# Supporting Information

# Alumina-supported cobalt-adeninate MOF membranes for $CO_2/CH_4$ separation

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## Experimental

N,N'-dimethylformamide (DMF) was dried over 3 Å molecular sieves for 1 day prior to use. Other chemicals were obtained via commercial sources and used directly without further purification. Preparation of cobalt butyrate and valerate salts is based on previous reported procedures (T. Li, D. Chen, J. E. Sullivan, M. T. Kozlowski and J. K. Johnson, *Chem. Sci.*, 2013, **4,** 1746).

## Synthesis of I seeds

Stock solutions of cobalt butyrate (0.05 M) and adenine (0.05 M) in dry DMF were prepared. To a Schlenk tube (40 mL) were added cobalt butyrate solution (9.0 mL; 0.45 mmol), and adenine solution (27.0 mL; 1.35 mmol). After the solution was frozen in liquid nitrogen and evacuated to 200 mTorr, it was heated in a 130 °C oven (24 h). Gray fine powder was collected, washed (dry DMF, 3X), and kept in fresh DMF.

## Synthesis of II seeds

Stock solutions of cobalt valerate (0.05 M) and adenine (0.05 M) in pre-dried DMF were prepared. To a Schlenk tube (40 mL) were added cobalt valerate solution (9.0 mL; 0.45 mmol), and adenine solution (27.0 mL; 1.35 mmol). After the solution was frozen in liquid nitrogen and evacuated to 200 mTorr, it was heated in a 130 °C oven (24 h). Gray fine powder was collected, washed (dry DMF, 3X), and kept in fresh DMF.

**Powder X-ray diffraction (PXRD)** patterns were collected using a Bruker AXS D8 Discover powder diffractometer equipped with a Cu Kα X-ray source at 40 kV, 40 mA. Scan speed and step size were set at 0.2 s per step and $0.02^{o}$ per step respectively. The samples were spread evenly on a glass slide and data were collected from $5^{o} < 2\theta < 45^{o}$.

## Scanning Electron Microscopy (SEM)

**I** and **II** seeds were loaded onto double-sided adhesive conductive carbon tape and sputtered with a layer of palladium. Scanning electron microscopy (SEM) images were taken using a Philips XL-30 field emission scanning electron microscope under SE mode.

## $CO_2/CH_4$ separation studies

The separation performance of the **I** and **II** membranes for equimolar $CO_2/CH_4$ 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 $65^{o}C$, $100^{o}C$ and $150^{o}C$ respectively.

