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# Bilayer asymmetric-based metal-organic frameworks membrane for blue energy conversion

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#### HIGHLIGHTS

#### G R A P H I C A L A B S T R A C T

- Heterogeneous membrane with asymmetric channel surface and angstromscale cavities for ionic conduction.
- Permselective ion transport through the heterogenous membrane mediated by negatively charged channel surface.
- The synergistic effect of the bilayer MOF-on-MOF membrane explored for osmotic energy harvesting.
- Numerical simulation explains the preferred direction of ion diffusion through the bilayer membrane

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#### ABSTRACT

The conversion of Gibbs free energy at the interface of solutions with salinity gradients into electrical energy is essentially a means of mitigating environmental pollution and bolstering the availability of new energy sources to enhance the renewable energy portfolio. However, a three-dimensional (3D) sub-nanofluidic membrane with high ion conductivity and selectivity for a reverse electrodialysis (RED) based osmotic energy conversion in both aqueous and organic solutions remains largely unexplored. Herein, we engineered a bilayer metal organic frameworks (MOFs) membrane with polystyrene sulfonated angstrom-size channels in UiO-66-NH<sub>2</sub> base layer and isoreticular MIL-88B membrane as the top layer to enhance permselectivity and high-performance salinity gradient energy generation. The angstrom-size windows in the heterogeneous membrane with a negatively charged channel surface endow the UiO-66-NH<sub>2</sub>(PSS)/MIL-88B membrane with a pieferred direction of ion conduction. Collectively, these features of the bilayer angstrofluidic channel membrane promote diffusion-driven osmotic energy conversion of 32.46 Wm<sup>-2</sup> and permeability of 526.60 Am<sup>-2</sup> at the interface of 500-fold aqueous work condition and 3.89 Wm<sup>-2</sup> from 100-fold salinity gradient in LiCl-methanol. This work sheds light on the

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#### 1. Introduction

As the urgency to replace the polluting energy generation technologies, meet the surging energy demand and reverse global climate emergency grows, the development of renewable energy resources has become increasingly important [1,2]. Hydro, solar, and wind energy are the leading renewable energies that contributed about 1230 GW, 849 GW and 825 GW, respectively, in 2021 to the global energy mix [3]. However, the severe intermittent nature of solar and wind energy impacts the continuous and reliable energy supply required from these renewable resources [4]. Recently, renewable energy in the form of osmotic energy, harnessed at the interface of solutions of different salinity levels, such as seawater and river water, has emerged as a sustainable, ubiquitous, and limitless energy resource with zero carbon emissions [5]. Osmotic energy (also known as blue energy) remains largely untapped within the realm of hydropower, and it is estimated that this abundant resource at the interface of seawater and river water could generate between 1.4 and 2.6 TW, equivalent to 9-17 % of the global electricity demand [6]. Waste organic solutions produced in most chemical and other related industries are often incinerated, causing the release of significant amounts of greenhouse gases and environmental pollution [7]. Through the utilization of ion-selective membranes (ISM), it is possible to convert the chemical potential at the interface of aqueous resources and waste organic solutions with a salinity gradient into electrical energy using a reverse electrodialysis (RED) technique [8]. The salinity gradient drives ions through the ISM to create electrochemical potential that is realized as ionic current and osmotic power [9]. The ionic current and the osmotic power density generated from the selective ionic flux through the membrane depend directly on the ionic permeability and selectivity of the membrane [10]. However, conventional ISMs used in the RED process exhibit low ionic flux and poor ion selectivity, resulting in low power conversion efficiency [11] and power density that is far less than the commercialization and industrial development bench mark of 5  $Wm^{-2}$  [12,13]. Also, due to these limitations in addition to chemical instability, most of the ISMs are unable to provide efficient osmotic power conversion from different solutions operating under different work conditions [14]. Consequently, there is a significant need for the development of novel ISMs that work under different environmental conditions to address osmotic energy harvesting in both aqueous and non-aqueous solutions with salinity gradient.

Metal-organic frameworks (MOFs), porous materials with high crystallinity, tunable architecture and multifunctionalities, have been shown to possess nano- and sub-nanoscale pore and window-cavity structures [15]. These emerging materials have shown great promise in ion conduction applications such as natural resource (particularly lithium and uranium) extraction [16–18], osmotic energy conversion [19,20], biosensing [21,22], battery separators and electrodes [23,24], desalination and other fields [25–27]. However, the primary bottlenecks in MOF design and synthesis remain the balancing of ion permeability (output current) and ion selectivity (output voltage) to enhance the performance of MOF in salinity gradient energy capture [28].

Inspired by the ultra-high ion conductivity and selectivity in biological ion channels, diverse nanofluidic MOF-based membranes are emerging as technological breakthrough platforms for osmotic energy conversion [29,30]. For instance, the ions present in resting electrocytes of electric eel enter and travel through sub-nanoscale biological ion channels in cytomembranes to an extracellular environment to generate ~75 mV transcellular potential to subdue prey and ward off potential predators [31–33]. As a result, the ultra-efficient sub-nano size ionic channels in electric eel continue to inspire the development of artificial ion channels for salinity gradient power harvesting. An illustrative instance includes the fabrication of an anion-based composite MOF membrane from UiO-66-NH<sub>2</sub> and anodic aluminum oxide (AAO) membrane with sub-nanochannels to mimic the biological ion channels of electric eel for salinity-gradient energy conversion. A power density of  $1.47 \text{ Wm}^{-2}$  was generated from mixing synthetic seawater and freshwater [20]. Similarly, a heterogeneous membrane of AAO substrate and UiO-66-NH<sub>2</sub> was constructed with ion channel functionalized with poly (sodium 4-styrenesulfonate) to enhance osmotic energy harvesting. The heterogenous membrane, PSS@UiO-66-NH<sub>2</sub>/AAO, achieved 6.32 Wm<sup>-2</sup> at the interface of 50-fold KCl salinity gradient [34].

