Preparation and Photoconductivity of Ethylenediamine-Bridged Iron Phthalocyanine Polymer [PcFe(eda)]ₙ

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ABSTRACT: An ethylenediamine (eda)-bridged iron phthalocyanine (FePc) polymer [PcFe(eda)]ₙ was synthesized by the complexing of ethylenediamine and FePc. Through electric field poling, a novel low-dimensional [PcFe(eda)]ₙ–PVDF film was obtained. The characterization of the film by DSC, angle-dependent XPS, FT–IR Reflection Absorption Spectroscopy (FTIR–RAS) revealed that the planes of phthalocyanine rings were parallel to the film surface. The photoconductivities of the photoreceptors (P/Rs) made from polarized or unpolarized [PcFe(eda)]ₙ–PVDF film and different charge transfer materials were measured. It was found that the photoconductivities of P/Rs from [PcFe(eda)]ₙ were much better than those of P/Rs from FePc, and after the orientation of electric field, the photoconductivities of P/Rs from [PcFe(eda)]ₙ increased greatly. These changes were ascribed to the effects of the low dimension of the molecular and material structure. In ESR spectra, both the complexation of FePc and ethylenediamine and the polarization of electric field raised the charge carrier density, which suggesting that in low-dimensional materials the intramolecular and intermolecular charge transfer interactions may increase significantly, resulting in the improvement of photoconductivities. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 1769–1774, 1997

Key words: phthalocyanine polymer; photoconductivity; electric field polarization; low dimension

INTRODUCTION

A kind of one-dimensional conductor through the coordination of macrocycles (Mac) [e.g., phthalocyanine (Pc), 1,2- and 2,3-naphthalocyanine (Nc), or tetrabenzoporphyrin (TBP)], transition metal atoms (e.g., M = Fe, Ru, Co, etc.) and containing delocalizable π electrons axial bridging ligands (L) [L = pyrazine (pyz), tetrazine (tz), diisocyanobenzene (dib), bipyridine (bpy), etc.] to form linear polymeric stacked arrangements [MacML]ₙ was extensively investigated.[1] The polymers, inside which the electrons were easy to move, could be used as good semiconducting materials even without doping. Recently, many studies on photoconductivity of the kind of the polymer were reported.[2–4] Unlike conductors, photoconductors, which have been extensively applied in photovoltaic cells and xerographic photoreceptors of copiers and laser printers, are not aimed at high dark conductivity but high conductivity under exposure. Therefore, the ligands containing delocalizable π electrons are not necessary. On the other hand, the material structure of photoconductive materials, such as polymorphs (different molecular stacking arrangements), particle size (surfacial area), conformation of molecules, etc., greatly influenced photosensitivity. So the design of photoconductive materials' molecular structure and material structure, which may enhance not only intramolecular charge transfer but also intermolecular charge transfer, is preferred.

For this purpose, an ethylenediamine (eda)-bridged iron phthalocyanine (FePc) polymer [PcFe-(eda)]$_n$ was synthesized, then polarized by an electric field, giving a new type of low-dimensional photoconductive material, which exhibited much better photoconductivity than that of the monomer, FePc.

EXPERIMENTAL

Reagents and Equipment

Iron phthalocyanine (FePc), N,N′-dimethyl-4-aminobenzaldehyde-1,1′-diphenylhydrazone (DMPP), and N,N′-diethyl-4-aminobenzaldehyde-1-phenyl-1′-(α-naphthyl)hydrazone (α-NP) were synthesized in our lab. Ethylenediamine (eda), poly(vinylene difluoride) (PVDF), and other reagents were commercially available (A.R.).

IR spectra were recorded on a NIC-5DX Fourier transform infrared spectrometer; UV-Vis spectra of the samples ($\sim 10^{-3}$ mg/mL in DMF) were taken on a DU-50 spectrophotometer; elemental analyses data were determined on a Perkin−Elmer 240C elemental analyzer; DSC curves were recorded on a Perkin−Elmer DSC-7 Differential Scanning Calorimeter under N$_2$, scanning rate was 20°C/min; thermogravimetric analyses were performed on a PRT-1 model thermobalance in enclosed air; FT−IR Reflection Absorption Spectra (FTIR-RAS) were obtained on a FTS-185 IR spectrometer; angle-dependent XPS examinations were carried out by a ESCALAB MK-II X-ray photoelectron spectrometer, using a AlK$_\alpha$ X-ray source with an energy of 1486.6 eV, the electron taken off angles (the angle between the normal to the film surface and the entrance to the energy analyzer) were −15, 0, 15, 30, and 45°; the samples were also analyzed by a FE-IXG electron spin resonance (ESR) spectroscope as solid powder under room temperature, sweep range 3300 ± 500 G, microwave frequency 9.236 GHz, power 4 mW, modulation frequency 100 kHz, amplitude 6.3G, g-values and the areas of the absorption peaks were calibrated by standards of *Mn* and diamond, respectively.

