

X-Ray Diffraction Study of Crystal Structure and Thin Films of Chromium(II) Phthalocyaninate

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Crystal structure of Cr(II) phthalocyaninate (CrPc) was determined by means of single-crystal X-ray diffraction. It was shown that after vacuum sublimation CrPc crystallized as a β -polymorph, which was isostructural to β -polymorphs of other metal phthalocyanines. When deposited onto glass substrate by organic molecular beam deposition, CrPc formed thin films with strong preferred orientation, consisting of α -polymorph. It was shown that both β -CrPc powder and α -CrPc films were unstable in air and transformed to Cr(OH)Pc. X-Ray diffraction (XRD) studies showed that β -CrPc polycrystalline powder after storage in air (relative humidity 20 %) began to exhibit the first signs of degradation already in 1 hour, while the first changes in XRD patterns of α -CrPc films became noticeable only after a few days. Annealing of α -CrPc films at 250 °C in air at a relative humidity of 70 % leads to their faster conversion to Cr(OH)Pc, and the resulting films have a high degree of crystallinity.

Keywords: Chromium phthalocyanine, XRD, single crystal, thin films, 2D GIXD.

Дифрактометрическое исследование кристаллической структуры и тонких пленок фталоцианината хрома(II)

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Кристаллическая структура фталоцианината хрома(II) (CrPc) была определена методом монокристаллической дифракции. Было показано, что после вакуумной сублимации CrPc кристаллизуется в виде β -полиморфа, который изоструктурен β -полиморфам фталоцианинатов других металлов. При осаждении на стеклянную подложку методом термического осаждения из газовой фазы CrPc образует тонкие пленки, состоящие из α -полиморфа, с сильной преимущественной ориентацией. Было показано, что как поликристаллический порошок β -CrPc, так и пленки α -CrPc нестабильны на воздухе и переходят в Cr(OH)Pc. Первые изменения в дифрактограммах порошка β -CrPc становятся заметны уже через час после их контакта с воздухом, в то время как изменения в дифрактограммах пленок α -CrPc начинают фиксироваться только через несколько дней. Отжиг пленок α -CrPc при 250 °C на воздухе при относительной влажности 70 % приводит к их более быстрому превращению в Cr(OH)Pc, при этом полученные пленки обладают высокой степенью кристаллическости.

Ключевые слова: Фталоцианинат хрома, рентгеновская дифракция, монокристаллы, тонкие пленки, 2D GIXD.

Introduction

Metal phthalocyanines (MPcs) belong to the class of tetrapyrrole complexes and attract the attention of researchers due to their wide applications in catalysis,^[1,2] photodynamic therapy,^[3] chemical sensing and electrochromic devices.^[4,5] Among them chromium phthalocyaninates demonstrate attractive electrochemical behavior and catalytic activity.^[6,7] For instance, Obirai *et al.*^[7] have demonstrated the catalytic activity of electrosynthesized chromium tetraaminophthalocyanine towards oxidation of nitric oxide and nitrite.

For the application in most electronic devices phthalocyanines should be deposited as thin films. It is known that the structure of thin films has a significant effect on their properties and characteristics. It was shown that thin films of chromium phthalocyanine (CrPc) could be deposited using vacuum deposition techniques, but they were not stable in air and oxidized to Cr(OH)Pc.^[8] However, Ercolani *et al.*^[9] reported that α -polymorph of CrPc was stable in air. Since it is well known that other metal phthalocyanines such as CoPc^[10,11] and ZnPc^[12,13] are deposited onto substrate surface as α -polymorphs, it is suggested that air stable CrPc thin films can be obtained if CrPc is deposited onto the substrate surface as α -polymorph.

Despite a number of adducts of chromium phthalocyaninates with solvents like tetrahydrofuran and dimethoxyethane, *e.g.* PcCrI(THF), PcCrI₃(THF), [PcCr(THF)₂]SbF₆, [K(DME)₄]₂[PcCr], [K₆(DME)₄]₂[Pc₄Cr]₂ and *etc.*^[6,14–19] were structurally characterized, the structure of single crystals of unsubstituted CrPc was not determined so far. For this reason, all previous studies of CrPc thin films were not supported by single crystal structural data.

Thus, the main goal of this paper was to determine the single crystal structure of CrPc and study the structural organization, phase composition and air stability of CrPc thin films using X-ray diffraction techniques.

