Molecular Assembly Structures and Physical Properties of 2,3-Diaminophenazine

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Keywords: 2,3-Diaminophenazine, Proton-electron transfer, Proton conduction, Molecular assembly, Hydrogen bond

2,3-Diaminophenazine (DAP) exhibits significant fluorescent emission in solution, which has been utilizing in the field of ion recognition as a fluorescent probe. Large π-π conjugated system and hydrogen bonding interactions of DAP derivative enables the formation of protonated salt of $HDAP^+$ to exhibit a unique self-assembly structure, forming a network of water channels and the proton conduction pathway. In this study, we prepared the single crystals of $(HDAP^+)(Cl^-)•3(H_2O)$, which crystal structure, redox behavior, , dielectric properties, and proton conduction property were evaluated.

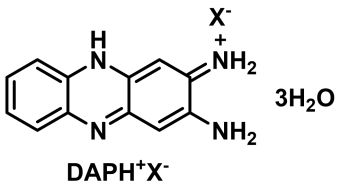

Fig.1 Molecular structure of $HDAP^+X^-$

Protonated 2,3-diaminophenazine salt of $(HDAP^+)(Cl^-)•3(H_2O)$ was obtained by the addition of aqueous $FeCl_3$ solution into *o*-phenylenediamine under ambient conditions. By recrystallizing the precipitation with deionized water, purple single crystals of the $(HDAP^+)(Cl^-)•3(H_2O)$ can be obtained. Single crystal X-ray structural analysis revealed that the $HDAP^+$ molecules forms a water channel network suitable for proton conduction through hydrogen-bonding network (Fig. 2a). Dielectric spectra showed temperature and frequency dependent behavior above 360 K, suggesting dynamic behavior of polar structural unit. The semicircular trace of the Cole-Cole plots at high temperatures indicates its proton conduction properties (Fig. 2b). The proton conductivity at 430 k was 1 nS cm^{-1} with an activation energy of 0.88 eV.

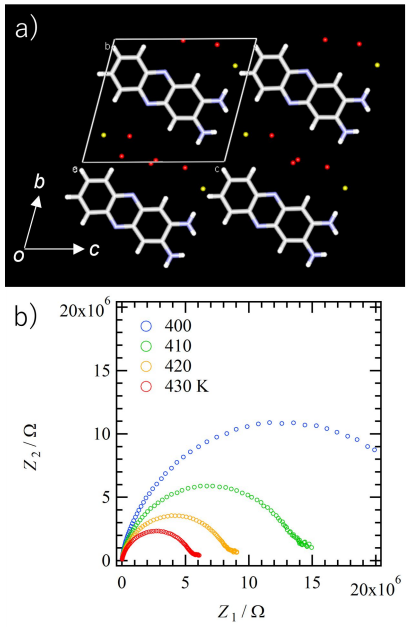

Fig. 2 Crystal structure and dielectric response of $(HDAP^+)(Cl^-)•3(H_2O)$. Unit cell viewed along the *a*-axis. b) *T*-dependent Cole-Cole plots and c) log σ−T^{-1} plots.