Polaron pair mediated triplet generation in polymer/fullerene blends

Stoichko D. Dimitrov*, Scot Wheeler, Dorota Niedzialek, Bob C. Schroeder, Hendrik Utzat, Jarvist M. Frost, Jizhong Yao, Alexander Gillett, Pabitra S. Tuladhar, Iain McCulloch, Jenny Nelson and James R. Durrant*

Nature Communications (DOI:10.1038/ncomms7501)

1.Introduction

1.1 Organic solar cells (OSC) (Figure 1)

1. Photoexcitation
2. Exciton diffusion
3. Electron transportation
4. Charge separation
5. Charge transportation

⇒ **Efficient charge separation leads high performance OSC.**

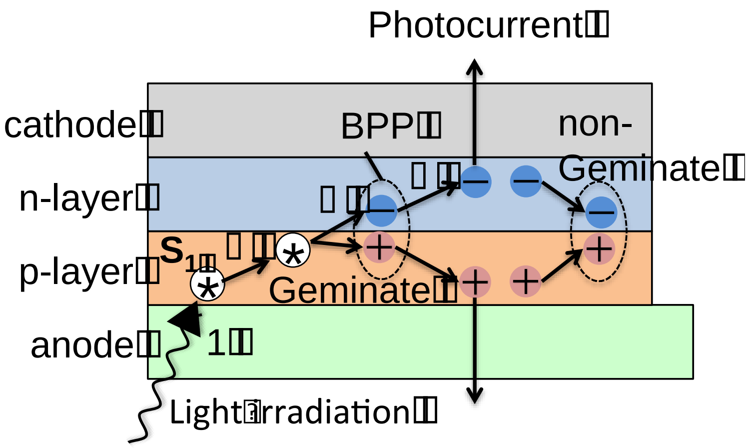

Figure 1. Organic solar cells

1.2 Triplet generation in OSC

- **Triplet and CS generation pathway (Figure 2)**
  - Bound polaron pair (BPP) is that coulombically bounded electron-hole pair.
  - BPP are converted into charge separate state (CS) and triplet exciton.

⇒ **Triplet generation causes current loss.**

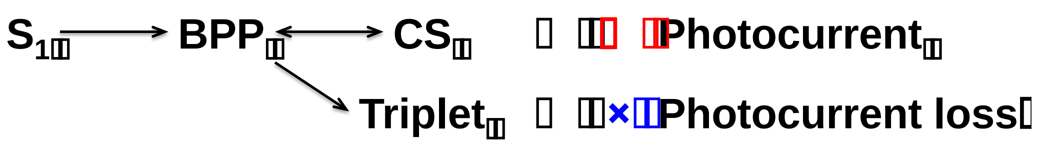

Figure 2. CS state generate dynamics in OSC

- **Two BPP generation pathways; Geminate and non-Geminate (Figure 1)**
  - Geminate recombination pathway

  BPP made from exciton transform into exciton.
  - non-Geminate recombination pathway

  BPP made from free electron and hole transtorm into exciton.

  non-Geminate triplet generation is reported.[1]

  Geminate one is forecasted.[2]

⇒ However, **triplet generation via geminate recombination is NOT reported.**

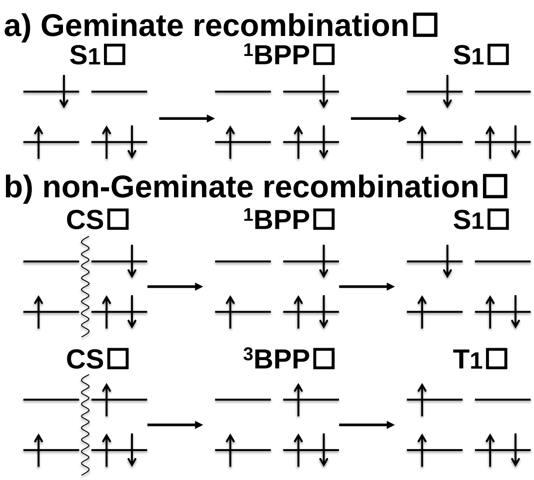

Figure 3. Recombination types

1.3 This work

- The authors investigated **Geminate triplet generation**.
- They indicated guide to control Geminate triplet generation.

