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POLYMER-BASED MATERIALS FOR HARVESTING SOLAR ENERGY (*PHASE*)

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Lead Institution University	University The Pennsylvania State
	University of Massachusetts Lowell University of Pittsburgh
of Massachusetts Amherst	
EFRC-Funded Collaborators	
Significant US Collaborators with no direct EFRC funding	Oak Ridge National Laboratory Temple University

4. COMPARISON OF ACCOMPLISHMENTS AND GOALS/OBJECTIVES

From the synthesis of new materials to the fabrication of the *most* efficient single junction OPV, in over 120 peer-reviewed publications (see Appendix 8) with over 1,200 total citations (***doubling*** each year), PHaSE researchers have made fundamental contributions with significant and sustained impact to the field of OPV. Scientific highlights of the Center include:

- *Polymer Morphologies with High PCE.* **Russell** with Wu (South China University of Technology) optimized the bulk heterojunction morphology of PTB7:PCBM solar cells, to achieve a PCE of 9.77% (9.61%, CPvT-certified), and with Chen (Nankai U), **Russell** developed a rhodium end-capped oligothiophene/$PC_{71}BM$ solar cell with PCE = 8.99% (CPvT-certified), the highest for a single-junction device based on a molecular species.
- *Aqueous Co-Assembly of Polymer Nanoparticles (NPs):* **Venkataraman**, **Lahti**, and **Russell** developed a transformative, environmentally friendly, water-based co-assembly process of pre-fabricated organic semiconductor NPs yielding devices with PCE = 2.1%, the highest PCE for any organic NP-based solar cell.
- *Zwitterionic Polymer Interlayers:* **Emrick** and **Russell** made novel conjugated polymer zwitterions (CPZs) in a new approach for interfacial modification layers (interlayers) in OPVs, which increased PCE by 50-500% for different electrode/interlayer combinations.
- *P3HT Nanostructures with Tunable Electronic Properties:* **Emrick** and **Barnes** generated mechanically robust P3HT nanofibers with tunable internal crystalline aggregation by chemical crosslinking; **Venkataraman** and **Barnes** showed tunability in the internal aggregate structure of P3HT NPs through advanced processing.
- *Polymer NP Superlattices.* **Venkataraman**, **Barnes**, **Dinsmore**, and **Sumpter** introduced the concept of polymer NP superlattices for use in OPVs and demonstrated the influence of NP size and structure on their photophysical behavior.
- *Kinetically Trapped BHJ Mesoscale Morphologies.* **Emrick**, **Hayward**, **Russell**, and **Balazs** demonstrated a general technique for achieving co-continuous nanocomposite morphologies by the jamming of NPs, with size scale controlled by segmental interactions.
- *Active-Layer Materials with Highly Tunable Electronic Properties.* **Thayumanavan**, **Coughlin**, **Lahti**, and **Briseno** developed polymer and oligomer systems with near-panchromic absorption and planar geometries to enhance π-π interactions.

The goals outlined below are drawn primarily from the goals and work described in the May 2012 scientific review of the PHaSE EFRC by the DOE BES, and in a 2013 intra-PHaSE review of research directions undertaken by PHaSE EFRC co-directors and its Internal Advisory Committee. Major PHaSE goals below arise from DOE BES grand challenges (*science.energy.gov/bes/efrc/research/ grand-challenges*). Also, a number of investigations on mesoscale properties are crucial to optimizing active layers in organic photovoltaic (OPV) devices. Brief summaries of accomplishments made toward meeting each goal are listed. Selected accomplishments are described in more detail subsequently in Section 5. Brief summaries of accomplishments made toward meeting each goal are listed. Selected accomplishments are described in more detail subsequently.

****Goal** – Synthesize conjugated chromophores that absorb throughout all (panchromic) or most of the visible solar spectrum for molecules/polymers/assemblies. Computational prediction of absorption properties for synthetically achievable structures is an important companion goal.

***Accomplishments**

- Multiple push-pull molecular and polymer chromophores with band onsets from 550-1000 nm and molar absorptivities to 260,000 $L^{-1}M^{-1}$ (**Lahti-Thayumanavan, Coughlin-Lahti**) have been made and characterized. Several of these have been incorporated into test OPV devices.

- Dithienylpyrrole-co-benzothiadiazole copolymers with varying substitution (alkyl, alkoxyaryl) on the pyrrole group have been made using direct arylation polymerization and have solid film band onsets to just over 700 nm. Both electronic and (especially) processing properties depend strongly on the substituents. These systems perform well in test OPV devices (see below) (**Lahti**).
- Polymer HOMO energies and band gaps for experimentally known electron acceptor type polyarylene vinylenes (with strong acceptor arylene groups such as benzothiadiazole) and for push-pull polymers between dithienylpyrrole and strong acceptor arylenes are so well predicted by density functional theory (DFT) computational methodology that these computations are now being used to select experimentally related polymers for synthesis. (**Lahti-Venkataraman-**Wong[Drexler]).

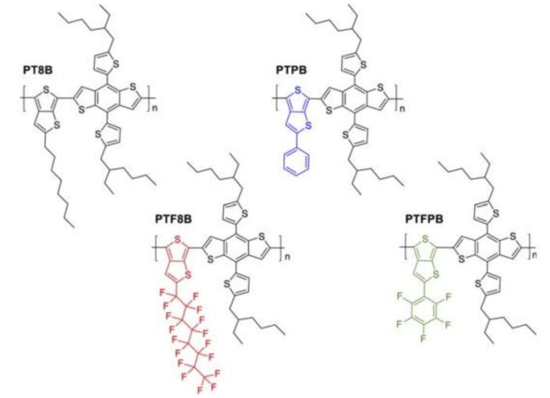

Fig. 1: Example, new low band gap systems: PTB series copolymers with hydrocarbon and fluorocarbon side chain substitution.

- Thieno[3,4-b]thiophene monomers having varying alkyl, aryl, perfluoroalkyl, and perfluoroaryl substitution were copolymerized with dithienylbenzodithiophene units by direct arylation polymerization to give PTB copolymers (**Fig. 1**) with strong absorption out to 1.56 eV in films (**Coughlin-Lahti**). These have HOMO/LUMO energy levels that are well aligned for use as electron donor materials in ITO/PCBM type OPV devices, and are being tested for such use (**Coughlin**).

****Goal** -- Identify and induce/control effects of molecular or polymer packing and self-assembly as a means of improving or simplifying OPV fabrication, and of testing and improving OPV charge mobility. This includes achieving balanced hole/electron charge transport in organic polymer thin films and nanoparticle assemblies, with high open-circuit voltages and large short-circuit currents in OPVs. This requires predictable tuning of organic HOMO and LUMO energies (E_{HOMO}, E_{LUMO}), and band gaps (E_g), plus matching E_{HOMO}, E_{LUMO} to cathode and anode materials.

