Supporting Information

Humidity-triggered single-crystal-to-single-crystal structural transformations in a Zn(II) coordination polymer displaying unusual activation energy change in proton conductivity

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Preparation. All chemicals and solvents used in the synthesis were of reagent grade and were used as received. All manipulations were performed under aerobic conditions.

[Zn(H_2SSA)$_2$(H_2O)$_2$]·7.1H_2O (1·7.1H_2O)**:** Complex **1** was prepared by solvothermal reactions. The solid mixture of $ZnCl_2$ (0.042 g, 0.31 mmol) and 5-sulfosalicylic acid hydrate (0.066 g, 0.303 mmol) was dissolved in 0.70 mL of THF. The reaction solution was transferred to a disposal pipet and sealed with the flame. After 24 h in 100 ^{o}C, colorless crystals were obtained with a yield of 88%. Anal. Calcd. for $C_{14}H_{28.2}O_{21.1}S_2Zn$: C, 25.34; H, 4.28; S, 9.66. Found: C, 25.36; H, 3.97; S 10.04.

{[Zn(H_2O)$_6$]·2H_2SSA·2H_2O}0.4H_2O (2·0.4H_2O)**:** Complex **2** was obtained from complex **1** under a specific temperature and humidity conditions. After the crystals of **1** were stored under 30 ^{o}C and 70% RH condition for 24 h, colorless crystals of **2** were formed through a structural change. Anal. Calcd. for $C_{14}H_{26.8}O_{20.4}S_2Zn$: C, 25.83; H, 4.15; S, 9.85. Found: C, 25.46; H, 4.03; S, 10.24.

[Zn(H_2O)$_6$]·2H_2SSA·4H_2O (**3**): After the crystals of **2** were stored under 40 ^{o}C and 80% RH condition for 48 h, colorless crystals of **3** were formed through a structural change. Anal. Calcd. for $C_{14}H_{30}O_{22}S_2Zn$: C, 24.73; H, 4.45; S, 9.43. Found: C, 24.57; H, 4.02; S, 9.38.

Physical Measurements. Powder X-ray diffraction were recorded using Cu Kα (λ =1.5406 Å) on a Rigaku Uitima III diffractometer with a scan speed of 2°/min and a step size of 0.01°. Water adsorption experiment was performed by volumetric method using a Micrometrics ASAP2020 instrument at 298K. Elemental analysis for C, H, and S was performed at the Elemental Analysis Service Center of Sogang University.

Impedance analyses. AC impedance data were obtained using a pellet (0.5 cm in diameter) pressed at 1000 kg for a couple of minutes. The thickness of the pellet was ranging from 0.04 to 0.07 cm. Measurements were carried out using Solatron SI 1260 Impedance/Gain-Phase Analyzer and 1287 Dielectric Interface with Pt pressed electrodes and applied AC voltage amplitude of 100 mV and frequency range of 10^6 – 0.1 Hz. For sample measurements, the pellet was placed in a homemade sample holder composed of Pt-based electrodes, which was located in an ESPEC SH-222/Benchtop temperature- and humidity-controlled chamber.

