

An Approach to an Ideal Molecule-Based Mixed Conductor with Comparable Proton and Electron Conductivity

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ABSTRACT: We synthesized a molecule-based proton–electron mixed conductor (PEMC), Pt(III) dithiolate complex with 1,4-naphthoquinone skeletons. The π -planar Pt complex involves a π -stacking column, which is connected with each other by one-dimensional hydrogen bonding chains composed of water molecules. Room-temperature (RT) proton conductivity is $8.0 \times 10^{-5} \text{ S cm}^{-1}$ under ambient condition, which is more than two orders higher than that of the isomorphous Ni complex ($7.2 \times 10^{-7} \text{ S cm}^{-1}$). The smaller activation energy (0.23 eV) than that of the Ni complex (0.42 eV) possibly originates from the less dense water, which promotes the reorientational dynamics, in the Pt complex with expanded lattice; namely, negative chemical pressure upon substitution of Ni by a larger Pt. In addition, the Pt complex shows a relatively high RT electronic conductivity of $1.0 \times 10^{-3} \text{ S cm}^{-1}$ brought about by the π -columns, approaching an ideal PEMC with comparable proton and electron conduction.

INTRODUCTION

Proton–electron mixed conductors (PEMCs) have been the subject of intensive research over past years because of their potential applicability for gas sensors, actuators, water electrolysis, and fuel cells.¹ To date, most existing PEMCs are inorganic metal oxides such as perovskites² or organic polymers such as PEDOT:PSS (PEDOT: poly(3,4-ethylenedioxythiophene), PSS: poly(4-styrenesulfonate)).³ The former provided a practical way of applying electrodes for fuel cells at elevated temperatures, whereas the latter constitutes significant engineering drawbacks due to their non-crystalline form. To guide the rational design of prominent PEMCs, the correlation between the proton/electron transports and structural geometries (i.e., molecular and crystal structures) must be well understood; however, the study of the relationship between structure and properties is still in its infancy.

Molecule-based PEMCs, especially of π -conjugated metal complexes are a promising platform because of their high designability with defined structures based on numerous combinations of metal ions and organic ligands. Metal dithiolate complexes have been the subject of extensive research as representative single-component electronic conductors.⁴ It is apparent that introduction of multiple sulfur atoms is responsible for the increased dimensionality and the decreased HOMO–LUMO energy gap. Although the chemical modification of the ligands can introduce Lewis basic sites that are indispensable for the proton transport via Grotthuss mechanism (or proton hopping),⁵ it is fair to say that the research for proton conduction is still limited as compared with the electron conduction in the metal dithiolate complexes.

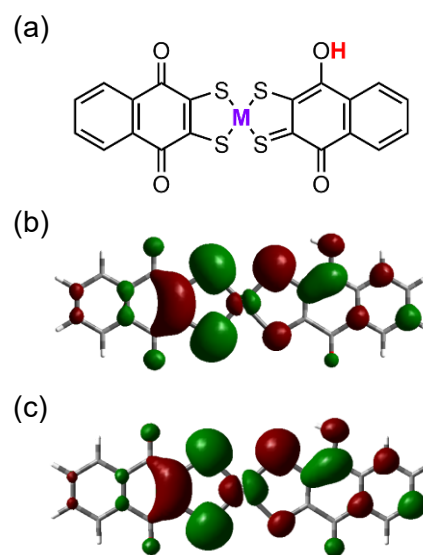


Figure 1. (a) Molecular structure of $[M^{III}(\text{Hnqdt})(\text{nqdt})]$ ($M = \text{Ni}$ or Pt). Calculated singly occupied molecular orbitals of (b) $[\text{Ni}^{III}(\text{Hnqdt})(\text{nqdt})]$ and (c) $[\text{Pt}^{III}(\text{Hnqdt})(\text{nqdt})]$.

