Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Electropolymerized thin films with microporous architecture enabling molecular sieving in harsh organic solvents under high temperature

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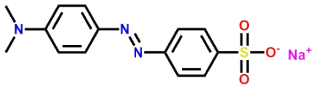
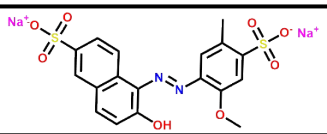
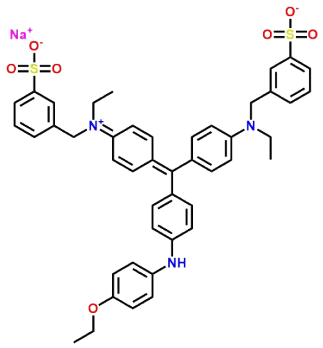
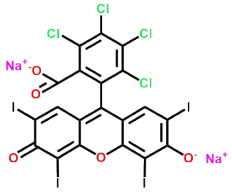
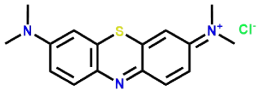
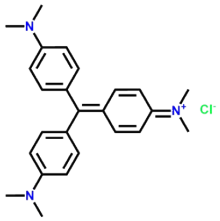
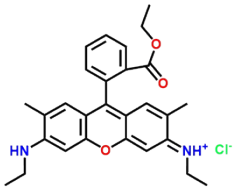
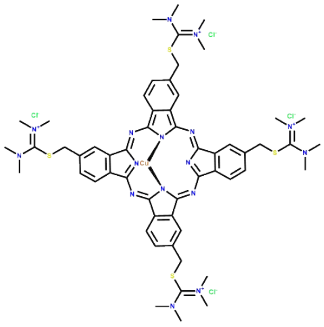
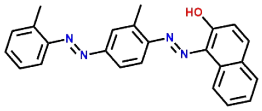
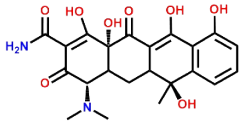
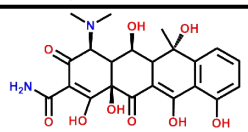
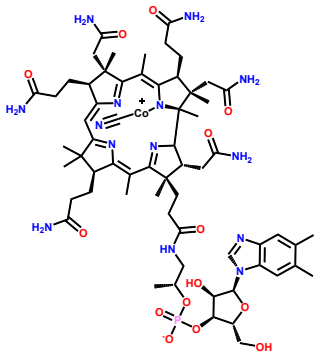
Table S1. Properties and structure of solutes used as marker for molecular separation in this work.

Solute	Chemical Formula	MW (g mol^{-1})	Net Charge
Methyl Orange (MO)		327.33	–1
Allura Red AC (ARAC)		496.42	–2
Brilliant Blue R (BBR)		826	–1
Rose Bengal (RB)		1017.65	–2
Methylene Blue (MB)		319.9	+1
Crystal Violet (CV)		407.99	+1
Rhodamine 6G (R6G)		479.02	+1

Alcian Blue (AB)		1298.86	+4
Sudan IV (SIV)		380.44	0
Tetracycline		444.43	0
Oxytetracycline		460.46	0
Vitamin B_{12} (VB12)		1355.37	0

