Journal Club July 4th, 2013

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External Quantum Efficiency Above 100% in a Singlet-Exciton-Fission-Based Organic Photovoltaic Cell

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Science **2013**, *340*, 334.

1. Introduction

1.1 Approaches to overcome the Shockley-Queisser limit

<The Shockley-Queisser limit (SQ limit)>

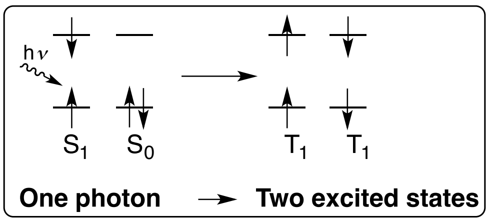
• Maximum PCE for a single p-n junction solar cell is ~ 31%.

<To overcome SQ limit>

• Tandem structure, light concentration, multi exiton generation (singlet fission), etc.

1.2 Singlet fission

<Mechanism>



→ Photocurrent can double!

→ Key to overcome the SQ limit.

• Detail calculation results: Transition via a dark state (D) (**Figure 1**).[1]

• Optical absorption does not generate dark state (dipole forbidden).

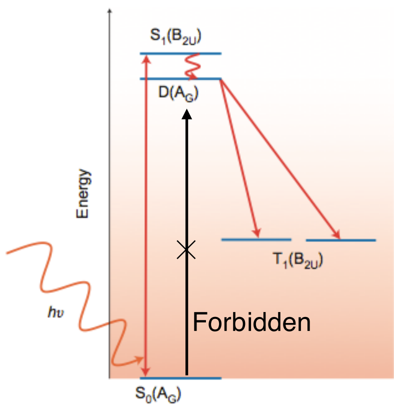


Figure 1. Mechanism of singlet fission.[1] S_1 or D could exist within either a monomer or a dimer, whereas T_1 states are necessarily localized on individual monomers.

<Materials>

• Acenes, rubrene, isobenzofuran, etc. (**Figure 2a**)

• Requirements:

(1) $E(S_1) > 2 \times E(T_1)$ (The case without thermal activation)

(2) Transition from S_1 to D (**Figure 2b**).[1]

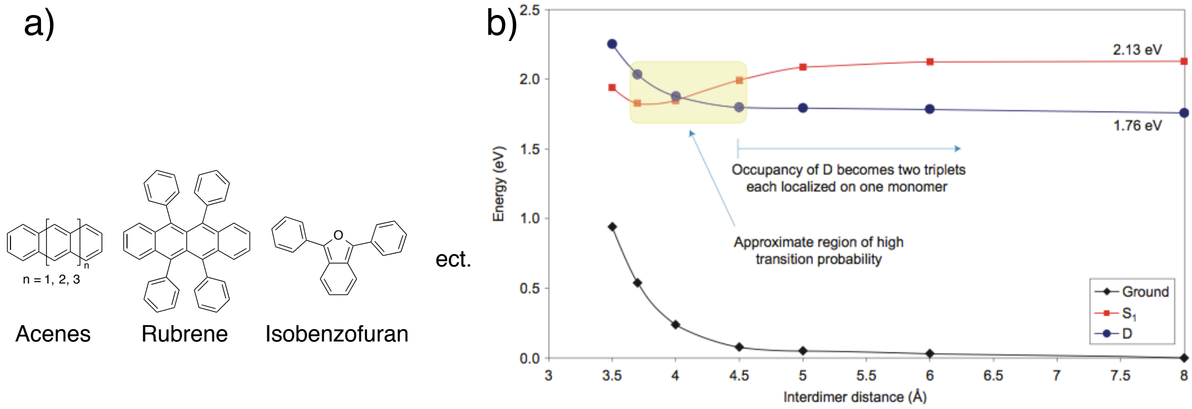


Figure 2. (a) Chemical structures of singlet fission materials. (b) Energies of excited states of a parallel pentacene dimer as a function of separation distance.[1] The mechanism for singlet fission can be described in terms of a state crossing from S_1 to D.

1.3 Singlet fission in organic electronics

• Photodetectors using singlet fission of pentacene were reported in 2009 by the authors.[2]

• Carrier generation between pentacene (T_1)/C_{60} has been observed without external voltage.[3]

• Singlet fission in organic photovoltaics was reported by the authors.[4]

• External quantum efficiency (EQE) > 100% in organic solar cells has not been reported.

1.4 This work

< Singlet fission in organic photovoltaics >

• EQE > 100% in organic solar cells.

• Break the conventional barrier of one electron per photon.

<Difficulties>

• Deactivation of triplet exitons

(1) Decrease the film thickness of pentacene.

(2) P3HT layer as an exciton blocking layer (**Figure 3a**).

