Electronic Supplementary Information (ESI†)

Defining sulfonation limits of poly(ether-ether-ketone) for energy-efficient dehumidification

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1. Polymer characterization

Table S1. Polymers designation and physical properties

Sample Name	Sulfonation Time (h)	DoS (%)	Density (g cm^{-3})	Mw (g mol^{-1})
P0	0	0	1.30±0.02	288.09
P1	1	3.81±0.065	0.30±0.05	299.54
P2	3	6.12±0.075	1.00±0.02	310.36
P3	6	10.50±0.10	1.46±0.05	326.27
P4	8	18.91±0.12	1.45±0.03	356.87
P5	12	25.37±0.17	0.52±0.02	380.35
P6	16	37.07±0.17	0.44±0.06	422.92
P7	48	46.40±0.20	0.70±0.02	456.83

Table S2. Elemental analysis of the polymers and their degree of sulfonation (DoS)

Polymer	%C	%H	%O	%S	DoS (%)	R.U. Mw
P0	79.08±0.03	4.285±0.025	16.635±0.005	0	0	288.09
P1	76.315±0.015	4.10±0.02	17.035±0.055	1.505±0.025	3.815±0.065	299.54
P2	74.495±0.025	3.995±0.035	19.09±0.03	2.42±0.03	6.125±0.075	310.36
P3	71.18±0.04	3.78±0.03	20.875±0.035	4.15±0.04	10.50±0.10	326.27
P4	64.35±0.09	3.25±0.025	24.835±0.035	7.495±0.035	18.915±0.115	356.87
P5	58.915±0.055	3.18±0.03	27.86±0.15	10.045±0.065	25.37±0.17	380.35
P6	49.135±0.075	2.96±0.03	33.24±0.01	14.665±0.005	37.075±0.175	422.92
P7	40.825±0.085	2.78±0.03	38.015±0.015	18.38±0.07	46.40±0.20	456.83

Table S3. Thermal decomposition stages of the SPEEK (P1–P7) polymers. PEEK (P0) is included for comparison.

Polymer	1st decomposition temperature (ºC)	2nd decomposition temperature (ºC)	3rd decomposition temperature (ºC)
P0	n.a.	n.a.	500±5
P1	150±3	222±2	374±3
P2	152±5	223±3	371±3
P3	142±4	222±3	360±2
P4	166±5	269±2	404±4
P5	n.a.	278±4	366±3
P6	n.a.	274±1	367±4
P7	n.a.	273±4	401±3

n.a.=not applicable

Table S4. Glass transition temperature and melting point of the synthesized polymers

Polymer	**T_g (°C)**	**T_m (°C)**
P0	172±2	335±2
P1	169±4	308±4
P2	171±3	309±4
P3	160±4	308±5
P4	185±2	316±1
P5	156±5	319±3
P6	164±2	314±2
P7	186±5	306±2

2. Performance

Table S5. Water uptake comparison of the developed polymers with the state-of-the art materials

Adsorbent	RH (%)	Water uptake (%)	Reference
UiO-66	40	35.1	1, 2
	50	36.3	
	60	37.4	
	70	38.2	
	80	39.1	
	90	45.9	
MIL-101(Cr)	40	81.5	3-6
	50	158.2	
	60	161.7	
	80	167.5	
	90	169.2	
SAPO-34	40	29.9	7
	50	30.6	
	60	31.1	
	70	31.5	
	80	31.9	
	90	32.5	
Ionogel	40	29	8
	50	37	
	60	47	
	70	59	
	80	81	
	90	145	
Y-shp-MOF	40	6	9
	50	7	
	60	17	
	70	42	
	80	49	
	90	50	
	95	50	
SAP	40	6.00	10
	50	18.8	
	60	33.65	
	70	49.3	
	80	67.3	
	90	98.5	
	95	129	
PCHM-MOF	40	4.61	11

	50	6.14	
	60	18.64	
	70	111.84	
	80	167.85	
	90	166.96	
BIT-66	40	4.80	12
	50	5.39	
	60	38.36	
	70	56.04	
	80	56.96	
	90	59.24	
	95	64.45	
MIL-100 (Fe)	40	36.37	13
	50	51.81	
	60	53.26	
	70	54.56	
	80	56.09	
	95	60.68	
MIL-160	40	35	14
	50	36	
	60	36	
	70	36	
	80	37	
	90	37	
	95	37.9	
MIP-200	40	41	14
	50	42	
	60	43	
	70	43	
	80	44	
	90	45	
MOF-801	40	28	15
	50	29	
	60	30	
	70	31	
	80	32	
	90	32	
P3	40	42.1	This work
	50	52.6	
	60	67.2	
	70	85.6	
	80	116.7	
	90	195.0	
	95	299.7	
P4	40	43.9	This work

	50	55.6
	60	70.0
	70	90.7
	80	126.7
	90	197.8
	95	323.6

Table S6. Hydrogen bond interactions within the polymers.

