Supporting Information

Exceptional high selectivity of hydrogen/methane separation on a phosphonate-based MOF membrane with exclusion of methane molecules

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1. Materials and Synthesis

All starting chemicals were obtained from commercial sources and used without further purification. The synthesis of $[Ni_{1.5}(4,4'\text{-bipy})_{1.5}H_3L(H_2O)_3](H_2O)_7$ was carried out using the literature method[1]. Typically, 2,4,6-trimethylbenzene-1,3,5-triyl)tris(methylene)triphosphonic acid (H_6L, 0.10 g, 0.25 mmol), $NiSO_4{\cdot}6H_2O$ (0.09 g, 0.38 mmol), 4,4'-Dipyridine (0.06 g, 0.38 mmol) and 15 ml water were added into a Telfon-lined stainless container (20 mL) and was sealed. The container was heated to 413 K for 72 hours and cooled to room temperature over a period of 24 hours. After filtration and was washed with deionized water, blue crystals were obtained.

(1) Membrane preparation

The seeds of MOF precursors (**1**) were deposited on PAAM substrate by vacuum plate method. Firstly, the as-synthesized crystals of **1** were milled into powders and were suspended in water to prepare aqueous suspension which contained ca. 0.2 wt% of MOF seeds. Then, the seed deposited PAAM was treated by a secondary growth of **1** under hydrothermal conditions to form the continuous membrane. In a typical procedure, 15 ml deionized water was added into a solid mixture of L (0.10 g, 0.25 mmol), $NiSO_4{\cdot}6H_2O$ (0.09 g, 0.38 mmol) and 4,4'-Dipyridyl (0.06 g, 0.38 mmol). The mixture solution was sealed and heated to 413 K for 72 h. At last, the MOF membrane was taken out and rinsed three times with distilled water to remove any solvent on the surface of MOF membrane, and then vacuum dried at 378 K for 6 h for permeance test.

(2) Sonication test

The membranes prepared at different temperatures were placed in water, and were sonicated in an ultrasonic machine (LC-CXJ01 600W) at room temperatures for 20 minutes, with the sonication frequency of 100 Hz and a power of 300 Watt.

2. Gas permeance experiments

The gas permeance set up is composed of two gas inlet ports, one permeance cell, four pressure sensors, two buffer tanks, one set of gas chromatograph, one computer and several valves and pipelines connecting them (see schematic illustration in Fig. S1).

In a typical gas permeance experiment, the **1**@PAAM-413 was sealed into a stainless steel permeance cell tightly. Before gas permeance tests, the membrane was activated in suit at 378 K using an external heater for 1.5 hour. The test temperature was controlled from 298 K to 353 K, and the pressure gap was controlled at 0.1 to 0.3 MPa. The test time was determined by the equibrium state of permeation measurements. When the pressure sensor reaches a constant reading, the test was continued for another 12 hours. At a steady state, the relationship between permeate pressure and time should be linear. The slope of the linear region of the pressure response curve was used to calculate permeance.

The single gas permeance was calculated from equation I :

$$P = \frac{V}{R \times T \times p_h \times A} \times \frac{d_p}{d_t} \qquad (1)$$

Where, P is the permeance (mol/Pa·m^2·s); V is the volume of low-pressure chamber (L); R is gas constant; T is the test temperature (K); p_h is the gas pressure in the high-pressure chamber (Pa); A is the area of the membrane; dp/dt is the change of pressure per unit time in the low-pressure chamber (Pa/s). The selectivity was calculated by the ratio of single gas permeance. The constitutions of outlet gases in binary component gas permeance experiments were detected by chromatograph.

