Highly selective and high-performance osmotic power generators in subnanochannel membranes enabled by metal-organic frameworks

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The electric organs of electric eels are able to convert ionic gradients into high-efficiency electricity because their electrocytes contain numerous “subnanoscale” protein ion channels that can achieve highly selective and ultrafast ion transport. Despite increasing awareness of blue energy production through nanochannel membranes, achieving high-performance energy output remains considerably unexplored. Here, we report on a heterogeneous subnanochannel membrane, consisting of a continuous UiO-66-NH₂ metal-organic framework (MOF) and a highly ordered alumina nanochannel membrane. In the positively charged membrane, the angstrom-scale windows function as ionic filters for screening anions with different hydrated sizes. Driven by osmosis, the subnanochannel membrane can produce an exceptionally high Br⁻/NO₃⁻ selectivity of ~1240, hence yielding an unprecedented power of up to 26.8 W/m² under a 100-fold KBr gradient. Achieving ultrahigh selective and ultrafast osmotic transport in ion channel–mimetic MOF-based membranes opens previously unexplored avenues toward advanced separation technologies and energy-harvesting devices.

INTRODUCTION

Ionic gradients are in ubiquitous existence in biological membranes, and thus, selective osmotic transport of ions in biological ion channels is of fundamental significance in physiological functions of natural systems. For example, Electrophorus electricus (or the commonly known electric eel) is capable of converting ionic gradients into high-voltage electricity of up to 600 V using a large number of asymmetric “subnanoscale” protein ion channels on the electrocytes (Fig. 1), which can regulate fast ion transport with high efficiency (2). Motivated by this high-efficiency ionic gradient power system, considerable efforts have been made on the exploration of the reverse electrodialysis–based ion-selective membranes using nanoscale single-pore (3–7) and multi-pore (8–12) devices. Moreover, nanofluidics-based heterogeneous membranes (13–19), which can rectify ion transport for boosting energy harvesting from ionic gradients, have been widely exploited. However, unlike for nanopore- and nanochannel-based membranes, osmotic power harvesting with subnanochannel membranes remains significantly unexplored. Although there have been few reports on osmotic harvesting for about 1-nm-scale membranes with lamellar two-dimensional materials (20, 21), the output performance was still limited due to non-uniform channel structures and limited mass transportation area, which can increase the membrane resistance for osmotic ion transport.

Metal-organic frameworks (MOFs), porous crystalline materials composed of metal clusters and organic linkers, have emerged as a promising platform for diverse applications from energy to environment (22–24) because of their narrow distribution of ordered channels, high surface area for transport, and tailorable surface properties. Although few publications have examined the potential use of the MOF-based membranes as an osmotic power generator (25, 26), the output performance is still not too high (<3 W/m²) compared with the conventional nanochannel membranes.

Most recently, a series of studies appeared, which showed that the voltage-driven ion transport can be regulated by in situ growing the UiO-66–based MOFs into a single 12-μm polyethylene ter-ephthalate (PET) nanochannel (27, 28). Significantly improved cation selectivity can be observed by tailoring surface chemistry of UiO-66 crystals. In light of their high stability in water (29) and numerous ordered three-dimensional channels comprising ~5- to 7-Å windows and ~8- to 11-Å cavities (fig. S1) (30), whose sizes are comparable to most of the hydrated ions (e.g., K⁺: 6.62 Å and Cl⁻: 6.64 Å) in water (31), the UiO-66–based MOFs are excellent candidates as an ion-selective membrane material for osmotic power harvesting. However, to the best of our knowledge, high-efficiency subnanochannel UiO-66–based MOF membranes for harvesting energy from ionic gradients are yet to be exploited.

