



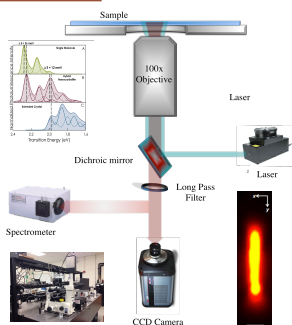
Chemical Imaging of Structure and Exciton Dynamics in Nanoscale Assemblies of Organic Semiconductors

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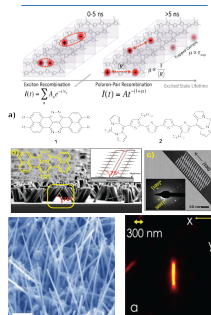
Fluorescence Imaging and Spectroscopy of Nanomaterials

- We use photoluminescence (PL) and scanning probe techniques to probe packing structure and exciton dynamics in nano-cluster and nano-wire assemblies of organic semiconductors.
- Analogous to single-molecule spectroscopy, we interrogate isolated nanosystems to probe directional interactions referenced to the pi-stacking directions
- How can chromophore coupling be "tuned" to selectively enhance charge/exciton transport?
- Disentangling "bright" and "dark" interactions in nanoscale assemblies?



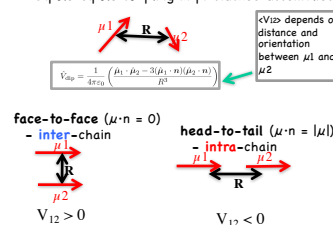
Directional control of energy/charge transport in organic semiconductors

- Role of molecular packing geometry? Programmed by molecular architecture?
- Role of sign, magnitude, and direction of different intermolecular couplings
- Isolated crystalline nanowires as a material platform
- optical polarization (excitation or emission) referenced to specific crystallographic directions.

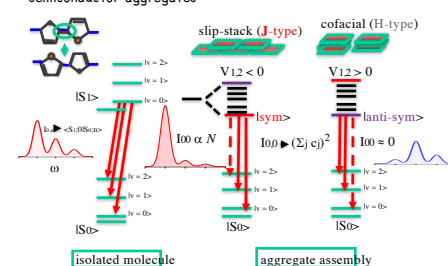


Spectral Signatures of Chromophore Coupling: HJ Aggregate Model

Dipole-dipole coupling in pi-stacked assemblies

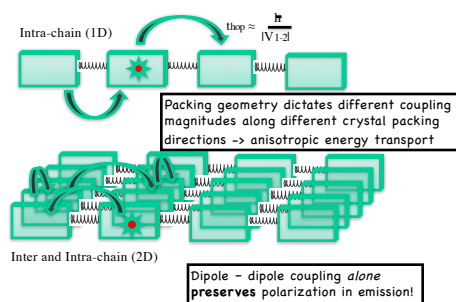


Vibronic signatures of directional coupling in organic semiconductor aggregates

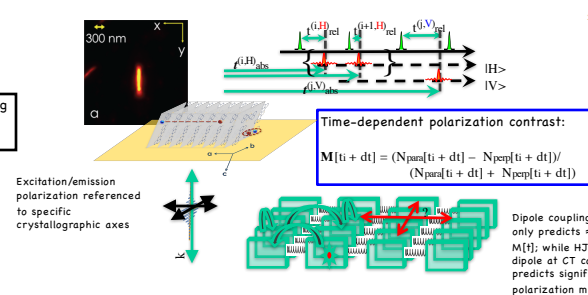


F. Spano, Acc. Chem. Res. 43, 429 (2010)

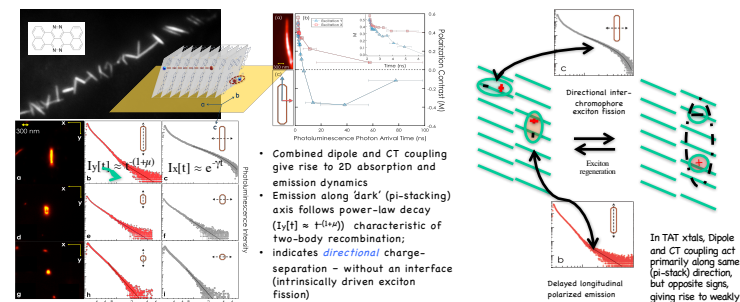
Exciton hopping in 2D assemblies



Time- and polarization resolved probing of directional coupling

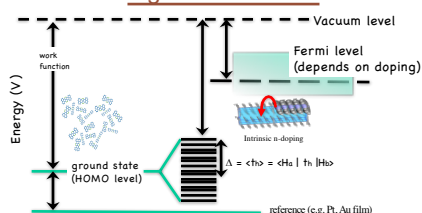


Anisotropic decay dynamics and directional charge separation in TAT nanowires

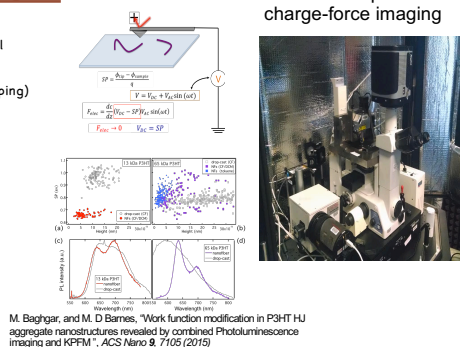


J. A. Labadie, H. B. Thompson, S. R. Marques, N. Colletti, A. L. Briseno, and M. D. Barnes, "Directional charge separation in organic semiconductor nanowires", *Nature Communications* 7, 10629 (2016)

Disentangling 'bright' and 'dark' couplings in organic nanowires

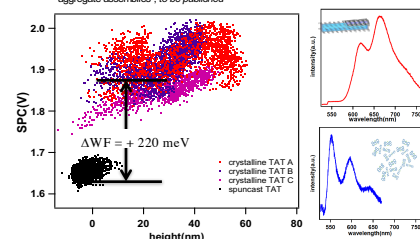


- Comparing isolated (uncoupled) molecule to TAT crystal, expect *increase* in SPC (decrease in WF) of $\langle \text{tho} \rangle$; theory predicts +75 meV
- Combined effect of HOMO shift and intrinsic doping (depends on volume)?



Applications to TAT nanoclusters and nanowires

P. Wang, and M. D. Barnes, "Disentangling bright and dark couplings in HJ aggregate assemblies", to be published



- Vibronic intensity ratio (bright coupling) proxy for pi-stacking order
- Observe a positive ($\approx +200 \text{ mV}$) change (less negative) in HOMO for TAT xtals relative to disordered films
- Combined HOMO shift and intrinsic doping?

Future Directions

- Temperature dependence of charge-separation/exciton regeneration
- Evolution of HJ (combined dipole and CT) coupling in TAT (and other) small-molecule semiconductors
- Near-field probes of anisotropic exciton mobility in crystalline nanowires
- Combined PL and EFM techniques to probe ground state coupling energies and correlation with packing structure (i.e., Rubrene polymorphs, other synthetic organic SCs)

