Electronic Supplementary Information

Brønsted acid Mediated Covalent Organic Framework Membranes for Efficient Molecular Separation

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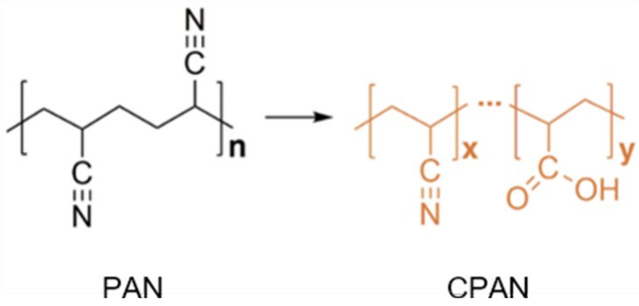


Fig. S1. Schematic presentation of the PAN transformed into CPAN.

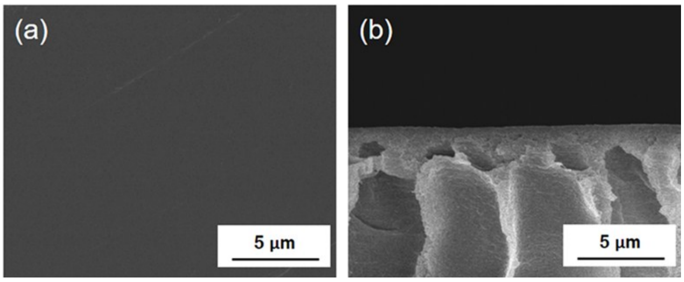


Fig. S2. Morphology of CPAN support membranes. (a) Surface SEM image. (b) Cross-sectional SEM image.

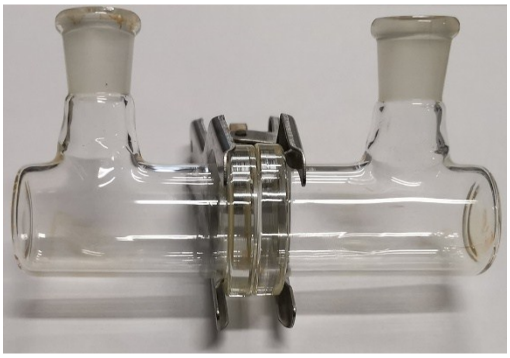


Fig. S3. Homemade diffusion cell used for the preparation of COF-JLU2 membranes.

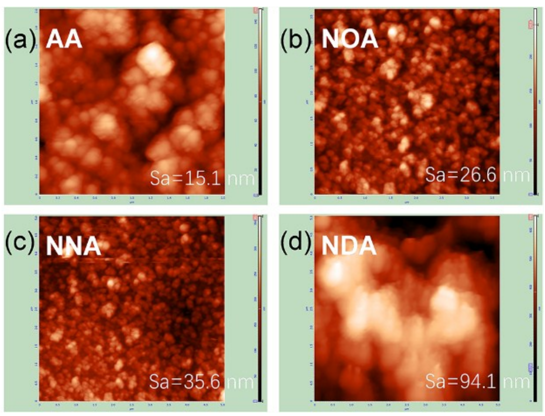


Fig. S4. AFM images of membranes. (a) mediated by AA. (b) mediated by NOA. (c) mediated by NNA. (d) mediated by NDA.

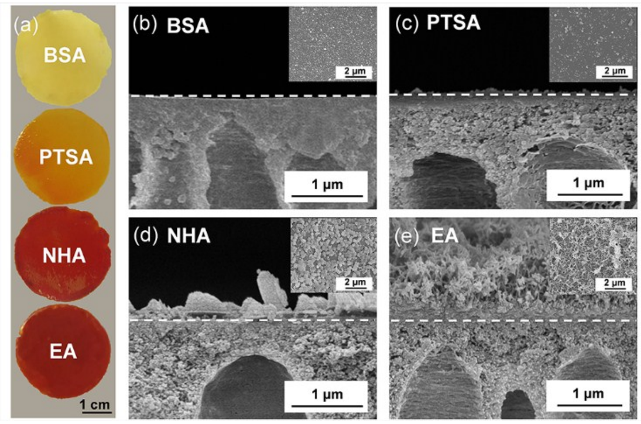


Fig. S5. (a) Digital photograph of membranes mediated by BSA, PTSA, NHA and EA, respectively; (b) Cross-sectional and top-view HRSEM images of membranes mediated by BSA. (c) Cross-sectional and top-view HRSEM images of membranes mediated by PTSA. (d) Cross-sectional and top-view HRSEM images of membranes mediated by NHA. (e) Cross-sectional and top-view HRSEM images of membranes mediated by EA.

