Analysis of Molecular Properties of Hole Transport Molecules Using Molecular Orbital Theory

Takayuki Shoda, Akiteru Fujii and Tetsuo Murayama
Yokohama Research Center, Mitsubishi Chemical Corporation
Yokohama, Japan
Shinji Aramaki
Odawara Reprographic Products Center, Mitsubishi Chemical Corporation
Odawara, Japan

Abstract

Polarizabilities and dipole moments of the existing hole transport molecules with different mobility were measured. The zero-field mobility determined by TOF technique correlated with dipole moments and polarizabilities. These results suggested that smaller dipole moment and larger polarizability of hole transport molecules are preferable properties for hole transport. Polarizabilities and dipole moments of the existing hole transport molecules were also calculated using semiempirical molecular orbital theory based on modified neglect of diatomic overlap (MNDO). The calculated polarizabilities and dipole moments strongly correlated with observed values. The fact implies that the calculated polarizability and the calculated dipole moment are good indices to develop new high mobility hole transport molecules. Semiempirical molecular orbital calculations were also applied to design new high mobility hole transport molecules.

Introduction

It is very important to investigate hole transport phenomena in molecularly doped polymers for design of new hole (carrier) transport molecules (CTMs) of organic photoreceptors. Usual hopping site distance, which is controlled by concentration of hole transport molecule in polymer matrix, is around 10Å. These hole transport molecules interact very weakly, and the charge carriers (holes) would be localized on one hole transport molecule in molecularly doped polymer.

Recently, the hole transport of a variety of molecularly doped has been studied actively. Many authors have shown the exponential dependence of the average intermolecular distance, square root of electric field, and temperature of the hole mobility in molecularly doped polymers. The small polaron hopping theory[1-4] and the disorder theory[5-8] have been accepted as the plausible explanations for the hole transport properties in molecularly doped polymers. It is

very useful for development of new CTMs to investigate relationship between parameters used in these theories and physical properties of hole transport molecules. Several experimental data indicate that increasing the polarity of the transport molecule has decreased the hole mobility in doped polymers[9-11] and in vapor-deposited molecular glasses.[12-13] Borsenberger et al. have analyzed the effect of dipole moments based on disorder formalism and divided the energetic disorder parameter σ into a dipolar component and a van der Waals component.[14-16] The dipolar component relates the dipole moment through the expression by Young.[17]

In this paper, we analyze the relationship between the hole mobility and the polarizabilities as well as the dipole moments of hole transport molecules. We compared these observed molecular properties to the results calculated by molecular orbital theory on the existing CTMs. Finally, we try to design new CTMs by using calculated polarizability and calculated dipole moment as guiding principles to develop high mobility CTMs.

Experimental

The molecular structures of the charge transport materials (CTMs) used in this study are illustrated in Fig. 1. These molecules are electron-donative, and a charge carrier is a hole. Solutions of these materials were prepared by dissolving 1:1 weight ratios of CTMs and bisphenol-A-polycarbonate in solvent which is the mixture of 1,4-dioxane and THF. Then the resulting solutions were coated onto Al-deposited poly(ethylene terephthalate) substrates that had previously been coated with β-oxytitanium phthalocyanine-dispersed poly(vinyl butyral) as a charge generation layer (CGL). Samples were dried at 125°C for 20 min and then 55°C for 48 h. The typical thickness of the charge transport layer (CTL) was 10 to 15μm. Al was then vacuum-deposited onto the free surface of the CTL to form a semi-transparent counter electrode. A standard time-of-flight technique was used to measure hole drift mobility.

After application of voltage, carriers were generated in the CGL when excited with light from a xenon flash lamp monochromated with a 700 nm interference filter. The displacement of a sheet of holes induced by the excitation of the CGL was time-resolved. To minimize distortion of the internal field by the injected charge, the exposures were filtered such that the total charge injected into the CTL was less than 0.05CV, where C is the sample capacitance, and V the applied voltage. The transient photocurrent was measured with a current-voltage amplifier (Keithley 428) and a digital storage oscilloscope (Nicolet model 3091). All transit times were obtained on log-log current-versus-time plots, and the shoulder identifies the transit time τ which is related to the drift mobility μ through the relation $\tau = L^2/\mu V$, where L is the thickness of the sample. Zero field mobility was obtained by plotting the mobility vs. square root of electric field, followed by extrapolating to zero field.