Polymer	DoS (%)	Number of hydrogen bonds
P0	0	0
P1	10.50	7
P2	18.915	16
P3	25.37	17
P4	37.075	19
P5	46.40	27

Table S7. Comparison of water uptake at varying DoS

Sr. No.	DoS (%)	Water uptake (%)	Liquid/vapor	Reference
1	44.5	34.9	Liquid	[16]
2	38	19.7	Liquid	[17]
3	46	24.4	Liquid	[17]
4	58	35.9	Liquid	[17]
5	66	44.8	Liquid	[17]
6	75	51.4	Liquid	[17]
7	80	61.4	Liquid	[17]
8	85	119.7	Liquid	[17]
9	48	5	Liquid	[18]
10	64	12	Liquid	[18]
11	66	19	Liquid	[18]
12	67	19	Liquid	[18]
13	79	23	Liquid	[18]
14	33	41	Liquid	[19]
15	64	32	Liquid	[20]
16	80	71	Liquid	[21]
17	98	40	Liquid	[22]
18	93	67	Liquid	[23]
19	47	100	Liquid	[17]
20	80	37	Liquid	[24]
21	69	23	Liquid	[25]
22	33	41.5	Liquid	[26]
23	53	27	Liquid	[27]
24	52	28.7	Liquid	[28]
25	59	30	Vapor	[29]
26	75	41	Vapor	[29]

27	0	0.79	Vapor	This work
28	3.8	82.5	Vapor	This work
29	6.1	192.4	Vapor	This work
30	10.5	299.7	Vapor	This work
31	18.9	323.6	Vapor	This work
32	25.3	46.9	Vapor	This work
33	37.1	19.1	Vapor	This work
34	46.4	23.3	Vapor	This work

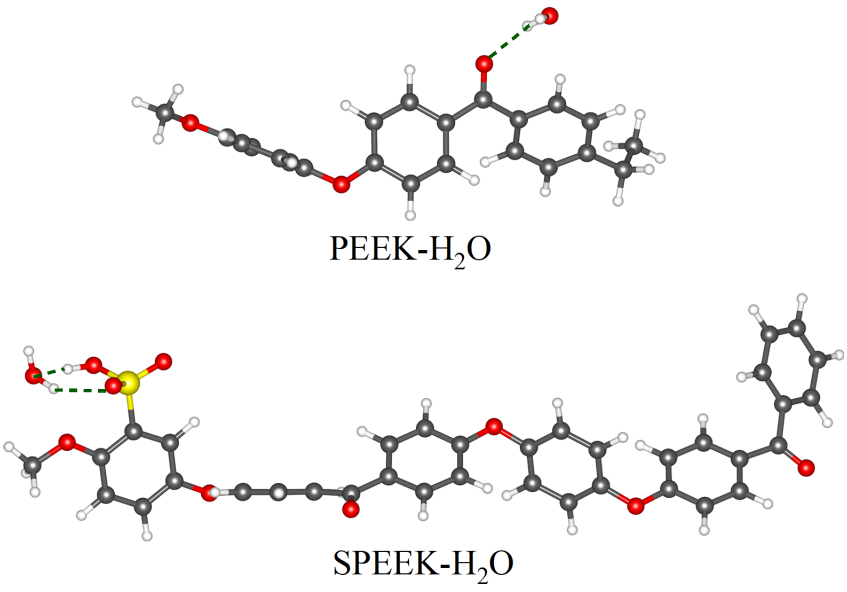

Fig. S1. Energy-minimized polymeric units of PEEK and SPEEK interacting with a water molecule.

