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Crystal Structures and Properties of Large Protonated Water Clusters Encapsulated by Metal−Organic Frameworks

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Abstract: A large ionic water cluster $H(H_2O)_{28}^+$, consisting of a water shell $(H_2O)_{26}$ and an encaged species $H(H_2O)_2^+$ as a center core, was trapped in the well-modulated cavity of a porous metal−organic framework (MOF) $\{[Co_4(dpdo)_{12}(PMo_{12}O_{40})_3]^-\}_\infty$ and structurally characterized. Degeneration of the protonated water cluster $H(H_2O)_{28}^+$ into a smaller cluster $H(H_2O)_{21}^+$ and recovery of $H(H_2O)_{28}^+$ from the resulting $H(H_2O)_{21}^+$ cluster in a reversible way demonstrated the unusual stability of the protonated water clusters $H(H_2O)_{28}^+$ and $H(H_2O)_{21}^+$ in the robust crystal host. Proton transport and proton/potassium ion exchange through the channels of the crystal host have been investigated by a well-established fluorometry method. X-ray fluorescence experiments and X-ray structural analyses of the exchanged crystals confirmed the occurrence of the proton/potassium ion-exchange reaction and the transformation of the protonated water cluster $H(H_2O)_{28}^+$ to an ionic cluster $K(H_2O)_{27}^+$. Comparison of the H^+/K^+ exchange of $H(H_2O)_{28}^+$ with that of its neighboring protonated water cluster $H(H_2O)_{27}^+$ suggested that the abundance of hydrogen bonds associated with the hydronium/water cluster in the $H(H_2O)_{28}^+$ cluster was essential for proton transport through the Grotthuss mechanism. On the basis of the results, our porous network could be described as a synthetic non-peptide ion channel, in terms of not only structural features but also the functions addressed. Direct observation of the structures of various large ionic water clusters trapped by porous MOFs, coupled with the proton/ion-exchange processes and the reversible dehydration/rehydration, provided valuable insights into the aqueous proton transfer and its mobility pertaining to the large protonated water clusters in the condensed phase.

Introduction

Water has probably received more scientific and technological interest than any other substance, because water is a major chemical constitute of our planet's surface and as such has been indispensable for the genesis of life, and also because it exhibits a fascinating array of unusual properties in pure form and as a solvent. The deceptively simple water molecule forms one of the most complex liquids and solids, and investigation continues to focus on all forms of water, including small clusters, bulk water, and a magnetite of ice polymorphs. While significant progress on these topics has been made over the decades, systems of water-solvated ions, for instance, proton and alkali cations, are not yet completely clear. It is far more difficult to characterize the structures of these solvated ions, particularly the solvated proton, despite the fact that the nature of the proton in water is a fundamental aspect of aqueous chemistry.[1,2] A powerful way to test the validity of various theoretical methods uses gas-phase protonated water clusters, $H^+(H_2O)_n$, as convenient models for the study of the so-called "aqua proton" in an isolated form as well as the proton solvation processes. Investigation of water clusters of various sizes can lead to precise structural information on hydrogen-bonding motifs in diverse chemical environments. The combination of effective computational techniques with new laser spectroscopy experiments has generated a wealth of information regarding the intricate details of how the proton interacts with water molecules as well as the structural and dynamic aspects of protonated water clusters $H^+(H_2O)_n$, with $n = 6-27$.[3−5] However, the dynamics resulting from the excess internal energy of the large protonated water clusters $H(H_2O)_n^+$ ($n > 20$) in the gas phase blurs the structural distinction and its spectroscopic manifestations.[6]

Since the lattice of a crystal host could offer an attractive environment to stabilize various topologies of neutral and ionic water clusters, recent studies have been focused on unraveling structural and morphological characteristics of water co-crystallized with various chemical entities, providing quantitative characterization of the hydrogen-bonded networks that exist in

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(1) Rini, M.; Magnes, B. Z.; Pines, E.; Nibbering, E. T. J. *Science* **2003**, *301*, 349–352.
(2) Roscioli, J. R.; McCunn, L. R.; Johnson, M. A. *Science* **2007**, *316*, 249–254.
(3) Zwier, T. S. *Science* **2004**, *304*, 1119–1120.
(4) Miyazaki, M.; Fujii, A.; Ebata, T.; Mikami, N. *Science* **2004**, *304*, 1134–1137.
(5) Singh, N. J.; Park, M.; Min, S. K.; Suh, S. B.; Kim, K. S. *Angew. Chem., Int. Ed.* **2006**, *45*, 3795–3800.
(6) Shin, J. W.; Hammer, N. I.; Diken, E. G.; Johnson, M. A.; Walters, R. S.; Jaeger, T. D.; Duncan, M. A.; Christie, R. A.; Jordan, K. D. *Science* **2004**, *304*, 1137–1140.

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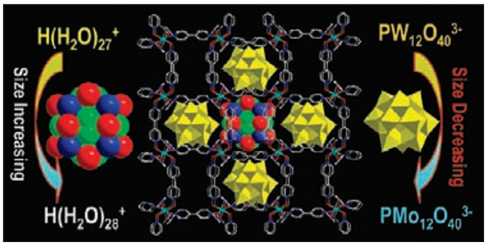

Figure 1. View of the synthetic strategy for control over cationic water clusters through encapsulation in a crystal host by replacing $PW_{12}O_{40}^{3-}$ anion with a slightly smaller $PMo_{12}O_{40}^{3-}$ analogue in a self-assembly process. The wire/stick diagram represents the robust $[Co_4(dpdo)_{12}]_\infty$ framework, the polyhedral diagram represents the 3− charged heteropolyacid anion that occupies three-quarters of the cavities, and the space-filling diagram represents the possible water cluster that occupies a quarter of the cavities of the MOFs, respectively.

aqueous solution.[7−12] These topics continuously generate considerable interest among both theoretical and experimental chemists, and the crystallographic characterization of a neutral polyhedral $(H_2O)_{21}$ cluster has been recently reported by Ye et al.[13] However, the isolation and stabilization of new, discrete protonated water clusters larger than $H^+(H_2O)_{21}$ in a crystal host are still challenging scientific endeavors due to the high mobility of the proton and the relatively weak but complex intermolecular bonding as well as the possible size dependence of clathrate hydrate structures.[3]

For quite a long time, we have been interested in encapsulating ionic hydrated species by synthetic receptors.[14,15] Recently, we explored simple building blocks (4,4′-bipyridine-*N*,*N*′-dioxide (dpdo) and Co^{2+} ions) for the synthesis of a 3D porous network with a cubic symmetry, $[Co_4(dpdo)_{12}][H(H_2O)_{27}(CH_3CN)_{12}][PW_{12}O_{40}]_3$ (compound **1**), with the aid of a large $PW_{12}O_{40}^{3-}$ anion as the template and pillar (the middle of Figure 1).[15] In this crystal host, a large protonated water cluster $H(H_2O)_{27}^+$, in which an unattached hydronium core ion is surrounded by a water shell $(H_2O)_{26}$ and located at the crystallographic center of the host, has been encapsulated. Since this 3D $[Co_4(dpdo)_{12}]_\infty$ framework is structurally robust and flexible to some extent, we assume that if the $[PW_{12}O_{40}]^{3-}$ anion were substituted by a smaller $[PMo_{12}O_{40}]^{3-}$ anion, the framework structure would likely be slightly changed and the size of the pores could be finely tuned. By this approach, the size of protonated water clusters encapsulated in the pores could be increased gradually up to one with the next larger number of waters, as schematically shown in Figure 1, so that the various hydrogen bond networks relative to the proton in the large protonated water clusters could be systematically and quantitatively investigated.

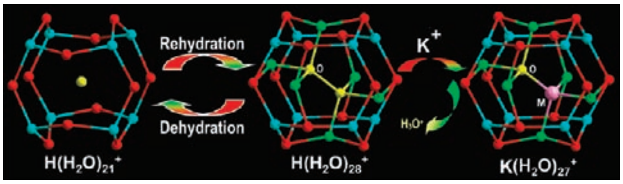

Figure 2. View of the single crystal-to-single crystal reversible dehydration/rehydration between protonated water clusters $H^+(H_2O)_{21}$ and $H^+(H_2O)_{28}$ within the cavity of a MOF as well as the proton/potassium exchange between the crystal host and bulk solution. The red, blue, and cyan balls represent water molecules located at different positions in the protonated water clusters, whereas the yellow and pale balls represent the possible hydronium and potassium ions, respectively.

