2 for the price of 1

UNSW AUSTRALIA

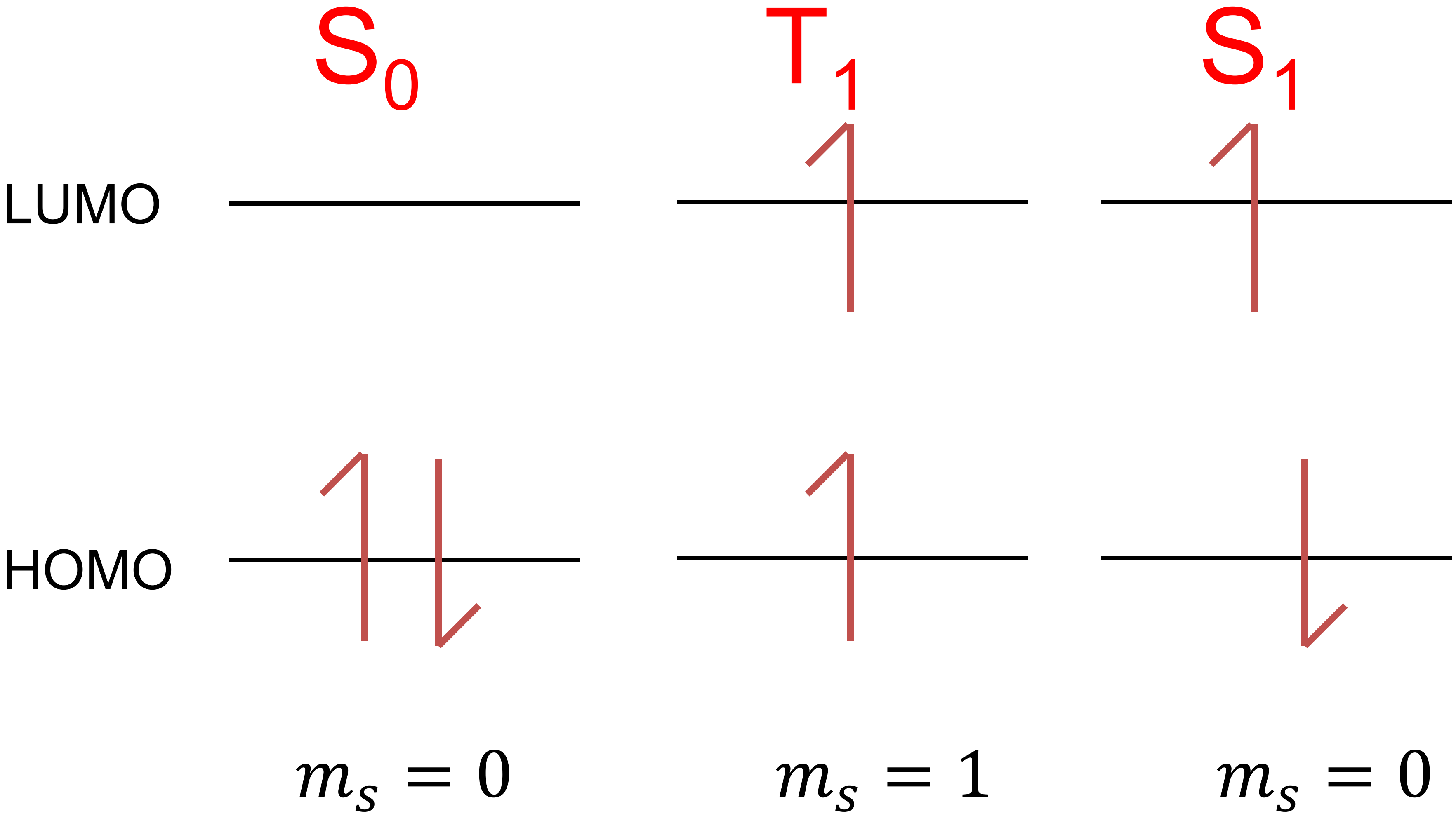
Never Stand Still Engineering School of Photovoltaic and Renewable Energy Engineering

Murad J Y Tayebjee

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



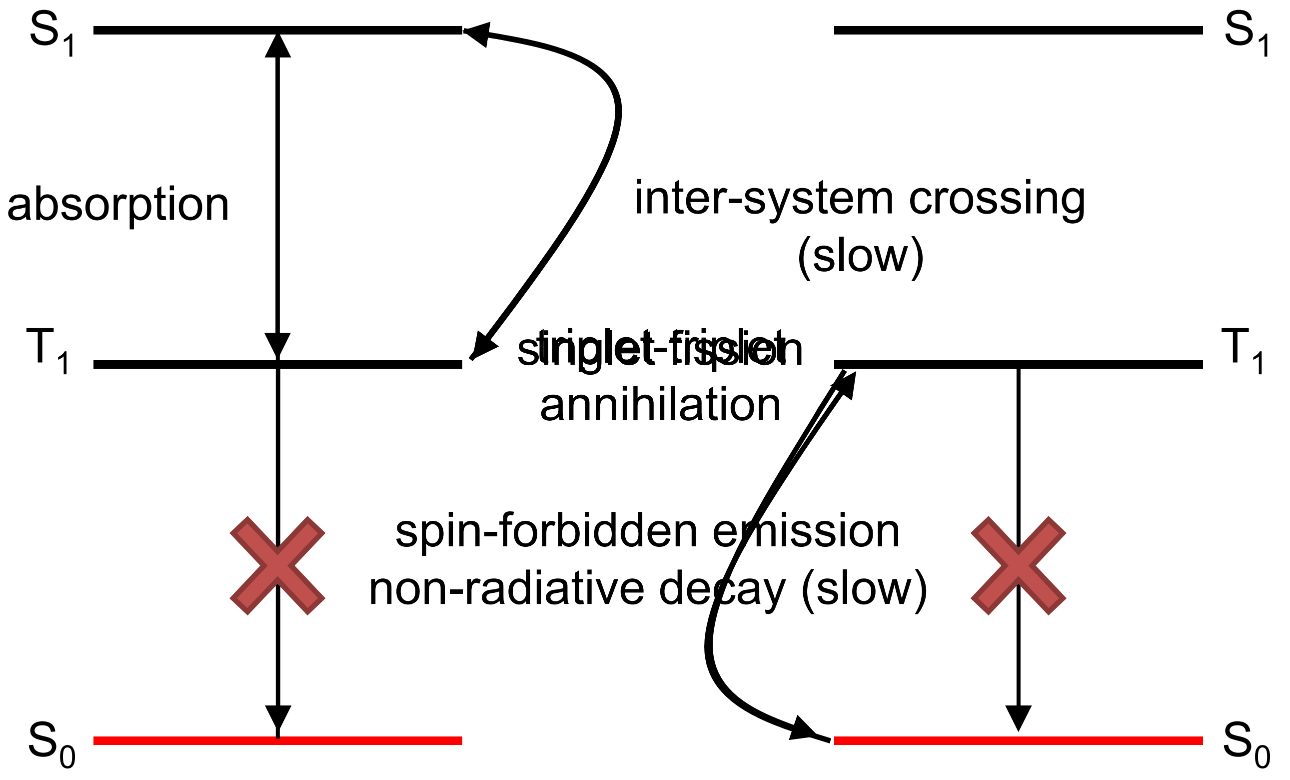
S_0 T_1 S_1

LUMO

HOMO

$m_s = 0$ $m_s = 1$ $m_s = 0$

Singlet Fission



absorption

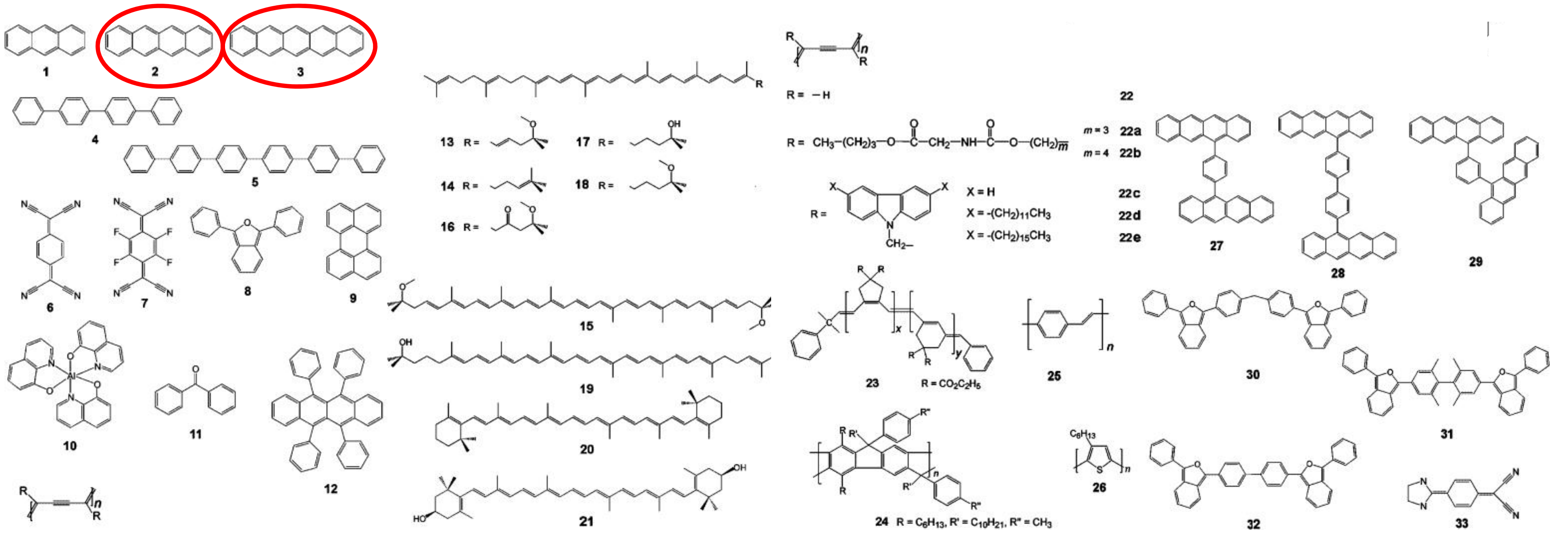
inter-system crossing
(slow)

singlet fission

triplet-triplet
annihilation

spin-forbidden emission
non-radiative decay (slow)

Molecules

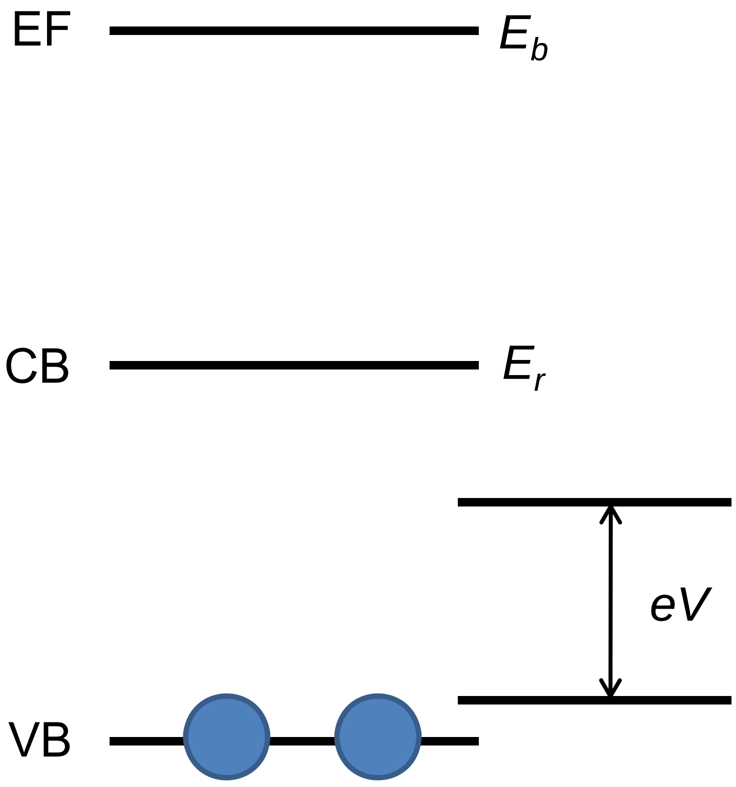


Smith, M., Michl, J., *Chem. Rev.*, (2010) **110**, 6891.

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

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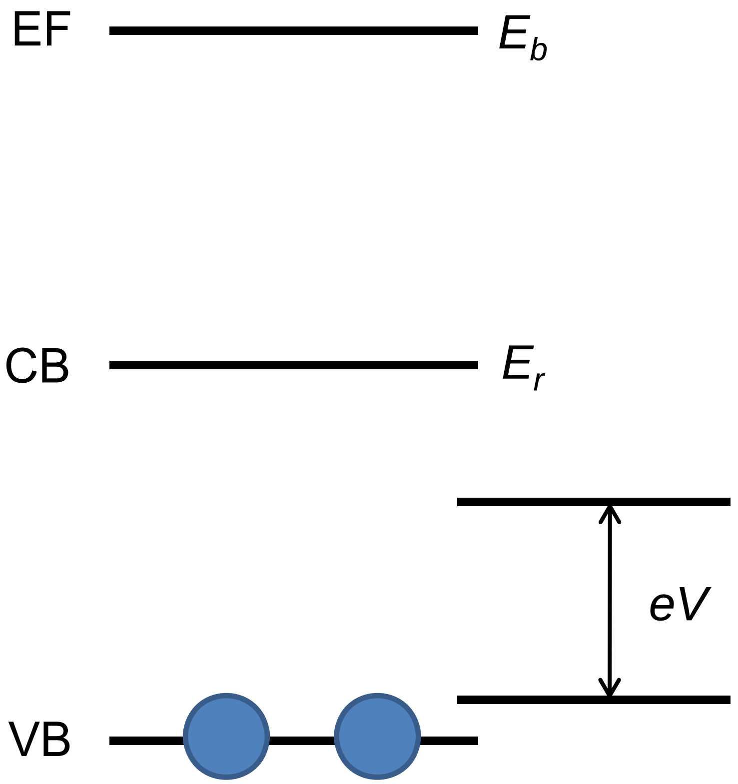


