First Observation of NIR 4f–4f Luminescence through the Energy Transfer from the SOMO π* Doublet in Nitronyl Nitroxide Radical Lanthanide(III) Complexes

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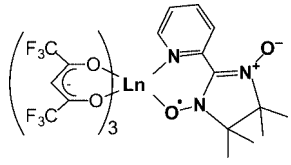
This study demonstrates the first observation of energy transfer from the doublet state of the nitronyl nitroxide radical ligand in Ln^{III} complexes, exerting the light-harvesting antenna effect on the NIR luminescence for the first time.

Introduction

With the aim of obtaining low-cost near-infrared (NIR) light sources for communications or sensing and biological applications, there have been a number of investigations concerning lanthanide(III) complexes with aromatic imines or organic dyes where the triplet states and/or ligand-to-metal charge transfer (LMCT) play crucial roles in the energy transfer as photosensitizers exerting antenna effects.[1–3] Lanthanide complexes having nitroxide radical(s) could have intriguing emitting properties with regards to the differences in the spin multiplicity of ligand excited states on going from triplet (organic compounds) to doublet (radicals) states. From magnetic studies on nitroxide radical complexes,[4] Luneau and Reber et al. reported the luminescence spectra of uncoordinated[5] and coordinated nitroxides,[6] where attempts were made to understand the electronic states[5] or to seek qualitative trends between the luminescence and the magnetic interaction.[6] During our endeavor to reveal the magneto-optical properties of metal complexes with nitronyl or imino nitroxide radicals such as NIT2py [4,4,5,5-tetramethyl-2-(2′-pyridyl)-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide] or IM2py [4,4,5,5-tetramethyl-2-(2′-pyridyl)-4,5-dihydro-1*H*-imidazol-1-oxyl][7–9] as well as of the Ln^{III}–Cr^{III} dinuclear complexes,[10–11] the emission spectra afforded information on the energy transfer from the nitroxide SOMO π* or the Cr^{III} ^2E state to the 4f state. Therefore, the SOMO π* of the nitroxide radical in lanthanide complexes could be expected to become a potential light harvesting antenna. However, there has been no report on Ln^{III} complexes exhibiting NIR 4f–4f luminescence associated with the SOMO π* of the NIT2py radical ligand to 4f energy transfer.

In this article the NIR luminescence is examined for the $[Ln^{III}(hfac)_3(NIT2py)]$ complex in the solid state (Scheme 1) with regards to energy transfer or the antenna effect.



Scheme 1. Schematic molecular structure of $[Ln(hfac)_3(NIT2py)]$.

Results and Discussion

The employed lanthanide(III) complexes are classified into three groups: (i) non-emissive (Lu^{III}: **1**), (ii) Vis-emissive (Eu^{III}: **2**; Sm^{III}: **3**), (iii) NIR-emissive (Nd^{III}: **4**; Tm^{III}: **5**; Yb^{III}: **6**).

The lanthanide complexes **1–6** show similar UV/Vis band patterns with peaks or shoulders near 550 nm and molar absorption coefficients of $\varepsilon_{max} \approx 350–380$ $mol^{-1}\,dm^3$ and $\varepsilon_{514} \approx 250$ $mol^{-1}\,dm^3$, which are assigned to the intraligand n–π* transition of the NIT2py ligand. Therefore, the photoexcitation conditions are not very different from one another at 541 nm.

The absorption and luminescence spectra of the non-emissive 4f–4f complex (**1**) exhibits a vibronic structure (Figure 1). Since the band contours of the two spectra show a mirror image relationship, the luminescence at 9–15×10^3 cm^{-1} is the intraligand doublet-doublet (D-D) luminescence from only one SOMO π* excited state, in con-

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trast to the (NITBzIm)Ln^{III} complexes which were claimed to have two SOMO π* states from the emission spectra.[8]

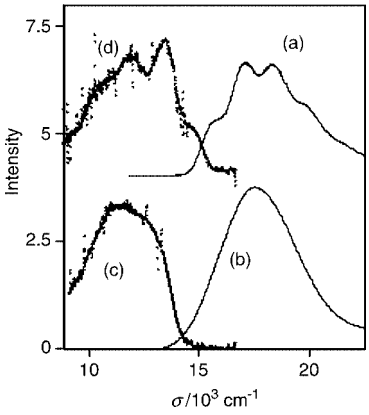

Figure 1. UV/Vis spectra (dotted lines) in CH_2Cl_2 at 180 K and luminescence spectra (solid lines) in the solid state at 180 K of **1** (a) and (d) and NIT2py ligand (b) and (c), respectively.

