VAPOR/VAPOR-SOLID INTERFACIAL GROWTH OF COVALENT ORGANIC FRAMEWORK MEMBRANES ON ALUMINA HOLLOW FIBER FOR ADVANCED MOLECULAR SEPARATION

Field of Invention

The present invention generally relates to molecular separations, and more particularly relates to covalent organic framework membranes on alumina hollow fibers for separation of chemical species.

Background

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Chemical separations account for a substantial portion of industrial energy consumption, and there is a constant need for more efficient separation processes. Organic solvent nanofiltration (OSN) represents an energy-efficient process for small molecule separation in solvent mediums compared to conventional methods like distillation and liquid-liquid extraction. However, the dense and amorphous nature of the commonly used polymeric membranes poses challenges in terms of the permeance-selectivity "trade-off" and poor stability when exposed to organic solvents. Although a limited range of organic solvent-resistant membranes such as DuraMem™ (Evonik) and PuraMem™ (Evonik) were developed, it is difficult to find polymeric membranes that simultaneously possess the required permeability and selectivity. There are some limitations in using DuraMem™ (Evonik) and PuraMem™ (Evonik), including low permeability and the need for relatively elevated operating pressure to overcome the resistance posed by their small pore sizes. Hence, there is a critical need to develop membranes resistant to a wide range of solvents and enable the separation of small molecules while maintaining high permeability and selectivity.

Covalent organic frameworks (COFs) are a class of porous crystalline materials made up of organic molecules linked by covalent bonds, forming two-dimensional (2D) or three-dimensional (3D) networks with well-defined pores. In particular, 2D COFs have emerged as an attractive material for membrane separation application, as one-directional (1D) pore channels can be formed by stacking the COF layers and it offers high porosity and sieving ability at the same time. To date, interfacial polymerization (IP) has been successfully used to

fabricate COF membranes as self-standing flat sheets or attached on flat substrates, which, however, faces the limitations of upscaling and practical applications.

The development of crystalline COFs involves the formation of highly ordered, periodic structures through covalent bonds between the organic building blocks (monomers). It is influenced by various factors, including the choice of monomers, reaction conditions (temperature, time, and solvent), and the presence of a catalyst. The first step for the crystallization process of high-quality COFs is the selection of appropriate organic monomers containing reactive functional groups to form covalent bonds. The selected monomers are mixed in a suitable solvent and/or appropriate catalyst. The solvent choice affects the solubility of the monomers and the reaction kinetics.

The general mechanism for COF growth is (1) nucleation, (2) polymerization, (3) crystal growth and (4) activation. Nucleation involves the formation of small clusters of seed crystals from the precursor mixture. These clusters with the presence of reactive functional groups serve as a starting point for COF growth. The nucleation sites provide a framework for further polymerization. The functional groups on the monomer react with each other to form covalent bonds, assembled in an orderly structure, extending the polymer chains. This step is often thermally activated and the reaction conditions (i.e. temperature, concentration, and time) need to be carefully controlled to promote uniform growth. As the polymerization continues, the COF structure grows outwards from the nucleation sites resulting in a highly ordered two-dimensional (2D) lattice structure. For some liquid-based reactions, the as-synthesized COF may undergo activation steps such as thermal or chemical treatments (i.e. solvent evaporation or washing), to remove the starting precursors. Translating this mechanism into synthesizing high-quality, crystalline, thin-film COF membranes is challenging due to the constraints of the solid substrate and the need for precise control over the reaction conditions.

Prior reports have engaged a vapor phase of either one of the two monomers or the solvent (and catalyst) for the growth of well-ordered COF membranes. However, the involvement of the liquid phase still poses great challenges for these strategies to be extended to curved and porous substrates (e.g. hollow fibers) simply because liquid does not spread evenly on such substrates.

Membrane fabrication is a complex and multidisciplinary field due to the influence of film's structure, thickness, crystallinity, and uniformity, consequently, affecting its performance and scale of production. A desirable membrane is simple to fabricate, with minimal defects, controlled film thickness, homogeneous, robust stability, and high throughput.

Many of 2D and 3D materials have shown promising membrane separation performance, but face big issues related to stability and durability under various operating conditions such as acidic, alkalic, solvent, and high-pressure systems.

Issues such as membrane fouling, chemical degradation, mechanical stability, and low resistance to harsh operating conditions can limit the lifespan and performance of membranes. Developing materials that can withstand demanding environments and exhibit long-term stability is crucial for practical applications.

Cost-effectiveness and commercial viability are also critical considerations for the widespread adoption of novel membranes. The availability and cost of materials, production techniques, and maintenance requirements impact the economic feasibility of implementing novel membrane technologies.

Most reported COF-layered membranes are flat-sheet membranes due to the ease of manufacturing and operations. However, in larger operations, hollow-fiber modules offer the highest membrane surface areas per unit volume due to their inherent compact design. Hollow-fiber membranes are well-suited for cross-flow filtration, where the feed solution flows tangentially across the membrane surface rather than directly through it. Cross-flow filtration helps prevent fouling and concentration polarization, enhancing the membrane's longevity and performance. Flat sheet membranes are typically used in dead-end or direct flow filtration, which can be more prone to fouling. Hollow-fiber membrane systems are relatively easy to scale up for industrial applications. Adding more fibers or modules can increase the processing capacity, making them adaptable to various production scales. Whilst, scaling up flat-sheet membrane systems can be more complex.

Hollow-fiber membranes can have two primary flow configurations: (1) inside-out; and (2) outside-in. Inside-out refers to the feed flowing through the inner lumen of the hollow fibers; outside-in flow, on the other hand, involves the flow of the feed solution on the outside surface of the fiber, with the permeate collected from the inner lumen. It has been reported that COF-layered membranes have grown on the external surface of tubular support membranes utilizing the outside-in configuration (Fan, H., *et al.*, *Angew. Chem. Int. Ed. Engl.* **2018**, *57*(15), 4083-4087). Inside-out configuration in NF is preferred over outside-in due to the following operation advantages: reduced fouling, easier to clean, reduced risk of abrasive wear, and better concentration polarization tolerance.

However, growth of COF on the inner lumen has generally been eschewed due to the current methods of synthesizing not being able to grow a consistent layer on a curved surface geometry. Current methods such as solvothermal, layer-by-layer assembly, and interfacial polymerization used for the synthesis of COF-based membranes are encumbered by complex reaction conditions, poor control over pore structure, and optimized to only flat-sheet membranes. Additionally, the confined space of the lumen limits accessibility making it difficult to achieve homogeneous nucleation and subsequently uniform COF deposition.

Therefore, to overcome at least one of the aforementioned problems, there exists a need for new COFs for separation of chemical species.

Summary of Invention

Aspects and embodiments of the invention are provided in the following numbered clauses.

1. A membrane suitable for separation of chemical species, the membrane comprising:
a ceramic substrate having a first surface and a second surface;
an anchoring chemical layer on the first surface of the ceramic substrate; and
a covalent organic framework (COF) layer on the anchoring chemical layer.

2. The membrane according to Clause 1, wherein the anchoring chemical layer is covalently bonded to the ceramic substrate and to the COF layer.

3. The membrane according to Clause 1 or Clause 2, wherein the anchoring chemical layer is a polymeric material having a plurality of amine groups and a plurality of hydroxyl groups, where:
at least some of the plurality of amine groups are covalently bonded to at least some of the COFs in the COF layer, optionally wherein the COF incorporates the plurality of amine groups within its structure; and
at least a portion of the oxygen atoms in the hydroxyl groups have reacted with the first surface of the ceramic substrate to provide covalent bonds between the anchoring chemical layer and the ceramic substrate.

4. The membrane according to any one of the preceding clauses, wherein the anchoring chemical layer is a polymeric material formed from a monomeric compound having an amine group and two hydroxyl groups on adjacent carbon atoms, optionally wherein the polymeric

material formed from a monomeric compound having an amine group and two hydroxyl groups on adjacent carbon atoms on an aromatic ring.

5. The membrane according to Clause 4, wherein the anchoring chemical layer is selected from one or more of the group consisting of a polydopamine, a poly-norepinephrine, and a poly-levodopa, optionally wherein anchoring chemical layer is a polydopamine.

6. The membrane according to any one of the preceding clauses, wherein the ceramic substrate is selected from one or more of a zirconia, a yttria-stabilised zirconia, a titania, a silica and an alumina.

7. The membrane according to Clause 6, wherein the ceramic substrate is an alumina.

8. The membrane according to any one of the preceding clauses, wherein the ceramic substrate is selected from a flat substrate, a hollow fiber substrate having one or more lumens running through it.

9. The membrane according to Clause 8, wherein the ceramic substrate is a hollow fiber substrate having one or more lumens running through it and the first surface is the surface of the lumen(s).

10. The membrane according to any one of the preceding clauses, wherein the COF is formed from a first organic monomer comprising a plurality of amine groups and a second organic monomer comprising a plurality of carbonyl groups (e.g. aldehyde groups).

11. The membrane according to Clause 10, wherein the first organic monomer is selected from one or more of the group consisting of ethylenediamine, 2,4-diaminopyridine, benzidine, 9,9-dimethyl-9*H*-fluorene-2,7-diamine, benzene-1,3,5-triamine, tris(4-aminophenyl)methane, 4,4',4''-(1,3,5-triazine-2,4,6-triyl)trianiline, and, more particularly, *para*-phenylenediamine (Pa), 2,5-dichlorobenzene-1,4-diamine (Pa2Cl), hydrazine (Hz), 3,5-diamino-1,2,4-triazole, melamine, optionally wherein the first monomer is Pa2Cl or, more particularly, Pa.

12. The membrane according to Clause 10 or Clause 11, wherein the second organic monomer is selected from one or more of the group consisting of terephthaldehyde, 2,5-dimethylbenzene-1,4-dicarbaldhyde, 4,4'-biphenyldicarboxaldehyde, glyoxal, succinaldehyde, 2,5-deoxy-denzene-1,4-dicarbaldehyde, and 1,1'biphenyl-3,4',5-tricarbaldehyde, 1,3,5-tris(4-

formylphenyl)benzene (TFP), more particularly, 1,3,5-triformylphloroglucinol (Tp), optionally wherein the second monomer is Tp.

13. The membrane according to any one of the preceding clauses, wherein the COF layer is formed from:

(a) 1,3,5-triformylphloroglucinol (Tp) and P-phenylenediamine (Pa) (TpPa);

(b) Tp and 2,5-dichlorobenzene-1,4-diamine (Pa2Cl) (TpPa2Cl); or

(c) Tp and hydrazine (Hz) (TpHz),

optionally wherein the COF layer is formed from TpPa2Cl or, more particularly, TpPa.

14. The membrane according to any one of the preceding clauses, wherein the COF layer has one or more of the following properties:

(ai) the COF layer is defect free;

(aii) the COF layer has a compact structure;

(aiii) the COF layer is crystalline in nature;

(aiv) the COF layer has a thickness of from 100 to 1,000 nm, such as from 120 to 500 nm; and

(av) an internal pore size of the COF is from 0.3 to 2 nm, such as from 0.5 to 1.8 nm, such as from 1 to 1.5 nm.

15. The membrane according to any one of the preceding clauses, wherein the membrane displays one or more of the following properties:

(bi) a water permeance of from 75 to 250 L m^{-2} h^{-1} bar^{-1}, such as from 100 to 150 L m^{-2} h^{-1} bar^{-1}, such as from about 120 to about 140 L m^{-2} h^{-1} bar^{-1};

(bii) an ethanol permeance of from 170 to 190 L m^{-2} h^{-1} bar^{-1};

(biii) a methanol permeance of from 200 to 220 L m^{-2} h^{-1} bar^{-1};

(biv) an acetone permeance of from 430 to 470 L m^{-2} h^{-1} bar^{-1};

(bv) an acetonitrile permeance of from 450 to 470 L m^{-2} h^{-1} bar^{-1};

(bvi) a dimethylformamide permeance of from 20 L m^{-2} h^{-1} bar^{-1};

(bvii) a dimethylsulfoxide permeance of from 10 to 30 L m^{-2} h^{-1} bar^{-1}, such as from 15 to 20 L m^{-2} h^{-1} bar^{-1};

(bviii) a molecular weight cut-off (MWCO) of from 200 to 1,000 Daltons, such as from 550 to 700 Daltons;

(bix) an operating temperature range up to about 350 °C; and

(bx) an operating pressure of from 1 to 100 bar, optionally wherein the operating pressure is from 1.5 to 10 bar, such as about 2 bar.

16. A method of forming a membrane suitable for separation of chemical species, the method comprising the steps of:

(a) providing a ceramic substrate having a first surface and a second surface that is coated on a first surface with an anchoring chemical layer; and

(b) subjecting the ceramic substrate to an interfacial chemical vapour deposition polymerization reaction for a period of time at a temperature to form a COF, by exposing the ceramic substrate to an environment comprising a first vapour stream comprising at least a first COF precursor monomer and a second vapour stream comprising at least a second COF precursor monomer, wherein the first and second COF monomers are deposited on the anchoring chemical layer and react to form a COF layer.

17. The method according to Clause 16, wherein step (b) is repeated from 1 to 10 further times.

18. The method according to Clause 16 or Clause 17, wherein the period of time is from 1 hour to 24 hours, such as from 3 hours to 10 hours, such as about 8 hours.

19. The method according to any one of Clauses 16 to 18, wherein the temperature of step (b) in Clause 16 is from 100 to 250 ºC, such as about 170 ºC.

20. The method according to any one of Clauses 16 to 19, wherein after step (b) of Clause 16, the anchoring chemical layer is covalent bonded to the ceramic substrate and to the COF layer.

