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together by hydrogen-bonding interactions, i.e., each unit cell contains 12 water molecules. The geometry of the 12 oxygen atoms in a unit cell can be described as a six-rung ladder with one rung at one end and two rungs at another end being rotated by approximately 90° with respect to the central axis of the nanochannel, while the oxygen ladder itself is along the axial direction of the nanochannel. Measurement of the temperature-dependent dielectric constant of the water wire reveals that the water wire exhibits large dielectric anomalies at approximately 175 and 277 K, respectively, significantly different from that of bulk water. More interestingly, the measurement of temperature- and frequency-dependent dielectric constants and temperature-dependent dielectric hysteresis of the 1D water wire indicates that the 1D wire undergoes a phase transition between 1D ferroelectric ice and 1D liquid at approximately 277 K. A single-phase ferroelectric ice is now produced within a nanochannel.

This 1D ice is spontaneously formed within a 3D supramolecular architecture of \(\text{[Cu}^{II}\text{Cu}^{I}\text{CDTA}]_{n}\) \(\cdot\) \(6\) \(\text{H}_2\text{O}\) \((\text{I})\) (Dataset S1) prepared by the reaction of \(\text{H}_2\text{CDTA}\) (0.364 g, 1.0 mmol), \(\text{Cu}^{II}\) (0.199 g, 1.0 mmol), \(4,4'\)-bpy (0.156 g, 1.0 mmol), and 10 mL water under the hydrothermal condition. Crystallographic analysis at 123 K indicates that the asymmetric unit of \((\text{I})\) contains half an independent divergent \(\text{Cu}^{II}\) ion, one monovalent \(\text{Cu}^{I}\) ion, half a CDTA\(^-\) ligand, one \(4,4'\)-bpy ligand, and three water molecules. Each \(\text{Cu}^{II}\) ion, located in the octahedral structure, is coordinated by two \(\text{N}\) atoms and four modenate carboxylate groups from one CDTA\(^-\) ligand to form a metalloligand [\(\text{Cu}^{II}\text{CDTA}\)]\(^2-\). Each \(\text{Cu}^{I}\) ion, located in the T-shaped structure, is coordinated by two \(\text{N}\) atoms, respectively, from two \(4,4'\)-bpy ligands and one monodentate carboxylate group from one metalloligand [\(\text{Cu}^{III}\text{CDTA}\)]\(^2-\) (Fig. 1A). The T-shaped coordination mode for the copper ion indicates existence of the \(\text{Cu}^{I}\) species, consistent with the observation of magnetic property of \((\text{I})\) (Fig. S1).

The two adjacent \(\text{Cu}^{II}\) ions, bridged by one \(4,4'\)-bpy ligand, in which its terminal \(\text{N}\) atom coordinates with one \(\text{Cu}^{II}\) ion, forms a 1D chain of \(\text{[Cu}^{II}\text{Cu}^{I}\text{CDTA}]_{n}\)\(^{2+}\). Connection of the adjacent 1D chains of \(\text{[Cu}^{II}\text{Cu}^{I}\text{CDTA}]_{n}\)\(^{2+}\) through the metalloligand of \(\text{[Cu}^{III}\text{CDTA}]_{n}\) with its two \(\text{O}\) atoms coordinating respectively with two \(\text{Cu}^{II}\) ions from two adjacent 1D chains leads to a 2D \(\delta\) network \(\text{[Cu}^{II}\text{Cu}^{III}\text{CDTA}]_{2}\)\(^{2+}\) (Fig. 1B) which further extends to a threefold interpenetration network as shown in Fig. 1C and D. The 3D supramolecular architecture of \((\text{I})\) can be viewed such that the 1D water wire \((\text{H}_2\text{O})_{12}\) acts as proton donor and is hydrogen bonded to the carboxylate of \(\text{[Cu}^{III}\text{CDTA}]_{n}\) from the adjacent threefold interpenetration networks, as illustrated in Fig. 1E.

