New Europium(III)-TTA Complex Containing 2-Pyrrolidone as Coligand to Application as Luminescent Sensor: PbII and Ethanol in Gasoline

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This work describes the synthesis and application of an europium(III) complex, [Eu(TTA)3(2-pyr)(H2O)], containing 2-thienoyltrifluoroacetonate (TTA) and 2-pyrrolidone (2-pyr) as ligands, obtained as white solid and soluble in ethanol. In solution, the complex showed red emission, characteristic of the EuIII emission in the solid state (λexc = 375 nm and λem = 612 nm). The complex was tested with PbII, CdII, and HgII ions in water. The effect of metal ions was monitored and evaluated by hypersensitive transition 5D0 → 7F2 (612 nm). The results show that PbII suppresses the complex luminescence and presents high sensitivity, according to the values for the Stern-Volmer constant (KSV = 2300 L mol⁻¹), showing good linearity, i.e., determination coefficient (R²) of 0.9913, and low limit of detection (LOD = 6.03 µM). Luminescence quenching increased with the increasing concentration of PbII. These results indicate that the synthesized complex is a potential luminescent sensor for detecting PbII in a simple and fast way, being applicable for routine environmental analysis. When applied as an ethanol sensor in gasoline, the complex hypersensitive transition intensity decreased with the increasing volume of ethanol in gasoline, reaching the values of R² = 0.9815 and LOD = 4.94% v/v.

Keywords: europium(III), 2-pyrrolidone, lanthanides, luminescent sensor

Introduction

Due to their luminescent properties, lanthanide ions compounds arouse the interest of the industry in developing new technologies.1-8 Lanthanides are particularly interesting for the spectroscopic properties of their trivalent ions, resulting from the 4f-4f electron transition.9 Although prohibited by the Laporte rule, the Judd-Ofelt theory postulates that these transitions occur due to the influence of coordination geometrical symmetry, which in most cases has asymmetric structures.10 The coordination number of lanthanide compounds is usually greater than six,11-13 presenting point groups with coordination number equal to seven, such as mono-capped octahedron (C₇₅) or a mono-capped trigonal prism (C₉₄),14 equal to eight, such as square antiprism (D₄d) and bi-capped trigonal prism (C₉₅),15 or even equal to nine, as occurs with tri-capped trigonal prism (C₉₆) or capped square antiprism (C₉₈).16,17

As f orbitals are shielded by the 5s and 5p orbitals, 4f-4f transitions are little influenced by the ligand field, generating narrow-band emissions similar to those of the free metal, which are always located in the same region.18 Lanthanides have a low molar absorption coefficient. As the direct excitation of lanthanide ion is not very efficient for emitting light, the use of ligands is necessary to perform the ligand to metal energy transfer process known as the antenna effect.19-21

From this process, the energy absorbed by the ligand passes from low-energy singlet to the high-energy singlet (S₀ → S₁), possibly involving an intersystem crossing of the high energy singlet to the triple excited state of the ligand...
(S₁ → T₁). Thus, this process may imply energy transfer from S₁ or T₁ to each emitting level of the lanthanide, especially regarding the triplet state for having a relative longer lifetime.²²-²⁵ Among the lanthanides, Eu³⁺ ions are capable of emitting red light, Tb³⁺ green light, Sm³⁺ orange light, and Tm³⁺ blue light in the visible region, whereas Dy³⁺ and the Sm³⁺ emit lights in the near-infrared region.²⁶-³²

In its excited state (D₀ ca. 17267 cm⁻¹), the Eu³⁺ ion have lower energies than most organic ligand triplet states, thus being widely used.³³ Likewise, β-diketones ligands are among the most used to obtain compounds with high light emission efficiency since their structures present chelating capacities and are favored by the π → π* transitions.³⁴-⁴⁰

