Metal-organic framework enables ultraselective polyamide membrane for desalination and water reuse

Yue Wen†, Ruobin Dai†, Xuesong Li†, Xingran Zhang†, Xingzhong Cao2, Zhichao Wu†, Shihong Lin3*, Chuyang Y. Tang4*, Zhiwei Wang†

While reverse osmosis (RO) is the leading technology to address the global challenge of water scarcity through desalination and potable reuse of wastewater, current RO membranes fall short in rejecting certain harmful constituents from seawater (e.g., boron) and wastewater (e.g., N-nitrosodimethylamine (NDMA)). In this study, we develop an ultraselective polyamide (PA) membrane by enhancing interfacial polymerization with amphiphilic metal-organic framework (MOF) nanoflakes. These MOF nanoflakes horizontally align at the water/hexane interface to accelerate the transport of diamine monomers across the interface and retain gas bubbles and heat of the reaction in the interfacial reaction zone. These mechanisms synergistically lead to the formation of a crumpled and ultrathin PA nanofilm with an intrinsic thickness of ~5 nm and a high cross-linking degree of ~98%. The resulting PA membrane delivers exceptional desalination performance that is beyond the existing upper bound of permeselectivity and exhibited very high rejection (>90%) of boron and NDMA unmatched by state-of-the-art RO membranes.

INTRODUCTION

The escalating global water shortage motivates sustainable water resource management for supplying clean, safe, and adequate water (1, 2). To date, reverse osmosis (RO) has become a leading technology to address the severe shortages in fresh water supply through desalination and wastewater reuse (3, 4). Although existing polyamide (PA) RO membranes exhibit high water-salt selectivity with salt rejection beyond 99% (for seawater desalination), they remain inadequate in removing certain harmful and regulated constituents from seawater and wastewater (5, 6).

For example, N-nitrosodimethylamine (NDMA), a carcinogenic disinfection by-product commonly found in the RO permeate of wastewater reuse plants (7), is regulated in California with a stringent action level as low as 10 parts per trillion (8). As commercial RO membranes show unsatisfactory rejection of NDMA [30 to 80% for laboratory-scale tests (9–11) and merely 5 to 60% for pilot- to full-scale systems (12)], energy-intensive advanced oxidation processes are required to destroy NDMA in RO permeates (13, 14). The poor rejection of NDMA is attributed to its small molecular weight (74 g mol⁻¹) and uncharged state at neutral pH (13, 15). Another challenge faced by commercial RO membranes in seawater desalination is the inadequate removal of boron, which is charge neutral [as B(OH)₃ at neutral pH] with a small molecular weight of 61.8 g mol⁻¹. Because of the low boron rejection (approximately 40 to 80%) by commercial RO membranes (16, 17), the desalinated permeate often requires an additional second-pass RO treatment, which increases the cost, energy consumption, and footprint of seawater desalination plants. The poor rejection of these important species by commercial RO membranes calls for the development of ultraselective RO membranes for more cost-effective seawater desalination and wastewater reuse.

As steric hindrance plays a critical role in solute rejection by RO membranes (10, 11), efforts have been dedicated to reducing the free volume of the PA active layers (5, 18). However, these approaches for improving of solute rejection sacrifice water permeance (5, 9, 19). While other efforts to fabricate more selective membranes have been attempted beyond the PA framework, such as incorporating porous nanomaterials (20, 21), stacking two-dimensional (2D) nanoflakes (22, 23), and integrating biomimetic nanochannels (1, 24, 25), no study has, thus far, reported the production of a defect-free membrane that effectively rejects small neutral solutes, such as NDMA and boron, without compromised water permeance.

The performance of the thin-film composite (TFC) RO membrane is primarily dependent on the properties of the PA active layer (26), which is fabricated via an interfacial polymerization (IP) reaction between an amine monomer, e.g., m-phenylenediamine (MPD), and an acyl chloride monomer, e.g., trimesoyl chloride (TMC) (27). As the IP process involves extremely fast and uncontrolled reaction at the water/oil interface (28), achieving desired PA properties toward both fast water transport and outstanding solute rejection remains technically challenging.

