

Rational Control of Ionic Conduction of Encapsulated Ionic Liquid by Fluorination of Isorecticular Metal–Organic Frameworks

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ABSTRACT: Hybrid materials have attracted much attention in solid-state conductors because of their great advantage in various combinations of components. In this study, the control of ionic conductivity of ionic liquid (IL), which is encapsulated in micropores of metal–organic frameworks (MOFs), has been realized by the chemical modification of the ligands of MOFs for the first time. When IL, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ((EMI)(TFSA)), is encapsulated into the pores with a 50% volumetric filling level, it shows the highest ionic conductivity when encapsulated in the fluororous MOF among the three isorecticular zinc-based microporous MOFs; the ionic diffusivity is one order of magnitude higher than that of (EMI)(TFSA)-encapsulated non-fluororous MOF. Computational simulations indicate that the mobility of (EMI)(TFSA) in non-fluororous framework is significantly restricted due to abundant C–H...F interactions, whereas the introduction of fluorine atoms on the ligands suppresses the C–H...F interactions, thereby showing the highest ionic conductivity. On the other hand, the ion migration of encapsulated (EMI)(TFSA) is not greatly affected by the fluorination of the ligands at a 100% filling level, because the possible different IL distributions with a 50% filling level is largely eliminated for the fully occupied (EMI)(TFSA).

Introduction

Ion batteries have played a pivotal role as energy storage devices because of their high energy density and cyclability.^{1–5} Given that liquid electrolytes as the indispensable component are highly controversial due to their flammability and susceptibility to leakage, solid-state electrolytes, known for their high safety, are one of the most promising alternatives of current researches.⁶ Recently, hybrid materials, which consist of host and guest materials, have become increasingly important because of their high designability for integrating the solid-state electrolytes using diverse components. For guest materials, ionic liquids (ILs), which are entirely composed of ions and melt at room temperature, have been investigated as potential electrolytes because of their high ion density and ionic conductivity.^{7–11} Notably, the former results in their negligible vapor pressure and inflammability, which endow them with higher safety compared to conventional liquid electrolytes. For host materials with porous structures, it is well-established that metal–organic frameworks (MOFs) can control their porous properties such as porous structure and surface potential by judiciously selecting the component metal ions (or clusters) and organic linkers.^{12–15} However, to date, efforts to control the ionic conductivity in IL-encapsulated MOF hybrid materials have been devoted to regulating the filling ratio or species of the encapsulated ILs.^{15–22} The control of ionic conductivity by modifying ligands of MOFs while keeping the porous structure has not yet been

accomplished, although functional groups of the ligands can have a significant interaction with guest molecules encapsulated in the pores.

In this study, we focused on the difference in binding energy between C–H...F and C–F...F interactions, primarily arising from the low polarizability of fluorine (Figure 1a).^{23–}

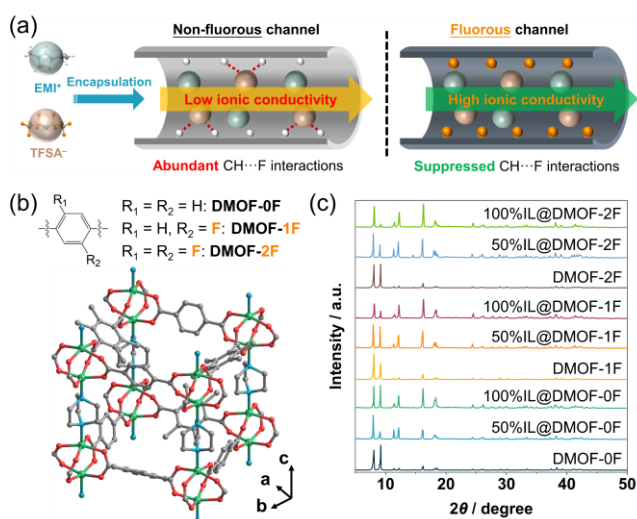


Figure 1. (a) Schematic image of ionic conduction of fluorinated IL in non-fluororous (left) and fluororous (right) channels. (b) Crystal structure of DMOF-0F. (c) PXRD patterns of DMOF-xFs, 50%IL@DMOF-xFs, and 100%IL@DMOF-xFs.

