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Photoconductivity study on silicon dichloride phthalocyanine

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Abstract

The photoconductivity of silicon dichloride phthalocyanine ($SiCl_2Pc$) is studied. The results show that $SiCl_2Pc$ has good photoconductivity but that its photoconductivity decreases after solvent treatment. We emphasize the effects of induction and orientation on the photoconductivity of $SiCl_2Pc$ by poly(vinyl difluoride) (PVDF) and an electric field. The results indicate that there may exist a polar induction effect of PVDF on $SiCl_2Pc$; an electric field force can make PVDF and $SiCl_2Pc$ dispersed in it orientate along the electric field direction, and the polarization value P reaches 0.42. Both induction and orientation can increase the photoconductivity of $SiCl_2Pc$.

Keywords: Photoconductivity; Silicon dichloride phthalocyanine

1. Introduction

It is well known that amorphous silicon is one of the most developing and promising inorganic photoconductive materials because of its low price, nontoxicity and good spectral response. However, its difficulty in film forming prevents further study. We know that phthalocyanines are very stable and lasting organic photoconductive materials [1], so we think that combining phthalocyanine with silicon may increase the photoconductivity. Although silicon dichloride phthalocyanine ($SiCl_2Pc$) was synthesized in the early 1960s [2], its photoconductivity has not been reported until now. $SiCl_2Pc$ is a polar molecule because of its two chloride atoms. Our carrier generation mechanism study on metal phthalocyanine (MPc) compounds shows that there exists a partial charge transfer from phthalocyanine ring to metal ($Pc \rightarrow M$) in the metal phthalocyanine molecule, which is represented as $M^{\delta-}Pc^{\delta+}$. We find that introducing factors which enhance $Pc \rightarrow M$ partial charge transfer may improve the photoconductivity of phthalocyanines; in contrast, introducing factors that reduce $Pc \rightarrow M$ partial charge transfer will decrease the photoconductivity of phthalocyanines [3]. Therefore $SiCl_2Pc$ may have good photoconductivity. In this paper we first add poly(vinyl difluoride) (PVDF) as an inducer to increase the polarity of $SiCl_2Pc$ and enhance $Pc \rightarrow M$ partial charge transfer, and then try to introduce molecular orientation and polarity of PVDF and $SiCl_2Pc$ through an electric field force.

2. Experimental details

2.1. Materials and equipment

Triphenylamine (TPA), poly(vinyl difluoride) (PVDF) and the other reagents were commercially available and of analytical grade. Silicon dichloride phthalocyanine ($SiCl_2Pc$), *N*,*N*,*N*′,*N*′-tetraphenyl benzidine (TPD) and poly(vinyl carbazole) (PVK) were synthesized and purified in our laboratory according to published procedures [4–6].

Photoconductive properties were determined on a GDT-II model photoconductivity-measuring device. Polarization spectra were measured on a Hitachi 850 fluorescence spectrophotometer.

2.2. Preparation of double-layered photoreceptor device

A double-layered photoreceptor device (PRD) was made by coating an interface layer (IFL) of poly(methyl methacrylate) (PMMA), a charge generation layer (CGL) of $SiCl_2Pc$ dispersed in PVDF or PMMA and a charge transportation layer (CTL) of TPD–PVK on an aluminium plate in that order.

The CGL was coated by two means: (a) coating with no electric field; (b) coating in an electric field $E = 1.67 \times 10^5$ V m^{-1} (see Fig. 1).

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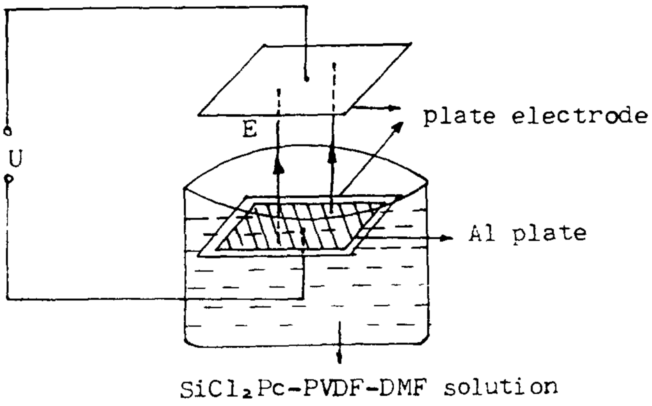


Fig. 1. Experimental set-up for solution coating CGL in electric field $E = 1.67 \times 10^5$ V m^{-1}.