One of the major issues at stake for a deeper understanding of the structure of solvated proton in water today is whether there are particularly stable structures for the entire protonated water cluster that appear as a function of cluster size. To test the possibility of the existence of stable protonated water clusters within the robust metal−organic frameworks (MOFs), crystal-to-crystal dehydration and rehydration experiments were carried out on these protonated water clusters. By virtue of the robustness of the frameworks, a stable, large protonated water cluster $H^+(H_2O)_{21}$ can be obtained by dehydration of the above-mentioned $H^+(H_2O)_{28}$ cluster, and this newly formed protonated water cluster $H^+(H_2O)_{21}$ can be restored to $H^+(H_2O)_{28}$, completing a reversible process (Figure 2, left) in the cavity of the MOF. The direct observation of two different types of protonated water clusters with unusual stability and their reversible transformation within the same cavity, a unique environment provided by the crystal host, could bring us closer to understanding the structural aspects and dynamic processes in forming proton hydrates.[16,17]

Furthermore, the most important aspect of the aqueous proton is its anomalously high mobility,[18,19] and the concerted proton transfer via the Grotthuss mechanism is a key step in acid−base chemistry.[20,21] Therefore, it is of paramount importance to explore the conditions for the occurrence of the proton transport associated with finite clusters in order to get a clear picture of the chemistry of these protonated water clusters and the relevant bulk aqueous solutions.[22,23] Along this line, cation-driven proton-transfer processes from the protonated water clusters in the crystal host to the bulk aqueous solution were extensively investigated through a well-established fluorometry method.[24,25] Exchange of potassium ions with proton hydrates included in

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(7) Dai, F. N.; He, H. Y.; Sun, D. F. *J. Am. Chem. Soc.* **2008**, *130*, 14064–14065.
(8) Ene, C. D.; Madalan, A. M.; Maxim, C.; Jurca, B.; Avarvari, N.; Andruh, M. *J. Am. Chem. Soc.* **2009**, *131*, 4586–4587.
(9) Xie, Y. S.; Ni, J.; Zheng, F. K.; Cui, Y.; Wang, Q. G.; Ng, S. W.; Zhu, W. H. *Cryst. Growth Des.* **2009**, *9*, 118–126.
(10) Wang, Y.; Okamura, T.-A.; Sun, W. Y.; Ueyama, N. *Cryst. Growth Des.* **2008**, *8*, 802–804.
(11) Rodriguez-Cuamatzi, P.; Vargas-Diaz, G.; Hopfl, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 3041–3044.
(12) Ghosh, S. K.; Bharadwaj, P. K. *Angew. Chem., Int. Ed.* **2004**, *43*, 3577–3580.
(13) Cao, M. L.; Wu, J. J.; Mo, H. J.; Ye, B.-H. *J. Am. Chem. Soc.* **2009**, *131*, 3458–3459.
(14) Zhang, B. G.; Guo, D.; Duan, C. Y.; Cai, P.; Meng, Q. J. *Chem. Commun.* **2003**, 1836–1837.
(15) Wei, M. L.; He, C.; Hua, W. J.; Duan, C. Y.; Li, S. H.; Meng, Q. J. *J. Am. Chem. Soc.* **2006**, *128*, 13318–13319.
(16) Takeya, S.; Ripmeester, J. A. *Angew. Chem., Int. Ed.* **2008**, *47*, 1276–1279.
(17) Mao, W. L.; Mao, H.-K.; Goncharov, A. F.; Struzhkin, V. V.; Guo, Q.; Hu, J.; Shu, J.; Hemley, R. J.; Somayazulu, M.; Zhao, Y. *Science* **2002**, *297*, 2247–2249.
(18) Marx, D.; Tuckerman, M. E.; Hutter, J.; Parrinello, M. *Nature* **1999**, *397*, 601–604.
(19) Headrick, J. M.; Diken, E. G.; Walters, R. S.; Hammer, N. I.; Christie, R. A.; Cui, J.; Myshakin, E. M.; Duncan, M. A.; Johnson, M. A.; Jordan, K. D. *Science* **2005**, *308*, 1765–1769.
(20) Garczarek, F.; Gerwert, K. *Nature* **2006**, *439*, 109–112.
(21) Mohammed, O. F.; Pines, D.; Dreyer, J.; Pines, E.; Nibbering, E. T. J. *Science* **2005**, *310*, 83–86.
(22) Asmis, K. R.; Pivonka, N. L.; Santambrogo, G.; Brümmer, M.; Kaposta, C.; Neumark, D. M.; Wöste, L. *Science* **2003**, *299*, 1375–1377.
(23) Asthagiri, D.; Pratt, L. R.; Kress, J. D. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 6704–6708.
(24) Sakai, N.; Matile, S. *J. Phys. Org. Chem.* **2006**, *19*, 452–460.
(25) Sidorov, V.; Kotch, F. W.; Abdrakhmanova, G.; Mizani, R.; Fettinger, J. C.; Davis, J. T. *J. Am. Chem. Soc.* **2002**, *124*, 2267–2278.

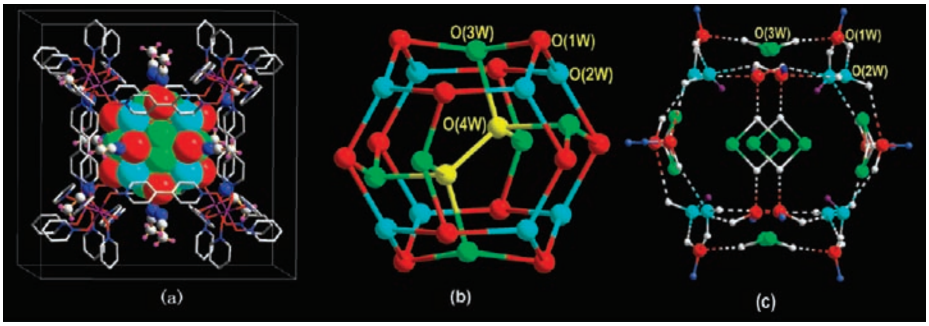

Figure 3. Perspective views of (a) the hydrophilic environment in which the $H^+(H_2O)_{28}$ cluster is located; (b) a $H^+(H_2O)_{28}$ cluster composed of a molecular ice shell $(H_2O)_{26}$ and a dimeric water ion core, with hydrogen atoms omitted for clarity; and (c) the hydrogen-bonding patterns of the $(H_2O)_{26}$ water shell, showing its six identical $(H_2O)_8$ octagonal faces and the statistically distributed water molecules O(3W) within these octagonal faces. The oxygen atoms of water molecules O(1W), O(2W), O(3W), and O(4W) are drawn in red, cyan, green, and yellow, respectively. The small balls represent the hydrogen atoms of water molecules, which are involved in hydrogen bonds with the $(H_2O)_{26}$ framework (white) and hydrogen bonds with acetonitrile molecules (dark blue), as well as those dangling inside the shell (pink).

the protonated water clusters results in the formation of a unique $K^+(H_2O)_{27}$ water cluster, providing an opportunity to structurally characterize large ionic water clusters (Figure 2, right).[26−29]

Results and Discussions

Structural Characterization of Large Protonated Water Cluster $H^+(H_2O)_{28}$. Reaction of $CoHPMo_{12}O_{40}$ with dpdo in acetonitrile/water solution gave a new compound, $\{[Co(dpdo)_3]_4(PMo_{12}O_{40})_3[H(H_2O)_{28}(CH_3CN)_{12}]\}_n$ (**2**). X-ray crystallographic study reveals that compound **2** is composed of a non-interwoven 3D framework with cubic cavities and guest molecules. Each Co(II) ion is coordinated by six identical dpdo ligands, forming an ideal octahedral coordination geometry, while each dpdo ligand bridges two identical Co(II) centers alternatively to form the 3D framework. Although the Co···Co separations in all directions are 11.62 Å, half of an axial length, the windows of the cubic cavities seem to be rectangular since the N(dpdo)−O(dpdo)−Co(II) angles are not right angles but ca. 120°. The Keggin structure $PMo_{12}O_{40}^{3-}$ anions, with a diameter of about 10.4 Å, fit the cubic cavities very well, avoiding potential interpenetrations of the framework. Since the template anion $PMO_{12}O_{40}^{3-}$ is typically trivalent and the corresponding $Co(II)(dpdo)_3$ unit of a cubic cavity is positive divalent, only some of the cavities would be filled by the anions as charge compensation. As evidenced by X-ray analysis, three-quarters of the cavities are occupied by $PMo_{12}O_{40}^{3-}$ anions, and another quarter of the cavities are filled with large water clusters. Under the current synthetic and crystallization conditions, protonation on the surface of a Keggin structure $PM_{O12}O_{40}^{3-}$ anion is unlikely,[30,31] and the most likely scenario is that the water cluster is protonated to maintain electrical neutrality throughout the crystal. Around each water cluster, eight Co^{2+} ions are situated at the vertexes of the cubic cavity, and six identical $PMo_{12}O_{40}^{3-}$ anions sit in six neighboring cavities. These ionic species together form a specific pseudo-spherical static field, which not only is an ideal environment for stabilizing ionic water clusters but also repels the excess proton toward the center of the water cluster rather than keeping it located on the surface. Along with those moves, it is also found that there are weak C−H(acetonitrile)···$O(PMo_{12}O_{40}^{3-})$ hydrogen bonds with a C···O separation of 3.202(5) Å between the acetonitrile molecule and polyanion and strong O−H(water cluster)···N(acetonitrile) hydrogen bonds with a N···O separation of 2.877(4) Å and N···H−O angle of 147(4)° between the water cluster and acetonitrile molecule. Consequently, these acetonitrile molecules form an amphiphilic global shield layer with their hydrophobic methyl groups pointing toward the outer polyanions and the hydrophilic C≡N ends directing toward the center of the cavity, providing a hydrophilic environment that is beneficial to the molecular recognition and stabilization of specific water clusters.

