Electronic Supplementary Information

Bistable N-H•••N Hydrogen Bonds for Reversibly Modulating the Dynamic Motion in an Organic Co-crystal

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Experimental details

All the chemical reagents were purchased as high purity (AR grade) and used without any further purification. The organic co-crystal of 1,2-diazabicyclo(2.2.2)octane bis(thiourea) (1) [dabco = 1,2-diazabicyclo(2.2.2)octane] has been synthesized in aqueous solution of dabco and thiourea in a ratio of 1:2. Variable-temperature X-ray single crystal diffraction experiments were performed on a Rigaku Saturn70 diffractometer with Mo/Cu-Kα radiation (λ = 0.71073/1.5406 Å). Absorption corrections were applied by using multi-scan program.[1] Crystal structures were solved by direct methods and refined by the full-matrix method based on F^2 using the *SHELXLTL* software package using *SHELXS-97*.[2] All non-hydrogen atoms positions were located using difference Fourier methods as implemented in *SHELXL-97*. All of the non-hydrogen atoms were refined anisotropically and the positions of the hydrogen atoms were generated geometrically.

Solid-state nuclear magnetic resonance (NMR) experiments were carried out on a Varian Infinityplus-300 spectrometer with a 4 mm double-resonance MAS probe at resonance frequencies of 299.8, and 75.4 MHz for ^{1}H and ^{13}C, respectively. ^{13}C CP/MAS NMR spectra were acquired at a spinning rate of 6 kHz and a recycle delay of 10 s. [13]C−[1]H dipolar couplings were measured using the DIPSHIFT experiment under 6 kHz MAS with a recycle delay of 10 s. [3] The time domain data were fit to give the apparent dipole coupling strengths in DIPSHIFT experiment. The true [13]C−[1]H dipolar couplings were calculated on the basis of apparent dipole coupling strengths and PMLG scaling factor. The [13]C T_1 values of CH_2 group in (dabco) were measured using the Torchia sequence [4] as a function of temperature. The data were fitted to an exponential decay function to extract [13]C T_1 values. The sample temperatures were calibrated by the chemical shifts of $Pb(NO)_3$ under the similar condition in the variable temperature NMR experiments.

XRPD patterns were recorded by an X-ray diffractometer (Rigaku Corporation SCXmini). Differential scanning calorimetry (DSC) is measured by a differential thermal analyzer of Netzsch DSC 200 F3 under nitrogen atmosphere in aluminum crucibles with the heating/cooling rate of 10 K/min. The specific heat measurement was performed on a PPMS-9T instrument in the temperature range of 2−293 K. Dielectric experiments were carried out on crystal specimen by TH2828 Precision LCR Meter at different frequency with an applied electric field of 0.5 V. The electrodes were made by sputtering silver onto both sides of samples and attaching copper leads with silver paste. Calibration of standard capacitor reveals that the experimental errors are within ± 1% accuracy.

Table S1. Crystal data and structural refinement details of **1** at 298 K and 100 K.

