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## Drastic rearrangement of self-assembled hydrogen-bonded tapes in a molecular crystal†

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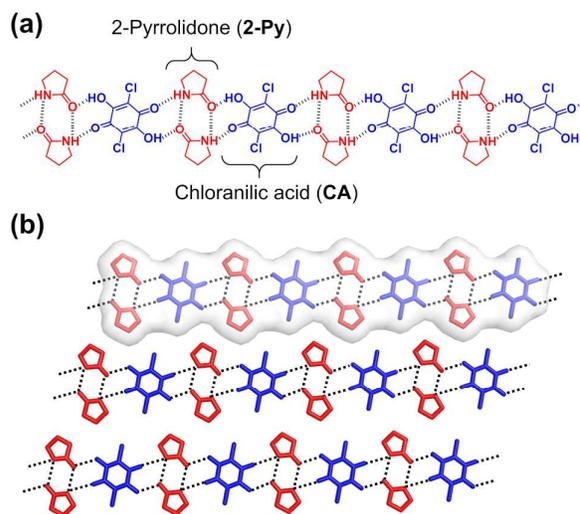
**A 2:1 hydrogen-bonded crystal of 2-pyrrolidone and chloranilic acid shows structural phase transitions accompanied by the drastic rearrangement of hydrogen-bonded tapes. Such a phenomenon is attributed to the selective and directional character of hydrogen bonds.**

A single-crystal-to-single-crystal (SCSC) polymorphic transformation is a phenomenon that occurs when a structural phase transition takes place with retention of single crystallinity.<sup>1</sup> It is a promising platform for investigating the structure–property relationship before and after the transition. In particular, crystals showing a large and anisotropic SCSC transformation have recently attracted much attention because of their potential applicability, not only to electronic but also to biomedical tools such as chemical sensors, mechanical actuators, and artificial muscles.<sup>2</sup> Most SCSC transformations are mainly driven by conformational change or molecular reorientation of isolated molecules,<sup>3</sup> and anisotropic molecular assemblies enable the collective translation with an anisotropic character.

Hydrogen bonds (H-bonds) are selective and directional interactions;<sup>4</sup> therefore, they can provide important clues for the formation of anisotropic molecular assemblies of proton donor and acceptor molecules. However, H-bonded assemblies have been largely limited to the purpose of unidirectional proton transfer for ferroelectric<sup>5</sup> and soliton<sup>6</sup> properties. In this report, we demonstrate a SCSC transformation with an unprecedentedly large translation of sheets consisting of H-bonded tapes for the first time. Furthermore, this H-bonded crystal shows an irreversible two-step SCSC transformation.

Slow evaporation of an acetonitrile solution containing 2-pyrrolidone (2-Py) as a proton acceptor and chloranilic acid (CA) as

a proton donor (4:1 molar ratio) gave red rhombic blocks. The crystal with 2:1 stoichiometry is identical to that reported previously (referred to as High-B).<sup>7</sup> In contrast, rapid cooling of the hot acetonitrile solution to room temperature gave orange plates, which are a new polymorph of 2:1 co-crystals (referred to as High-A; see ESI† for synthetic details). High-A belongs to the space group *P*-1, and the asymmetric unit contains two 2-Py molecules and one CA (Table S1, ESI†). Figure 1a shows an H-bonded tape composed of 2-Py and CA, in which two 2-Py molecules form a dimer through double complementary N–H⋯O H-bonds (N⋯O distances of 2.93 and 2.94 Å vs. sum of the van der Waals radii: 3.07 Å<sup>8</sup>). The dimers are connected by a CA through N–H⋯O (N⋯O distances of 3.01 and 3.03 Å) and O–H⋯O (O⋯O distances of 2.57 and 2.59 Å vs. sum of the van der Waals radii: 3.04 Å<sup>8</sup>) H-bonds to construct an infinite H-bonded tape. The tapes are arranged in a parallel fashion so as to engage with each other along the side-by-side direction (Figure 1b), although there is no van der Waals contact. Sheets



