Structural investigation of a hydrogen bond order–disorder transition in a polar one-dimensional confined ice†

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The hydrogen-bond arrangement within crystalline 2,3,6,7,10,11-hexahydroxytriphenylene tetrahydrate (HHTP·4H2O) undergoes an order–disorder transition at 240 K, as evidenced by the emergence and disappearance of systematic absence violations in variable-temperature single-crystal X-ray diffraction measurements. The low-temperature ordered phase is polar with ferroelectric coupling between neighbouring one-dimensional ice-like columns of hydrogen-bonded H2O molecules. At temperatures above 240 K the material adopts a paraelectric state characterised by the absence of long-range ordering between column polarisations. We discuss the mapping of this phase transition onto the problem of frustration on the canonical Ising square lattice, and suggest that HHTP·4H2O is an obvious candidate for exploring switchable ferroelectric behaviour in confined ices.

Whether the dipolar nature of the water molecule might be translated into a polar form of ice is a question that has its origin in the very earliest studies of hydrogen bonding in solid phases of water.1,2 The configurational entropy of bulk ices is such that, to date, the only successful approaches to developing polar phases have involved symmetry lowering via e.g., surface layer deposition3,4 and dimensionality reduction in confined phases;5,6 even the nature of the supposedly-polar ice XI obtained on ion doping at low temperatures remains controversial.3,7,8 For some time, the focus of confinement studies has been on water-filled carbon and inorganic nanotubes.9–14 However, the primary application of polar ices—namely, in ferroelectric devices—relies on switchable bulk dipolar alignment, which is difficult for nanotube conglomerates; consequently the design strategy has recently shifted to exploiting aligned voids within nanoporous crystalline hosts.15,16 So, for example, water confined to nanochannels in the framework material La2CuII[NH(CH2COO)2]6 exhibits antiferroelectric ordering below the confined liquid ↔ solid transition at 350 K;17 likewise, 1D “water wires” within a copper-based coordination polymer [CuII2CuIII(CDTA)(4,4′-bpy)] have been shown to undergo a spontaneous transition between liquid and ferroelectric states at 277 K.18

Despite the observation of dielectric hysteresis in the ferroelectric phase of [CuII2CuIII(CDTA)(4,4′-bpy)], perhaps the most obvious distinction between the formation of polar states in these confined ices and that in traditional ferroelectric phases such as PbTiO3 is that polarisation always seems to emerge on cooling from a liquid parent state rather than from a paraelectric phase.21 This suggests there exists only minimal distinction between the energy scales associated with long-range dipole alignment within and between nanopores and is likely the origin of the relatively weak and temperature-specific ferroelectric hysteresis observed for these systems.18

In this paper, we study the temperature-dependent evolution of 1D ice polarisation in the crystalline molecular hydrate HHTP·4H2O [Fig. 1].20 We show that 1D water-filled channels within HHTP·4H2O exhibit a well-defined polar ↔ paraelectric transition; as such the material is an excellent candidate for investigation into ice-based ferroelectric responses. HHTP-containing systems are of intense current interest in the field of molecular framework materials, where they are favoured for their thermal robustness and attractive porosity/sorption properties.22,23 Our focus is not on any covalent network assembled from HHTP, but rather on the hydrate of the molecule itself. As in all known HHTP cocrystals, the structure of this hydrate [shown in Fig. 1(b)] is dominated by the stacking of triphenylene cores into 1D columns;19,20,24 indeed this motif reflects the well-known role of triphenylene as the structural basis for a large and separate family of discotic liquid crystals.25 The surface of these columns is decorated by hydrophilic –OH groups, and consequently the voids between columns are ideally suited to water coordination. In the single previous structural study of HHTP-
anomalously large considering the temperature at which data were collected. In order to rationalise these crystallographic observations, we prepared a single-crystal sample of HHTP-4H$_2$O and measured its X-ray diffraction pattern as a function of temperature (see ESI† for synthesis and experimental details). During low-temperature data collection, we observed that the intensity of some reflections was temperature dependent: they were strongest at the lowest temperatures but undetectable at 240 K. Making use of the associated reflection conditions, we could assign to the low-temperature structure the space group $P2_1cn$, which is a maximal subgroup of $Pbn$ obtained by removing the inversion symmetry operation. Subsequent refinement of the 100 K data set in this lower-symmetry setting gave an improved structural model in which both the hydrogen-bonding connectivity and water O atom displacement parameters made physical sense. This model is illustrated in Fig. 2(a), and full structural details are given as ESI†.