Synthesis of Ethylenediamine-Bridged FePc Polymer [PcFe(eda)]$_n$

A mixture of 1.017 g FePc ($\sim$ 1.79 mmol) and 0.20 mL ethylenediamine ($\sim$ 2.67 mmol) in 80 mL DMF was stirred with N$_2$ under room temper-

ature for 72 h. Then the slurry was filtered, the filtrate was precipitated by water, and the precipitate was washed by water, and dried at 60°C in vacuum, giving 0.7925 g product as green powder (yield, 70.5%).

ANAL. Calcd. for C$_{34}$H$_{24}$N$_{10}$Fe [MW = 628.48]: C, 64.97, H,3.82, N,22.29. Found: C,62.40, H,3.71, N,20.87.

Preparation of the Electric Field Poled Film

A dispersion solution of [PcFe(eda)]$_n$ (0.4 wt %) and poly(vinylene difluoride) (PVDF) (1.6 wt %) in DMF was coated on Al substrate and heated at about 50°C in an electric field (E = 5 × 10^4 V/m). After the solvent evaporated an ordered film was obtained. The film was about 1 μm thick.

Photoconductivities of the Electric Field Poled Film

The electric field poled [PcFe(eda)]$_n$−PVDF film was taken as the charge-generation layer (CGL), associated with different charge-transportation layers (CTLs, 50 wt % DMPP or α-NP in bisphenol-A-polycarbonate, about 40 μm thick), giving a novel type of low-dimensional double-layered photoreceptor (P/R). Comparingly, the P/Rs consisting of a CGL made from FePc−PVDF (1 : 4 wt %) film with or without polarization by electric field and corresponding CTLs were also prepared. The photoconductivities of P/Rs were measured on a GDT-II model photoconductivity measuring device, using a 5 W, 24 V visible lamp as a light source to gain photoinduced discharge curves (PIDC) of P/Rs. From PIDC we obtained $\Delta V_1\%$, which is the percentage of potential discharge after 1 s of exposure, $t_{1/2}$, which is the time from the original potential to half under exposure, and $E_{1/2}$, which is the product of $t_{1/2}$ multiplied by I (intensity of light). The $E_{1/2}$ can indicate photosensitivity. The smaller the $E_{1/2}$ is, the higher the photosensitivity is.

