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(54) **Title**: PROCESS FOR COATING SUPPORT SURFACE WITH POROUS METAL-ORGANIC FRAMEWORK

(57) **Abstract**: Provided is a process for coating at least part of a surface of a support with a porous metal-organic framework comprising at least one at least bidentate organic compound coordinated to at least one metal ion. The process comprises the following steps: (a) spraying the at least one part of the support surface with a first solution comprising the at least one metal ion; (b) spraying the at least one part of the support surface with a second solution comprising the at least one at least bidentate organic compound; wherein step (b) is carried out before, after or simultaneously with step (a), to form a layer of the porous metal-organic framework.

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PROCESS FOR COATING SUPPORT SURFACE WITH POROUS METAL-ORGANIC FRAMEWORK

Description

The present invention relates to a process for coating at least part of a surface of a support with a porous metal-organic framework ("MOF").

Processes for coating with metal-organic frameworks have been described in the prior art.

WO2009/056184 A1 describes, for example, spraying a suspension comprising a metal-organic framework onto materials such as nonwovens.

DE 10 2006 031 311 A1 proposes applying adsorptive materials such as metal-organic frameworks to support materials by adhesive bonding or another method of fixing.

The formation of a layer of MOF by means of bonding to gold surfaces by means of self-assembly monolayers is described by S. Hermes et al., J. Am. Chem. Soc. 127 (2005), 13744-13745 (see also S. Hermes et al. Chem. Mater. 19 (2007), 2168-2173; D. Zacher et al., J. Mater. Chem. 17 (2007), 2785-2792; O. Shekhah et al., J. Am. Chem. Soc. 129 (2007), 15118-15119; A. Schroedel et al., Angew. Chem. Int. Ed. 49 (2010), 7225-7228).

MOF layers on silicone supports are described by G. Lu, J. Am. Chem. Soc. 132 (2010), 7832-7833.

MOF layers on polyacrylonitrile supports are described by A. Centrone et al., J. Am. Chem. Soc. 132 (2010), 15687-15691.

Copper-benzenetricarboxylate MOF on copper membranes is described by H. Guo et al., J. Am. Chem. Soc. 131 (2009), 1646-1647.

The production of an MOF layer on an aluminum support by dipping and crystal growing is described by Y.-S. Li et al., Angew. Chem. Int. Ed. 49 (2010), 548-551. Similar subject matter is described by J. Gascon et al., Microporous and Mesoporous Materials 113 (2008), 132-138 and A. Demessence et al., Chem. Commun. 2009, 7149-7151 and P. Küsgen et al., Advanced Engineering Materials 11 (2009), 93-95.

The electrodeposition of an MOF film is described by A. Doménech et al., Electrochemistry Communications 8 (2006), 1830-1834.

MOF layers have likewise been used for coating capillaries (N. Chang et al., J. Am. Chem. Soc. 132 (2010), 13645-13647).

Despite the processes for coating a support surface with a porous metal-organic framework which are known from the prior art, there is a need for improved processes.

It is an object of the present invention to provide an improved process.

The object is achieved by a process for coating at least part of a surface of a support with a porous metal-organic framework comprising at least one at least bidentate organic compound coordinated to at least one metal ion, which comprises the steps

(a) spraying of the at least one part of the support surface with a first solution comprising the at least one metal ion;
(b) spraying of the at least one part of the support surface with a second solution comprising the at least one at least bidentate organic compound,

where step (b) is carried out before, after or simultaneously with step (a), to form a layer of the porous metal-organic framework.

It has been found that spraying-on of the first and second solution results in spontaneous formation of the metal-organic framework in the form of a layer on the support surface. Here, it is particularly advantageous that homogenous layers can be obtained. Spraying enables a faster production process than dipping processes to be carried out. The adhesion can be increased, so that bonding agents may be able to be dispensed with.

Step (a) can be carried out before step (b). Step (a) can also be carried out after step (b). It is likewise possible for step (a) and step (b) to be carried out simultaneously.

