



# Article Aggregation and Conductivity in Hot-Grown Petroporphyrin Films

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**Abstract:** As a follow-up to our study on aggregation of metal-etioporphyrin complexes (Colloids Surf. A. Physicochem. Eng. Asp. 2022, 648, 129284), we considered thin films of three isomers of copper(II) etioporphyrin deposited on hot substrates. Despite the almost identical absorption spectra of isomers, their solid-state superstructures differ remarkably both in form and size. The lateral conductivity of films is much less sensitive to an isomer-type, regardless of the substrate temperature. However, the dark conductivity of cold-grown films is about two orders of magnitude higher than that of hot-grown films, whereas the photoconductivity of the latter is 100–1700 times greater, depending on the isomer.

Keywords: etioporphyrins; films; surface; aggregation; conductivity



In the preceding paper [1], we described the effect of regioisomerism of metalloetioporphyrins on the morphology and microcrystalline structure of their films obtained by thermal evaporation in vacuum. A molecular film was grown on a substrate fixed on a holder without intentional heating or cooling. During the growth process it was noticed that, along with the other growth parameters, the substrate temperature influences both the visual appearance (hence structure) and properties (conductivity) of the resulting thin films. In the present work, the copper etioporphyrin isomers I, II, and III were deposited on hot substrates. The term "hot" here means the temperature of the substrate holder that enables a sustainable film growth at a desired rate without obstructive re-sublimation of the molecules from the heated surface. This temperature was found to be about 100  $^{\circ}$ C for the most volatile compound in the series and maintained at this level for all others to ensure uniformity of the growth conditions. Etioporphyrin molecules in thus obtained films showed very peculiar aggregation motifs that depend on the peripheral isomerism of the macroligand much stronger than in the films deposited on an unheated (=cold) substrate. In addition, the DC conductivity was assessed in both cold- and hot-deposited films, which can be viewed as a first step towards applications of these materials in organic electronics [2].

# 2. Materials and Methods

Experimental procedures and analytical methods were the same as previously described [1], except for the substrate temperature ( $T_g = 100$  °C); the thickness of films was also 100 nm. For the photoelectrical measurements, the films were deposited on ceramic (Al<sub>2</sub>O<sub>3</sub>) substrates with a pre-patterned array of planar interdigital electrodes, IDE [3–6].



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). The actual temperature of both the quartz crucible, from which the InCl-EtioP-I powder was evaporated using resistive heating, and the massive copper stage, on which the substrates were fixed, was controlled by a thermocouple. In each case, the temperature was precisely set by an AC-DC power supply. The current-voltage characteristics were measured with a Keithley SCS-4200 station in the dark and under illumination of 100 mW/cm<sup>2</sup> in a shielded stainless steel chamber filled with ultrapure argon (99.998%) after proper purging to avoid the environmental influences. We also tested the photoconductivity of samples after exposure to air and found no great difference, at least during measurements. The values of specific conductivity  $\sigma$  at room temperature were derived from the linear section of the I–V curve—Table 1. Given the IDE geometry, the transition from the ohmic I–V section to the space charge-limited currents occurs at a bias of 12–14 V or greater depending on a sample [4]. Then, the films were heated in air to 120 °C and cooled back to room temperature with a stop every 10  $^{\circ}$ C so as to obtain steady-state I–V dependencies. Using the points on the cooling arm, the Arrhenius-type dependence of logarithm  $\sigma$  vs. reciprocal absolute temperature T was plotted for each sample and the value of thermal activation energy  $E_{act}$  was calculated using the equation  $\sigma = const \times exp(-E_{act}/kT)$  [4,7]. Typically, 2–4 samples of each type were measured until reproducible results were obtained. We decided to use only copper complexes in this study since for nickel etioporphyrin-I, the deposition process on both cold and hot substrates is different [1], which lowers the relevance of the comparison. The results on the morphology and properties of vacuum-deposited films of Ni-EtioP-I and -II complexes will be published elsewhere.

Table 1. Some parameters of copper etioporphyrin isomers in thin films.

