2 for the price of 1

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Outline

• What is singlet fission?
• The potential of singlet fission technologies
• The effect of chromophore coupling on singlet fission rates
• Observing intermediate states in the singlet fission process using magnetic resonance spectroscopy
Molecular states of interest

\[ S_0 \quad T_1 \quad S_1 \]

\[ \text{LUMO} \quad \text{HOMO} \]

\[ m_s = 0 \quad m_s = 1 \quad m_s = 0 \]
Singlet Fission

- Absorption
- Singlet fission annihilation
- Inter-system crossing (slow)
- Spin-forbidden emission non-radiative decay (slow)
Molecules

Part 1: The Potential of Singlet Fission for Photovoltaic Devices
Exciton fission solar cells

- Exciton fission threshold, $E_b$
- Band gap, $E_r$
- Fission can occur in
  - Bulk inorganic semiconductors (impact ionization)
  - Low-dimensional inorganics
  - Rare-earth materials
  - Organic molecular crystals
Exciton fission solar cells

• Exciton fission threshold, $E_b$
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• Fission can occur in
  – Bulk inorganic semiconductors (impact ionization)
  – Low-dimensional inorganics
  – Rare-earth materials
  – Organic molecules

$E_F$ $E_r$

$E_b$

$eV$

CB $E_r$

VB
Entropy as a driving force

\[ \Delta U = 2E_r - E_b \]
\[ \Delta A = \Delta U - T\Delta S = 0 \]
\[ \Delta U = T\Delta S \]
\[ T\Delta S = 2E_r - E_b \]

That is: \( E_b/E_r \) can be less than 2 for \( T>0 \)

Tayebjee et al. JPCL, 2012, 3, 2749-2754.
**Detailed Balance Limiting Efficiency**

![Graph showing energy levels and efficiency](image)


More realistic device limiting efficiencies

Conclusions and Progress

• Tetracene on silicon is theoretically well-matched to give high device efficiencies
• In principle, a tetracene layer could be applied on top of a silicon cell to enhance the overall efficiency. (Initially proposed by Dexter in 1979)
• However triplet injection/dissociation at the tetracene/silicon interface has not been achieved yet:
  – Devices have been made by several groups, but none show a >100% quantum yield in the EQE spectrum
• More work needs to be done to understand organic/inorganic interfaces.
Part 2: Singlet Fission in TIPS-Pentacene Nanoparticles
Why nanoparticles?

- Nice systems to study
  - Solution state
  - Have some control over size
  - Have some control over morphology
- Device fabrication by spin-coating aqueous solutions
- TIPS-Pn 200% fission yield in thin films
Why nanoparticles?
Particle Characterization

Z-average: ~150 nm
PDI: 0.2

The Role of Interchromophore Coupling

Morphology

- Type II is similar to thin films where fission yield is 200%
- So we expect fission to be much more efficient in the Type II nanoparticles
Transient Absorption

Type I

![Type I Absorption Spectra](image)

Type II

![Type II Absorption Spectra](image)

Ultrafast Polarization Anisotropy

Photoluminescence Anisotropy Decay

- We expect there to be no decay in anisotropy in
  - Type II regions
  - Exciton traps
- We expect the anisotropy to decay when
  - Excitons migrate within Type I regions
  - Excitons migrate across crystalline grain boundaries
Ultrafast Time-resolved Photoluminescence

Summary of Nanoparticle Results

• Do to the slow crystallization process used to generate Type II nanoparticles, singlet exciton traps were generated and actually slowed the rate of fission
• Both short-range and long-range morphology play a role in the rate of singlet fission
Part 3: Singlet Fission in Bipentacenes
Quantitative Fission in Bipentacenes

\[
R = \text{NODIPS}
\]

\[n = 2: \text{BP2} \]
\[3: \text{BP3}\]

![Graph showing extinction coefficient vs. wavelength for different compounds](image_url)
Anomalous Triplet Lifetimes

Sanders, et al., *JACS*, 2015, 137 (28), pp 8965–8972
Transient Absorption: Triplet Yield but Not Triplet-Triplet Coupling

\[ \begin{align*}
S_0 & \quad \text{Optical Pump} \\
S_1 & \quad \text{fs pulsed laser} \\
(TT) & \quad \text{Internal conversion} \\
\end{align*} \]

\[ \begin{align*}
\text{Photo-induced absorption} & \quad \text{Optical Probe} \\
\text{Photo-induced bleach} & \quad \text{2T} \\
\end{align*} \]
Transient EPR: Nature of Spin States

$S_1$ (TT) Internal conversion

$S_0$

Optical Pump

Microwave Probe

$\sim 10 \text{ eV}$

$\sim 40 \mu \text{eV}$
The Spin Hamiltonian

\[ \hat{\mathcal{H}} = \hat{H}_z + \hat{H}_{zf} s + \hat{H}_{ee} \]

- Zeeman:
  - Splits states with different \( m_s \) under an applied field
- Zero-field splitting:
  - Splits states of individual triplets
- (TT) interaction:
Zero Field Splitting of Triplet States

\[ \hat{H} = \hat{H}_z + \hat{H}_{zfs} + \hat{H}_{ee} \]

\[ |y\rangle \quad \downarrow 2E \quad |x\rangle \quad \downarrow D \quad |z\rangle \]

\[ |0\rangle \rightarrow |-> \]

\[ B_z (\text{mT}) \]

