Curcuminoid Ligands for Sensitization of Near-Infrared Lanthanide Emission

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Fluorescent lanthanide complexes were synthesized using a non-phenolic analog of curcumin as the principal chromophoric chelating ligand. Sensitized, near-infrared fluorescence is observed in these complexes as a result of photo-excitation of the chromophoric ligands, population of the molecular triplet state, and transfer of energy to the emitting lanthanide ion. For the purpose of intra-molecular energy transfer, the triplet states of curcuminoid ligands are more favorably matched with the excited electronic states of neodymium and ytterbium ions than those associated with less conjugated β-diketonate ligands. Sensitization of fluorescence through an internal redox reaction, thought to occur in other ytterbium complexes, is predicted to be less probable under the present circumstances.

KEY WORDS: Lanthanide; curcumin; chelate; sensitized fluorescence; near-infrared.

INTRODUCTION

Chelated lanthanide ions represent a unique class of fluorescent compounds that feature narrow-band emission in the visible or near-infrared region, sensitized through intra-molecular energy transfer from photo-excited organic ligands. Fluorescent biological tags [1] and electro-luminescent devices [2] are among the numerous, diverse applications for which materials of this category have been implemented. Sensitization efficiency in most cases is influenced by the energetic proximity of the molecular triplet state of the chromophoric ligand to the excited electronic levels of a particular lanthanide element [3,4]. Accordingly, efforts have been made to identify ligands that best satisfy the unique sensitization requirements of each fluorescent lanthanide [4]. Substituted β-diketonates are among the most commonly used ligand systems, and perform quite satisfactorily in conjunction with certain lanthanides, but are not universally applicable. Lanthanide complexes comprised of acetylacet-onate, benzoylacetonate, and dibenzoylmethide ligands have molecular triplet states in the vicinity of 25,000, 22,000, and 20,500 cm^{-1}, respectively. These ligands, or analogs thereof, have been employed with considerable success to sensitize visible-emitting lanthanides such as dysprosium, europium, samarium, and terbium.
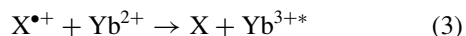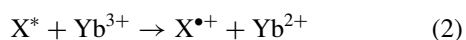
The trivalent ions of neodymium and ytterbium emit light in the near-infrared region, and are notable in terms of the relatively low energies of their principal emitting levels (Yb^{3+} ^{2}F$_{5/2}$, $\sim$10,500 cm^{-1}; Nd^{3+} ^{4}F$_{3/2}$, $\sim$12,000 cm^{-1}). The energy differences between each of these emitting levels and the molecular triplet states of the ligand systems described earlier are substantial. Since it is generally advantageous to minimize these differences in order to enhance the sensitization process, efforts have been made to identify sensitizing chromophores having molecular triplet states that are more energetically suitable [5–14]. Highly conjugated ligand systems, conducive to visible excitation, form lanthanide complexes having correspondingly lower molecular triplet state energies than the simple β-diketonate ligands noted earlier. For example, the incorporation of fluorescein and eosin chromophores into diethylenetriamine-pentaacetic acid derivatives allows visible-wavelength excitation and attendant sensitization of erbium, neodymium, and ytterbium [5].

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Similar results have been obtained for mono-thio-β-diketonate complexes of neodymium and ytterbium [6]. Various porphyrinate ligands have been used successfully to sensitize near-infrared lanthanide luminescence [7,8].

