

# Effect of Covalent Organic Frameworks Containing Different Groups on Properties of Sulfonated Poly (Ether Ether Ketone) Matrix Proton Exchange Membranes

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**Table. S1. Amount of raw materials required for preparing SPEEK/TpPa-SO<sub>3</sub>H composite membranes**

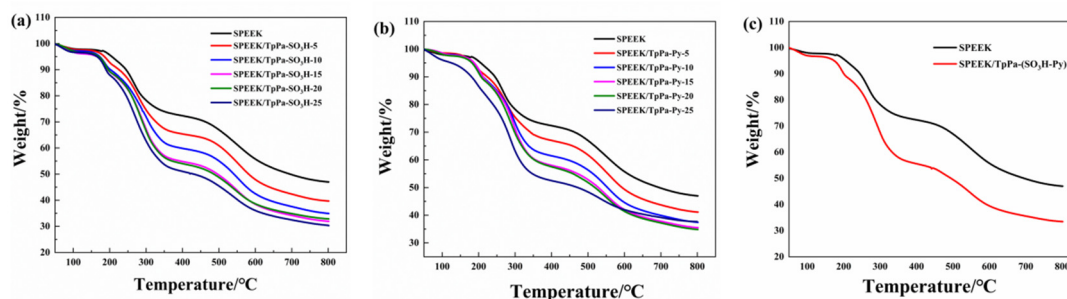
COFs mass				20 wt%
percentage (wt%)	Tp (g)	Pa-SO <sub>3</sub> H (g)	PTSA (g)	SPEEK solution (g)
5	0.0070	0.0094	0.0430	1.6380
10	0.0140	0.0188	0.0860	1.6380
15	0.0210	0.0282	0.1290	1.6380
20	0.0280	0.0376	0.1720	1.6380
25	0.0350	0.0470	0.2150	1.6380

**Table. S2. Amount of raw materials required for preparing SPEEK/TpPa-Py composite membranes**

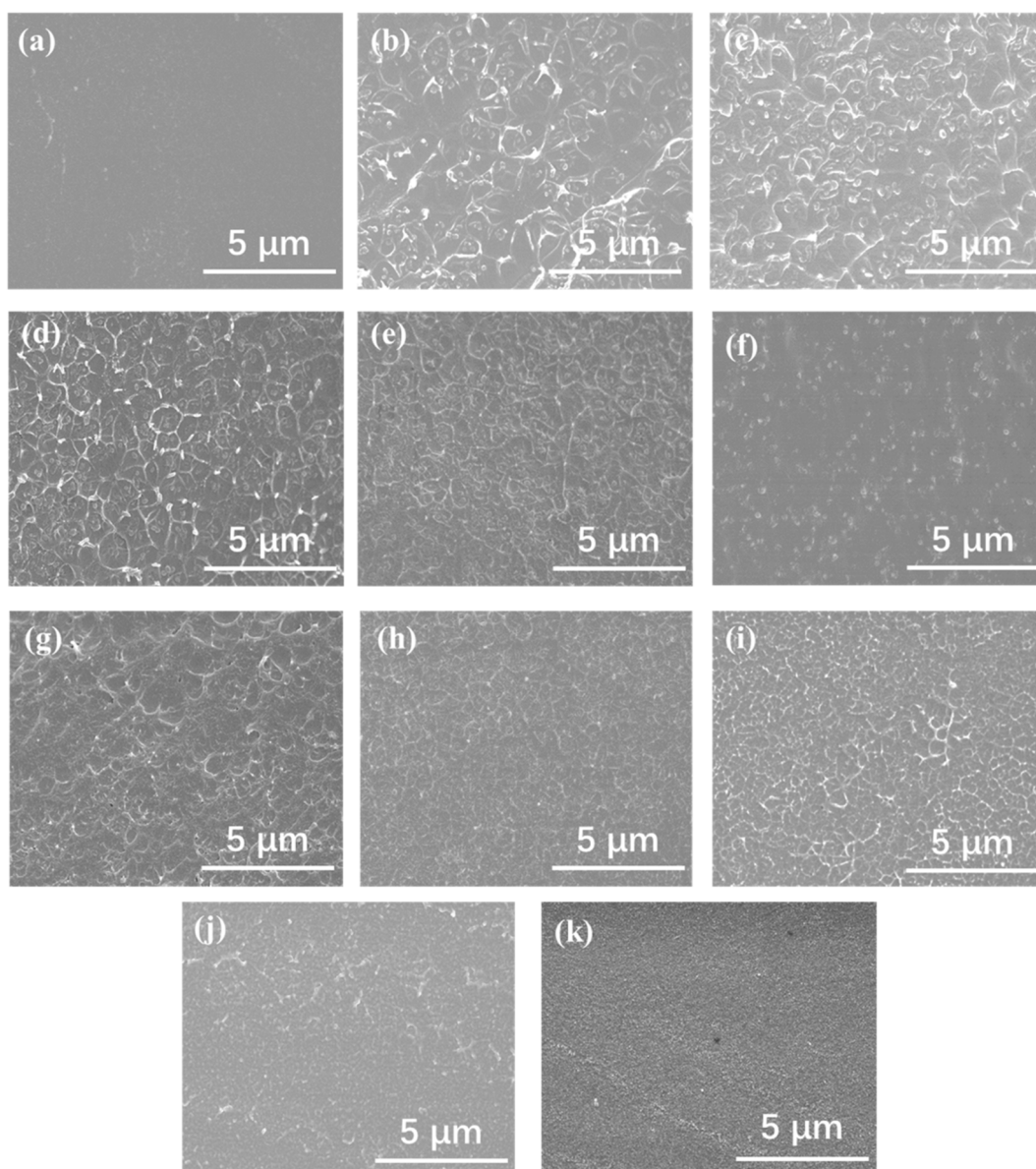
COFs mass				20 wt%
percentage (wt%)	Tp (g)	Pa-Py (g)	PTSA (g)	SPEEK solu- tion (g)
5	0.0092	0.0072	0.0430	1.6380
10	0.0184	0.0144	0.0860	1.6380
15	0.0276	0.0216	0.1290	1.6380
20	0.0368	0.0288	0.1720	1.6380
25	0.0460	0.0360	0.2150	1.6380

