

Supporting Information

Anomalous Water Molecule and Mechanistic Effect of Water Nanotube Cluster Confined to Molecular Porous Crystal

Makoto Tadokoro*, ¹ Takashi Ohhara, ² Yuhki Ohhata, ¹ Takaaki Suda, ¹ Yuji Miyazato, ¹ Takeshi Yamada, ³ Tatsuya Kikuchi, ³ Ichiro Tanaka, ⁴ Kazuo Kurihara, ² Masaharu Oguni, ⁵ Kazuhiro Nakasuji⁶ Osamu Yamamuro,³ and Kuroki Ryota²

¹Department of Chemistry, Faculty of Science, Tokyo University of Science, Kagurazaka 1-3, Shinjuku-ku, Tokyo 162-8601, Japan, ²Neutron Science Research Center, Japan Atomic Energy Research Institute, 2-4 Shirane Shirakata, Tokai, Naka-gun, Ibaraki 319-1195 Japan, ³Neutron Science Laboratory, Institute for Solid State Physics, University of Tokyo, 106-1 Shirakata, Tokai, Naka-gun Ibaraki 319-1106, Japan, ⁴Department of Biomolecular Functional Engineering, College of Engineering, Ibaraki University, 4-12-1 Nakanarisawa-cho, Hitachi, Ibaraki 316-8511, Japan, ⁵Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8551, Japan, ⁶*Department of Subject of General Education, Fukui University of Technology, 3-6-1 Gakuen, Fukui City, Fukui 910-8505.*

Corresponding author: Prof. Makoto Tadokoro (tadokoro@rs.kagu.tus.ac.jp)

Contents

1. METHODS

1-1. Preparation of Crystal 1.

1-2. Neutron crystal structure analysis.

1-3. Neutron scattering analysis.

2. References

3. Supporting Figures

Figure 1S.

Figure 2S.

Figure 3S.

Figure 4S.

Figure 5S.

Figure 6S.

1. METHODS

1-1. Preparation of Crystal 1. The H₂O solution (10 cm³) containing [Co(H₂bim)₃](NO₃)₃ (0.16 g, 0.24 mmol) was added to H₂O (5 cm³) dissolved H₃TMA (0.026 g, 0.12 mmol) and LiOMe (0.012 g, 0.32 mmol) to give orange powder precipitates. The suspension was heated to 120 °C and dissolved completely. This solution was kept over night at 45 °C to obtain orange hexagonal crystals 1. The orange crystal 2 was prepared by the same method of 1 except for D₂O instead of H₂O. Elemental analyses of crystal 1 in vacuum dry at 100°C, found C, 45.62%, H, 3.64%, N, 22.91%; calculated values for [Co^{III}(Hbim)₃](trimesic acid)·2.5H₂O: 45.45%, H, 3.67%, N, 23.56%. TG (thermogravimetric analysis): 35.03%, Calcd by 35.02% at 20 H₂O.

