Supporting information

Insight into the structures and properties of polyamide lithium extraction nanofiltration membranes by molecular dynamics simulation

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The specific simulation steps for RDF of the oxygen atoms of water with PIP and QSPIP

Initial molecular structures of PIP and QSPIP were constructed using Materials Studio 2019. Atomic charges for both molecules were derived using the RESP fitting method. Subsequently, two cubic simulation boxes simulation box (5 nm × 5 nm × 5 nm) were prepared: one containing 50 PIP molecules and the other containing 50 QSPIP molecules. Each box was inserted 2000 water molecules to model aqueous diffusion behavior. The General AMBER Force Field (GAFF) was applied to PIP and QSPIP, while the TIP3P model was used. Both prepared systems underwent sequential simulation stages: (1) a 2 ns energy minimization to eliminate unfavorable contacts, followed by (2) a 10 ns NPT ensemble simulation (T = 300 K, P = 1 bar) to achieve thermodynamic equilibrium.

The fractional free volumes (FFV) are typically defined as the relative void space within a polymer membrane, representing the unoccupied molecular-scale space in the polymer. The Free Accessible Volume (FAV) refers to the method of probing the accessible volume with hard spherical particles of specific radii, which enables a more realistic estimation of the accessible free volume for penetrating polymer structures.

$$FFV = \frac{V_f}{V_f + V_o} \times 100\%$$

where V_f is defined as the free volume in the system that is unoccupied by the atoms of the polymer, V_o refers to the space actually occupied by atoms or molecules.

$$FAV = \frac{V_{acc}}{V_{sp}} \times 100\%$$

where V_{acc} is the accessible volume of polymer, and V_{sp} is the specific volume of polymer.

Table S1 21-step equilibration protocol.

Step	Ensemble	Conditions (K,bar)	Length (ps)	Step	Ensemble	Conditions (K,bar)	Length (ps)
			21-step equilibration [1]				
1	NVT	1000	50	**12**	NPT	300, 25000	5
2	NVT	300	50	**13**	NVT	1000	5
3	NPT	300, 1000	50	**14**	NVT	300	10
4	NVT	1000	50	**15**	NPT	300, 5000	5
5	NVT	300	100	**16**	NVT	1000	5
6	NPT	300, 30000	50	**17**	NVT	300	10
7	NVT	1000	50	**18**	NPT	300, 500	5
8	NVT	300	100	**19**	NVT	1000	5
9	NPT	300, 50000	50	**20**	NVT	300	10
10	NVT	1000	50	**21**	NPT	300, 1	800
11	NVT	300	100				

[1] Abbott LJ.; Hart KE.; Colina CM. Polymatic: a generalized simulated polymerization algorithm for amorphous polymers. *Theoretical Chemistry Accounts* 2013, 132, 1334.

Table S2 The simulated cross-linking degree and density values of PIP-TMC and QSPIP-TMC.

	Model 1	Model 2	Model 3	Average values
	PIP-TMC			
Density (g/cm^3)	1.24	1.24	1.25	1.24
Cross-linking degree (%)	82.8	82.6	83.0	82.8
	QSPIP-TMC			
Density (g/cm^3)	1.19	1.16	1.19	1.18
Cross-linking degree (%)	83.5	83.0	83.6	83.4

Table S3 The C, O and N element composition and O/N.

Items	PIP-TMC	PIP-TMC-Expt. Data [1]	PIP-TMC-Expt. Data [2]	QSPIP-TMC
C (%)	69.73	71.25	71.74	72.38
O (%)	16.38	15.69	15.45	12.17
N (%)	13.89	13.06	12.82	15.45
O/N	1.18	1.21	0.83	0.79

[1] Tian J.; Chang H.; Gao S.; Zhang R. How to fabricate a negatively charged NF membrane for heavy metal removal via the interfacial polymerization between PIP and TMC? *Desalination* 2020, 491, 114499.