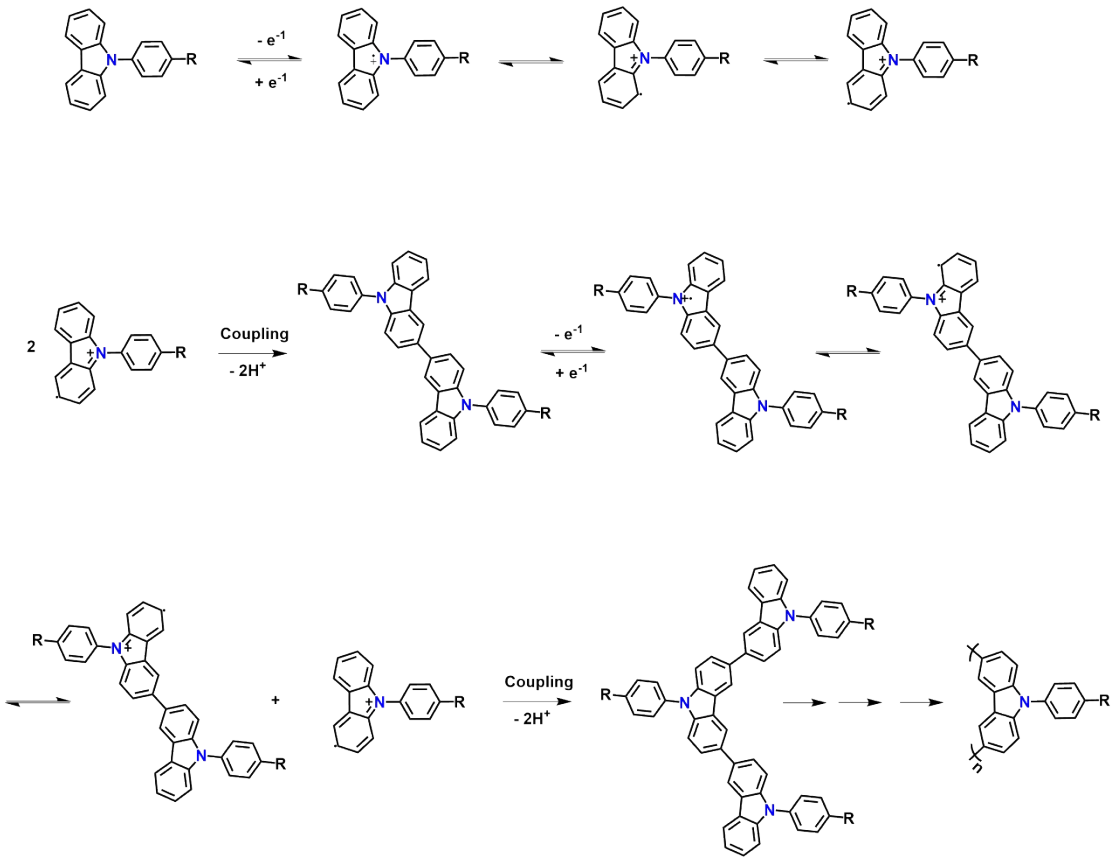


Figure S1. The electropolymerization mechanism of TCTA.[1]

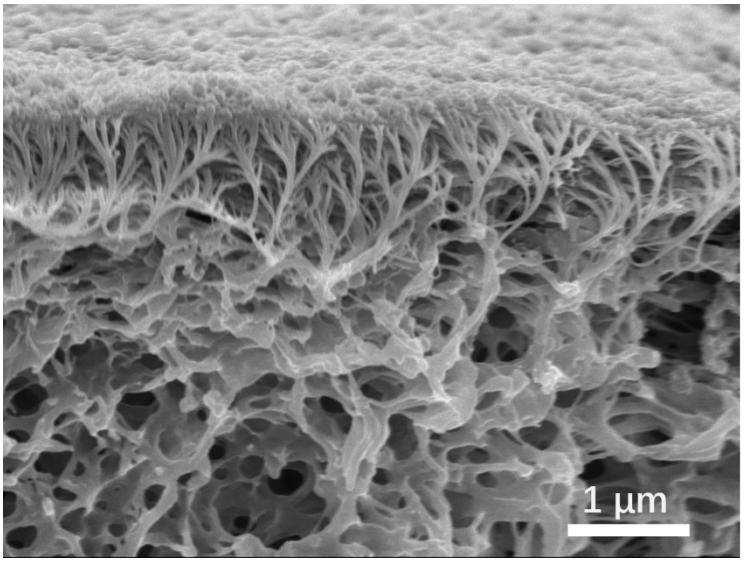


Figure S2. Cross-section of TCTA-EP membrane on CNT/PP support.

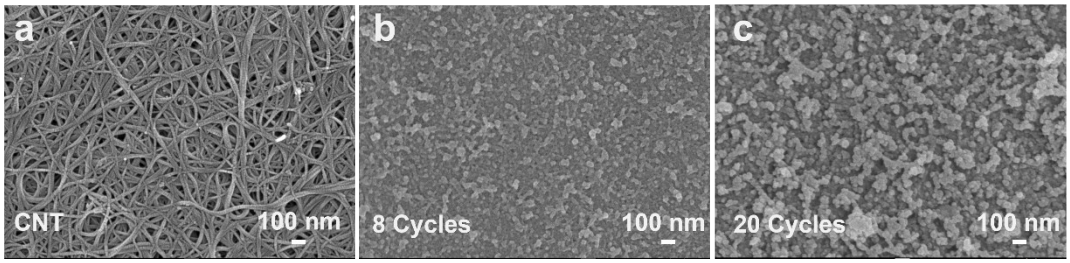


Figure S3. SEM images present the membrane morphology of TCTA-EP film with different number of CV cycle at scan rate of 50 mV s^{-1}.

