Supporting Information

Integration of Phosphorylated MOF/COF Core-Shell Structures into Hybrid Membrane for High-Temperature Fuel Cell Application

Kumar Divya [a], Liu qing qing [a], Ravi Murali [b], Muhammad Rehman Asghar [a], Huiyuan Liu [a], Weiqi Zhang [a], Qian Xu [a], Jianwei Ren [c], Huaneng Su [a,*]

[a] *Institute for Energy Research, Jiangsu University, 301 Xuefu Road, Zhenjiang 212013, PR China*

[b] *School of Materials Science and Engineering Jiangsu University, 301 Xuefu Road, Zhenjiang 212013, PR China*

[c] *Department of Chemical Engineering, University of Pretoria, cnr Lynnwood Road and Roper Street, Hatfield 0028, South Africa*

*Corresponding author

E-mail address: suhuaneng@ujs.edu.cn

Table S1 Blend composition of SPEEK and SPEEK/MOF, SPEEK/COF and SPEEK/CM hybrid membranes

Membrane code	Blend composition (10 wt. %)				NMP (Solvent wt. %)	Phosphoric acid (PA) (%)
	(Polymer, wt. %) SPEEK	(Additive, wt. %)				
		MOF	COF	Core shell 'CM'		
SPEEK	**100**	**-**	**-**	**-**	**90**	**85**
PASPMOF-0.5	**99.5**		**-**	**-**	**90**	
PASPMOF-0.75	**99.25**		**-**	**-**	**90**	
PASPCOF-0.5	**99.5**	**-**	**0.5**	**-**	**90**	
PASPCOF-0.75	**99.25**	**-**	**0.75**	**-**	**90**	
PASPCM-0.5	**99.5**	**-**	**-**	**0.5**	**90**	
PASPCM-0.75	**99.25**	**-**	**-**	**0.75**	**90**	

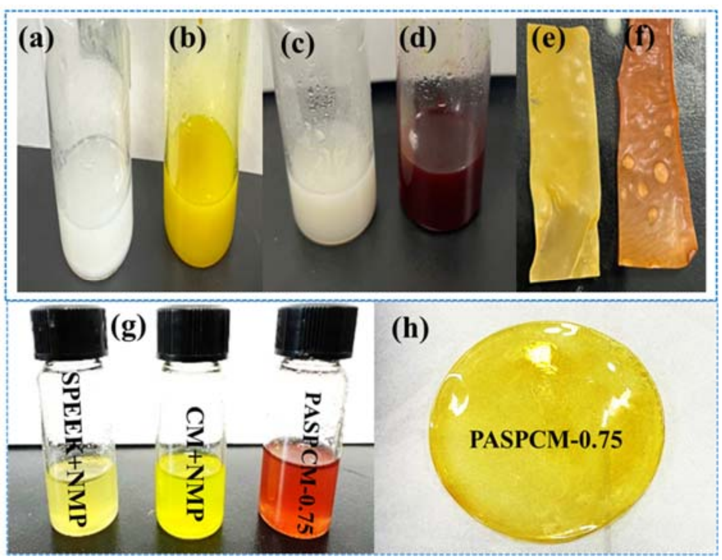

Fig.S1 Polymer and filler dispersing into NMP solution in the following combination (a)NMP+0.75% UiO-67 (Milky white), (b) NMP+ 0.75 wt.%COF (dark yellow), (c) NMP+SPEEK+0.75wt.% UiO-67 (White) (d) NMP+SPEEK+ 0.75 wt.% COF (e)after PA doping Film of PASPMOF-0.75 (no cracks on the film), (f) PASPCOF-0.75 (high degree of swollen with uneven film) (g)Polymer and filler dispersing into NMP solution in the following combination SPEEK+NMP (pale yellow), NMP+ 0.75 wt.%CM (yellow), NMP+SPEEK+0.75wt. CM (Red) (h) after PA doping Film of PASPCM-0.75.

