

# Periodic Multilayers of Perylene-3,4:9,10-tetracarboxylic Dianhydride and Chloroindium Phthalocyanine: Limitations to Long-Term Stability

A. Schmidt, L.-K. Chau,<sup>†</sup> V. S. Valencia,<sup>‡</sup> and N. R. Armstrong\*

University of Arizona, Department of Chemistry, Tucson, Arizona 85721

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The linear optical properties of periodic ultrathin multilayers of perylene-3,4:9,10-tetracarboxylic dianhydride (PTCDA) and chloroindium phthalocyanine (ClInPc) change after exposure to ambient environments. This discoloration extends over a period of months. The B- and Q-bands of ClInPc decrease significantly in intensity, while the PTCDA absorbance spectra are unchanged. ClInPc and PTCDA multilayers alone are stable in air over the same period of time. UV-vis spectroscopy and X-ray photoelectron spectroscopy (XPS) are in agreement with a destruction of the Pc chromophore. This reaction may be initiated by reaction of the anhydride groups of PTCDA with ambient moisture, forming carboxylic acids, as seen by XPS. Control experiments show that PTCDA hydrolyzes in the presence of water and that ClInPc degrades if exposed to acids. These results impact the device implications for long-term use of PTCDA/phthalocyanine assemblies.

## Introduction

The complimentary spectral and electronic properties of phthalocyanine and perylene dyes make them attractive for heterojunction formation.<sup>1-3</sup> Perylene dianhydride dyes, such as perylene-3,4:9,10-tetracarboxylic dianhydride (PTCDA) have been shown to exhibit n-type behavior as polycrystalline thin films.<sup>1</sup> PTCDA has been used to form heterojunctions with various phthalocyanine thin films, including the tri- and tetravalent metal Pcs.<sup>2,3</sup> Multilayer thin films of PTCDA have also been created with other aromatic species, to study effects of exciton confinement.<sup>3</sup> Most phthalocyanines (Pc) show p-type electronic behavior, although they are more properly defined as an insulator which exhibits p-type electrical responses due to the high concentration of electron acceptor defect sites and chemical impurities.<sup>1</sup> The potential applications for these multilayer configurations in optical communication devices<sup>1-3</sup> make it important to evaluate their stability. The necessary stability for many applications has to be at least 1 year

(ca. 10 000 h). The reactivity of aromatic dianhydrides toward hydrolysis<sup>4</sup> makes the long-term stability of such thin-film materials suspect.

The stability of such PTCDA/Pc heterojunctions is investigated here with chloroindium phthalocyanine (ClInPc). ClInPc is a widely used model substance for organic semiconductors and their heterojunction formation.<sup>1</sup> We show here that the destruction of the Pc chromophore in the PTCDA/ClInPc system may be caused by slow hydrolysis of the PTCDA layers in a multilayer assembly. As a result, multilayers of PTCDA and ClInPc do not meet stability requirements, if special precautions, such as encapsulation, are not taken.

## Experimental Section

PTCDA (Aldrich) and ClInPc (synthesized after the method described in ref 5; see Figure 1, were purified twice by vacuum gradient sublimation. Elemental analysis (C, H, N; Desert Analytics, Tucson) showed these dyes to be at least 97% pure.

All multilayer samples were produced by vacuum sublimation (base pressure 10<sup>-8</sup> Torr) on sapphire substrates (Rolyn; 0.5 mm thick, 0.5 in. diameter). Each sample consisted of 20 periods of alternating *x* monolayers (ML) of PTCDA and *y* ML of ClInPc, where 2 ≤ *x*, *y* ≤ 5. PTCDA was always the first deposited monolayer. Thin films of pure PTCDA or ClInPc were 120 and 80 ML thick, respectively. Detailed investigations about the structure of these films will be discussed elsewhere.<sup>6</sup> All samples were stored in the ambient laboratory atmosphere, covered, in the dark, at room temperature.

