

Abstract

of the dissertation thesis titled

“Synthesis and spectral features of flavones in which intra- and intermolecular proton transfer occurs”

The doctoral dissertation thesis is devoted to investigations of inter- and intramolecular proton transfer in the excited state (ESPT) in various hydroxyflavone derivatives (hydroxy-2-phenylchromen-4*H*-ones).

7-Hydroxyflavone and its derivatives were selected for investigations of the intermolecular (“solvent-assisted”) ESPT and photodissociation reactions. It was found that spectral features of the compounds depend on the hydrogen-bonding ability of a media. In aqueous solutions, absorption and fluorescence of 7-hydroxyflavones depend on pH/ H_0 . Such dependence is due to coexistence of these compounds in three protolytic forms (cationic, neutral, and anionic) in the ground state and in four forms (cationic, two neutral tautomers, and anionic) in the excited state *via* protolytic dissociation reactions. Solvent-assisted ESPT transformation of one neutral tautomeric form to another in acidic and neutral media is most probably a two-step process including protolytic dissociation followed by protonation. Thermodynamics and kinetics of photodissociation processes in 7-hydroxyflavones investigated are finely tuned by the mesomeric electronic effect of a substituent at position *para* of the benzene ring. 7-Hydroxy-4'-methoxyflavone exhibits the most intensive and multiband fluorescence among the 7-hydroxyflavones investigated and can be prospectively applied as multiparametric fluorescent sensor of pH or level of media organization.

The phenomenon of coupled Excited State Intramolecular Proton Transfer (ESIPT) and protolytic dissociation was investigated in 3,7-dihydroxyflavone. It has been found, that in the 1–8 pH range, the compound undergoes a cascade of transformations in the excited state involving two neutral and two monoanionic tautomeric forms. ESIPT observed in monoanionic species is unusually slow and reversible. Coexistence of two monoanionic tautomeric forms is

the reason of dual fluorescence of 3,7-dihydroxyflavone in basic solutions, which is one of the most intensive ones reported so far for aqueous media. For these reasons, 3,7-dihydroxyflavone exhibits attractive features of ratiometric fluorescence sensor of pH and compounds of low deprotonating ability.

To facilitate efficient synthesis of 3,7-dihydroxyflavone using Algar-Flynn-Oyamada (AFO) reaction, its pathway was thoroughly analyzed. The conducted calculations enabled to draw conclusions as to the most probable mechanism of the AFO reaction. Furthermore, discovered relations between yields of variously substituted 3-hydroxyflavones and calculated atomic partial charges explained influence of the electron-releasing substituents on outcome of undergoing reactions. The research undertaken enabled synthesis of 3,7-dihydroxyflavone with a good yield.

Novel carbonyl derivatives of 3,7-dihydroxyflavone were designed and synthesized in order to investigate the Double ESIPT (ESIDPT). Spectral behavior of the compounds and excited state tautomeric transformations investigated experimentally revealed that ESIDPT occurs in one of them. ESIDPT occurs *via* stepwise mechanism and leads to the tautomeric species exhibiting abnormally low rate constant of radiative deactivation and consequently very low fluorescence quantum yield. The investigations of various hydroxyflavone derivatives containing carbonyl substituents reveal that proton transfer occurs in the excited state of all of them, which opens new horizons in design and creation of new ESIPT and ESIDPT fluorophores.

The thesis is structured in the following way. ESPT phenomena, their importance for fluorescence spectroscopy, as well as compounds selected for research together with the aims of investigations are described in Introduction section. Chapter 1 is a brief review of methods of synthesis of hydroxyflavones as well as their spectral properties conditioned by ESPT. Methods of synthesis and investigations carried out in the research undertaken are described in Chapter 2. The most significant in author's opinion findings together with the supporting them experimental and theoretical evidences are discussed in Chapter 3.