Very recently, we synthesized a dithiolate complex of nickel(III) with d^7 electron configuration formed with 1,4-naphthoquinone skeletons as Lewis acidic/basic sites, $[\text{Ni}^{III}(\text{Hnqdt})(\text{nqdt})] \cdot 4.2\text{H}_2\text{O}$ (nqdt^{2-} : 1,4-naphthoquinone-2,3-dithiolate; **Ni-H**; Figure 1a).⁶ It showed both proton and electron conduction; however, room-temperature (RT) proton conductivity is less than RT electronic conductivity by four orders of magnitude. Thus it is apparent that the estab-

lishment of rational design of molecule-based PEMCs, especially for the increase in proton conductivity, is a key to develop an ideal PEMC that shows comparable proton and electron conduction. The prominent mixed (ambipolar) conduction can lead to the high hydrogen permeation flux desirable for hydrogen separation membranes.^{1,2,7}

Considering the fact that Grotthuss-type proton conductivities of some metal complexes⁸ and acid-doped polymers⁹ were steadily decreased by applying physical pressure, application of “negative” chemical pressure¹⁰ by substitution of Ni(III) by a larger atom to expand the crystal lattice may lead to the increase in proton conductivity. We note that there are very limited physical methods to apply negative pressure.¹¹ In this study, therefore, we synthesized the Pt(III) counterpart, [Pt(Hnqdt)(nqdt)], and found that the RT conductivities for proton and electron approach each other compared with those in **Ni-H** mainly owing to the significant increase in proton conductivity.

RESULTS AND DISCUSSION

(NH₄)[Pt^{III}(nqdt)₂] was synthesized following the reported procedures for (NH₄)[Ni(nqdt)₂]⁶ and (TBA)₂[Pt(nqdt)₂].¹² Crude product of the protonated complex, [Pt^{III}(Hnqdt)(nqdt)], was obtained by the addition of hydrochloric acid to a methanol solution of (NH₄)[Pt(nqdt)₂]. Cation exchange from NH₄⁺ to H⁺ was confirmed by the disappearance of an N–H stretching band at 3170 cm^{−1} in the infrared (IR) spectrum (Figure S1), although the proton might be partially shared with water molecules in the lattice forming the hydrogen bonding network. Details of the synthetic procedures are given in Supporting Information. Vapor diffusion of diethyl ether into a methanol solution of the crude [Pt(Hnqdt)(nqdt)] yielded black rod-shaped single crystals, whereas black polycrystalline product was yielded by the rapid addition of diethyl ether to an acetone solution of the crude [Pt(Hnqdt)(nqdt)] followed by the sonication of a dispersed water of the precipitation. Powder X-ray diffraction (XRD) measurements showed that the polycrystalline sample is isostructural with the single-crystalline sample (Figure S2). Chemical composition was determined as [Pt(Hnqdt)(nqdt)]·3.6H₂O (**Pt-H**) by the elemental analysis of polycrystalline sample (Calcd for Pt₁C₂₀H_{16.2}O_{7.6}S₄: C, 34.24; H, 2.33; N, 0.00%. Found: C, 34.43; H, 2.03; N, 0.08%).¹³

Single-crystal XRD measurements revealed that **Pt-H** belongs to a monoclinic lattice with space group *I2/m* at 298 K (Figure 2a)¹⁴ and is isostructural with **Ni-H**. A central platinum atom is located at an inversion center and an asymmetric unit contains a quarter of [Pt(Hnqdt)(nqdt)] molecule, adopting a perfect square planar environment ($\tau_4 = 0$).¹⁵ As well, a hydrogen atom bound to quinoid oxygens is positionally disordered over four equivalent sites due to the crystallographically imposed symmetry. Oxygen atoms of water molecules, as indicated by elemental analysis, are located on three crystallographically independent sites (O2, O3, and O4). Given that PLATON/SQUEEZE¹⁶ estimated a residual electron count of 36 e[−], corresponding to 3.6 water molecules per [Pt(Hnqdt)(nqdt)] molecule, occupancies of the water oxygens were refined with the restriction of the sum of oxygen atoms to 3.6 per [Pt(Hnqdt)(nqdt)] molecule (0.726(9) for O2, 0.725(9) for O3, and 0.350(9) for O4). We

note that the value is in good accordance with that estimated from the elemental analysis of polycrystalline sample.