Amphiphilic nanoflakes with highly asymmetric surface wettability (29, 30) have garnered considerable attention in drug delivery (31), catalysis (32), and oil recovery (33). Inspired by their great potential in interfacial properties regulation (34), here, we develop an ultraselective PA RO membrane by enhancing the IP process at the interface to create a crumpled, free-standing, and ultrathin nanofilm with an intrinsic thickness (δₘₜ) of ~5 nm and a high cross-linking degree of ~98%. The amphiphilic metal-organic framework (MOF) nanoflakes self-assemble at the water/hexane interface and regulate the heat dissipation and the interfacial transport of MPD monomers during IP (Fig. 1B). This process, namely, MOF assembly regulated IP (MARIP), results in an ultrathin PA nanofilm with unprecedentedly high rejections of NDMA (90.3 ± 0.4%) and boron (94.2 ± 0.2% at pH 8).

1State Key Laboratory of Pollution Control and Resource Reuse, Shanghai Institute of Pollution Control and Ecological Security, School of Environmental Science and Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, China. 2Department of Civil and Environmental Engineering, Vanderbilt University, Nashville, TN 37235-1831, USA. 3Department of Civil Engineering, University of Hong Kong, Pokfulam Road, Hong Kong S.A.R., China. 4Corresponding author. Email: shihong.lin@vanderbilt.edu (S.L.); tangc@hku.hk (C.Y.T.); zwwang@tongji.edu.cn (Z.Wa.) 5These authors contributed equally to this work.
The mechanisms of amphiphilic nanoflakes in enhancing IP were further investigated using Doppler broadening energy spectroscopy (DBES), isothermal titration calorimetry (ITC), and molecular simulations.

**RESULTS**

**Formation of free-standing PA nanofilm via MARIP**

Amphiphilic CuBDC (copper-1,4-benzene dicarboxylate) MOF nanoflakes with a large porosity, high aspect ratio, and asymmetric wettability were used for regulating the IP process. The fabricated MOF nanoflakes were extremely thin lamellar sheets with a lateral dimension of 1 to 2 μm and a thickness of ~2 nm (Fig. 1, C to F). The Raman spectra showed characteristic peaks at 864, 1137, 1434, and 1611 cm⁻¹, confirming the crystalline structure of MOF nanoflakes (Fig. 1G) (35). The x-ray diffraction (XRD) pattern exhibited the typical structure of MOF nanoflakes (Fig. 1H) (35). The out-of-plane XRD pattern showed two reflections, corresponding to (201) and (402) crystallographic planes of MOF structure that were perpendicular to the layers and the pores. The pore size (~1.41 nm) was substantially larger than the water molecules (~2.8 Å), ensuring the rapid transport of water molecules.

The large difference in surface energy between the hydrophilic segments (i.e., ─COOH groups from BDC on the edges of nanoflakes) and the hydrophobic segments (i.e., aromatic and aliphatic sites from BDC organic linkers exposed in the lateral dimensions) led to strong adsorption of CuBDC at the interface, resulting in a continuous interfacial self-assembly of the MOF nanoflakes (fig. S2) (36). The formation of the interfacial MOF layer was corroborated by the
exceptional ability of MOF nanoflakes to stabilize oil/water mixture. When MOF nanoflakes were added in an oil/water mixture, stable oil-in-water emulsions formed spontaneously and almost immediately (fig. S3A), as the MOF nanoflakes effectively reduced the interfacial tension (fig. S3B). The self-assembly of MOF nanoflakes at the interface was also supported by molecular dynamics (MD) simulation that showed the alignment of nanoflakes along the interface (see details in the Supplementary Materials and movie S1).

The ultrathin PA nanofilm was first fabricated using MARIP at a support-free water/hexane interface with the interfacial self-assembly of MOF nanoflakes (Fig. 1I) and then transferred onto a polyether-sulfone (PES) substrate for further tests. The PA membranes obtained with MOF dosages of 0.05, 0.10, and 0.20 weight % (wt%) are denoted as MARIP-0.05, MARIP-0.1, and MARIP-0.2, respectively, and the membrane formed via free interface polymerization without MOF was named as FIP and used as a control. To identify the position of MOF nanoflakes in the water/hexane system relative to that of the PA layer, the PA nanofilms were further analyzed by x-ray photoelectron spectroscopy (XPS) and XRD. The Cu element was not detected on the top surface of the PA nanofilms (fig. S4A) but became increasingly abundant at the bottom surface with increasing MOF dosage (fig. S4B). XRD patterns (fig. S4C) on the bottom surface of PA nanofilms formed via MARIP exhibited the (402) crystallographic plane of the MOF structure, suggesting that MOF nanoflakes align in parallel to the bottom surface of the nanofilm.

