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The Role of Driving Energy and Delocalized States for Charge Separation in Organic Semiconductors

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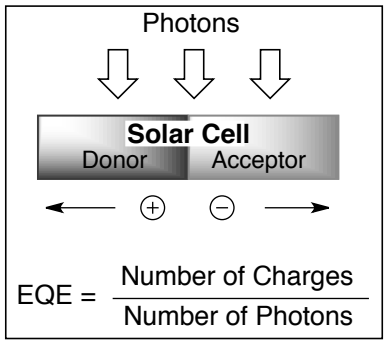
1. Introduction

1.1. The importance of charge separation in organic photovoltaics (OPVs)

- The number of electrons generated per the number of photons irradiated (EQE: external quantum efficiency) varies from low (<10%) to high (>70%) depending on the device.
- Among various reasons, the charge separation in the interface plays an important role in the difference of EQE.



1.2. Current understanding of the photon-to-charge conversion in OPVs

① Donor molecules are pumped up to singlet excited states by incident light.

② The energy of the singlet excited states (singlet excitons) diffuse to the interface of donor and acceptor.

③ The excitons undergo ultrafast (<100 fs) generation of charge transfer (CT) states.

④ **Charge separation occurs. The details are discussed later**.

⑤ Separated charges (SCs) diffuse to the electrode and are collected.

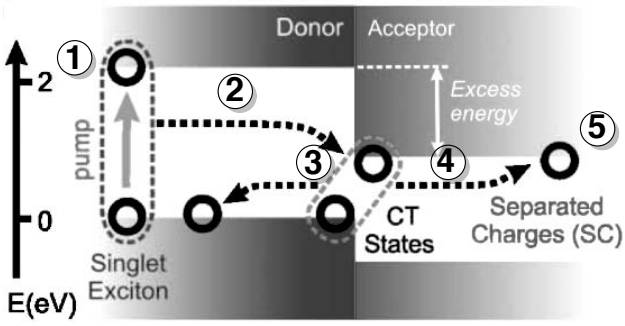


Figure 1. Photon-to-charge conversion in OPVs

- In order to generate SCs from CT states (③->④), CT states should overcome the Coulomb attractive force of ~200 meV.[1]
- However, there are several reports that the charge separation occurring quite efficientry (~100%).[2]
- The mechanism to overcome the force and achieve long-range charge separation remains unanswered.

2. Pump-push experiments for elucidation of the role of excess energy

2.1 Experimental procedure

① Above-gap pump pulse was illuminated to generate singlet excited states.

② The excited states produce "hot" CT (CT_n) states, where the delocalization of charge takes place (discussed in section 3.3).

③ The CT_n states are cooled down to CT_0 states, where the charge has lower energy and is more localized.

④ IR push pulse that selectively causes CT_0->CT_n transition is illuminated.

⑤ The number of SCs generated by IR push pulse is estimated by calculating the change of photocurrent with and without the push pulse (δPC/PC).

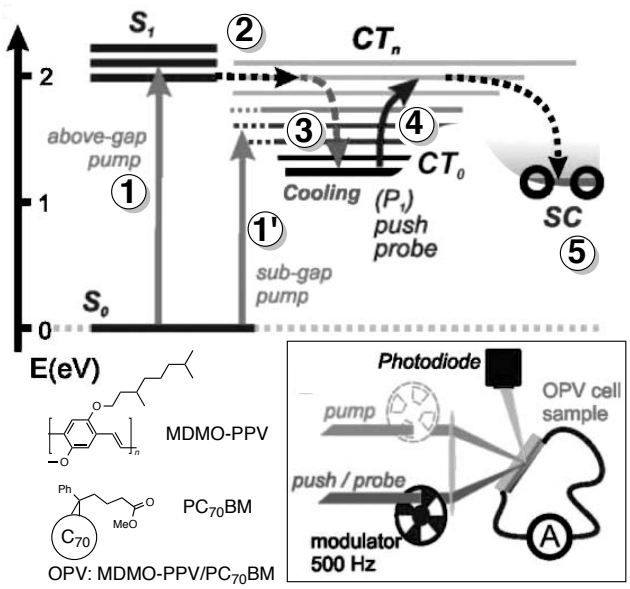


Figure 2. Schematic image of pump-push experiment.

2.2. Results and discussion

- Figure 3 shows the amount of photocurrent generated by the irradiation of CT_0 states by the IR push pulse, relative to the photocurrent generated without the IR push pulse.
- The decay time is the life time of CT_0 states.
- When below-gap pump pulse was illuminated (Figure 2, ①'), direct S_0 to CT_n transition occures. In this case, the CT_n states have ~0.5 eV lower energy than the CT_n states generated via above-gap pump experiment.

