Visible light sensitisation of europium(III) luminescence in a 9-hydroxyphenal-1-one complex

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The 9-hydroxyphenal-1-one ligand forms stable 3 : 1 complexes with trivalent lanthanides, in which it acts as an antenna suitable for the visible light excitation (up to 475 nm) of the trivalent europium ion.

Trivalent lanthanide ions are known for their bright luminescence of high colorimetric purity.[1] This luminescence arises from f–f transitions, which means that the emission bands are narrow. As a result, complexes of lanthanide ions emitting in the visible have found applications in several areas, such as photonics, imaging and sensing.[2] Usually, one tries to find a ligand system which can serve as an antenna, in order to harvest the excitation light and transfer it towards the lanthanide ion. Because of the forbidden nature of the f–f transitions, this allows much denser population of the excited states of the lanthanide, resulting in stronger emission. In these antenna systems, it is important that the triplet energy level of the antenna is well-positioned towards the lanthanide accepting energy level (which can, but does not have to be the emitting level). If the triplet level is too low in energy, it is obvious that no light can be transferred towards the lanthanide. If the triplet is positioned too high, the excitation light will be high frequency light, situated in the UV. This can be unwanted and even harmful for living tissue, in the case of bio-sensing applications. Furthermore, no cheap pump sources are available in the UV.

Given the advantages of visible light excitation, it is surprising that only very few europium-based materials which allow visible light sensitisation have been reported. Ternary complexes of β-diketonates with 1,10-phenanthroline have been published with absorption bands in the region 380–400 nm, whereas certain Schiff base systems containing europium have been mentioned as well, although their efficiency decreased drastically with increasing wavelength of the excitation light.[3] One system offering sensitisation with light with wavelengths longer than 400 nm has been described by Werts *et al.*[4] However, the adducts of a push–pull chromophore such as Michler's ketone to a lanthanide tris(β-diketonate) reported by these authors are only stable in non-coordinating solvents like benzene and toluene. This limits their applicability significantly. Furthermore, these adducts could not be obtained in the solid state but had to be made *in situ.*

The 9-hydroxyphenal-1-one molecule (HPHN, Fig. 1) has been the subject of numerous theoretical studies, due to the strong intramolecular hydrogen bonding between the 9-hydroxy proton and the 1-carbonyl oxygen atoms and due to its electron-rich three-ring structure.[5] Derivatives of the 9-hydroxyphenal-1-one molecule have been used as dyes for the coloring of clothes.[6] Whereas complexes of 9-hydroxyphenal-1-one with the elements B and Be, as well as with transition metal ions have been reported in the literature; to our knowledge, no lanthanide complexes with the same ligand have been described up till now.[7]

We have synthesised the first lanthanide complexes with the 9-hydroxyphenal-1-one ligand and here we present the spectroscopic properties (absorption, excitation and emission spectra) of the Eu(III) complex **1**, as well as the crystal structure of its DMF adduct, shown in Fig. 2.

Compound **1** has been prepared by deprotonating three equivalents of the ligand HPHN in ethanol with an aqueous solution of ammonia, followed by the dropwise addition of one equivalent of $EuCl_3 \cdot 6H_2O$ in ethanol. The solution was left to stir over night, after which a yellow precipitation of **1** had been formed. Crystals suitable for X-ray diffraction were obtained after slow evaporation of a solution of **1** in DMF at room

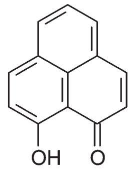

Fig. 1 Chemical structure of 9-hydroxyphenal-1-one (HPHN).

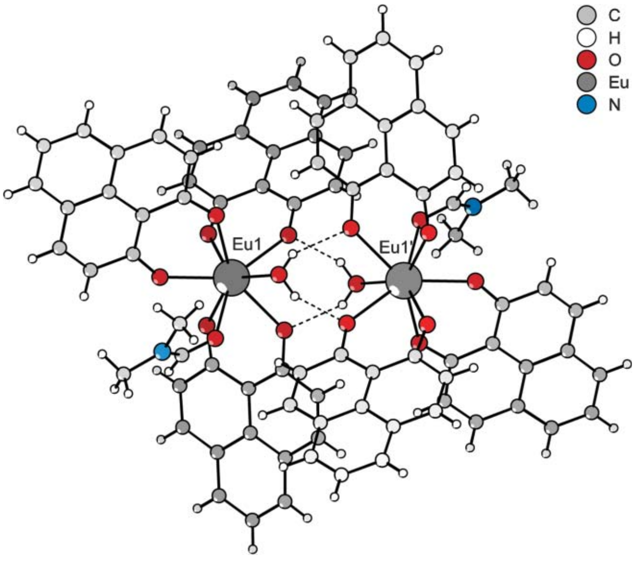

Fig. 2 A view showing two $Eu(PHN)_3(H_2O)(DMF)$ moieties attached by hydrogen bonds. The Eu1′ refers to the atom at equivalent position (1 – *x*, –*y*, –*z*).

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temperature. The crystallised compound has the composition $[Eu(PHN)_3(H_2O)(DMF)]\cdot(HPHN)$ with one free ligand molecule in the asymmetric unit.

