

Supporting Information

Enhanced stability and separation efficiency of graphene oxide membranes in organic solvent nanofiltration

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Table S1. Performances of GO-based membranes for molecular separations in organic solvents

	Materials	Thickness	Solvent permeance (L m ⁻² h ⁻¹ bar ⁻¹)	Rejection
Yang et al. ^{S1}	HLGO	8 nm	7.5 (methanol)	99% for Chrysoidine G (249 g mol ⁻¹)
Aba et al. ^{S2}	GO hollow fiber membrane (wet)	1.5 μm	3.97 (methanol)	97% for MO (327.3 g mol ⁻¹)
Chong et al. ^{S3}	GO hollow fiber membrane	150 nm	2.8 (water); 7.54 (acetone)	90% for methyl red (269.3 g mol ⁻¹) in water
Hua et al. ^{S4}	TPP/GO/HPE I	62 nm	14.9 (ethanol)	95% for Alcian blue (1299 g mol ⁻¹)
	TPP/GO/HPE I/PSS		3.1 (ethanol)	97% for Rose Bengal (1017 g mol ⁻¹)
Li et al. ^{S5}	GO/PI	70 nm	1 (ethanol)	95.34% for vitamin B12 (1355.4 g mol ⁻¹)
This work	GO/BA	60 nm	3.5 (methanol)	95% for AF (585.54 g mol ⁻¹); 99.0% for VB12

References:

- S1. 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.
- S2. N. F. D. Aba, J. Y. Chong, B. Wang, C. Mattevi and K. Li, *J. Membr. Sci.*, 2015, **484**, 87.
- S3. J. Y. Chong, N. F. Aba, B. Wang, C. Mattevi and K. Li, *Sci. Rep.*, 2015, **5**, 15799.
- S4. D. Hua and T.-S. Chung, *Carbon*, 2017, **122**, 604.
- S5. B. Li, Y. Cui, S. Japip, Z. Thong and T.-S. Chung, *Carbon*, 2018, **130**, 503.

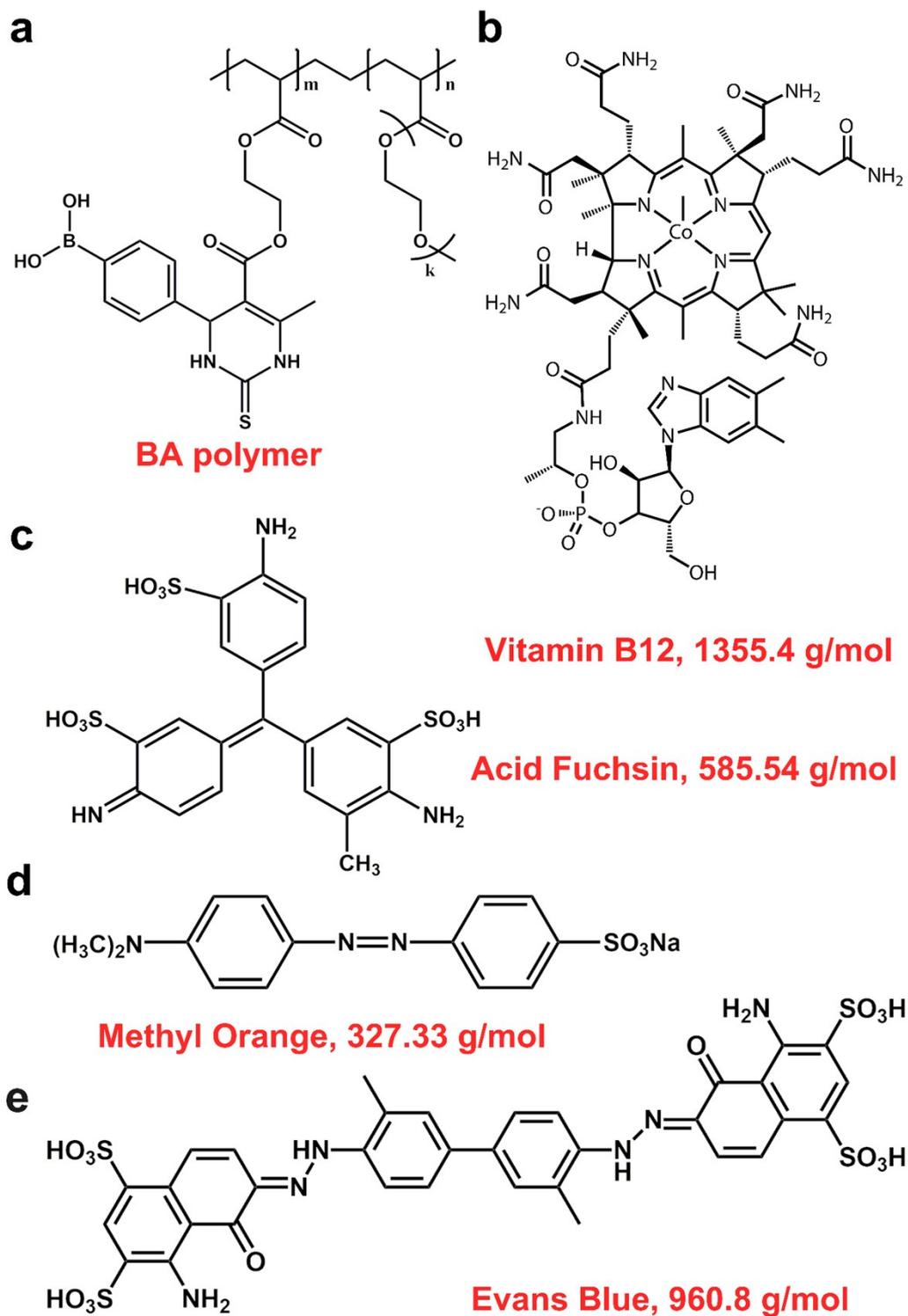


Fig. S1 Chemical structures of BA polymer (a), vitamin B12 (b), acid fuchsin (c), methyl orange (d) and Evans blue (e).