UV-vis spectroscopy was performed in transmission mode using a double-beam spectrophotometer (Hitachi U-2000) with 1 nm resolution. All spectra were corrected for background substrate.

<sup>†</sup> Present address: Center for Bioengineering, FL-20, University of Washington, Seattle, WA 98195.

<sup>‡</sup> Previously V. S. Williams; currently at Sandia National Laboratories, P.O. Box 5800, Albuquerque, NM 87185-0338.

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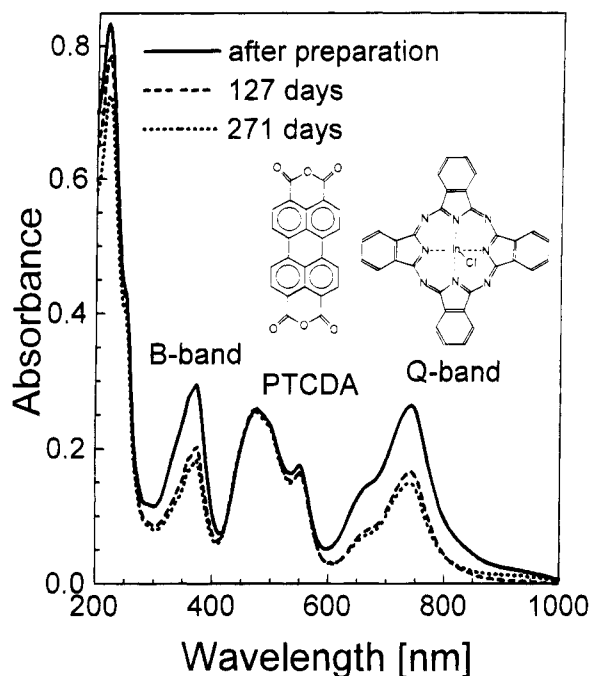
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**Figure 1.** UV-vis absorbance spectra of 20 periods of (5 ML PTCDA/2 ML ClInPc) at different ages. The B- and Q-band of ClInPc decreases, while the PTCDA spectral features remain stable. The chemical structure of the molecules is shown in the inset.

**Table 1. Stoichiometric Ratios for 20(*x*ML PTCDA/*y*ML ClInPc) Samples Several Months after Preparation, Determined by XPS**

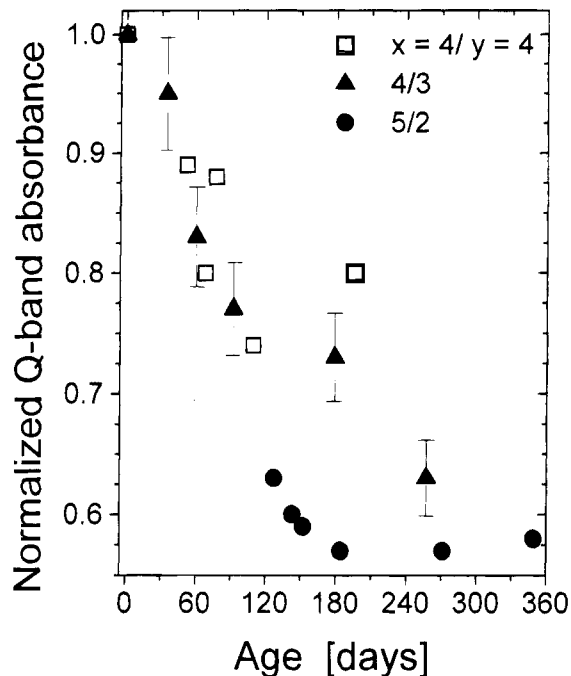
	Cl/In	N/In
expected	1/1 = 1.0	8/1 = 8.0
<i>x</i> = 4/ <i>y</i> = 4: after 2 months	1.3 ± 0.2	4.8 ± 0.7
<i>x</i> = 4/ <i>y</i> = 4: after 14 months	0.54 ± 0.08	3.1 ± 0.5
<i>x</i> = 5/ <i>y</i> = 5: after 7 months	0.60 ± 0.09	1.2 ± 0.2
<i>x</i> = 5/ <i>y</i> = 2: after 19 months	0.67 ± 0.10	1.0 ± 0.2

