

## Amorphous Molecular Materials with High Carrier Mobilities: Thiophene- and Selenophene-Containing Tris(oligoarylenyl)amines

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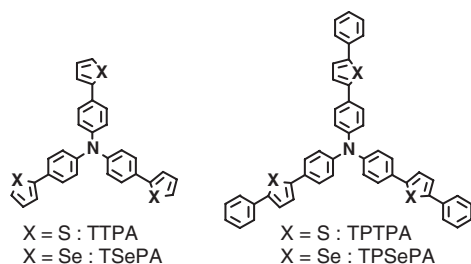
(Received June 14, 2004; CL-040683)

A novel class of amorphous molecular materials, thiophene- and selenophene-containing tris(oligoarylenyl)amines, were developed. They were found to exhibit high hole drift mobilities greater than  $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at an electric field of  $1.0 \times 10^5 \text{ V cm}^{-1}$  at 293 K in their amorphous glassy states. These values are of the highest level among those reported for organic disordered systems.

Charge transport in organic disordered systems plays an important role in the operation of organic electronic and optoelectronic devices, e.g., photoreceptors in electrophotography, electroluminescent devices, and photovoltaic devices.

Organic disordered systems such as polymers and molecularly doped polymers, where low molecular weight organic compounds are dispersed into polymer binders, have been studied extensively. We have performed a series of studies on the creation of low molecular-weight organic compounds that readily form stable amorphous glasses above room temperature, namely, "amorphous molecular materials."<sup>1</sup> The creation of amorphous molecular materials has enabled studies of charge transport in their amorphous glassy states without polymer binders.<sup>1-3</sup> Recently, there have been numerous studies on charge transport in amorphous molecular materials.<sup>4-7</sup> It has been revealed that amorphous molecular materials exhibit drift mobilities in the range from  $10^{-5}$  to  $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , greatly depending upon the structures of materials.<sup>3</sup> Materials that exhibit drift mobilities of the order of  $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  have been limited in number.<sup>4,6,7</sup>

It is a challenging subject to develop amorphous molecular materials with one order greater drift mobilities,  $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ cm}^{-1}$ , in the amorphous glassy state. In the light of the consideration that oligoarylenes exhibit high hole mobilities of ca.  $1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ,<sup>3</sup> and that the incorporation of the thiophene or selenophene ring may result in a higher degree of planarity of the oligoarylene unit, leading to better intermolecular overlap of  $\pi$  electrons, we have designed and synthesized a new class of amorphous molecular materials, thiophene- and selenophene-containing tris(oligoarylenyl)amines, tris[4-(2-thienyl)phenyl]amine (TTPA), tris[4-(5-phenylthiophen-2-yl)phenyl]amine (TPTPA), tris[4-(2-selenyl)phenyl]amine (TSePA), and tris[4-(5-phenylselenophen-2-yl)phenyl]amine (TPSePA).



TTPA and TPTPA were synthesized by the coupling reactions of tris(4-iodophenyl)amine with the corresponding oligoarylenylmagnesium bromide in tetrahydrofuran (THF) in the presence of 1,3-bis(diphenylphosphino)propane nickel(II) chloride as a catalyst. TSePA and TPSePA were synthesized by the coupling reactions of tris(4-iodophenyl)amine with the corresponding oligoarylenylzinc chloride in THF in the presence of tetrakis(triphenylphosphine)palladium as a catalyst. They were identified by mass spectrometry,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopies, and elemental analysis.<sup>8</sup>

These tris(oligoarylenyl)amines were found to form amorphous glasses above room temperature when the melt samples were cooled, as evidenced by differential scanning calorimetry (DSC), X-ray diffraction, and polarized light microscopy. The glass transition temperatures of TTPA, TPTPA, TSePA and TPSePA were 70, 83, 80, and 105 °C, respectively, as determined by DSC. To our knowledge, TSePA and TPSePA are the first examples of selenium-containing amorphous molecular materials.

Hole drift mobility was measured by a time-of-flight method. An appropriate amount of material was heated to melt on an indium-tin-oxide (ITO)-coated glass, which was pressed by another ITO glass and then cooled with ice water. The cell was mounted in a cryostat and irradiated with pulsed  $\text{N}_2$  laser light (wavelength: 337 nm, pulse duration: 3 ns).

All the molecular glasses of TTPA, TPTPA, TSePA, and TPSePA exhibited nondispersive transient photocurrents in the wide range of temperatures and electric fields. The transit time ( $t_\tau$ ) was determined from the cusp of the plot of  $\log i_{\text{ph}}$  vs  $\log t$ , where  $i_{\text{ph}}$  and  $t$  represent the transient photocurrent and time, respectively, according to the Scher–Montroll theory.<sup>9</sup> The hole drift mobility ( $\mu$ ) was calculated from the formula  $\mu = L^2/t_\tau V$ , where  $L$  is the thickness of the sample and  $V$  is the applied voltage. The hole drift mobilities of these molecular glasses were found to exceed  $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  as shown in Table 1. These values are of the highest level among those reported for organic disordered systems.

