

# Proton Conduction in Paddlewheel-Type Dinuclear Platinum(III) Complex System Including Neutral and Protonated 1,2,4-Triazole

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**ABSTRACT:** 1,2,4-Triazole (trz) is a heterocyclic base with high proton affinity, making it an excellent candidate as a hopping site for fast proton transport. In this study, we synthesized two paddlewheel-type dinuclear platinum complexes:  $(\text{Htrz})_2[\text{Pt}_2(\text{sq})_4(\text{trz})_2] \cdot 3(\text{H}_2\text{O})$  (**1**) and  $(\text{Bu}_4\text{N})_2[\text{Pt}_2(\text{sq})_4(\text{trz})_2] \cdot 3(\text{H}_2\text{O})$  (**2**), where  $\text{H}_2\text{sq}$  is squaric acid. Crystallographic study revealed that, in contrast to complex **2**, complex **1** is the first example of an integration involving  $\text{N}-\text{H} \cdots \text{N}$  hydrogen-bonding interaction between neutral and protonated trz in the solid. Complex **1** exhibited a high proton conductivity of  $1.0 \times 10^{-4} \text{ S cm}^{-1}$  at 25 °C and 98% relative humidity, which was significantly higher than that of **2** ( $8.5 \times 10^{-8} \text{ S cm}^{-1}$  under the same conditions). Infinite hydrogen-bonding networks, including  $\text{trz}-\text{Htrz}^+$  pairs, were apparently responsible for the high proton conduction observed in complex **1**.

## 1. INTRODUCTION

Solid proton conductors play a pivotal role in diverse applications such as energy storage and fuel cells.<sup>1–5</sup> To date, tremendous efforts have been devoted to exploring new and more advanced materials and investigating the underlying mechanism of the structure-property correlations.<sup>6–11</sup> Current research on proton-conducting materials primarily focuses on three main categories: organic polymer materials, inorganic materials, and organic-inorganic hybrid materials. Organic polymers, such as Nafion and sulfonated poly(ether ether ketone) (SPEEK), are extensively studied materials for proton transport because of the presence of acidic functional groups under hydrated conditions.<sup>12–15</sup> Nevertheless, the absence of long-range ordered structures makes it difficult to understand the structure-property relationship when designing advanced proton conductors. Partial substitution of lower valent dopants has been successfully employed to achieve proton conduction in perovskite-type oxides such as  $\text{Sr}(\text{Zr},\text{Y})\text{O}_{3-\delta}$  and  $\text{Ba}(\text{Ce},\text{Y})\text{O}_{3-\delta}$ .<sup>16,17</sup> Despite the use of structurally defined oxides with high proton conductivity in various electrochemical devices, including fuel cells, the degradation of thermodynamic stability under fuel-cell operating conditions remains an unsolved problem. Organic-inorganic hybrid materials, including metal-organic frameworks (MOFs) or porous coordination polymers (PCPs), are composed of various combinations, such as organic cations/metal complex anions, metal complex cations with organic ligands and inorganic anions, and neutral metal complexes with organic ligands.<sup>18–23</sup> The judicious design or choice of components has provided prominent proton conductors, especially based on the control of the  $\text{p}K_a/\text{p}K_b$  of metal ions or organic ligands and introducing Lewis acidic/basic sites into the ligands or as guest species to facilitate proton carriers and activate proton-hopping events.

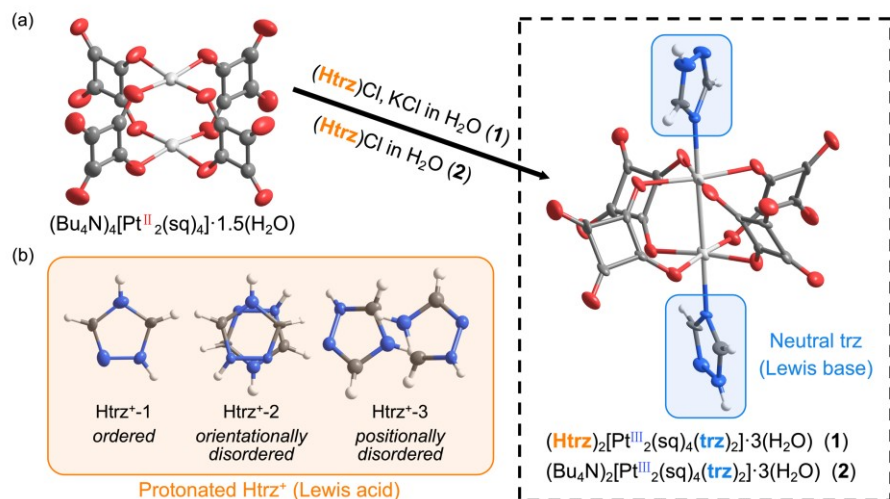
It is known that heterocyclic bases such as imidazole, 1,2,3-triazole, and 1,2,4-triazole (hereafter termed trz) have been utilized as key components for proton conductors owing to the formation of  $\text{N}-\text{H} \cdots \text{N}$  hydrogen bonding networks.<sup>24,25</sup>

In particular, their conjugated acids possess both Lewis acidic and basic sites, thereby promoting fast proton relays between neighboring molecules. Among them, our theoretical calculations at the density functional theory DFT/B3LYP level predicted that the difference in total energy between neutral and protonated species, corresponding to proton affinity,<sup>26,27</sup> of trz ( $-208.26 \text{ kcal mol}^{-1}$ ) is significantly lower than those of imidazole ( $-233.92 \text{ kcal mol}^{-1}$ ) and 1,2,3-triazole ( $-221.65 \text{ kcal mol}^{-1}$ ). This result clearly indicates that trz is a promising platform for realizing fast proton hopping between neutral and protonated trz, which inevitably results in high proton conductivity. To the best of our knowledge, there is only one report on the synthesis of metal complex system that includes protonated trz ( $\text{Htrz}^+$ ) cations and trz-coordinated complex anions,  $(\text{Htrz})_2[\text{Mo}_3\text{O}_6(\text{O}_2)_4(\text{trz})_2] \cdot \text{H}_2\text{O}$ .<sup>28</sup> However, the  $N,N'$ -bridging trz ligands lack Lewis basic sites to construct the proton-conducting pathways, although the trinuclear molybdenum(VI) complex has been used as an acid catalyst for reactions such as alcoholysis and epoxidation.

