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Direct Observation of Molecular Images of Lanthanide Phthalocyanines

II. Behavior of Small Particles and Crystal Growth Mechanism

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Tiny crystallites in thin films of lanthanide phthalocyanines ($Ln\mathrm{Pc}_2\mathrm{H}$, Ln = Nd, Tb, Er, Tm, Yb, and Lu) prepared by epitaxial growth on KCl have been studied by means of high-resolution electron microscopy. It has been found that small organic particles show anomalous crystal structures which do not exist in the bulk state and that there are two kinds of fixed orientational relationships between the tiny $Ln\mathrm{Pc}_2\mathrm{H}$ particles. A crystal growth mechanism has been advanced. It is suggested that the strong adsorption between the molecules and the substrate, by which the four nitrogen atoms of the ligand facing the KCl substrate surface are located close to the potassium ions, dominates initially the epitaxial nucleation and that the existence of geometric isomers results in the formation of ordered twins. According to the geometry between the molecules and the twins, it is inferred that the rotation angle between the two ligands of a molecule is 36.9° in both the tetragonal and orthorhombic phases.

Introduction

Over several decades many studies have been made on the semiconductivity, photoconductivity, photochemical reactivity, photosynthetic activity, luminescence, and fluoroescence of metal–phthalocyanines (*M*Pc) with highly conjugated structures (*1–3*). Furthermore, some interests have also been shown concerning the application of these complexes as catalysts, polymers, and pigments (*4, 5*). With further investiga-

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tions made on the sandwich-type derivatives of phthalocyanine (MPc_2 or MPc_2H), their applied fields shall become more extensive. A knowledge of the morphology and the internal structure of small particles of these compounds is important for the understanding of the reaction mechanism involved in the catalytic process as well as many phenomena in materials science of organic crystals which are considerably different from metal crystals in chemical and physical properties. In order to study the structures of tiny particles, high-resolution electron microscopy (HREM) was used and some interesting results were obtained for ultrafine metallic particles.

It was reported earlier (*6*) that there are obvious differences between the thin film grown on KCl and that on NaCl: the former consists mainly of the tetragonal phase with a large number of ordered twins, the latter mostly of the orthorhombic phase and only a few twins. Our observation of small $LnPc_2H$ particles by means of HREM is motivated by both their structural characteristics and crystal growth mechanism. It is revealed that small particles of organic crystals, which are held together by weak van der Waals forces, are different from the crystal structure in the bulk state. From the fact that a rigorous orientation relationship exists between the small particles, it is suggested that the epitaxial nucleation is strongly controlled by the oriented adsorption of individual molecules on the substrate surface caused by the electronic interaction between them. Moreover, it is postulated that the rotation angle between the two ligands of a molecule in both the tetragonal and orthorhombic phases can be determined from the geometry of molecular arrangement and twin relationship. The experimental method has been described in detail in a previous paper (*6*).

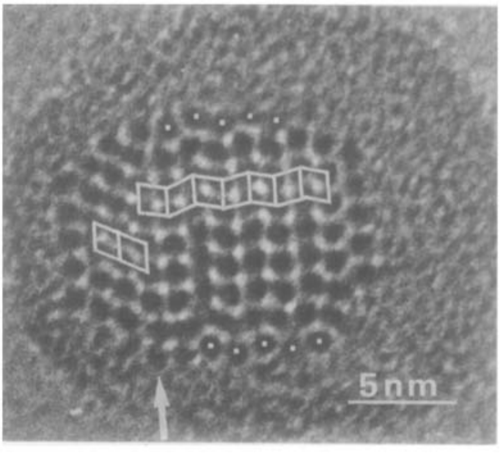

FIG. 1. Molecular image of small $LuPc_2H$ particle grown on KCl with only short-range order of the packing of $LuPc_2H$ columns.

Behavior of Small Particles

The crystal growth process can be arrested by cutting off the power supply to the substrate heater or even leaking air into the vacuum evaporator to suppress the movement of molecules on the substrate surface. The size of the particles deposited on KCl is from a few hundreds to several nanometers. The small particles in the HREM images presented here are of medium size since the contrast produced by the ultrafine particles consisting of only a few layers of molecules is too low to be examined.

