Anion Stripping as a General Method to Create Cationic Porous Framework with Mobile Anions

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Ⓢ *Supporting Information*

ABSTRACT: Metal−organic frameworks (MOFs) with cationic frameworks and mobile anions have many applications from sensing, anion exchange and separation, to fast ion conductivity. Despite recent progress, the vast majority of MOFs have neutral frameworks. A common mechanism for the formation of neutral frameworks is the attachment of anionic species such as F^- or OH^- to the framework metal sites, neutralizing an otherwise cationic scaffolding. Here, we report a general method capable of converting such neutral frameworks directly into cationic ones with concurrent generation of mobile anions. Our method is based on the differential affinity between distinct metal ions with framework anionic species. Specifically, Al^{3+} is used to strip F^- anions away from framework Cr^{3+} sites, leading to cationic frameworks with mobile Cl^- anions. The subsequent anion exchange with OH^- further leads to a porous network with mobile OH^- anions. New materials prepared by anion stripping can undergo ion exchange with anionic organic dyes and also exhibit much improved ionic conductivity compared to the original unmodified MOFs.

Metal organic frameworks (MOFs) are porous materials assembled from metal ions or clusters and organic ligands and have shown potential applications in fields such as gas storage and adsorption,[1] catalysis,[2] drug delivery,[3] electrochemistry, and photoelectrochemistry.[4] Recent reports have also demonstrated high proton conductivities.[5] Water-mediated proton-conducting MOFs operating at low temperatures and anhydrous proton-conducting MOFs working at intermediate temperatures[6] have been well investigated. The design flexibility and framework stability have made MOFs a versatile platform for different types of ion conducting materials. The crystalline nature of MOF materials further allows precise determination of their structures,[7] providing an opportunity to probe the conduction mechanism, which is vital to the rational design and development of new generations of ion conductors.

Fuel cells are among a number of viable options to address today's energy and environmental concerns.[8] Ion exchange membranes are a crucial component of fuel cells, acting as a barrier between the fuel and the oxidizing agent while transporting charges from one electrode to another within the cell. Although current state-of-art fuel cells employ Nafion-family proton conductors,[9] anion exchange membrane fuel cells are now attracting growing interest due to their potential advantages,[10] especially their favorable oxygen reduction kinetics, which would allow for less platinum loading on the electrodes or even nonprecious metal catalysts during the electrochemistry process. While significant efforts have been put into developing MOFs for proton exchange membrane fuel cells, few studies have been reported on anion-conducting MOFs that could be utilized in anion exchange membrane fuel cells.[11]

Anion conductivity can be achieved with the same strategy used for the synthesis of cationic frameworks.[12] However, unless there are special factors at play, the direct synthesis of stable and porous MOFs favors neutral frameworks. Given the fact that a large pool of neutral frameworks are available, postsynthetic methods[13] that allow the conversion of neutral frameworks into cationic ones are highly desirable. Here, we demonstrate a method (termed anion stripping) that can be used to accomplish this task. By taking advantage of the stronger affinity of F^- to Al^{3+} than to Cr^{3+} or Fe^{3+}, this method uses Al^{3+} to strip Cr^{3+}-bonded F^- ions away from Cr^{3+} sites and replaces charge-balancing framework-attached F^- anions with mobile Cl^- and OH^- anions. (Scheme 1)

The postsynthetic modification of the original MIL-100[14] (denoted as MIL-100-Cr-F and MIL-100-Fe-F) was performed in two steps, through exchange of F^- with Cl^- and OH^- sequentially. The removal of strongly bonded F^- on Cr^{3+} or Fe^{3+} in MIL-100-Cr-F or MIL-100-Fe-F was achieved by soaking their respective pristine powders in $AlCl_3$ solutions. For

Scheme 1. Illustration of the anion stripping process with $AlCl_3$[a]
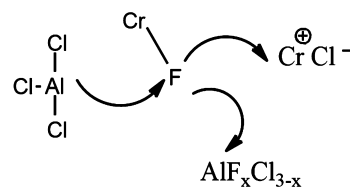
[a]Use of the concentrated NaCl solution (5 M) resulted in no stripping of F^-, and no inclusion of Cl^- was observed.

