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

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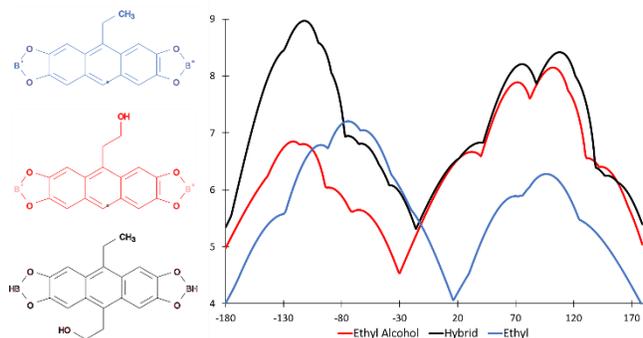
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This investigation is comprised of two parallel objectives: (1) to understand how embedding of acene chromophores in covalent organic frameworks affects their electronic and photophysical properties, and (2) to explain the origin of excited-state lifetime 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 in this award period.

### Progress of the Research

*Structural and electronic properties of acene-linked COFs.* Building on our previous study (in *J. Mater. Chem. A*) of the COF environment's influence on electronic energy levels and couplings between embedded acenes, we have investigated the stacking behavior and electronic properties of acene-linked COFs with bulky substituents. Of special interest to us are substitutions that may enhance the likelihood of singlet fission (SF), the creation of two triplet excitons from one singlet exciton.

We have developed a screening approach called contact profile analysis to identify chemical substitutions that can promote herringbone-like orientations between acene layers; such orientations have proven favorable for enhancing electronic couplings and SF rates in organic crystals. Interestingly, we have found that contact profiles for singly substituted acene linkers are approximately additive (Fig. 1), that is, the sum of the contact profiles provides a rough estimate for the contact profile of an asymmetrically disubstituted acene linker. However, there are deviations that



**Figure 1** Contact profiles of substituted anthracene dimers: relative energies (in eV) versus angle between anthracene planes (in degrees) for (a) 9-ethyl; (b) 9-ethoxy; (c) 9-ethoxy-10-ethyl derivatives of anthracene with boronate ester linkages.

require an independent analysis of the disubstituted species. This result highlights the importance of rapid screening tools like this contact profile analysis to identify substitutions that show promise for enhancing SF in photoactive COF materials.

In parallel with the contact profile study, we have more closely examined energies and couplings in a small selection of substituted acene-COFs through density functional tight binding (DFTB) electronic structure and molecular dynamics simulations. 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 planning to report the details in the coming year so that this work can help experimental materials chemists determine whether such COFs might support SF.

*Modulation of charge transfer state lifetimes by encapsulation in mesoporous media.* Previously, we published results from a series of simulations to characterize the photophysics of 9-mesityl-10-methylacridinium ion (MesAcr<sup>+</sup>) in the gas phase, in acetonitrile solution, and encapsulated in a mesoporous aluminosilicate material to dissect the role of the dyad's environment on the charge separation and recombination processes. In this period, we extended the scope of these simulations to a small set of acridinium-based donor-acceptor complexes to determine how substitution by electron-donating or electron-withdrawing groups might influence the excited-state lifetime. Our initial results suggest that the reorganization energy, driving force, and excited-state lifetime are not significantly modulated by these substitutions. From these observations we would argue that future efforts to modulate the excited-state lifetime should focus on pore engineering to further reduce the reorganization energy and boost the activation free energy for charge recombination in these complexes.

*Enhancing charge carrier mobility in novel electroactive COFs.* In collaboration with the research team of Donglin Jiang (National University of Singapore), we have simulated charge carrier mobilities of newly developed electroactive COF materials. Through computation of reorganization energies (Fig. 2) and electronic couplings in the framework of constrained DFT configuration interaction (CDFT-CI), we have characterized electron and hole mobilities in these materials for comparison with experimental measurements. We are currently working to improve the model by sampling reorganization energies and electronic couplings from molecular dynamics simulations of representative two-layer fragments of the associated COFs.

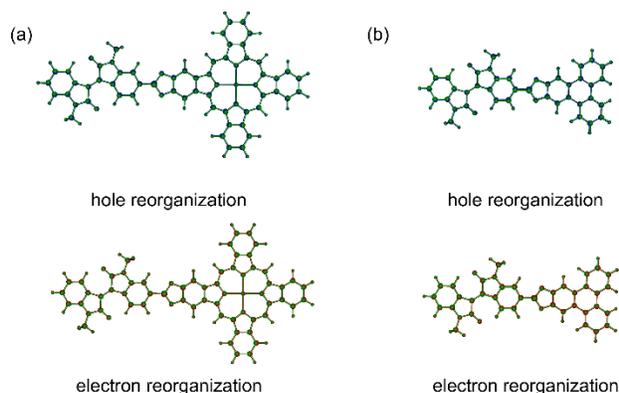
*Isomerization and tautomerization in photoactive COF materials.* Another new direction in this award period concerns the influence of COF embedding on the photoisomerization and tautomerization dynamics of compounds that undergo *cis-trans* isomerization and excited-state intramolecular proton transfer (ESIPT), respectively. Together with Nawe Kungwan (Chiang Mai University), we are performing mechanistic and molecular dynamics studies of these processes in COFs that have been prepared experimentally by the group of Kian Ping Loh (National University of Singapore). These simulations are taking advantage of our excited-state density functional tight binding ( $\Delta$ DFTB) code. By comparing the energetics of photoisomerization and tautomerization in these COFs to that of the free linkers, we are quantifying the influence of embedding on light-induced functionality in these COFs. We aim to report our findings in this area in the coming year.

### Impact on PI Development

The studies enabled by this PRF support have delivered preliminary results that formed the basis of an NSF CAREER proposal that was funded through the Division of Materials Research in 2019. Our PRF-sponsored activity has also continued to play an important role in our international collaborations. We are fortunate to exchange ideas and developments with two experimentalist partners at the National University of Singapore as part of our electroactive and photoactive COF research thrust. Furthermore, interactions stemming from this research have served as a catalyst for our collaborations with computational chemistry colleagues in Thailand: our research group currently hosts two student awardees of the highly competitive Royal Golden Jubilee scholarship and exchange program. Such international exchange enables us to share the US teacher-scholar model, specifically in a primarily undergraduate institutional context, with potential members of the future professoriate in other countries. Finally, the research supported by PRF contributed to the PI's successful tenure and promotion in 2019.

### Impact on Student Development

While the number of graduate (MS) students in the PI's group increased from one to three during this award period, undergraduate students continued to play a central role in the progress of our PRF-sponsored research. This year, our PRF support enabled summer research opportunities for two undergraduate students; engaged an additional undergraduate and two visiting scholars funded through other mechanisms; and provided partial support for one masters student at WWU. In addition, it supported student travel to regional and national conferences, including ACS National and Northwest Regional meetings, for poster and oral presentations describing this work. These professional development and networking opportunities have proven valuable: three of the undergraduates supported by this award since its inception have since entered chemistry or materials science graduate programs, both in the US and abroad. In-person connections with prospective advisors and thought leaders in the field, enabled by PRF travel support, helped foster the supported students' interest in graduate study and contributed significantly to their informed decision-making about the next steps in their respective careers in science.



**Figure 2** Limited structural reorganization was observed for electron depletion or addition in a core-linker segment of novel (a) CuPc-based and (b) triphenylene-based COF materials. Structures before and after reorganization are indicated by color, with the green structure representing the neutral compound.