Entropy as a driving force

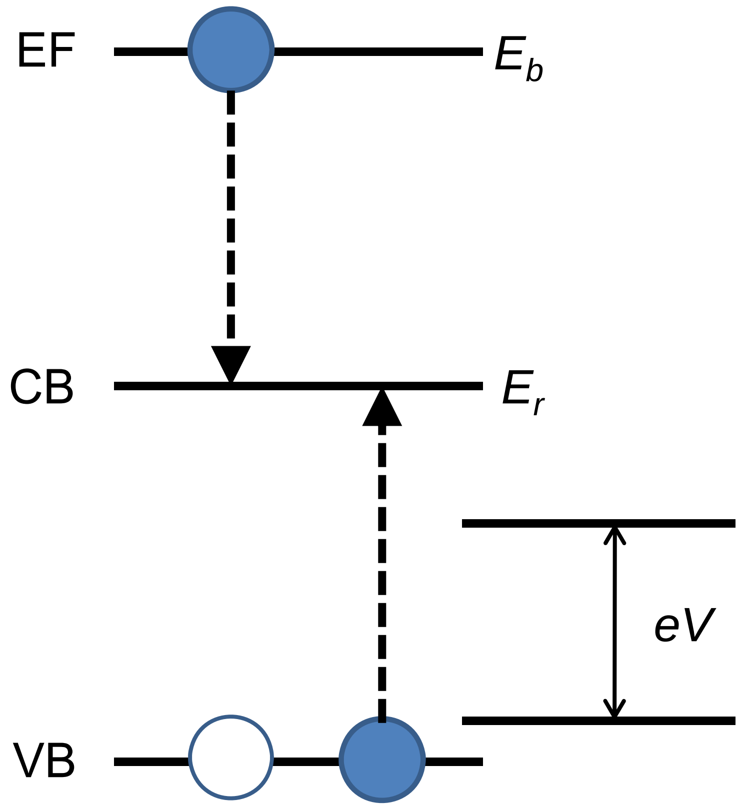
$\Delta U = 2E_r - E_b$

$\Delta A = \Delta U - T\Delta S = 0$

$\Delta U = T\Delta S$

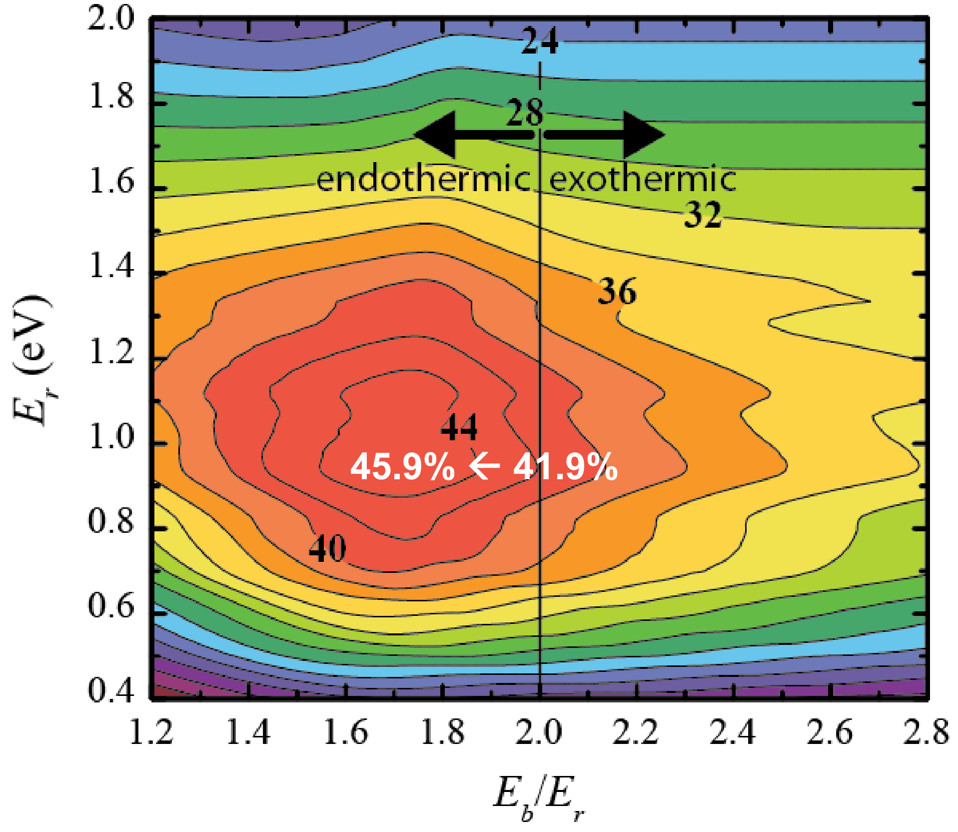
$\mathrm{T}\Delta S = 2E_r - E_b$

That is: E_b/E_r can be less than 2 for T>0!

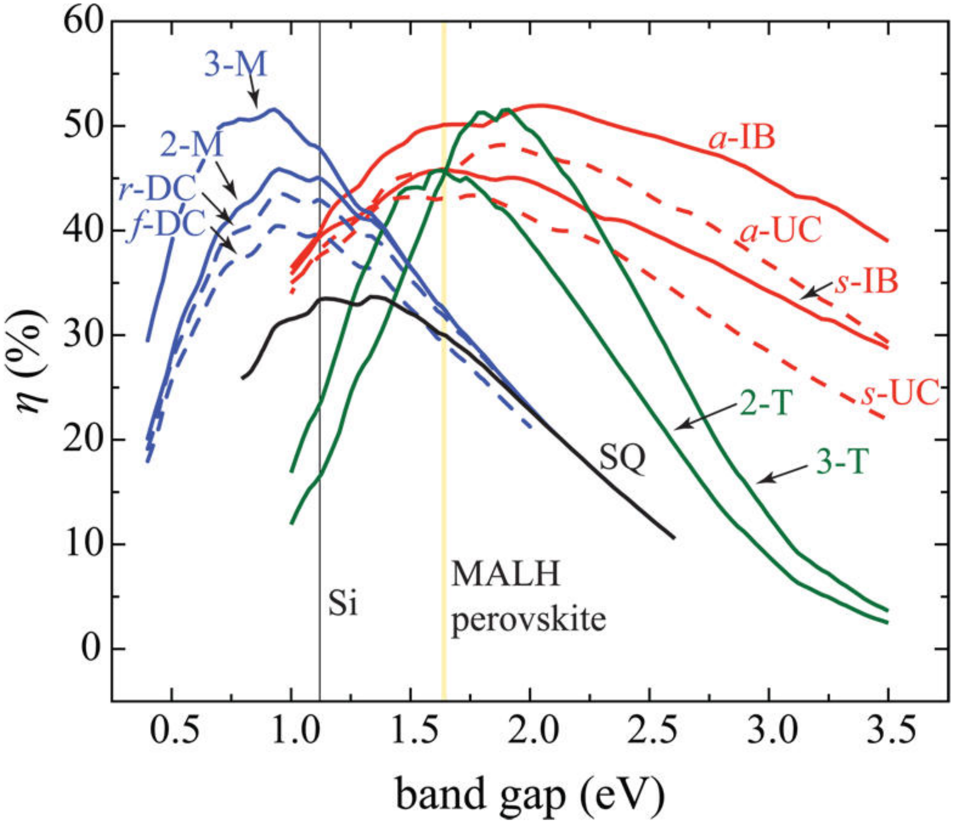


Tayebjee et al. JPCL, 2012, **3**, 2749-2754.

Detailed Balance Limiting Efficiency



Tayebjee, M., Gray-Weale, A., Schmidt, T., *JPCL*, (2012) **3**, 2749.

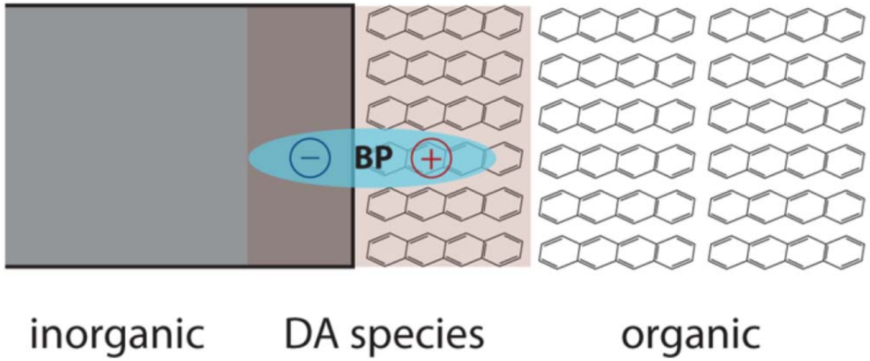


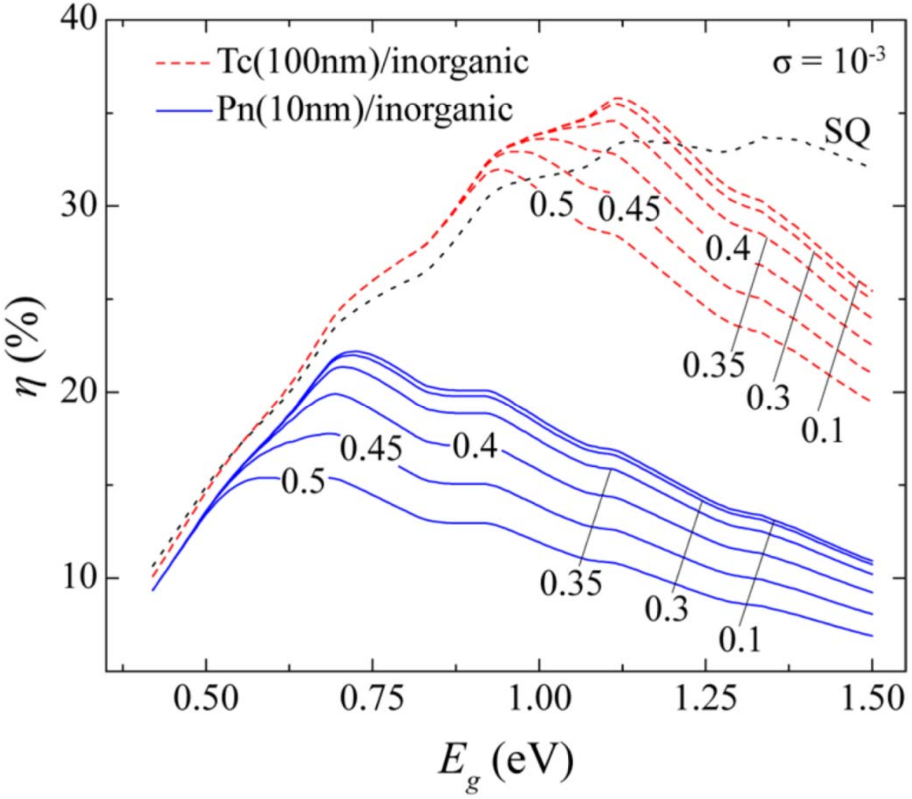
Tayebjee, M., McCamey, D., Schmidt, T., *JPCL*, (2015) **6**, 2367.

Trupke, T., Green, M., Wurfel, P., *JAP*, (2002), **92**, 1668.

Hanna, M., Nozik, A., *JAP*, (2006), **100**, 74510

More realistic device limiting efficiencies





Tayebjee, M., Mahboubi-Soufiani, A., Conibeer,G., *JPCC*, (2014) **118**, 2298.

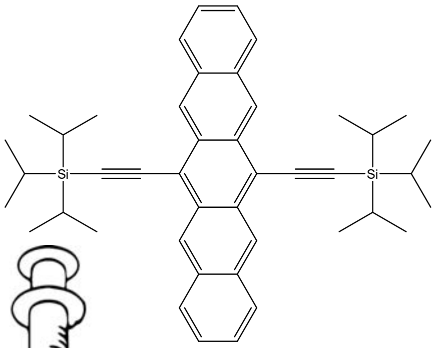
Conclusions and Progress

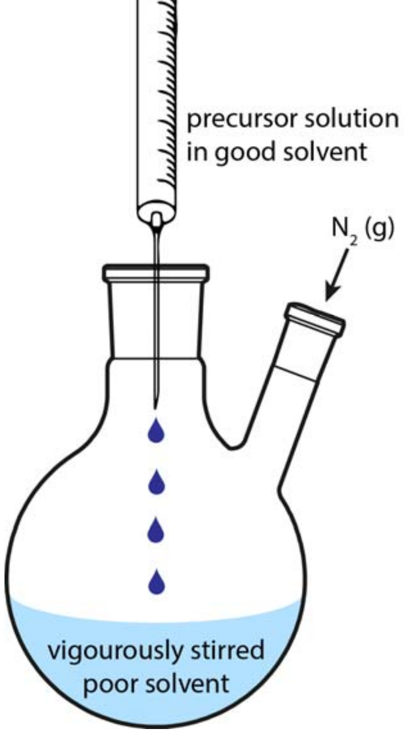
- Tetracene on silicon is theoretically well-matched to give high device efficiencies
- In principle, a tetracene layer could be applied on top of a silicon cell to enhance the overall efficiency. (Initially proposed by Dexter in 1979)
- However triplet injection/dissociation at the tetracene/silicon 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.

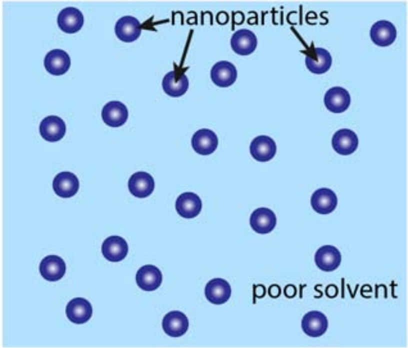
Part 2: Singlet Fission in TIPS-Pentacene Nanoparticles

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

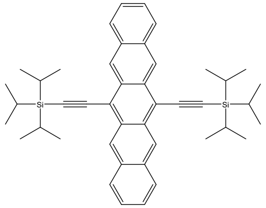


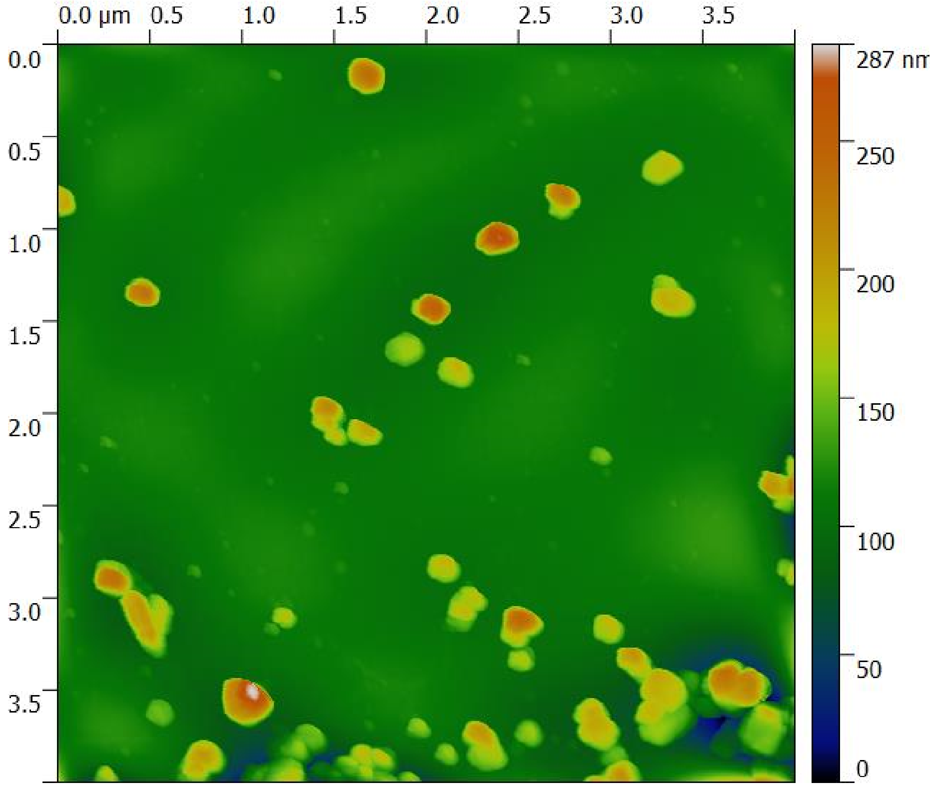


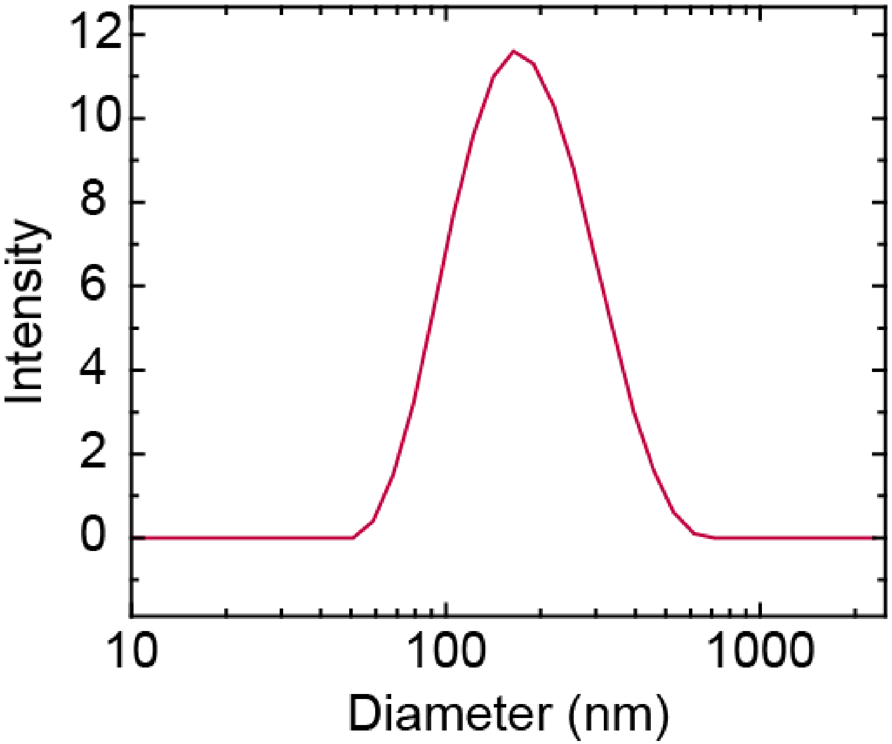


Why nanoparticles?

