Effects of Conjugated Polymer Incorporation on the Morphology and Energy Harvesting of Solution-Processed Phthalocyanine-Based Thin-Films

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ABSTRACT: Here, we investigate the morphology, spectral absorption bandwidth and energy transfer in solution processed phthalocyanine-based thin films blended with conjugated polymer materials with complementary absorption bands. Unary, binary, and ternary solutions of the solution processable phthalocyanine derivative 2,3,9,10,16,17,23,24-octakis(octyloxy)-29H,31H-phthalocyanine (Oct-Pc) and the conjugated polymers poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO) and poly(3-hexylthiophene) (P3HT) were used to prepare sub-55 nm thick unary-phase and blended thin-films. Spectroscopic analysis shows absorption band full-width-at-half-maximum (FWHM) values increase from between 60 and 160 nm for the individual materials to greater than 450 nm for the composite thin-film ternary blend due to the complementary bandgap energies and spectral absorption bands of the constituent materials. Additionally, photoluminescence and transient absorption measurements show very efficient transfer of excited state energy in the wider band-gap materials (donors) to the narrower band-gap material (acceptor). Resonant energy or charge transfer occurs with efficiencies between 90% and 100% for the various blends. Atomic force microscopy and grazing-incidence wide angle X-ray scattering data indicate that P3HT and Oct-Pc exhibit the poorest blending. This correlates with the lowest donor photoluminescence quenching efficiency due to the extended separation of the P3HT chains from Oct-Pc molecules. However, addition of a relatively small fraction of PFO disrupts Oct-Pc crystallinity and enables improved mixing and energy transfer between P3HT and Oct-Pc.

Introduction

The limited spectral overlap of conjugated organic molecular and polymer absorption bands with the solar spectrum (absorption spectrum full width at half maximum (FWHM) values are in the range 50 - 200 nm at visible wavelengths [1-8]) has led to synthesis of new absorber materials [9-13] and to development of tandem [13,14] and ternary blend device architectures for broadband solar energy harvesting [1-4]. In a ternary blend, an electron donor or acceptor material is added to a binary blend of two

organic semiconductors [2]. Cascading lowest-unoccupied molecular orbital (LUMO) level energies in ternary blend active materials leads to a transfer of energy typically from the higher bandgap material to the lower bandgap material *via* energy or charge transfer. In that way, the spectral absorption band of blended organic thin-films is effectively broadened compared to single-phase (i.e., unary-phase) and binary blend organic thin-films and can yield improved light harvesting across the solar spectrum. The presence (or absence) of a particular energy or charge transfer mechanism typically depends on relative highest-occupied molecular orbital (HOMO) and LUMO energies, the donor-acceptor separation distance, the relative ratios of the materials and spectral overlap between donor emission and acceptor absorption bands. Changes in crystallinity and morphology of ternary-blend organic thin-films compared to binary-blend thin-films have also been reported and can impact the absorption bandwidth and energy transfer favorably or unfavorably depending on the relative ratio, crystallinity and molecular organization of the constituent materials [15,16].

Since bulk-heterojunction (BHJ) thin films consisting of a binary blend of poly(3-hexylthiophene-2,5-diyl) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) are the most widely-studied, solution-processable organic thin-film active layers for photovoltaic applications, the majority of studies of organic ternary blend thin films to date have incorporated a third material into this binary blend system [2]. Poly(9,9-dioctylfluorene-co-benzothiadiazole) (F8BT) and poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7(2,1,3-benzothiadiazole)] (PCPDTBT) are two conjugated polymers that have shown potential as the third active material in P3HT:PCBM thin film [5-7]. For example, the P3HT:PCPDTBT:PCBM system, with weight ratio of 0.8:0.2:1, was reported to outperform the P3HT:PCBM 1:1 system in BHJ organic photovoltaic (OPV) devices after a thermal annealing step (PCE of 2.8% and 2.5%, respectively) [7]. The proposed mechanism for the performance improvement was a two-step charge transfer process: following excitation, electrons transferred

from PCPDTBT to PCBM and, subsequently, the remaining hole carriers on PCPDTBT transferred to P3HT prior to collection at the respective electrode.

