# Supporting information

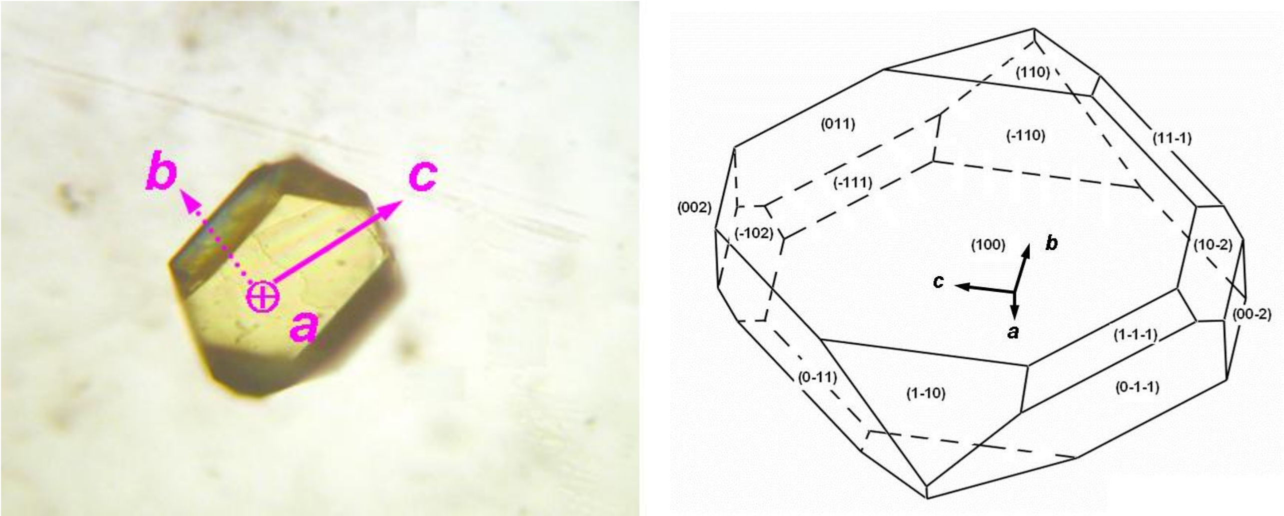

**Figure S1**. The obtained yellow crystal of **1** (left) and its growth habit determined by the X-ray powder diffraction (right).

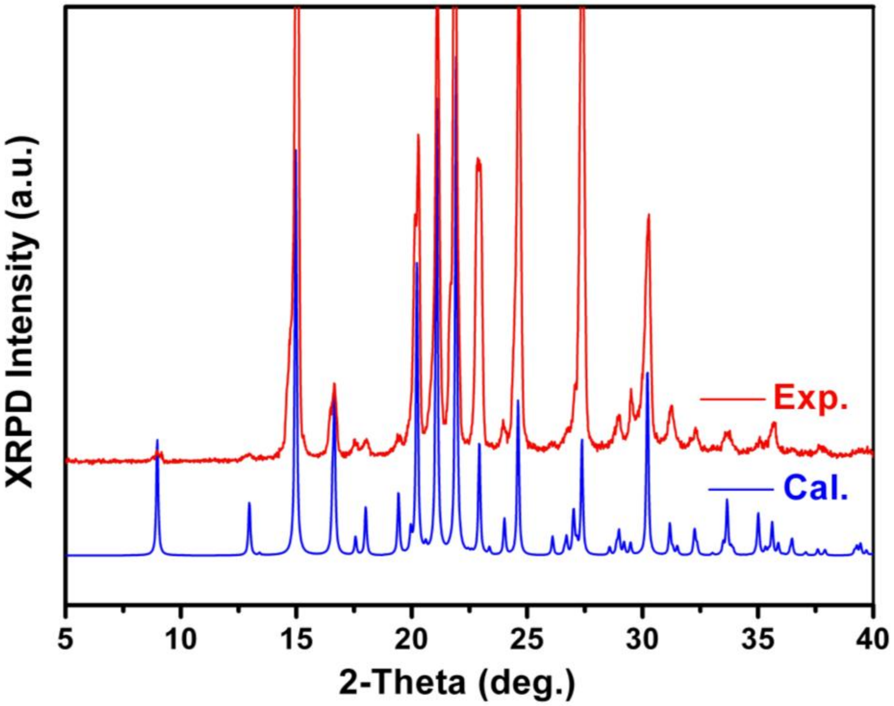

**Figure S2**. Calculated and experimental XPRD patterns on the polycrystalline samples of **1** at the room temperature, which fairly well confirms the purities of the obtained sample.

