

Epitaxial Growth and Molecular Orientation of Tetraphenylporphyrin Thin Film Vacuum-Evaporated on KCl

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Abstract

5,10,15,20-Tetraphenylporphyrin (H_2TPP ; $C_{44}H_{30}N_4$, $M_r = 614.75$) films were vacuum-evaporated onto a KCl (001) surface. High-resolution electron microscopy and electron diffraction patterns indicated that the H_2TPP crystal in the film is monoclinic with dimensions $a = 1.20$, $b = 1.90$, $c = 1.47$ nm, $\beta = 91^\circ$ and $Z = 4$. The rectangular crystallites grow epitaxially along four directions, the (101) plane of the crystal making parallel contact with the substrate surface and the b axis making an angle of $\pm 18.5^\circ$ with the KCl [100] or [010] directions. A high-resolution electron micrograph of the film showed fine structure in a thin crystal. Lattice fringes are aligned parallel with a spacing of 0.95 nm, and short parallel bands with a spacing of 0.38 nm are arranged obliquely in the lattice fringe. The optical diffraction pattern of the fine structure showed a long-period structure with an interval of 1.91 nm for every five bands. It is suggested that the planar molecules of H_2TPP orient themselves nearly perpendicular to the substrate surface.

Introduction

Metalloporphyrins play an important role in photo-biological phenomena of photosynthetic organisms as photon-collecting complexes in chlorophylls. Solar energy absorbed by porphyrins is transferred with high efficiency to the electron-transport system, which is integrated in a crystallographically ordered arrangement (Deisenhofer, Epp, Miki, Huber & Michel, 1985). A large number of attempts have been made to construct an artificial photosynthetic system using the photoelectrochemical properties of porphyrins (Calvin, 1978; Tabushi & Kugimiya, 1985). Thin solid porphyrin films have been attracting interest as an organic material for optoelectronic devices such as photovoltaic solar-energy converters (Kampas, Yamashita & Fajer, 1980; Harima & Yamashita, 1985), and as optical data-recording media by means of photochemical hole burning of metal-free base porphyrins (Volker & MacFarlane, 1979). In order to improve the efficiency of energy conversion, porphyrin derivatives, including various

central metals (Katsu, Tamagake & Fujita, 1980) and substituents (Yamashita, Kihara, Shimizu & Suzuki, 1982; Yamashita, Matsumura, Harima, Miura & Suzuki, 1984), have been synthesized so that photocurrent quantum yields of 20–30% have been achieved by the most efficient photovoltaic cells using vacuum-evaporated thin films (Yamashita, 1982). For the purpose of modelling photovoltaic cells with efficient energy transfer, close attention should be paid to the molecular arrangement of the porphyrins in thin films. Nevertheless, most of the photovoltaic organic materials studied so far have been amorphous or microcrystalline thin films deposited at random on metal electrodes. Few investigations have been made concerning the orientation of porphyrin crystals and their molecular arrangement in thin films.

It is well known that phthalocyanine compounds, synthetic analogues of porphyrins, show epitaxial overgrowth in thin films formed by vacuum-evaporation onto cleavage surfaces of alkali halides (Uyeda, Ashida & Suito, 1965). Their crystal structures and growth mechanisms were investigated by electron microscopy and electron diffraction (Ashida, 1966). The molecular arrangement of chlorinated copper phthalocyanine was directly determined by high-resolution electron microscopy (HREM) (Uyeda, Kobayashi, Suito, Harada & Watanabe, 1972); this was the first observation of a molecular image of a radiation-sensitive organic compound. HREM is particularly suited to the investigation of the local structure and molecular orientation in thin crystals which cannot be analyzed by X-ray diffraction methods.

In the present study, 5,10,15,20-tetraphenylporphyrin (H_2TPP , Fig. 1) films were vacuum-evaporated onto a KCl (001) surface. The crystal structure and orientation in the films were investigated by HREM, and by X-ray and electron diffraction.

