Supplementary Information

Ionic-Content-Driven Restructuring of Spirobisindane Ionene Networks: Implications for Mechanics, Self-Healing, and Gas Transport

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S1. Model Construction and Simulation Details

Monomer parameters were obtained from LigParGen (OPLS-AA). Polymer chains were generated algorithmically by repeating and connecting these units at predefined junction sites using a custom script; junctions generate new bond/angle/dihedral types, which were assigned by matching each to its chemically equivalent motif in the monomer. No reparameterization was performed. The resulting oligomers were placed at random initial positions within the simulation box to ensure an unbiased starting configuration prior to energy minimization and equilibration.

All molecular simulations were carried out using an all-atom representation in the `real` unit system under fully periodic boundary conditions. Short-range non-bonded interactions were truncated at 9,Å, and long-range electrostatics were evaluated using Ewald summation with a convergence tolerance of 10^{-4}. Atoms were modeled with explicit partial charges, and neighbor lists were updated every timestep using a 2,Å skin distance. Temperature and pressure control, integration settings, and cutoff schemes match the standard OPLS protocol applied to condensed-phase systems. The detailed mathematical expressions for all bonded, non-bonded, dihedral, and improper interactions used in these simulations are provided in Sec. S2.

Polymer configurations were equilibrated through a multistage protocol. Simulations utilized periodic cubic cells with side lengths of 65–75 Å (6.5–7.5 nm), containing approximately $\sim 2.3\times10^4$ to 3.5×10^4 atoms. First, the simulation cell was isotropically expanded while the system was heated to 600 K and propagated under Langevin dynamics combined with an *NVE* integrator to remove any unfavorable contacts. This was followed by an extended *NPT* equilibration at 600 K to relax the density. The system was then cooled in stages (600 K→450 K and 450 K→294 K) under *NPT* conditions, with additional equilibration at 294 K to ensure convergence of volume, pressure, and structural observables. Each stage was run for $\mathcal{O}(10^6$–$10^7)$ timesteps using a 1 fs timestep. Specifically, systems were equilibrated at 294 K for 5 ns; during the final 2 ns, density fluctuated within 0.5 % with no systematic drift, and chain conformational metrics reached stabilization. Configurations were saved at the end of each stage for subsequent production simulations, which consisted of 1 ns under NVT for thermodynamic sampling, followed by 1 ns under NVE to evaluate dynamical quantities such as MSD without thermostat interference.

Triaxial tension was applied by elongating the box along x at $10^{-6}\,\mathrm{fs}^{-1}$ while L_y and L_z remained fixed. Coordinates were affinely remapped, and engineering strain was defined as $\varepsilon(t) = [L_x - L_{x,0}]/L_{x,0}$, with $L_{x,0}$ taken from the undeformed state. The system was thermostatted at 374 K (Langevin) and integrated using *NVE* with displacement limiting. Normal stresses and the bonded/non-bonded energy decomposition (chain–chain, IL–IL, chain–IL) were tracked throughout deformation to strains of order 5. The post-healing tensile test used the identical loading protocol, except strain was referenced to the healed box length, $L_{x,0}^{\mathrm{heal}}$.

Self-healing was assessed by relaxing the deformed configuration from the end of the triaxial test. The simulation was continued at 600 K under isotropic *NPT* control (1 atm) with fixed box geometry in y and z and full barostat response in x. No external load was applied; $\sigma_{xx}, \sigma_{yy}, \sigma_{zz}$ therefore reflect only internal stresses generated during recovery. Engineering strain was monitored relative to the pre-deformation box length $L_{x,0}$. Bonded and non-bonded energy components (chain–chain, IL–IL, chain–IL) were recorded during healing to quantify interfacial recombination and structural recovery.

S2. Force-field functional form

All simulations employed an OPLS-type all-atom force field. The total potential energy is expressed as,

$$U_{\mathrm{tot}} = \sum_{\mathrm{bonds}} U_{\mathrm{bond}} + \sum_{\mathrm{angles}} U_{\mathrm{angle}} + \sum_{\mathrm{dihedrals}} U_{\mathrm{dihedral}} + \sum_{\mathrm{impropers}} U_{\mathrm{improper}} + \sum_{i<j} U_{\mathrm{nb}}(r_{ij})\,. \tag{S1}$$

Energies are reported in kcal mol^{-1}, distances in Å, and angles in degrees in the parameter tables (angles are converted to radians in the force evaluations). Atom labels refer to the atom types defined in Fig. S1.

Non-bonded interactions: Non-bonded interactions between atoms i and j consist of Lennard–Jones 12–6 and Coulomb terms,

$$U_{\mathrm{nb}}(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}. \tag{S2}$$

Lennard–Jones parameters are assigned per atom type as ε and σ (see Table S1). Cross interactions were generated using the arithmetic mixing rule,

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}, \qquad \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}. \tag{S3}$$

Bond stretching: Bonded pairs interact via a harmonic potential,

$$U_{\mathrm{bond}}(r) = k_r\,(r - r_0)^2, \tag{S4}$$

where k_r is the bond force constant (kcal mol^{-1} Å^{-2}) and r_0 is the equilibrium bond length (Å). The values of k_r and r_0 for each bond type are listed in Table S2.

Angle bending: Valence angles are described by a harmonic potential,

$$U_{\mathrm{angle}}(\theta) = k_\theta\,(\theta - \theta_0)^2, \tag{S5}$$

where k_θ is the angle force constant (kcal mol^{-1} rad^{-2}) and θ_0 is the equilibrium angle. The tabulated θ_0 values in Table S3, are given in degrees and are converted to radians internally for force evaluations.

Dihedral torsions: Proper torsions follow the standard OPLS Fourier series in the dihedral angle ϕ,

$$U_{\mathrm{dihedral}}(\phi) = \tfrac{1}{2}V_1(1+\cos\phi) + \tfrac{1}{2}V_2(1-\cos 2\phi) + \tfrac{1}{2}V_3(1+\cos 3\phi) + \tfrac{1}{2}V_4(1-\cos 4\phi), \tag{S6}$$

where V_1, V_2, V_3, V_4 (kcal mol^{-1}) are the dihedral coefficients listed in Table S4, and each row of that table is applied to the set of atom-type combinations indicated in the last column.

Improper torsions: Planarity and chirality are enforced using a Fourier-type improper potential for the improper angle ω,

$$U_{\mathrm{improper}}(\omega) = k_\chi\,[1 + d\cos(n\omega)], \tag{S7}$$

with amplitude k_χ (kcal mol^{-1}), phase parameter $d = \pm 1$, and integer periodicity n. The corresponding parameters (k_χ, d, n) for each improper type are given in Table S5.

