Supporting Information

The distinguishing of *cis-trans* isomer enabled *via* dielectric/ferroelectric signal feedback in supramolecular Cu(1,10-phenanthroline)$_2$SeO$_4$•(diol) system

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X-ray, DSC and dielectric measurements. Variable-temperature X-ray single-crystal diffraction data were collected on a Rigaku Saturn 724$^+$ diffractometer with *Mo–Kα* radiation (λ = 0.71073 Å) for **1** and **2**. Data processing including empirical absorption corrections was performed using the Crystalclear software package (Rigaku, 2018). The structures were solved by direct methods and refined by the full-matrix method based on F^2 by means of the SHELXLTL software package. Non-H atoms were refined anisotropically using all reflections with $I > 2\sigma$ (I). All H atoms were generated geometrically and refined using a "riding" model with $U_{iso} = 1.2U_{eq}$ (C and N). The asymmetric units and the packing views were drawn with DIAMOND (Brandenburg and Putz, 2005). Angles and distances between some atoms were calculated using DIAMOND, and other calculations were carried out using SHELXLTL. DSC was performed by heating and cooling the polycrystalline samples on a Perkin–Elmer Diamond DSC instrument in the temperature range 300–370 K with a heating rate of 10 K/min under nitrogen atmospheric pressure in aluminum crucibles. For dielectric measurements, the samples were made with single-crystals cut into thin plate perpendicular to the crystal *c*-axis. Silver conduction paste deposited on the plate surfaces was used as the electrodes. Complex dielectric permittivity was measured with a TH2828A impedance analyzer over the frequency range from 1 kHz to 1 MHz with an applied electric field of 0.5 V.

Ferroelectric and PFM measurements. For ferroelectric and pyroelectric measurements, the single-crystal sample is the same as the dielectric one. The hysteresis loops were recorded on a Radiant Precision Premier II using a Sawyer-Tower electric circuit at a measurement frequency of 20 Hz. For PFM measurements, PFM visualization of the ferroelectric domain structures was carried out using a commercial atomic force microscope system (MFP-3D, Asylum Research) on crystal sample along the *a*-axis. Conductive Pt/Ir-coated silicon probes (EFM, Nanoworld) were used for domain imaging and polarization switching studies. Resonant-enhanced PFM mode was used to enhance the signal, with a typical AC voltage frequency of about 360 kHz and AC amplitude of 5.0 V.

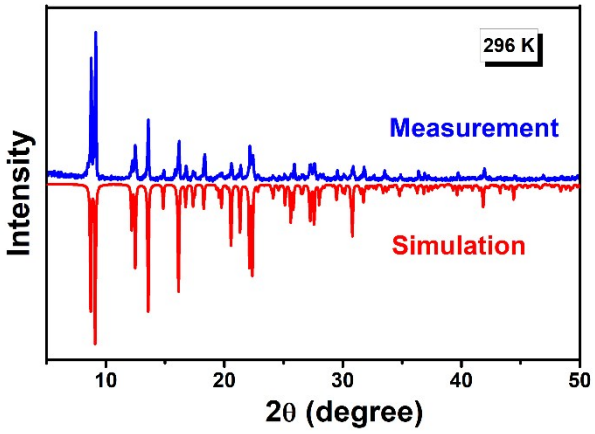

Fig. S1 Pattern of powder X-ray diffraction of **1** at 296 K.

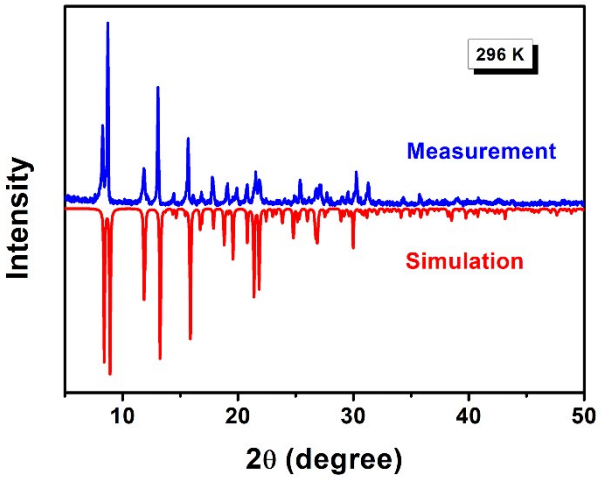

Fig. S2 Pattern of powder X-ray diffraction of **2** at 296 K.

