Photophysical properties of new europium(III) complexes with potential application as luminescent label

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Compounds containing lanthanide ions show an extensive range of applications in several areas, like displays, luminescent labels, sensors, etc. The narrow emission bands and the long emission lifetime make these compounds attractive to application as luminescent labels in biologic systems, because it makes possible the differentiation of the emission coming from the luminescent label from that coming from the biological moities. In order to be used as a luminescent label in a biological environment is desirable some properties, like, high quantum yield, solubility or dispersibility in water and functional groups that can interact with biomolecules. Therefore, the objective of this study is the synthesis of complexes with general formula $[Ln(tta)_3(L)]$ (Ln = La, Eu, Gd, trivalents and L=(2,2',6,6'-tetramethoxy-[3,3'-bipyridine]-4,4'-diyl)bis(diphenylphosphine oxide) (bpdpo) or pyrazino[2,3-f][1,10]phenanthroline (pyphen)) that shows high emission lifetime and quantum yield and may present, after futures structural changes, solubility or dispersibility in water. The ligand (2,2',6,6'-tetramethoxy-[3,3'-bipyridine]-4,4'-diyl)bis(diphenylphosphine oxide) (bpdpo) was obtained by the oxidation of the compound 4,4'-bis(diphenylphosphanyl)-2,2',6,6'-tetramethoxy-3,3'-bipyridine in toluene using H_2O_2 as oxidant agent. The oxidation was confirmed using ^{31}P-NMR, (δ 28,48 ppm) and FT-IR (δ(P=O) = 1115 cm^{-1}). The complexes $[Eu(tta)_3(L)]$ (L = bpdpo (A) e pyphen (B)) were synthetized by the substitution of the water molecules from the precursor complex $[Ln(tta)_3(H_2O)_2]$. The ligands L were dissolved in methanol, and added to the methanolic solutions from the precursor complex. The final solutions were stirred for 30 min at 60 °C until precipitation of the solids. The formation of the complexes was confirmed by FT-IR, ^{1}H e ^{31}P-NMR and photoluminescence spectroscopy. The emissions spectra of the europium complexes are showing in Figure 1. In all cases the transitions characteristic from the europium(III) ion, $^5D_0 \rightarrow {}^7F_J$ (J = 0 – 4), are detected. The change of the band profile ($^5D_0 \rightarrow {}^7F_2$ transition) in the complexes $[Eu(tta)_3(L)]$, compared to the precursor complex $[Eu(tta)_3(H_2O)_2]$, indicate that the chemical environment around the europium(III) ion was changed, indicating that the water molecules were replaced by the ligands. The substitution of the water molecules was confirmed by enhancement of the lifetime (0.886±0,001 ms and 0.753±0,003 ms in the complexes A and B, respectively) compared to the precursor complex (0.201±0,007 ms). Using the Horrocks equation, it was confirmed that no coordinated water molecules is detected in the complexes A and B. The high emission lifetime and the presence of nitrogen atoms free to interact with groups that can makes these complexes charged and make them potentials candidates to application as luminescent labels in biological environments.

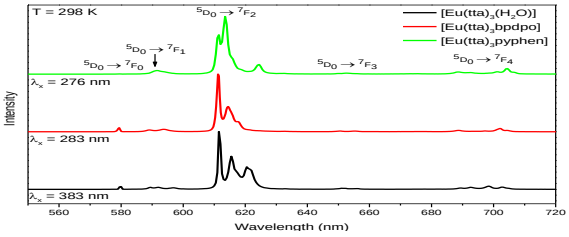

Figure 1: Emission spectra of the europium(III) complexes.

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