²⁵ To this end, a series of Zn-based microporous MOFs, $\text{Zn}_2(\text{xFBDC})(\text{tmBDC})(\text{DABCO})$ (hereafter **DMOF-xFs**), where x denotes the number of fluorine on the terephthalate ligands (xFBDC^{2-} ; $x = 0, 1$, and 2), was chosen as the host materials (tmBDC²⁻: tetramethylterephthalate, DABCO: 1,4-diazabicyclo[2.2.2]octane) mainly based on the following reasons: (1) Fluorination of **DMOF-xFs** can produce the isoreticular manipulation, enabling the systematic investigation of fluorination effects on ion-conducting behavior. Among a series of **DMOF-xFs**, the inclusion of tmBDC ligands endows the framework structure with high stability under aerobic conditions.²⁶ (2) The microporous framework structure (pore size ~ 0.6 nm) can provide a compelling platform for investigating the effect of fluorination on the pore wall-IL interactions.²⁷ We introduced a certain amount of 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ((EMI)(TFSA)), which is one of the most widely used fluorinated ILs in electrochemical applications, as the guest materials largely because of its excellent electrochemical and thermal stability.^{28–30} Electrochemical impedance measurements revealed that ion-conducting behavior of (EMI)(TFSA)-encapsulated **DMOF-xFs** (hereafter **IL@DMOF-xFs**) depends largely on the IL filling level, which is explained in terms of the C–H $\cdots$ F interactions. The present work would provide a new strategy for developing and understanding the ionic conducting hybrid materials.

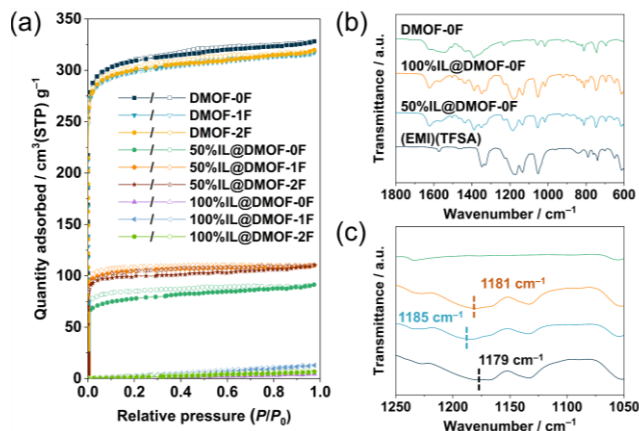


Figure 2. (a) N₂ gas adsorption/desorption isotherms of **DMOF-xFs**, **50%IL@DMOF-xFs**, and **100%IL@DMOF-xFs**. (b) FT-IR spectra of bulk (EMI)(TFSA), **DMOF-0F**, **50%IL@DMOF-0F**, and **100%IL@DMOF-0F**. (c) shows enlarged FT-IR spectra in the range of 1050–1250 cm⁻¹.

Results and Discussion

All the pristine **DMOF-xFs** ($x = 0, 1$, and 2) were synthesized using the solvothermal method according to the literature and activated at elevated temperature under vacuum (see experimental details in the Supporting Information and Figure S1).^{31,32} We note that attempts to obtain the single crystals of **DMOF-4F** (i.e., $x = 4$) with tetrafluoro-BDC ligands are presently unsuccessful. The crystal structures of pristine **DMOF-xFs** have been determined by single-crystal X-ray diffraction (SCXRD) measurements as reported in our previous paper.³² To recap briefly, the three **DMOF-xFs** are isomorphous in the tetragonal system, with terephthalate-based linkers (xFBDC^{2-} or tmBDC^{2-}) bridging the Zn dimers in the ab plane and DABCO units pillaring the dimers along

