Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

Supporting information

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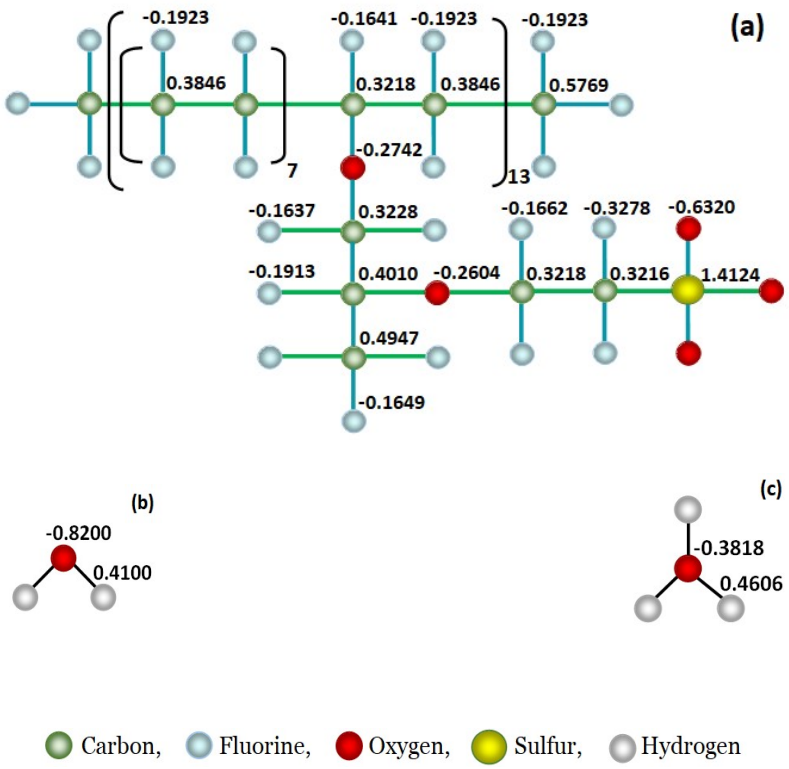

Figure S1. Partial charge of (a) Nafion® polymer, (b) water molecule and (c) hydronium ions

Table S1. Force fields used for the hydrated Nafion® system. CB = backbone carbon, C= sidechain carbon, S= sulfur, F= fluorine and O=oxygen

$E_{bond} = \frac{1}{2}k_b(r - r_0)^2$, $E_{angle} = \frac{1}{2}k_\theta(\theta - \theta_0)^2$, $E_{torsion} = k_\phi\left(1 + cos(n\phi - \phi_s)\right)$, $E_{L-J} = 4\varepsilon\{(\frac{r_0}{r})^{12} - (\frac{r_0}{r})^6\}$

E_{bond}	$r_0\,(nm)$	$k_b\,(kJ/mol/nm^2)$	E_{angle}	$\theta_0\,(degree)$	$k_b\,(kJ/mol/rad^2)$
CB-CB	0.1498	179627.6554	C(B)-C(B)-C(B)	122.5536	444.6499
C(B)-C	0.1530	292880.0000	C(B)-C(B)-F	118.3191	419.8083
C-O	0.1420	292880.0000	F-C(B)-F	121.5020	452.8745
C-S	0.1800	292880.0000	C-C-O	109.4710	418.4000
C-F	0.1336	253240.5748	C-O-C	125.2300	418.4000
S-O	0.1480	292880.0000	O-C-F	109.5700	418.4000
			F-C-S	110.3000	418.4000
			C-C-S	116.8100	418.4000
			C-S-O	102.6500	1464.4000
			O-S-O	115.5000	1464.4000

