



2-й Международный семинар по спектроскопии
и фотохимии макрогетероциклических
соединений 18–19 октября 2022 г.

Минск, БЕЛАРУСЬ

**Porphyrins as molecular probes of surface structure, optical
properties, and energy relaxation pathways for semiconductor
quantum dots**

E. Zenkevich^a, V. Sheinin^b, O. Kulikova^b, O. Koifman^b

^a*National Technical University of Belarus Prospect Nezavisimosti 65,
220013 Minsk, Belarus, e-mail: zenkev@tut.by*

^b*G.A. Krestov Institute of Solution Chemistry, Russian Acad. of Sciences,
153045 Ivanovo, Russia*

From the basic scientific and application point of view, the functionalization of semiconductor quantum dots (QDs) with suitable organic molecules or dyes is of great interest and the selection of appropriate dyes is crucial to tune the spectral-kinetic properties of QD-dye nanoassemblies.

Here, we present a comparative experimental data and quantum chemical calculations obtained for glutathione (GSH) stabilized QDs AgInS/ZnS upon their electrostatic interactions with positively charged 5,10,15,20-(tetra-N-methyl-4-pyridyl)porphyrin molecules in water at ambient temperature. Based on steady-state absorption/photoluminescence, time-resolved photoluminescence (TCSPC), and Raman spectroscopy, interface phenomena, photoluminescence quenching as well as pathways and mechanisms of exciton relaxation in “AgInS/ZnS QD – porphyrin” nanoassemblies are analyzed. Using the elaborated for the first time size-consistent quantum chemical atomistic 3D model for glutathione stabilized AgInS/ZnS QD, we propose a detailed physico-chemical mechanism for the interaction of the porphyrin molecule as molecular probes with the QD surface. It includes electrostatic interactions of the positively charged porphyrin free base molecule with negatively charged capping ligand (GSH), followed by a very fast metalation of porphyrin free base (formation of ligated Zn-porphyrin complex) which is directly fixed on the QD surface. Based on these results, it was evaluated that the strong “quasi-static” quenching of the QD photoluminescence is caused by two main competitive non-radiative processes – Förster resonance energy transfer AgInS/ZnS/GSH QD → Zn-porphyrin, and the electron tunneling beyond the AgInS/ZnS core under conditions of quantum confinement. The detailed analysis of the surface structure and interface phenomena in nanoassemblies based on semiconductor quantum dots and organic chromophores, is a key challenge for development of hybrid nanomaterials and their applications.

Acknowledgements. This work was supported by the program BSPSR program “Photonics and Electronics for Innovations (2021-2025, Belarus)”, RFBR grant № 18-53-00035 (Russia-Belarus), and Visiting Scholar Program of TU Chemnitz, Germany (E.Z., 2020-2021).