Abstract

In this thesis the pH dependency of the coordination modes of lanthanide complexes with macrocyclic ligands based on 1,4,7,10-tetraazacyclododecane skeleton was studied. The cyclen-based ligand structures in this work contained three acetate and one aminoethyl group with a *N*-alkyl-*N*-methylphosphonate substituent, DO3AN(R)P, where R is an alkyle substituent on the nitrogen atom of the pendant arm (R = methyl, benzyl).

Lanthanide complexes of a previously studied prototype ligand DO3ANP with secondary amino group (R = H) have shown interesting properties in the field of ^{31}P NMR imaging because of their various coordination properties, which allow *in situ* pH measurement. These complexes can also be used for monitoring the kinetics of the chemical exchange of the amino group proton in ^{1}H NMR imaging using the chemical exchange saturation transfer (CEST NMR). In this thesis, two new derivatives DO3ANMeP and DO3ANBnP were prepared in order to better understand the coordination modes changes in this ligand series. Also, their coordination behaviour with selected lanthanide ions was studied (Eu^{3+}, Gd^{3+}, Dy^{3+}, Yb^{3+}).

Based on a series of NMR and luminescence measurements, it was found out, that in acidic conditions the complexes containing DO3ANP motif bind a water molecule in their coordination sphere. However, in basic conditions, the water molecule coordination site is occupied by the coordinated pendant arm instead. This causes a significant change in the ^{31}P NMR chemical shift. For the derivatives containing tertiary amine on the pendant arm this effect was not observed anywhere on the pH scale between 2 and 10.

The second aim of this thesis was optimalization of the general synthetic pathway leading to DO3AN(R)P ligands. In general, these ligands were obtained by introducing a properly substituted aminoethyl group to the 1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid (DO3A) skeleton. A special attention was paid to the derivative caring a 2,2,2-trifluoroethyl group, which could potentially be used also for ^{19}F NMR imaging. Various methods for introducing the trifluoroethyl group were tested. The chosen synthetic precursor was prepared by a reduction of the corresponding trifluoroacetamide by several different routes using $LiAlH_4$ and BH_3 as reducing agents (including various reactions using *in situ* generated BH_3).