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Polymeric conducting anode for small organic transporting molecules in dark injection experiments

S. C. Tse, S. W. Tsang, and S. K. So^{a)}

Department of Physics, Hong Kong Baptist University, Kowloon Tong, Hong Kong, China
and Centre for Advanced Luminescence Materials, Hong Kong Baptist University,
Kowloon Tong, Hong Kong, China

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Poly(3,4-ethylenedioxythiophene) doped with polystyrenesulphonic acid (PEDOT:PSS) is used as a hole-injecting anode for small organic hole transporters in current-voltage (JV) and dark injection space-charge-limited current (DI-SCLC) experiments. The hole transporters under investigation are phenylamine-based 4,4',4''-tris(N -3-methylphenyl- N -phenyl-amino)triphenylamine (MTDATA), N,N' -diphenyl- N,N' -bis(1-naphthyl) (1,1'-biphenyl)-4,4'-diamine (NPB), and N,N' -diphenyl- N,N' -bis(3-methylphenyl)(1,1'-biphenyl)-4,4'-diamine (TPD). Clear DI-SCLC transient peaks were observed over a wide range of electric fields in all cases. For MTDATA and NPB, hole mobilities evaluated by DI experiments are in excellent agreement with mobilities deduced from independent time-of-flight technique. It can be concluded that, for the purpose of JV and DI experiments, PEDOT:PSS forms an Ohmic contact with MTDATA and a quasi-Ohmic contact with NPB despite the relatively low-lying highest occupied molecular orbital of the latter. In the case of TPD, hole injection from PEDOT:PSS deviates substantially from Ohmic injection, leading to a lower than expected DI-extracted hole mobility. The performances of other hole-injecting anodes for DI experiments were also examined. © 2006 American Institute of Physics. [DOI: 10.1063/1.2348640]

I. INTRODUCTION

Organic electronics has evolved into an important technology in optoelectronics as indicated by increasing appearances of fashionable consumer products such as high contrast flat panel displays.¹ There are also emerging applications in solar cells, photodetectors, and flexible electronic papers.²⁻⁴ At least one active organic electronic material is present in all of these devices. The material is usually processed into a very thin film through which a current passes. Thus the ability to characterize the conductivity of an organic film is of special importance in organic electronics.

Optical time-of-flight (TOF) technique is, perhaps, the most widely used method of quantifying the conductivity of organic electronic materials.⁵ In TOF, the organic material is sandwiched between two electrodes, one of which is transparent. After laser radiation, the transient photocurrent is monitored as charge carriers drift to the charge-collecting electrode under an applied voltage V . The carrier transit time (τ) is determined from the turning point in a plot of the photocurrent against time. Knowing the thickness (d) of the sample, one can deduce the carrier mobility from the relation $\mu = d^2 / (\tau V)$.

Besides TOF, dark injection space-charge-limited current (DI-SCLC) is a well-known technique for measuring carrier mobility in organic electronic materials.⁶⁻⁸ In a DI experiment, the sample has a configuration of anode/organic layer/cathode. The cathode is designed to be electron blocking if only the hole injection is examined. The sample is then subjected to a voltage pulse excitation. Under the special case in which (i) the anode/organic contact is Ohmic and (ii) the

organic/cathode contact is electron blocking, a transient electrical (hole) current can be observed after application of the pulse excitation. Figure 1 outlines the ideal transient current response for a trap-free organic semiconductor. The transient current density $J(t)$ can be computed from Poisson's equation for a trap-free material under the condition of unipolar Ohmic injection.⁹ From Fig. 1, at $t = \tau_{DI}$, $J(t)$ reaches a maximum value of J_{DI} . For $t > \tau_{DI}$, the transient current decays monotonically and asymptotically to a steady-state value of J_{SCL} . Two critical parameters can be extracted from the transient current density. First, the characteristic time τ_{DI} is the arrival time of the fastest carriers at the noninjecting electrode. τ_{DI} is related to the space-charge free carrier transit time τ by^{9,10}