2.3. *Photoconductivity measurement of double-layered photoreceptor device [7]*

The GDT-II model photoconductivity-measuring device was used with a visible lamp (5 W, 24 V) as light source to plot the photoinduced discharge curve (PIDC) of the PRD. In this measurement the surface of the PRD was negatively charged and charge carriers were generated in the CGL and injected into the CTL on exposure. From the PIDC we obtain the percentage of potential discharge after 1 s of exposure (ΔV_1) and the time from the original potential to half that value on exposure ($t_{1/2}$). The ΔV_1 and $t_{1/2}^{-1}$ values indicate the photosensitivity: the larger they are, the higher is the photosensitivity of the material.

3. Results and discussion

3.1. *Photoconductivity of silicon dichloride phthalocyanine*

One PRD was made with $SiCl_2Pc$ dispersed in PMMA as the CGL and TPD–PVK–PMMA (5:5:1 by weight) as the CTL. Its photoconductivity was measured and is given in Table 1.

From Table 1 we can see that $SiCl_2Pc$ has a high charge acceptance ($V_o = 890$ V), a low rate of dark discharge ($R_d = 43.2$ V s^{-1}) and a high rate of photodischarge ($R_p = 375$ V s^{-1}). The percentage of potential discharge after 1 s of exposure is $\Delta V_1 = 58.1\%$ and the time of half-discharge is $t_{1/2} = 0.69$ s. Under the same experimental conditions the $t_{1/2}$ and ΔV_1 values of CuPc are 3.92 s and 21.3% respectively. These indicate that $SiCl_2Pc$ has much better photoconductivity than CuPc.

Table 1 also gives the photoconductivity of $SiCl_2Pc$ treated with various solvents. We find that the ΔV_1 values of solvent-treated $SiCl_2Pc$ are smaller than ΔV_1 of untreated $SiCl_2Pc$ and that the $t_{1/2}$ values are longer, indicating that the photoconductivity of $SiCl_2Pc$ decreases after dipping in acetone, THF and CH_2ClCH_2Cl solvents. This occurs because the solvent treatment induces a morphological transformation of $SiCl_2Pc$ crystals [8] which results in a decrease in the photoconductivity of $SiCl_2Pc$.

3.2. *Influence of dispersant on the photoconductivity of $SiCl_2Pc$*

Fig. 2 and Table 2 reveal the influence of the dispersant on the photoconductivity of $SiCl_2Pc$. We find that compared with $SiCl_2Pc$ dispersed in PMMA, $SiCl_2Pc$ dispersed in PVDF has a larger ΔV_1 and a shorter $t_{1/2}$, indicating that $SiCl_2Pc$ dispersed in PVDF has better photoconductivity than $SiCl_2Pc$ dispersed in PMMA.

It has been proved that there exists a partial charge transfer from phthalocyanine ring to metal (Pc→M) in the metal phthalocyanine molecule, which is represented as $M^{\delta-}$ $Pc^{\delta+}$, and that all factors enhancing Pc→M partial charge transfer may improve the photoconductivity of phthalocyanines [3,9]. From the structure of $SiCl_2Pc$ (**1**) we find that the two chlorine atoms linked to Si can accept electrons strongly because of their large electronegativity, indicating that $SiCl_2Pc$ is a polar molecule. PVDF is a molecule with a permanent dipole moment due to the two fluorine atoms, while PMMA is a non-polar molecule. When PVDF is used as dispersant, its permanent dipole moment will induce $SiCl_2Pc$ molecules dispersed in it to generate an induced dipole moment. In other words, PVDF is an inducer and may increase the molecular polarization of $SiCl_2Pc$, hence enhancing Pc→M partial charge transfer. This is favourable to the photoconductivity of $SiCl_2Pc$.