***Accomplishments –**

- A major, multi-group PHaSE effort to develop surfactant-stabilized, organic polymer and molecule nanoparticles (NPs) has reached important milestones in the past year:
  - ❖ Polymer and molecule-based NPs have been fabricated in films (**Fig. 2**) by a highly reproducible, straightforward, ecologically low-impact, water-based process. At present regioregular (rr) P3HT NPs can be made with diameters down to 30 nm, and with low, 15% size dispersity. PCBM nanoparticles of similar size and dispersity have also been made. A patent for this methodology has been granted (USSN 15/301,365, **Venkataraman**).
  - ❖ Removal of excess SDS surfactant from PHaSE-processed P3HT NPs improves charge transport significantly over NP films that retain excess surfactant. Spray-coated films of rr-P3HT NPs made by the PHaSE process exhibit time-of-flight hole transport charge mobilities equal to those of pristine rr-P3HT films made by conventional spin coating. The surfactant-minimized films show charge transport that is much less trap limited, much less dispersive, and therefore more appropriate for electronic use (**Venkataraman-Lahti-Russell**).

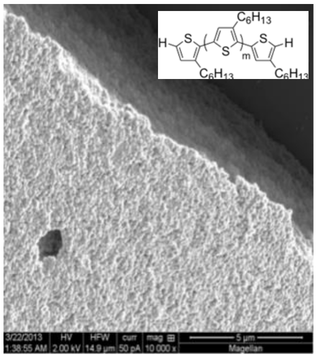

Fig. 2: Spray painted film made with rr-P3HT NPs stripped of excess SDS surfactant.

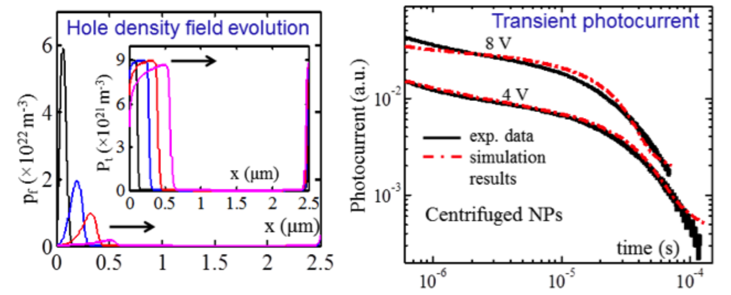

Fig. 3: (Left) Simulated evolution (with time as indicated by the arrows) of free and trapped (inset) hole density profiles in a P3HT sample consisting of a NP assembly with the excess surfactant molecules removed under a bias of 4 V. (Right) Least-squares fits of simulation predictions (red dot-dashed lines) to experimental data (black solid lines) for photocurrent evolution under various applied biases in P3HT films consisting of NP assemblies with the excess surfactant molecules removed. The modeled contact area of the film with the electrodes is A = 6 mm^2.

- ❖ Computational modeling is underway to determine ideal mixture ratios of hole and electron transporting NPs to maximize BHJ pathway connections in a randomly composed film, and yield optimum charge transport (**Venkataraman-Dinsmore**).
- ❖ Deterministic charge transport computational modeling fits experimental photocurrent evolution behavior very well for both hole transporting rr-P3HT thin films and for PHaSE type rr-P3HT NP assemblies (**Fig. 3**). The method is being extrapolated to make predictions for new conjugated materials being fabricated into NP films (**Maroudas-Venkataraman**).

- Fabrication procedures were identified to create highly networked, fibrillar morphologies for new generation hole transporting conjugated polymers:
  - ❖ Chloroform / polar secondary solvent mixtures optimize bulk heterojunction (BHJ) morphology in PDPPBT:PC$_{71}$BM films (**Fig. 4**) giving a very wide range of morphologies with OPV power conversion efficiencies (PCE) ranging from 0.6% to 5%. This finding significantly broadens the scope of presently used good/bad solvent mixture techniques for tuning BHJ morphology, which usually focuses on the vapor pressure differences between nonpolar solvents (**Russell**).
  - ❖ Structural changes in 98.5% regioregular rr-P3HT in varying temperature influence hole transport. Temperature dependent WAXD of regiorandom rra-P3HT indicates that intramolecular distance increases with thermal expansion. The constant interchain distance in rra-P3HT suggests that the charge hopping distance between chains in the amorphous phase of rr-P3HT is also temperature independent. The WAXD structural probe studies of temperature dependence for these morphologies are a guide for optimizing morphologies in other polymers having significant crystallinity (**Russell**-Duzhko),

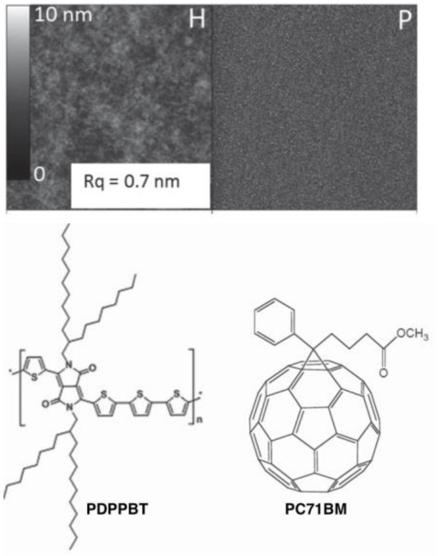

Fig. 4: AFM showing height (H) and phase (P) profiles of highest PCE film for PDPPBT:PC$_{71}$BM BHJ films; Rq = roughness.

****Goal** -- Develop and use polymer and organic molecular interlayer compounds and materials to improve electrode-organic interface transport, and to vary the "inherent" open circuit voltage (V_{OC}) that is typically set by HOMO and LUMO energy levels of electron donor and electron acceptor materials used in a BHJ device. Strong dipole-based effects in the interlayer materials (e.g., from permanent dipoles arising from zwitterionic substituents) induced desired variations, and can significantly alter OPV behavior with use of interlayer thickness as low as 5 nm.

***Accomplishments --**

- PCEs of BHJ polymer OPV devices were increased by >500% (0.92% to 5.78%) when PHaSE-developed zwitterion-substituted conjugated polymer (cpz-polymer) interlayers were incorporated (**Fig. 5**). The improvement arose from reducing the Ag cathode work function in the device, due to dipole alignment effects. An analogous, though lesser, effect (68% improvement) was seen in OPV devices using Al cathodes. Interlayer thickness was critical, with 5 nm thick films producing the most efficient devices. CPZ polymers like PTBTSB have good solvent orthogonality with lower polymer layers, and are readily fabricated into interlayers that are as effective or better than vapor-deposited LiF (**Emrick-Russell**-Duzhko).

