Final Technical Report
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Contractor: University of Massachusetts Amherst
Award Title: Chemical Microscopy of Conjugated Molecules and Hybrid Nanostructures
Reporting Period: 8/15/2005 – 11/14/2017
Prinicipal Investigator: Michael D. Barnes

Summary statement

This research program was focused on development of new material platforms and analytical spectroscopy methodologies for probing inter- and intra-molecular electronic processes in conjugated nanomaterials. A detailed understanding of the connection between molecular architecture, supramolecular/polymer assembly, and optoelectronic function is critical to the improvement in polymer-based optoelectronics, yet many questions remain outstanding as to how to 'program' specific inter-molecular couplings via molecular structure in order to achieve desired device performance (photostability, charge-separation and charge-transport efficiency). We combine single-molecule spectroscopy tools and new synthetic methodologies to probe intra- and inter-molecular coupling in small-molecule, oligomeric complex structures and crystalline nanoscale supramolecular assemblies in order to understand in detail, the structure-excitonic property relations and elucidate molecular design rules (distances, angles, etc) for improved performance in organic optoelectronics.

Summary of work over the most recent renewal period: Chemical Imaging of directional interactions in organic semiconductor nanowires

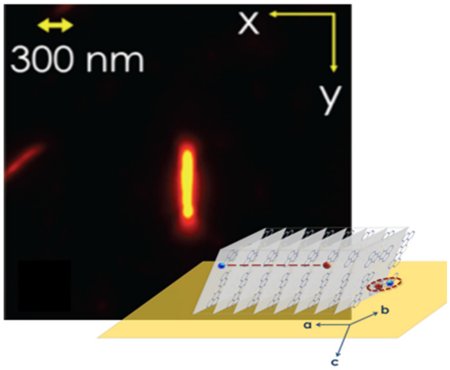

Figure 1. Fluorescence image and structural schematic (foreground) of an isolated TAT nanowire crystal. In this case the pi-stacking direction is aligned along the Y-axis in the lab frame, and optical polarization in either excitation or emission can be referenced to either the X or Y dimension.

Our recent work has focused on the chemical imaging of ordered assemblies of tetraazaterrylene (TAT), recently featured in *Materials Today*. Figure 1 shows a photoluminescence image and structural schematic of an isolated TAT nanowire crystal. In our experiments, the goal is to understand directional interactions in ordered molecular assemblies so that it is critical that we isolate individual nanowire crystals. In this format, the nanowire crystal plays a material role analogous to a single molecule in which different optical polarizations in either absorption or emission can be referenced to different directional interactions in the crystal. Quantitative modeling of the of the TAT absorption spectrum revealed the coexistence of two different aggregate types: An H-type Frenkel exciton (dipole-dipole) component, and a J-type charge transfer (CT) component, both of which act almost exclusively along the π-stack direction. The deeper implication of this work was the idea that directionality in both short- and long-range interactions might be tuned, leading to significantly enhanced control over energy and charge transport in crystalline assemblies of small molecule semiconductors. Further this provides a unique chemical imaging opportunity in which the balance between exciton coupling and charge transfer interactions (revealed by different optical spectroscopies) is defined by sub-Å displacements in both directions perpendicular to the pi-stacking axis.

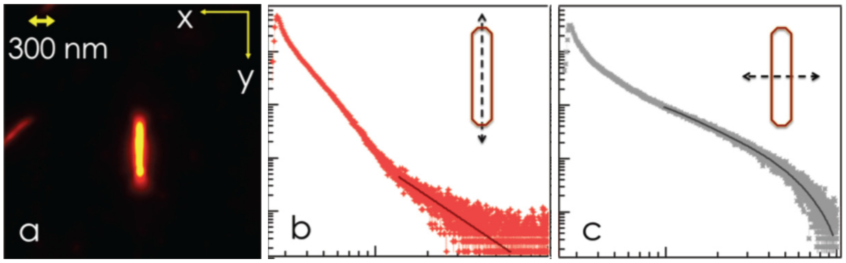

Figure 2. (a) PL image of TAT nanowire and experimental geometry. (b) Log-Log plot of PL counts vs. time for longitudinally (Y-) polarized emission, and (c) Log-Log plot of PL vs. time for transverse (X-) polarized emission. The X-polarized emission follows exponential decay, while the Y-polarized emission shows a delayed component following a power law.

