# Supplementary Information

# Highly crystalline and robust covalent organic framework membranes for predictable solvent transport and molecular separation

Hukang Guo [a, b], Jianxiao Jiang [a, b], Chuanjie Fang [a, b, *], Liping Zhu [a, b, c, *]

[a] *MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310058, P.R. China*

[b] *MOE Engineering Research Center of Membrane and Water Treatment Technology, Zhejiang University, Hangzhou 310058, P.R. China*

[c] *Center for Healthcare Materials, Shaoxing Institute, Zhejiang University, Shaoxing 312000, P.R. China*

* Corresponding author

Dr. Fang, fangchuanjie@zju.edu.cn

Prof. Zhu, lpzhu@zju.edu.cn

## 1. Figures

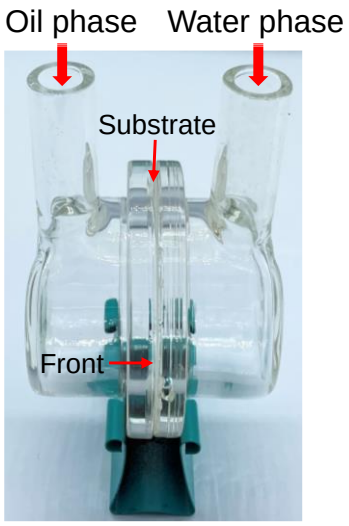



**Fig. S1.** Digital photograph of a homemade diffusion cell used for the growth of a COF-DT layer on a PAN support via interface polymerization.