the c axis (Figure 1b for **DMOF-0F** as an example). We note that the fast-rotating motion of DABCO units³³ have an unfavorable effect on the hydrogen-bonding interaction with component ions of (EMI)(TFSA). As shown in Figure 1c, the polycrystalline **DMOF-xFs** after the activation exhibit powder X-ray diffraction (PXRD) patterns identical to those simulated from the SCXRD measurements, indicating their high purity suitable for the following measurements. N₂ gas adsorption/desorption measurements revealed that the three **DMOF-xFs** have comparable surface areas and pore volumes, i.e., 1229 m² g⁻¹ and 0.51 cm³ g⁻¹ for **DMOF-0F**, 1192 m² g⁻¹ and 0.49 cm³ g⁻¹ for **DMOF-1F**, and 1197 m² g⁻¹ and 0.49 cm³ g⁻¹ for **DMOF-2F** (Figure 2a). Thus, it is noticeable that these **DMOF-xFs** have a microporous framework structure with similar porous properties, which apparently provides an optimal platform to investigate the effect of the fluorination of MOFs on ionic diffusion of guest ions in the micropores.

Three hybrid materials, namely (EMI)(TFSA)-encapsulated **DMOF-xFs**, were prepared by grinding (EMI)(TFSA) and each **DMOF-xF** in a mortar and annealed under vacuum for capillary action (see experimental details in the Supporting Information).^{34,35} where an adequate amount of (EMI)(TFSA) was weighted and mixed with each **DMOF-xF** to fill 50% of the pore space based on the calculated pore volume (hereafter **50%IL@DMOF-xF**). Figure 1c displays the PXRD patterns of **DMOF-xFs** before and after the encapsulation. Given that all the diffraction peaks remain the 2θ positions, it is obvious that the framework structure is well kept throughout the encapsulation process. As shown in Figure S2, scanning electron microscope (SEM) images revealed that the irregular morphology of pristine **DMOF-xFs** after grinding remained almost unchanged during the introducing of IL. Thermogravimetric (TG) profiles under N₂ atmosphere confirmed that **50%IL@DMOF-xFs** are thermodynamically stable up to approximately 300 °C (Figures S3–S5). It is known that the reduced thermal stability of (EMI)(TFSA) compared to the bulk state is associated with the suppressed thermal relaxation due to the electrostatic interaction with the pore surface.³⁶ N₂ gas adsorption/desorption isotherms of **50%IL@DMOF-xFs** show a considerable decrease in N₂ uptakes compared to pristine **DMOF-xFs** (i.e., 328 to 91 cm³ g⁻¹ for **DMOF-0F**, 317 to 110 cm³ g⁻¹ for **DMOF-1F**, and 320 to 110 cm³ g⁻¹ for **DMOF-2F**; Figure 2a). Notably, pore size distributions calculated using the non-local density functional theory (NLDFT) method suggest that the pore size of **DMOF-1F** (0.97 to 0.91 nm) and **DMOF-2F** (1.00 to 0.95 nm) remained almost unchanged after the IL encapsulation in contrast to the significant decrease in **DMOF-0F** (1.12 to 0.91 nm) as shown in Figures S6–S8. The unchanged pore size despite decreasing the pore volume in fluorinated MOFs is indicative of the inhomogeneous introduction of IL in the micropores due to the suppressed C–H $\cdots$ F interactions (see below). To investigate the ion-conducting behavior under a homogeneous filling condition, we prepare three **IL@DMOF-xFs** with 100% IL filling ratio (hereafter **100%IL@DMOF-xF**) using the same procedure as for **50%IL@DMOF-xFs**. The N₂ uptakes became negligible for **100%IL@DMOF-xFs** as shown in Figure 2a, and the gradual decrease in the N₂ uptake with increasing the IL filling level is compelling evidence of the

encapsulation of IL into the pores of **DMOF-xFs** rather than the deposit on the particle surface to interrupt the adsorption of N_2 gas.

Differential scanning calorimetry (DSC) measurements were performed on the six hybrid materials (i.e., $y\%$ **IL@DMOF-xFs**; $y = 50$ and 100) to evaluate the thermal behavior of (EMI)(TFSA) in the pores. As shown in Figure S9, bulk (EMI)(TFSA) exhibits an exothermic peak at -40°C upon cooling and an endothermic peak at -15°C upon heating, corresponding to the freezing and melting events, respectively. On the other hand, $y\%$ **IL@DMOF-xFs** showed little trace of the DSC peaks (Figure S9) indicating that (EMI)(TFSA) in the pores remains in the liquid state down to ca. -170°C due to the nanosize effect as reported previously.¹⁶ The calorimetric properties also affirmed the IL encapsulation into the pores of **DMOF-xFs**.

