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Supplementary Materials for

Smart covalent organic networks (CONs) with "on-off-on" light-switchable pores for molecular separation

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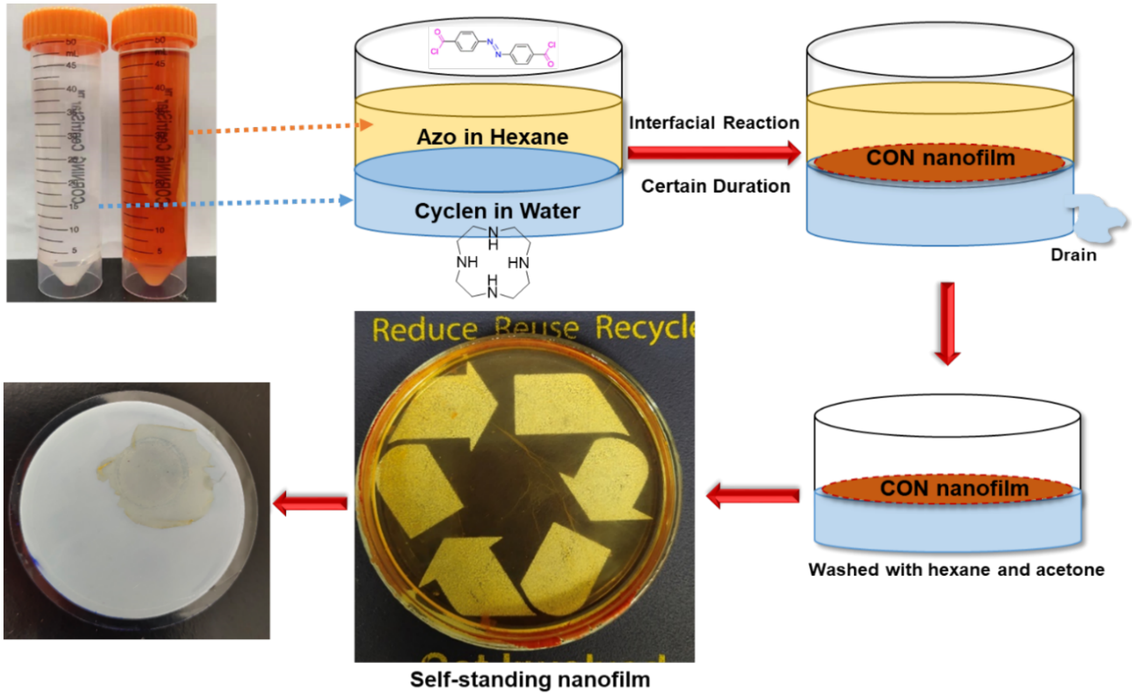
- References

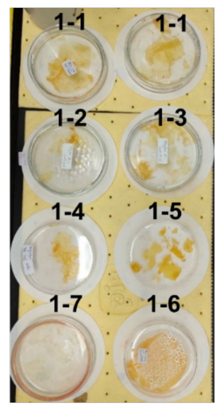
Other Supplementary Material for this manuscript includes the following:

(available at advances.sciencemag.org/cgi/content/full/6/34/eabb3188/DC1)

- Movies S1 to S5



System 1	1,4,7,10-Tetraazacyclododecane	Azobenzene-4,4'-dicarbonyl Dichloride	SDS (mmol/l)	Membranes	Note
1-1	0.5 mmol/100 mL H2O	0.2 mmol/100 mL Hexane	0	Thin, defect, low mechanical robust	×
1-2	1.0 mmol/100 mL H2O	0.2 mmol/100 mL Hexane	0	Thin, defect, low mechanical robust	×
1-3	1.5 mmol/100 mL H2O	0.2 mmol/100 mL Hexane	0	Thin, defect, low mechanical robust	×
1-4	0.5 mmol/100 mL H2O	0.2 mmol/100 mL Hexane	0.1	Thin, porous, defect	×
1-5	0.5 mmol/100 mL H2O	0.2 mmol/100 mL Hexane	0.5	Thick, porous, defect	×
1-6	0.5 mmol/100 mL H2O	0.2 mmol/100 mL Hexane	1.0	Thick, porous, defect	×



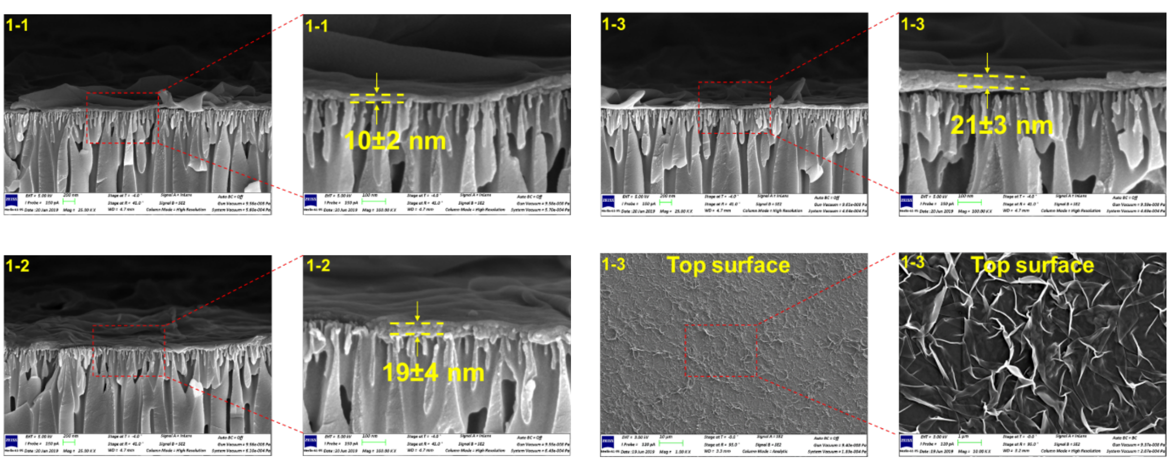
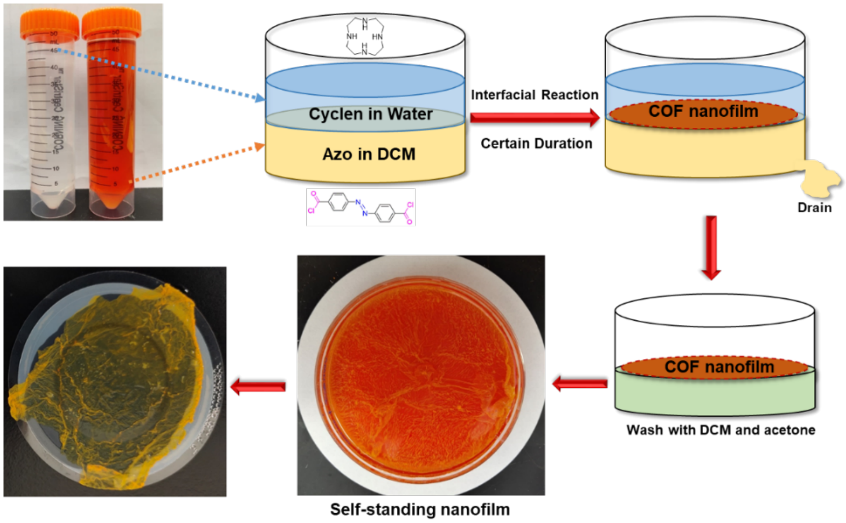
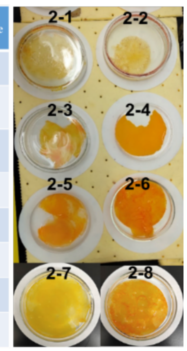
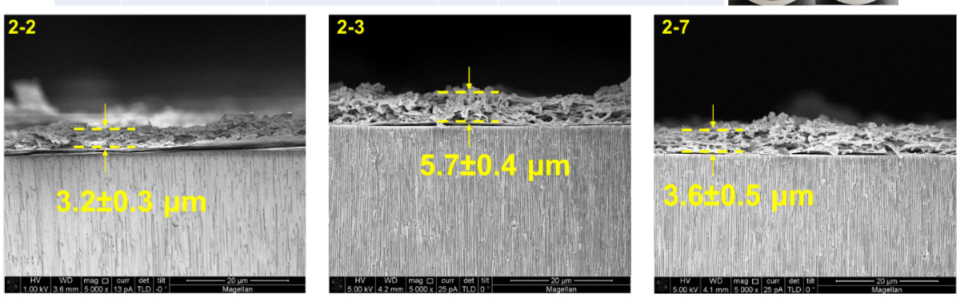


