

2014 GCEP Final Report

Organic Solar Cells

Investigators

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Abstract

In this project, we aim at combining the molecular design and device fabrication expertise of Bao, theoretical simulation expertise of Aspuru-Guzik, structural characterization expertise of Toney, and the large distributed computing power of IBM's World Community Grid (WCG) to rationally design organic semiconductors for charge transport and solar cells from a completely new angle. Moving away from molecular design from trial-and-error, we combine powerful theoretical tools and various characterization techniques to develop an inverse rational design methodology for novel organic semiconductors. We have seen a feasible path towards breakthroughs in materials performance by using this approach. Such a massive amount of computing resources has been first applied to atomic-scale modeling problems in material sciences. We have been able to develop new materials with high mobility and air stability that are critical for ubiquitous electronics applications.

Achievement 1: Role of Crystal Texture in Exciton Transport in Conjugate Polymer Thin Films

Controlling the thin film microstructure of an organic photovoltaic (OPV) device is of paramount importance for optimizing the solar energy conversion efficiency. We have recently shown that by changing the side chain of a semicrystalline conjugated polymer donor from a common aliphatic moiety to a siloxane-terminated chain, we achieved greater than order-of-magnitude improvements in the field-effect charge mobility of the polymer. In addition to the increase in charge mobility, we found that the crystallographic texture of the polymer with siloxane side chains was significantly altered, leading two dominant orientation motifs. In this work, we investigated the effect of varying crystallographic texture of our conjugated polymer on the diffusion length of low-energy optical excitations – a quantity that exerts a dominant influence on the desired length-scale of donor/acceptor phase segregation in a working OPV device. We find that although the crystal orientation of the siloxane-terminated polymer is nominally conducive to enhanced transport of optical excitations in the vertical (relevant) direction, the diffusion lengths of both polymers are comparable. This suggests that the long-range transport of electronic excited states is limited *not* by transfer within crystallites but by that of the amorphous regions connecting the crystallites.

Achievement 2: Polymorphism and Confinement in Thin Crystalline Fullerene Films

Fullerene derivatives continue to play a central role in organic photovoltaics, serving as a highly soluble electron acceptor and quasi-isotropic charge conductors. However, relatively little is known about the microstructure of the fullerene phase in a blend donor/acceptor solar device, and even less is known about the structure as a function of film thickness and thus vertical confinement. We have shown that for the most widely used fullerene acceptor PC[60]BM, the crystal structure depends strongly on the film thickness, with new polymorphs appearing as film thickness is increased. In addition, for films of order 100 nm, a novel phase develops that suggests supramolecular organization on length scales significantly exceeding the common fullerene unit cell dimensions. In contrast, we find neither evidence for thickness-induced polymorph formation nor appearance of extremely large unit cells in films of PC[70]BM, indicating that the size and anisotropy of the fullerene skeleton play a large role in the packing motifs of this class of electron acceptors.

Achievement 3: In-situ, High Speed X-ray Diffraction and Optical Microscopy to Explain Mechanism of Metastable Polymorph Formation in TIPS-Pentacene

The crystal structure an organic molecule has significant impact on its physical, biological and electronic properties. In the field of organic electronics, certain small molecular organic semiconductors (OSCs) can be crystallized in various metastable, lattice-strained polymorphic forms using the solution shearing method. In our previous year work, we demonstrated the lattice engineering based on solution-shearing methodology to allow us to access many possible new molecular packing that are not possible through other conventional methods. Using our method to incrementally introduce lattice strain, we alter the π - π stacking distance of 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS-pentacene) from 3.33Å to 3.08Å, and density functional theory calculations show an increase (36.9meV) in the charge transfer integral beyond that calculated (11.7meV) for the evaporated TIPS-pentacene thin film. These lattice strained polymorphs may have better electrical performance than the equilibrium OSC crystal. However, the mechanism of lattice strained OSC polymorph formation is not understood due to the lack of powerful tools for probing crystal growth kinetics. We used a combination of high speed optical microscopy and grazing incidence X-ray diffraction (GIXD) methods to shed light on the mechanism of crystal growth and polymorph selection of the OSC 6,13(bis-triisopropyl silylethynyl)pentacene (TIPS-pentacene) with micrometer spatial resolution and millisecond temporal resolution. Using the observations gathered from the in-situ optical imaging and GIXD, we grow TIPS-pentacene metastable polymorphs using spin-coating, a commonly used solution processing method. This work details how high speed GIXD can be used to probe crystal growth and polymorphism, and sheds light on the various design parameters that enable the growth of high performance OSC polymorphs.