$E_{torsion}$	n	ϕ_s	$k_\phi\,(kJ/mol)$	E_{L-J}	$\varepsilon\,(kJ/mol)$	$r_0\,(nm)$
X–C(B)–C(B)–X	3	0	2.0920	CB	0.3531	0.3460
CB–CB–CB–CB	3	180	6.7302	C	0.3979	0.3473
F–CB–CB–CB	3	180	8.6236	F	0.2075	0.3025
F–CB–CB–F	3	0	8.4567	O	0.4004	0.3033
X–C(B)–O–X	3	0	2.0920	S	1.4393	0.3590
X–C(B)–S–X	3	0	2.0920			

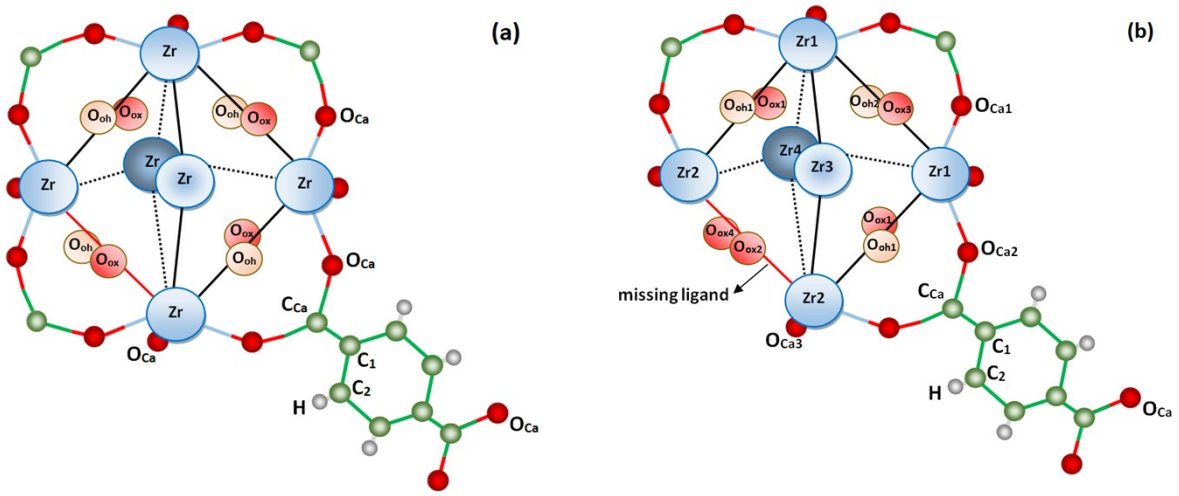

Figure S2. Schematic structure of (a) pristine UiO-66 with one representative ligand, (b) one missing ligand defected UiO-66 with an average coordination number (CN) of 11.5. All atom names have been shown in corresponding circles. O_{ox} is attributed to oxygen with no hydrogen bond and O_{oh} allocates to oxygen connected to hydrogen.

Table S2. Force field parameters of the covalent and noncovalent contributions to the pristine UiO–68 (see Figure S2 a)

E_{bond}	$r_0\ (nm)$	$k_b\ (kJ/mol/nm^2)$	E_{angle}	$\theta_0\ (degree)$	$k_b\ (kJ/mol/rad^2)$
C_{ca}-C_1	0.1499	208700.00	C_{ca}-C_1-C_2	120.10	617.00
C_{ca}-O_{ca}	0.1274	441400.00	C_{ca}-O_{ca}-Zr	134.90	298.00
C_1-C_2	0.1400	314000.00	C_1-C_{ca}-O_{ca}	118.20	165.00
C_2-C_2	0.1388	338200.00	C_1-C_2-C_2	120.10	464.00
C_2-H	0.1083	337600.00	C_1-C_2-H	119.40	280.00
O_{oh}-H_{oh}	0.0997	495700.00	C_2-C_1-C_2	119.90	449.00
Zr-O_{ca}	0.2212	52200.00	C_2-C_2-H	120.20	345.00
Zr-O_{oh}	0.2258	40300.00	Zr-O_{oh}-H_{oh}	114.90	161.00
Zr-O_{ox}	0.2070	81900.00	O_{ca}-C_{ca}-O_{ca}	123.30	648.00
			Zr-O_{oh}-Zr	105.20	738.00
			Zr-O_{ox}-Zr	118.90	556.00
			O_{ox}-Zr- O_h	67.20	174.00