RESULTS AND DISCUSSION

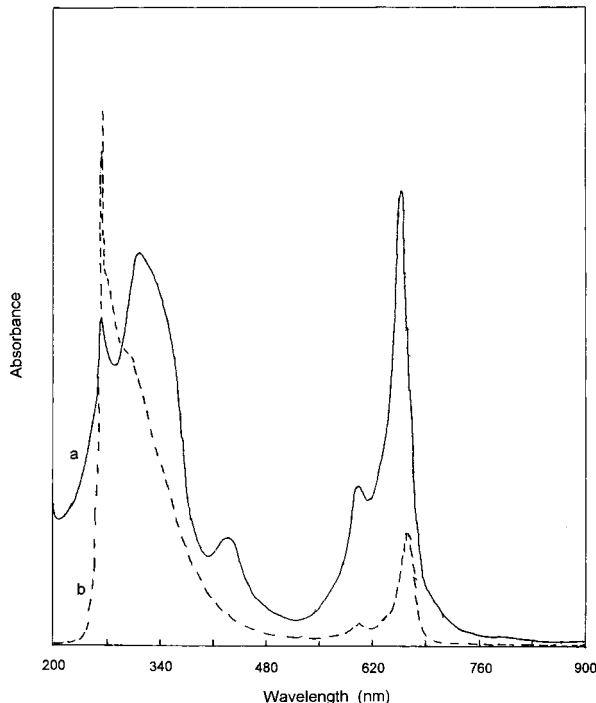### Synthesis of Phthalocyanine Polymer

Figure 1 was IR spectra of FePc and ethylenediamine-bridged FePc polymer [PcFe(eda)]$_n$. The polymer showed not only typical absorption at 1334, 1080, 915, 760, and 735 cm^{-1} of phthalocyanine, but also characteristic peaks at 3400 (N—H
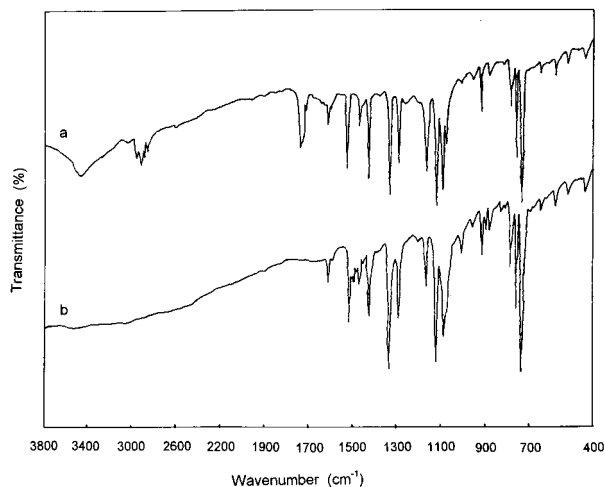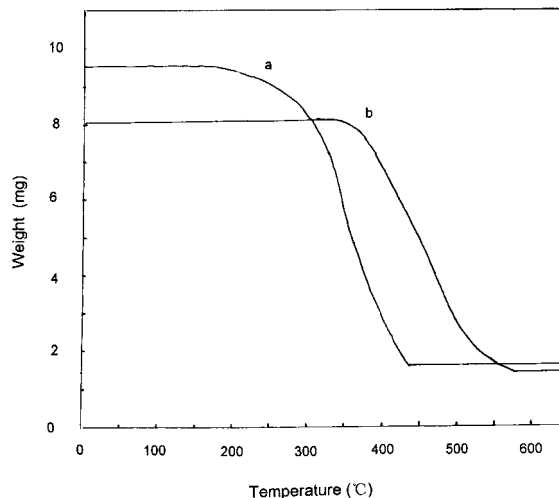
Figure 1 IR spectra of (a) [PcFe(eda)]$_n$; (b) FePc.

Figure 3 Thermogravimetric analyses of (a) [PcFe-(eda)]$_n$, 9.6 mg; (b) FePc, 8.1 mg.

stretching vibration), 2940 (C—H stretching vibration), and 1720 cm^{-1} (N—H bending vibration) of the ligand, ethylenediamine, suggesting that FePc really reacted with ethylenediamine.

The UV-Vis spectrum of [PcFe(eda)]$_n$ differed remarkably at the 200–400 nm range (Soret band) from that of the monomer, FePc (Fig. 2). Noticeably, a new peak at 436 nm appeared, which was ascribed to the charge transfer transi-

tions from full b$_{2g}$(d$_\Pi$) orbitals of Fe atoms in FePc to empty b$_{3u}$(2p$_x$*) of N atoms in ethylenediamine,[5] which furthermore supported the fact of the complexation of FePc and ethylenediamine.

From thermogravimetric studies of FePc and [PcFe(eda)]$_n$ (Fig. 3), we found that the polymer started to decompose in air at 184°C until 438°C, while FePc started to degrade in air at 354°C until 556°C. FePc exhibited higher thermal stability than [PcFe(eda)]$_n$. This result was easily understood. Moreover, from thermogravimetric data, we could estimate the degree of polymerization of [PcFe(eda)]$_n$. Because ethylenediamine given off during thermogravimetric procedure, it was assumed that the degradation residue was originated from the decomposition of Pc rings. Thus, the content of FePc moiety in the polymer was obtained as 92.81%, and the content by calculation was 90.45%, which indicated that the polymer, [PcFe(eda)]$_n$ was indeed synthesized, but the accurate MW of the polymer was not available because phthalocyanine polymer are slightly soluble even in DMF or chloronaphthlene.