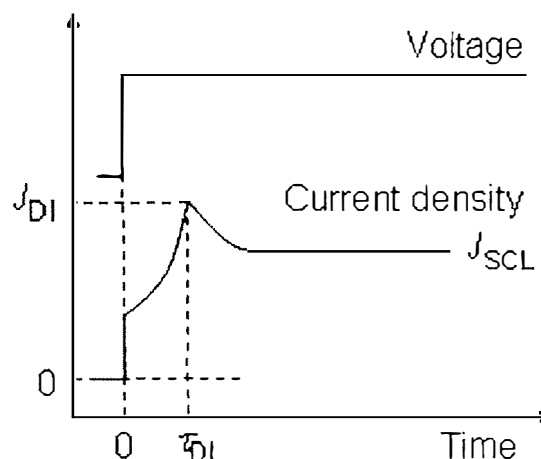


FIG. 1. An ideal DI-SCLC transient.

^{a)}Electronic mail: skso@hkbu.edu.hk

$$\tau_{DI} = 2(1 - e^{-0.5})\tau = 0.787\tau. \quad (1)$$

Hence the carrier mobility can be determined from DI experiments as outlined in Fig. 1. Second, the ratio J_{DI}/J_{SCL} should be 1.21.⁹ Departure from this ideal value of 1.21 may indicate that the injecting contact deviates from Ohmic injection. Alternatively, if the charge injection remains Ohmic, deviation of this ratio could also be a consequence of non-negligible charge diffusion or field dependent mobilities. A critical examination of this ratio under the condition of Ohmic injection has been reported elsewhere.¹¹ This paper primarily deals with the evaluation of carrier mobilities from DI experiments.

While the principles of DI-SCLC are well known, the application of the DI technique has encountered limited success due to the lack of Ohmic injecting electrodes.¹² For hole injection, many common small-molecule hole transporters have their highest occupied molecular orbitals (HOMOs) exceeding 5.3 eV.^{13–15} Ideally, it is possible to use high work function metals (e.g., Pt) for hole injection into the material of interest. In reality, whenever high work function metals are in contact with small molecules, it is very common to observe, e.g., by photoemission experiments, a higher than expected hole injection barrier.¹⁶ The origin of the deviation is still controversial, but it is believed to be associated with charge redistribution in the metal/organic interface.

This paper addresses the hole injection problem in DI experiments. We use poly(3,4-ethylenedioxythiophene) (PEDOT), doped with poly(styrenesulfonic acid) (PSS), as the hole-injecting anode. The hole transporters under examination are phenylamine-based 4,4',4''-tris(*N*-3-methylphenyl-*N*-phenyl-amino)triphenylamine (MTDATA), *N,N'*-diphenyl-*N,N'*-bis(1-naphthyl) (1,1'-biphenyl)-4,4'-diamine (NPB), and *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl) (1,1'-biphenyl)-4,4'-diamine (TPD). Figures 2(a) and 2(b) show their chemical structures and their HOMO levels. We show that PEDOT:PSS can behave effectively as a quasi-Ohmic contact for DI experiments. The hole mobilities deduced from DI measurements are in good agreement with those obtained independently from TOF.

II. EXPERIMENT

All samples for TOF, DI-SCLC, and current-voltage (I/V) measurements have the general structure of an organic layer sandwiched between two electrodes. The bottom anode was a patterned layer of indium tin oxide (ITO) on glass. Prior to film deposition, ITO substrates were exposed to UV ozone.¹⁷ A 100 nm layer of PEDOT:PSS (BAYTRON® P VP Al 4083, H.C. Starck GmbH) was spin-coated onto ITO. Afterwards, the substrate was annealed in air at 150 °C for 30 min to drive out residual moisture. MTDATA, NPB, or TPD were thermally evaporated onto the ITO substrate at a rate of 1 nm/s.¹⁸ A semitransparent Al film was subsequently evaporated on the organic layer as the cathode for the TOF samples. For DI-SCLC and I/V measurements, Ag was used as the hole-collecting and electron-blocking electrode. All film thicknesses were determined *in situ* by a calibrated quartz crystal sensor and *ex situ* by a profilometer. After coating, the samples were immediately housed inside a

