

# Electronic Supplementary Information

## Structures and Phase Transition of Multi-Layered Water Nanotube Network Confined to Nanochannels

Makoto Tadokoro,<sup>\*a,b</sup> Syoko Fukui,<sup>b</sup> Tadanori Kitajima,<sup>b</sup> Yuki Nagao,<sup>c</sup> Shin'ichi Ishimaru,<sup>d</sup>  
Hiroshi Kitagawa,<sup>c</sup> Kiyoshi Isobe<sup>e</sup> and Kazuhiro Nakasuji<sup>f</sup>

<sup>a</sup> Department of Chemistry, Faculty of Science, Tokyo University of Science, Kagurazaka 1-3, Shinjuku-ku, Tokyo, Japan. Fax: +81 3 3620 3858; Tel: +81 3 5228 8714; E-mail: tadokoro@rs.kagu.tus.ac.jp. <sup>b</sup> Department of Chemistry, Graduate School of Science, Osaka City University, Sugimoto 3-3-138, Sumiyoshi-ku, Osaka, Japan. Fax: +81 6 6605 2522; Tel: +81 6 6605 2547. <sup>c</sup> Department of Chemistry, Graduate School of Science, Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka, Japan. Fax & Tel: +81 92-642-2570; E-mail: hiroshiscc@mbox.nc.kyushu-u.ac.jp. <sup>d</sup> Department of Environmental Materials Science, School of Engineering, Tokyo Denki University, Takenisigakuenndai 2-1200, Inzei, Chiba, Japan. Fax: +81 476 46 8038; Tel: +81 476 46 8077; E-mail: ishimaru@cck.dendai.ac.jp. <sup>e</sup> Department of Chemistry, Graduate School of Science, Kanazawa University, Kadoma-cho, Kanazawa, Ishikawa, Japan. Fax: +81 76 264 5742; Tel: +81 76 264 5697; E-mail: isobe@cacheibm.s.kanazawa-u.ac.jp. <sup>f</sup> Department of Chemistry, Graduate School of Science, Osaka University, Machikaneyama-cho 1-1, Toyonaka, Osaka, Japan. Fax & Tel: +81 6 6850 5392; E-mail: nakasuji@chem.sci.osaka-u.ac.jp

E-mail: tadokoro@rs.kagu.tus.ac.jp

## Syntheses of 1 and 2

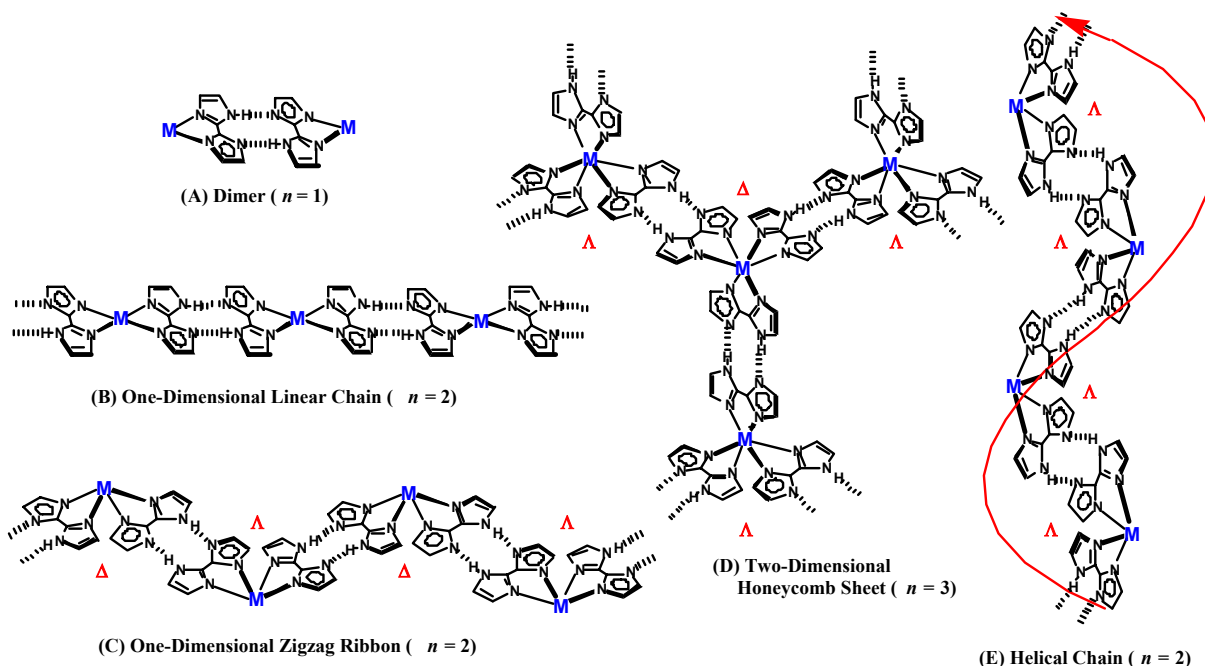
The H<sub>2</sub>O solution (10 cm<sup>3</sup>) containing [Co(H<sub>2</sub>bim)<sub>3</sub>](NO<sub>3</sub>)<sub>3</sub> (0.16 g, 0.24 mmol) was added to H<sub>2</sub>O (5 cm<sup>3</sup>) dissolved H<sub>3</sub>TMA (0.026 g, 0.12 mmol) and LiOMe (0.012 g, 0.32 mmol) to give orange powder precipitates. 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 D<sub>2</sub>O instead of H<sub>2</sub>O. 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<sup>III</sup>(Hbim)<sub>3</sub>](trimesic acid)·2.5H<sub>2</sub>O: 45.45%, H, 3.67%, N, 23.56%.

