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# Microscopic Mobility of Polarons in Chemically Doped Polythiophenes Measured by Employing Photoluminescence Spectroscopy

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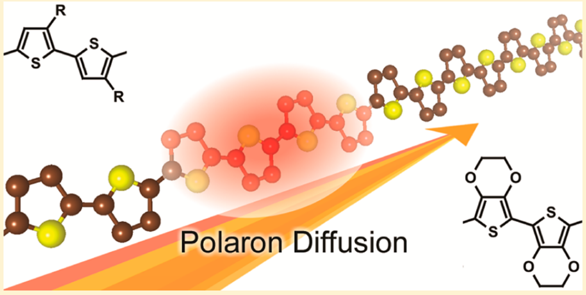
**ABSTRACT:** Doped conjugated polymers show high electrical conductivity due to doping-generated polarons, and understanding their transport properties is key to their practical use as transparent flexible electrodes. The transport properties have been widely studied in the field-effect transistor configuration, where the long-range transport affected by grain boundaries and conjugation breaks dominates. In contrast, spectroscopic measurements are sensitive to microscopic transport properties and have a potential to reveal the characteristic transport within an intrachain conjugation region. In this study, we show the photoluminescence of polarons in chemically doped polythiophenes to estimate microscopic carrier mobility through the relaxation dynamics of the photoexcited state of polarons. The estimated carrier mobility is 2 $cm^2 V^{-1} s^{-1}$ and larger than the reported highest value on the order of 0.1 $cm^2 V^{-1} s^{-1}$ in field-effect transistors. This study demonstrates the real-time observation of carrier diffusion and scattering in the conductive state of conjugated polymers.



**KEYWORDS:** *polythiophene, chemical doping, polaron, photoluminescence, one-dimensional diffusion*

High electrical conductivity, structural flexibility, and optical transparency in the visible region make doped polythiophenes one of the most promising materials for future transparent flexible electrodes. To increase their utilization in technological applications, understanding transport properties and investigating carrier mobility are crucial, especially estimation of the achievable upper limit of carrier mobility.

The transport properties of doped polythiophenes have been widely studied in the field-effect transistor configuration. The highest carrier mobility in the polythiophene field-effect transistor[1−8] is on the order of 0.1 $cm^2 V^{-1} s^{-1}$, while theoretical studies suggest much higher mobility in polythiophenes.[9−11] This discrepancy may arise from the transport properties in the field-effect transistor that reflects long-range transport, which is affected by grain boundaries and conjugation breaks.[9−13] Since it is highly probable that the maximum carrier mobility is achieved within a conjugation region on a polymer chain, an investigation of the microscopic transport properties within an intrachain conjugation region may help achieve maximum conductivity. Spectroscopic measurements are suitable for this because of their sensitivity to microscopic responses. In particular, ultrafast spectroscopy enables us to observe the initial stage of carrier dynamics in real time and to understand carrier diffusion and scattering within an intrachain conjugation region that are obscured by the later slow dynamics in the case of transport measurements.[14]

In pristine polythiophenes, as schematically shown in Figure 1a, the lowest optical absorption is due to the transition from the $\pi$ to the $\pi^*$ band, called $\pi-\pi^*$ transition, which lies in the visible region. When an electron is removed from a polymer chain, a positive polaron, i.e., a positive charge and an unpaired electron with a change in the bond alternation pattern between them, is generated on the chain (Figure 1b). In such doped polythiophenes, two polaron states, called P1 and P2, arise in the midgap region between the $\pi$ and $\pi^*$ bands. Emergence of the P1 and P2 states results in new optical transitions related to the two states in the infrared region at the expense of the $\pi-\pi^*$ transition, leading to optical transparency in the visible spectral region.[15−20]

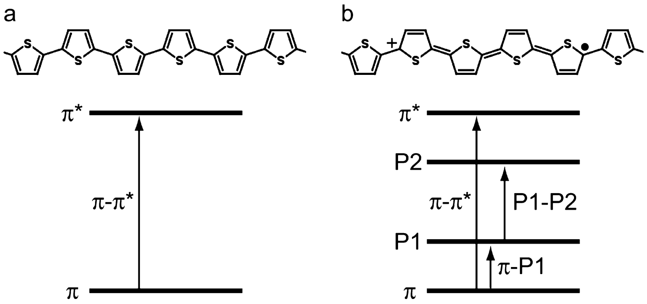


**Figure 1.** Schematic structures of polythiophenes: (a) undoped and (b) doped polythiophene. The corresponding energy diagrams are illustrated below the chemical structures.

