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<td>Author(s)</td>
<td>Hada, Miyako; Shioya, Nobutaka; Shimoaka, Takafumi; Eda, Kazuo; Hada, Masahiko; Hasegawa, Takeshi</td>
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Kyoto University
Comprehensive Understanding of Structure-Controlling Factors of a Zinc Tetraphenylporphyrin Thin Film Using pMAIRS and GIXD Technique


Abstract: The performance of an organic electronic device is significantly influenced by the anisotropic molecular structure in the film, which has long been difficult to predict especially for a solution process. In the present study, a zinc tetraphenylporphyrin (ZnTPP) thin film prepared by a solution process is chosen to comprehensively explore the molecular arrangement mechanism as a function of representative film-preparation parameters: solvent, film-preparation technique, and thermal annealing. The anisotropic structure is first analyzed by using the combination technique of infrared p-polarized multiple-angle incidence resolution spectrometry (pMAIRS) and grazing incidence X-ray diffraction (GIXD), which readily reveal the molecular orientation and crystal structure, respectively. As a result, the real dominant factor is found to be the “evaporation time of the solvent,” which determines the initial two different molecular arrangements, types-I and -II, while the thermal annealing is found to play an additional role of improving the molecular order. The correlation between the molecular orientation and the crystal structure has also been revealed through the individual orientation analysis of the porphyrin and phenyl rings.

Introduction

Organic semiconductors used for thin film electronic devices are made of polymeric or small-molecular materials. Most of the polymeric semiconductors represented by poly-(3-hexylthiophene-2,5-diyl) (P3HT) and poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) are highly soluble in an organic solvent, and thus a thin film can be prepared easily and inexpensively via a solution process such as the spin-coating techniques. The polymeric materials, however, have an intrinsic issue of a low charge mobility[1] due to a poor molecular ordering in the thin film.

In contrast, small-molecular materials represented by pentacene and dinaphtho[2,3-b:2′,3′-f]thieno[3,2-b]thiophene (DNTT) exhibit high charge mobilities[2] thanks to a high crystallinity in the thin film. Unfortunately, however, these representative compounds have a low solubility in an organic solvent, which makes the film preparation difficult via a solution process. In fact, the vacuum vapor deposition[3] and molecular beam epitaxy[4,5] methods, which are unsuitable for a mass production, are thus often employed.

To overcome the dilemma, solvent-soluble small-molecular semiconductors accompanying additional chemical groups with a high affinity to organic solvents have been developed[13-17] which are expected to possess both high solubility and high charge mobility. One of the materials is zinc tetraphenylporphyrin (ZnTPP; chart 1) that is composed of the porphyrin skeleton and four phenyl rings. By introducing the phenyl moieties, ZnTPP is made highly soluble in many organic solvents. Since porphyrin or phthalocyanine is a representative small-molecular organic semiconductor for electronic devices,[18] ZnTPP receives much attention as a promising compound and as a solution-processable small-molecular material for the devices.[19-22]
slowly in a drop-casted (DC) film. Therefore, an appropriate combination of a solvent (Chl or TCB) and a film-preparation technique (SC or DC) controls the solvent “evaporation time,” which finally controls the molecular arrangement in the film.

Another important film-preparation parameter is the “thermal annealing” technique, which is often used to order or convert the molecular arrangement in a thin film. For example, the thermal annealing improves the semiconductor properties (i.e., charge mobility, on/off ratio, etc.) of an etioporphyrin-I thin film.

In the present study, the film structure of a ZnTPP thin film is studied comprehensively and systematically for all the combinations of the three film-preparation parameters in terms of the molecular orientation and the crystal structure.

For the purpose, we have first employed the combined analytical technique of infrared p-polarized multiple-angle incidence resolution spectrometry (pMAIRS) and the grazing incidence X-ray diffraction (GIXD) technique. The combination technique is quite powerful to reveal the correlation between the molecular orientation and crystal structure in a thin film: the molecular orientation of each chemical group in the thin film is revealed quantitatively by using pMAIRS and GIXD provides the crystal structure (and/or crystallinity). As a result, the molecular arrangement in the ZnTPP film has been found to have a wide variety of the molecular orientation and crystal structure, which can readily be controlled by choosing an appropriate combination of only three film-preparation parameters.

