Electronic Supplementary Material (ESI) for Nanoscale.

Selective Interfacial Synthesis of Metal-Organic Frameworks on Polybenzimidazole Hollow Fiber Membrane for Gas Separation

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(Supporting Information)

Contents

Section S1: Experimental

General Remarks: 2-methylimidazole (*2*-mIm), Zinc Nitrate, 1,3,5-benzenetricarboxylic acid (BTC) and Cupric Nitrate was purchased from Sigma Aldrich chemicals. The solvents were purchased from Thomas Baker Chemicals. All starting materials were purchased from commercial source and used without further purification.

Optimized protocoal for the preparation of ZIF-8 *via* interfacial synthesis method [ZIF-8 ($CHCl_3/H_2O$)]

For the ZIF-8 ($CHCl_3/H_2O$) synthesis, the organic phase was prepared by adding 0.162 g of *2*-methylimidazole in 10 mL of $CHCl_3$. The resulting clear solution was used for the preparation of a thin ZIF-8 film by slow addition of a solution of 0.146 g of $Zn(NO_3)_2.6H_2O$ in 10 mL of water in it. The biphasic mixture was left to stand at room temperature for 6 hours (Figure S1a).

Optimized protocoal for the preparation of ZIF-8 *via* interfacial synthesis method [ZIF-8 (IBA/H_2O)]

For the ZIF-8 (IBA/H_2O) synthesis, the aqueous phase was prepared by adding 0.146 g of $Zn(NO_3)_2.6H_2O$ in 10 mL of water. The resulting clear solution was used for the preparation of a thin ZIF-8 film by slow addition of a solution of 0.162 g of *2*-methylimidazole in 10 mL of isobutyl alcohol (IBA) in it. The biphasic mixture was left to stand at room temperature for 6 hours (Figure S1b).

Optimized protocoal for the preparation of CuBTC *via* interfacial synthesis method [CuBTC ($CHCl_3/H_2O$)]

For CuBTC ($CHCl_3/H_2O$) synthesis, the aqueous phase was prepared by adding 0.68 g of $Cu(NO_3)_2.6H_2O$ in 10 mL of water. The resulting clear solution was used for the preparation of a thin CuBTC film by slow addition of a clear solution of 0.5 g of 1,3,5-benzenetricarboxylic acid (BTC) in 10 mL of $CHCl_3$ and 0.75 mL of triethylamine (TEA) in it. The biphasic mixture was left to stand at room temperature for 6 hours (Figure S1d).

Optimized protocoal for the preparation of CuBTC *via* interfacial synthesis method [CuBTC (IBA/H_2O)]

For CuBTC (IBA/H_2O) synthesis, the organic phase was prepared by adding 0.5 g of 1,3,5-benzenetricarboxylic acid (BTC) in 10 mL of $CHCl_3$ and 0.75 mL of triethylamine (TEA). The resulting clear solution was used for the preparation of a thin CuBTC film by slow

addition of a clear solution of 0.68 g of $Cu(NO_3)_2.6H_2O$ in 10 mL of water in it. The biphasic mixture was left to stand at room temperature for 6 hours (Figure S1c).

