Final Technical Report

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"Crystallization-driven assembly of conjugated-polymer-based nanostructures"

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Executive Summary

The goal of this project has been to improve our ability to simultaneously control the organization, and therefore the opto-electronic properties, of conjugated-polymer based materials across three different length-scales: 1) the molecular scale, in the sense of controlling growth and functionalization of highly crystalline semiconducting organic materials capable of efficient charge transport, 2) the nanoscale, in terms of positioning n- and p-type materials with domain sizes comparable to exciton diffusion lengths (~ 10 nm) to facilitate charge separation, and 3) the colloidal scale, such that well-defined crystalline nanoscale building blocks can be hierarchically organized into device layers.

As described in more detail below, the project was successful in generating powerful new approaches to, and improved fundamental understanding of, processing and self-assembly of organic and hybrid semiconducting materials across all three length-scales. Although the goals of the project were formulated with primarily photovoltaic architectures in mind, the outcomes of the project have significant implications for a variety of conjugated-polymer-based devices including field-effect-transistors for sensors and logic devices, as well as potentially thermoelectrics and battery electrode materials. The project has resulted in 10 peer-reviewed publications to date [1-10], with several additional manuscripts currently in preparation.

Accomplishments

Controlled growth of functional conjugated polymer nanofibers

While the ability of conjugated polymers to assemble from solution into crystalline nanofibers has been appreciated for many years, and used to significant extent to improve the performance of devices, we sought to obtain improved control over the growth of these nanowires, including the extension of such assembly approaches to polymers bearing a variety of different chemical functionalities. Poly(3-hexyl thiophene) (P3HT) represents one of the most intensively studied conjugated polymers and can be synthesized with a comparatively high level of control over molecular weight and functionality of both side chains and chain ends, thus making it a natural choice for our studies.

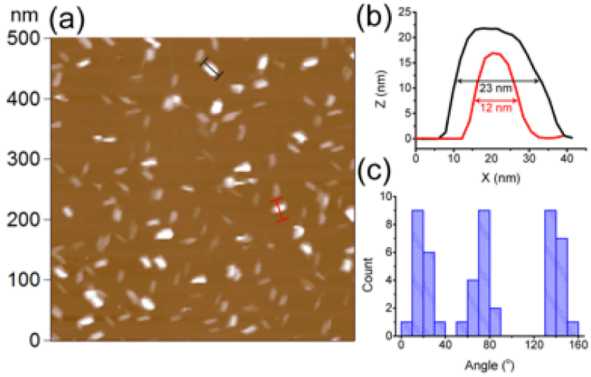

Figure 1. **(a)** *In situ* AFM image of P3HT nanofibers grown on HOPG for 3 h. **(b)** Height profiles corresponding to the colored lines in (a). **(c)** The distribution of orientation angles of the nanofiber long axis relative to the horizontal direction reveals three preferred orientations, suggesting epitaxy.

A key finding of the current project is that surfaces coated with graphene (or graphite) enable selective nucleation of crystalline P3HT nanofibers from metastable supersaturated solutions of the polymer, as summarized in Figure 1 [8]. This result is important from at least two perspectives. First, the resulting materials present an important opportunity in the design of organic photovoltaic devices, since graphene represents an attractive alternative to ITO for transparent electrodes, while the vertical growth of pi-stacked nanowires is an ideal geometry for a bulk-heterojunction device layer. Second, the system represents an ideal platform for fundamental studies of the crystallization of conjugated polymers. For example, analysis of growth kinetics revealed a

saturation in film thickness as a function of time, indicating that the growing tips of nanofibers must be poisoned, e.g., due to the accumulation of defects in the lattice structure. This observation correlates well with measurements of seeded crystal growth kinetics in bulk suspensions, which revealed anomalously low Avrami exponents suggesting poisoning of growing nanofibers, and therefore the difficulty of achieving "living" crystallization of P3HT-based nanofibers. Although our initial study focused on only a single molecular weight of P3HT, we have since been able to extend it to a variety of molecular weights, as well as a second polymer, poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene] (PBTTT), which has superior electronic characteristics compared to P3HT. A manuscript describing the generalization of the technique and a comparison of the growth kinetics is planned for 2017.

