Electronic Supplementary Information (ESI):

Highly permeable and selective amino-functionalized MOF CAU-1 membrane for CO$_2$/N$_2$ separation

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Materials

Chemicals were used as received: 2-amino-1,4-benzenedicarboxylic acid (H$_2$N-H$_2$BDC) (>99%, J&K Scientific Ltd.), Aluminium chloride hexahydrate (>99%, J&K Scientific Ltd.), Methanol, ethanol (>99%, Tianjin Kermel reagent Co., Ltd.). Asymmetric porous α-Al$_2$O$_3$ tubes with α-Al$_2$O$_3$ buffer layers of a nominal pore size of 200 nm and porosity of 30–35% (Foshan Ceramics Research Institute of China: 13mm o. d., 9mm i. d.) were used as supports.

Membrane Preparation

Preparation of CAU-1 seeds

The CAU-1 seeds were prepared by mixing AlCl$_3$·6H$_2$O (2.261 g, 9.36 mmol) and H$_2$N-H$_2$BDC (0.568 g, 3.14 mmol) dissolved in methanol (30 ml) followed by heating the resulting mixtures at 398 K for 5 h according to the recipe reported by the Stock et als.$^1$. After filtration, a yellow microcrystalline product was obtained. The as-synthesized product contains large amounts of chloride ions, which can be removed by stirring the CAU-1 microcrystalline three times in deionized water (2000 ml per 0.5 g CAU-1) 15 h. And stirring the CAU-1 crystal three times in methanol to removed H$_2$O for 15 h (2000 ml per 0.5 g CAU-1). The product was isolated and dried at 373 K in vacuum oven for 72 h.

Seeding the support using CAU-1 seeds

The hot dipping coating proposed in our previous work $^2$ was applied to deposit CAU-1 seeds onto the surface of the support. The preheated (373 K) tube with two ends sealed with Teflon plugs was dipped into well-dispersed 0.1 wt% CAU-1 seed methanol solution for about 20 seconds, and followed by drying at 373 K for overnight. The outer surface of the dried supports was rubbed carefully with cotton to remove the superfluous seeds that loosely packed on the surface. The seeding procedures were repeated to coat the well-dispersed 0.1 wt% CAU-1 seeds once more. Subsequently, the support was heated in an oven at 373 K to fix the CAU-1 seeds layer on the support.

Secondary synthesis of CAU-1 membrane

The CAU-1 membrane was prepared by the secondary solvothermal growth from a clear solution. The membrane synthesis solution was prepared by compounding AlCl$_3$·6H$_2$O (1.77 g, 7.32 mmol) and H$_2$N-H$_2$BDC (0.44 g, 2.42 mmol) dissolved in a total volume of 35 ml of methanol in ethanol mixture (1:2 v/v) using an ultrasonic
bath according to the previous report. The $\alpha$-Al$_2$O$_3$ tube was placed vertically in a Teflon-lined stainless steel autoclave which was filled with synthesis solution, and heated at 398 K in air oven for 12 hours. Considering the strong interaction of water molecule with amino group in CAU-1 pore wall that demanded high temperature to empty water molecules, after solvothermal reaction, the as-synthesized membrane was washed with methanol instead of water (2000 ml) five times for 45 hours under stirring to remove the chloride ions and occluded NH$_2$-H$_2$BDC linker until the chloride element was under Energy-dispersive X-ray spectroscopy (EDXS) detection as shown in Figure S6.

**Characterization**

Scanning electron microscopy (SEM) images and Energy-dispersive spectroscopy (EDS) of the CAU-1 crystals and membrane were taken with a NOVA NANO SEM 450 (FEI Company) microscope at an acceleration voltage of 20 kV and a working distance of 8-13 mm after gold coating. X-ray diffraction (XRD) patterns were collected on a Philips Analytical X-ray diffractometer using Cu Kα radiation (30 mA and 40 kV). The adsorption properties of the CAU-1 crystals collected from the membrane autoclave were carried out with an adsorption analyzer (MICROMERITICS INSTRUMENT CORP, ASAP-2020M) at different temperature.

**Permeation of single gas and separation of mixed gases**

The synthesized CAU-1 membrane still contained the guest molecules in its cavities. So before gas permeation test, the membrane was activated to remove occluded methanol by drying in vacuum oven at 323 K for 12 h, followed by flowing H$_2$ gas on stream in the permeation cell through the membrane at temperature 323 K until the H$_2$ flux was constant. The gas permeation properties of the CAU-1 membrane was investigated using gases of H$_2$ (0.289 nm), CO$_2$ (0.33 nm), CH$_4$ (0.38 nm), N$_2$ (0.364 nm) and SF$_6$ (0.55 nm) in a permeation set up as shown in Figure S1. The values in brackets are the kinetic diameters of the various gases, respectively. The membrane was placed in a home-made stainless steel module with a cylindrical geometry. Graphite was used as sealing between the membrane and the module. For the single gas measurements, the feed flow rates were set to 200 ml min$^{-1}$. The pressures at both of membrane sides were constant at 1 bar. For all the measurements of single and binary gas systems, Ar was used as sweep gas with volumetric flow rate of 200 ml min$^{-1}$. In the case of the mixed gas measurements feed flow rate was constant with a total volumetric flow rate of 200 ml min$^{-1}$. The pressures at the feed and permeate sides were both constant at 1 bar. Before the measurement of each gas species, the permeation apparatus was dried and purged with the respective gas to avoid the disturbance from previous gas and impurities (H$_2$O) permeation during measurements. The composition of feed and permeate streams were measured using GC9600 (SHIMAZU) gas chromatograph, equipped with GDX-501 and 5A molecular
sieve column. The permeance $P_i$ for the permeating gas $i$ is defined as:

$$P_i = \frac{N_i}{\Delta P_i \times A}$$

Where $N_i$ is the permeating flux of component $i$ (mol/s), $\Delta P_i$ is the transmembrane pressure difference of component $i$ (Pa), and $A$ is the membrane area (m$^2$). The separation factor $\alpha_{i,j}$ is defined as: the ratio of the molar fractions $Y$ of the component $i$ and $j$ in the permeate divided by the ratio of the molar fractions $X$ of $i$ and $j$ in the feed. Therefore, the separation factor for CO$_2$ can be calculated as:

$$\alpha_{CO_2,j} = \frac{Y_{CO_2}/Y_j}{X_{CO_2}/X_j}$$

**Fig. S1** Schematic diagram of the gas permeation apparatus.$^4$
Results and Discussions

Fig. S2 The crystal structure of CAU-1, the yellow and blue sphere illustrates the distorted octahedral and tetrahedral cages with effective diameters of approximately 1 nm and 0.5 nm formed by the brick \( \{ \text{Al}_8(\text{OH})_4(\text{OCH}_3)_8 \}^{12+} \) respectively, access to the cages is through small triangular windows with a free aperture of 0.3-0.4 nm.

Fig. S3 XRD patterns of CAU-1 seeds and membranes: simulated CAU-1 powder (a); CAU-1 seed used in this work (b); the CAU-1 seeded layer (c); the CAU-1 membrane (d)
Fig. S4 SEM images of CAU-1 seeds used in this work (a); the surface and cross-section of CAU-1 seeded layer (b, c); the surface and cross-section of α-Al₂O₃ support (d, e)

Fig. S5 Optical pictures of (1) α-Al₂O₃ tube; (2) CAU-1 seeded support; (3) the CAU-1 membrane on α-Al₂O₃ tube; (4) the outer diameter of α-Al₂O₃ tube; (5) the length of α-Al₂O₃ tube
Fig. S6 The elemental content analysis of the cross-section of CAU-1 membrane: the (a), (b), (c) is corresponding to the line of a, b, c of the SEM image

Fig. S7 CO₂, CH₄ and N₂ adsorption isotherms of CAU-1 powders collected from the membrane autoclave
<table>
<thead>
<tr>
<th>membrane</th>
<th>T(K)</th>
<th>V_{CO2}/V_{N2}</th>
<th>P_{CO2} (mol m^{-2}·s^{-1}·Pa^{-1})</th>
<th>α_{CO2/N2}</th>
<th>Separation Index^{[b]}</th>
<th>Ref.</th>
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<td>NaY</td>
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<td>1.5×10^{-6}</td>
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<td>1.5×10^{-7}</td>
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<td>0.80</td>
<td>[7]</td>
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<td>T</td>
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<td>5.5×10^{-8}</td>
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<td>SAPO-34</td>
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<tr>
<td>NH₂-SAPO-34</td>
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<td>50:50</td>
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<td>ZIF-7</td>
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<td>1^{[a]}</td>
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<td>[12]</td>
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<td>88:22(160kpa)</td>
<td>4.5×10^{-7}</td>
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<td>88:22(445kpa)</td>
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<td>70</td>
<td>3.45</td>
<td>[21]</td>
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<td>17.4</td>
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<td>22.82</td>
<td>2.84</td>
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^{[a]} Ideal separation factor. ^{[b]} \pi = (CO_2 permeance \times (selectivity - 1)) \times permeate pressure

**Table S2** Separation performances of CAU-1 membranes for the separation of CO₂/N₂ mixtures (1:1) at 298 K and 0.1 Mpa

<table>
<thead>
<tr>
<th>CAU-1 membrane</th>
<th>CO₂ permeance (mol/m²·s·Pa)</th>
<th>N₂ permeance (mol/m²·s·Pa)</th>
<th>Separation factor</th>
<th>Average separation factor</th>
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</thead>
<tbody>
<tr>
<td>M1</td>
<td>7.27×10^{-7}</td>
<td>3.59×10^{-8}</td>
<td>20.2</td>
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<tr>
<td>M2</td>
<td>7.38×10^{-7}</td>
<td>3.46×10^{-8}</td>
<td>21.3</td>
<td>20.5</td>
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<td>M3</td>
<td>7.21×10^{-7}</td>
<td>3.61×10^{-8}</td>
<td>20.0</td>
<td></td>
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</table>
Reference