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A Luminescent Anion Sensor Based on a Europium Hybrid Complex

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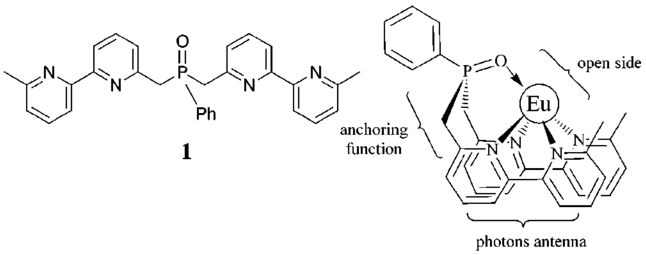
Over the past few decades, considerable attention has been devoted to the design of luminescent labels and sensors, since they offer the real possibility to solve critical analytical problems in growing fields of social and economical importance.[3,4] For example, the widespread use of nitrogen- and phosphorus-rich fertilizers in agriculture has ensured that nitrates and phosphates are major pollutants in soils and wastewater. Although nitrate is not considered toxic to humans, its metabolites may be carcinogens.[5] Most of the sensors used to analyze nitrates in food, fertilizers, or plant tissues are based on the principle of ion exchange and lack sensitivity.[6] Undoubtedly the development of highly selective ionophores able to monitor anions at the subnanomolar range remains a major goal for contemporary analytical science. In this context, an ever-growing interest revolves around the design of luminescent lanthanide labels possessing excited-state lifetimes in the ms range.[7] Among such systems, the Ln(III) texaphyrins exhibit significant affinities for oxyanions but suffer from poor luminescence properties.[8]

In seeking to design an improved anion sensor we have capitalized on the realization that the P═O group binds tightly to lanthanide cations.[9] Furthermore, it is known that bipy fragments act as effective photon antennae for Ln cations. Putting together these two ideas, we have synthesized the bis-bipyridine-phenylphosphine oxide ligand **1**,[10] which appears to possess all the features to be a good luminescent anion sensor when complexed with lanthanide cations. The pentadentate ligand in fact ensures that the first coordination sphere of the Ln cation is incompletely saturated, thereby leaving vacant coordination sites for interaction with the incoming anion. A schematic representation of the ligand and the coordination pocket available for lanthanide binding is sketched in Scheme 1.

Scheme 1



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The relevant europium complexes [Eu·**1**]X_3 ($X = NO_3^-$ or $CF_3SO_3^-$) were prepared by mixing stoichiometric amounts of **1** with the corresponding Eu-salt in a CH_2Cl_2/MeOH mixture for the nitrate or in CH_3CN for the triflate salt. On the basis of mass spectroscopy, it was established that both complexes possess a stoichiometry of one ligand to one Eu, an assignment supported by elemental analysis.

IR spectra of all complexes in the solid state displayed features characteristic of the ligand ($\nu_{C=C}$, $\nu_{C=N}$, $\nu_{P=O}$) and of the anion employed. For nitrate, the splitting between the two highest frequency bands attributed to the NO_3^- vibrations ($\Delta\nu = 170$ cm^{-1}) is in keeping with a bidentate chelating mode of approximate C_{2v} local symmetry. Coordination of the P(O) to the europium is substantiated by splitting of the P═O absorption band with an average shift of 15 cm^{-1} toward lower energy. For the triflate complex, this shift is increased to 75 cm^{-1}. Stretching vibrations corresponding to triflate anions ($\nu_{s(SO2)} = 1029$ cm^{-1} and $\nu_{as(SO3)} = 638$ cm^{-1}) point to coordination in the first coordination sphere, while bands at 573 and 517 cm^{-1} (ν_{Eu-O}) also indicate the presence of coordinated water in the solid state.