Fig. S1. Fabrication process, reaction conditions, and results of the freestanding CON films via water and hexane system. Photo credits: Jiangtao Liu.



System 2	1,4,7,10-Tetraazacyclododecane	Azobenzene-4,4'-dicarbonyl Dichloride	SDS (mmol)	K2CO3 (mmol)	Membranes	Note
2-1	0.5 mmol/100 mL H2O	0.5 mmol / 100 mL DCM	0	0	Thin, defect	×
2-2	0.5 mmol/100 mL H2O	1.0 mmol / 100 mL DCM	0	0	Thick, porous, defect	×
2-3	1.0 mmol/100 mL H2O	1.0 mmol / 100 mL DCM	0	0	Thick, porous, defect	×
2-4	1.5 mmol/100 mL H2O	1.0 mmol / 100 mL DCM	0	0	Thick, defect	×
2-5	0.5 mmol/100 mL H2O	1.0 mmol / 100 mL DCM	0.1	0	Thick, porous, defect	×
2-6	0.5 mmol/100 mL H2O	1.0 mmol / 100 mL DCM	1.0	0	Thick, porous, defect	×
2-7	1.0 mmol/100 mL H2O	0.5 mmol / 100 mL DCM	0	0.1	Thick, gel, defect	×
2-8	1.5 mmol/100 mL H2O	1.0 mmol / 100 mL DCM	0	0.2	Thick, gel, defect	×





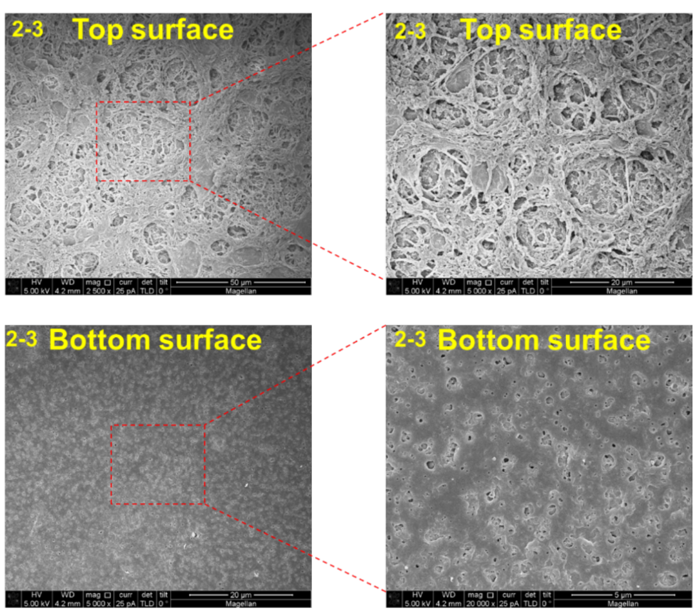
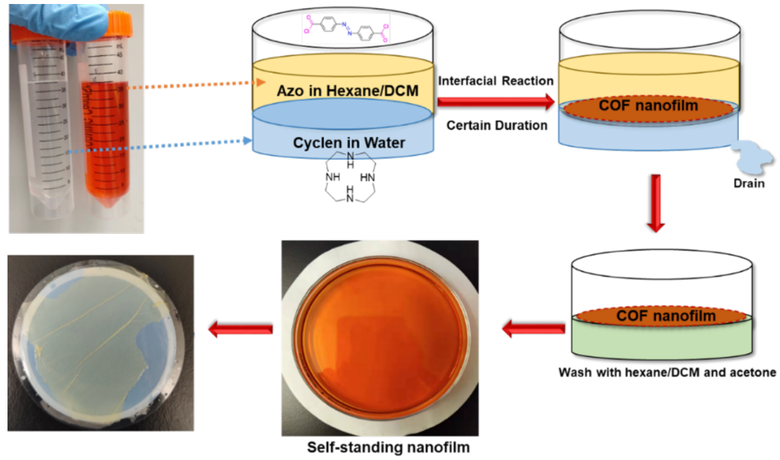
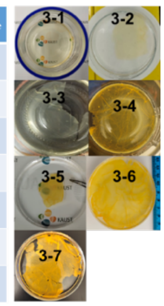
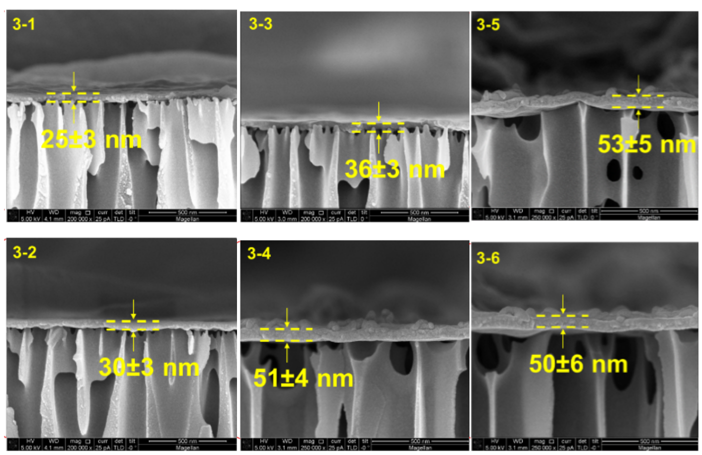


