Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Interfacial growth of 2D MOF membranes *via* contra-diffusion for CO_2 separation

Shuangshuang Jiang,[a] Xinli Shi,[a] Yucong Zu,[a] Fuxing Sun,*[a] Guangshan Zhu*[b]

[a]*State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun, 130012, PR China. E-mail: fxsun@jlu.edu.cn*

[b]*Key Laboratory of Polyoxometalate Science of the Ministry of Education, Faculty of Chemistry, Northeast Normal University, Changchun, 130024, PR China. E-mail: zhugs@jlu.edu.cn*

Table of Contents:

1. Supporting Tables and Figures

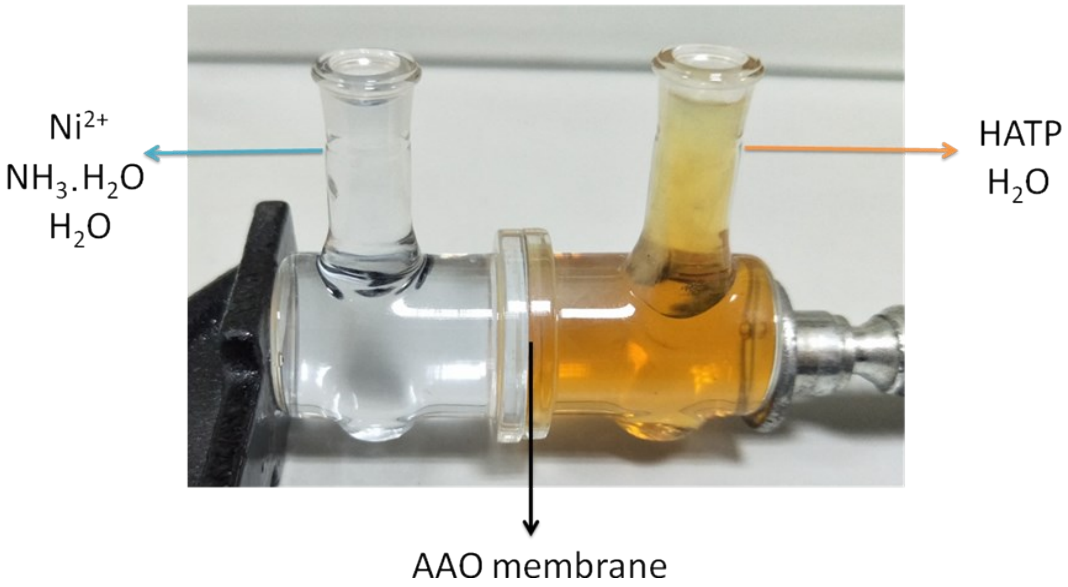

Fig. S1 Digital photograph of the home-made contra-diffusion cell.

