Electronic Supporting Information

Ionic Liquids Functionalized Multi-Walled Carbon Nanotubes/Zeolitic Imidazolate Framework Hybrid Membranes for Efficient H_2/CO_2 Separation

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1. Experimental details:

1.1 Materials

Porous α-Al_2O_3 disks (30 mm in diameter, 3 mm in thickness, Angtai Electronic Ceramics Co. Ltd) were used as supports. Cobalt(II) nitrate hexahydrate (Co $(NO_3)_2 \cdot 6H_2O$, 99%, J&K Scientific Ltd.), benzimidazole (BIM, 99%, Aladdin Chemistry Co. Ltd), 3-Aminopropyltriethoxysilane (APTES, 98%, Aladdin Chemistry Co. Ltd), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][Tf2N], purity>99%), purified multi-walled carbon nanotubes (CNTs, length: 10-30μm, inner diameter: 5-10nm, purity: >95%), *N,N'*-dimethylformamide (DMF, ≥99.5%, Sinopharm Chemical Reagent Co. Ltd), sodium hydroxide (NaOH, ≥96%, Beijing Chemical Works), ethanol (C_2H_5OH, ≥97%, Beijing Chemical Works) were used without further purification.

1.2 Preparation of ZIF-9 Membrane

One side of porous α-Al_2O_3 disk was polished with 1500 grit SiC sandpaper to get a smooth surface for the growth of membrane, and abundant deionized water was used to wash off the impurities by ultrasonic. In order to gain concentration of hydroxyl groups on the surface of support, the α-Al_2O_3 disk was soaked in saturated NaOH solution for 24 hours. After that, the support was ultrasonically dealt with abundant deionized water again and dried at 90°C for 2 hours. The supports were dissolved in the mixture solution of 0.4 g APTES (coupling agent, 2% volume fraction), 24 ml ethanol and 1 ml deionized water for 24 hours, followed by being cleaned using ethanol and finally dried.[1]

Co $(NO_3)_2 \cdot 6H_2O$ (0.6 g) was dissolved in 40 ml DMF (solution I) and BIM (0.52 g) was dissolved in 20 ml DMF (solution II). Both of these two solutions were thoroughly stirred to guarantee the intensive mixing. Then solution I was poured into a 100 ml autoclave. The support with the unpolished side coated by Teflon tape was hanged in the solution I vertically for 30 minutes. After that, solution II was transferred into and the autoclave was sealed. The mixture solution was heated up to 110°C in 2 hours. After

crystallization at 110°C for 72 hours, ZIF-9 membrane was produced. The sample was washed by ethanol several times and soaked in the abundant ethanol for 24 hours. Then the sample was activated in a vacuum oven at 90°C for 24 hours. Finally, the ZIF-9 membrane formed successfully.

1.3 Preparation of ILs functionalized CNTs suspension

CNTs were carried out using the following procedure: pristine CNTs (0.2g) were added to a solution of H_2SO_4 (200ml) and HNO_3 (200ml), which were stirred vigorously at 80 °C for 24 h. Then the acidulated CNTs were disposed by filtration and washed with deionized water until filtrate became neutral. The solid was dried under high vacuum for 12 h at 70 °C to get 0.1 g acidulated CNTs. Then the 0.1 g acidulated CNTs and 0.2 g ILs were added to the 20 ml ethanol solution which was under ultrasound for 1 h and stirred vigorously at 65 °C for 24 h under a N_2 atmosphere.[2] The resulting product was then repeatedly washed with ethanol at room temperature to filter the unbound ILs. Finally, the resulting CNTs were added to the 20 ml ethanol solution which was under ultrasound for 1 h and stirred vigorously for 24 h at room temperature. The CNT@IL suspension was prepared.

