

Material Design of Organic Thin Films for Bipolar Charge Transport

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Polymeric thin films molecularly doped with low-molecular-weight compounds have attracted much attention as a class of charge-carrier-transporting organic materials and have been widely used in practical organic photoreceptors for electrophotography. Since the charge-carrier transport in such a system is a chain of redox processes between the neutral molecules and the corresponding radical ions,¹ electron-donating and electron-withdrawing dopants have potential ability to transport positive (hole) and negative (electron) charges, respectively. Then polymeric films doped with both electron donors and acceptors are expected to be capable of transporting bipolar charges. A few such bipolar charge-transport materials (BCTMs) have been reported.^{2,3} The reason is that few electron acceptors that have sufficient compatibility with binder polymers are known^{2,4-6} and that electron acceptors generally interact with electron donors to form charge-transfer complexes^{2,4,5} that may perturb charge transport. In a charge-transfer complex of poly(*N*-vinylcarbazole) (PVK) as an electron donor and 2,4,7-trinitro-9-fluorenone (TNF) as an electron acceptor, the only well-known BCTM, Gill reported that the complexed carbazole pendants lose hole-transporting ability.^{2b} For bipolar charge transport, the materials should be designed with the interaction between donor and acceptor dopants as well as their individual charge-transporting nature taken into consideration. From its applications in electrophotography to optoelectronics, the development of BCTMs provides an interesting study.

Recently, we have found a novel electron-transporting compound, 3,5-dimethyl-3',5'-di-*tert*-butyl-4,4'-diphenylquinone (MBDQ),⁷ which has an electron affinity comparable to that of TNF and much higher compatibility with common binder polymers than TNF. MBDQ with its chemical structure shown in Figure 1 exhibits the excellent electron drift mobility in its molecularly doped polymeric films and does not interact with electron donors easily due to its bulky alkyl substituents. No charge-transfer absorption could be observed in the mixtures of MBDQ and hole-transporting electron donors such as aromatic amine and hydrazone derivatives, in contrast with the case of TNF. Thus, MBDQ is a favorable candidate for the electron acceptors in the bipolar charge-transport system mentioned above.

Here we present a member of this class of BCTMs based on MBDQ. The present member consists of MBDQ as an electron acceptor, *N,N,N',N'*-tetrakis(*m*-methylphenyl)-

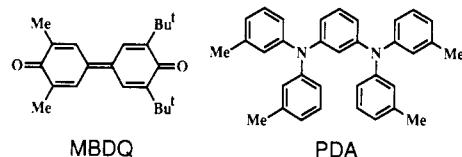


Figure 1. Molecular structures of the electron (MBDQ) and hole (PDA) transport compounds used in this study.

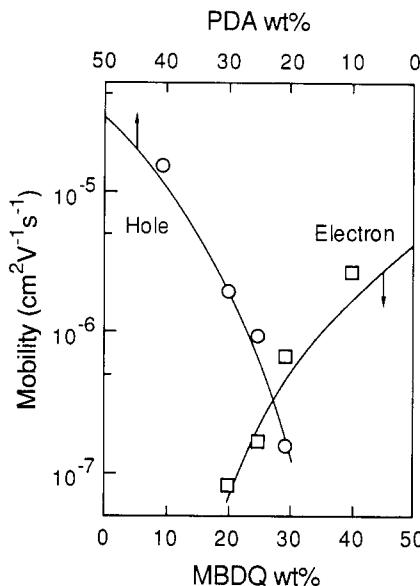


Figure 2. Electron (□) and hole (○) mobilities in the bipolar charge transport system with various dopant concentrations; total dopant concentration 50 wt %. The solid curves show the concentration dependences of the electron and hole mobilities for the cases of only MBDQ and PDA, respectively. Mobility measurements were carried out in a field of 5×10^5 V cm⁻¹ at room temperature.

1,3-diaminobenzene (PDA) as an electron donor and polycarbonate⁸ as a binder polymer.

MBDQ was synthesized by the oxidative coupling of 2,6-dimethylphenol and 2,6-di-*tert*-butylphenol and purified by column chromatography and recrystallization.⁷ PDA, an excellent hole-transporting compound,⁹ was synthesized by Ullmann condensation of 1,3-diaminobenzene and *m*-iodotoluene and purified by column chromatography and vacuum distillation. The homogeneous composite films were easily obtained by the simple solvent-cast technique owing to high solubility and compatibility of PDA and MBDQ. The hole and electron drift mobilities of the films prepared were measured by the standard time-of-flight transient photoconduction method using a nitrogen gas laser pulse. The films incorporating each of PDA and MBDQ in more than ca. 20 wt % showed well-defined transient photocurrents due to hole and electron transports. Figure 2 shows the variation of hole and electron drift mobilities with each dopant concentration under the whole dopant concentration remaining at 50 wt %. The hole mobility increases predominantly with an increase in the PDA concentration, and the electron mobility also increases with an increase in the MBDQ concentration. When a composite film incorporates ca. 20 wt % PDA and ca. 30 wt % MBDQ, its hole and electron mobilities are equal and exceed 10^{-7} cm² V⁻¹ s⁻¹ (ca. 3×10^{-7} cm² V⁻¹ s⁻¹) in a field of 5×10^5 V cm⁻¹ at room temperature. To our knowledge, this is the best data

