

Title: 1,4-Dihydropyrrolo[3,2-*b*]pyrroles- synthesis and optical properties

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The main objective of my PhD project was to gain deep insight into the synthesis, reactivity and optical properties of analogs and derivatives of pyrrolo[3,2-*b*]pyrroles, which in the future may be applied in photonics or organic electronics. I have started with optimization of the novel methodology for the synthesis of tetraarylopyrrolo[3,2-*b*]pyrroles developed in our laboratory. Condensation between aromatic aldehydes, aromatic amines and diacetyl leads to 1,4-dihydropyrrolo[3,2-*b*]pyrrole derivatives. It turned out that addition of catalytic amount of *para*-toluenesulfonic acid to the reaction mixture significantly improves reaction's yield. Having optimized methodology in hand, I designed novel compounds possessing pyrrolo[3,2-*b*]pyrrole core taking advantage of the fact that position 3 and 6 of intrinsically electron-excessive core offer an ideal reacting site for both oxidative coupling and direct arylation. I have synthesized unprecedented penta- and hexaarylopyrrolo[3,2-*b*]pyrroles which adopt propeller-like architectures. These compounds possess intriguing optical properties, and astonishingly high values of two photon absorption cross section, given their limited conjugation. The next goal was to synthesize flat, ladder-type analogs possessing pyrrolo[3,2-*b*]pyrrole core. Scrupulous design of *ortho*-arylbenzaldehydes gave rise to the synthesis of tetraarylopyrrolo[3,2-*b*]pyrroles susceptible to oxidative aromatic coupling. Indeed treating these compounds with iron(III) chloride produces π -expanded ladder-type analogs of pyrrolo[3,2-*b*]pyrroles. All the final dyes are blue-emitters. They exhibit very narrow emission curves, which is of great importance in OLED technology. Building upon these results I have designed the synthesis of curved heterocyclic analogs of polycyclic aromatic hydrocarbons. These compounds adopt helicene-like shape due to the steric repulsion between adjacent benzene rings. They possess very interesting optical properties including solvatochromism. The latter one is very intriguing since such phenomenon was reserved for dipolar molecules. The final chapter of my research was serendipitous discovery regarding the influence of steric hindrance in intramolecular oxidative aromatic coupling. I have obtained completely new chromophore built upon pyrrolopyrrolium salt core possessing spiro carbon atom. These compounds exhibit moderately intense red fluorescence. Comprehensive studies on the synthesis and optical properties of pyrrolo[3,2-*b*]pyrroles contributed to better understanding of their nature and can open the door to the optoelectronic applications in the future.