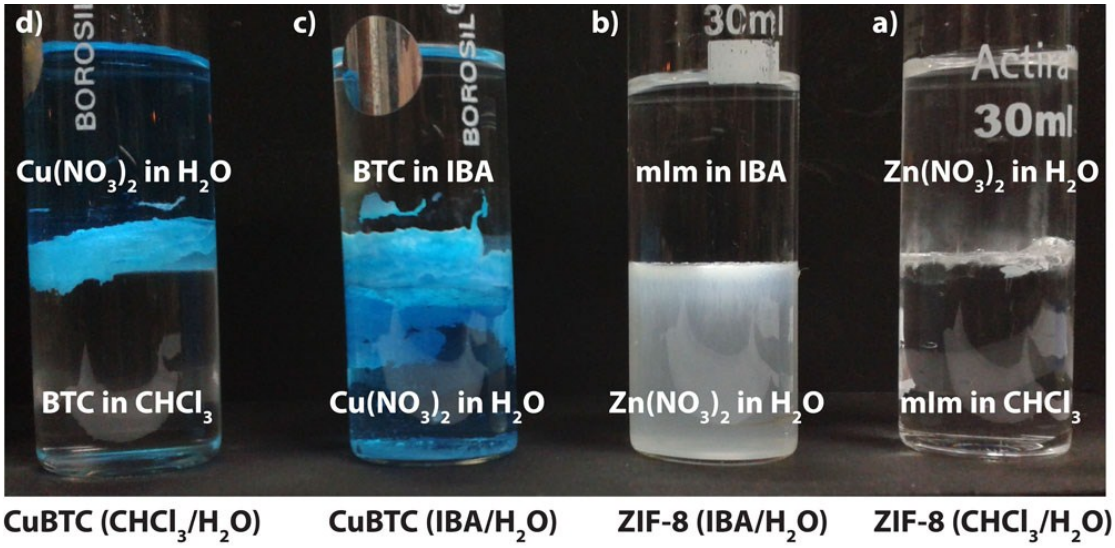

Figure S1. a-d) Demonstrating the synthesis of ZIF-8 and CuBTC using $CHCl_3$/water and IBA/water as solvent systems via interfacial synthesis method.

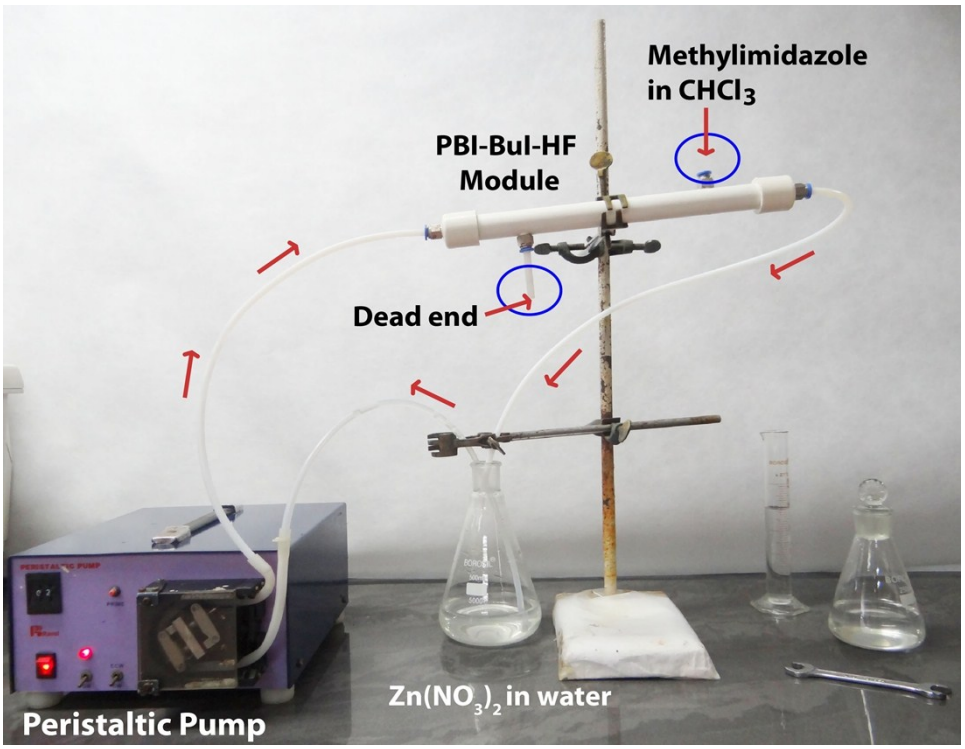

Figure S2. Circulation setup for the growth of ZIF-8 on inner surface of PBI-BuI hollow fibers (ZIF-8@PBI-BuI-In).

