Advantages of admittance spectroscopy over time-of-flight technique for studying dispersive charge transport in an organic semiconductor

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We show that admittance spectroscopy (AS) is a better technique than time of flight (TOF) to study the charge transport properties in dispersive materials. The hole transport properties of N,N'-diphenyl-N,N'-bis(1-naphthyl)(1,1'-biphenyl)-4,4'-diamine (NPB) doped with different traps were evaluated by AS and TOF techniques. It was found that both techniques can show clear signals for measuring the mobility of NPB doped with shallow traps. When NPB was doped with deep traps, the AS signals were still clear for mobility extraction. In sharp contrast, the TOF transients become featureless and the carrier transit time cannot be determined. The validity of AS in mobility determination was demonstrated by comparing the extracted AS to TOF mobilities. Generally, the hole mobilities extracted by these two techniques were in excellent agreement. In addition, we will demonstrate that AS can be employed to measure carrier dispersion. © 2009 American Institute of Physics. [doi:10.1063/1.3251409]

I. INTRODUCTION

Charge carrier transport is one of the most crucial factors that govern the performance of optoelectronic devices, e.g., organic light emitting diodes (OLEDs), organic thin film transistors, organic photovoltaic cell (OPVs), etc.[1–3] To understand the charge transport behaviors inside such devices, many researches have been devoted to measure the carrier mobility of the organic films.[4,5] Experimentally, time of flight (TOF) is perhaps the most general technique to extract the carrier mobility of organic materials.[6] In TOF, free charge carriers are photogenerated by a pulsed laser. The mobility is determined by the transit time τ of the leading charge carrier transporting through the organic film. Since TOF technique is independent of the electrical contact at the metal/organic interface, the problems of charge injection can be neglected. Thus, TOF can be viewed as a standard means to measure carrier mobilities. TOF, however, suffers from several limitations. Due to the finite photon penetration length of laser, a thick film is required to provide a well-defined flight distance, which results in large material consumption. Moreover, traps (intrinsic or extrinsic) may be presented inside the organic film, resulting in a highly dispersive TOF transient, hindering the extraction of τ. Thus, TOF appears not to be a practical means for mobility evaluation in dispersive material. Yet, there are still abundant interests in measuring the mobilities of many dispersive organic materials. Prime examples are the organic blends inside a bulk heterojunction solar cell, which is now a hot topic in OPVs.[7–9] Due to carrier dispersion or trapping, transit time technique such as TOF is not the best choice in evaluating carrier mobilities in dispersive materials. There is a clear need to look for an alternative.

In this study, we show that admittance spectroscopy (AS) is a better technique than TOF to study the charge transport properties in dispersive materials. AS is known to be a powerful technique for carrier mobility evaluation.[10–12] Previous reports showed that AS can be successfully applied to extract the mobility of amorphous organic materials. A representative example is the hole mobility measurement of N,N'-diphenyl-N,N'-bis(1-naphthyl)(1,1'-biphenyl)-4,4'-diamine (NPB).[13] NPB is a well-recognized hole transporter in OLEDs and it possesses trap-free hole transporting property.[14] To examine the feasibility of AS and TOF in the determination of carrier mobility in dispersive materials, we intentionally doped some traps into NPB. The hole mobility measurement of doped NPB by AS and TOF will be compared. The dopants used were rubrene (Rb), 4-(dicyanomethylene)- 2- methyl-6- (p-dimethylaminostyryle)4H-pyran (DCM1), and copper phthalocyanine (CuPc). Their chemical structures and highest occupied molecular orbitals (HOMO) are shown in Fig. 1. The dopants have a higher-lying HOMO relative to the host, i.e., NPB. The dopant molecules form traps in NPB and the trap depth E_t is approximately equal to the HOMO energy difference between the dopant and the host material.[15] Generally, larger trap depth should result in more dispersive charge transport. Besides studying carrier mobilities, we demonstrate that AS can also be employed to measure carrier dispersion.

