

Electronic Supporting Information

Defect-engineered UiO-66-NH₂ modified thin film nanocomposite membrane with enhanced nanofiltration performance

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1. Experimental Section

Materials: Trimesoyl chloride (TMC), (+)-10-camphorsulfonic acid (CSA), zirconium chloride ($ZrCl_4$), N,N-dimethylformamide (DMF), 1,4-benzenedi-carboxylic acid (H_2BDC), 2-aminoterephthalic acid ($BDC-NH_2$), benzoic acid (HBC), acetic acid (HAc), ethanol, methanol, hydrochloric acid (HCl), sodium hydroxide (NaOH), nitric acid (HNO_3) and sodium sulfate (Na_2SO_4) were ordered from Aladdin Co., Ltd (China). Diethylene glycol, Triethylene glycol, glucose, D(+)-Sucrose, raffinose and α -cyclodextrin used for MWCO tests were received from Shanghai Macklin Biochemical Technology Co., Ltd. (China), Ltd. Triethylamine (TEA) and n-hexane were obtained from Sinopharm Chemical Reagent Co., Ltd. (China). Piperazine (PIP) was supplied by J&K Chemical Reagent Co., Ltd. (China). Commercial polysulfone ultrafiltration membrane (PSF, MWCO = 20 kDa) was supplied by RisingSun Membrane Technology Co., Ltd. (China). Deionized (DI) water was produced by a water purifier of Millipore. All aforesaid chemicals applied in this work received no further purification before use.

Synthesis of nanofillers: UiO-66 was synthesized by dissolving 1 mM $ZrCl_4$, 1 mM H_2BDC and 1 mL HAc into 30 mL DMF solution. The reaction was maintained in a Teflon reactor at 120°C for 24 h. After cooled to room temperature, the products were centrifuged at 10000 rpm for 5 min and washed with methanol 3 times. The resulting powder was dried at 60°C for 24 h. Synthesis procedure and recipes of UiO-66- NH_2 were similar to the process of UiO-66 except for the replacement of 1 mM H_2BDC to 1 mM $BDC-NH_2$.

Specifically, D-UiO-66- NH_2 was prepared through a defect engineering method of modulator control and post acid treatment. 0.5 mM $ZrCl_4$, 1 mM $BDC-NH_2$, 15 mM HBC and 1 mL HAc were dissolved into 20 mL DMF solution. The products were obtained by transferring the mixture into a Teflon reactor at 120°C for 24 h before centrifuged at 10000 rpm and washed with methanol. Then the solids were treated by 1 M HCl (10 mL) for 30 min to activate the defects D-UiO-66- NH_2 . After centrifugation, the yellow brown products were washed with DI water, DMF, and methanol before dried at 60°C for 24 h. Due to the similarity of the coordination mode, excess ligands of HBC will compete with the origin ligands of 2-aminoterephthalic acid ($BDC-NH_2$) during the formation of D-UiO-66- NH_2 .

However, the benzoate (BC) can only connect with one Zr_6 cluster, which is more vulnerable when facing the attack of acid, resulting in a higher tendency to break away from the frameworks under the HCl treatment and induce missing-linker defects.

Preparation of membranes: The TFC and TFN membranes were prepared using a classical interfacial polymerization (IP) method on commercial polysulfone ultrafiltration membrane. The PSF substrate was immersed in the DI water all night to remove the impurities before membrane fabrication. The membrane was rolled to wipe off the water on the surface and dried in the air for 2 min before saturated by a water solution containing 0.35 wt% PIP, 1 wt% CSA, and 2% (v/v) TEA for 2 min. After poured out the superfluous water solution, the membrane was rolled again and dried in the air for another 2 min. Then 0.1 wt% TMC/n-hexane organic solution was added onto the surface to react with PIP for 60 s. The obtained membrane was heated at 60°C for 15 min and stored in DI water. The modified TFN nanofiltration membranes were fabricated by dispersing 0.012 wt% of UiO-66, UiO-66-NH₂ and D-UiO-66-NH₂ into the TMC/n-hexane solution. The corresponding TFN membranes were labeled as TFN-U, TFN-UN and TFN-DUN, respectively.

