Evolution of the Photoactivity of Chloroaluminum Phthalocyanine and Related Materials upon Heat Treatment

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Thin films and powders of chloroaluminum phthalocyanine (ClAlPc) have been heat treated at 300 °C over various time periods (1–60 min). The same treatment has been applied to a highly photoactive ClAlPc, which is both structurally and chemically modified by anion uptake (Gastonguay, L.; et al. *J. Electrochem. Soc.* **1992**, *139*, 337). The evolution of the photoactivity of the films (monitored photoelectrochemically) as well as their absorbance in the visible and near-infrared (NIR), their surface morphology, and their crystalline structure have been examined upon heating. Weight losses of the powders and their differential thermal calorimetry have also been measured. After heat treatments at 300 °C for 60 min the following characteristics are obtained for all films: (i) a blue-shifted absorbance in the visible (the maximum of the Q band is at 630 nm); (ii) a low photoactivity of the resulting stable phase; (iii) the disappearance of the absorbance in the NIR for the structurally and chemically modified ClAlPc. This goes along with a drop of the photoactivity by at least one order of magnitude; (iv) a common film morphology (sharp-cornered parallelepipedic needles perpendicular to the substrate); (v) the same electron diffraction pattern for all films, characterized by four interplanar distances for $d \geq 5$ Å. The electron diffraction patterns may be interpreted either in terms of a slight modification of the triclinic lattice reported for ClAlPc single crystal or in terms of a cofacial stacking of the ClAlPc molecules. Heat treatments at 300 °C of ClAlPc thin films also demonstrate that Pc layers sublimed at 2000 Å min^{-1} are amorphous or organized only at very short range, for more than 75% of the film. This characteristic is responsible for the easy diffusion of H$^+$ in the disorganized phase, followed by its reaction with O_2^- and the uptake of anions which compensates for the loss of negative charges in highly photoactive structurally and chemically modified ClAlPc. The anions (Cl$^-$, Br$^-$, I$_3^-$, I$^-$) taken up during the modification of ClAlPc are lost as hydrogen halides or I$_2$ during the heat treatment. The maximum loss rate happens at temperatures between 130 and 150 °C depending upon the anion involved.

Introduction

Phthalocyanines (Pcs) are one of the most important families of pigments used in xerographic imaging where their photoconductive properties are appreciated in charge generating layers.[1-3] Recently, interest has been focused on these dyes because some of the Pcs are sensitive in the near-infrared region (NIR; 750–850 nm). This is an essential characteristic for the development of laser beam printers and digital copiers equipped with laser diodes or LED arrays.[4-7]

Molecular solids like Pcs display various polymorphic structures with extremely different photoconducting properties. As a general rule, it appears that the Pcs absorbing in the NIR are also the ones which show the largest photoactivity under polychromatic illumination. This is true, for instance, for x-H$_2$Pc (8) τ-H$_2$Pc,[8,9] solvent-modified MgPc,[10] and for some Pcs containing tri- or tetravalent metals.[11,12]

Changes in the absorption spectra of the Pcs are related to the arrangement of the molecules in the solid. The electronic spectrum of x-H$_2$Pc can be interpreted as that of a dimer of parallel macrocycles.[13] On the other hand, Pcs with a trivalent[14,15] or tetravalent metal characterized by only one axial ligand[16] are found to be cofacially stacked in a linear assembly aligned along the metal halide or metal–oxo bond, or are in an assembly where molecules are staggered to form a slipped stack arrangement. These changes in the absorption spectra are interpreted in terms of interactions between the transition dipoles situated in

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the plane of the macrocycles. From this theory[17] a blue or a red shift (relative to the monomer absorption spectrum in solution) is expected for the cofacial or slipped stack arrangements, respectively. The latter arrangement is the most photoactive.

Our interest in Pcs has been focused on aluminum phthalocyanines and particularly on chloroaluminum phthalocyanine (ClAlPc). It is possible to induce structural modifications of the pigment and follow their influence on the photoactivity of the film by measuring its photoelectrochemical characteristics. The goal is to unravel the parameters having the largest influence on the photoactivity of this molecular semiconductor.

ClAlPc is a blue dye absorbing strongly in the visible. The film absorbance spans the 550–850-nm region (Q band) with a maximum at about 730 nm (where the linear absorption coefficient it 5×10^4 cm^{-1}) and a shoulder at about 670 nm. Under polychromatic illumination of 35 mW cm^{-2}, the short circuit photocurrent, J_{sc}, of a 4000-Å-thick ClAlPc film is 0.25 mA cm^{-2} (immediately after contact with an I_3^-/I^- redox solution at pH 3).[18]

For a sublimation rate of 2000 Å min^{-1}, the ClAlPc film is made of a tight assembly of rods grown in a direction perpendicular to the substrate. The rods have a mean diameter of 500 Å and a length equivalent to the thickness of the film. Changing the sublimation rate changes only the diameter of the crystallites (from a mean value of about 1500 Å for a sublimation rate of 200 Å min^{-1} to 400 Å for 10 000 Å min^{-1}).[19,20] All films are porous. The ClAlPc rods are partially amorphous and partially crystalline.[21] However, the ratio of these two phases is unknown. The crystalline phase displays the same triclinic slipped stack structure as the one reported by Wynne[14] for ClAlPc single-crystal platelets. In the films, the planes of the phthalocyanine macrocycles are parallel to the substrate[21,22] and seem to correspond to the plane $(3\,1\,\overline{13})$ of the crystal lattice. This orientation agrees with the interplanar distances, d, observed by TEM for $d > 4$ Å.[20] X-ray diffraction of ClAlPc powder and of a thick (15 μm) film yields essentially one major peak at $2\theta = 27.09°$ (CuKα) corresponding to $d = 3.29$ Å. This is the macrocycle interdistance in the crystal.[23]

ClAlPc is a p-type semiconductor. This electrical property results from the interaction of the Pc with oxygen to form $Pc^+O_2^-$.[24] It is possible to induce structural transformations in ClAlPc by contact of the thin film with aqueous acidic solutions containing various salts.[18,19] The chemical composition of the film changes during these transformations. There is a diffusion of H^+ into the solid. Upon contact with H^+, the following reaction happens in the film:

$$Pc^+O_2^- + H^+ \rightarrow HO_2^{\bullet} + Pc^+$$

Anions from the solution are then uptaken in the solid phase in order to maintain the electrical neutrality of the film. The uptake of I_3^-, I^-, or Br^- has been demonstrated by X-ray absorption spectroscopy.[25,26] As ClAlPc transformations were performed with 15 different salts, other anions were also expected to be found in the structure of the modified films. However, only two kinds of absorption spectra have been observed after all the transformations: the first one is characterized by the growth of a peak at 835 ± 8 nm at the expense of the Q band absorption in the visible (I-type transformation). The second one is characterized by both a blue and red shift of the Q band resulting in peaks at 638 ± 11 and 805 ± 6 nm, respectively[18] (H-type transformation). Transformations I or H performed on ClAlPc powder demonstrate a partial hydrolysis of the pigment (20–30%). The chemical composition of the powder after I_3^- or Br^- uptake is either $(ClAlPc + HOAlPc)^{0.10+}(I_3^-)_{0.10}$ or $(ClAlPc + HOAlPc)^{0.14+}(Br^-)_{0.14}$.[23]

The structural and chemical modifications of ClAlPc films are interesting because they can result in large increases of the photoactivity (depending upon the salt used).[18] The best J_{sc} values for I-type transformations are obtained with KI (J_{sc} = 0.80–0.85 mA cm^{-2}) while for H-type transformations, the best values are obtained with KCl or KBr (J_{sc} = 0.85–1.0 mA cm^{-2}). All short-circuit photocurrents are measured under polychromatic illumination of 35 mW cm^{-2} in an I_3^-/I^- electrolyte at pH 3 after completion of the transformation. The shape of the action spectra for both kinds of transformations only differ above 700 nm, extending more in the near infrared region in the case of transformation I. Curiously, there is no peak in the action spectrum of ClAlPc after H-type transformations that corresponds to the peak at 637 ± 11 nm in the absorption spectrum.