Section S2: FT-IR Analysis

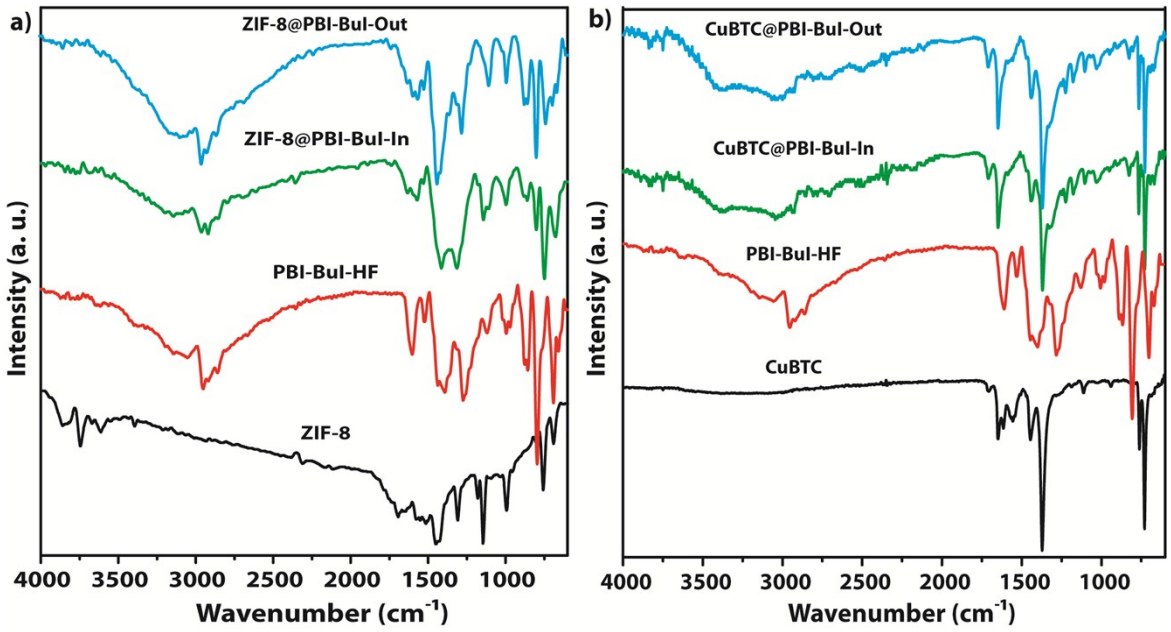

Figure S3. FT-IR of a) ZIF-8@PBI-BuI (both In and Out); b) CuBTC@PBI-BuI (both In and Out) composite membranes in comparison with pristine PBI-BuI-HF, ZIF-8 and CuBTC.

Section S3: Stereo Microscopy Images

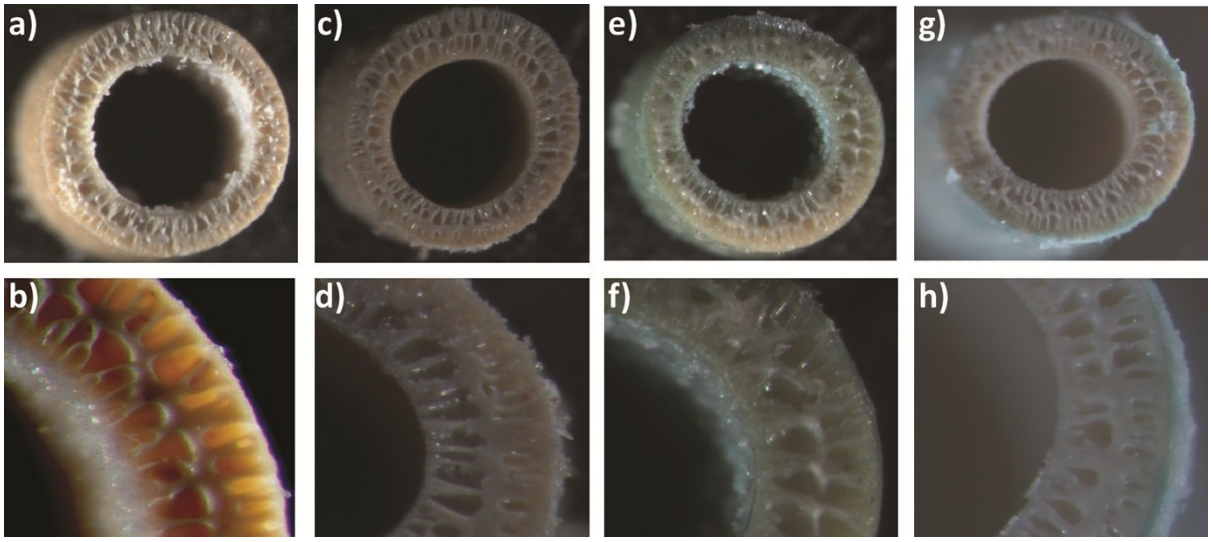

Figure S4. Stereo microscopy images showing MOF growth on PBI-Bu-HF: a), b) ZIF-8@PBI-BuI-In; c), d) ZIF-8@PBI-BuI-Out; e), f) CuBTC@PBI-BuI-In; and g), h) CuBTC@PBI-BuI-Out composites.