### Crystal Structure Data for crystal 1 at 23 °C

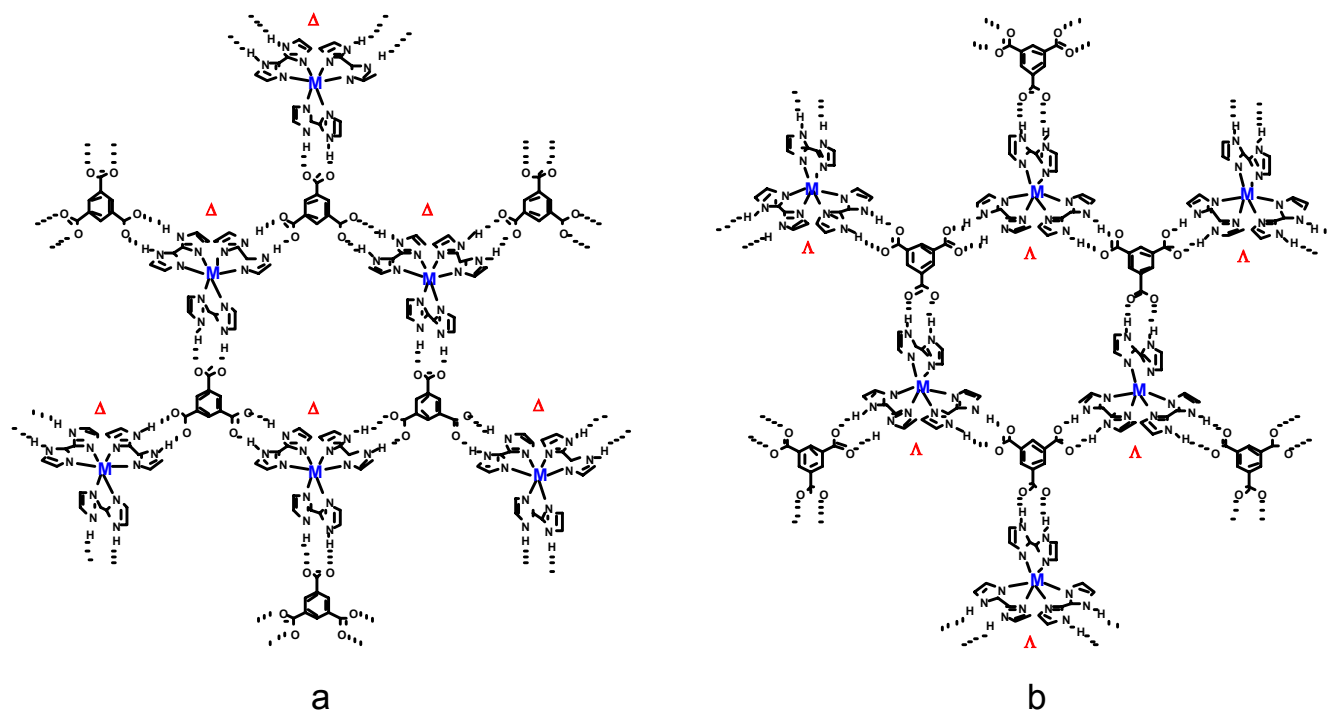
Single crystal **1** of this material at 23.0°C are  $C_{27}H_{67}N_{12}O_{29}Co$ ,  $F_w = 1082.28$ , monoclinic of space group  $C2/c$  (no. 15), with cell dimensions;  $a = 16.403(5)$  Å,  $b = 29.471(7)$  Å,  $c = 10.954(6)$  Å,  $\beta = 90.24(3)^\circ$ ;  $V = 5295(3)$  Å<sup>3</sup> and  $Z = 4$ ,  $D_{calcd} = 1.358$  gcm<sup>-3</sup>,  $\mu(Mo-K\alpha) = 4.18$  cm<sup>-1</sup>. A total of 4648 ( $R_{int} = 0.044$ ) independent reflections having  $6.0^\circ < 2\theta < 50.0^\circ$  were collected on a computer-controlled Rigaku ASC-7R (rotating anode) four-circle auto-diffractometer using  $\omega$ - $2\theta$  scan and graphite monochromatic Mo-K $\alpha$  ( $\lambda = 0.71069$ Å) radiation. The structure was solved using direct method techniques with the SIR 92 and Full-matrix least-squares refinement. The non-hydrogen atoms were located and then refined anisotropically except for the confined water oxygen atoms. The hydrogen atom positions were fixed geometrically at calculated distances. The resulting parameters have been refined to converge  $R_1$  (unweighted, based on  $F_o$ ) = 0.0880 for 257 parameters ( $I > 3.00 \sigma(I)$ ) on 2157 reflections. Maximum and minimum highest peaks in the final differential map are 0.56 and  $-0.41$  e<sup>-</sup>/Å<sup>3</sup>, respectively and goodness of fit = 1.23. Further details of the data collection and structure solution of **1** at 23°C are provided as crystal data in pdf files containing the Electric Supplementary Information Available.

