Relationship Between Molecular Properties of Hole Transport Molecules and Field Dependence of Hole Mobility

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Abstract

The electric field dependence of drift mobility was obtained by Time Of Flight (TOF) technique on several hole transport molecules in polymer binder. The electronic properties of carrier transport molecules obtained from experiment and molecular orbital calculation were compared to the electric field dependence of drift mobility. The slope of drift mobility clearly showed the linear dependence on dipole moment of CTM.

Introduction

Hole transport phenomena in molecularly doped polymers (MDPs) have been widely discussed as the one of the most important research issues to develop new organic photoreceptor's materials. The small polaron hopping theory[1-4] and the disorder theory[5-8] have been accepted as the convincing explanations for the hole transport properties in such MDP systems. The electric field dependence of drift mobility that is the slope of drift mobility to the square root of electric field was discussed by using the Gaussian disorder model[9-11] and the dipolar trap model.[12,13] Dipole moment of CTM is an important molecular property for electric field dependence of drift mobility in these papers. There is still not so clear relationship between dipole moment of CTM and the electric field dependence of drift mobility in MDP. And the relationship between other molecular properties of CTM and the electric field dependence has not so investigated vigorously. In our previous work,[14-16] we investigated several molecular properties and the roles of these properties on carrier transport by using both experimental and computational techniques.

In this paper, we study the relationship between the electric field dependence of drift mobility and some CTM molecular properties.

Experimental

The molecular structures of the charge transport materials (CTMs) used in this study are illustrated in Figure 1. The drift mobility was obtained by using a standard Time-Of-Flight (TOF) technique.[17] The layered organic photoreceptor samples were prepared by following the scheme as shown in our previous work.[14,15]

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]. Dielectric constant of CTM solution was obtained from the ratio of capacitance of CTM solution to that of air at room temperature and 100KHz measurement frequency by using LF impedance analyzer (HP4192A) and the sample cell (ANDO denki's AS-20468). Refractive index of dilute 1,4-dioxane solutions of CTMs in the quarts liquid sample cell was measured at room temperature by using 1150nm He-Ne laser.

Computational Methods

Ab initio restricted Hartree-Fock calculation with 6-31G* basis set function was carried out to obtain electronic spatial extension of ground state's wave function by using Gaussian98 program.[20]

Dimerization energies of CTMs (CTM1-CTM10) were obtained by following the scheme described in our previous work.[16] The MOPAC93[21] and PCK91[22] were used in the dimerization energy calculation.

Results and Discussions

Figure 2 shows the electric field dependence of drift mobility. The slope of drift mobility against the applied external electric field, dielectric constant of CTM solutions, refractive index of CTM solutions, electronic polarizabilities of CTMs, dipole moments of CTMs, and dimerization energies are shown in Table 1

Figure 3 shows the comparison between dimerization energy of CTM molecule and the field dependence of drift mobility. Dimerization energy could be consider as a guideline for the disorder of MDP structure derived by aggregation of CTM molecules in the coating process of CTL. The electric field dependence of drift mobility shows little correlation to the dimerization energy of CTM. This fact implies that CTLs prepared by the using these CTMs have the same magnitude of positional disorder in the CTL structure.

Electronic polarizability is a linear component of electric charge displacement, when an electric field is applied to a molecule. If carrier transport molecule has a diffuse charge cloud, the charge cloud of carrier transport molecule deform largely by applying the electric field, because the charge cloud does not be strongly attracted by nucleus. Therefore, carrier transport molecule with diffuse charge cloud should have a large polarizability. So, we compared observed electronic polarizability to electronic spatial extension (<ΦGS|r2|ΦGS>) calculated by ab initio MO theory.