The Vis-emissive complexes **2** and **3** only demonstrated the intraligand D-D luminescence at 15 K. This results from the energy transfer from the 4f levels to the SOMO π* level, as compared with the cases of [Eu^{III}(hfac)$_3$(IM2py)][7a] and [Eu^{III}(hfac)$_3$(NITBzim or IMBzim)] [hfac = hexafluoroacetylacetonate; NITBzim = 2-(2-benzimidazolyl)-4,4,5,5-tetramethylimidazolin-1-oxyl 3-oxide; IMBzim = 2-(2-benzimidazolyl)-4,4,5,5-tetramethylimidazoline 1-oxide].[6] For [Eu^{III}(hfac)$_3$(IM2py)], the visible 4f–4f luminescence was observed by excitation at 222 nm corresponding to the intraligand hfac transition, but not by excitation at 465 nm corresponding to the intraligand IM2py transition at room temperature; exhibiting the energy transfer from the triplet state of the ancillary hfac ligand.[8a] However, at 5 K the 4f–4f luminescence of the (IM2py)Eu complex was observed by Ar^+ laser excitation.[6b–6d] The present (NIT2py)Eu^{III} complex only gives the intraligand (NIT2py) luminescence, probably due to the lower lying SOMO π* in NIT2py compared with the SOMO π* in IM2py[8a], as shown in Figure 2. On the other hand, the luminescence behavior of [Eu(NITBzim)$_2$(NO$_3$)$_3$] is similar to that of the present NIT2py complex, whereas [Eu(hfac)$_3$(NITBzim or IMBzim)] demonstrates both the intraligand and visible 4f–4f luminescence.[6b–6d] This difference results from the relative location between the SOMO π* band envelope of nitroxide radicals and the emissive 4f energy levels as can be seen in Figure 2.

As shown in Figure 3, the NIR 4f–4f emissive complexes gave typical 4f–4f luminescence at 7490 cm^{-1} ($^4F_{3/2}\rightarrow{}^4I_{13/2}$), 9400 cm^{-1} ($^4F_{3/2}\rightarrow{}^4I_{11/2}$), 11100 cm^{-1} ($^2F_{3/2}\rightarrow{}^4I_{9/2}$) for **4** and 10000 cm^{-1} ($^3H_4\rightarrow{}^3H_6$), 12500 cm^{-1} ($^3F_3\rightarrow{}^3H_6$) for **5** and ca. 10000 cm^{-1} ($^2F_{5/2}\rightarrow{}^2F_{7/2}$) for **6**. These facts indicate that the energy transfers occur from the SOMO π* to the 4f excited levels. The 4f–4f transitions of these complexes are located below the NIT2py SOMO π* state. This behavior is analogous to the case of the energy transfer from the $^2E(Cr^{III})$ to the 4f levels for the Cr–Nd and Cr–Yb dinuclear complexes, [(acac)$_2$Cr(bpypz)Ln(hfac)$_3$],[10d,11] but

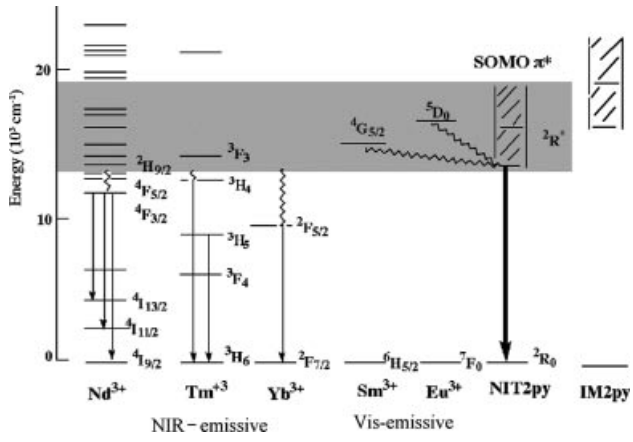

Figure 2. Energy levels for the Ln complexes and nitroxide radicals.

different from that for the corresponding complexes, [(acac)$_2$Cr(ox)Ln(HBpz$_3$)$_2$], which exhibit the simultaneous 3d–3d and 4f–4f luminescence at low temperature.[11] In our recent luminescence study of (NIT2py)- and (IM2py)Cr^{III} complexes, it is found that the NIT2py and IM2py radicals exert the antenna effect, showing a fast energy transfer from the SOMO π* to the $^2E/^2T_1(Cr^{III})$ state.[9] These findings suggest that the SOMO π* doublet state of the nitroxide radical could be of potential for visible-light sensitization of NIR luminescence as a light-harvesting antenna. This could be required for possible candidates of NIR light sources or multiplex assays to simultaneously detect a mixture of lanthanide ions with narrow luminescence peaks by visible-light excitation. This is because of the lower lying NIT2py SOMO π* band range existing within the emissive 4f levels compared with that of IM2py and NITBzim or IMBzim.