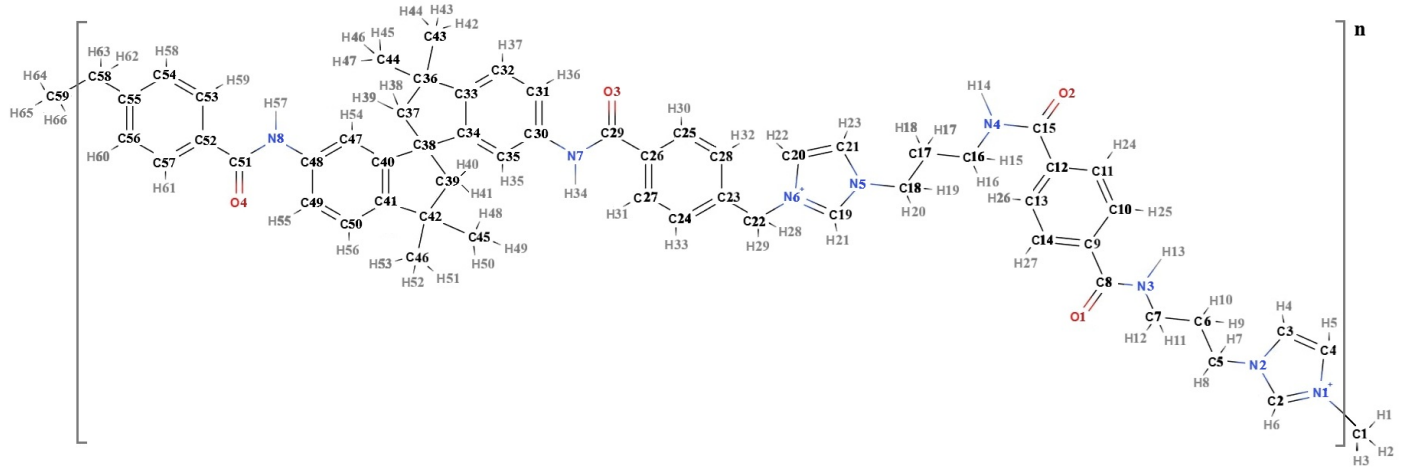


Fig. S1 Atom-type map for a single repeat unit of the SBI-TC-API-PA1 monomer. All atom labels correspond directly to the identifiers used in the pair, bond, angle, dihedral, and improper parameter tables.

Table S1 Unique pair interaction parameters. Each pair entry (type i–j) uses the atom labels defined in Fig. S1

ε (kcal mol^{-1})	σ (Å)	N_{types}	Atom-type combinations
0.21	2.96	4	O1; O2; O3; O4
0.17	3.25	8	N1; N2; N3; N4; N5; N6; N7; N8
0.066	3.5	19	C1; C16; C17; C18; C22; C36; C37; C38; C39; C42; C43; C44; C45; C46; C5; C58; C59; C6; C7
0.03	2.42	28	H4; H5; H6; H13; H14; H21; H22; H23; H24; H25; H26; H27; H30; H31; H32; H33; H34; H35; H36; H37; H54; H55; H56; H57; H58; H59; H60; H61
0.03	2.5	38	H1; H2; H3; H7; H8; H9; H10; H11; H12; H15; H16; H17; H18; H19; H20; H28; H29; H38; H39; H40; H41; H42; H43; H44; H45; H46; H47; H48; H49; H50; H51; H52; H53; H62; H63; H64; H65; H66
0.07	3.55	40	C2; C3; C4; C8; C9; C10; C11; C12; C13; C14; C15; C19; C20; C21; C23; C24; C25; C26; C27; C28; C29; C30; C31; C32; C33; C34; C35; C40; C41; C47; C48; C49; C50; C51; C52; C53; C54; C55; C56; C57

Table S2 Unique bond parameters listed by atom pair. Atom labels correspond to Fig. S1

k_r (kcal mol^{-1} Å^{-2})	r_0 (Å)	N_{types}	Atom-type combinations
337.0	1.449	2	C7-N3; C16-N4
512.0	1.375	2	C3-C4; C20-C21
400.0	1.49	4	C8-C9; C12-C15; C26-C29; C51-C52
434.0	1.01	4	H13-N3; H14-N4; H34-N7; H57-N8
477.0	1.343	4	C2-N1; C2-N2; C19-N5; C19-N6
490.0	1.335	4	C8-N3; C15-N4; C29-N7; C51-N8
570.0	1.229	4	C8-O1; C15-O2; C29-O3; C51-O4
337.0	1.475	5	C1-N1; C5-N2; C18-N5; C22-N6; C58-N1
317.0	1.51	6	C22-C23; C33-C36; C34-C38; C38-C40; C41-C42; C55-C58
427.0	1.381	6	C3-N2; C4-N1; C20-N6; C21-N5; C30-N7; C48-N8
268.0	1.529	13	C5-C6; C6-C7; C16-C17; C17-C18; C36-C37; C36-C43; C36-C44; C37-C38; C38-C39; C39-C42; C42-C45; C42-C46; C58-C59
367.0	1.08	24	C2-H6; C3-H4; C4-H5; C10-H25; C11-H24; C13-H26; C14-H27; C19-H21; C20-H22; C21-H23; C24-H33; C25-H30; C27-H31; C28-H32; C31-H36; C32-H37; C35-H35; C47-H54; C49-H55; C50-H56; C53-H59; C54-H58; C56-H60; C57-H61
469.0	1.4	30	C10-C9; C10-C11; C11-C12; C12-C13; C13-C14; C14-C9; C23-C24; C23-C28; C24-C25; C25-C26; C26-C27; C27-C28; C30-C31; C30-C35; C31-C32; C32-C33; C33-C34; C34-C35; C40-C41; C40-C47; C41-C50; C47-C48; C48-C49; C49-C50; C52-C53; C52-C57; C53-C54; C54-C55; C55-C56; C56-C57
340.0	1.09	38	C1-H1; C1-H2; C1-H3; C5-H7; C5-H8; C6-H9; C6-H10; C7-H11; C7-H12; C16-H15; C16-H16; C17-H17; C17-H18; C18-H19; C18-H20; C22-H28; C22-H29; C37-H38; C37-H39; C39-H40; C39-H41; C43-H42; C43-H43; C43-H44; C44-H45; C44-H46; C44-H47; C45-H48; C45-H49; C45-H50; C46-H51; C46-H52; C46-H53; C58-H62; C58-H63; C59-H64; C59-H65; C59-H66

