the samples were equilibrated in a closed container over water, at room temperature overnight, in an attempt to attain the maximum amount of hydrate water. In contrast to $K_5Sb_5P_2O_{20}$, two distinctive regions can be seen in the TGA curves of the substituted samples (Figure 11). The majority of water is lost below 100 °C in the substituted samples. Above ~100 °C, the amount of water lost is almost identical in both the substituted and $K_5Sb_5P_2O_{20}$ samples (Figure 11). The two regions in the TGA curves of the substituted samples (i.e., I and II) are attributed to two types of water: surface and lattice water; $K_5Sb_5P_2O_{20}$ has only lattice water. The adsorption of surface water in the substituted samples could be due to their smaller particle size (hence larger surface area) compared with that of $K_5Sb_5P_2O_{20}$. Alternatively, the substitution of Nb/Ta for the more electronegative Sb (Table II) is expected to increase the formal charge on the lattice oxygen in $K_5Sb_{5-x}M_xP_2O_{20}$, which results in a more hygroscopic sample.

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New Class of Electron Acceptors Having High Polymer Dispersibility, Unsymmetrically Substituted Diphenoquinones, and Their Application as Electron Transport Materials

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A new class of electron acceptors, unsymmetrically substituted diphenoquinones with methyl and bulky alkyl substituents, has been developed for electron-transport compounds, which possess high dispersibility in a wide range of polymers owing to their unsymmetrical and bulky substitutions. 3,5-Dimethyl-3′,5′-di-*tert*-butyl-4,4′-diphenoquinone (MBDQ), a representative member of these acceptors, dispersed molecularly in polycarbonate exhibited electron mobilities over 10^{-6} cm^2/V s at a conventional concentration of 40 wt %, which are the highest for electron transport in molecularly doped polymers. The photoinduced discharge measurements demonstrated that electrons can be injected from titanylphthalocyanine into the MBDQ-doped polycarbonate, indicating a possible application to xerography.

Introduction

Charge-transport phenomena in molecularly doped polymers (MDPs) have attracted considerable attention because of their technological importance as charge-transport materials for organic photoreceptors in xerography.[1] These materials are also of interest for the basic understanding of charge transfer in amorphous organic solids. Usually, these are supplied as binary solid solutions that are comprised of a transport-active molecule and a film-forming polymeric binder. From the chemical point of view, charge transport in such MDPs is an electric-field-driven chain of redox processes between neutral molecules and the corresponding radical ions, i.e., cation and anion radicals for positive (hole) and negative (electron) charge transport, respectively.[2-4] It is, therefore, required that the molecules for hole and electron transport should be electron-donating and electron-accepting in their ground states, respectively.

A large number of hole-transporting electron donors have emerged so far, and many of them, such as arylamine and hydrazone derivatives, have been widely used in practical xerographic photoreceptors. The hole transport in MDPs, therefore, has been extensively investigated.[2-17] The hole mobilities are largely in the range 10^{-4}–10^{-8} cm^2/V s and increase with an increase in dopant concentration. In most cases, the mobilities are thermally activated with a field-dependent activation energy that may be also temperature-dependent.[7,9,11,14,15,21e]

In contrast to the abundance of hole-transport materials, only a few electron acceptors have been reported as elec-

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tron-transport molecules.[18-22] The main reason is that electron acceptors are generally characterized by their poor dispersibility in polymers. Of electron-transporting acceptors reported so far, 2,4,7-trinitro-9-fluorenone (TNF) is the most known and investigated example.[18] However, TNF is poorly dispersible in common binder polymers although extraordinarily compatible only with an electron-donating polymer, poly(*N*-vinylcarbazole) (PVK), owing to the charge-transfer complexation. The electron mobility of TNF–PVK is as low as on the order of 10^{-7} cm^2/V s, and the charge-transfer absorption in the visible region is disadvantageous in many applications. Since TNF has been furthermore registered as a carcinogenic compound, the practical use of it and its analogues has been discouraged rapidly.

