Supramolecular Chemistry

Formation of Two-Dimensional Supramolecular Icelike Layer Containing $(H_2O)_{12}$ Rings**

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Water is still not fully understood, though intensive investigations have been performed both experimentally and theoretically[1] because of its fundamental importance in biological and chemical processes.[2] Structural information of small water clusters is the first step towards understanding the behavior of bulk water. Thus, there has been an extensive investigation of water structures in recent years. A variety of water clusters including hexamers,[3,4] octamers,[5,6] and decamers,[7] found in a number of crystal hosts, have been structurally characterized and display very different configurations.

Structurally, the low-dimensional polymeric water/ice lies in between water clusters and bulk water and has physical properties closely associated with those of bulk water. However, understanding the growth of larger water clusters and how the clusters link to form a large network is still challenging, though some polymeric water phases consisting of basic water tetramer and hexamer subunits have been reported.[8–11] Very recently, two 2D water/ice layers containing large 12-[12] or 18-membered[13] water rings have been observed in solid states, which provide novel structural aspects of water and new insights into water with implications in biological environments. In this context, we describe two 1D and 2D water morphologies observed in the supramolecular solid-state complexes bpedo·2 H_2O (**1**) and bpedo·5 H_2O (**2**; bpedo = *trans*-bis(4-pyridyl)ethylene dioxide). The strong capability of O,O′-bifunctional 4-pyridyl spacers of forming hydrogen bonds with water molecules is known in supramolecular chemistry and crystal engineering.[14] Thus, employing such a compound is expected to facilitate the formation of various degrees of water aggregates.

Compounds **1** and **2** were obtained from methanol and aqueous solution, respectively. Single-crystal X-ray diffraction analysis[15] revealed that the hydrogen-bonding association of water molecules in compound **1** leads to the formation of 1D segregated water chain along the [001] direction (Figure 1). The chain consists of a sequence of O1w-O1w-O2w-O2w (Oxw = water oxygen center) with inversion centers lying in between two O1w and two O2w units. The inversion center leads to disorder of the water hydrogen atoms in the chain over two positions because of symmetry-imposed hydrogen-bonding interactions. The remaining hydrogen atom on each water is bonded to a bpedo moiety, which links the water chains in *trans*-mode (Scheme 1 a) into a 2D sheet (Figure 1). There are significant π–π interactions between adjacent bpedo molecules in the sheet which are separated by a distance of 3.22 Å.

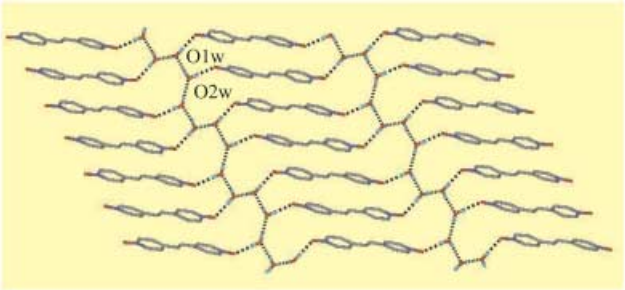
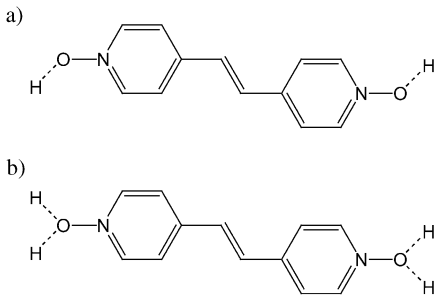


Figure 1. 2D sheet consisting of 1D segregated water chains and bpedo linker molecules in **1**.



Scheme 1. Hydrogen bonding of bpedo to water; a) *trans* mode, b) μ_4-hydrogen-bond mode.

