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# Supporting Information

## Ultrathin fluorinated self-cleaning membranes via coordination-driven metal-bridged assembly for water purification

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## Experimental Procedures

### Methods

The cross-section morphology and elemental mapping of MBFM/PAN were captured by transmission electron microscopy (TEM, JEOL-2100F, Japan). The membrane sample was encapsulated by epoxy resin and cut into thin (~90-100 nm) slices by Ultratome (Leica EM UC6). The slice-shaped samples were then deposited on micro grid copper holders.

The chargeability of the dyes was measured by a zeta potential analyzer (Zetasizer Nano ZS90, UK). The dye adsorption of the MBFM(40)/PAN membrane was measured by immersing membrane (membrane area=4.1 $cm^2$) into a 50 mL beaker with 30 mL of feed solution (100 ppm dye). After 3-day adsorption, the dye concentration of feed was determined by a UV-vis spectrophotometer and the amount of adsorbed dyes ($M_{dye}$, μg/$cm^2$) on the membrane was calculated by Equation (S1),

$$M_{dye} = \frac{V_s}{A} \times (C_0 - C_3) \qquad \text{(S1)}$$

where the $C_0$, $C_3$ (μg/mL) were the dye concentration at the beginning and after 3 days, respectively, $V_S$ (mL) was the volume of solution and the A ($cm^2$) was the membrane area.

The interactions between metal ions ($Fe^{3+}$ and $Na^+$) and organic ligands (phosphate/sulfonate) were carried out with Material Studio software via the Forcite molecular mechanics module.[1,2] The phosphate and sulfonate ligands were set to be completely deprotonated for coordination reaction. The electrostatic non-bond energy was used to evaluate the interaction between metal ions and ligands.

## Materials

Nafion®, developed by Dupont in 1960, is a kind of perfluorosulfonate acid polymer consisting of a hydrophobic polytetrafluoroethylene backbone and functional perfluorovinyl ether branched chains terminated by hydrophilic sulfonic acid groups (Fig. S1). Herein, a 5% Dupont Nafion® (D520) solution (Polymer content, 5.0 wt. % min, 5.4 wt. % max; Water content, 45±3 wt. %; VOC content, 50±3 wt. %; Specific gravity, 0.92-0.94; Viscosity, 10-40 cP at 25 ℃ and 40 $sec^{-1}$ shear rate) was supplied by Hesen electric Co. (Shanghai, China).

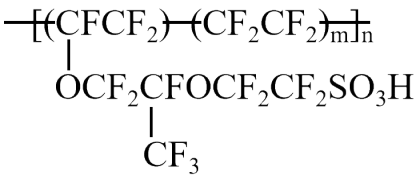

Fig. S1. Chemical structure of Nafion®

# Results

## Figures

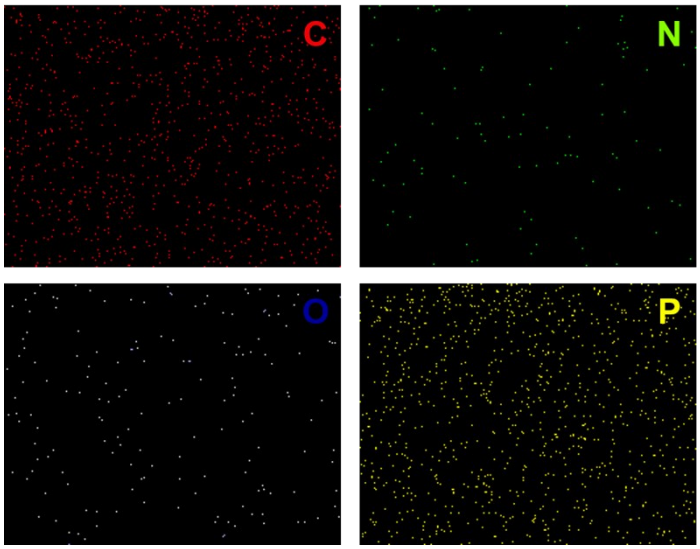


Fig. S2. Elemental mapping images of PA-absorbed PAN substrate.