Characterization of the Electric Field Poled Film

Displayed in Figure 4 were DSC curves of [PcFe(eda)]$_n$–PVDF film (1) and [PcFe(eda)]$_n$–PVDF film (2) coated with or without electric field, respectively. It was observed that the melting point (T_m) of 1 was 0.83°C higher than that of 2, and melting heat of 1 was 0.21 J/g greater than that of 2. What caused it? It was the effect of poling of the electric field. Due to molecular

**Figure 2** UV-Vis spectra of (a) [PcFe(eda)]$_n$, —; (b) FePc, $\cdots$.
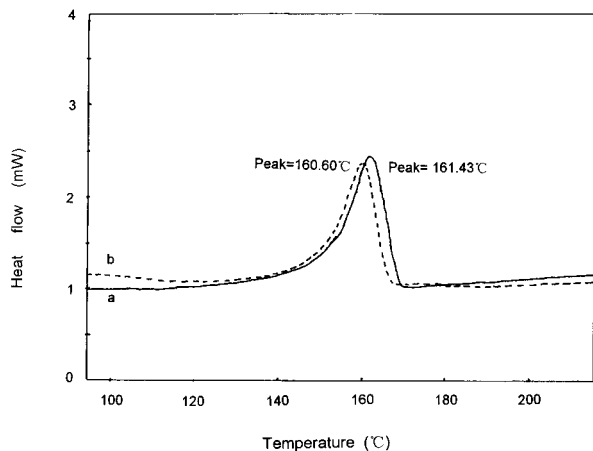
Figure 4 DSC curves of (a) [PcFe(eda)]$_n$−PVDF film coated in the electric field (1.68 mg, —); (b) [PcFe(eda)]$_n$−PVDF film coated without the electric field (1.54 mg, · · ·).

preferential alignment in the film poled by electric field, free energy of the film decreased, blocking the movements of polymer molecules, resulting in the changes of thermal properties of the film.

Presented in Figure 5 were the data of [PcFe(eda)]$_n$−PVDF film cast in an electric field from angle-dependent XPS examinations. The intensity ratios, Fe$_{3p3}$/C$_{1S}$ exhibited a peak as (the angle of the sample with respect to the analyzer) was 0°, implying the preferential orientation of the main chains of [PcFe(eda)]$_n$ normal to the film surface, i.e., Pc rings stacked parallel to the film surface.
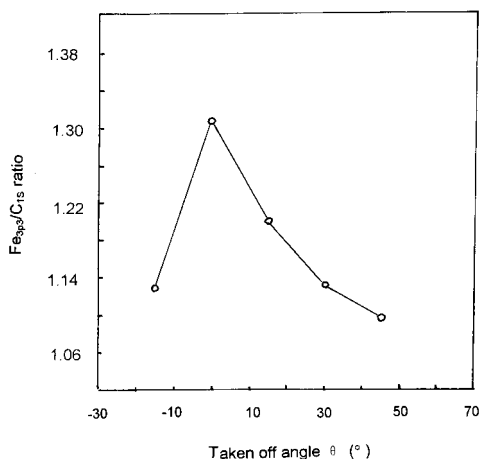
Figure 5 Fe$_{2p3}$/C$_{1s}$ ratios of the [PcFe(eda)]$_n$−PVDF film made in the electric field at different taken off angles.
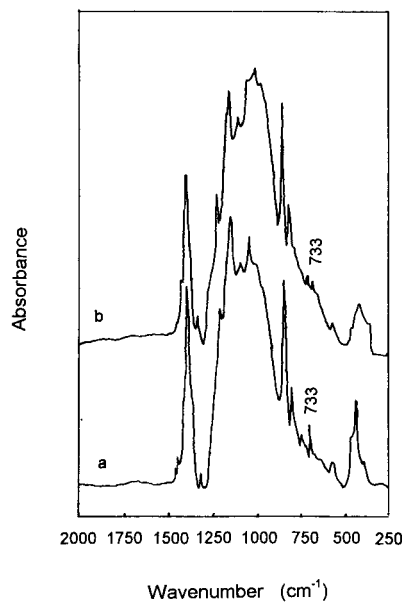
Figure 6 FTIR-RAS of the [PcFe(eda)]$_n$−PVDF film made in the electric field (a) GIR; (b) RIR.

