Mixed-matrix membranes (MMMs) comprising polymer matrices and metal-organic frameworks (MOFs) provide efficient and economic CO₂ separation. One major challenge is to construct continuous and defect-free MMMs due to poor MOF/polymer compatibility. Here, this protocol describes the step-by-step details for synthesis of desired linkers that allow the fabrication of new polymerizable MOFs containing vinyl groups (BUCT MOFs) and the preparation procedures of defect-free MMMs with enhanced MOF/polymer interfacial adhesion and boosted gas separation performances.
Protocol

Synthesis and characterization of polymerizable MOFs for the preparation of MOF/polymer mixed matrix membranes

Ziman Chen,1,2,3,* Yahui Zhang,2 Qingmei Song,2 Liang Ma,1,2 and Yongqin Lv1,2,4,*

1Beijing Advanced Innovation Center for Soft Matter Science and Engineering, State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China
2Beijing Key Laboratory of Bioprocess, College of Life Science and Technology, Beijing University of Chemical Technology, No 15 North Third Ring East Road, Chaoyang District, Beijing 100029, China
3Technical contact
4Lead contact
*Correspondence: zmchen@mail.buct.edu.cn (Z.C.), lvyq@mail.buct.edu.cn (Y.L.)

https://doi.org/10.1016/j.xpro.2021.101039

SUMMARY

Mixed-matrix membranes (MMMs) comprising polymer matrices and metal-organic frameworks (MOFs) provide efficient and economic CO₂ separation. One major challenge is to construct continuous and defect-free MMMs due to poor MOF/polymer compatibility. Here, this protocol describes the step-by-step details for synthesis of desired linkers that allow the fabrication of new polymerizable MOFs containing vinyl groups (BUCT MOFs) and the preparation procedures of defect-free MMMs with enhanced MOF/polymer interfacial adhesion and boosted gas separation performances.

For complete details on the use and execution of this profile, please refer to Chen et al. (2021).

BEFORE YOU BEGIN

Gas separation has become a promising technology to alleviate the increasing level of greenhouse gas carbon dioxide (CO₂) (D’Alessandro et al., 2010). Compared with conventional separation techniques, the membrane-based separation has attracted extensive attention owing to their relatively low cost, good processability, and less energy consumption (Baker and Low, 2014; Bernardo et al., 2009; Brunetti et al., 2010; Javaid, 2005; Rezakazemi et al., 2014). Nevertheless, most of the polymer membranes are subjected to the “trade-off” effect between the selectivity and permeability. In this respect, researchers have developed the mixed matrix membranes (MMMs) which incorporated low-cost polymer matrix and organic/inorganic fillers to overcome this obstacle by synergistic action between the different components (Dechnik et al., 2017; Guo et al., 2019; Park et al., 2017). Metal-organic frameworks (MOFs), also known as porous coordination polymers (PCPs), are constructed by organic ligands and various metal ions. MOFs possess unique structural features, such as large specific surface area and tunable porosity. These abundant structural merits underpin their widespread applications in the gas separation field especially in the MMMs fabrication (Denny et al., 2016; Guo et al., 2021; Lin et al., 2014, 2018; Seoane et al., 2015; Shahid et al., 2015). However, one major issue was that the poor interfacial compatibility between MOF fillers and polymer matrices partly restrained the separation performance. Therefore, in this protocol, we report a synthetic strategy and characterization of polymerizable MOFs containing vinyl groups (named BUCT MOFs, BUCT=Beijing University of Chemical Technology) (Scheme 1), which allow preparation of defect-free MMMs with enhanced MOF/polymer interfacial adhesion and facilitated superior gas separation performances. At first, the desired linkers (linker 1
and linker 2) are synthesized from the starting material 2,5-dihydroxy-1,4-benzenedicarboxylic acid (compound 1), then the corresponding BUCT MOFs are prepared via the coordination of Zn-oxo clusters with organic linkers, afterward, the MOF/polymer MMMs are prepared by a simple thermally initiated free radical polymerization. Before one begins, the following preparations need to be carried out.

Preparation of solutions and reagents (for the synthesis of organic linker)

© Timing: 30 min

1. Preparation of stock solutions during step i in Scheme 1
   a. Prepare 400 mL saturated sodium hydrogen chloride (NaHCO₃) solution by adding 180 g NaHCO₃ into 400 mL deionized water. The stock solution should be stored at 4°C.
   b. Prepare 400 mL saturated sodium chloride (NaCl) solution by adding 50 g NaCl into 400 mL deionized water. The stock solution should be stored at 4°C.