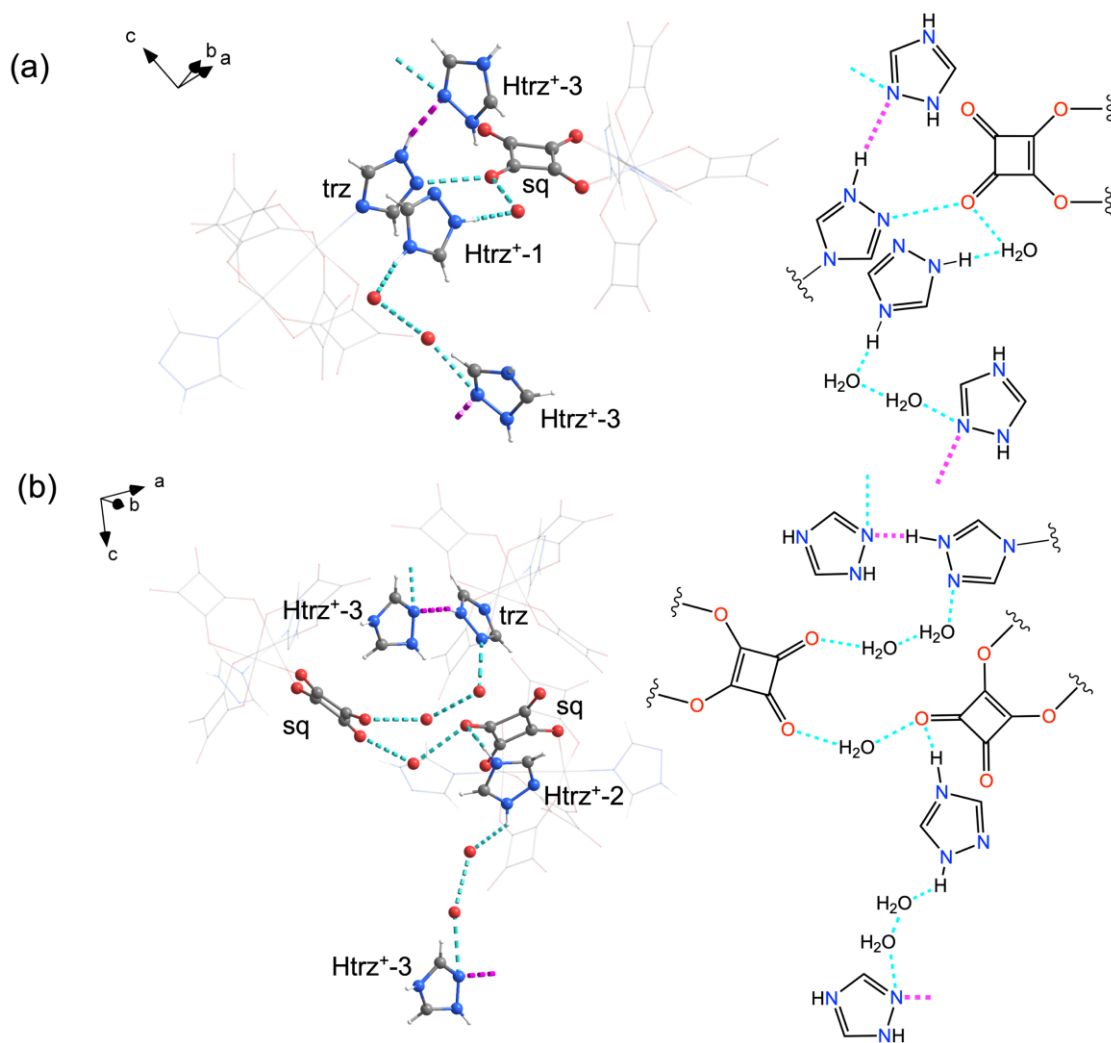
In this study, we present the first approach to simultaneously incorporate neutral trz moieties with active Lewis basic sites into metal complex anions and  $\text{Htrz}^+$  cations as their counterparts. We utilized paddlewheel-type dinuclear Pt (III) complex anions, in which the  $\text{Pt}_2$  units coordinate with four squarate ( $\text{sq}^{2-}$ ) ligands at the equatorial positions and two trz ligands at the axial positions. As discussed later, sq ligands can assist in the formation of proton-conducting pathways in the crystal. Two complexes,  $(\text{Htrz})_2[\text{Pt}_2(\text{sq})_4(\text{trz})_2] \cdot 3(\text{H}_2\text{O})$  (**1**) and  $(\text{Bu}_4\text{N})_2[\text{Pt}_2(\text{sq})_4(\text{trz})_2] \cdot 3(\text{H}_2\text{O})$  (**2**), were synthesized from the precursor,  $(\text{Bu}_4\text{N})_4[\text{Pt}_2(\text{sq})_4] \cdot 1.5(\text{H}_2\text{O})$  with Pt(II)-paddlewheels with no axial ligands, to investigate the effect of hydrogen-bonding interactions between neutral and protonated trz species on proton conduction.