Experimental

CrPc was synthesized according to the procedure described elsewhere.^[9] The obtained dark violet powder was crushed in an agate mortar and purified by gradient sublimation in vacuum (10^{-5} Torr) at 430 °C in a glass tube. The resulting product was small needle-shaped crystals with dark violet color and metallic luster, which is typical for metal phthalocyanines. CrPc thin films were deposited by an organic molecular beam deposition technique in vacuum (10^{-5} Torr) onto glass substrates. The substrate temperature was 80 °C. The nominal thickness of the films was 150–200 nm. After preparation, all samples (polycrystalline powder, single crystals, thin films) were stored in a desiccator.

Crystal structure of CrPc was determined at 298 K using a Bruker X8 Apex single-crystal diffractometer (MoK α sealed X-ray tube with a graphite monochromator, APEX CCD-detector). APEX3 software package (SAINT, SADABS)^[20] was used for raw frame collection, data reduction, absorption correction and unit cell refinement. The structure solution was performed in Olex2 1.2.10^[21] with SHELXT-2018/2^[22] and SHELXL-2018/3^[23] used for the solution and structure model refinement, respectively. Powder and thin film diffraction patterns were recorded using a Shimadzu XRD-7000 diffractometer (CuK α , Bragg-Brentano scheme vertical θ - θ goniometer with a scintillation counter detector). Diffraction peak profiles were fitted using the Voigt function.

2D GIXD (GIWAXS) patterns of CrPc thin films were obtained using a Bruker DUO single-crystal diffractometer (Incoatec I μ S_{Cu} Cu-anode microfocus tube, Apex II CCD detector). A thin glass substrate with CrPc film was placed in the special sample adapter and mounted onto the goniometer head. The primary X-ray beam angle of incidence was about 0.5°. 2θ position of the CCD detector was set at 0°; the distance from the sample to the detector was 80 mm.

UV-Vis spectra were recorded using a UV-Vis-3101PC “Shimadzu” spectrophotometer. IR spectra were recorded using a Vertex 80 FTIR spectrometer.

To investigate stability of CrPc powders and films the samples were heated at different conditions in a glass ampoule that was filled with air or vacuumized. Moist air was prepared by its bubbling through distilled water. The relative humidity (RH) inside the tube was controlled with a commercially available digital humidity meter IT-8.

Results and Discussion

A reasonably large (0.3 mm×0.05 mm×0.05 mm) CrPc single crystal was mounted onto a nylon loop with epoxy resin. Particular attention was paid to ensure that the crystal was completely coated with epoxy resin to prevent its decomposition under the influence of atmospheric moisture. The unit cell parameters and refinement details of a CrPc single crystal are given in Table 1. CrPc crystallizes in $P2_1/n$ space group with molecules arranged in the herringbone pattern, which is identical to high-temperature β -polymorphs of other metal phthalocyanines, *e.g.* β -CuPc,^[24] β -CoPc,^[25] β -ZnPc,^[26] *etc.* The packing diagram of CrPc molecules is shown in Figure 1.

The distance between two molecules in a stack (mean square plane through all non-hydrogen atoms) is 3.349 Å,

Table 1. Unit cell parameters and refinement details of a CrPc single crystal.

Compound	CrPc
Formula	C ₃₂ H ₁₆ N ₈ Cr
F.W.	564.53
Temperature, K	298
Crystal system	monoclinic
Space group	$P2_1/n$
a , Å	14.6544(14)
b , Å	4.8399(4)
c , Å	17.3324(17)
β , °	105.699(2)
Volume, Å ³	1183.46(19)
Z	2
ρ_{calc} , g·cm ⁻³	1.584
Goof	1.024
2θ range for data collection, °	3.24÷56.54
Data completeness up to 50° 2θ , %	100
R_{int} , %	3.62
R_1 , %	4.37
CCDC No.	1956459