charge balance, chloride ions enter the pore to replace F⁻. Following the modification, the solid was collected by filtration and washed several times to remove extra ions that might be adsorbed on the solid surface. Considering that OH^- conductors are desirable in fuel cells, MIL-100-Cr-Cl powders were further soaked in NaOH solution to exchange Cl^- with OH^-. While the conversion of MIL-100-Cr-Cl into MIL-100-Cr-OH was successful, the conversion of MIL-100-Fe-Cl failed since it appeared unstable under the alkaline conditions used here.

Crystallinity and porosity of samples after the modification were monitored by PXRD and N_2 adsorption measurements. As indicated by the PXRD results in Figure 1a, modified
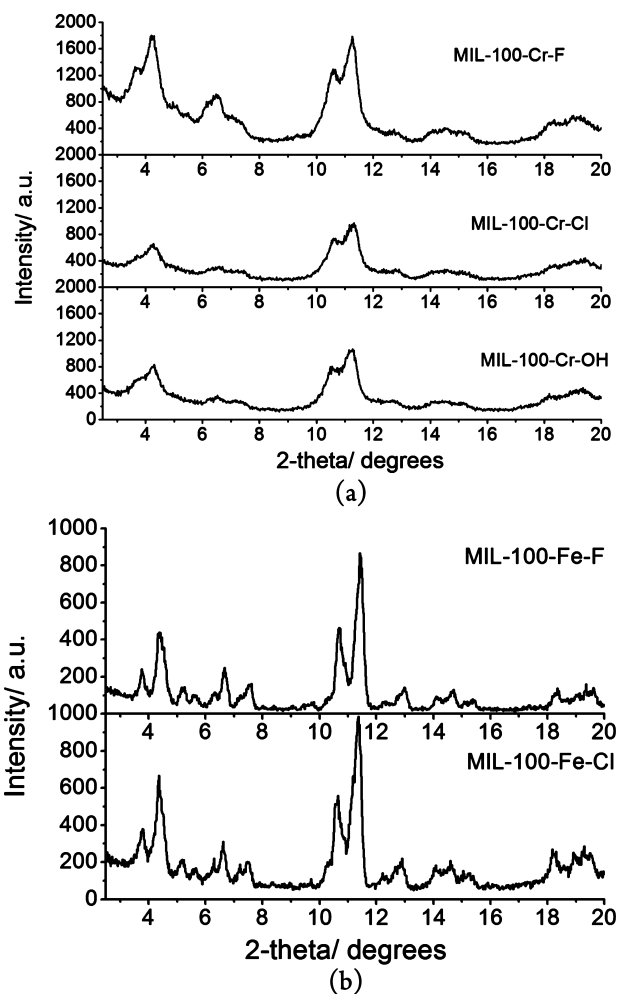

Figure 1. PXRD patterns of MIL-100-Cr-F (a), MIL-100-Fe-F (b), and their modified forms.

samples (MIL-100-Cr-Cl and MIL-100-Cr-OH) remained highly crystalline, even though some peaks were broadened, likely due to the reduced particle size caused by the modification. As for MIL-100-Fe-Cl, no any loss of crystallinity was detected by the PXRD analysis (Figure 1b). Furthermore, the porosity of MIL-100-Cr-Cl and MIL-100-Fe-Cl remained intact as shown by the N_2 adsorption data (Figure S2). MIL-101-Cr-Cl[15] also stayed intact after the modification (Figure S3).

The successful replacement of F⁻ by Cl⁻ in MIL-100-Cr and MIL-100-Fe was confirmed by the EDX analysis. The SEM images (Figures S7a and S8a) show the as-prepared samples as

small octahedra. Both as-synthesized MIL-100-Cr-F and MIL-100-Fe-F have F peaks on the EDX spectra (Figures S7b and S8b), because F is bonded to Cr^{3+} or Fe^{3+}. However, no F peaks were detected for MIL-100-Cr-Cl or MIL-100-Fe-Cl, while new Cl^- peaks appeared (Figures S7c and S8c).

