

Crystal Structure and Luminescence of $[\text{Eu}(\text{TTA})_3 \cdot \text{DAF}] \cdot 0.5\text{C}_7\text{H}_8$ Complex Excited by Visible Light

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The non-ionic europium(III) complex $[\text{Eu}(\text{TTA})_3 \cdot \text{DAF}] \cdot 0.5\text{C}_7\text{H}_8$ (TTA = 2-thenoyltrifluoroacetate, DAF = 4,5-diazafluoren-9-one) was synthesized. The structural determination has been carried out. DAF coordination induces the both excitation spectra in the solid state and solution having a red shift and sensitizes Eu^{3+} luminescence under visible light excitation.

Keywords Eu(III) complex, crystal structure, visible light excitation, luminescence, energy transfer

Introduction

The design and synthesis of luminescence complexes have attracted considerable attention due to their potential uses as molecular photonic devices,¹ fluorescent sensors,² or luminescent chemical probes.^{3,4} The long lifetime of the excited states of the lanthanide ions and their sharp light emission are an advantage in these application. It is well known that in a typical luminescence complex the various steps of the overall process involving absorption of light, transfer, and reemission at lower wavelength are performed separately by distinct parts of the complex. According to these results, much effort has been devoted to the investigation of synthetic strategies for the design of suitable encapsulating ligands which can efficiently optimize the luminescent properties of lanthanide ions by facilitating the well-known light conversion process. The ligands in luminescent lanthanide complexes contain, besides coordination groups, one or more sensitizing chromophores (antennae) which are

needed to overcome the excitation bottleneck formed by the inherently small absorption cross sections of the lanthanide ions. The antenna absorbs the light and consecutively transfers the energy to the lanthanide ions.⁵ For possible applications, it would be the most advantageous to have antenna that absorbs significantly at wavelengths longer than 400 nm and then transfers the excitation energy efficiently and irreversibly to the lanthanide ion. However, for luminescent Eu^{3+} and Tb^{3+} complexes, the excitation window appears to be limited to the near-UV due to the energetic constraints posed by the photo-physics of sensitized lanthanide luminescence.⁶ There is little research work which described Eu^{3+} complexes containing chromophores that absorb at wavelengths longer than 400 nm.⁷ Although the mixed complexes of certain β -diketonates and *O*-phenanthroline display absorption bands in the region 380—400 nm, but the luminescence quantum yields are quite low. In order to search for improved antenna chromophores for lanthanide ions, we have undertaken a study of intramolecular energy transfer between organic chromophores and lanthanide chelates in solid state. In this paper we report the luminescence of $[\text{Eu}(\text{TTA})_3 \cdot \text{DAF}] \cdot 0.5\text{C}_7\text{H}_8$ and its crystal structure.

Experimental

Synthesis

All the chemicals are of analytical grade and used

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without further purification. 4,5-Diazafluoren-9-one and $\text{Eu}(\text{TTA})_3 \cdot 2\text{H}_2\text{O}$ were prepared according to the literature procedures.^{8,9}

Complex $[\text{Eu}(\text{TTA})_3 \cdot \text{DAF}] \cdot 0.5\text{C}_7\text{H}_8$ was prepared as follows: All solvents were treated before use as usual, and 4,5-diazafluoren-9-one (0.182 g, 1 mmol) and $\text{Eu}(\text{TTA})_3 \cdot 2\text{H}_2\text{O}$ (0.936 g, 1 mmol) were refluxed in toluene/chloroform (1:1) (20 mL) for 2 h. The resulting yellow mixture was left standing for several days to obtain crystalline complex with 70–75% yield. mp: 168–170°C. Anal: $\text{C}_{38.5}\text{H}_{22}\text{F}_9\text{N}_2\text{O}_7\text{S}_3\text{Eu}$, Calcd: C 44.31, H 2.10, N 2.68. Found: C 44.87, H 2.47, N 2.61.

