Structures and Properties of Supramolecular Assemblies Constructed by Pyrizine Derived Ligand

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Crystal engineering, a study of manipulating packing structures of crystalline materials, has an aspect as a derivation of functionalities or physical properties. Especially, supramolecular coordination assemblies with hydrogen bonding network have often shown fascinating structures, dynamics, or functionalities. It is not only these individual factors but also correlations among them that attract most researchers.

One of the most effective strategies to obtain hydrogen bonding network in packing is to select a ligand with numerous hydrogen bonding accepter sites in its structure. $tdpd^{2-}$ ($tdpd^{2-}$ = 2,3-dicyano-5,6-pyrazinediolate) is a pyrizine derived ligand with six hydrogen bonding accepter sites in its structure, and, on account of these sites, numerous supramolecular assemblies have been generated.[1-3] In this research, six unprecedented supramolecular coordination assemblies constructed by $tdpd^{2-}$ have been synthesized.

The obtained compounds can be divided into two types; tdpd mono formed systems (**1**-**4**) and bis formed systems (**5**, **6**). For mono formed systems, each has different assembled structures with different dimension; 1-D chain, 2-D sheet, and 3-D network, without hydrogen bonding network by H_2O molecules. Especially, for the 3-D network system, including Cu^{II} as a central metal ion, the EPR spectroscopic measurement indicates magnetic interaction among localized spins (S = 1/2) of Cu^{II} ions. On the other hand, both of the bis formed systems have hydrogen bonding networks by H_2O molecules in the 2D sheet-like assembled structure (Fig. 1) and along the 1D chains (Fig. 2), for **5** and **6**, respectively. To observe behaviors of H_2O molecules in the packings and structural dynamics of **5** and **6**, proton conductivities and water adsorption properties have been investigated. Proton conductivities at RH = 100% are σ_{363K} = 4.493×10^{-7} S cm^{-1} with E_a = 0.180eV and σ_{363K} = 7.243×10^{-7} S cm^{-1} with E_a = 0.139eV for **5** and **6**, respectively, and these values of E_a are attributed to Grothuss mechanism. Furthermore, the isotherm of **6** shows that the H_2O uptake increases with multi steps in the adsorption process, indicating structural changes with soaking H_2O molecules.

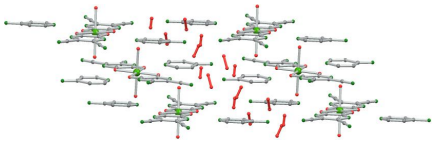

Fig.1 2D-Supramolecular Structure of **5**

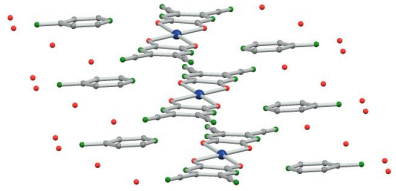

Fig.2 1D-Supramolecular Structure of **6**

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