1.4 CNT@IL layer covering the ZIF-9 crystal

CNT@IL/ZIF-9 hybrid membrane was synthetized using heat treatment of layer-by-layer deposition method. The α-Al_2O_3 supported ZIF-9 membrane was horizontally placed on the CNT@IL suspension for an hour and then evaporated at 80 °C in an air oven for 30 minutes. CNT@IL deposition was repeated for 20 cycles to obtain a dense CNT@IL layer on the surface of ZIF-9 crystals. After this deposition, the CNT@IL/ZIF-9 membrane was further activated at 70 °C in the air oven overnight.[3]

1.5 Preparation of CNT/ZIF-9 membrane

CNTs were carried out using the following procedure: pristine CNTs (0.2g) were added to a solution of H_2SO_4 (200ml) and HNO_3 (200ml), which was stirred vigorously at 80 °C for 24 h. Then the acidulated CNTs were disposed by filtration and washed with deionized water until the filtrate became neutral. After that the resulted CNTs were dried under high vacuum for 12 h at 70 °C to get 0.1 g acidulated CNTs. The acidulated CNTs were added to the 20 ml ethanol solution which was under ultrasound for 1 h and stirred vigorously for 24 h. The α-Al_2O_3 supported ZIF-9 membrane was horizontally placed on the CNTs solution for an hour and then solvent evaporated at 80 °C in an air oven for 30 minutes. CNTs deposition was repeated for 20 cycles. Finally, the CNT/ZIF-9 membrane was further activated at 70 °C in the air oven over night.

1.6 Preparation of IL/ZIF-9 membrane

ILs was carried out using the following procedure: 0.2 g ILs was added to the 20 ml ethanol which was stirred for 1 h. The concentration of ILs solution is 1.3 wt %, which is comparable to that in the preparation of CNT@IL/ZIF-9 membrane (1.2 wt %). The α-Al_2O_3 supported ZIF-9 membrane was horizontally placed on the ILs solution for an hour without applying any pressure gradient. After the membrane was loaded, membranes were dried at 80 °C in an air oven for 30 minutes.[4] This process was repeated for 20 cycles. Finally, the IL/ZIF-9 membrane was further activated at 70 °C in the air oven over night.

2. Characterization techniques and results

2.1 Characterization

Powder X-ray diffraction analysis of the membranes were performed on a SHIMADZU XRD-6000-X-ray diffractometer in reflection mode with Cu Ka radiation (λ = 1.5406 Å). The 2θ range from 5° to 50° was scanned with a step size of 0.05°. Scanning electron micrographs (SEM) (FEI, a XL-30 ESEM-FEG microscope, US) were applied to check the morphologies of the membranes. Gold-coated specimens were used to increase the conductivity and the measurements were carried out under 10-20 kV acceleration. The specimens for transmission electron microscope (TEM) observation were prepared by ultrasonicating samples in ethanol and dropped on a copper grid, which were obtained on a JEOL 3010 transmission electron microscope operating at 200 kV. Thermogravimetric and decomposition analyses were performed on a TGA/DSC 1/1100 SF instrument. The temperature ranges from 50°C to 800 °C in air at a heating rate of 10 °C /min. Fourier transform infrared spectroscopy (FTIR) was checked by using a FTIR-8400 (Shimadzu Corp., Japan) with a scan range from 500 to 4000 cm^{-1}. The Raman spectra were operated with a laser Raman microscope (Renishaw invia) with a 633 nm Ar line as the excitation source. The spectra were measured in a backscattering configuration with a triple monochromator at intervals of 1.5 cm^{-1}. The laser power was 0.5 W.

2.2 Permeation and separation of single gas

Single gas permeation was measured in home-made devices. The supported CNT@IL/ZIF-9 membrane was sealed in a permeation module with silicone O-rings. The feed gases were fed to the top side of the membrane. Before the measurement of each gas species, the permeation apparatus was purged with the respective gas to avoid the disturbance from previous gas permeation. During measurements, exactitude manometers and temperature transducers were used to control the pressure and temperature, respectively. The downstream side was contacted with the atmosphere (~0.1 MPa), and the pressure at the feed side was controlled with the exactitude manometer. The effective area of the CNT@IL/ZIF-9 membrane was estimated to be around 3.14 cm^2. The permeation experiments were carried out for four single gases (H_2, N_2, CH_4 and CO_2) in this study. The permeation rates of these gases were recorded using the soap film flowmeter. The ideal separation factor of gases was calculated as the ratio of their permeation. To confirm the reliability of results, each measurement has been repeated at least five times. [3] The permeation (P_{per}) was calculated as follows:

$$P_{\mathrm{per}} = \frac{\frac{V}{t}}{R \cdot T \cdot \left(\frac{\Delta \mathrm{P}}{P_0}\right) \cdot A}$$

where, V is the total volume of gas permeated in the soap film flowmeter, t is the operating time, R is the constant of 8.314 $Pa \cdot m^3/(mol \cdot K)$, T is the testing temperature, ΔP is the pressure drop, P_0 is the atmosphere pressure, and A is the membrane area.[5,6]

