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 $\sim600\,cm^{-1}$ 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.
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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 absorbtivity 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 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 $Ru(bpy)_3^{2+}$ (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]

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

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 $2.3 \times 10^4 \, M^{-1} \, m^{-1}$. Based on its large absorptivity, the band is assigned to the symmetry allowed $\pi-\pi^*$ 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

transfer from an orbital which is localized on the imidazole group to one consisting of the pyridine group. The DV-Xα method calculation provides a HOMO-LUMO gap of 3.43 eV (361 nm) as compared to the lowest absorption band at 3.78 eV (328 nm).

The free biz ligand 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 317 nm (Fig. 1b) and matches very well with the absorption profile of the ligand. In MeOH solutions, the ligand shows a broad and unstructured emission that originates from the singlet excited state (Fig. 1c). The
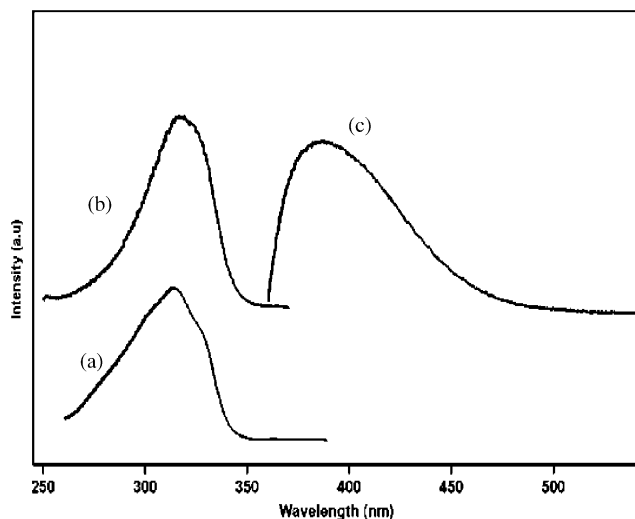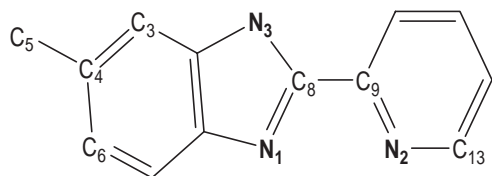

Fig. 1. Spectra of the biz ligand in MeOH solution: (a) absorption spectrum of a 4×10^{-5} M solution in MeOH; (b) excitation spectrum monitored at 400 nm. The calculated molar extinction coefficient (ε) of the band at 320 nm is 2.3×10^4 M^{-1} cm^{-1}; (c) emission spectrum for excitation with 330 nm.

Scheme 1. Structure of 6-methyl-2-(2-pyridyl)-benzimidazole (biz).

emission band maximizes at 385 nm. Upon coordination, a lower-energy emission originating from the triplet state is also observed at ~ 473 nm, indicating the importance of heavy ion effect [15] in initiating the singlet to triplet inter-system crossing (ISC) phenomenon in this system.

3.2. Energy transfer in the Cm^{3+}–biz system

Among the actinides, Cm^{3+} possesses the largest separation between its ground state manifold and the luminescent, first excited-state. As a result, the non-radiative, de-excitation processes within the metal f–f transitions are relatively minimal, and curium is one of the most luminescent actinide ions.

The emission spectrum for the 1:1 (Cm^{3+}:biz) complex is shown in Fig. 2a. The band consists of two regions. At the shorter wavelength region a broad and weak band is observed at ~ 473 nm, along with a much weaker band at ~ 382 nm. These bands correspond to the ligand's triplet and singlet emissions, respectively. Concomitantly, the characteristic Cm^{3+} emission corresponding to the $^6D_{7/2} \rightarrow {}^8S_{7/2}$ transition is observed at 602 nm.

