Novel 1-D Water Nanowires in Crystal of an Organic Host

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Novel infinite columnar/helical structures of hydrogen-bonded water molecules in an organic host crystal, constructed by the crystallographic symmetry operation, provide the structural scaffold for evaluating one-dimensional water nanowires.

Water clusters play an important role in the stabilization of supramolecular systems both in solution and in the solid state. Thus, their structural study is important for obtaining a molecular level description of the properties of bulk water, leading to better understanding the structure and behavior of water molecules in biological systems. Up to the present, extensive studies have been carried out as to the structures of ice[1] and small water clusters of $(H_2O)_n$, $n < \approx 20$,[2] which has a 3- or 2-D hydrogen-bonded network of associated water molecules. In contrast, a 1-D wire structure of water molecules is thought to be flexible and rarely formed as the stable construction under the usual situation; although the 1-D water nanostructures were recently reported in the crystal structures of some zeolites, these were only possible under the high pressure.[3] However, herein, we report the crystal structures of two kinds of water nanowires, Wire-I and -II, formed in an organic host. These nanowires have 1-D and regularly ordered columnar/helical structures formed by hydrogen-bonded water molecules, whose diameters are 1.642 and 0.639 nm, respectively. At the present time, the study of 'nanowire' is a hot topic[4] and many new material nanowires have been reported. Thus, we believe that these experimentally observed, not computationally simulated, water nanowires provide the structural basis for the physicochemical investigation and dynamic simulation of 1-D water structures in pores across membranes, peptides or carbons.

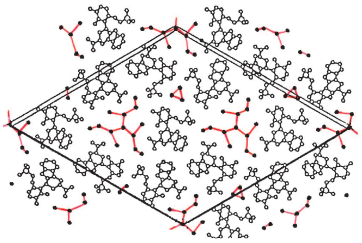

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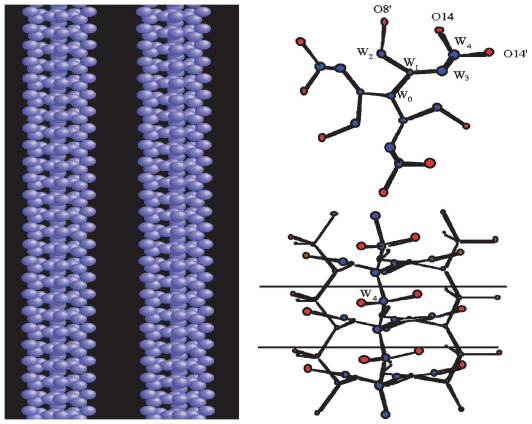
Figure 1. Crystal structure of the supramolecular assembly of **1** and water molecules, viewed from the crystallographic *c*-axis. The hydrogen-bonded water clusters are shown with red lines and form two kinds of frameworks of Wire-I and -II constructed by 39 and 9 water molecules per one unit cell, respectively.

Crystal samples were obtained from a mixture of an aqueous solution of L-tryptophan and pyridoxal 5-phosphate. In solution, both compounds formed a cyclized Schiff base, 3-carboxy-1-{3-hydroxy-2-methyl-5-[(phosphonooxy)methyl]-4-pyridyl}-1,2,3,4-tetrahydro-β-carboline (**1**). Figure 1 shows the crystal structure of this hydrate compound (space group $R3$, $Z = 9$).[5]

One unit cell contains nine **1** molecules, three Wire-I units, and three Wire-II units. All 48 water molecules in one unit cell participate in forming Wire-I and -II. In the ice structure,[1] water molecules are linked with four neighbours through hydrogen bonds and form a tetrahedral framework. In such a framework, each water molecule occupies the same position with respect to the others and plays the same role in the 3-D network structure. In contrast, water molecules reported here assume positions different from one another and play different roles from those of water molecules in the ice structure. Interestingly, these water nanowires take the absolute configurations, because of the co-crystallization with the optically active **1** molecules. The absolute structures of these two nanowires are shown in Figures 2 and 3.



(a) (b)

Figure 2. (a) Intrawire hydrogen-bonding framework of Wire-I (stereoscopic view by CPK model), viewed along to the *c*-axis. (b) The top and side views (ball-and-stick model) of its structural unit, together with the hydrogen-bonding oxygen atoms (red circles) of **1**, are shown in the upper and lower panels, respectively, where the structure interposed with two lines is the building unit of Wire-I. Water molecules are shown with blue-colored spheres and the sticks show the intermolecular hydrogen bonds. The water clusters are infinitely connected to each other along the crystallographic *c*-axis through their intermolecular hydrogen bonds and are stabilized by the hydrogen bonds to the phosphate, carboxyl and phenol O atoms of the adjacent **1** molecules.

