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Short communication

Domino-like thermal phase transition of 2,3-bis(phenylethenyl)-5,6-dicyanopyrazine crystal

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ABSTRACT

The single crystals of 2,3-bis(phenylethenyl)-5,6-dicyanopyrazine, **1** underwent a morphological phase transformation from a yellow crystal to an orange one via a thermal phase transition without the crystal state collapsing. The transformation began at a single starting point in the yellow crystal and then spread out into the whole crystal like a domino at 174.5 °C. This phenomenon was confirmed using the differential scanning calorimetry (DSC) and the X-ray crystal analysis. The crystal lattice transformation of compound **1** was explained in terms of the lattice contraction and the intermolecular π–π interaction in the solid state.

1. Introduction

The solid-state chemistry of organic materials has attracted a great attention because of their functionalities such as their optical and/or magnetic properties [1–4], reactivities [5,6], and phase transition [7–12] in electronics and photonics caused by the molecular stacking in aggregates. Many functionalities of organic materials are induced by the π-electron oriented intermolecular interactions that can control these diverse phenomena [13–15]. Thus, the intermolecular π–π interactions that are caused by strong molecular stacking are very significant to inducing special functionalities such as the crystal morphology and phase transition in the solid state.

Recently, reports showed that bis(phenylethenyl)-dicyanopyrazine, **1**, exhibited a crystal morphology with two types of crystals [16–18]. One, a red-colored crystal, was obtained from the recrystallization of **1** from a solution of tetrahydrofuran and acetonitrile (v/v = 1/1). The other was a yellow-colored crystal that was obtained from benzene (see Fig. 1). Not only did the two crystals exhibit different colors but also different photochemical reaction behaviors. The yellow crystal underwent a polymerization in the solid state under irradiation, whereas the orange crystal was photochemically inert.

In this work, we found that bis(phenylethenyl)-dicyanopyrazine, **1**, morphologically transformed from the yellow crystal to the orange crystal at 174.5 °C. The X-ray crystal analysis and the differential scanning calorimetry (DSC) were measured in order to clarify the specific crystal thermal transformation with respect to the intermolecular π–π interaction, which had an influence on the phase transition of **1** in the crystal state.

2. Experimental section

2.1. Materials

Compound **1** was synthesized with the known method [18]. The single crystal of **1** was obtained from dilute solution by controlling the rate of evaporation of solvent. Compound **1** gave yellow colored crystal from benzene solution. The crystal analysis data of the single crystal of **1** in room temp. was reported in the literature [18].

2.2. Instrumental analysis

Thermal behaviors of single crystals of **1** were investigated using a Mettler differential calorimetry 821e. (5 mg per sample, temperature rate: 10 °C/min).

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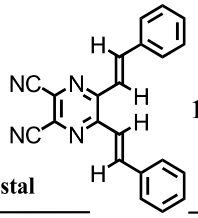

1

Yellow Crystal

Crystal symmetry	**Monoclinic, C2/c**
Lattice parameters	**a (Å) = 13.202(3)** **b (Å) = 12.274(3)** **c (Å) = 12.233(3)** **β (°) = 117.38(2)** **D_c (gcm^{-3}) = 1.261** **Z = 4** **R 0.040** **Rw 0.036**

Red Crystal

Crystal symmetry	**Monoclinic, C2/c**
Lattice parameters	**a (Å) = 13.192(2)** **b (Å) = 12.263(2)** **c (Å) = 12.126(2)** **β (°) = 117.49(1)** **D_c (gcm^{-3}) = 1.276** **Z = 4** **R 0.053** **Rw 0.074**

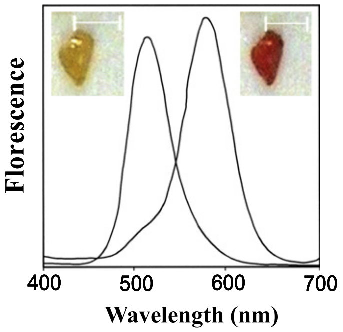

Fig. 1. Crystal morphology of **1** and the crystal data.

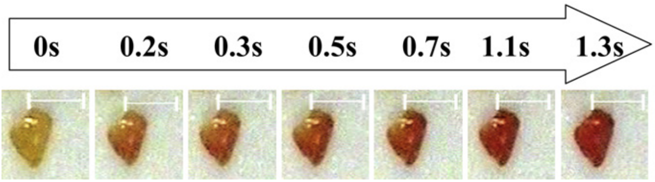

Fig. 2. Thermal color change of crystal **1** (scale bar: 780 μm).

Gel permeation chromatography (GPC): the analyzer was composed of a Shimadzu LC-10A pump, a Shodex DEGAS KT-16 degassor, and a Sugai U-620 column oven. A combination of two polystyrene gel columns of Toso TSK gel G4000 H8 and G2500 H8 was used with chloroform as an eluent at 35 °C. The molecular weight was calibrated with respect to polystyrene standards.

The color change evaluation of the crystal **1** with temperature was monitored using high temperature observation equipment (SP-5000DS).

