

# Synthesis and Photoconductivity Study of Phthalocyanine Polymers. I. PAA-CuPc(NO<sub>2</sub>)<sub>2</sub>

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## SYNOPSIS

Cu-dinitro-diamino phthalocyanine was synthesized and converted to the diazonium salt. Polyacrylamide bonded CuPc(NO<sub>2</sub>)<sub>2</sub> [PAA-CuPc(NO<sub>2</sub>)<sub>2</sub>] (I) was synthesized by hot polymerization of acrylamide and this diazonium salt. Polymer (I) is water soluble and contains about 7 mol % CuPc(NO<sub>2</sub>)<sub>2</sub> rings, which are covalently bonded to PAA. Polymer (I) shows good photoconductivity, which is much better than that of the corresponding phthalocyanine monomers. By doping with iodine (I<sub>2</sub>), the photosensitivity of polymer (I) is increased, which through fluorescence analysis is explained by the fact that a charge-transfer complex (CTC) of polymer (I) with I<sub>2</sub> is formed. The influence of interface layer (IFL) and charge-transportation material (CTM) on the photoconductivity of polymer (I) were also studied.

## INTRODUCTION

Phthalocyanine compounds are typical organic photoconductive materials because of their broad infrared and visible region response.<sup>1</sup> However, their insolubility and difficulty in film-forming prevent further detailed study. Therefore, synthesis of soluble phthalocyanine polymers and study of their photoconductivity bear great theoretical importance and applied value.

So far, several articles have reported on the synthesis of phthalocyanine polymers, however, there are few studies on their photoconductivity. There are four types of phthalocyanine polymers:

1. Polymers involving the bridging of phthalocyanine units by exocyclic groups attached to the benzene rings,
2. A single benzene ring is fused into two phthalocyanine cycles,
3. The central metal ions are bridged by oxygen atoms to form the polymeric linkages, and

4. The phthalocyanine unit is covalently bonded or grafted onto the polymer chain.

In this article, we describe bonding phthalocyanine on polymer chains in order to obtain soluble polymers and study their photoconductivity.

## EXPERIMENTAL

### Materials and Equipment

CuCl, urea, phthalic anhydride (PA), triphenylamine (TPA), acrylamide, and the other reagents were commercially available and of analytical grade. Polyvinylcarbazole (PVK) and N,N,N',N'-tetraphenyl-benzidine (TPD) were synthesized in our laboratory.<sup>2,3</sup>

IR spectra were recorded on a NIC-5DX Fourier Transform Infrared Spectrometer. UV/VIS spectra were taken on a DU-50 spectrophotometer. Elemental analyses were determined on a Perkin-Elmer 240C Elemental Analyzer. Photoconductive properties were performed on a GDT-I model photoconductivity measuring device. Fluorescence spectra were recorded on an RF-850 Fluorescence Spectrophotometer.

Synthesis of 3-Nitrophthalic acid is described in Ref. 4.

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### Synthesis and Reduction of Tetranitro Copper Phthalocyanine<sup>1</sup>

Tetranitro copper phthalocyanine [CuPc(NO<sub>2</sub>)<sub>4</sub>] was prepared from 3-nitrophthalic acid, urea, CuCl, and a catalyst by melting method.<sup>1,7</sup>

Anal. Calcd. for CuPc(NO<sub>2</sub>)<sub>4</sub> (C<sub>32</sub>H<sub>12</sub>N<sub>12</sub>O<sub>8</sub>Cu, 755.5): C, 50.83%; N, 22.24%; H, 1.59%. Found: C, 50.77%; N, 22.53%; H, 1.92%.

The infrared spectrum (KBr) of CuPc(NO<sub>2</sub>)<sub>4</sub> shows absorption bands at 1540 cm<sup>-1</sup> and 1340 cm<sup>-1</sup> (characterized absorption of ArNO<sub>2</sub>).

In our reduction of CuPc(NO<sub>2</sub>)<sub>4</sub>, two nitro (—NO<sub>2</sub>) groups were reduced to amino groups.

Anal. Calcd. for dinitro-diamine CuPc(C<sub>32</sub>H<sub>16</sub>N<sub>12</sub>O<sub>4</sub>Cu, 695.5): C, 55.21%; N, 24.16%; H, 2.30%. Found: C, 55.15%; N, 24.11%; H, 2.70%.

