Metal–Organic Frameworks

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Introduction of an Ionic Liquid into the Micropores of a Metal–Organic Framework and Its Anomalous Phase Behavior**

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Abstract: *Controlling the dynamics of ionic liquids (ILs) is a significant issue for widespread use. Metal–organic frameworks (MOFs) are ideal host materials for ILs because of their small micropores and tunable host–guest interactions. Herein, we demonstrate the first example of an IL incorporated within the micropores of a MOF. The system studied consisted of EMI-TFSA (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide) and ZIF-8 (composed of $Zn(MeIM)_2$; H(MeIM) = 2-methylimidazole) as the IL and MOF, respectively. Construction of the EMI-TFSA in ZIF-8 was confirmed by X-ray powder diffraction, nitrogen gas adsorption, and infrared absorption spectroscopy. Differential scanning calorimetry and solid-state NMR measurements showed that the EMI-TFSA inside the micropores demonstrated no freezing transition down to 123 K, whereas bulk EMI-TFSA froze at 231 K. Such anomalous phase behavior originates from the nanosize effect of the MOF on the IL. This result provides a novel strategy for stabilizing the liquid phase of the ILs down to a lower temperature region.*

Ionic liquids (ILs) are promising materials as novel solvents for such processes as chemical reactions,[1] extraction,[2] catalysis,[3] and gas absorption.[4] Moreover, ILs have been recently used as safe electrolytes in secondary batteries,[5] electric double-layer capacitors,[6] dye-sensitized solar cells,[7] and fuel cells.[8] These applications come from their desirable properties, such as nonflammability, negligible volatility, high electrochemical and thermal stability, and high ionic conductivity. Decreasing the melting point (m.p.) temperature of ILs is one of the most significant issues for the widespread use of ILs. The phase behavior and the structure of ILs have been studied in detail,[9] and various efforts have been devoted to lowering the m.p. of the ILs, such as changing the structure of the component ions,[10] adding other ILs or organic compounds,[11] and confining the ILs into fine pores.[12] The melting points of ILs were lowered by tens of degrees Kelvin when the ILs were incorporated within mesoporous materials, such as porous glasses[12a] or mesoporous silica.[12c] However, there has been no report on lowering the m.p. of ILs by confinement within micropores less than 2 nm in diameter, where the m.p. is expected to be lowered drastically without chemical modification.

Metal–organic frameworks (MOFs) are a novel group of materials with a large number of uniformly sized micropores. Various properties of MOFs have been studied, such as gas adsorption,[13] separation,[14] catalysis,[15] magnetic,[16] electronic,[17] and optical[18] properties, as well as ionic conductivity.[19] MOFs can be designed for several different aspects, such as pore size, framework topology, surface area, and inner surface properties. As MOFs are highly designable, they have significant potential as novel host materials for small guest molecules. Herein, we report the first example of an IL incorporated within the micropores of a MOF (Figure 1) and the phase behavior of the IL inside of the MOF micropores. We have used a thermally and chemically stable MOF, ZIF-8 (composed of $Zn(MeIM)_2$; H(MeIM) = 2-methylimidazole),[20] and a thermally stable and low-viscosity IL, EMI-TFSA (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide).

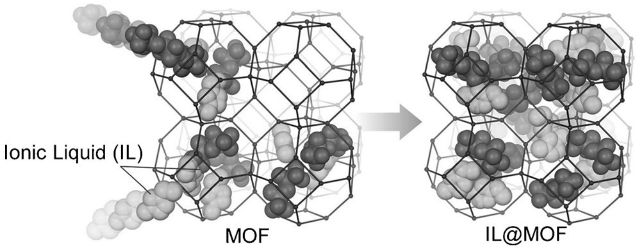

Figure 1. Representation of the incorporation of the IL into the micropores of the MOF.

