DOE-BES Final Report for DE-SC0010419

Title: Analysis of Organic Electron Materials using Neutron Scattering

Awarded to: University of California, Davis

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Dates: August 1 2013 through July 31 2022

Abstract: Neutron scattering is a powerful suite of measurement techniques that enable unique analysis of structure and dynamics of a wide variety of materials. Specifically, neutrons interact strongly with protons, which enables excellent contrast in light element organic materials that cannot be obtained with any other measurements. This series of three proposals focused on using inelastic neutron scattering (INS) to study the vibrations (dynamics) of the organic molecules involved in organic electronic devices. Our main goals were to demonstrate that INS is capable of elucidating new, useful, and unique knowledge about organic electronic samples that could be used to improve the function of devices or to solve outstanding problems that could not be solved using other measurement techniques. Since all of the goal involved using INS or other neutron techniques to do something "new" a large part of the effort was focused on complex data interpretation and development of modeling workflows that could be used by other members of the organic electronics community to study their materials. To facilitate the goal of making INS measurements more accessible to a broader community and for a wider range of materials, we optimized and engineered the computational workflows to be well documented, publicly available, and user friendly. The individual titles of the three sequential DOE-BES awards are: (1) Engineering doping profiles in organic semiconducting materials, (2) Measurement and modeling of molecular dopant structure and dynamics, and (3) Quantification of Dynamic Disorder in Electronic and Excitonic Organic Materials. For readability, this report is organized to highlight the progress of the research thematically. Many of the ideas started in one grant period and then spilled over into later awards and collaborative research.

Detailed Report:

(1) Engineering doping profiles in organic semiconducting materials

The central question of the first award (2013-16) was to quantify the diffusion rate of molecular dopants within an organic semiconducting polymer. All semiconductor devices are made up of a mixture of intrinsic and doped layers/domains. Doped domains have conductivity many orders of magnitude higher than the intrinsic domains, which is how electrical current is controlled in the devices. Inorganic semiconductors are doped using substitutional atoms that add or remove electrons within the crystalline matrix of the semiconductor. In contrast, organic semiconductors are doped using additional molecules that either accept or donate electrons. For all devices, it is critical to have excellent spatial control of the location and density of the dopant species for the device to function properly.

As of 2013, it was known that molecular dopants in organic semiconductors were able to diffuse within the semiconducting matrix at low temperatures, which made the resulting devices unstable. However, the dopant diffusion rate had not been quantified nor was there an accepted mechanism that explained the diffusion of large molecules with >20 atoms. More importantly, there was no measurement technique that was capable of measuring the diffusion rate of an organic dopant within the matrix of an organic semiconductor because there is no contrast. We attempted to measure the diffusion rate in several different ways including using fluorescence quenching and NEXAFS spectroscopy as part of this award, but were unable to quantify the diffusion rate. We also noticed that molecular dopants prefer polymers with polar side chains[1-4] These observations led to later collaborative papers related to the doping mechanism of organic semiconductors and the role that polar side chains play in this mechanism.[5]

To quantify the dopant diffusion rate using neutrons, we synthesized a new and unique dopant that was labeled with a single protonated methyl group that could be measured in the background of a deuterated semiconducting polymer. This new dopant was based on the molecular structure of the well-studied molecular dopant F4TCNQ and had the useful property that it was 100x more soluble than F4TCNQ, which made it preferable for solution processing.[6] We then used quasi-elastic neutron scattering (QENS) to measure the temperature dependent motion of the methyl group on the dopant within a matrix of a deuterated semiconducting polymer called poly-3-hexylthiophene (P3HT). We found that QENS was able to detect the motion of the methyl group over small times and distances but did not fully quantify the time/distance range of diffusive motions that were necessary for an organic electronic device. So, we also measured the fluorescence quenching of P3HT films that were doped with methyl-F4TCNQ and F4TCNQ. This technique was able to measure dopant diffusion over micrometers for samples heated over minutes. We found that the methyl group acted as an anchor that reduced the diffusion rate by 100x. This paper was in many ways a landmark paper that changed how the whole organic electronics community thought about synthesizing dopants, measuring dopant diffusion, and controlling the location of dopants in organic semiconducting devices.[7]

Through the process of trying to fabricate films with alternating domains of doped and undoped P3HT, we discovered a new effect: the addition of a molecular dopant to the semiconducting polymer film greatly reduced the solubility of the film in non-polar solvents because the doped film became a molecular salt polymer$^+$dopant$^-$. This observation has several important consequences. First it led to the idea that the polymer deposition and addition of the dopant could be separated into two distinct steps, which we named Sequential solution doping.[8] Sequential doping of semiconducting polymers is now the standard for the entire organic electronics community and has led to numerous records in conductivity, mobility, and is the basis of many grants on organic thermoelectric materials and devices.[9] Second, the observation of doping induced insolubility means that dopants could be used as method to create patterning contrast between semiconducting polymer domains. The research on the patterning method really took off, leading to numerous research articles that were based on data taken between 2014-16 [2, 4, 10-16] The Moulé group has separately focused on using dopant induced solubility control as a patterning mechanism and has since received three follow-on NSF awards based that focus on semiconductor patterning (Award numbers 1636385, 1804690, and 2208009) with combined funding of ~$2,000,000 and written a highly cited review paper on polymer doping.[11] The Moulé group also recently filed two different preliminary patent applications, the second of which UC Davis is aggressively pursuing in 2023.