In the 1D ice \((\text{H}_2\text{O})_{12}\), there exist three crystallographically independent water molecules, O1w, O2w, and O3w (Fig. 1F). Each O1w acts as both proton acceptor and donor to connect with the adjacent two O1w, forming a cyclic water tetramer whose plane is slightly twisted but normal to the central axis of the nanochannel. Four O2w (each hydrogen-bonded to one O2w and one O3w, respectively) and four O3w (each hydrogen-bonded to one O3w and one O2w) form a cyclic and boat-like water octamer. Each crystallographically independent water molecule has a fully occupied \(\text{H}\) atom \((\text{H}1\text{wa} \text{for} \text{O}1\text{w}, \text{H}2\text{wa} \text{for} \text{O}2\text{w}, \text{and} \text{H}3\text{wa} \text{for} \text{O}3\text{w}).\) The fully occupied \(\text{H}\) atoms for O1w and O2w are hydrogen-bonded, respectively, to O4 and O1 from carboxylate of [\(\text{Cu}^{III}\text{CDTA}\)]\(^2-\), whereas O3w is hydrogen-...
bonded to O1w. The remaining H atoms of the water molecules are disordered and treated as half-occupied. As a consequence, the 1D ice (H₂O)₇₉₆ can be viewed as a water tetramer acting as a proton acceptor and boat-like water octamer acting as a proton donor (Fig. 1F). The calculated density (29) for the 1 D ice is 1.038 g/cm³, significantly higher than that of 0.9167 g/cm³ for the bulk ice at 0 °C (7).

When the guest water was fully removed, the nanochannel (1) retained its structure (Fig. S2), allowing measurement of the dielectric constants for (1) and water-free (1) (E = 1.0 V, 10 kHz) from 45 to 298 K. As shown in Fig. 2, the real part of dielectric constant (ε') for (1) along the a axis exhibits a large temperature dependence. It is nearly constant (ε' ≈ 40) below 100 K but then rises to a broad peak with a maximum ε' ≈ 260 at around 170 K. As the temperature was further raised to 298 K, a sharp dielectric peak appeared with the maximum ε' ≈ 381 at around 277 K. Because the ε' for (1) along the b and c axes and for water-free (1) along the a axis (ε' ≈ 30) is almost temperature-independent over the entire range, we can conclude the temperature-dependent ε' for (1) along the a axis corresponds to the water wire. The ε' for the water wire is dramatically different from that of bulk water (ε'(H₂O) ≈ 90 at 273 K) and exhibits high anisotropy compared to bulk water (30).

To establish the basis for the temperature-dependent behavior of the water wire, the dielectric constants for (1) and its deuterated form [Cu₄Cu⁵(CDTA)(4,4'-bpy)]⁺ 60(D₂O) (1a) (Dataset S2) along the a axis were measured at various frequencies from 1 kHz to 10 MHz. As the frequency was raised throughout this range (Fig. 3A), the broad dielectric peak for (1) shifts to high temperature and its ε' decreases from 293 to 82. At first glance, the temperature- and frequency-dependent ε' for (1) exhibits the characteristic behavior of a relaxor ferroelectric (the typical strong dispersion effects often being ascribed to the freezing-in of ferroelectric clusters; refs. 31 and 32). The broad dielectric peak, however, does not represent a phase transition, but a dielectric relaxation phenomena, because the broad peak of ε' for (1) (especially that for (1a)) decreases rather than increases with the increase of frequency (33).

Consistent with this observation is that the temperature-dependent dielectric constant (ε') decreases rather than increases for (1) with the increase of frequency (33).

Given that (1) crystallizes with a the centrosymmetric space group Pdd2, what causes the ferroelectricity of the water wire? To address this question, the structure of water wire was analyzed in greater detail. Even though the positions of oxygen atoms in the crystal structure can be fully determined from the X-ray diffraction (XRD) experiment, the exact positions of hydrogen atoms cannot. As mentioned above, however, O1w and O2w each hydrogen-bond with O1 and O4 in the host nanochannel, thereby hindering the tendency for disordered hydrogen atoms. This hindrance limits the orientation of remaining hydrogen atoms of O1w and O2w, so they can only rotate along the axis of the O1⋯O1w and O4⋯O2w, respectively, to maximize hydrogen-bonding interactions in the water wire.

