Oriented Single-Crystal-to-Single-Crystal Phase Transition with Dramatic Changes in the Dimensions of Crystals

Guangfeng Liu, Jie Liu, Yang Liu, and Xutang Tao*

State Key Laboratory of Crystal Materials, Shandong University, Jinan, Shandong 250100, P. R. China

S *Supporting Information*

ABSTRACT: We report here a new polymorph of cocrystal CuQ_2-TCNQ that shows an oriented single-crystal-to-single-crystal phase transition along its *a*-axis at ambient conditions. Upon mechanical stimulation, it converts into another polymorph accompanied by almost doubling its length and halving its thickness. Our crystallographic studies indicate the dramatic changes in crystal dimensions resulted from the prominent changes of molecular stacking patterns. A reasonable mechanism for the phenomenon was proposed on the basis of the structural, microscopic, and thermal analysis.

Understanding structure−property relationships in molecular polymorphs is an essential part of crystal chemistry.[1] Many crystal materials have been found to exhibit distinct properties (i.e., ferroelectricity, conductivity, and magnetism) in different crystalline phases.[2] However, the relationship between the changes in crystal physical dimensions and crystal structure during a phase transition has remained relatively unexplored. This aspect is fundamental and important for an intuitive grasp of the molecular packing mechanism, which may have important technical implications for molecular mechanical actuators and artificial muscles.[3] The magnitude of crystal size change during a phase transition depends on the structural mismatch between the original and final lattices. Thus, normally the mismatch is quite small to preserve the integrity of a single crystal; otherwise the crystal will collapse.[4] In this sense, a single-crystal-to-single-crystal (SCSC) phase transition with remarkable size changes could provide us with a good model to study the correlation between the changes in the crystal interior and its morphology. Here, we report a new crystal phase of a classical cocrystal, 7,7,8,8-tetracyanoquinodimethane-*p*-bis(8-hydroxyquinolinato)copper(II) (CuQ_2-TCNQ, Form II), whose dimensions change drastically (∼100% increase in length and 50% reduction in thickness) under mechanical stimulation (Figure 1 and Movie S1), similar to the malleable deformation of metals. However, it was confirmed by the single-crystal X-ray diffraction (SCXRD) studies that the visible deformation process is a strict oriented SCSC phase transition, which enables us to obtain concrete information about the changes in crystal packing on the same sample after the phase transition. Thus, this particular SCSC phase transition provides a good model to understand the structure−property relationships between crystal dimension changes and crystal structures.

The structure of cocrystal CuQ_2-TCNQ (Form I), first reported by Williams and Wallwork, belongs to triclinic system,
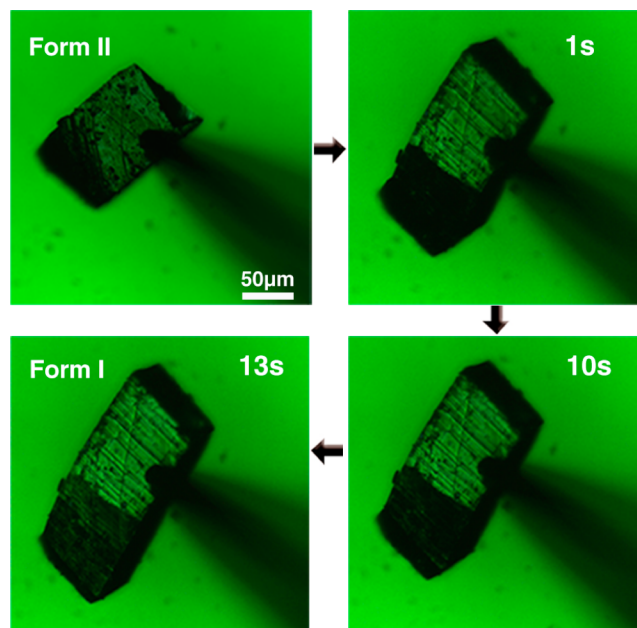

