DEVELOPMENT OF FLUOROSENSOR FOR SELECTIVE AND SENSITIVE DETERMINATION OF LN(III) IONS

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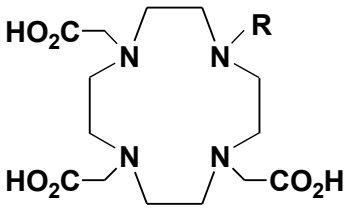
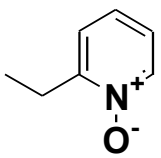
Ln(III) complexes of macrocyclic ligands are utilized in medicine and preclinical research as MRI (Gd), optical (Eu/Tb or Yb/Nd luminescence in VIS or NIR region) or nuclear probes for diagnostics and/or for cancer treatment (*e.g.* metal radioisotopes ^{90}Y, ^{153}Sm, ^{166}Ho, ^{177}Lu in nuclear medicine). For biomedical applications, such complexes should exhibit a high thermodynamic stability as well as kinetic inertness under physiological conditions and their knowledge of thermodynamic/kinetic properties is important to evaluate their possible *in vivo* applications. We studied the kinetic, thermodynamic and analytical properties of Ln(III) complexes of the mono(pyridine-*N*-oxide) analogue of the H_4dota macrocylic ligand (H_3do3a-pyNO, Scheme 1). It was found that this ligand forms thermodynamically stable and kinetically inert Ln(III) complexes. Its Eu(III) and Tb(III) complexes exhibit a strong long-lived fluorescence as a result of the antenna effect of the pyridine-*N*-oxide fluorophore pendant arm. Using an excitation wavelength of 286 nm, this ligand can be employed as a fluorogenic reagent for the determination of Eu(III) and Tb(III) at pH 6.5 and c_L = 1 mM detected luminescence at 615 nm for Eu(III) complex and at 547 nm for Tb(III)complex. Detection limits are at concentrations around 1.0 μM and linearity of the method spans over 2 orders of magnitude. The method was applied to artificial and real samples (spiked mineral waters, extracts from luminophore CRT dust) with satisfactory results. The method is simple and rapid without interference of other metal ions.



R	Ligand
H	H_3do3a
CH_2COOH	H_4dota
	H_3do3a-py^{NO} = H_3L

Scheme 1 The formulas of macrocyclic ligands discussed in the text