Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Molecular Dynamics Simulations of Side Chain Pendant of Perfluorosulfonic Acid Polymer Electrolyte Membranes

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Supporting Information

Table S1. Force field parameters for side chain pendants (Dow, Aciplex and Nafion).

Atom	σ (nm)			ε (kJ mol^{-1})		
C	0.350			0.276144		
F	0.295			0.221752		
S	0.355			1.406000		
O	0.300			0.711280		
O	0.296			0.711280		
Bond	r (nm)			k_b(kJ mol^{-1} nm^{-1})		
C-F	0.1332			307105.6		
C-C	0.1529			224262.4		
C-O	0.1410			267776.0		
C-S	0.1810			185769.6		
S-O	0.1440			585760.0		
Bond angle	θ_0 (deg)			k_θ (kJ mol^{-1} rad^{-1})		
F-C-F	109.1			644.336		
F-C-S	109.5			418.400		
F-C-C	109.5			418.400		
F-C-O	109.8			425.000		
C-C-C	112.5			488.273		
C-C-O	109.5			418.400		
C-O-C	116.9			694.544		
C-S-O	108.9			619.232		
O-S-O[a]	119.0			870.272		
Dihedral angle	Dihedral coefficient (kJ mol^{-1})					
	C_0	C_1	C_2	C_3	C_4	C_5
C-C-C-F[b]	0.2460	-0.3285	0.5831	1.8585	7.4668	0.3716
F-C-C-F[b]	0.7084	0.6226	0.9997	0.3564	14.9016	-6.1012

F-C-C-O[b]	0.1936	1.0729	0.6616	1.9442	12.1706	-6.6721
C-C-S-O[b]	-0.5741	1.0065	-0.5901	0.9551	11.2104	-0.0044
C-C-O-C[c]	47.1740	-44.0367	1.7176	-6.8656	0.0	0.0
F-C-O-C[c]	45.1736	46.0834	3.0942	-159.279	0.0	0.0

[a]Ref. No. 59, [b]Periodic function (this work-from eq. 2), and [c]Periodic function (this work-from eq. 3)

Table S2. Box length and density (ρ) obtained from a 10 ns equilibration run for side chain pendant/water mixtures at 300 K.

λ	Dow		Aciplex		Nafion	
	Box length (Å)	ρ (g cm^{-3})	Box length (Å)	ρ (g cm^{-3})	Box length (Å)	ρ (g cm^{-3})
3	60.550	1.680	66.089	1.736	66.670	1.732
6	64.392	1.563	69.521	1.634	69.904	1.636
9	67.975	1.479	72.502	1.559	72.917	1.565
12	71.003	1.419	75.209	1.497	75.632	1.503
15	74.062	1.370	77.896	1.448	78.290	1.451

Table S3. Box length and density (ρ) obtained from a 10 ns equilibration run for side chain pendant/water mixtures at 350 K.

λ	Dow		Aciplex		Nafion	
	Box length (Å)	ρ (g cm^{-3})	Box length (Å)	ρ (g cm^{-3})	Box length (Å)	ρ (g cm^{-3})
3	61.643	1.590	67.461	1.631	66.841	1.632
6	65.646	1.483	70.682	1.545	71.507	1.550
9	69.003	1.407	73.865	1.468	74.208	1.479
12	72.373	1.353	76.952	1.408	76.914	1.424
15	75.181	1.309	79.173	1.376	79.667	1.380

Table S4. Diffusion coefficients (D_A) of hydronium ions in side chain pendant/water mixtures obtained from a 20 ns production run.

SSC pendant	Temperature (K)	D_A ($\times 10^{-5}$ cm^2 sec^{-1})				
		λ=3	λ=6	λ=9	λ=12	λ=15
Dow	300	0.0323	0.1303	0.2401	0.3570	0.4599
	320	0.0590	0.2632	0.4880	0.5764	0.6811
	335	0.1124	0.3265	0.5861	0.8042	1.0104
	350	0.1568	0.5141	0.8326	1.1348	1.1939
Aciplex	300	0.0175	0.0979	0.1824	0.2858	0.3193
	320	0.0339	0.1699	0.3196	0.4579	0.5662
	335	0.0548	0.2302	0.4456	0.6083	0.7930
	350	0.0988	0.3457	0.6385	0.8899	0.9414
Nafion	300	0.0180	0.0751	0.1430	0.2193	0.2275
	320	0.0361	0.1286	0.2470	0.3110	0.4674
	335	0.0537	0.2054	0.3720	0.4706	0.5298
	350	0.0774	0.2812	0.4665	0.5820	0.7540

Table S5. Diffusion coefficients (D_A) of water in side chain pendant/water mixtures obtained from a 20 ns production run.

