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DIRECT MOLECULAR IMAGING OF LOW DIMENSIONAL SOLIDS
BY HIGH RESOLUTION ELECTRON MICROSCOPY

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Abstract High resolution electron microscopy was performed to characterize the structure of metal complexes of cyano-compounds formed by solid state reactions. Examples of molecular images are presented to show normal and faulted arrangements in the lattice.

INTRODUCTION

Recently, the adoption of thin films is gathering its importance as a study mode of the status of low dimensional crystals. The knowledge of molecular arrangement in thin films can be most effectively obtained by electron microscopy and selected area electron diffraction (SAD).

Although highly accurate crystal data should be given by X-ray diffraction structure analysis, electron microscopy is also esteemed for the capability of revealing the local and oriented structures. Owing to the rapid progress in the instrumentation as well as in the image formation theory, the recognizable locality has reached the order of single molecule and even that of constituent atoms in the ultimate case. Thence the state of molecular packing in thin crystalline films is currently studied on the basis of direct imaging by using conventional high resolution electron microscope (HREM).

The potentiality of visualization of atoms was predicted even before the evolution of electron microscope. However it was only 1970 that the first molecular images were taken¹ to establish a possible approach to the visualization of atoms. The essential drawback that the lens defect limits the ultimate resolution is an inevitable difficulty against this purpose. To overcome this difficulty, shorter wavelengths must be adopted as theoretically proposed by Scherzer.² In 1974, a 500kV electron microscope was constructed at Kyoto University to achieve the atomic resolution as proved with the high resolution images of chlorinated Cu-phthalocyanine reproduced in Fig. 1. Nowadays, conventional 200kV instruments are widely used for high resolution structure studies. The present report is to introduce some recent results obtained with thin films of low dimensional crystals produced as the results of solid state surface reactions.

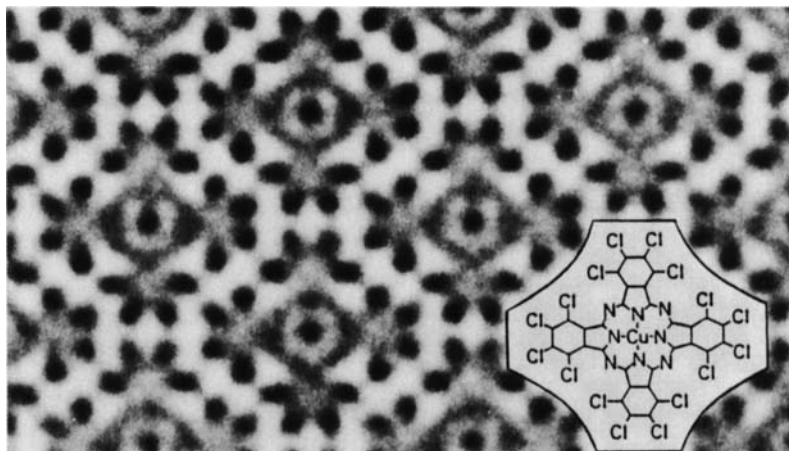


Fig. 1. High resolution molecular images of chlorinated Cu-phthalocyanine showing constituent Cl and Cu atoms as well as benzene and porphyrin rings
N. Uyeda *et al.*, *Chem. Scripta*, 14, 47 (1978/79).

