# **Electronic Supporting Information**

# Facile preparation of COFs composite membranes for nanofiltration by stoichiometric spraying layer-by-layer selfassembly

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#### 1. Experimental Section

*Materials:*1,4-dioxane (Diox, 99.0%), acetic acid (HAc, 99.5%), ethanol, acetone, dichloromethane (DCM), ethyl acetate (EA) and sodium hydroxide (NaOH, 99%) were bought from Beijing chemical factory. Water-soluble aniline blue (98%), acid orange red (98%), acid magenta (98%), methyl blue (98%), chrome black T (98%), and Congo Red (98%) were provided by Beijing Inoke Co., Ltd. 1,4-diaminobenzene (PDA, 99.0%, Adamas) and 1,3,5-benzenetricarboxaldehyde (TFB, 98%, Zhengzhou Ames Chemical Co., Ltd.) were employed. Polyacrylonitrile ultrafiltration membranes (PAN, MWCO 50,000) were provided by Beijing Saipuruite Company.

**Preparation of COF-LZU1 membrane:** PAN ultrafiltration membranes were immersed in NaOH aqueous solution (1 mol L<sup>-1</sup>) at 30 °C for 1 h, and then rinsed using DI water and dried at room temperature. The PDA and TFB dioxane solution were sprayed onto the PAN membrane alternately with stoichiometric ratio, and reacted under vacuum at 30 °C. The obtained COF-LZU1 membranes were rinsed using ethanol and dried.

*Nanofiltration:* The filtration was carried out using a 50 mg L<sup>-1</sup> dyes solution at 25°C. The permeance (P, L m<sup>-2</sup> h<sup>-1</sup> MPa<sup>-1</sup>) is expressed as Eq. (1):

$$P = \frac{V}{A \ t \ \Delta P} \tag{1}$$

where V is the permeate volume, t the time,  $\Delta p$  the trans-membrane pressure, A the effective membrane area (19.6 cm<sup>2</sup>). The rejection of dyes is calculated from Eq. (2):

$$R(\%) = \left(1 - \frac{C_p}{C_0}\right) \times 100 \tag{2}$$

where  $C_p$  and  $C_0$  denote the dye concentrations in the permeate and feed solution, respectively. The dye concentration was measured using an UV-vis spectrophotometer. In the nanofiltration process, the flux can be expresses with the resistance-in-serials model,

$$J_v = \frac{\Delta p}{\mu(R_a + R_b)} \tag{3}$$

where  $J_v$  is the membrane flux (L m<sup>-2</sup> h<sup>-1</sup>),  $R_a$  the resistance of PAN layer (m<sup>-1</sup>), and  $R_b$ 

the resistance of COFs layer (m<sup>-1</sup>)

*Stability and Post-treatment of the Membranes:* The solvent resistance of COMs was evaluated by immersing the COMs in various solvents, i.e., deionized water (DI water), ethanol, acetone, dichloromethane (DCM), and ethyl acetate (EA) at room temperature for 14 days and then used to filter 50 mg L<sup>-1</sup> of water-soluble aniline blue solution. And the operational stability of COF-LZU1 membrane was evaluated by filtering 50 mg L<sup>-1</sup> of water-soluble aniline blue solution for 45 h. To eliminate defects and pinholes in the COF-LZU1 layer and further improve the rejection, post-treatment was conducted by immersing COF-LZU1 membranes in diluted TFB and PDA solutions (in 1, 4-dioxane) with different concentrations under vacuum at room temperature for two days. After rinsing with DCM, THF and acetone, and activation by solvent exchange with methanol (3 times), the COF-LZU1 membranes were used to filter 50 mg L<sup>-1</sup> of acid orange red solution.

