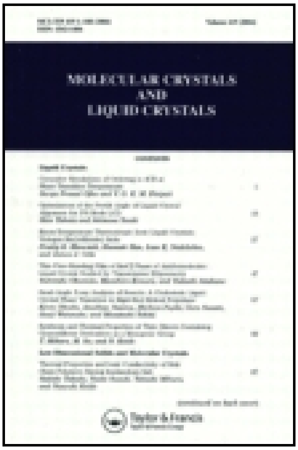

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# Epitaxial Growth of 5,10,15,20-Tetraphenylporphyrin Metal Complexes and Their Photovoltaic Properties

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# EPITAXIAL GROWTH OF 5,10,15,20-TETRAPHENYLPORPHYRIN METAL COMPLEXES AND THEIR PHOTOVOLTAIC PROPERTIES

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ABSTRACT Epitaxial growth of 5,10,15,20-tetraphenylporphyrin metal complexes (MTPP; M = Zn, Mg, Co, VO) and their photoelectrochemical properties were investigated. MTPP crystals grew epitaxially on a KCl (001) surface by a physical vapor deposition method. All the crystals belong to the tetragonal system. The (100) plane of MTPP crystals is parallel to the KCl (001) plane, and the [100] axis is parallel to the KCl <120> axis. Photoelectrochemical properties were measured in the indium-tin oxide(ITO)/MTPP/$I_3^-$,$I^-$/Pt system.

## INTRODUCTION

Porphyrin films attract interests as a functional material in solar energy conversion.[1] Many porphyrin derivertives with various central metals and substituents were prepared in order to improve the photovoltaic properties.[2] Most of photoelectrochemical investigations using organic semiconductors have been made for amorphous or polycrystalline thin films. A $H_2$TPP film orientation-controlled exhibited higher photocurrent three times than that of its polycrystalline film.[3] The results suggensts that a molecular arrangement and a crystal orientation in films play an important role in photovoltaic properties of organic cell.

In this paper, MTPP films were prepared on a KCl cleavage surface and the molecular arrangement in the film was observed by electron microscopy. The photoelectrochemical properties of films were investigated in wet cells.

## RESULTS AND DISCUSSION

Figure 1 shows electron micrographs and selected area electron diffraction patterns of the ZnTPP films deposited on a KCl and ITO substrates. The film deposited on a KCl substrate (a) was