Conjugated small molecule absorbers have great potential as sensitizers in OPVs as many have absorption bands that occur in the UV and near-infrared range [8-19]. When incorporated into a ternary system, this allows for a broader absorption band compared to what can typically be achieved with conjugated polymer-based absorber blends. Work by Sharma *et al.* and Choi *et al.* demonstrated that P3HT:PCBM devices incorporating solution processable molecules such as diketopyrrolopyrrole with a cyanovinylene-4-nitrophenyl unit (DPP-CN) or 9,18-(di-2-hexyldecyl)-2,11-dimethoxy-9,18-dihydrobenzo[5,6]-s-indaceno[1,2-b]indeno[2,1-h]carbazol-6,15-dione (HMBI) show improved PCE [8,9]. The P3HT:DPP-CN:PCBM ternary blend extended the absorption edge from 630 nm to 750 nm when compared to the binary blend [8]. Due to the cascading relative offsets of the HOMO and LUMO energy levels, charge transfer was the primary mechanism of electronic interaction proposed between the three materials in the P3HT:DPP-CN:PCBM system, similar to that of the aforementioned polymer blend cases. The HMBI:P3HT:PCBM system extended the blue edge of the absorption band of the binary blend from a wavelength of ~400 nm to below a wavelength of 350 nm [9]. The HMBI:P3HT:PCBM system exhibited a long-range, Förster resonance energy transfer (FRET) process from HMBI to P3HT and then a charge transfer process from P3HT to PCBM.

Other small molecule-based ternary blend systems have employed one or more phthalocyanine derivatives [15-19] to broaden the OPV active layer spectral absorption band and improve overall PCE compared to a binary blend active layer. Phthalocyanines are particularly attractive as materials for solar energy harvesting because their bandgap energy can be tuned close to the ideal value of 1.4 eV dictated by the Shockley-Queisser limit [20-22]. The main drawback is the limited solubility of most phthalocyanine-derivatives in organic solvents which inhibits their uniform deposition via coating or printing methods. Blending of conjugated polymers with phthalocyanine derivatives, such as copper phthalocya-

nine (CuPc), has been suggested to improve the stability and performance of CuPc-based OPV devices [23]. However, investigations of the film forming properties, morphology and energy transfer efficiency in sensitized or blended solution-processable phthalocyanine-based thin films have not been reported. Here, the film forming properties, the absorption spectral bandwidth, and the extent and efficiency of energy transfer in thin-films of a solution-processable phthalocyanine derivative (2,3,9,10,16,17,23,24-octakis(octyloxy)-29H,31H-phthalocyanine (Oct-Pc)) sensitized with the conjugated polymers (poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO) and/or poly(3-hexylthiophene) (P3HT)) are investigated. The complementary absorption bands of the materials generate a broadened absorption spectrum, spanning more than 450 nm, in the ternary blend thin film. Efficient sensitization of Oct-Pc by both conjugated polymers is demonstrated despite significant differences in the extent of spectral overlap between the conjugated polymers and the Oct-Pc. This study also investigates morphological properties of the organic semiconductor ternary blend thin-films compared to binary blends and the unary phase films and the effect of blend morphology on the efficiency of energy transfer.

Methods

Materials. The three organic semiconductors were chosen based on the following criteria. (i) Since the film casting technique was solution based, organic semiconductors that were highly soluble in the same organic solvent were selected. This allowed homogeneous blending of the different molecules in solution prior to casting and ensured a high degree of physical interaction between the materials in the cast film, thereby allowing energy/charge transfer to occur [1]. (ii) Each semiconductor was chosen so that its absorption spectrum was spectrally separated to reduce overlap, allowing for a broader absorption band. (iii) Lastly, the emission spectra of the two higher-bandgap-energy semiconductors overlapped with the absorption spectra the two lower-bandgap-energy semiconductors [24].

