Coordination-Chemistry Control of Proton Conductivity in the Iconic Metal−Organic Framework Material HKUST-1

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S *Supporting Information*

ABSTRACT: HKUST-1, a metal−organic framework (MOF) material containing Cu^{II}-paddlewheel-type nodes and 1,3,5-benzenetricarboxylate struts, features accessible Cu^{II} sites to which solvent or other desired molecules can be intentionally coordinated. As part of a broader investigation of ionic conductivity in MOFs, we unexpectedly observed substantial proton conductivity with the "as synthesized" version of this material following sorption of methanol. Although HKUST-1 is neutral, coordinated water molecules are rendered sufficiently acidic by Cu^{II} to contribute protons to pore-filling methanol molecules and thereby enhance the alternating-current conductivity. At ambient temperature, the chemical identities of the node-coordinated and pore-filling molecules can be independently varied, thus enabling the proton conductivity to be reversibly modulated. The proton conductivity of HKUST-1 was observed to increase by ~75-fold, for example, when node-coordinated acetonitrile molecules were replaced by water molecules. In contrast, the conductivity became almost immeasurably small when methanol was replaced by hexane as the pore-filling solvent.

M etal−organic frameworks (MOFs) are an intriguing class of crystalline materials that can be readily assembled by combining metal ions (components of nodes) and multitopic organic ligands (structural linkers) via coordination chemistry, typically under solvothermal reaction conditions.[1] Often characterized by large internal surface areas and extended nanoscale porosity, MOFs are being examined as candidate materials for applications in chemical separations,[2] gas storage,[3] heterogeneous catalysis,[4,5] sensing,[6] ion exchange,[7] and drug delivery.[8] Recently, another potential property of MOFs, electrical conductivity—and, in particular, proton conductivity—has begun receiving attention. This attention comes in part from fundamental scientific interest in ionic conductivity[9,10] in new environments, in part from a desire to use conductivity as a real-time reporter on sorption of molecular guests,[11] and in part because of the need for new proton-conducting materials capable of better performance than existing materials when deployed as membranes in proton exchange membrane (PEM) fuel cells.[9]

To date, only two approaches have been used to engender proton conductivity in MOFs. The first centers on incorporating carboxylic, sulfonic, or phosphonic acid species as channel-accessible functionalities on framework linkers.[12] The second entails physically introducing proton donors and/or carriers such as ammonium ion, carboxylic acid species, or 1*H*-1,2,4-triazole into the pores of already-synthesized framework compounds.[13] Here we report on a third approach: a poor proton donor, in this case H_2O, is bound to an otherwise open coordination site of a node- or linker-based metal cation. Binding substantially increases the acidity of the incorporated molecule, enabling it to donate a proton to hydroxylic guest molecules (in this case MeOH) and thereby rendering conductive the network of hydrogen-bonded guest molecules filling the framework material's pores and channels. As shown below, we find that this approach can increase proton conductivity by close to 2 orders of magnitude.

While any of several MOFs featuring open coordination sites[3c,14] should be capable of capitalizing on this new approach, we limited our study to HKUST-1, a nanoporous crystalline material constructed from paddlewheel-coordinated $(Cu^{II})_2$ nodes and 1,3,5-benzenetricarboxylate (BTC) linkers[15] (Chart

Chart 1. Illustrations of (a) the HKUST-1 Structure in a Two-Dimensional View along the (100) Direction and (b) an HKUST-1 Node with the Cu-Paddlewheel Environment
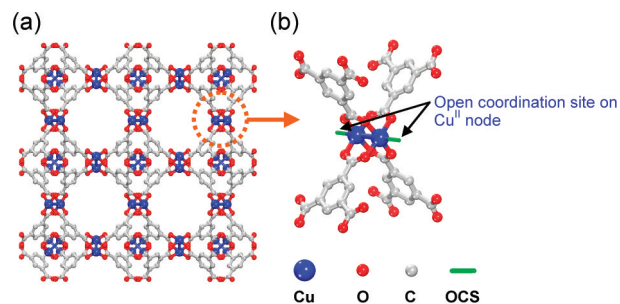
1). The ease of preparation of HKUST-1, together with the presence of weakly axially coordinating Cu^{II} sites,[16] have made it one of the most widely studied MOFs. One intriguing study by Yazaydin and co-workers showed the importance of Cu^{II}-coordinated water in CO_2 adsorption.[17] Other studies have revealed the importance of the open form of the metal site (obtained by axial-ligand removal) for Lewis acid catalysis[5] and selective adsorption.[18] For systematic studies of proton conductivity, we examined the "as synthesized" version of

