Experimental Evidence of Reversible Crystalline State Transformation of 2,2':6',2''-Terpyridine: Visualization and Seed Effect

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Abstract

We have succeeded in causing reversible polymorphic transformation of 2,2':6',2''-terpyridine (terpy). By contacting a template terpy crystal with the target crystal, reversible orthorhombic-to-monoclinic transformation occurred directly without via melting state. The transformation process is successfully visualized and it is found that the template crystal influences the transition temperature itself.

Keywords

Crystallization, Polymorphism, Solid-State Transformation, Terpyridine

1. Introduction

Terpyridine has been widely used as ligands for metal-organic complex system, and it alone shows interesting properties in a solid state. Mutai *et al.*, reported two crystal structures of 2,2':6',2''-terpyridine (**Figure 1**, expressed as terpy hereafter) [1]. In **Figure 2**, two crystal structures of terpy are shown using reported crystallographic data [2] [3]. A remarkable difference between the two crystal structures is their molecular packing motif. The orthorhombic form has columnar stacks of the molecules, while the monoclinic form has a sandwich herringbone motif. Solid-state transformations of terpy were also reported and their results are summarized in **Figure 2**. Orthorhombic form can be transformed into the monoclinic form by heating. However cooling of the monoclinic form resulted in no opposite transformation by our own test. On the other hand, further heating of the transformed monoclinic form leads to melting and solidification as orthorhombic form occurred by cooling

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Figure 1. Molecular structure of 2,2':6',2''-terpyridine.

Figure 2. Crystal structure of orthorhombic and monoclinic forms of terpy and schematic representation of phase transformation of terpy previously reported [1]. Orthorhombic form of terpy transformed into monoclinic form by heating and opposite transformation was not occurred directly. Monoclinic form may be changed into orthorhombic form via melting state.

the melt. Thus reproducible phase transformation has been achieved indirectly via melting state.

Here a question arises as to why opposite monoclinic-to-orthorhombic transformation does not occur and/or how to do that. Is there a steric hindrance? The purpose of this study is to achieve a reversible orthorhombic-to-monoclinic transformation. In addition, crystal-state change caused by the transformation is successfully visualized.

2. Experimental

2.1. Materials

Commercially available terpy reagent (Tokyo Kasei) was used. In the reagent, traces amount of, at least, two impure species were included, one of which was estimated as 2,2',6',2''-terpyridine-3'-ol by us and the other was not identified yet. Thus purification of the reagent was done by column chromatography. Details of the method is described elsewhere [1].

2.2. Preparation of Two Polymorphism of Terpy

Terpy was dissolved in toluene/hexane mixed solvent (1:1 vol%) at 313 K and it was cooled to 278 K to commence crystallization. Resulting crystals were picked up and were washed several times. Structures of the crystals were confirmed as orthorhombic form by comparing the measured powder XRD pattern with a theoretical XRD pattern calculated using a crystal structure data [2] [3]. Melting point of the orthorhombic crystals was reported as 359 - 361 K [1].

Monoclinic form crystals were prepared by transformation of the orthorhombic crystals. Orthorhombic crystals prepared were grounded for 10 min, this is found very important for reliable transformation by us, and the crystals were heated to 362 K to commence crystalline-state transformation. The resulting crystal structure was recognized as monoclinic form by X-ray power diffraction measurement. The melting point of the monoclinic form crystals was estimated as 364 K in good agreement with the reference data [1].

In-situ observation of the crystalline state transformation was done using two types of crystals prepared as follows. A large orthorhombic crystal was cut into two pieces at the center of the crystal. To a left edge of the one piece (orthorhombic), a small size monoclinic crystal was in contact with as shown in **Figure 3**. Another piece of the crystal was used as it is for comparison.

2.3. Solid-State Transformation

The crystal prepared was put onto a hot stage. Temperature of the hot-stage was gradually elevated until some change in the crystalline state was recognized. In some test, cooling of the resulting crystal (or melt) was also carried. Observation of the crystal was done using a CCD camera.

3. Results and Discussion

Orthorhombic crystal without any modification, showed often no change in crystal structure only by the thermal treatment. Although repeated experiments were performed for confirmation, only melting of the orthorhombic crystals were occurred at around melting temperature of the crystal in most cases. This means no transformation from orthorhombic to monoclinic had occurred. On the other hand, when orthorhombic crystal, which was in contact with a monoclinic small crystal as shown in **Figure 3**, was used, obvious change occurred as shown in **Figure 4**. Initially, the crystal was transparent (a), but 6 second after the temperature reached 347 K, left edge of the crystal became slightly whitish (b). Interestingly, the whitish area expanded to the right with the progress of time (b-h) as if it was a transformation wave (see Supporting Information Movie S1. This transformation process can be more clearly seen by the movie). This change in crystal state has been completed within 60 sec.