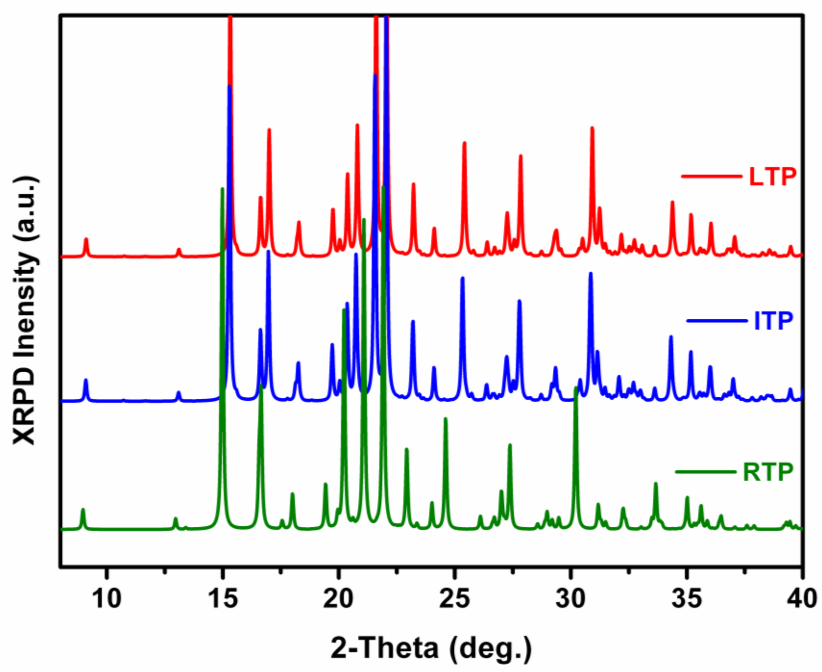

**Figure S3.** Comparison of the variable-temperature X-ray powder diffraction patterns of **1** on the basis of structure determination. The results indicate that spectra in LTP and ITP are well coincident while the patterns in RTP change obviously, explicitly confirming the phase transition of **1**.