Figure 1 is the molecular image of a small growing $LuPc_2H$ particle. Similar to all other high-resolution electron micrographs in this paper, a black disk corresponds to a molecular column rather than a single molecule in a crystal. The arrangement of these molecular columns only have short-range order and no definite Bravias lattice can be derived from this image. As discussed previously (*6*), the rotation angle between two ligands of a molecule may vary within a limited range. It is suggested that the lattice energy in the above-mentioned structures can be reduced by the change of molecular

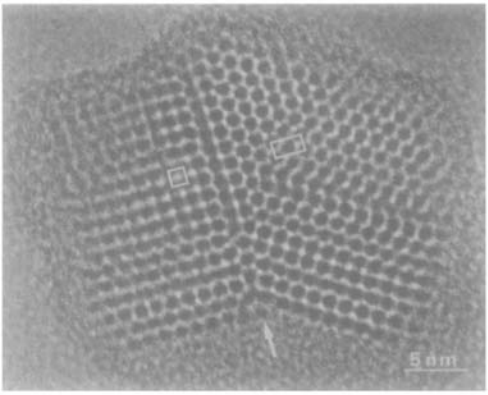

FIG. 2. Molecular image of $LuPc_2H$ with slightly deformed tetragonal and orthorhombic lattices, respectively.

shapes. At the crystal edge, the molecular columns marked by white points are located at irregular positions. These columns take up the preferable sites so that each of them often have four neighbors instead of three as in the usual case, resulting in a widening of their contact areas with their neighbors. The increased surface tension is balanced by the increased intermolecular forces due to enlarged contact areas so that these irregular positions are stable for molecular stacking. Following the crystal growth, other molecular columns form outside this edge, this will cause the molecular columns at the original irregular positions to move to regular sites. The contrast around the particles is somewhat higher than that of the carbon film. This is possibly caused by the disorder molecules existing around these crystallites.

It is concluded by the comparison of Fig. 1 with Fig. 2 that the degree of the order of molecular arrangement is enhanced with an increase of the size of small particles. In Fig. 2, the left and right part of the crystallite divided by the arrow consist mainly of slightly deformed tetragonal and orthorhombic phases, respectively. It is obvious that the structure of the crystallite shown in Fig. 2 resembles more the tetragonal or orthorhombic phase than that shown in Fig. 1 does. According to the morphology, it seems that the crystallite shown in Fig. 2 consists of a pair of twins, but this is not true since the crystallite is composed of two parts having different crystal structures, though some stacking faults exist in both of them.

The interesting structural image of a $LuPc_2H$ crystallite is shown in Fig. 3. The molecules in the center of the crystallite are packed in the tetragonal form (T), but those at the edge are arranged in the orthorhombic form (O). This is a common phenomenon in the initial stage of particle growth on KCl (see also Figs. 4 and 5). It was mentioned previously (*6*) that the films grown on KCl consist mostly of the orthorhombic phase. These characteristics of crystal growth result from the interaction between these molecules and the substrate, which will be discussed in the next section. In the central part of the crystallite, the interaction between the molecules and the substrate is strong and this leads to the formation of the tetragonal structure; at the boundary of the crystallite, the interaction between the molecules and the substrate

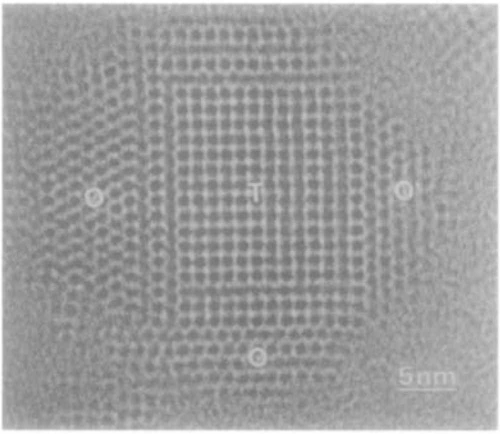

FIG. 3. Molecular image of $LuPc_2H$ with the tetragonal structure in the center marked by T and the orthorhombic structures at the edge by O.

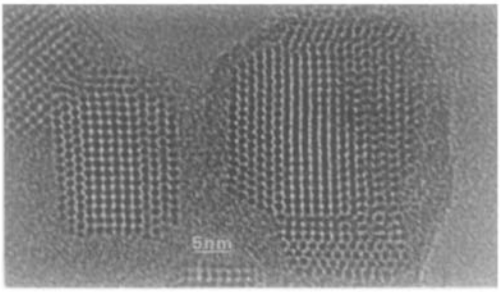

FIG. 4. Molecular image of two small $LuPc_2H$ particles having almost parallel orientation.

becomes weak because of the increase of surface tension, and this causes the generation of orthorhombic phase as a consequence of surface action and the close packing of the molecules.

