Molecular Orientation–Photoconductivity Relationship Study of Phthalocyanine Polymer-Oriented Thin Films

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ABSTRACT: The molecular orientation–photoconductivity relationships of several kinds of phthalocyanine polymer (PPc)-oriented thin films have been studied in double-layered photoreceptor devices, where the charge-generation layers (CGLs) are phthalocyanine polymer-oriented thin films and the charge-transportation layers (CTLs) are composed of hole transporting materials of tetraphenyl benzidine or hydrazone. The oriented thin films containing PPc dispersed in polyvinyl difluoride (PVDF) were prepared by the electric field orientation. The results showed that the photosensitivities of the phthalocyanine polymer (PPcs)-oriented thin films were higher than those of the unoriented PPcs thin films, and varied with their molecular structures and the molecular stacking in the films. This was thought to be due to the molecular orientation effect, which was demonstrated by the analyses of the polarized fluorescence, DSC, FTIR reflection absorption spectroscopy (FTIR-RAS), and angle-dependent XPS. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 2331–2339, 2000

Key words: photoconductivity; oriented thin film; phthalocyanine polymer

INTRODUCTION

Since phthalocyanine polymer (PPc) emerged in the 1950s, many phthalocyanine polymers (PPcs) have been synthesized because of their interesting optical, magnetic, catalytic, electrochemical, semiconductive, and photoconductive properties.[1–8] As a kind of promising photoconductive material, PPcs have been widely investigated.[9–12] Many factors, such as impurity, particle size, crystallographic orientation, molecular stacking arrangements, and conformation of molecules are known to have an effect on the photogeneration efficiency of PPcs. Therefore, with the emergence of the supramolecular thin films, one of the inter-

esting things is how to fabricate PPc ultrathin films. So far, several techniques have been used to obtain the ultrathin layers:[13] (a) the poling of initially nonpolar polymer films,[14,15] (b) the Langmuir-Blodgett (LB) assembly of polar monolayers,[16,17] and (c) the defined growth of films of polar polymers by self-assembly[18,19] or grafting.[20,21] Phthalocyanine polymer ultrathin films with unique and ordered molecular structures had been fabricated through the LB technique[22] and self-assembly.[23] However, little is known about the relationship between the photoconductive property and the molecular stacking arrangements in the phthalocyanine polymer films.

Two kinds of phthalocyanine polymers have been synthesized in our lab: (a) one-dimensional bridged polymeric phthalocyanine, such as 4,4′-diamino-diphenyl ether bridged polymeric SiPc,[24] and (b) polymers containing phthalocyanine (Pc) units, including homopolymer containing Pc
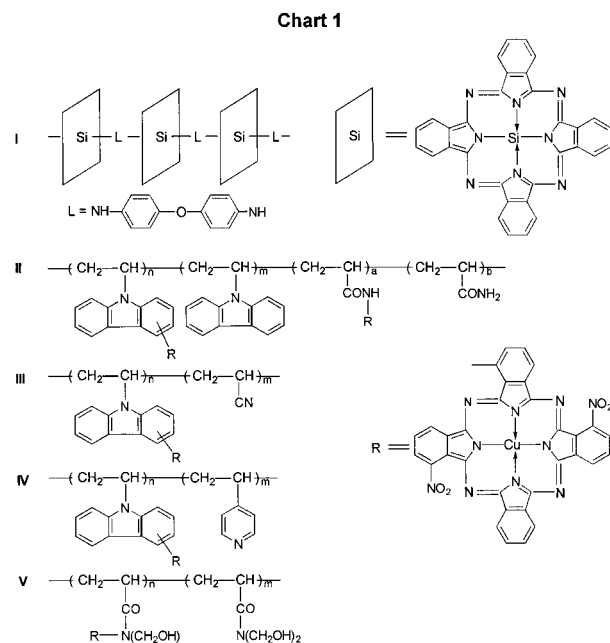
Chart 1

Chart 1 Chemical structural formulas of polymeric phthalocyanines (PPcs).

units, for example, polyacrylamide-bonded copper phthalocyanine,[25] and copolymer containing Pc units, such as poly(vinylcarbazole-co-acrylamide)–bonded copper phthalocyanine.[26] Their photoconductivity studies showed that the one-dimensional bridged polymeric phthalocyanines exhibited higher photosensitivity than most polymers containing Pc units. The results suggested that the one-dimensional molecular structure might be favorable to the photoconductivity. So, if the PPcs molecules can stack in an orderly fashion during the film forming, the photoconductivity may be increased further.

