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## COMMUNICATION

## Remarkably Enhanced Proton Conduction of $\{\text{NBu}_2(\text{CH}_2\text{COOH})_2\}[\text{MnCr}(\text{ox})_3]$ by Multiplication of Carboxyl Carrier in the Cation

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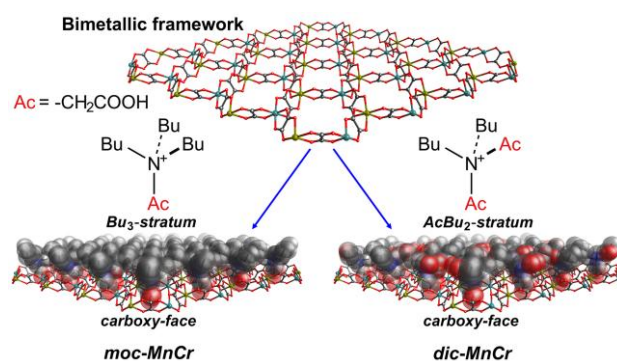
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Hisashi Ōkawa,<sup>\*a,b</sup> Kazuya Otsubo,<sup>\*a</sup> Yukihiro Yoshida<sup>a</sup> and Hiroshi Kitagawa<sup>\*a</sup>

The proton conduction of  $\{\text{NBu}_2(\text{CH}_2\text{COOH})_2\}[\text{MnCr}(\text{ox})_3]$  (*dic-MnCr*) is studied in comparison with its analogous  $\{\text{NBu}_3(\text{CH}_2\text{COOH})\}[\text{MnCr}(\text{ox})_3]$  (*moc-MnCr*). The proton conductivity is enhanced remarkably by the multiplication of the carboxyl carrier in the cation, from  $5.2 \times 10^{-7} \text{ Scm}^{-1}$  at 90% RH (25 °C) in *moc-MnCr* to  $1.8 \times 10^{-3} \text{ Scm}^{-1}$  at 95% RH (25 °C) in *dic-MnCr*.

Studies of proton-conductive materials have come into the limelight for their potential application to the solid-state electrochemical devices.<sup>1</sup> Most recent works are based on metal-organic frameworks (MOFs)<sup>2</sup> because MOFs enable the rational design of proton transfer pathways in their frameworks. Various approaches have been employed to generate proton conduction in MOFs. Generally adopted is the incorporation of proton-carrier groups like hydroxy,<sup>3</sup> carboxyl,<sup>4–8</sup> phosphono<sup>9–11</sup> or sulfo<sup>12–15</sup> groups in the framework of MOFs by assembling metal ions and organic sources functionalized with these carrier groups. We have adopted another approach based on the bimetallic MOFs:  $(\text{A})[\text{M}_b^{\text{II}}\text{M}_a^{\text{III}}(\text{ox})_3]$ .<sup>16–18</sup> They have the layer constitution of the honeycomb-based bimetallic sheets and the intercalation of the  $\text{A}^+$  cations between the sheets. Proton transfer pathway is formed between the bimetallic sheets by introducing proton carrier(s) into the cationic component. This approach has the advantage of evaluating the proton conduction for various

cations while maintaining the layered network of the MOFs. In



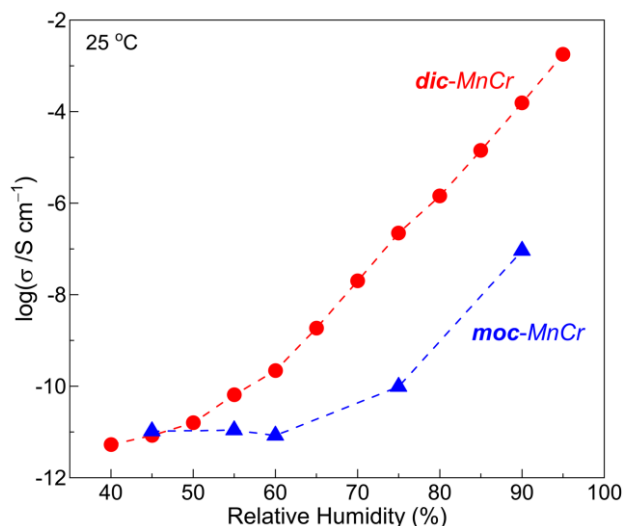
**Fig. 1** The dissymmetric sheet of *moc-MnCr* (left) with the carboxy-face and the *Bu*<sub>3</sub>-stratum and that of *dic-MnCr* (right) with the carboxy-face and the *AcBu*<sub>2</sub>-stratum. The *AcBu*<sub>2</sub>-stratum of *dic-MnCr* is drawn based on the powder X-ray diffraction analysis (see ESI). Manganese, chromium, carbon, nitrogen and oxygen atoms are drawn in yellow, green, grey, blue and red,