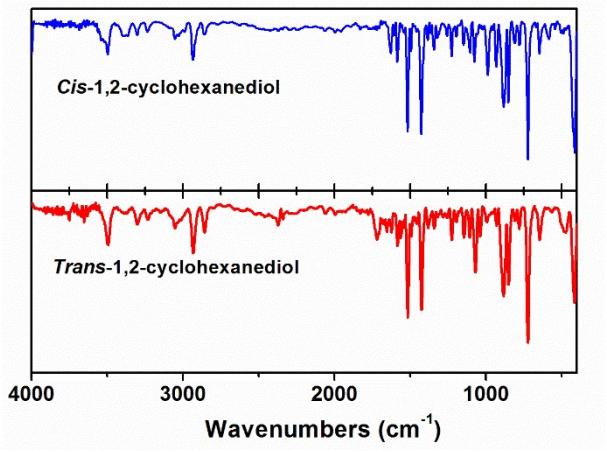

Fig. S3 IR spectra of **1** and **2**.

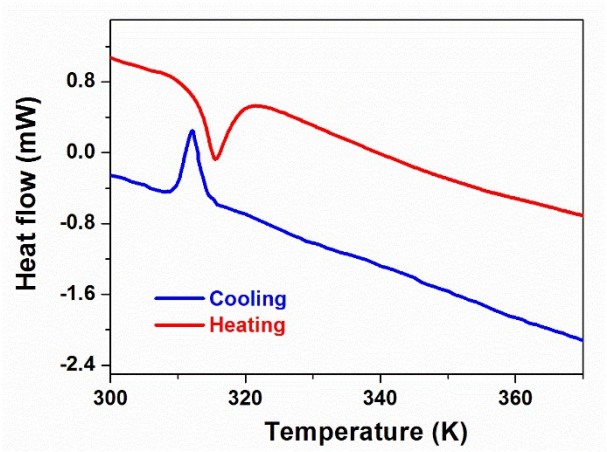

Fig. S4 DSC curve for **1**, showing an above-room-temperature phase transition.

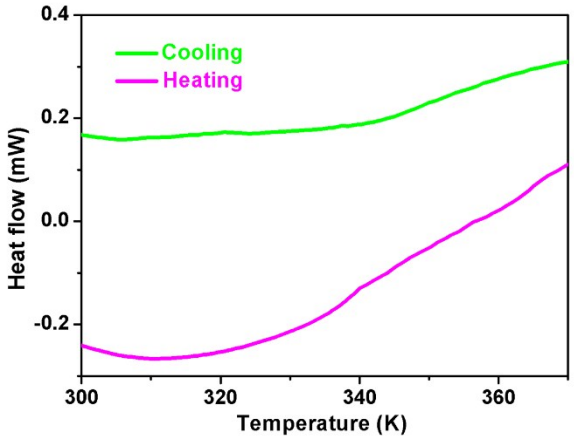

Fig. S5 DSC curves for **2**, showing no observed thermal anomaly.

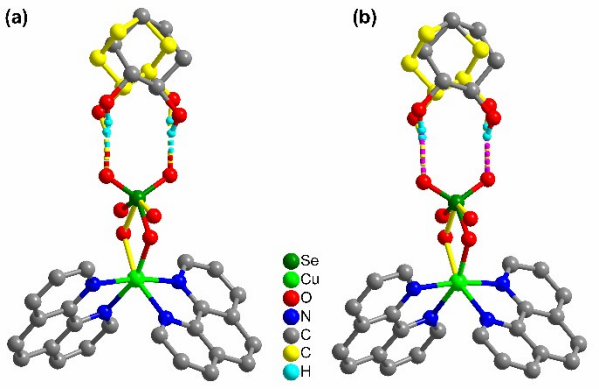

Fig. S6 Molecular structures of **2** in the RTP (a) and HTP (b), respectively. The pink and yellow dashes stand for the hydrogen-bonding interactions between host part of *bis*(1,10-phenanthroline-k^2N,N')(selenato-O)copper(II) and guest *trans*-1,2-cyclohexanediol molecule.