Based on the above criteria, the three organic semiconductors chosen for the ternary blend in this study were: poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO; number average molecular weight, $M_n = 48,352$ Da; polydispersity index (PDI) = 3.74); regioregular P3HT ($M_n = 24,091$ Da; PDI = 2.2; regioregularity $\geq 96\%$), and 2,3,9,10,16,17,23,24-octakis(octyloxy)-29H,31H-phthalocyanine (Oct-Pc; molecular weight = 1540.24 Da) [25]. All materials were purchased from Sigma Aldrich and were used without further purification.

Film Fabrication and Characterization. Thin-film samples were fabricated by spin coating solutions of the organic semiconductors, in chloroform, onto glass substrates. The concentrations of the solutions were 2 g L^{-1} for PFO, 5 g L^{-1} for P3HT, and 10 g L^{-1} for Oct-Pc. These concentrations were chosen so that the peak absorbance of each material in the thin-films was similar in magnitude and were limited by the solubility of Oct-Pc in chloroform (upper limit of $\sim 12\text{ g L}^{-1}$). To dissolve the materials in chloroform, solutions were heated to 40°C and sonicated in a water bath for 30 min. $20\text{ }\mu\text{L}$ of the solution was dynamically dispensed onto a glass substrate spinning at 6000 rpm and the substrate was allowed to spin for 1 min.

Film thickness and surface topography were evaluated using atomic force microscopy (AFM; Veeco Digital Instruments Nanoscope III, tapping mode, antimony-doped silicon AFM probe tips with a nominal tip radius of 8 nm). Prior to film thickness measurements, a region of the organic thin-film was physically removed to expose the substrate. Subsequently, AFM scans of a film/substrate region of the sample were acquired and the step size from the top of the film to the substrate surface was extracted from the scans, yielding the film thickness [15].

Grazing-incident wide angle X-ray scattering (GIWAXS) patterns were acquired using the X9 undulator-based beamline in the National Synchrotron Light Source at Brookhaven National Laboratory. Samples were measured under vacuum ($\sim 40\text{ Pa}$) using an incident X-ray beam angle of 0.10° and photon energy of 13.5 keV. The incident beam was focused onto the sample using Kirkpatrick-Biaz mirrors,

which provided a 100 μm wide $\times$ 50 μm high spot at the sample position whose footprint spread along the sample in the direction of propagation. The 2D GIWAXS patterns for each sample were analyzed by taking vertical (out-of-plane) and horizontal (in-plane) line scans. The GIWAXS data provided information on the packing, relative crystallinity and internal structure of the thin-film samples [26,27].

Absorption spectra were obtained using a transmission-based, fiber-coupled UV-Visible spectrometer (S.I. Photonics, Inc., Model 440). Photoluminescence (PL) spectra of the thin-films were acquired using a custom-built PL spectroscopy system capable of three different laser excitations: 355 nm (third harmonic of a Nd:YVO₄ laser operating with 0.6 ns pulse duration, a repetition rate of 25 kHz and an average power density at the sample of 4 mW cm^{-2}); 532 nm (continuous-wave laser diode; average power density at the sample of 26 mW cm^{-2}); and 633 nm (HeNe continuous-wave laser; average power density of 29 mW cm^{-2}). PL emission from the samples was collected, collimated and focused onto the entrance slits of an imaging spectrometer (Andor Shamrock SR 303i) for spectral acquisition.

For time-resolved pump-probe (i.e., transient absorption) measurements, the pulses of a Ti:Sapphire oscillator (Spectra Physics, Tsunami) were amplified in a home-built multi-pass Ti:Sapphire amplifier, which resulted in 0.4 mJ, 70 fs pulses at 790 nm with a repetition rate 1.25 kHz. The output of the amplifier was split into probe and pump beams using a beam splitter. The pump branch was directed to drive a non-collinear optical parametric amplifier (NOPA, Topas White) followed by the second-harmonic generation unit which produced a 3.5 mW train of $\sim$ 25 fs excitation pulses at a wavelength of 370 nm. The probe beam was delayed with the help of a computer-controlled motion controller and focused into a 2 mm sapphire plate to generate a white light continuum. The white light was spatially overlapped with the pump beam in the plane of the thin-film sample. In order to reduce sample heating effects, the thin-film was placed in a quartz cuvette filled with water. To measure the optical density (i.e., absorbance) change (ΔOD), the probe signal was collected by a detector (Thorlabs, DET110) and a monochromator (Oriel MS257 with a 1200 lines/mm grating). The typical power of the pump beam was

200 mW at the thin-film sample. The polarization of the pump beam was set at the magic angle (54.7°) relative to that of the probe beam.