$$\sigma = \frac{L(cm)}{A(\pi r^2) * R(\Omega)}$$

Crystallographic Structure Determination. X-ray data for **1** and **3** were collected on a Bruker SMART APEXII diffractometer equipped with graphite-monochromated Mo Kα radiation (λ =0.71073 Å). Preliminary orientation matrix and cell parameters were determined from three sets of ω scans at different starting angles. Data frames were obtained at scan intervals of 0.5° with an exposure time of 10 s per frame. The reflection data were corrected for Lorentz and polarization factors. Absorption corrections were carried out using SADABS. The structures of **1** and **3** were solved by direct methods and refined by full-matrix least-squares analysis using anisotropic thermal parameters for non-hydrogen atoms with the SHELXTL program. All hydrogen atoms were calculated at idealized positions and refined with the riding models. X-ray data of **2** was collected using synchrotron radiation (λ = 0.7000 Å) and a 2D-SMC ADSC Quantum-210 detector with a Pt-coated Si double crystal under a cooling stream of N_2 at the Pohang Accelerator Laboratory. The ADSC Quantum-210 ADX program was used for data collection and HKL3000 was used for cell refinement, data reduction, and absorption corrections. The structure was solved by direct methods and refined by the full-matrix least-squares method using anisotropic thermal parameters for non-hydrogen atoms with the SHELXTL program. Crystal data for **1**: empirical formula = $C_{14}H_{14}O_{16}S_2Zn$, M_r = 567.74, T = 296(2) K, monoclinic, space group C2/*c*, a = 29.1076(10) Å, b = 5.2452(2) Å, c = 20.7121(8) Å, β = 133.431(4)°, V = 2296.41(18) Å^3, Z = 4, D_{calc} = 1.642 g cm^{-3}, μ = 1.326 mm^{-1}, 21520 reflections collected, 2850 unique (R_{int} = 0.0365), $R1$ = 0.0374, $wR2$ = 0.1322 [$I > 2\sigma(I)$]. Crystal data for **2**: empirical formula = $C_{14}H_{26}O_{20}S_2Zn$, M_r = 643.84, T = 100(2) K, triclinic, space group P-1, a = 6.5970(13) Å, b = 7.4350(15) Å, c = 13.278(3) Å, α = 74.22(3)°, β = 88.27(3)°, γ = 77.73(3)°, V = 612.2(2) Å^3, Z = 1, D_{calc} = 1.746 g cm^{-3}, μ = 1.266 mm^{-1}, 7149 reflections collected, 3646 unique (R_{int} = 0.0428), $R1$ = 0.0499, $wR2$ = 0.1519 [$I > 2\sigma(I)$]. Crystal data for **3**: empirical formula = $C_{14}H_{30}O_{22}S_2Zn$, M_r = 679.87, T =

100(2) K, triclinic, space group P-1, a = 6.520(6) Å, b = 7.123(6) Å, c = 14.542(13) Å, α = 92.562(8)°, β = 96.661(8)°, γ = 102.857(8)°, V = 652.2(10) Å^3, Z = 1, D_{calc} = 1.731 g cm^{-3}, μ = 1.199 mm^{-1}, 14888 reflections collected, 3244 unique (R_{int} = 0.0491), $R1$ = 0.0437, $wR2$ = 0.1413 [$I > 2\sigma(I)$].

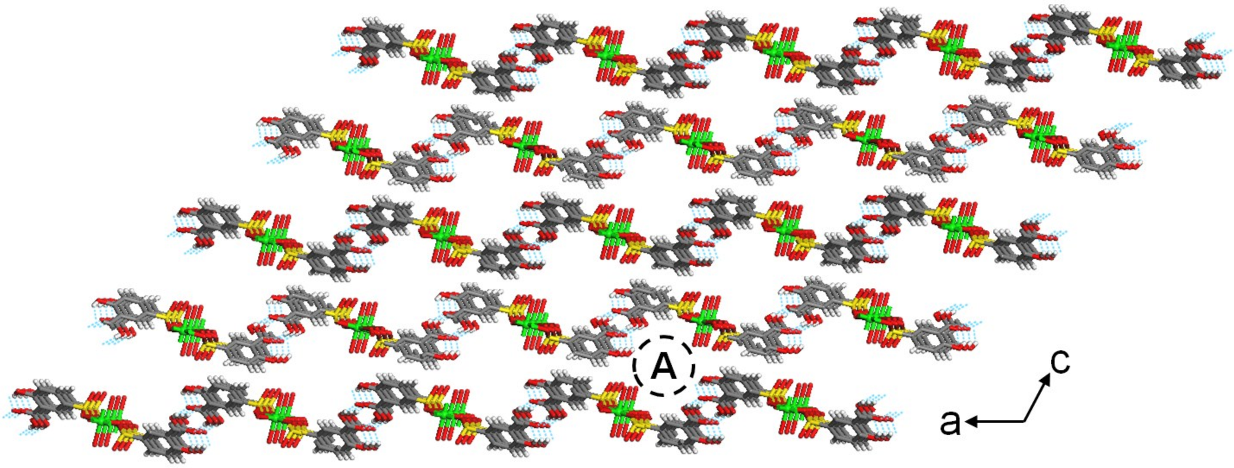


Fig. S1 Structure of **1** showing the packing diagram in the *ac* plane. **A** indicates the pore developed along the *b* axis.