Insight into the nature of the species formed in solution has been gleaned by studying the dependence of the spectral profile on ligand concentration. The details of these studies were reported previously [11]. Although the concentration of the initial CmCl$_3$ is low (5 mmol), inner sphere Cl$^-$ ligation is expected in MeOH, as suggested previously for non-aqueous solvents [16]. The emission maximum at 599.2 nm (Fig. 2 in Ref. [11]) is red-shifted when compared to the band reported in aqueous media [17] 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 absorption and/or emission band [18].

Upon the addition of the biz ligand in a 1:1 ratio, the emission maximum red-shifts to 602 nm, and the intensity increases significantly. Further addition of the ligand beyond the 1:1 mole ratio results in the growth of a shoulder at 605 nm. The intensity of the sensitized emission increases and the shoulder becomes a well-

Table 1
Energy levels (eV) and orbital configuration of HOMO and LUMO of the biz ligand by the DV-Xα calculation method

Orbital	Energy (eV)	Contribution to the orbital (%)
2nd LUMO	2.718	C10 (26); C11 (26); C12 (28); N2 (20)
LUMO	1.965	C3 (4.4); C4 (5.4); C6 (1.1); C7 (7.6); C8 (11); C9(15) C10 (6) ; C11 (4); C12 (15.6); N1(12.3); N3 (4.5);N2 (11)
HOMO	−1.463	C1 (6.2); C2 (5.7); C3 (8.4); C4 (16); C7 (13.2); C8(13.9); C10 (3.9); C12 (4.7); N1 (18.4); N2 (3); N3(3)
SHOMO	−1.891	C1 (6.9); C2 (13.1); C3 (13.6); C4 (2); C6 (27.2); C7(9); C8 (2.8); C10 (1.3); C12 (1.5); N1(4)

Both the SHOMO (second highest occupied orbital) and the HOMO consist of contributions from the $2p_\pi$ atomic orbitals, whereas the LUMO consists of contributions from the $2p_{\pi*}$ atomic orbitals. Percentage contributions are given in parentheses. Note that $>82\%$ and $>94\%$ contributions to the HOMO and SHOMO, respectively, are derived from the imidazole group. The contributions from the pyridine group to the two lowest unoccupied orbitals is $>52\%$ and 98%.
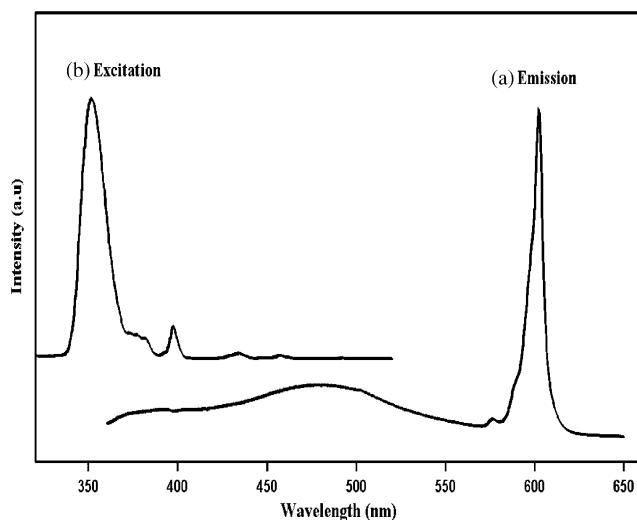
Fig. 2. (a) Emission spectrum of Cm^{3+}:biz (1:1) in MeOH solution. The spectrum was collected upon ligand excitation at 351 nm. (b) Excitation spectrum collected by monitoring the curium emission at 600 nm.

defined band as the ligand ratio increases. These changes are indicative of stepwise complexation at the metal center.

