Exotic water state in hydrophilic nanospace of porous coordination polymers

Authors: Tomoaki Ichii1*, Takashi Arikawa1, Kenichiro Omoto2, Nobuhiko Hosono2, Hiroshi Sato2, Susumu Kitagawa2, Koichiro Tanaka1,2*

Affiliations:
1Department of Physics, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan.
2Institute for Integrated Cell-Material Sciences, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan.

*Corresponding to: kochan@scp.kyoto-u.ac.jp (K.T.); ichii.tomoaki.46v@st.kyoto-u.ac.jp (T.I.)

Abstract:
Nanoconfined water exhibits physical properties not seen in the bulk phase due to confinement effects. In this study, using highly designable nanopores of porous coordination polymers, we discovered an exotic water state between solids and liquids. Single-crystal X-ray diffraction found that nanoconfined water has a discrete symmetry like solid ices, but infrared spectroscopy showed the existence of broken hydrogen bonds like liquid water. Because there exist no solid-liquid critical points in the bulk phase diagram, the water state does not correspond to any bulk state. We showed that the theoretically predicted solid-liquid supercritical-like state is realized even at standard ambient conditions in hydrophilic nanospaces.

Main Text:
Water is ubiquitous in nature and plays a crucial role in biological and chemical systems (1–5). The intermolecular interactions of hydrogen bonds (H-bonds) in liquid water induce characteristic properties, such as dynamic network rearrangements at (sub-)picosecond scale, maximum density at 4 °C, and the highest specific heat capacity of all liquids except ammonia (6–9). However, when liquid water is confined within a nanoscale space, the structure and dynamics are dominated by not only H-bonds but also the size, geometry, and inner wall properties of the confined space. It is interesting to note that nanoconfined water shows different physical properties from bulk water even at the same temperature and pressure.

So far, many research groups have performed studies on nanoconfined water using porous materials like zeolites, carbon nanotubes (CNTs), and silica (10–16). They observed that confinement effects occur in spaces narrower than 100 nm scale and can be classified into two regimes. The first regime appears in spaces from 2 nm to few tens of nanometers, where the confined water is conceptually divided into a water core with bulk liquid-like properties and a shell of surface water with properties different from bulk water (10, 11). The local surface water and its electrostatic forces affect the collective behavior of bulk liquid-like water, resulting in a higher viscosity and proton mobility than bulk water (12,
The second regime appears in spaces narrower than 2 nm, where only surface water exists (14–16). In this regime, nanoconfined water is strongly affected by the geometry restrictions and overlapped potentials of the inner-walls, giving rise to exotic properties: hydrophobic confinements in the 1 nm-size quasi-one-dimensional (1D) nanospace of CNTs realizes a supercritical gas-like structure of water at ambient temperature and pressure (15). Hydrophilic confinements of water in quasi-1D nanospaces also have the possibility to realize unexpected H-bond states, which should be much different from CNTs owing to the strong surface potentials. However, the study of such water states remains unexplored because of the difficulties in preparing hydrophilic 1 nm-size quasi-1D nanospaces.

The completely regular and highly designable nanopores of porous coordination polymers (PCPs) shed new light on this issue (17, 18). The recent remarkable progress in the design and synthesis of PCPs has made it possible to precisely control the size, dimensions, and inner wall properties of nanopores at nanoscale (0.4–2 nm) (18), which completely differs from conventional nanoporous materials. This feature of PCPs enables us to explore anomalous water states induced by a hydrophilic quasi-1D nanospace. In this paper, we first discover an exotic water state with a discrete symmetry like solid ices and broken H-bonds like liquid water. The absence of solid-liquid critical points in the bulk phase diagram indicates that the nanoconfined water does not correspond to any bulk states. Our results show that hydrophilic confinements of quasi-1D nanospace realize a solid-liquid supercritical-like state that is theoretically predicted to exist at high pressure (≈10 MPa) in the same size of CNTs.

We synthesized a water-adsorbing PCP that is composed of copper ions and isophthalates (see Supplementary Information). The water sorption isotherm was measured at 298 K, as shown in Fig. 1A. At higher relative pressures $P/P_0$ where $P_0$ is the saturated water vapor pressure, the PCP contains three water molecules per copper ion (PCP-1). At $P/P_0 = 0.04$, the data exhibits a very sharp desorption feature, corresponding to the release of two water molecules (referred to as “guest water” hereafter) per copper ion (PCP-2). The remaining water molecule in PCP-2 (referred to as “coordinated water”) is strongly bound to the copper ion through a coordination bond as shown below. Heavy water sorption isotherms were also measured (Fig. S1), and we verified that the adsorption properties exhibit no isotope effects.

We performed single-crystal X-ray diffraction (SXRD) analysis of PCP-1 (Fig. S2) to investigate whether nanoconfined water in PCP-1 has a discrete symmetry like solid ices or continuous symmetry like gas vapor and liquid water. Fig. 1B shows the unit cell of PCP-1, which is a two-dimensional (2D) sheet structure with a square lattice framework. The 2D sheets are stacked along the c-axis (Fig. 1C) with a separation distance of 6.9 Å, creating 1 nm-size quasi-1D channels that can accommodate water. We observed the positions of oxygen atoms in confined water molecules using SXRD, which shows that water in a quasi-1D nanospace has a discrete rotational and translational symmetry like solid ices even at room temperature. There are three types of oxygen atoms in the water molecules for each copper ion in different environments (colored red, blue, and purple). The red-colored oxygen atoms are in close proximity to the copper ions (green) and strongly bound by a coordination bond (coordinated water). In contrast, the other two oxygen atoms (blue and purple) are located near the center of the channel at different positions along the c-axis (sites I and II in Fig. 1C, respectively). The distances between the blue and purple
oxygen atoms and nearby oxygen atoms on the inner wall are 2.8 and 3.2 Å, respectively (Fig. 1B), indicating that these are the guest water weakly bound by H-bonds (19) and released at $P/P_0 = 0.04$. These analyses are supported by powder crystal X-ray diffraction (PXRD) and simulation results (Fig. S3). The distance between the four water molecules (2.9 Å) at sites I and II suggest the existence of tetramer H-bonding structure (Fig. 1B) (19). However, the tetramers at sites I and II are separated by a distance of 3.3 Å or 3.6 Å, indicating no or considerably weak H-bond interactions between the tetramers (Fig. 1C) (19, 20). The guest water density ($d$) is estimated to be 1.0 g/cm³ at 298 K. This is close to the density of liquid water: 0.997 g/cm³ at 298 K, 0.1 MPa (20). We also confirmed that there are no differences between the framework structures of PCP-1 and PCP-2 (Fig. S3).

To investigate the surface potential on the inner walls, we measured the infrared (IR) spectrum of PCP-2 without guest water (blue curve in Fig. 2A). It shows two sharp absorption peaks (H1 and H2) owing to the OH stretching modes of coordinated water. This interpretation was confirmed by the isotopic effect observed for the two absorption peaks (see Supplementary Information). The IR spectrum of PCP-2 with coordinated D₂O (red curve in Fig. 2A) shows new absorption peaks (D1 and D2) at frequencies that are 21/2 times lower than those of H1 and H2, respectively(21). As shown by the black curves in Fig. 2A, each peak is well-defined by the Lorentz function with parameters shown in Table 1, which means that the structural inhomogeneity of coordinated water is negligible. Due to the strong correlation between the resonance frequency of the OH stretching mode and H-bond length (O-O distance between water molecules), the peaks H1 (at 3450 cm⁻¹) and H2 (at 3655 cm⁻¹) can be assigned to H-bonded OH (HB-OH) with a H-bond length of ~3 Å and non-H-bonded OH (Free-OH)(19), respectively. The number of H1 and H2 arms determined from the absorbance area normalized by oscillator strength are almost the same (see Supplementary Information), which means that every coordinated water molecule has both HB-OH and Free-OH arms. The crystallographic data (data file S1) shows that several oxygen atoms (colored brown in Fig. 2C) are located within ~3 Å. However, only one atom satisfies the tetrahedral geometry formed by the sp³ hybrid orbital of the oxygen atoms in coordinated water molecules. As shown in Fig. 2C, the HB-OH arm of coordinated water is H-bonded to an oxygen atom of an isophthalate in the adjacent layer, and the other OH arm is directed to the interior of the 1D nanochannel, which makes the inner wall hydrophilic.