For all data sets, we were able to refine a satisfactory structural model based on the $Pbn$ solution of ref. 20; however, on close examination of the diffraction patterns themselves, we realised that a set of weak reflections forbidden in the $Pbn$ space group were unaccounted for by such a model. The intensity of these reflections was temperature dependent: they were strongest at the lowest temperatures but undetectable at 240 K. Making use of the associated reflection conditions, we could assign to the low-temperature structure the space group $P2_1cn$, which is a maximal subgroup of $Pbn$ obtained by removing the inversion symmetry operation. Subsequent refinement of the 100 K data set in this lower-symmetry setting gave an improved structural model in which both the hydrogen-bonding connectivity and water O atom displacement parameters made physical sense. This model is illustrated in Fig. 2(a), and full structural details are given as ESI†.

The distinction between $P2_1cn$ and $Pbn$ structural models for low-temperature HHTP-4H$_2$O is crucial because the former is a polar space group whereas the latter is non-polar. Indeed the structural feature responsible for polarity within the $P2_1cn$ model is precisely the ice-like hydrogen-bonding network...
within the water-filled channels: i.e., the ice rules break inversion symmetry [Fig. 2(b)]. While there are two polar 1D ice chains within the crystallographic unit cell, these are related to one another by the crystal symmetry in a way that reinforces the polarisation component parallel to the a crystal axis [Fig. 3]. In fact the chain geometry is of interest in its own right within the context of helical polymer motifs:29 it takes the rarely-observed form of a so-called “directed meso-helix”, an object with polarisation components both along and normal to the helix axis.26 So whereas the polarisation associated with 1D ices is usually parallel to the confinement axis,16,18 in this system the net polarisation is perpendicular to the crystallographic axis. Arrows have been drawn on each meso-helix to emphasise the direction of O–H···O hydrogen-bond donation. (c) Structure inversion has the effect of switching the direction of each O–H···O hydrogen bond, and hence reversing the polarisation along a. The left and centre panels illustrate the ice-like network for these two polarisation states. At temperatures above 240 K, HHTP·4H2O exists in a paraelectric phase in which both states occur throughout the crystal structure, with no long-range correlation between neighbouring ice-like chains. The resulting average structure has Pbcn symmetry and is most meaningfully understood in terms of an equal-population superposition of the two polarisation states.

The transition from polar to paraelectric states of HHTP·4H2O can be quantified using an order parameter derived from the intensities of those reflections unique to the P2₁cn space group (see ESI†). Fig. 4 shows the temperature evolution of a small relevant portion of the diffraction pattern across the transition: here the three reflections (011) (031) and (071) are forbidden in Pbcn and can be seen to decrease in intensity with heating. For each of these reflections, the corresponding order parameter $\xi$ was calculated for each temperature according to

$$\xi(kl) = \frac{I(0k1)}{I(042)}^{1/2}$$

where $\xi$ is a temperature-independent scaling parameter, $I(hkl)$ is the measured intensity of the (hkl) reflection, and the parent (042) reflection was used for normalisation for its combination of strong intensity at all temperatures and well-defined peak profile. The parameter $\xi$ takes the value of zero within the paraelectric regime and is non-zero whenever there is long-range correlation of the 1D ice polarisations. The temperature dependence of $\xi$ for these three reflections is illustrated in Fig. 4, where the values at 240 K should be interpreted as the
result obtained by integrating background fluctuations in the diffraction images. In the absence of a well-defined discontinuity in the function $\xi(T)$, we can conclude that the phase transition is likely to be second-order in nature. By comparing the results of heating and cooling runs, we find no evidence of hysteresis at likely to be second-order in nature. Relevant sections of the single-crystal diffraction patterns are shown in the inset; these illustrate the disappearance of (0k1); $k = 2n + 1$ reflections on heating towards $T_c$. The nearest-neighbour square lattice Ising model discussed in the text predicts a sharper transition (thin line) than is observed experimentally.33 The inclusion of frustrated next-nearest-neighbour terms in the ordering Hamiltonian is known to give rise to a temperature dependency similar to the empirical curve fit shown here [bold line; eqn (5)].

To interpret the order parameter variation shown in Fig. 4 we construct a mapping of the polarisation state of HHTP-4H2O onto the square Ising model. Each 1D ice chain is capable of adopting either one of two configurations consistent with the ice rules—these are the orientations related to one another by the inversion centre present in $Pbcn$ but absent in $P2_{1}2_{1}2_{1}$—and so can be assigned one of the two states $e\in\{1,-1\}$ allowed in an Ising model. For each 1D chain there are four equidistant nearest-neighbours to which its polarisation ($\xi_{m}$) will be coupled via subtle reorganisation of the connecting HHTP molecules [Fig. 5(a)]. The corresponding energy scale $J_{nn}$ is (by symmetry) identical for all nearest-neighbours of all chains, giving the canonical Hamiltonian

$$\mathcal{H} = -J_{nn} \sum_{i,j=nn} e_{i} e_{j}.$$  (2)

