Supplementary Information

Tuning Anhydrous Proton Conduction in Single-Ion Polymers by Crystalline Ion Channels

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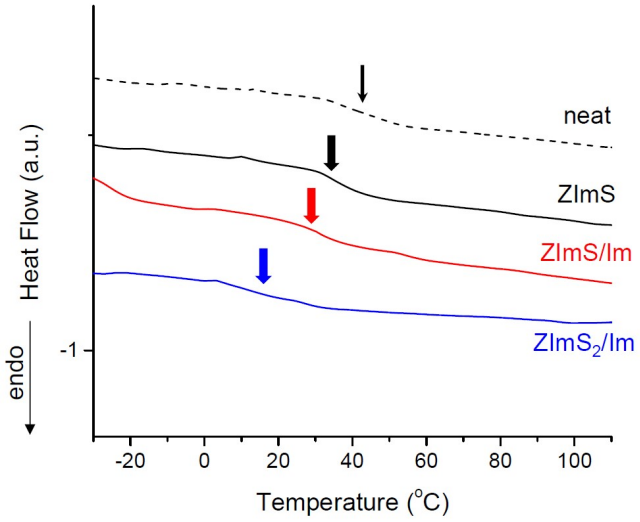
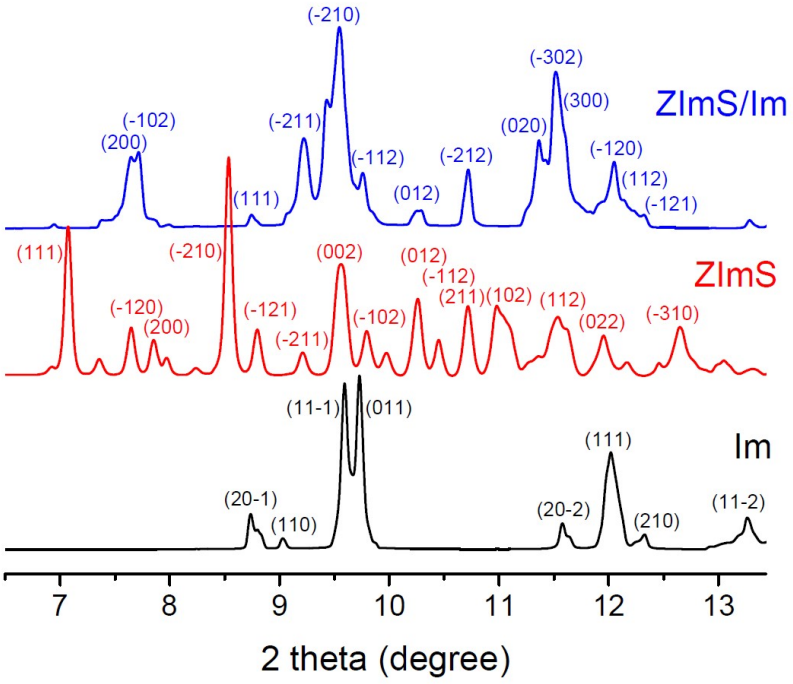
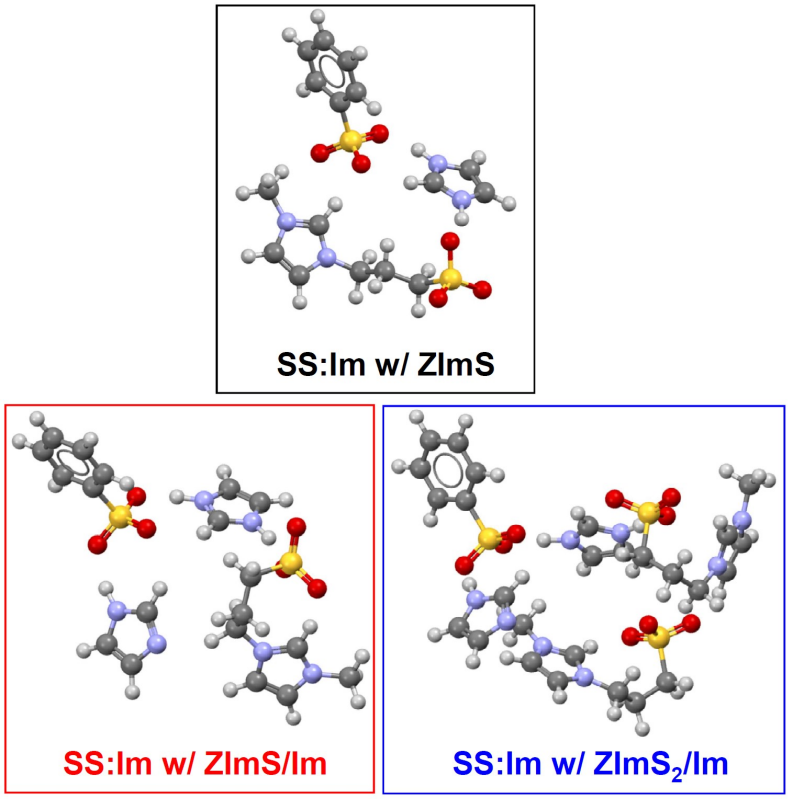
Supplementary Figures