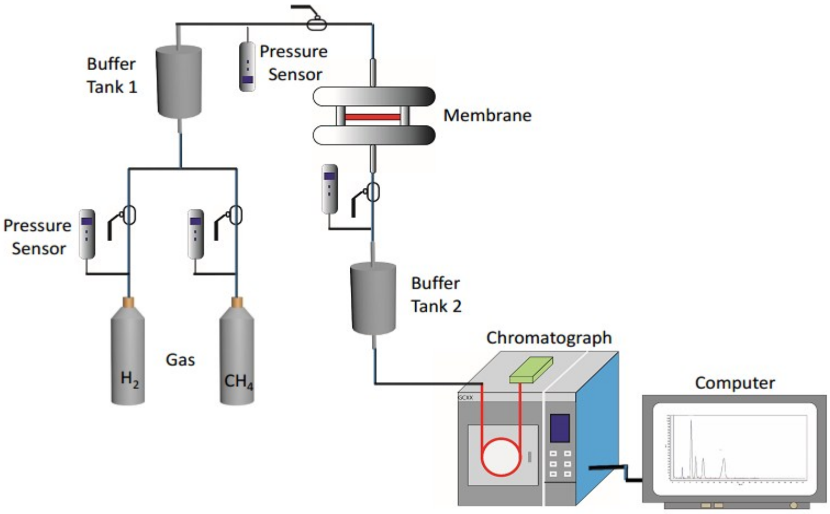


Fig. S1 Measurement equipment of separation process for single-component or binary component gas

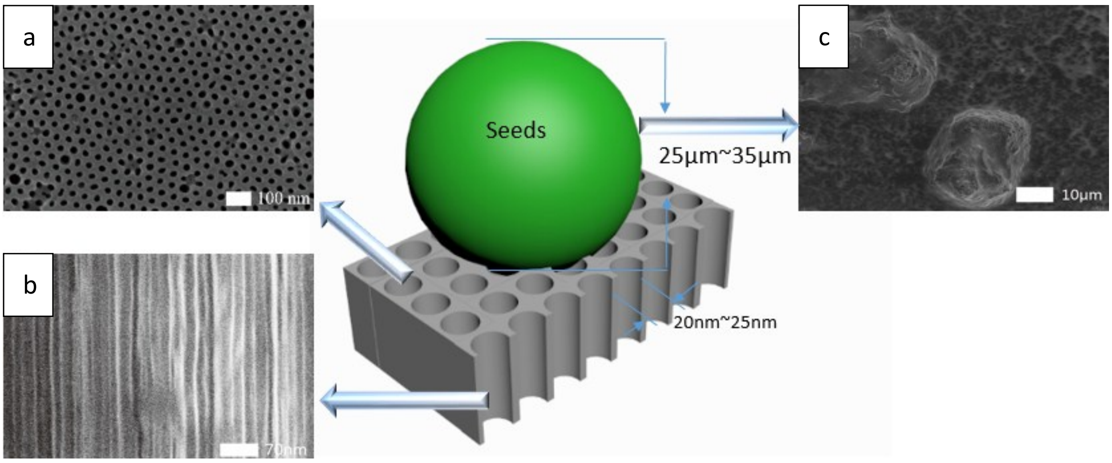


Fig. S2 The pattern of the seed deposited PAAM, (a)seeds, (b)the top view SEM image for PAAM, (c)the cross-section SEM image for PAAM