Isomer	$T_g$	$\lambda^Q_{max}$ , nm	$\lambda^B_{max}$ , nm	$\sigma$ , S/cm	$E_{act}$ , eV	$I^L/I_D$
Cu-EtioP-I	cold	575	392	$1.3\times 10^{-8}$	0.6	6.1
	hot	573	390	$8 \times 10^{-11}$	0.9	$6.3 \times 10^2$
Cu-EtioP-II	cold	$\sim$ 570	396	$1 \times 10^{-7}$	0.75	5.0
	hot	$\sim$ 571	394	$1 \times 10^{-10}$	0.8	$2.1 \times 10^3$
Cu-EtioP-III	cold	575	394	$6 \times 10^{-8}$	1.0	8.1
	hot	573	386	$2 \times 10^{-10}$	1.0	$1.4 \times 10^4$

 $T_g$  = grow temperature, either 25 °C (cold) or 100 °C (hot);  $\lambda_{max}^{Q,B}$  = maximum of absorption band, either Q- or B-(Soret)—Figure 1;  $\sigma$  = specific conductivity of films (in the lateral direction);  $E_{act}$  = thermal activation energy of conductivity;  $I^L/I_D$  = light-to-dark current ratio at 12 V, light = 1 Sun—Figure S7.



**Figure 1.** EAS of copper(II) etioporphyrin films on hot substrates, inset—spectra of solutions in toluene from [1].

## 3. Results and Discussion

As seen from Figure 1, there are minor differences in the electronic absorption spectra (EAS) for the three Cu-EtioP isomers deposited on the hot glass/ITO substrate. Moreover,

temperature does not affect the position of the absorption bands—Table 1. The only remarkable feature is a decrease in intensity of Q-bands relative to the B-band in the spectra of the hot-grown films (Figure S1), which might suggest a change in intermolecular interaction [8]. However, the bathochromic shift of bands due to J-type aggregation [9] is about 10 nm for all three isomers, i.e., the same as in the cold-grown films [1]. The solution spectra of I, II, and III-isomers are nearly identical—Figure 1, inset. Spectra of films deposited on other transparent substrates, such as optical glass and quartz glass, do not qualitatively differ from those deposited on glass/ITO.

As shown previously [1], the similarity of spectral profiles of different isomers in the solid state does not necessarily imply a similar morphology of films deposited on an unheated (cold) substrate. In Figure 2, SEM images of the films deposited on cold and hot substrates are compared. The morphology of hot-grown films is coarser and more clearly reflects the unique packing motif inherent in each isomer. This motif must be associated with the structural features of the molecules that are essential for their self-assembling, with symmetry in this case. So, the Cu-EtioP-I forms the rounded objects with a lateral size of up to 1  $\mu$ m—Figure 2. These objects are composite and they closely resemble the balls of threads, which makes one wonder how such threads progressively grow on a flat substrate (a spiral or spindle-like growth?). Notably, the molecule of the I-isomer has a rotation-type  $C_{4h}$  symmetry. The II-isomer forms large ingrown needles that are oriented mostly parallel to the substrate surface, although in some cases, they are inclined and protrude above the surface of the film—Figure 2. The surface of films consisting of molecules of the least symmetrical Cu-EtioP-III features variously shaped grains whose size does not exceed 0.3–0.4  $\mu$ m.



**Figure 2.** SEM images of the Cu-EtioPs films deposited on cold (**top panels**, from [1]) and hot (**bottom panels**) silicon substrates in similar conditions, insets—molecular structures and symmetry of isomers. The white mark in the left top corner corresponds to 1 μm.

Unevenly spaced huge protruded grains and the softness of molecular aggregates make it difficult to scan the surface of hot-grown films by atomic-force microscopy in the conventional semi-contact mode. The height difference on the surface relief ranges from a few hundred nanometers to a micron, depending on the probability of an AFM tip meeting a large-sized object; some results are shown in Figure S2. The XRD patterns of films deposited on cold and hot substrate are compared in Figure 3. In all cases, no new diffraction maxima were detected in the hot-grown films. However, the Cu-EtioP-I films deposited on a hot substrate show a tremendous increase in the intensity of the low-angle diffraction peak at 6.9 degrees, while other peaks practically disappear. The peak at 20.8 degrees is most likely a tripled diffraction order of a strong peak at 6.9 degrees.

In the previous article, we tentatively assigned the peak at 6.9 degrees to a metastable phase that appears in the films of I-isomers of metal-etioporphyrins [1]. It now becomes clear that this phase is quite stable and tends to dominate in hot-grown Cu-EtioP-I films.

