

Photoconductivity and Photovoltaic Effect of Charge-Transfer Complex of Poly[4-phenyl-2,6-(*p*-phenoxy)quinoline] and 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone

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SYNOPSIS

A new polymer containing a heterocyclic quinoline unit in the main chain, poly[4-phenyl-2,6-(*p*-phenoxy)quinoline] (PQ), was synthesized by an acid-catalyzed self-condensation reaction. We have found that PQ, which is generally a good insulator itself, can show photoconductivity when doped with an electron acceptor. From the UV-VIS absorption spectra, we found that PQ can form a charge-transfer (CT) complex with an electron acceptor, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). The CT complex of the PQ-DDQ mixture showed distinct photoconductivity. Employing the DDQ composition ranging from 5 to 10 wt %, the ratio of dark and photoconductivity was calculated to be about 1 : 100 at an applied electric field of 10^5 V/cm. Additionally, the bilayer sample of PQ/DDQ exhibited a significant photovoltaic effect. The photovoltaic current increased with increasing photointensity. The open-circuit voltage was measured ranging from 0.4 to 0.7 V and the photovoltaic conversion efficiency was calculated to be 10^{-3} – $10^{-2}\%$. The PQ film treated with DDQ vapor showed a relatively higher photovoltaic effect than that of the sample treated with DDQ solution. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Recently, the application of organic polymers to optoelectrical technology has attracted great attention by virtue of advantages of structure variability, ease of fabrication, possibility of mass production, good mechanical property, and high functionality.¹⁻⁵ A number of polymeric systems have been studied and evaluated with regard to photoconductive and photosensitive properties because of the increasing demand for such materials in electrophotography and related processes.³⁻⁷ Since the photoconductive properties of poly(*N*-vinylcarbazole) (PVK) were first reported in 1957, the interest in photoconductive polymers centered on PVK and other polymeric structures containing a carbazole unit as an active

chromophore.⁸⁻¹¹ We synthesized a new heterocyclic polymer, poly[4-phenyl-2,6-(*p*-phenoxy)quinoline] (PQ),¹² containing a quinoline unit in the main chain by employing the acid-catalyzed self-condensation reaction of 4-amino-4'-acetyl-3-benzoyl-diphenylether. Because of wholly aromatic chemical structure, PQ showed high thermal stability with no weight loss up to 550°C both in air and nitrogen. Contrary to other heterocyclic polymers, PQ has good solubility in common organic solvents such as chloroform and tetrahydrofuran, so that homogeneous film could be easily prepared from the solution by casting or spin-coating methods. In our previous papers,^{12,13} we reported that PQ has a strong tendency to form a charge-transfer (CT) complex with various electron acceptors. We also reported^{12,13} that the CT complex of PQ and 2,4,7-trinitro-9-fluorenone (TNF) showed a photoconductive property and a photovoltaic effect. Based on these papers,^{12,13} we were motivated to prepare a uniformly doped film

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by mixing PQ as an electron donor and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as an electron acceptor. Photoconductivity and the photovoltaic effect of this CT complex system were investigated and compared with those of the CT complex of PQ and TNF.

EXPERIMENTAL

Sample Preparations

Mixture Film (PQ-DDQ)

The synthetic procedure for PQ was well described in our previous reports.^{12,13} Great care must be taken to purify the final polymer, dopant, and solvents used in this study because minute traces of impurities can rapidly deactivate excited molecules. Using the PQ-DDQ solution (concn 0.05–2.0 wt %) in 1,1,2,2-tetrachloroethane (TCE), the film was cast on an indium tin oxide (ITO) glass ($2.5 \times 2.5 \text{ cm}^2$). After complete drying, a semitransparent gold electrode (diameter 1.5 cm) was deposited on the mixture film of PQ-DDQ by vacuum evaporation at 10^{-6} – 10^{-5} Torr. The thickness of mixture films was measured using a Taylor-Hobson Talysurf 10M.