The MIL-88B MOF unit, with its unique hexagonal structure and 3D topology, has drawn much interest in the sustainable energy application fields particularly lithium ion batteries [35,36], sodium batteries [37], lithium-sulphur batteries [38], solar cells [39], aqueous zinc-ion batteries [40], seawater electrolysis [41], microbial fuel cells [42] mainly due to its open-framework crystal structure and multivalence states. Additionally, MIL-88B has been employed in diverse environmentally beneficial applications [43–46]. Compare to other MOFs, MIL-88B exhibit excellent structural flexibility, chemical stability and abundant raw sources [46]. The structural flexibility and the multivalence state make the MIL-88B an ideal MOF candidate to integrate with other materials to achieve a synergistic effect for different applications.

Nanoporous composite membranes have been explored for their unique ability to balance the trade-off between ion permeability and selectivity for separation and extraction applications [16,47,48], as well as osmotic power harvesting [10,29,49]. For instance, a ZIF-8 membrane intercalated with polystyrene sulfonate (PSS) on highly ordered alumina nanochannel membrane (ANM), ZIF-8/PSS@ANM, was reported for osmotic energy harvesting in an organic solvent. An outstanding power density of 23.4 Wm<sup>-2</sup> was achieved from the interface of 2 M LiCl-Methanol with pure methanol solvent [50]. From these examples, it is obvious that combining the benefits of angstrom-scale passage cavities with chemical modification to mimic biological ion channels decorated with functional groups that control the hydrationdehydration processes underlying angstrofluidic ion transports will enhance the blue energy harvesting [51-53] We envisage that the biomimetic angstrofluidic ion channels will enhance ion permeability and selectivity to promote salinity gradient energy capture in both aqueous and organic solutions.

Herein, inspired by the sub-nano size potassium ion channels found in nature, we demonstrate a hybrid angstrofluidic channel membrane consisting of UiO-66-NH2 and MIL-88B, with the base layer intercalated with the negatively charged guest polymeric molecule, PSS. The bilayer metal-organic frameworks (MOF-on-MOF) with hierarchical pore structure was constructed from layer-by-layer deposition method. The UiO-66-NH<sub>2</sub>(PSS)/MIL-88B membrane benefits from the differential pore shape and channel surface charge to regulate transmembrane ion conduction in both aqueous and non-aqueous solutions for osmotic power conversion. The UiO-66-NH2 base layer has a wide array of triangular pore aperture of  $\sim 6$  Å, tetrahedral cavities of  $\sim 8$  Å and octahedral channel of ~11 Å [16]. The MIL-88B has an isoreticular structure with an average pore diameter of  $\sim 6$  Å [54]. The presence of a wide array of pores in the UiO-66 promotes better ion permeability and the isoreticular small ion channels in the MIL-88B serve as ion filters that screen ions based on their hydrated size. Additionally, these two MOF materials use the same terephthalate ligand and can easily be linked together through this common ligand [55]. Furthermore, the two MOFs have been used for various applications in different media and have been shown to be stable in both aqueous and organic solutions. The introduction of the negatively charged PSS molecules changes the space charge of the angstrom-size channels in UiO-66-NH2 and induces charge

asymmetry in the MOF-on-MOF membrane. The PSS-mediated charge in the angstrom-scale channel surfaces enhances ionic conductivity and permselective transport in the bilayer membrane. The synergistic effects of steric sieving and electrostatic interactions result in the energy conversion of  $5.60 \text{ Wm}^{-2}$  at the interface of simulated sea and fresh water. The power density was further enhanced to  $32.47 \text{ Wm}^{-2}$  with a higher permeability of  $526.60 \text{ Am}^{-2}$  achieved by using a 500-fold salinity gradient, while generating  $3.89 \text{ Wm}^{-2}$  from a 100-fold LiCl-methanol gradient. This work offers a new perspective on the design of angstrofluidic hybrid membranes aimed at enhancing selective ion transport for high-performance salinity gradient energy generation in both aqueous and organic solvent conditions.

## 2. Experimental section

#### 2.1. Materials

Tris(hydroxymethyl)aminomethane (Tris,  $\geq$ 99.8 %), dopamine hydrochloride (PDA,  $\geq$ 98 %), polyethyleneimine (PEI, M<sub>W</sub> = 800), 2-aminoterephthalic acid (99 %), zirconium(IV) chloride ( $\geq$ 99.5 %), poly (sodium 4-styrenesulfonate) (PSS, average M<sub>w</sub> ~ 70 k), hydrochloric acid (HCl, 37 % w/w), iron(III) nitrate nonahydrate ( $\geq$ 99.95 %), terephthalic acid (98 %), *N*,*N*-dimethylformamide (DMF, 99.8 %) and acetonitrile ( $\geq$ 99.9 %) were purchase from Sigma Aldrich. The anodized aluminum oxide (AAO) membrane ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, hydrophilic, pore size: 0.02 µm) was purchased from Whatman. The salts (LiCl, NaCl, KCl, MgCl<sub>2</sub> and CaCl<sub>2</sub>) were supplied by Sigma-Aldrich Co. and are in a reagent purity state. All aqueous solutions were prepared with ultrapure deionized water (18.2 MΩ).