The different growth characteristics of *Ln*Pc_2H on KCl and NaCl are explained on the basis of a study on the mutual orientation between the small particles grown on KCl. Typical micrographs are presented in Figs. 4 and 5. Two small particles in Fig. 4 are almost parallel though they are not in contact with each other, and the somewhat stronger contrast around these particles is possibly produced by the molecules in disorder. When these two islands coalesce, they form either a single crystal or two domains with a boundary between them. Although the distance between the two small particles in Fig. 5 is larger than 8 nm, they still have a definite relative orientation of about 37°. With further growth, the tetragonal twins of 36.9° or 53.1° will appear. The mutual orientation between all particles in the films studied in this work is similar to the above cases: either parallel or having a relative angle of about 37°.

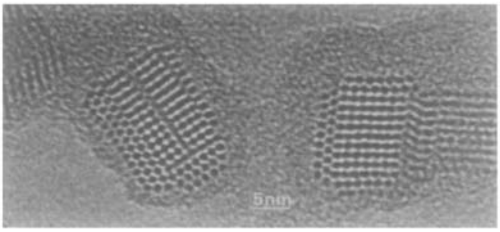

FIG. 5. Molecular image of two small $LuPc_2H$ particles with a relative angle of about 37°.

Crystal Growth Mechanism and Discussion

The phenomena mentioned above can be interpreted in the light of the topography of the substrate surface, the interaction between the substrates and the deposits, molecular shape, and intermolecular forces. The cleavage face of the KCl crystal is the (001) lane, in which K and Cl ions, drawn as hollow and hatched circles, respectively, alternate in the [100] and [010] directions with a spacing of 0.314 nm (Fig. 6). According to Kobayashi (*7*), the electrons in the phthalocyanine molecule have the highest density at the bridge nitrogen atoms, such as *m*, *n*, *p*, and *q* in Fig. 6. This causes an electrophilic effect to occur at these nitrogen atoms (*8*). According to Ashida (*9*), the potassium ion has an electron-attractive

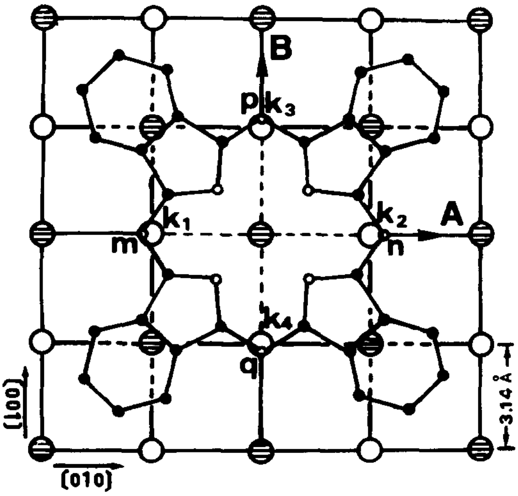

FIG. 6. The orientation of the deposited phthalocyanine molecule relative to the lattice structure of the cleavage face of KCl (k_1, k_2, k_3, and k_4 are Cl ions, while *m*, *n*, *p*, and *q* are bridge N atoms).

force so that the bridge nitrogen atoms of phthalocyanine facing the (001) plane of the substrate surface possibly superpose on the potassium ions on the cleavage face. Four nitrogen atoms (e.g., *m*, *n*, *p*, and *q*) on the *A* and *B* molecular axes, parallel to the [010] and [100] directions of KCl, respectively, superpose on potassium ions (e.g., k_1, k_2, k_3, and k_4), while the four phenyl branches of the molecule spread along the [110] and $(1\bar{1}0]$ directions of the substrate. The phthalocyanine ligands of $Ln\mathrm{Pc_2H}$ molecule should have the same property as the phthalocyanine molecule since they have the same structure. Following the principle mentioned above, the lower ligands of $Ln\mathrm{Pc_2H}$ molecules (dotted lines) are adsorbed on the KCl surface, and the phenyl branches of the lower ligands of not only the same isomers but also the different ones are parallel to each other as shown in Fig. 7. A loose tetragonal lattice of 1.404 nm is composed of the four molecules located at A, B, C and D. In addition to the interaction between molecules and substrate, the model of molecular arrangement on substrate is also governed by intermolecular forces, which may cause a slight adjustment of the lattice parameter to 1.35 nm as described in detail before (*6*). E is the favorable position for a molecule to form an orthorhombic unit with the two molecules located at B and D if only the interaction between the substrate and the molecules is concerned. In order to pack as close to an exact orthorhombic unit as possible, the molecule located at E has to rotate and also to move slightly to a new position. Owing to the steric hindrance between this molecule and those at B and D, a higher energy is required. It is possible that the molecule at E moves to F during its rotation and movement leading to the formation of tetragonal lattice together with both molecules at B and D. In other words, it is favorable for $Ln\mathrm{Pc_2H}$ molecules to form the tetragonal phase rather than the orthorhombic lattice on KCl substrate. This may be the reason for the film grown on KCl consisting mainly of the tetragonal phase.