The infrared spectrum (KBr) of dinitro-diamine CuPc shows absorption bands at 1610 cm<sup>-1</sup> (amine —NH<sub>2</sub> stretching) and 1340 cm<sup>-1</sup>, 1530 cm<sup>-1</sup> (characteric absorption of ArNO<sub>2</sub>).

### Synthesis of Water Soluble Polyacrylamide Bonded CuPc(NO<sub>2</sub>)<sub>2</sub><sup>5</sup>

Polyacrylamide bonded CuPc(NO<sub>2</sub>)<sub>2</sub> [PAA-CuPc(NO<sub>2</sub>)<sub>2</sub>] (I) was synthesized by hot polymerization of acrylamide and the diazonium salt of dinitro-diamine CuPc. The infrared spectrum (KBr) of polymer (I) shows absorption bands at 750, 900, 1040, 1090, and 1120 cm<sup>-1</sup> (typical absorption of phthalocyanine polymer<sup>6</sup>).

UV/VIS spectrum (water): 624.0 nm (Abs. 1.034)

331.0 nm (Abs. 0.983)

213.0 nm (Abs. 1.910)

From experimental values for polymer (I): C, 49.11%; N, 13.83%; H, 4.05%, we can calculate the mol content of CuPc(NO<sub>2</sub>)<sub>2</sub>:

7.0%, calculated from the analysis of carbon,

7.8%, calculated from the analysis of nitrogen.

### Preparation of Double Layered Photoreceptor Device and Measurement of Its Photoconductivity<sup>7</sup>

The double layered photoreceptor device (P/R) was made by coating an interface layer (IFL) of polymethyl-methacrylate (PMMA), a charge generation layer (CGL) of polyacrylamide bonded CuPc(NO<sub>2</sub>)<sub>2</sub> (I), and a charge transportation layer (CTL) of

TPD-PVK, TPA-PVK, or TPD-TPA-PVK on an aluminium plate, in order.

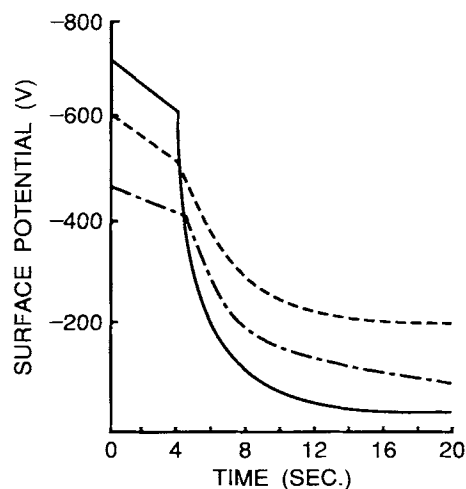
A GDT-I model photoconductivity measuring device was used with a 5W, 24V visible lamp as light source to plot the photoinduced discharge curve (PIDC) of the P/R. In this measurement, the surface of the P/R was negatively charged, and hole charge carriers were generated in CGL and injected into CTL under exposure. From PIDC, we obtained ( $\Delta V_1\%$ ), which is the percentage of potential discharge after 1 sec of exposure, and  $t_{1/2}$ , which is the time from original potential to half under exposure. The  $t_{1/2}^{-1}$  can indicate photosensitivity. The bigger the  $t_{1/2}^{-1}$ , the higher the photosensitivity.

## RESULTS AND DISCUSSION

### Photoconductivity of Polyacrylamide Bonded CuPc(NO<sub>2</sub>)<sub>2</sub> (I)

Polyacrylamide bonded CuPc(NO<sub>2</sub>)<sub>2</sub> (I) is soluble in water and dimethyl sulfoxide (DMSO), and slightly soluble in tetrahydrofuran (THF), alcohol, and acetone organic solvents. We made double layered photoreceptor devices (P/R) using the solution coating method. The film forming was good, and the film was thin and uniform.

