

## Photoluminescence and Raman Studies of Curium and Americium Complexes of 6-Methyl 2-(2-Pyridyl)-benzimidazole: Evidence for an Efficient Intramolecular Energy Transfer

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Received July 3, 2003

The 6-methyl-2-(2-pyridyl)-benzimidazole (biz) ligand coordinates with the actinide species in solution, and the complexes display efficient intramolecular energy-transfer processes. The energy transfer in the Cm(III)–biz system proceeds in a nonradiative mode, whereas a radiative mode is the principal mechanism in the Am(III)–biz system.

Direct f–f excitation in actinide and lanthanide ions is inherently inefficient, as they represent Laporte forbidden transitions. One strategy used to circumvent this low absorptivity involves coordination with energy transmitting ligands, usually one with chromophores of high molar extinction coefficients. Ligands possessing aromatic and/or heteroaromatic groups are easily excited by near-UV radiation and, hence, are capable of enhancing excited-state energy transfers in donor/acceptor systems. In this regard, highly luminescent lanthanide complexes of cryptands,  $\beta$ -diketones, and several other macrocyclic ligands have been studied extensively.<sup>1</sup> The rich body of literature on “sensitized” luminescence involving lanthanide systems contrasts with the minimal attention given to the corresponding transuranium species. To the best of our knowledge, studies

involving “sensitized” emissions in transuranium complexes are limited to the  $\beta$ -diketonate systems,<sup>2</sup> which were studied some three decades ago. Emission enhancement through ligand “sensitization” is particularly important in actinide research both for trace level analyses and because the hazards associated with the materials necessitate efficient and selective ultraviolet and visible luminescent probes.

Among the actinides, Cm<sup>3+</sup> possesses the largest separation between its ground-state manifold and the luminescent first excited state. As a result, the nonradiative de-excitation processes within the metal f–f transitions are relatively minimal and make curium a strongly luminescent actinide ion. Previous studies<sup>3</sup> have suggested laser induced fluorescence as a viable technique for trace level analysis of the Cm<sup>3+</sup> ion. However, by selecting the energy transmitting ligand, it is possible to attain a significant increase in the emission quantum yield through a “sensitized” emission phenomenon.

Herein we report coordination and luminescence enhancement in curium and americium complexes with the 6-methyl 2-(2-pyridyl)-benzimidazole ligand (biz). Considering the environmental importance and consequences of actinide speciation, the present findings may have an important ramification in trace analysis of these materials.

The biz ligand itself emits weakly both in the solid and in MeOH solutions. The excitation spectrum of a dilute solution ( $\sim 10^{-5}$  M in MeOH) of the ligand maximizes at 320 nm and matches very well with the absorption profile. The absorption band maximizes at 315 nm with a shoulder at 330 nm (extinction coefficient ( $\epsilon$ ),  $2.3 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>). The solution emission at 385 nm is rather broad (full width at half-maximum, fwhm = 62 nm) and unstructured,

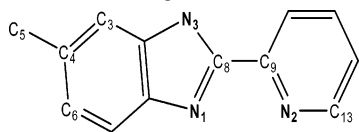
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**Chart 1.** Structure of the Biz Ligand.

