Claims

1. A polycrystalline metal-organic framework membrane comprising:

a substrate material having a surface; and

a polycrystalline metal-organic framework attached to the surface of the substrate material, wherein the polycrystalline metal-organic framework is formed from:

a secondary building unit having the formula Ia or Ib:

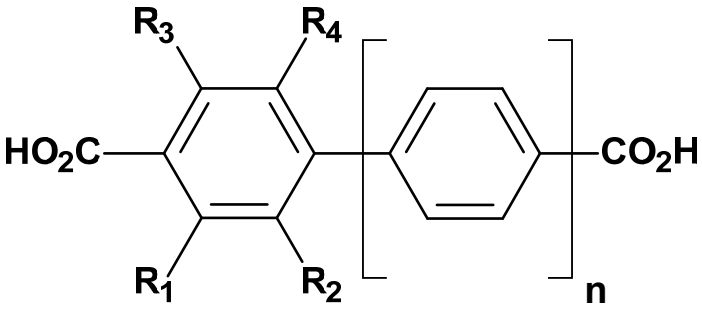
$$M_6O_4(OH)_4 \qquad \text{Ia},$$

where M is selected from Zr, Hf, and Ti; or

$$M'_6(OH)_8 \qquad \text{Ib}$$

where M' is selected from Sm, Y, Dy, Er, Gd, and Ce; and

a ligand selected from fumaric acid, butynedioic acid, squaric acid, naphthalene-2,6-dicarboxylic acid, [2,2'-bipyridine]-5,5'-dicarboxylic acid, or a ligand having formula II:



II

, where:

R_1 is selected from H, halo, OR_{5a}, SR_{5b}, C_1 to C_5 alkyl, NO_2, $NR_{5c}R_{5d}$, SO_3H, CF_3, or CO_2H;
R_2 is selected from H, halo, OR_{6a}, SR_{6b}, C_1 to C_5 alkyl, NO_2, $NR6_cR_{6d}$, SO_3H, CF_3 or CO_2H;
R_3 is selected from H, halo, OR_{7a}, SR_{7b}, C_1 to C_5 alkyl, NO_2, $NR_{7c}R_{7d}$, SO_3H, CF_3, or CO_2H;
R_4 is selected from H, halo, OR_{8a}, SR_{8b}, C_1 to C_5 alkyl, NO_2, $NR_{8c}R_{8d}$, SO_3H, CF_3 or CO_2H;
R_{5a-5d}, R_{6a-6d}, R_{7a-7d}, R_{7a-7d} are each independently selected from H or C_1 to C_5 alkyl; or
R_1 and R_2 or R_3 and R_4 form, together with the carbon atoms to which they are attached to a C_6 aromatic ring; and n is 0, 1 or 2.

2. The membrane according to Claim 1, wherein the substrate material is selected from one or more of a polymer, a ceramic (e.g. alumina), a carbon cloth, a metal, and a metal oxide.

3. The membrane according to Claim 2, wherein, when the substrate material is alumina, then the secondary building unit has formula Ia, where M is Zr, Hf or Ti, or the secondary building unit has formula Ib.

4. The membrane according to any one of the preceding claims, wherein the polycrystalline metal-organic framework is a UiO-66-type metal-organic framework.

5. The membrane according to any one of the preceding claims, wherein:
R_1 is selected from H, halo, OR_{5a}, SR_{5b}, C_1 to C_5 alkyl, NO_2, $NR_{5c}R_{5d}$, SO_3H, CF_3, or CO_2H;
R_2 is selected from H, OR_{6a}, SR_{6b}, CF_3 or CO_2H;
R_3 is selected from H, halo, OR_{7a}, SR_{7b}, C_1 to C_5 alkyl, $NR_{7c}R_{7d}$, SO_3H, CF_3, or CO_2H; and
R_4 is selected from H, F, OR_{8a}, SR_{8b}, CF_3 or CO_2H.

6. The membrane according to any one of the preceding claims, wherein:
when two or more of R_1 to R_4 are not H, then the non-H substituents are identical to each other; and/or
n is 0 or 1 (e.g. n is 0).

