Photoexcited carriers in organic light emitting materials and blended films observed by surface photovoltage spectroscopy

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The electronic structure of the widely-used light emitting materials, 2,5-*bis*(5-tert-butyl-2-benzoxazolyl) thiophene (BBOT), poly(*N*-vinylcarbazole) (PVK) thin films have been characterized using surface photovoltage spectroscopy. The photo-induced charge separation and transfer processes in both blend films of PVK:BBOT and PVK:TPD:BBOT, where TPD is N,N'-diphenyl-N,N'-*bis*(3-methylphenyl)-$[1,1'$-biphenyl]-$4,4'$-diamine have also been investigated. The results of the photo-induced contact potential difference (CPD) change show that BBOT film is an electron-transporting material while PVK film is a hole-transporting one. The photoluminescence and electroluminescence results of the blend films suggest an exciplex interaction between BBOT and PVK or TPD. A positive CPD change due to photo-excitation of the BBOT in PVK:BBOT blend film is attributed to electron trapping at the localized state induced by dispersed BBOT species. In the PVK:TPD:BBOT blend films, a positive CPD change, which starts at the same transition energy as in the former blend film but is significantly enhanced, is observed and explained in terms of charge transfer between the involved energy structures of the blend components. The dependence of the observed effects on the blend composition and ensuing electronic structure is discussed.

I. INTRODUCTION

Electronically active organic molecular materials/films are widely studied in optical electronic devices, such as light emitting devices and solar cells.[1–3] Organic materials may have a tunable electronic energy gap through chemical synthesis/modification, and low cost for device fabrication.

The disadvantage of organic solids is the low density and mobility of their charge carriers due to the weak van der Waals interaction between the molecules. Blend films provide a simple way of improving charge carrier transport within the film by mixing component materials with the opposite charge carrier type to improve the efficiency of the device or obtain a desirable spectral distribution.[2–9] Also in a blended system, a new excited state, giving a different emission color from each of the individual components, i.e., exciplex can be formed. Exciplex emission from light emitting devices has attracted some attention.[10–15] In photo-excited processes, an exciplex is a result of exciton dissociation and charge transfer between the excited/ground state donor and the ground/excited state acceptor components.

Some techniques operating under vacuum, such as ultraviolet photoemission spectroscopy (UPS), x-ray photoelectron spectroscopy (XPS), and the Kelvin probe method (KPM),[16–19] have been used in studying organic thin films. They mainly focus on metal/organic interface electronic structure and electrostatic information, such as interface dipole, work function, electronic energy level, and chemical reaction at interfaces. They can be difficult to use on films fabricated in air.[20,21] Also, they do not provide insight into

the carrier transporting type and excitation processes in the organic (blend) film, which are clearly a prerequisite for optimal selection of the component materials for blend film-based devices.

Given the surface work function of a semiconductor both in dark and under photoexcitation, surface photovoltage spectroscopy (SPS) has been used as an efficient tool for determination of the conductivity type and surface/interface electronic states of inorganic semiconductors, by measuring the contact potential difference (CPD) spectrum.[22] Recently, this technique has also been used to investigate the electronic structure and photo-induced charge processes of the organic electronic materials and organic–inorganic interfaces.[23–27]

2,5-*bis*(5-tert-butyl-2-benzoxazolyl) thiophene (BBOT), poly(*N*-vinylcarbazole) (PVK) and N,N'-diphenyl-N,N'-*bis*(3-methylphenyl)-$[1,1'$-biphenyl]-$4,4'$-diamine (TPD) are widely used in organic light emitting devices.[8–11,28,29] In this paper, we report the characterization of the carrier transporting types and electronic states of the BBOT and PVK films using SPS. Furthermore, we investigate the photo-excited carrier separation and transfer processes in both blend films of PVK:BBOT and PVK:TPD:BBOT. Both the films showed exciplex interactions in their electroluminescence when used as the emissive layers in light emitting devices.[11]