The literature reported many luminescent lanthanide compounds for various applications. Lucena et al.⁴¹ reported a ZnAl₃₋ₓLnₓO₄ (where Ln = Eu³⁺ or Tb³⁺) enabled the marking of ammunition and clearly identified luminescent gunshot residue (GSR). The identification can be performed visually by direct UV irradiation of any surface containing GSR particles. Destefani et al.⁴² reported the evaluation of acute toxicity of the complex [Eu(PIC)₃(NMK)]ₙ, which has as ligands picric acid (PIC) and N-methyl-caprolactam (NMK), applied as luminescent marker for the visual identification of GSR. Devi et al.⁴³ synthesized a series of smart luminescent Eu³⁺ complexes with five different ligands [Eu(DBM)₃] as fluorescent sensor to Hg²⁺, using functionalized phenanthro-imidazole derivatives as the neutral ligands and dibenzyloxymethane (DBM) as the anionic ligand and red light-emitting diodes (LEDs) were fabricated by integrating a near-ultraviolet (NUV). Wang et al.⁴⁴ reported europium(III) chelated nanoparticles (EuNPs) conjugated to monoclonal antibodies specific to the O-specific polysaccharide fractions of Escherichia coli 0157:H7. The EuNPs were used as fluorescent nanoparticle immunochromatographic strips, which enable rapid and quantitative detection in food samples. Zmojda et al.⁴⁵ reported luminescent studies on germanate glasses doped with Eu³⁺ ions for photonic applications. Zhang et al.⁴⁶ reported a biodegradable film enabling visible light excitation of hexanuclear Eu³⁺ complex [Eu₂(TTA)₃CPT-TPY] (TTA = 2-thienyltrifluoroacetone; CPT-TPY = 2,2',4,4',6,6-hexakis-(4-[(2,2'-6',2''-terpyridinyl)-4'-ylphenoxy]-1,3,5,2-λ⁵,4λ⁶,6λ⁷-triazatrisphosphinine) for various applications. Li et al.⁴⁷ synthesized a luminescent europium metal-organic framework [Eu(Hbptc)(H₂O)]ₙ (Hbptc = biphenyl-2,3,3',5'-tetracarboxylate) for selective sensing of pollutant small organic molecules. Zhou et al.⁴⁸ reported a ZnSe quantum dot based ion imprinting technology for fluorescence detecting Cd²⁺ and Pb²⁺ ions on a 3D rotary paper based microfluidic chip. Sun et al.⁴⁹ reported a lanthanide metal-organic frameworks (Ln-MOFs) {[Ln(L)(ox)₂(H₂O)₂]H₂O}ₙ (Ln = Pr, Nd, Sm and Eu) constructed by 5-hydroxyisophthalic acid (H₁L) and oxalate (ox) through solvothermal methods as luminescent sensor to acetone and Cu²⁺. Chen et al.⁵⁰ synthesized a three lanthanide metal-organic frameworks (LnMOFs) [Ln₂L₃(H₂O)₉] (Ln = Eu³⁺, Tb³⁺ and Gd³⁺) adopting the ligand of cyclobutane-1,1,1,1,1,1,5,5,5-hexafluoro-2,4-pentanedione (HIP) where HIP is 5-hydroxyisophthalate) for detecting picric acid and macrodantin. Zhai et al.⁵¹ reported an europium metal-organic framework (Eu-MOF), [Eu(L)(OAc)(DMA)]ₙ (DMA = N,N-dimethylacetamide) as luminescence probe for detecting Al³⁺, Li et al.⁵² reported lanthanide polyhedral ({[Ln₂(bpda)₃(H₂O)₃]·H₂O}ₙ (Ln = Tb or Dy) that have been synthesized with 2,2'-bipyridine-4,4'-dicarboxylate (H₂bpda) as fluorescence sensor to Hg²⁺. Zheng et al.⁵³ synthesized an europium based metal-organic framework (Eu-MOF), Eu₄₃ (L = 4'-4-carboxyphenyl)-2,2'-6',2''-terpyridine), under hydrothermal conditions, and used it as a solid luminescence sensor for Fe³⁺, Yan et al.⁵⁴ synthesized an oleic acid (OA)-capped β-NaYF₄: 20%Yb, 0.5%Tm upconversion nanoparticles (UCNPs) [OA-UCNPs] for Cu²⁺ sensing. Xu et al.⁵⁵ reported a Eu³⁺ functionalized Zr-based metal-organic framework as fluorescent probe for Cd²⁺ detection in aqueous environment. Lou et al.⁵⁶ reported a “blue-to-red” colorimetric method for determination of Hg²⁺ and Ag⁺ based on stabilization of gold nanoparticles (AuNPs) by redox formed metal coating in the presence of ascorbic acid (AA). Lian et al.⁵⁷ reported a [[Yb(TTTPC)-(H₂O)]₃·3Cl·NO₃·0.5DMA·6H₂O]ₙ synthesized in conventional aqueous solutions with H₂TTTPC ligands (H₂TTTPC = 1,1',1''-(2,4,6-trimethylbenzene-1,3,5-triyl)(methylene)-tris(pyridine-4-carboxylic acid), DMA = N,N-dimethylacetamide) for highly selective and sensitive luminescent sensor for Pb²⁺ over mixed metal ions. Yang et al.⁵⁸ synthesized nanoporous coordination polymers {[La₂(PDA)₃(H₂O)]H₂O}ₙ (PDA = pyridine-2,6-dicarboxylate) and {[Pr₂(PDA)₃(H₂O)]H₂O}ₙ as selective luminescent probes of Pb²⁺, Ca²⁺ and Cd²⁺ ions. Fonseca et al.⁵⁹ reported a terbium(III)-based metal-organic framework as a luminescent sensor to detect the adulteration of ethanol fuel with methanol.

The literature reported the great versatility of the use of lanthanides with 2-thienyltrifluoroacetone (TTA) and others coligands. Xue et al.⁶⁰ reported lanthanide complexes [Yb(fac)₃(H₂O)]₂, Yb(TTA)₃(H₂O)₃, Nd(TTA)₃(H₂O)₃ (fac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione) functionalized nanofibrillated cellulose (Ln-NFC) nanopapers with near-infrared (NIR) luminescence to bring
a brilliant future for UV filters. Teotonio et al.\textsuperscript{62} reported a [Eu(TTA)\textsubscript{3}(NO\textsubscript{3})(TPPO)\textsubscript{2}] (TPPO = triphenylphosphine oxide) (bis-TTA complex) and [Eu(TTA)\textsubscript{3}(TPPO)\textsubscript{2}] (tris-TTA complex) where was evaluated the photoluminescent and triboluminescent behavior. Li et al.\textsuperscript{63} reported a novel organic-inorganic mesoporous luminescent hybrid containing Ln\textsuperscript{III} (Eu\textsuperscript{III}, Tb\textsuperscript{III}) complexes covalently attached to the functionalized ordered mesoporous SBA-15 (Santa Barbara amorphous-15), which were designated as Ln(TTA-SBA-15),bpy and Ln(DBM-SBA-15),bpy (bpy = 2,2'-bipyridine), respectively, obtained by sol-gel process. Li et al.\textsuperscript{64} synthesized nanocomplexes NaGdF\textsubscript{4}:Yb,Er@SiO\textsubscript{2}@Eu(TTA)\textsubscript{3} Phen (2-thenoyltrifluoroacetone, TTA), (1,10-phenanthroline monohydrate, Phen) showing the ligand-sensitized Eu\textsuperscript{III} complexes attached to the outer surface of SiO\textsubscript{2}. The green (542 nm) and red (610 nm) light were excited by NIR and UV illumination, respectively. In this context, this work uses a Eu\textsuperscript{III} compound with 2-thenoyltrifluoroacetonate (TTA) and 2-pyrrolidone (2-pyr) ligands as a luminescent sensor to identify Pb\textsuperscript{II} in water and ethanol in gasoline.