## 2. RESULTS AND DISCUSSION

The crystallographic data for all compounds are listed in Table S1. As shown in Figure 1a, the pre-



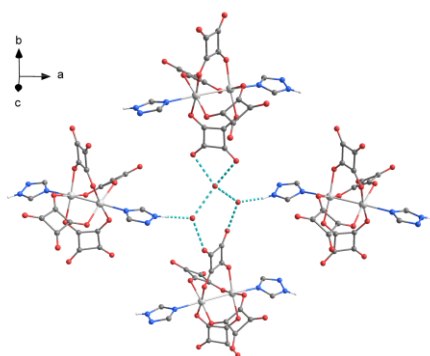
**Figure 1.** (a) Paddlewheel-type platinum dinuclear complex molecules in (left)  $(\text{Bu}_4\text{N})_4[\text{Pt}_2(\text{sq})_4] \cdot 1.5(\text{H}_2\text{O})$  and (right) **1** and (b) three kinds of crystallographically independent Htrz<sup>+</sup> cations in **1**, determined by crystallographic data at 298 K for  $(\text{Bu}_4\text{N})_4[\text{Pt}_2(\text{sq})_4] \cdot 1.5(\text{H}_2\text{O})$  and 100 K for **1** (grey, C; white, H; blue, N; silver, Pt; red, O).



**Figure 2.** Hydrogen bonding networks in (a and b) **1** (cyan dotted lines), where only the short contacts forming the infinite hydrogen bonding networks are shown. In (a) and (b), the numbering of Htrz<sup>+</sup> cations corresponds to that in Figure 1. The purple dotted lines in (a) and (b) show the N–H···N hydrogen-bonding contact between neutral and protonated trz. Schematic representations of hydrogen bonding networks are shown in right side.

cursor,  $(\text{Bu}_4\text{N})_4[\text{Pt}_2(\text{sq})_4]\cdot 1.5(\text{H}_2\text{O})$ , involves eclipsed paddle-wheel platinum dimers with four sq ligands, in which intra-dimer Pt–Pt distance was determined 2.99(5) Å. Given that the structural geometry aligns well with that of the paddlewheel-type Pt(II) dimer in  $\text{Ba}_2[\text{Pt}_2(\text{sq})_4]\cdot 6(\text{H}_2\text{O})$ ,<sup>29</sup> it is apparent that the Pt ions in  $(\text{Bu}_4\text{N})_4[\text{Pt}_2(\text{sq})_4]\cdot 1.5(\text{H}_2\text{O})$  are in a divalent state, as expected from its composition.

Complex **1** crystallized as a monoclinic system with space group  $P2_1/c$ . The asymmetric unit contains one and two half-Htrz cations, one  $[\text{Pt}_2(\text{sq})_4(\text{trz})_2]$  complex molecule, and two guest water molecules. Two platinum atoms are bridged by four sq ligands in the crystal, with a Pt–O distance of 2.00(3)–2.03(3) Å (Table S2), to form a paddlewheel-type dinuclear complex molecule (Figure 1a). The  $\text{PtO}_4$  unit is twisted by ca. 21° from the eclipsed structure, in contrast to  $(\text{Bu}_4\text{N})_4[\text{Pt}_2(\text{sq})_4]\cdot 1.5(\text{H}_2\text{O})$ . Along the axial direction, two neutral trz molecules coordinate to the  $\text{Pt}_2$  core in an  $\eta^1$  coordination mode with a Pt–N distance of 2.13(4) and 2.15(4) Å. The Pt–Pt distance within the dimer was determined to be 2.60(5) Å, which is apparently shorter than that in paddlewheel Pt(II) dimers including  $(\text{Bu}_4\text{N})_4[\text{Pt}_2(\text{sq})_4]\cdot 1.5(\text{H}_2\text{O})$ , but more comparable to those in paddlewheel Pt(III) dimers.<sup>29–33</sup> To compensate for the charge in the crystal, three crystallographically independent protonated triazolium ( $\text{Htrz}^+$ ) cations act as proton sources: one is ordered ( $\text{Htrz}^+-1$ ) and the other two are orientationally ( $\text{Htrz}^+-2$ ) or positionally ( $\text{Htrz}^+-3$ ) disordered (Figure 1b). The occupancy of the oxygen atoms in the guest water molecules was refined by restricting the sum of the oxygen atoms to three per  $(\text{Htrz})_2[\text{Pt}_2(\text{sq})_4(\text{trz})_2]$  unit, as determined by elemental analysis. We verified the water content using thermogravimetric analysis (TGA); the profile shows an initial weight loss of 4.8% up to about 80 °C, which corresponds to three water molecules (4.6% by weight) (Figure S1). The crystallographic data suggested that there were several electron density peaks in the lattice; we assigned the four peaks to water oxygen atoms with occupancies of 1.0, 0.85(1), 0.61(1), and 0.54(1).

