Exciton dissociation in solar cells:

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Outline

• **Introduction** - Excitons & photovoltaics

• Charge transfer (CT) excitons on organic semiconductor surfaces:

• Direct time domain observation of 2D polarons

• Extracting hot or multiple carriers from inorganic quantum dots:
The conventional solar cell: \textit{p-n junction}

- Light absorption & charge separation occur in same location
- Charge separation by build-in electric field

UMN solar car
Excitonic solar cells

The Coulomb barrier problem

Exciton: an electron-hole pair

Molecular or Frenkel exciton in an organic semiconductor or inorganic quantum dot

Charge transfer exciton at a D/A interface

Large binding energy ($\gg kT$) due to the low dielectric constant!

$$V = -\frac{e^2}{4\pi\varepsilon\varepsilon_0 r}$$
What drives exciton dissociation?

• How does a Frenkel exciton dissociate?

\[ \Delta_{LUMO} > B_{ex} \]

• How does a CT exciton separate?

\[ \Delta \mu, \text{ but …} \]
Probing electron dynamics in the *time* domain: femtosecond two-photon photoemission

Lindstrom, Zhu *Chem. Rev.* (06)
How do charge carriers separate in an organic heterojunction solar cell?

i) Light absorption

ii) Exciton diffusion

iii) Exciton dissociation

iv) Charge transport
Previous suggestion of “long distance” geminate e-h pair in exciton dissociation

Morteani et al. PRL 92, 247402 (2004)
Previous evidence for the need of excess energetic driving force in exciton dissociation

Nanocrystalline polythiophene/PCBM

Amorphous polythiophene/PCBM

Coulombically bound radical pair (BRP)

Ohkita et al. JACS 130, 3030 (2008)
Charge transfer exciton: a toy model

\[ \hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{4\pi\varepsilon_0 \varepsilon |\vec{r}_o + \vec{r}|} \]
Experimental realization of the toy model for CT excitons

\[ \varepsilon_{PC} = 5.3, \varepsilon_o = 1.0 \quad \rightarrow \quad \bar{\varepsilon} = 3.2 \]
What is the binding energy of a CT exciton (geminate pair)?

How to overcome this binding energy in charge separation?
The model system: crystalline pentacene thin films grown on Bi

Sadowski et al, Appl Phys Lett 2005
Thayer et al, Phys Rev Lett 2005
2PPE spectra: IPS & CT exciton

$\nu_1 = 4.16 \text{ eV}$
$\nu_2 = 1.39 \text{ eV}$
Spatial distribution of IPS & CT exciton $\Psi$

Nonane overlayer quenches both IPS and the CT exciton state

IPS shows dispersion & CT exciton state is localized.

$|\Psi|^2$ is on the surface

$E - E_F$ (eV)

$2$PPE intensity

C9 overlayer
- 0.0 ML
- 0.5 ML
- 1.0 ML

$E_F = 1.5 m_e$

Binding energy (eV)

$k_\parallel$ ($\text{Å}^{-1}$)
Origin of charge transfer excitons

\[ \hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2 \gamma}{4\pi \varepsilon_0 |\vec{r}_o + \vec{r}|} - \frac{e^2 \beta}{4\pi \varepsilon_0 \varepsilon} \]

\[ \beta = \frac{\varepsilon - 1}{\varepsilon + 1} \quad \gamma = \frac{2}{\varepsilon + 1} \]
Simulation results: the delocalized image band

- $E_B$ (eV)
- $k$ (Å$^{-1}$)
- $n = 30$
- $x$ (nm)
- $y$ (nm)
- pure IPS

Levels:
- 1s
- 2s
- 2p
- 1p
Simulation results: the localized CT excitons

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<th>1s</th>
<th>1p</th>
<th>1d</th>
<th>1f</th>
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Simulation: CT exciton binding energies

energy scale $E_{CTE}$
- internal Coulomb energy of the exciton
- $0 = \text{bottom of IPS band (continuum)}$

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<th>Orbital</th>
<th>Energy (eV)</th>
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<tr>
<td>3s</td>
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</table>
Seeing hot excitons at higher $h\nu$

UV pump from HOMO

1 ML pentacene
CT excitons - the complete picture

1 ML pentacene

Pump: 4.38 eV; Probe: 1.46 eV
All CT excitons show no dispersion: photo-ionization destroys the quasi-particle!