$E_{torsion}$	n	ϕ_s	$k_\phi\ (kJ/mol)$	E_{L-J}	$\varepsilon\ (kJ/mol)$	$r_0\ (nm)$
C_{ca}-C_1-C_2-C_2	2	180	17.400	Zr	0.2887	0.2783
C_{ca}-C_1-C_2-H	2	180	8.000	O_{ox}	0.4004	0.3033
C_1-C_{ca}-O_{ca}-Zr	2	180	24.700	O_{oh}	0.4004	0.3033
C_1-C_2-C_2-C_1	2	180	15.350	O_{ca}	0.4004	0.3033
C_1-C_2-C_2-H	2	180	18.100	C_{ca}	0.3979	0.3473
C_2-C_1-C_{ca}-O_{ca}	2	180	8.300	C_1	0.3979	0.3473
C_2-C_1-C_2-C_2	2	180	15.850	H_{oh}*	0.2846	0.0636
C_2-C_1-C_2-H	2	180	12.950	H	0.2846	0.0636
H-C_2-C_2-H	2	180	8.300			
O_{ca}-C_{ca}-O_{ca}-Zr	2	180	2.200	* H_{oh} is connected to O_{oh}		

Table S3. Force field parameters of the covalent and noncovalent contributions to the defected UiO–68 with one missing ligand and 66 with an average coordination number of 11.5 (see Figure S2 b)

E_{bond}	$r_0\ (nm)$	$k_b\ (kJ/mol/nm^2)$	E_{angle}	$\theta_0\ (degree)$	$k_b\ (kJ/mol/rad^2)$
C_{ca}-C_1	0.1499	208700.00	C_{ca}-C_1-C_2	120.10	617.00
C_{ca}-O_{ca1}	0.1274	441900.00	C_{ca}-O_{ca1}-Zr_1	136.00	286.00
C_{ca}-O_{ca2}	0.1275	440300.00	C_{ca}-O_{ca2}-Zr_1	135.10	317.00
C_{ca}-O_{ca3}	0.1274	438100.00	C_{ca}-O_{ca2}-Zr_2	134.90	313.00
C_1-C_2	0.1400	314000.00	C_{ca}-O_{ca3}-Zr_1	136.40	302.00
C_2-C_2	0.1388	338200.00	C_{ca}-O_{ca3}-Zr_2	131.10	283.00
C_2-H	0.1083	337600.00	C_{ca}-O_{ca3}-Zr_3	136.10	300.00
O_{oh1}-H_{oh1}	0.0997	495400.00	C_{ca}-O_{ca3}-Zr_4	136.70	299.00
O_{oh2}-H_{oh2}	0.0996	496700.00	C_1-C_{ca}-O_{ca1}	118.40	173.00