3. The SEM images of membranes

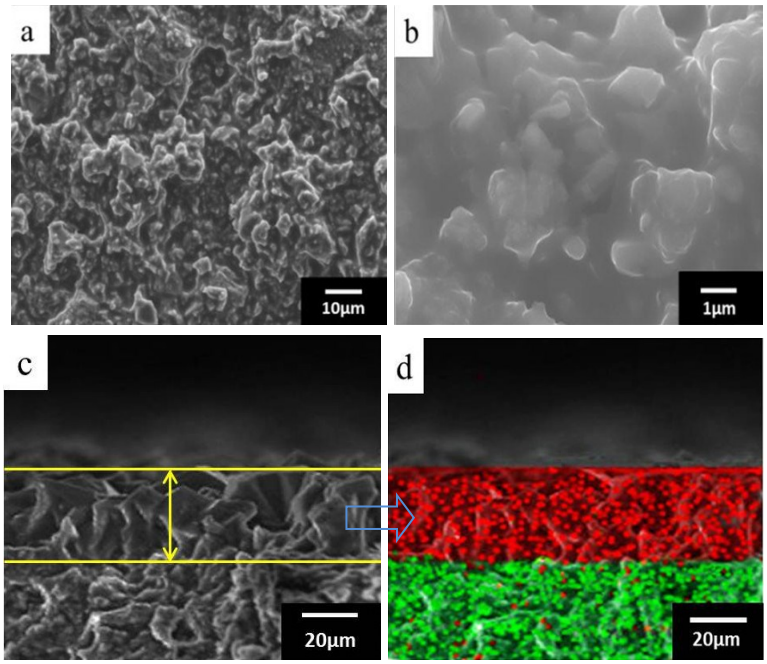

Fig.S1. Top view (a, b), cross-section (c) SEM images and the Energy Dispersive Spectrometer (EDS) mapping (d) of the cross-section (red: Co as tracer for IL/ZIF-9; green: Al as the tracer for the support) of IL/ZIF-9 membrane.