Inspired by subnanoscale ion channels in biologic membranes, we design a heterogeneous subnanochannel membrane, UiO-66-NH₂@ANM, prepared with a continuous subnanoscale UiO-66-NH₂ MOF membrane and a highly ordered alumina nanochannel membrane (ANM) support, for osmotic energy harvesting (Fig. 1). In this ion channel–mimetic membrane, the narrow NH₂-containing window-cavity channel structures are considered as ionic filters and ionic conductors for boosting osmotic ion transport with high anion selectivity. In view of a large number of subnanochannels in UiO-66-NH₂ membrane, numerous nanosubnanochannel interfaces are formed between the two membranes of UiO-66-NH₂@ANM, and thus, the large-sized ANM can act as an ion-storage layer for improved ion transport (17). The resulting UiO-66-NH₂@ANM can achieve an unprecedented power density of up to 26.8 W/m² under a 100-fold KBr gradient, while nearly negligible power for KNO₃ at the same concentration gradient, yielding an amazingly high Br⁻/NO₃⁻ selectivity of ~1240. Achieving ultrahigh selective and ultrafast osmotic transport in the ion channel–mimetic MOF-based membrane paves avenues for next-generation sustainable energy generation and desalination.
RESULTS

Fabrication of UiO-66-NH2@ANM

The heterogeneous subnanochannel membrane, UiO-66-NH2@ANM, was fabricated by in situ solvothermal synthesis of a dense UiO-66-NH2 crystal layer on the NH2-functionalized ANM support with the presence of an optimized amount of modulator, benzoic acid, which can assist control of the crystal size of UiO-66-NH2 (Fig. 2A, see more details in Materials and Methods) (32). The ANM was fabricated by the two-step anodization strategy as reported previously (8), followed by postmodification with 3-aminopropyltriethoxysilane (APTES) under nitrogen to obtain the NH2-functionalized ANM support. The modification of an APTES monolayer, which can act as a covalent linker between UiO-66-NH2 and ANM, is important here to fabricate a continuous dense UiO-66-NH2 crystal layer because of the poor heterogeneous nucleation between UiO-66-NH2 and porous substrates (33). The successful modification of APTES onto ANM was confirmed by the x-ray photoelectron spectroscopy spectra (Fig. S2A). Zeta potential measurements of the ANM and NH2-functionalized ANM also confirmed that the latter was still positively charged in neutral solution after the modification of amine moieties on the channel walls (Fig. S2B).

The successful growth of a large-scale (over 250 μm × 250 μm) continuous and pinhole-free UiO-66-NH2 layer on the highly ordered ANM was confirmed by the top view and cross-sectional view scanning electron microscopy (SEM) images of UiO-66-NH2@ANM (Fig. 2, B and C). The thicknesses of the UiO-66-NH2 layer and ANM were ~750 nm and ~17.4 μm, respectively (Fig. 2C and fig. S2C), and the average pore diameter and pore density of the ANM layer were ~56 nm and ~5.2 × 109 pores/cm2, respectively (fig. S2, D and E). The x-ray diffraction (XRD) patterns of UiO-66-NH2@ANM also confirmed the successful synthesis of UiO-66-NH2 crystals (fig. S2F). The contact angle measurements of UiO-66-NH2@ANM displayed that its ANM side was hydrophilic and the UiO-66-NH2 side was more hydrophilic (Fig. 2D), advantageous to ion and water transport. The N2 sorption isotherms of UiO-66-NH2 crystals revealed that they had high Brunauer-Emmett-Teller (BET) surface areas of 1106 m2/g (fig. S3A) and were composed of ca. 6- to 7-Å window apertures and majorly about 1.24-nm cavities of ordered MOF channels (Fig. 2E). Originating from the existence of NH2 functional groups, UiO-66-NH2 was positively charged with a zeta potential of about 35 mV in neutral salt solution (fig. S3B), indicating an anion selectivity. The zeta potential of 35 mV at 10 mM KCl corresponds to a surface charge density of ~8.6 mC/m2, calculated by \( \sigma_s = k_F^2 \sinh \left( \frac{F \zeta}{RT} \right) \) (34), where \( \varepsilon_f \) is the dielectric constant of fluid, \( \kappa \) is the reciprocal of the Debye length, \( R \) is the gas constant, \( T \) is the fluid temperature, \( F \) is the Faraday constant, and \( \zeta \) is the measured zeta potential of UiO-66-NH2. The anion-selective property of the UiO-66-NH2 layer was also confirmed by the energy-dispersive x-ray spectroscopy mappings of UiO-66-NH2@ANM after it was immersed in 0.1 M KCl solution for 30 min (fig. S4). The strength of chlorine signals was stronger than that of potassium on the UiO-66-NH2 surface. Because the ANM is also positively charged in neutral solution, the fabricated UiO-66-NH2@ANM is entirely anion selective and of symmetric charge nature.

