

Supporting Information

Amphoteric Metal-Organic Framework Subnanochannels with pH-Tuneable Cation and Anion Sieving Properties

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Experimental Section

Chemicals

Lithium chloride (LiCl), potassium bromide (KBr), potassium iodide (KI), calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), formic acid (HCOOH), and 1,2,4-benzenetricarboxylic acid (BDC-COOH) were purchased from Sigma–Aldrich. 2-Aminoterephthalic acid (BDC-NH₂) was purchased from Alfa Aesar. Methanol, zirconium (IV) chloride (ZrCl_4), sodium chloride (NaCl), potassium chloride (KCl), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), potassium nitrate (KNO_3), potassium sulfate (K_2SO_4), acetic acid (CH_3COOH), hydrochloric acid (HCl) and sodium hydroxide (NaOH) were purchased from Merck. Ion-track polyethylene terephthalate (PET) membranes were purchased from GSI Helmholtz Centre (Darmstadt, Germany). Milli-Q water (18.2 M Ω cm) was used in the experiments and measurements.

Preparation of bullet-shaped PET subnanochannel (SNC) membranes

PET membranes (12 μm thick, with single or multiple ion tracks in the center) were simultaneously etched by 6 M NaOH + 0.025% sodium dodecyl diphenyloxide disulfonate from one side and 6 M NaOH from the other side at 60 °C to produce single or multiple bullet-shaped nanochannels. During the etching process of the single-channel membrane, voltage was applied across the membrane at 1 V using a picoammeter (Keithley 6487), and the current was observed via the picoammeter to monitor the etching process. When the current or etching time reached the required value, the etching process was terminated by adding a mixture of 1 M KCl and 1 M HCOOH aqueous solution to neutralize the alkaline etching solution. Then, the membrane was thoroughly washed with water. The morphologies, diameters, and cross sections of the nanochannels were observed using scanning electron microscopy (SEM) on multi-channel membranes (channel density 10⁸/cm²) prepared under the same etching conditions as single-channel membranes.

Preparation of PET-MOF nanochannel membranes by interfacial growth method

The PET nanochannel membrane was clamped into a home-made interfacial synthesis apparatus consisting of two cells. Metal ion solution and ligand solution were prepared and sonicated for 30 min, and then they were added to each side of cell. The details of the solution compounds are summarized in Table S1. Acetic acid (AA) was added in the synthesis of MOFs with mixed ligands to enhance the solubility of BDC-NH₂ in water.

Table S1. Compounds of solution for the preparation of PET-MOF nanochannels

MOFs	Metal ion solution		Ligand solution		
	ZrCl ₄	Solvent	BDC-NH ₂	BDC-COOH	Solvent
	(mg)	(10 mL)	(mg)	(mg)	(10 mL)
UiO-66-NH ₂	600	DMF	480	0	DMF
UiO-66-MIX1 (UiO-66-(NH ₂) _{0.75} (COOH) _{0.25})	600	Water/AA* = 4:1	360	135	Water/AA = 4:1
UiO-66-MIX2 (UiO-66-(NH ₂) _{0.5} (COOH) _{0.5})	600	Water/AA = 4:1	240	270	Water/AA = 4:1
UiO-66-MIX3 (UiO-66-(NH ₂) _{0.25} (COOH) _{0.75})	600	Water/AA = 4:1	120	405	Water/AA = 4:1
UiO-66-COOH	600	Water	0	541	Water

*AA= Acetic acid

The interfacial synthesis equipment was then sealed into a Teflon autoclave and heated in an oven at 100 °C for 48 h. After the autoclave cooled down, the PET-MOF nanochannel membranes with UiO-66-type MOFs were washed with water and kept in water at room temperature.

Preparation of UiO-66-type MOF nanocrystals

To prepare UiO-66-type MOF nanocrystals, the metal ion solution and ligand solution in Table S1 were simply mixed in a Teflon autoclave and kept stirred for 30 min. The Teflon autoclave was then sealed and heated in an oven at 100 °C for 48 h. After the autoclave cooled, the UiO-66-type MOF nanocrystals were washed with water and ethanol, and vacuum dried at 80 °C for 12 h.

Characterizations

X-ray diffraction (XRD) patterns were recorded in the 2θ range of 5–85° at room temperature using a Bruker D8 Advance A25 X-ray diffractometer operating under Cu K α radiation (40 kV, 40 mA) at a step size of 0.02° and a count time of 1.6 seconds per step. SEM images and energy-dispersive X-ray spectroscopy (EDX) analysis were taken with a field-emission scanning electron microscope (Zeiss Sigma, Germany, equipped with an Oxford Instruments 100 mm² SSD detector). The zeta potential of MOF crystals was determined using a Zetasizer (Malvern Panalytical). Nitrogen sorption isotherms at 77 K were obtained using a surface characterization analyzer (Micromeritics 3Flex), and the samples were degassed at 180 °C for 48 h prior to the measurements. Low pressure volumetric nitrogen adsorption isotherms up to 1 bar were measured with a Micromeritics 3Flex gas sorption analyzer. The BET surface area and pore size were determined using by measuring N₂ isotherms at 77 K in a liquid nitrogen bath and then using Micromeritics software for calculations. TGA analysis was tested by a Mettler Toledo TGA 2 system. The MOFs weighed in an alumina crucible were heated from 25 °C to 800 °C at 5 °C/min under an air purge at 50 mL/min. FTIR spectra were taken by FTIR Frontier spectrometer (Perkin Elmer).