Experimental

Materials

Europium(III) oxide (Eu\textsubscript{2}O\textsubscript{3}) and the ligands 2-theoyltrifluoroacetonate (TTA = C\textsubscript{8}H\textsubscript{4}F\textsubscript{3}O\textsubscript{2}S) and 2-pyrrolidone (2-pyr = C\textsubscript{4}H\textsubscript{7}NO) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Eu\textsubscript{2}O\textsubscript{3} was converted to its respective chloride using concentrated hydrochloric acid.\textsuperscript{39} Characterization of complex

The europium(III) compound with TTA, [Eu(TTA)\textsubscript{3}(H\textsubscript{2}O)\textsubscript{2}], was synthesized according to an adapted literature procedure.\textsuperscript{65} The percentage of europium in the complex was determined by complexometric titration with 0.01 mol L\textsuperscript{-1} standard EDTA (ethylenediamine tetraacetic acid) solution using ortho-xyleneol orange as indicator. Carbon, hydrogen, and nitrogen (CHN) elemental analysis was performed using the PerkinElmer 2400 series II Elemental Analysis Instrument (Waltham, Massachusetts, USA). Infrared spectra were obtained from the spectral region of 4000 to 400 cm\textsuperscript{-1} using a KBr tablet in transmittance mode and a PerkinElmer FTIR GX spectrometer (Waltham, Massachusetts, USA) at room temperature. Thermogravimetry analysis (TGA) was performed using a TG 60-H Shimadzu thermobalance (Kyoto, Japan) at a flow rate of 50 mL min\textsuperscript{-1} and a heating rate of 10 °C min\textsuperscript{-1}, under the temperature range of 25 to 800 °C and ambient atmosphere. Solid-state Ultraviolet-Visible (UV-Vis) spectroscopy analysis was performed in the 200-800 nm region using a PerkinElmer spectrometer (Waltham, Massachusetts, USA). Photoluminescence spectra (excitation and emission) were obtained using a FLUOROLOG3 ISA/JobinYvon Horiba (Edison, New Jersey, USA) spectrofluorometer equipped with a Hamamatsu R928P photomultiplier, the SPEX 1934 D phosphorimeter, a 450 W Xe lamp, and a pulsed 150 W Xe-Hg lamp.

Synthesis of the [Eu(TTA)\textsubscript{3}(2-pyr)(H\textsubscript{2}O)] complex

[Eu(TTA)\textsubscript{3}(2-pyr)(H\textsubscript{2}O)] was synthesized according to an adapted literature procedure.\textsuperscript{40} First, 2-pyr (0.20 g, 2.35 mmol) was added dropwise to a methanol solution (30 mL) of [Eu(TTA)\textsubscript{3}(H\textsubscript{2}O)\textsubscript{2}] (1.20 g, 1.40 mmol) and left stirring overnight. The resulting white solid was washed with water to remove the excess 2-pyr ligand, dried, and stored at room temperature. The scheme represents the synthesis of the complex (Figure 1).

Selectivity study of metals

Ions from heavy metals are major polluters, posing significant risks both to human health and the environment. Ions such as Ni\textsuperscript{II}, Hg\textsuperscript{II}, Zn\textsuperscript{II}, Cd\textsuperscript{II}, Pb\textsuperscript{II}, Cu\textsuperscript{II}, and Cr\textsuperscript{IV} are not easily degraded when compared to conventional organic pollutants. Most of them are highly toxic and cancerous, raising concern due to their cumulative capacity in living organisms.\textsuperscript{66,67} Considering that, we investigated the effect of metal ions on the luminescence of the [Eu(TTA)\textsubscript{3}(2-pyr)(H\textsubscript{2}O)] complex using three heavy metals, namely Pb\textsuperscript{II}, Cd\textsuperscript{II}, and Hg\textsuperscript{II}. For each metal, aqueous solutions were prepared from their respective nitrates in a 2.41 × 10\textsuperscript{-3} mol L\textsuperscript{-1} concentration. An ethanolic solution of the complex was also prepared in a 6.50 × 10\textsuperscript{-5} mol L\textsuperscript{-1} concentration. Then, 0.500 mL of each metal aqueous solution was individually mixed with 2.500 mL of the solution containing [Eu(TTA)\textsubscript{3}(2-pyr)(H\textsubscript{2}O)]. The mixtures were stirred and analyzed in the spectrofluorometer.

Detection of ethanol content in gasoline

Type ‘A’ gasoline (without additives) and ethanolic solution of the complex in the concentration of 6.50 × 10\textsuperscript{-5} mol L\textsuperscript{-1} were used in the experiment. Gasoline was mixed with ethanol in proportions ranging from 0-100% (v/v), stirred, and analyzed on the spectrofluorometer. This experiment sought to evaluate the behavior of the ethanol/complex when mixed with gasoline to verify whether
it would be applicable as a luminescent sensor for identifying gasoline adulteration by photoluminescence.

**Results and Discussion**

**Characterization of [Eu(TTA)$_3$(2-pyr)(H$_2$O)]**

The results obtained from carbon, hydrogen, and nitrogen (CHN) elemental analysis and complexometric EDTA titration suggest the formation of the stoichiometric compound [Eu(TTA)$_3$(2-pyr)(H$_2$O)].

C$_{28}$H$_{21}$EuF$_9$NO$_8$S$_3$ calcd. (%): Eu$_{III}$ 16.49, C 35.98, H 2.24, N 1.45; measured: Eu$_{III}$ 16.54, C 36.61, H 2.30, N 1.52; FTIR $\nu$ / cm$^{-1}$ (Figure S1, Supplementary Information (SI) section) $\nu_{as}$C=O (1536(s)), $\nu_{s}$C=O (1623(s)), $\nu$C−N (1496(s)); TTA free: $\nu_{s}$C=O (1654(s)) and 2-pyr free: $\nu_{s}$C=O (1662(s)), $\nu$C−N (1467(s)). Molar conductance in acetonitrile: 4.41 cm$^2$ Ω$^{-1}$ mol$^{-1}$. Yield 85%. Based on the molar conductance in acetonitrile, we may rightfully infer that the compound is nonelectrolyte, thus indicating that the three TTA are linked to the first coordination sphere of the complex, similarly to the [Eu(TTA)$_3$(NMC)(H$_2$O))] (NMC = N-methyl-ε-caprolactam) studied by Borges et al.$^{39,40}$

