Membranes with outstanding performance that are applicable in harsh environments are needed to broaden the current range of organic dehydration applications using pervaporation. Here, well-intergrown UiO-66 metal-organic framework membranes fabricated on prestructured yttria-stabilized zirconia hollow fibers are reported via controlled solvothermal synthesis. On the basis of the adsorption–diffusion mechanism, the membranes provide a very high flux of up to ca. 6.0 kg m⁻² h⁻¹ and excellent separation factor (>45 000) for separating water from i-butanol (next-generation biofuel), furfural (promising biochemical), and tetrahydrofuran (typical organic). This performance, in terms of separation factor, is one to two orders of magnitude higher than that of commercially available polymeric and silica membranes with equivalent flux. It is comparable to the performance of commercial zeolite NaA membranes. Additionally, the membrane remains robust during a pervaporation stability test (≈300 h), including exposure to harsh environments (e.g., boiling benzene, boiling water, and sulfuric acid) where some commercial membranes (e.g., zeolite NaA membranes) cannot survive.

1. Introduction

Pervaporation, a membrane separation process based on the adsorption–diffusion mechanism,[1] has been considered as a promising energy-efficient technology for molecular-scale liquid/liquid separations.[2] Quite a few pervaporation membranes have been made commercially available for organic dehydration.[2a] However, new membrane materials that are able to provide enhanced performance and hold robustness in harsher conditions are still on demand to extend the current range of organic dehydration.

Metal-organic frameworks (MOFs) or porous coordination polymers have emerged as a family of porous crystalline materials composed of metal-containing units stitched together by organic ligands.[3] Their wide topological varieties and customizability in chemistry render MOFs as superior membrane materials for diverse potential applications.[4] Recently, a number of promising results have been reported in fabricating polycrystalline MOF membranes for gas separation.[5,6] Nevertheless, the investigation of these membranes for pervaporation is still in its infancy, particularly in systems involving water.[4,7] Expediting the development of MOF membranes in pervaporation is extremely challenging, as it may require novel qualified MOF materials and defect-free membranes need to be fabricated on porous substrates.

As a subfamily of MOFs, a series of chemical and thermally stable zirconium(IV) MOFs (Zr-MOFs) have been unveiled since 2008.[8] UiO-66 (UiO stands for University of Oslo) is a prototypical Zr-MOF, with a formula of Zr₆O₄(OH)₄(BDC)₆ (BDC = 1,4-benzene-dicarboxylate) and fcu topology (Figure 1a). Its aperture size is around 0.6 nm, as estimated from crystallographic data.[8a] This material possesses hydrophilic adsorption sites since plenty of hydroxyl groups are involved in its framework.[8b] Very recently, we developed UiO-66 membranes for water desalination.[9] The membranes exhibited high rejection for multivalent ions. However, its water flux is moderate. In this study, UiO-66 polycrystalline membranes with outstanding pervaporation performance were developed on prestructured substrates using controlled solvothermal synthesis. The membranes can effectively dehydrate biofuels (e.g., butanol), biochemicals (e.g., furfural), and other organics (e.g., tetrahydrofuran, THF) with excellent stability (Figure 1a).

2. Results and Discussion

2.1. Yttria-Stabilized Zirconia (YSZ) Hollow Fiber Substrates

Porous ceramic YSZ hollow fibers (HFs) were specially designed and used as substrates in virtue of their merits, which include high packing density, low transport resistance, easy scale-up, good mechanical strength, and outstanding chemical and thermal stability.[10] Since UiO-66 is constructed by zirconium clusters and BDC ligands,[8] another reason to employ this type of substrate is that they could possibly provide zirconium to chemically bond with BDC ligands (discussed below), thus promoting the.
heterogeneous nucleation of UiO-66. The HF geometry was carefully created via a combined phase inversion/sintering approach. As shown in Figure 1b–e, the as-synthesized HF is ≈1.1 mm in outer diameter. The wall with a thickness of around 200 µm contains three sponge-like layers sandwiching two layers of microchannels. The sponge layers contribute to mechanical strength enhancement and also provide relatively smooth surfaces (outer layer, pore size is around 80 nm) for depositing additional thin membrane layers, while the microchannel layers would reduce resistance for molecule permeation.

