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Porous organic hydrate crystals: structure and dynamic behaviour of water clusters

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4-Nitrostyrylpyridine hydrochloride forms porous crystals stabilized by cation- π and NO₂····CI interactions that involve water clusters with a T5(2) motif in the channels. The crystals reversibly release and re-uptake water molecules. Solid-state ¹⁷O NMR spectroscopic analyses revealed the behaviour of the water molecules present in the channels.

The design and synthesis of porous materials possessing water channels have attracted a lot of recent attention due to their potential utility in terms of proton conductivity¹ and dielectric properties² and as a model³ for the naturally occurring membrane water channel proteins, aquaporine⁴ and gramicidin.⁵ Various types of porous materials involving water clusters have been reported, including carbon nanotubes⁶ (CNTs), pillar[5]arens,⁷ porous organic crystals,⁸ metal-organic frameworks⁹ (MOFs) or porous coordination polymers⁹ (PCPs). Among these materials, the design of molecular organic crystals possessing porosity is relatively difficult as crystal packing relies on various noncovalent bonds. Nevertheless, such crystals remain attractive as they possess several advantages in terms of structural diversity and flexibility as well as being more environmentally friendly than other materials.

We have previously reported that styrylpyridine hydrochloride molecules form hydrate crystals that involve water channels surrounded by columns arranged in a head-to-tail fashion¹⁰ through cation- π interactions.^{11,12} This prompted us to develop readily accessible and more stable porous organic crystals by modifying the styrylpyridine structure. Among the various derivatives surveyed, we found that 4-nitrostyrylpyridinium salts form unusual porous hydrate crystals involving an infinite water tape constructed from pentamer water clusters.¹³

It has been well documented that the structure and dynamic properties of the water clusters significantly contribute to the performance of the materials.^{1a,7b,8e,9a} Therefore, exploitation of the dynamic properties of the water clusters would be of great importance. In this communication, we report the structure of novel porous organic crystals as well as the dynamic behaviour of the water clusters present in the channels.

The recrystallization of (E)-4-(4-nitrostyryl)pyridine $(1)^{14}$ from MeOH in the presence of 1.2 equiv of conc HCl produced hydrate crystals of the corresponding HCl salt, **1**·HCl·3H₂O, suitable for X-

ray structural analysis (Scheme 1). Thermogravimetric analysis of the crystals showed a 10.9 wt% loss at 343 K, confirming the existence of 3 equiv of H_2O molecules. The crystal system was orthorhombic with a $P2_12_12_1$ space group.



Scheme 1. Preparation of the 1·HCl·3H₂O hydrate crystals



Fig. 1 Packing diagram of $1 \cdot \text{HCl} \cdot 3\text{H}_2\text{O}$ along the *a* axis.

Fig. 1 shows the crystal packing structure of $1 \cdot \text{HCl} \cdot 3\text{H}_2\text{O}$ along the *a* axis. It is clear that the molecules form columns, and that the four columns form an infinite hydrophobic channel that involves water molecules. The diameters of the channel are approximately 6.8 Å and 3.2 Å on the major and minor axes, respectively, which are close to those of the naturally occurring membrane water channels of aquaporine $(2.8\text{ Å})^4$ and gramicidin (ca. 4Å).⁵ The molecules were

arranged in a head-to-tail and face-to-face fashion to form columns as shown in Fig. 2a; the structure of which is similar to those previously reported for styrylpyridine derivatives.¹⁰ The distance between the centroids of the pyridinium and aryl moieties is 3.775Å, suggesting that the columns are stabilized by cation- π interactions. The chloride anion forms a H-bond with NH and is located between the nitro groups of the upper and lower layers through electrostatic interactions. The distances between the Cl^{-...}NO₂ are 3.354Å and 3.415Å. This also contributes to stabilize the head-to-tail column structure, forming a stronger framework to maintain the channels. To the best of our knowledge, this Cl-...NO2 interaction has not yet been reported. The columns are linked together through H-bonds between the oxygen atoms of the nitro group and the several C-H groups of the next column (Fig. S3). In addition, the chloride anion bridges between the columns via H-bond networks of NH···Cl···HC (Fig. 2b). It should be noted that this channel is chiral due to it having a chiral space group similar to those of naturally occurring water channels.



Fig. 2 Packing diagrams of $1 \cdot \text{HCl} \cdot 3\text{H}_2\text{O}$, showing (a) a side view and (b) four molecules with H-bond networks.



Fig. 3 Packing diagrams of $1 \cdot \text{HCl} \cdot 3\text{H}_2\text{O}$, showing (a) a water cluster in a channel and (b) a water cluster with chloride ions forming Hbonds. The displacement ellipsoids are drawn at the 50% probability level.