The absorption spectrum of [Eu·**1**]$(CF_3SO_3)_3$ in acetonitrile (Figure 1a) is dominated by transitions centered on the bipy moieties, since the phenyl chromophore linked to the P-atom has a much lower molar absorption coefficient. Complexation of Eu^{3+} cations shifts the lowest-energy absorption band from $\lambda_{max} = 291$ nm ($\epsilon = 28\,000$ M^{-1} cm^{-1}) in the free ligand to 312 nm ($\epsilon = 17\,450$ M^{-1} cm^{-1}) for the complex. Such a variation in the $\pi \rightarrow \pi^*$ transitions centered on the bipy moieties is indicative of coordination to Eu-center and could be used to determine a stability constant ($\log \beta = 5.8 \pm 0.5$ M^{-1} for the formation of a 1/1 ligand to Eu stoechiometry).[11] Interestingly, this bathochromic shift becomes less pronounced in solvents with increasing coordinative affinity such as methanol ($\lambda_{max} = 294$ nm; $\epsilon = 21\,400$ M^{-1} cm^{-1}) or water ($\lambda_{max} = 292$ nm; $\epsilon = 22\,000$ M^{-1} cm^{-1}). Upon excitation into the absorption bands of the ligand in acetonitrile at 20 °C, the [Eu·**1**]$(CF_3SO_3)_3$ complex luminesces weakly ($\Phi^{12} = 0.026$, $\tau = 0.80$ ms) (Figure 1b). The luminescence excitation spectrum is very similar to the absorption spectrum, confirming that energy transfer from the ligand to the metal ion occurs. Addition of tetrabutylammonium triflate (100 equiv) has no observable effect on either absorption or luminescence spectra, in keeping with a weak interaction of the triflate anion with the Eu center in solution.[13]

Addition of tetrabutylammonium nitrate (Figure 1b), chloride, fluoride, or acetate to an acetonitrile solution of [Eu·**1**]$(CF_3SO_3)_3$

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(3) (a) *Fluorescent Chemosensors for Ion and Molecule Recognition*; Czarnik, A. W., Ed.; American Chemical Society: Washington, DC, 1992. (b) *Chemosensors for Ion and Molecule Recognition*; Desvergne, J.-P., Czarnik, A. W., Eds.; NATO Advanced Study Institute Series; Kluwer Academic Publisher: Dordrecht, 1997.

(4) (a) Mayer, A.; Neuenhofer, S. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1044. (b) Fabbrizzi, L.; Poggi, A. *Chem. Soc. Rev.* **1995**, 197. (c) De Silva, A. P.; Gunaratne, Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515. (d) Prodi, L.; Bolletta, F.; Montalti, M.; Zaccheroni, N. *Coord. Chem. Rev.* **2000**, *205*, 59.

(5) Ellis, G.; Adatia, I.; Yazdanpanah, M.; Makela S. K. *Clin. Biochem.* **1998**, *31*, 195.

(6) Bühlmann, P.; Pretsch, E.; Bakker, E. *Chem. Rev.* **1998**, *98*, 1593.

(7) (a) Carnall, W. T. *Handbook on the Physics and Chemistry of Rare Earth*; Gschneidner, K. A., Jr., Eyring, L., Eds.; North-Holland Publishing Co.: Amsterdam, 1979; Vol. 3, p 171. (b) Sabbatini, N.; Guardigli, M.; Manet, I.; Ziessel, R. In *Calixarenes 2001*; Asfari, Z., Böhmer, V., Harrowfield, J., Vicens, J., Eds.; Kluver Academic Publishers: Dordrecht, The Netherlands, 2001; p 583 and references therein.

(8) (a) Lisowski, J.; Sessler, J. L.; Mody, T. D. *Inorg. Chem.*, **1995**, *34*, 4336. (b) Lisowski, J.; Sessler, J. L.; Lynch, V.; Mody, T. D. *J. Am. Chem. Soc.* **1995**, *117*, 2273.

(9) Baaden, M.; Berny, F.; Boehme, C.; Muzet, N.; Schurhammer, R.; Wipff, G. *J. Alloys Compd.* **2000**, *303*, 104.

(10) Douce, L.; Charbonnière, L.; Cesario, M.; Ziessel, R. *New J. Chem.* **2001**, *25*, 1024.

(11) Association constant was obtained in anhydrous $CH_3CN/TBAPF_6$ 0.01 M by monitoring changes in the UV−vis absorption spectra of ligand solutions (5×10^{-3} to 10^{-5} M) titrated by increasing amounts of $[Eu(OTf)_3]$ (10^{-4} to 5×10^{-5} M). The spectral changes were fitted to the following equation $\mathbf{1} + Eu^{3+} \rightleftharpoons [Eu{\cdot}\mathbf{1}]^{3+}$ using the Specfit software (see ref 14).

(12) Luminescence quantum yields (uncertainty ± 15%) were determined using $[Ru(bpy)_3]^{2+}$ as standard ($\Phi = 0.028$ in aerated water), Nakamaru, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2697.

(13) Bünzli, J.-C.; Milicic-Tang, A. *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Jr.; Eyring L., Eds.; North-Holland Publishing Co.: Amsterdam, 1995; Vol. 21, p 305.