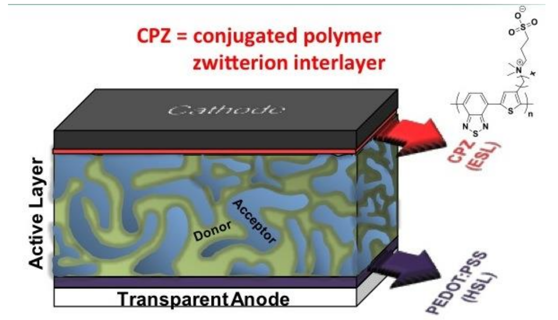

Fig. 5: Scheme the design of a BHJ OPV device using Ag or Al cathode, donor = PTB7, acceptor = PC71BM, with a CPZ, permanent dipole substituted polymer as a thin interlayer.

- Two novel fulleropyrrolidines bearing tertiary amine (C_{60}-N) or zwitterionic sulfobetaine (C_{60}-SB) moieties were tested as cathode buffer interlayers in OPV devices. Charge mobility studies using bilayer OPV devices shows C_{60}-N to have the higher electron transport mobility, and provides a truly Ohmic contact with superior device performance under those device conditions. These findings were used to produce a record PCE single junction OPVs (see below, **Emrick-Russell**-Duzhko).

****Goal --** Directly probe the electronic and structural nature of freely-solvated versus aggregating polymer chains, aggregation behavior as fabrication solvents are removed, and the formation of varying thin film morphologies when annealed or otherwise morphologically manipulated post-deposition. The influence of ordering and alignment on photovoltaic performance is considerable, therefore spectroscopic, computational, and structural (in situ x-ray diffraction and x-ray scattering [XRD, XRS], AFM, cAFM, etc.) probes of "as-fabricated" nanostructures and films are invaluable for understanding *why* successful fabrication strategies work.

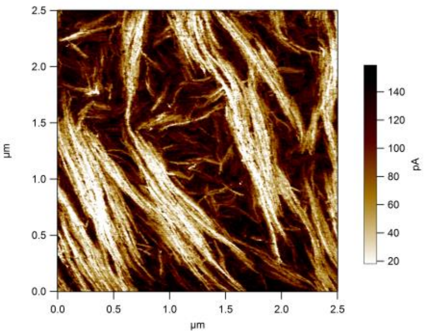

Fig. 6: cAFM of a polymer/PCBM BHJ.

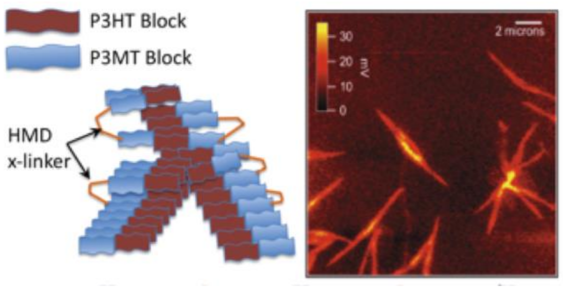

Fig. 7: (Left) Scheme showing branched nanostructure made from crosslinked P3HT-P3MT diblock copolymers. (Right) Surface potential contrast image of nanostructures show spatially varying work function.

***Accomplishments**

- A new collaboration (**Barnes-Briseno-**Spano[Temple]) to model π-stacking with electronic behavior shows excellent correlation of experimental absorption spectral features for crystalline nanopillars of tetraazaterrylene derivatives with specific crystal packing motifs, when the spectra are modeled using DFT and semiempirical INDO/S computational modeling of dyad and larger cluster models for the crystal lattice. A model that incorporates some degree of X—X → X^+—X^- charge transfer in a pi-stack gives superior agreement with experiment, compared to a model using Frenkel exitons alone.

- cAFM measurements (including Kelvin probe force microscopy and electrostatic force microscopy) have been successfully deployed to show the variation in BHJ for films of active layer polymers, PCBMs, and molecules, which are assembled by the same methodology used to incorporate these components into OPV devices. cAFM for spray-coated mixtures of single-component organic NPs using PHaSE-developed methodology shows completely different, granular BHJ from the highly fibrillar, connective patterns seen (**Fig. 6**) in mixed-solvent fabricated BHJs using PCBM and conjugated electron donor copolymers (**Venkataraman-Lahti**).
- Surface potential contrast imaging of P3HT cross-linked with poly(3-methanol-2,5-thiophenediyl))=P3MT shows nanoscale detail in a variety of nanostructures. Kelvin probe force microscopy (KPFM) reveals the nanostructures (**Fig. 7**) to have spatially varying work function with individually cross-linked nanoribbons and 'brittle-stars'. The nanoribbons show highly crystalline central cores with disordered P3HT toward the ribbon ends, as evidenced by contact potential changes (**Barnes-Emrick**).

****Goal --** Integrate the results of the various specific areas of progress described above, to improve OPV device performance. Particular targets are PCE increases by new fabrication strategies and increased device active area, using the most promising materials and morphological tuning strategies.

***Accomplishments --**

- PTB7 and PCE10 (high performance, new generation electron donor material polymers for organic photovoltaics) were fabricated into single junction BHJ OPVs with $PC_{71}BM$ as an electron acceptor material. The BHJ morphologies were optimized by a combination of high boiling additives plus thermal annealing, with various cathode metals used (Ca, Al, Ag, Cu, Au). Fabrication of OPV devices with addition of a 5-55 nm thick interlayer of fulleropyrrolidine with a tertiary amine (C_{60}-N) or a zwitterionic sulfobetaine (C_{60}-SB) gave single-junction PCE up to 8.91% with a Ag electrode (NREL certified), and a record high 9.78% with a Ca electrode (**Emrick-Russell**-Duzhko).
- Dithienylpyrrole-co-benzothiadiazole copolymers with varying substitution (alkyl, alkoxyaryl) on the pyrrole group have been made using fairly new direct arylation polymerization, characterized, and incorporated into test organic photovoltaic (OPV) devices (**Lahti**) having PCE up to 5.1% after initial morphological optimization work. Polymer HOMO energies and band gaps for these are well predicted by computational methodology using 1-D repeat unit symmetry; this method is now being used to select new targets with desired electronic properties (**Lahti-Wong**[Sandia]).
- A bis(hydroxyaryl)anilino-squaraine SQ-OH used as electron donor material with $PC_{71}BM$ gives PCE = 4.8% after morphological optimization. Grazing incident angle x-ray diffraction (GIXD) shows "as-fabricated" SQ-OH/$PC_{71}BM$ films to have varying amounts and sizes of SQ-OH crystallites, depending on the fabrication procedure used. OPV films form 48 nm SQ-OH crystallites (resonant soft x-ray scattering) in a largely $PC_{71}BM$ matrix for devices made by using a mixed solvent plus diiodooctane (DIO) slow-evaporating additive with thermal annealing. (**Thayumanavan-Lahti-Russell**).
- Fluorine-substituted di(aryl)anilino-squaraines SQ-F and SQ-CF3 added to P3HT give increased PCE to 4.6% for "in-air" fabricated OPV devices using $PC_{61}BM$; this performance is much higher than for in-air devices made with P3HT alone, and is comparable to PCE for *highly optimized* P3HT OPV devices without SQ additives (**Thayumanavan-Kumar**[**UM-Lowell**]**-Lahti**).
- Small molecule, molecular additives (electron acceptor fluorenes or anthracene substituted by donor diarylamines) increase relative PCE by 33% in Grätzel type D709-based DSSCs when added in 1-3 mM concentrations to DSSC iodide/iodine dye-recharging solution, up to 4% absolute PCE for devices made in open air. The improvements do not arise from improved light

