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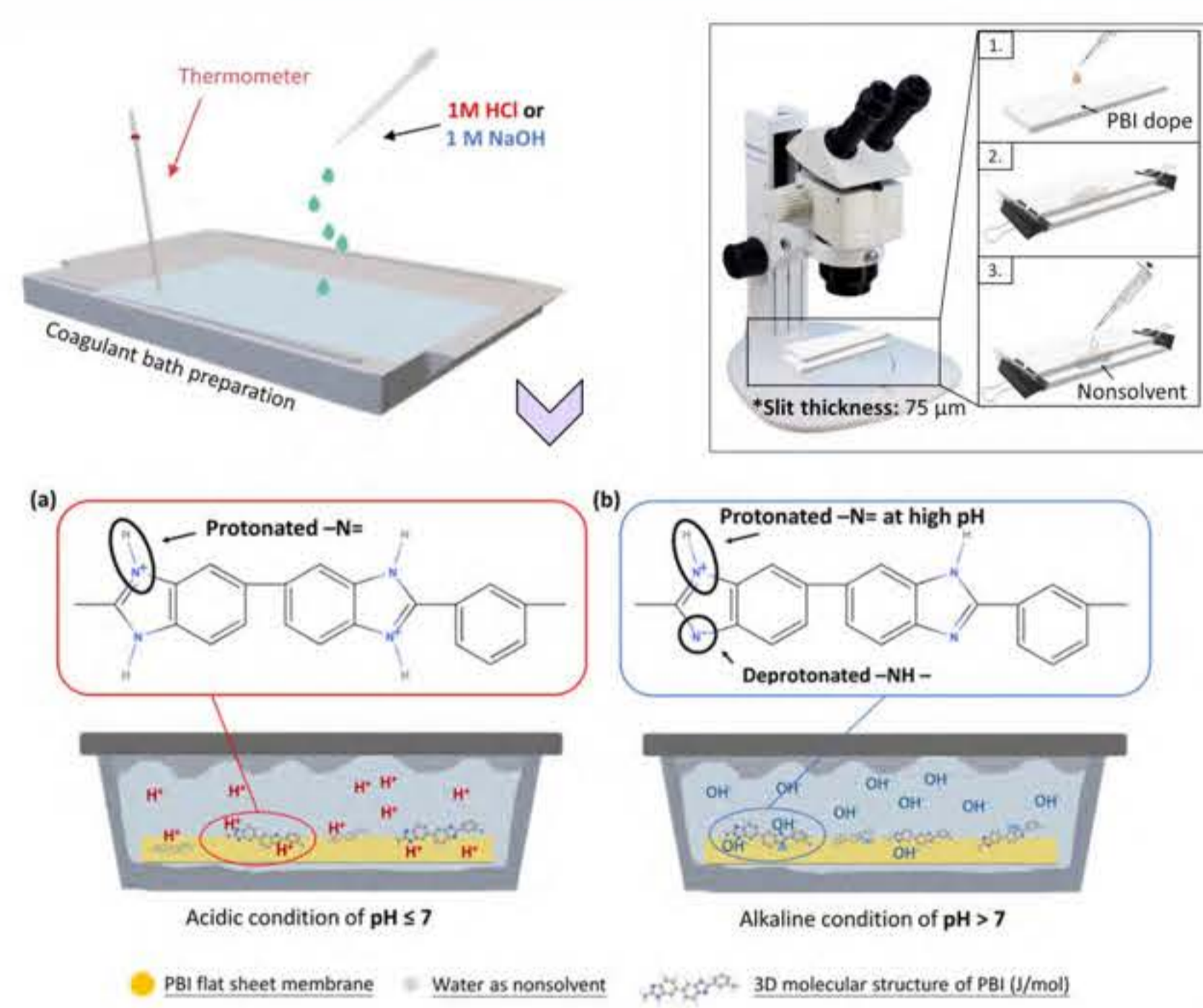
pH-tunable and pH-responsive polybenzimidazole (PBI) nanofiltration membranes for Li⁺/Mg²⁺ separation

