

Proton-electron coupling and mixed conductivity in a hydrogen-bonded coordination polymer

Received: 24 June 2024

Accepted: 22 January 2025

Published online: 03 February 2025

Minju Park ¹, Huiyeong Ju ², Joohee Oh ^{3,4}, Kwangmin Park ¹,
Hyunseob Lim ^{3,4} , Seok Min Yoon ^{5,6}  & Intek Song ¹ 

The fundamental understanding of coupled proton-electron transport in mixed protonic-electronic conductors (MPECs) remains unexplored in materials science, despite its potential significance within the broader context of mixed ionic-electronic conductors (MIECs) and the possibility of controlled diffusion of protons using hydrogen-bond networks. To address these limitations, we present a hydrogen-bonded coordination polymer Ni-BAND ($\{[\text{Ni}(\text{bpy})(\text{H}_2\text{O})_2(\text{DMF})_2](\text{NO}_3)_2 \cdot 2\text{DMF}\}_n$), which demonstrates high mixed protonic-electronic conductivity at room temperature. Through detailed analysis, we unravel the coupled transport mechanism, offering insights for the rational design of high-performance MPECs. We demonstrate the practical implications of this mechanism by examining the humidity-dependent synaptic plasticity of Ni-BAND, showcasing how MPECs can expand into traditional MIEC applications while leveraging their unique proton-mediated advantages.

Mixed protonic-electronic conductors (MPECs) are materials capable of conducting both protons and electrons^{1–5}. This dual conductivity enables the exploration of interactions between proton and electron, specifically proton-electron coupling (PEC). On a microscopic scale, this is exemplified by proton-coupled electron transfer (PCET), where the movement of protons and electrons enhances their mutual transfer^{6,7}. This mechanism is critical for redox reactions involving hydrogen, such as water splitting, photosynthesis, and respiration. Consequently, MPECs have been extensively studied to facilitate PCET in various electrochemical processes like the hydrogen oxidation reaction (HOR) or the oxygen evolution reaction (OER)^{1,8}.

Beyond the microscopic scale, PEC is crucial in transport phenomena within MPECs. This importance is evident from the broader category of mixed ionic-electronic conductors (MIECs), where ionic-electronic coupling significantly impacts material properties. For

example, ion-electron interactions influence the contrast ratio in electrochromic devices, determine the number of states in neuromorphic devices, and affect the transconductance in electrochemical transistors⁹. Moreover, ion-electron interactions can induce doping effect, which significantly improves the materials' conductivity. The significance of PEC is further supported by the unique characteristics of protons compared to other ions, such as their responsivity to environmental moisture and the transport through the Grotthuss mechanism. The moisture responsivity means that protons can be directly derived from moisture, allowing for relative humidity as a parameter to control the transport characteristics^{10,11}. The Grotthuss mechanism, which leverages hydrogen bond (H-bond) network, enhances transport mobility and establishes a strong structure-property correlation¹⁰. This is in contrast to the diffusion of other ions, which often suffers from randomized movement, making it more

¹Department of Chemical and Biological Engineering, Andong National University (ANU), 1375 Gyeongdong-ro, Andong, Gyeongbuk 36729, Republic of Korea. ²Research Center for Materials Analysis, Korea Basic Science Institute, Daejeon 34133, Republic of Korea. ³Department of Chemistry, Gwangju Institute of Science and Technology (GIST), 123 Cheomdangwagi-ro, Buk-gu, Gwangju 61005, Republic of Korea. ⁴Center for Quantum Conversion Research (QCR), Institute of Basic Science (IBS), 123 Cheomdangwagi-ro, Buk-gu, Gwangju 61005, Republic of Korea. ⁵Department of Chemistry, Gyeongsang National University, 501 Jinjudae-ro, Jinju, Gyeongnam 52828, Republic of Korea. ⁶Research Institute of Advanced Chemistry, Gyeongsang National University, 501 Jinjudae-ro, Jinju, Gyeongnam 52828, Republic of Korea. ✉e-mail: hslim17@gist.ac.kr; smyoon@gnu.ac.kr; songintek@anu.ac.kr

difficult to predict and optimize their transport^{12,13}. Therefore, with PEC, MPECs can advance the conventional uses of MIECs by improving their performance and providing material designability.

Despite these promising attributes, the exploration and utilization of PEC in MPECs presents significant challenges. For example, traditional oxide-based MPECs operate at very high temperature, such as 300 to 600 °C, limiting their study and applications under ambient conditions^{14,15}. Composite MPECs often show high conductivity for both electrons and protons at room temperature, their complex structures make it difficult to understand the underlying conduction and coupling mechanisms^{16–20}. Radical salts show extremely high electrical conductivity, but their single crystal form factor hinders practical applications, and their in-vacuo proton conductivity is relatively lower than that of the electrons^{21,22}.

Recent studies on MPECs have increasingly focused on metal-organic frameworks (MOFs), as their orderly structures enable systematic investigations of conduction mechanisms^{2–4}. While they incorporate H-bond network and extended π conjugation to enhance protonic and electronic conduction respectively, achieving a balancing between them within a single MOF remains challenging. Their conductivity levels are typically low and uneven for protons and electrons. The balanced conductivity for protons and electrons is particularly important for the optimized performance and applications^{23,24}. More importantly, the specific effects of PEC on these properties remain unclear.

To address this challenge, we combine design strategies from π -conjugated polymers and hydrophilic moieties using coordination chemistry. The former is inspired by poly(2,3-dihydrothieno-1,4-dioxin)-poly(styrenesulfonate) (PEDOT:PSS), a highly conductive π -conjugated polymer, which utilizes its conjugated backbone to stabilize doped states resulting from ion-electron coupling²⁵. The latter enables the diffusion of water molecules, leading to high proton conductivity as in Nafion²⁶. Applying these approaches, we design a hydrogen-bonded coordination polymer to have nickel (Ni) coordinated with ligands: 4,4'-bipyridine (bpy), water (aqua; H₂O), nitrate (NO₃[−]), and dimethylformamide (DMF). The bpy ligands are capable of bridging, allowing for formation of coordination polymers and enhancement of electrical conductivity^{27,28}. With NO₃[−] and H₂O ligands, they construct a wide variety of coordination polymers with extensive H-bond networks for efficient proton conduction^{29–31}. DMF facilitates charge transfer in coordination complexes³². Moreover, when utilized as a solvent, DMF enables scalable material preparation. For instance, its low surface tension and slow evaporation rate facilitate the spin coating process for creating thin films³³. The transport properties of these thin films are superior to commonly used pellet forms due to fewer grain boundaries. Additionally, DMF's polarity aids in forming polymer gels^{28,34}. These gel forms provide structural flexibility and support complex diffusion phenomena, making them ideal for soft electronics and bio-realistic applications^{35,36}.

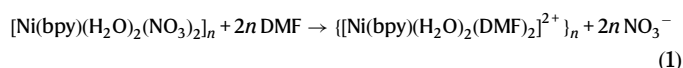
In this study, we investigate a hydrogen-bonded coordination polymer, termed Ni-BAND ([Ni(bpy)(H₂O)₂(DMF)₂](NO₃)₂·2DMF)_n, termed Ni-BAND, named after the center metal and the first letters of each ligand. Ni-BAND exhibits high electrical conductivity (0.24 S/cm, RH < 10%) and proton conductivity (0.09 S/cm, RH > 90%) at room temperature (Fig. 1). Experimental and theoretical analyses reveal that PEC has a critical role in transport properties through strong n-type doping and water adsorption. Notably, Ni-BAND exhibits a transition between electron- and proton-dominant transport regimes depending on humidity levels. In its gel form, Ni-BAND displays PEC-induced resistive switching behavior, suggesting potential applications as a neuromorphic gel that mimics synaptic behaviors and soft texture of biological tissues. Overall, this study emphasizes the critical role of PEC in MPECs by discussing transport dynamics, structure-property relationships, and neuromorphic applications.

Results

Synthesis, structural analysis, and characterization of Ni-BAND

The synthesis of Ni-BAND starts with the preparation of a precursor [Ni(bpy)(H₂O)₂(NO₃)₂]_n by reacting Ni(NO₃)₂·6H₂O with bpy in ethanol³⁷ (Fig. 2a). The precursor is then dispersed in DMF and left undisturbed in a sealed vial at room temperature, yielding blue, faceted crystals of Ni-BAND over a period of 72 h (Fig. 2b, c). For thin film preparation, the dispersion is directly spin-coated onto arbitrary substrates, including rigid substrates such as SiO₂/Si, quartz, and ITO glass as well as on flexible substrates like polyethylene terephthalate (PET) (Fig. 2d). The resulting film has a thickness of 300 nm, as confirmed by atomic force microscopy (Supplementary Fig. 1). Drop-drying with higher concentration yields a gel form instead (Fig. 2e). Such gelation from high concentration of precursors aligns with existing literature on MOF gelation³⁸.

Single-crystal X-ray diffraction (SCXRD) analyses revealed the crystal structures of Ni-BAND, showing a six-coordinate Ni(II) complex with two non-coordinated DMF and NO₃[−] molecules per unit cell (Fig. 3a, Supplementary Tables 1–4 and Supplementary Data 1). The coordination sphere includes two H₂O, two DMF, and two bridging bpy ligands in a trans configuration. This hints that the synthesis involves the net chemical reaction as follows²⁶:



The four rings of the bpy ligands in Ni-BAND exhibits near coplanarity with slight tilting, forming a one-dimensional bpy-Ni-bpy chain (Fig. 3b, c). Molecular orbital (MO) analysis reveals unique d- π conjugation along this backbone chain (Fig. 3d and Supplementary Fig. 2). The lowest unoccupied molecular orbital (LUMO), and its nearest unoccupied molecular orbitals (UMOs) exhibit delocalized states along bpy-Ni-bpy. In contrast, the highest occupied molecular orbital (HOMO) and its nearest occupied molecular orbitals (OMOs) display localized states (see Supplementary Note 1).

