PHYSICAL REVIEW B **84**, 205208 (2011)

High-pressure optical studies of donor-acceptor polymer heterojunctions

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(Received 8 October 2011; published 14 November 2011)

Bulk heterojunction polymer solar cells are based on a composite blend of two materials with electron donating and electron accepting properties. We present optical studies of a ladder-type poly(para-phenylene) and a regioregular poly(3-hexylthiophene) polymer blended with a fullerene derivative under hydrostatic pressure. The photoluminescence and absorption spectra reveal different pressure coefficients for the pristine polymer compared with the blended system. Using a phenomenological model to determine the volume change of the system under pressure, we attribute the difference in the pressure coefficient to a change in the band-edge offset at the heterojunction upon enhanced interaction. The band-edge offset is found to increase with increasing pressures for both the ladder-type and thiophene systems.

DOI: 10.1103/PhysRevB.84.205208 PACS number(s): 78.55.Kz, 62.50.−p, 78.40.Me, 84.60.Jt

I. INTRODUCTION

Although the area of donor-acceptor polymer heterojunctions for photovoltaic applications has grown tremendously in the last decade, there are still several underlying questions regarding optical processes, charge generation, and charge transport phenomena across these heterojunctions that are not well understood. The most efficient organic solar cells use a phase-separated composite blend of two materials forming a type-II heterojunction. Major breakthroughs with efficiencies reaching over 8% have been recently reported.[1] A composite of poly(3-hexylthiophene) (P3HT) as the electron donating polymer and [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM) as the electron accepting material yields 4–5% power conversion efficiency (PCE).[1,2] Several low band gap polymers, which can be achieved by alternation of donor and acceptor units in the polymer chain, are being developed to better harvest the solar spectrum.[3]

A typical type-II heterojunction formed by blending a conjugated polymer with PCBM is shown in Fig. 1(a). At the simplest level, excitons are stable if their Coulombic binding energy is higher than the band-edge offsets. On the other hand, if the band offset energy is greater than the exciton binding energy, the exciton can dissociate to form free charges (polarons) as shown schematically by the arrow in Fig. 1(a). A series of recent reports indicate that the process of photoinduced charge separation in polymer heterojunctions involves charge transfer complex (CTC) states that are formed at the interface of the polymer and fullerene phases in the blend. These CTC states are formed deep inside the optical gap of the polymer and fullerene constituents.[4,5] The exact role of CTC states in controlling PCE is still debatable. A recent work shows that interfacial polarons generated with below-gap excitation do not effectively contribute to the photocurrent density in solar cells for typical thicknesses of polymer films used in current solar cell architecture.[6]

Typically, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels in the pristine systems are experimentally known; however, experimental verification of the true band offset in the blended system remains a challenge. Theoretical work by Koster and co-workers shows that the band offset energy has a huge impact on the solar cell efficiency; a 0.1 eV decrease in the LUMO offset (between the donor and acceptor) in P3HT:PCBM solar cell [as shown in Fig. 1(a)] results in 1% increase in the overall PCE.[7] In light of this, an accurate measurement of the band offset energy and how it is impacted by intermolecular interactions in a donor-acceptor blended system are necessary for designing new materials to enhance solar cell efficiencies.

Hydrostatic pressure has played a major role in determining the structure-property relationship and interchain/intrachain interactions in pristine π-conjugated polymers and molecules.[8–10] Continuous-wave (CW) spectroscopy under pressure reveals redshift and broadening of the photoluminescence (PL) spectra, which is interpreted in terms of a strong overlap of the π-electron wave function and strong interchain interactions.[11] Destabilization of localized states as in methylated ladder-type poly-para-phenylene (LPPP)[12] and changes in the backbone planarization of oligophenyls[9] are other attributes of enhanced interaction in these systems. Time-resolved PL of blended fluorene-based copolymers sheds light on the changes in excited state dynamics upon enhanced intermolecular interaction at the heterojunction.[13] Representative pressure data from a donor polymer versus donor:acceptor blend show differences at higher pressures, as seen in Fig. 1. This is discussed in detail in Sec. III A.