this work, we report the proton conduction of  $\{\text{NBu}_2(\text{CH}_2\text{COOH})_2\}[\text{MnCr}(\text{ox})_3]$  (*dic-MnCr*) in comparison with  $\{\text{NBu}_3(\text{CH}_2\text{COOH})\}[\text{MnCr}(\text{ox})_3]$  (*moc-MnCr*), to examine the carboxyl multiplication effect upon proton conduction. The preparation of *dic-MnCr* is given in Electronic Supplementary Information (ESI).

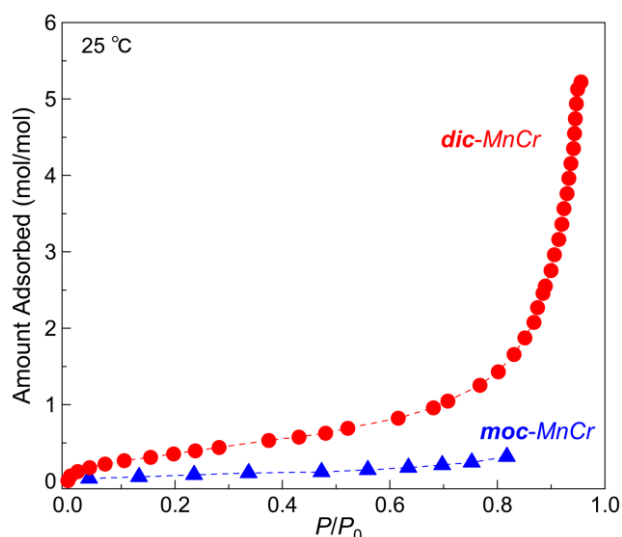
<sup>a</sup> Division of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan. Email: okawa134@outlook.jp, kazuya@kuchem.kyoto-u.ac.jp, kitagawa@kuchem.kyoto-u.ac.jp

<sup>b</sup> Department of Chemistry, Graduate School of Science, Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan.

†Electronic Supplementary Information (ESI) available: Experimental details, powder X-ray diffraction, FTIR, TG and Nyquist plots. See DOI: 10.1039/x0xx00000x



**Fig. 2** Relative humidity dependences of the proton conductivity of *dic-MnCr* (circles) and *moc-MnCr*<sup>17</sup> (triangles) at 25 °C. Due to sample stability at highly humidified condition, the conductivity plots for *moc-MnCr* are shown up to 90% RH.



**Fig. 3** The water adsorption isotherms of *dic-MnCr* (circles) and *moc-MnCr*<sup>17</sup> (triangles) at 25 °C.

The structure of *moc-MnCr* was reported previously.<sup>17</sup> The structural characteristics relevant to the present discussion are shortly mentioned below. In the crystal,  $\{\text{NBu}_3(\text{CH}_2\text{COOH})\}^+$  ions are aligned in one direction with the insertion of the carboxyl group into the honeycomb cavity and the orientation of the  $\text{NBu}_3$  residue in the interlayer space (Fig. 1, left). The bimetallic sheet is dissymmetric with respect to two faces. One face is characterized by the carboxyl OH groups protruding out of the cavities. The face is defined as the “*carboxy-face*”. The other face is covered by the stratum of *n*-butyl groups ( $\text{Bu}_3\text{-stratum}$ ) from the  $\text{NBu}_3$  residues. The proton transfer occurs through the interlayer space between the *carboxy-face* of one sheet and the  $\text{Bu}_3\text{-stratum}$  of the adjacent sheet. A similar layer structure is supposed for *dic-MnCr* because of the