Table S3 Unique angle parameters (i–j–k). Atom labels match those in Fig. S1

k_θ (kcal mol^{-1} rad^{-2})	θ_0 (°)	N_{types}	Atom-type combinations
40.0	109.5	1	C34-C38-C40
38.0	118.4	2	C7-N3-H13; C16-N4-H14
51.65	110.58	2	C6-C5-N2; C17-C18-N5
80.0	109.7	2	C6-C7-N3; C17-C16-N4
80.0	111.2	2	C23-C22-N6; C55-C58-N1
35.0	121.6	4	H4-C3-N2; H5-C4-N1; H22-C20-N6; H23-C21-N5
35.0	130.7	4	C3-C4-H5; C4-C3-H4; C20-C21-H23; C21-C20-H22
50.0	121.9	4	C7-N3-C8; C15-N4-C16; C29-N7-C30; C48-N8-C51
70.0	109.8	4	C2-N1-C4; C2-N2-C3; C19-N5-C21; C19-N6-C20
70.0	115.5	4	C9-C8-N3; C12-C15-N4; C26-C29-N7; C52-C51-N8
80.0	120.4	4	C9-C8-O1; C12-C15-O2; C26-C29-O3; C52-C51-O4
80.0	122.9	4	N3-C8-O1; N4-C15-O2; N7-C29-O3; N8-C51-O4
35.0	119.8	6	C8-N3-H13; C15-N4-H14; C29-N7-H34; C30-N7-H34; C48-N8-H57; C51-N8-H57
85.0	120.0	8	C10-C9-C8; C11-C12-C15; C13-C12-C15; C14-C9-C8; C25-C26-C29; C27-C26-C29; C51-C52-C53; C51-C52-C57
63.0	112.4	10	C1-N1-C2; C1-N1-C4; C2-N1-C58; C2-N2-C5; C3-N2-C5; C4-N1-C58; C18-N5-C19; C18-N5-C21; C19-N6-C22; C20-N6-C22
58.35	112.7	11	C5-C6-C7; C16-C17-C18; C36-C37-C38; C37-C36-C43; C37-C36-C44; C37-C38-C39; C38-C39-C42; C39-C42-C45; C39-C42-C46; C43-C36-C44; C45-C42-C46
63.0	114.0	11	C33-C36-C37; C33-C36-C43; C33-C36-C44; C34-C38-C37; C34-C38-C39; C37-C38-C40; C39-C38-C40; C39-C42-C41; C41-C42-C45; C41-C42-C46; C55-C58-C59
35.0	109.5	19	H1-C1-N1; H2-C1-N1; H3-C1-N1; H7-C5-N2; H8-C5-N2; H11-C7-N3; H12-C7-N3; H15-C16-N4; H16-C16-N4; H19-C18-N5; H20-C18-N5; C23-C22-H28; C23-C22-H29; H28-C22-N6; H29-C22-N6; C55-C58-H62; C55-C58-H63; H62-C58-N1; H63-C58-N1
70.0	120.0	22	N1-C2-N2; C3-C4-N1; C4-C3-N2; N5-C19-N6; C20-C21-N5; C21-C20-N6; C22-C23-C24; C22-C23-C28; C31-C30-N7; C32-C33-C36; C33-C34-C38; C34-C33-C36; C35-C30-N7; C35-C34-C38; C38-C40-C41; C38-C40-C47; C40-C41-C42; C42-C41-C50; C47-C48-N8; C49-C48-N8; C54-C55-C58; C56-C55-C58
33.0	107.8	28	H1-C1-H2; H1-C1-H3; H2-C1-H3; H7-C5-H8; H10-C6-H9; H11-C7-H12; H15-C16-H16; H17-C17-H18; H19-C18-H20; H28-C22-H29; H38-C37-H39; H40-C39-H41; H42-C43-H43; H42-C43-H44; H43-C43-H44; H45-C44-H46; H45-C44-H47; H46-C44-H47; H48-C45-H49; H48-C45-H50; H49-C45-H50; H51-C46-H52; H51-C46-H53; H52-C46-H53; H62-C58-H63; H64-C59-H65; H64-C59-H66; H65-C59-H66
63.0	120.0	30	C10-C9-C14; C10-C11-C12; C11-C10-C9; C11-C12-C13; C12-C13-C14; C13-C14-C9; C23-C24-C25; C23-C28-C27; C24-C23-C28; C24-C25-C26; C25-C26-C27; C26-C27-C28; C30-C31-C32; C30-C35-C34; C31-C30-C35; C31-C32-C33; C32-C33-C34; C33-C34-C35; C40-C41-C50; C40-C47-C48; C41-C40-C47; C41-C50-C49; C47-C48-C49; C48-C49-C50; C52-C53-C54; C52-C57-C56; C53-C52-C57; C53-C54-C55; C54-C55-C56; C55-C56-C57
35.0	120.0	40	H6-C2-N1; H6-C2-N2; C9-C10-H25; C9-C14-H27; C10-C11-H24; C11-C10-H25; C12-C11-H24; C12-C13-H26; C13-C14-H27; C14-C13-H26; H21-C19-N5; H21-C19-N6; C23-C24-H33; C23-C28-H32; C24-C25-H30; C25-C24-H33; C26-C25-H30; C26-C27-H31; C27-C28-H32; C28-C27-H31; C30-C31-H36; C30-C35-H35; C31-C32-H37; C32-C31-H36; C33-C32-H37; C34-C35-H35; C40-C47-H54; C41-C50-H56; C48-C47-H54; C48-C49-H55; C49-C50-H56; C50-C49-H55; C52-C53-H59; C52-C57-H61; C53-C54-H58; C54-C53-H59; C55-C54-H58; C55-C56-H60; C56-C57-H61; C57-C56-H60
37.5	110.7	41	C5-C6-H9; C5-C6-H10; C6-C5-H7; C6-C5-H8; C6-C7-H11; C6-C7-H12; C7-C6-H9; C7-C6-H10; C16-C17-H17; C16-C17-H18; C17-C16-H15; C17-C16-H16; C17-C18-H19; C17-C18-H20; C18-C17-H17; C18-C17-H18; C36-C37-H38; C36-C37-H39; C36-C43-H42; C36-C43-H43; C36-C43-H44; C36-C44-H45; C36-C44-H46; C36-C44-H47; C38-C37-H38; C38-C37-H39; C38-C39-H40; C38-C39-H41; C42-C39-H40; C42-C39-H41; C42-C45-H48; C42-C45-H49; C42-C45-H50; C42-C46-H51; C42-C46-H52; C42-C46-H53; C58-C59-H64; C58-C59-H65; C58-C59-H66; C59-C58-H62; C59-C58-H63