Both transformations result in some changes in the film morphology. They are minimal after an I-type (a slight increase in rod diameter at the expense of the number of rods per unit area). However, spectacular changes occur for the most photoactive H-type transformations. In this case, the rods are transformed into needles of about the same section but these needles have their long axis oriented in a plane parallel to the surface. This change of 90° in the orientation of the molecule is also observed by X-ray absorption spectroscopy at the C_{1s} and N_{1s} edges.[22]

Structural changes also occur during both transformations of ClAlPc films. It is somewhat puzzling that both the I and H kinds of modifications seem to produce the same electron diffraction pattern, which is different from the non transformed film. It can be fitted by a monoclinic structure. Some amorphous regions are still present in the transformed film. The X-ray diffraction diagram of a 15-μm-thick sublimed ClAlPc film or the ClAlPc powder is characterized by a very strong peak at $2\theta = 27.09°$ (d = 3.29 Å). After transformation by I_3^- (I-type) or Br^- (H-type) uptake, a new peak appears in the diffraction diagram at $2\theta = 25.81°$ (d = 3.45 Å). The immersion of ClAlPc in

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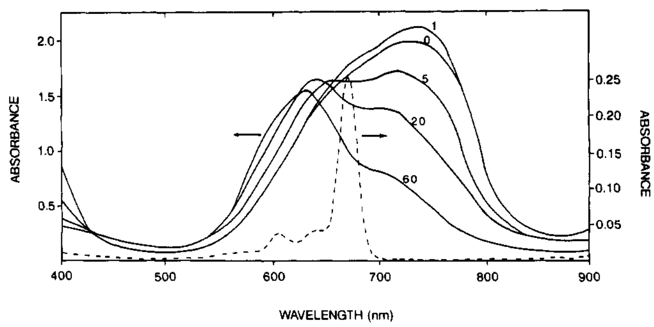

Figure 1. Evolution of the absorption spectrum of a 4000-Å-thick ClAlPc film after heat treatments at 300 °C for various time periods in min. The absorption spectrum of ClAlPc in solution (in arbitrary units) is given for comparison.

the aqueous solutions of I_3^- or Br^- results only in a partial transformation of the material. For the ClAlPc powder, the intensity of the new peak at $2\theta = 25.81°$ represents only 11% of the intensity of the peak at $2\theta = 27.09°$. The percentage rises to 47% for the film of the same material.[23]

The results presented in this paper are related to the behavior of ClAlPc films (before and after transformation) during heat treatment. Changes in absorbance, photoactivity, morphology, and crystalline structure of the films have been monitored in order to shed more light on this complex system.

Experimental Section

The ClAlPc synthesis and its elemental analysis have been given elsewhere.[19] The electrode preparation (sublimation of ClAlPc films, under vacuum, onto SnO_2 (ρ_s = 25–30 Ω sq^{-1})), their electrochemical measurements (always performed with an I_3^-/I^- (0.005 M/0.4 M) solution at pH 3 (HCl)) as well as the sample preparation and the deduction of interplanar distances for transmission electron microscopy (TEM) have been explained in detail in ref 18.

Heat treatments of nontransformed and transformed ClAlPc films were first performed under a flow of N_2. All measurements reported in the result section were however obtained in ambient air because no difference was found in the results by switching from N_2 to air. Films were usually heat treated at 300 °C for periods of 1–60 min but various temperatures ranging from 100 to 400 °C were also used.

Thermogravimetric analyses (TGA) were used to measure eventual weight changes of nontransformed and transformed ClAlPc powders under heat treatment. The thermal transition curves were also recorded on the same powders by differential scanning calorimetry (DSC). Both TGA and DSC measurements were performed on a Shimadzu TGA/DSC Model 50 instrument at a scanning temperature rate of 10 °C min^{-1} under a nitrogen flow of 20 mL min^{-1}.

Results

Absorption Spectra and Photoelectrochemistry. Figure 1 presents the evolution of the absorption spectrum of a 4000-Å-thick ClAlPc film after being heat treated at 300 °C for various time periods given in min. From this figure, it can be seen that there is a progressive blue shift of the Q band maximum from 730 to 630–640 nm. A slight and reproducible increase in the film absorbance also appears after 1 min at 300 °C.

The corresponding short-circuit photocurrents, J_{sc}, and open-circuit photovoltages, V_{oc}, of heat-treated ClAlPc films are given in Table I. As all measurements were performed in I_3^-/I^- solution at pH 3, the ClAlPc films have the possibility to be modified, as previously reported,[25] by I_3^- uptake. However, there is barely any I-type modification of the films after a heat treatment of 5 min, and no modification at all after heat treatments of 20 or 60 min. J_{sc} and V_{oc} values reported in Table I for 0 and 1 min have of course been measured after completion of the I-type transformation. The higher J_{sc} found after 1 min is in agreement with the improved absorbance of the film.

Table I. Evolution of the Short-Circuit Photocurrent, J_{sc}, and Open-Circuit Photovoltage, V_{oc}, of Nonmodified ClAlPc Films[a] as a Function of the Heat Treatment Time at 300 °C

time (min)	J_{sc}[b] (mA/cm²)	V_{oc}[b] (mV)	time (min)	J_{sc}[b] (mA/cm²)	V_{oc}[b] (mV)
0	0.89	96	20	0.13	16
1	1.00	95	60	0.14	18
5	0.25	16			

[a] Sublimation rate: 2000 Å/min. Thickness: 4000 Å. [b] Polychromatic illumination at 35 mW/cm². Redox electrolyte: I_3^-/I^- (0.005 M/0.4 M) at pH 3.

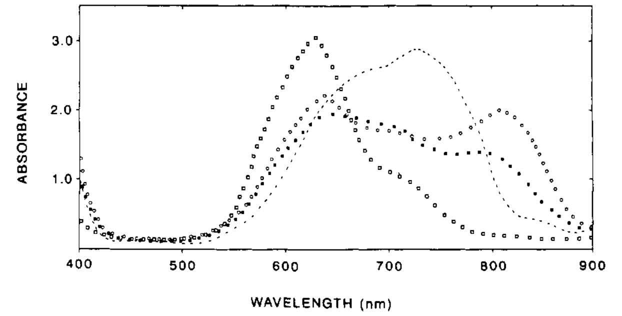

Figure 2. Evolution of the absorption spectrum of a 4000 Å thick ClAlPc film (- - -) which has been first H-type modified by immersion in an aqueous acidic solution containing 0.1 M of KCl (○), then heat treated at 300 °C during 1 min (■) or 60 min (□).

Heat treatments have also been performed at 100 °C on ClAlPc films with the result that, within experimental error, there is no detectable change in the photoactivity of the films, even after heat treatment for 2 h at that temperature. Heat treatments have also been performed for 1 min on a series of ClAlPc films at temperatures varying between 100 and 400 °C, followed by the measurement of their absorption spectra and photoactivities in I_3^-/I^- solution. J_{sc} values remain constant at about 0.8 mA cm^{-2} from 100 to 200 °C, then increase up to 1.0 mA cm^{-2} at 300 °C (the same value as the one reported in Table I). A decrease in J_{sc} (down to 0.48 mA cm^{-2} at 400 °C) is observed for temperatures above 300 °C. Accordingly, there is also a blue shift in the Q band maximum of the absorption spectrum of the ClAlPc film.