The [Pt(Hnqdt)(nqdt)] molecule with a nearly flat geometry forms a uniform π -stacking column through short heteroatomic S···S contacts (3.56 Å vs. sum of van der Waals radii: 3.60 Å¹⁷) along the *a* axis (Figure 2b). It is possible that the short interplanar distance (3.50 Å) indicates the formation of significant π - π interactions, affording an infinite electronic conduction path. Our density functional theory (DFT) calculations using B3LYP with 6-31++G(d,p) (C, H, O, and S) and SDD (Ni and Pt) basis set predicted that the singly occupied molecular orbital (SOMO) of [Pt^{III}(Hnqdt)(nqdt)], extends to the π -conjugated plane (Figure 1c) as in the case of [Ni^{III}(Hnqdt)(nqdt)] (Figure 1b), which allows the electronic conduction within the π -stacking column. Along the side-by-side direction, the columns are connected to each other with O–H···O hydrogen bonds via water molecules (O···O: 2.26 Å vs. sum of van der Waals radii: 3.04 Å;¹⁷ Figure 2c). As shown in Figure 2d, the water molecules (O2 and O3) form a one-dimensional (1D) hydrogen bonding network along the *a* axis, which is parallel to the π -stacking column.

Electronic band structure of **Pt-H** was calculated using Perdew–Burke–Ernzerhof (PBE) functional and projector-augmented-wave pseudopotential on the crystallographic

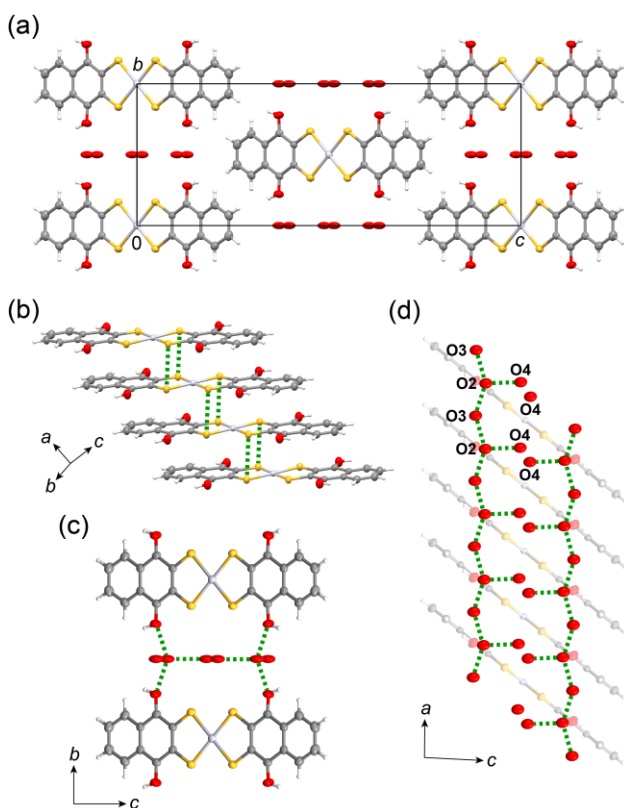


Figure 2. Crystal structure of **Pt-H** (gray, C; white, H; red, O; yellow, S). (a) Molecular arrangement viewed along the *a* axis. (b) Uniform π -stacking column through short heteroatomic S···S contacts shown by green dotted lines. (c) Side-by-side intermolecular O–H···O hydrogen bonds shown by green dotted lines. (d) One-dimensional hydrogen bonding network of water molecules through O–H···O hydrogen bonds shown by green dotted lines.

