Article

Rare Earth-Indomethacinate Complexes with Heterocyclic Ligands: Synthesis and Photoluminescence Properties

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In this work, synthesis, characterization and photophysical properties of trivalent rare earth complexes with a nonsteroidal anti-inflammatory drug [the indomethacinate (indo), presenting formulas $RE(indo)_3(H_2O)_x$ (x = 3, for Eu^{3+} and Gd^{3+}, and x = 4 for Tb^{3+}), $RE(indo)_3(bipy)$ and $RE(indo)_3(phen)$ (bipy: 2,2'-bipyridine, and phen: 1,10-phenanthroline)] were investigated. Based on photoluminescent results, the intramolecular energy transfer process from T_1 triplet states of indo, phen and bipy ligands to the $^5D_0$ emitting level of the Eu^{3+} ion in the coordination compounds is discussed. Accordingly, it is proposed two possible intramolecular energy transfer mechanisms between indomethacinate ligand and rare earth ions, which involve the participation of excited electronic states of the heterocyclic ligands as intermediate ones.

Keywords: indomethacin, rare earth, heterocyclics, photoluminescence, energy transfer

Introduction

In recent decades, metallotherapeutic drugs based on transition metal and trivalent rare earth ions have attracted considerable attention owing to their potential applications in medicine as anti-inflammatory,[1] antitumor,[2] antiproliferative,[3] antifungal,[4,5] antiviral[6,7] and antimicrobial.[8] Many of these compounds present enhanced biomedical activity, reduced toxicity[1] and diminished collateral effects as compared with non-coordinated parent drugs. Among various classes of metallotherapeutic drugs, those based on the nonsteroidal anti-inflammatory drugs (NSAIDs) from the carboxylate or oxicam families have received particular attention because of their great ability to coordinate to different metal ions, resulting thermodynamically and kinetically stable complexes.

The molecular structures of NSAIDs are characterized by the presence of chromophore groups and low-lying triplet state with energy in the range of 20,000-25,000 cm^{-1}, which may act as luminescent sensitizers for trivalent rare earth ions.[9] Additionally, molecules of NSAIDs may act as multidentate ligands for RE^{3+} ion through their hard N– and O– sites. It is well-known that RE^{3+} ions play a wide range of roles in fluoroimmunoassay methods,[10] therapy[11] and as luminescent probe for biomolecules[12] due to their unique spectroscopic properties such as narrow emission bands, high luminescence intensities and the long lifetimes of the $^{2S+1}L_J$ emitting levels. Furthermore, the rare earth ions may be indirectly excited via coordinated ligand (antenna effect) in a spectral region far from those where emission is generally monitored.

Recently, Zhou *et al.*[13] have investigated the structural and photophysical properties of two new rare earth complexes where carprofen has acted as effective luminescence

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sensitizer for the Tb^{3+} ion, but not for the Eu^{3+} ion. Luminescence properties of the Tb^{3+} complexes with ibuprofen and orthofen containing additional organic bases were also studied by Teslyuk *et al.*[9] in order to propose an analytical method to determine NSAID drugs. The chemiluminescent method, based on Eu^{3+} emission for the determination of naproxen in pharmaceutical and urine, has been developed by Kaczmarek.[14]

Among NSAID drugs, indomethacin (1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indole-3-acetic acid (Hindo)) (Figure 1) is considered one of the most clinically investigated.[1] Its coordination complexes with transition metals have been extensively investigated in terms of structural and spectroscopic properties.[15] Generally, these complexes present other donor ligands because indomethacinate (indo) cannot saturate the coordination sphere of the metal ions. In the case of the rare earth complexes, neutral ligands such as heteroaromatic and phosphine oxide ligands have been not only used for this purpose, but have been shown that they may also play an essential role in the luminescence sensitization that involves either a direct intramolecular energy transfer to the metal ion or an indirect mechanism via energy transfer to other ligands. The main evidences for this latter mechanism were reported for Eu^{3+}-tris(diketonate) complexes,[16-18] however, the interligand energy transfer in rare earth complexes is still not clear.
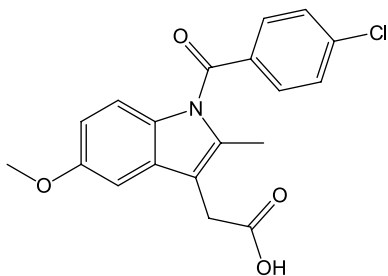

Figure 1. Molecular structural formula of the indomethacin ligand (Hindo).

In particular, excited triplet states of some heteroaromatic ligands are almost resonant with that for indomethacinate (indo) ligand, consequently, these states may contribute to an operative interligand energy transfer in which the heteroaromatic ligands act as energy acceptor from ionic ligands and, subsequently, transfer their energy to the trivalent rare earth ion increasing the luminescence intensity. Thus, the investigation of this intramolecular energy process may contribute to design of new highly luminescent complexes based on carboxylate ligands for different practical applications. Besides, up to now, to the best of our knowledge, no investigation has been carried

out on the quantitative photophysical properties of the RE^{3+} coordination compounds in the solid state containing indomethacin.

Herein, it is reported the synthesis, characterization, intramolecular ligand-to-metal energy transfer and photophysical properties study of the RE^{3+} complexes (where RE^{3+}: Eu^{3+}, Gd^{3+} or Tb^{3+}) with indomethacinate (indo) and ancillary heteroaromatic ligands (2,2'-bipyridine (bipy), and 1,10-phenanthroline (phen)), in the solid state. Photoluminescent properties of the Eu^{3+} complexes have been thoroughly investigated taking into account the radiative (A_{rad}) and non-radiative (A_{nrad}) emission coefficients, experimental intensity parameters (Ω_2 and Ω_4) and emission quantum efficiency (η). Additionally, the synthesized complexes may be used to perform new methods for luminescence determination of NSAID drugs and potential application as target medicine.[9]

