

# Novel Electron Transporting Quinone Compounds with Extended $\pi$ -Conjugate System

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## Abstract

Novel quinone compounds **1-3** with extended  $\pi$ -conjugate system shown in Figure 1 have been designed as an electron transporting compound for fabricating single-layer organic photoreceptors (OPC) useful for positive charging. We synthesized them and examined their properties. They showed suitable electron accepting properties and good compatibilities to a binder resin. The electron transporting behavior will be discussed based on the fundamental experiments of its electric field, temperature, and intermolecular distance dependencies in molecularly doped system, and analyzed applicability of small-polaron hopping to electron transport in the materials.

required to develop an excellent electron transporting material (ETM) for fabricating high-sensitive single-layered organic photoreceptor for positive charging.

It is considered that preferably ETM has electron withdrawing as a molecule and has a widely spread conjugate system within a molecule<sup>2)</sup>. Several compounds has been developed so far, but generally these have unfavorable point in lower compatibility with the binder resin used widely. Then we have tried to design and synthesize several ETMs for higher electron mobility and compatibility with a binder resin. In this paper, synthesis and electron transporting behavior of some quinone compounds are described.

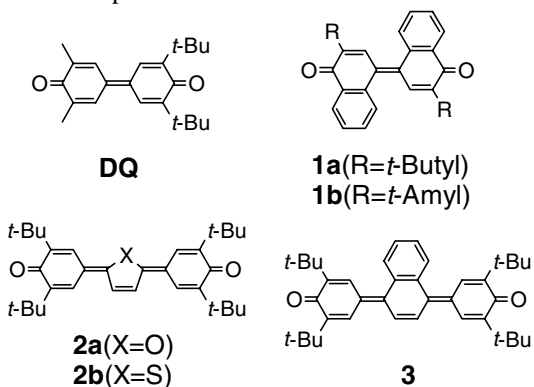


Figure 1. Quinone compounds in this study

## Introduction

Organic photoreceptor has been widely used in electro-photographic systems in place of inorganic one because of its high productivity and safety. There are mainly two types in organic photoreceptors, the single-layered and double-layered ones. We have developed the single-layered organic photoreceptor drum for positive charging. This type of device structure has the advantages in the points of lower ozone generation at the charging<sup>1)</sup> and better image quality compared with the double-layered organic photo-receptor drum for negative charging. It is, however, crucially

## Molecular Design

Electron transporting compounds in this study were designed on the basis of the following concepts.

- Keeping a suitable electron accepting property.
- Expanding the conjugate system
- Improvement of compatibility to a binder resin.

Previously, we succeeded in developing electron transporting diphenylquinone derivatives (**DQ**) shown in Figure 1 by introducing asymmetric substituents to ensure the polymer compatibility<sup>2,3)</sup>. On the basis of this compound, it was expected to enhance intermolecular overlap of electron orbital and compatibility to binder polymers without special substituents owing to naphthalene skeleton as well. The advanced intermolecular overlap of electron orbitals was expected by spreading  $\pi$ -conjugate system in two directions (Figure 2). One is lateral against the axis connecting two quinone groups with replacing phenyl ring of diphenylquinone with naphthalene ring; (Figure 2-i, compound **1**), the other is longitudinal with introducing terphenyl skeleton; (Figure 2-ii, compound **2,3**). It was also expected to be more compatible to binder polymers without special substituents because of the intramolecular distortion caused by introducing naphthyl group or asymmetric skeleton. We have already reported about the syntheses and properties of compound **1**<sup>4,5)</sup> and **2**<sup>6)</sup>. In this paper, the synthesis and properties of compound **3** are

described, and we try to clarify the relation between electron mobility and molecular structure.

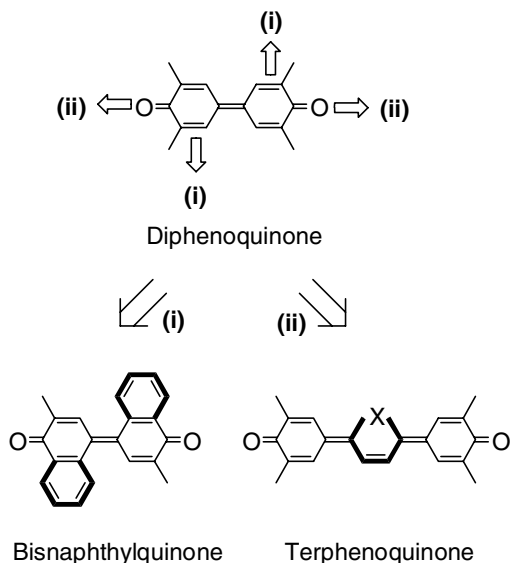


Figure 2. Molecular design in this study

## Experimental

### Synthesis of Quinone Compounds

Bisnaphthylquinone derivatives **1** were synthesized by simple oxidative coupling reaction of 2-alkyl-1-naphthol<sup>47</sup>. Terphenoquinone **2** were synthesized by Grignard reaction between furan or thiophene and phenol derivatives and following oxidation<sup>7,8)</sup>.