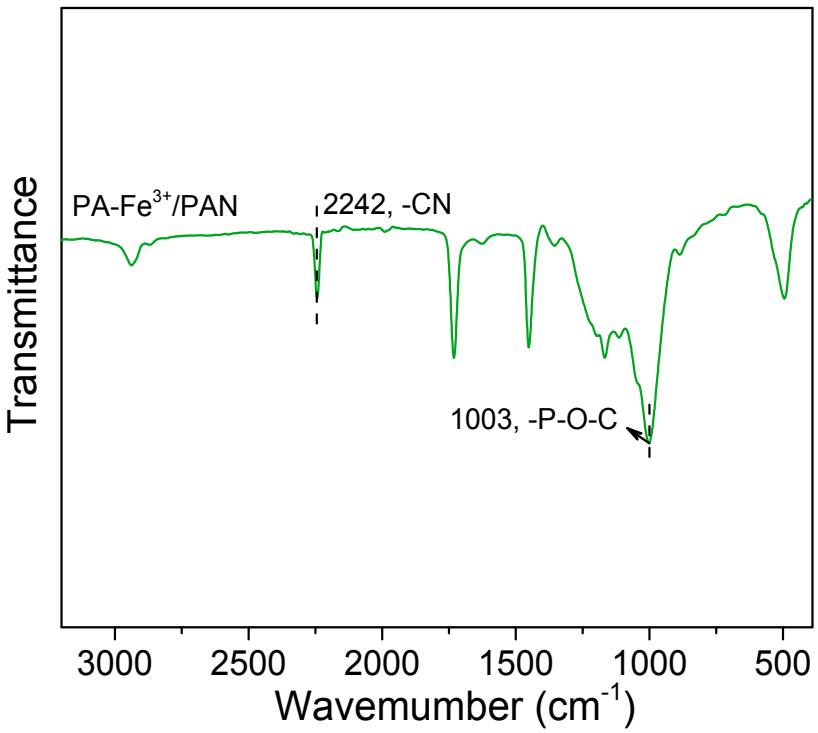


Fig. S3. FTIR spectrum of PA-$Fe^{3+}$/PAN.

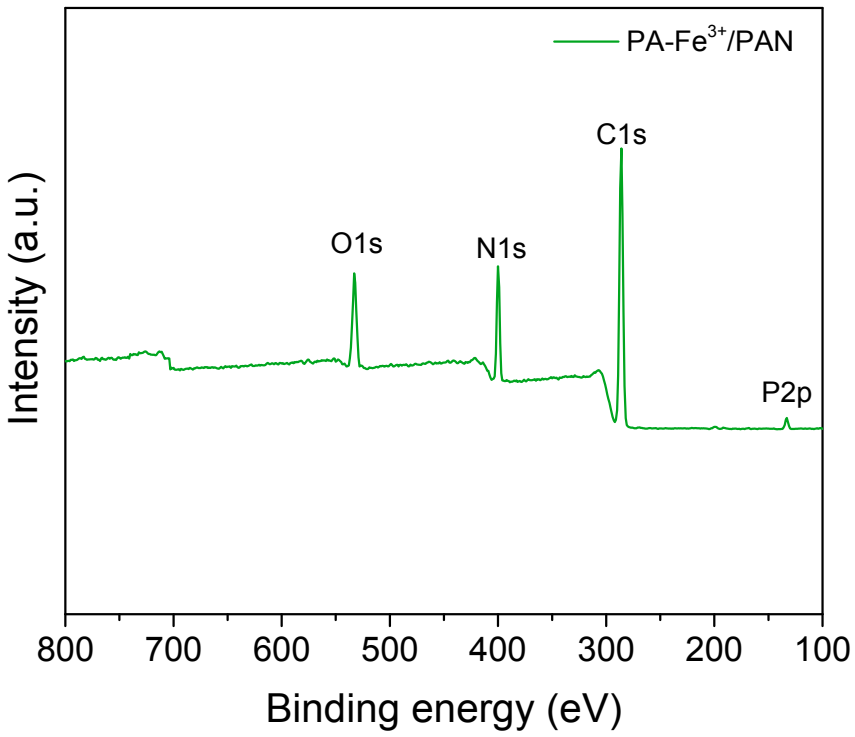


Fig. S4. XPS spectrum of PA-$Fe^{3+}$/PAN.

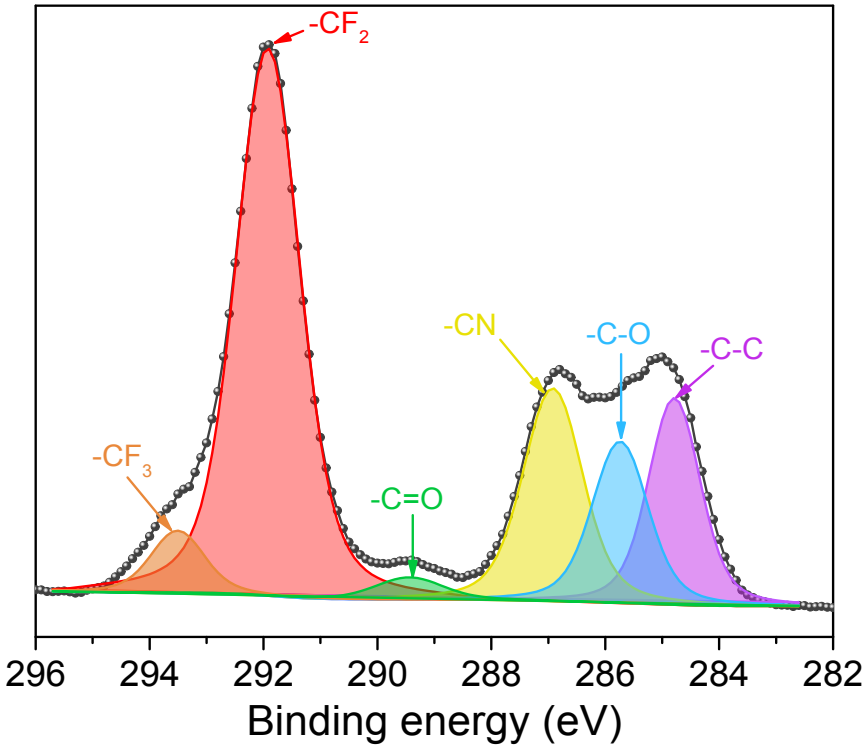


Fig. S5. High-resolution C1s core-level spectrum resolving results of MBFM(40)/PAN.