1.4 Strategy

- Two silaindacenodithiophene (SiIDT) copolymer / [6,6]-phenyl C71 butyric acid methyl ester (PC70BM) blend films, which show contrasting excited state energetics and solar cell device performance.
- Both blend had similar S1-T1 gap but **different S1-CS gap (Figure 4)**

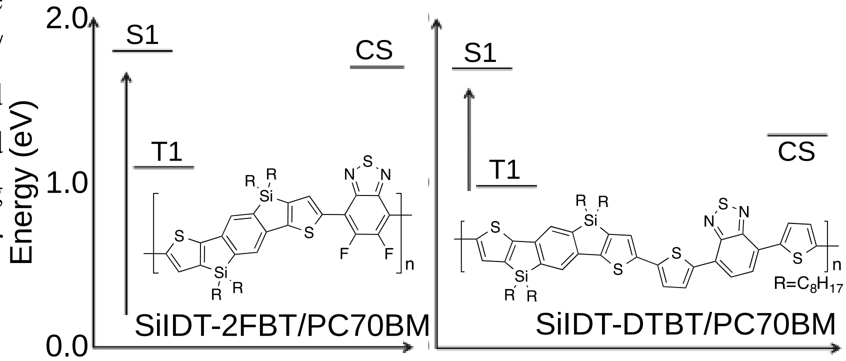

Figure 4. Structure and energy level

2.Results and discussion

2.1 Device performance of polymer fullerene blends

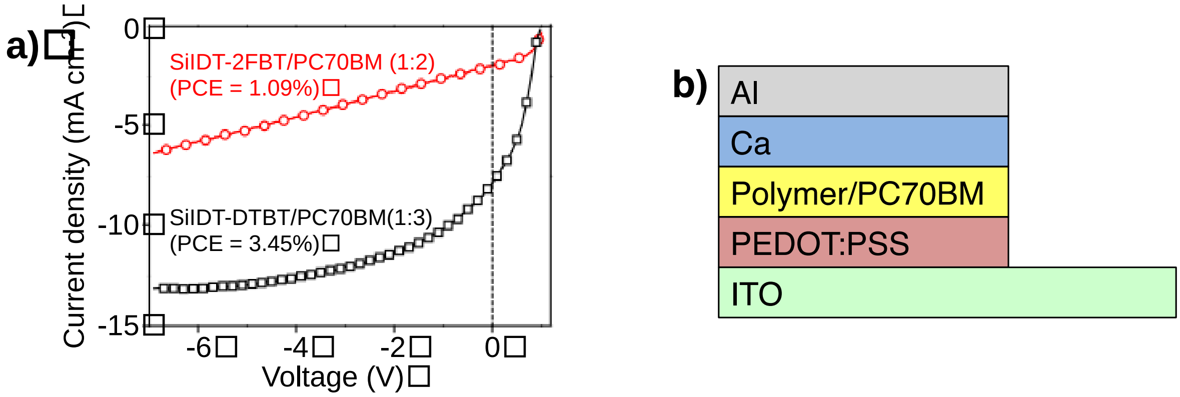

Figure 5. device performance (a) and structure (b)

- DTBT device has better performance than 2FBT one. (Figure 5)

2.2 Optical measurement and state dynamics of polymer/fullerene blend films

- Photoluminescence properties of SiDT-2FBTand SiDT-2FBT/PC70BM
  Both blend have very high quenching yield >96%. (Figure 6)

⇒ Triplet did not generate via inter system crossing.

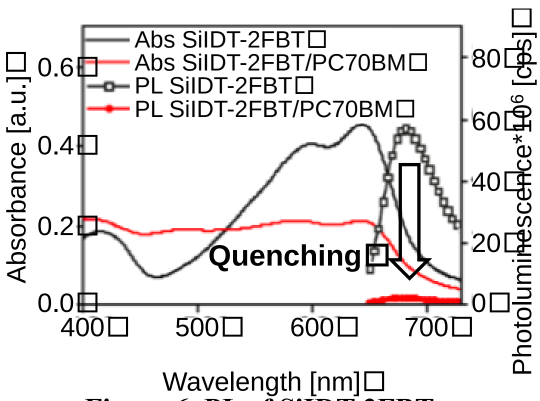

Figure 6. PL of SiIDT-2FBT

- Triplet generation in SiIDT-2FBT/PC70BM blend film
  - Transient absorption (TA) of SiIDT-2FBT/PC70BM film at N_2 (Figure 7a)

  The absorption band at 1,100 nm dominates the spectra in the first microsecond, while the blue-shift 1,000 nm absorption band is dominant at later delay times.