resemblance of the powder X-ray diffraction pattern with that of *moc-MnCr*<sup>17</sup> (see Figs. S1 and S2 in ESI). Fourier transform infrared spectrum also supported the formation of the MnCr bimetallic layer structure as shown in Fig. S3 in ESI. The sheet of *dic-MnCr* has the *carboxy face* on one side and the stratum of the  $-\text{N}(\text{CH}_2\text{COOH})\text{Bu}_2$  residues (*AcBu}\_2\text{-stratum}*) on the other side (Fig. 1, right). The *AcBu}\_2\text{-stratum}* has some hydrophilic character in contrast to the hydrophobic nature of the  $\text{Bu}_3\text{-stratum}$  in *moc-MnCr*. The *AcBu}\_2\text{-stratum}* is probably disordered with respect to the conformation of the  $\text{N}(\text{CH}_2\text{COOH})\text{Bu}_2$  residues unless otherwise restricted. In Fig. 1, the disordered feature of the *AcBu}\_2\text{-stratum}* is shown based on the powder X-ray diffraction analysis (see ESI). Similar to *moc-MnCr*,<sup>17</sup> *dic-MnCr* is stable up to 300 °C as confirmed by thermogravimetric analysis (see Fig. S4 in ESI).

The proton conductivity vs. relative humidity (RH) profile of *dic-MnCr* at 25 °C is shown in Fig. 2 along with the profile of *moc-MnCr* for comparison. The proton conductivity of *moc-MnCr* is virtually invariant with  $\sim 1.1 \times 10^{-11} \text{ S cm}^{-1}$  in the 45–60% RH range and then increases to a moderate conductivity of  $5.2 \times 10^{-7} \text{ S cm}^{-1}$  at 90% RH. On the other hand, the conductivity of *dic-MnCr* increases from  $5.3 \times 10^{-12} \text{ S cm}^{-1}$  at 40% RH to a high value of  $1.8 \times 10^{-3} \text{ S cm}^{-1}$  at 95% RH. Obviously the *AcBu}\_2\text{-stratum}* is involved in the proton conduction under humidification conditions. Selected Nyquist plots of *dic-MnCr* are also shown in Figs. S5–S9 in ESI. The water adsorption isotherm of *dic-MnCr* is given in Fig. 3. Contrary to virtually no water adsorption in case of *moc-MnCr*,<sup>17b</sup> the water uptake in *dic-MnCr* increases to one molecule at  $\sim 70\%$  RH and then runs up to ca. 5 molecules at 95% RH. The Grotthuss mechanism<sup>19</sup> and the Vehicle mechanism<sup>20</sup> are proposed to explain the proton transfer in solid compounds. The Grotthuss mechanism refers to the proton mediation by infinite network of hydrogen bonds while the Vehicle mechanism refers to the transfer of  $\text{H}_3\text{O}^+$  through space. In the water adsorption isotherm of *dic-MnCr*, the saturation tendency above 90% RH is particularly noteworthy. This can be regarded as the completion of hydrogen-bonded network between the *carboxy-face* and the *AcBu}\_2\text{-stratum}*. It is well known that the activation energy of proton transfer ( $E_a$ ) is informative to inspect the proton conduction mechanism. In general, the  $E_a$  is lower than 0.5 eV for the Grotthuss mechanism whereas higher than 0.5 eV for the Vehicle mechanism.<sup>21</sup> To examine the proton transfer in *dic-MnCr* in regard to the water adsorption process, the activation energies were evaluated at different RHs by the Arrhenius plots of the proton conductivities (Fig. 4). Judging from the RH dependence of  $E_a$ , the proton conducting mechanism in *dic-MnCr* is similar to that of the Vehicle mechanism below 80% RH, whereas it is likely that the Grotthuss mechanism is dominant above 90% RH. Note that *dic-MnCr* shows unique RH sensitive  $E_a$  values that straddle the energy range between Vehicle- and Grotthuss-type proton conducting mechanisms.<sup>22</sup>

