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## **Supporting Information**

## Electrospun nanofiber substrates that enhance polar solvent separation from organic compounds in thin-film composites

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Comprising 11 pages: 5 tables and 6 figures.



Table S1. Molecular structure of dyes used in this work

Cross-linking duration(h)	S <sub>total</sub> /( m <sup>2</sup> ·g <sup>-1</sup> )	V <sub>total</sub> /( cm <sup>3</sup> ·g <sup>-1</sup> )
0	8.01	0.021
8	9.04	0.024
24	9.26	0.030

Table S2. Effect of cross-linking duration on the specific surface area and porevolume of PAN nanofibers

Solvent	Substrates	Cross-linking duration(h)	Reduction ratio of solid content gel content after 48h
DMF	asymmetrical	8	1.04%
	nanofibrous	8	1.74%
DMSO	asymmetrical	8	5.54%
	nanofibrous	8	0.90%

Table S3. Weight loss of cross-linked substrates degraded in aprotic solvents

Cross-linking duration(h)	d-spacing(Å)	particle size(nm)		
0	5.22	9.62		
4	5.20	9.34		
6	5.19	8.71		
8	5.23	10.01		
24	5.28	8.92		

Table S4. D-spacing and particle sizes of nanofibrous substrates

	Membrane	Solute	Rejection (%)	Marker MW (g mol <sup>-1</sup> )	Permeance (L m <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	Reference
1	PA/PAN nanofibous-8	Sudan4	99.2	380	9.9	This work
2	PA/PAN	Oleic acid	93	282	6.0	55
3	(PIM-1/PEI)/PAN	HPB	91	535	3.6	56
3	PIM-1/PAN	HPB	73	535	6.0	50
4	PA/cross-linked P84	Styrene Oligomers	98	236	1.5	57
5	NH <sub>2</sub> -MWCNT/P84	Methylene Blue	99.8	320	2.26	58
6	(PA/MOFs)/P84	Styrene Oligomers	96	236	3.9	59
7	MIL-101/ZIF-11/P84	Sunset Yellow	90	450	13.2	60
8	(Ultrathin PA)/P84	Naphthalene Brown	99.9	400.3	19.11	61
9	(UiO-66-NH <sub>2</sub> )/PI	Tetracycline	99	444	20.0	62
10	(PS-b-PEO/PAA)/alumina	Polyethylene Glycols	80	370	0.1	63
11	Inopor TiO <sub>2</sub> /alumina	Victoria Blue	99	506	0.4	64
12	0.8Cu-BTC/PPSU	Reactive Orange 16	93.4	600	3.3	65
13	PA/PSF	Crystal Violet	90	407	2.0	66
14	PA/ZIF-8/PSF	Sunset Yellow	90	450	8.7	67
15	Cross-linked PANI	Styrene Oligomers	97	236	0.8	68

## Table S5. A comparison of the MeOH permeability and Sudan4 (Mw 380.44 gmol<sup>-1</sup>) dye rejection rates between our membranes and literature.



Fig S1. The fabrication process for thin film composite membranes based on PAN nanofibrous substrates



Fig S2. N1s XPS spectra for the 8h cross-linked PAN substrates, (a) 8h crosslinked asymmetrical substrates and (b) 8h cross-linked asymmetrical substrates on surface ,(c) 8h cross-linked asymmetrical substrates and (d) 8h cross-linked asymmetrical substrates with 300 s depth profiling.



Fig S3.Cross-linking and size effects on mechanical properties



Fig S4. UV-vis absorbance spectra of the feed and permeate of four basic dyes in methanol.



Fig S5. Molecular weight cut-off (MWCO) of the PA/8h-cross-linked nanofibrous substrates



Fig S6. Zeta potential of PA/8h-cross-linked nanofibrous substrates as a function of the pH value.