X-ray photoelectron spectroscopy (XPS) data were acquired at room temperature with a VG ESCALAB MKII spectrometer using an Mg K $\alpha$  source (1.2536 keV). The analyzer pass energy was set to 50 eV (mode CAE50) or 20 eV (mode CAE 20) and the energy increment to 0.1 eV. Data analysis was carried out using standard background correction schemes.<sup>7</sup> The photoemission peak intensities were corrected for background, transmission function of the analyzer and the photoemission probability.<sup>7</sup> Such corrected peak intensities were used to determine the stoichiometric ratio of different atoms in the samples (Table 1). The binding energies were referred to the (aromatic) carbon 1s peak with the position set at 284.7 eV.

FT-IR measurements of ClInPc in KBr pellets was performed with a Nicolet 510P FT-IR spectrometer (4 cm<sup>-1</sup> resolution). The spectra were baseline corrected.

## Results and Discussion

UV-vis absorbance spectra were measured at different times following formation of the PTCDA/ClInPc multilayers. An example is shown in Figure 1 for a (5 ML PTCDA/2 ML ClInPc)  $\times$  20 sample. Absorbance features are seen which are attributable to PTCDA (200 and 500 nm) and to ClInPc (B-band at 380 nm and the Q-band at around 750 nm). With increasing sample age the B- and Q-bands of the ClInPc decrease, while peak positions and the band shapes (peak ratios) remain



**Figure 2.** Normalized absorbance of different PTCDA/ClInPc multilayers as a function of sample age. The ClInPc Q-band maxima were measured immediately after preparation and were normalized to unity. The number of PTCDA monolayers, *x*, and ClInPc monolayers, *y*, of a single period is given in the inset (*x*/*y*). The experimental errors are shown for one series.

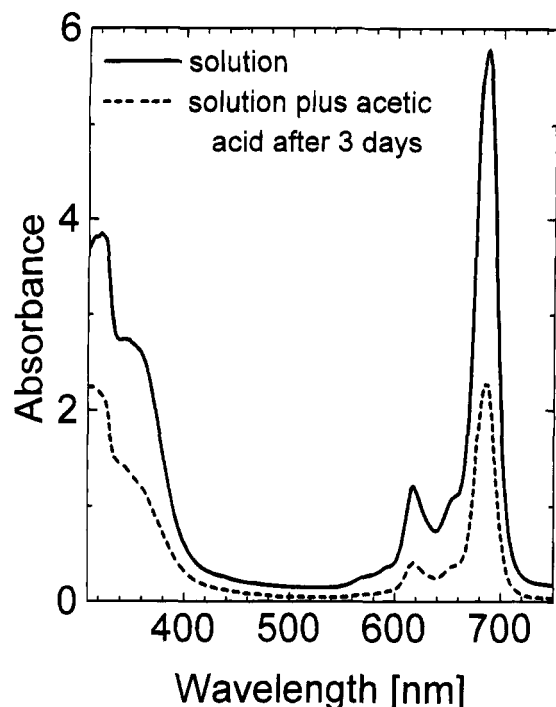
unchanged. The PTCDA and ClInPc pure control thin films do not show a significant decrease in absorbance for up to 390 days. We have to conclude that PTCDA mediates the discoloration. Errors in the measured and normalized absorbance spectra are approximately 5%.

In Figure 2, the results for several samples of different composition are shown in a plot of the Q-band absorbance maximum as a function of sample age. The peak intensities of the initial Q-band absorbance spectra measured directly after film preparation are normalized to unity. The maximum absorbance decreases nonlinearly with increasing sample age, over a period of months, following preparation. The decrease in Pc Q-band absorbance is faster for those multilayers which had larger coverages of PTCDA in each film, relative to ClInPc. Our data base is not large enough to determine a quantitative dependence on the ratio of PTCDA to ClInPc.

