

## Supporting Information

### Synthesis and CO<sub>2</sub>/CH<sub>4</sub> separation performance of Bio-MOF-1 Membranes

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#### Synthesis of Bio-MOF-1 seeds

Bio-MOF-1 crystals were prepared employing the synthesis protocol reported by Rosi's group (see for example: An, J.; Geib, S. J.; Rosi, N. L. *J. Am. Chem. Soc.* **2009**, *131*, 8376). In a typical Bio-MOF-1 crystals were prepared employing a solution with a composition of adenine (0.25 mmol), 4,4'-biphenyl dicarboxylic acid (BPDC) (0.5 mmol), zinc acetate dehydrate (0.75 mmol), nitric acid (2 mmol), DMF (13.5 mL), and water (2 mL). This solution was placed in a sealed Teflon-line autoclave and heated to 130°C for 24h. The resultant solution was centrifuged at 3000 rpm and washed with DMF. This step was repeated 3 times. The resultant crystals were dried under Argon at 125°C for 2h. All chemicals were purchased from Sigma-Aldrich; except DMF (Acros Organics).

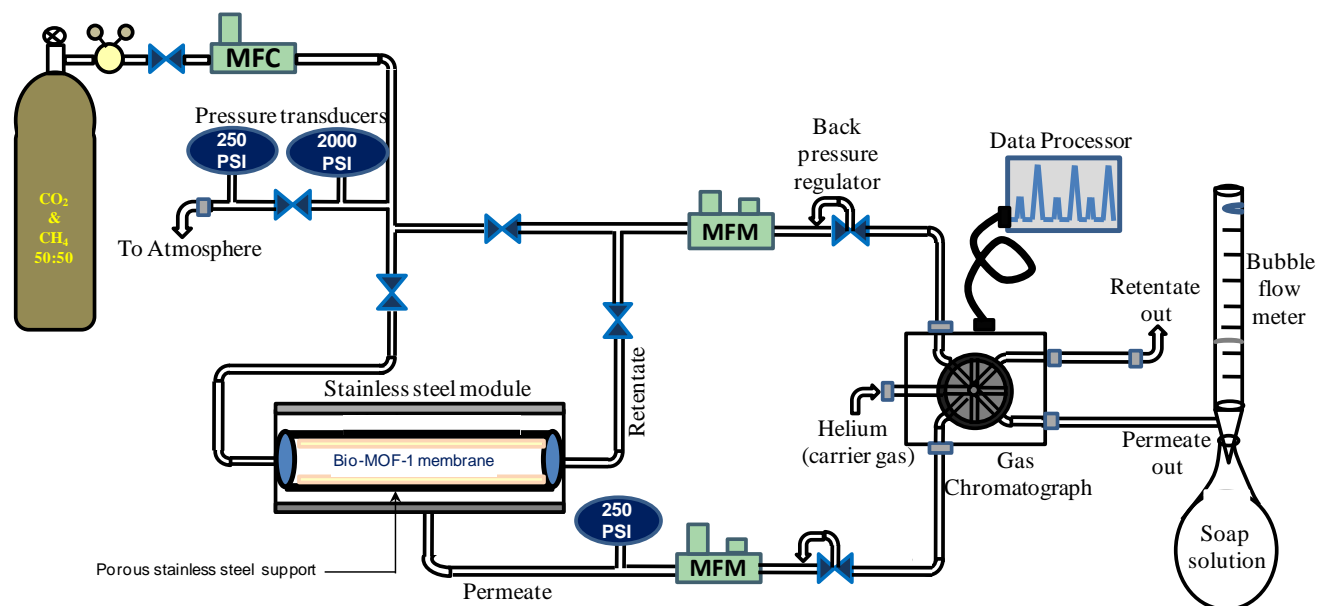
#### Characterization

The morphological features of Bio-MOF-1 crystals were inspected with a FE-SEM (FEI Nova 600) with an acceleration voltage of 6 kV. The crystalline structure was analyzed by XRD patterns collected on a Bruker D8 Discover diffractometer at 40 kV, 40mA with Cu K $\alpha$  radiation. The surface area and adsorption-desorption isotherm measurements were carried out on a Micromeritics Tristar 3000 porosimeter at 77 K using liquid nitrogen as coolant. Prior to the nitrogen adsorption experiments, the samples were degassed at 403K for 3 h. Adsorption

isotherms for CO<sub>2</sub> and CH<sub>4</sub> were measured at room temperature using water as the coolant. The quantitative analysis of elemental carbon, hydrogen, and nitrogen were carried out at Midwest Microlab, LLC (Indianapolis).

