Electronic Supplementary Information (ESI) for

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

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Experimental Details

Sample preparation: Chloranilic acid (CA) was obtained from TCI Chemical Industry (Tokyo, Japan) and purified by recrystallization from aqueous solution. 2-Pyrrolidone (2-Py) was obtained from Nacalai Tesque (Kyoto, Japan) and used as received without further purification. Orange plate crystals of High-A were prepared by rapid cooling of a hot acetonitrile solution (120 mL) containing CA (2.12 g, 10.2 mmol) and 2-Py (3.40 g, 39.9 mmol) to room temperature (5.5 h), while stirring. Red rhombic block crystals of High-B were prepared by slow evaporation of an acetonitrile solution (1.01 L) containing CA (2.09 g, 10.0 mmol) and 2-Py (3.41 g, 40.0 mmol) at room temperature.

Single-crystal X-ray structural analysis: Crystallographic data at typical temperatures were collected using the synchrotron X-ray at the BL02B1 beam-line in SPring-8 with a Rigaku Mercury 2 CCD detector (λ = 0.703010 Å).[1] Variable-temperature experiments were performed on a laboratory X-ray diffractometer (Rigaku XtaLAB P200) with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). A single crystal was mounted on a glass fibre with epoxy resin and cooled by a stream of cooled nitrogen gas. The structures were solved by direct methods (SHELXT[2]) and refined by full-matrix least-squares refinement on F^2 (SHELXL[3]) using the CrystalStructure[4] software package. The positions of all atoms, including hydrogen atoms, were refined in the general least-squares cycle with no restraints. All non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were refined isotropically.

(1) Crystallographic data were deposited with the Cambridge Crystallographic Data Centre: deposition nos. CCDC 1838517 (High-A at 298 K), 1838519 (Low-B at 100 K), 1838518 (High-B at 298 K) and 1838516 (High-B at 100 K).

(2) G. M. Sheldrick, *Acta Crystallogr*., 2015, **A71**, 3.

(3) G. M. Sheldrick, *Acta Crystallogr*., 2008, **A64**, 112.

(4) CrystalStructure 4.2.5: Crystal Structure Analysis Package, Rigaku Corporation, Tokyo, Japan.

Table S1. Cell parameters and crystallographic information for each form of 2:1 co-crystal of 2-pyrrolidone and chloranilic acid

	High-A	Low-B[a]	High-B[a]	High-B[a]
Formula	$C_{14}H_{16}Cl_2N_2O_6$	$C_{14}H_{16}Cl_2N_2O_6$	$C_{14}H_{16}Cl_2N_2O_6$	$C_{14}H_{16}Cl_2N_2O_6$
Formula weight	379.20	379.20	379.20	379.20
Temperature (K)	298	100	298	100
Wavelength (Å)	0.703010	0.703010	0.703010	0.703010
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1
Colour	Orange	Orange	Orange	Orange
a (Å)	8.1575(9)	4.6904(17)	4.987(3)	4.9143(16)
b (Å)	10.3671(12)	8.921(3)	7.592(4)	7.458(2)
c (Å)	11.0921(13)	9.833(3)	11.718(6)	11.698(4)
α (°)	74.290(5)	103.357(7)	72.926(6)	73.270(5)
β (°)	75.655(5)	96.447(7)	89.449(6)	89.528(6)
γ (°)	67.442(5)	93.984(7)	71.157(6)	69.737(5)
V (Å^3)	822.93(17)	395.8(2)	399.6(4)	383.2(2)
Z	2	1	1	1
Calcd density (g cm^{-3})	1.530	1.591	1.576	1.643
μ (mm^{-1})	0.410	0.426	0.422	0.440
F(000)	392	196	196	196
Crystal size (mm^3)	0.09 × 0.04 × 0.01	0.14 × 0.06 × 0.02	0.14 × 0.06 × 0.02	0.14 × 0.06 × 0.02
Total reflections	10883	5200	5228	4220
Unique reflections	3744	1799	1821	1393
Parameters used	281	141	141	141
R_{int}	0.0603	0.0830	0.0658	0.0613
Goodness-of-fit	0.946	1.028	0.944	1.065
R_1 [$I > 2\sigma(I)$]	0.0491	0.0535	0.0520	0.0434
wR_2 (all reflections)	0.1333	0.1428	0.1302	0.1120
max, min $\Delta\rho$ (e Å^{-3})	0.25, -0.24	0.60, -0.60	0.31, -0.23	0.38, -0.38

[a] Data taken from the same piece of single crystal during the temperature-sweeping process.