Each protonated water cluster in the cavity of compound **2** comprises a $(H_2O)_{26}$ water shell acting as a "sub-host" and a dimeric protonated water ion core as a "guest" (Figure 3b). Eight water molecules O(2W) and another 12 water molecules O(1W) are linked together, forming a $(H_2O)_{20}$ hexahedron with each of its faces depicted as an octagonal water ring $(H_2O)_8$. Twelve hydrogen atoms H(1WB) and 12 hydrogen atoms H(2WB) situate at the 24 identical edges of the hexahedral $(H_2O)_{20}$, respectively, forming O(1W)−H···O(2W) or O(1W)···H−O(2W) hydrogen bonds[32] with O···O separations of about 2.84 Å. The residual space of the cavity is filled by an additional six water molecules O(3W) that embed in the six faces of the $(H_2O)_{20}$ hexahedral shell, respectively, by forming two identical O(1W)···H−O(3W) hydrogen bonds with hydrogen atoms H(3WA). In the faces of the water cage, the chairlike hexagonal ring O(1W)−O(2W)−O(1W)−O(3W)−O(1W)−O(2W) is quite similar to that in cubic ice, I_c, which has been reported as a building block in many forms of ice and relevant liquid.[33,34] Notably, such a special structure could be derived from the pentagonal dodecahedral water cluster, one of the most stable

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(26) Hashimoto, K. H.; Morokuma, K. *J. Am. Chem. Soc.* **1994**, *116*, 11436–11443.

(27) Barnett, R. N.; Landman, U. *Phys. Rev. Lett.* **1993**, *70*, 1775–1778.

(28) Bush, M. F.; Saykally, R. J.; Willams, E. R. *J. Am. Chem. Soc.* **2008**, *130*, 15482–15489.

(29) Hertel, I. V.; Hüglin, C.; Nitsch, C.; Scgulz, C. P. *Phys. Rev. Lett.* **1991**, *67*, 1767–1770.

(30) Kanda, Y.; Lee, K. Y.; Nakata, S.; Asaoka, S.; Misono, M. *Chem. Lett.* **1988**, 139–142.

(31) Yang, J.; Janik, M. J.; Ma, D.; Zheng, A.; Zhang, M.; Neurock, M.; Davis, R. J.; Ye, C.; Deng, F. *J. Am. Chem. Soc.* **2005**, *127*, 18274–18280.

(32) Due to the space group in which the lattices of compound **2** crystallized, the 24O(1W)···O(2W) interactions are identical. The hydrogen atom H(2WB) attached to water molecule O(2W) and the hydrogen atom H(1WA) attached to water molecule O(1W) are refined to be partly occupied, each O(1W)···O(2W) hydrogen bond having the SOF fixed at 0.5. In this case, the O(1W)···O(2W) hydrogen bond can be either O(1W)−H···O(2W) or O(1W)···H−O(2W) type.

(33) Mishima, O.; Stanley, H. E. *Nature* **1998**, *396*, 329–335.

(34) Loubeyre, P.; LeToullec, R.; Wolanin, E.; Hanfland, M.; Hausermann, D. *Nature* **1999**, *397*, 503–506.

water clusters previously reported,[35,36] in which each O···O hydrogen bond of the pentagonal rings is broken by inserting a disordered water molecule O(3W) with the volume of the whole water shell expanded. As a consequence, the pentagonal ring is transformed into a hexagonal ring, the most common building block of ice[37] and bulk water.[38] The $(H_2O)_{26}$ shell formed, with O_h symmetry, is also of particular interest as it could be used as a model for simulating water···water interactions and/or the physical properties of water in both the condensed phase (such as bulk water and ice) and the gas phase (such as small isolated water clusters).

The 28-mer protonated water cluster has been reported as the second smallest water cluster $H^+(H_2O)_n$ that exhibits clear intensity enhancement in the mass spectrum.[39−42] Nagashima et al.[40] conducted one of the earliest Monte Carlo simulations for $H^+(H_2O)_{28}$ based on the model developed by Matsuoka et al.[43] for H_2O-H_2O interactions and the potential function given by Buffey and Brown[44] for $H_3O^+-H_2O$ interactions. Their calculations showed that a pentakaidecahedral $5^{12}6^3$ cage enclosing a protonated water dimer $H_3O^+-H_2O$ is exceptionally stable, in accord with the experimentally observed intensity anomaly at $n = 28$. The $5^{12}6^3$ cage is prolate-like, composed of 26 water molecules, and known to exist in condensed phases as water hydrates.[45] The separation between the two oxygen vertexes along the long axis of the cage is about 1 nm, allowing the cavity to hold two water molecules comfortably.[46] Such a structure of the 28-mer protonated water cluster would help us to determine the detailed structure of $H^+(H_2O)_{28}$ we obtained in the condensed phase, since our 6^{12} cage has a size similar to that of the $5^{12}6^3$ cage in the theoretical model. The 12 O(water)−H bonds dangling around the cluster and interacting with 12 acetonitrile molecules seem to resemble the 12 dangling OH bonds carried by $H_3O^+-H_2O@(H_2O)_{26}$ in Nagashima's model, rather than the 11 OH bonds of the $H_2O-H_2O@H^+(H_2O)_{26}$ postulated in the recent theoretical investigations.[47]

Due to the space group in which the compound crystallized, the oxygen atoms of water molecules (or hydronium ions) in the center core could be statistically distributed in eight identical positions that match up with the eight vertexes of an ideal cube (not shown). The edge length of this cube is about 1.50 Å, and its face diagonal is about 2.12 Å in length, both shorter than 2.29 Å, the limit for intermolecular O···O interactions.[48] In this case, the most likely distribution of the two water molecules is on the ends of each body diagonal of the cube statistically with an O(4W)···O(4W) distance of 2.60 Å. The electronic residue at the crystallographic center is refined as one hydrogen atom[49] in consideration of the above-mentioned specific pseudo-spherical static field around the water cluster. The other hydrogen atoms associated with the dimeric center core are also found to be involved in the hydrogen bonds linking the center core with the outer water shell $(H_2O)_{26}$.

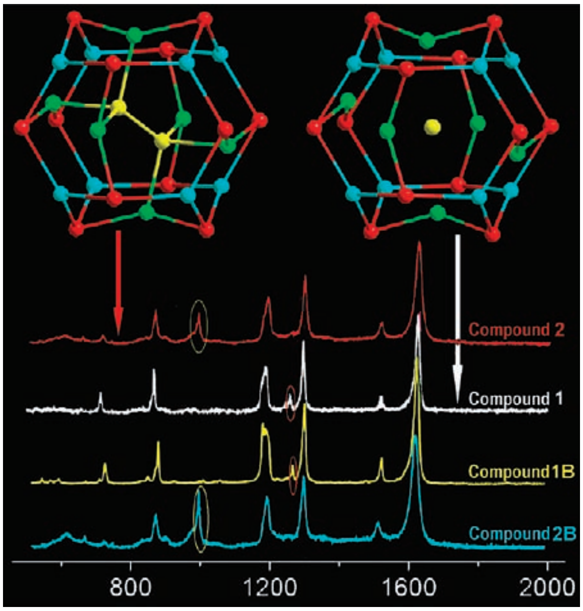

Figure 4. Single-crystal laser Raman spectra of compounds **1** and **2**, as well as compounds **1B** and **2B** obtained from compounds **1** and **2**, respectively, through a dehydration/rehydration procedure (vide infra) in the range of 500−2000 cm^{-1} at 293 K, excited with the 488 nm line laser.