2.2. Formation and Characterization of UiO-66 Membranes

UiO-66 polycrystalline membranes were fabricated on the pre-structured YSZ HF by an in situ solvothermal approach via careful control of the heating duration, composition, and temperature of the synthetic mother solutions. A standard preparation recipe is given in the Experimental Section. To understand the membrane formation mechanism, scanning electron microscope (SEM), X-ray diffraction (XRD), and Fourier transform infrared-attenuated total reflection (FTIR-ATR) characterizations were conducted as shown in Figure 2. A schematic diagram is given in Figure S1 (Supporting Information). First, after 2 h of heating, a very thin amorphous gel layer was formed on the surface of the substrate, as confirmed by the SEM images (Figure 2a,b) and XRD patterns (Figure 2i and Figure S2 (Supporting Information)). This is possibly caused by the aggregation of gel particles formed in the mother solution, which were transported to the substrate due to Brownian motion and chemical interaction between the ligands and substrate (discussed below). During the consequent synthesis, heterogeneous nucleation occurred probably at the interface of the gel and the solution (Figure 2c,d), the only place where both the ligand and metal source were present in abundance. The diffraction peaks of UiO-66 crystals started to rise in the XRD pattern (Figure 2i and Figure S3 (Supporting Information)). Meanwhile, further gel settlement could still be proceeding, which buried and disturbed some of the UiO-66 nuclei (Figure 2c,d). After this nucleation period, crystals propagated through the gel network and then sank to the substrate (Figure 2e,f) by consuming the gel around them. The particle size of UiO-66 crystal is around 100 nm at this stage. This propagation process was followed by or parallel with the aggregation and densification of nanocrystals. With prolonged heating, crystal growth took place (Figure 2g–l) by acquisition of nutrients from bulk solution, from nearby unreacted amorphous gel and small UiO-66 crystals (Ostwald ripening). A well-intergrown membrane layer (Figure 2i–k) was finally formed after 48 h continuous heating after narrowing intercrystalline gaps (Figure 2g).

Since this membrane was prepared with simultaneous growth and nucleation, UiO-66 crystals emerging on the surface of membrane layer were identified in the SEM image (Figure 2k). As demonstrated by the XRD pattern (Figure 2i), a pure phase polycrystalline UiO-66 membrane with random orientation was fabricated. The UiO-66 grains are ≈0.3–0.8 µm in size with sharp edges (Figure 2i). The membrane thickness is ca. 1.0 µm (Figure 2j,k), which is only half of what was previously reported for a UiO-66 membrane, because the designed YSZ hollow fibers can not only provide relatively smooth surface but also promote the heterogeneous nucleation.

To verify whether chemical interactions between the ligands and substrate exist or not, FTIR-ATR characterization was carried out. Bare YSZ powders were prepared by grinding the
sintered YSZ HF and then dispersed in the same solution that was used for membrane fabrication without adding the zirconium source. After heating for 48 h at 120 °C, the powders were isolated and thoroughly rinsed and dried. As indicated in Figure 2m, the bare YSZ powders did not exhibit relevant absorption in the frequency range between 1350 and 1710 cm⁻¹, whereas in the case of BDC ligands, strong peaks were presented in virtue of the stretching vibration of carboxyl groups (1423 and 1674 cm⁻¹) and phenyl rings (1574 cm⁻¹). After the above treatment with BDC ligands, clear peaks appeared in the IR spectra of YSZ powders (Figure 2m, middle). Considerable blue/red shifts were observed corresponding to the stretching vibration of carboxyl groups (1440 and 1658 cm⁻¹) and phenyl rings (1593 cm⁻¹).[11] These data signify that chemical bonds were established between the ligands and substrate, probably between the carboxyl and zirconium. This chemical interaction provides an evidence to disclose the energy-dispersive X-ray spectroscopy (EDXS) mapping (Figure 2k). Although no visible UiO-66 crystals were recognized in the bulk substrate (Figure 2i), slight intrusion of the C signal (grey) into the substrate (Y signal, light grey) was detected. This might be due to the fact that the substrate was chemically modified by the BDC ligands during membrane preparation. The chemical interaction can enhance the adhesion of the membrane layer to the substrate to a large extent, and consequently the membrane stability is improved.

