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Supporting Information

Polybenzimidazole-based mixed membranes with exceptional high water vapor permeability and selectivity

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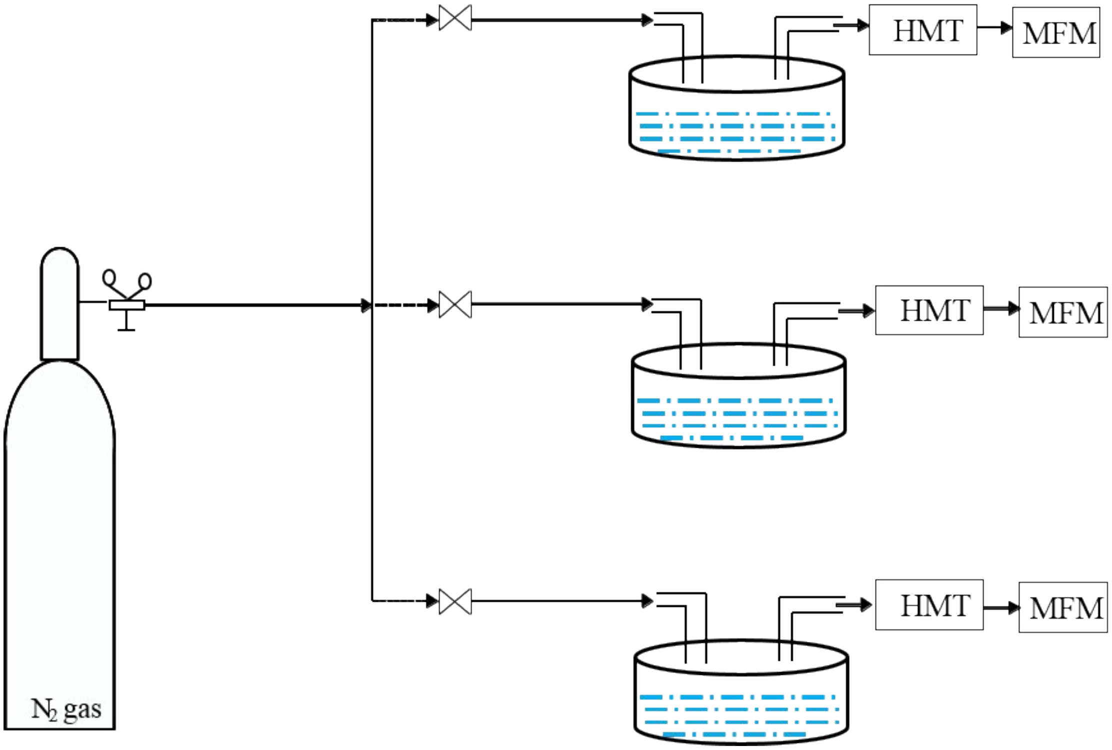

Figure S1: Schematic presentation for measuring water vapor permeation through the mixed matrix membranes. Humidity & temperature sensor (HMT) and mass flow meter (MFM).

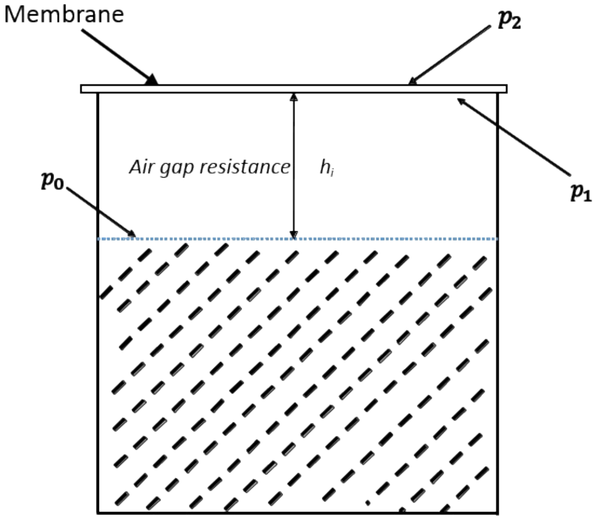

Figure S2: Schematic diagram for apparent and actual water vapor pressure values obtained from a water vapor permeability cup.

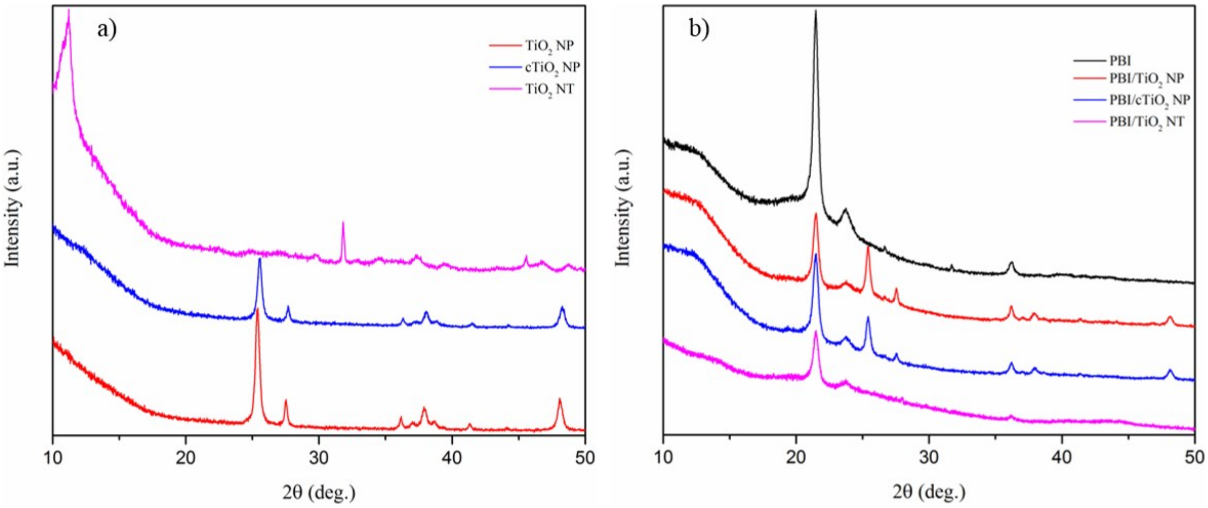

Figure S3: The WXRD pattern for: a) TiO_2 nanoparticles, carboxylated TiO_2 ($cTiO_2$) nanoparticles and TiO_2 nanotubes; b) PBI and the mixed matrix membranes containing the fixed amount of TiO_2 nanoparticles, $cTiO_2$ nanoparticles and TiO_2 nanotubes.