By comparison, the smaller congener $H^+(H_2O)_{27}$ of compound **1** contains almost the same $(H_2O)_{26}$ water shell as in compound **2** but a different center core, namely a single oxygen species, with the shortest O···O separation related to the center core being 3.57 Å. Considering the most rational distribution of charges in the solid-state structure of **1** with cubic symmetry, it is suggested that the excess proton might be positioned in the center and occur in the context of the H_3O^+ (Eigen) form of a hydronium ion.[50] A conformation calculation at the B3LYP/6-31g** level with the positions of oxygen atoms fixed suggests that the excess proton resides inside the clathrate structure. The two structurally different protonated water clusters obtained, with neighboring numbers, i.e., $H^+(H_2O)_{28}$ and $H^+(H_2O)_{27}$, offer us a great opportunity to observe the essential variation of the structural features pertaining to clathrate hydrates and their formation, which is one of the major issues related to understanding the proton in water.[3] By further comparison of the structures of compounds **1** and **2**, it is found that the Co−O bond distances and the O−Co−O and Co−O−N bond angles of compounds **2** are 2.057(3) Å, 90.2(1)°, and 118.3(1)°,

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(35) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: New York, 1997; Chapters 8 and 9.

(36) Ripmeester, J. A.; Tse, J. S.; Rarcliffe, C. I.; Powell, B. M. *Nature (London)* **1987**, *325*, 135–136.

(37) Fletcher, N. H. *The Chemical Physics of Ice*; Cambridge University Press: Cambridge, UK, 1970.

(38) Eisenberg, D.; Kauzmann, W. *The Structure and Properties of Water*; Oxford University Press: New York, 1969.

(39) Echt, O.; Kreisle, D.; Knapp, M.; Recknagel, E. *Chem. Phys. Lett.* **1984**, *108*, 401–407.

(40) Nagashima, U.; Shinohara, H.; Nishi, N.; Tanaka, H. *J. Chem. Phys.* **1986**, *84*, 209–214.

(41) Schindler, T.; Berg, C.; Niedner-Schatteburg, G.; Bondybey, V. E. *Chem. Phys. Lett.* **1996**, *250*, 301–308.

(42) Lee, S. W.; Freivogel, P.; Schindler, T.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1998**, *120*, 11758–11765.

(43) Matsuoka, O.; Clementi, E.; Yoshimine, M. *J. Chem. Phys.* **1976**, *64*, 1351–1361.

(44) Buffey, I. P.; Brown, W. B. *Chem. Phys. Lett.* **1984**, *109*, 59–65.

(45) Sloan, E. D. *Nature* **2003**, *426*, 353–363.

(46) Khan, A. *Chem. Phys. Lett.* **1996**, *258*, 574–580.

(47) Wu, C.-C.; Lin, C.-K.; Chang, H.-C.; Jiang, J.-C.; Kuo, J.-L.; Kllein, M. L. *J. Chem. Phys.* **2005**, *122*, 074315.

(48) Day, V. W.; Hossain, M. A.; Kang, S. O.; Powell, D.; Lushington, G.; Bowman-James, K. *J. Am. Chem. Soc.* **2007**, *129*, 8692–8693.

(49) The presence of electron residue at the crystallographic body center in a cubic crystal system is not a guarantee that the excess proton is situated at the special position. It might also be caused by an average of the identical positions of these disordered species near the body center, such as the excess proton of the disordered hydrate hrdronium $H_3O^+\cdot H_2O$, or it might come from crystallographic noise.

(50) Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1–19.

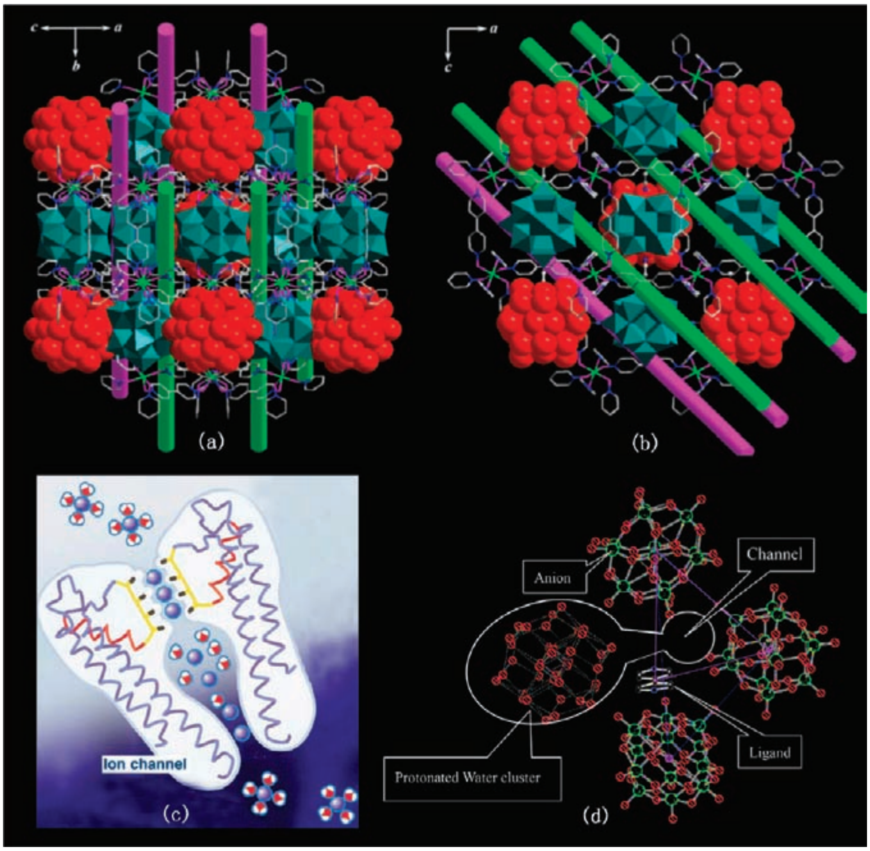

Figure 5. Packing diagrams of **2** showing the potential ionic channels: view along the (1,0,1) and (0,1,0) directions (a) and (b), respectively. (c) Simple representation of the KcsA K^+ channel with its ion conduction pore dilated to about 10 Å in diameter to keep the K^+ ions in a watery, high-dielectric environment (reprinted with permission from ref 70). (d) Perspective view of a channel constrained by the polyoxomolybdate anions and the dpdo ligands as well as the protonated water cluster.

respectively, similar to those observed in the crystal structure of compound **1**, i.e., 2.043(3) Å, 90.6(1)°, and 119.2(1)°, respectively. Additionally, the separation between the center of the protonated water cluster $H^+(H_2O)_{28}$ and the oxygen atoms (O1W) in the outer water shell $(H_2O)_{20}$ is about 4.58 Å, slightly larger than in $H^+(H_2O)_{27}$ (4.50 Å). These results demonstrate that subtle variation of the structures of these MOFs could lead to significant structural differences in the protonated water clusters that settle in their cavities. The ability to selectively obtain these two protonated water clusters with different structures by finely tuning the pore sizes of MOFs provides an opportunity to quantitatively and systematically explore some biologically important issues related to the water clusters.

Single-crystal laser Raman spectra of compounds **1** and **2** and related compounds at room temperature were recorded to identify the protonated water species described above. The spectra of **1** and **2** both exhibit one strong absorption band at about 1185 cm^{-1} that arises from the anions[51] and two strong absorption bands at 1295 and 1625 cm^{-1} ascribable to the dpdo ligands,[52] respectively, consistent with the similarity of their crystal hosts (Figure 4). The most noticeable feature might be the appearance of a new band at about 980 cm^{-1} in the spectrum of compound **2** but not in that of compound **1**, which contains the $H^+(H_2O)_{27}$ species,[52] suggesting the existence of new hydrogen-bonding patterns in the $H^+(H_2O)_{28}$ cluster of compound **2**, even though further quantitative analysis is still needed for precise assignment of the remaining bands. Since the $H^+(H_2O)_{27}$ and $H^+(H_2O)_{28}$ clusters that appear in the two compounds, respectively, have almost the same $(H_2O)_{26}$ shell structure and there are no water•••hydronium interactions in the $H^+(H_2O)_{27}$ cluster as discussed above, the new type of hydrogen bond in the $H^+(H_2O)_{28}$ cluster likely pertains to the water•••hydronium interactions within the center core or between the ionic center core and the $(H_2O)_{26}$ shell.[53]

Detailed structural analysis of compound **2** shows that it contains potential ionic channels passing through the frameworks and surrounded by the water clusters and heteropolyacid anions. As shown in Figure 5, each channel is perpendicular to and passes through a right triangle defined by three identical anions in a (1,1,1) plane, together with a dpdo ligand that compresses the channel down to 3.3 Å in radius. On this plane, an ionic water cluster sits by the triangle, forming a square with these three anions. These unique structural features of compound **2**, i.e., the high-dielectric conduction pores with their radii up to about 10 Å and the long channels with their radii of about 3.3 Å, are reminiscent of the central cavity and selective filter in the K^+ channel, such as the KcsA K^+ channel.[54,55] It is likely that these channels only admit passage of some small species, such as K^+ ions, hydronium ions, or water molecules.

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(51) Thouvenot, R.; Fournier, M.; Franck, R.; Rocchiccioli-Deltcheff, C. *Inorg. Chem.* **1984**, *23*, 598–605.