Hydrostatic pressure studies were important in determining band offset parameters in GaAs/AlAs interfaces in the mid 1980s.[14,15] Photoluminescence experiments from such heterojunctions under pressure were used to vary the band offset and this information was then used to extract the magnitude of the offset at ambient pressure. In this work we present optical spectroscopic studies of two blended systems under hydrostatic pressure: phenyl-substituted LPPP (PhLPPP):PCBM and P3HT:PCBM. A comparison of the PL and absorption spectra from the blended system with the pristine donor polymer shows differences in the pressure coefficient, which is attributed to a change in the band offset of the heterojunction as a function of pressure. The volume change in the pristine and blended systems under pressure is found to be similar using the optical data. By comparing the pressure coefficient of the optical band gap of the pristine

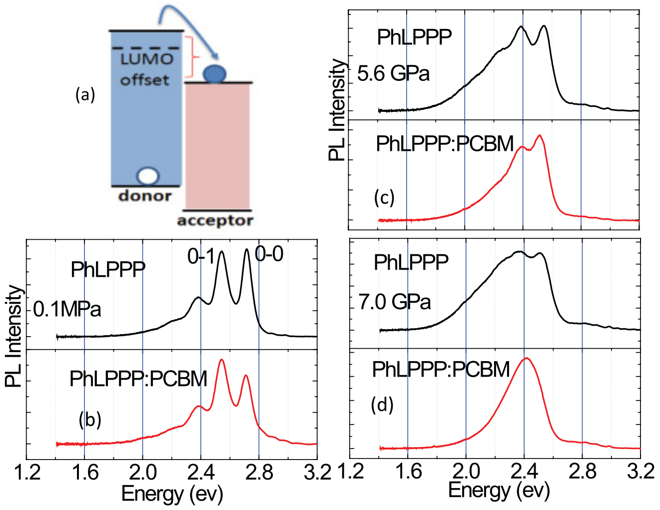

FIG. 1. (Color online) (a) Schematic of a donor-acceptor heterojunction with the hole left behind in the HOMO level of the donor and the electron being transferred to the LUMO of the acceptor. (b)–(d) PL from pristine and blended PhLPPP:PCBM at various pressures.

and blended systems, and C_{60} under pressure, the magnitude of the LUMO offset is determined as a function of pressure. To our knowledge this is the first time such a methodology has been utilized to extract the band-edge offset in organic heterojunctions under enhanced intermolecular interactions. We present the experimental details in Sec. II, followed by our experimental results of photoluminescence and absorption under pressure in Sec. III A. In Sec. III B we discuss a phenomenological model for determining the configuration coordinate parameters under pressure, followed by the LUMO offset energy of both PhLPPP:PCBM and P3HT:PCBM under pressure in Sec. III C.

II. EXPERIMENTAL DETAILS

PhLPPP containing a trace concentration of covalently bound Pd atoms was used as the donor polymer[16] along with PCBM, purchased from Sigma Aldrich, as the acceptor in a 2:1 concentration. The pristine and blended films were cast from dichlorobenzene. The pressure studies were conducted in a Merrill-Bassett-type diamond anvil cell (DAC) with cryogenically loaded argon as the pressure medium. The pressure was measured using the luminescence of a ruby chip located in the pressure chamber. The optical properties of the pristine donor polymer films were also measured under pressure. The PL spectra were excited using the 351 nm line of an Ar ion laser. The luminescence excitation and absorption spectra were analyzed with an Ocean Optics 2000 spectrometer with 25 micron slits. An advantage of using PhLPPP in this study is that both absorption and PL can still be tracked at high pressures in blended films. The higher concentration of the donor polymer in blends (compared to what is used in PV cells) ensured that the luminescence was still observable at higher pressures. Although this work does not take triplet excitation into account, prior work shows that the presence of triplet excitons in PhLPPP enhances solar cell efficiency over singlet-state-only photovoltaic (PV) cells.[17] We also present PL results under pressure from a blended P3HT:PCBM (3:1) film; absorption studies were not feasible in this film due to its thickness.

III. ELECTRONIC STATES UNDER PRESSURE

A. PL and absorption results

Figures 1(b)–1(d) compare the PL spectra obtained from pristine PhLPPP films to those from PhLPPP:PCBM blended films at selected values of pressure. The atmospheric pressure data (0.1 MPa) clearly show that the donor emission is identical for the two films. The slight difference in the ratio of the intensity of the vibronic peaks (0-0/0-1) in the pristine and blended film is due to differences in the thickness of the films, which is difficult to control on the diamond anvil. The 5.6 and 7.0 GPa data clearly show that the vibronic peak position and the shape of the PL spectra are different for the pristine and blended films at higher pressures. To obtain the individual vibronic energies and peak widths, the spectra were systematically fitted with four Gaussian peaks at all pressures.