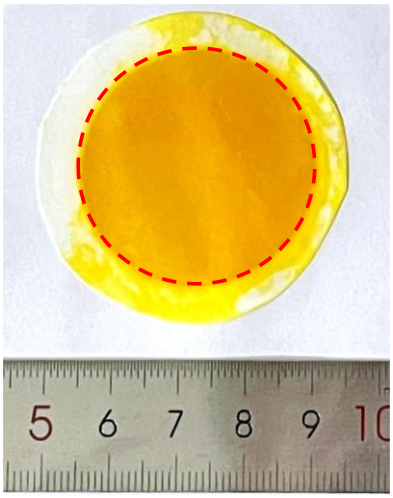



**Fig. S2.** Digital photograph of the COF-DT-2.7/PAN membrane.

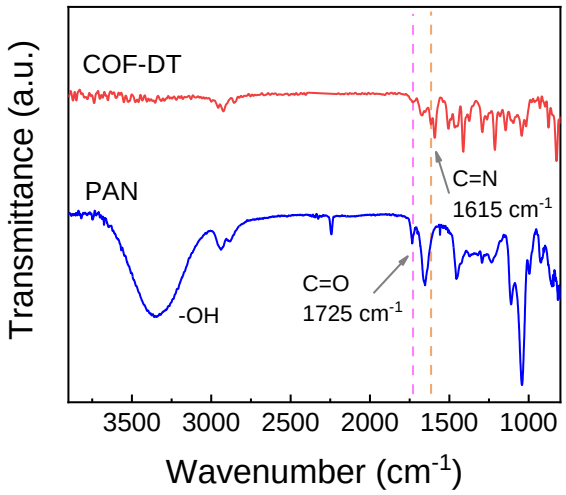



**Fig. S3.** ATR-FTIR spectra of the COF-DT/PAN and pristine PAN membranes.

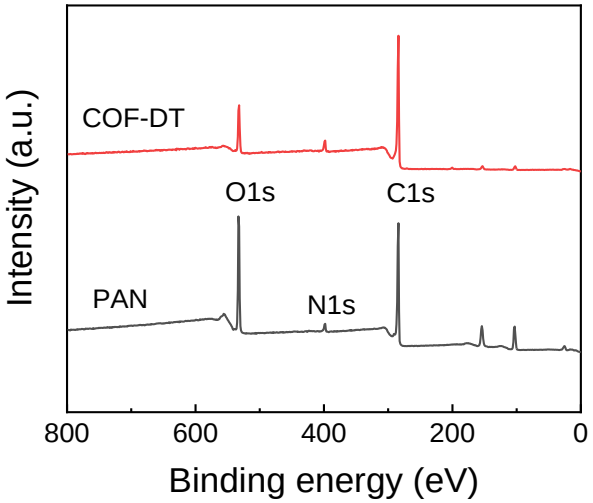



**Fig. S4.** XPS spectra of the COF-DT/PAN and pristine PAN membranes.

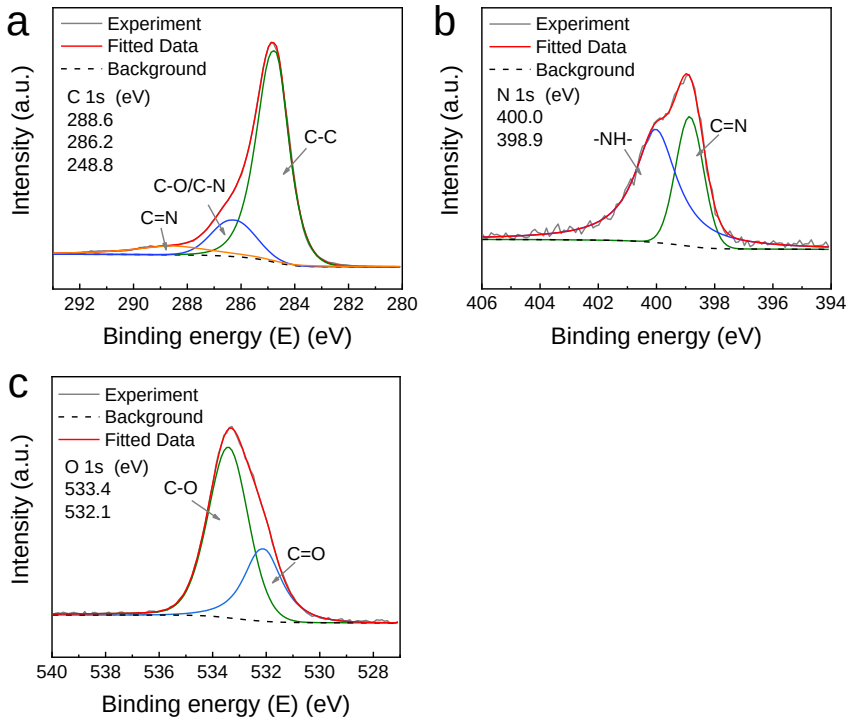



**Fig. S5.** High-resolution XPS spectra of C 1s (a), N 1s (b), and O 1s (c) for the COF-DT/PAN membrane.

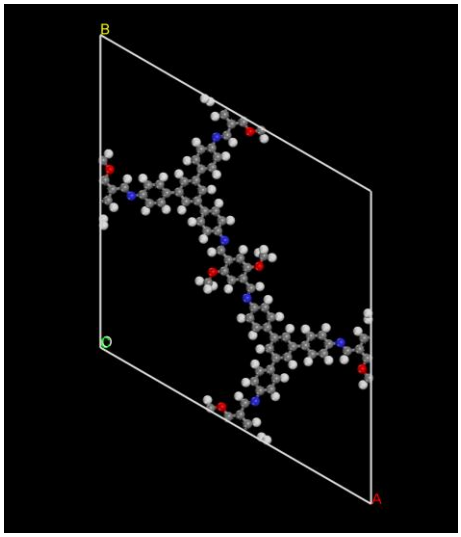