Figure 3. A schematic illustration of the terpy crystal used for reversible orthorhombic-to-monoclinic crystal transformation. A small monoclinic crystal of terpy is in contact with the large orthorhombic crystal for transformation.

Figure 4. Photographic pictures of orthorhombic-to-monoclinic transformation process at 347 K. (a) Just before the transformation; (b) after 6 s, change in crystalline state occurred from the area in contact with the monoclinic small crystal. The boundary, shown by arrow, between changed (left) and unchanged (right) parts moved to left side; (c) 22 s; (d) 31 s; (e) 38 s; (f) 45 s; (g) 53 s; (h) 57 s. Scale bar = 1 mm.

In order to identify the structures of changed and unchanged part of the crystals, another orthorhombic crystal in contact with a monoclinic small crystal was allowed to cause the crystal state change at 347 K (the same temperature with that of Figure 4). In this case, the change has been stopped at a middle of the crystal by lowering the temperature as shown in Figure 5. Left side (changed part) and right side of the crystal were collected and XRD pattern of them were measured. As shown Figure 5, it was identified that left-side crystal and right-side crystal were monoclinic and orthorhombic, respectively. Based on these results, the change in crystalline state shown in Figure 4 indicate visualization of orthorhombic-to-monoclinic crystal transformation.

It is interesting to point out that during the transformation process in Figure 4, the temperature was kept at 347 K. This is much lower than orthorhombic-to-monoclinic transformation temperature (356 K). Did the seed crystal of target structure lowered the transition temperature? If it is, what is the definition of transformation temperature? Now, we have such fundamental questions, however, further investigations are required to answer the questions.

In the next step of this research, opposite transformation (monoclinic to orthorhombic) is investigated. As the same with the literature [1], pure monoclinic crystals did not transform into orthorhombic. Thus, we have decided to cause the transformation in the presence of target structure (orthorhombic). At first, an orthorhombic crystal was allowed to be transformed into monoclinic as the same way as described above. In this case, however, the transformation was stopped at the middle of the crystals just by cooling. The resulting crystal, which had both monoclinic (left side) and orthorhombic (right side) structures as shown in Figure 6(a), was used for the reverse (monoclinic-to-orthorhombic) transformation experiment. The crystal was set at room temperature to commence phase transformation. As expected, from the monoclinic-orthorhombic boundary as shown by arrow in Figure 6(a), dark region was appeared and it was developed to left side. The dark region was recognized as orthorhombic by XRD as shown in Figure 7. XRD examination showed this phenomena was caused by direct transformation of monoclinic-to-orthorhombic form. By this transformation, corruption of the crystal, transition of single crystal to polycrystalline, occurred and transmission of the light was reduced. It is interesting, this reverse transition was very slow compared with orthorhombic-to-monoclinic transformation.

Figure 5. Powder-XRD patterns of transformed (shown by “Left”) and untransformed (“Right”) parts of a terpy crystal. In this case, orthorhombic crystal (upper-left inset picture) was transformed into monoclinic form and the transformation was stopped at the center of the crystal (upper-right inset picture). The crystal was cut into two pieces and XRD patterns of the two pieces were measured, respectively. Calculated orthorhombic (bottom) and monoclinic (second from the bottom) form patterns were also shown for polymorphism estimation.

Figure 6. Photographic pictures of opposite monoclinic-to-orthorhombic transformation process of terpy. The starting crystal (a) was made by stopping the orthorhombic-to-monoclinic transformation at the center of the crystal. Thus left- and right-sides of the boundary, marked by arrow, have monoclinic and orthorhombic structures, respectively. With progress of time, the boundary moved to left-side as shown in (b)-(h); (b) 6 h; (c) 12 h; (d) 18 h; (e) 24 h; (f) 48 h; (g) 72 h; (h) 96 h. The transformed area became opaque, showing collapse of the crystal.

Figure 7. Powder-XRD patterns of opaque crystals in Figure 6 and calculated orthorhombic and monoclinic form patterns were also shown.

4. Conclusion

From the experimental results, reverse transformation of terpy crystal was found possible in the presence of a seed crystal which has the target crystal structure. The dynamic process of the reversible transformation was visualized. In addition, transition temperature may be lowered by the presence of target structure.

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Supporting Information