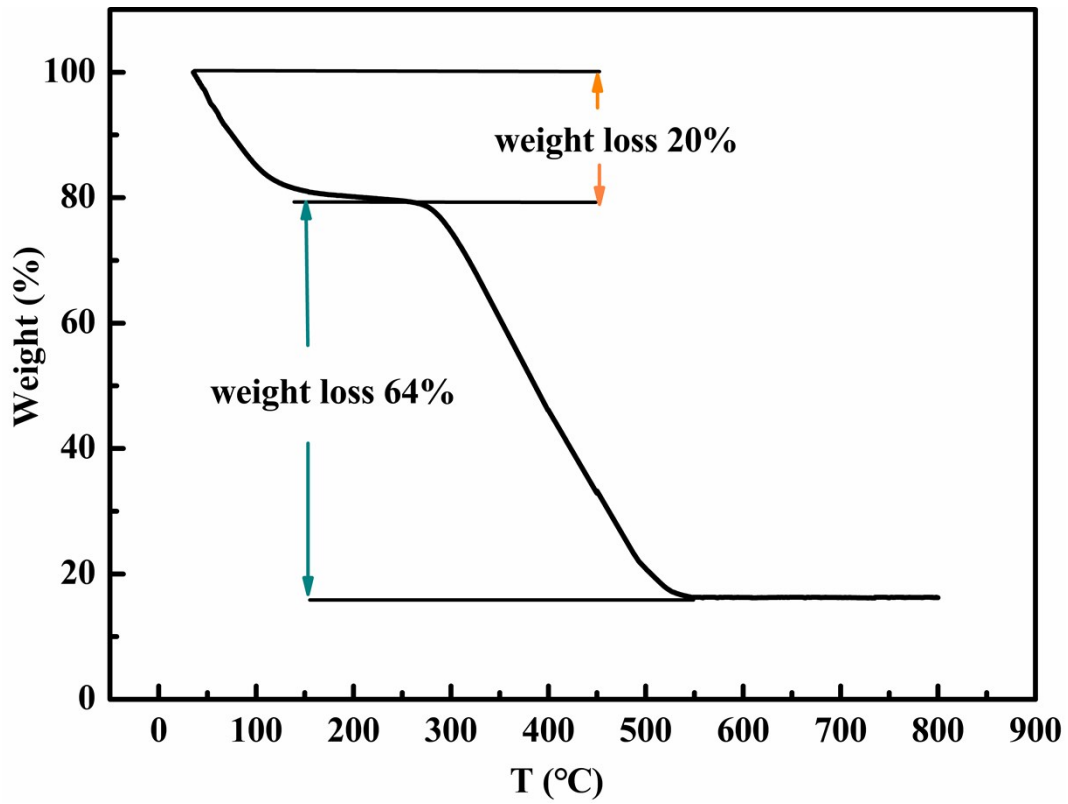

Fig. S2 The TGA curve of peeled $Ni_3(HITP)_2$ powder.

Table S1 Textural pore properties data for the peeled MOF powder and reported by literatures

Sample	S_{BET} (m^2 g^{-1})	V_{total} (cm^3 g^{-1})	Pore size (nm)	Ref
$Ni_3(HITP)_2$	884.7±0.9	/	1.3, 1.6	1
$Ni_3(HITP)_2$	530	0.53	1.4, 1.7-2	2
$Ni_3(HITP)_2$	628.23	0.512	0.8, 2.1	3
$Ni_3(HITP)_2$	458	/	/	4
$Ni_3(HITP)_2$	421/340	/	/	5
Peeled $Ni_3(HITP)_2$	638.8	/	1.5	6
Peeled $Ni_3(HITP)_2$	900.7	1.6	1.4-2, 4.5-7.5	This work

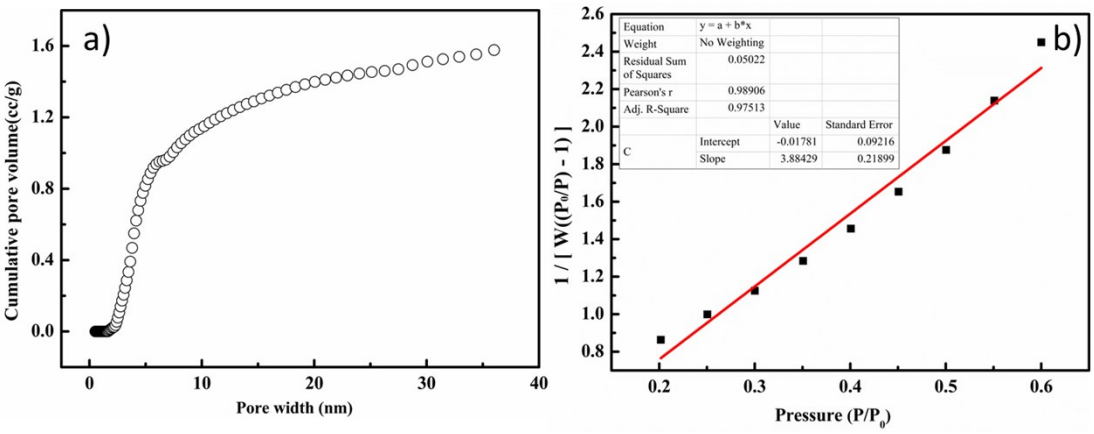

Fig. S3 a) The total pore volume and b) BET plot of $Ni_3(HITP)_2$ powder peeled of the membranes

