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Photoelectric Effect of Metallophthalocyanine Derivatives

Ryo Hirohashi,* Toyohide Tanaka, Yoshihiro Koshijima, and Masafumi Kamiyama
Department of Image Science and Engineering, Faculty of Engineering, Chiba University,
Yayoi-cho 1-33, Chiba-shi 260
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Synopsis. The photoelectric effect of copper phthalocyanine derivatives ($CuPcR_4$) in a dispersed system in polycarbonate (PC) has been investigated with a sandwich-typed cell configuration of Au/$CuPcR_4$ in PC/Ag. When the incident irradiation was directed through the Ag electrode, the photocurrent and photovoltage were observed for all $CuPcR_4$ cells. It has been concluded that the photoelectric characteristics are not missed and that the values of the work functions of all $CuPcR_4$ derivatives are between 4.67 and 4.78 eV.

Metallophthalocyanines (MPc) have been shown to be characteristic of the photoconductivity between visible and infrared irradiation. These materials are used in the field of imaging technology as organic photoconductors[1] or as organic solar cells.[2] The thin films of MPc are prepared by vacuum evaporation,[3] ion sputtering,[4] and a dispersed system in a polymer.[5] We have investigated the photoelectric effect of copper phthalocyanine derivatives ($CuPcR_4$) in a dispersed system in polycarbonate. These $CuPcR_4$ were synthesized by sulfonylation of CuPc or by the Wyler method[6] of trimellitic anhydride with urea.

Experimental

Materials (Specimen). The $CuPcR_4$ derivatives used in the present experiments were synthesized by the methods shown in Fig. 1. The structures of $CuPcR_4$ derivatives are shown in Fig. 2. Though the positions of the substituents in $CuPc(CONH_2)_4$ and $CuPc(COCl)_4$ could be determined in the synthetic processes, the positions of $CuPc(SO_2Cl)_4$ obtained by a substitution reaction of CuPc could not confirmed. Purification of these $CuPcR_4$ derivatives by sublimation at about 600 °C was not successful.

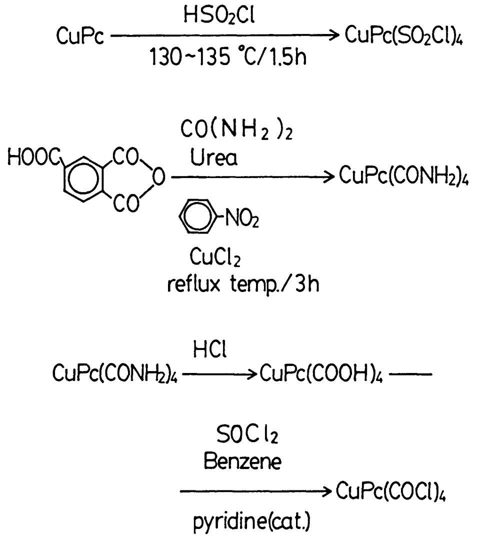

Fig. 1. The synthetic process of CuPc derivatives.

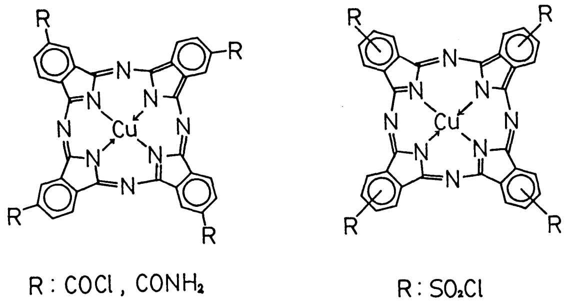

Fig. 2. The molecular structure of CuPc derivatives. The positions of the substituents in $CuPc(COCl)_4$ and $CuPc(CONH_2)_4$ are determined, but $CuPc(SO_2Cl)_4$ is not confirmed.