**Morphology and properties of PA nanofilms from MARIP**

The PA films fabricated using MARIP are morphologically very different from the PA film fabricated using FIP without MOF (Fig. 2A and fig. S5). Compared with the smooth PA film formed at the free interface without MOF, PA films that formed via MARIP have “ridge-and-valley” structures with substantially increased surface roughness (fig. S6A). Transmission electron microscopy (TEM) images revealed overwhelmingly dark MOF nanoflakes underneath the PA matrix of MARIP membranes (Fig. 2B). The MOF nanoflakes occupied more projected area with increasing MOF concentration used in MARIP. The distinct morphological differences are associated with the different IP processes: In FIP, the heat released from the reaction of MPD and TMC rapidly dissipated across the free interface; in MARIP, however, the MOF nanoflakes acted as a barrier against heat dissipation across the interface and induced a substantial local temperature gradient that caused interfacial hydrodynamic instability of the hexane layer driven by Rayleigh-Bénard convection (37). The accumulation of heat where polymerization occurred led
to the local formation of gas nanobubbles that roughened the PA nanofilms (27, 38).

To confirm the role of MOF nanoflake assembly in MARIP, we further fabricated Mix-MOF PA membrane by adding TMC/hexane solution to the system immediately (within 5 s) after MOF nanoflakes were added to water (without forming an interfacial self-assembly). Without horizontal alignment at the interface, the MOF nanoflakes were incorporated into the nanofilm during the IP process. In the absence of interfacial confinement by the self-assembled MOF layer, the Mix-MOF PA membrane resembled those of the FIP membrane (figs. S7 and S8) and did not exhibit the ridge-and-valley structure observed in PA membranes formed via MARIP. Both the permeance and salt rejection of Mix-MOF membrane were notably inferior to PA membranes fabricated using MARIP (fig. S8C), which suggests the critical role of the interfacial MOF self-assembly. Furthermore, while layering the MOF/hexane solution on the MPD/water solution, MPD diffused into the hexane phase and eventually deposited on the MOF surface upon hexane evaporation. To illustrate the impact of the predeposited MPD monomer, we performed a control experiment with no MPD preloading. In comparison to MARIP-0.1, membranes obtained without MPD preloading presented a slightly less-rough ridge-and-valley structure and a minor decrease in water permeance and salt rejection (fig. S9), which implies that the preprecipitated MPD on MOF film may also contribute to the formation of ultraselective MARIP membranes.

The surface area ratio (SAR) of the nanofilm, i.e., the ratio of the 3D surface area over the projected area, was estimated from the TEM images (Fig. 2C). SAR increased markedly from 1.6 ± 0.4 for the FIP membrane to 3.4 ± 1.1, 7.1 ± 1.2, and 7.9 ± 1.8 for MARIP-0.05, MARIP-0.1, and MARIP-0.2 membranes, respectively (Fig. 2D). The increased SAR is likely caused by the presence of more nanovoids (Fig. 2, C and E). These nanovoids enhance water uptake (39) and provide a large effective area for water permeation, thus resulting in a higher water permeability. The scanning electron microscopy (SEM) micrographs of the bottom surface show that both the quantity and size of the openings increased with a larger dosage of MOF nanoflakes (fig. S10), which could provide more channels for water transport through the PA nanofilm. In addition to a larger SAR, the TEM cross-sectional images (Fig. 2C) also show that the intrinsic thickness decreased substantially from 13.6 ± 1.7 nm for the FIP film to 8.6 ± 1.3, 5.3 ± 1.6, and 5.9 ± 0.9 nm for MARIP-0.05, MARIP-0.1, and MARIP-0.2 nanofilms, respectively (Fig. 2E). The intrinsic thickness of the PA films represents the characteristic length for transmembrane water transport (38, 40) and differs from the apparent thickness (i.e., the thickness of the crumpled PA structure), which increased with MOF nanoflakes addition (fig. S11). The PA films fabricated using MARIP were intrinsically much thinner than the PA active layers in TFC membranes fabricated using conventional IP (25 to 35 nm; fig. S12) or PA nanofilms reported elsewhere (38, 40).

Furthermore, the enhanced transport of MPD due to reduced free-energy barrier (41) substantially improved the cross-linking degree of PA nanofilms (Fig. 2F based on XPS results) from 74.9 ± 3.9% for the FIP film to 92.8 ± 3.1, 97.7 ± 0.9, and 95.7 ± 2.9% for MARIP-0.05, MARIP-0.1, and MARIP-0.2 nanofilms, respectively. Deconvolution of C1s, O1s, and N1s high-resolution spectra confirmed an increase of N—C=O moiety and a decrease of O—C≡O and R-NH₂ moieties (fig. S13 and table S1). The increased degree of cross-linking, as corroborated by less-negative zeta potential (fig. S14A) and reduced carboxyl group density (fig. S14B), resulted in higher solute rejection. The denser PA nanofilm from MARIP was further confirmed by DBES. As a lower $S$ parameter represents a smaller free volume (or subnanometer pores) (42), the consistently lower range of the $S$ parameter of MARIP-0.1 as compared to that of PA films formed in FIP or conventional IP with support layer indicates that MARIP-0.1 has a smaller free volume (Fig. 2G).