Characterization: The chemical properties of these nanofillers were verified by Fourier transform infrared spectroscopy (FTIR, Thermo Scientific Nicolet iS5, USA). The dispersibilities and particle sizes of UiO-66, UiO-66-NH₂ and D-UiO-66-NH₂ were analyzed by dynamic light scattering analysis (DLS, Brookhaven ZetaPALS, USA). Besides, to investigate the crystal characteristics of the synthesized nanofillers, X-ray diffraction powder pattern (XRD, Bruker AXS D8, Germany) was employed. The thermo gravimetric analyses of the UiO-66, UiO-66-NH₂ and D-UiO-66-NH₂ were compared using a thermal gravimetric analyzer (TGA, SDT Q600, USA). The samples were heated to 1000°C at the rate of 3°C/min and under air atmosphere. The nitrogen adsorption/desorption isotherms of the nanofillers were plotted by Micromeritics (ASAP-2020, USA). The nanofillers were outgassed at 100°C for 8 h before analysis. Zeta potentials of the nanofillers were obtained by a zeta potential analyzer (Brookhaven ZetaPALS, USA) with the pH ranging from 3 to 10. The averages were taken from three repeated measurements. The morphologies of the nanofillers and membranes

were observed by field emission scanning electron microscope (FESEM, FEI Quanta 250F, USA). To explore the membrane hydrophilicity, water contact angles (WCA, Krüss DSA30, Germany) of the membranes were measured. The roughnesses of the TFC and TFN membranes were analyzed by an atomic force microscopy (AFM, Bruker MultiMode8, Germany) in areas of 4 square microns. Surface charges of the membranes were measured by a zeta potential analyzer (Anton Paar SurPASS 3, Austria) with the pH ranging from 3 to 10. The elementary compositions of the membranes were investigated using an X-ray photoelectron spectroscopy (XPS, PHI Quantera II, Japan). The salt concentration was determined using a conductance meter (INESA DDSJ 308A, China). The loadings of MOFs on membranes were calculated by electron-coupled plasma atomic emission spectrometry (ICP-AES, Optima 7000 DV, USA). The results and calculations were presented in Table S3, ESI†. The nanofillers and membranes were digested by NaOH and HNO₃.

Filtration and separation tests: The nanofiltration performances of the membranes were measured using a lab-scale cross-flow model with the feed solution of 1 g/L Na₂SO₄ under 4 bar at ambient temperature. The flow rate was 4.8 L/min using a diaphragm pump (SF-52848-800P, China). The effective filtration area of the membrane was 12.56 cm². Before tested with the feed solution, membrane coupons were pre-pressurized using DI water under 10 bar for 30 min to stabilize the membrane permeance. The permeance (P, LMH/bar) and rejection (R, %) are calculated by following equations:

$$P = \frac{V}{S \times \Delta t \times (\Delta p - \Delta \pi)} \quad (1)$$

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (2)$$

where S (m²), Δt (h), Δp (bar), Δπ (bar), V (L), C_p (g/L) and C_f (g/L) are corresponding to the effective filtration area of the membrane, filtration time, pressure difference across the membrane, osmotic pressure difference, permeated water volume, solute concentrations in the permeate and the feed solutions, respectively. The molecular weight cut-offs (MWCOs) of prepared membranes were tested with 1 g/L of diethylene glycol (MW= 62.07 Da), triethylene glycol (MW= 150.17 Da), glucose (MW= 180.16 Da), d(+)-Sucrose (MW= 342

Da), raffinose (MW= 504 Da) and α -cyclodextrin (MW= 972 Da). The concentrations of these organics in permeate and feed solution were measured by a total organic carbon analyzer (TOC-VCSH, Shimadzu, Japan). The MWCOs of our membranes were corresponding to the molecular weight of 90% rejection. The calculation of rejection was the same as equation (2).