**Fig. S6.** Unit cell of the AA stacking mode of the COF-DT (O, red; N, blue; C, grey).

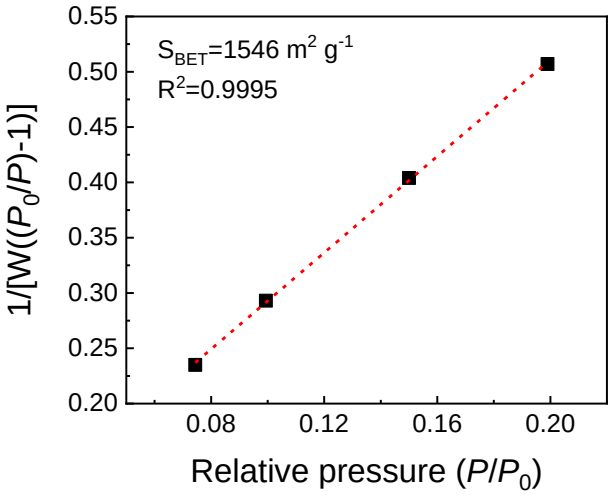



**Fig. S7.** BET plot calculated from the $N_2$ adsorption isotherm.

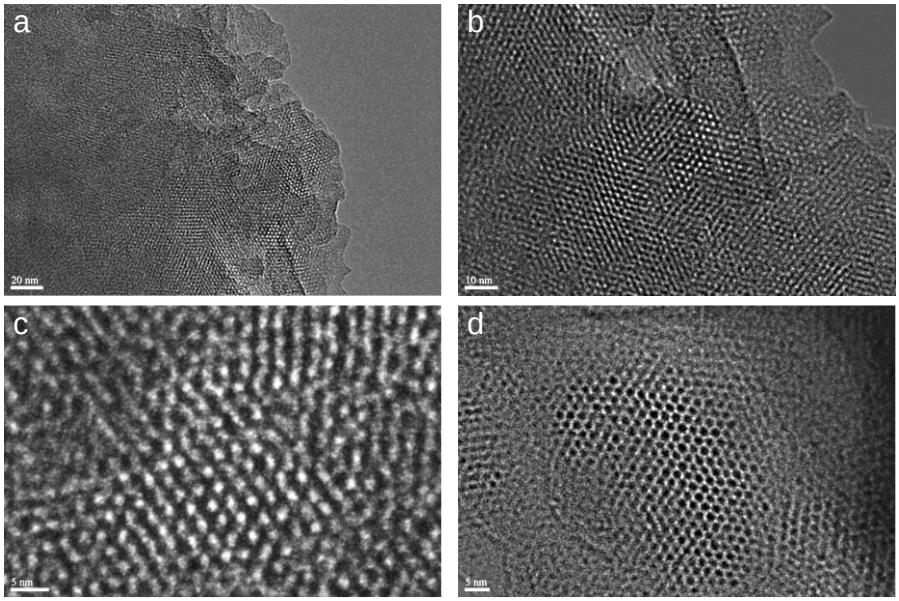



**Fig. S8.** HRTEM images of the COF-DT-2.7 film under different magnifications.

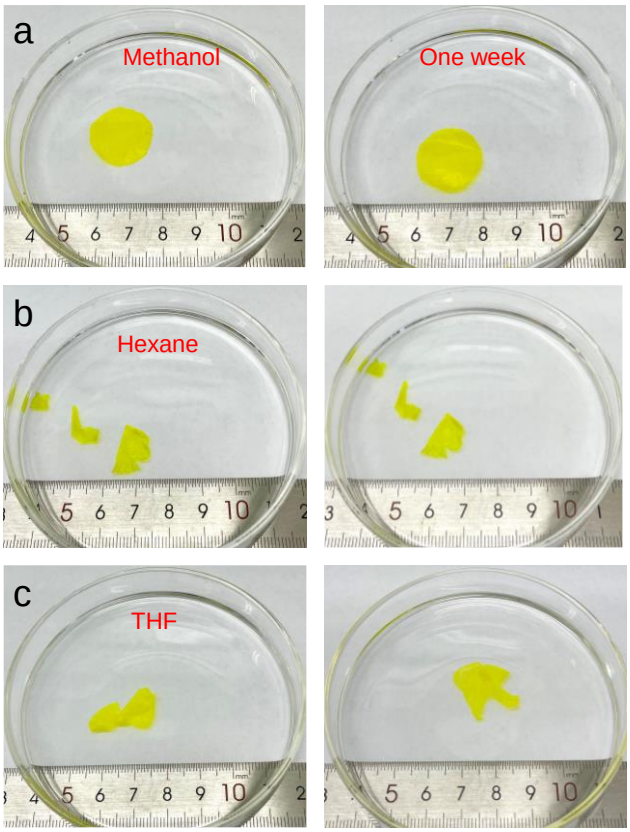



**Fig. S9.** Digital photographs of COF-DT-2.7 films before and after treatment for one week in methanol (a), hexane (b), and THF (c).