Compound **2** contains an ordered 2D hydrogen-bonded water layer (Figure 2 a). Hydrogen-bonding association generates a 12-membered water ring consisting of six O3w, four O1w, and two O2w centers, which is symmetric over a crystallographic twofold axis passing through O1w. These 12-membered rings are fused together to form a 2D supramolecular $(H_2O)_{12}$ morphology with a corrugated sheet (Figure 2 b). The geometric parameters of the $(H_2O)_{12}$ ring are summarized in Table 1. The average O···O separation of 2.748 Å (90 K) or 2.776 Å (295 K) in the supramolecular $(H_2O)_{12}$ morphology is very close to the corresponding value of 2.759 Å in ice I_h.[16] Furthermore, the average O-O-O angle of 109.7° observed in $(H_2O)_{12}$ morphology is strikingly similar to the tetrahedral geometry, in agreement of the preferred tetrahedral hydrogen-bond arrangement for ice I_h, which further indicates the resemblance between $(H_2O)_{12}$ morphology and ice I_h.

In contrast to the recently observed ice layer, comprising $(H_2O)_{12}$ ring plus a dangling water molecule, which occurs only at very low temperature (20 K),[12] our $(H_2O)_{12}$ morphology can exist in a wide temperature range. The hydrogen-

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[**] This work was supported by the National Science Fund for Distinguished Young Scholars (20125104), NSFC No. 20221101, and the Research Fund for the Doctoral Program of Higher Education (20010001020).

  DOI: 10.1002/ange.200353097

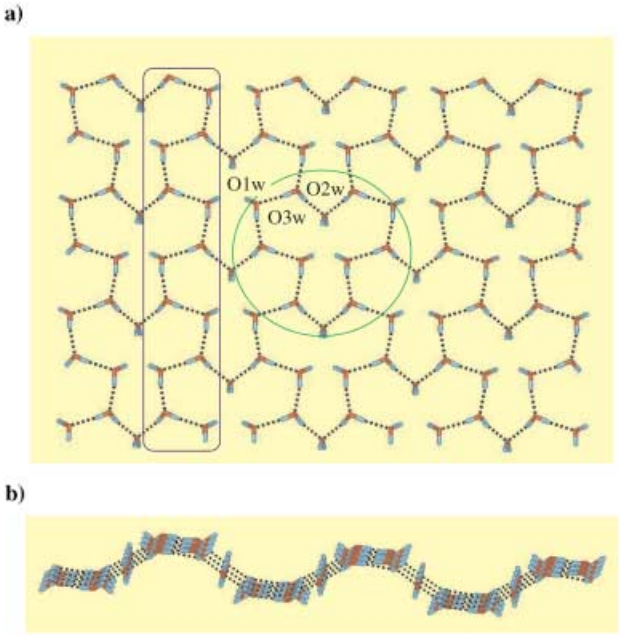

Figure 2. Supramolecular $(H_2O)_{12}$ water layer in **2**; a) Top view, the $(H_2O)_{12}$ ring is circled in green. The local structure boxed in blue shows a segregated chain similar to that in **1**. b) Side view.

Table 1: Hydrogen-bond parameters in compounds **1** and **2**.[a]

D–H···A	D–H [Å]	H···A [Å]	D···A [Å]	∢D-H···A [°]
		Compound **1**		
O1W-H···O1W	0.77(3)	1.98(4)	2.754(2)	176(4)
O1W-H···O2W	0.75(4)	2.04(4)	2.797(2)	175(4)
O2W-H···O2W	0.86(4)	1.91(4)	2.770(2)	174(5)
O2W-H···O1W	0.79(4)	2.01(4)	2.797(2)	172(3)
O1W-H···O1	0.88(2)	1.85(2)	2.722(2)	171(2)
O2W-H···O2	0.86(2)	1.89(2)	2.756(2)	174(2)
		Compound **2**		
O1W-H···O3W	0.85(2)	1.90(2)	2.7338(11)	168(2)
O3W-H···O2W	0.85(2)	1.94(4)	2.7759(9)	169(2)
O3W-H···O1W	0.85(2)	1.89(2)	2.7344(10)	172(2)
O1W-H···O1	0.87(2)	1.969(4)	2.7999(9)	159(2)
O2W-H···O1	0.86(2)	1.89(2)	2.7268(8)	166(2)