Current measurement

The ionic transport properties of PET nanochannel membranes were studied using I-V curves. Ionic currents were measured with a Keithley 6517B picoammeter (Keithley Instruments, Cleveland) on two PTFE chambers, which were separated by a piece of PET nanochannel membrane. The two chambers were filled with chloride salt solutions at the same concentration. Ag/AgCl electrodes and Pt electrodes were used to apply a transmembrane potential across them for the testing of cation selective transport and anion selective transport, respectively. The transmembrane potential used in this work was scanned from -1 to $+1$ V. The pH of the electrolyte solutions was adjusted with 1 M HCl and 1 M KOH solutions. All pH values and current measurements in this work were taken at room temperature. In this work, each test was repeated at least three times to obtain the average current values at different voltages.

Ion selectivity based on ion currents

For quantitative comparison, the selectivity ratio (SR) of the mono-valance cation over the di-valance cation is calculated as the ratio of the respective current at the same transmembrane voltage (i.e., -1 or $+1$ V) according to equation (1) in consideration of the valence difference.

$$SR_{MCl/M^*Cl_2} = \left| \frac{I_{MCl}}{I_{M^*Cl_2}} \right| \cdot \frac{Z_{M^*}}{Z_M} \quad (1)$$

where I_{MCl} and $I_{M^*Cl_2}$ are the currents of mono-valance cation chloride electrolytes and di-valance cation chloride electrolytes, respectively, at the same concentration; Z_M and Z_{M^*} are the valence values of the mono-valance cations and di-valance cations, respectively.

Similarly, the selectivity ratio (SR) of the mono-valance anion over the di-valance anion is calculated as the ratio of the respective current at the same transmembrane voltage (i.e., -1 or $+1$ V) according to equation (2) in consideration of the valence difference.

$$SR_{KA/K_2B} = \left| \frac{I_{KA}}{I_{K_2B}} \right| \cdot \frac{Z_B}{Z_A} \quad (2)$$

where I_{KA} and I_{K_2B} are the currents of potassium mono-valence anion electrolytes and potassium di-valence anion electrolytes, respectively, at the same concentration; Z_A and Z_B are the valence values of the mono-valence anions and di-valence anions, respectively.

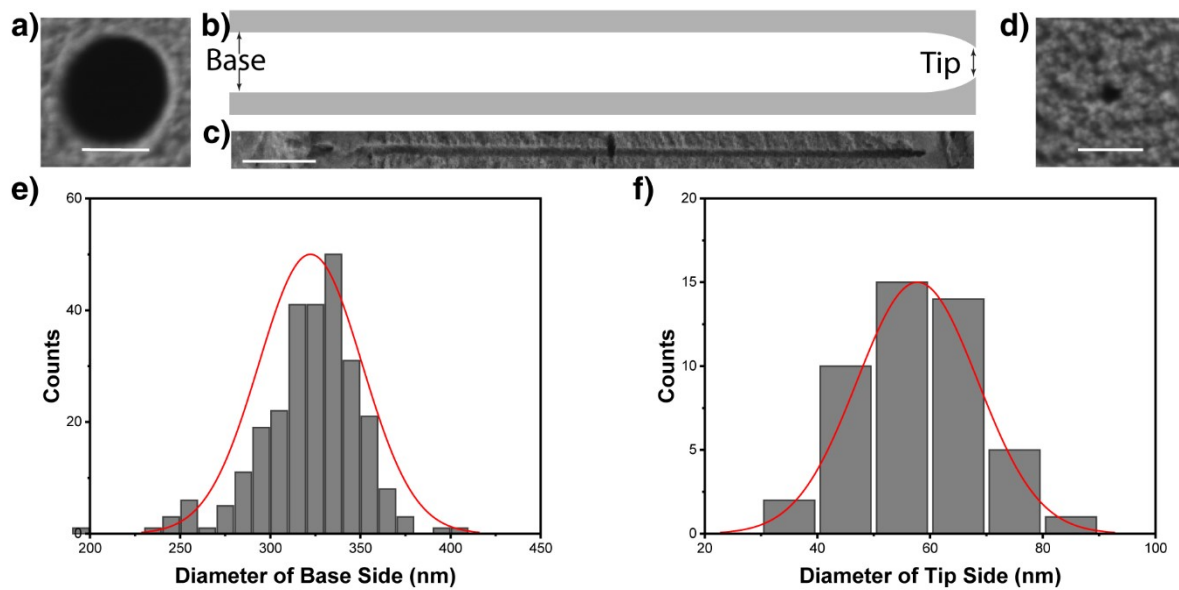


Fig. S1 Characterization of bullet-shape channel through PET membrane. a) SEM image of the base side. Scale bar is 200 nm. b) Scheme of cross section. c) SEM image of cross section. Scale bar is 1 μ m. d) SEM image of the tip side. Scale bar is 200 nm. e,f) Diameter distributions of (e) base side and (f) tip side with average values of 322.3 ± 28.7 nm and 57.8 ± 10.7 nm, respectively.