The resulting layer of the porous metal-organic framework can preferably be dried. If step (a) and (b) are not carried out simultaneously, a drying step can additionally be carried out between the two steps.

The drying of the resulting layer of the porous metal-organic framework can, in particular, be effected by heating and/or by means of reduced pressure. Heating is carried out, for example, at a temperature in the range from 120°C to 300°C. The layer is preferably dried at at least 150°C.

Spraying can be carried out by means of known spraying techniques. Spraying with the first, second or both with the first and the second solution is preferably carried out in a spraying drum.

The solutions can be at different temperatures or the same temperature. This can be above or below room temperature. The same applies to the support surface. The first solution or the second solution or both the first and the second solution is/are preferably at room temperature (22°C).

The first and second solutions can comprise identical or different solvents. Preference is given to using the same solvent. Possible solvents are solvents known in the prior art. The first solution or the second solution or both the first and second solutions is/are preferably an aqueous solution.

The support surface can be a metallic or nonmetallic, optionally modified surface. Preference is given to a fibrous or foam surface.

Particular preference is given to a sheet-like textile structure comprising or consisting of natural fibers and/or synthetic fibers (chemical fibers), in particular with the natural fibers being selected from the group consisting of wool fibers, cotton fibers (CO) and in particular cellulose and/or, in particular, with the synthetic fibers being selected from the group consisting of polyesters (PES); polyolefins, in particular polyethylene (PE) and/or polypropylene (PP); polyvinyl chlorides (CLF); polyvinylidene chlorides (CLF); acetates (CA); triacetates (CTA); polyacrylic (PAN); polyamides (PA), in particular aromatic, preferably flame-resistant polyamides; polyvinyl alcohols (PVAL); polyurethanes; polyvinyl esters; (meth)acrylates; polylactic acids (PLA); activated carbon; and mixtures thereof.

Particular preference is given to foams for sealing and insulation, acoustic foams, rigid foams for packaging and flame-resistant foams composed of polyurethane, polystyrene, polyethylene, polypropylene, PVC, viscose, cellular rubber and mixtures thereof. Very particular preference is given to foam composed of melamine resin (Basotect).

A particularly suitable support material is filter material (including dressing material, cotton cloths, cigarette filters, filter papers as can, for example, be procured commercially for laboratory use).

The first solution comprises the at least one metal ion. This can be used as metal salt. The second solution comprises the at least one at least bidentate organic compound. This can preferably be in the form of a solution of its salt.

The at least one metal ion and the at least one at least bidentate organic compound form the porous metal-organic framework by contacting of the two solutions directly on the support surface to form a layer. Metal-organic frameworks which can be produced in this way are known in the prior art.

Such metal-organic frameworks (MOF) are, for example, described in US 5,648,508, EP-A-0 790 253, M. O'Keeffe et al., J. Sol. State Chem., 152 (2000), pages 3 to 20, H. Li et al., Nature 402, (1999), page 276, M. Eddaoudi et al., Topics in Catalysis 9, (1999), pages 105 to 111, B. Chen et al., Science 291, (2001), pages 1021 to 1023, DE-A-101 11 230, DE-A 10 2005 053430, WO-A 2007/054581, WO-A 2005/049892 and WO-A 2007/023134.

As a specific group of these metal-organic frameworks, “limited” frameworks in which, as a result of specific selection of the organic compound, the framework does not extend infinitely but forms polyhedra are described in the recent literature. A.C. Sudik, et al., J. Am. Chem. Soc. 127 (2005), 7110-7118, describe such specific frameworks. Here, they will be described as metal-organic polyhedra (MOP) to distinguish them.

A further specific group of porous metal-organic frameworks comprises those in which the organic compound as ligand is a monocyclic, bicyclic or polycyclic ring system which is derived at least from one of the heterocycles selected from the group consisting of pyrrole, alpha-pyridone and gamma-pyridone and has at least two ring nitrogens. The electrochemical preparation of such frameworks is described in WO-A 2007/131955.