**Separation performance of PA nanofilms from MARIP**

The separation performance of the PA membranes was evaluated using cross-flow filtration. The FIP membrane had a relatively low water permeance and low salt rejection, even lower than that of TFC-PA membrane prepared via conventional IP with a support layer. In contrast, the water permeance of the MARIP-0.1 and MARIP-0.2 membranes was 262 and 277% of that of the FIP membrane, respectively (Fig. 3A). The marked permeance enhancement for PA membranes formed from MARIP was attributed to the following factors: (i) the larger effective area for water transport and (ii) the lower intrinsic thickness of the active layer that reduces the water transport distance. As shown in Fig. 3A, the MARIP membranes also exhibited excellent salt rejection. Notably, the NaCl rejection was markedly improved from 95.4 ± 0.5% (FIP) to 99.5 ± 0.1% (MARIP-0.1) and 99.1 ± 0.2% (MARIP-0.2), as a result of the higher cross-linking degree of the PA membranes from MARIP. The MARIP-0.1 and MARIP-0.2 membranes outperformed laboratory-made and commercial RO membranes by having the highest water/NaCl selectivity for a given permeance or the highest permeance for a given water/NaCl selectivity (Fig. 3B and section S2.3).

The water/solute selectivity, especially for very small neutral molecules, is of great significance for RO applications in desalination and potable reuse of wastewater (13). The FIP membrane exhibits low rejection of boron (57.1 ± 2.6%) and NDMA (71.3 ± 1.4%) because of its low degree of cross-linking (Fig. 3C). In contrast, much higher rejection of both species was achieved with the MARIP membranes. As a result of the high degree of cross-linking, MARIP-0.1 and MARIP-0.2 membranes exhibited extremely high rejection of NDMA (90.3 ± 0.4 and 90.1 ± 1.1%, respectively) and boron (90.1 ± 3.4 and 90.2 ± 2.8%, respectively) at neutral pH. Even higher boron rejection (Fig. 3D) was reached by the MARIP-0.1 membrane at a higher pH (94.2 ± 0.2% at pH 8), which generally favors the boron rejection by shifting its speciation toward the more negatively charged species (43). Compared with the laboratory-scale, pilot-scale, and full-scale TFC RO membranes in recent literature (Fig. 3E and tables S2 and S3), the MARIP-0.1 membrane exhibited unprecedentedly high rejection of both boron (pH 8) and NDMA.

The MARIP-0.1 membrane outperformed membranes reported in literature in boron rejection, featuring the highest water/boron selectivity (Fig. 3F) and transcending the existing performance upper bound on the selectivity versus permeance plot. With the MARIP-0.1 membrane, a single-pass seawater RO can produce water with a sufficiently low boron level that meets the irrigation and drinking water standard of the World Health Organization (44), which can translate to a substantial reduction of capital cost by eliminating the second-pass RO dedicated for boron removal in conventional seawater RO plants.

**DISCUSSION**

IP is a complex and nonequilibrium process, where two monomers polymerize rapidly and irreversibly near the interface between two...
immiscible phases. In MARIP, the amphiphilic MOF nanoflakes were used to enhance IP process to obtain an ultraselective PA layer with simultaneous improvement of water permeance and selectivity. We hypothesize that the ultraselectivity of PA membranes from MARIP is attributable to the combined effects of (i) accelerated IP reaction resulting from increased interfacial temperature due to hindered heat dissipation and (ii) facilitated trans-interface transport of MPD caused by the reduced energy barrier (Fig. 4) and enhanced electrostatic attraction at the interface.

The exothermal nature of IP process plays a critical role in PA nanofilm formation. The heat release rate is closely related to PA nanofilm formation, and the intensive heat release accelerates the whole reaction process and enhances the cross-linking degree of the polymer matrix (45). The local temperature rise could lead to “interfacial boiling,” facilitating degassing of the solution to generate bubbles that led to the formation of nanovoid structure in the resulting PA film (27). The heat release rate during IP process, measured by ITC, is shown in Fig. 4A and fig. S15. With MOF nanoflakes at the interface, the heat release rate was remarkably higher than that of the control sample (fig. S15). The addition of MOF nanoflakes nearly tripled the average heat release rate compared to that of the control FIP reaction (Fig. 4A). The addition of MOF nanoflakes accelerated the IP process, which, in turn, released more heat, creating a positive feedback loop to promote a highly vigorous IP process. The accelerated IP process substantially improved the cross-linking degree (and thus the selectivity) of the resulting PA nanofilms.

