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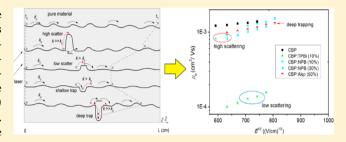
# Charge Transport in Mixed Organic Disorder Semiconductors: Trapping, Scattering, and Effective Energetic Disorder

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Supporting Information

ABSTRACT: The effects of trapping and scattering on the transporting properties of organic disorder semiconductors have been studied by time-of-flight (TOF) method. Tris-(8hydroxyquinoline)-aluminum (Alq<sub>3</sub>), 2,2',2"-(1,3,5-benzenetriyl)-tris-(1-phenyl-1H-benzimid-azole) (TPBi), and N,Ndiphenyl-N,N-bis(1-naphthyl)-(1,1'-biphenyl)-4,4'diamine (NPB) are doped into 4,4'-N,N'-dicarbazolebiphenyl (CBP) to form traps and scatters with various energy level differences. It is found that the low scatters significantly reduce the mobility and make the TOF transients, while the deep traps



and high scatters would not significantly reduce the mobility and change the nondispersive behavior of the TOF transients. The main difference between deep traps and high scatters is that the deep traps induce a great reduction of the photocurrent, while the high scatters do not obviously decrease the photocurrent. The experimental results are well explained by the Miller-Abrahams hopping model and the effective energetic disorder. Furthermore, a theoretical method is established to determine the demarcation between the shallow trap (low scatter) and the deep trap (high scatter) in terms of energy level differences. These results may shed light on the understanding of charge transport in mixed organic semiconductors.

# 1. INTRODUCTION

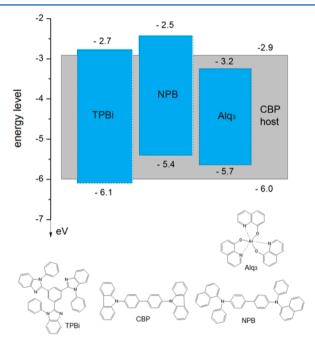
Mixed organic disorder semiconductors have great potential for wide applications in the fields of organic light emitting diodes (OLEDs)<sup>1-5</sup> and heterojunction organic photovoltaics (OPVs).6-8 However, a general and fundamental understanding of how charge traps and scatters affect charge transport in these materials, which is essential to our comprehension of the physicochemical processes in organic electronic devices, has yet to be realized. Charge transport in disorder organic semiconductors has been widely accepted as a field-assisted, thermally activated hopping process between the localized transporting states.<sup>9,10</sup> The weak interactions between the molecules and the great degree of energetic disorder make charge transport more sensitive to charge traps and scatters for the organic semiconductors, as compared to their inorganic counterparts.

Charge traps and scatters in organic semiconductors have several origins, including chemical impurities, geometric disorder, and "Coulomb traps" formed from bound holeelectron pairs, 11 among which the ones originated by chemical impurities are most common and have been widely studied in OLEDs and OPVs. Trap energies are located in the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the material, and scatter energies are either higher than the LUMO (for electron transport) or lower than the HOMO (for hole transport). Several studies have suggested that even a very small amount of traps or scatters can change the mobility of the

mixed organic materials. Traps have been found to reduce the hole mobility of N', N'-bis(3-methylphenyl)-(1,10-biphenyl)-4,4'-diamine (TPD) for 1 order of magnitude, and traps with an depth of  $0.2~{\rm eV}$  can induce more significant reduction than those with a depth of  $0.1~{\rm eV}.^{12}$  The study on hole mobility of *N*,*N*-diphenyl-*N*,*N*-bis(1-naphthyl)-(1,1'-biphenyl)-4,4'diamine (NPB) has suggested that traps can induce significant reduction in hole mobility due to the additional trap residing time, while there is a slight reduction for scattering as the total transit path is increased by carrier scattering.<sup>13</sup> Ma et al.<sup>14</sup> have also concluded that doping molecules as traps increases the density of traps and decreases the hole mobility, whereas doping molecules as scatters does not obviously affect hole transport as the density of traps are not increased. Lots of effort has been made to interpret why traps and scatters play different roles, and energetic disorder has been the focus of the discussions. Through temperature varying mobility measure and the analysis by the Gaussian disorder model (GDM), 15 the energetic disorders of the mixed organic semiconductors have been obtained. 12,13,16 Results show that in the trapping situations, the energetic disorders increase, 12,13 while in the scattering situations, the energetic disorders are almost identical to the pristine case. 13,16 The energetic disorder seems to well interpret the difference between trapping and scattering. However, a larger energetic disorder in trapping situation is contradictory