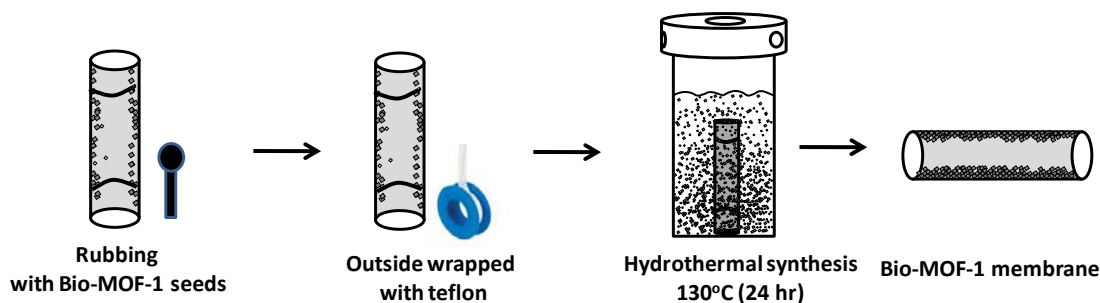
### CO<sub>2</sub>/CH<sub>4</sub> separation studies

The separation performance of the Bio-MOF-1 membranes for equimolar CO<sub>2</sub>/CH<sub>4</sub> gas mixture was measured in a separation system shown in Figure S1. The membranes were mounted in a stainless steel module with silicone O-rings as seals on both ends. The driving force across the membrane was provided by pressure drop. In all separation experiments, the pressure drop was 138 KPa and the permeate pressure was 99.5 KPa (atmospheric pressure). The gas flux was measured by a soap film bubble flow meter. The total feed flow rate was 100 mL/min. The compositions of the feed, retentate, and permeate streams were measured, after attaining the steady state, using a gas chromatograph (SRI instruments, 8610C) equipped with a thermal conductivity detector and HAYESEP-D packed column. The oven, injector and detector temperatures in the GC were kept at 65°C, 100°C and 150°C respectively.



