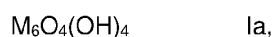


Claims

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:

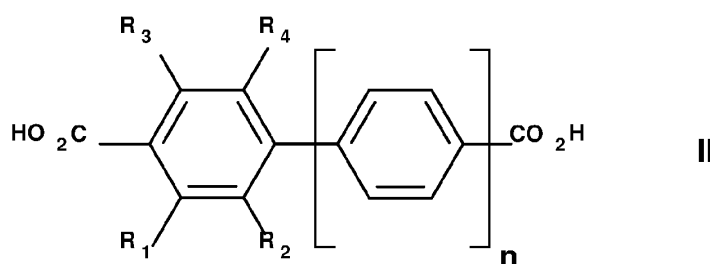


where M is selected from Zr, Hf, and Ti; or



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:



, where:

R₁ is selected from H, halo, OR_{5a}, SR_{5b}, C₁ to C₅ alkyl, NO₂, NR_{5c}R_{5d}, SO₃H, CF₃, or CO₂H;
 R₂ is selected from H, halo, OR_{6a}, SR_{6b}, C₁ to C₅ alkyl, NO₂, NR_{6c}R_{6d}, SO₃H, CF₃ or CO₂H;
 R₃ is selected from H, halo, OR_{7a}, SR_{7b}, C₁ to C₅ alkyl, NO₂, NR_{7c}R_{7d}, SO₃H, CF₃, or CO₂H;
 R₄ is selected from H, halo, OR_{8a}, SR_{8b}, C₁ to C₅ alkyl, NO₂, NR_{8c}R_{8d}, SO₃H, CF₃ or CO₂H;
 R_{5a-5d}, R_{6a-6d}, R_{7a-7d}, R_{8a-8d} are each independently selected from H or C₁ to C₅ alkyl; or
 R₁ and R₂ or R₃ and R₄ form, together with the carbon atoms to which they are attached to a C₆ 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:
R₁ is selected from H, halo, OR_{5a}, SR_{5b}, C₁ to C₅ alkyl, NO₂, NR_{5c}R_{5d}, SO₃H, CF₃, or CO₂H;
R₂ is selected from H, OR_{6a}, SR_{6b}, CF₃ or CO₂H;
R₃ is selected from H, halo, OR_{7a}, SR_{7b}, C₁ to C₅ alkyl, NR_{7c}R_{7d}, SO₃H, CF₃, or CO₂H; and
R₄ is selected from H, F, OR_{8a}, SR_{8b}, CF₃ or CO₂H.
6. The membrane according to any one of the preceding claims, wherein:
when two or more of R₁ to R₄ 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-diethoxyterephthalic 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.