Figure 2 shows the evolution of the absorption spectrum of a 4000-Å-thick ClAlPc film which has been first H-type modified by 12-h contact with an aqueous acidic solution containing 0.1 M of KCl (or KBr) (○) and then heat treated at 300 °C during 1 (■) and 60 min (□). The NIR peak which is characteristic of the H-type modification completely disappears after 60 min of heat treatment. The final spectrum shows a maximum absorbance of the Q band at 630 nm, a wavelength similar to the blue shifted absorption peak always present in the spectrum after H-type modification.

The corresponding short-circuit photocurrents and open-circuit photovoltages of heat treated ClAlPc films following their H-type modification by KCl are given in Table II. As for the as-sublimed ClAlPc films (Table I), J_{sc} and V_{oc} values reported in Table II indicate a drastic decrease of the photoactivity after heat treatments ≥5 min. On the other hand, contrarily to what is happening

Table II. Evolution of the Short-Circuit Photocurrent, J_{sc}, and Open-Circuit Photovoltage, V_{oc}, of ClAlPc Films[a] Modified with KCl or KI as a Function of the Heat Treatment Time at 300 °C

salt	time (min)	J_{sc}[b] (mA/cm^2)	V_{oc}[b] (mV)	salt	time (min)	J_{sc}[b] (mA/cm^2)	V_{oc}[b] (mV)
KCl	0	1.00	110	KI	0	0.85	95
	1	0.64	64		1	0.56	60
	5	0.21	17		5	0.19	16
	20	0.11	16		20	0.12	16
	60	0.12	18		60	0.11	17

[a] Sublimation rate: 2000 Å/min. Thickness: 4000 Å. [b] Polychromatic illumination at 35 mW/cm^2. Redox electrolyte: I_3^-/I^- (0.005 M/0.4 M) at pH 3.

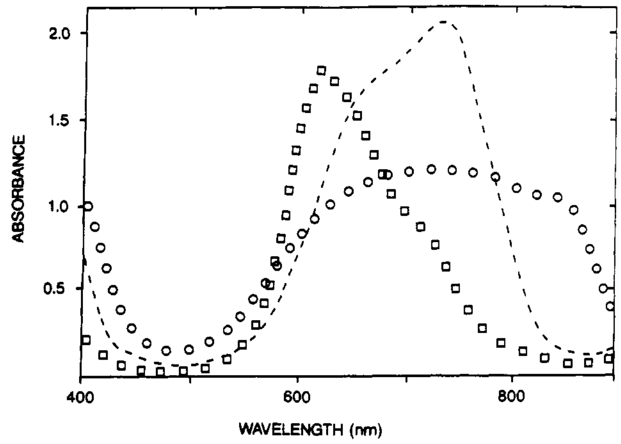

Figure 3. Evolution of the absorption spectrum of a 4000-Å-thick ClAlPc film (- - -) which has been first I-type modified by immersion in an aqueous acidic solution containing 0.1 M of KI (○) and then heat treated at 300 °C during 60 min (□).

with as-sublimed ClAlPc, the photoactivity of the modified film drops after only 1 min at 300 °C. This is accompanied by a decrease of the NIR absorbance (Figure 2).

When H-type modified ClAlPc films are heat treated at 200 °C for 120 min, a value of J_{sc} = 0.4 mA cm^{-2} is obtained. Such a decrease in photoactivity is obtained at 300 °C after a heat treatment of less than 5 min (Table II).

Figure 3 shows the absorption spectrum of an I-type ClAlPc film, modified by 12-h contact with an aqueous acidic solution containing 0.1 M KI (○), followed by a 60-min heat treatment at 300 °C (□). The corresponding J_{sc} and V_{oc} values for various heat treated films at 300 °C are also reported in Table II. The same conclusions about the photoactivity can be drawn for I or H type modified ClAlPc films.

Figure 4 presents the action spectra (normalized at 100% of their maximum) of a ClAlPc film 4000 Å thick, which has been first H-type modified with KCl during 12 h (○) and then heat treated at 300 °C during 1 min (■) and 60 min (□). Although after 1 min at 300 °C, J_{sc} decreases from 1.0 mA cm^{-2} to 0.64 mA cm^{-2} under polychromatic light (Table II) and from a maximum quantum efficiency of 16% to 9%, it is important to notice that there is barely no change between the shapes of the curves represented by the open circles and full square points of the action spectra. On the other hand, the corresponding absorption spectra (Figure 2) display a marked decrease of the absorbance of the NIR peak. The quantum efficiency of the modified film after 60 min of heat treatment at 300 °C is only 0.6%. This decrease in the photoactivity of the ClAlPc film confirms the statement made about the NIR band being responsible for the high photoactivity of ClAlPc[18] or the other Pcs with similar long wavelength absorption.[8-12] It also shows that the highly photoactive structure which is obtained for ClAlPc after H-type modification is quite unstable and can be easily transformed to a stable but poorly photoactive structure by increasing the heat treatment temperature.

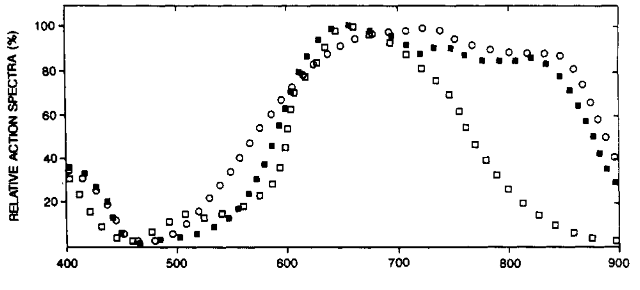

Figure 4. Evolution of the action spectrum of a 4000-Å-thick ClAlPc film which has been first H-type modified by immersion in an aqueous acidic solution containing 0.1 M of KCl (○), followed by a heat treatment at 300 °C during 1 min (■) and during 60 min (□).

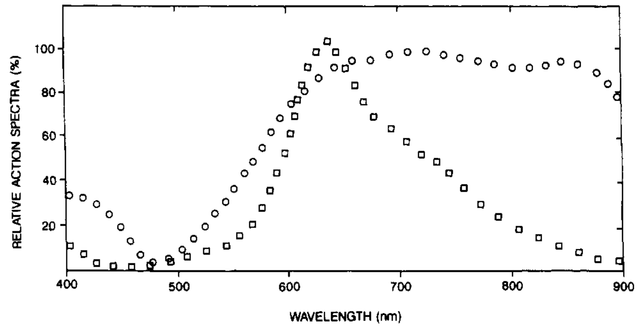

Figure 5. Evolution of the action spectrum of a 4000-Å-thick ClAlPc film which has been first I-type modified by immersion in an aqueous acidic solution containing 0.1 M of KI (○), followed by a heat treatment at 300 °C during 60 min (□).

Figure 5 shows the action spectra of a ClAlPc film I-type modified with KI during 12 h (○), followed by a 60 heat treatment at 300 °C (□). In this case, the maximum quantum efficiencies are 12 and 0.6% before and after 60 min of heat treatment, respectively. The quantum efficiencies in both Figures 4 and 5 are defined as the number of electrons collected per 100 incident photons.