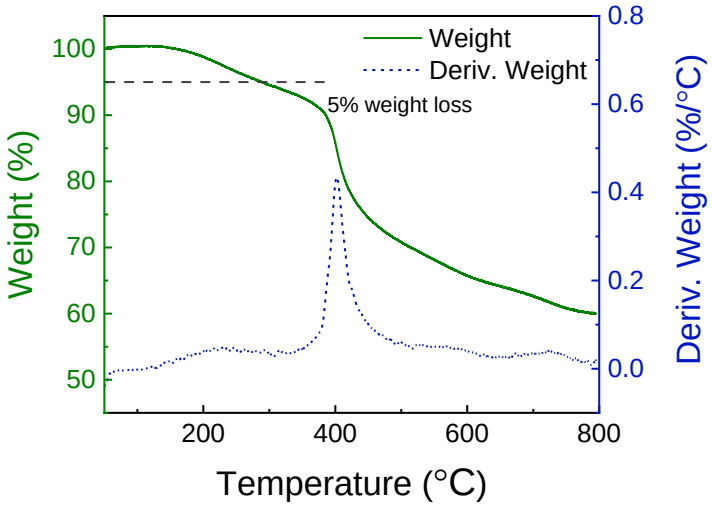



**Fig. S10.** TGA and DTG curves of the COF-DT-2.7 film under $N_2$.

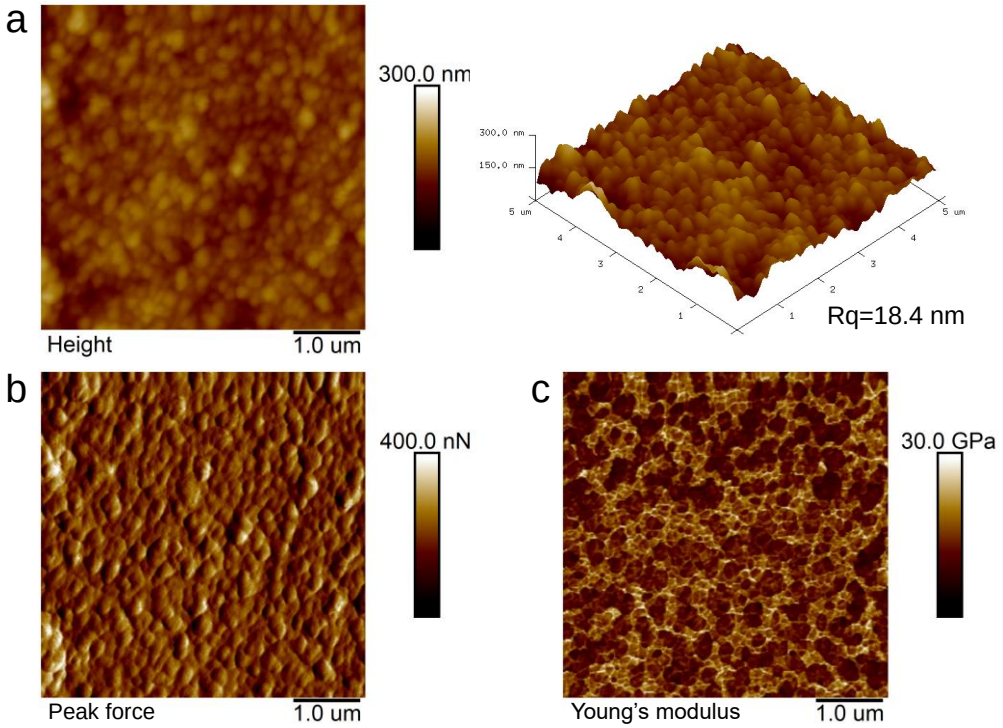



**Fig. S11.** AFM images of the COF-DT-2.7 film measured by height (a), peak force (b), and Young's modulus (c) modes.

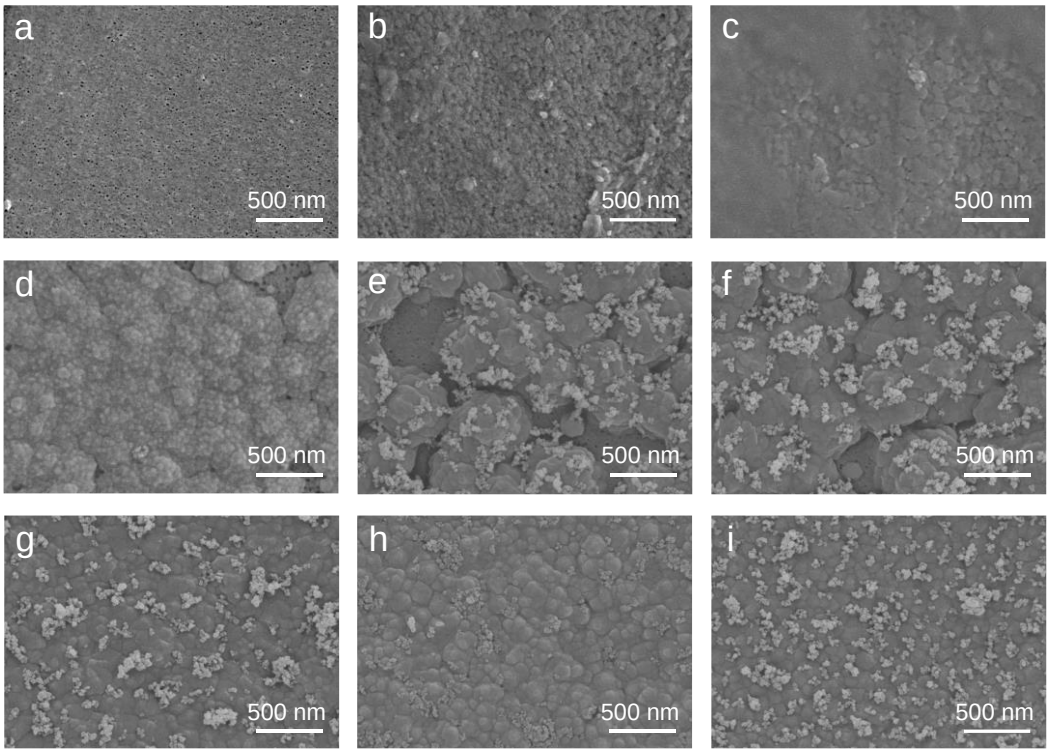



**Fig. S12.** Surface SEM images of the PAN (a), COF-DT-0.9/PAN (b), COF-DT-1.2/PAN (c), COF-DT-1.5/PAN (d), COF-DT-1.8/PAN (e), COF-DT-2.1/PAN (f), COF-DT-2.4/PAN (g), COF-DT-2.7/PAN (h), COF-DT-3.0/PAN (i) membranes.