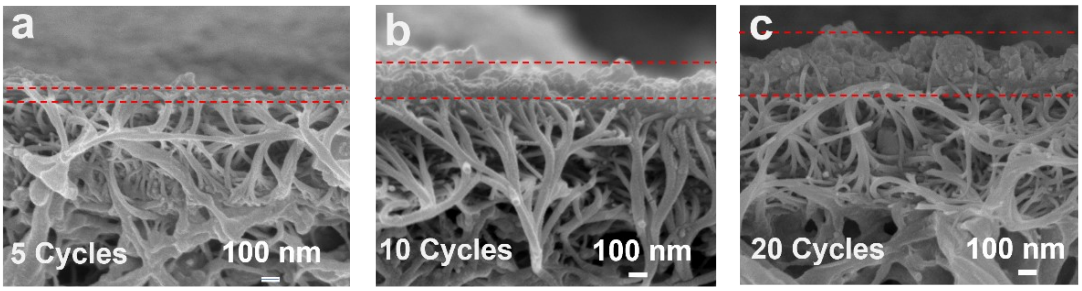


Figure S4. SEM images present the cross section of TCTA-EP film with different number of CV cycle at scan rate of 50 mV s^{-1}.

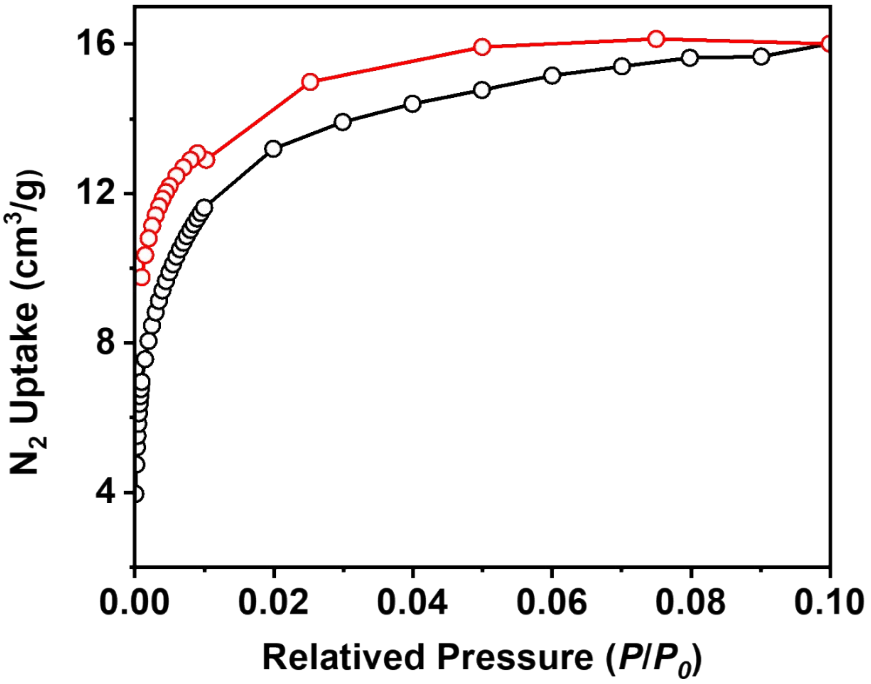


Figure S5. Nitrogen sorption isotherm of TCTA-EP films measured at 77 K. 5 mg of material was collected for the measurement.

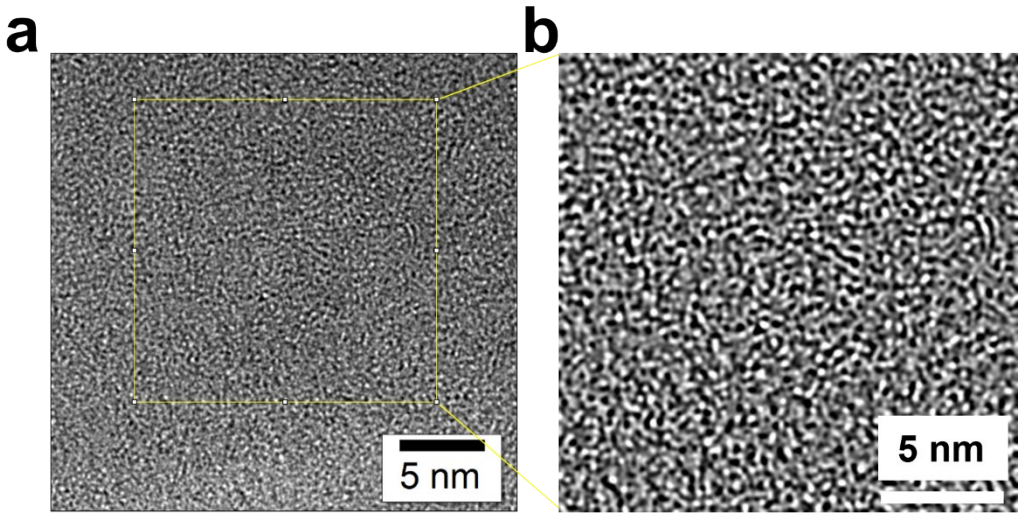


Figure S6. The TEM image of the TCTA-EP-8 membrane. (a) Original TEM image. (b) TEM image with higher contract processed by Image J software.