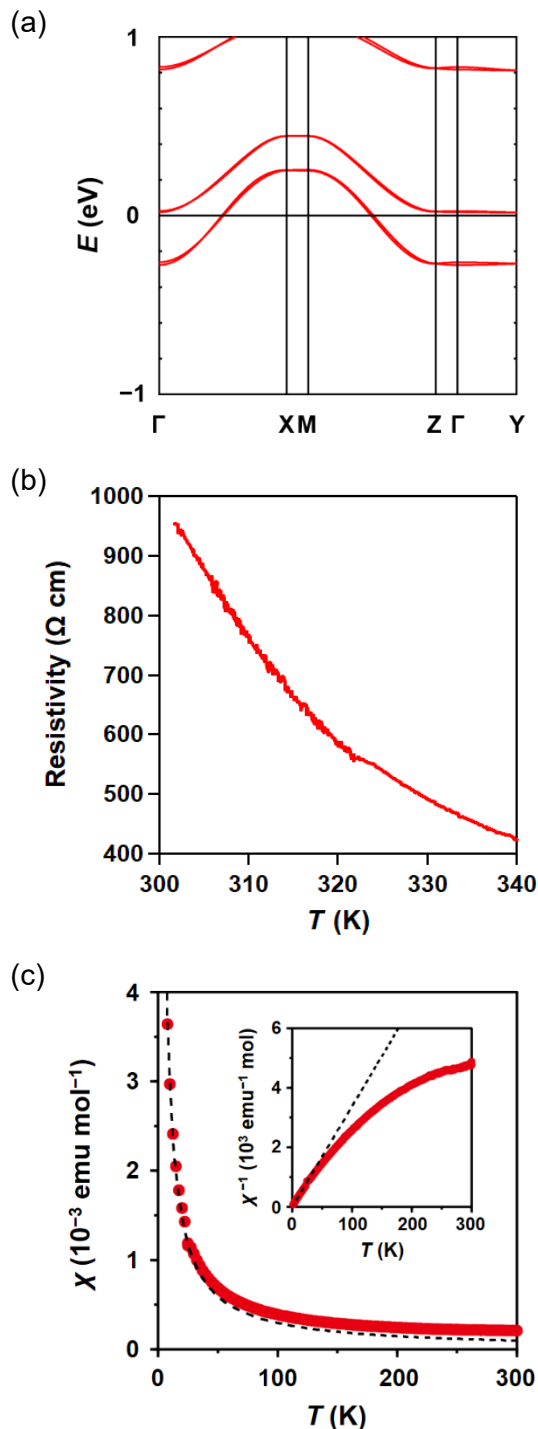


Figure 3. (a) Calculated band dispersion of [Pt(Hnqdt)(nqdt)] in **Pt-H** at 298 K, where Γ , X, M, Z, and Y are (0, 0, 0), (1/2, 0, 0), (1/2, 0, 1/2), (0, 0, 1/2), and (0, 1/2, 0), respectively. (b) Temperature dependence of electronic resistivity of a single crystal of **Pt-H** along the stacking direction. (c) Temperature dependence of magnetic susceptibility (χ) of polycrystalline **Pt-H** under an applied magnetic field of 5 kOe. Inset is the temperature dependence of χ^{-1} . Black dotted lines represent the calculated susceptibilities for the Curie law with 7.9% of $S = 1/2$ spin.

data obtained at 298 K. Figure 3a shows the band structure calculated without Hubbard correction U . We note that the band structure near the Fermi level is not substantially changed by U (Figure S3). It is apparent that the band is much more dispersive along the a direction than along the other directions because of the formation of π -stacking column. There is a half-filled band across the Fermi level with a bandwidth (W) of 533 meV.

It is apparent that the unpaired electron of d^7 configuration of Pt(III) is responsible for the electron conduction in **Pt-H**, although it is more or less delocalized over the complex molecule. To shed light on electronic transport behavior, the dc resistivity of a single crystal of **Pt-H** was measured along the stacking direction using a standard four-probe method. The conductivity (σ_e) was estimated to be $1.0 \times 10^{-3} \text{ S cm}^{-1}$ at RT, which is fairly high for a neutral π -planar metal complex.¹⁸ As shown in Figure 3b, **Pt-H** shows semiconducting behavior with a small activation energy (E_a) of 0.22 eV. Magnetic susceptibility (χ) of polycrystalline sample of **Pt-H** was measured under an applied magnetic field of 5 kOe. Figure 3c shows the temperature dependence of χ after subtracting the core diamagnetic contribution approximated by Pascal's constants ($-2.49 \times 10^{-4} \text{ emu mol}^{-1}$).¹⁹ Although the χ value follows the Curie law with 7.9% of $S = 1/2$ spin at low temperatures, a deviation from the Curie law was observed above ca. 50 K. The deviation is even more marked when the reciprocal of χ is plotted as a function of temperature (inset of Figure 3c). Similar temperature-independent behavior ($1.06 \times 10^{-4} \text{ emu mol}^{-1}$ at 300 K after subtracting the Curie component) has been found in several neutral π -planar metal complexes that show semiconducting transport behavior.²⁰ As the value is apparently lower than that expected from the $S = 1/2$ Curie spin ($1.25 \times 10^{-3} \text{ emu mol}^{-1}$) despite having a uniform chain, it is likely that **Pt-H** lies in the vicinity of the Mott-Hubbard boundary.