Fluorescent emission from certain chelated ytterbium complexes contradicts the notion that sensitization can occur only under conditions that specifically favor intra-molecular energy transfer. Most notable in this regard are complexes in which large energy differences exist between the molecular triplet state and the ytterbium excited state. A classic example involves sensitization of ytterbium fluorescence by dibenzoylmethide ligands [15]. This process appears to be extraordinarily efficient despite an energy difference greater than $10,000 \, \text{cm}^{-1}$. The sensitization of ytterbium fluorescence by terphenyl-based ligands [16] is perhaps, even more remarkable. In this instance, the energy of the molecular triplet state of the lanthanide complex is nearly $15,000 \, \text{cm}^{-1}$ greater than that of the $^2F_{5/2}$ emitting level of ytterbium. It is important to note that among the fluorescent lanthanide elements, ytterbium represents a special case in which intra-molecular energy transfer may not be solely responsible for sensitization. It has been postulated that a photo-induced electron transfer mechanism may play a substantial role in sensitizing ytterbium fluorescence in certain complexes [17,18]. According to the mechanism outlined later, photo-excitation (1) of the chromophoric ligand or host molecule results in the production of a molecular radical cation (2), and reduction of the chelated Yb^{3+} to Yb^{2+}. Spontaneous electron back-transfer (3) recycles the chromophore while yielding a finite fraction of excited-state Yb^{3+} ions.

$$X + h\nu \rightarrow X^* \tag{1}$$

$$X^* + Yb^{3+} \rightarrow X^{\bullet+} + Yb^{2+} \tag{2}$$

$$X^{\bullet+} + Yb^{2+} \rightarrow X + Yb^{3+*} \tag{3}$$

Although the notion of ytterbium fluorescence sensitization occurring through photo-induced electron transfer has been met with certain skepticism [19,20], there has not been a plausible alternative explanation for sensitized ytterbium emission observed under circumstances that do not favor intra-molecular energy transfer.

The present investigation examined the utility of curcuminoids as novel sensitizing ligands for ytterbium and neodymium. Curcumin (bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione) is a natural product derived from *Curcuma longa* (turmeric) [21,22]. The enolic form of the curcumin molecule is functionally similar to substituted β-diketonates in terms of metal complexation, but has more extensive π-electron conjugation and longer wavelength absorption. Natural curcumin

has been utilized for some time as a spectrophotometric complexing agent for boron [23]. Curcumin also forms complexes with a variety of transition metals, and specific efforts have been made to examine the cytotoxic properties of this category of compounds [24]. Interest in this area has led to the synthesis of novel curcuminoids [25,26].

Despite their metal-chelating abilities and unique spectroscopic properties, curcuminoids have not been previously examined as sensitizers for lanthanide fluorescence. A triplet state energy of approximately $14,000 \, \text{cm}^{-1}$ has been reported for the curcumin enolate in dioxane solution [21]. Dysprosium, europium, samarium, and terbium, all having emitting levels at energies greater than $14,000 \, \text{cm}^{-1}$, are not amenable to sensitization by curcuminoids. However, in view of the arguments presented earlier, curcuminoid ligands appear to be ideally suited for sensitization of fluorescent emission from ytterbium and neodymium. We have demonstrated that enolization of curcuminoids, and subsequent complexation of Nd^{3+} and Yb^{3+} ions by the β-diketonate moiety, yields stable *tris* complexes that emit near-infrared fluorescence under visible light excitation. This communication describes the synthesis and spectroscopic characterization of curcuminoid complexes of these lanthanides.

EXPERIMENTAL

The objective of the present investigation was to prepare *tris*-curcuminoid complexes of ytterbium and neodymium similar to the diketonate complexes described earlier. Commercially available curcumin contains minor amounts of demethoxycurcumin and bis-demethoxycurcumin. There is no question that all three natural curcumin analogs readily complex trivalent lanthanide ions. However, to facilitate preparation of soluble, homogeneous lanthanide complexes, we elected to synthesize a curcuminoid ligand having the formula (bis(3,4-dimethoxyphenyl)-1,6-heptadiene-3,5-dione). Similar non-phenolic curcuminoids have been synthesized for photophysical studies [22,27]. Lewis base adducts of chelated lanthanide compounds typically yield higher fluorescence emission intensities due to increased saturation of lanthanide coordinating sites, and attendant exclusion of energy-quenching water molecules [9,28,29]. In order to mitigate quenching of the near-infrared emissions of neodymium and ytterbium, the curcuminoid complexes prepared during the present investigation included 1,10-phenanthroline as a neutral auxiliary ligand.
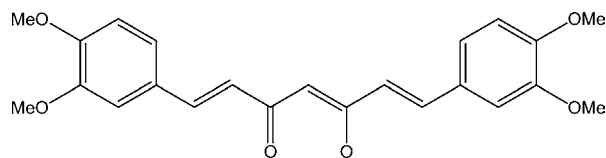
Fig. 1. Molecular structure of the non-phenolic curcuminoid enolate.