Figure S7. Water contact angle (WCA) of CNT/PP membrane.

Table S2. Physical properties of the solvents used in this study.

Solvents	Viscosity η at 25 °C (mPa·s) ‡	Total Hansen solubility parameter δ_T ($MPa^{1/2}$) †	δ_p ($MPa^{1/2}$)⊥	Kinetic diameter d_k (nm)ǂ	Molar Diameters d_m (nm)*
Hexane	0.294	14.9	0	0.43	0.75
Acetone	0.306	20.1	10.4	0.47	0.62
Methanol	0.539	29.6	12.3	0.38	0.51
Ethanol	1.081	26.5	8.8	0.45	0.57
DMF	0.816	24.8	13.7	0.50	0.63

‡Viscosity parameter η was obtained from reference[2];

†Total Hansen solubility parameter (δ_T) was obtained from reference[3];

⊥δ_p is solubility parameter due to dipole forces[4];

ǂKinetic diameter d_k was obtained from reference[5];

*Molar diameter (d_m) was calculated from: $d_m = 2 \times (3V_m/4\pi N_A)^{1/3}$; where N_A is the Avogardo's number[6].

Figure S8. TCTA-EP-8 membrane with diameter of 3.5 cm.

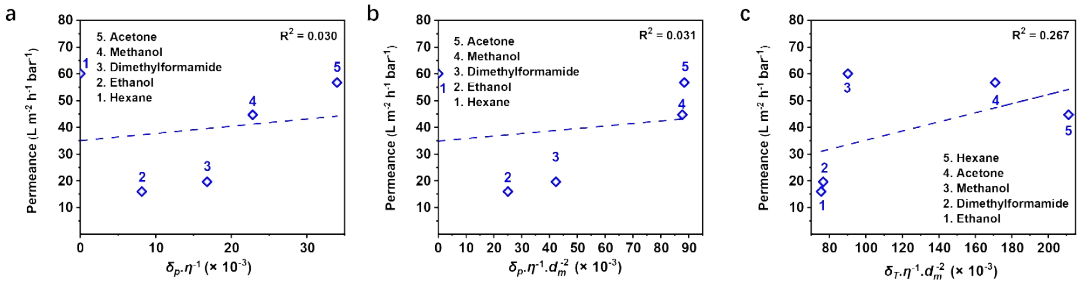


Figure S9. The organic solvent permeance of TCTA-EP-8 membrane against (a) solubility parameter (δ_p) multiplied by inverse of viscosity, (b) solubility parameter (δ_p) multiplied by inverse of viscosity and molar diameter and (c) solubility parameter (δ_T) multiplied by inverse of viscosity and molar diameter.

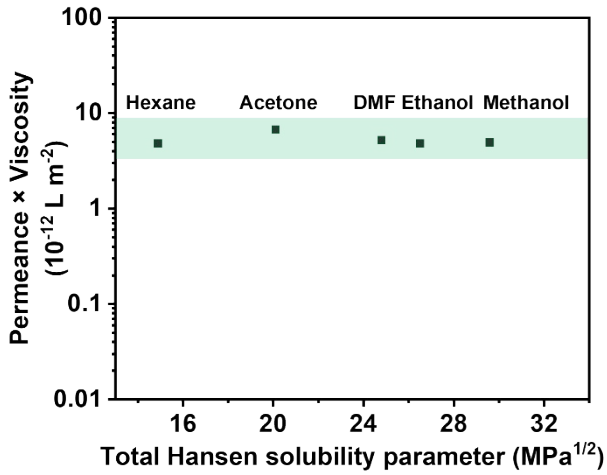


Figure S10. Product of permeance and viscosity of different solvents as a function of total Hansen solubility parameter for TCTA-EP-8 membrane.

Supplementary Note I: Estimation of three-dimensional minimum box size of various solutes.