Table S4 Unique dihedral parameters (i–j–k–l). Atom labels correspond to the annotated monomer in Fig. S1

V_1 (kcal mol^{-1})	V_2 (kcal mol^{-1})	V_3 (kcal mol^{-1})	V_4 (kcal mol^{-1})	N_{types}	**Atom-type combinations**
-1	-0.35	0	0	2	C6-C5-N2-C2; C17-C18-N5-C19
0	0.462	0	0	2	C6-C7-N3-C8; C17-C16-N4-C15
0.845	-0.962	0.713	0	2	N4-C16-C17-C18; C5-C6-C7-N3
1	-0.35	0	0	2	C6-C5-N2-C3; C17-C18-N5-C21
2.392	-0.674	0.55	0	2	N2-C5-C6-C7; C16-C17-C18-N5
-1.013	-0.709	0.473	0	4	N2-C5-C6-H9; N2-C5-C6-H10; H17-C17-C18-N5; H18-C17-C18-N5
0	0	0.464	0	4	N4-C16-C17-H17; N4-C16-C17-H18; H9-C6-C7-N3; H10-C6-C7-N3
0	6.089	0	0	4	O1-C8-N3-C7; O2-C15-N4-C16; O3-C29-N7-C30; O4-C51-N8-C48
2.3	6.089	0	0	4	C9-C8-N3-C7; C12-C15-N4-C16; C26-C29-N7-C30; C52-C51-N8-C48
0	1.1	0	0	8	N3-C8-C9-C10; N3-C8-C9-C14; N8-C51-C52-C53; N8-C51-C52-C57; C11-C12-C15-N4; C13-C12-C15-N4; C25-C26-C29-N7; C27-C26-C29-N7
0	4.9	0	0	8	O1-C8-N3-H13; O2-C15-N4-H14; O3-C29-N7-H34; O4-C51-N8-H57; C9-C8-N3-H13; C12-C15-N4-H14; C26-C29-N7-H34; C52-C51-N8-H57
0	10.75	0	0	8	N2-C3-C4-N1; N2-C3-C4-H5; H4-C3-C4-N1; H4-C3-C4-H5; N6-C20-C21-N5; N6-C20-C21-H23; H22-C20-C21-N5; H22-C20-C21-H23
1.3	-0.2	0.2	0	12	C33-C36-C37-C38; C34-C38-C39-C42; C36-C37-C38-C34; C36-C37-C38-C39; C36-C37-C38-C40; C37-C38-C39-C42; C38-C39-C42-C41; C38-C39-C42-C45; C38-C39-C42-C46; C40-C38-C39-C42; C43-C36-C37-C38; C44-C36-C37-C38
0	2.1	0	0	16	O1-C8-C9-C10; O1-C8-C9-C14; O4-C51-C52-C53; O4-C51-C52-C57; C11-C12-C15-O2; C13-C12-C15-O2; C25-C26-C29-O3; C27-C26-C29-O3; C31-C30-N7-C29; C31-C30-N7-H34; C35-C30-N7-C29; C35-C30-N7-H34; C47-C48-N8-C51; C47-C48-N8-H57; C49-C48-N8-C51; C49-C48-N8-H57
0	5	0	0	18	C3-C4-N1-C1; C3-C4-N1-C2; C3-C4-N1-C58; C4-C3-N2-C2; H4-C3-N2-C2; C4-C3-N2-C5; H4-C3-N2-C5; H5-C4-N1-C1; H5-C4-N1-C2; H5-C4-N1-C58; C20-C21-N5-C18; C20-C21-N5-C19; C21-C20-N6-C19; C21-C20-N6-C22; H22-C20-N6-C19; H22-C20-N6-C22; H23-C21-N5-C18; H23-C21-N5-C19
0	10	0	0	18	N1-C2-N2-C3; N1-C2-N2-C5; N2-C2-N1-C1; N2-C2-N1-C4; N2-C2-N1-C58; N5-C19-N6-C20; N5-C19-N6-C22; H6-C2-N1-C1; H6-C2-N1-C4; H6-C2-N1-C58; H6-C2-N2-C3; H6-C2-N2-C5; N6-C19-N5-C18; N6-C19-N5-C21; H21-C19-N5-C18; H21-C19-N5-C21; H21-C19-N6-C20; H21-C19-N6-C22
0	0	0.462	0	27	C33-C36-C37-H38; C33-C36-C37-H39; C33-C36-C43-H42; C33-C36-C43-H43; C33-C36-C43-H44; C33-C36-C44-H45; C33-C36-C44-H46; C33-C36-C44-H47; C34-C38-C39-H40; C34-C38-C39-H41; H38-C37-C38-C34; H38-C37-C38-C40; H39-C37-C38-C34; H39-C37-C38-C40; C40-C38-C39-H40; C40-C38-C39-H41; H40-C39-C42-C41; H41-C39-C42-C41; C41-C42-C45-H48; C41-C42-C45-H49; C41-C42-C45-H50; C41-C42-C46-H51; C41-C42-C46-H52; C41-C42-C46-H53; C55-C58-C59-H64; C55-C58-C59-H65; C55-C58-C59-H66