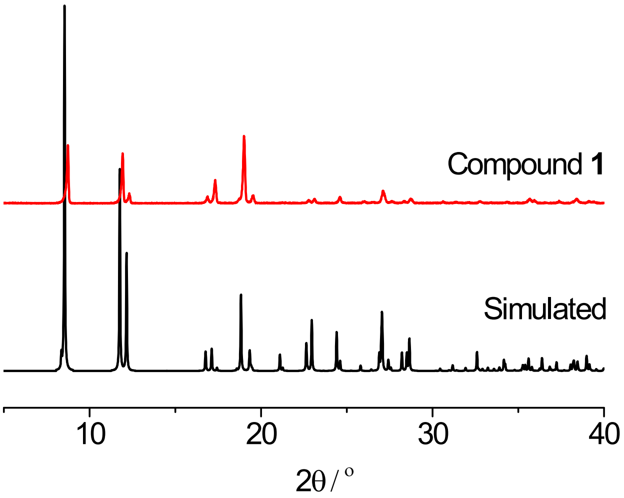


Fig. S2 PXRD profile of **1** and the simulated pattern derived from single crystal structure.

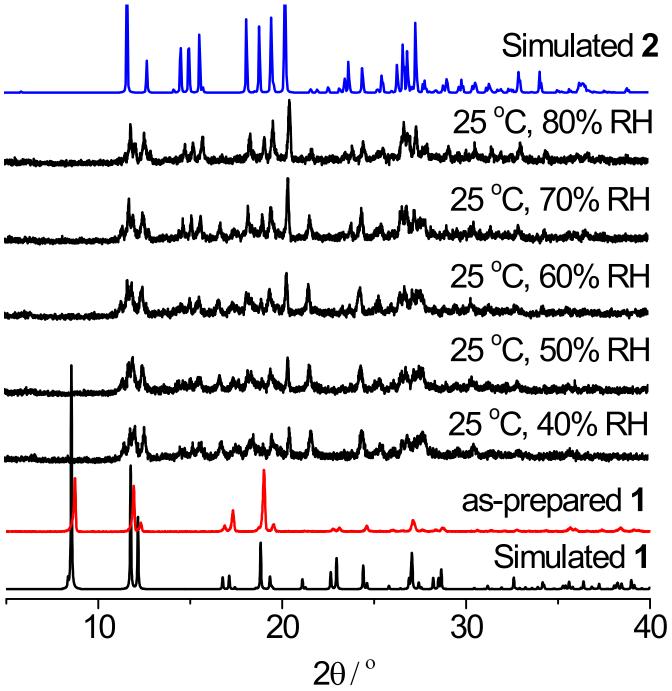


Fig. S3 PXRD data of **1** upon exposure to different humidity at 25 °C.