The electric-field and temperature dependencies of the charge carrier drift mobilities of these molecular glasses were analyzed in terms of the disorder formalism (Eq 1), which assumes that charge transport in disordered systems occurs by hopping through a manifold of states, subject to fluctuations in both the hopping site energies (energetic disorder) and the intermolecular wavefunction overlap (positional disorder),<sup>10</sup>

$$\mu = \mu_0 \exp \left[ - \left( \frac{2\sigma}{3kT} \right)^2 \right] \exp \left\{ C \left[ \left( \frac{\sigma}{kT} \right)^2 - \Sigma^2 \right] E^{1/2} \right\} \quad (1)$$

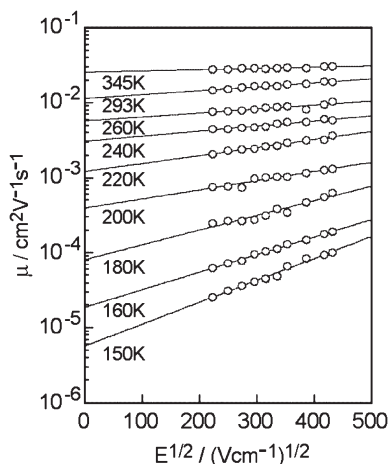
where  $\sigma$  and  $\Sigma$  are the parameters that characterize the energetic and positional disorder, respectively,  $\mu_0$  represents a hypothetical mobility in the energetic disorder free system,  $E$  is the electric

field,  $k$  is the Boltzmann constant,  $T$  is the temperature, and  $C$  is an empirical constant.

Figure 1 shows the electric field dependencies of the hole drift mobilities at various temperatures observed for the TSePA molecular glass. The hole drift mobilities followed the electric field dependence of  $\exp(SE^{1/2})$ , where  $S$  represents a coefficient. Hole drift mobilities at the zero electric field,  $\mu(E=0)$ , were obtained by the extrapolation of the electric field dependence of the hole drift mobilities to the zero electric field. The values of  $\mu_0$  and  $\sigma$  were obtained from the intercept and the slope, respectively, of the linear plot of the logarithm of  $\mu(E=0)$  vs  $T^{-2}$ . The  $\Sigma$  value was determined from the intersection at  $S=0$  in the linear plot of  $S$  vs  $(\sigma/kT)^2$ , where  $(\sigma/kT)^2 = \Sigma^2$  holds. The hole transport parameters based on the disorder formalism for these molecular glasses are summarized in Table 1.

The results show that while  $\Sigma$  and  $C$  values for TTPA, TPTPA, TSePA, and TPSePA are more or less similar to those for many other amorphous molecular materials, the pre-exponential factor  $\mu_0$  for these molecular glasses are approximately one order of magnitude greater than those for a number of amorphous molecular materials. In addition, the  $\sigma$  values for these molecular glasses are relatively small as compared with other amorphous molecular materials. It is therefore indicated that the high hole drift mobilities observed for these molecular glasses are attributed both to the large pre-exponential factor  $\mu_0$  and to the relatively small energetic disorder  $\sigma$ .

The pre-exponential factor, namely, the hypothetical mobility in the absence of energetic disorder, is thought to be determined by the intrinsic charge-transporting ability of the mole-



**Figure 1.** Electric field dependencies of hole drift mobilities for the molecular glass of TSePA.

**Table 1.** Hole drift mobilities and charge transport parameters determined for the molecular glasses of TTPA, TPTPA, TSePA, and TPSePA in terms of the disorder formalism

Material	$\mu$ / $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ <sup>a</sup>	$\mu_0$ / $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$	$\sigma$ /eV	$\Sigma$	$C$ / $(\text{cmV}^{-1})^{1/2}$
TTPA	$1.1 \times 10^{-2}$	$1.1 \times 10^{-1}$	0.064	1.1	$3.3 \times 10^{-4}$
TPTPA	$1.0 \times 10^{-2}$	$1.8 \times 10^{-1}$	0.075	1.3	$4.1 \times 10^{-4}$
TSePA	$1.5 \times 10^{-2}$	$1.6 \times 10^{-1}$	0.063	1.8	$3.6 \times 10^{-4}$
TPSePA	$1.1 \times 10^{-2}$	$1.1 \times 10^{-1}$	0.067	1.0	$3.7 \times 10^{-4}$