*Characterization:* The morphology of the membranes was characterized by a field emission scanning electron microscopy (SEM, Hitachi S-4800, Japan, EDS, XFlash 6160, BRUKER). Atomic force microscopy (AFM) measurements were performed using a Digital Instrument Multimode Nanoscope in the tapping mode under ambient conditions. The morphology of the particles was analyzed with FEI Talos F200S transmission electron microscope. The functional groups of COF membranes were analyzed by Fourier transform infrared spectroscopy (FTIR, Affinity-1, Shimadzu, Japan). The crystal structure of the membranes was analyzed by X-ray diffraction analyzer (Shimadzu, XRD-6000, Cu k $\alpha$ ), and surface analyses were performed by Xray photoelectron spectroscopy (XPS, Thermofisher, ESCALAB 250Xi, England). Nanoindentation (G200) was used for testing the binding force between COF-LZU1 layer and PAN substrate. Nitrogen sorption/desorption of MOFs were measured on a static volumetric adsorption of COF-LZU1 and PAN/ COF-LZU1 were measured on a static volumetric adsorption system(Boynton Beach, Florida), and the Brunauer-Emmett-Teller(BET) surface area and pore diameter were calculated.



### 2. Figures and Tables





N Ka1\_2



**Figure S1.** Characterization of COF-LZU1/PAN membrane. (a) FTIR spectra. (b) and (c) Mapping of N elements of the cross-section. (d) The selected area electron diffractions (SAED) characterization.



**Figure S2.** N element XPS characterization. (a) N element XPS of PAN pristine membrane. (b) N element XPS of COF-LZU1/PAN membrane.



**Figure S3.** Nanoindentation characterization of COF-LZU1/PAN membrane. (a) Nanoindentation test. (b) Critical load value. (c) Hardness.



**Figure S4.** (a)N<sub>2</sub> absorption/ desorption isotherm spectra of COF-LZU1 and PAN/ COF-LZU1 membranes. Pore distribution of (b) COF-LZU1 and (c) COF-LZU1/PAN membrane.



Figure S5. Effect of HAc concentrations on the membranes surface (SEM). (a) 0 mol  $L^{-1}$ . (b) 0.05 mol  $L^{-1}$ . (c) 0.15 mol  $L^{-1}$ . (d) 0.3 mol  $L^{-1}$ .



Figure S6. Effect of HAc concentrations on the membranes surface (AFM). (a, e) 0 mol  $L^{-1}$ . (b, f) 0.05 mol  $L^{-1}$ . (c, g) 0.15 mol  $L^{-1}$ . (d, h) 0.3 mol  $L^{-1}$ .



**Figure S7.** Effect of numbers of LbL layers on the SEM of membranes. (a, b) PAN pristine membrane. (c, d) 1 layer. (e, f) 2 layers. (g, h) 3 layers. (i, j) 4 layers.



**Figure S8.** Effect of numbers of LbL layers on AFM of membranes surface. (a, f) PAN membrane. (b, g) 1 layer. (c, h) 2 layers. (d, i) 3 layers. (e, j) 4 layers.



Figure S9. Effect of PDA concentrations on SEM of membranes surface. (a)  $0.069 \text{ mol } L^{-1}$ . (b)  $0.035 \text{ mol } L^{-1}$ . (c)  $0.023 \text{ mol } L^{-1}$ . (d)  $0.014 \text{ mol } L^{-1}$ .



**Figure S10.** Effect of PDA concentrations on the AFM of membranes surface. (a, e) 0.069 mol  $L^{-1}$ . (b, f) 0.035 mol  $L^{-1}$ . (c, g) 0.023 mol  $L^{-1}$ . (d, h) 0.014 mol  $L^{-1}$ .



Acid orange

Mw=350.32





Acid magenta Mw=585.54

0 0=\$-0- Na+

0



Congo red Mw=696.68

Mw=461.38

**Chrome black T** 



Aniline blue Mw=737.72

Methyl blue Mw=799.80

`Ş́≈o °Ó Na⁺

Figure S11. Formula and molecular weight of different dyes.



**Figure S12.** SEM of COFs/PAN membranes after immersing in different solvents for 14 days. (a) Deionized water. (b) Ethanol. (c) Acetone. (d) Dichloromethane. (e) Ethyl acetate.



**Figure S13.** Revolution of permeance and rejection of membranes after immersing in different solvents for various time. (a) Deionized water (b) Ethanol. (c) Acetone. (d) Dichloromethane. (e) Ethyl acetate.



