Dynamics of excitons in thin-film aggregates of cyanine dyes

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Orlando, April 19, 2012
Molecular aggregates

Thin-film J-aggregates

- Few molecular layers
- Self-assembly
- Room temperature
- Spatial order on the scale of 100 nm

Deposition generalizes to many sulfopropyl dyes

Thin film cyanine dye J-aggregates

Brian Walker
Bawendi group, MIT

• Spectra can be tuned by changing the dye
Molecular aggregates

Photonic devices:
Strong exciton-photon coupling in organic cavities

Photosensitization:
Fluorescence enhancement from DCM molecules on a J-aggregate film

Biomimicry:
Photosynthesis in green sulfur bacteria
Intermolecular resonance coupling

\[ H_{\text{Coulomb}} = \frac{1}{2} \frac{1}{4\pi\varepsilon_0} \sum_{ij} \frac{e^2}{|r_i - r_j|} \]

Förster interactions

Singlet excitons in aggregates

Existing claims:
• Frenkel excitons delocalized over tens of molecules
• Large diffusion length (up to 100 nm at room T)
• Signatures of wave-like exciton propagation

Concerns:
• Lattice structure is not well characterized
• Transport properties are measured indirectly
• Transport regime is hard to model quantum mechanically

Our approach:
• ab-initio computation of molecular and lattice properties
• Phenomenological parameters fitted to experiments
• Exciton dynamics is quantum
• extraction of transport parameters
Dynamics model

- Monte-Carlo time propagation of exciton wave function on a lattice
- Haken-Reneker-Strobl model for coupling to the environment
- Phenomenological parameters: thermal noise, lattice imperfections
  - static disorder, Gaussian distribution of transition frequencies
  - dynamic disorder, white noise with the dephasing rate $\Gamma$
Molecules

TC

TDBCK

U3
Intra-molecular excitations

oscillator strength density (eV$^{-1}$)

> 98% HOMO $\rightarrow$ LUMO

- Hybrid functional PBE0
- Triple-$\zeta$ basis set
- Polarizable environment - COSMO
• 2D map of the Forster interaction computed ab-initio and fitted with an extended dipole model

Molecular monolayer

Fitting lattice structure to J-band shift

• Ly is varied
• Lx is fixed = length of the molecule + 2*VdW radii

J-band shift

Brickstone model

D. Möbius and H. Kuhn, J. Appl. Phys. 64, 5138 (1988)
Exciton dynamics

Initial conditions

J-band: Initial site
Exciton population dynamics
Exciton dynamics

Coherences

- Coherence = two-sites one-time correlation functions
Exciton coherence dynamics

Static disorder 70 meV
Dynamic disorder 30 meV
Exciton population dynamics

Ballistic and diffusive transport

\[ \langle M_{xx}^{(2)}(t) \rangle \]
\[ \langle M_{yy}^{(2)}(t) \rangle \]

ballistic (≈ \( t^2 \))

diffusive (≈ t)
Exciton dynamics

Initial conditions

- TDBC - DOS
- Static disorder 70 meV
- ‘Diffusion band’ different from J-band
- Different maximum in each direction
Exciton population dynamics

Dephasing dependence

Diffusion coefficient in 2D TDBC film from exciton-exciton annihilation
Akselrod, et. al. PRB 82, 113106 (2010)
Exciton population dynamics

2D maps of diffusion constants

- $D_{xx}$ TDBC
J-aggregate in cavity

A simple model

J-band

Site - cavity coupling
\(~0.1\) meV

Cavity mode decay
J-aggregate in cavity

J-band polaritons

Diffusion

Change in the diffusion constant is about 3% only
Conclusions

• Ab-initio molecular properties
• Haken - Reineker – Strobl model for noise
• Monte Carlo wave function exciton transport
• Model can be extended to device structures
• Computed transport coefficients are comparable to experimental results

Concerns:
• Need more data on lattice structure
• Need temperature dependences
• Need direct measurements of exciton diffusion

Acknowledgements

Stephanie Valleau
Harvard

Man-Hong Yung
Harvard

Alex Eisfeld
MPI, Dresden; also @ Harvard

MIT guys
Gleb Akselrod
Bulovič group

Brian Walker
Bawendi group
(now at Oxford)

Dylan Arias
Dorthe Eisele
Nelson group

Alan Aspuru-Guzik
Harvard
Thank you for your attention!
Excitation dynamics

Monte Carlo propagation of the wave function

System initialization
- J-aggregate Hamiltonian
- Initial state $|\Psi(0)\rangle$

Random choice

Scattering
$|\Psi(t)\rangle = S|\Psi(t)\rangle$

Unitary propagation
$|\Psi(t + dt)\rangle = e^{-i\tilde{H}dt}|\Psi(t)\rangle$

Average over an ensemble
Molecular monolayer

J-band shift

Convergence
Intermolecular resonance coupling

Förster and Dexter interactions

\[ H_{\text{Coulomb}} = \frac{1}{2} \frac{1}{4\pi\varepsilon_0} \sum_{ij} \frac{e^2}{|r_i - r_j|} \]
More molecules

Three 2-level molecules, site basis

$X^{(3)}$

$X^{(2)}$

$X^{(1)}$

$X^{(0)}$

Coherent interactions with optical fields

Optical relaxation is along the same paths
Molecular monolayer

Coupling strength

+55 meV

-70 meV

-20 meV

Dexter contribution is small
Coupling regimes

**Weak:** $V \ll \Gamma$

- Excitons jump incoherently between molecules
- Environment thermalizes excitons on single molecules

**Strong:** $V \gg \Gamma$

- Molecular excitations form bands – coherent coupling between sites
- Coupling to the environment enters as thermalization between bands
Intermediate coupling, $V \approx \Gamma$

- Molecules are coupled coherently
- Coupling to the environment enters as frequency diffusion
- Excitons are NOT thermalized
Exciton dynamics

Population transfer between dyes

Static disorder 70 meV
Dynamic disorder 30 meV
Exciton population dynamics

Disorder dependence

Dynamic disorder 50 meV
HRS vs jump model

![Graph showing the relationship between second moment $M^2$ and static disorder (meV). The graph compares HRS and jump models.](image-url)