21. The method according to any one of Clauses 16 to 20, wherein the anchoring chemical layer is a polymeric material having a plurality of amine groups suitable to form covalent bonds with the first COF precursor monomer and has a plurality of hydroxyl groups, where at least a portion of the oxygen atoms in the hydroxyl groups have reacted with the first surface of the ceramic substrate to provide covalent bonds between the anchoring chemical layer and the ceramic substrate.

22. The method according to any one of Clauses 16 to 21, wherein the ceramic substrate having a first surface and a second surface that is reacted on a first surface with an anchoring chemical layer precursor monomer material that comprises at least one amine group and at least one (e.g. 2) hydroxyl group to form the anchoring chemical layer by polymerisation of the anchoring chemical layer precursor monomer material and the formation of a plurality of

covalent bonds between the first surface of the ceramic substrate and the formed anchoring chemical layer.

23. The method according to Clause 22, wherein the anchoring chemical layer precursor monomer material is selected from one or more of the group consisting of dopamine, norepinephrine, L-DOPA (Levodopa) with amine and catechol-like structures.

24. The method according to Clause 23, wherein the anchoring chemical layer is a polydopamine.

25. The method according to any one of Clauses 16 to 24, wherein the ceramic substrate is selected from one or more of a zirconia, a yttria-stabilised zirconia, a titania, a silica and an alumina, optionally wherein the ceramic substrate is an alumina.

26. The method according to any one of Clauses 16 to 25, wherein the ceramic substrate is selected from a flat substrate, a hollow fiber substrate having one or more lumens running through it.

27. The method according to Clause 26, wherein the ceramic substrate is a hollow fiber substrate having one or more lumens running through it and the first surface is the surface of the lumen(s).

28. The method according to any one of Clauses 16 to 27, wherein the first COF precursor monomer comprises a plurality of amine groups and the second COF precursor monomer comprises a plurality of carbonyl groups (e.g. aldehyde groups).

29. The method according to Clause 28, wherein the first COF precursor monomer is selected from one or more of the group consisting of ethylenediamine, 2,4-diaminopyridine, benzidine, 9,9-dimethyl-9*H*-fluorene-2,7-diamine, benzene-1,3,5-triamine, tris(4-aminophenyl)methane, 4,4',4''-(1,3,5-triazine-2,4,6-triyl)trianiline, and, more particularly, *para*-phenylenediamine (Pa), 2,5-dichlorobenzene-1,4-diamine (Pa2Cl), hydrazine (Hz), 3,5-diamino-1,2,4-triazole, and melamine, optionally wherein the first monomer is Pa2Cl or, more particularly, Pa.

30. The method according to Clause 28 or Clause 29, wherein the second COF precursor monomer is selected from one or more of the group consisting of terephthaldehyde, 2,5-dimethylbenzene-1,4-dicarbaldhyde, 4,4'-biphenyldicarboxaldehyde, glyoxal, succinaldehude,

2,5-deoxy-denzene-1,4-dicarbaldehyde, and 1,1'biphenyl-3,4',5-tricarbaldehyde, 1,3,5-tris(4-formylphenyl)benzene (TFP), more particularly, 1,3,5-triformylphloroglucinol (Tp), optionally wherein the second COF precursor monomer is Tp.

31. The method according to any one of Clauses 16 to 30, wherein:

(a) the first COF precursor monomer is P-phenylenediamine (Pa) and the second COF precursor monomer is 1,3,5-triformylphloroglucinol (Tp);

(b) the first COF precursor monomer is 2,5-dichlorobenzene-1,4-diamine (Pa2Cl) and the second COF precursor monomer is 1,3,5-triformylphloroglucinol (Tp);

(c) the first COF precursor monomer is hydrazine (Hz) and the second COF precursor monomer is 1,3,5-triformylphloroglucinol (Tp).

32. A method of using a membrane as described in any one of Clauses 1 to 15 in a process of separating a first organic compound from a second organic compound, the method comprising the steps of:

(a) providing a membrane as described in any one of Clauses 1 to 15;

(b) passing a first mixture comprising a first organic compound and a second compound that is organic or inorganic compound through the membrane using a suitable pressure to provide a second mixture comprising the first organic compound, with the second organic compound either being absent from the second mixture or is substantially reduced in amount.

33. A device to manufacture a membrane suitable for separation of chemical species, the device comprising:

a reaction chamber suitable for housing a ceramic membrane;

a first feed vessel fluidly connected to the reaction chamber;

a second feed vessel fluidly connected to the reaction chamber;

a first gas source connector fluidly connected to the first feed vessel; and

a second gas source connector fluidly connected to the second feed vessel, wherein the first and second feed vessels comprise a means or apparatus suitable to vaporise a monomeric material suitable to form a COF; and

the reaction chamber comprises a means or apparatus suitable to provide a temperature in the reaction chamber to maintain the monomeric material suitable to form a COF in a gaseous state, a means or apparatus suitable to purge the monomeric material suitable to form a COF from the reaction chamber, and a means or apparatus to remove said monomeric material from the reaction chamber, optionally the means or apparatus that to remove said monomeric material from the reaction chamber also recirculates it back into the reaction chamber.

Drawings

FIG. 1 depicts photo images of (a) polydopamine (PDA)-coated alumina hollow fiber, (b) the experimental setup of the vapor/vapor-solid (V/V-S) membrane synthesis method, and (c) COF-coated alumina hollow fiber.

FIG. 2 depicts (a) and (b) a schematic illustration of the fabrication of TpPa-1 COF membrane (1,3,5-triformylphloroglucinol, Tp and p-phenylenediamine, Pa as monomers) on PDA-modified aluminum hollow fiber substrate by a vapor/vapor-solid (V/V−S) interfacial growth method. Octanoic acid (OA) was used to dissolve the Tp and Pa monomers.

FIG. 3 depicts (a) attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) spectra Tp, Pa, TpPa-1/Alumina, PDA-modified alumina (curved), and (b) X-ray diffraction (XRD) patterns of TpPa-1/Alumina and PDA-modified alumina (flat alumina substrate was used for COF growth and characterization).

FIG. 4 depicts (a) cross-sectional SEM image of TpPa-1/Alumina, (b) energy dispersive X-ray spectroscopy (EDS) image of Al, O, N and C, and (c and d) top view SEM images of TpPa-1/Alumina (COF grown on alumina hollow fiber substrate).

FIG. 5 depicts (a) cross-sectional SEM image of pristine alumina hollow fiber substrate, (b) its corresponding EDS image of Al, O, N and C, and top view SEM images of (c) pristine and (d) PDA-modified alumina hollow fiber substrate.

FIG. 6 depicts scanning electron microscopy (SEM) images of TpPa-1/Alumina with different reaction time of (a, b, c) 12 h, (d, e, f) 24 h, and (g, h, i) 48 h at 170 °C.

FIG. 7 depicts (a)-(f) transmission electron microscopy (TEM) images of TpPa-1 COF scratched from the lumen of TpPa-1/Alumina (8 h, 170 °C).

FIG. 8 depicts (a)-(f) SEM images TpPa-1/Alumina obtained after 8 h reaction at 170 °C at the different inner surface locations of the hollow fiber substrate.

FIG. 9 depicts the effects of (a) reaction time (T = 170 °C, Tp and Pa concentration = 2 mg/mL) and (b) monomer concentrations (reaction time = 8 h, T = 170 °C) on water permeance and

CR rejection of TpPa-1/Alumina. The error bar shows the standard error of three sample collected in the test.

FIG. 10 depicts the effect of reaction temperature on water permeance and dye rejection of TpPa-1/Alumina with 8 h of growth duration and starting concentration of both monomers at 2 mg/mL. The error bar shows the standard error of three sample collected in the test.

FIG. 11 depicts organic solvent and aqueous nanofiltration performance, (a) molecular dye rejection of TpPa-1/Alumina in water, ethanol, and methanol, (b) permeance of protic and aprotic organic solvents through TpPa-1/Alumina versus the solvent properties, and (c) long-term stability test for separation of CR dye in methanol solution over 80 h. The error bar shows the standard error of three sample collected in the test. The error bar shows the standard error of three sample collected in the test.

FIG. 12 depicts long-term stability test for separation of Congo Red dye and sodium sulfate salt in aqueous solution over 100 h. The error bar shows the standard error of three sample collected in the test.

FIG. 13 depicts condensation of aldehyde and amine monomers for synthesis of TpPa2Cl and TpHz COFs.

FIG. 14 depicts characterization of TpPa-1, TpPa2Cl, and TpHz COF membranes grown alumina substrate by 3 cycles of V/V−S method, (a) XRD patterns (grown on the flat substrate), (b) ATR-FTIR spectra, (c) N 1s XPS peak and (d) Cl 2p XPS peak of TpPa2Cl.

FIG. 15 depicts XRD patterns of (a) TpPa-1/Alumina, (b) TpPa2Cl/Alumina and (c) TpHz/Alumina obtained by 1, 2 and 3 reaction cycles; comparison of XRD patterns with powdered (d) TpPa-1, (e) TpPa2Cl, and (f) TpHz COF and their corresponding simulated XRD patterns.

FIG. 16 depicts cross-sectional and top view SEM and EDS images of TpPa2Cl/Alumina obtained by 1 reaction cycle (a, d, g), 2 reaction cycles (b, e, h) and 3 reaction cycles (c, f, i).

FIG. 17 depicts cross-sectional and top view SEM and EDS images of TpPa-1/Alumina obtained by 1 reaction cycle (a, d, g), 2 reaction cycles (b, e, h), and 3 reaction cycles (c, f, i).

FIG. 18 depicts cross-sectional and top view SEM and EDS images of TpHz/Alumina obtained by 1 reaction cycle (a, d, g), 2 reaction cycles (b, e, h), and 3 reaction cycles (c, f, i).

FIG. 19 depicts organic solvent and aqueous nanofiltration performance of TpPa2Cl/Alumina obtained by 1, 2 and 3 reaction cycles: (a) molecular dye rejection in water, (b) permeance of pure water, acetone, ethanol, methanol and DMSO; Organic solvent and aqueous nanofiltration performance of TpHz/Alumina obtained by 1, 2 and 3 reaction cycles: (c) molecular dye rejection in water; (d) permeance of pure water; and (e) molecular structure of TpHz. The error bar shows the standard error of three sample collected in the test.

FIG. 20 depicts organic solvent and aqueous nanofiltration performance of TpPa-1/Alumina obtained by 1, 2 and 3 reaction cycles: (a) molecular dye rejection in water; and (b) permeance of water, acetone, ethanol, methanol and DMSO. The error bar shows the standard error of three sample collected in the test.

FIG. 21 depicts (a) organic solvent nanofiltration (OSN) performance of TpPa-1/Alumina and TpPa2Cl/Alumina obtained by 1, 2 and 3 reaction cycles for separation of GA from DMSO, and (b) performance comparison of our membranes with several polymeric polymers in the literature. The error bar shows the standard error of three sample collected in the test.

FIG. 22 depicts TpPa OSN solute performance with increasing thermal cycles.

FIG. 23 depicts a setup for COF fabrication.

FIG. 24 depicts monomers for COFs.

FIG. 25 depicts substrate recycling.

FIG. 26 depicts an inside out cross-flow filtration module.

FIG. 27 depicts uniform and compact coating with tunable COF layer thickness.

Description

It has been surprisingly found that the membranes disclosed herein enable separation of small molecules while maintaining high permeability and selectivity. Further, the methods disclosed herein may be used to grow crystalline and ordered COF membranes on targeted solid

surfaces including curved surfaces efficiently, are simple and do not require a vacuum condition which is necessary for chemical vapor deposition (CVD, a conventional method for making COF membranes).

Thus, in a first aspect of the invention, there is provided a membrane suitable for separation of chemical species, the membrane comprising:

a ceramic substrate having a first surface and a second surface;
an anchoring chemical layer on the first surface of the ceramic substrate; and
a covalent organic framework (COF) layer on the anchoring chemical layer.

In embodiments herein, the word "comprising" may be interpreted as requiring the features mentioned, but not limiting the presence of other features. Alternatively, the word "comprising" may also relate to the situation where only the components/features listed are intended to be present (e.g. the word "comprising" may be replaced by the phrases "consists of" or "consists essentially of"). It is explicitly contemplated that both the broader and narrower interpretations can be applied to all aspects and embodiments of the present invention. In other words, the word "comprising" and synonyms thereof may be replaced by the phrase "consisting of" or the phrase "consists essentially of" or synonyms thereof and *vice versa*.

The phrase, "consists essentially of" and its pseudonyms may be interpreted herein to refer to a material where minor impurities may be present. For example, the material may be greater than or equal to 90% pure, such as greater than 95% pure, such as greater than 97% pure, such as greater than 99% pure, such as greater than 99.9% pure, such as greater than 99.99% pure, such as greater than 99.999% pure, such as 100% pure.

As used herein, the singular forms "a," "an," and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a composition" includes mixtures of two or more such compositions, reference to "an oxygen carrier" includes mixtures of two or more such oxygen carriers, reference to "the catalyst" includes mixtures of two or more such catalysts, and the like.

When used herein, the term "a membrane suitable for separation of chemical species" refers to a membrane suitable for use in chemical separations.

When used herein, the term "an anchoring chemical layer" refers to a layer formed of a chemical that is capable of attaching to both the ceramic substrate and the covalent organic framework (COF) layer. Said anchoring chemical layer is sandwiched between the substrate

and the COF, thereby strongly attaching one to the other. This mode of attachment may be because the constituent component of the anchoring chemical layer is able to form covalent bonds to both the ceramic substrate and the COF layer.