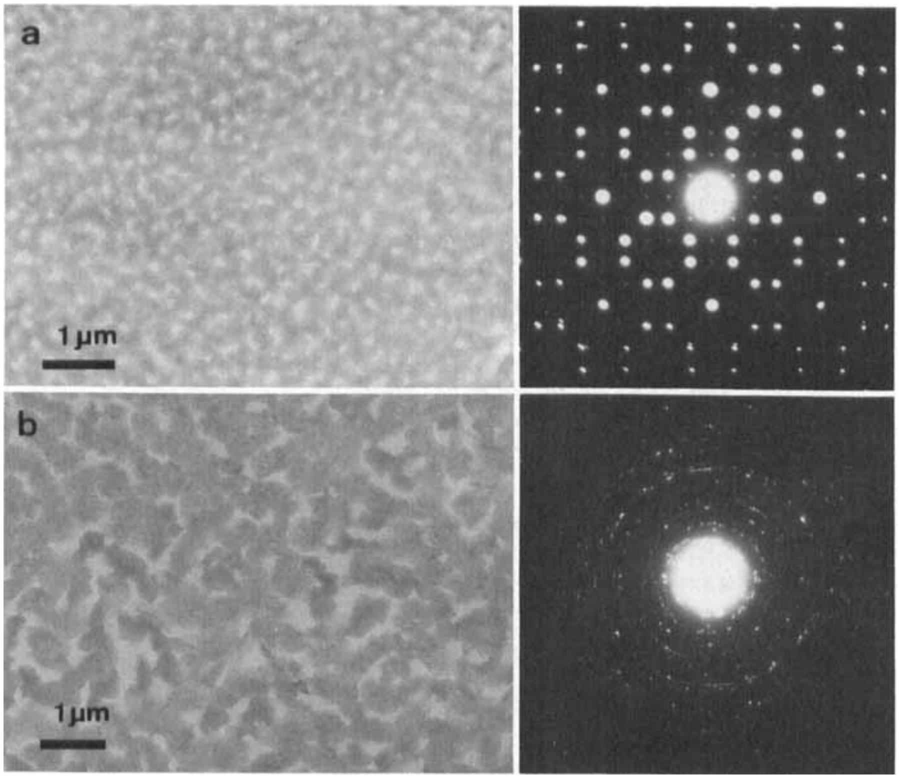


FIGURE 1 Electron micrographs and electron diffraction patterns of the ZnTPP films deposited on KCl (a) and ITO glass (b).

composed of crystals which grew epitaxially on the substrate. The electron diffraction pattern consisted of superposition of two tetragonal single pattrens, and the angle between the two patterns was 37°. On the other hand, the film deposited on an ITO substrate (b) was composed of crystallites, so that the electron diffraction showed a ring pattern. The crystal belonged to a tetragonal system, and the lattice constants were as follows: a = 1.34, c = 0.97 nm, which agreed well with those of $ZnTPP \cdot H_2O$ crystal.[4] The c-axis of the crystal was perpendicular to the KCl (001) plane, and the a-axis was parallel to the KCl <210> direction.

Figure 2 shows $2\theta/\theta$ X-ray diffraction patterns from the original powder of ZnTPP (a), the film deposited on the KCl (b), and the film on the ITO glass (c). The pattern from



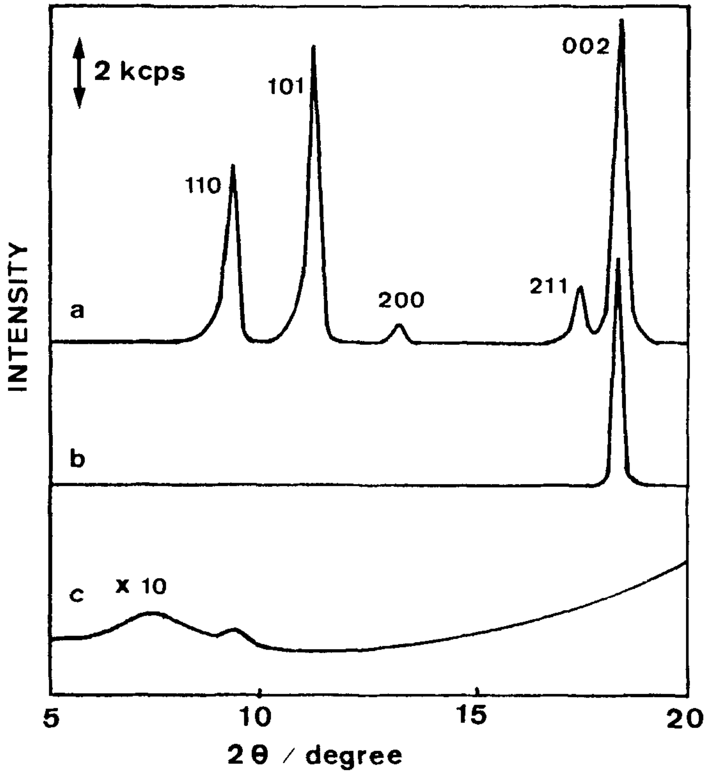


FIGURE 2 X-ray diffraction of the original powder (a), the film deposited on KCl (b), and the film on ITO glass (c).

powder showed diffraction peaks of the tetragonal crystal. The film deposited on the KCl showed only one reflection from the (002) plane. This indicates that the ZnTPP crystals grew epitaxially all over the substrate taking its (001) plane paralell to the substrate. No clear peak was observed for the film deposited on the ITO glass, which was caused by crystallines with random orientation.

After separating the epitaxial film from the KCl substrate in water, the MTPP film was mounted on an ITO glass as an electrode. Figures 3 (a) and (b) show current-voltage characteristics in the dark and under illumination of the polycrystalline and oriented ZnTPP electrodes, respectively.