Particle Characterization





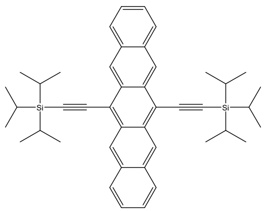


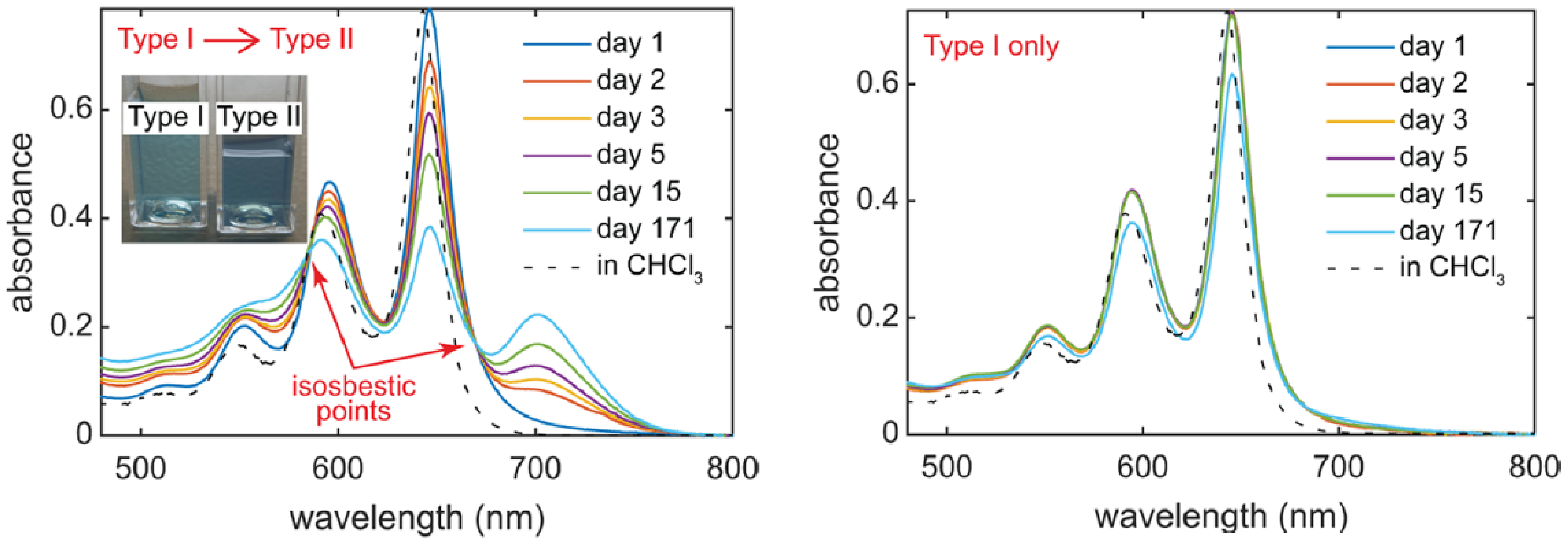
Z-average: ~150 nm

PDI: 0.2

Tayebjee, M., Schwarz, K., MacQueen, R., Dvorak, M., Lam, A., Ghiggino, K., McCamey, D., Schmidt, T., Conibeer, G. *JPCC.*, (2016) **120**, 157.

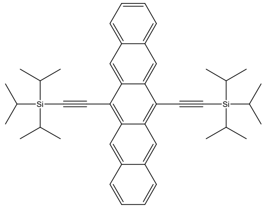
The Role of Interchromophore Coupling



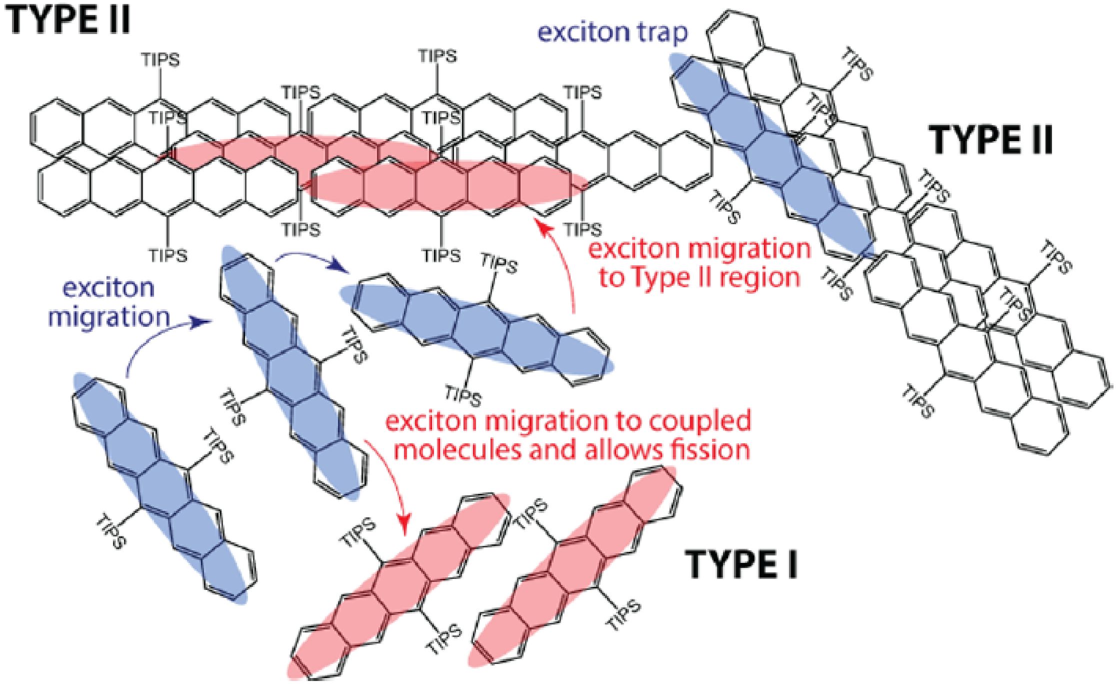


Tayebjee, M., Schwarz, K., MacQueen, R., Dvorak, M., Lam, A., Ghiggino, K., McCamey, D., Schmidt, T., Conibeer, G. *JPCC.*, (2016) **120**, 157.

Morphology

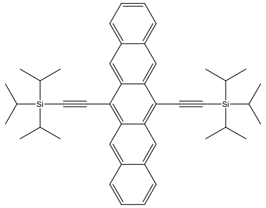


- Type II is similar to thin films where fission yield is 200%
- So we expect fission to be much more efficient in the Type II nanoparticles

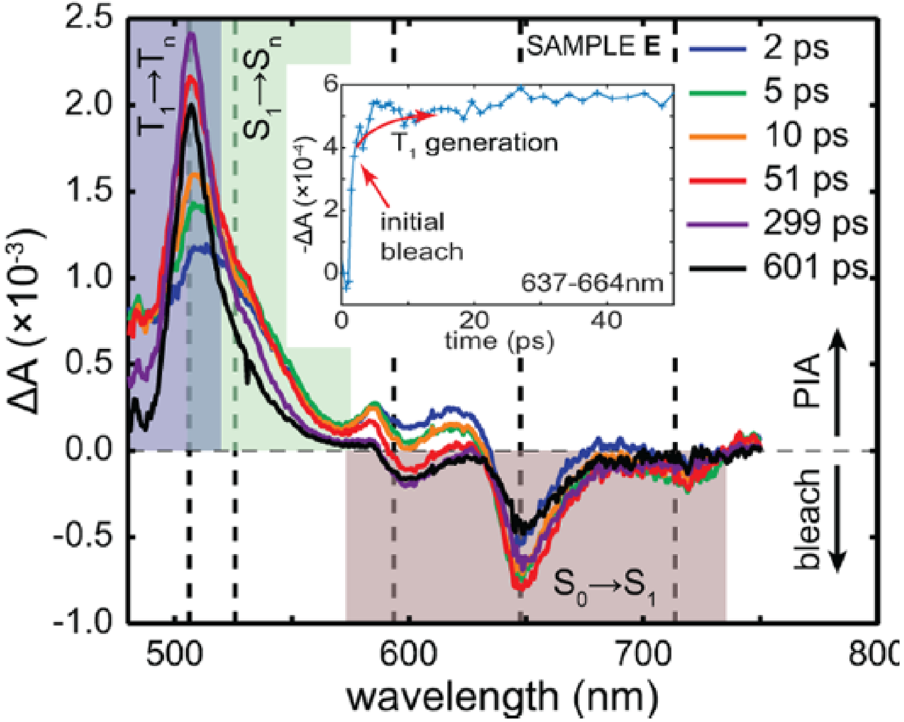


Tayebjee, M., Schwarz, K., MacQueen, R., Dvorak, M., Lam, A., Ghiggino, K., McCamey, D., Schmidt, T., Conibeer, G. *JPCC.*, (2016) **120**, 157.

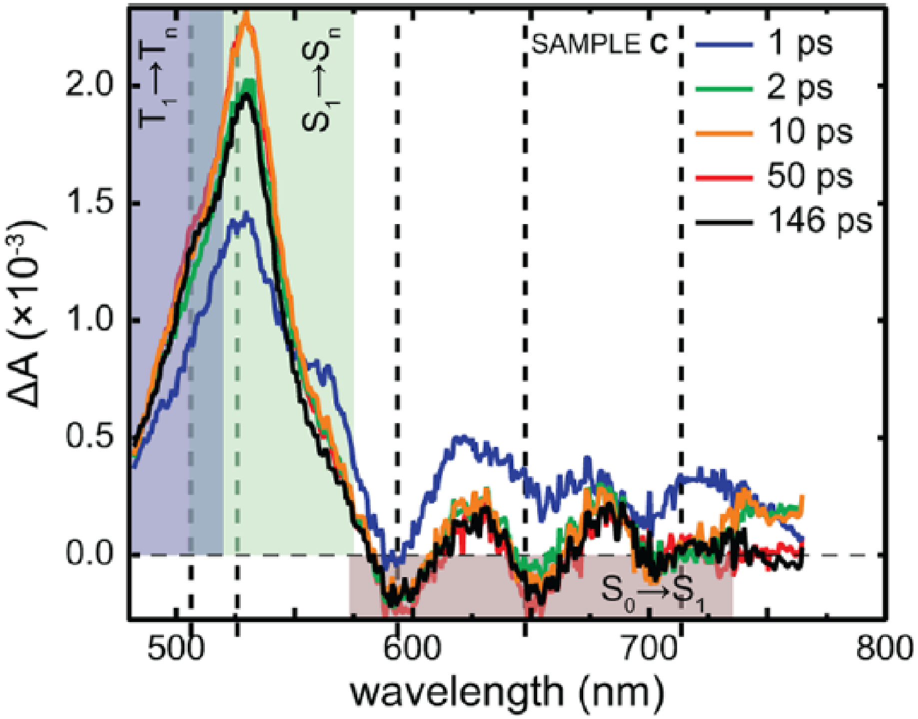
Transient Absorption



Type I

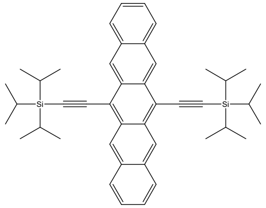


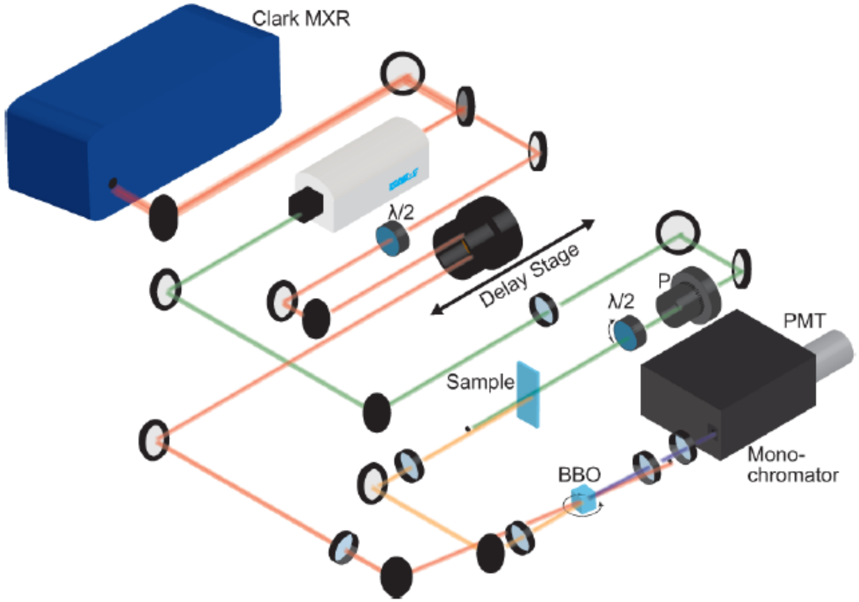
Type II

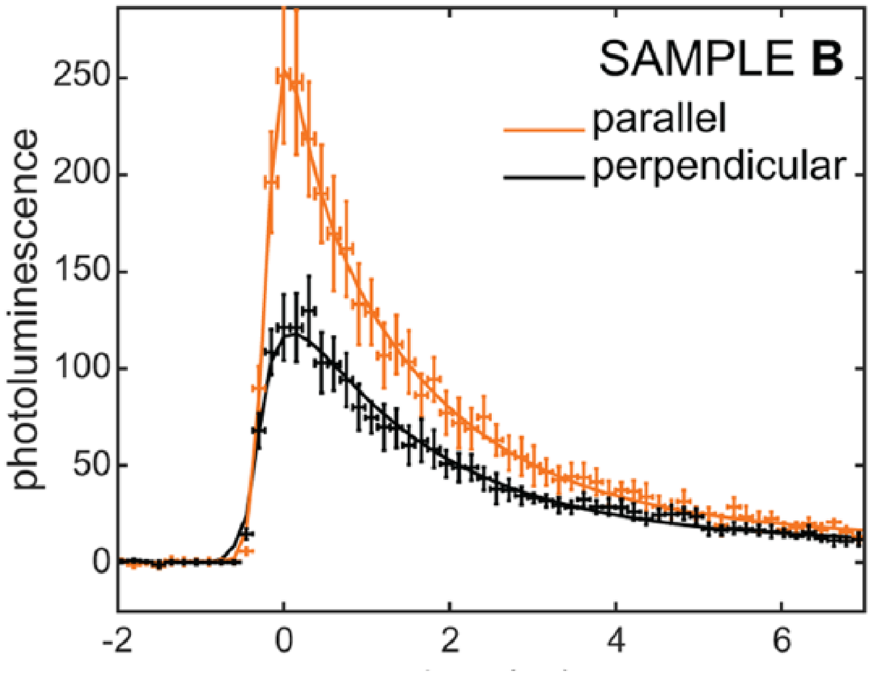


Tayebjee, M., Schwarz, K., MacQueen, R., Dvorak, M., Lam, A., Ghiggino, K., McCamey, D., Schmidt, T., Conibeer, G. *JPCC.*, (2016) **120**, 157.