harvesting (low optical density), but apparently by improving the iodide/iodine electron shuttle efficacy -- the additives do not work without the iodide/iodine component (**Lahti-Kumar**[**UM-Lowell]**).

- Increasing device active area from 0.1 to 0.25 mm^2 using a slot-die coating process (**Fig. 8**) for a PTB7-PC$_{71}$BM OPV device gave only a slight decrease in PCE from 6.23% to 5.43%. The 0.25 mm^2 area device compares well to the 7.1% PCE of a device using a "classic" spin-coated BHJ film with only a 0.06 mm^2 active area (**Russell**).

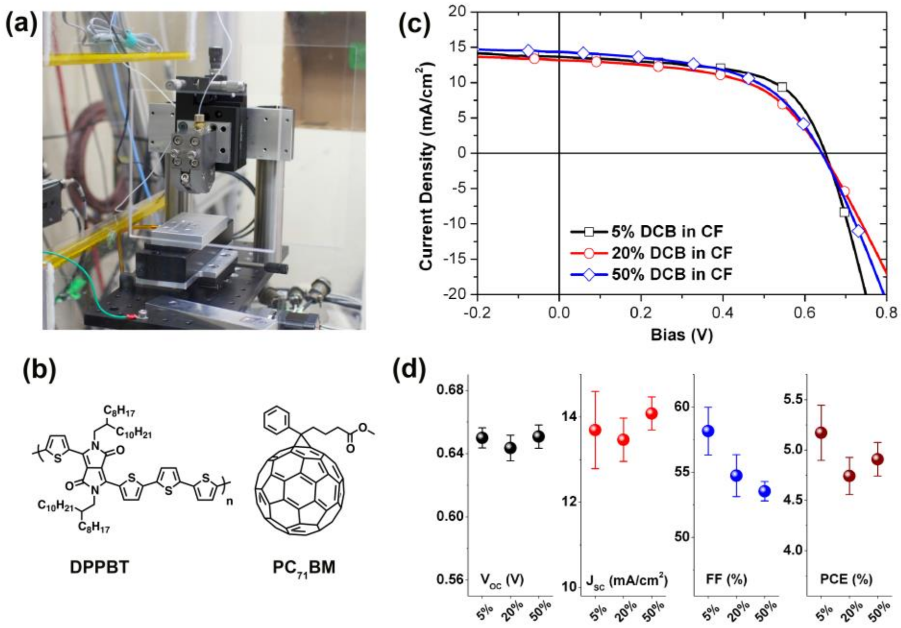

Fig. 8: (a) Mini slot die instrument; (b) conjugated polymer donor and PC71BM acceptor; (c) I-V curves of BHJ devices fabricated by slot die coating using different solvent compositions; (d) device performance statistics. DCB = *ortho*-dichlorobenzene, CF = chloroform

5. MAJOR EFRC ACTIVITIES, RESULTS, FINDINGS, ACHIEVEMENTS

- **Interlayers for Improving Photovoltaic Performance**

Emrick and **Russell**, working with PHaSE Facility Director Duzhko, have shown that conjugated polymers bearing zwitterionic sulfobetaine side chains (CPZ polymers) can readily be processed into ESLs that give up to 5-fold increases in PCE relative to control OPV devices that do not use the ESL, depending on the cathode material. The magnitude of PCE improvement is comparable or better than that achieved in devices using LiF ESLs. The CPZ polymers provide a low temperature methodology for adding ESLs, since they can be spin coated from polar solvents that are orthogonal to those that dissolve typical neutral organic conjugated active layer polymers. For tests using the hole transport layer PTB7 and the interlayer CPZ polymers the best device PCE was 7.74% for an ITO/PEDOT-PSS/PTB7:PC$_{71}$BM/PTBTSB-2/Ag device having a PTBTSB-2 interlayer of 5 nm thickness. The PCE improvement (relative to devices without ESLs) arises largely from increases in V$_{OC}$ and FF. The increase in V$_{OC}$, in turn, is attributed to the largest interfacial dipole value (–0.96 eV) induced in this study, at the PTBTSB-2/Ag interface. Carbon K-edge total electron yield (≈10 nm) and Auger electron yield (≈1 nm) NEXAFS spectra (obtained in collaboration with D. DeLongchamp at NIST) used to assess polymer chain orientation at different film thicknesses indicate that the CPZ polymers assume a face-on orientation with respect to the underlying active layer, and that the aliphatic portions of the chains are not oriented normal to the film surface. The zwitterionic side chains of the CPZ polymers can be considered as dipoles fixed rigidly to the conjugated backbone, directing the negative charges towards the cathodic surface. This orientation should and does reduce the cathode work function, but only for the first monolayer or so: the strong distance dependence of the dipole interface effect is consistent with a thin, 5 nm film of CPZ polymer providing optimal effects.