FORMATION AND STRUCTURE OF METAL TCNQ COMPLEXES

When thin bilayered films of metal(M) and TCNQ are produced by successive vacuum evaporation on a single crystal face, M·TCNQ complexes are slowly formed turning into blue in color. Obviously, the reaction is based on the diffusion of metal ions due to charge transfer mechanism. A preliminary inspection by selected area diffraction indicated that the axes of segregated columns of TCNQ and metal are normal to the substrate face. Fig. 2 shows two examples of HREM images of Ag and Al·TCNQ taken with a conventional instrument (JEM-200CX) operated at 200kV. Apparently, the crystal assumes a nearly tetragonal symmetry with two dimensional cell constants are $a=12.5\text{\AA}$ and 12.4\AA , respectively. As obvious from the inset illustrations, the image elements such as the square net of obtuse zigzag lines and slightly oblong blocks can be interpreted in terms of images of TCNQ molecules projected along the column axes, while the dark dot located at each corner of square mesh is the image of metal column, Ag or Al, as projected along their aligning directions. Although the crystallographic symmetry is different from those reported by Konno et al.³ and Richard et al.⁴ in regard to K-complex, the general molecular arrangement is almost isomorphic with the normal complex crystal. The relative contrast between Ag and Al ions well parallels the relative electron scattering power of both ions. The results of observation revealed that these complexes are isomorphic and that the resulted complex always keeps a certain topotactic relationship with the axial orientation of the mother crystal of TCNQ, that is, a regularity exists between the molecular orientations in both crystals. The metal species so far found to follow the above solid

state reaction mechanism are Li, Na, K, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pd, Ag, Cs, Au and Tl. A similar phenomenon of solid state complex formation was also found for a reaction of TCNQ and anthracene,⁵ although it was confirmed that the product does not assume the segregated column structure but form a D-over-A structure as reported by Williams *et al.*⁶

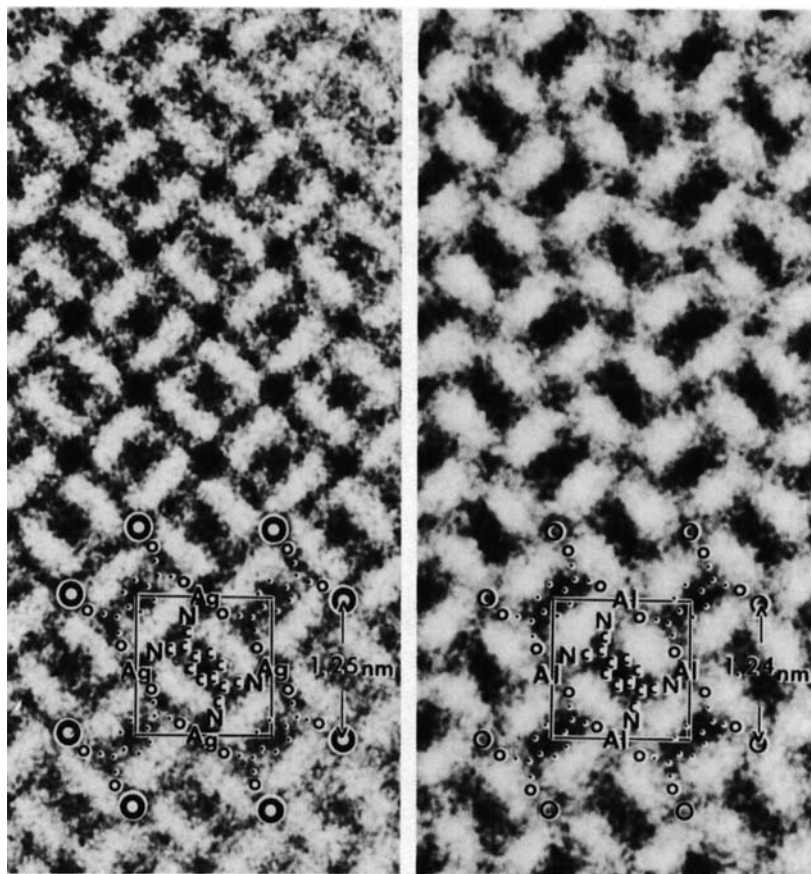


Fig. 2. High resolution structure images of complex crystals of TCNQ with Ag and Al both formed by solid-solid diffusion