The project also made major strides in the assembly of crystalline conjugated polymer nanofibers bearing functional groups that can be used for crosslinking to improve stability, or attachment of other species to aid processing. In particular, we focused on two different, and highly versatile, groups placed at the end of the alkyl substituents of poly(3-alkyl thiophenes). In the first case, thiol functional groups were installed, allowing the nanowires to be reversibly crosslinked and uncrosslinked through mild chemical oxidation and reduction steps [5]. In the second case, we made use of azide groups, which provide irreversible UV-induced crosslinking. Importantly, as much as 20 mol% of the azido-thiophene monomer could be incorporated into a random copolymer with P3HT without significantly reducing the ability of the copolymer to crystallize into nanofibers. Due to this high density of azide functional groups, UV-induced reaction of only ~ 50% was sufficient to provide crosslinked nanowires with excellent thermal and solvent stability, while leaving behind many sites for further chemical modification of nanofibers using azide-alkyne "click" chemistry [9]. For example, Figure 2 shows crosslinked P3HT nanofibers coated with poly(ethylene glycol) chains in this manner, which allowed the fibers to be subsequently suspended in, and processed into devices from, polar solvents including alcohols and water. In the effort to move toward organic electronic components that can be processed from "green" solvents, this strategy has considerable potential.

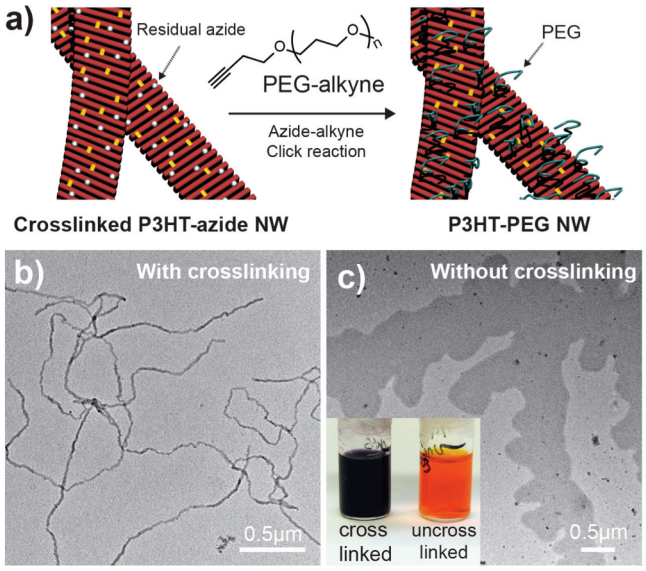

Figure 2. (a) Schematic of "click" functionalization of photo-crosslinked P3HT-azide nanofibers and TEM images of **(b)** successfully functionalized wires and **(c)** dissolved polymer obtained by functionalization of uncrosslinked wires (inset: photograph of the respective suspension/solution).

Finally, the experience developed in growth and structural characterization of well-defined nanofibers through this project fed directly into two collaborative studies of the photophysical properties of P3HT nanofibers with the group of Barnes at UMass. Significant differences were found in the extent of *H*-type aggregate coupling (corresponding to inter-chain pi-pi overlap) and *J*-type coupling (corresponding to intra-chain conjugation) as a function of the degree of polymer regioregularity and solvation of the nanofibers [2], as well as chain folding of P3HT [4].

Crystallization-driven assembly of hetero-nanostructures

The second main goal of the project was to move beyond nanostructures of a single material, to heterostructures incorporating two different semiconducting materials placed in well-defined spatial arrangements. Toward this goal, we focused on two major sub-themes: (i) conjugated-polymer nanofibers with chemically functionalized edges, and (ii) coupled crystal modification in mixtures of conjugated polymers and small molecules.