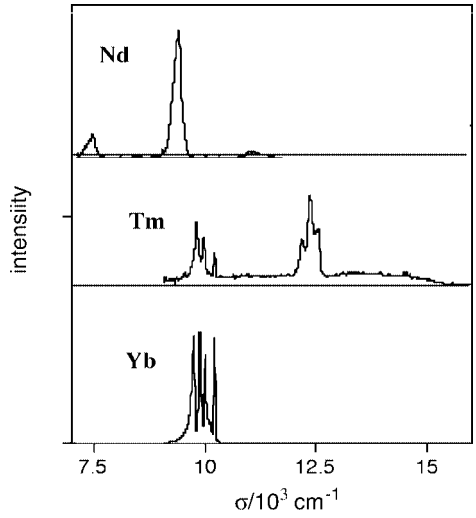

Figure 3. Luminescence spectra in the solid state at 15 K of [Ln(hfac)$_3$(NIT2py)] (top to bottom: **4**, **5**, **6**).

Conclusion

In summary, we observed the 4f–4f NIR luminescence of the (NIT2py)Ln^{III} complexes at 15 K through the direct

energy transfer from the SOMO π* doublet state to the 4f levels for the first time. Since there was no observation of the simultaneous luminescence for the NIR-emissive Ln^{III} complexes, it appears that the NIT2py radical exerts an antenna effect as a light-harvesting ligand. It is invaluable to clarify the difference between the doublet (SOMO π*)-to-4f direct energy transfer in nitroxide complexes and the triplet-to-4f indirect energy transfer through intersystem crossing from the singlet to triplet state in nonradical organic ligands,[2,3] e.g., in relation with the LMCT for Eu^{III}[12] or Yb^{III} complexes.[13]

Further photophysical and photochemical studies will be needed for the development of new photosensitizers for NIR light sources. This would be made feasible by tuning the emissive states with a variation of the substitution of NIT radicals such as benzimidazole in the nitroxide radical Ln^{III} complexes.

Experimental Section

Measurements: The NIR absorption spectra were recored with a Perkin–Elmer Lambda 19 spectrophotometer at room temperature in chloroform solution. The luminescence spectra were measured with a SPEX 1269 spectrometer with excitation by an Ar^+ laser (514.5 nm). The focus distances for the excitation and emission were 25 cm and 1.3 m, respectively. The excitation and emission slit widths were 4 mm and 2 mm, respectively. The dispersed signal was detected by a Ge-pin photodiode (North Coast EO-817L) cooled by liquid nitrogen.

Preparation of Complexes: The (NIT2py)Ln^{III} complexes were prepared by a modified literature method.[2a] NIT2py (1 mmol) was added to a solution of $[Ln(hfac)_3(H_2O)_2]$ (1 mmol) in $CHCl_3$/EtOH (1:1) (20 mL). The resulting violet solution was stirred at room temperature. After 1 d, violet elongated crystals with no crystallization solvent were obtained. The Eu^{III}, Lu^{III} and Yb^{III} complexes were stable at –5 °C, while the other Ln^{III} complexes were stable at room temperature. $C_{27}H_{19}F_{18}LuN_3O_8$ (1030.40): calcd. C 31.47, H 1.86, N 4.08; found C 31.92, H 1.92, N 4.15. $C_{27}H_{19}F_{18}N_3O_8Yb$ (1028.47): calcd. C 31.53, H 1.86, N 4.09; found C 32.04, H 1.93, N 4.09. $C_{27}H_{19}F_{18}N_3NdO_8$ (999.67): calcd. C 32.44, H 1.92, N 4.20; found C 34.19, H 2.38, N 4.21. $C_{27}H_{19}F_{18}N_3O_8Tm$ (1024.37): calcd. C 31.66, H 1.87, N 4.10; found C 31.43, H 1.80, N 4.11.

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