Fig. S2. Fabrication process, reaction conditions, and results of the freestanding CON films via water and dichloromethane system. Photo credits: Jiangtao Liu.



System 3	1,4,7,10-Tetraazacyclododecane	Azobenzene-4,4'-dicarbonyl Dichloride	Reaction time (h)	Membranes	Note
3-1	0.5 mmol/100 mL H2O	0.2 mmol / 100 mL Hexane/DCM	24	Thin, defect	✗
3-2	0.5 mmol/100 mL H2O	0.5 mmol / 100 mL Hexane/DCM	24	Thin, defect free	✓
3-3	1.0 mmol/100 mL H2O	0.5 mmol / 100 mL Hexane/DCM	24	Thick, defect free	✓
3-4	1.5 mmol/100 mL H2O	0.5 mmol / 100 mL Hexane/DCM	24	Thick, defect free	✓
3-5	1.5 mmol/100 mL H2O	0.5 mmol / 100 mL Hexane/DCM	48	Thick, defect free	✓
3-6	1.5 mmol/100 mL H2O	0.5 mmol / 100 mL Hexane/DCM	72	Thick, defect free	✓
3-7	1.5 mmol/100 mL H2O	0.5 mmol / 100 mL Hexane/DCM(3/2)	72	Thick, defect free	✓





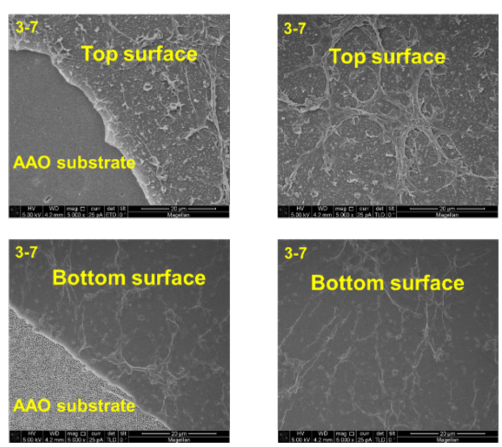


Fig. S3. Fabrication process, reaction conditions, and the results of the freestanding CON films via water and hexane/dichloromethane (4/1) system. Photo credits: Jiangtao Liu.

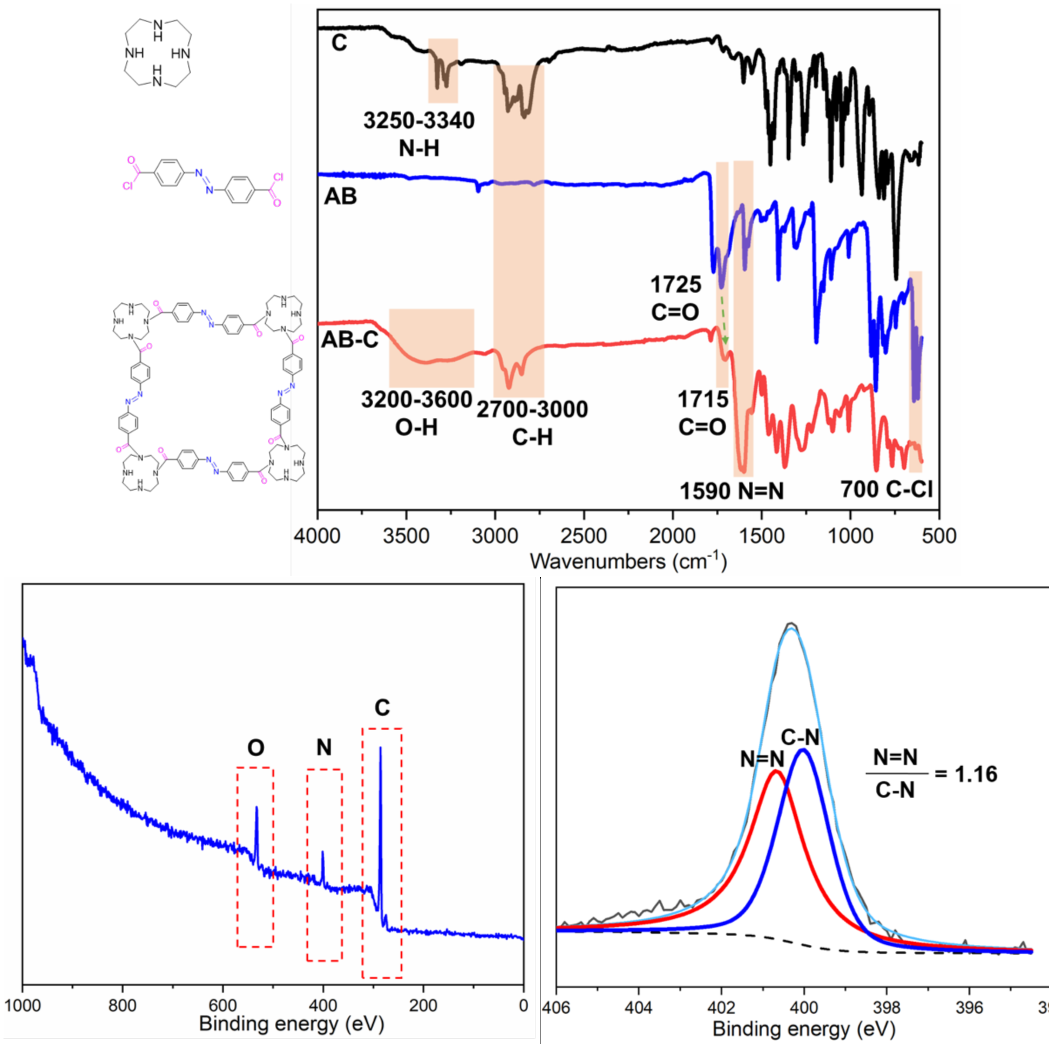


Fig. S4. ATR-FTIR spectra of the monomers and free-standing CON films. Note: 1,4,7,10-tetraazacyclododecane (cyclen, C), azobenzene-4,4'-dicarbonyl dichloride (AB), and covalent organic networks (AB-C). XPS spectra and N_{1s} analysis of the freestanding *trans*-CON film, the N_{1s} peak was deconvoluted into two peaks at 400.5 eV (N=N from azobenzene units) and 399.8 eV (C-N from cyclen units).