II. EXPERIMENT

BBOT, PVK (average MW 1 100 000), and TPD were purchased from Aldrich, and used as received. Figure 1
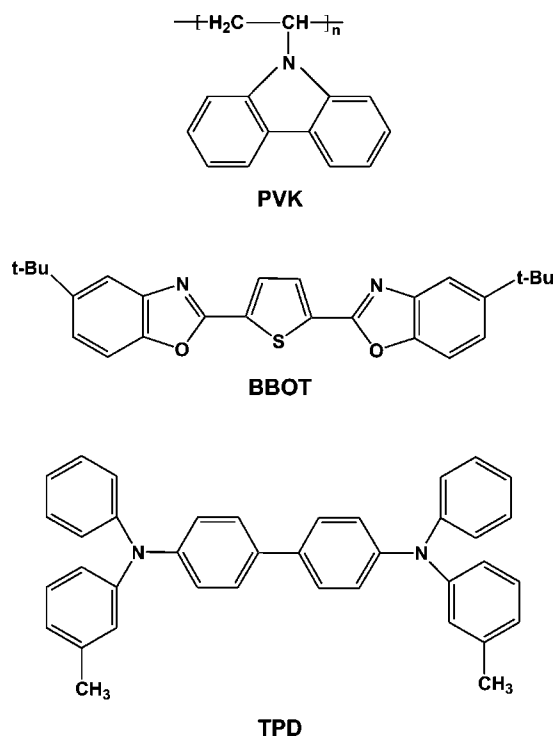
FIG. 1. Molecular schematics of PVK, BBOT, and TPD.

FIG. 2. Absorption spectra of the PVK (a), TPD (b), BBOT (c) single-component films, PVK:BBOT (d) and PVK:TPD:BBOT (e) blend films. Insert: photoluminescence spectra of PVK (a), BBOT (b), TPD (c) single-component films and electroluminescence spectra of the ITO/PVK:BBOT/Al (d) and ITO/ PVK:TPD:BBOT/Al (e) devices at 18 V bias. The spectra are normalized and vertically shifted for clarity.

shows their molecular structures. The PVK film, PVK:BBOT, and PVK:TPD:BBOT blend films were prepared by spin-coating from 1,1,2-trichloroethane solutions. Unless noted, the PVK:BBOT blend film was prepared from the PVK:BBOT solution with 30 wt. % BBOT (PVK, 0.05 mol l^{-1}; BBOT, 0.01 mol l^{-1}). For the PVK:TPD:BBOT blend film, the PVK:TPD:BBOT solutions were prepared by addition of 10 wt. % TPD into the PVK:BBOT solution with 30 wt. % BBOT. The films were heat-treated at 70 °C for 1 h. The blend films have a thickness range of 50–60 nm as measured by a Taylor Hobson Talystep. The BBOT film was obtained by evaporation at a pressure of $\sim$10^{-5} Torr, with a thickness of about 100 nm. Indium-tin-oxide glass (ITO) (Rs: 5–15Ω/$\square$) was used as film substrates for CPD measurements and glass slides for optical measurements. ITO glass was ultrasonically cleaned in ethanol, acetone, dichloromethane for 10 min each, and dried with nitrogen. Before film preparation, ITO glass was irradiated using an UV lamp (250 W) for 15 min to keep the same substrate condition as for the light-emitting device.

The absorption spectra were measured utilizing a Varian Cary 500 UV-Vis-NIR spectrophotometer. The photoluminescence (PL) spectra were measured by a Perkin-Elmer LS 50B luminescence spectrometer. The CPD spectra were obtained using a Kelvin probe arrangement (Besocke Delta Phi, Germany). The CPD was measured between the sample and the Au grid vibrating reference probe. It is described by $V_{CPD}=(1/e)(W_S-W_R)$.[22] A double 0.25 m grating monochromator (Oriel MS257) was used to provide illumination with a 300 W Xe lamp used as the light source. The Kelvin probe measures an averaging signal in a 2.5 mm diameter area. All CPD spectra were obtained after sufficient equilibration had been achieved in the
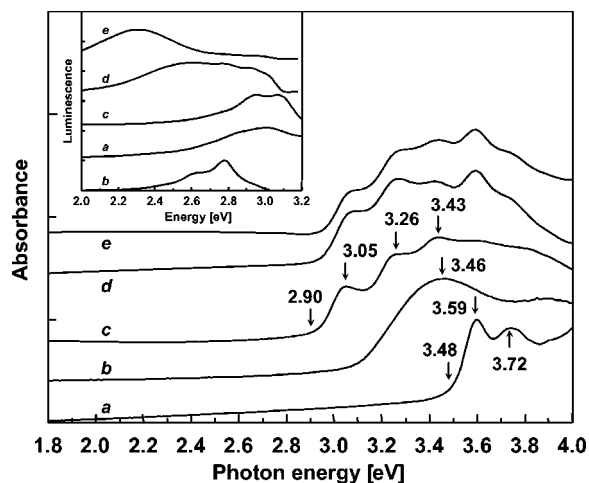
dark, indicated by an essentially constant dark CPD before scanning. All measurements were conducted in air at room temperature.

