

Morphological Change of Cocrystal Bis(8-Quinolinolato) Copper(II): 7,7,8,8-Tetracyanoquinodimethane Polymorphism

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Abstract

We studied cocrystal of bis(8-quinolinolato) copper(II) (CuQ_2) and 7,7,8,8-tetracyanoquinodimethane (TCNQ), which change dramatically crystal shape in a moment by adding press on crystal face. Single crystal was prepared by dissolving CuQ_2 and TCNQ in chloroform by evaporation of the solution at ambient conditions. We investigated about crystal structure and morphological change properties. We proclaim that this phenomenon is solid phase transition to Form I from Form II, it is caused by pressure on the crystal face (001) of Form II and the crystal expansion direction is the side face (100). We take note of the common structure between polymorph and explain that this transition occurs by the structure like dominoes falling. We obtained a correlation between molecular level structure change and macroscopic shape changes.

Keywords

Crystal Morphology, Crystal Structure, Organic Compounds

1. Introduction

Cocrystal has been attracting attention a variety of fields because they can be changed physical-chemical property without modifying the molecular structure. For example, these may improve physical property as solubility, bioavailability, stability, hygroscopicity, and compressibility of active pharmaceutical ingredients without change curative effect [1] [2]. Furthermore, in the functional material, it is possible to form Charge Transfer Complex (CT Complex) by combining a molecule which is likely to emit electrons (Donor) and a molecule

which is easy to receive electrons (Acceptor), so this is expected to exhibit conductivity, magnetism, conductive property, remarkable modulation of optical characteristics and unique structural change. Excellent properties may be exhibited even for inexpensive molecules. If we combine appropriate molecules, and it is an excellent method in cost and time reduction because complicated routes such as synthesis are not required.

The property is different between polymorphisms, because the crystal structure differs though it is the same molecule. Therefore, we need to understand the relationship between the crystal structure and its properties, but the research has not been done sufficiently. To understand the structure-property relationship in this molecular crystal, we need to determine the precise role of various non-covalent interactions within the crystal structure. In particular, it is thought that the reconstruction of interaction such as C-H...O or π -stacking have an effect in the case of mechanical reaction of crystals such as phase transition, deformation, mechanochromic luminescence, but research on the role of interaction in these dynamic phenomena has not been advanced much. If we can elucidate the movement of such molecules in the crystal, it will contribute to the prevention of deterioration of medicines (tablet processing) and organic semiconductors [3] [4]. However, few papers have clarified the relationship between structural changes at the molecular level and macroscopic shape changes.

In this work, we investigated two polymorphisms of bis(8-quinolinolato) copper(II) (CuQ_2) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) cocrystal. Previous studies have reported that phase transformation occurs with morphological changes due to pressure, but the details of interactions and the reasons for the spread on the transition have not been clarified [5]. We aimed to elucidate the phase transformer mechanism of CuQ_2 -TCNQ cocrystal polymorphism by clarifying the intermolecular interaction affecting the transition behavior by pressure.

2. Materials and Methods

2.1. Materials

Bis(8-quinolinolato)copper(II) (CuQ_2 , 95.0% purity) and 7,7,8,8-Tetracyanoquinodimethane (TCNQ, 98.0% purity) were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), chloroform and dichloromethane were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

2.2. Single Crystal Preparation

Form II was prepared by adding 1 equiv each of the corresponding CuQ_2 and TCNQ in chloroform followed by slow evaporation of the solution at ambient conditions. The crystals were obtained after 4 - 6 days.

2.3. Characterization

2.3.1. Single Crystal X-Ray Structure Analysis

Single crystal X-ray diffraction data were collected on a Rigaku XtaLAB P200

diffractometer using graphite monochromated Mo K α radiation at 20°C \pm 1°C. The data were processed with the Rigaku Crystal Clear software. Structure solution and refinements were executed using SIR2011 [6] (Form II) SHELXT Version 2014/4 [7] (Form I), and using SHELXL Version 2014/7 [8] (Form I, II). The structure was solved by and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model and full-matrix least-squares refinement.

