New Electron Transport Materials with High Drift Mobility Comparable to Hole-Transporting Materials

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Abstract

New electron transport materials having the following general structure shown in Figure 1 have been developed. We synthesized them and examined their properties. These compounds showed good compatibility to a polycarbonate and good solubility in common organic solvents. Electron transport properties of these compounds were investigated. Electron drift mobilities have been measured as a function of the concentration and electric field by the conventional time-of-flight technique. They showed nondispersive electron transport in composition films. The values of electron mobility ranged from 10^{-8} to 10^{-4} cm^2/Vs as the molecular concentration was varied from 20 to 60 wt%.
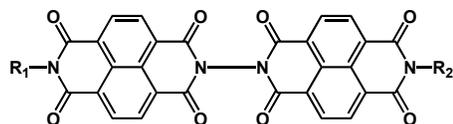
Figure 1. The general structure of electron transport materials in this study

Introduction

Charge transport in molecularly doped polymers (MDP) has been investigated because of its importance to fundamental charge-transport studies in amorphous organic materials and its application in electrophotography. The charge transport in amorphous materials of active molecules is an electric field driven chain of redox processes involving neutral molecules and their charged derivatives, i.e., positive and negative states for hole and electron transport, respectively. The mobilities are very low, strongly field and temperature dependent, as well as dependent on the molecule structure, dopant concentration, and the host polymer.

While hole transport has been widely investigated, there have been few reports of electron transport in these materials. 2,4,7-trinitorofluorenone (TNF) is known as an electron transport material, it shows poor solubility in organic solvent, poor dispersibiliy in binder polymers, and high toxicity.[1] Diphenoquinone (DPQ) derivatives have been described as nonmutagenic (Ames test), electron transport materials.[2] There are, however, indications that electron mobilities are generally lower than hole mobilities.

Recently, the single-layered OPC has been attracted attention because of its possibility of a high resolution imaging[3,4]. The single-layered OPC is usually used for positive charging, therefore has the advantage in the points of lower ozone generation at the charging. The single-layered OPC is comprised charge generation material (CGM) dispersed in charge transport material/binder polymer. The holes and electrons are photogenerated on the CGM. It is necessary in the single-layered OPC to transport electrons from bulk to the positively charged OPC surface. It is required to developed an excellent electron transport material (ETM) for fabricating high sensitive single-layered OPC.

This report describes a development of new electron transport materials and an investigation of electron transport property of them doped polycarbonate.

Experimental
Synthesis

We have developed a series of the naphthalene-tetracarboxylic diimide dimmers (Dimmer). The synthesis of these materials was done in three steps. First, 1,4,5,8-naphthalene-tetracarboxylic acid anhydride was reacted with amine compounds to form monoimide derivatives. In the second step, monoimide was reacted with hydrazine monohydrate. Finally, this intermediate was reacted with monoimide to form final compounds. These compounds were purified by column chromatography on silica gel and recrystallization several times. Table 1 showed alkyl structures of electron transport materials in this study.

Table 1: Molecular Structures of Electron Transport Materials in this Study

Dimmer	R1	R2
1	3-pentyl	3-pentyl
2	3-pentyl	2-hentyl
3	2-hentyl	2-hentyl
4	2-octyl	2-octyl
5	2-octyl	2-ethylhexyl

Film Preparation

The sample films were prepared by the simple solvent-cast technique using a wired bar on an aluminum substrate from chloroform solutions. The resulting wet films were dried in a vacuum oven for 2 h at 60℃. Bisphenol-Z type polycarbonate (PC-Z) was used as binder polymers. The doping concentration of the samples was varied in the range of 20-60% by weight dimmer in PC-Z. A semitransparent gold electrode was vacuum deposited on the surface of the organic transport layer. The sample thicknesses were between 7 and 11 μm.

Drift Mobility Measurement

The drift mobilities were measured by the time-of-flight (TOF) technique. Photoexcitation was carried out by 3-ns exposure of 337-nm radiation derived from N_2 laser. At most concentrations

and applied fields, transient photocurrents were nondispersive. The transit times, τ, were determined from the double logarithmic plot of the transient photocurrent curve. The charge carrier drift mobility, μ, was calculated from the expression $\mu = L^2/(\tau V)$, where L is the sample averaged thickness and V is the applied voltage. All measurements were performed in vacuum.