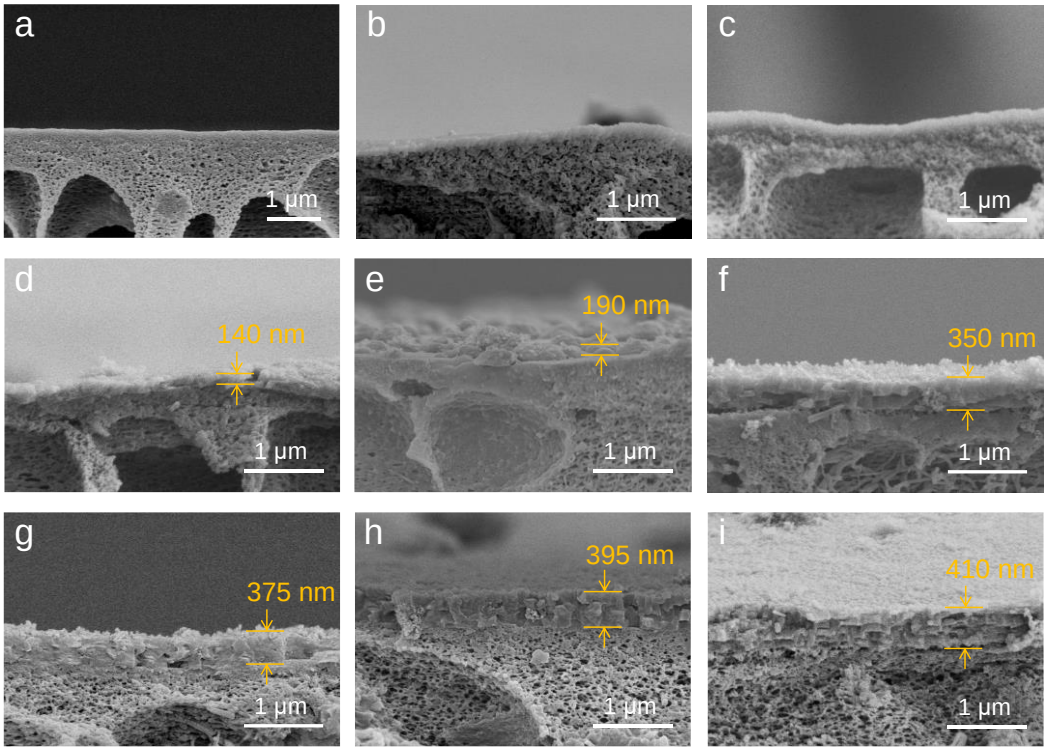



**Fig. S13.** Cross-section SEM images of the PAN (a), COF-DT-0.9/PAN (b), COF-DT-1.2/PAN (c), COF-DT-1.5/PAN (d), COF-DT-1.8/PAN (e), COF-DT-2.1/PAN (f), COF-DT-2.4/PAN (g), COF-DT-2.7/PAN (h), COF-DT-3.0/PAN (i) membranes.