Electrochemical impedance spectra of **Pt-H** were measured using a compressed pellet of the polycrystalline sample, which was sandwiched by Nafion membranes as electron blocking electrodes (Figure S4). The proton conductivity (σ_p), which was estimated by fitting the Nyquist data (Figure 4a) with an appropriate equivalent circuit (Figure S5), is as high as $8.0 \times 10^{-5} \text{ S cm}^{-1}$ at RT under ambient condition. It is noteworthy that the value is more than two orders higher than that of **Ni-H** under the same conditions ($7.2 \times 10^{-7} \text{ S cm}^{-1}$; Figure S6),⁶ and is among the highest ever reported for a neutral π -planar metal complex. As shown in Figure 4a, the RT σ_p value is relatively insensitive to humidity; $9.9 \times 10^{-5} \text{ S cm}^{-1}$ at 30%RH and $1.3 \times 10^{-4} \text{ S cm}^{-1}$ at 90%RH. Given that the occupancy of O4 site is the lowest (0.35 at 298 K) among the oxygen of water molecules, the extra water molecules introduced under high RH condition are preferentially accommodated at the O4 sites. Because the 1D hydrogen-bonding network is composed only of O2 and O3 sites, it is possible that the introduction of the extra water molecules has little effect on proton conductivity.

As shown in Figure 4b, the proton conductivity follows Arrhenius-type activated behavior with $E_a = 0.23 \text{ eV}$, which was estimated based on the equation, $\sigma_p T = A \exp(-E_a/k_B T)$, where A is the pre-exponential factor and k_B is the Boltzmann constant. It is noteworthy that the E_a value, which falls well within the Grotthuss regime,⁵ is apparently lower than

that of **Ni-H** (0.42 eV).⁶ Reflecting on the expanded lattice of **Pt-H** ($V = 1138.8(6) \text{ \AA}^3$) by 1.5% relative to that of **Ni-H** ($V = 1121.8(9) \text{ \AA}^3$) as expected, it is most likely that less dense water in **Pt-H** (0.85 g cm^{-3} vs. 0.96 g cm^{-3} in **Ni-H**) modifies the reorientational dynamics in the favorable direction of increased proton transport. The positive activation volume must be a reflection of the importance of the relaxation process over the proton transfer process between neighboring hopping sites in determining the proton transport in this system.²¹ We note that the formation of single-well potential for the proton motion, which is expected from the short O...O distances,²² leads to the low energy barrier for the proton transfer process. Because electron densities on protonated and unprotonated quinoid oxygens in $[\text{Pt}^{\text{III}}(\text{Hnqdt})(\text{nqdt})]$ (-0.65232 and -0.52632 , respectively) predicted by DFT calculations are comparable to those in $[\text{Ni}^{\text{III}}(\text{Hnqdt})(\text{nqdt})]$ (-0.64823 and -0.52261 , respectively), the difference in pK_a is too small to influence proton conductivity of the complexes. Accordingly, the effect of metal ions on proton conduction is mainly driven by the less dense water due to the expansion of the lattice. To our best of

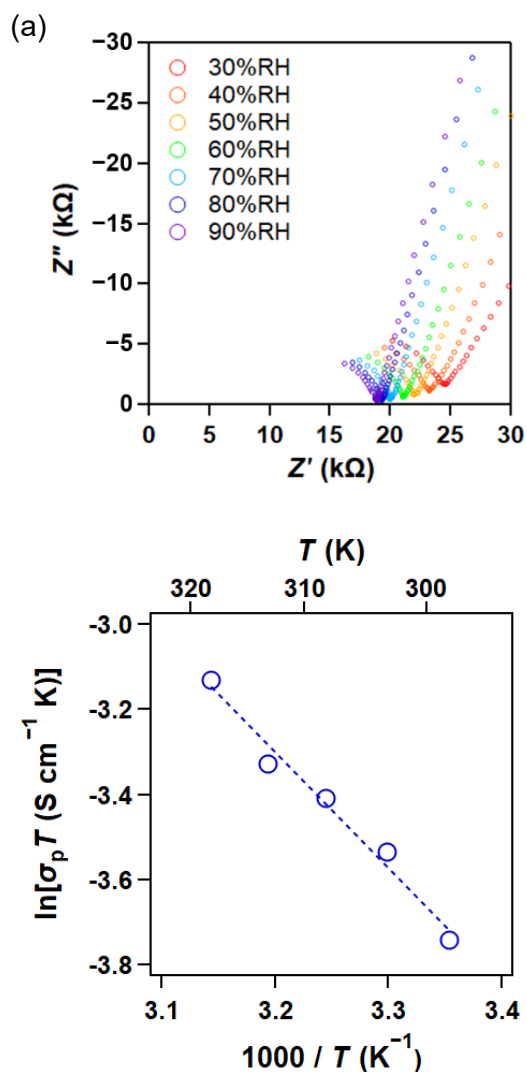


Figure 4. (a) Nyquist plots of the impedance spectra of **Pt-H** under several RH. (b) Arrhenius-type activated behavior of proton conductivity (σ_p) of **Pt-H** under ambient condition. A dotted line is fitted to the Arrhenius equation.

