

Photoswitchable supramolecular systems based on carboxyl derivatives of thiacalix[4]arene and their complexes with Zn(II) and Tb(III) ions

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Abstract

© ISUCT Publishing. New lower rim functionalized thiacalix[4]arenes 7 and 8 in 1,3-alternate conformation containing photoswitchable azobenzene fragments and carboxyl groups as cation binding sites were obtained. The structure of the obtained compounds was established by 1D and 2D NMR^{1H} spectroscopy and MALDI-TOF mass spectrometry. The ability of compounds 7 and 8 to form nanoaggregates in solution was studied by dynamic light scattering (DLS) both in the presence of cations of d/f elements and without them. Compound 7 forms in the solution time-stable nanoparticles with a diameter of about 3.5 nm, which, according to molecular modeling, are monomers. A similar result has been obtained for complexes based on Zn(II) and Tb(III) cations in different metal/ligand ratios (from 1:1 to 4:1). The metal/ligand=2:1 stoichiometry determined by the UV-titration method for the complexes based on compound 7 indicates the formation of intramolecular chelate complexes typical for calixarenes in the 1,3-alternate conformation. Irradiation of macrocycle 7 solutions at a wavelength of 254 nm (8 W) for 30 minutes resulted in a small decrease of size of the nanoparticles till 2-2.5 nm. Obviously, compound 7 in cis form becomes more compact, which was confirmed by quantum-chemical modeling. A similar result is observed for the complexes with Zn(II) cations. For the Tb(III) ions which are considered as harder acids relative to Zn(II) cations, accordingly to HSAB theory, the aggregation process leads to increasing of nanoparticle size due to the interaction of Tb(III) cations with peripheral cis-N=N groups of compound 7. In contrast to macrocycle 7, compound 8 with Zn(II) and Tb(III) cations forms complexes of 1:1 stoichiometry. This leads to dramatic changing of aggregation behaviour of compound 8 compared to compound 7 either in the absence or in the presence of metal ions in the solution. Photoisomerization of the macrocycle 8 afforded an increasing (up to 2000 nm) of the size of the nanoaggregates observed in the solution. Thus, the formation of nanoscaled aggregates based on synthesized macrocycles and their complexes with Zn(II) and Tb(III) cations depends significantly on the availability of carboxyl groups for intermolecular interactions and the ability of metal ions to bind peripheral cis-azo groups. So, it has been shown that on the basis of synthesized macrocycles and their complexes with Zn(II) and Tb(III) cations, the photoswitchable supramolecular systems able to be controlled by the light irradiation can be created.

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Keywords

Azobenzene, External stimuli, Photoswitchable nano-sized aggregates, Tb complexes,

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