

## Promotion of Low-Humidity Proton Conduction by Controlling Hydrophilicity in Layered Metal–Organic Frameworks

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### Supporting Information

**ABSTRACT:** We controlled the hydrophilicity of metal–organic frameworks (MOFs) to achieve high proton conductivity and high adsorption of water under low humidity conditions, by employing novel class of MOFs,  $\{NR_3(CH_2COOH)\}[MCr(ox)_3] \cdot nH_2O$  (abbreviated as **R-MCr**, where R = Me (methyl), Et (ethyl), or Bu (*n*-butyl), and M = Mn or Fe): **Me-FeCr**, **Et-MnCr**, **Bu-MnCr**, and **Bu-FeCr**. The cationic components have a carboxyl group that functions as the proton carrier. The hydrophilicity of the cationic ions was tuned by the  $NR_3$  residue to decrease with increasing bulkiness of the residue:  $\{NMe_3(CH_2COOH)\}^+ > \{NEt_3(CH_2COOH)\}^+ > \{NBu_3(CH_2COOH)\}^+$ . The proton conduction of the MOFs increased with increasing hydrophilicity of the cationic ions. The most hydrophilic sample, **Me-FeCr**, adsorbed a large number of water molecules and showed a high proton conductivity of  $\sim 10^{-4}$  S  $cm^{-1}$ , even at a low humidity of 65% relative humidity (RH), at ambient temperature. Notably, this is the highest conductivity among the previously reported proton-conducting MOFs that operate under low RH conditions.

Recent studies on metal–organic frameworks (MOFs) have shown that their designable framework architectures and specific pore surfaces are of potential interest to chemists studying various functionalities of solid-state materials, such as selective gas sorption,<sup>1</sup> heterogeneous catalysis,<sup>2</sup> magnetism,<sup>3</sup> and electrical conductivity.<sup>4</sup> Proton conductivity is now regarded as a new functionality of the porous MOFs<sup>5</sup> and has attracted great interest, not only for scientific studies, such as biological systems,<sup>6</sup> but also for practical investigation.<sup>7</sup> MOFs can provide well-designed pores for proton-conducting pathways and include various conducting media, such as water molecules in the pores. The various interactions between the pores and the guest molecules, such as hydrophilic or hydrophobic interactions, may contribute to introduction of guests as conducting media into the pores. To date, we have studied the introduction of acid molecules and water molecules into the pores as proton carriers and conducting media, respectively, and have succeeded in synthesizing highly proton-conductive MOFs.<sup>5a,b</sup> Other groups have also reported on MOFs showing proton conduction.<sup>5h–o</sup>

We have focused on the hydrophilic interaction that strongly affects the affinity to water molecules and have intended to explore the good proton conductors operating even under ambient conditions (i.e., low humidity and low temperatures). In general, water-mediated proton conductors (e.g., Nafion) require high-humidity conditions.<sup>7a,8a–c</sup> On the other hand, anhydrous proton conductors (e.g., solid acids and imidazole-based materials) require high temperatures.<sup>7a,8d–g</sup> MOFs also show a similar tendency and do not exhibit high proton conductivity under ambient conditions. They require highly humid conditions, near to 100% relative humidity (RH),<sup>5a–k</sup> or high temperatures, above 100 °C.<sup>5l–n</sup> It is a prime issue for practical proton conductors that are intended to operate under ambient conditions, and this is because water molecules easily desorb from these materials under low humidity because of their low affinity; avoiding this desorption is necessary for efficient proton transport under ambient conditions. These facts illustrate that the controlling of hydrophilicity of the pores is of key importance in designing MOFs with high proton conductivity under ambient conditions.

