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Visible-Light-Sensitized Near-Infrared Luminescence from Rare-Earth Complexes of the 9-Hydroxyphenalen-1-one Ligand

Rik Van Deun,* Pascal Fias, Peter Nockemann, Kristof Van Hecke, Luc Van Meervelt, and Koen Binnemans

Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, B-3001 Leuven (Heverlee), Belgium

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The unique absorption properties of the 9-hydroxyphenalen-1-one (HPHN) ligand have been exploited to obtain visible-light-sensitizable rare-earth complexes in 1:3 and 1:4 metal-to-ligand ratios. In both stoichiometries (1:3, tris, $Ln(PHN)_3$; 1:4, tetrakis, $A[Ln(PHN)_4]$, with Ln being a trivalent rare-earth ion and A being a monovalent cation), the complexes of Nd(III), Er(III), and Yb(III) show typical near-infrared luminescence upon excitation with visible light with wavelengths up to 475 nm. The X-ray crystal structures of the tris complexes show solvent coordination to the central rare-earth ion, whereas in the tetrakis complexes, the four PHN^- ligands form a protective shield around the central ion, preventing small solvent molecules from coordinating to the rare-earth ion, at least in the solid state.

The electronic absorption bands of the organic molecules mostly used as ligands in coordination complexes of trivalent lanthanide ions are often situated in the ultraviolet (UV) part of the electromagnetic spectrum.[1-4] Direct sensitization of rare-earth luminescence by excitation in the lanthanide's 4f levels is inefficient because of the small molar absorptivity ϵ (typically lower than 10 M^{-1} cm^{-1}), unless powerful excitation sources such as lasers are used.[5,6] Therefore, the large molar absorptivity of the organic ligands is often used to absorb a great deal of light and transfer this energy to the central metal ion. This process is known as the *antenna effect*.[7-10] For this process to be efficient, it is important that the triplet level of the ligand is situated slightly above the accepting energy levels of the lanthanide ion (ideally about 1500 cm^{-1}). Because the accepting energy levels of the visible luminescing lanthanides are all situated at relatively high energy positions (typically between 17 000 and 23 000 cm^{-1}), it is obvious that the absorption bands of the antenna are likely to be located in the UV region. By careful selection of the antenna chromophore, however, it is possible to allow visible light sensitization.[11-14] Earlier, we illustrated this for red Eu(III) luminescence.[15]

In this Communication, we show that the 9-hydroxyphenalen-1-one (HPHN) ligand is a good antenna for the visible-light sensitization of near-infrared (NIR) emission in rare-earth complexes. Additionally, we comment on the influence of two different stoichiometries and look at the effect of a solution versus a powdered sample.

The chemical structure of the HPHN molecule is depicted in Figure 1. It can be considered as a "polycyclic" β-diketone, in which the large delocalization of the π electrons accounts for a shift of the absorption bands to longer wavelengths than those, for example, in dibenzoylmethane.[16] β-Diketones are well-known as ligands for rare-earth complexes.[17-19]

Furthermore, the absence of an α-H atom is beneficial for NIR luminescence because C−H bonds in close proximity to the rare-earth ion can easily deactivate the excited states in a nonradiative way.[20,21]

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* To whom correspondence should be addressed. E-mail: rik.vandeun@chem.kuleuven.be.

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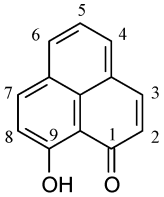

Figure 1. Chemical structure of HPHN, including the numbering scheme.

To obtain complexes in a 1:3 metal-to-ligand ratio, 3 equiv of the ligand HPHN was dissolved in ethanol containing a few drops of a 30% ammonia solution at 50 °C. An ethanolic solution of 1 equiv of the rare-earth chloride was added slowly to this solution, and the resulting complex, obtained as a yellow powder, was collected by filtration, washed, and dried thoroughly. In the case of the 1:4 metal-to-ligand ratio, 4 equiv of ligand was used, with NaOH or NEt_4OH (Et = ethyl) as the base. If one would use ammonia as the base in the tetrakis reaction, the ammonium counterion would donate a H atom to one of the ligands, resulting in the formation of significant amounts of the tris complex. In the case of the Na^+ and NEt_4^+ counterions, this cannot occur. This ammonia−ammonium equilibrium has also been observed in tetrakis rare-earth quinolinate complexes.[22] Both synthetic procedures (to obtain both tris and tetrakis complexes) yield pure materials. No mixtures were formed.

Elemental analysis results of the tris complexes suggest the presence of small amounts of water in the compounds, which is in agreement with the crystal structure that was reported earlier for the Eu(III) complex.[15] However, also in the case of the tetrakis complexes, the calculated and experimental elemental analysis results match only when one takes into account the presence of one to four water molecules.[23] Indeed, the materials were found to be hygroscopic.

