

Spatial Conformation and Charge Recombination Properties of Polythiophene Derivatives with Thienylene–Vinylene Side Chains Investigated by Static and Femtosecond Spectroscopy

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We report herein the photophysics of three two-dimensional polythiophene derivatives, with different lengths of thienylene–vinylene conjugated side chains, in comparison with regioregular poly(3-hexylthiophene) (P3HT). In solution, an evolution from stimulated emission to photoinduced absorption (PIA) at emission peak is discovered with increasing length of side chains, indicating larger steric hindrance by longer side chains. The exciton lifetime is reduced by a factor of five when the thienylene–vinylene side chain is prolonged to three units. In the film form, we investigate the dynamics of the two PIA bands, assigned to intrachain exciton and interchain polaron pairs, respectively. The analysis of the dynamics suggests that their intrachain exciton decays are similar to the one-dimensional P3HT. The recombination possibility of delocalized interchain polaron pairs occurring in 0.9 ps is reduced with longer thienylene–vinylene side chain samples. Compared with regioregular P3HT film, which self-organizes to form lamellae crystal morphology, the morphologies of these three two-dimensional polythiophenes are amorphous, attributed to the large steric hindrance caused by the existence of side chains. This design of polythiophene derivatives provides the reduction of recombination possibility for delocalized interchain polaron pairs generated in the polymer.

1. Introduction

Polythiophene and its derivatives, a class of promising candidates for organic optoelectronic devices such as polymer light-emitting diodes (PLEDs),^{1,2} polymer field-effect transistors (PFETs),^{3,4} and polymer solar cells (PSCs),^{5–8} have attracted much attention since the discovery of conducting polyacetylene in 1977.⁹ Especially for PSCs, interest in polythiophene greatly increases because of its lower band gap and much higher carrier mobility compared with other polymers.¹⁰ To date, Heeger's group has reported the fabrication of polymer-based photovoltaic cells with power conversion efficiency (PCE) of 6.1%, using the alternating thiophene copolymer in bulk heterojunction composites with the fullerene derivative [6,6]-phenyl C₇₀-butyric acid methyl ester (PC₇₀BM).⁶ Another series of thiophene derivatives with different electron-withdrawing functional groups has been developed lately for PSCs that exhibits the highest PCE values of 7.7%.⁷ More improvements require the designing of new functional polymers, as well as understanding the photophysical processes in the materials. In bulk heterojunction (BHJ) materials, photoinduced charge transfer and charge separation have been discovered. Mobile carriers are generated usually via a two-step process: initial ultrafast electron transfer from the electron donor to acceptor to form an intermediate charge transferred state (CT), followed by the separation of CT states to mobile carriers.¹⁰ The detailed photophysical processes vary to some extent in different materials. From MDMO-PPV to PCBM, the initial electron transfer process is as fast as 45 fs according to Sariciftci's work.¹¹ In comparison, from oligo(th-

ienylenevinylene) (OTV) to PCBM, the electron transfer lasts for ~14 ps,¹² which is 2 orders slower than the former. The separation of CT states occurs on the time scale of several tens of picoseconds. The efficiency of PSCs also depends on other factors, such as absorption bandwidth, carrier mobility in bicontinuous networks, film morphology, and annealing conditions.^{13–15}

In order to explore the potential of polythiophene derivatives, chemical modification is widely used by substitution/addition of specific moieties or side chains to modulate electronic and morphology structures. Using a donor–acceptor approach, several types of low band gap copolymers have been chemically synthesized to better harvest the solar radiation, such as poly(isothianaphene), poly(benzothiadiazole–pyrrole–thiophene), polyfluorene, poly(thienopyranazine), and so on.^{7,16} Cross-linked polythiophenes with vinylene–terthiophene–vinylene conjugated bridges were synthesized to improve charge transportation in PSCs.¹⁷ Li and Chen^{18,19} reported solar cells with PCE of 3.2% and 2.5% using two-dimensional polythiophenes as donors, which possess alkylthiophene conjugated side chains with and without vinylene linkers.