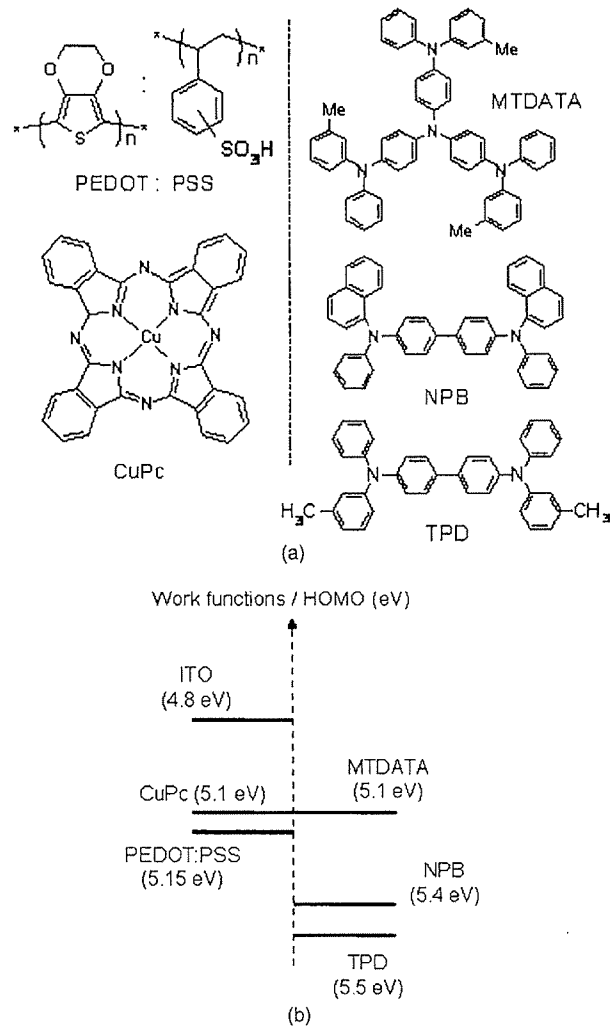


FIG. 2. (a) Chemical structures and (b) HOMO levels of CuPc, PEDOT:PSS, MTDATA, NPB, and TPD. The work function of ITO is also shown in (b).

vacuum cryostat. All measurements were carried out at room temperature.

Details of the TOF experimental setup were described elsewhere.¹³ Briefly, the sample structure was ITO/phenylamine(d μm)/Al (15 nm), where d varied between 3 and 8 μm. A dc power supply was used to provide an electric field of 0.01–1 MV/cm across the sample. A pulsed N_2 laser at 337.1 nm was used to generate free charges near the Al electrode. The photogenerated carriers moved through the sample under the external electric field and drifted to the ITO electrode. A current sensing resistor R in series with the sample converted and magnified the photocurrent into a proportional voltage reading. A digital oscilloscope was used to capture the voltage across R .

In DI experiments, a rectangular voltage pulse (amplitude 1–100 V, pulse duration 12 ms) was applied to the sample using a pulse generator (HP model 241B). The general sample structure was ITO/PEDOT:PSS/phenylamine(d μm)/Ag (100 nm), where d varied between