Section S4: SEM Images

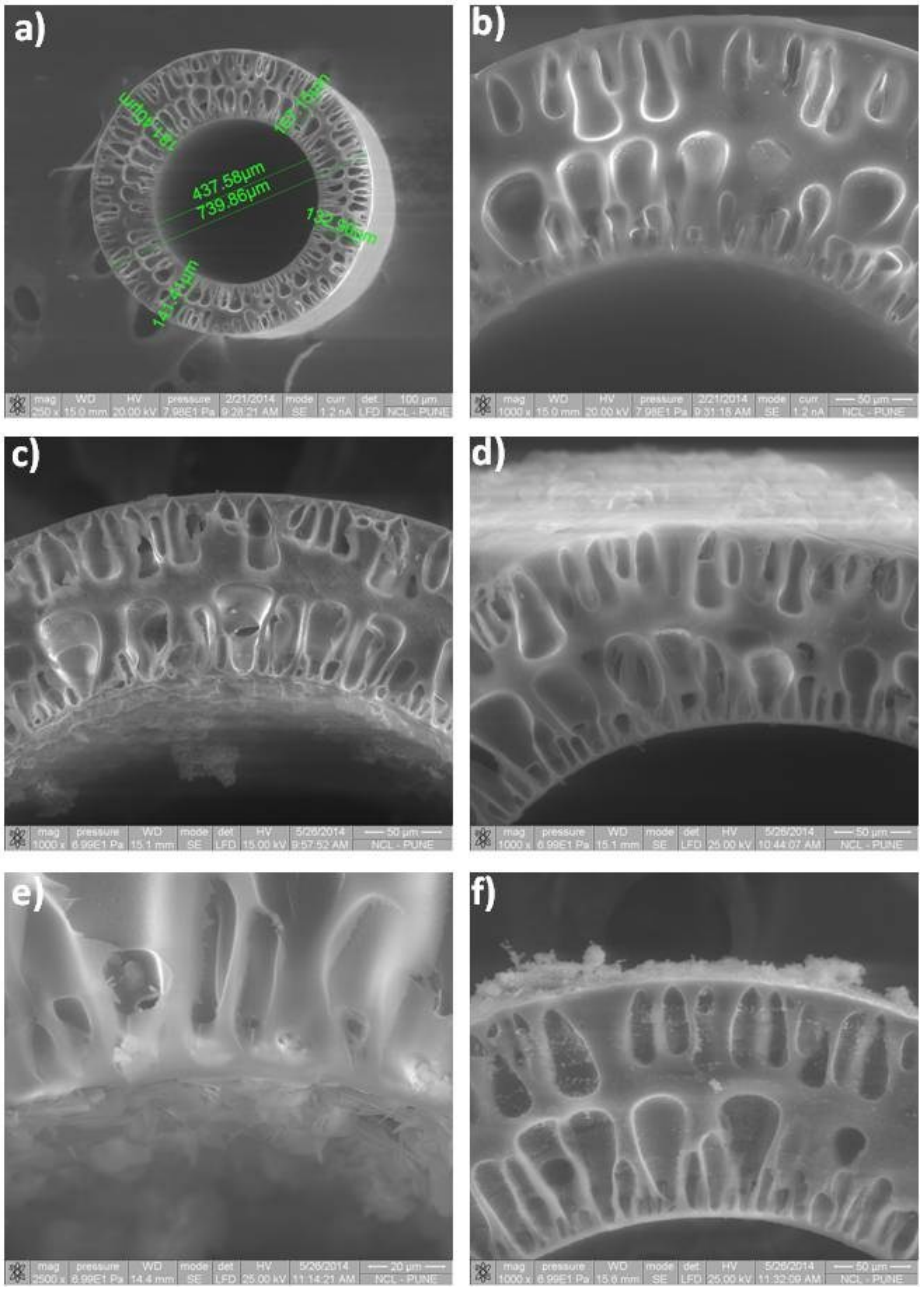

Figure S5. SEM images showing the cross section of a) and b) PBI-BuI hollow fiber; c) ZIF-8@PBI-BuI-In; d) ZIF-8@PBI-BuI-Out; e) CuBTC@PBI-BuI-In; and f) CuBTC@PBI-BuI-Out composite membranes respectively.