One example of the first approach is summarized in Figure 3. Here, P3HT polymers bearing a ligand functionality (either thiol or phosphonic acid) were first synthesized and allowed to assemble into crystalline nanofibers. Since the chain ends cannot pack into the crystalline polymer lattice, they are almost entirely confined to the edges of the fibers. Subsequent incubation of these fibers with CdSe nanoparticles therefore led to adsorption of particles along the fiber edges, and even bundling into larger superstructures consisting of alternating domains of P3HT and CdSe [1]. This alternating placement of p-type polymer and n-type inorganic semiconductor with ~ 10 nm domain sizes is anticipated to facilitate charge transfer between the materials; consistent with this expectation, photoluminescence measurements of the hybrid nanostructures showed almost complete quenching of fluorescence from CdSe. In a second example along similar lines, block copolymers of P3HT and a poly(3-alkyl thiophene) bearing amine groups at the alkane chain end were assembled and reacted with di-isocyanate functionalized fullerenes [6]. In this case, reaction with difuctional fullerenes provided not only chemical crosslinking of the fibers (and therefore thermal and solvent stability), but also yielded photoluminescence quenching and ambipolar charge transport characteristics.

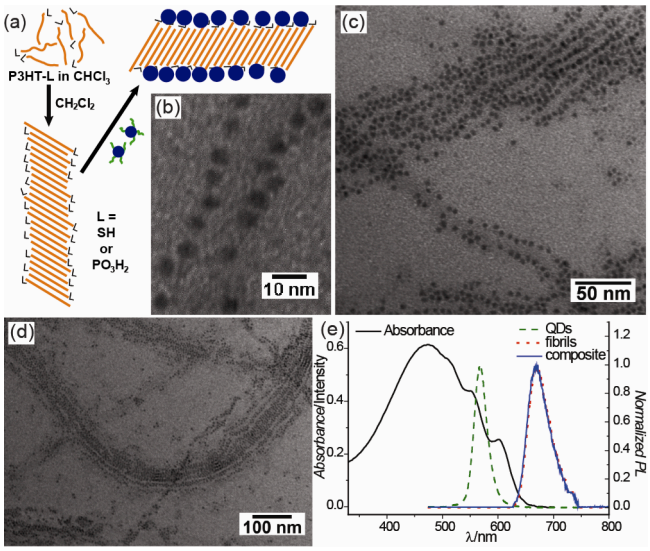

Figure 3. **(a)** Schematic illustration of hybrid nanowire assembly by nanoparticle adsorption to ligand-functionalized polymer nanowires. **(b)** – **(d)** TEM images showing individual fibers flanked by CdSe nanoparticles and larger scale "superhighway" bundles. **(e)** UV-vis absorbance of composites, and photoluminescence spectra.

In the second main approach, we studied crystallization in mixtures of conjugated polymers, primarily P3HT, with conjugated small molecules, primarily *N*,*N*'-dioctyl perylene diimide (PDI). Remarkably, a mixture of these two materials cast from ortho-dichlorobenzene (*o*-DCB) yields "shish-kebab"-like heterostructures (Figure 4c), consisting of a central

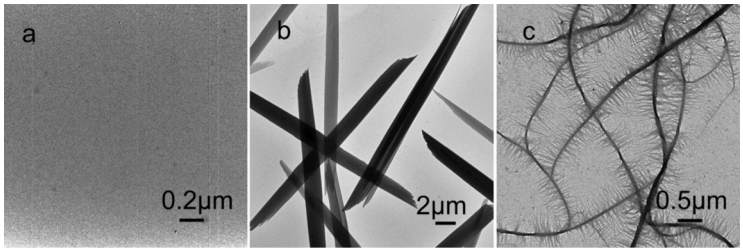

Figure 4. (a) When P3HT is cast from *o*-DCB, little if any crystallization takes place, while **(b)** casting PDI from *o*-DCB leads to large (several μm wide) crystals. Casting a mixture of the two materials, however, yields shish kebab nanostructures where PDI forms the central wire.

