

**Final Technical Report
For
DOE Grant No. DE-FG02-98ER45737**

Development of a Scanning Transmission X-Ray Microscope

Polymer Thin Films and Self Assembled Monolayers: Pattern Formation and Surface Interactions

NEXAFS Microscopy and Resonant Scattering of Polymeric Materials

**Organic Heterojunction Devices:
Structure, Composition, and Performance at <20 nm Resolution**

Fundamental Science of High Open Circuit Voltage Excitonic Solar Cells

Control of Interface- and Mesoscopic Structure in High Performance Organic Solar Cells: Towards a Predictive Device Paradigm

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d. Accomplishments

d.1. Overview

This document represents the cumulative, final technical report for Grant No. DE-FG02-98ER45737, the title of which has changed with each funding period, but the research pursued is within a coherent overall theme of methods and technique developments that exploit contrast at the carbon absorption edge to characterize complex organic materials and the use of these synchrotron radiation-based methods for important research challenges in polymer physics and Materials Science. The last three funding periods focused on organic devices and in particular organic solar cells (OSCs), owing to their extra-ordinarily complex morphology, yet high potential as a cheap and printable power-conversion technology.

Funding from this grant was acknowledged in at least 102 scientific papers, including many that are highly cited and/or are published in high profile journals. The main highlights include the following:

- The development of the most successful and world leading scanning transmission soft x-ray microscope (STXM), awarded the Advanced Light Source (ALS) Klaus Halbach Award for innovative instrumentation
- The pioneering development of Resonant Soft X-ray Reflectivity and Resonant Soft X-ray Scattering (R-SoXR/R-SoXS) methods (Appl. Phys. 2005 and APL 2006)
- The co-development of a dedicated R-SoXS facility at the ALS (Res. Sci. Instr. 2013)
- The discovery of miscibility in organic solar cell blends (JCPL 2010)
- The first quantitative measurement of domain composition in organic solar cells (Advanced Materials, 2013)
- The discovery of scattering anisotropy in organic materials due to bond orientation distributions (Nature Materials, 2012)
- The discovery that molecular bond orientation can be quantified in complex three dimensional morphologies and related to OSC device performance (Nature Photonics, 2014)
- The discovery and delineation of the first quantitative relations between χ interaction parameter, morphology and function in organic solar cells (Nature Materials, 2018)

Overall visibility of the Program: This grant provided the majority of the funding for the PI over the last 20 years and the research supported by this grant enjoyed and continues to enjoy high visibility. The PI has delivered ~180 invited presentations during the budget period including 4 Plenary Lectures at national or international meetings and the Sayers Lecture at NCSU. The vast majority of the content of these presentations was based on research supported by this grant.

PI Ade is listed as a 2017 WoS Highly Cited researcher, a result largely based on the support from this grant.

d.2. Selected scientific accomplishments

d.2.1. Development of world leading X-ray microscopes.

PI Ade lead a small team to develop a scanning transmission soft x-ray microscope (STXM) at a bending magnet beamline at the Advanced Light Source (ALS). It is the most successful, most productive and world leading STXM. Key components and concepts (particularly the control software and laser interferometry) were also used in a second, undulator-based STXM at the ALS. These developments revolutionized STXM technology and were awarded the Advanced Light Source ***Klaus Halbach Award***, given annually for the most innovative instrumentation. The instrument was commercialized by Accel and installed at various synchrotron radiation facilities around the world, including the Swiss Light Source, the Canadian Light Source, Diamond, and BESSY-II. The instrument paper describing this development is highly cited with currently 545 citations in WoS.

This technology and successor STXM instruments at the ALS also formed the basis of pioneering experiments by ALS staff in ptychography, which together with microscopy and photon correlation spectroscopy, is a considerable component of the scientific case for the ALS-U, the major upgrade project for the ALS.

d.2.2. Development of experiments complementary to STXM: Resonant Soft X-ray Reflectivity and Resonant Soft X-ray Scattering.