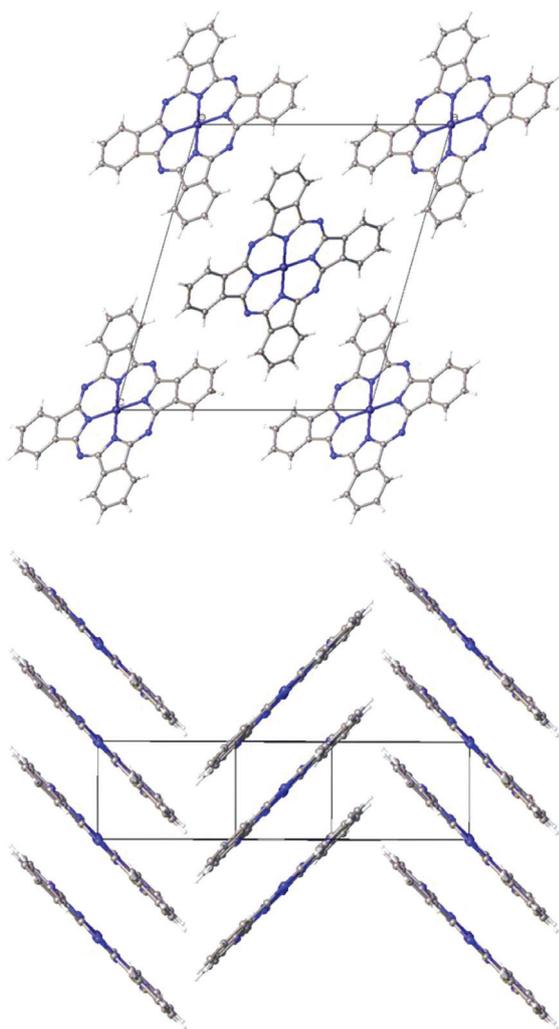


Figure 1. Packing diagram for CrPc molecules.

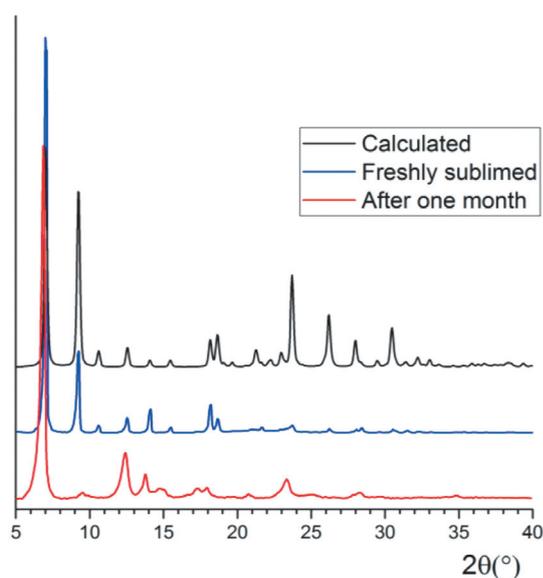


Figure 2. XRD patterns of CrPc: calculated from single-crystal data (black line), for the freshly sublimed powder (blue line) and the powder after storage for a month in air at RH 20 % (red line).

while the stacking angle (angle between the stacking direction and the plane of molecule) is 43.78° for CrPc, which is similar to β -polymorphs of other metal phthalocyanines: CuPc (3.342 \AA and 44.24°), CoPc (3.320 \AA and 44.07°) and ZnPc (3.338 \AA and 43.45°).

It is worth mentioning that unlike other $M(\text{II})\text{Pc}$ ($M = \text{Cu, Zn, Co, Ni}$) CrPc is not stable in air. To investigate stability of CrPc powders and films the XRD patterns of freshly prepared samples were compared with those after storage in air at RH 20 % for 1 month, after 1 hour annealing at 250°C in vacuum ($5 \cdot 10^{-5}$ Torr), after 1 hour annealing at 250°C in air at RH 20 % and after 1 hour annealing at 250°C in air at RH 70 %.

Figure 2 shows diffraction patterns of the freshly sublimed CrPc powder and the powder after storage for a month in air (RH 20 %) in comparison with the pattern calculated from single crystal data. The diffraction pattern of the freshly sublimed CrPc powder is identical to the calculated one, confirming that no other crystal phases are present in the bulk sample. Different relative intensities of diffraction peaks are caused by strong texture of the sample because CrPc crystals are shaped like needles and cannot be grinded in the mortar because of their sensitivity to moisture. X-ray diffraction studies showed that chromium phthalocyanine polycrystalline powder after storage in air (RH 20 %) for 1 hour already began to exhibit the first signs of degradation. After one week, CrPc completely lost its crystallinity. When observed under a microscope, freshly sublimed CrPc crystals looked like dark violet needles with metallic luster, but after one week they acquired a twisted appearance. However, one more week later the powder started to crystallize slowly to Cr(OH)Pc. The diffraction patterns of the CrPc powder after its storage for a month in air (RH 20 %) differ from that of freshly sublimed powder, indicating the formation of a different crystalline phase. The measured interplanar distances and relative peak intensities for the powder after storage for a month in air are given in Table 2. According to the data reported by Ercolani *et al.*^[9] this crystalline phase can be identified as Cr(OH)Pc.