During the IP process, MPD monomers diffuse from aqueous phase to the organic phase to form the PA nanofilm in organic phase near the interface (28). The diffusivity of amine monomers in the reaction zone is of critical importance, i.e., a higher diffusivity benefits faster and more complete IP, leading to the formation of a denser PA matrix. The diffusivity of MPD from water to hexane phase was measured by monitoring the MPD concentration in hexane by ultraviolet-visible (UV-vis) spectrophotometry with/without the presence of MOF nanoflakes. The diffusivity of MPD to hexane phase increased notably in the presence of MOF nanoflakes (Fig. 4B), which was attributed to the reduced local energy minima...
for MPD transport caused by MOF nanoflakes. The periodic distribution of hydrophilic Cu—O groups and hydrophobic benzene ring groups of the MOF nanoflakes changed the energy landscape for MPD diffusion, thereby facilitating the trans-interfacial transport of MPD monomers and regulating the kinetics of the IP process (28, 49). Moreover, the hydrophobic sites (exposed aromatic and aliphatic sites from BDC organic linkers) of the amphiphilic MOF nanoflakes facilitated the accumulation of the MPD molecules by hydrophobic interaction at the water/hexane interface, leading to a greater initial MPD concentration gradient to drive the trans-interfacial transport (28). The greater initial concentration gradient has also been validated by the results of control NMPL membrane (fig. S9). The intensified IP due to the rise of local temperature and the enhancement in MPD transport led to the formation of the dense PA active layers.

We further performed MD simulation of heat dissipation across the water/hexane interface to confirm that the presence of interfacial MOF hinders heat dissipation. After 4 ns of the heat input, the atoms near the MOF/hexane system had higher temperature with a uniform distribution (Fig. 4C). The equilibrium temperature at the interface in the water/MOF/hexane system was substantially higher than that of the interface in the water/hexane system (Fig. 4D), which was mainly because of the larger interfacial thermal resistance in the presence MOF (movies S2 and S3). For the water/hexane system, the transfer of heat produced in IP was mainly resisted by the water/hexane interface with a thermal resistance of 4.38 × 10−9 m K W⁻¹ (table S5). In the water/MOF/hexane system, however, the heat transfer was resisted by the MOF/hexane interface, MOF, and MOF/water interface with a total thermal resistance of 1.39 × 10−8 m K W⁻¹ (table S6). MD simulation also shows that MPD molecules prefer to stay at the water/hexane interface where they have the lowest free energy (Fig. 4E). This can be explained by the fact that the hydrophilic amino groups of MPD could form strong hydrogen bonds with water, while the hydrophobic benzene rings have a higher affinity to hexane. The energy penalty for MPD to enter the hexane phase from the interface is ~9.3 kT at 25°C, suggesting that partition of MPD into the hexane phase is highly unfavorable unless there is a strong concentration gradient sustained by the IP process that constantly consumes MPD. The addition of the MOF nanoflakes changes the energy landscape for interfacial MDP diffusion. Although the overall energy penalty for MPD transport to the hexane phase from the aqueous phase or from the interface is not reduced, the presence of the MOF nanoflakes at the water/hexane interface creates many local energy minima in the free-energy curve that now becomes highly “zigzagging” (Fig. 4F). These local energy minima result in metastable states with relatively small energy penalties in between, thereby facilitating the trans-interface transport of MPD.

As the pore size of MOF is similar to the molecular size of MPD (fig. S20, A and B), the zigzagging of the free-energy curve is likely attributable to the periodic distribution of hydrophilic Cu—O groups and hydrophobic benzene ring groups of MOFs along the transport direction. While the strong molecular attraction between amino groups of MPD and Cu—O groups of MOF nanoflakes reduced the free energy, the repulsion between amino groups and benzene ring...
groups increased the free energy. In the presence of multiple local minima, the transport of MPD across the water/hexane interface only needs to overcome the largest of the energy penalties between two adjacent minima, which is considerably (~48%) lower than that in an MOF-free system. In other words, the reduced maximum energy penalty due to the presence of interfacial MOF assembly facilitates transport of MPD across the interface.