The evidence for the replacement of F⁻ by Cl⁻ and for the mobility of Cl^- ions was further shown by the precipitation experiment with $AgNO_3$ (see Supporting Information (SI)). By soaking MIL-100-Cr-Cl in the $AgNO_3$ solution, no precipitation was observed, ruling out the possible surface-adsorbed Cl^- residues on the powder. Next, the Cl^- was displaced out of the pores into the solution by anion exchange with the concentrated $NaNO_3$ solution. As a result, the NO_3^- exchanged solution readily underwent the precipitation reaction with Ag^+ ions in the solution (Figure S6), which not only confirmed the presence of Cl^- ions in the pores but also their mobility.

The exchange of OH^- for Cl^- in MIL-100-Cr-OH could first be inferred from the decreased Cl/Cr ratio (based on the EDX data) following the exchange of Cl^- with OH^- (Table S1). Because a fixed amount of anions are required to balance the charge, the decreased Cl/Cr ratio following the exchange with OH^- suggests that some Cl^- anions had been replaced with OH^-.

Further support for the inclusion of the OH^- anion into the framework comes from solid-state NMR spectroscopy. Figure 2
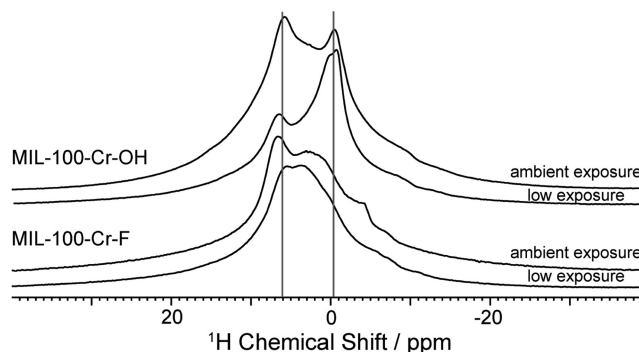

Figure 2. ¹H spectra for MIL-100-Cr-F and MIL-100-Cr-OH obtained from solid-state NMR.

shows ¹H spectra for MIL-100-Cr-F and MIL-100-Cr-OH under conditions of low and ambient exposure to moisture. Inclusion of OH^- correlates with an additional peak at −0.2 ppm, while increasing hydration leads to increased downfield peak intensity at 6.1 ppm. We therefore assign these peaks to the hydrogens of hydroxide and water, respectively. Both peaks are found to relax quickly (Figure S9), consistent with direct association with the paramagnetic Cr sites. A third spectral component, centered at ∼3.7 ppm, is assigned to hydrogens on the aromatic ligands. These assignments are consistent with similar observations in other paramagnetic MOF systems.[16] Two-dimensional (2D) chemical-shift−chemical-shift correlation experiments allow better resolution of the three sites, as shown in the SI. Also evident in the 2D spectrum is a "ridge" of more slowly relaxing hydrogens that we tentatively assign to nonspecifically adsorbed water within the porous framework.

The mobility of Cl^- anions was further confirmed by ion exchange[17] with anionic organic dye molecules (See SI). Figure 3 shows the UV−vis spectra for a series of Orange G (OG) solutions that were treated by the original MIL-100-Cr-F and modified MIL-100-Cr-Cl (labeled as MIL-100-Cr-Cl-0, 1, 3,
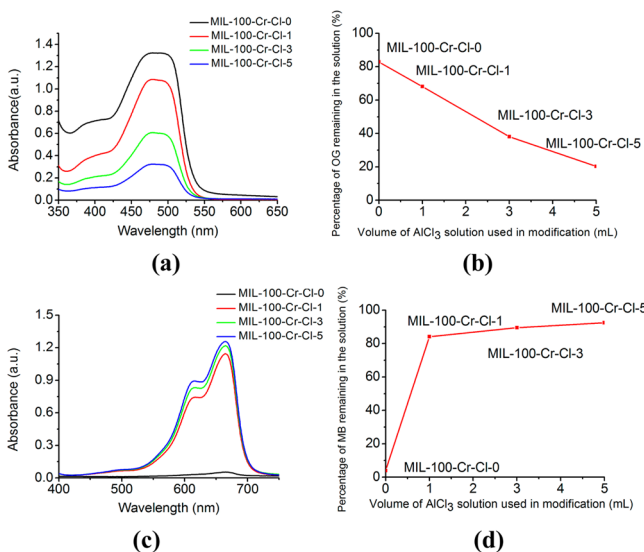
Figure 3. UV−vis absorbance and remaining percentage of OG (a, b) and MB (c, d) treated by MIL-100-Cr-F and its modified forms.

