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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-interactive anion tri(4-pyridyl)hexaazaphenylene (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 states^{4,5} by deepening a local minimum energy state to trap kinetic states. For this purpose, we designed a multi-interactive molecule, tri(4-pyridyl)hexaazaphenylene 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 ligand^{6a} 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 NH₄TPHAP 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 NH₄TPHAP and NaTPHAP with clearly different features: one phase keeps high crystallinity (denoted by NH₄ (or Na) TPHAP-**A**) under humid conditions; the other has a low crystallinity (NH₄ (or Na) TPHAP-**B**). NH₄TPHAP-**A** single crystal was obtained by slow recrystallization from dilute MeOH solution; NH₄TPHAP-**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 NH₄TPHAP-**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

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with forming pores surrounded by six pyridine rings (Fig. 1a,c, red-dotted line). Both $\text{NH}_4\text{TPHAP-A}$ and NaTPHAP-A form π - π stacking columns at hexaazaphenalene (HAP) skeletons⁹ 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 $\text{NH}_4\text{TPHAP-A}$ loosely bind TPHAP^- by hydrogen bonding (H-bonding) interactions; $\text{N1A}(\text{NH}_4^+) \cdots \text{N}(\text{Pyridine})$: 2.891(2) Å; $\text{N2A}(\text{NH}_4^+) \cdots \text{N}(\text{HAP})$: 2.990(4)-3.485(4) Å (Fig S2, ESI).

Similarly, the structure of NaTPHAP-A has disordered Na^+ and loose binding; $\text{Na}^+ \cdots \text{N}(\text{HAP})$ distance is 3.0(3)-3.6(2) Å (Fig S3, ESI). In contrast, both of the single crystals of $\text{NH}_4\text{TPHAP-B}$

$\text{NH}_4\text{TPHAP-B}$, which is the isostructure of KTPHAP , all dimer units bridged by NH_4^+ are strongly connected by NH_4^+ ($\text{N}(\text{NH}_4^+) \cdots \text{N}(\text{HAP})$ bond distance is 2.987(1)-3.189(1) Å (Fig. 1e,f and S4, ESI).⁷ 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).

The ion conductivities of these materials were significantly correlated with initial structure and atmospheric humidity (Fig. 3). We used *ac* impedance spectroscopy to measure the conductivity of compressed pellets of each crystal under various relative humidities (RH). The conductivities of all materials increased more than 2 order of magnitude as humidity became higher. These observations clearly indicate that water adsorption accelerates ion conduction. In addition, the conductivity measurement under deuterated water conditions (95% RH, 30 °C) gave similar conductivities ($\text{NH}_4\text{TPHAP-A}$; $2.95 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$, NaTPHAP-A ; $9.77 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$, $\text{NH}_4\text{TPHAP-B}$; $2.23 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$, NaTPHAP-B ; $1.29 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$, ESI) to those which were measured under normal water conditions. These results indicate that the main charge carrier is not proton. Therefore, the possible mechanism of the ion conduction in these systems were based on the migration of Na^+ and NH_4^+ . Their migration can be accelerated by water adsorption which reduces the interaction between the ions and the framework. A-phases showed drastic conductivity changes from negligible (insulating) at 50% RH to $10^{-3} \text{ S}\cdot\text{cm}^{-1}$ at 95% RH. These high conductivities are comparable to cation-exchanged Nafion.¹⁰ Na^+ ions are less mobile ($5.19 \times 10^{-8} \text{ m}^2\text{s}^{-1}\text{V}^{-1}$) than NH_4^+ ions ($7.63 \times 10^{-8} \text{ m}^2\text{s}^{-1}\text{V}^{-1}$) in water.¹¹