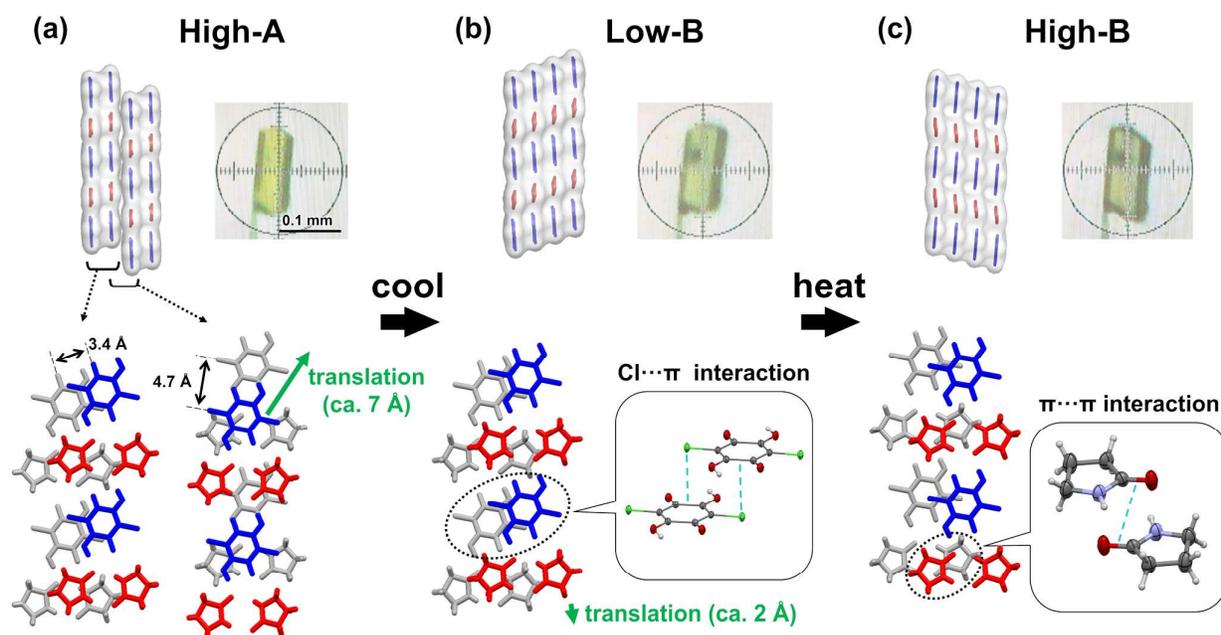
**Figure 1.** (a) H-bonded tape formed by double H-bonds between 2-pyrrolidone (2-Py) dimers and chloranilic acids (CA) in High-A. (b) Sheet structure of the H-bonded tapes, in which the opaque surface indicates the van der Waals surface. Hydrogen atoms are omitted for clarity. 2-Py and CA molecules appear in red and blue, respectively.

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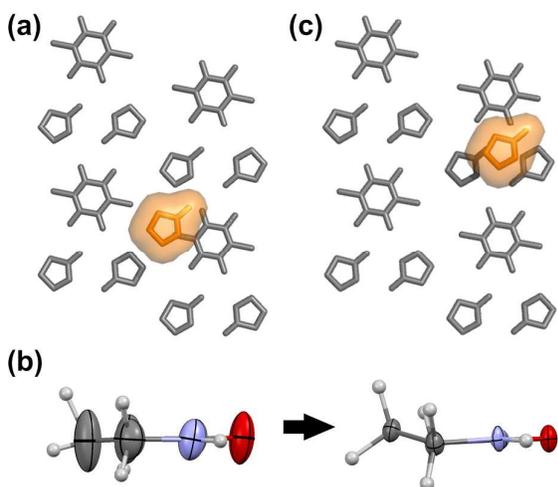


**Figure 2.** Side view of stacked tapes (top left), crystal morphology (top right), and face view of stacked tapes (bottom) of (a) High A at 298 K, (b) Low B at 100 K, and (c) High B at 298 K. In bottom panels, 2-Py and CA molecules, appearing in red and blue, respectively, are placed in the front of grey molecules, and green arrows indicate the translation of the sheet during the transitions (a) between High-A and Low-B and (b) between Low-B and High-B. Blue dotted lines in the insets show short contacts of (b) Cl... $\pi$  between CA molecules and (c)  $\pi$ ... $\pi$  between 2-Py molecules (grey: carbon, white: hydrogen, purple: nitrogen, green: chlorine, red: oxygen).