Bilayer Film (PQ/DDQ)

PQ film was cast on an ITO glass using the spin-coating method. After drying the solvent completely, one bilayer sample of PQ/DDQ was prepared using 2-butanone solution of DDQ (concn 2 wt %). The solution was poured onto the surface of the mother film and then spread using the spin-coating system. The other bilayer sample of PQ/DDQ was prepared by the vapor-doping method. DDQ vapor was doped onto the surface of the mother film. Then, an Al electrode (diameter 1.5 cm) was deposited on the completely dried film under vacuum. Each film was cast at constant speed to make the thicknesses identical. The thickness of bilayer films was measured to be the same as that of the mixture films.

UV-VIS Absorption Spectra

Absorption spectra of the solutions as well as the thin films were recorded with a Shimadzu UV-240 double-beam scanning spectrophotometer. Solution samples (concn $5 \times 10^{-3} \text{ M}$) were measured in a standard $1 \times 4 \text{ cm}^2$ quartz cell and thin films were measured on a quartz plate. In the case of the thin-film sample, the PQ film was cast on fused silica and DDQ was doped onto PQ film using DDQ vapor.

Photoconductivity Measurement

The dark and photoconductivity currents of the mixture film of PQ-DDQ were measured using a Keithley 247 dc high-voltage power supply at room temperature. A 400 W Oriel xenon lamp was used as a UV-VIS light source.

Photovoltaic Effect Measurement

A bilayer sample (ITO//PQ/DDQ//Al) was connected to the Keithley 617 electrometer for measuring the photovoltaic effect. UV-VIS light was irradiated onto the opposite side of the ITO electrode and the short-circuit photocurrent always flowed from the ITO to the Al electrode in the external circuit. The applied voltage ranged from 0.0 to 0.8 V and the light source was the same as that used for photoconductivity measurement.

RESULTS AND DISCUSSION

We examined^{12,13} the solution mixtures between PQ and some common electron acceptors, such as iodine, TNF, and DDQ to check the capability for CT complex formation. From the UV-VIS absorption spectra, we found that PQ can form CT complexes with these electron acceptors. Generally, the introduction of an electron-donating and -accepting group into a π -electron conjugated system makes the HOMO energy increase and LUMO energy decrease. The CT complex formation, therefore, causes the energy gap to decrease between HOMO energy and LUMO energy, resulting in a red shift of absorption maxima. The CT band, due to the CT transition of the electron from the HOMO of the donor to the LUMO of the acceptor, is generally considered to provide the potential for photoconductivity. When PQ was doped with DDQ as an electron acceptor, the color immediately changed from the light yellow of PQ and DDQ to dark brown, which indicates the formation of the CT complex. The UV-VIS spectra of PQ, DDQ, and the PQ-DDQ (1 : 1) mixture show this formation in terms of the appearance of a new absorption tail around 400 nm (see Fig. 1). The TCE solution of PQ showed an absorption maximum at around 350 nm, but the shape of the absorption maximum for PQ-DDQ became broader and the wavelength was red-shifted. This implies that PQ interacts with a DDQ to give the CT complex. The photovoltaic action spectra is illustrated in Figure 2. The wavelength of the maximum current peak is consistent with that of the absorption maximum in the UV-VIS spectra.

As expected, the PQ film cast with the electron acceptor formed a CT complex showing good photoconductivity. Figure 3 shows the photoconductivities of the CT complex films at various concentrations of DDQ in the PQ matrix. Comparing the dark and photoconductivity of each sample, we conclude that 5–10 wt % of an electron acceptor is the most effective composition for the CT complex. In addition, characteristics of dark and photocurrent density for PQ doped with DDQ are shown in Figure 4. The photocurrent was 1×10^{-6} A/cm² at 1×10^5 V/cm and the dark current was 1×10^{-9} A/cm² at the same applied electric field. The difference between dark and photocurrent increased with increasing electric field and photointensity at the same electric field.