2.3. Separation Performance and Stability of UiO-66 Membranes

The synthesized membrane contained guest molecules within its cavities before activation. An on-stream pervaporation test (see the Experimental Section and Figure S4 (Supporting Information)) was conducted to empty the cavities and to monitor the activation process simultaneously. An n-butanol aqueous solution was applied (5.00 wt% water, 30 °C) as feed. At the early stage of activation, considerable n-butanol molecules could pass through the membrane together with water (Figure 3). This is understandable because the kinetic diameters of water (ca. 0.3 nm) and n-butanol (ca. 0.5 nm) molecules are smaller than the aperture of UiO-66 (around 0.6 nm). Following the activation, water concentration increased gradually in permeate because of the increase of water flux, although the total flux did not change obviously (Figure 3). After around a
24-hour continuous pervaporation test, water concentration in the permeate reached a plateau value of ≈99.60 wt% with a total flux around 1.20 kg m⁻² h⁻¹. It is suspected that the hydrophilic adsorption sites, i.e., hydroxyl groups, in the cavities were partly hindered by some guest molecules before activation. These guest molecules could be removed by passing through water and n-butanol molecules during activation process. Therefore, more hydrophilic adsorption sites were open and available to preferentially adsorb water against n-butanol molecules. This is why an enhancement of water flux and water/n-butanol selectivity was accomplished after activation.

After activation, a stability test of the membrane was carried out toward water/n-butanol and water/furfural solutions (5.00 wt% water in each solution, 30 °C). Butanol is a representative next-generation biofuel and furfural (furan-2-carbaldehyde) is a promising platform biochemical. Both of them can be commercially produced in water medium from biomass. As shown in Figure 3, benefiting from the excellent chemical stability of UiO-66 materials and good attachment of membrane layer to substrate, the membrane remained robust even after a treatment with boiling benzene and water. No discernible degradation of membrane performance was observed during the following test of more than 200 h. In both cases of water/n-butanol and water/furfural separations, the water concentration in permeate was equal or higher than 99.60 wt%. When the feed was switched from n-butanol to furfural aqueous solution, the total flux was increased to around 1.80 kg m⁻² h⁻¹. This is attributed to the enhanced chemical potential of water in the feed side (see the Experimental Section). In order to further check the membrane stability, H₂SO₄ was introduced to the feed (pH ≈ 2), which is a benchmark acid catalyst for producing biofurfural. The membrane kept robust even in this acid solution (Figure 3).

Apart from purifying n-butanol and furfural, the membrane performance was evaluated for separating water from other typical biofuels (e.g., i-butanol and ethanol) and organics (e.g., propanol, THF, and acetone) at elevated temperatures. As illustrated in Table 1 and Tables S1 and S2 (Supporting Information), the selectivity of water over organic molecules increased with the increase of organic kinetic diameters in virtue of the size-selective diffusion in the pervaporation process. The selectivity and water permeance changed with feed concentration and temperature (Table 1 and Table S1 (Supporting Information)); this indicates that water adsorption has limitations toward harsh conditions are restricted. Polymeric membranes (e.g., poly(vinyl alcohol)) have poor solvent stability and inorganic membranes (e.g., zeolite NaA) are unstable in the presence of acid or high water content feed. The above mentioned stability test data reveal that the newly developed UiO-66 membrane is capable of being used in harsh conditions, which may broaden the industrial applications of pervaporation.