From Figure 1 and Table I, we find that polymer (I) has good charge acceptance ( $V_o$ ) as high as 706 V and low residual potential ( $V_R$ ) of 42 V. The surface potential decreases suddenly at the beginning of exposure. The rate of dark discharge ( $R_d$ ) is as



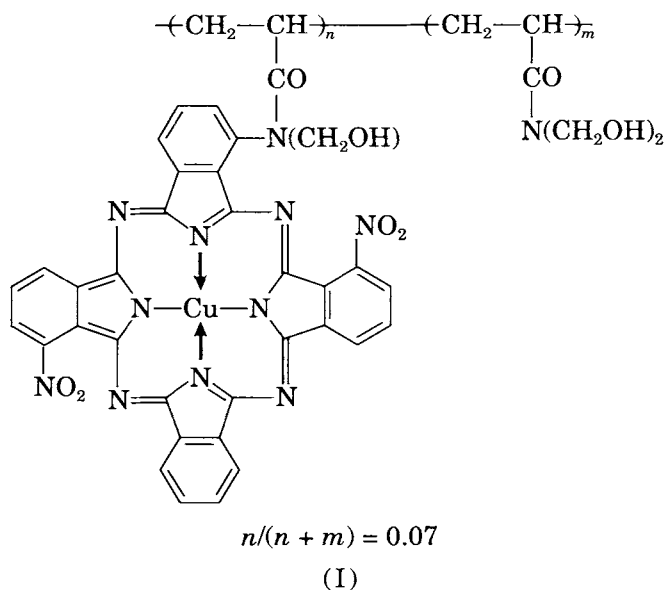
**Figure 1** Photoinduced discharge curve of photoreceptor from polymer (I) (—), CuPc(NO<sub>2</sub>)<sub>4</sub> (---), and CuPc (-----).

**Table I** Photoconductivity of Polymer(I), CuPc(NO<sub>2</sub>)<sub>4</sub>, and CuPc

CGM	V <sub>o</sub> (V)	V <sub>R</sub> (V)	R <sub>d</sub> (V/sec)	R <sub>p</sub> (V/sec)	ΔV <sub>1</sub> %	t <sub>1/2</sub> (sec)	t <sub>1/2</sub> <sup>-1</sup> (1/sec)
Polymer(I)	706	42	9	397	53.4	0.92	1.09
CuPc(NO <sub>2</sub> ) <sub>4</sub>	463	102	14	108	24.2	4.25	0.24
CuPc	598	200	18	142	26.4	4.84	0.21

small as 9 V/sec, while the rate of photo discharge ( $R_p$ ) is as large as 397 V/sec. The time of half discharge  $t_{1/2}$  is 0.92 sec, the percentage of potential discharge after 1 sec exposure ( $\Delta V_1\%$ ) is 53.4%, showing good photoconductivity. Comparing with those of CuPc(NO<sub>2</sub>)<sub>4</sub> and CuPc monomers, we find that, under the same condition, polymer (I) has a bigger value of  $V_R$  and smaller  $R_d$ , which shows that polymer (I) has much better photoconductivity than CuPc(NO<sub>2</sub>)<sub>4</sub> and CuPc monomers.

From the structure of polymer (I), we can see that there are strong electron-acceptor ( $-\text{NO}_2$ ), and also electron-donor ( $-\text{N}:$ ) groups on the same polymer chain. The interaction of the electron-acceptor  $-\text{NO}_2$  and electron-donor  $:\text{N}-$  may help the charge carriers move, hence enhancing photoconductivity.



### Photoconductivity of Polymer(I) Doped with Iodine (I<sub>2</sub>)

The dopant I<sub>2</sub> was added to polymer (I), and the P/R were prepared by the same procedure mentioned above. Their photoconductivities were measured and are listed in Table II.

As shown in Table II, after adding I<sub>2</sub>, almost all of  $\Delta V_1\%$  values are increased, while  $t_{1/2}$  values decreased, that is, the photosensitivity of polymer (I) could be increased by adding I<sub>2</sub> in the range of 0–75% by weight. For CTM (Charge-Transportation Material) of TPD:PVK:PMMA = 5:2.5:1, the photoconductivity reaches a maximum at 15 wt % I<sub>2</sub>;

