Efficient sensitized emission in Yb(III) pentachlorotropolonate complexes†

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New Yb(III) complexes based on the pentachlorotropolonate (pctrop) ligand show enhanced infrared emission when excited in the orange organic chromophore. Yb(pctrop)$_3$(DMF-d_7)$_2$ presents the highest reported quantum yield for a nonfluorinated infrared-emitting organolanthanide complex.

Optical materials with trivalent lanthanide ions are of interest due to the variety of monochromatic and intense light emissions arising from the (partially forbidden) intraconfigurational f–f transitions.[1] In particular, some of them show relatively long-lived photoluminescence (PL) in the near infrared (NIR) region of the spectrum, which has applications in a number of fields, including biology and telecommunications.[2] Organolanthanides allow for enhanced optical properties due to the possibility of increasing the rare-earth concentration and for exciting the lanthanide emitter *via* allowed absorptions in organic chromophores[3] (sensitization).

Among NIR emitters, Er^{3+}, Nd^{3+} and Yb^{3+} have been widely studied for their favourable emitting energies and potential for long-lived, efficient luminescence. However, NIR-emitting organolanthanides usually show low efficiencies (and short lifetimes in the order of a few microseconds or less). This is due to the multiphonon de-excitation[2,4] caused by the coupling of high energy oscillators (C–H, O–H, N–H) in the organic ligands or the solvent to the electronic levels of the rare-earth. Strategies to overcome this problem include filling the coordination sphere of the lanthanide with bulky multidentate ligands, thereby

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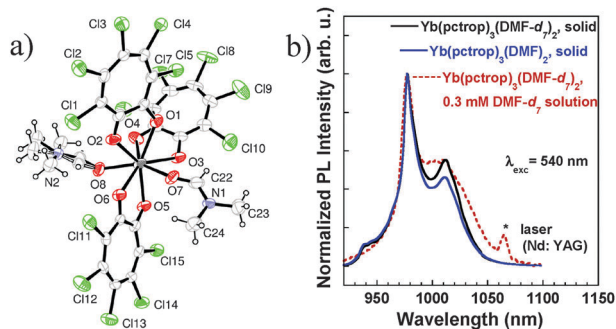
excluding the high energy oscillators of solvent molecules[5] and, importantly, the use of deuterated or halogenated ligands.[6] Thus, the lower energy of vibrations with respect to their hydrogenated counterparts allows for increasing the lifetime of the NIR transitions to tens of microseconds, and even longer.[6,7]

Numerous past and recent studies have been devoted on the one hand to determining the influence of the nature and position of the different groups on the efficiency and on the other hand to exploring conjugated and aromatic chromophores.[6–9] However, little has been published on perhalogenated ligands with low energy chromophores, nor on chlorinated ligands in general.[10]

Our work demonstrates the most efficient Yb^{3+} organometallic molecule without fluorine. In this new complex, sensitization is provided by a perhalogenated low energy chromophore ligand, namely pentachlorotropolonate (2,3,4,5,6-pentachloro-7-oxocyclohepta-1,3,5-trienolate, pctrop).[11] In this study, we analyze the sensitization mechanism, the effect of chlorination and the behaviour in the solid and solution phases. We also report surprisingly favourable results regarding the suitability (in terms of PL efficiency) of *N,N*-dimethylformamide (DMF) as a neutral ligand, particularly in its per-deuterated form, DMF-d_7.

Tropolone (2-hydroxycyclohepta-2,4,6-trien-1-one) has been shown to deprotonate easily (pK_a 6.7) to form the bidentate tropolonate ligand, which forms complexes with a number of trivalent lanthanides.[12] The tropolonate ion sensitizes IR-emitting lanthanides allowing for emission upon indirect excitation in the UV–blue range.[13] Strategies to exploit this sensitization in longer-lived systems involving NIR emitters have been proposed, including ingenious *trans*-domain mechanisms in which energy is absorbed in an organic shell around an inorganic nanoparticle.[14] Herein, we employ the pentachlorinated analogue of this ligand to coordinate to Yb^{3+} to form a crystalline ytterbium tris(perchlorotropolonate) (Fig. 1) complex with no additional cations. The heavy chlorine atoms in the pctrop ligand play a twofold role: firstly, they contribute a chlorinated shell around the ytterbium; secondly, they provide enhanced intersystem crossing (ISC) due to the increased spin–orbit interaction caused by their large atomic number. In sensitized emission processes

Fig. 1 (a) ORTEP view of the [Yb(pctrop)$_3$(DMF)$_2$] complex. (b) NIR emission spectra of the complexes in solid and solution upon excitation of the organic chromophore's absorption band.