| Empirical formula	$C_8H_{20}N_6S_2$	$C_8H_{20}N_6S_2$
Formula weight	264.42	264.42
Temperature/K	298(2)	100(2)
Radiation	Mo-Kα (0.71073 Å)	Mo-Kα (0.71073 Å)
Crystal system	Monoclinic	Monoclinic
Space group	*C2/c*	*C2/c*
a/Å	9.685(6)	19.106(7)
b/Å	7.867(5)	15.504(7)
c/Å	18.241(11)	18.03(3)
α/deg	90	90
β/deg	95.266(11)	95.648(15)
γ/deg	90	90
Volume/ Å³	1384.0(14)	5315.0(9)
Z	4	4
Calculated density/g cm⁻³	1.269	1.322
Absorption coefficient/mm⁻¹	0.372	0.387
F(000)	568	2272
Crystal size/mm	0.35×0.25×0.10	0.35×0.25×0.15
Limiting indices	-11<=h<=12, -9<=k<=10, -23<=l<=23	-24<=h<=24, -20<=k<=19, -23<=l<=22
Reflections collected / unique	5134 / 1528 [*R*(int) = 0.0326]	18174 / 5867 [R(int) = 0.0588]
GOF	1.019	1.222
R_1, wR_2 [*I*>2σ(I)]	0.0397/0.1033	0.1021/0.2841
R_1, wR_2 (all data)	0.0589/0.1192	0.1148/0.3114
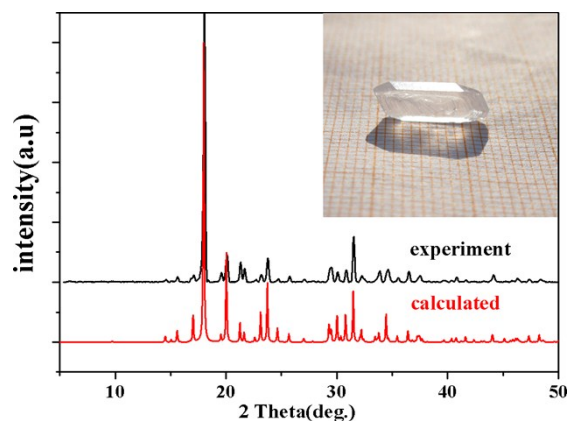
Figure S1. The well-matched experimental and calculated PXRD patterns at room temperature confirm the purity of **1**; The inset is the grown crystal of **1** with size of 12.5×5.8×3.6 mm^3.
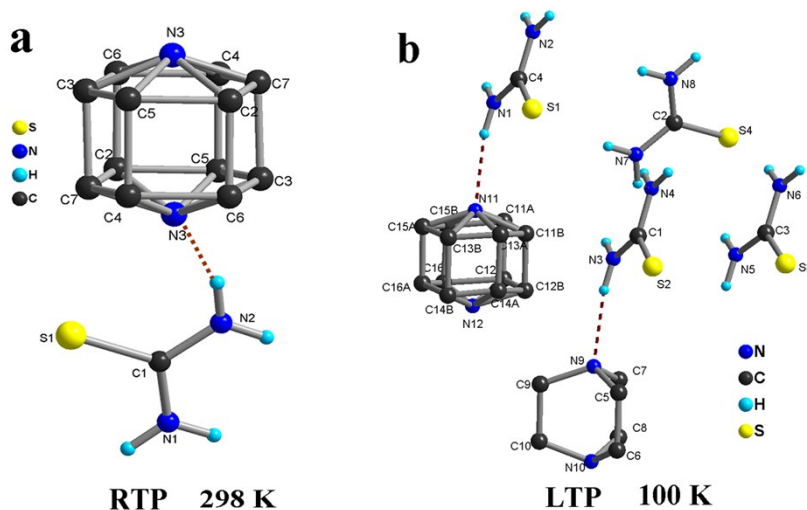

Figure S2. Asymmetric unit of **1** in RTP (a) and LTP (b), of which dabco molecule locates in the disordering and ordering respectively. N-H•••N hydrogen bonds connect the dabco and thiourea together.
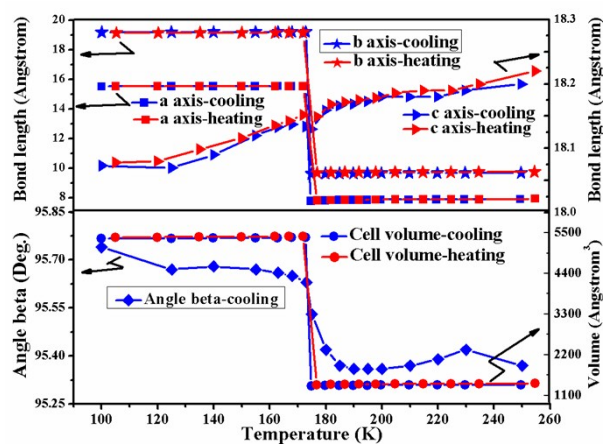

