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Structural Correlations in the Generation of Polaron Pairs in Low-bandgap Polymers for Photovoltaics

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1. Introduction

1.1 Mechanism of photocurrent generation in organic photovoltaic cells (OPVs)

(1) Exciton generation and exciton diffusion

Light absorption generates excited states. The excitons diffuse to the interface between donor and acceptor (DA).

(2) Charge transfer (CT)

The exciton gives an electron to the acceptor molecule. The CT state is bound by the Coulomb interaction.

(3) Charge dissociation

The CT state dissociates into free charges (carriers).

(4) Charge transport

Hole and electron are transported toward electrodes.

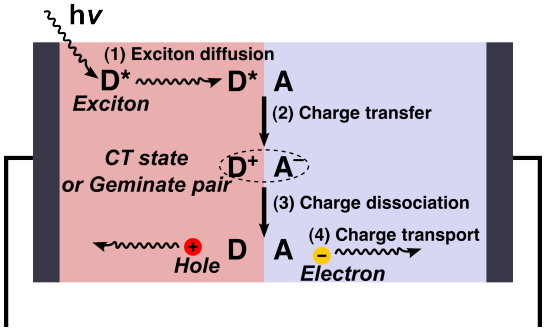
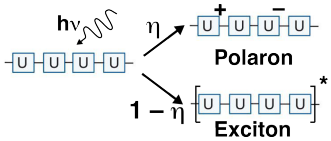


Figure 1. The schematic illustration of the photocurrent generation mechanism.

1.2 Excited states of polymers for OPVs

<Exciton and polaron>

• Excitation by light produces not only neutral excitons, but also polaron pairs (anion and cation pairs) in the pristine donor polymers.



Scheme 1. Polaron and exciton generation.

• Investigations on excited state suggest that the yield of polaron pairs (η) is 1~30%. [1,2]

• It remains a crucial question to correlate the excited states with polymer structures.

<Benefits for OPVs>

• The energy offset of the lowest unoccupied molecular orbital (LUMO) levels of DA is considered to afford the dissociation of the stongly bound exciton (0.5~1 eV), which results in the voltage loss in OPVs (**Figure 2**).

• Polaron pairs would be easy to separate since polaron pairs have weaker binding than excitons (The voltage loss should be small).

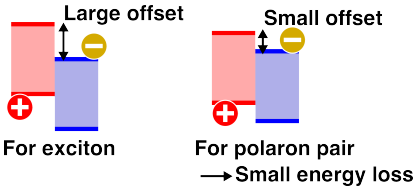


Figure 2. The illustration of the energy level alignments of large offset (left) case and small offset case (right).

1.3 Polymer materials for OPVs

• Representative examples of polymer materials (**Figure 3**)

• Donor-acceptor co-polymers have been recently utilized to obtain the absorption in the long wavelength region.

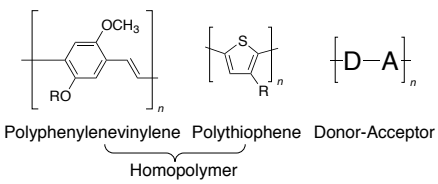


Figure 3. The chemical structures of the representative polymer materials.

1.4 This work

• DA structure is advantageous for the polaron pair generation?

• The authors focused on the polaron pair yield (η), dynamics and relation of the chemical structures of DA type polymers.

• They employ transient absorption (TA) spectroscopy.

• A series of donor-acceptor co-polymers were examined.

• The distance of DA units and the acceptor strength

➔ Strong influence on the generation yield and the recombination dynamics of polaron pairs

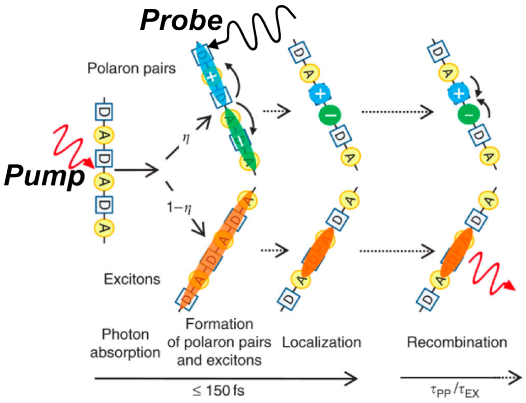


Figure 4. The photoinduced generation of polaron pairs (top) and excitons (bottom).

2. Results and Discussion

2.1 Ground- and excited-state absorption

• The ground-state absorption spectra of a series of co-polymers (**Figure 5 a**-**d**) are measured and the pump light wavelengths were determined (**Figure 5 e**-**h**).

