CLAIMS

1. A method of forming a covalent organic framework (COF) membrane, comprising:

i) forming a membrane substrate by:

a) impregnating a porous polymer with a pore-forming agent in order to form an impregnated polymer;

b) at least partially carbonising the impregnated polymer at a temperature of 150 °C to 500 °C in order to form the membrane substrate;

wherein the membrane substrate is characterised by a crystallinity of 10% to 70% relative to the porous polymer; and

ii) interfacially polymerising amino monomers and acyl monomers on a surface of the membrane substrate in order to form the COF membrane;

wherein the acyl monomers are aldehyde monomers.

2. The method according to claim 1, wherein the amino monomer comprises at least two amino moieties; and/or

wherein the acyl monomer comprises at least two aldehyde moieties.

3. The method according to claim 1 or 2, wherein the acyl monomer is selected from 1,3,5-triformylphloroglucinol, 1,3,5-triformylbenzene, terephthalaldehyde, 4,4'-biphenyldicarboxaldehyde, 2,5-bis(2-propynyloxy)terephthalaldehyde, 2,5-dimethoxyterephthalaldehyde, 4,4'-biphenyldialdehyde, tetrathiafulvalene-tetrabenzaldehyde or a combination thereof; and/or

wherein the amino monomer is selected from p-phenylenediamine (PDA), hydrazine hydrate (HZ), 1,3,5-tris(4-aminophenyl)benzene (TAPB), 3,3-dihydroxybenzidine (DHBD), 2,2'-bipyridine-5,5'-diamine, 4,4'-azodianiline, 4,4',4''-(1,3,5-triazine-2,4,6-triyl)trianiline, 4,4',4''-(1,3,5-triazine-2,4,6-triyl)tris(1,1'-biphenyl)trianiline, benzidine, 2,5-diethoxy-terephthalohydrazide, 2,5-diaminebenzene-1,4-disulfonic acid, 2,5-diaminebenzenesulfonic acid, triphenylene hexamine, 1,4-phenylenediamine, melamine, 2,5-dimethylbenzene-1,4-diamine or a combination thereof.

4. The method according to any one of claims 1 to 3, wherein the interfacial polymerisation comprises:

a) homogenously coating the surface of the membrane substrate with amino monomers in order to form a surface coated with amino monomers;

b) homogenously coating the surface coated with amino monomers with acyl monomers; and

c) polymerising the amino monomers to the acyl monomers.

5. The method according to any one of claims 1 to 4, wherein the polymerisation is performed in the presence of an acid at a concentration 0.1 mM to 10 mM, and/or
wherein the polymerisation is performed at a temperature of 40 °C to 90°C and/or for 2 h to 60 h.

6. The method according to any one of claims 1 to 5, wherein the pore-forming agent is an inorganic metal salt selected from calcium nitrate, calcium chloride, magnesium chloride, sodium nitrate, potassium carbonate, aluminium nitrate or a combination thereof; and/or
wherein the porous polymer is selected from polyacrylonitrile (PAN), polyethersulfone (PES), polyvinylidene fluoride (PVDF), polysulfone, sodium alginate, chitosan, polydimethylsiloxane, polyvinyl alcohol, poly(ether-ether-ketone), poly(methyl methacrylate) (PMMA), polytetrafluoroethylene (PTFE) or a combination thereof.

7. The method according to any one of claims 1 to 6, wherein the impregnation step is performed for at least 1 h;
wherein the impregnated polymer is carbonised at a temperature of 200 °C, and/or for 30 min to 360 min; and/or in the presence of oxygen.

8. The method according to any one of claims 1 to 7, wherein the membrane substrate is characterised by a degree of carbonisation relative to the porous polymer of at least 20%; and/or
wherein the membrane substrate is characterised by an increase in pore size relative to the porous polymer of 5 times to 100 times.