Although the Franck−Condon states of absorption and relevant linear[15,17,18,20] and nonlinear optical responses[21] in doped polythiophenes have been studied to date, the relaxation

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of the photoexcited states has received little attention. The relaxation of the photoexcited state is due to two competing processes: radiative and nonradiative processes. In general, nonradiative processes include carrier scattering (such as inelastic scattering by carriers and trap at a defect), multiphonon scattering, and energy transfer. Photoluminescence (PL) spectroscopy provides information on the nonradiative processes through observation of the competing radiative process. In particular, time-resolved PL measurements enable us to obtain the rate of nonradiative processes; for example, the rate of carrier scattering and, in turn, the carrier diffusion constant can be obtained. Therefore, the femtosecond time-resolved PL measurement is a powerful method to study ultrafast carrier dynamics.

The PL of polarons in doped polythiophenes has not been reported yet. In this paper, we report the PL of polarons in regioregular head-to-tail poly(3-hexylthiophene-2,5-diyl) (abbreviated P3HT) doped with $ClO_4^-$ and poly(3,4-ethylenedioxythiophene)−poly(styrenesulfonate) (abbreviated PEDOT−PSS). We observe a PL band with a peak at ∼1.3 eV with vibronic structures in the two types of doped polythiophenes with an excitation of the P1−P2 transition. The ultrafast decay of PL intensity is fitted to a stretched-exponential function and shows no energy dependence, indicating that photoexcited polarons decay because of diffusion-induced relaxation on the one-dimensional polymer chain. We estimate the carrier mobility from the time evolution of PL intensity, which is larger than the reported highest value in a field-effect transistor.

## ■ RESULTS AND DISCUSSION

**Absorption Spectra.** Figure 2a shows the typical absorption spectra of undoped (pristine) and doped spin-coated P3HT films. Doping was performed by immersing the film into an acetonitrile solution (0.050 mol/L) of $Cu(ClO_4)_2$ and then rinsing it in pure acetonitrile.[21,22] The immersion times were 1 min (red curve), 6 min (green curve), and 2 h (blue curve). The spectrum of the undoped film shows an absorption peak at 2.42 eV with fine structures at 2.06, 2.24, and 2.60 eV. These structures are assigned to an exciton band associated with the $\pi-\pi^*$ transition (Figure 1a) and its vibronic sidebands;[23] the zero-phonon line is located at 2.06 eV, and higher phonon lines are separated by 0.18 eV (vibrational energy of the C═C stretching mode[24]). In contrast, in the spectrum of the doped film (red curve), the absorbance associated with the $\pi-\pi^*$ transition decreases, and two absorption bands appear at 0.6−0.7 and 1.6 eV. They are attributed to the transition from the $\pi$ band to the P1 state ($\pi$−P1 transition) and that from the P1 state to the P2 state (P1−P2 transition), respectively[18] (Figure 1b). Vibronic sidebands are not observed in the present doped sample, while chemically doped $\pi$-conjugated oligomers in solution show sharp absorption bands of the $\pi$−P1 and P1−P2 transitions with clear vibronic sidebands.[25,26] It is suggested that the absorption bands broaden inhomogeneously because the dopant ions ($ClO_4^-$) are nonuniformly distributed in the film sample.

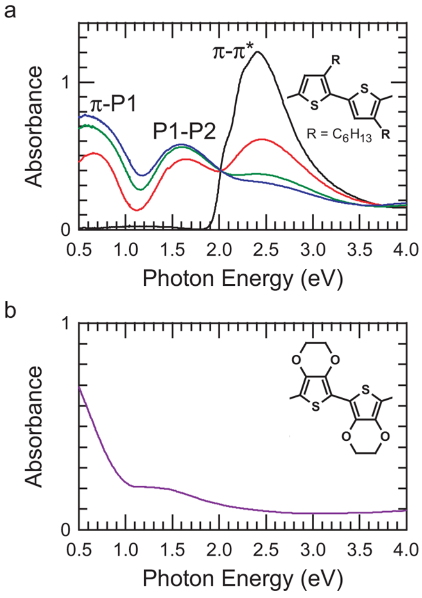

**Figure 2.** Absorption spectra. (a) Absorption spectra of undoped (pristine) and doped spin-coated P3HT films. The doping (immersion) times are 1 min (red), 6 min (green), and 2 h (blue). (b) Absorption spectrum of spin-coated PEDOT−PSS film. The insets show the chemical structures of the respective polythiophenes.