and 5, respectively, corresponding to different amount of AlCl$_3$ used for anion stripping, details in SI). The decreasing absorbance of OG solutions (following exchange with Cl$^-$) was the direct evidence of increased anion-exchange abilities of modified MIL-100-Cr-Cl, due to the high mobility of Cl$^-$. For the original unmodified MIL-100-Cr-F, the only way to trap OG is by physical adsorption of both organic anions (OG^{2-}) and its counter cations (i.e., Na$^+$). But for modified MIL-100-Cr-Cl with mobile Cl$^-$ ions, the exchange of Cl$^-$ anions with OG^{2-} anions could take place, leading to an improved uptake of OG^{2-} anions. With more mobile Cl$^-$ ions introduced into the framework, more OG^{2-} can be exchanged into the pores, as evidenced in Figure 3b.

In addition to significantly improved anion exchange property, the conversion of neutral MIL-100-Cr-F into cationic MIL-100-Cr-Cl had a dramatic effect on their cation exchange properties.[18] Positively charged methylene blue (MB) was chosen here. The MB solution turned almost clear when unmodified neutral MIL-100-Cr-F was soaked in them for 1 day, showing a good adsorption ability by neutral MIL-100-Cr for MB. The higher adsorption ability of neutral MILs for MB$^+$ than for OG^{2-} is likely due to relatively smaller size of MB cation than OG anion (Table S2). However, a dramatic decrease in the adsorption ability for MB cations took place even after neutral MIL-100-Cr-F was treated with a small amount of AlCl$_3$ (Figure 3c,d). This result can be explained by the fact that the cationic framework MIL-100-Cr-Cl obtained from our modification repels cationic dyes, while neutral unmodified MIL-100-Cr-F is more receptive to cationic dyes. Similar results were obtained for both MIL-100-Fe (Figure S4) and MIL-101-Cr (Figure S5)

The conversion of neutral MIL-100-Cr-F (as well as the Fe form) into MIL-100-Cr-Cl with mobile chloride led to a dramatic enhancement in their ion-conduction properties. To characterize the ion conductivity of MIL-100-Cr-Cl, AC impedance measurement was performed on pellet samples (See SI). A representative Nyquist plot is shown in Figure S10, which consists of a semicircle at the high-frequency region and a spike tail at the low-frequency region. The low-frequency tail corresponds to the blocking effect at the electrolyte-electrode interface, consistent with the fact that the ions are unable to

diffuse into the stainless steel plate. Here, bulk and boundary contributions to the total resistivity are not resolved clearly into two separate semicircles at the high-frequency region. Analysis on MIL-100-Cr-Cl in ambient environment gave a conductivity of 1.4×10^{-6} S cm^{-1} and rose up to 1.6×10^{-5} S cm^{-1} as the relative humidity increased to 99.9% (Figure 4). Similar trend
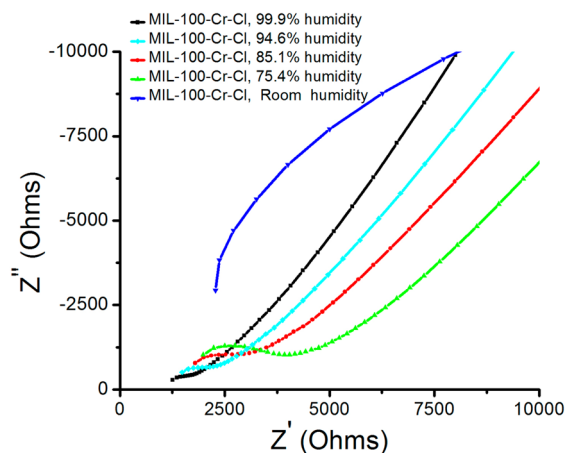

