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Electronic Supplementary Information (ESI)

Effect of Ionic Groups on the Morphology and Transport Properties in a Novel Perfluorinated Ionomer Containing Sulfonic and Phosphonic Acid Groups: A Molecular Dynamics Study

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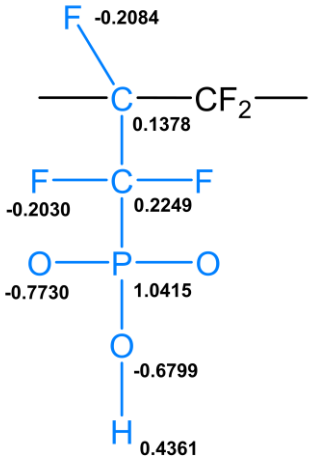

Fig. S1 RESP2 partial charge of the phosphonic acid side chain.

Table S1. Force field parameters of the phosphonic acid side chain.

		R_0 (nm)	K_b (KJ/mol/nm^2)
E_{bond}	C-P	0.1911	127769.10
	P-O(P)	0.1496	491803.35
	P-O(PH)	0.1640	227641.70
	O-H	0.0964	132979.80
	C-F	0.1355	482839.20
	C-C	0.1560	202656.40

		ϕ_s (deg)	n	K_ϕ (KJ/mol)
$E_{dihedral}$	X-C-P-O	0	3	0.9302
	X-P-O-H	0	3	2.7906

		θ (deg)	K_θ(KJ/mol/deg^2)
E_{angle}	C-C-P	122.8810	1145.4570
	F-C-P	107.1860	747.2961
	C-P-OP	105.2560	802.8955
	C-P-O(PH)	101.7190	646.3194
	O(P)-C-O(P)	124.0050	381.4145
	O(P)-C-O(PH)	109.0590	729.5632
	P-O(PH)-H(OP)	111.1570	381.4145

		σ (nm)	ε (KJ/mol)
$E_{L\text{-}J}$	P	0.3697	1.3389

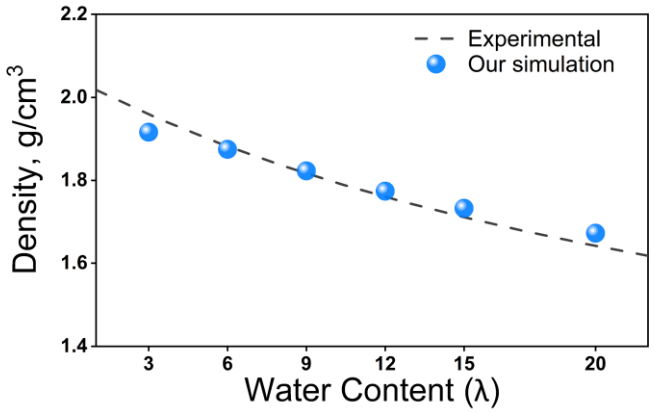

Fig S2. Experimental and simulated densities of Nafion 1144 (PFSA in this study) at different hydration level.

Table S2. Simulated densities (g/cm^3) of PFSA, PFSA-PFPA and PFPA at different water contents.

λ	PFSA	PFSA-PFPA	PFPA
3	1.9162	1.9242	1.9228
6	1.8749	1.8755	1.8814
9	1.8228	1.8215	1.8113
12	1.7741	1.7716	1.7590
15	1.7329	1.7259	1.7131
20	1.6729	1.6620	1.6473

