Final Report Project 22-26

A New Approach to Multielectron Photocatalysis

Summary:

Solar energy can be used to make hydrogen or hydrocarbons. But these chemical reactions usually need to absorb multiple electrons to happen. Usually, only one absorbed photon can can generate a single electron, meaning multiple photons must be absorbed, accumulating electrons, which leads to reduced yield. In photoredox catalysis, where one electron is transferred at a time to solve this problem, the highly reactive intermediates cause side reactions and reduce the selectivity. The main goal of this project is to understand how multielectron photocatalysis can be improved by using the exciton multiplication process called singlet fission. Towards this end a singlet fission dimer was prepared and we were able to investigate and provide chemical insights to the nature of the singlet fission generated multiexcited triplet pair state (^{1}TT) with implications for electron transfer reactions from SF materials. We demonstrated that electron transfer from the ^{1}TT state in a tetracene dimer can occur through two different mechanisms. The findings have been submitted for publication and is available as a preprint at ChemRxiv (10.26434/chemrxiv-2025-jw8kc)

Project report:

To directly produce fuels from solar energy through photocatalysis would have a profound societal impact. It would enable the storage of intermittent solar energy and the direct use of the fuel in transportation infrastructure. However, realising cost-effective and efficient photocatalysis for solar-fuel production remains a key challenge. For solar-fuel production of hydrogen (H_2) or hydrocarbons, chemical reactions often require multiple electrons to proceed. Typically, one absorbed photon at most generates one electron. Consequently, multiple photons must be absorbed, leading to electron accumulation and potential losses in yield.

Therefore, the primary objective of this project is to develop and demonstrate a novel and more efficient approach for multielectron photocatalysis by harnessing the exciton multiplication process known as singlet fission (SF). Although singlet fission has been recognised since the 1960s, it has not been explored for its potential in photocatalysis. As a multi-exciton generation process, singlet fission holds the promise of overcoming the significant challenge of accumulating electrons through consecutive photon absorption.

In essence, this study aims to investigate the potential of singlet fission (SF) to enhance photocatalytic multi electron reactions. SF, a process where an excited singlet state splits into two triplet states is described by:[3]

$$S_0S_0 \xrightarrow{h\nu} S_0S_1 \rightleftarrows {}^1TT \rightleftarrows {}^1[T\ldots T] \rightleftarrows T_1 + T_1$$

Where S_0, S_1, and T_1 are the ground state singlet, first excited singlet and first excited triplet state, respectively. ^{1}TT and ^{1}[T$\cdots$T] are the strongly, and weakly correlated triplet pair states, respectively. Which excited states are best suited for charge extraction remains a question of

ongoing debate. In the funded project we clearly illustrated the chemical difference between the triplet pair and free triplet state in tetracene dimers in relation to electron transfer.

Method:

The project commenced with the synthesis of SF dimers, molecules comprising two identical chromophores known to undergo SF in solid state. The choice fell on TIPS-Tetracene as it is a soluble and high yielding SF chromophore. The first dimer (Methoxy-dimer figure 1) that was targeted turned out to be too weakly coupled to allow for efficient SF.

