Singlet Fission

More Efficiency out of the Solar Spectrum

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Organic Electronics (Seminar Talk)

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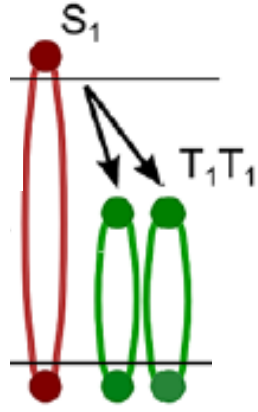

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4 May 2017

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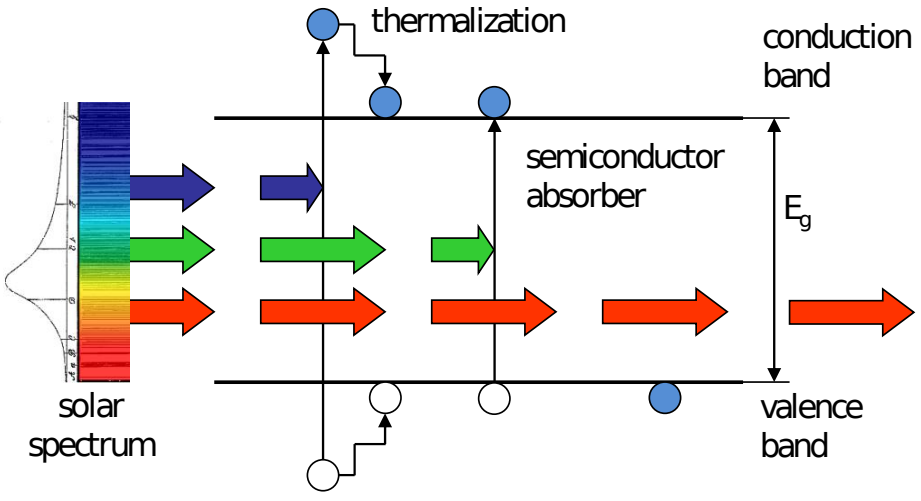
Presentation Overview

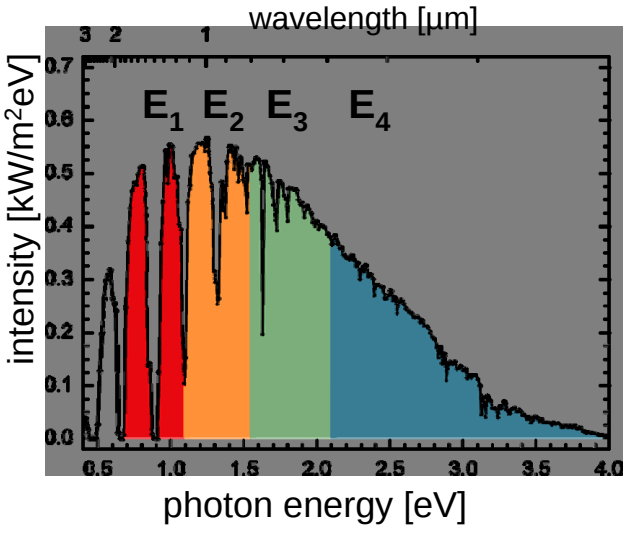
- Efficiency Limit in Photovoltaics
- Singlet Fission and Triplet-Triplet Annihilation
- Singlet Fission: Basics
- Intersystem-Crossing & Spin-Orbit Coupling
- Singlet Fission: Process I
- Singlet Fission: Process II
- Singlet Fission: Material Example
- Singlet Fission: Detection Techniques
- Singlet Fission: Trends & Challenges
- Aknowledgements

Efficiency Limit in Photovoltaics

Photovoltaics efficiency from Solar Spectrum is limited (Shockley-Queisser Limit $\sim 34\%$)



Source: Lips, Klaus (FU Berlin, HZB) Analytics for Photovoltaics 2016 Lecture Notes