The general suitability of metal-organic frameworks for absorbing gases and liquids is described, for example, in WO-A 2005/003622 and EP-A 1 702 925

These specific groups are particularly suitable for the purposes of the present invention.

The metal-organic frameworks according to the present invention comprise pores, in particular micropores and/or mesopores. Micropores are defined as pores having a diameter of 2 nm or less and mesopores are defined by a diameter in the range from 2 to 50 nm, in each case corresponding to the definition given in Pure & Applied Chem.

57 (1983), 603 - 619, in particular on page 606. The presence of micropores and/or mesopores can be checked by means of sorption measurements which determine the absorption capacity of the MOF for nitrogen at 77 kelvin in accordance with DIN 66131 and/or DIN 66134.

The specific surface area, calculated according to the Langmuir model (DIN 66131, 66134), of an MOF is preferably greater than 10 m^2/g, more preferably greater than 20 m^2/g, more preferably greater than 50 m^2/g. Depending on the MOF, it is also possible to achieve greater than 100 m^2/g, more preferably greater than 150 m^2/g and particularly preferably greater than 200 m^2/g.

The metal component in the framework according to the present invention is preferably selected from groups Ia, IIa, IIIa, IVa to VIIIa and Ib to VIb. Particular preference is given to Mg, Ca, Sr, Ba, Sc, Y, Ln, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ro, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, Al, Ga, In, Tl, Si, Ge, Sn, Pb, As, Sb and Bi, where Ln represents lanthanides.

Lanthanides are La, Ce, Pr, Nd, Pm, Sm, En, Gd, Tb, Dy, Ho, Er, Tm, Yb.

As regards the ions of these elements, particular mention may be made of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Sc^{3+}, Y^{3+}, Ln^{3+}, Ti^{4+}, Zr^{4+}, Hf^{4+}, V^{4+}, V^{3+}, V^{2+}, Nb^{3+}, Ta^{3+}, Cr^{3+}, Mo^{3+}, W^{3+}, Mn^{3+}, Mn^{2+}, Re^{3+}, Re^{2+}, Fe^{3+}, Fe^{2+}, Ru^{3+}, Ru^{2+}, Os^{3+}, Os^{2+}, Co^{3+}, Co^{2+}, Rh^{2+}, Rh^{+}, Ir^{2+}, Ir^{+}, Ni^{2+}, Ni^{+}, Pd^{2+}, Pd^{+}, Pt^{2+}, Pt^{+}, Cu^{2+}, Cu^{+}, Ag^{+}, Au^{+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Tl^{3+}, Si^{4+}, Si^{2+}, Ge^{4+}, Ge^{2+}, Sn^{4+}, Sn^{2+}, Pb^{4+}, Pb^{2+}, As^{5+}, As^{3+}, As^{+}, Sb^{5+}, Sb^{3+}, Sb^{+}, Bi^{5+}, Bi^{3+} and Bi^{+}.

Very particular preference is given to Mg, Ca, Al, Y, Sc, Zr, Ti, V, Cr, Mo, Fe, Co, Cu, Ni, Zn, Ln. Greater preference is given to Mg, Ca, Al, Mo, Y, Sc, Mg, Fe, Cu and Zn. In particular, Mg, Ca, Sc, Al, Cu and Zn are preferred. Very particular mention may here be made of Mg, Ca, Al and Zn, in particular Al.

The term “at least bidentate organic compound” refers to an organic compound which comprises at least one functional group which is able to form at least two coordinate bonds to a given metal ion and/or to form one coordinate bond to each of two or more, preferably two, metal atoms.