Surface charge–governed ion transport of UiO-66-NH2@ANM

Because the UiO-66-NH2 MOF channels fabricated comprise two major characteristic pore sizes, one of which is from triangular windows in the range of about 6 to 7 Å and the other is from octahedral cavities of diameters about 12.4 Å (Figs. 2E and 3A), the heterogeneous UiO-66-NH2@ANM should display apparent surface charge–governed ion transport (35) at high electrolyte concentration. To demonstrate this, the ion transport properties of UiO-66-NH2@ANM were examined by monitoring the transmembrane ionic current by using a custom-made electrochemical cell (see details in Materials and Methods). Figure 3B shows the current-time (I-t)
measurement of UiO-66-NH₂@ANM recorded in 0.01 M KCl (pH 6.1) solution by alternating an applied voltage bias between +1 and −1 V. Each cycle lasted for 6 min without break, and the entire experiment was done for a total period of 48 min, displaying a superior ion transport stability of the membrane. Figure S5 further shows the current-voltage (I-V) characteristics of UiO-66-NH₂@ANM at concentrations between 0.001 and 0.1 M. For all concentrations tested, the current at the positive voltage is slightly larger than that at the negative voltage of the same magnitude, indicating that UiO-66-NH₂@ANM can rectify ionic current with the rectification ratios of about 2.06, 1.41, and 1.14 at 0.001, 0.01, and 0.1 M KCl, respectively. Similar to earlier reports with nanoscale membranes (36), the rectification ability of the subnanoscale UiO-66-NH₂@ANM decreases with increasing salt concentration, which can be ascribed to the stronger screened effect on surface charges of channels at higher concentrations (37). The weak ion rectification can be attributed to the asymmetric wettabilities and pore sizes of the heterogeneous membrane prepared, both of which induce two different and opposite preferred ion transportation directions (38). We then further analyzed the transmembrane conductance as a function of the KCl concentration ranging from 1 μM to 3 M (Fig. 3C). As shown, the ionic conductance starts to deviate from the bulk value tendency (gray curve) when the salt concentration is below 1 M, indicating the apparent surface charge–governed ion transport phenomenon. The inset in Fig. 3C schematically depicts the Debye length of ~0.3 nm on the charged MOF channel at 1 M KCl, which is comparable to the half window size of UiO-66-NH₂ that we prepared, indicating again its subnanoscale structures. This originates from the earlier report that the channel conductance is governed by its surface charges when the overlapping of the electric double layers in the solid-state channel becomes notable (35). The hydrophilicity, subnanoscale pore structures, and rectified ion transport of the heterogeneous membrane prepared could shed light on the further application in osmotic power generation.