Physical measurements

Elemental analyses were performed on a Perkin-Elmer 240C analytical instrument. Fluorescence and phosphorescence spectra were obtained with AB₂ spectrometer. Liquid N₂ cooling was used to obtain phosphorescence spectra at low temperature (77 K). A mixed solvent (4:3:3 DMF/methanol/ether by volume) was used to obtain clear rigid glasses at 77 K as follows: First, the compounds were dissolved in hot DMF (ca. 50°C) and cooled to room temperature. Next, methanol and ether were added and the solution was carefully cooled in a quartz tube in liquid nitrogen to make a glass suitable for emission spectral evaluation.

Caution: Rapid cooling in liquid nitrogen or rapid heating while part of the sample is still a glass can cause cracking of the quartz tube in which the rigid mixed-solvent sample is housed.

The quantum yields of the Eu(III) complexes were measured with $[\text{Ru}(2,2'\text{-bipy})_3]^{2+}$ ($\phi = 0.028$ in aerated water¹⁰) as the standard. In order to give comparisons of emission in intensities, corrections for instrument response, inner filter effects, and phototube sensitivity were made.¹¹ A correction for differences in the refraction indices was introduced where necessary.

Crystal structure determination

Yellow crystalline blocks of composition $[\text{Eu}(\text{TTA})_3 \cdot \text{DAF}] \cdot 0.5\text{C}_7\text{H}_8$, suitable for X-ray diffraction studies, were obtained by evaporation of a toluene/chloroform (1:1) solution of the complex. The intensity data were collected on a Siemens SHELXTL P4 diffractometer

with graphite-monochromatic Mo K_α radiation ($\lambda = 0.071073$ nm) at 293(2) K using a crystal of approximate dimensions 0.53 nm × 0.32 nm × 0.28 nm. Crystallographic data are listed in Table 1. The data were corrected for Lorentz and polarization effects during data reduction using XSCANS.¹² The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL version 5.03.¹³ All the non-hydrogen atoms were refined anisotropically. All computations were carried out using the SHELXTL-PC Program Package.¹³ Selected bond lengths and bond angles are listed in Table 2.

Full crystallographic details, excluding structure factors, have been deposited at Cambridge Crystallographic Data Centre (CCDC).

Results and discussion

Description of the structure

ORTEP drawing of $[\text{Eu}(\text{TTA})_3 \cdot \text{DAF}] \cdot 0.5\text{C}_7\text{H}_8$ is shown in Fig. 1. The complex crystallized in the monoclinic system with space group ($P2_1/c$). Data show that the complex is eight-coordinated Eu(III) ion containing six oxygen atoms from the TTA and two nitrogen atoms from the DAF, and these atoms lie at the apices of a slight distorted square antiprism. But, the symmetry around the central europium ion is approximately C_2 . The carbonyl group of DAF does not ligate to the europium ion and the unit cell contains four $[\text{Eu}(\text{TTA})_3 \cdot \text{DAF}]$ and two toluene molecules disordered over four positions with structure occupancy factor 0.5.

A least square plane was fitted to the four oxygen atoms [O(3)O(4)O(5)O(6)] from the two TTA ligands with an average deviation of 0.00707, which forms the bottom square face of the square antiprism (Fig. 2). The TTA ligand spans are 0.2763 and 0.2748 nm while the other oxygen-oxygen distances are 0.2947 and 0.3109 nm. All angles in the square face are 90° within the experimental error. A least squares plane was fitted to the two nitrogen atoms and two oxygen atoms [O(1)-O(2)N(1)N(2)] from DAF and TTA with a deviation of 0.02765 forming the upper square face of the antiprism. The span of DAF is 0.2942 nm while that of the TTA ligand is 0.2780 nm. The dihedral angle between [O(3)O(4)O(5)O(6)] and [O(1)O(2)N(1)N(2)] is 4.8°. The average Eu—O bond length is 0.2369 nm.