2.3.2. Scanning Electron Microscope (SEM)

Scanning Electron Microscope was conducted using JSM-7100 (Japan Electron Optics Laboratory), acceleration voltage is 2.0 kV, working distance is 25 mm, irradiation current is 8 A.

3. Results and Discussion

3.1. Morphological Change of CuQ₂-TCNQ Cocrystal

The obtained crystal was observed morphological change by pressure on the largest surface with a metal needle (Figure 1). The obtained crystal and the crystal after the morphological change was found to be respectively Form II and Form I by single crystal X-ray structural analysis, thus the morphological change was single crystal—single crystal phase transition (Table 1).

Table 1. Summary of the crystallographic data for CuQ₂-TCNQ cocrystals.

	Form II ^a	Form II ^b	Form I ^c	Form I ^b
Temperature	293 K	298 K	293 K	298 K
Crystal System	triclinic	triclinic	triclinic	triclinic
Space Group				
<i>Z</i>	1	1	1	1
Formula Weight	556.04	556.03	556.04	556.03
<i>a</i> (Å)	8.0483(11)	8.0350(5)	7.154(6)	7.127(5)
<i>b</i> (Å)	8.2666(15)	8.2606(6)	7.552(6)	7.543(5)
<i>c</i> (Å)	9.7787(13)	9.7665(7)	12.033(18)	12.014(5)
α (deg)	77.164(15)	77.260(1)	83.70(10)	83.495(5)
β (deg)	73.536(14)	73.554(1)	88.895(10)	88.783(5)
γ (deg)	78.163(15)	78.132(1)	67.78(5)	67.724(5)
<i>V</i> (Å ³)	601.26(17)	599.26(7)	598.0(12)	593.6(6)
ρ (g/cm ³)	1.536	1.541	1.544	1.555
<i>R</i> (int)	0.0214	0.0171	0.2070	0.0215
<i>R</i> ₁	0.0246	0.0253	0.0821	0.0285
<i>wR</i> ₂	0.0683	0.0760	0.2056	0.0776

a: Data from single crystal before phase in this study. b: Data from reference. c: Data from crystal after the phase transition in this study.

At the same time, we obtained the plane index of Form I and Form II. The pressure surface and extended surface was (001), (100) on Form II and respectively changed $(11\bar{1})$, (001) on Form I, and the direction of the transition was found (Figure 1). Detailed morphological changes are shown in Figure 2. At first, the crystal was broken by pressure (0 - 10 s), and then the crystal moved while the form changed and jumped from 20 s to 32 s. The crystal shape change was completed after 52 s. The crystal after this transition had a regular layered structure. When we observed the crystal surfaces before and after the transition, we found that Form II had a small difference in height and uniformity, while Form I had a large difference in height. The length of crystal increased dramatically, but the crystal was getting thinner. Therefore, the crystal density does not seem to change much (Figure 3).

3.2. Mechanism of the Transition of Form II

Crystal Structure

We fixed the crystal structure according to the direction of structural change and found a common structure. It is a layered structure indicated by gray squares in which CuQ_2 and TCNQ are alternately arranged and a laminated structure in which the layers are stacking. We considered this crystal structure as domino aligned, thus it was thought that this laminated structure shifted like one domino falling after another by the pressure to (001), and the transition propagated. The angle formed by the layer structure with respect to the crystal surface is also larger in Form I than in Form II (Figure 4). Therefore, the interactions of both



Figure 1. The direction of structural change of Form II before transition and Form I after transition by pressure on Form II crystal surface (001).

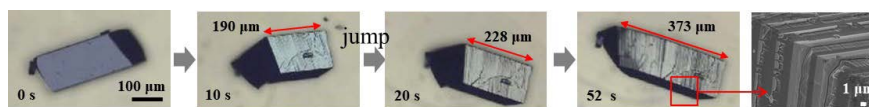


Figure 2. The morphological change of Form II by pressure and SEM image of Form I after morphological change.