**Osmotic power conversion through UiO-66-NH₂@ANM**

The osmotic power conversion efficiency of UiO-66-NH₂@ANM prepared was tested with the same electrochemical cell in the presence of a salinity gradient (Fig. 4A, see details in Materials and Methods). Because both UiO-66-NH₂ and ANM are positively charged in neutral solutions, applying a salinity gradient through the composite membrane will lead to a net flow of anions, generating a diffusion potential (Vdiff) and diffusion current (Idiff). Figure 4B illustrates the I-V curves of UiO-66-NH₂@ANM under the two opposite configurations of 1000-fold KCl gradient. Note that in Fig. 4B, the electrode calibration with the redox potential (V_redox) arising from the uneven potential drop occurring on the two Ag/AgCl electrode–solution interfaces immersed in different salinity solutions has been performed (see section S2 and table S1) (13). Consequently, Vdiff and Idiff originating from the pure osmotic transport can be directly read from the intercepts on the voltage and current axes, respectively. Figure 4B indicates that when the concentrated solution was in contact with the UiO-66-NH₂ side, the absolute values of Vdiff and Idiff were ~72.7 mV and ~1.81 μA, respectively. Under the reverse salinity gradient with the concentrated solution in contact with the ANM side, both the absolute values of Vdiff and Idiff decreased to ~46.1 mV and ~1.05 μA, respectively. The preferential direction for anion transport decreases the internal resistance of the heterogeneous membrane, calculated as Rm = Vdiff/Idiff, by approximately 9.3% in the former setup, beneficial to harvesting energy.
from salinity gradients with higher performance (13). Hereafter, we hence kept the compartment facing the UiO-66-NH2 side filled with concentrated solutions in the following tests, which is consistent with earlier reports with anion selectivity of heterogeneous membranes (14).

As the next step, we tested the osmotic power conversion (including $V_{\text{diff}}$ and the diffusion current density, $J_{\text{diff}}$) of UiO-66-NH2@ANM under a series of concentration gradients using KCl. The lower concentration was fixed at 1 mM, and the higher concentration was elevated from 10 to 3000 mM. Note that although the achieved power density is smaller than all the reported state-of-the-art anion-selective nanochannel membranes (13–19), the output is still below the value of the commercial benchmark (5 W/m²).

We also tested the osmotic power generation of UiO-66-NH2@ANM by mixing artificial seawater (500 mM NaCl) and river water (10 mM NaCl). As shown in fig. S6, the maximum output power density was about 2.96 W/m² under this 50-fold NaCl concentration gradient. Note that although the achieved power density is smaller than the above value with using KCl (4.93 W/m²) under the same concentration gradient, it is still higher than all the reported state-of-the-art anion-selective nanochannel membranes (14, 15, 39–41) to the best of our knowledge (table S2). The demoted osmotic power when using NaCl can be attributed to the larger hydrated diameter of Na⁺ ions (7.16 Å) than the K⁺ ions (6.62 Å) (31). However, because the subnanoscale membrane is highly anion selective and composed of a large number of ordered window-cavity channel structures, the demotion in osmotic power with other larger-size cations is not notable.

**Fig. 3. Surface charge–governed ion transport in UiO-66-NH2@ANM.** (A) Schematic of the (i) heterogeneous UiO-66-NH2@ANM, (ii) illustrated lattice structure of the UiO-66-NH2 membrane, which has (iii) ordered window size of 6 to 7 Å. (B) Dynamic current measurements of UiO-66-NH2@ANM recorded in 0.01 M KCl solution with an external bias alternating between +1 and −1 V. (C) Transmembrane ionic conductance of UiO-66-NH2@ANM as a function of the KCl concentration varying from 10⁻⁶ to 3 M. It indicates that the membrane conductance starts to deviate from the bulk value (gray line) at a high concentration of 1 M (corresponding to a Debye length of ~0.3 nm; inset), showing the apparent surface charge–governed ion transport phenomenon even in high saline condition owing to the subnanoscale channels of UiO-66-NH2.

Highly selective and high-performance osmotic power generation

Note that the hydrated diameter of the major transporting anions, Cl⁻, considered here is 6.64 Å (31), which is within the window sizes (ca. 6 to 7 Å) of UiO-66-NH2 that we prepared. This drives us to think whether there is a possibility to use the other electrolytes (e.g., KBr) with a smaller hydrated anion diameter for improved osmotic power generation. We then investigated the osmotic power generation of the heterogeneous subnanochannel membrane, UiO-66-NH2@ANM, by using four anion types of electrolytes with different hydrated diameters (Fig. 5). Here, we fixed the higher concentration at a high saline condition of 1000 mM (corresponding to a Debye length of 0.3 nm) to minimize the surface charge effect and the lower
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concentration at 10 mM. Because the heterogeneous subnanochannel membrane is entirely positively charged, the difference in osmotic powers shown in Fig. 5 comes primarily from major transporting anions. The current densities of UiO-66-NH₂@ANM in KBr and KCl were over one order of magnitude higher than those in KNO₃ and Na₂SO₄ (Fig. 5A). The achieved maximum power densities were ca. 26.8, 11.0, 0.0216, and 0.0497 W/m² for KBr, KCl, KNO₃, and Na₂SO₄, respectively (Fig. 5B). Similar to the behaviors of current density, UiO-66-NH₂@ANM outputs the osmotic power densities in KBr and KCl that are higher than those in KNO₃ and Na₂SO₄ systems.