Zr_1-O_{ca1}	0.2182	59700.00	C_1-C_{ca}-O_{ca2}	118.50	166.00
Zr_1-O_{ca2}	0.2201	49000.00	C_1-C_{ca}-O_{ca3}	118.20	171.00
Zr_2-O_{ca2}	0.2240	40300.00	C_1-C_2-C_2	120.10	464.00
Zr_1-O_{ca3}	0.2194	53500.00	C_1-C_2-H	119.40	280.00
Zr_2-O_{ca3}	0.2193	51800.00	C_2-C_1-C_2	119.90	449.00
Zr_3-O_{ca3}	0.2207	52200.00	C_2-C_2-H	120.20	345.00
Zr_4-O_{ca3}	0.2208	50700.00	Zr_1-O_{oh1}-H_{oh1}	115.60	154.00
Zr_1-O_{oh1}	0.2281	35400.00	Zr_2-O_{oh1}-H_{oh1}	116.50	154.00
Zr_2-O_{oh1}	0.2251	46400.00	Zr_3-O_{oh1}-H_{oh1}	115.90	156.00
Zr_3-O_{oh1}	0.2263	38700.00	Zr_1-O_{oh2}-H_{oh2}	114.50	165.00
Zr_1-O_{oh2}	0.2262	41000.00	Zr_4-O_{oh2}-H_{oh2}	114.50	151.00
Zr_4-O_{oh2}	0.2323	22500.00	O_{ca1}-C_{ca}-O_{ca1}	123.30	652.00
Zr_1-O_{ox1}	0.2071	85600.00	O_{ca2}-C_{ca}-O_{ca2}	123.30	638.00
Zr_2-O_{ox1}	0.2009	123700.00	O_{ca3}-C_{ca}-O_{ca3}	123.00	642.00
Zr_4-O_{ox1}	0.2063	85100.00	Zr_1-O_{oh1}-Zr_2	101.80	719.00
Zr_2-O_{ox2}	0.2072	88200.00	Zr_1-O_{oh1}-Zr_3	104.10	672.00
Zr_3-O_{ox2}	0.2035	96800.00	Zr_1-O_{oh2}-Zr_1	104.50	713.00
Zr_1-O_{ox3}	0.2077	78300.00	Zr_1-O_{oh2}-Zr_4	104.00	715.00
Zr_3-O_{ox3}	0.2072	77800.00	Zr_1-O_{ox1}-Zr_2	118.30	443.00
Zr_2-O_{ox4}	0.2087	69200.00	Zr_1-O_{ox1}-Zr_4	120.80	429.00
Zr_4-O_{ox4}	0.2258	3700.00	Zr_1-O_{ox3}-Zr_1	117.80	532.00
			Zr_1-O_{ox3}-Zr_3	118.80	540.00
			Zr_2-O_{oh1}-Zr_3	102.70	711.00
			Zr_2-O_{ox1}-Zr_4	111.30	584.00
			Zr_2-O_{ox2}-Zr_2	110.90	595.00