### 2.2. Fabrication of UiO-66-NH<sub>2</sub>(PSS)/MIL-88B membranes

The AAO membrane substrate was immersed in a 50 mM Tris-HCl buffer solution (pH 8.5) containing 2 mg mL<sup>-1</sup> of PDA and 2 mg mL<sup>-1</sup> of PEI for 6 h. At the end of the 6 h, the AAO membrane coated with PDA-PEI was washed thoroughly and then soaked overnight in Milli-Q water to remove excess chemical residues and then dried at room temperature. UiO-66-NH<sub>2</sub>(PSS) was first synthesised on the PDA-PEI modified AAO membrane, followed by MIL-88B. The metal precursor solution for UiO-66-NH<sub>2</sub> was prepared by dissolving 0.2067 g of ZrCl<sub>4</sub> (0.89 mmol) in 16.7 mL of DMF and 3.3 mL of HCl as a coordination modulator. 0.1 wt% (40 mg) of PSS was mixed into the metal precursor solution, 0.2267 g of 2-aminoterephthalic acid (1.25 mmol) was dissolved in 20 mL of DMF to prepare the ligand solution. The metal precursor and ligand solutions were subsequently mixed and transferred into a Teflon-lined autoclave vessel together with the PDA-PEI modified AAO membrane and heated for 3 h at 80 °C. The UiO-66-NH<sub>2</sub>(PSS) coating was repeated for another cycle. MIL-88B was then synthesised on top of the UiO-66-NH<sub>2</sub>(PSS) layer. 0.4848 g of iron (III) nitrate nonahydrate (1.2 mmol) and 0.1994 g of terephthalic acid (1.2 mmol) were dissolved in 18 mL of DMF and 18 mL of acetonitrile. The mixture was then transferred into a Teflon-lined autoclave vessel together with the UiO-66-NH<sub>2</sub>(PSS) membrane and heated for 5 h at 90 °C.

# 2.3. Characterisation

Surface morphologies of the membranes were examined using scanning electron microscopy (SEM; JEOL JSM-7800F). Crystallographic data of the MOF membranes were obtained using a Rigaku MiniFlex benchtop X-ray diffractometer (XRD) with a Cu anode tube, through an angular range of 5 to 40° 20 with a step size of 0.03° and speed of 2° min<sup>-1</sup>. The surface chemistry of the membranes was examined via Fourier transform infrared spectroscopy (FT-IR, Shimadzu IRTracer-100) in attenuated total reflectance (ATR) mode with wave-numbers of 400–4000 cm<sup>-1</sup>.

The N2-adsorption-desorption experiment was conducted using a

Micromeritics ASAP 2020 surface area and pore size analyser. The samples (60 mg) were degassed under reduced pressure ( $<10^{-2}$  Pa) at 180 °C for 24 h prior to measurements. The temperature was maintained at 77 K with a liquid N<sub>2</sub> bath. The BET surface area was calculated over the relative pressure range between 0.05 and 0.30, and the total pore volume was calculated at a relative pressure of approximately 0.95.

#### 2.4. Electrical measurement

Ion conduction and salinity gradient energy generation experiments were conducted in an electro-chemical workstation, SP-300 potentiostat (BioLogic Science Instrument) with a pair of Ag/AgCl electrodes in an H-type electrochemical cell. The fabricated MOF-on-MOF membrane is sandwiched between to two halves of the H-cell filled with same volume and same concentration of electrolyte for ion conduction experiment and different concentrations of the same electrolyte for salinity gradient energy generation. The effective testing area of the MOF-on-MOF membrane for ionic conduction and salinity gradient energy conversion experiments is ~0.03 mm<sup>2</sup>. For transmembrane conductance, ionic current is measured from the application of voltage ranging from -800 to +800 mV with a pair of Ag/AgCl electrodes.

# 2.5. Permeation experiments

The diffusion of ion through the MOF-on-MOF membrane was conducted in an H-cell.

The MOF-composite membrane was sandwiched between deionized water and a fluorescent dye in the H-cell to measure the ion permeation. The feed compartment was filled with 0.1 mM fluorescent dyes ((Rhodamine 6G (Rh (+), orange or sulforhodamine (Rh (-), purple) solution of 40 mL, and the permeate side was filled with the same volume of deionized water. The permeate conductivity was analysed with a conductivity meter at different time intervals for a period of 30 min.

# 2.6. Osmotic energy generation

The osmotic energy conversion measurement is similar to ion conduction experimental setup except that the electrochemical setup is connected to an external load resistor. The stable diffusion current is measured at the input resistance and the power density calculated from Eq. (1).

$$P_d = \frac{I^2 R_L}{S} \tag{1}$$

In this equation, I is the current,  $R_L$  is the external electrical load resistance and S is the effective surface area of ion conduction of the membrane.

# 2.7. Molecular dynamic simulation

The combination of crystallographic data from public databases such as Chemtube3D and, American Mineralogist Crystal Structure Database (AMCSD), and Materials Project websites, along with computational tools like Avogadro for composite membrane design, OBGMX for force field parametrization, Python scripts for pre-processing, and DFT methods for charge determination enabled the successful setup and execution of molecular dynamics simulations for UiO-66-NH<sub>2</sub>(PSS)/ MIL-88B. Detail parameter analysis presented in the supporting information (SI). These simulations provided valuable information about the membrane's ion transportation behaviour, structural stability, and potential applications in various fields. The molecular dynamics simulation was conducted using the Large-scale Atomic/Molecular Massively Parallel Simulator (GROMACS) with a time step of 2 fs. We utilized the OPLS-AA force field for the MOF and water structures, ensuring accurate representation of the interactions within the system. The simulations were carried out in the NPT ensemble at 300 K and 1 atm using the NoséHoover thermostat and Berendsen barostat. Van der Waals interactions were calculated with a cut-off distance of 12 Å, and the Particle Mesh Ewald (PME) method was employed for long-range electrostatic interactions. The initial structures of UiO-66-NH<sub>2</sub> and MIL-88B were optimized using DFT calculations to ensure geometrical accuracy before the simulations.