Experimental

Materials

The indomethacin ligand was extracted from the INDOCID® drug using ethyl acetate as solvent and purified in a flash column chromatography on silica gel (Tedia, SiliaFlash® F60 40-63 μm, 230-400 mesh), using a mixture of hexane and ethyl acetate (1:1) as eluent. The commercially available 2,2'-bipyridine (bipy) 99% and 1,10-phenanthroline (phen) monohydrated 99% heteroaromatic ligands were purchased from Sigma-Aldrich and were used without previous purification. The rare earth chlorides ($RECl_3 \cdot 6H_2O$) were prepared by the reaction between their corresponding rare earth oxides, RE_2O_3 (99.999%) (RE: Eu^{3+} and Gd^{3+}) and Tb_4O_7 (99.999%) from Sigma-Aldrich, and concentrated hydrochloric acid (37%, Merck) as reported in the literature.[19,20]

Instrumentation

C, H and N analyses were performed on a microanalytical analyzer model 2400 (PerkinElmer). Infrared absorption spectra were recorded in a Shimadzu FTIR spectrophotometer model IRPrestige-21 by using the technique of KBr pellets in the interval of 400-4000 cm^{-1}. Thermogravimetric analyses (TGA) of the RE^{3+}-indomethacinate complexes from room temperature to 900 °C were conducted with a thermobalance model DTG-60H Shimadzu by using platinum crucibles with approximately 2 mg of complexes. A dynamic synthetic air atmosphere (50 mL min^{-1}) and a heating rate of 10 °C min^{-1} were used as instrumental conditions. Steady-state luminescent spectra were acquired by using a Horiba

JobinYvon Fluorolog-3 spectrofluorimeter presenting double grating 0.22 m monochromator (SPEX 1680) and a 450 W Xenon lamp as excitation source. Luminescence decay data were also collected by using a phosphorimeter SPEX 1934D accessory coupled to the Fluorolog-3 spectrofluorimeter.

Synthetic methodology

Synthesis of the RE(indo)$_3$(H$_2$O)$_x$ complexes

A NaOH aqueous solution (1 mol L^{-1}) was added slowly (dropwise) to a suspension of indomethacin ligand (400.0 mg, 1.12 mmol) in 50 mL of water until the apparent pH value of ca. 7, followed by the dropwise addition of a RECl$_3$·6H$_2$O aqueous solution (0.37 mmol: 135.6 mg (EuCl$_3$·6H$_2$O), 137.4 mg (GdCl$_3$·6H$_2$O) and 138.2 mg (TbCl$_3$·6H$_2$O)), yielding immediately a yellow solid precipitate. The powder samples were filtered, washed thoroughly with cooled water and dried under reduced pressure (358.9 mg, 76% for Eu^{3+}; 312.8 mg, 66% for Gd^{3+}; and 308.6 mg, 65% for Tb^{3+}); CHN anal. calcd. for C$_{57}$H$_{51}$Cl$_3$EuN$_3$O$_{15}$ (**1**): C, 53.64; H, 4.03; N, 3.29; found: C, 53.46; H, 4.17; N, 3.17; FTIR (KBr) ν / cm^{-1} 3390m, 3088w, 2992w, 2926m, 2849w, 2833w, 1682s, 1591s, 1545s, 1477s, 1416s, 1402s, 1323s, 1229s, 1090m, 1014w, 924w, 835w, 754w; CHN anal. calcd. for C$_{57}$H$_{51}$Cl$_3$GdN$_3$O$_{15}$ (**2**): C, 53.42; H, 4.01; N, 3.28; found: C, 53.49; H, 4.15; N, 3.35; FTIR (KBr) ν / cm^{-1} 3418m, 3088w, 3069w, 2994w, 2955w, 2928w, 2833w, 1682s, 1591s, 1553s, 1477s, 1435s, 1400s, 1369s, 1323s, 1230s, 1148m, 1090m, 1070m, 1036m, 1014w, 926w, 835w, 754w; CHN anal. calcd. for C$_{57}$H$_{53}$Cl$_3$TbN$_3$O$_{16}$ (**3**): C, 52.61; H, 4.11; N, 3.23; found: C, 52.26; H, 4.08; N, 3.03; FTIR (KBr) ν / cm^{-1} 3424m, 3088w, 3067w, 2994w, 2928m, 2849m, 2833w, 1682s, 1591s, 1553s, 1477s, 1437s, 1400s, 1321s, 1229s, 1148m, 1090m, 924m, 835m, 754m.

Synthesis of the RE(indo)$_3$(bipy) complexes

To a solution of bipy (37.4 mg, 0.24 mmol) in ethyl acetate (10 mL) was added dropwise a solution of RE(indo)$_3$(H$_2$O)$_x$ complexes (0.24 mmol: 300.0 mg for Eu^{3+}, 307.5 mg for Gd^{3+}, and 308.0 mg for Tb^{3+} complex) in ethyl acetate (40 mL). A precipitate (yellow powder) was obtained after the solvent evaporation. The product was thoroughly washed with cooled ethyl acetate (ca. 10 mL), filtered and dried under reduced pressure resulting in yellow solid (281.5 mg, 84% for Eu^{3+}; 289.2 mg, 86% for Gd^{3+}; and 276.2 mg, 82% for Tb^{3+}). Although the complexes are very soluble in several solvents (dichloromethane, chloroform, ethyl acetate, acetone, toluene, etc.), and all attempts to obtain single crystals were unsuccessful; CHN anal. calcd. for C$_{67}$H$_{53}$Cl$_3$EuN$_5$O$_{12}$ (**4**): C, 58.38; H, 3.88; N, 5.08; found

(%): C, 57.76; H, 3.84; N, 5.07; FTIR (KBr) ν / cm^{-1} 3428w, 3069w, 3042w, 2992w, 2926w, 2832w, 1682s, 1601s, 1566s, 1477s, 1458s, 1437s, 1398s, 1321s, 1227s, 1148m, 1088m, 1036m, 924w, 835m, 756m; CHN anal. calcd. for C$_{67}$H$_{53}$Cl$_3$GdN$_5$O$_{12}$ (**5**): C, 58.15; H, 3.86; N, 5.06; found: C, 57.26; H, 4.24; N, 4.93; FTIR (KBr) ν / cm^{-1} 3428w, 3071w, 2990w, 2928w, 2849w, 2832w, 1682s, 1601s, 1566s, 1477s, 1458m, 1437s, 1321s, 1227s, 1148m, 1088m, 1036m, 1014m, 924w, 835m, 756m; CHN anal. calcd. for C$_{67}$H$_{53}$Cl$_3$TbN$_5$O$_{12}$ (**6**): C, 58.08; H, 3.86; N, 5.05; found: C, 57.26; H, 4.36; N, 4.96; FTIR (KBr) ν / cm^{-1} 3428w, 3084w, 2990w, 2926w, 2849w, 2833w, 1682s, 1603s, 1564s, 1477s, 1437s, 1317s, 1227s, 1148m, 1090m, 1036m, 926m, 835m, 756m.