Ab initio molecular dynamics (AIMD) simulation (see Materials and Methods) was carried out to study the positions of the water molecules within the nanochannel. We selected one channel (containing 256 atoms, including 12 H₂O molecules) as the model system for the AIMD simulation. All the dangling bonds on the outer surface of the nanochannel were terminated by hydrogen atoms. All the heavy atoms (except hydrogen) on the wall were fixed to the XRD measured positions, and they were not relaxed during the geometry optimization and AIMD simulation. The initial orientations of hydrogen atoms were randomly assigned. During the 12.5-ps AIMD simulation (with temperature fixed at 300 K), we observed little movement in oxygen atom positions, with only small fluctuations in the dihedral angles around the hydrogen-bonding interactions (see Movie S1). The oxygen atom positions along the a axis were measured at various frequencies in the range of 1–10 MHz (Fig. 3B). Similar to that for (1), the broad dielectric peak of for (1a) also shifts to high temperature and its ε' decreases with increasing frequency, whereas the broad peak of ε' for (1a) decreases with the increase of frequency. However, the maximum ε' of (1a) for the sharp peak appears at approximately 285 K, which is approximately 8 K higher than that for (1), showing the “deuteration effect” that influences the phase transition temperature of the water wire.

To gain more insight into the positions of hydrogen atoms under an external electric field and to evaluate the magnitude...
of polarization under the external field, classical molecular dynamic simulation was employed (see Materials and Methods). In the molecular dynamics (MD) simulation, all the oxygen atoms were fixed at the positions determined by the measured crystal structure while the orientations of O-H bonds were allowed to relax. From a snapshot of 1D ice under the external electric field in the \( a \) direction, one can see that one hydrogen atom of the O1w forms a hydrogen bond either with symmetry-related O1w (Fig. 5B) or the symmetry-related O3w (Fig. 5C). Likewise, one hydrogen atom of O2w forms a hydrogen bond either with O3w (Fig. 5B) or symmetry-related O2w (Fig. 5C). For the O3w, one hydrogen atom either forms a hydrogen bond with O2w or symmetry-related O3w. Note that the snapshots in Fig. 5B and C show states in which most O-H bonds point along the electric field, and that the snapshots in Fig. 5B and C have the opposite electric field directions. The average dipole moment per 12 water molecules in a channel along the \( a \) axis (\( \mu \)) is \(-25.1 \) and \(-25.0 \) D, respectively, in two opposite fields. Clearly, the hydrogen-bonding interactions among water molecules in the water wire and the host (1) is of critical importance to the inherent ferroelectricity of the 1D ice. The water-host hydrogen bonds do not break and reform while the remaining hydrogen atoms of the water molecules in the 1D ice rotate alternately under the opposite electric field. As a result, the polarity of the 1D ice can be reversed by reversing the external electric field, as shown in Fig. 5B and C. Consistent with this structural explanation is that the magnitude of \( \varepsilon' \) (about 1.576) with \( f = 1 \) kHz at 277 K was nearly 40 times larger than at 50 K (Fig. 4). The dielectric phase transition is due to molecular motion rather than fast electronic motion (34).

Water is the most abundant liquid on Earth and it plays a key role in many biological and chemical processes and material sciences (35). However, its role in many phenomena is not fully understood despite a myriad of studies (36–38). Here, based on the confinement within the 3D supramolecular architecture of \([\text{Cu}^2\text{Cu}^2\text{CDTA}(4,4'-\text{bpy})_2]_n\), we have produced a 1D ice \((\text{H}_2\text{O})_{12}^\text{trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid monohydrate (H}_4\text{CDTA,}}\))

**Materials and Methods**

**Sample Preparation.** For \([\text{Cu}^2\text{Cu}^2\text{CDTA}(4,4'-\text{bpy})_2]_n\cdot 6\text{H}_2\text{O (1), trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid monohydrate (H}_4\text{CDTA,}}\)
Fig. 5. (A) A snapshot of water molecules (plotted in a ball and stick model) and vicinal atoms of nanochannel (plotted in a line model) at 10 ps from an AIMD simulation with temperature controlled at 300 K. Classical MD snapshots of the 1D ice in an external electric field whose direction is (B) along the -a axis and (C) along the a axis, respectively. In B and C, the red and green balls denote to O and H atoms, respectively, and the orange dashed lines denote hydrogen bonds.