Received: August 9, 2012 Published: August 27, 2012 with the well-known comprehension of the energetic disorder as the width of the distribution of the localized states, according to which the scatters can increase the energetic disorder identically as the traps, especially when the energy level difference between the host material and the traps (or the scatters) is smaller than the energetic disorder of the host material; thus the traps (or the scatters) are sure to participate in charge transport. To sum, a generalized realization of the effects of charge trapping and scattering is still a problem, and the contribution of charge trapping and scattering to the energetic disorder needs to be clarified.

In this work, the effects of traps and scatters on charge transport in mixed organic semiconductors are investigated by TOF. 4,4'-N,N'-Dicarbazolebiphenyl (CBP) is used as the host material. Three dopants, tris-(8-hydroxyquinoline)-aluminum (Alq<sub>3</sub>), 2,2',2"-(1,3,5-benzenetriyl)-tris-(1-phenyl-1*H*-benzimid- azole) (TPBi), and NPB, are used to form traps and scatters of various ratios in the CBP host. All of these materials are widely used as transporting materials with good film-forming properties and stabilities. 9,10 The hole and electron mobilities of pristine CBP are around  $10^{-3} \, \mathrm{cm}^2/(\mathrm{V} \, \mathrm{s})$ , which is orders of magnitude larger than the dopants used in this study according to previous reports. 9,17-19 The energy levels and chemical structures of the materials are shown in Figure 1. Hole



**Figure 1.** Energy levels and chemical structures of the organic semiconductors.

and electron mobilities under various electric fields are measured. The results show that low scatters and shallow traps induce a significant reduction in mobility, while high scatters and deep traps would not significantly decrease the mobility. According to the Miller–Abrahams hopping model, we conclude that shallow traps and low scatters participate in charge transport to a great degree as their energy level difference ( $\Delta E$ ) with the host is small, while high scatters and deep traps hardly participate in charge transport due to the thermodynamically controlled low hopping rate between these states and the host states, which is resulting from the large  $\Delta E$ . As a result, the shallow traps and the low scatters enlarge the

effective energetic disorder of the mixed semiconductors and decrease mobility significantly, while the deep traps and high scatters would not contribute to the effective energetic disorder and just induce a slight reduction in mobility resulting from the elongated transporting manifold. Moreover, a theoretical method is established to determine the demarcation between the shallow trap (low scatter) and the deep trap (high scatter) in terms of  $\Delta E$ , and our conclusions for the CBP hosted system can be extended to other systems with this demarcation.

#### 2. EXPERIMENTAL METHODS

In the present study, to confirm the trapping and scattering situations in this mixed system, the HOMOs of all four materials, and the LUMOs of CBP and Alq3, were measured by a cyclic voltameter, with a linear correlation with ferrocene (4.8 eV).20 The LUMOs of TPBi and NPB were from ref 20. The TOF samples had a structure of ITO/CBP: dopants (x) (2)  $\mu$ m)/Mg:Ag (100 nm), where x is the mol percentage of the dopants. The organic layer was deposited inside a high vacuum evaporator at 10<sup>-6</sup> Torr onto ITO glass, each material with an evaporation source. The coating rate for the organic materials was about 0.2 nm/s. Thicknesses of the organic layer were monitored in situ with a quartz crystal sensor. After coating, the sample was packaged with a glass plate under a controlled N<sub>2</sub> atmosphere. A nitrogen pulsed laser (pulse width 10 ns, wavelength 355 nm, beam size 3.14 mm<sup>2</sup>) was used as the excitation light source, which is directed from the ITO side to generate a thin sheet of excess carriers near the ITO/organic interface. The transient photocurrent signals were recorded by a digital storage oscilloscope with a current sensor resistor (R) of 50  $\Omega$ , and then the transit time ( $t_{\rm T}$ , the time that the carriers pass through the organic film) was measured from the double-logarithmic plot of the transient photocurrent. With the applied bias V and the thickness L, the charge mobility could be calculated as  $L^2/t_TV$ . All of the TOF experiments were done at the temperature of 298 K.