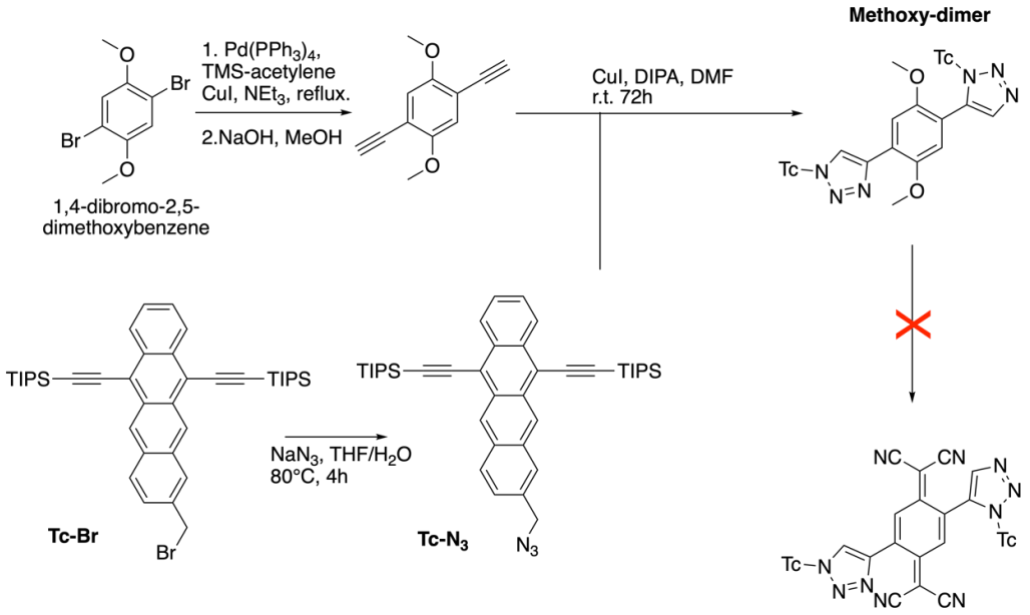

Figure 1. Synthetic route to first singlet fission dimer.

A redesigned SF dimer (Figure 2), similarly linked as the first dimer at the 2-position, however with continuous conjugation through an ethynyl-phenyl-ethynyl bridge, was then prepared. Instead of methoxy-groups longer hexyloxy-groups were used to increase the solubility. Many of the same starting materials and intermediates could be reused in for the second synthesis. The second dimer proved suitable for the study of electron transfer from both the ^1TT and T_1 states.

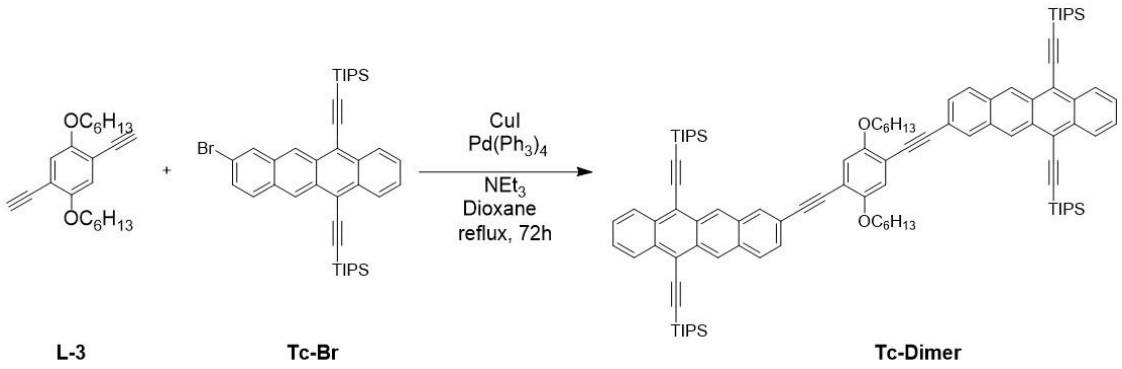

Figure 2. Synthetic route to second singlet fission dimer

Time-resolved fluorescence and transient absorption spectroscopy was used to follow the excited state dynamics. These techniques revealed the formation of the ^{1}TT state. Notably, the

^{1}TT state transitions to form only one free triplet, a common problem for SF dimers that are strongly to moderately coupled. However, this proved to offer an ability for us to specifically probe the different excited states. By using electron acceptors and donors with different redox potentials and varying the concentration of these, we were able to tune electron to occur from either the ^{1}TT or T_1 states.

Results:

The study revealed that electron transfer from the ^{1}TT state can occur through two distinct mechanisms, depending on the energetically accessible pathways. When there's insufficient driving force for electron transfer from a single T_1, the ^{1}TT state behaves similarly to the S_1 state, allowing a maximum of one electron transfer event per photon absorption. However, if electron transfer from T_1 is feasible, it becomes energetically viable to extract two electrons from ^{1}TT in a sequential, or potentially through a concerted, mechanism. Consequently, while the initial steps of SF are highly efficient (^{1}TT formation), if T_1 formation is limited, as is often the case with many dimers, only excessively high acceptor (donor) concentrations will yield electron transfer yields exceeding 100% if the ^{1}TT can be accessed. This emphasises the paramount importance of accounting for the relative redox potentials of the acceptor and donor compared to the T1 energy when designing solar cell and photoredox catalyst dimers.

The study has been submitted for publication and is currently available as a prepring on ChemRxiv: 10.26434/chemrxiv-2025-jw8kc.