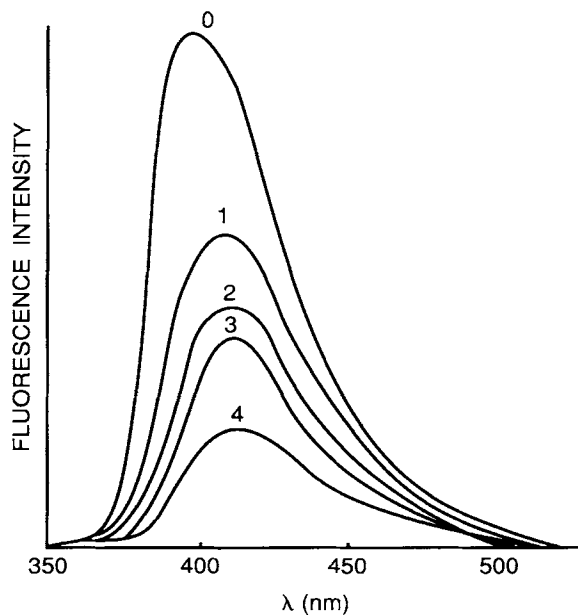
for CTM of TPD:PVK:PMMA = 5:1:1, when I<sub>2</sub> content is 65 wt %, photoconductivity is best.

Keeping the concentration of THF solution of polymer (I) unchanged while increasing the concentration of I<sub>2</sub> ([I<sub>2</sub>]) continually, we observe that the fluorescence intensity of polymer (I) decreases continually, but no exciplex fluorescence band appears at a longer wavelength (Fig. 2). A linear correlation between  $F_0/F$  and [I<sub>2</sub>] is obtained, where  $F_0$  and  $F$  are fluorescence intensities of polymer (I) when [I<sub>2</sub>] is equal to zero and a certain value  $c$ ,

**Table II** Photoconductivity of Polymer(I) Doped with I<sub>2</sub>

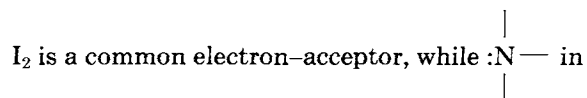
CTM	I <sub>2</sub> Content(wt %)	R <sub>d</sub> (V/sec)	R <sub>p</sub> (V/sec)	ΔV <sub>1</sub> %	t <sub>1/2</sub> (sec)	t <sub>1/2</sub> <sup>-1</sup> (1/sec)
TPD:PVK:PMMA = 5:2.5:1 (wt)	0	9	397	53.4	0.92	1.09
	15	12	721	68.3	0.53	1.89
	25	11	602	66.5	0.61	1.64
	40	12	371	60.4	0.69	1.45
	55	11	375	59.6	0.69	1.45
	65	9	397	55.0	0.84	1.19
	75	14	341	55.8	0.84	1.19
TPD:PVK:PMMA = 5:1:1 (wt)	0	13	487	52.9	0.92	1.09
	15	12	435	52.7	0.92	1.09
	25	11	457	58.2	0.84	1.19
	40	10	509	63.0	0.76	1.32
	55	15	449	65.3	0.69	1.45
	65	13	524	69.7	0.48	2.08
	75	18	449	63.3	0.69	1.45

respectively, as shown in Figure 3. The linear  $F_0/F$  vs.  $[I_2]$  plots may be attributed to the following three mechanisms: (a) forming charge transfer complex (CTC) at ground state; (b) forming exciplex; (c) quenching by physical collision. From Figure 2, we find no exciplex fluorescence band, so the second mechanism should be excluded. The third mechanism belongs to the diffusion control process, which may be neglected. Therefore, the first mech-

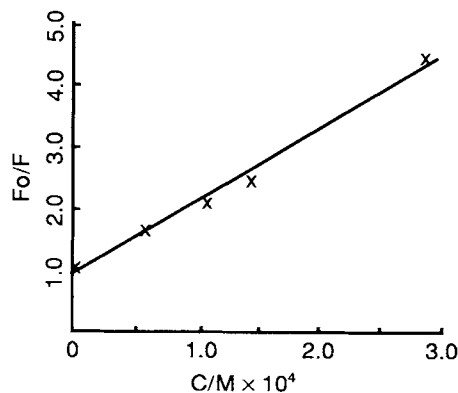


**Figure 2** Fluorescence spectra of polymer (I) with different  $[I_2]$ .  $\lambda_{ex} = 347.5$  nm. 0,  $[I_2] = 0$ ; 1,  $0.586 \times 10^{-4}$  M; 2,  $1.172 \times 10^{-4}$  M; 3,  $1.465 \times 10^{-4}$  M; 4,  $2.931 \times 10^{-4}$  M.