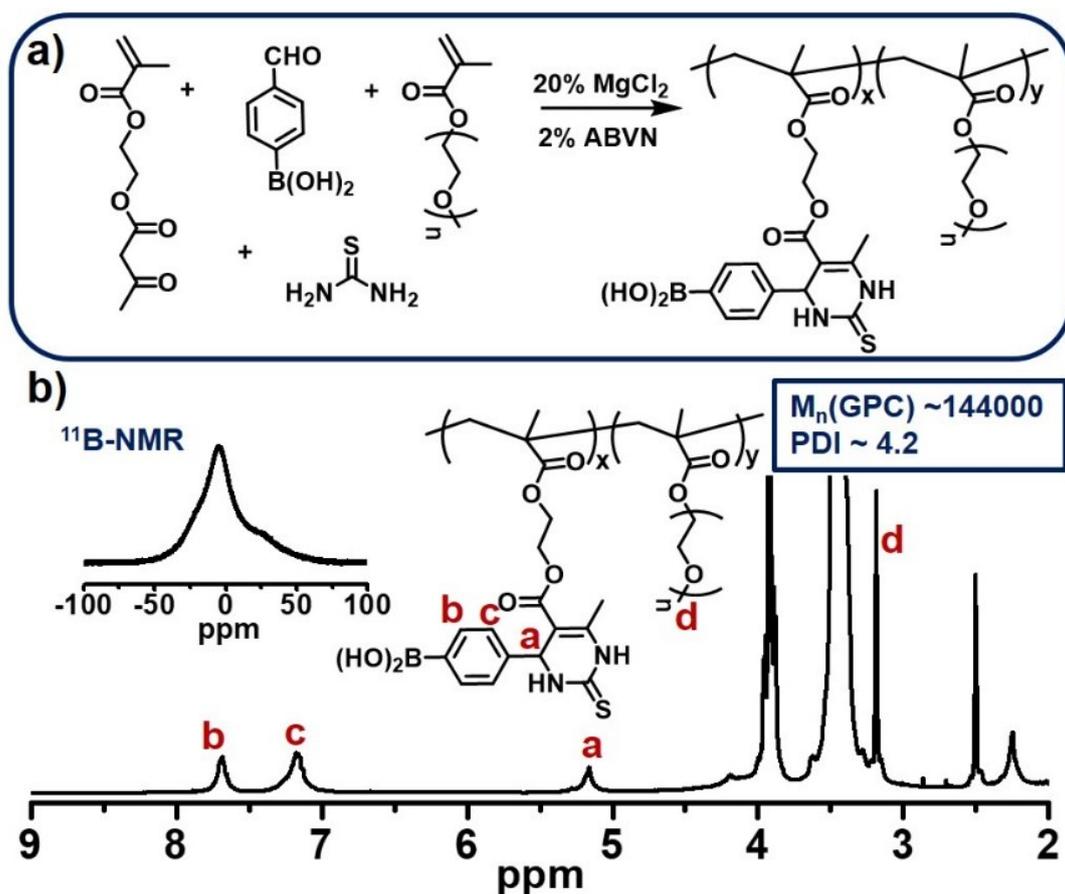


Fig. S2 (a) One pot preparation of BA polymer via the combination of the Biginelli reaction and radical polymerization. (b) ¹H and ¹¹B NMR spectra (DMSO-*d*₆ + D₂O, 400 MHz) of BA polymer.

In a 100 mL Schlenk tube, AEMA (2.14 g, 10.0 mmol), 4-formylphenylboronic acid (1.50 g, 10.0 mmol), thiourea (1.14 g, 15.0 mmol), MgCl₂ (0.19 g, 2.0 mmol), polyethylene glycol maleate (PEGMA, M_n: 950 g mol⁻¹; 9.50 g, 10 mmol) and 2,2'-Azobis(2,4-dimethyl)valeronitrile (ABVN, 0.05 g, 0.2 mmol) were mixed in 20.0 mL of acetic acid. The tube was sealed with a rubber septum and purged by nitrogen flow for 20 min, then kept in a 70 °C oil bath for 12 h. The polymerization was quenched using an ice-water bath. Then the mixture was precipitated in diethyl ether for 3 times and dried under vacuum to obtain the pure BA polymer for further characterization and use.

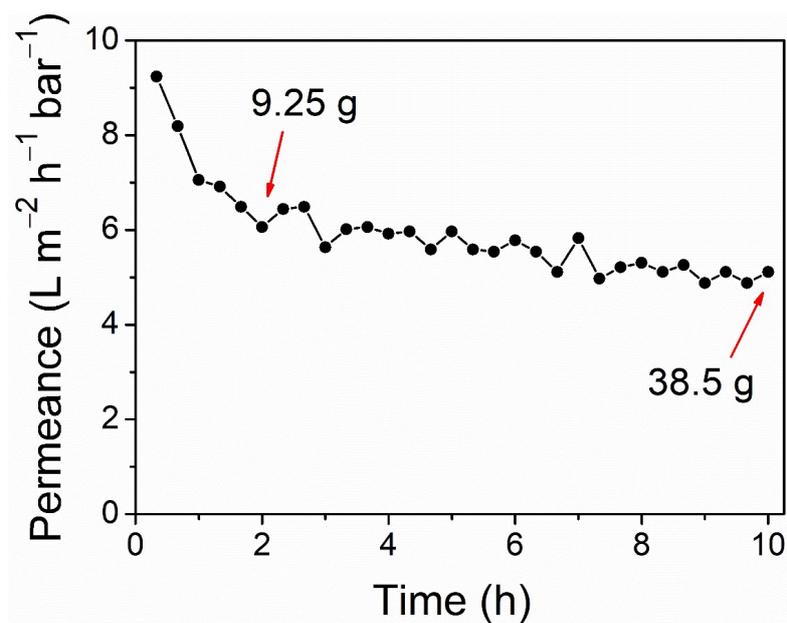


Fig. S3 A typical process of stabilizing a 44-GO-0.5BA-T membrane by filtrating methanol to achieve a steady flux.