In the present article, photoconductivity–molecular orientation relationships of PPcs shown in Chart 1 were investigated by a photoinduced xerographic discharge technique. PPcs dispersed in polyvinyl difluoride (PVDF)-oriented thin films were made by electric field orientation.

EXPERIMENTAL

Materials and Equipment

The synthesis and characterization of PPcs are listed in Table I. The charge-transportation materials (CTMs) of N,N,N',N'-tetraphenyl benzidine (TPD) and N,N'-diethylaminobenzaldehyde α-naphthylhydrazone (NH) were synthesized and purified according to the previous studies.[28,29] Polyvinylcarbazole (PVK) was also synthesized according to the reported procedure.[30] PVDF, polymethyl methacrylate (PMMA), and the other reagents were commercially available and in analytical grade.

Polarized fluorescence spectra were obtained on an RF-850 Fluorescence Spectrophotometer. The anisotropy spectra were recorded by the following equation:

$$A(\lambda) = [I_{//}(\lambda) - G \cdot I_{\perp}(\lambda)]/[I_{//}(\lambda) + 2G \cdot I_{\perp}(\lambda)],$$

where G is corrected factor, and $I_{//}$ and $I_{\perp}$ are fluorescent intensities when the directions of the polarizer and the analyzer are parallel to and perpendicular to each other, respectively. The bigger the A value is, the higher the degree of the molecular orientation. DSC curves were recorded on a DSC-7 differential scanning calorimeter at a heating rate of 10°C/min in N_2. FTIR reflection

Table I   Preparation of Polymeric Phthalocyanines (PPcs)

PPcs	Monomer	Solvent	Temp (°C)	Content of Pc (mol %)	Ref.
I	SiPcCl$_2$[a] + DDE[b]	quinoline	200	—	24
II	DAS-CuPc[c] + VK[d] + AA[e]	H$_2$O	60	29.6 (wt %)	26
III	VK-CuPc[f] + AN[g]	DMF[h]	70	0.074	27
IV	VK-CuPc + VP[i]	DMF	70	0.086	27
V	DAS-CuPc + AA	H$_2$O	60	7.0	25

[a] SiPcCl$_2$ = dichloride silicon phthalocyanine.
[b] DDE = 4,4′-diamino-diphenyl ether.
[c] DAS-CuPc = diazonium salt of dinitro-diamine CuPc.
[d] VK = vinylcarbazole.
[e] AA = acrylamide.
[f] VK-CuPc = vinylcarbazole bonded dinitro CuPc.
[g] AN = acrylonitril.
[h] DMF = dimethylformamide.
[i] VP = 4-vinylpyridine.

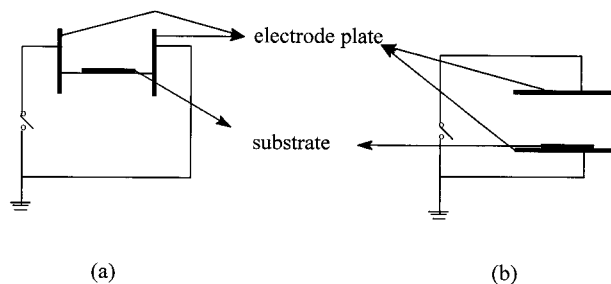(a)   (b)

Figure 1 Schematic diagram of electric field orientation: (a) orientation in a parallel electric field; (b) orientation in a perpendicular electric field.

absorption spectra (FTIR-RAS) were recorded using a Digilab FTS-20E IR spectrophotometer. The experimental setup for the measurement of grazing-incident reflection (GIR) spectra was made by Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. The angle of incidence in the GIR and the reflection IR (RIR) measurements was 75 and 26°C, respectively. In both GIR and RIR investigations, the uncoated smooth stainless steel plate was used as the reference, the scanned times was 64, and no polarizer was used. Angle-dependent XPS examinations were carried out on an ESCALAB MK-II X-ray photoelectron spectrometer using an Al K_{α} X-ray source with an energy of 1468.6 eV. The sample could be rotated so that the electron tak-off angle can be changed.

Preparation of PPcs-Oriented Thin Film[31]

PPcs-oriented thin films were obtained through the electric field orientation. A substrate was put to the surface of a polyvinyl tetrafluoride supported plate [Fig. 1(a)], or to the surface of one electrode plate directly [Fig. 1(b)]. The substrate is a quartz plate for the polarized fluorescence, angle-dependent XPS, and DSC measurements; a stainless steel plate for the FTIR reflection absorption experiment; an aluminum plate overcoated a PMMA layer for the photoconductivity measurement. The dimethylformamide (DMF) dispersion containing PPc and PVDF in a weight ratio of 1 : 4 was prepared first, then the DMF dispersion was covered on the substrate. An external electric field was applied, and the substrate was heated at about 50°C until the DMF solvent was slowly evaporated completely, giving a thin film containing PPc and PVDF (abbreviated as PPc–PVDF film). The direction of the electric field may be parallel to or perpendicular to the plane of

the substrate. It was defined as the orientation in a parallel electric field (4.0×10^5 V/m) [Fig. 1(a)] or the orientation in a perpendicular electric field (1.0×10^5 V/m) [Fig. 1(b)], respectively, here.