Synthesis of the RE(indo)$_3$(phen) complexes

To a solution of phen monohydrated (47.5 mg, 0.24 mmol) in ethyl acetate (10 mL) was added dropwise a solution of RE(indo)$_3$(H$_2$O)$_x$ complexes (0.24 mmol: 300.0 mg (Eu^{3+}), 307.5 mg (Gd^{3+}) and 308.0 mg (Tb^{3+})) in ethyl acetate (40 mL). A precipitate (yellow powder) was obtained after the solvent evaporation. The product was thoroughly washed with cooled ethyl acetate (ca. 10 mL), filtered and dried under reduced pressure resulting in yellow solid (279.5 mg, 82% for Eu^{3+}; 280.5 mg, 82% for Gd^{3+}; and 267.2 mg, 78% for Tb^{3+}). Although the complexes are very soluble in several solvents (dichloromethane, chloroform, ethyl acetate, acetone, toluene, etc.), and all attempts to obtain single crystals were unsuccessful; CHN anal. calcd. for C$_{69}$H$_{53}$Cl$_3$EuN$_5$O$_{12}$ (**7**): C, 59.09; H, 3.81; N, 4.99; found: C, 58.73; H, 3.98; N, 5.55; FTIR (KBr) ν / cm^{-1} 3437w, 3076w, 2992w, 2926w, 2832w, 1680s, 1607s, 1553m, 1477s, 1427s, 1356s, 1325s, 1227s, 1148m, 1088m, 1068m, 920m, 833m, 754m; CHN anal. calcd. for C$_{69}$H$_{53}$Cl$_3$GdN$_5$O$_{12}$ (**8**): C, 58.87; H, 3.79; N, 4.97; found: C, 57.63; H, 4.24; N, 4.86; FTIR (KBr) ν / cm^{-1} 3447m, 3078w, 2992w, 2953w, 2953w, 2832w, 1678s, 1607s, 1589s, 1556m, 1477s, 1427s, 1398s, 1356s, 1229s, 1144m, 1090m, 1069m, 922w, 837m, 754m. CHN anal. calcd. for C$_{69}$H$_{53}$Cl$_3$TbN$_5$O$_{12}$ (**9**): C, 58.80; H, 3.79; N, 4.97; found: C, 57.36; H, 3.91; N, 4.85; FTIR (KBr) ν / cm^{-1} 3597w, 3428w, 3078w, 2992w, 2953w, 2928w, 2832w, 1678s, 1609s, 1589s, 1557m, 1477s, 1427s, 1356s, 1325s, 1229s, 1148m, 1090m, 922m, 835m, 754m.

Results and Discussion

Synthesis and characterization

Elemental analysis data of the rare earth indomethacinate complexes are in agreement with the ratios metal:indo:water and metal:indo:heteroaromatic equal to 1:3:3 for hydrated

complexes (**1** and **2**), 1:3:4 for hydrated complex (**3**) and 1:3:1 for rare earth complexes (**4-9**) which contain bipy and phen as ancillary ligands.

FTIR spectrum for indomethacin ligand extracted from the INDOCID® drug is in agreement (Figure S1 in the Supplementary Information (SI) section). Figure 2 shows the FTIR spectra for the Eu^{3+}-indomethacinate complexes, while FTIR spectra for Gd^{3+} and Tb^{3+} are presented in Figures S2 and S3 in the SI section. In general, the absorption spectra for the RE^{3+} complexes (**1-3**) exhibit a broad band in the range of 2600-3400 cm^{-1} that is assigned to the O–H stretching of the water molecules. As can be seen, this band is not present in the vibrational spectra for the complexes containing the heteroaromatic ancillary ligands, indicating that water molecules have been substituted by neutral ligands. The characteristic absorption bands assigned to the carboxylic group (COOH) of the Hindo free ligand, e.g., ν(O–H) at 3300 cm^{-1} and ν(C=O) at 1734 cm^{-1}, have been substituted by the intense absorption bands assigned to ν_{as}(COO) (at 1613 cm^{-1}) and ν_s(COO) (at 1416 cm^{-1}) of the carboxylate group of the RE^{3+} complexes (**2**). Furthermore, the values for $\Delta[\Delta_{as}(COO) - \Delta_s(COO)]$ are falling in the range of 197 cm^{-1} for all the complexes (**1-9**), indicating that indo ligand is coordinated to the RE^{3+} as chelating or bridging mode.[21-23] These results strongly suggest that those complexes are either binuclear or coordination polymers. Moreover, the absorption bands around 1468 and 1423 cm^{-1} indicate that bipy and phen heteroaromatic ligands are coordinated to the metal ions through their nitrogen atoms.[16,24]
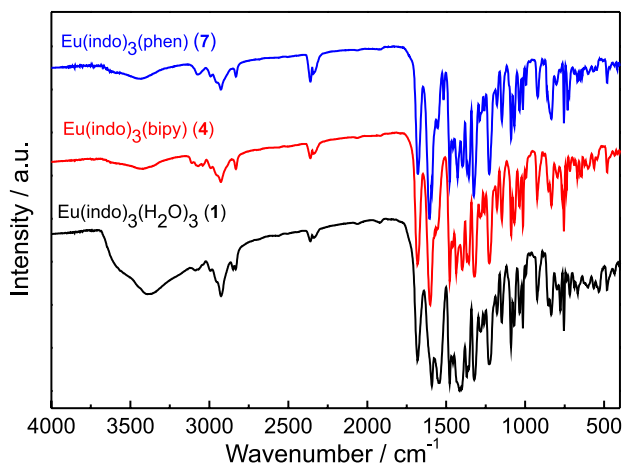

Figure 2. FTIR absorption spectra of the Eu^{3+} complexes (**1**, **4** and **7**) recorded in the range of 4000-400 cm^{-1} in KBr pellets.

