

Molecule-based Proton–Electron Mixed Conductor with the Highest Ambipolar Conductivity

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ABSTRACT: Proton–electron mixed conductors (PEMCs) are an essential component for potential applications in hydrogen separation and energy conversion devices. However, the exploration of PEMCs with excellent mixed conduction, which is quantified by the ambipolar conductivity, $\sigma_{\text{amb}} = \sigma_e \sigma_H / (\sigma_e + \sigma_H)$ (σ_e : electronic conductivity; σ_H : proton conductivity), is still a great challenge, largely due to the lack of structural characterization of both conducting mechanisms. In this study, we prepared a molecule-based proton–electron mixed-conducting cation radical salt, $(\text{ET})_4[\text{Pt}_2(\text{pop})_2(\text{Hpop})_2] \cdot \text{PhCN}$ (ET: bis(ethylenedithio)tetrathiafulvalene, pop^{2-} : $\text{P}_2\text{H}_2\text{O}_5^{2-}$), by electrocrystallization. The salt shows metallic electronic conduction, which arises from the $(\text{ET})_2^{+\bullet}$ layers, with a high σ_e value ($1\text{--}2 \text{ S cm}^{-1}$ at room temperature). The metallic state was corroborated by magnetic susceptibility measurement and band structure calculation. The salt also shows superprotonic conduction ($\sigma_H = 2.1 \times 10^{-2} \text{ S cm}^{-1}$ at room temperature under dried conditions), which relies on the one-dimensional (1D) hydrogen-bonding network of protonated paddlewheel-type Pt-dimer complex anions, $[\text{Pt}_2(\text{pop})_2(\text{Hpop})_2]^{2-}$. Crystallographic and computational studies revealed the presence of infinite intra- and intermolecular O–H $\cdots$ O hydrogen bonds, which show a double-well-like potential energy curve with a negligible energy barrier in the 1D chain, facilitating Grotthuss-type proton hopping via Lewis basic sites. Among the structurally-defined PEMCs, the present salt displays the highest room-temperature σ_{amb} value of $2.1 \times 10^{-2} \text{ S cm}^{-1}$ even under dried conditions. The σ_{amb} value has the same order as those of reported perovskites-type metal oxides at high temperatures and achieves a level that is beneficial for the practical applications.

INTRODUCTION

Proton–electron mixed conductors (PEMCs) have manifested their significance over past several decades as essential components in practical applications such as hydrogen separation, gas sensors, actuators, and fuel cells.^{1–3} Over a long period, inorganic metal oxides, such as perovskites,^{4,5} and organic polymers, such as PEDOT:PSS [PEDOT: poly(3,4-ethylenedioxythiophene); PSS: poly(4-styrenesulfonate)]^{6,7} have been extensively studied as potential PEMCs. However, to effectively design advanced PEMCs, a major challenge lies in clarifying the relationship between the mixed conduction and structural characteristics, which remains poorly understood due to their undefined structures and conducting mechanisms.

Molecule-based solids are emerging as a promising platform for introducing multifunctionality based on the established structure–property relationship because of their high designability and well-defined structures. For example, the coexistence of electronic conductivity with magnetism, including spin crossover,⁸ magnetic ordering,^{9,10} and single-molecule magnetism,¹¹ has been achieved by judicious design or choice of cationic π -conjugated molecules and metal complex anions. Regarding PEMCs, Day and his coworkers have reported the first proton–electron mixed conducting cation radical salt, combining cationic bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET;

Figure 1a) molecules with metal oxalate complex anions and 18-crown-6.¹² The salt showed a relatively high room-temperature ambipolar conductivity (σ_{amb}), defined by the equation $\sigma_{\text{amb}} = \sigma_e \sigma_H / (\sigma_e + \sigma_H)$ (σ_e : electronic conductivity; σ_H : proton conductivity), in the order of $10^{-3} \text{ S cm}^{-1}$, which is crucial for hydrogen permeability in the hydrogen separation process.^{13–16} However, the σ_{amb} value is still insufficient for PEMCs to be used in hydrogen separation at an industrial level ($> 10^{-2} \text{ S cm}^{-1}$).^{1,2,17,18} In addition, in the aforementioned salt, the activation energy for proton conduction (E_a) is very high ($> 1.0 \text{ eV}$), suggesting proton conduction primarily through the vehicle mechanism, involving the transfer of a protonated Lewis base in space;^{19–21} however, it remains unclear whether the species of the Lewis base is H_2O or NH_3 , which is a serious obstacle to the further development of molecule-based PEMCs. Very recently, our group reported a molecule-based PEMC with $\sigma_{\text{amb}} \sim 10^{-6} \text{ S cm}^{-1}$, in which partially oxidized TTF molecules are arranged in a hydrogen-bonding framework of protonated paddlewheel-type Pt-dimer complex anions.²² The semiconducting transport behavior ($\sigma_e = 1.3 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature) is well-explained by the localized electrons in the one-dimensional (1D) TTF arrays, whereas the proton conduction ($\sigma_H = 2.8 \times 10^{-6} \text{ S cm}^{-1}$ at room temperature) is attributed to the infinite O–H $\cdots$ O hydrogen-bonding networks through phosphonic acid moieties in the Pt-dimer. Crystallographic study revealed