### Crystal Structure Data for crystal **1** at $-75\text{ }^{\circ}\text{C}$ .

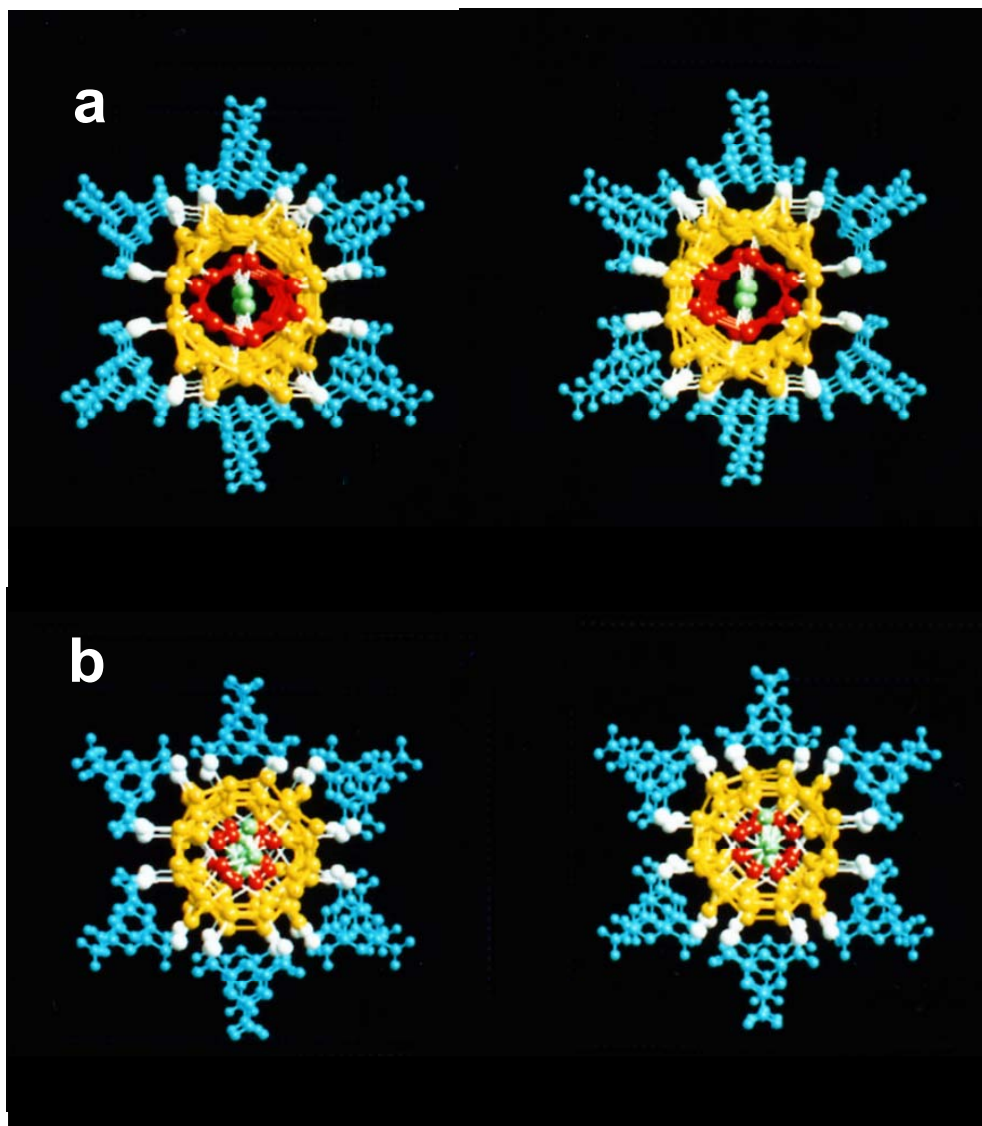
Single crystal **1** of at  $-75.0\text{ }^{\circ}\text{C}$  are  $\text{C}_{81}\text{H}_{183}\text{N}_{36}\text{O}_{78}\text{Co}_3$ ,  $F_w = 3086.42$ , monoclinic of space group  $C2/c$  (no. 15), with cell dimensions;  $a = 16.7257(19)\text{ \AA}$ ,  $b = 29.142(3)\text{ \AA}$ ,  $c = 32.264(3)\text{ \AA}$ ,  $\beta = 92.939(4)^{\circ}$ ;  $V = 15705(2)\text{ \AA}^3$  and  $Z = 4$ ,  $D_{\text{calcd}} = 1.305\text{ gcm}^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 4.16\text{ cm}^{-1}$ . A total of 16262 ( $R_{\text{int}} = 0.043$ ) independent reflections having  $2\theta_{\text{max}} < 55.0^{\circ}$  were collected on a computer-controlled Rigaku/MSM Mercury CCD auto-diffractometer using Lorenz-polarization corrections and graphite monochromatic Mo-K $\alpha$  ( $\lambda = 0.71070\text{ \AA}$ ) radiation. The structure was solved using direct method techniques with the Shelxs-97 and Full-matrix least-squares refinement (Shelxl-97). The non-hydrogen atoms were located and then refined anisotropically. Only the O(40) has a 0.5 occupancy factor because of disordering. The hydrogen atom positions were fixed geometrically at calculated distances. All hydrogen atoms of water molecules are not refined and omitted. The resulting parameters have been refined to converge  $R_1$  (unweighted, based on  $F_o$ ) = 0.095 for 900 parameters ( $I > 3.00\sigma(I)$ ,  $2\theta < 54.97^{\circ}$ ) on 10351 reflections. Maximum and minimum highest peaks in the final difference map are 0.038 and  $-0.004\text{ e}^{-}/\text{\AA}^3$ , respectively and goodness of fit = 1.09. Further details of the data collection and structure solution of **1** at  $-75\text{ }^{\circ}\text{C}$  are provided as crystal data in pdf files containing the Electric Supplementary Information Available.