To advance further the utility of NEXAFS to a range of complex carbonaceous materials such as polymers and their blends, PI Ade was instrumental in pioneering Resonant Soft X-ray Reflectivity and Resonant Soft X-ray Scattering (R-SoXR/R-SoXS) methods (*Appl. Phys. Lett. 2005, Appl. Phys. Lett. 2006*). His team was the first to use R-SoXS on structured polymeric materials and on organic devices. These methods have unique advantages. R-SoXS corresponds to what is usually referred to as Ultra-small X-ray Scattering (USAXS), yet does not require highly collimated beams. It has also high and selective contrast so that even samples as thin as 50 nm can be readily investigated in transmission. These developments and the unique potential and opportunity they presented lead to the construction of a dedicated R-SoXS facility at the ALS (*Res. Sci. Instr. 2013*), which is now the most productive (by publication) soft x-ray facility at the ALS, even though it uses only 50% of the time at an undulator beamline.

d.2.3. Pioneering work in organic solar cells: Paradigm changes

The PI and his group were the first to discover miscibility in organic solar cell (OSCs) blends within the amorphous regions of OSC devices (*JCPL 2011*). This led to a change in paradigm of how the devices are conceptualized and are depicted in schematics. The mixed amorphous domains and their beneficial and detrimental impact have been widely studied ever since. This work was followed with the first quantitative measurement of domain composition in the mixed regions in

OSCs (*Advanced Energy Materials 2013*). A general body of work based on the characterization of high efficiently OSCs and various model material systems followed, most of which have been published in excellent journals. This body of work established heuristic relationships between miscibility and device performance. It eventually led to the first quantitative miscibility-structure-function relationship delineated below (*Nature Materials 2018*). Most publications continue to be highly cited.

d.2.4. Molecular alignment relative to domain interfaces.

Collins et al. (*Nature Materials, 2012*) discovered anisotropic scattering patterns in OSC blends when polarized photons are used for R-SoXS characterization. The origin of anisotropy arises from the molecular orientation of one or both of the components relative to the discrete local donor/acceptor interfaces in OSCs, and can be studied even though these interfaces are only locally developed and randomly distributed and randomly oriented within the active layer of the OSC. Tumbleston et al. (*Nature Photonics 2014*) utilized this anisotropy in scattering and with advanced analysis succeeded to establish the importance of the degree of molecular ordering (DMO) of several donor polymers in polymer:fullerene BHJ solar cells. The films were cast using PC₆₁BM as an acceptor from several different solvents with and without fluorine substitution on the polymer backbones. The polymers used were PNDT–DTBT, PBnDT–DTBT, and PBnDT–FTAZ. We have shown for the first time that the DMO is likely a critical morphological parameter for polymer:fullerene solar cells with a bulk heterojunction architecture. More generally, since the molecular orientation at donor-acceptor interfaces has been demonstrated both theoretically and experimentally in bilayer to be important to the photovoltaic process in small molecule devices, the DMO is likely an important measure in a broad range of organic solar cells. As polarized R-SoXS is currently the only scattering technique that can probe non-crystalline organic molecular orientation, it will remain a key technique for future research into many organic systems.

d.2.5. Revealing the special nature of FTAZ

Collaborative work with the You group (materials synthesis) and the Neher group (device characterization), coupled to the morphological characterization of the Ade group revealed one of the secrets to great performance of the FTAZ material and the importance of charge transport (*JACS 2014*). Fluorination has been shown in many materials to improve performance, although the details are still debated. Given that device characteristics depend on many parameters, deriving structure-property relationships has been very challenging. In the case of FTAZ and related copolymers, a single parameter, hole mobility, determines the fill factor of several hundred nanometer thick bulk heterojunction photovoltaic devices based on a series of copolymers with varying amount

