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Articles

Luminescence Behavior of Europium Complexes in Sol–Gel Derived Host Materials

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The narrow emission bands of europium(III), particularly the laser-active 610-nm band, make it useful as an optical source. Previous solution studies demonstrated that Eu^{3+} chelate complexes have superior fluorescence properties with respect to salts such as $EuCl_3$ and $Eu(NO_3)_3$, both of which have recently been doped into gel matrices. To study the liquid-phase and solid-state properties of Eu^{3+} complexes relative to $EuCl_3$, tris(4,4,4-trifluoro-1-(2′-thienyl)-1,3-butanedionato-*O*,*O*′)europium(III) dihydrate and piperidinium tetrakis(4,4,4-trifluoro-1-(2′-thienyl)-1,3-butanedionato-*O*,*O*′)europate(III) were introduced into silica gel by the sol–gel method. The luminescence behavior of the solid-state samples was studied during the sol–gel aging process by means of absorption, emission, and excitation spectroscopy. The complexes were found to have notably higher quantum efficiencies than $EuCl_3$, in both solution and the solid state, and their absorption and spontaneous-emission cross sections were 2–3 orders of magnitude higher.

Introduction

The sol–gel method has been shown to be a suitable approach for the preparation of novel luminescent materials. Much recent work has focused on the development of solid-state tunable dye laser media using organic dye dopants,[1-12] and several researchers have demonstrated laser action in such media.[1-7] Typically, dopants are incorporated into gel hosts via dissolution of soluble species into the initial precursor sol. Solutions may be spin-coated onto various substrates, pulled into free-standing fibers or cast into bulk monoliths. Thus, these gel-based media appear to be promising candidates for the development of new bulk lasers and integrated optical device sources. Unfortunately, organic dyes photodecompose, thereby limiting useful application lifetimes.[2,3,8] Efforts have been directed toward improving the photostability of dye-doped gel materials through matrix optimizations and more recently materials possess substantially enhanced stability behavior.[6,9-11] A second problem associated with organic dye-doped materials involves luminescence quenching at high laser repetition rates, as intersystem crossing to relatively long-lived triplet states tends to reduce the stimulated emission cross section of these systems at pump-pulse rates greater than 5 Hz. For these reasons, it is of interest to explore alternative luminescent species for use in optical source applications. The research presented herein seeks to extend earlier work regarding luminescent sol–gel derived matrices to include complexed rate-earth ion dopants.

Compounds containing rare-earth ions have long been used as phosphors and laser materials because of their sharp, intensely luminescent *f*–*f* electronic transitions. In particular, europium(III) has five narrow emission bands corresponding to the $^5D_0 \rightarrow {}^7F_i$ transitions, where $i = 0$, 1, 2, 3, 4. The strongest transition, $^5D_0 \rightarrow {}^7F_2$, occurs at approximately 610 nm, the characteristic "europium red" luminescence.[13] Among their widespread applications, europium(III) phosphors have been used as red emission sources in cathode-ray tubes.[13] The $^5D_0 \rightarrow {}^7F_2$ transition has also been shown to exhibit laser emission under appropriate conditions in Eu^{3+}-doped crystals and glasses[14] and from Eu^{3+} organometallic complexes in solution.[15]

Mack *et al.*, Sanchez, and Campostrini *et al.* have previously examined the luminescence behavior of $EuCl_3$[16,17]

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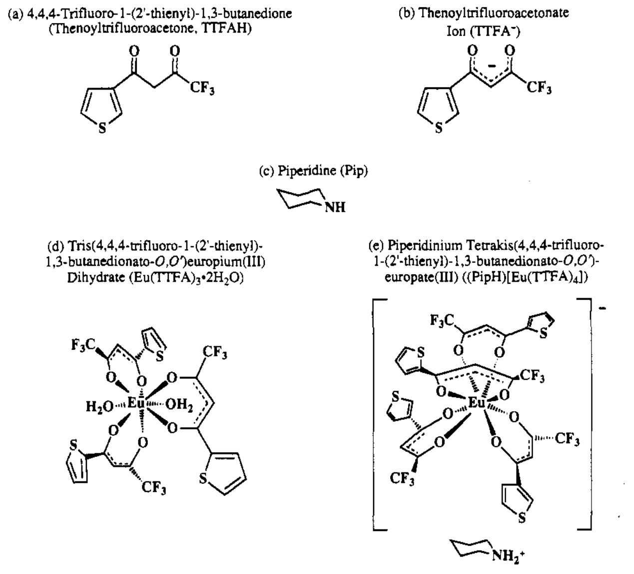