Synthesis of Curcuminoid Complexes

The curcuminoid ligand was prepared using 3,4-dimethoxybenzaldehyde (vanillin methyl ether) according to the method outlined in [25]. The molecular structure of the enolic form of the synthesized curcuminoid ligand shown in Fig. 1 illustrates the extensive conjugation that gives rise to visible wavelength absorption. To prepare the Nd(curc)$_3$(phen) complex, the curcuminoid ligand (0.170 g, 0.43 mmol), 1,10-phenanthroline (0.025 g, 0.14 mmol) and N,N-diisopropylethylamine (75 μL, 0.43 mmol) were dissolved in 10 mL acetone with stirring. An aqueous solution of NdCl$_3$ (0.14 mmol) was added and stirring continued for 30 min. Addition of water (40 mL) caused precipitation of the complex as a yellow solid that was collected on a medium frit and washed with water (0.146 g, 69%). Yb(curc)$_3$(phen) was prepared similarly.

Spectroscopic Measurements

A Cary 5 UV-Vis-NIR spectrophotometer was used to record absorption spectra for solution-state ligands and lanthanide complexes. All fluorescence measurements were performed at room temperature using dry powders of the curcuminoid complexes, finely dispersed (approximately 10% w/w) within a polytetrafluoroethylene (PFE) powder host, and pressed into 13-mm diameter pellets. Front-surface excitation of the pellets was accomplished using 150-W high-pressure xenon lamp and a 0.22-m monochromator equipped with a 1200 g/mm diffraction grating. The nominal spectral bandpass for excitation was 7.2 nm. Fluorescence emission spectra (850–1150 nm) were recorded using a 0.125-m spectrograph equipped with a 1024-element linear diode array detector and a 600 g/mm diffraction grating. A long-pass optical filter was used to reject source radiation. Raw emission data were corrected to compensate for the spectral response of the array detector. Wavelength calibration for the emission spectrograph was accomplished using second-order diffraction of visible emission lines from a mercury discharge lamp.

RESULTS AND DISCUSSION

Figure 2 shows the absorption spectrum of the non-phenolic curcuminoid in methanol solution at a concentration of 3×10^{-5} mol/L. With the exception of a small hypsochromic shift in the visible-wavelength absorption maximum to 418 nm, the spectrum closely resembles that of natural curcumin [22,30]. The shift in
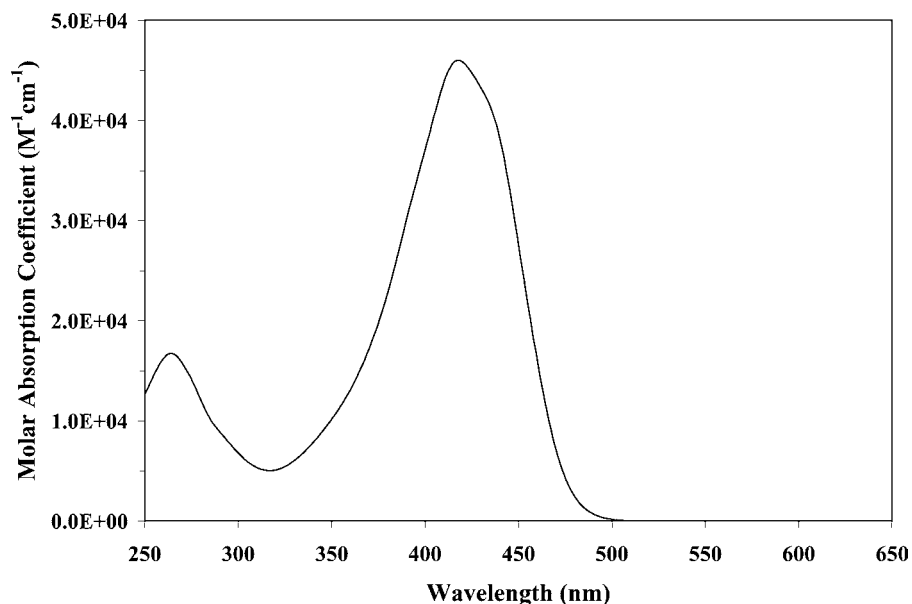