Figures 5 and 6 show the I-V characteristics for PQ thin film of which the surface was treated both with DDQ solution and with DDQ vapor to form

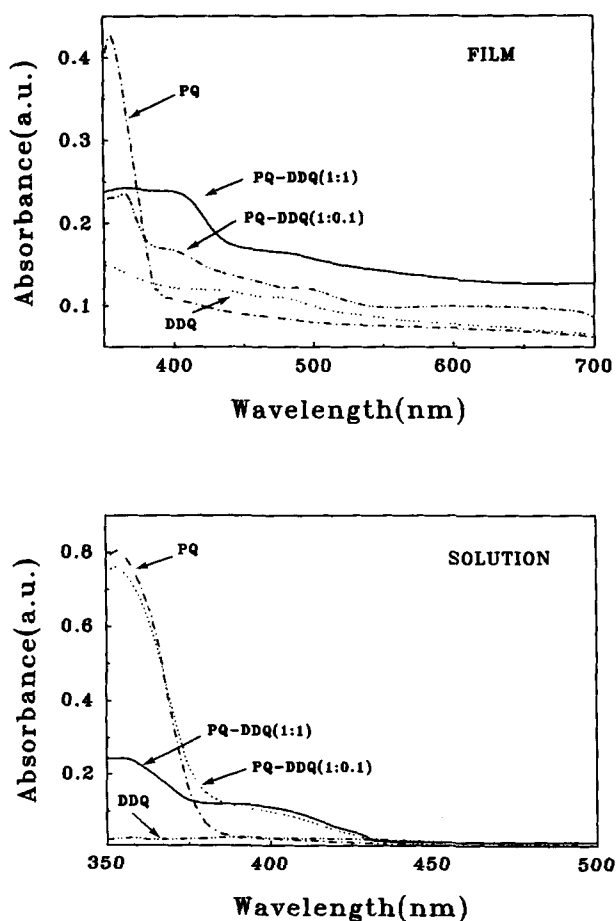


Figure 1 Absorption spectra of PQ, DDQ, and the PQ-DDQ mixture both in the solution and the solid state. Total concn of each solution: 5×10^{-3} M.

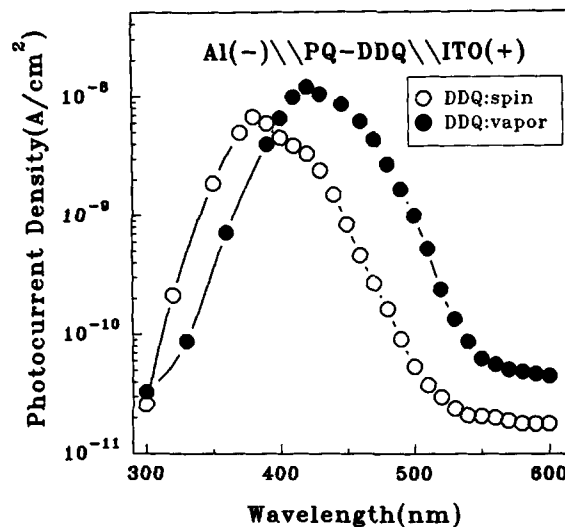


Figure 2 Photocurrent of the bilayer sample of PQ-DDQ with the change of spectral wavelength.

the CT complex at the interface. The photocurrent was measured at 10^2 – 10^3 times larger than the dark current. The photovoltaic current was 0.0–0.7 V in the system, as shown in many other organic polymers of the *p*-type semiconductor when contacted to an Al electrode. Such photovoltaic current may be due to a Schottky potential barrier at the interface between metal electrode and an *n*-type layer of the PQ/DDQ complex and to a difference in the work functions when using the Al and ITO electrode. The

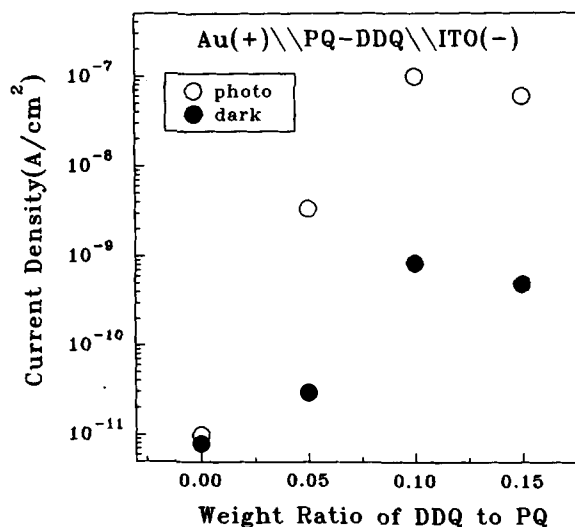


Figure 3 Dark and photocurrent of PQ-DDQ complex with the change of DDQ concentration. Electric field: 3×10^4 V/cm.

