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Photophysics and morphology of poly(3-dodecylthienylenevinylene)-[6,6]-phenyl-C₆₁-butyric acid methyl ester composite

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A series of low band gap poly(3-dodecylthienylenevinylene) (PTV) with controlled morphological order have been synthesized and blended with the electron acceptor [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) for organic photovoltaic devices. Two polymers with the most and least side chain regioregularity were chosen in this work, namely the PTV010 and PTV55, respectively. Using photoluminescence, photo-induced absorption spectroscopy, and atomic force microscopy, we find no direct evidence of photoinduced charge transfer between the two constituents, independent of the bulk-heterojunction morphology of the film, although the possibility of formation of P⁺/C₆₀⁻ charge transfer complex was not completely ruled out. The large exciton binding energy ($E_b = 0.6$ eV) in PTV inhibits the photoinduced electron transfer from PTV to PCBM. In addition, excitons formed on polymer chains suffer ultrafast (<ps) intrachain decay to the dark 2A_g state in both PTV010 and PTV55 cases, whereas excitons generated on PCBM molecules undergo energy transfer only to PTV55 in the blend film. Thus, the addition of PCBM increases the photoluminescence yield with respect to neat polymer yield. The efficiency of the energy transfer process is shown to depend on the degree of polymer and PCBM intermixing within the film, which in turn is governed by the polymer chain orders. The effect of such intermixing on the resulting kinetics of photo-induced excitations is also discussed. Our results show limited effect of polymer crystallinity of PTV to its excitonic properties, much the contrary of the case with poly(3-hexylthiophene) which has similar chemical structure with PTV. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4720091>]

Motivated by the progress of poly(3-hexyl)thiophene (P3HT), which has been one of the most commonly used donor polymers for bulk heterojunction organic photovoltaics,¹⁻⁴ recently there have been a large effort and interest in another class of polymer, namely the polythienylenevinylene (PTV).⁵⁻⁸ PTV has a chemical structure that is very similar to P3HT, yet lower bandgap (1.8 eV) which provides a better match with the solar spectrum in organic photovoltaic application. Surprisingly, PTV based devices have consistently yielded poorer performance in comparison with those employing P3HT.⁸⁻¹¹ There are, of course, many factors that determine device efficiency including choice of electrodes and contact resistances, as well as other factors which are governed by photo-active layer morphology. In particular, the chemical modification of the backbone by the attachment of ordered, or regioregular, side chains lead to improved device performance and highlighted the effect of the semi-crystalline polymer morphology on absorption, charge transport, and phase segregation within the bulk heterojunction (BHJ).¹²⁻¹⁵ Majority of previous PTVs do not have controlled arrangement in side chain (called regioregularity), PTV studied here was a series of poly-3-dodecylthienylenevinylene (PDDTV) with different degrees of regioregularity synthesized by Horner-Emmons reaction between the aldehyde and phosphonate groups of two difunctionalized comonomers.⁸ By varying the feed ratio

of the two monomers, a series of PDDTV's with different degrees of regioregularity were produced.⁸ We focus on the two polymers with full regioregularity where the dodecyl side chains are perfectly aligned up with 100% head-to-tail ratio, and full regiorandomness when the side chains are randomly oriented with 25% head-to-tail ratio (Fig. 2(a)), and refer to them as PTV010 (regular) and PTV55 (random), respectively.

In our previous work, we have shown how regioregularity has affected photophysics of neat PTVs.¹⁶ In order to guide effective improvement on organic photovoltaic devices based on this series of PTVs, it is desirable to investigate the photophysics of PTV (as electron donor) and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) (as electron acceptor) blend, and the influence of regioregularity on electronic interaction between polymer and PCBM. PTV studied here is intrinsically dark with very small photoluminescence (PL) quantum efficiency ranging from 10^{-5} - 2×10^{-4} .¹⁶ The transient photoinduced absorption (PIA) shows that the primary intrachain exciton (1B_u) decays within few hundreds fs to a "dark" exciton (2A_g) below it¹⁷; subsequently, the 2A_g exciton may undergo intersystem crossing to long-lived triplets, or be trapped into long-lived polarons, as revealed by continuous wave (cw) PA measurements.¹⁶ In this letter, we demonstrate through PIA and PL spectroscopy and atomic force microscope (AFM) morphological characterization that there is no observable charge transfer in PTV:PCBM blend films regardless of the regioregularity of PTV. Our results are compared with two types of polymer:PCBM composites:

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one, composite of non-luminescent polymer such as polydiacetylene (PDA) with PCBM; two, regioregularity controlled polymer such as P3HT with PCBM which has shown definite photoinduced charge transfer.