IR spectroscopy was additionally used to study

Table 2. Measured interplanar distances and relative peak intensities of Cr(OH)Pc XRD pattern.

d_{exp} (\AA)	I_{exp} (%)
12.92	100
9.281	2.5
7.153	21.3
6.434	7.2
5.984	8.3
5.124	5.3
4.943	4.0
4.275	1.0
3.817	8.7
3.560	3.4
3.165	2.6
3.016	0.6
2.579	1.0

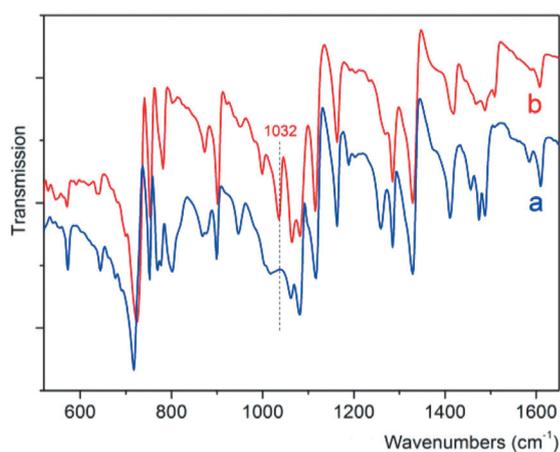


Figure 3. IR spectra of freshly sublimed (a) and stored for a month in air (RH 20 %) (b) CrPc powders.

the degradation of CrPc powder. IR spectra of freshly sublimed CrPc powder and the same powder stored for a month in air (RH 20 %) are shown in Figure 3. The additional comparatively intense band at 1032 cm^{-1} corresponding to Cr-O stretching vibrations appears in the spectrum of CrPc powder stored for a month in air. Besides, the group of bands at $715\text{--}770\text{ cm}^{-1}$ shifts by $3\text{--}7\text{ cm}^{-1}$ to the higher wavenumbers after the prolonged contact of CrPc with air moisture. These changes can also be a clear indication of CrPc powder degradation and its transformation to Cr(OH)Pc upon interaction with H_2O present in the air.

Several XRD patterns of CrPc films are shown in Figure 4. The XRD pattern of CrPc film taken immediately after its deposition contain one strong peak with $d = 12.79\text{ \AA}$ and two weak peaks with $d = 6.38\text{ \AA}$ and $d = 3.23\text{ \AA}$. The absence of other diffraction peaks and the fact that two

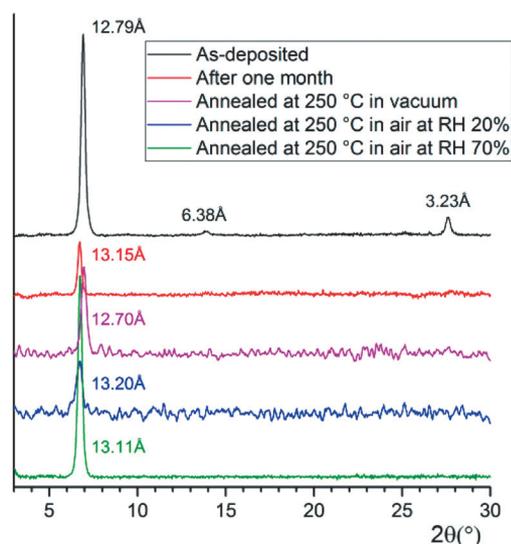


Figure 4. XRD patterns for CrPc thin films: as-deposited (black line), after storage in air at RH 20 % for 1 month (red line), after 1 hour annealing at $250\text{ }^\circ\text{C}$ in vacuum (magenta line), after 1 hour annealing at $250\text{ }^\circ\text{C}$ in air at RH 20% (blue line), and after 1 hour annealing at $250\text{ }^\circ\text{C}$ in air at RH 70 % (green line).

weak peaks have interplanar distances equal to $\frac{1}{2}$ and $\frac{1}{4}$ of the interplanar distance of the strong peak indicate that the CrPc film has strong preferred orientation relative to the substrate surface.