Figure S3. Temperature dependences of the unit cell parameters of **1** with a mode of heating and cooling.
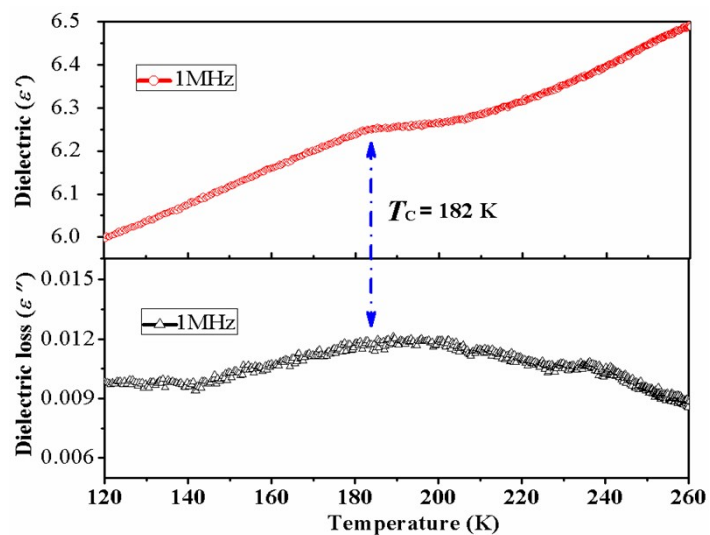
Figure S4. Temperature dependency of the real part ε' (up) and the imaginary part ε'' (down) of the dielectric permittivity of **1** with crystal.
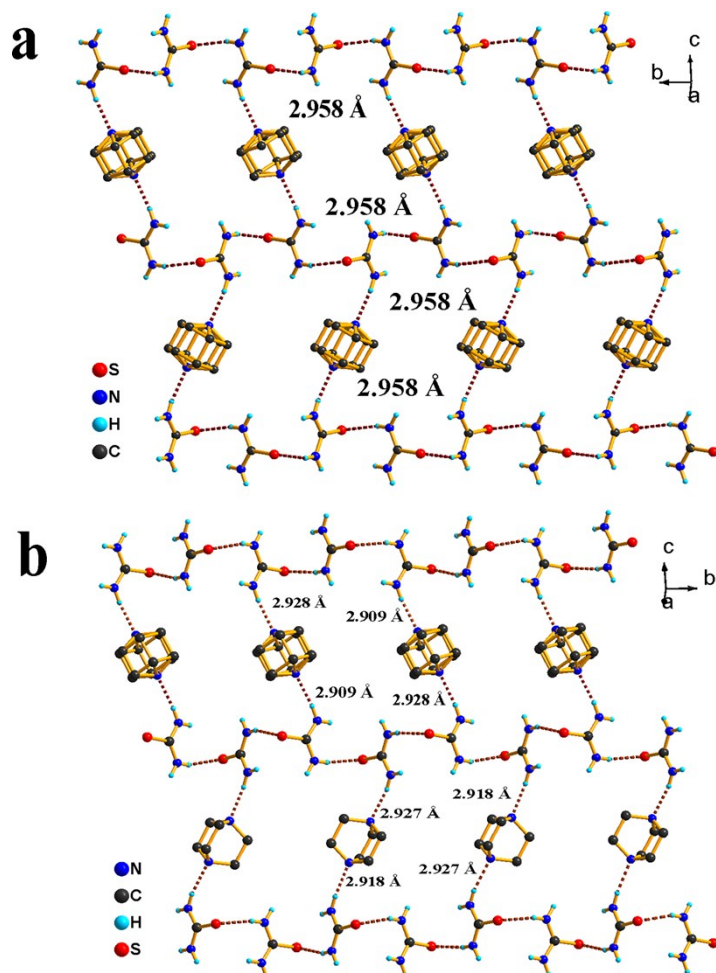

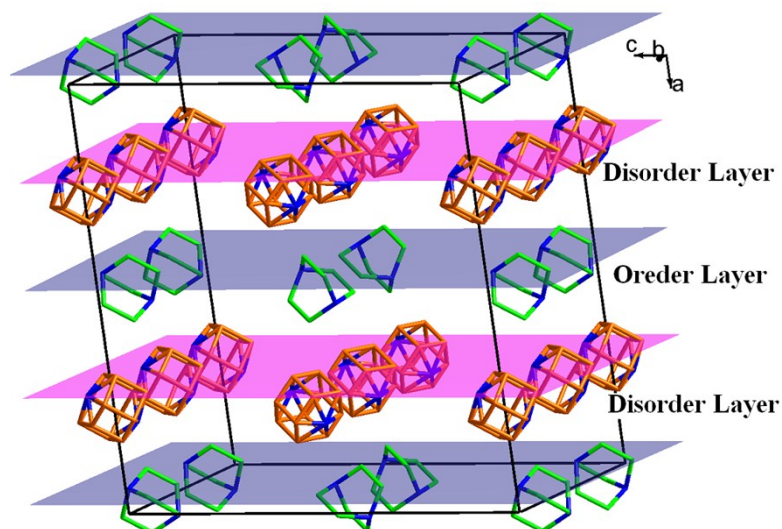Figure S5. N-H•••N hydrogen bond configuration of **1** in RTP and LTP.