III. RESULTS AND DISCUSSION

A. Carrier transporting types and electronic states

Figures 2(a) and 2(c) show the absorption spectra of PVK and BBOT single-component films. The characteristic absorption of the PVK film peaks at about 3.59 eV, and 3.72 eV. The BBOT film absorption is characterized by three bands at 3.05 eV, 3.26 eV, and 3.43 eV. According to the measured absorption, the optical gap energies (π-π^*) of the PVK and BBOT films are 3.59 eV and 3.05 eV, respectively.

Figures 3(a)–3(c) are the CPD spectra of the blank ITO, BBOT, and PVK films deposited on ITO. The ITO substrate starts a negative CPD change from about 3.2 eV, corresponding to the band-to-band transition. The BBOT and PVK films have the characteristic CPD changes at 2.90 eV and 3.48 eV, respectively. These are caused by the photoinduced charge redistribution due to the optical gap transitions of the two species.

In organic solid-state films, the carrier transport gap is the separation between the highest occupied molecular orbital (HOMO) and the lowest unoccupied orbital (LUMO). The HOMO and LUMO are analogous to the valence and conduction bands of inorganic semiconductors but the carrier transport is by hopping. The difference between the transport gap and the optical gap, i.e., the binding energy of the Frenkel exciton, may be large.[30] While there is no report of the transport gap of BBOT, PVK has a transport gap of about 4.4 eV, which is about 0.8 eV higher than the π-π^* optical gap.[31] The illumination-induced CPD change of PVK film
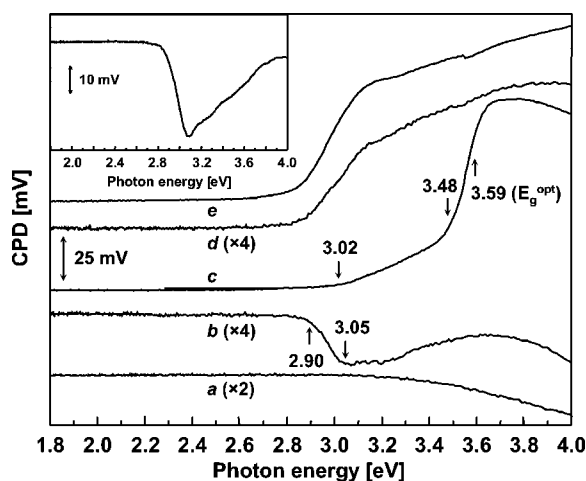
FIG. 3. CPD spectra of the ITO (a), BBOT (b), and PVK (E_g^{opt} denotes the optical gap) (c), single-component films, PVK:BBOT (d), and PVK:TPD:BBOT (e), blend films. Insert: the CPD spectrum of a PVK:BBOT film from a PVK:BBOT solution with 43% BBOT. The spectra are vertically shifted for clarity.

shows charge redistribution following the generation of a singlet Frenkel exciton, rather than a direct photoexcitation from HOMO to LUMO. As a neutral excited state, the exciton itself cannot cause charge redistribution. The discussed CPD change must be a result of the photo-generated Frenkel exciton dissociation into free carriers. Without loss of generality, the CPD change of BBOT may also be governed by the same mechanism (the extreme condition is that the exciton binding energy is a few meVs, as in inorganic semiconductor).