[2] Peng H.; Tang Q.; Tang S.; Gong J.; Zhao Q. Surface modified polyamide nanofiltration membranes with high permeability and stability. *Journal of Membrane Science* 2019, 592, 117386.

Table S4 The water content of the simulated membranes in comparison with the experimental and simulated results in literatures.

Items	Theoretical works		Experimental works		This study	
	Ref [1]	Ref [2]	Ref [3]	Ref [4]	PIP-TMC	QSPIP-TMC
Water content (wt%)	14-31	21.22-21.61	20	23	17.29	26.39

[1] Wang L.; Dumont RS.; Dickson JM. Molecular dynamic simulations of pressure-driven water transport through polyamide nanofiltration membranes at different membrane densities. *RSC Advances* 2016, 6, 63586-63596.

[2] He J.; McCutcheon JR.; Li Y. Effect of different manufacturing methods on polyamide reverse-osmosis membranes for desalination: Insights from molecular dynamics simulations. *Desalination* 2023, 547, 116204.

[3] Lee J.; Doherty CM.; Hill AJ.; Kentish SE. Water vapor sorption and free volume in the aromatic polyamide layer of reverse osmosis membranes. *Journal of Membrane Science* 2013, 425, 217-226.

[4] Kotelyanskii MJ.; Wagner NJ.; Paulaitis ME. Atomistic simulation of water and salt transport in the reverse osmosis membrane FT-30. *Journal of Membrane Science* 1998, 139, 1-16.
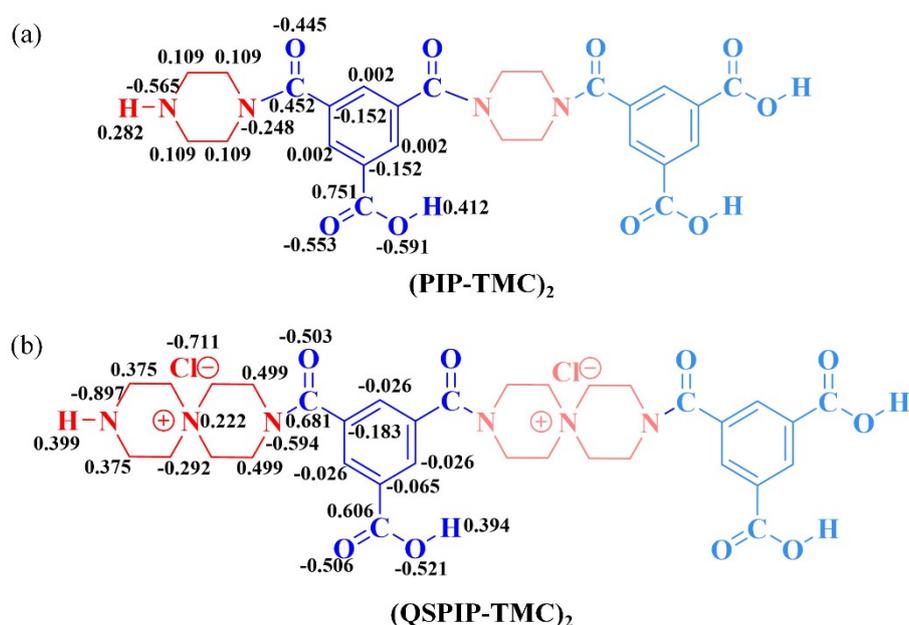
Figure S1 Chemical structures and partial charges of (PIP-TMC)$_2$ and (QSPIP-TMC)$_2$.
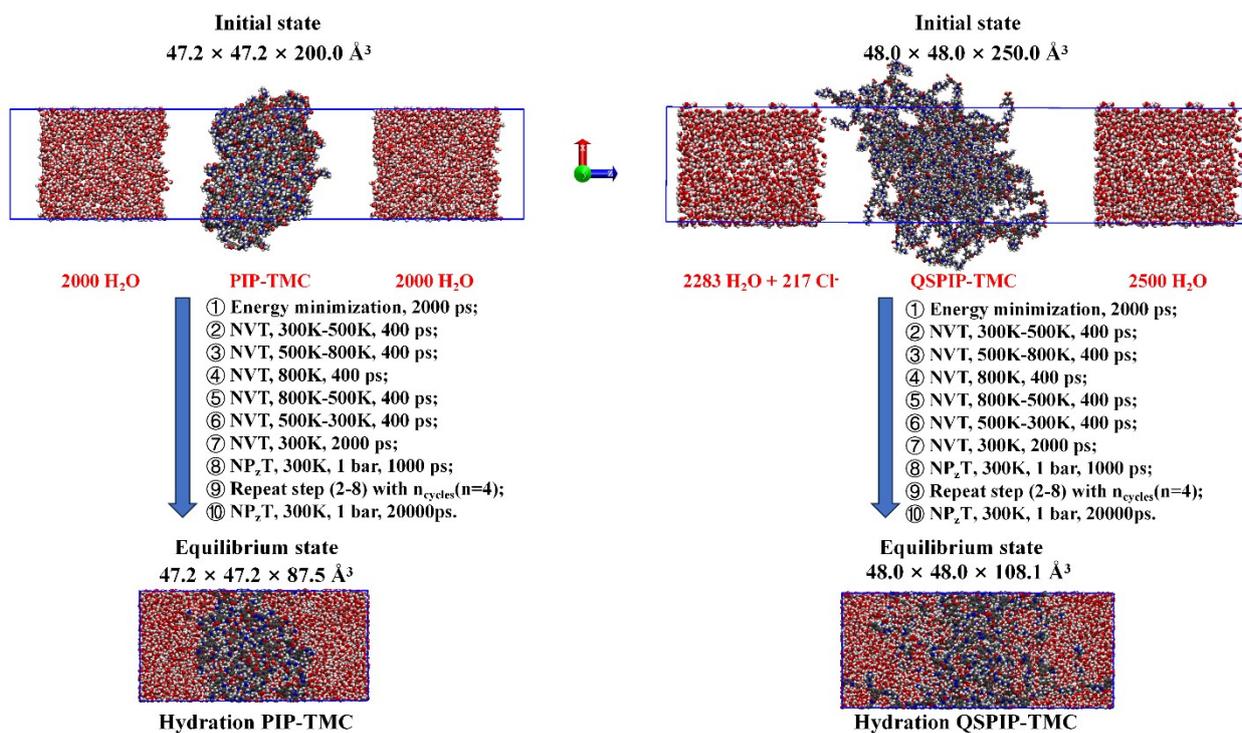
Figure S2 The initial and equilibrium states for the hydration PIP-TMC and QSPIP-TMC matrixes.
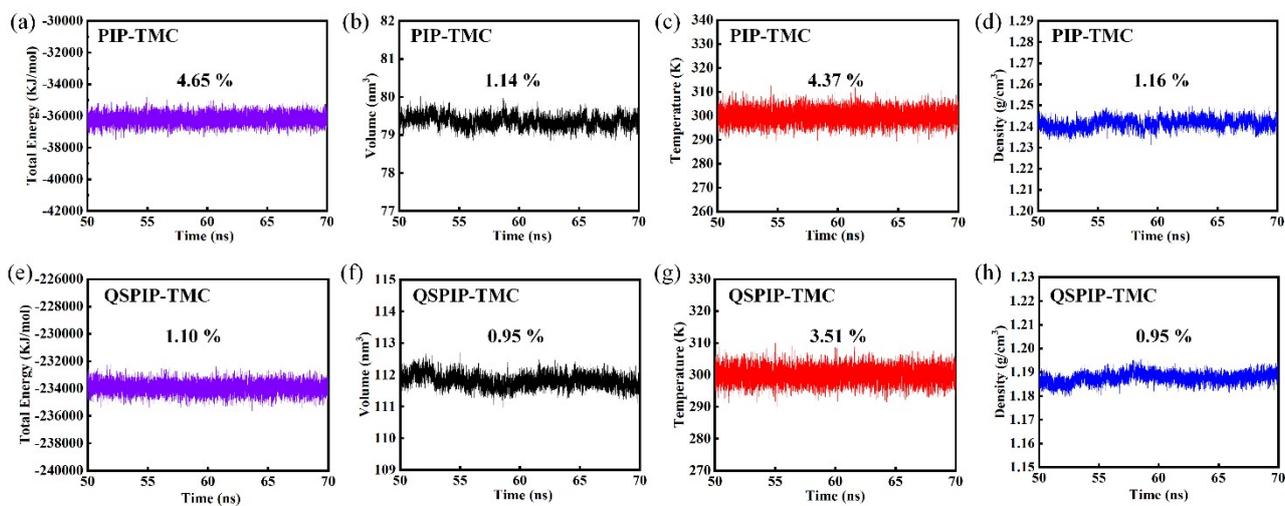