  The long-lived signal at 1,000 nm absorption band is assigned polymer polaron state.[3,4]
  - Transient kinetics of SiDT-2FBT/PC70BM film at N_2 and O_2 (Figure 7b)

  Only the fast decay phase is quenched by molecular oxygen, thus 1,100 nm absorption band is assigned to triplet.

⇒ **Triplet is generated in only SiIDT-2FBT/PC70BM** (No triplet in SiIDT-DTBT/PC70BM)

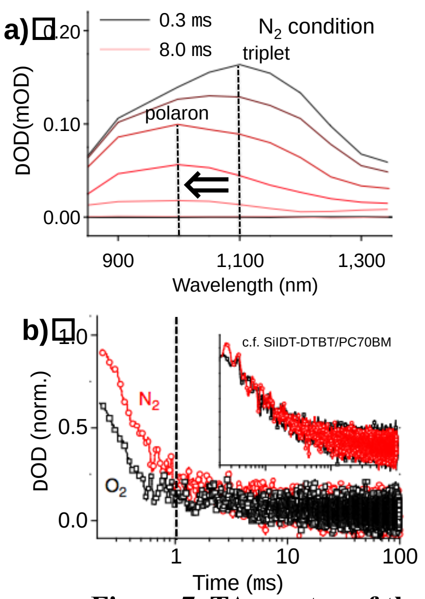

Figure 7. TA spectra of the SiIDT-2FBT/PC70BM.

- **Triplet generation monitored SiIDT-2FBT and SiIDT-2FBT/PC70BM blend film**
  - **Femtosecond TA spectra of SiIDT-2FBT film (Figure 8a)**

  1,300 nm absorption band is assigned to polymer singlet, and its lifetime is ~160 ps.
  - **Femtosecond TA spectra of SiIDT-2FBT/PC70BM film(Figure 8b)**

  Polarons based state intermediate triplet generation, thus they assigned to BPP.

⇒ **S1+BPP (at 0.3 ps) → BPP (at 100 ps) → T1+polarons (at 6 ns)**

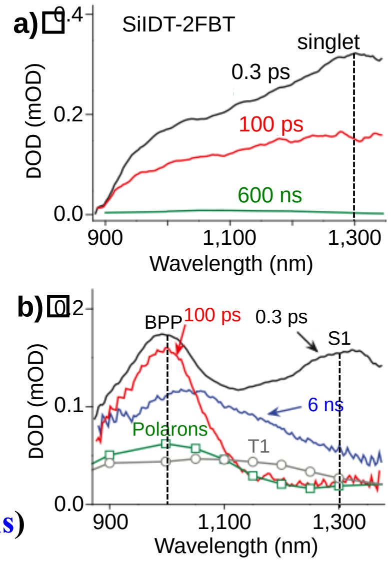

Figure 8. Femtosecond TA spectroscopy of SiIDT-2FBT

- Excitation density and triplet exciton generations (Figure 9)

  Non-Geminated triplet generation increase triplet amount with excitation density.

  Vgem = [Ex density],

  Vnon-gem = [electron]*[hole]=$[\text{Ex density}]^2$

  Triplet exciton amount is independent of excitation density <20μJ cm^{-2}.