After 1 hour annealing at $250\text{ }^\circ\text{C}$ in vacuum (10^{-5} mbar) (Figure 4, magenta line) CrPc thin film does not show any noticeable changes (the diffraction pattern looks more noisy because of the less acquisition time). The interplanar distance of the strongest peak becomes slightly smaller because of the reduced mechanical stress in CrPc crystallites. At the same time, annealing in air at RH 20 % leads to the noticeable changes of the XRD pattern (Figure 4, blue line). After 1 hour annealing at $250\text{ }^\circ\text{C}$ the intensity of the first diffraction peak reduces significantly, while its interplanar distance increases to 13.2 \AA . This may be due to the transformation of CrPc to Cr(OH)Pc. At the same time, after 1 hour annealing at $250\text{ }^\circ\text{C}$ in air at RH 70 % the intensity of the diffraction pattern increases because of the formation of Cr(OH)Pc films with the higher crystallinity. The diffraction peak on its XRD pattern has a slightly less interplanar distance compared to the film annealed in air at RH 20 %.

Storage of the film in air (RH 20 %) at room temperature without heating (Figure 4, red line) also leads to similar changes in the XRD pattern, but the resulted film exhibits the less degree of crystallinity. It is worth mentioning that these changes are much slower than in the case of β -CrPc powders. The first signs of degradation begin to appear in XRD patterns only in several days.

The XRD data of CrPc thin films are in good agreement with their UV-Vis spectra. The optical absorption spectra of the as-deposited film, the film after 1 hour annealing at $250\text{ }^\circ\text{C}$ in vacuum, after 1 hour annealing at $250\text{ }^\circ\text{C}$ in air at RH 20 % and RH 70 % are given in Figure 5. The as-deposited CrPc film is characterized by a wide characteristic absorption Q-band in the region of $500\text{--}800\text{ nm}$ with the absorption maximum at 640 nm . It is known that the Q-band in UV-Vis spectra of phthalocyanine films is sensitive to their structure and phase composition.^[27]

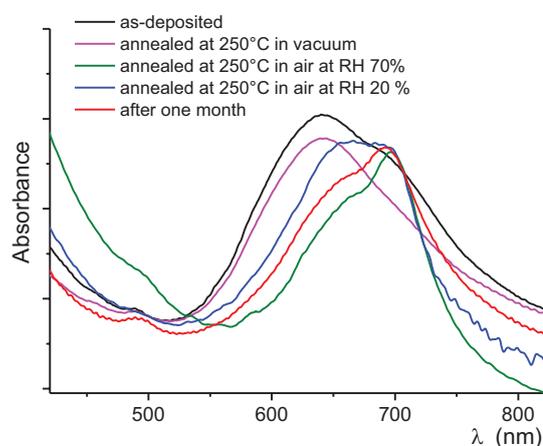


Figure 5. Optical absorption spectra of CrPc thin films: as-deposited (black line), after storage in air at RH 20 % for 1 month (red line), after 1 hour annealing at $250\text{ }^\circ\text{C}$ in vacuum (red line), after 1 hour annealing at $250\text{ }^\circ\text{C}$ in air at RH 20 % (blue line), and after 1 hour annealing at $250\text{ }^\circ\text{C}$ in air at RH 70 % (green line).

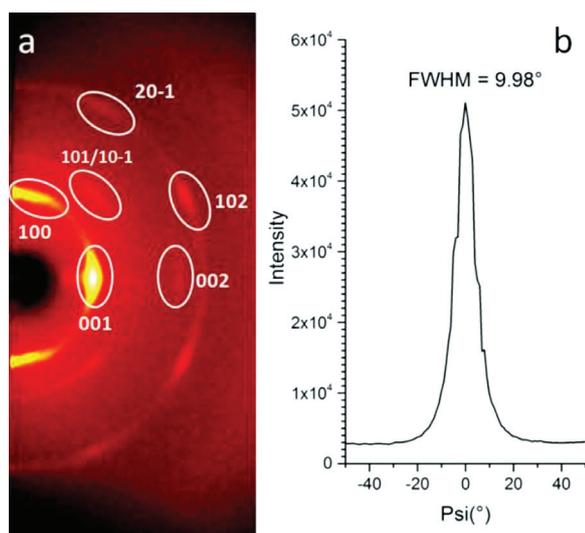


Figure 6. 2D GIXD pattern of as-deposited CrPc thin film (a) and azimuthal profile (phi scan) of the (001) peak (b).