Zr_2-O_{ox2}-Zr_3	118.30	443.00
Zr_2-O_{ox4}-Zr_2	110.50	827.00
Zr_2-O_{ox4}-Zr_4	103.00	851.00
O_{oh1}-Zr_1-O_{ox1}	69.00	223.00
O_{oh1}-Zr_1-O_{ox3}	67.90	212.00
O_{oh1}-Zr_2-O_{ox1}	70.80	258.00
O_{oh1}-Zr_2-O_{ox2}	69.50	318.00
O_{oh1}-Zr_3-O_{ox2}	69.50	239.00
O_{oh1}-Zr_3-O_{ox3}	68.10	170.00
O_{oh2}-Zr_1-O_{ox1}	67.90	259.00
O_{oh2}-Zr_1-O_{ox3}	68.20	220.00
O_{oh2}-Zr_4-O_{ox1}	67.20	320.00
O_{ox1}-Zr_2-O_{ox4}	74.50	182.00
O_{ox1}-Zr_4-O_{ox4}	70.60	387.00
O_{ox2}-Zr_2- O_{ox4}	69.50	453.00

$E_{torsion}$	n	ϕ_s	$k_\phi\,(kJ/mol)$	E_{L-J}	$\varepsilon\,(kJ/mol)$	$r_0\,(nm)$
C_{ca}-C_1-C_2-C_2	2	180	17.400	Zr_1	0.2887	0.2783
C_{ca}-C_1-C_2-H	2	180	8.000	Zr_2	0.2887	0.2783
C_1-C_2-C_2-C_1	2	180	15.350	Zr_3	0.2887	0.2783
C_1-C_2-C_2-H	2	180	18.100	Zr_4	0.2887	0.2783
C_2-C_1-C_2-C_2	2	180	15.850	O_{ox1}	0.4004	0.3033
C_2-C_1-C_2-H	2	180	12.950	O_{ox2}	0.4004	0.3033
H-C_2-C_2-H	2	180	8.300	O_{ox3}	0.4004	0.3033
O_{ca1}-C_{ca}-O_{ca1}-Zr_1	2	180	1.850	O_{ox4}	0.4004	0.3033
O_{ca2}-C_{ca}-O_{ca2}-Zr_1	2	180	1.650	O_{oh1}	0.4004	0.3033
O_{ca3}-C_{ca}-O_{ca3}-Zr_1	2	180	2.100	O_{oh2}	0.4004	0.3033
O_{ca3}-C_{ca}-O_{ca3}-Zr_2	2	180	2.950	O_{ca1}	0.4004	0.3033
O_{ca3}-C_{ca}-O_{ca3}-Zr_3	2	180	2.850	O_{ca2}	0.4004	0.3033
O_{ca3}-C_{ca}-O_{ca3}-Zr_4	2	180	2.450	O_{ca3}	0.4004	0.3033
C_2-C_1-C_{ca}-O_{ca1}	2	180	8.300	C_{ca}	0.3473	0.3979
C_2-C_1-C_{ca}-O_{ca2}	2	180	8.300	C_1	0.3473	0.3979
C_2-C_1-C_{ca}-O_{ca3}	2	180	8.300	C_2	0.3473	0.3979
C_1-C_{ca}-O_{ca1}-Zr_1	2	180	21.000	$H_{oh1}{}^*$	0.0636	0.2846
C_1-C_{ca}-O_{ca2}-Zr_1	2	180	24.350	$H_{oh2}{}^*$	0.0636	0.2846
C_1-C_{ca}-O_{ca2}-Zr_2	2	180	22.350	H	0.0636	0.2846

C_1-C_{ca}-O_{ca3}-Zr_1	2	180	22.050	
C_1-C_{ca}-O_{ca3}-Zr_2	2	180	19.750	* H_{oh1} and H_{oh1} are connected to O_{oh}
C_1-C_{ca}-O_{ca3}-Zr_3	2	180	21.650	
C_1-C_{ca}-O_{ca3}-Zr_4	2	180	19.100	

Table S4. Partial charges of pristine and defected UiO-66 obtained from ChelpG method.

UiO-66 Pristine		UiO-66 Defected	
Atom	Partial charge (e)	Atom	Partial charge (e)
Zr	2.370	Zr_1	2.374
O_{ox}	-1.083	Zr_2	2.336
O_{oh}	-1.037	Zr_3	2.375
O_{ca}	-0.683	Zr_4	2.363
C_{ca}	0.764	O_{ox1}	-1.074
C_1	-0.135	O_{ox2}	-1.104
C_2	-0.106	O_{ox3}	-1.091
H_{oh}	0.497	O_{ox4}	-1.109
H	0.152	O_{oh1}	-1.039
		O_{oh2}	-1.026
		O_{ca1}	-0.682
		O_{ca2}	-0.683
		O_{ca3}	-0.685
		C_{ca}	0.764
		C_1	-0.135
		C_2	-0.106
		H_{oh1}	0.496
		H_{oh2}	0.490
		H	0.152