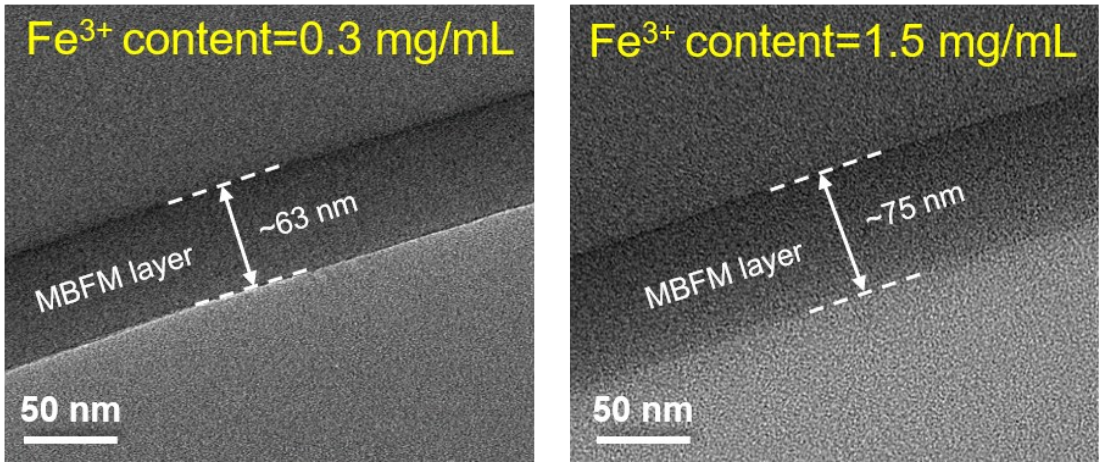


Fig. S6. Cross-sectional high-resolution TEM images of MBFM/PAN with varied $Fe^{3+}$ content. The assembly time of Nafion® is 40 min.

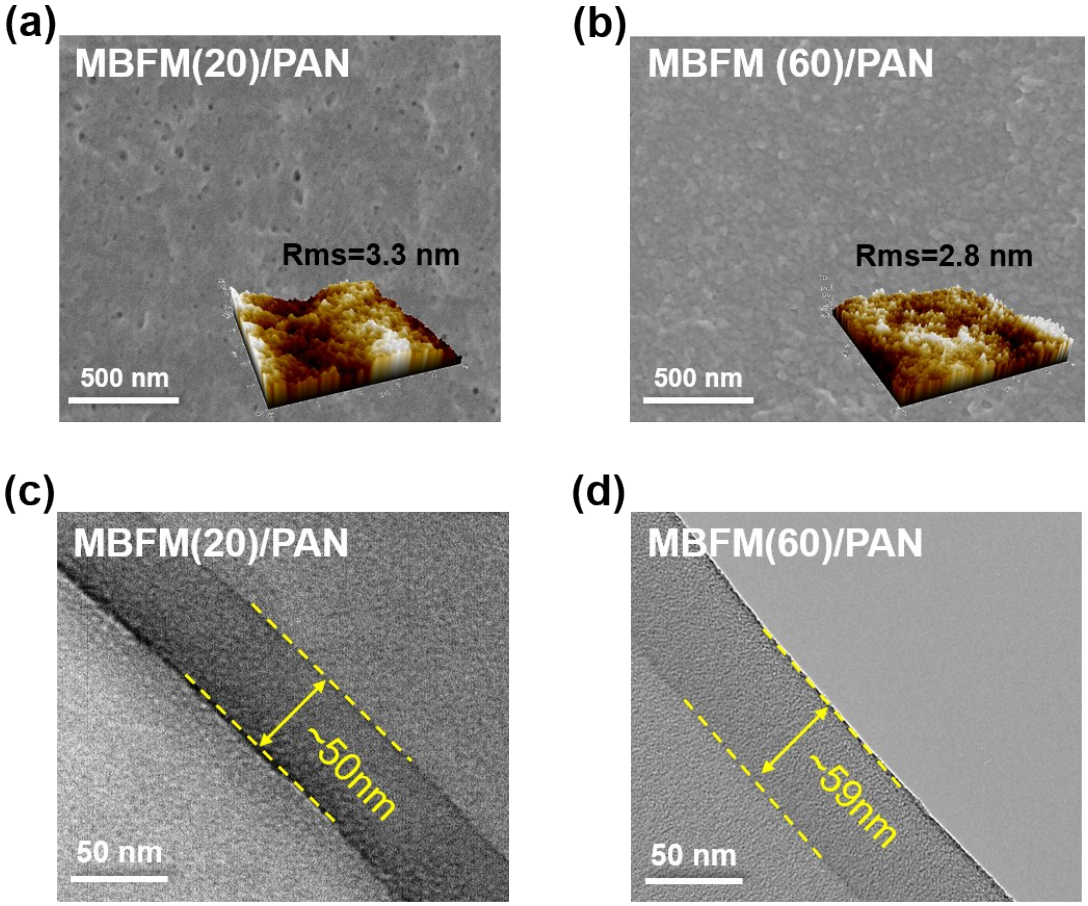


Fig. S7. (a-b) Surface morphologies of MBFM(20)/PAN and MBFM(60)/PAN. Insets: AFM images of MBFM(20)/PAN and MBFM(60)/PAN. (c-d) Cross-sectional high-resolution TEM images of MBFM(20)/PAN and MBFM(60)/PAN. The $Fe^{3+}$ content is 0.9 mg/mL.