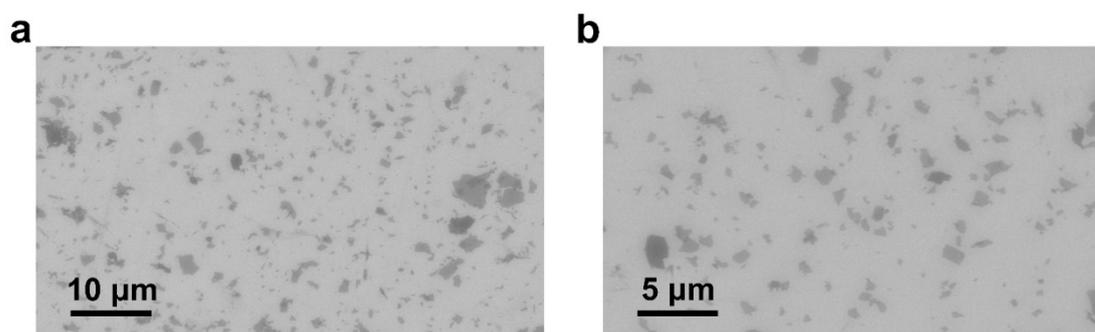


Fig. S4 (a, b) SEM images of GO sheets in different resolutions.

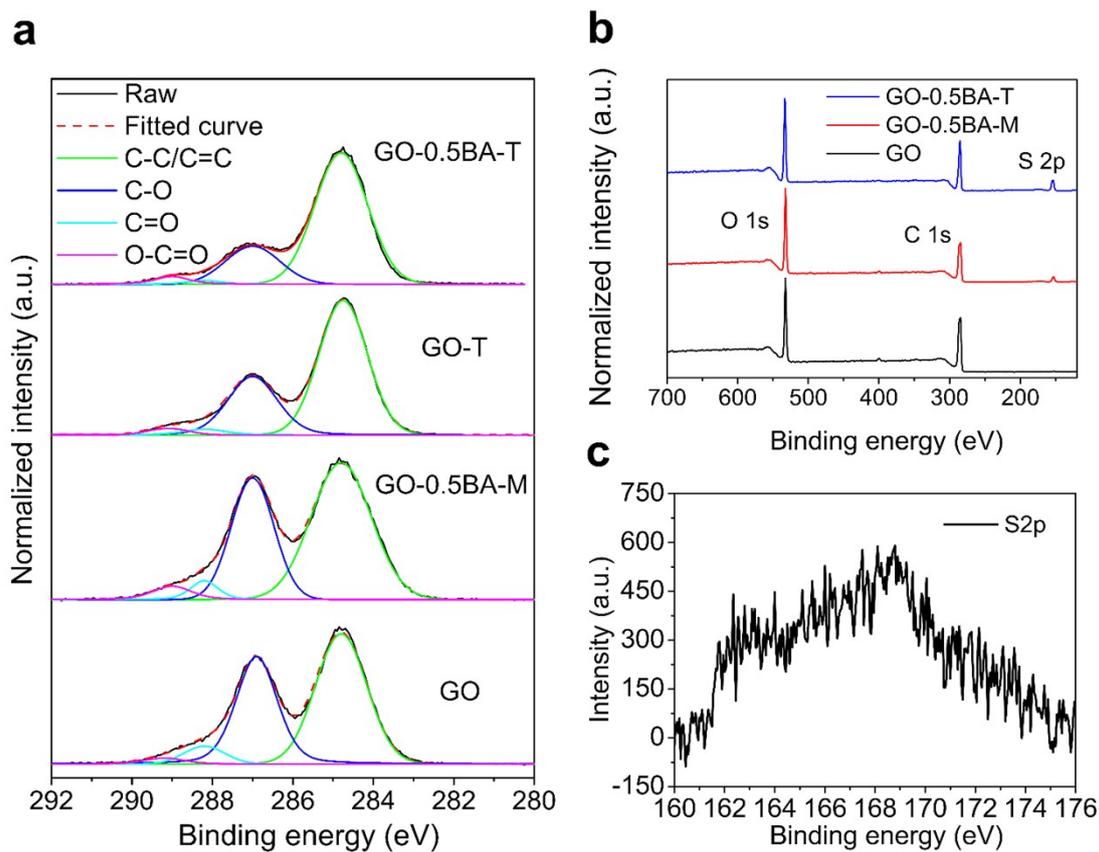


Fig. S5 (a) C1s XPS spectra of GO, GO-0.5BA-M, GO-T and GO-0.5BA-T membranes. (b) XPS survey spectra of GO, GO-0.5BA-M and GO-0.5BA-T membranes. (c) S 2p XPS spectra of a GO-0.5BA-T membrane.