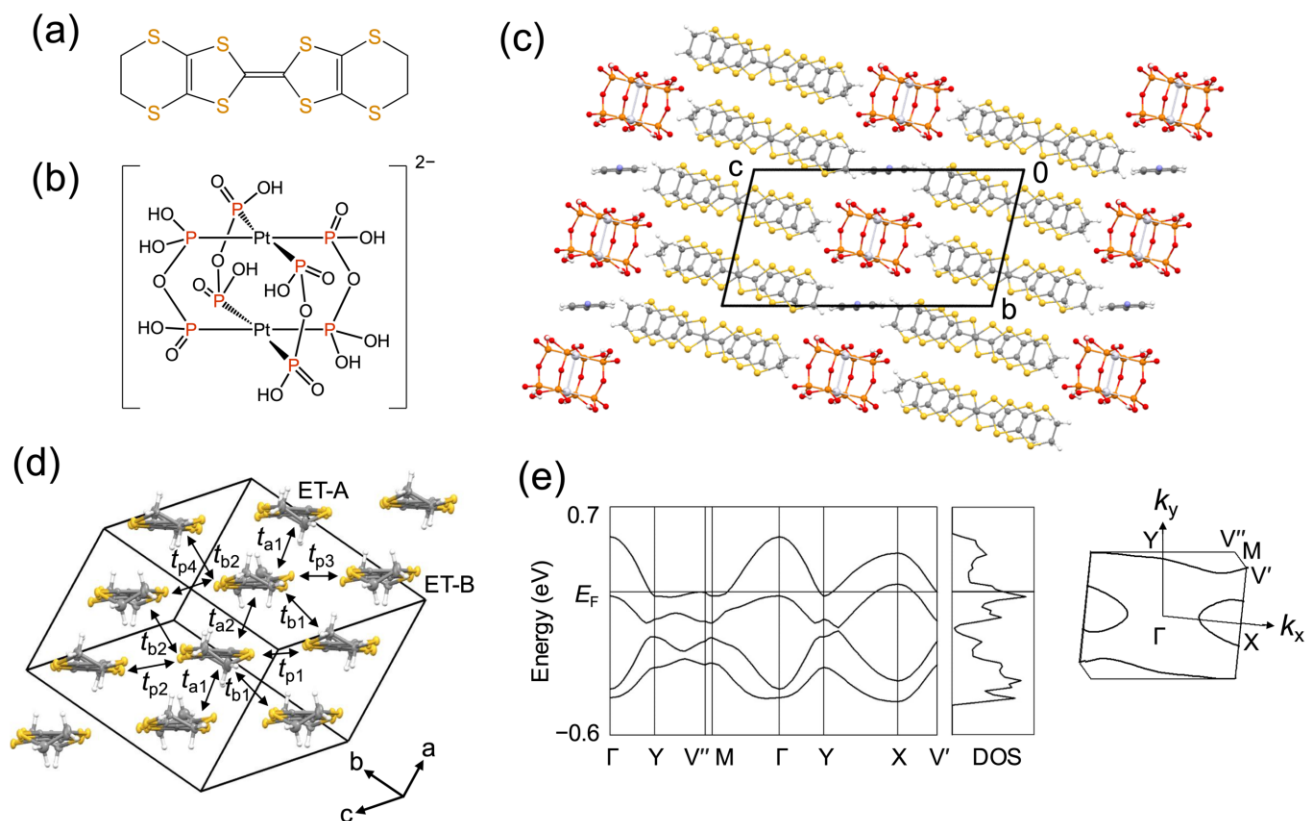


Figure 1. Molecular structures of (a) ET and (b) $[\text{Pt}_2(\text{pop})_2(\text{Hpop})_2]^{2-}$ anion. (c) Crystal structure of β'' -(ET) $_4[\text{Pt}_2(\text{pop})_2(\text{Hpop})_2]\cdot\text{PhCN}$ (**1**) viewed along the a axis. (d) β'' -type ET packing pattern in **1**. Calculated transfer integrals at 100 K are $t_{a1} = -58.2$ meV, $t_{a2} = -43.8$ meV, $t_{b1} = -176.7$ meV, $t_{b2} = -163.8$ meV, $t_{p1} = -97.0$ meV, $t_{p2} = 53.0$ meV, $t_{p3} = 92.9$ meV, and $t_{p4} = 95.6$ meV. (e) Calculated band dispersion, density of states (DOS), and Fermi surface of **1** at 100 K. The horizontal line shows the Fermi energy (E_F). Color code in (c) and (d): C, gray; H, white; N, blue; O, red; P, orange; Pt, silver; S, yellow.

that the proton conduction predominantly occurs through the Grotthuss mechanism;^{23,24} however, the presence of potential extra proton in the O-H...O bonds may disturb the sequential proton hopping for high σ_H .