FT−IR Reflection Absorption Spectroscopy (FTIR-RAS) (Fig. 6) also confirmed the result. When the infrared light incident at grazing angle (GIR), vibrations having transition moments approximately perpendicular to the surface are expected to appear with enhanced intensity while those having transition moments nearly parallel to the surface are expected to appear weakly or not at all comparing with those of incidence at small angle (RIR). In Figure 6, the peaks at 1231 and 1170 cm^{-1} that were assigned to C—F stretches of PVDF were stronger in GIR than those in RIR, while the peaks at 1073, 1030, and 1005 cm^{-1} that were assigned to C—C stretches of main chains in PVDF reduced to weaker shoulders compared with those in RIR, indicating that C—F bonds of PVDF oriented along the direction of the external electric field, perpendicular to the film surface, and main chains of PVDF aligned parallel to the film surface. Of particular interest was the absorption observed at 733 cm^{-1} in GIR, which was assigned as C—H out-of-plane bending mode in the phthalocyanine ring,[6] disappeared in RIR, suggesting that the dipolement of C—H out-of-plane vibration was perpendicular to the film surface, i.e., the phthalocyanine rings were polarized in the direction parallel to the film surface. This was coincident with the result from angle-dependent XPS examinations.

**Table 1   The Effects of Molecular Structure and Material Structure on the Photoconductivities of FePc and [PcFe(eda)]$_n$**

| CGL	CTL	E $(10^4$ V/m)	V_o (V)	V_R (V)	I (lux)	ΔV_1 %	$t_{1/2}$ (s)	$E_{1/2}$ (lux·s)
FePc	DMPP	0	996	177	800	20.19	3	2400
FePc	DMPP	5	1492	281	800	27.43	2.3125	1850
FePc	α-NP	0	894	173	800	34.89	1.875	1500
FePc	α-NP	5	943	185	800	37.19	1.6875	1350
[PcFe(eda)]$_n$	DMPP	0	1024	202	800	44.59	1.25	1000
[PcFe(eda)]$_n$	DMPP	5	1037	182	800	63.45	0.5	400
[PcFe(eda)]$_n$	α-NP	0	1164	140	800	60.21	0.625	500
[PcFe(eda)]$_n$	α-NP	5	2062	174	800	82.35	0.25	200
[PcFe(eda)]$_n$	α-NP	5	1843	140	200	62.27	0.6875	137.5

Photoconductivities of the Electric Field Poled [PcFe(eda)]$_n$–PVDF Film

Shown in Table I were the photoconductive data of FePc–PVDF film and [PcFe(eda)]$_n$–PVDF film prepared with or without the electric field, respectively. From the data, it was found that the polymer exhibited much better photoconductivities than the monomer, FePc. When α-NP was taken as CTL, the polymer had a much smaller $t_{1/2}$ (0.625 s), a much greater ΔV_1% (60.21%), and a much smaller $E_{1/2}$ (500 lux·s). The photoconductivity of [PcFe(eda)]$_n$ rised two times greater than that of FePc. Interestingly, electric field poling greatly influenced the photoconductivity of [PcFe(eda)]$_n$, while the electric field had little effect on the photoconductivity of FePc. For [PcFe-(eda)]$_n$, when α-NP as CTL, $t_{1/2}$ decrease to 0.25 s from 0.625 s, ΔV_1% rised to 82.35% from 60.21%, $E_{1/2}$ reduced to 200 lux·s from 500 lux·s after orientation by the electric field. The photoconductivity of [PcFe(eda)]$_n$ improved by 1.5 times! Comparingly, the photoconductivity of FePc merely rised by 11.1% after poled by the electric field.

What caused it? We thought that it was the low dimension of molecular and material structure of the electric field poled [PcFe(eda)]$_n$–PVDF film that probably accounted for the improvement of photoconductivity. The effects of molecular structure may be: (1) after the complexation of FePc and ethylenediamine, because of the overlapping of Π-Π orbitals in phthalocyanine rings, an "electron channel" may form along the main chains of [PcFe(eda)]$_n$, in which electrons were easy to migrate; (2) owing to the occurring of the charge transfer from full $b_{2g}(d_\Pi)$ orbitals of Fe atoms to the empty $b_{3u}(2p_x^*)$ of N atoms in [PcFe(eda)]$_n$