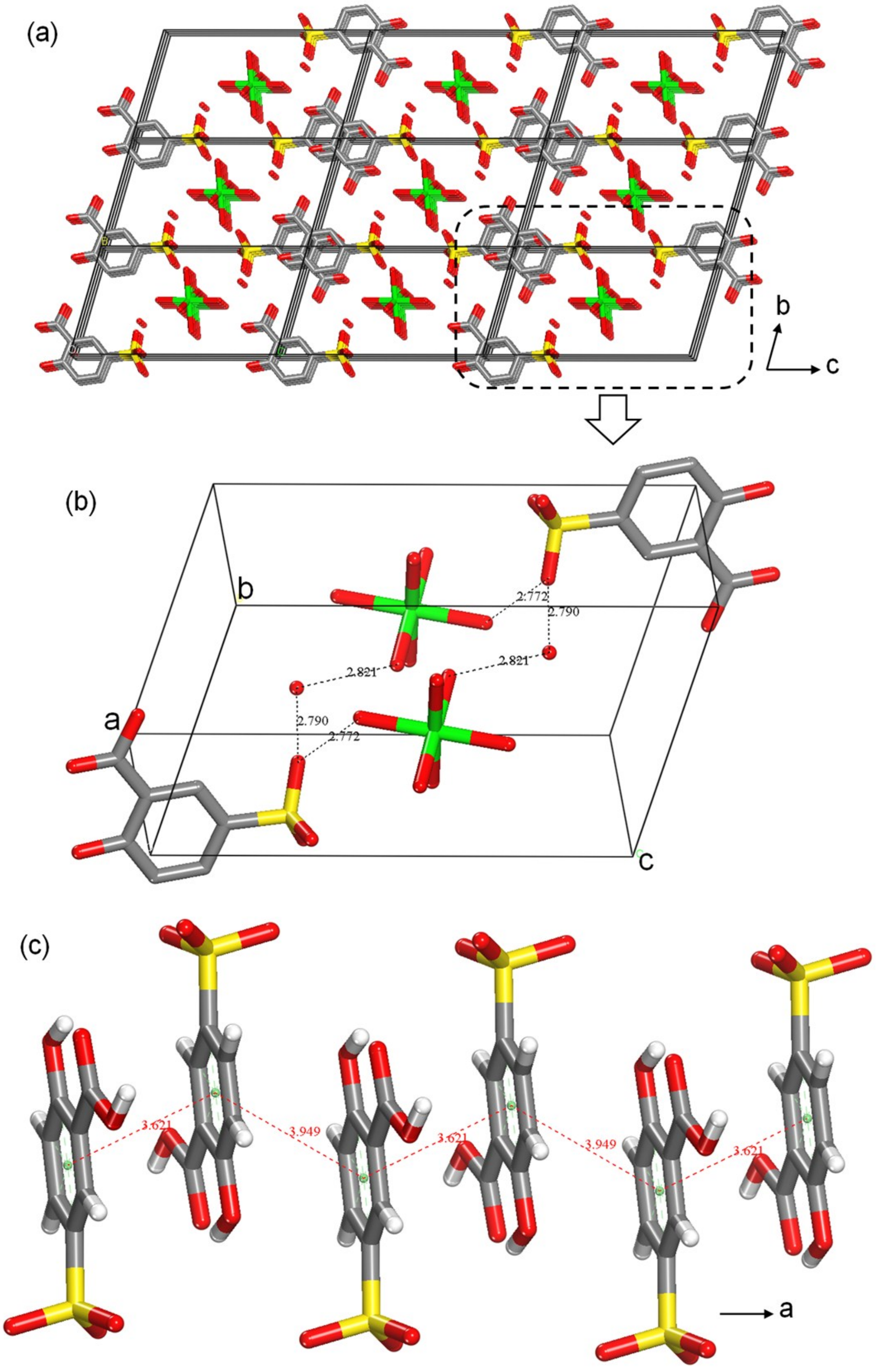


Fig. S4 (a) Extended structure of **2** showing the packing diagram in the *bc* plane. (b) Structure of **2** in the unit cell. The dotted lines represent hydrogen bonding interactions. (c) π-π stacking forces between benzene rings (centroid distances are 3.621 and 3.949 Å).