For a strong diffraction peak at 6.9 degrees arising in a hot-grown film, the rocking curve (omega scan) can be reliably measured. The full width at half maximum is 0.6 degrees, which indicates a very high degree of texture. This fact disagrees with the morphology of Cu-EtioP-I film as viewed with SEM/AFM in Figures 2 and S2, and we cannot offer a consistent explanation of such a disagreement. Perhaps, the internal structure of a "ball of threads" is actually rather complex, such that it allows molecules to retain their preferred orientation with respect to the substrate. Since the lattice parameters for this thin-film phase are unknown, it is not possible to determine the orientation. In the XRD patterns of the films of II and III isomers, the intensity of all peaks related to hot-grown films decreases, whereas the number and relative intensity of the peaks remain unchanged—Figure 3. Given equal nominal thickness of molecular layers in all batches, this can be explained by decreased strength of the crystallites texture in hot-grown films, which, again, is not consistent with the SEM/AFM images in Figures 2 and S2. Crystallinity of Cu-EtioP-III is stronger suppressed by deposition on a hot substrate: the intensity of peaks is reduced by a factor of five (Figure 3).



**Figure 3.** XRD patterns of Cu-EtioPs films deposited on cold (from [1]) and hot silicon substrates; assignment of peaks for Cu-EtioP-III is discussed in Appendix A.

It seems natural to assume that the morphological singularity of etioporphyrin isomer films would result in variations of their macroscopic properties, the most interesting of which is electrical conductivity. Therefore, we examined the conductive properties of the films that were similarly deposited on the IDE substrates maintained at either cold of hot temperature  $T_g$ —Table 1. These are commercially available substrates consisting of a highdielectric support (finely polished polycorundum  $p-Al_2O_3$  plates) equipped with a pair of photolithographically patterned 60 nm thick multi-pin electrodes (nickel) spaced 30  $\mu$ m apart [1]—Figure S6. Thus, the growth surface in the electrode channel is not the same as in the Si(111) wafers used for SEM/AFM and XRD measurements; in its dielectric nature and roughness, it is close to the glass used for optical measurements. The morphology of films grown on dissimilar substrates (glass and Si) is compared in Figures S3–S5. It may be concluded that the substrate material definitely affects the morphology of the growing etioporphyrin layer; in particular, those grown on insulating technical substrates are more textured—cf. [10]. However, the general trends demonstrated by the isomers continue.

The values of  $\sigma$  are low, which is typical of weakly bound molecular solids [6,8], with no lucid correlation with an isomer type. Similarly to phthalocyanines, the dark conductivity in copper etioporphyrins is most likely of extrinsic nature and associated with the presence of thermally activated charge carriers (holes) [2,4,5]. *E*<sub>act</sub> increases in the isomeric row I $\Rightarrow$ II $\Rightarrow$ III, remaining basically the same for cold- and hot-grown films—Table 1. The most obvious distinction between cold- and hot-grown films consists in the two-orders-of-magnitude lower conductivity and in a largely increased photosensitivity; these parameters are likely to be interrelated. A decrease in the dark conductivity in hot-grown films can be explained by the fact that, despite the appearance of large-sized grains with a presumably high conduction ability, there exist well-defined intergrain boundaries, deep voids, etc., which limit the charge transport—Figure 2. Nonetheless, the results in Table 1 are somewhat surprising, since the morphology of films composed from different isomers, e.g., the size, shape, composition, and orientation of grains, differ very strongly, whereas the conductivity parameters change either slightly or monotonically.

Note that the value of  $\sigma$  corresponds to the lateral transport of charge carriers across the film, it may change when measured in the vertical direction, i.e., in the sandwich electrode geometry [5], as the films are textured. Therefore, a slight variation of  $\sigma$  depending on the isomer type can be assigned to the existence of a very thin underlayer that bridges the electrodes and, hence, determines the charge transport in the channel. This layer could be amorphous or somehow oriented [10], so that the correlation of  $\sigma$  with the bulk film morphology would be minimal; in hot samples, it becomes thinner. To rule this hypothesis out, one needs to do measurements on the sandwich-type cells with a varying bottom electrode material (this work is underway currently).

On the other hand, such a strong increase in the photo-assisted conductivity of hotgrown Cu-EtioP-III films cannot be solely due a decrease in the dark-current signal—Table 1. The mechanisms underlying the photoconductivity in the polycrystalline porphyrin-type materials are recently reviewed in [2]. The photosensitivity reaches  $1.4 \times 10^4$  for the IIIisomer, which is a very high value for for an IDE-based cell with a top-evaporated molecular layer [6,8]. Therefore, the photo-activated transfer of charge carriers in moderately biased cells seems to be more efficient across a film consisting of densely packed, highly textured crystallites of Cu-EtioP-III (Figures 2 and S3), probably due to the reduced barrier heights. In other words, the bulk morphology of films begins to play its role in the conductivity of illuminated devices.