# 3. THEORETICAL BASIS

According to the Miller–Abrahams hopping model,  $^{21}$  the hopping rate between an occupied state i and an unoccupied state j is

$$v_{ij} = v_0 e^{-2r_{ij}/a} \begin{cases} e^{-\Delta E/kT} & , \Delta E = \varepsilon_j - \varepsilon_i \ge 0 \\ 1 & , \text{else} \end{cases}$$
 (1)

where  $v_0$  is the prefactor rate,  $r_{ij}$  is the distance between an occupied state i and an empty state j, a is the average localization length of the hopping states, T is the absolute temperature, k is the Boltzmann constant, and  $\varepsilon_i$  and  $\varepsilon_j$  are, respectively, the localized energy of state i and state j.

The GDM introduces Gaussian density of states (DOS) for the localized transporting sites and uses the Miller–Abrahams hopping rate. The empirical equation for the dependence of charge carrier mobility  $\mu$  on field E and temperature T suggested by GDM is

$$\mu = \mu_{00} \exp\left[\frac{1}{2} \sum^{2} - \left(\frac{2}{3} \frac{\sigma}{kT}\right)^{2}\right]$$

$$\times \exp\left(C\left[\left(\frac{\sigma}{kT}\right)^{2} - \sum^{2}\right] E^{1/2}\right)$$
(2)

where  $\mu_{00}$  is a prefactor mobility,  $\sum$  is the positional disorder that characterizes the spatial orientation of the states,  $\sigma$  is the energetic disorder, and k is the Boltzmann constant.

## 4. RESULTS

The roles (traps or scatters) that TPBi, Alq<sub>3</sub>, and NPB play in hole transport or electron transport of CBP host are shown in Table 1. According to Table 1, CBP:TPBi belongs to low

Table 1. Roles the Dopants Played in Hole Transport and Electron Transport of CBP

	hole transport		electron transport	
material	role in CBP	$\Delta E \text{ (eV)}$	role in CBP	$\Delta E$ (eV)
TPBi	low scatter	0.1	low scatter	0.2
NPB	deep trap	-0.6	high scatter	0.4
$Alq_3$	deep trap	-0.3	deep trap	-0.3

scattering situation in hole and electron transporting; CBP:NPB (hole), CBP:Alq $_3$  (hole), and CBP:Alq $_3$  (electron) belong to the deep trapping situation; and CBP:NPB (electron) belongs to the high scattering situation.

Hole and electron TOF transients of pure CBP and the mixed organic semiconductors are measured under various bias, and the TOF transients measured under 100 V are depicted in Figure 2. The hole TOF transient of pure CBP is a typical nondispersive one with an evident plateau, and we see that introduction of deep traps (NPB (10%, 30%) and Alq<sub>3</sub> (50%)) does not change the nondispersive behavior. However, introduction of shallow scatters (TPBi (10%, 30%)) changes

the TOF transient to dispersive ones, and the dispersive behavior is more evident for the 30% TPBi-doped films. The corresponding hole double-logarithmic plots (Figure 2c) indicate that the transition time,  $t_{\rm T}$ , of the films with deep traps do not change much, while for the film with 10% of TPBi shallow scatters,  $t_{\rm T}$  increases 10-fold. Also, when the amount of TPBi increases to 30%, the TOF transient is too dispersive to determine  $t_{\rm T}$ . For the electron TOF transients, high scatters (NPB (10%, 30%)) and deep traps (Alq<sub>3</sub> (50%)) do not change the nondispersive behavior and would not significantly increase  $t_{\rm T}$ ; the dispersive behavior of the TOF transients and the significant increasing of  $t_{\rm T}$  in the shallow scattering situations (CBP: TPBi (10%) and CBP: TPBi (30%)) are also found.