The simulation also shows that MPD molecules transport through the MOF framework via “flipping” motions (movie S4), which might be attributed to the benzene ring rotation under the thermal disturbance (fig. S20, C and D). This flipping facilitates MPD molecules to overcome the periodic potential barrier, which benefits the rapid transport of MPD. The simulation results are consistent with experimental observation of increased MPD diffusivity in the presence of MOF nanoflakes (Fig. 4B). We note that, regardless of the presence of the interfacial MOF assembly, there always exists a positive energy penalty for the trans-interface transport of MPD alone. In a real IP process, however, the polymerization reaction in the hexane phase consumes the MPD and maintains a concentration gradient to sustain trans-interface transport. While MD simulations, considering all aspects of the IP process, are computationally prohibitive, the results supporting MOF-facilitated transport in the absence of polymerization should equally apply in the presence of polymerization.

In summary, we have developed a MARIP process to fabricate highly cross-linked and ultraselective PA membranes with performance transcending the upper bound of permselectivity tradeoff. Not only these membranes have a substantially higher water permeance compared with that of commercial TFC-PA membranes (~125% enhancement) but they also achieved unprecedentedly high rejections (>90%) of small neutral molecules (e.g., boron and NDMA) that are regulated but challenging for existing RO membranes to remove. The MARIP membrane transcended the existing performance upper bound on the selectivity versus water permeance plot (A/B versus A). We note that such a performance evaluation framework was developed on the basis of the solution-diffusion model and the assumption that B is a constant for a given salt and a given membrane (50). However, recent literature rightfully questioned the validity of the solution-diffusion model and assumption of B being a constant and an intrinsic membrane property parameter (51, 52). Therefore, the comparison between performance of the MARIP membrane and that of the existing membranes, especially those measured with different solution and operating conditions, should be interpreted with caution.

PA membranes from MARIP enable the production of water that meets the stringent standard for potable water quality, rendering it promising for highly efficient seawater desalination and wastewater reuse. The mechanisms for forming these high-performance membranes in the presence of amphiphilic MOF nanoflakes include the confinements of trans-interface heat transfer and gas nanobubbles formed in situ and the enhancement of the trans-interface transport of diamine monomers. These factors together promote the formation of a highly cross-linked, ultrathin, and corrugated PA active layer that is both highly water permeable and exceptional in rejecting salts and micropollutants.

**METHODS**

**Preparation of MOF-regulated free-standing membrane**

The free-standing PA membrane was prepared by fabricating a PA active layer at a free aqueous-organic interface, i.e., via FIP. Briefly, for the pristine FIP membrane, the MPD aqueous solution (2.0 wt%) was added to a glass container, followed by carefully pouring 0.10 wt% TMC/hexane solution onto the surface of MPD solution. The total reaction time for IP was 1 min. The resultant PA active layer was picked up on a substrate and rinsed with sufficient hexane to remove the unreacted TMC. The PA active layer was then floated on a water surface and transferred to PES membrane. For the MOF-regulated free-standing membrane (see Fig. 11), before the adding of TMC/hexane solution, the MOF/hexane solution (0.05, 0.10, and 0.20 wt%) was carefully spread onto the surface of MPD solution, ensuring that the surface was fully covered by the MOF/hexane solution. The system was then placed at room temperature for 10 min until all the hexane was evaporated, which enabled the MOF nanoflakes to assemble at the interface (53). Then, the TMC/hexane solution was carefully added onto the preformed thin MOF layer along the wall of the glass container by using a pipette to initiate the IP reaction. The obtained membranes using MARIP are denoted as MARIP-0.05, MARIP-0.1, and MARIP-0.2 membranes with MOF dosages of 0.05, 0.1, and 0.2 wt%, respectively.

**Conventional TFC membrane preparation**

The conventional TFC membrane was fabricated using a conventional IP method according to our previous work (54). Briefly, the PES substrate was first immersed in 2.0 wt% MPD aqueous solution for 2 min. The excess MPD solution was removed by nitrogen gas using an air knife. Then, the 0.10 wt% TMC/hexane solution was poured onto the substrate surface for 45 s, resulting in the formation of PA nanofilm on the substrate. After thoroughly rinsing with hexane, the membrane was cured at 75°C for 5 min. The resultant membrane (TFC-PA) was stored in deionized (DI) water at 4°C for further characterization and tests.