• To determine the polaron absorption wavelengths, the co-polymers oxidized with $SbCl_5$ and the absorption spectra of the solution of hole polarons (polymer cations) were measured.

➔ The difference spectra of the neutral polymers and the hole polarons (oxidized polymers) are shown in **Figure 5 i**-**l** (solid lines).

• To determine the exciton absorption, the TA spectra of polymers were measured (**Figure 5 i**-**l**, square dots).

➔ Exiton absorption and polaron absorption were observed.

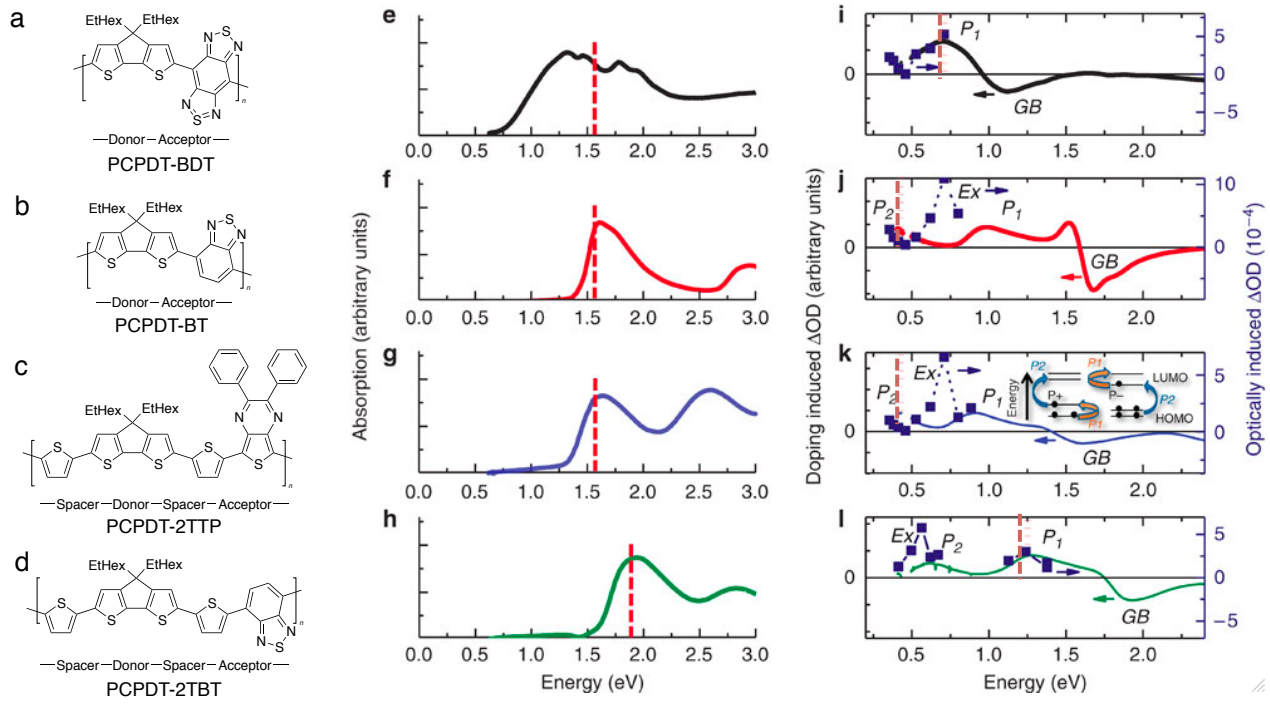


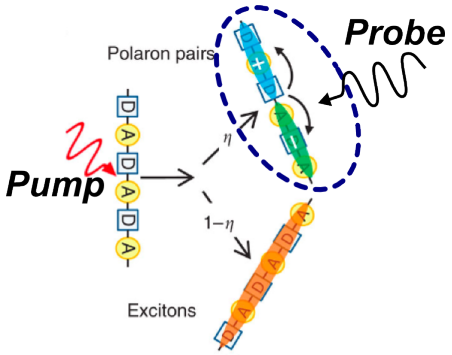
Figure 5. Excitons and polaron pairs spectra of co-polymers. Chemical structures of the co-polymers: (**a**) PCPDT-BDT, (**b**) PCPDT-BT, (**c**) PCPDT-2TTP and (**d**) PCPDT-2TBT. Absorption spectra of: (**e**) PCPDT-BDT, (**f**) PCPDT-BT, (**g**) PCPDT-2TTP and (**h**) PCPDT-2TBT. The vertical dashed lines indicate the pump photon energies for transient absorption (TA) experiments. (**i**) PCPDT-BDT, (**j**) PCPDT-BT (**k**) PCPDT-2TTP, (**l**) PCPDT-2TBT doping-induced ΔOD spectra as solid lines obtained by $SbCl_5$ to the respective polymer solutions. *GB* indicates ground-state bleaching, P_1 first polaron band, *Ex* exciton absorption band P_2 second polaron band. The squares show the transient absorption spectra recorded at zero time delay between the pump and probe beam. The vertical dashed lines indicate the choice of probe photon energies for determining the polaron pair yields in the experiments of **Figure 6**. The inset in (**k**) sketches the P_1 and P_2 polaron transitions.