The hole and electron mobilities under various fields are depicted in Figure 3. The hole mobility and electron mobility of pure CBP are in the order of  $10^{-3}~\rm cm^2/(V~\rm s)$ . Low scatters of 10% induce 1 order of magnitude's reduction in mobility; however, there is only a slight reduction for high scattering and deep trapping in mobility. Both the logarithmic electron mobility and the logarithmic hole mobility vary linearly with the square root of the applied electric field, which is in agreement with the Poole–Frenkel law:  $^{22}$ 

$$\mu = \mu_0 \exp(\beta E^{1/2}) \tag{3}$$

where  $\mu_0$  is the mobility at zero electric field, and  $\beta$  is the Poole–Frenkel factor that represents the slope of the field dependence of the mobility. For further analysis, the zero electric filed mobility ( $\mu_0$ ) and the Poole–Frenkel factor ( $\beta$ ) of the films are extracted according to the Poole–Frenkel law and

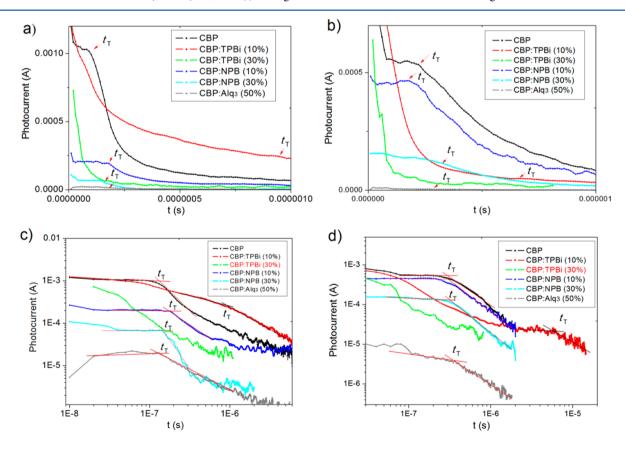
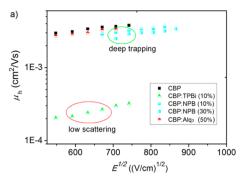


Figure 2. Hole (a) and electron (b) TOF transients of the pure and doped films under 100 V, and their corresponding double-logarithmic plots (c and d).



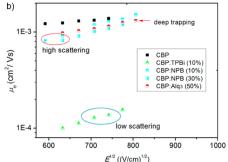
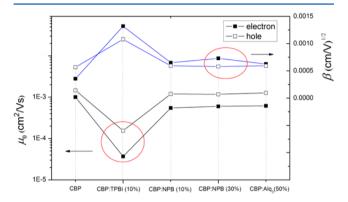


Figure 3. Hole (a) and electron (b) mobilities under various fields.

depicted in Figure 4. Both  $\mu_0$  and  $\beta$  of the materials with deep traps or high scatters are near identical to that of pure CBP;



**Figure 4.** Zero field mobilities  $(\mu_0)$  and Poole–Frenkel factor  $(\beta)$  of pure CBP and the mixed organic materials.

however, for the material with low scatters,  $\mu_0$  is much smaller and  $\beta$  is much larger. The opposite change trends of  $\ln \mu_0$  and  $\beta$  are in accordance with the GDM, where  $\ln \mu_0$  and  $\beta$  can be expressed as:<sup>15</sup>