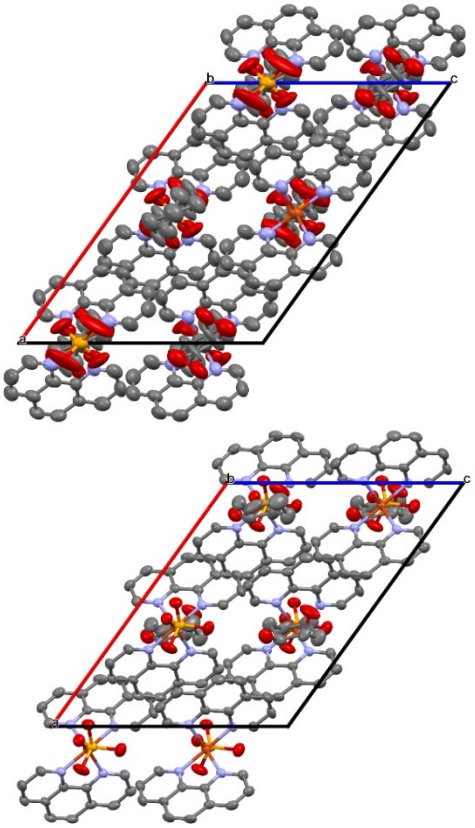

Fig. S7 Comparison of the crystal structures of **1** (lower) and **2** (upper) in RTP, showing the similarities of the packing. H atoms were omitted for clarity.

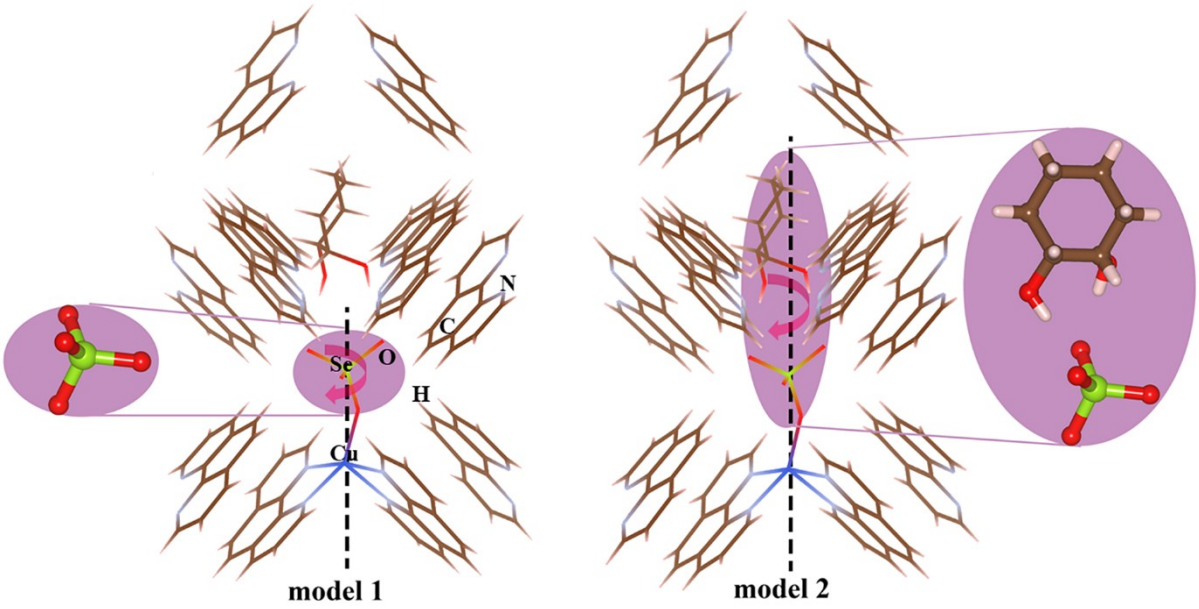

Fig. S8 Proposed two rotation types. Mode 1, including the rotation of the SeO_4^{2-} anions. Mode 2, including the rotation of the SeO_4^{2-}–diol as a rigid part. The rotational groups were drawn in the 'ball-and-stick' model and covered with shadow. The black dashed lines represent the (pseudo) C_2 rotation axis.

