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Crystallinity-dependence of ionic conductivity in ion pairs of multi-interactive anion

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Ammonium and sodium salts (ion pairs) of multi-inte ractive anion tri(4-pyridyl)hexaazaphenalene (TPHAP−) showed completely different ion-conductive properties depending on the crystal structures. TPHAP columnar crystals showed high conductivity to $10^{-3}$ S·cm$^{-1}$ while retaining their structures even in humid condition, whereas TPHAP dimer crystals exhibited conductivity $\sim 10^{-5}$ S·cm$^{-1}$ with crystallinity deterioration. The main unit structures induced by multi-interactivity realized different water accessibility, which explains the differences in their ion conductivity and stability against humidity.

Intermolecular interactions play critical roles in functional materials, crystal engineering, and biological systems.1-3 In such systems, molecules that have multi-point interactions are important components because they can stabilize meta-stable states4,5 by deepening a local minimum energy state to trap kinetic states. For this purpose, we designed a multi-interactive molecule, tri(4-pyridyl)hexaazaphenalene anion (TPHAP−) which has multi-point interaction sites composed of nine nitrogen atoms in the same π-plane.6 Using this molecule, we trapped a kinetic coordination network composed of TPHAP ligand6a and prepared diverse coordination networks from the same crystallization setup by changing only solvent or additives.6b Importantly, the potassium salt KTPHAP shows humidity-dependent conductivity with reversible structure transformation by hydration/dehydration.7 This result indicates that water and K$^+$ strongly influence structural change with interaction of TPHAP−.

Here we report ion conducting properties of two new TPHAP salts, ion pairs of NH$_4$TPHAP and NaTPHAP which were isolated as two kinds of phases: highly water-stable phase A and phase B which can readily deteriorate under high humidity. At 95% RH, the A-phases were more conductive than the B-phases by two orders of magnitude. The existence of different crystalline phases indicates that we can prepare various structures by exploiting the multi-interactive nature of TPHAP−. These properties in both phases can be explained by considering main structural unit, which is a 1-D column or dimer of TPHAP ion pair. Water accessibility strongly affects their water-stable crystallinity and the ion conductivity.

We obtained two crystalline phases of both NH$_4$TPHAP and NaTPHAP with clearly different features: one phase keeps high crystallinity (denoted by NH$_4$(or Na) TPHAP−-A) under humid conditions; the other has a low crystallinity (NH$_4$(or Na) TPHAP−-B). NH$_4$TPHAP-A single crystal was obtained by slow recrystallization from dilute MeOH solution; NH$_4$TPHAP-B single crystal was obtained by quick recrystallization from concentrated MeOH solution. NaTPHAP-A crystalline powder was obtained by vapour diffusion using MeOH solution and ethyl acetate; NaTPHAP-B single crystal was obtained using the same method with more ethyl acetate vapour in a smaller crystallization vial than in the case of NaTPHAP−-A crystal (Fig. S1, ESI). This sensitivity of crystallization to condition indicates that TPHAP− can respond to very small change of environment effects by forming completely different structures.5,6

The crystal structures of NH$_4$TPHAP−-A and NaTPHAP−A were solved by single-crystal X-ray analysis and by ab initio X-ray powder diffraction (XRPD) analysis (ESI),8 respectively (Fig. 1). Both phases are stable under air and have the same structural features; owing to highly symmetrical structure of TPHAP−, they are spread onto 2-D layer in hexagonal shape.
with forming pores surrounded by six pyridine rings (Fig. 1a,c, red-dotted line). Both NH$_4$TPHAP-A and NaTPHAP-A form π–π stacking columns at hexaazaphenalene (HAP) skeletons along the b- and the c-axes with the distances of 3.40 Å and 3.34 Å, respectively (Fig. 1b,d). The remaining open spaces are occupied by counter cations (NH$_4^+$, Na$^+$) and severely-disordered water molecules. Two disordered NH$_4^+$ in NH$_4$TPHAP-A loosely bind TPHAP$^-$ by hydrogen bonding (H-bonding) interactions; N1A(NH$_4^+$)--N(Pyridine): 2.891(2) Å; N2A(NH$_4^+$)--N(HAP): 2.990(4)-3.485(4) Å (Fig S2, ESI). In contrast, both of the single crystals of NH$_4$TPHAP-B, which is the isostructure of KTPHAP, all dimer units bridged by NH$_4^+$ are strongly connected by NH$_4^+$·(N(NH$_4^+$))=⁻N(HAP) bond distance is 2.987(1)-3.189(1) Å (Fig. 1e,f and S4, ESI). This tight binding protects the crystal from disruption by interaction with air and escape of water from the system. In contrast, in single crystals of NaTPHAP-B, the dimers are formed by dipole-dipole interactions and simple π–π stacking between TPHAP’s. Furthermore, interaction between the dimers is too weak to maintain crystallinity. Therefore, its crystallinity drastically decreases in air because of MeOH escape (Fig. S5, ESI).