Experimental

H_2TPP , obtained from Tokyo Chemical Industry Co. Ltd, was purified by sublimation in a nitrogen atmosphere at a pressure below 1 kPa and at 673 K. A

KCl (001) surface, to be used as a substrate, was cleaved in air and immediately mounted on a heater in a vacuum chamber. The substrate was preheated at 423 K for 1 h and kept at room temperature under vacuum (1×10^{-4} Pa). The purified H_2TPP was evaporated onto the substrate from a quartz crucible heated with a tungsten coil. The deposition rate and thickness were monitored with an oscillating quartz thickness meter. The deposited film was reinforced with an amorphous carbon film by the indirect deposition method. The KCl substrate was then dissolved away by floating on water and the specimen transferred to a microgrid coated with a gold film. The (111) lattice image from gold ($d = 0.235$ nm) provided an accurate magnification calibration. The unit-cell dimensions were determined from electron diffraction patterns, using the lattice spacings of gold as reference. The relative orientation between the deposited and the substrate crystals was estimated from shadow-casting of chromium along the KCl [100] direction. Electron micrographs and electron diffraction patterns were obtained with a JEOL JEM-200CX instrument equipped with a high-resolution pole piece ($C_s = 2.0$ mm). The HREM observations were carried out by means of a minimum-dose system (Fujiyoshi, Kobayashi, Ishizuka, Uyeda, Ishida & Harada, 1980) at 120 kV accelerating potential. An optical transform was obtained from the electron micrograph using an He-Ne gas laser. The X-ray work was carried out with Cu $K\alpha$ radiation and a Rigaku RINT-1500 instrument equipped with a thin-film attachment. The H_2TPP film on the KCl substrate was placed on a rotating disk and the glancing angle between the incident X-ray beam and the substrate KCl face was fixed at 0.5° . The X-ray diffraction pattern was recorded on a strip chart.

Results and discussion

The crystal growth and the orientation of H_2TPP deposited on a KCl (001) surface depends on the

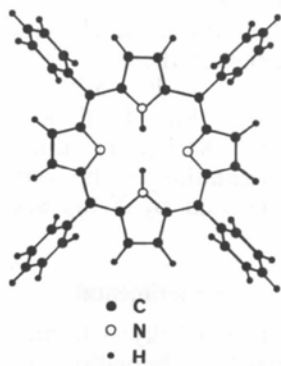


Fig. 1. Molecular structure of H_2TPP .

deposition rate as well as the substrate temperature. Thin epitaxial films on the substrates kept at room temperature were obtained at growth rates of less than 9.0 nm min^{-1} in thickness. For higher substrate temperatures the thin crystallites aggregated to form rectangular islands with identical orientation (Yanagi, Takemoto, Hayashi & Ashida, 1990). Fig. 2 shows an electron micrograph of the H_2TPP crystals deposited on KCl kept at 373 K. The crystals, with an average thickness of 90 nm, are rectangles, the long sides of which run along four directions, two of them at an angle of 37° and the other two orthogonal to the former. This angular relation is made clear by the selected-area electron diffraction pattern shown in Fig. 3. The pattern can be explained as the result of superposition of four identical single-crystal patterns, which are rotated at the angles made by each crystallite shown in Fig. 2. The orientation of two directions crossing at right angles can be attributed to the crystallographic symmetry of the KCl (001) surface, as reported previously for the epitaxial growth of metal phthalocyanines (Ashida, Uyeda & Suito, 1966) and long-chain molecules (Ueda, 1987) on KCl.

Fig. 4 shows the orientation of the H_2TPP crystals relative to the substrate crystal surface. The direction

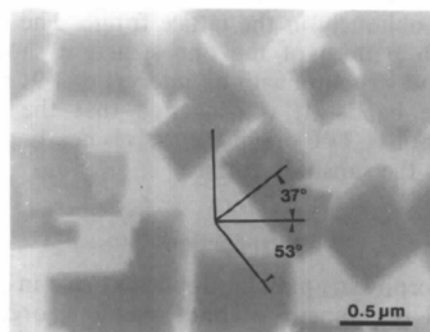


Fig. 2. Electron micrograph of H_2TPP crystals growing epitaxially on a KCl (001) surface kept at 373 K.