Blend solutions of concentration 5 mg/ml in *o*-dichlorobenzene were prepared from PTV and PCBM at 1:1 weight ratio. Films were then cast onto sapphire substrates and allowed to dry for over 24 h before measurements. Thickness measurement was performed by a Dektak profilometer, yielding values on the order of 100 nm for spin coated film and on the order of micrometers for drop cast film. All optical experiments were conducted using a standard PIA setup.¹² An Ar⁺ laser beam at $\hbar\omega = 2.5$ eV modulated at various frequencies, f (10 Hz to 5 kHz), was used for excitation, and an incandescent tungsten/halogen lamp was used as the probe. The PIA signal was measured using a lock-in amplifier referenced at f , a monochromator, and various combinations of gratings, filters, and solid-state photodetectors spanning the spectral range $0.3 < \hbar\omega$ (probe) < 2.7 eV. For PIA and PL measurements, films were mounted inside a Jannis coldfinger cryostat to provide temperature as low as 10 K. The PIA signal is calculated as $\Delta T/T = (T - T_{\text{pump}})/T$, where T_{pump} is the transmission measured while the pump excitation is incident on the sample, and T is the transmission without pump. We used a Veeco Dimension 3100 AFM to profile the surface of PTV. The AFM was set on tapping mode, the tip velocity of the cantilever was set to 20 $\mu\text{m/s}$ and 10 $\mu\text{m} \times 10 \mu\text{m}$ height and phase images were generated.

The absorption of a 1:1 blend of PTV and PCBM film is a linear combination of mainly the absorption from the polymer below 2.5 eV, and predominantly that of PCBM above 2.5 eV (not shown in this paper). Therefore there is no ground state charge transfer between these two constituents.

Figure 1 shows the PL of films of the two neat PTVs, namely PTV010 (regio-regular) and PTV55 (regio-random), and their blends with PCBM with a 1:1 weight ratio. PTV is intrinsically non-luminescent due to the order of $E(2^1A_g) < E(1^1B_u)$.¹⁷ PTV010 film has very weak PL (Fig. 1(a), black circle), whereas PTV55 is not luminescent at all (Fig. 1(b), black circle). The weak PL from PTV010 was not quenched in the PTV010:PCBM blend film (Fig. 1(a), red circle), and the PL acquires a new feature at 1.7 eV which can be attributed to PCBM emission (Fig. 1(a), red circle).¹⁸ The possibility of energy transfer from PTV010 to PCBM is ruled out since the bandgap of the polymer (~ 1.8 eV) is smaller.¹⁶ It is more likely that direct absorption by PCBM accounts for this emission as the two constituents have comparative absorption at the pump energy of 2.54 eV. The PL of PTV010:PCBM blend (Fig. 1(a), red circle) was a simple superposition of PL from PTV (Ref. 16) and PCBM.¹⁸

Regardless of the favorable energy alignment between PTV and PCBM (Fig. 2(b)), there is no occurrence of photoinduced electron transfer. Similar observation was reported in a blend of another nonluminescent polymer PDA with fullerene (C_{60}),¹⁹ and was mainly attributed to the high exciton binding energy of PDA, which inhibits electron transfer onto C_{60} . The exciton binding energy of PTV was measured by electroabsorption to be 0.6 eV,¹⁷ which is even higher than that of PDA (0.5 eV). Therefore, it is no surprise that we did not observe evidence of charge transfer in PTV/