The planar backbone conformation of PhLPPP [as seen in the inset of Fig. 2(a)] results in clear vibronic features both in the PL and absorption spectra. The 0-0 vibronic energy of the PL and the absorption spectra of PhLPPP are plotted in Figs. 2(a) and 2(b) for both pristine and blended samples. The optical band gap in the blended sample has a slightly lower energy compared to the pristine sample. This is most likely due to a charge transfer upon mixing the two systems; a higher PCBM concentration results in a further lowering of the band gap. We note that in both cases (blended and pristine) the optical band gaps of the donor polymers, PhLPPP and P3HT, were measured. CW spectroscopy does not yield any exciplex emission under pressure in these systems.

A redshift of the π-π^* transition is seen in all conjugated molecules and polymers under pressure.[11] A shift to lower energies of the electronic spectra reflects a higher degree of overlap of the π-electron wave function upon increasing the pressure. Figures 2(a) and 2(b) clearly show that the rate of shift of the PL/absorption energies are different for the pristine and blended PhLPPP samples. The solid lines are quadratic fits over the entire pressure range; the linear component is similar to the values listed in Table I. P3HT:PCBM also shows a slightly higher pressure coefficient compared to pristine P3HT. We point out that blended samples in this work have a higher concentration of the donor polymer compared to typical donor-acceptor ratios used in solar cells. Table I lists the linear component of the pressure coefficient (by fits up to 5 GPa) for the 0-0 absorption/PL vibronic peak from pristine and blended PhLPPP and P3HT.

In this work we have not measured the optical properties of PCBM separately as a function of pressure but rather use the pressure coefficient of the absorption edge of C_{60} found in the literature. Since the bulk modulus of C_{60} and conjugated molecules/polymers are similar ($\sim$10 GPa),[11] a simple approximation is to assume that the only effect of hydrostatic pressure is to decrease the lattice constant of the overall system,[18] according to $P = -B\Delta V/V = -3B\Delta a/a$,

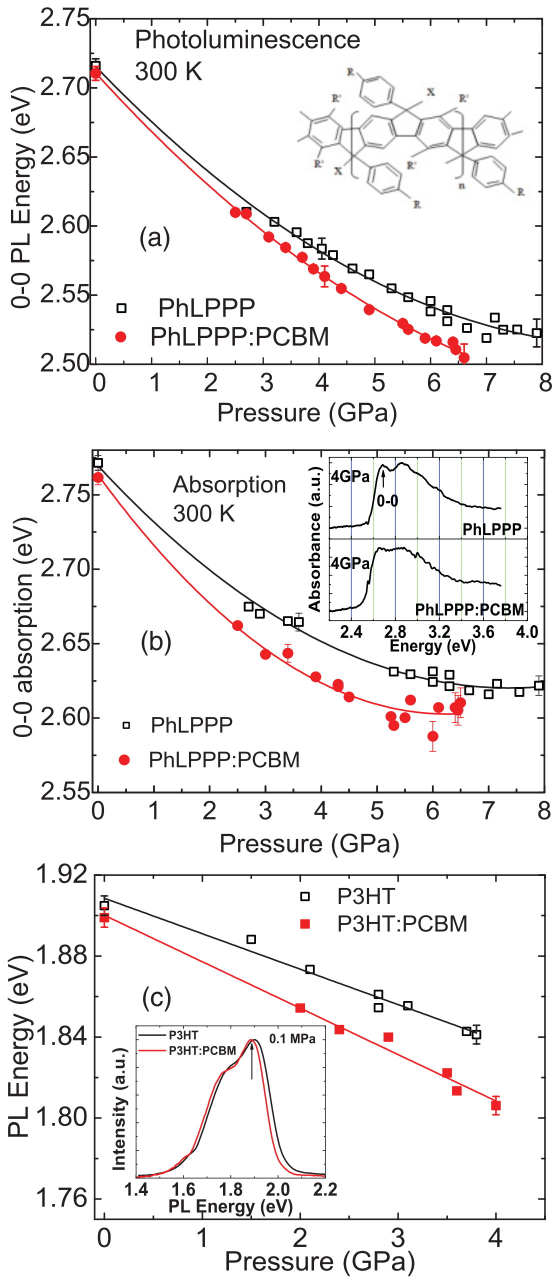

FIG. 2. (Color online) The energy position of the 0-0 vibronic peak in PL (a) and absorption (b) of pristine PhLPPP and blended PhLPPP:PCBM as a function of pressure. The inset in (a) shows the chemical structure of PhLPPP; the inset in (b) shows the absorption spectra of PhLPPP and PhLPPP:PCBM at 4 GPa. The arrow denotes the 0-0 absorption peak. (c) Peak position of the central PL peak of P3HT in the pristine and blended samples as a function of pressure. The inset shows the PL spectra of P3HT and the blended sample at 0.1 MPa. The arrow denotes the central PL peak.

