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Ultrafast nonlinear transparency driven at a telecom wavelength in an organic semiconductor system

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Ultrafast nonlinear transparency driven at a telecom wavelength in an organic semiconductor system

Abstract
Ultrafast laser-induced transparency is demonstrated using femtosecond (fs) pump-probe experiments in the organic P3HT:PCBM (donor:acceptor) blend structure. For above band gap pumping, ultrafast transient signals strongly depend on the probe photon energy. Most intriguingly, for below band gap pumping at 0.95 eV, or 1.3 µm at a telecom wavelength, a huge transmission increase up to 30% only during the laser pulse ~100 fs is observed as a pump-driven, quasi-instantaneous suppression of absorption for the high photon-energy energy probe beam. We attribute the observed laser-driven transparency to dynamic Franz-Keldysh effect, at least one order of magnitude stronger compared to the multiphoton nonlinearities. Our results may be used for development of low-cost, beyond 100 Gbit/s optical switching devices.

Keywords
Franz-Keldysh effect, Femtosecond lasers, Organic semiconductors, Photoexcitations, Optical computing, Optical modulators, Exciton dynamics, Excitation energies

Disciplines
Electrical and Electronics | Engineering Physics

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Ultrafast nonlinear transparency driven at a telecom wavelength in an organic semiconductor system

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ABSTRACT
Ultrafast laser-induced transparency is demonstrated using femtosecond (fs) pump-probe experiments in the organic P3HT:PCBM (donor:acceptor) blend structure. For above band gap pumping, ultrafast transient signals strongly depend on the probe photon energy. Most intriguingly, for below band gap pumping at 0.95 eV, or 1.3 µm at a telecom wavelength, a huge transmission increase up to 30% only during the laser pulse ~100 fs is observed as a pump-driven, quasi-instantaneous suppression of absorption for the high photon-energy energy probe beam. We attribute the observed laser-driven transparency to dynamic Franz-Keldysh effect, at least one order of magnitude stronger compared to the multiphoton nonlinearities. Our results may be used for development of low-cost, beyond 100 Gbit/s optical switching devices.

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Ultrafast optical components are highly demanding in fast optoelectronics especially for future optical telecommunications.1 Recently there has been great effort to develop next generation 40 and 100 Gbit/s optical data transmission based on time-division multiplexing (TDM) and wavelength-division multiplexing (WDM).2-5 The speed of conventional optoelectronic devices is limited by the response of the electronics rather than fast optical processes. It is a largely unexplored territory thus far for ultrafast all-optical switching and wavelength conversion in sub-picosecond (ps), with low cost, organic P3HT:PCBM Bulk heterojunction (BHJ) structures, where P3HT is poly(3-hexyl thiophene) and PCBM is [6,6]-phenyl-C60 butyric acid methyl ester.

Most ultrafast optical components developed with inorganic semiconductors6 are based on the electro-optic Pockels’ effect,7 nonlinear effects,8 phase transformation,9 photonic crystals,10,11 or multiphoton absorption.12 Organic electronic devices have niche applications complementing inorganic ones in thin and light weight applications.43-45 Although they present potential obstacles, notably long-term stability, these have been resolved for applications such as organic LED (OLED) displays and organic solar cells by encapsulation, UV shielding, oxygen and humidity barrier, and active materials.46,47 BHJ organic photovoltaic (OPV) cells having low band gap donors and fullerene acceptors have great potential due to their easy fabrication and low cost, e.g., role to role processing, inkjet printing, and screen print.48-50 Yet the ultrafast nonlinear optical effects in inorganic materials has been relatively less studied.

Searching for non-perturbative regime in organic semiconductors under intense, off-resonant pump pulse provides an interesting opportunity for ultrafast nonlinear optoelectronics. Band structure of solids arises from electrons in a spatially periodic potential. The same electrons in the presence of strong time periodic potential (an AC
field of sufficient strength) lead to substantial modifications of near band gap absorption, since the light field cannot be treated as a small perturbation, i.e., non-perturbative effect. For instance, in bulk semiconductor GaAs huge (∼40%) laser-induced below-band-gap absorption and above-band-gap transparency induced by an intense laser beam were observed; this was explained by the dynamic Franz-Keldysh effect (DFKE).15-16,51 This process does not create real charge carriers/excitons so the effect disappears rapidly when there is no strong pump beam. Using this effect ultrafast switching is possible with an ultrashort pulsed laser. However, the non-perturbative regime in organic semiconductors has not been identified.