In addition, Ni-BAND features extensive H-bond networks (Fig. 3e). A unit cell of Ni-BAND features 14 unique H-bonds meeting Steiner's criteria for H-bonds in solids: bond distance less than 3 Å and angles greater than 110°³⁹ (Supplementary Table 5). Notably, strong H-bonds are found between the non-coordinated molecules (NO₃[−] and DMF) and the H₂O ligands; the distance between O5 from DMF and O6 from H₂O is 2.713 Å, and that between O2 from NO₃[−] and O6 from H₂O is 2.737 Å (Fig. 3c). H-bonds are also present among adjacent unit cells, including weak C-H...O types. Multiple H-bond pathways form between the coordinated water ligands, exhibiting a range of bond strengths (Supplementary Fig. 3).

The powder X-ray diffraction (PXRD) patterns correspond closely with the theoretical patterns derived from single crystals and exhibit stability under vacuum conditions (Supplementary Fig. 4). While most patterns match with each other, the diffraction pattern shows slight shifts toward lower diffraction angles in peaks near $2\theta = 25^\circ$, specifically those corresponding to the (12-1) and (20-2) crystallographic planes that run parallel to the bpy-Ni-bpy chains. These shifts can be attributed to non-uniform distortions caused by water molecule incorporation between the bpy-Ni-bpy chains⁴⁰. XRD studies on thin films further show that they exhibit preferred orientation. In regions of small-angle diffraction below 10°, where diffraction from the (001) and (010) planes is anticipated, in-plane diffraction obtained by grazing-incidence X-ray diffraction (GIXRD) exclusively reveals the (001) planes (Fig. 3f). Conversely, the out-of-plane diffraction pattern shows solely the (010) planes. The former plane intersects the bpy-Ni-bpy plane, whereas the latter lies along the bpy-Ni-bpy axis (Fig. 3g). This suggests that in thin films the bpy-Ni-bpy planes tend to lie on the substrate surface rather than orienting vertically (Fig. 3h). In the gel

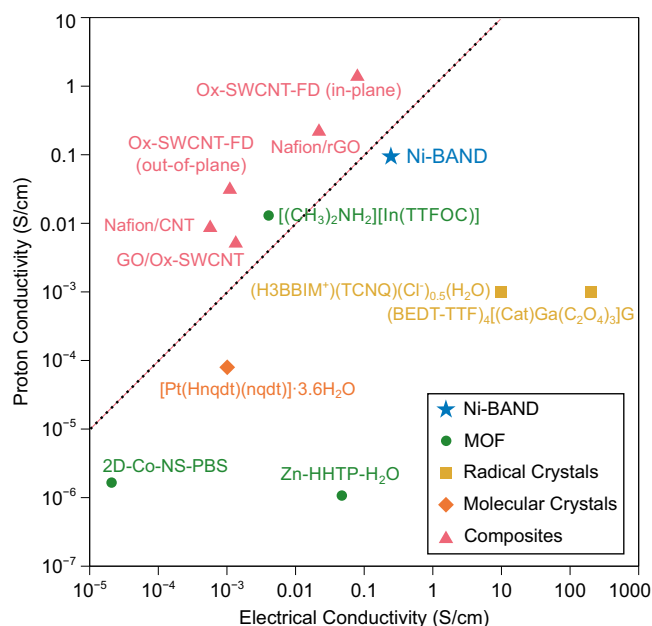


Fig. 1 | Room-temperature electrical and proton conductivities of mixed protonic-electronic conductors including this study (Ni-BAND). Proton conductivities were measured under humid (RH > 90%) conditions, except for the radical crystals (measured in vacuum). Electrical conductivities were obtained under humid conditions, except for Ni-BAND (dry) and Zn-HHTP-H₂O (RH 30%). Dashed line indicates equal proton and electron conductivities. Data sources: Ox-SWCNT-FD¹⁶, Zn-HHTP-H₂O², Nafion/rGO¹⁷, [(CH₃)₂NH₂][In(TTFOC)]³, GO/Ox-SWCNT¹⁸, [Pt(Hnqdt)(nqdt)]·3.6H₂O⁵, Nafion/CNT¹⁹, 2D-Co-NS-PBS⁴, (BEDT-TTF)₄[(Cat)Ga(C₂O₄)₃]G²¹, (H3BBIM*)(TCNQ)(Cl)_{0.5}(H₂O)²². HHTP hexahydroxy-triphenylene, Ox-SWCNT oxidized single-walled carbon nanotube, FD freeze-drying, rGO reduced graphene oxide, TTFOC tetrathiafulvalene octacarboxylates, nqdt 1,4-naphthoquinone-2,3-dithiolate, CNT carbon nanotube, 2D-Co [Co₂(OH)₆(H₂O)₃(C₄H₄O₄)₄]·7 H₂O, NS nanosheets, PBS phosphate buffer solution, BEDT-TTF bis(ethylenedithio)tetrathiafulvalene, Cat H₃O⁺ or NH₄⁺, G [(Cat)₂(crown-6 ether)]·5 H₂O, H3BBIM 2-(2-1H-benzimidazolyl)-1H-benzimidazolium, TCNQ 7,7,8,8-tetracyano-p-quinodimethane. Source data are provided as a Source Data file.

form, the diffraction patterns are generally weaker, reflecting a less crystalline structure (Supplementary Fig. 4). They also suggest the presence of short-range order among the polymer chains as well as swelling of the lattice structure within the gel, pointing to the potential for a hierarchical gel form in Ni-BAND.

X-ray photoelectron spectroscopy (XPS) analysis confirms the formation of Ni-BAND thin films without detectable impurities (Supplementary Fig. 5). The Ni2p spectrum shows a single oxidation state with two additional satellite peaks. The observed 2p_{3/2} peak at 855 eV aligns with the expected binding energies for octahedral Ni²⁺-O (-856 eV) and Ni²⁺-N (-854 eV) in Ni-BAND^{41,42}. The lack of a peak at 857 eV indicates the complete consumption and removal of the starting reagent Ni(NO₃)₂⁴³. The chemical environment is further validated by the O1s spectrum showing two distinct components (metal-bound oxygen at -530 eV and oxygen in NO₃⁻, H₂O, and DMF at -532 eV)^{44,45}, and the N1s spectrum displaying distinct peaks for NO₃⁻ nitrogen (-406 eV) and pyridinic/metal-coordinated nitrogen (-399 eV)^{42,46}. Thermogravimetric analysis (TGA) shows loss of water and DMF at 100 °C and 150 °C, providing additional confirmation of the material's composition (Supplementary Fig. 6).

Proton-electron coupled transport in Ni-BAND

The presence of d-π conjugation and extended H-bond network suggests that Ni-BAND can potentially conduct both electrons and protons. To investigate this dual transport, thin film devices with gold (Au) electrodes were fabricated (Fig. 4a). Utilizing films instead of pellets enhances practical applications due to scalability and improved molecular interconnectivity, which reduces barriers to charge transport. In this filmic form, environmental moisture can interact with the H-bond network, facilitated by hydrophilic moieties like NO₃⁻, DMF and H₂O⁴⁷ (Fig. 3h).

Direct current (DC) conductivity measurements reveal highly conductive nature of Ni-BAND. Two-electrode *I-V* measurements showed linear response, and four-point probe measurements revealed a DC conductivity of 0.20 S/cm at ambient conditions (25 °C and 50% RH) (Fig. 4a). This value exceeds that of the record for structurally similar 1D MOF with d-π conjugations (0.094 S/cm in DDA-Cu) and hydrogen-bonded organic frameworks (1.35 × 10⁻⁶ S/cm in MUV-20b)^{48–50}. The devices demonstrate air stability, exhibiting a decent

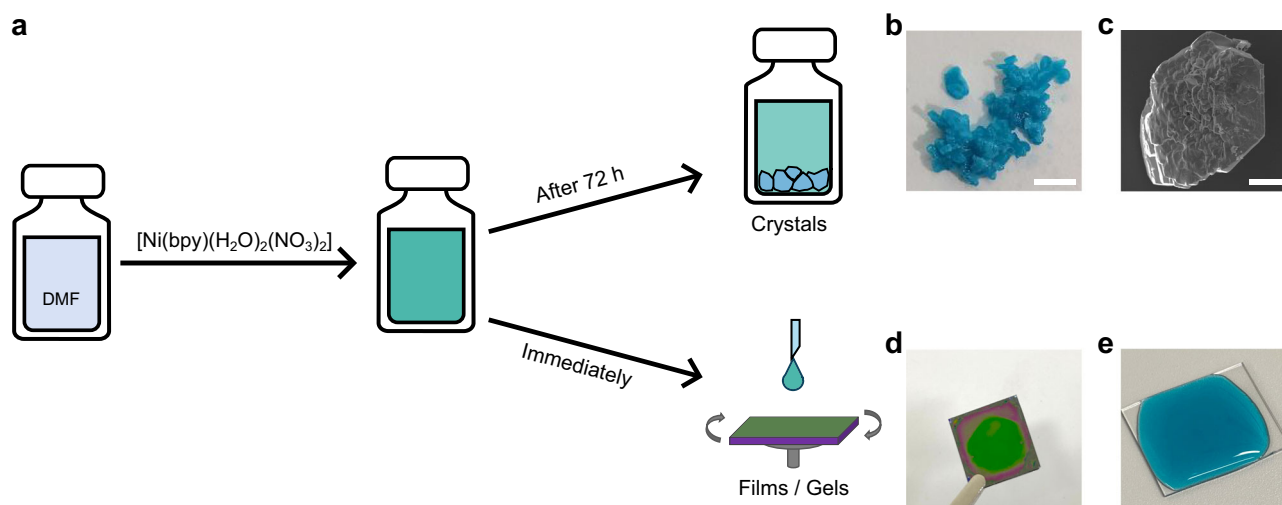


Fig. 2 | Synthesis and visualization of Ni-BAND crystals, thin films, and gels. **a** Schematic illustration of Ni-BAND synthesis, showing the dissolution of the precursor ([Ni(bpy)(H₂O)₂(NO₃)₂]) in DMF (center), yielding crystals (top right) and films or gels (bottom right). **b** Photograph of as-synthesized Ni-BAND crystals. The

scale bar denotes 5 mm. **c** Scanning electron microscope image of Ni-BAND crystals. The scale bar denotes 200 μm. **d** Photograph of Ni-BAND films prepared on a SiO₂(300 nm)/Si substrate (1.5 cm × 1.5 cm). **e** Photograph of Ni-BAND gel (2 cm × 2 cm) prepared on a glass substrate.

