Abstract in English

Synthesis and photophysical properties of novel merocyanine dyes

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The main objective of my PhD course was to gain deep insight the synthesis and optical properties of rhodols, which might be applied in cell imaging and STED microscopy. I have started with development of the synthesis rhodols possessing endocyclic sulfone fragment. This was achieved via the 3-step synthesis of corresponding rhodamines, followed by the substitution of dimethylamino moiety with the oxygen atom. Having new sulfone-rhodols in hand, I decided to modify one of them by incorporation of hexyl chain with the quaternary phosphonium center at the terminal position to make the dye suitable for cell imaging. These compounds possess intriguing optical properties i.e. high fluorescent quantum yields and high Stokes shifts as well as excellent photostabilities.

The next goal was to develop the synthetic approach towards rhodols from coumarins via Knoevenagel condensation. For this purpose, I have synthesized 4-hydroxycoumarins possessing diethylamino moiety and the coumarin analogue with the annulated nitrogen atom at the position 7 and after additional 3 steps I have obtained 3-formyl-coumarins as the rhodol precursors. This double Knoevenagel condensation of 3-formyl coumarins with dimethyl 1,3-acetonedicarboxylate is absolutely unprecedent, because at the second step the source of carbonyl group is lactone ester, which is typically considered to be inert in this type of reactions. I have performed a huge part of work trying to find the best conditions for this condensation. In this case I tried various Lewis acids, bases, solvents, different temperature and the reaction time. Besides, on the basis of the electronic spectroscopy I have developed a convenient method for screening multiple experiments in the tiny scale to evaluate conversion and yields of reactions without workup and purification. As a matter of fact, the best catalyst revealed to be piperidine. This reaction allowed me to obtain new rhodols possessing two ester groups in 13-28% yield. The obtained rhodols demonstrate excellent quantum yields: 0.47 – 1.00 in DCM and DMSO.

The final of my research was a discovery of an extraordinary straightforward one-step synthesis of rhodols from *m*-aminophenols and tetrafluorohydroxybenzaldehyde. This method is similar to classic Friedel-Crafts condensation with a difference that a molecule of HF forms during the reaction instead of water as in the original method. The reaction successfully proceeds in toluene or xylene at elevated temperatures and does not require any bases or other additives. The product precipitates from the reaction mixture and can be purified via simple recrystallization. This approach is applicable to *m*-aminophenols, 4-hydroxy-7-aminocoumarins and

hydroxyaminonaphthalenes, that allowed me to obtain an uncommon π-expanded linear rhodol and π-expanded rhodol analogues. This is the first representative of π-expanded rhodols with the additional benzene ring from amino side possessing the linear chromophore.