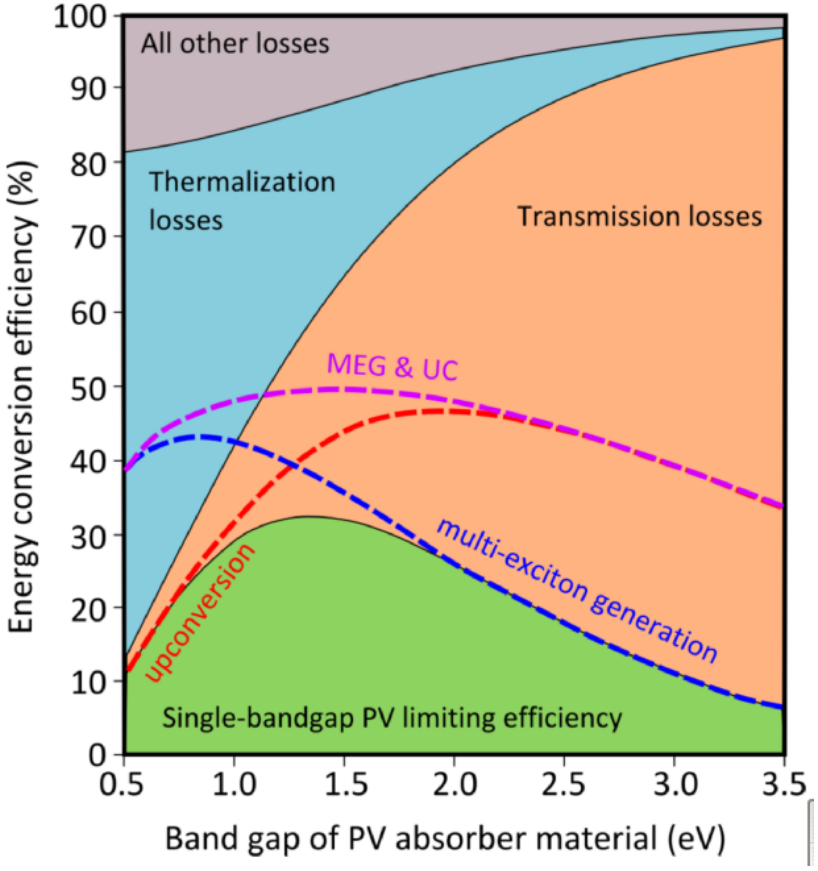


Wasted Energy
$\rightarrow$ Possible to collect?

Solutions:
- ~~Non-Linear Optics~~ ($\omega' = 2\omega$)
- Multi-layer design
- Up- & Down-Conversion

Singlet Fission & Triplet-Triplet Annihilation

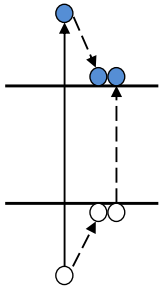
More Efficiency from Solar Spectrum with Up-&Down-Conversion



Source: Lips, Klaus (FU Berlin, HZB)
Analytics for Photovoltaics 2016 Lecture Notes

Up-Conversion (UC)
low E photons **added** to E_g
→ Triplet-Triplet Annihilation (TTA)

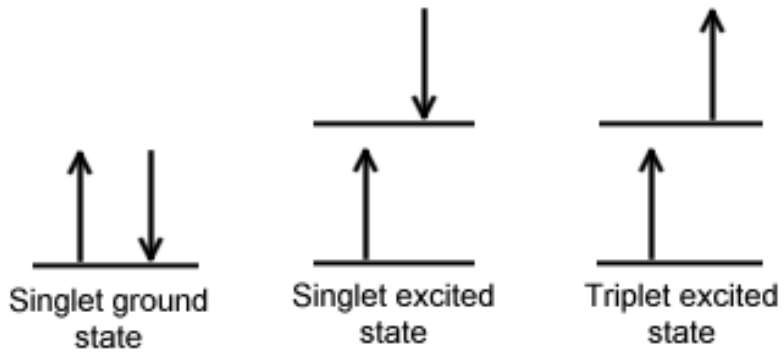
Down-Conversion (DC)
high E photons **split** to E_g
(Multi-Exciton Generation (MEG))
→ Quantum Dots (inorganic)