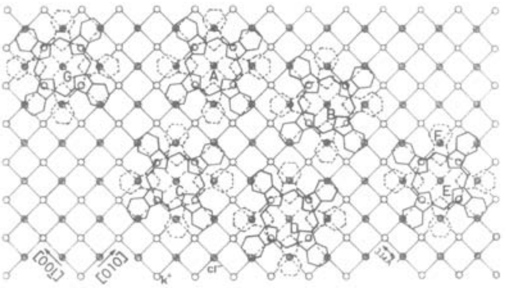

FIG. 7. The structure of the cleavage face of KCl and the deposited molecules of $Ln\mathrm{Pc_2H}$ (*Ln* cations omitted); the lower ligands take an orientation as shown in Fig. 6, and A, B, C, and D form a tetragonal unit.

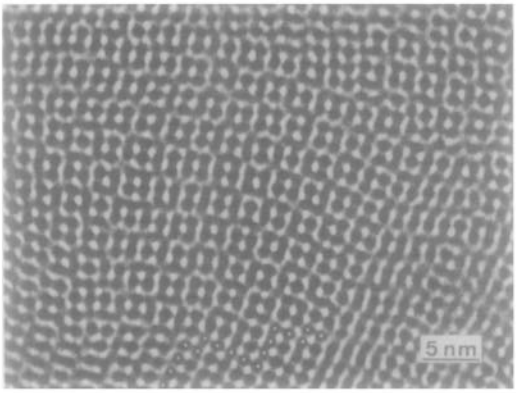

FIG. 8. Molecular image of $\mathrm{NdPc_2H}$ growing on KCl. The tetragonal structure is surrounded by the white points at the lower part, and most of the molecular columns in the confused region are arranged with four molecular columns as a group.

Figure 8 is a molecular image of $\mathrm{NdPc_2H}$ growing on KCl. In the central part the bright dots do not lie on a crossgrid pattern. In other words, the arrangement of $\mathrm{NdPc_2}$ molecules is neither tetragonal nor orthorhombic, though they often appear as squares. From this irregular pattern it is suggested that one-dimensional molecular columns form before the three-dimensional crystal (*10*), and that the molecular columns seem to be mobile, often in groups of four, on the KCl surface during the transformation from the disordered state to a tetragonal crystal, which exists at the bottom of Fig. 8 adjacent to this disordered region (the boundary is marked with white dots). This might serve as proof of the preferential formation of the tetragonal phase on KCl surface as discussed above since these units of four molecular columns exist in the tetragonal lattice, but not in the orthorhombic one.

The crystal growth of evaporated film is governed by two factors: the rate of nucleation and its growth. When $LnPc_2H$ is deposited onto a cleavage face of KCl, fast nucleation caused by the strong electronic adsorption and good matching between the molecules and the substrate occurs not only at the steps but may also occur on the smooth parts of the substrate surface and results in a large number of fine crystallites as reported above (*6*).

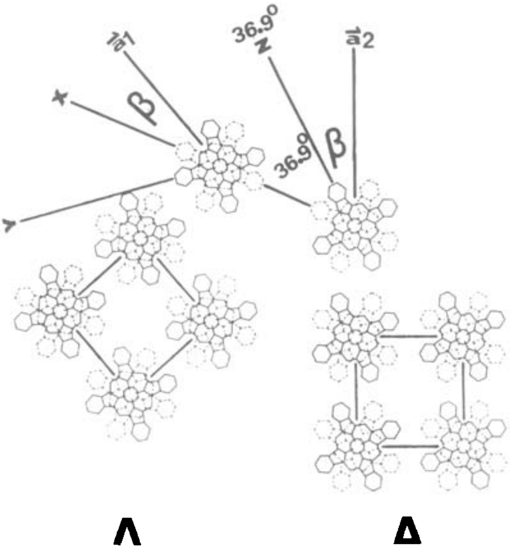

FIG. 9. The relationship of the twins and the rotation angle between two ligands of a $LnPc_2H$ molecule. The [100] directions of two crystals consisting of Δ- or Λ-form isomers respectively are indicated by a_1 and a_2, *X* represents the direction determined by the two phenyl branches of the lower ligands of a molecule, and *Y* or *Z* corresponds to the direction of the phenyl branches of the upper ligands of a Δ- or a Λ-form molecule, respectively.