Continued on next page

Table S4 - continued from previous page

V_1 (kcal mol^{-1})	V_2 (kcal mol^{-1})	V_3 (kcal mol^{-1})	V_4 (kcal mol^{-1})	N_{types}	**Atom-type combinations**
0	0	0.3	0	66	C5-C6-C7-H11; C5-C6-C7-H12; H7-C5-C6-C7; H7-C5-C6-H9; H7-C5-C6-H10; H8-C5-C6-C7; H8-C5-C6-H9; H8-C5-C6-H10; H9-C6-C7-H11; H9-C6-C7-H12; H10-C6-C7-H11; H10-C6-C7-H12; H15-C16-C17-H17; H15-C16-C17-C18; H15-C16-C17-H18; H16-C16-C17-H17; H16-C16-C17-C18; H16-C16-C17-H18; C16-C17-C18-H19; C16-C17-C18-H20; H17-C17-C18-H19; H17-C17-C18-H20; H18-C17-C18-H19; H18-C17-C18-H20; C37-C36-C43-H42; C37-C36-C43-H43; C37-C36-C43-H44; C37-C36-C44-H45; C37-C36-C44-H46; C37-C36-C44-H47; C37-C38-C39-H40; C37-C38-C39-H41; H38-C37-C38-C39; H39-C37-C38-C39; C39-C42-C45-H48; C39-C42-C45-H49; C39-C42-C45-H50; C39-C42-C46-H51; C39-C42-C46-H52; C39-C42-C46-H53; H40-C39-C42-C45; H40-C39-C42-C46; H41-C39-C42-C45; H41-C39-C42-C46; C43-C36-C37-H38; C43-C36-C37-H39; C43-C36-C44-H45; C43-C36-C44-H46; C43-C36-C44-H47; C44-C36-C37-H38; C44-C36-C37-H39; C44-C36-C43-H42; C44-C36-C43-H43; C44-C36-C43-H44; C45-C42-C46-H51; C45-C42-C46-H52; C45-C42-C46-H53; C46-C42-C45-H48; C46-C42-C45-H49; C46-C42-C45-H50; H62-C58-C59-H64; H62-C58-C59-H65; H62-C58-C59-H66; H63-C58-C59-H64; H63-C58-C59-H65; H63-C58-C59-H66
0	0	0	0	74	H1-C1-N1-C2; H1-C1-N1-C4; H2-C1-N1-C2; H2-C1-N1-C4; H3-C1-N1-C2; H3-C1-N1-C4; C6-C7-N3-H13; N6-C22-C23-C24; N6-C22-C23-C28; H7-C5-N2-C2; H7-C5-N2-C3; H8-C5-N2-C2; H8-C5-N2-C3; H11-C7-N3-C8; H11-C7-N3-H13; H12-C7-N3-C8; H12-C7-N3-H13; H15-C16-N4-H14; H15-C16-N4-C15; H16-C16-N4-H14; H16-C16-N4-C15; C17-C16-N4-H14; H19-C18-N5-C19; H19-C18-N5-C21; H20-C18-N5-C19; H20-C18-N5-C21; C23-C22-N6-C19; C23-C22-N6-C20; H28-C22-N6-C19; H28-C22-N6-C20; H28-C22-C23-C24; H28-C22-C23-C28; H29-C22-N6-C19; H29-C22-N6-C20; H29-C22-C23-C24; H29-C22-C23-C28; C32-C33-C36-C37; C32-C33-C36-C43; C32-C33-C36-C44; C33-C34-C38-C37; C33-C34-C38-C39; C33-C34-C38-C40; C34-C33-C36-C37; C34-C33-C36-C43; C34-C33-C36-C44; C34-C38-C40-C41; C34-C38-C40-C47; C35-C34-C38-C37; C35-C34-C38-C39; C35-C34-C38-C40; C37-C38-C40-C41; C37-C38-C40-C47; C39-C38-C40-C41; C39-C38-C40-C47; C40-C41-C42-C39; C40-C41-C42-C45; C40-C41-C42-C46; C50-C41-C42-C39; C50-C41-C42-C45; C50-C41-C42-C46; C54-C55-C58-N1; C54-C55-C58-C59; C54-C55-C58-H62; C54-C55-C58-H63; C55-C58-N1-C2; C55-C58-N1-C4; C56-C55-C58-N1; C56-C55-C58-C59; C56-C55-C58-H62; C56-C55-C58-H63; H62-C58-N1-C2; H62-C58-N1-C4; H63-C58-N1-C2; H63-C58-N1-C4

Continued on next page

Table S4 - continued from previous page

V_1 (kcal mol^{-1})	V_2 (kcal mol^{-1})	V_3 (kcal mol^{-1})	V_4 (kcal mol^{-1})	N_{types}	**Atom-type combinations**
0	7.25	0	0	120	N7-C30-C31-C32; N7-C30-C31-H36; N7-C30-C35-C34; N7-C30-C35-H35; N8-C48-C49-C50; N8-C48-C49-H55; C9-C10-C11-C12; C9-C10-C11-H24; C10-C11-C12-C13; C10-C11-C12-C15; C11-C10-C9-C8; C11-C10-C9-C14; C11-C12-C13-C14; C11-C12-C13-H26; C12-C13-C14-C9; C12-C13-C14-H27; C13-C14-C9-C8; C13-C14-C9-C10; C15-C12-C13-C14; C15-C12-C13-H26; C22-C23-C24-C25; C22-C23-C24-H33; C22-C23-C28-C27; C22-C23-C28-H32; C23-C24-C25-C26; C23-C24-C25-H30; H24-C11-C12-C13; H24-C11-C12-C15; C24-C23-C28-C27; C24-C23-C28-H32; C24-C25-C26-C27; C24-C25-C26-C29; H25-C10-C9-C8; H25-C10-C9-C14; H25-C10-C11-C12; H25-C10-C11-H24; C25-C26-C27-C28; C25-C26-C27-H31; H26-C13-C14-C9; H26-C13-C14-H27; C26-C27-C28-C23; C26-C27-C28-H32; H27-C14-C9-C8; H27-C14-C9-C10; C28-C23-C24-C25; C28-C23-C24-H33; C29-C26-C27-C28; C29-C26-C27-H31; H30-C25-C26-C27; H30-C25-C26-C29; C30-C31-C32-C33; C30-C31-C32-H37; H31-C27-C28-C23; H31-C27-C28-H32; C31-C30-C35-C34; C31-C30-C35-H35; C31-C32-C33-C34; C31-C32-C33-C36; C32-C33-C34-C35; C32-C33-C34-C38; H33-C24-C25-C26; H33-C24-C25-H30; C33-C34-C35-C30; C33-C34-C35-H35; C35-C30-C31-C32; C35-C30-C31-H36; H36-C31-C32-C33; H36-C31-C32-H37; C36-C33-C34-C35; C36-C33-C34-C38; H37-C32-C33-C34; H37-C32-C33-C36; C38-C34-C35-C30; C38-C34-C35-H35; C38-C40-C41-C42; C38-C40-C41-C50; C38-C40-C47-C48; C38-C40-C47-H54; C40-C41-C50-C49; C40-C41-C50-H56; C40-C47-C48-N8; C40-C47-C48-C49; C41-C40-C47-C48; C41-C40-C47-H54; C42-C41-C50-C49; C42-C41-C50-H56; C47-C40-C41-C42; C47-C40-C41-C50; C47-C48-C49-C50; C47-C48-C49-H55; C48-C49-C50-C41; C48-C49-C50-H56; C51-C52-C53-C54; C51-C52-C53-H59; C51-C52-C57-C56; C51-C52-C57-H61; C52-C53-C54-C55; C52-C53-C54-H58; C53-C52-C57-C56; C53-C52-C57-H61; C53-C54-C55-C56; C53-C54-C55-C58; H54-C47-C48-N8; H54-C47-C48-C49; C54-C55-C56-C57; C54-C55-C56-H60; H55-C49-C50-C41; H55-C49-C50-H56; C55-C56-C57-C52; C55-C56-C57-H61; C57-C52-C53-C54; C57-C52-C53-H59; H58-C54-C55-C56; H58-C54-C55-C58; C58-C55-C56-C57; C58-C55-C56-H60; H59-C53-C54-C55; H59-C53-C54-H58; H60-C56-C57-C52; H60-C56-C57-H61