In Fig. 4, the activation energies below 80% RH vary significantly depending upon the RH investigated. This fact implies that the degree of conformational disorder of *AcBu<sub>2</sub>-stratum* is dependent on RH to influence the proton transfer through the interlayer space. Above 90% RH, the *carboxy-face* and the *AcBu<sub>2</sub>-stratum* work together in forming the hydrogen-bonded network. In the resulted network, the *AcBu<sub>2</sub>-stratum* must be ordered with the same conformation about the -N<sub>2</sub>AcBu<sub>2</sub> residues. We suppose that the Vehicle ↔ Grotthuss interconversion is accompanied by the “disordered” (below 80% RH) ↔ “ordered” (above 90% RH) phase interchange in the *AcBu<sub>2</sub>-stratum*. A sharp increase of water adsorption was observed at this humidity range (~80% RH, see Fig. 3). In addition, XRPD pattern of hydrated form also suggested the expansion of interlayer spacing and structural transition induced by water-vapour adsorption (see Fig. S10 in ESI). These results would support this assumption.

In conclusion, the proton conduction of {NBu<sub>2</sub>(CH<sub>2</sub>COOH)<sub>2</sub>}[MnCr(ox)<sub>3</sub>] (*dic-MnCr*) is remarkably enhanced relative to {NBu<sub>3</sub>(CH<sub>2</sub>COOH)}[MnCr(ox)<sub>3</sub>] (*moc-MnCr*) by the multiplication of the carboxyl carrier in the cation component. Studies on analogous MOFs composed of tri(carboxyl)- or tetra(carboxyl)-ammonium ions are underway.

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## Conflicts of interest

There are no conflicts to declare.

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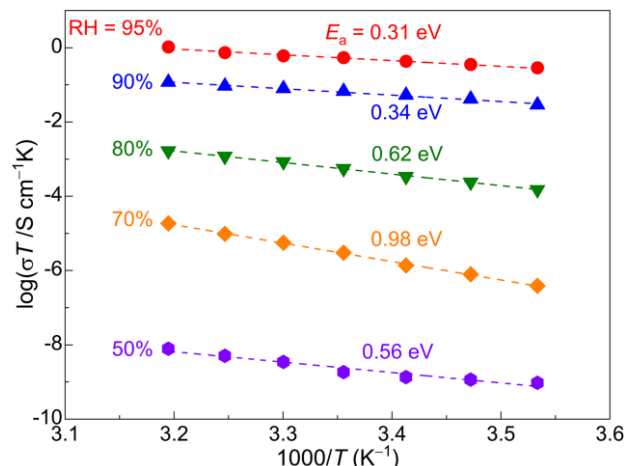
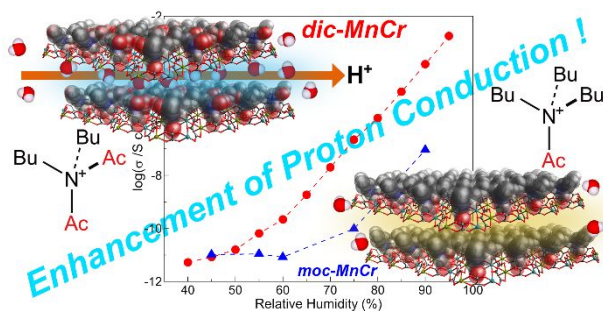


Fig. 4 Arrhenius plots of the proton conductivity for *dic-MnCr* at different RHs.

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$\{\text{NBu}_2(\text{CH}_2\text{COOH})_2\}[\text{MnCr}(\text{ox})_3]$  (*dic-MnCr*) shows significantly enhanced proton conduction ( $1.8 \times 10^{-3} \text{ Scm}^{-1}$  at 95% RH) relative to  $\{\text{NBu}_3(\text{CH}_2\text{COOH})\}[\text{MnCr}(\text{ox})_3]$  by the multiplication of the carboxyl carrier in the cation.



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#### ORCID information for Authors

Dr. Kazuya Otsubo: 0000-0003-4688-2822

Dr. Yukihiro Yoshida: 0000-0003-4630-9559

Prof. Hiroshi Kitagawa: 0000-0001-6955-3015