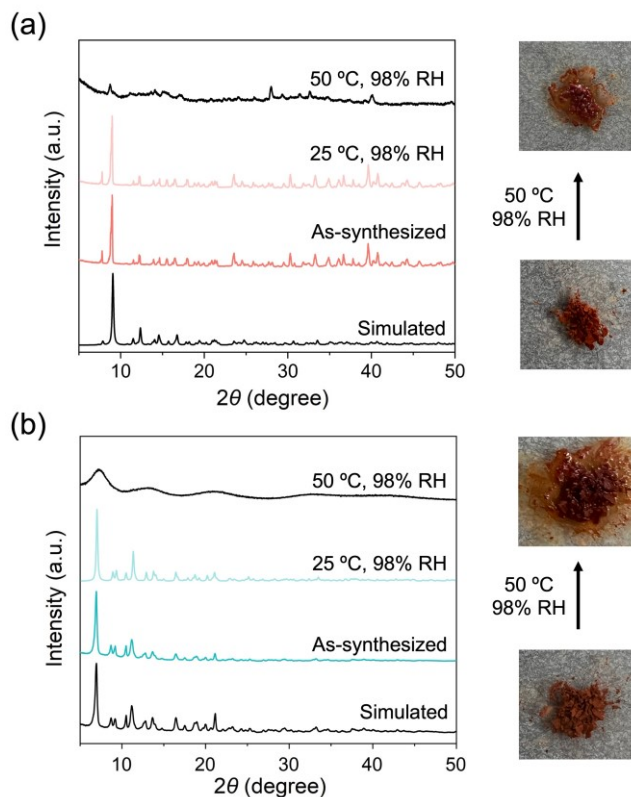


**Figure 3.** Hydrogen bonding contacts in complex **2** (cyan dotted lines).

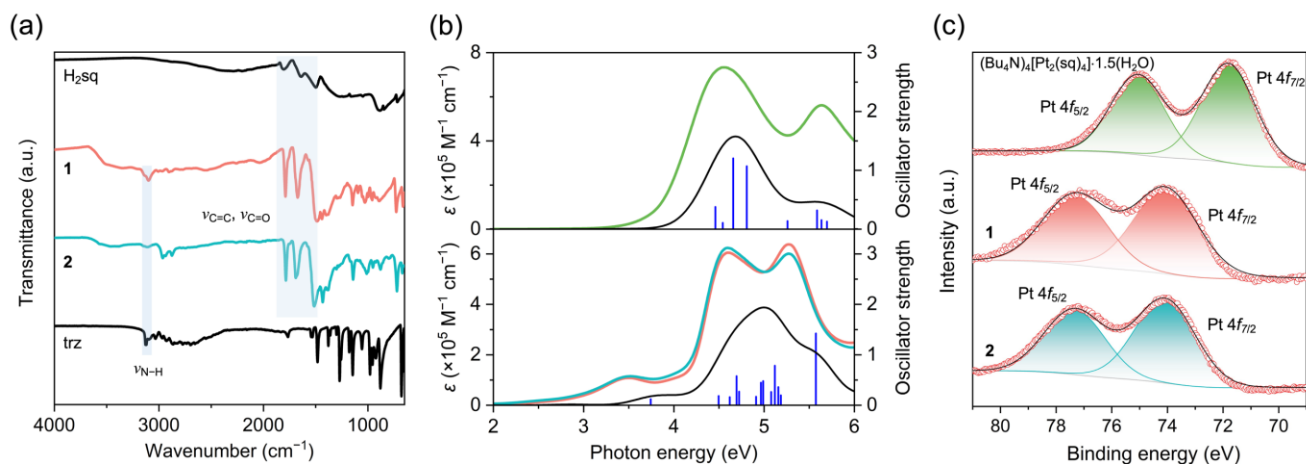
In a unit cell, there are two arrays of  $[\text{Pt}_2(\text{sq})_4(\text{trz})_2]^{2-}$  complex molecules, related by an inversion center, along the  $c$  axis (Figure S2). In each array, the dimers that are rotated by 90° with respect to dimers are related by the  $c$ -glide plane at  $y = 0.25$  or  $0.75$ . The  $[\text{Pt}_2(\text{sq})_4(\text{trz})_2]^{2-}$  complex molecules are surrounded by Lewis-base water molecules and Lewis-acidic  $\text{Htrz}^+$  cations. Whereas ordered  $\text{Htrz}^+-1$  cations are located between the neighboring arrays at  $y \sim 0.25$  and  $0.75$ , disordered  $\text{Htrz}^+-2$  and  $\text{Htrz}^+-3$  cations are located at  $y \sim 0$  and  $0.5$ .

The crystal structure contains two crystallographically-independent hydrogen-bonded networks composed of  $\text{Htrz}^+$  cations, coordinated trz, coordinated sq, and guest water, as illustrated in Figures 2a and 2b. Notably, both hydrogen-bonding networks include N–H...N hydrogen bonds between trz and  $\text{Htrz}^+$  ( $\text{N}\cdots\text{N}$  distance: 2.82(1) Å vs. sum of the van der Waals radii: 3.10 Å<sup>34</sup>). The networks also contain O–H...O hydrogen bonds with an O...O distance of 2.69(6)–2.82(5) Å (sum of the van der Waals radii: 3.04 Å<sup>34</sup>) between the guest water and sq ligands and O–H...N hydrogen bonds with an O...N distance of 2.69(6)–2.80(9) Å (sum of the van der Waals radii: 3.07 Å<sup>34</sup>) between trz and sq ligands.