knowledge, **Pt-H** represents the first example showing the increased proton conductivity by applying negative chemical pressure in molecular proton conductors, although the relationship between the lattice parameter and proton conduction properties has been reported in some perovskite oxides [e.g., $\text{BaCe}_{1-x}\text{Zr}_x\text{RE}_{0.1}\text{O}_3$ ($\text{RE} = \text{Nd, Gd}$)]²³ and inorganic solid acids [e.g., $\text{AH}(\text{CO}_4)_2$ ($\text{A} = \text{NH}_4, \text{Rb, Cs}$; $\text{C} = \text{S, Se}$)]²⁴. Assuming that the compressibility of bulk water, 0.45 GPa^{-1} ,²⁵ is applicable to the water molecules in the present complexes, the negative chemical pressure applied to the water molecules in the complexes upon the substitution of Ni with Pt is estimated to be approximately 0.24 GPa. The RT conductivities for proton ($\sigma_p = 8.0 \times 10^{-5} \text{ S cm}^{-1}$) and electron ($\sigma_e = 1.0 \times 10^{-3} \text{ S cm}^{-1}$) in **Pt-H** approach each other compared with those in **Ni-H** ($\sigma_p = 7.2 \times 10^{-7} \text{ S cm}^{-1}$ and $\sigma_e = 4.1 \times 10^{-3} \text{ S cm}^{-1}$),⁶ recognizing it as a more ideal PEMC with ambipolar diffusion along the same crystallographic axis.

CONCLUSIONS

We synthesized a new molecule-based PEMC, $[\text{Pt}(\text{Hnqdt})(\text{nqdt})] \cdot 3.6\text{H}_2\text{O}$ (**Pt-H**), which involves a π -stacking column and a hydrogen bonding network. The RT proton conductivity under ambient condition is more than two orders higher than that of the isomorphous Ni complex. It appears that application of negative chemical pressure upon substitution of Ni by a larger Pt is responsible for the increased proton conductivity. The **Pt-H** shows comparable high conduction for proton and electron, leading to the highest level of molecule-based PEMC. The present work opens an avenue for exploring not only more advanced PEMCs but also undesigned proton-coupled electron conductors based on π -planar metal complexes. The metal complexes have great advantage of their diverse combinations of metal ions and ligands as well as the chemical modification of the ligands, which facilitating the design and control of their proton-electron transport properties.

ASSOCIATED CONTENT

Supporting Information

Experimental details, IR spectra (Figure S1), powder XRD patterns (Figure S2), band structure obtained from DFT calculations (Figure S3), schematic of impedance spectroscopic measurements (Figure S4), Nyquist plot of impedance spectrum (Figure S5), and temperature dependence of σ_p (Figure S6).

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Notes

The authors declare no competing financial interests.

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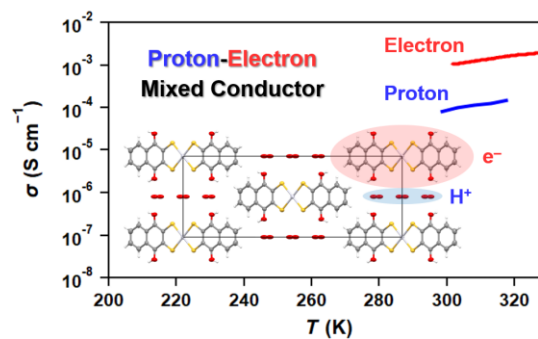
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We synthesized a new molecule-based proton–electron mixed conductor (PEMC), a hydrated Pt dithiolene complex with naphthoquinone skeletons. The proton conductivity is more than two orders higher than that of the isostructural Ni complex, possibly owing to the application of negative chemical pressure upon substitution of Ni by Pt. The comparable proton and electronic conductivities in this complex lead to the highest level of molecule based PEMC.
