2013 GCEP 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 solar cells from a completely new angle. Instead of molecular design from intuition, we will combine powerful theoretical tools and various characterization techniques to develop an inverse rational design methodology for novel materials. By doing so, we see a feasible path towards breakthroughs in performance. Such a massive amount of computing resources has not been previously applied to atomic-scale modeling problems in material sciences. For organic semiconductors to find ubiquitous electronics applications, the development of new materials with high mobility and air stability is critical.

Achievement 1: 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 2: 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 3: 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 4: Development of high efficiency polymer/polymer solar cells

Bulk heterojunction (BHJ) organic solar cells (OSCs) have received enormous attention in the past two decades for the attractive features of low cost, flexible device, and solution processability. To improve and optimize the devices performance, enormous work has focused on the chemical modifications to polymeric donors by expanding the absorption range, increasing hole mobility, and enhancing the charge separation efficiency. Up till now, fullerene derivatives play dominant roles in serving as acceptors in BHJ OSCs, while few polymer materials have been examined as electron acceptors in all-polymer OSCs. The reported PCE of solar cells using polymer acceptors reached about 2%. In spite of the merely moderate efficiency achieved so far, binary polymeric blends of donor and acceptor materials present a number of distinct advantages over the polymer-fullerene recipe. First, polymeric acceptors are more effective solar-light harvesting systems and may be tailored to complement the absorption of the donors through chemical modifications. Second, excitons and charge carriers diffuse and transport efficiently in polymer (acceptor) phase. Additionally, polymer acceptors with high molecule weight are more compatible with polymer donors and likely produce more stable phase separation between donor and acceptor.

We have developed new materials that achieved polymer-polymer blend with a PCE up to 4.5%. This is almost two times higher than the reported record.

Achievement 5: 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 6: continued to develop the Clean Energy Project – our computational high-throughput screening on the WCG

Over the past year, we have continued to improve and expand many of *the Clean Energy Project* (CEP) components and diversified the molecular library by new additions based on the suggestions from our experimentalist collaborators. To date we have performed 150 million density functional theory calculations on 2.3 million molecules with 24 million conformers. We have used more than 15,000 years of volunteer computing time provided by the IBM World Community Grid (WCG) accumulating 400 TB of data. Recently, we have extended our disc-based storage capacity to well over 700TB and have introduced an additional long-term data storage and backup solution via a tape vault. We have also greatly bolstered our empirical calibration scheme for the computational results that help us to better compensate for the systematic discrepancies between theoretical and experimental data. Our current OE12 trainings and calibration set with about 1500 real molecules includes detailed metadata to specify the context and origin of the underlying experimental numbers. 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. These will be made available to the chemistry community in the coming few months.

Achievement 7: further developed the Clean Energy Project Database, CEPDB, with a public launch date at June 2013

The development of CEPDB has made substantial progress over the last year and it is increasingly becoming the organizational centerpiece of the project. The CEPDB is populated with the results from 150 million first principles calculations and now has a size reaching up to 70GB. 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 based on various models. The database will be made publicly available by the end of June 2013 and provide a hub for exchange of experimentally available data to further elaborate and improve the models. Through the database top performing materials and their properties will be available to the scientists around the world who would like to incorporate those molecules into their own research. Therefore, the database will provide a framework for further development of the photovoltaics as well as facilitate collaboration among scientists.

Publications

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2) H. Li[1], G. Giri[1], J. Tok, Z. Bao, "Toward High-Mobility Organic Field-Effect Transistors: Control of Molecular Packing and Large-Area Fabrication of Single-Crystal Based Devices." MRS Bulletin, 2013. Invited Review.

3) D.-M. Smilgies, R. Li, G. Giri, K. W. Chou, Y. Diao, Z. Bao, and A. Amassian, "Look fast: Crystallization of conjugated molecules during solution shearing probed in-situ and in real time by X-ray scattering." Phys. Status Solidi RRL, 2013, 7 (3): 177–179.

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6) G. Giri, et. al In-situ, High Speed X-ray Diffraction and Optical Microscopy to Explain Mechanism of Metastable Polymorph Formation in TIPS-Pentacene. In preparation.

7) G. Giri, et. al. Control of Polymeric Semiconductor Molecular Packing using Solution Shearing. In Preparation.

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12) D. H. Kim, J. Mei, K. Schmidt, A. L. Ayzner, G. Giri, A. L. Appleton, M. F. Toney, Z. Bao. "Sequential Solution-Processed, Nanostructured Quasi-Bilayer Polymer Photovoltaics Using Selective Solvents." Submitted to Energy & Environmental Science.

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