Figure S3 The fluctuations of total energy, volume, temperature, and density of both PIP-TMC and QSPIP-TMC membranes along z-axis.
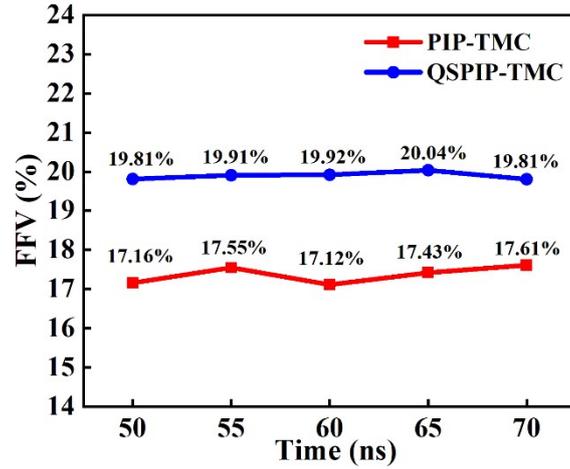
Figure S4 The fractional free volume (FFV) in PIP-TMC and QSPIP-TMC systems at 50 ns, 55 ns, 60 ns, 65 ns, and 70 ns.
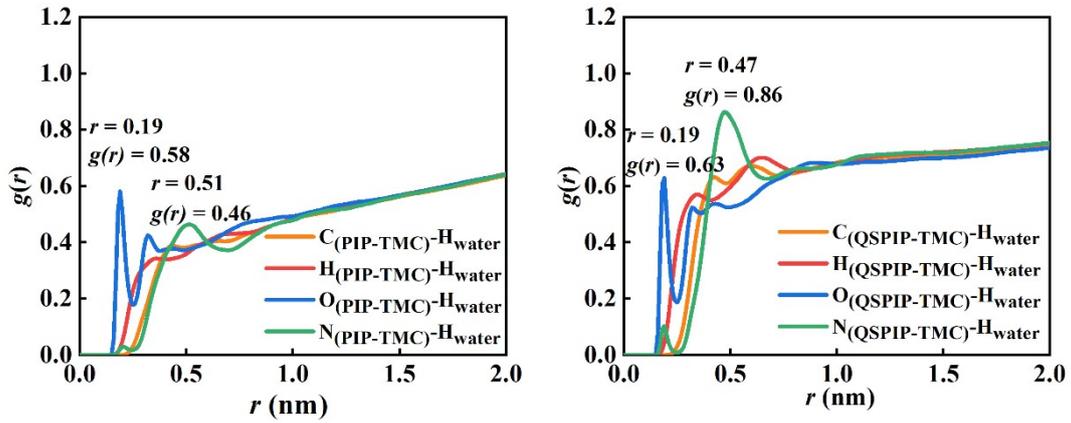