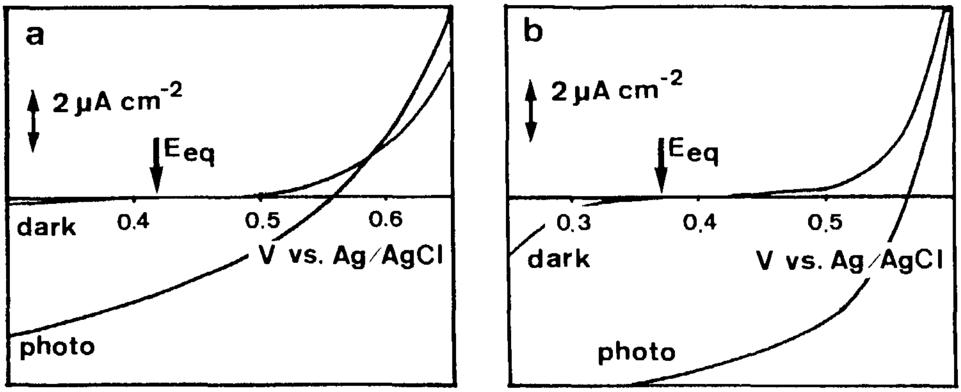


FIGURE 3 Current-voltage curves in the dark and under illumination of the polycrystalline (a) and oriented (b) ZnTPP electrodes, respectively.

The thickness of the ZnTPP films were about 200 nm for both cases. The illumination was carried out with white light of 100 mW $cm^{-2}$ from the side of electrolyte solution to the ZnTPP films. The current-voltage curves in the dark indicate a rectifying behavior due to a p-type semiconduction of ZnTPP. The cathodic photocurrent observed under illumination is due to a band-bending of ZnTPP downward at the inteface between the ZnTPP and the $I_3^-/I^-$ solution. The photoelectrochemical data are listed in Table I. The fill factor for the oriented film was an extremely high value of about 0.46. This may be caused by orientation effect of the ZnTPP crystal.

TABLE I Photoelectrochemical data for the ZnTPP films.

| | Polycrystalline film | Oriented film |
|---|---|---|
| Isc /μA $cm^{-2}$ | 3.88 | 7.19 |
| Voc /mV | 140.0 | 197.5 |
| Imax /μA $cm^{-2}$ | 2.13 | 5.06 |
| Vmax /mV | 82.5 | 130.0 |
| ff | 0.323 | 0.463 |
| η' | $1.8 \times 10^{-4}$ % | $6.6 \times 10^{-4}$ % |

The molecular arrangements and the molecular packing in the epitaxial film are shown schematically in Fig.4. The

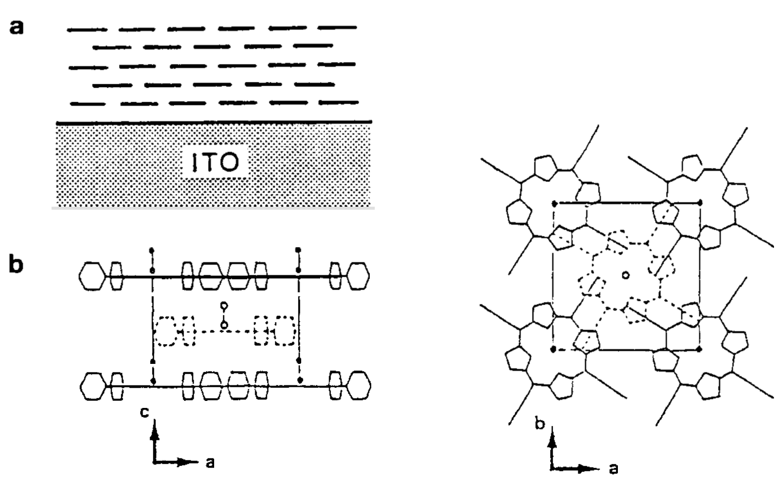


FIGURE 4 Schematic diagrams of the molecular arrangement (a) and the molecular packing (b) in the epitaxial film electrode.

planar MTPP molecules stack with its molecular plane paralell to the substrate surface. In this film, a carrier mobility seems to be larger than that of the polycrystalline film because of the high orientation.

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