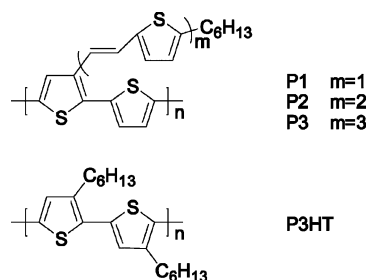
Recently, different types of chemical modified polythiophenes with conjugated side chains have been synthesized.^{17–20} Excited state dynamics of P3HT and photophysical processes in P3HT-based polymer solar cells have been explored by a variety of spectroscopic methods.^{10,26–28} Ohkita and co-workers investigated the charge carrier formation in a series of polythiophene/fullerene blend films by transient absorption spectroscopy on microsecond to millisecond time scales.²¹ However, research on the photophysical processes in chemical modified polythiophene derivatives on pico- or femtosecond time scales, which can be a guide for the chemical modification of more efficient solar cell materials, is quite limited. Li's group recently

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SCHEME 1



synthesized some two-dimensional polythiophenes with different lengths of thienylene–vinylene side chains. Reports revealed that the performance of their PSCs fabricated from the two-dimensional polythiophene was superior to that from P3HT in the same condition.^{18,19} Therefore, in this paper, we studied the photophysical processes of two-dimensional polythiophenes with different lengths of side chains in a series by a variety of optical probe techniques and compared the results with that of the well-known material, P3HT, widely used in PSCs.

2. Experimental Section

The P3HT was purchased from Nichem Fine Technology Co. Ltd., with MW of 68 000. The two-dimensional polythiophenes P1, P2, and P3 were synthesized by Li's group.¹⁹ Scheme 1 shows the molecular structures of P3HT and three two-dimensional polythiophenes (P1, P2, and P3) with different lengths of thienylene–vinylene side chains. Ultraviolet–visible (UV–vis) absorption and emission spectra were recorded with an Agilent 8453 UV–vis spectroscopy system and a Hitachi F-2500 fluorescence spectrophotometer, respectively, at room temperature. The concentration for steady absorption measurement was 40 $\mu\text{mol/L}$ in chlorobenzene and reduced to 4 $\mu\text{mol/L}$ for steady emission measurement. The film samples were drop cast onto quartz substrates from chlorobenzene solution.

The transient absorption (TA) spectroscopy measurements were carried out with a dual-beam femtosecond setup consisting of a second harmonic (415 nm) of a Ti:sapphire chirped-pulse amplification system (Spitfire, Spectra Physics) as the pump (with repetition rate of 1 kHz and pulse duration of 140 fs) and a white light continuum generated in a 1 cm thick water cell as the probe. The pump beam was modulated mechanically at exactly half the repetition rate of the CPA system (500 Hz), and $\Delta T/T$ or ΔOD was detected with a phase sensitive technique using lock-in amplifiers. In order to reduce noise, a separate reference beam, passing through the sample at a different spot, was taken from the probe beam. The TA spectra were recorded by a scanning monochromator in the range of 420–1000 nm. Group velocity dispersion in the probe was compensated by shifting the delay line in order to keep a pump–probe delay independent of wavelength. During measurements, all samples were placed in a rotating sample cell, and the film samples were covered by a slice of clean quartz for protection of oxidation. At each probe wavelength, the PIA decay time constants were obtained by first deconvoluting the experimental signal from the correlation Gaussian time profile of pump and probe (characterized by a fwhm of ca. 500 fs) and then fitting to a sum of exponential terms.

The X-ray diffraction measurements were performed by using a Bruker D8 diffractometer system, equipped with a Ge (220) monochromator. The X-ray wavelength was Cu K α 1 radiation at 1.5406 Å.