[a] Data are taken from the structures determined at 90 K.

bonded network of our $(H_2O)_{12}$ morphology does not show any significant changes on going from 90 to 295 K, which suggests structural uniformity. Moreover, the ice layer described here exhibits a novel topological motif with a pseudo C_{3v} symmetry, which differs from the reported irregular $(H_2O)_{12}$ ice phase.[12] Compared with 2D supramolecular $(H_2O)_{18}$ morphology which is structurally similar to liquid water,[13] the O···O separation in our $(H_2O)_{12}$ morphology is 0.1 Å shorter.

The remaining four hydrogen atoms per $(H_2O)_{12}$ water ring are bonded to two bpedo molecules, which act as bridges in a μ_4-hydrogen-bond fashion (Scheme 1b) to link these 2D water layers into a 3D network (Figure 3). The bpedo bridges are interweaved each other such that pyridine rings of one bpedo unit form π–π interactions with those of another. Notably, the water chain in **1** and layer in **2** can be viewed as

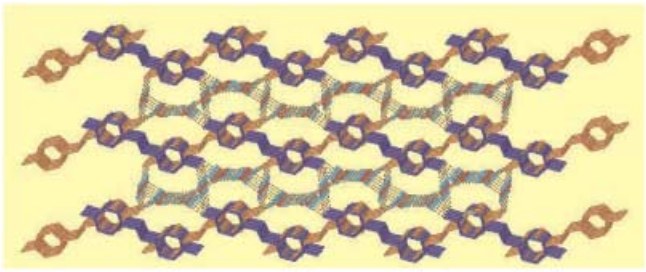

Figure 3. 2D supramolecular $(H_2O)_{12}$ water layers in **2** are connected by interweaved bpedo spacers into a 3D network.

building blocks, which are pillared by bpedo spacers to extend the dimensionality of the structure. In this sense, the water chain and layer are different from reported water clusters and other morphologies, which are situated within the host cavities or channels generated by organic or inorganic moieties.

The two compounds are interconvertible in the corresponding solvents. Recrystallization of **1** from water gave **2**, while dissolving **2** in methanol yielded **1**. The structural variation from 1D water chain in **1** to 2D water layer in **2** may be rationalized as follows: Within the methanol solution, the methanol presumably prevents the further growth of the water chain, while the water chain tends to grow in size without limitation in a water-enriched solution. A clear relationship between the two water phases exists. The water layer in **2** can be regarded as an evolution of water chain in **1** by adding water between the chains. The local structure of the $(H_2O)_{12}$ water layer (circled in blue in Figure 2a) displays a segregated chain motif, very similar to that observed in **1**. The extra water molecules are interspersed between water chains and bridge the neighboring chains to give the 2D layer. On the other hand, strong hydrogen-bonding ability of pyridine oxide linker employed here also plays a crucial role in promoting and stabilizing the aggregation of water molecules, thereby leading to the higher membered water rings. Compared with compound **1**, compound **2** easily loses its lattice water in air, which reflects the relatively weak interactions with the organic moiety in **2**. The hydrogen-bonding parameters give more evidence about the stability of the compounds. In **2** the average O···O separation of 2.763 Å between water layer and bpedo spacer is slightly longer than the average intrawater-layer O···O separation of 2.748 Å, while in **1** the average O···O separation of 2.739 Å between water chain and bpedo is significantly shorter than the average intrawater-chain hydrogen-bond length of 2.780 Å. These parameters imply that the water in **1** is more strongly affiliated to the organic spacers than in **2**.

In summary, structural variation from 1D water chain to 2D layer is realized by varying the crystallization conditions. The unique 2D ice layer has a great similarity with ice I_h and features a novel $(H_2O)_{12}$ ring. As water molecules play a crucial role in contributing to conformation, stability, function, and dynamics of biomacromolecules, the new water phases may provide insight into the hydrogen-bonding motif of the aqueous environment in living systems and enhance understanding of the 2D structural aspects of water.