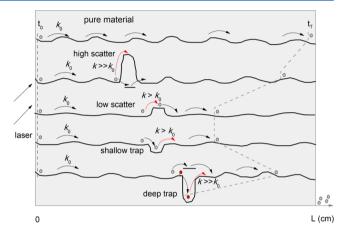
$$\ln \mu_0 = \ln \mu_{00} + \sum^2 /2 - (2\sigma/3kT)^2 \tag{4}$$

$$\beta = C[(\sigma/kT)^2 - \Sigma^2] \tag{5}$$

# 5. DISCUSSIONS

I. The Effects of Traps and Scatters on Mobility. As seen in Figure 3, deep trapping and high scattering just induce a slight reduction in mobility; however, shallow scattering induces significant reduction in mobility. Results in the works by So et al. have also shown that shallow trapping (with the energy level difference  $\Delta E \leq 0.2$  eV, for hole transporting of TPD:Rubrene film, TPD:DCM1 film, <sup>12</sup> NPB:DCM1 film, and NPB: DCM2<sup>13</sup> film) can induce significant reduction in mobility. These results indicate that  $\Delta E$ , that is, the depth of the traps or the height of the scatters, is a crucial factor for charge transport in mixed organic semiconductors, besides the roles (traps or scatters) the dopants play in the host. Here, we use the Miller–Abrahams hopping model to explain how  $\Delta E$  make differences in the effects of traps and carriers on charge transport.

Figure 5 shows the sketch of the localized hopping transports in the pure disorder materials, and disorder materials with high scatters, low scatters, shallow traps, or deep traps. In the pure material, we assume the carriers hop without traps or scatters,



**Figure 5.** The localized hopping transports in the pure disorder material, and the disorder materials with high scatters, low scatters, shallow traps, and deep traps.

and pass through the organic layer at  $t_{\rm T}$ . In the low scattering and shallow trapping situations, as  $\Delta E$  is small, the hopping rate (k) between the host states and the scatters (or the traps) is not far smaller than the hopping rate between the host states  $(k_0)$  according to eq 1 (as  $\Delta E/kT$  is small); hence, shallow traps and low scatters can participate in charge transport to a great degree. As a result, the carriers are greatly slowed by the hoping between the host states and the low scatters or the shallow traps, and hence the mobility sharply decreases.

In the high scattering situation, as the hopping rate to the high scatters (k) is orders of magnitude smaller than the hopping rate between the host states  $(k_0)$  (because of the large  $\Delta E$ ), the carriers tend to hop to other nearby host states instead of the high scatters. As a result, the transporting manifold elongates, while the rate of each hopping does not change much, and hence the mobility just slightly decreases. In the deep trapping situation, carriers are easy to capture by the deep traps, but the escaping rate from the deep traps is far smaller than  $k_0$  due to the large  $\Delta E$ , which leads to a large trap residing time  $(t_{\rm tr}, t_{\rm tr} \propto \exp(\Delta E/kT))$  of the carriers. <sup>12,23</sup> According to eq 1,  $t_{\rm tr}$  could be thousands of times larger than the relaxation time of carriers at the host states. In such a long time, carriers that go by the traps tend to hop to other nearby host states, just as in the high scattering situation. Hence, the mobility slightly decreases due to the elongation of the transporting manifold. From the discussions above, we can conclude that the deep traps and high scatters have similar effects on mobility due to the thermodynamically controlled low hopping rate between these states and the host states, so mobility will not sharply decrease until the continuous

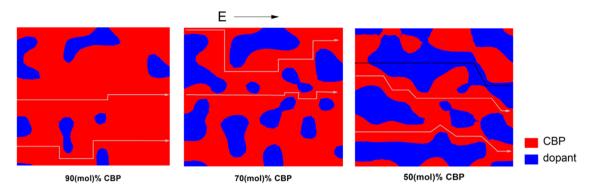


Figure 6. 2D simulations of the transporting sites  $(10 \times 10)$  of the mixed organic materials. The sites of CBP and the dopant are determined by random coordinates. The arrows represent the transporting manifold in the deep trapping and high scattering situations.