<sup>a</sup>Measured at an electric field of  $1.0 \times 10^5 \text{ Vcm}^{-1}$  at 293 K.

cule and the degree of intermolecular wavefunction overlap. The energetic disorder  $\sigma$ , namely, the fluctuation of the hopping site energy, is understood as determined both by the variation of molecular geometry caused by bond rotation and by the fluctuation of polarization energy resulting from van der Waals and charge-dipole interactions. It is thought that the incorporation of the thiophene- and selenophene-containing oligoarylene unit enhances the intrinsic charge transporting ability and/or the degree of intermolecular wavefunction overlap and that the synthesized molecules with symmetrical structures reduce energetic disorder because of a small degree of variation of the molecular geometry.

In summary, novel thiophene- and selenophene-containing tris(oligoarylenyl)amines were developed. They were found to exhibit high hole drift mobilities exceeding  $10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ , which are of the highest level among those reported for organic disordered systems. It is shown that the high hole drift mobilities are attributable to a large pre-exponential factor and to a relatively small energetic disorder in terms of the disorder formalism. The present study provides a new molecular design concept for amorphous molecular materials with high mobilities, paving the way for future development of amorphous molecular materials with high-performance charge transport.

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- 8 **TTPA**. Yield: 34%. Mass (TOF):  $m/z = 491$  ( $M^+$ ).  $^1\text{H}$ NMR (750 MHz, THF- $d_8$ ):  $\delta$  7.03 (dd, 3H), 7.12 (d, 6H), 7.29 (d, 3H), 7.30 (d, 3H), 7.55 (d, 6H).  $^{13}\text{C}$ NMR (188 MHz, THF- $d_8$ ):  $\delta$  123.2, 124.9, 125.2, 127.4, 128.6, 130.4, 144.7, 147.4. Anal. Calcd. for  $\text{C}_{30}\text{H}_{21}\text{NS}_3$ : C, 73.28; H, 4.30; N, 2.85; S, 19.56. Found: C, 73.31; H, 4.26; N, 2.82; S, 19.16%. **TPTPA**. Yield: 7%. Mass (EI):  $m/z = 719$  ( $M^+$ ).  $^1\text{H}$ NMR (600 MHz, THF- $d_8$ ):  $\delta$  7.16 (d, 6H), 7.24 (t, 3H), 7.33 (d, 3H), 7.36 (dd, 6H), 7.37 (d, 3H), 7.61 (d, 6H), 7.65 (d, 6H).  $^{13}\text{C}$ NMR (150 MHz, THF- $d_8$ ):  $\delta$  124.3, 124.9, 125.2, 160.0, 127.2, 128.0, 129.6, 130.2, 135.2, 143.6, 143.9, 147.5. Anal. Calcd for  $\text{C}_{48}\text{H}_{33}\text{NS}_3$ : C, 80.07; H, 4.62; N, 1.95; S, 13.36. Found: C, 79.96; H, 4.61; N, 1.91; S, 13.35%. **TSePA**. Yield: 21%. Mass (TOF):  $m/z = 635$  ( $M^+$ ).  $^1\text{H}$ NMR (400 MHz, THF- $d_8$ ):  $\delta$  7.10 (d, 6H), 7.25 (dd, 3H), 7.44 (dd, 3H), 7.51 (d, 6H), 7.94 (dd, 3H).  $^{13}\text{C}$ NMR (100 MHz, THF- $d_8$ ):  $\delta$  125.1, 125.3, 127.8, 130.1, 131.1, 132.4, 147.5, 150.9. Anal. Calcd for  $\text{C}_{30}\text{H}_{21}\text{NSe}_3$ : C, 56.98; H, 3.35; N, 2.21; Se, 37.46. Found: C, 56.78; H, 3.38; N, 2.31%. **TPSePA**. Yield: 15%. Mass (EI):  $m/z = 863$  ( $M^+$ ).  $^1\text{H}$ NMR (600 MHz, THF- $d_8$ ):  $\delta$  7.14 (d, 6H), 7.24 (t, 3H), 7.34 (dd, 6H), 7.48 (d, 3H), 7.53 (d, 3H), 7.55 (d, 6H), 7.59 (d, 6H).  $^{13}\text{C}$ NMR (150 MHz, THF- $d_8$ ):  $\delta$  125.2, 126.4, 126.4, 127.1, 127.6, 128.1, 129.6, 132.3, 137.3, 147.5, 149.7, 149.9. Anal. Calcd for  $\text{C}_{48}\text{H}_{33}\text{NSe}_3$ : C, 66.98; H, 3.86; N, 1.63; Se, 27.52. Found: C, 66.77; H, 3.86; N, 1.63%.
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