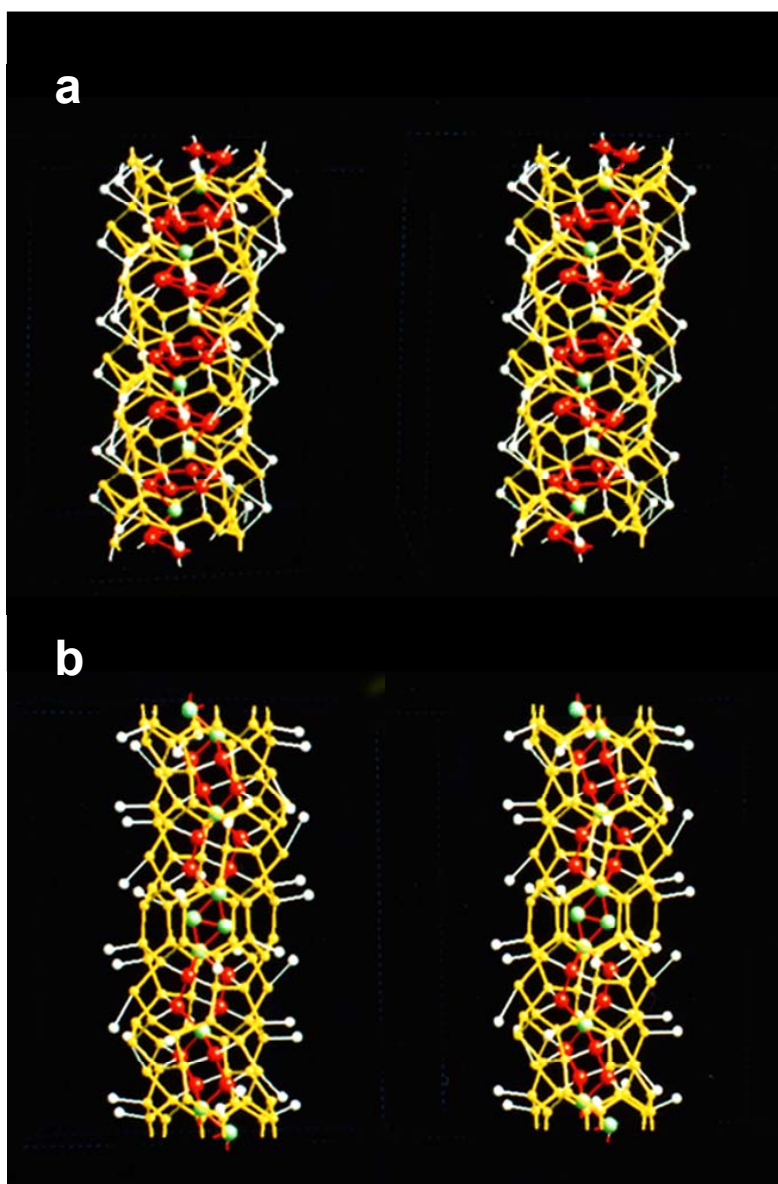
**Fig. 1S** Schematic representations of multi-dimensional assemblies formed by transition-metal complexes with the controlled configurations and regulated the number of  $\text{Hbim}^{-1}$  ligands: A) “**Zero-Dimensional Dimer**” constructed by the complementary intermolecular hydrogen bonds between  $\text{Hbim}^{-1}$  ligands in the metal complexes coordinated by only one  $\text{Hbim}^{-1}$  ligand. B) “**One-Dimensional Linear Chain**” assembled by the metal complexes with *trans*-configuration coordinated by at least two  $\text{Hbim}^{-1}$  ligands. C) “**One-Dimensional Zigzag Ribbon**” assembled by the metal complexes with two  $\text{Hbim}^{-1}$  ligands in *cis*-configuration. D) “**Two-Dimensional Honeycomb Sheet**” linked by three intermolecular hydrogen bondings of the metal complexes with three  $\text{Hbim}^{-1}$  ligands. The sheet is constructed by hydrogen bondings with alternate linkage between different optical isomers of  $\Delta$  and  $\Lambda$  types. E) “**Helical Chain**” assembled by intermolecular hydrogen bondings between the same optical isomers of  $\Delta$  or  $\Lambda$  containing at least two  $\text{Hbim}^{-1}$  ligands. The symbol “ $n$ ” represents the number of  $\text{Hbim}^{-1}$  ligands coordinated to transition metal ions.



**Fig. 2S** Schematic representations of hybrid honeycomb sheet networks formed from new complementary alternative H-bonds between three carboxylic groups of the trimesic acid and three Hbim<sup>-1</sup> ligands of the Δ optical isomers (Δ-sheet) **a**, or the Λ ones (Λ-sheet) **b**, of [Co<sup>III</sup>(H<sub>2</sub>bim)<sub>3</sub>]<sup>3+</sup> complexes.