The spectroscopic results are also consistent with an earlier EXAFS complexation studies conducted by Yaita et al. on $Am^{3+}-$ and Nd^{3+}–biz systems, where the dominance of the mono- and bis-coordinated species (M–biz and M(biz)$_2$ complexes) in alcoholic solutions have been reported [19]. In acidic media, as in our case, the EXAFS results indicated that a maximum of only two biz ligands coordinate, even at a 1:4 (M:biz) ratio, in a bidentate fashion. Hence, 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 most intense excitation band for the direct f–f absorption is usually observed at ~ 395 nm. Addition of the Biz ligand in a 1:1 mole ratio provides a dramatic change in the excitation spectrum of the system (Fig. 2b). The band at 351 nm with full-width at half-maximum (FWHM) of 16 nm becomes dominant, although direct f–f excitation in this region provides negligible emission. Hence, the broad excitation band at 351 nm corresponds to the ligand-centered π–π^* transition. Compared to the free ligand spectrum, the band is red-shifted by ~ 3100 cm^{-1} in the complexes. Comparison of the excitation intensities at 351 and 395 nm indicates that the sensitized emission (via the 351 nm excitation) is nearly 60 times larger than the direct metal centered f–f excitation (at 395 nm), indicating that the ligand-centered transition is the principal route for the delivery of excited energy into the curium's $5f^n$ electronic levels.

The emission spectrum for the 1:1 (Cm^{3+}–biz) complex is shown in Fig. 2b. The band consists of two

regions. At the shorter wavelength region a broad and weak band is observed at ~ 473 nm, along with a much weaker band at ~ 382 nm. These bands correspond to the ligand's triplet and singlet emissions, respectively. Concomitantly, the characteristic Cm^{3+} emission corresponding to the $^6D_{7/2} \rightarrow {}^8S_{7/2}$ transition is observed at 602 nm.

Depending on the chelate, several attributes influence the effectiveness of energy transfers from the lowest triplet state of the coordinating ligand to one of the f-species electronic levels. These factors include donor–acceptor distances, spectral overlap between the donor emission and acceptor absorption bands, and the involvement of ligand centered and/or ligand to metal ion charge transfer states. The most important factor involves the position of the lowest triplet state of the ligand relative to the acceptor f-ion level [20,21].

Latva et al. [22] have recently studied several ligands and established a correlation between the energies of the lowest triplet state and the luminescence quantum yields involving several lanthanide ions. For an efficient energy transfer, the first step involves energy absorption by the organic chromophore to its singlet excited state. Ligands with large extinction coefficients are preferred for maximizing the efficiency of the energy transfer process. This step is followed by intersystem crossing to the triplet state, where the exited energy is then intramolecularly transferred to the acceptor resonance level.

As shown in Fig. 1, the free biz ligand displays an emission originating only from a singlet state at ~ 385 nm. Emission from the triplet state is absent, indicating the inefficiency of intersystem crossing in the ligand system. However, upon coordination with actinide and/or lanthanide ions, the ligand-centered optical transitions are influenced significantly, both in position and intensity. First, the absorption band red shifts by as much as 3100 cm^{-1} in the complexes, as compared to the free ligand, indicating that coordination with the f-species lowers the π–π^* transition. Second, the triplet emission at ~ 473 nm in the complexes is dominant, although only singlet emission at 385 nm dominates in the free ligand emission. This indicates that intersystem crossing from singlet to the triplet state is facilitated by coordination to heavy metal atoms in solution.

The efficiency of energy exchange between the lowest triplet state of the ligand and the acceptor f-ion level is dependent on the relative transfer and back-transfer rates [23]. In highly efficient systems, the back transfer step is minimized and/or eliminated once the energy is transferred to the metal center. A reduced back transfer requires that the triplet state be at a sufficiently higher level than the acceptor level. Accumulated data on lanthanide systems indicate that energy gaps ranging from ~ 1000 to 1850 cm^{-1} are adequate to minimize the back transfer process from the acceptor level to the

ligand center [24]. It would be of interest to extend the validity of this approach to the transuranium systems.