7. The membrane according to any one of the preceding claims, wherein the ligand is selected from fumaric acid, butynedioic acid, squaric acid, naphthalene-2,6-dicarboxylic acid, [2,2'-bipyridine]-5,5'-dicarboxylic acid, terephthalic acid, 2-fluoroterephthalic acid, 2-chloroterephthalic acid, 2-bromoterephthalic acid, 2-iodoterephthalic acid, 2-hydroxyterephthalic acid, 2-mercaptoterephthalic acid, 2-methylterephthalic acid, 2-nitroterephthalic acid, 2-aminoterephthalic acid, 2-sulfoterephthalic acid, 2-(trifluoromethyl)terephthalic acid, benzene-1,2,4-tricarboxylic acid, 2,3-dihydroxyterephthalic acid, 2,3-dimercaptoterephthalic acid, 2,5-difluoroterephthalic acid, 2,5-dichloroterephthalic acid, 2,5-dibromoterephthalic acid, 2,5-diiodoterephthalic acid, 2,5-terephthalic acid, 2,5-dihydroxyterephthalic acid, 2,5-dimercaptoterephthalic acid, 2,5-dimethylterephthalic acid, 2,5-diaminoterephthalic acid, 2,5-bis(trifluoromethyl)terephthalic acid, 2,5-diemthoxyterephthalic acid, benzene-1,2,4,5-tetracarboxylic acid, 2,5-disulfoterephthalic acid, 2,5-diethoxyterephthalic acid, 2,5-diisopropylterephthalic acid, 2,3,5,6-tetrafluoroterephthalic acid, 2,3,5,6-tetrahydroxyterephthalic acid, 2,3,5,6-tetramethylterephthalic acid, 2,3,5,6-tetrakis(trifluoromethyl)terephthalic acid, benzene-1,2,3,4,5,6-hexacarboxylic acid, [1,1'-

biphenyl]-4,4’-dicarboxylic acid, [1,1’:4’,1’’-terphenyl]-4,4’’-dicarboxylic acid, and naphthalene-1,4-dicarboxylic acid.

8. The membrane according to Claim 7, wherein the ligand is selected from or 2-aminoterephthalic acid or 2,5-dihydroxyterephthalic acid.

9. The membrane according to any one of the preceding claims, wherein the substrate material is provided in the form of a mesh, a sheet or in the form of hollow fibers (e.g. porous alumina ceramic hollow fibers) and other arrangements that are obtainable by the folding of a mesh, a sheet and hollow fibers.

10. The membrane according to any one of the preceding claims, wherein the polycrystalline metal-organic framework attached to the surface of the substrate material has a thickness of from 20 nm to 20 μm, such as from 800 nm to 20 μm, such as from 2 μm to 20 μm.

11. A method of using a polycrystalline metal-organic framework membrane as described in any one of Claims 1 to 10 in a process of separating a fluid into a filtrate fluid and a retentate fluid, the process comprising the steps of:
(a) providing a fluid in need of separation to a polycrystalline metal-organic framework membrane as described in any one of Claims 1 to 10;
(b) allowing or enabling a portion of the fluid to pass through the polycrystalline metal-organic framework membrane to provide a filtrate fluid and thereby providing a filtrate fluid; and
(c) collecting the filtrate fluid and retentate fluids.

12. The method according to Claim 11, wherein the fluid to be separated is selected from: a mixture of gases; an aqueous solution comprising one or more inorganic materials; an aqueous solution comprising one or more organic materials; an aqueous solution comprising one or more inorganic materials and one or more organic materials; a mixture of organic liquids; a mixture of one or more organic liquids and water; a mixture of one or more organic liquids and one or more organic materials; a mixture of one or more organic liquids and one or more inorganic materials; a mixture of one or more organic liquids, one or more organic materials and one or more inorganic materials; a mixture of water, one or more organic liquids and one or more organic materials; a mixture of water, one or more organic liquids and one or more inorganic materials; and a mixture of water, one or more organic liquids, one or more organic materials and one or more inorganic materials.