As functional groups via which the abovementioned coordinate bonds are formed, particular mention may be made by way of example of the following functional groups: $-CO_2H$, $-CS_2H$, $-NO_2$, $-B(OH)_2$, $-SO_3H$, $-Si(OH)_3$, $-Ge(OH)_3$, $-Sn(OH)_3$, $-Si(SH)_4$, $-Ge(SH)_4$, $-Sn(SH)_3$, $-PO_3H$, $-AsO_3H$, $-AsO_4H$, $-P(SH)_3$, $-As(SH)_3$, $-CH(RSH)_2$, $-C(RSH)_3$

$-CH(RNH_2)_2$ $-C(RNH_2)_3$, $-CH(ROH)_2$, $-C(ROH)_3$, $-CH(RCN)_2$, $-C(RCN)_3$, where R is, for example, preferably an alkylene group having 1, 2, 3, 4 or 5 carbon atoms, for example a methylene, ethylene, n-propylene, i-propylene, n-butylene, i-butylene, tert-butylene or n-pentylene group, or an aryl group comprising 1 or 2 aromatic rings, for example 2 C_6 rings, which may optionally be fused and may, independently of one another, be appropriately substituted by at least one substituent in each case and/or may, independently of one another, in each case comprise at least one heteroatom such as N, O and/or S. In likewise preferred embodiments, mention may be made of functional groups in which the abovementioned radical R is not present. In this respect, mention may be made of, inter alia, $-CH(SH)_2$, $-C(SH)_3$, $-CH(NH_2)_2$, $-C(NH_2)_3$, $-CH(OH)_2$, $-C(OH)_3$, $-CH(CN)_2$ or $-C(CN)_3$.

However, the functional groups can also be heteroatoms of a heterocycle. Particular mention may here be made of nitrogen atoms.

The at least two functional groups can in principle be bound to any suitable organic compound as long as it is ensured that the organic compound bearing these functional groups is capable of forming the coordinate bond and of producing the framework.

The organic compounds comprising the at least two functional groups are preferably derived from a saturated or unsaturated aliphatic compound or an aromatic compound or a both aliphatic and aromatic compound.

The aliphatic compound or the aliphatic part of the both aliphatic and aromatic compound can be linear and/or branched and/or cyclic, with a plurality of rings per compound also being possible. The aliphatic compound or the aliphatic part of the both aliphatic and aromatic compound more preferably comprises from 1 to 15, more preferably from 1 to 14, more preferably from 1 to 13, more preferably from 1 to 12, more preferably from 1 to 11 and particularly preferably from 1 to 10, carbon atoms, for example 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10 carbon atoms. Particular preference is given here to, inter alia, methane, adamantane, acetylene, ethylene or butadiene.

The aromatic compound or the aromatic part of the both aromatic and aliphatic compound can have one or more rings, for example two, three, four or five rings, with the rings being able to be present separately from one another and/or at least two rings being able to be present in fused form. The aromatic compound or the aromatic part of the both aliphatic and aromatic compound particularly preferably has one, two or three rings, with one or two rings being particularly preferred. Furthermore, each ring of said compound can independently comprise at least one heteroatom, for example N, O, S, B, P, Si, Al, preferably N, O and/or S. The aromatic compound or the aromatic part of the both aromatic and aliphatic compound more preferably comprises one or two C_6 rings, with the two being present either separately from one another or in fused form. In particular, mention may be made of benzene, naphthalene and/or biphenyl and/or bipyridyl and/or pyridyl as aromatic compounds.

The at least bidentate organic compound is more preferably an aliphatic or aromatic, acyclic or cyclic hydrocarbon which has from 1 to 18, preferably from 1 to 10 and in particular 6, carbon atoms and additionally has exclusively 2, 3 or 4 carboxyl groups as functional groups.

The at least one at least bidentate organic compound is preferably derived from a dicarboxylic, tricarboxylic or tetracarboxylic acid.