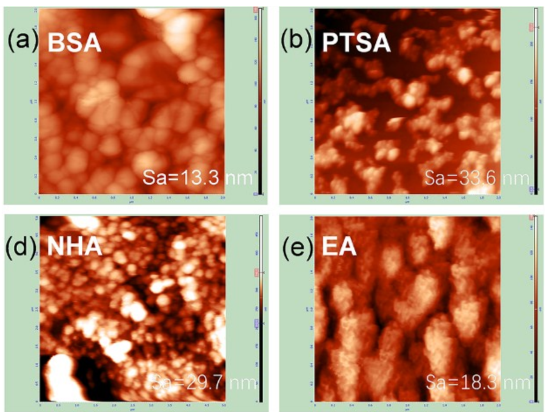


Fig. S6. AFM images of membranes. (a) mediated by BSA. (b) mediated by PTSA. (c) mediated by NHA.(d) mediated by EA.

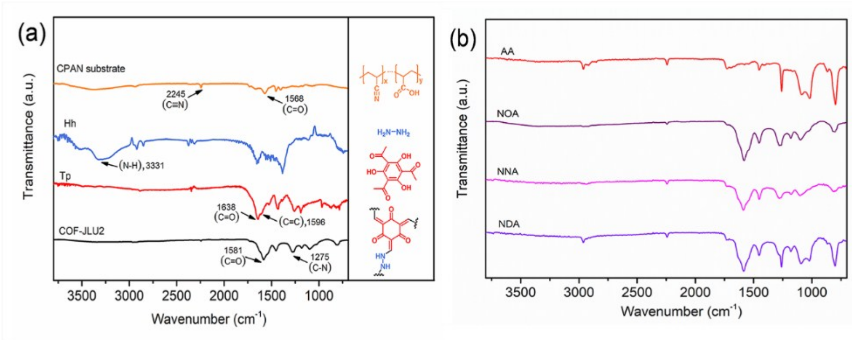


Fig. S7. (a) FT-IR spectra of CPAN substrate, Tp, Hh and COF-JLU2, respectively. (b) FT-IR spectra of membranes mediated by AA, NOA, NNA and NDA, respectively.

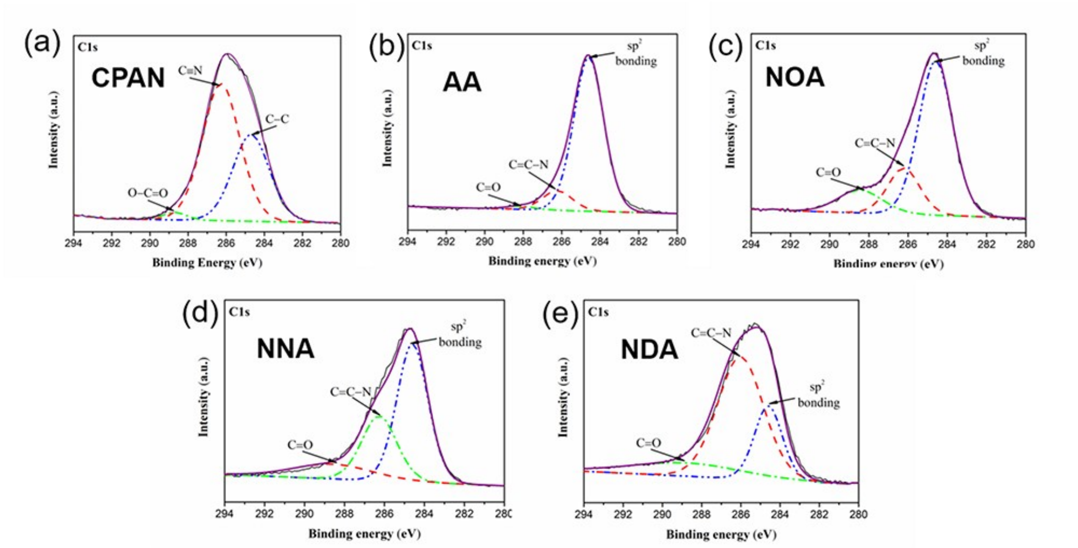


Fig. S8. (a) C1s XPS spectra of CPAN support. (b) C1s XPS spectra of membrane mediated by AA. (c) C1s XPS spectra of membrane mediated by NOA. (d) C1s XPS spectra of membrane mediated by NNA. (e) C1s XPS spectra of membrane NDA.