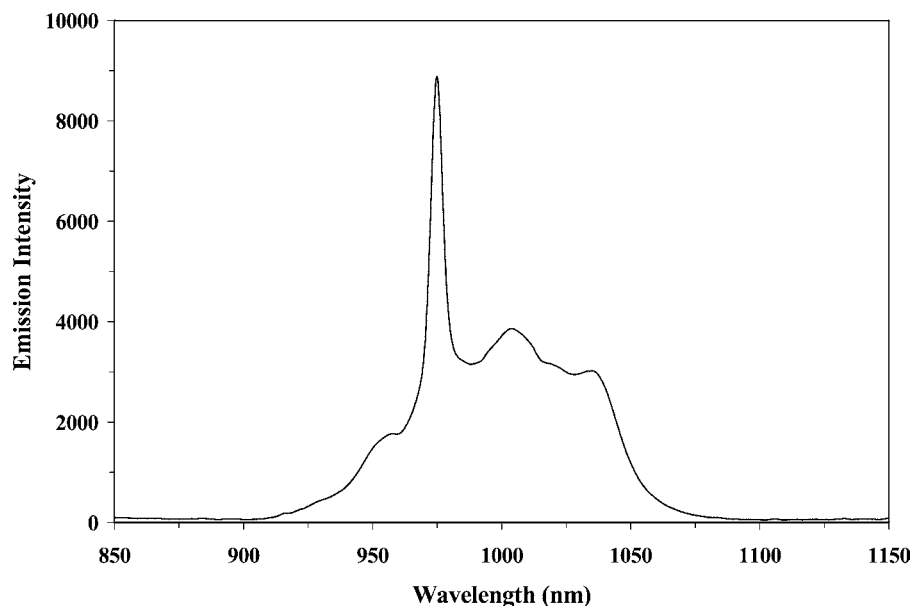**Fig. 2.** Absorption spectrum of the non-phenolic curcuminoid in methanol solution at a concentration of 3×10^{-5} mol/L.

Fig. 3. Fluorescence emission spectrum of $Yb^{3+}(curc)_3(phen)$.

peak absorption wavelength can be attributed to a slight difference in π-electron conjugation. It is reasonable to assume that the triplet state energies of the non-phenolic curcuminoid and natural curcumin are similar with regard to intra-molecular energy transfer to chelated lanthanide ions.

Figure 3 shows the fluorescence emission spectrum acquired during 418 nm excitation of the $Yb^{3+}(curc)_3(phen)$ complex. The emission peak at 974 nm has a full width at half maximum of less than 10 nm, and corresponds to a $^2F_{5/2} \rightarrow {}^2F_{7/2}$ electronic transition. Additional weak emissions correspond to electronic transitions terminating at the remaining J levels of the $^2F_{7/2}$ manifold [31]. The curcuminoid triplet state energy is considered favorable for intra-molecular energy transfer to the Yb^{3+} ion. Photo-induced electron transfer, postulated to increase the yield of excited-state Yb^{3+} ions in other compounds [17,18], is much less likely to play a significant role in the present curcuminoid complex. The viability of this pathway depends to a large extent on the energy of the *singlet* excited state of the chromophoric ligand system. This energy represents the driving force for the reversible redox reaction that initiates production of excited-state Yb^{3+} ions. The following expression (Eq. (1)), adapted from Ref. [17], was used to forecast the spontaneity of this mechanism.