Dipole moments and polarizabilities were determined by measuring the dielectric constant and refractive index of several concentrations of dilute 1,4-dioxane solutions of CTMs, following the procedures described in the literature.[18-19] A concentration extrapolation was applied to dielectric constant and refractive index measurements in order to eliminate solute-solute interactions.
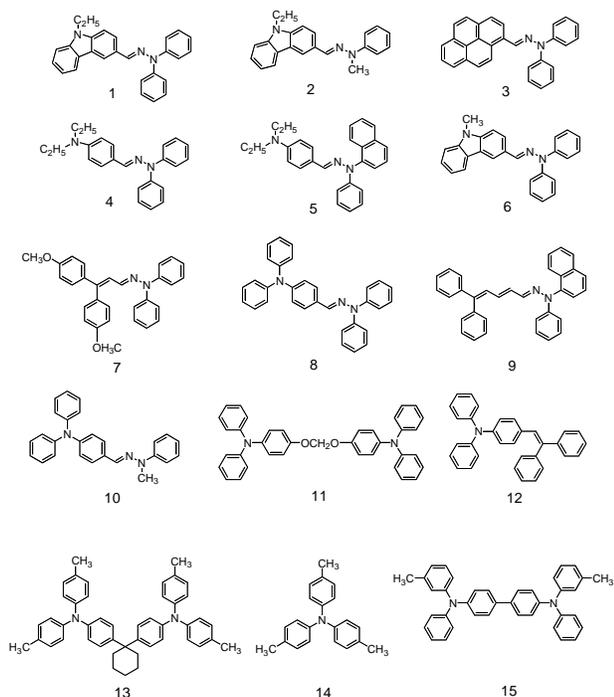

Figure 1. Molecular structures of the existing charge transport molecules

Computational Methods

The MOPAC93[20] program was used to carry out the restricted Hartree-Fock (RHF) calculation based on the Parametric Method number 3 (PM3) [21] method of the Modified Neglect of Diatomic Overlap(MNDO). Molecular structures of CTMs were optimized by the Eigenvector Following (EF)[20] technique. Dipole moment was calculated from the atomic charges and lone-pair electrons in the MOPAC93. Isotropic polarizability was obtained at 0 eV radiation energy by using the POLAR keyword.

Results and Discussions

Table 1 shows the hole mobility, polarizabilities and dipole moments of molecules described in Figure.1. Figure 2 and 3 show the mobility as a function of polarizabilities and dipole moments. These figures show that the zero-field mobility increase with increasing polarizabilities, while the zero-field mobility decrease with increasing dipole as reported before[9-11]. These results imply that the CTM, which have larger polarizability and smaller dipole moment, is desirable for hole mobility.

Table 1. Mobility, polarizabilities, and dipole moments of the existing hole transport molecules.

CTM	$\mu(E=0)$[a] ($10^{-6}cm^2/Vs$)	$\mu(E=300kV/cm)$[b] ($10^{-6}cm^2/Vs$)	α[c] ($+^3$)	p[d] (Debye)
1	0.94	6.2	59.13	2.67
2	0.092	0.87	48.57	2.57
3	1.4	9.6	62.34	2.48
4	0.27	2.6	49.78	3.37
5	0.26	2.4	57.73	3.34
6	0.60	4.4	57.78	2.65
7	0.58	4.1	65.86	3.48
8	2.8	12	65.57	2.51
9	5.5	21	71.59	2.57
10	1.9	9.1	56.11	2.35
11	1.6	5.7	74.79	1.78
12	14	30	62.27	1.25
13	11	19	86.53	1.38
14	17	29	38.24	0.95
15	6.7	15	75.72	1.39

a) Zero-field mobility at 297K.
b) Mobility under 300kV/cm at 297K
c) Polarizability
d) Dipole moment