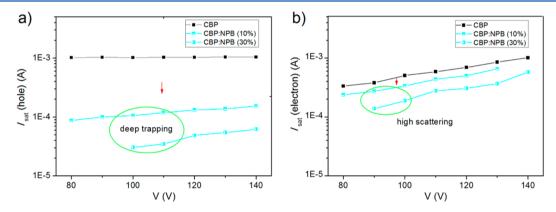


Figure 7. The saturation photocurrents (plateau currents) of (a) the hole TOF transients of pure CBP and the deep trapping situation, and (b) the electron TOF transients of pure CBP and the high scattering situation.

transporting manifolds of the host states disappear. From Figure 3, we see that even when the deep trapping dopant increases to 50%, mobility shows no obvious decrease. To explain this surprising phenomenon, 2D simulations of the transporting sites of the mixed organic materials are made and shown in Figure 6. The results show that continuous transporting manifolds (white arrows) still exist when 50% of dopant is induced.

However, a significant difference also exists between the deep trapping and high scattering. From Figure 5, we see that carriers are captured in the traps while scatters do not capture the carriers. So we may infer that the saturation photocurrent, that is, the plateau photocurrent of the TOF transient, can be much smaller in the deep trapping situation than in the high scattering situation. The plateau photocurrents of the CBP:NPB films in Figure 2a (deep trapping situations) and Figure 2b (high scattering situations) are within our prediction. Furthermore, the saturation photocurrents ( $I_{\rm sat}$ ) of the CBP:NPB films under various bias are depicted in Figure 7, through which we see deep traps induce a reduction of 1 order of magnitude in  $I_{\rm sat}$  while there is only a slight reduction for high scatters.

II. The Effective Energetic Disorder. There seems to be a contradiction between the experimental energetic disorder and the theoretical energetic disorder in the previous temperature varying studies. <sup>12,13,16</sup> In this part, we proposed the concept of "effective energetic disorder" ( $\sigma_{\rm eff}$ ) and demonstrate its consistency with the experimental energetic disorder.

The energetic disorder has been widely accepted as the width of the localized DOS, that is, the standard deviation of the distribution of the localized energy. Following this theoretical

definition, the energetic disorder of the mixed system can be exactly expressed by

$$\sigma_{\rm m}^2 = (1 - x)\sigma_{\rm A}^2 + x\sigma_{\rm B}^2 + x(1 - x)(\Delta \varepsilon)^2 \tag{6}$$

where x is the concentration of the impurity,  $\sigma_A$  and  $\sigma_B$  are, respectively, the energy disorder of the host and the impurity,  $\Delta \varepsilon = \varepsilon_A - \varepsilon_B$ , where  $\varepsilon_A$  and  $\varepsilon_B$  are, respectively, the LUMOs (or HOMOs) of the two constituents (the derivation of eq 6 can be found in the Supporting Information). Equation 6 indicates that the contributions of traps and scatters to energetic disorder are identical in theory. However, why does the experimental energetic disorder induced by trapping and scattering differ in some reports? 12,13 In the discussions above, we have concluded that the shallow traps and low scatters participate in charge transport to a great degree, while the deep traps and high scatters hardly participate in charge transport. This conclusion suggests that the energetic disorder should only include the contribution of the states that participate in charge transport to ensure its practical applicability, and this is what the "effective energetic disorder" refers to.

According to the definition of the effective energetic disorder  $(\sigma_{\rm eff})$ ,  $\sigma_{\rm eff}$  of the materials with high scatters or deep traps would be almost identical to the energetic disorder of the pure material, while  $\sigma_{\rm eff}$  of the materials with low scatters or materials with shallow traps could be expressed by eq 6, which is increased by  $x(1-x)(\Delta\varepsilon)^2$ , as compared to the pure material (if  $\sigma_{\rm A} \approx \sigma_{\rm B}$  or x is small). A recent Monte Carlo simulation by Tamika et al. has indicated that with  $\sigma_{\rm A} = \sigma_{\rm B} = 0$  eV and  $\Delta\varepsilon = \pm 0.05$  eV (which is among the low scattering or shallow trapping situation), the source drain current  $(I_{\rm SD})$  as a function