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EMI-TFSA incorporated into ZIF-8 (denoted as EMI-TFSA@ZIF-8) was obtained through a simple mixing method. ZIF-8 powder was dried at 423 K overnight under vacuum to remove guest molecules from the micropores. EMI-TFSA was mixed with activated ZIF-8 in a mortar at molar ratios of 0.14:1, 0.37:1, and 0.57:1, where EMI-TFSA theoretically occupies the volume of the micropores at 25, 66, and 100%, respectively. The mixtures were heated and stored overnight to enhance the diffusion of EMI-TFSA into the micropores. As shown in the powder X-ray diffraction (XRD) patterns (Figure 2), the crystal structure of ZIF-8 remained stable even after mixing with EMI-TFSA and subsequent heating. We also observed a change in the relative intensities of the peaks. In particular, with increasing amounts of EMI-TFSA incorporated within the pores of ZIF-8, the intensities of the 011 and 013 peaks decreased and increased, respectively. These results suggest that the electron density inside the micropores of ZIF-8 was changed as a result of the introduction of EMI-TFSA.

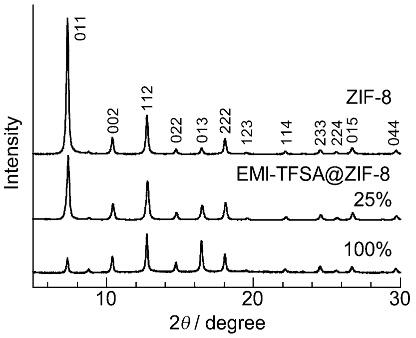

Figure 2. Powder XRD patterns of ZIF-8 and EMI-TFSA@ZIF-8. Ratios of volumetric occupancies of EMI-TFSA to pore volume of ZIF-8 are 25% and 100%. Plane indices were assigned with reference to a previous report.[20]

To confirm the presence of EMI-TFSA inside the micropores, nitrogen gas adsorption and infrared absorption (FTIR) measurements were carried out. Figure 3 shows the N_2 adsorption and desorption isotherms. Type-I adsorption[21] was observed both with and without incorporated EMI-TFSA. This result indicates that the microporous nature was maintained even after introduction of the IL. The pore volume of ZIF-8 decreased by 29% after the introduction of EMI-TFSA, and this result is consistent with the theoretical calculated value (25%). The FTIR spectra of EMI-TFSA, ZIF-8, and EMI-TFSA@ZIF-8 are shown in Figure S2 in the Supporting Information. Bands at 1060, 619, and 516 cm^{-1} in the FTIR spectrum of EMI-TFSA@ZIF-8 can be assigned to EMI-TFSA and show a blue shift from the bands of the bulk EMI-TFSA. The blue-shifted bands can be explained by the disaggregation of the ions into a few ion pairs as a result of nanosizing within the micropores. Using the van der Waals volumes of the EMI^+ cations and the $TFSA^-$ anions,[22] we confirmed that the storage capacity of each micropore of ZIF-8 was only three pairs or less. From these N_2 adsorption and FTIR measurements, we concluded that EMI-TFSA was successfully introduced into the micropores of ZIF-8 without any destruction of the framework.

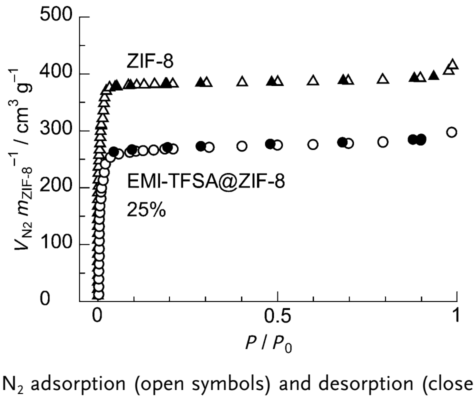

Figure 3. N_2 adsorption (open symbols) and desorption (closed symbols) isotherms of ZIF-8 and EMI-TFSA@ZIF-8 at a volumetric occupancy of 25% at 77 K.