In this paper we demonstrate ultrafast optical switching using low cost, easily fabricated organic OPV cells based on P3HT:PCBM films which is a mixture of random oriented organic semiconductors. Recent studies showed that such P3HT:PCBM-based solar cells can readily yield power conversion efficiencies (PCEs) of 4% to 6%.17-19 When the pump energy is 0.95 eV (1.3 µm) which is well below the band gap of P3HT, the huge modulation up to 30% is observed as a pump-driven, quasi-instantaneous suppression of absorption for the high energy probe photons. This transient nonlinear transparency exists only during the laser pulse ∼100 fs, which we attribute to DFKE. In addition to providing observations of non-perturbative phenomena in organic electronics, these are potentially relevant to the development of, among others, beyond 100 GHz optical switching devices.

The P3HT:PCBM blends and pristine P3HT thin films were prepared as described in the supplementary material. Basic optical and electrical properties as well as charge carrier dynamics of P3HT:PCBM are reported before.20-29 The dynamics of our P3HT and P3HT:PCBM samples were studied via ultrafast transient transmission spectroscopy using a pulsed probe beam, ∼100 femtosecond (fs) white-light continuum (WLC) generated from a 3-mm-thick sapphire crystal, from 2.50 eV to 1.68 eV with less than 1 µW total average power (inset Fig. 1(c)). An ultrafast Ti:Sapphire laser generating 35 fs pulses at 1 kHz repetition rate, with a central wavelength of 800 nm, was used to drive the pump and probe beams.30-32 The pump beam was generated from an optical parametric amplifier (OPA), generating high-power fs pulses with tunable wavelength in the visible and infrared spectral regions. The average power of the pump beam is 8 mW for 640 nm and 1.05 mW for 1.3 µm through a 2 mm pinhole. The transmission of the probe beam, from WLC, through the sample was collected and passed through a computer-controlled spectrometer, where its intensity was then recorded. A reference beam, split from the WLC probe, was also passed through the spectrometer and simultaneously recorded, canceling out laser noise. The pulse width of pump and probe beam is 100-140 fs slightly depending on the wavelength. During experiments, the air-sensitive samples were placed in a continuous flow nitrogen purge box to minimize degradation. The transient transmission difference ∆T/T (negative absorption difference, ∆T = -ΔA) was measured with pump-probe delays with a motorized stage. It is increased by ground state photo bleaching and decreased by photo-induced absorption.

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gaps of P3HT and PCBM are 2.0 eV and 2.4 eV, respectively (inset Fig. 1(a)).33-37 The main absorption peaks in P3HT:PCBM blend are near 2.3 eV from π–π absorption of P3HT and above 3 eV from fullerene absorption in PCBM. Optical band gaps of P3HT and PCBM from absorption measurements are 1.9 eV and 2.0 eV, which are lower than HOMO–LUMO gaps due to broadened energy levels from disorder in conjugated polymers.38 In our experiment, the pump photon energy is set to either 1.96 eV, which is slightly above the optical band gap of P3HT, or below that of PCBM, or 0.95 eV, which is well below the optical band gaps.

Fig. 1(a) shows the representative transient transmission dynamics of P3HT:PCBM blend. The pump energy is 1.96 eV (14 µJ/cm²). The increase in the transmission is due to ground state photo bleaching.31 It consists of multiple decay channels
from sub-ps, low frequency probes below the P3HT gap are more sensitive to strongly-bound charge transfer (CT) excitons or polarons in BHJ films that generate mid-gap CT states by attracting $\pi$ and $\pi^*$ bands into the gap. This is consistent with the band alignment of BHJ samples shown in Ref. 28. Specifically, the probe photon energy dependence lower than 1.82 eV down to 1.68 eV shows a pronounced increase in $\Delta T/T$ amplitude in P3HT:PCBM while the transient signals quickly diminish in pristine P3HT films as shown in Fig. 2. The associated, three characteristic temporal components, $\approx 1$ ps, 10 ps and $\approx 100$s of ps, seen in the BHJ films can be attributed to CT excitation formation, cooling of hot CT states and long time charge separation at D/A interface. These results confirm that ultrafast absorption spectroscopy reveals different transient charge carrier dynamics after photoexcitation in P3HT and P3HT:PCBM BHJ, consistent with the prior literature.20–29