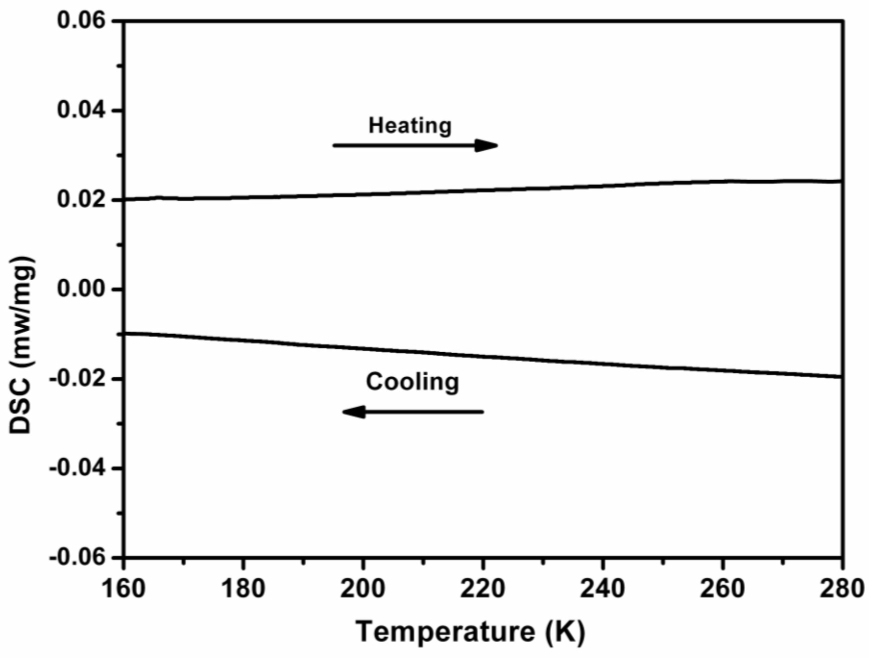

**Figure S4**. DSC traces of **1** measured in the temperature range of 160-290 K.

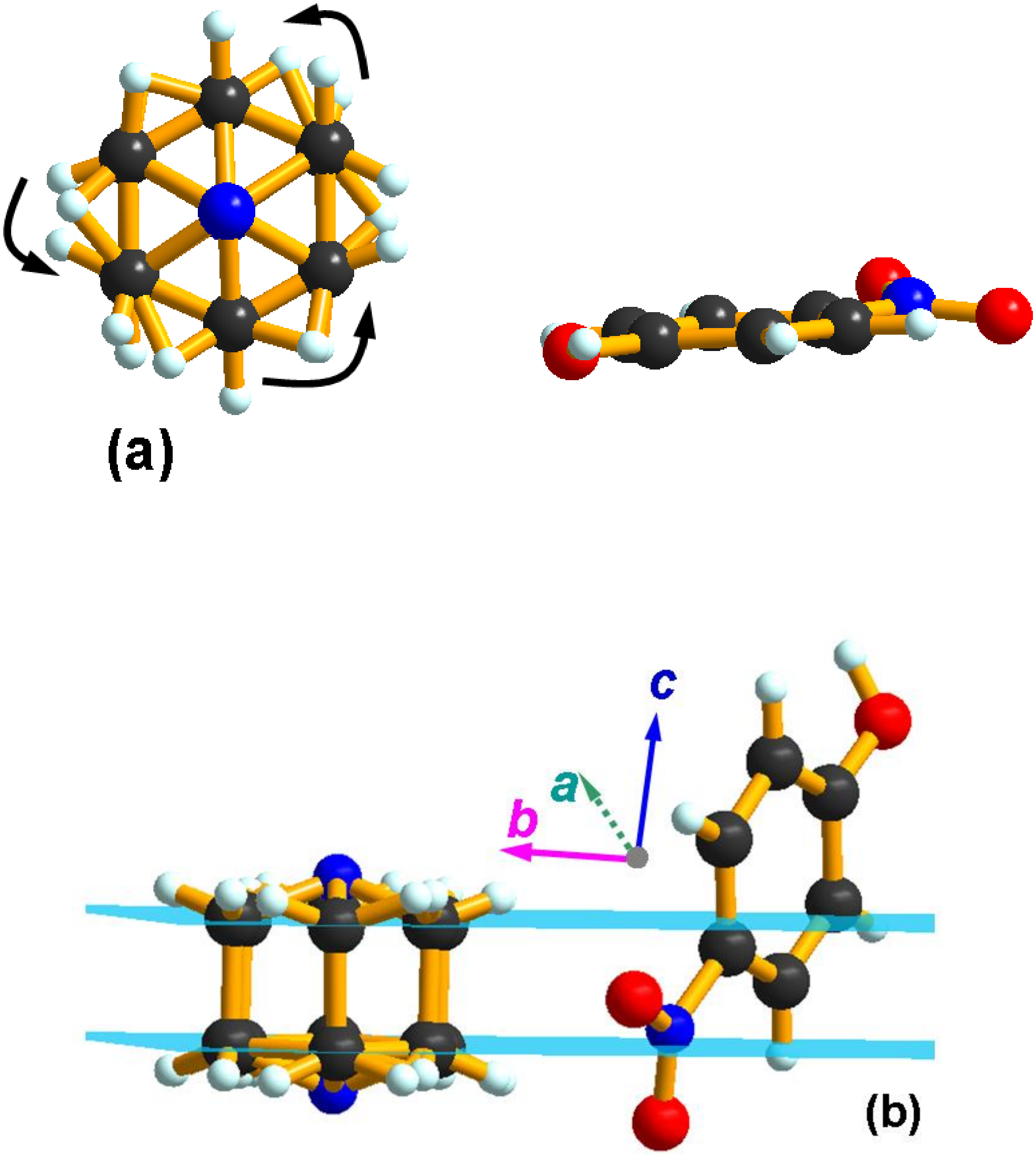

**Figure S5**. (a) Schematic illustration for the rotational motions of room-temperature dabco molecule in **1** viewed along the N-N axis direction. All the bonded-hydrogens are split owing to the disordings of rotational motions of dabo; (b) Corresponding plane through carbon atoms in dabco. The rotational N-N axis lies along the direction of the normal for the current coplane, which is almost parallel to the crystallographic *c*-axis.