1-2. Neutron crystal structure analysis. The crystal 1 used at neutron structure analysis had grown up to a size of 3.90 x 1.05 x 0.44 mm³ for several weeks and the Bragg's reflections were gathered by the 2-D neutron data-correction apparatus BIX-III diffractometer [1][2] at Japan Atomic Research Institute. The crystal 1 used at neutron structure analysis had grown up to a size of 3.90 x 1.05 x 0.44 mm³ for several weeks. Crystal 1 included into a closed glass capillary (φ 1.6 mm) was fixed on an aluminum pin and mounted on the BIX-III diffractometer, equipped with a 2-D neutron data-correction imaging plate, [3] set up at the JRR-3M reactor of the Japan Atomic Energy Research Institute (JAERI). The results of neutron crystal analysis of 1 at 293 K are C₂₇H₆₁N₁₂O₂₆Co, *F*_w = 542.00, monoclinic of space group *C*2/*c* (#15), with cell dimensions; *a* = 16.338(2) Å, *b* = 29.335(2) Å, *c* = 10.909(2) Å, β = 90.336(10)°, *V* = 52228.3(12) Å³ and *Z* = 8, *D*_{calc} = 1.377 gcm⁻³, neutron (λ = 1.51000 Å), *R*₁ = 12.33%, *wR*₂ = 23.20%. Maximum and minimum highest peaks in the final differential map are 0.093 and -0.107 e⁻/Å³, respectively and goodness of fit = 1.238 for 397 parameters (All, 2θ < 114°) on 3565 reflections. The neutron diffraction data were collected by the ω scan method (oscillation range Δω = 1.0 °) at 293 K using perfect-silicon-crystal-monochromated neutron radiation (λ = 1.51000 Å). Since BIX-III is a single-axis cylindrical diffractometer, there is a large blind region around the rotation axis. To reduce the blind region, data (ω-scan (Δω = 0.5°)) were collected by changing the angle value of the aluminum pin (about 180, 135, and 90°) instead of changing the χ circle position for the ordinary X-ray diffractometer. Reflections were integrated with the *Denzo* program and the data collections without absorption correction were carried out with *Scalepack* program. [4] The positional parameters of non-hydrogen atoms were constrained using the coordinates of II as an initial model. The refinement was on *F*₂ against all reflections by full-matrix least squares using SHELXL-97. Hydrogen atoms were observed in difference Fourier maps (neutron-scattering- length density maps) as negative and positive peaks. All water molecules included into WNT were fixed into two O–H distances as 0.96(2) Å, and the H···H one as 1.51(3) Å in a water molecule. Each O(8), O(14), H(4A), H(5A), H(5B), H(8A), H(8B), H(9B), H(14A) and H(14B) atom is calculated as an isotropic refinement. In neutron analysis, a cobalt atom was also treated with an isotropic refinement since it had a small cross section on neutron atomic scattering. Numerical absorption correction was done using the face indices determined by the SMART

CCD diffractometer with the *ABSG* program. [5]

1.3. Neutron Scattering Analysis. The quasi-elastic neutron scattering (QENS) data of 1 were measured with a time-of-flight (TOF) spectrometer AGNES of the Institute for Solid State Physics, The University of Tokyo. This instrument is installed at the cold neutron guide (C3-1) of JRR-3, Japan Atomic Energy Agency (Tokai, Ibaraki, Japan). [6][7] Neutrons with a wavelength of 4.22 Å (for standard mode) or 5.50 Å (for high resolution mode) are extracted with an array of five PG(002) monochromators and pulsed with a double Fermi chopper. The pulsed neutrons are scattered by a sample and detected with 328 ³He tube detectors arranged in a wide detector bank covering scattering angles of 10-130°. The energy resolution, energy range, and *Q* range at the standard mode, which was used in this experiment, are 120 µeV, $-4 < \Delta E < 20$ meV, and $0.2 < Q < 2.7$ meV, respectively. Small pieces of the crystals 1 were wrapped with aluminium foil and loaded in a concentric double-cylinder aluminium can (40 mm in height, 14.0 mm in inner diameter of the outer cylinder, 12.0 mm in outer diameter of the inner cylinder). The sample was then sealed by using an indium gasket. The amount of the sample was ca. 1.8 cc and the thickness of the sample was about 0.5 mm corresponding to the transmission of neutron beam of about 85%. The sample was set in a top-loading type cryostat and immediately cooled down to 276 K. The elastic (fixed-window) scan was first performed from 276 K to 100 K in a cooling direction, and then from 100 K to 300 K in a heating direction to investigate hysteresis effects of the transition. The temperature step was 5 ~ 10 K and the duration of each measurement was 1 h. Full data sets of quasielastic and inelastic scattering were recorded at 150, 266, 256, and 246 K taking about 15 h for each point. Bulk water was also measured at 266, 276, 286 and 296 K for comparison.