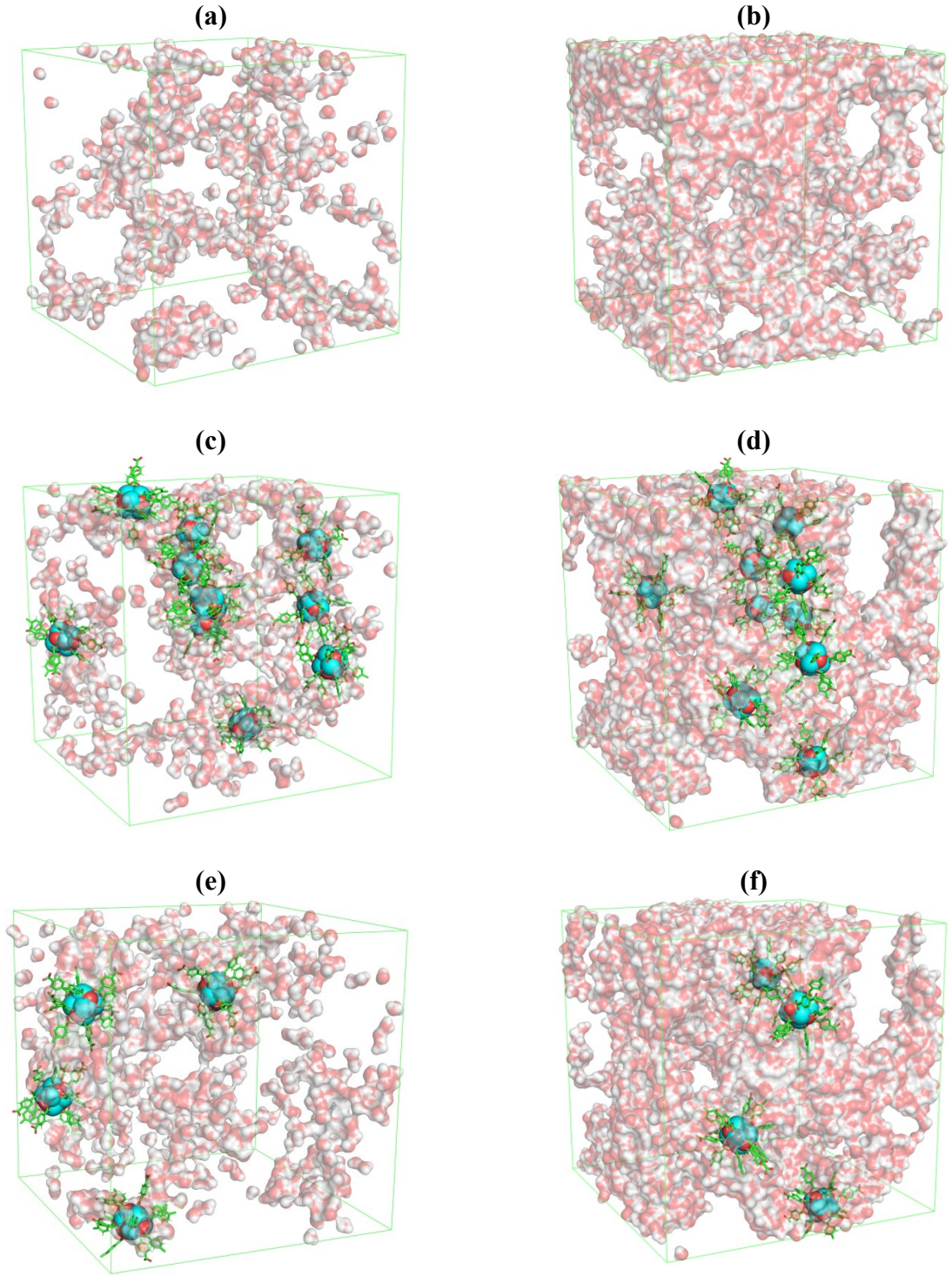

Figure S3. Final snapshots of pure Nafion® at λ = 3 (a) and 15 (b), hybrid Nafion® UiO-5wt%-P for λ = 3 (c) and 15 (d), hybrid Nafion® UiO-2wt%-P for λ = 3 (e) and 15 (f). Aqueous clusters tend to be more spherical around Zr-nodes in hybrid membranes especially at lower λ. Nafion® chains are not shown for better representation.