# 3. Results and discussion

#### 3.1. Fabrication and characterisation of the MOF-on-MOF membrane

Fig. 1a illustrates the fabrication process of the bilayer MOF-on-MOF heterostructure, UiO-66-NH<sub>2</sub>(PSS)/MIL-88B membrane for ion transport and salinity gradient energy conversion. Firstly, anodic aluminum oxide (AAO) substrate is functionalized with polydopamine/polyethyleneimine (PDA/PEI). This is followed by the growth of UiO-66-NH<sub>2</sub> thing film intercalated with PSS by in-situ encapsulation method. The MIL-88B thin film is subsequently grown on the UiO-66-NH<sub>2</sub>(PSS) layer to form the bilayer UiO-66-NH2(PSS)/MIL-88B membrane. Scanning electron microscopy (SEM) is used to characterise the morphological features of the MOF-on-MOF membrane. The SEM characterisation of the PDA/PEI modified AAO, UiO-66-NH2(PSS), UiO-66-NH2(PSS)/MIL-88B membranes (Fig. 2a) shows that the deposited MOF layers are continuous without any visible defects. The nanorods of the MIL-88B have been grown successfully on the UiO-66-NH<sub>2</sub>(PSS) thin film (Fig. 2b). The cross-sectional SEM of the monolayer UiO-66-NH<sub>2</sub>(PSS) thin film (Fig. 2c) and the bilayer UiO-66-NH<sub>2</sub>(PSS)/MIL-88B membrane (Fig. 2d) reveal the integration of the MIL-88B on top of the UiO-66-NH<sub>2</sub>(PSS) base layer through the heteroepitaxial growth process [56] to form a hybrid membrane. The crystallinity of the UiO-66-NH<sub>2</sub>(PSS)/ MIL-88B membrane and the substrate was studied using X-ray Diffraction (XRD) and the XRD pattern of the UiO-66-NH<sub>2</sub>(PSS) film on the AAO-PEI/PDA exhibits distinct peaks at 7.3° and 8.4° (Fig. 2e), similar to what has been reported in literature [16].

The MIL-88B film displays standard characteristic peaks at 20 positions of 9.08 and 10.66°, which is consistent with the peaks from the simulated MIL-88B pattern from datable and in literature [57]. In addition, the peaks of the UiO-66-NH<sub>2</sub>(PSS) and MIL-88B films are visible in the bilayer UiO-66-NH<sub>2</sub>(PSS)/MIL-88B membrane (Fig. 2e). Furthermore, the XRD pattern for the hybrid membrane after being subjected to osmotic energy conversion test is similar to the pristine membrane, indicating good stability (Fig. S1a) of the heterostructured MOF. The surface chemistry of the bilayer MOF-on-MOF membrane and its substrate is further characterised through Fourier transform infrared (FTIR) (Fig. 2f). The formation of the UiO-66-NH<sub>2</sub> is identified through the Zr-O bond stretching at 700 cm<sup>-1</sup> and the N-H bond from the amino functional group, NH<sub>2</sub>, has a broad peak ranging from 2600 to  $3600 \text{ cm}^{-1}$ . The intercalated PSS in the UiO-66-NH<sub>2</sub>(PSS) is evident at peaks spanning 1008 to 1188  $\text{cm}^{-1}$ , which is associated with the R-SO<sub>3</sub> stretching present in the pure PSS molecule. The Fe-O stretching vibrations at 548 cm<sup>-1</sup> and C—O at 1506 cm<sup>-1</sup> are signature stretching bonds in the MIL-88B as reported previously [58]. There are no observable peaks in the AAO substrate functionalized with PEI/PDA. The adsorption isotherms of the individual layers of the MOF-on-MOF membrane shown in Fig. S1b indicate their permanent porosity with a type-I characteristic isotherm with BET surface area of 772 and 120  $m^2g^{-1}$  and total pore volume 0.72 and 0.09 cm<sup>3</sup>g<sup>-1</sup> of UiO-66-NH<sub>2</sub>(PSS) and MIL-88B, respectively. The differential channel shape and asymmetric channel surface charge of the heterogeneous membrane intercalated with nucleophilic guest molecule, PSS, to regulate the conduction of ion to create osmotic potential [59]. These asymmetric properties of the MOF-on-MOF membrane closely mimic phosphorylated multifunctional ion channels found in cellular machinery [60].



**Fig. 1.** Fabrication process of the heterogenous MOF-on-MOF angstrofluidic membrane with ion conduction and its application for osmotic power conversion in both aqueous and organic solutions. (a) Schematic illustration of the bilayer UiO-66-NH<sub>2</sub>(PSS)/MIL-88B membrane fabrication process. (b) Schematic representation of the experimental set-up for salinity gradient energy conversion and the illustration of ion conduction pathway arrowed to the left. (c) Salinity gradient energy conversion in aqueous and organic solutions arrowed to the right.



**Fig. 2.** (a) Surface morphology of PDA/PEI functionalized AAO, UiO-66-NH<sub>2</sub>(PSS), and UiO-66-NH<sub>2</sub>(PSS)/MIL-88B membranes. (b) SEM image near the edge of UiO-66-NH<sub>2</sub>(PSS)/MIL-88B membranes. Cross sectional SEM images of (c) UiO-66-NH<sub>2</sub>(PSS) and (d) UiO-66-NH<sub>2</sub>(PSS)/MIL-88B membranes. (e) XRD spectra of UiO-66-NH<sub>2</sub>(PSS)/MIL-88B, UiO-66-NH<sub>2</sub>(PSS), and PDA/PEI coated AAO, membranes and their corresponding simulated patterns from powder diffraction-4 (PDF-4) crystallography database. The symbols ( $\blacklozenge$ ), (x) and (\*) represent the peaks for MIL-88B, and PDA/PEI coated AAO and UiO-66-NH<sub>2</sub>(PSS) phase, respectively. (f) FTIR spectra of UiO-66-NH<sub>2</sub>(PSS)/MIL-88B, UiO-66-NH<sub>2</sub>(PSS), and PDA/PEI coated AAO, MIL-88B, UiO-66-NH<sub>2</sub>(PSS) phase, respectively. (f)

# 3.2. Ion conduction in the MOF-on-MOF membrane

The sub-nanofluidic channels with charged surface of the bilayer MOF-on-MOF membrane provide high-speed ionic conduction pathways. To elucidate the ionic conduction across the UiO-66-NH<sub>2</sub>(PSS)/ MIL-88B membrane, the ionic transport characteristic of the bilayer membrane was evaluated from the current-voltage (*I-V*) measurements in NaCl solution of different concentrations. The UiO-66-NH<sub>2</sub>(PSS)/MIL-88B membrane was sandwiched between two chambers of an H-type electrochemical cell filled with NaCl solutions (Fig. 3a). Symmetric *I-V* curves from -800 mV to 800 mV were recorded from 1 mM to 1000 mM NaCl using an in-house made Ag/AgCl electrodes. The transmembrane current increases with increasing electrolyte concentration from  $\sim$ 0.5  $\mu$ A at 1 mM to  $\sim$ 400  $\mu$ A at 1000 mM (Figs. 3b and S2a).