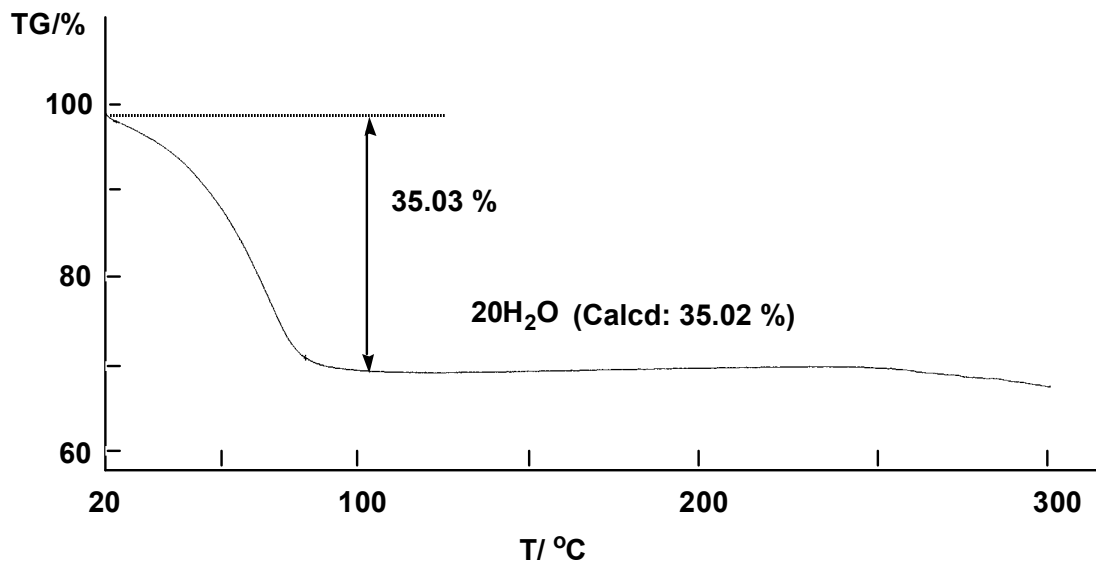
**Fig. 3S** Stereoviews of crystal structures for **1** above the phase transition temperature at 23°C (**a**) and below the phase transition temperature at -75°C (**b**): perspective views of the multi-layered structure representing units of the two channels along the *c* axis confining **a**, a one-dimensional hierarchical water-tube and **b**, a hierarchical ice-like tube, respectively. Trimesic acids containing into the outer wall of the channel as building blocks are shown by the blue spheres and solid lines. The yellow spheres and solid lines describe H-bonding between water molecules in the primary water-tube stabilized by strong interactions with the oxygen atoms (white spheres) of the trimesic acid of the outer wall. For clarity, H-bonding greater than 2.7 Å (i.e. the mean value of H-bonding distance) was omitted. The red spheres and solid lines represent H-bonding between water molecules in the secondary water-layer and the green spheres show water molecules in the tertiary water domain, respectively.



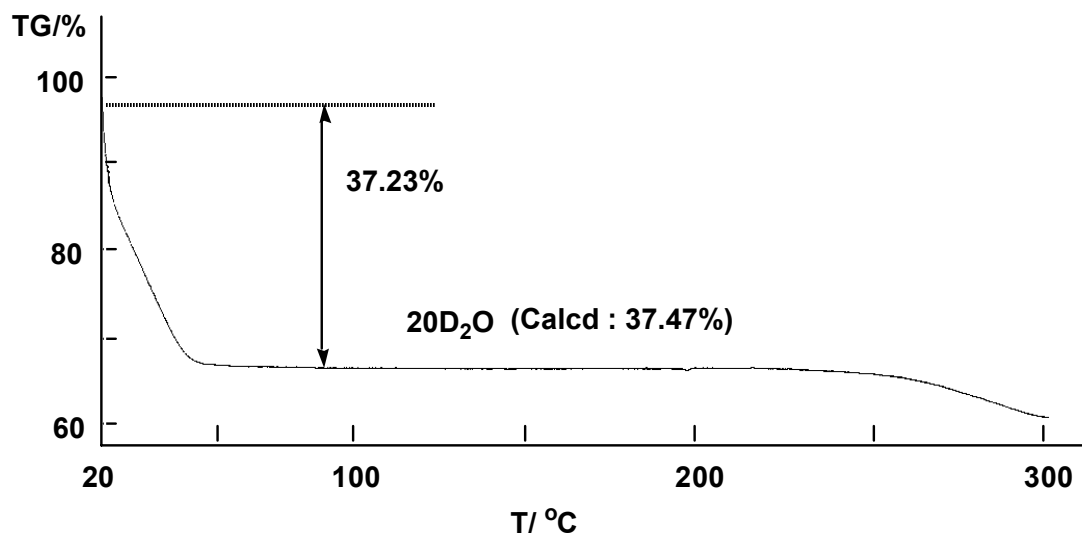
**Fig. 4S** Stereoviews of crystal structures for **1** above the phase transition temperature at 23°C (**a**) and below the phase transition temperature at -75°C (**b**): Stereoviews of the side crystal structures of **a**, the hierarchical water-tube above the phase transition temperature and **b**, the hierarchical ice-like tube below the phase transition temperature: yellow, red and green spheres indicate water molecules in the primary water-tube, secondary water-layer and tertiary water-segment, respectively. The solid red lines show H-bonding between water molecules in the secondary and tertiary water-domains and the solid yellow lines also describe it between them in the primary water-tube with the oxygen atoms (white spheres) of the trimesic acid (H-bonding greater than 2.7 Å were omitted for clarity). **a**, water clusters of the secondary and tertiary domains with quasi-planar hexagonal rings at an inclination of  $\sim 30^\circ$  bridged by water molecules in the tertiary segment. **b**, the ice-like tube construct has a one-dimensional poly-spiro chain formed from alternative H-bonds between the  $C_s$  water tetramers and the two water hexagons with chair-like structural isomers.