In general, the physical consequences of mixing of coupled exciton and charge transfer states can be profound: In cases where the sign of both interactions are positive (the HH aggregate), exciton transport along the dominant coupling direction is strongly enhanced, while in the case where both interactions are negative (the JJ aggregate) charge transport is enhanced. TAT crystals represent an interesting intermediate case in which the exciton coupling interaction is positive, while the CT interaction is negative giving rise to an HJ aggregate. The physical consequence of this destructive interference between the coupling modes is the existence of interchromophore excitons (where the positive and negative charges are shared between adjacent molecules) with low exciton binding energy – i.e. high dissociation probability along the direction of interaction. In our recent publication in *Nature Communications*, we have observed directly the spectroscopic signature of this intrinsic directional exciton fission. Figure 2 shows the PL decay from an isolated TAT nanowire decomposed into emission polarized along the chromophore (X) axis, and the pi-stacking (Y) axis. The X-polarized emission follows normal first-order kinetics (exponential decay) as expected for excitations localized on individual molecules. The Y-polarized emission however follows *second*-order kinetics, i.e a power-law decay described by $I(t) \approx A\, t^{-\mu}$ where A is an amplitude, t is the time, and μ is the power law exponent. This power law decay derives from exciton fission along the pi-stacking axis, followed by exciton regeneration at longer time by a polaron capture mechanism. To our knowledge, this is the first observation of directional charge separation in organic semiconductors, and suggests some exciting new directions in organic optoelectronics such as polarization-based optical switching and organic photovoltaics.

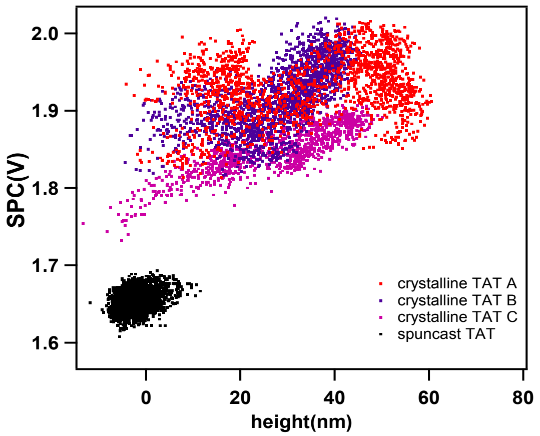

Figure 3. Comparison of surface potential contrast (SPC) between TAT nanowire crystals and spun-cast TAT films. Higher SPC means less negative HOMO level; the nanowire crystals have a ground state energy that is ≈ 200 meV above that of uncoupled TAT molecules. Comparison of equal height signatures (where intrinsic charge doping is minimal) gives a work function difference of ≈ 80 meV – very close to $\langle t_h \rangle$ computed by Spano and coworkers.

In addition to our efforts on polarized optical measurements on isolated nanowire crystals, we have been exploring combined spectral and electric force scanning probe imaging of isolated TAT crystals in an effort to disentangle excited state interactions (which combine both coupled exciton and CT interactions) from ground state interactions themselves which modify the energy location of the highest occupied molecular orbital (HOMO). In ordered molecular assemblies, the ground states of neighboring molecules interact via hole transfer described by the matrix element , $\langle t_h \rangle = \langle H_i \mid t_h \mid H_j \rangle$ where $H_{i,j}$ are the ground state HOMO levels for neighboring molecules i, and j, and t_h is the single particle operator describing hole transfer between them. In TAT crystals, the magnitude of this interaction is computed to be 75 meV; for a completely ordered system (neglecting intrinsic doping) where each molecule contributes two electrons, the coupled ground state should be elevated in energy by t_h. Figure 3 shows preliminary results from different TAT nanowire crystals. We observe an elevation of the ground state (relative to disordered spun-cast TAT films) of ≈ 200 meV which is close to what would be expected for both ground state coupling and intrinsic n-type doping from the nitrogen centers on the TAT molecules. We are close to completing a study correlating work function changes (via Kelvin Probe Force Microscopy, KPFM) with pi-stacking disorder inferred from vibronic intensity ratios in the PL spectra. While there is still more work to be done in this project, the preliminary results are very exciting, showing a convergence to a ground state elevation of ≈ 80 meV in the limit of very small nanowire structures.

Integrated Photoluminescence and Kelvin Probe Force Microscopy (KPFM) mapping of surface electronic properties in organic semiconductors

In our integrated photoluminescence/KPFM setup, our aim is to disentangle ground state interactions that modify the energy location of the highest occupied molecular orbital (HOMO) from excited state interactions. For example, the polarization mixing revealed in time- and polarization-resolved PL measurements derive from combined coupled exciton and charge-transfer interactions, while modifications in the work function derive only from "dark" ground state interactions. The combined wavelength resolved PL is an essential component of the measurement scheme where pi-stacking order is inferred from vibronic intensity ratios. This allows us to correlate changes in the work function (energy location of the HOMO) with molecular packing changes.