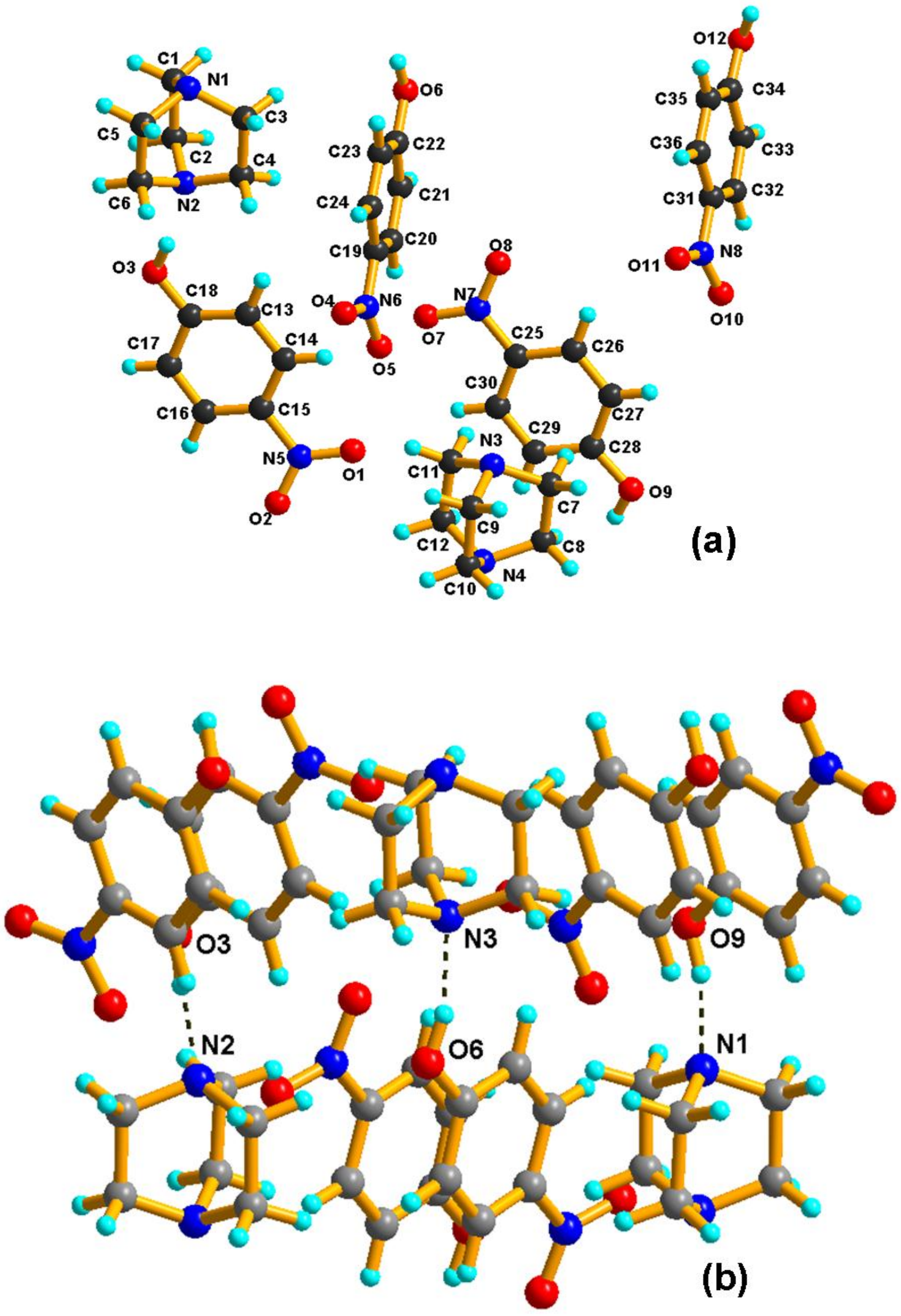

**Figure S6**. (a) Molecule structure of **1** with atomic labellings at the LT phase, in which all the dabco molecules have become much more ordered; (b) Several strong N-H···O H-bonds are shown as the black dashed lines between N atoms of the dabco and O atoms of *p*-nitrophenol moieties.

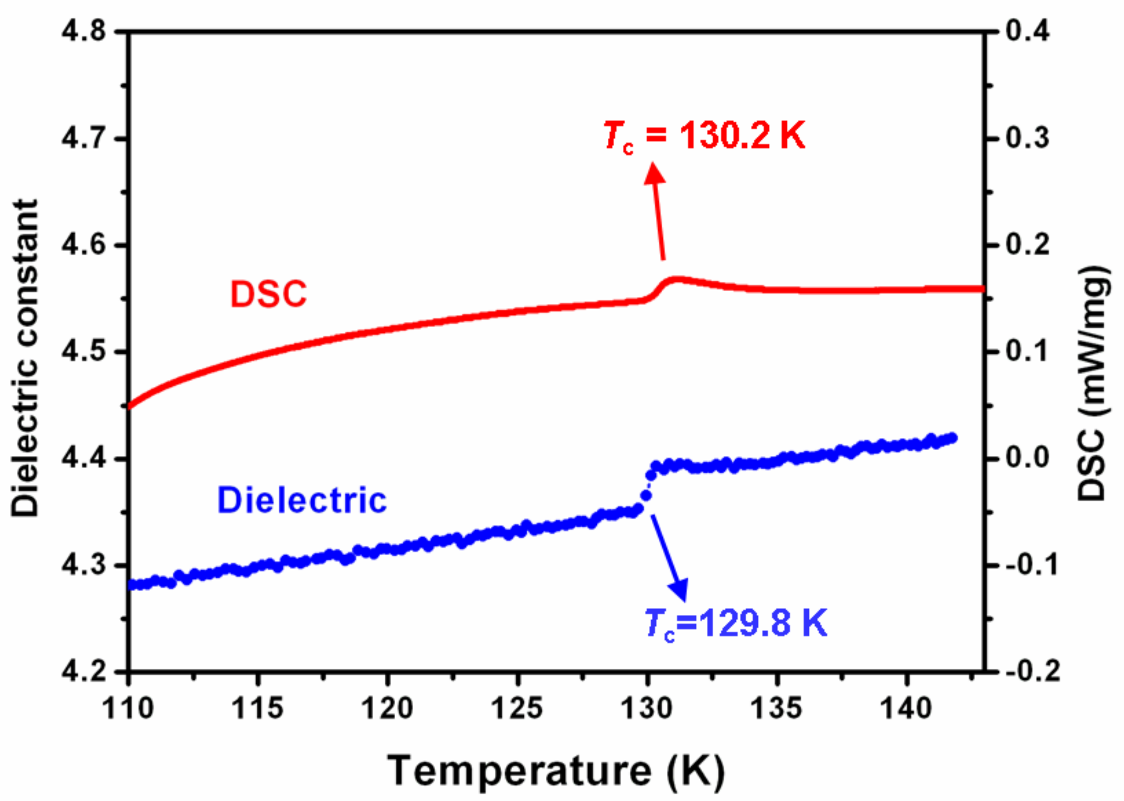

**Figure S7**. DSC and dielectric traces measured on the polycrystalline powder of the deuterated analog of **1** in the heating mode. The observed anomalies confirm the existence of phase transition. However, phase-transition temperature is still located around 130 K and the absence of deuterium isotope effect exclude the possible motions of proton.