3.3. Comparison of the Cm^{3+}–biz with Tb^{3+}–biz systems

The excitation spectrum of the Tb^{3+}–biz system, monitored at the terbium emission band at 620 nm is shown in Fig. 3a. The ligand-centered band at 344 nm is dominant in the spectrum providing clear evidence for the intramolecular energy transfer processes. The emission spectrum of the Tb^{3+}–biz system is shown in Fig. 3b for the 1:1 (Tb^{3+}:biz) ratio. The spectrum was collected after ligand-centered excitation at 344 nm. Broad ligand-centered emission bands are observed at 382 and ~475 nm. The former band is consistent with the band displayed by the free ligand (Fig. 1c) and originates from its singlet state. The broad band at ~475 nm is a consequence of the enhanced intersystem crossing due to the ligand's coordination to the heavy metal ion [15,24]. In addition to the ligand-centered bands, the spectrum also consists of the "sensitized" metal centered f–f transitions that appear at the tail of the ligand's triplet emission band. The f–f bands are observed at 488.6, 543.7, 586, and 620 nm, and correspond to the $^5D_4 \rightarrow {}^7F_6$, $^7F_5$, $^7F_4$, $^7F_3$ transitions, respectively.

The lowest triplet state of the ligand, situated at ~21,100 cm^{-1}, is in resonance with the emitting first excited $^5D_4$ level of Tb^{3+}. Since the second excited $^5D_3$ state of Tb^{3+} is positioned at >5000 cm^{-1}, it is reasonable to assume that all of the exited energy is transferred directly to the emitting $^5D_4$ level located at 20,500 cm^{-1}. The energy difference between the triplet state of the ligand and the $^5D_4$ level of Tb^{3+} is about 600 cm^{-1}. Although, the energy-match up between the donor/acceptor levels is expected to enhance the forward transfer, a separation of ~600 cm^{-1} is less than ideal to eliminate entirely the back-transfer process [22,24]. As a result, the ligand-centered emissions are dominant. Prior work on Tb^{3+} systems have indicated that competitive back transfer processes from excited Tb(III) to the ligand center reduces the efficiency, even when the energy difference between the $^5D_4$ and the lowest triplet state is as large as 1800 cm^{-1} [25].

The energy transfer process in the Cm^{3+}–biz system proceeds as depicted in Fig. 4. The second excited $^6D_{5/2}$ level is in resonance with the ligand's triplet state and therefore serves as the acceptor level for the initial transfer. The excitation then cascades, non-radiatively, to the emitting $^6D_{7/2}$ level located at ~16,700 cm^{-1}. The characteristic curium emission is observed at ~602 nm and originates from this excited state.

Comparison of Figs. 2 and 3 indicate that the ligand emission is minimal in the curium system, indicating that upon optimal conditions the luminescence efficiency is higher for curium than for terbium. The quantum yield data of the two systems are also consistent with this assertion. The "sensitized" emission of the Cm^{3+}–biz system increases to 6.2%, compared to the 0.26% value attained for the metal centered excitation prior to ligand addition. In contrast, the quantum yield of the sensitized emission of the Tb^{3+}–biz system (0.03%) is almost identical with that of the direct f–f excitation.

A plausible explanation for this difference is that the gap between the curium acceptor and the ligands triplet is slightly higher in the Cm^{3+}–biz complex than in the terbium system. The triplet donor in the curium system is situated ~1000 cm^{-1} above the $^6D_{5/2}$ acceptor level,
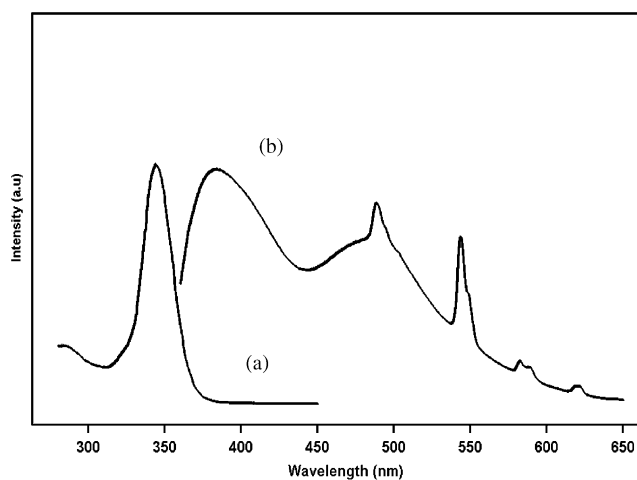