We followed our previous research to obtain the three-dimensional minimum box size of the solutes.[7] The molecule structures of the solutes were firstly optimized in Chem3D via MM2 program to achieve minimized energy for the molecule conformation (Minimum RMS gradient was set as 0.01). Multiwfn 3.8 (dev) software[8] was then applied to obtain the three-dimensional minimum box size covering the van der Waals surface of the solutes molecules (**Figure S11**) by inputting the optimized molecule structures in the software. It is noted that the metal ions of the dyes are not included in box. The critical diameter *d** defines the smallest permeable diameter of the solute molecules [9-11]. The equivalent diameter of the circle equals to the smallest area of plane on the molecule box is defined as the critical diameter *d** of the solute.

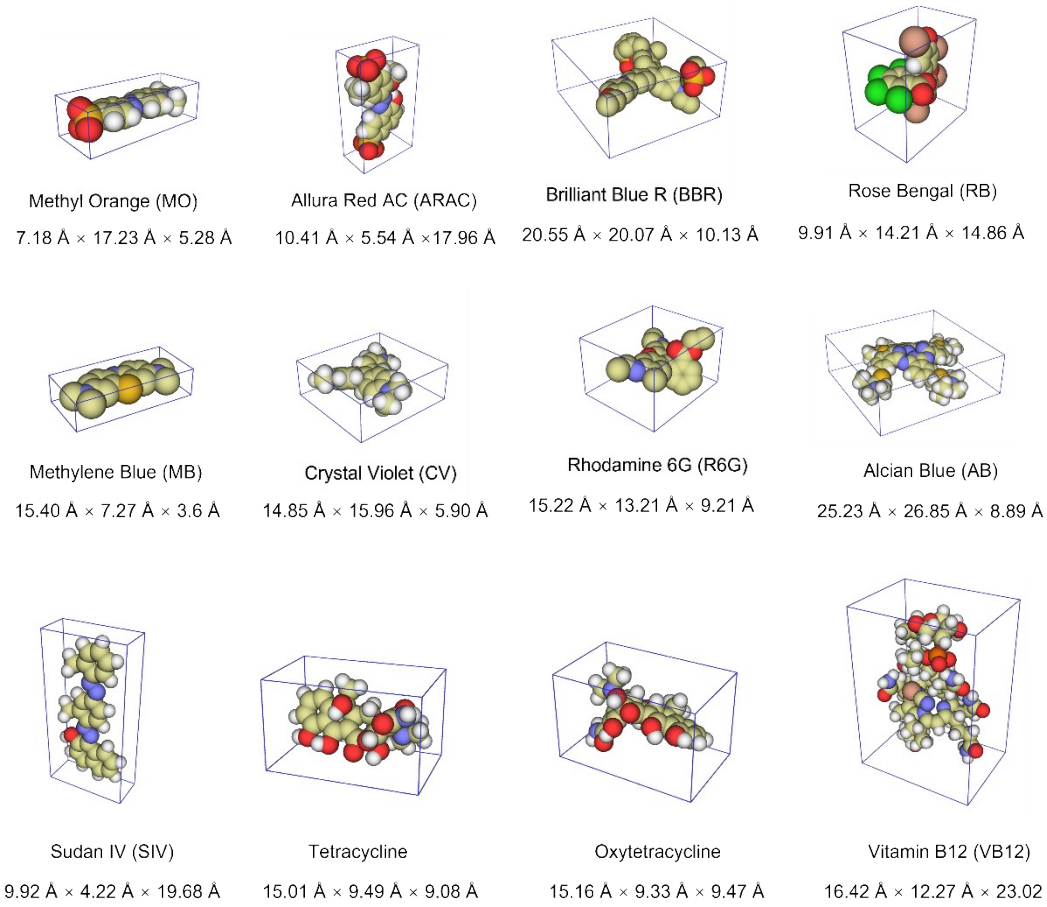


Figure S11. The chemical structure and the three-dimensional minimum box size of the solute molecules used in molecular separation experiment.

Supplementary Note II. Calculation of pore size distribution of TCTA-EP-8 membrane.