Results and Discussion

Molecular orientation in a ZnTPP film prepared from a Chl solution: Figure 1 shows pMAIRS spectra of the ZnTPP thin films prepared from the Chl solution (denoted as “Chl films”). The red and blue lines are the in-plane (IP) and out-of-plane (OP) spectra, respectively. The spectra of a–d in Figure 1 correspond to the samples a–d listed in Table 1, respectively. The band assignments of the spectra of ZnTPP were made after a DFT calculation, and the results are summarized in Table S1 (Supporting Information). The C–H out-of-plane deformation vibration ($\gamma$(C–H)) band of an aromatic ring appears in the low wavenumber region of 900–650 cm$^{-1}$, while the C–H in-plane deformation vibration ($\delta$(C–H)) band appears in 1600–950 cm$^{-1}$. The $\gamma$(C–H) and $\delta$(C–H) modes have transition moments perpendicular and parallel to the aromatic ring plane, respectively. In particular, the $\gamma$(C–H) mode is fortunately highly localized on the ring with a strong absorption coefficient, which is quite useful for analyzing the molecular orientation of the ring.$^{[23,29]}

As found in the Chl-SC film (Figure 1a), the pMAIRS-IP and -OP spectra have comparable band intensities in all the regions, which straightforwardly indicates that ZnTPP in the film has a random orientation. After annealing this film (denoted as “Chl-SC-A film”; Figure 1b), the bands at 798 and 718 cm$^{-1}$, both of which are assigned to the $\gamma$(C–H) modes of ‘porphyrin’ ring ($\gamma$(C–H)$_{\text{por}}$; Figure 2a),$^{[40-42]}$ develop significantly in the OP spectrum.

![Figure 1. Infrared pMAIRS spectra of the ZnTPP thin films prepared from the Chl solution.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent</th>
<th>Film-preparation technique</th>
<th>Annealing</th>
<th>Evaporation time</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>Chl</td>
<td>Spin-Coating (SC)</td>
<td>×</td>
<td>Short</td>
</tr>
<tr>
<td>(b)</td>
<td>Chl</td>
<td>SC</td>
<td>Annealed</td>
<td></td>
</tr>
<tr>
<td>(c)</td>
<td>Chl</td>
<td>Drop-Coating (DC)</td>
<td>×</td>
<td></td>
</tr>
<tr>
<td>(d)</td>
<td>Chl</td>
<td>DC</td>
<td>Annealed</td>
<td></td>
</tr>
<tr>
<td>(e)</td>
<td>1,2,4-trichlorobenzene (TCB)</td>
<td>SC</td>
<td>×</td>
<td>Long</td>
</tr>
<tr>
<td>(f)</td>
<td>TCB</td>
<td>SC</td>
<td>Annealed</td>
<td></td>
</tr>
<tr>
<td>(g)</td>
<td>TCB</td>
<td>DC</td>
<td>×</td>
<td></td>
</tr>
<tr>
<td>(h)</td>
<td>TCB</td>
<td>DC</td>
<td>Annealed</td>
<td></td>
</tr>
</tbody>
</table>
Figure 2. Schematic diagram of the vibration modes and the angles between the substrate surface normal and the direction of the transition moment: the angles of $\phi_{\text{por}}$ and $\phi_{\text{ph}}$ correspond to the $\gamma$(C–H)$_{\text{por}}$ (a) and $\gamma$(C–H)$_{\text{ph}}$ (b) modes, respectively.

Considering the surface selection rule of the pMAIRS spectra (see Experimental), the porphyrin ring should lie parallel to the substrate, that is, the face-on orientation.

The phenyl ring, on the other hand, is remained to have a random orientation as indicated by the intensity ratio of the $\gamma$(C–H) bands of the ‘phenyl’ ring ($\gamma$(C–H)$_{\text{ph}}$; Figure 2b) at about 700 cm$^{-1}$ between the IP and OP spectra. This trend is also found for the Chl-DC film (Figure 1c) and the annealed Chl-DC film (“Chl-DC-A film”; Figure 1b): the thermal annealing makes the molecular orientation improved for the porphyrin ring, while the phenyl ring is kept un-oriented (as summarized in Table 2).