Table 1
Photoconductivity of $SiCl_2Pc$ [a] in various solvents

$SiCl_2Pc$	V_o (V)	R_d (V s^{-1})	R_p (V s^{-1})	ΔV_1 (%)	$t_{1/2}$ (s)	$t_{1/2}^{-1}$ (s^{-1})
Untreated	890	43.2	375	58.1	0.69	1.45
Dipped in acetone (72 h)	1187	40.0	375	46.8	1.13	0.88
Dipped in THF (72 h)	882	43.2	375	45.9	1.13	0.88
Dipped in CH_2ClCH_2Cl (72 h)	945	49.6	250	50.5	0.94	1.06

[a] 20% $SiCl_2Pc$ is dispersed in PMMA as the CGL; IFL thickness about 2 μm, CGL thickness about 8 μm, CTL thickness about 30 μm.

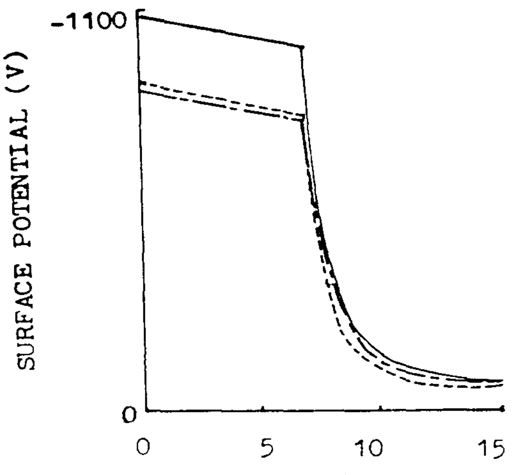
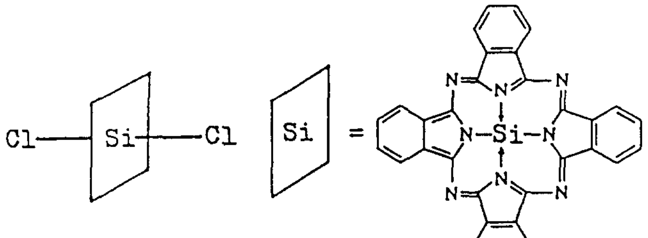


Fig. 2. PIDCs of PRDs from 20% $SiCl_2Pc$ dispersed in PMMA (- - - - - -, $E=0$), PVDF (– – – – –, $E=0$) and PVDF (———, $E=1.67\times10^5$ V m^{-1}).



(1)

Therefore it is the induction effect of PVDF on $SiCl_2Pc$ that leads to better photoconductivity of $SiCl_2Pc$ dispersed in PVDF than that of $SiCl_2Pc$ dispersed in PMMA.

3.3. Influence of electric field on the photoconductivity of $SiCl_2Pc$

From Fig. 2 and Table 2 we also find that by coating $SiCl_2Pc$–PVDF in an electric field (EF) $E=1.67\times10^5$ V s^{-1}, the photoconductivity of the PRD is better than that of the PRD obtained by coating $SiCl_2Pc$–PVDF without an EF. For the 20 wt.% $SiCl_2Pc$ system the charge acceptance of the PRD coated in the EF is higher than that of the PRD coated without the EF, and ΔV_1 increases to 68.5% from 63.2% while $t_{1/2}$ decreases to 0.44 s from 0.56 s. For different proportions of the $SiCl_2Pc$–PVDF system the same conclusion can be drawn.

To explain the above results, two CGL films were prepared by coating DMF solution of 20% $SiCl_2Pc$ dispersed in PVDF and removal of the solvent by evaporation with no electric field and with an electric field of 1.67×10^5 V s^{-1} respectively (see Fig. 1). The films were uncovered and their fluorescent emission polarization spectra were recorded (Fig. 3).