The blue curve in Fig. 2B shows the IR absorption spectrum of PCP-1 adsorbing guest water. A broad absorption band (H3) is observed in the frequency range of the OH stretching modes. H3 shows an approximately 21/2 times isotopic shift by replacing all the guest and coordinated H₂O with D₂O (red curve in Fig. 2B), indicating that H3 is due to the adsorbed H₂O. The broad absorption band H3/D3 is decomposed into three Gaussian functions and one Lorentz function (H4/D4) as shown in Fig. 2B. These are assigned to OH stretching modes with strong (3202 cm⁻¹), intermediate (3390 cm⁻¹), weak (3539 cm⁻¹), and no H-bond (H4, 3630 cm⁻¹) (22). The existence of weak H-bonded and free OH arms is a characteristic of liquid water not seen in solid ices. We can estimate the number of Free-OH arms in PCP-1 from the absorbance area of H4 peak normalized by oscillator strength. Table 1 shows that the absorbance area of H4 peak is almost the same as that of H2 (Free-OH of coordinated water). Because of the small difference in peak position between H2 and H4, their oscillator strengths are comparable to each other (8). Therefore, the number of Free-OH arms in PCP-1 is almost the same as in coordinated water (four per unit cell). Based on this knowledge of the H-bond state of guest and coordinated water molecules, we can uniquely identify the H-bond network structure of the guest water as shown in Fig. 2D. Due to the negligible interaction between tetramers (Fig. 1C), guest water molecules on
site I have Free-OH arms. As a result, the average H-bond number of guest water is 3, which lies between those of liquid water (2.2 (15) and 2.6 (23)) and solid ices (∼4 (24)). Interestingly, this means that despite the discrete symmetry like solid ices, guest water does not satisfy Pauling’s ice rule which states that each water molecule offers/accepts two hydrogen atoms to/from two neighboring molecules and has four H-bonds (24).

We also investigated a dynamic property of guest water molecules by time-lapse IR spectroscopy. We prepared PCP-1 adsorbing the mixture of H2O and D2O. We exposed the sample to D2O gas vapor and measured the spectral changes in H3, which provides information about the diffusion dynamics of guest water molecules. The result is shown in Fig. 3A. D3 gradually increased in height with time (t), whereas H3 gradually decreased. These spectral changes are attributed to the exchange of guest H2O/HDO with D2O molecules outside the nanochannels. The H3 area normalized by oscillator strength provides the number of hydrogen atoms per unit cell, \( n_{H\text{-atom}}(t) \), which is shown in Fig. 3B (see Supplementary Material). It decreases exponentially (green curve), as expected from the 1D diffusion model (25),

\[
n_{H\text{-atom}}(t) \propto \exp(-t/\tau) \tag{1}
\]

The time constant \( \tau = 3.8 \times 10^3 \) s determined from the fit allows us to deduce the diffusivity (D) of water in the nanochannel using the following relation (25),

\[
\tau = \frac{l^2}{3D} + l/\alpha \tag{2}
\]

Here, \( l \) and \( \alpha \) are the lengths of the 1D nanochannel and surface permeability, respectively. The root-mean-square of the channel length \( \langle l^2 \rangle^{1/2} \) is 0.8 \( \mu \)m (Fig. S4). The surface permeability is unknown, but at least a positive number. This allows us to determine the lower limit of diffusivity as \( 0.6 \times 10^{-16} \) m\(^2\)/s, which is higher than that of ice VII (\( < 2.6 \times 10^{-19} \) m\(^2\)/s at 300 K, 10 GPa (26)). Since microscopic molecular diffusion is induced by the hopping process, this result shows that the structural rearrangements of guest water tetramers occur faster in PCP-1 than in solid ices at the same temperature.

Previous studies on confined water in the 1 nm-size hydrophobic nanospace of CNTs have reported its continuous symmetry and intermediate H-bond number of 1.2 between gaseous and liquid water at ambient pressure and temperature (15). This corresponds to a liquid-gas supercritical-like structure in the bulk phase diagram (15). On the other hand, our results show that water molecules in the 1 nm-size hydrophilic nanospace have a discrete symmetry and intermediate H-bond number between solid ice and liquid water. This indicates a solid-liquid supercritical-like structure. However, it is commonly believed that a solid-liquid critical point does not exist, because of the famous symmetry argument that an isotropic liquid cannot continuously transform into a solid with a discrete symmetry (27). In fact, there is no solid-liquid critical point in the bulk phase diagram of water (8). Therefore, the water state in the hydrophilic nanospace of PCP-1 is exotic with no corresponding states in the bulk phase diagram.

Then, what is the observed water state in the quasi-1D hydrophilic nanospace? Recently, the intriguing possibility of the solid-liquid critical point has been reported for strongly confined water under high pressure. The simulation showed the existence of continuous phase change between square ice phase and liquid phase in 1 nm-size CNTs (28). The water state in PCP-1, the 1D array of square water with a larger diffusivity than solid ice at room
temperature and intermediate H-bond number between solid ice and liquid water, nicely fits into this phase boundary at ambient temperature and high pressure (28). These results indicate that the hydrophilic inner wall in PCP-1 plays the role of effective high pressure because the surface potential localizes the guest water molecules. In this study, we illustrated the remarkable ability of hydrophilic nanochannels to induce exotic states of water even at ambient conditions, which would enable us to facilitate new chemical reactions and control structural changes in biological molecules.

References and Notes:
1. G. W. Robinson, S.-B. Zhu, S. Shing, M. W. Evans, Water in Biology, Chemistry and Physics: Experimental Overviews and Computational Methodologies. (World Scientific, 1996).
2. I. Ohmine, S. Saito, Water dynamics: Fluctuation relaxation, and chemical reactions in hydrogen bond network rearrangement. Acc. Chem. Res. 32, 741–749 (1999).
3. F. Zhu, E. Tajkhorshid, K. Schulten, Theory and Simulation of Water Permeation in Aquaporin-1. Biophys. J. 86, 50–57 (2004).
4. P. Ball, Water as an active constituent in cell biology. Chem. Rev. 108, 74–108 (2008).
5. M. Smits et al., Ultrafast energy flow in model biological membranes. New J. Phys. 9, 390–390 (2007).
6. G. S. Kell, Density, Thermal Expansivity, and Compressibility of Liquid Water from 0°C to 150°C: Correlations and Tables for Atmospheric Pressure and Saturation Reviewed and Expressed on 1968 Temperature Scale. J. Chem. Eng. Data. 20, 97–105 (1975).
7. D. Luzar, A. & Chandler, Hydrogen-bond kinetics in liquid water. Nature. 379, 55–57 (1996).
8. D. Eisenberg, W. Kauzmann, The Structure and Properties of Water (Oxford Univ. Press, London, New York, 1969).
9. K. E. Bett, J. B. Cappi, Effect of Pressure on the Viscosity of Water. Nature. 207, 620–621 (1965).
10. S. Gruener, T. Hofmann, D. Wallacher, A. V. Kityk, P. Huber, Capillary rise of water in hydrophilic nanopores. Phys. Rev. E. 79, 67301 (2009).
11. S. Kerisit, C. Liu, Molecular Simulations of Water and Ion Diffusion in Nanosized Mineral Fractures. Environ. Sci. Technol. 43, 777–782 (2009).
12. L. Li, Y. Kazoe, K. Mawatari, Y. Sugii, T. Kitamori, Viscosity and wetting property of water confined in extended nanospace simultaneously measured from highly-pressurized meniscus motion. J. Phys. Chem. Lett. 3, 2447–2452 (2012).
13. T. Tsukahara, W. Mizutani, K. Mawatari, T. Kitamori, NMR studies of structure and dynamics of liquid molecules confined in extended nanospaces. J. Phys. Chem. B. 113, 10808–10816 (2009).
14. E. Mamontov et al., Dynamics of water in LiCl and CaCl₂ aqueous solutions confined in silica matrices: A backscattering neutron spectroscopy study. Chem. Phys. 352, 117–124 (2008).
15. T. Ohba, Size-dependent water structures in carbon nanotubes. Angew. Chem. Int. Ed. 53, 8032–8036 (2014).
16. I. C. Bourg, C. I. Steefel, Molecular dynamics simulations of water structure and diffusion in silica nanopores. J. Phys. Chem. C. 116, 11556–11564 (2012).
17. O. M. Yaghi et al., Reticular synthesis and the design of new materials. *Nature*. **423**, 705–714 (2003).
18. S. Kitagawa, R. Kitaura, S. Noro, Functional Porous Coordination Polymers. *Angew. Chem. Int. Ed.* **43**, 2334–2375 (2004).
19. T. Steiner, The hydrogen bond in the solid state. *Angew. Chem. Int. Ed.* **41**, 48–76 (2002).
20. A. Khan, A Liquid Water Model: Density Variation from Supercooled to Superheated States, Prediction of H-Bonds, and Temperature Limits. *J. Phys. Chem. B.* **104**, 11268–11274 (2000).
21. I. V. Stiopkin et al., Hydrogen bonding at the water surface revealed by isotopic dilution spectroscopy. *Nature.* **474**, 192–195 (2011).
22. J. B. Brubach, A. Mermet, A. Filabozzi, A. Gerschel, P. Roy, Signatures of the hydrogen bonding in the infrared bands of water. *J. Chem. Phys.* **122**, 184509 (2005).
23. J. Zielkiewicz, Structural properties of water: Comparison of the SPC, SPCE, TIP4P, and TIP5P models of water. *J. Chem. Phys.* **123**, 104501 (2005).
24. V. F. Petrenko, R. W. Whitworth, *Physics of Ice* (Oxford University Press, 1999).
25. L. Heinke, Z. Gu, C. Wöll, The surface barrier phenomenon at the loading of metal-organic frameworks. *Nat. Commun.* **5**, 1–6 (2014).
26. E. Katoh, H. Yamawaki, H. Fujihisa, M. Sakashita, K. Aoki, Protonic Diffusion in High-Pressure Ice VII. *Science.* **295**, 1264–1267 (2002).
27. Stanley H, *Introduction to Phase Transitions and Critical Phenomena* (Oxford Univ Press, London, 1971).
28. K. Mochizuki, K. Koga, Solid–liquid critical behavior of water in nanopores. *Proc. Natl. Acad. Sci.* **112**, 8221–8226 (2015).
Acknowledgments:

Funding: S.K., H.S., N.H., and T.A. are thankful to the Japan Society for the Promotion of Science (JSPS) for KAKENHI Grant-in-Aid for Specially Promoted Research (25000007). S.K., H.S., and N.H. acknowledge the financial support of Scientific Research (S) (18H05262). N.H. acknowledges JSPS for a KAKENHI Grant-in-Aid for Young Scientists (B) (16K17959) and Scientific Research (B) (18H02072). K.T. is thankful to the Scientific Research (S) (17H06124). Author contributions: T.I., T.A., S.K., and K.T. conceived the experiments. T.I. built the set-up, performed the experiments and analyzed the experimental data with contributions from T.A. and K.T. K.O., N.H., and H.S. synthesized and characterized the PCP sample. T.I., T.A., and K.T. developed the analytical model. All the authors contributed to discussing the results and writing the paper. Competing interests: Authors declare no competing interests. Data and materials availability: All data necessary to support the conclusions are available in the manuscript or supplementary materials. The x-ray crystallographic coordinate for a structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre under deposition number CCDC 1893959.

Supplementary Materials:

Materials and Methods
Supplementary Text
Figures S1-S16
Tables S1-S3
References (29-40)
Data File S1
**Fig. 1. Water adsorbing PCP.** (A) Desorption isotherm of water adsorbing PCP at 298 K. The adsorption isotherm is also measured and the same as the desorption isotherm (Fig. S1). (B) The unit cell of the crystal structure of PCP-1. Atoms are colored as follows: Cu, green; C, gray; O of isophtalates, brown; O of coordinated water, red; O of guest water, blue and purple. Hydrogen atoms are omitted. The magnified view shows the tetramer water structure with distances between oxygen atoms. (C) Side view of the 1D nanochannel with adsorbed water molecules showing isolated water tetramers in site I and II.

**Fig. 2. Hydrogen bond structure of coordinated and guest water.** (A) The IR absorption spectra of PCP-2 adsorbing only coordinated H$_2$O (blue line) and D$_2$O (red line) at 295 K below 4 % RH. The small peaks (2800 ~ 3100 cm$^{-1}$) correspond to the CH stretching modes of the framework. The black broken and solid lines are the result of Lorentz curve fittings of absorption peaks due to coordinated H$_2$O and D$_2$O, respectively. (B) The IR absorption spectra of PCP-1 adsorbing H$_2$O (blue line) and D$_2$O (red line) under 30 % RH. Each IR band is well decomposed into three Gaussian functions (black dashed) and one Lorentz function (solid line). Yellow and cyan dashed lines are the sum of four deconvoluted functions of the red and blue line, respectively. (C) The schematic diagram of H-bond structure of coordinated water in PCP-2. Hydrogen atoms are colored by cyan. (D) The schematic diagram of H-bond structure of coordinated and guest water in PCP-1.
Fig. 3. Dynamic properties of guest water. (A) The series of IR absorption spectra after the exposition to D$_2$O vapor. (B) The number of hydrogen atoms per unit cell ($n_{H\text{-atom}}(t)$). The green solid line shows curve fitting results with exponential functions.

Table 1. Results of peak positions, FWHMs, and ratio of absorbance area for Lorentz fitting of coordinated H$_2$O and D$_2$O in Fig. 2A and H4&D4 in Fig. 2B.

|     | Peak position (cm$^{-1}$) | FWHM (cm$^{-1}$) | Ratio of absorbance area |
|-----|--------------------------|------------------|--------------------------|
| H1  | 3450                     | 140              | 4.8                      |
| H2  | 3655                     | 33.5             | 1                        |
| H4  | 3630                     | 50.9             | 0.91                     |
| D1  | 2544                     | 73.5             | 2.1                      |
| D2  | 2706                     | 36.8             | 0.76                     |
| D4  | 2689                     | 50.8             | 0.85                     |
Supplementary Materials for

Exotic water state in hydrophilic nanospace of porous coordination polymers

Tomoaki Ichii¹*, Takashi Arikawa¹, Kenichiro Omoto², Nobuhiko Hosono², Hiroshi Sato², Susumu Kitagawa², Koichiro Tanaka,¹,²*

*Correspondence to: kochan@scphys.kyoto-u.ac.jp (K.T.); ichii.tomoaki.46v@st.kyoto-u.ac.jp (T.I.)

This PDF file includes:

Materials and Methods
Supplementary Text
Figs. S1 to S16
Tables S1 to S3
References (29–40)

Other Supplementary Materials for this manuscript include the following:

Data File S1
**Materials and Methods**

**Materials**

All solvents, organic and inorganic reagents are commercially available, and were used without further purification. Single crystals of PCP-1 were prepared according to previously reported procedures. Microwave syntheses were performed using Biotage model Initiator. Single-crystal X-ray crystallographic analysis was performed using Rigaku model XtaLab P200 diffractometer equipped with a Dectoris PILATUS 200 K detector, using a VariMax Mo Optic with MoKa radiation (\(\lambda = 0.71075\) Å) and a confocal monochromator. Thermogravimetric analyses (TGA) were performed on a Rigaku model Thermo plus EVO under dry N\(_2\) atmosphere at 30 ºC (Fig. S3c). For H\(_2\)O desorption, powder crystals of PCP-1 were exposed to dry N\(_2\) atmosphere for ca. 2 h at 30 ºC to remove guest H\(_2\)O to provide powder crystals of PCP-2. PXRD of the resultant PCP-2 were measured under dry N\(_2\) atmosphere at 30 ºC (Fig. S3c). For H\(_2\)O adsorption, resultant powder crystals of PCP-2 were exposed to open air for ca. 0.5 h at 30 ºC to absorb guest H\(_2\)O to provide PCP-1. PXRD of the resultant powder crystal were measured under open air at 30 ºC (Fig. S3d).

**Synthesis of single crystals of Cu(ipa)·3H\(_2\)O (PCP-1)**

5-Methylysothioic acid (H\(_2\)ipa) (272 mg, 1.51 mmol, 1.0 eq) and H\(_2\)O (10 mL) were placed in a pressure vessel, which was stirred at 150 ºC for 1 h using a microwave reactor. After cooling down to room temperature, to the mixture was added Cu(NO\(_3\))\(_2\)·2.5H\(_2\)O (353 mg, 1.51 mmol, 1.0 eq) in H\(_2\)O (10 mL). After standing the mixture at 150 ºC for 5 days, Cu(ipa)·3H\(_2\)O (PCP-1) was obtained as blue block single crystals. After washing with H\(_2\)O, the resultant single crystals were stored in H\(_2\)O (10 mL). After standing the mixtures at 30 ºC for ca. 2 h at 30 ºC to remove guest H\(_2\)O to provide powder crystals of PCP-2. PXRD of the resultant PCP-2 were measured under dry N\(_2\) atmosphere at 30 ºC (Fig. S3c).