From the viewpoint of utilizing organic materials fully in optoelectronics, it is strongly desired to develop electron-transport materials as a counterpart to hole-transport materials that are already in practical use. In dispersion-based systems, the poor dispersibility leads to phase separation, i.e., aggregation of the molecules, which deteriorates their optical and electrical properties.[17,19,21b] For this purpose, the compounds must be designed taking polymer dispersibility as well as electron-accepting nature into consideration.

It is known that the introduction of an alkyl substituent into molecules may improve their dispersibility in organic polymers and solubility in organic solvents. On the basis of this concept, some alkylated derivatives of TNF and its analogues have been recently developed, which exhibited higher dispersibility than that of TNF itself.[20,21] In a previous communication,[23] we presented a novel electron-transporting compound, MBDQ, which is nonmutagenic (Ames test), possesses sufficient electron affinity comparable to TNF, and exhibits high polymer dispersibility in a wide range of polymers, which is unexpected for electron acceptors.

In the present paper, we report the syntheses and molecular properties of this new class of electron acceptors represented by MBDQ, unsymmetrically alkyl-substituted diphenoquinones. In addition, their electron-transport properties in a polycarbonate matrix and possible application to xerographic photoreceptors are described.

Experimental Section

Syntheses. Many have reported that 3,5,3′,5′-tetraalkyl-4,4′-diphenoquinones can be synthesized by the oxidative self-coupling of the corresponding 2,6-dialkylphenols.[24,25]

The symmetrical diphenoquinones with cyclohexyl (**1a**), *tert*-butyl (**1b**), isopropyl (**1c**), and methyl (**1d**) substituents were synthesized according to the method reported by Menger and Carnahan,[25] which is characterized by the high yield and the ease in workup.

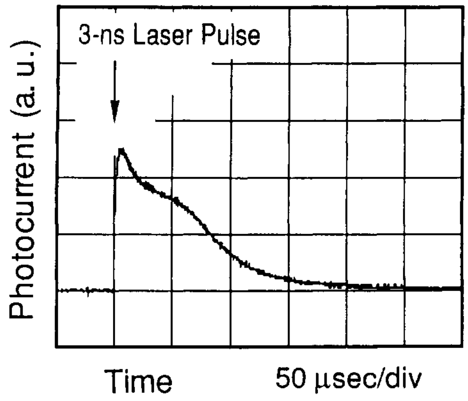

Figure 1. Typical time-of-flight signal due to electron transport for tetraalkyldiphenoquinone-doped PC-Z (80 wt % MBDQ, 6-μm thickness). $F = 40$ V/μm, $T = 25$ °C.

To obtain new unsymmetrical diphenoquinones **2a–c**, the coupling method was applied to mixtures of two kinds of phenols.[23] No attempts to optimize synthetic conditions were made. 3,5-Dimethyl-3′,5′-di-*tert*-butyl-4,4′-diphenoquinone (**2b**, i.e., MBDQ) was prepared in the following manner: A mixture of 2,6-dimethylphenol (30 mmol) and 2,6-di-*tert*-butylphenol (30 mmol) in chloroform (120 mL) was vigorously stirred at 50–55 °C for 2 h with fine powder of potassium permanganate (240 mmol) as an oxidizing reagent. The insoluble solids (inorganic salts and a large part of **1d** produced) were then removed by filtration, and the resulting filtrate was evaporated to dryness under reduced pressure. This gave the desired cross-coupling product **2b** and two kinds of self-coupling byproducts, **1b** and **1d**. **2b** was separated roughly from the byproducts by extraction with ethanol and then completely by column chromatography on silica gel (Merck silica gel 60) with dichloromethane as eluant. Recrystallization from hexane gave yellowish red needles of **2b**, λ_{max}(CH$_2$Cl$_2$) 422 nm; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.37 (s, 18 H), 2.17 (s, 6 H), 7.68 (s, 2 H), 7.71 (s, 2 H). Anal. Calcd for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70; M, 324. Found: C, 81.42; H, 8.65; M$^+$, 324.