When used herein, the term "covalent organic framework" (COF) refers to a porous two- or three-dimensional structure formed from organic building blocks. Covalent organic frameworks comprise pores, and the size and shape of the pores will depend on the organic blocks the COF is formed from.

It will be appreciated that the anchoring chemical layer may be coated on the first surface of the ceramic substrate and/or or chemically bonded to the first surface of the ceramic substrate, and the COF layer may be coated on the anchoring chemical layer and/or chemically bonded to the anchoring chemical layer.

In some embodiments of the present invention that may be mentioned herein, the anchoring chemical layer may be covalently bonded to the ceramic substrate and to the COF layer.

In some embodiments of the present invention that may be mentioned herein, the anchoring chemical layer may be a polymeric material having a plurality of amine groups and a plurality of hydroxyl groups. In such embodiments, at least some of the plurality of amine groups may be covalently bonded to at least some of the COFs in the COF layer. Without wishing to be bound by theory, the COF may incorporate the plurality of amine groups within its structure. In such embodiments, at least a portion of the oxygen atoms in the hydroxyl groups may have reacted with the first surface of the ceramic substrate to provide covalent bonds between the anchoring chemical layer and the ceramic substrate.

When used herein, the term "a polymeric material having a plurality of amine groups and a plurality of hydroxyl groups" refers to any suitable polymeric material that has more than one amine group and more than one hydroxyl group. As the skilled person will appreciate, the polymeric material may contain other components, additives and/or impurities.

In some embodiments of the present invention that may be mentioned herein, the anchoring chemical layer may be a polymeric material formed from a monomeric compound having an amine group and two hydroxyl groups on adjacent carbon atoms.

In some embodiments of the present invention that may be mentioned herein, the anchoring chemical layer may be a polymeric material formed from a monomeric compound having an amine group and two hydroxyl groups on adjacent carbon atoms on an aromatic ring.

As explained above, the anchoring chemical layer may be any suitable polymeric material that has more than one amine group and more than one hydroxyl group. For example, the anchoring chemical layer may be selected from one or more of the group consisting of a polydopamine, a poly-norepinephrine, and a poly-levodopa. In some embodiments of the present invention that may be mentioned herein, the anchoring chemical layer may be a polydopamine.

Any suitable ceramic substrate may be used. For example, the ceramic substrate may be selected from one or more of a zirconia, a yttria-stabilised zirconia, a titania, a silica and an alumina. In some embodiments of the present invention that may be mentioned herein, the ceramic substrate may be alumina.

The ceramic substrate may have any suitable configuration. For example, the ceramic substrate may be selected from a flat substrate, and a hollow fiber substrate having one or more lumens running through it. In some embodiments of the present invention that may be mentioned herein, the ceramic substrate may be a hollow fiber substrate having one or more lumens running through it and the first surface is the surface of the lumen(s). For example, the ceramic substrate may be a hollow fiber substrate having one or more lumens running through it and the first surface is the surface of the lumen(s), and has an inside-out configuration.

In some embodiments of the present invention that may be mentioned herein, the COF may be formed from a first organic monomer comprising a plurality of amine groups and a second organic monomer comprising a plurality of carbonyl groups. For example, the carbonyl groups may be aldehyde groups.

Any suitable organic monomer may be used as the first organic monomer. For example, the first organic monomer may be selected from one or more of the group consisting of ethylenediamine, 2,4-diaminopyridine, benzidine, 9,9-dimethyl-9*H*-fluorene-2,7-diamine, benzene-1,3,5-triamine, tris(4-aminophenyl)methane, 4,4',4''-(1,3,5-triazine-2,4,6-triyl)trianiline, and, more particularly, *para*-phenylenediamine (Pa), 2,5-dichlorobenzene-1,4-diamine (Pa2Cl) and hydrazine (Hz). In some embodiments of the present invention that may be mentioned herein, the first monomer may be Pa2Cl or, more particularly, Pa.

Any suitable organic monomer may be used as the second organic monomer. For example, the second organic monomer may be selected from one or more of the group consisting of terephthaldehyde, 2,5-dimethylbenzene-1,4-dicarbaldhyde, 4,4'-biphenyldicarboxaldehyde, glyoxal, succinaldehude, 2,5-deoxy-denzene-1,4-dicarbaldehyde, and, more particularly, 1,1'biphenyl-3,4',5-tricarbaldehyde1,3,5-triformylphloroglucinol (Tp). In some embodiments of the present invention that may be mentioned herein, the first monomer may be Tp.

For example, the COF layer may be formed from:

(a) 1,3,5-triformylphloroglucinol (Tp) and P-phenylenediamine (Pa) (TpPa);

(b) Tp and 2,5-dichlorobenzene-1,4-diamine (Pa2Cl) (TpPa2Cl); or

(c) Tp and hydrazine (Hz) (TpHz),

In some embodiments of the present invention that may be mentioned herein, the COF layer may be formed from TpPa2Cl. In some embodiments of the present invention that may be mentioned herein, the COF layer may be formed from TpPa.

In some embodiments of the present invention that may be mentioned herein, the COF layer may have one or more of the following properties:

(ai) the COF layer is defect free;

(aii) the COF layer has a compact structure;

(aiii) the COF layer is crystalline in nature;

(aiv) the COF layer has a thickness of from 100 to 1,000 nm, such as from 120 to 500 nm; and

(av) an internal pore size of the COF is from 0.3 to 2 nm, such as from 0.5 to 1.8 nm, such as from 1 to 1.5 nm.

The term "compact structure" is intended to mean that the COF layer is a dense layer with uniform thickness, which is distinctly different from a porous substrate with mesopores. This is a qualitative measurement, which may be seen using scanning electron microscope images and such uniformly thick and dense layers may be seen in Fig. 16a-f (cross-section images) of the application as filed.

The full width half maximum of the peak in a XRD pattern may be used to calculate crystallite size (i.e., crystallinity) by using Scherrer equation. The sharper the peak, the larger the crystallite size.

Scherrer equation:

$$D = 0.9\lambda/B\cos\theta,$$

where B is the full-width half maximum of the peak, θ is half of the diffraction angle, D is the crystallite size, and λ is the wavelength of X-ray.

With reference to FIG. 14, the peak at lower angle is diffraction by (100) lattice and the big hump is (001) lattice of COFs. The crystallinity in [100] direction (parallel to COF layer) is higher than that in [001] direction (perpendicular to the layer, or along the thickness of the membrane). Taking TpPa2Cl XRD curve (middle one in FIG. 14a), the crystallite size estimated in [100] and [001] direction using the Scherrer equation is around 6.8 and 0.6 nm, respectively. As such, the COF defined herein is crystalline.

In some embodiments of the present invention that may be mentioned herein, the membrane displays one or more of the following properties:

(bi) a water permeance of from 75 to 250 L m^{-2} h^{-1} bar^{-1}, such as from 100 to 150 L m^{-2} h^{-1} bar^{-1}, such as from about 120 to about 140 L m^{-2} h^{-1} bar^{-1};

(bii) an ethanol permeance of from 170 to 190 L m^{-2} h^{-1} bar^{-1};

(biii) a methanol permeance of from 200 to 220 L m^{-2} h^{-1} bar^{-1};

(biv) an acetone permeance of from 430 to 470 L m^{-2} h^{-1} bar^{-1};

(bv) an acetonitrile permeance of from 450 to 470 L m^{-2} h^{-1} bar^{-1};

(bvi) a dimethylformamide permeance of from 20 L m^{-2} h^{-1} bar^{-1};

(bvii) a dimethylsulfoxide permeance of from 10 to 30 L m^{-2} h^{-1} bar^{-1}, such as from 15 to 20 L m^{-2} h^{-1} bar^{-1};

(bviii) a molecular weight cut-off (MWCO) of from 200 to 1,000 Daltons, such as from 550 to 700 Daltons;

(bix) an operating temperature range up to about 350 ºC; and

(bx) an operating pressure of from 1 to 100 bar, optionally wherein the operating pressure is from 1.5 to 10 bar, such as about 2 bar.

It is noted that materials having such properties are unusual and unexpectedly good.

Details of the permeance and MWCO measurement techniques are provided in the examples section below.

In a second aspect of the invention, there is provided a method of forming a membrane suitable for separation of chemical species, the method comprising the steps of:

(a) providing a ceramic substrate having a first surface and a second surface that is coated on a first surface with an anchoring chemical layer; and

(b) subjecting the ceramic substrate to an interfacial chemical vapour deposition polymerization reaction for a period of time at a temperature to form a COF, by exposing the ceramic substrate to an environment comprising a first vapour stream comprising at least a first COF precursor monomer and a second vapour stream comprising at least a second COF precursor monomer, wherein the first and second COF monomers are deposited on the anchoring chemical layer and react to form a COF layer.

The first COF precursor monomer and the second COF precursor monomer may be mixed with a solvent before introducing them as the vapor precursors in the reaction vessel. Upon heating the reaction vessel, these precursors containing the monomers may be vaporized and transported through convective heat transfer. They may be deposited and reacted on the ceramic substrate surface. The precursor molecules may form initial clusters or nuclei on the ceramic substrate. These nuclei may serve as the starting point for COF thin-film growth. Once nucleation occurs, the precursor molecules on the ceramic substrate surface may begin to self-assemble, creating strong covalent bonds between the functional groups, leading to the growth of the solid COF structure. The thin film may expand from the nucleation sites, extending both laterally across the substrate and vertically (thickness), forming a layered structure. As the polymerization continues, the COF lattice structure emerges, and the covalent bonds between the building blocks may create a highly ordered, crystalline structure.

In some embodiments of the present invention that may be mentioned herein, step (b) may be repeated from 1 to 10 further times.

Without wishing to be bound by theory, the thickness of the membrane may be tuned from 100 to 500 nm by adjusting the number of reaction cycles accordingly.

In some embodiments of the present invention that may be mentioned herein, the period of time may be from 1 hour to 24 hours, such as from 1 hour to 10 hours, such as from 1 hour to 8 hours, such as from 1 hour to 3 hours, such as from 3 hours to 24 hours, such as from 3 hours to 10 hours, such as from 3 hours to 8 hours, such as from 8 hours to 24 hours, such as from 8 hours to 10 hours, such as from 10 hours to 24 hours, such as about 8 hours.

In some embodiments of the present invention that may be mentioned herein, the temperature of step (b) in the second aspect of the invention may be from 100 to 250 ºC, such as about 170 ºC.

In some embodiments of the present invention that may be mentioned herein, after step (b) of the second aspect of the invention, the anchoring chemical layer may be covalent bonded to the ceramic substrate layer and to the COF.

In some embodiments of the present invention that may be mentioned herein, the anchoring chemical layer may be a polymeric material having a plurality of amine groups suitable to form covalent bonds with the first COF precursor monomer and has a plurality of hydroxyl groups, where at least a portion of the oxygen atoms in the hydroxyl groups have reacted with the first surface of the ceramic substrate to provide covalent bonds between the anchoring chemical layer and the ceramic substrate.

In some embodiments of the present invention that may be mentioned herein, the ceramic membrane may have a first surface and a second surface that is reacted on a first surface with an anchoring chemical layer precursor monomer material that comprises at least one amine group and at least one (e.g. 2) hydroxyl group to form the anchoring chemical layer by polymerisation of the anchoring chemical layer precursor monomer material and the formation of a plurality of covalent bonds between the first surface of the ceramic substrate and the formed anchoring chemical layer.

Any suitable anchoring chemical layer precursor monomer material may be used. For example, the anchoring chemical layer precursor monomer material may be selected from one or more of the group consisting of dopamine, norepinephrine, L-DOPA (Levodopa) with amine and catechol-like structures.

The anchoring chemical layer and ceramic substrate of the second aspect of the invention are as discussed above.

In some embodiments of the present invention that may be mentioned herein, the first COF precursor monomer may comprise a plurality of amine groups and the second COF precursor monomer comprises a plurality of carbonyl groups. For example, the carbonyl groups may be aldehyde groups.

Any suitable COF precursor monomers may used as the first COF precursor monomer. For example, the first COF precursor monomer may be selected from one or more of the group consisting of ethylenediamine, 2,4-diaminopyridine, benzidine, 9,9-dimethyl-9H-fluorene-2,7-diamine, benzene-1,3,5-triamine, tris(4-aminophenyl)methane, 4,4',4''-(1,3,5-triazine-2,4,6-triyl)trianiline, and, more particularly, para-phenylenediamine (Pa), 2,5-dichlorobenzene-1,4-

diamine (Pa2Cl), hydrazine (Hz), 3,5-diamino-1,2,4-triazole, and melamine. In some embodiments of the present invention that may be mentioned herein, the first COF precursor monomer may be Pa2Cl. In some embodiments of the present invention that may be mentioned herein, the first COF precursor monomer may be Pa.

In some embodiments of the present invention that may be mentioned herein, the second COF precursor monomer may be selected from one or more of the group consisting of terephthaldehyde, 2,5-dimethylbenzene-1,4-dicarbaldhyde, 4,4'-biphenyldicarboxaldehyde, glyoxal, succinaldehude, 2,5-deoxy-denzene-1,4-dicarbaldehyde, and 1,1'biphenyl-3,4',5-tricarbaldehyde, 1,3,5-tris(4-formylphenyl)benzene (TFP), more particularly, 1,3,5-triformylphloroglucinol (Tp). In such embodiments of the present invention that may be mentioned herein, the second COF precursor monomer may be Tp.

