SYNTHESIS AND STABILITY OF ZIRCONIUM AND HAFNIUM PHTHALOCYANINES WITH OUT-OF-PLANE DOPAMINE LIGAND

Fedosova N.[1], Tretyakova I.[1], Chernii S.[1], Gerasymchuk Y.[2], Bilyy R.[3], Rotaru A.[4], Kovalska V.[1], Chernii V.[1]

[1]V.I. Vernadskii Institute of General and Inorganic Chemistry NASU, Kyiv, Ukraine

[2]Institute of Low Temperature and Structure Research PAS, Wroclaw, Poland

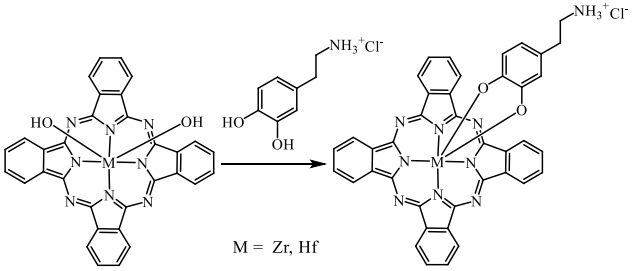
[3]Lectinotest R&D, Lviv, Ukraine

[4]"Petru Poni" Institute of Macromolecular Chemistry, Iasi, Romania

natalifedosovaia@gmail.com

This work is devoted to the synthesis, stability and optical properties of zirconium and hafnium phthalocyanine complexes with an out-of-plane coordinated dopamine ligand. The choice of dopamine as a ligand is based on the fact that it contains an aliphatic amino group suitable for covalent interaction with various substrates, in particular, biomolecules. As a rule, phthalocyanine complexes with out-of-plane ligands are synthesized starting from the corresponding zirconium (hafnium) dichloride or dicarboxylate phthalocyanines [1, 2]. In the course of the work, it was established that, based on dichloride complexes, the reaction proceeds with low yields, and dopamine does not react with dicarboxylate complexes at all. Therefore, the necessary complexes were obtained from the corresponding dihydroxophthalocyanine derivatives (Scheme). In the process of synthesis, water is released, which does not affect the course of the reaction, the yields of final products are about 75 %.

In the NMR spectra of the obtained compounds, there are signals corresponding to 16 protons of the phthalocyanine macrocycle in the region of 9.0–8.0 ppm, as well as signals of the out-of-plane ligand in the region of 7.9–7.7, 5.5–5.0, and 2.3–2.1 ppm. The analysis of integral intensities indicates the coordination of only one dopamine ligand to the central metal atom of the phthalocyanine macrocycle.



Scheme. Synthesis of zirconium and hafnium phthalocyanines with out-of-plane coordinated dopamine

The obtained complexes are soluble in aqueous and buffer media, their UV-Vis spectra show the typical patterns of phthalocyanine complexes with the characteristic B and Q bands at about 330 and 690 nm, respectively. It was established by UV-Vis spectroscopy that the obtained complexes are stable in cell culture media not less than 48 hours.

This work was supported by the Horizon 2020 MSCA RISE Grant No 872331 "Non-biased fluorescent dyes as markers of drugs for optical in cellulo and in vivo imaging"

1. Z Ou, R Zhan, LA Tomachynski et all. *Macroheterocycles*, **2011**, 4(3), 164–170.

2. YS Gerasymchuk, VY Chernii, LA Tomachynskii et all. *Optical Materials*, **2010**, 32 (9), 1193–1201.