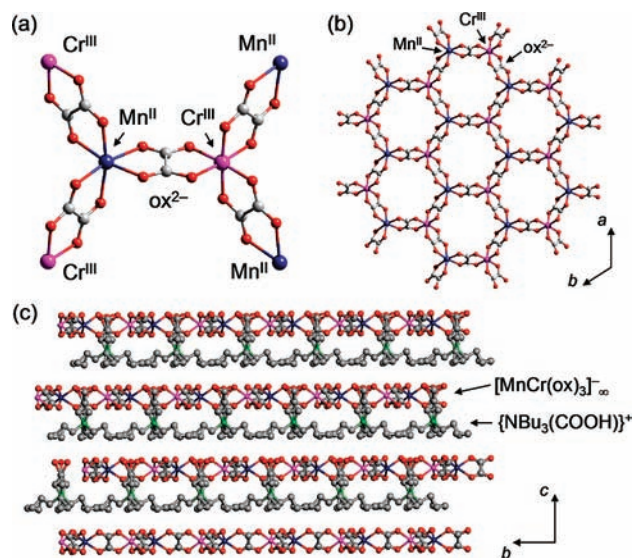
Here, we discuss the promotion of proton conduction under ambient conditions by employing oxalate-bridged layered MOFs,  $\{NR_3(CH_2COOH)\}[MCr(ox)_3] \cdot nH_2O$  (R = Me (methyl), Et (ethyl), or Bu (*n*-butyl), and M = Mn or Fe) (abbreviated as **R-MCr**), having a cationic component composed of carboxylic acid groups that can function as the proton carriers. The hydrophilicity of the cationic ions was tuned by the  $NR_3$  residue and decreases with increasing bulkiness of the residue, i.e.,  $\{NMe_3(CH_2COOH)\}^+ > \{NEt_3(CH_2COOH)\}^+ > \{NBu_3(CH_2COOH)\}^+$ . These MOFs exhibited proton conductivity under various humidity conditions, dependent on their hydrophilicity. The most hydrophilic sample, **Me-FeCr**, showed a high proton conductivity of  $\sim 10^{-4}$  S  $cm^{-1}$ , accompanied by a large adsorption of water molecules, even at low humidity, such as 65% RH.

**Me-FeCr**·3H<sub>2</sub>O, **Et-MnCr**·2H<sub>2</sub>O, **Bu-MnCr**, and **Bu-FeCr** were synthesized by reacting (NH<sub>4</sub>)<sub>3</sub>[Cr(ox)<sub>3</sub>]·3H<sub>2</sub>O, MnCl<sub>2</sub>·4H<sub>2</sub>O, or FeCl<sub>2</sub>·6H<sub>2</sub>O and  $\{NR_3(CH_2COOH)\}Br$  in methanol (details are given in the Supporting Information (SI)). **Et-FeCr** was also obtained, but this was not used in this

Received: January 5, 2012

Published: March 12, 2012

work because of contamination from impurities. The crystal structure of **Bu-MnCr** was determined from single-crystal X-ray diffraction measurements (Figure 1). The Mn ions are linked



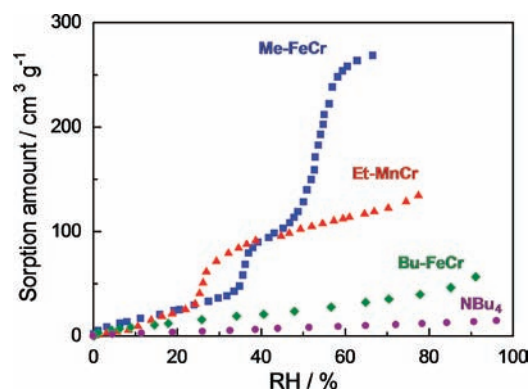
**Figure 1.** The crystal structure of **Bu-MnCr**. (a) Representation of the coordination geometry around  $\text{Mn}^{\text{II}}$  and  $\text{Cr}^{\text{III}}$ , (b) the honeycomb layer structure, and (c) stacking view along the layers.

by  $[\text{Cr}(\text{ox})_3]^{3-}$  units to form a honeycomb-based two-dimensional (2-D) framework comparable to those observed in analogous MOFs.<sup>9</sup> The average Cr–O and Mn–O bond distances were 1.975 and 2.189 Å, respectively. The cationic ions are perpendicularly aligned with the 2-D layer, with the carboxyl groups residing in each honeycomb cavity. The interlayer space was mostly occupied by the  $\text{NBu}_3$  residues of the cationic ions, suggesting that the hydrophilic nature of interlayer space can be controlled by them.