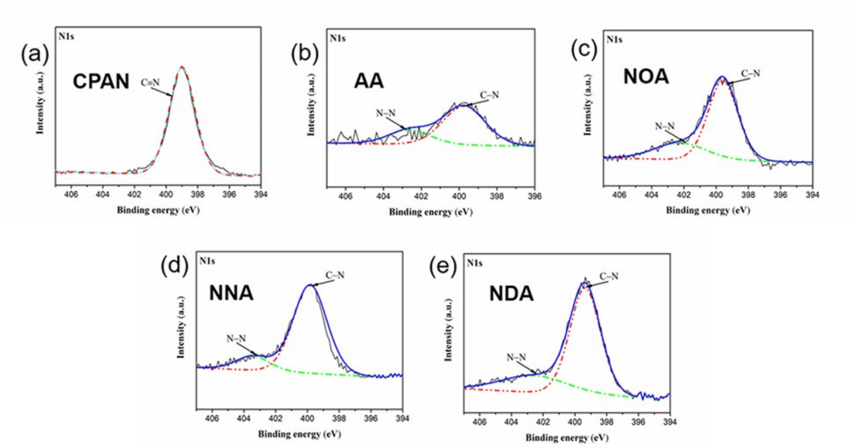


Fig. S9. (a) N1s XPS spectra of CPAN support. (b) N1s XPS spectra of membrane mediated by AA. (c) N1s XPS spectra of membrane mediated by NOA. (d) N1s XPS spectra of membrane mediated by NNA. (e) N1s XPS spectra of membrane NDA.

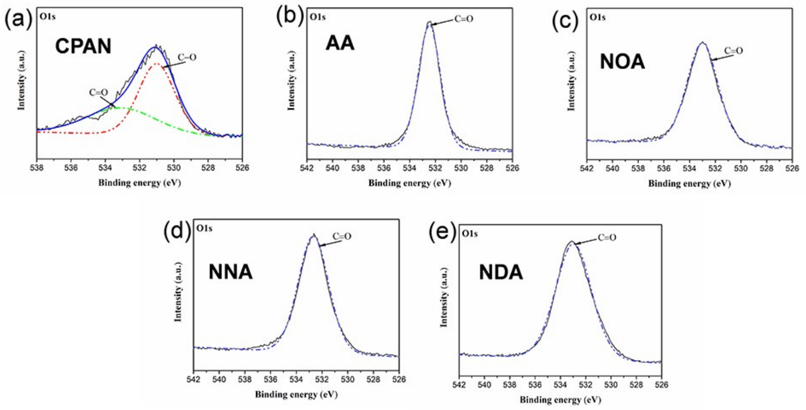


Fig. S10. (a) O1s XPS spectra of CPAN support. (b) O1s XPS spectra of membrane mediated by AA. (c) O1s XPS spectra of membrane mediated by NOA. (d) O1s XPS spectra of membrane mediated by NNA. (e) O1s XPS spectra of membrane NDA.

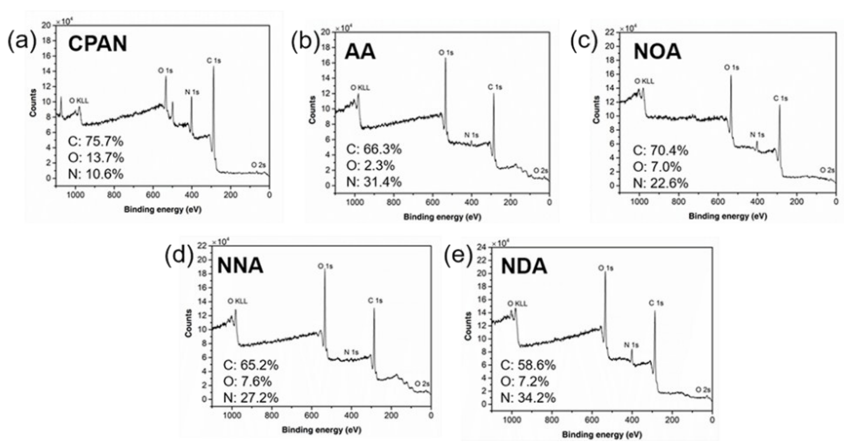


Fig. S11. (a) XPS survey spectra of CPAN support. (b) XPS survey spectra of membrane mediated by AA. (c) XPS survey spectra of membrane mediated by NOA. (d) XPS survey spectra of membrane mediated by NNA. (e) XPS survey spectra of membrane mediated by NDA.