Figure 4. Nyquist plot of MIL-100-Cr-Cl under various humidity.

was observed for MIL-100-Fe-Cl (Figure S13), which had a lower conductivity of about 1.3×10^{-6} S cm^{-1} at low humidity, but reached 6.0×10^{-5} S cm^{-1} at 99.9% RH. Considering the comparable charge carrier concentration, significant difference in conductivities between MIL-100-Cr-Cl and MIL-100-Fe-Cl might be related to the differing Cl$^-$ mobility within the framework, resulting from different interaction between Cl$^-$ ions and frameworks, especially the metal ions (Cr^{3+} vs Fe^{3+}) with open metal sites but different Lewis hardness. The conductivity shown here is within the range of other MOF-based ion conductors, which mostly varies from 10^{-3} to 10^{-7} S cm^{-1}.[5d]

To further demonstrate the significant enhancement in conductivity following our postsynthetic modification, the ac impedance measurement was also performed on unmodified MIL-100-Cr-F and MIL-100-Fe-F at 99.9% RH (Figures S11 and S15). The radius of the semicircle at the high-frequency region was significant larger than the modified one, indicating the poor conducting nature of unmodified MIL-100-Cr-F and MIL-100-Fe-F.

When Cl$^-$ ions were partially replaced by OH$^-$ in MIL-100-Cr, we could still observe increasing conductivity for MIL-100 Cr-OH as the humidity increased (Figure S14). However, it was lower than that of MIL-100-Cr-Cl. The decreased conductivity might be due to the stronger interaction between OH$^-$ and the framework, resulting in the lower mobility of OH$^-$ compared to Cl$^-$ ions. When the sample was heated up while maintaining the same relative humidity, smaller semicircle appeared at the high-frequency region, corresponding to an enhanced conductivity. This trend was expected from the Arrhenius relationship, which indicated the temperature dependence of charge carrier mobility. In fact, the conductivity of MIL-100-Cr-OH was found to follow the linear relationship with temperature in the Arrhenius plot, as shown in Figure 5.

In summary, we have presented an effective approach to produce cationic MOFs with mobile anions by postsynthetic modification on a neutral framework. A significant enhancement in the ion conductivity was observed following the F$^-$
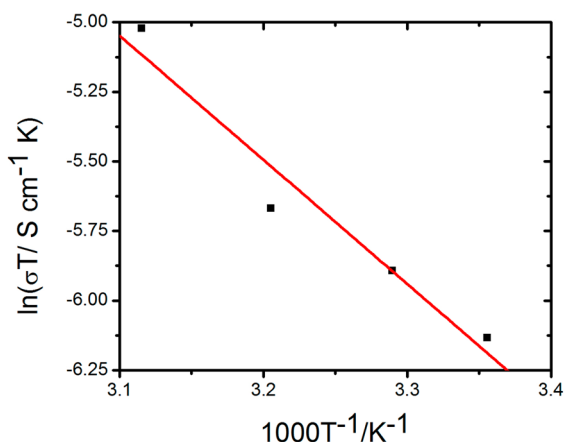
Figure 5. Arrhenius plot for MIL-100-Cr-OH (E_a = 0.38 eV).

stripping, coupled with the introduction of mobile Cl^-/OH^- anions. The mobility of extra framework anions was also confirmed by anion exchange with charged organic dyes. The synthetic method reported here should be generally applicable to other materials as well and represents a new avenue for the development of cationic framework materials with potential applications in fuel cells.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Experimental details and additional figures. 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.

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