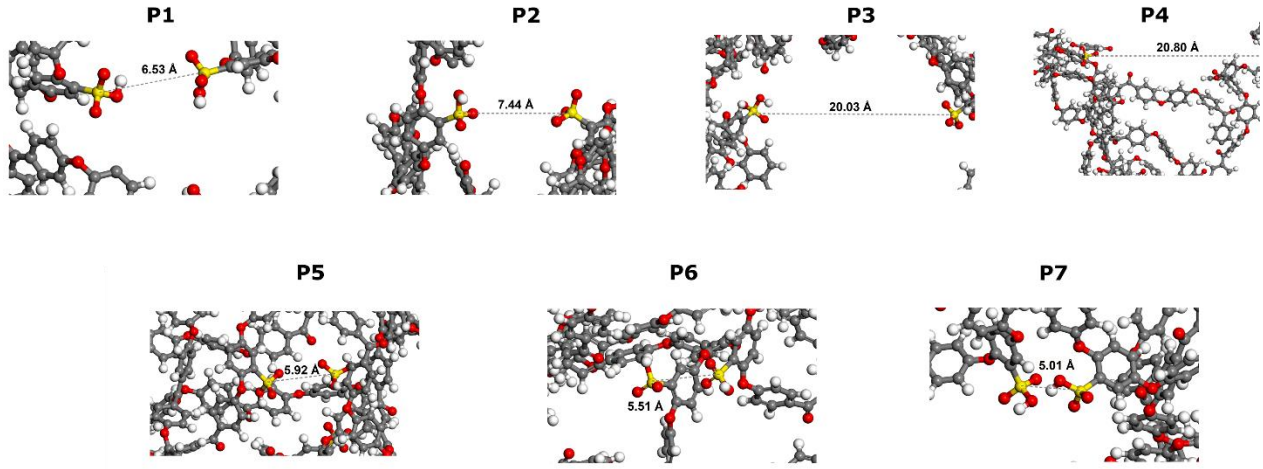

Fig. S2. Calculated S-S distances between SO_3H groups in the SPEEK polymer matrix.

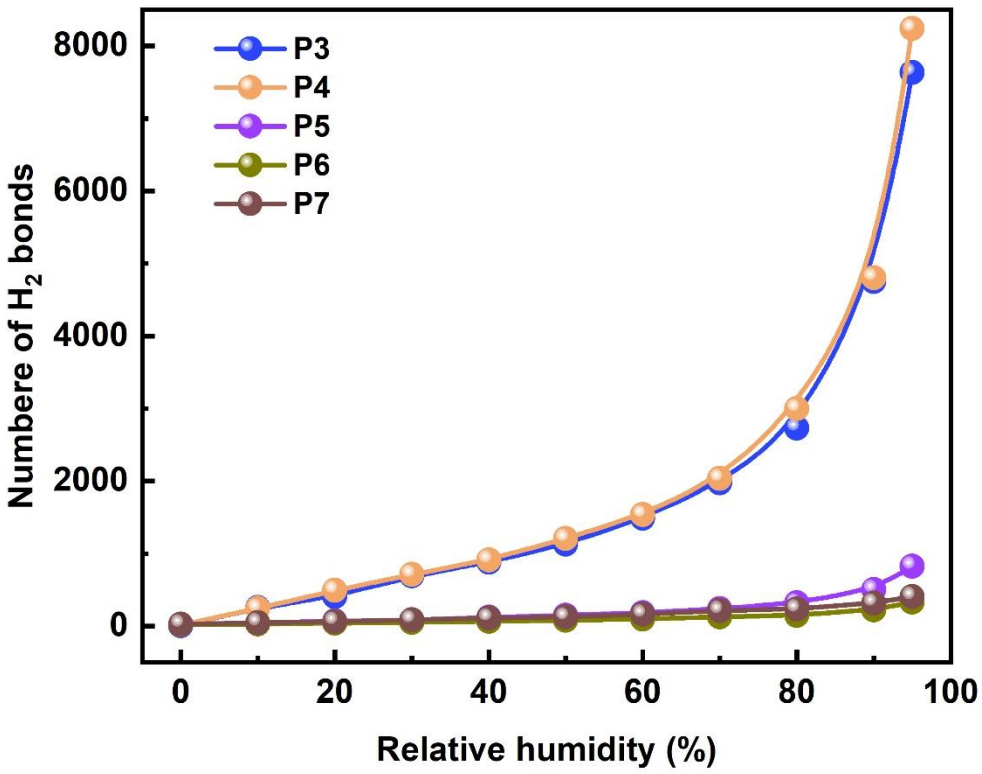

Figure S3. Hydrogen bond interactions of the SPEEK polymers as a function of RH.