where P is the pressure, B is the bulk modulus, V is the volume, and a is the lattice constant. From the differences in the pressure coefficients of the pristine and blended samples, one may be inclined to attribute this to a difference in volume change of the blended sample compared to the pristine one, which as we see in the following section is not the case. Since x-ray diffraction studies under pressure from these samples are challenging, we estimate the volume change under pressure utilizing the optical data.

TABLE I. Pressure coefficient of the 0-0 PL and absorption vibronic peaks. These parameters were obtained by a linear fit to the peak energies up to 5 GPa.

Sample	α_{0-0} (PL) (meV/GPa)	α_{0-0} (abs.) (meV/GPa)
PhLPPP	-32.4 ± 2.0	-29.4 ± 2.7
PhLPPP:PCBM	-36.2 ± 1.3	-36.1 ± 3.1
P3HT	-17.5 ± 1.1	
P3HT:PCBM	-22.9 ± 1.1	

B. Configuration coordinate parameters

Using a phenomenological model that was proposed by Drickamer and Frank,[19] one can estimate the separation between the ground and excited electronic states in configuration coordinate space upon photoexcitation as a function of pressure. This method gives an estimate of the volume change under pressure. Figure 3(a) shows a schematic configuration coordinate diagram, where the ground and excited electronic states are displaced by Δ at atmospheric pressure. In this simple scheme, we consider only a single configuration coordinate Q and ignore the electronic degeneracy. The impact of pressure may be represented as an increase in the configuration interaction, which significantly changes the energies associated with optical and thermal transitions. A

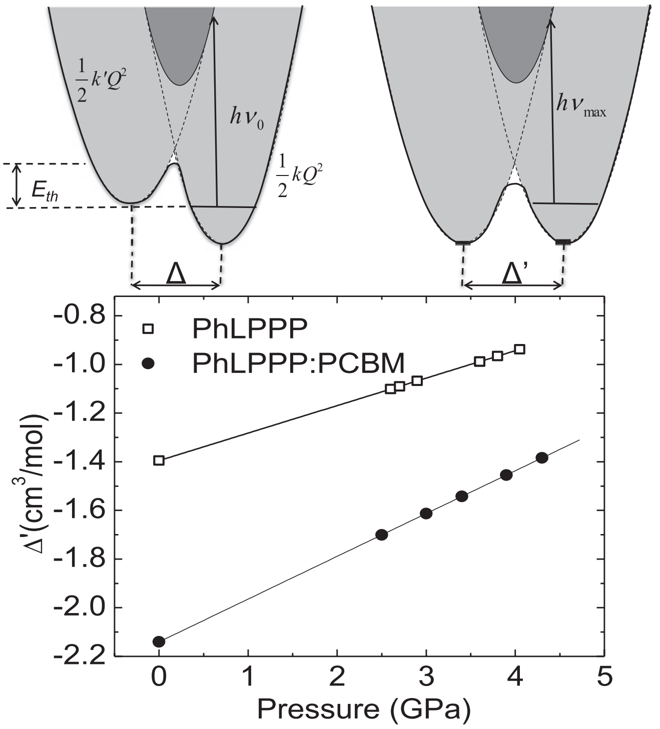

FIG. 3. Top: Schematic configuration coordinate diagram at atmospheric (left) and high pressure (right). E_{th} is E_0 at 1 atm. Bottom: Displacement of the potential energy minima (Δ') as a function of pressure in PhLPPP and PhLPPP:PCBM.