The Fourier transformed infrared spectroscopy (FTIR) (Figure S1) showed that the band associated with the asymmetrical stretch, $\nu_{as}$C−O (1536 cm$^{-1}$), absent in the free ligand spectra, corroborating with ligands coordination. Both TTA and 2-pyr present $\nu$C=O, but they cannot be distinguished because they occur in the same region. The presence of the stretch vibration $\nu$C−N and its wavenumbers shift to larger values concerning free 2-pyrolidone ligand suggests that this ligand is coordinated. Thus, the $\nu$C−O displacement in TTA and 2-pyr suggest that these ligands are coordinated by carbonyl oxygen. Also, the spectrum of the complex presented the characteristic water $\nu$O−H vibrational mode in the 3000-3500 cm$^{-1}$ region, suggesting the presence of water.$^{69}$

The thermogravimetry analysis (Figure S2, SI section) presented three main events of mass loss. From 25 to 76 °C, the compound is very stable. The first mass loss occurred from 76 to 120 °C, as an endothermal event. This first stage was related to the water output of coordination (experimental: 1.98%, calculated: 1.96%), corroborating the suggested stoichiometry. The following two steps are exothermic and occurred with peak temperatures at 289 and 456 °C, related to the thermal degradation of organic ligands, 2-tenoitrifluoracetone and 2-pyrolidone. The second weight loss (58.99%) occurred from 120 to 395 °C, which was attributed to the decomposition of two TTA and 2-pyr molecules. The third stage with about 20.91% mass loss started at 395 °C, finished at 540 °C, the mass loss percentage was near the loss of one TTA molecule from the complex. Complete degradation of the Eu$_{III}$ complex
occurs at 540 ºC, with a total mass loss of 81.88% (residue mass: 18.12%). The total mass loss calculated was 80.99%, considering that the residue is Eu₂O₃ (calculated: 19.01%).

The absorption spectrum in the ultraviolet-visible (UV-Vis) region (Figure S3, SI section) showed bands with maximum absorption at 268 nm, attributable to π → π* intraligand electronic transitions, and an intense band in the 330 nm region, attributable to n → π* transitions. The excitation spectrum (Figure 2a) showed an intense broad band in the 250-450 nm assigned to S₀ → S₁ and bands assigned to the 4f-4f transitions overlapped by the ligand band. The 4f-4f transitions are originated from the 7 F₀ ground state to the excited levels 5 L₉ (360 nm), 5 H₄ (379 nm), 5 L₇ (385 nm), 5 L₅ (393 nm) and 5 D₃ (415 nm) excited states and remain approximately invariable in each Eu³⁺ complex. So, the 4f-4f transitions overlapped by the ligand band can be also an efficient channel for the photoluminescence for the compounds. And it is possible to identify the bands 7 F₀ → 5 D₃ (451 nm), 7 F₀ → 5 D₂ (466 nm), 7 F₀ → 5 D₁ (526 nm), 7 F₀ → 5 D₀ (580 nm).

At room temperature, the emission spectrum (Figure 2b) of the compound in solid-state showed the regions of the intraconfigurational transitions, 5 D₀ → 7 F₄ with maximum emission at 612 nm, 5 D₀ → 7 F₂ followed by 591 nm, 5 D₀ → 7 F₃, 652 nm, 5 D₀ → 7 F₅, and 700 nm, 5 D₀ → 7 F₆. The presence of the 5 D₀ → 7 F₂ transition, a hypersensitive electric dipole transition whose intensity is higher than that of the 5 D₀ → 7 F₁ transition (allowed by a magnetic dipole transition), suggests that the compound does not have an inversion center and that Eu³⁺ is in chemical environment of low symmetry. Experimental intensity parameters, Ωₖ, for the [Eu(TTA)₃ (2-pyr)(H₂O)] complex were determined from the emission spectra using the following equation 1.

\[
\Omega_k = \frac{4e^2\omega^3 A_{0k}}{3\hbar c^3 \chi F_j \| U^{(k)} \| \|^2 D_j^*}
\]

where e is the electron elementary charge, ω is the angular frequency, c is the speed of light and χ is the Lorentz local field correction term, given by χ = n(n² + 2)²/9 and \( ^7 F_j \| U^{(k)} \| \|^2 D_j^* \) is a squared reduced matrix element with value of 0.0032 for the \( ^{3}D₀ \rightarrow ^{3}F₂ \) transition and 0.0023 for the \( ^{3}D₀ \rightarrow ^{3}F₁ \) transition. The refractive index (n) has been assumed equal to 1.5.

In this work, the \( ^{3}D₀ \rightarrow ^{3}F₆ \) transition was not observed experimentally, consequently, the experimental Ωₖ parameter could not be estimated. The spontaneous emission coefficient, A₀₀ = 0.31 × 10⁻¹⁰(n)²[(ν₀₁)²], leading to an estimated value around 50 s⁻¹ for the refractive index (n) defined above. In equation 2, the Ω₀₀ term, where \( J = 2 \) and 4, represents the spontaneous emission coefficients of the \( ^{3}D₀ \rightarrow ^{3}F₂ \) and \( ^{3}D₀ \rightarrow ^{3}F₁ \) transitions, which can be calculated from \( ^{3}D₀ \rightarrow ^{3}F₁ \) reference transition (magnetic dipole mechanism), therefore this transition is practically insensitive to chemical environment changing, equation 2.

\[
A_{0j} = \frac{\sigma_{0j} S_{0j} A_{01}}{S_{0j} \sigma_{0j}} A_{01}
\]

where S₀₁ and S₀ₖ are the areas under the curves of the \( ^{3}D₀ \rightarrow ^{3}F₁ \) and \( ^{3}D₀ \rightarrow ^{3}F_j \) transitions, with S₀₁ and σ₀₁ being their energy barycenters, respectively.

The lifetimes (τ) of the [Eu(TTA)₃ (2-pyr)(H₂O)] complex were obtained from the photoluminescence decay curves (Figure S4, SI section) using the equation I(t) = I(0) exp(-t/τ) and a curve fitting program, where I(t) is the intensity at time t, t is time and I(0) is the intensity in the initial time equal to zero (t = 0). The quantum efficiency of the 5 D₀ emitting level (θ) for the Eu³⁺ complex are presented in Table 1 and were calculated from the ratio A_rad / A_total, where A_rad and A_total are radiative and total rates assigned to the decay processes of the 5 D₀ emitting level, respectively. In this case, the A_rad values were obtained by summing the radiative spontaneous coefficients due to the \( ^{1}D₀ \rightarrow ^{3}F₁ \) transitions, while A_total were determined from the lifetime values of the \( ^{3}D₀ \) emitting level (τ) by considering the reciprocal relation between these properties (A_total = 1/τ).