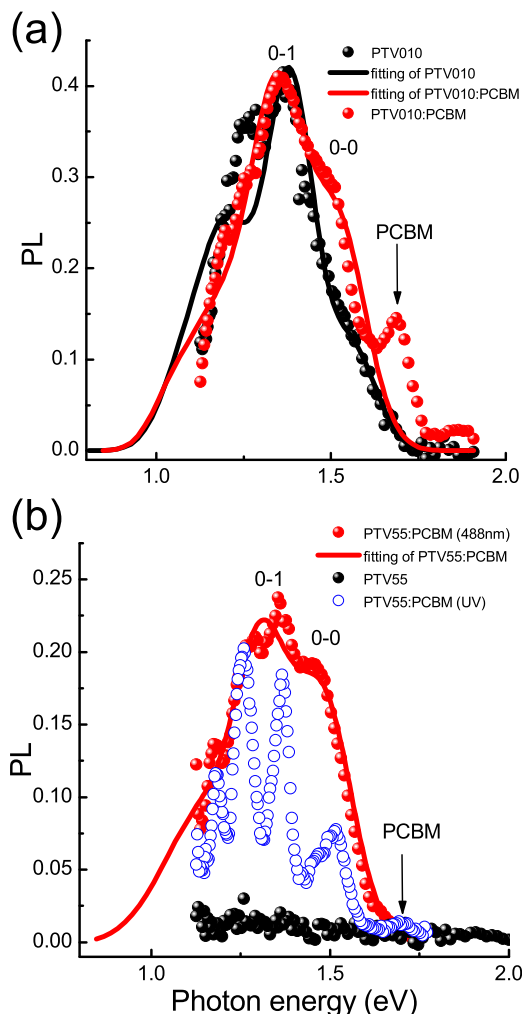


FIG. 1. (a) The PL spectra of films of PTV010 (black circle) and PTV010:PCBM blend with 1:1 weight ratio (red circle). The line through data points is fit using a modified Franck-Condon model using the equation $I(\omega) \sim (n\hbar\omega)^3 [\alpha\Gamma(\hbar\omega - E_0) + \sum (S^m/m!) \Gamma(\hbar\omega - (E_0 - mE_p))]$, where S is the Huang-Rhys parameter which defines the electron-phonon coupling strength; m is the number of the vibrational modes involved in the transition; E_0 is the PL onset at $\sim E(1^1B_u)$; E_p is the strongest coupled vibrational energy, which is taken to be 0.18 eV for C=C stretching vibration; (b) Same as in (a) but for PTV55 film and PTV55:PCBM blend film. As a comparison, the PL spectrum of PTV55:PCBM blend film excited by UV light (blue empty circle) was also shown. The arrow in (a) and (b) indicates the PL from PCBM. All the data were not corrected by the response of grating-si detector, however, all PL were normalized to the 0-1 band intensity for comparison.

PCBM blend. However, unlike the case with PDA/ C_{60} system, where the addition of C_{60} had no effect on the weak PL of PDA,¹⁹ the addition of PCBM instead “brings out” PL in PTV55 film (Fig. 1(b)). This was explained by Förster resonant energy transfer from PCBM to PTV55. Figure 2 illustrates this process. The singlet exciton generated in PCBM transfers its energy to PTV55, creating an exciton that recombines radiatively. In order to prove this scenario, we used UV excitation (3.7 eV) for the same PTV55:PCBM film, and the PL intensity was four times that of the PL when excited by visible (2.5 eV) after normalizing to the pump intensity. Not only so, very weak PL from PCBM itself at 1.7 eV was observed (Fig. 1(b), blue empty circle).¹⁸ Since PCBM has stronger UV absorption than PTV55, more PL is expected from PTV55 upon energy transfer from PCBM.

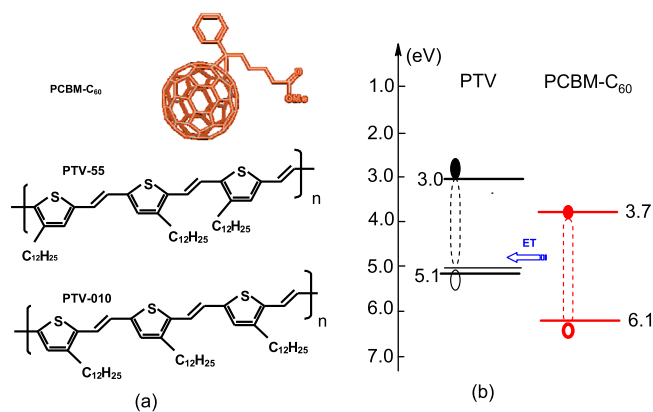


FIG. 2. (a) Molecular structures of [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) and poly(3-dodecylthienylenevinylene) (PTV). Shown are PTV with two regioregularities: PTV55 (regiorandom) and PTV010 (regioregular); (b) Energy levels of PTV:PCBM blend. The broken line shows the highest occupied molecular orbital (HOMO) of PTV55. ET stands for energy transfer from PCBM to PTV.