2. References

- [1] Tanaka, I., Kurihara, K., Chatake, T. & Niimura, N. Neutron diffractometer for biological crystallography-3 (BIX-3). *J. Phys. Soc. Jpn., Suppl.* **A70**, 459-461 (2001).
- [2] Tanaka, I., Kurihara, K., Chatake, T. & Niimura, N. A high-performance neutron diffractometer for biological crystallography (BIX-3). *J. Appl. Crystallogr.* **35**, 34-40 (2002).
- [3] Haga, Y., Kumazawa, S. & Niimura, N. Gamma-ray sensitivity and shielding of a neutron imaging plate. *J. Appl. Crystallogr.* **32**, 878-882 (1999).
- [4] Otwinowski, Z. & Minor, W. *Processing of x-ray diffraction data collected in oscillation mode, methods in enzymology*. eds. by Carter, C. W. Jr., Sweet, R. M., Academic Press, Vol. 276, Part A, 307-326 (1997).

- [5] Coppens, P. Absorption Correction Based on Face Indexing and Integration on a Gaussian Grid, *Crystallographic Computing*, p.255 (1970) in *PLATON*. (Spek, A. L. Single-crystal structure validation with the program *PLATON*. *J. Appl. Crystallogr.* **36**, 7-13 (2003)).
- [6] Kajitani, T., Shibata, K., Ikeda, S., Kohgi, M., Yoshizawa, H., Nemoto, K. & Suzuki, K. Construction of the TOF-type cold-neutron spectrometer, AGNES. *Physica. B* **213/214**, 872-874 (1995).
- [7] Yamamuro, O., Inamura, Y., Kawamura, Y., Watanabe, S. Asami, T. & Yoshizawa, H. Activity report of neutron science laboratory, *Institute of Solid State Physics, University of Tokyo*, **12**, 12-15 (2005).

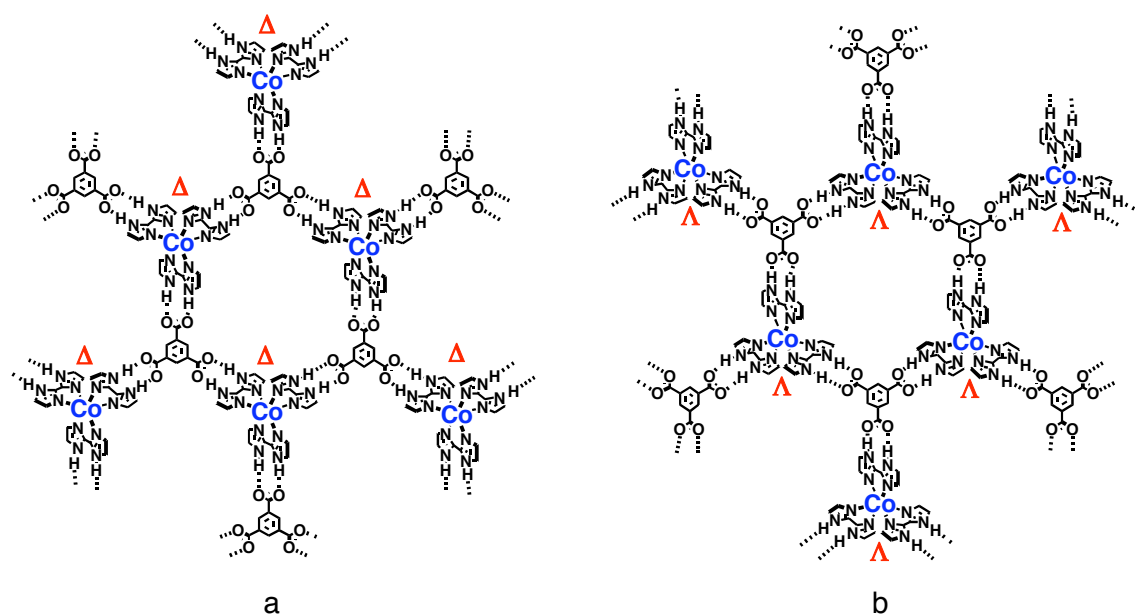


Figure 1S

Schematic representations of hybrid honeycomb sheet networks formed from new complementary alternative H-bonds between three carboxylic groups of the $[\text{TMA}]^{3-}$ and three Hbim^{-1} ligands of the Δ optical isomers (Δ -sheet) a, or the Λ ones (Λ -sheet) b, of $[\text{Co}^{\text{III}}(\text{H}_2\text{bim})_3]^{3+}$ complexes.