Results and Discussion

The chemical structures of the three organic semiconductors employed in this study and an electronic energy level diagram are displayed in Figure 1a-d [28-32]. All of the materials were soluble in chloroform and were cast into unary, binary or ternary blend thin-films with thicknesses ranging from $\sim 5 - 55$ nm. The concentrations of the organic semiconductors in solutions containing one or more of the semiconductors were fixed at 2 g L^{-1} , 5 g L^{-1} and 10 g L^{-1} for PFO, P3HT and Oct-Pc, respectively.

Figure 1. Chemical structures of (a) PFO, (b) P3HT, and (c) Oct-Pc. (d) Energy level diagram of the three organic semiconductors shown in (a)-(c) with approximate HOMO, LUMO and band-gap energies shown [8-24]. (e) - (h): AFM images ($1.75 \mu\text{m} \times 1.75 \mu\text{m}$) of the surface topography of spin-coated thin-films of: (e) PFO; (f) P3HT; (g) Oct-Pc; and (h) the PFO:P3HT:Oct-Pc ternary blend.

As a result, the binary and ternary thin-films that were cast from blended solutions exhibited thicknesses that corresponded well to the summation of the unary phase thin-film thicknesses of the corresponding materials. For example, average film thicknesses of 5 nm, 15 nm, and 32 nm were measured for the single phase PFO, P3HT and Oct-Pc films, respectively, and the ternary blend film was found to have an average film thickness value of 54 nm which corresponded well to the sum of the respective unary-phase film thicknesses.

Film Morphology and Molecular Order. Figure 1e-h shows surface topographies of PFO, P3HT, Oct-Pc single component thin-films, and the PFO:P3HT:Oct-Pc ternary blend thin-film acquired using tapping-mode AFM. PFO and P3HT formed smooth films with root mean square (RMS) roughness values of 0.48 nm and 0.25 nm, respectively. The Oct-Pc thin-film exhibited a more crystalline surface structure with rod-like domains [31]. This yielded an increased surface roughness of 1.39 nm. However, the surface roughness of the ternary blend thin-film was only 0.47 nm. Although the ternary blend thin-film had a higher overall concentration of material and the Oct-Pc concentration was larger than that of PFO and P3HT, the topography showed new and distinct fibrillar features. This was likely due to a change in molecular organization or crystalline structure of one or more of the materials in the blend relative to that in the single phase [32].

Thin-Film X-ray Scattering Characterization. Grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were carried out to further assess the nanoscale morphology of the thin-film blends (Figure 2). The ultra-thin-film of PFO appeared to be mostly amorphous. P3HT showed predominantly the “face-on” molecular configuration with a relatively high degree of order, based on the distinct intermolecular X-ray scattering peak at small q values [33]. Oct-Pc was significantly more crystalline than the conjugated polymers, with sharp, well-defined X-ray scattering peaks in both the 1-D and 2-D X-ray scattering profiles. The binary blend of PFO:P3HT exhibited scattering peaks similar to that of the unary scattering profiles. The binary blend of PFO:P3HT exhibited scattering peaks similar to

Figure 2. 1D, in-plane grazing-incidence wide-angle X-ray scattering profiles of: (a-c) single-component; (d-f) binary blend; and (g) ternary blend thin-films with concentrations of 2, 5 and 10 g L⁻¹ for PFO (blue), P3HT (green) and Oct-Pc (red), respectively. Insets show 2D diffraction patterns for their respective sample with the intensity scale shown in the inset in (a). The scale bars inset in the 2D diffraction patterns are for the in-plane scattering vector (q_x) and all scale bars are 0.5 Å⁻¹. All 1D scattering profiles were extracted by taking a line profile of the corresponding 2D pattern along the direction indicated by the pink line in the inset of (d).