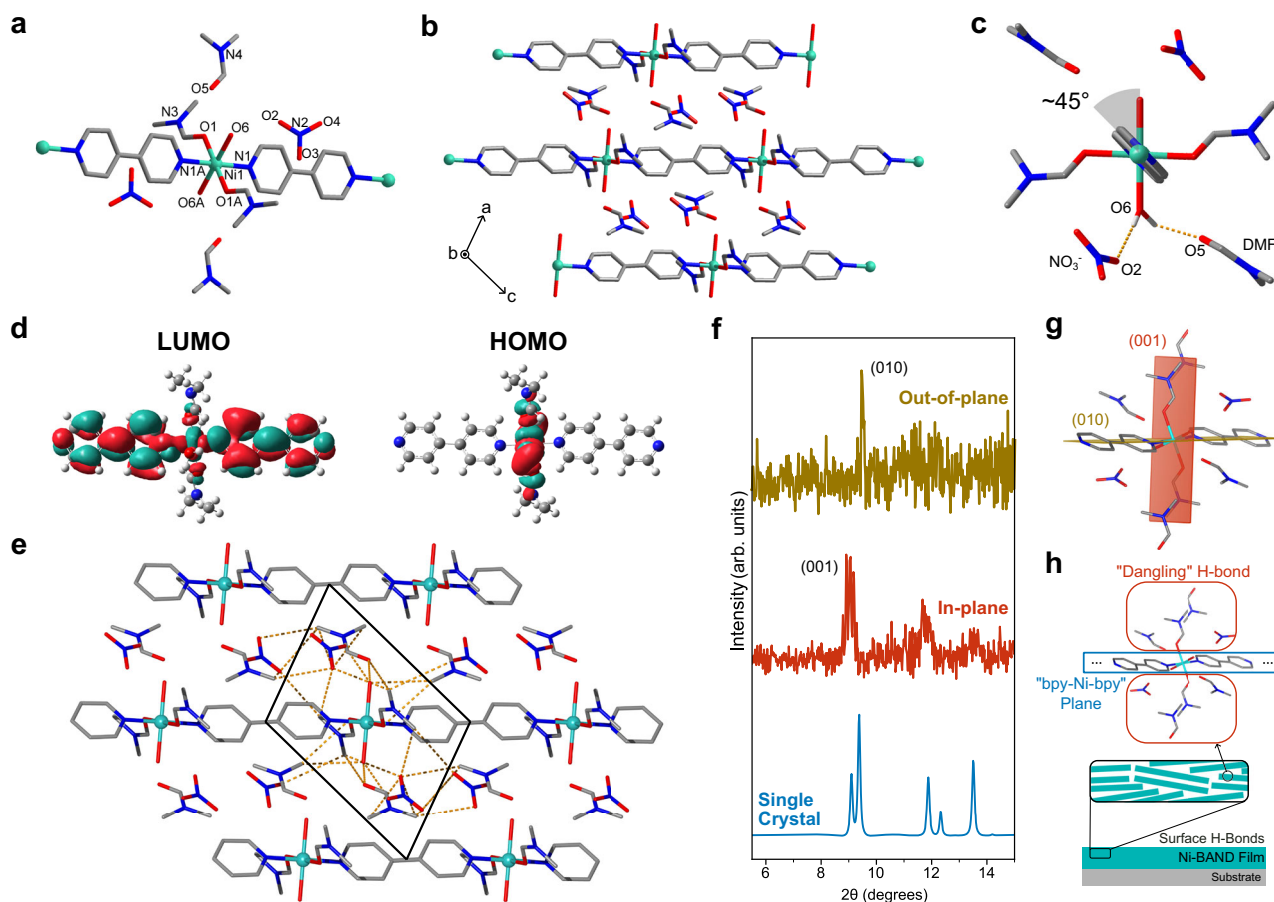


Fig. 3 | Crystal structure and X-ray diffraction analysis of Ni-BAND. **a** Unit cell structure. **b** Crystal packing showing parallel bpy-Ni-bpy chains. **c** Coordination sphere of Ni(II) center viewed along the bpy-Ni-bpy axis. Yellow dashed lines represent H-bonds. **d** HOMO and LUMO diagrams of $[\text{Ni}(\text{bpy})_2(\text{DMF})_2(\text{H}_2\text{O})_2]^{2+}$. The atomic colors are identical to **(a)**, except for hydrogen shown in white. Orbital signs are represented by red and green shading with isovalue of $0.02 \text{ e}/\text{u}^{-3}$. **e** H-bond network (yellow dashed lines) viewed in the same perspective as in **(b)**. Unit cell

outlined in black. Complete H-bond parameters are listed in Supplementary Table 5. **f** In-plane and out-of-plane XRD patterns of Ni-BAND thin films. **g** Crystallographic representation showing the (010) plane (yellow shading) and (001) plane (red shading) relative to the unit cell. **h** Schematic of Ni-BAND film on substrate with inset showing stacked bpy-Ni-bpy planes and terminal H-bonds. Source data are provided as a Source Data file.

retention of the conductance when exposed to air for over a month (Supplementary Fig. 7).

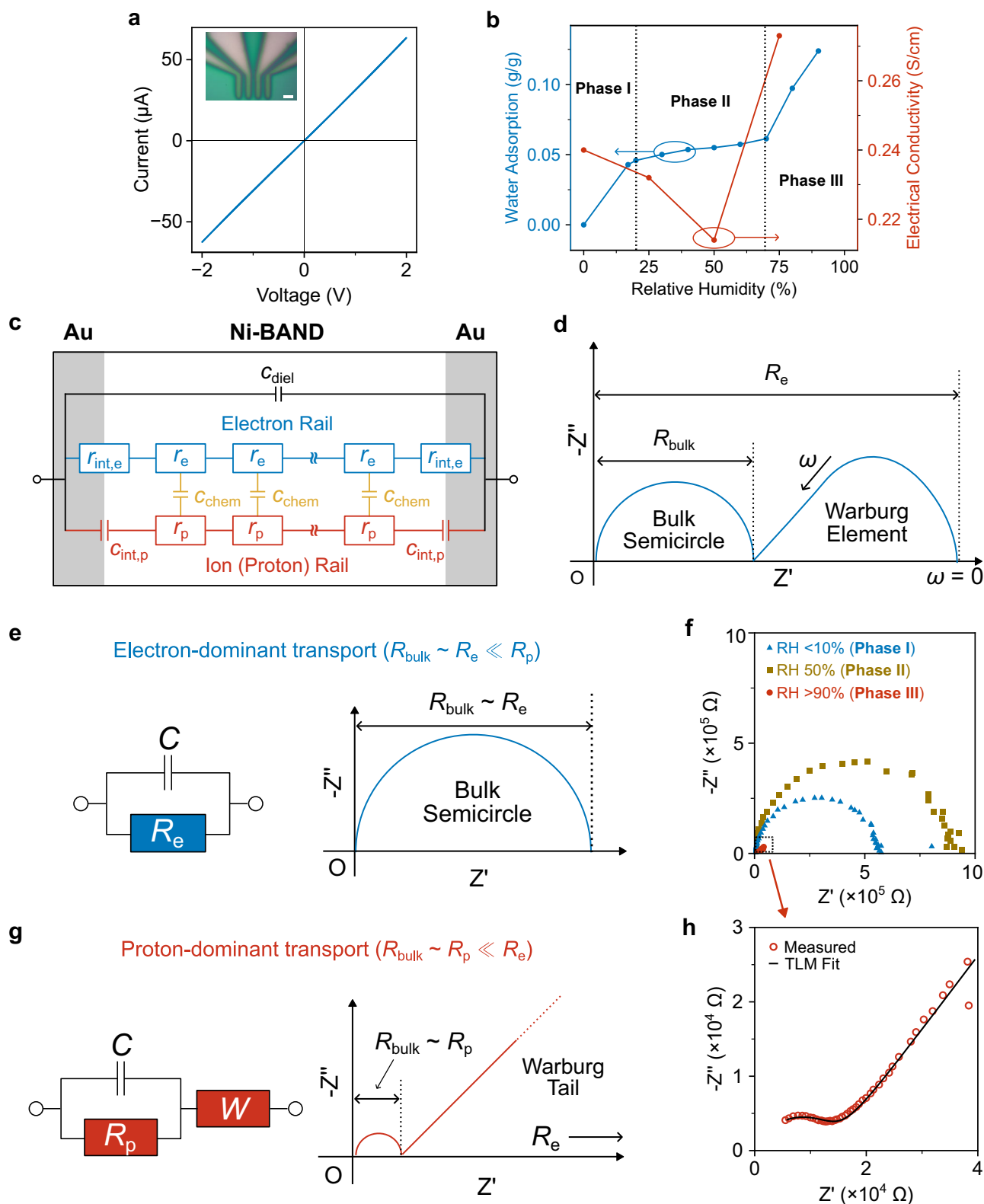
To understand the potential contribution of protons to the overall transport, Ni-BAND's responses to varying humidity levels were examined. Water vapor adsorption isotherm revealed three distinct phases: initial sharp uptake (Phase I, <30% RH), plateau region (Phase II, 30–70% RH), and secondary uptake (Phase III, >70% RH) (Fig. 4b). Negligible N_2 adsorption (surface area $\sim 9 \text{ m}^2/\text{g}$, Supplementary Fig. 8) suggests that the water uptake occurs through multilayer formation with hydrophilic components such as NO_3^- , DMF, and H_2O , mirroring the behavior of non-porous polymers like Nafion[®]^{26,51,52}. It also aligns with the PXRD peak shift near $2\theta = 25^\circ$ as discussed above.