SSC pendant	Temperature (K)	D_A ($\times 10^{-5}$ cm^2 sec^{-1})				
		λ=3	λ=6	λ=9	λ=12	λ=15
Dow	300	0.2097	0.5201	0.8542	1.0739	1.2662
	320	0.3580	0.8606	1.3120	1.6571	1.9425
	335	0.5562	1.2149	1.7907	2.2278	2.5225
	350	0.7354	1.6351	2.2614	2.8246	3.1875
Aciplex	300	0.1220	0.4545	0.7081	0.9467	1.1004
	320	0.2319	0.7165	1.1305	1.4255	1.7134
	335	0.3650	0.9167	1.4267	1.8755	2.2655
	350	0.5248	1.2890	1.8975	2.4173	2.8161
Nafion	300	0.1380	0.3978	0.6520	0.9626	1.1158
	320	0.2392	0.5713	1.0210	1.3198	1.6121
	335	0.3860	0.8935	1.4253	1.7164	2.0581
	350	0.5040	1.1295	1.8252	2.2710	2.5097

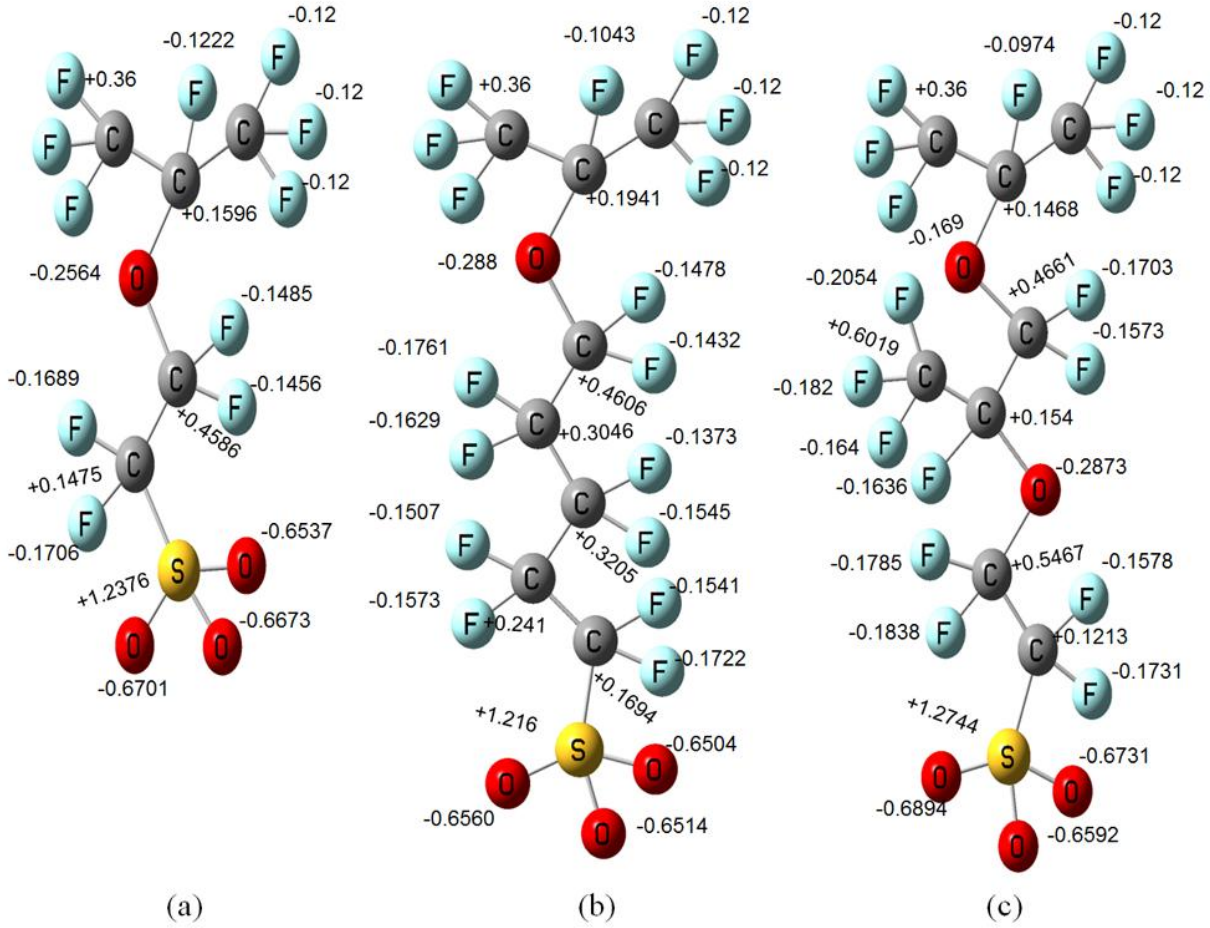

Figure S1: Partial charges for a) Dow, b) Aciplex and c) Nafion side chain pendant of PFSA ionomer membrane.

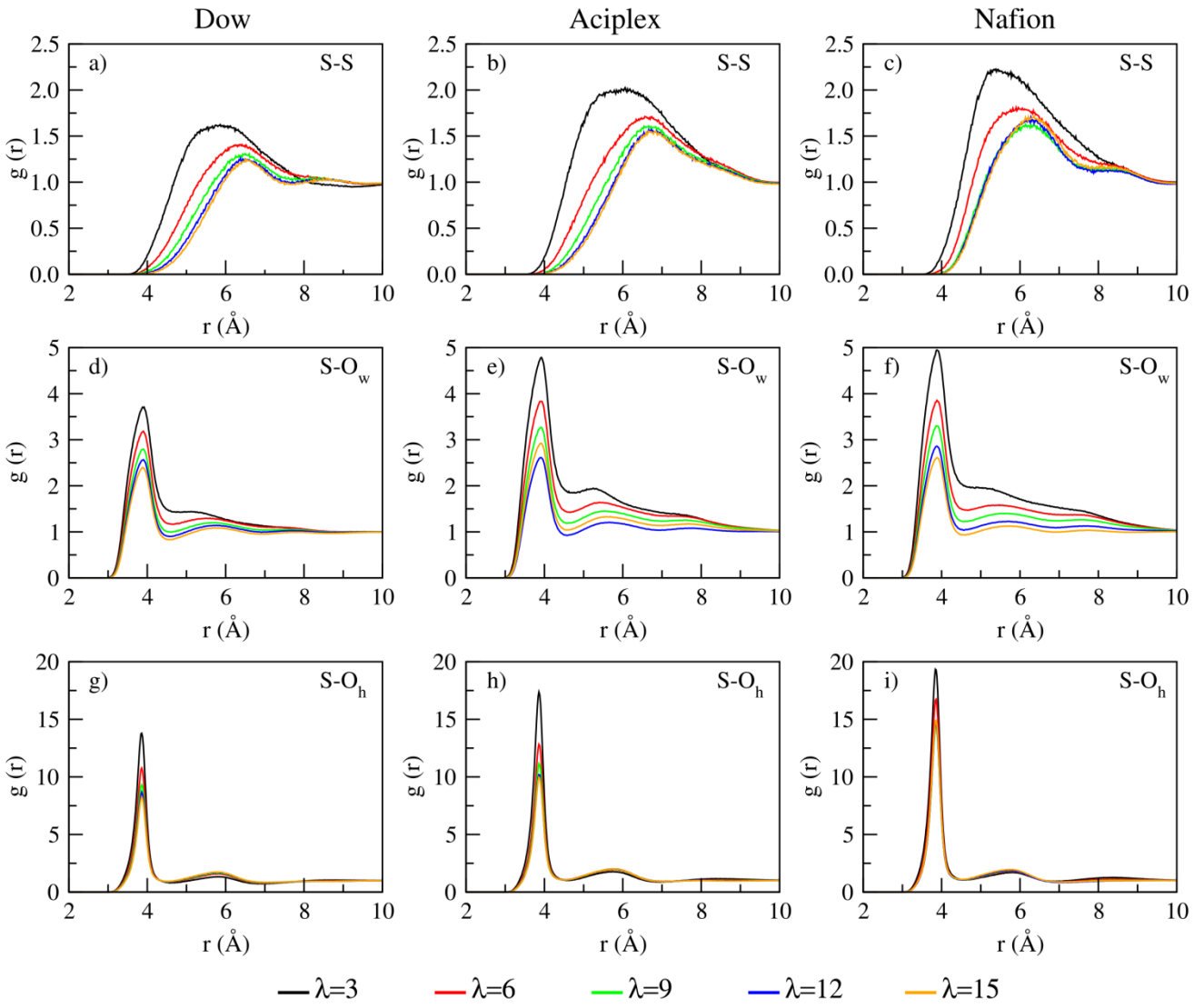

Figure S2: a-c) S-S, d-f) S-O$_w$ and g-i) S-O$_h$ RDFs at 350 K.