Table S5 Improper torsion parameters. Atom labels follow Fig. S1

k_χ (kcal mol^{-1})	d	n	N_{types}	**Atom-type combinations**
10.5	-1.0	2.0	4	C8-C9-N3-O1; C15-C12-N4-O2; C29-C26-N7-O3; C51-C52-N8-O4
0.0	-1.0	2.0	5	N1-C1-C2-C4; N1-C2-C4-C58; N2-C2-C3-C5; N5-C18-C19-C21; N6-C19-C20-C22
2.5	-1.0	2.0	40	C2-H6-N1-N2; C3-C4-H4-N2; N3-C7-C8-H13; C4-C3-H5-N1; N4-C15-C16-H14; N7-C29-C30-H34; N8-C48-C51-H57; C9-C10-C14-C8; C10-C11-C9-H25; C11-C10-C12-H24; C12-C11-C13-C15; C13-C12-C14-H26; C14-C13-C9-H27; C19-H21-N5-N6; C20-C21-H22-N6; C21-C20-H23-N5; C23-C22-C24-C28; C24-C23-C25-H33; C25-C24-C26-H30; C26-C25-C27-C29; C27-C26-C28-H31; C28-C23-C27-H32; C30-C31-C35-N7; C31-C30-C32-H36; C32-C31-C33-H37; C33-C32-C34-C36; C34-C33-C35-C38; C35-C30-C34-H35; C40-C38-C41-C47; C41-C40-C42-C50; C47-C40-C48-H54; C48-C47-C49-N8; C49-C48-C50-H55; C50-C41-C49-H56; C52-C51-C53-C57; C53-C52-C54-H59; C54-C53-C55-H58; C55-C54-C56-C58; C56-C55-C57-H60; C57-C52-C56-H61

S3. Additional structural analyses for 4-mer systems

Figures S2 and S3 report the RDF and neighbor-density analyses for hydrogen–nitrogen and hydrogen–oxygen interactions in 4-mer systems. They are the 4-mer counterparts to Figs. 7 and 8, computed using the same analysis protocol.

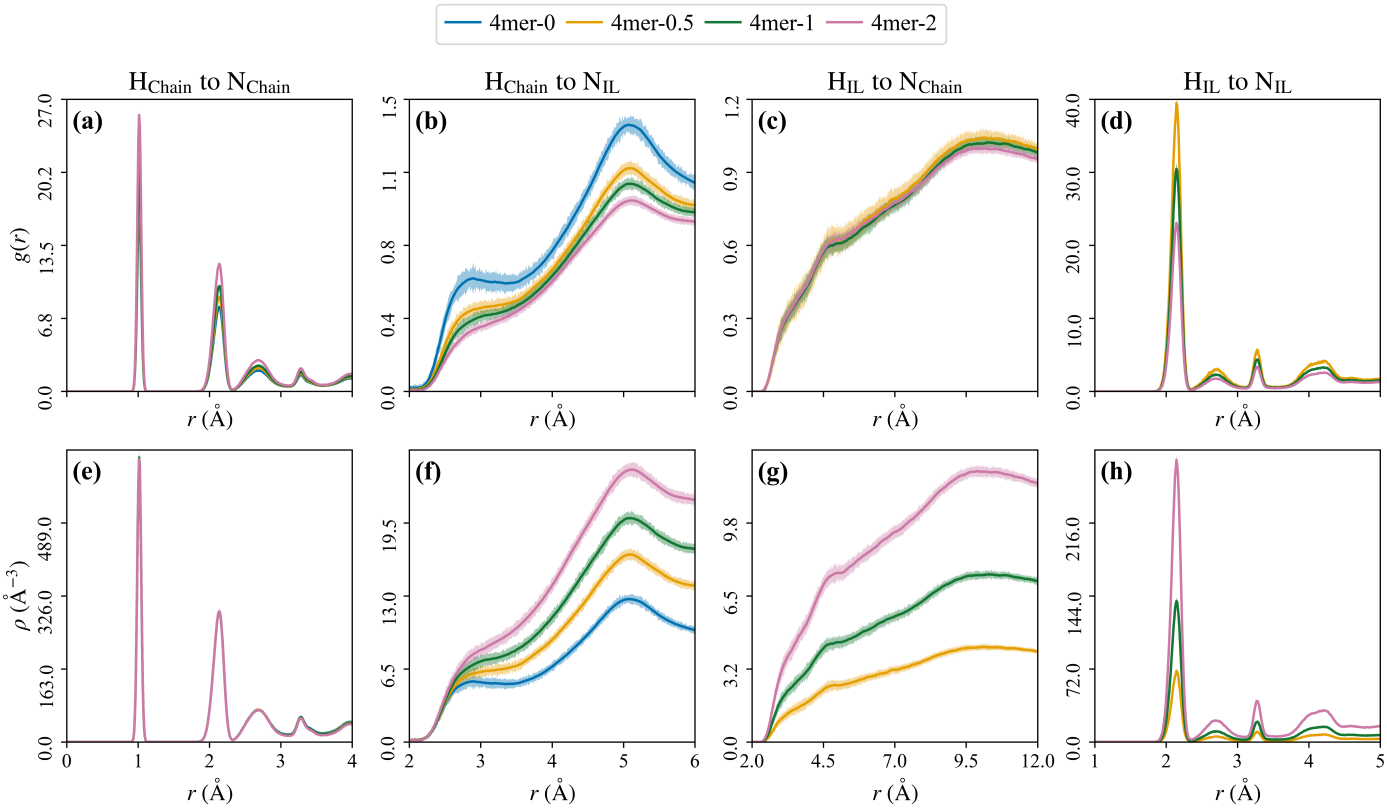


Fig. S2 RDF and neighbor density analysis for hydrogen and nitrogen interactions among chain-to-chain, chain-to-IL, and IL-to-IL pairs in 4-mer systems.

S4. CO_2 binding configurations

Figure S4 shows the initial (pre-optimization) CO_2 placements on representative polymer and IL fragments for all binding motifs. Some distinct starting orientations converge to similar optimized geometries, and the configurations in Fig. S4 document these different initial placements.

S5. MSD of 8-mer systems

Figure S5 and Table S6 report the MSD curves and power-law fit parameters for the 8-mer systems. These results correspond to the 4-mer analyses presented in Fig. 20 and Table 3.