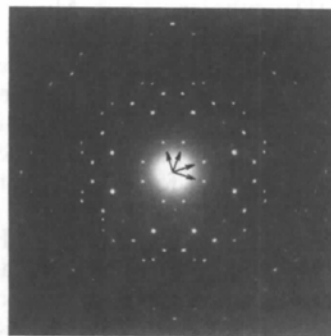


Fig. 3. Electron diffraction pattern of H_2TPP crystals growing epitaxially on a KCl (001) surface kept at 373 K.

of the KCl [100] axis was determined from the shadows of crystals with a truncated pyramidal morphology. The straight line which coincides with the KCl [100] direction crosses the edges of the crystals at $\pm 26.5^\circ$. At lower substrate temperatures, the H_2TPP deposits grow as thinner crystals (Yanagi, Takemoto *et al.*, 1990). Fig. 5 shows an electron micrograph and an electron diffraction pattern of an H_2TPP single crystallite deposited on a KCl substrate kept at 298 K. The rectangular crystallite of about 6 nm in thickness adopts the same orientation as the crystallite deposited on the KCl substrate kept at 373 K (see Fig. 4). The lattice image can be seen in the rectangular crystallite. The lattice fringes, with a spacing of 0.95 nm, are aligned at an angle of 45° to the sides of the rectangular crystallite. Thus, the lattice fringes are at an angle of 18.5° to the KCl [100] and [010] directions. The diffraction pattern shown in Fig. 5(b) is the single-crystal pattern which is a component of the superposed pattern shown in Fig. 3. A series of spots on the equator correspond to the interplanar spacing of 1.90 nm. The layer lines composed of strong diffraction spots show the interplanar spacing of 0.38 nm^{-1} and weak spots appear on four lines with an equidistance of 1.90 nm^{-1} between the strong layer lines. The H_2TPP crystal has polymorphs and the structures have been given as tetragonal with $a = 1.5125$, $c = 1.394$ nm and $Z = 4$ (Hamor, Hamor & Hoard, 1964) and as triclinic with $a = 0.644$, $b = 1.042$, $c = 1.241$ nm, $\alpha = 96.06$, $\beta = 99.14$, $\gamma = 101.12^\circ$ and $Z = 1$ (Silvers & Tulinsky, 1967). The lattice spacings obtained from the crystal in the film did not coincide with those of the crystal structures given previously. Therefore, the crystals in the film vacuum-evaporated on KCl seem to have a different structure and/or orient in a special way. In order to obtain the diffraction pattern from the basal plane, the specimen was rotated and tilted against the incident electron beam. The net patterns shown

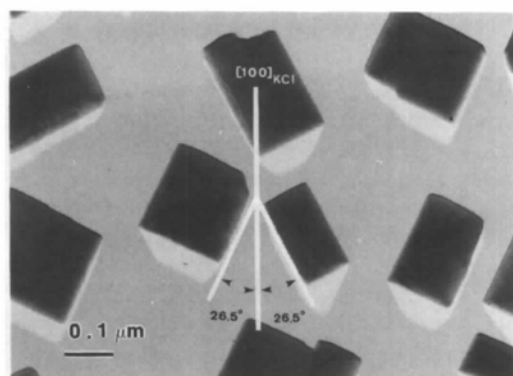


Fig. 4. Electron micrograph of H_2TPP crystals showing the angular relation by shadow-casting of chromium along the KCl [100] direction.

in Figs. 6(a) and 6(b) were obtained when the specimen was tilted by about 51 and 39° , respectively, around an axis normal to the lattice fringes of the crystallites. The diffraction spots on the equators of both diffraction patterns gave the lattice spacing of 1.90 nm, which is twice the spacing of the lattice fringes shown in Fig. 5(a). This common equatorial axis was assigned to the b^* axis. The lattice spacings of the vertical directions were 1.20 and 1.47 nm, from the diffraction spots in Figs. 6(a) and 6(b), respectively. The former was assigned to the a^* axis and the latter to the c^* axis. Thus, the reciprocal-lattice dimensions were determined to be $a^* = 0.833$, $b^* = 0.526$, $c^* = 0.680 \text{ nm}^{-1}$, $\alpha^* = 90$ and $\gamma^* = 90^\circ$

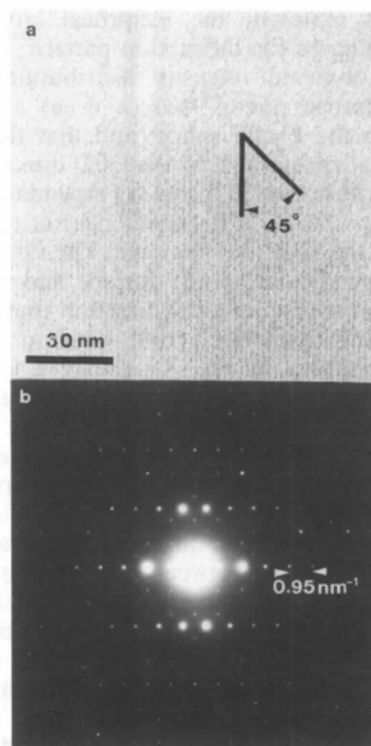


Fig. 5. (a) Electron micrograph and (b) electron diffraction pattern of an H_2TPP single crystal deposited on a KCl (001) surface kept at 298 K.