Photoreceptor Fabrication and Photoconductivity Measurement

The photoconductive properties of PPc–PVDF-oriented thin films were studied in double-layered photoreceptors (P/Rs). A schematic cross section of a double-layered photoreceptor (P/R) is shown in Figure 2. The procedure for preparation of the photoreceptor is as follows: the mixture of PPc dispersed in PVDF (PPc : PVDF = 1 : 4, by wt) was coated onto the surface of an aluminum (Al) substrate through the electric field orientation introduced above. The Al substrate was precoated with a 1 μm-thick interface layer (IFL) of PMMA. The PPc–PVDF oriented layer (0.5 μm) was taken as the charge-generation layer (CGL). On top of the CGL, a 30 μm-thick TPD-PVK-PMMA (5 : 5 : 1, by wt) or NH–PMMA (1 : 1, by wt) charge-transportation layer (CTL) was coated, and a double-layered P/R was obtained.

The photoconductivity measurements were made on a GDT-II model photoconductivity measuring device by a photoinduced xerographic discharge technique.[32] A 5-W, 24- visible lamp was used as a light source. The measurement included charging, dark decaying, exposure, and erasing four steps, which is the basis of the xerographic process used in copying machines. Several parameters can be obtained from the measurement: charged initial surface potential (V_0), residual potential (V_r), dark decay (R_d), photo decay (R_p), percentage of potential discharge after 1 s of exposure (ΔV_1), time from the initial potential to half under exposure ($t_{1/2}$), and half discharge energy ($E_{1/2}$). The photosensitivity of the P/R is expressed as $E_{1/2}$, which is the product of **I** and $t_{1/2}$, where **I** is the light intensity. A good photocon-
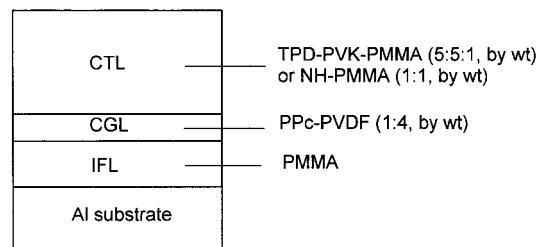

Figure 2 A schematic cross section of a double-layered photoreceptor (P/R).

Table II Xerographic Data of P/Rs from PPc–PVDF Oriented Thin Films

CTL	CGL	$E \times 10^{-5}$ (V/m)	V_0 (V)	V_r (V)	R_d (V/s)	R_p (V/s)	ΔV_1 (%)	$t_{1/2}$ (s)	I (lux)	$E_{1/2}$ (lux·s)
TPD : PVK :	**I**-PVDF	0^a	945	187	50	250	65.2	0.50	800	400
PMMA		1^b	953	148	10	425	72.2	0.50	200	100
= 5 : 5 : 1 (by wt)		1^c	1007	164	53	500	72.6	0.38	800	304
	II-PVDF	0^a	753	156	26	312	65.4	0.50	800	400
		1^b	857	125	50	350	74.8	0.38	200	76
		1^c	1468	210	54	500	77.9	0.25	800	200
	III-PVDF	0^a	1093	226	30	325	56.2	0.75	800	600
		1^b	1031	179	20	375	72.2	0.44	800	352
		1^c	1242	242	65	500	64.1	0.56	800	448
	IV-PVDF	0^a	788	116	36	375	60.9	0.63	800	504
		1^b	507	50	33	187	72.9	0.31	800	248
		1^c	992	171	54	500	68.4	0.44	800	352
	V-PVDF	0^a	582	85	4	375	61.3	0.75	800	600
		1^b	1187	226	43	500	68.5	0.69	200	138
		1^c	867	160	39	375	69.1	0.44	800	352
NH : PMMA	**I**-PVDF	0^a	570	93	13	312	62.7	0.69	800	552
= 1 : 1 (by wt)		1^b	1117	195	69	375	78.2	0.31	800	248
		1^c	613	89	40	387	71.4	0.38	800	304
	II-PVDF	0^a	875	91	16	375	61.9	0.69	800	552
		1^b	1398	179	75	500	81.7	0.25	800	200
		1^c	1078	148	59	375	76.0	0.31	800	248
	III-PVDF	0^a	648	78	20	250	56.4	0.88	800	704
		1^b	621	121	35	275	67.1	0.50	800	400
		1^c	804	117	22	362	64.0	0.63	800	504
	IV-PVDF	0^a	685	66	15	325	59.2	0.75	800	600
		1^b	1273	226	52	500	68.9	0.44	800	352
		1^c	773	128	22	375	61.8	0.69	800	552
	V-PVDF	0^a	605	85	18	312	56.0	0.81	800	648
		1^b	539	74	26	325	70.3	0.44	800	352
		1^c	679	89	26	500	72.3	0.50	800	400