The molecular size cut-off value of TCTA-EP-8 membrane was taken as the critical diameter d^* of the solute at which the membrane rejection equals to 90%. The pore size distribution of TCTA-EP-8 membrane was determined by the rejection of neutral solutes with different critical diameter d^* (See more details in **Supplementary Note I**), including Sudan IV (MW = 380.44 g mol^{-1}, d^* = 0.73 nm), Tetracycline (MW = 444.43 g mol^{-1}, d^* = 1.05 nm), Oxytetracycline (MW = 460.46 g mol^{-1}, d^* = 1.06 nm) and Vitamin B_{12} (MW = 1355.37 g mol^{-1}, d^* = 1.60 nm). The probability density function curve was obtained with the assumptions[12]: (1) Ignoring the steric and hydrodynamic interactions between the neutral solutes and the pore of the membrane; (2) The mean effective pore size of the TCTA-EP-8 membrane (μ_p) equals to the geometric mean diameter of the solute (μ_s) with a measured rejection of 50%; (3) It is assumed that the geometric standard deviation of the TCTA-EP-8 membrane (σ_p) is the geometric standard deviation (σ_g), defining as the ratio of d^* at rejection equals to 84.13% and 50%. Based on the above assumptions, the pore size distribution of TCTA-EP-8 membrane can be characterized by the probability density function (PDF)[13]

$$\frac{dR(d_p)}{dd_p} = \frac{1}{d_p \, ln \, \sigma_p \sqrt{2\Pi}} exp\left[- \frac{\left(ln \, d_p - ln \, \mu_p\right)^2}{2(ln \, \sigma_p)^2} \right]$$

where d_p is the pore size of the membrane.

Supplementary Note III: Adsorption of the TCTA-EP membranes.

To exclude the contribution of adsorption effects on dye rejections, TCTA-EP-8 membranes with area of 0.196 cm^2 were immersed in 5 mL dye solutions (50 ppm) and stirred at 300 rpm at room temperature for one week. Three different dyes including Sudan IV (neutral, MW = 380.44 g mol^{-1}), Allura Red AC (negatively charged, MW = 496.42 g mol^{-1}), and Rhodamine 6G (positively charged, MW = 530.0 g mol^{-1}) were used and the dye concentration of solutions before and after immersion was quantified by UV-Vis spectrometer (**Figure S12**).

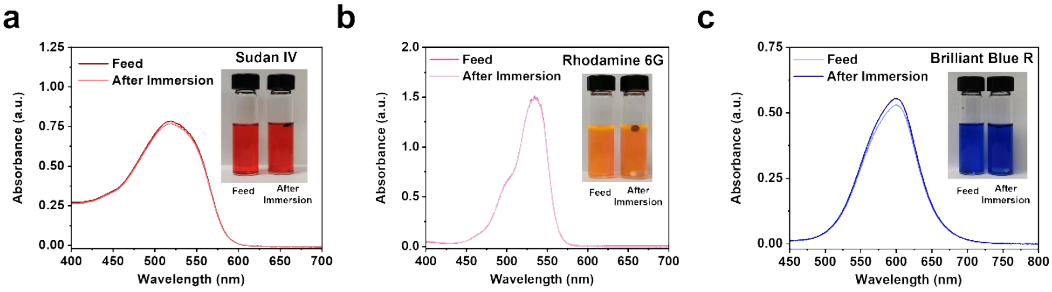


Figure S12. UV absorption spectra of solutes ((a) Sudan IV, (b) Rhodamine 6G, (c) Brilliant Blue R) in DMF before and after the immersion of TCTA-EP-8 membrane for 1 week. Inserts present the photos of the feed and feed solution after immersion of TCTA-EP-8 membrane.

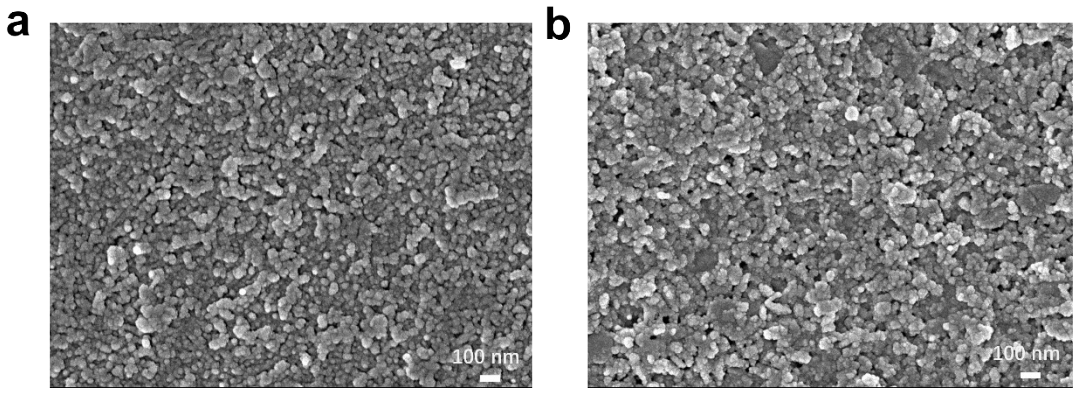


Figure S13. (a) Surface morphology of TCTA-EP-8 membrane (a) before and (b) after cross-flow test.

