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One-dimensional Tube-like $\{5^{12}6^2\}_n$ Water Clusters Stabilized in a Molecular Nanoporous Framework

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Water nanotube clusters (WNTs) contained in nanochannels of molecular porous crystal are prepared. The structure of these WNT is almost the same as that of partial clathrate-hydrate type-I, which is constructed from 1-D $\{5^{12}6^2\}_n$ water clusters stabilized under ambient atmosphere. The WNT has a structural phase transition at −53.5 °C from the solid to liquid state.

Investigation of some water-molecule clusters formed in the interstitial space of supramolecular crystals has attracted attention as an important method to understand the behavior of bulk water and ice.[1] However, since most of the water clusters are actually small in unit cell and stabilized by direct H bonding with supramolecules, they display no macroscopic behavior of bulk water such as a phase transition and a glass one. We have constructed huge water clusters in porous molecular crystals with one-dimensional nanochannels by self-organization of designed molecular building blocks.[2] The water nanotube clusters (WNTs) in the channel spaces show a structural phase transition, and the crystal structure of WNT corresponding to the melting state is also observed. Interestingly, the crystal structure of WNT, stabilized by H bonds with porous outer walls is constructed from a partial structure $\{5^{12}6^2\}_n$ of type-I clathrate hydrates.

In a previous study, WNTs with an infinite tube-like structure have successfully been confined to channel cavities of a nanoporous crystal $\{[\mathrm{Co^{III}(H_2bim)_3}](\mathrm{TMA})\}_n$ (**1**) ($\mathrm{H_2bim}$ = 2,2′-biimidazole, $\mathrm{H_3TMA}$ = trimesic acid) with $[\mathrm{Co^{III}(H_2bim)_3}]^{3+}$ and TMA^{3-}.[2] On undergoing condensation and fusion at the melting point of −28 °C, the WNT undergoes a reversible phase transition. Furthermore, some H-bonding networks of structural water molecules that are stabilized only on the interface in the WNT, which H bond with carboxylic oxygen atoms in the outer wall of the nanoporous channels, are observed by neutron crystal structure analysis.[3] In this study, a molecular building block $[\mathrm{Ru(H_2bim)_3}]^{3+}$ is designed, in which the Ru^{3+} ion radius ($\phi \approx 0.82$ Å), derived by Shannon,[4] is larger than the Co^{3+} ion radius ($\phi \approx 0.69$ Å). The isostructural crystal $\{[\mathrm{Ru^{III}(H_2bim)_3}](\mathrm{TMA})\}_n$ (**2**) along with crystal **1** is self-organized from $[\mathrm{Ru(H_2bim)_3}]^{3+}$ and TMA^{3-} in water, and the characteristics are compared. The characteristics of the WNT generally change with a change in molecular building blocks forming the nanoporous framework.

Figure 1 shows the results of the differential scanning calorimetry (DSC) measurement of **2**. The melting temperature of WNT confined to nanometer-scale regions with diameters greater than ca. 2 nm usually conforms to the Kelvin equation, which shows the capillary freezing point depression[5] and decreases with a decrease in the diameter of the region. The melting temperature of the WNT of **2** is −53.5 °C. It can be maintained in the liquid state in the form of stable supercooled water down to temperatures lower than those required for maintaining the WNT of **1** in the liquid state (−28 °C). Most water molecules in the WNT affect strong interactions of the WNT with the outer wall of the nanoporous channel. Therefore, the tendency of the melting temperatures of **1** and **2** to shift toward lower values is probably attributed to the difference between hydrophilic interactions occurring on the channel surface (which are affected by channel sizes) and hydrophobic interactions occurring on the channel surfaces of CNTs.[6] One of the reasons why the WNT of **2** is maintained in the formation of supercooled water down to a low temperature of −53.5 °C has been revealed in a previous study of bulk water, in which imaging-plate X-ray diffraction of supercooled water was carried out.[7] The model contains two water molecules in one pore of a $5^{12}6^2$ tetradecahedron unit. This model is comparable to the aggregation of water molecules in the supercooled region. Therefore, our WNT with the $\{5^{12}6^2\}_n$ structures can be maintained as supercooled water down to almost −60 °C, because its structure is comparable to the water molecule structure in Pauling's cluster model.[8]

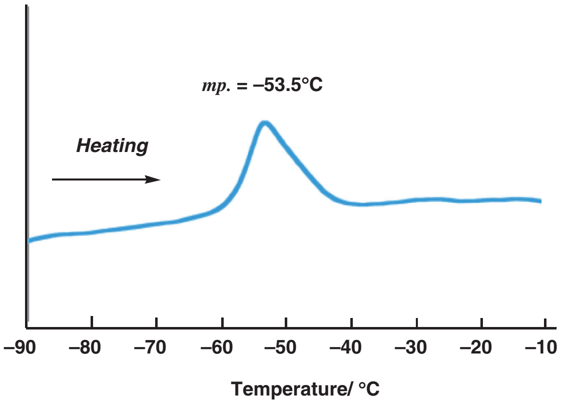

Figure 1. Result of DSC measurement of **2** is shown from −90 to −10 °C at a velocity of 10 °C min^{-1}.