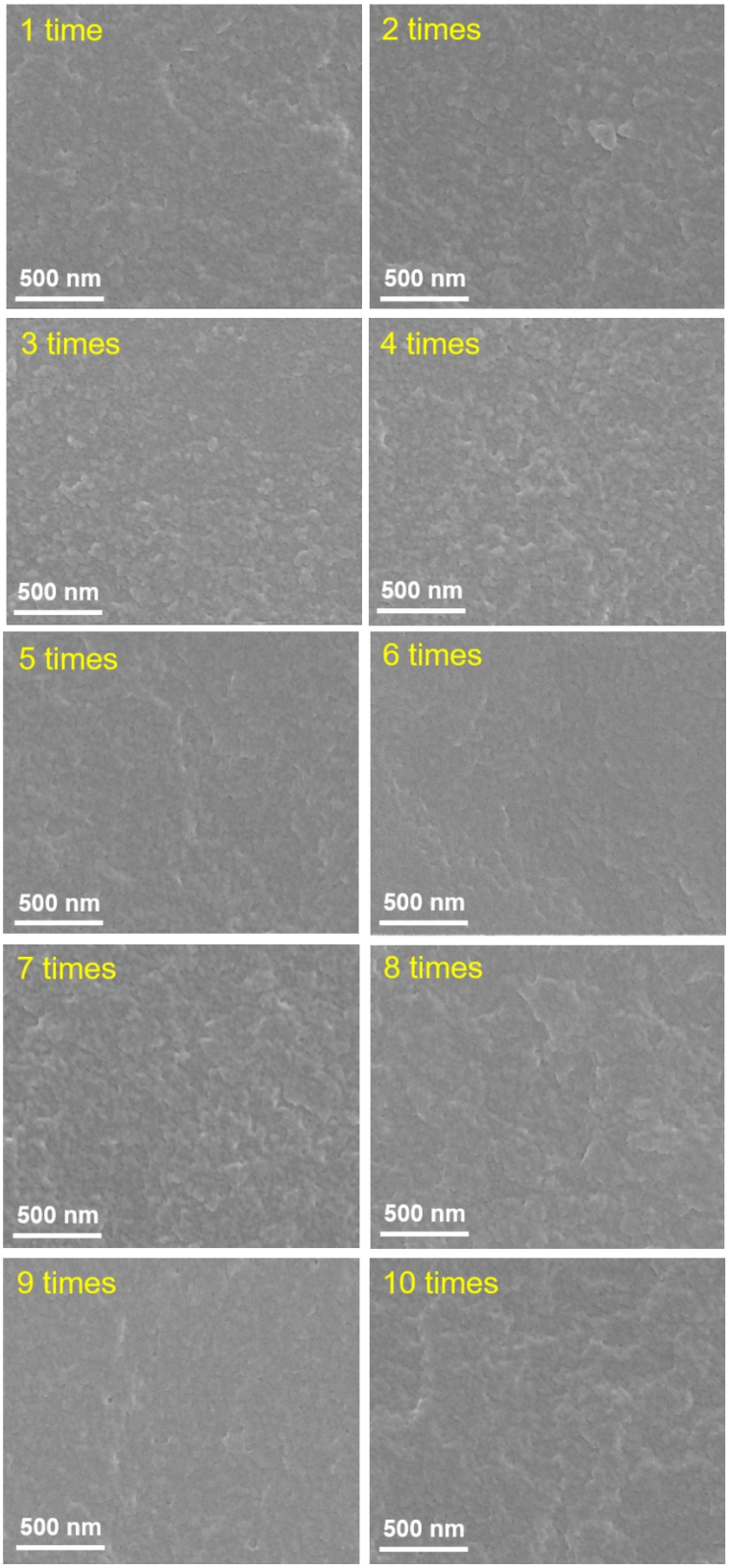


Fig. S8. Surface morphology of MBFM(40)/PAN fabricated by Nafion® solution with different usage times.

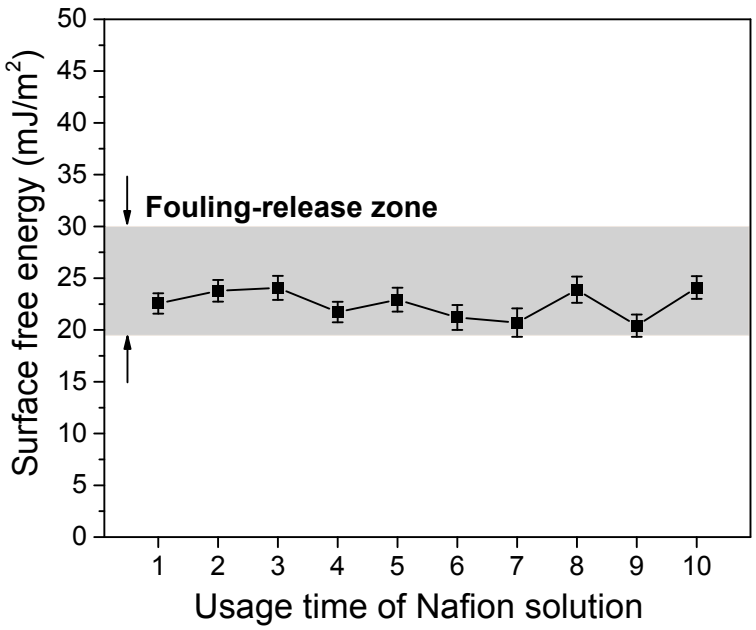


Fig. S9. Surface energy of MBFM(40)/PAN fabricated by Nafion® solution with different usage times.