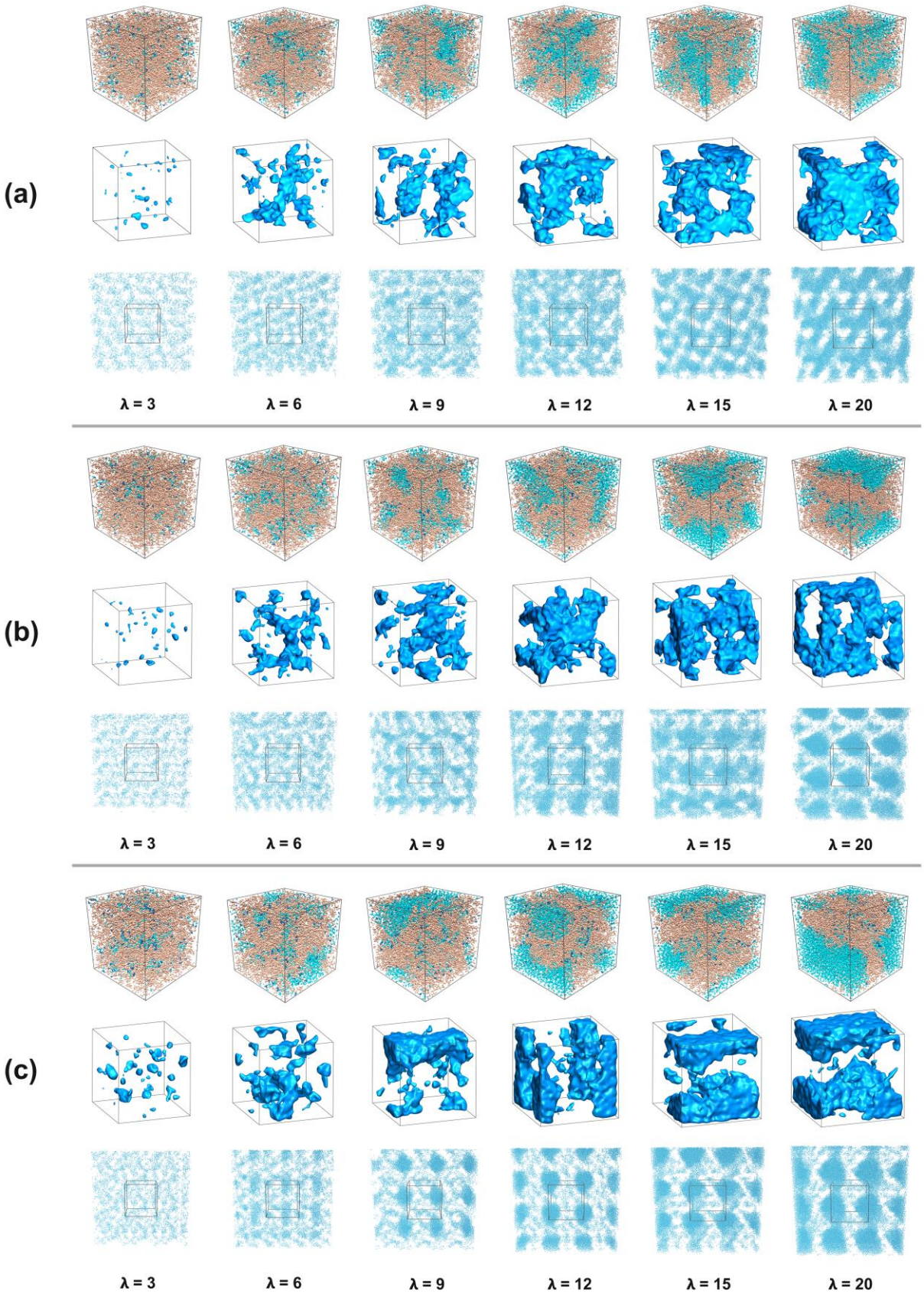

Fig. S3 Snapshots of the simulation box (upper row), iso-surface representations of the aqueous domain (middle row) and periodic snapshots of the aqueous domain (bottom row) of (a) PFSA, (b) PFSA-PFPA and (c) PFPA systems at different water contents. In the simulation snapshots, atoms of water molecules, hydronium ions and ionomers are depicted in cyan,

blue and orange, respectively. The iso-surfaces of the aqueous domain are shown in blue. Periodic snapshots are taken in two dimensions of the simulation box, with all oxygen atoms in water molecules and hydronium ions depicted in cyan.