It is known that carboxylic acid anhydrides can be hydrolyzed by water to form carboxylic acids, catalyzed by acids or bases.<sup>4</sup> The meso-bridging aza nitrogens of a phthalocyanine molecule are slightly basic;<sup>8a</sup> adsorption of water by chloroaluminum phthalocyanine films has been reported to occur at these sites.<sup>8b</sup> The presence of water in the PTCDA/ClInPc multilayers, coupled with the basic nature of the meso-bridging aza nitrogens, is likely to enhance the hydrolysis of anhydride groups in PTCDA.<sup>4</sup> Significant amounts of water are not present in the as-prepared films multilayer films, because the Knudsen cells for the sublimation of both PTCDA and ClInPc in UHV are held above 250 °C. However, the water necessary to start the hydrolysis can diffuse into

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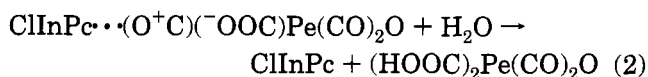
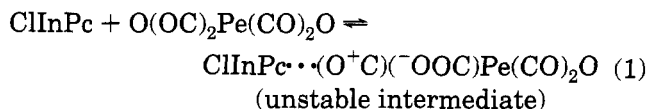
**Figure 3.** UV-vis absorbance of ClInPc dissolved in pyridine. Shown are the spectrum of the original solution and the spectrum 2 days after acetic acid was added to the solution (ca. 0.1% wt/wt). Both B- and Q-band absorbance decreases.

the film from the ambient environment after preparation. The resulting carboxylic acid groups are likely to have  $pK_a$  values near those of benzoic acid (4.2 in water).

That such acid groups render the Pc molecule unstable is strongly suggested by studies of Pc stability in acidic solutions: ClInPc was dissolved in pyridine to a concentration of  $10^{-5}$  M and glacial acetic acid (ca. 0.1% wt/wt) was added to the solution. For these solutions the Pc Q-band spectra decreased in intensity by 40% in 2 days, compared to the original spectrum (see Figure 3), while the position of the peak maximum is unchanged. Added acetic acid apparently causes the same discoloration effect as observed in the UV-vis absorbance spectra of aged PTCDA/ClInPc multilayer samples. Similar results were found for solutions of ClInPc in concentrated sulfuric acid. The different time scale for this reaction in the thin solid film as compared to the solutions is probably due to a long induction period for the reaction to occur in the solid state and the slow diffusion of water into the film.

It has been reported that the treatment of metal-phthalocyanines (like Co- and Cu-Pc) with acids led to protonation (visible as a redshift in the Q-band absorbance) and/or dissociation of the metal.<sup>9</sup> We note here that no red-shift of the Q-band was observed for ClInPc after treatment with acetic acid. Therefore, the decrease in absorbance without change of the peak position indicates a destruction of the Pc chromophore (see below). The same experiments were done by us with chloroaluminum phthalocyanine solutions in pyridine. The UV-vis absorbance also decreases after adding acetic acid. This reaction is therefore not restricted to ClInPc alone, but will probably occur in other trivalent metal Pcs as well.