Figure 1. SCSC phase transition process with the (001) plane of Form II as pressure-bearing surface.

space group $P\bar{1}$, with unit cell parameters of $a = 7.120(7)$, $b = 7.540(8)$, and $c = 12.000(12)$ Å.[5] In our experiments, CuQ_2 and TCNQ were cocrystallized by ultrasonic dispersion in chloroform and then evaporation of the solvent at room temperature (see Supporting Information). The new polymorph of CuQ_2-TCNQ (Form II) also belongs to the triclinic system, space group $P\bar{1}$, with unit cell parameters of $a = 8.0350(5)$, $b = 8.2606(6)$, and $c = 9.7665(7)$ Å; its unit cell volume (599.26 Å^3) is slightly bigger than that of Form I (591.2 Å^3) (Table S1).

The Form II crystal is morphologically stable in the ambient environment. However, once the (001) face of a Form II crystal was pricked with a metal needle, remarkable dimensional changes were observed. The Form II crystal completely transformed into Form I without breakage, which means Form II is metastable relative to Form I at room temperature. This phase transition process usually lasts for a few seconds. Figure 2a shows the morphological changes of the crystal in such a transition, where the length of the crystal was approximately doubled and the surface defects of the crystal
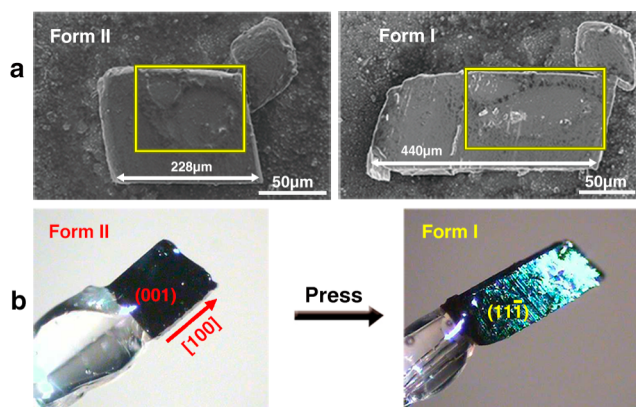
Figure 2. (a) Scanning electron microscopy images of the crystal before and after phase transition. The changes of surface defects on the crystal are shown in the yellow rectangles. (b) Face-indexing graphics of the same piece of crystal before and after the phase transition.

exhibited extended dimensions. Atomic force microscopy images (Figure S1) of Form II crystal before and after the phase transition show that wrinkles formed on the crystal surface after the transition. During such a transition, the Form II crystal transformed into Form I along the [100] direction (Figure 2b), and the (001) plane of Form II changed into the (11$\bar{1}$) plane of Form I on the same crystal. Furthermore, the phase transition was also found when the (010) plane of Form II was mechanically stimulated (Figure S2 and Movie S2). Nevertheless, we have not observed the phase transition when the (100) plane was the pressure-bearing face. These observations suggest that the phase transition is anisotropic.

Differential scanning calorimetry (DSC) measurements were performed on polycrystalline samples with size distribution of 0.1−1 mm to study the thermodynamic relations between the two polymorphs. As shown in Figures 3 and S3, upon heating,
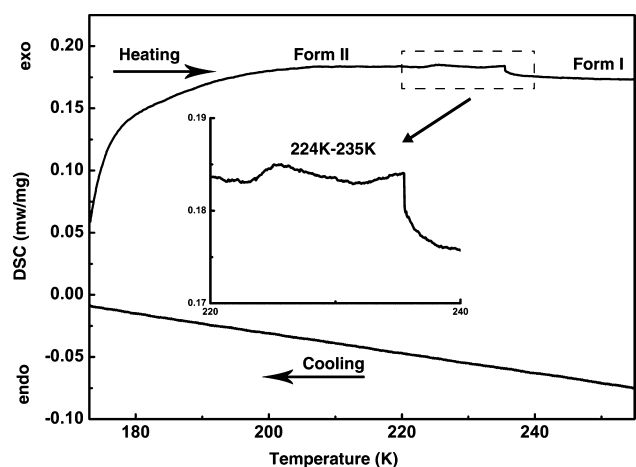

Figure 3. DSC curves of Form II (size distribution of 0.1−1 mm) with rate of 10 K min^{-1} in a heating−cooling cycle.