Raman spectra were measured to investigate the intermolecular interaction between the encapsulated IL and the frameworks (Figure S10). The peak at 740 cm^{-1} , which is attributed to the CF_3 bending vibration coupled with the S–N–S stretching vibration in (EMI)(TFSA),³⁷ exhibited a negligible shift after the encapsulation. However, Fourier transform infrared (FT-IR) spectra of **IL@DMOF-xFs** (Figures 2b, 2c and S11) exhibited a striking difference from that of bulk (EMI)(TFSA). Taking **IL@DMOF-0F** as an example, the CF_3 antisymmetric stretching mode,³⁸ which was observed at 1179 cm^{-1} in bulk (EMI)(TFSA), shows a slight but distinct blue shift in $y\%$ **IL@DMOF-0F** (1185 cm^{-1} for $y = 50$ and 1181 cm^{-1} for $y = 100$), indicating the existence of ion-framework Coulombic interactions between TFSA⁻ anions and **DMOF-0F**. The interaction can be readily assigned to the $\text{CH}\cdots\text{F}$ hydrogen bonding interaction, where the hydrogen atom comes from BDC, tmBDC, or DABCO ligand.

Given that one of the most striking effects of the ion-framework interactions is the ionic conduction of (EMI)(TFSA) encapsulated in the pores, AC impedance spectroscopy measurements of all the hybrid materials were performed in the temperature range of 25 and 60°C under dried conditions (30% relative humidity (RH)). PXRD and FT-IR measurements confirmed that the structure of **IL@DMOF-xFs** remained almost intact during the measurements (Figures S12–S17). As shown in Figures 3a–3c, the ionic conductivity (σ) of compressed pellets of all the hybrid materials exhibits a steady increase with increasing the IL filling level; i.e., 1.1×10^{-10} to $3.8 \times 10^{-5}\text{ S cm}^{-1}$ at 25°C for **50%IL@DMOF-0F** to **100%IL@DMOF-0F**, 1.6×10^{-10} to $5.0 \times 10^{-5}\text{ S cm}^{-1}$ for **50%IL@DMOF-1F** to **100%IL@DMOF-1F**, and 9.0×10^{-10} to $2.7 \times 10^{-5}\text{ S cm}^{-1}$ for **50%IL@DMOF-2F** to **100%IL@DMOF-2F**. The ion-conducting behavior of **100%IL@DMOF-xFs** is comparable to those of reported **IL@MOF** hybrid materials (Table S1). It is noteworthy that the σ value of **50%IL@DMOF-2F** is one order higher than those of **50%IL@DMOF-0F** and **50%IL@DMOF-1F**, possibly associated with the reduced ion-framework interactions by the fluorination of BDC ligands (see below). On the other hand, the ionic conductivity of **100%IL@DMOF-2F** has the same order of magnitude as those of **100%IL@DMOF-0F** and **100%IL@DMOF-1F**. A possible explanation is that the different distributions of IL in the pores of **50%IL@DMOF-xFs**, namely, the preferential IL occupations near the pore surface of the non-fluorous MOF