The europium ion exhibits a coordination number of eight with a quadratic antiprismatic coordination sphere.† The 9-hydroxyphenal-1-one ligands are coordinating in a bidentate fashion. Additionally one DMF solvent molecule and a water molecule is coordinated to the lanthanide ion. The water molecule forms strong hydrogen bonds (distance H···O: 2.04(10) Å and 2.03(7) Å, respectively) to the oxygen atoms of two ligands of a second europium-tris-9-hydroxyphenal-1-one moiety, resulting in the formation of dimeric couples.

Complex **1** exhibits the characteristic red europium emission upon excitation with visible light (up to 475 nm). Fig. 3 shows a combination of the absorption, excitation and emission spectra. As can be seen, the maxima in the absorption spectrum coincide nicely with the maxima in the excitation spectrum, although the peak heights are not the same. Three bands can be distinguished: one in the UV, centered at 250 nm, one in the near-UV, centered at 350 nm, and a third band, located in the visible, at 458 nm. From Fig. 3, it can be understood that the energy transfer from the ligand to the europium ion is most efficient upon excitation in the bands located at the longest wavelengths. Indeed, even though the band at 458 nm has the lowest intensity in the absorption spectrum, it has a high intensity in the excitation spectrum. From literature, it was found that the triplet level of the ligand is situated at 17277 cm^{-1} or 579 nm (determined in *n*-hexane).[8] This is very similar to the energetic position of the $^5D_0$ level of the trivalent europium ion (determined in water).[9] This means that the energetic position of the triplet level is at the lower limit for sensitisation of europium luminescence.

The quantum yield of **1** was determined by means of an integrating sphere and was found to be 0.5%, whereas the lifetime has been found to be 10 µs (THF solution excited at 458 nm). This is somewhat shorter than usually found, possibly because of the rather poor shielding of the europium ion. The quantum yield is comparable to that of the well-known β-diketonate complex $Eu(dbm)_3\cdot 2H_2O$ (dbm = dibenzoylmethanate) and also to that of a recently published europium nitrobenzoato complex.[10] However, neither of these complexes allows visible light sensitisation. Two possible reasons for the low quantum yield can be considered: (1) the position of the triplet level of the ligand, resulting in possible back energy transfer and (2) the fact that the europium ions are not very well shielded from the environment. The importance of the caging effect of the ligands around the lanthanide in terms of water exclusion has been mentioned before.[11]

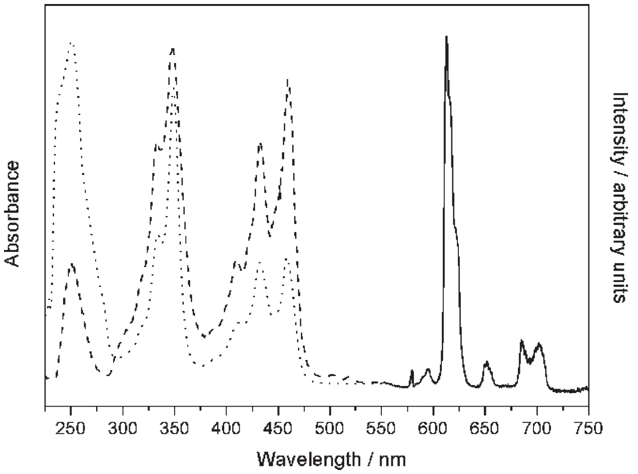

Fig. 3 Absorption spectrum (dotted line), excitation spectrum (dashed line) and emission spectrum (solid line) of **1** in THF at room temperature.

In conclusion, we have synthesised the first lanthanide complexes with the 9-hydroxyphenal-1-one ligand and we have shown that Eu^{3+} luminescence can be sensitised by visible light (up to 475 nm). To circumvent the coordination of solvent molecules to the lanthanide ions, we are currently investigating tetrakis complexes (stoichiometry $NEt_4[Ln(PHN)_4]$, with Ln being a trivalent lanthanide ion and NEt_4 tetraethyl ammonium). Preliminary results on the europium complex are very promising (better shielding while solubility and visible light excitation remain similar). We are also extending the research towards near-infrared emitting lanthanides (Nd^{3+}, Yb^{3+} and Er^{3+}). The 9-hydroxyphenal-1-one ligand seems to be a very good sensitiser for near-infrared luminescence as well.

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Notes and references

† Crystal data for compound **1**: crystals grown from DMF, intensity data were collected on a SMART 6000 diffractometer equipped with CCD detector using Cu-Kα radiation (λ = 1.54178 Å). The images were interpreted and integrated with the program SAINT from Bruker,[12] $C_{55}H_{38}EuNO_{10}$, M = 1024.82, triclinic, $P\bar{1}$ (no. 2), a = 13.6463(2), b = 13.8170(2), c = 14.7689(2) Å, α = 110.7920(10)°, β = 115.3580(10)°, γ = 98.4080(10)°, V = 2201.02(5) $Å^3$, T = 300 K, Z = 2, D_c = 1.564 g cm^{-3}, μ(Cu-Kα) = 10.739 mm^{-1}, F(000) = 1036, 8110 independent reflections (R_{int} = 0.0847). Final R = 0.0392 for 7085 reflections with $I > 2\sigma(I)$ and ωR_2 = 0.0886 for all data. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL program package.[13] Non-hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode with isotropic temperature factors fixed at 1.2 times U(eq) of the parent atoms (1.5 times for methyl groups), except for H52, H56 and H57 which were directly localised from the Fourier difference map. CCDC 252086. See http://www.rsc.org/suppdata/cc/b4/b414703k/ for crystallographic data in .cif or other electronic format.

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