To date, the cationic ET molecule, which possesses an extended π -conjugated system compared to TTF, has been combined with diverse transition-metal complex anions, leading to tremendous success in the search for new molecule-based metals and superconductors.^{9,25–27} In the salts, the assembly of monocationic ET dimers, $(\text{ET})_2^{+\bullet}$, can provide a half-filled conduction band, and the electronic conducting behavior varies depending on the arrangement of the ET molecules.^{26,28–30} Given that the counter anion has a significant effect on the ET packing structure, the judicious design of the metal complex anions can not only introduce Lewis acidic sites that are indispensable for achieving the proton transport but also modify the ET arrangement that is responsible for controlling the electronic transport. Thus, ET cation radical salts seem to be rather traditional but can provide new and more advanced PEMCs by rationally designing the protonic metal complex anions.

In this study, we prepared an ET-based proton-electron mixed-conducting cation radical salt, $(\text{ET})_4[\text{Pt}_2(\text{pop})_2(\text{Hpop})_2]\cdot\text{PhCN}$ (**1**) (pop^{2-} : $\text{P}_2\text{H}_2\text{O}_5^{2-}$), by the electrooxidation of ET in the presence of protonated paddlewheel Pt(II) dimers, $[\text{Pt}_2(\text{pop})_2(\text{Hpop})_2]^{2-}$ (Figure 1b). This salt demonstrates remarkable properties for proton-

electron mixed conduction; namely, metallic behavior with a high electronic conductivity ($\sigma_e = 1\text{--}2$ S cm^{-1}) and superprotonic conductivity ($\sigma_H = 2.1 \times 10^{-2}$ S cm^{-1}) at room temperature, even under dried conditions. Infinite hydrogen-bonding networks formed by the $\text{pop}^{2-}/\text{Hpop}^-$ ligands coordinated to Pt ions in a paddlewheel manner are responsible for the Grotthuss-type proton conduction with a low E_a value (0.15 eV). In particular, the salt shows the highest room-temperature σ_{amb} value of 2.1×10^{-2} S cm^{-1} among the structurally-defined materials, which is comparable to those of reported perovskites at high temperatures (> 850 °C) and the value required for the above-mentioned practical applications.^{1,2,17,18}

RESULTS AND DISCUSSION

Synthesis and Crystal Structure. Single crystals of **1** were successfully obtained using an electrooxidation method. A benzonitrile solution of ET and Pt-dimer precursor, $(\text{Bu}_4\text{N})_2[\text{Pt}_2(\text{pop})_2(\text{Hpop})_2]$,³¹ was added to the H-type cell and electrolyzed under a constant current (1.0 μA) at 20 °C over a period of 2 weeks, yielding dark brown elongated plate crystals of **1** (Figure S1; see Supporting Information for the details). Elemental analysis ensures the composition determined from the single-crystal X-ray diffraction (SCXRD) analysis. (see Supporting Information) We note that the obtained crystals remain stable even after storage in air for eight months (Figure S2).

Crystal structure of **1** was determined by SCXRD measurements at different temperatures: 100, 150, 200, 250, 273, and 298 K [Table S1; see the CIF files for details (2404979–2404984)]. The salt **1** crystallizes in a triclinic lattice with space group $P\bar{1}$, and the asymmetric unit contains two ET molecules (hereafter, ET-A and ET-B), half $[\text{Pt}_2(\text{pop})_2(\text{Hpop})_2]^{2-}$ ion, and half guest PhCN molecule. Bond length analysis³² revealed that the charges of the ET-A and ET-B are +0.23(7) and +0.61(7), respectively, at 298 K, which are possibly a sign of the development of charge disproportionation. It was suppressed by decreasing temperature; the charges were +0.34(7) and +0.47(7), respectively, at 100 K (Figure S3). Given that a pair of ET-A and ET-B form a dimer unit (see below), the charge of each dimer is almost temperature-independent and close to +1.

As shown in Figure 1c, the salt has a layered structure constructed by layers of ET and layers of Pt-dimers and PhCN. In the ET layer, cationic ET molecules are stacked along the *a* axis to achieve β'' -type packing pattern²⁸ within the *ab* plane (Figure 1d). Adjacent ET molecules are connected by short S...S contacts (3.43–3.56 Å vs sum of the van der Waals radii: 3.60 Å; ref. 33).^{34–36} The electronic band structure of **1** at 100 K was calculated by assuming uniform charge distribution of ET layer (i.e., +0.5 on each ET) within a tight-binding model based on the extended Hückel method (Figure 1e).³⁷ The values of the transfer integral (*t*), which relates to the overlap integral (*s*) between the highest occupied molecular orbitals (HOMOs) of ET^{0.5+} molecules according to the equation, $t = Es$ ($E = -10$ eV), were estimated to be −58.2 and −43.8 meV along the stacking direction ($//a$; t_{a1} and t_{a2}), −176.7 and −163.8 meV along the side-by-side direction ($//b$; t_{b1} and t_{b2}), and −97.0, 53.0, 92.9, and 95.6 meV along the oblique direction (t_{p1} – t_{p4}) (Figure 1d). The upper band is half-filled with a bandwidth (*W*) of 517 meV, whereas the on-site Coulomb repulsion on the ET dimer (U_d), calculated as $U_d = 2|t_{b1}|$,^{38,39} is 353 meV. The value of U_d/W (0.68), which is related to the electron correlation, strongly suggests that the salt has metallic electronic state. The Fermi surface consists of a quasi-1D electron-like surface along the k_y direction and a hole-like pocket at the X point, as observed in other β'' -type ET salts, such as β'' -(ET)₂AuBr₂⁴⁰ and β'' -(ET)₂SF₅CH₂CF₂SO₃.⁴¹