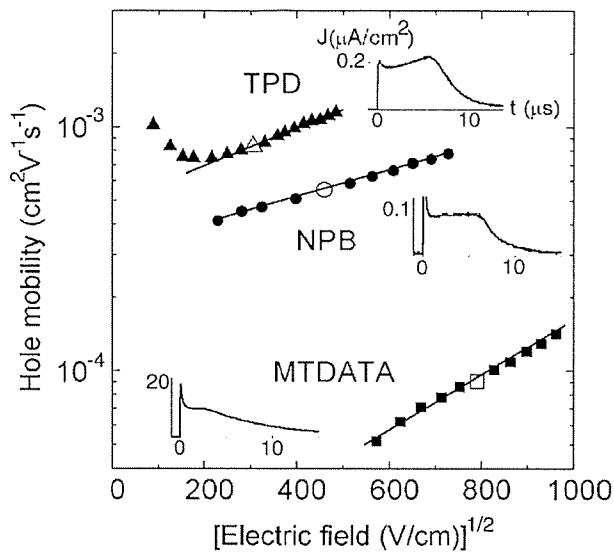


FIG. 3. TOF mobilities of MTDATA, NPB, and TPD at room temperature. For each material, an example of TOF transient is shown. The open symbols are the corresponding data points from which the transients were taken. The film thicknesses for MTDATA, NPB, and TPD were 3.5, 7.55, and 5.13 μm , respectively.

0.7 and 5.2 μm . The DI-SCLC current was detected in a manner similar to TOF experiments. The carrier mobility can be calculated as follows:

$$\mu = \frac{0.787d}{\tau_{\text{DI}}F} = \frac{0.787d^2}{\tau_{\text{DI}}V}, \quad (2)$$

where $F=V/d$ is the applied electric field. For the DI-SCLC samples, additional JV measurements were performed with a computer-controlled Keithley Source-Measure Unit (model 236). During all the measurements, the samples were kept at room temperature in a vacuum cryostat with a pressure less than 10^{-3} torr.

III. RESULTS AND DISCUSSIONS

Phenylamine compounds, including MTDATA, NPB, and TPD, are very important hole transporting materials for organic light-emitting diodes (OLEDs). Figure 3 summarizes their room temperature field dependent hole mobilities μ derived from TOF experiments from our laboratory under identical sample preparation procedures. The values of the hole mobilities are comparable to those in the literature.^{12,13,19,20} For each material, a typical TOF hole transient signal is shown alongside μ in Fig. 3. Among the three phenylamines, TPD has the highest hole mobilities while MTDATA has the least. For an applied field strength F exceeding 40 kV/cm, the hole mobilities roughly follow a Poole-Frenkel dependence, in which $\mu \sim \exp(\beta F^{0.5})$. The factor β in the exponent is the Poole-Frenkel slope and it can be deduced directly from the slope of μ in Fig. 3. β is a measure of the sensitivity of the mobility with respect to the applied electric field. From Fig. 3, β is smallest for NPB and largest for MTDATA, indicating that the hole mobility is least sensitive to F in the case of NPB.

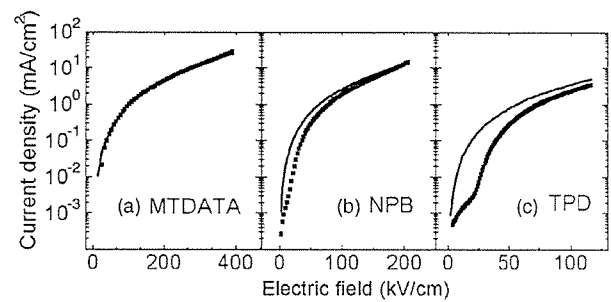


FIG. 4. Current-voltage characteristics of PEDOT:PSS/ phenylamine/ Ag devices. Solid lines are fits to the experimental JV using SCLC theory.