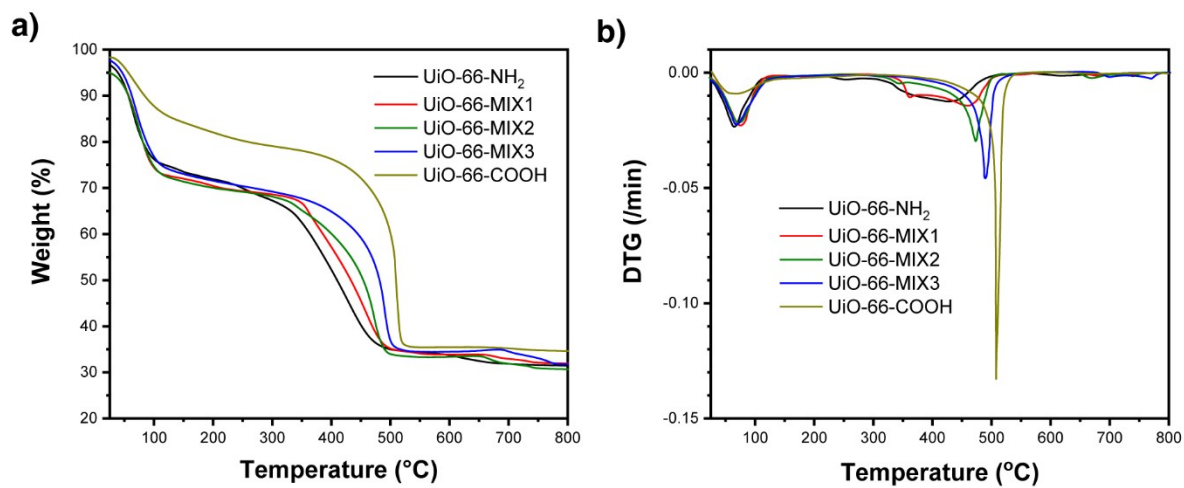


Fig. S2 TGA-DTG curves of UiO-66-X MOFs.

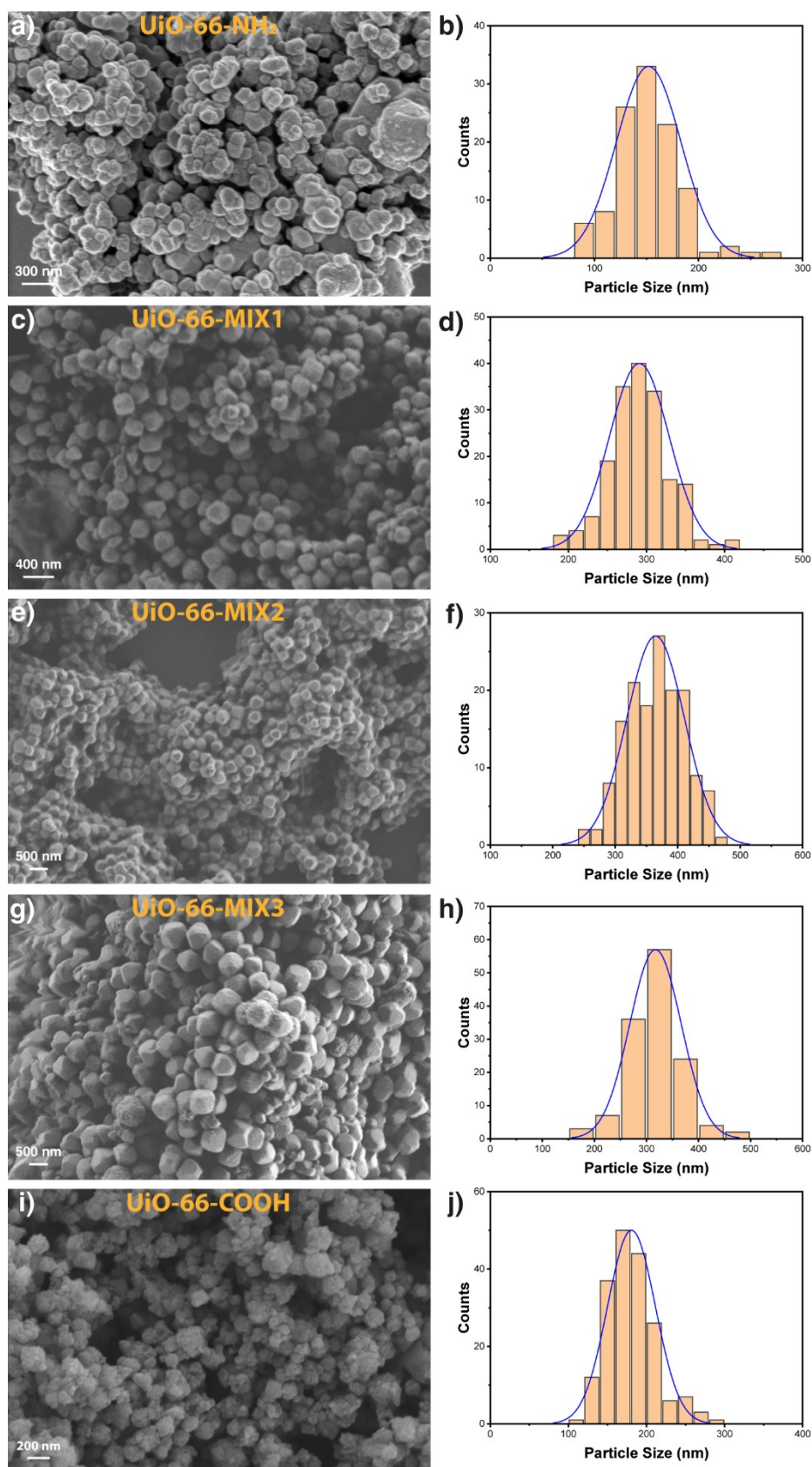


Fig. S3 SEM images (left) and size distributions (right) of UiO-66-NH₂, UiO-66-MIX1, UiO-66-MIX2, UiO-66-MIX3, UiO-66-COOH seeds, respectively. The mean sizes of UiO-66-NH₂,

UiO-66-MIX1, UiO-66-MIX2, UiO-66-MIX3, UiO-66-COOH seeds are 152.1 ± 31.0 nm, 290.1 ± 38.3 nm, 364.7 ± 46.2 nm, 317.3 ± 49.5 nm, and 180.8 ± 30.7 nm, respectively.

