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# A New Polymorph of Hydroxyaluminum Phthalocyanine. Characterization and Photoactivity

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Sublimed films of α-form hydroxyaluminum phthalocyanine (α-PcAlOH) can be transformed into a novel polymorph by a treatment with aqueous acid solutions. The spectroscopic characterization of the new polymorph, showing its particular visible and IR spectra and X-ray diffraction pattern was achieved by comparing with other polymorphs. The dimorphic transformation of PcAlOH is also associated with a dramatic enhancement in photoactivity as shown in the performance of a photoelectrochemical cell based upon a PcAlOH/redox junction.

Phthalocyanines are known to exist in different polymorphic forms, depending on their molecular stacking arrangements in the solid state.1) The transformation of one form into another one (dimorphic transformation) can be accomplished by several techniques including thermal2) and organic solvent treatments,3) acid ball-milling4) and inert solvent grinding.5) It has been shown that the metastable α-form of metal phthalocyanine is transformed into the stable β-form through various intermediate forms depending on the properties of organic solvents.3) Their forms are distinguished by X-ray diffraction, electron microscopy techniques and optical (visible and IR) spectroscopy. The dimorphic transformation reorganizes the molecular arrangement within the solids and at the same time changes the optical, electrical and photoconductivity properties of the phthalocyanines. In this paper, we would like to report a new dimorphic transformation of the α-form of hydroxyaluminum phthalocyanine (induced by an acid treatment) into a new polymorph and the dramatic enhancement of its photoactivity.

Hydroxyaluminum phthalocyanine (PcAlOH) compound was prepared as follows. Chloroaluminum phthalocyanine was first synthesized by heating o-phthalonitrile and $AlCl_3$ in quinoline, and the washed product was heated in 30% $NH_4OH$ solution in the presence of pyridine6) to give PcAlOH. The product was then washed by repeated solvent extraction techniques. The α-form was obtained by first adding PcAlOH to concentrated sulfuric acid, then pouring the solution into ice water and finally filtering the solid. Thin films of α-form PcAlOH were obtained by evaporation under vacuum ($10^{-5}$-$10^{-6}$ Torr) on substrates (pyrex and tin-oxide-glasses, polished aluminum plate, $CaF_2$ plate) maintained at room temperature. Absorption spectra were recorded by an LKB 4050 spectrometer, FT-IR spectra by a Nicolet 170 SX and

X-ray diffraction patterns by a Siemens diffractometer model D 500 (employing CuK$_\alpha$ radiation). The treatment consisted simply of dipping the sublimed thin film samples into aqueous acid solutions at room temperature. The photoelectrochemical cell was constructed in a one compartment glass cell with a Pt foil (3 x 3 cm$^2$ x 0.1 mm) as a counter electrode and an aqueous electrolyte ($10^{-1}$ M $Na_2SO_4$, $10^{-4}$ M $I_3^-$, and $10^{-1}$ M $I^-$). The PcAlOH film side on NESA was faced to the illumination, and the counter electrode was placed 1 cm behind the NESA glass. The cell voltage and current were measured using a Keithley 616 digital electrometer. Action spectra measurements were made with a Yvon-Jobin monochromator and a 300 W tungsten lamp.

The visible absorption spectra of a thin film of PcAlOH as deposited (a) and after 20 h of exposure to an aqueous potassium monophthalic acid solution (2%, curve g) are shown in Fig. 1. The untreated film presented only one absorption band at 640 nm, a characteristic of the α-form. When dipped in a 2% aqueous acid solution (e.g. potassium monophthalic acid, nitrophthalic acid, trifluoroacetic acid or hydrochloric acid), PcAlOH thin films showed different absorption spectra. A new and intense absorption peak appeared at 840 nm, accompanied with a decrease in the intensity of the peak at 640 nm. The new peak at 840 nm is not the protonated form of PcAlOH because extensive washing of PcAlOH films with water showed the same absorption spectrum. Based on the absorbance of the peak at 840 nm, the efficiency of the acid treatment of similar films is as follow: HCl > $CF_3CO_2H$ > nitrophthalic acid ~ phthalic acid.

