Acene-based Architectures for Singlet Fission

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Abstract (English)

Singlet fission (SF) is a promising photophysical process for enhancing the efficiency of next-generation photovoltaic and optoelectronic devices by generating two triplet excitons from one photoexcited singlet state. Despite extensive investigation, the molecular factors governing efficient SF, particularly the role of intermolecular geometry, interchromophore distance, and electronic coupling, remain incompletely understood. This dissertation advances the mechanistic understanding of SF and provides molecular-design guidelines for acene-based chromophores, with particular emphasis on pentacene derivatives.

Chapter 1 introduces singlet fission and its energy requirements, the stability and functionalization of acenes, and the use of acene dimers as model systems for mechanistic studies. Chapter 2 describes the synthesis of pentacene dimers containing *para*-phenylene, *meta*-phenylene, and adamantyl spacers connected through phenylethynyl linkers of different lengths. Their steady-state photophysical properties are discussed, and ultrafast transient absorption spectroscopy, performed by collaborators, is used to elucidate excited-state dynamics and singlet-fission pathways.

Chapter 3 focuses on the synthesis of resorcin[4]arene cavitands functionalized with pentacene or tetracene chromophores. These switchable systems were designed to reversibly modulate chromophore proximity, thereby enabling investigation of how conformational changes influence SF dynamics. UV-vis spectroscopy was employed to probe the conformational switching of these architectures upon addition of external stimuli.

The results described in Chapter 3 revealed the limited stability of pentacene derivatives under acidic conditions, motivating a detailed investigation of the chemical reactivity of TIPS-pentacene and related acene derivatives. Chapter 4 therefore examines the stability and reactivity of these acenes under acidic conditions. UV-vis titration, UV-vis-NIR spectroscopy, and EPR analysis support a radical-cation-mediated reaction pathway in the acid-mediated dimerization of TIPS-pentacene.

Finally, Chapter 5 summarizes the major findings of this dissertation and provides an outlook for the future design of acene-based systems for singlet fission studies

Chapter 6 contains detailed synthetic procedures and spectroscopic characterization data for compounds discussed in this dissertation.