Ultrafast Polarization Anisotropy



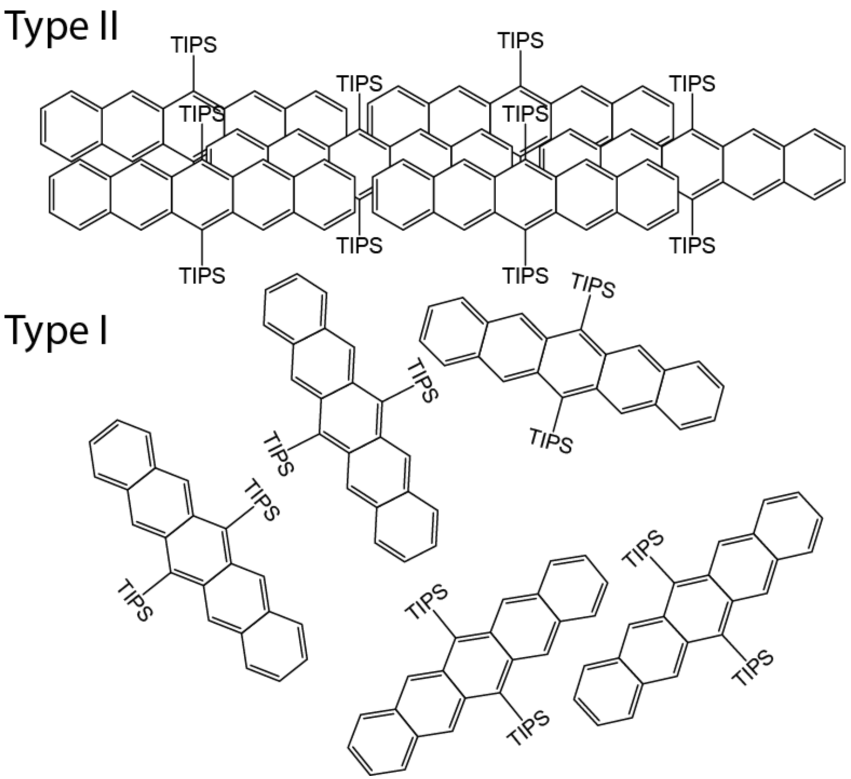




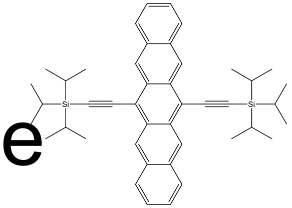
Tayebjee, M., Schwarz, K., MacQueen, R., Dvorak, M., Lam, A., Ghiggino, K., McCamey, D., Schmidt, T., Conibeer, G. *JPCC.*, (2016) **120**, 157.

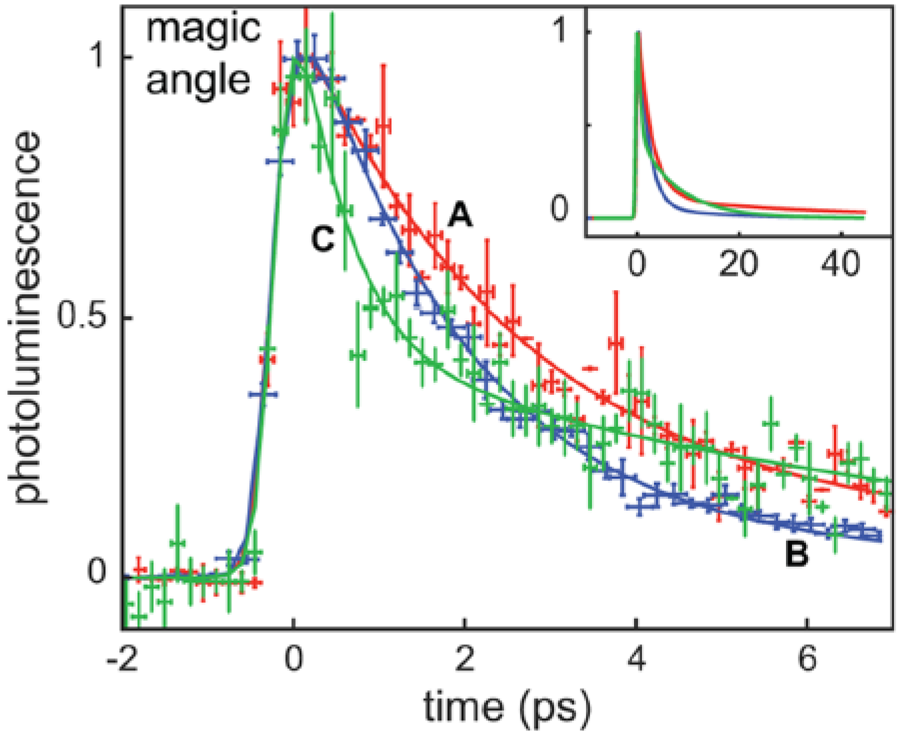
Photoluminescence Anisotropy Decay

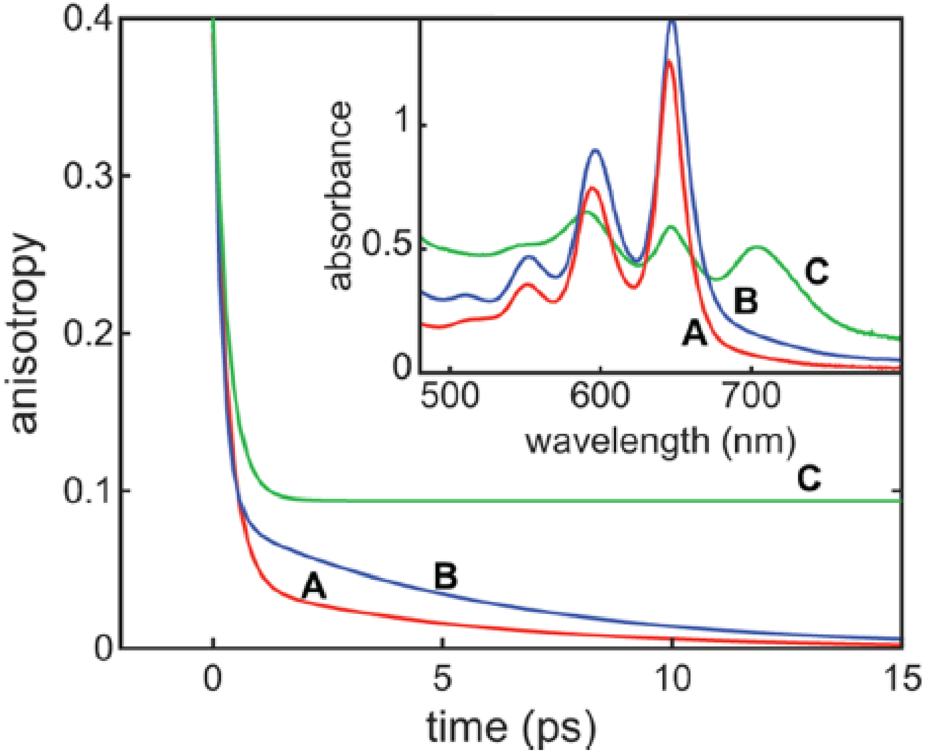
- We expect there to be no decay in anisotropy in
  - Type II regions
  - Exciton traps
- We expect the anisotropy to decay when
  - Excitons migrate within Type I regions
  - Excitons migrate across crystalline grain boundaries



Ultrafast Time-resolved Photoluminescence







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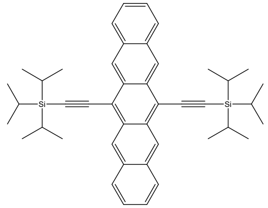
Schmidt, T., Conibeer, G. *JPCC.*, (2016) **120**, 157.