The longer Eu—N bond lengths (average 0.2663 nm) may be related to the steric requirement and to the relatively weak coordination capability of the nitrogen atoms. Because of the unequal Eu—N and Eu—O bond lengths, the upper square face is translated parallel to the bottom face with the two oxygen atoms of the upper face lying closer to the rotation axis of the ideal an-

tiprism. The Eu—N distance is longer than the previous report¹⁴ (0.2488 nm for [Eu(Mentb)₂](ClO₄)₃, Mentb = Methyl-tris(*N*-alkylbenzimidazol-2-(methyl) amines), 0.2501 nm for [Eu(*n*-Prmtb)₂](ClO₄)₃, *n*-Prmtb = *n*-Propyl-tris(*N*-alkylbenzimidazol-2-(methyl) amines) which results in occurrence of the complex substitute reaction in polar solvent.

Table 1 Crystallographic data for complex [Eu(TTA)₃·DAF]·0.5C₇H₈

Empirical formula	C _{38.5} H ₂₂ F ₉ N ₂ O ₇ S ₃ Eu
Formula weight	1043.72
Temperature	293(2) K
Wavelength	0.071073 nm
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>C</i>
<i>a</i> (nm)	1.0083(2)
<i>b</i> (nm)	2.2339(5)
<i>c</i> (nm)	1.9061(4)
β (°)	90.96(3)
Volume, <i>Z</i>	4.293(2) nm ³ , 4
Density (calculated)	1.615 Mg/m ³
Absorption coefficient	1.694 mm ⁻¹
<i>F</i> (000)	2060
Crystal size (mm)	0.48 × 0.37 × 0.23
θ _{min} , θ _{max} (°)	1.82, 25.06
Limiting indices	-1 ≤ <i>h</i> ≤ 12, -1 ≤ <i>k</i> ≤ 26, -22 ≤ <i>l</i> ≤ 22
Reflections collected	9509
Independent reflections	7584 [<i>R</i> (int) = 0.0797]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	7541/0/543
<i>S</i>	1.034
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0673, <i>wR</i> ₂ = 0.1670
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1374, <i>wR</i> ₂ = 0.2440
Largest diff. peak and hole	1408 and -670 e/nm ³
(Δ/σ) _{max}	0.000

$$W = 1/[\sigma^2(F_o^2) + (0.1200P)^2 + 3.0000P], P = (F_o^2 + 2F_c^2)/3$$

Table 2 Selected bond distances (nm) and angles (°) for [Eu(TTA)₃·DAF]·0.5C₇H₈

Eu—O(1)	0.2389 (8)
Eu—O(2)	0.2379 (8)
Eu—O(3)	0.2360 (7)
Eu—O(4)	0.2361 (8)
Eu—O(5)	0.2362 (8)
Eu—O(6)	0.2361 (8)
Eu—N(1)	0.2699 (10)
Eu—N(2)	0.2626 (10)
O(1)-Eu-O(2)	71.3 (3)
O(3)-Eu-O(4)	71.7 (3)
O(5)-Eu-O(6)	71.2 (3)
N(1)-Eu-N(2)	67.1 (3)

The average O—Eu—O angle within the chelate rings is 71.4°. The average N—Eu—N angle is 67.1°. The ability of both TTA and DAF to shield europium(III) ion completely with O-donors and N-donors from the addition of bound water molecules is important for the design of Ln(III) supramolecular photonic devices since coordinated water molecules are frequently efficient quenchers of Ln(III) luminescence.³

Solution luminescence

When Eu(TTA)₃·2H₂O and DAF in toluene/chloroform (1:1) are mixed, a red glow emerges from the

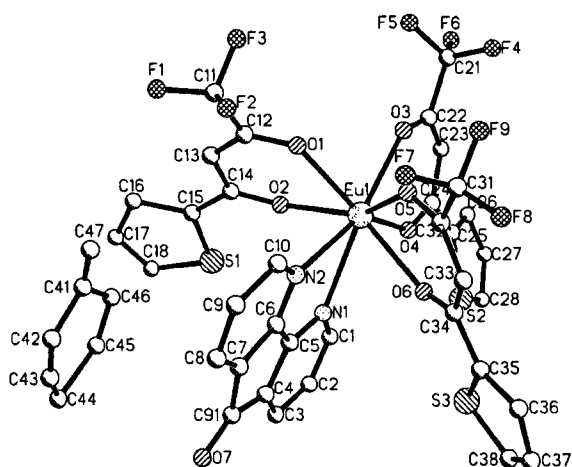


Fig. 1 Molecular structure of complex $[\text{Eu}(\text{TTA})_3 \cdot \text{DAF}] \cdot 0.5\text{C}_7\text{H}_8$ (all hydrogen atoms are omitted for clarity).