2. Preparation of stock solutions during step ii in Scheme 1
   a. Prepare 30 mL 1.0 M hydrochloric acid (HCl) stock solution by adding 2.5 mL concentrated HCl into 27.5 mL deionized water. The stock solution should be stored at 4°C.
### KEY RESOURCES TABLE

| REAGENT or RESOURCE | SOURCE | IDENTIFIER |
|---------------------|--------|------------|
| **Chemicals**       |        |            |
| Anhydrous methanol (99.9%, SuperDry, with molecular sieves, water ≤ 30 ppm) | J&K Scientific Ltd (Beijing, China) | CAS: 67-56-1 |
| Thionyl chloride (SOCl₂) | Macklin (Shanghai, China) | CAS: 7719-09-7 |
| N,N'-dimethylformamide (DMF) | Fuchen Chemical Regent (Tianjin, China) | CAS: 68-12-2 |
| Hydrochloric acid (HCl) | Fuchen Chemical Regent (Tianjin, China) | CAS: 7647-01-0 |
| Ethanol (AR, 95%) | Aladdin (Shanghai, China) | CAS: 64-17-5 |
| Dichloromethane (CH₂Cl₂) (AR) | Macklin (Shanghai, China) | CAS: 75-09-2 |
| Sodium hydrogen chloride (NaHCO₃) (AR) | Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) | CAS: 144-55-8 |
| Sodium chloride (NaCl) (AR) | Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) | CAS: 7647-14-5 |
| Anhydrous sodium sulfate (Na₂SO₄) (AR) | Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) | CAS: 15124-09-1 |
| Sodium hydroxide (NaOH) (AR) | Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) | CAS: 1310-73-2 |
| Zinc nitrate hexahydrate (Zn(NO₃)₂ - 6H₂O) | J&K Scientific Ltd (Beijing, China) | CAS: 10196-18-6 |
| 4,4'-Bipyridine | J&K Scientific Ltd (Beijing, China) | CAS: 553-26-4 |
| Poly(ethylene glycol) methyl ether acrylate (PEGMEA) (Mₙ, 480 g/mol) | J&K Scientific Ltd (Beijing, China) | CAS: 32171-39-4 |
| Poly(ethylene glycol) diacrylate (PEGDA) (Mₙ, 700 g/mol) | J&K Scientific Ltd (Beijing, China) | CAS: 26570-48-9 |
| 2,5-Dihydroxy-1,4-benzenedicarboxylic acid | Sigma-Aldrich (St. Louis, USA) | CAS: 610-92-4 |
| 4-Vinylbenzyl chloride | Macklin (Shanghai, China) | CAS: 1592-20-7 |
| 2,2’-Azobis(2-methylpropionitrile) (AIBN) | Macklin (Shanghai, China) | CAS: 78-67-1 |
| 2-Mercaptoethanol | Macklin (Shanghai, China) | CAS: 60-24-2 |
| 8-Bromo-1-octene | Heowns (Tianjin, China) | CAS: 2695-48-9 |
| 1,8-Octanedithiol | ADAMAS-BETA (Shanghai, China) | CAS: 1191-62-4 |
| **Deposited data** |        |            |
| BUCT-1 crystal structure | This paper | CCDC number: 2053658 |
| BUCT-2 crystal structure | This paper | CCDC number: 2052358 |
| Original data | This paper | Mendeley Data: https://doi.org/10.1016/j.isci.2021.102560 |
| **Other** |        |            |
| Ultrasonic cleaning machine | Ningbo Xinzi Biotechnology Co., Ltd (Shanghai, China) | SB-3200D |
| Teflon reactor (100 mL) | Beijing Ke Hua Jing Wei Scientific Co., Ltd (Beijing, China) | N/A |
| Vacuum drying oven | Shanghai Bluepard Instruments Co., Ltd (Shanghai, China) | DZF-6050 |
| Rotary evaporator | Xi’an Heb Biotechnology Co., Ltd (Xi’an, China) | RE-3000E |
| Blast drying oven | Shanghai Bluepard Instruments Co., Ltd (Shanghai, China) | DHG-9070A |
| 400 MHz Bruker AVANCE III NMR spectrometer | Bruker | N/A |
| JEOL JSM-7610F field emission scanning electron microscope | Hitachi High-Technologies (Japan) | N/A |
| Spectrum One FTIR spectrometer | Perkin Elmer (USA) | N/A |
| Constant volume/variable pressure apparatus | Suzhou Xinwang Membrane Technology Co., Ltd (Suzhou, China) | FHM-PermCe |
| Gas Chromatograph | Beijing Beifen Ruli Analytical Instrument Co. Ltd (Beijing, China) | SP-3420A |
| Chromatography Column for GC | Beijing Femis Analysis Technology Co., Ltd (Beijing, China) | Porapak Q (2 m * 3 mm) |