The observed polarizability and dipole moment are compared with the values calculated by the semiempirical molecular orbital calculation in Figure 4 and Figure 5, respectively. Figure 4 and Figure 5 show that the calculated polarizability and dipole moment strongly correlate to the observed values. This fact implies that polarizability and dipole moment could be estimated by the semiempirical molecular orbital theory before new CTM is synthesized. Moreover, it would be expected to design the preferable CTM for mobility using the calculated polarizability and dipole moment, because figure 2 and figure 3 imply that the CTM which have larger polarizability and smaller dipole moment is desirable for hole mobility.
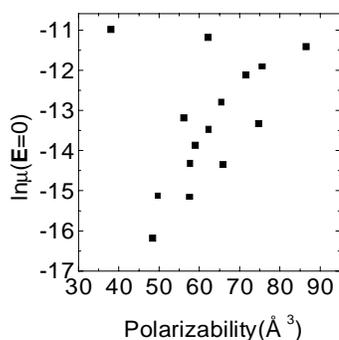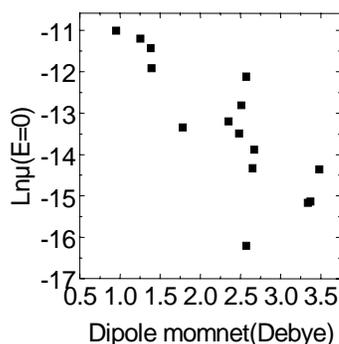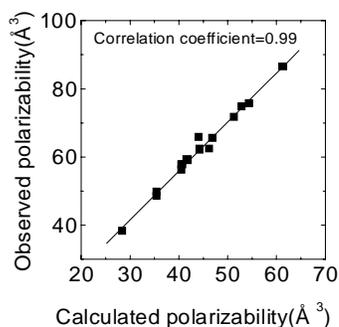
*Figure 2. lnμ(**E**=0) vs. Polarizability*

*Figure 3. lnμ(**E**=0) vs. Dipole moment*

Figure 4. Calculated polarizability vs. Observed polarizability
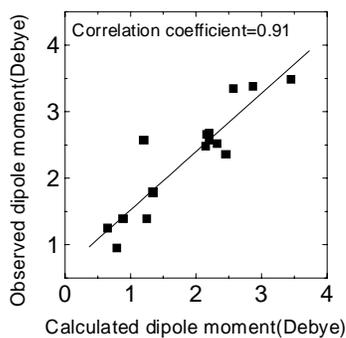

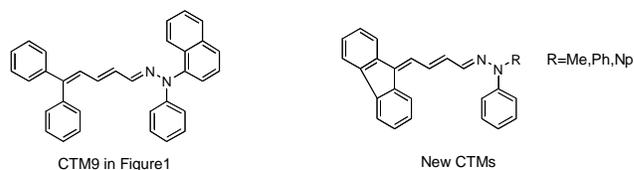*Figure 5. Calculated dipole moment vs. Observed dipole moment*

Figure 6 New CTMs to assess our guiding principle to high mobility CTMs

Therefore, we tried to design the new CTMs around CTM9 which have the highest mobility in hydrazone compounds in figure 1 using the calculated polarizability and dipole moment. Figure 6 shows the proposed CTMs. Figure 6 includes the CTMs, which would have the mobility lower than CTM9, to assess our guiding principle to design higher mobility CTMs. The calculated polarizabilities and the calculated dipole moments of the new proposed CTMs are shown in Table 2. Table 2 suggests that the New CTM-Np would have higher mobility than CTM 9.

The Highest Occupied Molecular Orbital(HOMO) of CTM9 and the proposed CTMs in figure 6 are shown in figure 7. Figure 7 shows that the π conjugation of the new CTM-Np extends to fluorenone unit, while that of CTM9 does not distribute on the vertical phenyl ring to π conjugation system. This fact also implies that the proposed new CTM-Np is more favorable for hole mobility than CTM9.

Table 2. Molecular weight, calculated polarizabilities, calculated dipole moments, and calculated ionization potentials of the new hole transport molecules.

CTM	Mw[a]	α[b] ($+^3$)	p[c] (Debye)	Ip[d] (eV)
CTM9	450.58	51.42	2.20	8.32
New CTM-Me	336.44	40.04	2.07	8.35
New CTM-Ph	398.51	49.02	2.10	8.25
New CTM-Np	448.57	54.17	2.11	8.33

a)   Molecular weight. b)Polarizability
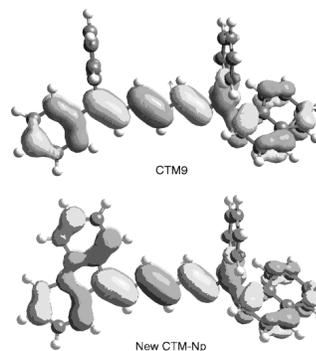
c)   Dipole moment d)Ionization potential

Figure 7. Highest Occupied Molecular Orbital(HOMO) of new CTMs with that of CTM 9.