Achievement 4: Measured Charge Transfer Rates at Well-defined Donor/acceptor Interfaces Using Core-Hole-Clock Spectroscopy to Gain Insight into the Dependence of Transfer Rates on Electronic Coupling

Determining the electronic structure and the electron transfer dynamics at donor/acceptor interfaces in organic photovoltaics is of great importance for engineering the next generation of high efficiency organic solar cells. Most often either the donor and/or acceptor molecules have

anisotropic shapes, which suggests that the dynamics of electron transfer at the donor/acceptor interface may depend strongly on relative orientation. Although theoretical results exist in support of this hypothesis, to date there has been no experimental evidence in support of this. In order to address this issue, we have prepared model donor/acceptor heterojunction films with well-defined interfacial donor/acceptor orientation. Using synchrotron X-ray absorption spectroscopy and X-ray scattering, we have verified control over the relative orientation. We then used the core-hole-clock formalism of resonant photoemission spectroscopy to directly measure the photoinduced electron transfer rate from our model donor (copper phthalocyanine (CuPc)) to the model acceptor (C60). When the donor is oriented “face-on” (i.e. strong interaction) with respect to the acceptor, we find an upper limit of 50 fs for the transfer time, which is significantly shorter than the reported > 200 fs transfer time for the edge-on orientation of CuPc with C60. These results underscore the importance of engineering donor/acceptor interfaces with strong electronic coupling.

Achievement 5: Explored Effects of Side-chain Engineering and Film Microstructures on OPV Performance Using Sequential Processing

The ideal microstructure in an OPV thin film must strike a fine balance between maximizing the rate of exciton dissociation at the heterojunction, which favors small domains, and minimizing the rate of bimolecular recombination while optimizing charge carrier mobilities, which favor large electron-hole separations (i.e. large domains). We have recently shown a dramatic improvement in the polymer field-effect mobility via side chain engineering using a conjugated backbone that yields good overlap with the solar emission spectrum. By changing the solubilizing sidechain from a common branched aliphatic moiety (PII2T-Ref) to a linear saturated carbon chain terminated by siloxane groups (PII2T-Si), we observed a significant decrease in the polymer π -stacking distance between backbones. In order to investigate how this sidechain engineering affects vertical charge transport in a solar cell device, we prepared blends of PII2T-Ref and PII2T-Si with a common electron acceptor PCBM. Since OPV devices overwhelmingly require some post-processing, and since the possible processing parameter space is enormous, we chose to concentrate on how a common solvent additive 1,8-diiodooctane (DIO) affects device performance as a function of sidechain moiety.

The process of film formation upon solvent evaporation lies far from equilibrium, and controlling the thin film microstructure is a very difficult task. For conjugated polymers as donors, the typical metastable thin film states that result involve a coexistence of crystalline and amorphous polymer regions, aggregated acceptor regions, as well as complex intermixed phases possessing varying degrees of disorder. In order to gain more control over the final morphology, we processed both D and A sequentially, so as to maximize the individual components *separately*, thereby inducing the proper D/A nanostructure.

Achievement 6: Effects of Odd-Even Side Chain Length of Alkyl-Substituted Diphenyl-dithiophenes on First Monolayer Thin Film Packing Structure

A range of low-cost and large-area applications are emerging from the field of organic electronics, such as solid-state lighting, solar cells and displays. Different performance parameters such as luminescence efficiency in organic light-emitting diodes (OLEDs), power conversion efficiency in organic photovoltaic cells (OPV) or field-effect mobility in organic

field-effect transistors (OFETs) are strongly determined by the morphology of the thin films and by the packing and orientation between individual molecules. Specifically, molecular packing strongly impacts the electronic coupling between molecules and the resulting charge carrier mobility. As a result, developing and understanding methods to control molecular packing of organic semiconductors by molecular design as well as processing control have been actively pursued by many research groups. In particular, we have been interested in molecular design rules for controlling thin film packing structures. We have been able to determine the precise molecular packing structures for thin films of pentacene, TIPSE-pentacene, and a series of fluorine-bithiophene oligomers from grazing incidence X-ray diffraction (GIXD) data combined with numerical fitting. This development is important for structure-property relationship studies because it allows us to understand organic semiconductor packing on substrates that are directly used for device fabrication.