II. EXPERIMENTAL

Details of TOF and AS techniques have been reported elsewhere.[6,12,13] Figure 2(a) shows the schematic diagram of the AS measurement. Generally, AS sample had a structure of anode/organic layer/cathode. For AS hole mobility measurement, it requires the organic material to form an Ohmic contact with the anode and an electron-blocking cathode. The relaxation of charge density of the sample is monitored under a dc biased voltage V_{dc} superimposed with a small

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ac excitation v_{ac} with a frequency f. Experimentally, the ac current response i_{ac} is measured and the complex admittance Y can be obtained as

$$Y(\omega) = \frac{i_{ac}}{v_{ac}} = G + iB = G + i\omega C, \tag{1}$$

where $i^2 = -1$, $\omega = 2\pi f$, and G, B, and C are the conductance, susceptance, and capacitance, respectively. Previously, we showed that Y can be deduced analytically and is given by[12]

$$Y(\Omega) = \frac{\varepsilon A}{\tau_{dc} d}\left\{\frac{\Omega^3}{2i[0.75\tilde{\mu}(\Omega)]^2\left[1 - \exp\left(\frac{-i4\Omega}{3\tilde{\mu}(\Omega)}\right)\right] + 1.5\tilde{\mu}(\Omega)\Omega - i\Omega^2}\right\}. \tag{2}$$

In Eq. (2), ε is the permittivity of the organic material and A and d are the active area and the thickness of the sample, respectively. The normalized frequency is defined as $\Omega = 2\pi f \tau_{dc} = \omega\tau_{dc}$. The normalized mobility is defined as $\tilde{\mu}(\Omega) = \mu(\Omega)/\mu_{dc}$, where $\mu_{dc} = d^2/(V_{dc}\tau_{dc})$ is the dc mobility and τ_{dc} is the average transit. A convenient way to extract the carrier mobility is to measure the frequency-dependent capacitance by an impedance analyzer and the negative differential susceptance $-\Delta B$ can then be calculated by $-\Delta B = -2\pi f(C - C_{geo})$, where $C_{geo} = \varepsilon A/d$ is the geometric capacitance. By plotting $-\Delta B$ versus f, it generally yields a maximum at a distinct frequency $f_r = \tau_r^{-1}$ as shown in Fig. 2(a). From Eq. (2) and computer simulations, the characteristic time τ_r and the average transit time τ_{dc} are related by $\tau_{dc} = 0.56\tau_r$.[12] From the known thickness of the organic layer d and electric field F, the carrier mobility can then be determined by

$$\mu_{dc} = d/(\tau_{dc}F) = d/(0.56\tau_r F). \tag{3}$$

In this study, all AS samples had a structure of indium-tin-oxide (ITO)/hole injection layer (HIL)/doped NPB (1.5% in volume)(2 μm)/Al(100 nm). For simplicity, all doped samples are represented with the notation NPB:X, where X is the name of the dopant. For NPB:Rb and NPB:DCM1, a 50 nm (3,4 ethylenedioxythiophene)/polystyrene sulfonic acid (PEDOT:PSS) was used as the HIL. PEDOT:PSS has been demonstrated to achieve nearly Ohmic contact with NPB.[14] However, it should be noted that the PEDOT:PSS cannot form an Ohmic contact with the NPB:CuPc layer. This may be attributed to the injected holes, which were strongly trapped by the CuPc molecules at the interface (see Fig. 1, $E_t \sim 0.3$ eV). Thus, a 20 nm NPB layer was inserted between the PEDOT:PSS and the doped NPB layer to facilitate hole injection. Aluminum was finally evaporated to form an electron-blocking layer. For this report, all AS measurements were taken at a slightly elevated temperature of $T = 311$ K to facilitate the injection of holes from the anode.

The schematic diagram of TOF hole mobility measurement is shown in Fig. 2(b). All TOF samples had a structure of ITO/doped NPB(8–9 μm) (1.5% in volume)/
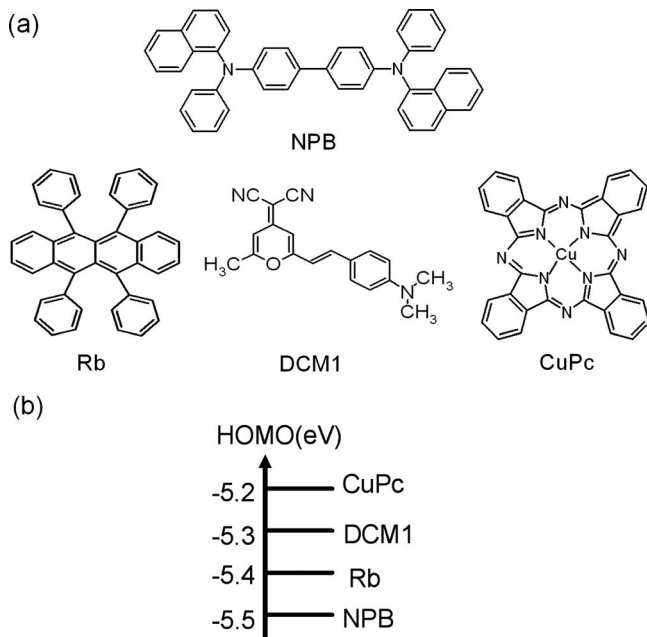