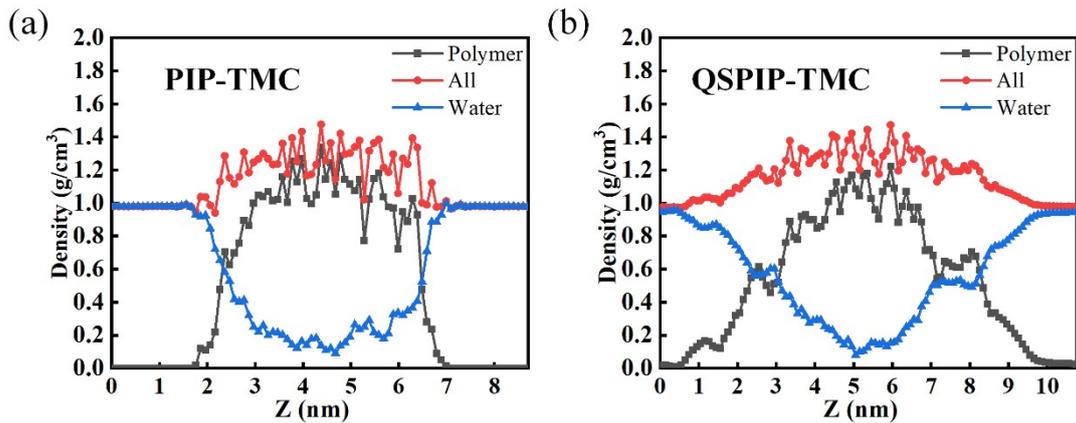**Figure S5** RDF profiles for PIP-TMC-H_2O and QSPIP-TMC-H_2O systems.