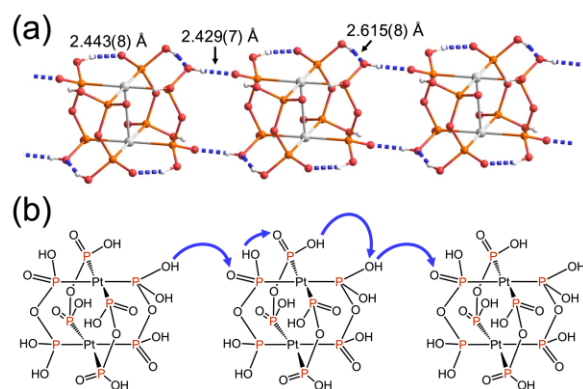


Figure 2. (a) Intra- and intermolecular O-H...O hydrogen bonds (blue dotted lines) of $[\text{Pt}_2(\text{pop})_2(\text{Hpop})_2]^{2-}$ ions in **1**. (b) Schematic representation of proton hopping pathway, as indicated by blue arrows. Color code in (a): H, white; O, red; P, orange; Pt, silver.

The protonated state of the Pt-dimer was assessed by examining the bond lengths determined by SCXRD analysis, according to the fact that the P-OH bond length is significantly longer than that of the P=O bond.⁴² As shown in Table S2, three of the four non-bridging P-O bonds are regarded as P-OH bonds in the two ligands (i.e., Hpop⁻), whereas the other two ligands have two single- and two double-bond characters in the non-bridging P-O bonds (i.e., pop²⁻).³¹ Given that X-ray photoelectron spectroscopy (XPS) demonstrated the valence state of Pt ions to be +2 (see below), the presence of two protonated Hpop⁻ ligands

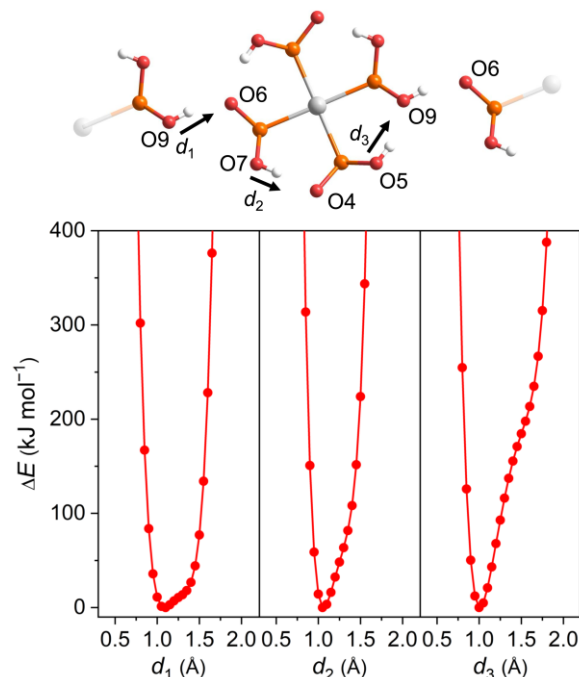


Figure 3. Potential energy curves of the proton in inter- and intramolecular O-H...O hydrogen bonds (O9-H9...O6, O7-H7...O4, and O5-H5...O9 from left to right) in **1**, using the crystal structure determined by the SCXRD measurement at 100 K. The curve in the O5-H5...O9 hydrogen bond was calculated with the assumption that H9 is attached to the neighboring O6. d_1 , d_2 , and d_3 represent the O9-H9, O7-H7, and O5-H5 distances, respectively (top panel). Color code: H, white; O, red; P, orange; Pt, silver.

ligands in a Pt-dimer results in the dianionic state of $[\text{Pt}_2(\text{pop})_2(\text{Hpop})_2]^{2-}$ units in **1**, which guarantees the charge neutrality with (ET)₂⁺ in the composition. In the anionic layer, the Pt-dimers form a 1D infinite chain along the *a* axis through double complementary O-H...O hydrogen bonds between the intermolecular adjacent Hpop⁻ ligands (O...O distance: 2.429(7) Å vs sum of the van der Waals radii: 3.04 Å;³³ Figure 2a). We note that the O...O distance lies between the typical values affording a single- (ca. 2.20 Å) and double- (ca. 2.66 Å) well potential energy curves of the proton in an O-H...O hydrogen bond.⁴³ In addition, there are intramolecular O-H...O hydrogen bonds with an O...O distance of 2.443(8)–2.615(8) Å. Theoretical calculations predicted that the intra- and intermolecular O-H...O hydrogen bonds show a double-well-like potential energy curve with a negligible barrier (Figure 3).^{43–45} Thus, it is obvious that the protons in the hydrogen bonds are

highly active to facilitate the efficient proton hopping in the 1D infinite chain.