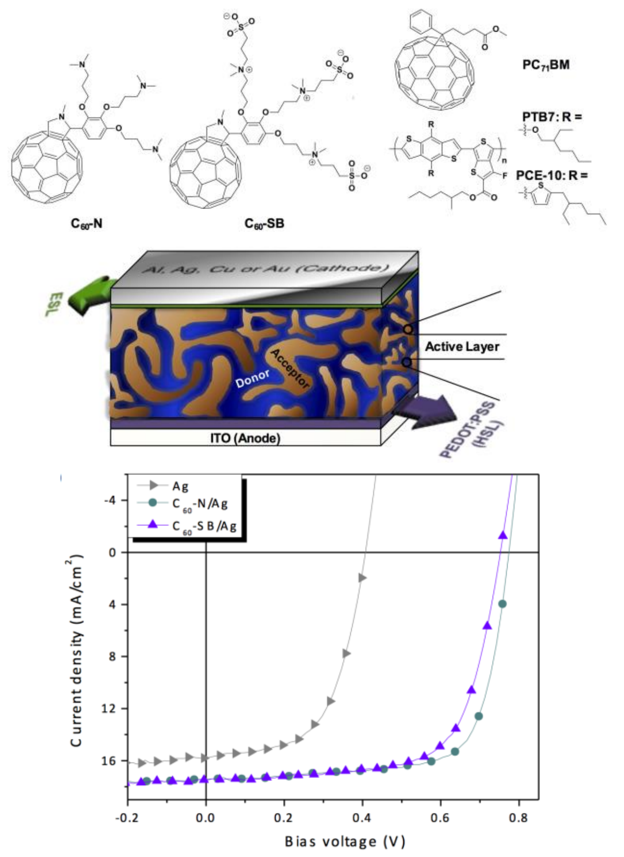

Fig. 9: Representative J–V characteristics for ITO/PEDOT:PSS/PCE-10:PC71BM/(fulleropyrrolidine)/ cathode OPVs with bare Ag cathodes and with ~15 nm-thick C60-N or C60-SB ESLs.

Emrick and **Russell**, working with PHaSE Facility Director Duzhko, recently investigated fulleropyrrolidines bearing a tertiary amine (C60-N) or a zwitterionic sulfobetaine (C60-SB) as cathode ESLs in single junction polymer solar cells. Compared to ITO/PEDOT-PSS/PCE-10/(no ESL)/Ag OPV devices that gave PCE = 2.75%, spin coated devices using a C60-N ESL gave a single-junction record PCE = **9.78**% (**Fig. 9**). Overall, PCEs exceeding 8.5 % were obtained for OPVs made with Al, Ag, Cu or Au cathodes, with V$_{OC}$ ~0.75 V being obtained regardless of the cathodic metal used. PCE > 6 % was obtained over a wide range of interlayer thicknesses (~5–55 nm) using both C60-N and C60-SB. Ultraviolet photoelectron spectroscopy (UPS) indicates that an interfacial energy “pinning” effect causes the essentially cathode-independent device performances. A work function of 3.65 eV is obtained for Ag, Cu and Au when a thin layer of C60-N is placed in contact with each metal. UPS and charge mobility studies indicate that C60-N provides a truly Ohmic contact under the tested device conditions. The relative ease of making C60-N and C60-SB, combined with their ability to create highly efficient OPVs, makes these fulleropyrrolidines excellent models and candidates for further optoelectronic integration.

- **Targeting Nanoscale-Networked, Fibrillar Active Layer Morphologies**

Crystalline nanofibers (or nanowires) of poly (3-hexylthiophene) – one of the most studied polymers for OPV applications - have attracted a great deal of interest because of the potential for efficient exciton or charge migration along specific directions (transverse or parallel) with respect to the nanofiber axis, processes which strongly depend on structural order and molecular packing within the aggregate. Solution-based assembly of such crystalline structures opens new possibilities for controlled interfacing. However, the inherent fragility of nanowire assemblies is a key limitation, so preserving their pristine aggregate (π-π stacking) structure is seen as essential for efficient long-range charge-transport. **Emrick** group recently made cross-linked block-copolymer nanofibers from P3HT-b-P3MT and P3HT-b-P3ST (**Fig. 10**) that are mechanically robust, and can be coated onto surfaces, re-suspended, and/or mixed with a variety of dopants.

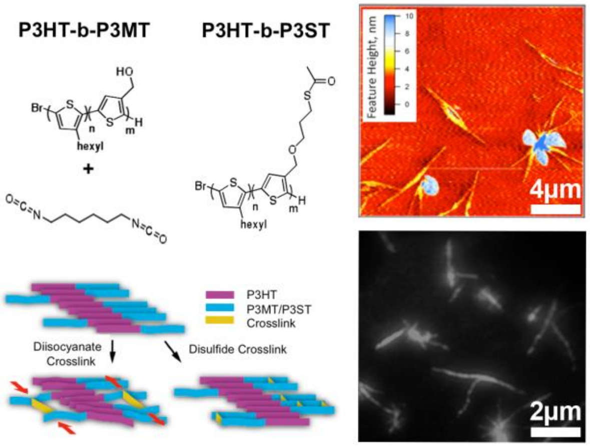

Fig. 10: (Left) Structural schematic of the P3HT-P3MT/P3ST diblock copolymers. Purple bars indicate lamellar assembly of the P3HT blocks, while the blue P3MT (P3ST) blocks participate in the cross-linking (yellow). (Top right) AFM surface height image of P3MT-crosslinked nanofibers showing different morphologies (wires, ribbons, and nanosheet "clover-leaf" structures). (Bottom right) Photoluminescence image of dilute P3HT-b-P3MT cross-linked nanofibers cast on glass.

Barnes and **Emrick** then probed the extent to which cross-linking perturbs the crystalline aggregate, and how different cross-linking strategies can tune electronic properties such as photoluminescence and charge separation efficiency. While the two nanofiber families have similar gross structure (and almost identical pre-cross-linked absorption spectra), they have completely different photophysics. P3ST di-block nanofibers show almost unchanged excitonic coupling after cross-linking. Cross-linked P3MT nanofibers show photoluminescence similar in electronic origin, vibronic structure, and lifetime, to un-aggregated P3HT molecules, suggesting almost complete extinction of excitonic coupling. Films of these materials were probed by bulk photoluminescence measurements and by nanoscopic AFM and cAFM (Kelvin Probe Force Microscopy), as shown in **Fig. 10**. Overall, for the P3ST system, the spatial extent of the cross-linking is approximately commensurate with the inter-lamellar spacing, giving a minimally perturbed aggregate structure. For the P3MT system, the cross-linking induces a high degree of strain on the P3HT aggregate block, disrupting both intra- and inter-chain coupling.

- **Soft Matter Nanoparticles: A General Strategy for Bulk Heterojunction Fabrication?**

PHaSE has made major time and personnel investment in trying to devise a more generalizable methodology for fabricating donor-acceptor BHJ films from organic components, that the typically Edisonian variation of component concentrations, solvent mixtures, additives (such as DIO), and thermal annealing that can be quite different for every new component tested. **Venkataraman**, **Barnes**, and **Dinsmore** summarized such a potential methodology in 2011, for binary mixtures of organic nanoparticles (NPs) to crease BHJ superlattices for photovoltaics. The basic goal is to pre-assemble organic electron donor and acceptor components into separate nanoparticles, that are then hierarchically assembled in BHJ films: the main variables would be use of different ratios of particles with different diameters to alter the number and types of charge flow pathways in the films. This is shown schematically in **Fig. 11**.