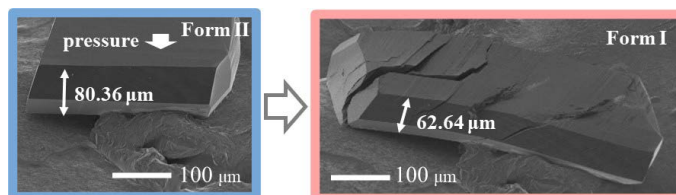


Figure 3. SEM images of morphological change of thickness of Form II and Form I by transition.

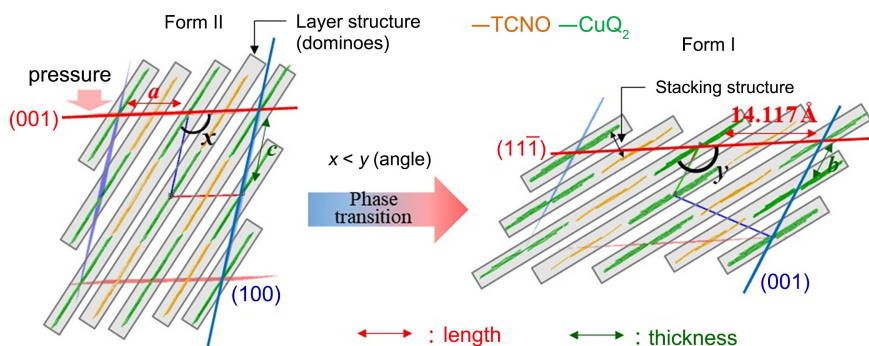


Figure 4. Schematic diagram of structure change from Form II to Form I.

layered and laminated structures were compared in Form I and Form II. The layered structure is formed by alternating TCNQ and CuQ₂ and the interactions are formed in the same way. Comparing the distances of interactions existing in the layers, N...H (I: 2.646 Å, II: 2.544 Å), O...H (I: 2.660 Å, II: 2.590 Å), C...H (I: 2.887 Å, II: 2.817 Å), H...H (I: 2.300 Å, II: 2.171 Å), the distance of Form II was found to be shorter than that of Form I. Therefore, it was suggested that Form II has a stronger layered structure. The interactions in the stacking structure are similar in terms of π -stacking and C...C interactions, but there is a big difference that Form I has only interactions between TCNQ...TCNQ. Form I was found to have a closer interaction distance between the laminations, which is believed to result in a very stable laminate structure. Therefore, it was thought that the structural change such as domino is caused by the following mechanism. Form II is held by interlayer interactions, which hold the molecules in the crystal in a domino-like configuration. But dominoes can start to fall apart the dominoes are knocked over and the stable structure is Form I. We think that the reason why the single crystal—single crystal phase transition was possible but Form II show macroscopic morphological changes also comes from the mechanism that domino falls while being held.

4. Conclusion

We could obtain a single crystal of Form II and observed solid phase transition to single crystal of Form I with morphological change by pressure. We revealed that the transition of Form II was caused on the (001) plane by pressure and expanded to the (100) direction. Thus, we can find the direction of structural change, and determine the generality of the trend from the crystal structure. It is a layered structure in which CuQ₂ and TCNQ are alternately arranged and a stacking structure. We thought that this transition would occur like a domino phenomenon, because the layer structure corresponds to a single domino and stacking. This mechanism is due to the fact that Form II has a strong layer structure, while interaction between stacked structure is weaker than Form I. Also, the ratio agreed between lattice length change and macroscopic shape change by the transition. Hence, our results indicate the usefulness for establishing the role of weak noncovalent interactions in solid-state dynamic pheno-

mena, such as stress-induced phase transformation, and it is important in the context of solid-state crystal engineering.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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