For example, the at least bidentate organic compound is derived from a dicarboxylic acid such as oxalic acid, succinic acid, tartaric acid, 1,4-butanedicarboxylic acid, 1,4-butenedicarboxylic acid, 4-oxopyran-2,6-dicarboxylic acid, 1,6-hexanedicarboxylic acid, decanedicarboxylic acid, 1,8-heptadecanedicarboxylic acid, 1,9-heptadecanedicarboxlic acid, heptadecanedicarboxylic acid, acetylenedicarboxylic acid, 1,2-benzenedicarboxylic acid, 1,3-benzenedicarboxylic acid, 2,3-pyridinedicarboxylic acid, pyridine-2,3-dicarboxylic acid, 1,3-butadiene-1,4-dicarboxylic acid, 1,4-benzenedicarboxylic acid, p-benzenedicarboxylic acid, imidazole-2,4-dicarboxylic acid, 2-methylquinoline-3,4-dicarboxylic acid, quinoline-2,4-dicarboxylic acid, quinoxaline-2,3-dicarboxylic acid, 6-chloroquinoxaline-2,3-dicarboxylic acid, 4,4'-diaminophenylmethane-3,3'-dicarboxylic acid, quinoline-3,4-dicarboxylic acid, 7-chloro-4-hydroxyquinoline-2,8-dicarboxylic acid, diimidedicarboxylic acid, pyridine-2,6-dicarboxylic acid, 2-methylimidazole-4,5-dicarboxylic acid, thiophene-3,4-dicarboxylic acid, 2-isopropylimidazole-4,5-dicarboxylic acid, tetrahydropyran-4,4-dicarboxylic acid, perylene-3,9-dicarboxylic acid, perylenedicarboxylic acid, Pluriol E 200-dicarboxylic acid, 3,6-dioxaoctanedicarboxylic acid, 3,5-cyclohexadiene-1,2-dicarboxylic acid, octanedicarboxylic acid, pentane-3,3-dicarboxylic acid, 4,4'-diamino-1,1'-biphenyl-3,3'-dicarboxylic acid, 4,4'-diaminobiphenyl-3,3'-dicarboxylic acid, benzidine-3,3'-dicarboxylic acid, 1,4-bis(phenylamino)benzene-2,5-dicarboxylic acid, 1,1'-binaphthyl-dicarboxylic acid, 7-chloro-8-methylquinoline-2,3-dicarboxylic acid, 1-anilino-anthraquinone-2,4'-dicarboxylic acid, polytetrahydrofuran 250-dicarboxylic acid, 1,4-bis(carboxymethyl)piperazine-2,3-dicarboxylic acid, 7-chloroquinoline-3,8-dicarboxylic acid, 1-(4-carboxy)phenyl-3-(4-chloro)phenylpyrazoline-4,5-dicarboxylic acid, 1,4,5,6,7,7-hexachloro-5-norbornene-2,3-dicarboxylic acid, phenylindanedicarboxylic acid, 1,3-dibenzyl-2-oxoimidazolidine-4,5-dicarboxylic acid, 1,4-cyclohexane-dicarboxylic acid, naphthalene-1,8-dicarboxylic acid, 2-benzoylbenzene-1,3-dicarboxylic acid, 1,3-dibenzyl-2-oxoimidazolidene-4,5-cis-dicarboxylic acid, 2,2'-

