Rational Control of Ionic Conduction of Encapsulated Ionic Liquid by Fluorination of Isoreticular Metal-organic Frameworks

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The hybrid materials of ionic liquids (ILs) and metal-organic frameworks (MOFs) have attracted much attention in solid-state conductors because of their great advantage in various combinations of components.[1,2] 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. 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). To this end, a series of Zn-based microporous MOFs, Zn_2(xFBDC)(tmBDC)(DABCO) (hereafter **DMOF-*x*F**s), where x denotes the number of fluorine on the terephthalate ligands (xFBDC^{2-}; x = 0, 1, and 2),[3] was chosen as the host materials (tmBDC^{2-}: tetramethylterephthalate, DABCO: 1,4-diazabicyclo[2.2.2]octane). 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. Electrochemical impedance measurements revealed that (EMI)(TFSA)-encapsulated **DMOF-2F** (hereafter **IL@DMOF-2F**) exhibits the highest ionic conductivity, which is explained in terms of the suppressed C–H···F interactions based on vibrational and computational studies. The present work would provide a new strategy for developing and understanding the ionic conducting hybrid materials.

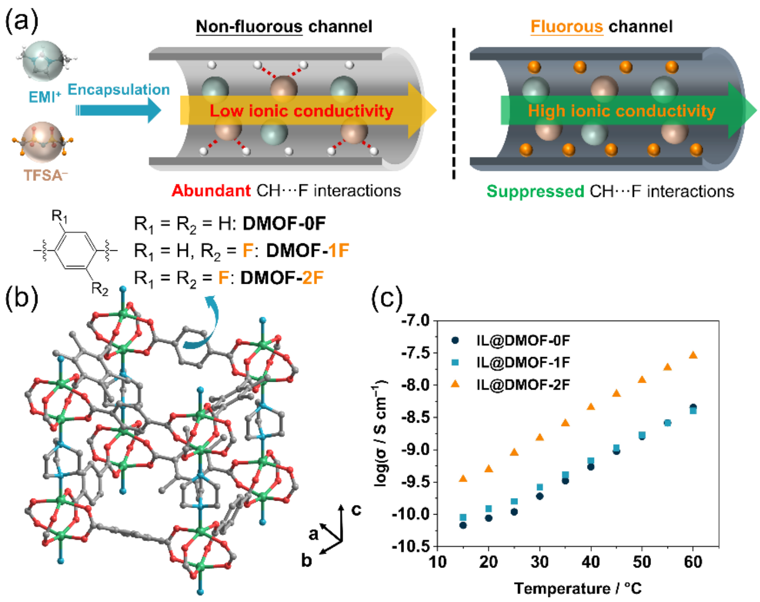

Figure 1. (a) Schematic image of ionic conduction of fluorinated IL in non-fluorous (left) and fluorous (right) channels. (b) Crystal structure of **DMOF-*x*F**s. (c) Temperature dependence of ionic conductivity (σ) of **IL@DMOF-*x*F**s.

References

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