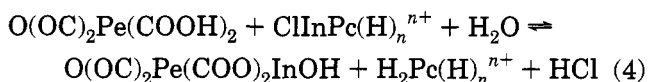
A possible reaction mechanism for the degradation of ClInPc in the ClInPc/PTCDA multilayers is proposed below. The bridging aza nitrogen in ClInPc is a base<sup>8a</sup> and catalyzes the hydrolysis of the anhydride group in PTCDA.<sup>4</sup> For simplicity, only one anhydride group is shown in the equations to react:



where Pe represents the perylene ring. Acid dissociates from hydrolyzed PTCDA and protonates the bridging aza nitrogens in ClInPc:



with  $n \leq 4$ . This is likely to weaken the In-N bonds in ClInPc and lead to the dissociation of the metal from the phthalocyanine:



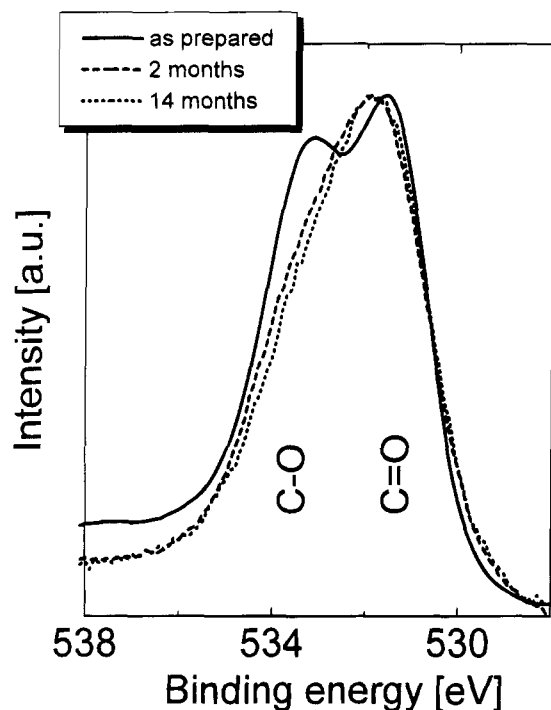
This may be followed by the decomposition of the protonated and demetallated Pc by an unknown mechanism. From this reaction mechanism (1)–(4) we expect that chlorine is lost, because HCl gas can leave the film. It is not clear if HCl plays a role in the further reaction of the Pc.

Surface analysis data were used to confirm such reactions in the near surface region of thin films. Oxygen(1s) peaks in XPS spectra of a PTCDA/ClInPc film were examined. In Figure 4 the normalized oxygen(1s) peaks are shown for a sample with 20 periods of 4 ML PTCDA and 4 ML ClInPc at different ages. The as-prepared film shows a peak for the carbonyl oxygen at 531.6 (fwhm 1.4 eV) and a peak for the singly bonded oxygen at 533.4 eV (fwhm 1.8 eV). This finding is identical to a pure PTCDA film grown in UHV.<sup>10</sup> (The ratio of 2:1 for C=O and C–O for the as-prepared sample is not obvious from Figure 4 because a shakeup loss of the C=O peak increases the observed intensity of the C–O peak.<sup>10,11</sup>) The results for the aged multilayer PTCDA/ClInPc samples are strikingly different. After storage for 2 months in ambient environments only a single O(1s) peak with an additional shoulder can be resolved. Fitting these peaks show that the main peak is at 531.6 eV and that the energy separation between shoulder and peak is  $1.5 \pm 0.1$  eV, while the separation in the as-prepared film is  $1.8 \pm 0.1$  eV. After storage for 14 months the shape of the peak has not changed significantly; only the area of the shoulder is decreased, as can be seen from Figure 4. To show that this behavior is caused by hydrolysis of PTCDA, we prepared a thin-film powder sample of PTCDA on gold and exposed it for several days to water (Milli-Q