Compound **3** was synthesized by three-steps reaction using 1,4-dibromonaphthalene as a starting material<sup>9)</sup>. Grignard reagent prepared from 1,4-dibromonaphthalene (3.9 g, 13.6 mmol) and magnesium (4 eq.) was vigorously stirred with 2,6-di-*t*-butyl-1,4-benzoquinone (1 eq.) in THF at reflux temperature. And obtained hydroxide was oxidized in chloroform solution by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; 0.5g, 3 mmol). The resulting solution was evaporated and purified by column chromatography on silica gel with chloroform as eluent. Compound **3** was obtained as dark greenish purple powder by recrystallization from hexane. The total yield was 11%.

### Compatibility to a Binder Resin

Compatibility of quinone compounds was evaluated with observation of the microcrystals on the molecularly dispersed film. The film was prepared as follows: the dichloromethane solution of quinone compound and binder resin (20-80/100, weight ratio) was cast onto aluminum substrate followed by drying at 60°C for 30 min. Z-type polycarbonate (TS-2020, Teijin Chemicals Ltd., Japan) was used as a binder resin.

### Evaluation of Redox Potentials

Redox potential (vs. Ag/Ag<sup>+</sup>, silver nitrate) as an evaluation of the electron acceptance was measured with cyclic voltammetry (Polarographic Analyzer P-100: Yanaco, Japan) by using a dichloromethane solution incorporated with tetra-butyl-ammonium perchlorate at a sweep rate of 100 mV/s.

### Electron Drift Mobility Measurements

The electron drift mobility measurements were made by conventional time-of-flight (TOF) technique. The film (about 5 μm thick) for this measurement was prepared by dissolving mixtures of the appropriate quinone compound and binder resin in dichloromethane. And then bar-drawing the resulting solutions onto aluminum substrate followed by drying at 60°C for 30 min., and semi-transparent gold electrode was then vacuum-deposited onto the layer. Photoexcitation was carried out by 3-ns exposure of 337-nm radiation derived from N<sub>2</sub> laser. The mobility μ was calculated from the conventional expression  $\mu = L^2/\tau V$ , where L is the film thickness, τ transit time and V the applied voltage.

### Xerographic Properties of Single-Layer OPC

Single-layer OPC was prepared by a bar-drawing method. X-form metal free phthalocyanine (Fastgen Blue, Dainippon Ink & Chem. Inc., Jpn.) as a charge generation material (4 weight part ratio), *N,N'*-diphenyl-*N,N'*-di-*m*-tolyl-(1,1'-biphenyl)-4,4'-diamine as a hole transporting material (80), Z-type polycarbonate (100), and **DQ** or **1b** as ETM (35) were dispersed together by an ultrasonic welder in THF. The solution cast onto an aluminum substrate, almost 20 μm thick. These steps were followed by drying at 100°C for 30 minutes.

Evaluation of xerographic properties for positive charging was performed by the electrostatic paper analyzer (EPA-8100, Kawaguchi Electric Works). Photosensitivity was evaluated with half decay exposure ( $E_{1/2}$ ) and residual surface potential ( $V_r$ ) in completing the illumination. An initial surface potential ( $V_0$ ) was set up to +800 V. Monochromatic light (780 nm) through a band pass filter was used as incident light source and the light power was 10 μWcm<sup>-2</sup> and the incident time was 1 second.

## Results and Discussion

### Properties of Quinone Compounds

The characteristics of quinone compounds **1-3** are summarized in Table 1. From this table, compound **1** and **3** introducing naphthyl group or asymmetric skeleton were found to enhance the superior polymer compatibility comparable to **DQ** having unsymmetrical substituents. Compound **2** was similar compatibility. Compounds **1-3** exhibited a red shift of the UV absorption against **DQ** due to the extension of the π-conjugation.

Reduction potentials (1st) of quinone compounds measured by cyclic voltammetry were ranged between -0.70 and -0.93 V (vs. Ag/Ag<sup>+</sup>). This results indicate that quinone

compounds have enough electron affinity on the basis of the requirement so as to have a stronger electron affinity than O<sub>2</sub> (reduction potential = -1.1 V)<sup>2)</sup> for ETMs of organic photoreceptor.