Table 1. Pervaporation performance of UiO-66 membranes for separating water from typical biofuels, biochemicals, and organics based on duplicate experiments. The temperature of feed composition was set at 70 °C except for tetrahydrofuran (THF) and acetone aqueous solutions, where the temperature was 50 °C. It is outside detection by Ggs Chromatography (GC) when the concentration of organics is lower than 0.02 wt%.

| Feed [10.00 wt% water] | Total flux [kg m⁻² h⁻¹] | Water permeance [10⁻⁵ mol m⁻² s⁻¹ pa⁻¹] | Water con. in permeate [wt%] | Selectivity | Separation factor |
|------------------------|-------------------------|-------------------------------------------|-----------------------------|------------|-----------------|
| Water/ethanol          | 3.73 ± 0.12             | 3.62 ± 0.13                               | 86.12 ± 0.20                | 68.0 ± 1.2 | 55.8 ± 1.0      |
| Water/n-propanol       | 4.65 ± 0.10             | 3.73 ± 0.09                               | 97.40 ± 0.23                | 168 ± 17   | 337 ± 30        |
| Water/i-propanol       | 4.62 ± 0.09             | 3.75 ± 0.07                               | 98.71 ± 0.11                | 641 ± 55   | 689 ± 55        |
| Water/n-butanol        | 5.38 ± 0.12             | 3.50 ± 0.08                               | 99.79 ± 0.02                | 835 ± 81   | 4280 ± 470      |
| Water/i-butanol        | 4.81 ± 0.11             | 3.13 ± 0.07                               | >99.98                      | >13 400    | >45 000         |
| Water/furfural         | 5.95 ± 0.08             | 3.08 ± 0.04                               | >99.98                      | >2360      | >45 000         |
| Water/THF              | 4.06 ± 0.11             | 7.29 ± 0.20                               | >99.98                      | >99 000    | >45 000         |
| Water/acetone          | 3.99 ± 0.12             | 7.26 ± 0.22                               | 99.45 ± 0.03                | 4760 ± 260 | 1630 ± 90       |

*The water permeance increased when THF and acetone solutions were employed as feed because the adsorption of water was enhanced when the temperature decreased.*
an influence on the membrane performance to some extent, which verified the hypothesis proposed in the above activation process.

The membranes developed in this work exhibit a very high performance for separating water from i-butanol, furfural, and THF in terms of an ultrahigh separation factor (>45 000) and appealing flux of up to ca. 6.0 kg m\(^{-2}\) h\(^{-1}\) based on duplicate experiments (Table 1). These results prove that the as-synthesized polycrystalline membranes were well-intergrown and the membrane fabrication method is reproducible. The membrane performance, in terms of separation factor, is one to two orders of magnitude higher than that of commercially available polymeric and silica membranes with equivalent flux (Table S3, Supporting Information).\(^{15a,b}\) It is comparable to the performance of commercial zeolite NaA membranes.\(^{15c}\) The excellent stability together with outstanding membrane performance recommend UiO-66 to be a novel hydrophilic pervaporation membrane, which may potentially widen the current application range of commercial membranes. The high water concentration in permeate remained, even when the concentration and temperature of feed solutions were modulated (Figure 4b,c). Due to the enhanced chemical potential of water molecules, the total flux goes up with the increase of temperature and water concentration in feed solutions, although molecule diffusivity heavily relies on temperature.

### 3. Conclusion

In summary, a new type of membrane for organic dehydration was developed based on zirconium metal-organic frameworks. The as-synthesized UiO-66 membranes supported on prestructured YSZ hollow fibers provided excellent performance for purifying typical biofuels, biochemicals, and organics under harsh environments, which outperformed the commercially available membranes for pervaporation. The properties of Zr-MOFs, including high stability and tunable structures and functional groups, suggest that these types of material have great potential to be developed as next-generation pervaporation membranes.