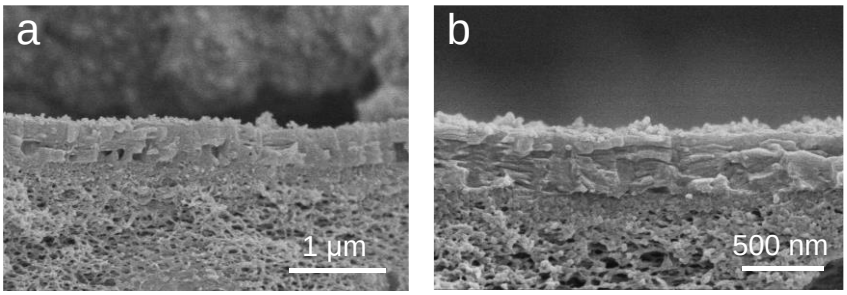



**Fig. S14**. Cross-section SEM images of the COF-DT-3.0/PAN membrane with different magnification factors.

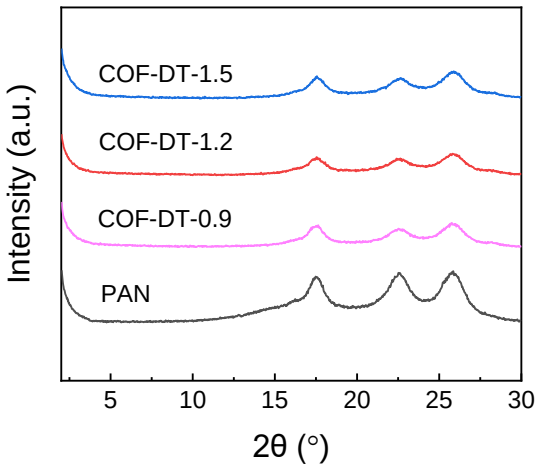



**Fig. S15.** XRD patterns of various COF-DT/PAN membranes prepared using different TAPB concentrations.

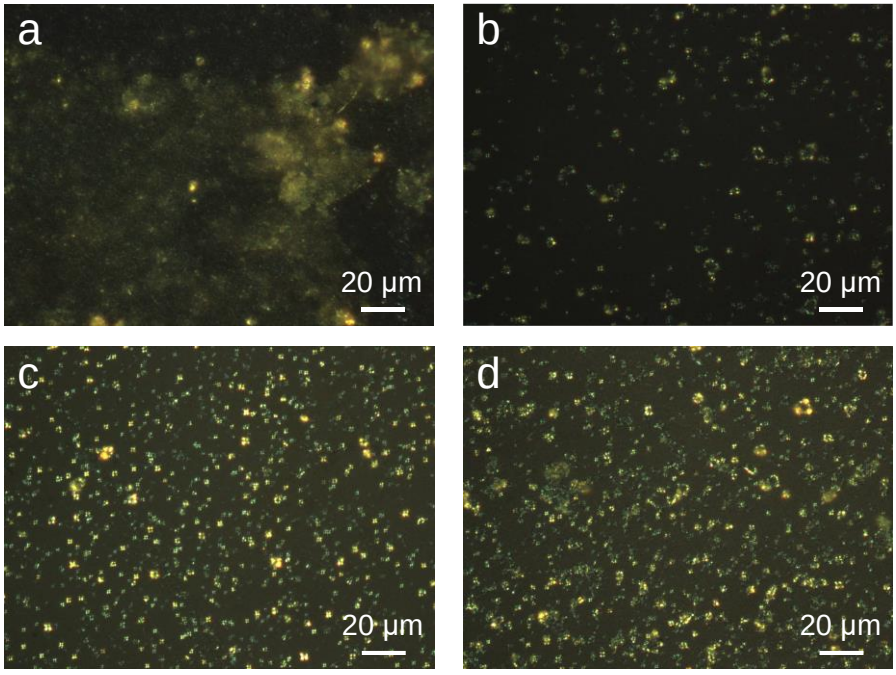



**Fig. S16.** Microscopic images of the COF-DT-2.1 (a), COF-DT-2.4 (b), COF-DT-2.7 (c), COF-DT-3.0 (d) films.

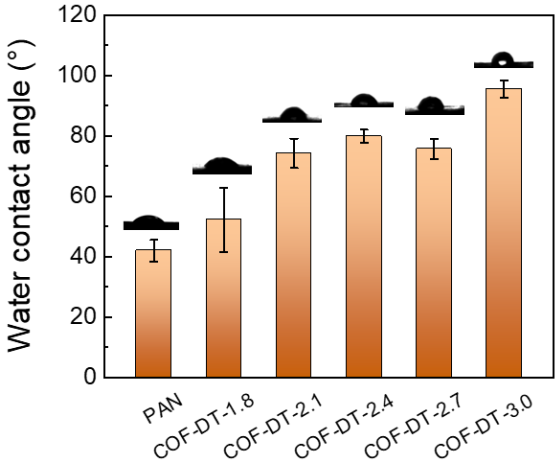



**Fig. S17.** Water contact angels of the PAN (a), COF-DT-1.8/PAN (b), COF-DT-2.1/PAN (c), COF-DT-2.4/PAN (d), COF-DT-2.7/PAN (e), COF-DT-3.0/PAN (f) membranes.

