

Thermosalient effect of a diketopyrrolopyrrole dye between two polymorphs with different crystal systems and molecular arrangements

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Two polymorphs of a *N, N'*-dipropylated diketopyrrolopyrrole dye, one yellow and the other orange, were obtained. The yellow polymorph showed a mechanical response upon heating. The X-ray analytical results indicated that the yellow polymorph changed into the orange one during the mechanical response, with a significant change in molecular conformation, molecular arrangement, and space group.

Dynamic molecular crystals¹ can transfer energy efficiently through external mechanical stimuli such as heat, light, and pressure on a macro-, micro-, or nano-scale.² These mechanical movements, which include explosion,²⁻⁷ bending,⁸⁻¹⁵ curling,¹⁶⁻¹⁸ jumping,^{2, 19-21} and rotation,²² make it easier to visually understand the change in organic crystals. In a dense and regularly packed crystal lattice, the conversion of energy due to external stimulation has recently attracted widespread attention owing to its potential wide range of applications, including in smart materials such as artificial muscles, biomimetic techniques, and technomimetics.²³⁻²⁹ The thermosalient effect, which is a mechanical response due to heat stimulation, was first reported by Etter *et al.* in 1983.³⁰ This interesting phenomenon generally produces a limited but definite change in the crystal unit cell parameters with phase transition, resulting in anisotropic changes. In almost all cases associated with this thermosalient effect, dynamic behaviour occurs due to the sudden release of accumulated energy during the phase transition with no space group change.³¹ Recently, Mittapalli *et al.* reported halogen-substituted *N*-salicylideneaniline derivatives with a thermosalient effect.^{32,33} Among the five compounds reported in their paper, one compound exhibited a thermosalient effect with a change of

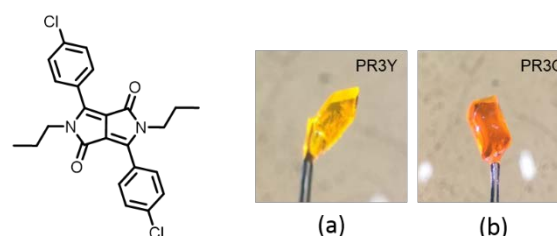


Fig. 1 Chemical structure and two differently coloured polymorphs of PR3.

space group, unlike the existing compounds showing a thermosalient effect. Form I of this compound, which was crystallised in the monoclinic space group $P2_1/c$, changed into form II, which belonged to the triclinic space group $P\bar{1}$, with cracking upon heating. In addition, these two forms were found to have significant differences in the molecular arrangement, as well as in the dihedral angle of the molecule. This is a rare example of the reported thermosalient effect because this effect has been generally considered to originate from a significant anisotropic lattice change without any changes in crystal system and space group.³²

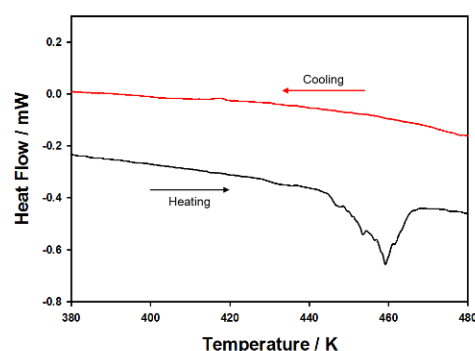


Fig. 2 DSC curve in which the phase transition of PR3Y was recorded.

During our polymorph hunting on a *N, N'*-bispropylated diketopyrrolo dye [3,6-bis(4-chlorophenyl)-2,5-dipropyl-2,5-dihydropyrrolo[3,4-

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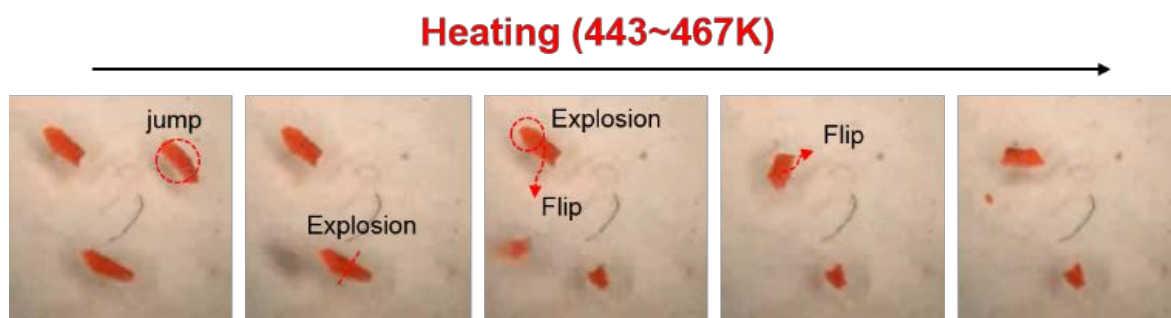