**Result of single-crystal X-ray crystallographic analysis for PCP-1 at 298 K**

Crystal data for C\(_9\)H\(_{12}\)CuO\(_7\)·F\(_w\) = 295.74, tetragonal, space group P4/nmm, \(a = b = 19.0629(3)\) Å, \(c = 6.91407(17)\) Å, \(V = 2512.53(8)\) Å\(^3\), \(Z = 8\), \(\rho_{\text{calc}} = 1.563\) g cm\(^{-3}\), \(\mu = 1.7571\) mm\(^{-1}\), \(T = 298\) K, \(\lambda(\text{MoK}\alpha) = 0.71075\) Å, \(2\theta_{\text{max}} = 50.0°\), 17310/1232 reflection collected/unique (\(R_{\text{int}} = 0.0221\)), \(R_1 = 0.0384 (I > 2\sigma(I))\), \(wR_2 = 0.1243\) (for all data), GOF = 1.079, largest diff. peak and hole 0.82 / −0.75 eÅ\(^{-3}\). Hydrogen atoms of H\(_2\)O molecules were not assigned. CCDC deposit number 1893959.

**PXRD of powder crystals of PCP-1 and PCP-2**

Reversible H\(_2\)O desorption/adsorption behaviors of PCP-1 and PCP-2 were monitored by PXRD under open air or dry N\(_2\) atmosphere at 30 ºC (Fig. S3). For H\(_2\)O desorption, powder crystals of PCP-1 were exposed to dry N\(_2\) atmosphere for ca. 2 h at 30 ºC to remove guest H\(_2\)O to provide powder crystals of PCP-2. PXRD of the resultant PCP-2 were measured under dry N\(_2\) atmosphere at 30 ºC (Fig. S3c). For H\(_2\)O adsorption, resultant powder crystals of PCP-2 were exposed to open air for ca. 0.5 h at 30 ºC to adsorb guest H\(_2\)O to provide PCP-1. PXRD of the resultant powder crystal were measured under open air at 30 ºC (Fig. S3d).
Upon exposure of PCP-1 to dry N₂ atmosphere at 30 ºC for ca. 2 h, PXRD pattern of PCP-1 changed to that of PCP-2, as evidenced by a distinct increase in the intensity of 110 diffraction ($2\theta = 6.5^\circ$, Fig. S3b,c). Furthermore, upon exposure of the resultant powder crystals of PCP-2 to open air, PXRD pattern of PCP-1 restored, as evidenced by the decrease in 110 diffraction ($2\theta = 6.5^\circ$, Fig. S3c,d). These reversible changes in the PXRD patterns suggest that PCP-1 reversibly releases/captures the guest H₂O upon exposure to dry N₂ atmosphere or ambient air at 30 ºC without degradation of its host framework.

**SEM observation of PCP-1.**
Field-Emission Scanning electron microscopy (FE-SEM) observations of powdery PCP-1 were performed with a HITACHI model SU-5000 operating at 15 kV. The dried samples deposited on carbon tape were coated with osmium using an osmium coater (Vacuum Device model HPC-20) prior to the observations.

**Synthesis of powder crystals of Cu(ipa)•3H₂O (PCP-1) and Cu(ipa)•H₂O (PCP-2)**
5-Methylisophthalic acid (H₂ipa) (195 mg, 1.1 mmol, 1.0 eq) and H₂O (54 mL) were placed in a pressure vessel, which were stirred at 150 ºC for 1 h using a microwave reactor. After cooling down to room temperature, to the mixture was added Cu(NO₃)₂•2.5H₂O (256 mg, 1.1 mmol, 1.0 eq) and pyridine (80 µL) in H₂O (10 mL). After stirring of the mixture at 150 ºC for 1.5 h, blue powder crystals were obtained. The resultant powder crystals were collected by decantation, washed successively with EtOH (7.5 mL x 3) and H₂O (15 mL x 3), and dried under ambient air to afford Cu(ipa)•3H₂O (PCP-1) (77.67 mg, 0.26 mmol, 24%) as blue powder crystals. The PXRD and TGA of the resultant material supported formation of PCP-1 in powdery form (Fig.S5, S6).

The guest H₂O of the powder crystals of PCP-1 were selectively removed upon standing PCP-1 under dry N₂ atmosphere or reduced pressure around room temperature, allowing us to obtain the monohydrated product, Cu(ipa)•H₂O (PCP-2), as characterized by following PXRD and TGA data (Fig.S5, S6).

**TGA of powder crystals of PCP-1**
TG profiles of powder crystals of PCP-1 were obtained in two distinct methods; measured with (i) constant and (ii) valuable heating-rate experiments.

(i) TGA of powder crystals of PCP-1 measured with constant heating rate (5 ºC/min)
TG profile of PCP-1 (Fig. S6) measured with constant heating rate (5 ºC/min) showed two distinct weight losses around 30–70 ºC (A) and 70–120 ºC (B), corresponding to the losses of the guest H₂O (2 molecules per one Cu(II)) and the coordinating H₂O (1 molecule per one Cu(II)), respectively (29).

The decomposition of the sample beyond 300 ºC is confirmed by the sharp weight loss in the TG profile.

(ii) TGA of powder crystals of PCP-1 measured with valuable heating rate
Powder crystals of PCP-1 were firstly exposed to dry N₂ atmosphere with a constant temperature condition (30 ºC) for 240 min, then the temperature was increased up to 500 ºC with the heating rate of 5 ºC/min. The weight reduction of the sample was monitored in time course as described on Fig. S7.

· **0–240 min (constant temperature condition (30 ºC))** Upon exposure of the sample to dry N₂ atmosphere at 30 ºC, a definite weight loss (C: 2 H₂O per one Cu(II) center) followed by plateau was observed.

· **240 min–330 min (heating at 5 ºC/min)** Upon increasing the temperature from 30 ºC with the heating rate of 5 ºC/min, a definite weight loss (D: 1 H₂O per one Cu(II) enter) followed by plateau was observed.
The weight loss followed by plateau observed as \( \text{C} \) (2 H\(_2\)O per one Cu(II) center) suggests PCP-1 selectively released guest H\(_2\)O upon exposure to dry N\(_2\) atmosphere at 30 °C to afford PCP-2. The weight loss observed as \( \text{D} \) (1 H\(_2\)O per one Cu(II) center) suggests loss of coordinating H\(_2\)O from PCP-2 upon heating. The decomposition of the sample beyond 300 °C (300 min) is confirmed by the sharp weight loss in the TG profile.

Samples for IR measurements

The sample was a pellet (~ 100 µm thickness) made by pressing microcrystalline powder sample of PCP-1 (the typical size is 0.67 µm as shown in Fig. S4). The pellet was placed in a chamber, wherein the humidity was regulated to control the adsorbed water amount in PCP-1. Chamber volume is \( \pi \times 1.28 \text{ cm} \times 1.28 \text{ cm} \times 0.7 \text{ cm} = 1.1 \text{ cm}^3 \). The low humidity below 4 % is achieved by flowing dry air into the chamber. The high humidity (~30 %) is obtained by the mixture of dry air and saturated steam. The humidity in the chamber is measured by means of a digital humidity meter (Model CTH-1100, Custom, Tokyo). The IR spectra were performed at ambient temperature by using Hyperion Fourier Transform Infrared (FTIR) microscope connected to the Bruker VERTEX 80v spectrometer at a spectral resolution of 4 cm\(^{-1}\). The steady states of coordinated and guest water were measured by 64 accumulation scans. IR spectra during the adsorption dynamics of guest water were measured by repeated data collection mode of Bruker VERTEX 80v spectrometer by accumulating 4 scans. It took 4 s per one IR data. The flow rate of D\(_2\)O molecules into the chamber is around 1 lpm. The used D\(_2\)O gas molecules were evaporated from 99% concentration of D\(_2\)O (CAS. No. 7789-20-0, Cambridge Isotope Laboratories Inc., product code DLM-4-99-1000).