E - E_{Fermi} (eV)

$E_{kin} = \frac{(\hbar k)^2}{2m}$

m = 1.5 m_e

Dispersion measurement carried out at $h\nu_1 = 4.38$ eV & $h\nu_2 = 1.46$ eV; time delay = 80 fs.
CT excitons on thick pentacene films

>20 nm pentacene/Si(111)

Pump: 4.59 eV; Probe: 1.53 eV
Why do CT excitons on pentacene decay so fast?

Short lifetimes: resonance with LUMO+x bands

Pump-probe delay (fs)

1 ML

> 10 ML

E-E_F (eV)

110 fs

40 fs

60 fs

120 fs

90 fs

Pump-probe delay (fs)
Surface CT excitons are general: tetracene

- 20 nm tetracene/Si(111)
- Tuning $h\nu$ to reach each resonance

IPS (standing up)

IPS (lying down)

CT$_{1s}$

$E-E_F$ (eV)

Time delay (fs)

$E-E_F$ (eV)

Time delay (fs)

$E-E_F$ (eV)

Time delay (fs)

$E-E_F$ (eV)

Time delay (fs)
The difference between surface CT excitons and the toy D/A model
The “hot” mechanism for charge carrier separation in organic photovoltaic

Conclusion: Charge separation at a D/A interface in OPV must involve “hot” CT excitons!

n > 1

- Less CT binding energy
- Longer lifetime
- More delocalization
- Better electronic coupling (energy denominator!)
Other interesting systems….
Summary 1

- Charge transfer excitons are seen on the crystalline pentacene and tetracene surfaces.

- Hot CT excitons are necessary in organic heterojunction photovoltaic.
Challenge to theory/simulation: *breaking up the quasiparticle*

\[ \hat{k} = \hat{k}_A - \hat{k}_D \]

\[ \Psi(\hat{k}, \hat{\rho}) \]

*What is the role of delocalization on interfacial charge separation?*
Polarons & localization

Electronic-nuclear coupling

Defects

Energetics of self-trapping:

\[ \Delta E_{ST} = E_{pol} + E_{loc} \]

Polarization gain (negative)

Localization penalty (positive) \( \approx 0.5 \cdot BW \)

\[ \Delta p \cdot \Delta x \geq h \]
Self trapping not observed.

Tetracene/Silicon(111), 150 K, thick film (> 20 nm)

Energy relaxation negligible:
No lattice polaron formation.
2D polarons that are absent in 3D

Model: NaCl/Cu(111)

Not an organic, but same physics...
Polaron formation in time-energy domain

NaCl conduction band (CB)
\[ \tau_{\text{trap}} = 62 \pm 8 \text{ fs}, \ \tau_{\text{decay}} = 120 \pm 20 \text{ fs} \]
\[ \Delta E = 60 \pm 10 \text{ meV} \]

NaCl interface band (IB)
\[ \tau_{\text{trap}} = 135 \pm 47 \text{ fs}, \ \tau_{\text{decay}} = 230 \pm 20 \text{ fs} \]
\[ \Delta E = -85 \pm 10 \text{ meV} \]

Where is the $|\psi|^2$? Effect of an overlayer

3ML NaCl/Cu(111) 1 ML nonane/3ML NaCl/Cu(111)

"bulk" polaron

NaCl/Cu Interface polaron

image polaron
Polaron formation in the momentum domain

Parallel dispersions

3 ML NaCl/Cu(111)

Conduction band

Interface band
Why does an electron polaron form in a 2D NaCl film but not in 3D NaCl?

\[ \Delta E_{ST} = E_{pol} + E_{loc} + E_{bond} \]

Bulk crystal: 
-0.5 eV  2.5 eV  -1.0 eV  \( \Delta E_{ST} \approx 1.0 \text{ eV} \)

Thin film (1 unit cell thick): 
-1.0 eV  1.7 eV  -1.0 eV  \( \Delta E_{ST} \approx -0.3 eV \)

More deformable and narrower bandwidth in a thin film. Delocalization \( \rightarrow \) localization!

Does it apply to thin films in general? Quantum wells?
Conclusion 2

• TR-2PPE of NaCl/Cu(111) provides time-domain evidence of a 2D polaron.

• Polaron or self-trapped excitons must be important to exciton dissociation at organic D/A interfaces (not directly observed in the time domain yet.....)
Challenge to theory/simulation: *delocalization + localization*

\[ \vec{k} = \vec{k}_A - \vec{k}_D \]

Now add localization from electron-nuclear coupling & trapping!

*My head is spinning…*