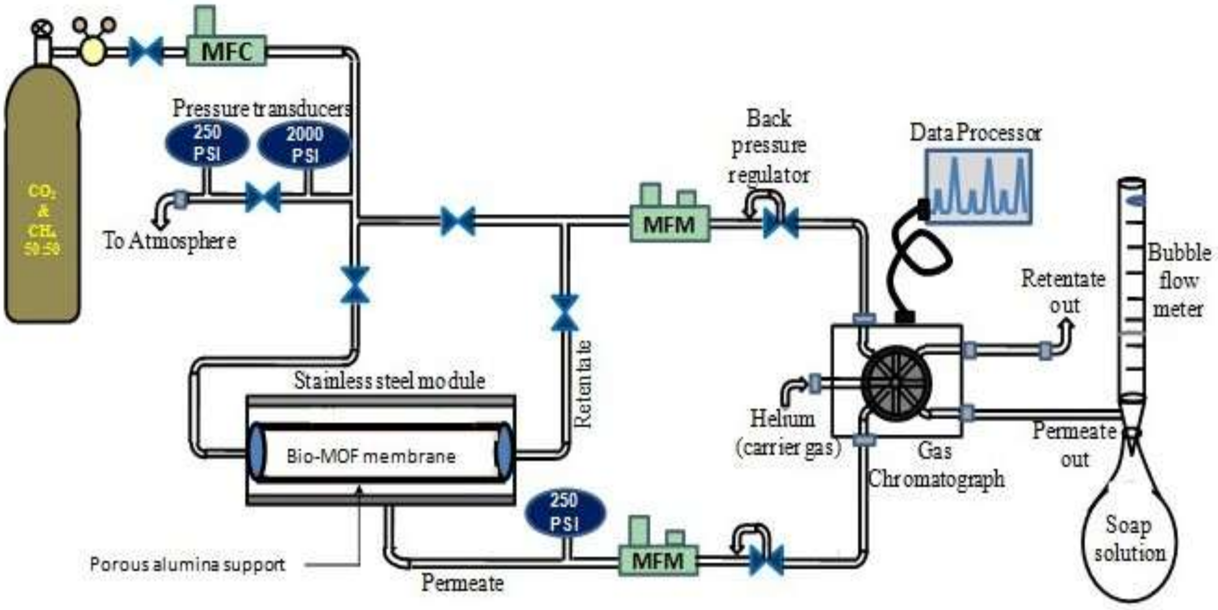

**Figure S1.** Separation system used for $CO_2/CH_4$ gas mixture separation experiments

## Experimental procedure for I and II membranes synthesis

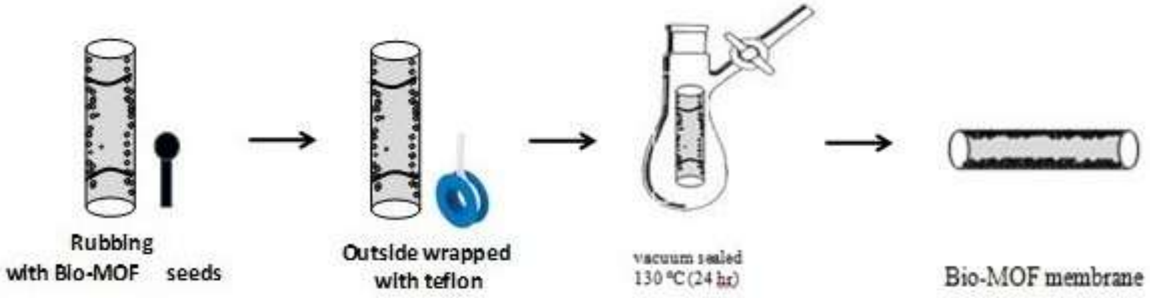

**Figure S2.** Schematic showing the steps for the preparation of **I** and **II** membranes

Figure S2 shows a schematic of the different steps employed to synthesize the **I** and **II** membranes. In general, the membranes were synthesized by rubbing the inside surface of the porous alumina tubes with dry **I** and **II** seeds using cotton swabs. Then, the rubbed porous supports, with their outside wrapped with Teflon tape, were then placed vertically in a Schlenk tube and filled with synthesis gel. It was then vacuum sealed and heated in 130 °C oven for 24 h. The Schlenk tube was allowed to cool down before open. The membranes were washed with dry dimethyl formamide. Multiple layers (5, 7) were applied following the same procedure. The membranes were dried and stored at 373K prior to the separation tests.