Single crystals of tetraethylammonium ytterbium(III) tetrakis(phenalenonate) were obtained by slow diffusion of diethyl ether into a dimethylformamide solution of the complex. The X-ray diffraction data confirm the presence of a tetrakis complex (Figure 2). The crystallized compound has the composition $NEt_4[Yb(PHN)_4]\cdot Et_2O$ (PHN = 9-hydroxyphenalen-1-onate). The Yb(III) ion is surrounded by four PHN^- ligands and exhibits a coordination number of 8 with a strongly distorted quadratic antiprismatic coordination sphere. The ligands are coordinated in a bidentate fashion. No evidence of solvent coordination to the central lanthanide ion was found in the crystal structure. This indicates that the water molecules found by CHN analysis are most likely present as water of crystallization.

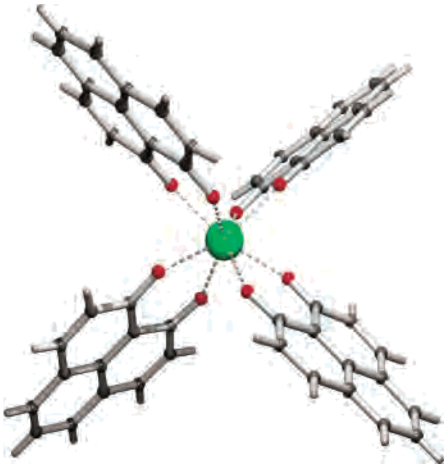

Figure 2. Molecular structure of the tetraethylammonium ytterbium(III) tetrakis(phenalenonate) (the tetraethylammonium counterion has been omitted for clarity).

The complexes exhibit characteristic NIR luminescence upon excitation with visible light of 460 nm. This wavelength corresponds to absorption from the ground state to the lowest singlet level of the ligand. The absorption spectra of the tris and tetrakis complexes look similar. This indicates that the energy levels of the ligands are unaffected by the stoichiometry of the complex. The combined absorption and emission spectra of tetraethylammonium tetrakis(phenalenonate) complexes of Nd(III), Er(III), and Yb(III) in tetrahydrofuran (THF) are shown in Figure 3. In this figure, the black solid line depicts the absorption spectrum of the tetrakis Nd(III) complex, whereas its emission spectrum is shown as the blue solid line. It contains three characteristic emission bands at 895, 1060, and 1335 nm, corresponding to the $^4F_{3/2} \rightarrow {}^4I_J$ lines ($J = {}^9/_2, {}^{11}/_2$, and ${}^{13}/_2$). The emission spectrum of the Er(III) complex is shown as the dotted red line and exhibits one characteristic band at 1530 nm, corresponding to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ line. Finally, the Yb(III) complex, drawn as the green dashed line, exhibits one emission band at 970 nm, corresponding to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ line.

The luminescence decay times of the Nd(III) ($^4F_{3/2}$), Er(III) ($^4I_{13/2}$), and Yb(III) ($^2F_{5/2}$) levels in $Ln(PHN)_3$ and $NEt_4[Ln(PHN)_4]$ have been recorded in THF and dimethyl sulfoxide (DMSO). The resulting values are given in Table 1. The order of magnitude of these decay times is comparable with that of other rare-earth complexes in similar solvents, although comparison of the decay time values of the tetrakis

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(23) CHN elemental analysis results for tris complexes. $Nd(PHN)_3\cdot H_2O$. Elem anal. Calcd for $C_{39}H_{21}O_6Nd\cdot H_2O$: C, 62.64; H, 3.10. Found: C, 62.43; H, 3.11. $Er(PHN)_3\cdot {}^1/_2H_2O$. Elem anal. Calcd for $C_{39}H_{21}O_6Er\cdot {}^1/_2H_2O$: C, 61.48; H, 2.91. Found: C, 61.55; H, 2.99. $Yb(PHN)_3\cdot 3H_2O$. Elem anal. Calcd for $C_{39}H_{21}O_6Yb\cdot 3H_2O$: C, 59.62; H, 3.08. Found: C, 59.33; H, 3.07. CHN elemental analysis results for tetrakis complexes. $NEt_4[Nd(PHN)_4]\cdot H_2O$. Elem anal. Calcd for $C_{60}H_{48}NO_8Nd\cdot H_2O$: C, 67.14; H, 4.70; N, 1.30. Found: C, 67.38; H, 4.99; N, 1.15. $NEt_4[Er(PHN)_4]\cdot 4.5H_2O$. Elem anal. Calcd for $C_{60}H_{48}NO_8Er\cdot 4.5H_2O$: C, 62.16; H, 4.96; N, 1.21. Found: C, 62.04; H, 4.89; N, 0.85. $NEt_4[Yb(PHN)_4]\cdot 3H_2O$. Elem anal. Calcd for $C_{60}H_{48}NO_8Yb\cdot 3H_2O$: C, 63.32; H, 4.78; N, 1.23. Found: C, 63.28; H, 4.69; N, 1.15.