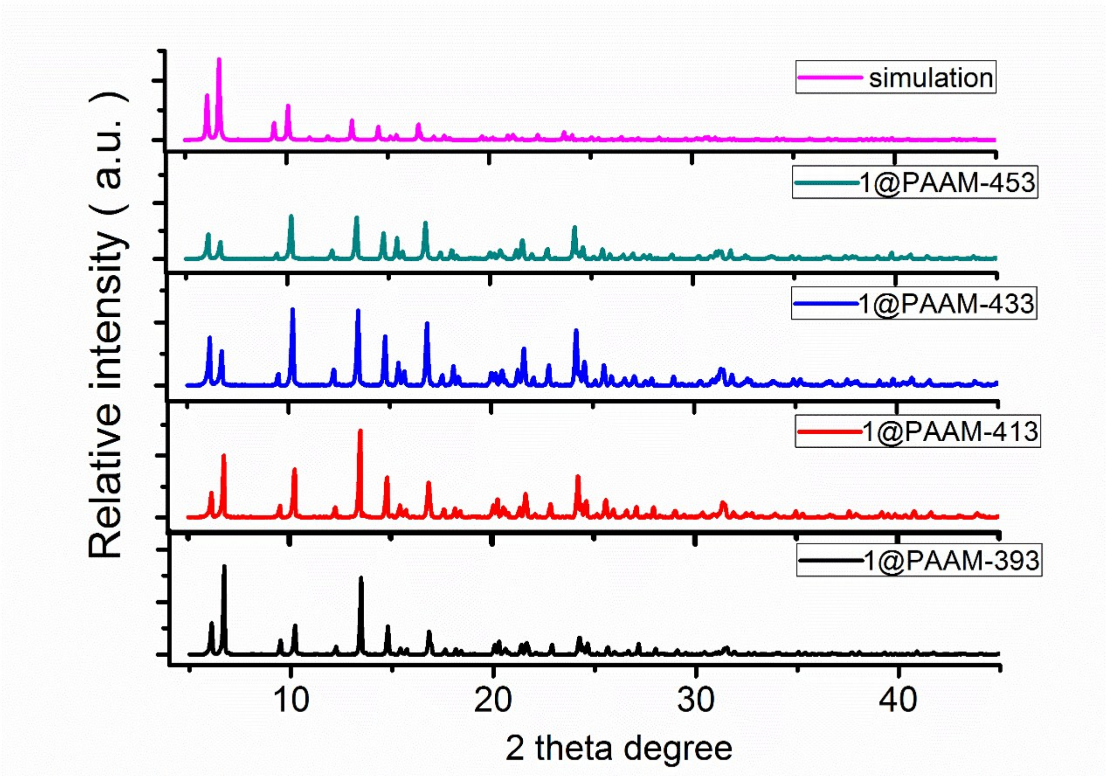
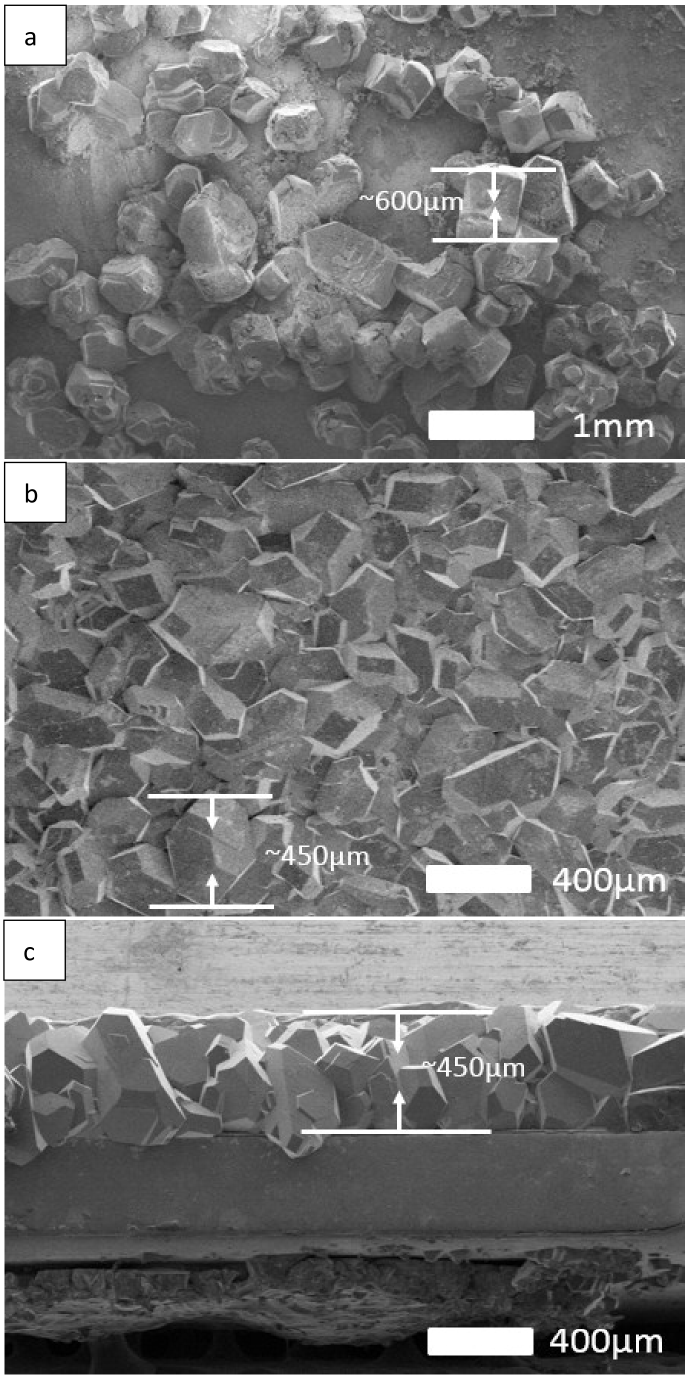