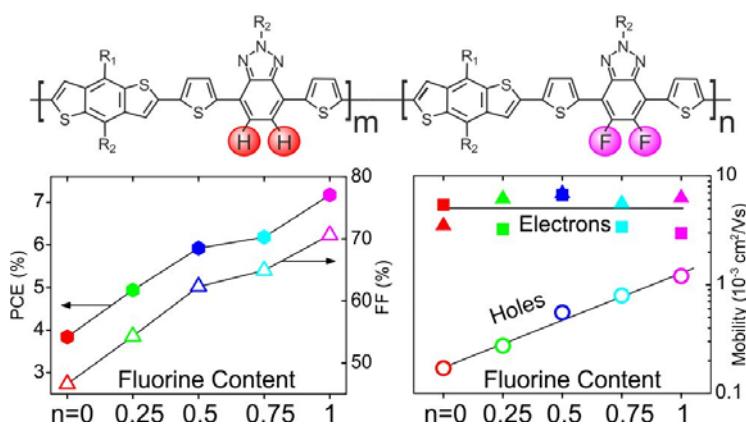


Figure 1. Performance and carrier mobilities for random copolymer with varying fluorine content. The morphology was carefully characterized by the Ade group including domain size, average purity and molecular packing. This is one of the most complete and sophisticated characterization of any OPV system.

of fluorine substitution. We showed that the steady increase of the hole mobility with the fluorine content was related to changes in polymer molecular ordering. Importantly, all other parameters, including the efficiency of free charge generation and the coefficient of non-geminate recombination are nearly identical for the copolymers, including the fully hydrogenated HTAZ. Our work emphasizes the need to achieve high mobility in combination with strongly suppressed charge recombination for thick devices required by mass production technologies. At least in FTAZ, the “fluorine-effect” had no bearing on the charge generation efficiency and thus is counter to several models previously advocated based on less complete characterization.

d.2.6. Linear ISI-FF variations in high efficiency small molecule devices

In collaboration with UCSB groups (Bazan and Nguyen), we investigated high efficiency small molecules systems. We brought our unique measurements fully to bear in these systems. By characterizing the morphology as completely as possible, including average domain purities, we can draw unique conclusions. For example, whereas the role of molecularly mixed domains in organic photovoltaic devices for charge generation was extensively discussed in the literature at the time, the impact on these domains on charge recombination and thus fill factor was largely unexplored. A combination of soft X-ray techniques enabled the quantification of phases at multiple length scales to reveal their role in reducing charge recombination in a highly efficient solution processed small molecule system (p-DTS(FBTTh₂)₂). A clear relationship between the average domain purity and the device fill-factor is revealed for the first time (see Figure 2). The results establish the complex interrelationship between average phase purity, domain size and structural order and highlight the requirement of optimal combination of phase purities and/or volume fractions to diminish bimolecular and geminate recombination in solution processed small molecule solar cells.

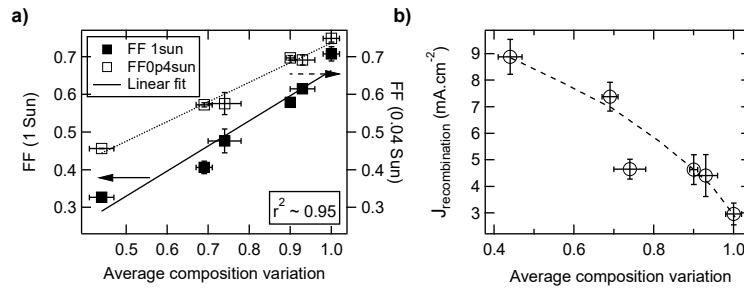


Figure 2: (a) Variation of FF (at 1 Sun illumination) (inset: FF at 0.04 Sun illumination) as a function of average composition variation, i.e. average domain purity. FF strongly correlates with average domain purity (Pearson’s ($r^2 \sim 0.95$)); (b) monotonic decrease of recombination current calculated from maximum power condition relative to $J_{\text{ph}}(-5\text{V})$ with average composition variation (broken line is shown as a guide to the eye).

Figure 2 highlights the requirement of optimal combination of phase purities and/or volume fractions to diminish bimolecular and geminate recombination in solution processed small molecule solar cells.

d.2.7. Record efficiency devices

In collaboration with the He group from HKUST, we unraveled the special characteristics and processing routes of three structurally similar donor materials that all yield exceptional OPV performance, including several unconventional fullerenes and open-literature record performance. Amazingly, ten polymer:fullerene combinations have achieved efficiency above 10%. (Liu, Nature Communication, 2014). This manuscript is highly cited with currently ~1,500 citations in WoS.

d.2.8. Predicting morphology: Quantitative χ -fill factor relations.