As the next step, we analyzed the selectivity ratios of the present subnanoscale UiO-66-NH₂@ANM and those of the nanoscale ANM (Fig. 5E and table S4). Because UiO-66-NH₂@ANM outputs the lowest power in KNO₃, the selectivities of the subnanochannel and nanochannel membranes reported here were estimated as a ratio of osmotic powers recorded in different anion types of electrolytes and KNO₃, which is different from the earlier reports using the voltage-driven ionic currents/conductances to calculate ion selectivity (45, 47), to emphasize the contribution of osmotic ion transport. The subnanoscale UiO-66-NH₂@ANM achieved the amazingly high Br⁻/NO₃⁻ and Cl⁻/NO₃⁻ selectivities of up to ~1240 and ~509, respectively, but the nanoscale ANM can enable the corresponding selectivities of ~13.3 and ~7.46 only. It is known that ions in water are hydrated and the hydrated ionic diameters are larger than the dehydrated ones (31). Of UiO-66-NH₂, the sub-1-nm-scale windows can function as ionic filters for screening hydrated ions and enhancing ion selectivity, whereas the nanometer-scale cavities can act as ionic conductors for boosting osmotic ion transport (45).

To quantity the magnitude by which the importance of the subnanoscale UiO-66-NH₂ layer contributes to the selective and promoted osmotic transport, we then compared the output powers from the present subnanoscale UiO-66-NH₂@ANM with those from the nanoscale ANM in different anion-type electrolytes at a 100-fold salinity gradient (Fig. 5D, fig. S7, and table S4). Note that in this study, we adopted the ~25-nm-diameter ANM in the comparison because of its apparently higher selectivity than the ~56-nm-diameter ANM. In KBr and KCl, the subnanochannel membrane UiO-66-NH₂@ANM outputted powers notably higher than the ANM; however, the reverse trends were observed in KNO₃ and Na₂SO₄. Compared with the nanoscale ANM, UiO-66-NH₂@ANM showed the appreciably amplified power densities of up to 1.92 and 1.13-fold in KBr and KCl, respectively. However, in KNO₃ and Na₂SO₄, the powers generated by UiO-66-NH₂@ANM largely decreased by 96.9 and 87.6%, respectively. Similar behavior can also be found in the osmosis-driven short-circuit currents between UiO-66-NH₂@ANM and ANM depicted in Fig. 5C and fig. S7C. Note that the achieved maximum power densities of the ANM were as low as ~0.69 and ~0.40 W/m² in KNO₃ and Na₂SO₄, respectively, ascribed to the strong absorption of nitrate and sulfate ions by alumina surfaces (46), which leads to an apparent decrease of the surface charges on the ANM. Subsequently, in the same electrolytes, the osmotic power was further decreased to approaching zero value using the heterogeneous subnanochannel membrane UiO-66-NH₂@ANM. Apparently, the promoted and demoted osmotic power efficiencies between UiO-66-NH₂@ANM and ANM stem from the existence of the subnanoscale window-channel structures of the UiO-66-NH₂ membrane layer, which function as either ionic conductors for boosting osmotic ion transport or ionic filters for hindering ion passage. Although the presence of NH₂ groups is capable of facilitating the anion transport, the angstrom-sized pore windows play a role in sieving hydrated anions.