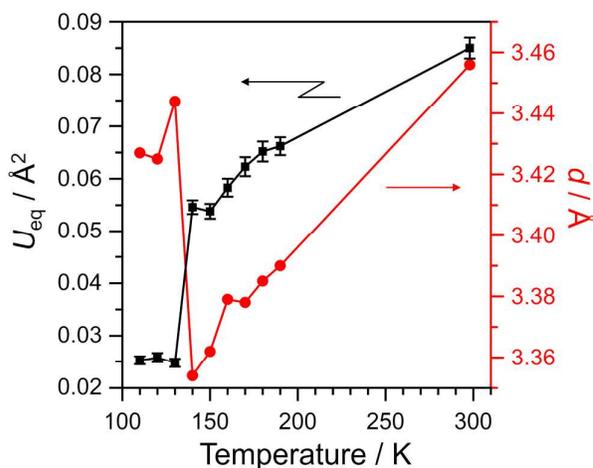
consisting of the tapes are alternately stacked with different overlapping patterns. In one pattern, adjacent tapes overlap with a shift by ca. 3.4 Å almost perpendicular to C=O bonds of CA, whereas the other pattern involves a shift by ca. 4.7 Å almost perpendicular to C–Cl bonds of CA (Figure 2a). In contrast to the latter, with no van der Waals contact, the former involves Cl... $\pi$  interactions<sup>9</sup> between adjacent CA molecules (Cl...C distance of 3.43 Å vs. sum of the van der Waals radii: 3.45 Å<sup>8</sup>) to form a dimeric sheet. Figure 2a shows four tapes viewed along the side-by-

side direction, in which each component molecule forms a pair within the dimeric sheet, resulting in alternating columns with a [2-Py...2-Py...CA...CA] repeat unit.

On cooling, the dimeric sheet in High-A exhibits a drastic translation by ca. 7 Å, which corresponds to more than half of a repeat unit of a H-bonded tape (Figure 2b; referred to as Low-B). The magnitude of the translation greatly exceeds that of reported SCSC transformations in H-bonded crystals (less than ca. 5 Å).<sup>10</sup> The translation leads to an unprecedented transformation from alternating columns to uniform segregated columns; i.e., the Cl... $\pi$



**Figure 3.** Molecular packing of (a) High-A and (c) Low-B viewed perpendicular to the molecular planes, in which the orange opaque surface indicates the 2-Py molecule with a significant out-of-plane thermal motion in High-A. In (a) and (c), hydrogen atoms are omitted for clarity. (b) Side view of the 2-Py molecule in High-A (left) and Low-B (right), where the 50% probability thermal ellipsoids are shown (excluding the hydrogen atoms).



**Figure 4.** Temperature dependence of equivalent isotropic thermal parameter of 4-carbon position of 2-Py with a significant out-of-plane thermal motion in High-A ( $U_{eq}$ ; black squares) and intersheet distance between dimeric sheets in High-A ( $d$ ; red circles).

interactions observed only within the dimeric sheet in High-A are present in all intersheet spacings in Low-B. Relative to High-A, Low-B adopts the same space group with a halved unit cell volume.

In kinetically stable High-A, one of the crystallographically independent 2-Py molecules, which is arranged with respect to the cavity of a sheet in a neighbouring dimer (Figure 3a), exhibits a significant out-of-plane thermal motion (equivalent isotropic thermal parameter  $U_{\text{eq}} = 0.085(2) \text{ \AA}^2$  for a 4-carbon position at 298 K; Figure 3b).<sup>11</sup> On the other hand, the 2-Py molecule in Low-B is positioned away from the cavity when viewed along the stacking direction (Figure 3c). As shown in Figure 4, the  $U_{\text{eq}}$  value experiences a sharp drop at about 130 K because of the transition from High-A to Low-B, and eventually attains a near plateau ( $0.0253(8) \text{ \AA}^2$  at 110 K), to adopt an envelope conformation (Figure 3b). Of particular importance is that the intersheet distance between dimeric sheets in High-A (d) shows an increase the transition temperature. This result provides compelling experimental evidence that the drastic transformation loses the closely packed structure to gain the additional CA...CA interactions and it is mainly triggered by reduction of the thermal motion of the 2-Py molecules.