### 4. Experimental Section

**Preparation of YSZ Hollow Fibers:** The YSZ hollow fibers were fabricated by a phase inversion combined sintering method.\(^{10}\) 120 g of YSZ powders (30–60 nm, 3 mol% yttria, Inframat Advanced Materials, LLC), 20 g of polyethersulfone (Radial A300, Ameco Performance, USA), and 1.0 g of dispersant (Arlacel P135, polyethylene glycol 30-dipolyhydroxystearate, Uniqema) were dispersed by ball milling in 80 g of dimethylsulfoxide (HPLC grade, VWR), to form a ceramic suspension with a high homogeneity and stability. After degassing, the resultant suspension was transferred to a metallic syringe and extruded through a tube-in-orifice spinneret (2.0 mm outer diameter, 1.0 mm inner diameter) to obtain the hollow fiber precursors in water bath with a dope (bore) flow rate of 5.0 mL min\(^{-1}\) (10 mL min\(^{-1}\)) and air gap of 2.0 cm. Then, the hollow fiber precursors were sintered at 1150 \(^{\circ}\)C to gain mechanical strength.

**Preparation of UiO-66 Membranes:** Controlled in situ solvothermal growth approach was employed to fabricate UiO-66 membranes on the prestructured YSZ hollow fibers (80 mm in length). The synthetic mother solution was prepared by dissolving 0.419 g of ZrCl\(_4\) (99.5%, Sigma-Aldrich), 0.299 g of BDC ligands (98%, Sigma-Aldrich), and 0.0320 g of deionized (DI) water (Analytic lab, AEX, Imperial College London) in 67.5 g of N,N-dimethylformamide (DMF, 99.8%, VWR) with the assistance of ultrasonic. Then, this clear solution was transferred
into a Teflon-lined stainless steel autoclave where a hollow fiber was placed vertically with both ends sealed to allow membrane growing on the outer surface. Afterward, the autoclave was placed in a convective oven and heated at 120 °C for 48 h. After cooling, the membrane was flushed with DMF and dried under ambient condition.

Characterizations: The SEM images coupled with EDXS were performed on a LEO Gemini 1525 instrument at an accelerating voltage of 5 and 20 kV, respectively. Panalytical Xpert XRD (using Cu Kr radiation, λ = 0.154 nm at 40 kV and 40 mA) was employed to analyze the crystalline structure of powders, membranes, and substrates. FTIR-ATR spectra were recorded on a spectrometer (Spectrum 100, PerkinElmer). The feed and permeate concentrations in the pervaporation test were measured by an off-line GC (GC 3900, Varian Inc.).

Pervaporation: The performance of the membranes was assessed via pervaporation test for separating water from organics (Figure S4, Supporting Information). Each time, 10 min was given to the system for stabilization before collecting samples. The pressure of the permeate side was kept at around 250 Pa. During the stability test, feed concentration was kept constant by compensating the loss of water to permeate. The total permeation rate (Equation (1)) was measured by weighing the condensed permeate

![Math formula](image)

where \( W \) refers to the weight of permeate (kg), \( A \) the membrane area (m²), \( t \) the duration (h) of the sample collection. The separation factor (Equation (2)) is defined as

![Math formula](image)

where \( X_{\text{water}} \) and \( Y_{\text{water}} \) denote the mass fraction of water in the feed and permeate sides, respectively. Membrane permeance (Equation (3)) is flux normalized by the chemical potential

![Math formula](image)

where \( J_i \) refers to the flux of permeate \( i \), \( p_i \) the chemical potential of component \( i \). The chemical potential was simulated using the computer program CHEMCAD. The selectivity (Equation (4)) is defined as

![Math formula](image)

where \( P_{\text{water}} \) and \( P_{\text{organic}} \) refer to the permeance of water and organic, respectively.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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