The humidity dependence of the four-point probe DC conductivity revealed a complex transport behavior, implying strong coupling between electrons and protons. The conductivity shows a distinctive J-shaped response to humidity levels, with a minimum at 50% RH (Phase II) (Fig. 4b), reminiscent of the mobility-dopant concentration relationship in MIECs. That is, the decreased electrical conductivity in Phase II can be attributed to the low concentration of protons acting as Coulombic traps for electrons, whereas in Phase III, the elevated concentration of protons enhances doping effect and electrical conductivity through band-like transport. This behavior can be further modulated by humidity-induced structural changes: lattice expansion in Phase II impedes intermolecular electron transfer, while

in Phase III, the pronounced doping effect overcomes these structural limitations.

Electrochemical impedance spectroscopy (EIS), when coupled with transmission line model (TLM) analysis, provides comprehensive insights into charge transport mechanisms beyond the scope of DC conductivity measurements, particularly for mixed conductors^{9,53,54}. The TLM framework employs an intuitive equivalent circuit model that helps interpret the unique impedance response patterns of these complex systems (Fig. 4c, d; see Supplementary Note 2). The TLM analysis reveals distinct transport behaviors across the humidity phases. In Phases I and II, the Nyquist plots show semicircular responses without Warburg elements, indicating electron-dominant transport (Fig. 4e, f). Despite Ni-BAND's extensive H-bond network connecting adjacent H_2O ligands, the presence of weak H-bond fragments makes it less suitable for efficient proton transport under low to intermediate humidity levels, leaving electrons as the primary charge carriers (Supplementary Fig. 3). The larger semicircle in Phase II correlates with the decreased DC conductivity, supporting the proposed electron-trapping mechanism by sparse protons.

Phase III exhibits a small high-frequency semicircle and a Warburg tail, suggesting transition to proton-dominant transport despite significant electrical conductivity (Fig. 4g, h). Multilayer formation in Phase III enhances H-bond connectivity, potentially allowing for efficient proton transport, despite having relatively weak C-H $\cdots$ O hydrogen bonds^{52,55,56}. Theoretical calculations indicate H_2O ligands



as potential proton sources, with the O-H bond energy of 4.85 eV (lower than pure water's 7.11 eV) (Supplementary Fig. 9). This is consistent with the previous studies showing the acidity of H_2O ligands in proton conductors with positively charged framework^{57–59}. The estimated proton conductivity reaches 0.09 S/cm, indicating superprotonic conductivity ($>10^{-2}$ S/cm).³ The estimated activation energy is 0.22 eV, consistent with the Grotthuss mechanism (Supplementary Fig. 10).

This mixed proton-electron conductivity corresponds with the high electrical conductivity of Ni-BAND through n-type doping. The optical band gap of 1.28 eV derived from Tauc plot and the valence band maximum (VBM) energy of 1.17 eV versus the Fermi level from ultraviolet photoelectron spectroscopy (UPS) indicate the Fermi level positioning near the conduction band minimum (CBM) (Fig. 5a, b). Temperature-dependent conductivity measurements revealed an Arrhenius activation energy of 0.06 eV, characteristic of shallow donor

Fig. 4 | Humidity-dependent transport properties of Ni-BAND. **a** Current-voltage (I - V) characteristics of Ni-BAND film on SiO_2/Si substrate with Au electrodes (± 2 V range). Inset: optical microscopic image of device. The scale bar denotes 200 μm . **b** Water vapor adsorption isotherm at 298 K (blue) and electrical conductivities (red) measured under varying relative humidity (RH) levels. **c** Transmission line model schematic for Au electrode device with circuit elements describing electron rail resistance (r_e), proton rail resistance (r_p), electron interfacial resistance ($r_{\text{int},e}$), proton interfacial capacitance ($C_{\text{int},p}$), chemical capacitance (C_{chem}), and dielectric capacitance ($C_{\text{die},e}$). **d** Simulated impedance spectrum based on model in (c), where

R_{bulk} represents the bulk resistance of the MIEC (MPEC) channel, R_e and R_p as the resistance along the electron and proton rails, respectively, and ω as the AC sweeping frequency. Equivalent circuit models and corresponding impedance spectra of MPEC with electron-dominant (e) and proton-dominant transport (g), where C and W represent capacitive and Warburg elements, respectively. Experimental impedance spectra at varying humidity levels (f) and magnified view (h). Black line in h shows fit using the circuit model in (g). Fitting parameters: R_p , $1.40 \times 10^4 \Omega$; C , $8.34 \times 10^{-9} \text{ F s}^{\alpha-1}$ ($\alpha = 0.639$); W , $7.00 \times 10^5 \Omega \text{ s}^{1/2}$. Source data are provided as a Source Data file.

states (Fig. 5c). This n-type doping aligns with the MO analysis, where electrons utilize delocalized states of LUMO and nearest UMOs.

In MPECs, proton-electron coupling requires n-type doping to maintain charge neutrality, similar to the ion-electron coupling observed in MIECs⁹. The n-type doping is further enhanced by structural disorders, particularly nitrate vacancies present in polycrystalline films and gels (Fig. 5d–g). DFT calculations show that these defects simultaneously reduce the band gap, promote n-type doping, and enhance band dispersion along the bpy-Ni-bpy chain (see Supplementary Note 1). Bader charge analysis confirms that the n-doping effect is stabilized in the framework due to bpy ligands in the conjugated bpy-Ni-bpy chain. The bpy ligands, known for their electron-accepting properties in coordination complexes, accommodate excess electrons and prevent the reduction of Ni(II) centers⁶⁰ (Supplementary Table 6).

Ni-BAND's conductivity behavior shows parallels with well-studied systems. Its electron transport resembles PEDOT:PSS, which exhibits minimal conductivity in its dedoped state but shows high conductivity upon doping, where its conjugated backbone holds the doped charges²⁵. Simultaneously, Ni-BAND's extensive H-bond network facilitates water adsorption and proton transport mechanisms reminiscent of Nafion. The humidity-dependent transport measurements confirm the coupling between protons and electrons, ultimately promoting n-type doping to maintain charge balance⁵⁶. While PEC and structural disorders may individually present minor effects, their synergistic interaction enables effective n-doping in Ni-BAND, analogous to extrinsic semiconductors where minimal dopant concentrations can dramatically alter electrical properties⁶¹.

The significant role of proton-electron coupling in Ni-BAND's transport contrasts with previous studies. Su et al.'s³ work attributed electrical conductivity to pseudocapacitance arising from redox processes, and Choi et al.'s² study treated protonic and electronic conductivities as separate. Moreover, Ni-BAND presents a viable alternative to He et al.'s⁴ strategy of isolating these conduction types within a single material. These insights not only clarify the intricate dynamics of charge transport but also inspire approaches to material design.

Neuromorphic potential of Ni-BAND synaptic devices

Building on PEC, Ni-BAND was assessed for its potential in memristors, an emerging application for MIECs^{9,35,62}. Memristors are critical for their ability to remember resistance states, enabling learning processes through synaptic plasticity^{63,64}. Therefore, they are considered fundamental components for neuromorphic computing, which seeks to emulate the brain's architecture to advance sustainable artificial intelligence. The potential of MPECs in memristors is particularly promising due to the critical role of moisture-derived protons in resistive switching behaviors of interface-type memristors¹¹. Additionally, the strong structure-transport relationship provided by the Grotthuss mechanism enables the systematic design of these memristors. Therefore, investigating Ni-BAND memristors could illustrate how MPECs might expand the traditional applications of MIECs by leveraging PEC, as discussed in the Introduction.

Ni-BAND films with Au electrodes exhibited a small pinched hysteresis at high sweeping voltages (–15 V to 15 V), a fingerprint of

memristors^{63,65} (Supplementary Fig. 11a). Although increasing the bias to –30 V to 30 V produced a larger hysteresis loop, it remained still too small to effectively study memristive properties and posed a risk of damaging the films (Supplementary Fig. 11b). To address this issue, a gel form of Ni-BAND, which shows higher resistance, was introduced to maximize the memristive properties (Fig. 6a, b). The higher resistance of the gel form compared to the film may be attributed to the swollen DMF solvent and lower crystallinity. This exploration of neuromorphic gels specifically offer benefits such as inherent flexibility and stretchability, which make them ideal for applications in printable electronics, wearable devices and soft robotics^{35,66}.