3,5-Dimethyl-3′,5′-dicyclohexyl-4,4′-diphenoquinone (**2a**) was similarly prepared and recrystallized from hexane/ethanol (1:1 v/v) to give orange microcrystals, λ_{max}(CH$_2$Cl$_2$) 424 nm; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.4–1.8 (complex, 20 H), 2.18 (s, 6 H), 2.88 (m, 2 H), 7.61 (s, 2 H), 7.76 (s, 2 H). Anal. Calcd for $C_{26}H_{32}O_2$: C, 82.94; H, 8.57; M, 376. Found: C, 82.89; H, 8.57; M$^+$, 376.

3,5-Dimethyl-3′,5′-diisopropyl-4,4′-diphenoquinone (**2c**) also was similarly prepared and recrystallized from methanol to give purple columns, λ_{max}(CH$_2$Cl$_2$) 421 nm. Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16; M 296. Found: C, 80.93; H, 8.21; M$^+$ 296. In mass spectrometry, a peak (m/z 312) was observed in the region heavier than the molecular ion. The impurity level was less than about 5%.

Physical Measurements. Cyclic voltammetric measurements of diphenoquinones were performed in acetonitrile with a sweep rate of 10 mV/s using 0.1 M [n-Bu$_4$N][ClO$_4$] electrolyte, a Beckman platinum working electrode, and a standard calomel reference electrode (SCE).

Electronic absorption spectra of thin films (thickness ca. 0.2 μm) of MBDQ with and without a polymeric binder, poly(4,4′-cyclohexylidenediphenyl carbonate) (PC-Z, Mitsubishi Gas Chemicals), which were spin-coated on a quartz slide from dichloromethane solutions, were measured as coated and after heating at 60 °C.

Time-of-Flight Measurement. Electron mobilities of diphenoquinones dispersed in PC-Z were measured in vacuo by the conventional time-of-flight technique.[12,15] The sample films were prepared by the simple solvent-cast technique using a wired bar on an aluminum substrate from dichloromethane solutions. These films were dried in air at 60 °C for 5 min and in vacuo at room temperature for 2 h and then provided with a semitransparent gold electrode by vacuum deposition. The thickness of the dried films ranged from 5 to 10 μm (typically 6 μm). The films were photoexcited through the gold electrode by a nitrogen laser pulse (ca. 3-ns duration). The well-defined transient photocurrents were observed only when the gold electrode was negatively biased. This

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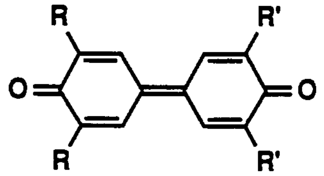
Table I. Molecular Properties of Symmetrical and Unsymmetrical Diphenoquinones



diphenoquinone				solubility, mmol/L		dispersibility	
	R	R′	E_{red}, V vs SCE	in hexane	in CH_3CN	in PC-Z[a]	mp, °C
1a	cyclohexyl	cyclohexyl	*b*	0.1	0.0	*c*	262–265
1b	*tert*-butyl	*tert*-butyl	−0.51	45	3.1	25	245–247
1c	isopropyl	isopropyl	−0.45	61	36	30	202–204
1d	methyl	methyl	−0.44	0.3	1.2	*c*	216–218
2a	methyl	cyclohexyl	−0.45	12	7.1	40	196–197
2b	methyl	*tert*-butyl	−0.48	52	57	80	180–181
2c	methyl	isopropyl	−0.45	137	460	80	124–126

[a] The maximum concentration in wt % up to which amorphous films could be obtained by the film-fabrication technique described in the Experimental Section. [b] Insoluble in CH_3CN. [c] Insoluble in casting solvents.

fact demonstrates that the mobile charge carrier is not a hole but an *electron*. It should be noticed here that the shoulders identifying the transit times τ were discernible in the photocurrent signals, as exemplified in Figure 1. The mobilities were determined from the conventional expression, $\mu = L^2/\tau V$, where L is the film thickness and V is the applied voltage. No dependences of the mobilities on film thickness were observed, which indicates that phenomena related to delayed generation can be neglected. Measurements in dry air and oxygen gas gave the same mobilities as in vacuo within experimental error, which suggests that electron-accepting oxygen gas does not significantly affect electron transport in the present systems.