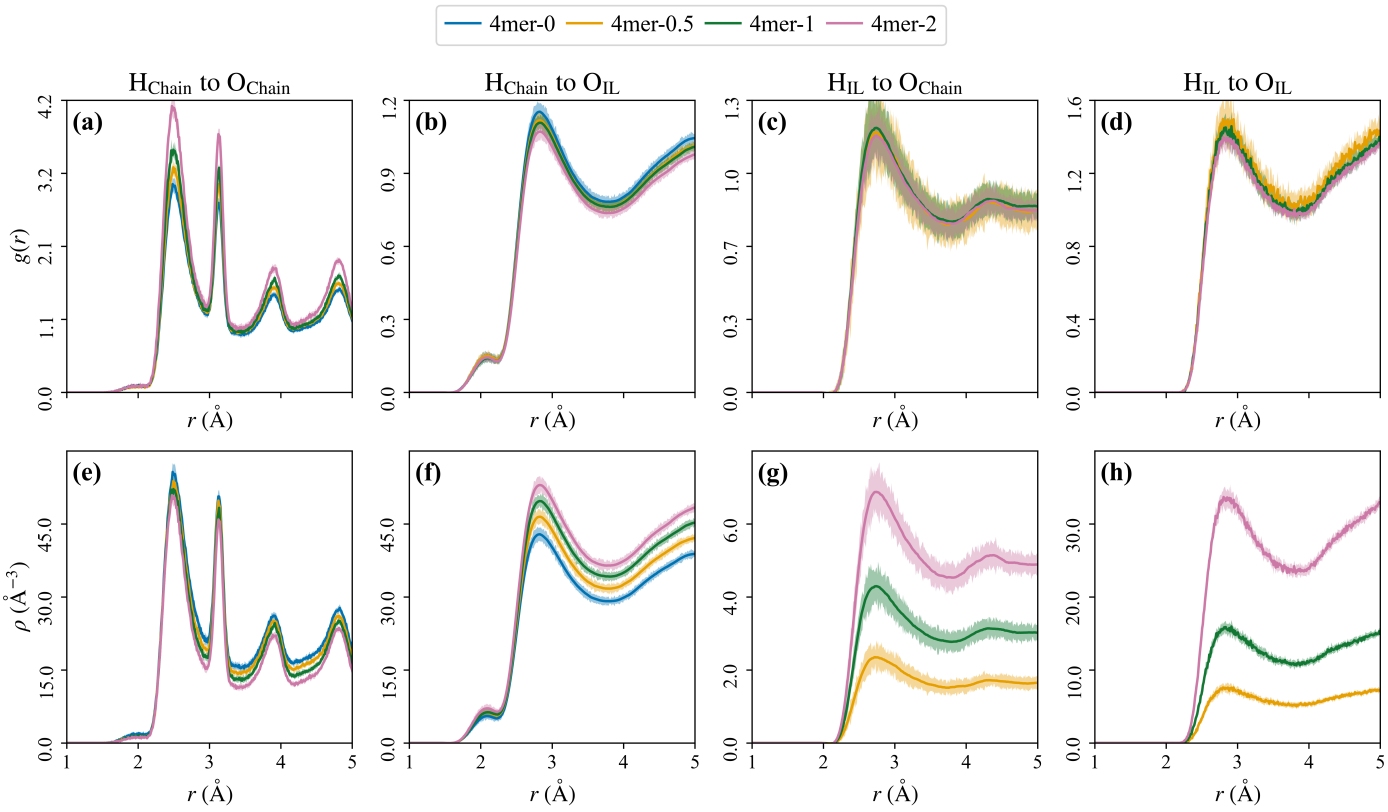
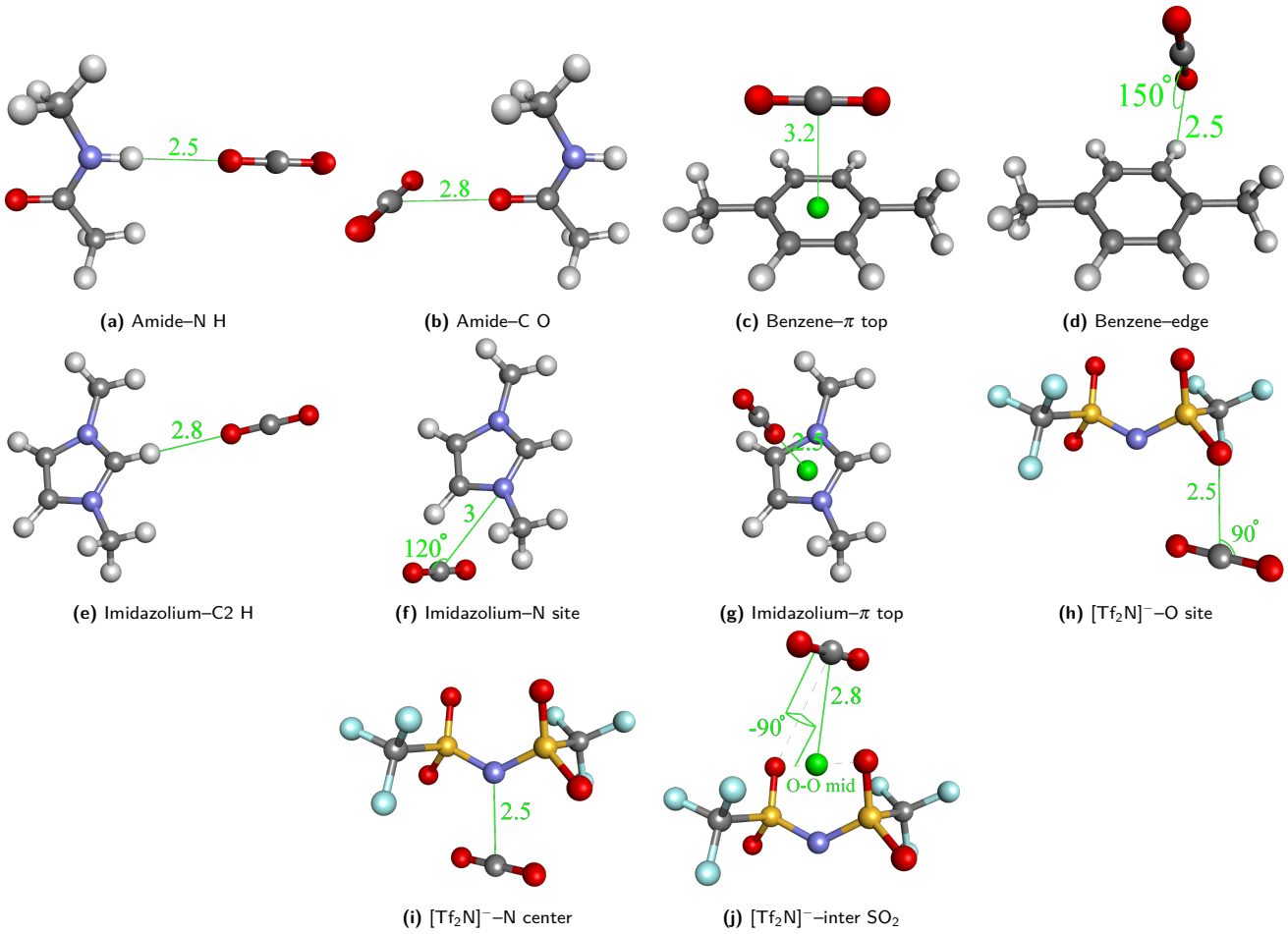


Fig. S3 RDF and neighbor density analysis for hydrogen and oxygen interactions among chain-to-chain, chain-to-IL, and IL-to-IL pairs in 4-mer systems.