Electronic States. Powder X-ray diffraction (PXRD) pattern of the polycrystalline sample of **1** matched well with that simulated from SCXRD data (Figure S4 and S5), indicating the high purity of the polycrystalline sample suitable for the following characterizations. XPS measurements were performed to examine the valence state of the Pt ions (Figure S6). The spectrum exhibits two peaks of Pt $4f_{5/2}/4f_{7/2}$; the binding energy of the $4f_{7/2}$ peak (73.75 eV) is clearly comparable to that reported for a congeneric divalent salt, $K_4[Pt_2(pop)_4]$ (73.7 eV).^{46,47} In addition, the Pt–Pt distance in the Pt-dimer (2.94 Å), determined by the SCXRD analysis, is comparable to those in paddlewheel Pt(II) dimers.^{48–50} Thus, it is evident that the Pt ions in **1** are in a divalent state, as demanded by the charge neutrality in the salt.

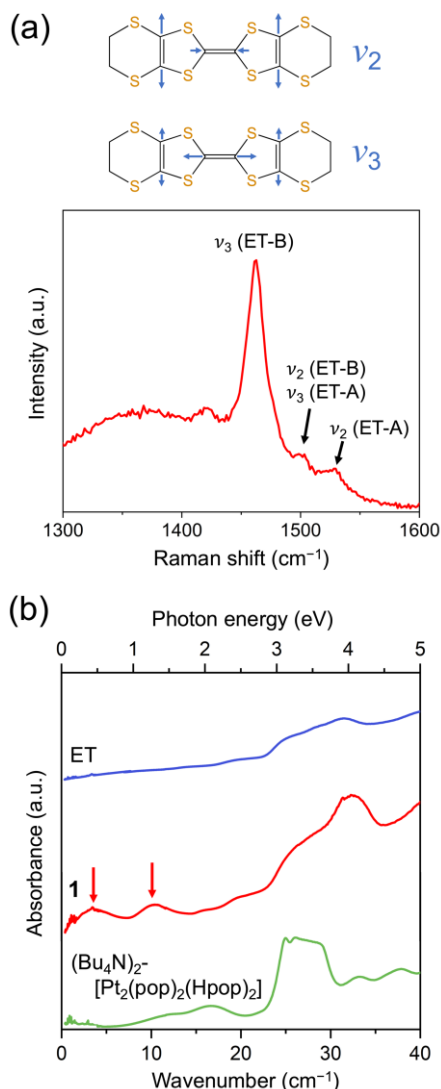


Figure 4. (a) Raman spectrum of **1** in the frequency region of ν_2 and ν_3 modes, with the polarization direction of the incident light parallel to the crystallographic a axis. The top panel shows an illustration of the ν_2 and ν_3 modes in an ET molecule. (b) UV-vis-NIR spectra of **1** (red), ET (blue), and $(Bu_4N)_2[Pt_2(pop)_2(Hpop)_2]$ (green) measured on the dispersed KBr pellets (see text for red arrows).

Raman measurements were performed on a single crystal of **1** to gain information on the charge state of ET molecules. It is known that there is an approximately linear relationship between the charge degree of ET molecule and the Raman-active C=C stretching frequencies.^{51–54} In this study, Raman-active ν_2 and ν_3 modes, which are predominantly the C=C stretching vibrations in the TTF moiety (top panel in Figure 4a), were used to estimate the charge state of ET molecules in **1**. Figure 4a shows the Raman spectrum of **1**, with an incident light polarized along the crystallographic a axis. An intense band at 1470 cm^{-1} is assigned to the ν_3 mode of the charge-rich ET (i.e., ET-B), which must show a ν_2 band at approximately 1500 cm^{-1} , as observed. It seems that the 1500 cm^{-1} -band also corresponds to the ν_3 mode of the charge-poor ET (i.e., ET-A), and the ν_2 mode of ET-A is visible at 1529 cm^{-1} . The spectral results unequivocally confirmed the charge disproportionation indicated by the bond length analysis.

Ultraviolet–visible–near-infrared (UV-vis-NIR) absorption spectroscopy was performed to elucidate the electronic state of ET layers in **1**. As shown in Figure 4b, the spectrum of **1** exhibits two distinct low-energy bands at 3.1×10^3 and $10.4 \times 10^3\text{ cm}^{-1}$. The former band is reminiscent of the so-called A band, defined as the intermolecular charge

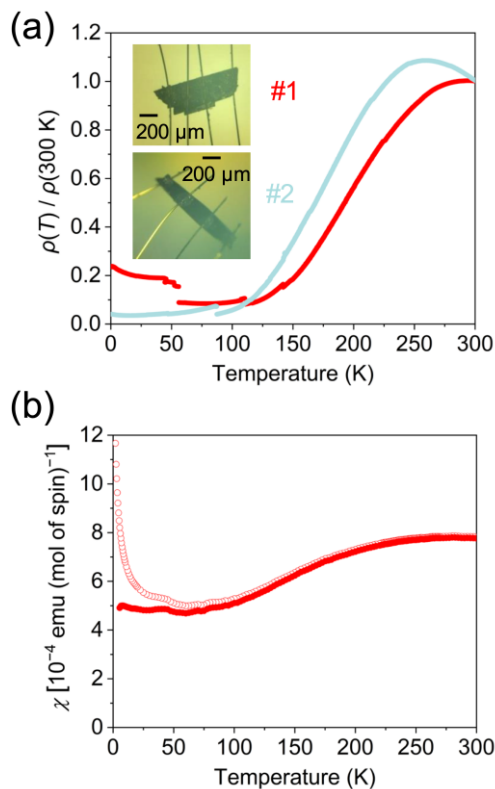


Figure 5. (a) Temperature dependence of the DC resistivity (ρ) normalized to its value at 300 K of two different single crystals of **1** (red: #1, pale blue: #2) along the stacking direction ($//a$). Insets are the photographs of the crystals attached with four gold wires. (b) Temperature dependence of magnetic susceptibility (χ) of polycrystalline **1** in an applied magnetic field of 10 kOe (red open circles). Red closed circles indicate the χ values after subtracting 0.4% of the Curie tail. Both measurements were conducted during the cooling process.