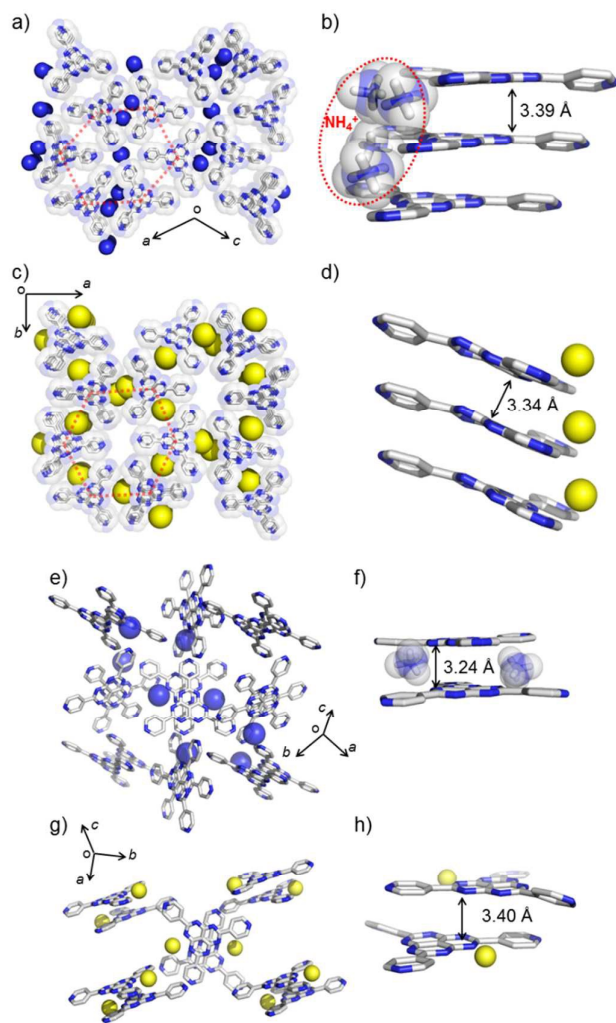


Figure 1. Initial crystal structures. a) Overview of $\text{NH}_4\text{TPHAP-A}$ structure; b-axis projection, b) Infinite π - π stacking of $\text{NH}_4\text{TPHAP-A}$, c) Overview of NaTPHAP-A structure; c-axis projection, d) Infinite π - π stacking of NaTPHAP-A , e) Overview of $\text{NH}_4\text{TPHAP-B}$ structure, f) Dimer unit of $\text{NH}_4\text{TPHAP-B}$, g) Overview of NaTPHAP-B structure, h) Dimer unit of NaTPHAP-B . Hydrogen and crystal solvents are omitted for clarity. Colour code: C, grey; N, blue; Na^+ , yellow sphere, NH_4^+ , blue sphere.

and NaTPHAP-B consist of dimer units of TPHAP^- which are bound by counter cations (Fig. 1e-h). In the crystal structure of

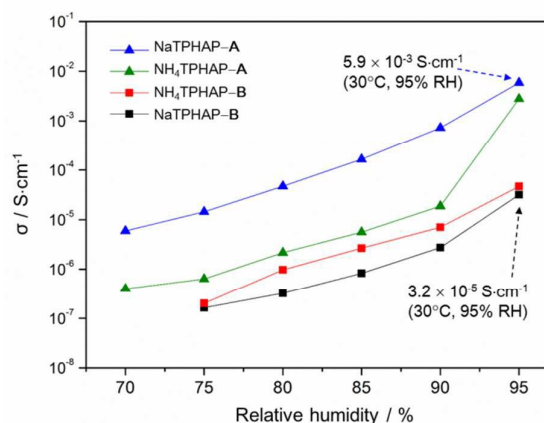


Figure 2. Ionic conductivity σ of different crystalline phases of NaTPHAP and NH_4TPHAP measured at 30 °C versus relative humidity. Note that the highest ionic conductivity values in NaTPHAP-A and NaTPHAP-B . (Detailed values are described in Table S1, ESI).