[a] PPc PVDF films were made without an electric field.
[b] PPc PVDF films were made in a perpendicular electric field.
[c] PPc PVDF films were made in a parallel electric field.

ductive material should have a low V_r, R_d, $t_{1/2}$, and $E_{1/2}$ value and a high R_p and ΔV_1 value,; especially, the smaller the $E_{1/2}$ value the higher the photosensitivity.

RESULTS AND DISCUSSION

Photosensitivity of PPc–PVDF-Oriented Thin Films

The photoconductive properties of the PPcs-oriented thin films were studied in double-layered P/Rs where the PPcs–PVDF-oriented thin films were used as CGLs. The xerographic data were summarized in Table II. We found that, whether TPD–PVK–PMMA or NH–PMMA was used as

CTM, the five kinds of PPcs–PVDF films made in a perpendicular or a parallel electric field had smaller values of $t_{1/2}$ and $E_{1/2}$ and higher values of R_p and ΔV_1, when compared to those corresponding films coated without an electric field. These observations indicate that the photosensitivities of the PPcs-oriented thin films made in both perpendicular electric fields and parallel electric fields were higher than those of the corresponding PPcs films made without an electric field. For example, take TPD–PVK–PMMA as CTM, the **I**–PVDF-oriented films made in a perpendicular electric field, and a parallel electric field had lower $E_{1/2}$ values (100 and 304 lux · s, respectively) than the **I**–PVDF film made without an

electric field (400 lux · s). This suggests that the photosensitivities of the PPcs–PVDF films might be improved by the electric field orientation.

It was noticed from Table II that, when TPD–PVK–PMMA was used as CTM, the $E_{1/2}$ values of PPc–PVDF films oriented in a perpendicular electric field decreased from 400, 400, 600, 504, and 600 lux · s to 100, 76, 352, 248, and 138 lux · s for **I**, **II**, **III**, **IV**, and **V**, respectively. If NH–PMMA was used as CTM instead of TPD–PVK–PMMA, the $E_{1/2}$ values also decreased from 552, 552, 704, 600, and 648 lux · s to 248, 200, 400, 352, and 352 lux · s for **I**, **II**, **III**, **IV**, and **V** , respectively. It can be concluded that the $E_{1/2}$ value decreasing degree or the photosensitivity increasing degree is followed by **II** > **V** > **I** > **IV** > **III** for CTM of TPD–PVK–PMMA when compared to those of the corresponding PPcs films made without an electric field. The following sequence of photosensitivity enhancement is also observed when NH–PMMA acts as CTM: **II** > **I** > **V** > **III** > **IV**. If PPc–PVDF films were oriented in a parallel electric field, the improvement of photosensitivity was followed by the order: **II** > **V** > **IV** > **III** > **I** for CTM of TPD–PVK–PMMA, and **II** > **I** > **V** > **III** > **IV** for NH–PMMA CTM.

In addition, we also found from Table II that the $E_{1/2}$ values of PPc–PVDF-oriented films made in a perpendicular electric field were lower than those of the corresponding films made in a parallel electric field, no matter whether the CTM was TPD–PVK–PMMA or NH–PMMA. This indicates that the photosensitivities of PPc–PVDF-oriented thin films made in a perpendicular electric field were higher than those of the corresponding PPc–PVDF-oriented thin films made in a parallel electric field. This suggests that the orientation in a perpendicular electric field is more favorable to the photogeneration efficiency other than in a parallel electric field.