**Table. S3. Amount of raw materials required for preparing SPEEK/TpPa-(SO<sub>3</sub>H-Py) composite membranes**

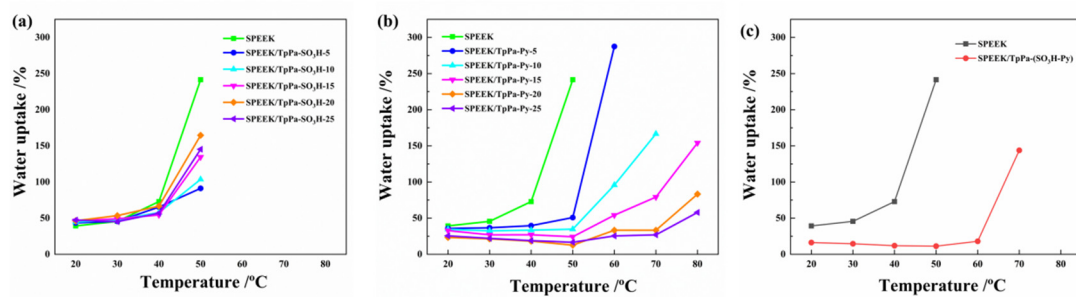
COFs mass					20 wt%
percentage (wt%)	Tp (g)	Pa-SO <sub>3</sub> H (g)	Pa-Py (g)	PTSA (g)	SPEEK so- lution (g)
20	0.0316	0.0213	0.0214	0.1720	1.6380

**Figure S1. TGA of membranes: (a) SPEEK and SPEEK/TpPa-SO<sub>3</sub>H, (b) SPEEK and SPEEK/TpPa-Py, (c) SPEEK and SPEEK/TpPa-(SO<sub>3</sub>H-Py).**

