

Abstract in English

The advancement of organic electronic materials relies heavily on the ability to design and synthesize new molecular frameworks with tunable optoelectronic properties. My research integrates synthetic organic chemistry with materials science, focusing on donor-acceptor (D-A) conjugated fluorophores belonging to the group of fused polycyclic aromatic and heteroaromatic hydrocarbons, which are multiply functionalized for light-emitting applications. Through my doctoral studies, I developed new synthetic strategies, explored fundamental structure property relationships. In addition to that, I also established versatile molecular design platforms that enable high-efficiency emission and controllable photophysical behavior. I also discovered various phenomena operating in these systems, like aggregation-caused quenching (ACQ), aggregation-induced emission (AIE), and twisted intramolecular charge transfer (TICT). The presented dissertation is part of a broad project aimed at the development of a new class of multi-substituted anthracene derivatives obtained *via* the *phospho*-Friedel-Crafts-Bradsher (F-C-B) cyclization. The main goal of this work was to develop novel synthetic routes for anthracene functionalization, primarily on peripheral rings, and to investigate photophysical, chemical, and electrochemical properties of the synthesized derivatives. Such compounds revealed high fluorescence quantum yields, significant photostability, and unique electronic properties.

The introduction part of this dissertation provides a general overview of a few classes of phosphorus substituted anthracene derivatives, which were obtained in the dissertation. Section 1.4, primarily concentrates on the synthesis and properties of phosphoryl (P=O) substituted anthracene derivatives, such as phosphine oxides, phosphine sulfides, phosphine selenides and phosphonates, the characteristic feature of which is multiply substitution by electronically diverse substituents. This section serves as a significant reference point for the achievements realized within this research area.

The results and discussion part of this dissertation focuses on the synthesis of multi-substituted anthracene derivatives containing diphenylphosphoryl, their thio- and seleno derivatives as well as diethoxyphosphoryl moieties, leading to several significant contributions. This part also helps to understand the electronic and optical properties of anthracenes and higher acenes through strategic incorporation of phosphorus substituents. Starting with section 3.1, which focuses on the one-pot three-step synthesis of 10-(diphenylphosphoryl)anthracenes, the C-O-P to C-P(=O) rearrangement is followed by the *phospho*-F-C-B cyclization. This strategy enabled the introduction of electron-withdrawing phosphorus moieties under mild conditions and provided access to anthracene derivatives with high photoluminescence quantum yields up to 95% yield in solution and > 95% in solid, and tunable emission properties. These findings were published in the *J. Org. Chem.* 2025, 90, 13, 4580-4590. In another project published in *Angewandte Chemie Int.Ed.* 2025, e202508168 (Section 3.3), I contributed to the synthesis and characterization of a phosphorus substituted (hetero)acene and corresponding substrates *via* the *phospho*-F-C-B

cyclization. A brief overview of these findings is presented in sections 3.1 and 3.3, with comprehensive details available in the enclosed publications.

The obtained anthracene derivatives in section 3.1, substituted with bromine at the position 7 were utilized to further expand the synthesis of more π -conjugated anthracene derivatives. The Sonogashira cross-coupling was employed to introduce various electron-donating and electron-withdrawing substituents *via* phenylethynyl linkages at the 7-position of anthracene (Section 3.2). As a result of this work, a series of 10-(diphenylphosphoryl)-7-(phenylethynyl)anthracenes was obtained, which exhibited pronounced solvent-dependent photophysical properties, particularly twisted intramolecular charge transfer (TICT) in compounds bearing dimethylamino or dicyanovinyl groups. Detailed characterization of the resulted 10-(diphenylphosphoryl)-7-(phenylethynyl)anthracenes derivatives by spectroscopic (UV-Vis absorption, fluorescence emission, quantum yields) and electrochemical (cyclic voltammetry) methods was performed. The manuscript containing these results is being prepared for submission.

The last section in this dissertation concerns the *ortho*-positional isomers of anthracene and carbazole derivatives containing phosphonate ester groups (Section 3.4). These compounds were synthesized *via* a three-step strategy incorporating the key *phospho*-F-C-B cyclization, followed by post-functionalization through the Knoevenagel condensation and the Sonogashira coupling in order to introduce ethynyl and dicyanovinyl moieties in new sets of post-functionalized *ortho*-positional isomers (section 3.5). These studies showed that a small change in the substitution pattern could significantly change fluorescence behavior, quantum yields, and redox potentials. Interestingly, some isomers showed quantum yields exceeding 90% and offered precise control over HOMO-LUMO energy levels. The results of the first part of this study are currently undergoing a peer review process, while the manuscripts for the subsequent studies are in preparation for submission.