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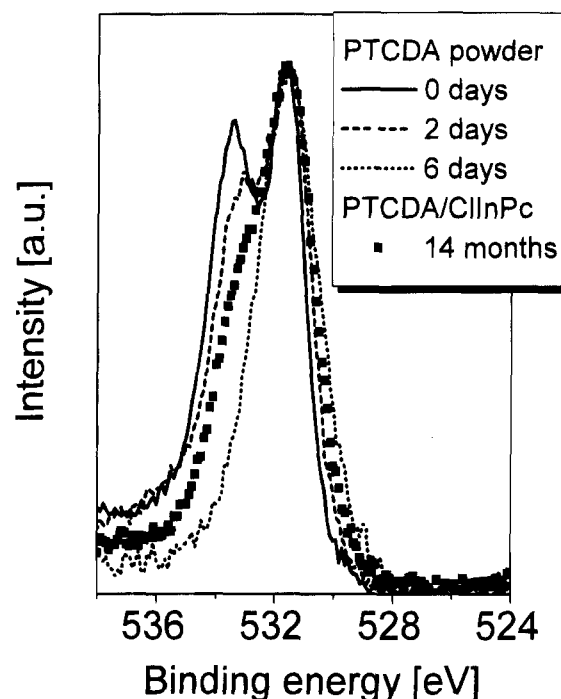
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**Figure 4.** XPS data (measured in the mode CAE50) for oxygen 1s peak of a 20(4 ML PTCDA/4 ML ClInPc) periodic multilayer sample after preparation, after storage for 2 and 7 months at ambient environment. The peak maxima were normalized.

quality). A powder sample was chosen to enhance the permeation of water into the bulk of PTCDA, which does not dissolve in water. Water was presented as a drop on top of the powder sample. XPS measurements were done before and at different steps during the exposure to water. Figure 5 shows the results for the film before and after 2 and 6 days of exposure. The second, smaller peak, initially at 533.4 eV decreases in intensity and the separation between the two peaks, as determined by a peak fit, decreases from 1.8 to 1.5 eV. The main peak stays at 531.6 eV during all experiments. It has been reported in ref 11 that in the carboxylic acid functionality  $\text{HOC}=\text{O}$ , with the carbon attached to an aromatic system, the doubly bound oxygen has a peak position of  $531.65 \pm 0.05$  eV and that the singly bound oxygen has a binding energy of  $533.14 \pm 0.08$  eV. The peak separation is therefore  $1.49 \pm 0.09$  eV, in good agreement with our finding of 1.5 eV and well below the initial separation of 1.8 eV in PTCDA, with an anhydride group  $\text{O}=\text{COC}=\text{O}$ . The result for the 14 months old multilayer sample is shown for comparison in Figure 5. It fits between a 2 and 6 day old sample directly exposed to water. The XPS spectrum of PTCDA in the multilayer sample exhibits the same characteristics as in the powder sample exposed to water. This shows that the PTCDA in a thin multilayer sample of PTCDA/ClInPc undergoes the same stoichiometric change as PTCDA directly exposed to water and strongly suggests that PTCDA in the multilayer samples is hydrolyzed. It also shows that the change in the multilayer samples is much slower compared to powder samples, which can be understood as a result of the slow diffusion of water into the initially water-free PTCDA/ClInPc multilayer film. The formation of carboxylic acid in the near surface region of PTCDA films, which is probed by XPS (ca. 10 nm total probing depth, i.e., at



**Figure 5.** XPS data (measured in the mode CAE20) for the oxygen 1s peak of a powder sample of PTCDA on gold. The lines show the results at different stages of exposure (0, 2, and 6 days) to water. The result for a 14 months old multilayer film are shown for comparison (■). The peak maxima were normalized.

least three complete periods of the multilayer), suggests that hydrolysis of anhydride groups to a carboxylic acid groups is likely to occur at minor quantity throughout a multilayer Pc/PTCDA film, as suggested by the nearly unperturbed UV-vis absorbance bands for the PTCDA chromophore. The UV-vis experiment probes the whole film depth, not only the surface, as does XPS.