Furthermore, the energy transfer creates excitons in PTV55 with excess energy (“hot” excitons) allowing for migration to more ordered domains with narrower distribution of conjugation lengths. This explains the red-shift as well as the narrowing of PL peaks as the pump energy is increased from 2.5 eV to ~4.0 eV where PCBM has appreciable absorption.¹⁸ The excitons generated in PTV55 by energy transfer from PCBM could be more likely to emit as compared to those generated by direct absorption by PTV55, as the latter quickly decay to the dark 2A_g state,¹⁷ whereas the former are generated with a delay and could arrive on conjugation segments for which the 2A_g state is already saturated. In PTV010:PCBM blend, no increase in PL from PTV010 is observed. The reason energy transfer from PCBM is apparent only in regiorandom PTV55 is due to the difference in film morphology as will be shown later in this paper.

We could fit the PL spectra using a modified Franck-Condon model that includes vibronic replica.^{20,21} Three parameters, which can be obtained from the fitting, are of importance. E_0 is the PL onset at $\sim E(1^1B_u)$; α is a parameter measuring the 0-0 “suppression degree” from H-aggregates in the film (Ref. 20 and references in), with $\alpha = 1$ for emission of isolated chains in dilute solution.²⁰ S is the Huang-Rhys parameter, which gives the coupling strength between the electronic transition and phonon modes. The best fitting of neat PTV010 PL spectrum yields $E_0 = E(1^1B_u) = 1.55$ eV, $\alpha = 0.30$, $S = 1.65$. On the other hand, fittings for PTV:PCBM blend films gave different parameters: for PTV010:PCBM, $E_0 = E(1^1B_u) = 1.51$ eV, $\alpha = 0.45$; for PTV55:PCBM, $E_0 = E(1^1B_u) = 1.47$ eV, $\alpha = 0.59$, $S = 1.1$ for both blend films. (See Ref. 32 for supplemental materials.) The value of α is less than 1 in all cases, consistent with the high crystallinity of the polymers in both neat¹⁶ and blend films observed in x-ray diffraction measurements (not shown). On the other hand, larger α in blend films shows more disorder in polymer chains, due to the interruption of PTV aggregates by PCBM molecules, as will be shown in AFM images in Figure 3. Going from neat polymer to blend, 0-0 transition energy E_0 was red-shifted, indicating more contribution from aggregates emission due to morphological change upon adding PCBM.

The more complete energy transfer in PTV55:PCBM blend (complete lack of PL from PCBM) comparing with in PTV010:PCBM was mainly due to morphological influence. As shown in Figure 3, the AFM of PTV010:PCBM shows severe and large phase segregation between polymer and PCBM (Fig. 3(d)), and the film is much rougher comparing with PTV55:PCBM (Fig. 3(b)). All these mean that the coupling between polymer and PCBM was much weaker in PTV010:PCBM blend, which is consistent with less efficient energy transfer from PCBM to PTV010 in this blend film. AFM images shown in Figure 3 indicate much better miscibility between PTV55 and PCBM, partly due to better solubility of PTV55 than PTV010 in dichlorobenzene.⁸ Very small contrast was observed in the phase image of PTV55:PCBM (Fig. 3(b)). This indicates that PTV55 and PCBM were well mixed forming tiny domains. The inset of Fig. 3(b) shown the same phase image with smaller contrast range (5°), and the polymer region (lighter color) and PCBM regions (darker color) are distinguishable. On the other hand, the separate domains in PTV010:PCBM are as large as microns. Since Förster energy transfer goes with $\sim 1/r^6$, the large separation of host (PCBM) and guest (PTV010) greatly reduced energy transfer rate.