Table S2. EDS mapping images of UiO-66-X MOFs seeds

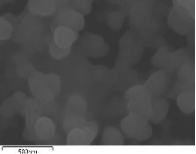
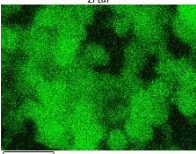
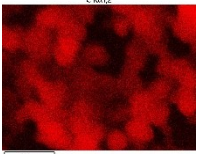
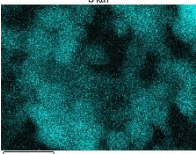
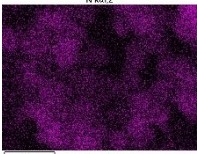
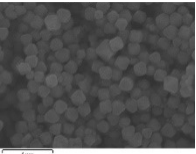
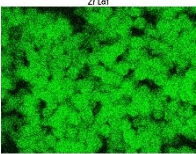
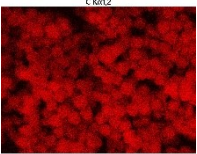
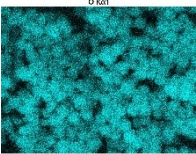
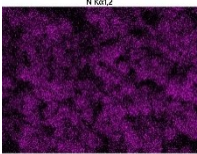
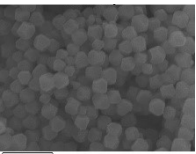
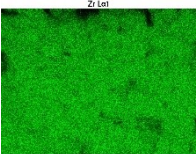
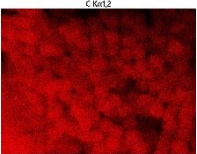
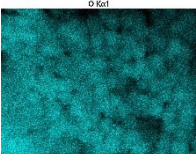
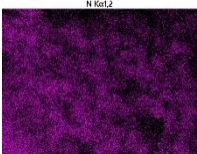
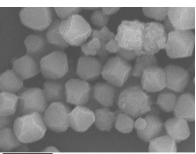
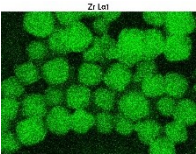
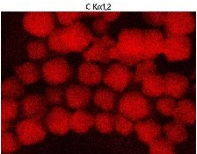
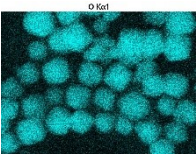
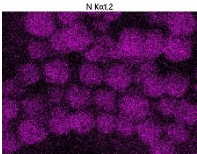
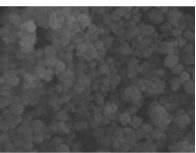
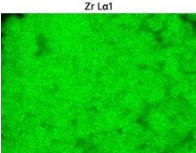
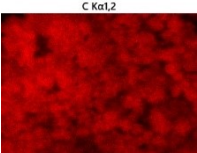
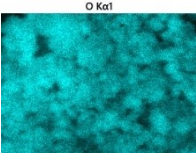
MOF	SEM	Zr	C	O	N
UiO-66-NH ₂					
UiO-66-MIX1					
UiO-66-MIX2					
UiO-66-MIX3					
UiO-66-COOH					N/A

Table S3. BET surface areas of UiO-66-X MOFs

MOFs	S_{BET} ($\text{m}^2 \text{g}^{-1}$)
UiO-66-NH ₂	745.5
UiO-66-MIX1	959.5
UiO-66-MIX2	860.6
UiO-66-MIX3	527.6
UiO-66-COOH	366.1