Form II crystals exhibited broad exothermic peaks from 224 to 235 K, which afterward was proved to correspond to the phase transition to Form I by variable-temperature SCXRD. The broad DSC peaks are caused by the broad size distribution of the sample.[6] (If using crystals with narrow size distribution, only a single exothermic peak appears, as shown in Figure S4.) Upon cooling, there are no heat flow peaks, which indicate that

the phase transition is monotropic.[7] Therefore, Form II is thermodynamically less favored than Form I.[8] For Form II crystals, slow heating (e.g., 1−10 °C/h) cannot trigger the phase transition because of the high degree of crystal perfection. So the metastable Form II crystals can exist in ambient environment. However, the phase transition can be triggered by introducing more defects in the crystal (rapid heating, e.g., 10 °C/min, in the DSC experiment or mechanical stimulation on specific faces of Form II). Moreover, it should be noted here that the phase transition is essentially different from the thermosalient effect (i.e., "jumping crystal"). The "jumping crystal" phase transition is defined as endothermic, and with positive change of unit cell volume, which is contrary to the phase transition here.[3c,d,6,9]

The cocrystals containing TCNQ are often known as charge-transfer complexes, in which the degree of charge transfer should be taken into account. The degree of charge transfer in a complex can be estimated from the geometry of TCNQ.[10] In the two polymorphs of CuQ_2-TCNQ, the ratios $c/(b + d)$ are very close to each other (0.479(2) for Form II and 0.478(2) for Form I; Figure S5 and Table S2), but slightly bigger than the value in neutral TCNQ (0.476), corresponding to degrees of charge transfer (ρ) of about 0.13(6) for Form II and 0.10(9) for Form I. This result indicates that there is basically no electronic state change between the two phases. This is further corroborated by the CN stretching frequency of the two phases, which is 2211 cm^{-1} in both cases (in neutral TCNQ the value is 2223 cm^{-1}; Figure S6).[11] Thus, the phase transition is different from the "neutral-to-ionic" phase transition in charge-transfer complexes, where the latter is always associated with great changes in electronic state and initiated by huge pressure (usually GPa in magnitude).[2a,c]