change in the PL/absorption linewidth with pressure implies different compressibility for the ground and excited electronic states. The force constants of the ground and excited states are represented by k and k', respectively. In pressure-induced thermal and optical processes, pressure selects the volume of the system as an appropriate configuration coordinate. Upon application of pressure P, the potential energy of the ground (V_g) and excited states (V_e) may be written as

$$V_g = \tfrac{1}{2}kQ^2 + PQ \tag{1}$$

and

$$V_e = \tfrac{1}{2}k'(Q-\Delta)^2 + PQ + E_0, \tag{2}$$

where E_0 is E_{th} at 1 atm [which is the difference between the bottom of the two wells at 1 atm, as shown in Fig. (3)]. By introducing a new coordinate Q' (where $Q' = 0$ for the new ground state), one can explicitly write the displacement Δ' at P as

$$\Delta' \equiv \Delta + P[1/k - 1/k']. \tag{3}$$

We direct the reader to Chapter 3 of Ref. 19 for a detailed derivation of the model. The PL energy at pressure P is given by

$$h\nu_{\max} = h\nu_0 + \frac{k}{k'}P\left[\Delta + \frac{P}{2}\tau\right], \tag{4}$$

where $\tau = [1/k - 1/k']$. The Gaussian half width of ($\delta E_{1/2}$) of the PL/absorption peaks in terms of the force constants and k_B as the Boltzmann constant is given by

$$\delta E_{1/2} = \left|\frac{k}{\sqrt{k'}\ln 2}(k_BT)^{1/2}[\Delta + P\tau]\right|. \tag{5}$$

Along with a redshift of the PL/absorption energies, a broadening of the vibronic peaks is also seen under pressure (see Fig. 4). For determining the configuration coordinate parameters only the linear part (~5 GPa) of the data (Fig. 2) was used. This reduces Eq. (4) to $(k/k')\Delta = \partial h\nu_{\max}/\partial P$. In the 5 GPa pressure regime, the linear pressure coefficients of the full width at half maximum (FWHM) of the vibronic peaks for the pristine and blended PhLPPP samples are 0.0062 ± 0.0015 eV/GPa and 0.0068 ± 0.0005 eV/GPa, respectively. Using Eqs. (4) and (5) we obtain the ratio of the force constants k/k' to be 1.19 and 1.16 for pristine and blended PhLPPP samples, respectively. This results in $\Delta = -1.39$ cm^3/mol and -2.14 cm^3/mol for pristine and blended PhLPPP, respectively.

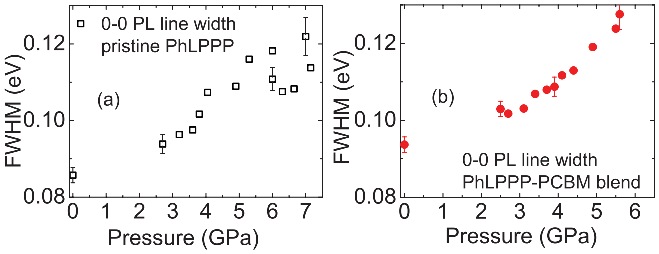

FIG. 4. (Color online) FWHM of the 0-0 PL vibronic in PhLPPP (a) and PhLPPP:PCBM (b).

From Eq. (3) one can deduce Δ' at higher pressures, which then gives an estimate of the change in volume with pressure. Figure 3(b) plots Δ' as a function of pressure yielding a 33% and 35% volume change for the pristine and blended samples, respectively, in the pressure range of 0.1 MPa and 5 GPa. A similar analysis carried out for P3HT and P3HT:PCBM shows ~2% volume change for both pristine and blended samples. Since P3HT is more crystalline compared to PhLPPP, it is not surprising that the overall volume change is smaller compared with PhLPPP.

C. LUMO offset

The above analysis shows that the difference in the redshift of PL/absorption energies in PhLPPP and PhLPPP:PCBM has an origin other than in the volume changes of the two systems. We attribute this difference to a change in the band-edge offset at the heterojunction upon enhanced interaction. Since the pressure coefficient of an exciplex emission could not be measured in the blended systems there is no internal metric for determining the band-edge offsets. However, from the pressure coefficients of the optical gap in pristine and the blended samples, and using the absorption edge data as a function of pressure in PCBM, one can estimate the LUMO offsets at the heterojunction, as outlined below.