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Figure 2. (a) Excitation, with \( \lambda_{exc} = 612 \) nm, and (b) emission, with \( \lambda_{exc} = 375 \) nm, spectra of the complex in solid-state, and (c) emission, with \( \lambda_{exc} = 375 \) nm, spectra of the complex (6.50 × 10⁻⁵ mol L⁻¹) in ethanolic solution.
The Table 1 shows the experimental values, obtained from the emission spectra, for the quantum efficiency (\(\eta\)), radiative (\(A_{\text{rad}}\)) and nonradiative (\(A_{\text{nrad}}\)) rates of spontaneous emission, lifetimes (\(\tau\)) and the Judd-Ofelt intensity parameters (\(\Omega_2\) and \(\Omega_4\)), for the Eu\(^{3+}\) ion in the complex.

The experimental data reveal that the substitution of the water molecule by a lactam increases the quantum efficiency of the europium complexes as noted by Borges et al.\(^\text{40}\). The value of \(\eta\) determined for this complex (\(\eta = 44\%\)) is not larger owing to the presence of one water molecule in the first coordinated sphere of the Eu\(^{3+}\) ion. This luminescence quenching is an effect of the vibronic coupling of the higher-energy OH oscillators and \(^5D_0\) emitting level causing a non-radiative dissipation of the energy. When compared with another complex reported in the literature [Eu(TTA)\(_3\)(NMC)(H\(_2\)O)], changes occur in the radiative coefficient (\(A_{\text{rad}}\)), the values of \(\eta\) are mainly associated to changes in the non-radiative rates (\(A_{\text{nrad}}\)). The experimental intensity parameters \(\Omega_2\) and \(\Omega_4\) of [Eu(TTA)\(_3\)(2-pyr)(H\(_2\)O)] present different values from those of [Eu(TTA)\(_3\)(NMC)(H\(_2\)O)] synthesized by Borges et al.,\(^\text{40}\) indicating that Eu\(^{3+}\) ions are in different chemical environments (Table 1). According to the literature, the \(\Omega_2\) value is the most influenced by small angular changes in the local geometry. This effect, together with changes in the ligating atom polarizability (\(\alpha\)), has been used to rationalize the hypersensitivity of certain 4f-4f transitions to changes in the chemical environment.\(^\text{40}\)

Selectivity study of metals

The emission spectrum of the mixture containing 2.50 mL of the complex in ethanolic solution and 0.500 mL of pure water (Figure 2c) showed the intracofigurational transitions \(^5D_0 \rightarrow ^7F_1\), \(^5D_0 \rightarrow ^7F_2\), \(^5D_0 \rightarrow ^7F_3\), and \(^5D_0 \rightarrow ^7F_4\). We used the hypersensitive transition \(^5D_0 \rightarrow ^7F_2\) (612 nm) as a reference to monitor possible metal-induced disturbances in the luminescence of the complex. As for the emission spectrum of the complex (Figure 3a), we verified that Pb\(^{II}\) decreased intensity by 12% at the reference transition (Figure 3b). Thus, the metal-induced luminescence quenching followed the order: Pb\(^{II}\) > Cd\(^{II}\) > Hg\(^{II}\). The effect of Pb\(^{II}\) in the presence of other metals was evaluated by mixtures of 0.500 mL of each metal at the concentration of \(2.41 \times 10^{-3}\) mol L\(^{-1}\), it was kept the same final volumes and equimolar concentrations of the ions to avoid the effect of dilution on luminescence.

Figure 3a shows that the luminescence intensity of the [Eu(TTA)\(_3\)(2-pyr)(H\(_2\)O)] solution with Pb\(^{II}\), Cd\(^{II}\) and Hg\(^{II}\) in ethanol solution with Pb\(^{II}\), Cd\(^{II}\) and Hg\(^{II}\) in aqueous solutions.
the increase in PbII concentration (Figure 4). The greater quenching caused by PbII may be explained by the energy absorption competition at the same wavelength of the ligand or by the complex-PbII interaction. The UV-Vis absorption spectrum of PbII in aqueous solution (Figure S5, SI section) showed an overlap with the complex excitation spectrum (Figure 2a), evincing the absorption competition between PbII and the europium(III) complex. Moreover, PbII ion electronic state has an empty p orbital, making it prone to become an electron-acceptor and thus weakening fluorescence.\(^{75,76}\)

The ratio \(I_0/I\) versus PbII concentration (Figure 4b) provides a coefficient of determination, \(R^2 = 0.9913\), and the equation may be adjusted as \(I_0/I - 1 = 2.3 \times 10^3 [PbII] - 0.7074\). With that, the ratio approaches the Stern-Volmer equation: \(I_0/I - 1 = K_{SV}[M]\), where \(I_0\) and \(I\) are the \(\overset{0}{D} \rightarrow \overset{2}{F}\) band emission intensities before and after metal addition, respectively; \([M]\) is the molar concentration of the metal ion; and \(K_{SV}\) is a Stern-Volmer constant that indicates quenching intensity.\(^{77}\) Based on the approximation, the \(K_{SV}\) value for \([Eu(TTA)\_3(2-pyr)(H_2O)]\) in the presence of PbII was equal to 2300 \(L \cdot mol^{-1}\). Limit of detection (LOD) was calculated using the equation LOD = \(3\sqrt{\sigma}/k\), where \(\sigma\) is the blank measurement standard deviation and \(k\) is the slope \(I_0/I\) vs. [PbII], reaching the value of 6.03 \(\mu M\). In a study conducted by Lin et al.,\(^{79}\) the authors evaluated an europium(III) coordination polymer as a sensor for PbII, finding \(K_{SV}\) to be equal to 33014 \(L \cdot mol^{-1}\) and LOD to 90.78 \(\mu M\) in water. Lin et al.\(^{79}\) synthesized europium(III) coordination polymer Eu-CPs, \([\{Eu_2(PBA)\_3(H_2O)\_3\}]\cdot DMF\cdot 3H_2O\), this compound exhibited 3D framework, what increases the weak bonding interaction between nitrogen atoms and PbII. This interaction perturbs the electronic structure of the ligand and reduce the energy transfer efficiency from the ligand to EuIII centers. In the present work \([Eu(TTA)\_3(2-pyr)(H_2O)]\) compound did not exhibit 3D framework.