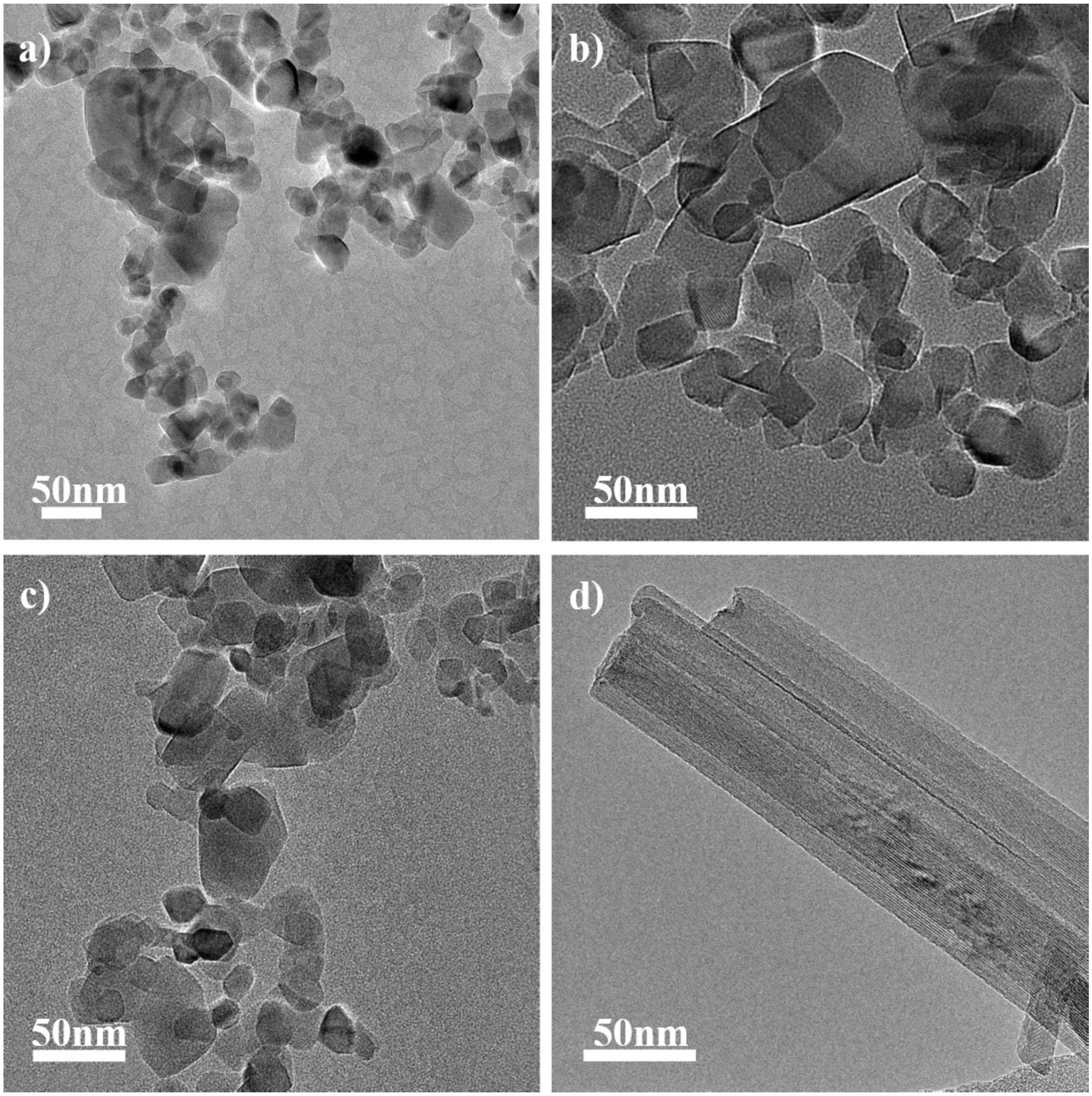

Figure S4: TEM images for: a) TiO_2 nanoparticles; b) alkali treated TiO_2 nanoparticles; c) carboxylated TiO_2 ($cTiO_2$) nanoparticles and d) TiO_2 nanotubes.

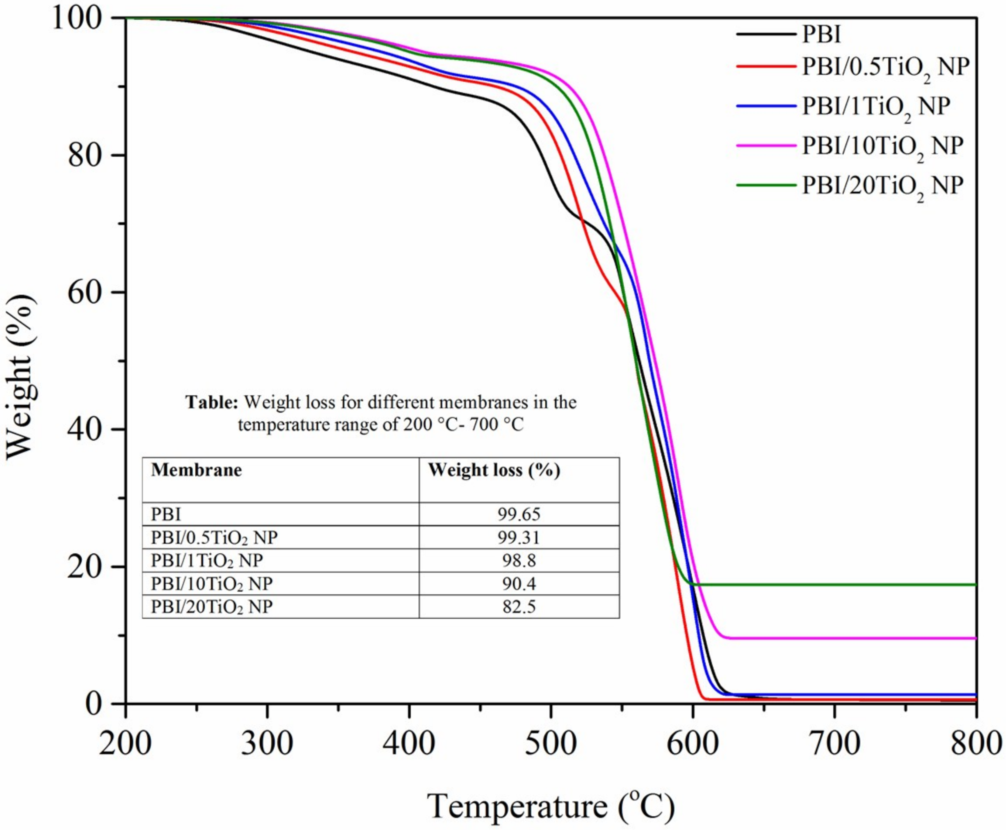

Table: Weight loss for different membranes in the temperature range of 200 °C- 700 °C