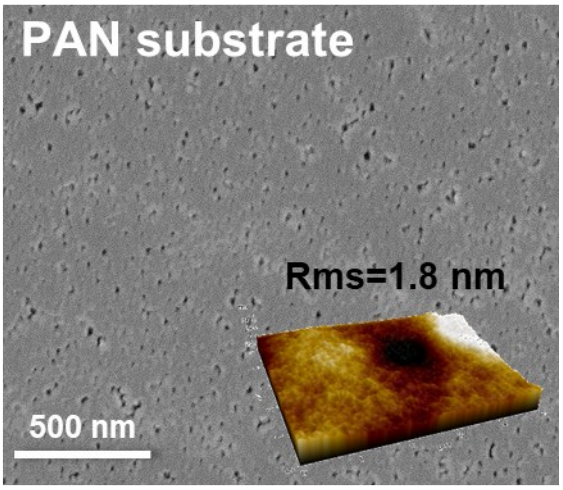


Fig. S10. Surface morphologies of the PAN substrate. Inset: AFM image of the PAN substrate.

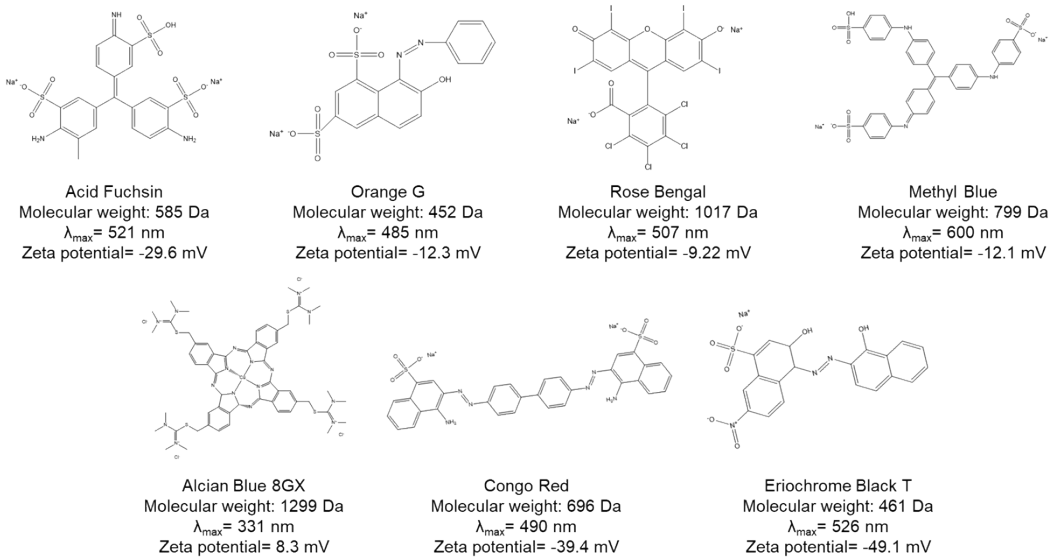


Fig. S11. Structural information of model organic dyes used in this work.

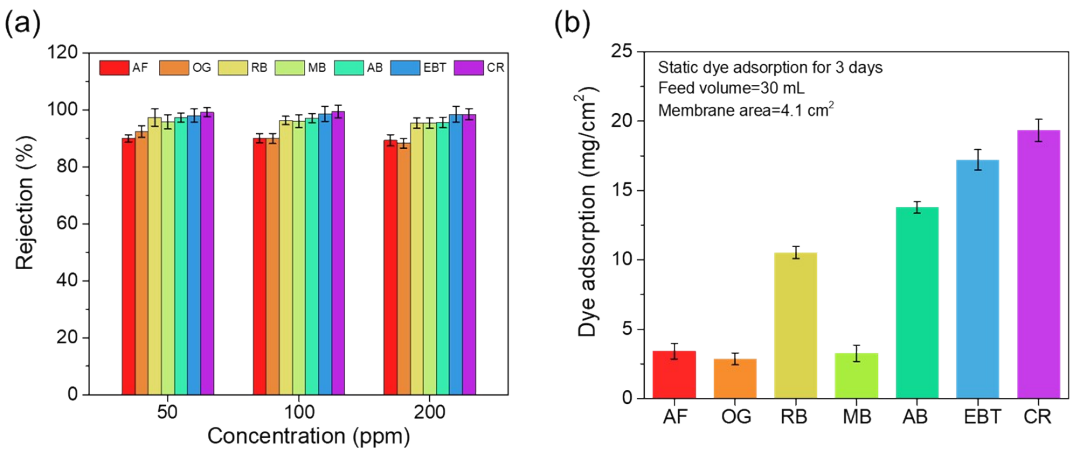


Fig. S12. (a) Dye rejections of MBFM(40)/PAN (AF: Acid Fuchsin, OG: Orange G, RB: Rose Bengal, MB: Methyl Blue, AB: Alcian Blue 8GX, CR: Congo Red, and EBT: Eriochrome Black T) with different feed concentrations. (b) Dye adsorption amount of MBFM(40)/PAN .