The presence of water molecules in the complexes (**1-3**) was also characterized by thermogravimetric analysis. TGA curves (Figure 3) present a weight loss around 3.5% in the temperature interval between 60-150 °C that is attributed to the release of three water molecules for the

complex (**1**) (similar to complex (**2**), see Figure S4 in the SI file). This result is similar to the thermal decomposition for the $Ce(indo)_3(H_2O)_3$ complex reported in reference.[15] Figure 3 also displays the TGA curves for the Eu^{3+} complexes (**4** and **7**) containing bipy and phen ligands.
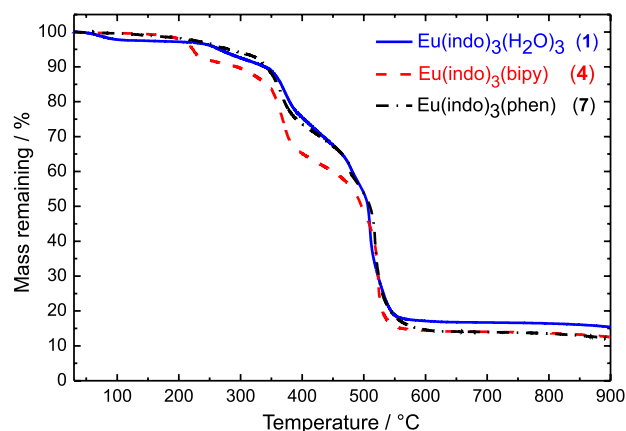

Figure 3. TGA curves of the complexes (**1**, **4** and **7**) recorded in the interval of 25-900 °C, using dynamic synthetic air atmosphere (50 mL min^{-1}) and a heating rate of 10 °C min^{-1}.

TGA curves for other coordination compounds are shown in Figures S4 and S5 in the SI section. For the complex (**3**), TGA curve shows a weight loss around 5% in the same temperature interval that is attributed to the release of four water molecules which corroborate with the CHN elemental analysis data. The resulting anhydrous compounds undergo thermal decomposition in successive steps that occur from 230 to 670 °C. In contrast to the hydrated complexes, TGA curves for the complexes (**4**) to (**9**) do not exhibit any weight loss until 150 °C, confirming the anhydrous form of these coordination compounds.

The coordination compounds (**3**, **6** and **9**) present successive steps that take place in the range of 300-750 °C, starting with a weight loss that corresponds to the release of the phen ligand. The TGA curves show that complexes with bipy ligand (**2**, **5** and **8**) are less stable than those ones containing phen ligand (**3**, **6** and **9**). The first weight loss of these complexes (around 170 °C) may be assigned to the release of the bipy ligand. However, no well-defined level is observed in the TGA curves owing to the subsequent decomposition of the $RE(indo)_3$ products. The final products remain stable until 900 °C for the thermal decomposition of all complexes, which can be assigned to the corresponding rare earth oxide, RE_2O_3 (RE: Eu and Gd) and Tb_4O_7.

Phosphorescent behavior

The emission spectra of the Gd^{3+} complexes (**2**, **5** and **8**) were recorded with excitation on the $S_0 \rightarrow S_1$

indomethacinate centered transition at 350 nm (Figure 4), showing two overlapped broad bands with maxima around 420 (blue region) and 500 nm (green region) assigned to the fluorescence ($S_1 \rightarrow S_0$) and phosphorescence ($T \rightarrow S_1$) intraligand transitions, respectively.
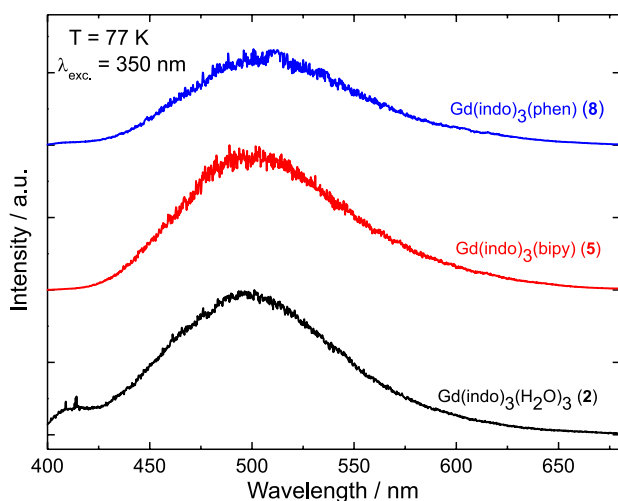

Figure 4. Phosphorescence spectra of the Gd^{3+} complexes (**2**, **5** and **8**), in solid state, recorded at liquid nitrogen temperature in spectral range of 400-700 nm, under excitation at 350 nm.

Since the highest intensity band is that due to the phosphorescence, the Gd^{3+}-indomethacinate complexes present green emission color under UV radiation excitation. Interestingly, no obvious difference between the emission spectra profiles of the Gd^{3+} complexes (**5** and **8**) and that for the precursor complex, **2**, is observed, indicating that photoluminescence properties of all the Gd^{3+} complexes are mainly due to the indomethacinate ligand coordinated to the RE^{3+} ion. For these coordination compounds, the indomethacinate triplet state (T_1) was determined taking into account the 0-0 phonon transition from the time-resolved phosphorescence spectra recorded with time delay of 0.04 ms (Figure S6 in the SI section).

