Volha Vetokhina
Ph.D. Thesis

**Spectroscopy, photophysics, conformational equilibria, and photoinduced tautomerization in selected bifunctional proton donor-acceptor azaaromatic molecules**

**ABSTRACT**

This work is devoted to a study of spectroscopic properties, photophysical processes and photochemical reactions in three series of trifunctional or bifunctional molecular systems having both a proton donor and acceptor centers. The aim of the work, *i.e.*, the qualitative and quantitative characterization of: (i) the photophysical parameters, (ii) the solvent-dependent rotamerization, and (iii) the ground and excited state tautomerization, was successfully realized with the use of steady-state and nanosecond and picosecond time-resolved UV-Vis spectroscopic methods, $^1$H NMR spectrometry, and quantum chemical computations. In order to study the solvent effects, the investigations have been performed in solutions and under supersonic jet isolation conditions.

The first family of compounds, 7-hydroxyquinoline-8-carbaldehydes (7-HQC), can exist in two tautomeric forms: **OH** (7-quinolinol) and **NH** (7(1$H$)-quinolinone). The compounds are composed of two moieties: a molecular “frame” (7-hydroxyquinolines, 7-HQ) and a proton “crane” (carbaldehyde group), and have been proposed to serve as models of a reversible optically driven molecular switch. The comparative studies of the spectroscopy and photophysics of the series of 7-HQC and 7-HQ and their prototropic reactions in a wide range of solvents allow us to explain the solvent-dependent mechanism of the ground and excited state long-range tautomerization.

The next two series of the studied compounds: (i) 2-(1H-pyrazol-5-yl)pyridines (2-PPs) and (ii) **indole derivatives** have the hydrogen bond donor and acceptor centers which are located in separate moieties, covalently linked by a single bond. The compounds can form syn (with the donor and the acceptor on the same side) and anti (with the two centers on the opposite sides) conformers via internal rotation around a single bond.

It is shown that 2-PPs are a rare example of molecules that exhibit three types of excited state proton transfer (ESPT) reactions: (i) intramolecular (ESIPT) in the syn form; (ii) intermolecular (ESDPT) in the dimers in nonpolar media, and (iii) solvent-assisted ESDPT in H-bonded 1:1 complexes with protic partners. The excited state processes are manifested by the appearance of dual luminescence and a bimodal irreversible kinetic coupling of the two fluorescence bands. Ground state syn-anti equilibria are detected and discussed. The fraction of the higher energy anti form varies for different derivatives and is strongly dependent on solvent polarity and hydrogen bond donor or acceptor ability.
On the contrary, spectroscopy and photophysics of selected bifunctional indole derivatives containing thiophene, thiazole, and furan, do not depend on solvent properties – independent of solvent polarity and hydrogen bond donor ability the compounds show strongly allowed and very efficient fluorescence. Due to the fact that the syn rotamers of these compounds are able to form cyclic, doubly hydrogen bonded complexes with protic partners which upon excitation can be efficiently deactivated in $S_1$ via internal conversion and/or proton transfer, such finding was not expected. On the other hand, the luminescence of 3-pyridin-4-yl-1H-indole (3-PI) is strongly quenched in alcohols and water. The mechanism of the excited-state deactivation leading to fluorescence quenching is proposed.