It is noteworthy that the morphology of the crystal dramatically changes during the SCSC transition at around 160–120 K (cooling rate of  $50 \text{ K min}^{-1}$ ; Movie S1, ESI†). The displayed facet deforms along the right diagonal direction, which corresponds to the microscopic transformation as shown in Figure 2b.

On heating, Low-B undergoes a second SCSC transition at around 170–200 K (heating rate of  $50 \text{ K min}^{-1}$ ). Crystallographic studies revealed that the high-temperature phase is identical with the foregoing High-B rather than High-A. In contrast to the first SCSC transition, in the second transition, the space group ( $P-1$ ) and unit cell volume ( $Z = 1$ ) remain unchanged. Each sheet collectively translates relative to the neighbouring sheet by ca.  $2 \text{ \AA}$  along the tape direction (Figure 2c). In High-B, intersheet  $\pi \cdots \pi$  interactions between ketone groups of 2-Py molecules ( $\text{C} \cdots \text{C}$  distance of  $3.34 \text{ \AA}$  vs. sum of the van der Waals radii:  $3.40 \text{ \AA}^8$ ) were observed, although there is no intersheet  $\text{Cl} \cdots \pi$  interaction between CA molecules. This result strongly indicates that the competition between intersheet CA...CA and 2-Py...2-Py interactions is a factor governing the second transition. Because High-B shows no sign of a phase transition upon varying the temperature (100–298 K), it is apparent that High-B is the most thermodynamically stable phase. Notably, the density of High-B at 100 K ( $1.64 \text{ g cm}^{-3}$ ) is higher than that of Low-B at 100 K ( $1.59 \text{ g cm}^{-3}$ ), possibly indicating the higher cohesive energy. During the second transition, the crystal deforms along the left diagonal direction (Movie S2, ESI†), and the morphology is distinct from that of High-A. Again, the deformation is closely related to the microscopic observation (Figure 2c).

In summary, we have demonstrated the first example of a remarkable SCSC transformation with anisotropic and collective large translations of H-bonded molecular assemblies. Because the directional character of H-bonds, as well as the thermal motion of components, is responsible for the peculiar behaviour in this system, our finding should open a new class of SCSC materials for practical applications, such as for mechanical actuators and artificial muscles. In particular, in H-bonded crystals composed of two or more components, there are several competing interactions between assemblies, which would lead to the large and anisotropic translation

by external stimuli. Such multicomponent H-bonded crystals also have the great advantage of their diverse combinations of proton donor and acceptor molecules, which would allow the rational design of SCSC materials with desired properties. Studies along this line are now in progress.

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## Conflicts of interest

There are no conflicts of interest to declare.