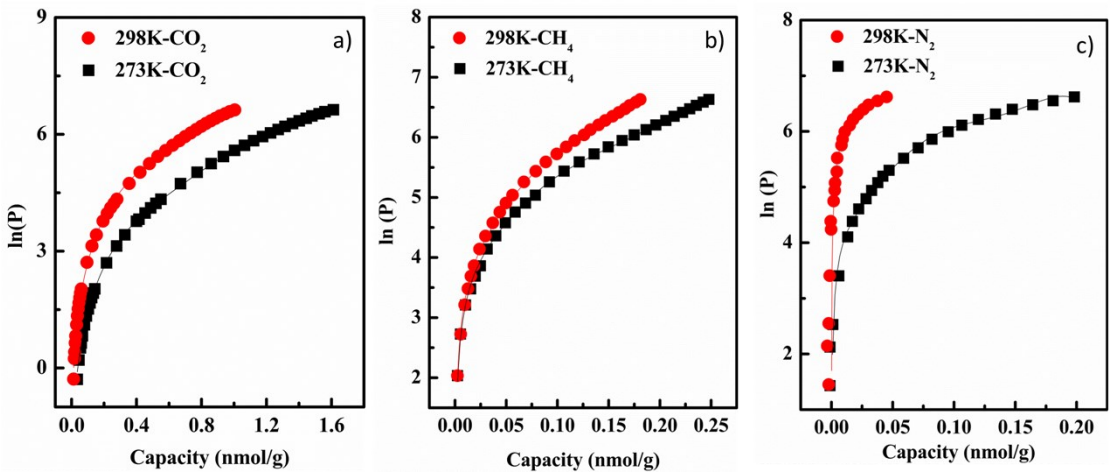

Fig. S4 CO_2, N_2 and CH_4 adsorption isotherms for $Ni_3(HITP)_2$ powder peeled of the membranes at 273 K, 298 K fitted by the dual-site Langmuir-Freundlich equation.

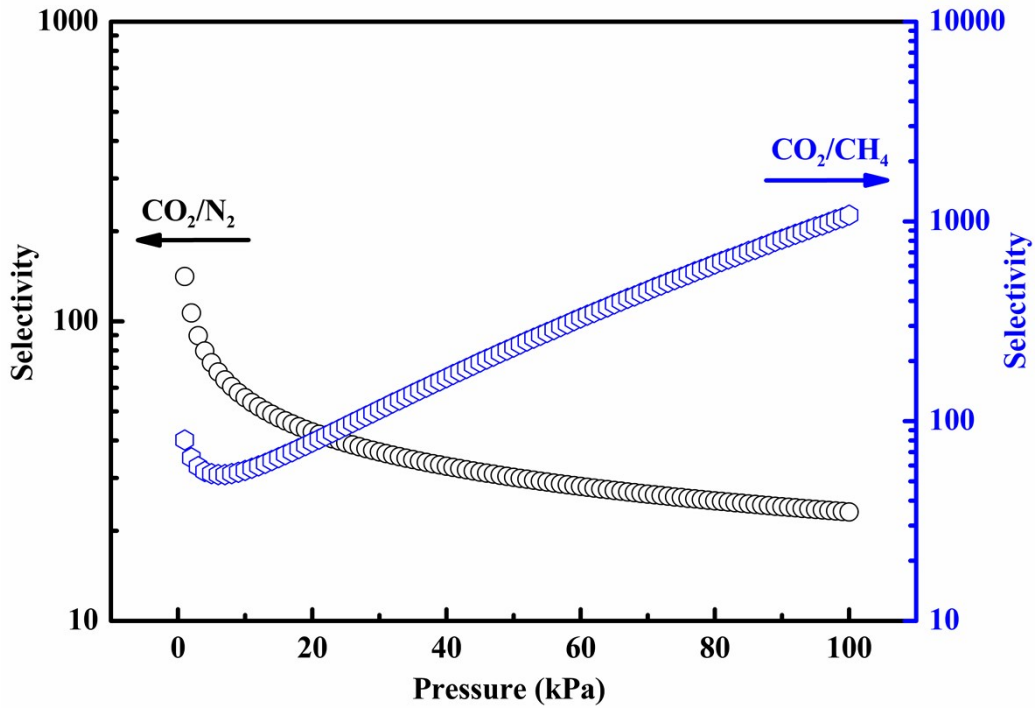

Fig. S5 The IAST selectivity of peeled $Ni_3(HITP)_2$ powder at 273 K.