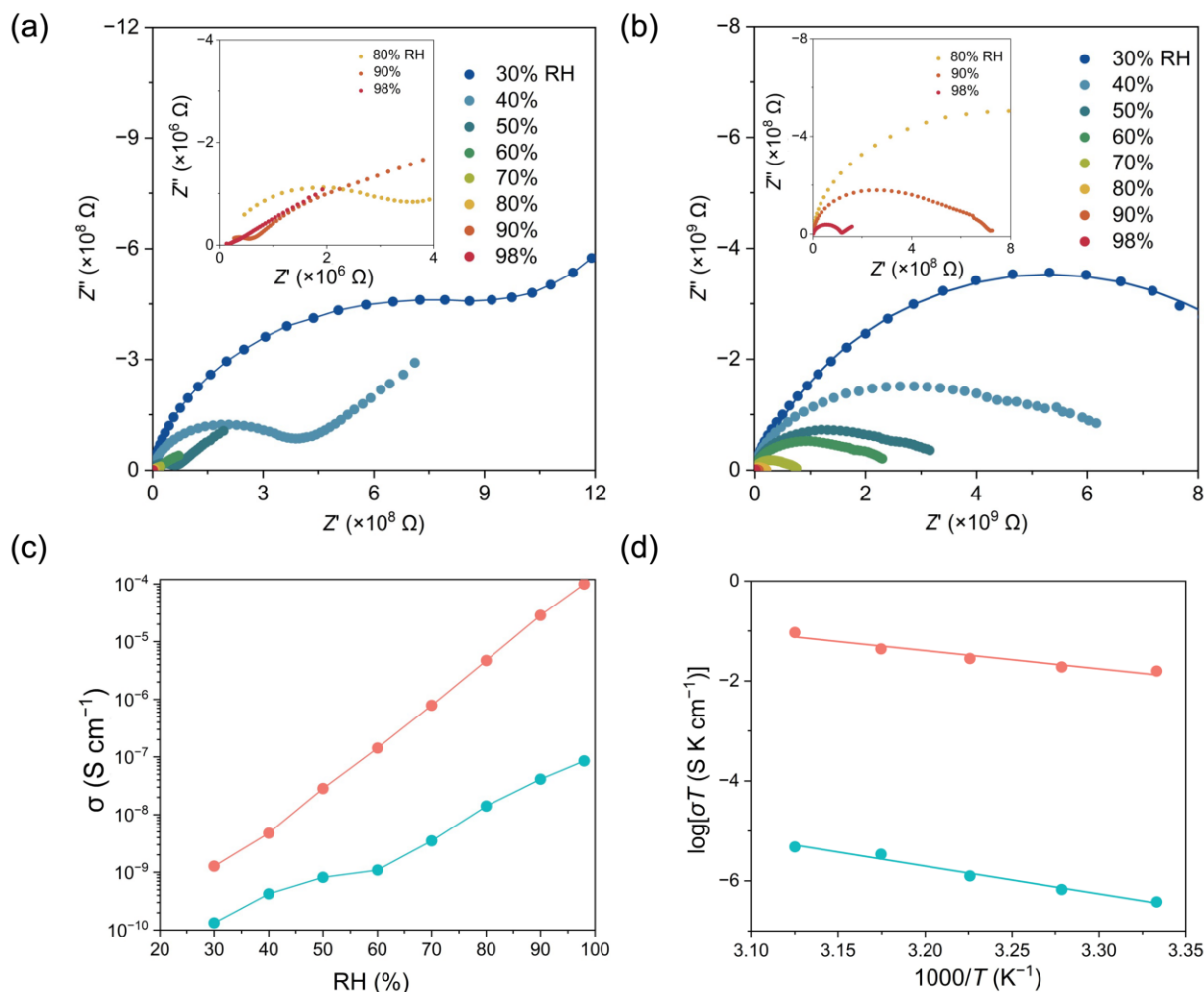
Complex **2** belongs to the orthorhombic system with the space group  $Pbcn$ . Similar to **1**, the  $\text{Pt}_2$  cores are bridged by four sq ligands, with trz molecules bound at the axial positions. The intra-unit Pt–Pt distance (2.60(5) Å) is comparable to that in **1**, implying the trivalent state of Pt ions. However, replacing the  $\text{Htrz}^+$  cations in **1** with bulky  $\text{Bu}_4\text{N}^+$  cations results in the interruption of the infinite hydrogen-bonding networks (Figures S2c and S2d), although there are O–H...O hydrogen bonds between sq and  $\text{H}_2\text{O}$ , as well as between  $\text{H}_2\text{O}$  molecules ( $\text{O}\cdots\text{O}$  distance: 2.70(8)–2.83(1) Å) (Figure 3). Additionally, there are N–H...O hydrogen bonds between trz and  $\text{H}_2\text{O}$  ( $\text{N}\cdots\text{O}$  distance: 2.71(8) Å). Bulky  $\text{Bu}_4\text{N}^+$  cations isolate the  $[\text{Pt}_2(\text{sq})_4(\text{trz})_2]^{2-}$  complex molecules from one another, thereby reducing their potential to interact with each other.



**Figure 4.** Powder X-ray diffraction (PXRD) patterns of polycrystalline samples of (a) **1** (red) and (b) **2** (blue). Simulated patterns obtained from the single-crystal X-ray diffraction (SCXRD) data are shown in black at bottom. Pale color and black patterns at top were obtained after standing the samples at 25 °C and 98% RH and 50 °C and 98% RH for 5 h, respectively. Photographs of the deliquescent states are shown in the right panel.



**Figure 5.** (a) Infrared spectra of **1** (red) and **2** (cyan) together with those of H<sub>2</sub>sq and trz (black). (b) UV-Vis spectra of (Bu<sub>4</sub>N)<sub>4</sub>[Pt<sub>2</sub>(sq)<sub>4</sub>·1.5(H<sub>2</sub>O)] (green), **1** (red), and **2** (cyan) in  $5 \times 10^{-6}$  M aqueous solution together with simulated spectra of [Pt<sub>2</sub>(sq)<sub>4</sub>]<sup>4-</sup> (black lines in the top panel) and [Pt<sub>2</sub>(sq)<sub>4</sub>(trz)<sub>2</sub>]<sup>2-</sup> (black lines in the bottom panel) based on TD-DFT calculations at the CAM-B3LYP/cc-pVTZ-PP/cc-pVDZ level. (c) Pt 4f XPS spectra of complex (Bu<sub>4</sub>N)<sub>4</sub>[Pt<sub>2</sub>(sq)<sub>4</sub>·1.5(H<sub>2</sub>O)], **1**, and **2**. The red open circles indicate the measured XPS data, whereas the black lines are the sum of the deconvoluted peaks.