At lower bias voltages (–20 V to 20 V), the devices exhibited a linear current-voltage (I - V) response, similar to that observed in film-based systems (Supplementary Fig. 12). However, when the voltage range was extended to –30 to 30 V, a pinched hysteresis began to appear, becoming more pronounced as the sweep rate decreased (Fig. 6d and Supplementary Fig. 13). The pinched hysteresis in Ni-BAND gel memristors is characterized by a gradual shift from a low-resistance state (LRS) to a high-resistance state (HRS) when subjected to significant positive or negative electrical biases (steps 1 to 2 and 3 to 4 in Fig. 6d). The device returns to LRS when the bias polarity is reversed (steps 2 to 3 and 4 to 1 in Fig. 6d). This behavior defines the Ni-BAND gel memristors as analog-switching, volatile memristors, making them suitable for use in neuromorphic computing systems^{67,68}.

The resistive switching mechanism in Ni-BAND memristors can be attributed to PEC (Fig. 6e). Specifically, the accumulation of protons at the electrode interface leads to a modification of the Schottky barrier height by trapping electrons. This phenomenon results in asymmetric Schottky barriers on each side of the electrodes, a known mechanism to induce memristive properties in Nb:STO and MoS_2 ^{11,68}. This hypothesis gains support from several observations. Firstly, pinched hysteresis is present in devices with inert Au electrodes, which do not form conducting filaments. Additionally, gradual changes in conductance during voltage sweeping—unlike the sudden transitions in filamentary memristors—further support this notion⁶⁹. Moreover, the reversible appearance and disappearance of pinched hysteresis when cycling between dry and humid conditions underscore the significance of protons in dictating memristive properties¹¹ (Fig. 6d and Supplementary Fig. 14). Returning to LRS upon bias polarity reversal is also noticeable in memristors based on Schottky barrier modifications, particularly under high bias voltages^{68,70}.

Ni-BAND gel memristors exhibited synaptic plasticity, mirroring the adaptability of biological synapses through potentiation and depression in response to applied pulse trains (Fig. 6c, f). Specifically, the conductance increased following a series of negative bias pulses and decreased after a series of positive bias pulses. This synaptic behavior parallels that observed in MoS_2 -based memristors, which exhibit a similar pinched hysteresis pattern as shown in Fig. 6d⁷⁰. This achievement marks the first demonstration of protonic memristors, which use protons as neurotransmitter and coordination polymers as the channel material to demonstrate synaptic plasticity. To the best of our knowledge, prior instances of synaptic behavior in memristors based on reticular materials primarily involved electroforming, where metal diffusion through these materials was the key operational mechanism^{71–73}. Moreover, the synaptic behaviors were maintained after 300 bending

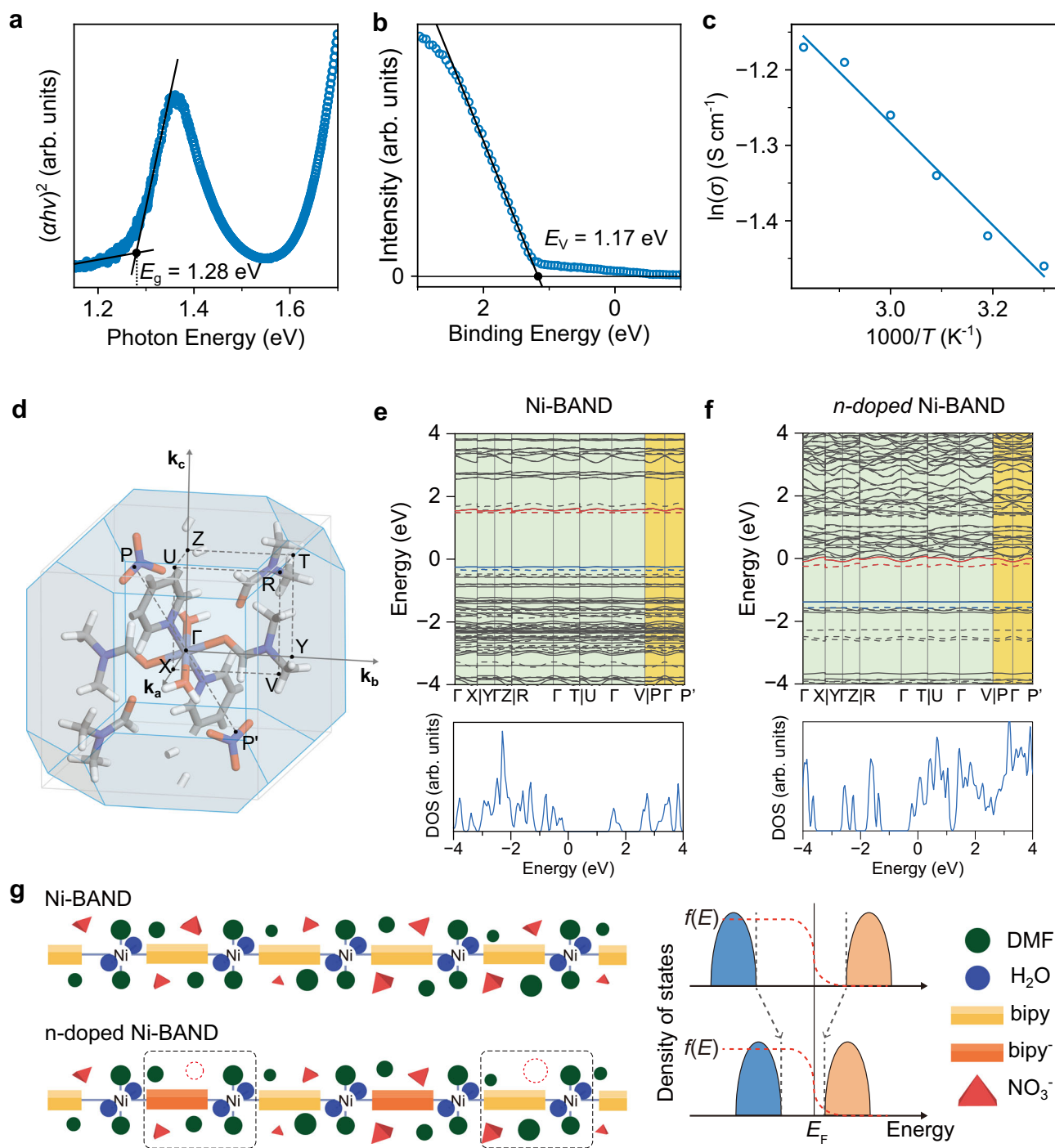


Fig. 5 | Electronic characterization and band structure of Ni-BAND. **a** Tauc plot from UV-Vis spectrum of Ni-BAND showing optical band gap, where α is absorption coefficient, h is the Planck constant, ν is the photon's frequency, and E_g is the band gap energy. Linear background fit parameters: slope, 37.4; y-intercept, -34.1 . Linera peak fit parameters: slope, 506; y-intercept, -634 . **b** UPS spectrum near the Fermi level, where E_v is the energy difference between the valence band maximum and the Fermi level. Linear fit parameters: slope, 2.01×10^5 ; y-intercept, -2.34×10^5 . **c** Arrhenius plot of electrical conductivities (σ) measured using four-point-probe measurement, where T is the measured temperature. Linear fit parameters: slope,

-0.6765 ; y-intercept, 0.7588 . **d** Optimized crystal structure of Ni-BAND in real space and its corresponding first Brillouin zone in reciprocal space. Fractional coordinates of all atoms are provided in Supplementary Data 2, and coordinates of high-symmetric points in the reciprocal space (Γ , X, Y, Z, R, T, U, V, P and P') are provided in Supplementary Table 7. Calculated electronic band structure (top) and density of states (bottom) for pristine (**e**) and NO_3^- removed, n-doped Ni-BAND (**f**). **g** Schematic representation and density of states upon n-doping. Source data are provided as a Source Data file.

cycles, indicating the flexibility of the gel and devices (Fig. 6f). This discovery highlights a striking resemblance between Ni-BAND gel devices and biological neurons; protons act akin to neurotransmitters, influencing the conductance or synaptic strength within a flexible and soft gel system, reminiscent of biological tissues.

Discussion

Our investigation into Ni-BAND reveals its distinctive mixed proton-electron conductivity, arising from its water-adsorbing properties and n-type doping in the system. A notable feature is strong PEC in Ni-BAND, characterized by transition of the major charge carrier