that of the unary P3HT film with a slight decrease in the degree of order (as evidenced by the increased width of the scattering peak). The other binary systems incorporating Oct-Pc show reduced crystallinity compared to the unary phase Oct-Pc film. In particular, the PFO:Oct-Pc film exhibited a dramatic decrease in the overall crystallinity of the Oct-Pc, which indicated a high degree of mixing of the two materials on the molecular scale. This was also observed in the ternary case. However, P3HT:Oct-Pc still showed many of the characteristic X-ray scattering peaks observed for the unary Oct-Pc film and the peak attributed to Oct-Pc's π - π stacking with a d -spacing of 19.7 Å was still very prominent [34,35]. This suggested that a degree of phase separation between P3HT and Oct-Pc occurred in the P3HT:Oct-Pc blend which was in agreement with the lower energy/charge transfer efficiencies reported below. Interestingly, in the ternary blend, there appeared to be improved mixing between the P3HT and Oct-Pc promoted by the relatively small percentage of PFO (~12 % by weight), as indicated by significantly reduced X-ray scattering from Oct-Pc.

Steady-State Optical Properties. Figure 3a-g shows the absorption and PL spectra of the unary, binary and ternary thin-films. The absorption maxima of the unary phase materials occurred at wavelengths of 393 nm and 544 nm for PFO and P3HT, respectively. Oct-Pc exhibited two strong absorption bands centered at 340 nm and 651 nm. Additionally, there was minimal spectral overlap of the dominant absorption peaks of each material. The full-width-at-half-maximum (FWHM) values of the lowest energy band of the absorption spectra for the single phase films were 55 nm, 162 nm and 167 nm for PFO, P3HT and Oct-Pc, respectively. The binary and ternary blend absorption spectra were almost direct summations of the individual absorption spectra of the constituent materials. This led to strong absorption spanning the near-UV and visible wavelength range, particularly for the ternary blend which exhibited a FWHM of more than 450 nm (Figure 3g).

Figure 3. Optical density, OD, (i.e., absorbance) and PL spectra of: (a-c) single-component; (d-f) binary blend; and (g) ternary blend thin-films with concentration of 2, 5 and 10 g L⁻¹ for PFO, P3HT and Oct-Pc, respectively. Vertical dotted lines represent the laser excitation wavelengths, λ_{ex} , solid black curves represent absorbance spectra and solid colored curves represent PL spectra (the color of the PL spectrum indicates the particular λ_{ex} used to excite the PL: blue indicates λ_{ex} = 355 nm; green indicates λ_{ex} = 532 nm; red indicates λ_{ex} = 633 nm, as represented by the vertical dotted lines). (h) Bar chart of percentage of solar absorption (relative to the AM1.5 solar spectrum) for the unary, binary and ternary blend thin-films. Both actual (black; determined from absorbance spectra of all film types) and expected (red; determined from a summation of the individual single-phase extinction spectra) solar absorption percentages are shown.

The PL spectra (acquired following excitation of the primary absorption transition of each material) of the single phase thin-films exhibited S_1-S_0 0-0 singlet exciton transitions at 430 nm, 666 nm and 776 nm for PFO, P3HT and Oct-Pc and characteristic vibronic structure at longer wavelengths (Figure 3a-c). The binary blends should exhibit emission from the lower bandgap acceptor material and notable quenching of emission from the donor material if significant charge/energy transfer occurs [24]. This was apparent for the PFO:P3HT and PFO:Oct-Pc binary blends (Figure 3d,e) when an excitation wavelength of 355 nm was employed. For both of these binary blends, PFO's characteristic emission spectrum was completely quenched and only emission from P3HT or Oct-Pc was observed. This was expected for the PFO:P3HT blend due to the significant spectral overlap of the PFO emission and the P3HT absorption band. For the PFO:Oct-Pc blend, the significant PFO emission quenching suggested that the Oct-Pc molecules and the PFO chains were in very close proximity to each other since the two materials have little spectral overlap between absorption and emission spectra. In this work, donor-acceptor distances less than ~ 1 nm are likely since the acceptors are present in higher concentrations than the donor molecules and the blends are in the solid state which favors intermolecular interactions. Additionally, due to the large conjugation lengths of PFO and P3HT, their excitons are relatively delocalized and can undergo rapid exciton migration or transfer to neighboring molecules [36,37]. Therefore, in the blended systems studied here short-range Dexter energy transfer and charge transfer can contribute to donor fluorescence quenching in addition to Förster resonance energy transfer. Both Dexter and Förster energy transfer require spectral overlap between donor emission and acceptor absorption and are not expected to cause a reduction of acceptor fluorescence [24]. This is the case for both the PFO:P3HT blend and the P3HT:Oct-Pc blend, whereby the PL intensity from the acceptor in the presence of the excited donor is greater than or equal to the PL intensity from the acceptor alone under the same excitation wavelength; see, for example the PL intensity of P3HT in Figure 3b and 3d under 355 nm excitation. Therefore, although charge transfer is possible, energy transfer is the most likely mecha-