用於分離 Li⁺/Mg²⁺ 的 pH 可調和 pH 響應型聚苯並咪唑 (PBI) 奈濾膜

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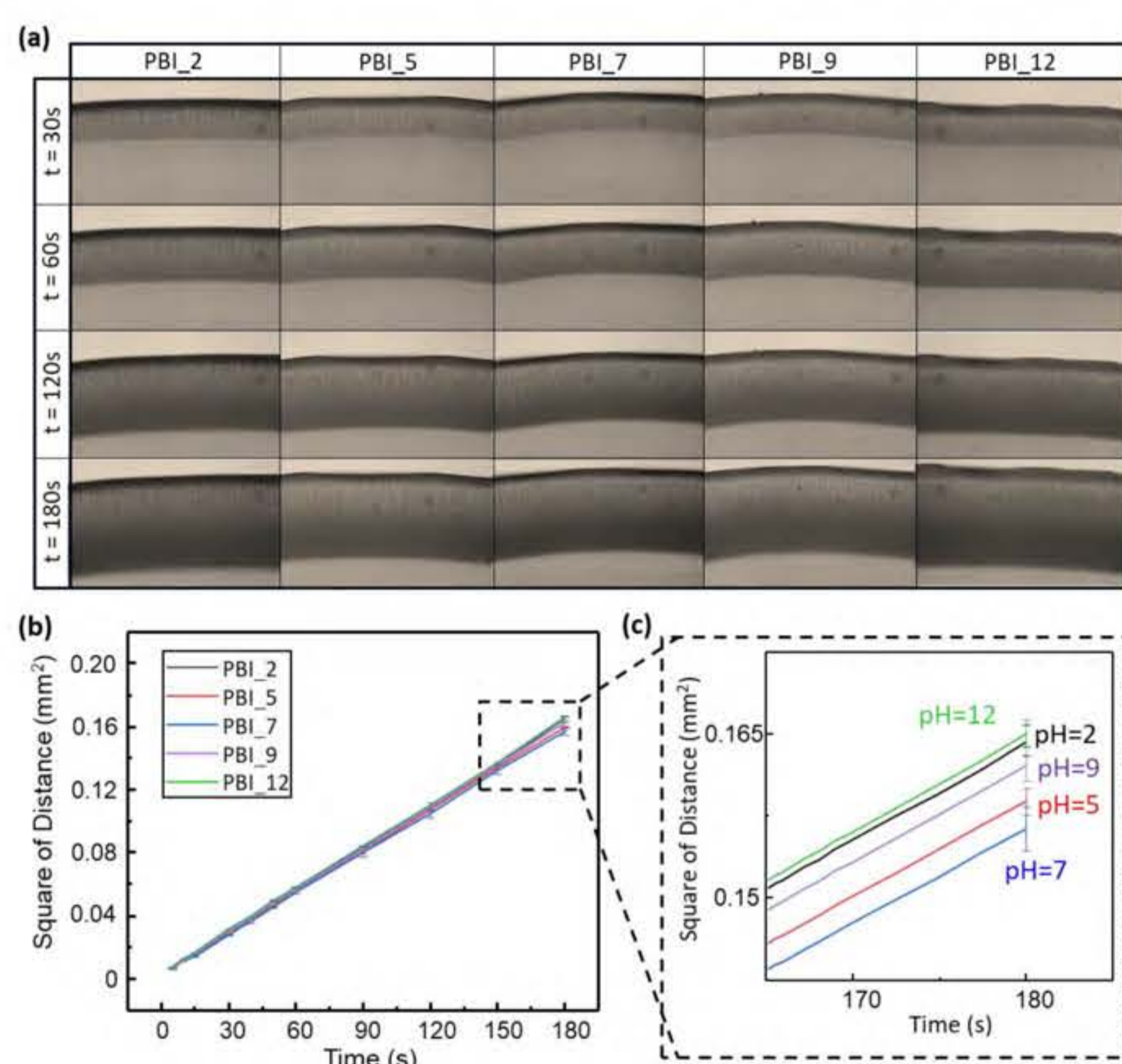
Schematic