The absence of the short-lived fluorescence emission band around 420 nm in those spectra (Figure 4) allowed for a more precise determination of the T_1 state energies, as following: 22,124, 21,882 and 21,552 cm^{-1} for the $Gd(indo)_3(H_2O)_3$ (**2**), $Gd(indo)_3(bipy)$ (**5**) and $Gd(indo)_3(phen)$ (**8**) complexes, respectively. These optical data indicate that triplet states of indo ligand should be in a good resonance condition of the emitting levels of the Eu^{3+} ion, acting as an efficient antenna for europium complexes.[16]

Luminescence spectra of the Eu^{3+}

As to the emission monitored on the intraconfigurational $^5D_0 \rightarrow {}^7F_2$ hypersensitive transition centered on the Eu^{3+}

ion (at approximately 612 nm), all excitation spectra for solid-state of the complexes (**1**, **4** and **7**) exhibit similar spectral profiles. These spectra (Figure 5) present a strong broad band in the range of 250-450 nm assigned to the $S_0 \rightarrow S_1$ transition belong to indo ligand, indicating that even in the complexes with bipy and phen, the luminescence sensitization mechanism of the Eu^{3+} ion started with radiation absorption by indomethacinate ligand. However, minor contributions due to the absorption from heterocyclic ligands are observed. It is worth noting that this band exhibits higher intensity than those ones from the intraconfigurational $^7F_0 \rightarrow {}^{2S+1}L_J$ transitions at around 468 and 525 nm, confirming the potential ability of the ligand to transfer energy to the Eu^{3+} ion.
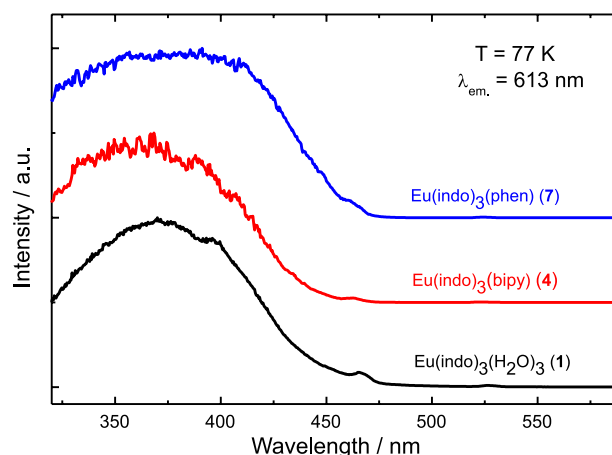

Figure 5. Excitation spectra of the Eu^{3+} complexes (**1**, **4** and **7**), in solid state, recorded at 77 K with emission monitored at 613 nm.

The emission spectra of all the RE^{3+} coordination compounds were recorded at 298 and 77 K, upon excitation on the ligand $S_0 \rightarrow S_1$ transition (at 350 nm) of the indomethacinate ligand (Figure 6). Under this condition, all the Eu^{3+}-indomethacinate coordination compounds (**1**, **4** and **7**) display high red luminescence at 77 K. A qualitative analysis shows that the Eu^{3+} complexes with ancillary heteroaromatic ligands (**4** and **7**) exhibit significantly higher luminescent intensities than the hydrated complex (**1**).

The emission spectra of the complex (**1**) in the range of 430-720 nm recorded at 298 and 77 K exhibit different spectral profiles (Figure 6). When recorded at 298 K, a broad band arising from intraligand transition is observed, that is only partially quenched in the emission spectrum recorded at 77 K. This band overlaps the standard set of well-resolved narrow emission bands owing to the Eu^{3+} centered transitions: $^5D_0 \rightarrow {}^7F_0$ (579 nm), $^5D_0 \rightarrow {}^7F_1$ (589 nm), $^5D_0 \rightarrow {}^7F_2$ (613 nm), $^5D_0 \rightarrow {}^7F_3$ (635 nm) and $^5D_0 \rightarrow {}^7F_4$ (717 nm).[24] On the other hand, one of the
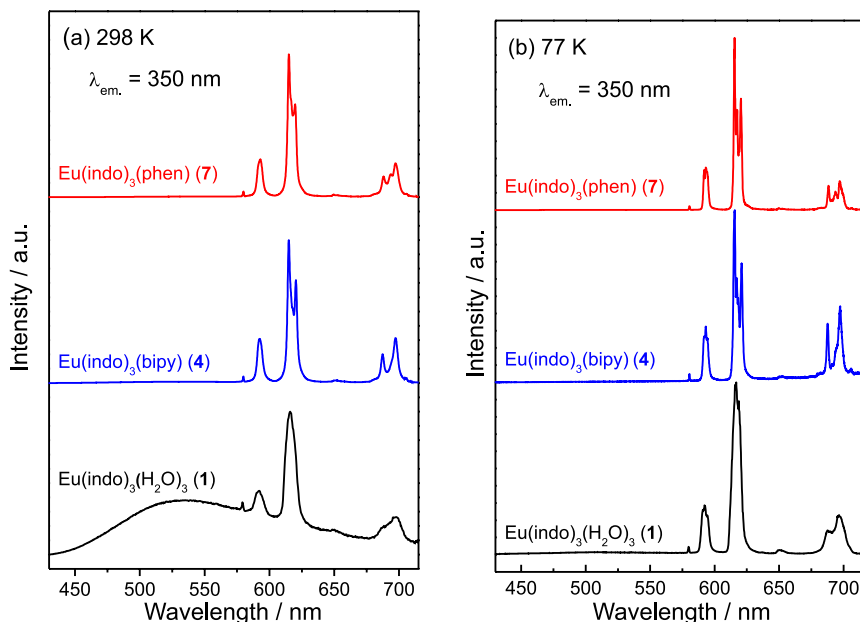
Figure 6. Emission spectra of the Eu^{3+} complexes (**1**, **4** and **7**), in solid state, measured at (a) 298 K and (b) 77 K, under excitation on the S_1 state of the indomethacinate ligand at 350 nm.

main features to be outlined from the photoluminescent spectra for complexes **4** and **7**, both recorded at 298 and 77 K, is the absence of the broad emission bands due to the indomethacinate fluorescence or phosphorescence. All of these photoluminescence spectra display similar spectral profile, in which only the intraconfigurational-4f^6 transitions are observed, being dominated by the well-characterized hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition allowed by forced electric dipole mechanism. It is also important to note the lower relative intensity ratio between the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ transitions in comparison with those for low symmetry Eu^{3+}tris-β-diketonate coordination compounds containing the bipy and phen, or their derivative ligands.[25,26] These results altogether suggest that a chemical environment around the rare earth ion is close to C_n or C_{nv} symmetry.