0.364 g, 1.0 mmol), copper acetic (Cu(CH₃COO)₂), H₂O, 0.199 g, 1.0 mmol), 4,4’-bipyridine (4,4’-bpy, 0.156 g, 1.0 mmol), and 10 mL distilled water were mixed while stirring at room temperature. When the pH of the mixture was adjusted to about 3 with 1.0 mol·L⁻¹ nitric acid, the solution was put into a 25-ml Teflon-lined Parr, heated to 150 °C for 3 d, and then cooled to room temperature at a rate of 3 °C·h⁻¹. Red stick crystals of (1) were collected in a yield of 30% based on Cu. Analysis calculated for Cu₂H₂Cu₂N₂O₄ (1) is as follows: C, 42.83; H, 4.86; N, 8.81; found: C, 42.99; H, 4.61; N, 8.68. IR (KBr pellet, cm⁻¹): 3431 s (strong), 3044 w (weak), 2929 (moderate); 2858 w, 1602 s; 1531 w, 1483 m; 1408 s; 1255 w; 1216 m; 1103 w; 993 w; 916 w; 891 w; 819 m; 800 m; 727 w; 633 w; 570 w; 476 v. Crystal data for 1a are red crystal, 0.30 × 0.15 × 0.08 mm³, orthorhombic, space group Fddd with a = 11.8037(5) Å, b = 24.8742(12) Å, c = 51.423(3) Å, V = 15.0981(12) Å³, M = 953.93, ρcalcd = 1.678 g·cm⁻³, μ = 1.752 mm⁻¹, F₀₀₀ = 7856, T = 123(2) K, K = 250.00. R(int) = 0.0312. Of the 10,335 reflections collected, 3713 are independent reflections (R(int) = 0.0312) and 2745 are observed reflections (I > 2σ(I)). On the basis of all these data and 255 refined parameters, R₁ (observed) = 0.0509, wR₂ (observed) = 0.1331, R₁ (all data) = 0.0557, and wR₂ (all data) = 0.1126 were obtained, GOF = 1.042.

Crystal Structure Determination. Data were collected with one single crystal on Oxford Gemini S Ultra using Mo-Kα radiation (λ = 0.71073) and equipped with Oxford Instruments at 123 K for (1), 250 K for (1b), 260 K for (1c), 277 K for (1d), and 298 K for (1e) (Databases 51, 53, 55, 56). Data of (1a) was collected on a Bruker SMART Apex CCD diffractometer using graphite-monochromatized Mo-Kα radiation (λ = 0.71073) at 123 K (Dataset 2). Absorption corrections were applied using the multiscan program SADABS. The structures were solved by direct methods (SHELXTL, version 5.10), and the non-H-atoms were refined anisotropically by a full-matrix least-squares method on F². CCDC 800743–800748 contain the supplementary crystallographic data for this paper as well. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Physical Measurements. Temperature-dependent dielectric constants were measured using the two-probe ac impedance method for frequencies from 1 kHz to 10 MHz (Wayne Kerr 6500B). A single crystal was placed into a cryogenic refrigeration system (Oxford Cryoemux). The electrical contacts were prepared using gold paste (Tokuriki 8560) to attach 25-μm gold wires to the single crystal. The P–E curve was measured using Radiant Precision Premier II.

Ab Initio Molecular Dynamics Simulation. Ab initio (Born-Oppenheimer) molecular dynamics simulation was performed using the QUICKSTEP program implemented in the CP2K package (39, 40). The Becke-Lee-Yang-Parr (41, 42) exchange correlation functional was selected, and the empirical dispersion correction (43, 44) to the density-functional theory (DFT) calculation (i.e., DFT-D calculation) was used to model the intermolecular dispersion. The Goedecker-Teter-Hutter (GTH) (45) norm-conserved pseudopotentials were utilized to account for the contribution of the core electrons. We also used the GTH-double-zeta-polarization Gaussian basis set along with a plane-wave basis set (with an energy cutoff of 280 Ryd) for the expansion of electronic wavefunctions. The AIMD simulation was performed in a constant-volume and constant-temperature ensemble with the temperature controlled at 300 K. The simulation cell contains 256 atoms, including 12 water molecules. The total AIMD simulation time was 12.5 ps (Movie 51).
Classical Molecular Dynamics Simulation. The classical MD simulations were performed using the Discover program implemented in the Material Studio 4.4 package (46). The consistent-valence force field was used with the atomic charges derived from the charge equilibration (47) method for the supramolecular structure, and the SPC (48) model was used for water. The simulation cell contains 1,648 atoms, including 96 water molecules. The initial structure was equilibrated at 290 K for 1 ns. After the equilibration, two additional MD simulations were performed, one in the external electric field (5.14 V/\,\text{nm}) along the 1D water wire, and another in opposite direction.