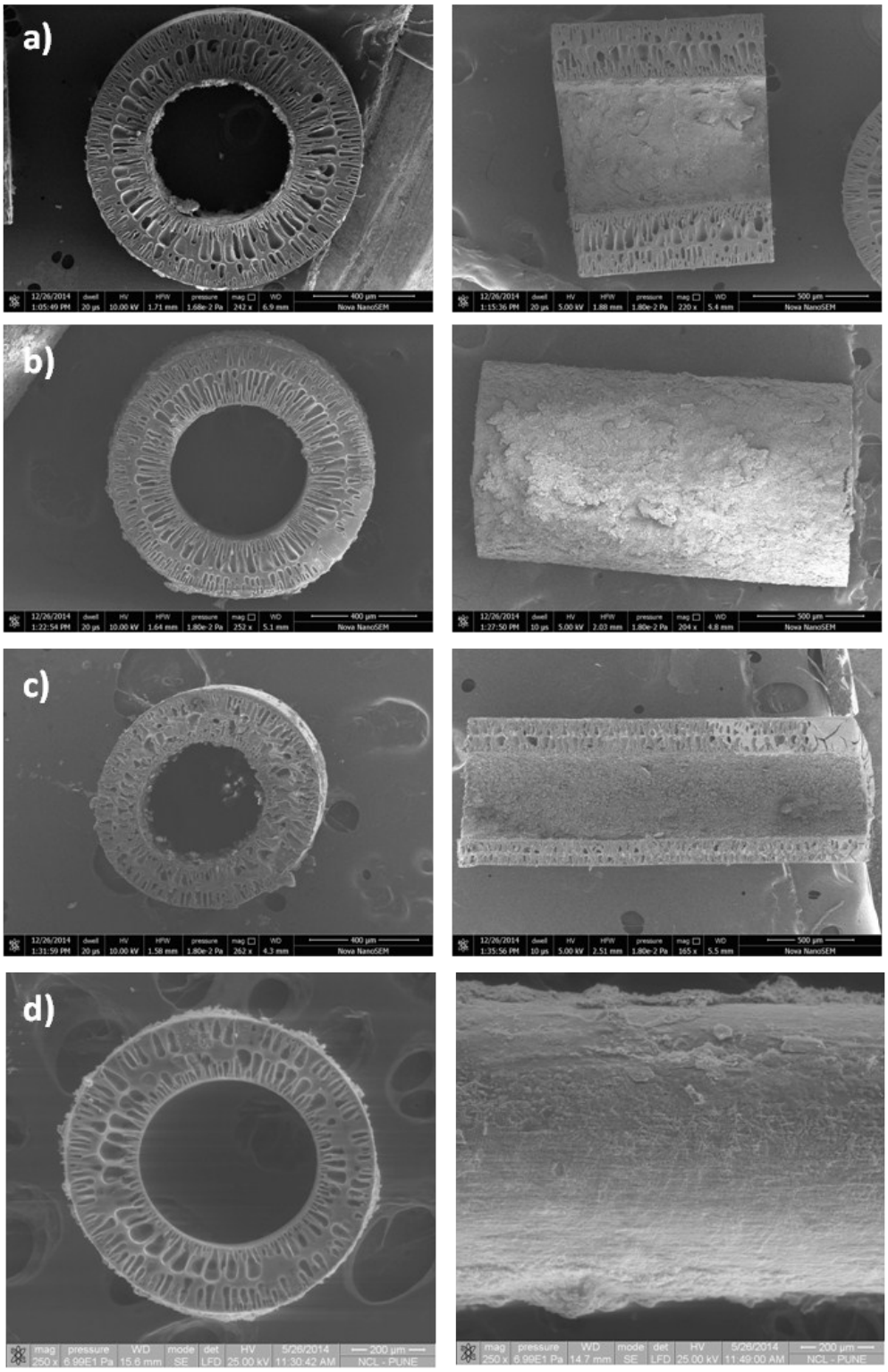

Figure S6. SEM images showing the cross section and cut along length of a) ZIF-8@PBI-BuI-In; b) ZIF-8@PBI-BuI-Out; c) CuBTC@PBI-BuI-In; and d) CuBTC@PBI-BuI-Out composite membranes respectively.