METAL TCNQF4 COMPLEX FORMED BY SOLID STATE REACTION

When TCNQF4 was evaporated on clean cleavage face of KCl, rapid color change into blue was observed as an evidence of CT complex formation. By the analysis of SAD patterns, it was found that the growth process was also based on the topotactic mechanism so that the resulted crystal always assumed a definite orientation. A HREM structure image is reproduced in Fig. 3 after noise elimination by photographic spacial averaging. The image appearance resembles those of M·TCNQ shown in Fig. 2. In spite of the improved sharpness of images as compared with the former ones, the body of each TCNQ molecule is thicker in width to reveal a barrel type feature, reflecting the presence of four substituted F atoms. From the intensity distribution of images, it was deduced that the normal of molecular plane is tilted by about 28° from the column axis. Since the tilt angle of ordinary TCNQ molecule in potassium complex is in a range of 9 and 16° , the molecules are rather deeply slanted in TCNQF4 case. Such a deep inclination was also reported by Wiygul et al. in regard to a DA complex with DBTTF.⁷ The dark dot at each mesh corner is interpreted in terms of the axial projection of K column.

Although the image of molecular lattice as well as the electron diffraction pattern apparently shows tetragonal symmetry, the extinction of reflections indicates that the space group is most possibly $P2_1/c$ of monoclinic system. With this lattice setting, b and c axes are supposed to run in the diagonal directions of the square lattice of the real image, for which the cell constants were estimated to be $b=c=12.17\text{\AA}$ while the a-axis nearly normal to the square lattice was found to be 3.39\AA from tilted diffraction.

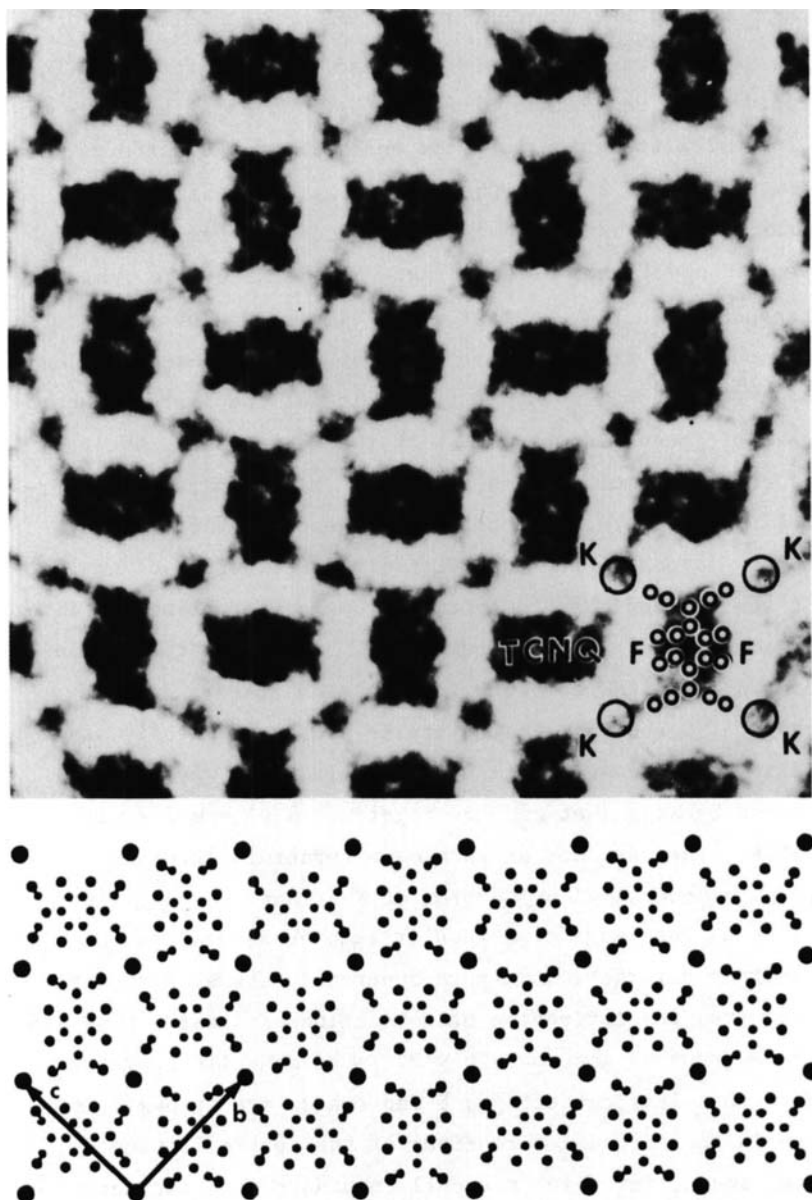


Fig. 3. High resolution structure image of $K \cdot TCNQF_4$ complex crystal projected along the axis of molecular column