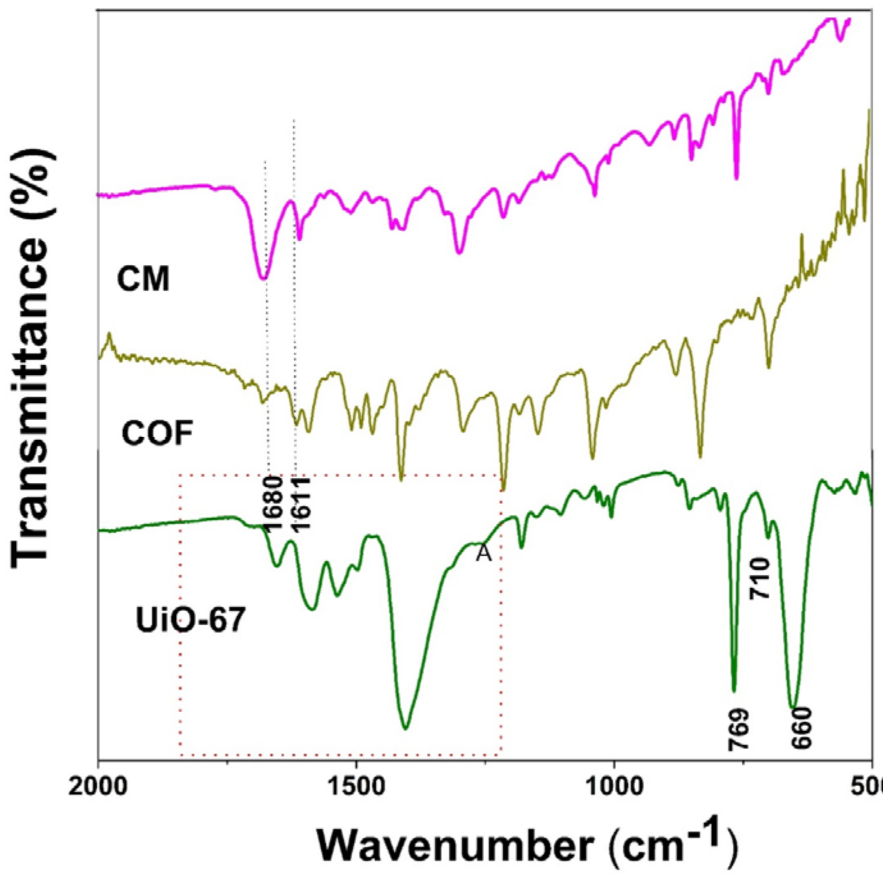

Fig.S2 FT-IR spectrum of UiO-67, COF and CM

Table S2 BET specific surface area, pore volume and pore size distribution

Materials	**BET Surface area (m^2 g^{-1})**	**Pore volume (cm^3 g^{-1})**	**Pore size (nm)**
UiO-67	1080	0.32	1.8
TAPB/DMTP COF	592	0.6	3.2
CM	872	0.04	1.8 and 3.9