Molecular Orientation–Photosensitivity Relationships

Why are the photosensitivities of PPcs–PVDF-oriented thin films higher than those made without an electric field? The answer may be found from their polarized fluorescent spectra. Figure 3 shows the dependence of the fluorescent anisotropy (A) on the emitted wavelength in PPc–PVDF films oriented in a parallel electric field. We observed from Figure 3 that all the PPcs–PVDF-oriented thin films made in a parallel electric field had large A values. For example, the A values of
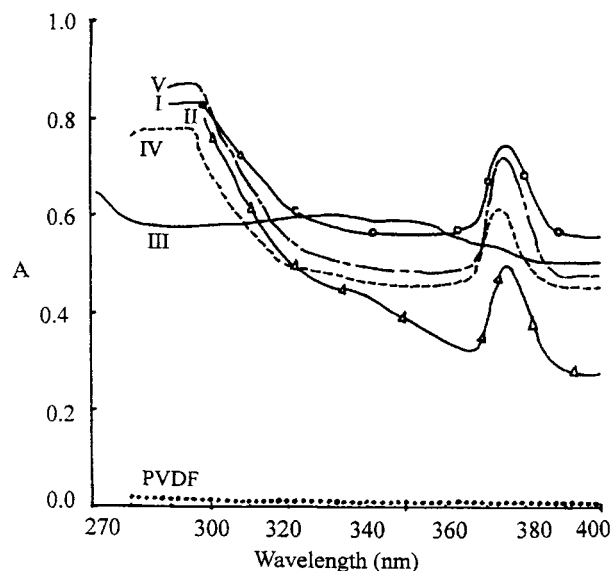

Figure 3 Anisotropy spectra from pure PVDF and PPc–PVDF (1 : 4, by wt)-oriented thin films made in a parallel electric field ($E = 4.0 \times 10^5$ V/m) at 50°C for 60 min, film thickness ≈1 μm, the excited wavelengths of **I**, **II**, **III**, **IV**, **V**, and PVDF are 290.3, 291.8, 256.1, 288.6, 291.4, and 280 nm, respectively.

V–PVDF-oriented film, were between 0.48–0.88, and had a peak at 373 nm. Although the overall anisotropy of pure PVDF film oriented in a parallel electric field was averaged to zero (A ≈ 0) because the pure PVDF had no fluorescent absorption. Therefore, only the orientation of the PPc molecules contributes to A values of PPc–PVDF-oriented thin films. In other words, the PPcs molecules orientate in the parallel electric field. As a result, the permanent dipole moment of the PVDF molecule is easy to polarize along the electric field direction, which may induce an electrical polarity of the PPc molecules dispersed in it and make both the molecules and dipole moment of the PPc orientate along the electric field also. The examinations of DSC can confirm the above conclusion. The melting heat (ΔH_f) of the **II**–PVDF and **V**–PVDF-oriented thin films made in a parallel electric fields was 37.78 and 39.82J/g, respectively. This was 4.37 and 3.33 J/g higher than that of the corresponding film coated without an electric field (33.41 and 36.49 J/g). This can be explained by the orientation of PVDF and PPcs molecules in the electric field. The high degree of the order in PPc–PVDF-oriented thin films led to the increase of ΔH_f values. So it is the orientation of the PPcs and PVDF molecules that is favorable to the charge carrier migration and, consequently, the photosensitivity increases.
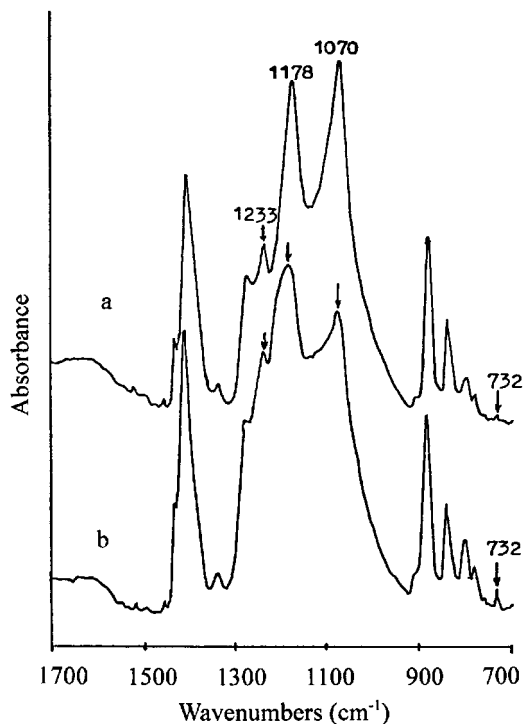
Figure 4 FTIR reflection spectra from **I**–PVDF-oriented thin film made in a perpendicular electric field ($E = 1.0 \times 10^5$ V/m): (a) RIR, (b) GIR.