In Wire-I, W_0 is located at a special point concerning the *x*- and *y*-positions and keeps the balance of the plane constituted by hydrogen-bonding network of W_1, W_2, and W_3 and their two sets translated by three-fold symmetry; W_1 is somewhat deviated from the plane because of the sp^3-directed hydrogen-bonding formations of W_0. Thus, the plane is constituted by ten hydrogen-bonded water molecules (W_0 and $\{W_1, W_2, W_3\} \times 3$ in Figure 2b upper panel) and is piled up at an interval of 0.473 nm (equals to the length of *c*-axis) along to the three-fold axis running parallel to *c*-direction. The neighboring planes are connect-

ed with each other by six hydrogen bonds of three water molecules, translated by a three-fold symmetry ($W_4 \times 3$ in Figure 2b lower panel). It is interesting to note that four atomic coordinates of W_1–W_4 are independent but within the range of hydrogen-bonding distance and angle, and the remains are all constructed by crystallographic symmetry operation in the structure of Wire-I. There are five types of hydrogen bonds in this wire unit. The intrawire O–O distances are in the range of 0.26(1) (W_0–W_1) to 0.29(1) (W_1–W_2) nm, and the hydrogen-bonded O–O–O angles range from 90(3)° (W_0–W_1–W_2) to 139(4)° (W_2–W_1–W_3). These distances and angles are in the range found in ice or water clusters.[1–3] The plane-stacked water nanostructures of Wire-I are novel and different from the linearly linked ones in the crystal structures of zeolites.

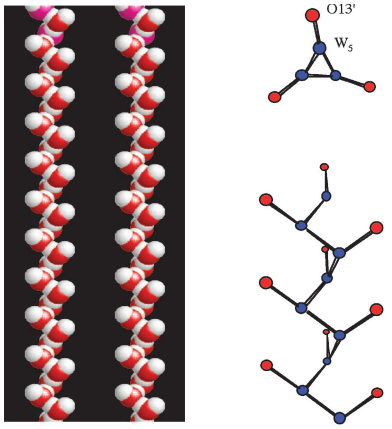


Figure 3. (a) Intrawire hydrogen-bonding framework of Wire-II (stereoscopic view by CPK model), viewed along to the c-axis, where the red and white colored spheres represent water oxygen and hydrogen atoms, respectively. (b) The top and side views (ball-and-stick model) of its structural unit, together with the hydrogen-bonding oxygen atoms (red circles) of **1**, are shown in the upper and lower panels, respectively. Water molecules are shown with blue-colored spheres and the sticks show the intermolecular hydrogen bonds. The water clusters are infinitely connected to each other along the crystallographic *c*-axis through their intermolecular hydrogen bonds and are stabilized by the hydrogen bonds to the phosphate O atoms of the adjacent **1** molecules.

In Wire-II, water molecules form an infinite helical structure around the three-fold screw axis, in which three water molecules compose one turn. The intrawire O–O distance and the hydrogen-bonded O–O–O angle are 0.26(1) nm and 93(3)°, respectively. The absolute structure of this water nanowire could be described as a left-handed helix.

The linearity of both water nanowires is completely perfect because of wire-structure formation around the crystallographic three-fold (Wire-I) or three-fold screw (Wire-II) axis. And these structures are assumed to be stable, as judged from that we already obtained needle crystals longer than 2 cm along the *c*-axis. In conclusion, we clarified the structures of two unique 1-D water nanowires in the crystal of **1** hexahydrate.

To our best knowledge, the water nanowires presented here are the first report on the 1-D water structures constructed by crystallographic symmetry operation and we believe that they provide the structural scaffold for evaluating 1-D water science, such as the water transfer or the conduction of protonic current through pores across membrane.

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5 Aqueous solution of equimolar (1 mM) PLP and L-tryptophan (free forms) were stirred for 1 h under heating at the room temperature (20 °C). Yellowish needle crystals of **1** were obtained by the slow vapour diffusion after a few weeks. Crystal density (1.378 g/cm^3) was measured by the flotation method using a C_6H_6/CCl_4 mixture. A single crystal with the dimension of $0.1 \times 0.1 \times 0.4$ mm^3 was sealed in a glass capillary with some mother liquid. All X-ray measurements at 20 °C were made on a Rigaku AFC7R diffractometer with graphite monochromated Cu Kα radiation ($\lambda = 1.5418$ Å) and a 12 kW rotating anode generator. X-ray crystal structure is of space group *R*3 (no. 146) with a hexagonal axis, where $a = b = 37.315(6)$ Å, $c = 4.734(4)$ Å. X-ray reflection intensities were collected using an ω-2θscan technique to a maximum 2θ value of <130°. The weak reflections ($F_O < 3\sigma(F_O)$) were rescanned to ensure good counting statistics. Stationary background counts were recorded on each side of the reflections. Four standard reflections monitored for every 100 reflection intervals showed no significant time dependence. An empirical absorption correction using the DIFABS program (N. Walker and Stuart, *Acta Crystallogr.*, **A39**, 158 (1983)) was applied, which resulted in transmission factors ranging from 0.88 to 1.15. The data were corrected for Lorentz and polarization effects. The structure was solved by direct method. All water molecules of crystallization were located by successive Fourier syntheses, in which a water molecule was located on a three-fold axis with the occupancy of 1/3. The non-hydrogen atoms were anisotropically refined by full-matrix least-squares method using SHELXL-97 (G. M. Sheldrick, "SHELXL-97 — A program for crystal structure refinement," University of Goettingen, Germany (1997)). The positions of hydrogen atoms were obtained from the difference Fourier map and were included isotropically in the calculation of $|F_c|$ values, but not refined. The positions of hydrogen atoms in Wire-I have not yet been determined. The final reliability factor is $R = 0.0734$ for 2028 reflections. CCDC 212442 contains the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.htm (or from the Cambridge Crystalllographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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