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Thiophene-Derivatized Pybox and Its Highly Luminescent Lanthanide Ion Complexes

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Lanthanide ion complexes have application in areas ranging from fluoroimmunoassays to materials science because of their light emission properties.[1] The luminescence is due to parity-forbidden and spin-forbidden f−f transitions, requiring thus the use of ligands as sensitizers. Numerous ligand designs have been described, from simple 2,6-pyridinedicarboxylic acid, shown to sensitize near-IR emission of Yb(III)[2] and utilized in standards for the determination of quantum yields of emission,[3] to more complex chelating architectures, capable of discriminating between different lanthanide ions and of yielding complexes with high quantum yields of luminescence.[4,5] Although pyridine-bis(oxazoline), Pybox, and its derivatives were extensively utilized by Aspinall and co-workers[6−8] in lanthanide ion complexes for enantioselective catalysis, they have never been reported as sensitizers for lanthanide luminescence. This ligand is extremely versatile, as it allows straightforward derivatization of the para position of the pyridine ring, as well as of the carbon atoms of the oxazoline ring.[6−10]

Here, we report for the first time its use as a sensitizer and describe the isolation of a highly luminescent complex of $Eu(CF_3SO_3)_3$ with thiophene-derivatized-Pybox, ThPybox. Highly luminescent solutions are obtained upon dissolution of the ligand in acetonitrile with $Ln(CF_3SO_3)_3$ in 3:1 stoichiometry, with quantum emission values of 76% for Ln = Eu and 59% for Ln = Tb. Preliminary studies with other Pybox derivatives synthesized in our laboratory also yield highly luminescent solutions.[11,12] The Eu(III) efficiency reported here with ThPybox as the sensitizer surpasses complexes recently described for which emission quantum yields in water were 21.5%−25.5%,[5,13] 16% in CH_2Cl_2,[14] and 2.3% in MeOH.[15] The efficiency for Tb(III) is also high and compares favorably with recently described systems, with values of 15%−45.5% in water,[16−18] 5.1% in THF,[19] 27% in CH_2Cl_2[14] and 63% in MeOH.[15] In the solvent acetonitrile, quantum yields of 1.3 and 4.7%, respectively, were reported for $[Ln(terpy)_3]^{3+}$ (Ln = Eu, Tb).[19,20] The excellent sensitization ability coupled with the versatility in derivatization makes this family of ligands very appealing for designing luminescent lanthanide ion complexes. The photophysical characterization of the luminescent solutions of Eu(III) and Tb(III) with ThPybox is reported here, along with X-ray crystallographic characterization. Solution speciation and spectroscopic details are presented in the Supporting Information.

ThPybox was synthesized through modified literature procedures (Scheme S1) in 7% overall yield from chelidamic acid. Stirring ThPybox with $Eu(CF_3SO_3)_3$ in 1:1 $MeOH/CH_3CN$ yielded X-ray quality crystals of a 2:1 metal complex (Figure 1a) within a few days. While only a 2:1 ligand-to-metal complex has been isolated with this ligand, depending on the initial ligand-to-metal ion stoichiometry in solution, complexes with different stoichiometries were isolated with other Pybox derivatives.[11] The complex discussed here crystallizes in the monoclinic space group *C*2/*c* with one ligand and 1.5 water molecules coordinated to the Eu(III) as well as 1.5 noncoordinated triflate ions in the asymmetric unit. The remaining coordination sphere and counter-ions are generated by symmetry. Eu(III) has a coordination number of nine and is bound to six nitrogen atoms of the two ThPybox ligands as well as three water molecules. The water molecules were most likely incorporated through the solvent. The Eu(III)−N distances are in the range 2.519−2.572 Å and the Eu(III)−O distances are in the range 2.434−2.484 Å (Table S2). The polyhedron around the metal ion is a slightly distorted tricapped trigonal prism with the oxygen of the center water molecule and the pyridine nitrogen atoms as the capping atoms. The packing structure is dominated by hydrogen-bonding interactions between the triflate counterions and the water molecules coordinated to Eu(III), weak hydrogen-bonding interactions between the triflate counterions and α-hydrogen atoms on the thiophene rings as well as short contacts between the fluorine and oxazoline oxygen (blue dashed lines, Figure 1b). The triflate ions provide for the electrical neutrality of the complex and stitch the complex cations together into a three-dimensional structure via hydrogen bonding.

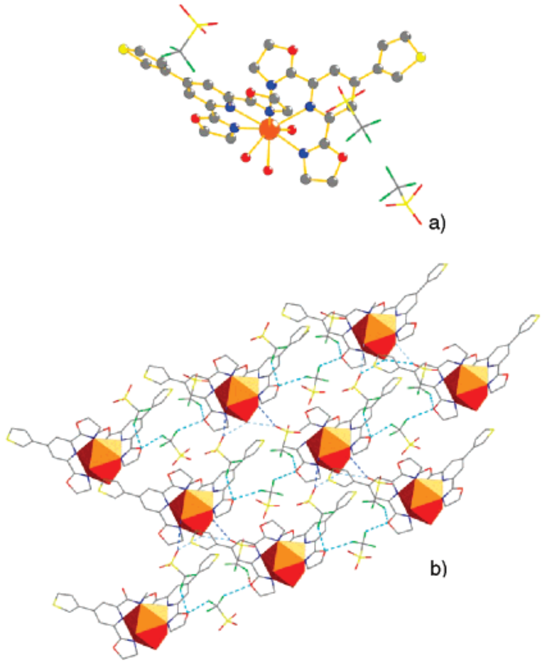

Figure 1. (a) Ball-and-stick and wire diagram of the 2:1 complex of ThPybox with $Eu(CF_3SO_3)_3$; (b) packing diagram, with polyhedral representation of Eu(III). Dashed bonds show selected intermolecular interactions of the triflate counteranions. Hydrogen atoms have been omitted for clarity.