To detect possible phase transitions of nanosized EMI-TFSA, differential scanning calorimetry (DSC) and solid-state ^{19}F static NMR measurements were conducted. Figure 4 shows the measured DSC diagrams. The bulk EMI-TFSA showed sharp peaks at 257 K upon heating and at 231 K upon cooling (the temperatures were taken at the top of the peaks). These peaks can be attributed to heat anomalies caused by melting and freezing, respectively. The reason for the freezing temperature being lower than the melting temperature comes from the supercooling of the liquid state.[23] In contrast, EMI-TFSA@ZIF-8 showed no peaks in the DSC measurements that could be derived from melting or freezing between 123 and 473 K. Weak anomalies appeared at almost the same temperatures of the melting and freezing of the bulk EMI-TFSA only in the case where the volumetric occupancy of EMI-TFSA was 100%. This result can be explained by the melting and freezing of the excess EMI-TFSA that was located outside the micropores of ZIF-8. The absence of a peak suggests that EMI-TFSA is prevented from freezing by a nanosize effect in the micropores of ZIF-8.

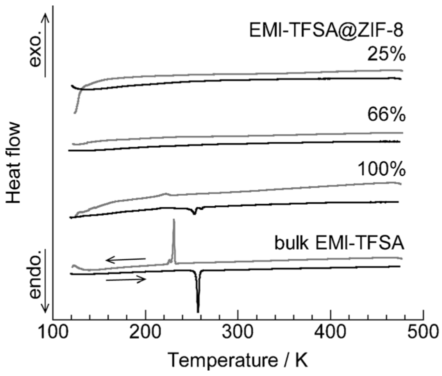

Figure 4. DSC curves of bulk EMI-TFSA and EMI-TFSA@ZIF-8 at volumetric occupancies of 25, 66, and 100%. Heating (black) and cooling (gray) curves recorded at a fixed scan rate of 5 $K\,min^{-1}$. Endo = endothermic heat flow, exo = exothermic heat flow.

Solid-state ^{19}F static NMR measurements were performed to study the motion of the $TFSA^-$ anions. The observed

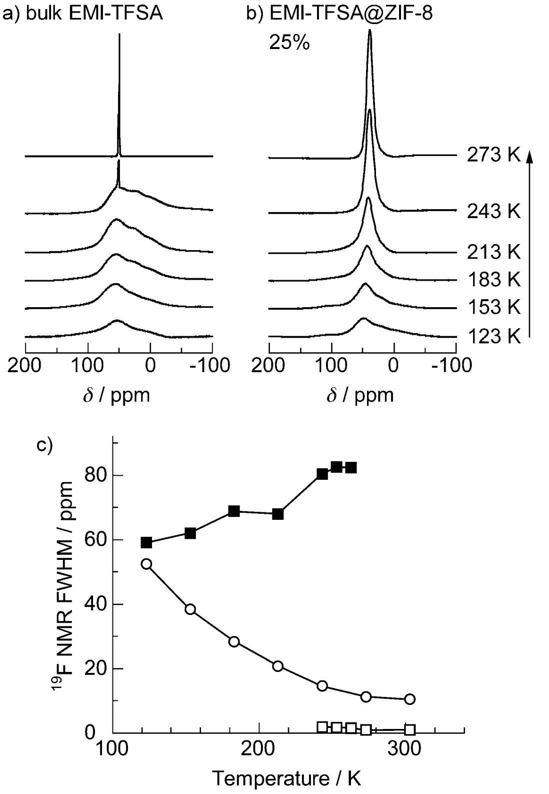

Figure 5. Solid-state ^{19}F static NMR spectra of a) bulk EMI-TFSA and b) EMI-TFSA@ZIF-8 at a volumetric occupancy of 25 % and c) their full widths at half maximum (FWHM). Open circles represent EMI-TFSA@ZIF-8; open squares represent sharp peaks and closed squares represent broad peaks of the bulk EMI-TFSA.