In some embodiments of the present invention that may be mentioned herein,

(a) the first COF precursor monomer may be P-phenylenediamine (Pa) and the second COF precursor monomer may be 1,3,5-triformylphloroglucinol (Tp);

(b) the first COF precursor monomer may be 2,5-dichlorobenzene-1,4-diamine (Pa2Cl) and the second COF precursor monomer may be 1,3,5-triformylphloroglucinol (Tp);

(c) the first COF precursor monomer may be hydrazine (Hz) and the second COF precursor monomer may be 1,3,5-triformylphloroglucinol (Tp).

Without wishing to be bound by theory, the integration of PDA-modification with the V/V−S method may eliminate the necessity for casting or spin coating procedures. The dilute vapor precursors chemical reactions may overcome the limitation for uniformed stable growth on curved surfaces, showcasing exceptional solvent performance and robustness without encountering any delamination issues.

In a third aspect of the invention, there is provided a method of using a membrane as described in the first aspect of the invention, in a process of separating a first organic compound from a second compound that is organic or inorganic, the method comprising the steps of:

(a) providing a membrane as described in the first aspect of the invention;

(b) passing a first mixture comprising a first organic compound and a second organic compound through the membrane using a suitable pressure to provide a second mixture comprising the first organic compound, with the second organic compound either being absent from the second mixture or is substantially reduced in amount.

In some embodiments of the present invention that may be mentioned herein, the first organic compound and the second organic compound may be selected from one or more of Rose Bengal (RB), Congo Red (CR), Acid Fuchsin (AF), Naphtol Blue Black (NBB), Methyl Orange (MO) and glycyrrhizic acid (GA).

In some embodiments of the present invention that may be mentioned herein, the first mixture may comprise the first organic compound and the second compound in a solvent. The solvent may be a protic solvent (e.g. water, ethanol, methanol, and isopropanol), an aprotic solvent (e.g. acetonitrile, acetone, hexane, dimethylformamide, dimethylacetamide, and dimethyl sulfoxide), or combinations thereof. The second compound may be an organic compound having a different size to the first organic compound or solid particles of an inorganic compound (e.g. solid particles of NaCl, $NaHCO_3$ or the like) that have a different size to the first organic compound. The second compound may be larger than the pore size of the COF.

In a fourth aspect of the invention, there is provided a device to manufacture a membrane suitable for separation of chemical species, the device comprising:

a reaction chamber suitable for housing a ceramic membrane;

a first feed vessel fluidly connected to the reaction chamber;

a second feed vessel fluidly connected to the reaction chamber;

a first gas source connector fluidly connected to the first feed vessel; and

a second gas source connector fluidly connected to the second feed vessel, wherein the first and second feed vessels comprise a means or apparatus suitable to vaporise a monomeric material suitable to form a COF; and

the reaction chamber comprises a means or apparatus suitable to provide a temperature in the reaction chamber to maintain the monomeric material suitable to form a COF in a gaseous state, a means or apparatus suitable to purge the monomeric material suitable to form a COF from the reaction chamber, and a means or apparatus to remove said monomeric material from the reaction chamber , optionally the means or apparatus that to remove said monomeric material from the reaction chamber also recirculates it back into the reaction chamber.

FIG. 23 depicts the device according to the fourth aspect of the invention. The device 2300 includes an inert gas cylinder 2310, mass flow controller (MFC) 2320, a first glass pressure vessel 2330 containing a monomer 1 solution 2331 disposed in an oil bath 2332, a second glass pressure vessel 2340 containing a monomer 2 solution 2341 disposed in an oil bath 2342, a tube furnace 2350 including a hollow fiber tube 2351, a pressure regulating valve 2360, a back pressure regulator 2361, a condenser 2370, and check valves 2380.

As will be appreciated, the present invention may be more energy-efficient and sustainable compared with conventional pharmaceutical separation methods (e.g. distillation), may provide improved safety in handling flammable solvents and enhanced separation efficiency and performance, especially in harsh environments (such as in DMSO, etc.).

Certain aspects of the invention that may be mentioned herein relate to the following numbered statements.

1. A membrane, comprising:
   (a) a ceramic substrate;
   (b) a polydopamine layer on the ceramic substrate; and
   (c) 1,3,5-triformylphloroglucinol P-phenylenediamine (TpPa) covalent organic frameworks (COF) layer on the polydopamine.

2. A method to fabricate a membrane, comprising the steps of:
   (d) coating a hollow fiber alumina substrate with polydopamine (PDA) to introduce reactive functional groups (amines) on the lumen surface of the alumina hollow-fiber substrate;
   (e) placing the polydopamine-coated hollow fiber alumina substrate on top of the two vessels which separately contain 1,3,5-triformylphloroglucinol (Tp) precursor and a P-phenylenediamine (Pa) precursor dissolved in octanoic acid as the solvent; and
   (f) performing interfacial chemical vapor deposition polymerization with the 1,3,5-triformylphloroglucinol (Tp) and P-phenylenediamine (Pa) precursors by exposing the hollow fiber alumina substrate to the vapor of the monomers via convective mass transfer at 170 °C for 8 hours. They are deposited and reacted on the modified PDA substrate surface (lumen) with strong adhesion.

Thus, as disclosed herein a vapor/vapor-solid (V/V-S) method can be successfully used to fabricate continuous and crystalline COF membranes (e.g. of TpPa-1, TpPa2Cl and TpHz COF) on a ceramic substrate with an anchoring chemical layer (e.g. a PDA-modified alumina hollow fiber substrate). This simple, versatile and one-step method allows both precursor monomers to vaporize and react at the pre-functionalized surfaces, either flat or curved, thus overcoming the processing challenges involving liquids. As shown herein as an example, the resultant TpPa-1 membrane of around 100 nm in thickness grown on alumina hollow fiber exhibits high water, ethanol, and methanol permeance of 150, 170, and 200 L m−2 h−1 bar−1, respectively, and a MWCO of 700 Da in all three solvents. It also displays high stability over

80 h of continuous operation of OSN and dye rejection. By increasing the V/V-S reaction cycle from 1 to 2 and 3, thicker membranes of around 250 nm and 500 nm can be yielded for all three COFs. As demonstrated in the examples below, TpPa2Cl/Alumina exhibits a remarkable OSN performance for the separation of a model API, glycyrrhizic acid (GA), from DMSO. High GA rejection rates of 90%, 95%, and 98% and the corresponding DMSO permeance of 20, 18, and 15 L m−2 h−1 bar−1 were obtained for TpPa2Cl/Alumina fabricated with 1-3 cycles. Owing to the ability of the V/V-S method to grow COF rapidly on curved surfaces, this allows for large-scale COF membrane fabrication, thereby enabling more advanced separation to be used more often and therefore enables a more sustainable pharmaceutical industry.

Further aspects and embodiments of the invention will now be discussed by reference to the following non-limiting examples.

Examples

Materials

1,3,5-triformylphloroglucinol (Tp, 98 %), was purchased from Shanghai Ichemical Co. Ltd. p-phenylenediamine (Pa, 99 %), 2,5-dichlorobenzene-1,4-diamine (Pa2Cl, 97%), hydrazine hydrate (Hz, 50-60 %), dopamine hydrochloride (98%), tris (hydroxymethyl)aminomethane (99.8%), copper(II) sulfate (99%), hydrogen peroxide (97%), and organic dyes Rose Bengal (RB, 95%), Congo Red (CR 97%), Acid Fuchsin (AF, 70%), Naphtol Blue Black (NBB, 80%), Methyl Orange (MO, 85%) and glycyrrhizic acid (GA, 95%) were purchased from Sigma-Aldrich. Methanol (MeOH, 99.9%), ethanol (EtOH, 99.5%), isopropyl alcohol (IPA, 99.7%), Acetone (Ace, 99.5%), dimethylformamide (DMF 99.8%), dimethyl sulfoxide (DMSO, 99.7%), dimethylacetamide (DMAc, 99.8%), acetonitrile (MeCN, 99.9%), and octanoic acid (OA, 99.7 %) were all purchased from Sigma Aldrich. Deionized water (resistivity over 18 MΩ cm) was obtained from a Millipore Q water purification system. The hollow-fiber alumina substrates (2.8×4.3×300 mm; pore size: 40 nm) were purchased from Coorstek. All materials and chemicals used in this work were used as purchased.

Analytical techniques

X-ray diffraction (XRD)

The XRD patterns of the COF membranes grown on flat alumina substrate were measured using a D2 Bruker X-ray diffractometer with Cu Kα radiation (λ = 1.54 Å) at a scanning rate of 10 °/min, and accelerating voltage and current of 30 kV and 10 mA, respectively. Data was collected using a 0.05 ° 2θ step scan from 2-40 ° with an exposure time of 2 s per step.

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR)

FTIR spectra were measured using Shimadzu IRPrestige-21 equipped with an attenuated total reflection (ATR) accessory featuring a ZnSe crystal (Shimadzu AIM 8800). Measurements were taken with 45 scans at a resolution of 4 cm^{-1} in the range from 400 to 4000 cm^{-1}. CHNS elemental analysis was done on an Elementa, Vario EL Cube.

Field emission-scanning electron microscopy (FESEM)

FESEM images were obtained using JEOL FESEM (JSM-6710F) at 5 kV with energy dispersive X-ray spectroscopy (EDS) spectra taken on Aztec Standard X-Max80.

Transmission electron microscopy (TEM)

TEM analysis was performed on JEOL HRTEM (JEOL 3010).

X-ray photoelectron spectroscopy (XPS)

XPS was measured using a Kratos Axis Supra spectrophotometer equipped with a dual anode monochromatic Kα excitation source.

Example 1. Modification of alumina hollow fiber substrate by polydopamine (PDA)

The alumina hollow fiber substrates were first wrapped with polytetrafluoroethylene (PTFE) tape to prevent the coating of PDA on the exterior surface. A quick dynamic coating process using $CuSO_4/H_2O_2$ trigger (C. Zhang *et al.*, *Angew. Chem., Int. Ed.* **2016**, *55*, 3054–3057; and M. Zhang *et al.*, *J. Membr. Sci.* **2022**, *657*, 120673) was adopted by circulating the aqueous solution containing 2 g/L of dopamine hydrochloride and 50 mM of tris (hydroxymethyl)aminomethane, 1.4 g/L of copper(II) sulfate, and 0.4 g/L of hydrogen peroxide vigorously through the lumen of the hollow fibers for 2 h at room temperature. Upon modification, the color of the substrates was changed from colorless to brown (FIG. 1a), indicating polymerization of dopamine to PDA and deposition of PDA on the surface. The substrates were then rinsed repeatedly with DI water, dried at 60 °C in a vacuum oven overnight, and stored at room temperature before further use.

Characterisation

With a wide range of available COF materials, TpPa with its β-ketoenamine carbon-nitrogen double bond linkage was chosen due to its high chemical stability and small aperture size of around 1.8 nm. A dynamic coating process using $CuSO_4/H_2O_2$ trigger for dopamine polymerization (C. Zhang *et al.*, *Angew. Chem., Int. Ed.* **2016**, *55*, 3054–3057; and M. Zhang *et al.*, *J. Membr. Sci.* **2022**, *657*, 120673) was applied to deposit PDA on the inner surface of

the alumina hollow fiber before the synthesis of COF layer. This method has been proven simple, quick, and effective in coating PDA stably on many different substrates including ceramic hollow fiber.

As shown in FIG. 1a, the color of the alumina hollow fiber at the inner surface changes to brown in just 2 h at room temperature. The primary role of PDA is to introduce the amine ($-NH_2$) functional groups to form a linkage with the aldehyde monomer (Tp) through Schiff base reaction. This allows the subsequent formation of the COF membrane being strongly attached to the alumina substrate. In a controlled study using bare alumina hollow fiber, it was observed that only random particles were yielded under the same condition.

Example 2. Synthesis of powder TpPa2Cl COF by solvothermal method

TpPa2Cl COF in powder form was synthesized by the Schiff-based reaction. Tp (30 mg, 0.142 mmol) and Pa2Cl (96 mg, 0.543 mmol) were dissolved in OA (30 mL) as the solvent. The mixture was subjected to solvothermal treatment at 150 °C under continuous stirring for 72 h. The resulting COF precipitate was washed with dimethylacetamide (DMAc) and dried in the 80 °C vacuum oven before PXRD characterization.

Example 3. Growth of COF membranes on PDA-modified alumina hollow fiber substrate by V/V−S interfacial grown method

The V/V−S method is engineered to achieve the desired properties of scalable, excellent, thin-film COF membranes. The process begins with the preparation of the substrate onto which the thin-film COF is to be deposited. The surface modification using polydopamine (PDA) is utilized to introduce reactive functional groups (amines) into the alumina hollow-fiber substrate. The choice of modification can influence the resulting film's adhesion and stability. The individual monomers (Tp and Pa) are mixed with the selected solvent (OA) before introducing them as the vapor precursors in the reaction vessel. Upon heating the reaction vessel, these precursors containing the monomers are vaporized and transported through convective heat transfer. They are deposited and reacted on the modified PDA substrate surface. The precursor molecules form initial clusters or nuclei on the substrate. These nuclei serve as the starting point for COF thin-film growth. Once nucleation occurs, the precursor molecules on the substrate surface begin to self-assemble, creating strong covalent bonds between the functional groups, leading to the growth of the solid COF structure. The thin film expands from the nucleation sites, extending both laterally across the substrate and vertically (thickness), forming a layered structure. As the polymerization continues, the COF lattice structure

emerges, and the covalent bonds between the building blocks create a highly ordered, crystalline structure.