**Figure S1.** Separation system used for CO<sub>2</sub>/CH<sub>4</sub> gas mixture separation experiments

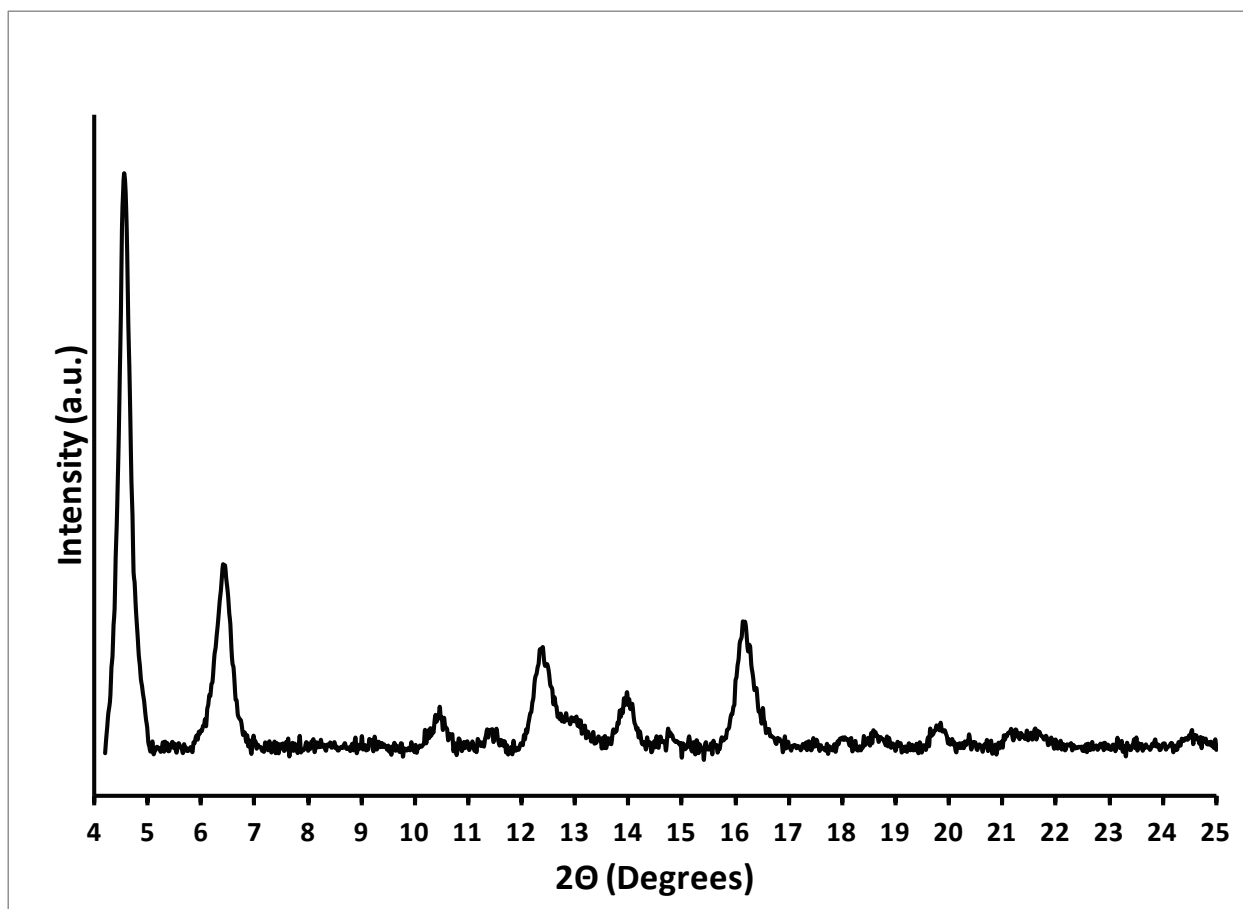
## Experimental procedure for Bio-MOF-1 membrane synthesis



**Figure S2.** Schematic showing the steps for the preparation of Bio-MOF-1 membranes

Figure S2 shows a schematic of the different steps employed to synthesize the Bio-MOF-1 membranes. In general, the membranes were synthesized by rubbing the inside surface of the porous stainless steel tubes with dry Bio-MOF-1 seeds using cotton swabs. Then, the rubbed porous supports, with their outside wrapped with Teflon tape, were then placed vertically in an autoclave and filled with synthesis gel. The hydrothermal treatment was carried out at 403 K for 24 h. The resulting membranes were gently washed with dimethyl formamide. Multiple layers (3,4 and 7) were applied following the same procedure. The membranes were dried and stored at 373K under Argon atmosphere prior to the separation tests.

For a membrane with pores in Knudsen diffusion range, the Knudsen diffusion selectivity is:  
 $(\text{molecular weight of CH}_4/\text{molecular weight of CO}_2)^{1/2} = 0.6.$



**Figure S3.** XRD pattern of Bio-MOF-1 membrane (M1)

The XRD of membrane M1 shown in Figure S4 corresponds to Bio-MOF-1 structure. The difference in peak intensity (between the main peak and secondary peaks) as compared to the XRD pattern of the seeds shown in Fig. 1a may indicate preferential orientation of the crystals, as confirmed in Figure 2b. This behavior has been observed in other MOF films: a) *J. Am. Chem. Soc.* 2010, 132, 76; b) *Chem. Commun.* 2008, 2441; c) *Eur. J. Inorg. Chem.* 2007, 60; d) *Chem. Mater.* 19, 2007, 2168.