in organolanthanides (Fig. 1b), the absorption occurs in the ligand; therefore a change in the spin number must take place in order to populate the trivalent lanthanide f multiplets. Moreover, it has been suggested that the sensitization of Yb^{3+} in organic chromophores involves an ISC step from organic states of spin singlet nature to triplet states.[2] Likewise, ISC interactions within the organic ligands cause a mixing of singlet and triplet states, which enhances the oscillator strength of (lower lying) states of triplet nature.[15] Apart from allowing for a lesser energy dissipation for the NIR emission, the existence of these low energy states in the organic ligands may enhance the resonance with the $^4F_{5/2}$ state of the Yb^{3+} ion (980 nm, $\sim$1.26 eV), thus favouring the energy transfer.

Fig. 1a shows the coordination environment of Yb in the X-ray crystal structure of [Yb(pctrop)$_3$(DMF)$_2$](0.5DMF) (see also ESI†). Yb^{3+} ions are charge-balanced by three pctrop anions. Thus, each metal ion is coordinated by eight oxygen atoms: two from each of the bidentate pentachlorotropolonate ions and one from each of the two directly coordinated neutral DMF molecules. Elemental analysis, performed after drying the crystals under reduced pressure, was consistent with the presence of only two DMF molecules per lanthanide ion, suggesting that the non-coordinated DMF is easily lost to form [Yb(pctrop)$_3$(DMF)$_2$]. It was this dried material that was used for subsequent PL studies.

The PL decay for the 980 nm Yb^{3+} $^2F_{5/2} \rightarrow$ $^2F_{7/2}$ emission (Fig. 2) in [Yb(pctrop)$_3$(DMF)$_2$] shows a double exponential behaviour with a major (90%) long lifetime component of 14 µs.
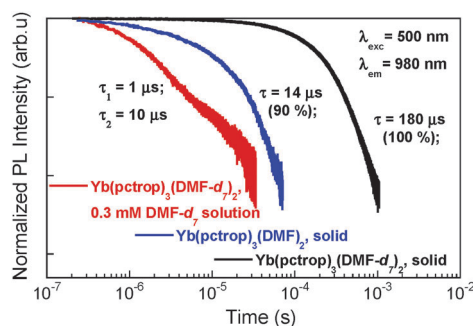

Fig. 2 PL decay curves (in the log–log scale) of [Yb(pctrop)$_3$(DMF-d_7)$_2$] and [Yb(pctrop)$_3$(DMF)$_2$] complexes. Note the contribution of two exponential components to the shape of the decay of the IR luminescence in the solution.

This value is slightly higher than the 12 µs obtained for the tetrakis tropolonate compound K[Yb(trop)$_4$][13] with all hydrogenated ligands surrounding the Yb^{3+} (but in which the hydrogen atoms are farther away on average than those of the coordinated DMF), and in the range of that of Yb hexafloroacetylacetonates, in which there is only one hydrogen atom per ligand in the vicinity of Yb, or some efficient Yb picolinates, quinolinates, *etc.*,[16] in which there is only one hydrogen atom per ligand in the vicinity of Yb. The values reported for the tropolonate-functionalized NaYF$_4$ nanoparticles[14] extend up to 68 µs. It is therefore interesting to find that, despite the presence of two coordinated highly hydrogenated molecules (each DMF molecule contains seven hydrogens), the pctrop–DMF complex solid shows a moderately long PL lifetime. The lack of O–H bonds plus the presence of all but two of the hydrogen atoms in the relatively distant *N*-methyl groups contribute to explaining this behaviour.[8,17] However, perchlorination provides only a modest increase with respect to the well shielded tropolonate tetrakis salt.[12,13]

The replacement of ordinary DMF by deuterated DMF (DMF-d_7) has important consequences in the PL decay (Fig. 2). It is known that deuteration increases the lanthanides' NIR PL lifetime as a result of the decrease of the energy of vibrations. In this case, the decay becomes 100% monoexponential, with a lifetime of 180 µs in the solid phase. DMF-d_7 solutions of this complex show a more complicated PL decay with a short component of 1 µs and a longer component of $\sim$10 µs (correspondingly 40% and 60% each). It is expected to find a shorter lifetime in the solution than in the solid due to the increase in the number of oscillators near the lanthanide caused by the solvation of the complex.