(the peak at 436 nm in Fig. 2), the photogenerated charge carrier pairs (e-h pairs) would separate immediately, raising the photogenerating efficiency, not like as in FePc, due to the spin-orbital coupling between the excited orbitals and the unpaired electrons in d orbitals of Fe atoms, the excited FePc may go back to the ground state with energy decaying. The assumption was supported by ESR study. As illustrated in Figure 7, [PcFe-(eda)]$_n$ showed superhyperfine splitting caused by ^{14}N atoms in ethylenediamine. Interestingly, FePc and [PcFe(eda)]$_n$ both exhibited a narrow absorption that g-value was 2.0014, close to that of free electron. For FePc, the peak-peak width of the absorption was 11.94 G, and for [PcFe(eda)]$_n$, the peak-peak width of the absorption was 9.44 G. Snow[7] thought that such narrow lines were usually associated with mobile electrons, so the spin density of the sample was the charge carrier
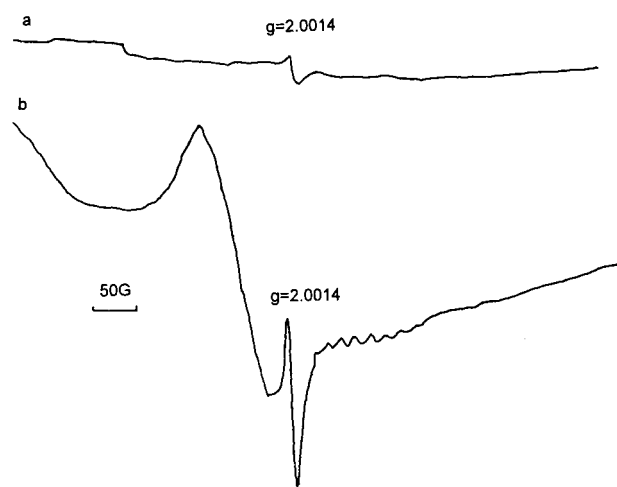
Figure 7   ESR spectra of (a) FePc; (b) [PcFe(eda)]$_n$.
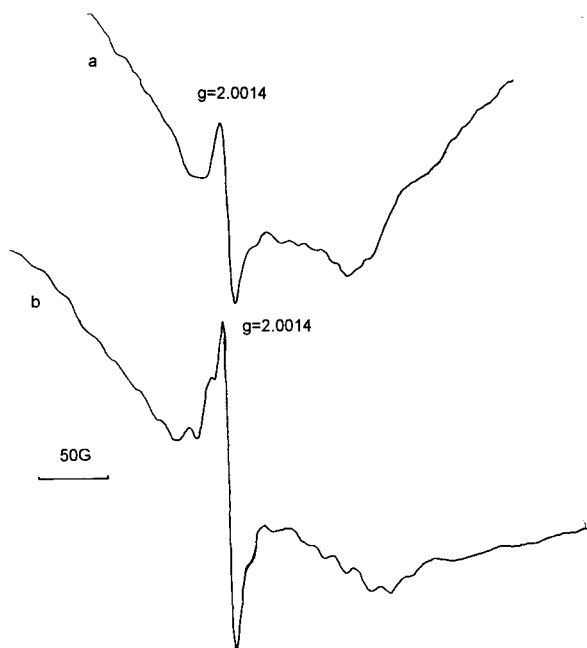
Figure 8 ESR spectra of (a) $[PcFe(eda)]_n$–PVDF film made without the electric field, receiver gain 4×10^2; (b) $[PcFe(eda)]_n$–PVDF film made with the electric field, receiver gain 2×10^2.

density. By calculation, we found that the charge carrier density of $[PcFe(eda)]_n$ was 1.447×10^{16} e/g, about three times than that of FePc (3.486×10^{15} e/g). Just because bridging bonds were formed between Pc rings in $[PcFe(eda)]_n$, Π-Π orbitals overlapping was larger, and spin exchange interactions were stronger, resulting in the narrowing of spin sign, which was favorable of hopping and migration of electrons, subsequently raising the charge carrier density and the photoconductivity. The effects of electric field poling may be: (1) after electric field orientation, $[PcFe(eda)]_n$ was aligned in the direction perpendicular to the film surface, and the direction

agreed with the direction of photoconduction; (2) the electric field poling may enhance intramolecular and intermolecular charge transfer, and the dipole–dipole interactions of polymers. The two reasons were suggested to contribute to the improvement of photosensitivity, which was also proved by ESR analyses. In Figure 8, through electric field poling, superhyperfine splittings or minor peaks appeared due to the change of material structure of $[PcFe(eda)]_n$–PVDF film, and the charge carrier density increased by 1.87 times from 9.237×10^{14} e/g to 2.563×10^{15} e/g. Thus, the photoconductivity improved dramatically.

From the above, we could say that molecular design and material engineering may be a good approach for the improvement of photoconductivity of the material.

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