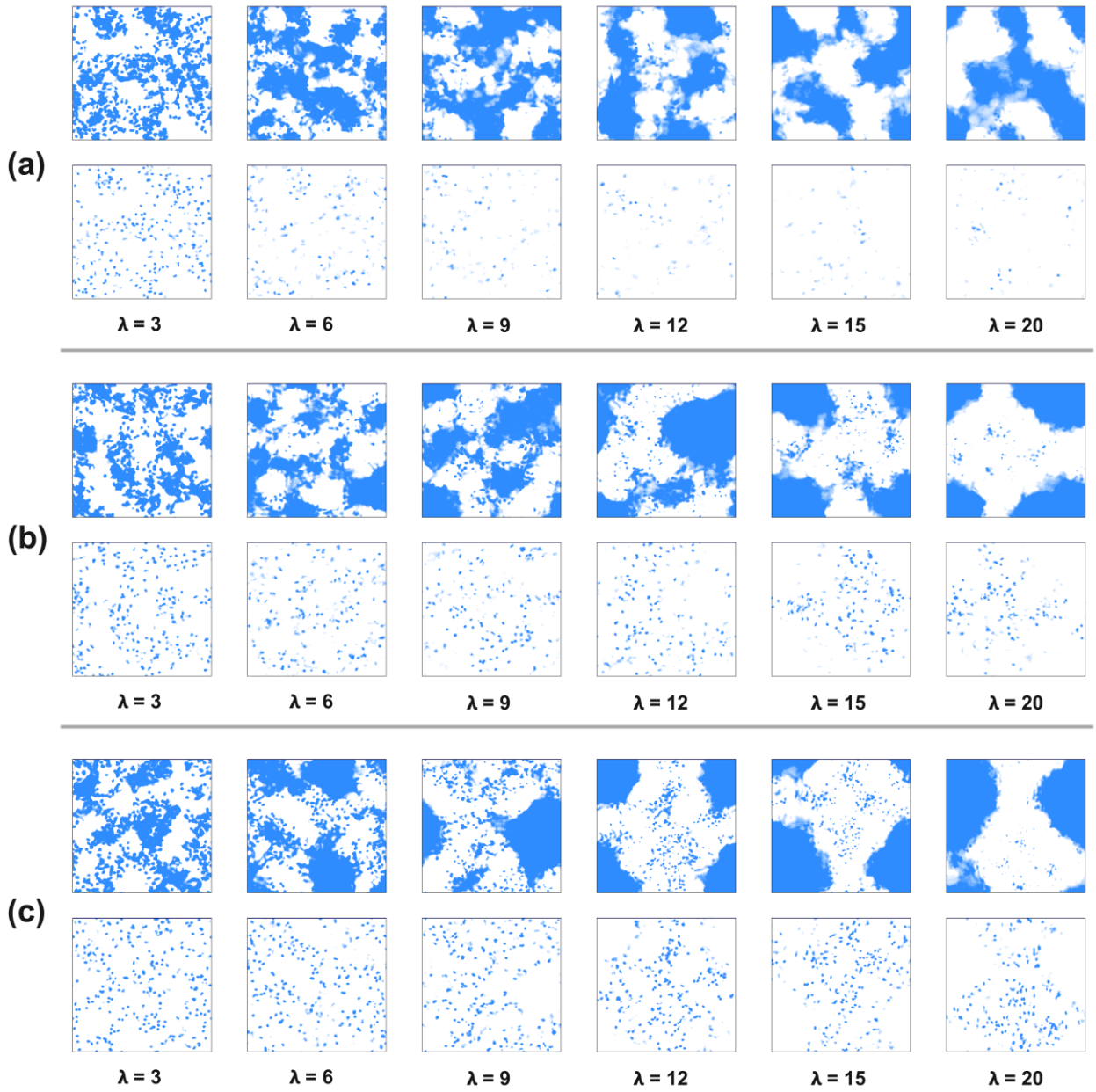

Fig. S4 2-D density maps of the aqueous domain (upper row) and the hydronium ions (bottom row) in (a) PFSA, (b) PFSA-PFPA and (c) PFPA systems at different water contents. The color bar in 2-D density maps ranges from white to blue, and the upper limit in each map is proportional to the respective total count of particles for normalization.

Table S3. Coordination number of the sulfonic/phosphonic acid groups around different ionic groups in PFSA, PFSA-PFPA and PFPA systems at different water contents.

λ	S-S_{PFSA}	S-$S_{PFSA\text{-}PFPA}$	P-P_{PPFA}	P-$P_{PFSA\text{-}PFPA}$	S-$P_{PFSA\text{-}PFPA}$
3	3.19	1.70	4.07	2.14	1.37
6	1.95	0.82	3.54	1.72	0.91
9	1.43	0.55	3.31	1.48	0.69
12	1.13	0.55	3.07	1.86	0.58
15	0.86	0.58	3.06	1.81	0.54
20	0.87	0.40	2.91	1.84	0.43

The cut-off radius for sulfur-sulfur, phosphorus-phosphorus and sulfur-phosphorus pairs is set to 0.68 nm, 0.78 nm and 0.66 nm, respectively, for determination of the coordination number.