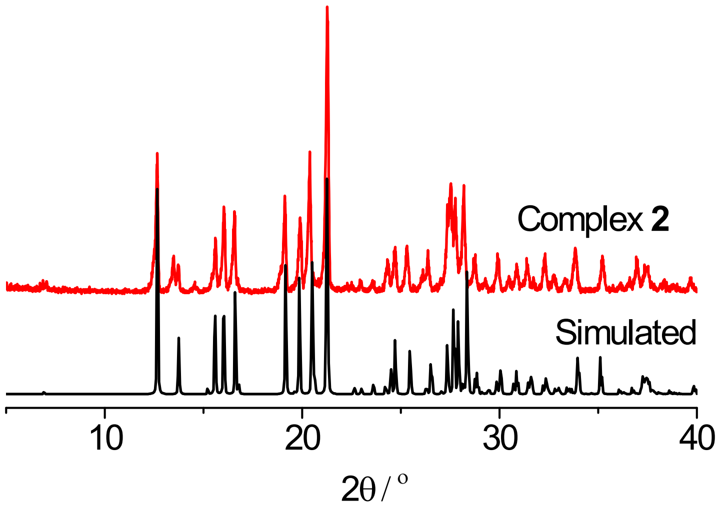
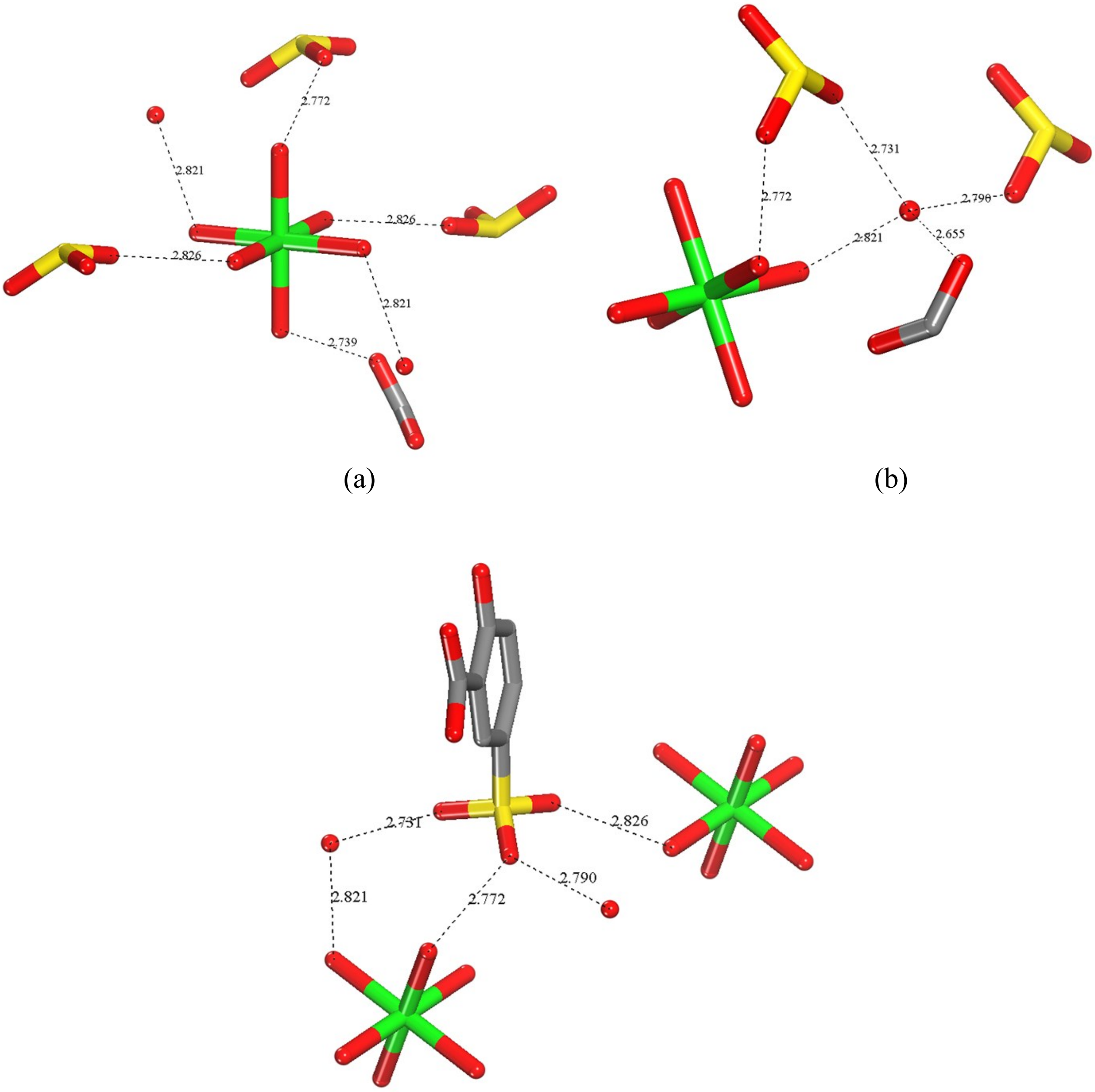


Fig. S5 PXRD profile of **2** and the simulated pattern derived from single crystal structure.



(a)

(b)

(c)

Fig. S6 Hydrogen bonding interactions around (a) $[Zn(H_2O)_6]^{2+}$, (b) H_2O, and (c) H_2SSA^- in **2**. The dotted lines denote hydrogen bonds.