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Fig. 4. Osmotic energy conversion of UiO-66-NH₂@ANM. (A) Schematic of our osmotic energy-harvesting device under a salinity gradient. (B) I-V curves of UiO-66-NH₂@ANM recorded under two opposite configurations of 1000-fold KCl gradient, where the redox potential contribution has been subtracted. The internal resistance (Rint) decreases by ~9.3% when the UiO-66-NH₂ layer faced a concentrated solution. (C) Diffusion potential (VDiff) and diffusion current (IDiff) as a function of concentration gradient. The lower concentration in contact with the ANM side was fixed at 1 mM. (D) Current density (open symbols) and power density (solid symbols) harvested under various KCl concentration gradients. The maximum output power densities achieved were ~2.19, 4.93, and 7.12 W/m² under 5-, 50-, and 500-fold concentration gradients, respectively.
On the contrary, the hydrated anions with smaller sizes (e.g., Br$^-$ (Fig. 5F), leading to an extremely low osmotic power performance. The presence of more uncharged, deprotonated NH$_2$ functional groups. The output power also decreases with the increase of testing area (Fig. 5G), which is expected because the enhanced access resistance and reduced ion selectivity (18) will undermine the conversion performance. However, we have to emphasize that our heterogeneous subnanochannel membrane was still able to achieve high-performance power as high as ~4.4 W/m$^2$ when using a testing area of 0.03 mm$^2$ (15, 42–44). This suggests the potential use of the UiO-66-based membranes in future industrial large-scale membrane applications.

### Stability test of UiO-66-NH$_2$@ANM

We also tested the stability of UiO-66-NH$_2$@ANM in aqueous solutions. The UiO-66-NH$_2$ side, after immersing the heterogeneous membrane in deionized water for 1 month, still kept continuous and dense structure (Fig. 6A), along with high crystallinity (Fig. 6B). We also soaked the UiO-66-NH$_2$ sample in high (i.e., 0.5 M) and different saline (e.g., KCl, KBr, KNO$_3$, and Na$_2$SO$_4$) environments for 7 days. XRD results shown in fig. S10 indicated that the structure of UiO-66-NH$_2$ retains its high crystallinity. The N$_2$ sorption isotherms of UiO-66-NH$_2$ shown in fig. S11 revealed that UiO-66-NH$_2$ can still contain about 77 and 75% BET surface areas after being soaked in 0.5 M KCl and 0.5 M KBr solutions, respectively. The slight decrease in surface area can be ascribed to the adsorption of high-concentration anions. The BET isotherm results validate again the high structural ability of UiO-66-NH$_2$ in saline environments. Such a good water and chemical stability of the UiO-66 MOF has been explained to be attributed to the strong Zr–O bond and the compact structure of metal clusters (29). Figure 6C illustrates the recordings of the short-circuit current of UiO-66-NH$_2$@ANM in 500 mM/10 mM KCl. The membrane can still retain 90.8% stable current operated for continuous 12 hours, revealing the potential of long-term operation for future application.

To further demonstrate the stability of osmotic power conversion performance with UiO-66-NH$_2$@ANM, we independently prepared a new membrane and tested its output power density in 1000 mM/10 mM KBr gradient for seven continuous days. As shown in Fig. 6D and fig. S12, only 12.8% decrease (from 26.5 to 23.1 W/m$^2$) of output power density can be observed. In addition, the cross-sectional...
for highly selective and high-performance osmotic power generators. The prototype work of anion-selective subnanochannel membranes can be further extended to cation-selective ones by tailoring functionality chemistry of UiO-66 pores, which will be identified as our future work and can lead to a new discovery of ionic devices. The mechanical property of heterogeneous subnanochannel membranes is expected to be improved by introducing high tensile strength porous polymer membranes as substrate support (18). We will also attempt different types of MOF membranes and identify experimental conditions, which may offer ultrafast osmotic ion transport and high-efficiency blue energy conversion in seawater-simulated (NaCl) conditions.