biquinoline-4,4'-dicarboxylic acid, pyridine-3,4-dicarboxylic acid, 3,6,9-trioxaundecanedicarboxylic acid, hydroxybenzophenonedicarboxylic acid, Pluriol E 300-dicarboxylic acid, Pluriol E 400-dicarboxylic acid, Pluriol E 600-dicarboxylic acid, pyrazole-3,4-dicarboxylic acid, 2,3-pyrazinedicarboxylic acid, 5,6-dimethyl-2,3-pyrazinedicarboxylic acid, 4,4'-diamino(diphenyl ether)diimidedicarboxylic acid, 4,4'-diaminodiphenylmethanediimidedicarboxylic acid, 4,4'-diamino(diphenyl sulfone) diimidedicarboxylic acid, 1,4-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 1,3-adamantanedicarboxylic acid, 1,8-naphthalenedicarboxylic acid, 2,3-naphthalenedicarboxylic acid, 8-methoxy-2,3-naphthalenedicarboxylic acid, 8-nitro-2,3-naphthalenedicarboxylic acid, 8-sulfo-2,3-naphthalenedicarboxylic acid, anthracene-2,3-dicarboxylic acid, 2',3'-diphenyl-p-terphenyl-4,4"-dicarboxylic acid, (diphenyl ether)-4,4'-dicarboxylic acid, imidazole-4,5-dicarboxylic acid, 4(1H)-oxothiochromene-2,8-dicarboxylic acid, 5-tert-butyl-1,3-benzenedicarboxylic acid, 7,8-quinolinedicarboxylic acid, 4,5-imidazoledicarboxylic acid, 4-cyclohexene-1,2-dicarboxylic acid, hexatriacontanedicarboxylic acid, tetradecanedicarboxylic acid, 1,7-heptane-dicarboxylic acid, 5-hydroxy-1,3-benzenedicarboxylic acid, 2,5-dihydroxy-1,4-dicarboxylic acid, pyrazine-2,3-dicarboxylic acid, furan-2,5-dicarboxylic acid, 1-nonene-6,9-dicarboxylic acid, eicosenedicarboxylic acid, 4,4'-dihydroxydiphenylmethane-3,3'-dicarboxylic acid, 1-amino-4-methyl-9,10-dioxo-9,10-dihydroanthracene-2,3-dicarboxylic acid, 2,5-pyridinedicarboxylic acid, cyclohexene-2,3-dicarboxylic acid, 2,9-dichlorofluorubin-4,11-dicarboxylic acid, 7-chloro-3-methylquinoline-6,8-dicarboxylic acid, 2,4-dichlorbenzophenone-2',5'-dicarboxylic acid, 1,3-benzenedicarboxylic acid, 2,6-pyridinedicarboxylic acid, 1-methylpyrrole-3,4-dicarboxylic acid, 1-benzyl-1H-pyrrole-3,4-dicarboxylic acid, anthraquinone-1,5-dicarboxylic acid, 3,5-pyrazoledicarboxylic acid, 2-nitrobenzene-1,4-dicarboxylic acid, heptane-1,7-dicarboxylic acid, cyclobutane-1,1-dicarboxylic acid 1,14-tetradecanedicarboxylic acid, 5,6-dehydronorbornane-2,3-dicarboxylic acid, 5-ethyl-2,3-pyridinedicarboxylic acid or camphordicarboxylic acid,

Furthermore, the at least bidentate organic compound is more preferably one of the dicarboxylic acids mentioned by way of example above as such.

The at least bidentate organic compound can, for example, be derived from a tricarboxylic acid such as

2-hydroxy-1,2,3-propanetricarboxylic acid, 7-chloro-2,3,8-quinolinetricarboxylic acid, 1,2,3-, 1,2,4-benzenetricarboxylic acid, 1,2,4-butanetricarboxylic acid, 2-phosphono-1,2,4-butanetricarboxylic acid, 1,3,5-benzenetricarboxylic acid, 1-hydroxy-1,2,3-propanetricarboxylic acid, 4,5-dihydro-4,5-dioxo-1H-pyrrolo[2,3-F]quinoline-2,7,9-tricarboxylic acid, 5-acetyl-3-amino-6-methylbenzene-1,2,4-tricarboxylic acid, 3-amino-

5-benzoyl-6-methylbenzene-1,2,4-tricarboxylic acid, 1,2,3-propanetricarboxylic acid or aurintricarboxylic acid.