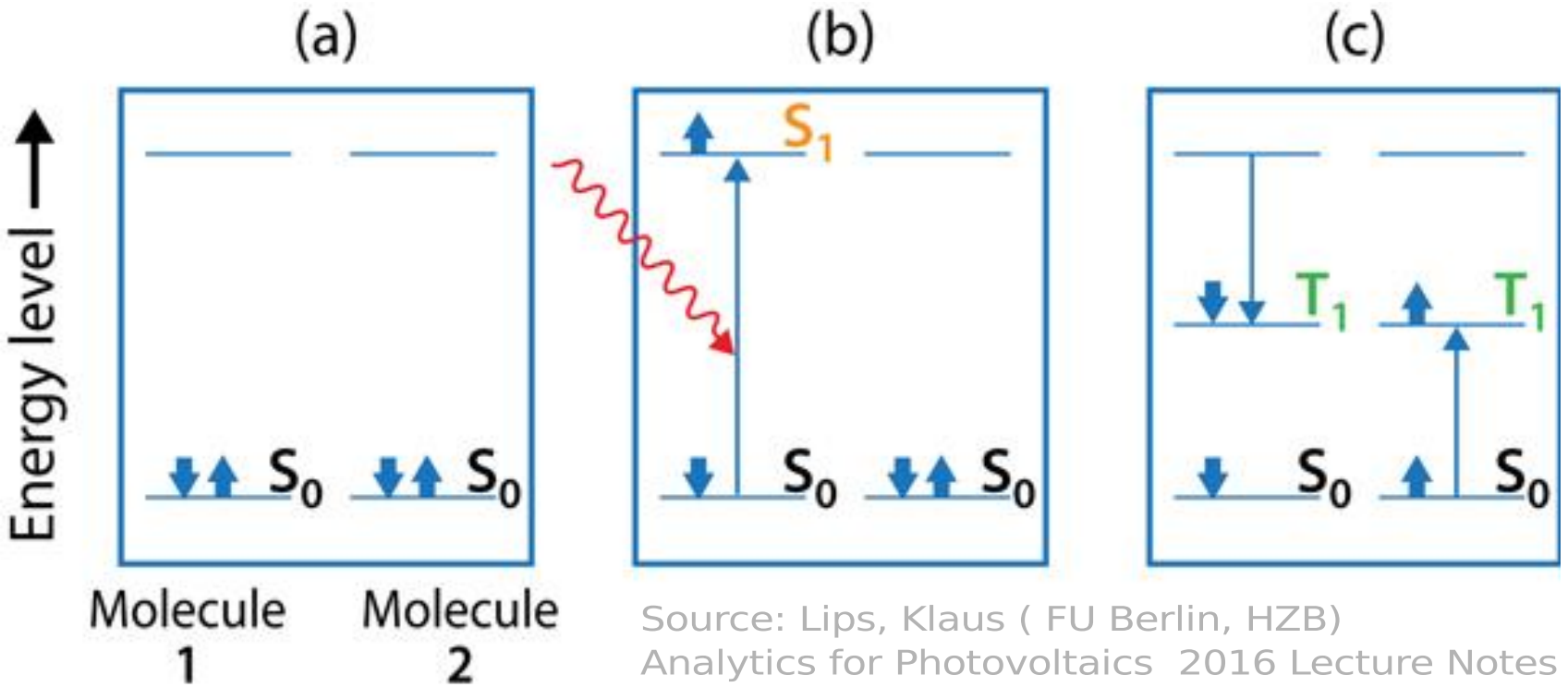
Downconversion/ Multi-Exciton Gen.

→**Singlet-Fission (SF)** (organic)