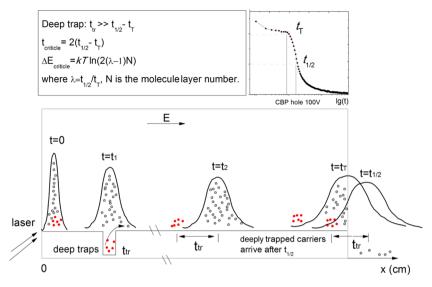


Figure 8. Transport of the free carriers (gray  $\bullet$ ) and the trapped–escaping carriers (red  $\bullet$ ), and the model of the critical  $\Delta E$ .

of the trap (or scatter) concentration (x) shows a quadratic polynomial behavior, which is in good accordance with the increment of energetic disorder given by eq 6. In this work, we have evidence to show the consistency of  $\sigma_{
m eff}$  with the experimental results. First, on one hand,  $\ln \mu_0$  of the materials with low scatters sharply decreases, and  $\beta$  of the materials with low scatters sharply increases (as shown in Figure 4), which can be attributed to the increasing of  $\sigma_{\text{eff}}$  according to eqs 4 and 5; on the other hand, both  $\ln \mu_0$  and  $\beta$  of the materials with deep traps or high scatters do not significantly change, which can be attributed to the unchanged  $\sigma_{ ext{eff}}$ . Results by So et al. also suggest that the experimental energetic disorder of the materials with high scatters is identical to that of the pure material, while the experimental energetic disorders of the materials with shallow traps increase by about 30%. 13 Second, shallow scatters change the TOF transients from nondispersive to dispersive, while high scatters and deep traps do not change the nondispersive behavior, as shown in Figure 2. The nondispersive and dispersive behavior of the TOF transient has been strongly related to the energetic disorder in the works by Bässler et al. 15,24 They have found that as the energetic disorder increases, the spatial distribution of the carriers becomes wider due to the thermodynamically controlled hopping, and hence the TOF transient changes to dispersive and the experimental transition time become longer.

III. The Demarcation of Deep Trap and Shallow Trap. In the discussions above, we have concluded the different effects of deep traps and shallow traps, as well as high scatters and low scatters, on charge transport. Deep traps and high scatters just induce a slight reduction in mobility and would not induce a big degree of dispersive trend in TOF transients, while shallow traps and low scatters induce significant reduction in mobility and a great degree of dispersive trend in TOF transients. The mechanisms of the differences have also been discussed. However, to make our conclusion convincible and generalized, a definite demarcation between the deep traps (high scatters) and the shallow traps (low scatters), that is, the critical  $\Delta E$ , is needed. An important difference from the shallow traps to the deep traps is that the shallow traps can result in a dispersive trend the TOF transients, which indicates the spatial distribution of the carriers has been broadened and the decay time of the photocurrent has been elongated by the shallow

traps. Although the carriers captured in deep traps can escape and arrive at the contra electrode, however, the time they arrive is much later than that of the uncaptured carriers because of the large trap residing time. Hence, these carriers will not broaden the spatial distribution of the uncaptured carriers that arrive around the time region of  $t_{\rm T}$ , and the determination of  $t_{\rm T}$  will not be disturbed (as shown in Figure 2c and d). Instead, the TOF transients always have a long tail plateau caused by the trapped carriers (as shown in Figure 2c, the CBP:NPB films). For the CBP:Alq<sub>3</sub> (50%) film, the long tail disappears as the trapped carriers may transport by the continuous manifolds of Alq<sub>3</sub>, which can be seen in Figure 6 (the black arrow).

Therefore, in our consideration, if the carriers captured by the traps arrive at the contra electrode long after  $t_{1/2}$  (the time at which the current has decreased to one-half of its plateau value), the trapped carriers are considered to not affect the spatial distribution of the untrapped carriers (as shown in Figure 8), then these traps belong to deep traps; however, if the carriers captured by the traps arrive before (or around)  $t_{1/2}$ , they are sure to affect the spatial distribution of the untrapped carriers and result in a more dispersive TOF transient, and then these traps are regarded as shallow traps.