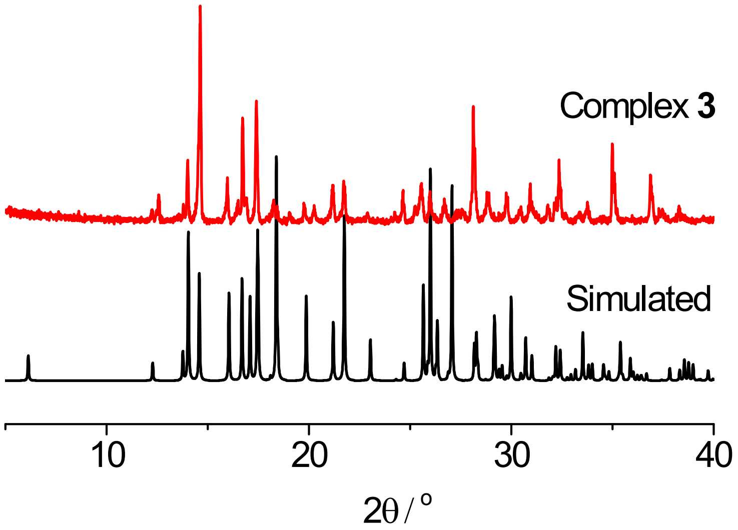


Fig. S7 PXRD profile of **3** and the simulated pattern derived from single crystal structure.