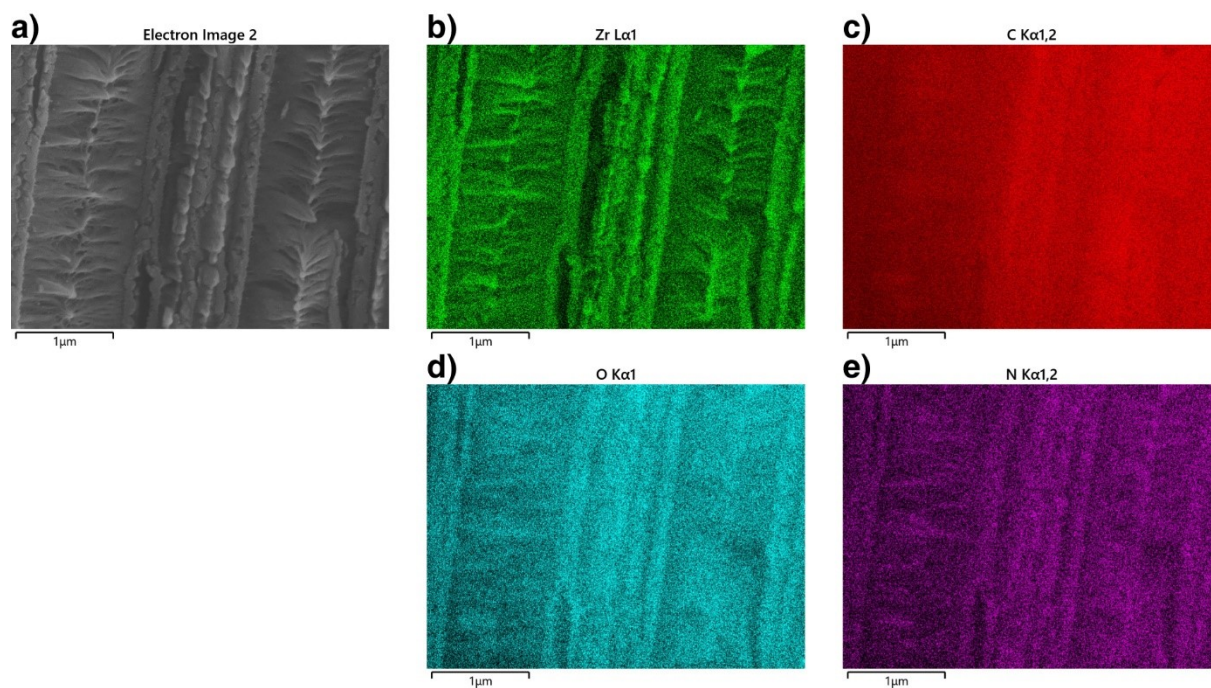


Fig. S4 EDX mapping of the cross section of PET-UiO-66-NH₂ multichannel membranes.

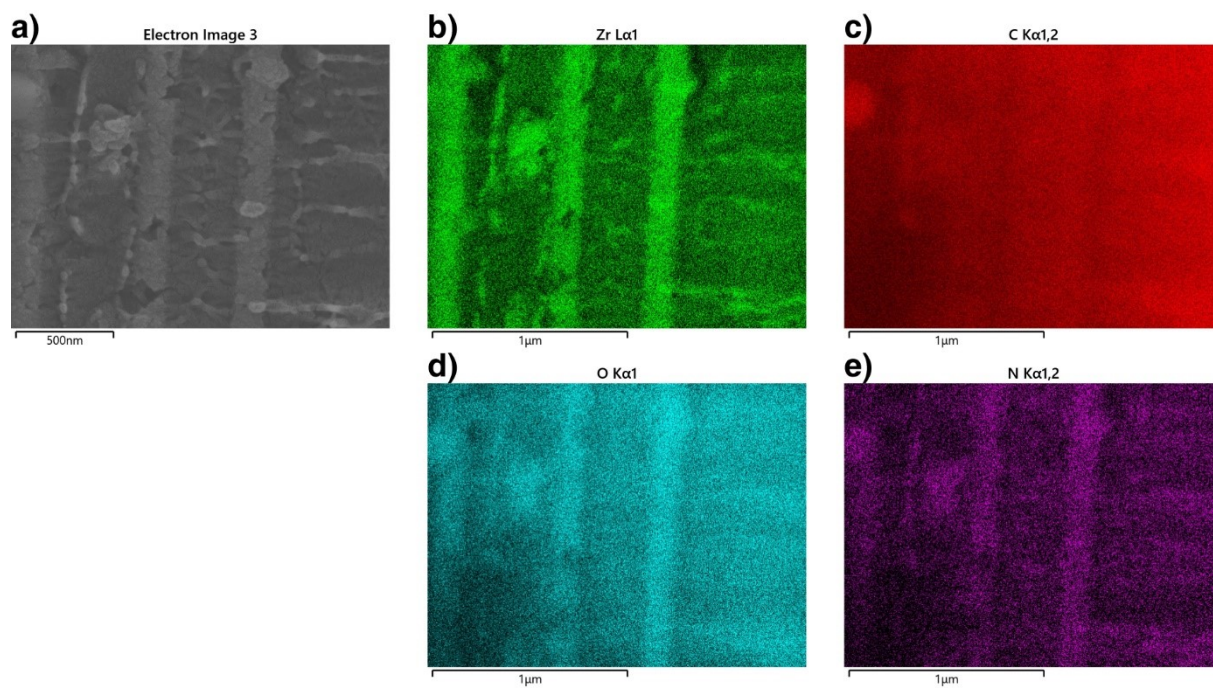


Fig. S5 EDX mapping of the cross section of PET-UiO-66-MIX1 multichannel membranes.

