

Simulating the Electronic Consequences of Embedding and Encapsulation of Photoactive Molecules within Porous Frameworks

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This investigation is comprised of two parallel objectives: (1) to understand how embedding of acene chromophores in covalent organic frameworks affects their electronic and photophysical properties, and (2) to explain the origin of excited-state lifetime enhancement of a small-molecule photocatalyst through encapsulation in a mesoporous aluminosilicate environment. These objectives are pursued principally through electronic structure modeling coupled with molecular dynamics simulations, with the following progress to date.

Progress of the Research

Structural and electronic properties of electroactive COFs. In this investigation, we are focused on the effects of chromophore embedding on the structural and electronic properties of a series of COFs possessing polyacene linkers (Fig. 1). Our motivating hypothesis is that with suitable chemical tuning, such COFs might support singlet fission (SF), the creation of two triplet excitons from one singlet exciton. Our simulations show that the embedded acenes preferentially adopt orientations at an angle relative to the COF plane at room temperature. Charge mobility through the COFs has been quantified as a function of the length of the embedded acene, and in our recent *J. Mater. Chem. A* publication, we have determined that room-temperature fluctuations in the COF structure have a *qualitatively* significant influence on the electron transport properties of the COF (Fig. 1c).

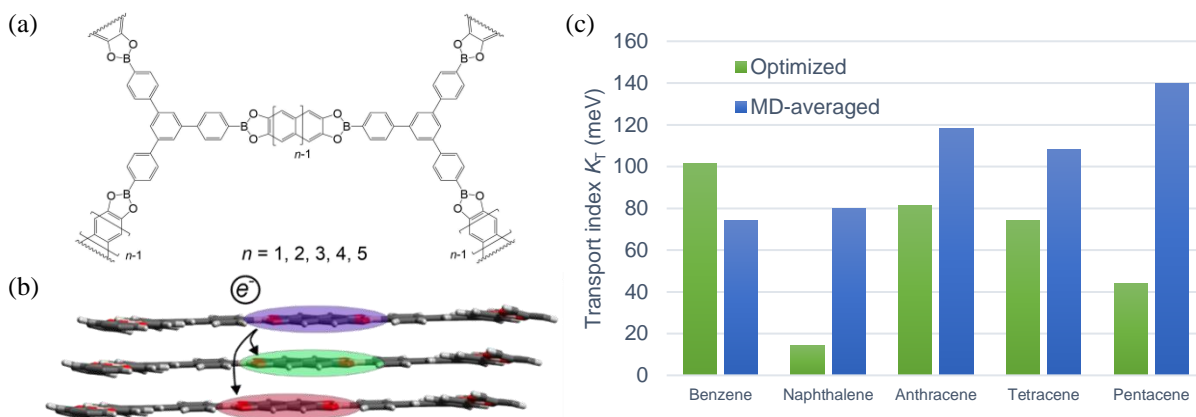


Figure 1 (a) Chemical structure of a family of acene-linked COFs. (b) Schematic illustrating vertical electron mobility along COF stacking direction. (c) Estimates of electron mobility obtained through ensemble averaging with DFTB-MD reveal a qualitatively different trend than estimates based on a single geometry for mobility versus acene length.

Current efforts in this investigation are focused on the stacking behavior of acene-linked COFs with bulky substituents. The goal of these simulations is to better understand how steric effects can assist in tuning the electronic coupling between COF layers and enhance the rate of singlet fission. We are developing a screening approach to identify chemical substitutions that can “lock” the acene linkers in orientations that have proven favorable for enhancing the electronic coupling in organic crystals. This “contact profile” analysis will be tested against full molecular dynamics simulations to refine the model and apply it to the identification of promising scaffolds for further investigation.

Modulation of charge transfer state lifetimes by encapsulation in mesoporous media. The 9-mesityl-10-methylacridinium ion (MesAcr⁺, at right in Fig. 2) has attracted significant attention – and some controversy – concerning the details of its charge-separation photochemistry. Recent experiments have introduced MesAcr⁺ into porous materials, for example, as a bridging unit in a mesoporous organosilica, and earlier claims of a long-lived charge-transfer state lifetime for MesAcr⁺ in solution have been extended to room temperature via encapsulation in AIMCM-41.