Although indomethacinate ligand dominates the antenna effect, emission data give evidences that excited states centered on the heterocyclic ligands (bipy and phen) can also play an important role as intermediate states in the intramolecular energy transfer from indomethacinate ligand to Eu^{3+} ion. A possible explanation for this behavior lies in the fact of heterocyclic ligands present their low-lying excited triplet states close in energy to the T_1 triplet excited state of the indomethacinate ligand. It is also close in energy to $^5D_0$ (ca. 17293 cm^{-1}) and $^5D_1$ (ca. 19027 cm^{-1}) emitting levels of the Eu^{3+} ion. According to the literature, the intramolecular energy transfer in the Eu^{3+}-indomethacinate complexes can be divided into two mechanisms, which is shown in Figure 7.[27,28]
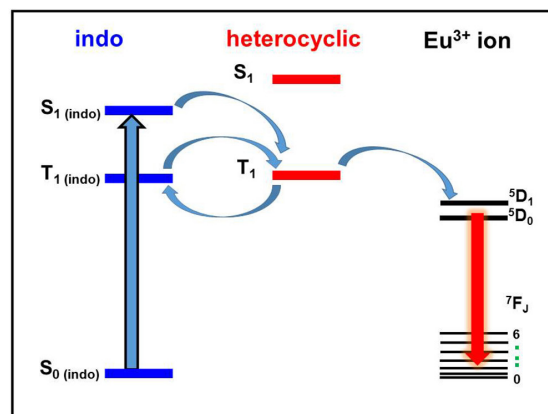

Figure 7. Partial energy level diagrams of the intramolecular energy transfer mechanisms for Eu^{3+}-indomethacinate complexes containing heterocyclic ligands. S_1 and T_1 represent excited singlet and triplet states, respectively.

For the first mechanism, indomethacinate ligand absorbs energy being excited to its S_1 states, and subsequently transfers this energy to the T_1 excited state belonging to heterocyclic ligand (Figure 7). Therefore, this latter ligand undergoes energy transfer from the intraligand triplet state to $^5D_1$ or $^5D_0$ levels of the Eu^{3+} ion ($T_1 \rightarrow {}^5D_1 \rightarrow {}^5D_0$), followed by radiative and non-radiative deactivation centered on the central metal ion ($^5D_0 \rightarrow {}^5F_J$). By means of the second mechanism, indomethacinate ligand absorbs energy being excited to its singlet state S_1, which undergoes intersystem crossing energy to the own T_1 state and transfers to the triplet excited level (T_1) of the heterocyclic ligand, followed by sensitization of the excited levels of the Eu^{3+} (Figure 7). In order to give an insight into the proposed

mechanisms above, it is listed the energies corresponding to the S_1 and T_1 excited states for all the coordinated ligands: S_1(indo) at 29,411 cm^{-1}, T_1(indo) at 21,790 cm^{-1}, S_1(phen) at 32,894 cm^{-1}, T_1(phen) at 22,100 cm^{-1}, S_1(bipy) at 30,300 cm^{-1} and T_1(bipy) at 22,100 cm^{-1}.

Following the standard methodology described by Sá *et al.*,[28] the photophysical properties of the Eu^{3+} ion into the novel complexes were quantitatively investigated. The spectroscopic parameters (A_{rad}), Judd-Ofelt intensity parameters (Ω_λ, $\lambda = 2$, 4 and 6) and emission quantum efficiency (η) were directly determined from the photophysical data.

The radiative rates (A_{rad}) of the Eu^{3+}-indomethacinate complexes were determined taking into account the following equation:[27]

$$A_{rad} = \sum_{J=2,4,6} A_{0J} = \sum_{J=2,4,6} \left(\frac{S_{0J}}{S_{01}}\right)\left(\frac{\sigma_{01}}{\sigma_{0J}}\right) A_{01} \qquad (1)$$

where, $A_{01} = 0.31 \times 10^{-11} \eta^3 \sigma^3$ and A_{0J} is the radiative rates assigned to the intraconfigurational $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_J$ (J = 2, 4 and 6) transitions, respectively. S_{0J} and σ_{0J} correspond, respectively, to the integrated intensities and barycenters of the intraconfigurational transitions. Each Judd-Ofelt intensity parameters (Ω_λ, $\lambda = 2$, 4 and 6) of the Eu^{3+} ion presents a direct correlation with the A_{0J} for a particular $^5D_0 \rightarrow {}^7F_J$ transition, which is expressed by the well-known equation reported in our previous work.[29]

Importantly, luminescence quantum efficiency (η) for the Eu^{3+}-indomethacinate complexes was determined from the product $\eta = A_{rad}\tau$, where τ is the luminescence decay lifetime of the $^5D_0$ emitting level. The values of τ were determined by the well-adjusted single-exponential luminescence decay curves of the Eu^{3+} complexes upon excitation and emission monitored at 350 and 613 nm, respectively. The non-radiative rate, A_{nrad}, was estimated from the difference between the value of A_{total} (1/τ) and A_{rad} value.

Table 1 presents the spectroscopic parameters obtained for all three Eu^{3+}-indomethacinate compounds at 298 and

77 K. As can be seen, the values of radiative rates for the complexes are comparable, indicating that no marked change occurs in the symmetry around the central metal ion when water molecules are substituted by the heterocyclic ligands or when the temperature is changed. On the other hand, a significant decrease in non-radiative rates (A_{nrad}) is observed when water molecules are replaced by those ligands, which is expected due to the ability of water molecules act as luminescence quenchers via multiphonon decay mechanism.[30]

Eu^{3+} complex (**1**) presents a considerably high dependence of A_{nrad} on the temperature in comparison with all of the other complexes investigated in this work (Table 1). This result suggests that there is the multi-phonon luminescent quenching effect, promoted by water molecules, and the additional luminescence quenching channel, probably a ligand-to-metal charge transfer state (LMCT). As a result, the luminescence quantum efficiency for the hydrated Eu^{3+}-indomethacinate complex at low temperature ($\eta = 20\%$) is the double of the value at room temperature ($\eta = 9\%$). The low values of η reflect the luminescence quenching of the Eu^{3+} ion. Such behavior agrees with what is observed for some Eu^{3+}-aromatic carboxylate coordination compounds reported in the literature.[31]

The A_{nrad} values of the complexes (**4**) and (**7**) are very low and practically independent of temperature. Although the low values of A_{rad} as compared with the Eu^{3+}-β-diketoante complexes reported in the literature,[30] which present values of A_{rad} close to 1000 s^{-1}, suggest that the low values of A_{nrad} contribute for the augment of emission quantum efficiency (η) in more than six times as compared with hydrated complex (**1**) (Table 1).