Venkataraman's group now can prepare rr-P3HT NPs with diameters down to 30 nm having <15% size variability. **Venkataraman** and **Dinsmore** have formulated water-based methodologies for either spray-coating NP films or fabricating (larger) NP films at a water-oil interface for removal. **Venkataraman**, **Lahti**, and **Russell** showed that rr-P3HT NP films exhibited photogenerated hole carrier charge transport even in the presence of excess SDS surfactant (used to stabilize the NPs), with much improved charge motilities in films that were subjected to a simple procedure to remove free surfactant from NP suspensions before spray coating. **Venkataraman** and **Maroudas** have found that the transport behaviors of the polymer NP films can be reproduced very well with deterministic computational models, allowing eventual extrapolation to behaviors of new materials using similar NP particle sizes.

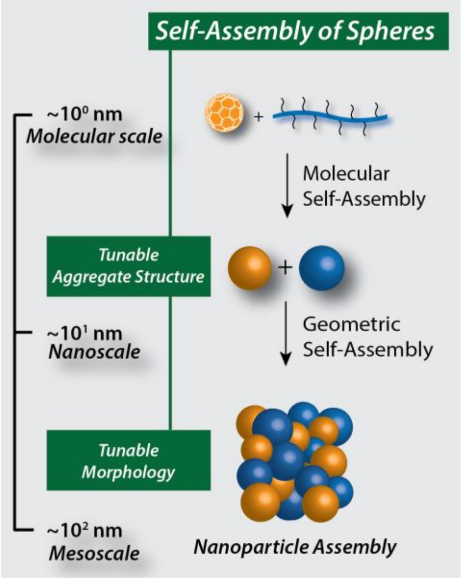

Fig. 11: Conceptual scheme for hierarchical pre-assembly of organic polymer and/or material NPs,that are subsequently assembled into larger BHJ

Venkataraman, **Lahti**, and **Dinsmore** showed that both binary mixtures of single component rr-P3HT and $PC_{61}BM$ NPs -- as well as binary component NPs using the same components -- show photoconversion behavior. While others have recently demonstrated photoconversion using binary component NPs, this is the first evidence that the most general strategy of using binary mixtures of single component NPs would give photoconversion. cAFM even shows regions having high and low hold transport mobility on the scale expected for a binary mixture of different NP components. Most notably, OPV devices made using binary mixtures of rr-P3HT and $PC_{61}BM$ NPs with a spray coated fabrication method have already be made with PCE = 2.1%, the highest PCE reported for any organic NP based OPV to date. This is comparable to PCEs obtained in unoptimized rr-P3HT:$PC_{61}BM$ spin coated BHJ OPV devices.

- ***In situ, Real Time* Characterization Under Commercially Relevant Conditions**

Tremendous efforts have been made wordwide to develop efficient light absorbing materials and devices. These advances have been achieved on laboratory scale devices and translation to large size scale devices has always been met with significant reductions in the PCE. Spin coating is routinely used to prepare laboratory-scale devices, while industrial processes have used blade or slot-die coating processes in a roll-to-roll (R2R) setting. These coating processes are fundamentally different in terms of solvent removal rate, which is critical in defining the kinetically-trapped morphologies encountered in the generation of the active layers in OPVs that result from a delicate interplay between the ordering and assembly of the hole-conducting polymer and a phase separation between the electron and hole conductors into bicontinuous morphologies.

The mismatch in device fabrication processes makes it difficult to translate quantitative results obtained from laboratory scale devices to commercially prepared large area devices, making optimization difficult. Using a mini-slot die coater (**Fig. 8**), **Russell** addressed this issue, where the commercial process was translated to the laboratory setting and *real time, in situ* to characterization of the active layer could be performed as films are cast from solution. The evolution of the morphology in the active layer was characterized under different drying conditions and a mechanism was proposed by which the morphology in the dried film is produced. This mini-slot die coater offers a simple, convenient, materials efficient route by which the morphology in the active layer can be optimized.

- ***Self- healing polymer sealant for encapsulating flexible solar cells***

Venkataraman used polyisobutylene (PIB)-based fully printable self-healing sealant for protecting organic photovoltaic (OPV) devices from degradation upon exposure to ambient environmental conditions. These sealants can be coated on flexible substrates using any roll-to-roll processing methods. PIB-based crosslinked sealants provide excellent device stability, especially the sealant made from the low molecular weight PIB. Additionally, this sealant provides healing of damage even under sunlight, albeit more slowly compared to that under UV light. Although various polymers such as polyvinyl alcohol, polyurethane, poly(methyl methacrylate) or poly(methyl methacrylate)-polyolefin have been used as a coating materials to protect organic active layers of OPVs from degradation. However, these polymers are also susceptible to degradation and crack formation upon prolonged exposure to unfavorable weather condition which ultimately allows moisture to pass through the coating and eventually damage the OPV systems. Furthermore, these coating materials are generally too permeable to moisture and oxygen. In this work, we demonstrated that PIB-based self-healing polymer sealants protect organic photovoltaics from damages caused by prolong exposure to hot and humid environmental conditions. The broad impact of this work is new materials for protecting the OPVs from environmental damages and providing enhanced life times of the OPVs which will benefit the society.

- ***Self- Raising efficiency of organic solar cells with electrotropic additives***

Incorporation of electrotropic additives with large molecular dipole moments into the bulk heterojunction layer of organic photovoltaic devices followed by electric field poling led to an increase of power conversion efficiency up to 7.97% from 7.17% for devices that did not utilize the additives and from 5.18% for devices with additives prior to poling. The improvement is due to more efficient extraction of photogenerated charge carriers, resulting in higher short circuit current density and fill factor. The observed effects are proposed to arise from a re-orientation of additive molecules in the external electric field, i.e., electrotropism, leading to a macroscopic alignment of their dipole moments. This leads to an increased built-in electrostatic potential difference in the device active layer post-poling. The dependence of device performance on the polarity of poling bias and reversibility of the effect are demonstrated, further supporting the proposed mechanism.