Membrane	**Weight loss (%)**
PBI	99.65
PBI/0.5TiO_2 NP	99.31
PBI/1TiO_2 NP	98.8
PBI/10TiO_2 NP	90.4
PBI/20TiO_2 NP	82.5

Figure S5: TGA for the mixed matrix membranes with varied amounts of TiO_2 nanoparticles. Inset table shows the weight loss observed for different membranes in the temperature range of 200 °C-700 °C.

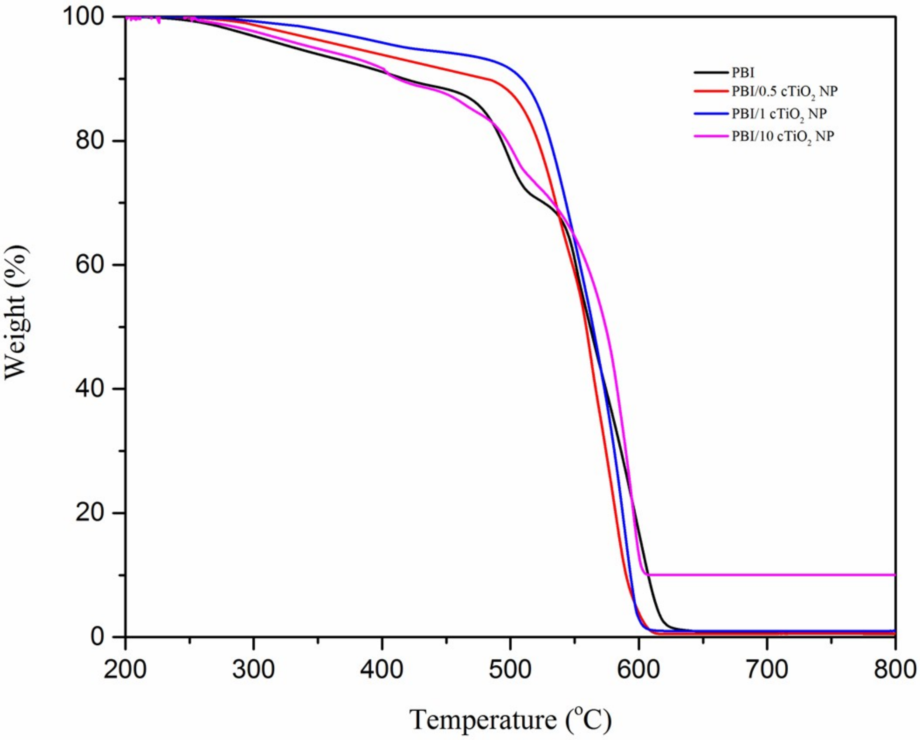

Figure S6: TGA of the mixed matrix membranes with varied amounts of carboxylic acid functionalized TiO_2 nanoparticles.

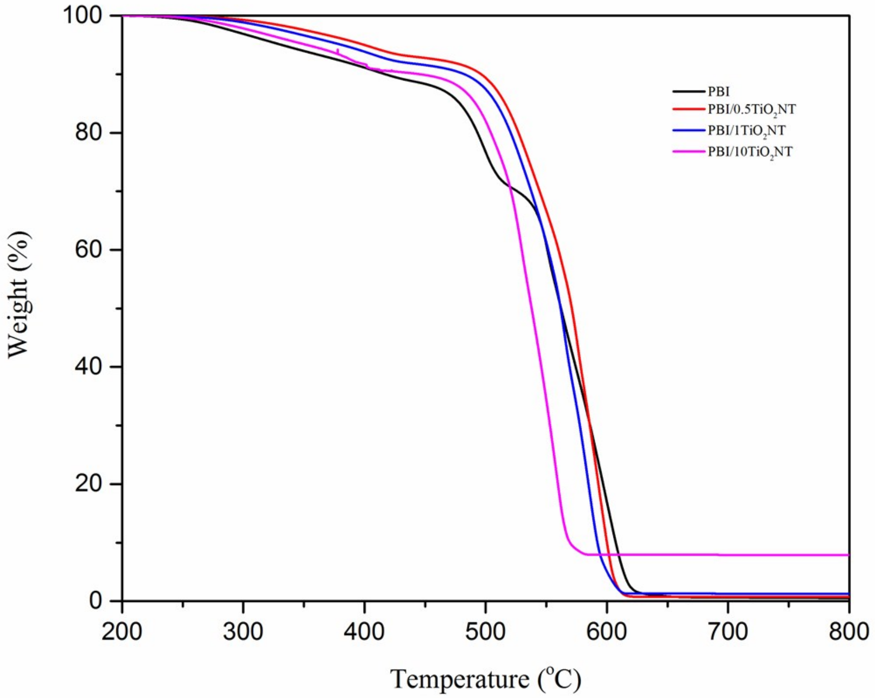

Figure S7: TGA of the mixed matrix membranes with varied amounts of TiO_2 nanotubes.