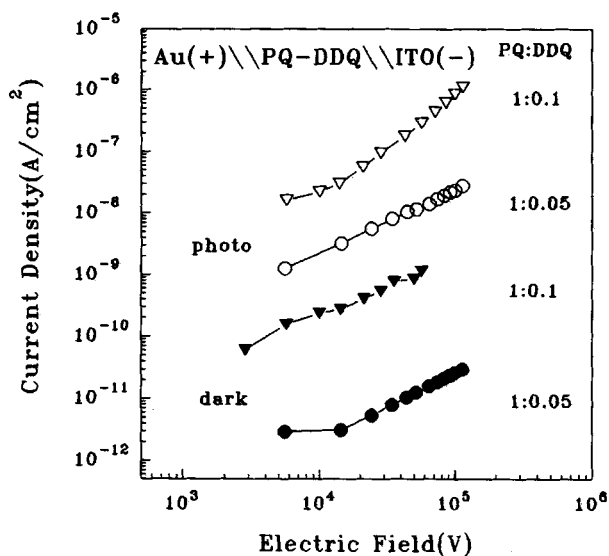


Figure 4 Photo and dark current of PQ-DDQ mixture.

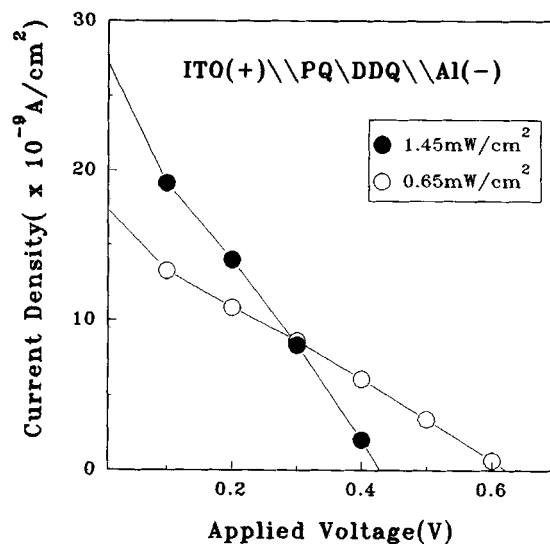


Figure 6 Photovoltaic effect of PQ/DDQ bilayer sample. DDQ: spin-coating method.

photovoltaic current at 0 V (I_{sc} , short-circuit current) increased with the increase of photointensity (Fig. 7). The photovoltaic conversion efficiency, η , can be estimated from the photocurrent density and the applied voltage, as shown in Figures 5 and 6, and the conversion efficiency (η) can be calculated from eq. (1)¹⁴:

$$\eta = 100 I_m V_m / P_i \quad (1)$$

where I_m is the photovoltaic current density; V_m ,

the photovoltage at maximum power output; and P_i , the incident power density.

The photovoltaic conversion efficiencies, η , were calculated to be 10^{-3} - $10^{-2}\%$. The PQ film that was treated with a DDQ vapor showed a relatively higher photovoltaic effect than did the sample treated with DDQ solution. From the photovoltaic effect of these heterogeneous bilayer samples it was found that conversion efficiency decreases with the increase of the photointensity and film thickness (see Fig. 8).

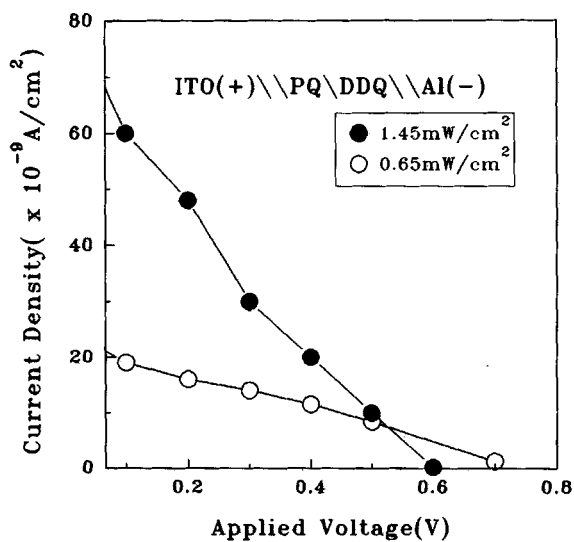


Figure 5 Photovoltaic effect of the bilayer sample of PQ/DDQ. DDQ: vapor-doping method.