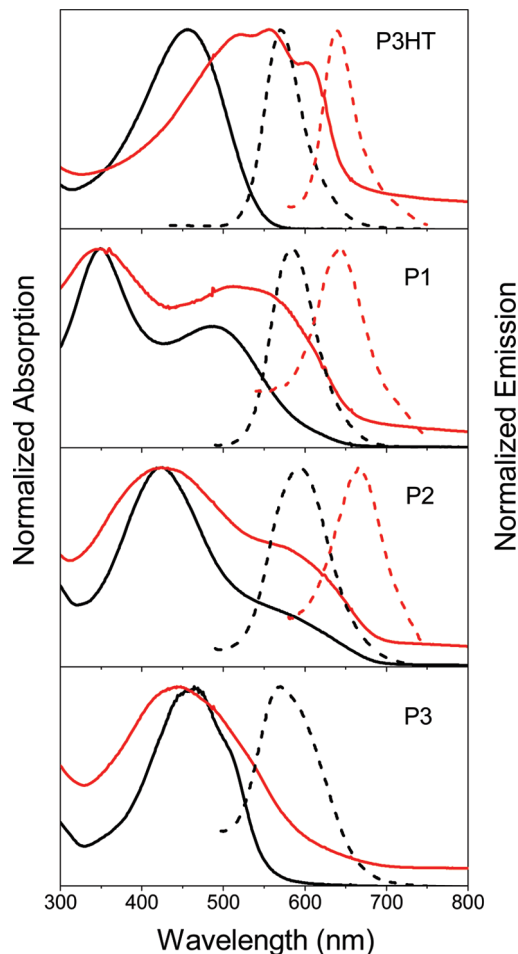


Figure 1. Steady absorption (—) and emission spectra (---) of P3HT, P1, P2, and P3 in dilute chlorobenzene solutions (black) and films (red) drop cast from chlorobenzene solutions.

3. Results and Discussions

3.1. Steady-State Absorption and Emission Spectroscopy.

The UV–vis normalized steady-state absorption and emission spectra of P1, P2, and P3 are presented in Figure 1 both in dilute chlorobenzene solutions and films, as well as those of P3HT for comparison. Both in solution and film phases, P1, P2, and P3 show two absorption bands: the one in the visible region originates from the π – π^* transition of the conjugated thiophene main chains which is the same as that in P3HT, and the other in the UV region is attributed to the thienylene–vinylene conjugated side chains.^{22,23}

In chlorobenzene solution, the absorption peak of side chains red shifts with the increasing of the side chain length, from 350 nm (for P1) to 464 nm (for P3). This is a direct result of increasing conjugation in side chains. In the visible region, the main chain absorption also red shifts from P3HT to P2, indicating a lower band gap of P1 (2.0 eV) and P2 (1.8 eV) due to the overall conjugation. The lower band gap benefits from the coplanarity of the thienylene–vinylene in the side chain conjugated with the thiophene ring in the main chain. However, for P3, the oversized side group brings strong twisting to the main chain, which breaks the backbone conjugation. Therefore, a blue shift of the visible band happens, and a shoulder at 505 nm appears in small amplitude. In this way, the oversized side chains decrease the π – π conjugation of the polymer P3. According to Li's and Chen's work,^{18,19} reducing the side chain density (the ratio of thiophene ring number with side group to that without side group for our samples is 1:1, so the density is