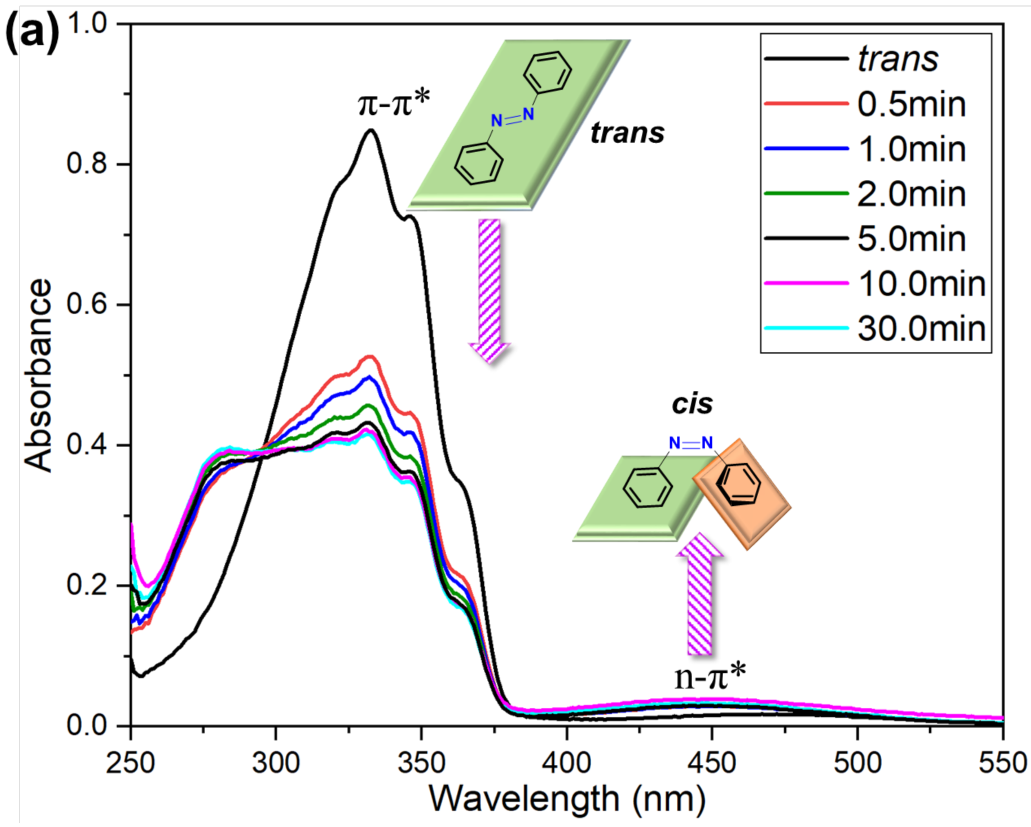


Fig. S5. UV-visible spectra of pure azobenene-4,4'-dicarbonyl dichloride *trans*-to-*cis* photoisomerization.