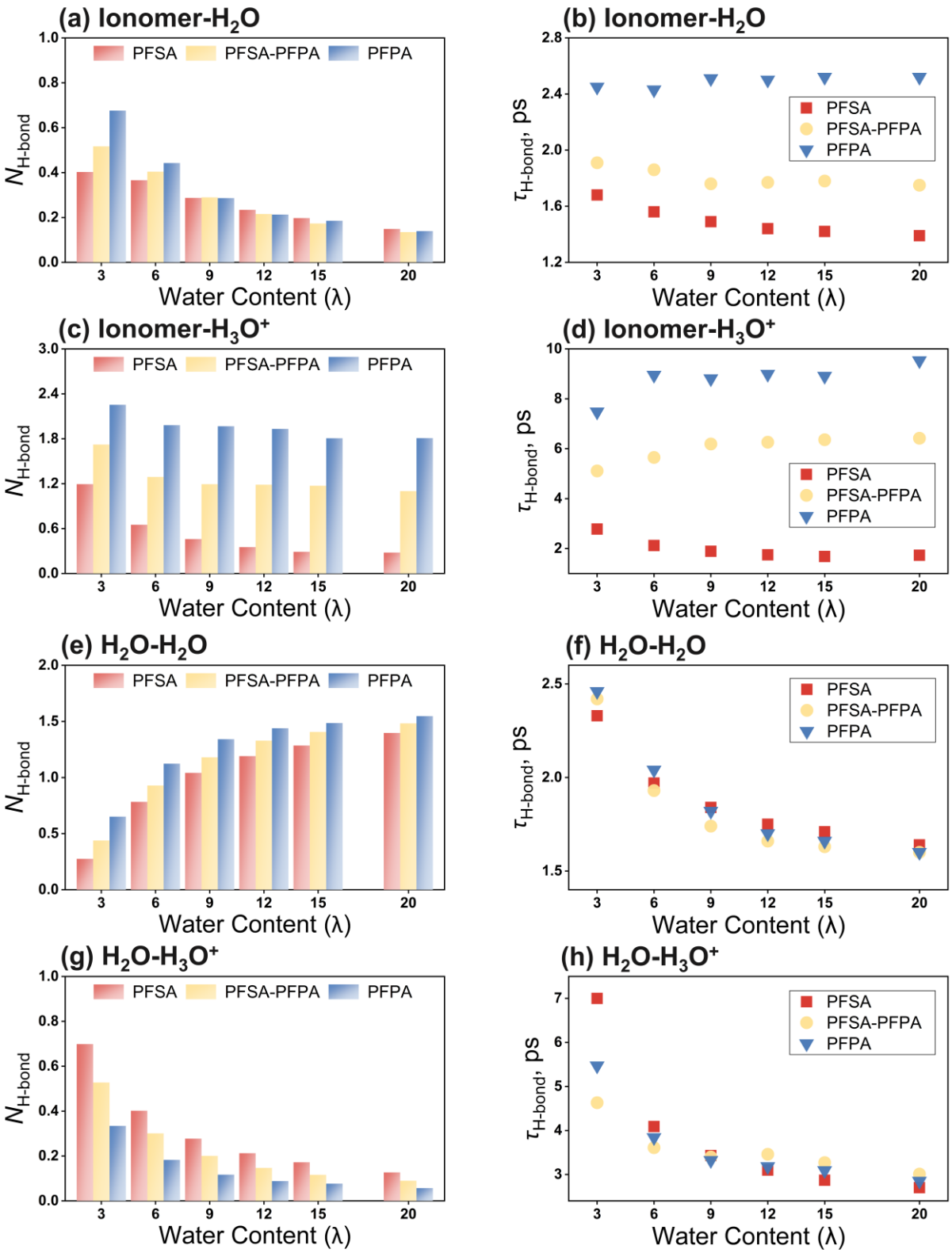

Fig. S5 Normalized average number ($N_{H\text{-}bond}$, left panel) and average lifetime ($\tau_{H\text{-}Bond}$, right panel) of hydrogen bonds formed between different donor-acceptor pairs in three systems at different water contents.