Figure 4(a) shows the PIA of PTV010:PCBM blend measured at two modulation frequencies: low 340 Hz and high 3 kHz. Comparing with the neat PTV010,¹⁶ the long-lived photoexcitations of the polymer, namely polarons

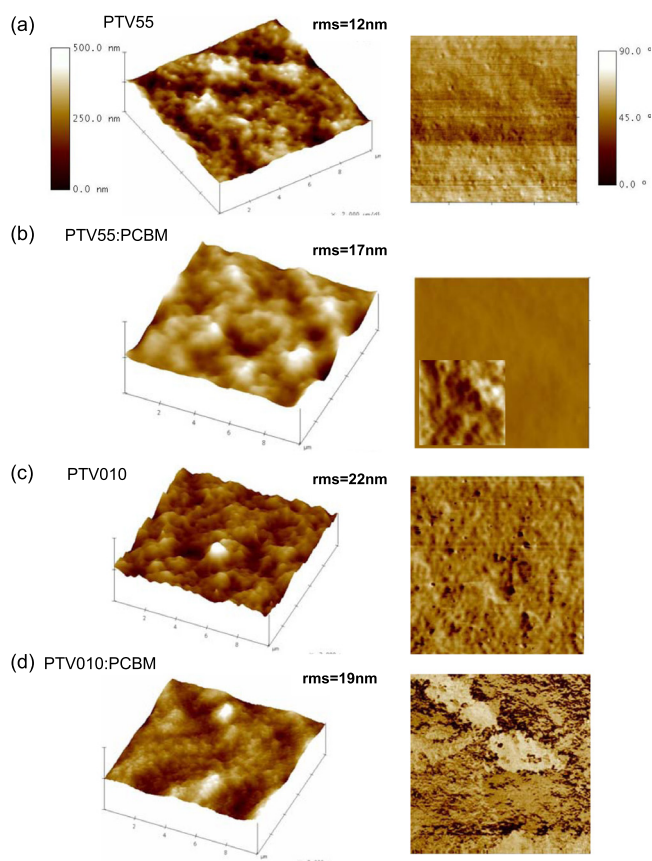


FIG. 3. The AFM images (left panel: topology; right panel: phase) of (a) PTV55; (b) PTV55:PCBM blend; (c) PTV010; and (d) PTV010:PCBM blend films on sapphire substrates. The scanning range is $10 \mu\text{m} \times 10 \mu\text{m}$. Height bar (peak to valley) represents 500 nm, and phase bar (contrast) represents 90°. The inset of (b) right panel is the phase image of a smaller scale (0 to 5°).

($P_1 \sim 0.31$ eV, $P_2 \sim 0.96$ eV) and triplet ($T \sim 1.2$ eV), are preserved in the blend film. Two new spectral features occurred in PTV010:PCBM blend film, the first being a broad band centered around 1.56 eV, and the second a shoulder at 1.3 eV. Both features were enhanced at high modulation frequency of 3 kHz, confirming that they are much faster than the original photoexcitations (polarons and triplet) from PTV010. The lifetime of both species is about $\tau_T^{\text{PCBM}} = 29 \mu\text{s}$, which is consistent with previous report about triplet state of PCBM molecules.¹⁸ Since these two peaks have similar frequency and pump intensity dependences, we assign the lower energy shoulder at 1.3 eV as the phonon replica of PCBM triplet absorption centered at 1.56 eV. The observed PCBM triplet energy is lower than previously measured,¹⁸ and this was interpreted by the PCBM molecules aggregate into crystals,²² and the crystallinity of PCBM was confirmed by glazing angle XRD measurement (not shown in this paper). Due to the variation of PCBM crystal sizes, there was a distribution of triplet state energy, which explains why the observed band was also broader than previously reported in C_{60} fine particles²³ and low concentration PCBM blend.²⁴ The superposition of PCBM triplet absorption peak with the photo bleaching (PB) of PTV010 was also responsible for the blue-shift of PB onset in PTV010:PCBM blend film, comparing the PB onset in neat PTV010 film.¹⁶ Note it is also plausible that the broad band was due to polaron pairs (or charge transfer complex P^+/C_{60}^-) as previously reported in polymer- C_{60} system,²⁵ or a mobile polaron generated via two-step process from the charge transfer complex as recently reported in P3HT/PCBM system.²⁶ However, we assign the transition centered at 1.56 eV to PCBM triplet absorption mainly due to the much shorter lifetime ($\sim 30 \mu\text{s}$) compared with either the polaron pair (comparable to polaron lifetime) from Ref. 25 or the mobile polaron ($\sim 100 \mu\text{s}$) from Ref. 26. Furthermore, the better mixing of PTV55 and PCBM would naturally boost the formation of P^+/C_{60}^- , if the band at 1.56 eV was indeed due to the polaron pair. However, in the PTV55:PCBM blend studied here, this absorption band was suppressed (green line in Fig. 4(a)) due to reduced triplet generation from competition of energy transfer to PTV55 from PCBM. Further experiments on spin characteristics of the long-lived photoexcitations are in process to finalize the assignment of this broad absorption near the band edge.