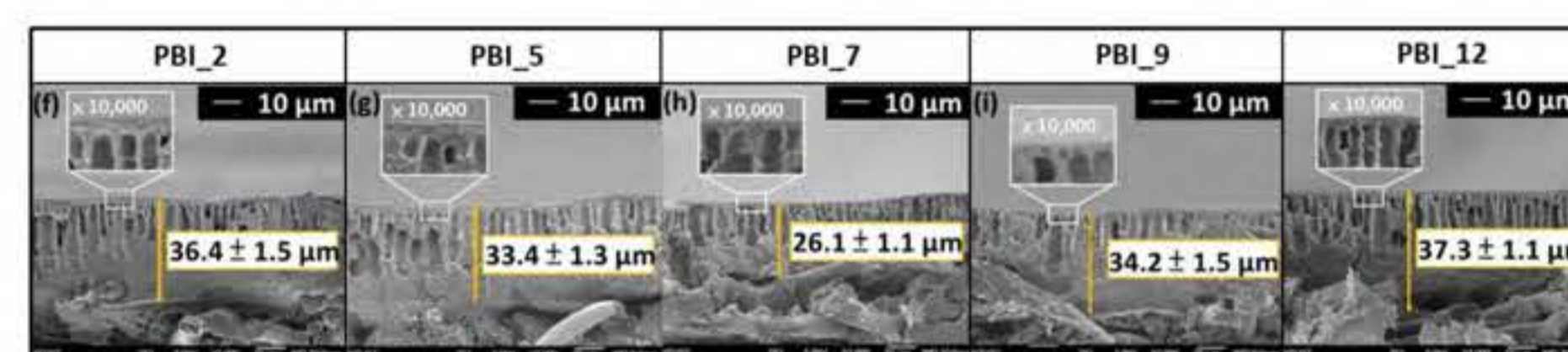
Abstract

Polybenzimidazole (PBI), a polymer known for its superior chemical stability, thermal properties, and mechanical resistance has been regarded as a suitable membrane material for a wide range of applications. Herein, we took advantage of these properties and its amphoteric nature that could endow the formed membranes with capabilities to have different states and responses in different pH conditions for enhanced nanofiltration (NF) performance. Integrally skinned asymmetric flat-sheet PBI membranes were fabricated using the nonsolvent-induced phase separation (NIPS) method under various pH in a coagulant bath. For the first time, we have thoroughly investigated the effects of nonsolvent acidity and alkalinity on PBI membrane formation and their performances. It was revealed that the membrane formed under pH 12 showed a doubled MgCl₂ rejection than the one formed under pH 7. Moreover, a green modification method was employed to enhance the membranes' sieving capabilities by using hyperbranched polyethyleneimine polymers (HPEIs) with different molecular weights (MWs). The PBI membrane formed under pH 12 and then surface modified with a HPEI of MW = 25,000 g/mol (i.e., PBI 12-25K membrane) has a molecular weight cut-off (MWCO) as low as 288 Da and an MgCl₂ rejection more than 97%. The membrane also displays pH-responsive characteristics for salt separation with unequal valence ratios of co-ions and counterions. It is able to show a competitive S_(Li,Mg) value for Li⁺/Mg²⁺ separation surpassing the state-of-the-art performance of commercial membranes.