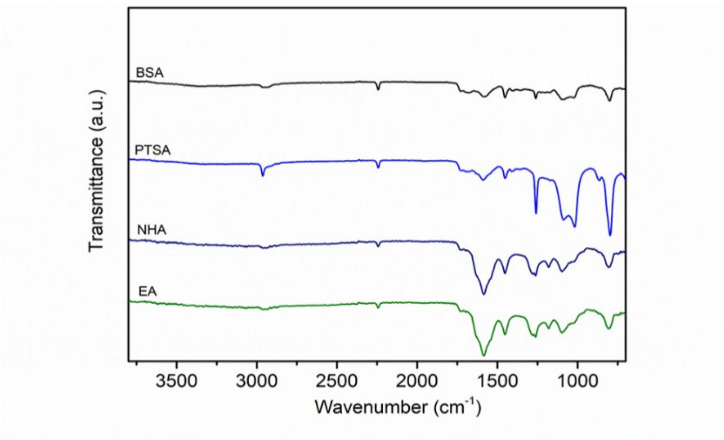


Fig. S12. FT-IR spectra of membranes mediated by BSA, PTSA, NHA and EA, respectively.

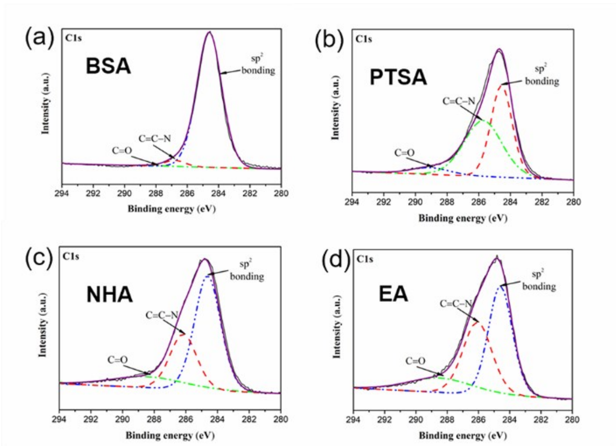


Fig. S13. (a) C1s XPS spectra of membrane mediated by BSA. (b) C1s XPS spectra of membrane mediated by PTSA. (c) C1s XPS spectra of membrane mediated by NHA. (d) C1s XPS spectra of membrane mediated by EA.

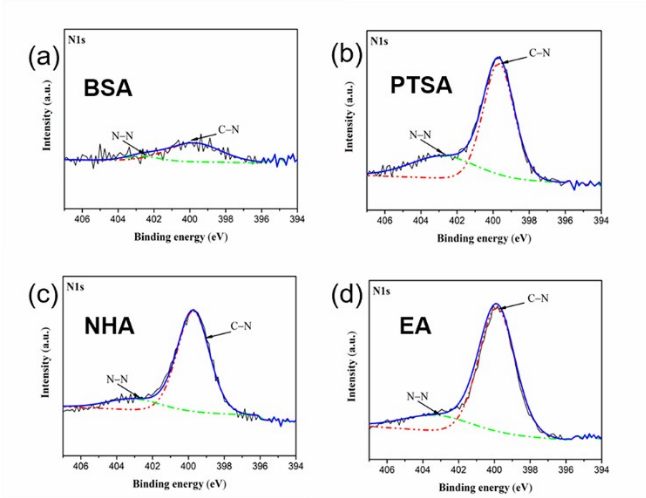


Fig. S14. (a) N1s XPS spectra of membrane mediated by BSA. (b) N1s XPS spectra of membrane mediated by PTSA. (c) N1s XPS spectra of membrane mediated by NHA. (d) N1s XPS spectra of membrane mediated by EA.

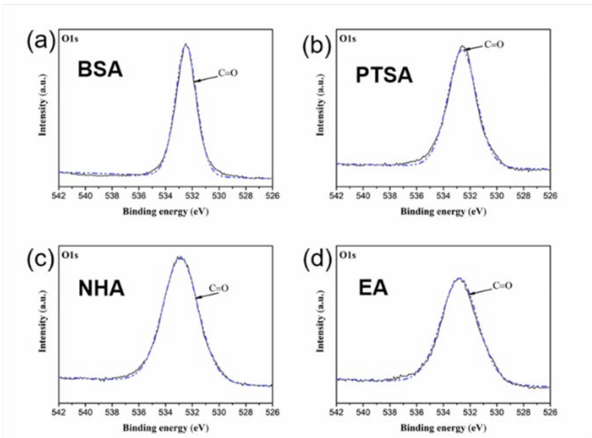


Fig. S15. (a) O1s XPS spectra of membrane mediated by BSA. (b) O1s XPS spectra of membrane mediated by PTSA. (c) O1s XPS spectra of membrane mediated by NHA. (d) O1s XPS spectra of membrane mediated by EA.