We did not observe the characteristic C_{60}^- anion absorption between 1.1 eV to 1.2 eV,²⁷ although it was possible that the C_{60}^- peak overlaps with the triplet peak (1.2 eV) of PTV. Since the polymer spectral features are all maintained when 50% by weight PCBM is added, we conclude that no appreciable charge transfer has occurred in the PTV/PCBM blends, regardless of regioregularity of PTV. The tightly bound excitons in PTV and the intra-chain sub-ps decay of these excitons into $2A_g$ state prevents the formation of charge transfer complex P^+/C_{60}^- .¹⁷

However, the lifetime of the original photoexcitations in PTV was greatly shortened. Fig. 4(b) shows the frequency dependence of both in-phase and quadrature PIA signals for PTV010 polaron (P_2) and triplet (T-PTV), as well as PCBM triplet (T-PCBM) in PTV010:PCBM blend film, and the lifetime derived from the cross point of the in-phase and

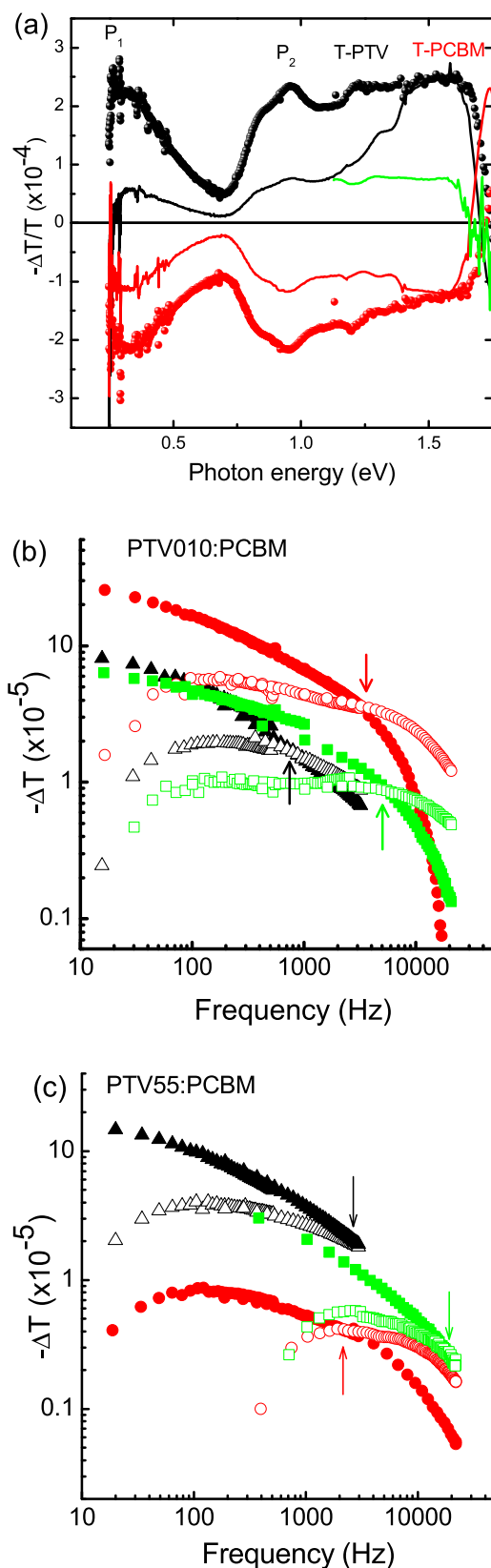


FIG. 4. (a) PIA spectra of PTV010:PCBM blend films measured at two modulation frequencies, 340 Hz (filled circle) and 3 kHz (solid line). Both in-phase (black) and quadrature (red) components were shown; Green line is the PIA spectrum of PTV55:PCBM blend at 3 kHz; The frequency dependence of the (b) PTV010:PCBM blend film, and (c) PTV55:PCBM blend film, for polaron (black, triangles) and polymer triplet (red, circles), and PCBM triplet (green, squares) measured both in-phase (filled) and in quadrature (empty). The laser intensity is 40 mW/cm². In both cases, the sample is at 10 K while under illumination with the 488 nm (2.54 eV) line from an Ar⁺ laser.

quadrature components²⁸ yield $\tau_T^{\text{PCBM}} = 29 \mu\text{s}$, which is consistent with previous measured PCBM triplet lifetime.²⁴ The lifetimes of polaron and triplet lifetime in PTV010:PCBM are: $\tau_p = 0.2 \text{ ms}$ for polaron and $\tau_T = 40 \mu\text{s}$ for triplet, comparing with $\tau_p = 0.2 \text{ ms}$ and $\tau_T = 40 \mu\text{s}$ in neat PTV010.¹⁶ We explain the shortening of lifetime for the polymer photoexcitations by two mechanisms: (1) the reduced electron-phonon coupling might reduce the activation energies of both species; and (2) the PCBM molecules may act as non-radiative recombination centers for such species, thus reducing the lifetime. Fig. 4(c) shows the frequency dependence of polaron and triplet in PTV55:PCBM blend film. It is