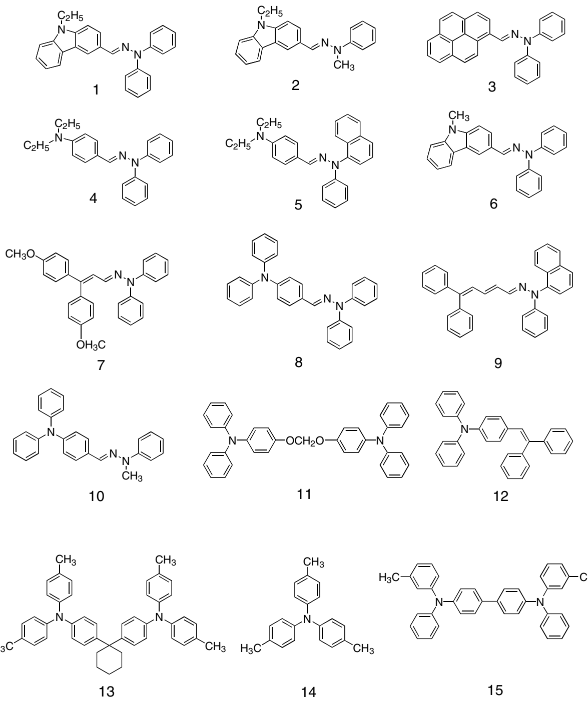

Figure 1 Molecular structures of the existing charge transport molecules.

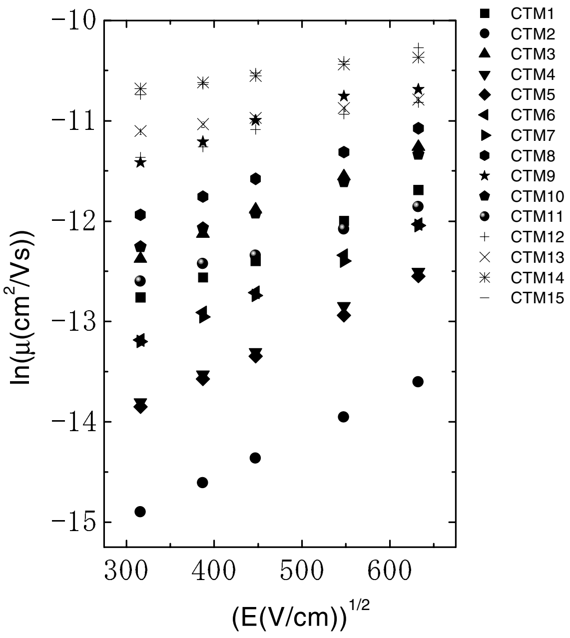

Figure 2 Electric field dependence of drift mobility

Table1 Slope of lnμ and CTM molecular properties

	Slope $^{a)}$ (x10^{-3})	D$^{b)}$ (Debye)	α$^{c)}$ (Å^{3})	ε$^{d)}$	n$^{e)}$	<r2>$^{f)}$	E_dim$^{g)}$ (kcal/mol)
CTM1	3.43	2.67	59.13	2.51	1.44	5028	-9.29
CTM2	4.10	2.57	48.57	2.53	1.44	4026	-11.41
CTM3	3.53	2.48	62.34	2.50	1.44	4677	-3.69
CTM4	4.15	3.37	49.78	2.71	1.44	4193	-8.89
CTM5	4.09	3.34	57.73	2.64	1.44	5285	-8.61
CTM6	3.64	2.65	57.78	2.53	1.44	4710	-6.31
CTM7	3.62	3.48	65.86	2.65	1.44	5687	-10.87
CTM8	2.73	2.51	65.57	2.47	1.44	6662	-9.94
CTM9	2.38	2.57	71.59	2.48	1.44	7385	-11.18
CTM10	2.91	2.35	56.11	2.47	1.44	5237	-8.80
CTM11	2.33	1.78	74.79	2.33	1.43	11353	-$^{h)}$
CTM12	1.46	1.25	62.27	2.32	1.44	5382	-$^{h)}$
CTM13	9.98	1.38	86.53	2.29	1.43	11143	-$^{h)}$
CTM14	1.01	0.95	38.24	2.28	1.43	2231	-$^{h)}$
CTM15	1.78	1.39	75.72	2.32	1.44	10031	-$^{h)}$

a) $\partial \ln\mu/\partial E^{1/2}$ b) Observed dipole moment
c) Observed electric polarizability
d) Dielectric constant of CTM solutions (Conc.:0.1 weight fraction)
e) Refractive index of CTM solutions (Conc.:0.1 weight fraction)
f) Electronic spatial extension calculated by ab initio MO
g) Dimerization energy calculated by semiempirical MO
h) Calculations have been not yet carried out.