The three water molecules in the channel, the oxygen atoms of which are indicated in O3-O5, are linked to one another through hydrogen bonds to form an infinite tape motif containing a T5(2) ring system¹⁵ (Figs 3a and 3b). The H atoms bonded to water oxygen atoms could not be found by a refinement except for H3 and H15. The O···O distances are in the range of 2.791Å to 2.938Å, which are close to those of previously reported pentamar cluster¹³ as well as the average of the O···O distances (~2.8Å) obtained by the CSD analysis.¹⁶ The water molecules are linked with the columns through O-H···Cl⁻ and O···H-C hydrogen bonds as shown in Figs. 2b and 3b. The three water molecules form different H-bonds; O3 and O4 form

H-bonds with both Cl⁻ and C-H, whereas O5 links with C-H alone. The details are shown in Table S5.

The channels can reversibly release and re-uptake water molecules in an open atmosphere as observed in the PXRD studies. Fig. 4a shows the simulated PXRD pattern for $1 \cdot \text{HCl} \cdot 3\text{H}_2\text{O}$. Heating of $1 \cdot \text{HCl} \cdot 3\text{H}_2\text{O}$ at 80°C for 3h gave rise to new peaks (Fig. 4b). Thermogravimetric analysis of the dehydrated crystals showed completion of the dehydration process. As the PXRD pattern of the dehydrate shows no noticeable broadening of the peaks, the crystallinity of the dehydrate is thought to be retained after dehydration, which differs significantly from the broadening patterns observed in previously reported dehydrated styrylpyridine hydrochloride.¹⁰ The differences in the PXRD patterns between the hydrate and dehydrate suggest that dehydration produces changes in the crystal structure.



Fig. 4 PXRD patterns of (a) the simulated $1 \cdot \text{HCl} \cdot 3\text{H}_2\text{O}$, (b) heating at 80°C for 3h, and (c) rehydrated at 58% relative humidity.

As a single crystal of 1 HCl 3H2O could not be retained through dehydration, the crystal structure of the resultant anhydrate 1 HCl remains unclear. To obtain an insight into the framework structure of the dehvdrate, solid-state ¹³C NMR spectra of the hvdrate and dehydrate were compared (Fig. S7). Differences were observed in the chemical shifts of the aromatic and pyridinium carbons between the two crystals: while the α -carbons next to the nitro group of the benzene ring and the 3-carbons of the pyridinium ring of the hydrate are equivalent, those of the dehydrate appear non-equivalent, indicating that the column structure was partially changed by dehydration. The orientation of the molecules in the column was confirmed by solid-state photodimerization. Irradiation of both hydrate and dehydrate crystals gave a synHT dimer^{10a} in quantitative yields (Scheme 2). This clearly shows that the head-to-tail orientation of the molecules was retained after dehydration. The good crystallinity of the dehydrate and the retention of head-to-tail orientation can be attributed to the cation- π and NO₂···Cl⁻ electrostatic interactions within the columns as well as H-bonds between columns, as described above. When the dehydrated powder was kept in a desiccator at 58% relative humidity for 24 h, the PXRD pattern was in close agreement with that of the simulated Journal Name

 $1 \cdot \text{HCl} \cdot 3\text{H}_2\text{O}$ (Figs. 4a and 4c). The time dependence of the PXRD measurements of $1 \cdot \text{HCl}$ under an atmosphere of water vapour shows no intermediate phase, suggesting that the trihydrate was directly restored from the dehydrate (Fig. S5). This facile reversible dehydration-hydration process is speculated to be the result of the hydrophobic environment of the channel.



Scheme 2. Irradiation of 1 HCl 3H₂O and the dehydrate crystal.

The dynamic behaviour of the water molecules in the porous organic crystals was clarified by solid-state ¹⁷O NMR analysis, which is more useful than conventional solid-state ¹H and ²H NMR analyses in that the former provides dynamic information on the whole water molecule. ¹⁷O NMR measurements were carried out at various temperatures using the ¹⁷O isotope-enriched compound. The ¹⁷O isotope enrichment of **1** HCl 3H₂O was performed through the exchange of $H_2^{16}O$ with $H_2^{17}O$ molecules by placing them in a $H_2^{17}O$ vapour atmosphere for 2 days at rt. Fig. 5 shows stationary ¹⁷O NMR spectra of 1·HCl·3H₂O measured in a sealed sample holder at temperatures from 143 K to 373 K. All the ¹⁷O NMR signals arose from the water molecules, and the crystal structure of 1·HCl·3H₂O was maintained throughout the NMR measurements, which was confirmed by solid-state ¹³C NMR analysis (Fig. S8). The lineshapes as a function of temperature were changed markedly, which is speculated to be associated with water molecule reorientation in 1.HCl·3H₂O. For convenience, all the ¹⁷O NMR spectra were classified into three phases, namely, Phase I (in the range of temperatures from 143 to 273 K), Phase II (from 273 K to 353 K), and Phase III (above 353 K).