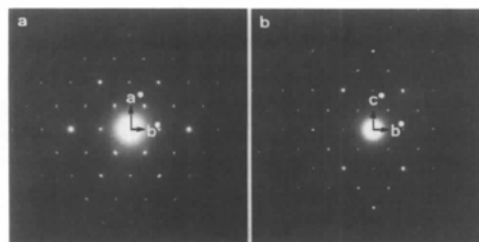


Fig. 6. Electron diffraction patterns of an H_2TPP single crystal tilted by (a) 51° and (b) 39° about the b^* axis.

from the analysis of the two-dimensional electron diffraction data. Fig. 7 shows the X-ray diffraction pattern from the H₂TPP film with the incident X-ray beam at an angle of 0.5°. Only two sharp peaks appeared, corresponding to the (202) and (312) planes, indicating that the (101) planes of the crystals are parallel to the substrate. From the X-ray data, the interplanar spacings of the (202) and (312) planes were 0.461 and 0.343 nm, respectively, and β was estimated to be 91°. Therefore, the H₂TPP film has the following unit-cell dimensions with monoclinic space group I_2 : $a = 1.20$, $b = 1.90$, $c = 1.47$ nm and $\beta = 91^\circ$.

On the basis of the crystal parameters thus determined, the diffraction pattern in Fig. 5(b) was indexed as shown schematically in Fig. 8. The large black dots represent the reciprocal lattice points corresponding to the diffraction pattern. It is found from the observed intensity distribution that the reciprocal-lattice points, $0k0$ (k even) and $2k\bar{3}$ (k odd) lie on the Ewald sphere and that the electron beam is incident parallel to the [302] direction of the crystal. Because the [302] axis is perpendicular to the (101) plane, the H₂TPP crystal has its (101) plane parallel to the KCl (001) surface. The (203) plane is nearly perpendicular to the surface and parallel to the b axis which is along the direction that makes an angle of 18.5° to the KCl [100] direction. The other small dots shown in Fig. 8 indicate a long-period structure of 1.91 nm, which is a fivefold spacing of the (203) plane, along the lattice fringe. The fine structure of the H₂TPP crystal was analyzed directly from a high-resolution electron micrograph and its optical diffraction pattern, as shown in Fig. 9. Fine bands can be observed in each fringe aligned in parallel. The spacing between the bands is 0.38 nm, which coincides with the (203) interplanar spacing, and band lines tilt to the lattice fringe by about $\pm 79^\circ$ as indicated by the white lines. The optical transform from the structure image reproduces the single-crystal electron diffraction pattern shown in Fig. 5(b). The weak spots marked with arrowheads can be observed in the pattern in addition to the basic

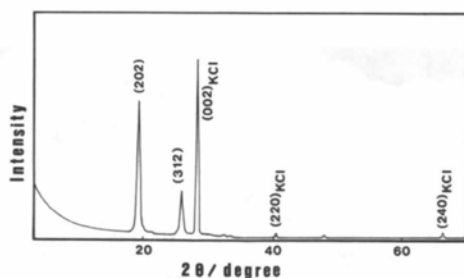


Fig. 7. X-ray diffraction of an H₂TPP film growing epitaxially on a KCl (001) substrate.

pattern. They correspond to the long-period structure of 1.91 nm mentioned above, in which an interval of five times the band spacing exists along the lattice fringe. Such a band structure in a column has been observed in phthalocyanine (Kobayashi, Fujiyoshi & Uyeda, 1982) and in octacyanophthalocyanine (Ashida, Ueda, Yanagi, Uyeda, Fujiyoshi & Fryer, 1988) crystals when their b axes are parallel to the substrate surface. In the case of phthalocyanine crystals, the planar molecules are piled up in parallel layers to form a herringbone structure in columns along the b axis. The intermolecular distance in such a column varies from 0.35 to 0.40 nm for macrocyclic ring compounds owing to the interaction of the π electrons. The band image is a projection of the molecules onto the (101) plane including the crystal b axis. In this projection the molecules are viewed along the molecular planes and imaged as dark bands.

