

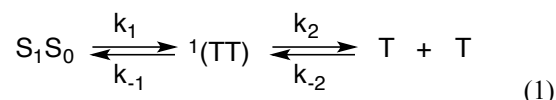
PRF#: 57843-ND4

**Project Title:** Acene Dimers: Synthesis, Structure, and Photochemical Properties

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**Narrative:** In this project, we propose to synthesize and study the photophysical properties of a series of acene-derived cyclophanes that have differing distance and geometries between the two acenes. Acenes are linear polyaromatic hydrocarbons some of which are capable of undergoing singlet fission (SF). This is a process that occurs between two chromophores wherein a (nominally localized) singlet excitation described as ( $S_1S_0$ ) undergoes a non-radiative conversion to a singlet-coupled pair of triplets ( $^1(TT)$ ). This multiexcitonic state can then convert to uncorrelated electronic excitations,  $T + T$  (Eq 1). This process can be rapid, provided that it is not significantly endergonic and that electronic coupling between the chromophores is favorable. For favorable energetics, the energy of  $S_1$  should be about two times (or greater) that of  $T_1$ .



The process can be rapid as it is spin allowed and can proceed via two pathways (Figure 1). One is dubbed “electron transfer”, the other “hole transfer”. In the “electron transfer” coupling, the excited electron in chromophore A is transferred to the LUMO of chromophore B and a ground state electron in chromophore B is transferred to the LUMO of chromophore A (Figure 1, left). By the hole transfer coupling, a ground state electron of chromophore B is transferred to the HOMO of chromophore A, and the other HOMO electron of chromophore A is transferred to the LUMO of chromophore B (Figure 1, right). Both pathways proceed via charge transfer (CT) states (i.e., the initial state wherein an electron has been transferred) that are virtually occupied during the energy transfer. These CT states can be coupled to both the starting state ( $S_1S_0$ ) and the product ( $^1(TT)$ ), and it is this coupling that permits the reaction to proceed and that we are probing using the molecules that we are synthesizing in this proposal.

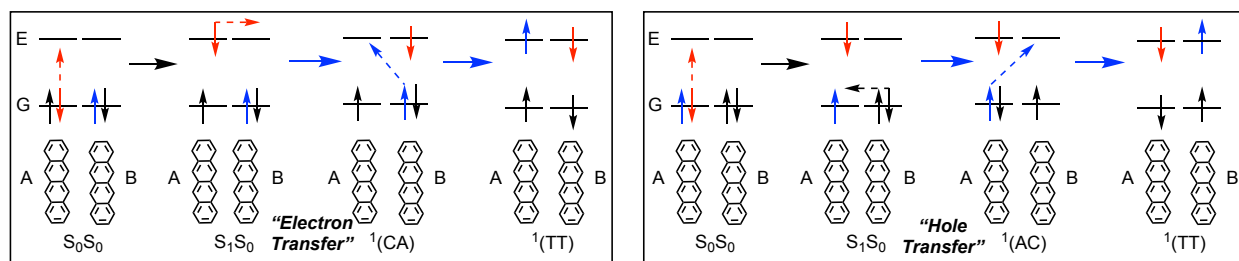


Figure 1

There are a relatively small number of chromophores that have the requisite energetics between  $S_1$  and  $T_1$  for efficient SF, with the most studied being the acenes, which are linear polyaromatic hydrocarbons. For naphthalene and anthracene, the energy of  $2xT_1$  is greater than  $S_1$ ; however, in longer acenes such as tetracene and pentacene  $2xT_1$  is either close to the energy of  $S_1$  or lower, rendering SF a potentially favorable process, so long as there is sufficient coupling between the chromophores.

In this proposal, we ask how spatial orientation and distance of chromophores impact the coupling of excited states in molecules that contain two chromophores, and how this coupling influences energy transfer among different excited states. To answer this question, we proposed to synthesize a series of bis-acene cyclophanes wherein the distance and geometry between the two acenes is systematically varied. Generalized renditions of the desired cyclophanes are shown in Figures 2a and 2b below. Note that the linkers, “A” and “A-A” can be varied to adjust the distance and geometry of the two acenes relative to each other. Once synthesized, the geometry will be determined by crystallographic methods and the rate and extent of singlet fission measured to determine and better understand the geometric factors that influence singlet fission.