Experimental Section

trans-bis(4-pyridyl)ethylene dioxide (bpedo) was prepared by oxidizing *trans*-bis(4-pyridyl)ethylene.[17] Recrystallization from methanol and aqueous solution gave yellowish block crystals of **1** and yellow prismatic crystals of **2**, respectively. Dissolving **1** in aqueous solution generated crystal **2**, whereas dissolving **2** in methanol solution gave compound **1**. No precautions were taken to exclude adventitious water during the experiments.

Received: October 15, 2003 [Z53097]

Keywords: hydrogen bonds · N ligands · supramolecular chemistry · water

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[15] Crystal data: Compound **1**, $C_{12}H_{14}N_2O_4$, $M_r = 250.25$, triclinic, $P\bar{1}$, $a = 8.9776(9)$, $b = 9.0771(10)$, $c = 9.2190(10)$ Å, $\alpha = 64.532(3)$, $\beta = 87.186(3)$, $\gamma = 62.796(4)°$, $V = 592.97(11)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.402$ Mg m^{-3}, $\mu = 0.107$ mm^{-1}, $F(000) = 264$, $GoF = 1.065$. A total of 4753 reflections were collected and 3063 are unique ($R_{int} = 0.0577$). $R1$ and $wR2$ are 0.0456 and 0.1303, respectively, for 228 parameters and 2615 reflections [$I > 2\sigma(I)$]. Compound **2**, $C_{12}H_{20}N_2O_7$, $M_r = 304.30$, orthorhombic, $Pbcn$, $a = 11.9300(8)$, $b = 7.2004(5)$, $c = 17.2426(12)$ Å, $V = 1481.15(18)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.365$ Mg m^{-3}, $\mu = 0.113$ mm^{-1}, $F(000) = 648$, $GoF = 1.060$. A total of 18374 reflections were collected and 2211 are unique ($R_{int} = 0.1008$). $R1$ and $wR2$ are 0.0392 and 0.1061, respectively, for 137 parameters and 2008 reflections [$I > 2\sigma(I)$]. The data were collected on a SMART CCD 1000 with MoKα radiation ($\lambda = 0.71073$ Å) at 90 K. Room temperature data have also been collected for both compounds: Compound **1**, $C_{12}H_{14}N_2O_4$, $M_r = 250.25$, triclinic, $P\bar{1}$, $a = 9.015(2)$, $b = 9.175(3)$, $c = 9.325(2)$ Å, $\alpha = 64.586(11)$, $\beta = 86.382(11)$, $\gamma = 62.618(6)°$, $V = 609.9(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.363$ Mg m^{-3}, $\mu = 0.104$ mm^{-1}, $F(000) = 264$, $GoF = 1.037$. A total of 2004 reflections were collected and 1811 are unique ($R_{int} = 0.0805$). $R1$ and $wR2$ are 0.0765 and 0.1952, respectively, for 217 parameters and 1446 reflections [$I > 2\sigma(I)$]. Compound **2**, $C_{12}H_{20}N_2O_7$, $M_r = 304.30$, orthorhombic, $Pbcn$, $a = 11.947(3)$, $b = 7.306(2)$, $c = 17.518(6)$ Å, $V = 1529.0(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.322$ Mg m^{-3}, $\mu = 0.109$ mm^{-1}, $F(000) = 648$, $GoF = 1.001$. A total of 6121 reflections were collected and 2125 are unique ($R_{int} = 0.0729$). $R1$ and $wR2$ are 0.0506 and 0.1270, respectively, for 137 parameters and 1337 reflections [$I > 2\sigma(I)$]. The structures were solved by direction methods and refined by a full matrix least-squares technique based on F^2 using SHELXL 97 program. CCDC-219926–219929 (for compounds **1** and **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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