The HOMO and LUMO energy levels of PCBM used here are −6.1 eV and −3.7 eV, respectively.[4] The HOMO level in PhLPPP was determined to be −5.27 eV using cyclic voltammetry. The LUMO energy level was estimated by adding the absorption edge energy (at 1 atm) to the HOMO energy, which may underestimate the energy value since the exciton binding energy is not taken into account. However, since the goal here is to estimate differences in the LUMO offset when the donor and acceptor molecules are treated separately versus when they form a heterojunction, the actual value of the exciton binding energy may not play a significant role. *Ab inito* theoretical calculation for anthracene under pressure shows a reduction in the excitonic binding energy with pressure.[20] In our experiments, since the binding energy of singlet excitons in both the donor polymer and PCBM will be lowered slightly upon increasing pressure, the effect may be negligible when we take the differences in the energies of the two systems. We further assume that the change in the band gap with increasing pressure predominantly arises from a shift of the LUMO level; i.e., the HOMO level in both PhLPPP and PCBM remains fixed and that the entire change in the band gap arises due to changes in the LUMO level. This is a reasonable approximation as theoretical calculations show the HOMO levels have smaller pressure-induced changes compared to the LUMO levels.[12]

Since the pressure coefficient of C_{60} (−71 meV/GPa) is known only up to 5 GPa,[21] the LUMO energies as a function of pressure in PCBM were estimated up to that value. The absorption pressure coefficients of PhLPPP and PhLPPP:PCBM were taken into account to determine the LUMO energies at different pressure values of PhLPPP in its pristine and blended form. The LUMO offsets (difference between PhLPPP and PCBM), when the donor and acceptor are treated separately versus when they form a heterojunction, are plotted in Fig. 5. The inset shows a similar trend for P3HT

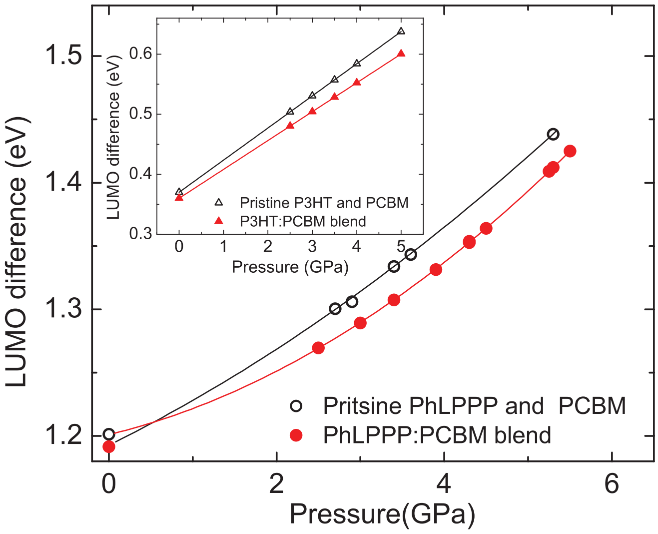

FIG. 5. (Color online) The LUMO energy difference between PhLPPP and PCBM as a function of pressure when the two are considered separately versus when they form a heterojunction. A polynomial second-order fit to the data is shown. The inset shows the same for the P3HT and PCBM system.

and PCBM, using the PL shift of P3HT and P3HT:PCBM under pressure.

The main observations are as follows: The blended heterojunctions have a lower band-edge offset compared to treating the donor and acceptor separately at all pressure values, and the LUMO offset increases with increasing pressure. The implications of these results are twofold. First, the band-edge offsets in donor-acceptor heterojunctions have slightly different values compared to arriving at these values by simply taking the HOMO/LUMO differences in the donor and acceptor material separately. Second, the LUMO offset increases with enhanced inter- or intrachain interactions. The latter may impact thermal annealing.[7] Undoubtedly the morphology and microstructure of the blended films impact charge separation and transport, which affect the overall PCE of organic solar cells. Our results show that an optimum phase microstructure with reduced intermolecular interaction may ensure a small LUMO offset between the donor and acceptor molecules, thus improving the PV efficiency.

IV. CONCLUSIONS

In conclusion, our experiments reveal a different pressure coefficient for the PL and absorption energies between a pristine donor polymer and the donor polymer:fullerene heterojunction. Using a phenomenological model, the volume changes of the pristine donor polymer and the heterojunction (blended system) as a function of pressure are found to be similar. We attribute the difference in the pressure coefficient to an increase in the band-edge offset with increasing hydrostatic pressure. The result is independent of the nature of the donor polymer; PhLPPP which is amorphous compared to regioregular P3HT shows a similar increase in the LUMO offset upon enhanced hydrostatic pressure. Such studies provide new directions for tailoring the properties of donor-acceptor heterojunctions toward improving the performance of organic solar cells. Our work also provides a platform for future theoretical modeling of polymer-fullerene heterojunctions and the impact of band-edge offset under enhanced interactions.

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