2. Figures and Tables

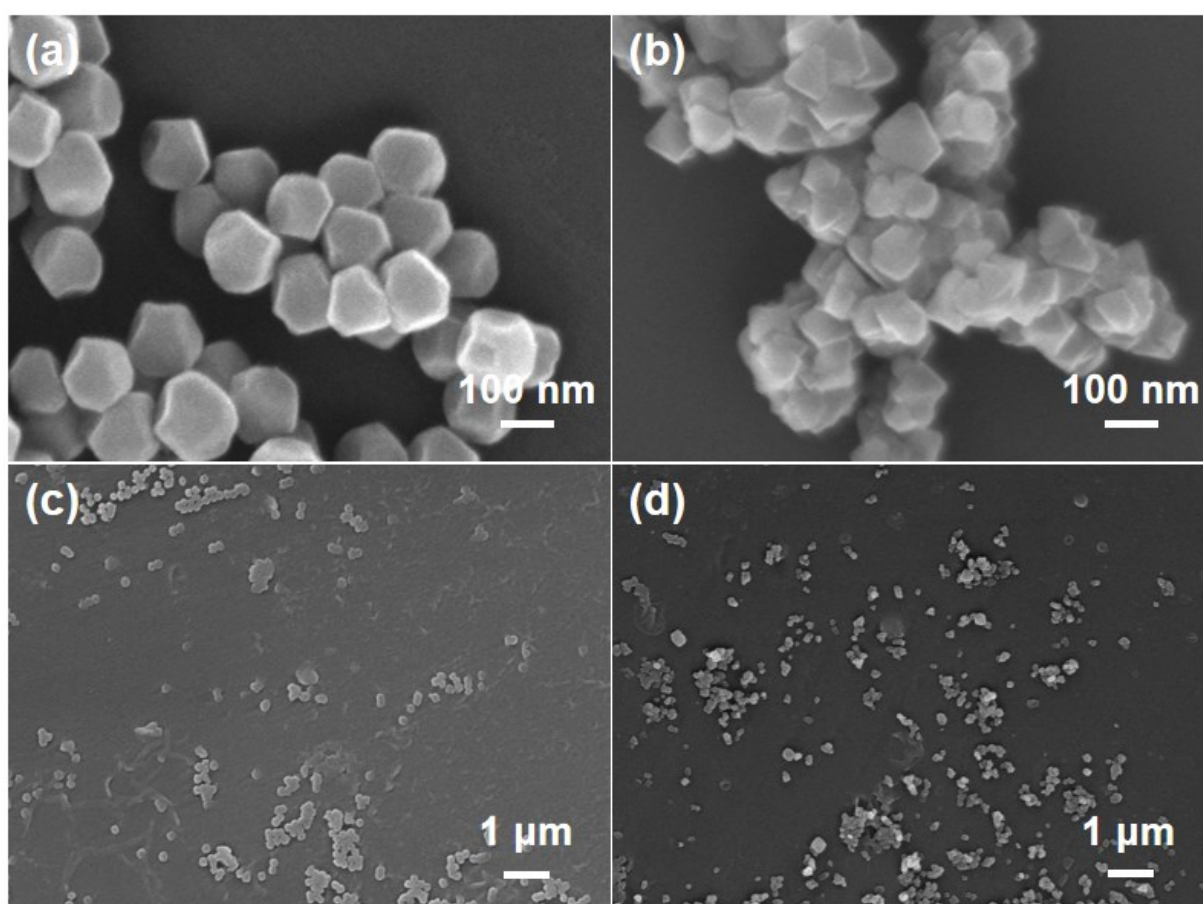


Fig. S1. SEM images of (a) UiO-66; (b) UiO-66-NH₂; (c) surface morphology of TFN-U; (d) surface morphology of the TFN-UN membrane