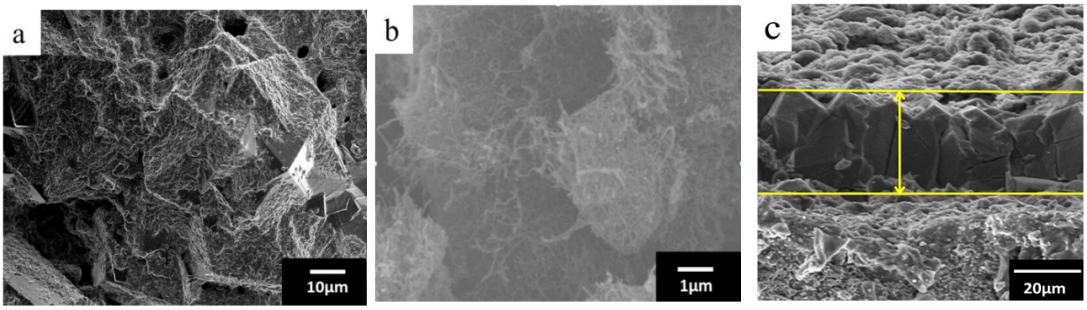

Fig. S2. Top view (a, b) and cross-section (c) SEM images of CNT/ZIF-9 membrane

4. The results of TGA, FT-IR and Raman spectra of membranes

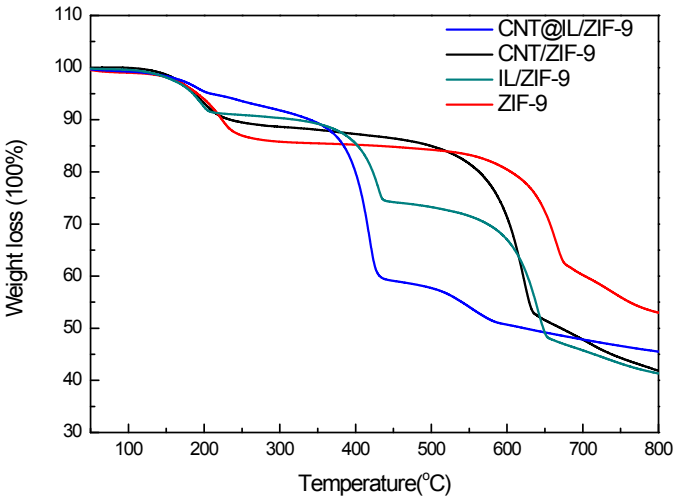

Fig. S3. TGA of the ZIF-9, IL/ZIF-9, CNT/ZIF-9 and CNT@IL/ZIF-9 membranes

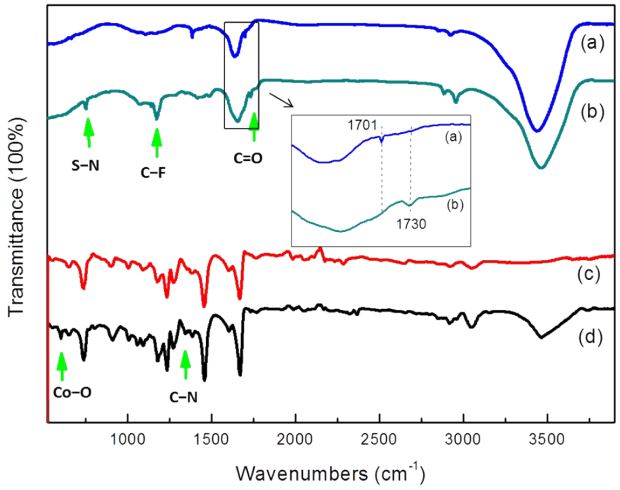

Fig. S4. FT-IR spectra of acidulated CNTs (a), CNT@IL (b), ZIF-9 (c) membrane and CNT@IL/ZIF-9 (d) membrane

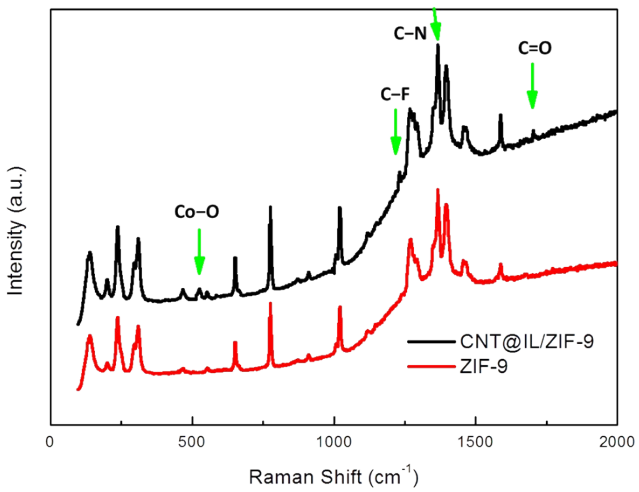

Fig. S5.Raman spectra of CNT@IL/ZIF-9 and ZIF-9 membranes

5. Comparison of the reported MOF membranes

Table S1. Comparison of gas permeability and ideal separation factors of membranes

Membrane	T (°C)	Permeance (10^{-8} mol·m^{-2}·s^{-1}·Pa^{-1})		Ideal separation factor	Ref.
		H_2	CO_2	H_2/CO_2	
IRMOF-3	25	152	62.4	2.44	S7
ZIF-78	25	11.1	1	11.07	S8
ZIF-7	220	4.55	0.35	13	S9
	25	6.04	1.33	4.54	S10
MIL-53	25	49.4	11.0	4.49	S5
ZIF-8	25	17.3	4.45	3.89	S11
	25	36	14	2.57	S12
	25	54.7	1.7	32.2	S13
	25	5730	336	17.05	S6
	25	21	2.36	8.90	S14
ZIF-90	225	30.8	4.1	7.51	S15
	225	29.6	1.37	21.6	
	200	25.0	3.42	7.30	S16
MMOF	25	1.21	0.34	3.57	S17
MOF-5	25	80	25	3.20	S18
Cu-BTC	25	74.8	14.8	5.05	S19
ZIF-9-67	25	1405	158	8.89	S1
$Zn_2(bim)_4$	120	91.8	0.32	290	S20
ZIF-100	25	6.3	0.08	77	S21
CNT@IL/ZIF-9	25	54.46	1.36	40.04	This study

6. Single gas permeances as well as the ideal separation factors at 25 °C and 1.0 bar

Table S2. Single gas permeance as well as the ideal separation factors of the CNT@IL/ZIF-9, IL/ZIF-9, CNT/ZIF-9 and ZIF-9 membranes at 25 °C and 1.0 bar.