2.2 Polaron pair yield

• The authors quantitatively probed the polaron pair formation.

• The probed light energies are shown as vertical dashed lines in **Figure 5 i-l**.

• **Figure 6** shows the rise and decay of the polaron pair density normalized by the number of photoexcitations, that is yield (η).



Scheme 2. Detection of polaron pairs.

<Acceptor ability>

• Co-polymers with acceptors having large electron affinities such as PCPDT-BDT and PCPDT-2TTP (**a**, **c**) exhibit the largest probability of polaron pair generation.

➔ The large electron affinity enhances the polaron pair generation.

<Spacer effect>

• PCPDT-2TTP and -2TBT (**c**, **d**) exhibit a longer initial recombination time of 5.9 and 8.8 ps than polymers w/o spacers.

➔ Spacers delay the recombination process.

➔ The initial decay is likely due to the on-chain recombination.

<DA structure effect>

• To compare DA type polymers with a homopolymer, P3HT was utilized.

• P3HT shows the lowest polaron yield (η = 8±2%) among the all materials.

➔ DA moieties within polymer are promoting polaron generation.

➔ In homopolymers polaron formation is less probable and eventually driven by the energetic disorder between the polymer chains.

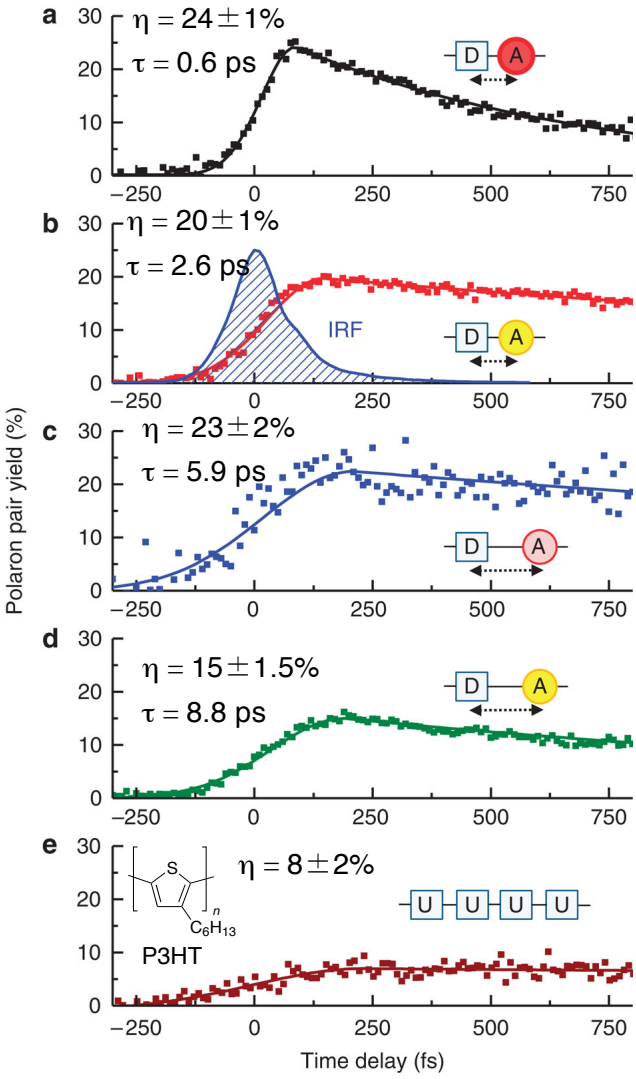
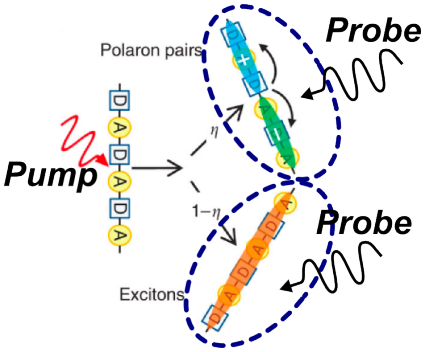