**Optional:** The resources listed above were only based on our experience. In principle, the chemicals and resources can be obtained from any reliable commercial sources and do not need to be limited to those listed in our table.
MATERIALS AND EQUIPMENT

**Stock solution of saturated NaHCO₃ solution (storage: 4°C)**

| Reagent                  | Final concentration | Amount  |
|--------------------------|---------------------|---------|
| NaHCO₃                   | saturated           | 180 g   |
| Deionized water          | n/a                 | 400 mL  |
| Total                    | n/a                 | 400 mL  |

**Stock solution of saturated NaCl solution (storage: 4°C)**

| Reagent | Final concentration | Amount |
|---------|---------------------|--------|
| NaCl    | saturated           | 50 g   |
| Deionized water | n/a         | 400 mL |
| Total   | n/a                 | 400 mL |

**Stock solution of dilute hydrochloric acid (storage: 4°C)**

| Reagent                              | Final concentration | Amount  |
|--------------------------------------|---------------------|---------|
| Concentrated hydrochloric acid (12.0 M) | 1.0 M               | 2.5 mL  |
| Deionized water                      | n/a                 | 27.5 mL |
| Total                                | n/a                 | 30 mL   |

**Note:** The saturated NaHCO₃ and NaCl solutions can be stored at 4°C for one day.

**Stock solution of dilute hydrochloric acid (storage: 4°C)**

| Reagent                              | Final concentration | Amount  |
|--------------------------------------|---------------------|---------|
| Concentrated hydrochloric acid (12.0 M) | 1.0 M               | 2.5 mL  |
| Deionized water                      | n/a                 | 27.5 mL |
| Total                                | n/a                 | 30 mL   |

**Note:** The 1.0 M HCl can be stored at 4°C for one month.

### STEP-BY-STEP METHOD DETAILS

#### Synthesis of organic linker

- **Timing:** 3 days

The initial step for the synthesis of BUCT MOFs requires the preparation of organic linkers, and the following steps mainly include the synthesis of two organic linkers. For the synthesis of organic linker, the first step (Step i in Scheme 1) is preparation of the precursor compound 2,5-dihydroxy-1,4-benzenedicarboxylate (compound 2). The second step (Step ii in Scheme 1) contains the nucleophilic substitution reaction between the precursor compound and halides as well as the hydrolysis of the ester group.

1. **Synthesis of the precursor compound 2,5-dihydroxy-1,4-benzenedicarboxylate (Step i in Scheme 1) (Chen et al., 2021)**
   a. Weigh 5 g (25.2 mmol) 2,5-dihydroxy-1,4-benzenedicarboxylic acid on the analytical balance and put it into the 500 mL single neck round bottom flask. Add 300 mL anhydrous methanol and sonicate for 5 min at 25°C to dissolve completely by using the ultrasonic cleaning machine. Then place the flask on a magnetic stirrer for stirring in 600 rpm at 25°C.
   b. Measure 6.563 mL (11 g, 0.1 mol) thionyl chloride (SOCl₂) with pipette and then transfer it into the 25 mL constant pressure dropping funnel carefully. Afterward, add the SOCl₂ into the above-mentioned flask over a 30 min period.
   c. **CRITICAL:** SOCl₂ should be measured in the fume hood and transferred quickly to avoid the hydrolysis reaction with water in the air.
   d. Transfer the reaction flask into the magnetic hot plate with an oil bath, stir at 600 rpm, and reflux at 70°C for 8 h. Then let it cool to 25°C.
d. Remove methanol using rotary evaporation under 220 mbar vacuum at 50°C, and dissolve the obtained solid in 200 mL dichloromethane (CH₂Cl₂).

e. Wash the organic phase with saturated NaHCO₃ aqueous solution, saturated NaCl solution, and deionized water, respectively. Place the dichloromethane solution into a conical flask.

f. Add 10 g anhydrous sodium sulfate into the conical flask to dry the organic solution for 30 min. Then filter the mixture by using Buchner funnel to obtain clear organic phase solution.

g. Remove the CH₂Cl₂ using rotary evaporation under 700 mbar vacuum at 50°C to obtain pure product.

h. Analyze the product by ¹H NMR (400 MHz, CDCl₃, 298 K, ppm): δ 9.97 (s, 2H, OH), 7.38 (s, 2H, Ar–H), 3.89 (s, 6H, CH₃); ¹³C NMR (400 MHz, CDCl₃, 298 K, ppm): 169.47, 152.91, 118.32, 117.76, 52.78.