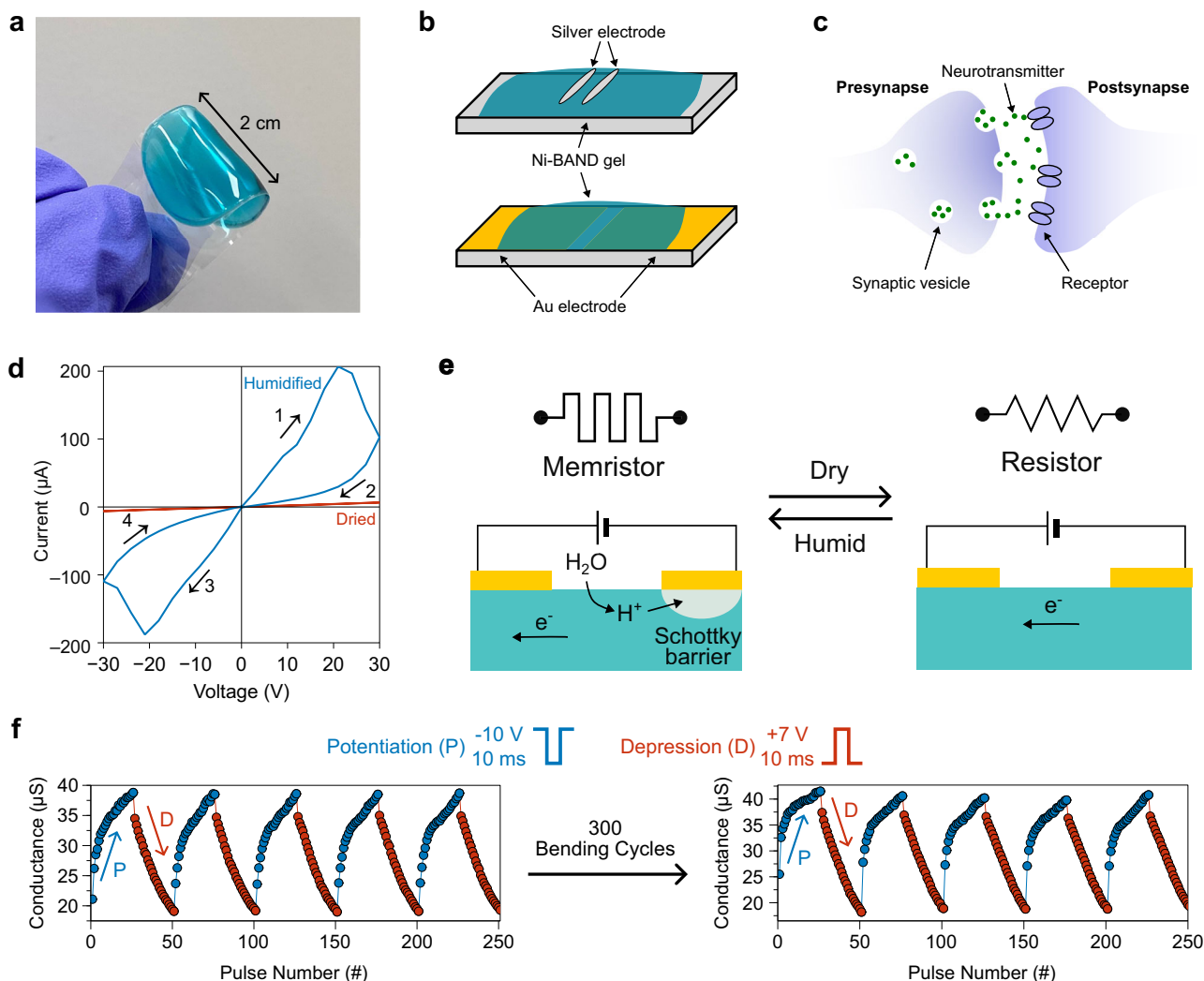


Fig. 6 | Neuromorphic characteristics of Ni-BAND gel memristors. a Photograph of Ni-BAND gel on flexible PET substrate. **b** Schematic of device structure with Ag and Au electrodes. **c** Schematic representation of synaptic transmission between pre- and post-synaptic terminals. **d** Current-voltage (I-V) characteristics under varying humidity conditions: as-prepared devices under ambient conditions (blue) and after overnight storage in dry Ar atmosphere (red). **e** Proposed transport

mechanism depending on environmental humidity. **f** Potentiation (P, blue) and depression (D, red) characteristics before (left) and after 300 bending cycles. (right) Applied voltage profile: set (−10 V, 10 ms), reset (+7 V, 10 ms), read (0.9 V, 10 ms). Each cycle consists of 25 alternating set (or reset) and read operations. Source data are provided as a Source Data file.

depending on humidity, underscores the importance of coupled transport for achieving high conductivity. It further facilitates resistive switching behavior in Ni-BAND, particularly in its gel form, suggesting its potential for application in synaptic devices. This shows how MPECs can broaden and enrich the applications of MIECs by bridging unique properties of protons through PEC. This research not only elucidates the interactions between protons and electrons within coordination polymers but also paves the way for applications of MPECs. By demonstrating their versatility beyond traditional electrochemical uses, this study positions MPECs as next-generation materials for electronics and iontronics.

Methods

Synthesis and preparation of crystals, thin films, and gels

The precursor for Ni-BAND was initially synthesized by dissolving 5 mmol of $\text{Ni}(\text{NO}_3)_2 \cdot 6(\text{H}_2\text{O})$ (Alfa aesar, 98%) and 5 mmol of 4,4'-bipyridine (Acros organics, 98%) into 6 ml of ethanol (Samchun, 99.8%). The precursor immediately began to form after mixing, further promoted by sonication. The precipitated precursor was then filtered through a nylon filter and rinsed with ethanol. The precursor was obtained with the yield

of 93.5%. The precursor was stored in dry conditions for the following synthesis processes.

For crystal synthesis, the precursor was dispersed into dimethylformamide (Samchun, 99.5%) to achieve a concentration of 0.1 g/mL. Note that during the dispersion, exposure to highly humid environments should be avoided, as moisture can inhibit proper precipitation and crystallization of the product. The dispersion was filtered through a nylon syringe filter (Hyundai Micro, NY045047A, pore size 450 nm). The filtered dispersion was sealed in a vial and allowed to stand undisturbed for 72 h at room temperature to precipitate blue crystals of Ni-BAND. The crystals were then filtered through a nylon filter, followed by rigorous rinsing with methyl isobutyl ketone (MIBK, Alfa aesar, 99%) to remove impurities. Ni-BAND crystals were obtained with a yield of 50.6%. Then, it was kept under vacuum for 24 h for further analysis.

For thin film preparation, the DMF dispersion of the precursors was prepared at 0.1 g/mL, which is identical to that used in the crystal growth. It was directly spin-coated onto various substrates, including SiO_2 (300 nm)/Si (Namkang Hi-tech, p-type), quartz (Hi-Solar), and PET. Spin-coating was conducted at 800 rpm for 10 s, followed by 2000 rpm for 60 s, resulting in a film of 300 nm in thickness. Prior to

spin coating, the substrate was treated with air plasma using a plasma cleaner (Alpha Science, PDC-32G-2) to enhance the film uniformity.

For gel formation, the concentration of the dispersion was 0.375 g/mL. Dip-coating or drop-drying a filtered dispersion onto arbitrary substrates results in a thick, separable gel.

Crystallographic and structural characterizations

Morphological examinations were conducted using an optical microscope (Nikon, Eclipse LV150NL) and a scanning electron microscope (Tescan, Vega II LMU). Thermogravimetric analysis was carried out with a Rigaku TG-8120 machine. Surface area and porosity analyses were performed via BET measurements utilizing a Microtrac MRB BELSORP MAX instrument. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Fisher Scientific Multilab-2000 instrument with an Al K α source. Ultraviolet photoelectron spectroscopy (UPS) was conducted on a Thermo Fisher NEXSA instrument with a bias voltage of -5 V. UV-Vis spectra were obtained using a Scinco S-3100 spectrophotometer.

Water vapor adsorption isotherms were obtained by measuring the weight changes depending on the humidity levels⁷⁴. Sample dry weights were first obtained immediately after complete drying (w_0). The samples were then placed in a chamber with controlled humidity and temperature (298 K). At each desired humidity level, the sample weight was measured once it reached a constant value (w_{wet}). The adsorbed water content was calculated as $(w - w_0)/w_0$.

The crystal structure of the crystallized sample was determined by SCXRD methods at the Korea Basic Science Institute (KBSI, Western Seoul Center, Korea). A single crystal was picked up with paratone oil and mounted on a Bruker D8 Venture PHOTON III M14 diffractometer equipped with a graphite-monochromated Mo K α ($\lambda = 0.71073$ Å) radiation source and a cold stream (-50 °C). Data collection and integration were performed using the software package of APEX3 (Bruker)⁷⁵. The absorption correction was performed by a multi-scan method implemented in SADABS⁷⁶. The structure was solved by direct method using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL-2018⁷⁷. All the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were added to their geometrically ideal positions.

Powder X-ray diffraction was performed using a Rigaku Ultima IV instrument equipped with CuK α radiation (2 kW). Grazing-incidence X-ray diffraction experiments were conducted with a Panalytical Empyrean instrument with CuK α radiation.

Electron and proton transport characterizations

Thin film devices were fabricated by sputtering Au for 80 s onto the films with a sputter (Cressington, Sputter Coater 108auto). Shadow masks defined the geometry of the electrodes. Four-point probe measurements were performed using a dedicated machine (Ossila, T2001A3). Two-point probe measurements were performed within a controlled gas/vacuum environment using a specialized probe station (Nextron, MPS-VAC) and a custom-made wired devices in a sealed vial. The injected Ar gas (99.999%) was monitored and controlled using mass flow controllers (Alicat, MC series). Each measurement was taken once after the target environment conditions (temperature, humidity, and pressure) had stabilized for a minimum of 30 min. To measure DC conductivity, a source meter (Keithley, 2636B SourceMeter) was used. For AC conductivity measurements, an oscilloscope (Tektronix, TBS 2102) and a function generator (Tektronix, AFG1062) were used with a shunt resistor. Electrochemical impedance spectroscopy (EIS) was collected over a frequency range spanning from 100 Hz to 1 MHz, applying an amplitude of 0.5 V without any DC bias, with the system exhibiting linear response. The acquired spectra were processed using the `impedance.py` package in Python⁷⁸. The conductivity (σ) was calculated based on the film's resistance (R), which was determined by the fitted circuit. This calculation was performed using the following

equation: $\sigma = l/(Rtw)$, where l represents the channel length, w is the channel width, and t is the film thickness.

For gel devices, gold (Au) electrodes were sputtered onto glass substrates. Ag electrodes were prepared using conductive paste⁷⁹. Channels were defined by masking the substrate before introducing the gel, thus configuring the devices with bottom electrodes. The bending experiments utilized a custom-built bending machine⁸⁰.