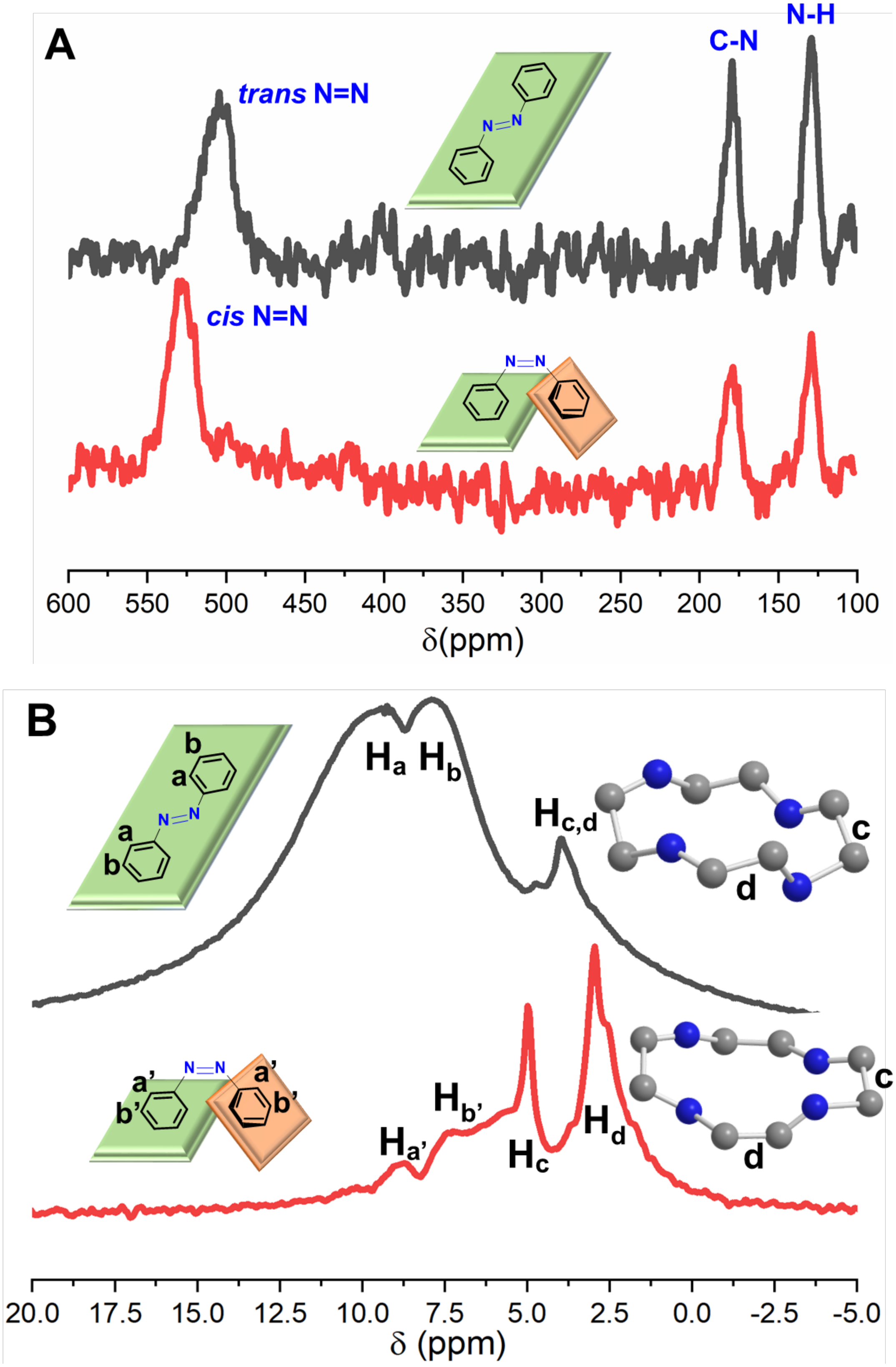


Fig. S6. (A) ^{15}N NMR and (B) ^{1}H NMR spectra of the freestanding *trans*-CON and *cis*-CON film.

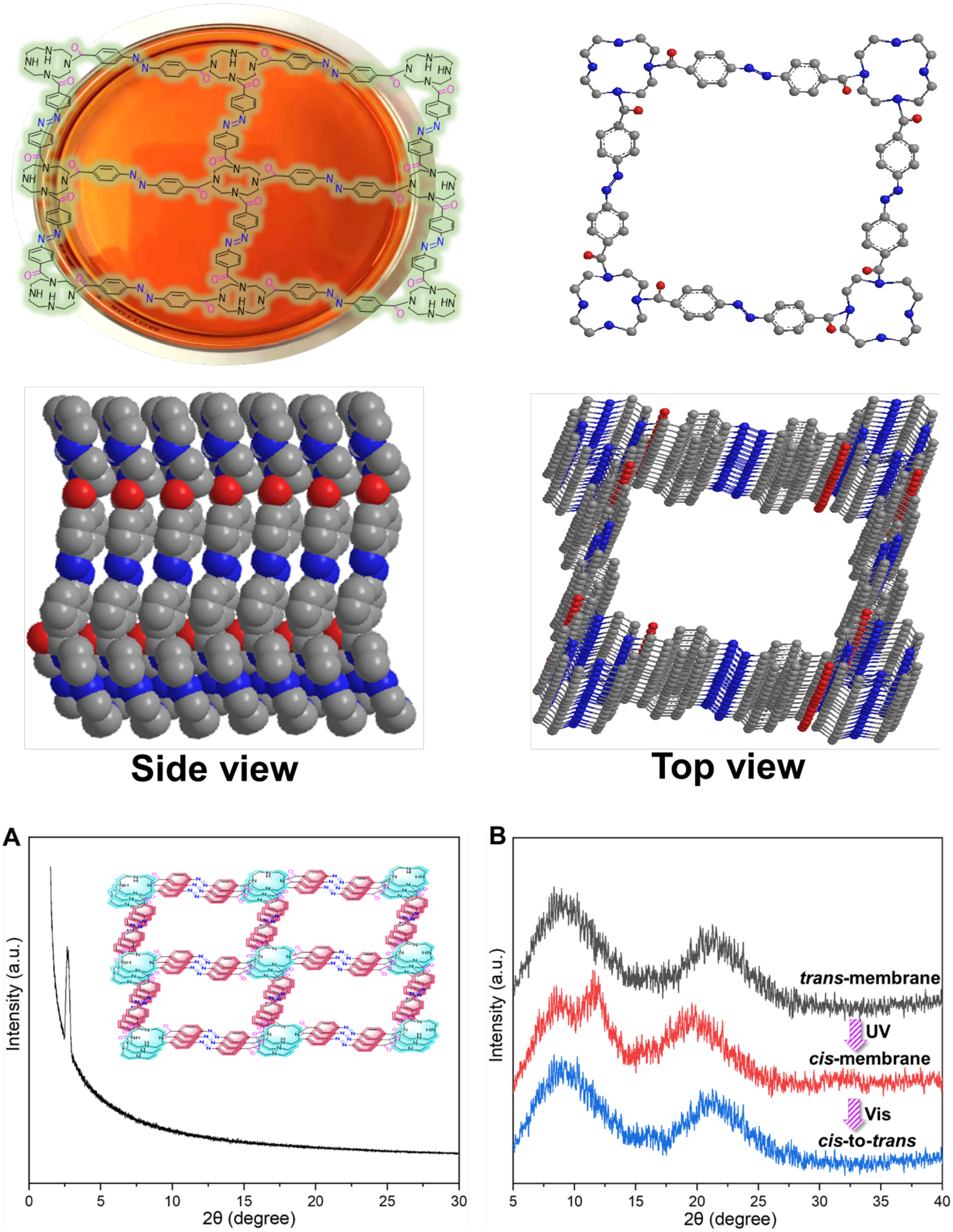


Fig. S7. (A) GID and (B) XRD spectra of the freestanding *trans*-CON and *cis*-CON film. Photo credit: Jiangtao Liu.