The monomers of the TpPa COF were first dissolved in two separated breakers, with 30 mg of Tp and Pa each (Tp:Pa molar ratio = 1:2) dissolved in 15 mL of OA by vigorous mixing. In a glass vessel, the PDA-modified membrane with its external surface wrapped with PTFE was placed on top of these two beakers containing the precursors. The vessel was covered with a silicon lid (FIG. 1b) and the entire setup was placed in an oven preheated at 170 °C for 8 h for one growth cycle. The Tp, Pa, and OA vapors were generated, assembled, and deposited on the lumen of the PDA-modified substrate. Upon the completion of the reaction, the membrane was washed with DMAc, ethanol, and methanol, dried in a 60 °C vacuum oven overnight, and stored at room temperature. The effects of several parameters were investigated including the reaction temperature, concentration of the precursors, reaction time, and no. of growth cycle.

Besides TpPa COF, two other COF membranes were also prepared with the same method by replacing Pa with Pa2Cl and Hz monomers. The molar ratio of Tp:Pa2Cl and Tp:Hz in the starting solutions was 1:3.8.

The balance between membrane stability, permeability, and rejection is often controlled by the thickness of the active layer. There is a trade-off between membrane thickness and permeability. Thicker membranes can hinder the diffusion of solutes through the material, which can reduce permeability. Thinner membranes may have stability issues and are prone to delamination, defects, and damage. To tune the membrane thickness, a thermal cycle approach was used for precise thickness control of the active COF layer. Repeating the V/V−S process with fresh monomers causes the COF growth onto the membrane substrate. With each additional cycle, the thickness of the COF active layer increases by 100-200 nm.

To increase the thickness of the COF membrane, the same substrate was also subjected to 2 times or 3 times the reaction cycle by using the fresh monomer solutions each time. The same experiment was performed using a porous flat alumina disk for characterization purposes.

As will be appreciated, the methods and COF membranes disclosed above may provide advantages such as smaller footprint size of the equipment, easier scaling up, less fouling and longer lifetime than conventional COF membranes, and recycling of ceramic substrates.

Characterisation

The experimental setup of the V/V−S synthesis is shown in FIG. 1b and 2. Tp and Pa monomers are dissolved in two separate beakers using OA as the solvent as well as the catalyst. At 170 °C in the oven, vapors of both monomers (V/V) are generated together with the solvent vapor. They are transported into the lumen of the fiber by natural convective mass transfer and deposited on the PDA-modified inner surface (S) of the hollow fiber. Such a simple V/V−S interface growth within as short as 8 h results in a TpPa-1 COF membrane as indicated by the reddish-brown color of the inner surface of the alumina hollow fiber (FIG. 1c). To confirm the formation of COF and analyze its structure, ATR-FTIR and XRD analyses were employed (FIG. 3). The analysis of COF grown on curved surfaces by XRD can be challenging. Therefore, COF deposited on a flat alumina substrate under the same reaction condition was used for XRD analysis. ATR-FTIR spectra (FIG. 3a) confirm the formation of COF from the observed C−N bond at 1258 cm^{-1} and C=C bond at 1585 cm^{-1}. The N−H stretching band of Pa monomer (3100–3370 cm^{-1}) and carbonyl stretching band of Tp monomer (1640 cm^{-1}) are not observed in TpPa-1/Alumina, indicating the monomer vapors react completely on the solid surface to form the COF structure. The XRD pattern (FIG. 3b) displays the characteristic (100) peak of TpPa-1 COF at around 4.7° and a broader peak at about 27° associated with the p-p interlayer stacking of (001) planes (C. A. Saiz *et al.*, *J. Membr. Sci.* **2018**, *546*, 120–127). The broad (001) peak is most likely due to the presence of only short-range orders in the membrane, which might be associated with the all-vapor and fast interfacial growth characteristics of the process. Nonetheless, the XRD result confirms that crystalline TpPa-1 structure is formed by the V/V−S method after 8 h, which is much shorter than those used in many liquid phase IP processes.

The cross-sectional scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) images of TpPa-1/Alumina (FIGS. 4a-b) depict a continuous COF thin-layer tightly attached to the surface of the alumina hollow fiber substrate. The thickness of the COF layer is approximately 80–100 nm. The top view SEM image (FIG. 4c) shows consistently the continuous layer with all gaps on the porous alumina substrate sealed (i.e. without visible defects or irregularities). A higher magnification image (FIG. 4d) shows that on top of the compact layer, there are larger particles of around 100 nm to a few hundred nanometers. Comparing the EDS images in FIG. 4b with that of the pristine substrate (FIG. 5b), a distinct COF thin layer was observed. The loose particles (FIGS. 4b-c) could be the grains of the substrate itself and wrapped with COF layers during V/V−S growth. Otherwise, they might be entirely COF particles outgrown from the underneath compact layer. It is believed that the former is more probable, based on further evidence from FIGS. 6-8. FIG. 6 shows by increasing the reaction time from 8 h to 12, 24, and 48 h, the surface becomes smoother accompanied by increased thickness. The thickness of the COF membrane is around 200 nm

after 48 h of growth duration. From the membrane prepared at 8 h, some particles from the surface were managed to be scratched off by a metal spatula for TEM analysis. As shown in FIG. 7, thin nanosheets are observed instead of dense particles, signaling that the surface of TpPa-1/Alumina is covered by continuous COF layers although the surface is not very even due to the small coating thickness. Furthermore, SEM images of specimens at different locations of the hollow fiber (FIG. 8) show that COF skin layers are consistently observed on the upper, lower, left, right, and middle surfaces of the inner lumen of the alumina hollow fiber. The gaps between the pristine grains of the porous alumina are sealed. Notably, there is no clear trend between the morphology of "loose" particles and their location, which indirectly excludes the possibility of forming loose COF particles, since there is no good explanation for V/V−S interface growth to produce distinctively different COF particle sizes at different locations. The observed difference is highly likely due to the inhomogeneity of the alumina substrate itself. All these results suggest the growth of crystalline and continuous TpPa-1 COF membrane on the inner surface of the hollow fiber substrate by our one-step V/V−S interfacial growth method.

Growth of COF membranes at the solid surface, in particular, curved surface is a complicated task. Compared to previously reported liquid-liquid (R. Wang *et al.*, *J. Membr. Sci.* **2019**, *586*, 274–280), liquid-air (D. B. Shinde *et al.*, *J. Am. Chem. Soc.* **2018**, *140*, 14342–14349), or solid-vapor (N. A. Khan *et al.*, *J. Am. Chem. Soc.* **2020**, *142*, 13450–13458) IP which all involve at least processing of one liquid phase, V/V−S method offers the unique advantage of growing COF membranes from all vapor phases on targeted solid surface efficiently. As will be appreciated, the process disclosed herein is extremely simple and does not require a vacuum condition which was necessary for chemical vapor deposition (CVD) reported elsewhere (S. Hao *et al.*, *Chem. Eng. J.* **2021**, *421*, 129750.).

Vapor-liquid-solid (VLS) phase reaction is limited to flat sheet membranes; limiting its large scale and practical applications. Flat-sheet membranes typically are limited in their surface area compared to hollow-fiber membranes, especially when creating large-scale flat-sheet membranes and assembling them into modules can be technically complex and expensive. VLS is limited to flat sheet membranes because organic precursors (either aldehyde or amine) dissolved in a suitable solvent can only be deposited onto a flat substrate. The choice of solvent and method of deposition (spin-coating or pre-assembly) is critical as it affects the resulting film quality and uniformity. Upon deposition, the precursor may form the initiating clusters or nuclei on the substrate, serving as starting points for COF growth. In contrast, the presently disclosed V/V−S method omits the casting or spin coating requirement of the liquid phase, with both monomers in the vapor phase and using PDA as anchor points for the

covalent attachment of the COF thin film. The PDA-modified layer, through a simple one-step immersion process, creates a homogeneous chemically active surface for COF to grow on the curved substrate.

Further, in VLS reaction, one of the liquid monomers first coated on the substrate may act as the excess reactant. The presently disclosed V/V–S method introduces both monomers in a dilute vapor phase. In the system disclosed herein, the precursor molecules are present in low concentrations within the vapor phase. This controlled dilution of precursors offers several advantages in COF thin-film fabrication. Without wishing to be bound by theory, dilute precursor conditions may prevent premature nucleation and uncontrolled growth, allowing for precise deposition on specific areas of the substrate. The dilute systems may also help control the kinetics of the chemical reaction involved in the film formation, which leads to more controlled growth rates. In a nutshell, the method disclosed herein reduces the need for monomer pre-assembly on the substrate surface and offers better thermodynamic and kinetic control of COF formation on the substrate.

Example 4. Performance studies of TpPa-1/Alumina

Organic solvent permeability, salt/dye separation, and active pharmaceutical ingredient (API, GA) separation

Organic solvent permeability, salt/dye separation, and API (GA) separation experiments were performed using a crossflow filtration setup with an applied pressure of 2 bar driven by a pump (Cole-Parmer Masterflex Digital Gear Pump). The solvent permeance was calculated using Equation 1, where J_i (L m^{-2} h^{-1} bar^{-1}) is the solvent permeance, v_i (L) is the volume of permeate collected, ΔP (bar) is the transmembrane pressure, A (m^2) is the effective area of the membrane, and t (h) is the elapsed time for permeate sample collection.

$$J_i = \frac{v_i}{\Delta P \times A \times t} \quad (1)$$

The permeance was calculated using data obtained after 1 h of continuous operation after the permeate flow became stable. For the molecular dye rejection test, the dyes were dissolved in selected solvents at a concentration of 100 mg/L. These dye solutions served as feed solutions to assess the nanofiltration performance. A UV-Vis spectrometer (UV-1800, Shimadzu) was used to quantify the concentrations of the dyes in the retentate, permeate, and feed solutions to obtain the separation performances of the membranes. The linear correlation of Beer-Lambert's law between absorbance and concentration was used to

determine the concentrations of the dye and API solutes. A calibration curve for each solute is constructed by preparing standard solutions of known concentrations and measuring their absorbance. For the mixture of dye and salt, the separation experiments were first tested for feed solutions containing 100 mg/L of dye and 1000 mg/L of salt Na_2SO_4. The membrane performance was also estimated using Equation (1) and Equation (2). The concentration of CR was determined using the UV-Vis spectrophotometer and the concentration of Na_2SO_4 was determined based on the conductivity measured with a conductivity meter (Myron L 6PIIFCE - Ultrameter II). Similarly, for the API separation test, GA was dissolved in water or DMSO at a concentration of 50 ppm as the feed solution. The concentration of GA was determined using the UV-Vis spectrophotometer. The membrane performance was also estimated using Equation (1) and Equation (2). The effective membrane area for these evaluations was 7.92 cm^2. Rejection was determined using Equation 2, where the concentration of the solute (C_p) in the feed solution was compared to that (C_f) in the permeate.

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (2)$$

Results and discussion

After confirming that continuous and crystalline TpPa-1 COF membrane is obtained by the V/V−S method on alumina hollow fiber, the performance of TpPa-1/Alumina for solvent permeation and dye rejection was evaluated in an inside-out and cross-flow module at 2 bar. Before detailed tests, the reaction parameters for membrane growth were first optimized by varying the reaction duration, monomer concentration and temperature. Based on water permeance and Rose Bengal (RB) rejection results (FIG. 9), TpPa-1/Alumina obtained with a reaction duration of 8 h and starting concentration of 2 $mgmL^{-1}$ for both monomers (Tp:Pa molar ratio = 1 : 2) exhibits the best performance (150 Lm^{-2} h^{-1} bar^{-1} and >99% rejection). When the reaction time is extended to 24 h, the water permeance is dropped to almost half due to a larger membrane thickness (around 200 nm vs 100 nm). The stochiometric molar ratio of Tp:Pa in COF is 1: 1.5. In the present disclosure, it was found that excess Pa is required to form good quality COF membranes, which could be due to partial oxidation of the amine functional group during the reaction since our reaction chamber also contains air. This can be avoided in future by designing a better reactor system that allows gas purging. With a lower reaction temperature at 150 °C, the membrane exhibits lower water permeance (35 Lm^{-2} h^{-1} bar^{-1}) and inferior dye rejection (FIG. 10). Reaction temperature higher than 170 °C was also attempted. However, the silicon lid cracked and resulted in vapor leakage. This issue could be avoided with a better design and the use of materials with higher thermal resistance.