• Reflection by glass substrate

(1) Antireflection by coating MgF_2.

(2) Light trapping (**Figure 3b**).

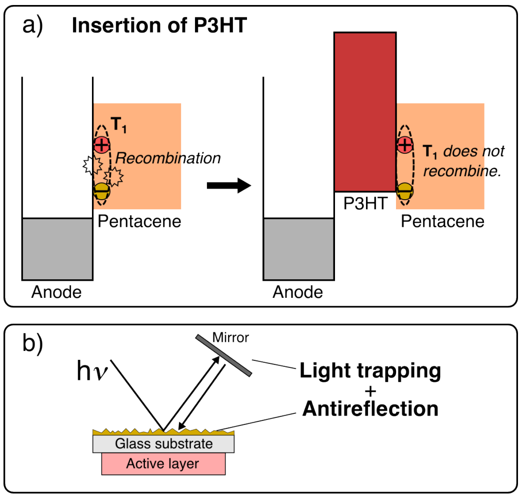


Figure 3. Schematic images of (a) exciton blocking, and (b) light trapping and antireflection methods.

2. Results and Discussion

2.1 Photovoltaic characterisitcs

<Device configuration> (**Figure 4**)

- Thin pentacene film (15 nm) to minimize triplet exciton loss.
- P3HT layer acts as triplet exciton blocking layer as well as hole extracting layer.
- MgF_2 antireflection coatings on the glass substrate to maximize light absorption.

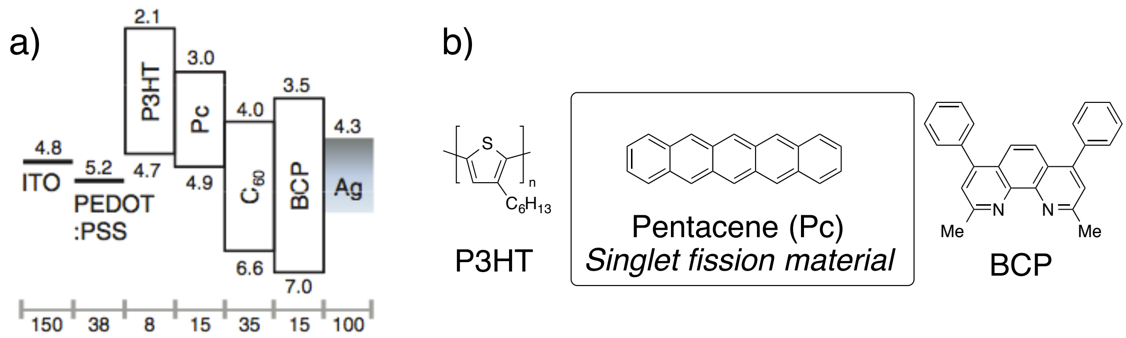


Figure 4. (a) Device architecture with the thickness (nm) of each layer, and (b) chemical structures of materials.

<External quantum efficiency (EQE) spectra and current-voltage characteristics>

$$\mathrm{EQE} = \frac{\text{Number of electrons}}{\text{Number of irradiated photons}}$$

→ EQE < 100% for conventional device, but EQE can exceed 100% for singlet fission device.

→ Reflection of photons by glass decreases EQE.

- Although the EQE was (82±1)% at vertical incidence of 670 nm light, EQE increased to (109±1)% at 10° incident angle with an optical trap mirror.
- The open circuit voltage is 0.36 V, which is limited by the $E(T_1)$ of pentacene (0.86 eV).

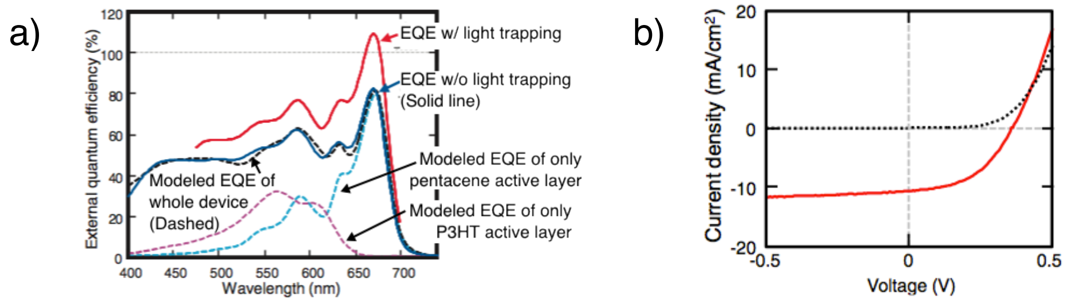
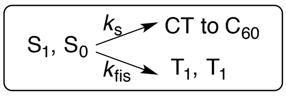


Figure 5. (a) EQE spectra of devices w/ and w/o optical trapping (solid), and simulated EQE spectra by optical fits from optical modeling (dashed). (b) Current-voltage curves under dark (dashed) and illumination of AM1.5G 100 mW/cm^2 solar simulated light (solid). The power conversion efficiency is (1.8±0.1)%.