FIG. 1. (a) Chemical structures of host material (NPB) and dopants. (b) HOMO energy diagram of host material and dopants.
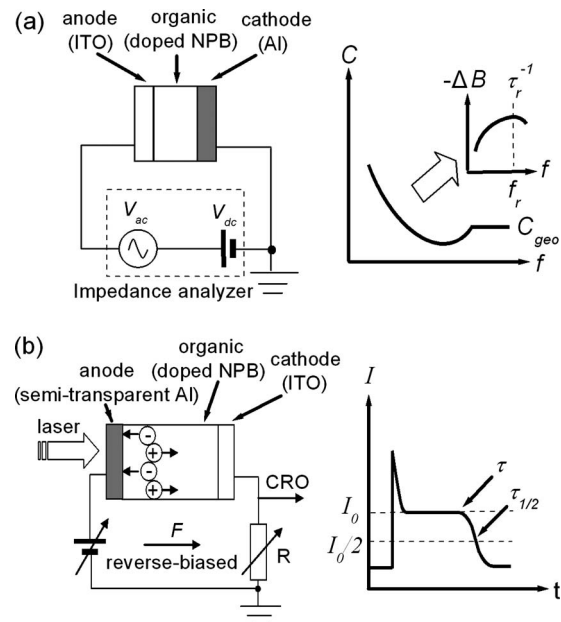

FIG. 2. Schematic diagram of (a) AS and (b) TOF experimental setup (left). Typical experimental signals are also shown (right).
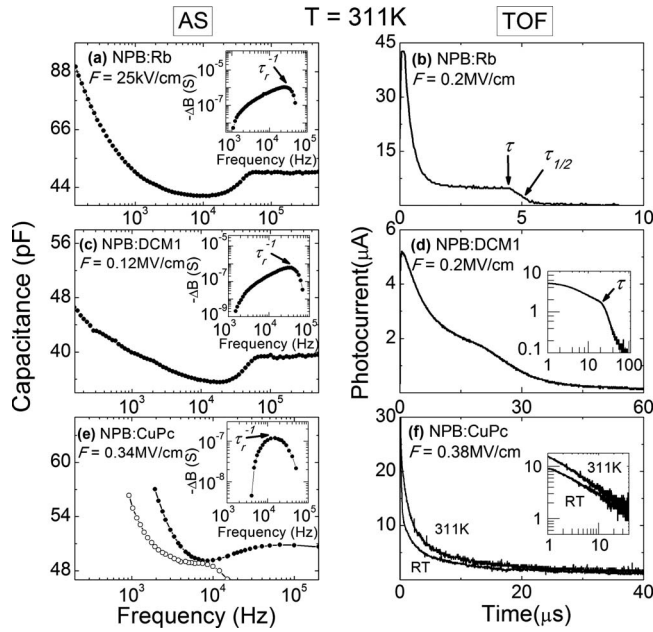
FIG. 3. The AS signals (left-hand panel) and TOF transients (right-hand panel) for NPB:Rb, NPB:DCM1 and NPB:CuPc at $T=311$ K. The open symbols shown in (e) are the AS signal of NPB:CuPc at room temperature. The insets in (a), (c), and (e) are the negative differential susceptance vs frequency plots. The insets shown in (d) and (f) are log-log plots of the TOF transients. In (f), the TOF transient at room temperature (RT) is also shown for reference.