Photoinduced Discharge Measurement. The potential of application of diphenoquinone-doped polymers as an electron transport layer (ETL) in double-layered xerographic photoreceptors was evaluated by a conventional photoinduced discharge (PID) test.[26] The photoreceptor devices, which were prepared on an aluminum substrate, consisted of a 16-μm amorphous film of 40 wt % MBDQ in PC-Z overcoated on a 0.5-μm charge-generation layer (CGL). The CGLs were coated from mixtures of a ball-milled tetrahydrofuran suspension of α-form titanylphthalocyanine (TiOPc) pigment[27] and a dichloromethane solution of PC-Z or poly(vinylbutyral) (S-LEC, Sekisui Chemical Co.) as a binder resin and then dried in vacuo at 60 °C for several hours. The PID measurements were performed with a systematic xerographic analyzer (EPA-8100, Kawaguchi electronic Works). The sample surfaces were charged positively by a 6-kV corotron. The light source was a halogen lamp (100 W, 2856 K). Monochromatic lights were obtained by using appropriate interference filters.

Results and Discussion

Molecular Properties. For electron transport, it is essential that the compounds have sufficient electron affinity. In addition, their radical anions are required to be stable chemically. If they undergo a chemical reaction, the electron transport would suffer drastic damage.[19] Symmetrically 3,5,3′,5′-tetraalkyl-substituted diphenoquinones are well-known as a class of electron acceptors having electron affinity comparable to TNF. Their radical anions are very stable owing to the steric protection of the reactive carbonyl groups by alkyl substituents.[28] In spite of the presence of alkyl substituents, however, their dispersibilities in binder polymers, although dependent on the kind of the substituents, are not good. To solve this problem, i.e., to enhance the polymer dispersibility, we have newly prepared unsymmetrically substituted ones. A limited number of unsymmetrically tetrasubstituted diphenoquinones have been synthesized so far.[29,30] Little is known concerning their properties.

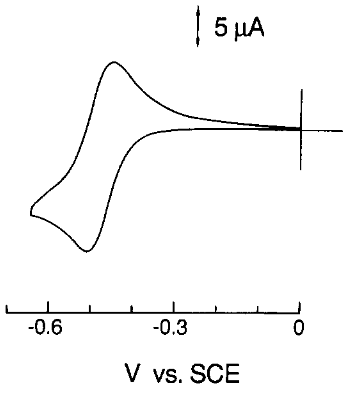


Figure 2. Cyclic voltammogram of a typical unsymmetrical diphenoquinone, MBDQ, in CH_3CN at Pt electrode; sweep rate 10 mV/s.

Figure 2 shows a typical example of the cyclic voltammograms of unsymmetrical diphenoquinones. All of them exhibited a reversible one-electron reduction wave like the symmetrical analogues.[28] Such reversibility implies the chemical stability of their radical anions. As can be seen in Table I, the half-wave reduction potentials E_{red}'s of the unsymmetrical diphenoquinones gave intermediate values between those of the corresponding symmetrical ones.

The solubility for two organic solvents and dispersibility in a typical binder polymer, PC-Z, of the unsymmetrical diphenoquinones are compared with those of symmetrical ones in Table I. All unsymmetrical diphenoquinones exhibited markedly higher solubility in both nonpolar (hexane) and strongly polar (acetonitrile) solvents than the corresponding symmetrical ones. In addition, the unsymmetrical substitution remarkably enhanced the dispersibility in PC-Z. We believe that these improvements are due mainly to their unsymmetrical molecular structure that could reduce the cohesive force between the molecules. This is implied by the fact that the melting points of the unsymmetrical diphenoquinones are much lower than those of the symmetrical analogues (see Table I). For xerographic applications, the dopant concentration in MDPs is typically 30–60 wt %. The unsymmetrical di-