The Judd-Ofelt intensity parameters (Ω_2 and Ω_4) present very similar values and reflect the small ratio between intensities of the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$ transitions (Table 1). Moreover, the Ω_2 values change only slowly when water molecules are substituted by neutral ligands in the first coordination sphere of the Eu^{3+} ion, indicating that the parameter is mostly influenced by small angular

Table 1. Experimental intensity parameters ($\Omega_{\lambda=2,4}$), radiative rate (A_{rad}), non-radiative rate (A_{nrad}), lifetime (τ) and emission quantum efficiency (η) of the $^5D_0$ emitting level determined for the Eu^{3+} complexes (**1**, **4** and **7**) recorded at 298 and 77 K

Coordination compound	Temperature / K	A_{rad} / s^{-1}	A_{nrad} / s^{-1}	Ω_2 / 10^{-20} cm^2	Ω_4 / 10^{-20} cm^2	τ / ms	A_{tot} / s^{-1}	η / %
$Eu(indo)_3(H_2O)_3$ (**1**)	298	477	4786	10.2	8.2	0.19	5263	9
	77	391	1570	7.9	7.1	0.51	1961	20
$Eu(indo)_3(bipy)$ (**4**)	298	366	222	7.1	7.0	1.70	588	62
	77	360	239	6.6	7.6	1.67	599	60
$Eu(indo)_3(phen)$ (**7**)	298	391	328	7.9	7.1	1.39	719	54
	77	337	317	6.9	5.3	1.53	654	51

changes in the local coordination geometry.[32-35] However, they are quite similar for Eu^{3+}-indomethacinate complexes containing heterocyclic ligands.

Luminescence spectra of the Tb^{3+}

Figure 8 shows the excitation spectra for Tb^{3+}-indomethacinate complexes recorded at 77 K in the spectral range of 250-550 nm. These spectra exhibit broad absorption bands with maxima at around 350 nm and a sharp absorption band located at 480 nm that reflect the indirect (via ligand) and direct excitation of the Tb^{3+} ion, respectively.

The emission spectra of Tb^{3+}-indomethacinate complexes were recorded at 298 and 77 K in the spectral range of 450-700 nm, under excitation on the intraligand
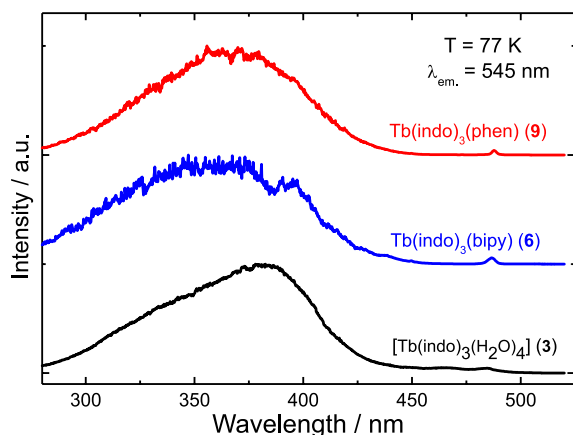

Figure 8. Excitation spectra of the Tb^{3+}-complexes (**3**, **6** and **9**), in solid state, recorded at 77 K with emission monitored at 545 nm.

$S_0 \rightarrow S_1$ transition (Figure 9). As shown in Figure 9a, all emission spectra measured at 298 K present a broad emission band due to the indomethacinate ligand that overlaps the sharp emission bands assigned to the intraconfiguration-$4f^8$ of the Tb^{3+} ion: $^5D_4 \rightarrow ^7F_6$ (480 nm), $^5D_4 \rightarrow ^7F_5$ (545 nm), $^5D_4 \rightarrow ^7F_4$ (584 nm), $^5D_4 \rightarrow ^7F_3$ (621 nm), and $^5D_4 \rightarrow ^7F_2$ (650 nm). The energy gap $\Delta E(T_{indomethacinate} - {}^5D_4)$ is only approximately 1000 cm^{-1}. These optical data indicate that the indomethacinate ligand is a better luminescence sensitizer for the Eu^{3+} than for the Tb^{3+} ion. This result is in according to Latva's empirical rule, which indicates that optimal sensitizing for Tb^{3+} and Eu^{3+} luminescence requires an energy gap between donor and acceptor states in gate 2100-4500 cm^{-1}. This fact indicates that energy back-transfer process from the Tb^{3+} ion to indo ligand is operative, acting as a luminescence quenching channel.