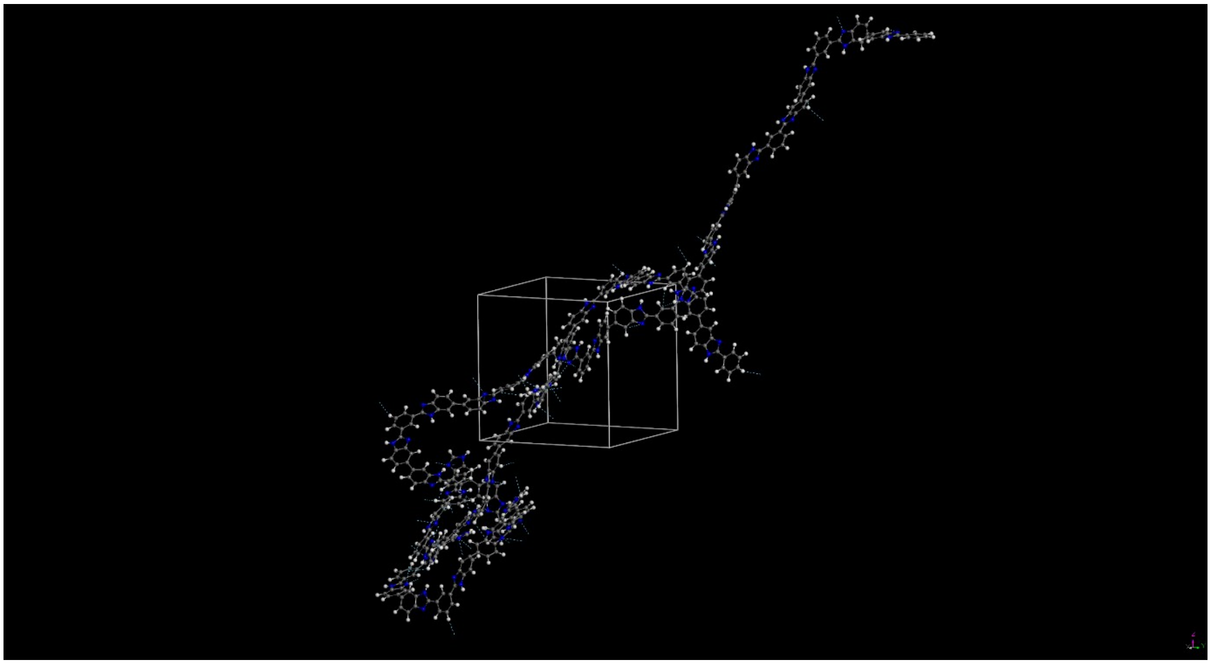

Figure S8: Hydrogen bond network formed in pure PBI, snapshots from MD simulations showing the H-bonds.

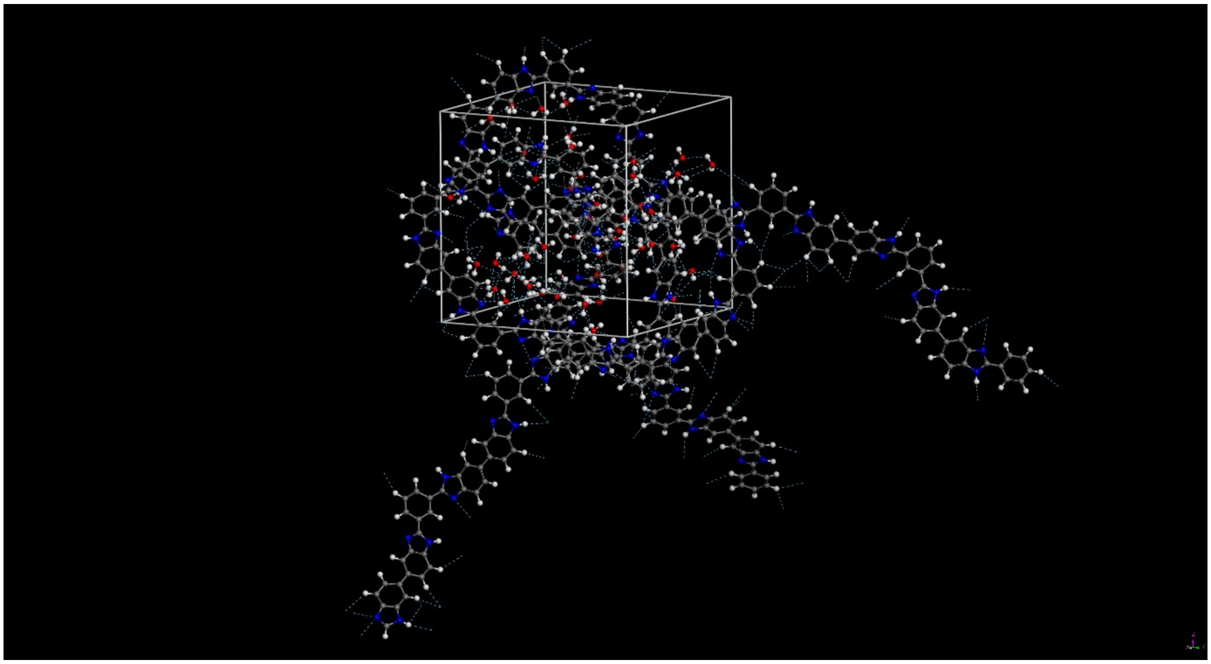

Figure S9: Hydrogen bond network formed in PBI-water cluster when water vapor activity *a=0.6*, snapshots from MD simulations showing the H-bonds.