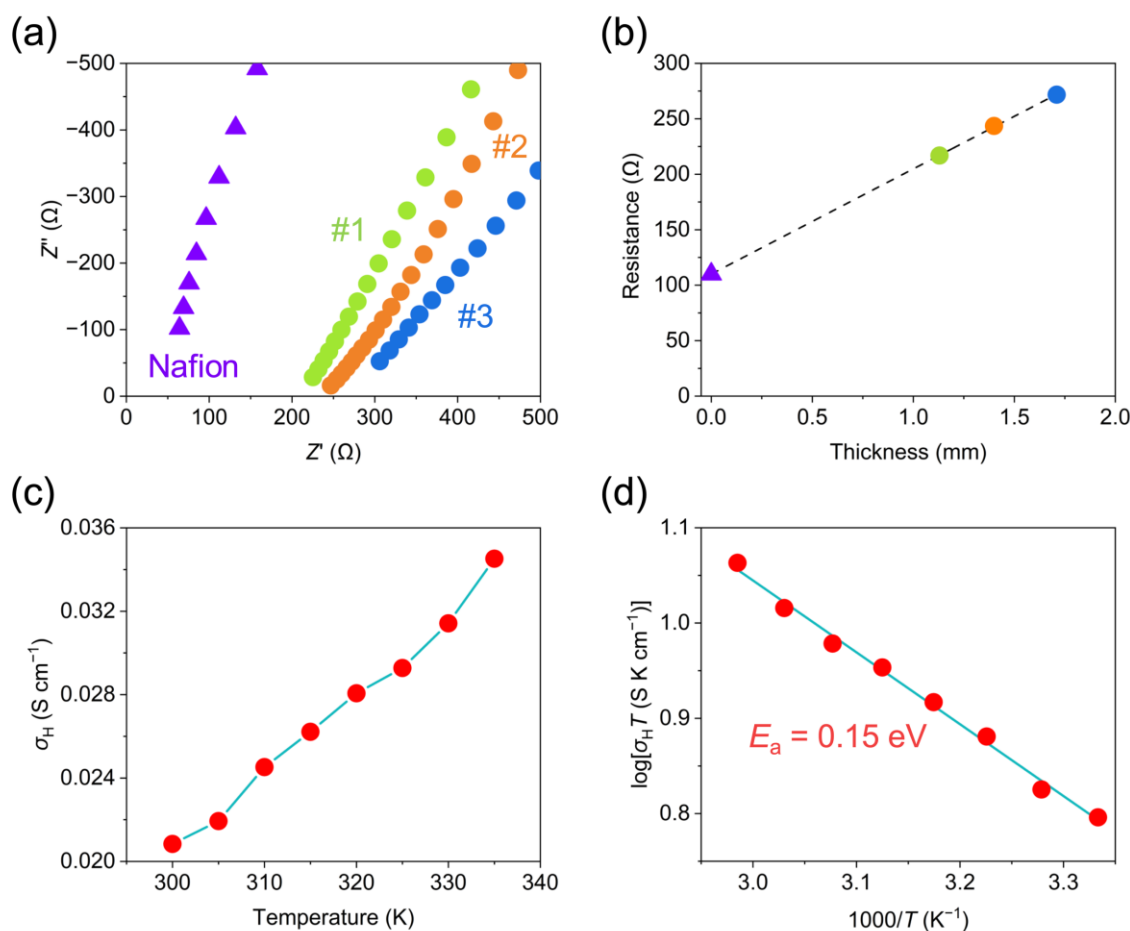


Figure 6. (a) Nyquist plots of the impedance spectra of pelletized **1** with different thicknesses (pale green: 1.13 mm (#1), orange: 1.40 mm (#2), blue: 1.71 mm (#3)) and a Nafion membrane (purple triangles) at 25 °C and 30% RH. (b) Relationship between the resistance and the thickness of the pellet of **1**, where the symbols are identical with those in (a). The intercept of the extrapolation line is consistent with twice the resistance of a Nafion membrane (see text for details). (c) Temperature dependence of average proton conductivity (σ_H) of the three pellets under 30% RH. (d) Arrhenius plot of $\sigma_H T$ under 30% RH, where the line is fit to the Arrhenius equation.