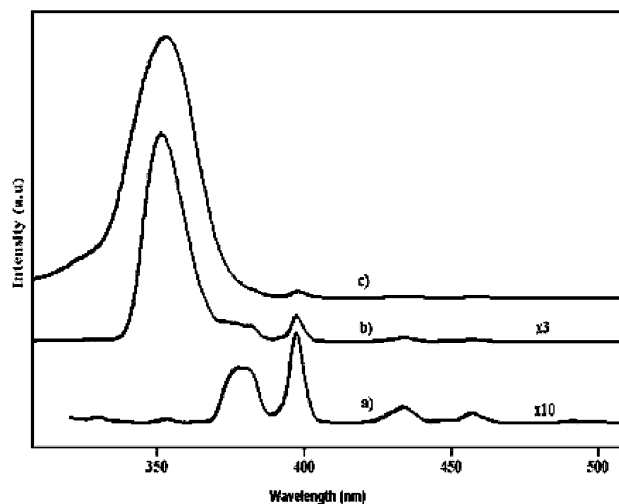
although the solid's spectrum shows progression with an average spacing of  $1420\text{ cm}^{-1}$ . The strong electron donating property of the benzimidazole group of the ligand (Chart 1) makes it facile to form an ILCT (intraligand charge transfer) transition to the pyridine moiety. This assertion is supported by our DV-X $\alpha$  theoretical calculations conducted on the ligand. The  $2p_{\pi}$  orbitals of the C and N atoms of the benzimidazole group contribute to the two highest occupied molecular orbitals. Their contributions to the HOMO and SHOMO (second highest occupied orbital) are 82% and 94%, respectively.<sup>4</sup> In contrast, the two lowest unoccupied orbitals show >52% and 98% contributions from the pyridyl group. As a result, the  $\pi$ - $\pi^*$  excitation is characterized by ILCT from the benzimidazole to the pyridyl moiety. The calculated HOMO-LUMO gap of 3.43 eV (361 nm) is comparable with the lowest absorption band found experimentally at 3.75 eV (330 nm).

Upon complexation<sup>5</sup> of  $\text{Cm}^{3+}$  with the biz ligand, the typically narrow and weak electronic transitions of curium are altered in both position and shape. The excitation spectrum shown in Figure 1a corresponds to a 5 mmol  $\text{CmCl}_3$  solution in MeOH obtained while monitoring the emitted light at 599.2 nm. The strongest bands at 397 and 378 nm correspond to the  $^8\text{S}_{7/2} \rightarrow ^6\text{I}_{11/2}$ ,  $^6\text{P}_{13/2}$  f-f transitions, respectively. As shown in Figure 1b, the 1:1  $\text{Cm}^{3+}$ -biz complex provides a dramatic change in its excitation spectrum. A band at 351 nm appears dominant, although direct f-f excitation in this region (Figure 1a) provides negligible emission. Hence, the excitation band at 351 nm corresponds to the ligand-centered  $\pi$ - $\pi^*$  transition. The band is red-shifted significantly ( $>3200\text{ cm}^{-1}$ ) when compared to the free ligand spectrum.

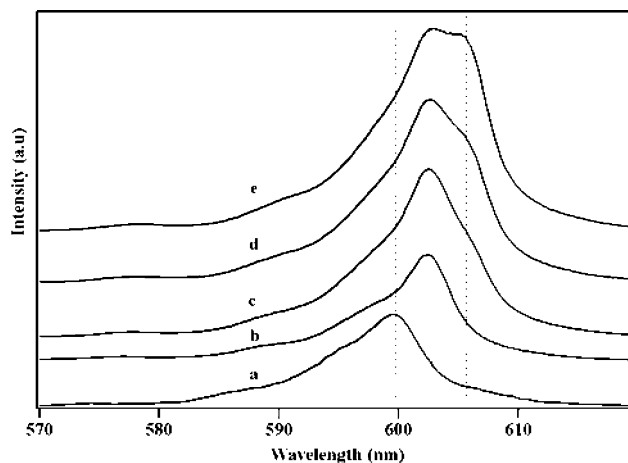
Insight into the nature of the species formed in solution has been gleaned by studying the dependence of the spectral profile on ligand concentration. Although the concentration of the initial  $\text{CmCl}_3$  is low (5 mmol), inner sphere  $\text{Cl}^-$  ligation is expected in MeOH, as suggested previously for nonaqueous solvents.<sup>6</sup> The emission maximum at 599.2 nm (Figure 2a) is red-shifted when compared to the band reported

(4) The HOMO is derived from the  $2p_{\pi}$  orbitals of N1, C4, C8, and C6 atoms with percentage contributions of 19%, 16%, 14%, and 13%, respectively. The LUMO is derived from  $2p_{\pi}$  orbitals of the C13, C9, N1, C8, and N2 atoms with percentage contributions of 16%, 16%, 12%, 11%, and 11%, respectively. Only the most significant contributions obtained by Mulliken population analysis are given. The atom numbering is as shown in Chart 1.

