Self-standing Covalent Organic Framework Membranes for Efficient Osmotic Energy Harvesting

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Undeniably, fossil fuels have powered modern civilization; however, after two centuries of extraction, global reserves of these non-renewable resources are approaching depletion. In contrast, the Gibbs free energy (ΔG) generated by salinity gradient mixing between seawater and freshwater remains one of the most significant yet underdeveloped renewable energy resources. Membrane-based reverse electrodialysis (RED) enables direct electricity generation from osmotic energy by harnessing the net ion flux driven by concentration gradients across ion-selective membranes. Therefore, developing ion-selective membranes with both high conductivity and high selectivity is particularly critical for efficient osmotic energy harvesting. Covalent organic frameworks (COFs) demonstrate remarkable potential for osmotic energy conversion due to their tunable nanochannel architectures, high porosity, and exceptional chemical stability. Herein, we demonstrate a facile solution-processing strategy for fabricating free-standing, micrometer-thick and crystalline membranes of imine-linked 2D ionic TpPa-(SO₃H)_X COF (X=0.5, 1, 1.5, 2). By systematically tuning the -SO₃H group density via stoichiometric control during COF synthesis, we achieved optimized charge-governed ion selectivity (quantitatively described by cation transference number, 0.943) in the nanochannels. Under salinity gradients mimicking seawater/riverwater conditions (0.5 M/0.01 M, NaCl), the device delivered an exceptional power output density of 24.6 W m⁻², representing a 4.9-fold enhancement over commercial benchmarks (5 W m⁻²).

Keywords: covalent organic framework, self-standing membrane, osmotic energy harvesting, ion.