FTIR reflection spectra of **I**–PVDF-oriented thin film made in a perpendicular electric field is shown in Figure 4. According to the measuring principle of the surface reflection absorption,[33] the absorption bands with dipole moments approximately perpendicular to the film surface are expected to appear with enhanced intensity in GIR spectrum in comparison with those in the RIR spectrum.[34] However, those bands with dipole moments nearly parallel to the film surface will appear weakly or disappear. In Figure 4, the weaker C—C stretching band at 1070 cm^{-1} and the two stronger C—F stretching bands at 1178 and 1233 cm^{-1} were observed in GIR when comparing to those in RIR spectrum. This indicates that the overall direction of the dipole moment of C—C and $C^{\delta+}$-$F^{\delta-}$ was parallel to and perpendicular to the film surface, respectively. So, in the perpendicular electric field, the dipole moment of $C^{\delta+}$-$F^{\delta-}$ in PVDF molecules oriented along the electric field direction, and perpendicular to the film surface. Meanwhile, the C—C main chains of PVDF aligned parallel to the film surface. The orientation model for PVDF in a perpendicular electric field is illustrated in Figure 5(a).

Because no absorption band was observed in the $700–800$ cm^{-1} region in the GIR of pure

PVDF-oriented film made in a perpendicular electric field, any absorptions of PPc–PVDF films in this region must be a result from PPc. Here, the absorption band at 732 cm^{-1}, assigned to the C—H out-of-plane bending in the phthalocyanine ring,[35] was used to investigate the stacking of phthalocyanine rings in PPc–PVDF films. Its vibration mode of the dipole moment was perpendicular to the plane of the phthalocyanine ring. As shown in Figure 4, the intensity of the band at 732 cm^{-1} was enhanced in GIR compared to that in RIR, indicating that the dipole moment was perpendicular to the film surface. From the relationship of the plane of phthalocyanine ring and its dipole moment vibration mode mentioned above, we might conclude that phthalocyanine rings in **I**–PVDF film were parallel to the film surface in the perpendicular electric field, as also shown in Figure 5(a).

Figure 6 is FTIR reflection spectra of **IV**–PVDF-oriented thin film made in a perpendicular electric field. It was seen that an enhanced intensity of C—C stretching band at 1074 cm^{-1}, while a decreased intensity of C—F stretching band at 1182 cm^{-1}, and almost disappeared band of C—H out-of-plane bending in phthalocyanine ring at 737 cm^{-1} were observed in GIR compared to those in RIR. These observations were different from
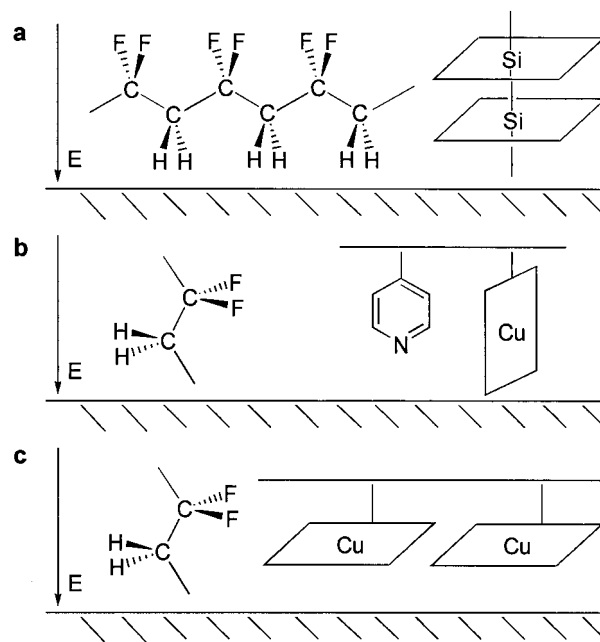

Figure 5 Orientation model of PVDF and PPcs in PPc–PVDF-oriented thin films made in a perpendicular electric field ($E = 1.0 \times 10^5$ V/m) based on collected data: (a) **I**–PVDF, (b) **IV**–PVDF, (c) **V**–PVDF.
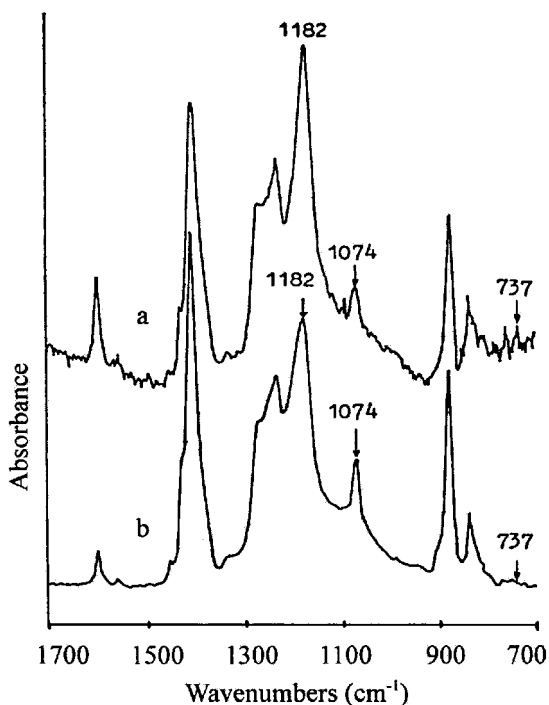
Figure 6 FTIR reflection spectra from **IV**–PVDF-oriented thin film made in a perpendicular electric field ($E = 1.0 \times 10^5$ V/m): (a) RIR, (b) GIR.