6. COST STATUS

PHaSE EFRC Budget Report Year 5

	Total	Projected	Current Spent/Enc.
Budget	$ 16,000,000	$16,000,00	$16,000,000

Equipment	(all of the original equipment line item budget has been expended)
Personnel	(all of the original personnel line item budget has been expended)

* Five-year equipment budget $1,260,000. Approval to purchase most equipment "up front" in the early years of the project was requested at the first EFRC Director's meeting (June 2009) and OK'd at that meeting. This was desired to allow a faster startup for the center, especially critical properties measurements needed to evaluate materials for possible utility in photovoltaic test devices. This procedure was discussed periodically during the ordering of major equipment in the first fiscal year of the project, including a site visit by Dr. Mark Pederson in early December 2009. This was also presented as part of the management and operations review for PHaSE that took place in mid-May 2010, which was overseen by DOE program officers (including Dr. Pederson) and by external reviewers. The management plan for PHaSE was approved following that review meeting. Accordingly, we have continued with this procedure for equipment purchasing since that time.

This summary does not include matching or additional funds from other sources that were used for capital equipment outlays.

Additional External support to PHaSE from UMass Amherst:

1. Support for Facility Director Extension Assistant Professor position: $45,225 salary and $823 benefits, per 9-month appointment
2. Space for Photovoltaic and Optical Spectroscopy Center: 1306 sq ft in two adjacent rooms
3. A 10% reduction of indirect cost rate from the UMass rate that was standard at the time PHaSE began, allowing more of the total costs to be allocated to direct costs.

Cumulative PHaSE EFRC Budget Report Years 1-5

Total	**Projected**	**Current**	**Spent/Enc.**	
Budget	$16,000,000	$16,000,000	$16,000,000	Total Costs
Equipment	1,260,000*	1,260,000	$1,260,000*	Direct Costs
Personnel	6,000,000	6,172,000	$5,840,000	Direct Costs

* Five-year equipment budget was $1,260,000. Approval to purchase most equipment "up front" in the early years of the project was requested at the first EFRC Director's meeting (June 2009) and approved at that meeting. This was desired to allow a faster startup for the center, especially critical properties measurements needed to evaluate materials for possible utility in photovoltaic test devices. This procedure was discussed periodically during the ordering of major equipment in the first fiscal year of the project, including a site visit by Dr. Mark Pederson in early December 2009. This was also presented as part of the management and operations review for PHaSE that took place in mid-May 2010, which was overseen by DOE program officers (including Dr. Pederson) and by external reviewers. The management plan for PHaSE was approved following that review meeting. Accordingly, we continued with that procedure for equipment purchasing.

Current budget = original budget numbers.

7. SCHEDULE STATUS

(a) Management Timelines. The original PHaSE EFRC proposal did not set Gantt-type timelines.

(b) Budget Schedule. The full 5-year PHaSE budget was front-loaded in August 2009 because PHaSE was funded through ARRA. All funds have been expended.

(c) Research and Organizational Milestones. PHaSE was created in 2009 as a new research center at UMass Amherst: it was not "spring-boarded" from a previously organized group of faculty or center. A number of milestones given below were specifically identified by the 2010 DOE BES Management Review, the 2012 Mid-term Scientific Review of PHaSE by DOE BES, and 2013 major internal review by the PHaSE Internal Advisory Board (Energy Research Group coordinators).

- *Expansion of the Center's External Advisory Committee* to six people was finalized.
- *Expansion of the Center's internal leadership group* was fully implemented.
- A *near-field scanning optical microscopy* (NSOM) *setup was successfully completed.*
- *Generally strengthened linkage of computational and experimental work* was done.
- *New high risk, high potential yield research foci targeted in Year 4* was accomplished through:

(i) *fabrication of polymer nanoparticles* (NPs) into test photovoltaic devices (achieveing 2.1% PCE by mixing P3HT NPs with PC61BM NPs, highest value in the world for this promising new technology) (**Venkataraman**, **Lahti**, **Dinsmore**)

(ii) *organic polymer zwitterion interlayers* were fabricated as thin (5 nm) layers by an orthogonal solvent procedure to tune electrode properties (**Emrick**, **Russell**)

(iii) the *polymer zwitterion interlayer technique* was *computationally modeled* by collaboration between **Russell** (UMass) and **Sumpter** (Oak Ridge)

(iv) a *new computational/experimental collaboration* between **Spano** of Temple University and **Barnes** of PHaSE at UMass was established and continues for the study of *exciton dynamics in aggregated, conjugated organic polymers and molecules*.

(v) push-pull polymers incorporating benzothiadiazole and dithienylpyrrolo-pyrrole (DPP) that were targeted in 2012 and 2013 PHaSE reviews were synthesized and tested in single junction, bulk heterojunction devices (**Lahti**, **Coughlin, Venkataraman**)

(vii) synthesis and photovoltaic testing is well advanced for a novel set of triarylamino-substituted squaraine compound being used as electron donor phases, both alone and in mixtures with conjugated polymers or with solution-fabricated perovskites; the work comes from a team comprising **Thayumanavan**, **Lahti**, and **Kumar** (UMass Lowell)

(viii) fabrication of bulk heterojunction (BHJ) *organic polymer, single-junction photovoltaic devices at or near the world's best PCE levels, e.g.,* a 8.91% NREL certified PCE with *FF* = 71.7% for a PCE10/PC$_{71}$BM photovoltaic device using an organic zwitterion interlayer (**Russell, Emrick**)

8. CHANGES IN APPROACH OR AIMS

There have been no major changes in the project aims or research strategy/approach. Work increasedin focus to fabricate test solar cells using the most promising new materials and methods to make them into bulk heterojunctions and other electronic assemblies.

9. PROBLEMS OR DELAYS

none

10. SABBATICALS, LEAVES OF ABSENCE, CHANGES OF KEY PERSONNEL OR TEAMING ARRANGEMENTS

These have been described in previous annual reports.

11. PRODUCTS AND TECHNOLOGY TRANSFER

(a) Journal and Book Publications

All papers, articles, and book chapters are listed at *www.energyfrontier.us* per DOE BES instructions.

From 1 August 2009 to 1 December 2016, *188 articles* have appeared or are in press acknowledging PHaSE EFRC support (not counting basic meeting abstracts). The se are provided in Appendix 1.