Theoretical calculations

Spin-polarized density functional theory (DFT) calculations were performed using the Vienna Ab-initio Simulation Package (VASP)^{81,82} to optimize the crystal structure and calculate fundamental electronic properties. The cell volume and ionic positions were optimized based on the crystal structure determined by SCXRD methods with fixed cell shape. The exchange-correlation energy was evaluated using the Perdew-Burke-Ernzerhof (PBE)⁸³ functional. The core electrons were replaced by projector augmented wave (PAW)⁸⁴ pseudo-potentials, expanded in a basis set of plane waves up to a cutoff energy of 400 eV. Electronic and ionic relaxations were performed until the total energy and atomic forces converged below thresholds of 10^{-5} eV and 0.05 eV/Å, respectively. A Γ -centered $4 \times 4 \times 3$ k-point grid was used for Brillouin zone sampling. The VASPKIT package⁸⁵ was used for the post-processing of the electronic band structure and density of states were displayed as sum of spin up and down. Molecular DFT calculations were performed using the Gaussian 16 program⁸⁶ to study orbital interactions in Ni-BAND. The B3LYP functional⁸⁷ and def2-TZVPP basis^{88,89} set were applied for molecular orbital calculations based on single point calculations from the VASP optimized structure.

Data availability

The X-ray crystallographic data for Ni-BAND have been deposited at the Cambridge Crystallographic Data Center (CCDC) under the database identifier CCDC: 2361111. Copies of the data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>. Source data are provided with this paper.

References

- Yan, B., Bisbey, R. P., Alabugin, A. & Surendranath, Y. Mixed electron–proton conductors enable spatial separation of bond activation and charge transfer in electrocatalysis. *J. Am. Chem. Soc.* **141**, 11115–11122 (2019).
- Choi, J. Y. et al. 2D conjugated metal-organic framework as a proton-electron dual conductor. *Chem* **9**, 143–153 (2023).
- Su, J. et al. High electrical conductivity in a 2D MOF with intrinsic superprotonic conduction and interfacial pseudo-capacitance. *Matter* **2**, 711–722 (2020).
- He, X.-L. et al. A mixed protonic–electronic conductor base on the host–guest architecture of 2D metal–organic layers and inorganic layers. *Adv. Sci.* **10**, 2205944 (2023).
- Kimura, Y. et al. An approach to an ideal molecule-based mixed conductor with comparable proton and electron conductivity. *Inorg. Chem.* **61**, 4453–4458 (2022).
- Huynh, M. H. V. & Meyer, T. J. Proton-coupled electron transfer. *Chem. Rev.* **107**, 5004–5064 (2007).
- Tybuski, R., Liu, T., Glover, S. D. & Hammarström, L. Proton-coupled electron transfer guidelines, fair and square. *J. Am. Chem. Soc.* **143**, 560–576 (2021).
- Liu, H. et al. Mixed protonic-electronic conducting perovskite oxide as a robust oxygen evolution reaction catalyst. *Electrochim. Acta* **282**, 324–330 (2018).
- Paulsen, B. D., Tybrandt, K., Stavrinidou, E. & Rivnay, J. Organic mixed ionic–electronic conductors. *Nat. Mater.* **19**, 13–26 (2020).
- Lim, D.-W. & Kitagawa, H. Proton transport in metal–organic frameworks. *Chem. Rev.* **120**, 8416–8467 (2020).

11. Kunwar, S. et al. Protons: critical species for resistive switching in interface-type memristors. *Adv. Electron. Mater.* **9**, 2200816 (2023).
12. Yang, Y. et al. Observation of conducting filament growth in nanoscale resistive memories. *Nat. Commun.* **3**, 732 (2012).
13. Li, M. et al. Directional Formation of Conductive Filaments for a Reliable Organic-Based Artificial Synapse by Doping Molybdenum Disulfide Quantum Dots into a Polymer Matrix. *ACS Appl. Mater. Interfaces* **14**, 44724–44734 (2022).
14. Gregori, G., Merkle, R. & Maier, J. Ion conduction and redistribution at grain boundaries in oxide systems. *Prog. Mater. Sci.* **89**, 252–305 (2017).
15. Park, C. Y., Lee, T. H., Dorris, S. E., Lu, Y. & Balachandran, U. Oxygen permeation and coal-gas-assisted hydrogen production using oxygen transport membranes. *Int. J. Hydrog. Energy* **36**, 9345–9354 (2011).
16. Nahar Rabin, N. et al. Enhanced mixed proton and electron conductor at room temperature from chemically modified single-wall carbon nanotubes. *RSC Adv.* **12**, 8632–8636 (2022).
17. Aragaw, B. A., Su, W.-N., Rick, J. & Hwang, B.-J. Highly efficient synthesis of reduced graphene oxide–Nafion nanocomposites with strong coupling for enhanced proton and electron conduction. *RSC Adv.* **3**, 23212 (2013).
18. Rabin, N. N. et al. Free-standing graphene oxide/oxidized carbon nanotube films with mixed proton and electron conductor properties. *Energy Adv.* **2**, 293–297 (2023).
19. Tortello, M., Bianco, S., Ijeri, V., Spinelli, P. & Tresso, E. Nafion membranes with vertically-aligned CNTs for mixed proton and electron conduction. *J. Membr. Sci.* **415–416**, 346–352 (2012).
20. Cao, L. et al. Phosphorylated graphene monoliths with high mixed proton/electron conductivity. *J. Mater. Chem. A* **6**, 8499–8506 (2018).
21. Akutsu-Sato, A. et al. The first proton-conducting metallic ion-radical salts. *Angew. Chem. Int. Ed.* **44**, 292–295 (2005).
22. Akutagawa, T., Hasegawa, T., Nakamura, T., Inabe, T. & Saito, G. Coupled protonic and electronic conduction in the molecular conductor [2-(2-1H-Benzimidazolyl)-1H-benzimidazolium]–TCNQ. *Chem. Eur. J.* **8**, 4402–4411 (2002).
23. Phair, J. W. & Badwal, S. P. S. Review of proton conductors for hydrogen separation. *Ionics* **12**, 103–115 (2006).
24. Tao, Z. et al. A review of advanced proton-conducting materials for hydrogen separation. *Prog. Mater. Sci.* **74**, 1–50 (2015).
25. Jeong, C., Kim, D. & Kim, F. S. Chemically dedoped PEDOT:PSS films with an amidine/polymer overcoating and their applications as a semiconducting channel in organic field-effect transistors and inverters. *Mater. Chem. Phys.* **284**, 126062 (2022).
26. Bharath, V. J. et al. Measurement of water uptake in thin-film Nafion and anion alkaline exchange membranes using the quartz crystal microbalance. *J. Membr. Sci.* **497**, 229–238 (2016).
27. Saha, R., Gupta, K. & Gómez García, C. J. Strategies to improve electrical conductivity in metal–organic frameworks: a comparative study. *Cryst. Growth Des.* **24**, 2235–2265 (2024).
28. Das, P. et al. 4,4'-Bipyridine-based Ni(II)-metalloge for fabricating a photo-responsive Schottky barrier diode device. *N. J. Chem.* **45**, 15920–15927 (2021).
29. Felloni, M. et al. Supramolecular interactions in 4,4'-Bipyridine cobalt(II) nitrate networks. *J. Supramol. Chem.* **2**, 163–174 (2002).
30. Barnett, S. A. & Champness, N. R. Structural diversity of building-blocks in coordination framework synthesis—combining M(NO₃)₂ junctions and bipyridyl ligands. *Coord. Chem. Rev.* **246**, 145–168 (2003).
31. Xiang, F. et al. Anhydrous proton conduction in crystalline porous materials with a wide working temperature range. *ACS Appl. Mater. Interfaces* **13**, 41363–41371 (2021).
32. Koo, J. Y. et al. Anisotropic electrical conductivity of a single-crystalline oxo-bridged Cr₄^{III} Mo₂^{VI} heterometallic complex. *Inorg. Chem.* **60**, 13262–13268 (2021).
33. Choi, J.-Y., Alford, T. L. & Honsberg, C. B. Solvent-controlled spin-coating method for large-scale area deposition of two-dimensional silica nanosphere assembled layers. *Langmuir* **30**, 5732–5738 (2014).
34. Zhang, T., Chang, G. & Guo, Q. Thermoreversible polymer gels in DMF formed from charge- and crystallization-induced assembly. *Polymers* **12**, 2056 (2020).
35. Kheirabadi, N. R., Chiolerio, A., Szaciłowski, K. & Adamatzky, A. Neuromorphic liquids, colloids, and gels: a review. *ChemPhysChem* **24**, e202200390 (2023).
36. Lee, H. et al. Hierarchical metal–organic aerogel as a highly selective and sustainable CO₂ adsorbent. *ACS Appl. Mater. Interfaces* **14**, 46682–46694 (2022).
37. Mauger-Sonnek, K., Streicher, L. K., Lamp, O. P., Ellern, A. & Weeks, C. L. Structure control and sorption properties of porous coordination polymers prepared from M(NO₃)₂ and 4,4'-bipyridine (M=Co²⁺, Ni²⁺). *Inorg. Chim. Acta* **418**, 73–83 (2014).
38. Zhuang, Z., Mai, Z., Wang, T. & Liu, D. Strategies for conversion between metal–organic frameworks and gels. *Coord. Chem. Rev.* **421**, 213461 (2020).
39. Steiner, T. The hydrogen bond in the solid state. *Angew. Chem. Int. Ed.* **41**, 48–76 (2002).
40. Yoon, S. M., Park, J. H. & Grzybowski, B. A. Large-area, freestanding MOF films of planar, curvilinear, or micropatterned topographies. *Angew. Chem. Int. Ed.* **56**, 127–132 (2017).
41. Duan, J., Chen, S. & Zhao, C. Ultrathin metal-organic framework array for efficient electrocatalytic water splitting. *Nat. Commun.* **8**, 15341 (2017).
42. Li, B. et al. Nanoreactor of nickel-containing carbon-shells as oxygen reduction catalyst. *Adv. Mater.* **29**, 1605083 (2017).
43. Moulder, J. F., Stickle, W. F., Sobol, P. E. & Bomben, K. D. *Handbook of X-Ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data* (Perkin-Elmer Corporation, Eden Prairie, Minn, 1992).
44. Meng, H., Jing, W., Xu, X., Yu, L. & Peng, Q. Nickel(II) nitrate hole-transporting layers for single-junction bulk heterojunction organic solar cells with a record 19.02% efficiency. *Angew. Chem. Int. Ed.* **62**, e202301958 (2023).
45. Chen, T. et al. In situ synthesis of Ni-BTC metal–organic framework@graphene oxide composites for high-performance supercapacitor electrodes. *ACS Omega* **8**, 10888–10898 (2023).
46. Jnido, G., Ohms, G. & Viöl, W. Deposition of zinc oxide coatings on wood surfaces using the solution precursor plasma spraying process. *Coatings* **11**, 183 (2021).
47. Xu, G., Otsubo, K., Yamada, T., Sakaida, S. & Kitagawa, H. Superprotonic conductivity in a highly oriented crystalline metal–organic framework nanofilm. *J. Am. Chem. Soc.* **135**, 7438–7441 (2013).
48. Shang, S. et al. A one-dimensional conductive metal-organic framework with extended π -d conjugated nanoribbon layers. *Nat. Commun.* **13**, 7599 (2022).
49. Kirlikovali, K. O. et al. An electrically conductive tetrathiafulvalene-based hydrogen-bonded organic framework. *ACS Mater. Lett.* **4**, 128–135 (2022).
50. Vicent-Morales, M. et al. Semiconductor porous hydrogen-bonded organic frameworks based on tetrathiafulvalene derivatives. *J. Am. Chem. Soc.* **144**, 9074–9082 (2022).
51. Rahman, M., Muttakin, M., Pal, A., Shafiullah, A. Z. & Saha, B. A statistical approach to determine optimal models for IUPAC-classified adsorption isotherms. *Energies* **12**, 4565 (2019).
52. Pili, S. et al. Enhancement of proton conductivity in nonporous metal–organic frameworks: the role of framework proton density and humidity. *Chem. Mater.* **30**, 7593–7602 (2018).
53. Bumberger, A. E., Nenning, A. & Fleig, J. Transmission line revisited—the impedance of mixed ionic and electronic conductors. *Phys. Chem. Chem. Phys.* **26**, 15068–15089 (2024).