10.1021/ja0118688 CCC: $20.00

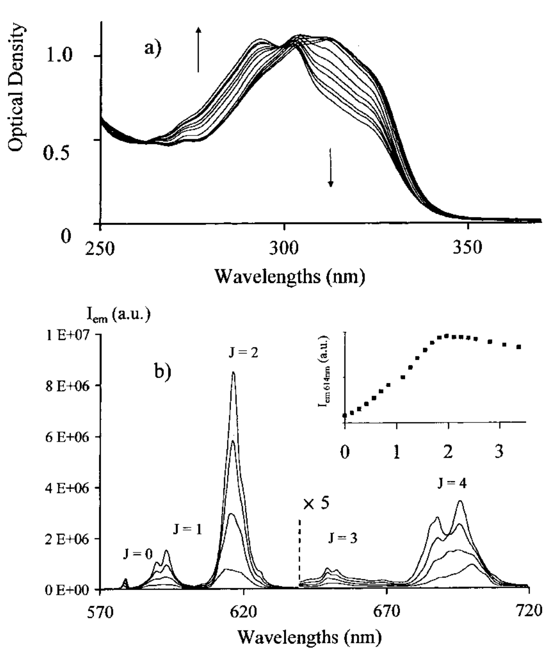

Figure 1. (a) Evolution of the UV−vis absorption spectrum of [Eu·**1**]-(OTf)$_3$ (5.36 × 10^{-5} M) in acetonitrile upon addition of increasing amounts of tetrabutylammonium nitrate. (b) Emission spectra of [Eu·**1**]-(OTf)$_3$ (7.45 × 10^{-5} M) in the presence of 0, 0.6, 1.0, and 2.0 equiv of TBANO$_3$, showing the increase of the $^5D_0 \rightarrow {}^7F_J$ transitions. Supporting electrolyte TBAPF$_6$, 0.01 M. Inset: Increase of I_{em} at 614 nm vs number of NO$_3$ equivalents.

greatly changed its photophysical properties. The most striking effect was observed for nitrate, where the emission yield increased by a factor of 11-fold upon addition of 2 equiv of salt (respectively 5, 1.8, and 1.5 for chlorides, acetates, and fluoride). Under these conditions, the excited-state lifetime and emission quantum yield reached values similar to that obtained with an authentic sample of [Eu·**1**](NO$_3$)$_3$ ($\Phi = 0.30$, $\tau = 1.45$ ms). Furthermore, it is worth noting that the structure of the luminescence profile changes during the titration with nitrate or with the other anions that progressively replace the loosely bound solvent molecules.

From the variation in the absorption spectra of an acetonitrile solution of [Eu·**1**](CF$_3$SO$_3$)$_3$ on addition of anion (Figure 1a) it was possible to calculate cumulative association constants[14] for the formation of complexes with one, two, or three anions.

$$[\mathrm{Eu}\cdot\mathbf{1}]^{3+} + \mathrm{X}^- \rightleftharpoons [\mathrm{Eu}\cdot\mathbf{1}\cdot\mathrm{X}]^{2+} \qquad \beta_1 = \frac{[(\mathrm{Eu}\cdot\mathbf{1}\cdot\mathrm{X})^{2+}]}{[(\mathrm{Eu}\cdot\mathbf{1})^{3+}] \times [\mathrm{X}^-]}$$

$$[\mathrm{Eu}\cdot\mathbf{1}]^{3+} + 2\,\mathrm{X}^- \rightleftharpoons [\mathrm{Eu}\cdot\mathbf{1}\cdot\mathrm{X}_2]^{+} \qquad \beta_2 = \frac{[(\mathrm{Eu}\cdot\mathbf{1}\cdot\mathrm{X}_2)^{+}]}{[(\mathrm{Eu}\cdot\mathbf{1})^{3+}] \times [\mathrm{X}^-]^2}$$

$$[\mathrm{Eu}\cdot\mathbf{1}]^{3+} + 3\,\mathrm{X}^- \rightleftharpoons [\mathrm{Eu}\cdot\mathbf{1}\cdot\mathrm{X}_3] \qquad \beta_3 = \frac{[(\mathrm{Eu}\cdot\mathbf{1}\cdot\mathrm{X}_3)]}{[(\mathrm{Eu}\cdot\mathbf{1})^{3+}] \times [\mathrm{X}^-]^3}$$

The cumulative association constants with increasing number of anions are gathered in Table 1. Except for chloride, three binding constants could be determined for each system, while the affinity of the Eu-complex for anions follows the trend: F$^-$ > AcO$^-$ > Cl$^-$ > NO$_3^-$. The association constants are very high in all cases and significantly different from those found by calorimetric titration for formation of [EuCl$_n$]$^{(3-n)+}$ species in DMF solution.[13,15] This discovery is in keeping with the pronounced π-acidic character of the hybrid ligand **1**.