(1) Stolka, M.; Yanus, J. F.; Pai, D. M. *J. Phys. Chem.* 1984, 88, 4707.
(2) (a) Schaffert, R. M. *IBM J. Res. Develop.* 1971, 15, 75. (b) Gill, W. D. *J. Appl. Phys.* 1972, 43, 5033.

(3) Borsenberger, P. M.; Chowdry, A.; Hoesterey, D. C.; Mey, W. J. *Appl. Phys.* 1978, 49, 5555.

(4) Ong, B. S.; Keoshkerian, B.; Martin, T. I.; Hamer, G. K. *Can. J. Chem.* 1985, 63, 147.

(5) McAneney, T. B.; Loutfy, R. O.; Ong, B. S.; Popovic, Z. D. U.S. Patent 4,559,287, 1985.

(6) Scozzafava, M.; Chen, C. H.; Reynolds, G. A. U.S. Patent 4,514,481, 1985.

(7) Yamaguchi, Y.; Tanaka, H.; Yokoyama, M. *J. Chem. Soc., Chem. Commun.* 1990, 222.

(8) The polycarbonate, derived from 4,4'-cyclohexylidenebisphenol, was obtained from Mitsubishi Gas Chemicals.

(9) Yokoyama, M. Advanced Printing of Paper Summaries of the Japan Hardcopy '88, 1988; p 51.

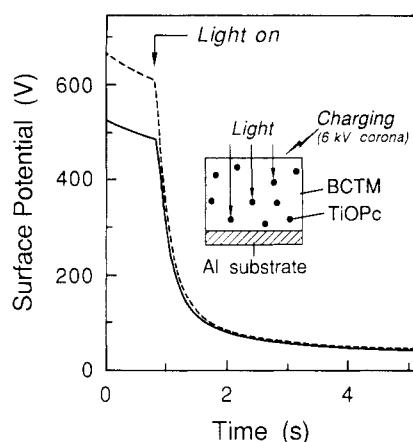


Figure 3. Photoinduced surface potential decay curves by the continuous irradiation of 630-nm light ($3.15 \mu\text{W cm}^{-2}$) for the photoreceptor with 0.5 wt % TiOPc pigment embedded in a BCTM (30 wt % MBDQ and 20 wt % PDA in polycarbonate): (—) positive charging; (---) negative charging. The optical density of the 17- μm photoreceptor was 0.51 in 630 nm (λ_{max} of TiOPc).

obtained for bipolar-charge-transporting organic materials. It should be noted in Figure 2 that the hole and electron mobilities of the present bipolar charge transport system are equal (within experimental error) to those of the films doped with only PDA or MBDQ separately. This finding clearly demonstrates that PDA and MBDQ function independently and do not interfere with each other in this system. Thus, it is emphasized that the present system provides a model for the material design of BCTMs.

In our laboratory, studies on the following two applications based on BCTMs are in progress: electroluminescent and electrophotographic devices. If fluorescent compounds that can capture both electrons and holes (i.e., recombine holes and electrons) are embedded in BCTMs, the resulting composite thin films may function as an electroluminescent device. On the other hand, if colored compounds that can separate the charges (i.e., generate holes and electrons) by light absorption are embedded, the resulting films may function as an electrophotographic photoreceptor that can work equally in both cases of positive and negative charging. An example of the latter is shown in Figure 3. The photoreceptor was prepared by embedding particles of titanylphthalocyanine (TiOPc) pigment as a charge-separation agent in the present bipolar charge-transport active matrix. As expected, its photoinduced discharge rates were quite independent of the polarity of charging. The electrophotographic properties of this novel type of photoreceptors will be presented in a forthcoming paper.

Cyclotrigallazane, $[\text{H}_2\text{GaNH}_2]_3$. Its Preparation, Structure, and Conversion to Cubic Gallium Nitride at 150 °C

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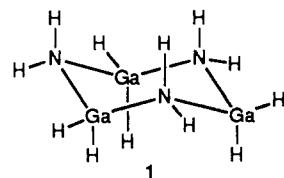
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As a III-V semiconductor having a bandgap of 3.5 eV,¹ there is interest in using gallium nitride in various op-

toelectronic devices. The known syntheses of bulk powders of GaN involve reactions of various gallium sources (Ga_2O_3 ,² Ga,³ or $[\text{NH}_4]_3[\text{GaF}_6]$ ⁴) with ammonia conducted at high temperatures (>900 °C) and result exclusively in gallium nitride having a wurtzite (hexagonal) structure. Reports of epitaxial thin films of cubic gallium nitride grown by molecular beam epitaxy or organometallic vapor-phase epitaxy on substrates such as GaAs,⁵ MgO,⁶ or cubic SiC⁷ have appeared. In this paper we describe the synthesis and structure of the novel trimer cyclotrigallazane and its reaction to give the first bulk samples of cubic GaN.