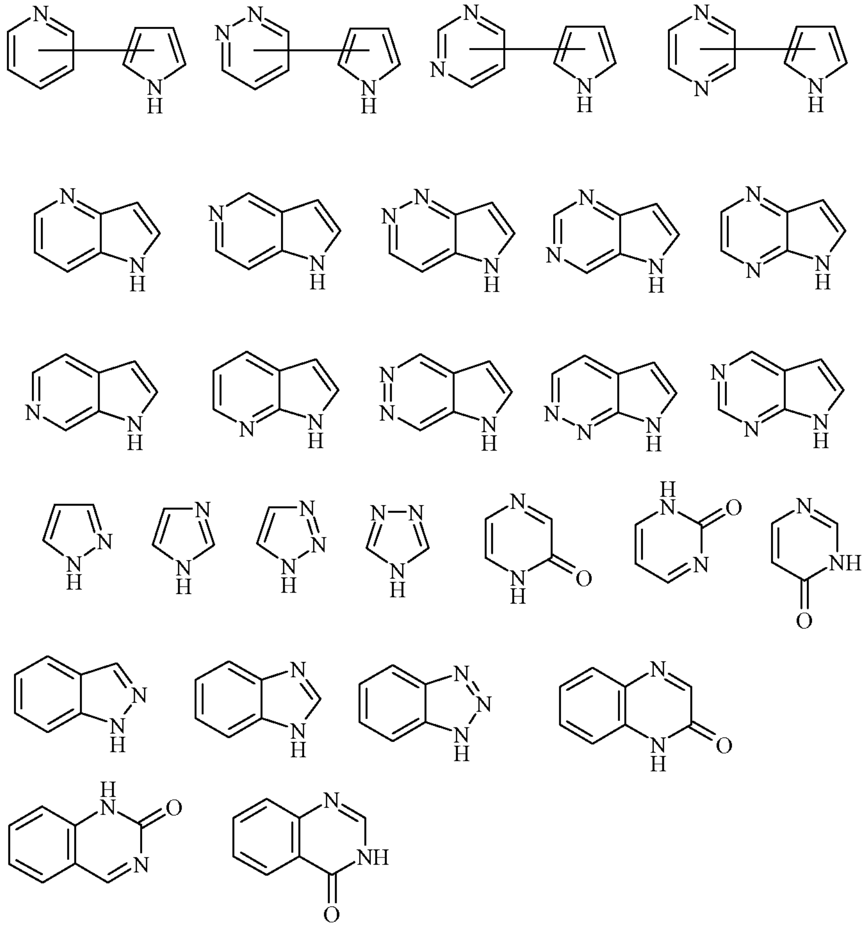
Furthermore, the at least bidentate organic compound is more preferably one of the tricarboxylic acids mentioned by way of example above as such.

Examples of an at least bidentate organic compound derived from a tetracarboxylic acid are

1,1-dioxidoperylo[1,12-BCD]thiophene-3,4,9,10-tetracarboxylic acid, perylenetetracarboxylic acids such as perylene-3,4,9,10-tetracarboxylic acid or (perylene-1,12-sulfone)-3,4,9,10-tetracarboxylic acid, butanetetracarboxylic acids such as 1,2,3,4-butanetetracarboxylic acid or meso-1,2,3,4-butanetetracarboxylic acid, decane-2,4,6,8-tetracarboxylic acid, 1,4,7,10,13,16-hexaoxacyclooctadecane-2,3,11,12-tetracarboxylic acid, 1,2,4,5-benzenetetracarboxylic acid, 1,2,11,12-dodecanetetracarboxylic acid, 1,2,5,6-hexanetetracarboxylic acid, 1,2,7,8-octanetetracarboxylic acid, 1,4,5,8-naphthalenetetracarboxylic acid, 1,2,9,10-decanetetracarboxylic acid, benzophenonetetracarboxylic acid, 3,3',4,4'-benzophenonetetracarboxylic acid, tetrahydrofurantetracarboxylic acid or cyclopentanetetracarboxylic acids such as cyclopentane-1,2,3,4-tetracarboxylic acid.

Furthermore, the at least bidentate organic compound is more preferably one of the tetracarboxylic acids mentioned by way of example above as such.

Preferred heterocycles as at least bidentate organic compound in which a coordinate bond is formed via the ring heteroatoms are the following substituted or unsubstituted ring systems:



Very particular preference is given to using optionally at least monosubstituted aromatic dicarboxylic, tricarboxylic or tetracarboxylic acids which can have one, two, three, four or more rings, with each of the rings being able to comprises at least one heteroatom and two or more rings being able to comprise identical or different heteroatoms. For example preference is given to one-ring dicarboxylic acids, one-ring tricarboxylic acids, one-ring tetracarboxylic acids, two-ring dicarboxylic acids, two-ring tricarboxylic acids, two-ring tetracarboxylic acids, three-ring dicarboxylic acids, three-ring tricarboxylic acids, three-ring tetracarboxylic acids, four-ring dicarboxylic acids, four-ring tricarboxylic acids and/or four-ring tetracarboxylic acids. Suitable heteroatoms are, for example, N, O, S, B, P, and preferred heteroatoms are N, S and/or O. Suitable substituents here are, inter alia, -OH, a nitro group, an amino group or an alkyl or alkoxy group.