**Figure S14.** Long-term stability of COF-LZU1 membrane in nanofiltration of water-soluble aniline blue.



**Figure S15.** SEM images of membranes post-treated in TFB and PDA solutions with different concentrations. (a, b) 0.2 mmol L<sup>-1</sup> TFB, 0.3 mmol L<sup>-1</sup> PDA. (c, d) 0.5 mmol L<sup>-1</sup> TFB, 0.75 mmol L<sup>-1</sup> PDA. (e, f) 1.0 mmol L<sup>-1</sup> TFB, 1.5 mmol L<sup>-1</sup> PDA. (g, h) 2.0 mmol L<sup>-1</sup> TFB, 3.0 mmol L<sup>-1</sup> PDA. (i, j) 10 mmol L<sup>-1</sup> TFB, 15 mmol L<sup>-1</sup> PDA.



Figure S16. Permeance and rejection of membranes post-treated in TFB and PDA solutions with different concentrations.

	Membrane type	Dye molecule	P (L m <sup>-2</sup> h <sup>-1</sup>	Rejection (%)	Ref
			MPa <sup>-1</sup> )		
Inorganic NF	Ceramic NF	Chrome black T	247.5	>96.8	[2]
membrane					
	PDDA/PSS	Methyl blue	82.5	92	[3]
	PES-SPMA	Reactive Dyes	145	98	[4]
Organic polymer	PDA/PEI/PPS	anionic dye MLB	96	99.4	[5]
NF membrane	PAA/PVA/GA	Congo red	42	96	[6]
	PVDF/nanoclay/	Methyl blue	500	75	[7]
	chitosan				
Organic-inorganic	ZIF-8/PSS	Methyl blue	265	98.6	[8]
blending	ZIF-8/PES	Rose Bengal	13	98.95	[9]
membranes	(NaSS-AC)/PS	Acid red	58	96	[10]
	PANI-TiO <sub>2</sub> /PSF	Reactive Black	42	81.5	[11]
		Chrome black T	756.0	98.2	
		Methyl blue	485.8	99.2	
	COF-LZU1/	Congo red	534.3	98.6	
	Alumina	Acid Fuchsin	580.5	91.4	[11]
		Rose Bengal	390.8	99.1	
COFs composite		Acid orange red	465.1	92.41	
membranes		chrome black T	462.5	90.20	
		acid fuchsin	433.2	94.24	This study
	COF-LZU1/PAN	Congo red	415.4	96.50	
		aniline blue	407.6	99.43	
		methyl blue	398.3	98.34	

## Table S1. Performance comparison among various membranes towards dyes rejection

#### References

- [S1] P. Chen, M. Xiao, Z. Zhong, Z. Feng, W. Xing, Y. Fan, Desalination 2017, 404, 102-111.
- [S2] H. Tang, S. Ji, L. Gong, H. Guo, G. Zhang, Polym. Chem. 2013, 4, 5621-5628.

[S3] A. V. R. Reddy, J. J. Trivedi, C. V. Devmurari, D. J. Mohan, P. Singh, A. P. Rao, S. V. Joshi, P. K. Ghosh, *Desalination* 2005, 183, 301-306.

[S4] X. Yan, Z. Li, K. Su, T. Fan, C. Lei, Chem. Eng. J. 2018, 341.

[S5] W. Lu, N. Wang, G. Zhang, S. Ji, AlChE J. 2013, 59, 3834-3842.

[S6] P. Daraei, S. S. Madaeni, E. Salehi, N. Ghaemi, H. S. Ghari, M. A. Khadivi, E. Rostami, *J. Membr. Sci.* 2013, **436**, 97-108.

[S7] R. Zhang, S. Ji, N. Wang, L. Wang, G. Zhang, J. R. Li, Angew. Chem. Int. Ed. 2015, 126, 9933-9937.

[S8] Y. Li, L. H. Wee, A. Volodin, J. A. Martens, I. F. J. Vankelecom, *Chem. Commun.* 2014, **51**, 918-920.

[S9] S. Duffy, J. Membr. Sci. 2006, 286, 342-350.

[S10]V. R. Pereira, A. M. Isloor, A. K. Zulhairun, M. N. Subramaniam, W. J. Lau, A. F. Ismail, *RSC Adv.* 2016.

[S11] H. Fan, J. Gu, P. H. Meng, A. Knebel, D. J. Caro, Angew Chem Int Ed 2018.