Technical Highlights over the duration of the grant

- Development of time- and polarization-resolved fluorescence imaging techniques

We developed a variant of time-tagged time-resolved fluorescence imaging to resolve polarization contrast from a single molecule or nanostructure with a time resolution limited by the electronic time-to-digital converter (4 picoseconds in our instrumentation). Using a Hanbury Brown-Twiss interferometer configuration and a pair of high timing precision avalanche photodiodes (APD) as photon counting devices that view orthogonal linear polarizations. The polarization-routed APD signals then provide a "photon-by-photon" record of the photoluminescence from the sample in terms of photon arrival time and polarization. Post-processing of the time/polarization record allows a reconstruction of the polarization contrast ("x" vs. "y" polarized) as a function of time. This technique can be easily applied to more mundane systems to recover, for example, rotational diffusion times in various media (solutions, polymer films, etc.) but we have shown this is most powerful as an experimental method to reveal directional interactions in nanowire systems that could ultimately be exploited for directional control over energy and charge transport in ordered semiconductor assemblies.

- Single-molecule chiroptical spectroscopy

In collaboration with Dhandapani Venkatraman at UMass Amherst, we developed the first fluorescence-based method for measuring chiral dissymmetries (essentially a circular polarization variant of a linear polarization contrast).

- Effects of charge attachment on quantum dot photoluminescence

In collaboration with Todd Emrick at UMass Amherst, we developed the first integrated fluorescence- and scanning probe methods for interrogating the effects of electron-donating ligands at the surface of quantum dots, and their role in suppressing fluorescence intermittency ("blinking") in quantum dot photoluminescence.

Graduate Students and Postdoctoral Researchers supported by this grant (2005-2017)

Postdoctoral Associates:

- Nathan Hammer (July 2005 – Aug 2007), currently Assistant Professor at University of Mississippi, Oxford, MI
- Kevin McCarthy (Sept 2006 – July 2008), currently Staff Scientist, Raytheon Corp., Andover MA.
- Sibel Ebru Yalcin (Aug 2010 – June 2012) Ph. D. Physics, July 2010, University of Massachusetts-Amherst
- Irene Dujovne (March 2011 – May 2012) Ph. D. Applied Physics, Columbia University
- Adam J. Wise (September 2012 – 2014) Ph.D. Chemistry, University of New Mexico

Past and Current Graduate Students:

- Pradeep Kumar, Ph. D. Univ. of Tennessee, July 2004. Thesis Title: "Effect of three-dimensional confinement on morphology and photophysics of semiconducting polymers." Currently at Hewlett-Packard, San Diego.

- Ruthanne Hassey-Paradise, Ph. D. University of Massachusetts-Amherst, Aug 2009. Thesis Title: "Single Molecule Chiroptical Spectroscopy". Current position Physical Chemistry Laboratory instructor and Lecturer, University of Massachusetts-Amherst.

- Michael Y. Odoi, Ph. D. University of Massachusetts-Amherst, June 2010. Thesis Title: "Time-resolved probes of exciton dynamics in nanostructured semiconductors". Currently a postdoctoral associate with Prof. Todd Krauss, University of Rochester, Rochester NY.

- Kevin T. Early, Ph. D. University of Massachusetts-Amherst, July 2010. Thesis Title: "Single-molecule probes of charge and energy exchange in quantum dot/conjugated organic nanosystems". Currently an NRC postdoctoral associate with Prof. David Nesbitt, JILA and University of Colorado, Boulder CO.

- Austin Cyphersmith, Ph. D. University of Massachusetts-Amherst, September 2012. Thesis Title "Dissymetries in fluorescence excitation and emission from coupled chiral chromophores". Has accepted postdoctoral position with Prof. Christine Payne (Georgia Tech) starting Oct. 1, 2012. Currently Director of Microscopy and Imaging Facilty, University of Illinois, Urbana-Champaign.

- Mina Baghgar, Ph.D. (Physics) University of Massachusetts-Amherst, March 2014. Thesis Title: "Optical and Scanning Probe Studies of Isolated P3HT (Poly-3-Hexylthiophene) Nanofibers". Currently working as a postdoctoral associate with Larry Silvera, Dept. of Physics, Harvard University.

- Joelle Labastide, Ph. D. (Chemistry) University of Massachusetts-Amherst, April 2015. Thesis Title: "Directional probes of exciton dynamics in nanostructured semiconductors."

- Sarah R. Marques, Ph. D. (Chemistry) University of Massachusetts-Amherst, August 2018. Thesis Title: "Evolution of H-J Coupling in Small-Molecule Organic Semiconductors."

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