(5) Solutions used in the complexation studies were prepared as follows. A 200 mM stock solution (A) of curium was prepared by dissolution of  $^{248}\text{CmCl}_3$  in 0.1 M HCl. Stock solution B consisted of 67 mM of the biz ligand in methanol. A 10  $\mu\text{L}$  portion of stock solution A was pipetted into microvolumetric flasks containing different amounts of the ligand solution (B). The total volume was adjusted to 400  $\mu\text{L}$  using MeOH, to provide a 5 mM  $\text{Cm}(\text{III})$  solution. The americium solutions were prepared in a similar fashion; using the  $^{243}\text{Am}$  isotope. All preparations were conducted in a glovebox suited for radiochemistry work.



**Figure 1.** Excitation spectra from MeOH solutions of (a)  $\text{CmCl}_3$ ; (b)  $\text{Cm}(\text{III})$ -biz (1:1); (c)  $\text{Cm}(\text{III})$ -biz (2:1).  $\text{Cm}(\text{III})$  is 5 mmol in all samples. Initial mole ratios are in parentheses. The pH was adjusted to 1 with HCl.



**Figure 2.** Emission spectrum of (a)  $\text{CmCl}_3$  and  $\text{Cm}(\text{III})$ -biz complexes having initial ratios of (b) 1:1, (c) 1:2, (d) 1:3, and (e) 1:4.

in aqueous media<sup>7</sup> and, hence, is in accord with the principle that complexation of actinide and/or lanthanide ion is often accompanied by a concomitant red-shift in the absorption and/or emission band.<sup>8</sup>

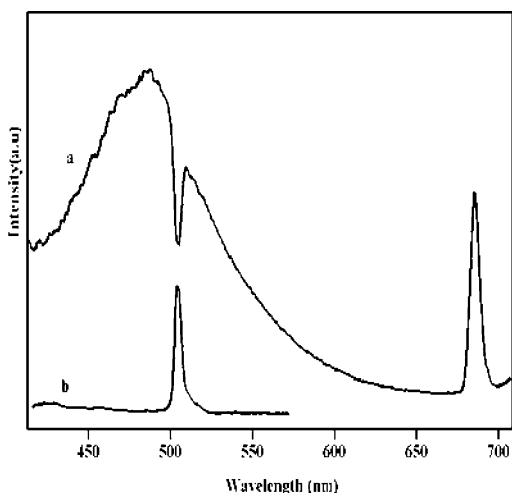
Upon the addition of the biz ligand at a 1:1 ratio, the emission maximum (Figure 2b) red-shifts further to 602 nm, and the intensity increases significantly. Further addition of the ligand beyond the 1:1 mole ratio results in additional increase in intensity of the sensitized emission. Compared to the 1:1 solution, the sensitized emission increases by a factor of  $\sim 3$ , 4, and 6 for the  $\text{Cm}^{3+}$ -biz initial ratios of 1:2, 1:3, and 1:4, respectively. These changes, together with the growth of a shoulder at 605 nm with increased ligand ratio (Figure 2d,e), are indicative of a stepwise complexation at the metal center.

Previous EXAFS complexation studies<sup>9</sup> on Am- and Nd-biz systems have indicated the dominance of the mono- and

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**Figure 3.** (a) Emission spectrum from a 1:1 Am–biz solution in MeOH. (b) Absorption spectrum of AmCl<sub>3</sub>. The “dip” at 505 nm matches with the  ${}^7F_0 \rightarrow {}^5L_6$  absorption of Am(III) suggesting that the energy transfer occurs in radiative mode.

bis-coordinated species in solution (M–biz and M(biz)<sub>2</sub> complexes). In acidic media, as in our case, the EXAFS studies also indicated that a maximum of only two biz ligands coordinate, even at a 1:4 (M–biz) ratio, at the metal center in a bidentate fashion. Complexation with curium should proceed similarly, and the emission peaks at 602 and 605 nm are taken to represent the mono- and bis-coordinated species that exist in equilibrium in solution.