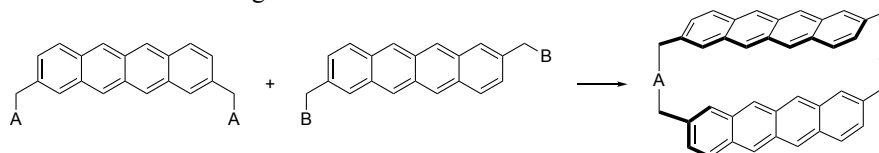


Figure 2a

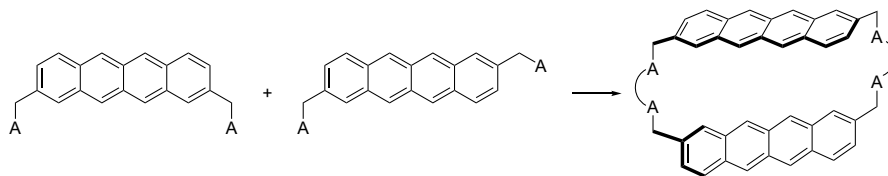
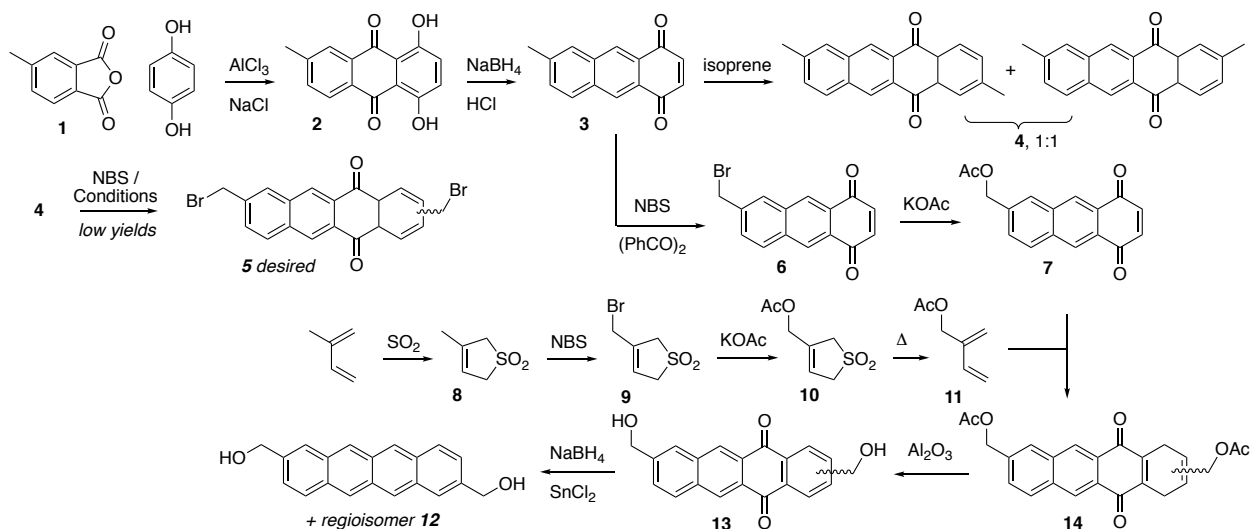


Figure 2b

During the past year, we have focused on the synthesis of the proposed acene cyclophanes. This poses several challenges, including, in some cases, the handling of sparsely soluble aromatic compounds, the synthesis of intermediates that are prone to decomposition and are difficult to purify, and the separation of compounds that are regioisomeric at remote sites.

Our strategy requires the synthesis of tetracene derivatives bearing benzylic functionality, including a suitable leaving group for coupling with linkers. In our initial attempts, we prepared quinone **4** as a mixture of regioisomers and studied its radical bromination under a variety of conditions (Scheme 1, **4** to **5**). Under our best conditions, we found that the desired product was produced in relatively small amounts with either monobromination observed as the major product or over bromination when greater equivalents of brominating agent are used. We therefore turned to a modified strategy that takes advantage of the efficient mono-bromination of a quinone, but wherein the oxidation at the other benzylic position is built in to the substrate. By this strategy, a functionalized isoprene unit (**11**) was prepared and subjected to a Diels-Alder reaction with functionalized quinone derivative, **7**. This produced **14** bearing a mixture of acetoxy regioisomers which will be separated later in the sequence. Subjecting this mixture to alumina/air provided the oxidized product **13** with concomitant loss of the acetate groups. Reduction with sodium borohydride followed by stannous chloride provided an orange material that is insoluble in chloroform, DMSO, or other common solvents.



Scheme 1

Moving forward, we will prepare derivatives of **14** wherein the hydroxyl groups are protected not as acetates, but as silyl ethers. Monodeprotection of these followed by coupling with a linker will then provide a dimer. Deprotection of the dimer followed by coupling with a second equivalent of the linker will provide the functionalized cyclophane. Variations in the identity and size of linker will provide cyclophanes wherein the tetracenes are spaced differently.

**Impact:** The impact of this award has been substantial as it has allowed me and the graduate student working on this project to explore a new avenue of research that would otherwise not be possible. Equally significantly, as a synthetic chemist, my lab is in a position to prepare complex molecules that less synthetic groups would not pursue and in collaboration with the co-PI on this project, we can combine expertise and explore areas of physical organic chemistry that would not otherwise be possible. This collaboration has tremendous impact on the graduate student working on this project as it exposed him to areas of science that he would not be exposed to otherwise, offering opportunities to greatly broaden his scientific exposure and expertise.

**Publications:** None to date.