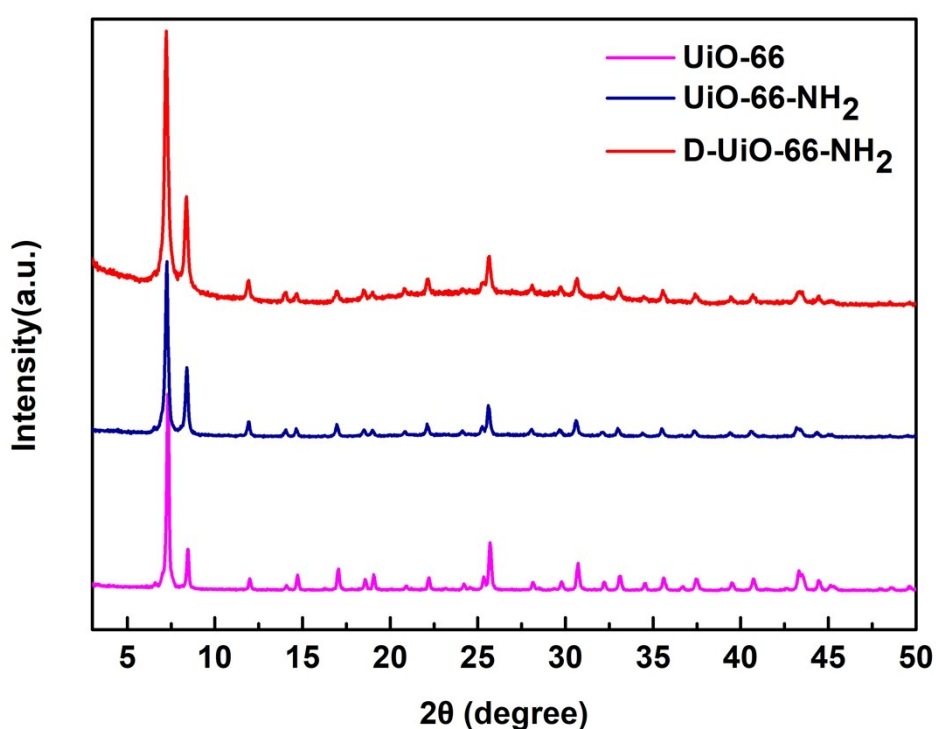


Fig. S2. PXRD patterns of UiO-66, UiO-66-NH₂, and D-UiO-66-NH₂

XRD results were investigated to confirm the crystallinity of synthesized nanofillers. Obviously, characteristic peaks at 7.36°, 8.48°, 17.08°, 25.68° and 33.12°, corresponding to the (111), (002), (004), (224), and (137) crystal planes of the UiO-66 type MOF, were appeared in all patterns, illustrating that the crystallization of D-UiO-66-NH₂ is well maintained after activated by HCl.