transfer transition ($ET^+ ET^0 \rightarrow ET^0 ET^+$) band in the partially oxidized ET array.^{26,55,56} Then it is most likely that the latter band arises from the intramolecular HOMO-2 to HOMO transition of an ET radical cation (so-called C band).^{26,55,56} The observation of A and C bands is consistent with the formation of two-dimensional layers of $(ET)_2^{+*}$, as evidenced by SCXRD and Raman spectroscopy results. Higher-energy bands ($> 12 \times 10^3$ cm⁻¹) of **1** are attributed to intramolecular transitions in the ET molecule^{56,57} and $[Pt(pop)_2(Hpop)_2]^{2-}$ anion.^{46,50}

Electronic Properties. DC resistivity measurements were performed on two different single crystals of **1** (#1 and #2) using the standard four-probe method with the current flowing along the *a* axis. As expected from the calculated band structure, #1 shows the metallic temperature dependence of resistivity (ρ) with a relatively high room-temperature electronic conductivity ($\sigma_e = 2.0$ S cm⁻¹; Figure 5a). Although #2 shows thermal activated behavior at around room temperature ($\sigma_e = 1.1$ S cm⁻¹ at room temperature), it undergoes metallic behavior down to 1.8 K after a resistivity maximum at ca. 250 K. We note that such

sample-dependent behavior, especially at around room temperature, has been reported in other ET-based conductors.^{58,59} It is possible that the suppression of metallic behavior at around room temperature in both crystals is a reflection of the subtle charge disproportionation of ET molecules, as indicated by the SCXRD data. As can be seen in Figure 5a, both crystals exhibit an abrupt resistivity jump at low temperatures. Given that the temperature varies from sample to sample, it is apparently caused by the formation of the crack growth in the crystal.

The magnetic susceptibility (χ) of polycrystalline **1** was measured under an applied magnetic field of 10 kOe (Figure 5b). The χ value after subtracting the core diamagnetic contribution approximated by Pascal's constants was estimated to be 7.82×10^{-4} emu (mol of spin)⁻¹ at 300 K. This value is greater than that for conventional organic metals ($< ca. 5 \times 10^{-4}$ emu (mol of spin)⁻¹),²⁶ possibly because of the partial suppression of itinerant electronic behavior by the subtle charge disproportionation of ET molecules at around room temperature. Thus, it is most likely that the steady decrease in χ upon cooling is associated with the di-

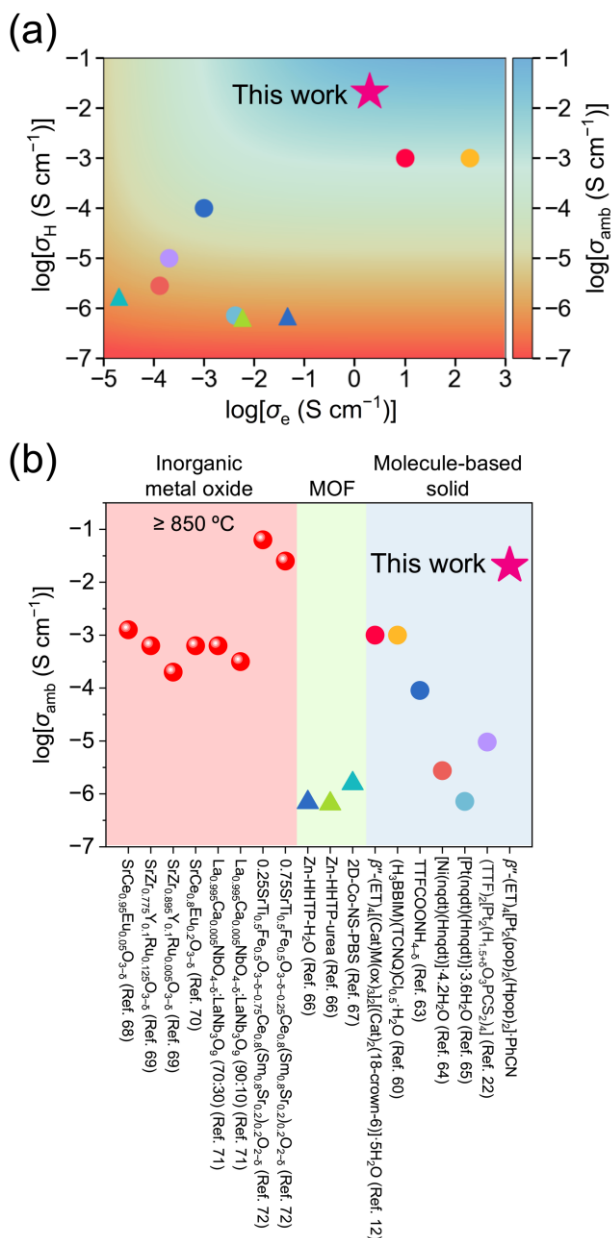


Figure 7. Comparison of the proton-electron mixed condition of **1** with those of reported PEMCs;^{12,22,60,63–72} (a) proton (σ_H) and electronic (σ_e) conductivities at room temperature under dried conditions and (b) ambipolar conductivity (σ_{amb}). Background color in (a) represents the σ_{amb} value. Cat: H_3O^+ or NH_4^+ ; TTF: tetrathiafulvalene; nqdt²⁻: 1,4-naphthoquinone-2,3-dithiolate; H3BBIM⁺: 2-(2-1*H*-benzimidazolyl)-1*H*-benzimidazolium; TCNQ: 7,7,8,8-tetracyanoquinodimethane; HHTP: hexahydroxytriphenylene.

sappearance of the charge disproportionation. Although the χ value exhibits a Curie-like upturn (0.4%) in the low-temperature region (< 50 K) due to crystal defects and/or Curie impurity, it is obvious that **1** shows Pauli paramagnetic behavior down to low temperatures, as expected from the metallic transport behavior.