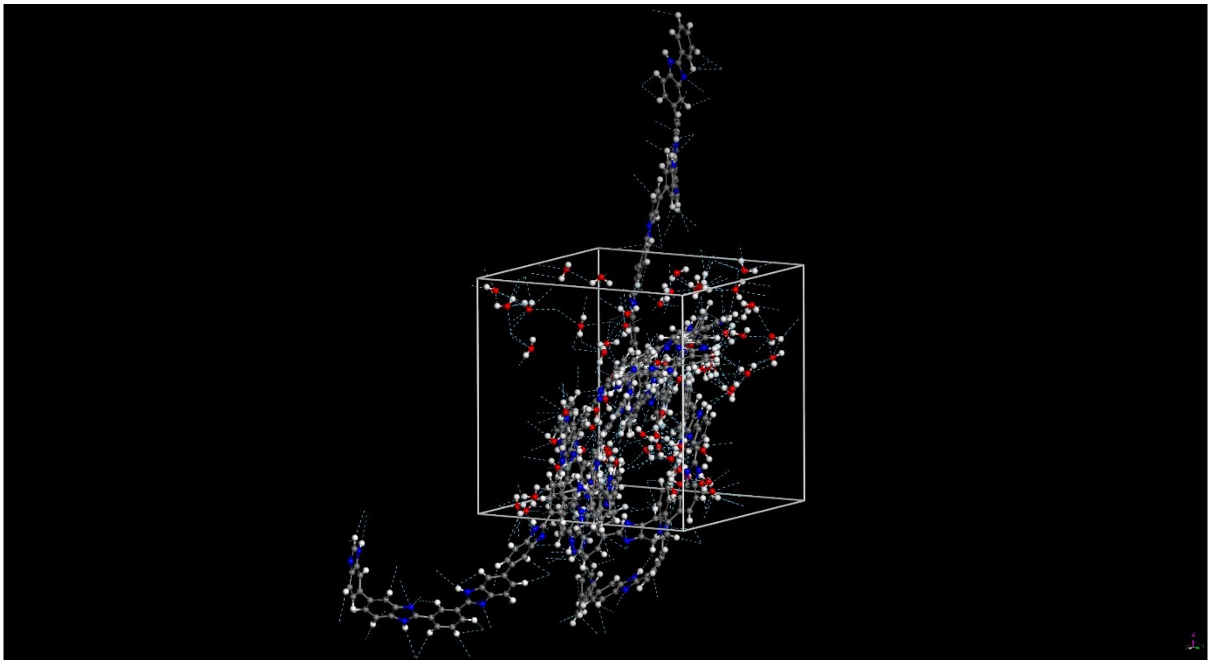

Figure S10: Hydrogen bond network formed in PBI-water cluster when water vapor activity *a=0.8*, snapshots from MD simulations showing the H-bonds.

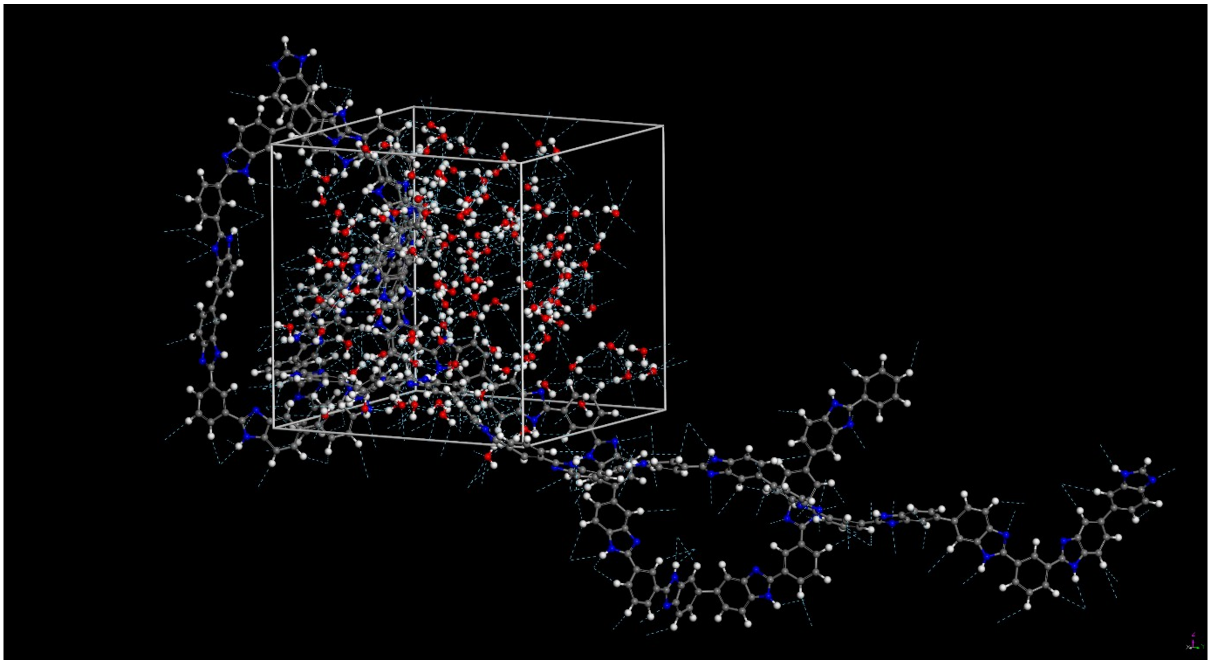

Figure S11: Hydrogen bond network formed in PBI-water cluster when water vapor activity *a=0.95*, snapshots from MD simulations showing the H-bonds.

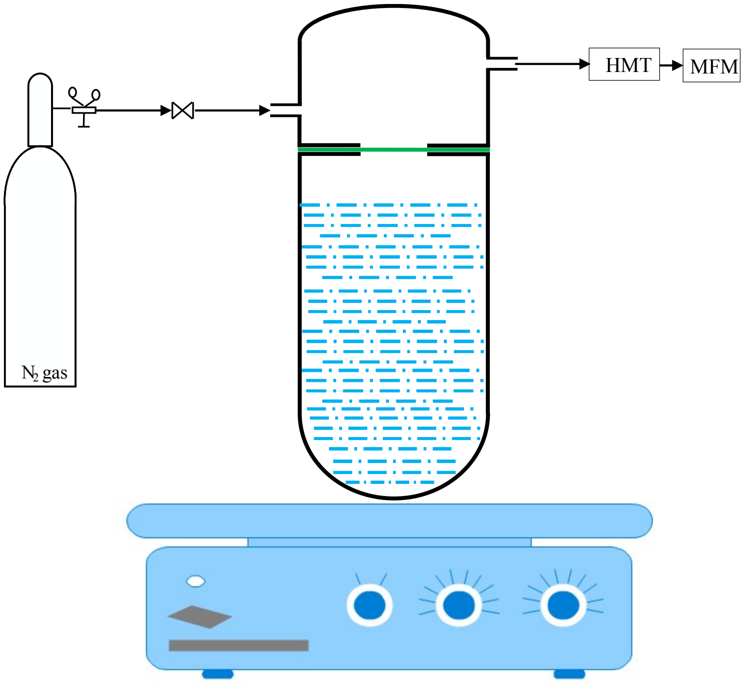

Figure S12: Schematic presentation of reactor used for esterification reaction. Humidity & temperature sensor (HMT) and mass flow meter (MFM).