13. A method of forming a polycrystalline metal-organic framework membrane as described in any one of Claims 1 to 10, the method comprising the steps of:

providing a seeded substrate having a surface seeded with seed crystals of the metal-organic framework, said seed crystals formed from a secondary building unit having the formula Ia or Ib and a ligand selected from fumaric acid, butynedioic acid, squaric acid, naphthalene-2,6-dicarboxylic acid, [2,2'-bipyridine]-5,5'-dicarboxylic acid, or a ligand having formula II, where formulae Ia, Ib and II are as described in any one of Claims 1 to 10; and

subjecting the seeded substrate to a first mother liquor comprising a solvent, a metal salt precursor and a ligand selected from fumaric acid, butynedioic acid, squaric acid, naphthalene-2,6-dicarboxylic acid, [2,2'-bipyridine]-5,5'-dicarboxylic acid, or a ligand having formula II as described above, for a first period of time under conditions sufficient to form a metal-organic framework membrane, wherein the metal salt precursor and the ligand are selected to form the same metal-organic framework as in the seed crystals.

14. The method of Claim 13, wherein the seeded substrate is formed by immersing a substrate having a surface in a second mother liquor that comprises a solvent, a metal salt precursor and a ligand selected from fumaric acid, butynedioic acid, squaric acid, naphthalene-2,6-dicarboxylic acid, [2,2'-bipyridine]-5,5'-dicarboxylic acid, or a ligand having formula II as described in any one of Claims 1 to 10 for a second period of time to provide a seeded substrate having a surface seeded with seed crystals of the metal organic framework, said seed crystals formed from a secondary building unit having the formula Ia or Ib and a ligand selected from fumaric acid, butynedioic acid, squaric acid, naphthalene-2,6-dicarboxylic acid, [2,2'-bipyridine]-5,5'-dicarboxylic acid, or a ligand having formula II, where formulae Ia, Ib and II are as described in any one of Claims 1 to 10.

15. A method of post-synthetic defect healing comprising the steps of:

(a) providing a polycrystalline metal-organic framework membrane as described in any one of Claims 1 to 10 in need of post-synthetic healing formed by the process of Claim 13;

(b) subjecting the polycrystalline metal-organic framework membrane in need of post-synthetic healing to a solution comprising a solvent a ligand selected from fumaric acid, butynedioic acid, squaric acid, naphthalene-2,6-dicarboxylic acid, [2,2'-bipyridine]-5,5'-dicarboxylic acid, or a ligand having formula II as described in Claim 1, for a period of time under conditions sufficient to achieve the post-synthetic healing, wherein the ligand are selected to form the same metal-organic framework as in the polycrystalline metal-organic framework membrane.

16. The method according to Claim 15, wherein the polycrystalline metal-organic framework membrane is formed from a secondary building unit of formula Ia, where M is Zr and the ligand is 2-aminoterephthalic acid.

17. A method of *in situ* healing, wherein the method comprises the steps of:

(a) providing a damaged polycrystalline metal-organic framework membrane, where the polycrystalline metal-organic framework membrane is as described in any one of Claims 1 to 10; and

(b) subjecting the damaged polycrystalline metal-organic framework membrane to a solution comprising a reaction solution comprising a solvent, a metal salt precursor, a ligand selected from fumaric acid, butynedioic acid, squaric acid, naphthalene-2,6-dicarboxylic acid, [2,2'-bipyridine]-5,5'-dicarboxylic acid, or a ligand having formula II as described above, and reactive reactive-containing secondary building units for a period of time under conditions sufficient to heal the damaged polycrystalline metal-organic framework membrane, wherein the metal salt precursor, the ligand and the reactive-containing secondary building units are selected to form the same metal-organic framework as in the damaged polycrystalline metal-organic framework membrane.

18. The method according to Claim 15, wherein the damaged polycrystalline metal-organic framework membrane if formed from a secondary building unit that has formula Ib, where M' is Sm and the ligand is 2,5-dihydroxyterephthalic acid.