Singlet Fission: Basics

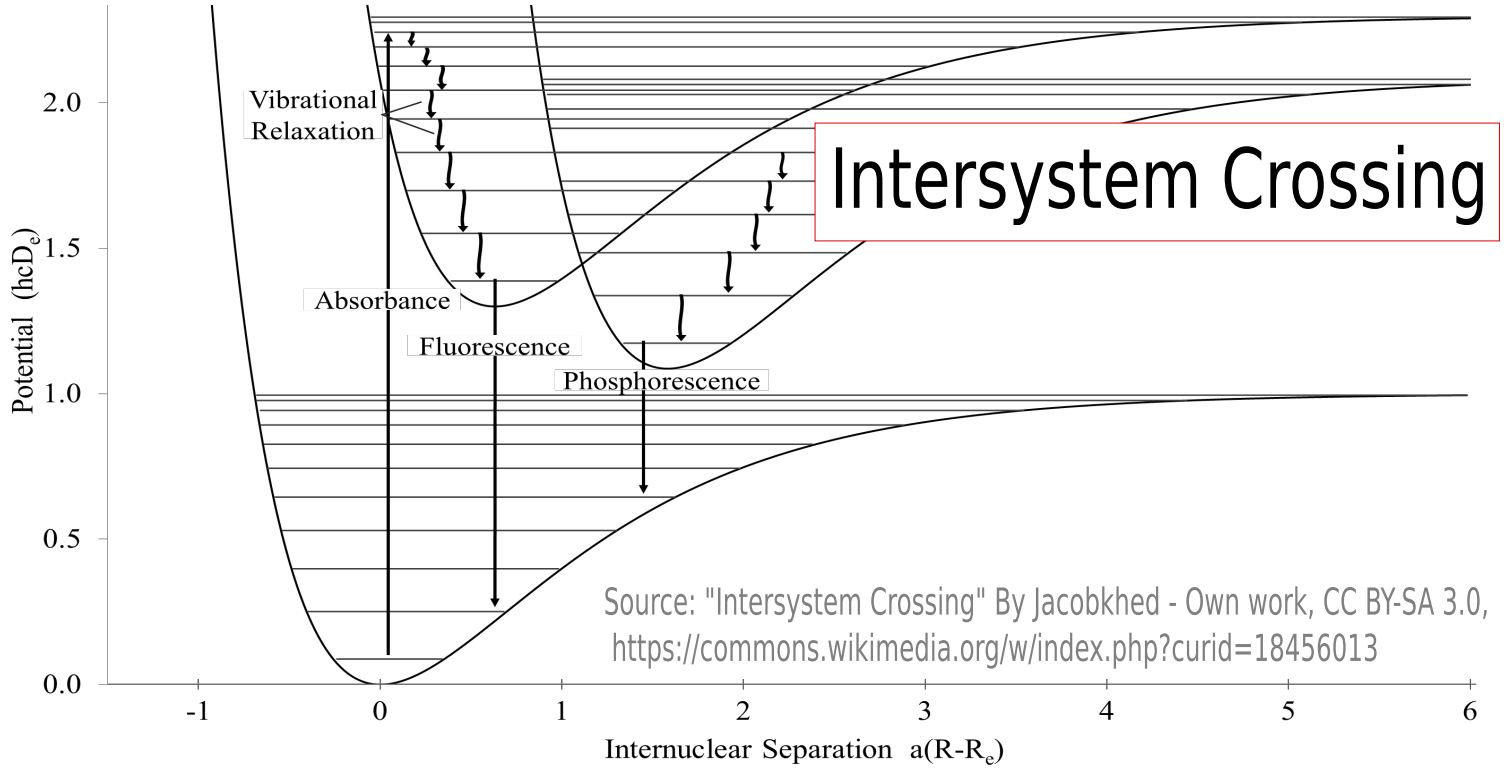


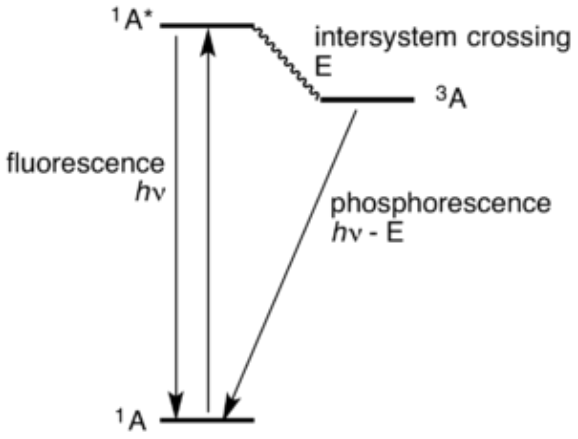
- T_1 lower than S_1 due to exchange interaction (we need $2E_{T1} \simeq E_{S1}$)
- **Spin Conservation** disallows competing thermal relaxation



Source: Lips, Klaus (FU Berlin, HZB)
Analytics for Photovoltaics 2016 Lecture Notes