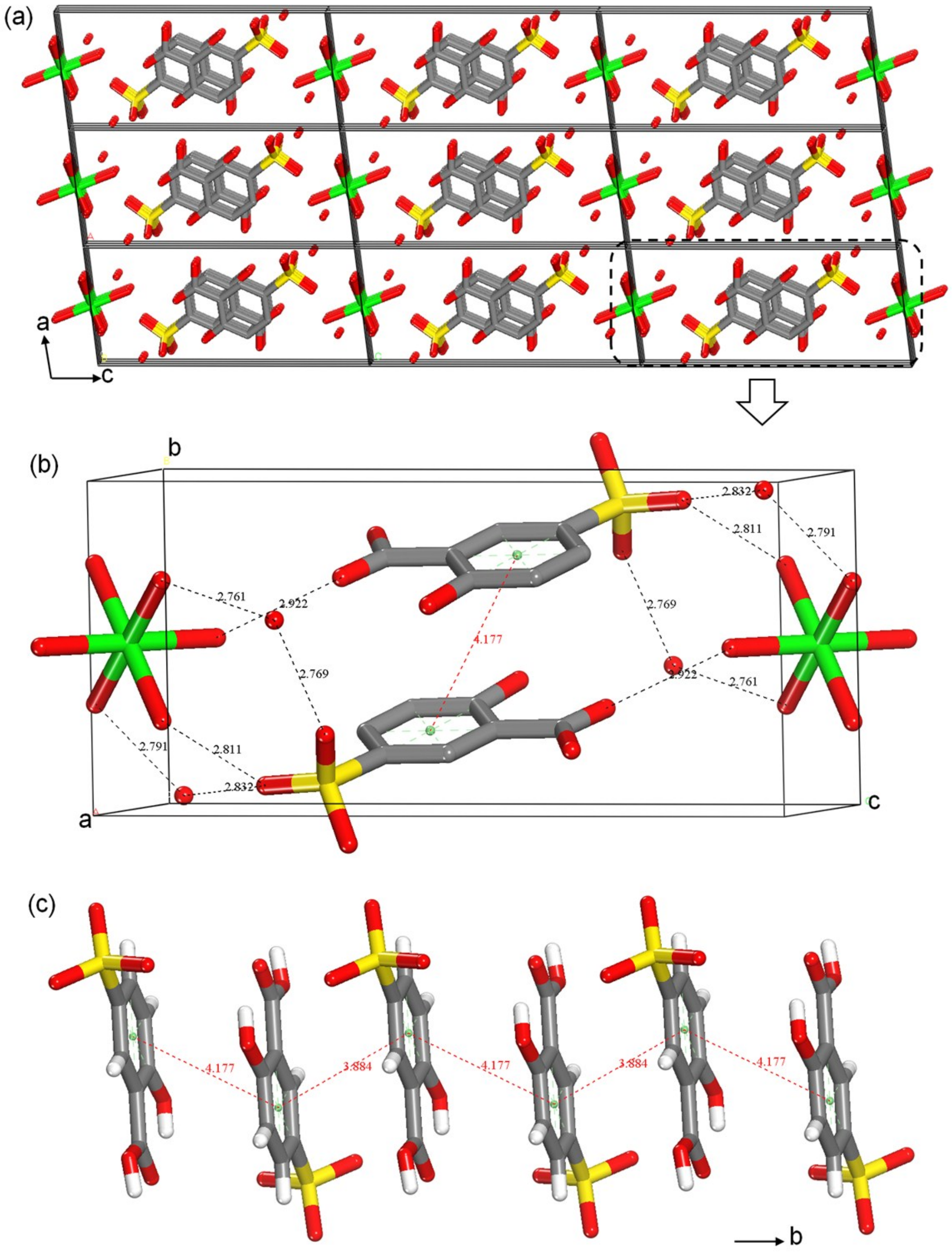
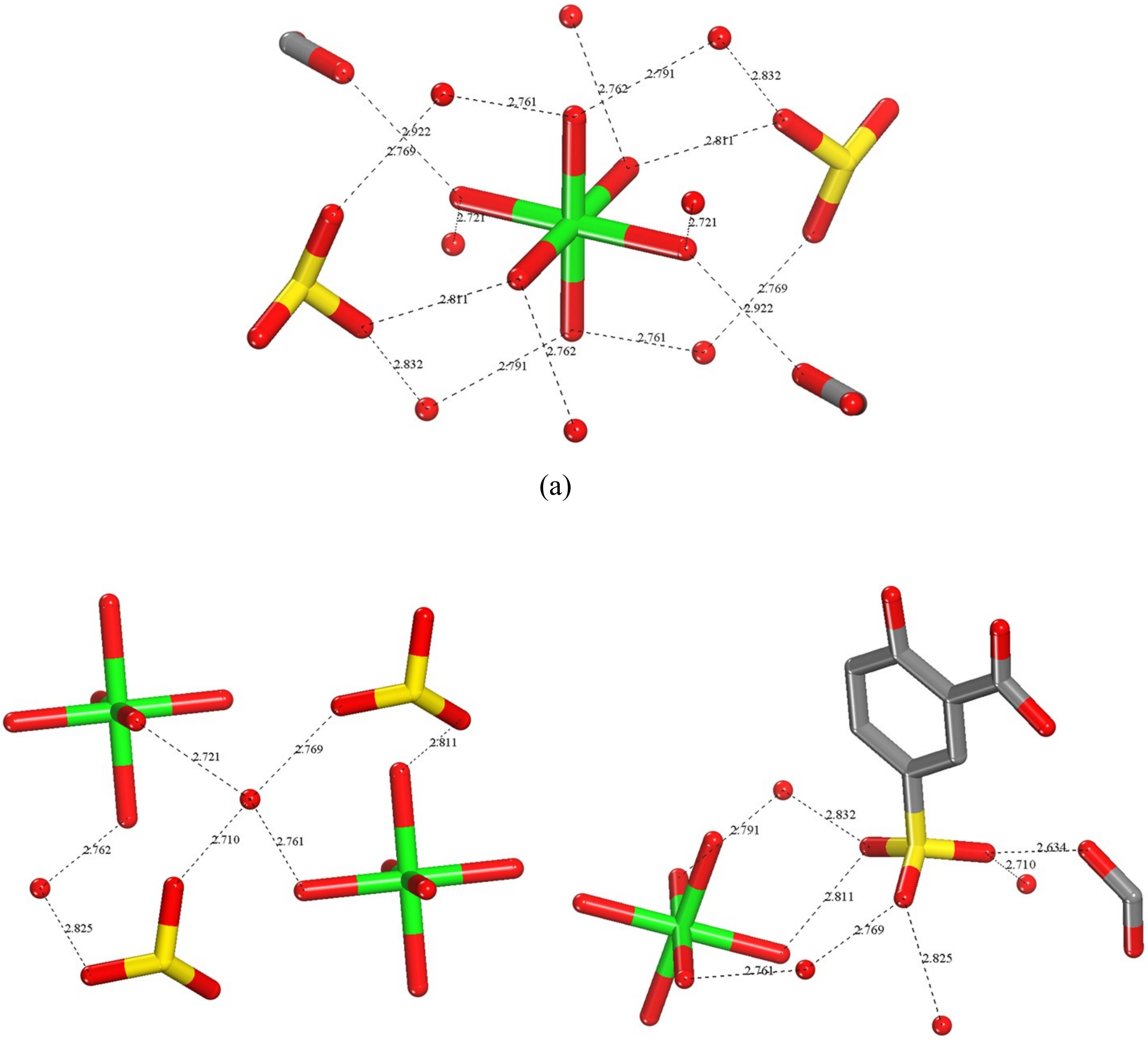