**Molecular orientation in a ZnTPP film prepared from a TCB solution:** Figure 3 shows pMAIRS spectra of the ZnTPP thin films prepared from the ‘TCB’ solution (denoted as “TCB films”). The spectra in Figure 3e-3h correspond to the samples e-h listed in Table 1, respectively. Since TCB exhibits a low-volatile character (b.p. 214°C) in contrast to Chl (b.p. 59°C), a long evaporation time is needed for obtaining a TCB film. The lower evaporation rate than that of Chl significantly influences the molecular orientation in the generated film: all the TCB films have an extremely large dichroic ratio between the OP and IP spectra in a wide wavenumber range as shown in Figure 3. This indicates that the ZnTPP molecules have highly oriented structures irrespective of the thermal annealing. With a similar discussion to that of the spectra in Figures 1b and 1d, the porphyrin ring in all the TCB films takes the face-on orientation. Note that the $\gamma$(C–H)$_{\text{por}}$ bands at 798 and 718 cm$^{-1}$ are shifted to 803 and 723 cm$^{-1}$, respectively, by changing the solvent from Chl to TCB. These band shifts will be discussed in detail later with related to XRD measurements.

Table 2. The correlation between the crystal structure and the molecular orientation in the ZnTPP thin film as a function of the film-preparation parameter.

<table>
<thead>
<tr>
<th>Film-preparation parameter</th>
<th>Molecular Orientation</th>
<th>Major molecular arrangement</th>
<th>Evaporation time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Porphyrin ring</td>
<td>Phenyl ring</td>
<td></td>
</tr>
<tr>
<td>Chl-SC</td>
<td>Random</td>
<td>Random</td>
<td>Amorphous (Type-I)</td>
</tr>
<tr>
<td>Chl-SC-A</td>
<td>Face-on</td>
<td>Random</td>
<td>Monoclinic (Type-I)</td>
</tr>
<tr>
<td>Chl-DC</td>
<td>Random</td>
<td>Random</td>
<td>Amorphous (Type-I)</td>
</tr>
<tr>
<td>Chl-DC-A</td>
<td>Face-on</td>
<td>Random</td>
<td>Monoclinic (Type-I)</td>
</tr>
<tr>
<td>TCB-SC</td>
<td>Face-on</td>
<td>Edge-on</td>
<td>Monoclinic (Type-II)</td>
</tr>
<tr>
<td>TCB-SC-A</td>
<td>Face-on</td>
<td>Edge-on</td>
<td>Monoclinic (Type-II)</td>
</tr>
<tr>
<td>TCB-DC</td>
<td>Face-on</td>
<td>Edge-on</td>
<td>Monoclinic (Type-II)</td>
</tr>
<tr>
<td>TCB-DC-A</td>
<td>Face-on</td>
<td>Edge-on</td>
<td>Monoclinic (Type-II)</td>
</tr>
</tbody>
</table>
The TCB films have another significant characteristic that even the γ(C–H)por band exhibits an apparent MAIRS dichroism for the band at 703 cm⁻¹, i.e., the IP band is much stronger than the OP one. Therefore, in the TCB films, the phenyl ring is concluded to stand perpendicularly on the substrate (the edge-on orientation) in contrast to the orientation of the porphyrin ring.

Another notable band is the δ(C–H) band of the phenyl ring (δ(C–H)ph) at 1440 cm⁻¹ appears dominantly in the OP spectrum. According to the DFT calculation, the transition moment of this band is parallel to the phenyl ring plane, and at the same time it is vertical to the phenyl-porphyrin bond, as shown in Figure 2c. In this manner, the TCB films have been found to have the phenyl ring with the edge-on orientation. In other words, the phenyl rings, which intrinsically have a rotational flexibility, are highly fixed in the TCB films. The highly oriented structure is thus found to be induced not by annealing, but by the slow-evaporation character of TCB (Table 2). The reason to induce this unique orientation will be revealed in the XRD part later.

In fact, the orientation of ZnTPP is improved by increasing the ‘evaporation time.’ For example, the TCB-SC film (Figure 3e) has a slightly inferior molecular orientation than that of the TCB-DC film (Figure 3g) as found at the bands of 803 cm⁻¹ on a fact that the drop-cast process needs a longer evaporation time than the spin-coating process. This suggests that a slower evaporation is preferable to a better crystallization, which would thus found to be induced not by annealing, but by the slow-evaporation character of TCB (Table 2). The reason to induce this unique orientation will be revealed in the XRD part later.

Analysis of Orientation Angle: Table 3 shows the orientation angles of the porphyrin and phenyl rings in the ZnPorph films revealed by pMAIRS using eq. (1), where Φpor and Φph are the angles of the ‘plane normal’ of the porphyrin and phenyl rings from the substrate normal, respectively (Figure 2). The angles of Φpor and Φph are evaluated by using the γ(C–H)por band at about 800 cm⁻¹ and the γ(C–H)ph band at about 700 cm⁻¹, respectively.