surprising that $\tau_p = 59 \mu\text{s}$, and $\tau_T = 66 \mu\text{s}$ in this blend film, whereas $\tau_T^{\text{PCBM}} = 9 \mu\text{s}$. All lifetimes are shorter than those in PTV010:PCBM blend (see Table I). We believe the much more efficient energy transfer in PTV55:PCBM plays a role in further reducing the lifetime of PCBM triplet, while the intermixing of PCBM molecules with PTV55 chains results in the shortening of lifetimes of polaron and triplet of PTV55. It appears that the polymer triplet lifetime is reduced by over two orders of magnitude while the polaron lifetime is reduced by only 25 times when PTV010 is blended with PCBM. This might be due to the closeness in energies of polymer triplet at 1.2 eV and the phonon replica of PCBM triplet at 1.3 eV, rendering it difficult to separate these two peaks.

In summary, we have conducted steady-state photophysics study of a series of low bandgap PTV with controlled regioregularity, blended with electron acceptor PCBM. Förster energy transfer was observed in the well mixed, electronically coupled regiorandom PTV55:PCBM blend, However, not in the regioregular PTV010:PCBM blend, due to the morphological variation resulted from polymer chain order. There were no new spectral features in PIA indicating the formation of a charge transfer complex, or separate charge species, unlike the case of P3HT:PCBM blend.^{29,30} All long-lived photoexcitations (i.e., polaron and triplet) in neat polymers were preserved, however, with much reduced lifetime (as much as two orders of magnitude). We explain the shortening of lifetime by energy transfer and increased trapping by the addition of PCBM. Our results were in consistency with recent report on very small electron transfer rate between oligo(thienylenevinylene)/fullerene composite.³¹ Our results have helped to explain the poor performance of OPV devices based on PTV and its derivatives, as the formation of PCBM triplet is detrimental to device efficiency and long term stability.²⁴

TABLE I. Lifetime of various photoexcitations in PIA spectra of neat PTV and PTV/PCBM blend films. P_2 and T are polaron and triplet for neat polymer, respectively; and PCBM-T is the triplet for PCBM molecules.

Film	P_2 (ms)	T (ms)	PCBM-T (ms)
PTV010	5.7	4.7	
PTV010:PCBM	0.20	0.040	0.029
PTV55	3.2	2.4	
PTV55:PCBM	0.057	0.066	0.0090

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