Similarly, the structure of NaTPHAP-A has disordered Na$^+$ and loose binding; Na$^+$--N(HAP) distance is 3.0(3)-3.6(2) Å (Fig S3, ESI). In contrast, both of the single crystals of NH$_4$TPHAP-B and NaTPHAP-B consist of dimer units of TPHAP$^-$ which are bound by counter cations (Fig. 1e-h). In the crystal structure of NH$_4$TPHAP-B, and NaTPHAP-B measured at 30 °C versus relative humidity. Note that the highest ionic conductivity values in NaTPHAP-A and NaTPHAP-B. (Detailed values are described in Table S1, ESI).
Figure 3. XRPD patterns. Simulated pattern from single crystal structure (dotted), initial powder (black) and hydrated powder (blue). a) experimental setting of XRPD measurement, b) NH₄TPHAP-A, c) NaTPHAP-A, d) NH₄TPHAP-B, e) NaTPHAP-B.

However, NaTPHAP-A showed higher conductivity (5.9 × 10⁻³ S·cm⁻¹) than NH₄TPHAP-A at 95% RH, though the crystals types have similar molecular packing. This is reasonable because larger interaction energy with water of Na⁺ enabled easier water adsorption than NH₄⁺ (vide infra). In addition, the conductivity of NH₄TPHAP-A increased abnormally under 95% RH; this result is consistent in the stronger stabilization effect by coulombic interaction of NH₄⁺---N (HAP or pyridine) (Tables S3, S4, ESI), the weaker interaction energy of NH₄⁺ with water than Na⁺ system which prevent the effective migration of NH₄⁺ within the system. On the contrary, TPHAP-dimer-based NH₄TPHAP-B and NaTPHAP-B crystals showed lower conductivities ≤ 3.2 × 10⁻⁵ S·cm⁻¹ at 95% RH.

We examined XRPD patterns under humid condition to investigate the hydration effect against the crystal structures and their conductivities (Fig. 3). NH₄TPHAP-A and NaTPHAP-A remained crystalline even at 95% RH, as does KTPHAP. To our surprise, neither A-phases showed significant pattern change. In contrast, the crystallinity of NH₄TPHAP-B and NaTPHAP-B decayed during hydration at 95% RH and 30 °C for 12 h. These different responses of crystallinity to hydration can be explained by their initial crystal structure, especially π-π stacking columnar structure or dimer structure.

A-phases have a stable columnar structure of TPHAP and each column is loosely bound by counter ions; the result is well-packed structure. This structural feature prevents water solvation which severely degrades the crystallinity. Instead, water can enter only the spaces in the crystals in which the cations are disordered but maintain interactions with TPHAP′ ((Na⁺ or NH₄⁺)---N(HAP)) even though their binding energies can be reduced. As a result, at 95% RH, the diffusion rate of the counter cations increases so the ion conductivity becomes high. In contrast, TPHAP dimer-based B-phase crystals include more free space than do A-phase, and provide more opportunity for water adsorption. Therefore, water adsorption caused the deterioration of initial ordered structures. However, the lower conductivity values of B-phase crystals than those of A-phase ones seem to be inconsistent because water adsorption can increase the diffusion rates of the cations which is linearly related to conductivity. The most reasonable explanation for this contradiction is the high stability of TPHAP and cation pair. Indeed, the complex can be clearly observed in the CS-ESI-MS spectrum using MeOH. This strong coulombic interaction impedes diffusion of the counter cations in water. An additional possibility is suggested by the slight increase of full width at half maximum with no change in intensity of XRPD patterns, indicating formation of finer powder by hydration. In fact, we confirmed the decrease of particle size by optical microscope. The observation suggests that a grain boundary effect may be operating: that water adsorption occurs mainly on the crystalline surface, so the grain boundary provides an effective conduction path.

In summary, we exploited the multi-interactive character of TPHAP to prepare two crystalline phases of NH₄TPHAP and of NaTPHAP. The crystallinity and structural features of ion pairs were closely related to their conductivity. The A-phases with infinite π-π stacking structure resisted degradation by high humidity conditions and have high conductivity. However, TPHAP-dimer based B-phases lost their crystallinity by hydration and showed low conductivity. This work emphasizes the importance of molecular interactions in design of hydrous ionic conducting systems.

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Notes and references


13 Diffusion constant $D$ can be described as $D = \sigma k T / C z^2 e^2$. Here $\sigma$ is ion conductivity, $k$ is Boltzmann constant, $C$ is carrier concentration, $z$ is ion valence and $e$ is elementary charge. See, *Modern Electro Chemistry vol 1: Ionics*, ed. J. O. Bockris and A. K. N. Reddy, Springer, 2nd edn, 1998.