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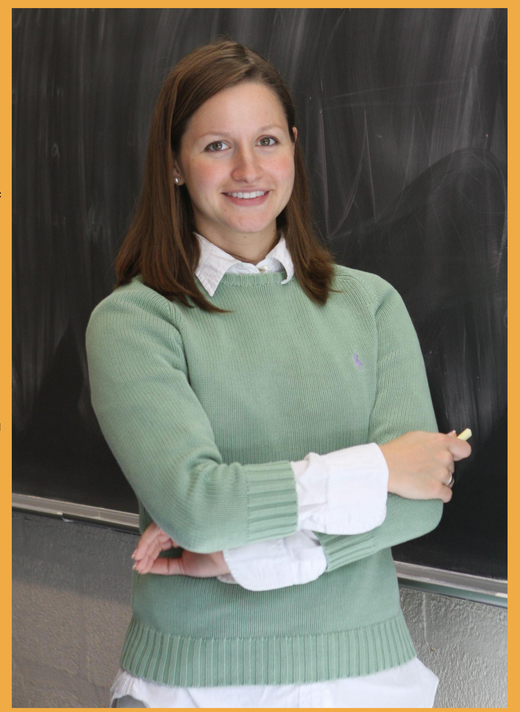
Rebecca Cantrell



The Morphology of C_{60}-Pentacene Heterojunction Interfaces for Photovoltaic Applications

The focus of my research is to predict optimal conditions for the thin film growth of small molecule organic semiconductors, which tends to be polymorphic and 3D, and hence poorly conducts electrons and holes. The motivation to grow thin films of organic semiconducting molecules with high electrical mobility is their suitability for electronic applications, especially display technologies, photovoltaic cells and RFID tags. Organic-based electronics are currently a $1B market, with projections of a $46B by 2016. They are attractive because of their low cost, but are also a challenge for device physicists due to their low energy conversion efficiency.[1] While material selection helps absorbance and quantum efficiency, the ability to effectively dissociate the exciton (electron-hole pair) and produce a photocurrent is **strongly influenced by the morphology adopted by the small molecules at the heterojunction interface:** The more direct or ordered the pathway for charges to travel once separated, the less likely they will be scattered or recombined. The aim of this research, then, is to determine the best way to direct thin film growth of anisotropically interacting organic materials on another by maximizing the probability of ordered, 2D, layer-by-layer growth. My results have already shown that the specific phase and morphology of the pentacene surface strongly affects the adsorption and diffusion properties of C_{60}, which are critical events in the deposition and growth of thin films.[2,3,4] Our atomistic Molecular Dynamics (MD) techniques showed that C_{60} molecules exhibit a distinct and highly anisotropic diffusion behavior on *bulk phase* pentacene that is not observed on *thin film* phase pentacene. This anisotropy is due to the slightly more tilted crystal structure of the bulk phase pentacene, which, in conjunction with the crystal's preferred herringbone pattern on the surface, produces "valleys" in which the C_{60} molecule is an almost exact fit.[4] The overall 2D diffusion coefficient for C_{60} on bulk phase pentacene is lower because, in this tilted configuration of pentacene, the pentacene exposes more of its pi-electron-rich face to the C_{60}, increasing the adsorption energy. From these results, we speculated that C_{60} molecules grown on bulk phase pentacene surfaces could be induced to produce a *structure-directing* thin film growth mode. Using our observations that the corrugation of the bulk phase can bias C_{60} diffusion along certain surface orientations, while attempting to thwart the tendency of C_{60} molecules to ignore the pentacene template, we considered systems of pentacene monolayers on a substrate (like metals) in which pentacene lies down on the surface rather than standing up (as in usual polymorphs). My recent results have demonstrated several processing routes to create highly conductive C_{60} nanowires (and introduced the concept of C_{60} biwires) using the tilt of the underlying pentacene surface as a means to alter the direction of growth and the propensity to grow nanowires,[5,6] as well as using the presence of pentacene step edges. My current research is focused on complementary algorithm development. I am creating a coarse-grained method of simulating C_{60} growth on pentacene that overcomes the limitations of MD in length and timescales and accesses experimental scales. I have developed a kinetic Monte Carlo (kMC) algorithm to incorporate a novel multiple-lattice system that allows me to model the growth of C_{60} molecules on pentacene. This work will be the first kMC (or any other) molecular simulation study of the growth of nonspherical molecules of type A on type B; all previous kMC simulations on related materials have been limited to the far easier task of growing like-on-like, *e.g., C_{60} on C_{60}.*[5] This code is also being made parallel *via* a "semi-rigorous synchronous sub-lattice" method[6], which should make at least millisecond time scales accessible. With such a technique in hand, I will be able to tune parameters such as temperature, deposition rate, and pentacene phase to map out all the resulting possible C_{60} growth patterns on a far larger scale than is possible with MD.