Isotopic substitutions

Isotopic substitution of guest and coordinated H\(_2\)O with D\(_2\)O was achieved just by exposing PCP-1 to D\(_2\)O vapour at ~30 % RH. The concentration of deuterium atoms of guest and coordinated water is controlled by exposing PCP-1 to the proper mixture of the deuterium oxide and distilled water (CAS. No. 7732-18-5, Wako Pure Chemical Industries Ltd., Osaka, product code 049-16787).

Isotope effects on peak widths of coordinated water in PCP-2

The peaks H1 and H2 can be assigned to the stretching modes of H-bonded OH (HB-OH) and non-H-bonded OH (Free-OH), respectively. This is also confirmed by the isotope effect on their peak widths. The widths of the absorption peaks due to the HB-OH stretching modes are strongly affected by the anharmonic coupling with lower frequency modes such as O-O vibration modes(31). The full width at half maximum (FWHM) is proportional to the reciprocal of the mass of hydrogen atom(32, 33). This suggests that the FWHM of HB-OH should be reduced by a factor of 2 by the isotope substitution. To confirm this point, we performed spectral shape analysis of the absorption peaks. Each peak is nicely described by the Lorentz function as shown by the black curves in Fig. 2A, which means the structural inhomogeneity of the coordinated water is negligible. This reflects the high crystallinity of the PCP-2 framework. The fitting results are summarized in Table1. The ratio of FWHMs between H1 and D1 is 140/73.5 = 1.90, which strongly suggests that peak H1 (D1) is due to HB-OH (HB-OD). In contrast, the FWHMs of H2 and D2 are almost the same (33.5/36.8 = 0.91), indicating that H2 (D2) is due to Free-OH (Free-OD).

Number of Free-OH and HB-OH arms in PCP-2

The absorbance area, when normalized by the oscillator strength, tells us the number of Free-OH and HB-OH arms in the PCP-2. Table 1 shows the absorbance area of HB-OH is 4.8 time larger than that of Free-OH. This is almost perfectly compensated by the increase in the oscillator strength by a factor of 5 ± 0.4 due to the H-bonding(8). After all, the IR absorption data suggests that there are equal number of
HB-OH and Free-OH arms. Considering the structural homogeneity, this result indicates that every single coordinated water molecule has both HB-OH and Free-OH arms.

**Time-lapse IR spectroscopy**

**1. IR spectra change during adsorption dynamics of guest water molecules**

A series of IR absorption spectra were recorded during guest water adsorption to reveal the adsorption dynamics of H-bonding at room temperature. Here, heavy water was used as guest water to allow us to spectrally separate coordinated H\(_2\)O and guest D\(_2\)O and observe changes in the H-bonding structure of the coordinated H\(_2\)O molecules during adsorption. Fig. S8 shows the transient IR absorption spectra during guest D\(_2\)O adsorption by PCP-2 under a controlled-humidity atmosphere. The time of 0 s corresponds to the point at which the nitrogen stream was switched from the dry (4% RH) to the wet (~30% RH) state while maintaining a constant flow rate. To highlight the initial adsorption process, the difference between the absorbance at 16 s and 0 s is shown by the solid curve in the inset. The two sharp peaks (D\(_1\)HDO and D\(_2\)HDO) observed here, which are similar to those found in Fig. 2A (D1 and D2), strongly indicate the formation of Free-OD and HB-OD at the beginning of the guest D\(_2\)O adsorption process. Close examination of the data reveals a slight difference between the peak frequencies of D\(_2\)HDO and D2 (dashed green curves, inset of Fig. S8). The peak position of D\(_2\)HDO is quite similar to that of the stretching modes of Free-OD for coordinated HDO (solid blue curve in Fig. S9b). This observation indicates the existence of coordinated HDO molecules. These spectral signatures suggest the following dynamics during the initial stage: incoming D\(_2\)O molecules first form H-bonds with coordinated H\(_2\)O, followed by ultrafast (typically in picoseconds\(^{35, 36}\)) exchange of deuterium and hydrogen atoms and breaking of the H-bonds (in nanoseconds\(^{37, 38}\)), resulting in coordinated HDO molecules.

After 16 s, a broad absorption band (D3) appears instead of the sharp absorption peaks. This change indicates that guest water molecules begin to form the tetramer H-bonding structures (Fig. 1B). Owing to the fast diffusion of water molecules (in nanoseconds), which is much shorter than the experimental timescale, almost all the guest molecules should exist in the stable tetramer form. The absorbance area of D3 monotonically increases with time, implying the steady intake of guest D\(_2\)O molecules into the nanopores. However, the H1 and H2 absorption peaks of coordinated H\(_2\)O change non-monotonically with time. This difference allows us to reveal selective adsorption dynamics inside the nanopores, as discussed below. The time evolution can be divided into three stages.

1) 0–120 s

The changes in the two peaks show opposite trends; the intensity of the higher frequency peak (H2) decreases whereas peak H1 increases in intensity and broadens. This change shows that the Free-OH arms of the coordinated water molecules are forming H-bonds with guest D\(_2\)O molecules. As a result, peak H2 red shifts and forms a lower frequency band (H3). These spectral changes suggest that site I is being occupied by guest D\(_2\)O molecules.

2) 120–180 s

Peak H2 (Free-OH) is no longer clearly observed and absorption band H3 does not change. These observations indicate that all the site I locations are filled with guest water molecules. Nonetheless, the absorption intensity corresponding to OD stretching modes increase, which suggests that guest water molecules are being adsorbed in site II. The absence of any spectral change in the H3 band during adsorption in site II reflects the negligible H-bonding interactions between adjacent water tetramers; otherwise, new HB-OH bonds would change the spectral shape of H3.

3) >180 s

The absorbance corresponding to guest D\(_2\)O (D3) increases, while the absorbance corresponding to the OH stretching modes (H3) decreases and then vanishes (red curve, Fig. S8). This result
shows that HDO or H₂O molecules are released from PCP-I and all hydrogen atoms are replaced by deuterium atoms.

To reveal the selective adsorption dynamics, we quantitatively deduced the number of water tetramers per unit cell in each site \( n_4(t) \) and \( n_4(t) \) from the IR intensities normalized by the oscillator strengths. The intensity decreases of the Free-OH and Free-OD peaks include information about \( n_4(t) \). In contrast, the increase in absorption intensity for the OD stretching modes gives the total mean number of adsorbed guest water tetramers \( (n_\text{total}(t)) \). The probability that all guest water molecules form the H-bonding number between guest water molecules of monomer, dimer, trimer, and tetramer in the 1D nanochannel is 0, 1, 2, and 4, respectively.

The stability of guest water tetramers during guest water adsorption

The much faster diffusion of guest water molecules than water uptake allows us to suppose that they are homogeneously distributed among the one-dimensional (1D) nanochannel. In this case, the adsorption process can be treated as a quasi-static one. Therefore, we can calculate the transient number distribution of water clusters (monomer, dimer, trimer, and tetramer) in the 1D nanochannel by using statistical thermodynamics. Here, we consider four cluster structures of monomer, dimer, trimer, and tetramer H-bonded to inner wall as shown in Fig. S10. We refer the total H-bonding energy of monomer, dimer, trimer, and tetramer as \( E_1, E_2, E_3, \) and \( E_4 \), respectively. The H-bonding number between guest water molecules of monomer, dimer, trimer, and tetramer and inner walls is 1, 2, 3, 4, respectively. The H-bonding number between guest water molecules and inner walls is 1, 2, 3, 4, respectively. Therefore, each total H-bonding energy of \( E_i \) are calculated as \( E_1 = E_w, E_2 = E_w + 2E_w, E_3 = 2E_H + 3E_w \), and \( E_4 = 4E_H + 4E_w \) when we define the water-water and water-inner wall of H-bonding interaction among clusters and \( E_H \) and \( E_w \), respectively. We also refer the number of monomer, dimer, trimer, and tetramer existing in the nanochannel as \( N_1, N_2, N_3, \) and \( N_4 \), respectively.