Figure 1. (a) 4,4,4-Trifluoro-1-(2′-thienyl)-1,3-butanedione or thenoyltrifluoroacetone (TTFAH), in its keto form. (b) Enolate form, thenoyltrifluoroacetonate (TTFA⁻). (c) Base piperidine (Pip). (d) Tris(4,4,4-trifluoro-1-(2′-thienyl)-1,3-butanedionato-*O,O′*)europium(III) dihydrate ($Eu(TTFA)_3{\cdot}2H_2O$).[24] (e) Piperidinium tetrakis(4,4,4-trifluoro-1-(2′-thienyl)-1,3-butanedionato-*O,O′*)europate(III)((PipH)[$Eu(TTFA)_4$]).[25]

and $Eu(NO_3)_3$[18] salts adsorbed into porous glasses and doped into sol–gel derived hosts. $EuCl_3$-doped silica gels produced in our laboratory were found to exhibit highly quenched luminescence. Thus, it is of great interest to modify the local environment of Eu^{3+} ions to improve their absorptive characteristics and to reduce nonradiative decay mechanisms from the excited state. One approach is the use of complex-forming ligands such as 4,4,4-trifluoro-1-(2′-thienyl)-1,3-butanedione (thenoyltrifluoroacetone or TTFAH, Figure 1). This method affords a rare-earth-metal ion that is substantially shielded from the immediate local surroundings by the organic ligand shell. Some ligands, such as TTFAH, are also highly asymmetric, thereby reducing the local-field symmetry of the metal ion and making the radiative transitions somewhat more allowed. Brecher *et al.* demonstrated that organometallic complexes of europium showed intense fluorescence in a variety of solutions, including protic systems such as ethanol and methyl methacrylate.[21] The emission cross sections of these complexes were found to be superior to inorganic salts, such as $EuCl_3$, after dissolution into comparable solvents. In the reported work tris(4,4,4-trifluoro-1-(2′-thienyl)-1,3-butanedionato-*O,O′*)europium(III) dihydrate and piperidinium tetrakis(4,4,4-trifluoro-1-(2′-thienyl)-1,3-butanedionato-*O,O′*)europate(III) metal-organic complexes have been doped into silica gel matrices. Luminescence behavior of the resulting composite material is described.

Syntheses

Europium(III) chelates were prepared using thenoyltrifluoroacetone (TTFAH), a *β*-diketone known to undergo keto–enol tautomerization. Although the keto form is heavily favored under most conditions, the enolic hydrogen is sufficiently acidic to dissociate in the presence of a base, forming thenoyltrifluoroacetonate (TTFA⁻), the relatively stable, conjugated enolate ion. The enolate form may react with metal ions to form organometallic complexes.[22] In the presence of stoichiometric quantities of Eu^{3+}, they can produce tris (1) or tetrakis (2) chelate complexes, depending upon the synthetic conditions used:

$$3Na(TTFA) + EuCl_3 \rightarrow Eu(TTFA)_3 + 3NaCl \quad (1)$$

$$4(PipH)(TTFA) + EuCl_3 \rightarrow (PipH)[Eu(TTFA)_4] + 3(PipH)Cl \quad (2)$$

where $(PipH)^+$ is the piperidinium ion. The indicated syntheses were initially described by Whan and Crosby[23] and later expanded by Brecher *et al.*,[21] who fully detailed the preparation of $Eu(TTFA)_3$ and (PipH)[$Eu(TTFA)_4$]. These complexes are highly soluble in *N,N*-dimethylformamide (DMF), which is known to be compatible with silicon alkoxide sol–gel preparative techniques.[24,25] Predicted complex structures are shown in Figure 1, and chemical compositions were verified by mass spectrometry analysis.[26,27] X-ray diffraction studies indicated that the recrystallized powders exist as polymorphic mixtures.

The host silica gel matrix was prepared by the hydrolysis and condensation of tetraethoxysilane (TEOS) according to the "sonogel" procedure as described by Esquivias and Zarzycki.[28] A 4:1 water-to-alkoxide mole ratio was used, with mild acid catalysis. Chelate-doped gel samples were prepared by the addition of 5 mM aliquots of the organoeuropium complex, dissolved in DMF, to the silica precursor solution. The resulting sol was subsequently cast into transparent polystyrene curvettes. The samples were kept in convered containers at room temperature until the onset of gellation, which occurred within 6–9 days. Aging and drying were allowed to proceed under ambient conditions over a period of several weeks. Dried xerogel samples retained approximately 20% of their original volume. The final number density of the organometallic guest species in the host gel matrix was calculated to be 3.0×10^{18} cm^{-3}.

Regarding the known toxicity of reagents used in this study, several of the precursors mentioned above, most notably DMF, piperidine, TEOS, and TTFAH, are believed to be slightly to moderately hazardous, thus requiring protection from contact with and inhalation of liquids or vapors.