54. Romero, M., Mombrú, D., Pignanelli, F., Faccio, R. & Mombrú, A. W. Mini-review: mixed ionic–electronic charge carrier localization and Transport in hybrid organic–inorganic nanomaterials. *Front. Chem.* **8**, 537 (2020).
55. Pardo, E. et al. High proton conduction in a chiral ferromagnetic metal–organic quartz-like framework. *J. Am. Chem. Soc.* **133**, 15328–15331 (2011).
56. Chand, S. et al. Metallo hydrogen-bonded organic frameworks (MHOFS) as new class of crystalline materials for protonic conduction. *Chem. Eur. J.* **25**, 1691–1695 (2019).
57. Tayade, S. B. et al. Proton conduction in a hydrogen-bonded complex of copper(II)-bipyridine glycoluril nitrate. *Dalton Trans.* **46**, 6968–6974 (2017).
58. Jeong, N. C., Samanta, B., Lee, C. Y., Farha, O. K. & Hupp, J. T. Coordination-chemistry control of proton conductivity in the iconic metal–organic framework material HKUST-1. *J. Am. Chem. Soc.* **134**, 51–54 (2012).
59. Zhu, S.-D. et al. A proton conductor showing an indication of single-ion magnet behavior based on a mononuclear Dy(III) complex. *J. Mater. Chem. C* **9**, 481–488 (2021).
60. Drover, M. W. et al. Octaboranonyl complexes of nickel: monomers for redox-active coordination polymers. *Chem. Eur. J.* **26**, 11180–11186 (2020).
61. Sze, S. M. & Ng, K. K. *Physics of Semiconductor Devices* (John Wiley & Sons, 2006).
62. Yao, Z. et al. Simultaneous implementation of resistive switching and rectifying effects in a metal-organic framework with switched hydrogen bond pathway. *Sci. Adv.* **5**, eaaw4515 (2019).
63. Chua, L. If it's pinched it's a memristor. *Semicond. Sci. Technol.* **29**, 104001 (2014).
64. Ielmini, D., Wang, Z. & Liu, Y. Brain-inspired computing via memory device physics. *APL Mater.* **9**, 050702 (2021).
65. Strukov, D. B., Snider, G. S., Stewart, D. R. & Williams, R. S. The missing memristor found. *Nature* **453**, 80–83 (2008).
66. Zhang, P. et al. Integrated 3D printing of flexible electroluminescent devices and soft robots. *Nat. Commun.* **13**, 4775 (2022).
67. Wang, R. et al. Recent advances of volatile memristors: devices, mechanisms, and applications. *Adv. Intell. Syst.* **2**, 2000055 (2020).
68. Zhou, H. et al. Design-dependent switching mechanisms of Schottky-barrier-modulated memristors based on 2D semiconductor. *Adv. Electron. Mater.* **9**, 2201252 (2023).
69. Zhu, J., Zhang, T., Yang, Y. & Huang, R. A comprehensive review on emerging artificial neuromorphic devices. *Appl. Phys. Rev.* **7**, 011312 (2020).
70. Li, D. et al. MoS₂ memristors exhibiting variable switching characteristics toward biorealistic synaptic emulation. *ACS Nano* **12**, 9240–9252 (2018).
71. Allendorf, M. D. et al. Electronic devices using open framework materials. *Chem. Rev.* **120**, 8581–8640 (2020).
72. Oh, J. & Yoon, S. M. Resistive memory devices based on reticular materials for electrical information storage. *ACS Appl. Mater. Interfaces* **13**, 56777–56792 (2021).
73. Li, T. et al. 2D oriented covalent organic frameworks for alcohol-sensory synapses. *Mater. Horiz.* **8**, 2041–2049 (2021).
74. Bontrager, N. C., Radomski, S., Daymon, S. P., Johnson, R. D. & Miller, K. M. Influence of counteranion and humidity on the thermal, mechanical and conductive properties of covalently crosslinked ionenes. *Polymer* **222**, 123641 (2021).
75. Bruker AXS, Inc. APEX3 (2019).
76. Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination. *J. Appl. Crystallogr.* **48**, 3–10 (2015).
77. Sheldrick, G. M. Crystal structure refinement with it SHELXL. *Acta Crystallogr. Sect. C* **71**, 3–8 (2015).
78. Murbach, M. D., Gerwe, B., Dawson-Elli, N. & Tsui, L. impedance.py: a Python package for electrochemical impedance analysis. *J. Open Source Softw.* **5**, 2349 (2020).
79. Cho, U., Kim, S., Shin, C. Y. & Song, I. Tabletop fabrication of high-performance MoS₂ field-effect transistors. *ACS Omega* **7**, 21220–21224 (2022).
80. Jeong, B.-Y. et al. Highly conductive self-healable rhenium oxide–polytetrahydrofuran composite for resilient flexible electrode. *ACS Mater. Lett.* **4**, 1944–1953 (2022).
81. Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169–11186 (1996).
82. Kresse, G. & Hafner, J. Ab initio molecular dynamics for liquid metals. *Phys. Rev. B* **47**, 558–561 (1993).
83. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
84. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **59**, 1758–1775 (1999).
85. Wang, V., Xu, N., Liu, J.-C., Tang, G. & Geng, W.-T. VASPKIT: a user-friendly interface facilitating high-throughput computing and analysis using VASP code. *Comput. Phys. Commun.* **267**, 108033 (2021).
86. Frisch, M. J. et al. *Gaussian 16 Rev. C.01* (2016).
87. Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **98**, 5648–5652 (1993).
88. Weigend, F. Accurate Coulomb-fitting basis sets for H to Rn. *Phys. Chem. Chem. Phys.* **8**, 1057–1065 (2006).
89. Weigend, F. & Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **7**, 3297–3305 (2005).

Acknowledgements

We thank Nak Cheon Jeong (DGIST) for insightful comments on this work. This research is funded by National Research Foundation of Korea (NRF) (2022R1A2C4002070 (S.M.Y.), RS-2023-00217555 (I.S.), and RS-2024-00455116 (I.S.)).

Author contributions

I.S. and S.M.Y. conceived the experiments and secured funding. M.P., H.J., K.P., and I.S. performed experiments. H.J. acquired and refined SCXRD data. J.O. and H.L. performed theoretical calculations. All authors were involved in the writing of the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at <https://doi.org/10.1038/s41467-025-56541-2>.

Correspondence and requests for materials should be addressed to Hyunseob Lim, Seok Min Yoon or Intek Song.

Peer review information *Nature Communications* thanks the anonymous reviewers for their contribution to the peer review of this work. A peer review file is available.

Reprints and permissions information is available at <http://www.nature.com/reprints>

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License, which permits any non-commercial use, sharing, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if you modified the licensed material. You do not have permission under this licence to share adapted material derived from this article or parts of it. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by-nc-nd/4.0/>.

© The Author(s) 2025