In this work, we define the deep traps by

$$t_{\rm tr} \ge 2(t_{1/2} - t_{\rm T}) \tag{7}$$

where  $t_{\rm tr}$  is the trap residing time, and  $t_{1/2}$  and  $t_{\rm T}$  are the half-time and the transition time of the pure material. According to the Miller–Abrahams model, we have

$$t_{\rm tr} = a/k_0 \cdot \exp(\Delta E/kT) \tag{8}$$

where a is the average length between the hopping sites and  $k_0$  is the average hopping rate in the pure material:

$$t_{\rm T} = a/k_0 \cdot N \tag{9}$$

where N = L/a is the molecule layer number of the film and L is the thickness of the film, and

$$t_{1/2} = \lambda \cdot t_{\mathrm{T}} \tag{10}$$

where  $\lambda$  is a factor obtained via the TOF transient of the pure material.  $\lambda$  represents the degree of the dispersive behavior (the larger is  $\lambda$ , the more dispersive is the TOF transient, and when  $\lambda = 1$ , the TOF transient is completely nondispersive), which is

close to the concept of tail broadening parameter W in the work by Tseng et al.<sup>25</sup>

Through eqs 7–10, we obtain the critical  $\Delta E$ , which is expressed as

$$\Delta E_{\text{critical}} = kT \ln(2(\lambda - 1)N) \tag{11}$$

For the TOF films in this work,  $L=2~\mu m$ ,  $a\approx 10~\text{Å}$  (according to the single crystal structure of CBP<sup>26</sup>), T=298~K, and  $\lambda$  is 2.5 for the hole transport and 3 for the electron transport, so we get  $\Delta E_{\text{critical}}=0.21~\text{eV}$  for hole transport and  $\Delta E_{\text{critical}}=0.22~\text{eV}$  for electron transport. According to the critical  $\Delta E$ , the trapping and scattering situations in Table 1 are convictive.

To generalize our conclusions for the CBP hosted system, we apply this model to the hole transport behaviors of TPD hosted system and NPB hosted system reported by So et al.  $^{12,13}$  The critical  $\Delta E$ 's of these systems are within 0.20–0.23 eV, and our conclusions of the effects of traps and scatters on charge transport are confirmed by the experimental results therein (see Table S1 in the Supporting Information). In addition, the experimental energetic disorders show a good accordance with what calculated by eq 6 (see Table S1 in the Supporting Information), except that the experimental disorders are found to be always larger than the theoretical results, which has been reported by Schein et al.  $^{27}$ 

## 6. CONCLUSIONS

The effects of trapping and scattering on charge transport in the mixed organic semiconductors have been investigated by the TOF method. We find that low scatters and shallow traps induce significant reduction in mobility, while there is only a slight reduction for high scatters and deep traps. The energy level difference between the traps (or scatters) and the host states,  $\Delta E$ , is a crucial factor to the effects of traps and scatters on charge transport, according to the Miller-Abrahams hopping model. We conclude that shallow traps and low scatters participate in charge transport to a great degree as  $\Delta E$ is small, while high scatters and deep traps hardly participate in charge transport due to their thermodynamic control low hopping rate with the host states, which is resulting from the large  $\Delta E$ . As a result, the shallow traps and the low scatters enlarge the effective energetic disorder of the mixed semiconductors and decrease mobility significantly, while the deep traps and high scatters would not contribute to the effective energetic disorder and just induce a slight reduction in mobility resulting from the elongated transporting manifold. Moreover, a theoretical method is established to determine the demarcation between the shallow trap (low scatter) and the deep trap (high scatter) in terms of  $\Delta E$ . This work helps to clarify the physical image of charge transport in mixed disorder semiconductors and may provide good guides to device design in organic electronics.

# ASSOCIATED CONTENT

#### S Supporting Information

Derivation of eq 6. Generalization of our conclusion to the TPD hosted system and NPB hosted systems<sup>12,13</sup> reported by So et al. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### **Notes**

The authors declare no competing financial interest.

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