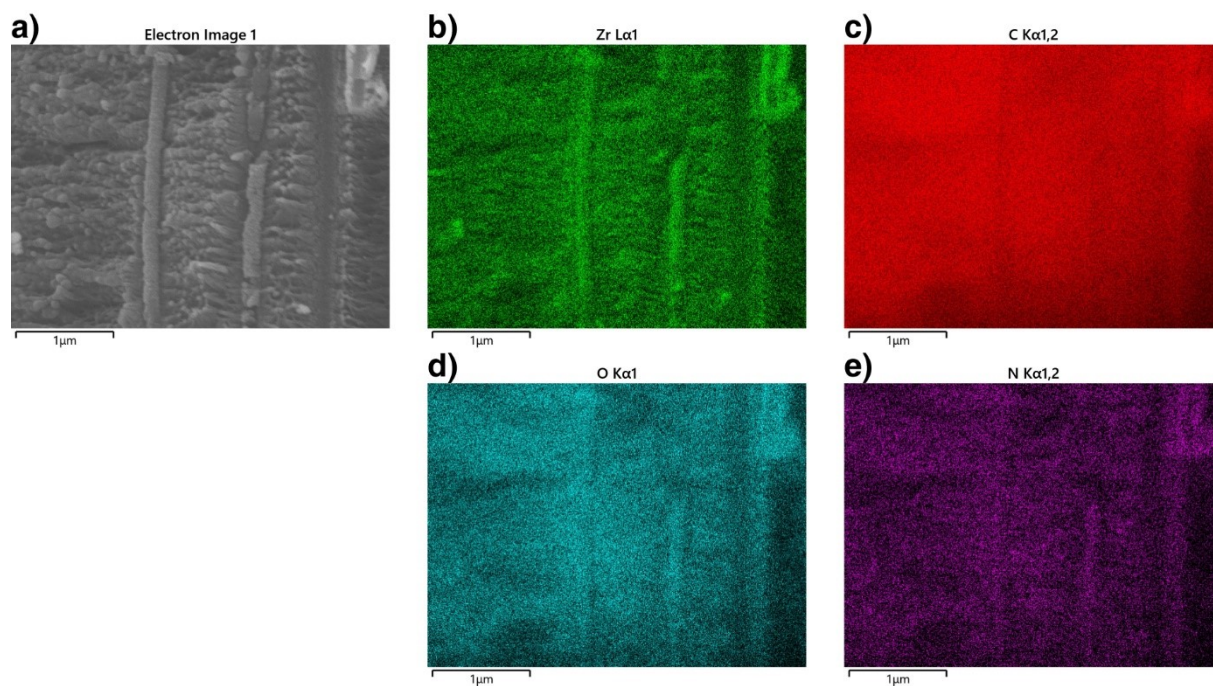


Fig. S6 EDX mapping of the cross section of PET-UiO-66-MIX2 multichannel membranes.

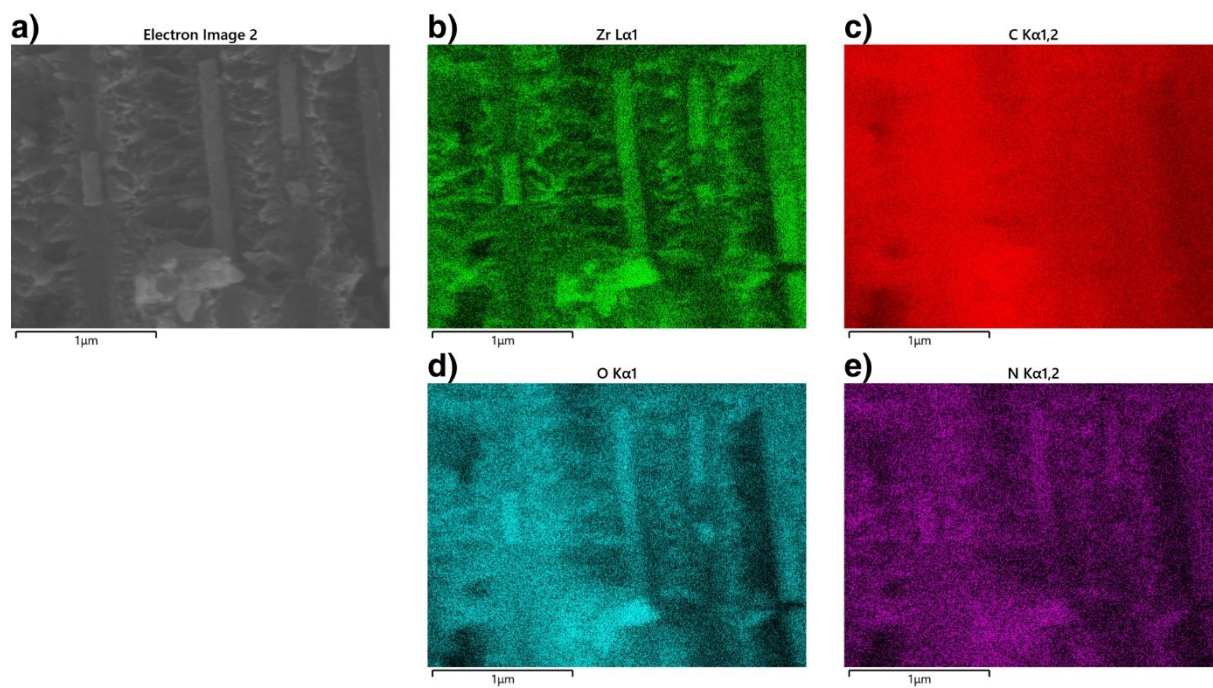


Fig. S7 EDX mapping of the cross section of PET-UiO-66-MIX3 multichannel membranes.