Zero Field Splitting of Triplet States

\[ \hat{H} = \hat{H}_z + \hat{H}_y + \hat{H}_x \]

\[ \begin{align*}
|^{5}(TT)_x \rangle & = \frac{1}{\sqrt{2}} (|xy\rangle + |yx\rangle) \\
|^{5}(TT)_y \rangle & = \frac{1}{\sqrt{2}} (|yz\rangle + |zy\rangle) \\
|^{5}(TT)_z \rangle & = \frac{1}{\sqrt{2}} (|xz\rangle + |zx\rangle) \\
|^{5}(TT)_a \rangle & = \frac{1}{\sqrt{2}} (|xx\rangle - |yy\rangle) \\
|^{5}(TT)_b \rangle & = \frac{1}{\sqrt{6}} (|xx\rangle + |yy\rangle - 2|zz\rangle)
\end{align*} \]

\[ \begin{align*}
|^{3}(TT)_x \rangle & = \frac{1}{\sqrt{2}} (|yx\rangle - |xy\rangle) \\
|^{3}(TT)_y \rangle & = \frac{1}{\sqrt{2}} (|yz\rangle - |zy\rangle) \\
|^{3}(TT)_z \rangle & = \frac{1}{\sqrt{2}} (|xz\rangle - |zx\rangle) \\
|^{1}(TT) \rangle & = \frac{1}{\sqrt{3}} (|xx\rangle + |yy\rangle + |zz\rangle)
\end{align*} \]


 Applied Magnetic Field

\[
\hat{\mathcal{H}} = \hat{H}_z + \hat{H}_{zs} + \hat{H}_{ee}
\]

\[|^{5}(TT)_{+2}\rangle = |++\rangle\]
\[|^{5}(TT)_{+1}\rangle = \frac{1}{\sqrt{2}} (|0+\rangle + |0+\rangle)\]
\[|^{5}(TT)_{0}\rangle = \frac{1}{\sqrt{6}} (2|00\rangle + (++\rangle + |++\rangle)\]
\[|^{5}(TT)_{-1}\rangle = \frac{1}{\sqrt{2}} (|--\rangle + |0-\rangle)\]
\[|^{5}(TT)_{-2}\rangle = |--\rangle\]
\[|^{3}(TT)_{+1}\rangle = \frac{1}{\sqrt{2}} (|+0\rangle - |0+\rangle)\]
\[|^{3}(TT)_{0}\rangle = \frac{1}{\sqrt{2}} (|--\rangle - |++\rangle)\]
\[|^{3}(TT)_{-1}\rangle = \frac{1}{\sqrt{2}} (|--\rangle - |0-\rangle)\]
\[|^{1}(TT)\rangle = \frac{1}{\sqrt{3}} (|00\rangle - |++\rangle - |--\rangle)\]

Pulsed Laser/cw-EPR **BP3** at 40K
Identifying the Spin States

- Initial spectrum is the quintet triplet pair state
- The final spectrum could be due to three different transitions based on the magnetic field resonance positions
  - $^5(TT)_{±1} \rightarrow ^5(TT)_{±2}$ ✗
  - $^3(TT)_{±1} \rightarrow ^3(TT)_{0}$ ✗
  - $T_0 \rightarrow T_{±1}$ ✓

**20 - 100 ns**

$^5(TT)_0 \rightarrow ^5(TT)_{+1}$

**5.1 - 5.2 μs**

$T_0 \rightarrow T_{+1}$
Identifying the Spin States

- Rabi oscillation frequency can be used to identify spin multiplicity
  \[ \Omega = \Omega_1 [S(S + 1) - M_S(M_S - 1)]^{1/2} \]
  - Nutation frequency ratio is expected to be \( \sqrt{3} = 1.73 \)
  - Experimental ratio is 1.69 ± 0.03
Dynamic Modelling

\[ \frac{dp}{dt} = Mp \]
Pulsed Laser/cw-EPR BP2 at 80K
Weakly Coupled Triplets

- Initial spectrum is the quintet triplet pair state
- The final spectrum cannot be explained by $T_0 \rightarrow T_{\pm 1}$ transitions
- We require weak coupling to accurately fit the spectrum
- This is evidence for triplet pair state dissociates into two triplets rather than intersystem crossing (TT) $\rightarrow$ $T_1 + S_0$

BP2 Nutation

- Rabi oscillation frequency can be used to identify spin multiplicity
- \( \Omega = \Omega_1 [S(S + 1) - M_s(M_s - 1)]^{1/2} \)
- Nutation frequency ratio is expected to be \( \sqrt{3} = 1.73 \)
- Experimental ratio is 1.5
- This departure from \( \sqrt{3} \) arises because the final triplets are weakly coupled
Temperature Dependent TA

**BP2**

- 300 K
- 240 K
- 180 K
- 120 K
- 80 K
- 50 K
- 30 K
- 7 K

**BP3**

- 300 K
- 240 K
- 180 K
- 120 K
- 80 K
- 50 K
- 30 K
- 14 K
- 7 K
Model Summary

- Isolated Triplet
- Decay

SF generated Triplet Pair

- Sensitization: $\tau = 25400$ ns
- Fission: $\tau = 270$ ns

Reaction Coordinate
Conclusions

• We observed quintets triplet-triplet-pairs in both BP2 and BP3
• The nature of the spin states involved in fission is much harder to understand using transient absorption – we can only observe the T₁ → Tₙ cross-section presented to the probe beam
• Using magnetic resonance and optical techniques in tandem allows for a full description of singlet fission
• Large triplet-triplet coupling is required for fission, but if it is too large triplet pairs may not be able to dissociate
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