Figure 2 shows X-ray diffraction patterns of the metastable α-form (a) and the new form n (b) of PcAlOH after treatment with aqueous acid solution.

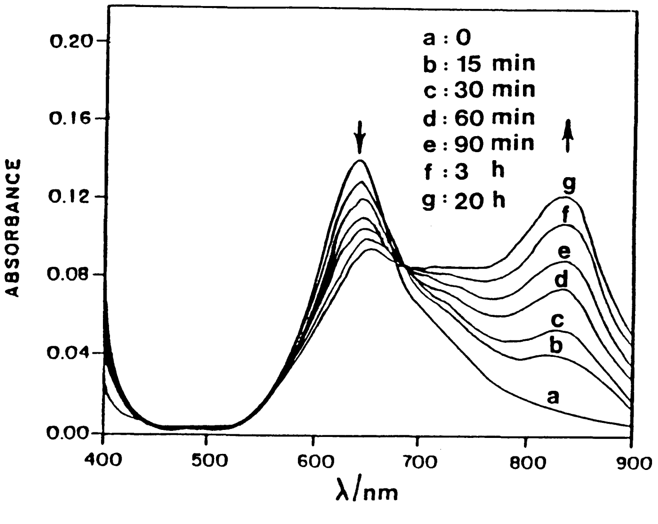

Fig. 1. Absorption spectra of PcAlOH before (a) and after acid treatment (b - g).

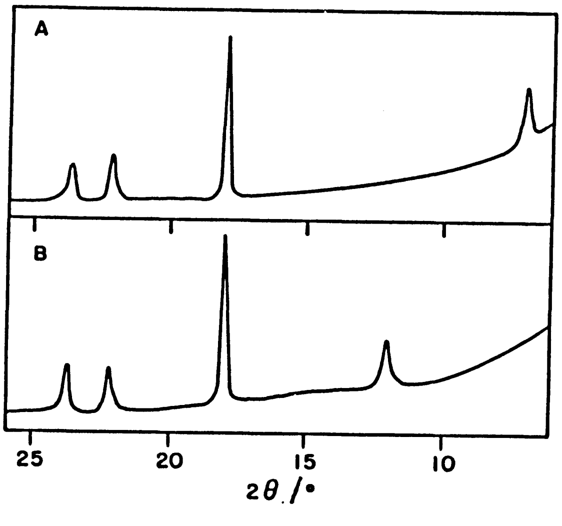

Fig. 2. X-Ray diffraction patterns of PcAlOH before (a) and after acid treatment (b).

FT-IR spectra of PcAlOH thin film evaporated on $CaF_2$ substrates before (a) and after (b) treatment with acids are shown in Fig. 3. Noticeable differences in the IR spectra were observed, particularly in the area of 1000 to 1200 $cm^{-1}$, where new absorption peaks appeared at 1134, 1118, and 1065 $cm^{-1}$ for the new polymorph. The formation of a complex between PcAlOH and phthalic acid can be eliminated because no IR carbonyl absorption was observed for the treated film (Fig. 3b).

The action spectra of PcAlOH films before (a) and after the treatment with phthalic acid (b) are shown in Fig. 4. The photovoltaic effect occurs mainly at the interface of PcAlOH and electrolyte. The photoresponse peak coincides fairly well with the absorption peak. The photovoltaic properties of thin PcAlOH film (230 Å) before and after treatment are summarized in Table 1.

