Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Comment on "1,4-Diazabicyclo[2.2.2]octane-based disalts showing non-centrosymmetric structures and phase transitions behaviors"

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Experimental Details

Single crystals of $(dabcoH_2)(BF_4)_2{\cdot}H_2O$ and $(dabcoH_2)(ClO_4)_2{\cdot}H_2O$ were grown from aqueous solutions containing stoichiometric amounts of 1,4-diazabicyclo[2.2.2]octane and HBF_4 or $HClO_4$ acid, respectively. The crystallization was carried out by a slow evaporation method at room temperature.

Calorimetric studies were performed in the temperature range 95–300 K using a differential scanning calorimeter Q2000 (TA Instruments). Indium standard was used to calibrate temperature and enthalpy and synthetic sapphire for specific heat calibration. The polycrystalline samples, prepared by grinding the single crystals, were heated/cooled with a rate of 10 K/min.

The single-crystal X-ray diffraction measurements were carried out with the graphite-monochromated Mo$K\alpha$ radiation on a Gemini A Ultra diffractometer. The temperature of the crystals was stabilized within ±0.1 K with a nitrogen stream generated by a Cryostream Plus (Oxford Cryosystems) attachment. The CrysAlis^{Pro} software[1] was used for data collection and processing. SHELXS97 and SHELXTL97 programs were used for structure solution and refinement.[2] The structures were refined by full-matrix least-squares method on all intensity (F^2's) data. Hydrogen atoms of water molecules were located in difference Fourier maps and refined with isotropic thermal parameters set at 1.2 times U_{eq} of the oxygen atoms. The H-atoms of $(dabcoH_2)^{2+}$ cations were located from the molecular geometry and refined in geometrically ideal positions after each cycle of the refinement. Crystallographic information files (CIFs) for the structures measured for $(dabcoH_2)(BF_4)_2{\cdot}H_2O$ and $(dabcoH_2)(ClO_4)_2{\cdot}H_2O$ were deposited in the Cambridge Crystallographic Database Centre as supplementary publications CCDC 1488023-1488026, 1502095 and 1502096.

Optical observations of ferroelastic domain structure were carried out with a polarizing microscope Eclipse E600 POL (Nikon) equipped with a Linkam cooling/heating stage THMSE 600. The temperature was stabilized with an accuracy of ±0.1 K. Thin crystal plates were oriented perpendicular to *a* axis of the room-temperature orthorhombic unit-cell.

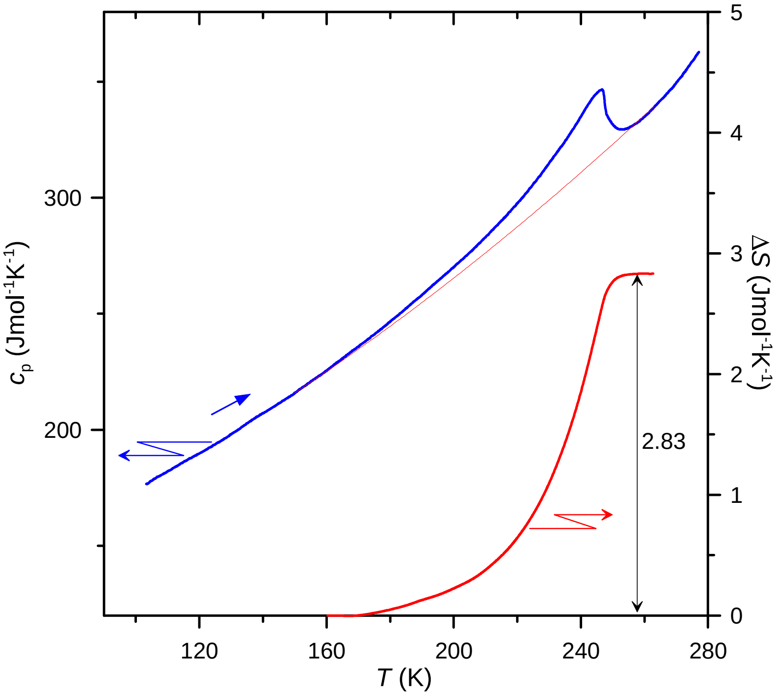

Figure S1. Specific heat and entropy change in the vicinity of second-order phase transition in $(dabcoH_2)(ClO_4)_2{\cdot}H_2O$

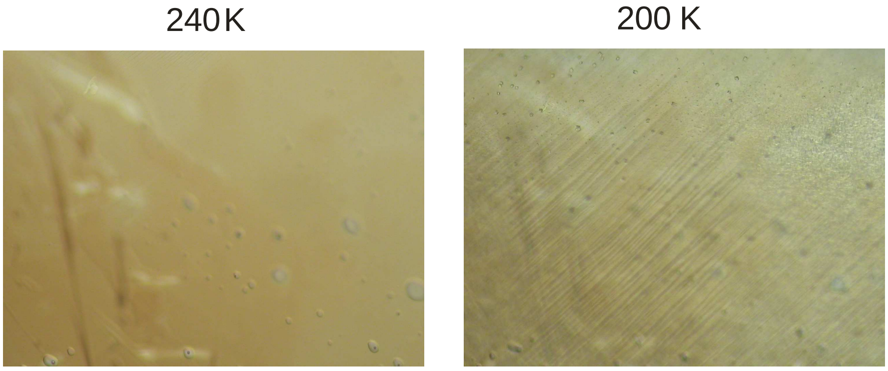

Figure S2. Crystal plate of (dabcoH$_2$)(BF$_4$)$_2$·H$_2$O viewed in polarized light in the high-temperature phase at 240 K and in the low-temperature phase at 200 K. A delicate pattern of the domain structure occurs in the low-temperature phase II (right photo).

References

1. *Oxford Diffraction CrysAlis^{Pro} version 171.34.40: Data Collection and Processing Software for X-Ray Diffractometers; Agilent Technologies: Santa Clara, CA, 2010.*

2. Sheldrick, G. M. *Acta Crystallogr*. **2008**, *A64* 112-122.