As a degenerate *n*-type semiconductor, the ITO substrate shows a negative CPD change under illumination of band gap energy. A fundamental function of SPS is to determine the carrier transport property (conductivity type) of an inorganic semiconductor.[22] At thermal equilibrium, an inorganic semiconductor surface is distinguished by a downward (*p*-type) or upward (*n*-type) band bending, due to majority carrier depletion in the surface space charge region (SCR). Under super band gap illumination, the band bending decreases due to redistribution of the photogenerated carriers, i.e., the surface work function decreases (increases) for an *n*-type (*p*-type) semiconductor. Thus, a positive (negative) CPD change indicates a *p*-type (*n*-type) semiconductor.

While both PVK and BBOT can be used as blue emitters in organic electroluminescent devices, the former is popularly used as a hole-transporting polymer and the latter is an electron-transporting material.[4–6,8–12,14,32] Consistent with their carrier transporting properties, PVK exhibits a positive polarity of the CPD change and BBOT a negative one under respective superoptical gap illumination.

The CPD change can be caused by two effects: a photo-induced surface/interface band bending change or the Dember effect.[22] For most inorganic semiconductors, the Dember effect, which arises from nonuniform carrier generation or recombination at high illumination, always increases the surface potential and shows a negative CPD change irrespective

of the carrier-transporting property of the measured material, due to the faster electron diffusion through the film bulk than that of the hole.[22] This characteristic may be unsuitable for an organic semiconducting film because hole mobility could be higher than that of electron in a hole-transporting material.[33] Analyzing the absorption intensity of the PVK film at optical gap energy shows about 80% of the incident light was transmitted through the film. Based on this consideration an almost-uniform absorption in the whole film region is expected. The Dember effect should not be the dominant process for the PVK and BBOT film. The measured CPD change of both the PVK and BBOT films should be due to the photoinduced band bending change at the film surface or interface with the ITO substrate.

The details of the electronic structure at the interface between the film and ITO substrate are beyond the scope of this paper. However, in CPD spectral analysis of a thin film one has to consider the space charge region (SCR) at the interface between the film and the substrate. An opposite polarity of the CPD change relative to the surface one would be measured if a strong interfacial SCR is formed and dominates the surface potential change. For such a mechanism, the film thickness change should influence the CPD signal due to the change of the effective light absorption at the interface region. We prepared thicker PVK and BBOT films and did not find a significant influence of the thickness on the dark surface work function and the CPD spectra. This shows that at the film thicknesses used, the CPD signal comes mainly from photoinduced charge separation at the film free surface rather than at the interface with the ITO substrate. This suggests that the PVK film surface has a downward surface band bending and a hole depletion surface layer, while BBOT has an upward surface band bending and an electron depletion surface layer. Considering the practical carrier transporting properties of PVK (hole-transporting) and BBOT (electron-transporting), this behavior is similar to *p*- or *n*-type inorganic semiconductor surface under thermal equilibrium.

The photon excites an electronic transition from ground state to the singlet Frenkel exciton state, i.e., a bound positive/negative charge pair. The exciton can either relax to the ground state or dissociate under an external electric field and as a result, release separated hole and electron.[31,34–36] The photoinduced CPD change of PVK and BBOT may be attributed to exciton dissociation under the surface potential, which puts a free hole in the π orbital (HOMO) of PVK or a free electron in π^* orbital (LUMO) of BBOT. They move along the surface field and as a result, the surface potential of PVK (BBOT) is changed by the charge redistribution at the surface. The electron (hole) can be trapped in defect/impurity states of PVK (BBOT) or enter into shallow states/band tail below the LUMO (above the HOMO).[22]

The present results, together with previous reports,[23,26] indicate the presence of surface band bending of organic films and that indeed SPS can efficiently characterize the conducting type of an organic semiconductor film. We note that the argument of an interface dipole layer (formed within several atomic thicknesses by charge transfer) rather than band bending at the organic layer/metal or inorganic semiconductor substrate was based on samples made and measured under

ultrahigh vacuum. However, carrier transfer in the organic material is unambiguously influenced by the ambient atmosphere in which the device is processed.[21,37,38] The differences in film preparation and measurement circumstances can result in controversial reports on the electronic properties. For example, the possibility of surface band bending of organic film was suggested due to surface O_2 doping.[21] It was also reported that the surface photovoltage of polymethine semiconducting films resulted from the space charge depletion layer at the front surface.[39]

Comparing the CPD spectra of the BBOT and PVK films, the intensity of the CPD change (surface photovoltage) of the former is much weaker than that of the latter. While the reason is not excluded from the weaker surface field of the BBOT film relative to PVK, it could be related to their difference in the extent of interaction among the molecules in the films. While PVK is a polymer, the BBOT film has a small shift (less than 0.1 eV) of absorption or photoluminescence spectra from dilute solution. This indicates weak electronic coupling among the molecules in the BBOT film, and photoexcited carrier transport among the molecules in the BBOT film could be less efficient than in PVK film.