**Figure 6.** Relative humidity (RH) dependent Nyquist plots of (a) **1** and (b) **2** at 25 °C, where the solid lines are the fit with the equivalent circuits shown in Figure S7. Insets show the enlarged plots for high-RH (80–98% RH) data. (c) RH dependence of proton conductivity (σ) of **1** (red) and **2** (blue) at 25 °C. (d) Arrhenius plots of proton conductivity of **1** (red) and **2** (blue) at 98% RH, where lines are fit to the Arrhenius equation.

The powder X-ray diffraction (PXRD) patterns of polycrystalline **1** and **2** matched well with those simulated from single-crystal XRD (SCXRD) data (Figures 4, S3 and S4), indicating the high purity of the polycrystalline samples suitable for the following characterisations. As shown in Figure 5a, the presence of sq ligands in **1** and **2** is manifested in the observation of a C=C stretching band at 1500 cm<sup>-1</sup> and symmetric and antisymmetric C=O stretching band at 1644 and 1806 cm<sup>-1</sup>, respectively.<sup>35</sup> The absence of O–H···O intermolecular hydrogen bonds, which were observed at 2286 cm<sup>-1</sup> in H<sub>2</sub>sq, further suggests the presence of sq<sup>2-</sup> species in the structure. In addition, both complexes showed the distinct bands at 3098 and 3143 cm<sup>-1</sup>, which are assignable to the N–H stretching mode of trz moieties. The presence of Bu<sub>4</sub>N<sup>+</sup> cations in **2** was verified by the observation of aliphatic C–H stretching bands at 2875 and 2962 cm<sup>-1</sup>.

The UV-vis spectra of all compounds were measured in a 5 × 10<sup>-6</sup> M aqueous solution (Figure 5b). In the UV region, (Bu<sub>4</sub>N)<sub>4</sub>[Pt<sub>2</sub>(sq)<sub>4</sub>·1.5(H<sub>2</sub>O)] exhibits characteristic bands at 5.65 eV ( $\epsilon \sim 5.6 \times 10^5$  M<sup>-1</sup> cm<sup>-1</sup>) and 4.55 eV ( $\epsilon \sim 7.3 \times 10^5$  M<sup>-1</sup> cm<sup>-1</sup>), which were primarily assigned to metal-to-ligand charge transfer (MLCT) arising from  $d\sigma^*(\text{Pt}_2)$  to  $\pi^*(\text{sq})$  transition based on the time-dependent DFT (TD-DFT) calculations at the CAM-B3LYP level (Tables S3 and S4 and Figures S5–S7). An additional band was observed at 3.51 eV ( $\epsilon \sim 1.0 \times 10^5$  M<sup>-1</sup> cm<sup>-1</sup>) for **1** and 3.51 eV ( $\epsilon \sim 1.1 \times 10^5$  M<sup>-1</sup> cm<sup>-1</sup>) for **2**, which mainly originates from  $\pi^*(\text{sq})$  to  $d\sigma^*(\text{Pt}_2) + \sigma^*(\text{Pt-trz})$  states, i.e., a mixture of ligand-to-ligand CT (LLCT) and ligand-to-metal CT (LMCT) transition. It is apparent that the additional band is closely related to the axial coordination of the trz ligands.

X-ray photoelectron spectra (XPS) measurements were performed to examine the valence states of the Pt ions (Figure 5c). The peaks at 77.3 and 74.1 eV observed for **1** and **2** are assigned to Pt 4f<sub>5/2</sub> and Pt 4f<sub>7/2</sub>, respectively, which are significantly higher than those of starting material (75.0 and 71.8 eV). Thus, it is evident that the platinum ions in **1** and **2** are in a trivalent state, whereas those in starting material are in a divalent state.<sup>36,37</sup> The oxidation of platinum ions during the reaction to yield **1** and **2** possibly arises from exposure to air,<sup>38–41</sup> and the trivalent state of the platinum ions is stabilized in an octahedral geometry with the axial coordination of trz. We note that the paddlewheel-type platinum(III) dimer complexes have diamagnetic ground state.<sup>42–45</sup>

The fact that complex **1** involves infinite hydrogen-bonding networks including direct N–H···N contacts between trz and Htrz<sup>+</sup>, prompted us to investigate its proton-conducting behavior. Before the AC impedance measurements, we evacuated the stability of complexes **1** and **2** under high humidity by monitoring changes in the PXRD patterns, which were recorded after the samples had been exposed to each relative humidity (RH) for five hours (Figure S8). The results showed that both complexes retained their crystal structures even at 98% RH.

Figures 6a and 6b present the Nyquist plots of the impedance spectra of pelletized **1** and **2**, respectively, at 25 °C under various humidity conditions (30–98% RH). For **1**, proton conductivity ( $\sigma$ ), calculated by fitting the plot with an equivalent circuit (Figure S9 and S10), was determined to be 1.3 × 10<sup>-9</sup> S cm<sup>-1</sup> at 30% RH. It steadily increased with increasing humidity, eventually reaching 1.0 × 10<sup>-4</sup> S cm<sup>-1</sup> at 98% RH (Figure 6c). It is worth noting that this value is comparable to those of