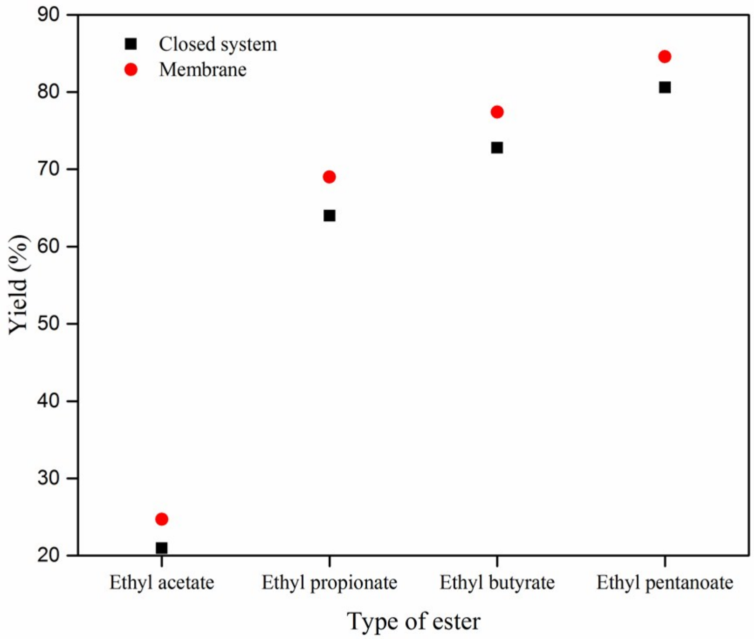

Figure S13: Effect of ester yield with membrane and with Al foil (closed system).

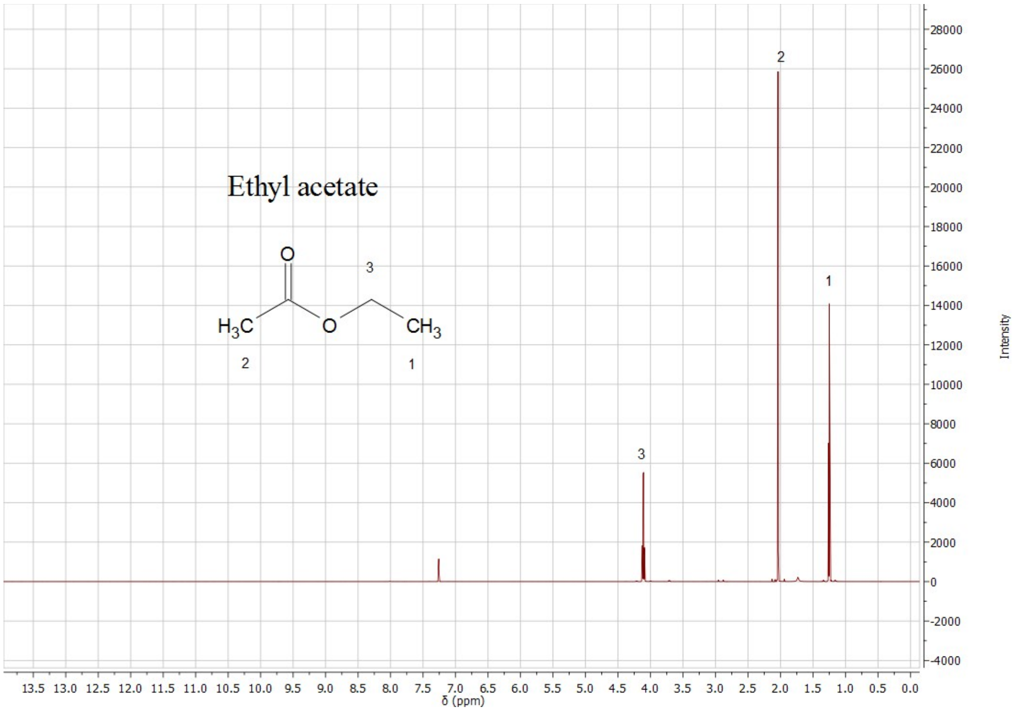

Figure S14: ^{1}H NMR spectrum of ethyl acetate when Al foil was used.

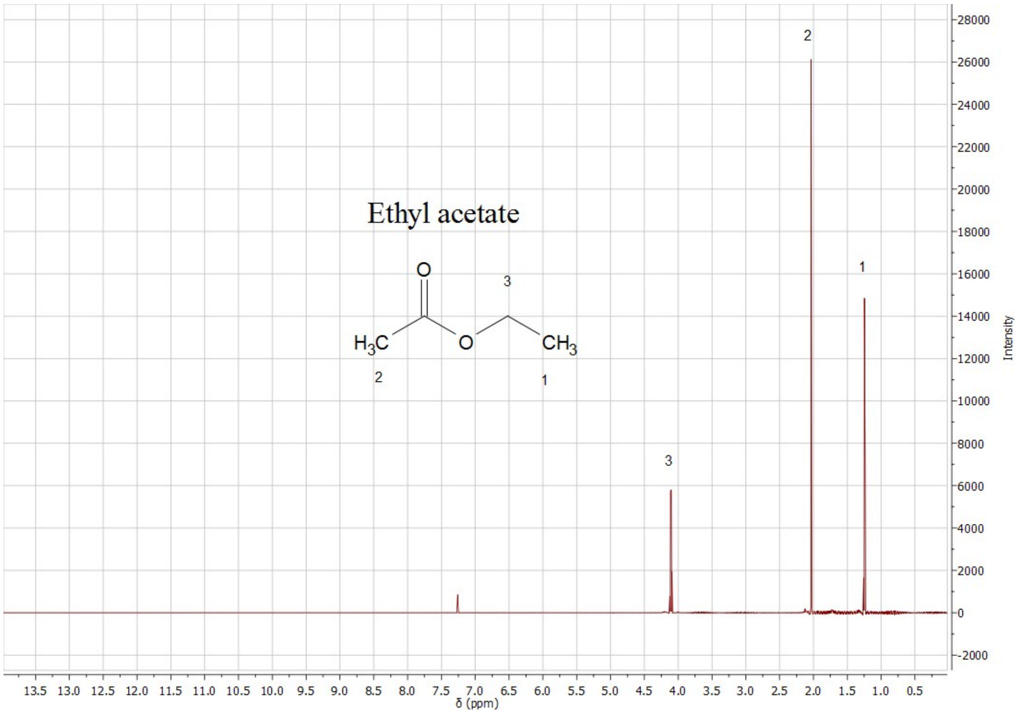

Figure S15: ^{1}H NMR spectrum of ethyl acetate prepared using PBI membrane.

