Electron Transfer Dynamics in Polymer Solar Cells Studied by Femtosecond Transient Absorption Measurements

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Abstract and Introduction:

Organic molecules offer a cheaper alternative to traditional bulk crystalline materials for solar cells. Unfortunately, none have yet shown efficiencies as high as those in silicon devices. Efficient solar cell materials must have an electronic band gap suitable for absorbing most of the radiation emitted by the sun, optimally 1.1-1.4 eV. So far, the band gaps of all organic polymers created for this purpose have been much higher or the molecules have been insoluble, preventing cheap production of efficient polymer solar cells. To improve the cost-efficiency of polymer solar cells, new soluble molecules are needed with smaller band gaps. PDTNT-DPPOD is a new such organic molecule synthesized by Dr. Yasuhiro Shirai of the Japanese National Institute for Materials Science (NIMS). It has a band gap of 1.37 eV and can act as an electron donor when paired with PCBM or C60 acceptor molecules.

In actual devices, however, the short-circuit current and open circuit voltages were lower than expected. In order to understand why, we use pump-probe spectroscopy to determine if electrons are being excited in the donor molecule and transferred to the acceptor molecules in solution.

Experimental Procedure:

We made three solutions of PDTNT-DPPOD dissolved in ortho-dichlorobenzene: PDTNT-DPPOD, PDTNT-DPPOD with PCBM, and PDTNT-DPPOD with C60. In all solutions, the concentration was 1 mg/mL. The mass ratio between PDTNT-DPPOD and PCBM/C60 was 1:1. For each pump-probe measurement, a 0.2 mm thick layer of one solution was flowed through a flow-cell using a 35 hz vibration pump. A pump pulse of 700 nm and a probe pulse of 670 nm were shone on the sample and the absorbance of the probe pulse was recorded. The delay between the two pulses was varied over a range of about 60 picoseconds. For the solutions of PDTNT-DPPOD alone and PDTNT-DPPOD with PCBM, the pump power was 10 mW and the probe power was 6 mW, at a repetition rate of 1 kHz. For the solution of PDTNT-DPPOD and C60, the pump power was 10 mW and the probe power was 4 mW at 1 kHz repetition, but the repetition was then lowered to 100 Hz to allow the system to return to the ground state between data point collection.

Results and Conclusions:

Pump-probe measurements of all three solutions showed a clear decrease in absorbance at zero delay between the pump and probe pulses. This indicates promotion of the ground state electrons to higher energy states, resulting in an absence of electrons that would have otherwise absorbed the probe pulse. We define the peak to steady-state ratio as the maximum decrease in absorbance over the end behavior decrease in absorbance (A/B in the figures).

PDTNT-DPPOD alone had the largest peak to steady-state ratio of 7.3, indicating most electrons excited by the pump pulse returned to the ground state 50 picoseconds later (Figure 1). The decay of the absorbance decrease was fitted by a two-exponential function with a fast portion corresponding to the singlet state decay and a slower portion corresponding to triplet state decay. PDTNT-DPPOD with PCBM had a lower peak to steady-state ratio of 4.9 indicating some electrons were captured by the PCBM acceptor and prevented from returning to the ground state (Figure 2). The decay still showed two separate exponential components corresponding to the singlet and triplet state decays however, indicating that many excited electrons were not captured. PDTNT-DPPOD with C60 had the lowest peak to steady-state ratio of 2.6, indicating a more efficient electron transfer than with PCBM (Figure 3). Additionally, the decay function had only a slow exponential component; the lack of an observed fast decay rate back to the ground state indicates efficient singlet charge transfer to the C60.