(52) Wei, M. L.; He, C.; Sun, Q. Z.; Meng, Q. J.; Duan, C. Y. *Inorg. Chem.* **2007**, *46*, 5957–5966.

(53) Bates, J. B.; Toth, L. M. *J. Chem. Phys.* **1974**, *61*, 129–137.

(54) Berneche, S.; Roux, B. *Nature* **2001**, *414*, 73–77.

(55) Valiyaveetil, F. I.; Leonetti, M.; Muir, T. W.; Mackinnon, R. *Science* **2006**, *314*, 1004–1007.

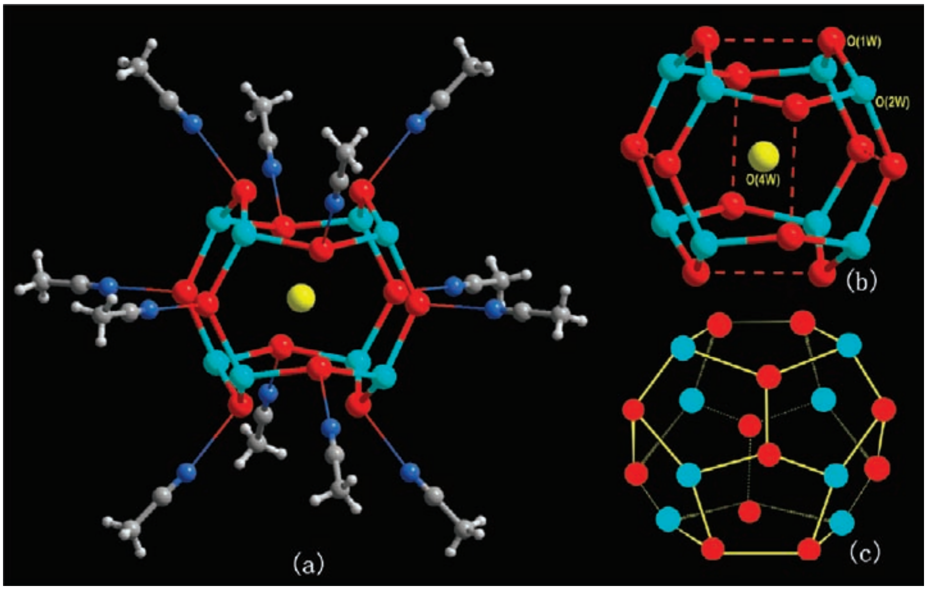

Figure 6. (a) Perspective view of a [$H^+(H_2O)_{21}(CH_3CN)_{12}$] cluster, showing the water shell $(H_2O)_{20}$. (b) Skeleton structure of the $H^+(H_2O)_{21}$ cluster formed by water molecules represented by O(1W) (red) and O(2W) (blue) and the center core by O(4W) (yellow). (c) Sketch map showing the hydrogen bonds in the ideal pentagonal dodecahedron shell composed of two different types of water molecules.

$H^+(H_2O)_{27}$↔ $H^+(H_2O)_{21}$ and $H^+(H_2O)_{28}$ ↔ $H^+(H_2O)_{21}$ Transformations. We also tried to thermally degrade the large protonated water clusters $H^+(H_2O)_{27}$ and $H^+(H_2O)_{28}$ in order to observe any possible structural consequence so that more useful structural information regarding these water clusters and their formations might be acquired. Thermal analyses of compounds **1** and **2** reveal small but significant weight losses in the temperature range 25−100 °C, concomitant with smooth endothermic curves. The weight losses of these two compounds are about 5% at 200 °C and less than 10% even after heating to 300 °C, and even when the samples were heated at 373 K under vacuum for 2 h, the crystallinity of compounds **1** and **2** was maintained. The crystalline compounds obtained from compounds **1** and **2** by heating are named as new compounds **1A** and **2A**, respectively. The identical space groups and nearly identical unit-cell dimensions between the original compounds and their dehydrated forms (i.e., **1** and **1A**, **2** and **2A**, respectively) indicate that the porous 3D frameworks and the main backbone of the protonated water cluster are retained. X-ray structural analyses of both compounds **1A** and **2A** exhibit identical protonated water clusters $H(H_2O)_{21}{}^+$, as shown in Figure 6. By comparing the structures of $H(H_2O)_{28}{}^+$ and $H(H_2O)_{27}{}^+$ clusters with that of $H(H_2O)_{21}{}^+$, it is found that, in the backbone of the $(H_2O)_{26}$ water shells, six water molecules (represented by O(3W) in Figure 3) initially in $H(H_2O)_{28}{}^+$ and $H(H_2O)_{27}{}^+$ clusters were removed upon dehydration. In the case of $H(H_2O)_{28}{}^+$, one of the two water molecules in the center core of $H(H_2O)_2{}^+$ was also lost, leaving a mono water molecule species $(H_3O)^+$ situated at the crystallographic center, which is evidenced by the absence of the band at 980 cm^{-1} in the single-crystal laser Raman spectra of compound **2A**.

Each of the resulting $H(H_2O)_{21}{}^+$ protonated water clusters has a hexahedral $(H_2O)_{20}$ shell, with each of its faces making an octagonal water ring as $(H_2O)_8$. The O(1W)···O(2W) separations in the hexahedral $(H_2O)_{20}$ shell of the $H(H_2O)_{21}{}^+$ cluster are revealed to be the same as those of the $H(H_2O)_{27}{}^+$ and $H(H_2O)_{28}{}^+$ clusters, respectively. It is also found that the shortest O···O separation between the water molecules in the center core and that in the water shell is ca. 4.04 Å, which is much longer than normal O···O hydrogen bonds, suggesting an isolated center core in the interior of the cluster. The excess proton should be localized on the water molecule at the center, forming an unattached hydronium ion as a center core, since only ionic species could be confined individually at the crystallographic center of the cluster by the strong and specific pseudo-spherical static field applied by the MOFs. Otherwise, a neutral water molecule was hardly isolated at the center, and it would be deviated from the center to the water shell via hydrogen bonds. Interestingly, the acetonitrile molecules surrounding the protonated water clusters in the cavities were not removed at all under the dehydration conditions, probably due to the relatively small diameters of the channels that selectively allow smaller species to pass through but not acetonitrile molecules. Last, these acetonitrile molecules seem to serve as linkers to connect the large polyoxotungstate or polyoxomolybdate anions with the water clusters.

It should be noted that the $H^+(H_2O)_{21}$ cluster, one of the most curious $H^+(H_2O)_n$ clusters to exist in the gas phase, was first reported by Searcy and Fenn[56] in 1974 as the discontinuity in the cluster ion intensity distribution or “magic number” at $n = 21$. There has been much speculation about the structure of the magic number cluster since water clathrates are known to trap methane and other gases in water cages composed of water dodecahedrons.[5,57] Searcy and Fenn suggested that the $H^+(H_2O)_{21}$ in the gas phase was derived from the pentagonal dodecahedron motif with one water molecule in the cage and a H_3O^+ ion on the surface. Though the structure of $H^+(H_2O)_{21}$ cluster we obtained is quite different from Searcy and Fenn’s model, the hexahedral $(H_2O)_{20}$ shell (Figure 6b) in our $H^+(H_2O)_{21}$ cluster could be thought of as being derived from the well-known pentagonal dodecahedron $(H_2O)_{20}$ (Figure 6c), with some of O···O hydrogen bonds in the pentagonal rings[35,36]

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(56) Searcy, J. Q.; Fenn, J. B. *J. Chem. Phys.* **1974**, *61*, 5282–5288.

(57) Davidson, D. W. In *Water: A Comprehensive Treatise*; Franks, F., Ed.; Plenum: New York, 1973, Vol. 2, pp 115−234.

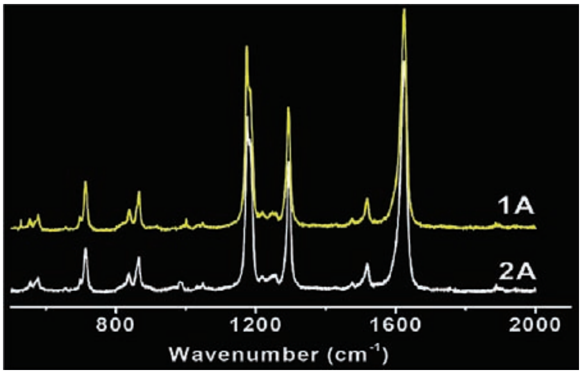

Figure 7. Single-crystal laser Raman spectra of compounds **1A** and **2A** in the range of 100−2000 cm^{-1} at 293 K. Those bands assigned to the H_3O^+ ion are indicated by arrows.