crystalline PDI nanowire flanked by P3HT nanofibers [3]. The mechanism of formation of these heterostructures, which we term 'coupled crystal modification', was determined to be as follows. P3HT adsorbs to crystals of PDI (primarily on the PDI (012) crystal faces), dramatically slowing the crystal growth rate and also changing the crystal shape, i.e., serving as a 'soluble additive' during PDI crystal growth. At the same time, the PDI crystals serve as efficient heterogeneous nucleating agents for crystalline P3HT fibers. Having understood this basic mechanism, we were subsequently able to use it to grow highly controlled hetero-crystalline nanostructures. Relying on P3HT to slow down the growth rate of PDI crystals, and ultrasonication to speed up the effective rate of crystal nucleation (possibly through fragmentation of existing nuclei), we were able to form short PDI "seed" crystals, that could be controllably extended in length by adding defined amounts of dissolved PDI in supersaturated solutions [7]. The preferred widths of the PDI crystals could also be tuned through the concentration of P3HT in solution. Finally, in addition to controlling the morphology of the PDI 'shish', the length of P3HT 'kebabs' formed during solvent evaporation could be varied through changes in overall P3HT/PDI ratio, thus providing access to a wide range of controlled heterostructures (e.g., Figure 5). Although our initial studies have focused on a limited set of constituent conjugated organic materials, we suspect that similar mechanisms of conjugated polymers adsorbing to, and nucleating from, other semiconducting organic nanocrystals should be quite general. Further, although our studies were conceived primarily with photovoltaic devices in mind, the ability to control growth of organic p/n heterostructures such as these may have important implications in a variety of other contexts, including logic devices (as described in the following section), sensors, and even thermoelectric devices.

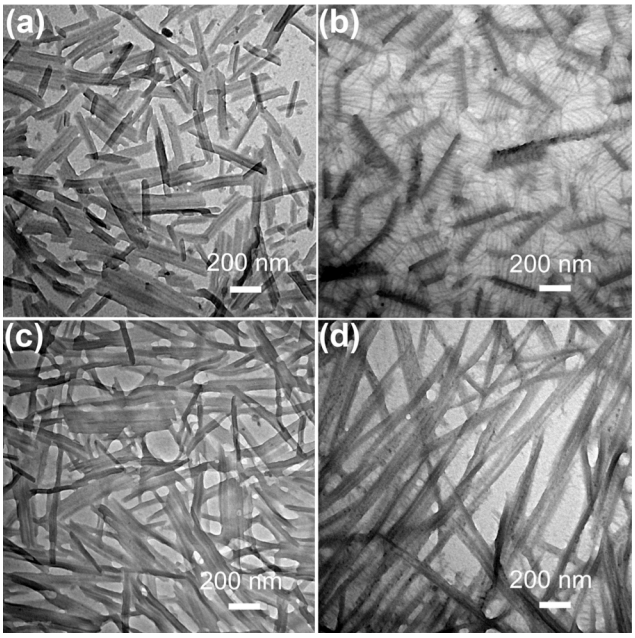

Figure 5. (a) PDI nanocrystal "seeds" prepared by sonication with P3HT can be extended with **(b)** additional P3HT, **(c)** additional PDI, or **(d)** both, yielding well-defined hybrid nanocrystals.

Colloidal-scale organization of nanocrystalline building blocks.

The final major goal of the project was to control organization of the precisely-defined building blocks developed in the first two goals into larger (device-scale) architectures through colloidal-scale assembly. Given the high level of control achieved in both lateral sizes and length distributions of PDI nanowires modified by P3HT, we decided to focus on this system for achieving higher-level assemblies.

As expected, PDI nanowires with sufficiently high aspect ratios (length/width) spontaneously form nematic phases in suspension. For example, Figure 6 shows cross-polarized optical micrographs of a series of suspensions with increasing aspect ratio: the shortest nanowires (length/width ~ 20) form an isotropic suspension, while the longest (length/width ~ 45) form a nematic phase, with a two-phase nematic/isotropic co-existence in-between. What is remarkable, however, is the exceedingly low volumetric loading at which this behavior takes place. Based on the Onsager criterion, we should expect a nematic phase to form for rods with

an aspect ratio of 40 only above a volumetric loading of ~ 10%. For the PDI nanowires here, however, this behavior is seen almost two orders of magnitude lower in concentration, i.e., at 0.16%. High-resolution microscopy studies suggest that while the nanowires are colloidally stable against macroscopic precipitation, they are not fully dispersed, instead tending to stick to each other. Thus, the effective aspect ratio of the resulting nanowire aggregates is apparently much larger than that of the primary nanocrystals, therefore yielding lyotropic liquid crystalline behavior even at low volumetric loadings. A manuscript describing these findings is currently in draft form and should be submitted by December, 2016 [11].