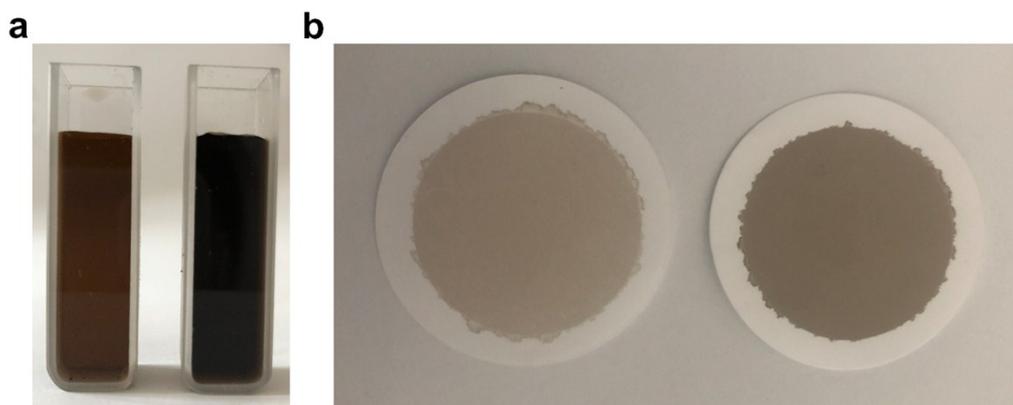


Fig. S6 (a) The digital photos of GO (left) and GO-0.5BA-T (right) dispersions. (b) The digital photos of 44-GO (left) and 44-GO-0.5BA-T (right) membranes on the nylon microfiltration membrane.

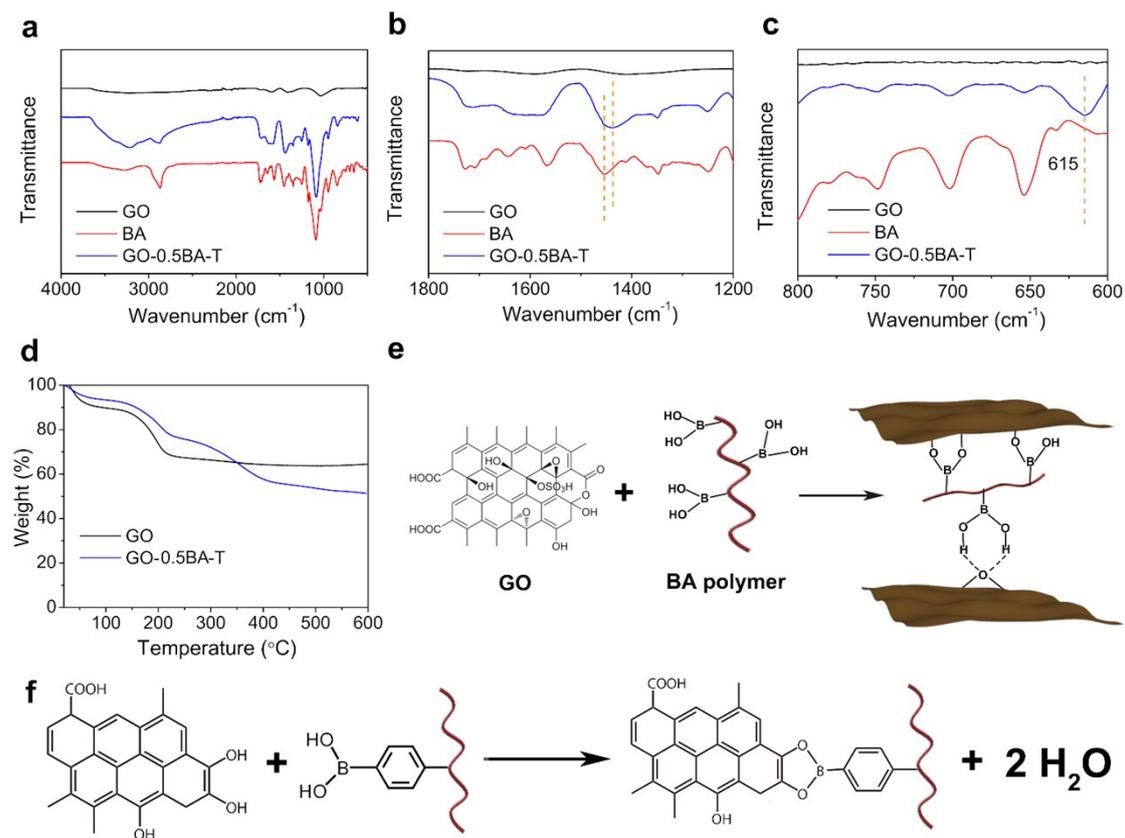


Fig. S7 (a) FTIR spectra and (b, c) magnified FTIR spectra of a GO membrane, BA polymer and a GO-0.5BA-T membrane. (d) Thermogravimetric (TGA) analyses of GO and GO-0.5BA-T membranes. (e) Schematic illustration of the covalent and noncovalent interactions between BA polymer and GO. (f) Reaction scheme between boronic moiety of BA polymer and the GO sheet.