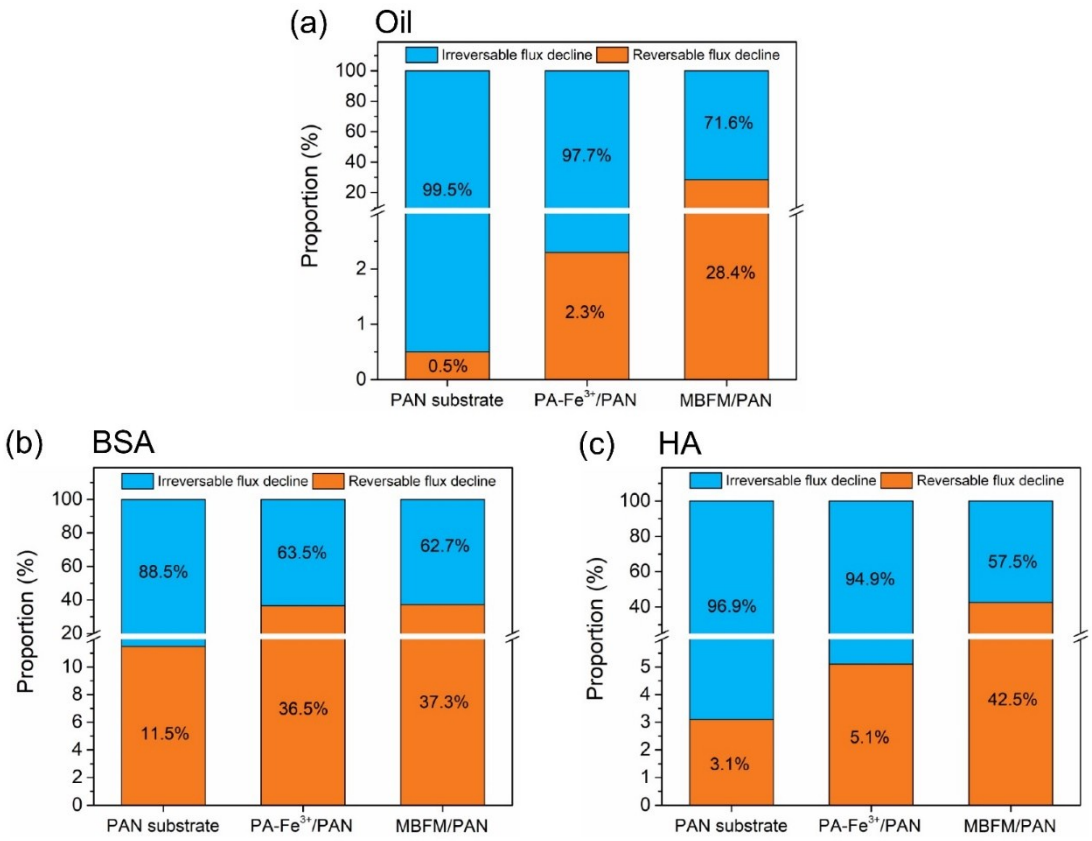


Fig. S13. The proportion of $DR_r$ ($PDR_r$) and $DR_{ir}$ ($PDR_{ir}$) to $DR_t$.

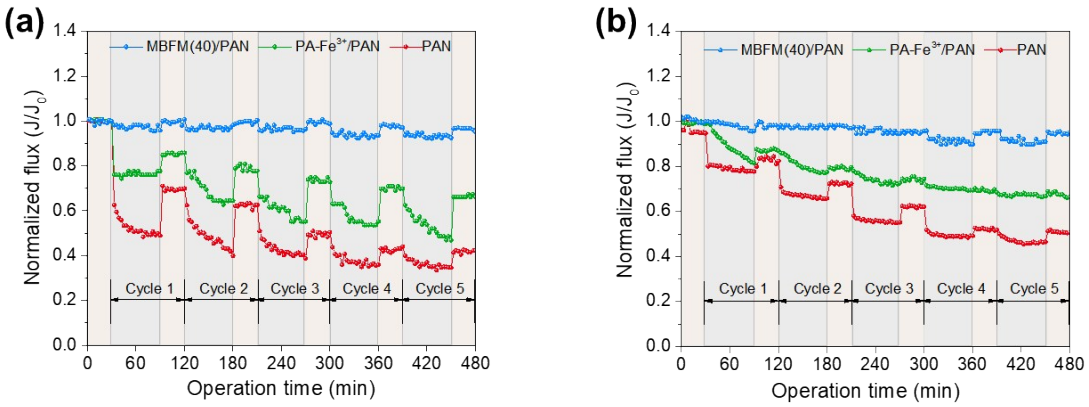


Fig. S14. Time-dependent normalized flux for PAN, PA-$Fe^{3+}$/PAN, and MBFM(40)/PAN membranes during five cycle filtration of (a) BSA solution and (b) HA solution.