The $N_{H\text{-}bond}$ for different donor-acceptor pairs in Fig. S5 are normalized to obtain comparative values for representations of the ability to form hydrogen bonds. The $N_{H\text{-}bond}$ for the ionomer-H_2O pair is normalized by the number of the water molecules, and that for the ionomer-H_3O^+ pair is normalized by the number of the hydronium ions. The $N_{H\text{-}bond}$ for the H_2O-H_2O and H_2O-H_3O^+ pairs are both normalized by the total number of the water molecules, which are considered as

the acceptors when forming hydrogen bonds. All the $N_{H\text{-}bond}$ decrease with increasing water content except for the hydrogen bonds formed between water molecules. The hydronium ions show excellent abilities to form hydrogen bonds, especially with the phosphonic acid-containing ionomers. Meanwhile, the $\tau_{H\text{-}Bond}$ decrease for all non-phosphonic-acid-associated donor-acceptors. The phosphonic acid groups in PFPA show distinct behaviors in forming hydrogen bonds with the hydronium ions compared to the sulfonic acid groups in PFSA. It can be concluded that strong interactions exist between the ionomers and the hydronium ions that are well maintained during hydration.

Table S4. Coordination number for water molecules and hydronium ions around different ionic groups in PFSA, PFSA-PFPA and PFPA systems at different water contents.

λ		S_{PFSA}	$S_{PFSA\text{-}PFPA}$	P_{PPFA}	$P_{PFSA\text{-}PFPA}$		S_{PFSA}	$S_{PFSA\text{-}PFPA}$	P_{PFPA}	$P_{PFSA\text{-}PFPA}$
3	H_2O	2.71	3.45	2.09	1.58	H_3O^+	2.42	2.12	2.41	2.74
6		4.92	5.45	3.19	2.93		1.60	1.30	2.09	2.23
9		5.83	6.00	3.23	3.25		1.22	1.00	2.02	2.07
12		6.37	6.27	3.26	3.14		1.10	0.92	2.00	2.11
15		6.68	6.31	3.56	3.19		0.85	0.91	1.89	2.11
20		6.81	6.74	3.54	3.24		0.81	0.75	1.85	2.01

The cut-off radius for $S\text{-}O_{water}$, $P\text{-}O_{water}$, $S\text{-}O_{hydronium\ ion}$ and $P\text{-}O_{hydronium\ ion}$ pairs is set to 0.46 nm, 0.74 nm, 0.45 nm and 0.42 nm, respectively, for determination of the coordination number.

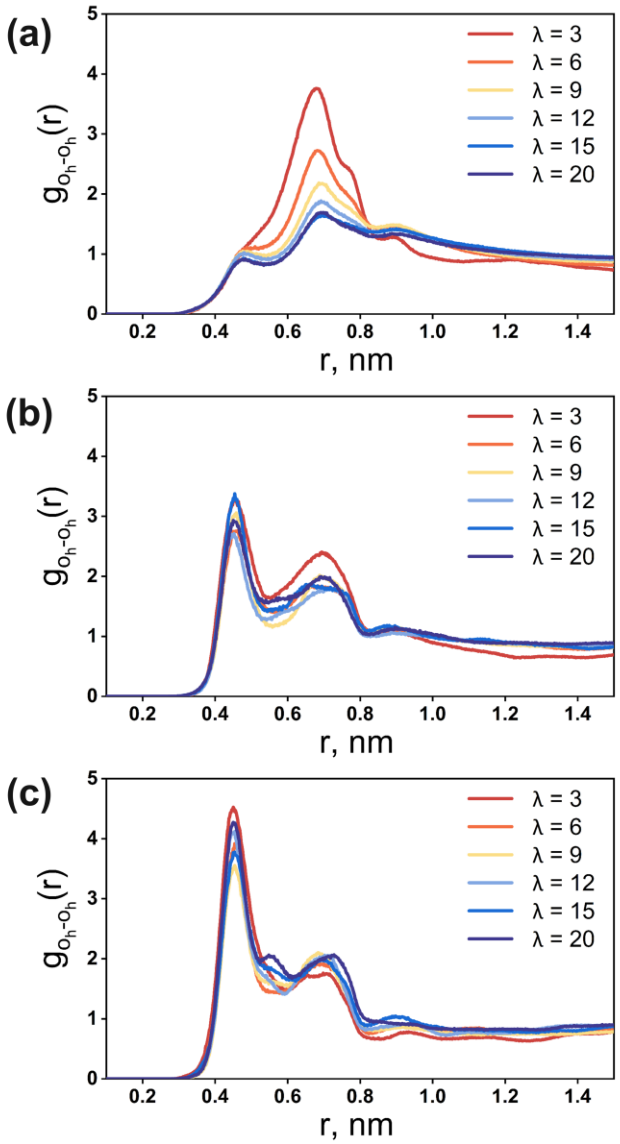

Fig S6. RDF curves of the hydronium ions around hydronium ions at different water contents in (a) PFSA, (b) PFSA-PFPA and (c) PFPA.