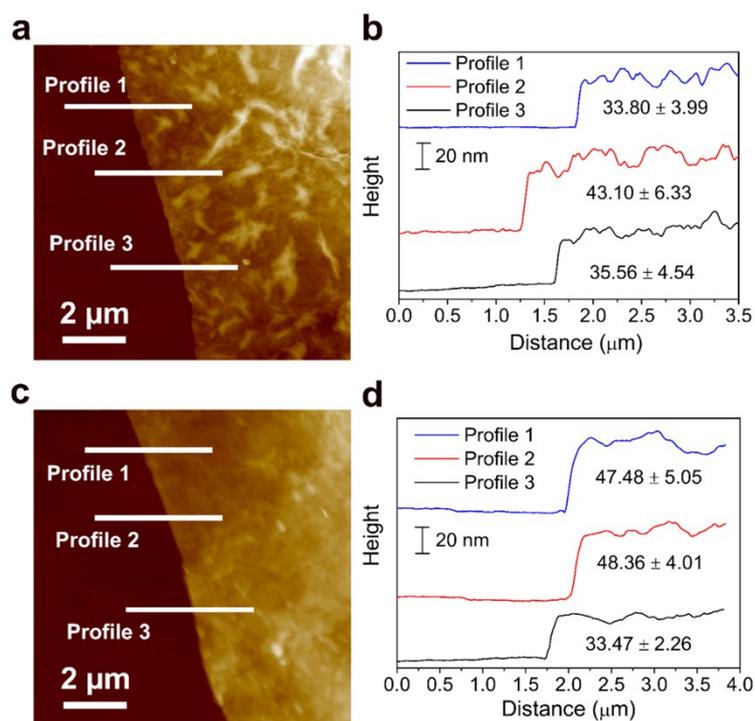


Fig. S8 AFM images and the corresponding height profiles of a 44-GO membrane (a, b) and a 44-GO-0.5BA-M membrane (c, d).

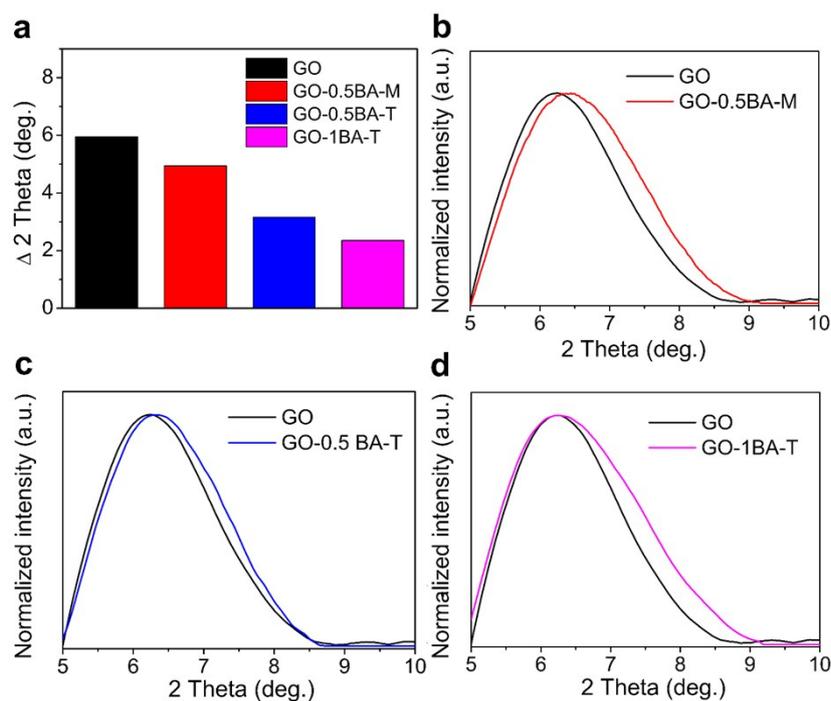


Fig. S9 (a) The differences of 2 Theta in XRD patterns between dried membranes and membranes in methanol. (b-d) The XRD patterns of GO, GO-0.5BA-M (b), GO-0.5BA-T (c) and GO-1BA-T (d) membranes in methanol.

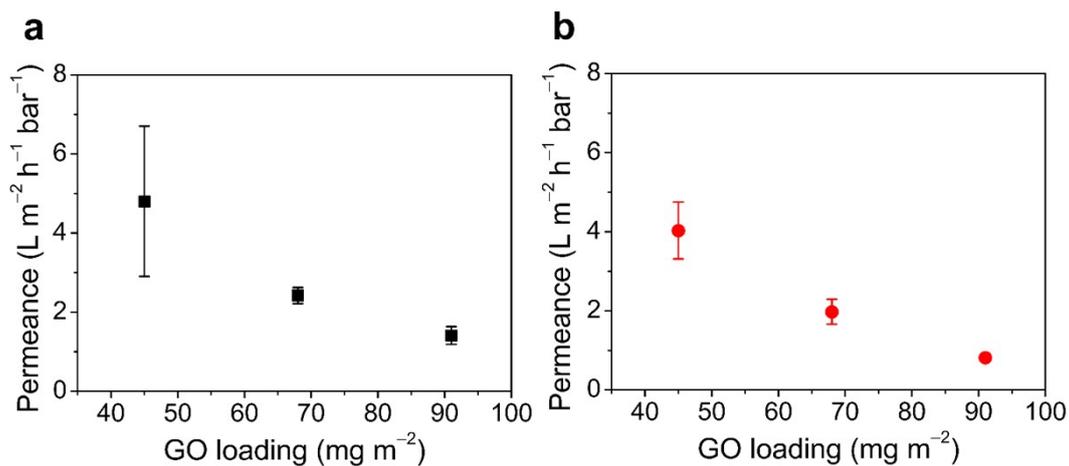


Fig. S10 The methanol permeances of m-GO (a) and m-GO-0.5BA-T (b) membranes with different GO loadings.