most molecule-based complexes including heterocyclic molecules such as pyridine, imidazole, triazole (Table S5).<sup>46–53</sup> The proton conductivity of **1** was not very significant, despite having the infinite hydrogen-bonding network. This behavior is possibly attributed to the inclusion of relatively long O···O (2.69(6)–2.82(5) Å) and O···N (2.69(6)–2.80(9) Å) contacts in the network. Given that the water vapor sorption isotherm exhibits a continuous increase in water uptake with increasing RH (Figure S11), the humidity-dependent conductivity provides strong evidence that protons are the primary charge carriers migrating via proton hopping through water molecules serving as Lewis basic sites. Lower water uptake in **2** compared with **1** despite including bulky Bu<sub>4</sub>N<sup>+</sup> cations is possibly attributed to the hydrophobic nature of Bu<sub>4</sub>N<sup>+</sup> cations. The temperature dependence of  $\sigma$  was measured at 98% RH up to 45 °C, above which both complexes began to deliquesce (Figure 4). As shown in Figure 6d, the  $\sigma$  value follows Arrhenius-type activated behavior, with an activation energy ( $E_a$ ) of 0.64 eV, estimated using the equation,  $\sigma T = A \exp(-E_a/k_B T)$  ( $A$ : pre-exponential factor,  $k_B$ : Boltzmann constant). The proton conductivity at 45 °C was estimated to be 2.9 × 10<sup>-4</sup> S cm<sup>-1</sup>. It is apparent that the formation of infinite hydrogen-bonding networks, possibly in addition to the direct trz···Htrz<sup>+</sup> contacts as mentioned above, is responsible for the relatively high  $\sigma$  values. Although the reason for the rather high  $E_a$  value remains unclear, possible proton tautomerism, explained by intramolecular proton transfer, within Htrz<sup>+</sup><sup>54</sup> and sq<sup>55</sup> species in the proton-conducting pathway may give rise to an energy barrier that must be overcome for the proton transfer process. The humidity and temperature dependences of the proton conductivity of **2** were strikingly different from those of **1**, as shown in Figures 6b and 6d. The room-temperature  $\sigma$  value was estimated to be 8.5 × 10<sup>-8</sup> S cm<sup>-1</sup> even at 98% RH, which is more than three orders of magnitude lower than that of **1** under the same conditions. The isolated hydrogen-bonding network (Figure 3) is a factor governing the observed lower proton conductivity and higher  $E_a$  value (1.10 eV). It is apparent that the acidic proton of Htrz<sup>+</sup> cations is responsible for the prominent proton conduction via the infinite hydrogen-bonding network. Replacing the hydrophilic Htrz<sup>+</sup> cations with hydrophobic Bu<sub>4</sub>N<sup>+</sup> cations not only eliminates the proton carriers but also prevents the formation of the network. Although MOFs and PCPs have received increasing attention as solid proton conductors in the past two decades,<sup>7–10,22</sup> molecule-based organic-inorganic hybrid materials, such as the present complex systems, have a considerable advantage in that the component molecules can self-assemble with hydrogen-bonding interactions, which can serve as proton-conducting pathways in the presence of proton carriers.

### 3. CONCLUSION

In conclusion, we successfully synthesized paddlewheel-type platinum dimer complexes in which dinuclear units with Lewis basic sq and trz ligands were combined with Htrz<sup>+</sup> (**1**) and Bu<sub>4</sub>N<sup>+</sup> (**2**) cations. The trivalent character of the platinum ions, verified by XPS analysis, led to the axial coordination of trz. A crystallographic study revealed that in contrast to complex **2**, complex **1** is the first structurally defined solid with infinite hydrogen-bonding networks, including neutral and protonated trz in a 1:1 stoichiometric ratio. The two species are directly connected via effective N–H···N hydrogen bonds to facilitate fast proton transfer between high-proton affinity bases. Consequently, the proton conductivity of **1** was more

than three orders of magnitude higher than that of **2** under the same conditions. These findings indicate a promising direction for developing a new family of molecular-based proton conductors including Lewis acids with different protonated states. Studies on this line are currently underway.

## 4. EXPERIMENTAL SECTION

**Materials.**  $\text{K}_2\text{PtCl}_4$ ,  $\text{HClO}_4$ ,  $\text{NaClO}_4$ ,  $\text{KCl}$ ,  $\text{AgClO}_4$ , and acetone were purchased from Fujifilm Wako Pure Chemical Industries.  $\text{H}_2\text{sq}$ , ascorbic acid,  $(\text{Bu}_4\text{N})\text{Cl}$ , and  $\text{trz}$  were obtained from Tokyo Chemical Industry. All the reagents were used without further purification. The water was deionized before use.

**Measurements.** Elemental analyses of C, H, and N were performed at the Elemental Analysis Center of the Faculty of Pharmaceutical Science, Kyoto University. FT-IR spectra were measured on a PerkinElmer Spectrum 100 FT-IR spectrometer in attenuated total reflection (ATR) mode. UV-vis spectra were obtained using a JASCO V-770 UV-visible/NIR spectrometer in the wavelength range 200–800 nm. Thermogravimetric analyses were conducted using a Burker TG-DTA 2000SA instrument under a  $\text{N}_2$  atmosphere. XPS spectra were collected on a Shimadzu ESCA-3400 X-ray photoelectron spectrometer using  $\text{Mg K}\alpha$  anode. PXRD patterns were recorded on a Rigaku MiniFlex600 diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). SCXRD data were collected on Rigaku XtaLAB P200 instrument with  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ) at 100 and 298 K. The structures were solved by the direct method using the SHELXS-2014 program<sup>56</sup> and refined by the full-matrix least-squares method on  $F^2$  using the SHELXL-2014 program.<sup>57</sup> Nonhydrogen atoms were refined anisotropically, whereas hydrogen atoms were positioned geometrically and refined using a riding model. The water vapor sorption experiments were carried out at 298 K using a BELSORP-max volumetric adsorption system (Microtrac BEL Corp.). AC impedance spectra of compressed pellets were collected using a Solartron SI 1260 Impedance/Gain-Phase Analyser and the 1296 Dielectric Interface in the frequency range of 1 MHz to 0.1 Hz with an applied AC voltage of 100 mV. Measurements were performed in humidity- and temperature-controlled chambers. Proton conductivity ( $\sigma$ ) was calculated based on the resistance ( $R$ ) estimated from the Nyquist plot (Figures S9 and S10). The calculation was performed using the equation,  $\sigma = L/RS$ , where  $L$  and  $S$  represent the thickness and area of the pellet, respectively.