Film Morphology. Being an assemblage of individual crystallites, ClAlPc films are porous.[18-20] As the photoactivity is tested photoelectrochemically, the I_3^-/I^- electrolyte has access to nearly the entire surface of each crystallite in the film. It is therefore important to verify that changes in the photoactivity with heat treatment are not resulting exclusively from morphological variations of the ClAlPc films.

Figure 6 displays the evolution, as seen by SEM, of the surface morphology of an as-sublimed, 4000-Å-thick ClAlPc film (a). After heating at 300 °C for 1 min, the treated film looks like the as-sublimed one but the surface morphology is altered if the film is heat treated for longer time periods: 5 (b) and 60 min (c). All pictures are taken at the same magnification. Although the number of crystallites per unit area seems to remain constant, they evolve from ill-defined cylindrical rods to sharp-cornered parallelepipedic needles having their long axis (equivalent to the thickness of a 4000-Å film) oriented also perpendicular to the substrate.

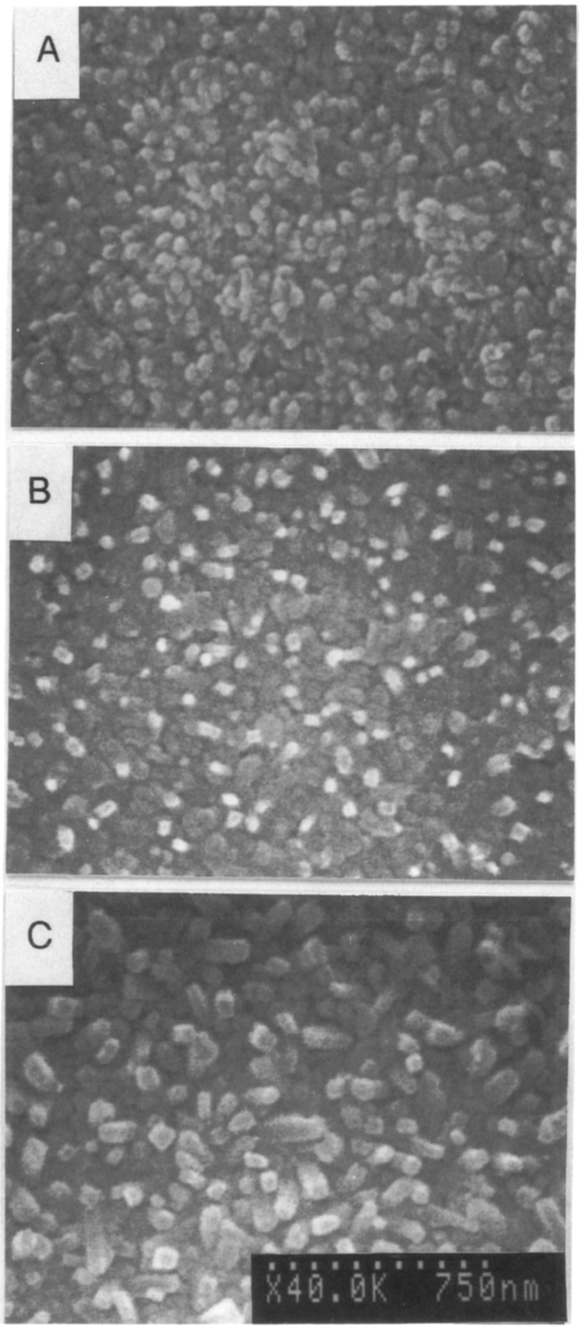

Figure 6. Surface morphology of a 4000-Å-thick ClAlPc film (a) as-sublimed or after heat treatment at 300 °C during 1 min, (b) during 5 min, and (c) during 60 min.

Figure 7 displays the evolution, as seen by SEM, of the surface morphology of a ClAlPc film after H-type modification with KCl (a). The latter film is then heat treated at 300 °C for 1 (b), 5 (c), and 60 min (d). All pictures are taken at the same magnification which is equivalent to the one used in the previous figure. The H-type transformed film (a) consists of sharp-cornered parallelepipedic needles having a section similar to that seen in Figure 6c. However, in this case, their long axes are in a direction parallel to the substrate. The film morphology does not change after 1 min of heat treatment but is completely modified for heat treatments ≥5 min. Figures 7d and 6c are quite similar.

At this point, it should be noted that the initial direction of the long axis of a crystallite belonging to a ClAlPc film, though tilted by 90° after an H-type modification with KCl, can be reset back along its initial direction if the H-type modification is followed by a heat treatment of the film.

Figure 8 displays the evolution, as seen by SEM, of the surface morphology of a ClAlPc film after I-type modification with KI, (a), followed by heat treatment at 300 °C for 60 min (b). All pictures are taken at the same magnification corresponding to the one used in Figures 6 and 7. In this case, the section of the cylindrical crystallites obtained after modification (Figure 8a) is somewhat larger than that of the as-sublimed crystallites (Figure 6a). However, after heat treatment, the morphology of the film displayed in Figure 8b is quite similar to the one shown in Figures 7d or 6c.

In conclusion, if all films remain porous, it is not possible to explain the changes in photoactivity of more than 1 order of magnitude that occur after heat treatment, on the basis of the total area of the crystallites in contact with the electrolyte. There is also a typical morphology (the sharp-cornered parallelepipedic needles of Figures 6c, 7d, and 8b) corresponding to heat-treated films of low photoactivity.

Structural Changes. Electron diffraction measurements were performed by TEM in order to detect any structural changes when as-sublimed or modified ClAlPc thin films are heat treated at 300 °C for various time periods. For these experiments, the molecular films have to be thinner ($\sim$1000 Å) than the ones used for photoelectrochemistry ($\sim$4000 Å thick). All selected area diffraction patterns show sharp crystalline reflections along with diffuse rings. All films therefore contain crystalline and amorphous regions. However, as a general rule, diffuse rings fade away for films heat treated for longer time periods. This occurs in parallel with a sharpening of the crystalline reflections, indicating an improved crystallinity for these films at the expense of the amorphous phase. This observation agrees with the morphological changes detected by SEM.

The interplanar distances, *d*, obtained from selected area diffraction patterns are displayed in Figure 9 for all heat-treated films. For comparison, the interplanar distances of as-sublimed ClAlPc and H-type modified ClAlPc with KCl, already reported,[18,21] are also given in Figure 9. Only *d* values ≥5 Å are included in this figure. These interdistances are indeed the most significant ones in the process of assigning a crystal lattice to the films. They correspond to the diffraction rings close to the transmitted electron beam spot which is the center of all rings. The width of each line in Figure 9 represents the uncertainty on the measurement of the ring diameter.

From Figure 9, it can be concluded that (i) all heat-treated films display the same diffraction pattern regardless of whether ClAlPc was H or I-type modified before heat treatment or not and (ii) even for 1 min at 300 °C, the diffraction pattern of heat-treated films is different from the one measured for as-sublimed or modified ClAlPc.