As shown in FIG. 11a, the TpPa-1/Alumina membrane obtained at 170 °C and 8 h exhibits excellent rejection of >95% for RB (973 Da) and >90% for Congo Red (CR, 696 Da) dissolved in all protic solvents (water, ethanol, and methanol). For smaller sized dyes, Napthol Blue Black (NBB, 616 Da) and Acid Fuchsin (AF, 585 Da), high rejection of >90% in water can still be obtained. However, the rejection drops in ethanol and methanol, especially in methanol. The rejection of AF in methanol is lower than in ethanol and water, especially near the MWCO. This difference is attributed to the multifactorial nature of solute-solvent-membrane interactions. Methanol generally has stronger solvation of the solute compared to ethanol, leading to a larger effective solute size. However, solvation also affects the membrane, with different solvents impacting membrane pore walls differently. In the present disclosure, the effective pore size of TpPa-1/Alumina is suggested to decrease in the order methanol-ethanol-water. Moreover, the lower affinity of methanol to the membrane compared to ethanol may enhance solute permeability, contributing to lower AF rejection. This is supported by higher pure solvent permeance rates for methanol compared to ethanol and water (FIG. 11b). For the smallest dye tested in this study, Methyl Orange (MO, 269 Da), poor rejection resulted in all solvents. Based on these results, the MWCO for our membrane is around 700 Da in water, ethanol, and methanol. The solvent permeance data of TpPa-1/Alumina for both protic and aprotic solvents are shown in FIG. 11b. The membrane exhibits high permeance for acetonitrile (450 L m^{-2} h^{-1} bar^{-1}) and acetone (430 L m^{-2} h^{-1} bar^{-1}), followed by methanol (200 Lm^{-2} h^{-1} bar^{-1}), ethanol (170 Lm^{-2} h^{-1} bar^{-1}) and water (150 L m^{-2} h^{-1} bar^{-1}). On the other hand, much lower permeances are obtained for DMF (20 L m^{-2} h^{-1} bar^{-1}), DMAc (18 L m^{-2} h^{-1} bar^{-1}), and DMSO (10 L m^{-2} h^{-1} bar^{-1}). Compared to COF-LZU1 deposited on alumina (S. Kandambeth *et al.*, *J. Am. Chem. Soc.* **2012**, *134*, 19524–19527) or ceramic (C. Zhang *et al.*, *Angew. Chem. Int. Ed.* **2016**, *55*, 3054–3057; and M. Zhang *et al.*, *J. Membr. Sci.* **2022**, *657*, 120673) hollow fiber in earlier works, the presently disclosed TpPa-1/Alumina displays a much higher water permeance but a larger MWCO. The higher water permeance could be due to a thinner membrane obtained in this study. Even though the pore size of TpPa-1 and COF-LZU1 is similar and should attribute to a similar MWCO, we observed a larger MWCO (500 vs 700 Da). In the same FIG. 11b, the permeance of these solvents is plotted against their physiochemical properties, $\delta^{-1}\eta^{-1}d^{-2}$, where δ is Hanson's solubility parameter, η is the kinematic viscosity and d is the molecular diameter (A. Buekenhoudt *et al.*, *J. Membr. Sci.* **2013**, *439*, 36–47). Solvent permeability is primarily determined by molecular size (second-order effect). Hanson's solubility parameter accounts for the dispersion, polarity, and hydrogen bonding of the solvent. The viscosity of the solvent affects its flow behavior and diffusion ability through the membrane. The plot shows a decent linear relationship between the permeance and the solvent properties, which enables a quick prediction of permeance given any solvent.

The long-term endurance of membranes in organic solvents is of critical importance for industrial organic solvent nanofiltration (OSN) applications. The operation stability of TpPa-1/Alumina was evaluated over 80 h of continuous cross-flow separation of CR from methanol. As shown in FIG. 11c, the membrane retains 91% of the initial permeance after 80 h with CR rejection remaining over 96%. The membrane exposed to this extended separation process remains intact and adheres stably to the substrate. These results and observations underline that the TpPa-1/Alumina exhibits excellent structural and chemical stability in prolonged contact with the organic solvent. Furthermore, previous studies have shown that COF membranes with sharp MWCO are effective for salt/dye separation (loose nanofiltration) (L. Valentino, M. Matsumoto *et al.*, *Environ. Sci. Technol.* **2017**, *51*, 14352–14359). Likewise, long-term salt/dye rejection was carried out using CR and sodium sulfate dissolved aqueous solution as the feed. FIG. 12 indicates that TpPa-1/Alumina has an extremely low dye penetration (<4%) and high Na_2SO_4 salt penetration (>85%) over the test. Water permeance in this case is reduced from 137 L m^{-2} h^{-1} bar^{-1} to 80 L m^{-2} h^{-1} bar^{-1} after 100 h, which could be attributed to an accumulation of salt molecules in pores of COF membrane, as well as possible membrane compaction. Compaction refers to the process by which the pores or channels within a membrane become gradually filled or blocked, often due to the accumulation of molecules on or within the membrane structure.

The performances of our TaPa-1/Alumina as well as those of several representative COF membranes fabricated by other methods are shown in Table 1. COF-based membranes though small-scale have shown impressive separation performance compared to commercial leading OSN membranes, such as DuraMem™ (Evonik) and PuraMem™ (Evonik) (G. M. Shi *et al.*, *J. Membr. Sci.* **2019**, *588*, 117202). For instance, DuraMem 500 exhibits a low acetonitrile permeance of 0.8 L m^{-2} h^{-1} bar^{-1} and AF rejection of 94.6% using a cross-flow flat-sheet configuration at 10 bar (N. Joseph *et al.*, *Adv. Funct. Mater.* **2017**, *27*). In the literature, a few COF membranes have shown excellent OSN performances. For example, the gradient COF membrane reported by Zhang and Liao's group exhibits excellent solvent permeance for methanol (176 L m^{-2} h^{-1} bar^{-1}) and hexane (270 L m^{-2} h^{-1} bar^{-1}) with a small MWCO of 472 Da (H. Zuo *et al.*, *Adv. Mater.* **2024**, *36*, 2305755). Compared with these COFs, our TpPa-1/Alumina demonstrates at least equivalent (if not better) performances and stability, but in an alumina hollow fiber module with continuous cross-flow operation.

Table 1. Comparison of aqueous and organic solvent nanofiltration performances of COF membranes fabricated by different methods.

Synthesis method	**COF**	**Membrane** **Solvent permeance (L m^{-2} h^{-1} bar^{-1})** **MWCO**	**Stability test condition**	**Substrate material** **Filtration setup** **Operating pressure**	**Reference**
Langmuir–Blodgett	TpPa-Py	Water 150 MeOH 170 EtOH 140 IPA 70 Hex 270 MeCN 250 ~700 Da	Nitroaniline filtration, 24 h	PAN, PSF, PVDF, or nonwoven PP Flat-sheet dead-end 1 bar	R. Shevate & D. L. Shaffer, *ACS Nano* **2022**, *16* (2), 2407-2418
	TpPa-Bz	Water 200 MeOH 220 EtOH 150 IPA 100 Hex 350 MeCN 300 ~800 Da			
Thermosolvent Diffusion Method	3D COF TFPM-HZ	Water 11 MeOH 44 EtOH 25 300 Da		PAN Substrate Flat-sheet Dead-End 1 bar	X. Shi *et al.*, *Angew. Chem. Int. Ed.* **2022**, *61*, e202207559

Vacuum filtration	GO/COF	Water 59 MeOH 60 EtOH 50 IPA 32 320 Da	Soaked in strong acid and base for 7 d; EtOH and MeOH filtration, 48 h	Nylon Flat-sheet dead-end 1-3 bar	L. Chen *et al.*, *Applied Materials Today* **2020**, *20*
Interfacial polymerization	PA/COF	MeOH 1.53 EtOH 7.98 DMF 5.5 479 Da	Soaked in DMF for 100 d, 14 d	PI Flat-sheet cross-flow	C. Li *et al.*, *J. Membr. Sci.* **2019**, *572*, 520-531
Langmuir–Blodgett	TFP-DHF M20	Water 60 MeOH 80 EtOH 40 IPA 25 Hex 120 MeCN 100 900 Da	Water, hexane acetonitrile, ethanol, isopropanol filtration, 30 h	AAO Flat-sheet dead-end 1 bar	D. B. Shinde *et al., J. Am. Chem. Soc.* **2018**, *140* (43), 14342-14349
Solid-vapor interface polymerization	TpPa-1	Water 411 MeOH 311 EtOH 289 MeCN 583 Ace 411	Water filtration, 30 cycles	PTFE Flat-sheet dead-end 0.5-1 bar	N. A. Khan *et al., J. Am. Chem. Soc.* **2020**, *142* (31), 13450-13458

		900 Da				
Interfacial polymerization	TpPa-1 COF-TFN	EtOH 60 DMF 5.5 375 Da	DMF filtration, 120 h	PI Flat-sheet cross-flow 2.5-20 bar	C. Yang *et al.*, *J. Membr. Sci.* **2021**, *637*
Interfacial polymerization	COP/PBI	Water 10.9–14.4 EtOH 2.4 MeCN 9.5 Ace 3.3 DMF 0.9 400–1000 Da	MeOH filtration, 10 h	PBI Flat-sheet dead-end 10 bar	A. Asadi Tashvigh & N. E. Benes, *Sep. Purif. Technol.* **2022**, *298*, 121589
Liquid phase polymerization and solvent vapor induced crystallization	TFP-PDA	Water 403 EtOH 270 MeOH 200 Hex 90 Ace 490 MeCN 519.6 800 Da	Water filtration, 96 h	ITO-coated disk Flat-sheet dead-end 0.5-3 bar	N. A. Khan *et al.*, *Nat. Commun.* **2022**, *13* (1), 3169
	TFP-TTA	Water 300 EtOH 250 MeOH 180			

		Hex 80 Ace 230 MeCN 420 800 Da				
Solvothermal growth	COF-LZU1	Water 76 450 Da	Water filtration, 80 h	Alumina tube, external Surface Cross-flow 5 bar	H. Fan *et al.*, *Angew. Chem., Int. Ed.* **2018**, *57* (15), 4083-4087
In situ growth	TAPA-BTCA	MeOH 224 EtOH 98 Acetone 395 Hexane 266 IPA 62 784 Da	IPA filtration, 175 h	PI hollow fiber, lumen and cross section Cross-flow 1 bar	Z. F. Gao *et al.*, *Sep. Purif. Technol.* **2022**, *294*, 121166
Interfacial polymerization	COF-LZU1	Water 28.5 500 Da	Water filtration, 96 h	Yttria-stabilized zirconia hollow fiber, external surface Cross-flow 5 bar	K. Banjerdteerakul *et al.*, *J. Membr. Sci.* **2023**, *683*, 121852
Porous PIL membrane templated synthesis	GCOM: TpPa-1	MeOH 176 EtOH 81 Hex 270 IPA 40	MeOH filtration 100 h	Free-standing flat sheet Cross-Flow 2 bar	H. Zuo *et al.*, *Adv. Mater.* **2024**, *36*, 2305755

		472 Da			
One-step V/V–S	TpPa-1	Water 150 EtOH 170 MeOH 200 Ace 436 MeCN 457 IPA 74 DMF 20 DMSO 10 700 Da	MeOH filtration, 80 h Water filtration, 100 h	Alumina hollow fiber Cross-flow 2 bar	The present disclosure
	TpPa2Cl	Water 140 EtOH 190 MeOH 214 Ace 469 DMSO 30.8 600 Da	-		
	TpHz	Water 150 550 Da	-		

Ethanol (EtOH), Methanol (MeOH), Acetonitrile (MeCN), Acetone (Ace) Hexane (Hex), Isopropanol (IPA), Dimethylformamide (DMF), Dimethylsulfoxide (DMSO), Graphene Oxide (GO), Polyacrylonitrile (PAN), PSF (Polysulfone), Polyvinylidene fluoride (PVDF), Polyamide (PA) Polyimide (PI), Polytetrafluoroethylene (PTFE), Aluminum Oxide (AAO), Polybenzimidazole (PBI), Indium tin oxide (ITO).

Therefore, the TpPa COF membrane on porous alumina substrate disclosed herein exhibits remarkable stability across two critical domains: loose nanofiltration; and organic solvent nanofiltration. Loose Nanofiltration (Loose NF) is a membrane-driven separation method positioned between Nanofiltration (NF) and Reverse Osmosis (RO) in the spectrum of pore size and selective separation. It specializes in effectively separating small to medium-sized molecules, typically within the molecular weight range of 200 to 1000 daltons, making it a versatile and precise filtration technique. OSN rejects solutes found in organic solvent applications involving non-aqueous solutions and organic compounds. This stability underscores its potential to address challenges in diverse separation scenarios, thus contributing to enhanced process efficiency. The ability to minimize fouling, enable continuous operation, enhance selectivity, and handle challenging feed streams makes crossflow filtration a preferred choice for efficient and effective separation processes.

Example 5. Characterization of TpPa2Cl and TpHz

To demonstrate the versatility of the V/V−S method, we synthesized two other COFs, TpPa2Cl (1,3,5-triformylphloroglucinol, Tp and 2,5-dichlorobenzene-1,4-diamine, Pa2Cl as monomers) and TpHz (1,3,5-triformylphloroglucinol, Tp and hydrazine hydrate, Hz as monomers) (FIG. 13). Compared to TpPa-1, TpPa2Cl has a slightly smaller aperture size of 1.5 nm due to the presence of two chloride groups in the amine monomer. TpHz has the smallest aperture size of 1.3 nm. Unlike TpPa-1 and TpPa2Cl consisting of the rigid and planar monomers, TpHz has a flexible skeleton, and the amine linkage can rotate and distort. It would be interesting to know the suitability of the V/V−S method for the synthesis of new COF membranes and how their properties differ.

In addition, besides a one-time reaction at 170 °C for 8 h, two and three V/V−S reaction cycles at the same condition were applied with the same substrate to increase the thickness of the COF membranes to achieve a good separation for a model API, glycyrrhizic acid (GA, 844 Da) from DMSO and water. GA is known for its anti-inflammatory properties and is used as a therapeutic drug in the treatment of Severe Acute Respiratory Syndrome Coronavirus 2 (SARS-CoV-2) infections. Similar to TpPa-1/Alumina, TpPa2Cl/Alumina and TpHz/Alumina (FIG. 14a) display similar XRD patterns with characteristics intralayer (100) and interlayer (001) peaks. The position of (100) peak is consistent with the aperture size of the three COFs at 4.7°, 4.8° and 7.0° for TpPa-1, TpPa2Cl and TpHz, respectively. The intensities of both (100) and (001) peaks for TpPa2Cl/Alumina and TpHz/Alumina are higher than those of TpPa-1/Alumina, indicating that they are more crystalline. In addition, there exists no obvious

difference in peak intensity among the membranes obtained with 1, 2 and 3 reaction cycles (FIG. 15). It also shows that the characteristic (100) peak at 4.7°, 4.8° and 7.0° in the XRD pattern of TpPa-1/Alumina, TpPa2Cl/Alumina and TpHz/Alumina, respectively, aligns well with that of the corresponding powdered COF and simulated pattern. The ATR-FTIR spectra (FIG. 14b) display C−N bond at 1223 cm^{-1} and C=C bond at 1558 cm^{-1} for TpPa2Cl/Alumina, and 1276 cm^{-1} and 1577 cm^{-1} for TpHz/Alumina, further confirming the formation of the β-ketoenamine linked framework structures. The presence of C−N bond is also reflected by the N 1s XPS peak of all the membranes at around 399 eV (FIG. 14c). Finally, Cl 2p peak of TpPa2Cl/Alumina (FIG. 14d) is centered at around 189 eV which is attributed to Cl−C bond.