The XPS measurements also allow us to determine the atomic ratio between In, Cl, and N in the Pc molecule. The results of two different samples are summarized in Table 1. For an aged samples with 4 ML PTCDA and 4 ML InPcCl the ratio between N/In is smaller than expected, and the ratio decreases with increasing age from 2 to 14 months. This shows that nitrogen atoms are lost and confirms that the Pc ring is degraded in the aged PTCDA/ClInPc multilayer system. The heavy metal In is not likely to form any product which can escape from the film, it is therefore used in all the XPS experiments as a reference. For the 2 months old sample the ratio Cl/In increased but is within the error identical to the expected value. After 14 months the ratio Cl/In is strongly decreased. A sample with 5 ML PTCDA and 2 ML ClInPc per period shows an decreased N/In ratio and a consistent decrease in the Cl/In ratio after 7 and 19 months. This indicates again the loss of nitrogen and also the loss of chlorine atoms from the aged sample, possibly due to the formation of HCl gas, as predicted by reaction 4. The loss of N in the sample with the higher PTCDA/ClInPc ratio are more severe, indicating that the PTCDA is responsible for the changes, as shown in Figure 2.

To check if the changes in the XPS spectra of the multilayer samples are caused by a reaction with an acid, we prepared two control samples of ClInPc powder on a gold substrate. The first of these control samples

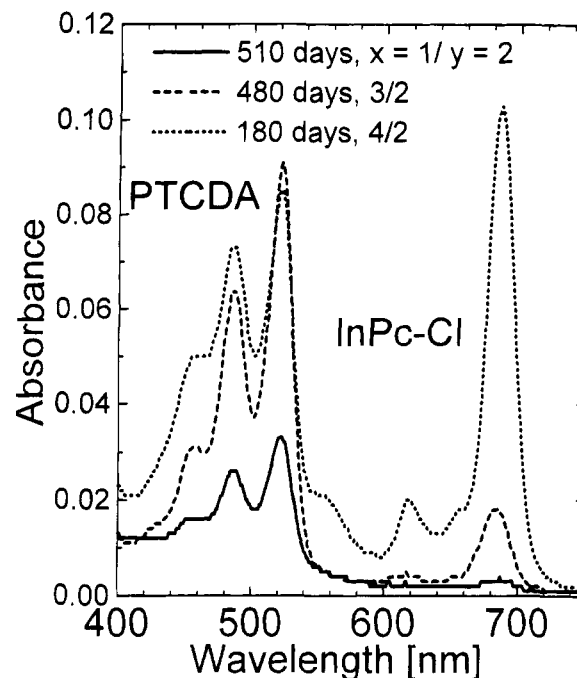
**Table 2. Stoichiometric Ratios for Powder Samples of ClInPc on Gold, Determined by XPS before and after Exposure to Glacial Acetic Acid**

	Cl/In	N/In
expected	1/1 = 1.0	8/1 = 8.0
as prepared	0.92 ± 0.14	7.2 ± 1.1
2 days of exposure	0.96 ± 0.14	5.6 ± 0.8
6 days of exposure	0.85 ± 0.13	4.8 ± 0.7
after 6 days of reaction with acetic acid in pyridine solution	0.20 ± 0.03	5.0 ± 0.8

was measured by XPS. The results are given in Table 2 and are within the error identical to the expected stoichiometric ratios for ClInPc. This sample was then exposed to glacial acetic acid, which was presented as a drop on the surface. The sample was measured after 2 and 6 days of exposure to the acid. Table 2 shows a small decrease in the ratios N/In and Cl/In, indicating a loss of nitrogen and chlorine. This effect is much clearer in a second control sample where ClInPc was dissolved in pyridine and glacial acetic acid (50% wt/wt) was added. After 6 days the reaction product was dried and measured by XPS. As can be seen in Table 2, the N/In and Cl/In ratios are drastically decreased. Nitrogen and chlorine are lost: the Pc ring is destroyed. Here again the sample changes are much smaller and slower if the reagent has to diffuse into the sample.