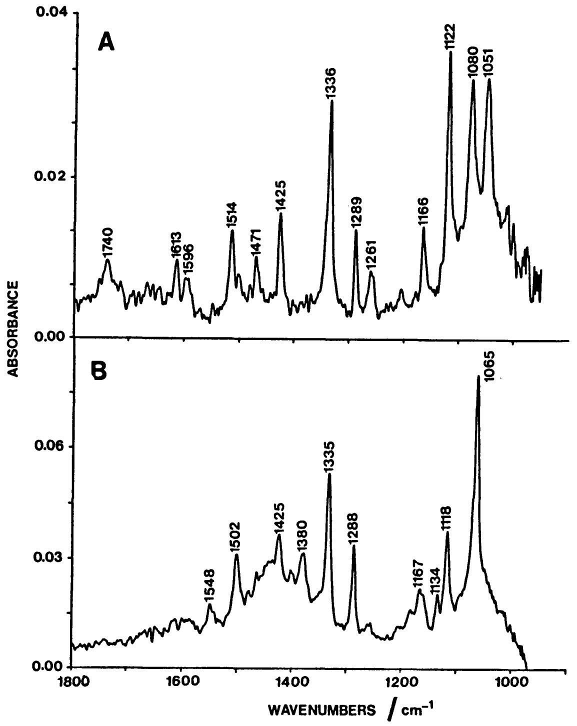

Fig. 3. Infrared spectra before (a) and after (b) acid treatment.

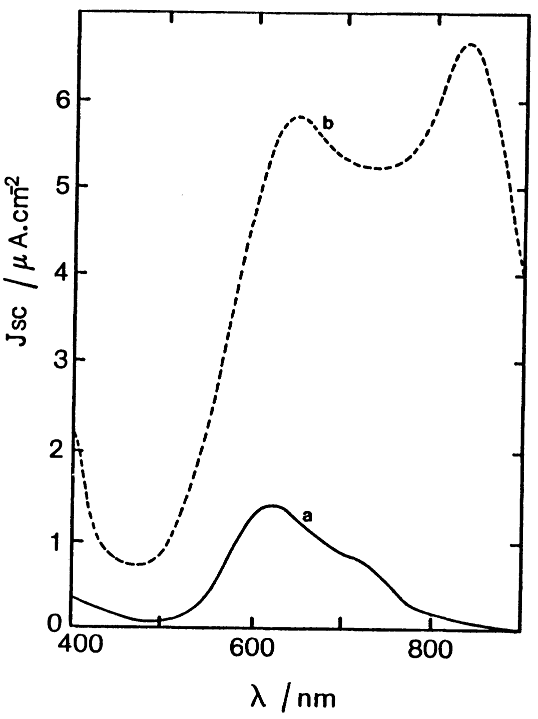

Fig. 4. Action spectra of a NESA/ PcAlOH/$I_3^-$/$I^-$/Pt cell before (a) and after (b) acid treatment.

Table 1. Electrical characteristics of NESA/PcAlOH/$I_3^-$/$I^-$/Pt photoelectrochemical cells (white light, 10 mW/$cm^2$)

| Redox | Thickness<br>Å | Treatment | $J_{sc}$<br>$\mu A \cdot cm^{-2}$ | $V_{oc}$<br>mV | ff | $\eta$<br>$10^{-3}$% |
|---|---|---|---|---|---|---|
| $I_3^-/I^-$ | 230 | before | 13.5 | 88 | 0.32 | 3.8 |
| $I_3^-/I^-$ | 230 | after | 31.5 | 102 | 0.53 | 17.0 |

Results from absorption spectra and X-ray diffraction indicate that the sublimed PcAlOH film $\alpha$-form is directly transformed into the new polymorph after exposure to aqueous acid solutions. The visible absorption spectrum of the new polymorph resembles that of the X-form for other metal phthalocyanines.[3)] However, the IR absorption spectrum and the X-ray diffraction patterns which present absorption peaks and diffraction lines different from those observed for the middle energy polymorphs (e.g. $\tau$, X, R or $\varepsilon$-form) are estimated to indicate a novel polymorph of PcAlOH. The structure of the $\alpha$ and $\beta$ form of PcM (M = divalent metals) have been determined and the structure of polymorphs such as X or $\varepsilon$-form has been assumed to have a dimeric structure of two neighbouring Pc molecules in a staggered configuration.[1,7)] The new polymorph PcAlOH could have a similar structure but because of the trivalent nature of the Al metal, other configurations are possible. Further structure determination is presently undertaken.

The photoactivity of the new PcAlOH polymorph is substantially increased by a factor of 6 for an optimized PcAlOH thin film and this is mainly due to a broader absorption band and an improvement of the junction rectifying behavior (i.e. decrease of the cell resistance up to a factor of 4 and increase of the fill factor up to 0.77, the highest value observed for an organic semiconductor) of an electrochemical cell NESA/PcAlOH/$I_3^-$/$I^-$/Pt.

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