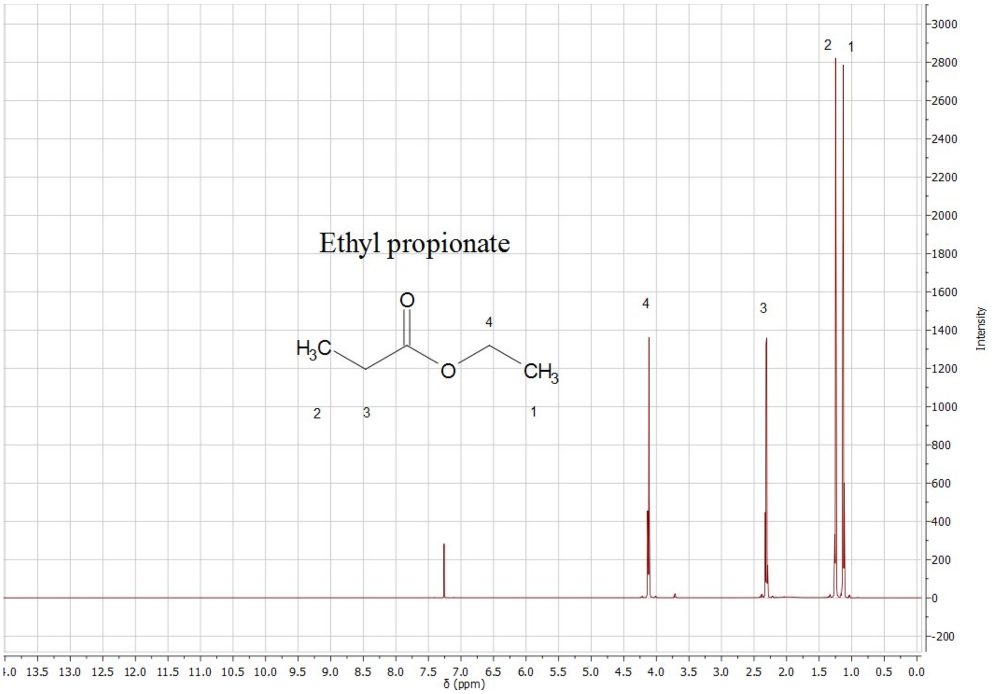

Figure S16: ^{1}H NMR spectrum of ethyl propionate prepared using PBI membrane.

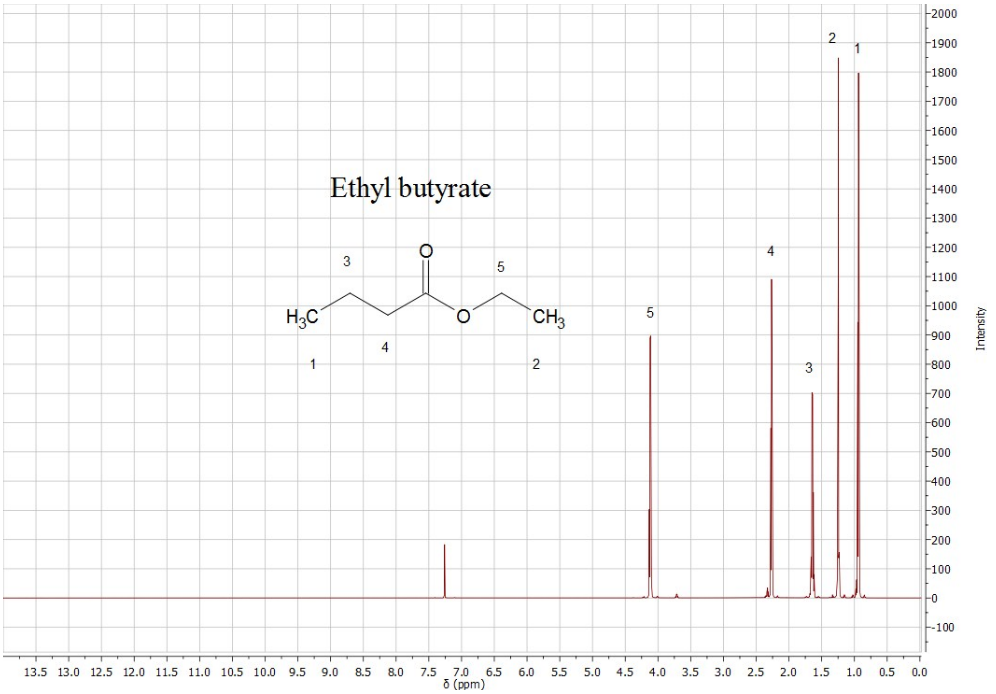

Figure S17: ^{1}H NMR spectrum of ethyl butyrate prepared using PBI membrane.

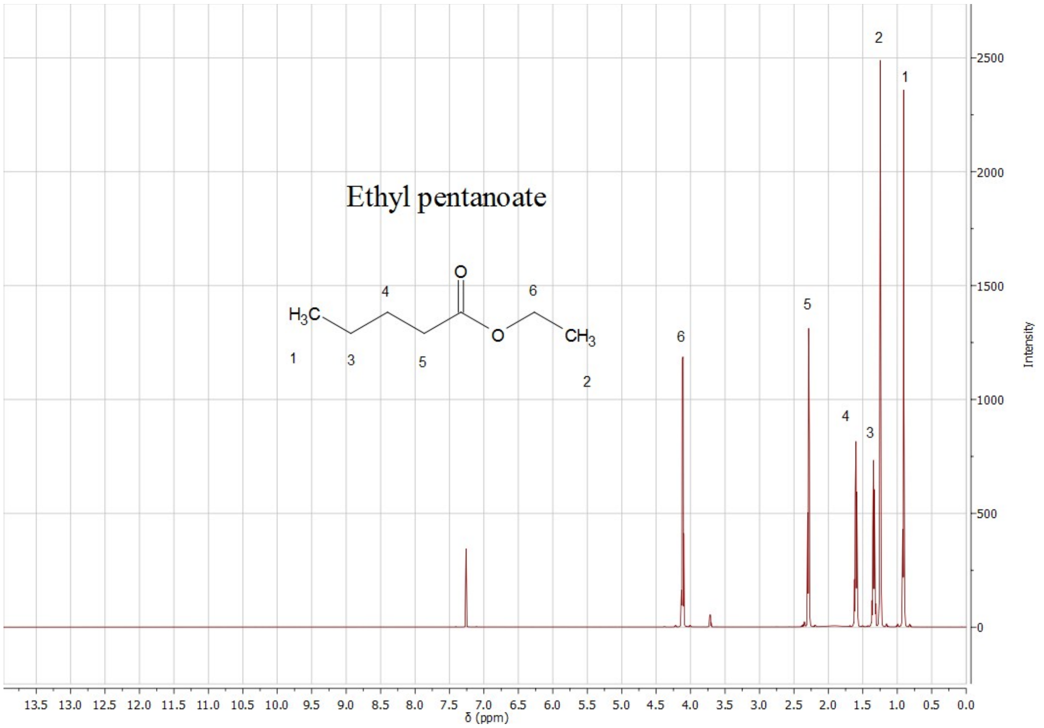

Figure S18: ^{1}H NMR spectrum of ethyl pentanoate prepared using PBI membrane.

