

Donor-acceptor pentacene analogs

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This dissertation reports the design, synthesis, and characterization of pentacene analogs incorporating the ***para*-quinodimethane (QDM)** core, which is highly polarized by non-symmetrically incorporated heteroatoms or groups, thereby creating a donor-acceptor system. Molecules with a non-symmetric QDM core, particularly interesting for their strong molecular polarization, remain largely unexplored and may lead to highly stable acene analogs. Therefore, the main goal was to develop synthetic routes to analogs of pentacene substituted at positions C5 and C12 with electronically distinct donor and acceptor heteroatoms/groups (**DA-pentacenes**), and to study how this functionalization influences their properties.

The first part of the research involves a comprehensive review of acenes, their diradicaloid behavior, and stabilization methods. Special focus is placed on heteroacenes and quinodimethane-derived systems, which enable access to open-shell or polarized structures while maintaining acene-like properties.

The first part of the experimental results discusses the synthesis and evaluates two strategies. The first, using polybrominated precursors, had low yields and unstable intermediates. The second, more efficient method employed functionalized terephthalate esters for forming C–N, C–S, and C–P bonds via palladium-catalyzed coupling reactions, followed by Friedel–Crafts cyclizations. Nucleophilic additions of lithiated reagents and controlled reductions produced various **DA-pentacenes**. Introduction of a carbonyl group required a separate synthetic pathway. The resulting **DA-pentacenes** include azasulfonyl, azaphosphine oxide and azaketone derivatives, whose steric and electronic environments were tuned through substituents varying in steric and electronic effects.

The second experimental part focuses on characterizing the properties of **DA-pentacenes**. The pentacene analogues exhibit narrow bandgaps with noticeable solvatochromism in absorption and emission, along with reversible redox behaviors consistent with strongly polarized electronic structures. A key achievement was demonstrating how solvent polarity and donor-acceptor strength influence the aromatic character of the central quinodimethane unit.

Overall, this work demonstrates practical synthetic methods for non-symmetric pentacene analogs, revealing how incorporation of highly polarized QDM affects their aromaticity, photophysics, redox properties, and stability. These findings emphasize the potential of polarized acene systems as tunable organic semiconductors for future optoelectronic applications.