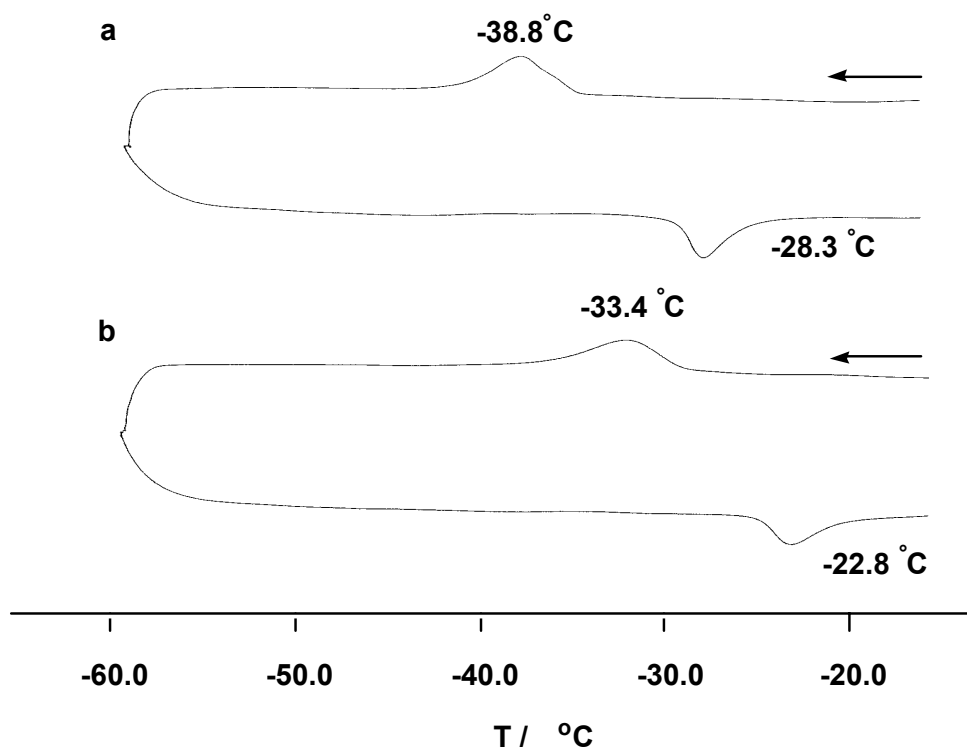
(a)



(b)



**Fig. 5S** The results of TG (Thermogravimetry) on crystal 1 containing water molecules (a) and crystal 2 containing heavy water molecules. Both crystals have approximately compositions of 20 H<sub>2</sub>O and 20 D<sub>2</sub>O for [Co(Hbim)<sub>3</sub>](TMA), respectively.



**Fig. 6S** DSC traces of **a**, crystal **1** (H<sub>2</sub>O molecules) and **b**, crystal **2** (D<sub>2</sub>O molecules) recorded at a heating rate of 10 °C min<sup>-1</sup>. The DSC measurements were carried out for **1** and **2** after coating with paraffin liquid. No peak corresponding to paraffin liquid was observed in the range of measurement.