An attempt was made to use the interplanar distances to identify the crystalline structure of the heat treatment ClAlPc phase. It was already demonstrated[22] that the planes of the Pc macrocycles of as-sublimed ClAlPc are parallel to the substrate. On the basis of similarities between the morphology of as-sublimed ClAlPc, heat treated or not (Figure 6), it is assumed that the planes of the Pc macrocycles are also parallel to the substrate after completion of the heat treatment. In both cases, the

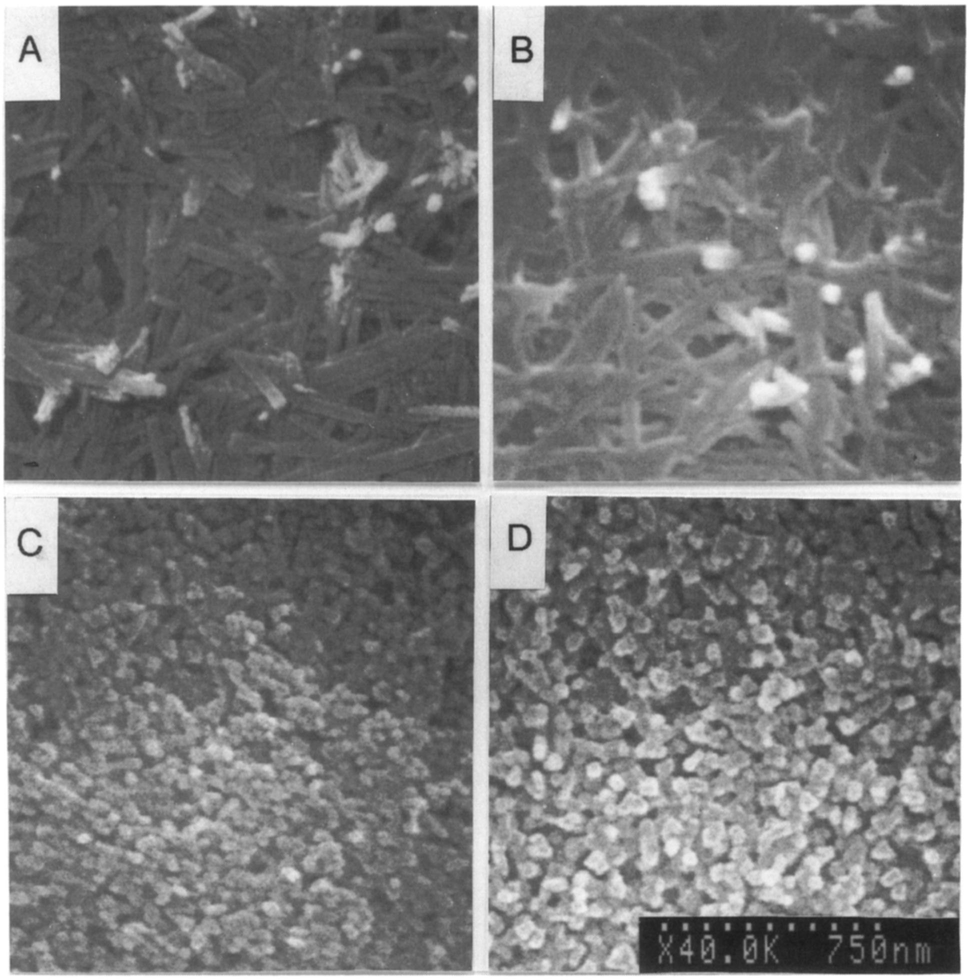

Figure 7. Surface morphology of a 4000-Å-thick ClAlPc film which has been first H-type modified by immersion of an aqueous acidic solution containing 0.1 M of KCl (a) and then heat treated at 300 °C during 1 (b), 5 (c), and 60 min (d).

crystallites are oriented with their long axis in a direction perpendicular to the substrate.

In the microscope, observations are made at zero tilt, so the film and therefore the ClAlPc macrocycle planes are perpendicular to the electron beam. In electron diffraction, the only active planes in the crystal lattice are those which are parallel to or at a small angle (θ <5°) from the electron beam. This condition greatly reduces the number of planes that actually diffract. By using the lattice parameters of the triclinic structure reported by Wynne for ClAlPc and the arrangement of the Pc molecules in the unit cell,[14] it was found[20] that the crystallographic planes (2$\bar{1}$0) and (1$\bar{2}$0) are characterized by d = 6.00 and 6.17 Å, respectively, (020) is characterized by d = 6.81 Å and (1$\bar{1}$0) is characterized by d = 9.67 Å. These interplanar distances fit with the three diffraction lines reported in Figure 9 for as-sublimed ClAlPc. The common perpendicular plane to those diffracting planes is near (3 1 $\overline{13}$). It is the crystallographic plane on which the macrocycles lie flat at an angle θ = 14° from (001).

The interplanar distances displayed in Figure 9 for heat treated ClAlPc can be obtained by slightly modifying the triclinic lattice parameters used for as-sublimed ClAlPc. The new parameters are listed in Table III along with the parameters reported by Wynne[14] for ClAlPc single crystal. It is found that the following crystallographic planes could participate to the diffraction: (1$\bar{2}$0) (120) (2$\bar{1}$0) (210) characterized by d = 5.68, 5.74, 5.77, and 5.84 Å, respectively; (020) and (200) for d = 6.35 and 6.53 Å, respectively; (1$\bar{1}$0) and (110) for d = 9.04 and 9.17 Å, respectively; (010) and (100) for d = 12.70 and 13.06 Å, respectively. These interplanar distances fit the four diffraction lines reported in Figure 9 for heat treated ClAlPc. The common perpendicular plane (within 5°) to all diffracting planes is (10$\bar{3}$). It is the crystallographic plane on which the macrocycles lie flat after heat treatment of the films at an angle 19.8° ≤ θ ≤ 20.1° from (001).

From Table III, one sees that only small changes in the lattice parameters are needed to fit the d values of Figure 9. It is difficult in the present case to know if parameter c is modified by heat treatment of ClAlPc because the corresponding axis is nearly parallel to the electron beam. Therefore, it is assumed that parameter c is unchanged. The same lattice parameters can be used to describe the structure of ClAlPc films which are first H or I-type modified, then heat treated at 300 °C.

At this point, it is necessary to point out that the interplanar distances obtained by TEM do not allow to ascertain univocally the crystal structure of the Pc. Indeed, if the triclinic structure with the lattice parameters given in Table III is justifiable for heat-treated ClAlPc on the basis of a slight variation of the initial lattice parameters characterizing as-sublimed ClAlPc, another structure can also describe the experimental interplanar distances of Figure 9. The lattice parameters of this second structure are given in Table IV. They are derived from the known single crystal structure of FGaPc.[15] According to that structure, the following crystallographic planes could

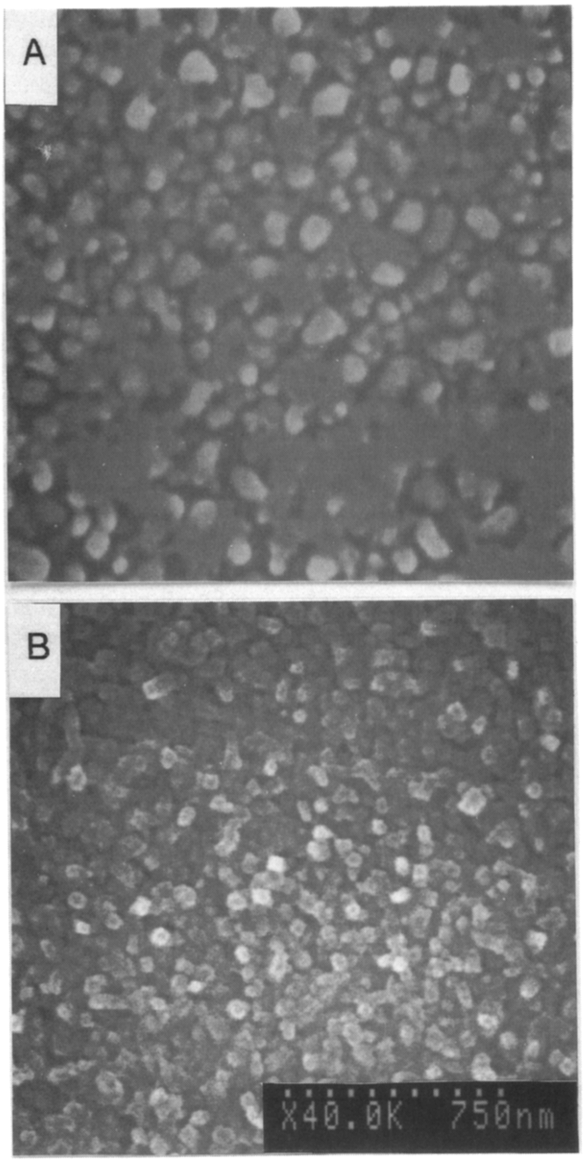

Figure 8. Surface morphology of a 4000-Å-thick ClAlPc film which has been first I-type modified by immersion in an aqueous acidic solution containing 0.1 M of KI (a), then heat treated at 300 °C during 60 min (b).