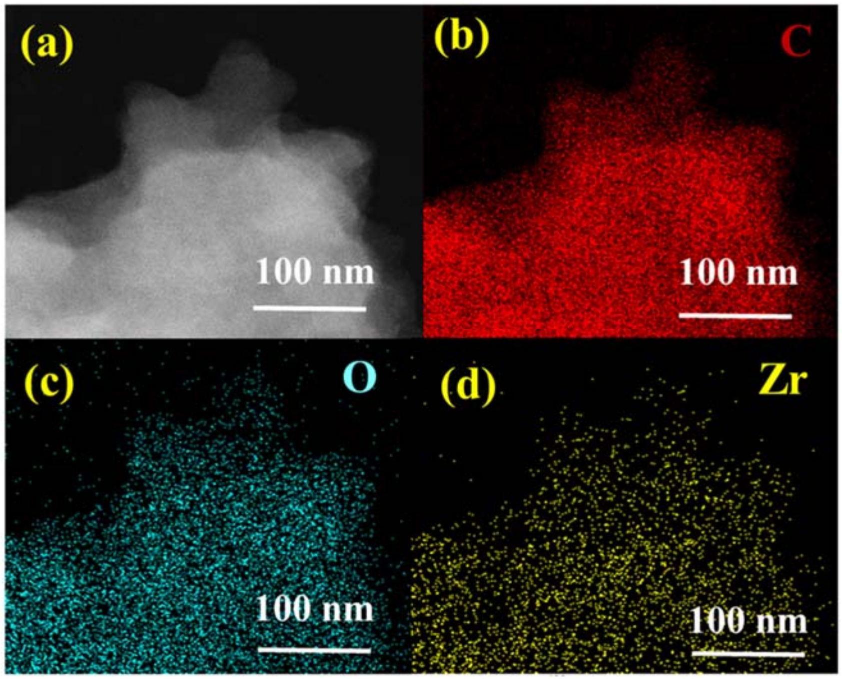

Fig.S3 Elemental mapping of CM core shell MOF

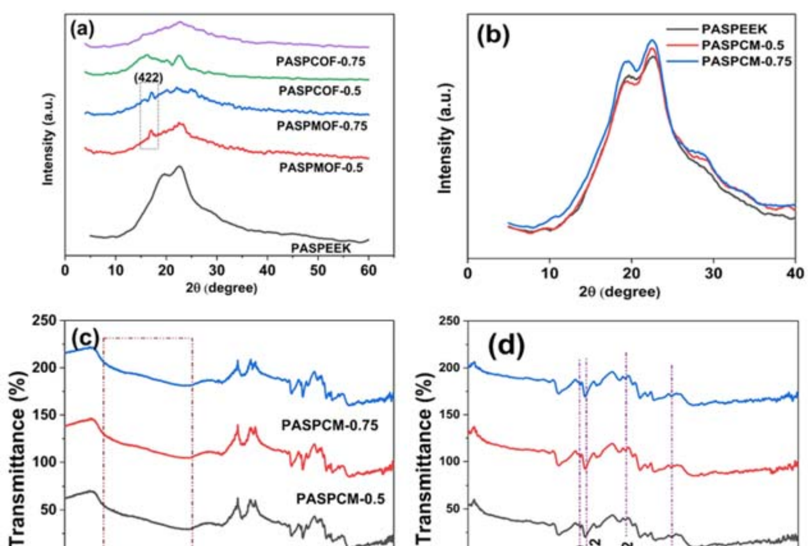

Fig.S4 (a, b) XRD pattern of PASPEEK, PASPMOF, PASPCOF and PASPCM hybrid membranes (c-d) FT-IR spectrum of PASPCM hybrid membranes

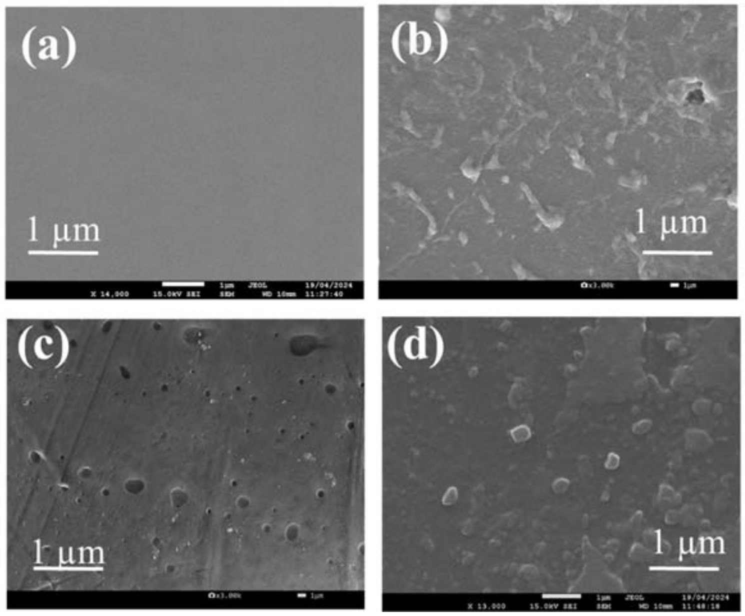

Fig.S5 SEM images of (a) PASPEEK, (b) PASPMOF-0.75, (c) PASPCOF-0.75 and (d) PASPCM-0.75 hybrid membrane