After the film annealing at 250 °C in vacuum, its spectrum remains almost unchanged. Annealing in air at 250 °C during 1 hour leads to the shift of the Q -band maximum to 696 nm with the appearance of shoulder at 663 nm. These changes were shown by XRD data to occur due to the formation of Cr(OH)Pc. The spectrum of the films annealed at 250 °C in air at RH 20 % corresponds to the mixture of CrPc and Cr(OH)Pc. The spectra of the films after storage in air at RH 20 % for 1 month and after 1 hour annealing at 250 °C in air at RH 70 % are similar to each other.

It is necessary to mention that the measured interplanar distances of all three peaks observed on the diffraction pattern of as-deposited CrPc film (Figure 4, black line) do not coincide with either those calculated from the single crystal data of β -CrPc (12.58 Å, 6.29 Å and 3.145 Å) or reported by Ercolani *et al.*^[9] for α -CrPc (12.55 Å, 6.30 Å and 3.16 Å). For this reason, it was impossible to determine the phase composition of CrPc thin film using only conventional XRD data. For this purpose, the as-deposited CrPc thin film was studied using a 2D GIXD technique described in more detail in our previous works.^[28,29] The 2D GIXD pattern of as-deposited CrPc film is shown in Figure 6a.

Instead of uniform diffraction rings, the localized diffraction spots are observed in the 2D GIXD pattern, which is typical for oriented thin films. The obtained 2D GIXD pattern does not match the pattern of β -polymorph of CrPc. For example, β -CrPc has only one diffraction peak (10-1) in the 2θ region from 6.5 to 7.5°, while two peaks azimuthally rotated 90° relative to each other are observed on the 2D GIXD pattern of as-deposited film. This pattern, however, is very similar to 2D GIXD patterns obtained from thin films of α -CoPc,^[28] which indicates that the investigated CrPc film crystallizes as an α -polymorph. Therefore, hkl indexes were assigned to the observed diffraction peaks by analogy with α -CoPc. Ercolani *et al.*^[9] assigned different hkl indexes to the diffraction pattern of α -CrPc, but since no structure data were available for α -CrPc, it was impossible at that time to say if such indexing was correct.

In order to estimate the degree of preferred orientation of CrPc thin film, 2D GIXD diffraction pattern was processed in a XRD2Dscan v.4.1.1 program.^[30] Figure 6b shows the azimuthal scan (phi-scan) of (001) peak, calculated by azimuthal integration in the 2θ region of $\pm 0.5^\circ$ from the (001) peak maximum. FWHM of the (001) peak azimuthal profile is 9.98°. Since the CrPc film has preferred orientation with the (001) lattice plane parallel to the substrate surface, the azimuthal profile of (001) peak clearly shows the distribution of the angles of inclination of CrPc crystallites relative to the substrate surface, that in this case varies in the range $\pm 10^\circ$ for most of crystallites.

Conclusions

In this work, crystal structure of Cr(II) phthalocyaninate was determined by the means of single crystal diffraction for the first time. It was shown that the CrPc powder obtained by sublimation in vacuum consisted of pure β -polymorph, which was isostructural to β -polymorphs of other metal phthalocyanines, *viz.* CuPc, CoPc, ZnPc, *etc.* When deposited onto a glass substrate by OMBD in vacuum, CrPc formed highly oriented films consisting of α -polymorph. It was shown that both β -CrPc powder and α -CrPc films were unstable in air and transformed to Cr(OH)Pc. X-Ray diffraction studies showed that β -CrPc polycrystalline powder after storage in air (RH 20 %) began to exhibit the first signs of degradation already in 1 hour, while the first changes in XRD patterns of α -CrPc films became noticeable only after a few days. Annealing of α -CrPc films at 250 °C in air at a relative humidity of 70 % leads to their faster conversion to Cr(OH)Pc, and the resulting films have a high degree of crystallinity.

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