As shown in Table 3, the orientation angles have a strong correlation with the evaporation time of the solvents. Note that, in the annealed TCB-DC film (denoted as “TCB-DC-A” film) taking the longest time to evaporate the solvent, Φpor and Φph are 11° and 78°, respectively. The orientation angle of 11° is surprisingly small as compared even with the Langmuir monolayer on water (27° ± 3°)[43] and the vacuum vapor-deposited film (28° ± 10°).[19] The Chi-SC film, in contrast, exhibits a nearly isotropic structure. In fact, both orientation angles of the porphyrin and phenyl rings (52° and 59°, respectively) are fairly closed to the magic angle, 54.7°, which quantitatively confirms the isotropic structure. In a similar manner, other discussions in the previous sections have also been confirmed more quantitatively as found in Table 3.

![Figure 4. Magnified pMAIRS spectra of the γ(CH)_por at ca. 800 cm⁻¹ in the annealed ZnPorph thin films. The wavenumber positions of 798 and 803 cm⁻¹ reflect to the type-I and -II crystals, respectively.](image-url)

### Table 3. The orientation angles of the porphyrin and phenyl rings. Φpor and Φph are the angles between the substrate normal and the direction of each vibration mode γ(C–H)por and γ(C–H)ph, respectively.

<table>
<thead>
<tr>
<th>Film-preparation parameter</th>
<th>Porphyrin ring</th>
<th>Phenyl ring</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Orientation</td>
<td>Orientation</td>
</tr>
<tr>
<td>Chl-SC</td>
<td>52 Random</td>
<td>59 Random</td>
</tr>
<tr>
<td>Chl-SC-A</td>
<td>31 Face-on</td>
<td>60 Random</td>
</tr>
<tr>
<td>Chl-DC</td>
<td>49 Random</td>
<td>51 Random</td>
</tr>
<tr>
<td>Chl-DC-A</td>
<td>39 Face-on</td>
<td>54 Random</td>
</tr>
<tr>
<td>TCB-SC</td>
<td>20 Face-on</td>
<td>70 Edge-on</td>
</tr>
<tr>
<td>TCB-SC-A</td>
<td>21 Face-on</td>
<td>73 Edge-on</td>
</tr>
<tr>
<td>TCB-DC</td>
<td>16 Face-on</td>
<td>73 Edge-on</td>
</tr>
<tr>
<td>TCB-DC-A</td>
<td>11 Face-on</td>
<td>78 Edge-on</td>
</tr>
</tbody>
</table>
the solvent evaporation time: the relative intensity of the band at 803 cm⁻¹ (correlated with type-II) to that at 798 cm⁻¹ (type-I) becomes larger with an increase of the evaporation time (as summarized in Table 2). This trend is also found in the un-annealed films (Figure S1). Therefore, the 'molecular arrangement' of ZnTPP in the thin film is expected to be controlled by changing the evaporation time as confirmed in the next section.

Crystal structure analysis by XRD measurements: To support the IR results in Figure 4, the ZnTPP films were investigated by using GIXD. Figure 5 shows the GIXD patterns of annealed films in both IP and OP diffractions, and all the GIXD-IP patterns of the films are different from the GIXD-OP ones. This difference apparently indicates that ZnTPP crystallites are highly oriented in the thin films, as found in the IR results.

The crystal of ZnTPP is known to have polymorphism.[46-48] In fact, the GIXD patterns are of two different patterns marked by asterisks (*) and dots (●) as found in Figure 5. The Chl-SC-A film (Figure 5a) has an asterisk peak in both IP and OP patterns. On the other hand, the TCB-SC-A film (Figure 5d) exhibits totally different peaks marked by the dots with no asterisk peaks. The rest films (Figures 5b and 5c) consist of the two patterns. By referring to the calculated XRD patterns from the crystal structure reported in a previous study, the asterisk and dot peaks are readily assigned to the two different monoclinic crystal systems (CCDC Refcode: ZZTTAY03[46] and ZNTPOR03,[48] respectively). In this manner, the GIXD patterns apparently indicate that the ZnTPP films are of two polymorphs. Since the pattern variation perfectly agrees with those of the pMAIRS spectra (Figure 4), the former and latter monoclinic crystal systems should correspond to the molecular arrangements of type-I and -II, respectively. The IR bands at 798 and 803 cm⁻¹ are thus assigned to the two different molecular arrangements.