2.2 Dependence of photocurrent and T_1 yield

<Photocurrent change (δ)> (**Figure 6A**)



($k_{fis}(B) = \chi(B)\, k_{fis}^0$)

• k depend on magnetic fields[2] and thickness[3].

• $\chi(B\!=\!0.4) = 0.85$ was obtained by the authors[2] using current dependence on magnetic field.

→ How about when using thickness dependence?

$$\delta = \frac{I(B) - I(0)}{I(0)} = \frac{k_S k_{fis}^0(\chi - 1)}{(2k_{fis}^0 + k_S)(\chi k_{fis}^0 + k_S)} \quad (1)$$

where $I(B)$ is the photocurrent as a function of magnetic field (B).

→ Thickness dependence was observed, and δ_{max} = – (2.7±0.1)% in 2-nm-thick layer (**Figure 6A**).

• From eq. 2, χ(B=0.4) = 0.85, identical to the value obtained in the ref. 2.

$$\chi = \frac{2\delta_{max}^{\ 2} + \delta_{max} + 1 + 2\sqrt{2}\delta_{max}\sqrt{\delta_{max} + 1}}{(\delta_{max} - 1)^2} \quad (2)$$

<T_1 yield (η_{fis})> (**Figure 6B**)

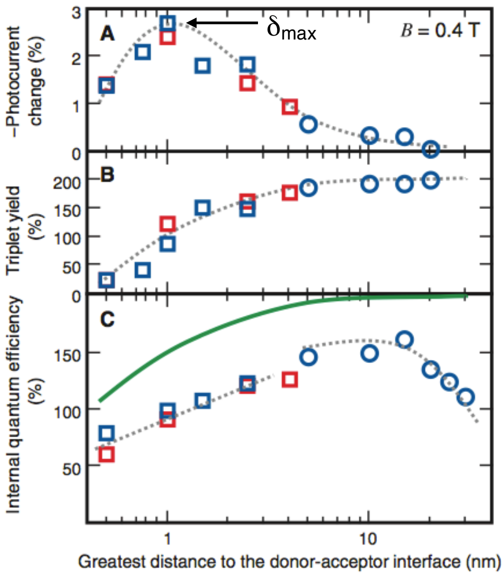


Figure 6. (A) The photocurrent change as a function of pentacene layer thickness. (B) The triplet yield as obtained from eq. 3. (C) A comparison of the magnetic field effect (solid line) with the internal quantum efficiency as determined from EQE measurements and the calculated optical absorption. Dashed lines are guides to the eye. Square symbols are measured in photodetector structures (stacked thin layers of donor and acceptor). Measurements in the solar cell structures (bilayer system of donor and acceptor) are circles. 3,4,9,10-Perylene tetracarboxylic bisbenzimidazole was used as acceptor to show generality (red squares).

$$\eta_{fis} = \frac{2}{1 + k_S/k_{fis}^0} = \frac{(1-\delta)\chi - 1 \pm \sqrt{(\delta(\chi+2) - \chi + 1)^2 - 8\delta^2\chi}}{(\delta+1)(\chi-1)} \quad (3)$$

• In thick films around 10 nm, η_{fis} ~ 200%, which corresponds to the simulated high IQE (**Figure 6B**, **6C**). Thickness > 15 nm, low IQE owing to triplet exciton diffusion limitations.

• Films with thickness < 5 nm, η_{fis} because of the competition between k_{fis} and k_S.

→ Thickness around 10-15 nm is the optimum to obtain high η_{fis} as well as high IQE.

3. Conclusion

• EQE above 100% was achieved using pentacene in organic photovoltaics.

• P3HT plays a key roll to block pentacene triplet excitons and to extrac holes.

• The optimum domain size of pentacene is 10-15 nm to obtain high η_{fis} as well as high IQE.

References: 1. Zimmerman, P. M.; Zhang, Z.; Musgrave, C. B. *Nat. Chem*. **2010**, *2*, 648. 2. Lee, J.; Jadhav, P.; Baldo, M. A. *Appl. Phys. Lett*. **2009**, *95*, 033301. 3. Chan, W. L.; Ligges, M.; Jailaubekov, A.; Kaake, L.; Miaja-Avila, L.; Zhu, X.-Y. *Science* **2011**, *334*, 1541. 4. Jadhav, P. J.; Mohanty, A.; Sussman, J.; Lee, J.; Baldo, M. A. *Nano Lett*. **2011**, *11*, 1495.