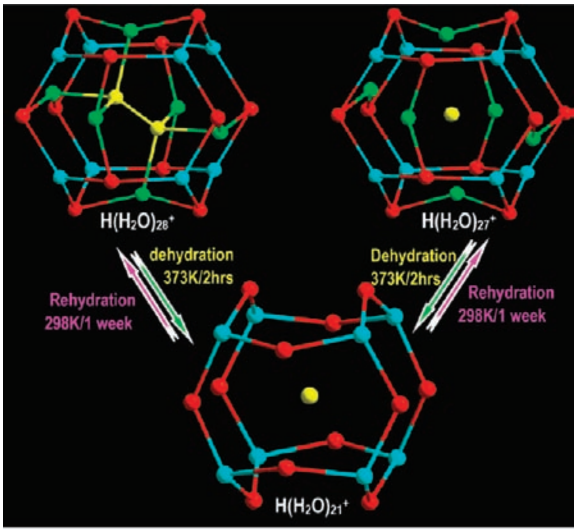

Figure 8. Thermodynamic transformations between $H(H_2O)_{28}{}^+/H(H_2O)_{27}{}^+$ and $H(H_2O)_{21}{}^+$ clusters with the center cores being changed from a hydrogen-bonded dimeric species in $H(H_2O)_{28}{}^+$ or a hydrogen-bonded mononuclear species in $H(H_2O)_{27}{}^+$ into an isolated mononuclear species. The different types of oxygen atoms of water molecules O(1W), O(2W), O(3W) and the center core one O(4W) are shown in red, cyan, green, and yellow, respectively.

being broken and the volume of the water shell being enlarged to adapt to the cavities of the 3D frameworks. For that, insertion of a water molecule into the edge (the O···O hydrogen bond) shared by two pentagonal rings would immediately lead to the formation of two hexagonal water rings. The $(H_2O)_{20}$ polyhedron in the $H^+(H_2O)_{21}$ cluster we obtained could be described as an intermediate, the faces of which are being changed between a hexagonal ring (the most common building block of ice and bulk water) and a pentagonal ring (the interesting unit of small isolated water clusters in the gas phase).

To investigate the reversibility of the transformations between the protonated water clusters ($H^+(H_2O)_{21}/H^+(H_2O)_{27}$, $H^+(H_2O)_{21}/H^+(H_2O)_{28}$), crystals of compounds **1A** and **2A** were kept in air for about a week and two new crystalline compounds, **1B** and **2B**, were obtained, respectively. Surprisingly, single-crystal X-ray analyses of compounds **1B** and **2B** clearly reveal that, in both compounds, the $H^+(H_2O)_{27}$ and $H^+(H_2O)_{28}$ clusters were respectively re-formed from the small protonated water clusters $H^+(H_2O)_{21}$ in compounds **1A** and **2A** as shown in Figure 8, which is also supported by the single-crystal Raman spectra of compounds **1B** and **2B** as well as the relevant compounds. As can be seen from Figure 4, the laser Raman spectrum of compound **1B** exhibits two bands at 1522 and 1260 cm^{-1}, assigned to the degenerate bending fundamentals υ_4 and υ_2 of the hydronium ion, which are also observed in the spectrum of compound **1**, indicative of the re-formation of the $H^+(H_2O)_{27}$ cluster. The single-crystal laser Raman spectrum of compound **2B** exhibits a band at about 980 cm^{-1} that does not appear in the spectra of compounds **1** and **1B**, probably pertaining to the water···hydronium interactions described for compound **2**. It is very likely that the structures of the water clusters in both compounds **2B** and **2** are identical.

The completely reversible dehydration/rehydration processes (i.e., $H^+(H_2O)_{21} \leftrightarrow H^+(H_2O)_{27}$ and $H^+(H_2O)_{21} \leftrightarrow H^+(H_2O)_{28}$) reveal that the various structural fashions, especially the different hydrogen-bonding patterns, of $H^+(H_2O)_{28}$ and $H^+(H_2O)_{27}$ are intrinsic and vary with the subtly different environments (cavities provided by the porous MOFs). It is clear that the sizes of water clusters can be finely tuned through modulating the robust crystalline MOFs, and this synthetic approach offers a distinct opportunity for systematically investigating protonated water clusters in condensed phases. Although these MOF-trapped species are actually different from the predicted protonated/ionic water clusters in the gas phase,[33] the direct observation of large ionic water clusters within porous MOFs and the reversible single crystal-to-single crystal dehydration/rehydration processes illustrate the unusual stability of the clusters $H^+(H_2O)_{28}$, $H^+(H_2O)_{27}$, and $H^+(H_2O)_{21}$ in the unique environments of the synthetic crystal hosts. This approach could be developed into a general method for acquiring X-ray pictures of the elusive protonated water clusters in the condensed phase, which will provide valuable direct mechanistic insights into aqueous proton chemistry not obtainable by other means.[16,17]

Proton/Ion Exchange between Ionic Water Clusters. The robust crystallinity of MOFs not only traps the usually non-isolatable water clusters but also facilitates their X-ray analysis, giving us a great opportunity to explore the proton transfer associated with these finite water clusters. Studies on proton transport from the protonated water clusters in the crystal hosts to the bulk aqueous solution were conducted by fluorometry using the standard protocol described previously.[24,25] Crystals of compound **2** (10 mg) were added into a water/acetonitrile (9:1) solution containing a pH-sensitive dye, 8-hydroxypyrene-1,3,6-trisulfonate (HPTS) (10 μM). The pH value of the solution was adjusted to about 7.4 by adding a Bu_4NOH solution, creating a pH gradient so that the protons included in the crystals could be driven out to the solution. Upon addition of KCl (0.1 M) or NaCl (0.1 M) to the above solution, the luminescence centered at 525 nm (excited at 460 nm) of the aqueous solution was quenched immediately, indicating a decrease of the pH value of the solution due to the increase of protons in the solution. This observation demonstrates that the protons were released from the crystals and, consequently, alkali metal ions in the solution entered into the crystals as charge compensators. Further fluorescence assays reveal a high ion transport mobility of compound **2**, with the first-order transport rate constant calculated to be 2.2×10^{-3} s^{-1} with the use of NaCl (0.1 M) (Figure 9). It is also revealed that the channels of compound **2** are able to discriminate between various monovalent cations. For example, when KCl was exploited, the transport rate constant of **2** shows a ca. 4.5-fold drop to 5.0×10^{-4} s^{-1}, whereas the addition of CsCl and tetrabutylammonium chloride

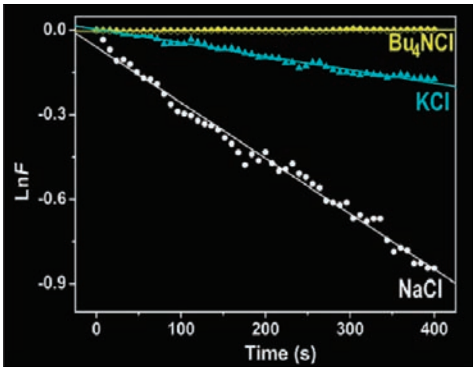

Figure 9. Time-dependent fluorescence plots of HPTS (10 μM) in water/acetonitrile (9:1) mixed solutions (pH = 7.4 ± 0.2) containing crystals of **2**, using 0.1 M Bu_4NCl (yellow diamonds), 0.1 M KCl (blue triangles), and 0.1 M NaCl (white circles), respectively (where F is equal to I_{460}/I_{403} and normalized; I_{460} and I_{403} are the emission intensities centered at 510 nm under 460 and 403 nm excitations, respectively).

into the solution did not cause any obvious luminescent change. In contrast, when the exact same experimental procedure was applied to the crystals of compound **1**, no significant luminescence changes of the aqueous solutions were measured in the presence of either KCl or NaCl, even at a higher concentration (0.5 M). X-ray luminescence spectra of the exchanged and well-cleaned crystalline solids from compound **2** exhibit typical K_α bands that arise from potassium or sodium atoms, unambiguously confirming the occurrence of proton/ion exchange in compound **2**. Without surprise, there are no significant peaks relative to K_α bands observed in X-ray luminescence spectra of the exchanged crystals from compound **1**. By comparison of the structures of compounds **1** and **2**, it was found that the most important difference between them is in the center cores of the protonated water clusters, despite their very similar structural features of the long ionic channels and $(H_2O)_{26}$ shells. Therefore, inhibition of proton transport in the case of compound **1** is likely ascribed to the "isolated" character of hydronium ion in the $H(H_2O)_{27}^+$ cluster; in contrast, the abundance of hydrogen bonds associated with the center ion core of the $H(H_2O)_{28}^+$ cluster seems essential for efficient proton transport in compound **2**, potentially through the Grotthuss mechanism.[58]

Though the concerted proton-transfer process under the Grotthuss mechanism has recently been studied in bulk solution by time-resolved spectroscopy[21] and ab initio molecular dynamics simulations,[18,23,59] there is no direct structural evidence of the proton-transfer mechanism associated with the large water clusters and bulk solution reported yet, due to the difficulties of finding suitable model compounds possessing appropriate hosts to trap large protonated water clusters as well as ion channels for the ingress and egress of protons. Over the years, while extensive efforts toward synthetic ion channels and pores have been made in the biochemical community based on organic molecules such as crown ethers, cyclic peptides, and rigid-rod β-barrels,[60−62] metal−organic scaffolds are definitely emerging as attractive architectures toward this purpose.[63−66] In terms of the structural features and the functions addressed here, our porous framework could be considered as a Werner-type synthetic non-peptide ion channel and may have applications in areas such as the detection and separation of ions and small molecules as well as catalysis owing to its easy synthesis, rigid structure, and adjustable porous sizes and chemical environments.