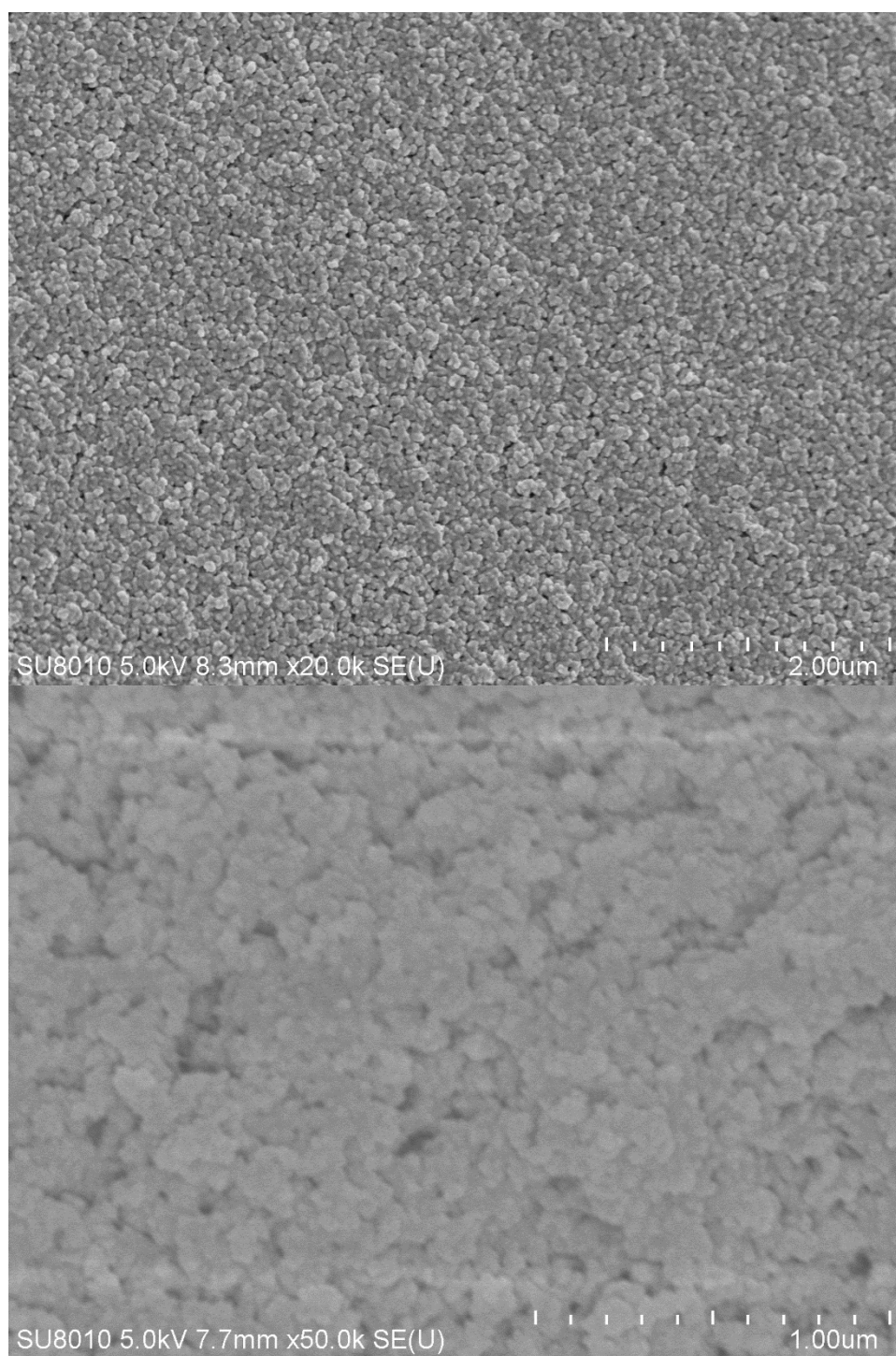
The thermal stability of SPEEK, SPEEK/TpPa-SO<sub>3</sub>H, SPEEK/TpPa-Py, and SPEEK/TpPa-(SO<sub>3</sub>H-Py) composite membranes were determined by TGA. SPEEK showed different degradation stages at 50-200°C, 200-450°C and 450-800°C. When the temperature is in the range of 50-200°C, the mass loss of SPEEK is due to the loss of water bound by physical or chemical action. The degradation of SPEEK in the temperature range of 200-450°C is mainly due to the decomposition of -SO<sub>3</sub>H, and may also be accompanied by the thermal decomposition of phenol caused by random chain fracture[1]. When the temperature is above 450°C, the main chain of SPEEK breaks and pyrolysis occurs. Compared with SPEEK membranes, the mass loss of SPEEK/TpPa-SO<sub>3</sub>H, SPEEK/TpPa-Py, and SPEEK/TpPa-(SO<sub>3</sub>H-Py) composite membranes before 200°C includes a large amount of proton carrier PTSA loaded in TpPa-SO<sub>3</sub>H, TpPa-Py, and TpPa-(SO<sub>3</sub>H-Py) channels. In the temperature range of 200-450°C, the mass loss of SPEEK/TpPa-SO<sub>3</sub>H and SPEEK/TpPa-(SO<sub>3</sub>H-Py) composite membrane includes not only the -SO<sub>3</sub>H group in SPEEK matrix, but also the -SO<sub>3</sub>H group in TpPa-SO<sub>3</sub>H skeleton structure. The weight loss in the range of 450-800 °C is caused by the fracture of SPEEK polymer chain and the decomposition of COFs skeleton. Therefore, compared with SPEEK membranes, the quality of thermogravimetric curves of SPEEK/TpPa-SO<sub>3</sub>H, SPEEK/TpPa-Py, and SPEEK/TpPa-(SO<sub>3</sub>H-Py) composite membranes decreased significantly.