anism is probable, where CTC is formed in the ground state.



polymer (I) is an electron-donor. Here we may say polymer (I) is an electron-donor molecule. The exciting light wavelength  $\lambda_{ex} = 347.5$  nm is selected so that the electron-donor molecule [polymer (I)] is excited. The excited energy absorbed by polymer (I) may be transferred to the acceptor molecule I<sub>2</sub> by radiationless promotion, which results in decreasing the electrons from the triplex state to the ground state and reducing the fluorescence intensity of the donor. When acceptor I<sub>2</sub> gets the excitation energy from the donor, its conductive band widens, which



**Figure 3** Linear correlation between  $F_0/F$  and  $[I_2]$ .

**Table III Influence of IFL on the Photoconductivity of Polymer (I)**

CGM	IFL	$V_o$ (V)	$V_R$ (V)	$Rd$ (V/sec)	$Rp$ (V/sec)	$\Delta V_1\%$	$T_{1/2}$ (sec)	$t_{1/2}^{-1}$ (1/sec)
a	No	462	5	56	316	81.8	0.38	2.63
	1.2 $\mu\text{m}$	706	42	9	397	53.4	0.92	1.09
b	No	400	19	54	342	79.4	0.38	2.63
	1.2 $\mu\text{m}$	550	26	12	371	60.4	0.69	1.45

<sup>a</sup> Polymer (I).

<sup>b</sup> Polymer (I):  $I_2 = 100:40$  (wt); CTM is TPD:PVK:PMMA = 5:2.5:1, 9.2  $\mu\text{m}$ .

**Table IV Influence of CTM on the Photoconductivity of Polymer (I)**

CTM (wt)	$Rd$ (V/sec)	$Rp$ (V/sec)	$\Delta V_1\%$	$t_{1/2}$ (sec)	$t_{1/2}^{-1}$ (1/sec)
TPD:PVK:PMMA = 5:2.5:1	10	471	54.4	0.92	1.09
TPD:PVK:PMMA = 5:1:1	13	487	52.9	0.92	1.09
TPD:PVK:PMMA = 5:5:1	45	188	34.2	1.76	0.57
TPD:PVK:PMMA = 2.5:5:1	24	406	56.1	0.84	1.19
TPA:PVK:PMMA = 5:2.5:1	9	164	14.5	4.92	0.20
TPA:PVK:PMMA = 5:5:1	21	498	40.5	1.30	0.77
TPA:PVK:PMMA = 2.5:5:1	26	153	21.9	3.23	0.31
TPD:TPA:PVK:PMMA = 2:1:1:1	14	188	45.3	1.15	0.87
TPD:TPA:PVK:PMMA = 2.5:2.5:1:1	17	281	50.3	1.00	1.00
TPD:TPA:PVK:PMMA = 1:2:1:1	12	198	39.8	1.46	0.68

Note: The thickness of IFL is about 1.2  $\mu\text{m}$ .

enhances the activity of electrons, and results in increasing the photoconductivity.

#### Influence of Interface-Layer on the Photoconductivity of the Polymer (I)

As shown in Table III, we see that under the same conditions, IFL has a great effect on the charge acceptance ( $V_o$ ), residual potential ( $V_R$ ) and the rate of dark discharge ( $Rd$ ). If there is no IFL,  $V_o$  and  $V_R$  are lower, but  $Rd$  is much larger. Therefore, although the  $\Delta V_1\%$  is larger and the  $t_{1/2}$  is shorter without the IFL, we still coat with IFL because of its slower  $Rd$ . In other words, IFL enhances the ability of charge acceptance and charge retention.

#### Influence of Charge-transport Material on the Photoconductivity of Polymer (I)

Table IV shows the influence of CTM on the photoconductivity of polymer (I). We find that the photoconductivity of polymer (I) varies with different kinds and proportions of CTM. Among the three charge transfer materials, TPD-PVK-PMMA is the best for polymer (I). When the weight proportions of TPD:PVK:PMMA are 5:2.5:1, 5:1:1, and 2.5:5:1,

the photoconductivities of P/R are better with large  $\Delta V_1\%$  and short  $t_{1/2}$ .

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