**Table S1**. Crystal data collection and structure refinement for **1**.

| | RTP, 293 K | ITP, 120 K | LTP, 100 K |
|---|---|---|---|
| Empirical formula | $C_{18}H_{22}N_4O_6$ | $C_{18}H_{22}N_4O_6$ | $C_{18}H_{22}N_4O_6$ |
| Formula weight | 390.40 | 390.40 | 390.40 |
| Crystal system, space group | Monoclinic, $P2_1/c$ | Triclinic, $P\bar{1}$ | Triclinic, $P\bar{1}$ |
| Unit cell dimensions | $a$ = 9.984(6) Å | $a$ = 9.805(5) Å | $a$ = 9.785(2) Å |
| | $b$ = 8.890(5) Å | $b$ = 13.762(6) Å | $b$ =13.7474(18) Å |
| | $c$ = 10.791(7) Å | $c$ = 13.774(7) Å | $c$ = 13.7474(18) Å |
| | $\beta$ = 99.593(9)° | $\alpha$ = 80.039(13)° | $\alpha$ = 80.157(14) ° |
| | | $\beta$ = 83.930(9)° | $\beta$ = 84.13(2) ° |
| | | $\gamma$ = 84.024(11)° | $\gamma$ = 84.13(2) ° |
| Volume | 944.4(10) Å$^3$ | 1813.3(15) Å$^3$ | 1805.7(5) Å$^3$ |
| Z, Calculated density | 2, 1.373 Mg/m$^3$ | 4, 1.430 Mg/m$^3$ | 4, 1.436 Mg/m$^3$ |
| Absorption coefficient | 0.105 mm$^{-1}$ | 0.109 mm$^{-1}$ | 0.109 mm$^{-1}$ |
| $F$(000) | 412 | 824 | 824 |
| Theta range for data collection | 4.04° - 25.00° | 2.30° - 27.39° | 1.51° - 23.99° |
| Limiting indices | -11<=h<=11, | -12<=h<=12, | -11<=h<=11, |
| | -10<=k<=10, | -16<=k<=17, | -15<=k<=13, |
| | -12<=l<=12 | -17<=l<=17 | -15<=l<=12 |
| Reflections collected / unique | 5754 / 1604 | 15084 / 7628 | 7724 / 5263 |
| | $R_{int}$ = 0.0341 | $R_{int}$ = 0.0917 | $R_{int}$ = 0.0189 |
| Max. and min. transmission | 0.9703, 0.9574 | 0.9628, 0.9455 | 0.9710, 0.9555 |
| Data / restraints / parameters | 1604 / 0 / 154 | 7628 / 0 / 506 | 5263 / 0 / 505 |
| GOF | 1.068 | 1.089 | 1.184 |
| Final $R$ indices [$I>2\sigma(I)$] | $R_1$ = 0.0461 | $R_1$ = 0.1768 | $R_1$ = 0.1050 |
| | $wR_2$ = 0.1303 | | $wR_2$ = 0.2386 |
| $R$ indices (all data) | $R_1$ = 0.0569 | $R_1$ = 0.1829 | $R_1$ = 0.1193 |
| | $wR_2$ = 0.1390 | | $wR_2$ = 0.449 |

**Table S2**. Selected $U_{eq}$ values for the atoms of dabco molecules at different temperatures, which is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor. The detailed $U_{ij}$ tensor ratio for dabco molecule for **1** at RT phase is $U_{eq}$ (N)/$U_{eq}$ (mean of carbon atoms) = 73.5/49; the value at IT phase is 27.5/19; the value at LT phase is 24.7/18. These findings reveal the successive order-disordered feature of the phase transition.

| Atoms | $U_{eq}$ , RTP | $U_{eq}$, ITP | $U_{eq}$, LTP |
|---|---|---|---|
| C7 | 68(1) | 28(1) | 22(1) |
| C8 | 69(1) | 26(2) | 24(1) |
| C9 | 80(1) | 29(1) | 25(2) |
| C10 | 80(1) | 28(1) | 27(1) |
| C11 | 69(1) | 27(2) | 25(2) |
| C12 | 75(1) | 27(1) | 25(2) |
| N1 | - | 18(1) | 17(1) |
| N2 | 49(1) | 20(1) | 19(1) |