2. Synthesis of organic linker (Step ii in Scheme 1) (Chen et al., 2021)

a. Weigh 2 g (8.8 mmol) precursor compound (2,5-dihydroxy-1,4-benzenedicarboxylate) on the analytical balance and put it into the 250 mL single neck round bottom flask. Then add 100 mL DMF into the flask and sonicate at 25°C for 5 min to dissolve completely by using the ultrasonic cleaning machine.

b. For linker 1, weigh 2.834 g (18.6 mmol) vinylbenzyl chloride and 5.491 g (39.8 mmol) potassium carbonate (K₂CO₃) on the analytical balance and transfer them into the flask containing precursor compound. Add 100 mL N,N₀-dimethylformamide (DMF) and sonicate at 25°C for 5 min to dissolve completely. For linker 2, only need to replace the vinylbenzyl chloride with 8-bromo-1-octene (3.548 g, 18.6 mmol), and the following steps are the same as the synthesis for linker 1.

c. Place the flask on a magnetic hot plate for stirring at 600 rpm and heating the mixture to 85°C for 12 h in the oil bath.

d. Remove the DMF using rotary evaporation under 6 mbar vacuum at 60°C, then add 80 mL methanol into the flask.

e. Add 0.804 g sodium hydrate (NaOH) (20.1 mmol) and 20 mL deionized water into the flask.

f. Place the flask on a magnetic hot plate, stir at 600 rpm, and heat the mixture at 80°C for 6 h. Let it cool to 25°C.

g. Remove the solvent using rotary evaporation under 45 mbar vacuum at 50°C and add 100 mL deionized water into the flask.

**CRITICAL:** The aqueous solution should be transparent, if not, filter the solution through Buchner funnel to obtain clear solution.

h. Acidify the aqueous solution to pH 6.5 with 1.0 M HCl in the ice water bath, to precipitate a large amount of solid.

i. Filter the obtained solid and wash with 100 mL deionized water.

d. Dry the solid under vacuum (~0.1 MPa) at 85°C for 12 h in the vacuum drying oven.

k. Analyze the product by ¹H NMR (400 MHz, CDCl₃, 298 K, ppm), linker 1: δ 13.07 (s, 2H, OH), 7.42–7.51 (m, 12H, Ar–H), 6.75 (m, 2H, CH), 5.86 (d, 2H, CH₂), 5.44 (d, 2H, CH₂), 5.17 (s, 4H, CH₂) ppm; ¹³C NMR (400 MHz, DMSO-d₆, 298K, ppm): δ 166.69, 150.22, 136.64, 136.53, 136.30, 127.46, 126.09, 116.09, 114.35, 70.22. Linker 2: δ 12.94 (s, 2H, OH), 7.21 (s, 2H, Ar–H), 5.81 (m, 2H, CH), 4.98 (m, 4H, CH₂), 3.96 (m, 4H, CH₂), 2.03 (m, 4H, CH₂), 1.67 (m, 4H, CH₂), 1.44–1.31 (m, 12H, CH₂); ¹³C NMR (400 MHz, DMSO-d₆, 298K, ppm): δ 166.96, 150.37, 138.78, 125.90, 115.47, 114.61, 69.10, 33.07, 28.64, 28.21, 25.12.

**Note:** The column chromatography separation could be an alternative option for further purification of the final product in step 2j.

### Synthesis of BUCT MOFs

© Timing: 2 days
3. For BUCT-1, weigh 0.5 g (1.16 mmol) linker 1, 0.181 g (1.16 mmol) 4,4'-bipyridine and 0.345 g (1.16 mmol) Zn(NO₃)₂·6H₂O by using an analytical balance and put into a clean 100 mL beaker. For BUCT-2, only need to replace linker 1 with linker 2 (0.485 g, 1.16 mmol), and the following steps are the same as the synthesis of linker 1.

4. Add 80 mL DMF into the beaker and homogenize the mixture by sonication at 25°C for 5 min. Afterward, add 4 mL ethanol into the beaker.