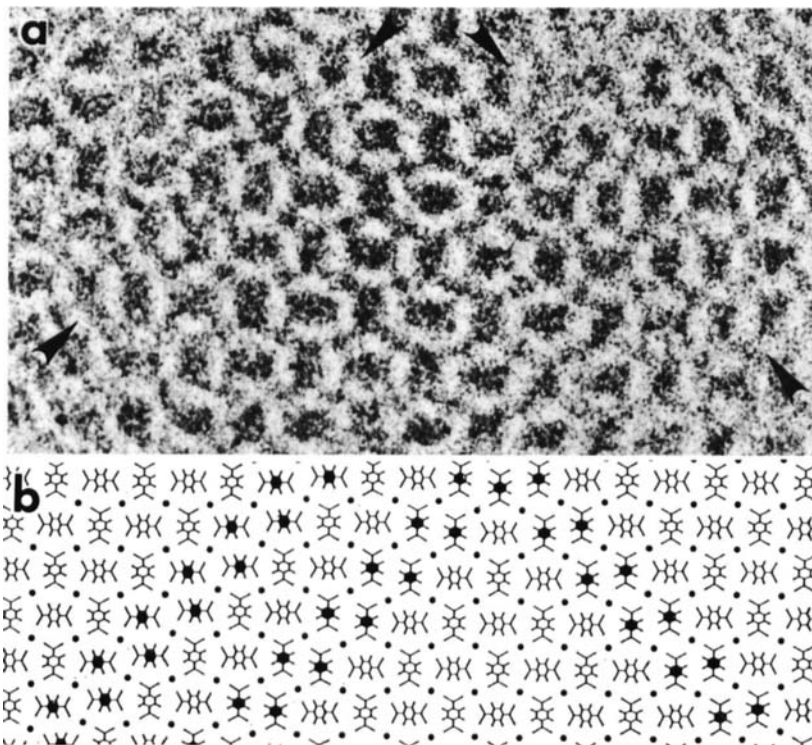


Fig. 4. Stacking faults of molecular arrays included in K·TCNQF4 crystal film.

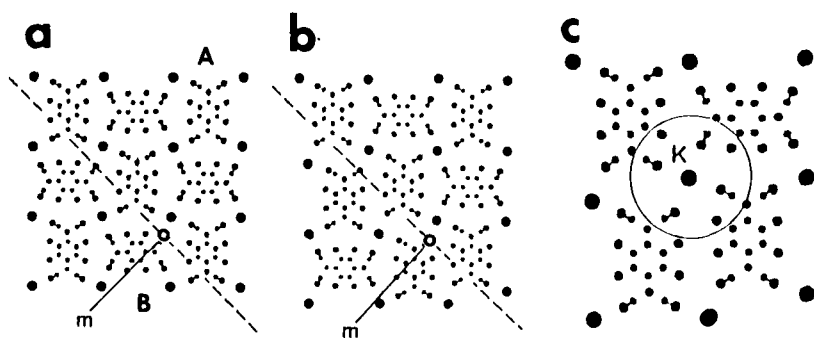


Fig. 5. Interpretation of stacking fault formation and the status of distorted structure around the potassium column

for normal TCNQ vacuum evaporated on KI cleavage face, although the reaction rate was rather slow. The instantaneous formation of complex observed with TCNQF4 is considered to be due to the electron affinity larger than TCNQ.