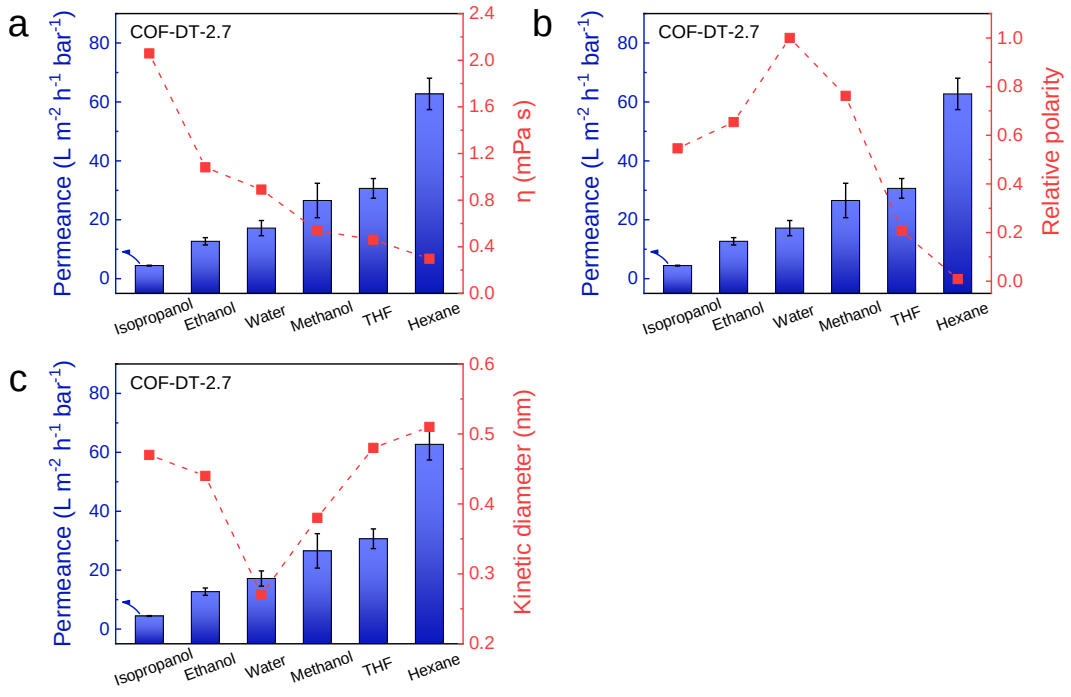



**Fig. S18.** The plots of solvent viscosity (a), relative polarity (b), and kinetic diameter (c) versus solvent permeance through the COF-DT-2.7/PAN membrane.

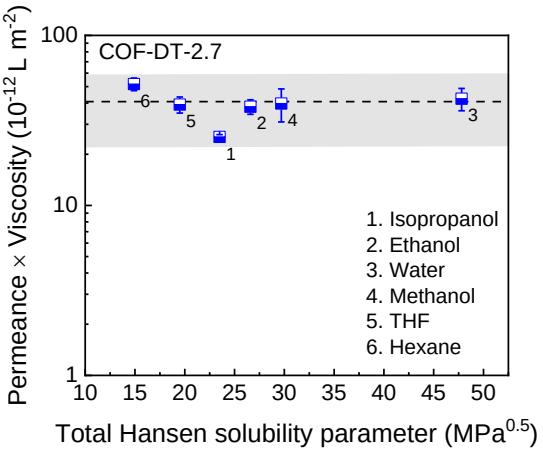



**Fig. S19.** Product of solvent permeance and viscosity as a function of the total Hansen solubility parameter for the COF-DT-2.7/PAN membrane.

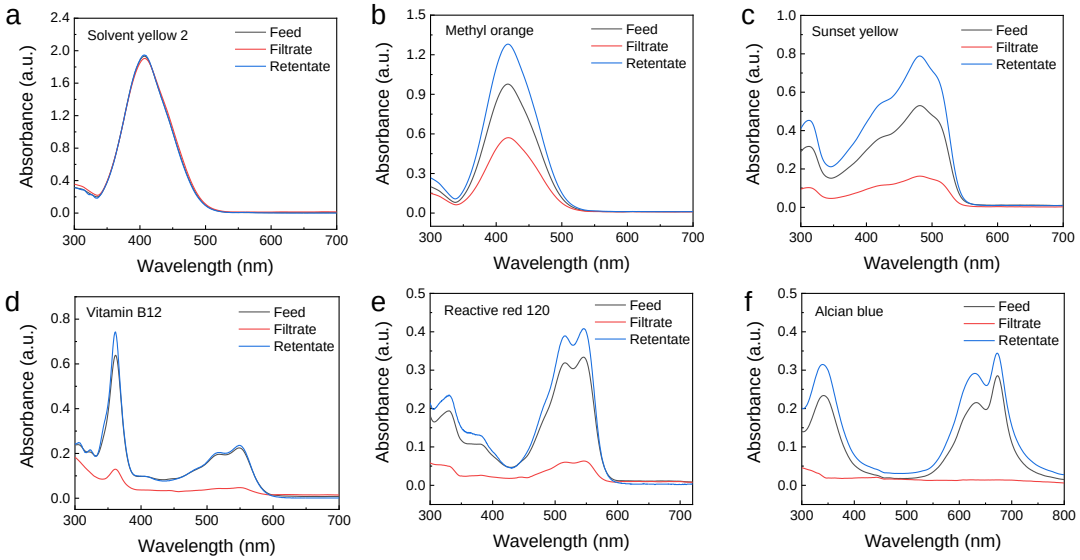



**Fig. S20.** UV-vis absorption spectra of various dye solution in ethanol (20 ppm) before and after filtration through the COF-DT-2.7/PAN membrane.