Spectroscopic Analysis

Luminescence characteristics were measured using a Spex Industries Model F112 spectrofluorimeter; absorption spectra were obtained using a Cary Model 5 spectrophotometer. Emission and excitation spectra were made in the "front face" orientation, and all spectra were corrected. Quantum efficiencies (*Q*) were calculated by

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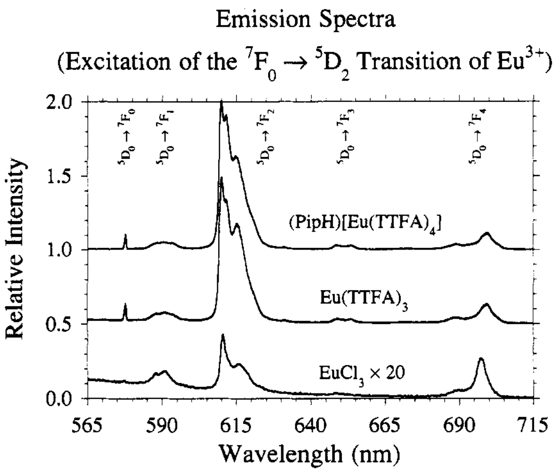

Figure 2. Emission spectra for (PipH)[Eu(TTFA)$_4$] (top, offset 1.0 relative intensity units), Eu(TTFA)$_3$ (center, offset 0.5 units), and EuCl$_3$ in aged silica gel. Spectra were normalized to the maximum emission intensity of (PipH)[Eu(TTFA)$_4$]. The spectrum of EuCl$_3$ has been increased by a factor of 20 times to make the salient structural features observable.

the reference technique of Demas and Crosby[29] using rhodamine 6G chloride in ethanol, reported to have a Q of 95%.[30] Absorption cross sections (σ_{Abs}) were calculated according to

$$\sigma_{\mathrm{Abs}} = \alpha_{\mathrm{Abs}}/\Delta N \tag{3}$$

where α_{Abs} is the absorption coefficient (cm^{-1}) at the excitation wavelength and ΔN is the difference between ground (N_0) and excited (N_1) state number densities (cm^{-3}).[31] Excited-state population densities were assumed to be negligible compared to the ground state population densities ($\Delta N \approx N_0$) under the spectrofluorometric excitation conditions used. The spontaneous-emission cross section (σ_{SpE}), a measure of the relative "brightness" of a luminous source, was obtained using the following:

$$\sigma_{\mathrm{SpE}} = Q\sigma_{\mathrm{Abs}} \tag{4}$$

Results and Conclusions

Figure 2 shows the emission spectra of (PipH)[Eu(TTFA)$_4$], Eu(TTFA)$_3$, and EuCl$_3$ in aged silica gel upon excitation of the $^7F_0 \rightarrow {}^5D_2$ europium transition. The maximum intensity of the $^5D_0 \rightarrow {}^7F_2$ peak (610–620 nm) in (PipH)[Eu(TTFA)$_4$] was observed to be slightly higher than that of Eu(TTFA)$_3$ and approximately 50 times that of EuCl$_3$. Only minor differences were seen between the relative emission peak heights of the various compounds when characterizing the organoeuropium spectra in DMF solution with respect to comparable concentrations in the silica precursor sol and the final dried silica gel. No indication of the presence of luminescent europium(II) species, known to have spectrally broad emission peaks near 428 and 507 nm in silicate materials,[32] was found.

Figure 3 shows the associated excitation spectra, detailing pump transitions resulting in radiative relaxation from the $^5D_0 \rightarrow {}^7F_2$ levels. Both chelates were observed to exhibit greatly increased $^5D_0 \rightarrow {}^7F_2$ luminescence emission cross section, by approximately an order of magnitude with respect to comparable EuCl$_3$-doped samples, following excitation of the $^7F_0 \rightarrow {}^5D_2$ transition. While this increase is notable, a substantially larger emission cross section results upon excitation of the chelate absorption band. Excitation of the ligand band, which couples (via ligand-to-metal charge transfer) into the $^5D_3$ (near 400 nm) and higher levels of europium(III), was observed to result in emission cross sections which were larger than comparable EuCl$_3$-doped gel samples by 3 orders of magnitude.