Section S5: Gas permeation unit, Permeance and Selectivity data.

Gas permeability measurements:

Single-gas permeation experiments using He, N_2, and C_3H_8 were performed at 35 °C using a variable volume method (Bhaskar *et al*. *J. Mater. Chem. A* **2014**, *2*, 12962). Upstream pressure of range 15 psi was used while maintaining permeates side at the ambient. The ideal selectivity was calculated from the ratio of the individual gas permeability. The permeance (P) was expressed in terms of GPU (Gas Permeation Unit) (1 GPU = $1x10^{-6}$ $cm.s^{-1}.cmHg^{-1}$). The gas permeance (P) can be expressed as,

$$\mathbf{P = J/AxTx\Delta p}$$

where, J is the flux (amount of gas transported per unit area per unit time), A is the active area, T is the time taken by the gas to permeate through the membrane, Δp is the pressure gradient across the membrane.

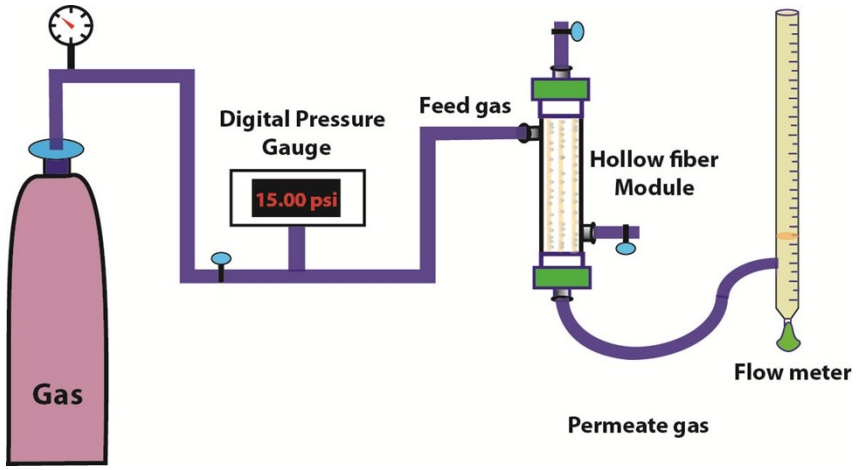

Figure S7. Schematic representation of gas permeation equipment set-up.

Table S1. **Permeance and Selectivity data.**

Hollow Fiber Membranes	P(He)	$P(N_2)$	$P(C_3H_8)$	$P(He)/P(N_2)$	$P(He)/P(C_3H_8)$
PBI-BuI-HF	6.01	5.81	5.29	1.04	1.14
ZIF-8@PBI-BuI-In	2	0.54	0.25	3.67	8.03
ZIF-8@PBI-BuI-Out	1.80	0.43	0.39	4.22	4.60
CuBTC@PBI-BuI-In	0.89	0.11	0.10	8.07	8.74
CuBTC@PBI-BuI-Out	1.31	0.11	0.08	12.05	17.02

*Permeance (P) expressed in GPU, (1 GPU = $1x10^{-6}$ cm s^{-1} cm Hg^{-1} = 3.348×10^{-10} mol m^{-2} s^{-1} Pa^{-1}).

Table S2. **Permeance and Selectivity data of some reported CuBTC@Support membranes.**

MOF	Substarte	$P(H_2)$ in GPU	$P(H_2)/P(N_2)$	Temp.	References
CuBTC	Copper net	4480.29	7	RT	*J. Am. Chem. Soc*., 2009, **131**, 1646
CuBTC	PSF	235.96	-	RT	*J. Mater. Chem. A*, 2013, **1**, 8828
CuBTC	α-Al_2O_3 discs	1194.74	3.7	RT	*Langmuir*, 2011, **27**, 4309
CuBTC	Porous SiO2 metal net	2986.86	8.91	25-60	*Chem. -Eur. J*., 2012, **18**, 10250
CuBTC	α-Al_2O_3 tube	119.47	8.66	RT	*J. Mater. Chem*., 2012, **22**, 10322
CuBTC	PBI-BuI-HF	1.31 (He)	12.05	RT	*This work*