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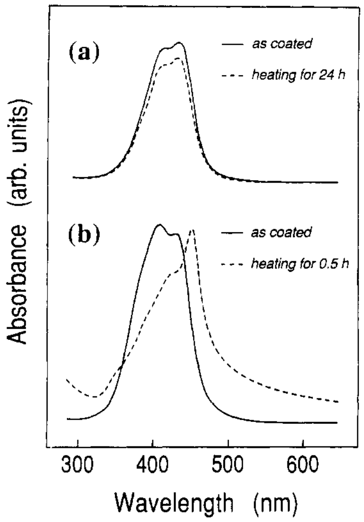

Figure 3. Absorption spectra of thin films (ca. 0.2 μm) of (a) 50 wt % MBDQ in PC-Z and (b) neat MBDQ. A little intensity loss by heating appears to be due to the sublimation of of MBDQ.

phenoquinones with *tert*-butyl (**2b**) and isopropyl (**2c**) substituents similarly exhibited sufficiently high dispersibility (more than 50 wt %) even in other common binder polymers such as poly(vinylbutyral), poly(vinyl chloride), polyester, and polystyrene.

Loutfy and Ong have recently proposed a spectroscopic evaluation for the dispersibility and stability of small molecules in polymers.[21a] In 4-(butoxycarbonyl)-9-dicyanomethylenefluorene (BCMF), which is the electron-transporting molecule that possesses, to our knowledge, the highest polymer dispersibility and mobility among those reported so far, they reported that the heat treatment (60 °C, 30 min) of its dispersion films, except for poly(vinyl chloride), causes a broadening of the absorption band and loss of absorption intensity due to the formation of molecular aggregates, which affect electron transport by acting as trapping sites.[21c] Figure 3 shows the absorption spectra of 50 wt % MBDQ-doped PC-Z and neat MBDQ as spin-coated and after heating at 60 °C. The spectra of the films as coated resemble closely the absorption of isolated MBDQ molecules in organic solvents. In the neat MBDQ film, however, the heat treatment for 30 min resulted in spectral change due to crystallization. On the other hand, the 50 wt % film exhibited little change even after heating for 24 h. These results indicate that the MBDQ molecules are molecularly dispersed in PC-Z and that the amorphous dispersion state is thermally stable even at a relatively high concentration of 50 wt %. Thus, the unsymmetrical diphenoquinones are favorable candidates for application as dispersion-based electron-transport materials and for fundamental studies of electron-hopping mechanism.

Electron-Transport Properties. The molecularly doped PC-Z films with diphenoquinones exhibited photoconduction due to electron transport as mentioned in the Experimental Section. On the basis of the hopping mechanism, a relationship between the mobility μ and distance between hopping sites R in MDPs is generally accepted:

$$\mu/R^2 \propto \exp(-2R/R_0) \tag{1}$$

where R_0 is a fitting constant, known as the charge localization radius.[18a] The mobility data at room temperature in a field of 50 V/μm are plotted in Figure 4 according to eq 1. The distance R was calculated by using the method used commonly in this field; that is, assuming each dopant molecule has a cubic shape, the center-to-center distance between molecules R is given by

$$R = (M/N_A dC)^{1/3} \tag{2}$$

where M is the molecular weight of dopant, N_A is Avogadro's number, d is the density, and C is fractional dopant concentration by weight. It should be noted in Figure 4 that all the data appeared on a single line. This suggests that the mobility of tetraalkyldiphenoquinones depends only on the center-to-center distance between diphenoquinone skeletons regardless of the kind of substituents. In other words, electrons are transported by hopping among π-conjugated diphenoquinone skeletons. From the slope of the line in Figure 4, a value of 1.4 Å was obtained for R_0, which compares with 1.8 Å for TNF[18a] (the only value reported for electron-transport materials) and 1.2–1.8 Å for a variety of hole-transport materials.[2,3,5,6,8]