Fig. S3 PXRD patterns of $[Ni_{1.5}(4,4'\text{-bipy})_{1.5}H_3L(H_2O)_3]\,(H_2O)_7$ membranes synthesized at different temperatures


a
~600µm
1mm
b
~450µm
400µm
c
~450µm
400µm

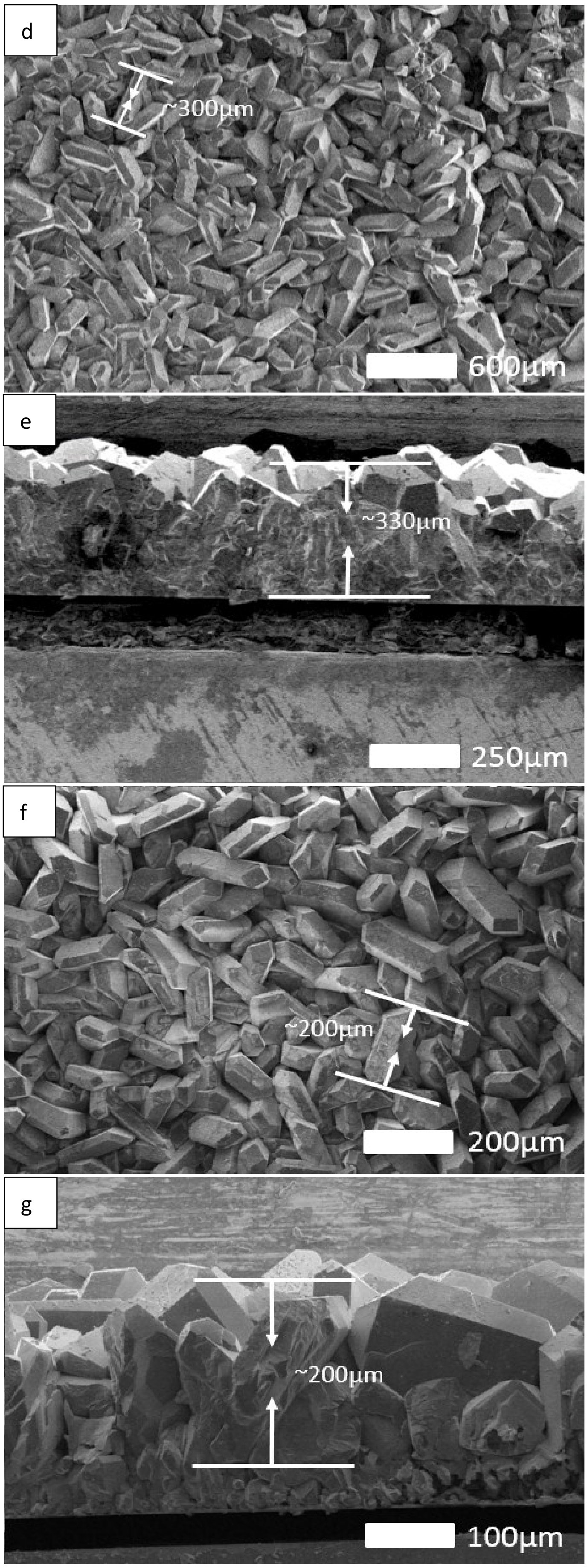

d
~300μm
600μm
e
~330μm
250μm
f
~200μm
200μm
g
~200μm
100μm

Fig. S4 The top view SEM images for (a)**1**@PAAM-393, (b)**1**@PAAM-413, (d)**1**@PAAM-433 (f)**1**@PAAM-453; and the cross-section SEM images for (c)**1**@PAAM-413, (e)**1**@PAAM-433 and (g)**1**@PAAM-453K