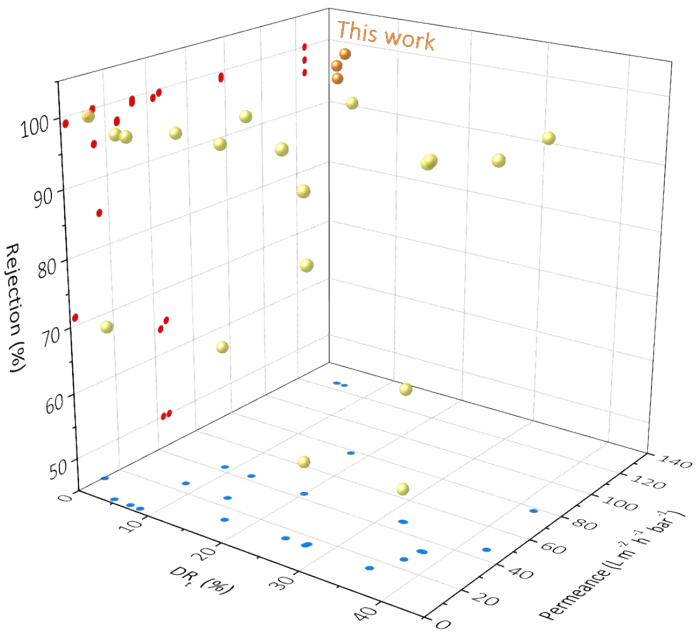


Fig. S15. Comparison on the antifouling and separation performance of MBFM(40)/PAN and the previously reported membranes in literatures.

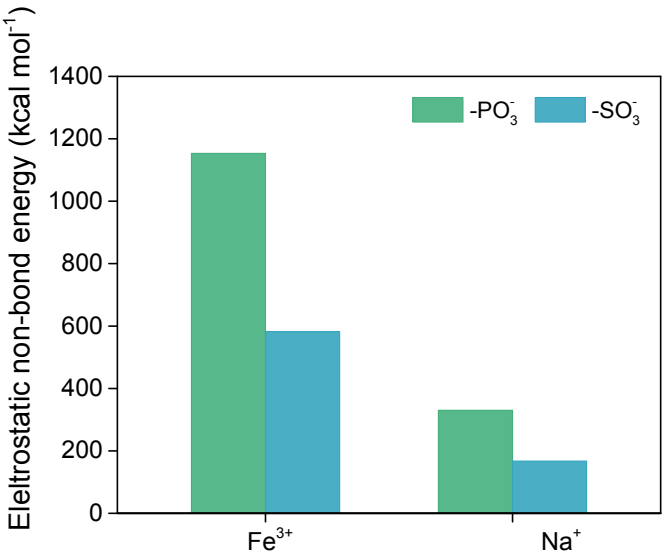


Fig. S16. Calculated electrostatic non-bond energy of metal ions ($Fe^{3+}$/$Na^{+}$) and ligands (phosphate/sulfonate) with the forcite molecular mechanics module.

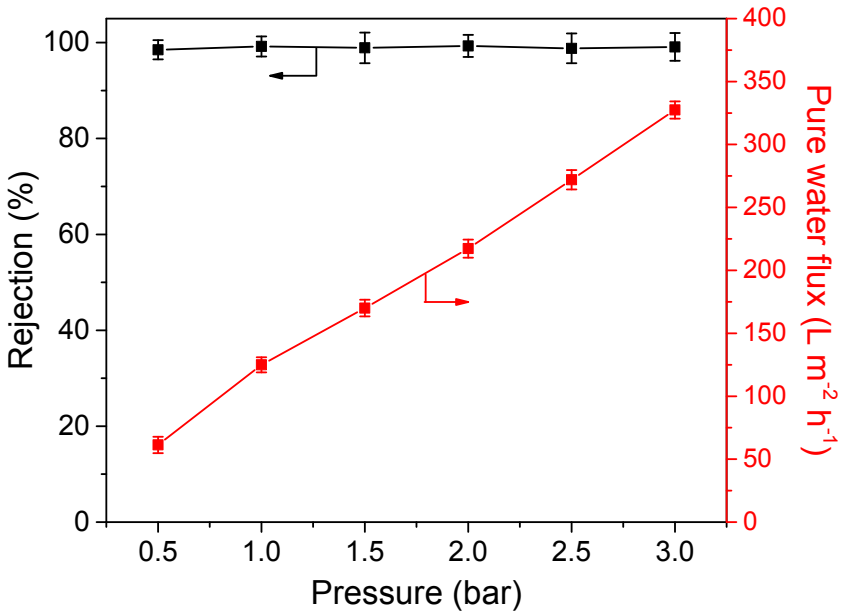


Fig. S17. The CR rejection and pure water flux of MBFM (40)/PAN under different driving pressure.

## Tables

Table S1. Surface elemental composition of PA-$Fe^{3+}$/PAN with varied $Fe^{3+}$ content.

| $Fe^{3+}$ content (mg/mL) | Elements content (at%) | | | | |
|---|---|---|---|---|---|
| | C | N | O | P | Fe |
| 0.3 | 47.6 | 7.9 | 32.3 | 7.7 | 4.5 |
| 0.9 | 62.8 | 8.5 | 15.8 | 4.6 | 8.3 |
| 1.5 | 73.4 | 12.8 | 8.3 | 1.9 | 3.6 |

Table S2. Surface elemental composition of MBFM/PAN with varied $Fe^{3+}$ content.