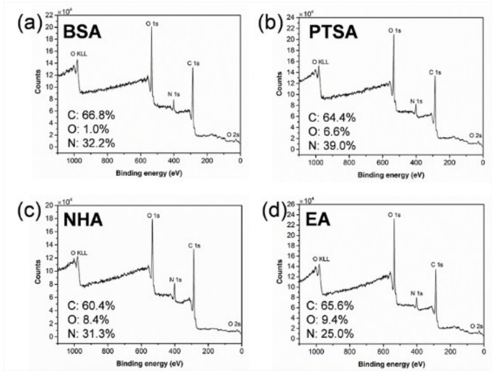


Fig. S16. (a) XPS survey spectra of membranes mediated by BSA. (b) XPS survey spectra of membranes mediated by PTSA. (c) XPS survey spectra of membranes mediated by NHA. (d) XPS survey spectra of membranes mediated by EA.

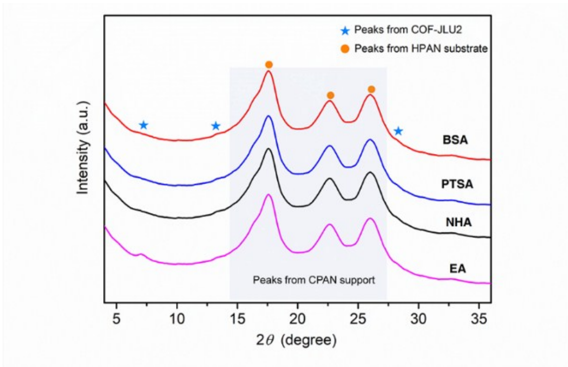


Fig. S17. GIWAXS results of membranes mediated by BSA, PTSA, NHA and EA, respectively.

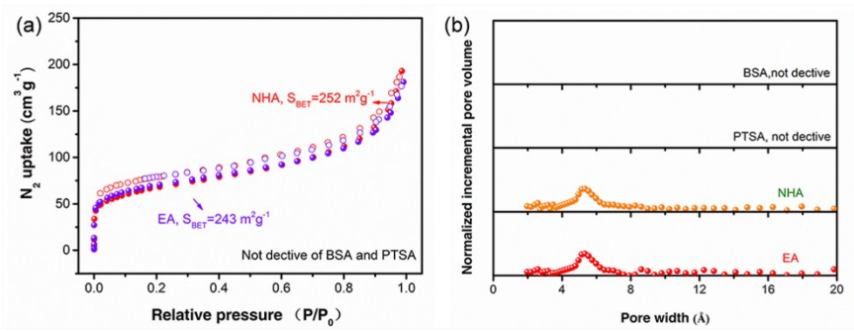


Fig. S18. (a) N_2 adsorption isotherm of membranes mediated by BSA, PTSA, NHA and EA. (b) aperture size distribution of membranes mediated by BSA, PTSA, NHA and EA.

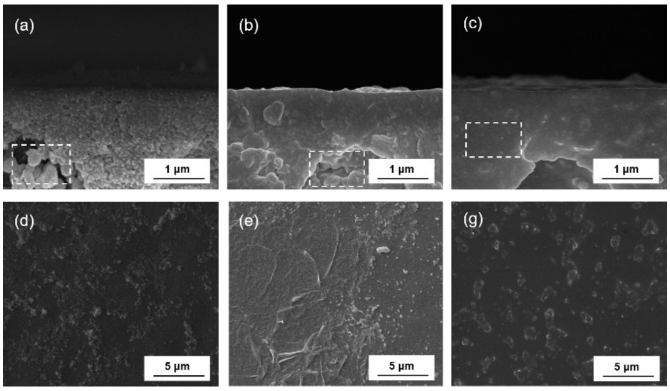


Fig. S19. HRSEM images of COF-JLU2 membranes mediated by Brønsted acids dissolved in aqueous phase. (a, d) cross-sectional and top-view images of membranes meidiated by AA. (b, e) cross-sectional and top-view images of membranes meidiated by NOA. (c, g) cross-sectional and top-view images of membranes meidiated by NDA.