No suboptical gap transition is observed in the BBOT film. The PVK film shows a transition at about 3.02 eV. This transition gives the same CPD change polarity as the optical gap transition. While the band tail effect is considered, this transition may also indicate a localized state because of the obviously different knee and large energy difference (0.57 eV) from the optical gap transition. This transition indicates a surface or bulk electron trap state [generally used in explaining the *p*-type conductivity or exciton dissociation of PVK (Refs. 31 and 34)] 0.57 eV below the π^* orbital, or a bulk localized energy level 1.38 eV (occupied) above the π orbital. Presently it is not clear if this state is related to the PVK molecular structure or defect state due to the film preparation process.

The identification of the weakly absorbing suboptical gap transition by absorption spectroscopy is easily blurred for the film sample due to the influence of the substrate and/or the film thickness. SPS is sensitive to the suboptical gap transition,[24,40] and because it only measures the surface potential change by the real light absorption, it is not influenced by light scattering, substrate absorption, etc. This is also clearly seen by comparing the CPD and absorption spectra of the PVK film, in the region of the suboptical gap absorption.

B. Photoinduced charge separation and transfer processes in PVK:BBOT and PVK:TPD:BBOT blend films

Figures 2(d) and 2(e) show the absorption spectra of PVK:BBOT and PVK:TPD:BBOT blend films. The absorption is the sum of the component electronic signatures, which suggests no new species (charge transfer complex) is formed at ground state during blending. However, as shown in the insert of Fig. 2, the EL spectra of the electroluminescent devices based on the PVK:BBOT and PVK:TPD:BBOT blend films (the same as PL emission) are dominated by

neither that of the PVK (3.01 eV) nor that of the BBOT (2.78 eV) or TPD (2.96 eV) component. The strongest emission band of the ITO/PVK:BBOT/Al device is centered at 2.61 eV. In the ITO/PVK:TPD:BBOT/Al device, a dominant emission band is centered at 2.30 eV. They have been attributed to the emission from the exciplex formed between BBOT and PVK (PVK^+BBOT^-) or between BBOT and TPD (TPD^+BBOT^-).[9,11]

Figure 3(d) shows the CPD spectrum of the PVK:BBOT blend film. The CPD change starts at the optical gap energy of the BBOT component. However, in contrast to that of the BBOT film [Fig. 3(b)], the BBOT transition in this blend film yields a positive CPD change. This suggests that in this blend film the dominant contribution from the BBOT to the CPD change does not come from the bulk phase state of BBOT, but is provided by charge transfer between the BBOT molecules and the PVK. The positive CPD change shows that the charge transfer effect results in net accumulation of photoinduced electrons at the surface region of the blend film. This means that the average work function of the PVK:BBOT blend film increases under illumination.

The photoinduced charge transfer can be attributed mainly to the electronic configuration of well-dispersed BBOT molecules acting as localized states in the PVK matrix. Figure 4(a) depicts the energy schematics for this charge transfer process in the PVK:BBOT blend film. Under illumination at the optical gap energy, the electron is pumped from the π orbital to the π^* orbital of the BBOT component, and the π orbital becomes an emptied molecular orbital. The 5.9 eV ionization potential of BBOT and 5.8 eV ionization potential of PVK (Ref. 9) yield about 0.1 eV π orbital energy offset between the two components. The emptied π orbital of the excited BBOT component may trap electrons from the π orbital of the ground state PVK, i.e., hole can be generated in PVK. The generated hole at the π orbital of PVK may be swept toward the film bulk while the excited electron is localized at the BBOT molecule. Therefore, a net negative charge is obtained near the surface, which results in an increased CPD.