CuPc(100nm) /Al(15 nm). The samples were reverse biased. A nitrogen pulsed laser ($\lambda=337.1$ nm) was irradiated on the semitransparent cathode/organic interface to generate electron-hole pairs. CuPc was used as a charge generation layer. Since it has strong absorption at 337.1 nm, over 90% of the incident photons were absorbed by the CuPc layer.[16] A dc power supply was used to provide the bias voltage for hole detection. Free holes are drifted toward the negatively biased anode. A digital oscilloscope was used to measure the applied voltage across the sensing resistor R, which was connected in series with the sample. The carrier transit time τ of the leading charge carrier transporting through the organic film can be determined from the turning point of the TOF transient [see Fig. 2(b)]. The carrier mobility for the fastest carrier can be extracted by

$$\mu = d/(\tau F). \tag{4}$$

III. RESULTS AND DISCUSSIONS

Figure 3 shows the representative frequency-dependent capacitances measured by AS (left-hand panel) and the TOF hole transients (right-hand panel) for different samples at $T=311$ K. For NPB:Rb, the Rb molecules form shallow traps in NPB. [see Fig. 1(b), $E_t \sim 0.1$ eV]. The dispersion in charge transport should not be too large. It is expected that both AS and TOF techniques show a clear signal for mobility extraction as shown in Fig. 3(a) and 3(b). From Fig. 3(a), the AS signal has a well-defined minimum capacitance C_{min} at an intermediate frequency and the capacitance attains to a steady value of about 50pF, which is the same as their respective geometric capacitance C_{geo}, at high frequencies. A

clear dip can be observed from the AS signal and τ_r can be determined from the peak of $-\Delta B$ versus f plot [see inset of Fig. 3(a)]. The AS mobility at certain frequency can then be computed by Eq. (3). On the other hand, the TOF transient for NPB:Rb shows a nondispersive characteristic with a very well-defined plateau and a sharp turning point as shown in Fig. 3(b). τ can be determined at the instant at which the plateau drops abruptly. The mobility can be obtained by using Eq. (4). It shows that both techniques are suitable to study some slightly dispersive materials.

To examine whether AS and TOF is feasible for mobility determination in more dispersive materials, two deep traps, DCM1 [Fig. 1(b), $E_t \sim 0.2$ eV] and CuPc [Fig. 1(b), $E_t \sim 0.3$ eV], were doped into NPB. We first discuss the effects of DCM1 on the AS and TOF measurement. From Fig. 3(c), we can see that the AS signals are still clear for mobility extraction when deep trap (DCM1) was doped into NPB. Similar to the case of NPB:Rb, the signal shows a clear dip and τ_r can be determined from the peak of $-\Delta B$ versus f plot [see inset of Fig. 3(c)]. In sharp contrast, the TOF signal of NPB:DCM1 is strongly influenced by the dopant. As shown in Fig. 3(d), the TOF transient becomes dispersive when DCM1 is introduced into NPB. The plateau region in the TOF signal is not evident and hence τ cannot be determined directly from the photocurrent transient. The hole transit time can only be defined from the log-log plot of the TOF signal [see inset of Fig. 3(d)]. This demonstrates that AS has an advantage for mobility extraction in dispersive materials. To further reveal the advantage of using AS technique to study dispersive materials, a deeper trap (CuPc) with large E_t of about 0.3 eV was doped into NPB [see Fig. 1(b)]. From Fig. 3(f), it can be seen that the TOF transients become highly dispersive for NPB:CuPc at room temperature (RT) and 311 K. The signal shows a monotonic decaying curve and τ cannot even be defined from the log-log plot of the photocurrent transient [see inset of Fig. 3(f)]. Contrarily, when AS method was used to study NPB:CuPc, the signal (closed symbols) retains its features for mobility determination as shown in Fig. 3(e). Obviously, it demonstrates that AS is superior over the TOF technique to study the charge transport inside highly dispersive materials as the AS signals are not easily affected by the deep traps. It should be noted that the carrier mobility of NPB:CuPc can only be determined by AS method when temperature is slightly elevated to 311 K or above. From Fig. 3(e), we cannot observe a clear dip for mobility determination from the AS data at room temperature (opened symbols). However, when temperature is increased to 311 K, a clear dip can be observed from the AS signal (closed symbols). It indicates that the injection of holes from the anode is improved.