As the immersion time increases (6 min, green curve), the suppression of the $\pi-\pi^*$ band and an enhancement of the $\pi$−P1 and P1−P2 bands are observed. This behavior indicates that doping increases with the increase in immersion time. Although the absorption spectrum of the doped film with a much longer immersion time of 2 h (blue curve) shows a slight increase in doping, the spectral features are similar to the spectrum of the 6-min-immersed film. Consequently, the doping level is almost saturated at the immersion time of 6 min, which is consistent with the result measured from THz time-domain spectroscopy.[22]

Figure 2b shows the absorption spectrum of a spin-coated PEDOT−PSS film. A large absorption band with the absorbance increasing toward lower energy and a weak shoulder at ∼1.5 eV are observed. The large absorption toward low energy is a result of the convolution of the Drude-like absorption of carriers[27] and the $\pi$−P1 transition. The shoulder arises because of the P1−P2 transition. The $\pi-\pi^*$ transition is almost completely suppressed, and its position is difficult to determine. The larger Drude-like absorption and the stronger suppression of the $\pi-\pi^*$ transition indicate that the carrier density is higher in the PEDOT−PSS than in the doped P3HT.

**PL Spectra.** Figure 3a shows the steady-state PL spectra of a doped drop-cast P3HT film (immersion time, 2 h) excited at 1.58 eV with different excitation densities (2.4−19.6 W $cm^{-2}$). By taking into account the reabsorption of PL emitted inside the sample, the correction of intensity was made in Figure 3 using the absorption spectrum. The PL spectra are similar except for the intensity. Before examining the details of the spectral shape, we confirmed that the observed PL is emitted from the photoexcited polarons. Early studies showed that the PL of excitons associated with the $\pi-\pi^*$ transition in polythiophenes[23] and other $\pi$-conjugated polymers[28] is due to the two-photon absorption with low-energy photons. In such cases, the PL intensity is quadratically dependent on the excitation density. In contrast, Figure 3b shows the linear dependence of peak intensity and spectral weight on excitation density. Their linear dependence indicates that the observed PL is associated not with multiphoton excitation processes but with a one-photon excitation process. Since the excitation photon energy of 1.58 eV is resonant with the P1−P2 transition of a polaron, the PL occurs because of the photoexcitation of

