

# Charge Carrier Dynamics in Benzoporphyrin Thin Films Investigated by Time-Resolved THz Spectroscopy

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**Abstract**— We performed optical pump-terahertz (THz) probe measurements to investigate the charge carrier dynamics of benzoporphyrin (BP) and BP-based bulk heterojunction (BHJ) thin films. In both samples, we observed an instantaneous appearance of transient THz signals which are attributed to polaron pairs. These polaron pairs recombine and/or trap in a defect site to localize within 1 ps time scale. From analysis of the transient complex conductivity spectra, we found that the conductivity spectra can be well reproduced by Drude-Smith model. For BP-based BHJ films, a faster decay dynamics of the transient THz signals was observed compared to BP films.

## I. INTRODUCTION

CONJUGATED organic semiconductors have been extensively studied because of promising applications for field-effect transistors and solar cells. One of the reasons for widespread interest is that solution-process can be used for fabrication of photovoltaic devices. This is a great advantage over silicon-based devices and potential for producing low-cost and flexible solar cells. Among these organic semiconductors, phthalocyanines and porphyrins have excellent optical and electronic properties [1-4]. It was shown that thermal conversion from precursor molecules is very useful and cost-effective method to fabricate thin films.

In order to improve a power conversion efficiency of such materials, it is indispensable to understand the detailed mechanism of charge generation, recombination, and charge carrier mobilities. In particular, transient absorption (TA) measurements have been used to probe the fundamental processes taking place in organic photovoltaic materials. Even though TA has high sensitivity and high time resolution to monitor the charge carrier dynamics, the assignment of the observed spectra is sometimes not straightforward because the electronic transitions are not directly related to the motion of charge carriers themselves.

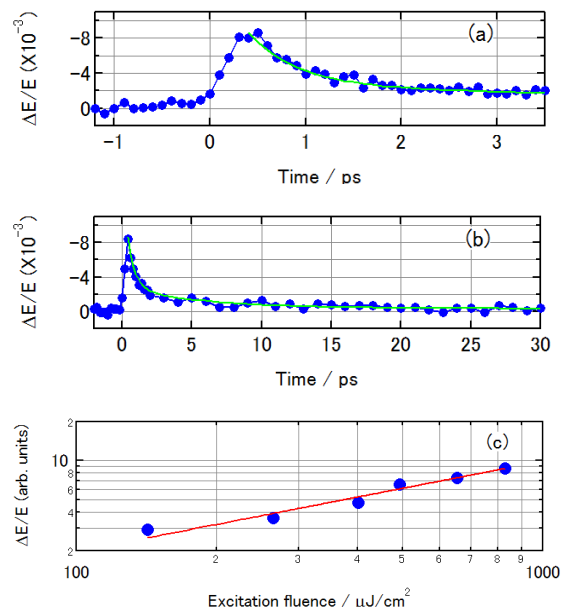
In this study, we performed optical pump-terahertz (THz) probe measurements to investigate the charge carrier dynamics of benzoporphyrin (BP) thin films and the corresponding BHJ thin films blended with [6,6]-Phenyl C<sub>61</sub> butyric acid methyl ester (PCBM). From analysis of the transient spectra in the THz region, it is possible to obtain information on the degree of localization of photo-generated charge carriers.

For measuring the dynamics in a broad THz range, the THz probe pulses were generated by a two-color femtosecond laser-induced plasma and sampled by an air-biased coherent detection [5,6]. The laser system was based on Ti:sapphire regenerative amplifier, producing a 100 fs pulse with center wavelength of 800 nm at a repetition rate of 1 kHz. In order to obtain information on the time dependence of the transient conductivity, we measured the change in peak amplitude of

THz waveform as a function of optical pump-THz probe delay. On the other hand, to measure the transient complex conductivity spectra, we scanned the time delays of optical pump and THz detection pulses synchronously at a fixed THz probe delay. We used UV pump pulse at 400 nm for optical excitation. BP and BP:PCBM (1:1) BHJ thin films were fabricated on the fused silica substrates by following the procedure reported elsewhere [3,4].

## II. RESULTS

Figure 1 displays the photo-induced change of THz electric field amplitude of BP thin film as a function of optical pump-THz probe delay measured at the peak of the THz transmission. The transient signal has an instantaneous decrease in amplitude and the majority of the signal decays with time constants of  $0.5 \pm 0.1$  ps and  $6.0 \pm 1.6$  ps. In this scan mode, the time dependence of the signals reflects the average photoconductivity of BP thin films. Figure 1(c) shows excitation fluence dependence of photo-induced change of THz electric field of BP thin films at the peak of the THz transmission.



**Fig. 1.** (a) and (b) Photo-induced change of THz electric field amplitude of BP films as a function of optical pump-THz probe delay measured at the peak of the THz transmission on two different time scales. Blue solid lines with filled circles and green lines represent the experimental results and the double exponential fits, respectively. Excitation fluence was  $530 \mu\text{J}/\text{cm}^2$ . (c) Excitation fluence dependence of photo-induced change of THz electric field of BP films at the peak of the THz transmission (blue filled circles). Red line represents the fit of power law to data.