IR and UV Spectera. The IR spectra from 700 to 800 cm^{-1} of the $CuPcR_4$ derivatives show characteristic absorption at 740 and 790 cm^{-1}; these $CuPcR_4$ derivatives were expected to have a β-type crystalline structure.[7] The IR absorption spectra did not change upon dipping in THF (tetrahydrofuran) for about 24 hours. Since there is no good solvent for these $CuPcR_4$ derivatives, each $CuPcR_4$ derivative was dipped in hot 1-chloronaphthalene for 48 hours. The UV and visible spectral peaks, thus obtained, are shown in Table 1.

Cell Structure. A sandwich-typed cell configuration of Au/$CuPcR_4$ in PC/Ag was used in the experiment; R and PC are substituents and polycarbonate, respectively. The semi-transparent electrode of Au and Ag were coated on the sample by an ion-sputtering method. PC was used as a binder: the $CuPcR_4$ derivatives were blended with PC (weight ratio of 1 to 2) by dispersing for 48 hours with ball-milling by the addition of THF; the resulting product formed into a film by a spin-coating method. The connection between the electrode and lead wire (Ag) was made by the use of an Ag paste (Du Pont).

Measurements. Measurements of the dark current and photocurrent were carried out in a cryostat in vacuum (ca. 10^{-5} Torr; 1 Torr≈133.322 Pa) through the Au or Ag electrode. The apparatus used for the current measurement and spectroscopy were a vibrating reed electrometer (Advantest TR-84M) and a monochromator (Nikon G-250), respectively. Work functions were measured using a low-energy UPS system (Riken Keiki AC-1).

Table 1. Wavelength of Absorption Peaks

	Solution/nm		Dispersed in PC/nm	
CuPc	608	688	650	734
$CuPc(COCl)_4$	628	694	600	710
$CuPc(SO_2Cl)_4$	644	717	605	720
$CuPc(CONH_2)_4$	642	710	632	705

Wavelength of absorption peaks observed on the solution of CuPc derivatives in 1-chloronaphthalene and on the dispersed system in polycarbonate.

Results and Discussion

Dark Current. The applied field dependence of dark current for Au/CuPc(SO_2Cl)$_4$ in PC/Ag cell structure is shown in Fig. 3. The observed nonlinearity indicates the presence of a barrier in this device. The highest dark conductivity is obtained in CuPc(COCl)$_4$, followed by CuPc(SO_2Cl)$_4$. The least conductive derivative on the dark state is CuPc-($CONH_2$)$_4$. We can note that the dark current is affected by the structure of each molecule.

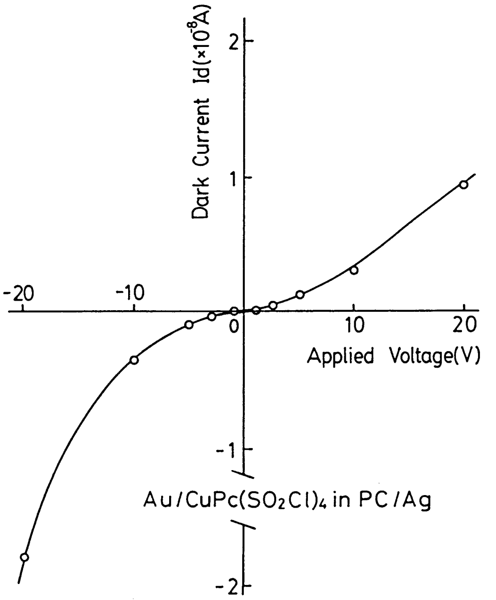

Fig. 3. Applied voltage dependence of dark current for Au/CuPc(SO_2Cl)$_4$ dispersed in PC/Ag cell structure. Applied voltage is measured on the basis of Ag electrode. Thickness of the cell is approximately 10 μm.

