Derivatives of pyrrolo[3,2-*b*]pyrrole exhibiting high two photon cross section

Anita Anna Janiga

Supervisor: Prof. Daniel T. Gryko

A practical synthesis of nonfused 1,4-dihydropyrrole[3,2-*b*]pyrroles in a domino reaction of aldehydes, primary amines, and butane-2,3-dione has been discovered. Six bonds are formed in a tandem process, which gives rise to tetrasubstituted pyrrole[3,2-*b*]pyrroles - the least studied among heteropentalenes. Unparalleled simplicity and versatility of this one-pot reaction, no chromatography, as well as superb optical properties, including high fluorescence quantum yield, have the potential to make 1,4-dihydropyrrole[3,2-*b*]pyrroles the molecules of choice for various applications. As a proof of principle, HeLa cell uptake of selected dyes was demonstrated. Moreover reactivity of invented dyes was studied comprehensively and series of 3,6-disubstituted derivatives was obtained.

The main goal of the PhD thesis was to synthesize the pyrrolo[3,2-*b*]pyrrole core-based dyes, presenting quadrupolar, acceptor-donor-acceptor general framework which exhibit high two-photon absorption cross-section (σ_2) and high fluorescence quantum yield (Φ_{fl}) for two-photon fluorescence microscopy application. Therefore unique, electron-excessive pyrrole[3,2-*b*]pyrrole moiety, linked *via* triple bonds was synthetized. It was demonstrated that the increase in molecular length of the chromophore effectively extends π-conjugation. The effect of structural variations on photophysical properties was studied in detail for these compounds. All of the π-expanded pyrrolo[3,2-*b*]pyrroles are fluorescent in solid and in the solution. Moreover the unprecedented ladder-type electron-rich hetero-hexacenes were synthesized. They constitute the most electron-rich ladder-type heteroacenes known to date and they possess strong blue-green fluorescence both in solution as well as in the solid state. Obtained bis(indolo[3,2-*b*])pyrrolo[3,2-*b*]pyrrole derivatives possess high lying HOMO level. Thanks to the combination of optical and electrochemical properties, these new functional dyes hold great promise in the broad field of opto-electronics.

In conclusion, obtained results are not only of theoretical significance, but they may also open the door to practical applications. The use of discovered approach can lead to the synthesis of a wide range of intrinsically electron-rich 1,4-dihydropyrrole[3,2-*b*]pyrroles, which can serve as ideal platforms in such diverse areas as fluorescent imaging and molecular electronics.