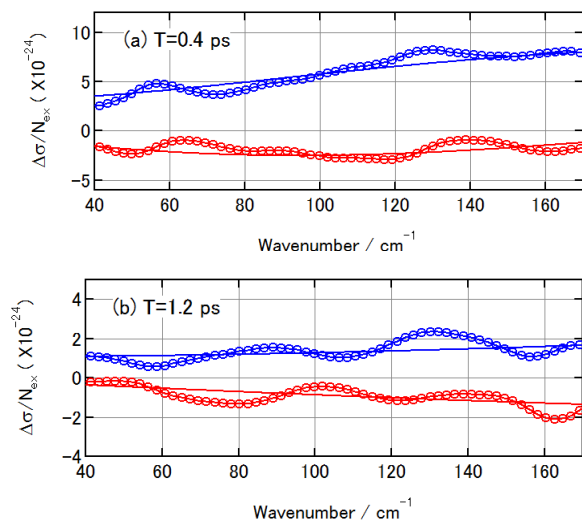
The excitation fluence dependence was fitted by a power law of the form with  $-\Delta E/E = Af^B$  where  $f$  is the excitation fluence. We observed sub-linear fluence dependence of the photoconductivity ( $B=0.70 \pm 0.07$ ).

Figure 2 shows the transient complex conductivity spectra of BP thin films measured at 0.4 ps and 1.2 ps. The real part of the conductivity spectrum increases at higher frequency and has positive value at lower frequency, which suggests that the response in the THz region is dominated by the mobile charge carriers. The imaginary part of the conductivity is negative, which approaches zero at lower frequency. This feature is different from what we expect from a classical Drude model. Generally, in disordered systems, the conductivity spectra can be described by Drude-Smith model [7]. To analyze our data, we used the following equation to fit the data by taking into

$$\frac{\tilde{\sigma}_{DS}(\omega)}{N_{ex}} = \frac{\varphi e^2}{m^* d} \frac{1}{1 - i\omega\tau} \left( 1 + \frac{c}{1 - i\omega\tau} \right) \quad (1)$$

where  $\tau$  is the carrier momentum relaxation time,  $\varphi$  is the quantum yield of the photon to carrier,  $m^*$  is the effective mass of the charge carrier and  $d$  is the absorption depth. The effect of the disorder is described by the parameter,  $c$ , which is related to the memory effect during the carrier scattering process. Since  $\varphi$  and  $m^*$  are unknown, we treat the first factor of the last expression in eq. (1) as a proportional constant and we can only determine the carrier momentum relaxation time,  $\tau$ , and the parameter,  $c$ . We found that  $\tau$  and  $c$  at 0.4 (1.2) ps are  $20.6 \pm 0.7$  ( $6.2 \pm 1.5$ ) fs and  $-0.83 \pm 0.01$  ( $-0.89 \pm 0.01$ ), respectively. At both time delays of 0.4 ps and 1.2 ps, the parameters,  $c$ , are close to one. This means that charge carriers are rapidly localized within 1 ps. We also found that the carrier momentum relaxation times are 5-20 fs.

As shown in Fig. 1, the THz transients rise immediately after the photo-excitation, which are due to instantaneous appearance of mobile charge carriers. We consider that exciton absorption is located at much higher frequency region compared to our observed one (40-170  $\text{cm}^{-1}$ ).



**Fig. 2.** Transient complex conductivity spectra of BP films measured at (a) 0.4 ps and (b) 1.2 ps. Blue (red) open circles are the real (imaginary) parts of transient conductivity obtained experimentally. The corresponding solid lines are the fits using a Drude-Smith model.

Based on dependence of excitation fluence, the results suggest that exciton-exciton annihilation causes the formation of the loosely bound polaron pairs where electron and hole are located at different BP units with small separation. These polaron pairs rapidly recombine and/or trap in a defect site to localize within a 1 ps time scale. These lead to the decay of the transient THz signals. Some portions of the polaron pairs dissociate to form mobile charge carriers, which are an origin of the slow decaying components on a few ps time scale.

For BP:PCBM BHJ thin film, we found that the transient signal decays with the time constants of  $0.2 \pm 0.1$  ps and  $2.9 \pm 0.5$  ps. Compared to BP films, we observed faster decaying dynamics on a ps time scale which means that mobile charge carriers are quenched before the charge separation takes place at the interfacial region of the BP and PCBM blends. However, about 10 % of the transient signal does not decay within 30 ps. This result shows that small portion of polaron pairs survive and are free to move.

### III. SUMMARY

We carried out optical pump-THz probe measurements to study the charge carrier dynamics of BP and BP:PCBM BHJ thin films. We found that the transient signals of BP films decay with the time constants of 0.5 ps and 6.0 ps. Based on excitation fluence dependence, we consider that exciton-exciton annihilation is an origin of the formation of the loosely bound polaron pairs and some of the polaron pairs dissociate to form mobile charge carriers. We also found that the conductivity spectra can be well reproduced by Drude-Smith model, meaning that charge carriers are rapidly localized within 1 ps. From comparison of the dynamics between BP and BP:PCBM BHJ films, we consider that mobile charge carriers are quenched before the charge separation takes place at the interfacial region of the BP and PCBM blends, even though a small portion of the carriers exist longer than a 30 ps time scale.

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