| $Fe^{3+}$ content (mg/mL) | Elements content (at%) | | | | | | |
|---|---|---|---|---|---|---|---|
| | C | N | O | S | P | Fe | F |
| 0.3 | 38.1 | 4.4 | 27.7 | 0.8 | 5.7 | 3.6 | 19.8 |
| 0.9 | 33.2 | 1.9 | 10.4 | 1.0 | 0.8 | 5.1 | 47.7 |
| 1.5 | 48.4 | 8.1 | 10.3 | 0.9 | 0.7 | 2.5 | 29.1 |

Table S3. Surface elemental compositions of PAN substrate, PA-$Fe^{3+}$/PAN and MBFM/PAN.

| Membrane name | Elemental content (at%) | | | | | | |
|---|---|---|---|---|---|---|---|
| | C | N | O | P | Fe | S | F |
| PAN substrate | 80.8 | 15.4 | 3.8 | — | — | — | — |
| PA-$Fe^{3+}$/PAN | 62.8 | 8.5 | 15.8 | 4.6 | 8.3 | — | — |
| MBFM(20)/PAN | 37.0 | 4.1 | 13.9 | 1.6 | 5.9 | 1.1 | 36.6 |
| MBFM(40)/PAN | 33.2 | 1.9 | 10.4 | 0.8 | 5.1 | 1.0 | 47.6 |
| MBFM(60)/PAN | 33.6 | 2.1 | 10.2 | 0.9 | 4.9 | 1.1 | 47.2 |

Table S4. Fluorine content of the previous-reported fluorine-based membranes.

| Membrane name | Fluorine content (at%) | Surface energy ($mJ/m^2$) | Ref. |
|---|---|---|---|
| MBFM(40)/PAN | 47.6 | 23.5 | This work |
| F3-PA/PES | 6.34 | 41.8 | [3] |
| FPA/TMC | 31.9 | 23.0 | [4] |
| F3-PDA/PES | 26.5 | 28.2 | [5] |
| F1.0-PA-60 | 26.5 | 46.1 | [6] |
| F-PAN-4 | 26.0 | 17.3 | [7] |
| PVDF/P(HFBM-SPP 50%) | 37.3 | 39.0 | [8] |
| PVDF/PBM-PEGMA-PHFBM | 34.7 | 29.1 | [9] |

Table S5. Comparison of the separation and antifouling performance of different membranes in literatures.

| Membrane name | Water permeance ($L\ m^{-2}\ h^{-1}\ bar^{-1}$) | Dye type | Dye rejection (%) | Foulant type | DRt (%) | FRR (%) | Ref. |
|---|---|---|---|---|---|---|---|
| MBFM(40)/PAN | 125.2 | Congo Red | 99.9 | Oil | 6.7 | 95.4 | This work |
| | | Eriochrome Black T | 97.8 | | | | |
| | | Methyl Blue | 96.5 | | | | |
| | | Alcian Blue 8GX | 95.8 | BSA | 7.5 | 95.3 | |
| | | Rose Bengal | 94.2 | HA | 7.3 | 95.8 | |
| | | Acid Fuchsin | 90.1 | | | | |
| | | Orange G | 89.5 | | | | |
| F3-PDA/PES | 43.1 | Congo Red | 99 | Oil | 20 | 93.4 | [5] |
| | | Orange GII | 64 | BSA | 12.7 | 94.5 | |
| | | Methylene Blue | 50 | HA | 8.9 | 98.6 | |
| HPAN-PEI-GA | 25.5 | Methylene Blue | 97.3 | SA | ~37 | ~62 | [10] |
| | | | | BSA | ~14 | ~86 | |
| | | Congo Red | 97.1 | HA | 8.1 | 91.7 | |
| NFM-3 | 15.6 | Reactive Red 49 | ~85 | BSA | 27.3 | 91.9 | [11] |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | Reactive Black 5 | ~87 | | | | |
| GQDs/PIP-TMC TFN | 14.5 | Congo Red | 99.9 | Oil | 35.28 | 85.26 | [12] |
| | | | | BSA | 24.66 | 91.85 | |
| | | Orange GII | 95 | HA | 27.23 | 99.06 | |
| PES-PIP-TMC-TA | 2.34 | Congo Red | 99 | SA | 6.8 | 96.5 | [13] |
| | | Methylene Blue | 71.2 | BSA | 8.2 | 95 | |
| | | Orange GII | 99 | HA | 4.5 | 99 | |
| | | Alcian Blue | 99 | | | | |
| NFM-3 | 12.8 | Reactive Black 5 | ~92 | BSA | ~17 | 94.5 | [14] |
| | | Reactive Red 49 | ~95 | | | | |
| ZIF-8/PEI–HPAN | 78 | Methyl Blue | 98.9 | BSA | 42 | ~58 | [15] |
| | | Congo Red | 99.2 | | | | |
| | | Acid Fusion | 87.2 | HA | 18 | ~82 | |
| | | Crystal Violet | 45.8 | | | | |
| GO-PSBMA | 11.98 | Reactive Black 5 | 99.2 | BSA | 0.18 | 94.4 | [16] |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | Reactive Red 49 | 97.2 | | | | |
| | | Methylene Blue | 99.6 | | | | |
| ZIF-8/PEI | 33 | Congo Red | 99.2 | BSA | 37.4 | 78.2 | [17] |
| | | Acid Fusion | 94.4 | HA | 37.7 | 87.8 | |
| | | Methyl Orange | 81.2 | | | | |

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