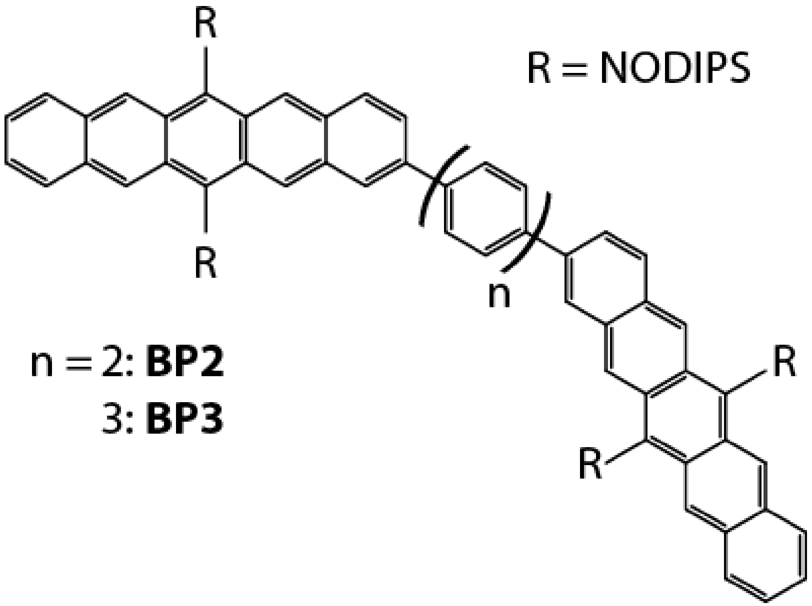
Summary of Nanoparticle Results



- 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

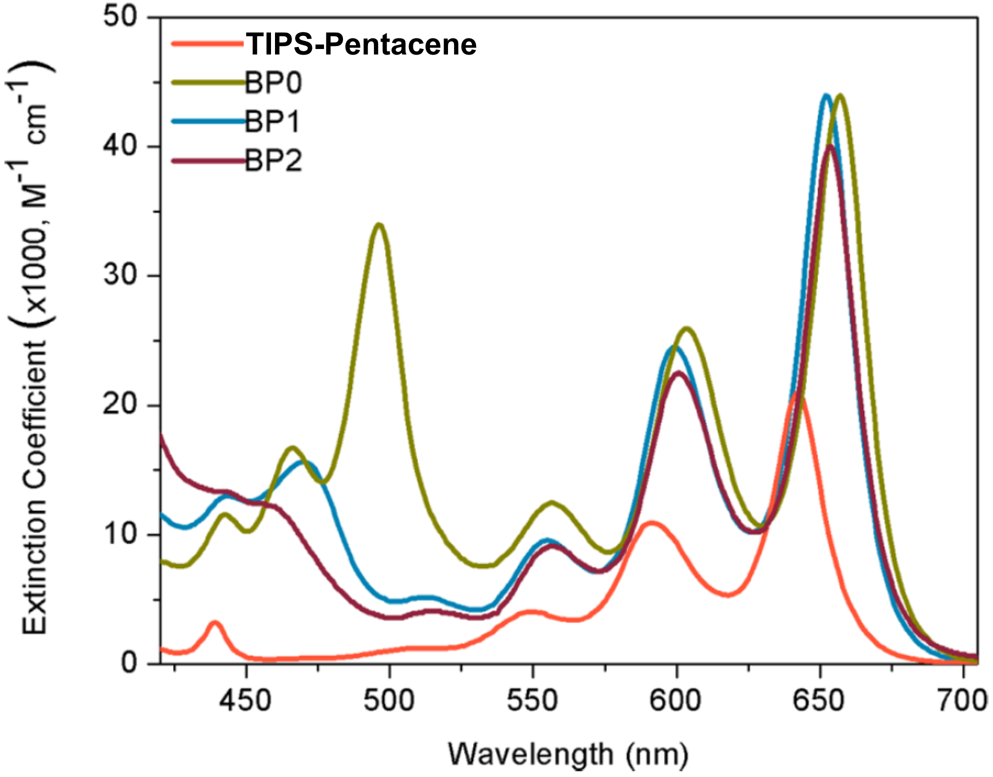
Part 3: Singlet Fission in Bipentacenes

Quantitative Fission in Bipentacenes



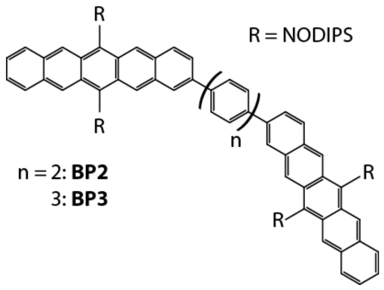
R = NODIPS

n = 2: **BP2**
3: **BP3**



Sanders, et al., *JACS*, **2015**, *137* (28), pp 8965–8972

Anomalous Triplet Lifetimes



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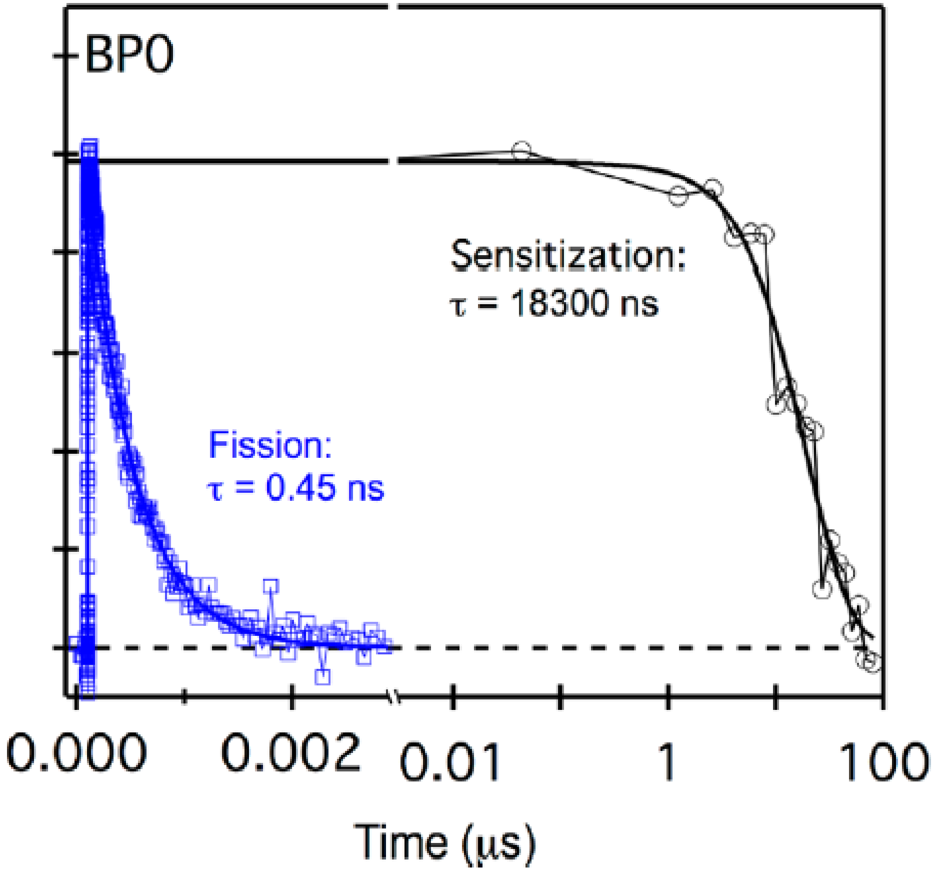
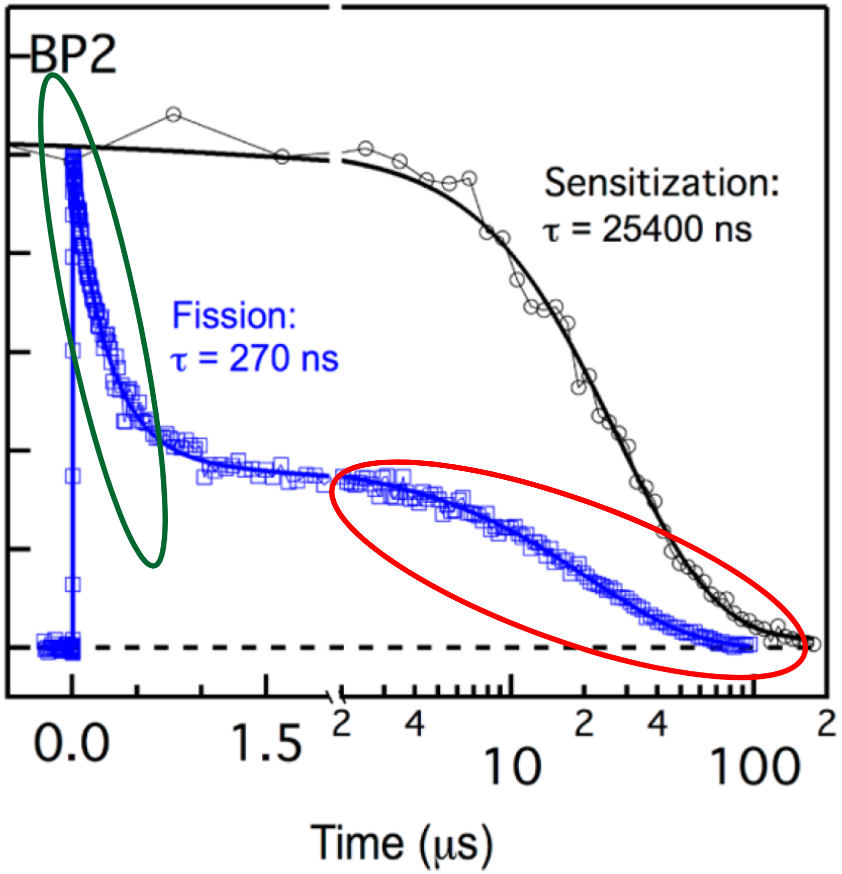
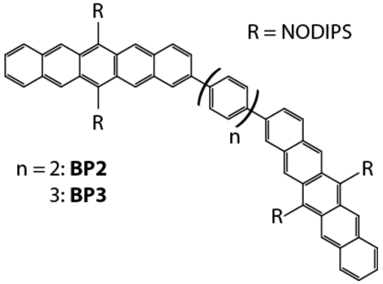
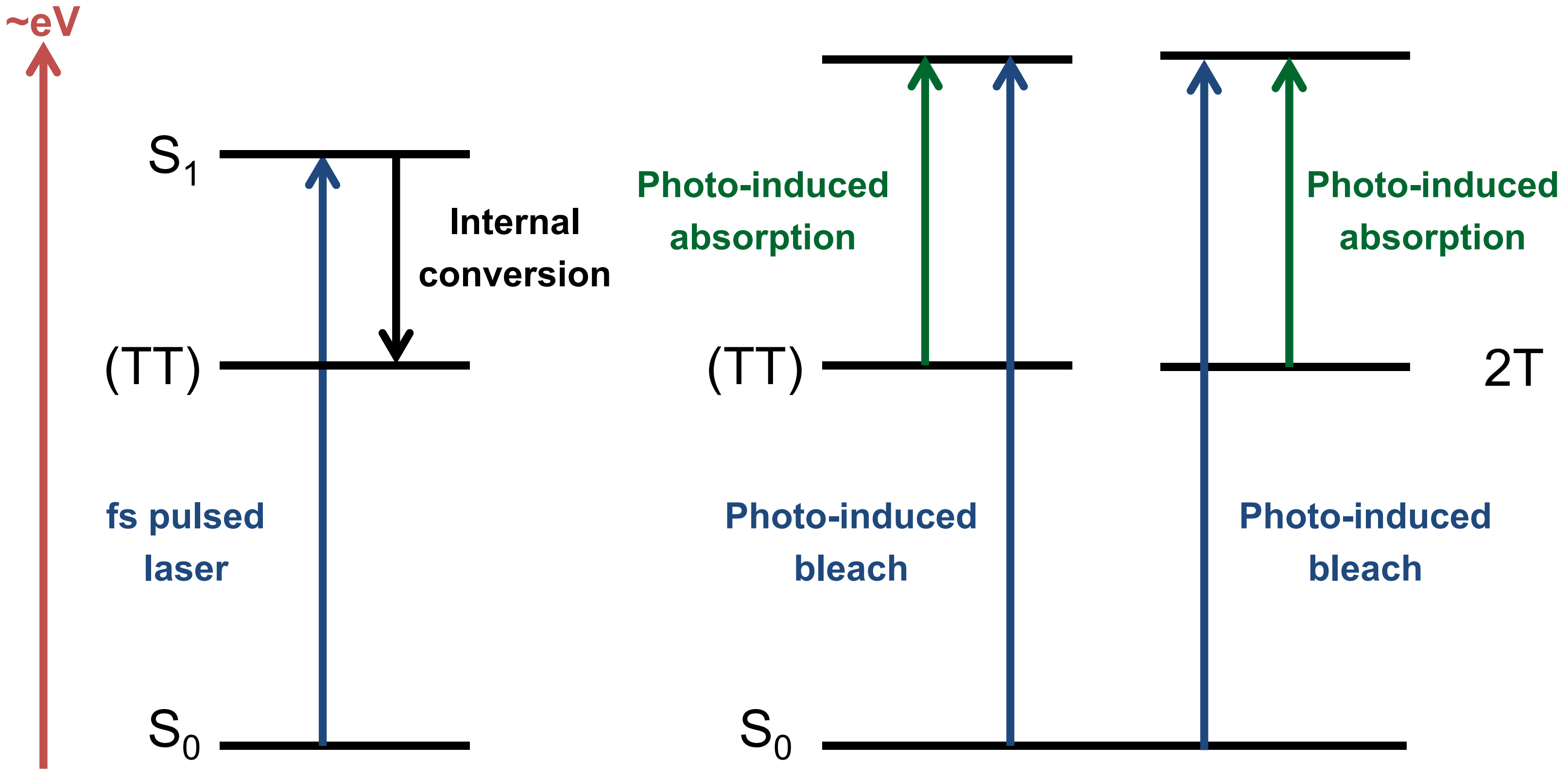




Sanders, et al., *JACS*, **2015**, *137* (28), pp 8965–8972

Transient Absorption: Triplet Yield but Not Triplet-Triplet Coupling





~eV

S_1

Internal conversion

(TT)

fs pulsed laser

S_0

Photo-induced absorption

(TT)

Photo-induced bleach

S_0

Photo-induced absorption

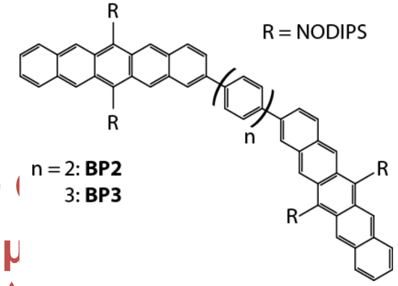
2T

Photo-induced bleach

Optical Pump

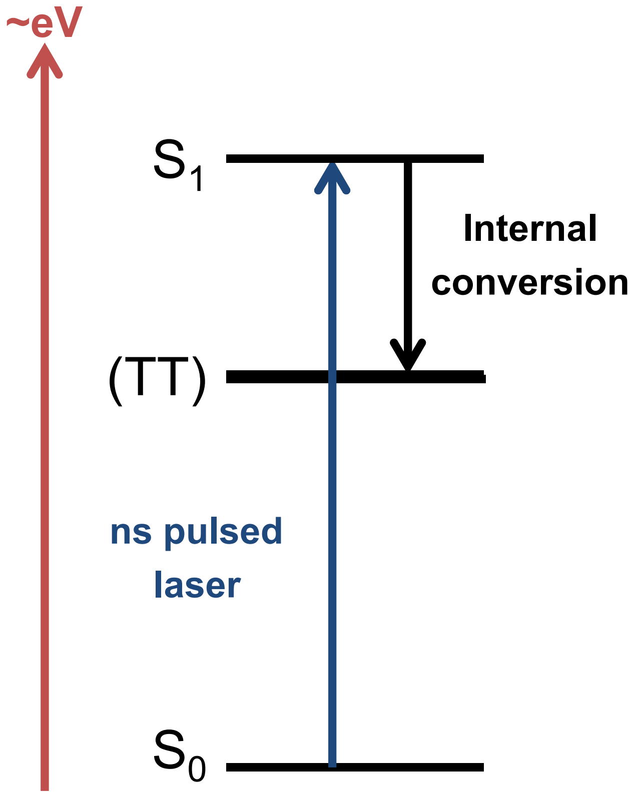
Optical Probe

Transient EPR: Nature of Spin States



R = NODIPS

n = 2: **BP2**
3: **BP3**

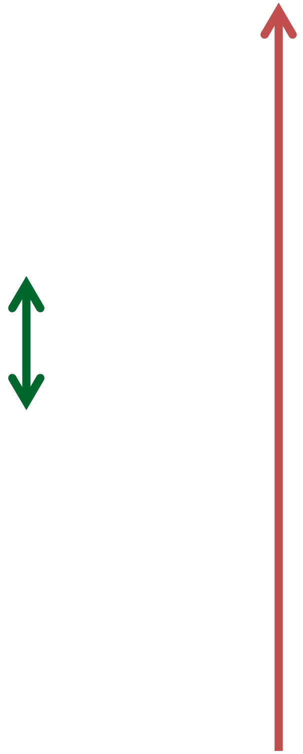


Internal conversion

ns pulsed laser

~10

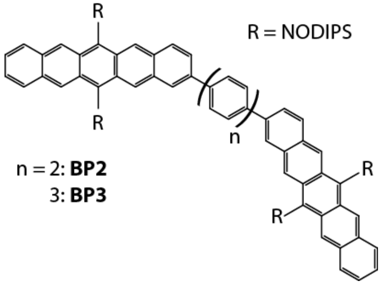
~40



Optical Pump

Microwave Probe

The Spin Hamiltonian



$$\hat{\mathcal{H}} = \hat{H}_z + \hat{H}_{zfs} + \hat{H}_{ee}$$

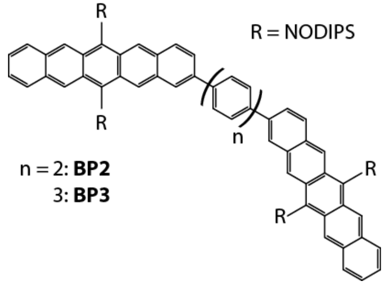
Zeeman

Splits states with different m_s under an applied field

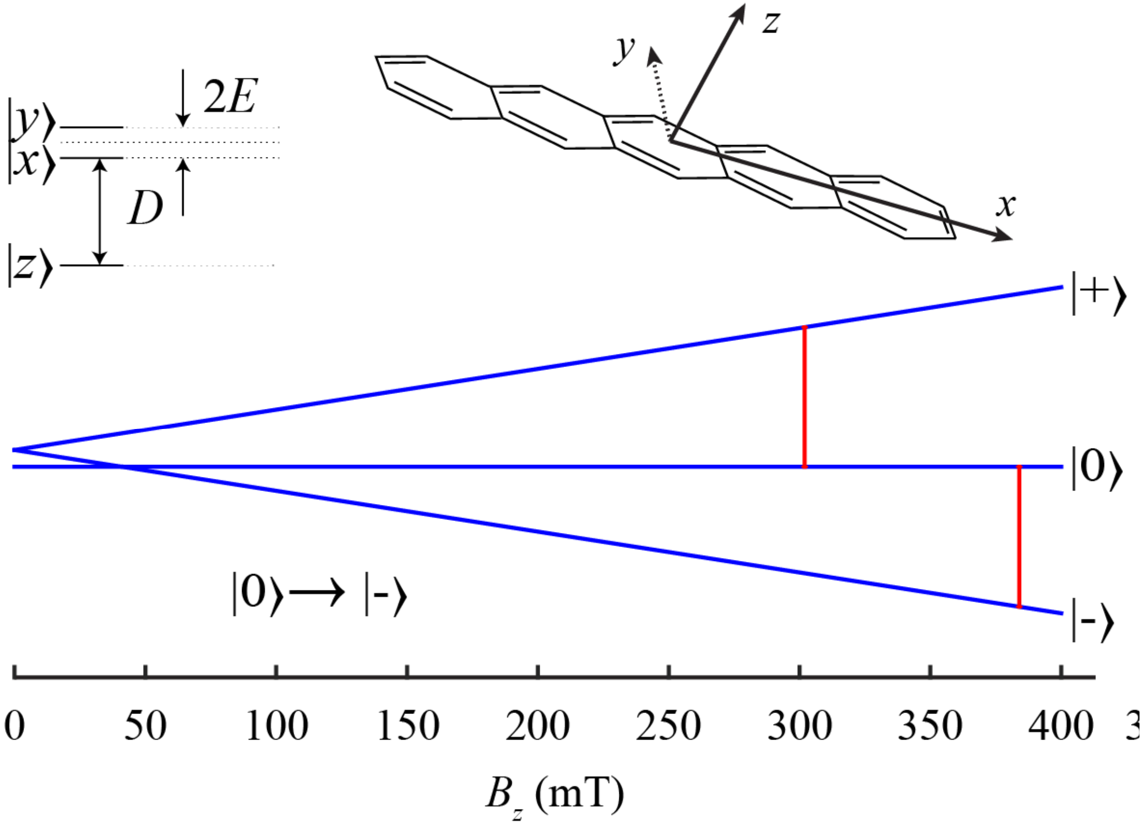
Zero-field splitting (splits states of individual triplets)