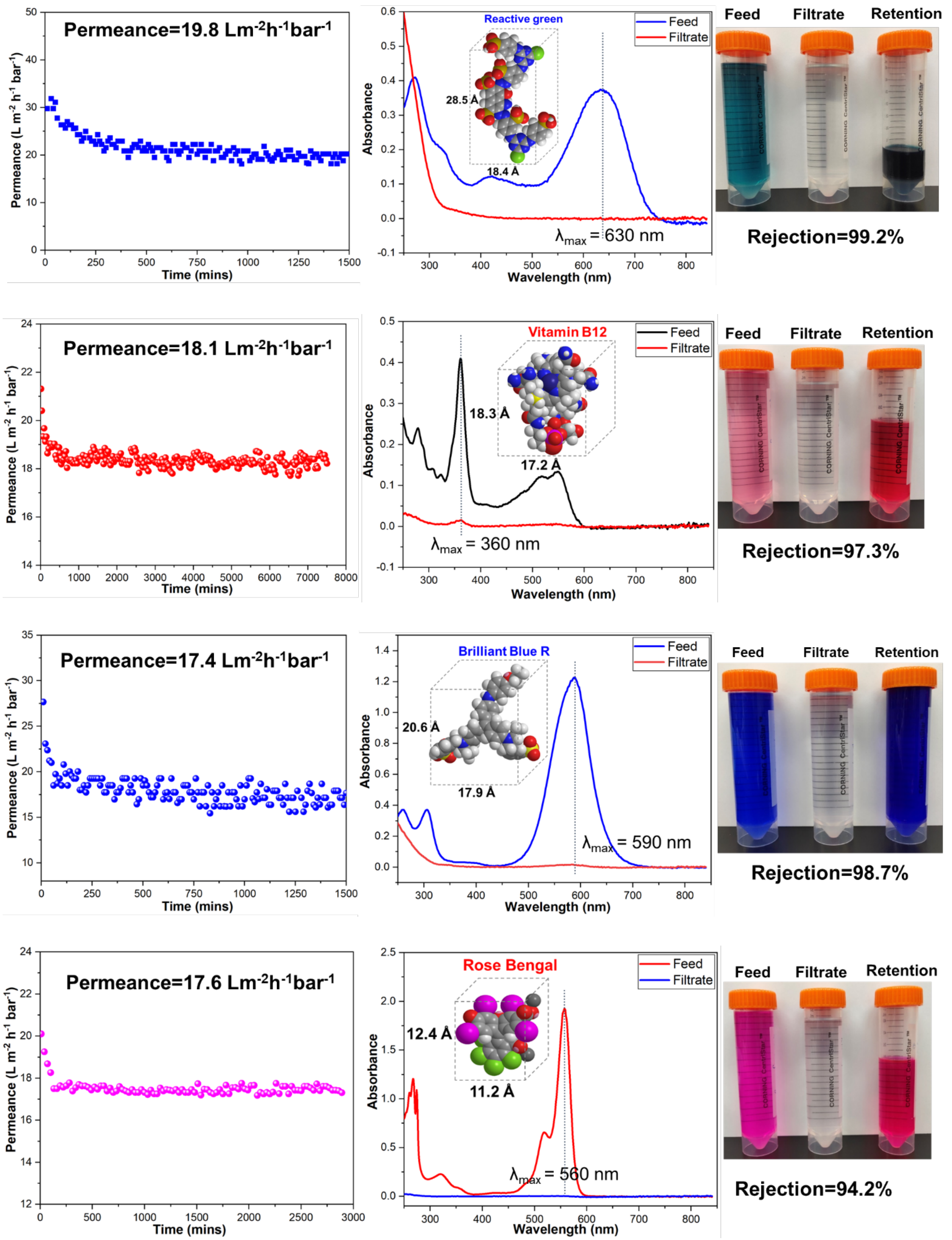


Fig. S8. Long-term permeance and UV spectra of dyes in methanol before and after filtration through the *trans*-CON membranes. (Inset) Photograph of the feed, filtrate, and retention of dye solution. Photo credits: Jiangtao Liu.

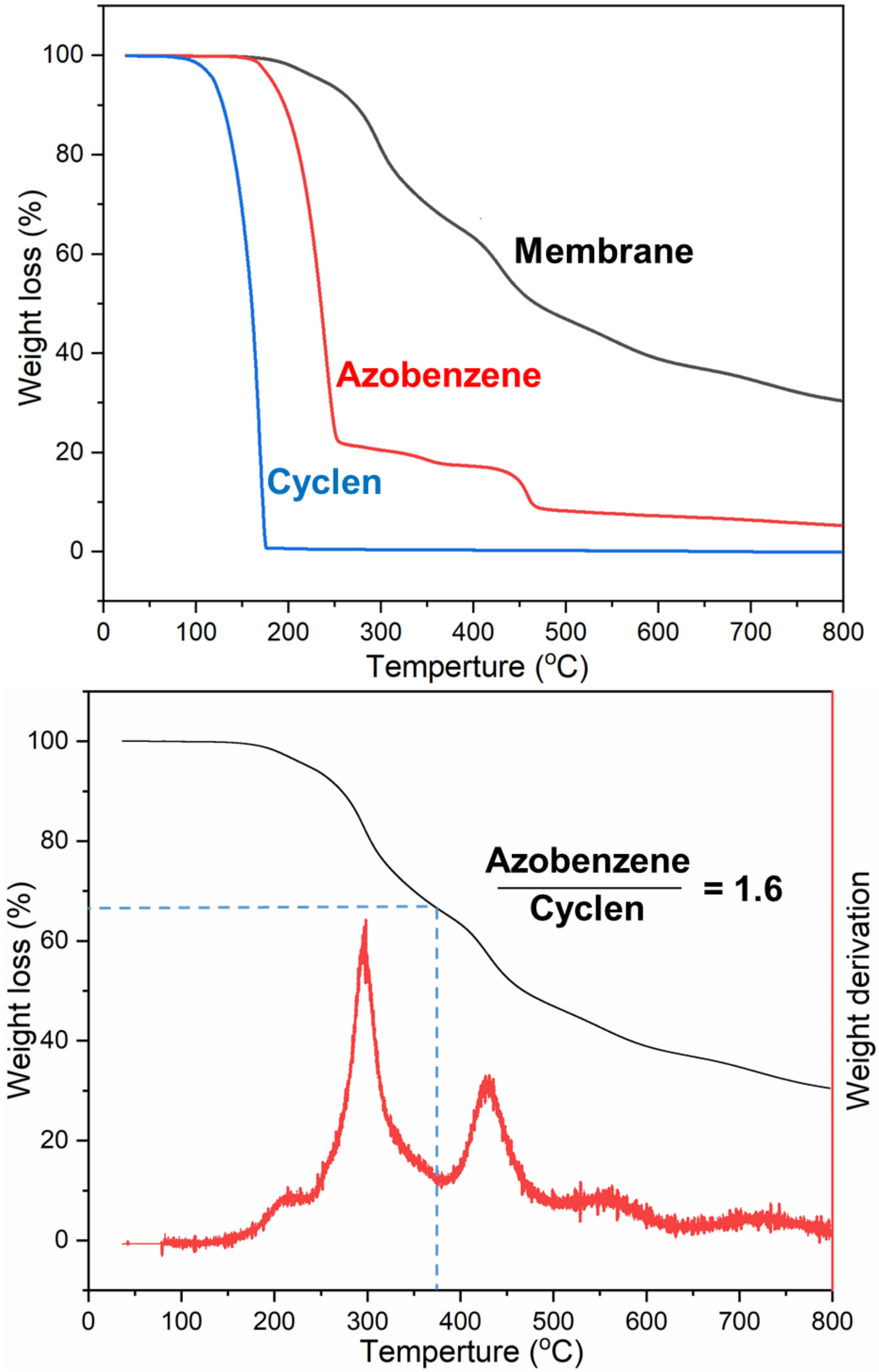


Fig. S9. TGA curves of monomers and CON membranes.