$$\Delta G^\circ = E\left(\frac{X^{\bullet+}}{X}\right) - E(X^*) - E\left(\frac{Yb^{3+}}{Yb^{2+}}\right) \qquad (1)$$

where ΔG° is the spontaneity of the photo-induced electron transfer mechanism; $E(X^*)$ the energy of molecular excited (singlet) state; $E(X^{\bullet+}/X)$ the reduction potential of the molecular radical cation; $E(Yb^{3+}/Yb^{2+})$ the reduction potential of bound ytterbium ion.

In the example described in Refs. [17,18], ytterbium was bound to proteins containing tryptophan. Table I lists the singlet excited state energy of tryptophan and the reduction potential of the corresponding radical cation. The calculated ΔG° value of -1.54 eV is indicative of the theoretical spontaneity of long-range electron transfer mechanism in this system. This pathway to fluorescence sensitization appears at least plausible in view of the considerable energy mismatch that exists between the molecular triplet state of tryptophan and the excited electronic state of ytterbium. It is reasonable to expect that

Table I. Thermodynamic Factors for Photo-Induced Electron Transfer in Ytterbium Complexes

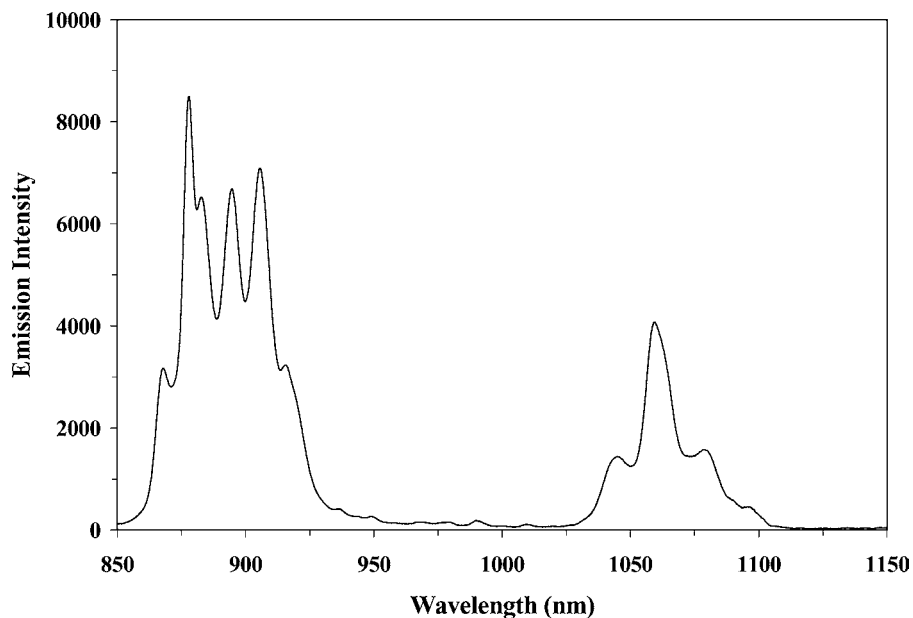|	Chromophore		
	Trp[a]	DB[b]	Curc.[c]
$E(X^*)$ (eV)	3.90	3.14	2.57
$E(X^{\bullet+}/X)$ (V)	1.13	0.87	0.94
$E(Yb^{3+}/Yb^{2+})$ (V)	-1.23	-1.23	-1.23
ΔG° (eV)	-1.54	-1.04	-0.40

[a] Tryptophan.
[b] Dibenzoylmethide enolate.
[c] Curcuminoid enolate.