Knowing the field dependent mobilities, one can readily predict how the JV characteristics of the materials under the condition of Ohmic injection contact. Following the work of Murgatroyd, the JV curve of a trap-free material should obey the form²¹

$$J = \frac{9}{8} \mu_0 \epsilon \exp(0.89 \beta \sqrt{F}) \frac{F^2}{d}, \quad (3)$$

where μ_0 is the mobility when $F=0$, and ϵ is the dielectric constant. If a material has a field independent carrier mobility, $\beta=0$. Equation (3) then reduces to the well-known Child's law.⁹ Figure 4 summarizes the measured JV characteristics for MTDATA, NPB, and TPD, using PEDOT:PSS as the hole-injecting anode and Ag as an electron-blocking cathode. The solid line in each panel in Fig. 4 is the corresponding theoretical fit to the experimental data using Eq. (3). For the case of MTDATA, the fit almost overlaps with the measured JV data in the entire range of applied voltage, indicating that indeed PEDOT:PSS forms an Ohmic contact to MTDATA and that hole conduction in MTDATA is trap-free. For NPB, the theoretical fit and the experimental data agree very well for about $F > 100$ kV/cm. Beyond this field, conduction is trap-free and space-charge-limited, and is dominated by bulk conduction of holes. The effect of anode contact is negligible. In the case of TPD, the experimental data deviate substantially from the theoretical fit at the low field region. It appears that a more substantial hole injection barrier [Fig. 2(b)] is present between PEDOT:PSS and the HOMO of TPD. The barrier limits the injection of holes from the polymeric anode into TPD and results in a current well below the theoretical JV curve. However, as the applied field F increases, the deviation becomes smaller.

Figure 5 shows the DI transient signals for MTDATA, NPB, and TPD. In all cases, the DI transient signals exhibit characteristics that resemble the ideal curve in Fig. 1. In each case, the DI signal reaches a peak at a well-defined time τ_{DI} and settles down to a steady-state value after a long time. Figure 6 shows a sequence of DI transients for NPB at high bias voltages. The DI transient grows progressively as the applied voltage increases. Simultaneously, there is a gradual reduction in τ_{DI} . Similar observations can be made for MTDATA and TPD. From Fig. 6 and Eq. (2), one can extract the hole transit time and hence the hole mobilities for NPB from DI technique alone. Similar analysis can be done for MTDATA and TPD. The results are summarized as open

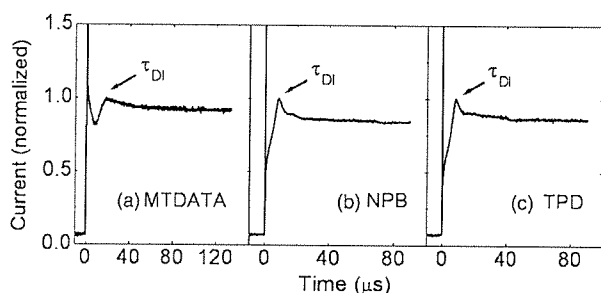


FIG. 5. Room temperature DI signals for MTDATA, NPB, and TPD under applied field strengths of 0.10, 0.09, and 0.09 MV/cm, respectively. The film thicknesses for MTDATA, NPB, and TPD were 0.76, 4.11, and 5.13 μm , respectively.

symbols in Fig. 7. In both Figs. 7(a) and 7(b), one can clearly see that hole mobilities derived from DI experiments are in excellent agreement with those deduced independently from TOF (solid symbols). The results for these two cases are entirely consistent with the JV results, which by themselves indicate that the contact between PEDOT:PSS and MTDATA (or NPB) is very close to Ohmic. For TPD, we can observe that there is substantial difference between the hole mobilities derived from DI and from TOF, especially when the applied field is small. Clearly, for TPD, the DI-derived hole mobility underestimates the true mobility.

Figure 2(b) provides the relevant energy diagram for interpreting the experimental observations. The work function of PEDOT:PSS is about 5.15 eV. When the PEDOT:PSS anode comes into contact with a layer of conjugated organic molecules (e.g., phenylamines), the hole injection barrier is, to a reasonable approximation, given by the energy difference between the HOMO level of the molecule and the work function PEDOT:PSS.²² Viewed in this manner, one expects that PEDOT:PSS should form an Ohmic contact with MTDATA and Schottky contacts with NPB and TPD with hole energy barriers of about 0.25 and 0.35 eV, respectively. Pre-