From the results of XRPD measurements (see the Supporting Information), it is clear that the structure of **Bu-FeCr** is fundamentally the same as that of **Bu-MnCr**. In the case of **Et-MnCr**, a similar pattern was observed, including a characteristic peak around  $2\theta = 9\text{--}13^\circ$  (for  $\text{Cu } K\alpha$  radiation), derived from the honeycomb layer framework.<sup>1f,5a,b,9</sup> However, there were additional peaks in **Me-FeCr** compared with **Bu-MnCr** or **Et-MnCr**, suggesting that it has a lower symmetry in its crystal structure. To confirm the structure of **Me-FeCr**, we performed unit cell indexing and Pawley fittings using the Material Studio software package. The monoclinic unit cells had space groups of  $P2$  or  $P2_1$ , which are successfully used for the fitting (Figure S2 (SI)). The cell parameters were essentially the same as those of previous oxalate-bridged 2-D layered MOFs,<sup>1f</sup> indicating that it also has a characteristic 2-D layered structure. The diffraction peak exhibiting maximum intensity was attributed to the (10–1) plane, corresponding to the periodic structure of the layers. The periodic distance between the layers of **Bu-MnCr**, **Bu-FeCr**, **Et-MnCr**, and **Me-FeCr** was determined to be 8.52, 8.49, 7.72, and 6.91 Å, respectively. According to the previous data of a similar MOF ( $\text{H}_2\text{dab}[\text{Zn}_2(\text{ox})_3]\cdot 2\text{H}_2\text{O}$  that has the periodic distance of 6.34 Å while it has two water molecules in interlayer space,<sup>1f</sup> they should have enough cavity space for the inclusion of several water molecules in the interlayer space.

Our magnetic studies add support for a similarity in the network structures of these MOFs. They showed a ferromagnetic ordering, with  $T_c = 5.6\text{--}5.9$  K for **Et-MnCr** and **Bu-MnCr** and  $T_c = 11.0\text{--}12.5$  K for **Me-FeCr** and **Bu-FeCr** (see the Supporting Information). These  $T_c$  values compare well to those found for oxalate-bridged 2-D layered compounds ( $T_c = 5\text{--}6$  K for **MnCr** and  $9.5\text{--}13$  K for **FeCr**).<sup>3b,5b,9</sup>

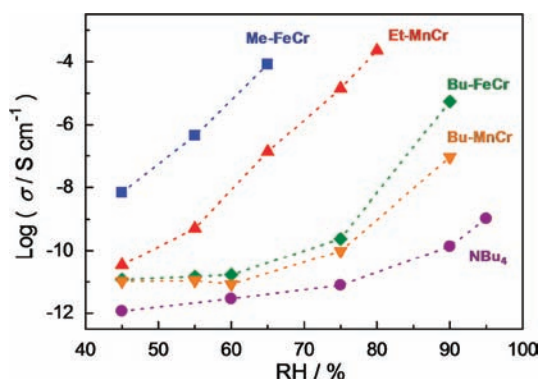
To examine the hydrophilicity and capacity for inclusion of water molecules of these MOFs, we measured their water adsorption isotherms. It is clear that each compound adsorbs water molecules to a different degree (Figure 2). **Me-FeCr** and



**Figure 2.** Water vapor adsorption isotherms of the MOFs at 298 K. The blue, red, green, and purple symbols correspond to **Me-FeCr**, **Et-MnCr**, **Bu-FeCr**, and **NBu<sub>4</sub>**, respectively.