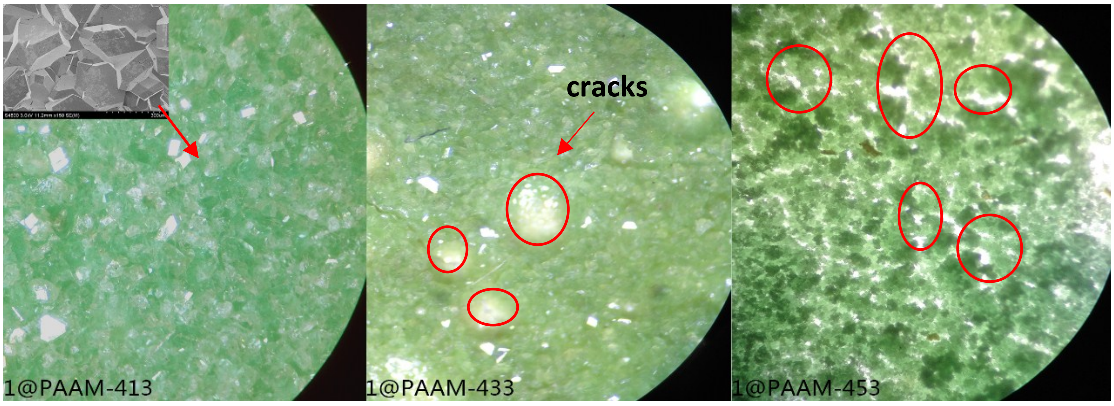


Fig. S5 The pattern of 1@PAAM prepared at different temperatures after sonication