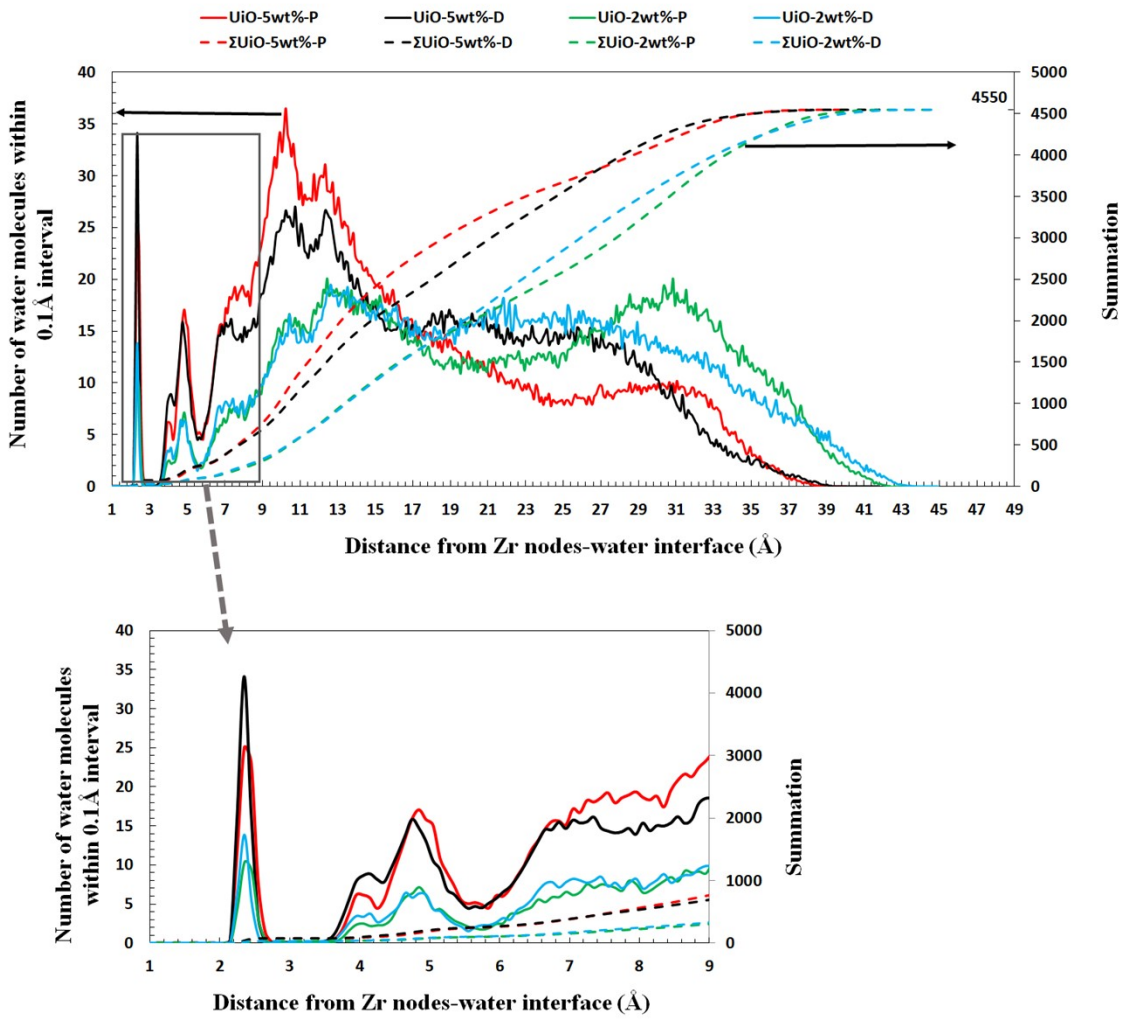

Figure S4. Histograms which are plotted as continuous curves of the closest distance between interface of water molecules with zirconium nodes of 5 and 2wt% pristine/defected doped polymers at λ = 15. The summation calculates the number of molecules within a given distance from the zirconium node/water interface.