Although the 1D nanochannel of the PCP sample have two kinds of site I and II, guest water molecules are selectively captured on the site I at early stage. Thus, we first neglect the site II and show that all guest water molecules form the H-bonding structure among site I. We consider the transient state when there are \( 4N_w \) guest water molecules in the 1D nanochannel with one kind of \( M \) site I. The combinations of \( N_i \) satisfy the condition of \( N_0 + N_1 + N_2 + N_3 + N_4 = M \) and \( N_1 + 2N_2 + 3N_3 + 4N_4 = 4N_w \) (\( N_0 \) is the number of empty sites in the 1D nanochannel). We calculated the probability \( p_4 \) that there are only tetramers in the 1D nanochannel. \( p_4 \) is calculated as follows.

\[
p_4(4N_w) = g_4(4N_w) \exp \left( \frac{N_w E_4}{k_BT} \right) / Z(4N_w)
\]

\[
g_4(4N_w) = \frac{M!}{(M-N_w)!N_w!} \sum_{\{N_i\} \in \mathcal{S}_4} \frac{\prod_{i=1}^4 \left( \begin{array}{c} N_0 + N_1 + N_2 + N_3 + N_4 = M \\ N_0 N_1 N_2 N_3 N_4 \end{array} \right)}{N_0! N_1! N_2! N_3! N_4!} \exp \left( \frac{\sum_{i=1}^4 E_i}{k_BT} \right)
\]

\[
Z(4N_w) = \frac{M!}{(M-N_w)!N_w!} \sum_{\{N_i\} \in \mathcal{S}_4} \frac{\prod_{i=1}^4 \left( \begin{array}{c} N_0 + N_1 + N_2 + N_3 + N_4 = M \\ N_0 N_1 N_2 N_3 N_4 \end{array} \right)}{N_0! N_1! N_2! N_3! N_4!} \exp \left( \frac{\sum_{i=1}^4 E_i}{k_BT} \right)
\]

\[
p_4 = \frac{4 \exp \left( \frac{A_{H} + 4E_w}{k_BT} \right)}{\exp \left( \frac{4E_1}{k_BT} \right) + 12 \exp \left( \frac{E_0 + 2E_1 + E_2}{k_BT} \right) + 6 \exp \left( \frac{2E_0 + 2E_1 + E_2}{k_BT} \right) + 12 \exp \left( \frac{2E_0 + E_1 + E_2}{k_BT} \right) + 4 \exp \left( \frac{3E_0 + E_4}{k_BT} \right)}
\]

When \( E_H = 2 \text{ kcal/mol} \) and \( E_w = 1.5 \text{ kcal/mol} \) (typical value of H-bonding energy on site I estimated from SXRD results in Fig. 1B), \( p_4 = 0.995 \). Also, we calculated \( p_4 \) at various \( 4N_w \) when \( M = \).
1000 which corresponds to 1 μm length of 1D nanochannels. The result in Fig. S11 shows that, during adsorption dynamics, almost all guest water molecules confined in the nanochannels with M site I exist in the stable form of the tetramer. This result is the same in the case of the 1D nanochannels with M sites II. The difference between site I and II is just the value of interaction between water and inner wall $E_w$. SXRD shows that water tetramers on site II also have the H-bonding interactions $E_w \sim 1$ kcal/mol. When $E_i = 2$ kcal/mol and $E_a = 1$ kcal/mol, $p_a$ is almost 1 as shown in Fig. S12. Therefore, in the case of 1D nanochannel with site I and II, it is also enough to consider only water tetramers during guest water adsorption.

### 3. Estimation of $n_f(t), n_H(t)$ and $n_{H\text{-atoms}}(t)$

In order to determine the number of water molecules in each site, it is essential to decompose the IR absorption spectra into the sum of the constituent elements. In this sample, we have H$_2$O, D$_2$O and HDO molecules due to the efficient isotope exchange. This prevents us from directly counting the number of H$_2$O or D$_2$O molecules. Instead, we counted the numbers of OH or OD arms ($m_i(t)$) from the spectra and converted them to $n_f(t), n_H(t)$ and $n_{H\text{-atoms}}(t)$. We have ten OH or OD stretching modes in total; H1 and H2 from coordinated H$_2$O molecules, D1 and D2 from coordinated D$_2$O molecules, D$_1$HDO and H$_2$HDO from coordinated HDO molecules with free-OH, H$_1$HDO and D$_2$HDO from coordinated HDO molecules with free-OD, and H3 and D3 from water tetramers.

The spectra of these components are shown in Fig. S13a. Except for H1, H3 and D3, we used the Lorentz fitting results that excellently reproduces the experimental data as shown in Fig. 2A (for H1, H2, D1, D2) and Fig. S9a and S9b (for H$_1$HDO, D$_2$HDO, D$_1$HDO, H$_2$HDO). H1 is obtained by subtracting a Lorentz function for H2 from the experimental data at 0 s shown in Fig. S8. This contains only H1 but also some additional absorption around 3200 ~ 3400 cm$^{-1}$. The absorption spectra of water tetramers are taken from the experimental data at 120 s in Fig. S8, where site I is fully occupied by water tetramers. We used data between 2000 ~ 2800 cm$^{-1}$ for D3 and 3200 ~ 3800 cm$^{-1}$ for H3.

Fig. S13b shows the fitting results for the data up to 180 s using ten spectral components. In the fitting, we imposed the following constraints; $m_{H1}(t) = m_{H2}(t), m_{D1}(t) = m_{D2}(t), m_{H1\text{-HDO}}(t) = m_{H2\text{-HDO}}(t) = m_{D1\text{-HDO}}(t) = m_{D2\text{-HDO}}(t)$. The data between 2800 cm$^{-1}$ ~ 3200 cm$^{-1}$ which contains absorption peaks due to the PCP framework is excluded in the fitting. The excellent fitting enables us to determine the spectral area of each component, $S_i(t)$. The number of arms are calculated as $m_i(t) = S_i(t)/f_i$, where $f_i$ is the oscillator strength. We determined the oscillator strengths as follows. First, we defined the oscillator strength of H2 ($f_{H2}$) as $S_{H2}(0)/4$ so that $m_{H2}(0) = S_{H2}(0)/f_{H2}$ is four, which corresponds to the initial state of four coordinated H$_2$O molecules per unit cell. The other oscillator strengths are defined as $f_i = f_{H2}*a_i/a_{H2}$; relative oscillator strength shown in Table S2).

We can calculate the total number of Free-OH/OD arms of coordinated water per unit cell $m_{\text{Free-OH/OD}}(t)$ as $m_{H2}(t) + m_{D2}(t) + m_{D2\text{-HDO}}(t) + m_{H2\text{-HDO}}(t)$. The decrease in $m_{\text{Free-OH/OD}}(t)$ from the initial value ($m_{\text{Free-OH/OD}}(0) = m_{H2}(0) = 4$) gives the total number of water tetramers on the site I per unit cell; $n_I(t)$

$$n_I(t) = (4 - m_{\text{Free-OH/OD}}(t))/4.$$ Similarly, the total number of adsorbed water tetramers ($n_{\text{total}}(t)$) is

$$m_{\text{total}}(t) = m_{H2\text{-HDO}}(t) + m_{D2\text{-HDO}}(t) + m_{H2\text{-HDO}}(t) + m_{D2\text{-HDO}}(t) + m_{D2\text{-HDO}}(t) + m_{H2\text{-HDO}}(t) + m_{H2\text{-HDO}}(t) + m_{H2\text{-HDO}}(t) + m_{H2\text{-HDO}}(t) + m_{H2\text{-HDO}}(t).$$

After 180 s where $n_I(t)$ reaches almost one, the spectral shape of the OD stretching mode begins to show a gradual change due to the isotope effect as shown in Fig. S14. As a result, the fitting procedure described above does not reproduce the IR spectra well. Therefore, we determined $n_I(t), n_D(t)$ and $n_{H\text{-atoms}}(t)$ without resorting to the spectral decomposition. First, we assumed $n_I(t)$ keeps staying at one; all site I are filled with water tetramers. Then, $n_D(t)$ can be calculated by subtracting the number of water molecules in site I and coordinated water molecules (both of which are four per unit cell) from the whole number of water molecules in the sample, which can be obtained from the spectra as

$$S'_{H2}(t)/f_{H2} + S'_{D2}(t)/f_{D2}/2; S'_{H3}(t) + S'_{D3}(t)$$

are the total area of the stretching modes of OD (2000 ~ 2800 cm$^{-1}$) and OH (2800 ~ 4000 cm$^{-1}$) in Fig. S8. When explicitly written, $n_D(t) = ([S'_{H2}(t)/f_{H2} + S'_{D2}(t)/f_{D2}]/2 - 8)/4$. In this calculation, we used constant $f_{H2}$ and $f_{D2}$ for all the data at different times (i.e., different isotope
4. Site-selective adsorption dynamics of guest water molecules