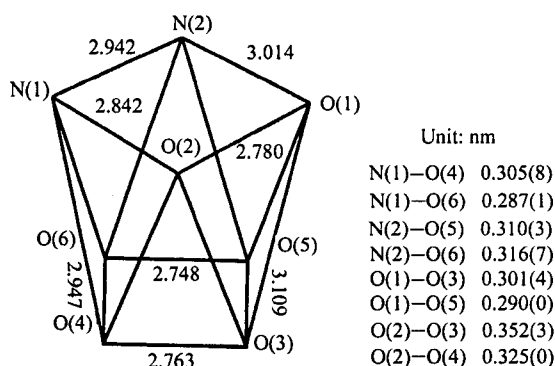


Fig. 2 Distorted square antiprism around the europium(III) ion in $[\text{Eu}(\text{TTA})_3 \cdot \text{DAF}] \cdot 0.5\text{C}_7\text{H}_8$.

solution under daylight illumination which is stronger than that of $\text{Eu}(\text{TTA})_3 \cdot 2\text{H}_2\text{O}$ because DAF coordination shields Eu^{3+} ion from water, also, increases the absorption efficiency of the visible light. The emission spectra (Fig. 3) demonstrates that this red glow is Eu(III) ion luminescence: the sharp peak at ~ 615 nm is characteristic of lanthanide ion emission.¹⁵ The quantum yield was found to be 0.11 in acetonitrile solution. Compared with $\text{Eu}(\text{TTA})_3 \cdot 2\text{H}_2\text{O}$ (Table 3), the DAF coordination leads the complex absorption band moving to red, and makes the corresponding excitation spectrum shift from 348 nm to 381 nm. The excitation spectrum is similar to that of Eu(III) complexes of 9-substituted-4,5-diazafluorene.^{16,17} There is a broad band at 250–300 nm, which is the emission from Eu^{3+} complex due to the oxygen atom $2p^6$ electron delocalization toward the empty $4f$ state of Eu^{3+} . When the solution was left in the ambient

for a few days the excitation spectrum changed a lot, only a broad band at 350 nm appeared, which is the same as $\text{Eu}(\text{TTA})_3 \cdot 2\text{H}_2\text{O}$. It means that $[\text{Eu}(\text{TTA})_3 \cdot \text{DAF}]$ complex is unstable in solution and DAF molecule is easy to lose. It is in accordance with the crystal structure, which shows that the bond lengths of Eu—N are longer and the bond strength is weaker. The emission spectrum of the title complex in the acetonitrile solution is the transitions of Eu(III) ion 5D_0 levels to the $^7F_{0-4}$ levels of the ground-state multiplet. The main emission occurs, as expected, in the $^5D_0 \rightarrow ^7F_2$ transition. The presence of $^5D_0 \rightarrow ^7F_0$ points to the Eu(III) ion at a site of C_n or C_s symmetry in solution. It is in accordance with the crystal structure which indicates C_s symmetry for the reported Eu(III) complex,¹⁸ and means that the structure of the Eu(III) complex in fresh solution is similar as that in solid state.