However, NaTPHAP-A showed higher conductivity ($5.9 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$) than $\text{NH}_4\text{TPHAP-A}$ at 95% RH, though the crystal types have similar molecular packing. This is reasonable because larger interaction energy with water of Na^+ enabled easier water adsorption than NH_4^+ (*vide infra*).¹² In addition, the conductivity of $\text{NH}_4\text{TPHAP-A}$ increased abnormally under 95% RH; this result is consistent in the stronger stabilization effect by coulombic interaction of $\text{NH}_4^+\cdots\text{N}$ (HAP or pyridine) (Tables S3, S4, ESI), the weaker interaction energy of NH_4^+ with water than Na^+ system which prevent the effective migration of NH_4^+ within the system. On the contrary, TPHAP-dimer-based $\text{NH}_4\text{TPHAP-B}$ and NaTPHAP-B crystals showed lower conductivities $\leq 3.2 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at 95% RH.

We examined XRPD patterns under humid condition to investigate the hydration effect against the crystal structures and their conductivities (Fig. 3). $\text{NH}_4\text{TPHAP-A}$ and NaTPHAP-A remained crystalline even at 95% RH, as does KTPHAP.⁷ To our surprise, neither A-phases showed significant pattern change. In contrast, the crystallinity of $\text{NH}_4\text{TPHAP-B}$ 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.

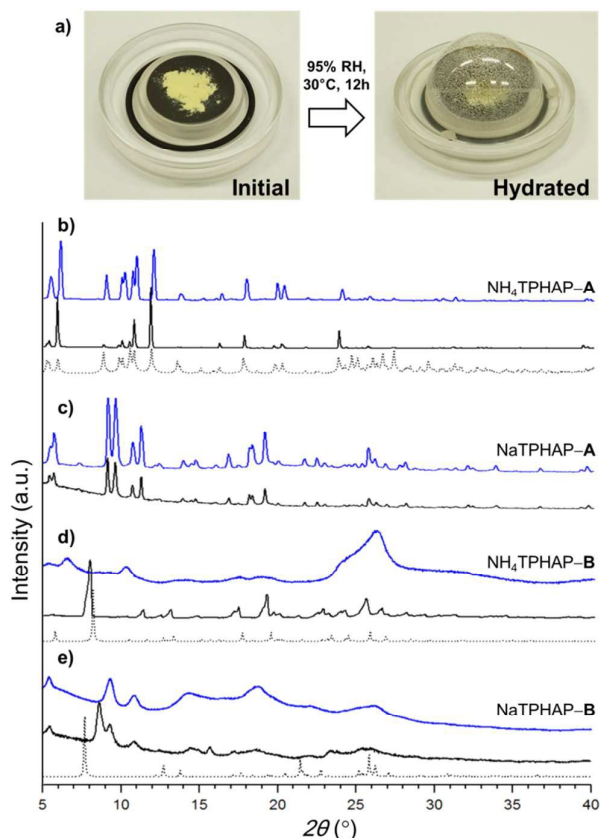


Figure 3. XRPD patterns. Simulated pattern from single crystal structure (dotted), initial powder (black) and hydrated powder (blue). a) experimental setting of XRPD measurement, b) $\text{NH}_4\text{TPHAP-A}$, c) NaTPHAP-A , d) $\text{NH}_4\text{TPHAP-B}$, e) NaTPHAP-B .

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^- ($(\text{Na}^+ \text{ or } \text{NH}_4^+)\cdots\text{N}(\text{HAP})$) 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.¹³ 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.^{6b} 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 NH_4TPHAP 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

- 1 *Supramolecular Chemistry*, ed. J. W. Steed and J. L. Atwood, Wiley, UK, 2nd edn, 2009
- 2 (a) D. Stock, A. G. W. Leslie and J. E. Walker, *Science*, 1999, **286**, 1700-1705; (b) N. Ban, P. Nissen, J. Hansen, P. B. Moore and T. A. Steitz, *Science*, 2000, **289**, 905-920; (c) N. H. Joh, A.