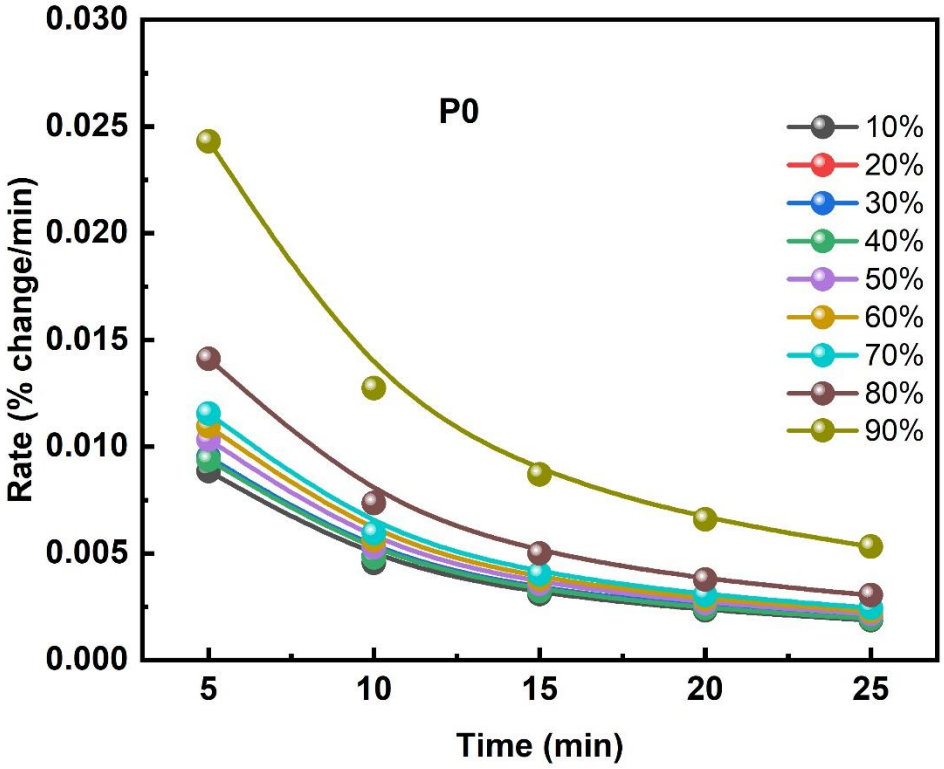

Figure S4. Water uptake rate of P0 at different relative humidity ranges from 10 to 90%.

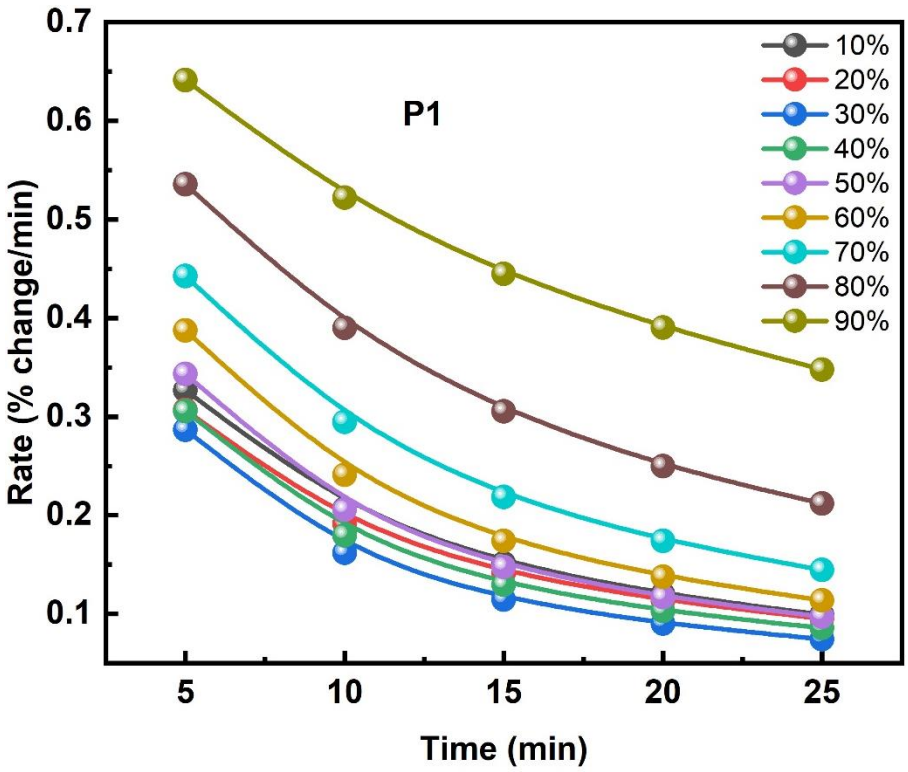

Figure S5. Water uptake rate of P1 at different relative humidity ranges from 10 to 90%.