The result is shown in figure 4. Figure 4 shows observed electronic polarizability correlates to the electronic spatial extension. This result demonstrates that electronic polarizability is a good guideline for overlap factor between wave functions of adjacent CTMs as we suggested in our previous work.[14,15]

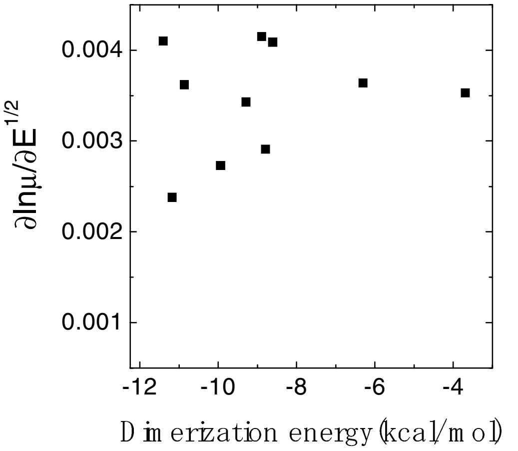

Figure 3 $\partial ln\mu/\partial E^{1/2}$ *vs dipole moment of CTM*

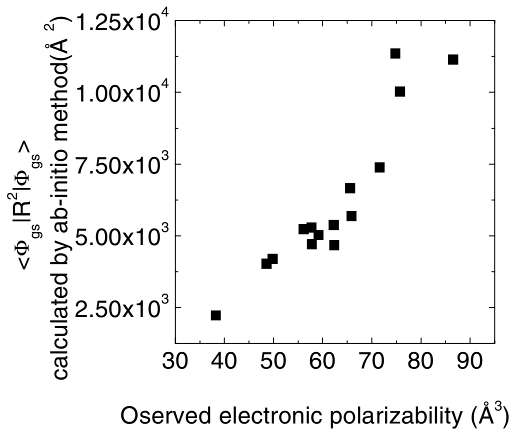

Figure 4 Observed electronic porarizability vs. electronic spatial extension of ground state wave function of CTM.

Figure 5 shows relationship between the observed electronic polarizability and the slope of lnμ. Figure 5 shows that electronic polarizability of CTM does not so correlate to the field dependence of drift mobility, although the CTMs with larger electronic polarizability seems to have the larger electric field dependence of drift mobility.

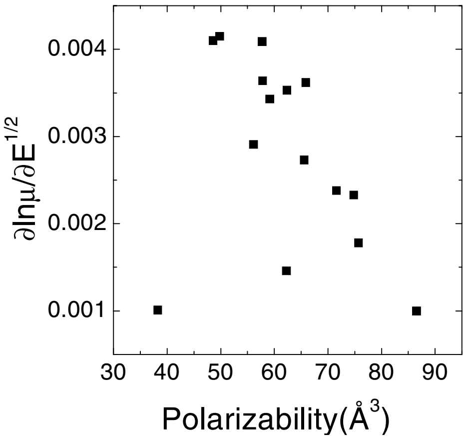

Figure 5 $\partial ln\mu/\partial E^{1/2}$ *vs. electronic polarizability of CTM*

Dielectric constants and dipole moments of CTMs are compared to the electric field dependence of drift mobility in figure 6 and figure 7, respectively. These figures show CTMs with the larger dielectric constant and larger dipole moment derive to the larger electric field dependence of drift mobility in CTL. These results imply that the dielectric property, which is induced by the change of the molecular orientation of CTM having permanent dipole moment, would be one of the important origins of the electronic field dependence. The slope of drift mobility clearly shows the linear dependence on dipole moment of CTM as shown in dipolar trap model,[12,13] rather than the quadratic dependence on that as shown in Gaussian disorder model.[9-11] This fact suggests that CTM molecules rotate in CTL at the temperature under the glass transition temperature of CTL binder polymer and the dipolar trap depth is reduced by the change of CTM molecular orientation.