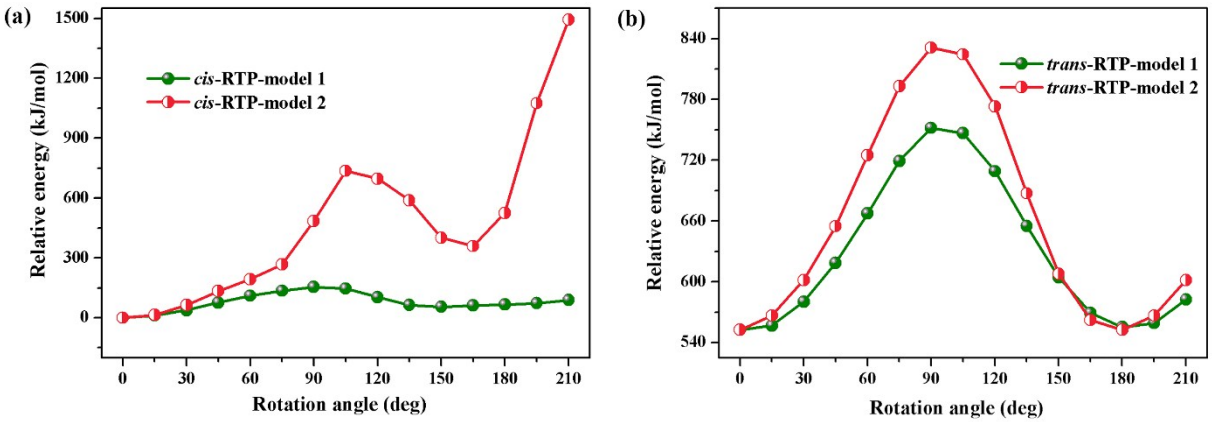

Fig. S9 Energy barrier of molecular rotation in **1**(*cis*) and **2**(*trans*). The relative energies are calculated with the rotation angles from 0˚ to 210˚ for the rotation mode **1** and mode **2** in RTP.

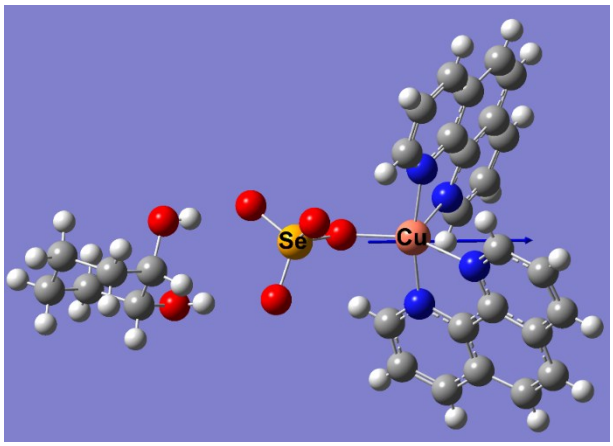

Fig. S10 Calculated dipole moments of the molecule by Gaussian software package. The dipole moment of **1** in RTP is shown as blue arrows pointing from Se to Cu.

Table S1 Crystal data and structure refinements for **1** and **2**.

Compound	**1**	**1**	**2**	**2**
Formula weight	683.07	683.07	683.07	683.07
Temperature	293 K	348 K	296 K	353 K
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*Cc*	*C*2/*c*	*C*2/*c*	*C*2/*c*
a/Å	17.320(3)	17.70(3)	18.25(3)	18.008(17)
b/Å	14.524(3)	14.592(18)	14.81(3)	14.686(11)
c/Å	13.424(4)	13.53(2)	13.65(4)	13.433(12)
α/deg	90	90	90	90
β/deg	125.116(8)	125.01(2)	125.12(3)	125.206(15)
γ/deg	90	90	90	90
Volume/Å^3	2762.3(11)	2862(7)	3018(12)	2903(4)
Z	4	4	4	4
Density/g cm^{-3}	1.643	1.585	1.503	1.563
R_1 [$I>2\sigma(I)$]	0.0456	0.1135	0.1344	0.0757
wR_2 [$I>2\sigma(I)$]	0.1005	0.2667	0.3397	0.1632
GOF	1.042	1.037	1.018	1.045