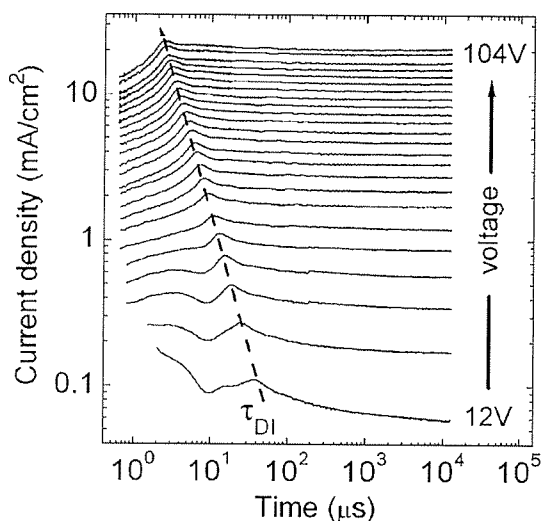


FIG. 6. A sequence of DI signals of NPB derived from a sample structure of PEDOT:PSS/NPB/Ag under different applied voltages. The applied voltage varied in steps of 4 V, starting from 12 V.

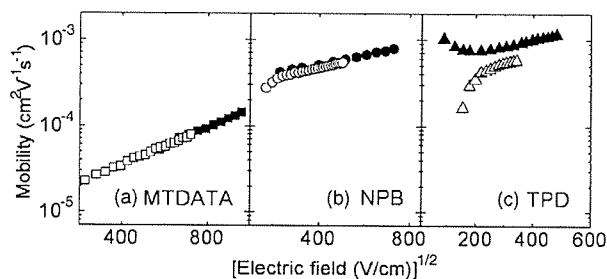


FIG. 7. Field dependent hole mobilities of MTDATA, NPB, and TPD at 290 K. The closed (\blacksquare) and open (\square) symbols represent the data obtained by TOF and DI-SCLC, respectively.

vious studies from computer simulations have dealt with the problem of charge injection from metal into organic charge transporters.^{23,24} When the barrier height is lower than about 0.3 eV, the metal/organic interface can be treated as Ohmic as the contact is capable of supplying the bulk of the organic material with SCLC current.²³ Our experimental results from the JV and DI experiments are entirely consistent with the reported computer-simulated results. For NPB, a hole injection barrier height of about 0.25 eV is lower than the crossover value of 0.3 eV. So for all practical purposes (JV and DI), the PEDOT:PSS/NPB interface can be treated as Ohmic, although technically a finite energy barrier does exist between PEDOT:PSS and NPB.

A similar reasoning can be applied, in principle, to the TPD data. A hole injection barrier height of 0.35 eV at the PEDOT:PSS/TPD interface is just in the neighborhood of the crossover value of 0.3 eV required for sustaining SCLC. From Ref. 23, charge injection is extremely sensitive to the barrier height in the vicinity of the crossover point. It is conceivable that a small increase of 0.1 eV above the crossover turns off carrier injection substantially, converting the metal/organic interface from an Ohmic into a Schottky contact. As a result, we observe deviations of the JV characteristics from the ideal SCLC [Fig. 4(c)]. Furthermore, the nominal hole mobilities extracted from DI results are also lower than those extracted from TOF [Fig. 7(c)]. The deviations from Ohmic behaviors are reduced as the applied voltage increases because the barrier height is lowered simultaneously.