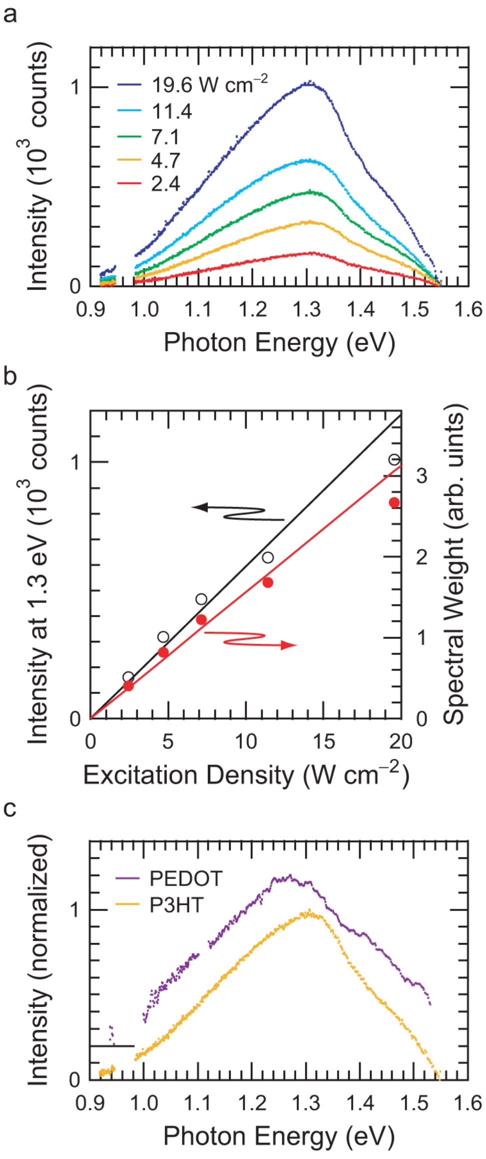

**Figure 3.** Photoluminescence spectra. (a) Steady-state photoluminescence (PL) spectrum and its dependence on excitation intensity of doped drop-cast P3HT film (doping (immersion) time, 2 h) excited at 1.58 eV. (b) Dependence of peak intensity and spectral weight of the steady-state spectrum on excitation density. (c) Steady-state PL spectrum of free-standing PEDOT−PSS film excited at 1.58 eV with an excitation density of 4.5 W cm$^{-2}$ (purple). For comparison, the steady-state PL spectrum of a doped P3HT film measured at a similar condition to that in (a) is also shown (orange). The baseline is shifted for display clarity.

polarons. This is supported by the result that the exciton PL from undoped P3HT films, which is situated above ∼1.2 eV and peaked at ∼1.6 eV,[29] was not detected in our measurements. Figure 3c shows the steady-state PL spectrum of a free-standing PEDOT−PSS film together with that of the doped P3HT film. Although side chains of the two polymers are completely different from each other (see the insets in Figure 2 for chemical structures of the two polythiophenes), the PL spectra are situated in a similar energy region, indicating that the observed PL is emitted not from some excited state related to the side chain but from the photoexcited polarons on polymer chains.

We then examine the PL spectral shape in Figure 3c. The PL spectrum of the doped P3HT (PEDOT−PSS) film shows a broad band with a peak at 1.30 (1.27) eV with fine structures at 1.47 (1.44) and 1.13 (1.09) eV. The fine structures are attributed to vibronic sidebands, because the energy separation of ∼0.17 eV corresponds to the C═C stretching mode of ∼0.17−0.18 eV in doped polythiophenes.[24] The vibronic sidebands of the C═C stretching mode in the spectra support the conclusion that the observed PL is emitted from photoexcited polarons on polymer chains. The reason that the vibronic sidebands are observed in the PL spectrum in contrast to the inhomogeneously broadened absorption spectrum is because the PL is predominantly emitted from photoexcited polarons with P1−P2 transition energy which is resonant with the excitation light and/or because the backbone planarization in the excited state might reduce the inhomogeneity.[29]

**Time Evolution of PL Intensity.** Figure 4a shows the time evolution of PL intensities in doped drop-cast P3HT films (immersion time, 1 and 6 min) excited at 1.55 eV with an excitation density of 0.39 $\mu$J cm$^{-2}$ per pulse. The upper two curves for PL at 1.1 eV in the P3HT films with 1 and 6 min immersion times show that the decay of PL intensity becomes fast with the increase in immersion time, i.e., with the increase in doping. The lower four curves for PL at 1.1, 1.2, 1.3, and 1.4 eV in the P3HT films with a 6 min immersion time show the same decay behavior within the error. Before examining the details of the decay behavior, we confirmed that the observed PL is emitted from the photoexcited polarons. Figure 4b shows the linear dependence of peak intensity at the time origin and integrated intensity of the time evolution of PL at 1.1 eV in the P3HT film with a 1 min immersion time on excitation density. Their linear dependence indicates that the observed PL is emitted from photoexcited polarons, and its time evolution reflects their linear decay process.

The time evolution of PL intensities in Figure 4a shows nonexponential decay, and the decay time is not constant over time. Consequently, we fit the time evolutions to a stretched-exponential function $I\ \exp[-(t/\tau)^{\beta}]$, which is convoluted with the instrument response function of the measurement system (a Gaussian form with a full width at half-maximum of 120 fs). When the parameters $\beta$ and $\tau$ are 0.27 (±0.02) and 70 (±20) fs, the fitting is fairly good for the 1-min-immersed film, as shown in Figure 4a (top black curve).[30] Similarly, a stretched-exponential function with $\beta$ of 0.31 (±0.02) and $\tau$ of 20 (±10) fs reproduces well the PL decay for the 6-min-immersed film (lower four black curves in Figure 4a). The time evolution of PL intensity in the free-standing PEDOT−PSS film in Figure 4c (excitation density, 0.39 $\mu$J cm$^{-2}$ per pulse) shows nonexponential decay and is fitted to a stretched-exponential function; $\beta$ and $\tau$ are 0.23 (±0.02) and 50 (±20) fs. Since the parameters $\beta$ and $\tau$ in the three samples have similar values, the relaxation process of photoexcited polarons is independent of the side chain.