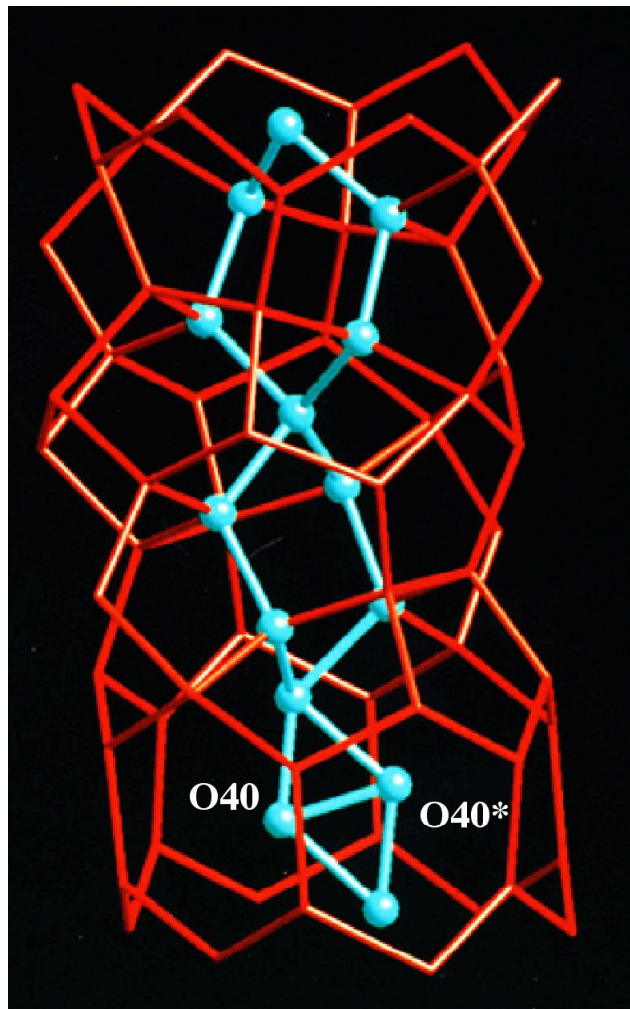


Figure 2S.

A view of the crystal structure for a unit of the three-layered INT into 1 below the phase transition temperature of -75°C . The red solid lines describe H-bonding between water molecules in the primary water-tube. The blue spheres and solid lines represent H-bonding between water molecules in the secondary water-layer and the tertiary water domain.