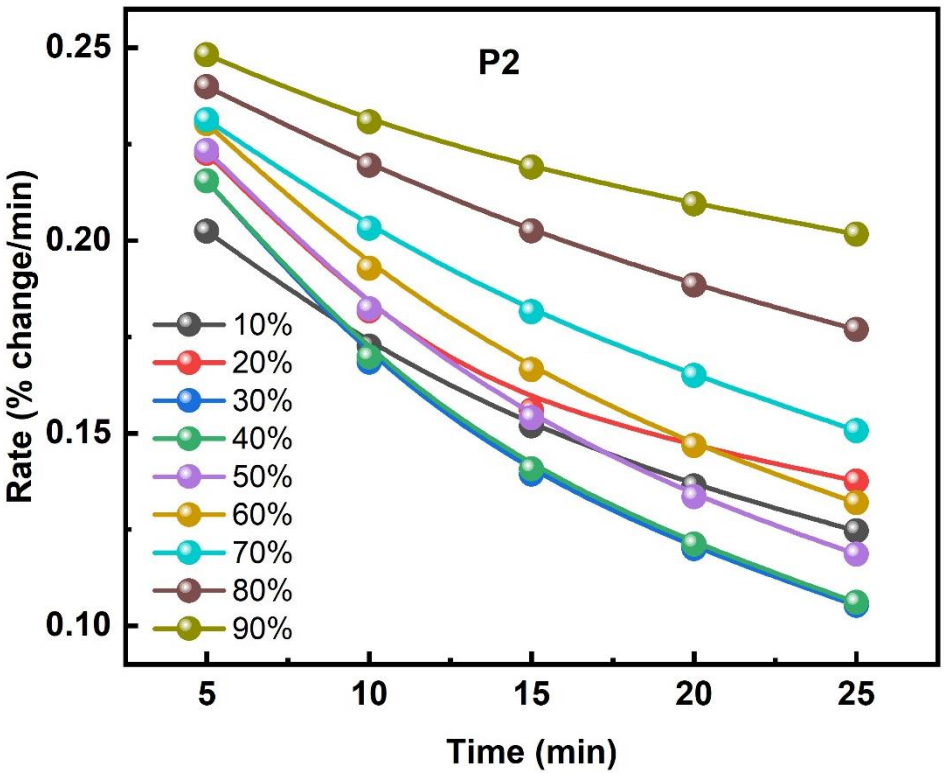

Figure S6. Water uptake rate of P2 at different relative humidity ranges from 10 to 90%.

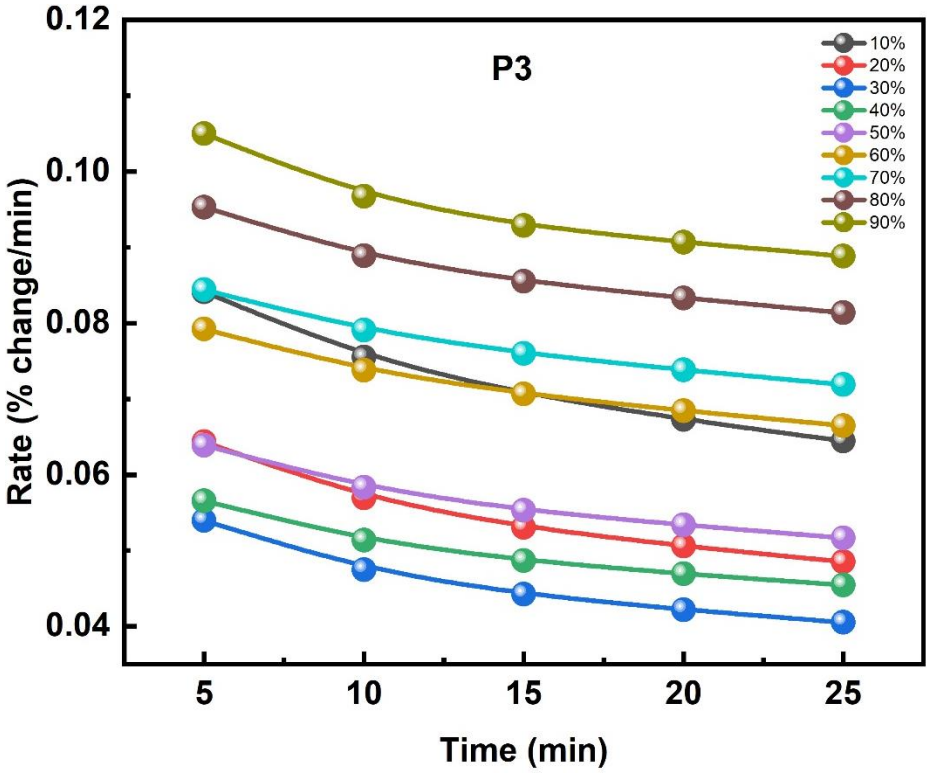

Figure S7. Water uptake rate of P3 at different relative humidity ranges from 10 to 90%.