Another difficult question related to semiconducting polymer doping relates to how the structure of the polymer is changed by the physical presence of the dopant and charging by the dopant. In principle, a conjugated polymer should have more quinone bonding along its backbone in the doped form, which would lead to structural changes to the side chains and increased planarity along the backbone. The Moulé group used INS measurements on the VISION instrument at Oak Ridge National Lab to measure the vibrational spectrum of the polymer P3HT with and without the presence of the molecular dopant F4TCNQ in order to determine the change in dynamics (stiffness) of the polymer backbone. Interpretation of this data was extremely difficult because no one had ever published detailed and quantitative comparison between the measured and simulated INS spectrum of such a complicated molecular system. INS is usually only used to study highly crystalline materials whereas P3HT/F4TCNQ is semi-crystalline. We demonstrated two important uses of INS. First, INS measurements and modeling showed that P3HT assumes several different crystalline configurations in all films, which could not be determined using x-ray diffraction measurements that averaged a much larger volume and selected only configurations that repeat over longer distances. Second, we demonstrated that addition of a dopant molecule caused structural modifications of the P3HT backbone consistent with greater dihedral planarity and also caused the side chains to assume a more uniform angle that is co-planar to the polymer backbone.[17] This project helped to crystallize our long term goal to model INS data for amorphous and semi-crystalline materials. We discussed our ideas about modeling in a review paper.[18]

(2) Measurement and modeling of molecular dopant structure and dynamics

Our second award focused exclusively on measurement and modeling of INS data. Our main goals were to use INS spectra and modeling to determine the phonon modes responsible for charge transport in organic semiconductor crystals and to develop modeling techniques that less computationally expensive so that more complex and less ordered samples could be studied using INS.

Modeling charge transport in high mobility organic semiconductors is difficult because the standard methods of hopping theory and band theory do not provide quantitative models. Hopping theory does not work because the hopping rate would have to be higher than the phonons (intermolecular vibrations) between nearest neighbor molecules. Band theory also does not work because it assumes that charges are delocalized across the full semiconductor whereas polarons (the charge carriers in organic semiconductors) are localized to within several monomers. In 2010, Troisi et. al. developed transient localization theory, which posited that the delocalization volume of a polaron within a crystal would dynamically fluctuate due to coupling to the bath of phonon modes. Thus, the charge mobility would be limited by the “dynamic disorder” of the molecular crystal. However, since no group had measured the phonon spectrum of any organic semiconductor, the theorists pretended that a single phonon bath mode could be used instead of a full phonon spectrum. The Moulé group sought to test this theory by measuring and modeling the phonon spectrum using the VISION spectrometer at ORNL and then predicting the charge mobility based on the measured electron-phonon coupling. We measured and modeled the phonon spectra of six well-known crystalline small molecule organic semiconductors and in collaboration with Troisi calculated the electron phonon coupling and predicted the charge mobility rate for those materials. Our prediction of charge mobility was over an order of magnitude more accurate for all materials than any group had previously achieved.[19, 20] These were landmark papers because it is the first time that anyone had accurately predicted charge mobility in organic semiconductors using a first principles simulation and we showed that our method was much better than any other method. Groups that assumed only a single phonon mode were >300% less accurate.

In this period, we also worked with the group of Enrique Gomez on modeling the side-chain and backbone dynamics of the polymer P3HT using QENS measurements. The Gomez group acquired the QENS measurements at ORNL and we helped with the molecular dynamics modeling of the data. The main result was that the side chain dynamics were correlated to the backbone dynamics. Essentially it means that in semiconducting polymers, the side chain motions (the tail) can in fact cause motions in the backbone (the dog). These motions in turn increase the dynamic disorder along the backbone, reducing the charge mobility.[21] These results and modeling were a strong motivator for our current work to use INS measurements to quantify phonon motions in polymers.

In 2016 I was on sabbatical in Germany. We collaborated with the group of Klaus Meerholz on morphological measurements of small molecule organic photovoltaic mixtures. As part of this collaboration, my group made SANS measurements at Garching of these material mixtures. We published a very nice paper examining how the side chain length of the merocyanine donor affects the domain size and mixing ratio of the donor and acceptor domains.[22]

(3) Quantification of Dynamic Disorder in Electronic and Excitonic Organic Materials

The largest challenge in simulating first the INS spectrum for organic semiconductors and then also the electron phonon coupling is the enormous computational expense, which was over 500,000 CPU hours per molecule. This computational expense greatly limited the applicability of the technique for predictive modeling of new materials. In our third award, we had to main goals. The first goal was to develop simulation techniques that would reduce the computational expense and make accurate prediction of charge mobility based on measured/simulated phonons a practical method. The second goal was to extend the prediction phonon mediated processes to the study of excitonic states in organic semiconductors. Since excitons are formed by light excitation, the first step was to develop a new instrument environment at the VISION instrument that enabled in-situ optical excitation of samples while measuring the INS spectrum.