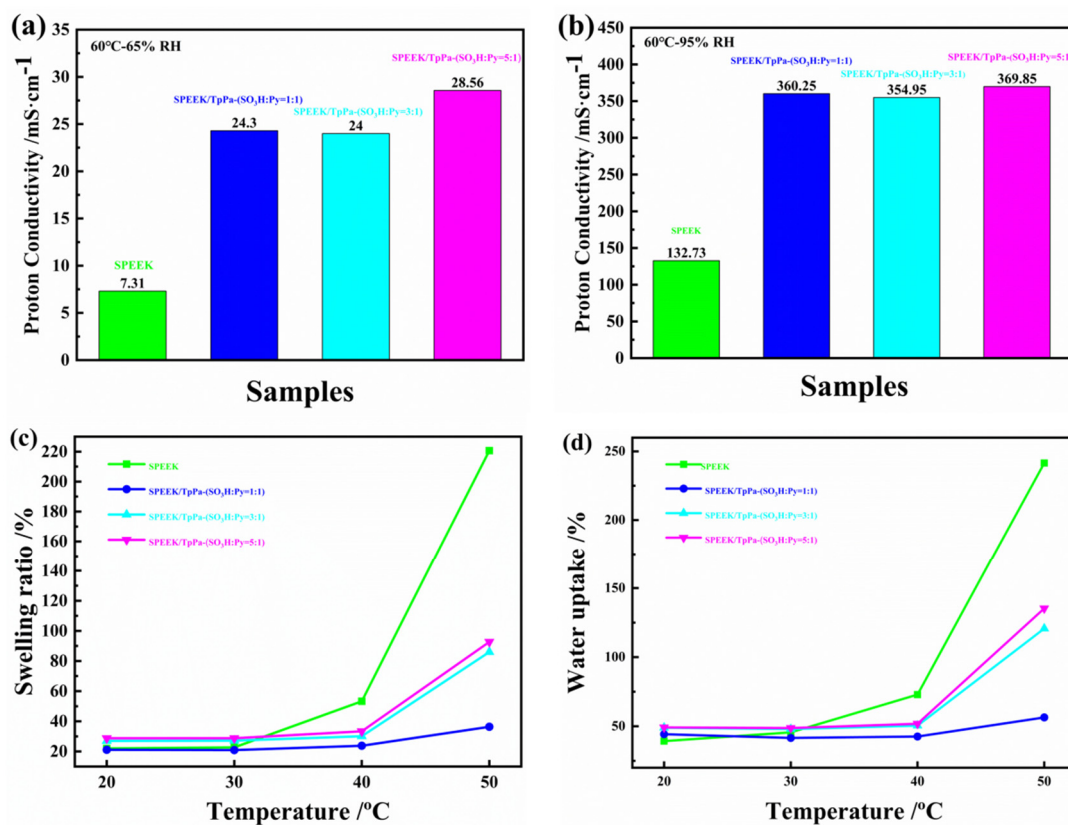
**Figure S2. SEM cross-section images of (a)SPEEK, (b)SPEEK/TpPa-SO<sub>3</sub>H-5, (c)SPEEK/TpPa-SO<sub>3</sub>H-10, (d)SPEEK/TpPa-SO<sub>3</sub>H-15, (e)SPEEK/TpPa-SO<sub>3</sub>H-20, (f)SPEEK/TpPa-SO<sub>3</sub>H-25, (g)SPEEK/TpPa-Py-5, (h)SPEEK/TpPa-Py-10, (i)SPEEK/TpPa-Py-15, (j) SPEEK/TpPa-Py-20, (k) SPEEK/TpPa-Py-25.**



**Figure S3. Water uptaking of membranes: (a) SPEEK and SPEEK/TpPa-SO<sub>3</sub>H, (b) SPEEK and SPEEK/TpPa-Py, (c) SPEEK and SPEEK/TpPa-(SO<sub>3</sub>H-Py).**



**Figure S4. SEM images of TpPa-(SO<sub>3</sub>H-Py) ( $\times 20000$ , and  $\times 50000$ ).**



**Figure S5. Properties of composite membranes with different ratios of sulfonic acid groups to pyridine groups: (a) proton conductivity at 60°C and 65% RH, (b) proton conductivity at 60°C and 95% RH, (c) swelling ratio, and (d) water uptaking.**

## References

- [1] Lakshmi, R. M.; Choudhary, V.; Varma, I., Sulphonated poly (ether ether ketone): Synthesis and characterisation. *Journal of materials science* **2005**, *40* (3), 629-636.  
<https://doi.org/10.1007/s10853-005-6300-2>.