Table S5. Coordination number of hydronium ions in the 1st and 2nd coordination shell around hydronium ions in PFSA, PFSA-PFPA and PFPA systems at different water contents.

λ		PFSA	PFSA-PFPA	PFPA		PFSA	PFSA-PFPA	PFPA
3		0.52	1.11	1.59		3.93	3.17	2.62
6	1st	0.40	0.86	1.19	2nd	2.77	2.42	2.62
9	CN,	0.35	0.79	1.03	CN,	2.18	2.22	2.47
12	H_3O^+-	0.31	0.69	1.05	H_3O^+ -	1.85	1.98	2.25
15	H_3O^+	0.28	0.76	0.99	H_3O^+	1.71	1.98	2.17
20		0.24	0.65	0.95		1.42	1.80	2.09

The cut-off radius for the 1st and 2nd coordination shell of the $O_{hydronium\ ion}$-$O_{hydronium\ ion}$ coordination pair is set to 0.55 nm and 0.81 nm, respectively, for determination of the coordination number.

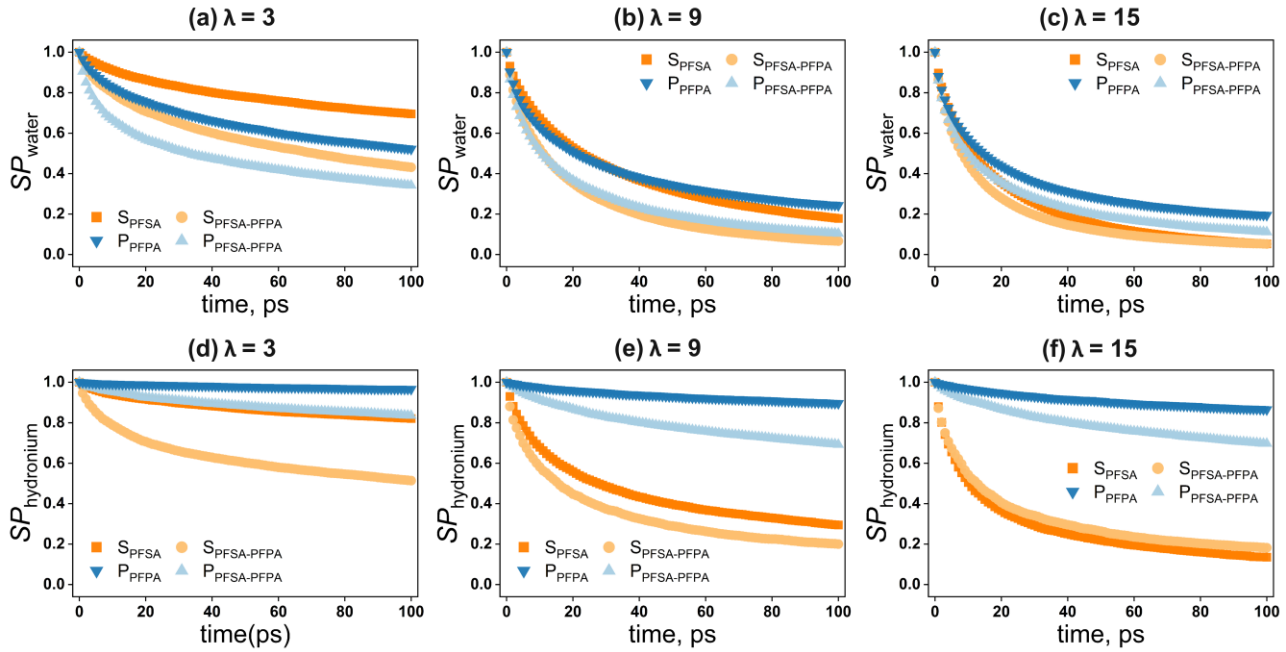

Fig. S7 Survival probability of water molecules (top row, SP_{water}) and hydronium ions (bottom row, $SP_{hydronium}$) around different ionic groups at different water contents.