Intersystem-Crossing & Spin-Orbit Coupling



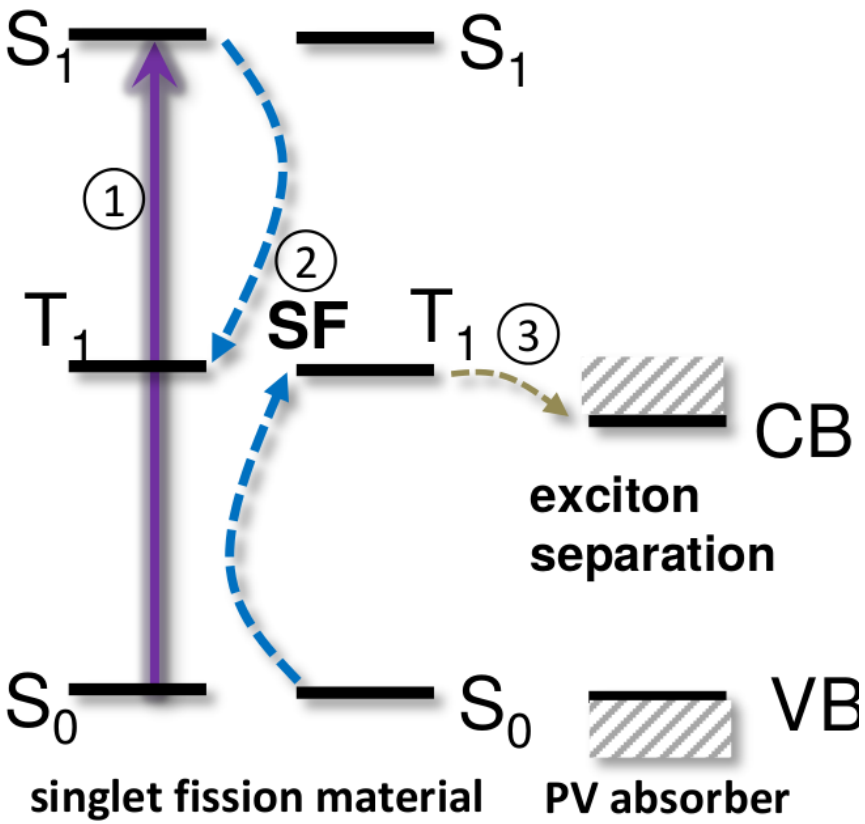


Non-Radiatively: Singlet to Triplet state
(reverse of the electron spin)

1- Overlap of vibrational levels
(little E loss/gain, $\sim kT$)

2- **Spin-Orbit Coupling**
(heavy-atom molecules and paramagnetic species)