⇒ **Triplet generation is dominated geminate pathway.**

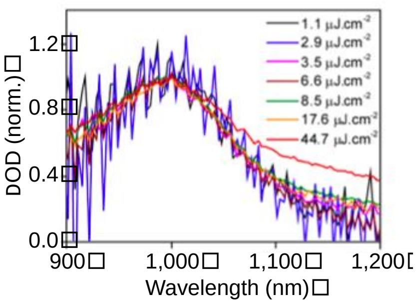

Figure 9. Excitation density dependent TA of 2FBT

2.3 Model for CS and T_1 generation

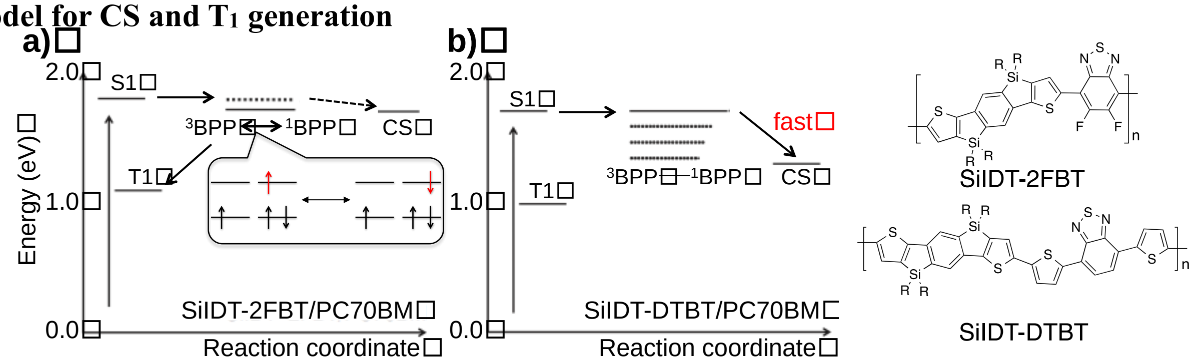

Figure 10. State dyagrams models[5,6]

- Model of triplet-generated film (SiIDT-2FBT/PC70BM) (Figure 10a)

Triplet-BPP (^{3}BPP) is easily generated, enabled by hyperfine interaction.
Geminate triplet generation is intermediated by ^{3}BPP.

- Model of no triplet-generated film (SiIDT-DTBT/PC70BM) (Figure 10b)

Convert from BPP to CS is accelerated by large energy gap between CS and BPP.

2.4 Electron field dependent generation of CS

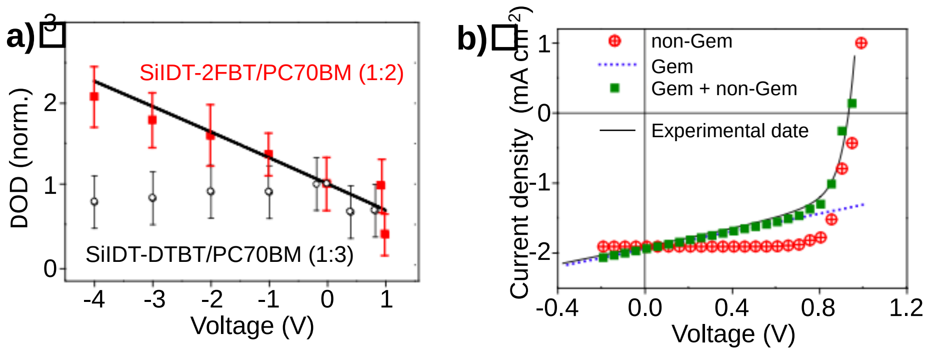

Figure 11. Voltage applied properties and reconstruction

- **Field-dependent polaron yield (Figure 11a)**

SiIDT-2FBT/PC70BM is dependent applied field, but SiIDT-DTBT/PC70BM.

⇒ BPP is generated.

- Causes of device performance loss (Figure 11b)

Reconstruction *J-V* curve (green square) assuming Geminate triplet and non-Gem is fit with experimental date (black curve)

3.Conclusion

- BPP state convert singlet-triplet easily and ^{3}BPP intermediate triplet generation.
- We can control geminate triplet generation by energy gap between S_1 and CS

4.References

1.A. Rao *et al. Nature*, **2013**, *500*, 435.
2.H. Ohkita *et al. J. Am. Chem. Soc.*, **2008**, *130*, 3030.
3. J. Nelson *Phys. Rev. B*, **2003**, *67*, 155209.
4. C. G. Shuttle *et al. Phys. Rev. B*, **2008**, *78*, 113201.
5. A. Köhler and D. Beljonnne *Adv. Funct. Mater.* **2004**, *14*, 11.
6. A. Monkman *et al. Phys. Rev. let.* **2001**, *86*, 1358.