Next, we investigate the crystal structure of the WNT of **2**. Figures 2a and 2b show the crystal structure of the WNT along the *b* and *c* axes, respectively, obtained by X-ray structure analysis at −20 °C, after the phase transition from the ice to the melting state. The connecting structure of water oxygen atoms in the WNT is also shown. The structural unit of a $5^{12}6^2$ tetradecahedron consists of twenty water molecules, which form two six-membered rings and twelve five-membered rings that H bond with two water molecules in the unit. The two faces of six-membered rings of consecutive $5^{12}6^2$ units joined end to end form a 1-D tube-like $\{5^{12}6^2\}_n$ structure. The water oxygen atoms (O(4), O(4)*, O(5), O(5)*, O(6), and O(6)*) of the primary hydrate sphere in the WNT, which might be directly connected to the carboxylic oxygen atoms (O(1), O(1)*, O(2), O(2)*, O(3),

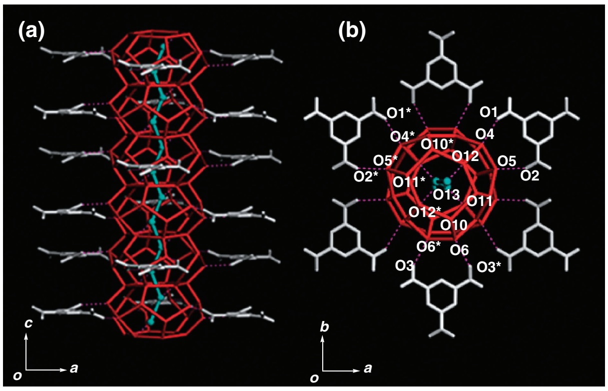

Figure 2. Crystal structure of WNT of **2** (a) along the *b* axis and (b) along the *c* axis. The red and blue lines denote the interconnections between water molecules. The $5^{12}6^2$ unit of the WNT is maintained by strong H bonds of the six carboxylic oxygen atoms of three TMA^{3-} molecules (white lines) in the porous framework.

and O(3)*) of TMA^{3-} in the outer wall, could determine the position of each of the oxygen atoms in spite of the WNT being in the melting state. Two heavily disordered water oxygen molecules O(13) and O(13)* are probably trapped inside the $5^{12}6^2$ unit by means of H bonds with O(12) and O(12)*, respectively. The structure of the WNT is almost the same as that of a partial cluster contained in type-I gas hydrates.[9] The actual structure of type-I clathrate hydrates is highly symmetric as it is a cubic crystal system; however, the WNT is slightly elongated and forms H bonds with six oxygen atoms of three carboxylic groups of three TMA^{3-} molecules in the outer wall (O(1)···O(5) = 2.688(4) Å, O(2)···O(4) = 2.700(4) Å, and O(3)···O(6) = 2.710(3) Å). Therefore, each $5^{12}6^2$ unit of the WNT has a triangular distortion that is elongated toward the H bonds formed with the outer wall. Out of the twenty water molecules forming the WNT, six form the primary hydrate sphere. Each secondary hydrate sphere of the WNT contains twelve water molecules (O(7), O(7)*, O(8), O(8)*, O(9), O(9)*, O(10), O(10)*, O(11), O(11)*, O(12), and O(12)*) which H bond with those in the primary hydrate sphere.[10] The average electron densities of each water molecule are calculated for a time-averaged electron density map observed by X-ray structure analysis. Thus, the position of each water molecule in WNT stabilized by H bonds with the outer wall may be identified in spite of the fluctuation of the WNT in the melting state. This fact is contrary to the fact that the position of the water molecules in the WNT of **1** cannot be identified, because of large thermal fluctuation.

A novel WNT is formed in nanometer-scale porous crystal **2** self-organized in water by molecular building blocks $[\mathrm{Ru}(\mathrm{H_2bim})_3]^{3+}$ and TMA^{3-}. The WNT has a $\{5^{12}6^2\}_n$ tube-like water cluster structure, which is almost the same as the structure of the water molecule cluster of type-I clathrate hydrate under normal temperature and pressure. Clathrate hydrate are generally stabile under extreme conditions;[11] however, the present WNT is stabile under normal hydrophilic conditions by means of H bonds formed by carboxylate oxygen atoms in the outer wall of the crystal. At temperatures lower than the melting temperature of **2** (−53.5 °C), the WNTs are transformed into ice-nanotube clusters (INTs). Therefore, the exact crystal structure of the WNT cannot be determined at extremely low temperature. Further, the density of WNTs of **2** is calculated to be 0.798 g cm^{-3}. This density value is considerably lower than those of ice I$_h$ (0.920 g cm^{-3} at 100 K and 0.1 MPa) and water (0.997 g cm^{-3} at 298 K and 0.1 MPa). The state of water molecules in the WNT is probably similar to a special low-density state such as supercritical water (0.348 g cm^{-3} at 647 K at 22 MPa) rather than normal water. In the future, by partially extracting mobile water molecules from the center of WNT under changing physical conditions such as temperature and humidity, we intend to achieve reversible insertion and removal of hydrophobic compounds such as methane and hydrogen from the WNT under normal temperature and pressure.

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10 The U_{eq} values for each water molecule are larger than those of each atom constituting the channel framework, because of the occurrence of thermal fluctuation in the melting state of the WNT. Therefore, no precise H-bonding distance between O atoms of WNT is calculated from the crystal structure. Each occupancy factor of the water oxygen atom in WNT is almost 1.0 except for the center of O(13) and O(13)* (ca. 0.5) in WNT. Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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