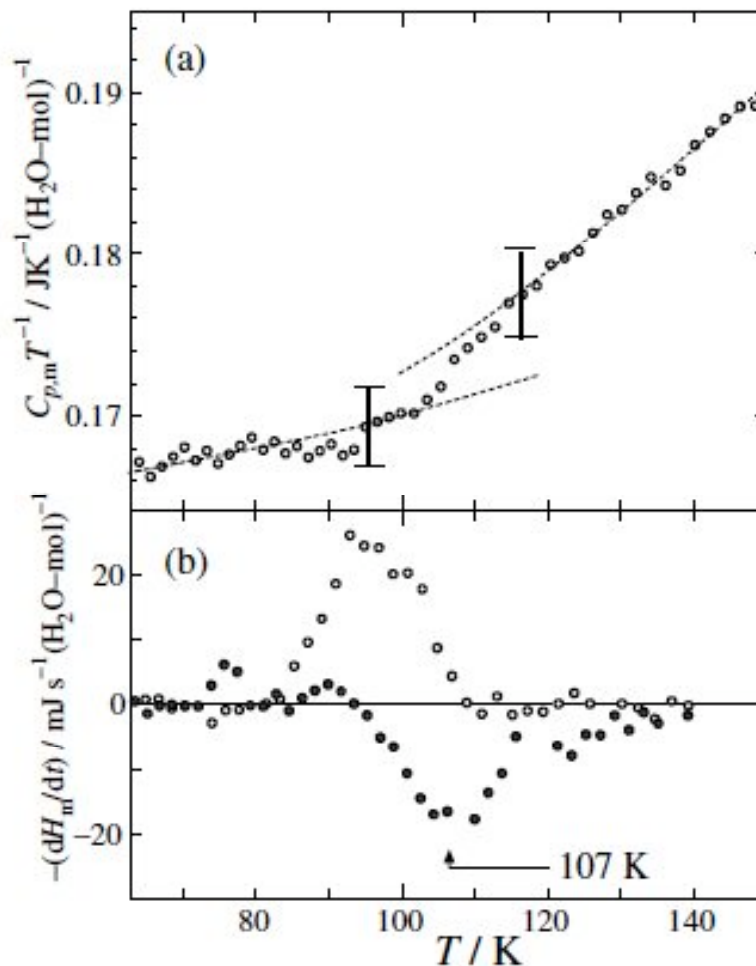


Figure 3S

Molar entropies (heat capacities divided by the respective temperatures) of the hydrate water (a) and spontaneous enthalpy-drift rates (b) on an enlarged scale at 70-150K. Upper and lower dotted lines in (a) represent the temperature dependences of the heat capacities under equilibrium and frozen-in states, respectively, expected at around a glass transition temperature of 107 K. The error bars stand for the magnitude of the imprecision in the data. Open and closed circles in (b) represent the data for the samples cooled rapidly at 2 K min^{-1} and slowly at 20 mK min^{-1} , respectively, before the measurements.^[12]