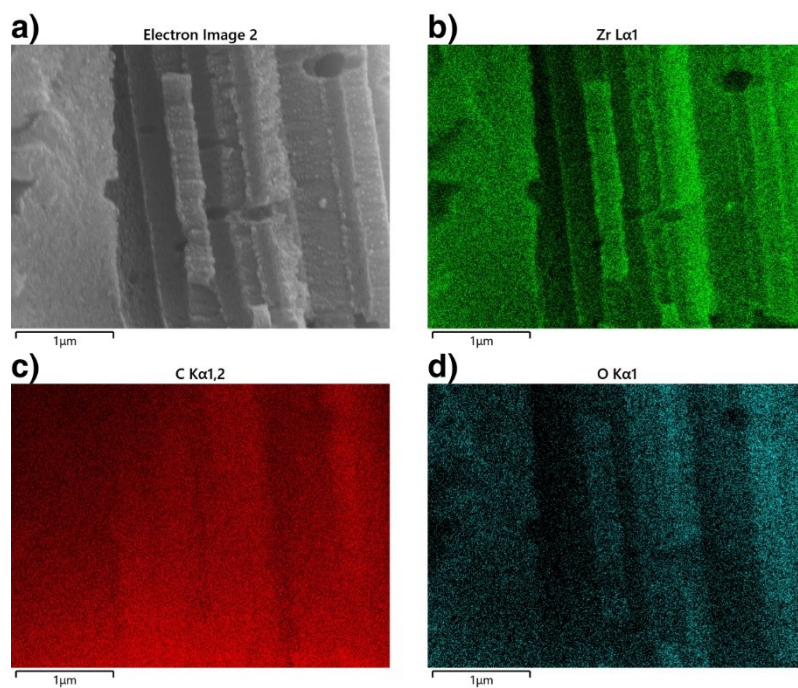


Fig. S8 EDX mapping of the cross section of PET-UiO-66-COOH multichannel membranes.

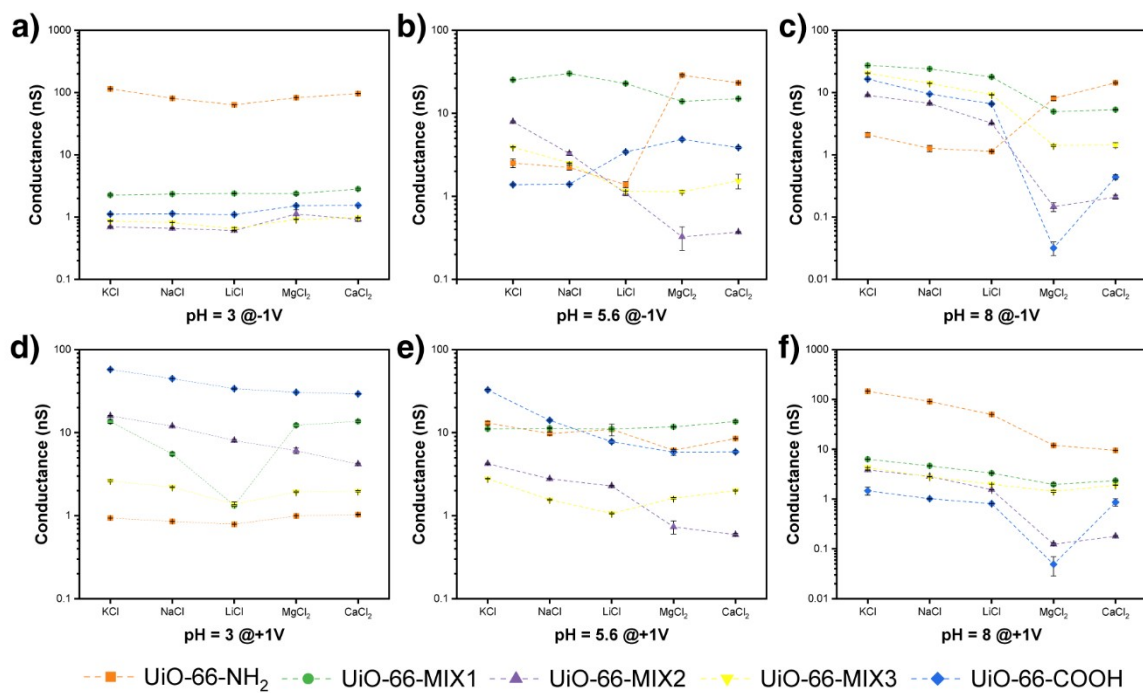


Fig. S9 Ionic conductances of PET-SNC with UiO-66-X MOFs measured in 0.1 M salt solutions (KCl, NaCl, LiCl, MgCl₂ and CaCl₂) at -1 V (a-c) and +1 V (d-f) under different pH values (pH = 3, 5.6 and 8).