The line-shapes in Phase I exhibit the effects of motional averaging with increasing temperature. It can be observed that from 143 to 193 K the spectral widths were roughly constant, although both edges gradually shrunk. After 193 K, the spectral widths significantly narrowed and the main peaks slightly shifted to the higher magnetic fields. New symmetric lines centered at approximately –45 ppm appeared at temperatures above 263 K. In the absence of a dynamic effect, the line-shape is expected to be more complicated as the solid-state ¹⁷O NMR spectrum is composed of three sub-spectra arising from three inequivalent oxygen sites. In the present case, however, the lowest temperature spectrum seems to show a line shape with dynamic averaging. The present observations, except for that at the lowest temperature, are consistent with the reported reorientations.¹⁷

The best-fitted ¹⁷O stationary spectra calculated at several temperatures are shown in Fig. S9. Given the exchange rate at each temperature, the activation energy for water reorientation can be determined by using the Arrenius law. An activation energy of $E_a = 15 \pm 5$ kJ mol⁻¹ was obtained by least-square fitting to the experimental data (Fig. S10). This is much smaller than those previously reported for ice and THF hydrates ($E_a = 30.12-59.8$ kJ mol⁻¹),^{17,18} indicating that the water molecular reorientations in 1·HCl·3H₂O proceeds more readily. This is thought to be due to the

hydrophobic environment of the channel, which results in weaker interactions with the channel.

At 273 K, the lowest temperature of Phase II, a critical change in line shape was observed in the ¹⁷O NMR spectrum. The spectrum consists of two components; a broad line and a narrow resonance line near 5 ppm. The broad component corresponds to the remaining peak observed in Phase I, and it was observed to disappear at higher temperatures. On the other hand, the narrow component corresponds to that for the rapid motion of water molecules. Apparently, the mobility of the water molecules is high in Phase II, but the motion was not assigned to isotropic motion; i.e., liquid water, because of the observed ¹⁷O chemical shift. Therefore, we expected that a fluid motion, such as the translation of water molecules or molecular hopping from one lattice point to another, takes place throughout the water channel, and Phase II can be characterized as an intermediate state between ice and liquid water. It should be noted that little difference was observed between the ¹³C NMR spectra in Phase I and II (Fig. S8), suggesting that the motion of the water had little influence of the structure of the channels.



Fig. 5 Stationary ¹⁷O NMR spectra of $1 \cdot \text{HCl} \cdot 3\text{H}_2\text{O}$ as a function of temperature.

From 303 K to 353 K, the broad line disappeared and the shape becomes much narrower, indicating that all of the water molecules were dynamically equivalent, and the motion is much faster than that in Phase I. As DSC measurements show an endothermic peak at temperatures over 353 K, the water molecules are thought to remain in the channels under confined conditions (Fig. S11). In Phase III

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(above 353 K), the isotropic line is centered at 0 ppm, suggesting that the water molecules exist in an equilibrium between the inside and the outside of the channel in a sealed sample holder. Although solid-state ¹⁷O NMR spectroscopy has been used for the investigation of water molecule behaviour in hydrate crystals,19 to the best of our knowledge, this is the first report on the dynamics of water clusters in the channels.

In summary, we found that 4-nitrostyrylpyridinium chloride forms porous crystals involving infinite water clusters with a T5(2) tape motif in the hydrophobic channels. The crystals reversibly release and re-uptake water molecules. The PXRD and the solid-state ¹³C NMR studies showed that the channel structure was partially changed after dehydration. The stability of the porous crystal structure can be explained by the contribution of cation- π and electrostatic Cl^{-...}NO₂ interactions within the columns and H-bond networks between columns. Solid-state ¹⁷O NMR analysis of the water clusters clarified the existence of three phases in terms of the dynamic properties. The activation energy of $\hat{E}_a = 15 \ \Box \ 5 \text{kJ mol}^{-1}$ in Phase I (143 K - 273 K) shows that water molecular reorientation proceeds readily in the hydrophobic channel. The mobility of the water molecules is high in Phase II (273 K - 353 K), but the motion could not be assigned to isotropic motion; therefore, Phase II can be characterized as an intermediate state between ice and liquid water. At temperatures higher than 353 K in a sealed sample holder (Phase III), the water molecules are in equilibrium between the inside and outside of the channel and behave like free water. These observations provide important insights into the development of new porous organic materials as well as the behaviour of water molecules in channels.

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Infinite water clusters with a T5(2) motif were observed in porous crystals of 4-nitrostyrylpyridine hydrochloride, the behavior of which was revealed by solid-state 170 NMR spectroscopic analyses. 97x35mm (300 x 300 DPI)