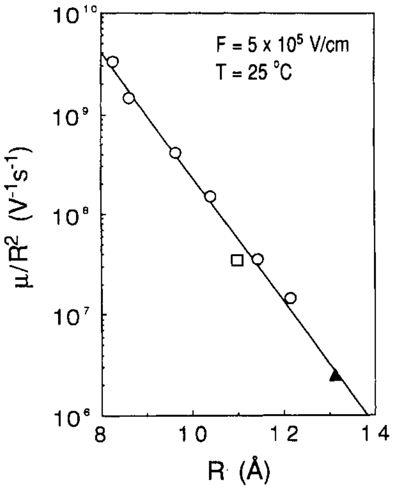

Figure 4. Dependence of electron mobilities on intermolecular distance in diphenoquinone-doped systems: ○ 25, 30, 40, 50, 70, and 80 wt % MBDQ; □ 40 wt % **2a**; ▲ 25 wt % **1b**.

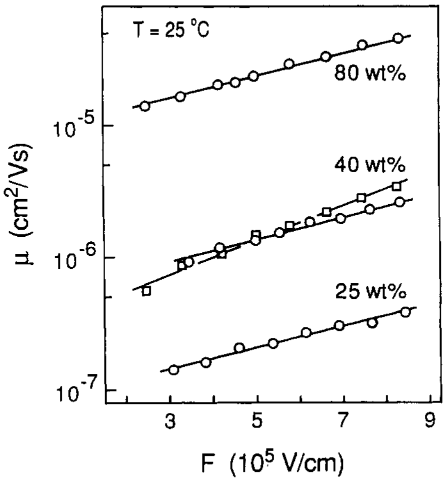

Figure 5. Field dependence of electron mobilities (○) of MBDQ in PC-Z at different concentrations. Also shown are data (□) for hole mobility of 40 wt % DEH in PC-Z.

Figure 5 shows the field dependence of the electron mobilities in samples doped with a typical unsymmetrical diphenoquinone, MBDQ, at different concentrations. The dependence is much weaker than that for TNF.[18a] We cannot unambiguously distinguish whether log μ vs F or $F^{1/2}$ provides a better linear fit in the narrow field range studied. At a widely used concentration of 40 wt %, the electron mobility attained the order of 10^{-6} cm^2/V s at room temperature. As compared under the same conditions, this value is about 1 order of magnitude higher than

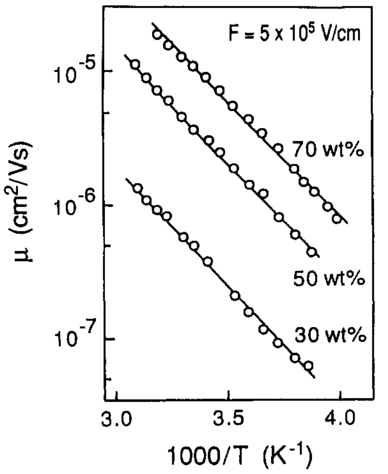

Figure 6. Arrhenius plots of electron mobilities of MBDQ in PC-Z at different concentrations.

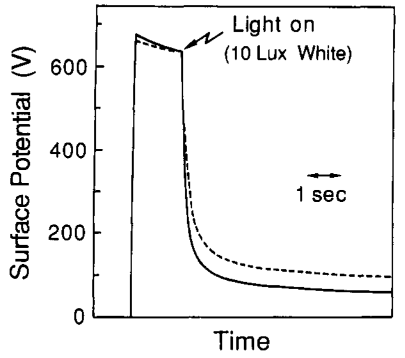

Figure 7. PID curves by 10-lux white light in the positive charging mode for double-layered photoreceptors with a 16-μm film of 40 wt % MBDQ in PC-Z as an ETL. CGL: TiOPc/S-LEC (1:1 by weight) (---), TiOPc/PDA/S-LEC (1:1:1) (—).

