PRF # 58739-UNI6
Photo-Oxidation of Thiophene-Containing Moieties in Dyadic Model Systems
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1. Research Progress

This project will characterize electronic dynamics in a series of custom-synthesized charge transfer dyads. A better understanding of light-driven charge transfer in thiophene-based compounds may improve photo-oxidative desulfurization methods used to refine petroleum.

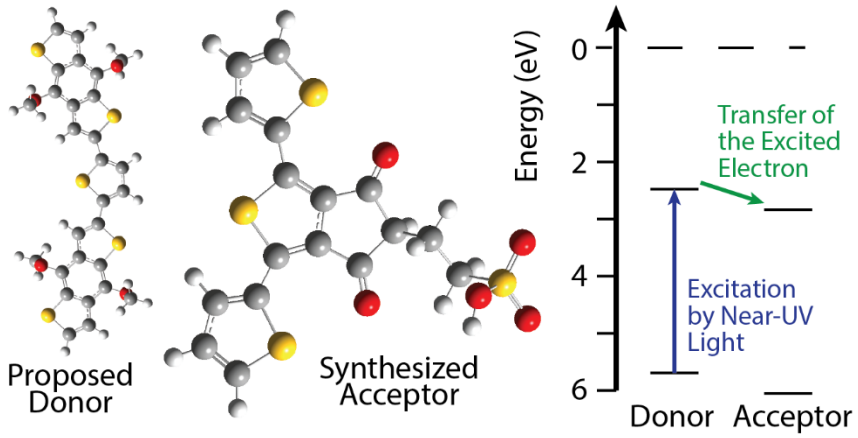

Figure 1: Geometry and Electronic Structure. *[LEFT] The predicted geometry of the acceptor and a proposed donor molecule. [RIGHT] The predicted electronic energy levels of the donor and acceptor, showing ~100 meV downhill path for excited electron transfer.*

To date the synthesis of one acceptor is complete (Figure 1). Ultimately, this acceptor will be chemically linked to a donor to form a macromolecular dyad. Electronic structure calculations using the CAM-B3LYP method demonstrate that the unlinked donor and acceptor molecules should provide the necessary energetic landscape for electronic relaxation through charge transfer. Electronic structure calculations were also used to explore the effects of the solvent environment and the protonation state of the acceptor.

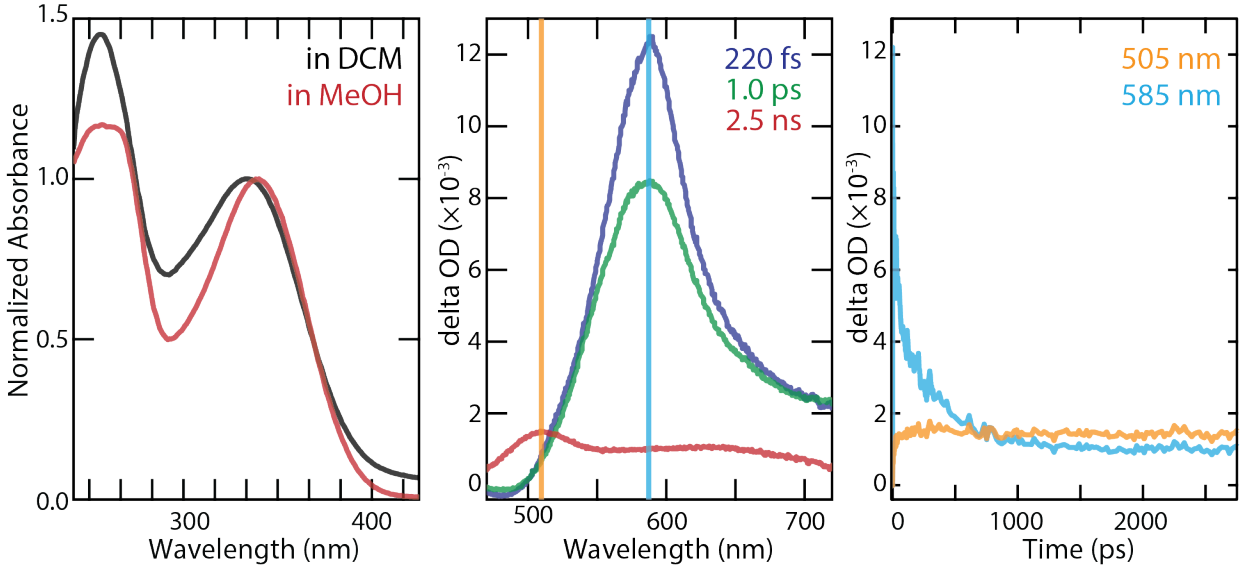

Figure 2: Static and Dynamic Spectroscopy of the Acceptor in Solution. *[LEFT] The absorbance spectrum of the acceptor displays only a small shift as the dielectric constant of the solvent varies. Transient absorbance spectra [CENTER] and kinetics [RIGHT] reveal multiple relaxation pathways and a long-lived excited state that survives beyond the ~3 ns range of the measurement.*

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Electronic relaxation dynamics in the acceptor molecule in various solvents have been characterized with static and dynamic spectroscopies (Figure 2). Varying the dielectric constant of the solvent produces only a small shift in absorbance and emission features. Transient absorbance spectra reveal excited state absorption that decays on multiple timescales, as well as a long-lived excited state feature that appears within in the first ten picoseconds and survives for a few hundred nanoseconds.

2. Student Impact

This award funded three undergraduate students as research assistants during the spring and throughout the summer. The team of students used absorbance and fluorescence spectroscopy to characterize several new molecules that we received from collaborators, including the electron acceptor synthesized by Prof. Lundin and her team. They also performed transient absorbance measurements at the Center for Nanoscale Materials at Argonne National Laboratory, and one student used Gaussian to predict the geometry and electronic structure of the molecules.

Funded research positions are critical to the scientific development of DePaul undergraduates, as many students cannot allocate time for research unless they can find paid positions. Visiting a national research facility also adds a formative experience for undergraduates from DePaul, exposing them to a variety of science careers they would not otherwise see and giving them a taste of the professional research environment.

The students are developing posters for our upcoming internal research conference, and one student is also preparing a manuscript for our internal journal of undergraduate research. They will also be encouraged to take their posters to regional conferences later in the year. Students will also be co-authors on an upcoming journal article, which we will begin to write after an upcoming trip to Argonne National Lab.

3. PI Impact

In the first year of this project we have gathered the bulk of a data set that should yield a high quality journal article, supporting progress towards tenure. Support for this project provides a clear direction for our research efforts in the near future. As synthesis of the proposed dyads comes to completion, we expect to collect a broader data set that should yield high impact results. We expect to develop proposals for additional funding based on these results over the coming year. This award will also fund travel to national conferences to present results.

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