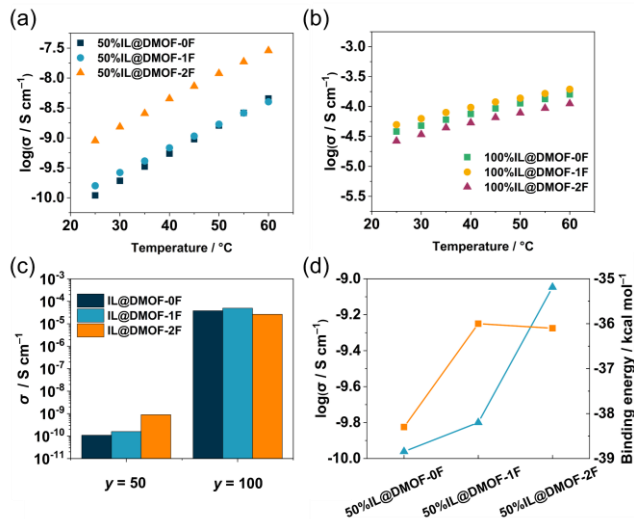


Figure 3. Temperature dependence of ionic conductivity (σ) of (a) **50%IL@DMOF-xFs** and (b) **100%IL@DMOF-xFs**. (c) Ionic conductivity of **50%IL@DMOF-xFs** ($y = 50$) and **100%IL@DMOF-xFs** ($y = 100$) at 25°C . (d) Ionic conductivity at 25°C (pale blue triangles) and calculated binding energy (orange squares) of **50%IL@DMOF-xFs**.

through the $\text{C-H}\cdots\text{F}$ interactions and near the core of the pores of the fluorous MOF like hydrophobic interactions, are largely eliminated in the fully occupied pore space of **100%IL@DMOF-xFs**, which leads to the comparable ionic conductivity as shown in Figure 3b. We note that this is the first example to demonstrate the control of ionic conductivity by chemically modifying the ligands while keeping the framework structure.

Ionic conductivity of all the hybrid materials exhibited the Arrhenius-type temperature dependence (Figures 3a and 3b). The activation energies (E_a s) estimated using the Arrhenius equation given by $\sigma T = A \exp(-E_a/k_B T)$ (A : pre-exponential factor; k_B : Boltzmann constant) of **100%IL@DMOF-xFs** (0.36 – 0.38 eV) are significantly lower than those of **50%IL@DMOF-xFs** (0.82 – 0.93 eV). The highest ionic conductivity was $4.3 \times 10^{-4}\text{ S cm}^{-1}$ when **100%IL@DMOF-1F** was heated at 85°C (Figure S18), which is the highest accessible temperature under the measurement conditions (30% RH).

To extract the mobility of component ions, the ion diffusivity (D) was estimated using the Nernst–Einstein equation, $D = ART/z^2 F^2$ (A : molar conductivity; $A = \sigma/M$, where M is the molar concentration, R : universal gas constant, z : charge of ions, F : Faraday constant). As expected from Figure 3b, the D values at 25°C of **100%IL@DMOF-xFs** ($2.6 \times 10^{-13}\text{ m}^2\text{ s}^{-1}$ for $x = 0$, $3.3 \times 10^{-13}\text{ m}^2\text{ s}^{-1}$ for $x = 1$, and $1.8 \times 10^{-13}\text{ m}^2\text{ s}^{-1}$ for $x = 2$) are significantly higher than those of **50%IL@DMOF-xFs**. It is noteworthy that the value of **50%IL@DMOF-2F** ($1.3 \times 10^{-17}\text{ m}^2\text{ s}^{-1}$) is one order higher than those of **50%IL@DMOF-0F** ($1.5 \times 10^{-18}\text{ m}^2\text{ s}^{-1}$) and **50%IL@DMOF-1F** ($2.2 \times 10^{-18}\text{ m}^2\text{ s}^{-1}$), confirming that **50%IL@DMOF-2F** involves the most mobile ions in the pores among the three **50%IL@DMOF-xFs**. These results are highly indicative of the lower interactions between TFSA⁻ anions and **DMOF-2Fs**.

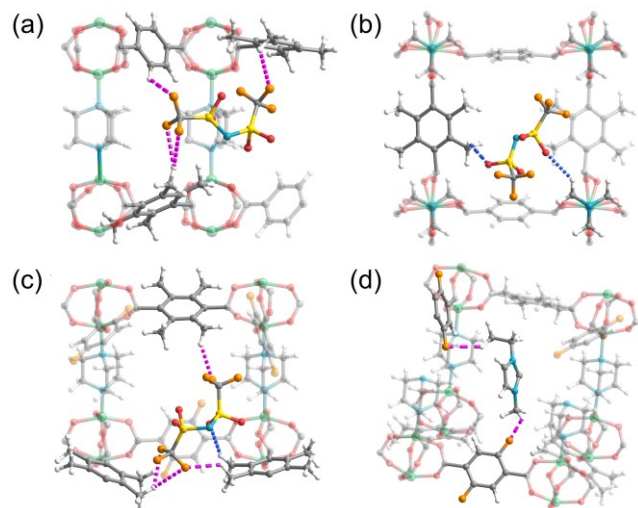


Figure 4. Simulated C-H...F short contacts (dotted pink lines) and C-H...O short contacts (dotted dark blue lines) in (a,b) **50%IL@DMOF-0F** and (c,d) **50%IL@DMOF-2F** frameworks. Frameworks without any interactions with IL are shown as translucent. Color code: C: grey; H: white; F: orange; N: blue; O: red; S: golden; Zn: green.