Achievement 7: *In silico* Designed and Predicted High Charge Carrier Mobility Compounds, Realized High Charge Carrier Mobility Experimentally

Despite the versatility of carbon, exploratory chemical synthesis in the vast chemical space can be hindered by synthetic and characterization difficulties. We showed that *in silico* screening of organic semiconductor materials can lead to the discovery of a new high-performance semiconductor. This work involved the theoretical screening of eight novel derivatives of the dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene semiconductor which has a maximum mobility of $8.3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Based on the charge transport parameters and the predicted crystal structures, we identified a novel compound expected to demonstrate a two-fold improvement in mobility over the parent molecule. Synthetic and electrical characterization of the compound is reported with single crystal field-effect transistors, showing a remarkable mobility of $13.7 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. This is one of the very few organic semiconductors with mobility greater than $10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ reported to date. More importantly, this is a significant step towards rationally designing organic semiconductors for efficient solar cells.

Achievement 8: Developed the Clean Energy Project Database CEPDB

The CEP results are compiled in the Harvard Clean Energy Project Database (CEPDB) which is made available as an open resource. The CEPDB is populated with the results from 150 million first principles calculations and now has a size reaching up to 70GB. It is designed for the storage and analysis of data on organic electronics. It allows to readily identify candidates with specific property combinations. The user interface allows searches with various data fields such as INChI, IUPAC, and common names, conversion to canonical SMILES, fingerprinting, a link to matplotlib for graphics, frontier orbital energies, and power conversion efficiencies. Currently, the CEPDB provides a simple interface to analyze the performance of the materials according to Scharber model. Moreover, it is flexible to employ other, potentially more advanced device performance models. It features regularly updated lists of the most promising OPV candidates as more data becomes available, as we improve the calibration scheme, and augment the data analysis capability. The CEPDB was released to the public in June 2013 under a Creative Commons Attribution ShareAlike license.

Achievement 9: Developed the Clean Energy Project – Computational High-Throughput Screening on the WCG

Over the past three years, we developed *the Clean Energy Project* (CEP) components such as the tools for molecule generation, automation of the quantum chemistry computations and data analysis. To date, we have performed 200 million density functional theory calculations on around 3 million molecules (~15 million conformers). We have used over 25,000 year of volunteer computing time provided by the IBM World Community Grid (WCG) accumulating around 0.75 PB of data, which is backed up via a tape vault storage solution. We have extended our current OE12 training and calibration data to include over 1500 reported PCE measurements, along with other related experimental values that we can use for compensating for systematic discrepancies between theoretical data and that observed experimentally. This data is stored with detailed metadata to specify the context and origin of the underlying experimental values. Based on the application of the Scharber model, we have identified the top 20,000 molecules with 10% or higher projected power conversion efficiency in donor acceptor solar cells. The high performing molecules are structurally analyzed and the moieties with the most amplified occurrence in the top candidates have been identified. We also performed cheminformatics analysis of the compounds with linear regression descriptor models.

Achievement 10: Performed Exciton Diffusion Calculations on the Dianthra[2,3-b:2',3'-f]thieno[3,2-b]thiophene Semiconductor:

We studied the singlet exciton diffusion in the dianthra[2,3-b:2',3'-f]thieno[3,2-b]thiophene molecular crystal by means of an approach that combines a stochastic time propagation of the excitonic wave function with molecular dynamics of the single crystal of the semiconductor and electronic structure calculations of the excited states. The fluctuation of the excited state energies (site energies) provides a good description of the dynamic disorder in the system. The exciton diffusion parameters obtained with this approach has been compared with the Haken-Strobl-Reineker model as well as with purely hopping picture.

Publications

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