HKUST-1, versions incorporating hydroxylic molecules as axial ligands, and a version incorporating a nonhydroxylic molecule as an axial ligand (Figure 1). Most experiments employed
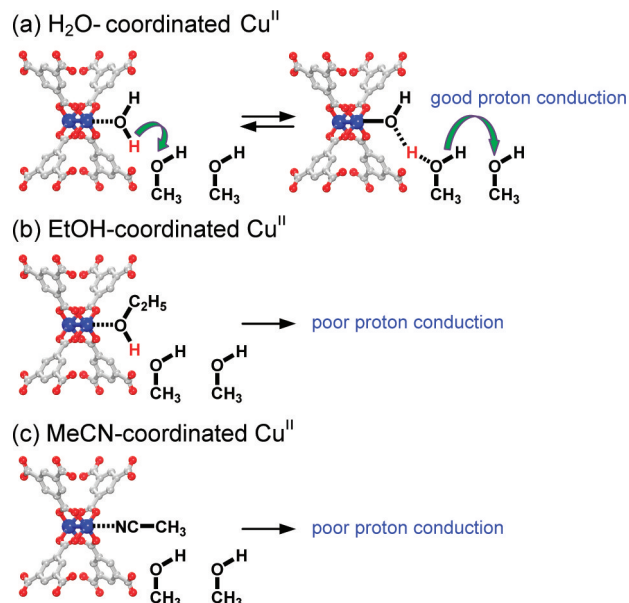

Figure 1. Qualitative representations of proton transfer from Cu^{II} centers coordinated with (a) water, (b) ethanol, and (c) acetonitrile.

Figure 2. (a) ^1H NMR spectra and (b) PXRD patterns of pristine-HK, H_2O-HK, EtOH-HK, MeCN-HK, and MeOH-HK as indicated (We designate desolvated HKUST-1 as HK). The numbers below each spectrum in (a) are relative peak areas.

methanol as the pore-filling solvent, but a few employed hexane. Key to the study was the ability to vary the chemical identities of the copper-coordinated molecules and the remaining channel-filling molecules independently.

"Pristine" HKUST-1 was prepared via solvothermal reaction of copper(II) nitrate and BTC in a mixed solvent of water and ethanol [for details, see section S-1 in the Supporting Information (SI)]. This form contains both H_2O and EtOH as coordinated molecules. To prepare pure H_2O-, EtOH-, MeOH-, or MeCN-coordinated HKUST-1, both H_2O and EtOH were removed via heating at 150 °C for 48 h under flowing nitrogen. Samples of the solvent-free material were then placed in an Ar-charged glovebox and allowed to coordinate H_2O, EtOH, MeOH, or MeCN by soaking in the corresponding neat liquid (see the SI). Figure 2a shows ^1H NMR spectra of pristine-HK, H_2O-HK, EtOH-HK, MeOH-HK, and MeCN-HK (HK = fully desolvated HKUST-1). The spectra were taken after each sample was dissolved in deuterated sulfuric acid, D_2SO_4.[19] The peak for three identical protons in BTC appears at ∼8.8 ppm, while peaks for the two identical CH_2 protons and three identical CH_3 protons in ethanol appear at 3.90 and 0.83 ppm, respectively. Additionally, the peaks for the three identical CH_3 protons of MeOH and MeCN appear at 3.65 and 1.88 ppm, respectively. However, the peak for water protons does not appear since sulfuric acid forms hydronium ions (nominally H_3O^+) featuring a peak at ∼10.6 ppm. On the basis of integration of these peaks, we found that 60% of the coordinated solvent molecules in pristine HKUST-1 were H_2O and 40% were EtOH and that these molecules were completely supplanted by H_2O, EtOH, MeOH, or MeCN in the corresponding modified HKUST-1 materials. The phase purity of pristine-HK, H_2O-HK, EtOH-HK, MeOH-HK, and MeCN-HK was confirmed via powder X-ray diffraction (PXRD) measurements (Figure 2b). The structural integrity of the MOF was well-preserved following these ligation-based
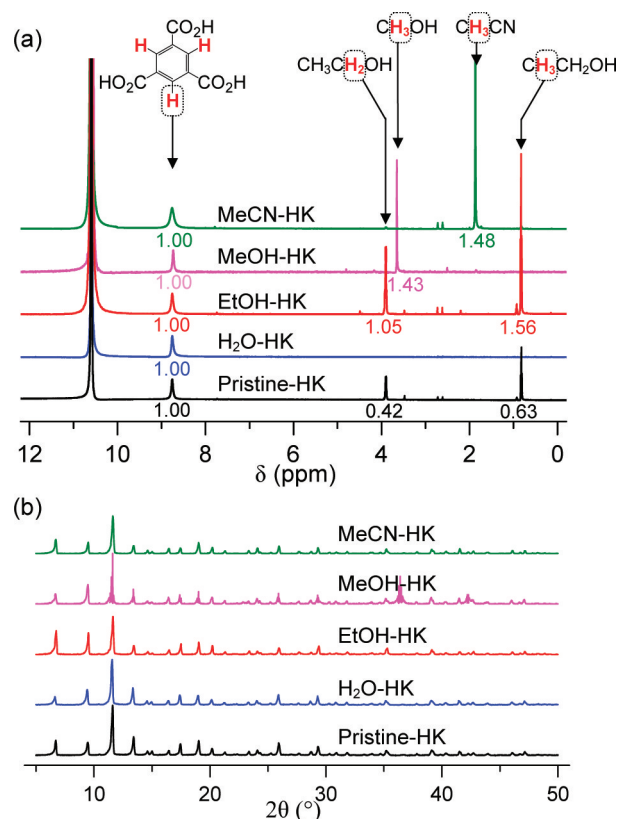
modifications. For conductivity measurements, disk-shaped pellets of the various versions of HKUST-1 were prepared by using a press and a die measuring 7.6 mm in diameter and 1.0 mm (±0.03%) in thickness. Silver epoxy was coated on the front and back faces of each pellet and used to anchor a pair of tin-coated copper wires. Each pellet was then placed in an oven at ∼60 °C for 40 min to cure the epoxy. Pellets were then exposed to methanol vapor (in dry N_2) at room temperature, after which variable-frequency alternating-current conductivity measurements (impedance measurements) were initiated.