From Fig. 3(d), the CPD change becomes relatively flat after 3.10 eV, and no sharp PVK characteristic transition can be distinguished. The CPD change could be "saturated" by the charge transfer from π orbital of the ground state PVK to that of the excited BBOT molecule, due to the strong BBOT absorption. Therefore, there would be no more electrons available to be excited from the π orbital to the π^* orbital of the PVK component.

A binary blend film morphology and structure depends on the concentrations of the two components. Phase separation has been demonstrated to be general in a blend film,[41,42] and is also true for the present PVK:BBOT blend film. As shown in the insert of Fig. 2, the emission bands from both PVK (3.01 eV) and BBOT (2.78 eV) phases were observed in the electroluminescent device of ITO/PVK:BBOT/Al. Therefore, it should be noted that the observed positive CPD change by BBOT photoexcitation could be an average effect of the dispersed BBOT molecules, PVK/BBOT interface and to a smaller extent of the pure BBOT surface region.
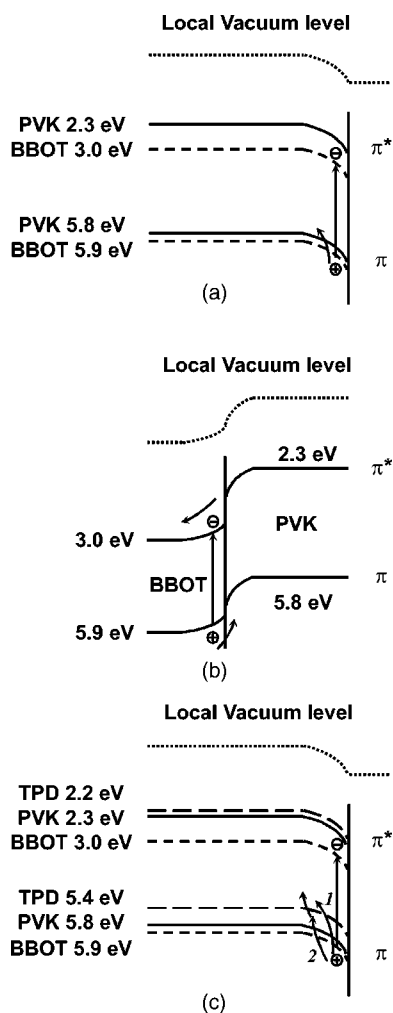
FIG. 4. Energy schematics for the charge transfer processes in PVK:BBOT (a and b) and PVK:TPD:BBOT (c) blend films. Models a and c are for well well-dispersed BBOT molecules as a localized state in the PVK or PVK:TPD matrix. Model (b) is for PVK:BBOT interface dominant CPD change at high BBOT concentration. In (c), *arrow 1*: direct electron transfer process from TPD to BBOT, *arrow 2*: electron transfer process from PVK to BBOT and subsequent from TPD to PVK.

Figure 4(b) shows the charge transfer process at a PVK:BBOT interface, which causes a negative contribution to the CPD change. When the size of the BBOT phase is so large that the contribution from the PVK/BBOT interface and the pure BBOT surface region dominate the CPD change, the total CPD change can be expected to be negative. This has been checked and verified by measuring the CPD spectra of the PVK:BBOT blend films with higher BBOT concentrations. As an example, the insert of Fig. 3 shows the CPD spectrum of a PVK:BBOT blend film from a PVK:BBOT solution with 43 wt % BBOT. A negative CPD change at the BBOT optical gap transition was observed. This indicates that at high concentrations, the BBOT can form a "massive" bulk phase in the blend film and the CPD could be dominated by the interface process as shown in Fig. 4(b). In comparison with the pure BBOT film, the CPD change is enhanced. It may indicate that the interface field of the BBOT phase is stronger than the surface field of a pure BBOT film, probably due to the alignment of the Fermi levels. Based on the magnitude of the CPD change, the contribution from the pure BBOT surface region can be neglected.

TPD has an ionization potential of 5.4 eV,[43] 0.4 eV lower than that of PVK. In a ITO/PVK:TPD:BBOT/Al device with 10 wt. % (or higher) TPD blending concentration, a new exciplex species TPD$^+$BBOT$^-$, rather than the PVK$^+$BBOT$^-$ species, has been observed. It seems to dominate the electroluminescence, owing to the stronger interaction of TPD with BBOT.[11] This shows that the hole is mainly transported or trapped in the TPD species.