	Permeance (10^{-8} mol·m^{-2}·s^{-1}·Pa^{-1})				Ideal separation factor		
	H_2	CO_2	N_2	CH_4	H_2/CO_2	H_2/N_2	H_2/CH_4
ZIF-9	710.60	84.43	303.80	248.32	8.42	2.34	2.86
CNT/ZIF-9	78.25	8.41	17.91	13.87	9.30	4.37	5.64
IL/ZIF-9	18.01	1.32	2.50	2.11	13.64	7.20	8.54
CNT@IL/ZIF-9	54.46	1.36	6.42	5.26	40.04	8.48	10.35

7. Single gas permeances of H_2 and CO_2 as well as the ideal separation factors for H_2/CO_2 at different testing conditions

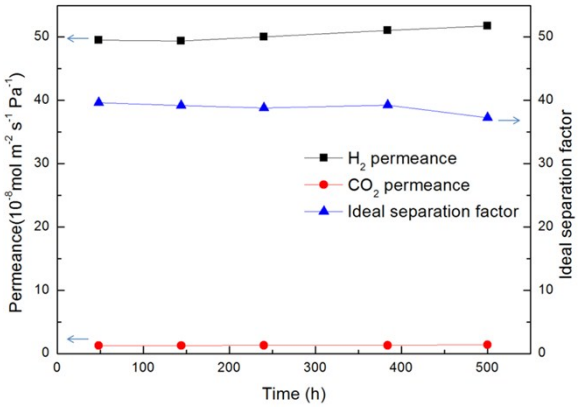

Fig. S6. Single gas permeances of H_2 and CO_2 as well as the ideal separation factors for H_2/CO_2 on the CNT@IL/ZIF-9 membrane as a function of time at 25°C and 1.0 bar

Table S3. Single gas permeances of H_2 and CO_2 as well as ideal separation factors for H_2/CO_2 at 25°C and 1.0 bar of 3 tested CNT@IL/ZIF-9 membranes

Membrane	Permeance (10^{-8} mol·m^{-2}·s^{-1}·Pa^{-1})		Ideal separation factor
	H_2	CO_2	H_2/CO_2
1	54.46	1.36	40.04
2	50.08	1.22	41.05
3	49.53	1.25	39.63

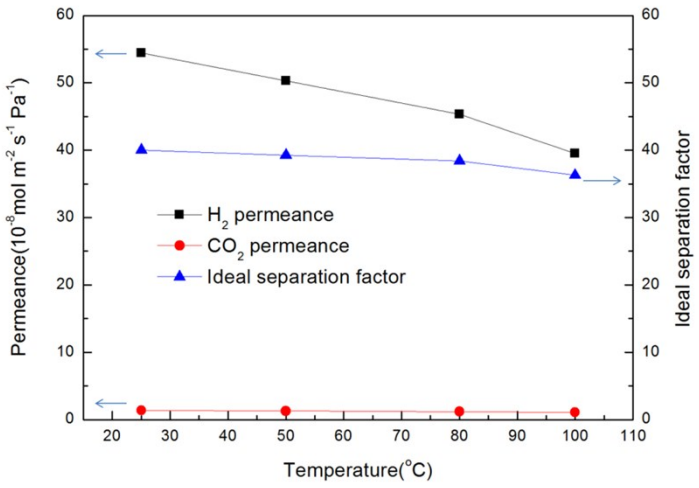

Fig. S7. Single gas permeances of H_2 and CO_2 as well as the ideal separation factors for H_2/CO_2 on the CNT@IL/ZIF-9 membrane as a function of the operation temperature at 1.0 bar