Fig. 3 HSM images of **PR3Y** crystals during heating.

c]pyrrole-1,4-dione, hereafter abbreviated as **PR3**], we found that one of its two polymorphs exhibited irreversible thermally induced dynamic behaviour. Crystal structure analysis of both polymorphs showed that this behaviour was based on a phase transition from one polymorph to another form, accompanied by a change in space group and molecular arrangement as a result of the conformational change of the alkyl substituent. To the best of our knowledge, our report is the first example to show the thermosalient effect accompanied by a significant change in molecular arrangement and space group as a result of the conformational change of the alkyl substituent.

The synthesis route of **PR3** and its characterisation data are shown in the electronic supplementary information (Figs. S1 – S3). Its crystallisation was tested under various conditions, and we found two differently coloured polymorphs, one yellow (**PR3Y**) [Fig. 1(a)] and the other orange (**PR3O**) [Fig. 1(b)]. X-ray diffraction-quality crystals of **PR3Y** were obtained by the liquid–liquid diffusion method using a combination of toluene/*n*-hexane and CHCl_3 /*c*-hexane. At room temperature, the propyl groups of molecules in **PR3Y** were found to be largely disordered. To solve this problem, the X-ray measurement was carried out at $-50\text{ }^\circ\text{C}$, and a crystal structure was obtained in which the disorder was still present on one of the propyl substituents. The disordered carbon atoms in the propyl group were refined by assuming that they were split into two possible occupied positions, C11A/C11B and C12A/C12B (Fig. S4). In the case of **PR3O**, crystals were obtained by a liquid–liquid diffusion

method using a combination of CHCl_3 /*n*-hexane and CH_2Cl_2 /*n*-hexane. Their crystallographic data are given in Table S1. We also carried out differential scanning calorimetry (DSC) measurements to determine their thermal stability. In the DSC measurement of **PR3Y**, a phase transition was observed while heating the crystals, with an endothermic peak in the temperature range of 443–467 K. This endothermic peak showed a sawtooth profile, a typical feature of the thermosalient effect,³¹ as shown in Fig. 2. This thermosalient transition was not reversible because no peak was observed upon cooling of **PR3Y** to $-50\text{ }^\circ\text{C}$ after the phase transition. Because no phase transition peak was observed in the DSC measurement of **PR3O** (Fig. S5), this observation suggests that **PR3O** is a stable phase. We then performed hot-stage microscopic (HSM) observation on the thermal response of **PR3Y** and found that the crystals of **PR3Y** were bursting and flipping when entire crystals started jumping, as shown in Fig. 3 and movie S1. The destruction of the crystals made it difficult to carry out single-crystal X-ray measurements after the mechanical response. This was led to the use of powder X-ray diffraction (PXRD) before and after the mechanical response. First, we checked the measured PXRD values of **PR3Y** and **PR3O** coincided with the simulated values (Fig. S6) to identify that there is no phase transition during sample preparation. And next, we examined how the **PR3Y** crystal changed after the mechanical response. As a result, the values of PXRD after the mechanical response were confirmed to match with the powder pattern of **PR3O**, as shown in Fig. 4. These experimental results indicated that the crystal of **PR3Y** changed to **PR3O** with the thermosalient effect. These results also suggest that these two polymorphs are monotropically related.³⁴

To identify the possible cause of the mechanical response of **PR3Y**, we carried out a detailed analysis of **PR3Y** in the crystal structure. First, because of the flexibility of the propyl group substituted on **PR3Y**, a relatively large thermal ellipsoid was found (Fig. S7). In several cases, thermosalient crystals having flexible substituents are related to the torsion of flexible substituents, and heating to the phase transition point causes the accumulation of strain in these flexible substituents.^{17, 35, 36} Then, after sudden release of the accumulated strain, the structure returns to the most energetically stable conformation. However, unlike conventional thermosalient molecules that exhibit similar molecular conformation before and after a phase transition, **PR3Y** changed to **PR3O** with a significant difference

