−Yb−H$_2$L stoichiometric ratio. X-ray diffraction data on single crystals show that the space group is the same as that for the homometallic Eu^{III} cluster, and the unit cell is very similar. The crystals are not of the highest quality, which prevented a more detailed analysis aiming at determining the Eu−Yb ratio. We have therefore turned to chemical analysis by transmission electron microscopy. Data collected on six to nine different spots of five different crystals yield an average Eu−Yb ratio of 1.0 ± 0.2 that is close to the stoichiometric ratio used in the crystallization process. Interestingly, the cluster displays dual Eu^{III}- and Yb^{III}-centered luminescence at both 10 (Figure 3) and 295 K. At low temperature, the spectra originating from Eu^{III} match closely those of $Eu\subset Na_6Eu_8L_{16}$; in particular, the contribution of Eu$_c^{III}$ to the $^5D_0 \leftarrow {}^7F_0$ transition is almost the same (1.3 ± 0.2% vs 1.6 ± 0.2%) and its lifetime is identical (0.24 ms). The latter data imply that more than 80% of the Yb^{III} ions occupy the peripheral sites and that they are most probably statistically distributed among these sites. As a consequence of the replacement of Eu^{III} ions by Yb^{III} ions, the quantum yield of the Eu^{III}-centered luminescence is reduced to 20 ± 2% in the Eu−Yb cluster. Moreover, the lifetime of the peripheral Eu$_p^{III}$ ions is shorter than that in the homometallic species and is clearly different for sites IIa (1.45 ± 0.05 ms at 10 K) and IIb (1.79 ± 0.04 ms at 10 K). Direct excitation of the Eu^{III} ions using either the $^5D_0 \leftarrow {}^7F_0$ or $^5D_2 \leftarrow {}^7F_0$ transitions yields essentially no Yb^{III} luminescence, so that excitation of the latter ion mainly occurs through the ligand strands. As a consequence, both the decrease in the Eu^{III} lifetime in going from Na_6Eu_9 to $Na_6Eu_{9-x}Yb_x$ ($x = 4$ and 5) and the differentiation between sites IIa and IIb most probably result from a deformation of the Eu^{III} sites consecutive to the incorporation of the smaller Yb^{III} ions, which brings deactivating oscillators closer to the Eu^{III} ions. Further investigations are being initiated in order to get better single crystals and to fully clarify this point by X-ray diffraction. Finally, although the Yb^{III} luminescence may appear to be modest with an apparent quantum yield of 0.22 ± 0.02% and a lifetime of 9.3 ± 0.1 μs at 295 K, it compares favorably with the emission obtained in deuterated organic solvents with sensitizers such as fluorescein (e.g., 0.23% in CD$_3$OD).[16]

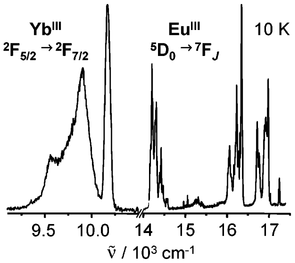

Figure 3. Luminescence spectra at 10 K [$\tilde{\nu}_{ex} = 28\,180$ (left) and 21 468 cm^{-1} (right)] of the polycrystalline $Na_6Eu_{9-x}Yb_xL_{16}$ cluster showing emission of both Yb^{III} and Eu^{III}.

A mixed Eu^{III}−Tb^{III} cluster has also been obtained, and its photophysical properties will be described in a subsequent paper, together with those of Na_6Er_9 and of the magnetic properties of the Na_6Ln_9 (Ln = Gd and Tb) compounds. In summary, we have synthesized new lanthanide cluster complexes with a high and controlled nuclearity, and initial photophysical investigation indicates that nonradiative deactivation processes are minimized, resulting in a sizable quantum yield for the Eu^{III} edifice. Moreover, this architecture can host different luminescent lanthanide ions, opening remarkable perspectives for developing multicolor emissive probes covering both the visible and NIR ranges.

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Supporting Information Available: X-ray crystallographic file in CIF format of the Na_6Eu_9 cluster and figures of the Na_6Eu_9 metallic core and of excitation and emission spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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