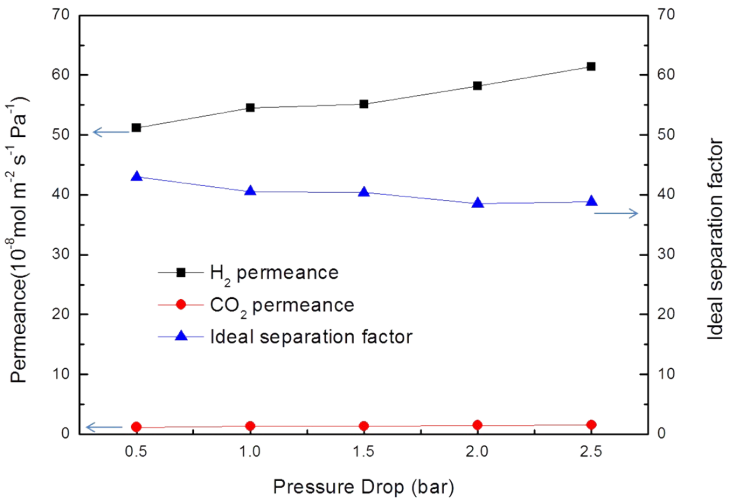

Fig. S8. Single gas permeances of H_2 and CO_2 as well as the ideal separation factors for H_2/CO_2 on the CNT@IL/ZIF-9 membrane as a function of the pressure drop at 25°C

References

S1 C. Zhang, Y. Xiao, D. Liu, Q. Yang and C. Zhong, *Chem. Commun.,* 2013, **49**, 600-602.

S2 M. Tunckol, E. Z. Hernandez, J. R. Sarasua, J. Durand and P. Serp, *Eur. Polym. J.*, 2013, **49**, 3770-3777.

S3 Z. Wang, J. Liu, L. Yan, Y. Wang and G. Luo, *Chin. J. Anal. Chem.,* 2002, **30**, 1053-1057.

S4 O. Tzialla, Ch. Veziri, X. Papatryfon, K. G. Beltsios, A. Labropoulos, B. Iliev, G. Adamova, T. J. S. Schubert, M. C. Kroon, M. Francisco, L. F. Zubeir, G. E. Romanos and G. N. Karanikolos, *J. Phys. Chem. C.*, 2013, **117**, 18434−18440.

S5 Y. Hu, X. Dong, J. Nan, W. Jin, X. Ren, N. Xu and Y. M. Lee, *Chem. Commun.*,2011, **47**, 737-739.

S6 Z. Xie, J. Yang, J. Wang, J. Bai, H. Yin, B. Yuan, J. Lu, Y. Zhang, L. Zhou and C. Duan, *Chem. Commun.*, 2012, **48**, 5977-5979.

S7 Y. Yoo, V. Varela-Guerrero and H. K. Jeong, *Langmuir*, 2011, **27**, 2652-2657.

S8 X. Dong, K. Huang, S. Liu, R. Ren, W. Jin and Y. S. Lin, *J. Mater. Chem*., 2012, **22**, 19222-19227.

S9 Y. Li, F. Liang, H. Bux, W. Yang and J. Caro, *J. Membr. Sci.,* 2010, **354**, 48-54.

S10 H. Bux, F. Liang, Y. Li, J. Cravillon, M. Wiebcke and J. Caro, *J. Am. Chem. Soc.,* 2009, **131**, 16000-16001.

S11 M. C. McCarthy, V. Varela-Guerrero, G. V. Barnett and H. K. Jeong, *Langmuir*, 2010, **26**, 14636−14641.

S12 Y. Pan and Z. Lai, *Chem. Commun*., 2011, **47**, 10275-10277.

S13 G. Xu, J. Yao, K. Wang, L. He, P. A. Webley, C. Chen and H. Wang, *J. Membr. Sci.*, 2011, **187**, 385-386.

S14 Q. Liu, N. Wang, J. Caro and A. Huang, *J. Am. Chem. Soc.*, 2013 , **135** , 17679-17682.

S15 A. Huang, N. Wang, C. Kong and J. Caro, *Angew. Chem. Int. Ed.*, 2012, **51**, 10551-10555.

S16 A. Huang and J. Caro, *Angew. Chem. Int. Ed*., 2011, **50**, 4979-4982.

S17 R. Ranjan and M. Tsapatsis, *Chem. Mater.,* 2009, **21**, 4920-4924.

S18 Y. Yoo, Z. Lai and H. Jeong, *Microporous Mesoporous Mater.,* 2009, **123**, 100-106.

S19 J. Nan, X. Dong, W. Wang, W. Jin and N. Xu, *Langmuir*, 2011, **27**, 4309-4312.

S20 Y. Peng, Y. Li, Y. Ban, H. Jin, W. Jiao, X. Liu and W. Yang, *Science*, 2014, **346**, 1356-1359.

S21 N. Wang, Y. Liu, Z. Qiao, L. Diestel, J. Zhou, A. Huang and J. Caro, *J. Mater. Chem. A.*, 2015, **3**, 4722–4728.