Density functional theory (DFT) is the most used and useful method to simulate the electronic states and phonon states of materials or molecules. When we used DFT to generate accurate simulations of INS spectra, however, the computation expense was extremely high because the simulation scale with the number of electrons cubed and an accurate of a supercell of organic molecules contained hundreds or thousands of atoms. We developed in parallel two different methods to reduce the computational expense of INS simulations and then compared the accuracy and expense of the methods. Molecular dynamics was the first choice because the simulation expense scales with the number of atoms squared. We simulated the INS spectrum using INS by taking a fourier transform of the velocity autocorrelation function and also found ways to simulated the background INS signal by estimating transitions to higher vibrational levels. The resulting simulation technique was more accurate than DFT for simulating the low energy INS spectrum for polymeric and amorphous samples.[23] Our second approach to lower computational cost was to use density functional tight binding (DFTB), which scales similarly to DFT, but only considers the valence electrons, so is generally about 1000x less expensive for the same sample as DFT. In order to improve the match to experiment we also used a machine learning approach called ChIMES that was developed at LLNL that corrected the repulsive forces between atoms. The DFTB/ChIMES method was in fact 1000x less expensive than DFT and led to a good fit to INS data across the full spectrum.[24] We next optimized the DFTB/Chimes and DFT methods for simulating INS spectra into an optimized, automated, and well commented workflow that could be implemented at national lab supercomputing centers. The workflow optimization reduced the computational expense by almost 100x using careful control of parallelization and optimization of each step in the workflow. We call our workflow

Davis Computational Spectroscopy (DCS-flow).[25] Finally, we performed a careful quantitative comparison between simulation methods for INS spectra. We found that DFT was the most accurate followed by DFTB/ChIMES, DFTB, machine learning methods or molecular dynamics.[26]

Once the complete workflow for simulating INS spectra and phonons was completed, we asked whether our workflow could be used to design new improved organic semiconductor materials. Unfortunately, the answer was NO. Although we could simulate the phonon modes very accurately, there was no way to use our simulation method to approach phonon engineering. The limitation that prevented phonon engineering is that each molecular system has 1000's of phonon modes and even very similar molecules had different dynamic motions or different contributions to the electron/phonon coupling at different energies. The dynamic disorder (σ^2) represents a thermal average of how the phonon modes affect the transfer integral (J). The electron/phonon coupling (g_{ij}) is written $g_{ij}^{l} = \nabla J_{ij,l} \cdot Q_l$ where $\nabla J_{ij,l}$ is the gradient of the transfer integral between molecules *i* and *j* for mode *l* and Q_l are the atomic displacements for mode *l*. σ^2 is a useful global measure, but summing over all atoms and modes does not allow for either a mode-by-mode (energy) or an atom-by-atom (spatial) analysis. We realized that we had been analyzing the energy spectrum because that is what a we measure with INS. Instead we started performing an atom-by-atom analysis which enabled us to map the relative contributions to the total dynamic disorder in relation to the molecular structure. This in turn gives us a tool to compare the contributions to dynamic disorder and thus the charge mobility between different molecular structures.[27] This paper will be extremely significant and will make INS the go-to tool for phonon engineering of molecular structures in the future.

In collaboration with catalysis groups at UC Davis, we made INS measurements of the metal-organic-framework MOF-UiO66. We found that the low energy portion of the INS spectrum could be used to examine the correlation between motions of defect sites and linker sites in the MOF, which in turn enabled us to determine the structure of the defect site with higher chemical, energetic, and dynamic specificity than had ever been performed before.[28] We believe that this will be a seminal paper in the MOF/catalysis field because of the ability to single out the spectroscopy of the defect site itself.

In collaborative work with an ultrafast spectroscopy group at UC Davis, we observed that excitonic (optical) excitation of semiconducting polymers in solution led to rapid changes in the backbone planarity of the polymer.[29] The implication is that excitons have large phonon contributions, that could be detected using the VISION spectrometer, but only if we could achieve a high density of optically excited states in-situ in the VISION spectrometer. Daniel Vong, a Moulé PhD student, applied for and received and DOE SCGSR award to work at ORNL with Luke Daemen at the VISION beamline to design and build a new sample environment for optically excited samples. He completed his work in 2022 and is writing his thesis that will include both designs of the new sample environment and the very first ever excited state INS measurements of optically excited phonons.

Summary: Over nine years the Moulé group focused on a wide range of scientific problems that involved a combination of organic electronic materials and neutron measurements. In most cases, the analysis of the data was extremely complicated because of the high complexity of the samples and first-of-a-kind analysis of the resulting data. Our goal remained fixed on increasing the range and complexity of samples that can be measured and interpreted using INS and also providing workflows that enable researchers to access INS with a lower entry barrier. All total there are 29 peer reviewed publications that have been cited a combined 1726 times (according to Google Scholar) as of 2/22/2023.

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