(TT) interaction

Zero Field Splitting of Triplet States

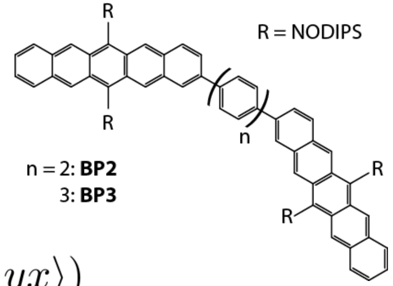


$$\hat{\mathcal{H}} = \hat{H}_z + \hat{H}_{zfs} + \hat{H}_{ee}$$

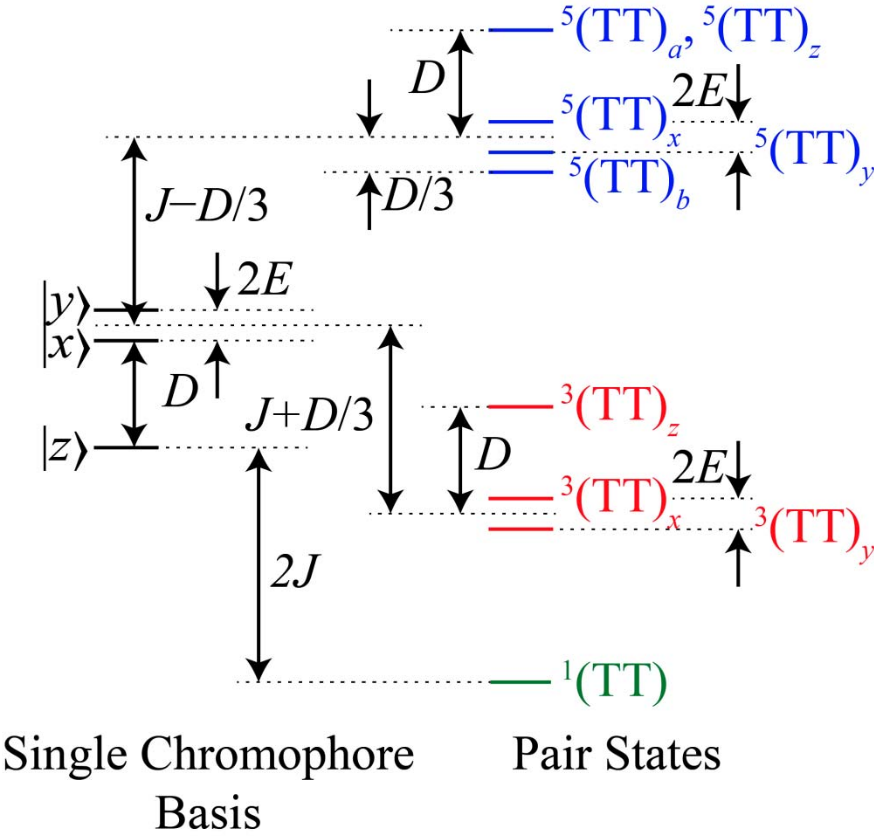


Stoll, S., Schweiger, A. *J. Mag. Res.* **2006**, *178* (1), pp 42-55

Zero Field Splitting of Triplet States



$$\hat{\mathcal{H}} = \hat{H}_z + \hat{H}_{zfs} + \hat{H}_{ee}$$



$$\left|^5(\mathrm{TT})_z\right\rangle = \frac{1}{\sqrt{2}}\left(|xy\rangle + |yx\rangle\right)$$

$$\left|^5(\mathrm{TT})_a\right\rangle = \frac{1}{\sqrt{2}}\left(|xx\rangle - |yy\rangle\right)$$

$$\left|^5(\mathrm{TT})_x\right\rangle = \frac{1}{\sqrt{2}}\left(|yz\rangle + |zy\rangle\right)$$

$$\left|^5(\mathrm{TT})_y\right\rangle = \frac{1}{\sqrt{2}}\left(|xz\rangle + |zx\rangle\right)$$

$$\left|^5(\mathrm{TT})_b\right\rangle = \frac{1}{\sqrt{6}}\left(|xx\rangle + |yy\rangle - 2|zz\rangle\right)$$

$$\left|^3(\mathrm{TT})_z\right\rangle = \frac{1}{\sqrt{2}}\left(|xy\rangle - |yx\rangle\right)$$

$$\left|^3(\mathrm{TT})_x\right\rangle = \frac{1}{\sqrt{2}}\left(|yz\rangle - |zy\rangle\right)$$

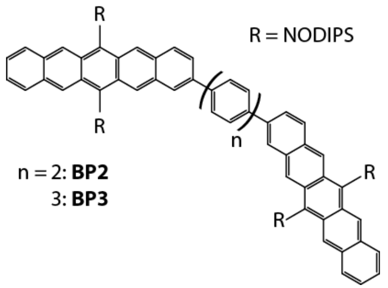
$$\left|^3(\mathrm{TT})_y\right\rangle = \frac{1}{\sqrt{2}}\left(|xz\rangle - |zx\rangle\right)$$

$$\left|^1(\mathrm{TT})\right\rangle = \frac{1}{\sqrt{3}}\left(|xx\rangle + |yy\rangle + |zz\rangle\right)$$

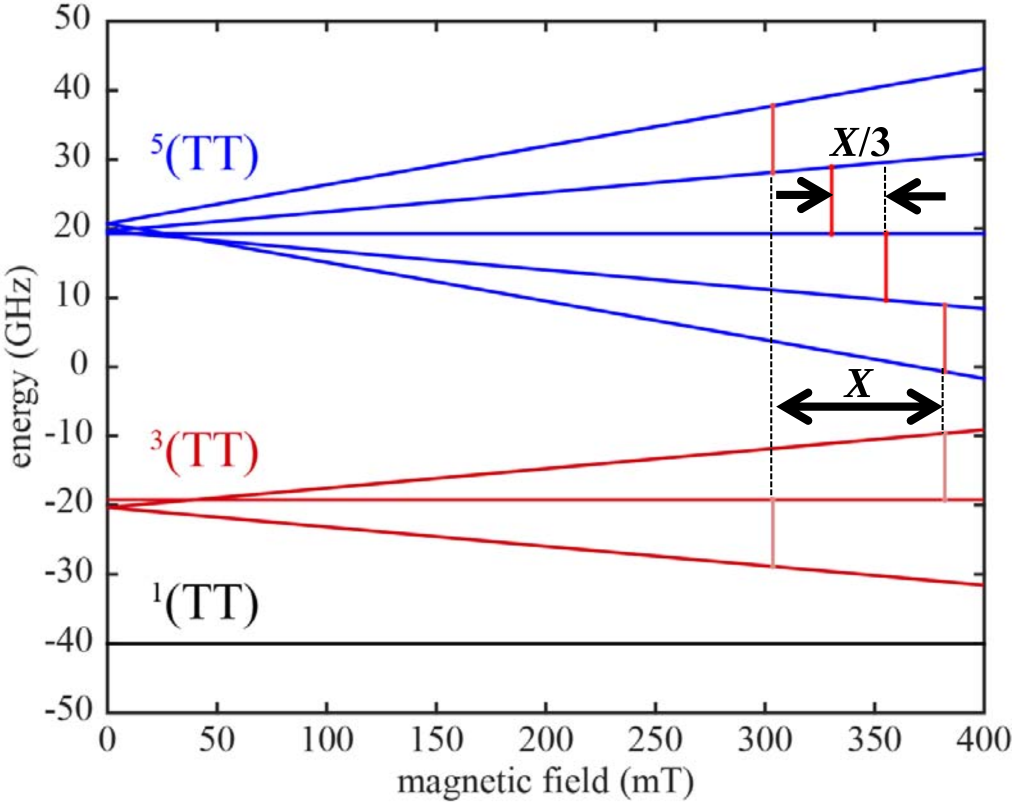
Merrifield, R. E., *Pure and Applied Chemistry,* **1971**, *27*(3), pp 481

Benk, H., Sixl, H., *Mol. Phys,* **1981**, *42*(4), pp 779-801

Applied Magnetic Field



$$\hat{\mathcal{H}} = \boxed{\hat{H}_z + \hat{H}_{zfs} + \hat{H}_{ee}}$$



$$\left|{}^5(\mathrm{TT})_{+2}\right\rangle = |{+}{+}\rangle$$

$$\left|{}^5(\mathrm{TT})_{+1}\right\rangle = \frac{1}{\sqrt{2}}\left(|{+}0\rangle + |0{+}\rangle\right)$$

$$\left|{}^5(\mathrm{TT})_{0}\right\rangle = \frac{1}{\sqrt{6}}\left(2\boxed{|00\rangle} + \boxed{|{+}{-}\rangle + |{-}{+}\rangle}\right)$$

$$\left|{}^5(\mathrm{TT})_{-1}\right\rangle = \frac{1}{\sqrt{2}}\left(|{-}0\rangle + |0{-}\rangle\right)$$

$$\left|{}^5(\mathrm{TT})_{-2}\right\rangle = |{-}{-}\rangle$$

$$\left|{}^3(\mathrm{TT})_{+1}\right\rangle = \frac{1}{\sqrt{2}}\left(|{+}0\rangle - |0{+}\rangle\right)$$

$$\left|{}^3(\mathrm{TT})_{0}\right\rangle = \frac{1}{\sqrt{2}}\left(|{+}{-}\rangle - |{+}{-}\rangle\right)$$

$$\left|{}^3(\mathrm{TT})_{-1}\right\rangle = \frac{1}{\sqrt{2}}\left(|{-}0\rangle - |0{-}\rangle\right)$$

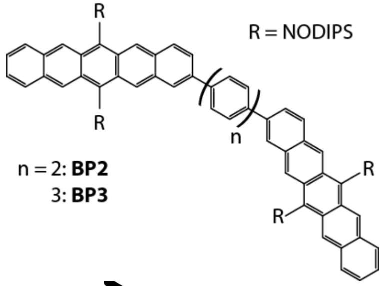
$$\left|{}^1(\mathrm{TT})\right\rangle = \frac{1}{\sqrt{3}}\left(\boxed{|00\rangle} - \boxed{|{+}{-}\rangle - |{-}{+}\rangle}\right)$$

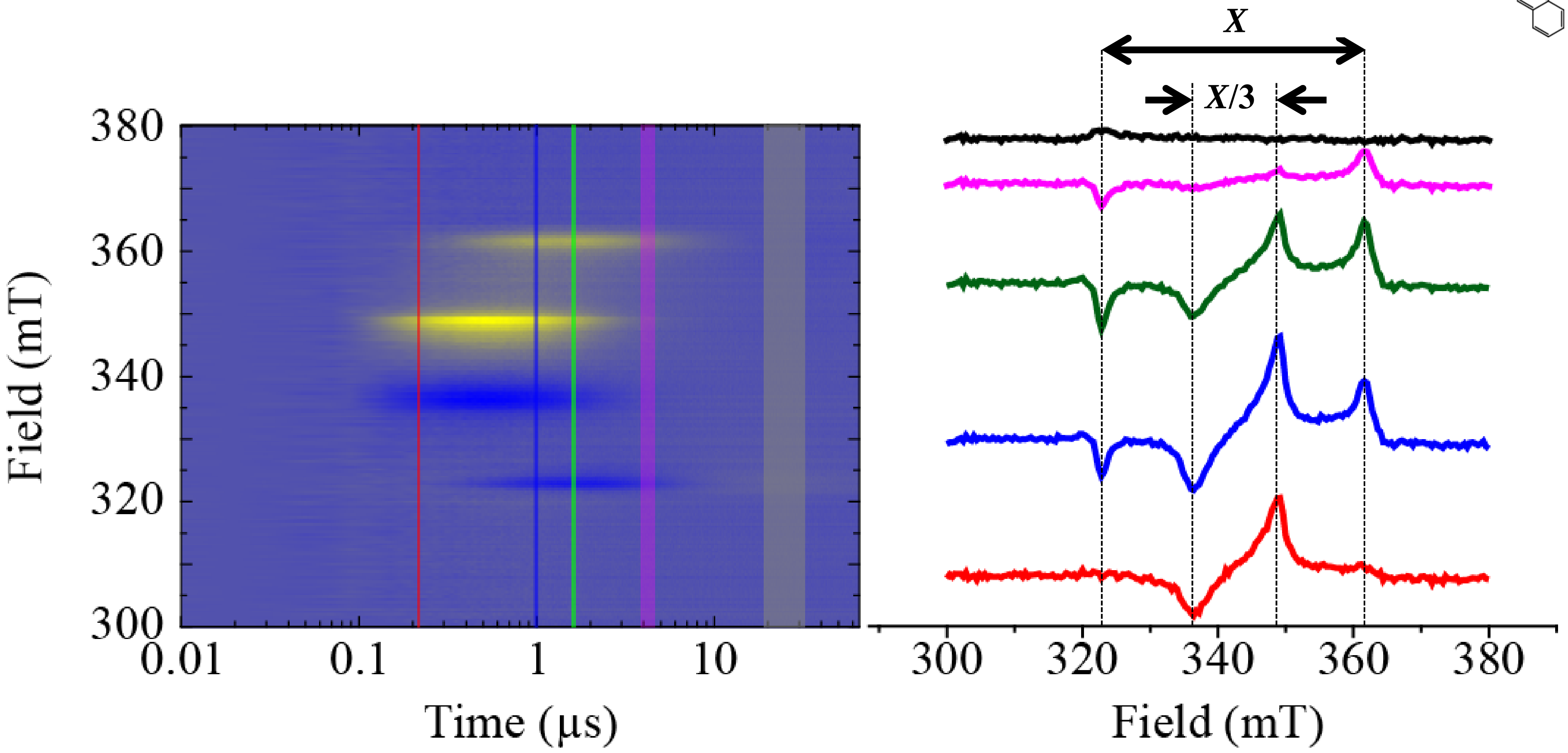
Merrifield, R. E., *Pure and Applied Chemistry,* **1971**, *27*(3), pp 481

Benk, H., Sixl, H., *Mol. Phys,* **1981**, *42*(4), pp 779-801

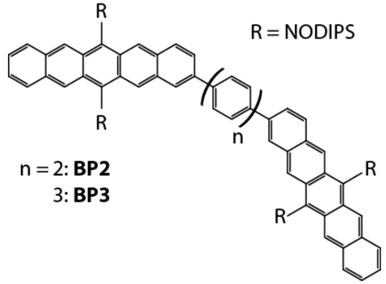
Burdett, J., et al. *Chem Phys Lett.*, **2013**, *585*, pp 1-10