participate to the diffraction: (021) and (02$\bar{1}$) characterized by d = 5.64 and 5.67 Å, respectively; (020) for d = 6.30 Å; (01$\bar{1}$) for d = 9.03 Å and (010) for d = 12.60 Å. These interplanar distances fit the four diffraction lines reported in Figure 9 for heat treated ClAlPc. The common perpendicular plane (within 5°) to all diffracting planes is (100). It is the crystallographic plane on which the macrocycles lie flat after heat treatment of the films.

If that structure prevails, heat treated ClAlPc molecules would be cofacially stacked in a way similar to the stacking of GFaPc or FAlPc.[27] The possibility of a cofacially stacked structure was also proposed for ClGaPc and OVPc.[11] Furthermore, epitaxial ClAlPc films grown on (001) KCl surfaces were shown by high-resolution electron microscopy to be cofacially stacked too.[28] The single-crystal structure of these cofacially stacked molecules has only be determined for FGaPc which was used as a starting reference in Table IV.

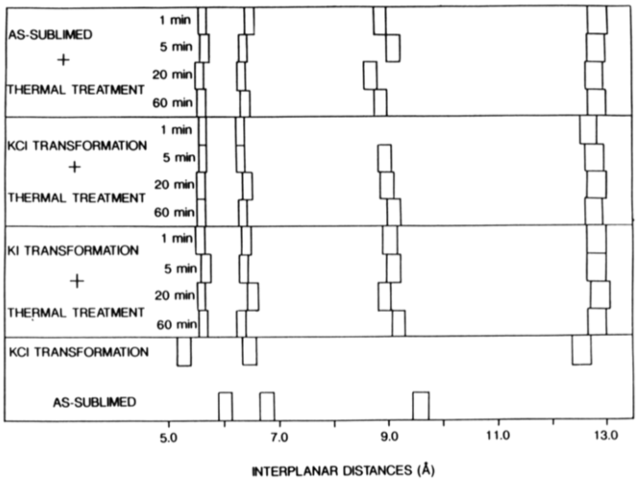

Figure 9. Interplanar distance for ClAlPc films which have been heat treated at 300 °C before or after H- or I-type modifications. Interplanar distances for as-sublimed ClAlPc and ClAlPc after H-type modification are given for comparison.

Table III. Lattice Parameters for As-Sublimed (A) ClAlPc and ClAlPc after Heat Treatment at 300 °C (B)

	A^a	B		A^a	B
a (Å)	13.7766	13.6–13.8	α (deg)	98.36	86–66 or 92–94
b (Å)	13.7754	12.70–12.75	β (deg)	108.6	108.6
c (Å)	14.0595	14.0595	γ (deg)	90.16	90.16

[a] From ref 14.

Table IV. Lattice Parameters for (A) FGaPc and ClAlPc after Heat Treatment at 300 °C (B)

	A^a	B		A^a	B
a (Å)	3.8711	3.8711	α (deg)	90.27	90.27
b (Å)	12.601	12.601	β (deg)	96.42	96.42
c (Å)	12.793	12.93	γ (deg)	91.28	91.28

[a] From ref 15.

On the basis of results already reported for FAlPc films,[19,24,30] cofacially stacked ClAlPc is expected to be characterized by (i) a blue-shifted absorption of the Q band relative to the Q band of the molecule in solution; (ii) a drastic reduction of the photoactivity. Both observations are confirmed experimentally. However, FAlPc is also known to become an organic conductor by iodine uptake.[31,32] This behavior is not observed for heat-treated ClAlPc films which remain unchanged upon immersion in the I_3^-/I^- redox couple in acidic solution.

It appears therefore, that electron diffraction patterns of Pc films like those presented in Figure 9 can only ascertain (i) the presence of a polycrystalline phase in the Pc film; (ii) the evolution of the crystalline phase upon structural modification. The exact structure of heat treated ClAlPc can only be determined by X-ray diffraction of a single crystal. The lattice parameters reported in Tables III and IV are based on several assumptions that could be confirmed or invalidated by further research.

TGA and DSC Measurements. Thermogravimetric analysis and differential scanning calorimetry were per-

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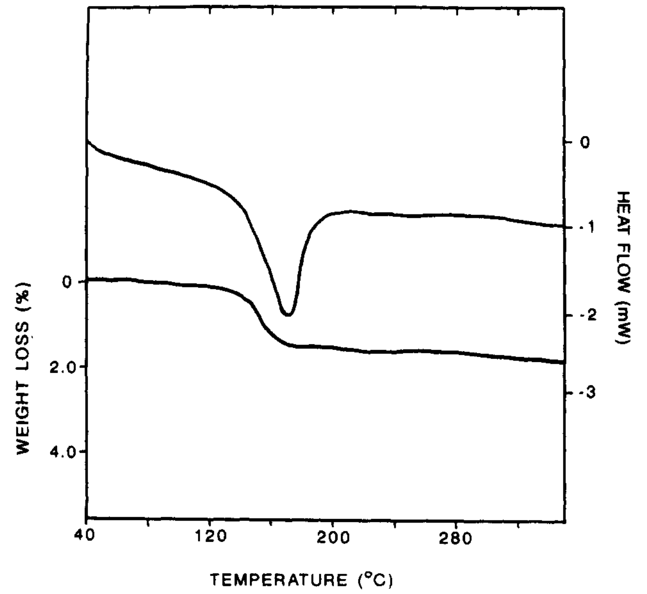

Figure 10. Thermogravimetry (lower curve) and differential scanning calorimetry (upper curve) of ClAlPc powders which have been first H-type modified by immersion in an aqueous acidic solution containing 0.1 M of KCl.

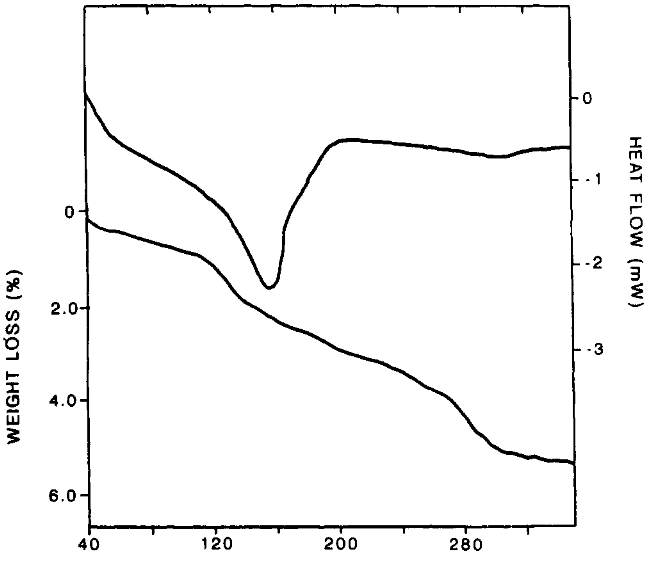

Figure 11. Thermogravimetry (lower curve) and differential scanning calorimetry (upper curve) of ClAlPc powders which have been first I-type modified by immersion in an aqueous acidic solution containing 0.1 M of KI.

formed on powders of as-sublimed ClAlPc and of H or I-type modified ClAlPc to monitor any weight losses and transitions in the material. On the temperature range probed (from 40 to 350 °C) there is no weight loss nor thermal transition detected for as-sublimed ClAlPc powder. This behavior is in agreement with the gradual crystallization of an amorphous phase during the entire temperature rise.