The mobility of CTL strongly depends on the condition how the sample is prepared. Therefore, each sample for the TOF measurement was prepared by dissolving each CTM in the same bisphenol-A-polycarbonate, 1,4-dioxane and THF solution to compare the mobility of New CTM-Np to the mobility of CTM9. The mobility of the new CTM-Np is shown with that of CTM9 in Figure 8. The mobility of new CTM-Np is also very high and is nearly the same as that of CTM9. We expected it would be somewhat higher than that of CTM9. Other factors affecting on the mobility should be considered to discuss small difference of the mobility between these CTMs. We are studying other CTMs to make sure the reliability of our guiding principle to design high mobility CTMs.
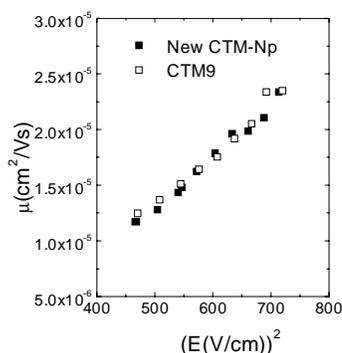

Figure 8. Comparison of the mobility between New CTM –Np and CTM9.

Conclusion

Polarizabilities and dipole moments of the existing hole transport molecules with different mobility were measured. The hole mobility correlated with dipole moments and polarizabilities. These results suggested that smaller dipole moment and larger polarizability are preferable for hole transport. Polarizabilities and dipole moments calculated by semiempirical molecular orbital theory strongly correlated to the observed polarizabilities and the observed dipole moments. These results implies that the calculated polarizability and the calculated dipole moment are good guiding principles to design new high mobility hole transport molecules.

References

1. J. X. Mack, L. B. Schein and A. Peled, *Phys. Rev.B* **39**, 7500(1989).
2. L. B. Schein, *Philos. Mag.* **65**, 795(1992).
3. L. B. Schein and J. X. Mack, *Chem. Phys. Lett.* **149**, 109(1988).
4. L. B. Schein, D. Glatz and J. C. Scott , Phys. Rev. Lett., **65**, 472(1990).
5. P. M. Borsenberger and D. S. Weiss, *Organic Photoreceptors for Xerography*, Marcel Dekker, New York, 1998.
6. G. Schönherr, H. Bässler and M. Silver, *Philos. Mag.* **44**, 47(1981).
7. H. Bässler, *Philos. Mag.* **50**, 347(1984).
8. H. Bässler, *Phys. Stat. Sol. B* **175**, 15(1993).
9. M. Sugiuchi and H. Nishizawa, *J. Imaging Sci. Technol.* **37,** 245 (1993).
10. Y. Kanemitsu and Y. Sugimoto, *Phys Rev. B* **46**, 14182 (1992).
11. R. H. Young and J. J. Fitzgerald, *J. Phys. Chem.* **99**, 4230(1995).
12. P. M. Borsenberger, E. H. Magin and J. Shi, *Physica B* **217**, 212(1996).
13. P. M. Borsenberger, W. T. Gruenbaum and E. H. Magin, *Jpn. J. Appl. Phys.* **35**, 2698(1996).
14. P. M. Borsenberger, E. H. Magin, M. B. ORegan and J. A. Sinicropi, *J. Polym. Sci. B* **34**, 317(1996).
15. P. M. Borsenberger and D. S. Weiss, *J. Imaging Sci. Technol.* **41,** 185 (1997).
16. W. T. Gruenbaum, E. H. Magin and P. M. Borsenberger, *Jpn. J. Appl. Phys.* **35**, 2704(1996).
17. R. H. Young, *Philos. Mag. B* **72**,435(1995).
18. K. D. Singer and A. F. Garito, *J. Chem. Phys.* **75**, 3572(1981).
19. K. D. Singer, J. E. Sohn, L. A. King, H. M. Gordon, H. E. Katz and C. W. Dirk, *J. Opt. Soc. Am. B* **6**, 1339(1989).
20. J.J. Stewart, MOPAC93 manual, FUJITSU LIMITED, 1993.
21. J.J. Stewart, J. Comp. Chem. **10**, 209(1989)

Biography

Takayuki Shoda received his Ph.D degree in chemistry from the University of Hokkaido at Sapporo in 1989. Since 1989 he has worked in Yokohama Research Center at Mitsubishi Chemical Corporation. He studies organic photoconductor and other organic photo-functional materials using both computational chemistry and analytical chemistry.