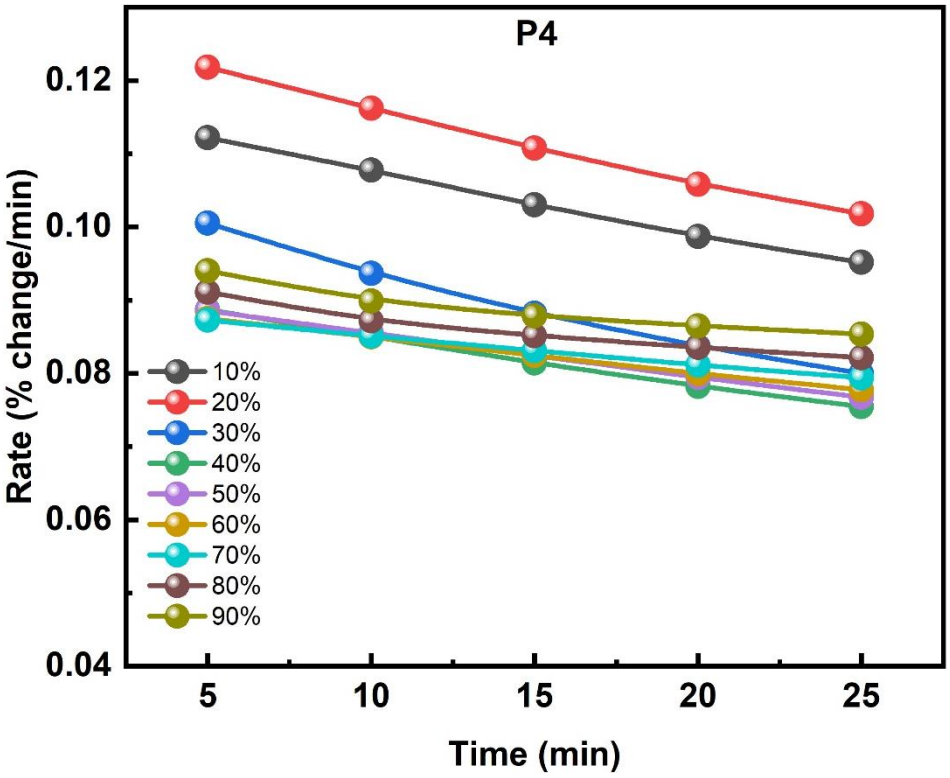

Figure S8. Water uptake rate of P4 at different relative humidity ranges from 10 to 90%.

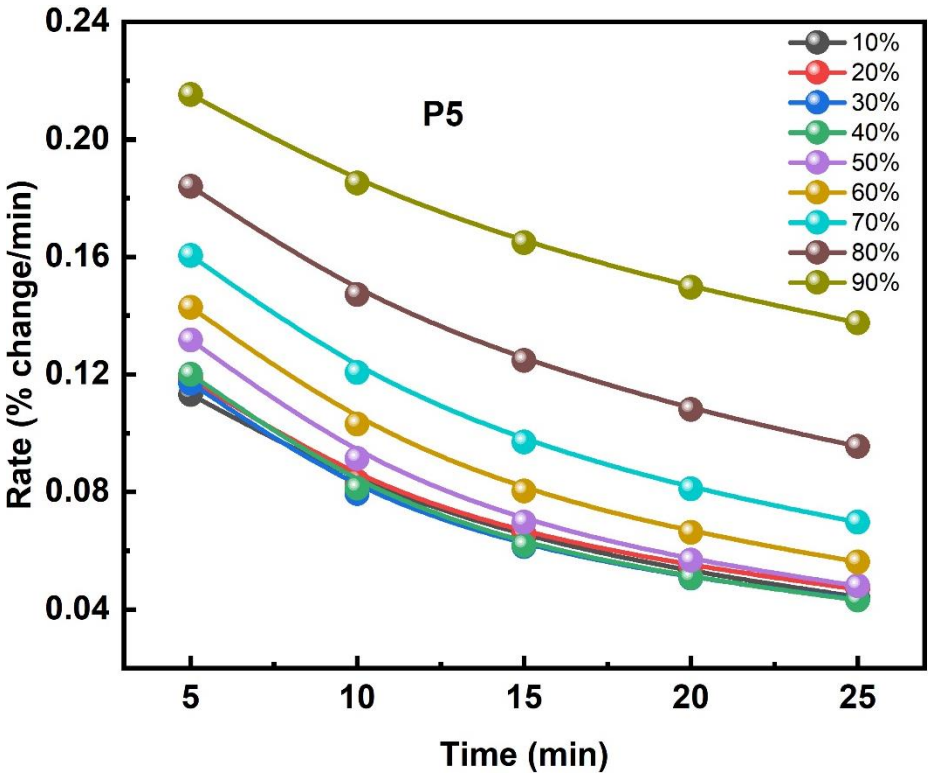

Figure S9. Water uptake rate of P5 at different relative humidity ranges from 10 to 90%.