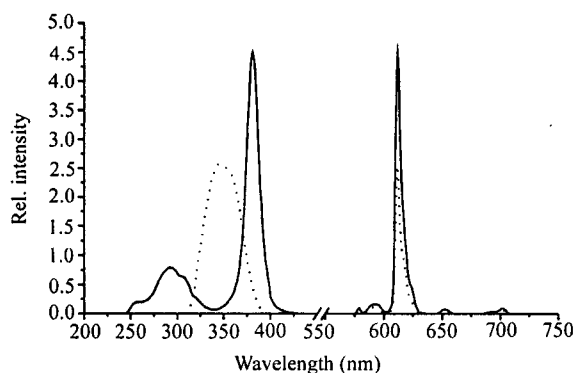


Fig. 3 Solution luminescence excitation ($\lambda_{\text{em}} = 612$ nm) and emission spectra of a solution of 10^{-5} M complex $[\text{Eu}(\text{TTA})_3 \cdot \text{DAF}] \cdot 0.5\text{C}_7\text{H}_8$ in acetonitrile [(---) spectra of complex as soon as prepared ($\lambda_{\text{ex}} = 381$ nm); (\cdots) spectra of complex standing left for a few days ($\lambda_{\text{ex}} = 348$ nm)].

The sensitization pathway in luminescent lanthanide complexes generally consists of excitation of the chromophore antenna into its singlet state, subsequent intersystem crossing of antenna to its triplet state, and energy transfer from the antenna triplet to the lanthanide ion,¹⁹ implying that energy of the triplet state must be sufficiently high. In view of the observation of efficiently sensitized Eu(III) luminescence upon excitation with visible light the singlet-triplet gap of the coordinated DAF must be more suitable than that of other organic chromophores used now. The Gd^{3+} complexes provide a

way to study the triplet state energy of the coordinated DAF. Having no electronic energy levels below 32000 cm^{-1} (310 nm), Gd^{3+} can not accept any energy from DAF. The phosphorescence emission of $\text{Gd}(\text{DAF})_4$ ($\lambda_{\text{ex}} = 341$ nm at 77 K) has a broad band peak at 478 nm. From the emission spectrum of $\text{Gd}(\text{DAF})_4$, the triplet state energy of the coordinated DAF is estimated to be 22421 cm^{-1} (446 nm). Because the Eu(III) and Gd(III) ions are very similar in charge and the distance between the metal cation and the DAF in the complexes, the effect of the metal ions on the ligands should also be similar. The triplet state energy is indeed sufficient to efficiently populate the 5D_0 luminescent state of Eu^{3+} (17500 cm^{-1}). The excited triplet state energy of TTA is around 21097 cm^{-1} .²⁰ As a result, it is possible that the energy transfers from DAF to Eu(III) ion directly, or via TTA to the Eu(III) ion in the $[\text{Eu}(\text{TTA})_3 \cdot \text{DAF}] \cdot 0.5\text{C}_7\text{H}_8$.

Table 3 Luminescence data of Eu(III) complexes

Complexes ^a	$^5D_0 \rightarrow ^7F_2$		Monochromaticity ^b
	λ_{ex} (nm)	λ_{em} (nm)	
a(l)	348	612	28
b(l)	381	612	28.4
c(l)	394	613	29.4
a(s)	400	611	18.3
b(s)	420	612	14.2
c(s)	392	613	12.6

^a a, $[\text{Eu}(\text{TTA})_3] \cdot 2\text{H}_2\text{O}$; b, $[\text{Eu}(\text{TTA})_3 \cdot \text{DAF}] \cdot 0.5\text{C}_7\text{H}_8$; c, $\text{Eu}(\text{TTA})_3 \cdot \text{L}$ (L = mono-(9-(4-hexadecylamino)-4, 5-diazafluorene)); l; solution; s: solid state. ^b $I_E(^5D_0 \rightarrow ^7F_2) / I_M(^5D_0 \rightarrow ^7F_1)$. Intensity I is the peak height of λ_{em} of $^5D_0 \rightarrow ^7F_2$, so, it does not represent that real fluorescence intensity.