Table S2 Comparison between the MOF membranes reported by literatures and this work. Permeance given in units of (10^{-8} mol m^2 s^{-1} Pa^{-1})

Membrane	CO_2 Permeability	CO_2/N_2 Ideal Selectivity	CO_2/CH_4 Ideal Selectivity	Ref.
Bio-MOF-1	110	/	2.6	7
ZIF-67	27.8	2.9	5.4	8
ZIF-69	2.36	2.2	2.7	9
ZIF-8	114	2.1	2.2	10
Bio-MOF-14	416	/	3.5	11
$[Cu_2L_2P]$	1.5	/	4～5	12
HKUST-1	28.1	1.0	1.7	13
$Cu(bipy)_2(SiF_6)$	3.85	0.9	0.9	14
CAU-1	1.46	0.7	0.8	15
JUC-150	1	0.6	0.9	16
Zn_2BzIm_3	0.81	0.8	1.0	17
ZIF-90	47.5	7.1	5.9	18
ZIF-7	900	13.6	13.5	19
sod-ZMOF-1	910	8.6	3.7	20
ZIF-8	3.5	7.0	7.1	21
Co-MOF-74	22.5	0.9	0.6	22
NH_2-MIL-53	0.18	0.9	0.9	23
$[Zn_2(cam)_2dabco]$	0.00733	0.5	0.5	24
ZIF-7-8	1.5	20	23.84	25
$Cu(dhbc)_2(bpy)$	3.83	22.8	19.6	26
ZIF-8	15	6.3	4.2	27
SIFSIX-3-Ni	45	/	9.9	28
$[Ni_2(Lasp)_2(bpe)]$	17.8	1.4	2.2	29
Fe-soc-MOF-1b	0.97	0.7	1.8	30
Cu-BTC/MIL-100	0.113	2.8	4.3	31
NH_2-MIL-125(Ti)	0.2	0.5	0.5	32
MIL-100(In)	90	3.8	1.1	33
ZIF-100	0.081	0.3	0.6	34
ZIF-8	4.45	3	3.3	35
CAU-10-H	400	/	4	36
COF-300-ZIF-8	2.67	/	0.5	37
ZIF-8	15.3	4.9	3.4	38
LDH-ZIF-8	0.187	3.1	10.3	39
ZIF-8/GO	35.8	3.1	3.2	40
ZIF-67	0.108	2.8	2.9	41
ZIF-8	652	4.3	5.4	42
$Ni_3(HITP)_2$	226	11.9	/	2
Ni-MOF	143	9.8	6.8	This work