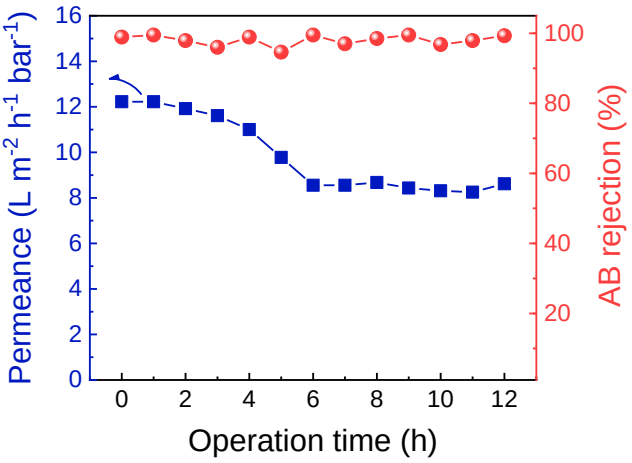
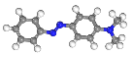
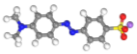
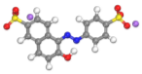
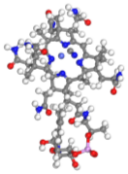
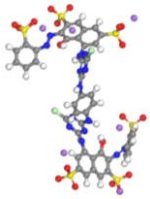



**Fig. S21.** Long-term separation stability of the COF-DT-2.7/PAN membrane toward the ethanolic AB solution in a crossflow filtration under 4 bar.

## 2. Tables

**Table S1.** Detailed properties of different dye molecules used in this work.

| Dye | Structure | Molecular size (Å) | Molecular weight (g/mol) | Charge | UV-vis absorption peak (nm) |
|---|---|---|---|---|---|
| Solvent yellow 2 |  | 15.7×7.0×4.1 | 225.29 | 0 | 408 |
| Methyl orange |  | 18.6×7.4×6.6 | 327.33 | − | 420 |
| Sunset yellow |  | 19.7×9.8×7.1 | 452.36 | − | 482 |
| Vitamin B12 |  | 22.6×17.1×7.0 | 1355.38 | 0 | 362 |
| Reactive red 120 |  | 25.3×17.2×12.4 | 1469.98 | − | 545 |

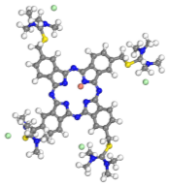
| | | | | | |
|---|---|---|---|---|---|
| Alcian blue |  | 26.1×24.5×15.4 | 1298.86 | + | 673 |

**Table S2.** Element compositions of membranes.

| Membranes | C (%) | N (%) | O (%) |
|---|---|---|---|
| PAN | 66.8 | 3.9 | 29.3 |
| COF-DT | 80.4 | 5.5 | 14.1 |

**Table S3.** Solvent properties.

| Solvent | Viscosity at 25 ℃ (mPa s) [1] | Relative polarity [2, 3] | Kinetic diameter (nm) [1, 4] | Total Hansen solubility parameter ($MPa^{0.5}$) [1] |
|---|---|---|---|---|
| Isopropanol | 2.06 | 0.546 | 0.47 | 23.5 |
| Ethanol | 1.08 | 0.654 | 0.44 | 26.6 |
| Water | 0.92 | 1 | 0.27 | 47.8 |
| Methanol | 0.54 | 0.762 | 0.38 | 29.7 |
| THF | 0.46 | 0.207 | 0.48 | 19.5 |
| Hexane | 0.29 | 0.009 | 0.51 | 14.9 |

## 3. References

1. A. Buekenhoudt, F. Bisignano, G. De Luca, P. Vandezande, M. Wouters and K. Verhulst, *J. Membr. Sci.*, 2013, **439**, 36-47.

2. Q. Yang, Y. Su, C. Chi, C. T. Cherian, K. Huang, V. G. Kravets, F. C. Wang, J. C. Zhang, A. Pratt, A. N. Grigorenko, F. Guinea, A. K. Geim and R. R. Nair, *Nat. Mater.*, 2017, **16**, 1198-1202.

3. P. J. Linstrom and W. G. Mallard, *J. Chem. Eng. Data*, 2001, **46**, 1059-1063.

4. J. Liu, S. Wang, T. Huang, P. Manchanda, E. Abou-Hamad and S. P. Nunes, *Sci Adv*, 2020, **6**, eabb3188.