Solid state luminescence

The emission spectra of $[\text{Eu}(\text{TTA})_3 \cdot \text{DAF}]$ complex in solid state and in solution are similar and both show five characteristic emission peaks of Eu(III) complex at ca. 580, 592, 614, 656 and 703 nm, respectively. However, $^5D_0 \rightarrow ^7F_2$ peak splits into three peaks at 612, 617 and 623 nm in solid state, which indicates that the environment of the Eu(III) is better defined in the solid state than in the solution. Fig. 4 shows the excitation spectrum of powder sample at room temperature, which is quite different from that in solution and is composed of a broad band from 225–500 nm peaking at 412

nm and 420 nm with four shoulders at 437, 452, 396 and 358 nm, and two sharp peaks at 309 nm and 465 nm. There appears a significant red shift in the excitation spectrum of the powder sample. The reason for this is the nephelauxetic effect, namely, the electron repulsion between the 4f electrons is decreased by DAF coordination, which results in a smaller splitting of the barycenters of the 7F and the 5D terms.²¹ The peak at 465 nm corresponds to the emission due to the stronger absorption from the transition of $^5D_2 \leftarrow ^1F_0$ of 465 nm.²¹ The broad band extending to 225 nm corresponds to the emission due to the oxygen atom $2p^6$ electron delocalization toward empty 4f state of Eu^{3+} .

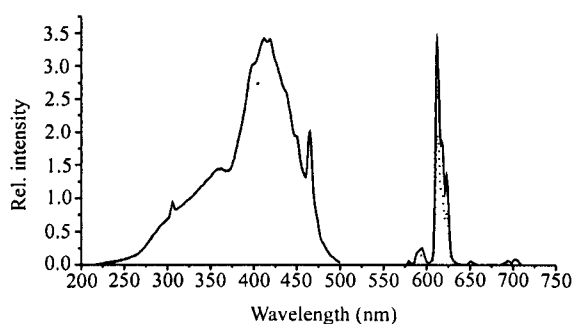


Fig. 4 Solid state luminescence excitation ($\lambda_{\text{em}} = 612$ nm) and emission spectra of complex $[\text{Eu}(\text{TTA})_3 \cdot \text{DAF}] \cdot 0.5\text{C}_7\text{H}_8$ [(—) spectrum of $\lambda_{\text{ex}} = 420$ nm; (···) spectrum of $\lambda_{\text{ex}} = 465$ nm.]

From Table 3 we can see that the excitation band of $[\text{Eu}(\text{TTA})_3 \cdot \text{DAF}]$ has 20 nm red shift from 400 nm to 420 nm and the intensity increases a lot at the longer wavelength side of the peak. Obviously, DAF coordination is responsible for this. Using the ratio of electronic dipolar transition intensity $I_E(^5D_0 \rightarrow ^7F_2)$ to magnetic dipolar transition intensity $I_M(^5D_0 \rightarrow ^7F_1)$ (here intensity I is peak height of $\lambda_{\text{em}}(^5D_0 \rightarrow ^7F_2, ^5D_0 \rightarrow ^7F_1)$) as a standard of monochromaticity, the I_E/I_M of $[\text{Eu}(\text{TTA})_3 \cdot \text{DAF}]$ is similar with that of $\text{Eu}(\text{TTA})_3$, but is better than that of Eu(III) complexes of 9-substituted-4, 5-diazafluorene which possesses very poor fluorescence properties^{16,17} due to the strong vibration coupling from alkyl chain attached to the complexes, also, due to a slight distortion in the symmetry of these complexes.

Conclusion

$\text{Eu}(\text{TTA})_3 \cdot 2\text{H}_2\text{O}$ forms the title complex with an-

tenna DAF. Crystal structure shows that Eu^{3+} locates at the center of a slight distorted square antiprism with C_2 symmetry. DAF coordination shields Eu^{3+} ion from water and induces both excitation spectra in the solid state and solution to produce a red shift, which sensitizes Eu^{3+} luminescence under visible light. The complex $[\text{Eu}(\text{TTA})_3 \cdot \text{DAF}]$ may be a good candidate as luminescent label in time resolved fluorescence microscopy, since visible light is less harmful to biological tissue than ultraviolet.

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