The CPD spectral measurement agrees well with this conclusion. Figure 3(e) shows the CPD spectrum of the PVK:TPD:BBOT blend film. Similarly to that of PVK:BBOT blend films, the CPD has a positive change at the same energy position as the optical gap energy of the BBOT component. However, the intensity of the CPD change is at least 5 times stronger than that of PVK:BBOT blend film. The TPD film absorption shows a broad band centered at 3.46 eV [Fig. 2(b)], and in both the CPD spectra of TPD and PVK:TPD films the CPD change starts at about 3.20 eV (not shown). Therefore, it may be concluded that the positive CPD change of the PVK:TPD:BBOT blend film is a result of the photoexcitation of BBOT and subsequent electron capture from the π orbital of the ground state TPD or PVK by the emptied π orbital of the excited BBOT. The enhanced (positive) CPD change indicates a more efficient electron accumulation at the surface region of the PVK:TPD:BBOT blend film, under photoexcitation of the BBOT component.

The reasons for the increased photoinduced charge transfer efficiency could be multiple because of the complex microstructural and molecular environment in a ternary blend film. Figure 4(c) shows a hypothesized energy schematic for two charge transfer models for the PVK:TPD:BBOT blend film. The electron capture from the π orbital of TPD by the emptied π orbital of the excited BBOT molecule may be efficient due to the lower ionization (oxidation) potential and higher hole mobility of TPD relative to PVK.[8,29] *Arrow 1* shows direct electron transfer from TPD to BBOT. The valence band offset is about 0.3 eV larger than that between PVK and BBOT components. One may be skeptical about the hole transfer without external bias at the 10 wt. % TPD blend. Such a blend may provide a distribution of TPD molecules with sufficiently small intermolecular distance so that the hole could hop between the TPD molecules at least at the surface region (under the surface field).

The second possibility is that electrons may be transferred from the π orbital of PVK to the emptied π orbital of the excited BBOT, followed by electron trapping at the π orbital of PVK from the π orbital of TPD. This would reduce the electron recombination ratio of the excited BBOT molecule and increase the charge transfer efficiency. *Arrow 2* shows the electron transfer process from PVK to BBOT and subsequently from TPD to PVK. In such a process, PVK plays the role of a charge-transfer bridge. Other mechanisms (for the enhanced positive CPD change) should also be considered. For example, can the dispersed TPD in BBOT change the

BBOT SPS spectrum from "*n*-like" to "*p*-like"? Can the interface field in the PVK be enhanced because of the introduction of TPD?

The electron transfer efficiency could be optimized by using the effect of the TPD concentration on the photoinduced charge transfer process. The improved charge transfer in such a ternary-blended system could be employed for photovoltaic or photoconductive devices combining operational efficiency with film quality/lifetime.

IV. SUMMARY

We have characterized the carrier transporting properties and surface electronic states of thin films of 2,5-*bis*(5-tert-butyl-2-benzoxazolyl) thiophene (BBOT) and poly(*N*-vinylcarbazole) (PVK), using surface photovoltage spectroscopy (SPS). BBOT is shown to be an electron-transporting material while PVK is a hole-transporting one. Furthermore, we have studied the photoinduced charge separation and transfer processes in blend films of PVK:BBOT and PVK:TPD:BBOT, where TPD is N,N'-diphenyl-N,N'-*bis*(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine. A positive contact potential difference (CPD) change at the BBOT optical gap transition in PVK:BBOT blend film rather than a negative one (as in the pure BBOT film) was observed, which suggests electron photoexcitation to the π orbital of BBOT molecule and subsequent electron transfer from the π orbital of the ground state PVK to the emptied π orbital of the excited BBOT molecule. In PVK:TPD:BBOT blend films, the positive CPD change due to BBOT photoexcitation is significantly enhanced in comparison with the PVK:BBOT blend film, which could be attributed to the more efficient electron transfer either directly from the π orbital of ground TPD to the emptied π orbital of the excited BBOT molecule or via PVK. This work shows that SPS is an efficient methodology for characterizing the electronic structure of the organic materials as well as the photoinduced charge separation and transfer in organic blend systems.

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