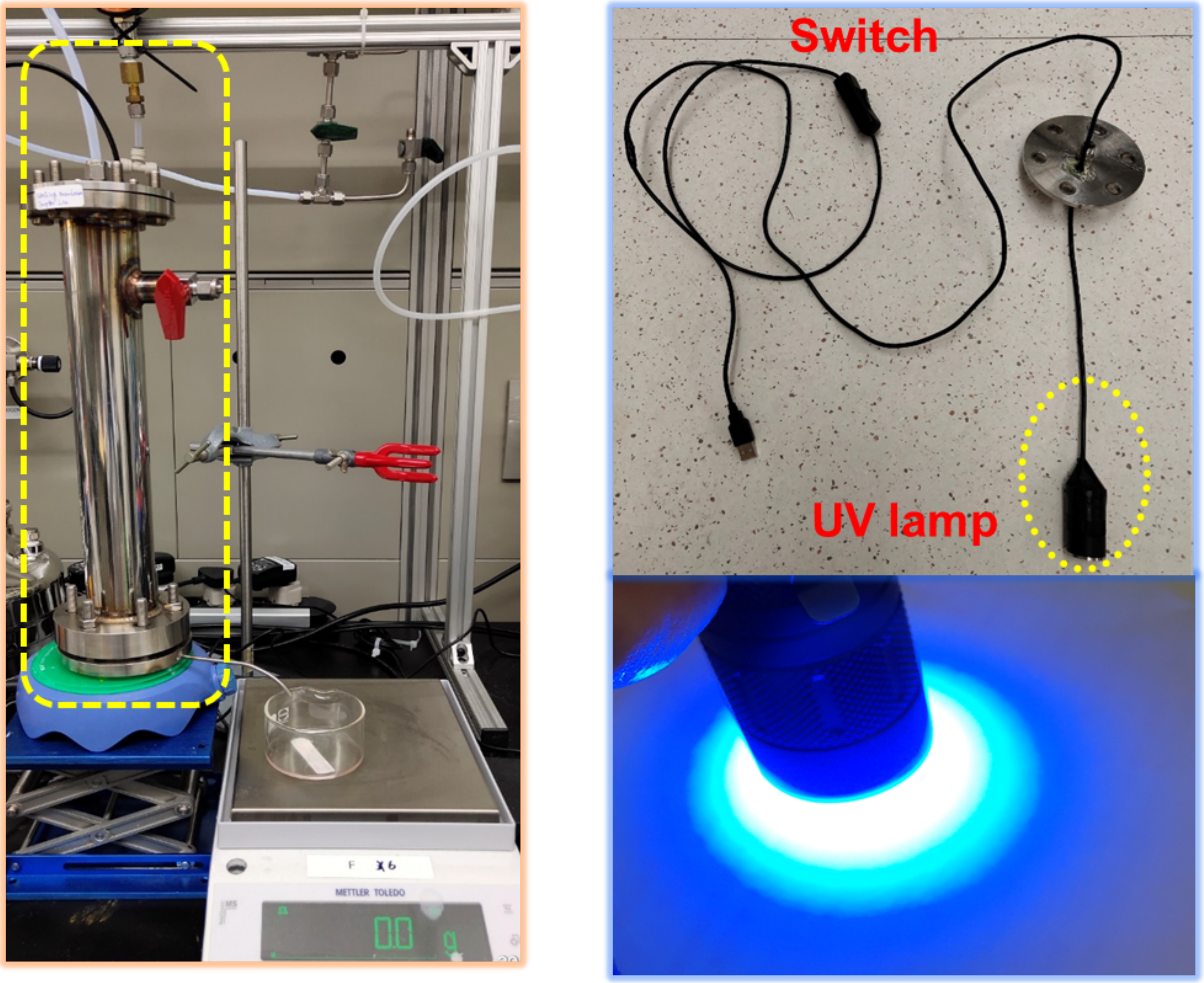


Fig. S10. Permeation cell equipped with UV lamp. Photo credits: Jiangtao Liu.

Table S1. Performance comparison beween various organic solvent nanofiltration membranes.