The SEM and EDS images of TpPa2Cl/Alumina (FIG. 16) show that dense and continuous skin layers are formed on the alumina hollow fiber substrate. The membrane thickness increases from approximately 120 nm to 250 nm and 500 nm upon successive growth cycles. Such flexibility in thickness control is expected advantageous for tailored applications. Similar membrane thickness tunning from around 100 nm to 500 nm is also achievable for TpPa-1/Alumina and TpHz/Alumina (FIGS. 17 and 18). The top view SEM images for all three COF membranes after 2 and 3 cycles of growth display higher numbers of large crystals on top of the compact layers. This phenomenon can be attributed to the introduction of fresh monomers during each cycle. The monomer vapors generated not only condense laterally to increase the thickness of the membrane but also in an orthogonal direction forming these COF crystals.

Example 6. Performance studies of TpPa2Cl and TpHz

The performance of TpPa2Cl and TpHz was studied by following the protocol in Example 4.

The characterization results obtained so far have confirmed that the V/V−S method is versatile and can be adapted to grow different COF membranes on curved substrates with controllable thickness. The OSN and dye rejection performance test was also conducted for TpPa2Cl/Alumina and TpHz/Alumina. FIGS. 19a and 9c demonstrate the pore size effect of COF on dye rejection. Between the two COFs, TpPa2Cl with a larger pore size gives an MWCO of around 600 Da in water for membrane obtained after 3 reaction cycles (500 nm in thickness). For thinner membranes obtained with 1 and 2 cycles, the MWCO is 700 Da. On the other hand, TpHz with a smaller pore size can reject >90% of AF (585 Da) and >70% of MO (269 Da) even with 1 cycle of reaction corresponding to around 100 nm in membrane thickness (FIG. 19c). Its MWCO should be between around 300–600 Da. The dye rejection of TpPa-1/Alumina obtained with different reaction cycles was compared (FIG. 20a) and no

difference in MWCO (700 Da) for TpPa-1 membranes of different thicknesses was found. This may be associated with its largest pore size among the three COFs. The MWCO is primarily determined by the pore size of the membrane or the effective pore size distribution. The crystalline structure of TpPa-1 COF provides a well-defined and consistent pore size distribution, which contributes to its selective molecular separation properties. Importantly, the crystalline structure and pore size distribution are typically consistent across the thickness of the COF layer. Even as the COF layer may be part of a thicker membrane, the selective properties of the COF remain intact. The additional thickness primarily serves mechanical or support functions without significantly altering MWCO. These observations underline that the TpPa-1/Alumina membrane exhibits minimal effects of physical aging, compaction, or swelling, and the separation layer adheres securely to the support without detachment.

The increase in thickness of the COF active layer affected the permeability more noticeably. As the active layer of the COF membrane becomes thicker, it introduces additional mass transfer resistance to the solvent due to increased tortuosity of the diffusion pathway. As shown in FIG. 19b, TpPa2Cl/Alumina obtained with 1 reaction cycle exhibits high and similar permeances as those of TpPa-1/Alumina shown earlier for acetone (469 L m^{-2} h^{-1} bar^{-1}), methanol (214 L m^{-2} h^{-1} bar^{-1}), ethanol (192 L m^{-2} h^{-1} bar^{-1}) and water (139 L m^{-2} h^{-1} bar^{-1}). Upon increase of the membrane thickness, these permeances decrease as expected. For TpPa2Cl/Alumina after 3 reaction cycles, the permeance drops to 214 L m^{-2} h^{-1} bar^{-1} (acetone), 136 L m^{-2} h^{-1} bar^{-1} (methanol), 132 L m^{-2} h^{-1} bar^{-1} (ethanol) and 100 L m^{-2} h^{-1} bar^{-1} (water). A similar trend was also found for TpPa-1/Alumina with more reaction cycles (FIG. 20b). The permeance of TpHz/Alumina is distinctively different from the other two COF membranes. A higher water permeance of 220 L m^{-2} h^{-1} bar^{-1} (1 cycle) to 140 L m^{-2} h^{-1} bar^{-1} (3 cycles) was obtained despite its smaller pore size (FIG. 19d).

DMSO is a widely used solvent for chemical reactions which has a high polarity and swelling effect. It is considered as an aggressive solvent and resistant to mass transfer through polymeric membranes. In general, membrane permeance of DMSO between 3–10 L m^{-2} h^{-1} bar^{-1} is considered impressive. Several polymeric membranes have been reported for OSN test using DMSO dissolved with dyes (FIG. 21).

The highest DMSO permeance reported is 6.3 L m^{-2} h^{-1} bar^{-1} with 89.5% RB rejection for a pyromellitic dianhydride–4,4'-diaminodiphenylmethane (PMDAMDA) polyimide membrane at an operating pressure of 25 bar (Y. Li *et al.*, *Ind. Eng. Chem. Res.* **2019**, **58**, 6712–6720). In the present disclosure, the performance of TpPa-1/Alumina and TpPa2Cl/Alumina

membranes was evaluated using DMSO dissolved with GA as a model API. As shown in FIG. 21a, our crystalline COF membranes, especially TpPa2Cl/Alumina, exhibit very promising performances. TpPa2Cl/Alumina membranes obtained after 1, 2, and 3 reaction cycles give excellent GA rejection rates of 90%, 95%, and 98% and DMSO permeance of 20, 18, and 15 L m^{-2} h^{-1} bar^{-1} at 2 bar. TpPa-1/Alumina membranes also demonstrate good rejection after 2 and 3 reaction cycles, as some defects are possibly sealed over the repeated cycles. However, the thicker membranes lead to lower permeance of DMSO. For TpPa-1/Alumina (3 cycle), the permeance is 3.5 L m^{-2} h^{-1} bar^{-1}. It is possible that the dichlorobenzene ring in TpPa2Cl provides a more polar and hence favourable environment for DMSO diffusion or flow in the pore channels of the membrane. As will be appreciated, the present invention displayed at least 3 times higher flux than conventional polymer membranes (FIG. 21b).

Example 7. COF-based membrane in waste treatment and upcycling OSN applications

To demonstrate the application of TpPa-1 in waste treatment and upcycling OSN, dilute solute-solvent systems were studied using 100 ppm of glycyrrhizic acid dissolved in DMSO running at 2 bar.

In detail, the membranes (TpPa-1/Alumina (1 cycle), TpPa-1/Alumina (2 cycle) and TpPa-1/Alumina (3 cycle)) exhibit a rejection rate of glycyrrhizic acid from DMSO ~90%, ~95%, and ~98% for 1, 2, and 3 cycles respectively (FIG. 22). Similarly, the excellent rejection observed for the molecules above the MWCO indicates that the membrane is performing as expected, selectively retaining larger molecules while allowing smaller ones to pass through. Permeability of DMSO 10 to 5 L m^{-2} h^{-1} bar^{-1} is excellent for OSN applications.

The inability to separate smaller APIs that are below the MWCO of a membrane is a common limitation in membrane-based separation processes. In the case of TpPa-1 COF membranes, their inherent pore size may not be suitable for separating smaller molecules.

Example 8. V/V–S fabrication of COF membranes on hollow fiber substrate

The control parameters of the setup (FIG. 23) for COF fabrication are provided below.

- Temperature (T_1, T_2, T_3, T_4, T_3 & $T_4 > T_1$ or T_2 (whichever is higher)
- Pressure (<5 bar)
- Flow rate of inert gas (f_{N2})

- Concentration of monomers (C_1, C_2)
- Types of monomer, solvent, coating layer (PDA, or other molecules) before COF growth
- Type of the substrate material (e.g., alumina, Yttria-stabilized zirconia)
- Configuration and dimension of substrate (e.g., single or multichannel)

With this setup and optimization of parameters, better quality membranes with higher crystallinity, uniformity in thickness, less defects, etc., for better performances, may be produced.

Further, the method disclosed herein may be applicable to a wide range of COF materials for different uses and applications, e.g. separation of APIs, solvents and salts.

Table 2. List of potential example COFs with various pore sizes for different uses and applications (FIG. 24).

COF	**Monomers**	**Pore Size (nm)**
LZU1	1,3,5-benzenetricarboxaldehyde (BTCA), Pa	1.9
TpPa-1	Tp, Pa	1.8
TpPa2Cl	Tp, Pa2Cl	1.5
TFP-TAPA	Tp, TAPA	1.2
CTF-BTD	2,1,3-benzothiadiazole-4,7-benzenedicarbonitrile (BTD)	0.65
SNW-1	terephthalate melamine	0.5

The key performance parameters include selectivity, permeability, tolerance to harsh solvent, and resistance to fouling.

Example 9. Substrate recycling

To demonstrate the recyclability of the substrate after the end of the lifecycle of COF membrane, the hollow fiber was placed in a muffle furnace and calcined with static air at 500 °C for 1 hour.

Results and discussion

FIG. 25 shows that it is feasible to remove COF layers after end-of-life by calcination and recycle the substrate for coating of fresh COF layers after PDA modification.

Comparative Example 1

Table 3. Comparison of COFs on hollow fiber.

One-step vapor phase (the present disclosure)	**One-pot, liquid phase** (H. Fan *et al.*, *Angew. Chem. Int. Ed.* **2018**, *57*, 4083–4087)	**Two-step, liquid phase** (K. Banjerdteerakul *et al.*, *J. Membr. Sci.* **2023**, *683*, 121852)	**Two liquid streams** (Z. F. Gao *et al.*, *Sep. Purif. Technol.* **2022**, *294*, 121166)
• Compact COF layer at inner surface • High permeance for water and common organic solvents • Suitable for harsh organic solvent	• Compact COF layer at exterior surface • Low water permeance • No organic solvent separation	• Loose COF layer at exterior surface • Very low water permeance • No organic solvent separation	• Loose COF film at the inner surface and COF particles scattered at the cross-section • No harsh solvent separation

Comparative Example 2

Table 4. Comparison of the present disclosure with commercial polymeric membranes.

Key parameters	**The present disclosure (COF)**	**SepPure (PEI, PBI)**	**Solv8 (PP)**	**Evonik (PI)**
Maximum membrane	Acetone: 436 Alcohol: 200 Acetonitrile: 457	Acetone: 4 Alcohol: 2.2 Acetonitrile: -	Acetone: - Alcohol: - Acetonitrile: ×	Acetone: 11 Alcohol: 6 Acetonitrile: 5

solvent permeance (L m^{-2} h^{-1} bar^{-1})	DMSO: 10 DMF: 20 DMAc: 18	DMSO: × DMF: - DMAc: -	DMSO: × DMF: - DMAc: ×	DMSO: - DMF: - DMAc: ×
Max T endurable (°C)	at least 200	60	130	50
Operating P (bar)	2	15	-	20-30
Configuration	Hollow fibre	Hollow fibre	Spiral wound	Flat sheet, spiral wound

-: data not available; ×: not compatible

Polymer: Polyethylenimine (PEI), polybenzimidazole (PBI), polypropylene (PP), polyimide (PI)

Organic solvent: Dimethyl sulfoxide (DMSO), dimethylformamide (DMF), dimethylacetamide (DMAc)

Conclusion

A vapor/vapor-solid (V/V−S) interfacial method to grow COF membranes specifically on the inner lumen surface of alumina hollow fiber was developed. In the presently disclosed method, both monomers are vaporized and introduced to the substrate as a vapor mixture (V/V). The unique V/V−S strategy allows a one-step, fast, and scalable process for the fabrication of high-quality COF membranes on both flat and curved substrates. Advanced membrane applications both in OSN and separation of organic dyes and API molecules were demonstrated with a cross-flow and inside-out configuration. The crystalline TpPa-1 membranes deposited on alumina hollow fiber demonstrate remarkably high permeance for both water and organic solvents, while also maintaining excellent selectivity over extended duration. The V/V−S method can also be extended to the synthesis of other COFs. The TpPa2Cl/Alumina membranes exhibit excellent OSN performance for a harsh solvent, dimethylsulfoxide (DMSO), and API separation.