Table S6 Power-law exponents A and α from MSD fits, $\mathrm{MSD}(t) = At^{\alpha}$, for the polymer, $[C_4mim]^+$ cation, and $[Tf_2N]^-$ anion in 8-mer systems. Time windows are listed in the table.

	Window 1		Window 2		Window 3	
	A	α	A	α	A	α
Polymer	(0.01-0.24)		(0.24-0.54)		(0.54-1.0) ns	
8mer-0	1.78	0.21	1.61	0.01	1.85	0.45
8mer-0.5	1.75	0.21	–	0.00†	1.81	0.37
8mer-1	1.82	0.21	–	0.00†	1.85	0.36
8mer-2	1.91	0.22	1.66	0.13	1.88	0.23
Cation	(0.01–0.49)		(0.49-0.87)		(0.87-1.0) ns	
8mer-0	–	–	–	–	–	–
8mer-0.5	5.65	0.20	5.75	0.27	5.47	0.08
8mer-1	5.70	0.20	5.90	0.30	5.78	0.23
8mer-2	5.80	0.20	6.00	0.25	5.90	0.08
Anion	(0.01-0.26)		(0.26-0.75)		(0.75-1.0) ns	
8mer-0	6.00	0.31	5.09	0.14	5.46	0.30
8mer-0.5	6.23	0.31	5.52	0.20	5.76	0.27
8mer-1	6.70	0.33	5.96	0.23	6.17	0.29
8mer-2	7.44	0.33	6.78	0.28	6.60	0.18

† Fits in this interval are noise-dominated and consistent with a plateau ($\alpha \approx 0$); small negative values may arise from MSD fluctuations.



(a) Amide–N H **(b)** Amide–C O **(c)** Benzene–π top **(d)** Benzene–edge

(e) Imidazolium–C2 H **(f)** Imidazolium–N site **(g)** Imidazolium–π top **(h)** $[Tf_2N]^-$–O site

(i) $[Tf_2N]^-$–N center **(j)** $[Tf_2N]^-$–inter SO_2

Fig. S4 Initial CO_2 binding configurations on representative polymer and IL fragments.

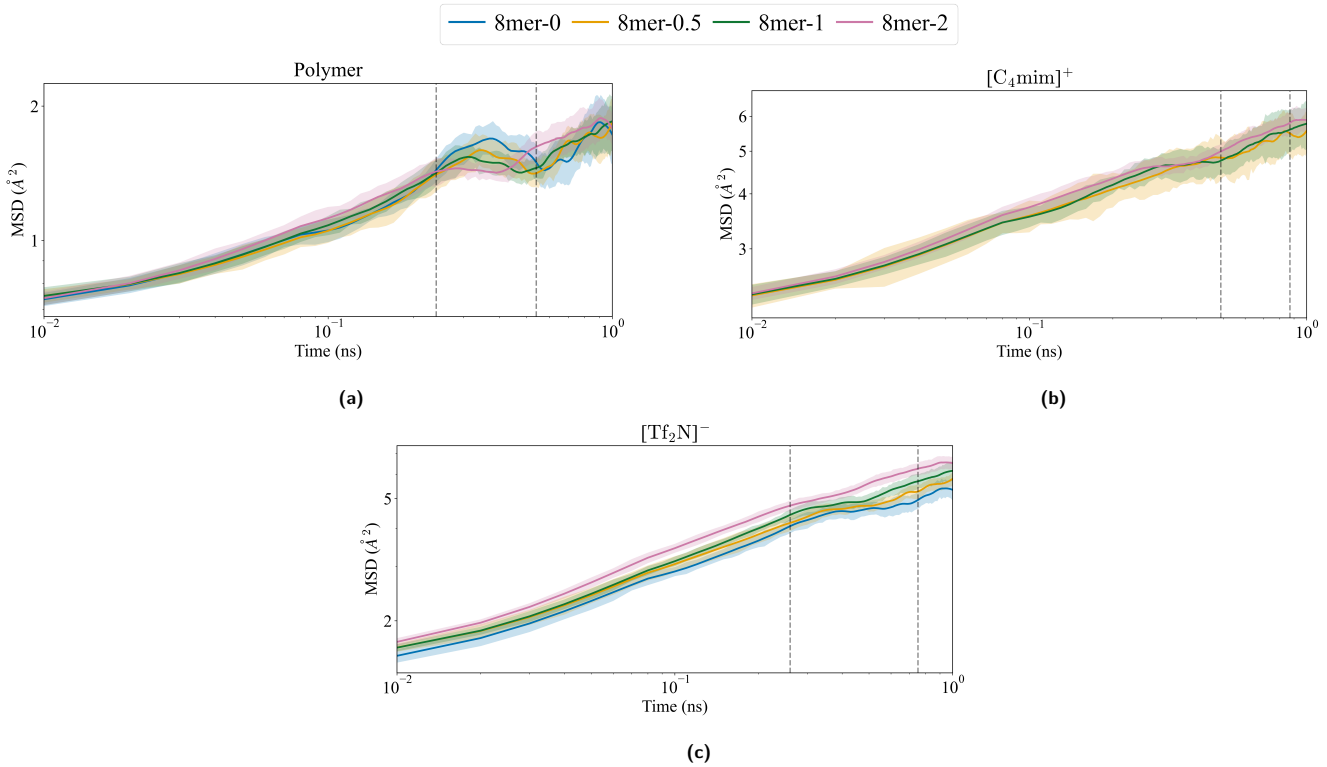


Fig. S5 MSD plotted on log–log scales for (a) 8-mer polymer chains, (b) $[C_4mim]^+$ cations, and (c) $[Tf_2N]^-$ anions as a function of IL concentration; shaded regions represent SD.