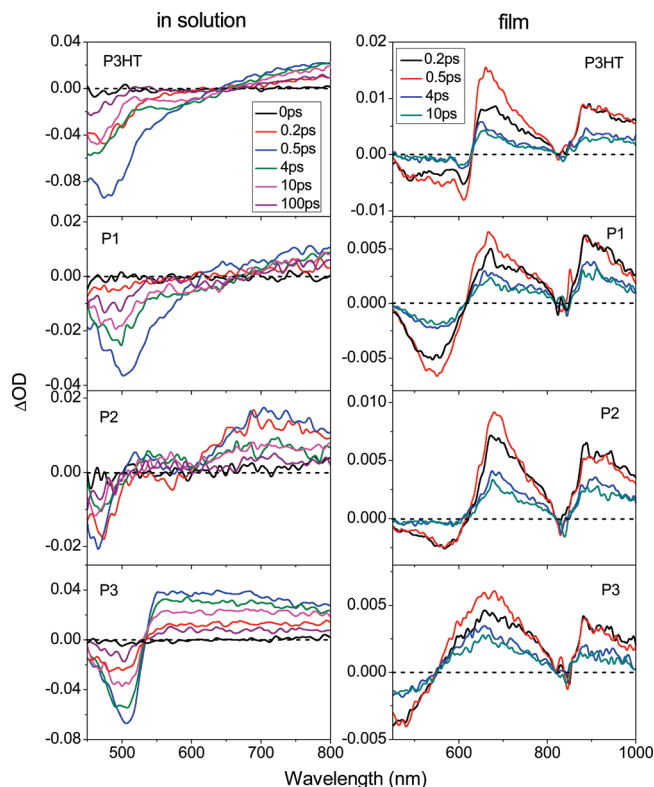


Figure 2. Transient absorption (TA) spectra at different delay times for P3HT, P1, P2, and P3 in chlorobenzene solution (left panel) and film (right panel), following excitation at 415 nm with pump intensity of $150 \mu\text{J cm}^{-2}$.

50%.) would be a pathway to solve the problem, that is to say, leaving larger space between side groups by inserting additional thiophene rings into the main chain.

The steady emission spectra of the polymers in chlorobenzene solution were excited at the absorption peaks of each polymer solution. For polymer P1, we discover that the emission peaks excited at the two absorption peak wavelengths (350 and 489 nm) are nearly the same. The phenomenon is also observed for P2 and P3. The emission spectra similarity of the two-dimensional polythiophenes excited at the two absorption peak wavelengths indicates that there is an intramolecular energy migration from the side chains to the main chains when the polymer is excited at the UV absorption peaks.²¹ In addition, the relative emission quantum efficiency in solution is 36:12:3:1, respectively, for P3HT, P1, P2, and P3.

The absorption and emission spectra of P3HT, P1, P2, and P3 films drop cast from chlorobenzene solutions are also given in Figure 1 for comparison with the data in solution. For P3HT, the absorption of film possesses a large red shift (106 nm) with featured vibronic structures compared with that in solution. The vibronic side bands are assigned to interchain or interplane interactions in the self-organized stacking lamellae reported in the region-regular P3HT films.^{24,25} But for the other three polymer films, the red shift of film absorption is much smaller than that of P3HT, indicating that the interchain interaction in P1, P2, and P3 is much weaker and the morphology of them may be different from that of P3HT. The emission intensity of P3 in film is too low to be detected.

3.2. Femtosecond Transient Absorption. The transient absorption (TA) spectra at different delay times for P3HT, P1, P2, and P3 in chlorobenzene solution and film are shown in Figure 2. In chlorobenzene solution (left panel), the transient spectrum exhibits a photobleaching (PB) band at 470, 500, 466,

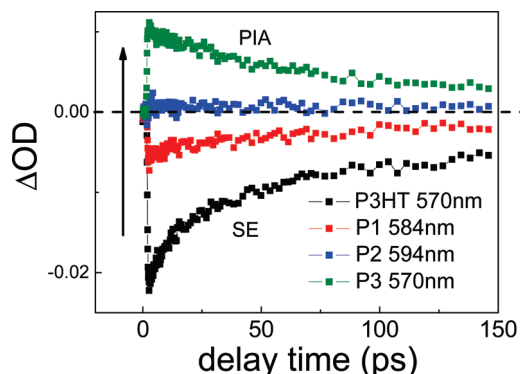


Figure 3. Transient signal decay profiles of P3HT, P1, P2, and P3 in solution probed at wavelengths of emission peaks.