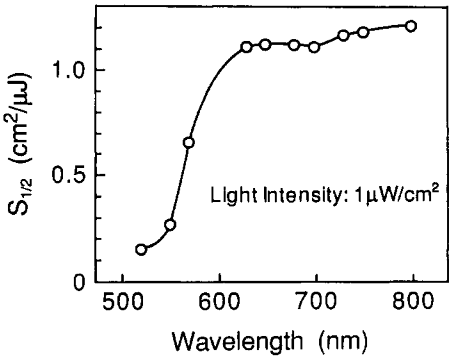

Figure 8. Spectral sensitivity $S_{1/2}$ of a double-layered photoreceptor consisting of 40 wt % MBDQ-doped PC-Z as an ETL and TiOPc/PDA/PC-Z (1:1:1 by weight) as a CGL. $S_{1/2}$ is defined as the reciprocal of the exposure energy required to photodischarge half of the initial surface potential.

for TNF[18a] and compatible to the hole mobility of *p*-(diethylamino)benzaldehyde–diphenylhydrazone (DEH),[12] a hydrazone derivative that is used in practical xerographic photoreceptors. At the maximum concentration, 80 wt %, high electron mobilities over 10^{-5} cm^2/V s were observed for the first time in MDPs.

Figure 6 shows the temperature dependence of the electron mobilities. The mobilities seem to obey the Arrhenius law. Independently of the dopant concentration, the activation energy is about 0.34 eV in a field of 50 V/μm and is much smaller than those (ca. 0.5 eV) for TNF[18a] and BCMF.[21e] This small value accounts for the higher electron mobility of MBDQ and, we suspect, comes from the small polarity of MBDQ molecule. The large polarity of TNF and BCMF may result in the large outer-sphere reorganization energy in electron transfer, which is considered to be an essential part of the activation energy.[4] Furthermore, the polarity could produce the cohesive force between molecules owing to dipole–dipole interaction, which would in turn lead to the aggregation. In addition, the bulky substituents of MBDQ can hamper the close contact between molecules. This is supported by the fact that MBDQ forms no or little charge-transfer complexes with electron donors,[31] in contrast with the cases of TNF[18a,20] and BCMF.[21b]

Application to Xerography. Latent image formation in xerography is accomplished by the imagewise exposure of a corona-charged photoreceptor.[1] Free charge carriers are created by photon absorption and then transported in appropriate directions, thereby decreasing the surface potential only in the exposed area. There has been a growing interest in utilizing layered structures in which the charge generation and transport functions are carried out in two separate layers. Most organic photoreceptors of practical use have the double-layered structure with a hole-transport layer as the upper layer. As a result, they work only in the negative charging mode. In the corona-charging process, however, the negative mode is inferior to the positive one with respect to the discharge stability and yield of ozone, a harmful gas to humans as well as photoreceptors. For this reason, organic photoreceptors that can work in the positive charging mode have been earnestly desired.[21d,22,31,32-35] Electron-transport materials enable us to fabricate such photoreceptors without changing the current double-layered configuration. As mentioned above, MBDQ-doped polycarbonate exhibits the electron mobility suitable for the practical use (more than 10^{-6} cm^2/V s) at a typical concentration of 40 wt %, and both field and temperature dependences of the mobility are relatively small. Figure 7 shows the PID curves for photoreceptors consisting of a 40 wt % MBDQ-doped PC-Z and TiOPc-based CGLs. The rapid photoinduced decay of positive surface potential was observed, whereas the photoreceptors exhibited no photodecay when charged negatively. These results indicate that electrons photogenerated in the TiOPc layer can be effectively injected into the electron-transporting MBDQ layer. Interestingly, the addition of *N,N,N′,N′*-tetrakis(*m*-methylphenyl)-1,3-diaminobenzene (PDA), a known hole-transporting electron donor,[16] to the CGL resulted in improvements in photosensitivity and residual potential as shown in Figure 7. Moreover, it was found that as a binder resin of the CGL, PC-Z gives better photosensitivity than the case of poly(vinylbutyral), S-LEC. Because no changes in the absorption spectrum of TiOPc were observed, these effects are not due to the spectral sensitization. The details of

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[35] Nakazawa, T.; Mutou, N.; Tsutsumi, M. Advanced Printing of Paper Summaries of the Japan Hardcopy '88, 1988; p 70. The photoreceptor presented therein, which has a single-layered structure with charge generation pigment embedded in a hole-transporting matrix, is, at present, the only organic one in commercial use that works in the positive charging mode. Its sensitivity was reported to be about 0.6 cm^2/μJ in the absorption region of the pigment.