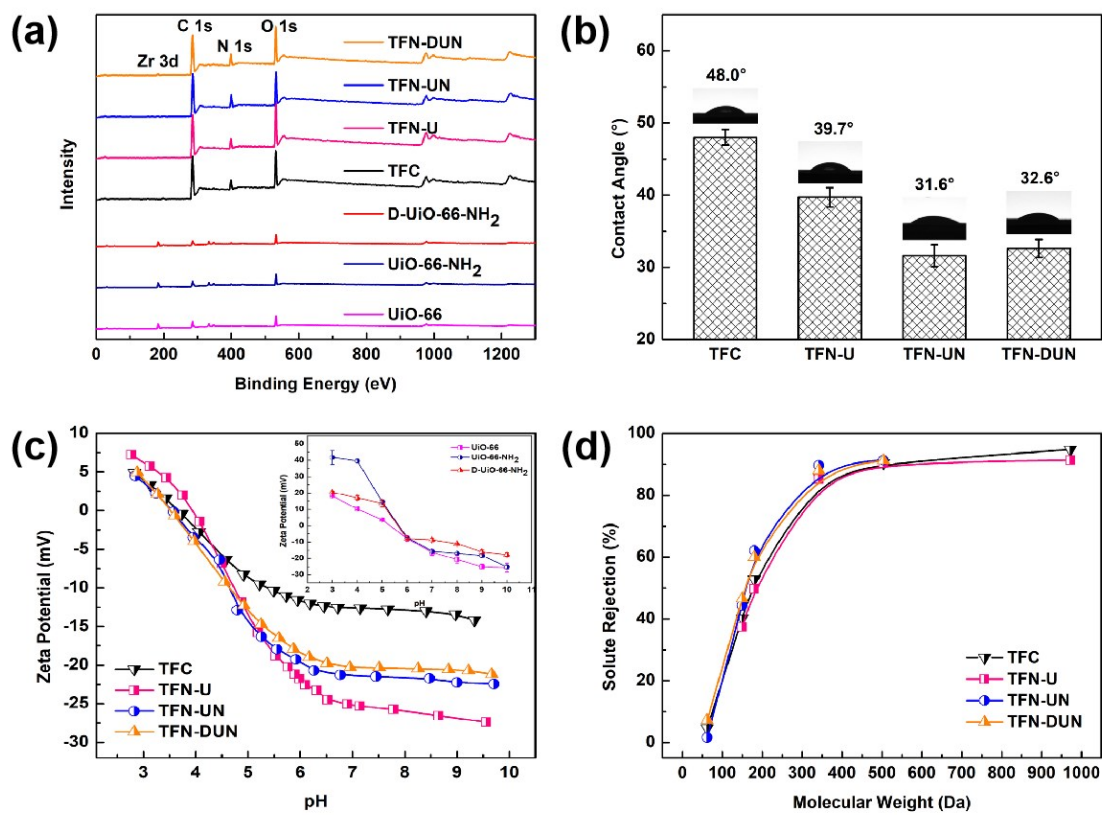


Fig. S3. (a) XPS results of nanofillers and membranes; (b) WCAs of membranes; (c) Zeta potential results of membranes and nanofillers (inset); (d) MWCOCs of membranes.

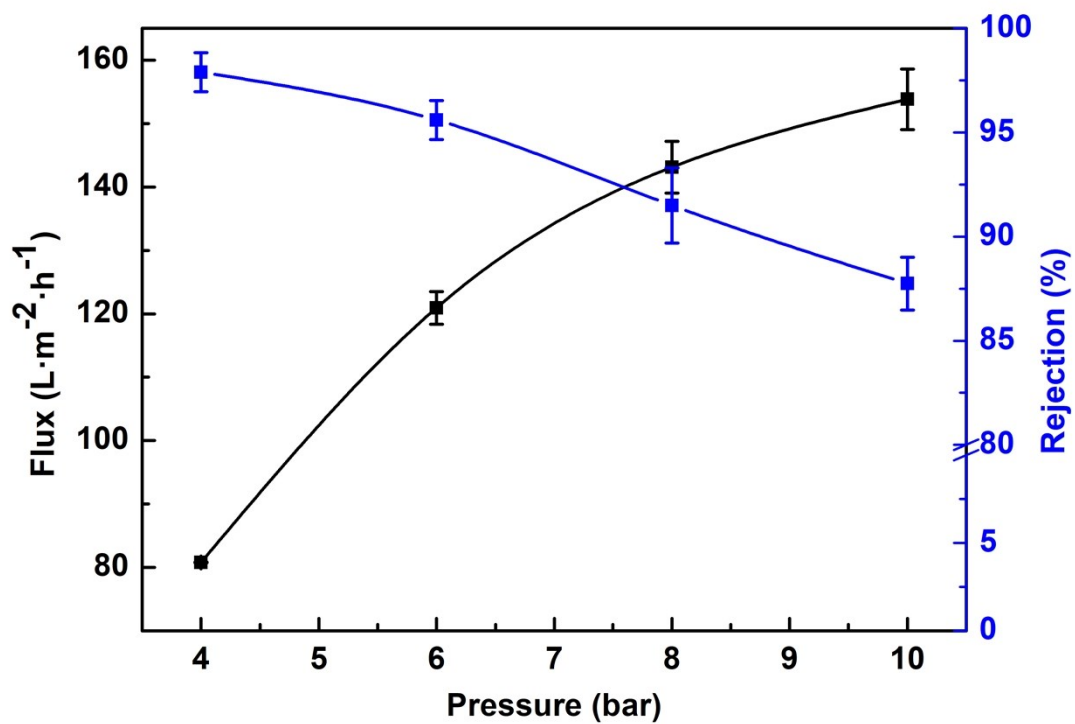


Fig. S4. Performances of TFN-DUN under various pressures

Owing to the concentration polarization phenomenon, the flux of TFN-DUN gradually levels off. Meanwhile, the rejection of TFN-DUN decreases with the increase of the operating pressure.