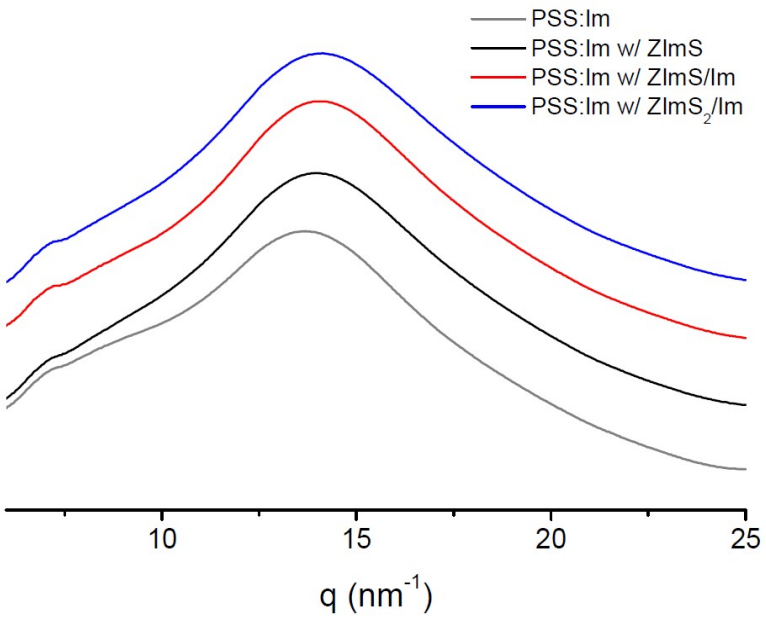
Supplementary Figure 1. Thermal transitions of PSS:Im-*b*-PMB with additives. DSC thermograms of PSS:Im-*b*-PMB (1.2-*b*-1.0 kg mol^{-1}) containing ZImS, ZImS/Im, and $ZImS_2$/Im, compared with that of neat PSS:Im-*b*-PMB, indicating a decrease in the T_g value of PSS:Im with additives. T_g of PMB (-68 °C) was not affected by additives.



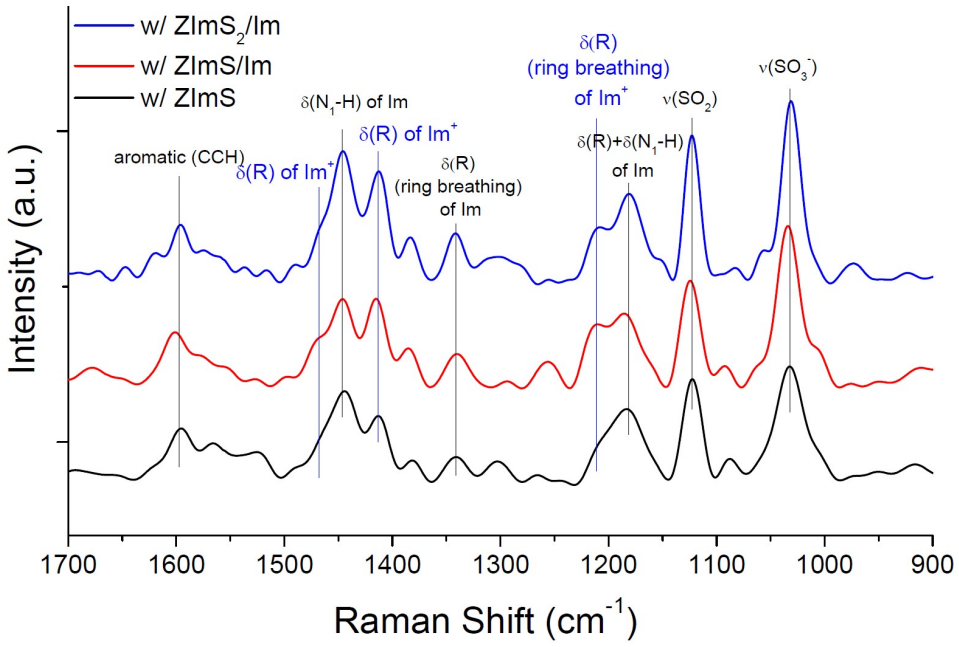
Supplementary Figure 2. Co-organization of ZImS and Im. WAXS profiles of neat Im, and neat ZImS, and ZImS/Im. Miller indices of the reflection planes (*hkl*) of each crystal were obtained by Mercury DSD 3.9 software, as given in the figure.