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electron generation and injection properties including these additive and binder effects will be presented in a further publication. The spectral response of the best photoreceptor obtained in this work is shown in Figure 8. The photoreceptor exhibited a high and flat sensitivity of about 1.2 cm^2/μJ in the absorption region of the TiOPc (600–850 nm). At present, these are the best data for all-organic double-layered photoreceptors that can work in the positive charging mode and are on a practical level.[35]

Conclusion

We have developed a new class of electron-transporting compounds, unsymmetrically substituted diphenoquinones. The unsymmetrical substitution remarkably enhanced not only the solvent solubility but also polymer dispersibility of diphenoquinone derivatives. High electron mobilities over 10^{-6} cm^2/V s were obtained for the first time in organic amorphous films with transport-active molecules dispersed in common binder polymers. Moreover, it has been found that electrons can be injected from TiOPc pigment into the diphenoquinone-doped polycarbonate, demonstrating the possible application to xerographic photoreceptors that can work in the positive charging mode.

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Photoselective Catalysis of Electroless Copper Solutions for the Formation of Adherent Copper Films onto Polyimide

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The photoreduction of potassium iron(3+) oxalate in the presence of palladium(2+) chloride results in the selective formation of palladium metal, which can catalyze copper plating from an electroless bath. This process is characterized by a rapid photospeed at several ultraviolet wavelengths, and selective electroless deposition of copper occurs only in the irradiated regions. A chemical treatment of the polyimide film, prior to treatment with the photocatalytic mixture results in excellent adhesion of the copper-plated pattern to polyimide. In an attempt to understand the mechanism for both adhesion and the photoformation of the active catalyst, an in situ X-ray photoelectron spectroscopic study was initiated. The results indicate base hydrolysis of the Kapton to form the disodium salt of polyamic acid, cation exchange at the polyamic acid groups, the rapid photoreduction of Fe^{3+} to Fe^{2+} and the slower reduction of Pd^{2+} to Pd^0. Mechanisms for copper–Kapton adhesion and for the photoformation of palladium metal are proposed based upon the results of this surface study. The described process utilizes aqueous solutions and thus is attractive for both manufacturing and environmental reasons. The simplicity of this method for creating selective copper circuit patterns and for producing highly adherent films of copper onto polyimide is highlighted.

Introduction

The metallization of dielectric materials is critical to the production of high-density microelectronic packaging components. The requirements placed upon the dielectric media have become increasingly stringent. Many microelectronic applications require low dielectric constants, thermal stability at elevated temperatures, a high degree of flexibility, and good tensile strength. Polyimides derived from pyromellitic dianhydride and oxydianiline (PMDA–ODA) have been extensively utilized because they meet the above requirements, are resistant to chemical attack, and are readily available as solutions, suspensions, and free-standing films.[1] Although several chemical and physical techniques for polymer metallization are available, these methods require polymer lithography to define the metal circuits.[2] Efforts to reduce the costs associated with the fabrication of multilayered packaging modules have stimulated research into alternate techniques for selective metallization. Photoselective metallization of polyimides via electroless plating offers several advantages including the elimination of lithographic steps, reduced fabrication costs, and simplicity.

Additive metallization via electroless deposition is initiated by a nobel-metal catalyst.[3] Several techniques have been explored for achieving selectivity of the active catalyst, which in turn provides selectivity of the plating process. Selective metal plating from electroless solutions was previously achieved by the UV-induced oxidation of tin(2+) colloids,[4] by the photoreduction of palladium(2+)-activated TiO$_2$ films,[5] by photoinhibition of active palladium–tin catalyst,[6] by the laser-induced decomposi-

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