Although fullerenes have been the dominant acceptor for organic solar cells for ~20 years an intense search for their replacement is underway to overcome disadvantages such as costs,

limited electronic structure engineering, and limited optical absorption. Numerous non-fullerene small molecule acceptors (SMA) have been reported in the past two years that show rapidly improving performance. The large number of ~2000 possible polymer:SMA systems and additional processing parameter combinations makes it extremely arduous using current combinatorial approaches to optimize the morphology of polymer:SMA blends and find the best material combination and corresponding optimized processing conditions. It is thus crucial to identify key material parameters that affect polymer:SMA morphology and to develop rational approaches of material selection and matching.

We have used bilayer interdiffusion quantified with Secondary Ion Mass Spectrometry (SIMS) to measure the phase diagram of a model system and to establish quantitative χ -FF relations (*Nature Materials*, 2018). We have also developed DSC methods to screen for χ and predict the suitability of a materials system. We believe these achievements will be considered seminal in a few years as they are the very first publication to establish any quantitative relation between thermodynamic properties and the limits they impose on the morphology and performance in a field that is largely progressing by trial and errors. The linear relation highlighted in Figure 2 between the root-mean-square composition variation (average purity) and the FF was a key ingredient in the quantitative model developed, attesting to the consistent and synergistic development of the work over the years while at the same time keeping the quality of the work and publications high. The χ -FF project was initially started with DOE funding, but due to the termination of the funding, had to be completed with ONR funding.

e. List of papers for which support from DOE is acknowledged

Publications in print in which support from this grant has been acknowledged are as follows:

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e. Comprehensive list of people working on the project.

Last Name, First Name	Average % of support obtained from grant	Role of person on the grant
Ade,Harald	9%	PI
Appel,Guenter Karl	80%	Post doc
Araki,Tohru	62%	Post doc
Carpenter,Joshua Howard	72%	Undergrad / Grad. Student
Chavez,John Lyndon	49%	Undergrad student
Collins,Brian Akira	61%	Post doc
Cottrell,Christopher R.	48%	Graduate student
Dhez,Olivier Renee	54%	Post doc
Ennis,David R	93%	Undergrad student
Gann,Eliot Hugh	5%	Graduate student
Ghasemi,Masoud	33%	Graduate student
Gu,Ziran	20%	Graduate student
Guignard III,Lewis Banner	46%	Undergrad student
Harton,Shane Edward	54%	Graduate student
Helms,Eric D	5%	Undergrad student
Hesterberg,Nikolai L	100%	Undergrad student
Hu,Shuming	14%	Graduate student
Hunt,Adrian Hartley	56%	Post doc
Jiao,Xuechen	71%	Graduate student
Kilcoyne,Arthur Lewis	61%	Research Asst. Professor

Kim,Ju Hyun	33%	Post doc
Li,Sen	31%	Graduate student
Ma,Wei	94%	Post doc
Mai,Cong	56%	Graduate student
McAfee,Terry Richard	10%	Graduate student
Melvin,Charles Evander	5%	Undergrad student
Meyer,Aric Paul	100%	Graduate student
Mukherjee,Subhrangsu	54%	Post doc
Nam,Daejin	5%	Graduate student
Schoell,Achim	100%	Undergrad student
Sellers,Kenneth Brandon	100%	Undergrad student
Seok,Jaewook	90%	Graduate student
Sherrill,Nathaniel Lawrence	92%	Undergrad student
Smith,Archie P	100%	Graduate student
Swaraj,Sufal	61%	Post doc
Tang,Maolong	12%	Graduate student
Tumbleston,John Richard	81%	Post doc
Urquhart,Stephen G	33%	Post doc
Walker,Matthew J.	12%	Graduate student
Wang,Cheng	75%	Graduate student
Watson,Anne M	100%	Undergrad student
Watts,Benjamin	100%	Post doc
Wei,Min	100%	Graduate student
Willis,Christine	100%	Undergrad student
Winesett,Donald A	23%	Graduate student
Yan,Hongping	55%	Graduate student
Ye,Long	25%	Graduate student
Zou,Ying	92%	Post doc

f. There is no unexpected funds.