## 4. Conclusions

A strong tendency of etioporphyrins to aggregate in films deposited on hot substrates in vacuum has been revealed. Elevated temperature is believed to provide for a rather equilibrium growth, at which the effect of peripheral isomerism of etioporphyrin molecules shows up most explicitly. As a result, thread-ball-like, needle-like structures, and bean-like supramolecular structures are formed by the I-, II- and III-isomers of copper etioporphyrin, respectively. In the former case, the growth mechanism appears to be amazing since the spirally twisted ordered aggregates lying tightly on the substrate surface give only one diffraction peak in the XRD pattern. A regular aggregation length amounts to 1  $\mu$ m in this case and exceeds 2  $\mu$ m in the case of II-isomer. This is probably a brighter example of the importance of molecular topography for self-assembling than that recently reported in [11] for saddle-shaped macrocycles with peripheral aliphatic chains.

Electrical conductivity in hot-grown films is by two orders of magnitude lower than in the cold-grown samples, while the molecular isomerism has no visual effect on the lateral charge transport parameters in both cases. However, the hot-grown films are highly photoconductive, especially in the case of Cu-EtioP-III, a light-to-dark current ratio of  $1.4 \times 10^4$  was measured in a planar cell with symmetrical contacts. This property can be used in design of economical and environmentally friendly planar detectors of visible light, considering the fact that metal-etioporphyrins-I and III can be found in nature as the components of fossil fuels and tissues (so-called petro- or geoporphyrins).

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/colloids6040077/s1, Figures S1–S7 and Tables S1–S4, CIF-file of Cu-EtioP-III crystallographic data.

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**Data Availability Statement:** Original SEM images at various magnifications, raw data of  $\sigma(T)$  dependencies and XRD patterns are available from the authors upon request.

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Conflicts of Interest: The authors declare no conflict of interest.

#### Abbreviations

The following abbreviations are used in this manuscript:

- IDE Interdigital electrodes
- ITO Indium-tin oxide layer
- AFM Atomic force microscopy
- SEM Scanning electron microscopy
- XRD X-ray diffraction

## Appendix A

In the previous work [1], we used single-crystal data for Cu-EtioP-I and Cu-EtioP-II available in the literature in order to analyze the experimental XRD patterns of powders and thin films. To our knowledge, no data are available for Cu-EtioP-III and for III-isomers of any metal-etioporphyrin in general. Moreover, the reviewers of that article expressed an interest in this problem in their comments. Although the issues of growth and analysis of single crystals lie somewhat beyond our expertise, we attempted to obtain macroscopic samples of Cu-EtioP-III suitable for single-crystal X-ray measurement. Eventually, the crystals were grown by vapor diffusion of methanol into the solution of Cu-EtioP-III in chloroform. The crystallographic data have been deposed in the Cambridge Crystallographic Data Centre under the deposition code CCDC 2201607 (geometric data available in Supplementary Tables S1–S4).



**Figure A1.** Comparison of experimental powder diffraction pattern of Cu-EtioP-III, green curve (from [1]) and simulated XRD-pattern, black curve (tuned cell).

## Comments:

- 1. An excellent coincidence between the diffraction curve reconstructed using a CIF-file and the XRD-pattern of freshly synthesized Cu-EtioP-III powder (Figure A1) confirms the reliability of the single-crystal experiment and the accuracy of obtained unit cell parameters.
- 2. According to the obtained data for the unit cell, the peaks at 7.5 and 8.7 degrees should be assigned to the diffraction planes (011) and (010), respectively, as shown in Figure 3, bottom panel. The tentative assignment of peaks made for the XRD patterns of Cu-EtioP-III in [1], Supplementary Materials, is therefore invalid.
- 3. It is now possible to conclude what is behind the changes in the relative intensity in Figure S3c. In most cases, there are two co-existing arrangements with respect to the substrate, in each of which flat Cu-EtioP-III molecules tilt away from the substrate surface, i.e., "standing-on" arrangement [1,10]. The tilt angle of molecular planes is 54.8° and 49.8° for (011) and (010) orientation, respectively—Figure A2. The Cu-EtioP-III films deposited on hot glass show a large increase in intensity of the (011) peak, accompanied by the drop of intensity of the (020) peak—Figure S3c. This indicates that the molecules prefer the (011) type of orientation only—Figure A2.



Figure A2. Cont.



**Figure A2.** Crystal packing of Cu-EtioP-III (**top center**), orientation of molecules: (**bottom left**)—(011) plane parallel to the substrate, (**bottom right**)—(010) plane parallel to the substrate.

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