2. Supporting References

1. Chen, T.; Dou, J.-H.; Yang, L.; Sun, C.; Libretto, N. J.; Skorupskii, G.; Miller, J. T.; Dincă, M. Continuous Electrical Conductivity Variation in M_3(hexaiminotriphenylene)$_2$ (M = Co, Ni, Cu) MOF Alloys. *J. Am. Chem. Soc.*, 2020, **142**, 12367-12373.
2. S. S. Jiang, X. L. Shi, F. X. Sun, G. S. Zhu, Fabrication of Crystalline Microporous Membrane from 2D MOF Nanosheets for Gas Separation, *Chem Asian J.*, 2020, **15**, 2371-2378.
3. D. Cai, M. Lu, L. Li, J. Cao, D. Chen, H. Tu, J. Li and W. Han, A Highly Conductive MOF of Graphene Analogue Ni_3(HITP)$_2$ as a Sulfur Host for High‐Performance Lithium-Sulfur Batteries, *Small*, 2019, **15**, 1902605.
4. A. Nazir, H. T. T. Le, C. W. Min, A. Kasbe, J. Kim, C. S. Jin and C. J. Park, Coupling of a conductive Ni_3(2,3,6,7,10,11-hexaiminotriphenylene)$_2$ metal-organic framework with silicon nanoparticles for use in high-capacity lithium-ion batteries, *Nanoscale*, 2020, **12**, 1629-1642.
5. M. K. Smith and K. A. Mirica, Self-Organized Frameworks on Textiles (SOFT): Conductive Fabrics for Simultaneous Sensing, Capture, and Filtration of Gases, *J. Am. Chem. Soc.*, 2017, **139**, 16759-16767.
6. Y. Zang, F. Pei, J. H. Huang, Z. H. Fu, G. Xu and X. L. Fang, Large-Area Preparation of Crack-Free Crystalline Microporous Conductive Membrane to Upgrade High Energy Lithium-Sulfur Batteries, *Adv. Energy Mater.*, 2018**, 8**, 1802052.
7. J. A. Bohrman, M. A. Carreon, Synthesis and CO_2/CH_4 separation performance of Bio-MOF-1 membranes, *Chem. Commun.*, 2012, **48**, 5130-5132.
8. P. Nian, Y. Li, X. Zhang, Y. Cao, H. Liu, X. Zhang, Zno Nanorod-induced Heteroepitaxial Growth of SOD Type Co-based Zeolitic Imidazolate Framework Membranes for H_2 Separation. *ACS Applied Materials & Interfaces*, 2018, **10 (4)**, 4151–4160.
9. Y. Y. Liu, G. F. Zeng, Y. C. Pan, et al, Synthesis of highly c-oriented ZIF-69 membranes by secondary growth and their gas permeation properties, *J. Membr. Sci.*, 2011, **379**, 46-51.
10. G. W. He, M. Dakhchoune, J. Zhao, Huang, S. Q. K. V. Agrawal, Electrophoretic Nuclei Assembly for Crystallization of High-performance Membranes on Unmodified Supports. *Adv. Funct. Mater.*, 2018, **28 (20)**, 1707427.
11. Z. Z. Xie, T. Li, N. L. Rosi, et al, Alumina-supported cobalt-adeninate MOF membranes for CO_2/CH_4 separation, *J. Mater. Chem. A.*, 2014, **2**, 1239-1242.
12. A. Betard, H. Bux, S. Henke, et al, Fabrication of a CO_2-selective membrane by stepwise liquid-phase deposition of an alkylether functionalized pillared-layered metal-organic framework $[Cu_2L_2P]_n$ on a macroporous support, *Microporous Mesoporous Mater.*, 2012, **150**, 76-82.

13. H. Guo, G. Zhu, I. J. Hewitt, S. Qiu, "Twin Copper Source" Growth of Metal-Organic Framework Membrane: $Cu_3(BTC)_2$ with High Permeability and Selectivity for Recycling H_2, *J. Am. Chem. Soc.,* 2009, **131**, 1646.

14. S. Fan, F. Sun, J. Xie, J. Guo, L. Zhang, C. Wang, Q. Pan, G. Zhu, Facile synthesis of a continuous thin $Cu(bipy)_2(SiF_6)$ membrane with selectivity towards hydrogen, *J. Mater. Chem. A.,* 2013, **1**, 11438.

15. S. Zhou, X. Zou, F. Sun, H. Ren, J. Liu, F. Zhang, N. Zhao, G. Zhu, Development of hydrogen-selective CAU-1 MOF membranes for hydrogen purification by 'dual-metal-source' approach, *Int. J. Hydrogen Energy,* 2013, **38**, 5338.

16. Z. Kang, M. Xue, L. Fan, L. Huang, L. Guo, G. Wei, B. Chen, S. Qiu, Highly selective sieving of small gas molecules by using an ultra-microporous metal–organic framework membrane, *Energy Environ. Sci*., 2014, **7**, 4053.

