

Coumarin derivatives with π -extended chromophore - synthesis and photophysical properties

Author: BSc Marek Krzysztof Charyton

Supervisor: Prof. Daniel Tomasz Gryko

The aim of this Doctoral Thesis was to develop a new, efficient method of the synthesis of coumarin-based compounds with an extended chromophore. Furthermore, the physicochemical properties and possible application of this novel class of functional dyes were also studied.

To begin with, the conditions of Knoevenagel's condensation, reported by Klimenko (L. Ya. Mainagashev, L. S. Klimenko, *Russ. Chem. Bull.*, 1996, 45, 2569), were deeply studied and subsequently modified in order to optimize and improve the reaction's yield. Klimenko's work describes reactions carried out between various 1-acyloxyanthraquinone derivatives and phenylacetonitrile. In my project in the model reactions, the reagents were replaced: 1-acyloxyanthraquinone with 1,5-dibenzoyloxyanthraquinone or 1,4-dibenzoyloxyanthraquinone while phenylacetonitrile with phenylacetic acid ester derivatives, respectively. The next stage was focused on studying the influence of time, temperature, solvents and added base on the overall reaction's yield as well as distribution of side and main products. This leads to a conclusion that the highest yield and the lowest amount of side products can be achieved under the following conditions: DMSO, K_2CO_3 , 100°C, 1 hour. A series of heretofore unknown biscoumarins exhibiting low photostability were obtained under these conditions. The next phase of my research was focused on explaining the process occurring while exposing these compounds to light. The biscoumarin derivatives exposed to light underwent transformation into stable pigments. Due to extremely low solubility, their structural analysis was very difficult. The mass measurements of the obtained pigments indicated a mass reduction by 4 units comparing to initial compounds. This allowed to conclude that the exposing to light leads to form two intramolecular bonds. Considering the mass decrease and drastic deterioration of solubility, 6π -electrocyclization was suspected resulting in obtaining a molecule possessing dibenzo[*fg,qr*]pentacene core. In order to improve solubility of the dibenzo[*fg,qr*]pentacene derivatives, the reaction was performed with a biscoumarin containing 4 hexyl groups. This modification allows the synthesis of a soluble dibenzo[*fg,qr*]pentacene product, enabling the analysis of the compound's structure. A soluble dibenzo[*fg,qr*]pentacene derivative was obtained both in the Mallory reaction (photochemical transformation) and via the intramolecular oxidative aromatic coupling.

Physicochemical measurements were performed for the poorly soluble biscoumarin derivatives, showing the quantum yield of fluorescence on moderate level (10-31%). The dibenzo[*fg,qr*]pentacene dye exhibits much stronger fluorescence equal to 90%.

Moreover electrochemical properties of pentacene derivatives were investigated. Cyclic chronovoltammetry has proven the semiconducting properties of the compounds, which allows the application as active materials in field transistors. The measurements show that two of the biscoumarins exhibit n-type of conductivity whereas one of the compounds behave as an ambipolar semiconductor. In addition, further investigation, carried out in cooperation with Kepler University in Linz, has proven that the obtained compounds can be used as promising photo-catalysts in the process of oxidation of H_2O to H_2O_2 in the presence of O_2 and light.

Subsequently, I discovered the synthesis of previously unknown aromatic compounds - benzofuraniminocoumarins *via* Knoevenagel condensation of 1,5-dibenzoyloxyanthraquinone and phenylacetonitrile derivatives. The spectroscopic measurements show that the obtained compounds exhibit weak fluorescence, however, after transformation into triflic imides, a significant bathochromic shift of absorption bands (approximately 70 nm) was observed followed by even larger shifts of the emission bands (70-100 nm) as well as a significant increase in the fluorescence quantum yield from moderate values for imines (4-40%) to very high ones for imides (above 90%). Moreover, this is the first scientific work describing the influence of electron-withdrawing substituent on the nitrogen atom on the optical properties of iminocoumarines. Solvatofluorochromism was also observed for these dyes.

In summary, this Thesis presents detailed researches among the synthesis and physicochemical properties of three new families of organic functional dyes based on π -extended coumarinoids. Due to the promising optical and electrochemical properties of the obtained compounds, they can be applied in the field of optoelectronic devices such as transistors or photo-catalysts.