Sensor to detect ethanol in gasoline

To evaluate the effect of the gasoline (ethanol mixture in the 0-100% (v/v) range) on the luminescence of the complex, we monitored the \(\overset{0}{D} \rightarrow \overset{2}{F}\) transition (at 612 nm) in \([Eu(TTA)\_3(2-pyr)(H_2O)]\) in aqueous solution with PbII at different concentrations (b) versus \(I_0/I\), and (c) luminescence of the mixtures with PbII at different concentrations, illuminated with a UV lamp at 365 nm at room temperature.

Figure 4. (a) Emission spectra (\(\lambda_{ex} = 375 \text{ nm}\)) monitoring the intensity of the \(\overset{0}{D} \rightarrow \overset{2}{F}\) transition (at 612 nm) of \([Eu(TTA)\_3(2-pyr)(H_2O)]\) in aqueous solution with PbII at different concentrations (b) versus \(I_0/I\), and (c) luminescence of the mixtures with PbII at different concentrations, illuminated with a UV lamp at 365 nm at room temperature.
blank measurement standard deviation and $k$ is the slope $(I_0/I)$ vs. ethanol (% v/v). Our results indicate that using the complex as a luminescent marker to identify ethanol in gasoline is a promising alternative for fuel quality control.

**Conclusions**

Our study verified that the use of $[^{3}E_{u}(TTA)_{3}(2-pyr)(H_{2}O)]$ complex as luminescent sensor is a promising alternative for detecting Pb$^{2+}$. We evaluated Pb$^{2+}$ concentration based on the luminescence quenching of the complex, finding a great sensitivity based on the values found for $K_{SV} = 2300$ L mol$^{-1}$, $R^2 = 0.9913$, and LOD = 6.03 µM. Our results reveal that the complex could be used for identifying and quantifying Pb$^{2+}$. We also tested the use of the complex as a luminescent marker to identify gasoline adulteration with the addition of ethanol, reaching the values of $R^2 = 0.9815$ and LOD = 4.94% v/v. These values indicate that the complex is sensitive and efficient, being promising for fuel quality control.

**Supplementary Information**

Supplementary data (spectral data, FTIR and UV-Vis, TG/DTG, and DTA) are available free of charge at http://jbcs.sbq.org.br as a PDF file.

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**Author Contributions**

Clebson de J. Macrino was responsible for the conceptualization, data curation, formal analysis, investigation, methodology, visualization, writing the original draft, review, and editing; Alex dos S. Borges for the conceptualization, data curation, formal analysis, investigation, methodology, visualization, writing the original draft, and review; Álvaro C. Neto for the conceptualization, data curation, formal analysis, investigation, methodology, visualization, writing the original draft, and review; Valdemar Lacerda Jr. and Wanderson Romão were responsible for the conceptualization, funding acquisition, investigation, methodology, project administration, resources, supervision; visualization, writing the original draft, review, and editing.