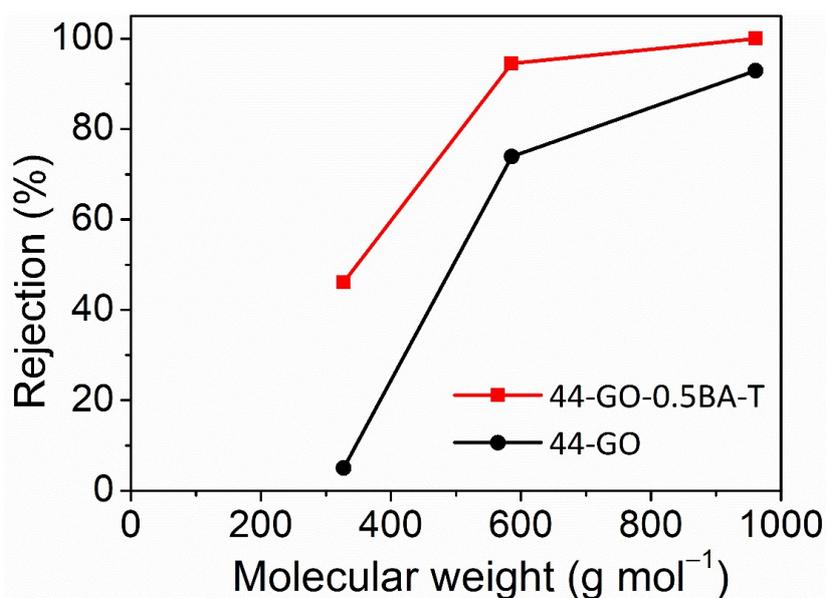


Fig. S11 MWCO curves of the 44-GO and 44-GO-0.5BA-T membranes in methanol.

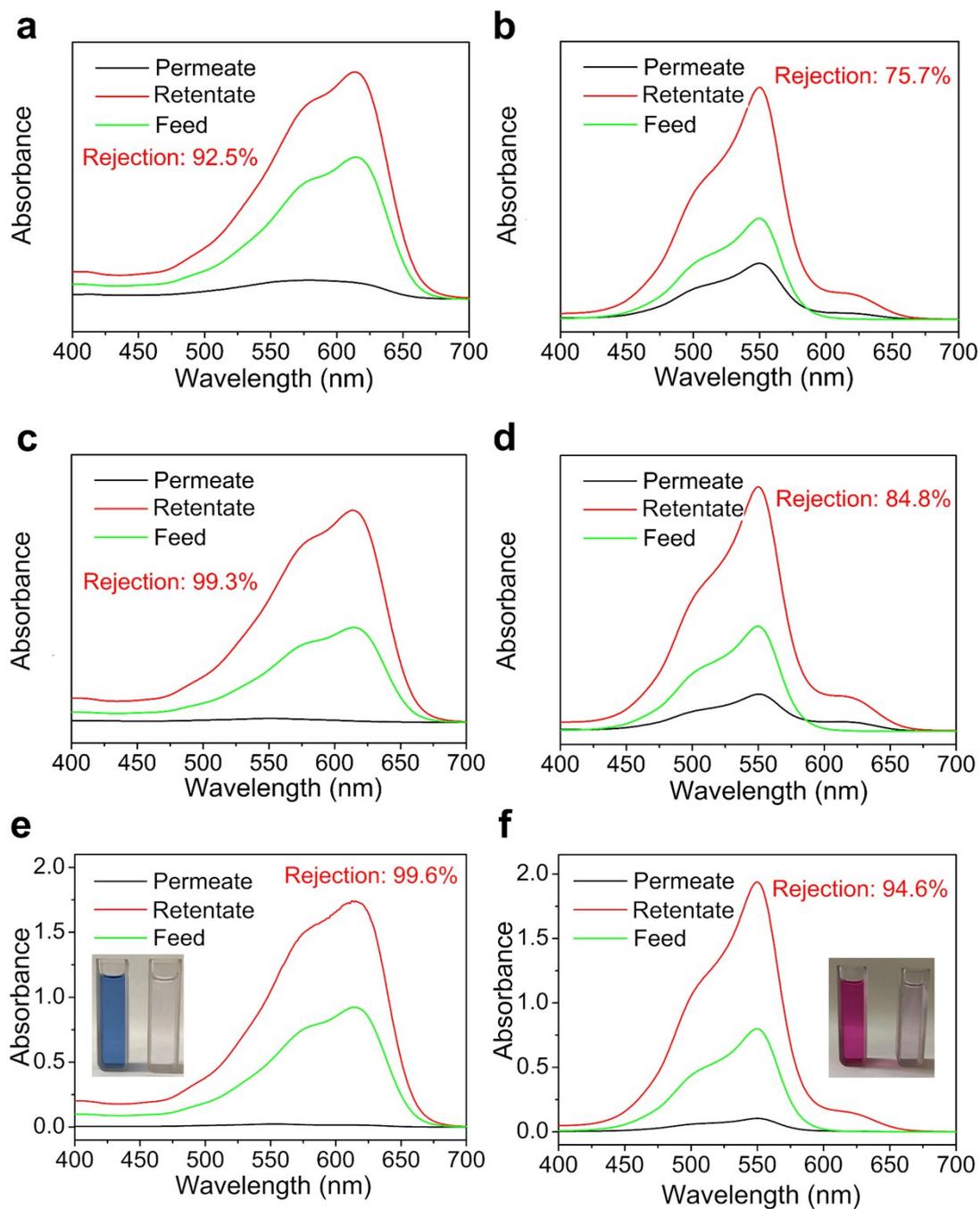


Fig. S12 UV-vis adsorption spectra of Evans Blue (a, c, e) and acid fuchsin (b, d, f) methanol solution before and after filtration through a 44-GO membrane (a, b), a 44-GO-0.5BA-M membrane (c, d) and a 44-GO-0.5BA-T membrane (e, f).