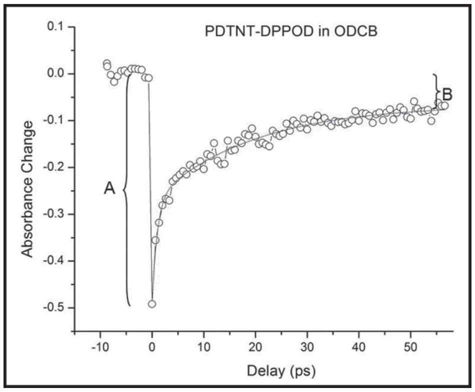

Figure 1: PDTNT-DPPOD undergoes rapid electron excitation, followed by a two-part exponential decay.

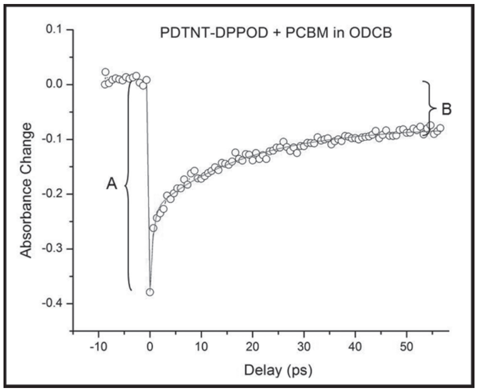

Figure 2: PDTNT-DPPOD with PCBM's moderate decrease in absorption indicates weak electron transfer.

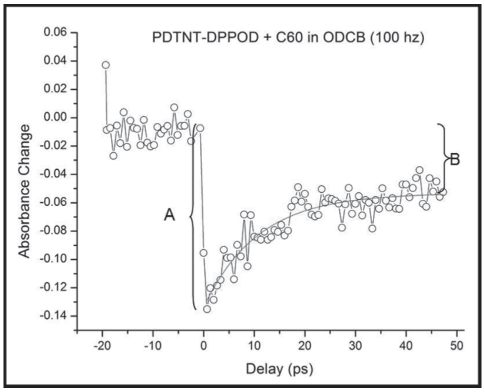

Figure 3: PDTNT-DPPOD with C60 has almost twice the absorption decrease of PCBM, indicating more efficient electron transfer.

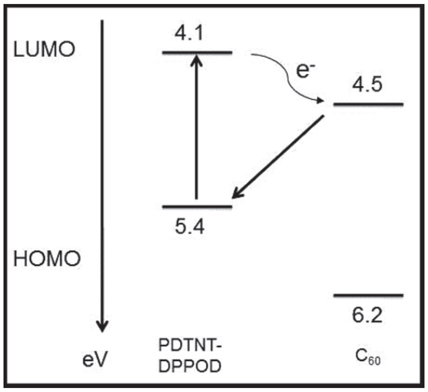

Figure 4: Electron excitation, charge transfer, and return to ground state/HOMO in PDTNT-DPPOD and C60.

PDTNT-DPPOD with C60 was originally measured at a repetition rate of 1 kHz, but that measurement never reached steady state. The measurement had to be repeated at 100 Hz because the absorbance of the system took longer to recover than for PDTNT-DPPOD alone. This indicates that charge transfer occurred from PDTNT-DPPOD's lowest unoccupied molecular orbital (LUMO) to C60's LUMO, which then had a longer recovery time back to PDTNT-DPPOD's highest occupied molecular orbital (HOMO) than from PDTNT-DPPOD's LUMO (Figure 4). This confirms device testing results that C60 served as a better electron acceptor than PCBM.

Future Work:

We have determined that the electron transfer process between PDTNT-DPPOD and PCBM is inefficient, likely because there is only a 0.1 eV difference in their LUMO energy levels. However, it is still unclear why solar cells made with PDTNT-DPPOD and C60 exhibit such low short-circuit current and open circuit voltage when compared with other molecules synthesized by Dr. Shirai's group. Fluorescence studies are needed to characterize the absorption wavelengths of different charge species for this molecule. To better understand device performance, nanosecond pump-probe measurements can be performed to determine carrier lifetime and recombination timescales. Solutions and films of thiophenes have also been known to exhibit different characteristics, so experiments should be performed with the film phase of this molecule.

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