- Min, S. Faham, J. P. Whitelegge, D. Yang, V. L. Woods, Jr. and J. U. Bowie, *Nature*, 2008, **453**, 1266-1270; (d) D. M. Rosenbaum, S. G. F. Rasmussen and B. K. Kobilka, *Nature*, 2009, **459**, 356-363.
- 3 G. D. Desiraju, *Angew. Chem. Int. Ed.*, 2007, **46**, 8342-8356.
- 4 (a) M. M. Gromiha and S. Seleveraj, *Prog. Biophys. Mol. Biol.*, 2004, **86**, 235-277; (b) M. Chaplin, *Nat. Rev. Mol. Cell Biol.*, 2006, **7**, 861-866.
- 5 (a) M. Kawano, T. Haneda, D. Hashizume, F. Izumi and M. Fujita, *Angew. Chem., Int. Ed.*, 2008, **47**, 1269-1271; (b) J. Martí-Rujas and M. Kawano, *Acc. Chem. Res.* 2013, **46**, 493-505; (c) H. Kitagarwa, H. Ohtsu and M. Kawano, *Angew. Chem., Int. Ed.*, 2013, **52**, 12395-12399.
- 6 (a) Y. Yakiyama, A. Ueda, Y. Morita, and M. Kawano, *Chem. Commun.*, 2012, **48**, 10651-10653; (b) T. Kojima, T. Yamada, Y. Yakiyama, E. Ishikawa, Y. Morita, M. Ebihara and M. Kawano, *CrystEngComm*, 2014, **16**, 6335-6344; (c) "Crystal Engineering of Coordination Networks Using Multi-Interactive Ligands", Y. Yakiyama, T. Kojima and M. Kawano, *Advances in Organic Crystal Chemistry: Comprehensive Reviews 2015*, ed. R. Tamura and M. Miyata, Springer, Tokyo, 223-240, 2015.
- 7 Y. Yakiyama, G. R. Lee, S. Y. Kim, Y. Matsushita, Y. Morita, M. J. Park and M. Kawano, *Chem. Commun.*, 2015, **51**, 6828-6831.
- 8 (a) M. Takata, B. Umeda, E. Noshibori, M. Sakata, Y. Saito, M. Ohno and H. Shinohara, *Nature*, 1995, **377**, 46-49; (b) S. Pagola, P. W. Stephens, D. S. Bohle, A. D. Kosar and S. K. Madsen, *Nature*, 2000, **404**, 307-310; (c) *IUCr Monographs on Crystallography 13*, ed. W. I. F. David, D. Shankland, L. B. McCusker and C. Baerlocher, Oxford University Press, Oxford, UK, 2002.
- 9 (a) S. Suzuki, Y. Morita, K. Fukui, K. Sato, D. Shiomi, T. Takui and K. nakasuji, *Inorg. Chem.*, 2005, **44**, 8197-8199; (b) S. Suzuki, K. Fukui, A. Fuyuhiko, K. Sato, T. Takui, K. nakasuji and Y. Morita, *Org. Lett.*, 2010, **12**, 5036-5039.
- 10 T. Okada, H. Satou, M. Okuno, and M. Yuasa, *J. Phys. Chem B.*, 2002, **106**, 1267-1273.
- 11 (a) *Tables of physical and chemical constants*, ed. G. W. C. LKaye and T. H. Lady, Longman, London, UK, 1973; (b) *Electrolyte solutions*, R. A. Robinson and R. H. Strokes, Butterworth, London, UK, 1959.
- 12 A. G. Volkov, S. Paula and D. W. Deamer, *Bioelectrochem. Bioenergetics*, 1997, **42**, 153-160.
- 13 Diffusion constant D can be described as $D = \sigma kT/Cz^2e^2$. Here σ 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.