Figure S6 The density distributions for PIP-TMC and QSPIP-TMC membranes.
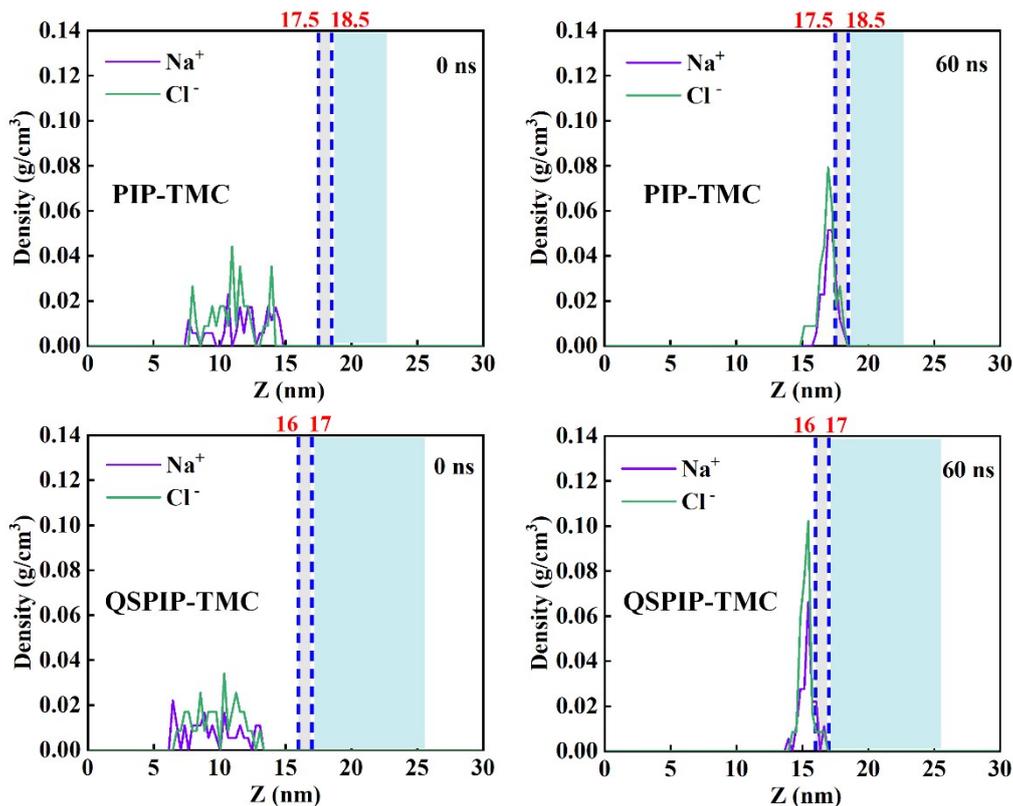
Figure S7 Density profiles of salt ions along the z-direction for PIP-TMC and QSPIP-TMC membranes at 0 ns MD and 60 ns MD. The gray shaded area denotes the interfacial region of membranes, and the blue area denotes the region of membranes.
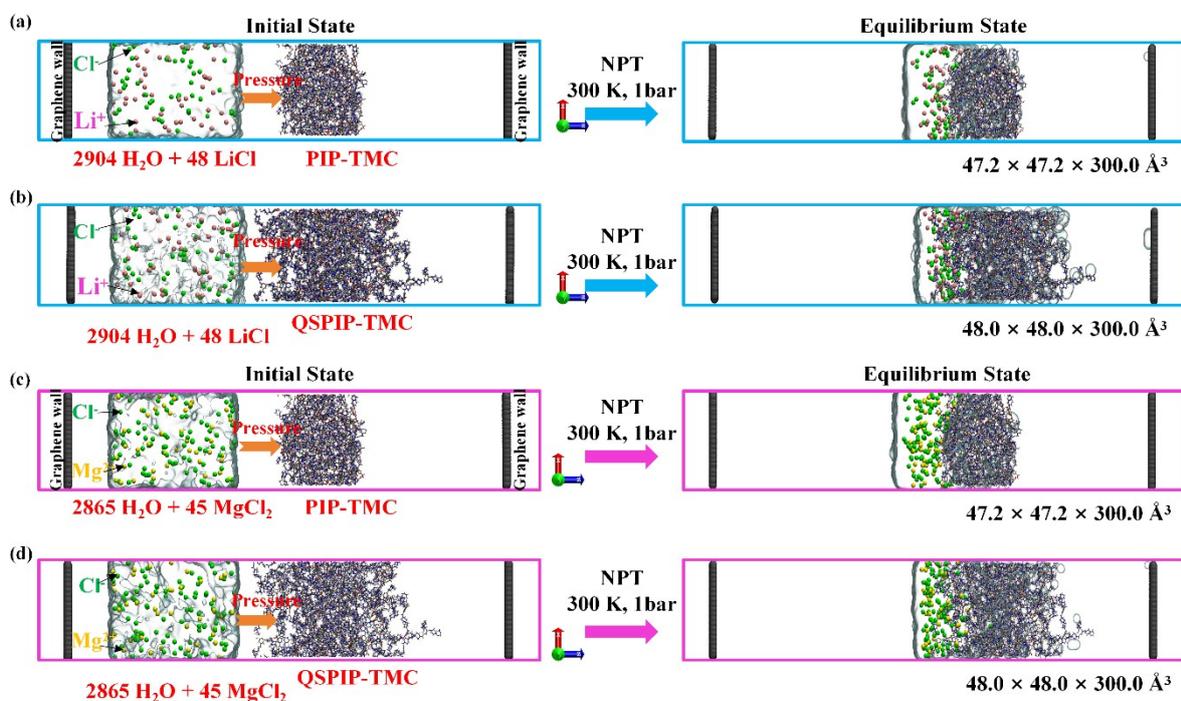