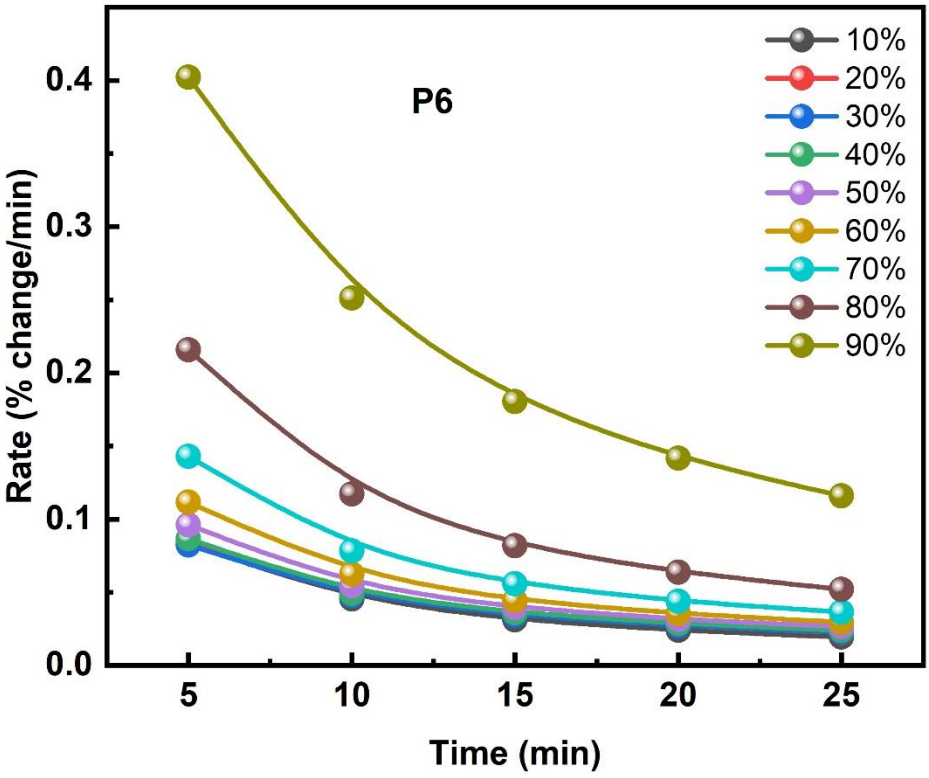

Figure S10. Water uptake rate of P6 at different relative humidity ranges from 10 to 90%.

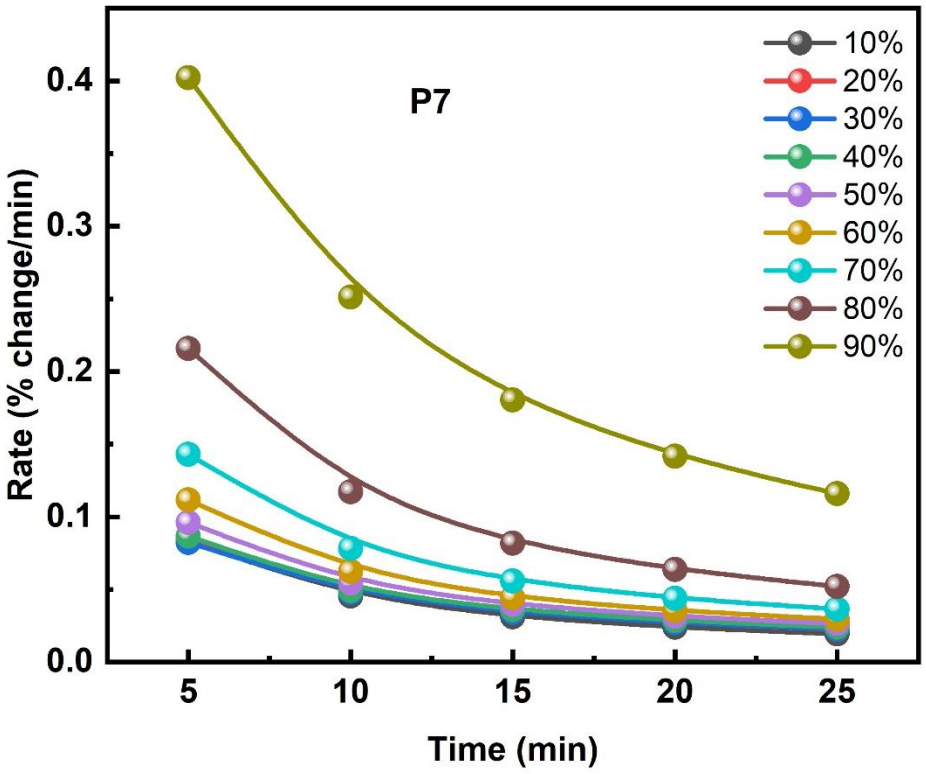

Figure S11. Water uptake rate of P7 at different relative humidity ranges from 10 to 90%.