On the other hand, Figure 10 shows the gravimetry and differential calorimetry associated with the thermal analysis of ClAlPc powder H-type modified with KCl during 24 h. An endothermic transition occurs during a 1.6% weight loss which proceeds at a maximum rate when the temperature is about 150 °C. Figure 11 is equivalent to Figure 10 for ClAlPc powder I-type modified with KI during 24 h. Two endothermic transitions occur during a 5.0% total weight loss which proceeds in 2 steps, with a maximum rate at about 130 °C for the first weight loss and at 290 °C for the second one. DSC shows that the first transition in Figure 11 seems to be equivalent to the transition in Figure 10. The second transition in Figure 11 appears only slightly endothermic even though its associated weight loss is similar to the one accompanied by the first transition. The same results are obtained for the I-type transformation with I_3^-/I^- solution during 24 h.

Such a double weight loss has already been mentioned for iodine-doped cobalt tetraphenylporphyrin (CoTPP)-I_x[33] or fluoroaluminum and fluorogallium phthalocyanines (FAlPcI$_x$ and FGaPcI$_x$).[32] For (CoTPP)I$_x$ in a low doped state ($x < 1$), iodine is removed at 240–260 °C. Two weight losses at 240–260 and 130–160 °C are observed for the highly doped (CoTPP)I$_x$ ($x > 1$). The nature of the two weight loss processes centered at 130 and 265 °C (where the rate of weight loss is maximum) for (FAlPcI$_x$)$_n$ was investigated by a combination of TGA and Raman spectroscopy. The latter technique was able to identify I_5^-/I_3^- in the doped polymer depending upon the value of x. The I_5^- or I_3^- signal disappears after the first weight loss process at 130 °C.

As far as our experiments are concerned, we used neutron activation analyses to relate the concentration of iodine in the film to the behavior of the TGA and DSC curves of I-type modified ClAlPc powders. When the latter material is I-type modified with I_3^-/I^- solution at pH 3 during 24 h, 5.7% (weight) of I is found in the powder.[23] When the modified powder is heated at 200 °C for 1 h, there is 0.25% (weight) of I remaining in the material. It corresponds to only 4.4% of the iodine present in the powder before the heating step at a temperature between the two weight losses of the TGA curve. On the other hand, when I-type modified ClAlPc is heated at 320 °C for 1 h, there is still 0.1% (weight) of I in the material.

Therefore, the first weight loss and endothermic reaction happening at 130 °C involves the departure (under the form of I_2 and HI) of nearly all iodine present as I_3^-[25] in the I-type modified ClAlPc with I_3^-/I^-. This is in agreement with what has already been published about iodine-doped porphyrins or phthalocyanines. For the second weight loss at 290 °C, it is proposed that it involves the sublimation of Pc fragments resulting from some decomposition reactions that would be catalyzed by the presence of iodine. Accordingly, the single weight loss at 150 °C in Figure 10 is explained by the departure of HCl from the ClAlPc that is H-type modified by KCl.

Discussion

From the results, it can be concluded that heat treatments at 300 °C greatly influence the characteristics measured for ClAlPc films, irrespective of whether the heat treatment occurs before or after an H or I-type structural modification of ClAlPc. For films heat treated during *60 min*, the following characteristics are always obtained:

(i) an absorbance in the visible (Q band) with a maximum at 630 nm;

(ii) a low photoactivity under polychromatic light (J_{sc} decreases at least by 1 order of magnitude) related to the disappearance of the absorbance in the NIR. The latter

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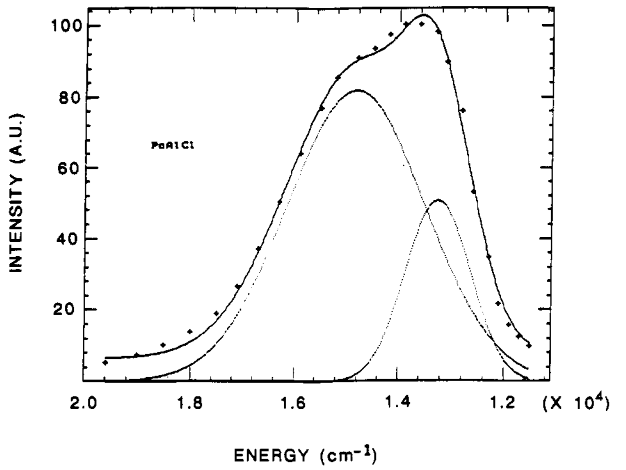

Figure 12. Deconvolution of the Q band of as-sublimed ClAlPc in two Gaussians. The experimental absorbances (+) are normalized to their maximum.

absorbance results from a structural reorganization of the film following the anion uptake;[18]

(iii) a common film morphology. All heat-treated films are made of a tight packing of sharp-cornered parallelepipedic needles having their long axis oriented perpendicular to the substrate;

(iv) the same electron diffraction pattern characterized by four interplanar distances for $d > 5$ Å. They are interpreted in terms of a slight modification of the triclinic lattice reported for ClAlPc[14] or in terms of a cofacial stacking of the ClAlPc molecules similar to the stacking of FGaPc.[15]

From the results obtained after a heat treatment of as-sublimed ClAlPc during *1 min*, it is possible to deduce that the sublimed films are mainly amorphous. Figures 1, 6, and 9 and Table I substantiate this conclusion. After 1 min at 300 °C, there is no drastic change in the Q band shape of ClAlPc (Figure 1) nor in the film morphology (Figure 6a) nor in the photoactivity of the film (Table I). However, Figure 9 indicates that the interplanar distances measured for the crystalline regions in the film are the same after 1 or 60 min but differ from those reported for as-sublimed ClAlPc before heat treatment.

If the structural changes occuring after 1 min have no effect either on the absorption spectrum or on the film's morphology or photoactivity, one is forced to conclude that only a small fraction of the as-sublimed ClAlPc film is crystalline. Therefore, the Q band shape, the film's morphology and photoactivity reflect the amorphous character of the majority of the phase. This hypothesis is verified by the deconvolution of the Q band of the as-sublimed ClAlPc absorption spectrum.

In solution in methanol, the non aggregated molecules display a strong and narrow absorption band centered at 670 nm (Figure 1). There are also two small peaks at 604 and 637 nm. In the amorphous solid phase, there will be a range of interactions between the molecules involved in all possible configurations. Blue and red shifts of various importances[17] are expected to occur with a probability following a Gaussian distribution centered at the energy corresponding to the maximum of the Q band absorption of the nonaggregated molecules in solution.