**Relaxation Process of Photoexcited Polarons.** We discuss the relaxation process of the photoexcited polarons. Earlier ultrafast time-resolved measurements for $\pi$-conjugated polymers indicated that the relaxation of photoinduced polaron states occurs mostly within 100 fs with a broad distribution of time scales by the coupling of the polarons to vibrational motions.[31,32] This suggests that the relaxation of photoexcited polarons in this study is also caused by the lattice relaxation. However, as shown in Figure 4a, the PL intensity in the P3HT

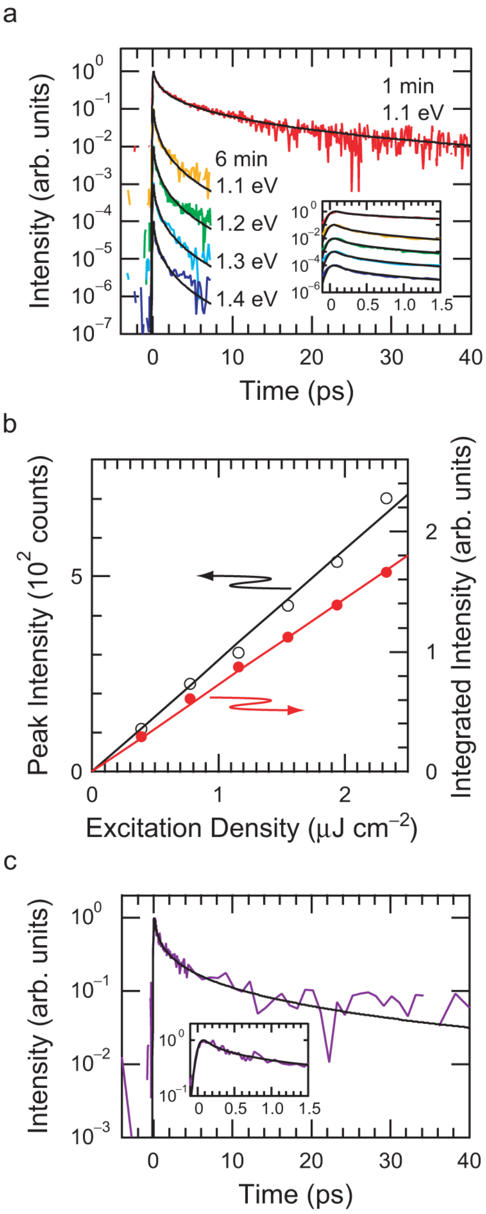

**Figure 4.** Time evolution of photoluminescence intensity. (a) Time evolution of photoluminescence (PL) intensities in doped drop-cast P3HT films (doping (immersion) time, 1 and 6 min) excited at 1.55 eV with an excitation density of 0.39 $\mu$J cm$^{-2}$ per pulse. The black curves are fitted results of stretched-exponential functions. (b) Dependence of peak intensity and integrated intensity of the time evolution of PL intensity at 1.1 eV in doped drop-cast P3HT film (immersion time, 1 min) on excitation density. (c) Time evolution of PL intensity at 1.1 eV in free-standing PEDOT−PSS film excited at 1.55 eV with an excitation density of 0.39 $\mu$J cm$^{-2}$ per pulse. The purple curve represents experimental results. The black curve is a fitted result of a stretched-exponential function.

film with a 6 min immersion time decays faster than that in the P3HT film with a 1 min immersion time. This result indicates that the relaxation of photoexcited polarons is caused by a doping-induced relaxation process, not by spontaneous relaxation processes.

The stretched-exponential function is often used for describing PL decay reflecting the relaxation processes due to excitation energy transfer in material ensembles and diffusion-induced relaxation.[33,34] Both relaxation processes are possible in doped polythiophenes. In our samples, owing to the inhomogeneity indicated by the absorption spectra in Figure 2, a photoexcited polaron (energy donor) finds another polaron (acceptor) with lower transition energy, and excitation energy transfer between them is expected. In the undoped P3HT solution and film,[29] excitation energy transfer of exciton toward polymer segments of longer conjugation lengths, i.e., lower transition energies, with the typical time constant of ~0.5−1 ps has been observed, and the PL decay becomes slower as the probed photon energy decreases. Consequently, the energy dependence of the PL decay should be observed if the PL decay in our experiments is determined by excitation energy transfer. However, the PL in the energy range 1.1−1.4 eV in the P3HT film with a 6 min immersion time in Figure 4a shows the same decay behavior. Therefore, relaxation of photoexcited polarons due to excitation energy transfer is ruled out, and we attribute it to diffusion-induced relaxation.