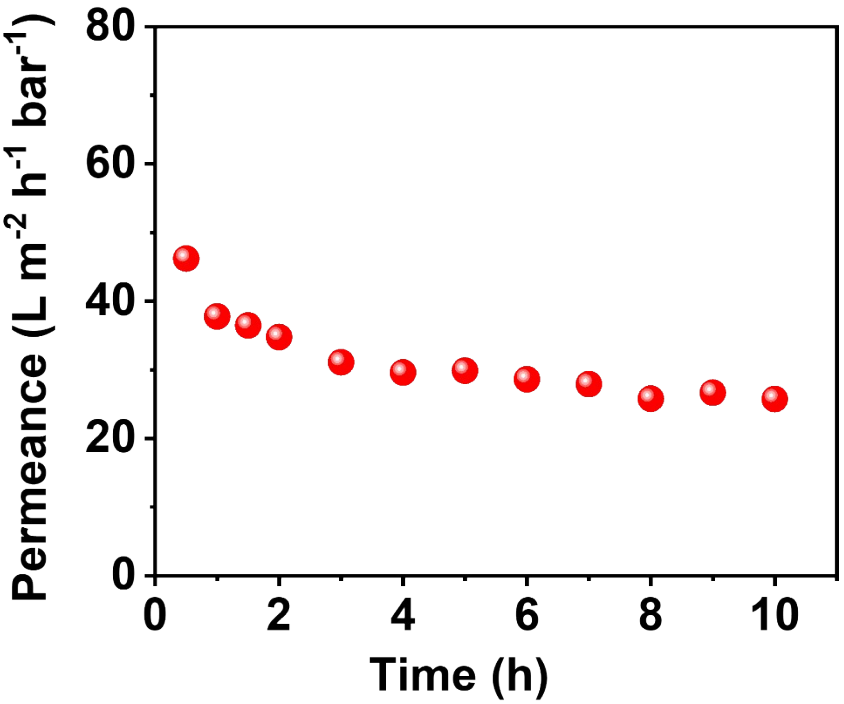


Figure S14. The pure DMF permeance of TCTA-EP-8 membrane under cross-flow mode.

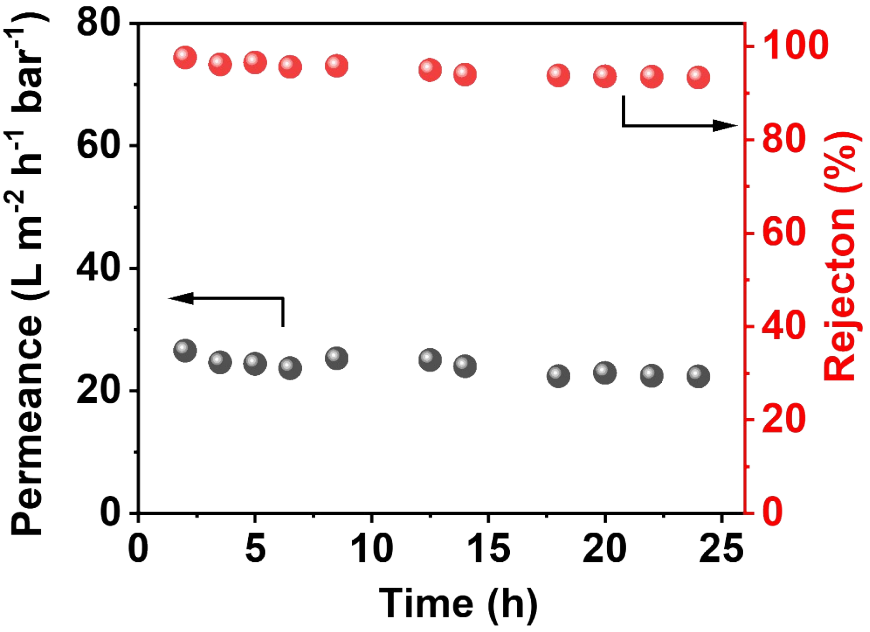


Figure S15. The cross-flow filtration performance of TCTA-EP-8 membrane. The feed solution was 50 ppm Allura Red AC (MW = 496.42 g mol^{-1}) in DMF.

Table S3. The membrane performance in DMF at high temperature in literature and this work.