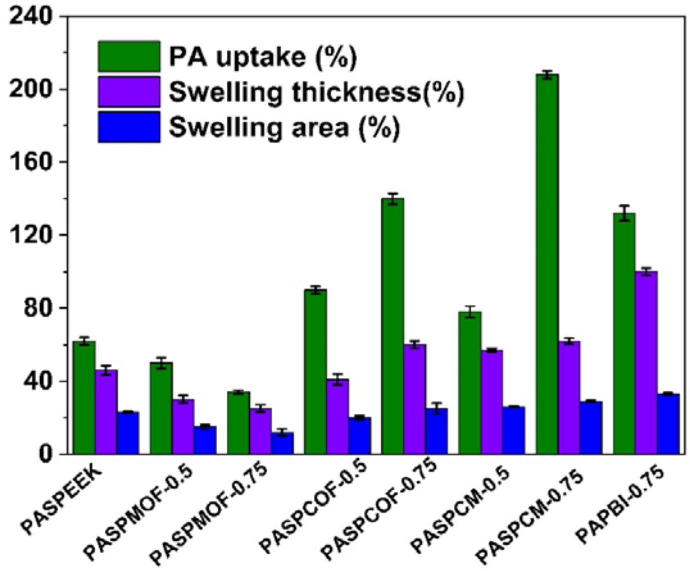

Fig.S6 (a) Phosphoric Acid doping in membrane increase swelling thickness, area and doping level

Table S3 Physicochemical properties such as PA uptake, swelling thickness, swelling area, of PASPEEK, PASPCM and PA PBI membranes

Membranes	PA uptake (%)	Swelling thickness (%)	Swelling area (%)
PASPEEK	62±2	46±2.5	23±0.6
PASPMOF-0.5	50±3	30±2	15±1
PASPMOF-0.75	34±1	25±2	12±2
PASPCOF-0.5	90±2	41±3	20±1
PASPCOF-0.75	140±3	60±2	25±3
PASPCM-0.5	78±3	57±0.9	26±0.35
PASPCM-0.75	208±2	62±1.5	29±0.5
PA-PBI	132±4	100±2	33±0.4

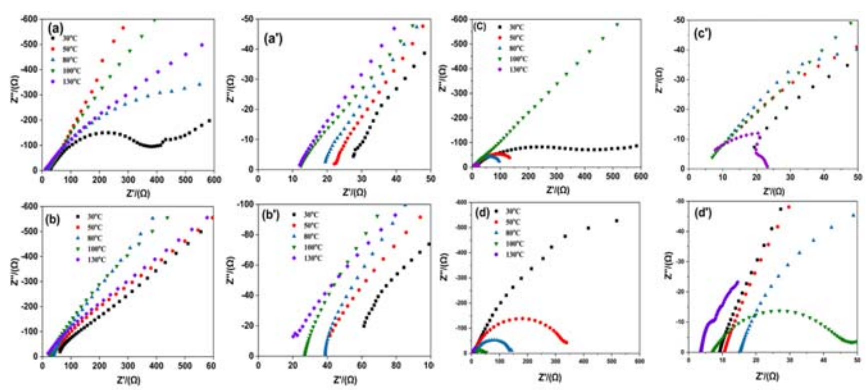

Fig.S6 AC impedance spectra (full spectrum represented as (a-d) and its relative extended graph denoted as (a´-d´)) **(a, a´)** PASPMOF-0.5, **(b b´)** PASPMOF-0.75**, (c, c´)** PASPCOF-0.5 and **(d, d´)** PASPCOF-0.75. Conductivity test performed at different temperature from 30-130 °C