**References**

1. Rostra, J. G.; Ferrer, F. J.; Espinós, J. P.; Elipe, A. R. G.; Yubero, F.; ACS Appl. Mater. Interfaces 2017, 9, 16313.
2. Du, P.; Bharat, L. K.; Yu, J. S.; J. Alloys Compd. 2015, 633, 37.
3. Ling, Q.; Song, Y.; Ding, S. J.; Zhu, C.; Chan, D. S. H.; Kwong, D. L.; Kang, E. T.; Neoh, K. G.; Adv. Mater. 2005, 17, 455.
4. Reichardt, C.; Schneider, K. R. A.; Saimuddin, T.; Wächtler, M.; McFarland, S. A.; Dietzke, B.; J. Phys. Chem. A 2017, 121, 5635.
5. Muller, G.; Dalton Trans. 2009, 44, 9692.
6. Jia, J.; Zhang, Y.; Zheng, M.; Shan, C.; Yan, H.; Wu, W.; Gao, X.; Cheng, B.; Liu, W.; Tang, Y.; Inorg. Chem. 2018, 57, 300.
7. Kumar, P.; Kanika; Singh, S.; Lahon, R.; Gundimeda, A.; Gupta, G.; Gupta, B. K.; J. Lumin. 2018, 196, 207.
8. Kuncewicz, J.; Dańbrowski, J. M.; Kyziol, A.; Brindell, M.; Łabuz, P.; Mazuryk, O.; Macyk, W.; Stochel, G.; Coord. Chem. Rev. 2019, 398, 113012.
9. Kariaka, N. S.; Smola, S. S.; Rusakova, N. V.; Dyakov, V. V.; Shishkina, S. V.; Silva, T. Y.; Trush, V. A.; Amirkhanov, V. M.; J. Lumin. 2020, 223, 117187.
10. Rosa, P. P. F.; Kitagawa, Y.; Hasegawa, Y.; Coord. Chem. Rev. 2020, 406, 213153.
11. Cotton, S. A.; Raithby, P. R.; Coord. Chem. Rev. 2017, 340, 220.
12. You, L. X.; Hao, J. H.; Qi, D.; Xie, S. Y.; Wang, S. J.; Xiong, G.; Dragutan, I.; Dragutan, V.; Ding, F.; Sun, Y. G.; Inorg. Chim. Acta 2019, 497, 119075.
13. Karraker, D. G.; J. Chem. Educ. 1970, 47, 424.
14. Yanagisawa, K.; Nakanishi, T.; Kitagawa, Y.; Seki, T.; Akama, T.; Kobayashi, M.; Taketsugu, T.; Ito, H.; Fushimi, K.; Hasegawa, Y.; Eur. J. Inorg. Chem. 2015, 28, 4769.
15. Burdett, J. K.; Hoffmann, R.; Fay, R. C.; Inorg. Chem. 1978, 17, 2553.
16. Kuramochi, Y.; Nakagawa, T.; Yokoo, T.; Yuasa, J.; Kawai, T.; Hasegawa, Y.; Dalton Trans. 2012, 41, 6634.
17. Bińzli, J. C. G.; Chauvin, A. S.; Vandevyver, C. D. B.; Bo, S.; Comby, S.; Ann. N. Y. Acad. Sci. 2008, 1130, 97.
18. Heffern, M. C.; Matoszuk, L. M.; Meade, T. J.; Chem. Rev. 2014, 114, 4496.
19. Braun, F.; Comba, P.; Grimm, L.; Herten, D. P.; Pokrant, B.; Wadepohl, H.; Inorg. Chim. Acta 2018, 484, 464.
20. Zhang, J. W.; Wang, C. R.; Liu, W. H.; Xu, S.; Liu, B. Q.; Inorg. Chim. Acta 2020, 508, 119648.
21. Bai, C.; Fu, X. Y.; Hu, H. M.; He, S.; Wang, X.; Xue, G. L.; Inorg. Chim. Acta 2020, 506, 119550.
22. Chen, W. T.; J. Solid State Chem. 2019, 284, 121160.
23. Ning, Y.; Zhu, M.; Zhang, J. L.; Coord. Chem. Rev. 2019, 399, 213028.
24. Abdelhamid, H. N.; Wilk-Kozubek, M.; El-Zohry, A. M.; Gómez, A. B.; Valiente, A.; Martín-Matute, B.; Mudring, A. V.; Zou, X.; Microporous Mesoporous Mater. 2019, 279, 400.
25. Jia, J. H.; Li, Q. W.; Chen, Y. C.; Liu, J. L.; Tong, M. L.; Coord. Chem. Rev. 2019, 378, 365.
26. Mauouche, R.; Belaid, S.; Benmerad, B.; Bouacida, S.; Freslon, S.; Daiguebonne, C.; Suffren, Y.; Calvez, G.; Bernot, K.; Roiland, C.; Pollèis, L.; Guillou, O.; Inorg. Chim. Acta 2020, 501, 119309.
27. Sun, Y.; Li, Q.; Wei, S.; Zhao, R.; Han, J.; Ping, G.; J. Lumin. 2020, 225, 117241.
28. Stan, C. S.; Rosca, I.; Sutiman, D.; Secula, M. S.; J. Rare Earths 2012, 30, 401.
29. Zhao, Y.; Wang, S.; Han, Y.; Zhang, J.; Liu, C.; Hu, X.; Zhang, Z.; Wang, L.; J. Lumin. 2020, 223, 117253.
30. Yang, D.; Liao, L.; Zhang, Y.; Guo, Q.; Mei, L.; Liu, H.; J. Lumin. 2020, 224, 117285.
31. Baklanova, Y. V.; Maksimova, L. G.; Lipina, O. A.; Tyutyunnik, A. P.; Zubkov, V. G.; J. Lumin. 2020, 224, 117315.
32. Herrmann, A.; Friedrich, D.; Zscheckel, T.; Rüssel, C.; J. Lumin. 2019, 214, 116550.
33. Kaczmarek, M.; J. Lumin. 2020, 222, 117174.
34. Binnemans, K.; Chem. Rev. 2009, 109, 4283.
35. Sizov, V. S.; Komissar, D. A.; Metlina, D. A.; Aminev, D. F.; Ambrozевич, S. A.; Nefedov, S. E.; Varaksina, E. A.; Metlin, M. T.; Mislavskii, V. V.; Taydakova, I. V.; Spectrochim. Acta, Part A 2020, 225, 117503.
36. Duan, Y. Y.; Wu, D. F.; Chen, H. H.; Wang, Y. J.; Li, L.; Gao, H. C.; Cu, J. Z.; Inorg. Chim. Acta 2020, 499, 119203.
37. Berezhnytska, O. S.; Savchenko, I. O.; Ivakh, N. B.; Rogotovs, O. O.; Trunova, O. K.; Rusakova, N. V.; J. Mol. Struct. 2020, 1201, 127160.
38. Bhat, S. A.; Ifitikhar, K.; Dyes Pigm. 2020, 179, 108383.
39. Borges, A. S.; Fulgêncio, F.; Silva, J. G.; Santos, T. A. R.; Diniz, R.; Windmüller, D.; Magalhães, W. F.; Araujo, M. H.; J. Lumin. 2019, 205, 72.
40. Borges, A. S.; Caliman, E. V.; Dutra, J. D. L.; Silva, J. G.; Araujo, M. H.; J. Lumin. 2016, 170, 654.
41. Lucena, M. A. M.; Sá, G. F.; Rodrigues, M. O.; Alves, S.; Talhavini, M.; Weber, I. T.; Anal. Methods 2013, 5, 705.