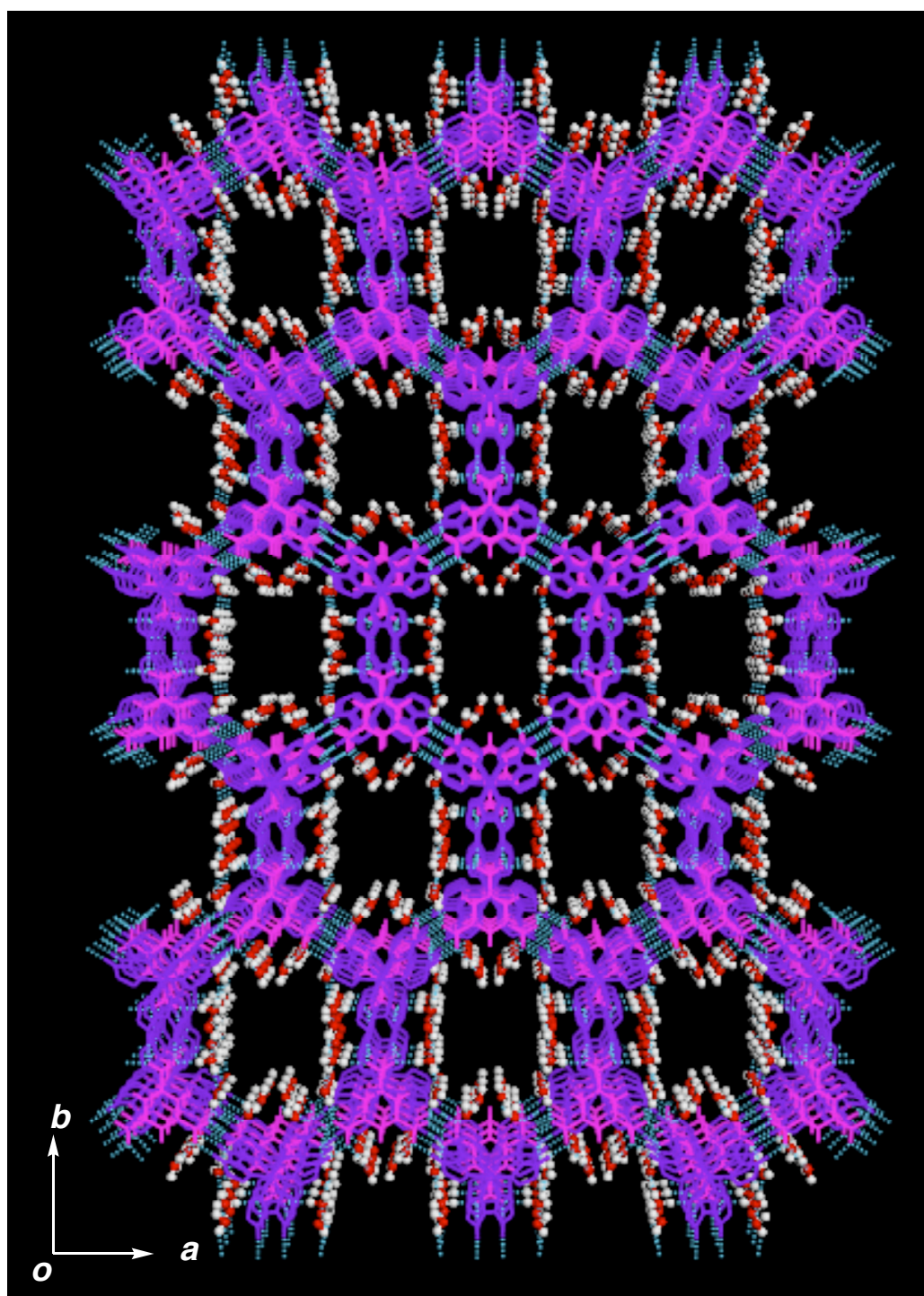


Figure 4S

Perspective view along the c axis of crystal 1

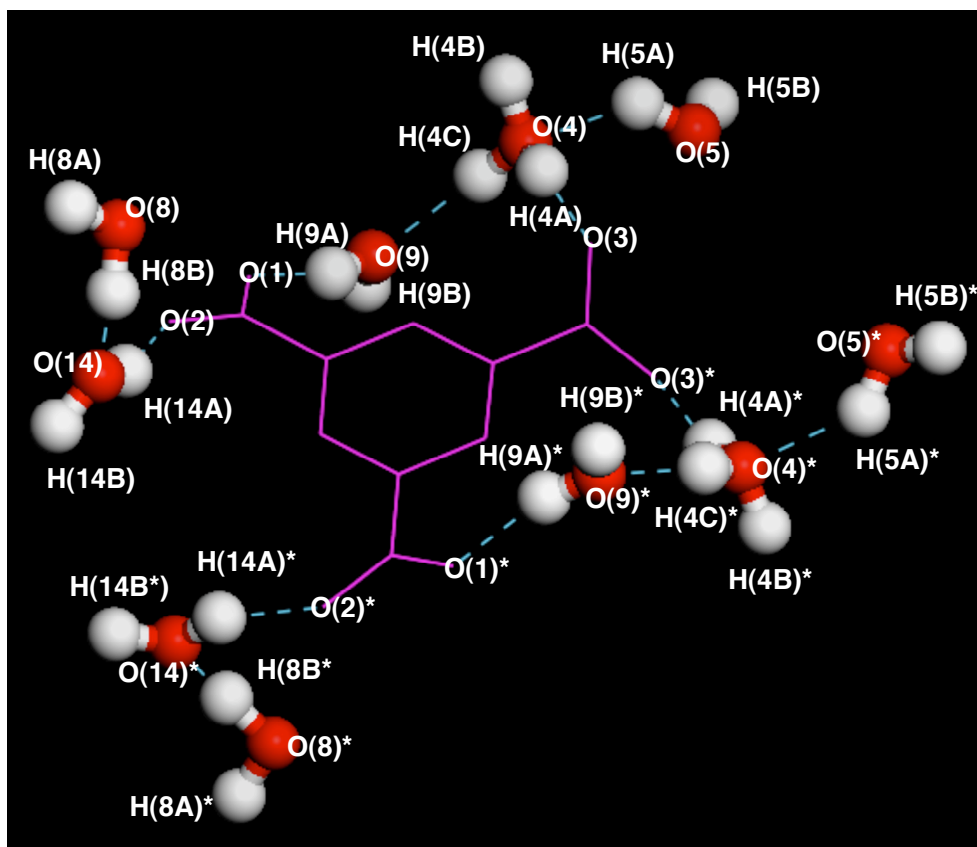


Figure 5S

Hydrogen bonding formation between [TMA]³⁻ and water molecules of structural water