As shown in Figure 3 and section S-2, plots of the imaginary component (Z'') versus the real component (Z') of the
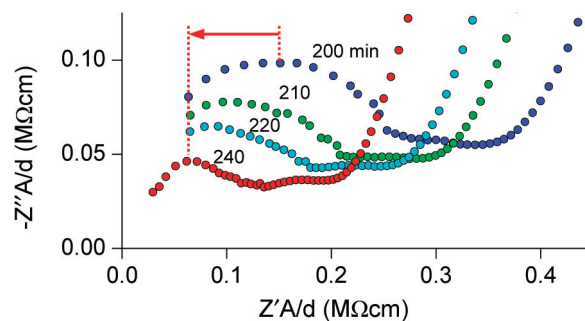

Figure 3. Impedance spectra of a H_2O-HK sample following exposure to MeOH vapor at room temperature. The arrow indicates that conductivity of the sample increases with increasing exposure time. See the SI for additional data.

impedance are dominated by a single arc that we ascribe to proton conduction (for details, see section S-3). Notably, the amplitude of the arc and its maximum along the Z' axis shift to progressively smaller values with increasing MeOH vapor exposure time. That is indicative of increasing conductivity (decreasing resistivity) and is to be expected as the pores slowly fill with MeOH, culminating in constant values for the conductivity. The limiting conductivities for both (hydroxylic) EtOH-HK and (nonhydroxylic) MeCN-HK were 0.2 μS cm^{-1}. These values are essentially identical to what we measured for carefully dried bulk MeOH (0.17 μS cm^{-1}; see the SI) and only slightly greater than what has been reported previously for highly purified bulk MeOH (0.04−0.11 μS cm^{-1}).[20,21] Taken together, these results indicate that neither coordinated acetonitrile nor coordinated EtOH enhances the conductivity within HKUST-1.

In contrast, H$_2$O-HK yielded a conductivity of 15 μS cm^{-1}, which is ∼90 times larger than that of bulk MeOH and ∼75 times larger than those of EtOH-HK and MeCN-HK (Figure
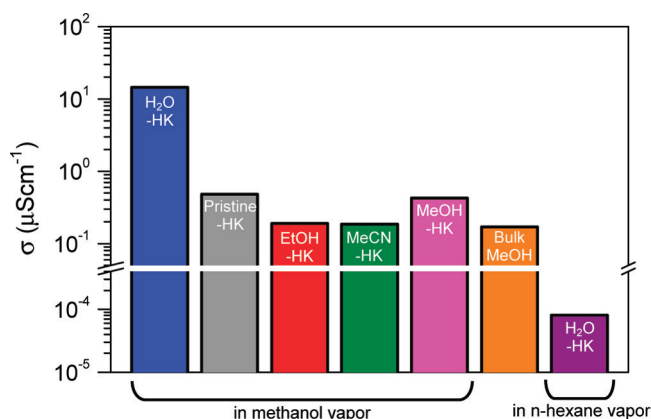

Figure 4. Proton conductivities of H$_2$O-HK, pristine-HK, EtOH-HK, MeCN-HK, MeOH-HK, and bulk MeOH under a MeOH or n-hexane atmosphere as indicated.