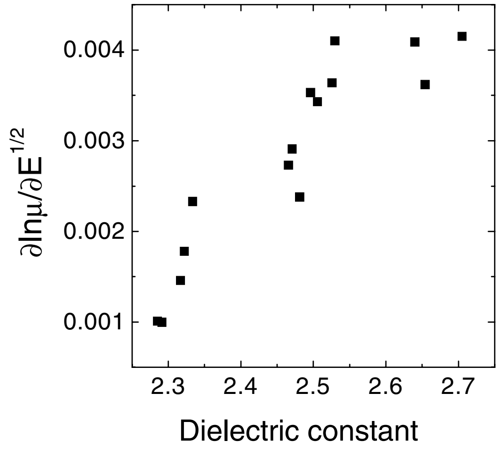

Figure 6 $\partial ln\mu/\partial E^{1/2}$ *vs Dielectric constant of CTM*

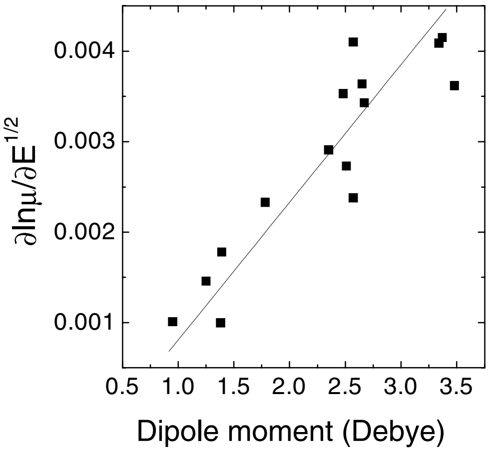

Figure 7. $\partial ln\mu/\partial E^{1/2}$ vs dipole moment of CTM

Conclusion

The relationship between the electric field dependence of drift mobility and several CTM molecular properties was investigated. The slope of drift mobility clearly shows the linear dependence on dipole moment of CTM as shown in dipolar trap model, rather than the quadratic dependence on that as shown in Gaussian disorder model. Observed electronic polarizability of CTM does not correlate to the field dependence of drift mobility, although the CTMs with larger electronic polarizability seems to have the larger electric field dependence of drift mobility. Dimerization energy obtained by semiempirical MO calculation does not show correlation to the field dependence of drift mobility.

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. Schöherr, 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. P. M. Borsenberger, and J. J. Fitzgerald, *J. Phys. Chem.* **97**, 4815(1993).
10. A. Dieckmann, H. Bässler and P. M. Borsenberger, *J. Phys. Chem.* **99**, 8136(1993).
11. R. H. Young and J. J. Fitzgerald, *J. Phys. Chem.* **99**, 4230(1995).
12. M. Sugiuchi and H. Nishizawa, *J. Imaging Sci. Technol*. **37**, 245 (1993).
13. S.V. Novikov and A.V. Vannikov, *J. Imaging Sci. Technol*. **38**, 355 (1994).
14. A. Fujii, T. Shoda, S. Aramaki, and T. Murayama, *J. Imaging Sci. Technol.* **43**, 430(1999)
15. T. Shoda, A. Fujii, S. Aramaki, and T. Murayama, *Proc. of IS&T' NIP 15: International Conference on Digital Printing Technol.* 651(1999)
16. T. Shoda, and T. Murayama, *Proc. of IS&T' NIP 16: International Conference on Digital Printing Technol.* 443(2000)
17. A. Melnyk and D.M. Pai, in *Physical Method of Chemistry*, Wiley Interscience, New York, Vol8, chap. 5(1993)
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. *Gaussian 98* (Revision A.9), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998..
21. J.J. Stewart, *MOPAC93 manual*, FUJITSU LIMITED, 1993.
22. D.E. Williams, PCK91; a *Crystal Molecular Packing Analysis Program,* Department of Chemistry, University of Louisville, Louisville, KY40292, E-mail:dew01@xray5.chem.louisville.edu

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.