Figure 3 shows the transient transmission of P3HT:PCBM with below band gap pumping at 0.95 eV to demonstrate DFKE effect, as illustrated in Fig. 3(a). The black line is undoped ground state band and the dotted green one is photo-induced bands due to DFKE. The pump induced blue shifts of the band gap increase the transmissions of the probe beam near the band gap. The estimated Keldysh parameter $\gamma \approx 0.14$ which is
clearly beyond the multi-photon regime and towards DFKE regime (see supplementary material for detail) based on the experimental condition used with peak intensity $I = 8.3 \times 10^{10}$ W/cm$^2$. This gives rise to the pump-induced nonlinear band shifts and transparency demonstrated below. The DFKE process is a virtual process with no real charge carriers/CT excitons created and exists only when a strong pump field is applied.

Fig. 3(b) plots the probe beam transmission at 2.07 eV (600 nm), which is slightly above the band edge of P3HT. The transmission increases by 6% at 1.7 mJ/cm$^2$ pumping power and up to 33% at the highest power used ~8.3 mJ/cm$^2$ (Fig. 3(c)) during the presence of pump pulse ~100fs. The inset shows that the peak intensities of P3HT:PCBM and P3HT are proportional to the pump intensity. The slope of the dashed lines in the inset are 4.0 for P3HT:PCBM and 2.7 for P3HT respectively. The observed fs laser-driven transparency in P3HT:PCBM blend is ~40–50% stronger compared to that in P3HT organic semiconductors under the same pumping condition. The similarity in the pump power dependence is reasonable since the electric field is not only generated by the charge separation but also electric field of incident pump during the laser pulse. Fig. 3(d) shows the long tail after 100 fs when the pump power is set to 5.9 mJ/cm$^2$ due to two photon process. This is most likely due to two pump photons rather than pump and probe photons since pump power is at least 1,000 times stronger than probe power. This two photon absorption effect doesn’t explain the pump-probe scan feature during the pulse. More importantly, the pump–probe scan with 1.7 ml/cm$^2$ pump, as shown in Fig. 3(d) (green), doesn’t show real carrier/CT excitons generation and only exhibit virtual excitation with a symmetric profile during the laser pulse which is consistent with DFKE. The absence of long tail >100 ps indicates no excitation generation and/or recombination seen in the strong pumping case. On the flip side, D/A interface does take a role in charge separation after the pump pulse that gives the longer decay time in Fig. 3(d).

The weak two photon absorption of the pump beam >150 fs is not caused by DFKE. Once the charge carriers are populated by the two photon absorption, the probe beam shows similar transient behavior as those in Figs. 1 and 2. This two photon absorption generates the real carrier/CT excitons during the pulse and exhibits long decay after the laser pulse that should be distinguished from DFKE. Please also note that two photon absorption involving one pump and one probe (much weaker) photons cannot account the observation either since it should be a much weaker effect compared to the two pump photon process. As discussed in Fig. 2, the photoinduced strongly-bound charge transfer excitons or polarons determine the long-lived transient responses in BHJ films while mobile singlet excitons in pristine P3HT films. Fig. 3 clearly identifies fs laser-driven transparency via DFKE as the observation of the non-perturbative regime in organic semiconductors that is distinct from ps bleaching to two photon absorption involving the generation of real carrier/CT exciton generations.

In conclusion, we have demonstrated 150 fs ultrafast transient transparency in P3HT and P3HT:PCBM blends with below band gap pumping. The ultrafast switching of 30% transmission difference is explained by a non-perturbative mechanism DFKE, which is a fast virtual process that is distinguished from two photon absorption involving real photoexcited charge carriers/CT excitons. The results demonstrate ultrafast manipulation of fundamental electronic properties of organic semiconductors and discover non-perturbative regime in this category of material. In the long run, such fundamental insights have significant implications in advancing organics-based above-terahertz speed modulators in ultrafast optoelectronics and in extending to other emergent photovoltaics materials.

See supplementary material for the sample preparation, pump-probe experiment, and the measurement of the probe wavelength and WLC chrip dispersion.

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