5. Transfer the mixture solution into the 100 mL Teflon reactor.

6. Heat the Teflon reactor at 85°C for 48 h using blast drying oven.

7. Wash the obtained pale yellow crystals with DMF (5 × 8 mL) and ethanol (3 × 8 mL).

8. Activate the crystals via immersing them in 20 mL CH₂Cl₂ for 8 h and dry under vacuum (−0.1 MPa) at 120°C for 12 h.

**Synthesis of BUCT MOFs single crystal**

- **Timing:** 2 days

To confirm the specific coordination structure of BUCT MOFs, we synthesized single crystals of MOFs with high quality according to the following steps as below.

9. For BUCT-1, weigh 10 mg (0.023 mmol) linker 1, 3.6 mg (0.023 mmol) 4,4’-bipyridine and 6.9 mg (0.023 mmol) Zn(NO₃)₂·6H₂O carefully by using an analytical balance and put into the 1 dram glass vial.

10. Add 1 mL DMF into the glass vial.

11. Homogenize the solution by sonication at 25°C for 5 min. Afterward, add 0.05 mL ethanol into the glass vial and seal the cap.

12. Heat the glass vial to 120°C for 48 h using blast drying oven.

13. Select a suitable single crystal of BUCT MOF and analyze the structure using Agilent Xcalibur (Eos, Gemini) single crystal diffractometers.

**Synthesis of MOF/polymer MMMs**

- **Timing:** 4 h

After obtaining BUCT MOFs with high crystallinity, the BUCT MOF-based MMMs were constructed according to the following steps as below.

14. Weigh 350 mg poly(ethylene glycol) methyl ether acrylate (PEGMEA), 150 mg poly(ethylene glycol) diacylate (PEGDA), 5 mg azobisisobutyronitrile (AIBN), and 150 mg BUCT MOF, then put them into a 10 mL centrifuge tube.

15. Homogenize the mixture by sonication at 25°C for 3 min.

16. Degas the mixture solution by purging with nitrogen for 5 min.

17. Fill the solution into a mold made up of two glass plates (40 mm x 60 mm x 1.5 mm) clamped together and separated with two Teflon strips with the thickness of 70 μm. The mold was shown in Figure 1.

   a. Photo image of separated three parts of the mold for membrane preparation: clips, glass plate, and Teflon trip.
   b. Photo image of the whole mold in top view.
   c. Photo image of the whole mold in side view.

18. Heat the mold in the blast drying oven at 65°C for 2 h.

19. Incubate the mold in water for 30 min to detach the membrane from the glass plates.

20. Wash the membrane with ethanol and dried at 85°C for 1 h.
Characterizations of MOF/polymer MMMs

Timing: 6 h

After the successful preparation of flexible stand-alone MOF/polymer MMMs, scanning electron microscopy (SEM) and fourier-transform infrared spectroscopy (FTIR) characterizations were adopted to evaluate the interfacial interaction between BUCT MOFs and polymer matrices. (Figure 2) (Chen et al., 2021).

Gas transport measurement of MOF/polymer MMMs

Timing: 4 days

Gas separation performance of membranes was determined using method reported previously (Ma et al., 2018, 2019; Tin et al., 2003). In detail, the gas permeation parameters were measured using single gases (CO₂ and CH₄) at 0.5 MPa pressure difference and 35°C. The permeability and selectivity of membranes were measured using a custom built constant volume/variable pressure apparatus (Figure 3) and the PID (Proportional-Integral-Derivative) diagram was shown in Figure 4. The gas separation performance of MOF/polymer membranes was displayed in Figure 5.

Measurement of the single gas permeabilities

21. Cut a 1 x 1 cm² piece of membrane and put it on the membrane holder, then put the holder into the permeation cell. The thickness of membrane is 130 μm. The temperature of the whole measurement system is 308 K.
22. Turn off the valve C1, DS, and the one which connects to the gas cylinder. Turn on the valve C2, C3, C4, and US. Turn on the vacuum pump for 5 min until the pressure of PG is lower than –13.0 psi.
23. Turn off valve C3, and turn on valve DS and V1 for 5 min, until the pressure of PT is lower than 1.0 bar.
24. Turn on valve C3 to vacuumize the whole system, until the pressure of PT is lower than 0.05 bar. The duration vacuum time is 30 min for CO₂, 3 h for N₂.
25. Turn off valve C3 and US, and turn on the intake valve for 30 s, until the pressure of PG is about 75 psi.
26. Turn on valve C1 for 2 s, and then turn it off immediately. Repeat this operation eight times. Afterward, turn off C1 and V1, and turn on valve US.