**MOF-mixed free-standing membrane preparation**

The MOF-mixed free-standing membrane was fabricated using the procedures similar to those in the MOF-regulated method as described above, except for the lack of evaporation process. The TMC/hexane solution was immediately (within 5 s) added to the system after the pouring of the MOF/hexane solution to exclude the assembling process. The concentration of the MOF/hexane solution was 0.1 wt%. The obtained membrane is denoted as the Mix-MOF membrane.

**Characterization methods**

Top surface, bottom surface, and cross-section morphologies of the membranes were observed by SEM (S4800, Hitachi, Japan). The TEM (TALOS F200X, Thermo Fisher Scientific, USA) was used to examine the membrane cross-sectional images. The intrinsic structure of the PA nanofilm including apparent thickness ($\delta_{app}$), intrinsic thickness ($\delta_{int}$), SAR, and void volume fraction ($f$) were determined from TEM images using the ImageJ software. A quartz crystal microbalance (QCM; Q-sense E4, Biolink Scientific, Sweden) was used to quantify the structural changes (i.e., $\delta_{int}$ and $f$) in PA nanofilms (54). The details of the TEM and QCM analysis can be found in the Supplementary Material.

The microstructure of PA films was characterized by a variable monoenergetic slow positron beam–coupled DBES (Institute of High Energy Physics, Beijing, China). Before DBES characterization, the membranes were thoroughly washed by pure water and dried. The DBES spectrum shows the information about the positron
annihilation event, where the depth profile of the cavity size distribution in PA films can be characterized by the S parameter. The water/hexane interfacial tensions were analyzed using an automatic surface tension meter (K100C-MK2, Krüss, Germany) following the Wilhelmy plate procedure.

To measure heat release rate during the IP reaction, ITC (Microcal PEAQ-ITC, Malvern, UK) was used to measure the exothermic reaction at the interface. Briefly, 100 µl of 2.0 wt% MPD/water solution was placed in the cell. Then, 0.1 wt% TMC/hexane solution (40 µl) was poured in the syringe. The heat release rate was monitored in every injection of TMC/hexane to MPD/water solution. For the MOF nanoflakes addition, before the titration, 10 µl of 0.10 wt% MOF/hexane solution was injected into the water surface in the cell. The cell was then kept open under the light until all the hexane was evaporated. Then, the TMC/hexane solution was injected to measure the heat release rate during IP reaction with the assistance of MOF nanoflakes.

To monitor the diffusion process of MPD monomers from aqueous phase with/without nanoflakes to organic phase through interface, the UV-vis spectrophotometer (TU1810, PERSEE, China) was modified, with the height of UV light 1 mm above the water/hexane interface. The change in absorbance at the monitoring point was recorded every 30 s once the hexane solution was added into the system. For the MOF addition, 0.10 wt% MOF/hexane solution was added to fully cover the surface of aqueous phase and evaporated thoroughly before the addition of hexane solution.

**Separation performance tests**

Membrane separation performance was tested using a laboratory-scale cross-flow filtration setup at 16.0 bar and 24 ± 0.1°C as described in our previous study ([55]). A membrane coupon (6.25 cm²) was precompacted with DI water at a cross-flow rate of 22.4 cm s⁻¹ for 6 hours before the measurement of water flux and salt rejection. Water flux (Eq. 1) was calculated by weighing the mass of the permeate over time

\[ J_W = \frac{\Delta m}{A_m \Delta t} \]  

where \( J_W \) (liter·m⁻²·hour⁻¹) is the water flux, \( \Delta m \) (g) is the mass of the permeate collected over a designated time interval (\( \Delta t \), hour), \( A_m \) is the membrane surface area (m²), and \( \rho \) (kg·liter⁻¹) is the density of water. The membrane water permeance (\( A \)) was determined as the ratio of water flux over the applied pressure.

The salt rejection was tested using a feed solution containing NaCl (2000 mg liter⁻¹). The salt rejection (\( R \)) was determined according to Eq. 2

\[ R = \left( 1 - \frac{C_p}{C_f} \right) \times 100\% \]  

where the conductivity of the feed \( C_f \) (mg liter⁻¹) and permeate \( C_p \) (mg liter⁻¹) was determined using an electrical conductivity meter (Cole-Parmer, USA).

The salt permeability coefficient (\( B \)) was determined using Eq. 3

\[ B = J_W \frac{1 - R}{R} \exp \left( - \frac{J_W}{k} \right) \]  

where the term \( \exp \left( - \frac{J_W}{k} \right) \) is used to correct the concentration polarization effect, and \( k \) is the mass transfer coefficient in the cross-flow cell calculated according to She et al. ([56]).