Besides non-Ohmic injection, alternative mechanism(s) could also be responsible for the TPD data. For example, it can be observed from Fig. 4(c) that at low current densities (say, at 25 kV/cm), the measured current density is about 50 times lower than the SCLC. Yet, a clear cusp is still observed in our DI-SCLC data at the same field strength. The first observation is an indication of a departure from SCLC in TPD while the latter observation can be taken as a confirmation of SCLC. The origin of the apparent contradiction is not clear to us. One possibility may be related to the nonuniform hole injection properties of PEDOT:PSS surface. It has been reported that the hole injection from a PEDOT:PSS layer to a polymer could be inhomogeneous due to nonuniform surface doping or morphological effects.²⁵ As a result, some parts of the PEDOT:PSS/TPD contact could have poor electrical contacts with TPD. The fact, together with the larger injection

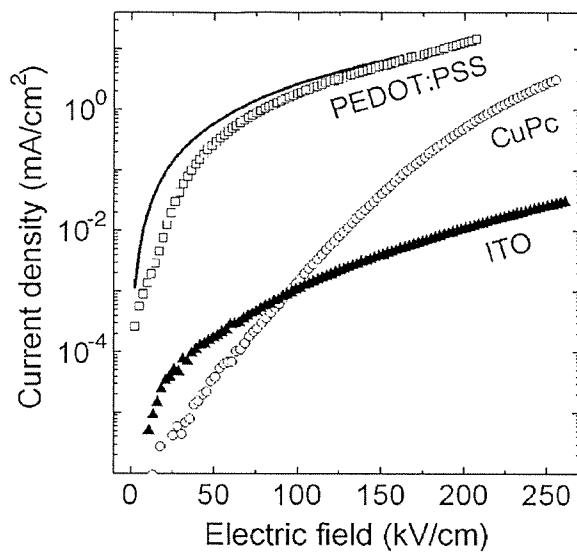


FIG. 8. Current-voltage characteristics of ITO/HIL/NPB/Ag devices using different HIL materials. The solid line is the theoretical trap-free space charge-limited current of NPB.

barrier in the PEDOT:PSS/TPD interface, may lead to an overall reduction in the injected current when compared to the SCLC. Despite the existence of these poor contact areas, there remain areas of good electrical contacts. So, clear DI-SCLC signals can still be observed.

The discrepancies between the DI and TOF in Fig. 7(c) deserve additional comments. From Fig. 3, one clearly observes a “bump” in the TOF signal of TPD. The precise origin of this bump is not known, but it could be due to a space charge layer near the charge-collecting electrode. If such a space charge layer is indeed present, then the carrier transit time would be reduced, resulting in an overestimation of the true carrier mobility from TOF, and hence a higher TOF mobility than the DI mobility. So the discrepancy between the TOF and DI results for TPD in Fig. 7(c) could be reduced if this factor is taken into account.

Apart from PEDOT:PSS, we attempted to use other high work function materials to act as hole injection layer for *JV* and DI measurements. Among the three hole transporters we are investigating, NPB is most relevant in OLED technology as it is thermally the most stable material. So we use NPB as a reference hole transporter and examine how hole-injecting materials affect the *JV* and DI experiments. The hole-injecting materials adopted are, besides PEDOT:PSS, ITO and CuPc. Their nominal work functions are shown in Fig. 2(b). Figure 8 shows the *JV* data for devices having the structure ITO/HIL/NPB/Ag, where HIL=hole injection layer can be ITO, CuPc, or PEDOT:PSS. The solid line, which acts as an upper bound for the experimental current density, is the computed *JV* curve using Eq. (3). Clearly, with the exception when HIL=PEDOT:PSS at high voltages, all devices operate well below the solid line, i.e., the condition of SCLC under the condition of Ohmic contact. As NPB is trap-free

for hole transports, the results indicate that among the three HI materials, only PEDOT:PSS can form Ohmic contact with NPB. Analogous DI experiments were carried out for samples with structures similar to those outlined in Fig. 8. Again, with the exception when HIL=PEDOT:PSS, the DI transients were featureless and no distinct τ_{DI} could be identified.

IV. CONCLUSION

We demonstrate that PEDOT:PSS can be used as an excellent hole injection material for small organic charge transporters. Applications of PEDOT:PSS as the hole injecting anode in DI experiments allow accurate determination of hole mobilities. It is conceivable that PEDOT:PSS can be employed in other electrical characterizations of organic materials that require Ohmic hole contacts.²⁰

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