temperature dependences of the ^{19}F NMR spectra and line widths for the bulk and nanosized EMI-TFSA materials are shown in Figure 5. In the bulk EMI-TFSA spectra, only a broad line was detected in the process of heating from 123 K to 213 K. A sharp line appeared at 243 K superimposed on the broad signal. Only a sharp line was measured at 273 K, and the broad signal vanished. This line sharpening is explained by "motional narrowing", namely, the line sharpening arising from free rotation and diffusion of the TFSA$^-$ anions. This implies that the bulk EMI-TFSA partly melted at approximately 243 K and completely turned into the liquid phase through further heating. The phase-transition behavior of the nanosized EMI-TFSA was drastically different from that of the bulk. Gradual and continuous narrowing occurred in the temperature range of 123–303 K. This result indicates that the nanosized EMI-TFSA in the micropores of ZIF-8 demonstrated no drastic motional change in this temperature range. The EMI-TFSA ions exist as only three or less ion pairs in each micropore of ZIF-8, as discussed above. This small number of ions is not enough to construct ordered crystal structures, and no phase transition between the solid and liquid phases is observed.

In summary, we have demonstrated the first example of an IL incorporated within the micropores of a MOF. EMI-TFSA was successfully introduced into the micropores of ZIF-8 through a simple mixing and heating method, which was confirmed by powder XRD, N_2 adsorption, and FTIR experiments. EMI-TFSA in the micropores of ZIF-8 showed no heat anomaly down to 123 K in the DSC measurements, whereas bulk EMI-TFSA showed freezing and melting at 231 and 257 K, respectively. In the solid-state ^{19}F static NMR spectra, EMI-TFSA in ZIF-8 showed a gradual and continuous narrowing of the line width on heating from 123 K to 303 K, whereas bulk EMI-TFSA showed a discontinuous change of line width arising from the free rotation and diffusion of TFSA$^-$ anions around its melting point. EMI-TFSA in ZIF-8 behaves as if free from boundaries between the solid and liquid phases. This result provides novel strategies for stabilizing the liquid phase of the ILs down to a lower temperature region and potentially provides strategies for controlling the dynamics of the ions by a nanosize effect and tunable host–guest interactions.

Experimental Section

Preparation of samples: The starting materials, ZIF-8 and EMI-TFSA, were purchased from Sigma–Aldrich Co. Ltd. (Basolite® Z1200) and Tokyo Chemical Industry Co. Ltd., respectively. ZIF-8 was dried at 423 K overnight under vacuum and mixed with EMI-TFSA in a mortar. The mixtures were heated and stored overnight to enhance the diffusion of EMI-TFSA into the micropores of ZIF-8. All preparation processes were carried out in a glove box filled with dried argon gas to prevent water adsorption on ZIF-8 and absorption into EMI-TFSA.

Physical measurements: Powder XRD measurements were performed using a Bruker D8 ADVANCE diffractometer ($\lambda = 1.54059$ Å; CuKα) in air. Nitrogen gas adsorption and desorption were measured at 77 K with an automatic gas adsorption apparatus, BELSORP-max (BEL Japan). FTIR spectra were obtained using the attenuated total reflectance (ATR) method on an ALPHA FTIR spectrometer with a platinum ATR module (Bruker) in a glove box. The spectra were obtained from 400 to 4000 cm^{-1} with a resolution of 2 cm^{-1}. DSC measurements were performed using a DSC3100SA (NETZSCH Japan). For DSC measurements, samples were hermetically sealed into aluminum pans in a glove box. The samples were first heated to 473 K, then cooled to 123 K, and then heated to 473 K again. The scan rate was fixed at 5 K min^{-1}. Solid-state ^{19}F static NMR measurements were performed at 376.5 MHz using a Bruker AVANCE II$^+$ 400 spectrometer. NaF aqueous solution was used at ambient temperature as the external standard. Samples hermetically sealed in glass tubes were cooled to 123 K and then heated to 303 K. The NMR spectra were obtained stepwise in the process of heating by applying a Fourier transform to the resulting free induction decay (FID) signal after a single $\pi/2$ pulse sequence.

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