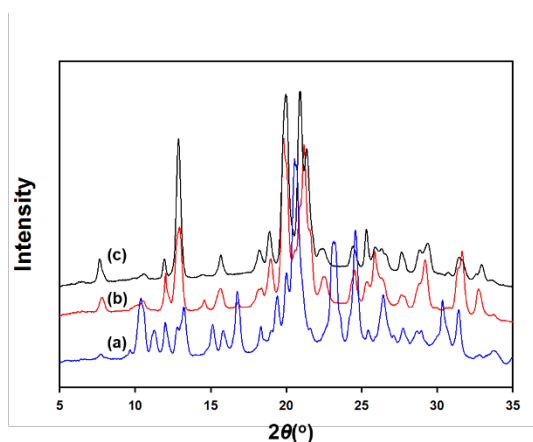


Fig. 4 PXRD peaks of (a) **PR3Y**, (b) **PR3O** and (c) after the mechanical response of **PR3Y**.

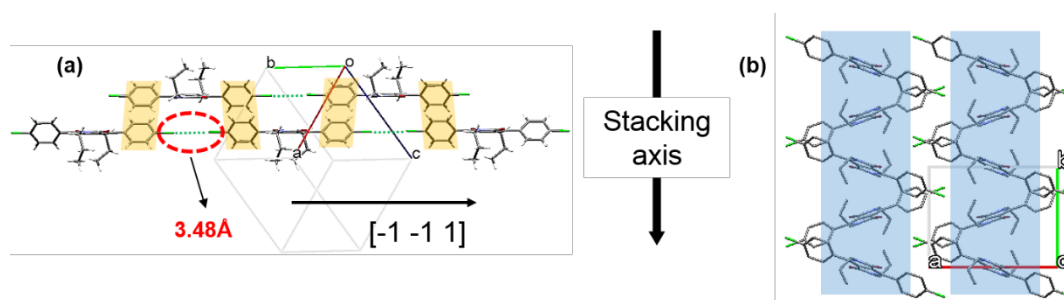


Fig. 5 (a) The one-dimensional chain of **PR3Y** propagating through the halogen interaction along the $[-1 -1 1]$ direction (green dotted line) with intermolecular π - π interaction (orange box) along the stacking axis. (b) The herringbone-like stacking arrangement of **PR3O** along b -axis (blue box).

in molecular conformation, molecular arrangement, and space group (from $P\bar{1}$ to $P2_1/c$) (Fig. 5, Fig. S7). In the crystal structure of **PR3Y**, a one-dimensional chain was formed by halogen interactions through the long molecular axis, and the chains were stacked on each other by π - π interactions [Fig. 5(a)]. However, the stable **PR3O** crystal structure showed a herringbone-like stacking arrangement without any specific intermolecular interactions [Fig. 5 (b)]. As a possible mechanism for the above considerable change, we can consider that the alkyl disorder of both sides in **PR3Y** resulted from the motion of the alkyl chain activated as temperature increased, which is related to the accumulation of energy.^{1, 37} The mechanical response might also be associated with the sudden release of this accumulated energy condensed in propyl groups and an optimisation of the crystal packing. Also, the metastable **PR3Y** crystals showed mechanical movement upon heating, even after being left at room temperature for several months, which indicates that **PR3Y** does not change into a stable **PR3O** form at ambient temperature without any thermal stimulation.

In summary, two polymorphs of the propylated diketopyrrolopyrrole dye were obtained, and one of the two showed several mechanical responses upon heating. We found this phenomenon was different from the phase transition categorised by the conventional thermosalient effect. Their X-ray analysis results indicated that disordered propyl groups may play an important role in the phase transition showing the heat-stimulated mechanical response. The above results may imply that the flexibility of the alkyl chain has the potential to affect the thermosalient effect. In the future, a detailed structural property correlation such as a lattice energy comparison between the two polymorphs and the dynamic behaviour of the substituents will be examined.

Conflicts of interest

There are no conflicts to declare.

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