a decreased intensity, were observed in GIR. All these results imply that the plane of phthalocyanine ring and the most dipole moment of C—F in PVDF are parallel to the film surface, as shown in Figure 5(c).

The sterically hindered effect may be responsible for the different stacking of the phthalocyanine rings in **IV**–PVDF and **V**–PVDF-oriented thin films made in a perpendicular electric field. Rigid carbazole rings exist except for pyridine rings linked to the **IV** main chain. It is difficult for the phthalocyanine rings bond to the carbazole groups to move and parallel the film surface. To **V**, however, there are no huge aromatic rings peripherally, which could allow for lying of the phthalocyanine rings.

In a summary, in a perpendicular electric field, phthalocyanine rings in **I** and **V** are parallel to the film surface, while the phthalocyanine rings in **IV** are perpendicular to the film surface. The stacking alignments of the phthalocyanine rings may be used to explain the photosensitivity. It seems that the lying phthalocyanine rings could absorb more photons, and hence, increase the efficiency of photogenerated charge carriers. That is
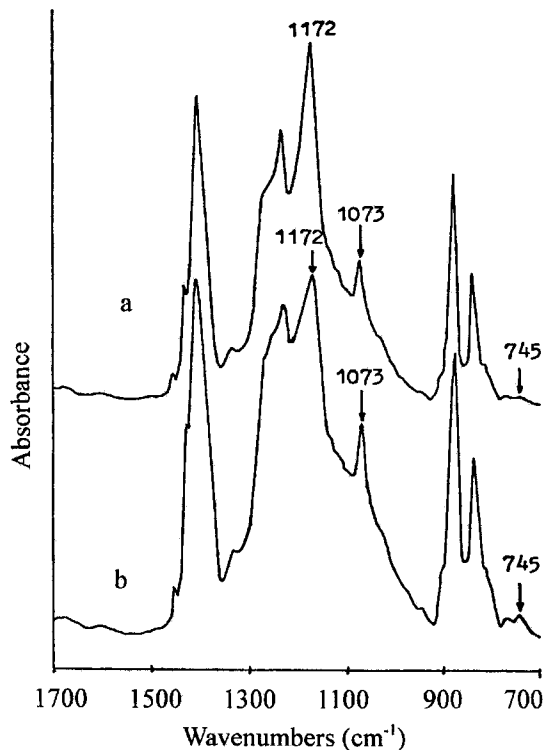
those of the above **I**–PVDF-oriented thin film completely. This indicates that the dipole moment of $C^{\delta+}$-$F^{\delta-}$ in PVDF tend to be parallel to the film surface, and that the plane of the phthalocyanine ring is perpendicular to the film surface [see Fig. 5(b)]. This may be related to the intramolecular charge transfer existing in **IV**. It is known that the phthalocyanine ring might act as an electron acceptor, while vinylpyridine can act as electron donor due to the —N:. Therefore, the intramolecular charge transfer might occur in **IV**, and resulting in –N:$^{\delta+}$, which may very well interact with the negatively polarity $F^{\Delta-}$ in the PVDF molecule. The interaction between the —N:$^{\Delta+}$ and the $F^{\Delta-}$ may lead to the fact that the net direction of dipole moment of $C^{\Delta+}$-$F^{\Delta-}$ in PVDF tend to be parallel to the film surface instead of orientate along the direction of the electric field.