Higher concentration of ions in the electrolyte solution provides more charge carriers, which increase the transmembrane current through the MOF-on-MOF membrane. The interconnected asymmetric pore heterostructure of the UiO-66-NH<sub>2</sub>(PSS)/MIL-88B shows no observable current rectification. This observation is attributable to an ohmic contact at the interface of the two MOF materials with almost identical pore cavities of ~6 Å in the constituent MOF membranes of the bilayer MOF-on-MOF membrane. The conductance-concentration curve (Fig. 3c) at various concentrations of NaCl through the bilayer membrane exhibits two distinct properties at 100 mM. The conduction of the electrolyte with concentration below 100 mM deviates from the linear bulk ionic conduction behaviour in the electrolyte with concentration above 100 mM (the red dashed lines). The ionic conduction of the electrolyte below 100 mM through the bilayer MOF-on-MOF gradually plateaued and becomes totally independent of the concentration of the electrolyte (black dashed lines). This observation shows that ionic transport in the membrane is totally controlled by surface-charge of the angstrofluidic channels which is consistent with the Electric Double Layer (EDL) theory [61]. This theory indicates that when the membrane channel size is less than or equal to twice the Debye length, the ionic conduction is entirely governed by surface charge with strong ion selectivity [62]. As a result, the thickness of the EDL was determined from

$$\lambda_D = \sqrt{\frac{\varepsilon \varepsilon_0 RT}{2n_{bulk} z^2 F^2}} \tag{2}$$

where  $\varepsilon$ ,  $\varepsilon_0$ , *R* and *T* denotes permittivity of water, the permittivity of a vacuum, universal gas constant and absolute temperature, respectively. The  $n_{bulk}$ ,  $z^2$  and  $F^2$  represents the concentration of the bulk solution, the valence number and Faraday's constant, respectively. The thickness of the EDL at 10 mM and 500 mM was calculated as ~30.4 and ~43 Å, respectively, which are far bigger than the pore size of both UiO-66-NH<sub>2</sub> and MIL-88B that shares a limiting pore window of ~6 Å. This means that the ion transport in the sub-nanochannel is fully dominated by surface charge. It should be noted that the surface charge density of an angstrom-scale channel cannot be determined from zeta potential characterisation which is a property of EDL and there is only stern layer formation in Angstrom-size channels [63]. To account for the specific ion specie conduction promoted by the surface charge from the



**Fig. 3.** Ion transport characteristics of the bilayer MOF-on-MOF membrane. (a) A schematic of the symmetric ion conduction in an electrochemical device for *I-V* measurement. (b) The *I-V* curves of the hybrid MOF-on-MOF membrane with concentration ranging from 1 mM to 1000 mM (c) Ionic conduction behaviour of the MOF-on-MOF membrane in different concentrations. (d) Time dependent conductivity profile of two oppositely charged fluorescent dyes ((Rhodamine 6G (Rh (+), orange) and sulforhodamine (Rh (–), purple) in permeation experiments in a neutral solution. (e) The ionic conductivity of the MOF-on-MOF membrane and its constituent membranes in 0.5 M NaCl. (f) The ionic conductance in the bilayer MOF-on-MOF membrane in 0.01 M NaCl ionic strength of different electrolytes.

intercalated PSS in the bilayer MOF-on-MOF membrane, we conducted ion permeation experiments with two fluorescent dyes with similar structural formula but opposite charges. The time dependent conductivity profiles of two fluorescent dyes, Rhodamine 6G (Rh (+)) and sulforhodamine (Rh(-)) shown in Fig. 3d. The MOF-on-MOF membrane is placed between DI water and 0.1 mM dye solution the conductivity of the DI water measured at different time intervals. At 30 mins, the conductivity of the positively charged Rhodamine 6G (Rh (+)) was over two times higher than the conductivity of the negatively charged sulforhodamine (Rh (-)) (Fig. 3d). It is worth pointing out that there was no observable colour change of the DI water in the permeation experiment after the testing period probably due to the low concentration of the dve in the permeate. In addition, ion permeability through the bilayer membrane and its constituent membranes sandwiched between 0.5 M NaCl and DI water was studied by measuring the conductivity the permeate side after 30 mins. The conductivity of 10.72, 46.10, 53.07 and 62.63 µS/cm was recorded in AAO-PDA/PEI, MIL-88B, UiO-66-NH<sub>2</sub>(PSS), and UiO-66-NH<sub>2</sub>(PSS)/MIL-88B respectively as seen in Fig. 3e. This observation could potentially be attributed to variations in pore architecture and the impact of intercalated charged polymeric guest molecules.

The ionic conductance of different electrolytes with ionic strength of 10 mM was further evaluated. The conductance increases in the order  $Li^+ < Mg^{2+} < Ca^{2+} < Na^+ < K^+$  (Fig. 3f). In an aqueous solution, the ions are hydrated with hydrated size ranging from 6.62 to 8.56 Å (Table S3). The sizes of the hydrated ions are bigger than the limiting channel size of 6 Å of the constituent membranes of the bilayer MOF-on-MOF membrane. This indicates that the ions will undergo some level of dehydration before traversing the membrane. The degree of dehydration is dependent on the hydration energy of the ion species and K<sup>+</sup> has the least hydration energy, the smallest hydrated ionic size with the least resistance to ionic transport, hence the highest ionic conductance. Furthermore, the MOF-on-MOF membrane has a better sieving effect on

the divalent ions due to their relatively bigger hydrated size than the monovalent ions and the intercalated PSS molecules preclude the conduction of the chloride ions [64].