27. Click the “Start” icon on the software to begin the measurement.

**Note:** All the measurements were conducted at 35°C with the pressure of gas collected in the upstream approaching 75 psi and keep it in a steady state.

**Measurement of the mixed gas permeabilities and selectivities**

For mixed gas permeation measurements, the receiving volume of the permeation cell was connected to a gas chromatograph (GC) by a valve (C5). All operations are the same as 1–6 steps, with minor difference in step 2. When turning on the valve DS and V1, also need to turn on the valve V3. The gas mixture contained 50% of CO2 and 50% of N2.

Permeability was determined from the rate of downstream pressure increase \( \frac{dp}{dt} \) using a custom-built constant volume/variable pressure instrument (Suzhou Faith & Hope Membrane Technology Co., Ltd.). The mixed gas steady-state permeation rate was calculated using the following equations (Ma et al., 2018; Tin et al., 2003):

\[
P_{CO_2} = \frac{273 \times 10^{10}}{760} \frac{y_{CO_2} VL}{AT} \left( \frac{26}{273} \right) \left( x_{CO_2} p_0 \right) \frac{dp_1}{dt}
\]

\[
P_{N_2} = \frac{273 \times 10^{10}}{760} \frac{1 - y_{CO_2} VL}{AT} \left( \frac{26}{273} \right) \left( 1 - x_{CO_2} \right) p_0 \frac{dp_1}{dt}
\]

---

**Figure 2. Characterizations of MOF/polymer MMMs**

(A) Photographs of BUCT-1 based MMMs (the MOF loading amount is 30 wt%).

(B) Scanning electron microscopy images of cross-sections of MOF/polymer MMMs.

(C) FTIR spectra of pristine BUCT MOFs, PEG monomers, and MOFs-based mixed matrix membranes.

Figure 2 reprinted with permission from Chen et al. (2021).
where $P$ is the permeability of the membrane to a specific gas (barrer), $V$ is the volume of the downstream chamber ($\text{cm}^3$), $L$ is the film thickness (cm), $p_1$ is the downstream permeate gas pressure (psi), $p_2$ is the upstream feed gas pressure (psi), $A$ is the effective area of the film ($\text{cm}^2$), $T$ is the experimental temperature (K), and $x_{CO_2}$ is the molar fraction of $CO_2$ in the feed gas (%). The separation factor for $CO_2$ to $N_2$ was calculated from the equation $\alpha = \frac{P_{CO_2}}{P_{N_2}}$.

**EXPECTED OUTCOMES**

This protocol allows for the synthesis of pillared-layer MOFs with polymerizable moieties using the "de novo" strategy. Compared with the reported post-synthetic modification (PSM) method (Albalad et al., 2018; Cohen, 2012, 2017; Garzón-Tovar et al., 2017; Morris et al., 2008; Yin et al., 2019), this strategy enables the formation of MOFs with highly accessible vinyl functionalities. At first, the functional organic ligand with vinyl groups was synthesized. After that, the vinyl-containing MOFs were prepared through the solvothermal method. NMR results verified the presence of vinyl groups in BUCT MOFs. The resulting mixed matrix membranes revealed superior MOF/polymer interfacial compatibility thanks to the high polymerizable reactivity of the double bonds in MOFs (Figure 4B). Moreover, these membranes exhibited significantly enhanced separation performances for $CO_2$/N$_2$ attributing to the improved MOF/polymer interface adhesion (Figure 5C).

**LIMITATIONS**

There are several limitations to this protocol. First, 2,5-dihydroxy-1,4-benzenedicarboxylic acid is not very stable as the starting material, and buy the small package of it and store it at 4°C as fresh as possible. It could be stable for one month under this storage condition. Second, for the step2a-2k in the Step-by-Step Method section, we directly perform the dialysis after the nucleophilic substitution reaction between the precursor compound and halides, this is not very precise and also might decrease the yield of final product. If possible, we would recommend to separate this process into two steps to obtain the intermediate product from nucleophilic substitution reaction. Third, for the preparation of MOF/polymer membranes, the grinding was required due to the big sizes of MOF samples which increased the workload and operation time. It is suggested to further optimize the reaction conditions to obtain MOF crystals with smaller sizes.

**TROUBLESHOOTING**

**Problem 1**

Low yield of precursor compound arising from the freshness and water sensitivity of SOCl$_2$ (step 1).
Potential solution
The SOCl₂ chemical was sensitive to water which would decrease the yield of precursor compound 2. In this regard, on one hand, the amount of SOCl₂ must be excessive. On the other hand, the constant pressure dropping funnel could be replaced with syringe injection to avoid contacting the air.