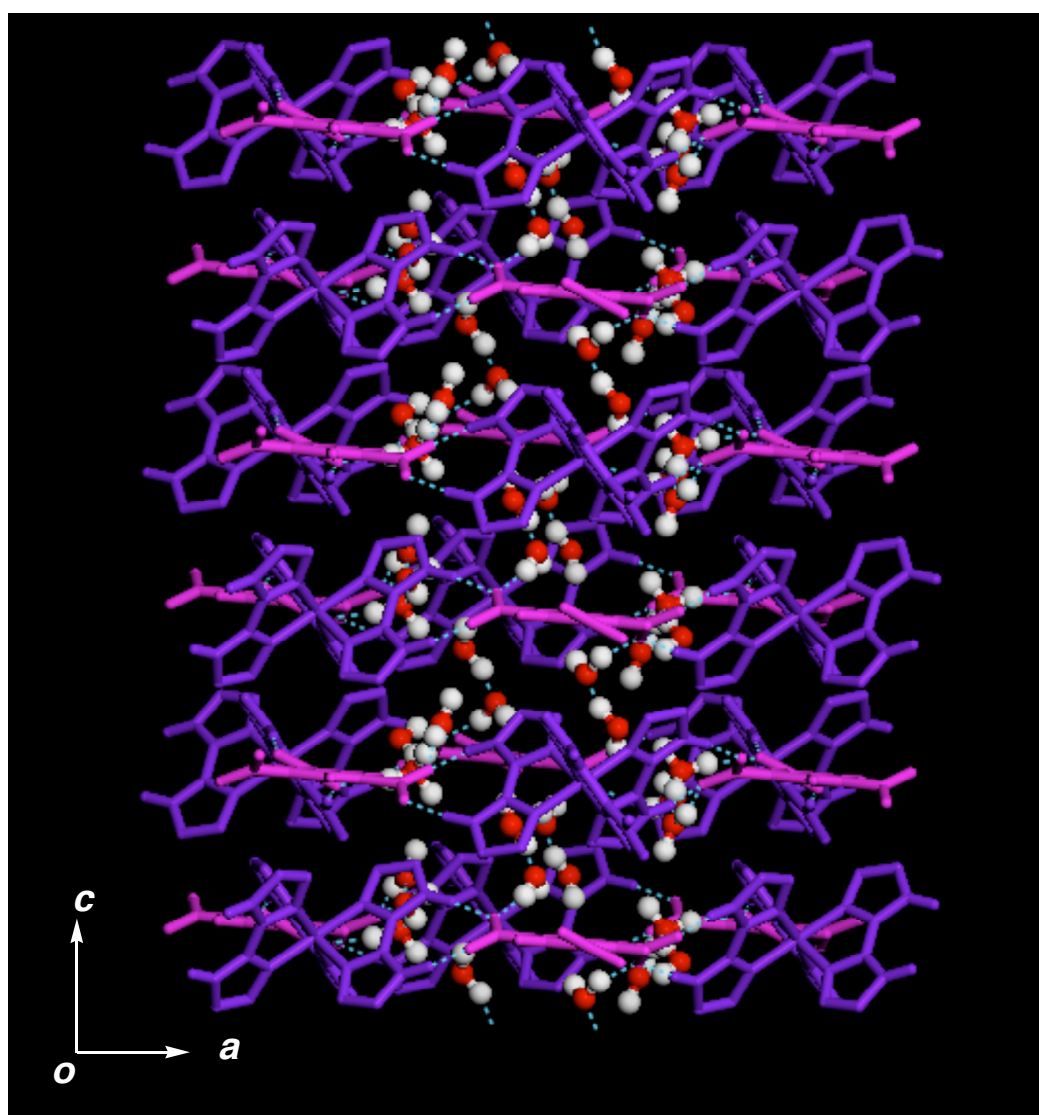


Figure 6S

Perspective view along the b axis and side view of WNT