**Et-MnCr** showed a large adsorption of water as the guest below 60% RH, while **Bu-FeCr** gradually adsorbed water, even at high humidity, suggesting that the interlayer spaces of **Me-FeCr** and **Et-MnCr** are more hydrophilic than are those of **Bu-FeCr**, and they have the potential to indicate proton conduction at low humidity. The isotherm of **Bu-MnCr** was similar to that of **Bu-FeCr**. The water contents in **Me-FeCr**, **Et-MnCr**, and **Bu-FeCr** were 268, 134, and 57  $\text{cm}^3 \text{g}^{-1}$  at the maximum allowable humidity, corresponding to 5.8, 3.2, and 1.6 water molecules per unit formula, respectively. The result of thermogravimetric analysis of **Me-FeCr** under a humidified condition (68% RH) also confirms the amount of adsorbed water molecules (see the Supporting Information). These compounds have instability limits at different humidities, and they deliquesce above their maximum allowable humidity, which are approximately 70% RH for **Me-FeCr**, 85% RH for **Et-MnCr**, and 95% RH for **Bu-FeCr** and **Bu-MnCr**. We also measured adsorption isotherms of the  $(\text{NBu}_4)[\text{MnCr}(\text{ox})_3]$  (abbreviated as **NBu<sub>4</sub>**) having the very hydrophobic cations, whose size is similar to that of the  $\{\text{NBu}_3(\text{CH}_2\text{COOH})\}^+$ , in the 2-D layered framework.<sup>3b</sup> It did not show apparent adsorption of water, suggesting that the carboxyl group also affects the hydrophilicity of the MOFs. It is clear that **Me-FeCr** has the largest capacity for water molecules, and this will play an important role in proton transport by forming a hydrogen-bonding network among the acid and water molecules at 40–65% RH. This may be because of the reduction in the alkyl groups contributing to a decrease in hydrophilicity and guest capacity in the interlayer spaces. These results indicate that the most hydrophilic MOF, **Me-FeCr**, may show high proton conductivity even under low humidity conditions.

To clarify the difference in the proton-conductive properties among the MOFs, we performed ac (alternating-current) impedance measurements under various humidity conditions using 2.5 mm  $\phi$  pellet samples having a thickness of  $\sim 0.8$  mm (details are shown in the Supporting Information). The proton conductivity of these compounds was estimated from the Nyquist plots (Figure S5 (SI)). The **Me-FeCr**, **Et-MnCr**, **Bu-FeCr**, and **Bu-MnCr** indicated proton conductivity of  $0.8 \times 10^{-4}$  (65% RH),  $1 \times 10^{-7}$  (65%),  $2 \times 10^{-11}$  (60%), and  $0.8 \times 10^{-11}$  S cm $^{-1}$  (60%), respectively, at low humidity conditions of  $\sim 65\%$  RH (Figure 3). There is a clear tendency that higher



**Figure 3.** Humidity dependence of the proton conductivity at 298 K. The blue, red, green, orange, and purple colors correspond to the proton conductivity of **Me-FeCr**, **Et-MnCr**, **Bu-FeCr**, **Bu-MnCr**, and **NBu<sub>4</sub>**, respectively.

proton conductivities are observed in the case of more hydrophilic compounds, under the same humidity conditions. According to the results of adsorption measurements, it should be due to the difference in water content among the MOFs, meaning that the hydrophilicity of the MOFs promote the proton conductivity under the low humidity. The most hydrophilic sample, **Me-FeCr**, showed the highest conductivity among the MOFs at 45–65% RH, and notably the maximum value of  $0.8 \times 10^{-4}$  S cm $^{-1}$  at 65% RH is the highest proton conductivity among proton-conductive MOFs operating under ambient conditions (Table 1).<sup>5</sup> **Et-MnCr**, **Bu-FeCr**, and **Bu-MnCr** showed proton conductivities of  $2 \times 10^{-4}$  (80% RH),  $5 \times 10^{-6}$  (90% RH), and  $0.9 \times 10^{-7}$  S cm $^{-1}$  (90% RH), respectively, at the maximum allowable humidity. There is a difference among the maximum allowable humidity conditions depending on the hydrophilicity, and the frameworks become unstable at higher humidity because of the need to retain a high number of water molecules. We also measured the proton conductivity for **NBu<sub>4</sub>**, which has no acidic sites but does have a