Fig. S8 (a) Extended structure of **3** showing the packing diagram in the *ac* plane. (b) Structure of **3** in the unit cell. The black dotted lines denote hydrogen bonding interactions. The centroid distance between benzene rings in **3** is 4.177 Å. (c) Stacking structure of H_2SSA^- moieties along the *b* axis. The red dotted lines show π-π contacts. The centroid distances are 3.884 and 4.177 Å, which are greater than those in **2**.



(a)

(b)

(c)

Fig. S9 Hydrogen bonding interactions around (a) $[Zn(H_2O)_6]^{2+}$, (b) H_2O, and (c) H_2SSA^- in **3**. The dotted lines denote hydrogen bonds.

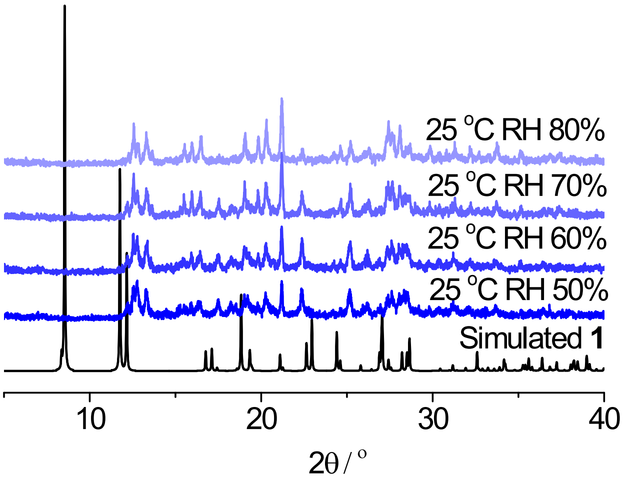


Fig. S10 PXRD profiles of **1** after exposure to the different relative humidity at 25 °C.

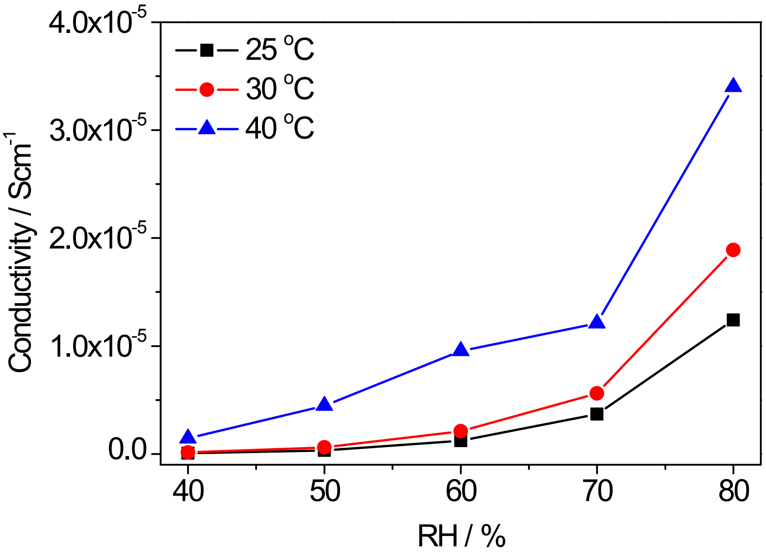


Fig. S11 Relative humidity (RH)-dependent conductivity of **1** at the indicated temperatures.