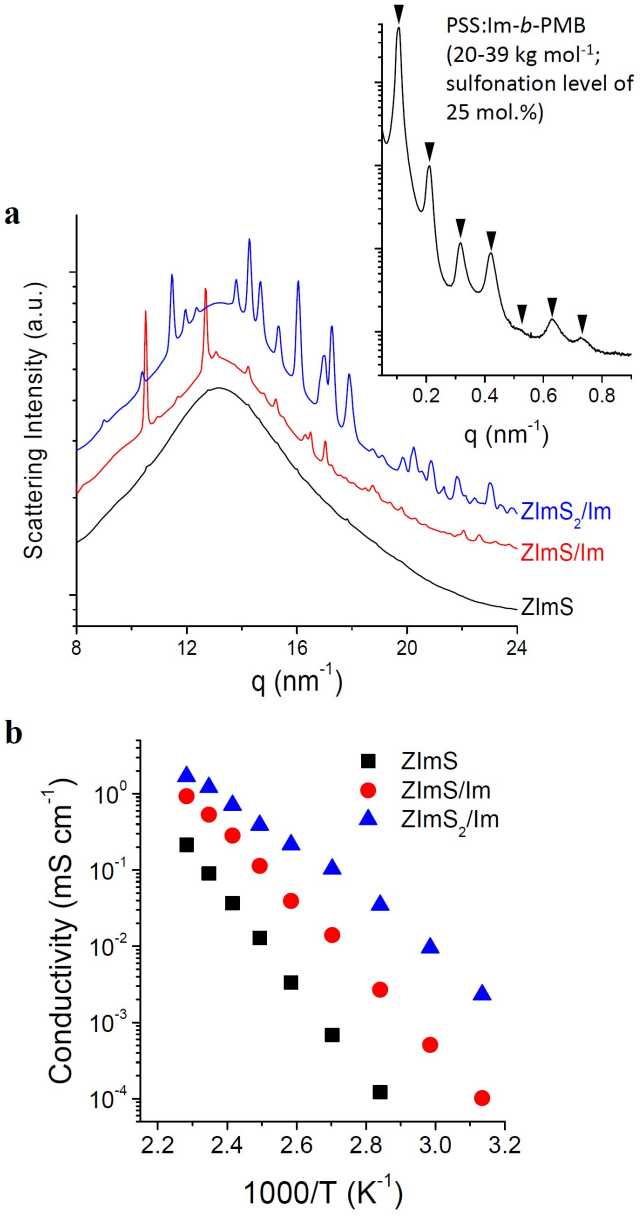
Supplementary Figure 3. Dissimilar dipolar orientations. Molecular conformations of SS:Im with incorporated ZImS and neutral Im, for which the geometries had been optimized by *ab initio* calculations based on the density functional theory (B3LYP/6-31G(d)).