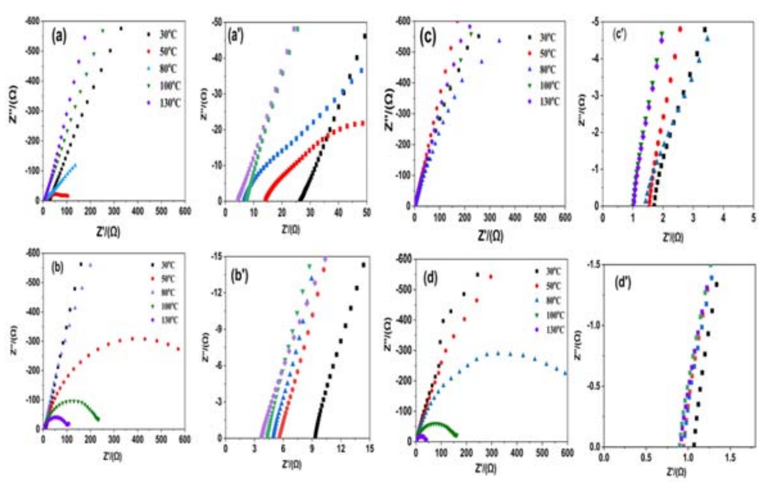

Fig.S7 AC impedance spectra (full spectrum represented as (a-d) and its relative extended graph denoted as (a´-d´)) **(a, a´)** PASPEEK, **(b b´)** PASPCM-0.5**, (c, c´)** PASPCM-0.75 and **(d, d´)** PA PBI membranes. Conductivity test performed at different temperature from 30-130 °C

Table S4 Anhydrous proton conductivity (different temperatures from 30-130°C) of PASPEEK, PASPCM and PA PBI membranes

Membranes	**Anhydrous Proton conductivity (S cm^{-1})**				
	30 °C	**50** °C	**80** °C	**100** °C	**130** °C
PASPEEK	0.5±0.2	0.9±0.4	1.7±0.2	1.9±0.2	3.2±0.4
PASPMOF-0.5	0.4±0.1	0.6±0.2	0.7±0.3	1.1±0.1	1.3±0.2
PASPMOF-0.75	0.1±0.1	0.3 ±0.1	0.4±0.1	0.6±0.3	0.6±0.2
PASPCOF-0.5	0.7±0.1	0.9±0.2	1.1±0.2	1.6±0.1	2.1±0.2
PASPCOF-0.75	0.9±0.1	1.2±0.3	1.4±0.1	1.9±0.2	3.5±0.3
PASPCM-0.5	1.4±0.3	2.3±0.3	2.7±0.1	3.0±0.1	4.3±0.3
PASPCM-0.75	4.0±0.2	4.5±0.1	5.8±0.4	6.6±0.4	7.7±0.4
PA-PBI	3.6±0.4	3.9±0.4	4.0±0.5	4.2±0.5	5.2±0.2