From Fig. 3 we can see that the polarization values of the film with the electric field are larger than those of the film with no electric field and that the maximum polarization value with the EF reaches $P=0.42$. The molecules and dipole moment of PVDF are easy to orientate in an electric field because of its permanent dipole moment, i.e. the electric field force can make the molecules and dipole moment of PVDF orientate so that the polarizability along the electric field direction (**E**) is very large whereas the polarizability along the other two directions is negligible in comparison. This may induce an electrical polarity of $SiCl_2Pc$ dispersed in PVDF and make both the molecules and dipole moment of $SiCl_2Pc$ orientate also. The result is that the photogenerated carriers can move more easily along

Table 2
Influence of dispersant and electric field on the photoconductivity of $SiCl_2Pc$ [a]

$SiCl_2Pc$ in CGL (wt.%)	Dispersant and electric field (EF)	V_o (V)	R_d (V s^{-1})	R_p (V s^{-1})	ΔV_1 (%)	$t_{1/2}$ (s)	$t_{1/2}^{-1}$ (s^{-1})
10	PMMA	695	33.6	250	50.7	0.94	1.07
	PVDF	609	28.8	250	60.4	0.62	1.60
	PVDF (EF) [b]	1132	48.8	375	61.4	0.56	1.78
20	PMMA	890	43.2	375	58.1	0.69	1.45
	PVDF	546	24.8	250	63.8	0.56	1.78
	PVDF (EF) [b]	1085	48.0	500	68.5	0.44	2.29
60	PMMA	707	26.4	250	45.0	1.25	0.80
	PVDF	785	32.0	375	64.4	0.50	2.00
	PVDF (EF) [b]	1671	80.0	500	66.7	0.44	2.29

[a] IFL thickness about 2 μm, CGL thickness about 8 μm, CTL thickness about 30 μm.
[b] CGL is coated in an electric field of 1.67×10^5 V m^{-1}.

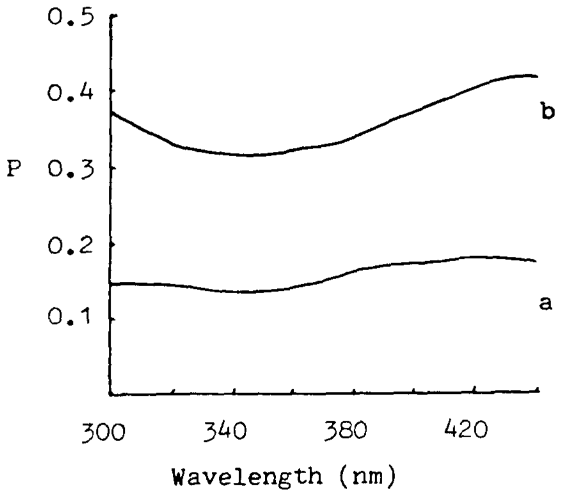


Fig. 3. Fluorescent emission polarization spectra of $SiCl_2Pc$–PVDF film (20:80 by weight), $\lambda_{ex}=280$ nm, film thickness about 5 μm: a, $E=0$; b, $E=1.67\times10^5$ V m^{-1}.

the polarization and the photoconductivity therefore increases.

4. Conclusions

(1) $SiCl_2Pc$ has better photoconductivity than CuPc but its photoconductivity decreases after solvent treatment.

(2) The photoconductivity of $SiCl_2Pc$ dispersed in PVDF is better than that of $SiCl_2Pc$ dispersed in PMMA, since the polarity induction effect of PVDF on $SiCl_2Pc$ may enhance Pc → M partial charge transfer.

(3) Coating $SiCl_2Pc$–PVDF in an electric field may improve the photoconductivity of $SiCl_2Pc$ further. The electric field force can cause the molecules and dipole moment of PVDF to orientate along the electric field direction in the CGL, which may also induce orientations of both the molecules and polarity of $SiCl_2Pc$ dispersed in PVDF. For the $SiCl_2Pc$–PVDF (20:80 by weight) system the polarization value P reaches 0.42. The result is that the photogenerated carriers can move more easily along the polarization and the photoconductivity therefore increases.

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