POTASSIUM-OCTACYANOPHTHALOCYANINE COMPLEX FORMATION

Another exchange reaction was also found by Ashida *et al.*⁸ when TCNB was vacuum evaporated on KI single crystal face. In this example, four TCNB molecules are condensed to form a macrocyclic ring of octacyanophthalocyanine[(CN)₈Pc] and, at the same time, produce a complex with K ion as a result of exchange reaction. By HREM observation, the complex crystal was found to assume a structure illustrated in Fig. 6, which is a projection of tetragonal lattice, $a=15.67\text{\AA}$ and $c=6.72\text{\AA}$, having symmetry of $P4/mcc$. The crystal consists of segregated columns of (CN)₈Pc and K ion. The Pc molecules are packed normal to the column axis with an intermolecular spacing of 3.36\AA . The molecular overlap is based on alternating rotation by $\pm 27.4^\circ$ in regard to the symmetry axis. A similar packing was reported by Schramm *et al.*⁹ for NiPc·I₃ complex.

It is noteworthy that (CN)₈Pc molecules in the complex are considered to exert certain intercolumnar interaction as they are mutually overlapped between two neighbor columns, where CN groups are antiparallely oriented in an alternating manner. As a result, four CN groups of a molecule are used to accommodate K ions while the other four act as arms to interact with surrounding four molecules in the nearest neighbor columns.

The strong reflections associated with the a -axis appear in the tilted diffraction patterns to give the above cell constant, weak reflections are also observed indicating the presence of a superlattice about 4 times larger than that of regular a -dimension.

An interesting finding is the appearance of stacking faults of molecular arrays which are included along the diagonal direction of square net. As reproduced in Fig. 4a, the faulted arrangement takes place resulting in an array of parallelly paired molecules which ruled out a diagonal array of perpendicularly oriented molecules to be sandwiched between them. The schematic representation in Fig. 4b is a wide view of molecular lattice where a few stacking faults run in a crystal along different diagonal lines.

The configuration of such a stacking fault can be interpreted in terms of a partial mirror operation to the molecular lattice. As illustrated in Fig. 5a, a partial mirror plane including one of the nitrogen column is considered to run along the diagonal direction. When all the lattice fully belongs to the area B is subjected to the mirror operation, the result will appear as shown in Fig. 5b. The net of K ion column between the paired molecular array is considerably distorted showing a good agreement with the real image in Fig. 3a. It is interesting to note that, in spite of such distortion, the four nitrogen atoms around K ion still keeps a similar configuration to that of the regular case as far as the 2D projection is concerned. It is also worth noting that the stacking fault of this type has not been found in the ordinary TCNQ complex so far. The formation of $K \cdot TCNQF_4$ complex is due to the exchange of iodine with TCNQF₄ on the ionic surface of KI single crystal. A similar exchange reaction was experienced also

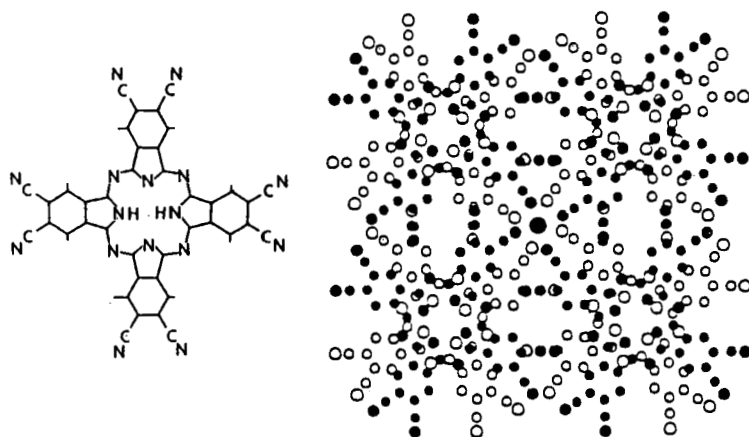


Fig. 6. Overlap structure of potassium complex of octacyanophthalocyanine formed on KI single crystal surface by exchange reaction

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