Pulsed Laser/cw-EPR **BP3** at 40K

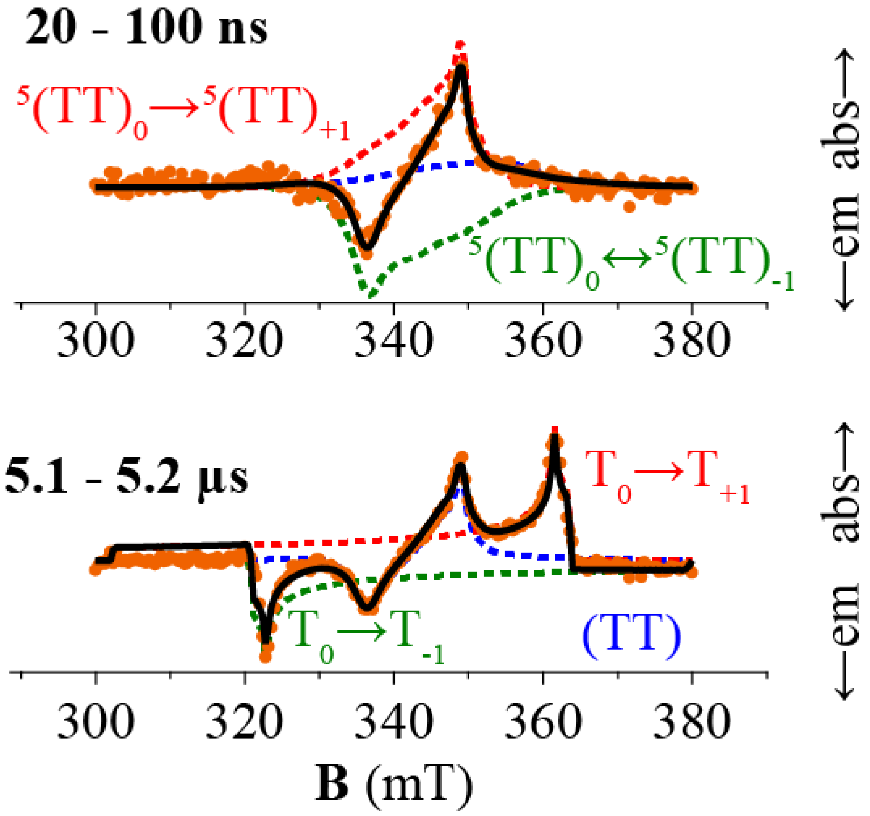




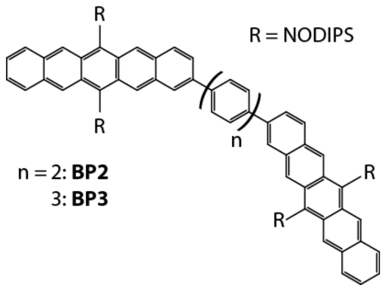
Identifying the Spin States



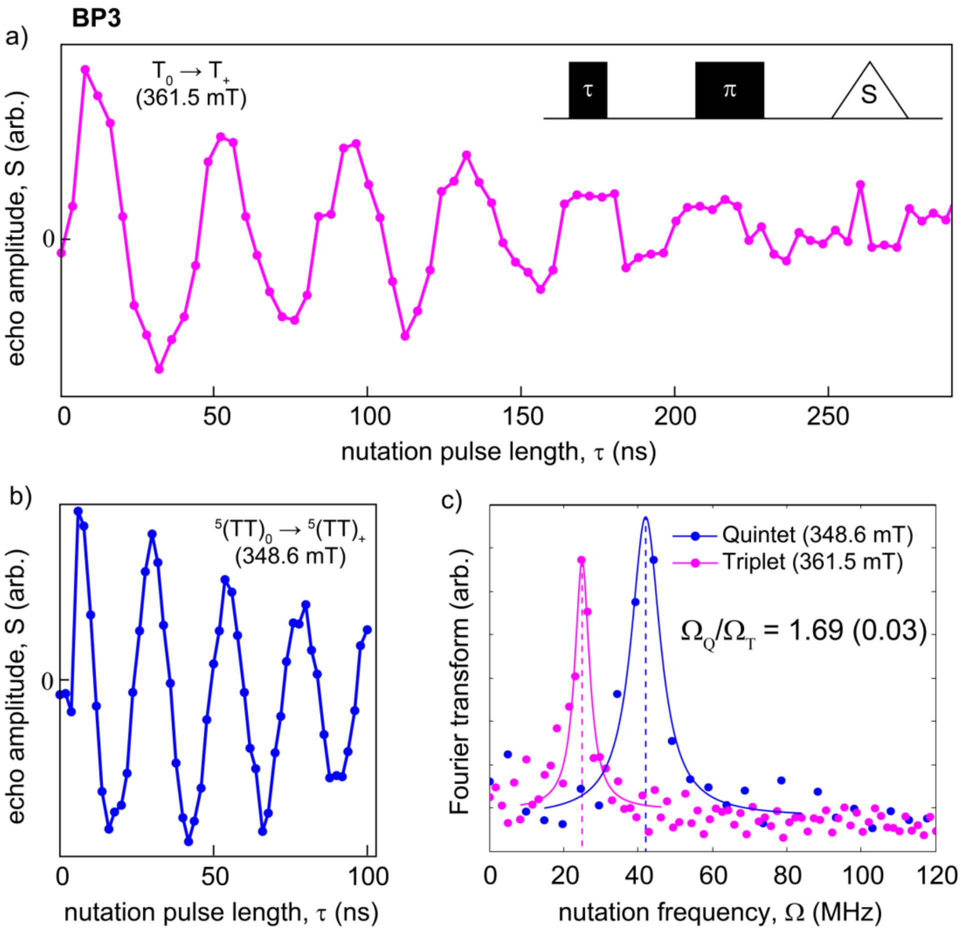
- Initial spectrum is the quintet triplet pair state
- The final spectrum could be due to three different transitions based on the magnetic field resonance positions
  - $^{5}(\mathrm{TT})_{\pm1} \rightarrow {}^{5}(\mathrm{TT})_{\pm2}$ ✗
  - $^{3}(\mathrm{TT})_{\mp1} \rightarrow {}^{3}(\mathrm{TT})_{0}$ ✗
  - $\mathrm{T}_0 \rightarrow \mathrm{T}_{\pm1}$ ✓



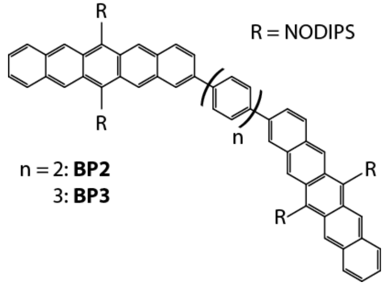
Identifying the Spin States



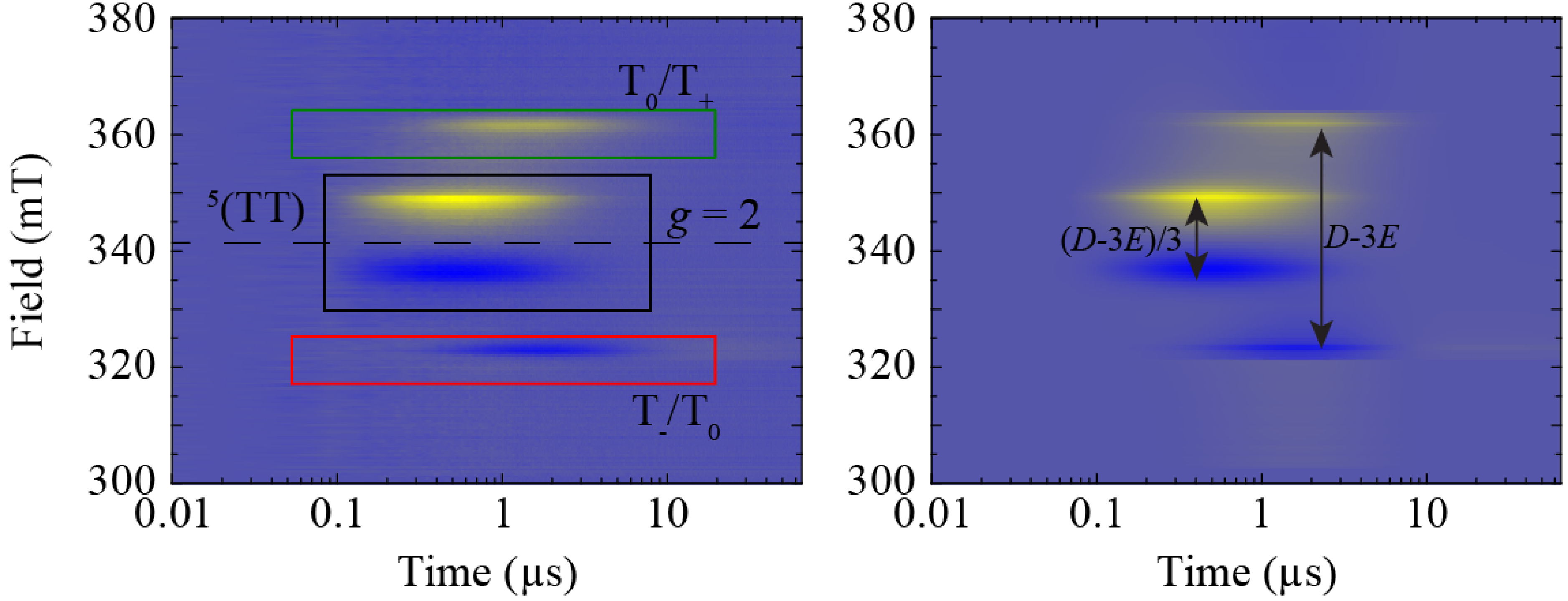
- Rabi oscillation frequency can be used to identify spin multiplicity
- $\Omega = \Omega_1[S(S+1) - M_s(M_S - 1)]^{1/2}$
- Nutation frequency ratio is expected to be $\sqrt{3} = 1.73$
- Experimental ratio is 1.69 ± 0.03



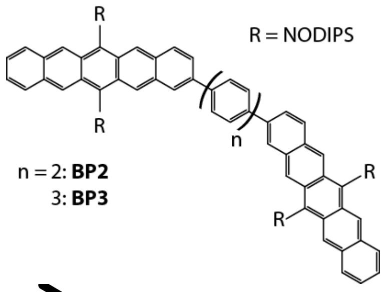
Dynamic Modelling

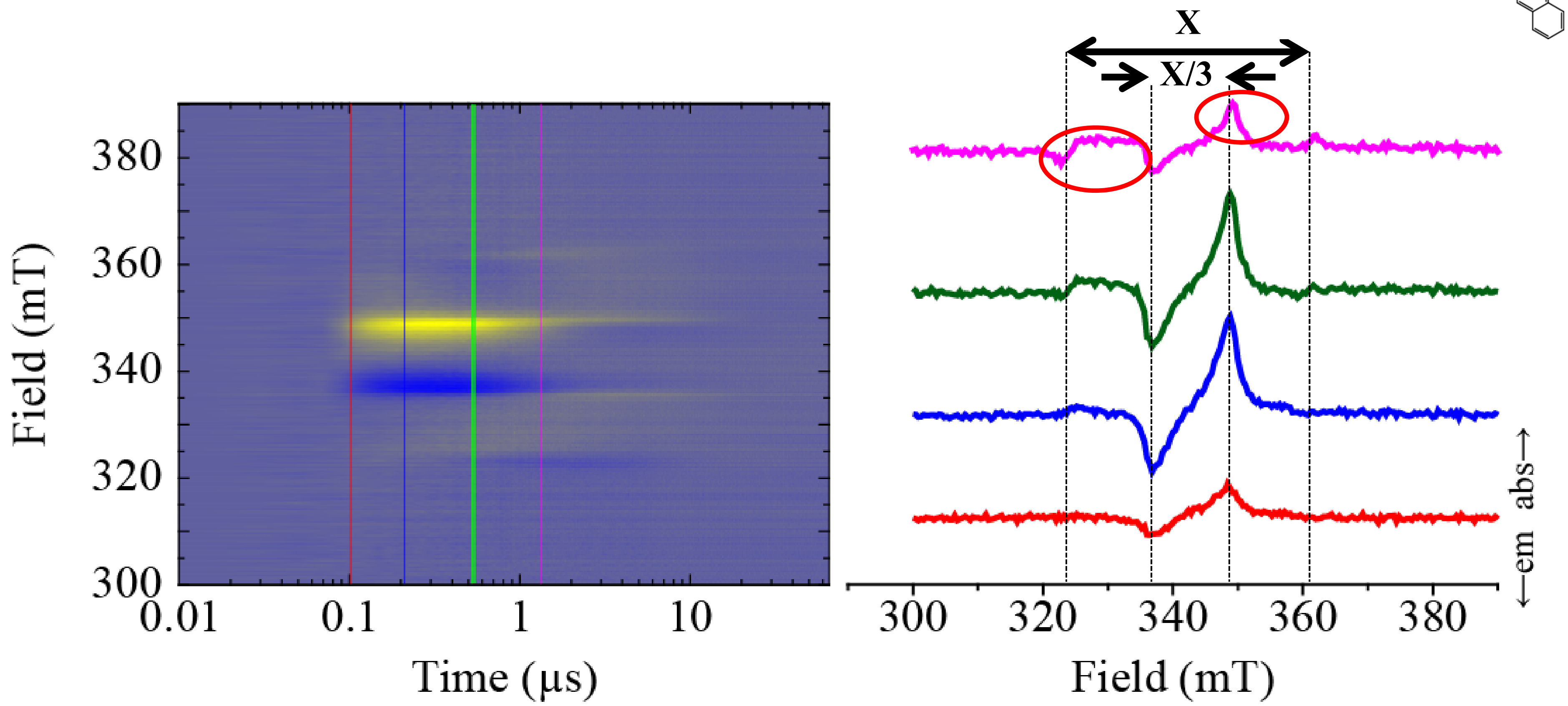


$$\frac{d\mathbf{p}}{dt} = \mathbf{M}\mathbf{p}$$

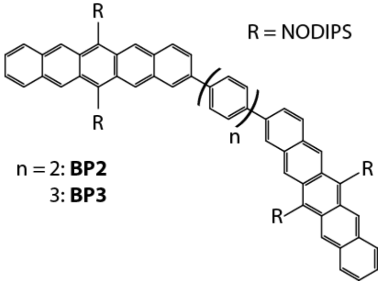


Pulsed Laser/cw-EPR **BP2** at 80K

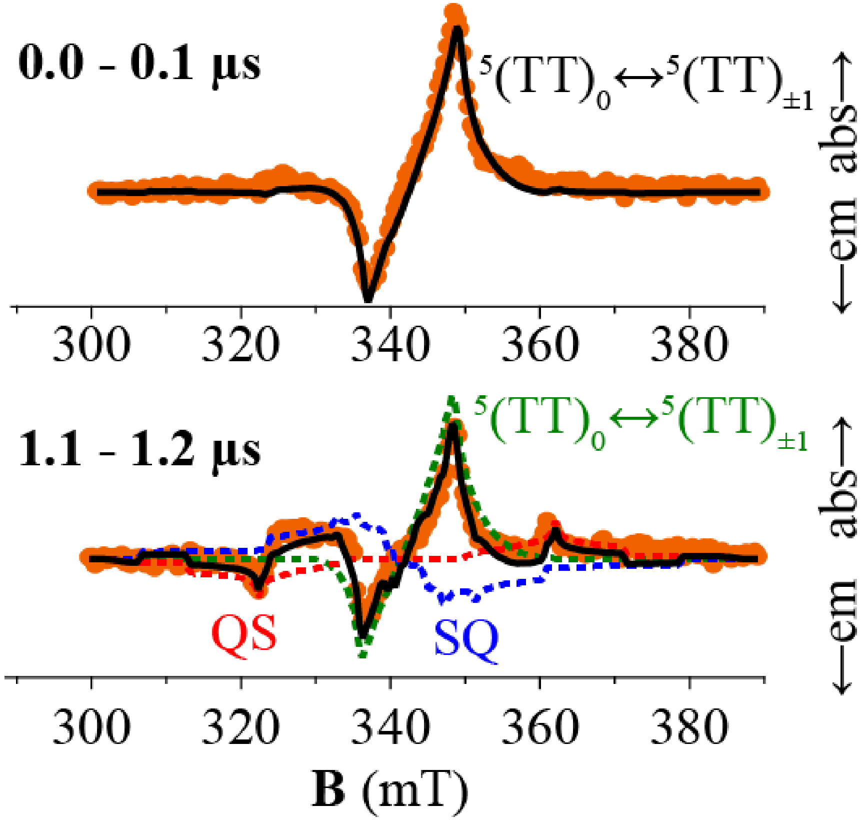




Weakly Coupled Triplets

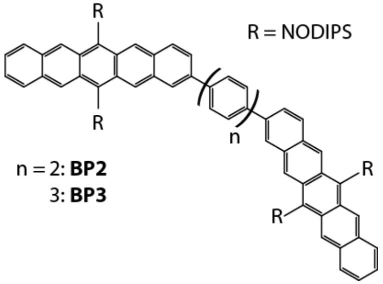


- Initial spectrum is the quintet triplet pair state
- The final spectrum cannot be explained by $T_0 \rightarrow T_{\pm1}$ transitions
- We require weak coupling to accurately fit the spectrum
- This is evidence for triplet pair state dissociates into two triplets rather than intersystem crossing (TT)→ T_1+S_0