Fig. 4. Fluorescence emission spectrum of $Nd^{3+}(curc)_3(phen)$.

photo-induced electron transfer may also occur in complexes in which the sensitizing chromophores are bound directly to Yb^{3+} ions. Dibenzoylmethide represents a category of β-diketonate ligands known to sensitize ytterbium fluorescence despite having triplet state energies that are unfavorable for intra-molecular energy transfer to this specific lanthanide ion [15]. The reduction potentials of the curcuminoid and dibenzoylmethide enolates were determined using cyclic voltammetry, and are listed in Table I along with the estimated singlet excited-state energies of these ligands. The ytterbium reduction potential, corrected to account for differences in binding constant between Yb^{3+} and Yb^{2+}, is also listed in Table I. The presence of phenanthroline as an auxiliary ligand was not considered in this assessment, since it is not, under the present circumstances, involved in the excitation of the lanthanide complexes (see later discussion).

The ΔG° values calculated for curcuminoid and dibenzoylmethide complexes of ytterbium were -0.40 and $-1.04\,eV$, respectively. Although the ΔG° value calculated for a ytterbium-dibenzoylmethide complex is less negative than that determined for the ytterbium–tryptophan system, the spontaneity for electron transfer might still be sufficiently large to account for the unexpected degree of fluorescence sensitization exhibited by the former. The ΔG° value calculated for photo-induced electron transfer in the ytterbium-curcuminoid complex predicts even less spontaneity. Given that the curcuminoid molecular triplet state is located in more favorable

energetic proximity to the excited electronic state of ytterbium, it is very likely that fluorescence sensitization in this case occurs exclusively through intra-molecular energy transfer.

In contrast to the easily reduced trivalent ytterbium ion, neodymium lacks a divalent oxidation state, and is not likewise amenable to participating in the redox reaction described earlier. Consequently, neodymium is entirely dependent on intra-molecular energy transfer for fluorescence sensitization [20]. Figure 4 is a fluorescence emission spectrum obtained by exciting the $Nd^{3+}(curc)_3(phen)$ complex at 418 nm. Individual emission features correspond to $^4F_{3/2} \rightarrow ^4I_{9/2}$ and $^4F_{3/2} \rightarrow ^4I_{11/2}$ electronic transitions of the Nd^{3+} ion. The spectral representation of nearly all of the J levels of the $^4I_{9/2}$ and $^4I_{11/2}$ manifolds provides some indication of the electrostatic crystal field splitting of these states.

It is notable that the phenanthroline adducts exhibited modestly enhanced fluorescence intensities overall, as compared to unsaturated curcuminoid complexes of both ytterbium and neodymium. Direct sensitization of neodymium has been reported in phenanthride-appended complexes, but required ultraviolet excitation [20]. The phenanthroline ligand, having a triplet state energy in excess of $21{,}000\,cm^{-1}$, is not involved in fluorescence sensitization under the present circumstances, since excitation of the curcuminoid complexes was performed in the visible region, at 418 nm. Coincident absorption by the curcuminoid chromophore, throughout the ultraviolet

region, precluded the possibility of achieving exclusive excitation of the phenanthroline ligand. It was not feasible, therefore, to examine direct energy transfer between phenanthroline and the lanthanide ion. The enhancement of fluorescence intensities noted earlier may simply be due to the intended exclusion of water molecules.

CONCLUSION

Intensely colored complexes of ytterbium and neodymium were prepared using a synthesized non-phenolic curcuminoid as the principal chromophoric ligand. Extended conjugation within the curcuminoid enolate permitted visible wavelength excitation of these complexes, resulting in near-infrared fluorescent emission from the chelated lanthanide ions. Sensitization of ytterbium fluorescence through a photo-induced electron transfer mechanism was not favored in the curcuminoid complex. Accordingly, near-infrared emission from ytterbium and neodymium could be attributed exclusively to intra-molecular energy transfer, brought about as a result of favorable energetic proximity between the molecular triplet state of the curcuminoid ligands, and the excited electronic states of the corresponding lanthanide ions.

ACKNOWLEDGMENT

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