Problem 2
Low purity of the final precursor compound (step 1).

Potential solution
If the final obtained precursor compound after step 1 was not pure, one alternative operation is recrystallization.

Problem 3
Low purity of the organic linker after acidification (step 2).

Potential solution
Sometimes the final product of organic linker was not very pure after acidification, considering this, it is alternative to choose the column chromatography separation to purify the final product.

Problem 4
The obtained BUCT MOFs are not crystals (step 7).

Potential solution
If the obtained BUCT MOFs are not crystals or show poor crystallinity, one potential solution is adding small amount of acid such as acetic acid to slow down the coordination speed between organic linker and metal ion.

Problem 5
The outcome for the gas transport is different from the expected results in the Gas Transport Measurement of MOF/polymer MMMs section.

Figure 4. Schematic diagram of dense membrane mixed gas permeation test apparatus
Potential solution
If the outcome for the gas transport is different from the expected results, one possible reason might originate from the preparation procedure of MOF/polymer MMMs. For instance, sometimes the MOFs and polymer matrix does not mix very well, and it will cause the uneven thickness in the MMMs. In this regard, we should optimize the mixing time of MOF materials and polymer matrix to ensure the adequate mixing.

RESOURCE AVAILABILITY

Lead contact
Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Yongqin Lv (lvyq@mail.buct.edu.cn).

Materials availability
All reagents generated in this study are available from the lead contact.

Data and code availability
The published article includes all datasets/code generated or analyzed during this study. Original data have been deposited to Mendeley Data: https://doi.org/10.1016/j.isci.2021.102560.

ACKNOWLEDGMENTS
The authors gratefully acknowledge the financial supports from the National Natural Science Foundation of China (22122801, 31961133004) and National Key R & D Program of China (2018YFA0902200).

AUTHOR CONTRIBUTIONS
Y.L. conceived and designed the experiments; Z.C. and Q.S. synthesized the BUCT MOFs. Z.C. characterized the properties of BUCT MOFs; Y.Z. and L.M. prepared the mixed-matrix membranes and measured their gas separation performances; and Y.L. and Z.C. wrote the manuscript.

DECLARATION OF INTERESTS
The authors declare no competing interests.
Ding, R., Zheng, W., Yang, K., Dai, Y., Ruan, X., Yan, X., and He, G. (2020). Amino-functional ZIF-8 nanocrystals by microemulsion based mixed linker strategy and the enhanced CO2/N2 separation. Sep. Purif. Technol. 236, 116209. https://doi.org/10.1016/j.seppur.2019.116209.

Garzón-Tovar, L., Rodríguez-Hermida, S., Imaiz, I., and Maspol, D. (2017). Spray drying for making cova lent chemistry: postsynthetic modification of metal-organic frameworks. J. Am. Chem. Soc. 139, 897–903. https://doi.org/10.1021/jacs.6b05138.

Guo, X., Qiao, Z., Liu, D., and Zhong, C. (2019). Mixed-matrix membranes for CO2 separation: role of the third component. J. Mater. Chem. A. 7, 24738–24759. https://doi.org/10.1039/C9TA0912F.

Guo, Z., Liu, Z., Zhang, K., Wang, W., Pang, J., Li, Z., Kang, Z., and Zhao, D. (2021). Stable metal-organic frameworks based mixed matrix membranes for Ethylenebenzene/N2 separation. Chem. Eng. J. 416, 129193. https://doi.org/10.1016/j.cej.2021.129193.

Javid, A. (2005). Membranes for solubility-based gas separation applications. Chem. Eng. J. 112, 219–226. https://doi.org/10.1016/j.cej.2005.07.010.

Li, H., Tuo, L., Yang, K., Jeong, H.-K., Dai, Y., He, G., and Zhao, W. (2016). Simultaneous enhancement of mechanical properties and CO2 selectivity of ZIF-8 mixed matrix membranes: interfacial toughening effect of ionic liquid. J. Mater. Sci. 51, 130–142. https://doi.org/10.1007/s10853-015-9201-4.

Lin, R., Ge, L., Hou, L., Strounina, E., Rudolph, V., and Zhu, Z. (2014). Mixed matrix membranes with strengthened MOFs/polymer interfacial interaction and improved membrane performance. ACS Appl. Mater. Inter. 6, 5609–5618. https://doi.org/10.1021/acsami.2014.03260.