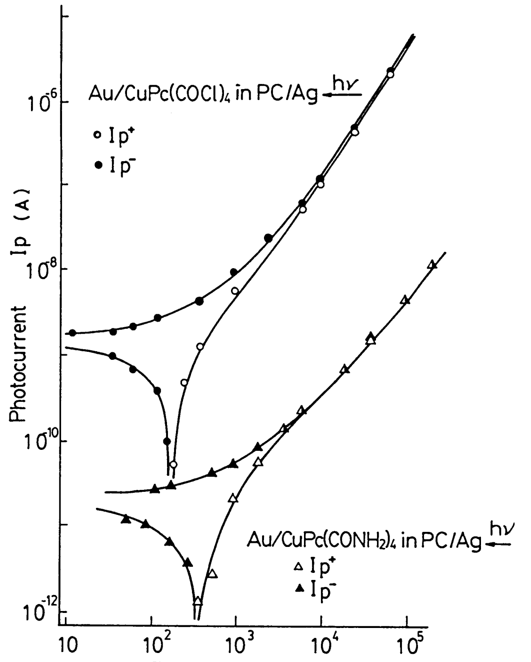

Fig. 4. Applied field dependence of photocurrent for Au/CuPcR$_4$ dispersed in PC/Ag type cells. R is substituent. The signs of I_p^+ and I_p^- represent the polarities of irradiated electrode. The magnitude of photocurrent is the absolute value.

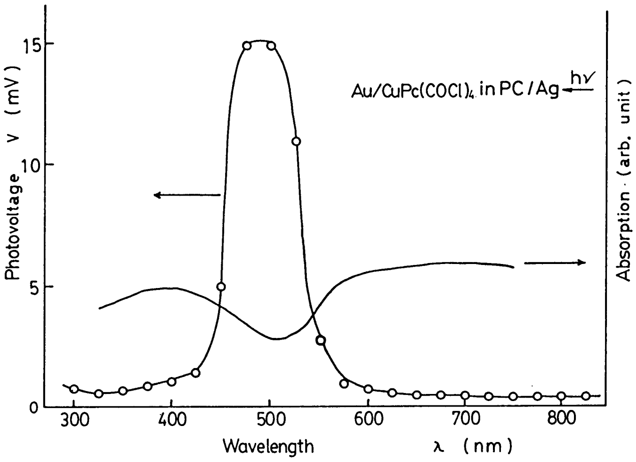

Fig. 5. Action spectrum of photovoltage for Au/CuPc(COCl)$_4$ dispersed in PC/Ag cell, and absorption spectrum of dispersed system (CuPc(COCl)$_4$ in PC. The thickness of the cell is approximately 10 μm. Irradiated electrode is Ag plane.

Photocurrent. The applied field dependences of the photocurrent are shown in Fig. 4. In this figure, the polarity signs of the current were determined by the polarity of the Ag electrode potential. The current and electric field are indicated in absolute value.[8] The photoelectric sensitivity is determined by the ratio of the photocurrent to the dark current (I_p/I_d); these ratios for CuPc($CONH_2$)$_4$, CuPc(SO_2Cl)$_4$ and CuPc-(COCl)$_4$ at about 10^3 V cm^{-1} were approximately 14.5, 7.4, and 4.8, respectively. These values may be rather higher than for dispersed systems. The current tends to greatly decrease around 10^2 V cm^{-1} (Fig. 4), indicating that it comes to equilibrium between the applied voltage and photovoltage.

Photovoltage. The photovoltages of CuPc($CONH_2$)$_4$, CuPc(SO_2Cl)$_4$, and CuPc(COCl)$_4$ generated by direct irradiation through the Ag electrode with a Xenon lamp, and then followed photocurrent measured by potentiometry, were approximately 200, 110, and 140 mV, respectively. When the Ag electrode is irradiated, the positive polarity of the photovoltage was obtained in all cases. The action spectrum of the photovoltage for Au/CuPc(COCl)$_4$ in PC/Ag cell is shown in Fig. 5. Due to the internal resistance of the voltmeter, the measured photovoltages are smaller than the true values, though the relative forms are not affected. In Fig. 5, the photovoltage peak is obtained in the wavelength region where absorption is the weakest. On the other hand, when the incident irradiation was directed through the Au electrode, a photovoltage was not generated. These result show that the photovoltage is generated not at the Au interface but, rather, only at the Ag interface. Consequently, a Schottky barrier could be formed between the CuPcR$_4$ and Ag interface. The work functions of Au and Ag are 4.78 and 4.67 eV, and these interfaces form ohmic and Schottky barrier, respectively. Therefore, the values of the work function of the $CuPcR_4$ derivatives are between 4.67 and 4.78 eV.

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