Normally, the SCSC transition is accompanied by relatively small changes of the original and final lattices to preserve the integrity of a single-crystalline phase.[3c,4] To understand the origin of the extraordinarily large changes in crystal dimensions of this phase transition, we investigated the change in packing patterns in the same piece of crystal before and after the phase transition. In Form II crystal (with dimensions 0.49 mm × 0.34 mm × 0.10 mm), each CuQ_2 molecule connected with two TCNQ and another two CuQ_2 molecules via moderate C—H···N (d/Å, θ/°: 2.54, 165.2), C—H···O (d/Å, θ/°: 2.59, 175.2), and weak C—H···C (d/Å, θ/°: 2.82, 141.3) interactions (Figure 4c). These intermolecular interactions propagate through the cocrystal structure to form 2D layers, with each layer making a dihedral angle of 55.6° with the (001) plane. The molecular layers stack along an axis of [100] direction with a repetition period equal to the length of the a-axis (8.035 Å; Figure 4a).[12] After the phase transition of the crystal into Form I (with new dimensions 0.95 mm × 0.34 mm × 0.05 mm; Figure 2b), the major face of the crystal has changed from the (001) plane of Form II to the (11$\bar{1}$) plane of Form I. Layered structure still appears in the Form I crystal, but with remarkably weakened intralayer hydrogen bonds of C—H···N (d/Å, θ/°: 2.647, 161.2), C—H···O (d/Å, θ/°: 2.669, 161.5), and C—H···C (d/Å, θ/°: 2.893, 136.4). More importantly, dramatic changes take place after the transition in the stacking pattern of the layers: each layer leans to the (11$\bar{1}$) face in Form I crystal with a dihedral angle of 27.7° along a stack axis of nearly [101] direction and a repeat distance of 14.098 Å (Figure 4b). The changes in the packing motifs of the molecular layers—the dihedral angle decreasing from 55.6° in Form II to 27.7° in Form I and the repetition period increasing
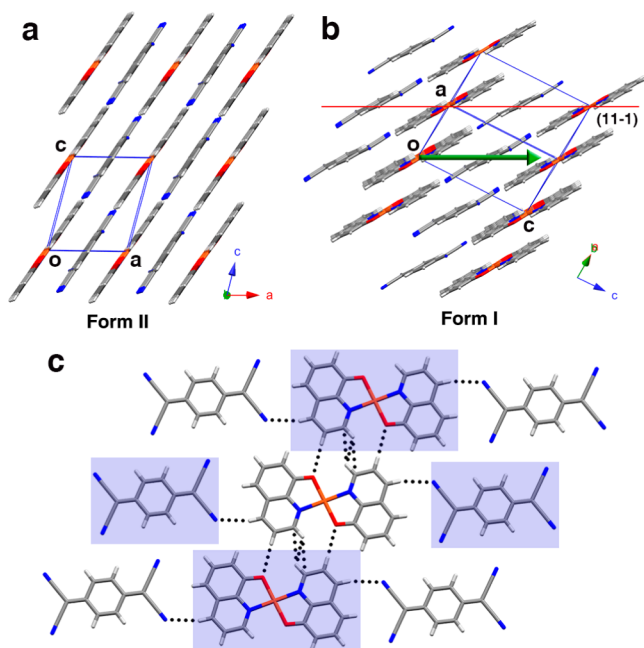
Figure 4. (a) Crystal packing of Form II (viewed down the *b*-axis). The molecular layers make an angle of 55.6° with (001), and the stack axis is [100]. (b) Crystal packing of Form I (view down [1$\bar{1}$0]). The molecular layers make an angle of 27.7° with (11$\bar{1}$), and the stack axis is nearly [101] (green arrow). (c) Layer structure shows C—H···N, C—H···O, and C—H···C interactions in both forms.

from 8.035 Å in Form II to 14.098 Å in Form I—result in the crystal being approximately half its original thickness and double its original length. On the other hand, the average interlayer separation is 3.30 and 3.32 Å for Form II and Form I, respectively, which suggests that the interlayer interactions are weaker than the intralayer interactions in both forms and the structures are anisotropic.

Variable-temperature SCXRD data of Form II were collected from 100 to 225 K at 25 K increments. The evolution of changes in the axial length as a function of temperature is shown in Figure 5. The unit cell parameters undergo huge
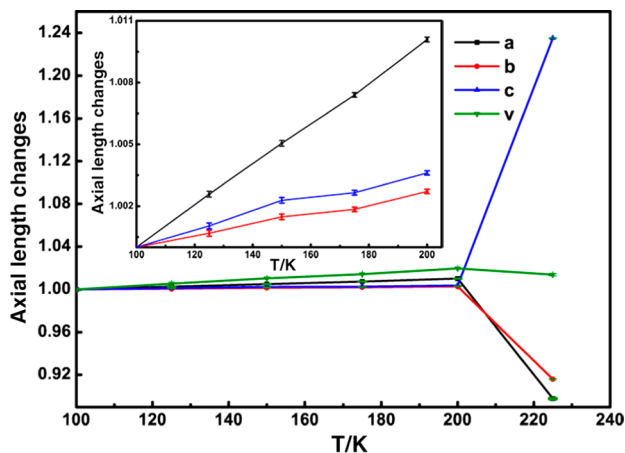
changes at 225 K corresponding to the occurrence of the phase transition, which is consistent with the result from the DSC experiment. Furthermore, it can be seen that the increasing rate of the *a*-axis is much bigger than that of the *b*-axis, in good agreement with the anisotropic nature of the crystal structure. This anisotropy and the oriented phase transition along the *a*-axis can be rationalized by the fact that the interlayer interactions (*a*-axis direction) are weaker than intralayer interactions (*b*-axis direction). On the other hand, for layered crystals, it has been suggested that the bigger the interplanar spacing, the smaller the attachment energy is, such that the crystals tend to slip along the crystallographic plane with the smallest attachment energy.[13] In Form II crystal, the interplanar spacings of (001) (9.226 Å) and (010) (7.926 Å) are significantly larger than for other planes (Figure S7). Therefore, only when the (001) or (010) plane acts as the pressure-bearing face can the phase transition be initiated.