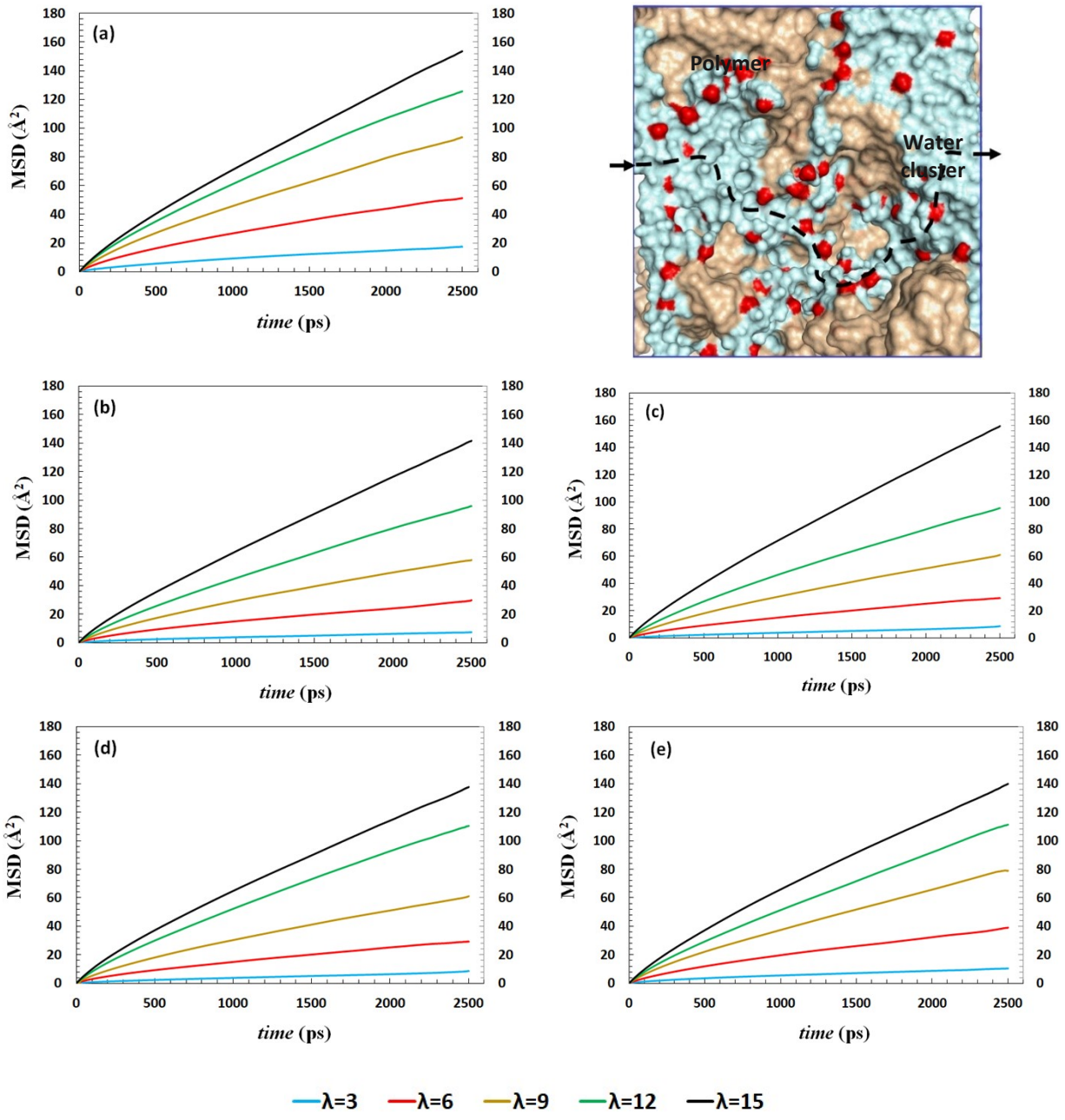

Figure S5. Mean square displacement of water molecules collected in 2.5ns of NVE microcanonical simulation. A schematic (top right) shows a potential pathway for diffusion of water molecules within hybrid membrane (cyan=water, red=hydronium ions, light brown=Nafion® chains). All MSDs are plotted for variety of water uptake λ = 3 to 15 for (a) pure, (b) UiO-5wt%-P, (c) UiO-5wt%-D, (d) UiO-2wt%-P and (e) UiO-2wt%-D.