Singlet Fission: Process I



Source: Lips, Klaus (FU Berlin, HZB)
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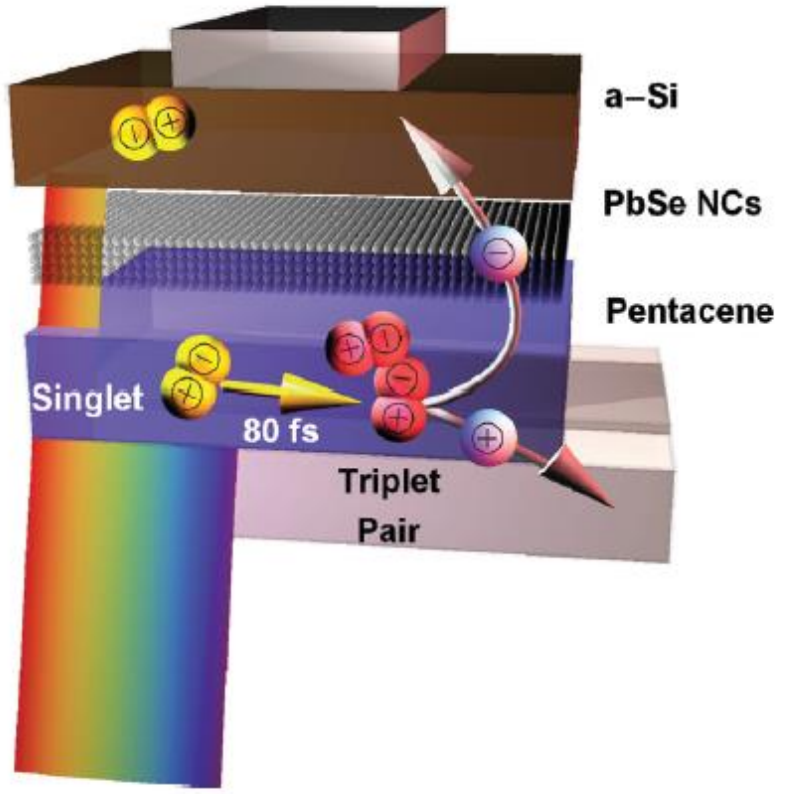
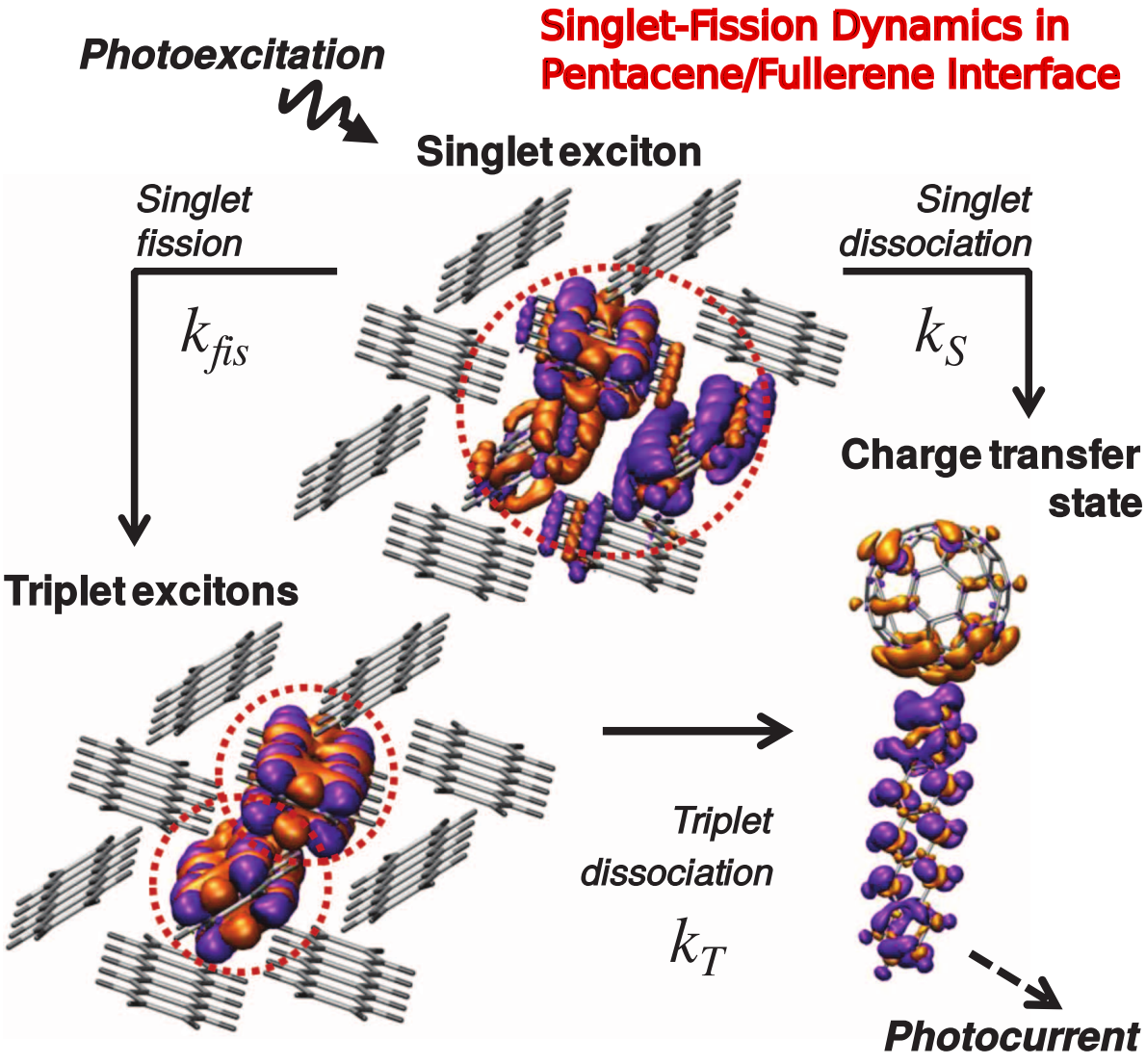


[3] Ehrler, Friend, Greenham et al., Appl. Phys. Lett. 101, 153507 (2012)

