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Citation: *Applied Physics Letters* **102**, 173302 (2013); doi: 10.1063/1.4803912

View online: <http://dx.doi.org/10.1063/1.4803912>

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***In-situ* monitoring of molecular vibrations of two organic semiconductors in photovoltaic blends and their impact on thin film morphology**

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(Received 12 February 2013; accepted 12 April 2013; published online 1 May 2013)

We report *in-situ* simultaneous monitoring of molecular vibrations of two components in organic photovoltaic blends using resonant Raman spectroscopy. Blend films were composed of a low bandgap copolymer thieno[3,2-b]thiophene-diketopyrrolopyrrole (DPPTTT) and (6,6)-phenyl-C₇₁-butyric acid ester (PC₇₀BM). Changes in Raman spectra associated with crystallization processes of each component and their impact on thin film morphology were studied during thermal annealing and cooling processes. Transition temperatures to crystalline phases in blends were measured at ~150 °C and ~170 °C for DPPTTT and PC₇₀BM, respectively. Such phase changes lead to modifications in local chemical composition reducing relative Raman peak intensities ($I_{\text{PC70BM}}/I_{\text{DPPTTT}}$) from ~0.4 in PC₇₀BM-rich domains to ~0.15 in homogeneous areas. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4803912>]

Conjugated polymer-based solar cells have promising potential for low cost solar cells.^{1,2} Recently, power conversion efficiency of ~8%-9% has been reported.³⁻⁵ Most of efficient organic solar cells are fabricated with the active layer composed of low bandgap polymer (electron donor): fullerene (electron acceptor) blends, in which the understanding of morphology of blend thin films is crucial to improve the performance of organic solar cells.^{6,7}

Raman spectroscopy is an inelastic light scattering-based technique which probes the vibrational modes of a material and it is a very valuable tool to probe the morphology of conjugated polymer:fullerene thin films.⁸⁻¹² It has a number of advantages including probing molecular order,^{8,12,13} molecular orientation,^{14,15} *in-situ* chemical reactions,¹⁶⁻¹⁸ and chemical mapping.^{9,12,19} Although Raman spectroscopy is a valuable tool to study the morphology of conjugated polymer:fullerene films, usually Raman spectrum of only one component (polymer) is probed. This is because fullerene molecules, such as (6,6)-phenyl-C₆₁-butyric acid methyl ester (PCBM), absorb at ultra-violet region, which produces small Raman scattering signal under visible laser excitation commonly used for the conventional Raman spectroscopy.

In this letter, we use a visible-light absorbing fullerene, (6,6)-phenyl-C₇₁-butyric acid ester (PC₇₀BM), so that the Raman scattering signal can be significantly enhanced by the resonant Raman effect.^{20,21} It is interesting to notice that there is no reported Raman spectrum of PC₇₀BM molecules. PC₇₀BM is technically important as it can increase the light absorption in visible energy range and it has been used to fabricate some of the most efficient organic solar cells up to date.^{3-5,22} The PC₇₀BM was blended with a new low bandgap co-polymer thieno[3,2-b]thiophene-diketopyrrolopyrrole-

based co-polymer (DPPTTT). It has been shown that DPPTTT has higher charge carrier mobilities among the low bandgap conjugated polymers and DPPTTT: PC₇₀BM solar cells have efficiency of 5.5%.²³ Here, we report that (i) both DPPTTT and PC₇₀BM Raman scattering signals are simultaneously observed in blend thin films, (ii) the molecular rearrangement of DPPTTT and PC₇₀BM in blend films during annealing and cooling processes is probed *in-situ* by monitoring the intensity of the Raman scattering signals from DPPTTT and PC₇₀BM, respectively, and (iii) the spatial distribution of phase-segregated components in the annealed blend films is probed directly by monitoring the Raman signal from PC₇₀BM relative to that from DPPTTT.

The DPPTTT was synthesised in house and its chemical structure (also PC₇₀BM) is shown in Figure 1. It has molecular weights, 102 kg/mol (M_w) and 14 kg/mol (M_n), respectively. PC₇₀BM was purchased from Solenne BV. For the pristine films preparation, 15 mg of DPPTTT or PC₇₀BM was dissolved in 1 ml of dichlorobenzene, the solutions were heated to 60 °C and stirred overnight, they were spin-cast at 1500 rpm for 2 min on oxygen-plasma etched glass substrates, producing film thickness of ~70 nm and ~30 nm for DPPTTT and PC₇₀BM, respectively. For the preparation of blend films, 6.7 mg of DPPTTT and 13.3 mg of PC₇₀BM were dissolved in a solvent mixture containing 0.8 ml chloroform and 0.2 ml dichlorobenzene. The blend solutions were stirred and heated up to 45 °C for an hour, and spin-cast at 2500 rpm for 60 s followed by 4000 rpm for 20 s, producing blend film thickness of ~300 nm. The solution and thin film preparation were carried out following the procedures reported.²³

We used a Raman microscopy (Renishaw InVia) in a back scattering configuration to perform Raman measurements on the DPPTTT, PC₇₀BM, and DPPTTT:PC₇₀BM films. The excitation wavelength is 488 nm (~0.9 mW) for

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the resonant Raman measurements. All the measurements were done in nitrogen environment to reduce degradation. The spectra were obtained with data acquisition time of 10 s and 3–5 data accumulations. The Raman spectra were background corrected using the Renishaw Wire 3.1 program. A Linkam hot/cool stage kit (THMS600) was used to control the temperature (22 °C–240 °C) for *in-situ* Raman measurements. The heating/cooling rate is 10 °C/min.