Protonic Properties. Finally, we measured the proton conductivity (σ_H) of **1** using its pelletized sample, sandwiched with two Nafion membranes as electron blocking electrodes (Figure S7).^{12,22,60} Figure 6a shows the Nyquist

plots obtained from AC impedance measurements at 25 °C under dried conditions (30% RH). We conducted the measurements of three pelletized samples with different thicknesses (#1: 1.13 mm, #2: 1.40 mm, and #3: 1.71 mm) to evaluate the intrinsic resistance because the impedance spectra exhibited only the linear-like plot due to the AC frequency limitation (< 1 MHz). As shown in Figure 6b, the resistance (R) estimated using the equivalent circuit displayed in Figure S8 shows the linear variation with the thickness, and the intercept resistance (110 Ω) is in good agreement with the value of a Nafion membrane (R_{Nafion}). Thus, the proton conductivity of **1** can be estimated based on the equation $\sigma_H = L/(R - 2R_{\text{Nafion}})S$, where L and S represent the thickness and area of the pellet, respectively (Figure S9). It is noteworthy that the σ_H value at 300 K under 30% RH (2.1×10^{-2} S cm⁻¹), which was estimated as the average of the three pellets, is exceptionally high. This value is of the same order of magnitude as that of the Nafion membrane at room temperature under wet conditions (ca. 7×10^{-2} S cm⁻¹).⁶¹ Figure 6c shows the temperature dependence of the average σ_H under 30% RH; the σ_H value steadily increases with increasing temperature. The Arrhenius-type activation behavior becomes more explicit when the logarithmic of $\sigma_H T$ is plotted as a function of the reciprocal of T (T : absolute temperature; Figure 6d). Using the equation $\sigma_H T = A \exp(-E_a/k_B T)$ (A : pre-exponential factor, k_B : Boltzmann constant), the E_a was estimated to be 0.15 eV, which indicates that proton transfer is governed by the Grotthuss mechanism ($E_a < 0.4$ eV),⁶² involving proton migration through an infinite hydrogen-bonding network. It is apparent that the presence of active proton in intra- and intermolecular O–H···O bonds (Figure 3) in the infinite hydrogen-bonding network (Figure 2b and S10) must be responsible for the sequential proton hopping, i.e., the Grotthuss-type proton conduction with a low E_a value. We note that the salt **1** is the first example of the metallic salt exhibiting Grotthuss-type proton conduction, where the hydrogen-bonding network was crystallographically identified as a proton conducting pathway. This is in contrast to the undefined proton conducting pathway in two reported molecule-based metallic salts with the fast proton conduction, which involve the $\text{H}_2\text{O}/\text{Cl}$ -disorder⁶⁰ and unidentified Lewis base species (H_2O or NH_3).¹² In addition, the salt **1** shows the highest σ_{amb} value in the order of 10^{-2} S cm⁻¹ (2.1×10^{-2} S cm⁻¹ at room temperature), which surpasses the values of all reported structurally-defined PEMCs, including molecule-based solids and metal-organic frameworks (MOFs) (Figure 7a and 7b).^{12,22,60,63–67} It is noteworthy that the σ_{amb} value is comparable to those of proton-electron mixed conducting perovskite-type metal oxides at high temperatures (Figure 7b).^{68–72} Apparently, the present metallic salt with σ_{amb} of the order of 10^{-2} S cm⁻¹ is a promising synthetic approach, aiming to achieve a level that is beneficial for the above-mentioned practical applications, such as hydrogen permeation membranes for hydrogen separation.^{1,2,17,18}

CONCLUSIONS

In summary, we synthesized the first example of the molecule-based metallic salt exhibiting superprotonic conductivity via the Grotthuss mechanism. The salt has a layered structure, constructed by layers of cationic ET mole-

cules and layers with protonated Pt-dimer complex anions. The β'' -type arrangement of ET molecules results in the metallic electronic state down to low temperatures. Intra- and intermolecular O–H...O hydrogen bonds, which show a potential energy curve with a negligible barrier, of the protonated Pt-dimer complex anions apparently construct the efficient proton conducting pathway. Remarkably, the salt shows the highest room-temperature ambipolar conductivity, even under dried conditions, among the structurally-defined PEMCs. The value in excess of 10^{-2} S cm $^{-1}$ is comparable to those of inorganic metal oxides, such as perovskite, at high temperatures (> 850 °C) and that required for industrial hydrogen separation. This work provides a strategic framework for designing and synthesizing new and high-performance molecule-based PEMCs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Details of experimental procedures, photograph of the sample, additional XRD data, XPS spectrum, TG profile, and additional impedance spectra.

Accession Codes

CCDC 2404979–2404984 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033.

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Notes

Any additional relevant notes should be placed here.

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