(b) Other Publications

- (We chose not to list basic meeting abstracts or other non-refereed publications.)
- The following articles acknowledging PHaSE-supported work were selected for special recognition in the relevant journals in which the articles were published. These cover art recognitions (including cover and frontpiece art) publicize PHaSE and the EFRC program.
    - (*Cover*) “Using Light To Guide the Motion of Nanorods in Photoresponsive Binary Blends: Designing Hierarchically Structured Nanocomposites” by Ya Liu, Olga Kuksenok, and Anna C. Balazs (**Balazs**, UPitt) for pages 12785-12795 of *Langmuir*, October 15, 2013: Vol. 29, Issue 41.
    - (*Frontpiece*) “Efficient Charge Transport in Assemblies of Surfactant-Stabilized Semiconducting Nanoparticles” by Monojit Bag et al. (**Venkataraman**, **Lahti**, **Russell**) for pages 6411-6415 of *Advanced Materials*, November 26, 2013: Vol. 26, Issue 44.
    - (*Frontpiece*) “Photovoltaic Effect at the Schottky Interface with Organic Single Crystal Rubrene” by Supravat Karak et al. (**Briseno**) for pages 1039-1046 of *Advanced Functional Materials,* February 26, 2014: Volume 24, Issue 8.
    - (*Frontpiece*) “Highly Stretchable Nanoparticle Helices Through Geometric Asymmetry and Surface Forces” by Jonathan T. Pham et al. (**Grason**, **Emrick**, **Crosby**) for pages 6703–6708 of *Advanced Materials*, December 10, 2013: Volume 25, Issue 46.
    - (*Editor's Choice Article*) “Highly Stretchable Nanoparticle Helices Through Geometric Asymmetry and Surface Forces” by Peng Liu et al. (**Russell**) has just appeared online at DOI:10.1021/cm500953e of *Chemistry of Materials*, April 14, 2014: dx.doi.org/10.1021/cm500953e.

(c) Selected websites that publicized, highlight, or use PHaSE work

- "PHaSE Energy Frontier Research Center at UMass Amherst" (*www.cns.umass.edu/efrc*).
  This site was significantly revamped this year in terms of content and format.
  Public site with details of PHaSE personnel, facilities, news, publication listing, useful links.
  Password protected secure intranet site includes PHaSE internal reporting site, presentation/discussion group archives, materials for use of External Advisory Committee members during virtual meetings.
- " Solar PHaSE. Advancing the frontiers of polymer-based photovoltaic research" (*www.umass.edu/researchnext/solar-phase*). Featured in March-(present) research news webpage from UMass Amherst Research Next.
- "Power Polymers -- Developing the next generation of solar cells" (*www.umass.edu/ researchnext/power-polymers*) and " Light Show: Next Generation of Solar Cells"

(*www.umass.edu/researchnext/light-show-next-generation-solar-cells*) still show PHaSE work from 2012-2013 at the research news webpage from UMass Amherst Research Next.

- "Science Works for U.S." (*www.scienceworksforus.org/massachusetts/scientists-seek-better-ways-to-harvest-sun-s-power-for-electricity*). Webpage for ScienceWorksForU.S., a project of the Association of American Universities. The specific page gives a summary of PHaSE's research as an Energy Frontier Research Center.
- "The Role of Molecular Architecture in Organic Photovoltaic Cells", (*pubs.acs.org/page/jpclcd/dv-video.html*). This is an American Chemical Society Office of Public Affairs video that describes findings supported (in part) by PHaSE. It is linked from a perspectives article published in *J. Phys. Chem. Lett*. by UMass Amherst PHaSE members -- the text article acknowledges PHaSE support.
- A Timeline of Photovoltaic Progress (*www.tiki-toki.com/timeline/entry/62320/Photovoltaics/#vars!date=1839-09-29_00:00:00!).* A "discovery" based website describing progress made in the area of photovoltaic cells, particularly in the area of organic-based solar cells (Plastic solar cells). The time line starts with Becquerel's observation of the photoelectric effect, and includes links to the DOE BES EFRC program at the DOE's description for the PHaSE center. The page is pitched at a level to interest any science-minded person, young to old.
- "Science Cinema" (*www.osti.gov/sciencecinema/product.biblio.jsp?osti_id=1027996*). From the DOE multimedia website, UMass Amherst video clip entry for EFRC program.

(d) Inventions, Patents, Disclosures

A table for patents field are in Appendix 2.

(e) Other Products (invited presentations, symposia, infrastructure improvements)

(i) *Symposia*

A PHaSE mini-symposium will be featured at the 14 May 2014 UMass Amherst Spring Polymer Event attended by numerous companies and organizations interested in applying polymer and materials science.

(ii) *Special Invited Presentations by PHaSE Leadership Members.*

PHaSE senior scientists made *over 75 invited and contributed presentations* at nationally meetings and venues, and *over a dozen invited* presentations *internationally*, describing work enabled by PHaSE support.

Examples by PHaSE Leadership Senior Investigators:

PHaSE co-director **Lahti** gave 4 international talks focusing on PHaSE work: Universidade de Minas Gerais, Belo Horizonte, Brazil (27 September 2013); Universidade Federal do Rio de Janeiro, Brazil (4 October 2013); Waseda University, Tokyo, Japan (9 October 2013); Keio University, Tokyo, Japan (9 October 2013). He also spoke about organic based photovoltaics to the ACS Connecticut Valley Section overseen round of the 2014 U.S. National Chemistry Olympiad held at UMass Amherst on 18 Mar 2014).

PHaSE co-director **Russell** gave invited international presentations at AIMR Tohoku University (18 March 2014) and Waseda University (18 March 2014). He also gave an invited talk at the 2014 Triennial Review of the Advanced Light Source at LBNL.

PHaSE ERG 1 coordinator **Emrick** spoke about “New functional hydrophilic polymers in materials applications,” at the ACS National Meeting (Dallas, 16 March 2014) and about “Directing assembly of polymer-functionalized nanoparticles in fluids and on substrates,” at the ACS National Meeting (Indianapolis, 8 September 2013).

PHaSE ERG 2 coordinator **Venkataraman** spoke about "Geometry and Entropy as New Tools for Self-Assembly”, at the Indo-US Symposium on Molecular Materials, Indian Institute of Science

(Bangalore, 15 July 2013) and about "Polymer Nanoparticle Assemblies" at the ACS National Meeting (Indianapolis, 10 Sept 2013).

PHaSE ERG 3 co-coordinator **Barnes** spoke about "Tuning Exciton Coupling in P3HT Nanostructures," at the ACS National Meeting (Indianapolis, 7 Sept 2013).

PHaSE ERG 3 co-coordinator **Maroudas** spoke about "Computational Analysis of Electronic and Mechanical Properties of Graphene/Diamond Superstructures," at the VII Brazilian Congress on Applied Thermodynamics (Uberlandia, MG, Brazil, November 2013).

(iii) *Infrastructure Improvements*

- University of Massachusetts Amherst, PHaSE Photovoltaic & Optical Spectroscopy Facility was established and continues to operate under independent funding.
- A *near-field scanning optical microscopy* (NSOM) *setup was successfully completed* and continues to operate under independent funding.

Appendix 1. PUBLICATIONS

1 Wang, Y. C. *et al.* Alkylthio substituted thiophene modified benzodithiophene-based highly efficient photovoltaic small molecules. *Organic Electronics* **28**, 263-268, doi:10.1016/j.orgel.2015.10.006 (2016)

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