**Table 1. Characteristics of quinone compounds**

| Compd.    | mp / °C   | Compatibility | $\lambda_{\max}^a$ / nm | $E_{\text{red}}^b$ (1st) / V (vs. Ag/Ag <sup>+</sup> ) |
|-----------|-----------|---------------|-------------------------|--|
| <b>1a</b> | 255 - 258 | <80wt%        | 486                     | -0.86  |
| <b>1b</b> | 199 - 201 | <80wt%        | 489                     | -0.90  |
| <b>2a</b> | 259 - 260 | <60wt%        | 563                     | -0.93  |
| <b>2b</b> | 272 - 274 | <60wt%        | 567                     | -0.88  |
| <b>3</b>  | 181 - 183 | <80wt%        | 579                     | -0.70  |
| <b>DQ</b> | 180 - 181 | <60wt%        | 422                     | -0.93  |

<sup>a,b</sup> In CH<sub>2</sub>Cl<sub>2</sub> solution

### Electron Drift Mobility of Quinone Compounds

From the measurements of transient photocurrent, charge transport of quinone compounds **1-3** was found to be fairly dispersive. Their electron mobilities for 40 wt% loaded quinone compounds in PC-Z at an electric field of  $5 \times 10^5$  Vcm<sup>-1</sup> at 294 K and the intermolecular distances (R) are summarized in Table 2. The intermolecular distance was calculated from the formula  $R = (M/N_A dC)^{1/3}$  where M is the molecular weight, N<sub>A</sub> the Avogadro's number, d the density (1.2 g/cm<sup>3</sup>) and C the weight percent of dopant. The electron drift mobility of compounds **1b** and **3** was obtained in the order of 10<sup>-6</sup> cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> even at 40wt% loading, similarly to **DQ**.

**Table 2. Electron mobilities and intermolecular distances of quinone compounds**

| Compd.    | $\mu^a$ / cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> | R / Å |
|-----------|---|-------|
| <b>1a</b> | $2.7 \times 10^{-7}$                                      | 11.1  |
| <b>1b</b> | $1.0 \times 10^{-6}$                                      | 11.4  |
| <b>2a</b> | $1.3 \times 10^{-7}$                                      | 11.8  |
| <b>2b</b> | $2.9 \times 10^{-7}$                                      | 11.9  |
| <b>3</b>  | $1.0 \times 10^{-6}$                                      | 12.3  |
| <b>DQ</b> | $1.6 \times 10^{-6}$                                      | 10.1  |

<sup>a</sup> Measured at  $E = 5 \times 10^5$  Vcm<sup>-1</sup> at 294K, 40wt% doped PC-Z

As shown in figure 3, however, if compared at the same intermolecular distance, these compounds **1b** and **3** give the larger electron mobility than that of **DQ**. This result seems to be due to the introduction of naphthalene skeleton to extend the  $\pi$ -conjugate plane.

To clarify the factors influencing electron mobility, we analyzed the transport properties of compound **3** based on the small-polaron hopping theory<sup>10,11)</sup>.

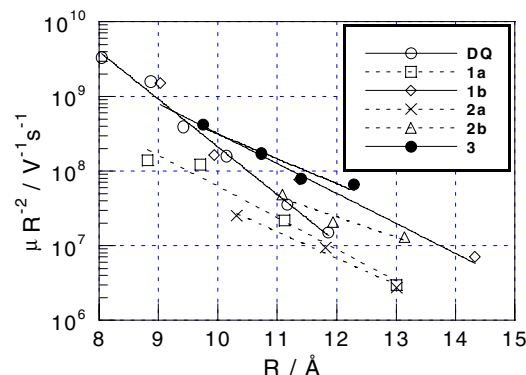


Figure 3. Dependence of electron mobilities as a function of intermolecular distance R

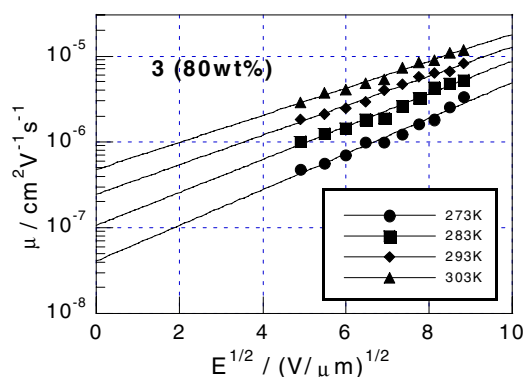


Figure 4. Field dependence of the electron mobilities at different temperatures

### Applicability of Small-Polaron Hopping Theory

The field dependence of mobility at various temperatures is plotted semi logarithmically in Figure 4. A linear relation fitted by a Gill's equation is observed between  $\ln \mu$  and  $E^{1/2}$ . The similar linear fits were obtained at each dopant concentration.

The zero-field mobility values  $\mu(E=0)$  were determined by extrapolation of the data shown in Figure 4. The zero-field mobility obeys Arrhenius law;  $\mu(E=0) = A \exp(-E_0/kT)$  where A is Arrhenius prefactor and  $E_0$  is activation energy.