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Austin Hooey Prize Winners

Jeisa Pelet

Combinatorial Libraries of Bi-functional Polymeric Vectors for siRNA Delivery

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Combinatorial chemistry can be a useful tool for the development of polymers as non-viral delivery systems. In this work, we developed polymer libraries to understand the structure-function relationship of these polymeric vectors for siRNA delivery. Characterization of these vectors allows the identification of optimal structural properties for efficient transport and delivery of siRNA into cells. Gene therapy has emerged as a promising technique to treat many chronic diseases, genetic disorders and even cancer. Furthermore, the recent discovery that RNA interference could be used as an approach to modulate protein expression in mammalian systems sparked a potential revolution in disease treatment. By taking advantage of this endogenous mechanism, gene silencing can be induced by sequence-specific cleavage of a messenger RNA coding for a specific protein, by means of a short interfering RNA (siRNA). Introducing siRNA into cells is limited by numerous challenges, predominantly the lack of effective delivery systems that can safely transport these macromolecules to their site of action while overcoming a manifold of barriers that hinder the delivery pathway. For siRNA delivery, synthetic vectors, including polymers[1], have increasingly gained attention primarily due to their easily controllable molecular composition. ***The goal of this research is to employ a combinatorial chemistry approach to design polymeric vectors for enhanced siRNA delivery through a mechanistic understanding of their structure-function relationships.*** Poly(acrylic acid) (pAA) was synthesized via reversible addition fragmentation chain transfer (RAFT) polymerization with controlled molecular weights[2]. Based on these precursors, polymer libraries were generated by conjugating two distinct moieties, agmatine (Agm) and D-(+)-galactosamine (Gal) at various ratios to the polymer side-chains[3]. Biophysical characterization of these polymer vectors, including binding affinity of polymers with siRNA, polyplex stability in the presence of other anionic species (heparin), polyplex effective diameter and zeta potential, were evaluated. In addition, assessment of cytotoxicity and transfection efficiencies mediated by these polymer vectors was carried out *in vitro* using MDAMB-231-luc cells as a model cell line. pAA was synthesized with four distinct M_n *, specifically 3kDa* (PDI=1.36), 5kDa (PDI=1.32), 10kDa (PDI=1.19) and 21kDa (PDI = 1.19). For each molecular weight, various combinations of Agm and Gal were substituted, for a total of 22 polymers under evaluation. Biophysical and biochemical characterization showed that both the Agm/Gal content and the molecular weight of the polymer precursor play important roles on the effectiveness of these vectors as siRNA delivery systems. From the *in vitro* data, polymer vectors identified as the best candidates will be evaluated for siRNA delivery *in vivo* (protein knockdown of Factor VII in mice). Combinatorial chemistry offers great flexibility and the advantage of simultaneous analyses of a wide chemical and structural parameter range. Mapping structure-function parameter space through polymer libraries is intended to understand the mechanisms of siRNA delivery leading to safer and more efficient delivery systems.

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