In Fig. S15, \( n_I(t) \) and \( n_H(t) \) are plotted on the left axis. While \( n_I(t) \) linearly increases, as shown by the yellow line, \( n_H(t) \) remains approximately 0 until 70 s. This adsorption order is probably due to differences in H-bonding strength at sites I and II. Because the local charge separation of OH is larger than that of CO owing to electronegativity differences between oxygen and carbon atoms, the H-bonding potential at site I \( (E_I) \) should be larger than that at site II \( (E_2) \). In fact, in site I, the distance between guest water molecules and the inner walls is 0.4 Å shorter than that in site II (Fig. 1B). Such a difference in H-bond lengths typically causes a potential energy difference of 1 kcal/mol\(^{-1}\). Because water tetramers have four H-bonds with the inner walls, \( E_2 - E_1 \) is estimated as 4 kcal/mol. As shown in the next section, this energy difference quantitatively explains the selective adsorption dynamics. After 70 s, \( n_I(t) \) also increases, and eventually, both \( n_I(t) \) and \( n_H(t) \) reach maximum values of one. As plotted on the right axis of Fig. S15a, \( n_{H,\text{atom}}(t) \) is constant until 180 s, indicating that no water molecules are desorbed from the nanopores. Around 180 s, \( n_{H,\text{atom}}(t) \) starts to decrease. Once sites I and II are completely occupied, \( n_{H,\text{atom}}(t) \) decreases exponentially, as shown by the green curve, revealing a constant rate of exchange for water molecules between the interior and exterior of PCP-1. This part of the data is plotted as Fig. 3B in the main text (the time origin is shifted).

5. Physical model of guest water adsorption dynamics

We will propose a physical model of the adsorption dynamics of guest water molecules. Since the time scale of the guest water intake (on the order of seconds to minutes. See Fig. S15a) is much longer than the thermal relaxation time (nanoseconds), the adsorption process can be treated as a quasi-static one. The number of water tetramers on each site can be quantitatively described by a quite simple model of statistical thermodynamics. The fact that water tetramers are isolated in the PCP-1 allows us to model the adsorption sites I and II as a collection of independent potential sites with different energies (Fig. S15b). The fast diffusion of water molecules inside the sample assures random distribution of water tetramers throughout the nanochannel. Under these circumstances, \( n_I \) and \( n_H \) can be calculated by the following ensemble averages:\(^{40}\),

\[
\begin{align*}
n_I(N) &= \frac{1}{M} \sum_{X=0}^{N} X \, p(N,X) \\
n_H(N) &= \frac{1}{M} \sum_{X=0}^{N} (N - X) \, p(N,X)
\end{align*}
\]

Here, \( M \) is the number of unit cells and \( p(N,X) \) is the probability that \( X \) out of \( N \) tetramers are on the site I. It is calculated as

\[
p(N,X) = \frac{g(X) \, \exp\left(-\frac{(N-X)\Delta E}{k_B T}\right)}{Z(N)}
\]

where \( g(X) \) is the statistical weight which denotes the number of equivalent energy states when \( X \) tetramers exist on the site I and \( Z(N) = \sum_{X=0}^{N} g(X) \, \exp\left(-\frac{(N-X)\Delta E}{k_B T}\right) \) is the partition function. \( \Delta E \) is the adsorption potential difference between site I and II \( 4(E_2 - E_1) \). \( g(X) \) is given by the following expression,

\[
g(X) = W(X) * W(N - X)
\]

where \( W(X) \) is the number of ways to arrange \( X \) water tetramers in \( M \) potential sites. \( W(X) \) is defined as:

\[\text{concentration} \] because these numbers are independent of the concentration of deuterium atoms (\( C=25, 50 \), and 75 %) as shown in Table S3. They are estimated from the absorbance area of OH and OD stretching modes when \( C=25, 50 \), and 75 % shown in Fig. S14. Finally, \( n_{H,\text{atom}}(t) \) are calculated by \( S_{H}(t)/f_{H3} \).
Let us use this model to describe the selective adsorption observed in Fig. S15a. Based on equations (1) and (2), we can calculate \( n_I \) and \( n_{II} \) as a function of \( n_{total} = N/M \). Fig. S15c shows the parametric plot of \( n_I \) and \( n_{II} \) against \( n_{total} \). The experimental data points (blue and purple dots) are well reproduced by our model (black curves) when \( \Delta E = 4(E_2 - E_1) \) is 2 kcal/mol.

6. Microscopic view of guest water adsorption dynamics

Fig. S16 summarizes the H-bond structure of coordinated water and adsorption dynamics of guest water molecules revealed in this paper. Before guest water adsorption, each coordinated water molecule has one HB-OH and Free-OH bond, respectively (Fig. S16a). Free-OH bonds are directed to the inner space and play a role of guest water attraction on the site I. When guest water adsorption starts, the incoming D2O molecules make H-bonding with coordinated water followed by isotope exchanges and H-bonding breaking (Fig. S16b). Guest water molecules diffuse over the 1D nanochannel and selectively adsorbed on the site I by forming a H-bonding unit of tetramer. After the filling of tetramers on the most of the sites I, guest water molecules start to occupy the site II (Fig. S16c). After most sites I and II are occupied, guest water exchange with gas water outside of the PCP-1 at a constant rate (Fig. S16d).
Fig. S1.
Adsorption and desorption isotherms of $\text{H}_2\text{O}$ (blue) and $\text{D}_2\text{O}$ (red) for water adsorbing PCP at 298 K.
Fig. S2.
ORTEP views (50% probability level) of PCP-1 based on single-crystal X-ray crystallographic analysis. Views from a) c-axis and b) b-axis. (C: gray, Cu: pale green, O: red, H: white).
Fig. S3.
PXRD profiles of PCP-1 and PCP-2 (CuKα, λ = 1.541 Å, 30 ºC). Simulated powder XRD patterns of a) PCP-1 and e) PCP-2. Experimental powder XRD patterns of b) PCP-1, c) PCP-2 prepared by exposing powder crystals of PCP-1 to dry N₂ atmosphere at 30 ºC for ca. 2 h, and d) PCP-1 prepared by exposing powder crystals of PCP-2 to open air at 30 ºC for ca. 0.5 h. (f) Schematic illustration of a sample stage for PXRD measurements equipped with a temperature controller, dry N₂ inlet, and a plastic cover.
**Fig. S4.**
Image of PCP-1 crystals taken by Scanning Electron Microscope (SEM). The average value of area is 0.64 µm².
Fig. S5.
PXRD profile of the powder crystals of **PCP-1** (30 °C, CuKα, λ = 1.541 Å).
Fig. S6.
TG profile of the powder crystals of PCP-1 measured with constant heating rate of 5 °C/min under N₂ atmosphere.
Fig. S7.
TGA profile of the powder crystals of PCP-1 measured with variable heating conditions under N₂ atmosphere (0 ~ 240 min: 30 °C (constant), 240 min ~ 330 min: heating late 5 °C/min.).
Fig. S8
Series of IR absorption spectra during the guest D$_2$O adsorption. “0 s” corresponds to the spectra before the D$_2$O adsorption. The blue line in the inset is the absorbance spectra difference between 16 s and 0 s. The dashed green and red line are the normalized absorption spectra of coordinated D$_2$O (Fig. 2A) and HDO (Fig. S9), respectively.
Fig. S9.
(a) IR absorption spectrum of coordinated HDO (H:5%, D:95%). H1_{HDO} and H2_{HDO} in the inset are due to HB-OH and Free-OH of coordinated HDO, respectively. Blue line is the result of Lorentz curve fitting of H1_{HDO} and H2_{HDO}. The fitting results are shown in Table S1. (b) IR absorption spectra of coordinated HDO (H:95%, D:5%) and D_{2}O are shown as red and green curves, respectively. The yellow curve in the inset is the absorption difference between red and green curves. D1_{HDO} and D2_{HDO} are due to the HB-OD and Free-OD of coordinated HDO, respectively. Blue line in the inset is the result of Lorentz curve fitting of D1_{HDO} and D2_{HDO}. The fitting results are shown in Table S1.
Fig. S10.
The possible cluster structures on the site I (a) and II (b). Green and black dot lines represent water-water and water-inner wall H-bonding interactions, respectively.
Fig. S11. Calculation results of $p_4$ for $\{E_H, E_w\} = \{2 \text{ kcal/mol, } 1.5 \text{ kcal/mol}\}$. 
Fig. S12.
Calculation results of $p_f$ for $\{E_{th}, E_w\} = \{2 \text{ kcal/mol, 1 kcal/mol}\}$. 
Fig. S13.
(a) IR absorption spectra of OH/OD bonds of coordinated and guest water (H3/D3), HB/Free-OH bonds of coordinated H2O (H1/H2), HB/Free-OH bonds of coordinated HDO (H1_{HDO}/H2_{HDO}), HB/Free-OD bonds of coordinated D2O (D1/D2), HB/Free-OD bonds of coordinated HDO (D1_{HDO}/D2_{HDO}). (b) The series of IR absorbance spectra and the fitting results (Black curves) by the ten absorption spectra shown in Fig. S13a.
Fig. S14.
IR absorption spectra of guest and coordinated water ($C = 75\%, 50\%, 25\%$, and $0\%$).
Fig. S15.
Modelling of the site selective adsorption dynamics of guest water. (a) The time evolution of $n_I(t)$, $n_{II}(t)$ and $n_{H-atom}(t)$ The yellow and green solid lines are the results of curve fittings by linear and exponential function, respectively. $n_I(t)$ after 180 s (blue dashed line) is supposed to be equal to $n_I(180 \text{ s})$. (b) $M$ sets of site I and II are regarded as $M$ sets of two independent potential sites for water tetramers. (c) The dependence of $n_I(t)$ and $n_{II}(t)$ on $n_{total}(t) = n_I(t) + n_{II}(t)$. After 180 s $n_I(t) = n_I(180 \text{ s})$ as shown by blue dashed line. The black solid lines are the calculations of statistical thermodynamics when $\Delta E = 4(E_2 - E_1) = 2 \text{ kcal/mol}$. 