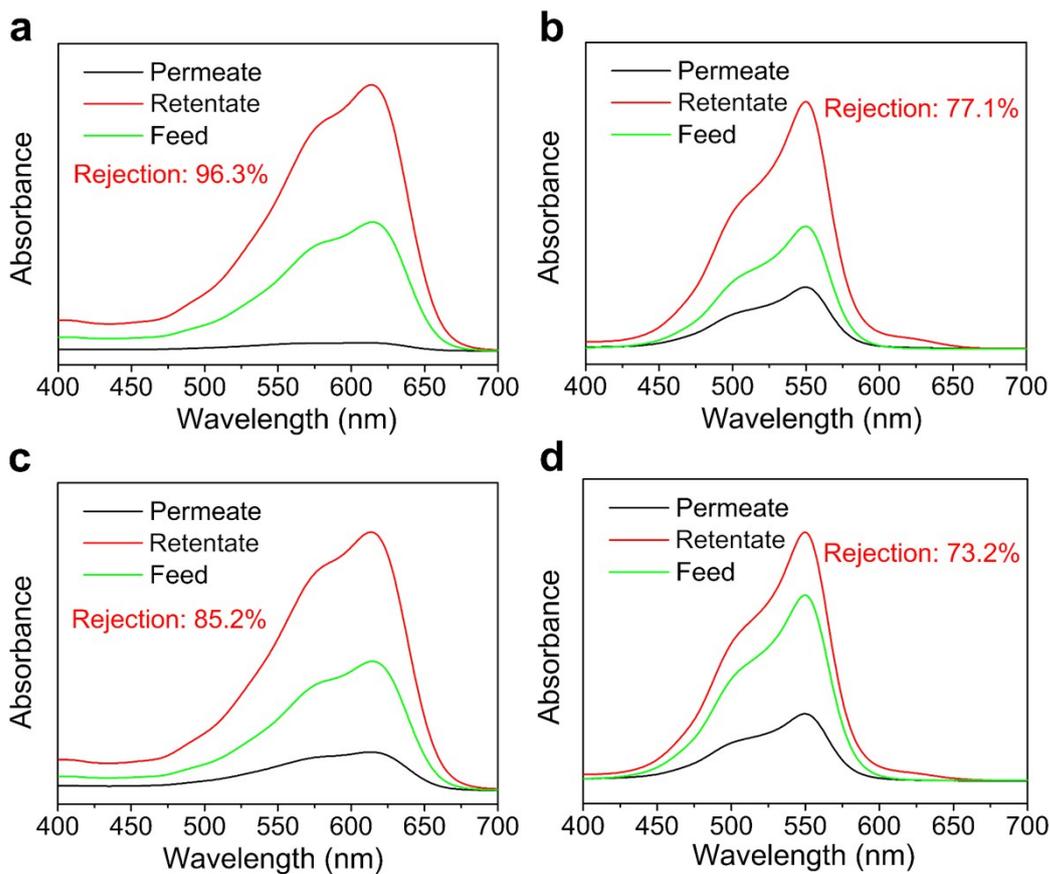


Fig. S13 UV-vis adsorption spectra of Evans Blue (a, c) and acid fuchsin (b, d) methanol solution before and after filtration through a 44-GO-0.1BA-T membrane (a, b) and a 44-GO-1BA-T membrane (c, d).

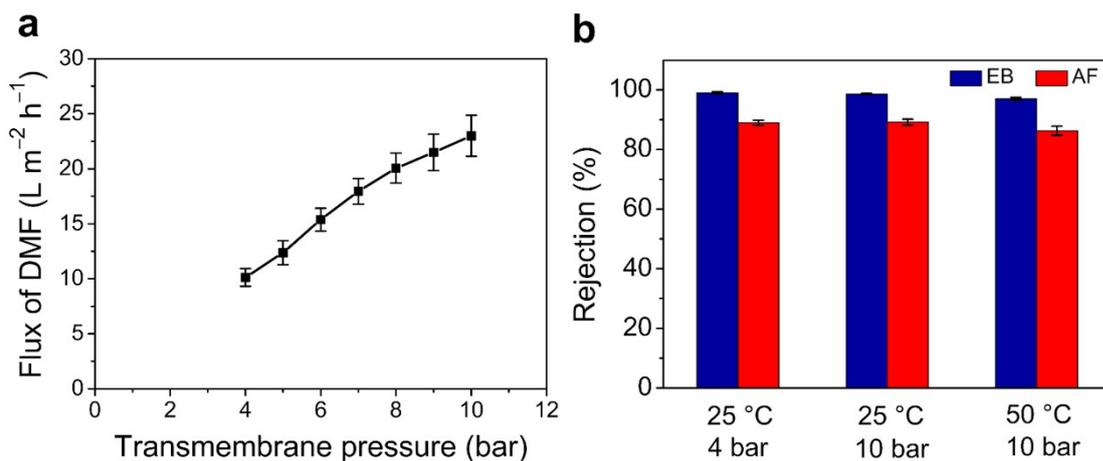


Fig. S14 (a) The variations of DMF flux with transmembrane pressure at the range of 4~10 bar. (b) The rejections for EB and AF in DMF solutions of the 44-GO-0.5BA-T membrane under different pressures and temperatures as indicated.