Ma, L., Svec, F., Li, Y., and Tan, T. (2019). In situ bottom-up growth of metal–organic frameworks in a crosslinked poly(electrolyte oxide) layer with ultrahigh loading and superior uniform distribution. J. Mater. Chem. A. 7, 20293–20301. https://doi.org/10.1039/C9TA05410D.

Ma, L., Svec, F., Tan, T., and Ly, V. (2018). Mixed matrix membrane based on cross-linked poly [electrolyte glycol] methacrylate and metal–organic framework for efficient separation of carbon dioxide and methane. ACS Appl. Nano Mater. 1, 2808–2818. https://doi.org/10.1021/acsanm.8b06493.

Morris, W., Doonan, C.J., Furukawa, H., Banerjee, R., and Yaghi, O.M. (2008). Crystals as molecules: post-synthesis covalent functionalization of zeolitic imidazolate frameworks. J. Am. Chem. Soc. 130, 12626–12627. https://doi.org/10.1021/ja805222q.

Nafisi, V., and Hág, M.-B. (2014). Development of dual layer of ZIF-8/PEBAX-2533 mixed matrix membrane for CO2 capture. J. Membr. Sci. 459, 244–255. https://doi.org/10.1016/j.memsci.2014.02.002.

Park, H.B., Kamcev, J., Robeson, L.M., Elimelech, M., and Freeman, B.D. (2017). Maximizing the right stuff: the trade-off between membrane permeability and selectivity. Science 356, eaab0530. https://doi.org/10.1126/science.aab0530.

Rezakazemi, M., Ebadi Amoooghian, A., Montazer-Rahmati, M.M., Ismail, A.F., and Matsuura, T. (2014). State-of-the-art membrane based CO2 separation using mixed matrix membranes (MMMs): an overview on current status and future directions. Prog. Polym. Sci. 39, 817–861. https://doi.org/10.1016/j.progpolymsci.2014.01.003.

Seoane, B., Coronas, J., Gascon, I., Benavides, M.E., Karvan, O., Caro, J., Kapteijn, F., and Gascon, J. (2015). Metal–organic framework based mixed matrix membranes: a solution for highly efficient CO2 capture? Chem. Soc. Rev. 44, 2421–2454. https://doi.org/10.1039/C4CS05043J.

Shahid, S., Nijmeijer, K., Nehache, S., Vankelecom, I., Deratani, A., and Quemener, D. (2015). MOF-mixed matrix membranes: precise dispersion of MOF particles with better compatibility via a particle fusion approach for enhanced gas separation properties. J. Membr. Sci. 492, 21–31. https://doi.org/10.1016/j.memsci.2015.05.015.

Song, Q., Nataraj, S.K., Roussevova, M.V., Tan, J.C., Hughes, D.J., Li, W., Bourgin, P., Alam, M.A., Cheeseam, A.K., Al-Muhtaseb, S.A., and Sivahanthi, E. (2012). Zeolitic imidazolate framework (ZIF-8) based polymer nanocomposite membranes for gas separation. Energy Environ. Sci. 5, 8359–8369. https://doi.org/10.1039/C2EE21964D.

Su, N.C., Sun, D.T., Beavers, C.M., Brit, D.K., Queen, W.L., and Urban, J.J. (2016). Enhanced permeation arising from dual transport pathways in hybrid polymer–MOF membranes. Energy Environ. Sci. 9, 922–931. https://doi.org/10.1039/C5EE06604A.

Tian, P., Zhang, T.S., Liu, Y., Wang, R., Liu, S.L., and Pramoda, K.P. (2003). Effects of cross-linking modification on gas separation performance of Matrimid membranes. J. Membr. Sci. 225, 77–90. https://doi.org/10.1016/S0376-7388(03)00805-5.

Xin, Q., Ouyang, J., Liu, T., Li, Z., Li, Z., Liu, Y., Wang, S., Wu, H., Jiang, Z., and Cao, X. (2015). Enhanced interfacial interaction and CO2 separation performance of mixed matrix membrane by incorporating polyethyleneimine-decorated metal–organic frameworks. ACS Appl. Mater. Inter. 7, 10665–10677. https://doi.org/10.1021/acsamat.10.071.

Yin, Z., Wan, S., Yang, J., Kurmoo, M., and Zeng, M.-H. (2019). Recent advances in post-synthetic modification of metal–organic frameworks: new types and tandem reactions. Coord. Chem. Rev. 378, 500–512. https://doi.org/10.1016/j.ccr.2017.11.015.