33
Fig. S16.
The schematic diagram of adsorption dynamics of guest water. (a) H-bonding structure of coordinated water before guest water adsorption. (b) The incoming D$_2$O molecules make H-bonding with coordinated H$_2$O, followed by ultrafast exchange of deuterium and hydrogen atom (typically in picoseconds) and breaking of H-bonding (in nanoseconds), which leaves HDO coordinated water molecules. Guest water molecules are selectively captured on site I and form the H-bonding structure of tetramer. This site-selectivity is induced by the difference of adsorption potential between site I and II. (c) After most site I are filled, guest water molecules start to stay at site II. (d) After most site I and II are occupied, guest water exchange with gas water outside of PCP at a constant rate.
Table S1. Results for Lorentz fitting of H1$_{HDO}$, H2$_{HDO}$, D1$_{HDO}$, and D2$_{HDO}$ of the OH/OD stretching modes in Fig. S9. The ratio of absorbance area of H1$_{HDO}$ and D1$_{HDO}$ are supposed to be the same as H1 and D1 in Table 1, respectively.

|        | Peak position (cm$^{-1}$) | FWHW (cm$^{-1}$) | Ratio of absorbance area |
|--------|---------------------------|------------------|--------------------------|
| H1$_{HDO}$ | 3453                      | 150              | 4.8                      |
| H2$_{HDO}$ | 3644                      | 24.3             | 0.53                     |
| D1$_{HDO}$ | 2550                      | 86.5             | 2.1                      |
| D2$_{HDO}$ | 2683                      | 24.4             | 0.34                     |
Table S2. Relative oscillator strength $a_i$; normalized value of absorbance area by the number per unit cell.

|                                | Ratio of absorbance area | Number per unit cell | Relative oscillator strength $a_i$ |
|--------------------------------|--------------------------|----------------------|-----------------------------------|
| HB-OH of coordinated H$_2$O (H1) | 4.8                      | 4                    | $a_{H1} = 4.8$                    |
| Free-OH of coordinated H$_2$O (H2) | 1                        | 4                    | $a_{H2} = 1$                      |
| HB-OD of coordinated D$_2$O (D1)  | 2.1                      | 4                    | $a_{D1} = 2.1$                    |
| Free-OD of coordinated D$_2$O (D2) | 0.76                     | 4                    | $a_{D2} = 0.76$                   |
| HB-OH of coordinated HDO (H$_1$HDO) | 4.8                      | 4                    | $a_{H1HDO} = 4.8$                 |
| Free-OH of coordinated HDO (H$_2$HDO) | 0.53                     | 4                    | $a_{H2HDO} = 0.53$                |
| HB-OD of coordinated HDO (D$_1$HDO) | 2.1                      | 4                    | $a_{D1HDO} = 2.1$                 |
| Free-OD of coordinated HDO (D$_2$HDO) | 0.34                     | 4                    | $a_{D2HDO} = 0.34$                |
| OH of coordinated and guest H$_2$O (H3) | 26.0                     | 24                   | $a_{H3} = 4.3$                    |
| OD of coordinated and guest D$_2$O (D3)  | 12.3                     | 24                   | $a_{D3} = 2.1$                    |
Table S3. The dependence of the concentration of deuterium atoms $C$ on relative oscillator strength $a_i$ of H3 and D3.

|            | Relative oscillator strength $a_i$ |
|------------|-----------------------------------|
| $a_{H3}$ (H$_2$O:100%, D$_2$O:0%) | 4.3                               |
| $a_{H3}$ (H$_2$O:75%, D$_2$O:75%) | 4.2                               |
| $a_{H3}$ (H$_2$O:50%, D$_2$O:50%) | 4.1                               |
| $a_{H3}$ (H$_2$O:25%, D$_2$O:25%) | 4.1                               |
| $a_{D3}$ (H$_2$O:0%, D$_2$O:100%) | 2.1                               |
| $a_{D3}$ (H$_2$O:25%, D$_2$O:75%) | 2.0                               |
| $a_{D3}$ (H$_2$O:50%, D$_2$O:50%) | 2.0                               |
| $a_{D3}$ (H$_2$O:75%, D$_2$O:25%) | 2.1                               |
Crystallographic Data S1.

Crystallographic information file (CIF) of PCP-1. CCDC number: 1893959
29. R. Q. Zou, H. Sakurai, S. Han, R. Q. Zhong, Q. Xu, Probing the Lewis acid sites and CO
catalytic oxidation activity of the porous metal-organic polymer [Cu(5-
methylisophthalate)]. *J. Am. Chem. Soc.* **129**, 8402–8403 (2007).

30. G. M. Sheldrick, *Program for refinement of crystal structures* (University of Gottingen,
Germany, 1997).

31. M. Bonn, M. J. P. Brugmans, A. W. Kleyyn, R. A. Van Santen, H. J. Bakker, Vibrational
dephasing mechanisms in hydrogen-bonded systems. *Phys. Rev. Lett.* **76**, 2440–2443
(1996).

32. J. Yarwood, G. N. Robertson, A new method of measuring the hydrogen bond stretching
frequency of a complex in solution. *Nature* **257**, 41–43 (1975).

33. R. M. Shelby, C. B. Harris, P. A. Cornelius, The origin of vibrational dephasing of
polyatomic molecules in condensed phases. *J. Chem. Phys.* **70**, 34 (1979).

34. T. Steiner, The hydrogen bond in the solid state. *Angew. Chem. Int. Ed.* **41**, 48–76 (2002).

35. S. Woutersen, H. J. Bakker, Ultrafast vibrational and structural dynamics of the proton in
liquid water. *Phys. Rev. Lett.* **96**, 5–8 (2006).

36. S. Meiboom, Nuclear Magnetic Resonance Study of the Proton Transfer in Water. *J. Chem. Phys.* **34**, 375–388 (1961).

37. M. Chen *et al.*, Jumping Diffusion of Water Intercalated in Layered Double Hydroxides.
*J. Phys. Chem. C.* **120**, 12924–12931 (2016).

38. S. Mitra, A. Pramanik, D. Chakraborty, R. Mukhopadhyay, Excess water dynamics in
hydrotalcite: QENS study. *Pramana J. Phys.* **63**, 437–441 (2004).

39. G. Gilli, P. Gilli, *The Nature of the Hydrogen Bond: Outline of a Comprehensive
Hydrogen Bond Theory* (Oxford University Press, 2009).

40. W. Greiner, L. Neise, H. Stöker, *Thermodynamics and Statistical Mechanics* (Springer-
Verlag, New York, 1995).