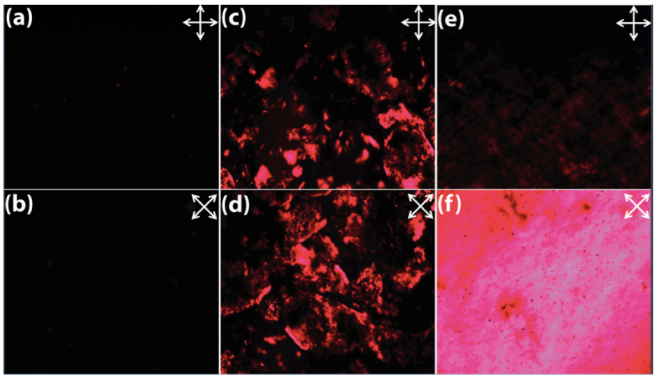

Figure 6. Cross-polarized optical micrographs of PDI nanocrystal suspensions (0.16 vol. %) with aspect ratios (length/width) of: (a, b) ~ 20 (c, d) ~ 30 and (e, f) ~ 45. Each image is 4 x 4 mm.

The tendency of these high aspect ratio crystalline structures to self-organize provides powerful opportunities to tailor the electronic properties of the resulting materials if the global (device-scale) alignment can be controlled. We suspect that a variety of different methods should allow for alignment (e.g., shearing, magnetic or electric fields, etc.), but have found a very simple method based on pinning of an evaporating droplet by a glass capillary tube placed on a substrate to be effective. As shown in Figure 7b, mixtures of PDI and P3HT cast in this manner yields aligned nanocrystal films (deposited in bands due to stick-slip motion of the contact line, i.e., the 'coffee-ring' effect). X-ray scattering and polarized optical microscopy measurements revealed a high degree of ordering, corresponding to a 2D order parameter of ~ 0.8 for both PDI and P3HT (where 1 represents perfect orientation and 0 is random). For appropriate ratios of the two materials, field-effect transistor device measurements conducted with the source and drain electrodes separated by a gap oriented along the direction of the PDI nanocrystals exhibited reasonably good n-type behavior, but not p-type behavior [10]. In contrast, the perpendicular electrode orientation gave good p-type behavior, but not n-type. Thus, these aligned hetero-nanocrystals represent a fundamentally new class of organic semiconductors that we term 'orthogonal ambipolar semiconductors'. We showed how such

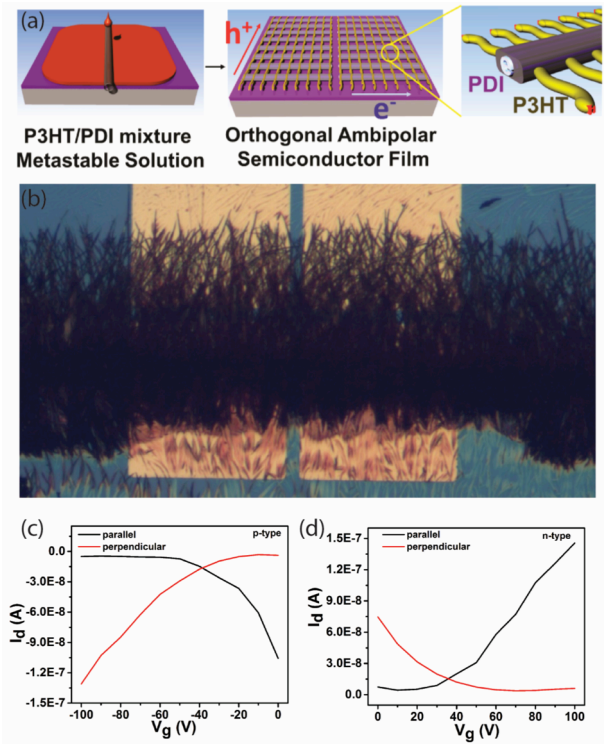

Figure 7 (a) Schematic illustration of aligned 'shish-kebab' film formation. **(b)** FET device architecture and an optical micrograph of a fabricated device. **(c)** FET devices show p-type behavior along the direction perpendicular to PDI nanowires, and **(d)** n-type behavior along the parallel direction.

materials could be used to build complementary logic gates (inverters, as well as 'NAND' and 'NOR' gates) out of a single film of semiconductor without any post-deposition modification steps needed to change the polarity of the charge carriers. Further, we demonstrated the fabrication of similar structures using both the better-performing conjugated polymer, PBTTT, as well as an alternative n-type molecule based on naphthalene diimide, suggesting that it should be possible to generalize this strategy to a wide variety of organic semiconductors.