nism for donor PL quenching for the PFO:P3HT and P3HT:Oct-Pc blends. However, at an excitation wavelength of 355 nm, there is a notable decrease in the Oct-Pc PL intensity in the presence of PFO (Figure 3e) compared to Oct-Pc alone (Figure 3c). This suggests that charge transfer is the dominant mechanism donor quenching mechanism in the PFO:Oct-Pc system.

In contrast to the PFO:P3HT and PFO:Oct-Pc binary blends, the PL spectrum from the P3HT:Oct-Pc binary blend exhibited residual P3HT emission in addition to emission from Oct-Pc when the donor (i.e., P3HT) was directly excited at a wavelength of 532 nm (Figure 3f). This incomplete quenching of P3HT's emission indicated that not all of the excitons generated in P3HT were transferred to Oct-Pc. The donor fluorescence quenching efficiency, E_T , in each blend due to either energy or electron transfer was estimated from the fluorescence intensity of the donor under direct excitation (i.e., the excitation laser wavelength falls within the absorption band of the donor) as follows [24]:

$$E_T = 1 - \frac{F_{DA}}{F_D} \quad (1)$$

where F_{DA} is the fluorescence intensity of the donor in the presence of an acceptor and F_D is the fluorescence intensity of the donor in the absence of an acceptor. Note that because the optical density of each material in the films remains constant (see Fig. 3; the optical density of the blends is the sum of the optical densities in the corresponding unary blends) and all of the films are optically thin (<55 nm thick) it is reasonable to assume that the number of excited donor molecules with and without the presence of the acceptor is constant. E_T values determined using Equation 1 for the blends studied in this work are shown in Table 1 along with the proposed dominant quenching mechanism(s).

Table 1. Donor fluorescence quenching efficiency values generated for each binary and ternary thin-film blend system calculated using Equation 1, along with proposed dominant energy/charge transfer mechanism.

Thin-Film Material Composition	E_T (%)	λ_{ex} (nm)	Proposed Mechanism
PFO:P3HT	99.9	355 nm	ET
P3HT:Oct-Pc	90.0	532 nm	ET

PFO:Oct-Pc	99.9	355 nm	CT
PFO:P3HT:Oct-Pc	99.9	355 nm	ET/CT
PFO:P3HT:Oct-Pc	92.7	532 nm	ET/CT

Highly efficient fluorescence quenching ($E_T = 99.9\%$; indicating rapid energy/charge transfer) was apparent for all blends with the exception of the P3HT:Oct-Pc binary blend ($E_T = 90\%$). However, a relatively small fraction of PFO added to the P3HT:Oct-Pc blend improved the energy transfer efficiency between P3HT to Oct-Pc to 92.7%. Compared to the P3HT:Oct-Pc binary blend, when P3HT was directly excited in the ternary blend, weaker emission from P3HT was observed in the ternary blend PL spectrum (Figure 3f,g). This may be due to the disruption of the Oct-Pc crystallinity caused by PFO chains which in turn allows for better intermolecular mixing between P3HT and Oct-Pc molecules. Therefore, even though PFO does not significantly broaden the absorption band of the ternary blend, it appears to play a role in reducing phase separation in the ternary blend and promotes more effective energy/electron transfer to the Oct-Pc.