Phase Inversion Analysis



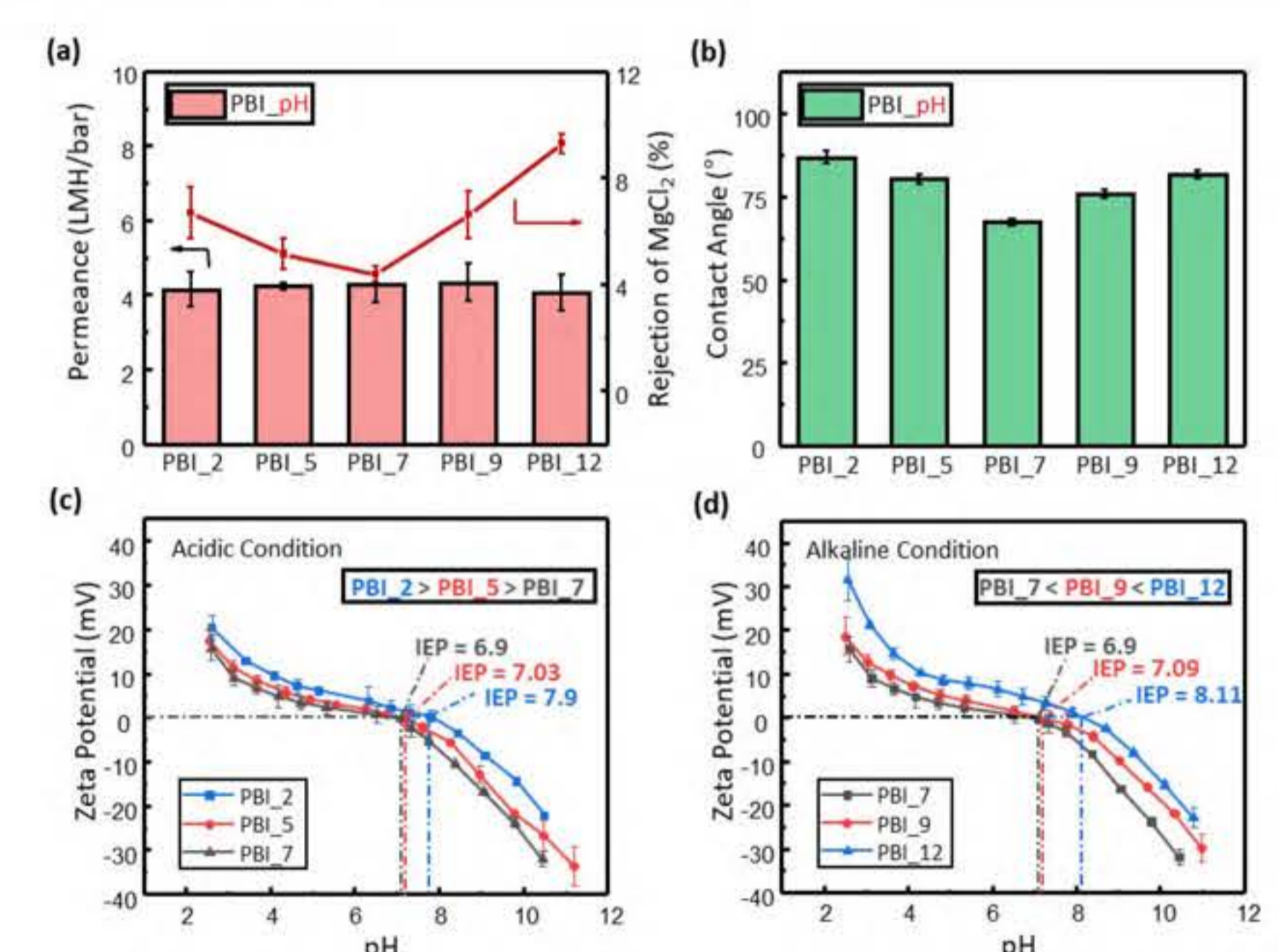
The longer the distance travelled by the dope, the thicker the membrane would be: pH₁₂ > pH₂ > pH₉ > pH₅ > pH₇



Membranes	Elemental composition (atm%)		
	N	C	O
PBI_2	8.2	68.6	23.2
PBI_5	9.4	72.4	18.2
PBI_7	10.3	74.6	15.1
PBI_9	8.1	66.8	25.1
PBI_12	7.7	68.7	23.6

N element is reduced with an increase in acidity and/or alkalinity of the coagulants.