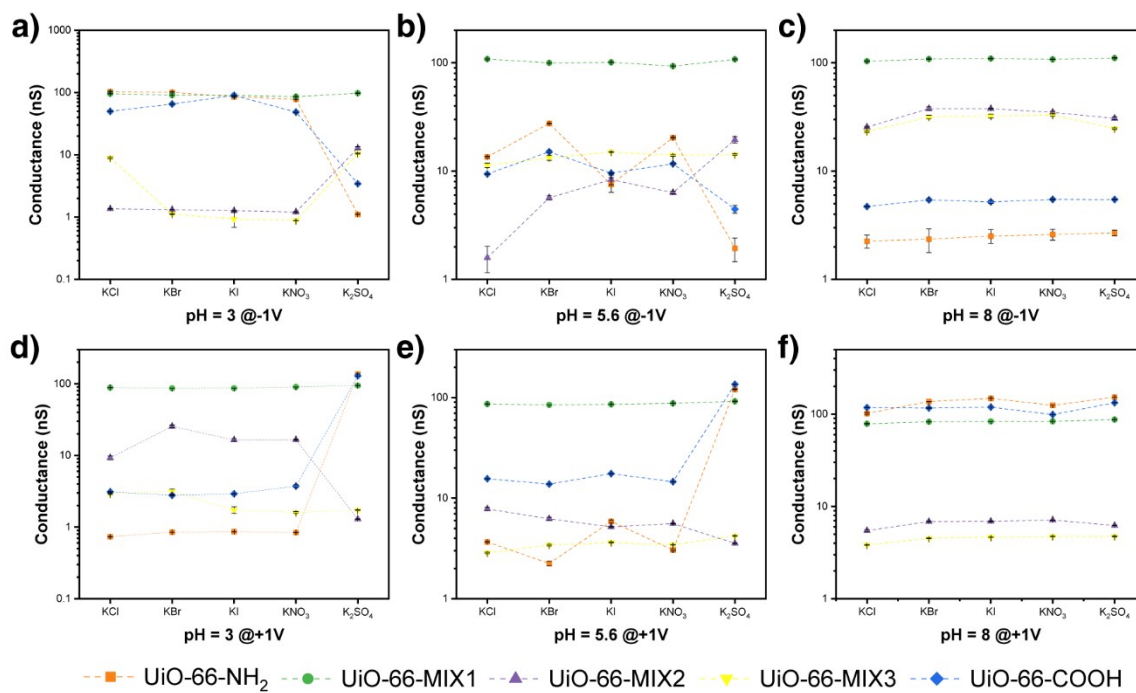


Fig. S10 Ionic conductances of PET-SNC with UiO-66-X MOFs measured in 0.1 M salt solutions (KCl, KBr, KI, KNO₃ and K₂SO₄) at -1 V (a-c) and +1 V (d-f) under different pH values (pH = 3, 5.6 and 8).

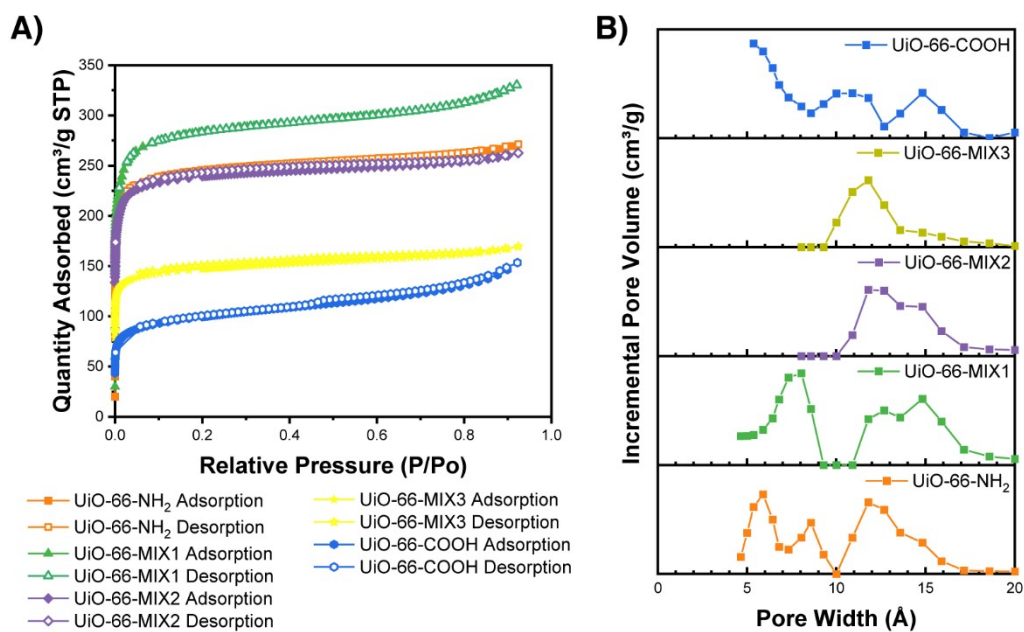


Fig. S11 A) Nitrogen gas adsorption isotherms and B) size distributions of UiO-66-X powders.

Table S4. Zeta potentials of UiO-66-X at various pH values

MOF	Zeta Potential (mV)		
	pH = 3	pH = 5.6	pH = 8
UiO-66-NH ₂	21.43 ± 1.05	-12.57 ± 0.58	-19.53 ± 0.33
UiO-66-MIX1	43.07 ± 0.94	-3.80 ± 0.40	-18.07 ± 1.30
UiO-66-MIX2	14.20 ± 0.16	-19.17 ± 1.03	-31.77 ± 0.21
UiO-66-MIX3	10.26 ± 0.71	-25.17 ± 1.25	-34.10 ± 0.57
UiO-66-COOH	8.65 ± 0.44	-22.93 ± 0.87	-27.53 ± 1.30

The UiO-66-X crystals were dispersed in water, and the concentration of the powder was ~ 0.05 mg mL⁻¹.

Table S5. Dehydrated/Hydrated Diameters of Ions¹

Ion	Dehydrated Diameter (Å)	Hydrated Diameter (Å)	Hydration enthalpy (KJ mol⁻¹)
K ⁺	2.66	6.62	-330
Na ⁺	1.90	7.16	-365
Li ⁺	1.20	7.64	-530
Mg ²⁺	1.30	8.56	-1945
Ca ²⁺	1.98	8.24	-1600
Cl ⁻	3.62	6.64	-365
Br ⁻	3.90	6.60	-335
I ⁻	4.32	6.62	-290
NO ₃ ⁻	5.28	6.70	-310
SO ₄ ²⁻	5.80	7.58	-1035

1. Y. Marcus, *Biophys. Chem.*, 1994, **51**, 111-127.