Transient Absorption. Time-resolved pump-probe (i.e., transient absorption) experiments were performed in order to directly examine the excited-state dynamics in the composite films and, more specifically, to confirm the energy transfer efficiency determined from steady-state fluorescence quenching measurements. Transient absorption decay profiles collected from P3HT, Oct-Pc, P3HT:Oct-Pc and the PFO:P3HT:Oct-Pc ternary blend are shown in Figure 4a for pump and probe wavelengths of 530 nm and 700 nm, respectively. At that pump wavelength, P3HT absorbs strongly (see the corresponding steady-state optical density (i.e., absorbance) spectrum in Fig. 3b), and, therefore, at the probe wavelength, the excited state of P3HT (i.e., P3HT^{*}) gave rise to strong excited-state absorption because the optical density (OD) of P3HT^{*} was higher than that of the ground-state P3HT at 700 nm (Fig. 4a). In contrast, Oct-Pc exhibited a characteristic bleach (i.e., a negative ΔOD signal in the transient absorption decay profile) because the optical density of the Oct-Pc excited state (Oct-Pc^{*}) was lower than that of its

ground state at the probe wavelength following excitation (see Fig. 3c which shows the strong absorbance of Oct-Pc at 700 nm). In Oct-Pc, the ground state bleach at 700 nm associated with the formation of the excited state of Oct-Pc (i.e., Oct-Pc^{*}) appears instantaneously within the time resolution of the measurement (~100 fs). In the P3HT:Oct-Pc and ternary blend films, the dominant light absorbing material is P3HT due to the far greater optical density of P3HT compared with both Oct-Pc and PFO at the pump wavelength of 530 nm (see Fig. 3a-c). As a result, in these samples the initial transient absorption

Figure 4. (a) Transient absorption decay profiles for selected single phase blends, the P3HT:Oct-Pc binary blend, and the ternary blend for a pump wavelength (λ_{pump}) of 530 nm and a probe wavelength (λ_{probe}) of 700 nm. (b) Temporal evolution of transient absorption spectra of the ternary blend with $\lambda_{pump} = 530 \text{ nm}$. (c) Steady-state optical density (i.e., absorbance) spectra of unary phase P3HT and Oct-Pc thin films, over the same wavelength range as for (b), showing the spectral cross-over in optical density between the two materials.

signal at $t = 0$ is dominated by the excited state of P3HT and is positive; however, it rapidly evolves into a bleach within 1 ps, consistent with a fast $\text{P3HT}^* + \text{Oct-Pc} \rightarrow \text{P3HT} + \text{Oct-Pc}^*$ electronic energy transfer process. The time-resolved spectra obtained from the ternary blend film in Figure 4b also show the rapid reduction of the ground state bleach signal (negative ΔOD signal) from P3HT below ~ 620 nm in less than 2 ps and the concomitant rapid change in the positive P3HT* signal to a negative ground state bleach signal from Oct-Pc above ~ 620 nm. This spectral cross over in the ground-state bleach between P3HT and Oct-Pc at 620 nm also agrees well with the spectral cross over in the steady-state optical density spectra for the two materials (Fig. 4c) and confirms rapid energy transfer between P3HT and Oct-Pc in the blended films.

Conclusions

The solution processable, thin-film ternary blend system reported here has the potential to enable an alternative to the stacked tandem organic photovoltaic device configuration with respect to overcoming the inherently narrow absorption bands of organic photovoltaic absorber materials. The thin-film ternary blend exhibited broadband absorption (> 450 nm) and $>90\%$ efficient energy/charge transfer between the components within the blend. While the polythiophene and the phthalocyanine derivatives exhibited strongly overlapping emission and absorption bands, respectively, they exhibited relatively poor mixing. However, introduction of a relatively small fraction ($\sim 10\%$ by volume) of polyfluorene improved mixing of the materials in the ternary blend and also resulted in an increase in the efficiency of energy transfer between polythiophene and the phthalocyanine derivative.

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