Comparing the GIR and RIR of **V**–PVDF-oriented thin film made in a perpendicular electric field (Fig. 7), we found that the band of C—H out-of-plane bending in the phthalocyanine ring at 745 cm^{-1} appeared in GIR almost disappeared in RIR. Meanwhile, the C—C stretching band at 1073 cm^{-1} with a slightly increased intensity, and the C—F stretching band at 1172 cm^{-1} with

Figure 7 FTIR reflection spectra from **V**–PVDF-oriented thin film made in a perpendicular electric field ($E = 1.0 \times 10^5$ V/m): (a) RIR, (b) GIR.
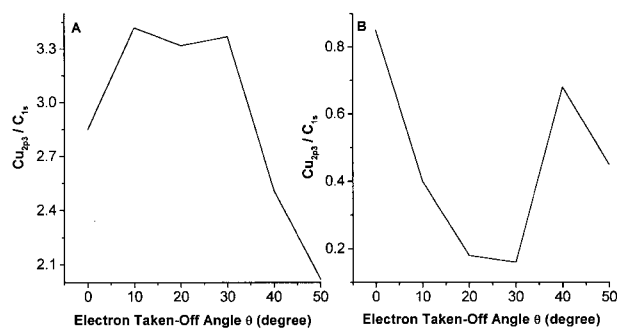
Figure 8   Variation in the ratio of Cu_{2p3} XPS signal to C_{1s} as a function of electron take-off angle for **V**–PVDF (1 : 4, by wt)-oriented thin film made in: (A) a perpendicular electric field ($E = 1.0 \times 10^5$ V/m); (B) a parallel electric field ($E = 4.0 \times 10^5$ V/m).

why the photosensitivities of **I**–PVDF and **V**–PVDF-oriented thin films made in a perpendicular electric field are increased much more than that of **IV**–PVDF-oriented thin film when compared to those of the corresponding PPc–PVDF-unoriented thin films.

Because no valuable information has been obtained in our experiments, no exact reason is known to explain why the improvement of photosensitivity of the five PPc–PVDF-oriented thin films made in a parallel electric field followed the order: **II** > **V** > **IV** > **III** > **I** for CTM of TPD–PVK–PMMA, and **II** > **I** > **V** > **III** > **IV** for NH–PMMA CTM. However, we tried to get some idea about why the photosensitivities of the five PPc–PVDF-oriented thin films made in a perpendicular electric field are higher than those made in a parallel electric field by FTIR-RAS and angle-dependent XPS techniques.

There is no obvious difference between GIR and RIR spectra of the five PPc–PVDF-oriented films made in a parallel electric field, suggesting that the degree of molecular orientation is too low to be detected by the FTIR-RAS technique. That is to say that the degree of molecular orientation in PPc–PVDF films made in a parallel electric field is lower than that made in a perpendicular electric field, which may be demonstrated by the angle-dependent XPS.

Angle-dependent XPS is an effective technique in molecular orientation investigations.[36] It has one important character that the photoelectron emission will be enhanced along the crystal axis direction,[37] which was interpreted as the "electron-channeling effect" caused by the photoelectronic crystal lattice diffraction.[38] Figure 8 shows the variation of the Cu_{2p3}/C_{1s} XPS signal ratios

plotted as a function of the electron take-off angle (θ) for the **V**–PVDF films made in perpendicular and parallel electric fields. A wide enhanced peak from 10 to 30° appeared for Cu_{2p3}/C_{1s} when **V**–PVDF thin film was made in a perpendicular electric field [see Fig. 8(a)]. This implies that the Cu_{2p3} photoelectron number taken off at this range of angles was the maximum, and a wide "electron channel band" was formed from 10 to 30° of the electron take-off angle. On the other hand, **V**–PVDF film made in a parallel electric field has two sharp photoelectron enhancement peaks appearing at $\theta = 0°$ and 40° for Cu_{2p3} [Fig. 8(b)]. This indicates that two "electron channels" were formed for Cu_{2p3}, which were 0° and 40° with respect to the normal of the film surface, respectively. The continuous "electron channel band" might mean a higher degree of molecular orientation than the two interrupted "electron channels." So, the higher photosensitivities of PPc–PVDF films made in a perpendicular electric field than those made in a parallel electric field may be due to the higher degree of molecular orientation in PPc–PVDF-oriented thin films.

CONCLUSIONS

Five kinds of PPc–PVDF-oriented thin films can be fabricated by the electric field orientation method. The molecular orientation in PPc–PVDF thin films is dependent on the direction of the applied electric field. The molecular orientation and the stacking alignments of phthalocyanine rings in oriented PPc–PVDF films greatly affect their photoconductive properties. Photosensitivities were higher in the oriented PPc–PVDF thin films than in the unoriented PPc–PVDF films due to the orientation. Higher photosensitivities were also observed in the oriented thin films made in a perpendicular electric field other than in a parallel electric field. This is very helpful for us to design the photoreceptor with excellent photoconductivity.

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