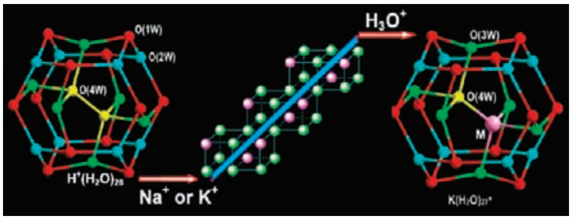

Figure 10. Scheme of the cation-driven proton transport through the channels from the protonated water cluster to the aqueous solution resulting in the replacement of the hydronium ion by an alkali cation. The oxygen atoms of water molecules O(1W), O(2W), O(3W) and the center core O(4W) as well as metal ions M are drawn in red, cyan, green, yellow, and pink, respectively.

The above-proposed exchange reaction has also been verified by the identification of a new potassium ion-containing compound, **3**, obtained either from a potassium/proton exchange upon compound **2** or an independent synthetic procedure. In this new compound, the 3D porous frameworks and the $(H_2O)_{26}$ water shells in compound **2** were well maintained except that the $H(H_2O)_{28}^+$ was substituted by a new ionic water cluster, $K(H_2O)_{27}^+$ (Figure 10, right). Generally speaking, a restricted cavity can be filled with an ion surrounded by the maximum of water molecules, the first hydrated shell, which largely depends on the size of the ion and the second hydrated shell confined by the cavity.[54,55] A K^+ ion is not able to form hydrogen bonds with water molecules, but it can be coordinated by water molecules. Since the hydration energy of K^+ (322 kJ/mol) is several times higher than the energy of hydrogen bonding between water molecules, the K^+ ion tends to locate in the interior of the water cluster so as to form K−O(water) coordination bonds as much as possible. Borrowing the off-centered structures of the ionic water clusters predicted by computational investigations, especially for the case of $Cs(H_2O)_{27}^+$[67] consisting of a H_2O-Cs^+ ion center core and a $(H_2O)_{26}$ water shell, the potassium ion water cluster in compound **3** was determined as a clathrate structure made up of a water shell $(H_2O)_{26}$ and a H_2O-K^+ ionic center core by X-ray diffractions and relevant spectroscopic studies shown above. The K^+ ion in the $K^+(H_2O)_{27}$ cluster is coordinated by three kinds of water molecules [O(3W), O(4W), and O(2W)], and the K(1)···O separations range from 2.67 to 2.80 Å, falling within the range of 2.58−2.92 Å for the K−O bond distances in the primary hydration shells of clusters $K^+(H_2O)_n$ with $n = 1-8$.[68] The K···O separations observed in the $K^+(H_2O)_{27}$ cluster are also similar to those found in the KcsA K^+ channel (2.70−3.08

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(58) Agmon, N. *Chem. Phys. Lett.* **1995**, *244*, 456–462.
(59) Tuckerman, M.; Laasonen, K.; Sprik, M.; Parrinello, M. *J. Chem. Phys.* **1995**, *103*, 150–161.
(60) Fyles, T. M. *Chem. Soc. Rev.* **2007**, *36*, 335–347.
(61) Davis, A. P.; Sheppard, D. N.; Smith, B. D. *Chem. Soc. Rev.* **2007**, *36*, 348–357.
(62) Litvinchuk, S.; Tanaka, H.; Miyatake, T.; Pasini, D.; Tanaka, T.; Bollot, G.; Mareda, J.; Matile, S. *Nat. Mater.* **2007**, *6*, 576–580.
(63) Fyles, T. M.; Tong, C. *New J. Chem.* **2007**, *31*, 655–661.
(64) Jung, M.; Kim, H.; Baek, K.; Kim, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 5755–5757.
(65) Jin, P.; Dalgarno, S. J.; Barnes, C.; Teat, S. J.; Atwood, J. L. *J. Am. Chem. Soc.* **2008**, *130*, 17262–17262.
(66) Sakai, N.; Matile, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 9603–9607.
(67) Selinger, A., Jr.; Castleman, A. W. *J. Phys. Chem.* **1991**, *95*, 8442–8444.
(68) Lee, H. M.; Kim, J.; Lee, S.; Mhin, B. J.; Kim, K. S. *J. Chem. Phys.* **1999**, *111*, 3995–4004.

Table 1. Crystallographic Data for Compounds **2**, **3**, **1A**, and **2A**

	2	**3**	**1A**	**2A**
empirical formula	$C_{144}H_{189}Co_4Mo_{36}N_{36}O_{172}P_3$	$C_{144}H_{186}Co_4KMo_{36}N_{36}O_{171}P_3$	$C_{144}H_{175}Co_4N_{36}O_{165}P_3W_{36}$	$C_{144}H_{175}Co_4Mo_{36}N_{36}O_{165}P_3$
formula weight	8958.78	8978.86	11997.43	8832.67
T/K	123	123	123	123
crystal system	cubic	cubic	cubic	cubic
space group	$Im\bar{3}$	$Im\bar{3}$	$Im\bar{3}$	$Im\bar{3}$
a/Å	23.229(1)	23.170(1)	23.160(1)	23.1496(7)
V/Å^3	12534(1)	12439(1)	12423(1)	12406.0(6)
Z	2	2	2	2
D_c/g·cm^{-3}	2.374	2.397	3.202	2.353
μ/mm^{-1}	2.128	2.160	16.979	2.145
reflns collected	136 700	38 718	37 856	37 752
unique reflns	2224	2745	2558	2558
R(int)	0.0425	0.0902	0.1068	0.0912
F(000)	8692	8708	10836	8466
$R_1(I > 2\sigma)$	0.0287	0.0497	0.0516	0.0444
wR_2(all data)	0.0669	0.0753	0.2115	0.0679
GOF	1.047	1.055	1.013	1.062

Å),[69] and the structure of $K^+(H_2O)_{27}$ is coincident with that in the central cavity of the K^+ channels, where the K^+ ion is surrounded by a hydration shell.[70]

Conclusions

Large ionic water clusters $H(H_2O)_{28}^+$, $K^+(H_2O)_{27}$, and $H(H_2O)_{21}^+$ were trapped and structurally characterized by finely modulating the pore sizes of 3D MOFs. The completely reversible dehydration/rehydration processes reveal that the large protonated water clusters are unusually stable in the cavities of the porous MOFs and that the various structural fashions of the protonated water clusters, especially the different hydrogen-bonding patterns, are intrinsic and vary with the subtle differences between the cavities. Proton-transfer studies suggested that the abundance of hydrogen bonds associated with the center ion core in the $H(H_2O)_{28}^+$ cluster is essential for the high mobility of aqueous protons. It is demonstrated that our porous network could be described as a synthetic non-peptide ion channel, in terms of not only structural features but also the functions addressed here. Direct observation of the structures of various large ionic water clusters trapped in the porous MOFs along with the reversible dehydration/rehydration processes and the proton/ion-exchange reactions provided valuable insight into the aqueous proton transfer and its high mobility relating to large protonated water clusters in the condensed phase.

Experimental Details

General and Measurements. All solvents and materials used for the syntheses were of reagent grade and used without further purification. α-$H_3PMo_{12}O_{40}$·$14H_2O$ and α-$H_3PW_{12}O_{40}$·$6H_2O$ were prepared according to a literature method[71] and characterized by IR spectra and thermogravimetric analyses. Elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 240C analyzer. IR spectra were recorded on a VECTOR 22 Bruker spectrophotometer with KBr pellets in the 400−4000 cm^{-1} regions at room temperature. X-ray fluorescence spectra were collected on an ARL9800-230XP spectrometer based on the solid films prepared using the single crystals of complexes. Fluorescence spectra were recorded on an AMINCO Bowman Series 2 fluorescence spectrophotometer. Laser Raman spectra of the single crystals of the title compounds were measured with a JY HR-800 spectrometer using the 488 Å line as the exciting source in the 100−2000 cm^{-1} regions.