9. A covalent organic framework (COF) membrane, comprising:

i) a membrane substrate comprising an at least partially carbonised porous polymer, the membrane substrate having a pore size of 100 nm to 800 nm, wherein the membrane substrate is characterised by a crystallinity of 10% to 70% relative to an uncarbonised porous polymer; and

ii) a COF layer interfacially polymerised on a surface of the membrane substrate, the COF layer formed from amino monomeric units and acyl monomeric units;

wherein the COF layer has a pore size of 0.5 nm to 10 nm.

10. The COF membrane according to claim 9, wherein the COF layer is characterised by at least one of the following:

a) a pore size of 0.8 nm to 2.4 nm;

b) a thickness of 50 nm to 500 nm;

c) an X-ray diffraction (XRD) 2θ value of 3° to 8°; and

d) a dye rejection of more than 90%.

11. The COF membrane according to claim 9 or 10, wherein when the amino monomeric unit is HZ, the COF membrane is characterised by at least one of the following:

i) a Evans blue rejection of more than 99.5%;

ii) a methyl blue rejection of more than 99.5%;

iii) a fuchsin acid rejection of more than 95%;

iv) a methyl orange rejection of more than 91%;

v) a water permeance of 50 L m^{-2} h^{-1} bar^{-1} to 800 L m^{-2} h^{-1} bar^{-1};

or wherein when the amino monomeric unit is DHBD, the COF membrane is characterised by a water permeance of 200 L m^{-2} h^{-1} bar^{-1} to 800 L m^{-2} h^{-1} bar^{-1}.

12. The COF membrane according to any one of claims 9 to 10, wherein the COF membrane is characterised by at least one of the following:

i) a polar aprotic solvent permeance of 10 L m^{-2} h^{-1} bar^{-1} to 100 L m^{-2} h^{-1} bar^{-1};

ii) a NMP permeance of 20 L m^{-2} h^{-1} bar^{-1} to 100 L m^{-2} h^{-1} bar^{-1};

iii) a DMSO permeance of 20 L m^{-2} h^{-1} bar^{-1} to 100 L m^{-2} h^{-1} bar^{-1};

iv) a $Pd(PPh_3)_4$ rejection of more than 95% in an organic solvent; and

v) a stability against organic solvents for at least 60 days, wherein the organic solvent is selected from DMF, NMP, DMSO, or a combination thereof.

13. The COF membrane according to any one of claims 9 to 12, wherein the membrane substrate is an organic membrane substrate having a pore size of 100 nm to 300 nm;

wherein the membrane substrate is characterised by a molecular weight cut-off (MWCO) of 500 kDa to 4000 kDa.

14. The COF membrane according to any one of claims 9 to 13, wherein the at least

partially carbonised porous polymer is 40% to 70% carbonised.

15. A method of recovering a compound from a solution, comprising nanofiltering the solution through the COF membrane according to any one of 9 to 14 in order to form a retentate and a permeate, wherein the compound is retained in the retentate.

16. The method according to claim 15, wherein a size of the compound is at least 60% relative to a pore size of the COF membrane;
wherein the COF membrane is characterised by a MWCO of 300 Da to 5000 Da; and/or wherein the method is characterised by a compound recovery yield of at least 90% and/or a compound recovery of at least 1 g.

17. The method according to claim 15 or 16, wherein the nanofiltration is performed under a pressure of 2 bar and/or under an inert atmosphere.

18. The method according to any one of claims 15 to 17, wherein the compound is an organometallic compound and/or an organic compound having a molecular weight of at least 600 Da.

19. The method according to any one of claims 15 to 18, wherein when the compound is a catalyst, the recovered catalyst is reusable in another catalytic cycle;
wherein the catalytic yield is substantially similar to a catalytic cycle using fresh catalyst;
wherein the recovered catalyst is reusable in at least 10 catalytic cycles.

20. The method according to any one of claims 15 to 19, wherein the method further comprises recovering a second compound from the permeate, comprising nanofiltering the permeate through a second COF membrane as disclosed herein in order to form a second retentate and a second permeate, wherein the second compound is retained in the second retentate; and wherein the second COF membrane has a smaller pore size relative to the first COF membrane.