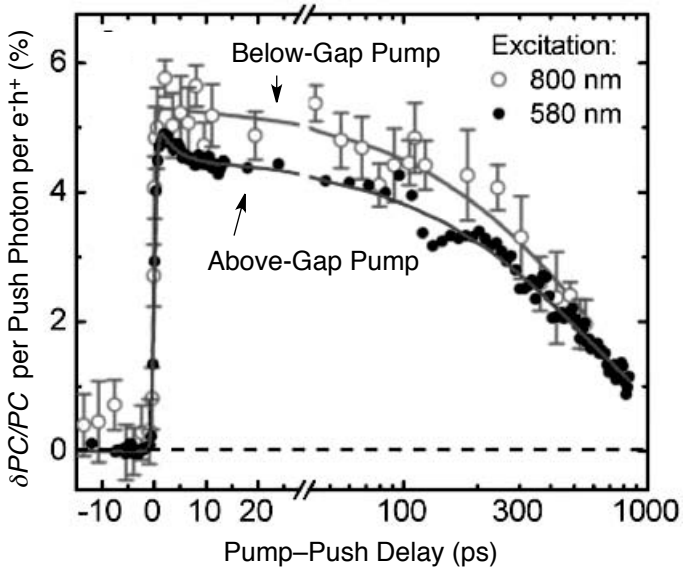


Figure 3. Relative photocurrent against pump-push delay.

- There was no difference between the transient of below-gap pump and above-gap pump. This indicates that large excess energy was not required for charge separation. *The role of "excess energy" is to access the CT_n states.*

3. Pump-push-probe experiment to elucidate dynamics of CT states

3.1 Experimental procedure

- Almost the same procedure as section 2.1. Instead of detecting photocurrent, the number of the sum of CT_0 states and SC states is measured by IR probe pulse.
- The IR probe pulse is not absorbed by CT_n states, where the charge is delocalized.

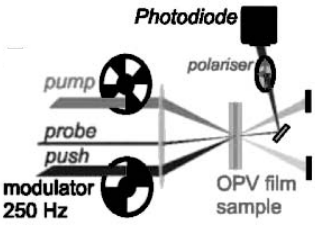


Figure 4. Schematic image of pump-push-probe experiment.

3.2 Results and discussion

- The number of the sum of CT_0 states and SC states is depicted in Figure 5a. When irradiated by push pulse, the number of charged states decreased a substantial fraction (~10%) indicating generation of CT_n states.
- The difference of the transient absorption of the probe pulse with and without the push pulse is depicted in Figure 5b. The intensity indicates the number of CT_n states after the push pulse.
- Two-step decrease of CT_n states was observed after the sudden increase of CT_n states by the push pulse.
  - The first rapid decay (~0.2 ps) is assigned to the relocalization of CT_n states to the neighboring CT_0/SC states (Figure 2, ④->⑤).
  - The second slow decay (~20 ps) is assigned to the generation of "mobile" charges. This indicates that *CT_n states induced "mobile" charges that contribute to the charge separation in the donor–acceptor interface.*