We have observed that the duration of the phase transition is several seconds. For a crystal with length of about 0.1 mm, the speed of the phase transition is approximately 0.01 mm/s. Such a phase transition is 10^7–10^8 times slower than the speed of elastic wave in solids, and also much slower than the speed of the thermosalient transitions.[6,14] This suggests that the phase transition is not a martensitic phase transformation, which is characterized by instantaneous and homogeneous movements,[15] but occurs by nucleation and gradual growth of macroscopic domains of the product lattice.[16] Additionally, the defects on the crystal surface are maintained and elongated after the phase transition (Figure 2a), which also suggests that the neighbors of every molecule are conserved within the 2D layers but the distances between them have increased. Thus, we propose a reasonable mechanism to describe the phase transition as follows: at first, mechanical stimulation on the surface of Form II crystals produces a large number of nuclei, which results in molecular rearrangement triggering the phase transition; then, reconstruction of the 2D layers takes place layer-by-layer; finally, the complete transition induces dramatic changes in the dimensions of the crystals.

In summary, we demonstrated a SCSC phase transition with remarkable crystal dimension changes. Crystal structure analysis before and after the transition indicates a reasonable mechanism by which the differences in the layer stacking patterns in two polymorphs are responsible for this oriented phase transition. The structure–property relationships between the changes of crystal size and crystal structures during the phase transition carry significant implications for crystal chemistry and molecular self-actuating devices. Further investigations to seek reversible phase transitions with similar behaviors on shape changes are currently in progress, through which we hope to get a deeper understanding of structure–property relationships in molecular polymorphism and find their applications in molecular mechanical actuators.

Figure 5. Variable-temperature unit cell data of Form II from SCXRD, showing that the Form II crystal could transform to Form I at 225 K on heating. Vertical error bars are contained within the markers. Inset: partial enlarged detail picture, showing the very different expansion coefficients with temperature for all axial lengths in Form II.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, Figures S1–S7, Tables S1 and S2, and Movies S1 and S2. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

txt@sdu.edu.cn

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Bernstein, J. *Polymorphism in Molecular Crystals*; Oxford University Press: New York, 2002.

(2) (a) Kumai, R.; Horiuchi, S.; Fujioka, J.; Tokura, Y. *J. Am. Chem. Soc.* **2012**, *134*, 1036. (b) Fu, D. W.; Cai, H. L.; Liu, Y.; Ye, Q.; Zhang, W.; Zhang, Y.; Chen, X. Y.; Giovannetti, G.; Capone, M.; Li, J.; Xiong, R. G. *Science* **2013**, *339*, 425. (c) Batail, P.; LaPlaca, S. J.; Mayerle, J. J.; Torrance, J. B. *J. Am. Chem. Soc.* **1981**, *103*, 951. (d) Broderick, W. E.; Eichhorn, D. M.; Liu, X.; Toscano, P. M.; Owens, S. M.; Hoffman, B. M. *J. Am. Chem. Soc.* **1995**, *117*, 3641.