- S_1 controls optical properties
- T_1 controls electrical properties

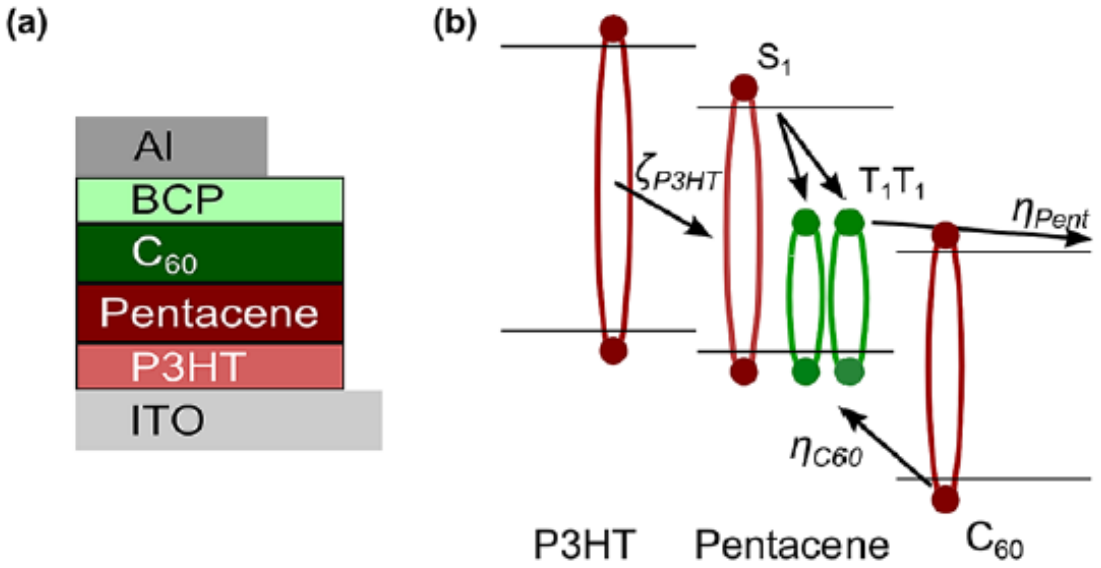
- Fission Probability
- Triplet-state lifetime
- Successful (2x) charge separation

Singlet Fission: Process II

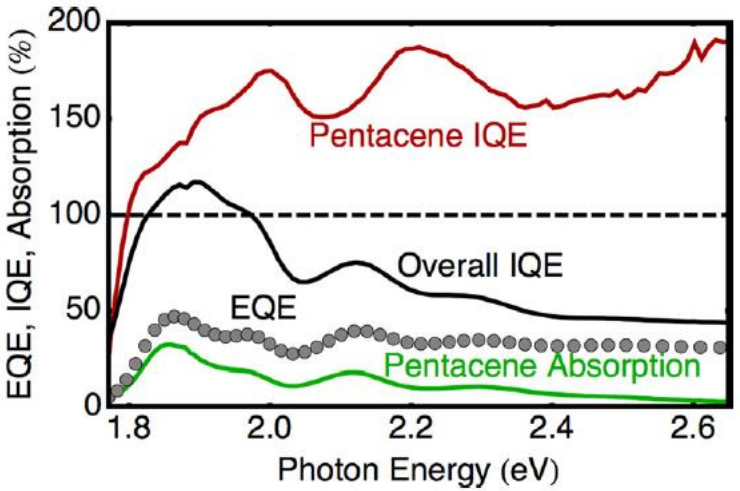


Source: Baldo, M.A. , Science 2013 "External Quantum Efficiency Above 100% in a Singlet-Exciton-Fission–Based Organic Photovoltaic Cell"

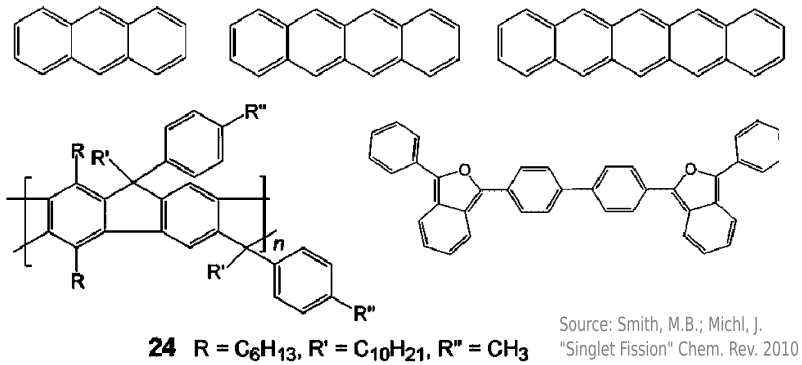
Singlet Fission: Material Example



Source: Tabachnyk et al., Appl. Phys. Lett. 103, 153302 (2013)