17. Y. Peng, Y. Li, Y. Ban, W. Yang, Two-Dimensional Metal-Organic Framework Nanosheets for Membrane-Based Gas Separation, *Angew. Chemie Int. Ed*.,. 2017, **56**, 9757.

18. K. Eum, C. Ma, D.-Y. Koh, F. Rashidi, Z. Li, C. W. Jones, R. P. Lively, S. Nair, Zeolitic Imidazolate Framework Membranes Supported on Macroporous Carbon Hollow Fibers by Fluidic Processing Techniques, *Adv. Mater. Interfaces*, 2017, **4**, 1700080.

19. F. Cacho-Bailo, S. Catalán-Aguirre, M. Etxeberría-Benavides, O. Karvan, V. Sebastian, C. Téllez, J. Coronas, Metal-organic framework membranes on the inner-side of a polymeric hollow fiber by microfluidic synthesis, *J. Memb. Sci.* 2015, **476**, 277.

20. B. A. Al-Maythalony, O. Shekhah, R. Swaidan, Y. Belmabkhout, I. Pinnau, M. Eddaoudi, Quest for Anionic MOF Membranes: Continuous sod-ZMOF Membrane with CO_2 Adsorption-Driven Selectivity, *J. Am. Chem. Soc.* 2015, **137**, 1754.

21. Y. Hu, J. Wei, Y. Liang, H. Zhang, X. Zhang, W. Shen, H. Wang, Zeolitic Imidazolate Framework/Graphene Oxide Hybrid Nanosheets as Seeds for the Growth of Ultrathin Molecular Sieving Membranes, *Angew. Chemie Int. Ed*.„ 2016, **128**, 2088.

22. X. Qin, Y. Sun, N. Wang, Q. Wei, L. Xie, Y. Xie, J.-R. Li, Nanostructure array assisted aggregation-based growth of a Co-MOF-74 membrane on a Ni-foam substrate for gas separation, *RSC Adv*., 2016, **6**, 94177.

23. W. Li, P. Su, G. Zhang, C. Shen, Q. Meng, Preparation of continuous NH_2-MIL-53 membrane on ammoniated polyvinylidene fluoride hollow fiber for efficient H_2 purification, *J. Memb. Sci*., 2015, **495**, 384.

24. K. Huang, S. Liu, Q. Li, W. Jin, Sep. Preparation of novel metal-carboxylate system MOF membrane for gas separation, *Purif. Technol*., 2013, **119**, 94.

25. Q. Hou, Y. Wu, S. Zhou, Y. Wei, J. Caro, H. Wang, Ultra-Tuning of the Aperture Size in Stiffened ZIF-8_Cm Frameworks with Mixed-Linker Strategy for Enhanced CO_2/CH_4 Separation, *Angew. Chemie Int. Ed*., 2019, **58**, 327.

26. Y. Ying, Z. Zhang, S. B. Peh, A. Karmakar, Y. Cheng, J. Zhang, L. Xi, C. Boothroyd, Y. M. Lam, C. Zhong and D. Zhao, Pressure-Responsive Two-Dimensional Metal-Organic FrameworkComposite Membranes for CO_2 Separation, *Angewandte Chemie*, 2021, **60**, 2-10.

27. Y. Miao, D. Lee, M. Dorneles De Mello, M. Abdel-Rahman, P. Corkery, J. A. Boscoboinik, H. Fairbrother and M. Tsapatsis, Electron beam induced modification of ZIF-8 membrane permeation properties, *Chem. Comm.*, 2021. DOI: 10.1039/D1CC00252J.

28. V. Chernikova, O. Shekhah, Y. Belmabkhout and M. Eddaoudi, Nanoporous Fluorinated Metal-Organic Framework-Based Membranes for CO_2 Capture, *ACS Applied Nano Materials*, 2020, **3**, 6432-6439.

29. Z. Kang, L. Fan, S. Wang, D. Sun, M. Xue, S. Qiu, In situ confinement of free linkers within a stable MOF membrane for highly improved gas separation properties, *CrystEngComm*., 2017, **19**, 1601.