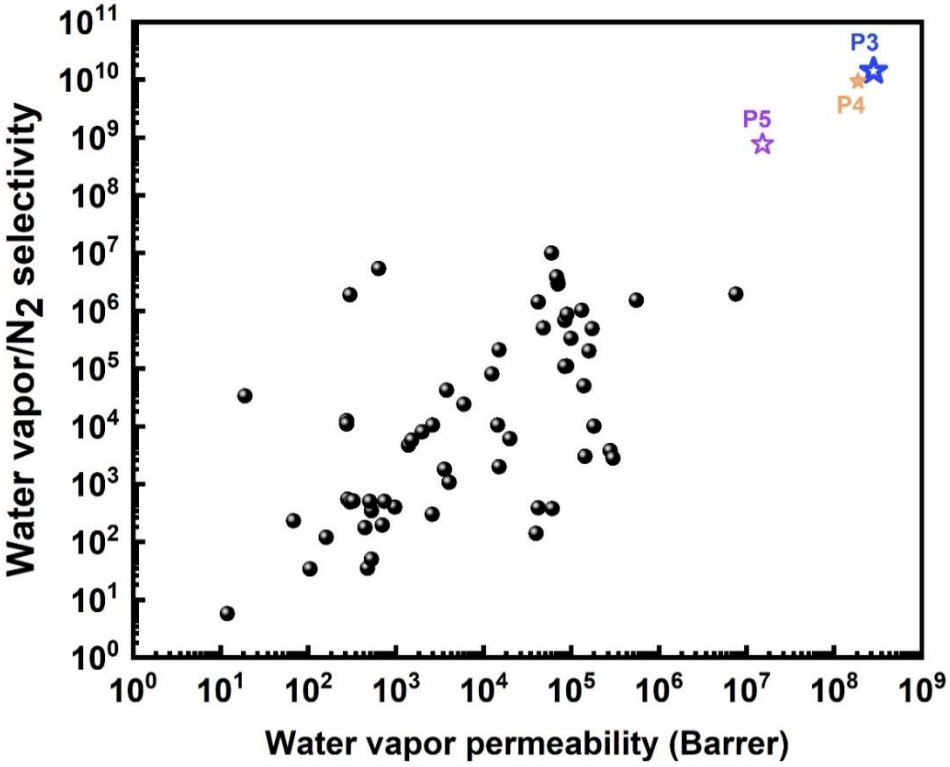

Figure S12. Performance of the theoretical membranes and comparison with the state-of-the art membranes for water vapor permeability and selectivity.

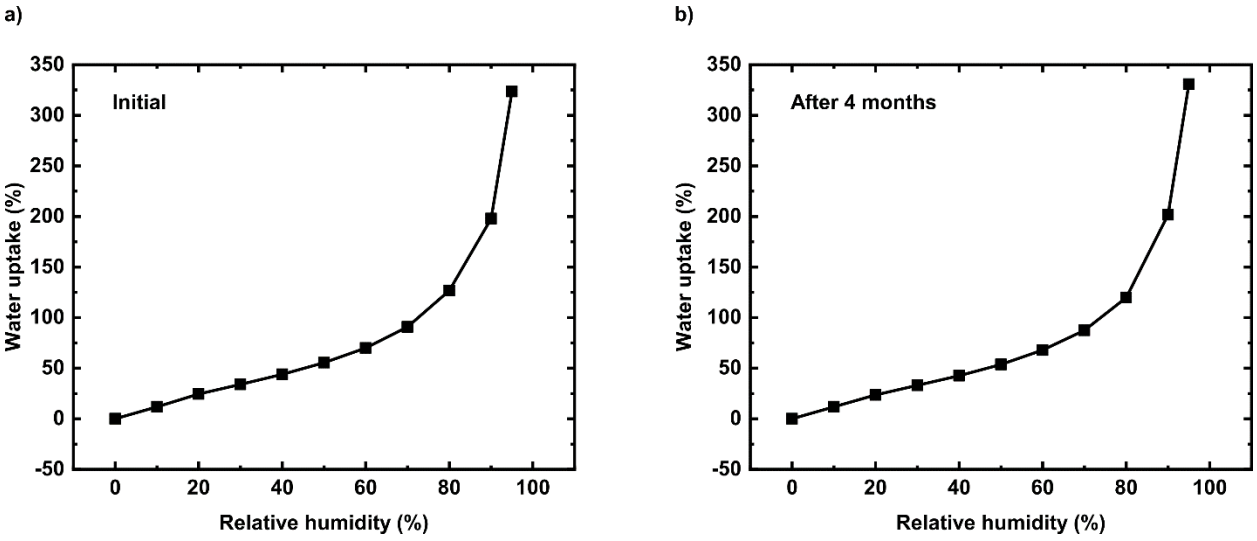

Figure S13. The water uptake versus relative humidity of P4 tested (a) initially, and (b) after 4 months. The polymer was stored under wet conditions during the 4 months.

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