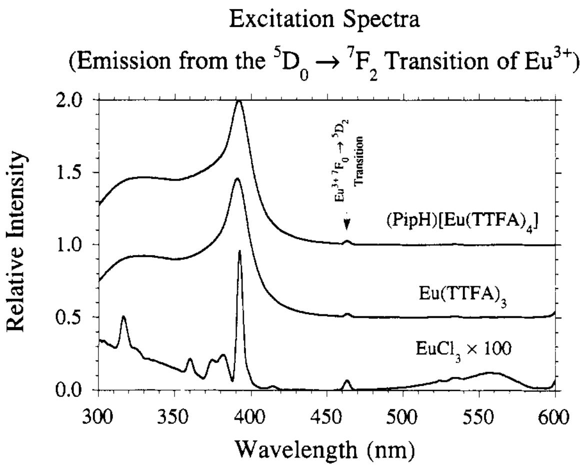

Figure 3. Excitation spectra for (PipH)[Eu(TTFA)$_4$] (top, offset 1.0 relative intensity units), Eu(TTFA)$_3$ (center, offset 0.5 units), and EuCl$_3$ in aged silica gel. Spectra were normalized to the maximum emission intensity of (PipH)[Eu(TTFA)$_4$]. The spectrum of EuCl$_3$ has been increased by a factor of 100 times to make the salient structural features observable.

Table I. Fluorescence Yield Comparison: Dopants in DMF Solution and Aged Silica Gel[a]

	λ_{ex}	α_{Abs} (cm^{-1})	σ_{Abs} (cm^2)	Q	σ_{SpE} (cm^2) (λ_{em} 612 nm)
1. Excitation of the Europium $^7F_0 \rightarrow {}^5D_2$ Transition, DMF Solution (6.02×10^{17} cm^{-3})					
EuCl$_3$	464.0	0.0007	1.1×10^{-21}	8.5%	9.1×10^{-23}
Eu(TTFA)$_3$	463.8	0.0051	8.5×10^{-21}	10.12%	8.7×10^{-22}
(PipH)[Eu(TTFA)$_4$]	463.9	0.0053	8.8×10^{-21}	10.6%	9.3×10^{-22}
2. Excitation of the Europium $^7F_0 \rightarrow {}^5D_2$ Transition, Silica Gel (3.10×10^{18} cm^{-3})					
EuCl$_3$	463.3	0.0087	2.9×10^{-21}	1.0%	2.9×10^{-23}
Eu(TTFA)$_3$	463.7	0.0193	6.4×10^{-21}	6.3%	4.1×10^{-22}
(PipH)[Eu(TTFA)$_4$]	463.6	0.0235	7.8×10^{-21}	5.9%	4.6×10^{-22}
3. Excitation of the Chelate, DMF Solution (6.02×10^{17} cm^{-3})					
Eu(TTFA)$_3$	389.5	1.34	2.2×10^{-18}	37.3%	8.3×10^{-19}
(PipH)[Eu(TTFA)$_4$]	389.0	1.50	2.5×10^{-18}	31.9%	8.0×10^{-19}
4. Excitation of the Chelate, Silica Gel (3.10×10^{18} cm^{-3})					
Eu(TTFA)$_3$	391.0	2.63	8.7×10^{-19}	15.8%	1.4×10^{-19}
(PipH)[Eu(TTFA)$_4$]	392.0	1.01	1.0×10^{-18}	22.2%	2.2×10^{-19}

[a] All the compounds in groups 1 and 3 were studied as 1.0 mM solutions (number density 6.0×10^{17} cm^{-3}) in *N,N*-dimethylformamide. The solid-state samples in groups 2 and 4 were calculated to have dopant number densities of 3.0×10^{18} cm^{-3}.

The effect of complex formation on the luminescence behavior of europium(III) in the gel hosts was examined by exciting the $^7F_0 \rightarrow {}^5D_2$ transition of Eu^{3+} at 464 nm, a lower excitation energy than the chelates' charge-transfer band. The complexes' quantum efficiencies and emission cross-sections were found to be significantly higher than those of EuCl$_3$ in solid- and liquid-phase hosts (Table I, sections 1 and 2), indicating that radiative relaxation processes associated with the Eu^{3+} ion are indeed enhanced by the chelate cage.

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The spontaneous-emission cross sections of the rare-earth-metal complexes, which are a measure of the radiation emission intensity from a given sample volume, were found to be 14 and 16 times larger for the tris and tetrakis chelates, respectively, than the comparable $EuCl_3$-doped silica gel material when excited at the $^7F_0 \rightarrow {}^5D_2$ transition (Table I, section 2). Luminescence behavior of the chelates greatly increased when pumped at wavelengths near 390 nm, corresponding to excitation at the red edge of the complexes' intense ultraviolet absorption bands (Table I, sections 3 and 4). The corresponding emission cross sections of gels doped with $Eu(TTFA)_3$ and $(PipH)[Eu(TTFA)_4]$ were observed to be 4800 and 7600 times larger, respectively, than comparable gel samples doped with $EuCl_3$. Quantum efficiencies of the chelate-doped gels were calculated to be between 15% and 23%. Rare-earth-metal complex doped silica gels have been observed to exhibit substantially improved luminescence characteristics with respect to comparable materials containing simple metal salts. The relatively high efficiency and large spontaneous-emission cross sections exhibited by these systems makes them promising candidates for potential use as optical sources.

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