30. Y. Belmabkhout, R. S. Pillai, D. Alezi, O. Shekhah, P. M. Bhatt, Z. Chen, K. Adil, S. Vaesen, G. De Weireld, M. Pang, M. Suetin, A. J. Cairns, V. Solovyeva, A. Shkurenko, O. El Tall, G. Maurin, M. Eddaoudi, Metal-organic frameworks to satisfy gas upgrading demands: fine-tuning the soc-MOF platform for the operative removal of H_2S, *J. Mater. Chem.* A, 2017, **5**, 3293.

31. W. Li, Y. Zhang, C. Zhang, Q. Meng, Z. Xu, P. Su, Q. Li, C. Shen, Z. Fan, L. Qin, G. Zhang, Transformation of metal-organic frameworks for molecular sieving membranes, *Nat. Commun*., 2016, **7**, 11315.

32. Y. Sun, Y. Liu, J. Caro, X. Guo, C. Song, Y. Liu, In-Plane Epitaxial Growth of Highly c-Oriented NH_2-MIL-125(Ti) Membranes with Superior H_2/CO_2 Selectivity, *Angew. Chemie Int. Ed.,* 2018, **57**, 16088.

33. Z. Dou, J. Cai, Y. Cui, J. Yu, T. Xia, Y. Yang, G. Qian, Preparation and Gas Separation Properties of Metal-Organic Framework Membranes, *Zeitschrift für anorganische und allgemeine Chemie,* 2015, **641**, 792-796.

34. M. C. McCarthy, V. Varela-Guerrero, G. V. Barnett, H.-K. Jeong, Synthesis of Zeolitic Imidazolate Framework Films and Membranes with Controlled Microstructures, *Langmuir*, 2010, **26**, 14636.

35. N. Wang, Y. Liu, Z. Qiao, L. Diestel, J. Zhou, A. Huang, J. Caro, Polydopamine-based synthesis of a zeolite imidazolate framework ZIF-100 membrane with high H_2/CO_2

selectivity, *J. Mater. Chem. A,* 2015, **3**, 4722.

36. H. Jin, A. Wollbrink, R. Yao, Y. Li, J. Caro, W. Yang, A novel CAU-10-H MOF membrane for hydrogen separation under hydrothermal conditions, *J. Memb. Sci.*, 2016, **513**, 40.
37. J. Fu, S. Das, G. Xing, T. Ben, V. Valtchev, S. Qiu, Fabrication of COF-MOF Composite Membranes and Their Highly Selective Separation of H_2/CO_2, *J. Am. Chem. Soc.*, 2016, **138**, 7673.
38. K. Eum, C. Ma, A. Rownaghi, C. W. Jones, S. Nair, ZIF-8 Membranes via Interfacial Microfluidic Processing in Polymeric Hollow Fibers: Efficient Propylene Separation at Elevated Pressures, *ACS Appl. Mater. Interfaces*, 2016, **8**, 25337.
39. Y. Liu, Y. Peng, N. Wang, Y. Li, J. H. Pan, W. Yang, J. Caro, Significantly Enhanced Separation using ZIF-8 Membranes by Partial Conversion of Calcined Layered Double Hydroxide Precursors, *ChemSusChem*., 2015, **8**, 3582.
40. Y. Hu, Y. Wu, C. Devendran, J. Wei, Y. Liang, M. Matsukata, W. Shen, A. Neild, H. Huang, H. Wang, Preparation of nanoporous graphene oxide by nanocrystal-masked etching: toward a nacre-mimetic metal-organic framework molecular sieving membrane, *J. Mater. Chem. A,* 2017, **5**, 16255.
41. P. Nian, Y. Cao, Y. Li, X. Zhang, Y. Wang, H. Liu, X. Zhang, Preparation of a pure ZIF-67 membrane by self-conversion of cobalt carbonate hydroxide nanowires for H_2 separation, *CrystEngComm*., 2018, **20**, 2440.
42. W. Li, P. Su, Z. Li, Z. Xu, F. Wang, H. Ou, J. Zhang, G. Zhang, E. Zeng, Ultrathin metal-organic framework membrane production by gel-vapour deposition, *Nat. Commun*., 2017, **8**, 406.