A vapor/vapor-solid (V/V−S) method was successfully demonstrated to fabricate continuous and crystalline TpPa-1, TpPa2Cl and TpHz COF membranes on PDA-modified alumina hollow fiber substrate. This simple, versatile and one-step method allows both precursor monomers to vaporize and react at the pre-functionalized surfaces, either flat or curved, thus overcoming the processing challenges involving liquids. The resultant TpPa-1 membrane of around 100 nm in thickness grown on alumina hollow fiber exhibits high water, ethanol, and methanol permeance of 150, 170, and 200 L m^{-2} h^{-1} bar^{-1}, respectively, and a MWCO of 700 Da in all

three solvents. It also displays high stability over 80 h of continuous operation of OSN and dye rejection. By increasing the V/V−S reaction cycle from 1 to 2 and 3, thicker membranes of around 250 nm and 500 nm can be yielded for all three COFs. Among them, TpPa2Cl/Alumina exhibits a remarkable OSN performance for the separation of a model API, glycyrrhizic acid (GA), from DMSO. High GA rejection rates of 90%, 95%, and 98% and the corresponding DMSO permeance of 20, 18, and 15 L m^{-2} h^{-1} bar^{-1} were obtained for TpPa2Cl/Alumina fabricated with 1–3 cycles. Owing to the ability of the V/V−S method to grow COF rapidly on curved surfaces, this study opens the possibilities of further research and development for large-scale COF membrane fabrication towards advanced separation and a more sustainable pharmaceutical industry.

The V/V−S method's feature lies in its exceptional capability to coat not only flat surfaces but also curved substrates, including the intricate lumen of hollow fibers; ensuring a continuous, defect-free coating across the entire membrane surface. This homogenous growth eliminates inconsistencies that may arise in traditional coating methods, resulting in enhanced separation efficiency and uniformity.

The filtration tests have elucidated the remarkably robust separation capabilities exhibited by our membranes when subjected to pharmaceutical feeds. These feeds consistently demonstrate compelling rejections exceeding 90%, underscoring the membrane's remarkable stability and efficiency in this demanding application.

By using thermal cycles, the tunability of COF membrane thickness offers a valuable advantage in achieving precise, selective, and efficient separations across a range of applications. This adaptability makes COF membranes a promising choice for addressing complex separation challenges in both laboratory and industrial settings.

Claims

1. A membrane suitable for separation of chemical species, the membrane comprising:
a ceramic substrate having a first surface and a second surface;
an anchoring chemical layer on the first surface of the ceramic substrate; and
a covalent organic framework (COF) layer on the anchoring chemical layer.

2. The membrane according to Claim 1, wherein the anchoring chemical layer is covalently bonded to the ceramic substrate and to the COF layer.

3. The membrane according to Claim 1 or Claim 2, wherein the anchoring chemical layer is a polymeric material having a plurality of amine groups and a plurality of hydroxyl groups, where:

at least some of the plurality of amine groups are covalently bonded to at least some of the COFs in the COF layer, optionally wherein the COF incorporates the plurality of amine groups within its structure; and

at least a portion of the oxygen atoms in the hydroxyl groups have reacted with the first surface of the ceramic substrate to provide covalent bonds between the anchoring chemical layer and the ceramic substrate.

4. The membrane according to any one of the preceding claims, wherein the anchoring chemical layer is a polymeric material formed from a monomeric compound having an amine group and two hydroxyl groups on adjacent carbon atoms, optionally wherein the polymeric material formed from a monomeric compound having an amine group and two hydroxyl groups on adjacent carbon atoms on an aromatic ring.

5. The membrane according to Claim 4, wherein the anchoring chemical layer is selected from one or more of the group consisting of a polydopamine, a poly-norepinephrine, and a poly-levodopa, optionally wherein anchoring chemical layer is a polydopamine.

6. The membrane according to any one of the preceding claims, wherein the ceramic substrate is selected from one or more of a zirconia, a yttria-stabilised zirconia, a titania, a silica and an alumina.

7. The membrane according to Claim 6, wherein the ceramic substrate is an alumina.

8. The membrane according to any one of the preceding claims, wherein the ceramic substrate is selected from a flat substrate, a hollow fiber substrate having one or more lumens running through it.

9. The membrane according to Claim 8, wherein the ceramic substrate is a hollow fiber substrate having one or more lumens running through it and the first surface is the surface of the lumen(s).

10. The membrane according to any one of the preceding claims, wherein the COF is formed from a first organic monomer comprising a plurality of amine groups and a second organic monomer comprising a plurality of carbonyl groups (e.g. aldehyde groups).

11. The membrane according to Claim 10, wherein the first organic monomer is selected from one or more of the group consisting of ethylenediamine, 2,4-diaminopyridine, benzidine, 9,9-dimethyl-9*H*-fluorene-2,7-diamine, benzene-1,3,5-triamine, tris(4-aminophenyl)methane, 4,4',4''-(1,3,5-triazine-2,4,6-triyl)trianiline, and, more particularly, *para*-phenylenediamine (Pa), 2,5-dichlorobenzene-1,4-diamine (Pa2Cl), hydrazine (Hz), 3,5-diamino-1,2,4-triazole, melamine, optionally wherein the first monomer is Pa2Cl or, more particularly, Pa.

12. The membrane according to Claim 10 or Claim 11, wherein the second organic monomer is selected from one or more of the group consisting of terephthaldehyde, 2,5-dimethylbenzene-1,4-dicarbaldhyde, 4,4'-biphenyldicarboxaldehyde, glyoxal, succinaldehyde, 2,5-deoxy-denzene-1,4-dicarbaldehyde, and 1,1'biphenyl-3,4',5-tricarbaldehyde, 1,3,5-tris(4-formylphenyl)benzene (TFP), more particularly, 1,3,5-triformylphloroglucinol (Tp), optionally wherein the second monomer is Tp.

13. The membrane according to any one of the preceding claims, wherein the COF layer is formed from:

(a) 1,3,5-triformylphloroglucinol (Tp) and P-phenylenediamine (Pa) (TpPa);

(b) Tp and 2,5-dichlorobenzene-1,4-diamine (Pa2Cl) (TpPa2Cl); or

(c) Tp and hydrazine (Hz) (TpHz),

optionally wherein the COF layer is formed from TpPa2Cl or, more particularly, TpPa.

14. The membrane according to any one of the preceding claims, wherein the COF layer has one or more of the following properties:

(ai) the COF layer is defect free;

(aii) the COF layer has a compact structure;

(aiii) the COF layer is crystalline in nature;

(aiv) the COF layer has a thickness of from 100 to 1,000 nm, such as from 120 to 500 nm; and

(av) an internal pore size of the COF is from 0.3 to 2 nm, such as from 0.5 to 1.8 nm, such as from 1 to 1.5 nm.

15. The membrane according to any one of the preceding claims, wherein the membrane displays one or more of the following properties:

(bi) a water permeance of from 75 to 250 L m^{-2} h^{-1} bar^{-1}, such as from 100 to 150 L m^{-2} h^{-1} bar^{-1}, such as from about 120 to about 140 L m^{-2} h^{-1} bar^{-1};

(bii) an ethanol permeance of from 170 to 190 L m^{-2} h^{-1} bar^{-1};

(biii) a methanol permeance of from 200 to 220 L m^{-2} h^{-1} bar^{-1};

(biv) an acetone permeance of from 430 to 470 L m^{-2} h^{-1} bar^{-1};

(bv) an acetonitrile permeance of from 450 to 470 L m^{-2} h^{-1} bar^{-1};

(bvi) a dimethylformamide permeance of from 20 L m^{-2} h^{-1} bar^{-1};

(bvii) a dimethylsulfoxide permeance of from 10 to 30 L m^{-2} h^{-1} bar^{-1}, such as from 15 to 20 L m^{-2} h^{-1} bar^{-1};

(bviii) a molecular weight cut-off (MWCO) of from 200 to 1,000 Daltons, such as from 550 to 700 Daltons;

(bix) an operating temperature range up to about 350 ºC; and

(bx) an operating pressure of from 1 to 100 bar, optionally wherein the operating pressure is from 1.5 to 10 bar, such as about 2 bar.

16. A method of forming a membrane suitable for separation of chemical species, the method comprising the steps of:

(a) providing a ceramic substrate having a first surface and a second surface that is coated on a first surface with an anchoring chemical layer; and

(b) subjecting the ceramic substrate to an interfacial chemical vapour deposition polymerization reaction for a period of time at a temperature to form a COF, by exposing the ceramic substrate to an environment comprising a first vapour stream comprising at least a first COF precursor monomer and a second vapour stream comprising at least a second COF precursor monomer, wherein the first and second COF monomers are deposited on the anchoring chemical layer and react to form a COF layer.

17. The method according to Claim 16, wherein step (b) is repeated from 1 to 10 further times.

18. The method according to Claim 16 or Claim 17, wherein the period of time is from 1 hour to 24 hours, such as from 3 hours to 10 hours, such as about 8 hours.

19. The method according to any one of Claims 16 to 18, wherein the temperature of step (b) in Claim 16 is from 100 to 250 ºC, such as about 170 ºC.

20. The method according to any one of Claims 16 to 19, wherein after step (b) of Claim 16, the anchoring chemical layer is covalent bonded to the ceramic substrate and to the COF layer.

21. The method according to any one of Claims 16 to 20, wherein the anchoring chemical layer is a polymeric material having a plurality of amine groups suitable to form covalent bonds with the first COF precursor monomer and has a plurality of hydroxyl groups, where at least a portion of the oxygen atoms in the hydroxyl groups have reacted with the first surface of the ceramic substrate to provide covalent bonds between the anchoring chemical layer and the ceramic substrate.

22. The method according to any one of Claims 16 to 21, wherein the ceramic substrate having a first surface and a second surface that is reacted on a first surface with an anchoring chemical layer precursor monomer material that comprises at least one amine group and at least one (e.g. 2) hydroxyl group to form the anchoring chemical layer by polymerisation of the anchoring chemical layer precursor monomer material and the formation of a plurality of covalent bonds between the first surface of the ceramic substrate and the formed anchoring chemical layer.

23. The method according to Claim 22, wherein the anchoring chemical layer precursor monomer material is selected from one or more of the group consisting of dopamine, norepinephrine, L-DOPA (Levodopa) with amine and catechol-like structures.

24. The method according to Claim 23, wherein the anchoring chemical layer is a polydopamine.

25. The method according to any one of Claims 16 to 24, wherein the ceramic substrate is selected from one or more of a zirconia, a yttria-stabilised zirconia, a titania, a silica and an alumina, optionally wherein the ceramic substrate is an alumina.

26. The method according to any one of Claims 16 to 25, wherein the ceramic substrate is selected from a flat substrate, a hollow fiber substrate having one or more lumens running through it.

27. The method according to Claim 26, wherein the ceramic substrate is a hollow fiber substrate having one or more lumens running through it and the first surface is the surface of the lumen(s).

28. The method according to any one of Claims 16 to 27, wherein the first COF precursor monomer comprises a plurality of amine groups and the second COF precursor monomer comprises a plurality of carbonyl groups (e.g. aldehyde groups).

29. The method according to Claim 28, wherein the first COF precursor monomer is selected from one or more of the group consisting of ethylenediamine, 2,4-diaminopyridine, benzidine, 9,9-dimethyl-9*H*-fluorene-2,7-diamine, benzene-1,3,5-triamine, tris(4-aminophenyl)methane, 4,4',4''-(1,3,5-triazine-2,4,6-triyl)trianiline, and, more particularly, *para*-phenylenediamine (Pa), 2,5-dichlorobenzene-1,4-diamine (Pa2Cl), hydrazine (Hz), and 3,5-diamino-1,2,4-triazole, melamine, optionally wherein the first monomer is Pa2Cl or, more particularly, Pa.

30. The method according to Claim 28 or Claim 29, wherein the second COF precursor monomer is selected from one or more of the group consisting of terephthaldehyde, 2,5-dimethylbenzene-1,4-dicarbaldhyde, 4,4'-biphenyldicarboxaldehyde, glyoxal, succinaldehude, 2,5-deoxy-denzene-1,4-dicarbaldehyde, and 1,1'biphenyl-3,4',5-tricarbaldehyde, 1,3,5-tris(4-formylphenyl)benzene (TFP), more particularly, 1,3,5-triformylphloroglucinol (Tp), optionally wherein the second COF precursor monomer is Tp.

31. The method according to any one of Claims 16 to 30, wherein:

(a) the first COF precursor monomer is P-phenylenediamine (Pa) and the second COF precursor monomer is 1,3,5-triformylphloroglucinol (Tp);

(b) the first COF precursor monomer is 2,5-dichlorobenzene-1,4-diamine (Pa2Cl) and the second COF precursor monomer is 1,3,5-triformylphloroglucinol (Tp);

(c) the first COF precursor monomer is hydrazine (Hz) and the second COF precursor monomer is 1,3,5-triformylphloroglucinol (Tp).

32. A method of using a membrane as described in any one of Claims 1 to 15 in a process of separating a first organic compound from a second organic compound, the method comprising the steps of:

(a) providing a membrane as described in any one of Claims 1 to 15;

(b) passing a first mixture comprising a first organic compound and a second compound that is organic or inorganic through the membrane using a suitable pressure to provide a second mixture comprising the first organic compound, with the second organic compound either being absent from the second mixture or is substantially reduced in amount.

33. A device to manufacture a membrane suitable for separation of chemical species, the device comprising:

a reaction chamber suitable for housing a ceramic membrane;

a first feed vessel fluidly connected to the reaction chamber;

a second feed vessel fluidly connected to the reaction chamber;

a first gas source connector fluidly connected to the first feed vessel; and

a second gas source connector fluidly connected to the second feed vessel, wherein the first and second feed vessels comprise a means or apparatus suitable to vaporise a monomeric material suitable to form a COF; and

the reaction chamber comprises a means or apparatus suitable to provide a temperature in the reaction chamber to maintain the monomeric material suitable to form a COF in a gaseous state, a means or apparatus suitable to purge the monomeric material suitable to form a COF from the reaction chamber, and a means or apparatus to remove said monomeric material from the reaction chamber , optionally the means or apparatus that to remove said monomeric material from the reaction chamber also recirculates it back into the reaction chamber.