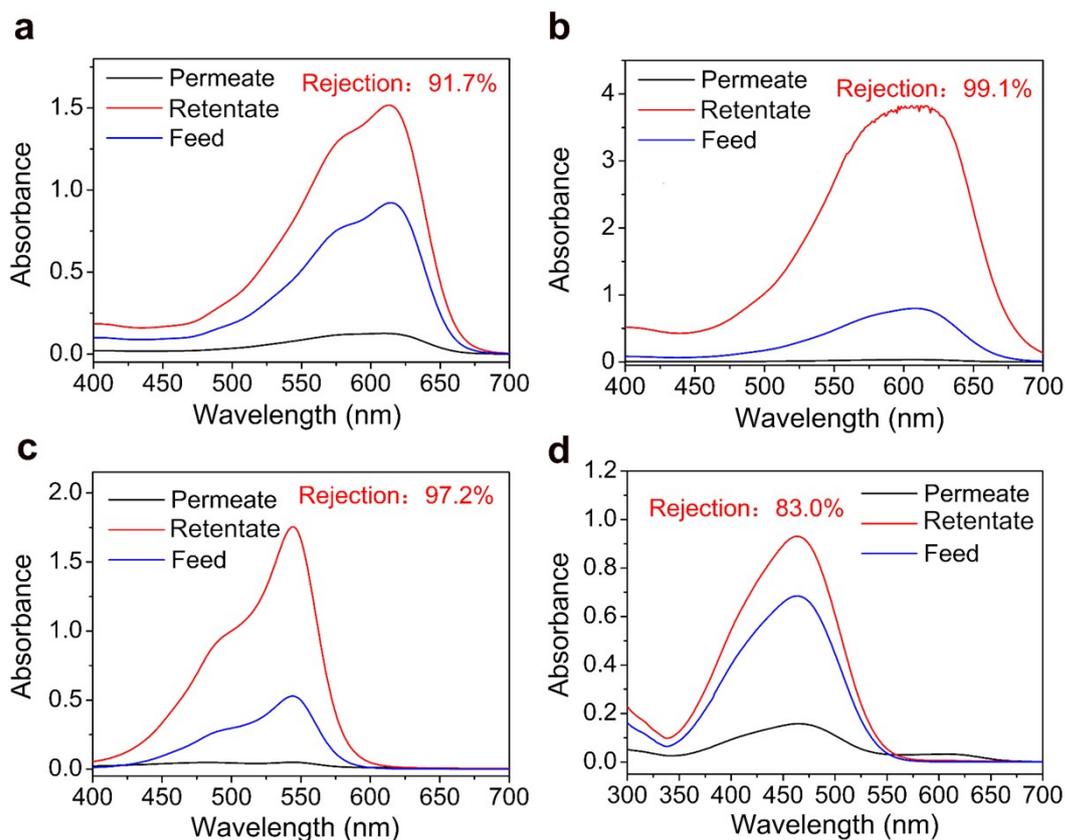


Fig. S15 UV-vis adsorption spectra of EB methanol solution (a), EB aqueous solution (b), AF aqueous solution (c) and MO aqueous solution (d) before and after filtration through a 44-GO-0.5BA-T membrane which was soaked in water for one month.

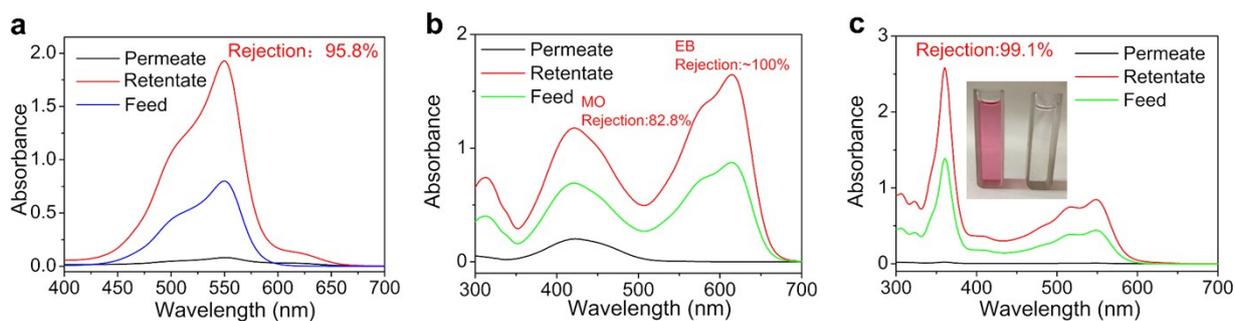


Fig. S16 (a) The UV-vis adsorption spectra of AF in methanol before and after filtration through a 44-GO-0.5BA-T membrane after soaking in water for one month. (b, c) The UV-vis adsorption spectra of mixed EB-MO solution (b) and VB12 (c) in methanol before and after filtration through a 44-GO-0.5BA-T membrane. Insert images were photos of feed solution (left) and permeate solution (right) of VB12 methanol solution.

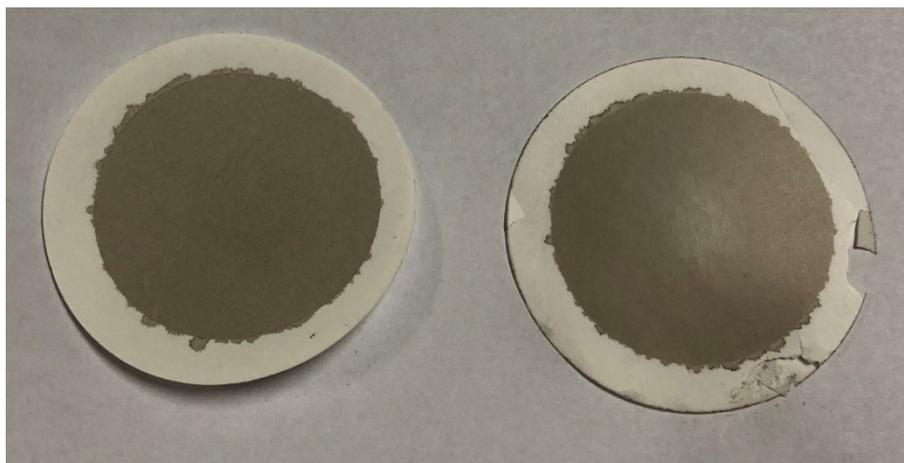


Fig. S17 The digital photos of 44-GO-0.5BA-T membranes on the nylon microfiltration membrane after soaking in 0.1 M HCl (left) and 0.1 M NaOH (right) under vigorous shaking for one and a half month.