Fig. 3. (a) Excitation spectrum of Tb^{3+}:biz (1:1) in MeOH solution. The spectrum was collected by monitoring the emission at 620 nm; (b) emission spectrum collected after ligand excitation at 344 nm.
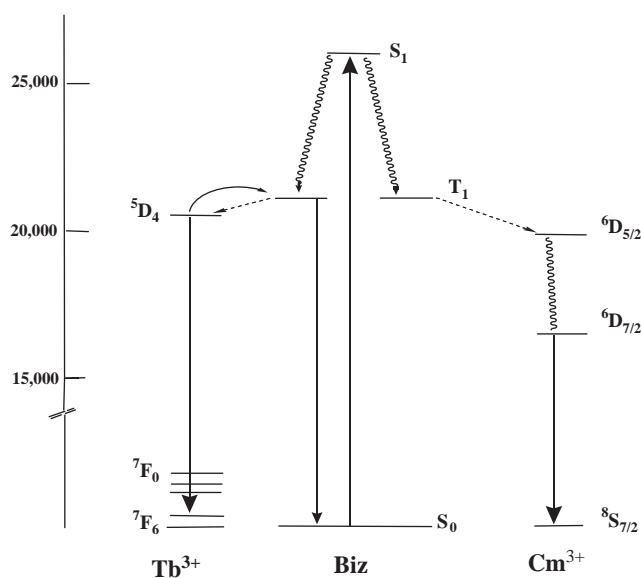

Fig. 4. Energy scheme for the absorption, energy transfer, and luminescence processes. The main energy acceptors and luminescent levels of curium and terbium are depicted.

while the corresponding gap in the terbium system is about $600 \, cm^{-1}$. According to the energy separation analogy discussed above, it is reasonable to assume a more competitive back transfer in the Tb^{3+}–biz as compared to the Cm^{3+}–biz system. The larger donor/acceptor gap in the latter would minimize the back transfer rate and maintains a balance between an efficient forward process and a reduced back transfer. A smaller energy difference would allow increased back transfer from the lowest resonance level of $^5D_4$ of Tb^{3+} to the triplet state of the ligand [25].

Several modifications of the biz ligand are believed essential to bring additional enhancement of the energy transfers and the luminescence efficiencies. For example, replacement of the proton at the imidazole N-site by heavier atoms would eliminate the coupling between the v_{N-H} vibrational manifold and the electronic transition. Ligands with v_{N-H} oscillators, having vibronic frequencies similar to v_{O-H}, are effective non-radiative deactivators of f-species excited states. Emission enhancement should be attained by eliminating a non-radiative pathway that may act as an energy sink, which would quench the emission. Other modifications we have considered include replacing various e-donating groups at the methyl substituent site. Such modifications are essential for tuning the energy match-up between the triplet state of the ligand and the acceptor f-level of the metal ion. For example, theoretical calculations have indicated that substitution of π-donor oxygen atoms at the benzimidazole ring destabilize the HOMO resulting in a red-shift of the lowest absorption transition [26]. Hence, systematic substitution of e-donating groups at the benzyl sites should influence the positions of the frontier orbitals and the energy match-up in donor/acceptor systems.

4. Conclusion

The 6-methyl-2-(2-pyridyl)-benzimidazole ligand coordinates with actinide and lanthanide species and efficiently enhances the emission from the metal ions. The position of the ligand's triplet state relative to the acceptor level is critical for the enhanced emission. In the curium complex the energy gap between the ligand's triplet state and the acceptor level is about $1000 \, cm^{-1}$, while in the terbium system the corresponding gap is $\sim 600 \, cm^{-1}$. The larger gap in curium reduces the energy back-transfer and the radiative yield is significantly higher. In the Tb case the smaller donor/acceptor gap enhances the back transfer rate and when compared to the curium system, the energy transfer is less efficient. The study provided an opportunity to develop a class of benzimidazole-based ligands suitable for sensitization of the transuranium species.

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