The diffusion-induced relaxation process gives rise to the decay behavior expressed by the stretched-exponential function. The value of $\beta$ = 1/3 corresponds to the one-dimensional diffusion of the photoexcited state toward relaxation centers in the long time region, while for two- and three-dimensional diffusion $\beta$ = 1/2 and 3/5, respectively.[35−37] The values of $\beta$ obtained in our experiments are 0.23, 0.27, and 0.31, and close to 1/3 rather than 1/2 and 3/5, indicating the photoexcited polarons diffuse one-dimensionally on the polymer chain. Femtosecond time-resolved PL measurements enable us to observe the fast transport that occurs within the polymer chain, although regioregular P3HT shows a highly ordered $\pi$ stacking, leading to the high transport properties between polymer chains, i.e., the high two- or three-dimensional transport.[38−40] It is noted that the recent study of polarization-resolved THz transmission through a doped regioregular P3HT film consisting of partially oriented polymer chains has indicated that the charge transport occurs mainly along polythiophene chains.[41]

In the present case, possible relaxation centers include structural defects and polarons. In chemically doped polythiophenes, dopants are in the vicinity of a polymer chain, resulting in structural defects such as torsion of the chain, and these defects might be the relaxation centers. However, undoped regiorandom P3HT films, where torsional defects are involved, show long-lasting exciton decay in the time regime of several hundreds of picoseconds.[42] Thus, torsional defects should not be the origin of the relaxation of photoexcited polarons, and the most plausible relaxation centers in the present case are polarons.

The photoexcited polarons diffuse one-dimensionally on the polymer chain, and the interaction with other polarons on the same and/or other chain occurs. Then, the photoexcited polarons decay by (1) forming bound states such as bipolarons[43−46] and polaron pairs ($\pi$-dimers)[47−49] with another polaron in the region with a low local density of polarons or (2) inelastically scattering other polarons in the polaron band in the region with a high local density of polarons. For scenario 1, the formation mechanism of a bipolaron we propose is electron transfer from a photoexcited polaron to other polaron, where the photoexcited polaron turns out to be a bipolaron and the other forms a bound state with the electron or is annihilated, leading to the relaxation of the photoexcited polaron and thus quenching of the PL. For the formation of a polaron pair, the generated polaron pair might still be in the excited state and be subject to radiative decay. In such a case, however, the luminescence band is situated in the energy region different from that of the polaron, because the electronic structure of the polaron pair is different from that of the polaron. For scenario 2, in analogy with the relaxation of a photoexcited carrier in a metal, the intraband scattering causes the relaxation of a photoexcited polaron and thus quenching of the PL.

The inverse of characteristic diffusion time $\tau$ is given by $2\pi^2(3/2)^3Dn^2$, where $D$ is the diffusion constant and $n$ is the one-dimensional density of relaxation centers.[35] Using $\tau$ = 70 fs and $n$ = 0.22 nm$^{-1}$ (estimated from a polaron density of 1.9 × 10$^{19}$ cm$^{-3}$),[22] the value of $D$ is estimated to be 5 × 10$^{-2}$ cm$^2$ s$^{-1}$ for the P3HT film with a 1 min immersion time. The diffusion constant is related to the mobility $\mu$ by $D = \mu k_B T/e$, where $k_B$ is the Boltzmann constant, $e$ is the elementary charge, and $T$ is the temperature. Consequently, the corresponding mobility is 2 cm$^2$ V$^{-1}$ s$^{-1}$. This value is in good agreement with that estimated for the P3HT film with a 6 min immersion time; using $\tau$ = 20 fs and $n$ = 0.41 nm$^{-1}$ (polaron density of 1.3 × 10$^{20}$ cm$^{-3}$),[22] the mobility is estimated to be 2 cm$^2$ V$^{-1}$ s$^{-1}$. For the PEDOT−PSS film, using $\tau$ = 50 fs and $n$ = 0.46 nm$^{-1}$ (polaron density of 1.8 × 10$^{20}$ cm$^{-3}$),[22] the mobility is estimated to be 0.6 cm$^2$ V$^{-1}$ s$^{-1}$.

