Polaron states and charge dynamics in doped conjugated polymers studied by various spectroscopic methods

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Abstract. Various spectroscopic data for doped conjugated polymers are reviewed and discussed. Chemical doping induces polaron states in the conjugated polymers. Two polaron states appear between the \( \pi \) and \( \pi^* \) states. Third harmonic generation spectroscopy reveals the multiply-resonant nonlinear optical processes using the polaron states. The terahertz measurements clarify the carrier localization, which is dependent on the doping levels. The ultrafast luminescence measurements reveal the relaxation process of the photoexcited states of the doped conjugated polymers.

1. Introduction
In organic electronics and nanotechnology, including the fields of organic conductors, electronic luminescent devices, field effect transistors (FET), and photovoltaic devices, mobile charges play important roles. The mobile charges often appear in the partially occupied \( \pi \) states of organic electronic systems. For example, in organic FET, the gate voltage controls the charge filling in the highest occupied molecular orbital (HOMO) or the lowest occupied molecular orbital (LUMO) [1] and realizes the partial occupation of these orbitals. In doped conjugated polymers, chemical doping gives the two polaron states (P1 and P2) in which the partially occupied \( \pi \) states are achieved [2].

Polarons induced by doping affect and change the pattern of the carbon skeleton in the conjugated chains, which leads to the emergence of new electronic states within the \( \pi-\pi^* \) gap. The spatial extent and anisotropy of the polarons are crucial to the usage of the polaron carriers. Moreover, it is important to understand the charge dynamics in the states where the polarons are on the conjugated chains. In this paper, the author reviews the electronic states in doped polythiophene, which is one of the most popular conjugated polymers, revealed by various optical experiments using femtosecond lasers. In the third-harmonic generation (THG) spectroscopy, the transition dipole moments between the polaron states and \( \pi (\pi^*) \) states are evaluated [3]. In the terahertz (THz) spectroscopy, the optical conductivity in the THz region is discussed [4–6]. Moreover, in the time-resolved luminescence measurement, the initial dynamics of the photoexcited states of the doped conjugated polymers are discussed [7]. From these optical properties of the doped states of the conjugated polymers, the nature of the carriers is discussed.

2. Doped poly(3-hexylthiophenes) [3, 4, 6]
The doped states of poly(3-hexylthiophenes) (P3HT), which are one of the main targets in this paper, are introduced in this section. Similar to most undoped conjugated polymers, the undoped P3HT has a
strong absorption peak, which is assigned to the \(\pi-\pi^*\) transition and is located at around 2.4 eV, as shown in figure 1(a) [3]. Chemical doping of P3HT is done by dipping the polymer into an acetonitrile solution of Cu(ClO₄)₂ both for regioregular and regiorandom P3HT. Even after taking the sample out of the dopant solution, the samples will remain stable for a sufficient amount of time for optical measurements. By changing the immersion time, we can control the degree of doping. The following laser experiments are performed for the samples which are taken out of the solution and placed in the air. By the chemical doping of P3HT, the absorption spectra related to the polaron states appear below the \(\pi-\pi^*\) transition and are shown in figure 1(b). \(\pi-\pi^*\) transitions are observed at around 0.6 eV and the P1-P2 transitions are at around 1.5 eV.

3. Spectroscopy for the polaron states

3.1. Third harmonic generation measurements [3]

In the THG experiments, a pulsed laser is irradiated on the sample and the generated third harmonic (TH) light is detected. The intensity of the TH light is compared with that of the reference sample and the third-order nonlinear susceptibility \(\chi^{(3)}\) is obtained. The spectra of \(\chi^{(3)}\) for the undoped and doped P3HT are shown in figure 1 [3]. The upper axis is the photon energy of the excitation laser, while the lower axis is the photon energy of the TH light. The absorption spectra are also plotted against the same lower axis. In the undoped sample, the peak positions of \(\chi^{(3)}\) and absorption in figure 1(a) are the same, indicating that three-photon resonance occurs. For the doped sample, the peak energy positions of \(\chi^{(3)}\) and that of the absorption are different. As the result of spectral analysis, one-photon resonance

Figure 2. Energy level structure of doped P3HT. Reprinted with permission from H. Kishida et al., Appl. Phys. Lett. 97, 103302 (2010). Copyright 2010 American Institute of Physics.
and three-photon resonance doubly occur as shown in figure 2 [3] and the spectral shape is determined. The spectral analysis also reveals the transition dipole moments between $\pi$, $\pi^*$, and the two polaron states. These experimental data reveal that the polaron states can contribute to the third-order nonlinear optical processes.