$E_0$  was almost constant irrespective of average intermolecular distance R and the Arrhenius prefactor A increases exponentially with a decrease in R. These results are in good agreement with a nonadiabatic behavior predicted by the small-polaron hopping theory:

$$\mu(E=0) = a_0 R^2 \exp(-2R/R_0) \exp(-E_0/kT)$$

where  $a_0$  is constant and  $R_0$  is the charge localization radius.

The values of  $a_0$ ,  $R_0$  and  $E_0$  were summarized in Table 3 with the values for **DQ**<sup>2)</sup> and compound **1**<sup>4,5)</sup>, **2**<sup>6)</sup> where  $E_p$  is the polaron binding energy ( $E_0 = E_p/2$ ).

**Table 3. The polaron parameters obtained for quinone compounds 1-3 doped PC-Z**

| Compd.    | $a_0 / \text{V}^{-1}\text{s}^{-1}$ | $E_p / \text{eV}$ | $R_0 / \text{Å}$ |
|-----------|------------------------------------|-------------------|------------------|
| <b>1a</b> | $1.6 \times 10^{23}$               | 0.87              | 1.1              |
| <b>1b</b> | $7.1 \times 10^{22}$               | 1.08              | 1.3              |
| <b>2a</b> | $1.3 \times 10^{22}$               | 1.12              | 1.4              |
| <b>2b</b> | $7.0 \times 10^{18}$               | 0.72              | 1.7              |
| <b>3</b>  | $5.1 \times 10^{25}$               | 1.26              | 1.4              |
| <b>DQ</b> | $3.0 \times 10^{23}$               | 0.98              | 1.2              |

$E_p$  is related to the structural changes between the neutral state and the corresponding ion state, and the stabilization of a single charged molecule by dipole polarization of the medium surrounding the charged molecule. And  $R_0$  corresponds to the decay length of the electronic wave function of the hopping site.

The value of  $E_p$  of all compounds except **1a** and **2b** seems to increase as the expansion of  $\pi$ -conjugated system and the value of  $R_0$  is almost larger than that of **DQ**.

As a result of molecular orbital calculation about compound **1**, it was observed the distortion at the central double bond<sup>4,5</sup> and can be presumed that **1** does not keep planar conformation even in neutral state. It can be understood, therefore, that **1** showed close  $R_0$  value due to the isolation of both quinone-parts.

Compound **2** was found to keep planar conformation by X-ray analysis<sup>7,8</sup>. So it is considered that intermolecular transporting was favorable, but electron mobility of compound **2** was smaller than **DQ**. We supposed the distribution of electron density has an important effect upon electron mobility when heteroatom was in existence.

As far as compound **3**, it nearly keeps planar conformation. It is considered that the expansion of  $\pi$ -conjugate system could extend the localization of electron and be effective to enhance electron transporting ability as expected.

Unfortunately, we could not observe an adiabatic behavior in these compounds with extended  $\pi$ -conjugate system, to which we expected strong intermolecular interaction like TPD of hole transporting material.

**Table 4. Half decay exposure ( $E_{1/2}$ ) and residual potential ( $V_r$ ) of the single-layer OPC using DQ or 1b for positive charging**

| Compd.    | $E_{1/2} / \mu\text{Jcm}^{-2}$ | $V_r / \text{V}$ |
|-----------|--------------------------------|------------------|
| <b>DQ</b> | 0.92                           | 32               |
| <b>1b</b> | 0.83                           | 26               |

### Xerographic Properties of the Single-Layer OPC

Table 4 shows the photosensitivity, both of  $E_{1/2}$  and  $V_r$ , of the single-layer OPC using **DQ** or **1b** as ETM for positive charging. The photosensitivity of OPC using **1b** was slightly higher than that of **DQ**. It is considered this result was caused by little effect of extended  $\pi$ -conjugation. The photosensitivity of the single-layer OPC using **1b** is enough high to use practically.

### Conclusion

We have developed some novel quinone compound as an electron transporting compound. It showed a suitable electron accepting property and a good compatibility to a binder resin. The electron drift mobility of the order of  $10^{-6} \text{cm}^2\text{V}^{-1}\text{s}^{-1}$  was obtained at 40 wt% loading, which was as high as diphenoquinone. As a result of analysis, it was suggested that the extension of  $\pi$ -conjugate system could be effective to enhance electron transporting ability.

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### Biography

Hideki Okada received the B. Eng. in 1993 and the M. Eng. in 1995 from Osaka University in Applied Chemistry. In 1995 he joined Kyocera Mita Co., Ltd. and now developing photoelectric materials as a Ph.D student under the direction of Prof. Masaaki Yokoyama in Graduate School of Engineering, Osaka University.