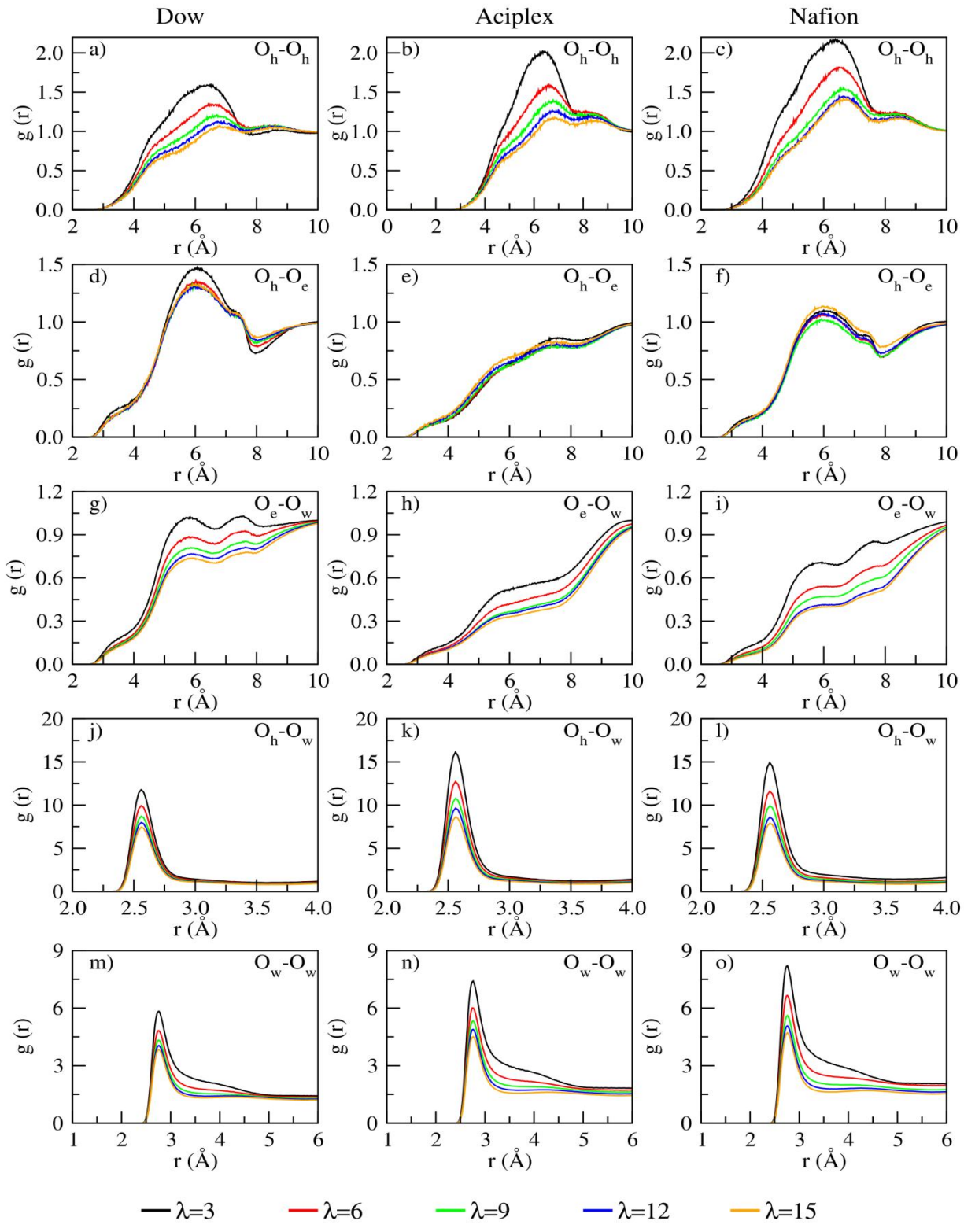

Figure S3: a-c) O_h-O_h, d-f) O_h-O_e, g-i) O_e-O_w, j-l) O_h-O_W and m-o) O_w-O_w RDFs at 350 K.