It has been proved that too high concentrations of long-lived lanthanides in organics-based solids can diminish the emission efficiency due to inter-ion interactions such as excitation hopping and cross-relaxation,[18] a phenomenon which has been exploited for cooperative conversion of radiation in ytterbium-based organophosphors.[19] We have produced [Y(pctrop)$_3$(DMF)$_2$](0.5DMF) crystals, which are isomorphous with the Yb analogue, and prepared a series of [Y$_{1-x}$Yb$_x$(pctrop)$_3$(DMF-d_7)$_2$] (0.1 < x < 0.9) to probe the effect of Yb–Yb interactions. We observed no change in luminescence lifetime upon decreasing the relative concentration of Yb: we therefore conclude that the complexes present an insulating character, possibly due to screening by the surrounding pctrop ligands and the separation of the encapsulated ions.

The remarkably long lifetime of the [Yb(pctrop)$_3$(DMF-d_7)$_2$] complex suggests a considerable PL efficiency. We have estimated the radiative lifetime τ_{rad} to be $\sim$1.22 ms in the solid (1.34 ms in the solution), which is comparable with the values of other organoytterbium complexes.[16,20] Thus, we have derived a quantum yield (efficiency) $\eta = \tau/\tau_{rad}$ around 15% for this compound. To the best of our knowledge, this value makes [Yb(pctrop)$_3$(DMF-d_7)$_2$] the most efficient non-fluorinated organoytterbium complex, to date. Importantly, we find that the suppression of multiphonon mechanisms of C–H bonds by substitution with C–D in the DMF neutral ligands achieves surprisingly high emission efficiency.[21]

Interestingly, perchlorotropolonate ligands allow for sensitization of the Yb^{3+} emission *via* excitation in the visible region at
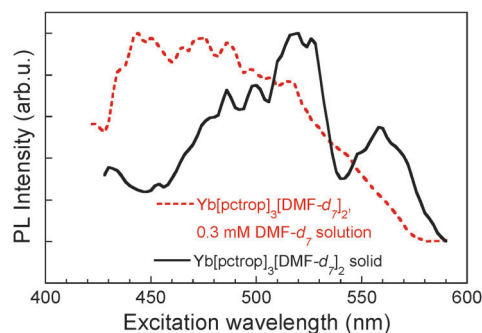
Fig. 3 Excitation spectra of the 980 nm luminescence from [Yb(pctrop)$_3$(DMF-d_7)$_2$] complexes in DMF-d_7 solution and in the solid phase.

wavelengths longer than 550 nm, as can be observed in the PL excitation spectrum, Fig. 3. This is advantageous from the point of view of not only decreasing the loss of energy $E_{exc} - E_{em}$ and using the existing long wavelength lasers, but also decreasing parasitic emissions from the surroundings of the complex, especially in imaging applications and biological environments. The visible absorption spectrum of the ytterbium(III) complex in DMF solution has a peak at 440 nm with a tail extending to 560 nm; in the solid state this is redshifted, reaching up to ∼600 nm. A low intensity, broad emission band between 450–700 nm, with a lifetime in the order of 50 ns (in the solid), is observed upon excitation at around 415 nm (see ESI†). A similar low energy band corresponding to triplet emission was observed in the tropolonate complexes.[22] The lifetime of this band was orders of magnitude longer due to the much decreased singlet-triplet mixing. All of these features prove that the organic spin multiplets are considerably mixed causing partially allowed absorption from states in the region around 520 nm.[2,10,15] These states and ISC-derived mixing favour coupling between the lanthanide and organic states. Still, this phenomenon requires phonon assistance due to the lack of resonance between the energies and density of states for the transitions: excited → relaxed in the organic part and the ground ($^2F_{7/2}$) → excited ($^2F_{5/2}$) state in the Yb^{3+} ion.[23] The mechanism for energy transfer from the organic part to Yb^{3+} is usually an uncertain subject in experiments involving UV excitation because it has been shown that organic–metal (back and forth) charge transfer transitions would be possible[24] in some complexes. The present case is an unambiguous example in which charge transfer Yb^{3+} + excited ligand → excited Yb^{2+} + ligand$^+$ involving the electronic cloud from the organic part is extremely unlikely, as the [Yb^{2+}, ligand$^+$] states necessarily require much higher energies than those available at 500–550 nm excitation.[22]

In conclusion, we report new organoytterbium complexes based on perchlorotropolonate and DMF ligands, which show enhanced 980 nm emission with sensitization in the blue to yellow range of the visible spectrum *via* low-lying states of the organic part. The choice of ligands makes the perdeuterated molecule the most efficiently sensitized non-fluorinated NIR-emitting organolanthanide to the best of our knowledge. Thus, we show that perchlorination is a valuable approach for enhancing the photophysical properties of these systems, which can be of particular practical significance in the search for shifted sensitization energies or if

perfluorination is difficult or the use of fluorine is to be avoided. This work opens the route to new ligands and organolanthanide complexes for photonic applications.

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