Figure 1(a) shows the absorption spectra of DPPTTT, PC₇₀BM, and DPPTTT:PC₇₀BM films before and after annealing up to 240 °C. While there are no significant changes in the absorption spectra of neat DPPTTT and PC₇₀BM films after the annealing, for the blend films, the absorption features from DPPTTT increase significantly upon annealing. We will discuss how this change in absorption spectra related to the Raman spectra obtained in the following sections. We also notice that the maximum absorption peak is located at 724 nm for neat DPPTTT film, at 745 nm after blending with PC₇₀BM, and at 715 nm after annealing of the blend films.

Figures 1(b)–1(e) show *in-situ* Raman spectra of DPPTTT and PC₇₀BM films when they were heated up to 240 °C and cooled back down to 22 °C. The nature of various vibrational peaks of DPPTTT and PC₇₀BM were first identified based on Raman spectra simulation of DPPTTT (dimer with side chains replaced by CH₃ group) and PCBM molecule (a similar fullerene to PC₇₀BM) using density functional theory (DFT) at the B3LYP/6-31G* and B3LYP/3-21G levels within the Gaussian 09 package (data not shown).²⁴ Here, the spectral regions containing the main conjugated backbone C=C vibrational modes of the molecules are shown as these modes are most sensitive to morphological changes in thin films.^{8,12,21}

For DPPTTT films, the Raman peak at 1515 cm⁻¹ is assigned to the anti-symmetry C=C stretching mode associated with the diketopyrrolopyrrole unit and the Raman peak at 1412 cm⁻¹ to the C=C stretching mode associated with the fused thiophene unit (Figures 1(b) and 1(c)). The peaks shift slightly to lower wavenumber (~3 cm⁻¹) when the films were heated to 240 °C, but their positions recovered

FIG. 1. Chemical structure of DPPTTT and PC₇₀BM (top left), (a) absorption spectra of DPPTTT, PC₇₀BM and blend films before and after annealing (240 °C), *in-situ* Raman spectra of DPPTTT film during heating (b) and cooling (c) processes, and PC₇₀BM film during heating (d) and cooling (e) processes. The Raman spectra are offset for clarity.

after cooling down to 22 °C. In addition, there is a shoulder peaking at 1502 cm⁻¹ of the 1515 cm⁻¹ main Raman peak. The intensity of this shoulder peak increases (relative to the 1515 cm⁻¹) with increasing temperature, but it reduces upon cooling. The 1502 cm⁻¹ peak may arise from the C=C stretching mode at the fused thiophene unit coupled with side-chain vibrational modes. Our assignments of the peaks at 1515 cm⁻¹, 1502 cm⁻¹, and 1412 cm⁻¹ are consistent with the peak positions of C=C stretching modes assigned for substituted pyrroles (~1565 cm⁻¹) and 2-substituted thiophenes (1514–1534 cm⁻¹, 1430–1454 cm⁻¹) based on infrared/Raman spectroscopy studies.²⁵

For PC₇₀BM films, the Raman peaks at ~1567 cm⁻¹ and ~1468 cm⁻¹ are assigned to the anti-symmetry and symmetry C=C stretch modes, respectively (Figures 1(d) and 1(e)). The intensities of these peaks are reduced and their positions are slightly shifted to lower wavenumbers (~4 cm⁻¹) upon heating, but their intensities and positions again recovered upon cooling. We consider that these reversible changes in the Raman peaks of both DPPTTT and PC₇₀BM films during heating and cooling processes indicate no significant irreversible phase transitions occurring in both films within the temperature ranges used here, which are consistent with no noticeable changes observed in their absorption spectra before and after thermal annealing (Figure 1(a)).