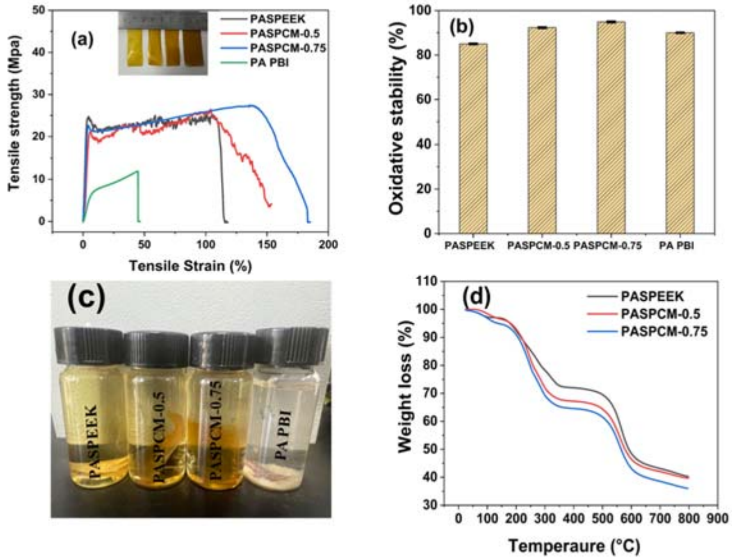

Fig.S8 (a) Tensile strength of pristine and hybrid SPEEK higher than Commercial PBI (b, c) Oxidative stability in Fenton reagent (Digital photograph of PASPEEK, PASPCM-0.5, PASPCM-0.75 and PA PBI membranes) (d) Thermal stability of PASPEEK and hybrid membranes.

Table S5 comparative mechanical stability of prepared PASPEEK, PASPCM and PA PBI membranes with other literature reported composite membranes

Membranes	**Mechanical stability (MPa)**	**References**
PA SPEEK	24.0	In this work
PASPCM-0.75	27.3	In this work
PA PBI	11.8	In this work
MIL-101(Cr)@OBPI	15	[1]
SPES/MOF	11.26	[2]
CBOPBI@MOF 30%	10.2	[3]
OPBI-Py@8 %	8.42	[4]
3 wt% Cu-TMA/sABPBI	7.70	[5]
PFSA@PTNF/TpPa-(SO_3H-Py)	23.3	[6]
40%UIO-66@OPBI	27.02	[7]

[1] G. Wei, Y. Liu, A. Wu, Y. Min, Z. Liao, R. Zhu, Y. Liang, L. Wang, Are complete metal-organic frameworks really responsible for improving the performance of high-temperature proton exchange membranes?, Materials Today Chemistry, 27 (2023) 101276.

[2] N. Anahidzade, A. Abdolmaleki, M. Dinari, K. Firouz Tadavani, M. Zhiani, Metal-organic framework anchored sulfonated poly(ether sulfone) as a high temperature proton exchange membrane for fuel cells, Journal of Membrane Science, 565 (2018) 281-292.

[3] Y. Wu, X. Liu, F. Yang, L. Lee Zhou, B. Yin, P. Wang, L. Wang, Achieving high power density and excellent durability for high temperature proton exchange membrane fuel cells based on crosslinked branched polybenzimidazole and metal-organic frameworks, Journal of Membrane Science, 630 (2021) 119288.

[4] B. Zhang, X. Li, S. Lv, X. Sun, H. Zhang, P. Zhou, Y. Chen, J. Zheng, S. Li, S. Zhang, High-performance polybenzimidazole composite membranes doped with nitrogen-rich porous nanosheets for high-temperature fuel cells, Journal of Membrane Science, 709 (2024) 123119.

[5] S. Moorthy, B. Maria Mahimai, D. Kannaiyan, P. Deivanayagam, Synthesis and fabrication of Cu-trimesic acid MOF anchored sulfonated Poly(2,5-benzimidazole) membranes for PEMFC applications, International Journal of Hydrogen Energy, 48 (2023) 36063-36075.

[6] X. Meng, L. Peng, Y. Wang, X. Li, Q. Peng, X. Zhang, C. Cong, H. Ye, Q. Zhou, Study on the properties of hybrid COF connected three-dimensional nanofiber structures in proton exchange membranes, International Journal of Hydrogen Energy, 71 (2024) 334-344.

[7] J. Chen, L. Wang, L. Wang, Highly Conductive Polybenzimidazole Membranes at Low Phosphoric Acid Uptake with Excellent Fuel Cell Performances by Constructing Long-Range Continuous Proton Transport Channels Using a Metal–Organic Framework (UIO-66), ACS Applied Materials & Interfaces, 12 (2020) 41350-41358.