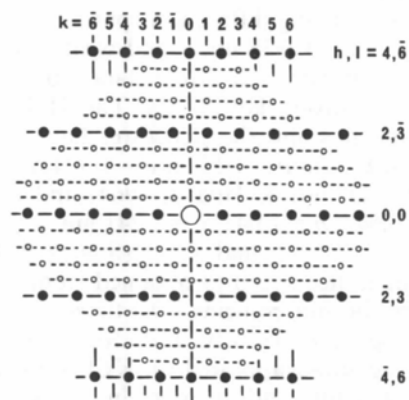


Fig. 8. Schematic diagram for interpretation of the diffraction pattern shown in Fig. 5(b).

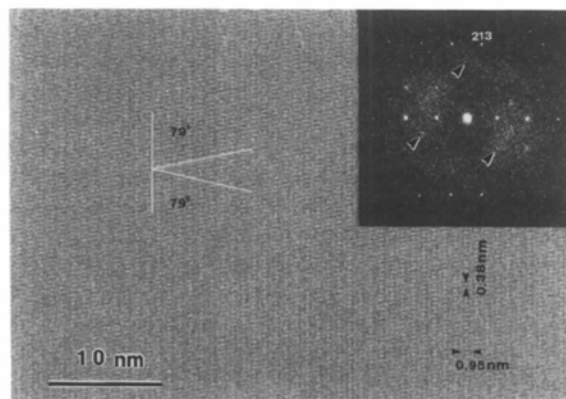


Fig. 9. High-resolution electron micrograph and its optical diffraction pattern (inset) of a thin H₂TPP crystal.

The stacking of H_2TPP molecules seems to be different from that of phthalocyanine, because the porphyrin ring is not planar but corrugated and the quasi-planar skeleton is easily deformable (Hamor *et al.*, 1964). Nevertheless, this projection image suggests that the planar molecules are almost normal to the substrate surface so that they are imaged as dark bands. From the molecular image and optical transform, the relationship of the molecular arrangement to the substrate face can be deduced (Fig. 10). All the molecular planes are almost normal to the substrate surface. The unit cell includes four molecules, two molecules indicated by solid lines situated in the (010) plane and the other two indicated by broken lines in the (020) plane. Two of them tilt by about $+11^\circ$ and the other two tilt by about -11° to the (203) plane, as shown by the open and shaded ellipses, respectively. The molecules along the a axis project onto the (101) plane at intervals of 0.38 nm, equal to d_{203} . Every fifth molecule is situated in the plane and thus gives rise to 1.91 nm periodicity.

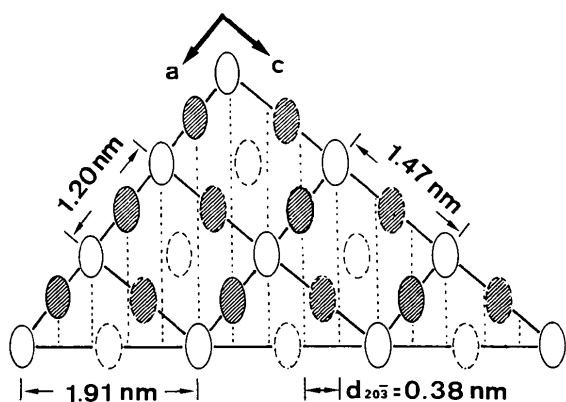


Fig. 10. Schematic diagrams of the molecular arrangement in an H_2TPP crystal orientated on the KCl substrate.

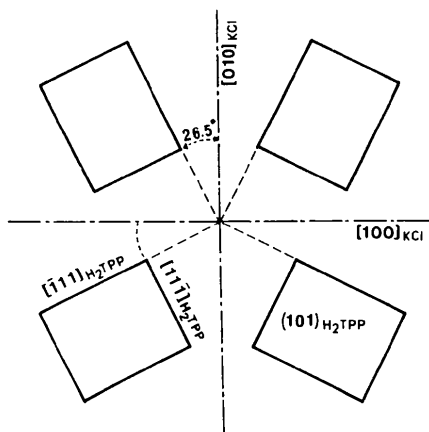


Fig. 11. Schematic diagram of the relative orientation between the H_2TPP crystals and the KCl substrate.