#### 3.3. Osmotic energy conversion from aqueous solutions

The salinity gradient energy conversion capacity of the heterogeneous MOF-on-MOF membrane is investigated with the membrane placed between electrolytes of asymmetric concentrations (0.5 M || 0.01; synthetic sea and fresh water in an electrochemical cell) as depicted in schematic in Fig. 1b. The salinity gradient drives the spontaneous diffusion of cations from the high concentration side to the low concentration region through the bilayer membrane, leading to the generation of a diffusion current and diffusion potential in the process. Two configurations of the concentration gradient for driving cation diffusion are considered, with the driving force originating either from the UiO-66-NH<sub>2</sub>(PSS) or MIL-88B side. The intercepts on the I-V curves represent two non-negligible quantities: open circuit voltage (V<sub>OC</sub>) on the horizontal axis and short circuit current (ISC) on the vertical axis. The different directions of the ion migration are shown on the right of Fig. 4a. The salinity gradient leads to transmembrane diffusion of ions which generates diffusion current and the migration of ions under electric field produces a drift current. For the forward salinity gradient orientation, ion diffuses from UiO-66-NH2(PSS) side to MIL-88B side, the absolute values of  $V_{OC}$  and  $I_{SC}$  are 105.59 mV and 1.15  $\mu$ A, respectively. The reverse gradient configuration involves ion diffusion from the MIL-88B side to UiO-66-NH<sub>2</sub>(PSS) side and 122.65 mV and 10.70  $\mu$ A, are recorded for  $V_{OC}$  and  $I_{SC}$ , respectively. The membrane internal resistance for the bilayer membranes is determined as  $V_{\text{OC}}/I_{\text{SC}}$ . The forward configuration has internal membrane resistance of 91.82 KΩ and 11.46 K $\Omega$  for the reverse orientation. This indicates that ion diffusion in the forward configuration from the UiO-66-NH<sub>2</sub>(PSS) side to the MIL-88B part is hampered by about eight times higher internal



**Fig. 4.** Osmotic energy conversion. (a) *I-V* curves of the bilayer membrane under the two salinity gradient configurations of forward and reverse diffusion and drift directions. For forward, ions migrated from the 0.5 M NaCl solution at the UiO-66-NH<sub>2</sub>(PSS) side to the 0.01 M at the MIL-88B side (violet curve) and for the reverse, ions diffuse from 0.5 M NaCl at the MIL-88B side to the 0.01 M at the UiO-66-NH<sub>2</sub>(PSS) side (red curve). The insert at the right shows the salinity gradient configurations with the ionic diffusion and drift directions. (b) *V-I* curves of the bilayer membrane under 5-, 50- and 500-fold salinity gradients of NaCl electrolyte with the Voc and Isc increasing as the salinity gradient increases. (c) The diffusion potential and cation transfer number at 5-, 50- and 500-fold salinity gradients of NaCl electrolyte. The 5-, 50- and 500-fold salinity gradients (d) transmembrane current density (e) power density with the external load resistance. The maximum power density of 1.47, 5.60 and 32.47Wm<sup>-2</sup> were attained in the 5-, 50- and 500-fold salinity gradient, respectively.

membrane resistance relative to the reverse configuration, hence the preferred high-speed ionic diffusion pathway is the reverse configuration. The reverse orientation is therefore selected for subsequent osmotic energy conversion parametric examination.

The transmembrane ionic conduction of the bilayer MOF-on-MOF membrane is further investigated in three different salinity gradients of NaCl: 0.5 M||0.1 M (5-fold), 0.5 M||0.01 M(50-fold) and 5 M ||0.01 M (500-fold). The ionic current positively correlates with the applied voltage in all the three concentration gradients (Fig. 4b). The V<sub>OC</sub> and I<sub>SC</sub> increase with increasing concentration gradient. The measured open circuit voltage (V<sub>OC</sub>) consist of diffusion potential (E<sub>diff</sub>) which is generated from the net-diffusion of ions across the MOF-on-MOF membrane and the redox potential (E<sub>redox</sub>) from the unequal potential drop at the electrode-electrolyte interface. The E<sub>diff</sub> is therefore described as.

$$E_{diff} = V_{OC} - E_{redox}$$
(3)

The  $E_{diff}$  is experimentally determined through electrode calibration by replacing the bilayer membrane with a non-ion selective membrane (Fig. S3). The  $E_{diff}$  of 31.26, 70.91 and 117.43 mV were determined from 5-, 50- and 500-fold concentration gradients, respectively (Fig. 4c). The ion transfer number (t<sub>+</sub>) of the bilayer membrane forms the basis of the  $E_{diff}$  which further defines the energy conversion efficiency of the membrane. Under the 5-, 50- and 500-fold concentration gradients, the ion transfer numbers of 0.92, 0.88 and 0.87, respectively, were determined for the MOF-on-MOF membrane (Fig. 4c). The increasing salinity gradients lead to a decrease in transfer efficiency, osmotic energy conversion efficiency, and ion selectivity (Figs. 4c and S4). This phenomenon may be attributed to the polarization effect occurring on the dilute solution side of the bilayer MOF-on-MOF membrane under higher salinity gradient due the build-up of counterions. Nevertheless, these results indicate that a substantial cation diffusion and significant power density can be attained from the salinity gradients.

To explore the osmotic energy conversion in the three different salinity gradients, the diffusion current is measured as an output against an external electrical load resistance ( $R_L$ ). The current densities of the three salinity gradients decline as the external electrical load resistance increases (Fig. 4d). The system's output power density ( $P_d$ ) [65] is calculated as