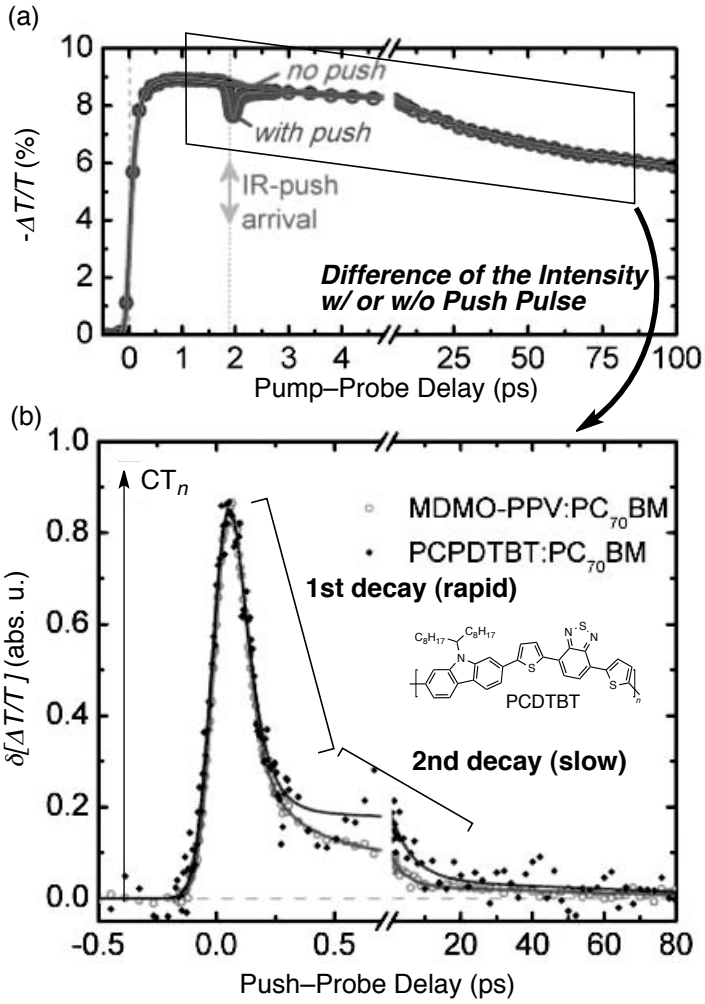


Figure 5. (a) Transient absorption. (b) Difference between with and without push measurements.

3.3 Theoretical investigation of CT_0 and CT_n states

- The average distance between hole and electron indicated that CT_n state has more delocalized charge density along the polymer backbone.
- The nature of average charge distance is dependent on the material as shown in the cases of P3HT/PCBM and P3HT/F8TBT.

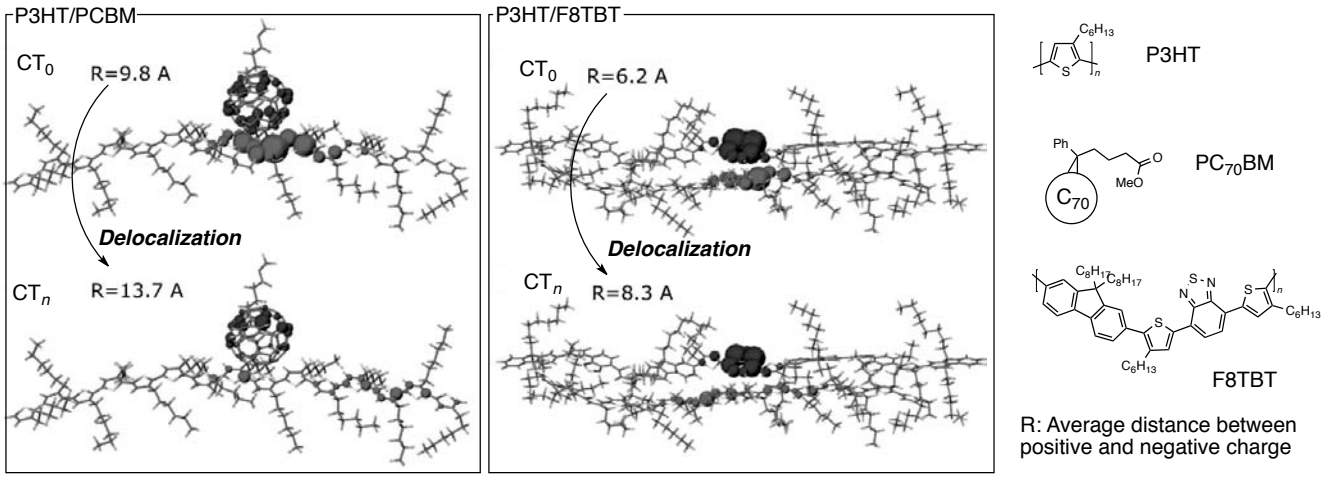


Figure 6. Charge distribution of CT_0 and CT_n states of two sets of donor/acceptor.

4. Conclusions

- The role of driving energy for charge separation is to form delocalized charge transfer state (CT_n), which facilitates long-range charge separation.
- Conventional model of charge separation through relaxation-assisted intermolecular hopping is not consistent with present result.
- Present study suggests two criteria for next generation OPV materials.
    1. Materials that support delocalized charge wave functions.
    2. Materials that have low reorganization energy with structural rigidity, which leads to suppression of torsion relaxation to charge-localized state (CT_n->CT_0).

5. References

(1) Gélinas, S.; Paré-Labrosse, O.; Brosseau, C. N.; Albert-Seifried, S.; McNeill, C. R.; Kirov, K. R.; Howard, I. A.; Leonelli, R.; Friend, R. H.; Silva, C. *J. Phys. Chem. C* **2011**, *115*, 7114–7119.

(2) Park, S. H.; Roy, A.; Beaupré, S.; Cho, S.; Coates, N.; Moon, J. S.; Moses, D.; Leclerc, M.; Lee, K.; Heeger, A. J. *Nat. Photon.* **2009**, *3*, 297–302.