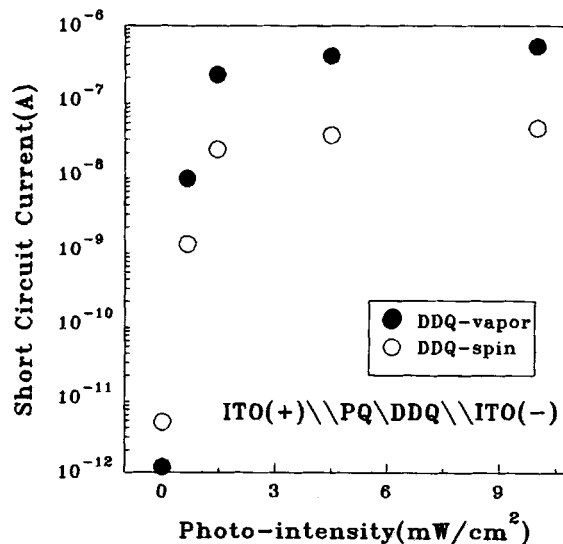


Figure 7 Relation between short-circuit photocurrent and photointensity. Film thickness: 0.8 μ m.

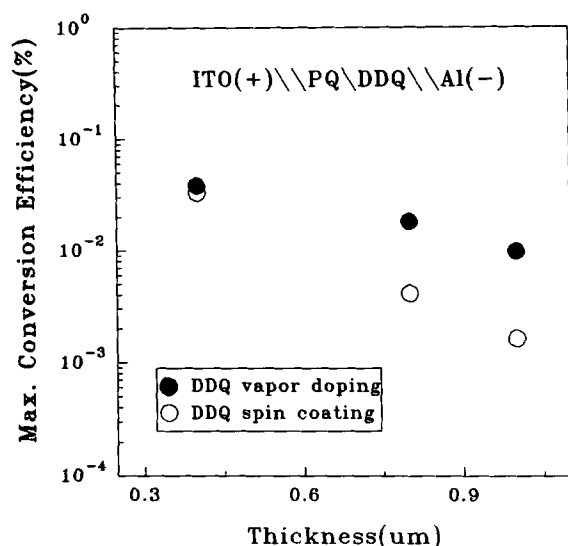


Figure 8 Dependence photovoltaic conversion efficiency on the film thickness of bilayer film of PQ/DDQ (1 : 0.1).

CONCLUSIONS

The mixture of PQ and DDQ was found to be a good CT complex as well as exhibiting distinct photoconductivity. Comparing the dark and photoconductivity of each sample, we conclude that 5–10 wt % of an electron acceptor in the polymer matrix is the most effective composition. The photocurrent was 1×10^{-6} A/cm² at 1×10^5 V/cm and the dark current was 1×10^{-9} A/cm² at the same electric field. The difference increased with increase of the electric field and photointensity. From the result of the dark and photoconductivity measurements, we conclude that the CT complex of PQ and DDQ also has strong potential for industrial use.

In addition, the bilayer sample of PQ and DDQ exhibited a comparable photovoltaic effect. The photovoltaic current at 0 V (I_{sc} , short-circuit current) increased with the increase of photointensity. The PQ film that was treated with a DDQ vapor showed a relatively higher photovoltaic effect than did the sample treated with DDQ solution. Because of the photovoltaic effect of these heterogeneous

samples, conversion efficiency decreased with the increase of the photointensity and the film thickness. The photovoltaic conversion efficiencies of bilayer samples, η , were calculated to be 10^{-3} – $10^{-2}\%$. The PQ film that was treated with a DDQ vapor showed a relatively higher photovoltaic effect than did the sample treated with DDQ solution. As the photointensity increased, the open-circuit voltage (V_{oc}) decreased and the short-circuit current (I_{sc}) increased.

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