$$P_d = \frac{I^2 R_L}{S} \tag{4}$$

In this equation, I is the current,  $R_L$  is the external electrical load resistance and S is the effective surface area of ion conduction of the membrane. The output power densities reached a maximum value at 9 KΩ, 8 KΩ and 4 KΩ for 5-, 50- and 500-fold salinity gradient, respectively, which represent the internal membrane resistance of the bilayer membrane. The internal membrane resistances recorded for the bilayer MOF-on-MOF in this study are lower than half the values previously reported [66,67]. The maximum power densities of 1.47, 5.60 and 32.47 Wm<sup>-2</sup> were attained in the 5-, 50- and 500-fold salinity gradient, respectively, as seen in Fig. 4e which correspond to 36, 30 and 28 % energy conversion efficiency in the MOF-on-MOF membrane (Fig. S4a). To contextualize the osmotic energy conversion of the MOF-on-MOF membrane, we also conducted energy conversion experiments using the constituent membranes (AAO-PDA/PEI, UiO-66-NH<sub>2</sub>(PSS), MIL-88B, UiO-66-NH<sub>2</sub>/MIL-88B) as illustrated in Fig.S5. In addition, we compared the power density captured with our MOF-on-MOF membrane with some reported state-of-the-art heterogeneous membranes (Tables S4 and S5) in a RED based-technology. The bilayer MOF-on-MOF angstrofluidic membrane has a higher power density than most heterogeneous membranes as shown in Tables S4 and S5. The high osmotic energy capture is attributed to the low membrane internal resistance as a result of the heterostructured nature of the membrane with interconnected angstrom-scale pore structure that is negatively charged with the polymeric guest molecules. These features endowed the UiO-66-NH<sub>2</sub>(PSS)/MIL-88B membrane with high-speed ion conduction and diffusion pathways, enhancing osmotic energy harvesting.

The osmotic energy conversion in the UiO-66-NH<sub>2</sub>(PSS)/MIL-88B membrane is further investigated in a 50-fold salinity gradient of different electrolytes. The electrolytes LiCl, NaCl, KCl, MgCl<sub>2</sub> and CaCl<sub>2</sub> yield 2.54, 5.60, 7.16, 4.04 and 2.89 Wm<sup>-2</sup> from the 50-fold salinity gradient interface, respectively, as shown in Fig. S6a. The highest osmotic power density was generated in K<sup>+</sup> electrolyte due to its smallest hydrated diameter of 6.62 Å, the lowest hydration energy of -295 KJmol<sup>-1</sup> and highest diffusion coefficient, and as a result, the K<sup>+</sup> experience the fastest transmembrane conduction, higher dehydration and rehydration before entering and exiting the angstrom-scale channel, respectively. The K<sup>+</sup> further undergoes a better charge separation in the

cation-selective UiO-66-NH<sub>2</sub>(PSS)/MIL-88B membrane, resulting in higher osmotic power conversion in the KCl than the other monovalent and divalent ions studied. The osmotic power generation stability of the MOF-on-MOF membrane is demonstrated in saline solution for 15 days (Fig. S6b) and the heterogenous membrane maintained a fairly stable energy conversion performance.

#### 3.4. Molecular mechanism of ion transport and energy conversion

To expand further on the mechanism of ion conduction through the bilayer MOF-on-MOF membrane, we conducted molecular dynamic simulation on the membrane. The molecular dynamic simulation of ion transport across the bilayer membrane was evaluated by fitting the bilayer membrane in between NaCl electrolyte with concentration gradient in two different configurations of the membrane (Fig. 5a). After the simulated time, it is observed that ions passing from the UiO-66-NH<sub>2</sub> (PSS) side of the bilayer membrane are temporarily adsorbed by the guest polymeric nucleophile (PSS) species. Ion diffusion originating from the MIL-88B side of the bilayer membrane, does not experience the



Fig. 5. Molecular dynamics simulation of ion transport across the UiO-66-NH<sub>2</sub>(PSS)/MIL-88 from either UiO-66-NH<sub>2</sub>(PSS) or MIL-88B side of the bilayer membrane. (a) The initial and final simulated interaction of ions with the sub-nanochannel surface of MIL-88B and UiO-66-NH<sub>2</sub> (PSS) membranes. (b) Ion diffusion comparison at the UiO-66-NH<sub>2</sub>(PSS) and MIL-88B membrane sides. (c) The difference between the initial and the final point for radius of gyration analysis. (d) Average electrostatics, vdW, and total energy between ions and membrane at the UiO-66-NH<sub>2</sub>(PSS) and MIL-88B membrane sides.

sudden disruption and are not trapped at the nanochannel surface. This observation indicates that the presence of the PSS in the UiO-66-NH<sub>2</sub> creates an energy surge wall barrier and act as ion filter that creates a zone of interaction between the channel surface with the arriving ions. Furthermore, this observation is akin to potassium channels found in cell membranes where the ion selective filter region is packed with negatively charged polar amino acids to regulate ion conduction and selectivity [68]. The ion diffusion across the bilayer membrane from the MIL-88B side however, experience almost no interaction with the channel surface. This leads to a superior ion diffusion from the MIL-88B side of the MOF-on-MOF membrane at 1.15 nm<sup>2</sup>ns<sup>-1</sup>, compared to the diffusion rate through the UiO-66-NH<sub>2</sub>(PSS) side (Fig. 5b). To elucidate further the underlining mechanism, a multi-faceted analysis is undertaken. The gyration radius analysis, as presented in Fig. 5c, provides further clarity. The expansion of the gyration radius on the MIL-88B side indicates a broader structural reconfiguration compared to the UiO-66-NH<sub>2</sub>(PSS) side. This expansion corresponds to an ion transport mechanism in which ions navigate through the MIL-88B side more effectively. This unique ion transport behaviour finds its root in the intricate interplay between the bilayer membrane's charge distribution and the specific MOF structures. On the UiO-66-NH<sub>2</sub>(PSS) side, the interaction between ions and the PSS induced negative charge results in ions being temporarily held at the front of the membrane. The energy analysis, depicted in Fig. 5d, mirrors this conduction mechanism, with energy profiles revealing the interplay between adsorption of ion and the intercalated PSS nucleophile that guide ion transport. This analyses collectively reaffirms the ionic conduction behaviour observed experimentally in Fig. 4a where the short circuit current of 1.15 µA and open circuit voltage of 105.59 mV were recorded for diffusive ion transport from the UiO-66-NH2 side of the MOF-on-MOF membrane as compare to the and 10.70 µA short circuit current and 122.70 mV open circuit voltage in the MIL-88B side. Both the experimental and the simulation results show that the bilayer MOF-on-MOF membrane exhibits a superior osmotic energy conversion characteristic with salinity gradient facing the MIL-88B side of the bilayer. The findings underscore the complex interplay between membrane surface charge and MOF structures, shedding light on how ions navigate these pathways, ultimately contributing to a comprehensive understanding of ion transport within such composite materials and subsequent salinity gradient energy conversion.