Table 1. Cumulative Association Constants for Complexes Formation with One, Two, and Three Anions in Acetonitrile Solution at 25 °C, Starting from the [Eu·**1**](OTf)$_3$ Complex

	Log β_1	Log β_2	Log β_3
NO$_3^-$	6.1 ± 0.3	11.0 ± 0.2	14.4 ± 0.7
Cl$^-$	6.9 ± 0.2	12.0 ± 0.2	<14.5
F$^-$	7.8 ± 0.7	15.5 ± 1.1	21.2 ± 1.2
AcO$^-$	6.9 ± 0.6	13.2 ± 0.8	19.1 ± 1.1

Evolution of the emission spectrum was also analyzed during the titration, confirming the luminescence enhancement (Figure 1b). The changes observed upon addition of nitrate and, in particular, the different structure of the more symmetry-sensitive transitions ($^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$) indicates that this anion coordinates to europium. As such, the anion must replace acetonitrile, water, or triflate molecules bound at the metal center. A similar effect can be ascribed to the other anions, which are also expected to be inserted in the first coordination sphere. Similar modulations of lanthanide luminescence have been observed in the presence of CO$_3^{2-}$, HCO$_3^-$, and organic anions.[16]

Taken together, these findings are consistent with the entry of anions such as F$^-$, AcO$^-$, Cl$^-$, NO$_3^-$ to the first coordination sphere of the [Eu·**1**](CF$_3$SO$_3$)$_3$ complex giving rise to drastic changes in the luminescence intensity. An appreciation of the above features led us to consider that the first anion coordinates to [Eu·**1**]$^{3+}$ to produce a dicationic species. This is corroborated by the fact that very slight modification of the UV−vis spectra is observed during the onset of the titration experiments. Addition of the second equivalent of anion has a more drastic influence on the absorption spectrum. This is in keeping with a concomitant coordination of the second anion with dissociation of a single bipy arm, leading to a monocationic species. It is worth noting that the increase of luminescence quantum yield and that of excited state lifetime are not parallel, indicating that the coordinated anion influences the efficiency of the energy-transfer processes from the ligand to the metal ion. Studies for correlating the structure of the various species to the efficiency of such processes are actually in progress in our laboratories. Finally, addition of the third anion has a more spectacular effect with an additional 30 nm hypsochromic shift of the most intense absorption band due to disassociation of the second bipy arm and formation of a neutral species. This process, as expected, typically leads to a decrease of the luminescence intensity.

We have therefore demonstrated that the present system registers anion binding by an increase in luminescence yield and lifetime. This provides the possibility to employ such complexes as luminescent sensors for anions; systems with this ability are much less common than cation sensors[17] and of great practical importance. This new system is particularly useful relative to other molecules because it allows detection of traces of halides and nitrates by luminescence monitoring at an europium center, whose long excited-state lifetime allows the enhancement of the signal-to-noise ratio with the use of time-resolved spectroscopy. The design of second-generation sensors, able to perform in coordinating solvents, might be achieved by rational design of locking bipy subunits such as the use of anionic bipy fragments.[18]

Supporting Information Available: Experimental details for the synthesis of the ligand and complexes, characterization of all new compounds. Absorption and luminescence spectrum of the [Eu·**1**](CF$_3$SO$_3$)$_3$ and [Eu·**1**](NO$_3$)$_3$ complexes in acetonitrile and experimental data for UV−vis titration experiments for each anion are also provided (11 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[14] (a) Binstead R. A. *SPECFIT*; Spectrum Software Associates: Chapell Hill, NC, 1996. (b) Gampp, H.; Maeder, M.; Meyer, C. J.; Zuberbühler A. D. *Talanta* **1985**, *32*, 257.

[15] Ishiguro, S.; Takahashi, R. *Inorg. Chem.* **1991**, *30*, 1854.

[16] Bruce, J. I.; Dickins, R. S.; Govenlock, L. J.; Gunnlaugsson, T.; Lopinski, S.; Lowe, M. P.; Parker, D.; Peacock, R. D.; Perry, J. J. B.; Aime, S.; Botta, M. *J. Am. Chem. Soc.* **2000**, *122*, 9674.

[17] Harriman, A.; Hissler, M.; Jost, P.; Wipff, G.; Ziessel, R. *J. Am. Chem. Soc.* **1999**, *121*, 14.

[18] Charbonnière, L.; Ziessel, R.; Guardigli, M.; Roda, A.; Sabbatini, N.; Cesario, M. *J. Am. Chem. Soc.* **2001**, *123*, 2436.