Europium(III) β-diketonate complexes showing emission from two-photons excitation

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Systems containing trivalent lanthanides ions have been the focus of several studies on biomarkers and sensors development. Due to their unique luminescent properties the lanthanide complexes can be used as a molecular probe for imaging or monitoring the change in intracellular pH, for example. The emission spectrum specific for each lanthanide ion and emission lifetime from microseconds to milliseconds are the main reasons for the interest in the use lanthanide as biomarkers, once it is possible to detect just the lanthanide emission eliminating the biological emission on imaging formation. A main drawback associate with those ions are the low molar absorption coefficient, however, the formation of complexes it is a way to solve this question through the antennae effect, in which the ligand absorbs the radiation and transfers to lanthanide ion which, in turn, emits on defined regions. Water solubility/dispersibility, kinetic stability and high lifetime emission of the lanthanide(III) complex are important factors for biological applications. Beyond the more usual on photon absorption, the two photon absorption is receiving interest, mainly in the study of biological systems. This technique concerns on the simultaneous absorption of two low energy photons followed by one photon emission of higher energy. To trivalent europium systems, the emission energy is around 612 nm (red emission). The main advantage associated with two photon absorption process is related to low energy excitation energy (above 700 nm to near infrared) implying on a deep biological tissue penetration. In this work, three β-diketone ligands and their respective europium(III) complexes were synthesized. The β-diketone ligand 1,3-di(pyridin-4-yl)propane-1,3-dione is already reported in the literature, however, the other two ligands (4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)-3-(pyridin-4-yl)propane-1,3-dione and 1,3-bis(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)propane-1,3-dione) have never been reported. The high conjugated systems were used to improve the molar absorptivity and the pyridine ring can shift the excitation wavelengths higher than 400 nm. Lastly, chains containing poly(oxyethylene) groups were used to improve the water-solubility. The ligands were characterized by nuclear magnetic resonance, mass spectrometry and vibrational spectrometry on infrared region. The main characterizations of complexes were photoluminescence, vibrational spectrometry on infrared region, thermal analysis and two photon absorption (2PA). At each trivalent lanthanide ion are three ligands coordinated on chelate mode and between two and three solvent molecules. The ligands and complexes show certain degree of water solubility. The complexes can be excited from 280 nm to wavelengths higher than 400 nm, showing two photon absorption from 700 nm to near 1000 nm. All of them have low symmetry, evidenced by the $^5D_0 \rightarrow {}^7F_2$ high intensity at emission spectra. The emission lifetimes are between 140 μs and 1,35 ms.

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