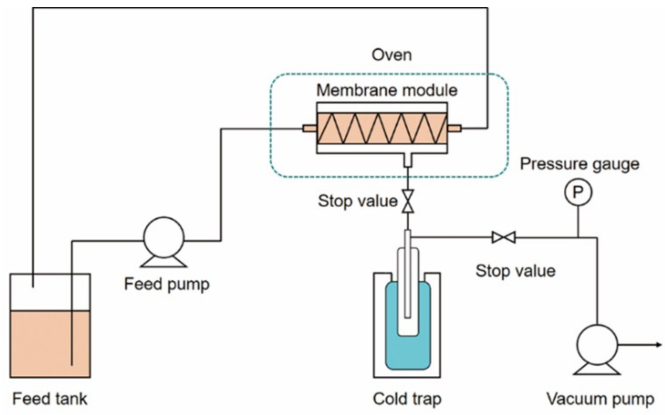


Fig. S20. Schematic presentation of steady-state alcohol dehydration measurement apparatus.

Table S1. Properties of Brønsted acid mediators.

Brønsted acid mediator	LogP

BSA	-1.67
AA	-0.28
PTSA	0.93
NHA	1.84
EA	2.37
NOA	2.43
NNA	2.82
NDA	3.96

Table S2. Structure and properties of small alcohols used as a marker for membrane dehydration process.

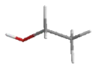
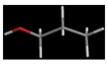
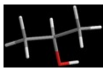
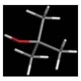
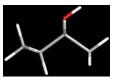
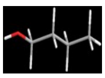
Name	Structure	Boiling point (K)	Critical temperature (K)	Molecular diameter (Å)
Ethanol		351.4	514.0	4.3
Propyl alcohol		370.4	536.8	4.6
Isopropyl alcohol		355.4	508.3	4.6
Tertiary butanol		355.6	506.2	4.8
Sec-butyl alcohol		372.8	536.2	4.8
n-butyl alcohol		390.9	563.3	5.1

Table S3. Butanol dehydration performances in literatures.

Membrane	Temperature (°C)	Feed solution	Total flux (g/m^2h)	Separation factor	Publication	Reference
GO/mPAN	70	10/90 wt% water/ n-butanol	4340	1791	2015	[2]
Hydrophobic silica	90	95/5 wt% water/ n-butanol	1500	15	2013	[3]
CS@GO/hollow fiber	70	10/90 wt% water/ n-butanol	10124	1523	2015	[4]
PMDA-ODA-S	40	10/90 wt% water/ butanol	1400	109.3	2016	[5]
GO-GTA membranes	60	15/85 wt% water/ n-butanol	2593	1883	2017	[6]
SiO_2 xerogel/CS MMMs	50	10/90 wt% water/ butanol	736	1498	2018	[7]
PVA/ceramic hollow fiber	80	5/95 wt% water/ n-butanol	1000	450	2006	[8]
PVA/PAN	60	5/95 wt% water/ n-butanol	250	350	1995	[9]
Pervap®2510	80	5/95 wt% water/ n-butanol	700	180	2004	[10]
6FDA-ODA-NDA/Ultem® 1010	60	15/85 wt% water/ n-butanol	390	2518	2009	[11]
BTESE hybrid silica (ETP-CVD)	95	5/95 wt% water/ n-butanol	1800	1100	2013	[12]
Hollow fiber silica	80	5/95 wt% water/ n-butanol	2920	1200	2005	[13]
P84/ceramic	95	5/95 wt% water/ n-butanol	1400	931	2008	[14]
Tubular silica	70	5/95 wt%	4500	600	2001	[15]

		water/ n-butanol				
PI/PEI dual-layer hollow fiber	60	15/85 wt% water/ n-butanol	846	1174	2009	[16]
Tubular silica	75	5/95 wt% water/ n-butanol	3000	250	2002	[17]
QP4VP/CMCNa	60	10/90 wt% water/ n-butanol	2241	1116	2013	[18]
ZIF-8/PBI	60	15/85 wt% water/ n-butanol	81	3417	2012	[19]
TR-PBO	80	10/90 wt% water/ n-butanol	58	390	2012	[20]
Methylated silica	60	6/94 wt% water/ n-butanol	1500	1000	2010	[21]
Tubular silica	70	5/95 wt% water/ n-butanol	2300	680	2001	[22]
COF/CNF	80	10/90 wt% water/ n-butanol	8530	3876	2019	[23]

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