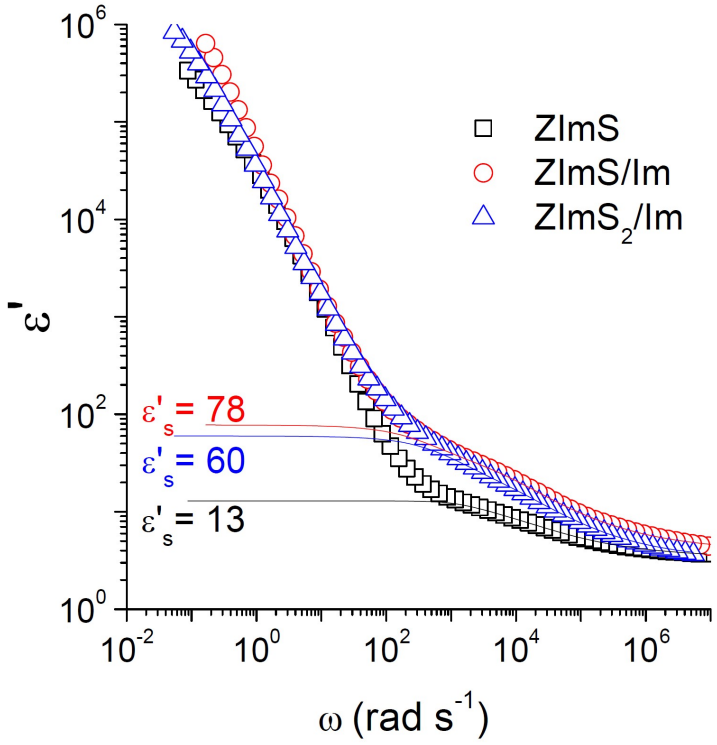
Supplementary Figure 4. Amorphous characteristics of PSS:Im homopolymers. WAXS profiles of PSS:Im homopolymers (1.2 kg mol^{-1} and sulfonation level of 20 mol.%) comprising ZImS, ZImS/Im, and $ZImS_2$/Im, compared with that of neat PSS:Im, measured at 25 °C. It is evident that all samples have amorphous ionic phases.



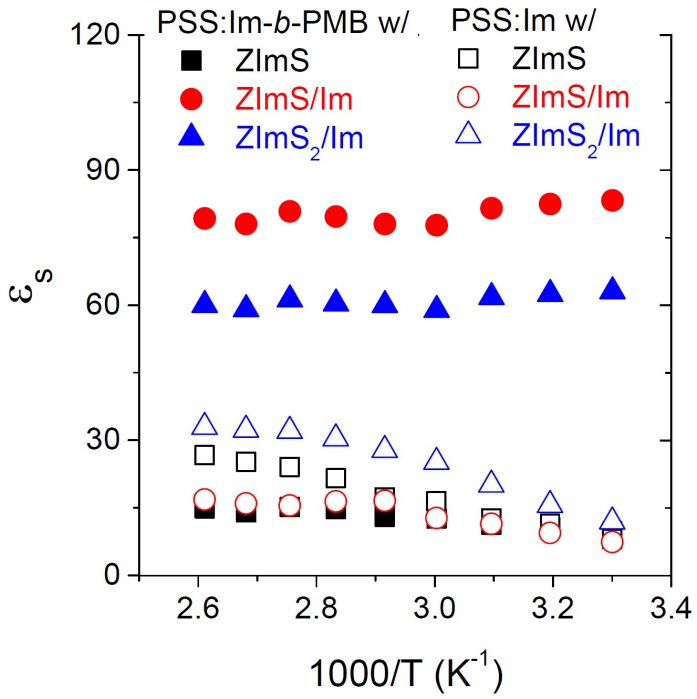
Supplementary Figure 5. Dissimilar proton dissociation degrees. Fourier transform Raman spectra of PSS:Im-*b*-PMB comprising ZImS, ZImS/Im, and $ZImS_2$/Im over the wavenumber ranges 900 – 1700 cm^{-1}. C–CH aromatic ring quadrant of PSS chains (at 1600 cm^{-1}) was used as an internal reference. As assigned in the figure, the absorption band at 1210 cm^{-1} indicates the ring breathing of Im^+, whereas that of neutral Im is shown at 1338 cm^{-1}. The peak at 1413 cm^{-1} signifies CH_3-N and CH_2-N stretching of Im^+, whereas that at 1446 cm^{-1} denotes the N-H stretching of neutral Im. From the intensity ratio, e.g., $I^{1210}/(I^{1210} + I^{1338})$, the degree of proton dissociation was calculated as 52%, 65%, and 54% for the samples containing ZImS, ZImS/Im, and $ZImS_2$/Im, respectively.