From these results, the orientational relationship between the deposited film and the substrate crystal is presumed to be as shown in Fig. 11. The crystallites adopt four sets of orientations as follows: $(101)_{H_2TPP} // (001)_{KCl}$, $[111]_{H_2TPP}$ crosses $[100]_{KCl}$ or $[010]_{KCl}$ at $\pm 26.5^\circ$. Two crystallites have a mirror-symmetry relationship to each other with respect to the KCl (100) and (010) planes. The epitaxial orientation of the crystals depends on the anisotropic adsorption of the molecules onto the substrate surface.

As reported in a paper by Yanagi, Ashida, Harima & Yamashita (1990) the orientated H_2TPP film exhibited a photocurrent quantum yield three times greater than that of a polycrystalline film. This enhancement in quantum yield was attributed to the perpendicular orientation of the planar molecules of H_2TPP to the surface of the substrate and this orientation of H_2TPP molecules was supported by an infrared spectroscopic study.

References

- ASHIDA, M. (1966). *Bull. Chem. Soc. Jpn*, **39**, 2632–2638.
 ASHIDA, M., UEDA, Y., YANAGI, H., UYEDA, N., FUJIYOSHI, Y. & FRYER, J. R. (1988). *Acta Cryst.* **B44**, 146–151.
 ASHIDA, M., UYEDA, N. & SUITO, E. (1966). *Bull. Chem. Soc. Jpn*, **39**, 2616–2624.
 CALVIN, M. (1978). *Acc. Chem. Res.* **11**, 369–374.
 DEISENHOFER, J., EPP, O., MIKI, K., HUBER, R. & MICHEL, H. (1985). *Nature (London)*, **318**, 618–624.
 FUJIYOSHI, Y., KOBAYASHI, T., ISHIZUKA, K., UYEDA, N., ISHIDA, Y. & HARADA, Y. (1980). *Ultramicroscopy*, **5**, 459–468.
 HAMOR, M. J., HAMOR, T. A. & HOARD, J. L. (1964). *J. Am. Chem. Soc.* **86**, 1938–1942.
 HARIMA, Y. & YAMASHITA, K. (1985). *J. Phys. Chem.* **89**, 5325–5327.
 KAMPAS, F. J., YAMASHITA, K. & FAJER, J. (1980). *Nature (London)*, **284**, 40–42.
 KATSU, T., TAMAGAKE, K. & FUJITA, Y. (1980). *Chem. Lett.* pp. 289–292.
 KOBAYASHI, T., FUJIYOSHI, Y. & UYEDA, N. (1982). *Acta Cryst.* **A38**, 356–362.
 SILVERS, S. J. & TULINSKY, A. (1967). *J. Am. Chem. Soc.* **89**, 3331–3337.
 TABUSHI, I. & KUGIMIYA, S. (1985). *J. Am. Chem. Soc.* **107**, 1859–1863.
 UEDA, Y. (1987). *Bull. Chem. Soc. Jpn*, **60**, 2011–2017.
 UYEDA, N., ASHIDA, M. & SUITO, E. (1965). *J. Appl. Phys.* **36**, 1453–1460.
 UYEDA, N., KOBAYASHI, T., SUITO, E., HARADA, Y. & WATANABE, M. (1972). *J. Appl. Phys.* **43**, 5181–5189.
 VOLKER, S. & MACFARLANE, R. M. (1979). *IBM J. Res. Develop.* **23**, 547–555.
 YAMASHITA, K. (1982). *Chem. Lett.* pp. 1085–1088.
 YAMASHITA, K., KIHARA, N., SHIMIZU, H. & SUZUKI, H. (1982). *Photochem. Photobiol.* **35**, 1–7.
 YAMASHITA, K., MATSUMURA, Y., HARIMA, Y., MIURA, S. & SUZUKI, H. (1984). *Chem. Lett.* pp. 489–492.
 YANAGI, H., ASHIDA, M., HARIMA, Y. & YAMASHITA, K. (1990). *Chem. Lett.* pp. 385–388.
 YANAGI, H., TAKEMOTO, K., HAYASHI, S. & ASHIDA, M. (1990). *J. Cryst. Growth*, **99**, 1038–1043.