Figure 6. Polaron pair generation and recombination dynamics. Time-resolved polaron pair absorption after photoexcitation, polaron yield (η) and recombination time (τ) for the co-polymers: (**a**) PCPDT-BDT, (**b**) PCPDT-BT, (**c**) PCPDT-2TTP, (**d**) PCPDT-2TBT and the homopolymer: (**e**) P3HT. The inset in **b** shows the pump-probe instrument response function (IRF) for 1.55 eV pump and 0.41 eV probe. The inset in **e** shows the chemical structure of P3HT.

2.3 Spectraly resolved dynamics of excitons and polaron pairs

• The population dynamics of polarons and excitons were probed.

• The measurement was performed at different pump-probe delay times (**Figure 7**).



Scheme 3. Detection of polaron and exciton.

• The insets of (**b**) and (**c**) suggest that the *Ex* band has a faster decay with respect to the P_2 bands.

• The faster decay of excitons with respect to polaron pairs has been already known in homopolymers.[1]

➔ The authors conclude that a faster decay for hot excitons than polaron pairs is a general behavior in π-conjugated polymers.

➔ It probably related to the lower electron-hole overlap in polaron pairs compared to excitons.

• *Ex* band does not show dynamics with time.

• Excitons do not evolve toward the polaron species.

➔ Within the time resolution of ~150 fs, excitons and polarons are formed independently at the zero pump-probe delay, and result in two populations with uncorrelated decay dynamics.

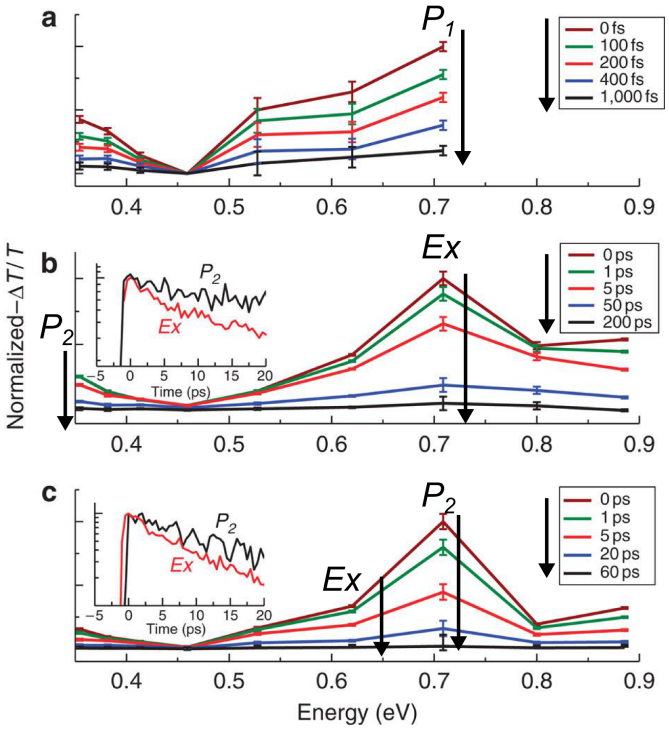


Figure 7. Exciton and polaron pair dynamics of: PCPDT-BDT (**a**), PCPDT-BT (**b**) and PCPDT-2TTP (**c**). The insets in (**b**) and (**c**) compare the normalized dynamics for excitons and polaron pairs on a tiem scale of 20 ps.

3. Conclusion

• The authors reported correlations on how the chemical structure of co-polymers in influencing the generation yield and the recombination dynamics of polaron pairs.

• The generation and the yield seems to depend on the electron affinity of the acceptor moiety, but also shows differences when the DA units are separated by the space units.

• Closely spaced DA systems suffer from a fast recombination occurring in a few picoseconds.

• The results provide better understanding of structre-property relationships in DA type co-polymers.

4. Reference

1. Sheng, C. X.; Tong, M.; Singh, S.; Vardeny, Z. *Phys. Rev. B* **2007**, *75*, 085206.

2. Piris, J.; Dykstra, T. E.; Bakulin, A. A.; Loosdrecht, P. H. M. V.; Knulst, W.; Trinh, M. T.; Schins, J. M.; Siebbeles, L. D. A. *J. Phys. Chem. C* **2009**, *113*, 14500.