4). We attribute this striking increase to the participation of coordinated water molecules as proton donors toward methanol, which increases the concentration of CH$_3$OH$_2^+$ well beyond what is achieved solely via autoprotolysis, thereby enhancing the proton conductivity (presumably via Grotthuss-type proton transfer, although mechanistic studies of this sort are beyond the scope of this preliminary study). The role of Cu^{II} is to enhance the acidity of ligated H$_2$O, a proposal for which there is ample chemical precedent.[22]

The absence of conductivity enhancement by coordinated MeCN, which lacks a dissociable proton, is understandable and consistent with our interpretation. In the case of ethanol coordination by Cu^{II}, we anticipated that the conductivity of methanol-infused HKUST-1 would at least somewhat exceed that of bulk methanol (since ethanol does possess a dissociable proton that could in principle be transferred to methanol in the same fashion as proposed for Cu^{II}-coordinated water). We attribute the lack of observable conductivity enhancement to the difference in acidity for ethanol versus methanol. While the acidity of water (pK_a = 14.0)[23] is 30 times greater than that of methanol (pK_a = 15.5),[24] the acidity of ethanol (pK_a = 15.9)[24] is 2.5 times *less* than that of methanol. Evidently, even with the enhancement of acidity provided by coordination to Cu^{II}, the conductivity contribution provided by EtOH is negligible.

Replacing EtOH with MeOH as the node-coordinated molecule and subsequently exposing the pore-evacuated material to MeOH vapor yielded a limiting conductivity of 0.43 μS cm^{-1}, ∼2.5 times that of purified and zeolite-dried bulk methanol and twice that of methanol-infused MeCN-HK (see above). We attribute the observed small enhancement to a modest lowering of the pK_a of MeOH upon coordination to Cu^{II}.

In the case of pristine-HK, we anticipated that the conductivity would fall midway between that for H$_2$O-HK and EtOH-HK, since 60% of the coordinated solvent molecules are water. Instead, upon exposure to MeOH vapor, pore-evacuated "pristine-HK" yielded a limiting conductivity of 0.5 μS cm^{-1}, which is much closer to that of EtOH-HK (Figure 4). At present, we lack a compelling explanation for this interesting observation.

Finally, the fact that noncoordinated proton-labile species are needed to engender significant conductivity was established via two more experiments. In one, H$_2$O-HK was exposed to n-hexane vapor and yielded a limiting conductivity more than 5 orders of magnitude below that obtained for H$_2$O-HK containing MeOH (Figure 4 and Figure S4 in the SI).[25,26] The second involved fully solvent-evacuated HKUST-1, which yielded a conductivity below the measurement threshold for our instrumentation.

In summary, postsynthesis modification of HKUST-1 via coordination of H$_2$O at open Cu^{II} (node) sites led to a large (∼75-fold) enhancement in proton conductivity, relative to a version containing nodes modified by acetonitrile, once the material's channels were infused with MeOH. The enhanced conductivity is ascribed to proton donation to MeOH by coordinated water, where the metal cations serve to enhance the acidity of the water molecules. While the study was limited to several variants of HKUST-1, this new approach to increasing proton conductivity should be transferrable to other MOF materials, including materials that offer open metal sites as components of linkers (e.g., MOFs featuring active-site-accessible metalloporphyrins or -salens as linkers). Acidity enhancements and therefore conductivity enhancements likely could be magnified by applying the strategy to MOFs such as Cr MIL-101 that contain ligand-accessible metal ions with higher charge than the Cu^{II} ions of HKUST-1.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and electrochemical impedance spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENTS

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(19) Prior to dissolution, noncoordinated guest molecules were selectively removed from all samples, including pristine-HK, by drying at ambient temperature for 1 h under dynamic vacuum. The same treatment was used to remove noncoordinated guest molecules from pristine-HK (i.e., 60:40 H_2O:EtOH-HK), H_2O-HK, MeCN-HK, EtOH-HK, and MeOH-HK prior to exposure to MeOH or hexane vapor and assessment of conductivity.

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(25) The most prosaic interpretation of the experiment is that even this tiny conductivity is due mainly to residual noncoordinated water or methanol rather than to *n*-hexane.

(26) Attempts to extend the study to water as the guest molecule yielded samples displaying no measurable conductivity. Subsequent PXRD measurements revealed that prolonged exposure to water vapor (∼2 h) resulted in an almost complete loss of MOF crystallinity. To the extent that the loss entails pore collapse, this would account for the absence of measurable conductivity.