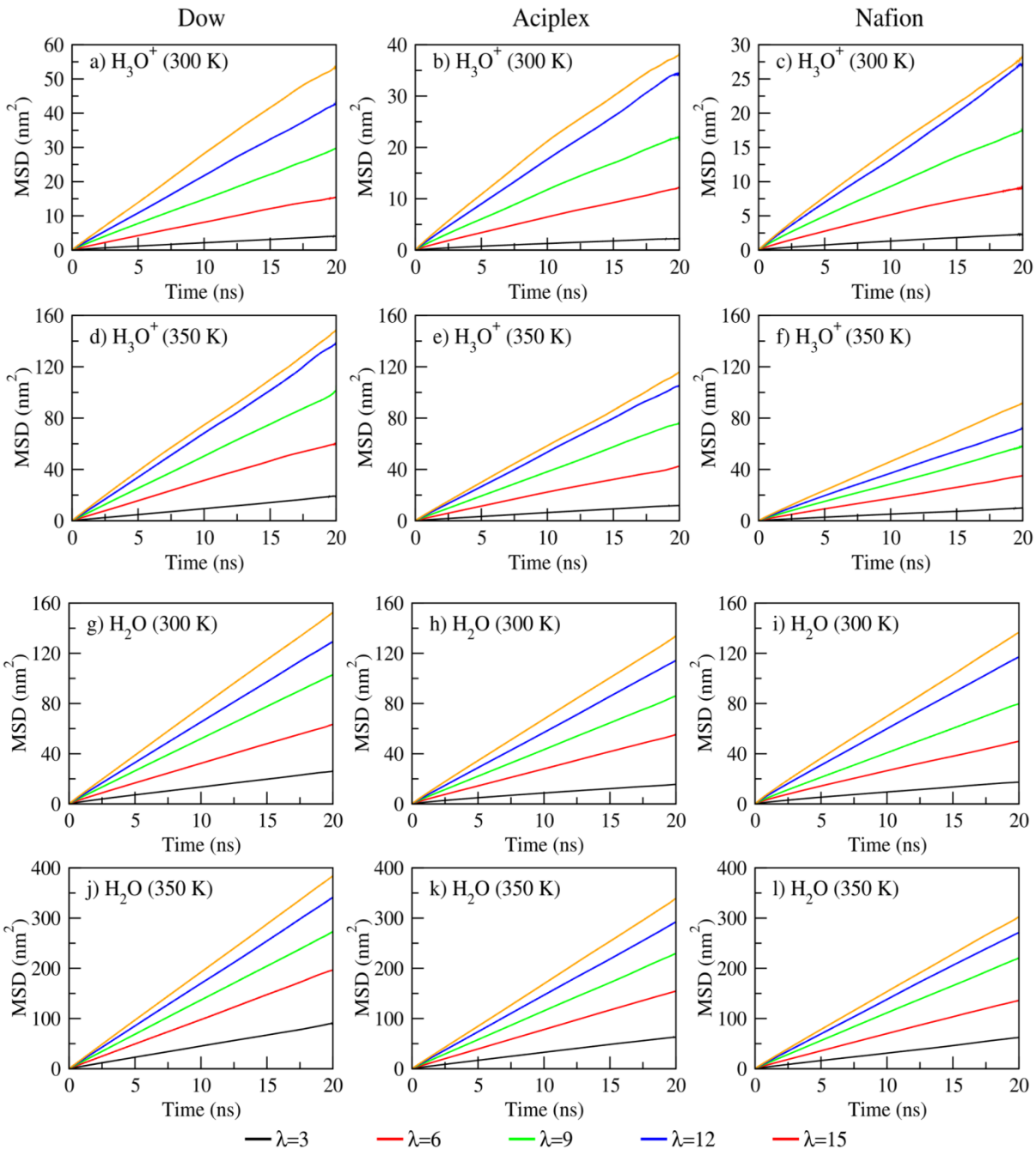

Figure S4. Mean Square Displacement of 1) hydronium ion a-c) at 300 K, d-f) at 350 K and 2) water g-i) at 300 K, j-l) at 350 K.

COMPLETE REFERENCE (50)

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