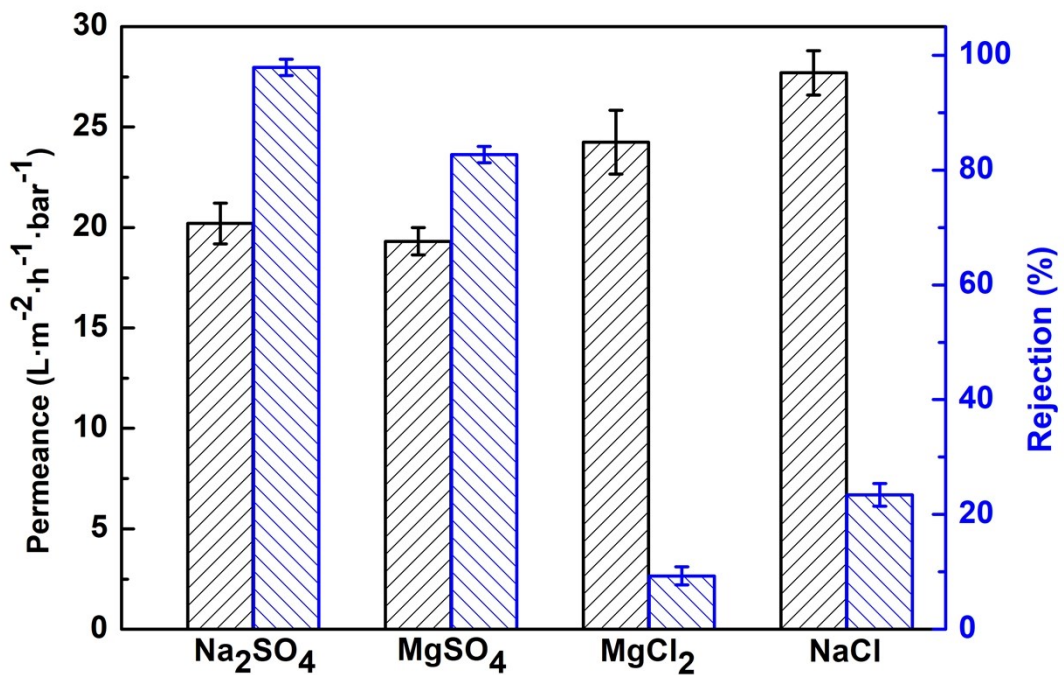


Fig. S5. Performances of TFN-DUN toward various salts

The size of the hydrated Cl^- is smaller than that of the hydrated SO_4^{2-} , therefore, the rejections of TFN-DUN to Na_2SO_4 and MgSO_4 are higher than to MgCl_2 and NaCl . In addition, the rejection to MgCl_2 is the lowest, because Mg^{2+} is more positive charged than Na^+ , leading to the unfavorable charge repulsive force between the negatively charged membrane and the salts.

Table S1 Specific surface areas and total pore volumes of nanofillers

Sample	Specific surface area (m²/g)	Total pore volume (cm³/g)
UiO-66	947	0.40
UiO-66-NH₂	877	0.49
D-UiO-66-NH₂	1217	0.62

Table S2. XPS results of TFC, TFN-U, TFN-UN and TFN-DUN layer composition

Sample	TFC	TFN-U	TFN-UN	TFN-DUN
C	68.51	66.58	67.45	62.54
N	11.60	10.80	11.67	11.08
O	19.86	20.88	19.53	18.44
C/N	5.91	6.16	5.78	5.65
O/N	1.71	1.93	1.67	1.66

The percentages of C, N and O from nanofillers were excluded.

Table S3. Loading amounts of MOFs in TFN-U, TFN-UN and TFN-DUN

Sample	Content of Zr (mg/mg)	Sample	Content of Zr (mg/cm²)	Loading of MOFs (mg/cm²)
UiO-66	0.3261	TFN-U	0.0139375	0.0427
UiO-66-NH₂	0.3126	TFN-UN	0.0136875	0.0438
D-UiO-66-NH₂	0.3298	TFN-DUN	0.014125	0.0428

The loading amounts of MOFs can be mirrored by the content of Zr element in the membrane. Hence, digestion experiments were adopted for dissolving Zr in the unite area of various membranes. It can be observed from Table S3 that loading amounts of different UiO-66 type MOFs in various membranes are quite similar.