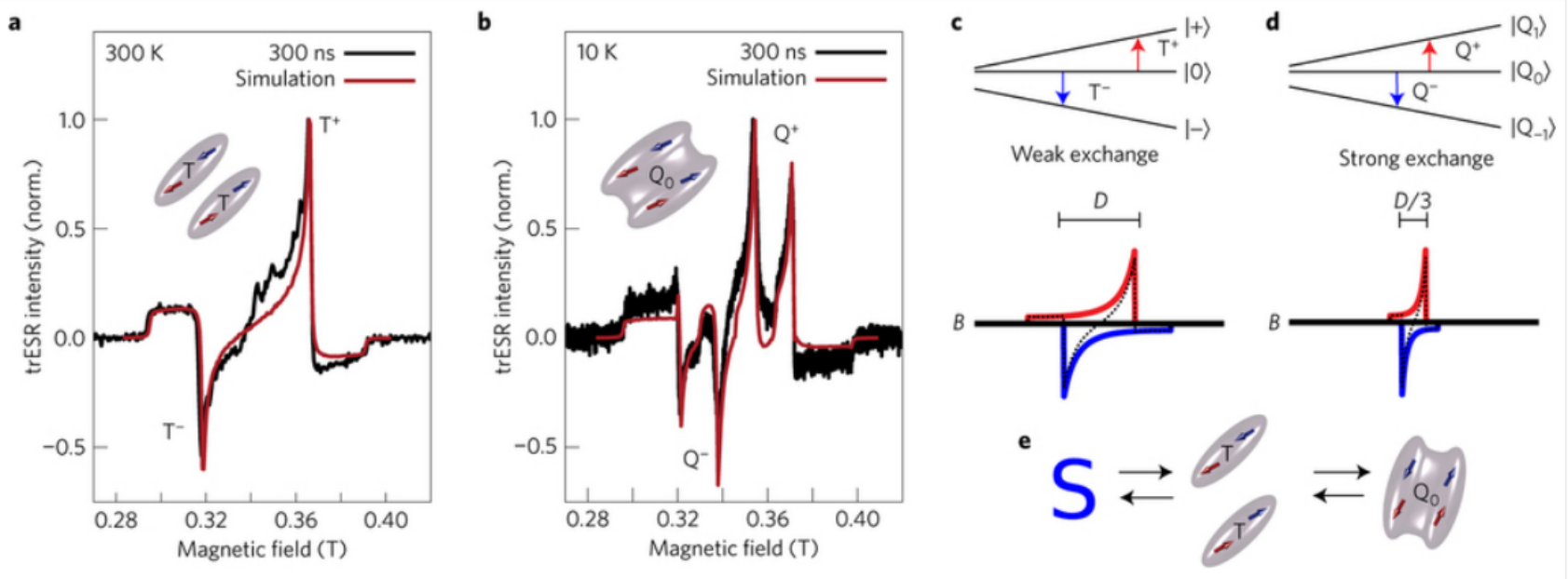
Source: Tabachnyk et al., Appl. Phys. Lett. 103, 153302 (2013)



Tetracene, Pentacene, Anthracene

Singlet Fission: Detection Techniques

- Photo-Luminescence (t-resolved)
- Magneto-Optical Techniques
  (change in Photo-Luminescence with $\vec{B}$ field through Zeeman interaction)
- Electron-Paramagnetic Resonance (EPR) and transient EPR
  (at FUB/HZB with TIPS-tetracene - soluable and change in E-states)



Source: Weiss, L. R., Bayliss, S. L., Kraffert, F., Thorley, K. J., Anthony, J. E., Bittl, R., Friend, R., et al. (2016). Strongly exchange-coupled triplet pairs in an organic semiconductor. Nature Physics

Singlet Fission: Trends & Challenges

Application

- tandem PV - SF(b)/M2(t): $47,7\%$ (Highest efficiency!)

Challenges:

- Cost & Long-term stability in sunlight
- Matching E-levels for fast (but low potential-loss) charge separation/transfer;
- Preventing premature charge injection from first S_1 while assuring efficient charge injection from T_1
- Max SF rate, min TTA rate; max absorption at all $E > E_g$
- Neighbouring molecules coupled in pair or higher agregates; **strong** coupling for fast SF
- Independent behaviour of both T_1; **weak** coupling for efficient charge separation

Aknowledgements

- Thanks to Klaus Lips and Rowan McQueen for the complete and well organized course "Analytics for Photovoltaics" (WS 2016) wherefrom I could have a lot of backup information and material
- Thanks to the EPR department of HZB - Alexander Schnegg, Shane Bonke - where I was allowed to do an Internship on the technique's field and contact more with the Solar Cells and Solar Fuels topics