Figures 4 and 5 exhibit a good correlation that the type-I arrangement decreases while the type-II one increases with increasing the solvent evaporation time. This suggests that the type-I arrangement has a kinetically stable structure; while the type-II arrangement is thermodynamically favorable. According to Ruan et al.,[48] two nitrogen atoms of the porphyrin ring are coordinated with the hydrogen atoms of the neighboring phenyl rings in the monoclinic arrangement. Since type-II corresponds to the monoclinic arrangement, the edge-on orientation of the phenyl ring in the type-II films should be induced by the coordination, which also accounts for the thermodynamically stable character.

The evaporation time also influences the ‘orientation of the crystallite’ via the crystallinity change. As found in Figure 5b, the Chl-DC-A film comprises both type-I and -II with a major and minor quantities, respectively. Some of the type-II peaks (indexed by 110, 020 and 201) appear commonly in the GIXD-IP and -OP patterns. On the other hand, ‘type-I’ component has only 10-1 peak in the IP pattern, while it yields only 110 peak in the OP one. This implies that the major component, type-I, is highly oriented, while the coexisting type-II has a nearly random orientation.

In a similar manner, the TCB-SC-A film (Figure 5c) is analyzed to have a reversed conclusion that type-II is the major component with a highly oriented structure, while the minor type-I component has a random orientation. Thus, the crystal orientation of types-I and -II also has an apparent correlation with the evaporation time of the solvent.

Influence of thermal annealing studied by XRD measurements: Thermal annealing of a film is another important factor of molecular ordering. In the previous section, all the analyses were performed on annealed films. To investigate the annealing effect, un-annealed films are also analyzed.

Figure 6 shows the GIXD-IP and -OP patterns of the un-annealed ZnTPP films. Of interest is that all the un-annealed films have no asterisk peak assigned to type-I; while the type-II peaks marked with dots appear. This means that the thermal annealing is necessary to generate the type-I 'crystal,' while the type-II crystal does not need annealing. This result looks strange when the IR results are taken into account. Since the un-annealed films of Chl-SC, Chl-DC and TCB-SC (Figure S1) exhibit the IR band at 798 cm⁻¹ assigned to type-I arrangement, they should yield the asterisk peaks. This is because pMAIRS reveals ‘molecular arrangement’ in both amorphous and crystal; whereas GIXD responds to both molecular arrangement and the crystallinity, which is limited in a crystal. The ‘molecular arrangement’ such as the monoclinic crystal systems of type-I and -II in an un-annealed film is determined at the initial stage immediately after the solvent evaporation, but it has poor ‘crystallinity.’ Since pMAIRS is sensitive to the molecular arrangement irrespective of the crystallinity, the γ(C–H)por band appears apparently. After the thermal annealing, the molecular order is improved to have a good crystallinity, which gives GIXD peaks in type-I.
In a similar manner, the type-II GIXD peaks of the annealed films are compared with those of the un-annealed ones (Figures 5 and 6). The annealed films apparently have stronger peaks than the un-annealed films, which confirms that crystallinity in type-II is improved by annealing the films.

As a conclusion, the effect of thermal annealing strongly depends on the initial state of molecular arrangement. Thus, the thermal annealing only helps improvement of the molecular order, and the solvent evaporation time is the dominant factor to determine the molecular arrangement of a ZnTPP film.

Conclusions

The molecular anisotropic structure of ZnTPP in films prepared by solution processes is comprehensively investigated by using a combinatorial technique of pMAIRS and GIXD. As a result, the molecular and crystal orientation, and the crystal structure are found to be controllable by the evaporation time of solvent depending on the two film-preparation parameters, a solvent and a film-preparation technique. The third parameter, thermal annealing, on the other hand, is found to mainly play a role for improving the crystallinity.

When a highly-volatile Chl solution is used for film-preparation, the porphyrin ring has the face-on orientation and this structure comes from the type-I arrangement; while in the TCB films taking the long time to become dried films, the type-II arrangement is generated where the porphyrin ring is highly oriented parallel to the substrate (11°), and the four phenyl rings on the porphyrin ring have a vertical stance (78°).

In addition, the component fraction and crystal orientation of types-I and -II are also correlated with the evaporation time. With increasing the evaporation time, the amounts of the type-I and -II crystallites are decreasing and increasing, respectively. In a similar manner, the crystal orientation of types-I and -II become inferior and improved, respectively, when a long evaporation time is taken. In this manner, the correlation between the molecular orientation and the crystal structure as a function of the film-preparation parameters is comprehensively revealed.