3.2. THz spectroscopy [4–6]

The dynamics of the charges in the doped conjugated polymers should be reflected in the low-frequency optical spectra. The optical conductivity spectra of the conjugated polymers, which are obtained from the time-domain THz spectroscopy, are discussed in this subsection. The THz spectra for the doped P3HT are shown in figure 3 [4]. With increased doping time, the absolute values of the optical conductivities also increase. The spectra are analyzed by the Drude-Smith model [8], in which the backward scattering of the carriers are considered. Such scattering leads to the localization of the carriers. In the analysis, the localization parameter $C$ ($-1 \leq C \leq 0$), carrier density $N$, and the relaxation time $\tau$ are calculated. $C = -1$ gives complete localization, while $C = 0$ is complete delocalization, where the model coincides with the normal Drude model. The data for regiorandom P3HT and PEDOT:PSS samples are also compared in figure 4. At low carrier density, the localization parameter is close to $-1$, which indicates that the states are insulating. Even at the highest carrier density, $C$ is below $-0.5$, which is in the region of localized states.

The anisotropy of the optical conductivity was reported for the oriented P3HT films fabricated by the rubbing method [6]. The optical conductivity parallel to the rubbing direction is significantly larger than that perpendicular to the rubbing direction. This fact indicates that the rubbing procedure aligns the polymer chains and that the charge motion governing the conductivity in the THz regions is along the polymer chain.

The THz measurements were extended to highly conducting polyanilines (PA) [5]. A highly conducting PA shows large optical conductivity values of over 500 S/cm. As a result of the spectral analysis by the Drude-Smith model, $C$ reaches $-0.23$. This value indicates that the localization mechanism is significantly weakened and that the true metallic state is realized in the highly conducting PA.

Figure 3. THz spectra of doped P3HT. Reprinted with permission from T. Unuma et al., Appl. Phys. Lett. 97, 033308 (2010). Copyright 2010 American Institute of Physics.

Figure 4. (a) Localization parameter $C$ and (b) relaxation time $\tau$ versus carrier density. Reprinted with permission from T. Unuma et al., Appl. Phys. Lett. 97, 033308 (2010). Copyright 2010 American Institute of Physics.
3.3. Luminescence and up-conversion measurements [7, 12]
Non-doped conjugated polymers such as polythiophenes are often luminescent [9]. On the other hand, the luminescence of the doped state is significantly quenched [10]. The quenching mechanism is not clear at present, but it is easily expected that the polaron states can be a path for the energy relaxation of the photoexcited states and one of the quenchers of the luminescence. However, luminescence from the doped states of P3HT was observed [7]. From the energy of the luminescence, it is assigned to the P2-P1 transition. The decay of the luminescence for the doped P3HT was measured using the up-conversion method. In the experiment, the excitation was done with an 80 fs laser pulse at 1.55 eV and the luminescence was probed at 1.1 to 1.4 eV. The sum frequency light of the luminescence and the gating pulse (1.55 eV, 80 fs) was detected. The time evolution of the luminescence (figure 5 [7]) is reproduced by a stretched exponential function. The decay time evaluated in the analysis of stretched exponential functions is approximately 30 fs. From the analysis, the mobility of the charges is estimated to be 2 cm²V⁻¹s⁻¹. This value is one order of magnitude larger than the macroscopically measured value [11]. The large mobility observed in the luminescence measurement reflects the fact that the up-conversion measurement detects the initial motion of the photocarriers and that various trapping or scattering processes do not work in such an ultrafast time region.

As for the PEDOT:PSS, a similar time evolution was observed [7]. Therefore, the relaxation process is inherent to the polythiophene backbone. In addition to the polaron luminescence, PEDOT:PSS shows the luminescence in the visible region under 3.08 eV excitation, which is assigned to the luminescence from the dopant polymer PSS [12]. This visible luminescence should be considered when we fabricate visible optical devices using PEDOT:PSS.

4. Conclusions
The polaron states and the charge dynamics in the doped conjugated polymers are discussed on the basis of the experimental results of various spectroscopic methods. The THG spectroscopy reveals the multiple resonance using both $\pi$ ($\pi^*$) states and polaron states. This clarifies that the polaron states and $\pi$ ($\pi^*$) states are not spatially separated, but that the $\pi$ ($\pi^*$) states and polaron states are significantly overlapped. The THz spectroscopy demonstrates the localization of the carriers in doped P3HT and the true metallic state in highly conducting polyaniline. These results suggest that the THz method is useful for the judgement of the metallic nature of the carriers. The time-resolved luminescence measurement for doped states clarifies the dynamics of the photoexcited states of the doped conjugated polymers. Thus, the various optical measurements using femtosecond lasers are a powerful tool for unravelling the physics of polarons in doped conjugated polymers.
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