pH-dependency

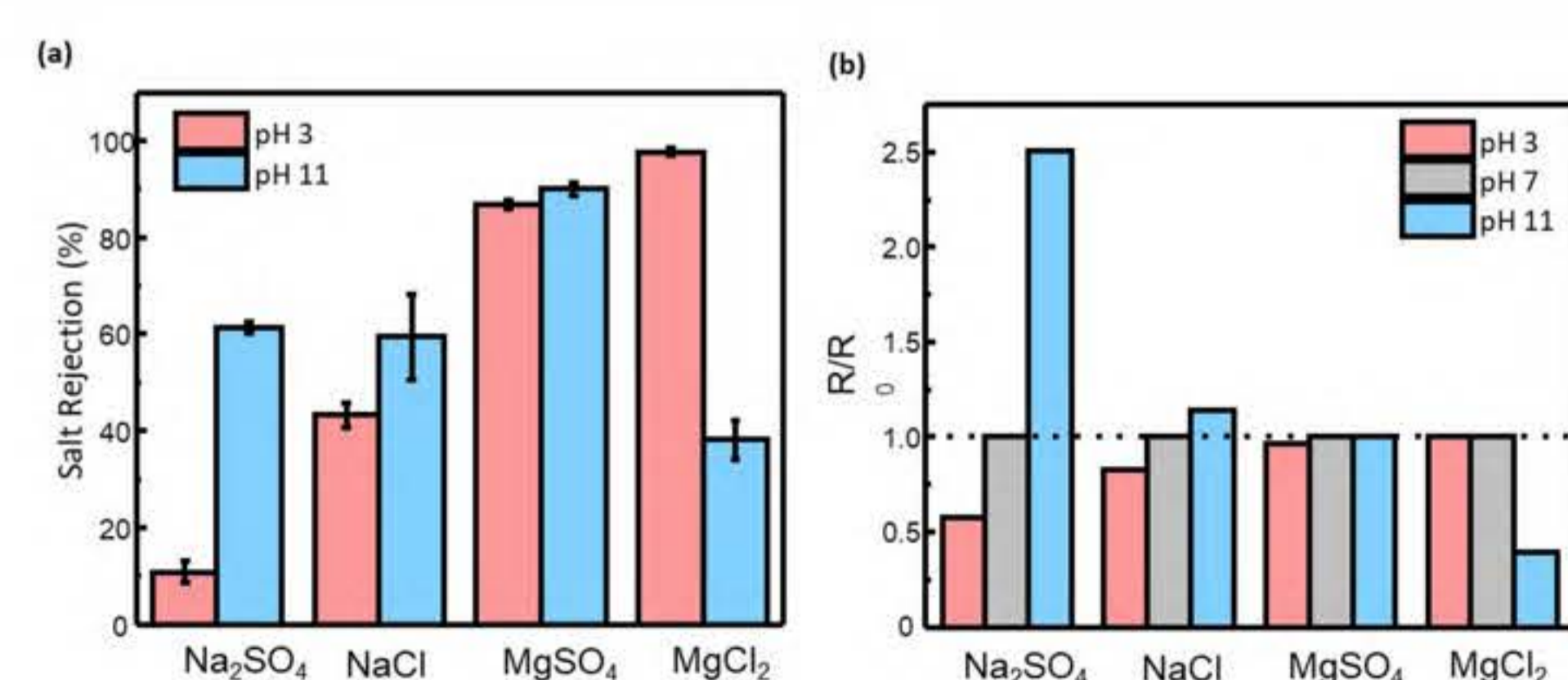


Higher rejection in lower and higher pH condition:

1. Thicker selective layer
2. Higher membrane charge

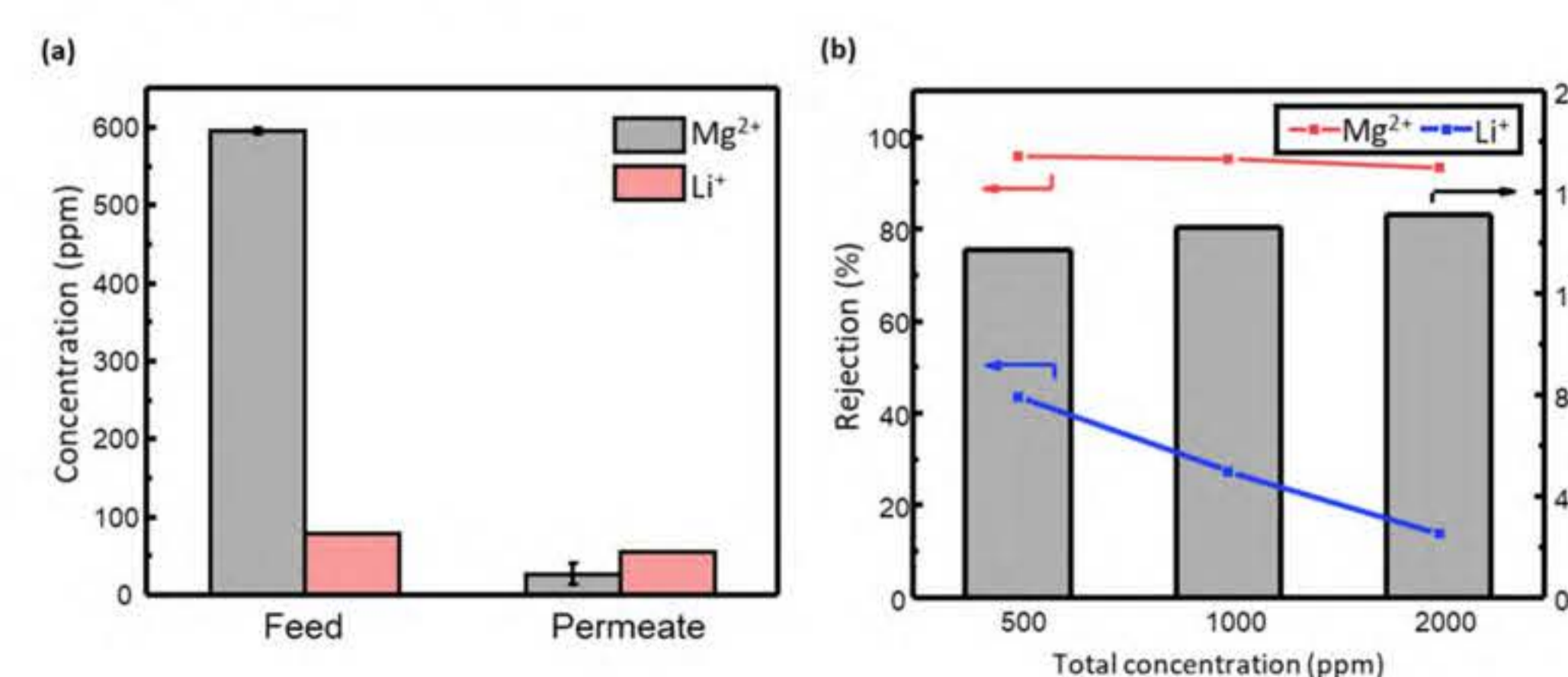
Optimum membrane: PBI_12

pH-responsiveness & Li⁺/Mg²⁺ Separation



Na₂SO₄ and MgCl₂ are more susceptible towards changes in feed pH because their valence ratios of co-ions and counterions are not equal to one.

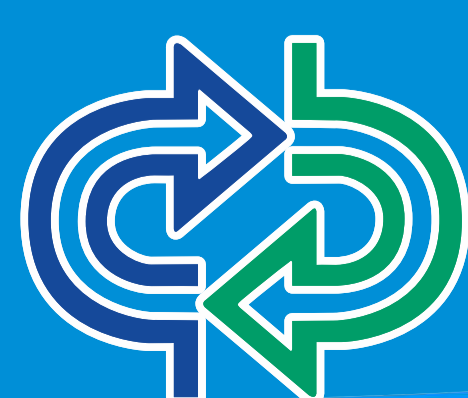
The NF tests were simulated by using LiCl and MgCl₂ salts with a weight ratio of 1:10.



Selected Publications

1. Setiawan, O., Huang, Y.H., Abdi, Z.G., Hung, W.S. and Chung, T.S.*, 2023. pH-tunable and pH-responsive polybenzimidazole (PBI) nanofiltration membranes for Li⁺/Mg²⁺ separation. *Journal of Membrane Science*, 668, p.121269.
2. Setiawan, O., Abdi, Z.G., Weber, M., Hung, W.S. and Chung, T.S.*, 2023. Employing sulfolane as a green solvent in the fabrication of nanofiltration membranes with excellent dye/salt separation performances for textile wastewater treatment. *Journal of Membrane Science*, 685, p.121942.
3. Austria, H.F.M., Subrahmanya, T.M., Setiawan, O., Widakdo, J., Chiao, Y.H., Hung, W.S.*, Wang, C.F., Hu, C.C., Lee, K.R. and Lai, J.Y., 2021. A review on the recent advancements in graphene-based membranes and their applications as stimuli-responsive separation materials. *Journal of Materials Chemistry A*, 9(38), pp.21510-21531.

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