Membrane	Temperature (℃)	Solute	Permeance (L m^{-2} h^{-1} bar^{-1})	Rejection (%)	References
Cross-Linked PBI	80	Polystyrene (MW = 1200 g mol^{-1})	~0.250	~70	[14]
APTS Cross-Linked PI	80	Polystyrene (MW = 236 g mol^{-1})	~0.183†	90*	[15]
M3	100	Polystyrene (MW = 610 g mol^{-1})	9	90	[16]
PEEK	80	Polystyrene (MW = 395 g mol^{-1})	0.067	~90*	[14]
PEEK	80	Pd	-	93	[14]
PEEK	85	Polystyrene (MW = 595 g mol^{-1})	0.2	75	[17]
PEEK	140	Polystyrene (MW = 595 g mol^{-1})	0.4	65	[17]
M_60	100	Allura Red AC (MW = 496 g mol^{-1})	24.1	~90	[7]

TCTA-EP-8	100	Allura Red AC (MW = 496 g mol^{-1})	33.1	94.4	This work

* The value was estimated from the rejection figure in the literature. † The value was calculated from the equation: Flux = –0.47 + 0.22*$e^{0.033*T}$, L m^{-2} h^{-1}, in the literature.

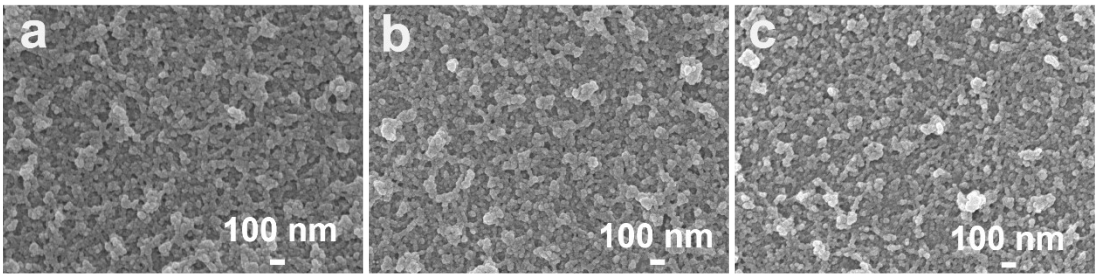


Figure S16. FESEM images of TCTA-EP-8 membranes after immersion in (a) 1.8 M in NaOH water, (b) 1.4 M H_2SO_4 in water and (c) 0.9 M triethylamine in DMF respectively for 7 days.

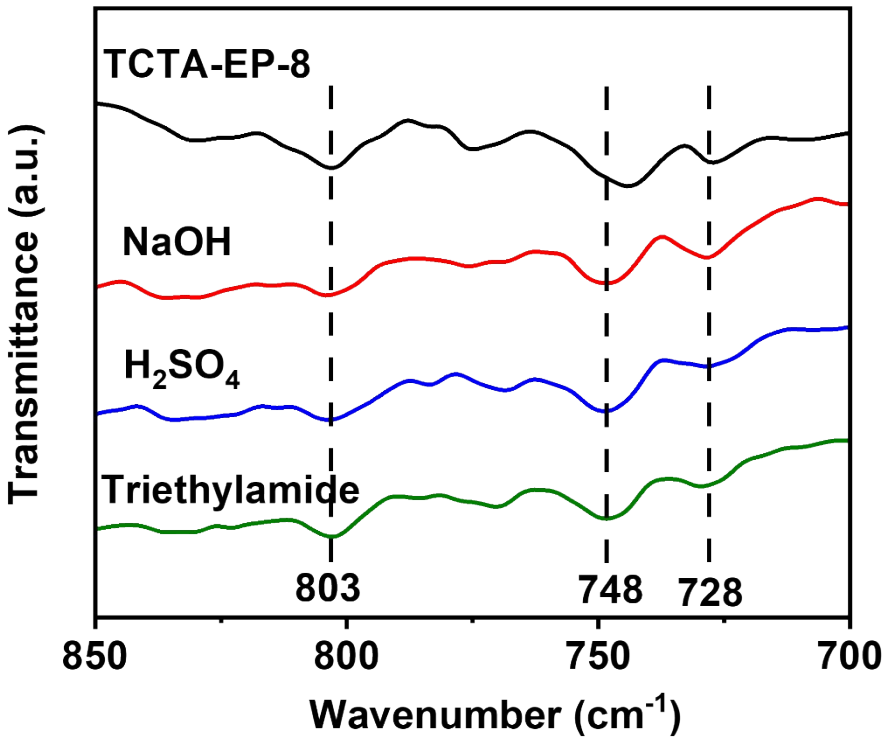


Figure S17. FTIR spectra of TCTA-EP-8 membranes after immersion in 1.8 M H_2SO_4 in water, 1.4 M NaOH in water and 0.9 M triethylamine in DMF respectively for 7 days.

Reference

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