Hydrogen-bonding interactions (Figure S1) in the range 2.7272 -2.8291 Å are seen between the triflate oxygen atoms and the water molecule oxygen atoms. Other interactions such as weak hydrogen bonding, as defined by Desiraju,[21] between fluorine atoms and C−H

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Table 1. Speciation Data of Ln(III)$(NO_3)_3$ with ThPybox in Acetonitrile Obtained by Absorption and Emission Titrations[a]

Ln(III)	method	log β_{11}	log β_{21}	log β_{31}
Eu	absorption	5.70 ± 0.07	10.70 ± 0.20	15.38 ± 0.10
	emission	5.15 ± 0.18	10.09 ± 0.11	14.34 ± 0.20
	average	5.43 ± 0.19	10.40 ± 0.23	14.86 ± 0.22
Tb	absorption	5.01 ± 0.17	9.10 ± 0.11	13.38 ± 0.14
	emission	4.75 ± 0.09	9.09 ± 0.07	12.10 ± 0.20
	average	4.88 ± 0.19	9.10 ± 0.13	12.74 ± 0.24

[a] Values are the average of at least three measurements with each technique. Sample absorption titration shown in Figure S5, Supporting Information.

Table 2. Photophysical Characterization of Ln(III)$(NO_3)_3$ with ThPybox in Acetonitrile in 3:1 Stoichiometry[a]

complex	ThPyboxEu	ThPyboxTb
Φ[%][b]	76.2 ± 6.6	58.6 ± 4.1
τ[ms]	2.097 ± 0.081	0.367 ± 0.032 0.019 ± 0.002
^{1}S[cm^{-1}][c]	28310 (28,610)	
^{3}T[cm^{-1}][c]	21080 (21,080)	

[a] [L] = 3[Ln(III)] ≈ 1×10^{-6} M. [b] Average of at least three measurements with different experimental conditions. [c] Measured in a solution with Ln = Gd at 77 K,[24] data in parenthesis is uncoordinated ligand.

moieties of the oxazoline or thiophene rings and F−O shorts contacts[22,23] are present in this structure (Figure S2).

These complexes, as well as others with similar Pybox ligands described elsewhere,[11,12] are highly luminescent in the solid state, as shown by the characteristic red or green color seen when the crystals are held under a handheld UV lamp ($\lambda = 254$ nm). When dissolved in methanol or acetonitrile luminescent solutions are obtained. While to date only a 2:1 complex was isolated in the solid state, other species are present in solution. To characterize these species ThPybox was titrated with Ln(III) nitrate in acetonitrile and the absorption and emission spectra of the resulting solutions were measured. Results of these speciation studies are summarized in Table 1 and are consistent with the formation of 1:1, 2:1 and 3:1 species in solution. The stability constants were obtained through independent absorption and emission titrations and are similar for both ions, with the Eu(III) species being slightly more stable. Through the use of speciation diagrams (Figure S3), conditions for the photophysical measurements were chosen to ensure that the main species in solution was the 3:1 species.

Absorption, excitation, and emission spectra for both metal ion complexes (Figure S4) show that the excitation spectra closely follow the absorption spectrum of the ligand. Further, the emission spectra of both Eu(III) and Tb(III) solutions show the characteristic transitions $^5D_0 \rightarrow {}^7F_J$ ($J = 1-4$) and $^5D_4 \rightarrow {}^7F_J$ ($J = 6-2$), respectively. As a result of almost complete quenching of the ligand centered emission in the case of the Tb(III) an increased background in the 450 to 500 nm region is seen. This translates into a quantum yield of emission of 58.6% (Table 2). This quantum yield is lower than the emission efficiency of 76.2% determined for Eu(III). However, both values are high and are accompanied by long luminescence lifetimes of ~2 ms for the Eu(III) and 367 μs for the Tb(III) species. The lifetime of the red emission could be determined from a single-exponential fitting of the decay curve and is consistent with the presence of one major luminescent species. In the case of the green emission, a double exponential had to be utilized. Closer inspection of the triplet emission spectrum of the ligand (Figure S6) reveals that the second component corresponds to residual ligand emission, which, as mentioned above, is not completely quenched by the Tb(III) and overlaps with the transitions of the metal ion.

In summary, ThPybox is a highly efficient sensitizer of Eu(III) and Tb(III) luminescence, as reflected in the high emission quantum yields of luminescence, which in the case of Eu(III) is up to three times as high as previously reported for other complexes. Further, the versatile chemistry of these ligands allows tuning of the sensitization ability and tailoring of the Ln(III) complex properties for specific applications. As such, Pybox and its derivatives show extreme promise as a new class of antennas for lanthanide ion emission.

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Supporting Information Available: Experimental details of the synthesis and spectroscopic characterization and X-ray crystallographic files in CIF. This material is available free of charge via the Internet at http://pubs.acs.org. X-ray crystallographic information files can also be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). CCDC 658540 contains the supplementary crystallographic data for the complex described in this paper.

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