**MATERIALS AND METHODS**

**Materials and chemicals**

The detailed information of all materials and chemicals is summarized as follows: aluminum foil (Al, 99.9995%; Strem Chemicals), oxalic acid (H$_2$C$_2$O$_4$, 99.8%; Showa), perchloric acid (HClO$_4$, 70%; Showa), chromium oxide (CrO$_3$, 99%; Showa), hydrochloric acid (HCl, 37%; Sigma-Aldrich), copper chloride (CuCl$_2$·2H$_2$O, 97%; Showa), phosphoric acid (H$_3$PO$_4$, 85%; Scharlau), 3-triethoxysilylpropylamine (APTES, ≥98%; Sigma-Aldrich), tolune (99.5%, JT Baker), zirconium (IV) chloride (ZrCl$_4$, 99.5+%-Zr; Strem Chemicals), N,N-dimethylformamide (DMF) (anhydrous, Macron), 2-ammonoterephthalic acid (BDC-NH$_2$, 99%; Sigma-Aldrich), benzoic acid (≥99.5%; TCI), sodium chloride (NaCl, 99%; Sigma-Aldrich), potassium chloride (KCl, 99%; JT Baker), potassium bromide (KBr, ≥99%; Honeywell Fluka), potassium nitrate (KNO$_3$, 99%; Alfa Aesar), and sodium sulfate (Na$_2$SO$_4$, 99%; Macron). Other solvents were purchased from ECHO Chemical Co. Ltd., Taiwan. All chemicals were used as provided. All aqueous solutions were prepared with deionized water (18.2 megohm-cm, Milli-Q).

**Preparation of NH$_2$-functionalized ANM support**

The ANM support with highly ordered straight channels was fabricated using the two-step anodization process as reported previously (8). First, a high-purity Al sheet was washed with acetone, ethanol, and water in sequence and then electrochemically polished with the HClO$_4$/ethanol solution (1:4 v/v) at 20 V for 90 s. The first anodization was carried out in 0.3 M oxalic acid under 50 V at 20°C for 30 min. Then, the disordered oxide layer was removed by the mixed solution (H$_2$PO$_4$/CrO$_3$/water) at 60°C for 1 hour. The second anodization was performed under the same condition of first anodization for 1 hour. To obtain a free-standing ANM support, the remaining aluminum was removed by the mixed solution (CuCl$_2$/HCl/water), followed by the etching of barrier layer carried out by 5 weight % (wt %) H$_2$PO$_4$ for 55 min at 30°C. Upon completion of the above steps, the ANM was then treated with APTES (0.02 M, in 40 ml of toluene) at 50°C for 3 hours under N$_2$ environment. After washing the modified ANM three times with toluene and ethanol, the membrane was cured in an oven at 110°C for 1 hour to ensure modification.

**Fabrication of UiO-66-NH$_2$@ANM**

First, a mixture of ZrCl$_4$ (0.116 g, 0.5 mmol), benzoic acid (5.06 g, 41.4 mmol), and DMF (30 ml) solution was stirred for 30 min in beaker. Then, the solution was transferred to 50-ml Teflon container and heated at 80°C for 2 hours. After cooling to room temperature,
membrane conductance was calculated at +1 V. For the output current density and redox potential, obtained by measuring the potential of the same formed with a Keithley 6487 picoammeter (Keithley Instruments, Cleveland, Ohio). A pair of Ag/AgCl electrodes was used, and the working electrode was placed in the compartment facing the UiO-66-NH$_2$ side for all measurements. For the analysis of ion transport, the I-V result was conducted in 0.01 M KCl solution by alternating an applied voltage bias between +1 and −1 V, and each cycle lasted for 6 min without break. The I-V results were recorded by changing the voltage between −2 and +2 V with 0.2-V steps, and the transmembrane conductance was calculated at +1 V. For the I-V curves in the osmotic energy conversion analyses, the contribution of the redox potential, obtained by measuring the potential of the same testing non-ion-selective micropore silicate wafer without UiO-66-NH$_2$@ANM, has been deducted. For the output current density and high-density nanoporous membrane measurement, an effective testing area of 0.03 mm$^2$ for ion transport was divided, consistent with previous studies (15, 42–44).

SUPPLEMENTARY MATERIALS
Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/7/10/eabe9924/DC1

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