$\{[Co_4(dpdo)_{12}][H(H_2O)_{28}(CH_3CN)_{12}](PMo_{12}O_{40})_3\}_\infty$ (2). α-$H_3PMo_{12}O_{40}$·$14H_2O$ (63 mg, 0.030 mmol) and $CoCl_2$·$6H_2O$ (75 mg, 0.030 mmol) were dissolved in water (1.5 mL), $CoHPW_{12}O_{40}$·nH_2O was obtained by evaporating the solution to dryness at 80 °C in a water bath. A solution (10 mL) of acetonitrile/water (3:2, v/v) was carefully layered over an aqueous solution of 4,4′-bipyridine-*N*,*N*′-dioxide hydrate (22 mg, 0.10 mmol), and then a solution of $CoHMo_{12}O_{40}$·nH_2O in an acetonitrile/water mixture (6:2, v/v) (4 mL) was carefully carefully added as a second layer. Black crystals that appeared after 4−5 weeks were collected and washed with water. Yield: 74 mg (86% based on polyoxometalates). Anal. Calcd (%) for $C_{144}H_{189}N_{36}O_{172}P_3Co_4Mo_{36}$: C, 19.30; H, 2.13; N, 5.63. Found: C, 18.83; H, 2.19; N, 5.28. IR (KBr): four characteristic vibrations resulting from the Keggin structure heteropolyanions, ν(Mo═Ot) 957, ν(Mo—Ob) 880, ν(Mo—Oc) 801, and ν(P—Oa) 1061 cm^{-1}; four characteristic vibrations resulting from dpdo molecules, ν(N—O) 1221, ν(ring) 1474, δ(C−H, in-plane) 1179, and δ(N—O) 839 cm^{-1}, as well as vibrations resulting from H—O and C—H (3383 and 3113 cm^{-1}).

$\{[Co_4(dpdo)_{12}][H(H_2O)_{21}(CH_3CN)_{12}][PMo_{12}O_{40}]_3\}_\infty$ (2A). Compound **2A** was prepared by heating crystals of complex **2** at 373 K for 2 h and subsequently cooling to 293 K. The whole process was performed in a vacuum using P_2O_5 as the desiccant. The IR spectrum was recorded as soon as the single crystals of **2A** were taken out from the vacuum desiccator. IR (KBr): four characteristic asymmetric vibrations resulting from heteropolyanions with the Keggin structure, ν(Mo═Ot) 957, ν(Mo—Ob) 880, ν(Mo—Oc) 801, and ν(P—Oa) 1061 cm^{-1}; four characteristic vibrations resulting from dpdo molecules, ν(N—O) 1221, ν(ring) 1474, δ(C−H, in-plane) 1179, and δ(N—O) 839 cm^{-1}.

$\{[Co_4(dpdo)_{12}][H(H_2O)_{21}(CH_3CN)_{12}][PW_{12}O_{40}]_3\}_\infty$ (1A). Compound **1A** was prepared by thermally treating the single crystals of complex **1**[15] using the same method described for **2A**. The IR spectrum was recorded as soon as the crystals of **1A** were taken out from the vacuum desiccator. IR (KBr): four characteristic asymmetric vibrations resulting from heteropolyanions with the Keggin structure, ν(W═Ot) 979, ν(W—Ob) 897, ν(W—Oc) 812, and ν(P—Oa) 1079 cm^{-1}; four characteristic vibrations resulting from dpdo molecules, ν(N—O) 1223, ν(ring) 1475, δ(C−H, in-plane) 1180, and δ(N—O) 839 cm^{-1}.

$\{[Co_4(dpdo)_{12}][H(H_2O)_{28}(CH_3CN)_{12}][PMo_{12}O_{40}]_3\}_\infty$ (2B). Compound **2B** was prepared by exposing crystals of **2A** in air for about 1 week. IR (KBr): four characteristic asymmetric vibrations resulting from heteropolyanions with the Keggin structure, ν(Mo═Ot) 957, ν(Mo—Ob) 881, ν(Mo—Oc) 802, and ν(P—Oa) 1062 cm^{-1};

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(69) Zhou, Y.; Morais-Cabral, J. H.; Kaufman, A.; MacKinnon, R. *Nature* **2001**, *414*, 43–48.

(70) MacKinnon, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 4265–4277.

(71) Rocchiccioli, D. C.; Fournier, M.; Franck, R.; Thouvenot, R. *Inorg. Chem.* **1983**, *22*, 207–216.

four characteristic vibrations resulting from dpdo molecules, ν(N—O) 1221, ν(ring) 1474, δ(C—H, in-plane) 1178, and δ(N—O) 839 cm^{-1}.

$\{[Co_4(dpdo)_{12}][H(H_2O)_{27}(CH_3CN)_{12}][PW_{12}O_{40}]_3\}_\infty$ (1B). Compound **1B** was prepared by exposing crystals of **1A** in air for about 1 week. IR (KBr): four characteristic asymmetric vibrations resulting from heteropolyanions with the Keggin structure, ν(W═Ot) 978, ν(W—Ob) 896, ν(W—Oc) 812, and ν(P—Oa) 1078 cm^{-1}; four characteristic vibrations resulting from dpdo molecules, ν(N—O) 1224, ν(ring) 1474, δ(C—H, in-plane) 1179, and δ(N—O) 838 cm^{-1}.

$\{[Co_4(dpdo)_{12}][K(H_2O)_{27}(CH_3CN)_{12}](PMo_{12}O_{40})_3\}_\infty$ (3). An acetonitrile/water (3:2, v/v) solution (10 mL) was carefully layered over an aqueous solution of 4,4′-bipyridine-*N*,*N*′-dioxide hydrate (33 mg, 0.15 mmol) and KCl (75 mg, 1.0 mmol), and then a solution of $CoHW_{12}O_{40}\cdot nH_2O$, formed by reaction of α-$H_3PW_{12}O_{40}\cdot 14H_2O$ (125 mg, 0.04 mmol) and $CoCl_2\cdot 6H_2O$ (10 mg, 0.04 mmol), in an acetonitrile/water mixture (6:2, v/v) (4 mL) was carefully added as a second layer over the buffer layer. Black block crystals appeared after the solution was left to stand for 4−5 weeks. Yield: 108 g (87% based on polyoxometalates). Anal. Calcd for $C_{144}H_{186}N_{36}O_{171}P_3Co_4W_{36}K$: C, 14.2; H, 1.5; N, 4.2. Found: C, 13.8; H, 1.4; N, 4.3. IR (KBr disk): ν(W═Ot) 960, ν(W—Ob) 880, ν(W—Oc) 800, ν(P—Oa) 1060, ν(N—O) 1220, ν(ring) 1475, and δ(C−H, in-plane) 1180 cm^{-1}, as well as vibrations resulting from H−O and C−H (3387 and 3088 cm^{-1}).

Crystallography. Crystallographic data for compounds **2**, **3**, **1A**, and **2A** are given in Table 1. These data were collected at 123 K on a Siemens SMART-CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using the SMART and SAINT programs.[72] The structures were solved by direct methods and refined on F^2 by using full-matrix least-squares methods with SHELXTL version 5.1.[73] Non-hydrogen atoms were refined anisotropically, except for the disordered oxygen atoms. Hydrogen atoms of the organic molecules were localized in their calculated positions and refined using a riding model. The hydrogen atoms of the water molecules for compound **2** at 123 K were found from the differenc Fourier maps and refined freely; the isotropic parameters of the hydrogen atoms attached to the water molecules O(3W) and O(4W) were fixed as 1.2 times the isotropic parameters of the atoms to which they were attached. For the crystal structures of compound **3**, hydrogen atoms on the water molecules were not treated. Some of the μ_2-O's in the anions were disordered into two positions with the site occupancy factor (SOF) fixed at 0.5 or 0.25 for the normal and special positions, respectively. The oxygen atoms of the P−O groups were also disordered into two positions with the SOF fixed at 0.25. For compounds **2**, **3**, **1A**, and **2A**, the water molecules of the type O(3W) positioned in each face of the $(H_2O)_{20}$ hexahedron were disordered with the SOF fixed at 0.25. The oxygen atoms of type O(4W) that sited in the center core were disordered with the SOF fixed at 0.08333 for compound **2**. For compound **3**, one of the water molecules and one of the alkali atoms occupied one of the four pairs of diagonal vertexes of the cube formed by the eight disordered identical positions with the SOF for each fixed at 0.04167.

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Supporting Information Available: Crystallographic data, in CIF format, of compounds **2**, **3**, **1A**, and **2A**. This information is available free of charge via the Internet at http://pubs.acs.org.

JA907023C

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[72] *SMART and SAINT*, Area Detector Control and Integration Software; Siemens Analytical X-ray Systems, Inc.: Madison, WI, 1996.

[73] Sheldrick, G. M. *SHELXTL V5.1, Software Reference Manual*; Bruker AXS, Inc.: Madison, WI, 1997.