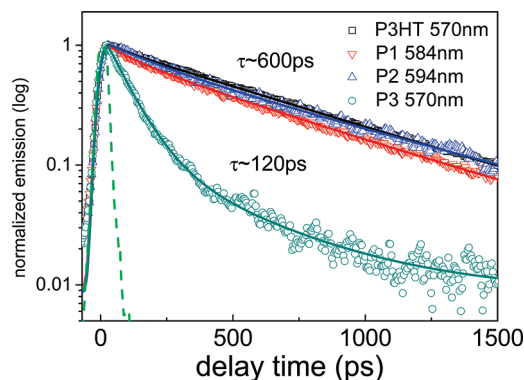


Figure 4. Time resolved fluorescence decay profiles for P3HT, P1, P2, and P3 solutions at emission peaks following excitation at 415 nm. Instrument response function (IRF) is given by the green dashed line. The experimental data and one or two exponential fitted results are given by open scatter dots and solid lines.

and 506 nm, respectively, for P3HT, P1, P2, and P3. The most interesting variation in transient spectra is the band of stimulated emission (SE), which usually locates around the emission peak wavelength in steady emission spectra. In P3HT solution, SE band locates at 570 nm. The intensity of the SE band for P1 reduces greatly at 584 nm. In the situation of P2, the transient signal at the emission peak almost reduces to zero. Negative SE signal turns to positive photoinduced absorption (PIA) signal at 570 nm for P3. Thus, we discover an evolution from SE band to PIA band in the series of polymers, from P3HT to P3, with the increasing of side chain length, as shown in Figure 3. From the evolution, we can conclude that larger side chain group will lead to more conformational defects along the main chain because of larger steric hindrance and strong twisting. The excitons excited in the main chain or transferred from the side chain will be quenched or trapped by the conformational defects, which is coincident with the emission quantum efficiency. With the appearance of defects, the nonemissive state competes with the emissive state and the negative SE signal evolves to positive PIA signal. The singlet state emissive lifetime, which was measured by picosecond time-resolved streak camera technique and given in Figure 4, is found to be composed of two components: a fast decay in 80–150 ps due to a defect related quenching mechanism and a slow decay in 400–600 ps for the deactivating of excitons. From P3HT to P2, the fast decay has small amplitude, from 10% to 25%. This yields an average lifetime of ~ 600 ps (where the average lifetime is given by $(a_1\tau_1 + a_2\tau_2)/(a_1 + a_2)$, τ values being the lifetimes and a values being their amplitudes) for P3HT, P1, and P2, in good accordance with literature reports.^{26,27} On the other hand, the

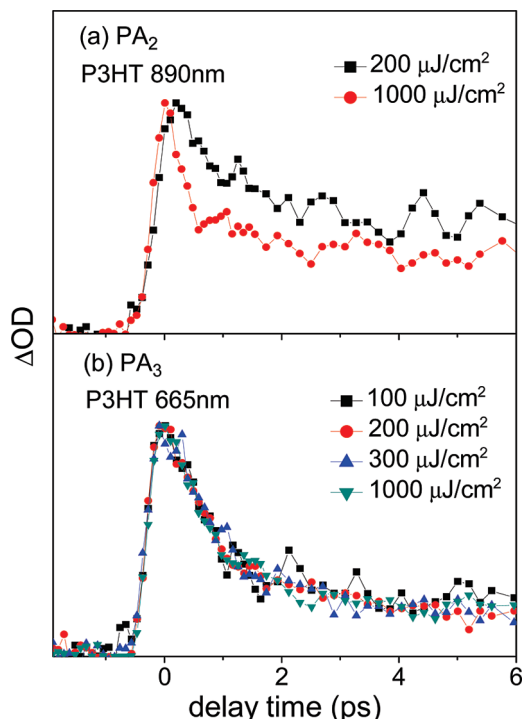


Figure 5. Transient decay profiles of PA₂ (a) and PA₃ (b) in P3HT film at different pump intensities.

amplitude of the fast decay abruptly increases to 90% for P3. The great amplitude reduces the average lifetime to 120 ps for P3. This can be attributed to the abrupt increasing of defect related quenching mechanism, such as twisting motion of the molecular chain, originating from the oversized side groups.

