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Intramolecular energy transfer in actinide complexes of 6-methyl-2-(2-pyridyl)-benzimidazole (biz): comparison between Cm^{3+} and Tb^{3+} systems

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Abstract

Coordination of the 6-methyl-2-(2-pyridyl)-benzimidazole ligand with actinide and lanthanide species can produce enhanced emission due to increased efficiency of intramolecular energy transfer to metal centers. A comparison between the curium and terbium systems indicates that the position of the ligand's triplet state is critical for the enhanced emission. The energy gap between the ligand's triplet state and the acceptor level in curium is about $1000\,cm^{-1}$, as compared to a $\sim 600\,cm^{-1}$ gap in the terbium system. Due to the larger gap, the back transfer with curium is reduced and the radiative yield is significantly higher. The quantum yield for this "sensitized" emission increases to 6.2%, compared to the 0.26% value attained for the metal centered excitation prior to ligand addition. In the terbium case, the smaller donor/acceptor gap enhances back transfer and the energy transfer is less efficient than with the curium system.

Keywords: Sensitized emission; Energy transfer; Actinide spectroscopy; *F*-elements; Photoluminescence

1. Introduction

Ligands possessing aromatic and/or heteroaromatic groups are easily excited with near UV radiation, and may be capable of enhancing excited-state energy transfers in donor/acceptor systems. The proper energy match-up between the triplet state of the ligand and an acceptor excited level is a necessary condition for the ligand to transfer its energy to the emitting metal ion. As direct *f–f* excitation in actinide and lanthanide ions are inherently inefficient, a strategy used to circumvent low absorbitivity involves coordination with energy transmitting ligands, usually one with chromophores of high molar extinction coefficients. Highly luminescent lanthanide complexes of cryptands [1], β-diketones [2,3], and several other macrocyclic ligands [4–8] have been studied extensively, although attention given to the corresponding actinide species has been minimal. To the best of our knowledge, studies involving "sensitized" emissions in transuranium complexes have been limited to the β-diketonate systems [9,10], which were studied some three decades ago. Such enhancements are particularly important with actinides as the hazards associated with them necessitate efficient and selective luminescent probes with ultraviolet and visible sensitizers. With energy transmitting ligands that have large absorption coefficients it is possible to increase significantly the emission quantum yield.

Attributes for maintaining strong sensitized luminescence include the formation of stable complexes with oxygen and/or nitrogen donating ligands that contain desirable chromophores. Once the intramolecular energy transfer occurs, the radiationless losses should be minimized to attain a highly efficient process. The position of the lowest triplet level of the ligand relative

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to the acceptor state is also an important factor that influences the quantum yield of *f*-element chelates in solution.

We have been engaged [11] in developing benzimidazole-based ligands suitable for intramolecular energy transfer processes with the transuranium elements. Systematic tuning of their energy levels through electron donating substituents can lead to energy match-up between the ligand's triplet ($^3\pi\pi^*$) state and the acceptor levels of the metal ions. In this paper we report coordination of the 6-methyl 2-(2-pyridyl)-benzimidazole (biz) ligand with Cm^{3+}, where the energy match up between the donor and acceptor levels provides a large enhancement to the sensitized emission of curium. The importance of the ligand's triplet level position in the overall energy transfer process was analyzed by comparing the Cm^{3+}–biz behavior with that of the Tb^{3+}–biz system.

2. Experimental

2.1. Material preparation

The complexing ligand used in this study was crystallized from a methanol solution by slow evaporation. The Cm-248 isotope was used for these experiments. All preparative work with curium was conducted in a glove box. A 10 μL portion of a 0.2 M stock solution of curium was mixed with the desired ligand ratios and the total volume adjusted to 400 μL with MeOH to provide a 5 mM solution for spectroscopic analysis. The spectroscopic measurements were conducted with in house designed quartz tubes, which have flat optical surfaces and a path length of 0.4 cm. The solution apparent pH was adjusted to 1 with HCl.

2.2. Spectroscopy

Luminescence investigations were conducted using an Instrument SA's optical system, that consisted of a monochromator (model 1000 M) attached with CCD, PMT and Infrared detectors. A 450 W Xe lamp was used as the light source. The system is interfaced with a personal computer and controlled by SpectraMax software. Data analyses were performed with Grams32 software (Galactic, version 5.1).

High-resolution spectroscopy studies were performed using an argon-ion laser (Coherent, model 306) and a double-meter spectrometer (Jobin-Yvon Ramanor model HG.2S). The resolution of the monochromator is $0.5\,\mathrm{cm}^{-1}$ at 514.5 nm. The monochromator is also interfaced with a personal computer; scanning and data collections are controlled by "LabSpec" software (version 3.04). Signal detection was acquired with a water cooled photo-multiplier tube (Hamamatsu R636).

The emission quantum yield (ϕ) was measured by relative method using quinine sulfate (0.1 mmol/L) in 0.1 M sulfuric acid solution and excited at 365 nm ($\phi = 0.56$) [12–14]. An aqueous solution of $\mathrm{Ru(bpy)}_3^{2+}$ (0.1 mmol/L) was also used as a secondary standard ($\phi = 0.042$). The integrated areas of the emission bands of the standard and sample were used in the comparison. Absorbance of both the standard and sample solutions were measured at the respective excitation wavelengths prior to the luminescence measurement and the data were used for correction purposes. The quantum yield calculation was performed using Eq. (1) [12]

$$\phi_{\mathrm{sp}} = \phi_{\mathrm{st}} \frac{[I_{\mathrm{sp}} {*} A_{\mathrm{st}} {*} \eta_{\mathrm{sp}}^2]}{[I_{\mathrm{st}} {*} A_{\mathrm{sp}} {*} \eta_{\mathrm{st}}^2]}, \tag{1}$$

where, ϕ is the quantum yield, I is the integrated area of the corrected emission band, A is absorbance at the excitation wavelength, η is refractive index (MeOH = 1.3288, and H_2O = 1.333 at 298 K), the subscripts sp and st correspond to sample and standard solutions, respectively. Dilute solutions were used to minimize inner filter effects. Deoxygenation of the standard solutions was accomplished by bubbling N_2 gas vigorously through the analyte for a minimum of 30 min.

3. Results and discussion

3.1. Spectroscopic studies on the biz ligand

The absorption spectrum of pure biz in MeOH solution is shown in Fig. 1a. The ligand absorbs strongly in the UV region maximizing at 317 nm and having a broad shoulder at ~328 nm. The absorption band at 317 nm has a large molar extinction coefficient (ε) of $2.3 \times 10^4\,\mathrm{M}^{-1}\,\mathrm{m}^{-1}$. Based on its large absorptivity, the band is assigned to the symmetry allowed π–π^* transition.

The strong electron donating property of the benzimidazole group of the ligand (Scheme 1) makes it facile to form an ILCT (intra-ligand charge transfer) transition to the pyridine moiety. This assertion is supported by our DV-Xα calculations conducted for the ligand. Detailed compositions of the frontier orbitals derived from Mulliken population analysis are given in Table 1. The HOMO and SHOMO (highest occupied and second highest occupied molecular orbitals, respectively) consist of 82% and 94% contributions from the $2p_\pi$ orbitals of the C and N atoms of the imidazole, respectively. In contrast, the two lowest unoccupied molecular (LUMO) orbitals have 52% and 98% contributions from the C and N atoms of the pyridine group. Hence, the lowest $\pi \rightarrow \pi^*$ band in this system corresponds to a charge