Membrane/Substrate	**Permeance ($L\ m^{-2}\ h^{-1}\ MPa^{-1}$)**	**Dye (g/mol)**	**Rejection (%)**	**References**
Freestanding *trans*-CON	22.6 (Methanol)	Indigo carmine (466)	49.3	This work
Freestanding *cis*-CON	19.3 (Methanol)	Indigo carmine (466)	94.7	This work
Freestanding *trans*-CON	17.4 (Methanol)	Brilliant Blue R (826)	98.7	This work
Freestanding PAR-BHPF	4.4 (Methanol)	Brilliant Blue R (826)	99.7	(2016) [50]
PAR-BHPF/PI	8.0 (Methanol)	Brilliant Blue R (826)	98.0	(2016) [50]
PAR-TTSBI/PI	6.0 (Methanol)	Brilliant Blue R (826)	99.9	(2016) [50]
PAR-DHAQ/PI	0.6 (Methanol)	Brilliant Blue R (826)	100.0	(2016) [50]
PAR-RES/PI	0.6 (Methanol)	Brilliant Blue R (826)	99.8	(2016) [50]
DuraMem DM150	0.48 (Methanol)	Acid fuschin (585)	100.0	(2015) [48]
PA/Cross-linked P84	12.6 (Methanol)	Acid fuschin (585)	99.9	(2015) [48]
PEI-sPPSU	100 (Ethanol)	Methyl Orange (327)	66.8	(2018) [51]
MWCNTs-COOH/P84	96 (Ethanol)	Rose Bengal (1017)	85.0	(2017) [52]
PEI-DBX/PBI	45 (Ethanol)	Tetracycline (444)	99.0	(2018) [53]
MPF-50	42 (Ethanol)	Raffinose (504)	41.0	(2005) [54]
Cross-linked PBI	37 (Ethanol)	Rose Bengal (1017)	100	(2014) [55]
MWCNTs-NH_2/P84	33 (Ethanol)	Eosin Y (648)	98.1	(2018) [56]
TPP/GO/HPEI/PSS	31 (Ethanol)	Rose Bengal (1017)	97.0	(2017) [57]
PA/crosslinking PI	27 (Ethanol)	Rose Bengal (1017)	100	(2015) [58]
PVDF-g-PS20	25 (Ethanol)	Rose Bengal (1017)	91.2	(2017) [59]
STARMEM™ 122	24.1 (Ethanol)	Sudan black (456)	94.1	(2010) [60]
PAN-Pebax/GO	19 (Ethanol)	Brilliant Blue G (854)	95.0	(2017) [61]
PI/POSS	12.6 (Ethanol)	Rose Bengal (1017)	99.0	(2017) [62]
PI	11.0 (Ethanol)	Methyl Orange (327)	95.0	(2017) [63]
PDA/PI	9.1 (Ethanol)	Methyl Blue (800)	99.0	(2017) [64]
COF-LZU1/AAO	53.4 (Ethanol)	Congo Red (697)	98.6	(2018) [65]
PA-COFs/PI	79.8 (Ethanol)	Rhodamine B (479)	99.4	(2019) [66]
TpPa-1/PAN	41.8 (Ethanol)	Congo Red (697)	99.0	(2019) [67]
TpPa/PSf	50.0 (Ethanol)	Congo Red (697)	99.5	(2018) [68]
TpPa/PVDF	60.0 (Ethanol)	Congo Red (697)	98.72	(2019) [69]
TpBD/PSf	33.6 (Ethanol)	Congo Red (697)	99.7	(2020) [70]
TpBD-Me/PSf	62.2 (Ethanol)	Congo Red (697)	99.2	(2020) [70]

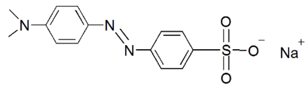
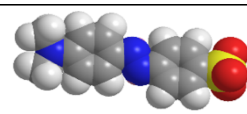
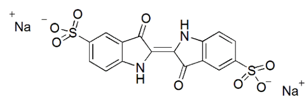
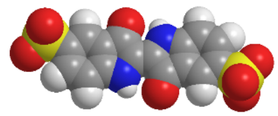
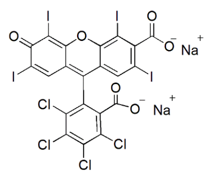
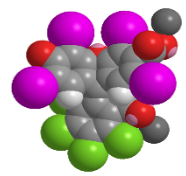
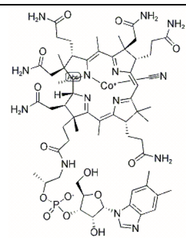
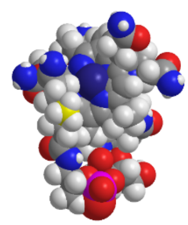
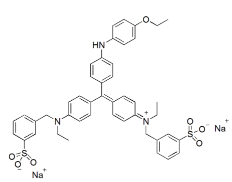
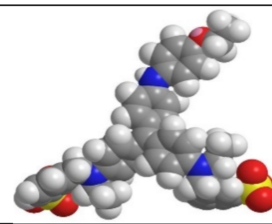
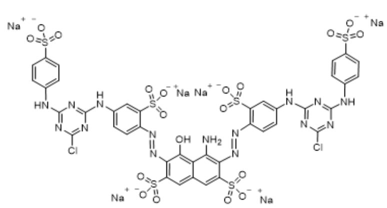
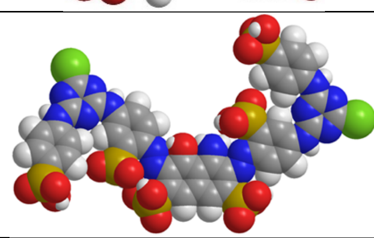
Table S2. Solvent properties: viscosity, relative polarity, kinetic diameter, and total Hansen solubility parameter.

Solvents	Viscosity at 25°C (mPa S)[71]	Relative polarity[72,73]	Kinetic diameter (nm)[1]	Total Hansen solubility parameter ($MPa^{1/2}$)[1]
Acetonitrile	0.342	0.460	0.51	24.4
Acetone	0.310	0.355	0.47	20.1
Methanol	0.539	0.762	0.38	29.7
Water	0.916	1.000	0.26	47.8
Ethanol	1.081	0.654	0.44	26.6
Isopropanol	2.058	0.546	0.47	24.6
Butanol	2.573	0.586	0.50	23.1
Dimethylformamide	0.816	0.386	0.55	24.8
p-Xylene	0.710	0.074	0.59	27.9
Toluene	0.555	0.099	0.58	18.2
Cyclohexane	0.908	0.006	0.60	16.8
Hexane	0.294	0.009	0.51	14.9

Table S3. Permeances of organic solvents through the self-standing *trans*- and *cis*-CON membranes.

Solvents	Permeance (L m^{-2} h^{-1} bar^{-1})	
	trans-CON	*cis*-CON
Acetonitrile	56.7±1.8	51.2±1.6
Acetone	48.2±1.3	45.7±1.4
Methanol	31.6±0.8	30.2±0.5
Water	22.1±0.4	20.4±0.2
Ethanol	12.4±0.6	12.6±0.5
Isopropanol	6.8±0.5	6.4±0.3
Dimethylformamide	4.3±0.4	4.5±0.3
p-Xylene	8.6±0.5	8.2±0.5
Toluene	10.2±0.7	12.4±0.6
Cyclohexane	15.8±0.8	14.3±0.7
Hexane	46.5±2.2	43.1±1.4

Table S4. The chemical structures, molar weights and dimensional parameters of various dyes.

Dyes	M_w (g/mol)	Chemical structure	3D molecular structure	Dimension (Å) ($L_1 \times L_2$, L_1 is the long end and L_2 is the short end)
Methyl Orange (MO)	327.3			14.6 × 5.2
Indigo Carmine (IC)	466.4			15.3 × 7.8
Rose Bengal (RB)	1017.6			12.4 × 11.2
Vitamin B12 (VB)	1355.4			18.3 × 17.2
Brilliant Blue R (BBR)	825.9			20.6 × 17.9
Reactive Green (RG)	1418.9			28.5 × 18.4

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