## Notes and references

- (a) N. K. Nath, M. K. Panda, S. C. Sahoo and P. Naumov, *CrystEngComm*, 2014, **16**, 1850; (b) P. Naumov, S. Chizhik, M. K. Panda, N. K. Nath and E. Boldyreva, *Chem. Rev.*, 2015, **115**, 12440; (c) P. Commins, I. T. Desta, D. P. Karothu, M. K. Panda and P. Naumov, *Chem. Commun.*, 2016, **52**, 13941; (d) T. Seki and H. Ito, *Chem. Eur. J.*, 2016, **22**, 4322. (e) A. Chaudhary, A. Mohammad and S. M. Mobin, *Cryst. Growth Des.*, 2017, **17**, 2893.
- (a) M. Morimoto and M. Irie, *J. Am. Chem. Soc.*, 2010, **132**, 14172; (b) G. Liu, J. Liu, Y. Liu and X. Tao, *J. Am. Chem. Soc.*, 2014, **136**, 590; (c) Z.-S. Yao, M. Mito, T. Kamachi, Y. Shiota, K. Yoshizawa, N. Azuma, Y. Miyazaki, K. Takahashi, K. Zhang, T. Nakanishi, S. Kang, S. Kanegawa and O. Sato, *Nat. Chem.*, 2014, **6**, 1079; (d) T. Taniguchi, H. Sugiyama, H. Uekusa, M. Shiro, T. Asahi and H. Koshima, *Nat. Commun.*, 2018, **9**, 538.
- (a) G. S. McGrady, M. Odlyha, P. D. Prince and J. W. Steed, *CrystEngComm*, 2002, **4**, 271; (b) E. V. Boldyreva, *Cryst. Eng.*, 2003, **6**, 235; (c) L. Dobrzycki, T. Zielinski, J. Jurczak and K. Wozniak, *J. Phys. Org. Chem.*, 2005, **18**, 864; (d) D. Das, E. Engel and L. J. Barbour, *Chem. Commun.*, 2010, **46**, 1676; (e) H. Takahashi and Y. Ito, *CrystEngComm*, 2010, **12**, 1628; (f) E. Marelli, N. Casati, F. Gozzo, P. Macchi, P. Simoncic and A. Sironi, *CrystEngComm*, 2011, **13**, 6845; (g) M. A. Asghar, Z. Sun, T. Khan, C. Ji, S. Zhang, S. Liu, L. Li, S. Zhao and J. Luo, *Cryst. Growth Des.*, 2016, **16**, 895.
- (a) G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, New York, 1st edn., 1997; (b) *The Weak Hydrogen Bond*, ed. G. R. Desiraju and T. Steiner, Oxford University Press, New York, 1999. (c) T. Steiner, *Angew. Chem. Int. Ed.*, 2002, **41**, 48.
- (a) S. Horiuchi, R. Kumai and Y. Tokura, *Chem. Commun.*, 2007, 2321; (b) S. Horiuchi and Y. Tokura, *Nat. Mater.*, 2008, **7**, 357; (c) S. Horiuchi, Y. Tokunaga, G. Giovannetti, S. Picozzi, H. Itoh, R. Shimano, R. Kumai and Y. Tokura, *Nature*, 2010, **463**, 789; (d) W. Zhang, R.-G. Xiong, *Chem. Rev.*, 2012, **112**, 1163; (e) A. S. Tayi, A. Kaeser, M. Matsumoto, T. Aida and S. I. Stupp, *Nat. Chem.*, 2015, **7**, 281; (f) T. Akutagawa, *Mater. Chem. Front.*, 2018, **2**, 1064.
- (a) A. S. Davydov, *Phys. Scr.*, 1979, **20**, 387; (b) Y. Kashimori, T. Kikuchi and K. Nishimoto, *J. Chem. Phys.*, 1982, **77**, 1904; (c) S. Yomosa, *J. Phys. Soc. Jpn.*, 1982, **51**, 3318; (d) S. Pnevmatikos, *Phys. Rev. Lett.*, 1988, **60**, 1534; (e) I. Takasu, T. Sugawara and T. Mochida, *J. Phys. Chem. B*, 2004, **108**, 18495.
- K. Gotoh and H. Ishida, *Acta Crystallogr.*, 2011, **C67**, o500.
- A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.
- (a) M. D. Prasanna and T. N. Guru Row, *Cryst. Eng.*, 2000, **3**, 135; (b) I. Saraogi, V. G. Vijay, S. Das, K. Sekar and T. N. Guru

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- Row, *Cryst. Eng.*, 2003, **6**, 69; (c) H. Matter, M. Nazaré, S. Güssregen, D.W. Will, H. Schreuder, A. Bauer, M. Urmann, K. Ritter, M. Wagner and V. Wehner, *Angew. Chem. Int. Ed.*, 2009, **48**, 2911.
- 10 For examples, see: (a) R. J. Davey, S. J. Maginn, S. J. Andrews, S. N. Black, A. M. Buckley, D. Cottier, P. Dempsey, R. Plowman, J. E. Rout, D. R. Stanley and A. Taylor, *Mol. Cryst. Liq. Cryst.*, 1994, **242**, 79; (b) D. P. Karothu, J. Weston, I. T. Desta and P. Naumov, *J. Am. Chem. Soc.*, 2016, **138**, 13298.
- 11 The dynamic nature of the out-of-plane thermal motion was confirmed by nuclear quadrupole resonance measurements: M. Donoshita *et al.*, unpublished work.

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