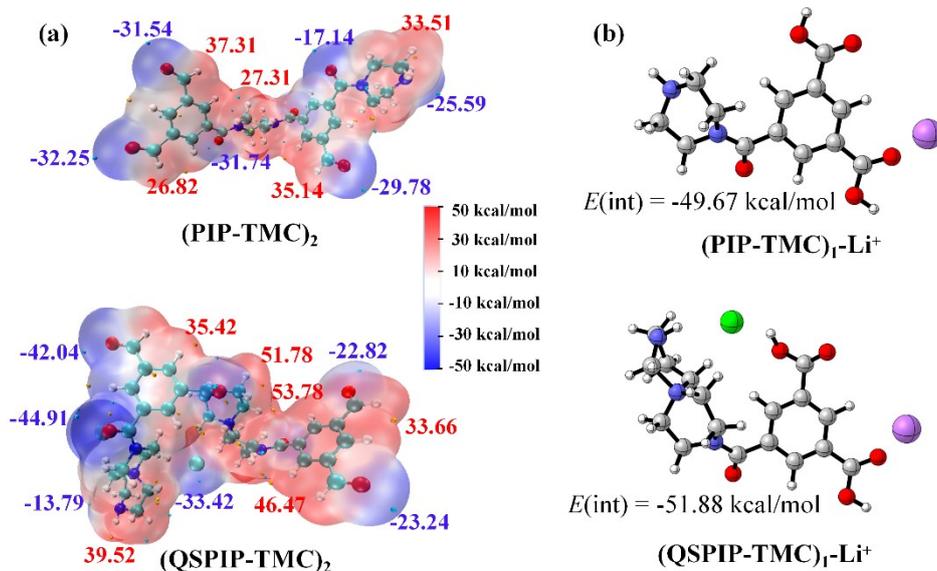**Figure S8** Snapshots of the initial and equilibrated states for the PIP-TMC-LiCl (MgCl$_2$)-H$_2$O and QSPIP-TMC-LiCl (MgCl$_2$)-H$_2$O systems.

Figure S9 (a) The electrostatic potential of (PIP-TMC)$_2$ and (QSPIP-TMC)$_2$; (b) The optimized structures of (PIP-TMC)$_1$-Li$^+$ and (QSPIP-TMC)$_1$-Li$^+$ and their interaction energies.
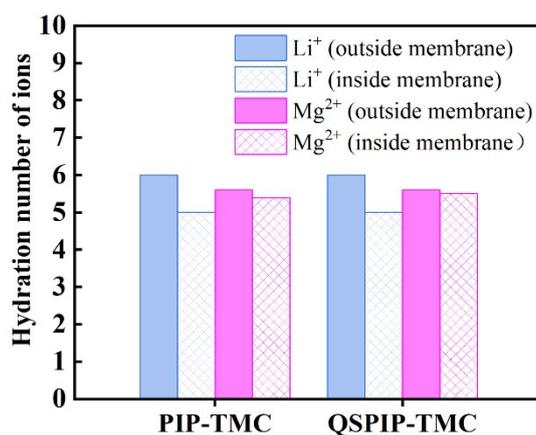

Figure S10 The hydration number changes of Li$^+$ and Mg^{2+} inside and outside the membranes
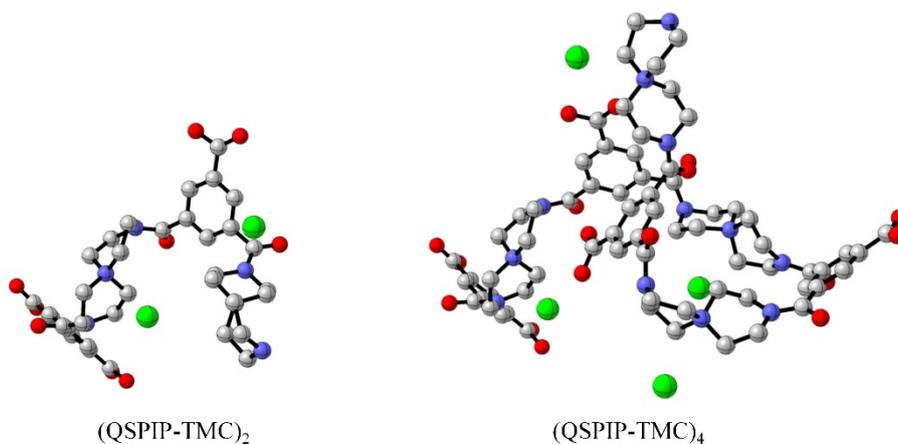

Figure S11 The optimized structures of (QSPIP-TMC)$_2$ and (QSPIP-TMC)$_4$ at the theoretical level of B3LYP/6-311+G(d,p).