For blend films, the intensities of 1515 cm⁻¹ and 1412 cm⁻¹ peaks (from DPPTTT) integrated over the peak

areas increase significantly from 150 °C (Figures 2(a) and 2(c)) upon heating. These intensities increase by ~40% when going from 150 °C to 170 °C, stay relatively constant from 170 °C to 210 °C, and increase significantly when annealed further up to 240 °C (~50% compared to that at 210 °C). These Raman intensities are irreversible when cooling down to 22 °C (Figures 2(b) and 2(c)). This is in dramatic contrast to the neat DPPTTT film, in which relatively constant intensities of the Raman peaks are observed (Figure 2(e)). The first transition temperature of ~150 °C observed here is correlated very well with the DPPTTT crystallization temperature measured by X-ray diffraction (XRD) in drop-cast blend films (not shown). Therefore, we can safely assign ~150 °C as a transition temperature of DPPTTT to more crystalline phase. The relatively constant Raman intensities of the neat DPPTTT film upon annealing is related to its already highly crystallized phase in the pristine film (not disrupted by PC₇₀BM molecules). Since the neat DPPTTT film is already highly crystallized, the additional thermal annealing produces no noticeable changes for further crystallization, different from the case of DPPTTT in the blend film upon annealing. This is consistent with similar absorption spectra obtained for both non-annealed and annealed neat DPPTTT films, but in contrast to significant changes in absorption for the blend films upon annealing (Fig. 1(a)). Such changes have also been reported for neat P3HT and P3HT:PC₆₀BM blend films.¹³

FIG. 2. *In-situ* Raman spectra of blend film during the heating (a) and cooling (b) processes. The grey bands indicate Raman signals from PC₇₀BM. Integrated intensities of Raman peaks at 1515 cm⁻¹ and 1412 cm⁻¹ during heating (c) and cooling (e) processes of DPPTTT:PC₇₀BM and DPPTTT films, respectively. Integrated intensities of Raman peaks at 1567 cm⁻¹ and 1468 cm⁻¹ during heating (d) and cooling (f) processes of DPPTTT:PC₇₀BM and PC₇₀BM films, respectively. For Figures 2(c)–2(f), the integrated Raman intensities are shown with respect to the values obtained at 22 °C before any thermal treatments.

In contrast, the origin of significant further increases in the Raman intensities upon annealing up to 240 °C is not clear. We consider that further increases in DPPTTT peaks may be induced by segregation of PC₇₀BM molecules from DPPTTT polymer matrix to form PC₇₀BM aggregates (see later section), which allows more DPPTTT chains to be crystallized and thus directly exposed to the Raman excitation, producing stronger Raman signals. Similar to the neat DPPTTT films, the intensity of the shoulder peak at $\sim 1502\text{ cm}^{-1}$ in blend films also increases (relative to the 1515 cm^{-1}) with increasing temperature and it recovers after cooling. These changes in Raman spectra of DPPTTT are also consistent with significantly enhanced absorption of DPPTTT in the blend film after thermal annealing (Figure 1(a)) indicative of better packed crystalline polymer chains.²⁶

On the other hand, the intensities of the 1567 cm^{-1} and 1468 cm^{-1} peaks (from PC₇₀BM) integrated over the peak areas in the blend films are relatively stable upon annealing up to 170 °C (Figures 2(a) and 2(d)). These intensities, however, tend to decrease from 170 °C to 190 °C ($\sim 17\%$) and further drop at 240 °C ($\sim 10\%$). The intensities decreased upon annealing are irreversible after cooling back to 22 °C (Figures 2(b) and 2(d)). Note that such irreversible changes in PC₇₀BM Raman peak intensities are not observed in neat PC₇₀BM films, in which the peak intensities decrease slightly with annealed temperatures, but they totally recover after cooling back to the room temperature (Figure 2(f)).

The transition temperature of $\sim 170\text{ °C}$ observed through Raman peak intensity changes is also found to be well correlated with the transition temperature measured by XRD in drop-cast blend films, in which the crystallization peaks of PC₇₀BM appear (not shown). Therefore, we assign this temperature as a transition temperature of PC₇₀BM to form its crystalline phase. The origin of further reduction in PC₇₀BM Raman peaks at higher temperatures is not clearly understood at the moment; although we speculate, this is due to smaller Raman scattering cross-section of PC₇₀BM molecules in aggregates (i.e., more aggregates, weaker Raman intensities). The PC₇₀BM absorption at the Raman excitation wavelength (488 nm) is expected to be reduced after the formation of aggregates due to considerable changes in its absorption profile (including spectral position), similarly as observed for PC₆₀BM.²⁷ It is interesting to notice in the blend films that PC₇₀BM crystallization seems to occur at slightly higher temperature ($\sim 170\text{ °C}$) than that required for DPPTTT crystallization ($\sim 150\text{ °C}$). This result may imply that enhanced crystallization of DPPTTT polymers assists the segregation and crystallization of PC₇₀BM molecules. This result can explain why the absorption of neat PC₇₀BM film does not change after annealing, but the absorption of PC₇₀BM in blend does change (Figure 1(a)). Also, the Raman peak intensity of neat PC₇₀BM film is reversible upon heating and cooling cycles, but that of PC₇₀BM in blend is not (Figure 2(f)).

FIG. 3. (a) and (b) AFM topography images of DPPTTT:PC₇₀BM blend film after thermal annealing at 140 °C and 170 °C, respectively. (c)–(e) *In-situ* optical micrographs of the DPPTTT:PC₇₀BM film annealed at 190 °C, 210 °C, and 240 °C, respectively. (f) Raman spectra of annealed (240 °C) blend film taken at domain and homogenous regions.