(3) (a) Kobatake, S.; Takami, S.; Muto, H.; Ishikawa, T.; Irie, M. *Nature* **2007**, *446*, 778. (b) Naumov, P.; Sahoo, S. C.; Zakharov, B. A.; Boldyreva, E. V. *Angew. Chem., Int. Ed.* **2013**, *52*, 9990. (c) Skoko, Ž.; Zamir, S.; Naumov, P.; Bernstein. *J. Am. Chem. Soc.* **2010**, *132*, 14191. (d) Sahoo, S. C.; Sinha, S. B.; Kiran, M. S. R. N.; Ramamurty, U.; Dericioglu, A. F.; Reddy, C. M.; Naumov, P. *J. Am. Chem. Soc.* **2013**, *135*, 13843.

(4) (a) Garcia-Garibay, M. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 8945. (b) Davey, R. J.; Maginn, S. J.; Andrews, S. J.; Black, S. N.; Buckley, A. M.; Cottier, D.; Dempsey, P.; Plowman, R.; Rout, J. E.; Stanley, D. R.; Taylor, A. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **1994**, *242*, 79.

(5) Williams, R. M.; Wallwork, S. C. *Acta Crystallogr.* **1967**, *23*, 448.

(6) Sahoo, S. C.; Panda, M. K.; Nath, N. K.; Naumov, P. *J. Am. Chem. Soc.* **2013**, *135*, 12241.

(7) Giron, D. *Thermochim. Acta* **1995**, *248*, 1.

(8) (a) Landenberger, K. B.; Bolton, O.; Matzger, A. J. *Angew. Chem., Int. Ed.* **2013**, *52*, 6468. (b) Grunenberg, A.; Henck, J.-O.; Siesler, H. W. *Int. J. Pharm.* **1996**, *129*, 147.

(9) (a) Lieberman, H. F.; Davey, R. J.; Newsham, D. M. T. *Chem. Mater.* **2000**, *12*, 490. (b) Etter, M. C.; Siedle, A. R. *J. Am. Chem. Soc.* **1983**, *105*, 641.

(10) (a) Kistenmacher, T. J.; Emge, T. J.; Bloch, A. N.; Cowan, D. O. *Acta Crystallogr.* **1982**, *B38*, 1193. (b) Chi, X.; Besnard, C.; Thorsmølle, V. K.; Butko, V. Y.; Taylor, A. J.; Siegrist, T.; Ramirez, A. P. *Chem. Mater.* **2004**, *16*, 5751.

(11) Chappell, J. S.; Bloch, A. N.; Bryden, W. A.; Maxfield, M.; Poehler, T. O.; Cowan, D. O. *J. Am. Chem. Soc.* **1981**, *103*, 2442.

(12) (a) Herbstein, F. H. *Crystalline Molecular Complexes and Compounds*; Oxford University Press: New York, 2005. (b) Visser, R. J. J.; Bouwmeester, H. J. M.; de Boer, J. L.; Vos, A. *Acta Crystallogr.* **1990**, *C46*, 852.

(13) (a) Varughese, S.; Kiran, M. S. R. N.; Ramamurty, U.; Desiraju, G. R. *Angew. Chem., Int. Ed.* **2013**, *52*, 2701. (b) Sun, C. C.; Kiang, Y. H. *J. Pharm. Sci.* **2008**, *97*, 3456.

(14) *CRC Handbook of Chemistry and Physics*, 55th ed.; Taylor & Francis: London, 1972.

(15) Porter, D. A.; Easterling, K. E. *Phase transformations in metals and alloys*; Chapman & Hall: London, 1992.

(16) Herbstein, F. H. *Acta Crystallogr.* **2006**, *B62*, 341.

593

dx.doi.org/10.1021/ja4102634 | *J. Am. Chem. Soc.* 2014, 136, 590−593