Figure S6. The crystalline array of **1** was constructed by alternately arranging the disordered and ordered motors in "operative state" and "dormant state" respectively
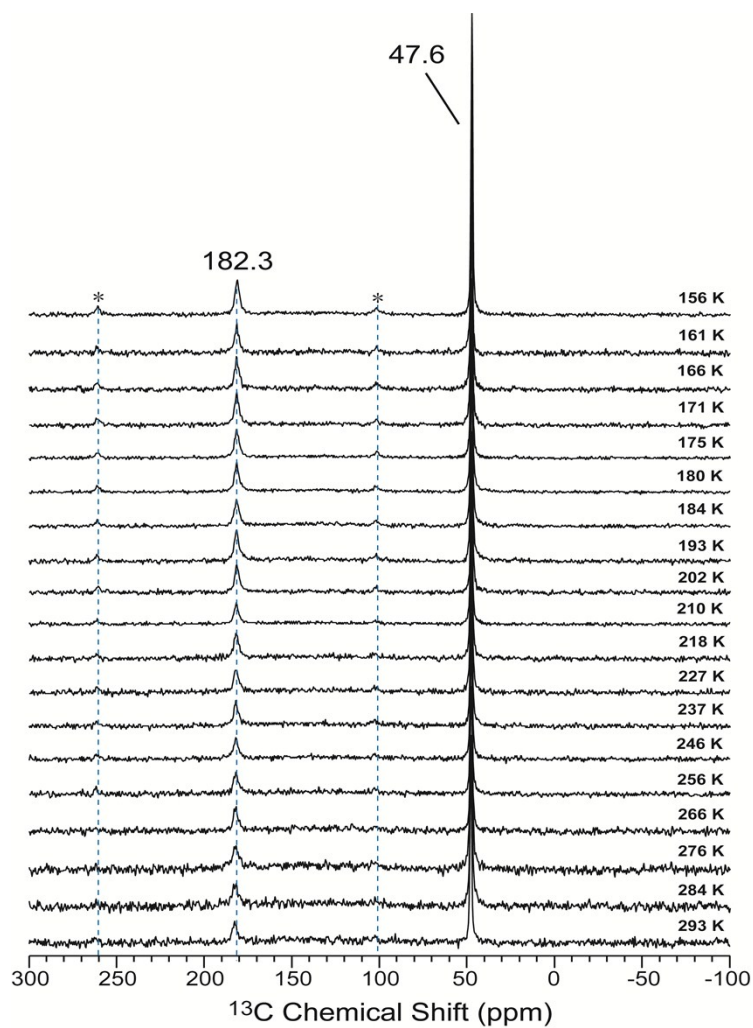

Figure S7. The ^{13}C CP/MAS NMR spectra of **1** at different temperatures. The signals at 47.6 ppm can be assigned to the carbon sites in dabco part of sample **1**. While the resonances at 182.3 ppm is unambiguously ascribed to C=S group. It can be

demonstrated that the main peaks from both the CH_2 sites of dabco and C=S group remain unchanged nearly in the temperature range of 293-156 K. It is noteworthy that the intensity of spinning sidebands from C=S and the CH_2 signal increases as the decrease of temperature from 293 to 227 K, and keeps almost unchanged upon further decrease the temperature. It can be revealed that the molecule of **1** become relatively rigid as the decrease of temperature from 293 to 227 K.
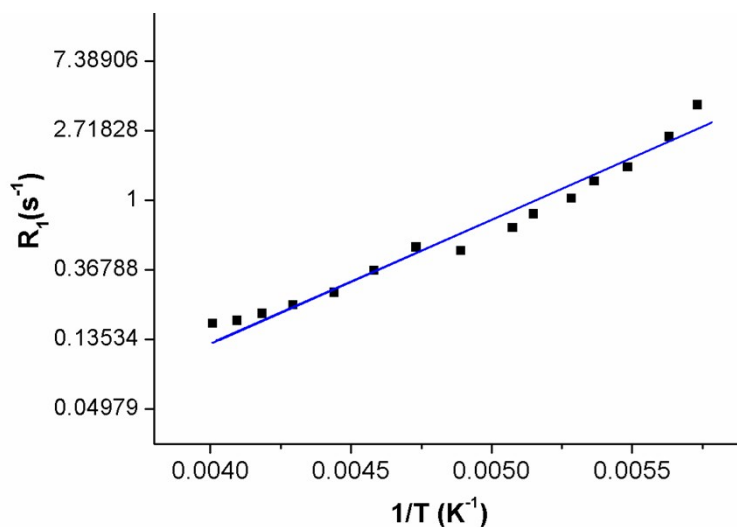

Figure S8. Temperature dependence of the ^{13}C spin-lattice relaxation rates (R_1) of dabco carbons in **1**.

References

[1] *APEX2, SADABS* and *SAINT.* Bruker AXS Inc.: Madison, Wisconsin, USA.. 2008.

[2] Sheldrick, G. M. SHELXL *97, Program for Crystal Structure Solution;* University of GÖttingen: GÖttingen, Germany, 1997.

[3] Hong, M.; Cross, J. D.; Rienstra, C. M.; Griffin, R. G.; Kumashiro, K. K.; Schmidt-Rohr, K. *J. Magn. Reson.* **1997**, *129*, 85.

[4] Torchia, D. A. *J. Magn. Reson.* **1978**, *30*, 613.