42. Destefani, C. A.; Motta, L. C.; Costa, R. A.; Macrino, C. J.; Bassane, J. F. P.; Filho, J. F. A.; Silva, E. M.; Greco, S. J.; Carneiro, M. T. W. D.; Endringer, D. C.; Romão, W.; Microchem. J. 2016, 124, 195.
43. Devi, R.; Rajendran, M.; Singh, K.; Pala, R.; Vaidyanathan, S.; J. Mater. Chem. C 2021, 9, 6618.
44. Wang, Q.; Long, M. Y.; Lv, C. Y.; Xin, S. P.; Han, X. G.; Jiang, W.; Food Control 2020, 109, 106894.
45. Zmojda, J.; Kochanowicz, M.; Miluski, P.; Golonko, P.; Baranowska, A.; Ragi, T.; Dorosz, J.; Kuwik, M.; Pisarski, W.; Pisarska, J.; Szal, R.; Mach, G.; Starzyk, B.; Lesnian, M.; Sitarz, M.; Dorosz, D.; Materials 2020, 13, 2817.
46. Zhang, D.; Zhang, Y.; Wang, Z.; Zheng, Y.; Zheng, X.; Gao, L.; Wang, C.; Yang, C.; Tang, H.; Li, Y.; J. Lumin. 2021, 229, 117706.
47. Li, R. F.; Zhang, T.; Liu, X. F.; Feng, X.; Inorg. Chem. Commun. 2016, 73, 170.
48. Zhou, J.; Li, B.; Qi, A.; Shi, Y.; Qi, J.; Xu, H.; Chen, L.; Sens. Actuators, B 2019, 305, 127462.
49. Sun, Z.; Li, H.; Sun, G.; Guo, J.; Ma, Y.; Li, L.; *Inorg. Chim. Acta* 2018, *469*, 51.
50. Chen, Z.; Yu, X.; Li, X.; Ye, Q.; Zhou, K.; Cai, Y.; Huang, L.; Li, Y.; Zeng, C.; *Inorg. Chem. Commun*. 2020, *112*, 107744.
51. Zhang, F.; Ma, J.; Huang, S.; Li, Y.; *Spectrochim. Acta, Part A* 2020, *228*, 117816.
52. Zhai, B.; Li, Z.Y.; Wub, Z.L.; Cui, J.Z.; *Inorg. Chem. Commun*. 2016, *71*, 23.
53. Li, R.; Zhang, Y.; Liu, X.; Chang, X.; Feng, X.; *Inorg. Chim. Acta* 2020, *502*, 119370.
54. Zheng, M.; Tan, H.; Xie, Z.; Zhang, L.; Jing, X.; Sun, Z.; *ACS Appl. Mater. Interfaces* 2013, *5*, 1078.
55. Yan, Q.; Chen, Z. H.; Xue, S. F.; Han, X. Y.; Lin, Z. Y.; Zhang, S.; Shi, G.; Zhang, M.; *Sens. Actuators, B* 2020, *268*, 108.
56. Xu, X. Y.; Yan, B.; *Sens. Actuators, B* 2016, *222*, 347.
57. Lou, T.; Chen, Z.; Wang, Y.; Chen, L.; *ACS Appl. Mater. Interfaces* 2011, *3*, 1568.
58. Lian, C.; Chen, Y.; Li, S.; Hao, M.; Gao, F.; Yang, L.; *J. Alloys Compd*. 2017, *702*, 303.
59. Yang, L.; Song, S.; Zhang, H.; Zhang, W.; Bu, Z.; Ren, T.; *Synth. Met.* 2011, *161*, 2230.
60. Fonseca, R. R.; Gaspar, R. D. L.; Raimundo Jr., I. M.; Laz, P. P.; *Rare Earths* 2019, *37*, 225.
61. Xue, B.; Zhang, Z.; Sund, Y.; Wang, J.; Jiang, H.; Du, M.; Chi, C.; Li, X.; *Carbohydr. Polym.* 2018, *186*, 176.
62. Teotonio, E. E. S.; Fett, G. M.; Brito, H. F.; Sá, W. M. F. G. F.; Felinto, M. C. F. C.; Santos, R. H. A.; *J. Lumin.* 2008, *128*, 190.
63. Li, Y.; Yan, B.; Li, Y.; *Microporous Mesoporous Mater.* 2010, *131*, 82.
64. Li, Y.; Jiao, J.; Yan, P.; Liu, L.; Wang, J.; Wang, Y.; Huang, L.; Liu, J.; Belfiore, L. A.; *Scr. Mater.* 2018, *152*, 1.
65. Charles, R. G.; Ohlmann, R. C.; *J. Inorg. Nucl. Chem.* 1965, *27*, 255.
66. Zou, Y.; Wang, X.; Khan, A.; Wang, P.; Liu, Y.; Alsaedi, A.; Hayat, T.; Wang, X.; *Environ. Sci. Technol.* 2016, *50*, 7290.
67. Wu, D.; Chen, L.; Lee, W.; Ko, G.; Yin, J.; Yoon, J.; *Coord. Chem. Rev.* 2018, *354*, 74.
68. Lyle, S. J.; Rahaman, M. M.; *Talanta* 1963, *10*, 1177.
69. Ugale, A.; Kalyani, N. T.; Dhoble, S. J.; *Mater. Sci. Energy Technol.* 2020, *3*, 51.
70. Oliveira, T. C.; Santos, H. P.; Lahoud, M. G.; Franco, D. F.; Freire, R. O.; Dutra, J. D. L.; Cuin, A.; Lima, J. F.; Marques, F. L.; *J. Lumin.* 2017, *181*, 196.
71. Chitnis, D.; Kalyani, N. T.; Dhoble, S. J.; *Optik* 2017, *130*, 237.
72. Marques, L. F.; Santos, H. P.; Oliveira, K. A.; Botezine, N. P.; Freitas, M. C. R.; Freire, R. O.; Dutra, J. D. L.; Martins, J. S.; Legnani, C.; Quirino, W. G.; Machado, F. C.; *Inorg. Chim. Acta* 2016, *458*, 28.
73. Donegá, C. D.; Alves Jr., S.; Sá, G. F.; *J. Alloys Compd.* 1997, *250*, 422.
74. Marques, L. F.; Cuin, A.; Carvalho, G. S. G.; Santos, M. V.; Ribeiro, S. J. L.; Machado, F. C.; *Inorg. Chim. Acta* 2016, *441*, 67.
75. Yan, Y. T.; Zhang, W. Y.; Zhang, F.; Cao, F.; Yang, R. F.; Wang, Y. Y.; Hou, L.; *Dalton Trans.* 2018, *47*, 1682.
76. Song, X. Z.; Wang, Y. X.; Yan, J. W.; Chen, X.; Meng, Y. L.; Tan, Z.; *ChemistrySelect* 2018, *3*, 9564.
77. Zeng, X.; Zhang, Y.; Zhang, J.; Hu, H.; Wu, X.; Long, Z.; Hou, X.; *Microchem. J.* 2017, *134*, 140.
78. Zhang, M. H.; Zhang, L. L.; Xiao, Z. Y.; Zhang, Q. H.; Wang, R. M.; Dai, F. N.; Sun, D. F.; *Sci. Rep.* 2016, *6*, 20672.
79. Lin, J.; Cheng, Q.; Zhou, J.; Lin, X.; Reddy, R. C. K.; Yang, T.; Zhang, G.; *J. Solid State Chem.* 2019, *270*, 339.
80. Romanel, S. A.; Cunha, D. A.; Castro, E. V. R.; Barbosa, L. L.; *Microchem. J.* 2018, *140*, 31.