A direct conformation of the hydrolysis of the anhydride group and the change in the phthalocyanine ring in the multilayer samples by FT/IR was not successful. The vibrational frequencies for In–N and In–Cl are below the cutoff from the sapphire substrate. Due to the long storage of the samples at ambient environment the surfaces are covered by organic impurities from the air. The hydrolysis is also only affecting a minor quantity of the anhydride groups. We therefore cannot investigate the reaction products on the sapphire substrate by FT-IR. Control experiments with pure ClInPc and ClInPc after treatment with glacial acetic acid (see above) were performed with powder samples in KBr pellets. In–Cl and In–N vibrations are below 400  $\text{cm}^{-1}$ ,<sup>12</sup> the influence of acid on the metal therefore cannot be investigated. We evaluated changes in the peak ratio between the C–N stretch vibration at 1335  $\text{cm}^{-1}$  and the C–H (out of plane bend) vibration at 727  $\text{cm}^{-1}$ ,<sup>12</sup> as well as the ratio between the C–N vibration at 1285  $\text{cm}^{-1}$  and the C–H (in plane bend) vibrations at 1119  $\text{cm}^{-1}$ .<sup>12</sup> The first ratio decreases by 17% and the second one by 29% if ClInPc is exposed to glacial acetic acid. This indicates a loss of nitrogen after the reaction with the acid, which is in accordance with the XPS data.

The possibility of Pc discoloration through changes in the packing structure of aged PTCDA/ClInPc multilayer films were also investigated. We dissolved three different aged PTCDA/ClInPc multilayer films in an equal amount of pyridine and measured the solution absorbance spectra. The cleaned substrates were checked to ensure that the films were completely dissolved. The number of Pc layers were equal for all samples, as was the area of the sample. An identical Pc absorbance is therefore expected for all three solutions if only structural changes in the films occurs. As shown in Figure



**Figure 6.** UV-vis absorbance spectra of three different 20-period PTCDA/ClInPc periodic multilayers samples dissolved in pyridine. The number of ClInPc layers per period is always 2 ML. Age of the film and the number of PTCDA monolayers,  $x$ , and ClInPc monolayers,  $y$ , of a single period are given in the inset ( $x/y$ ). This experiment shows that structural changes are not responsible for the discoloration.

6, the absorbance in the ClInPc spectral region decreases with age, while the ratio of the PTCDA absorbance between the samples are equal to the number of PTCDA layers in the different sample. This indicates that the Pc discoloration was not caused by a structural change of the ClInPc molecules in the aged PTCDA/ClInPc multilayer films.

## Conclusions

The characterization of PTCDA/ClInPc multilayers by UV-vis absorbance spectroscopy and XPS showed that a chemical reaction is responsible for the discoloration of the ClInPc in the aged multilayer samples. Structural changes in the films as a cause for the discoloration are ruled out. Control experiments with pure samples showed that (a) PTCDA undergoes a hydrolysis if exposed to water, (b) ClInPc reacts with acetic acid which leads to a decrease of the Q-band UV-vis absorbance and is accompanied by a loss of Cl and N as seen in XPS and FT-IR, and (c) pure ClInPc films do not show a discoloration, if they are exposed to ambient environment.

The similarity between the XPS and UV-vis results for the multilayer and control samples strongly suggests that the discoloration of ClInPc is caused by a destruction of the nitrogen-containing heterocycle by a reaction with acid and that this reaction in the multilayer samples is initiated by the hydrolysis of PTCDA, which leads to an acid. A possible reaction path of the hydrolysis of PTCDA and the demetallization of ClInPc is discussed in the text and is in accordance with the experimental findings. However, the actual reaction which leads to the destruction of the Pc rings is unknown.

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The formation of carboxylic acid due to hydrolysis of the dianhydride functionality in PTCDA is an undesirable outcome in their use in Pc/perylene multilayers and suggests that their application must be preceded by rigorous exclusion of moisture from the device. Potential solutions to this problem are under exploration, and may include the use of less reactive dianhydrides, such as *N,N*-dimethylperylene-3,4:9,10-bis(dicarboxamide). Such molecules have similar electronic and optical properties, but their reactivity toward hydrolysis is much smaller.

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