The Raman experiments lend support for strong coordination between the biz ligand and the actinide systems. The vibrational band of biz at 1003 cm<sup>-1</sup> (breathing mode of the heterocyclic ring<sup>10</sup>) is shifted to 1023 cm<sup>-1</sup>. A shift to higher wavenumbers is therefore indicative of strong coordination of the ligand to the Cm<sup>3+</sup> center.<sup>11</sup>

As with the Cm–biz system, exclusive excitation of the ligand in the Am–biz complexes provides emissions corresponding to an Am(III) f–f transition. The emission spectrum shown in Figure 3a exhibits a broad band at ~485 nm in addition to the characteristic  ${}^5L_6 \rightarrow {}^7F_2$  transition of Am(III) at 685 nm. Although the ligand-centered band at 485 nm is barely detectable in the spectrum of the free ligand, its intensity increases significantly in the presence of selected heavy lanthanide and actinide ions that have been studied. On the basis of these observations, the transition is assignable to the <sup>3</sup>ILCT state, where increased intersystem crossing (ISC) enhances the emission originating from the ligand’s triplet state (heavy atom effect).<sup>12</sup> The curium system provides similar enhancement but only at higher ligand

contents, suggesting that an efficient energy transfer to curium quenches the emission originating from the triplet excited state of the ligand.

A characteristic feature associated with the ligand-centered emission of the Am–biz system (shown in Figure 3a) is the presence of a large “dip” at 504 nm, indicating reabsorption of the emitted light at that wavelength. The absorption spectrum of Am(III) (shown in Figure 3b) facilitates the assignment of the reabsorption mechanism. A match between the dip at 504 nm and the  ${}^7F_0 \rightarrow {}^5L_6$  absorption band of Am(III) suggests that the energy transfer from the triplet state of the ligand to the  ${}^5L_6$  electronic level of Am(III) occurs by a radiative mode.

The intramolecular energy-transfer process is particularly pronounced with curium, where we were able to observe strong emission at 685 nm from a 20 μM Cm<sup>3+</sup> solution (in MeOH) using only a 400 W xenon lamp as the excitation source. Under similar experimental conditions, metal centered direct f–f excitation provided no detectable signal, indicating that the  $\pi$ – $\pi^*$  excitation, as an allowed transition, provides an efficient channel for the delivery of a significant amount of near-UV radiation into the Cm<sup>3+</sup> 5f<sup>5</sup> electronic levels. The quantum yield for this “sensitized” emission increases to 0.062, compared to the 0.0026 value attained for the metal-centered excitation prior to ligand addition.

We are now investigating the complexes involving several modifications of the biz ligand thought to be essential to further tune the energy match up between the  $\pi$ – $\pi^*$  level of the ligand and the acceptor f-levels of the actinide ion and enhance this energy-transfer process. One route to accomplish the former may be to vary the electron donating ability of the substituent at the methyl site of the benzyl group (Chart 1). Replacement of the proton at the imidazole N-site by a heavier atom should also eliminate the coupling between the  $\nu_{N-H}$  vibrational manifold and the electronic transition. It is known<sup>13</sup> that ligands with  $\nu_{N-H}$  oscillators, having vibronic frequencies similar to  $\nu_{O-H}$ , are effective nonradiative deactivators of excited f-species. Eliminating a nonradiative pathway that may act as an energy sink would be an important strategy to maximize the emission enhancement obtained through intramolecular energy transfers, and its application of these for trace level detection of actinide species.

**Acknowledgment.** This research was sponsored by the Division of Chemical Sciences, Geosciences and Biosciences, OBES, USDOE, under Contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed by UT-Battelle, LLC and the Japan Atomic Energy Research under the Japan-US Actinide program.

IC034759Y

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