If two nuclei with molecules of the same type are formed in neighboring regions on the KCl substrate, the mutual orientation between the molecules in them will be similar to the four molecules marked by A, B, C, and D in Fig. 7, and these two crystallites will be oriented in parallel similar to the two small particles shown in Fig. 4. On the other hand, if two molecules of different types come into contact, the relative orientation between them will resemble that existing between C and G molecules in Fig. 7 or the two small particles in Fig. 5. This will lead to the formation of ordered twins.

The relationship among the formation of tetragonal twins, the interaction between molecules and KCl substrate, as well as the existence of geometric isomers is schematically illustrated in Fig. 9. The two tetragonal units consist of Δ- and Λ-form isomers, respectively, and their [100] directions are labeled by a_1 and a_2. The *X* represents the [110] direction of the KCl substrate and therefore also the direction of phenyl branch of the lower ligands of both isomers, while *Y* or *Z* indicates the direction of the phenyl branches of the upper ligands of a Δ- or Λ-form molecule. According to the previous report (*6*), the angle between tetragonal twins, namely, that between a_1 and a_2 here, is 36.9°. Since the angle between *X* and a_1 is equal to that between *Z* and $a_2(\beta)$, the angle between *X* and *Z* will also be 36.9°. Thus it is proved that the rotation angle between two ligands of a $LnPc_2H$ molecule in the tetragonal phase is 36.9°. The molecular structure should be the same, no matter whether the molecules form a tetragonal or an orthorhombic lattice and this relative angle should also apply to the $LnPc_2H$ molecules in the orthorhombic phase, because both the lattices have the same *a* axial length.

The rotation angle between two ligands

of a sandwich-type metal phthalocyanine complex (*M*Pc$_2$ or *M*Pc$_2$H) has been determined in some cases, for example, NdPc$_2$H: 45° (*11*); β-NdPc$_2$H: 38° (*12*). Different molecular structures occur in different crystal structures as appeared in above examples. The change of the rotation angle is limited not only by the steric hindrance between two ligands of each molecule but also by that between those of neighboring molecules in a crystal, and this can be elucidated by the molecular stacking in the tetragonal phase. The smaller the rotation angle between two ligands of a molecule is, the closer the molecular packing in the tetragonal lattice is and the lower the lattice energy becomes. But the greater the deviation of the rotation angle from 45° is, which is the most symmetric and consequently the most stable configuration of an individual molecule, the greater will be its molecular deformation energy. Therefore the rotation angle is governed by the minimum total energy as the sum of the lattice energy and the molecular deformation energy. It can perhaps be imagined from the characteristics of the molecular packing in the tetragonal phase that, in this case, the smallest rotation angle between two ligands of a molecule permitted by the steric hindrance within a molecule has been achieved.

In the present experimental results, the crystallites in the film grown on NaCl have a random relative orientation. The strong oriented adsorption between the chloride ions and the bridge nitrogen atoms of phthalocyanine ligands, similar to that on KCl, does not take place probably because of the adsorbed water molecules on the cleavage surface of NaCl under the experimental conditions as pointed out by Ashida (*9*). The effect of NaCl on *Ln*Pc$_2$H molecules is similar to that of a smooth and strong attractive surface on which the deposited molecules can move relatively freely. The strong attractivity leads to the molecular packing parallel to the substrate surface, the smoothness causes the molecules to be mostly stacked in orthorhombic phase as a close-packing sequence and the crystallites to have a random mutual orientation and grow easily to large ones because of the difficulty of nucleation. The latter is confirmed by the following facts: the selective area electron diffraction of single crystal of the orthorhombic phase can frequently be seen in the films grown on NaCl, but such large orthorhombic or tetragonal crystals are rarely found in those grown on KCl.

Conclusion

Similar to small metallic particles, small particles of organic compounds are different from their bulk state in crystal structures. The molecules at the crystal boundary deviate from regular lattice positions to balance the intermolecular forces and the surface tension. Two kinds of mutual orientation between the *Ln*Pc$_2$H crystallites grown on KCl exist, either parallel or at an angle of 37°. The ordered twins of *Ln*Pc$_2$H result from the electronic adsorption between the molecules and the KCl substrate as well as the existence of geometric isomers.

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