

# Anhydrous Superprotonic Conduction in Molecular Crystals Utilizing $\pi$ -Electron-Coupled Proton Tautomerism

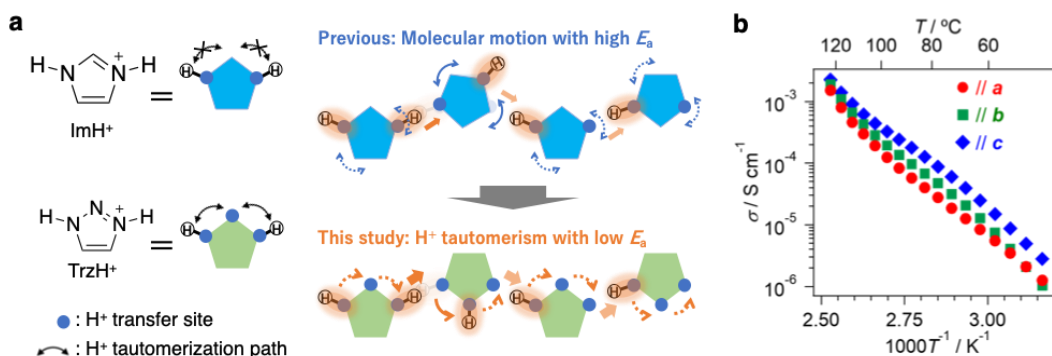
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Anhydrous organic proton ( $H^+$ ) conductors, which exhibit  $H^+$  conductivity without humidification, have attracted much attention as candidates for next-generation solid electrolytes in fuel cells. However, the previously reported ones with high  $H^+$  conductivities were acid- or base-doped polymers. Therefore, conduction mechanism remains unclear, and full control of  $H^+$  migration in solids have not been achieved. Utilization of molecular single crystals is highly important to investigate their conduction mechanism in detail.

In a molecular crystal, where constituent molecules are densely packed to construct an extended hydrogen-bond (H-bond) network, it is expected that, in addition to intermolecular  $H^+$  transfer, intramolecular  $H^+$  transfer from one side to the other side by molecular reorientation motion is necessary. In fact, we have investigated a series of imidazolium (**ImH** $^+$ ) dicarboxylates and revealed that, in addition to static factors such as formation of H-bonding networks and the acidities of the constituent molecules (i.e.  $\Delta pK_a$ ), **ImH** $^+$  librational motion is a key factor to achieve anhydrous  $H^+$  conductivity.[1–3] Very recently, we adopted phosphate anion (**H<sub>2</sub>PO<sub>4</sub> $^-$** ), which is known to bring about superprotonic transition in inorganic alkali phosphates by rotational motions, as counter anion of **ImH** $^+$ , and found that molecular motion of both acid and base contribute to anhydrous  $H^+$  conduction. However, realization of significant molecular motion in a crystal is difficult, and the activation energy ( $E_a$ ) of  $H^+$  conduction was often very high ( $>3$  eV), resulting in the low conductivity.

Here, we propose “H $^+$  tautomerism”, which is the fast intramolecular  $H^+$  transfer coupled with reconstruction of  $\pi$  electrons, i.e.,  $\pi$ -electron-coupled intramolecular  $H^+$  transfer, as a new strategy to avoid necessity of high-barrier molecular motion for  $H^+$  conduction. In this study, we focused on 1,2,3-triazolium (**TrzH** $^+$ ), which has three adjacent proton transfer sites, and investigated its **H<sub>2</sub>PO<sub>4</sub> $^-$**  salts. The single crystal exhibited isotropically superprotonic conductivities ( $> 10^{-3}$  S/cm) with quite low  $E_a$  of ca. 1 eV. The results show that  $H^+$  tautomerism can be a new strategy to develop anhydrous molecular superprotonic conductors.



**Fig. 1.** (a) (left) Molecular structures of **ImH** $^+$  and **TrzH** $^+$  with the schematic image of their possibility of the proton tautomerism, and (right) schematic images of proton conduction by molecular motion and proton tautomerism. (b) Temperature dependence of anhydrous proton conductivity of (**TrzH** $^+$ )(**H<sub>2</sub>PO<sub>4</sub> $^-$** ).

## References

- [1] Y. Sunairi, HM, *et al.*, *J. Phys. Chem. C* **122**, 11623 (2018). [2] Y. Sunairi, SD, HM, *et al.*, *J. Phys. Soc. Jpn.* **89**, 051008 (2020). [3] Y. Hori, SD, HM, *et al.*, *J. Phys. Chem. Lett.* **12**, 5390 (2021).