Table S1: Dual-mode parameters from Equation 7 for water sorption in PBI at 25 °C

Activity range	K_D (cm^{3}STP/cm^{3}Poly.atm)	b (atm^{-1})	C'_{H} (cm^{3}STP/cm^{3}Poly)
Sorption (0-0.6)	11773.9±940.7	237.35±761.34	13.64±27.63

Table S2: Comparison of the performance of fabricated membranes with state-of-the-art membranes

Sr. No.	Membrane material	Temperature (°C)	Water vapor permeance (GPU)	Water vapor permeability (Barrer)	Selectivity H_2O/N_2	Ref.
1	PSU HFM	32	529	-	50	[1]
2	[Emim][Tf_2N]	31	635	2.80×10^5	3.80×10^3	[2]
3	Stabilized triethylene glycol	15-30	223	1.50×10^4	2.0×10^3	[3]
4	PSU/Si-TFC	30	2.2×10^3	741	500	[4]
5	PSU/ HFM PA TFC	30	1.5×10^3	505	500	[5]
6	PESU/PDA-TFC (polydopamine)	30	3.2×10^3	-	195	[6]
7	PESU/PDA-TFC (polydopamine)	30	1.03×10^3	473	35	[7]
8	PEI/Pebax® 1657	21	1.8×10^3	3.6×10^3	1.8×10^3	[8]
9	PESU/CA+PEG2000	30	444	444	176	[9]
10	PSU/BA-TFC (3,5-diaminobenzoic acid)	30	2.2×10^3	105	34	[10]
11	PSU/TFC-TiO_2	30	1.1×10^3	282	548	[11]
12	PESU/TFC	30	2.0×10^3	160	119	[12]
13	PSU/TFC-cTiO_2	30	1.3×10^3	302	486	[13]
14	PSU/TFC-OH-TiO_2	30	1.4×10^3	327	510	[14]
15	NaA zeolite/Ni sheet	32	2.0×10^4	6.10×10^4	178 (H_2O/air)	[15]
16	PVA/LiCl-SS scaffold	31	1.7×10^3	3.0×10^5	2.8×10^3 (H_2O/air)	[16]
17	PVA/TiO_2 –SS scaffold	24	1.5×10^3	-	5.78×10^3 (H_2O/air)	[17]

18	Pebax® 1657/ GO (5-layer and 1.6% GO)	21	5.0×10^3	1.25×10^4	8.0×10^4	[18]
19	Gaphene oxide	30.8	3.0×10^4	1.82×10^5	1.0×10^4	[19]
20	Pebax® 1074	21	3.2×10^4	1.6×10^5	2.0×10^5	[20]
21	Polyactive ($PEO_{75}PBT_{25}$)	30	-	1.4×10^5	5.0×10^4	[21]
22	PSU/13X zeolite	30	127	1.45×10^4	1.04×10^4	[22]
23	SPEEK	30	-	6.0×10^4	1.0×10^7	[23, 24]
24	SPES	30	-	1.5×10^4	2.11×0^5	[25]
25	Polyether-polyurethane	50	3.2×10^3	4.2×10^4	390	[26]
26	Polyethylene	-	-	12	5.71	[27]
27	Polyvinylalcohal	-	-	19	3.33×10^4	[27]
28	Polypropylene	-	-	68	230	[27]
29	Polystyrene	-	-	970	400	[27]
30	Cellulose acetate	-	-	6.0×10^3	2.4×10^4	[27]
31	Ethyl cellulose	-	-	2.0×10^4	6.06×10^3	[28]
32	Polyvinylchloride	-	-	275	1.25×10^4	[27]
33	Polyamide (PA-6)	-	-	275	1.10×10^4	[27]
34	Polycarbonate	-	-	1400	4.7×10^3	[27]
35	Polyphenyleneoxide	-	-	4.1×10^3	1.07×10^3	[27]
36	PDMS	-	-	4.0×10^4	140	[27]
37	Polyimide (Kapton)	-	-	640	5.3×10^6	[27]
38	PAN	-	-	300	1.87×10^6	[27]
39	Polysulfone	-	-	2.0×10^3	8.0×10^3	[27]
40	Natural rubber	-	-	2.6×10^3	300	[27]
41	Polyethersulfone	-	-	2.62×10^3	1.05×10^4	[25, 29]
42	PVA/TEG	30	4.8×10^3	1.43×10^5	3.0×10^3	[30]
43	Poly(acrylamide-co-acrylic acid) (PAMAC)	35	-	109	-	[31]
44	ETS-4 TFN	30	1.4×10^3	527	346	[32]

45	EVOH/EVA/EVOH	25	-	2.9×10^3	4.8×10^4	[33]
46	PBI	22	2.1×10^3	4.2×10^4	1.42×10^6	This work
47	PBI/1% TiO_2 NP	22	3.5×10^3	7.1×10^4	2.90×10^6	This work
48	PBI/1% $cTiO_2$ NP	22	3.55×10^3	7.11×10^4	3.05×10^6	This work
49	PBI/0.5% TiO_2NT	22	3.4×10^3	6.8×10^4	3.9×10^6	This work

(PDMAEMA): poly(N,N-dimethylaminoethyl methacrylate)

(MMMs) composed of multiwalled carbon nanotubes (MWCNTs) dispersed in isotactic polypropylene (i-PP)

(PAMAC) poly (acrylamide-co-acrylic acid) composite

EVOH/EVA/EVOH: Poly (ethylene-*co*-vinyl alcohol)/ Poly (ethylene-*co*-vinyl acetate) three layer membranes

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