From the TA spectra of films, shown in the right panel of Figure 2, we find that there are two PIA bands for all these thiophene polymers: one in the visible region (650 nm–700 nm) and the other in the near IR around 900 nm, which are assigned to interchain polaron pairs and intrachain excitons, defined as PA₃ and PA₂ in ref 28, respectively. We compared the transient decay dynamics of the two bands in P3HT film under different pump intensities shown in Figure 5, from 100 to 1000 μJ cm⁻². The decay of PA₂ depends on the pump intensity, showing faster decay at higher intensity, which is due to the exciton–exciton annihilation above saturated pump intensity. However, the decay of PA₃ is independent of pump intensity. The initial decay of PA₃ can be fitted by power-law decay because of delocalized interchain polaron pairs recombination, which is in agreement with the diffusion-limited geminate recombination.²⁹ The comparison of the dependence on pump intensity and the power-law decay feature are coincident with Vardeny’s work^{28,30} and confirm the assignment of PA₂ and PA₃.

In order to investigate the chemical modification effect of the two-dimensional polythiophene in bulk materials, particularly on ultrafast dynamics, we compared the two PIA bands decay profiles of P3HT, P1, P2, and P3 in Figure 6, as well as the fitted results in solid lines by three exponential components, which is reasonable in the short time range although it is described by power-law decay in the initial several picoseconds above in Figure 5b for PA₃ band. The fitted parameters are summarized in Table 1. PA₂ decay profiles show the dynamics of intrachain excitons which are generated in the main chains. Because the photon energy of excitation we used is higher than the red edge of the polymer absorption spectrum, we interpret the ultrafast decay process τ_1 (0.6–0.8 ps) as the downhill energy transfer of “hot” excitons, which is an exciton cooling

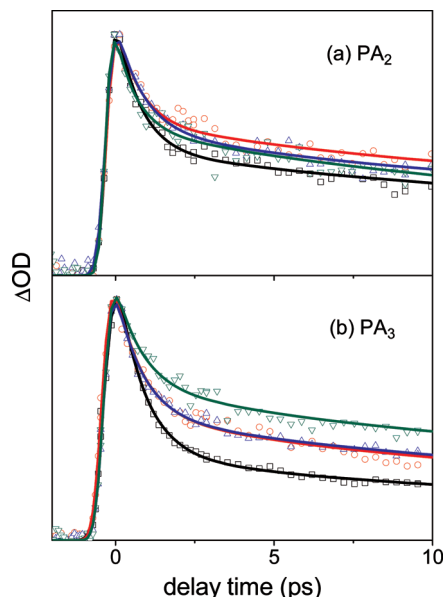


Figure 6. Transient decay profiles of PIA bands for P3HT, P1, P2, and P3 films. The excitation was 150 μJ cm⁻² at 415 nm. PA₂ bands (a) measured at 890 nm decay nearly the same for the different films with different lengths of side chains. PA₃ bands (b) were probed at 665 nm for P3HT (□, dark) and P1 (○, red), 690 nm for P2 (△, blue) and P3 (▽, cyan). The fitted results (the solid lines) are also shown in the figures.

TABLE 1: Decay Parameters of PA₂ and PA₃ Fitted by Three Exponential Functions for P3HT and the Other Two-Dimensional Polythiophenes

samples and probe wavelengths	fitted parameters (ps)		
	τ_1	τ_2	τ_3
PA ₂ band			
P3HT 890 nm	0.7 (60%)	13 (20%)	464 (20%)
P1 890 nm	0.7 (49%)	13 (24%)	457 (27%)
P2 890 nm	0.8 (51%)	11 (22%)	421 (27%)
P3 890 nm	0.6 (50%)	12 (29%)	460 (21%)
PA ₃ band			
P3HT 665 nm	0.9 (75%)	9 (13%)	254 (12%)
P1 665 nm	0.9 (60%)	11 (22%)	244 (18%)
P2 690 nm	0.9 (59%)	11 (21%)	242 (20%)
P3 690 m	0.9 (48%)	10 (24%)	247 (28%)