### Seeded alumina support

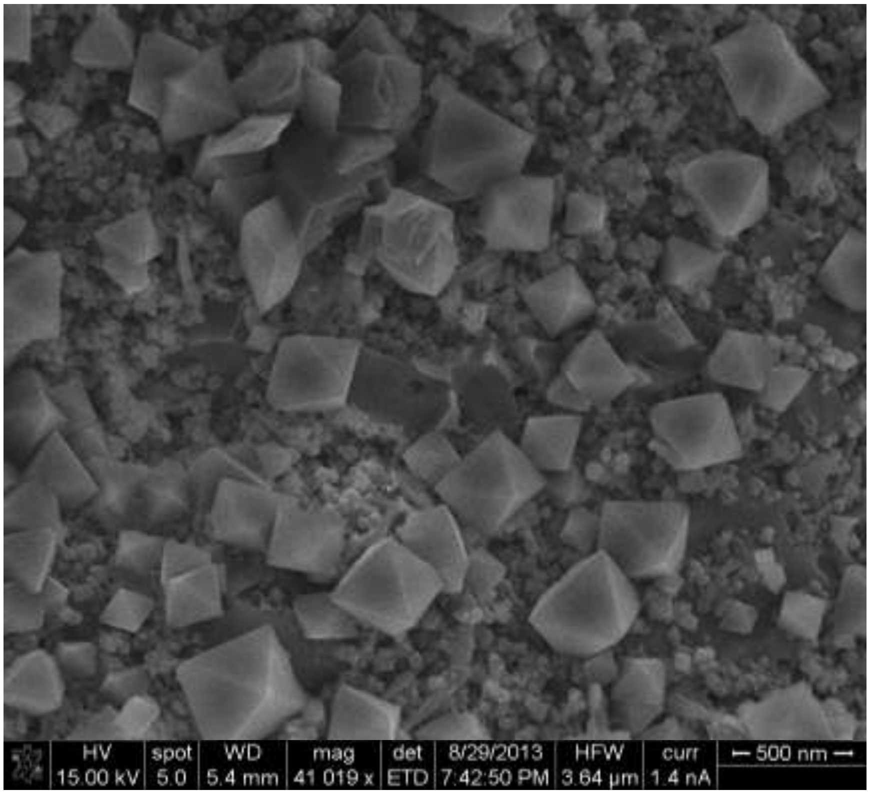

**Figure S3.** Representative SEM of a "seeded alumina porous support" with **II** crystals. This seeded support was used directly for the preparation of **II** membranes.

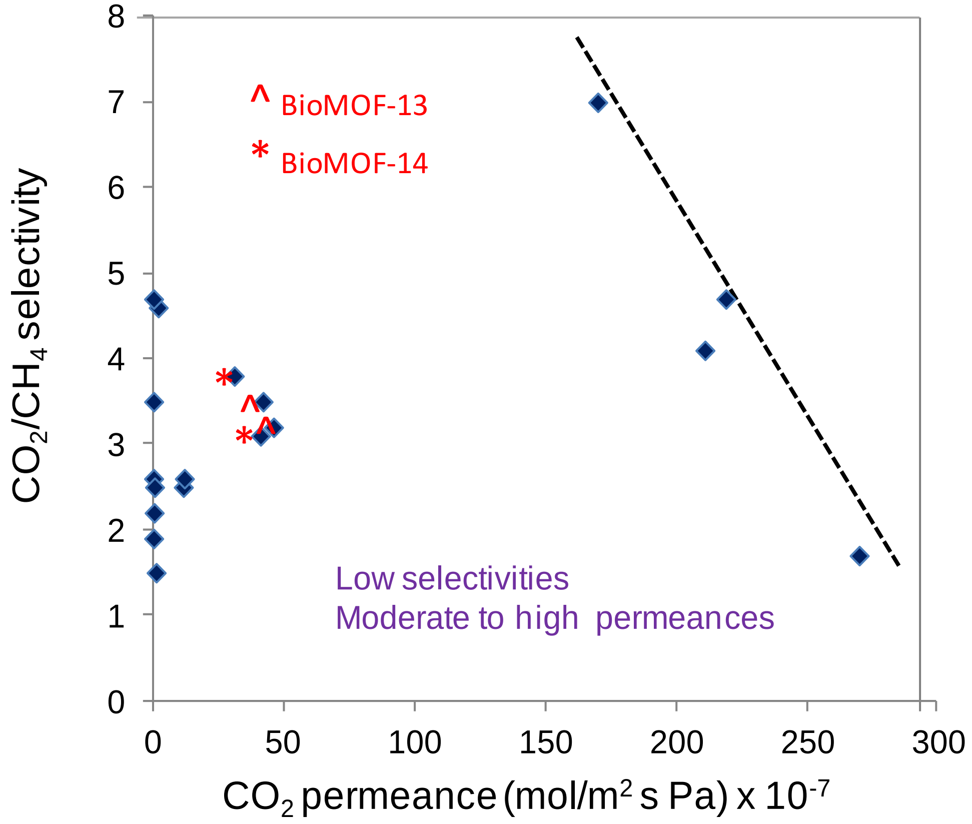

**Figure S4.** $CO_2/CH_4$ separation selectivies vs $CO_2$ permeances for MOF membranes. For comparison BioMOF-13 and BioMOF-14 membranes have been included.