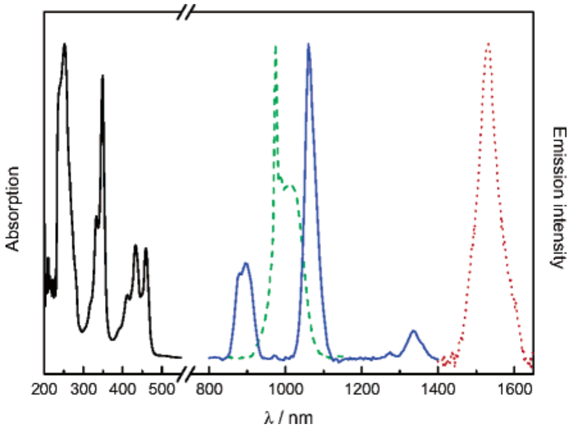

Figure 3. Combined absorption and emission spectra of tetraethylammonium tetrakis(phenalenonate) complexes of Nd(III) (absorption spectrum as the solid black line; emission spectrum as the solid blue line), Er(III) (emission spectrum as the dotted red line), and Yb(III) (emission spectrum as the dashed green line) in THF at room temperature ($\lambda_{exc} = 460$ nm; $c \approx 10^{-5}$ mol L^{-1}; signals are not to scale).

Table 1. Luminescence Decay Times (in Microseconds) of the Nd(III) ($^4F_{3/2}$), Er(III) ($^4I_{13/2}$), and Yb(III) ($^2F_{5/2}$) Levels in Ln(PHN)$_3$ (tris) and NEt$_4$[Ln(PHN)$_4$] (tetrakis) Complexes[a]

	Nd		Er		Yb	
	tris	tetrakis	tris	tetrakis	tris	tetrakis
powder	1.00	1.33	1.83	2.30	12.9	20.8
THF	0.70	0.73	1.50	1.54	9.12	9.31
DMSO	1.43	1.34	2.42	2.53	15.6	16.1

[a] $\lambda_{exc} = 355$ nm (third harmonic of the Nd:YAG laser), $c \approx 10^{-5}$ mol L^{-1}.

complexes in DMSO with those of tetraethylammonium rare-earth tetrakis(5,7-dichloroquinolinate) complexes in the same solvent indicates that the tetrakis(phenalenonates) are slightly superior (quinolinates: Nd(III) 1.18 μs, Er(III) 2.30 μs, and Yb(III) 15.6 μs).[24]

The effect of replacing the weakly coordinating solvent THF with the strongly coordinating solvent DMSO upon the value of the luminescence decay time is striking. While this is in agreement with what one would expect for tris complexes with water molecules coordinating to the central rare-earth ion (the DMSO molecules will be able to replace the water molecules, whereas the THF will not, and the lower stretching frequency of the S═O bond in DMSO makes DMSO a less powerful quencher than water), it is apparent that the same effect occurs in the case of the tetrakis complexes. As a matter of fact, the luminescence decay times of the tris complexes hardly differ from those of the tetrakis complexes (except for the pure powders vide infra). Upon comparing these decay time values, one could question the stoichiometry of the complexes in solution. Indeed, rare-earth β-diketonate complexes are known to be dynamic entities in solution, quickly exchanging ligands and yielding several species in solution.[17,18] When a freshly prepared solution of the NEt$_4$[Y(PHN)$_4$] complex in DMSO-d_6 was monitored by ^{1}H NMR as a function of time at room temperature, the dynamic nature of the complex was evidenced by the appearance of peaks from the tris complex Y(PHN)$_3$. Integration of the peaks at equilibrium indicated the presence of 11% of the tris complex and 89% of the tetrakis complex. The luminescence decay times for the solution measurements in Table 1 are, therefore, average values. Evidence for the fact that the tetrakis complexes do indeed show superior luminescent properties in comparison to their tris counterparts is given by the observation of the powdered samples. Although the increase in the luminescence decay time from tris to tetrakis is not spectacular, it is, nevertheless, significant (ranging from a 25 to 60% increase). The reason why the difference is not that striking could be found in the presence of C−H groups in close proximity to the lanthanide ion: indeed, especially the H atoms in the 2 and 8 positions on the ligand are rather close to the rare-earth ion. Nevertheless, the decay time values of the tetrakis powders compare well to the previously reported values of tetraphenylimidophosphinate (tpip) complexes, indicating that the rare-earth ions are efficiently shielded from the environment by the four PHN$^-$ ligands.[25,26] The Nd(PHN)$_3$ complex has been successfully doped into a thin film produced by polymer solution spin-casting techniques, yielding a working organic light-emitting device and showing its potential toward application.[27]

In conclusion, we have shown that the HPHN ligand can be used to sensitize NIR emission in rare-earth ions. Furthermore, because of its large delocalization, the ligand allows visible-light sensitization with wavelengths of up to 475 nm. The drawback of the dynamic nature of the complexes in solution could be overcome by using solid-state processing techniques. The luminescence decay times of the tetrakis powders compare well to the excellent times of the tpip complexes published earlier.

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Supporting Information Available: CIF file of the crystal structure, CCDC 626954. ^{1}H NMR spectrum of the tetrakis complex NEt$_4$[Y(PHN)$_4$] in DMSO-d_6, a description of the equipment, crystal structure data, and refinement details. This material is available free of charge via the Internet at http://pubs.acs.org.

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