To assess the intermolecular interaction from the computational viewpoint, the binding energy between IL and the frameworks was calculated from the difference of total energies using the grand canonical Monte Carlo (GCMC) method.³⁹ The calculated binding energies, i.e., $-38.3 \text{ kcal mol}^{-1}$ for **IL@DMOF-0F**, $-36.0 \text{ kcal mol}^{-1}$ for **IL@DMOF-1F**, and $-36.1 \text{ kcal mol}^{-1}$ for **IL@DMOF-2F**, under the assumption that a pair of component ions of (EMI)(TFSA) is present in the unit cell (equivalent to ca. 25% IL filling level) confirmed the weakest ion-framework interactions in **IL@DMOF-2F** (Figure 3d). As displayed in Figures 4a and 4b, the TFSA⁻ anion in **IL@DMOF-0F** interacts with the adjacent BDC and tmBDC ligands through C-H...F hydrogen bonds with a F...H distance of 2.56–2.74 Å (vs. the sum of the van der Waals radii: 2.67 Å; ref. 40). Besides, two oxygen atoms of sulfonyl groups in the TFSA⁻ anion have short interatomic contacts with a tmBDC ligand (O...H distance: 2.69 Å vs. sum of the van der Waals radii: 2.72 Å; ref. 40) and with a DABCO ligand (O...H distance: 2.71 Å). On the other hand, in **IL@DMOF-2F**, there is no indication of F...H interactions between the TFSA⁻ anion and BDC ligands, although the F...H interactions between the TFSA⁻ anion and tmBDC ligands were found (F...H distance: 2.53–2.77 Å; Figures 4c and 4d). The difference in ion-framework interactions between **IL@DMOF-0F** and **IL@DMOF-2F** is apparently as a consequence of the fluorination of BDC ligands, which can interrupt the C-H...F interactions in the favorable direction of increased ion migration. Accordingly, we could control the ionic conductivity of IL-encapsulated MOFs by chemically modifying the ligands for the first time. Because a vast number of combinations of ILs and MOFs, both of which have developed into an extensive independent field of research over the past three decades, are actually feasible to synthesize IL@MOF hybrid materials, application of the accumulated knowledge about chemical modifications of both systems would allow the rational control of ion-conducting properties of the hybrid materials.

Conclusion

In summary, (EMI)(TFSA) was encapsulated in a series of isorecticular microporous MOFs, namely, **IL@DMOF-0Fs**, **IL@DMOF-1Fs**, and **IL@DMOF-2Fs**, to explore new solid-state ionic conductors. The AC impedance spectroscopy revealed that the σ value of **50%IL@DMOF-2F** is one order of magnitude higher than those of **50%IL@DMOF-0F** and **50%IL@DMOF-1F**. Computational studies confirm that BDC ligands form C-H...F hydrogen bonds with TFSA⁻ anions in **50%IL@DMOF-0F** to suppress the ion diffusion in the pores. On the other hands, the introduction of fluorine atoms into the BDC ligands in **50%IL@DMOF-2F** inevitably suppresses the C-H...F hydrogen bonding interactions, which endow the high ionic conductivity. This work represents the first demonstration of controlling the ion diffusion and thus ionic conductivity in IL-encapsulated MOF hybrid systems by regulating the number of fluorine atoms in the ligands.

ASSOCIATED CONTENT

Supporting Information. Details of the synthesis and characterizations such as ¹H NMR, PXRD, SEM, TG, DSC, FT-IR, Raman, and gas sorption data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

Any additional relevant notes should be placed here.

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Table of Contents artwork