The topology of this coupled system is that of the square net and is two-dimensional because each 1D chain acts as a collective object. As such we can interpret the hydrogen bond order–disorder transition in HHTP-4H2O as a specific manifestation of the general and well-established problem of the square Ising model [Fig. 5(b)].33–35

In the case that nearest-neighbour interactions are the only interactions of relevance to the order–disorder process then the corresponding equilibrium behaviour of the square Ising model is known exactly.33 One anticipates a second-order phase transition between ordered (or, in the case of HHTP-4H2O, polar) and disordered (i.e., centrosymmetric) states at the critical temperature

$$T_{c} = \frac{J_{nn}}{k_{B} \ln(1 + \sqrt{2})}.$$  (3)

The temperature-dependence of the order parameter ($\equiv$ magnetization in Onsager’s formulation33) follows the closed form

$$\xi = [1 - \sinh^{-1}(2J_{nn}/k_{B}T)]^{1/8},$$  (4)

which predicts a more sudden variation in $\xi(T)$ near $T_{c}$ than we observe experimentally [Fig. 4].

In practice it is likely that next-nearest-neighbour interactions cannot altogether be neglected in a physical system such as we study here. The inclusion of appropriate additional terms into the Hamiltonian of eqn (2) leads to a surprisingly-complex (and still controversial) system for which no exact
solution is obtainable. Of relevance to the present situation is the observation that next-nearest-neighbour coupling constants $J_{nn}$ of opposite sign to $J_{nn}$ have the effect of reducing the order parameter at lower temperatures to give a thermal variation more similar to that which we find to occur in HHTP-4H$_2$O. This is the so-called ‘frustrated Ising model’, for which the phase transition is actually very weakly first-order. So there may be some suggestion that 1D ice polarisations couple in a ferroelectric sense for nearest neighbours in HHTP-4H$_2$O but in an antiferroelectric sense for next-nearest neighbours. Actually the situation is even more complex in this case because the orthorhombic crystal symmetry gives rise to two distinct types of next-nearest neighbours—a problem for which we are not aware of any prior theoretical groundwork. What is known is that the relationship between $J_{nn}$ and $T_c$ given in eqn (3) holds even for the frustrated Ising case, and so we can estimate the interchain coupling strength in HHTP-4H$_2$O to be $\sim 0.9$ kJ mol$^{-1}$. For comparison the interaction energy between two water molecules is estimated to lie between 18.8 and 30.1 kJ mol$^{-1}$, consequently, this system displays an excellent discrimination between inter- and intra-chain energy scales. In the absence of a closed form for the temperature dependence of the order parameter for a frustrated square Ising model, we have used an empirical fit in Fig. 4 of the form

$$\xi = \left( \frac{x}{1 + x} \right)^\nu,$$  

(5)

where $x = \xi(T - T_c)/T$, and $\xi$ and $\nu$ are constants.

We attribute the accessibility of a bona fide paraelectric state in HHTP-4H$_2$O to the very weak inter-chain coupling, which allows hydrogen bond disorder to occur without melting of the oxygen sublattice. We note specifically that the H$_2$O oxygen atom positions remain well-defined even at temperatures above $T_c \approx 240$ K; the larger-than-expected oxygen displacement parameter observed reflects only the superposition of two half-occupied oxygen sites associated with each of the two polarisation states. This observation distinguishes the behaviour of paraelectric HHTP-4H$_2$O from that of the high-temperature phases of the related 1D ices [Cu(C$_6$H$_4$NO$_2$)$_2$] and [Cu$_2$(C$_{6}$(CD)$_{3}$TA)[4,4'-bpy]], within which long-range diffusive motion of the H$_2$O occurs. Consistent with the small magnitude of $J_{nn}$ is the negligible difference in HHTP geometries we observe across the order–disorder transition, which in turn explains the remarkable weakness of the additional diffraction intensities associated with symmetry breaking.

In conclusion, we find that the molecular hydrate HHTP-4H$_2$O exhibits a hydrogen bond order–disorder transition near $T_c \approx 240$ K that is associated with the development at low temperatures of long-range ferroelectric coupling between polar 1D ice chains [Fig. 5(c)]. The phase transition behaviour we observe maps qualitatively onto the problem of ordering on the Ising square lattice, with the accessibility of a paraelectric phase at temperatures above $T_c$ suggesting that ferroelectric switching of the low-temperature polar phase should be possible. Indeed we intend to pursue this line of investigation in the immediate future. Finally, we note that our study also illustrates how molecular systems might host confined ice phases in a manner normally associated with porous covalent networks or carbon/inorganic nanotube arrays.

The authors gratefully acknowledge financial support from the EPSRC (EP/G004528/2) and the E.R.C. (Grant Ref.: 279705).

References