In the calculation, we assume that the formation of the bound states of polarons or the inelastic scattering of polarons occurs with a probability of one, and thus the estimated mobility is the lower bound. These values are larger than the reported highest value, on the order of 0.1 cm$^2$ V$^{-1}$ s$^{-1}$, in the field-effect transistor configuration.[1−3,8] This is because our estimated mobility reflects the one-dimensional short-range transport that is free from grain boundaries and conjugation breaks,[9,10,12,13] while the transport properties in the field-effect transistor are much more affected by them. Our values of mobility are consistent with those of photoinduced polarons in undoped polythiophenes obtained by optical-pump THz-probe measurements,[13] where short-range transport is observed.

The above estimate was done under a point particle approximation of a polaron, while the finite size of a polaron (3−5 thiophene rings) has been shown by electron spin resonance and absorption measurements[43,44] and theoretical calculations.[45,46] The finite size of a polaron decreases the effective distance between polarons; for example, for $n$ = 0.22 nm$^{-1}$, the corresponding interpolaron distance under a point particle approximation is 4.5 nm, while the finite size of a polaron with four thiophene rings (∼1.6 nm) makes an effective interpolaron distance of 2.9 nm. This effect causes a change in our estimation of mobility from 2 cm$^2$ V$^{-1}$ s$^{-1}$ to 0.8 cm$^2$ V$^{-1}$ s$^{-1}$. However, even in this case, the value is larger than 0.1 cm$^2$ V$^{-1}$ s$^{-1}$.

Since the samples in this study were subject to no special care during preparation and contained dopant ions, the intrachain conjugation length should not be as long as those reported in early studies, for example, ∼20−25 thiophene rings.[38] Thus, the polaron mobility in an ideal one-dimensional chain might be larger than that obtained in this study. It was demonstrated that the femtosecond time-resolved PL measurement is a powerful tool to investigate the polaron mobility through observation of relaxation processes of photoexcited states in doped polymers. Future studies on carrier-density- and structure-controlled polymers are expected to clarify the upper limit of the mobility in doped polymers.

## METHODS

**Sample Description.** P3HT used in this study was obtained from Sigma-Aldrich Co. (regioregularity >98.5%). P3HT films were fabricated by casting a chloroform solution of P3HT on quartz substrates. As thin (thick) films are suitable for absorption (PL) measurements, the spin-coating and drop-casting methods were used for fabrication of thin and thick films, respectively. Doping was performed by immersing the films into an acetonitrile solution (0.050 mol/L) of $Cu(ClO_4)_2$ and then rinsing them in pure acetonitrile.[21,22] In this immersion procedure, the doping is almost fully saturated before the total doping time of up to 6 min (carrier density 1.3 × 10$^{20}$ cm$^{-3}$).[22] The PEDOT−PSS used in this study was obtained from Sigma-Aldrich Co. (high-conductivity grade), where the carrier density was measured by early THz time-domain spectroscopy[22] to be 1.8 × 10$^{20}$ cm$^{-3}$. PEDOT−PSS films for absorption measurements were fabricated by spin-coating the as-purchased solution on $CaF_2$ substrates. For PL measurements, free-standing films were prepared: a PEDOT−PSS solution was drop-cast on glass substrates, and after drying under ambient conditions, the films were taken off the substrates.

**Experimental Setup.** Absorption spectra were measured using a commercial spectrophotometer. Steady-state PL spectra were measured under excitation by a CW laser diode at 784 nm (corresponding photon energy 1.58 eV). The excitation power was in the range 1.2 to 9.6 mW. PL was focused into a single-grating monochromator placed after a low-pass filter and detected by a liquid-nitrogen-cooled InGaAs photomultiplier. Spectral resolution was ∼6 meV. Spectral sensitivity was determined by measuring the spectrum of a standard tungsten lamp. Time-resolved PL measurements were carried out based on the frequency up-conversion technique[50,51] with a mode-locked Ti:sapphire laser (82 MHz, 800 nm (1.55 eV), 80 fs). The excitation power was in the range 10 to 60 mW. The time and spectral resolutions were 120 fs and 30 meV, respectively. The error of the fitting analysis with the deconvolution method is 10 fs. Steady-state and time-resolved PL measurements were performed using quasi-backscattering geometry. All measurements were conducted at room temperature.

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### Notes

The authors declare no competing financial interest.

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