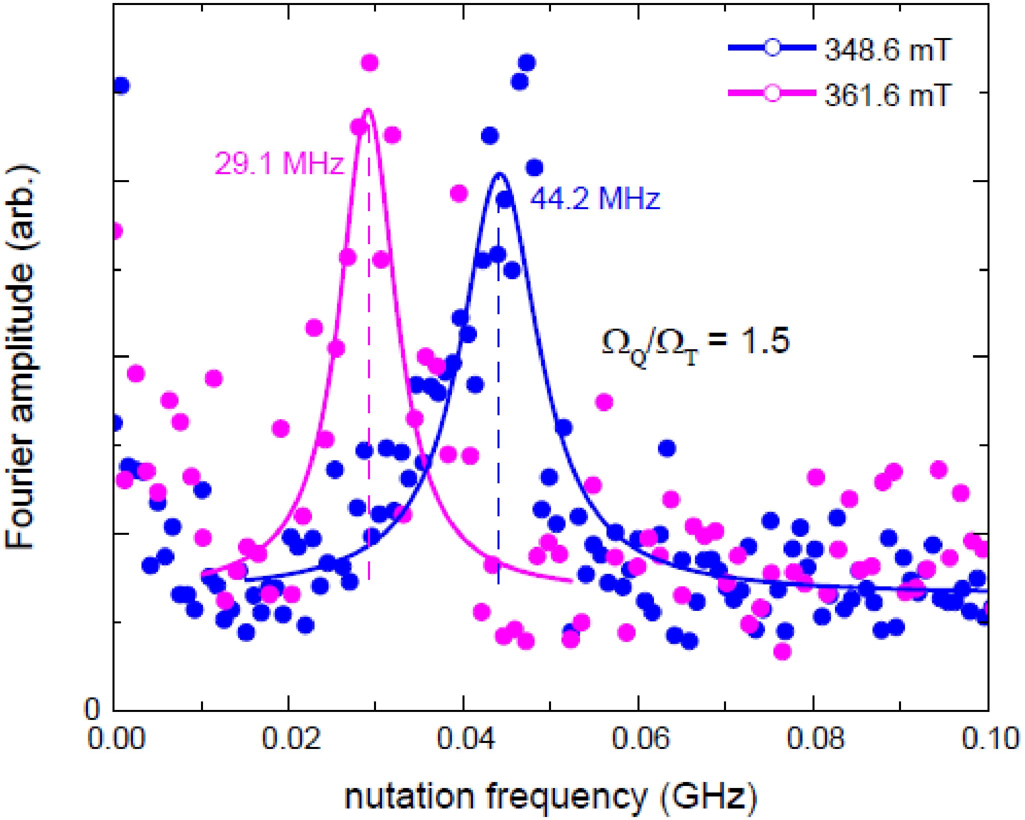


Benk, H., Sixl, H., *Mol. Phys,* **1981**, *42*(4), pp 779-801

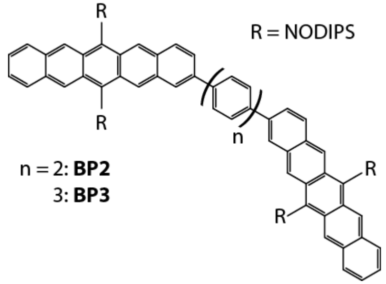
BP2 Nutation



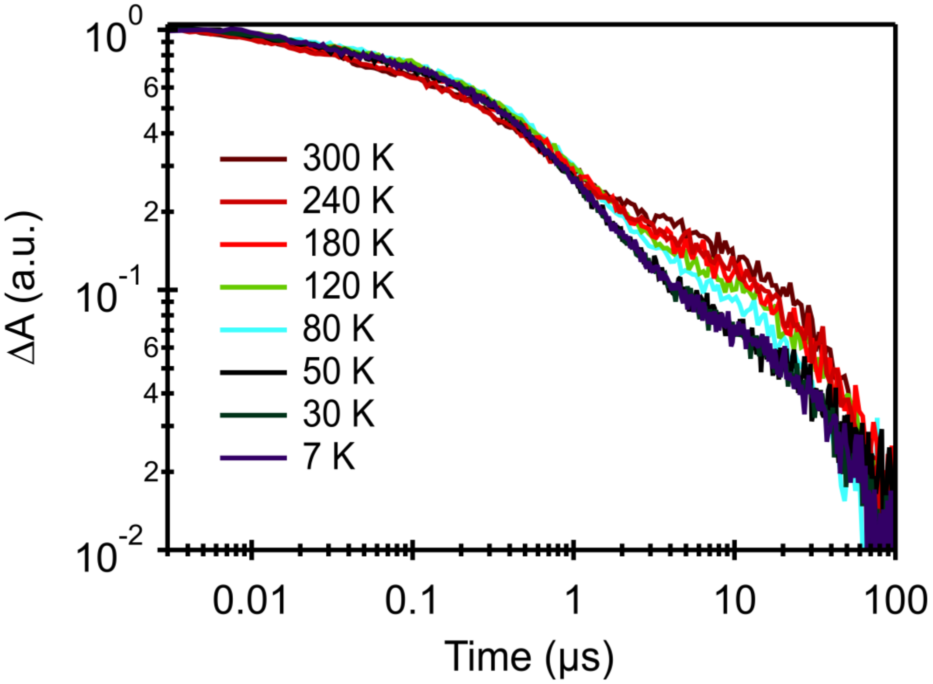
- Rabi oscillation frequency can be used to identify spin multiplicity
- $\Omega = \Omega_1[S(S+1) - M_s(M_S - 1)]^{1/2}$
- Nutation frequency ratio is expected to be $\sqrt{3} = 1.73$
- Experimental ratio is 1.5
- This departure from $\sqrt{3}$ arises because the final triplets are weakly coupled



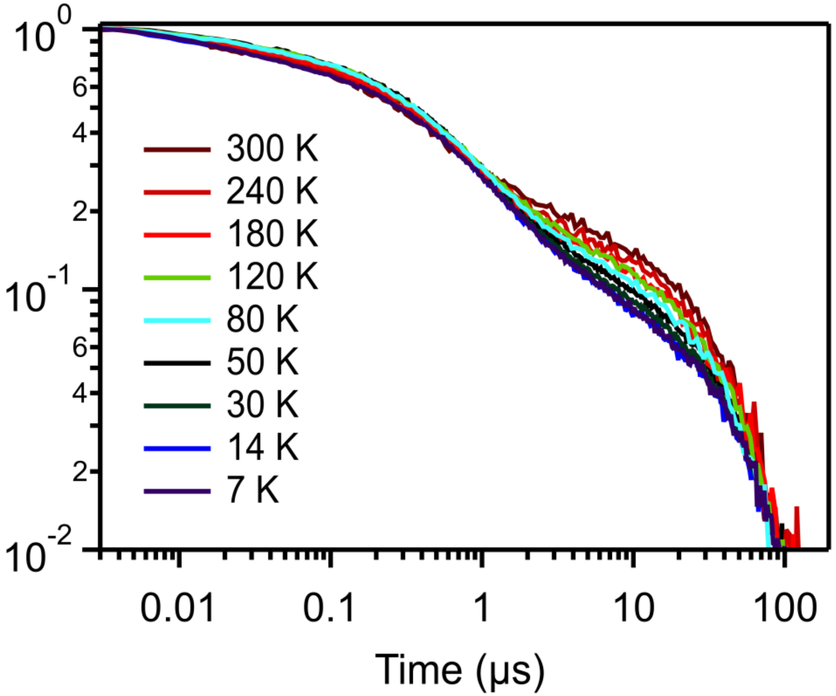
Temperature Dependent TA



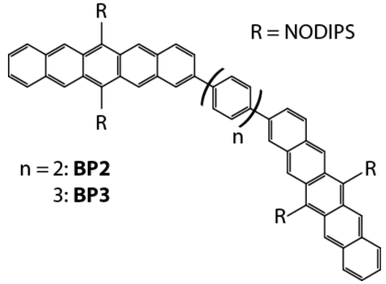
BP2

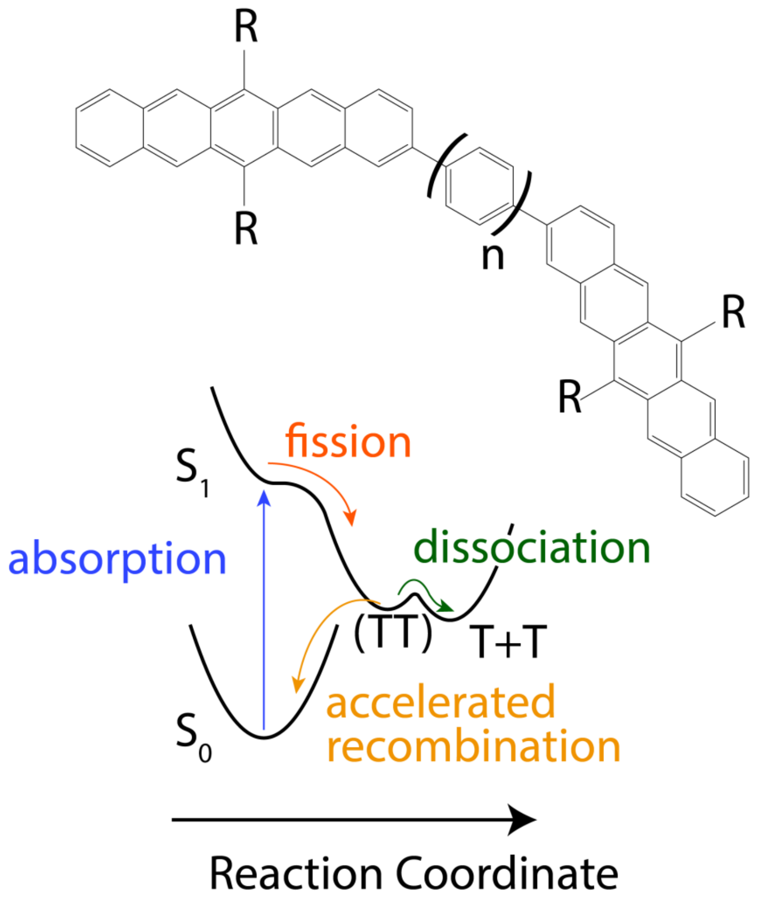


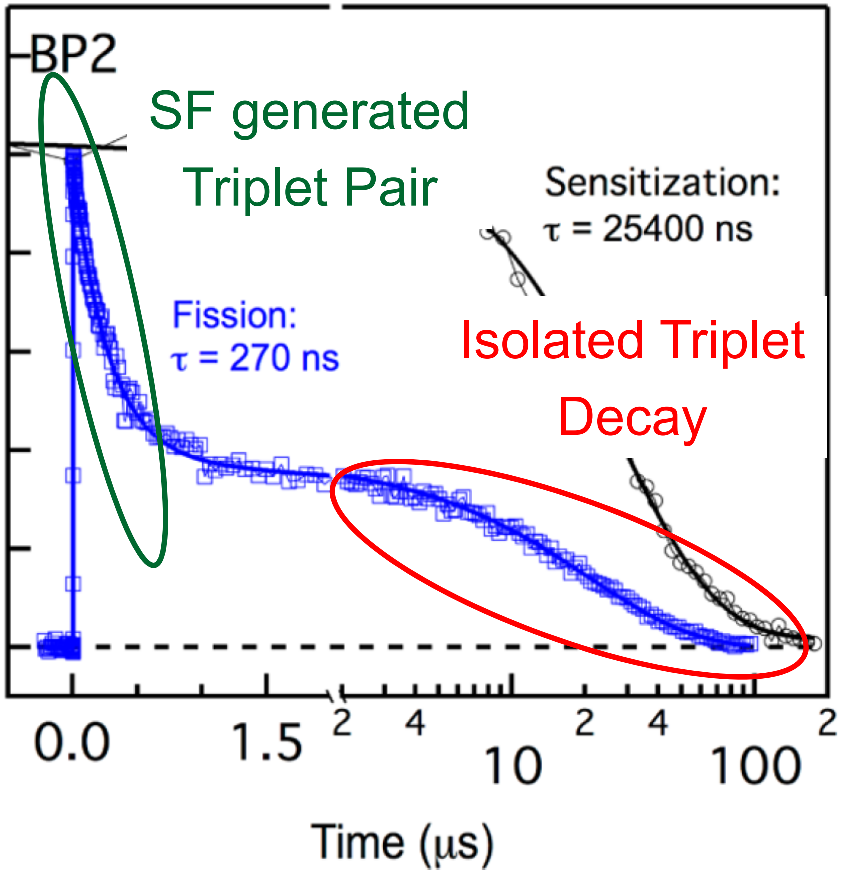
BP3



Model Summary







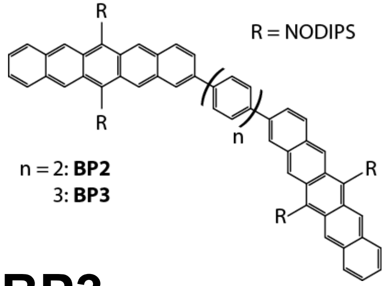
SF generated Triplet Pair

Sensitization: τ = 25400 ns

Fission: τ = 270 ns

Isolated Triplet Decay

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 $T_1 \rightarrow T_n$ 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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