**Computational.** DFT calculations based on the CAM-B3LYP-D3(BJ)<sup>58,59</sup> functional were performed using cc-pVTZ-PP<sup>60</sup> and cc-pVDZ<sup>61</sup> basis sets for the Pt and other atoms, respectively. Full geometry optimisations were performed with “Opt = Tight” keyword. In the present calculations, “Int = SuperFineGrid” was specified, and stabilities of the wave functions were confirmed by specifying the “Stable = Opt” keyword. For  $[\text{Pt}_2(\text{sq})_4]^{4-}$  and  $[\text{Pt}_2(\text{sq})_4(\text{trz})_2]^{2-}$  complexes, eighty and seventy excited states were calculated in the TD-DFT calculation, respectively. For all calculations, the solvent effect of water with  $\epsilon = 78.3553$  was modelled using the integral equation formalism variant of polarisable continuum model (IEF-PCM<sup>62</sup>). Computations were performed using the Gaussian 09 software package.<sup>63</sup>

**Synthesis of  $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$  stock solution.** The tetraaqua Pt(II) complex was synthesised according to a previously reported procedure.<sup>64</sup> Typically,  $\text{K}_2\text{PtCl}_4$  (3.5 g, 8.5 mmol) was

added to 400 mL of 1.0 M  $\text{HClO}_4$  solution. The mixture was bubbled with argon in dark conditions at 70 °C and stirred for 90 min until the potassium salt was completely dissolved. Then, 400 mL of 0.2 M  $\text{AgClO}_4$  solution was added slowly to the mixture over 8 h. The mixture was stirred under argon at 70 °C in the dark for seven days. Finally, a pale-yellow solution containing  $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$  ions was obtained by filtering to remove the precipitate. Because of the highly oxidising nature of  $[\text{Pt}(\text{H}_2\text{O})_4]^{2+}$ , an aliquot of the stock solution was used in the following reaction.

**Synthesis of  $(\text{Bu}_4\text{N})_4[\text{Pt}_2(\text{sq})_4] \cdot 1.5(\text{H}_2\text{O})$ .** Squaric acid ( $\text{H}_2\text{sq}$ , 570 mg, 5.0 mmol) was added to 100 mL of the stock solution. The mixture was heated to 55 °C for 2 h, during which the solution turned purple. A saturated solution of  $\text{NaClO}_4$  (10 mL) was added and the mixture was stirred for 7 d at room temperature in air. During this process, a black precipitate formed. The precipitate was dissolved in water (100 mL) and ascorbic acid (176 mg, 1.0 mmol) was added. After filtration the brown precipitate,  $(\text{Bu}_4\text{N})\text{Cl}$  (1.0 g, 3.5 mmol) was added to the yellow solution. After the solution was allowed to stand for 5 d at room temperature, bulk yellow crystals were formed at the bottom of the vial (134 mg, 47.4% yield based on  $\text{H}_2\text{sq}$ ). Elemental analysis calcd (%): C, 52.36; H, 8.07; N, 3.05. Found (%): C, 52.30; H, 8.22; N, 2.94.

**Synthesis of  $(\text{Htrz})_2[\text{Pt}_2(\text{sq})_4(\text{trz})_2] \cdot 3(\text{H}_2\text{O})$  (1).**  $(\text{Bu}_4\text{N})_4[\text{Pt}_2(\text{sq})_4] \cdot 1.5(\text{H}_2\text{O})$  (233 mg, 0.20 mmol) in water (30 mL) was stirred at room temperature for 1 h to yield a transparent yellow solution. Subsequently,  $\text{KCl}$  (1.06 g, 20 mmol) was added to the solution and stirred for 1 h. The addition of acetone (100 mL) yielded a yellow precipitate which was filtered and washed with acetone and ethanol. An excess of  $(\text{Htrz})\text{Cl}$  was added to the yellow aqueous solution (20 mL), and the solution was kept at room temperature overnight. Bulk red crystals were formed by slow evaporation of the red solution over five days (169 mg, 73.4% yield). Elemental analysis calcd (%): C, 24.62; H, 1.72; N, 14.35. Found (%): C, 24.35; H, 1.97; N, 14.54.

**Synthesis of  $(\text{Bu}_4\text{N})_2[\text{Pt}_2(\text{sq})_4(\text{trz})_2] \cdot 3(\text{H}_2\text{O})$  (2).**  $(\text{Bu}_4\text{N})_4[\text{Pt}_2(\text{sq})_4] \cdot 1.5(\text{H}_2\text{O})$  (233 mg, 0.20 mmol) was stirred in water (30 mL) at room temperature for 1 h to obtain a transparent yellow solution. Bulk red crystals formed after an excess amount of  $(\text{Htrz})\text{Cl}$  was added, and the solution was allowed to stand at room temperature for 3 d (151 mg, 65.8% yield). Elemental analysis (%): C 41.21, H 5.59, N 7.39. Found (%): C, 41.35; H, 5.76; N, 7.09.

## ASSOCIATED CONTENT

### Supporting Information

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

Full materials and methods, crystallographic data, supporting characterization data, and TD-DFT calculations including additional figures and tables as described in the Supporting Information.

### Accession Codes

CCDC 2351050–2351052 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](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge

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P. W., Y. Y., and H. K. conceived the research and designed the experiments. P. W. and T. I. synthesized the materials. TD-DFT calculations were performed by Y. N., whereas P. W., Y. Y., and H. K. cowrote the manuscript. All the authors discussed and commented on the paper.

### Notes

Any additional relevant notes should be placed here.

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## Table of Contents artwork