Results and Discussion
Molecular Properties
Figure 2 shows the concentration dependence of glass transition temperature, Tg, obtained Dimmer **3**. The Tg was determined from DSC experiments. No crystallization could be observed in any of the samples prepared for the whole 20-80 wt% concentration range. Dimmer **3** itself shows no glass transition. This shows good compatibility properties of these dimmer compound. The solubility for two organic solvents (THF and toluene) and compatibility to a typical binder polymer, PC-Z, of Dimmers are shown in Table 2.

There are two important factors for the improvement of the solubility. One is the length of the carbon atom attached to the imide nitrogen atom, the other is the number of the substitutions of the same carbon atom.

Electron-Transport Properties
Figure 3 shows the electric field dependence of the room temperature mobility in the films of Dimmer **2** dispersed in PC-Z at several concentrations. The concentration of the material is expressed in weight percent. The mobility data follow a straight line in a semilogarithmic representation as a function of the square root of the applied field at all dopant concentrations. At the maximum concentration, 60wt%, high electron mobilities over 10^{-4} cm^2/Vs is observed for the first time in MDP. This indicates that these mobility are comparable to that of N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD) in polycarbonate[5].

Table 2: Molecular Properties of Dimmers in this Study

Dimmer	Solubility (mmol/L)		Compatibility	m.p.
	THF	Toluene	(wt%)	(°C)
1	28.7	124.3	60	365-367
2	357.8	357.8	80	268-269
3	344.0	344.0	80	227-228
4	331.2	331.2	80	217-218
5	165.6	331.2	70	210-211
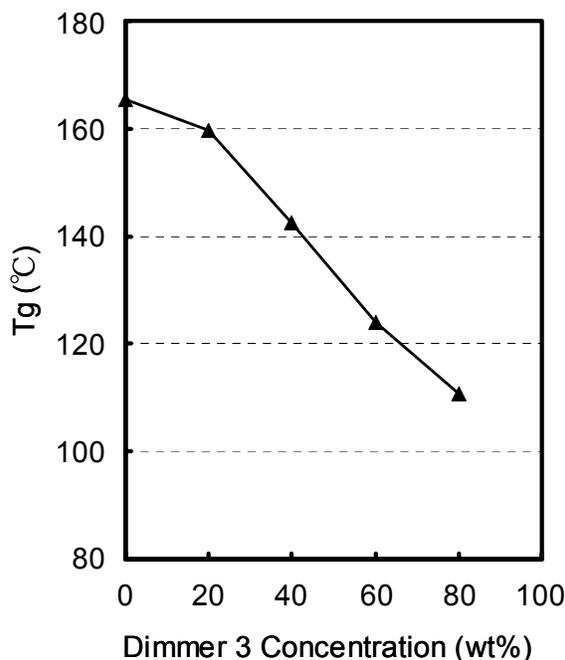
Figure 2. Dependence of glass transition temperature as a function of dopant concentration
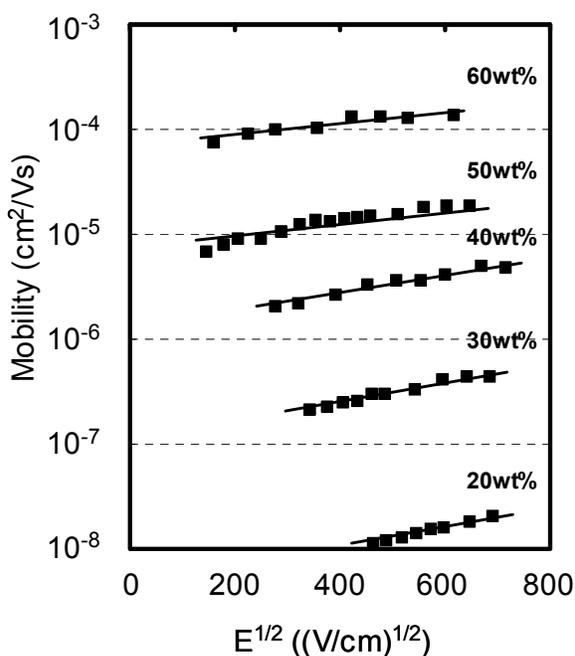
Figure 3. Dependence of electric field of the electron mobilities at different concentrations