Publications

(125 citations as per ISI Web of Science search on 10/12/16)

1. E.B. Pentzer, F.A. Bokel, R.C. Hayward, T. Emrick "Nanocomposite "Superhighways" by Solution Assembly of Semiconductor Nanostructures with Ligand-Functionalized Conjugated Polymers", *Advanced Materials, **24**, 2254-2258* (**2012**). DOI: 10.1002/adma.201104788

2. M. Baghgar, J. Labastide, F. Bokel, I. Dujovne, A. McKenna, A.M. Barnes, E. Pentzer, T. Emrick, R.C. Hayward, M.D. Barnes, "Probing Inter- and Intrachain Exciton Coupling in Isolated Poly(3-hexylthiophene) Nanofibers: Effect of Solvation and Regioregularity", *Journal of Physical Chemistry Letters*, **3**, 1674-1679 (**2012**). DOI: 10.1021/jz3005909

3. L. Bu, E. Pentzer, F.A. Bokel, T. Emrick, R.C. Hayward, "Growth of poly(3-hexyl thiophene)/perylene tetracarboxydiimide donor/acceptor shish-kebab nanostructures by coupled crystal modification", *ACS Nano*, **6**,10924-10929 (**2012**). DOI: 10.1021/nn3043836

4. M. Baghgar, J.A. Labastide, F. Bokel, R.C. Hayward, M.D. Barnes, "Effect of Polymer Chain Folding on the Transition from H- to J-Aggregate Behavior in P3HT Nanofibers", *The Journal of Physical Chemistry C*, **118**, 2229–2235 (2014). DOI: 10.1021/jp411668g

5. B.A.G. Hammer, M.A. Reyes-Martinez, F.A. Bokel, F. Liu, T. P. Russell, R.C. Hayward, A.L. Briseno, and T. Emrick, "Reversible, Self Cross-Linking Nanowires from Thiol-Functionalized Polythiophene Diblock Copolymers", ACS Applied Materials & Interfaces, 6,7705-7711 (2014). DOI: 10.1021/am500976w

6. B.A.G. Hammer, M.A. Reyes-Martinez, F.A. Bokel, F. Liu, T.P. Russell, R.C. Hayward, A.L. Briseno and T. Emrick, "Robust polythiophene nanowires cross-linked with functional fullerenes", *Journal of Materials Chemistry C*, **2**, 9674–9682 (2014). DOI: 10.1039/c4tc01898b

7. L. Bu, T.J. Dawson, R.C. Hayward, "Tailoring Ultrasound-Induced Growth of Perylene Diimide Nanowire Crystals from Solution by Modification with Poly(3-hexyl thiophene)", *ACS Nano*, **9**, 1878-1885 (2015). DOI: 10.1021/nn506795q

8. D.E. Acevedo-Cartagena, Jiaxin Zhu, Elvira Trabanino, Emily Pentzer, Todd Emrick, Stephen Nonnenmann, Alejandro L. Briseno, and Ryan C. Hayward, "Selective nucleation of poly(3-hexyl thiophene) nanowires on multilayer graphene substrates", *ACS Macro Letters*, 4, 483-487 (2015). DOI: 10.1021/acsmacrolett.5b00038

9. H. J. Kim, M. Skinner, A.L. Briseno, T. Emrick, B.J. Kim, R.C. Hayward, "Water Processable Polythiophene Nanowires by Photo-crosslinking and Click-functionalization", Nano Letters, 15, 5689-5695 (2015). DOI: 10.1021/acs.nanolett.5b01185

10. W. Huang, J.C. Markwart, A.L. Briseno, R.C. Hayward, “P3HT/PDI shish kebabs: orthogonal ambipolar semiconductors for complementary logic gates”, ACS Nano (2016). DOI: 10.1021/acsnano.6b03942

11. W. Huang, R.C. Hayward, “Poly(3-hexyl thiophene)-Modified “Living Crystallization” and Lyotropic Liquid Crystalline Behavior of Perylene Diimide Nanowires”, in preparation (2016).