3. Results and discussion

It was reported that bis(phenylethenyl)-dicyanopyrazine, **1**, showed the crystal morphology to give the yellow and orange colored crystals [16–18]. The polymorphism of **1** mainly resulted from the strong stacking tendency of the large π-electrons between the layer structures. The main crystallographic difference between these two crystalline polymorphs was caused by the repeating distance. The red crystal had a shorter *c*-axis than the yellow crystal. This distance corresponded to the interlayer distance of the π–π stacking [18].

Interestingly, the yellow crystal of **1** rapidly transformed to a red crystal after thermal treatment at 174.5 °C. Photographs of the color change of **1** were taken while placing the yellow crystal on a hot plate at room temperature and gradually increasing the temperature. At a temperature of 174.5 °C, the color change occurred instantly, as shown in Fig. 2.

This morphological transformation took place with a “domino” like phenomena that the process began at one terminal point of the yellow crystal, and the color change completely spread out to the other end point without any collapse (or volume change of the crystal). The response time was within 1 s for the 700 μm size crystal.

Furthermore, this phase transition was confirmed using differential scanning calorimetry (DSC). The red crystals of **1** exhibited a sharp endothermic peak at 257.8 °C, whereas the yellow crystals showed a main broad peak (258.7 °C) and another small peak (174.5 °C), which was located below the usual melting point (Fig. 3). The small peak at 174.5 °C was only found in the yellow crystal and was attributed to the endothermic lattice contraction from the yellow crystal structure to the orange crystal (vide supra), in Fig. 1.

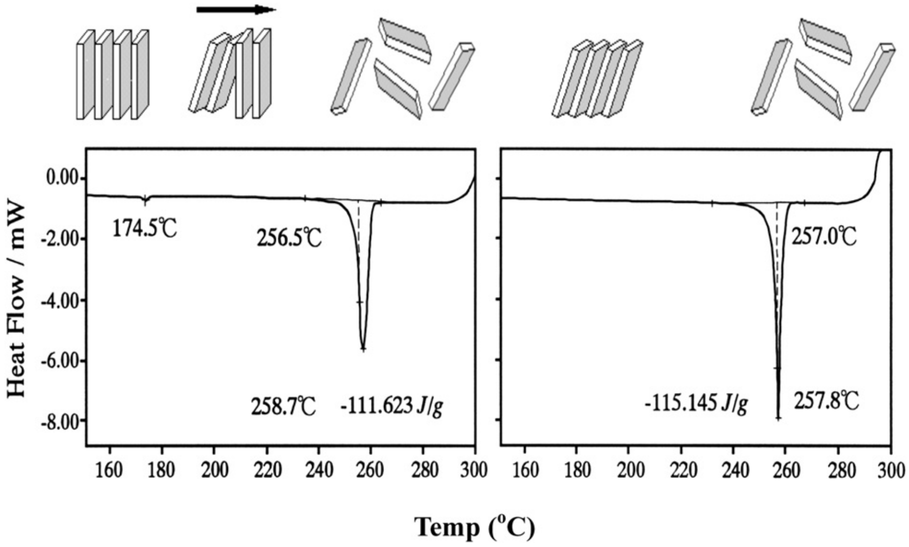

Fig. 3. Difference in the thermal properties between the yellow (left) and the red crystals (right) of the **1**. The schematic crystal lattice transformation is also shown at the top.

This small endothermic peak indicated that the crystal structure of the yellow crystal was less stable than the orange crystal, leading to a small energy gap between these phases.

Fig. 3 also shows the schematic crystal lattice transformation from the yellow to orange crystal. During heating of one point in the yellow crystal, the lattice started to contract at that point, which caused stress to the neighbor lattice. Then the contraction spread out to the whole crystal through a domino-like behavior in Fig. 2. The DSC results clearly showed that the contraction started at 174.5 °C, and the phase transition spread throughout the entire crystal. Obviously, the red crystal had a more contracted crystal packing structure than the yellow crystal because of the increased intermolecular $\pi-\pi$ interaction, which led to a bathochromic shift in the absorption and fluorescence spectra compared to the yellow crystal. This triggered the domino-like phase transition in the thermal transformation of the yellow crystal.

The cooperative spin lattice interaction induces the phase transition through photo-irradiation at a critical temperature, called the photo-induced domino effect [9,11,12]. Theoretically this effect was explained by a model composed of the localized electrons and lattices. The polymorphology and crystal transition of polythiophene and polystylene on the solvent vapor and thermal treatment were also reported [14,15].

However, the domino effect was not observed for the thermal transition of small molecules because the crystal lattice of the starting molecule was too easily distorted during the thermal phase transition.

4. Conclusion

In conclusion, the thermal phase transition of bis(phenylethenyl)-dicyanopyrazine, **1**, from the yellow crystal to the orange phase instantly occurred at a temperature of 174.5 °C. This transition triggered the local crystal contraction, and the color change completely spread throughout the entire crystal area through a domino-like behavior. We expect that this work should provide good insight into understanding the thermal and photochemical behaviors of solid-state organic compounds.

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