In this year of PRF support, we completed and published results from a series of simulations to characterize the photophysics of MesAcr⁺ in the gas phase, in acetonitrile solution, and encapsulated in AIMCM-41 to dissect the role of the dyad's environment on the charge separation and recombination processes. For the challenging case of the encapsulated dyad, we have developed a combined Monte Carlo / molecular dynamics approach to explore external and internal degrees of freedom on the dyad, respectively. The simulations reveal significant differences between the reorganization energy in the gas phase, in solution, and in the pore. Strikingly, the reorganization energy in the porous AIMCM-41 environment is slightly lower than in vacuum, leading to a greater activation barrier for charge recombination in the Marcus inverted region (Fig. 3). This finding challenges the commonly assumed partitioning of the reorganization energy into independent, positive inner-sphere and outer-sphere contributions.

We showed through this work that the environment dependence of the electron transfer parameters can be rationalized through a simple electrostatic model which can be used to estimate the relative charge-transfer state stabilization of related chromophores using only their geometries and atomic partial charges. A manuscript describing this work was recently published in *J. Phys. Chem. C*. We are currently continuing this line of inquiry through a comparative analysis of charge separation in other acridinium-based donor-acceptor complexes in AIMCM-41.

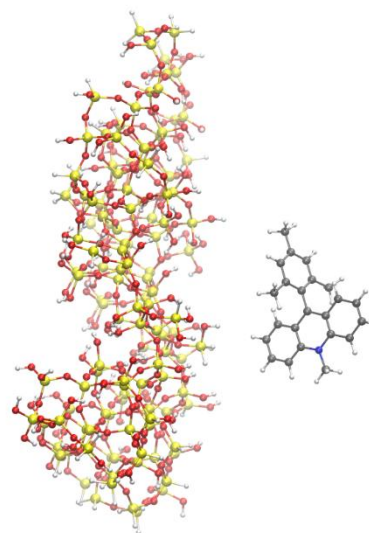


Figure 2 Snapshot of combined Monte Carlo / molecular dynamics simulation of MesAcr@AIMCM-41.

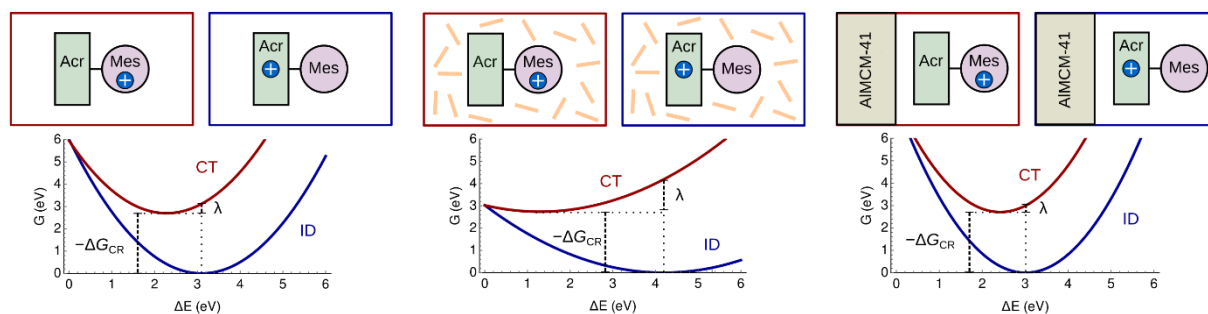


Figure 3 Marcus curves for charge recombination in MesAcr⁺ in vacuum, MeCN solution, and encapsulation in AIMCM-41, derived from DFT/MM, and DFT-in-DFTB molecular dynamics sampling, respectively.

Impact on PI Development

In addition to publication of the MesAcr⁺ encapsulation study, outcomes of our PRF support have been presented at 3 scientific meetings (local, national, and international). Our PRF-sponsored activity provided a basis for discussions that led to an opportunity for the PI to host a visiting PhD student for one year with support from the Royal Golden Jubilee Fellowship program of Thailand. PRF support has also been crucial in the generation of findings that have formed a basis for preliminary results for other investigations. During this award period, the PI received support from the NSF RUI program and was selected as a Cottrell Scholar of the Research Corporation for Science Advancement.

Impact on Student Development

Undergraduate students are central to the progress made to date in this project. The first author of the *J. Phys. Chem. C* publication stemming from this support completed the work as an undergraduate, and she is now pursuing a PhD in materials science. This project has funded summer research opportunities for a total of four undergraduate students and one masters student at WWU and has supported their travel to regional and national conferences for poster presentations – and one oral presentation at the Murdock College Science Research Conference – describing this work.