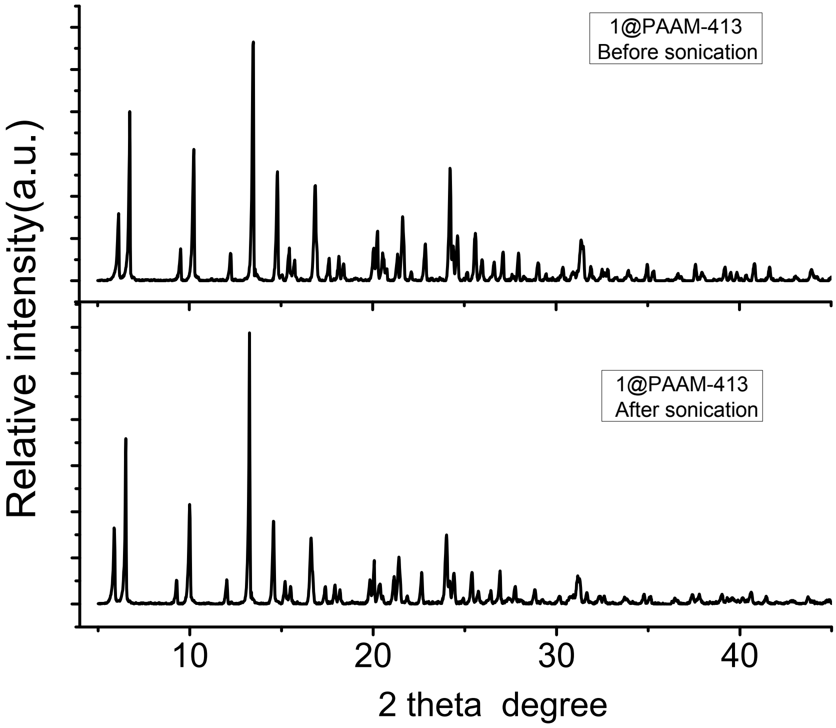


Fig. S6 PXRD patterns of 1@PAAM-413 before and after sonication

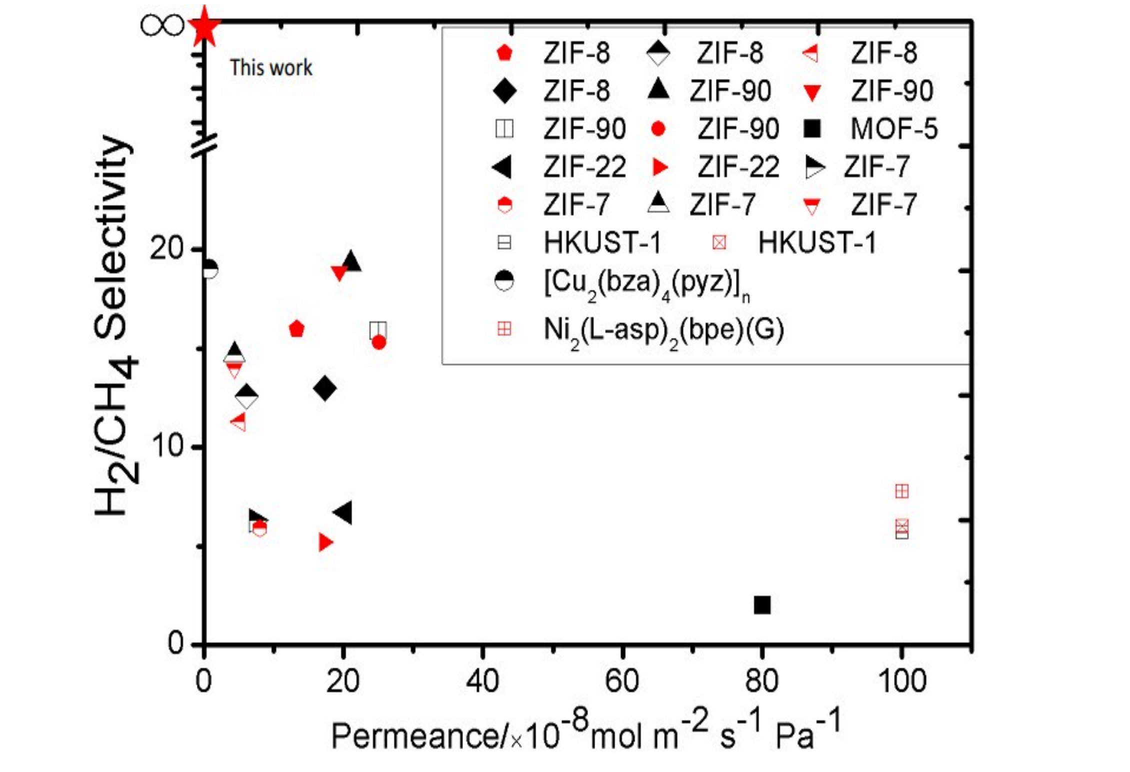


Fig. S7 H_2/CH_4 selectivity as a function of H_2 permeance for 1@PAAM-413 compared with other MOF membranes.

Table S1 Experimental separation factors of H_2/CH_4 with different MOFs membranes

MOF	Permeance of H_2 (×10^{-8} mol/Pa·m^2·s)	Selectivity for H_2/CH_4	Ref.
ZIF-8	15.44/13.27*	20.28/15.99*	2
ZIF-8	6.04/5.08*	12.58/11.29*	3
ZIF-8	17.3±3.7	13	4
ZIF-90#	21/19.4*	19.3/18.9*	5
ZIF-90#	25/25.1*	15.9/15.3*	6
MOF-5	470	~3	7
MOF-5	80	~2	8
ZIF-22	20.2/17.2*	6.7/5.2*	9
ZIF-7#	7.4/7.96*	6.29/5.9*	10
ZIF-7#	4.35/4.36*	14.7/14*	11
HKUST-1	~100	5.7	12
HKUST-1	100*	6	13
$[Cu_2(bza)_4(pyz)]_n$	0.69	19	14
Ni_2(L-asp)$_2$(bpe)·(G)	100*	7.77*	15
$Ni_{1.5}(4,4'\text{-bipy})_{1.5}\cdot H_3L\cdot(H_2O)_7$	0.144	Exceptionally high	This work

* Binary component gas

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