In the present study, because of the sublimation character of ZnTPP, the annealing was performed far below the melting point, which is a usual condition for small molecular compounds. In this case, the kinetically stable type-I arrangement keeps the arrangement, and it does not change into the thermodynamically stable type-II one. This confirms again that the molecular arrangement is not influenced by the annealing, but it is determined only by the solvent evaporation rate.

Experimental Section

Materials: Zinc(II) tetraphenylporphyrin (ZnTPP) was purchased from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan), which was used without further purification. Chloroform (Chl) was the ACS spectrophotometric grade with a purity of \( \geq 99.8\% \) and 1,2,4-trichlorobenzene (TCB) was the chromasolv grade with a purity of \( \geq 99\% \), which were both purchased from Sigma Aldrich (St. Louis, MO, USA).

Film Preparations: A Chl solution of ZnTPP with a volume of 20 \( \mu \)L at 10.0 mM was deposited on a silicon substrate using an Active (Saitama, Japan) ACT-300T Spincoater at 2000 rpm for 60 seconds to have a spin-coated (SC) film. In a similar manner, a TCB solution of 40 \( \mu \)L at 20.0 mM was used on the spin coater at 1000 rpm for a few seconds. The spinning time was changed depending on the character of the solvent. Since TCB has a weak affinity to the silicon substrate surface, for example, a spinning time was very short; otherwise most of the solvent would be thrown away. To have solvent-free films, several seconds and a few hours were spent, respectively, for the SC films made from the Chl and TCB solutions (abbreviated as “Chl-SC film” and “TCB-SC film,” respectively).

Drop-casted (DC) films were prepared by using a 2.0 mM Chl solution and a 4.0 mM TCB solution of ZnTPP (“Chl-DC film” and “TCB-DC film,” respectively). After spreading a solution with a volume of 40 \( \mu \)L on a silicon substrate, it was dried in ambient air for a minute and a few days, respectively, for the SC films made from the Chl and TCB solutions. The SC films were found to have the thickness of ca. 40 and 110 nm, respectively. All the films were prepared on a double-side polished silicon substrate with a square shape (40x20 mm²) in ambient air (25°C), and the thermal annealing was performed at 100°C for 2 hours on an IKA (Osaka, Japan) C-MAG HS 4 hot-stirrer.

IR band assignment by DFT Calculations: Quantum-chemical calculations were performed by using the Gaussian09 program package.\[^{[49]}\] The density functional theory (DFT) method was used with the B3LYP hybrid functional to calculate the molecular vibration frequencies and vibration modes. The 6-311G(d,p) basis set\[^{[50]}\] was used for Zn and the 6-311G(d,p) basis set\[^{[50]}\] was used for the other atoms.

Figure 6. GIXD-IP and -OP patterns of the un-annealed ZnTPP thin films. The diffraction peaks marked with black circles and asterisks are assigned to the type-I and -II crystals, respectively.

![Figure 6](image-url)
**ACKNOWLEDGEMENTS**

This work was financially supported by Grant-in-Aid for Scientific Research (A) (No. 15H02185 (TH)) and Grant-in-Aid for Young Scientists (B) (No. 26810075 (TS)) from Japan Society for the Promotion of Science, for which the authors thanks are due.

**Keywords:** pMAIRS • GIXD • molecular orientation • thin films • porphyrinoids

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**GIXD measurements:** GIXD measurements were performed by using a RIGAKU (Tokyo, Japan) SuperLab diffractometer with a Cu rotating anode X-ray generator operated at 40 kV and 30 mA (1.2 kW), generating the CuKα (λ = 0.15418 nm) radiation. The XRD in-plane (IP) and out-of-plane (OP) patterns (denoted as GIXD-IP and -OP patterns) were obtained in the range between 2θ = 1° and 30° having a sampling step of 0.01° with a scan speed of 1° min⁻¹. For all the XRD measurements, the parallel X-ray beam was incident on the sample at the fixed angle of α = 0.20° from the surface parallel.

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[48] W. J. Ruan, Z. A. Zhu, X. H. Bu, Z. H. Zhang, Y. Shao, Y. T. Chen, Chin. J. Struct. Chem. 1998, 17, 159-164. ZnTPP in the monoclinic single crystal reported in this paper is a monohydrate. ZnTPP of type-II in our thin films, however, is not hydrated (see the δ(H2O) region around 1650 cm⁻¹ in Figure 3). This suggests that the hydration is not important to have the type-II crystallites.
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Comprehensive Understanding of Structure-Controlling Factors of a Zinc Tetraphenylporphyrin Thin Film Studied by pMAIRS and GIXD Technique.