The CIE (International Comission on Illumination) color coordinates of the Eu^{3+}- and Tb^{3+}-indomethacinate complexes measured from emission spectra[35] recorded at 298 and 77 K are presented in Figure 10. According to these results, the emission color of the Eu^{3+} complex (**1**) is tunable from pink to red when temperature is lowed. This behavior reflects the complete quenching of the phosphorescence band from indomethacinate coordinated ligand for the emission spectrum recorded at 77 K. Besides, taking into consideration that the emission spectra of the Eu^{3+} coordination compounds (**4**) and (**7**) recorded at both temperatures are dominated by the intraconfigurational-$4f^6$ narrow emission bands centered on the Eu^{3+} ion, the CIE color coordinates are located in the red region of CIE
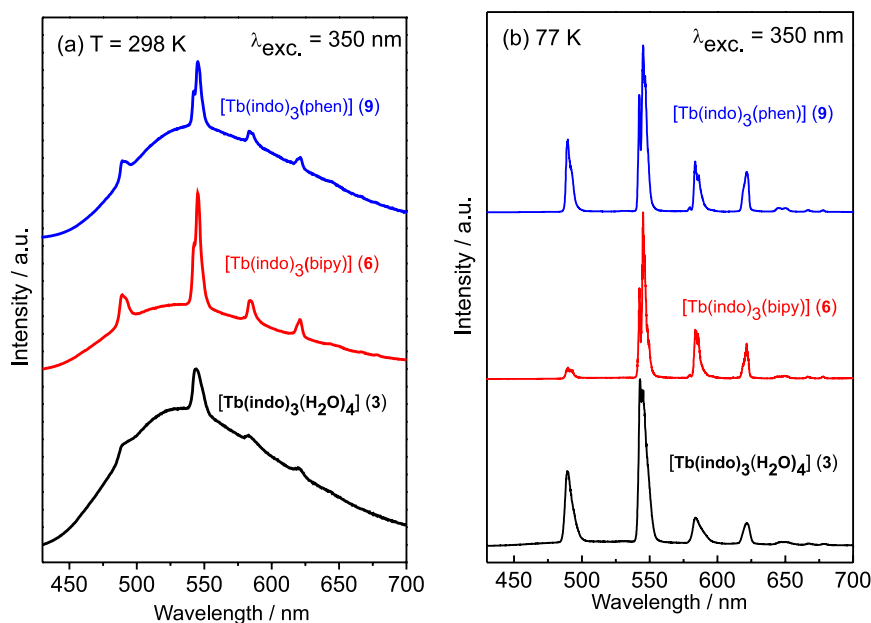

Figure 9. Emission spectra of the Tb^{3+} complexes (**3**, **6** and **9**), in solid state, recorded at (a) 298 and (b) 77 K, under excitation on the singlet state S_1 of the indomethacinate ligand at 350 nm.

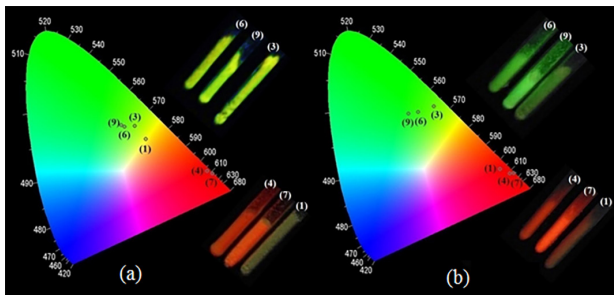chromaticity diagram, as expected. Thus, the europium complexes exhibit pure red emission color.

Figure 10. CIE chromaticity diagram presenting (x, y) color coordinates for Eu^{3+} and Tb^{3+} complexes at (a) room temperature and (b) liquid nitrogen temperature, under excitation at 350 nm. Photographs of the RE^{3+} complexes (insert) taken with a digital camera displaying the green and red emissions under UV irradiation lamp at 365 nm.

As mentioned above, all emission spectra of the Tb^{3+}-indomethacinate compounds recorded at 298 K exhibit the high intense phosphorescence band assigned to $T_1 \rightarrow S_0$ transition from indomethacinate ligand (Figure 9a). Therefore, they present CIE coordinates color in the green-yellow region. On the other hand, the green emission colors displayed by these complexes at 77 K reflect the dominating intensities of the narrow emission bands arising from the intraconfigurational-$4f^8$ transitions centered on the Tb^{3+} ion (Figure 9b).

Excitation spectra of the solid solutions $Eu_{0.5}Tb_{0.5}(indo)_3(H_2O)_3$ and $Eu_{0.5}Tb_{0.5}(indo)_3(L)$, where L: phen or bipy, have been also recorded at 77 K in order to investigate the monomeric or polymeric nature of the synthesized systems (Figure S7 in the SI section). These systems were prepared based on the experimental procedures for pure complexes, using equimolar mixtures of Eu^{3+} and Tb^{3+} ions. All excitation spectra (Figure S7 in the SI section) of the solid solutions recorded under emissions monitored at 679 nm ($^5D_0 \rightarrow {}^7F_4$ transition of the Eu^{3+} ion exhibit a narrow band at 487 nm, which corresponds to the intraconfigurational $^5F_6 \rightarrow {}^5D_4$ Tb^{3+}-centered transition. This result suggests that RE-indomethacinate complexes are dinuclear or polymeric systems. Similar results were also observed for RE-ibuprofen complexes containing donor nitrogen ligands[36,37] and for RE-dipivaloyl complexes with tppo as neutral ligand.[38]

Conclusions

Herein, nine novel rare earth indomethacinate complexes were successfully prepared using simple synthetic routes. The coordination compounds presenting formulas $RE(indo)_3(H_2O)_x$, $RE(indo)_3(bipy)$ and $RE(indo)_3(phen)$

(RE: Eu^{3+}, Gd^{3+} and Tb^{3+}, indo: indomethacinate ligand, bipy: 2,2'-bipyridine, and phen: 1,10-phenanthroline, x = 3 for Eu^{3+} and Gd^{3+} complexes, and x = 4 for Tb^{3+} complex) were characterized by elemental analysis of C, N and H, thermogravimetric analysis and infrared spectroscopic data. Based on photoluminescent parameters, non-radiative rates (A_{nrad}) were drastically decreased when water molecules were substituted by heterocyclic ligands, which improved significantly the emission quantum efficiencies of the complexes. On the other hand, the radiative rates (A_{rad}) and the Judd-Ofelt $\Omega_{\lambda = 2, 4}$ parameters were almost insensitive to the coordination changes.

Referring to the coordination of heterocyclic ligands, the intramolecular energy transfer processes in the RE^{3+} coordination compounds were also improved. The spectroscopic results indicated that T_1 excited states of the heterocyclic ligands play an important role as an intermediate state on the luminescence sensitization of the Eu^{3+} ion by the indomethacinate ligand. Finally, the properties of RE^{3+}-indomethacinate complexes in the solid state described in this work are highly appropriate for light conversion molecular devices, such as those used as luminescent markers for bioassays and bioimage fields.

Supplementary Information

FTIR spectra, thermogravimetric data and luminescence spectra for compounds **2**, **5**, **8**, **3**, **6** and **9** are available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgments

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