To assess the membrane separation performance, we further measured the rejection of the inorganic micropollutant [boron, molecular weight (MW) = 61.8 g mol⁻¹] and the very small neutral micropollutant (NDMA, MW = 74.1 g mol⁻¹). The concentration of boron (5 mg liter⁻¹ at pH 6) was determined by an inductively coupled plasma optical emission spectrometer (Agilent, 5110) ([21]). The NDMA rejection was analyzed using a liquid chromatography–mass spectrometer (LC-MS; U3000-QE, Thermo Fisher Scientific) with a feed solution of 890 µg liter⁻¹. The elevated feed concentration was proved to have no notable influence on NDMA removal ([57]) and could be detected by LC-MS directly without sample concentration. The NDMA-D6 (mass/charge ratio = 81) was used as an internal standard sample for quantification.

**Computation simulation**

To explore the effect of the MOF nanoflakes on the dissipation of reaction heat from the MOF/hexane interface to the water and hexane phases, we simulated the heat diffusion process in both water/MOF/hexane and water/hexane systems for comparison. A symmetrical setup of the thermal diffusion system was used in the simulation. Heat was continuously added to the two slabs at a specific rate by changing the velocity of the atoms, with two cold slabs at constant temperatures located in the water and hexane phases, respectively (fig. S17). Both the water/hexane system and water/MOF/hexane system contain 4172 water molecules, 936 hexane molecules, and 100 MPD molecules and 36 TMC molecules in the water and hexane phases, respectively. For water/MOF/hexane system, the MOF nanoflake has a size of 4 by 6 by 6 unit cells with periodic conditions in the y and z directions, which corresponds to a size of about 21 Å by 39 Å by 43 Å. The slabs for adding heat were in the hexane phase close to the MOF/hexane interface. The releasing rate of heat from the IP between MPD and TMC with an interfacial area of 1677 Å² was estimated to be 7.0 × 10⁻⁷ kcal mol⁻¹ ps⁻¹ according to the bond energy between MPD and TMC. The release rate of heat was determined by quantum calculations in combination with the measured diffusion rate of MPD across the MOF/hexane interface. Considering the sizes of the simulated system and MOF that were several orders smaller than that in the experiments, the rate of adding heat to the slabs, \( Q_i \), was set to 0.70 kcal mol⁻¹ ps⁻¹ to simulate the heat from the exothermic IP reaction. The cold slabs in the water and hexane phases were maintained at a temperature of 298 K with the Langevin thermostat, and heat would be removed from these two slabs because a microcanonical (NVE) ensemble was applied to the whole system. The damping factor of the Langevin thermostat was set to 0.1 ps according to the work of Li et al. ([58]). The amounts of heat removed from these two slabs in every unit time were accumulatively collected. The MD simulation was conducted with the Lammps package. All the slabs have a thickness of 5 Å. The simulations were run for 4,000,000 steps with a time step of 1 fs. The heat was added to the system every 10 steps, and the removed heat from the cold slabs were collected every 100 steps. Before the simulation of heat diffusion, the system had been fully equilibrated in an NPT ensemble at a temperature of 298 K and a pressure of 101.3 kPa. Because the system was symmetric in the x direction, we averaged the temperature profile of the system in the x direction.
SUPPLEMENTARY MATERIALS

1. H. B. Park, J. Kamcev, L. M. Robeson, M. Elimelech, B. D. Freeman, Maximizing the right
2. Bio-protocol.
3. Supplementary material for this article is available at https://science.org/doi/10.1126/
4. NVE thermodynamic ensemble at 298-K temperature. Two simulated lattices were constructed, i.e., one is the water/MOF/hexane system and the other is the water/MOF/hexane system. Both simulated lattices are composed of the same number of H2O (1043) and MPD (1) on the left, and hexane (234) on the right. In the MD model with MOF, the MOF nanoflake that is placed between water and hexane has the size of 4 by 6 by 6 unit cell and 21 Å by 39 Å, with periodicity in the y- and z-coordinate directions. Both lattice cell was separated into several sampling segments with the length of 0.5 Å (near the interface) and 1 Å (far from interface) (fig. S19). Each sampling segment consists of 1,000,000 steps, and each step lasts 1 fs. During the MD process, the MPD molecule was initially fixed at the center of each sampling segment with a spring potential and then the simulations were operated to obtain the final equilibrium state for umbrella sampling. The elastic coefficient of the spring used in umbrella sampling was set to 3 to 10 kcal mol⁻¹ Å⁻².

REFERENCES AND NOTES

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SUPPLEMENTARY MATERIALS

View/request a protocol for this paper from Bio-protocol.

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