Figure 12 presents the deconvolution of the Q band absorption of as-sublimed ClAlPc into two Gaussians. Note that the x axis is given in cm^{-1}. The area under the curves is therefore proportional to the oscillator strength of both fractions of ClAlPc.[34] The main Gaussian has its maximum at 1.48×10^4 cm^{-1} (676 nm). It represents the amorphous fraction of the film. A small difference between the maximum of absorption in the solid phase (676 nm) and in solution (670 nm) is not significant. Indeed, it has been demonstrated for oxytitanium phthalocyanine (OTiPc) that the absorption peak position was slightly affected (within about 20 nm) by the induced or permanent dipole of the solvent or its electron-donating or -withdrawing properties.[35] The other Gaussian has its maximum at 1.33×10^4 cm^{-1} (750 nm). It represents the red shifted crystalline fraction of the film. The area under the amorphous ClAlPc is 3.5 times the area under the crystalline phase. The film is therefore more than three-quarter amorphous. This is in agreement with the above deduction concerning the predominantly amorphous character of as-sublimed ClAlPc.

It could be objected that deconvoluting Figure 12 into two Gaussians is an oversimplification. If it might be justified to represent the amorphous part of the Q-band absorption of ClAlPc by a Gaussian, some structure is expected for the ordered phase. Its representation by a Gaussian too is indeed an oversimplification. However, Q-band absorption spectra of Pc films do usually show very little structure. Therefore we do not introduce a significant error in the conclusions drawn from the deconvolution of Figure 12 by using a Gaussian shaped Q-band absorption for the crystalline fraction of the as-sublimed ClAlPc film.

At this point, it should be stressed that it is because the as-sublimed ClAlPc film is mainly amorphous that H- or I-type structural reorganizations are possible. These film modifications are characterized by the appearance of an absorption in the NIR which was found to improve the Pc photoactivity.[8-12,18,19] However, for ClAlPc it is the result of anion uptake into the film. Indeed, it is observed that the redox couple I_3^-/I^- is not able to penetrate into as-sublimed ClAlPc once the film has been heated at 300 °C for a time period ≥20 min (Table I). At the same time, an improved crystallinity is noticed. This observation is consistent with high-resolution electron microscopy experiments performed to explain the mechanism of the doping process of polyoxogermanium phthalocyanine $(OGePc)_n$ by iodine.[36] In that case, it was found that stacking faults act as triggers for the doping reaction by providing openings to iodine in the crystal lattice. An amorphous phase is disorganized or organized only on a short-range scale. Therefore, it should be very permeable to anions. On the contrary, heat-treated ClAlPc, which is an annealed crystalline phase, could be quite defect free and therefore exempt of sites which could trigger the solid-state reaction.

Another reason for the lack of anion uptake in ClAlPc after heat treatment of the material could be the disappearance of the driving force of the reaction upon increase of the film temperature. It has been postulated[18,23] that the driving force for anion uptake is the electrical neutrality of the film which has been disrupted by the reaction of O_2^- (from $Pc^+O_2^-$) with H^+ diffusing from the solution. The result is an uncompensated positive charge on the Pc. If

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this reaction is the main mechanism of anion uptake, it means that the concentration of anions in the film is equivalent to the concentration of O_2^- before immersing the film into the solution. In other words, H- or I-type modifications of ClAlPc do not alter either the initial Pc^+ concentration or the conductivity of the film. Indeed, the same resistance was deduced from the slope of the forward *J–V* characteristics of ClAlPc films before and after I-type modification.[19]

It was demonstrated in this work that anions leave the film upon heating at 300 °C during 1 h (less than 2% of I initially present in the film after I-type modification with I_3^-/I^- remain after heat treatment). So does O_2, which desorbs above 150 °C from zinc, nickel, or copper phthalocyanines.[37–39] Heating to 150 °C only leads to a slight decrease in the XPS intensity of the O_2^- peak in lead phthalocyanine but oxygen is displaced by NO_2 at that temperature.[40] There is a possibility that the reaction of O_2 with the mainly amorphous as-sublimed ClAlPc or the rather polycrystalline heat treated film (after cooling down) could be different.

A drastic lowering of the O_2^- density in heat treated ClAlPc would result in a strong decrease of the anion uptake. However, this does not seem to happen since the resistances of the film (measured from the slope of the forward *J–V* characteristic) are the same before and after heat treatment. Only the photoactivity is different. One may therefore conclude that $Pc^+O_2^-$ densities in as-sublimed ClAlPc, before and after heat treatment are similar. They cannot be invoked to explain the lack of anion uptake in the heat-treated films.

It has been reported that $Pc^+O_2^-$ is also involved as a precursor in the photoactivity of Pcs and related molecules.[41,42] The most likely mechanism is via charge transfer from the Pc singlet to the $Pc^+O_2^-$ complex to leave a free hole in the Pc and a weakly trapped electron in the excited state of the complex. This photogeneration mechanism is a slight variation of the extrinsic photogeneration mechanism proposed by Popovic[43] (a singlet exciton promotes the electron of a negatively charged impurity into the conduction band of the host Pc material, the hole being generated by regeneration of the negatively charged impurity).

If ClAlPc always contains an identical concentration of $Pc^+O_2^-$ or Pc^+A^- (A^- being an anion like Cl^-, Br^-, I_3^-, etc...), how can we explain the reported differences in photoactivity. Changes from $Pc^+O_2^-$ in as-sublimed ClAlPc to Pc^+A^- upon modification occur with the appearance of a NIR absorbance. It indicates a structural reorganization of the Pcs into the new phase which is more photoactive. The new phase is not a polymorph of ClAlPc because it contains also various anions besides Pc molecules. However, various Pc polymorphs absorbing in the near infrared have also been obtained by milling, heating or by solvent treatment.[10,16,44,45] Their photoactivity is always higher than for their stable counterparts. Therefore, a high photogeneration efficiency is mainly a function of the stacking of the molecules rather than of the density of $Pc^+O_2^-$ complexes, provided the latter one is high enough.

It is interesting to notice that the improvement of the photoactivity of Pc's is not the only characteristic of the dye which is related to the appearance of an absorption in the near infrared. Non linear optical properties (χ^3) of Pcs also show enhanced χ^3 values (about 1 order of magnitude) upon red shifts in substituted or not substituted oxovanadium phthalocyanine (OVPc), OTiPc,[46,47] and substituted CuPc and H_2Pc.[48,49]

Conclusion

Heat treatments performed at 300 °C on ClAlPc thin films demonstrate that the Pc layer sublimed at 2000 Å min^{-1} is amorphous for more than three-quarters of the film. This characteristic is responsible for the easy diffusion of H^+ in the disorganized phase followed by its reaction with O_2^- and the uptake of anions to compensate for the loss of negative charges. The chemical modification of the phase accompanies a structural reorganization and a red shift of the Q band of the Pc which then displays photoactivity in the NIR.

The photoactive phase is not stable. By heat treatment, its structure evolves toward a mainly polycrystalline material via a loss of the incorporated anions (Cl^-, Br^-, I_3^-, I^-) as I_2 or hydrogen halides. The new crystalline phase does not show any NIR absorbance and its photoactivity is at least 1 order of magnitude lower than before heat treatment. The electron diffraction pattern of the new phase yields interplanar distances that can be fitted either with a triclinic lattice similar to the one characterizing the crystalline fraction of as-sublimed ClAlPc or a triclinic lattice similar to that of FGaPc characterized by a cofacial stacking of the Pc macrocycles. X-ray absorption spectroscopy at the Al K edge could help to define if the stacking of ClAlPc is cofacial after heat treatment of the material.

An investigation of the transport properties and conductivity measurements of the films before and after H- or I-type modifications, followed by a heat treatment are now necessary in order to understand why the resistance of the film remains constant through structural reorganizations or heat treatments.

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