Next, we investigate the validity of AS for mobility extraction in dispersive materials. The extracted average hole mobilities μ_{dc} by AS are compared to those measured by TOF. To have a fair comparison, the TOF mobilities are computed from the average carrier transit time $\tau_{1/2}$ rather than the fastest carrier transit time τ since AS measures the average mobility of the charge carriers. $\tau_{1/2}$ can be determined from the time for the transient to decay to one-half of the plateau value [see, e.g., Fig. 2(b)]. Figure 4 shows the field depen-
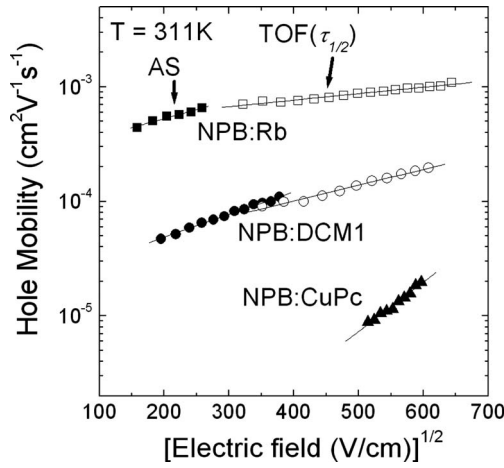
FIG. 4. Field dependent hole mobilities of NPB:Rb, NPB:DCM1, and NP-B:CuPc at $T=311$ K. The closed and opened symbols represent the data extracted from AS and TOF techniques, respectively. For NPB:CuPc, the carrier mobilities can only be measured by AS. The solid lines are the best fit of the mobility data.
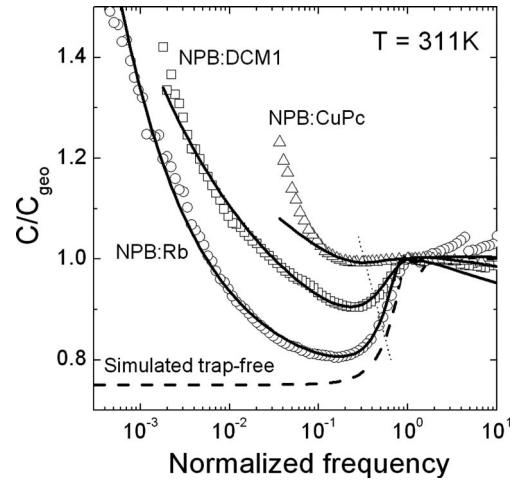

FIG. 5. Experimentally determined frequency-dependent capacitances of doped NPB. The solids lines are fits to data using Eqs. (1), (2), and (5). The dashed line is the simulated trap-free AS signal. The dotted line is the locus of f_r, which is related to the carrier transit time by $\tau_{dc}=0.56f_r^{-1}$. Details of dispersion parameters are summarized in Table I.

dent hole mobilities of doped NPB by AS and TOF. The solid and open symbols are the hole mobilities derived from AS and TOF, respectively. Generally, the two sets of data are in excellent agreement with each other. It shows that AS is a reliable technique to measure the carrier mobility in dispersive materials. It should be noted that the mobility of NPB-:CuPc can be only extracted by the AS method. However, the mobility of NPB:CuPc obtained from AS method is still reasonable. Since larger mobility reduction can be observed when the trap depth in NPB is increased.[15]

Our results demonstrate that for the more dispersive samples, carrier transit times can only be extracted by AS rather than TOF technique. The failure of TOF is probably related to the nature of data acquisition. TOF measures carrier transit times in the time domain. The measurement is affected by the combined RC time constant of the sample and the sensing resistor. For the highly dispersive sample (NPB:CuPc), the effective time constant is larger (due to the increase in sample resistance). The resulting TOF signal is then overwhelmed by the RC decay, rendering the determination of the transit time impossible. In contrast, AS extracts carrier transit times in the frequency domain. AS simultaneously probes the real and the imaginary parts of the complex impedance [Eq. (1)]. The extraction of the carrier transit time only needs to involve the imaginary part of the complex impedance (i.e., the frequency-dependent capacitance) and is independent of the conductivity of the sample. Thus the extraction of the carrier transit time remains effective for AS.