# 3.5. Osmotic energy conversion from organic solutions

We also investigated the bilayer UiO-66-NH<sub>2</sub>(PSS)/MIL-88B capacity to extract osmotic power from the interface of organic solutions with salinity gradients, leveraging the MOF-on-MOF membrane's stability under diverse working conditions. LiCl is chosen as the electrolyte due to its superior solubility in common organic solvents compared to other monovalent and divalent salts. This characteristic makes LiCl particularly suitable for use with commonly employed organic solvents in both the pharmaceutical and chemical industries. These common solvents are ethanol (EtOH), Isopropanol (IPA), methanol (MeOH), *N*, *N*-Dimethylformamide (DMF), and Dimethyl sulfoxide (DMSO), which aligns well with what has been previously reported in the literature [14,69]. A 10-fold concentration gradient of 0.1 molL<sup>-1</sup> and 0.01 molL<sup>-1</sup> LiCl in all the five organic solutions were employed to study the ionic transport process and energy conversion capacity of the bilayer MOF-on-MOF membrane.

The maximum osmotic current ( $I_{SC}$ ) of 1.16  $\mu$ A (Fig. 6a) and osmotic potential ( $V_{OC}$ ) of 123.04 mV (Fig. 6b) and were recorded in methanol and DMSO, respectively. As a result, the osmotic energy generating capacity of the bilayer MOF-on-MOF was determined as output power density [14]  $P = \frac{V_{0C} \times I_{SC}}{S}$  and 0.53, 2.55, 0.04, 1.13, 1.32 Wm<sup>-2</sup> Fig. 6c were recorded in ethanol, methanol, isopropanol, DMF and DMSO, respectively. The highest osmotic current and power density recorded from LiCl-Methanol is mainly due to the low viscosity of methanol, hence the energy carrier, Li<sup>+</sup> in the methanol diffuses faster across the MOF-on-MOF membrane than in the other organic solvents. As a result of this observation, the osmotic energy conversion in methanol is further examined in three different concentration gradients (10-fold; 0.1 M|| 0.01, 50-fold; 0.5 M||0.01 M and 100-fold; 1 M|| 0.01 M) index on an external circuit with external load resistance. The current density curves (Fig. 6d) are similar to those recorded in the aqueous solutions and the maximum output power density of 3.89, 1.32 and 0.19  $Wm^{-2}$  (Fig. 6e) were recorded in 100-, 50- and 10-fold respectively. These results compare favourably with other heterogeneous membranes reported for salinity energy conversion in organic solvents through reverse electrodialysis (as shown in Table S6). This underscores the potential of the UiO-66-NH<sub>2</sub>(PSS)/MIL-88B membrane for harnessing salinity gradient energy in various organic solvents and highlights the ability of the reverse electrodialysis technology to augment the renewable energy portfolio with salinity gradient energy from unconventional sources



Fig. 6. Osmotic energy conversion in organic solvents. (a) The short circuit current ( $I_{SC}$ ) (b) open circuit voltage ( $V_{OC}$ ) and (c) power density of the UiO-66-NH<sub>2</sub>(PSS)/MIL-88B in five common organic solvents. The 10-, 50- and 100-fold salinity gradients (d) transmembrane current density (e) power density with the external load resistance in LiCl-methanol.

while minimizing the environmental impact of waste organic solutions.

#### 4. Conclusion

In summary, we have engineered a bilayer metal-organic frameworks membrane that benefits from the array of pore architecture present in UiO-66-NH<sub>2</sub> with a channel space that negatively charged and isoreticular pore structured MIL-88B membrane as the top layer for osmotic energy conversion in both aqueous and different organic solutions. The UiO-66-NH<sub>2</sub>(PSS)/MIL-88B membrane with asymmetric pore shape and channel surface charge endows the MOF-on-MOF membrane with a preferred direction of an enhanced cation conduction. The angstrom-scale heterogeneous membrane with the nucleophilic energy domain serves as ion filters, restricting the transmembrane conduction of large-sized hydrated cations and at the same time enables high-speed transport of small-sized dehydrated cations across the membrane. These features collectively enhance the diffusion-driven ionic conduction in different work conditions generating 5.60 Wm<sup>-2</sup> at the interface of synthetic sea and freshwater and  $3.89 \text{ Wm}^{-2}$  at the interface of 100-fold salinity gradient in LiCl-methanol. In addition, the capacity to extract osmotic energy from diverse solvents and the 32.47 Wm<sup>-2</sup> osmotic power from 500-fold salinity gradient demonstrates the MOF-on-MOF membrane as an excellent osmotic energy conversion material. The simulation results indicate that the intercalated guest molecule, PSS, in the bilayer membrane plays a significant role in ion conduction. The energy barrier introduced by the polymeric guest molecule in the UiO-66-NH<sub>2</sub> channel modulates the speed of ion transport in the angstromsize channel by restricting ions entering from the UiO-66-NH<sub>2</sub> section through adsorption while ions from the Mil-88B side has no such hindrance. The slow flow of the ions arriving from UiO-66-NH<sub>2</sub> side, in addition to the dehydration of ions before entering the channel, results in a significant internal membrane resistance relative to ions arriving from the MIL-88B section. This work provides a new avenue to design angstrom-scale ion channels for osmotic energy conversion in both aqueous and non-aqueous environments.

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## CRediT authorship contribution statement

All authors contributed to Conceptualization, Writing, Review, and Editing. All authors have read and agreed to the published version of the manuscript.

#### Institutional review board statement

The study did not require ethical approval.

#### Informed consent statement

Not applicable.

# Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Data availability

The data supporting the findings of this work are available in the supporting material and as well as from the corresponding authors.

# Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.desal.2024.117968.

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