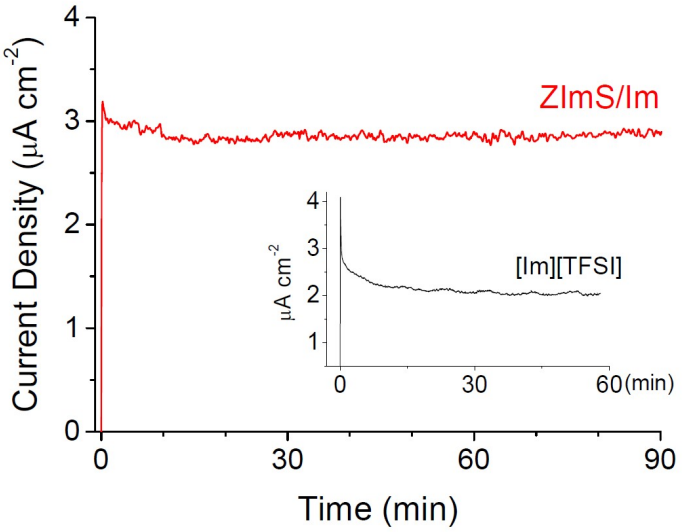
Supplementary Figure 6. High molecular weight PSS:Im-*b*-PMB comprising additives. **a**, WAXS profiles of PSS:Im-*b*-PMB (20-39 kg mol^{-1} and a sulfonation level of 25 mol.%) comprising ZImS, ZImS/Im, and ZImS$_2$/Im, measured at 25 °C. SAXS profile of neat PSS:Im-*b*-PMB displaying lamellar morphology (d_{100} = 56 nm) is shown in the inset. **b**, Temperature-dependent ionic conductivity of PSS:Im-*b*-PMB (20-39 kg mol^{-1}) comprising additives.



Supplementary Figure 7. Dielectric relaxation behavior. Representative dielectric permittivity spectra of PSS:Im-*b*-PMB copolymers with various additives, measured at 60 °C. The spectra with model fits were horizontally shifted to show the static dielectric constants, ε_s.



Supplementary Figure 8. Dissimilar dipolar arrangements. The static dielectric constants, ε_s, of PSS:Im-*b*-PMB and PSS:Im with the addition of ZImS, ZImS/Im, and $ZImS_2$/Im at different temperatures, revealing dissimilar dipolar arrangements in ionic phases of block copolymers and homopolymers.



Supplementary Figure 9. Polarization experiments. Current density profile of PSS:Im-*b*-PMB containing ZImS/Im, after polarizing the sample with ΔV of 100 mV. Symmetric cell was employed by sandwiching the polymer with carbon electrodes. PSS:Im-*b*-PMB containing ionic liquid was used as a control.

Supplementary Tables

Supplementary Table 1. **Crystal Structures and Lattice Parameters of Neat Im, Neat ZImS, and ZImS/Im Mixture**

	Im	ZImS	ZImS/Im
Crystal structure	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P1m1$
a (Å) (α)	9.8 (90°)	9.8 (90°)	11.1 (90°)
b (Å) (β)	5.5 (117°)	11.4 (98°)	7.0 (113.0°)
c (Å) (γ)	7.8 (90°)	8.1 (90°)	10.1 (90°)

Supplementary Table 2. Dielectric Relaxation Parameters of PSS:Im-*b*-PMB Block Copolymers Comprising ZImS, ZImS/Im, and ZImS$_2$/Im

PSS:Im-*b*-PMB	Dipolar moiety	Number density[a] (ν, nm^{-3})	Dipole moment[b] (m, D)	g[c]	V_p/V_m[d]
w/ ZImS	Ion pair (SO_3^- – Im^+)	0.36	7	0.4	0.8
	ZImS	0.32	17.5		
w/ ZImS/Im	Ion pair (SO_3^- – Im^+)	0.32	7	1.9	1.1
	Neutral pair (Im - ZImS)	0.39	19.3		
w/ ZImS$_2$/Im	Ion pair (SO_3^- – Im^+)	0.27	7	1.1	1.5
	Neutral pair (Im - ZImS)	0.32	19.3		
	ZImS	0.24	17.5		

[a]estimated from the group contribution method based on molecular structure.

[b]calculated using a DFT exchange-correlation functional, *B3LYP*.

[c]calculated using eq (1) at 343 *K*

[d]calculated using eq (2) at 343 *K*