Besides extracting carrier transit times and hence carrier mobilities, AS can also be employed to measure carrier dispersion. The normalized mobility $\tilde{\mu}(\Omega)$ in Eq. (2) can be written in the form[10,11,17]

$$\tilde{\mu}(\Omega) = \mu(\Omega)/\mu_{dc} = 1 + M(i\Omega)^{1-\alpha}, \qquad (5)$$

where M and α are the dispersion parameters. From Eqs. (1), (2), and (5), one can simulate the frequency-dependent capacitance by using three parameters, namely, μ_{dc}, M, and α. For a trap-free material with nondispersive carrier transport,

the dispersion parameters M and α should be equal to 0 and 1, respectively. An example of computer simulated frequency-dependent capacitances for trap-free materials ($M=0$, $\alpha=1$, and $\mu_{dc}=1\times10^{-3}$ cm^2/V s) are shown as a dash line in Fig. 5. We can see that the minimum of capacitance C_{min} is equal to $0.75C_{geo}$. In fact, the values of M, α, and C_{min}/C_{geo} can provide a guideline for studying carrier dispersion. To study how M, α, and C_{min}/C_{geo} change with carrier dispersion, the admittance data of doped NPB were fitted by Eqs. (1), (2), and (5), and the simulated results were shown as a solid line in Fig. 5. For NPB:Rb (slightly dispersive transport), the simulated result is in good agreement with our experimental data. The values of dispersion parameters M and α were found to be 0.03 and 0.50, respectively. The value of $C_{min}/C_{geo}=0.80$ is closed to the ideal value of 0.75. When DCM1 is doped into NPB (moderately dispersive transport), there is a clear change in the shape of the AS signal. The values of M and C_{min}/C_{geo} increase to 0.10 and 0.91, respectively, while the value of α decreases to 0.27. For NPB:CuPc (highly dispersive transport), the simulated result can only be fitted well with our experimental data at high frequency. At low frequency, our data deviate from the simulated result. Table I summarizes all the values of M, α, and C_{min}/C_{geo}. From the above results, it demonstrates that the fitting parameters M and α, which strongly depend on the shape of the AS signal, can be used to describe the carrier dispersion in organic solids. Generally, a more dispersive charge transport would result in a larger value of M and

TABLE I. Dispersion and transport parameters extracted from the AS signals in Fig. 5.

Sample	E_t (eV)	α	M	C_{min}/C_{geo}	τ_r (μs)	F (kV/cm)
Trap-free	0	1	0	0.75	6.5	67
NPB:Rb	~0.1	0.50	0.03	0.80	9.9	67
NPB:DCM1	~0.2	0.27	0.10	0.91	87	67
NPB:CuPc	~0.3	0.13	0.23	0.99	15	260

smaller value of α. The value of $C_{\min}/C_{\mathrm{geo}}$ would also larger and deviate from the ideal value of 0.75. In addition, the dispersion parameter α can provide an insight of the distribution of trap states inside disordered organic solids. According to the Scher and Montroll theory, the energy of localized states can be described as an exponential distribution,[18]

$$\rho(\varepsilon) = \rho_0 \exp\left(-\frac{\varepsilon}{k_B T_t}\right). \tag{6}$$

In Eq. (6), k_B is the Boltzmann constant and T_t is the characteristic temperature; the product $k_B T_t$ can be understood as the spread of trap energies, i.e., the width of the distribution $\rho(\varepsilon)$. The dispersion parameter α can be expressed as $\alpha = T/T_t$ with the condition $0 \le \alpha \le 1$ and $T \le T_t$. With the knowledge of α, we can compute the characteristic temperature T_t and hence the distribution of trap states can be evaluated. In our AS experiments, the values of α are in the order $\alpha_{\mathrm{Rb}} > \alpha_{\mathrm{DCM1}} > \alpha_{\mathrm{CuPc}}$ (see Table I). From the relation $\alpha = T/T_t$ ($0 \le \alpha \le 1$ and $T \le T_t$), it indicates that a smaller α would result in a larger T_t. Thus, it suggests that the distribution of traps states in NPB:CuPc is the broadest, while the one in NPB:Rb is the narrowest.

IV. CONCLUSION

In conclusion, we have demonstrated that AS is superior over the TOF technique to study the charge transport inside dispersive materials. For studying slightly dispersive charge transport (NPB:Rb), both techniques show clear signals for mobility extraction. The AS method, however, shows clear advantages in studying highly dispersive materials (NPB:CuPc). The AS signals remain clear for mobility determination when deep traps are present, while the TOF transients show highly dispersive characteristics without any indication of the carrier transit time. The extracted mobilities of NPB:Rb and NPB:DCM1 by AS are in excellent agreement with those obtained by TOF technique. It further demonstrated that AS is a reliable technique for mobility evaluation in dispersive materials. Additionally, the dispersion parameters M and α from AS can be employed to measure the carrier dispersion in organic solids.

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