2-D layered structure similar to that of our MOFs.<sup>3b</sup> This compound exhibited low proton conductivity, even at high humidity, because of the absence of proton carriers and water. From those results mentioned above, it is suggested that the dissociative protons of carboxylic acids and water molecules play the important roles as proton carriers and conducting media, which contribute to the high degree of proton conductivity in **Me-FeCr**, **Et-MnCr**, **Bu-FeCr**, and **Bu-MnCr**.

In summary, we have demonstrated the promotion in proton conductivity under ambient conditions by employing a novel class of MOFs with the carboxyl-containing cationic ions,  $\{NR_3(CH_2COOH)\}[MCr(ox)_3]$  (R = Me, Et, Bu, and M = Mn, Fe). The hydrophilicity of the cationic ions was tuned by the NR<sub>3</sub> residue, and this decreases with increasing bulkiness of the residue. The hydrophilicity of the cationic ions influenced the interlayer hydrophilicity, which is closely connected with the adsorption of water molecules and hence with the proton conduction in the MOFs. A high proton conduction of  $0.8 \times 10^{-4}$  S cm $^{-1}$  was observed at 65% RH, in **Me-FeCr**. This is the highest conductivity among proton-conducting MOFs operating under low humidity.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Synthetic procedure, physical measurements, XRPD measurements, X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The synchrotron XRPD measurements were supported by JASRI/SPring-8. This work was partly supported by the JSPS Research Fellowships for Young Scientists No. 21-4405, and Grants-in-Aid for Scientific Research No. 20350030 and No. 22108526.

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**Table 1.** Proton Conductivity of the MOFs under Ambient Conditions

compound	$\sigma$ (S cm $^{-1}$ )	RH (%)	T (K)	reference
<b>Me-FeCr</b>	$0.8 \times 10^{-4}$	65	298	this work
(NH <sub>4</sub> ) <sub>4</sub> [MnCr <sub>2</sub> (ox) <sub>6</sub> ]·4H <sub>2</sub> O	$3.0 \times 10^{-5}$	69	295	ref 5j
Co[Cr(CN) <sub>6</sub> ] <sub>2/3</sub> ·zH <sub>2</sub> O	$2.9 \times 10^{-5}$	69	293	ref 5i
{NH(prol) <sub>3</sub> }[MnCr(ox) <sub>3</sub> ]·2H <sub>2</sub> O <sup>a</sup>	$2.0 \times 10^{-6}$	65	298	ref 5b
(NH <sub>4</sub> ) <sub>2</sub> (adp)[Zn <sub>2</sub> (ox) <sub>3</sub> ]·2H <sub>2</sub> O <sup>b</sup>	$6.0 \times 10^{-6}$	70	298	ref 5a
Zn <sub>3</sub> (L)(H <sub>2</sub> O) <sub>2</sub> ·2H <sub>2</sub> O <sup>c</sup>	$1.4 \times 10^{-6}$	75	298	ref 5h
(HOC <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> dtoaCu <sup>d</sup>	$5.9 \times 10^{-8}$	70	300	ref 5g
Mn(dhbc)(H <sub>2</sub> O) <sub>2</sub> <sup>e</sup>	$3.5 \times 10^{-9}$	60	298	ref 5f

<sup>a</sup>prol =  $-C_3H_7OH$ . <sup>b</sup>adp = adipic acid. <sup>c</sup>L = 1,3,5-benzenetriphosphonate. <sup>d</sup>dtoa = dithioamide. <sup>e</sup>H<sub>2</sub>dhbc = 2,5-dihydroxy-1,4-benzoquinone.

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