The only previous report of the reaction between $(\text{Me}_3\text{N})\text{GaH}_3$ and NH_3 suggested the uncharacterized product was polymeric.⁸ In our hands H_2GaNH_2 was prepared in 75% yield simply by passing gaseous NH_3 over solid $(\text{Me}_3\text{N})\text{GaH}_3$ at room temperature for 1 h. The less-than-quantitative yield results from losses of the volatile gallane starting material, and higher yields can be achieved by condensing liquid ammonia directly on $(\text{Me}_3\text{N})\text{GaH}_3$. Even without further purification, elemental analysis of the white powder indicated the formula H_2GaNH_2 , and the lack of measurable carbon confirmed the quantitative displacement of trimethylamine.¹⁰ The highest mass peak observed by using EI mass spectrometry (20-eV ionizing voltage) was 262 amu, corresponding to the parent ion of the trimer minus one hydrogen. The extremely limited solubility of cyclotrigallazane in all common organic solvents precluded us from obtaining a ¹H NMR spectrum. The infrared spectrum of the powder dispersed in *n*-undecane reveals $\nu_{\text{N-H}}$ vibrations at 3297 and 3247 cm^{-1} and $\nu_{\text{Ga-H}}$ vibrations at 1890, 1865, and 1832 cm^{-1} . Careful sublimation at 40–50 °C and 0.05 Torr yielded a small number of clear, colorless crystals that were shown by single-crystal X-ray crystallography to consist of a six-membered ring in a chair conformation, 1,¹¹ similar to that observed in $[\text{H}_2\text{BNH}_2]_3$.¹²



Thermogravimetric analysis of cyclotrigallazane shows an abrupt weight loss (4.5%) at 150 °C followed by a

- (1) Illegems, M.; Dingle, R.; Logan, R. *A. J. Appl. Phys.* 1972, 43, 3797.
- (2) Schoonmaker, R. C.; Burton, C. E. *Inorg. Synth.* 1963, 7, 16.
- (3) Johnson, W. C.; Parsons, J. B.; Crew, M. C. *J. Phys. Chem.* 1932, 36, 2651.
- (4) Juza, R.; Hahn, H. *Z. Anorg. Allg. Chem.* 1940, 244, 111.
- (5) Mizuta, M.; Fujieda, S.; Matsumoto, Y.; Kawamura, T. *Jpn. J. Appl. Phys.* 1986, 25, L945.
- (6) Powell, R. C.; Tomasch, G. A.; Kim, Y. W.; Thornton, J. A.; Greene, J. E. Abstracts of Papers; Fall Meeting, Boston, MA; Materials Research Society: Pittsburgh, PA, 1989; F7.2.
- (7) Paisley, M. J.; Sitar, Z.; Posthill, J. B.; Davis, R. F. *J. Vac. Sci. Technol.* 1989, A7, 701.
- (8) Storr, A. *J. Chem. Soc. A* 1968, 2605.
- (9) Shriver, D. F.; Shirk, A. E. *Inorg. Synth.* 1977, 17, 42.
- (10) Anal. Calcd: Ga, 79.45; N, 15.96; H, 4.59; C, 0.00. Found: Ga, 79.70; N, 15.71; H, 4.46; C, 0.08 (Analitische Laboratorien in Engelskirchen, West Germany).
- (11) X-ray crystallographic data: monoclinic crystal system, $P2_1/m$ space group, $a = 8.079$ (8) Å, $b = 8.506$ (9) Å, $c = 8.079$ (8) Å, $\beta = 138.24$ (5)°, $Z = 2$, $V = 370$ (1) Å³, $T = -90$ °C, $R(F) = 0.119$, $R(wF) = 0.118$. Twinning of all crystals examined resulted in higher values of $R(F)$ and $R(wF)$. Full details of the structural solution are available in the supplementary material and will be reported separately. Structural data: Ga(1)-N(2) = 1.96 (2) Å, Ga(1)-N(2') = 1.96 (2) Å, Ga(3)-N(2) = 1.98 (2) Å, Ga(3)-N(4) = 1.96 (1) Å; N(2)-Ga(1)-N(2') = 100 (1)°, N(2)-Ga(3)-N(4) = 99.6 (9)°, Ga(1)-N(2)-Ga(3) = 117.0 (8)°, Ga(3)-N(4)-Ga(3') = 118 (1)°.
- (12) Corfield, P. W. R.; Shore, S. G. *J. Am. Chem. Soc.* 1973, 95, 1480.