Figure 4 shows the intermolecular distance dependence of the electron mobility. The mobility data in a field of 1.6×10^5 V/cm in Figure 3 are plotted. This figure indicates an exponential relationship between μ/R^2 and R. On the basis of the hopping

mechanism, a relationship between the mobility μ and intermolecular distance R in MDP is generally accepted[1]:

$$\mu/R^2 \propto \exp(-2R/R_0) \qquad (1)$$

where R_0 is the charge localization radius. The average distance between molecules, R, is calculated from the formula $R=(M/(N_A dC))^{1/3}$, where M is molecular weight, N_A is Avogadro's number(6.02×10^{23}) , and d is the density(1.2 g/cm^3), and C is fractional dopant cncentration by weight. The mobility data of other Dimmers with different alkyl substitution appear on the same line. In the same figure, the mobilities of N,N'-bis(1,2-dimethylpropyl)-1,4,5,8- naphthalene-tetracarboxylic diimide (NTDI) in PC-Z are plotted. As shown in figure 4, Dimmer **2** gives the larger electron mobility than that of NTDI at the same intermolecular distance. From the slope of the line in Figure 4, a value of 1.04 Å was obtained for R_0 of Dimmer **2** and 0.866 Å for NTDI. From the straight line extrapolated from the values for other intersite distance, the mobility of 100% Dimmer **2** is estimated as 1.6×10^{-3} cm^2/Vs. This value is the highest electron mobility among amorphous organic semiconductors.
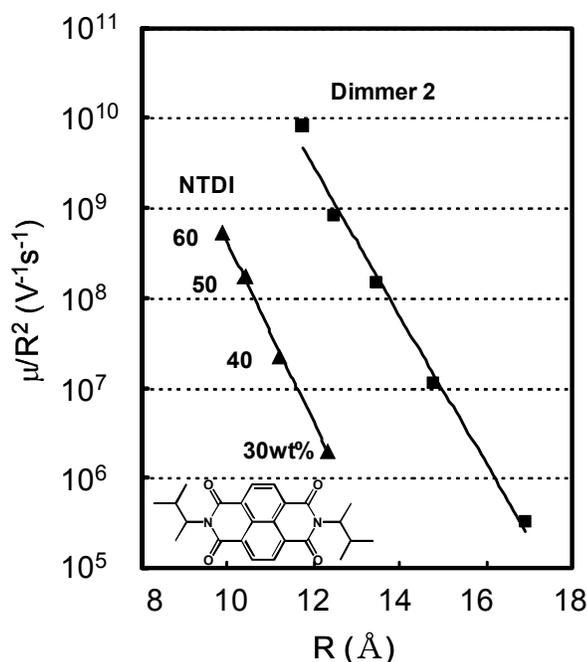
Figure 4. Dependence of intermolecular distance of the electron mobilities

The distance R is calculated assuming each dopant molecule has a cubic shape. The mobility data of all Dimmers follow eq. (1) suggests that the two naphthalene-tetracarboxylic units in a molecule behave as one hopping site. From this result, two mechanism are considered for the improvement of electron mobility. One is the fast electron transfer between two naphthalene-tetracarboxylic units, the other is the delocalization of radical anion state on the two units. These mechanism improve the mobility of electrons between naphthalene units within a molecule. As a result, intramolecular mobility shortens the effective hopping distance of transporting site between two molecules.

Conclusion

We have developed some novel electron transport materials, naphthalene-tetracarboxylic diimide dimmers. They showed good dispersibility in a polycarbonate and good solubility in organic solvent. High electron mobilities over 10^{-4} cm^2/Vs were obtained for the first time in organic solid solutions with transport active compounds dispersed in common binder polymer. As a result of analysis, it was suggested that the intramoleculare mobility of a charge in ETM could be effective to enhance charge transporting ability. This gives a novel molecular design concept for the ETM.

Acknowledments

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