process, migrating from high energy site to low energy site. The slower dynamics of τ_2 of about 12 ps and τ_3 around hundreds of picoseconds represents the isoenergetic energy transfer after the fast migration.³¹ For the reason of the similarity of main chains for P3HT and the three two-dimensional polythiophenes, the intrachain exciton dynamics decays similarly with each other, as shown in Figure 6a and Table 1. However, the decay profiles of PA₃ bands show a different feature. The fast decay in 0.9 ps (τ_1) exhibits the delocalized interchain polaron pairs recombination. With the increasing side chain length from zero unit (P3HT) to 3 units (P3), the amplitude of the recombination process decreases gradually, 75% for P3HT, 60% for P1, 59% for P2, and 48% for P3, as seen in Figure 6b and Table 1. This decrease shows us that the interchain polaron pairs, which are mobile and delocalized in material, recombine with a lower possibility in the polymer possessing a longer thienylene–vinylene side chain. The longer thienylene–vinylene side chains increase the distance between the polymer main chains, and the recombination possibility of the delocalized interchain polaron pairs is reduced. The localized interchain polaron pairs are less mobile and consequently have slower dynamics corresponding to τ_2 and τ_3 .³⁰

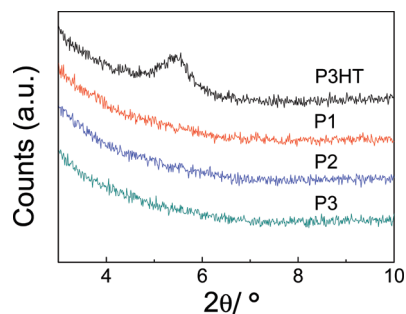


Figure 7. XRD measurements of P3HT, P1, P2, and P3 films.

According to Li's report,¹⁹ the PCEs of polymer based solar cells fabricated with two-dimensional polythiophenes (2.57% and 3.18%), which are very similar to P2, are higher than that fabricated with P3HT (2.41%) under the same experimental conditions. The two-dimensional polythiophene without vinylene linkers also exhibits higher open-circuit voltages (V_{oc}) when blended with fullerene as electron acceptors than the one-dimensional P3HT.¹⁸ This could be a new pathway to design more promising materials by chemical modification methods. According to our research, the two-dimensional design of polythiophene provides reduction of recombination possibility for delocalized interchain polaron pairs generated in the polymer, which could be a significant factor in the improvement of PSCs. Also, the two-dimensional design will possibly increase the communication between neighbor chains.^{18,19} The X-ray diffraction (XRD) measurements reveal that the micromorphology in the three two-dimensional polythiophenes is amorphous, while that of P3HT stacks in lamellae crystal structure, as shown in Figure 7. The diffraction peak of P3HT film fabricated by drop cast is in accordance with that by spin-coated.^{20,24} The amorphous structure of the two-dimensional polythiophenes also supports the analysis of steady state and transient spectra in chlorobenzene solution, showing twisting defects along the main chains, which are caused by the large steric hindrance in two-dimensional polythiophenes.

4. Conclusion

In this work, we have investigated the optical properties of P3HT and three two-dimensional polythiophenes with different lengths of side chains of thienylene–vinylene units, including steady-state absorption/emission spectra and ultrafast transient absorption spectra both in chlorobenzene solution and in drop cast film, as well as time-resolved emission spectra in solution and XRD measurement in film. From the steady-state spectroscopy studies in solution, we found that the overall conjugation strength increases with longer side chains (P3HT, P1, and P2), but the conjugation is reduced for P3 because of large steric hindrance and strong twisting brought by the oversized side chains. An evolution from SE band to PIA band in the series of thiophene polymers with the increasing of side chain length was discovered, which also originates from the steric hindrance in the two-dimensional thiophene polymers. In film samples, we mainly focused on the two PIA bands assigned to intrachain excitons (PA_2) and interchain polaron pairs (PA_3), which have a dependent and independent correlation with pump intensity, respectively. From the decay profiles of the PA_3 band, we deduced that the recombination possibility of delocalized interchain polaron pairs is reduced by the larger thienylene–vinylene side groups. This reduction does great contribution to the higher PCE of solar cell devices based on two-dimensional polythiophenes. Therefore, the two-dimensional thiophene strategy

could be a new pathway for designing more promising materials by chemical modification methods. Moreover, the two-dimensional polythiophenes show amorphous structure rather than lamellae crystal structure in P3HT.

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