Particularly preferred at least bidentate organic compounds are imidazolates such as 2-methylimidazolate, acetylenedicarboxylic acid (ADC), camphordicarboxylic acid, fumaric acid, succinic acid, benzenedicarboxylic acids such as phthalic acid, isophthalic acid, terephthalic acid (BDC), aminoterephthalic acid, triethylenediamine

(TEDA), methylglycinediacetic acid (MGDA), naphthalenedicarboxylic acids (NDC), biphenyldicarboxylic acids such as 4,4'-biphenyldicarboxylic acid (BPDC), pyrazinedicarboxylic acids such as 2,5-pyrazinedicarboxylic acid, bipyridinedicarboxylic acids such as 2,2'-bipyridinedicarboxylic acids such as 2,2'-bipyridine-5,5'-dicarboxylic acid, benzenetricarboxylic acids such as 1,2,3-, 1,2,4-benzenetricarboxylic acid or 1,3,5-benzenetricarboxylic acid (BTC), benzenetetracarboxylic acid, adamantanetetracarboxylic acid (ATC), adamantanedibenzoate (ADB), benzenetribenzoate (BTB), methanetetrabenzoate (MTB), adamantanetetrabenzoate or dihydroxyterephthalic acids such as 2,5-dihydroxyterephthalic acid (DHBDC), tetrahydropyrene-2,7-dicarboxylic acid (HPDC), biphenyltetracarboxylic acid (BPTC), 1,3-bis(4-pyridyl)propane (BPP).

Very particular preference is given to using, inter alia, 2-methylimidazole, 2-ethylimidazole, phthalic acid, isophthalic acid, terephthalic acid, 2,6-naphthalenedicarboxylic acid, 1,4-naphthalenedicarboxylic acid, 1,5-naphthalene-dicarboxylic acid, 1,2,3-benzenetricarboxylic acid, 1,2,4-benzenetricarboxylic acid, 1,3,5-benzenetricarboxylic acid, 1,2,4,5-benzenetetracarboxylic acid, aminoBDC, TEDA, fumaric acid, biphenyldicarboxylate, 1,5- and 2,6-naphthalenedicarboxylic acid, tert-butylisophthalic acid, dihydroxybenzoic acid, BTB, HPDC, BPTC, BPP.

Apart from these at least bidentate organic compounds, the metal-organic framework can also comprise one or more monodentate ligands and/or one or more at least bidentate ligands which are not derived from a dicarboxylic, tricarboxlic or tetracarboxylic acid.

Apart from these at least bidentate organic compounds, the metal-organic framework can also comprise one or more monodentate iigands.

Preferred at least bidentate organic compounds are formic acid, acetic acid or an aliphatic dicarboxylic or polycarboxylic acid, for example malonic acid, fumaric acid or the like, in particular fumaric acid, or are derived from these.

For the purposes of the present invention, the term “derived” means that the at least one at least bidentate organic compound is present in partially or fully deprotonated form. Furthermore, the term “derived” means that the at least one at least bidentate organic compound can have further substituents. Thus, a dicarboxylic or polycarboxylic acid can have not only the carboxylic acid function but also one or more independent substituents such as amino, hydroxyl, methoxy, halogen or methyl groups. Preference is given to no further substituent being present. For the purposes of the present invention, the term “derived” also means that the carboxylic acid function can be present as a sulfur analogue. Sulfur analogues are –C(=O)SH and its tautomer and -C(S)SH.

Suitable solvents for preparing the metal-organic framework are, inter alia, ethanol, dimethylformamide, toluene, methanol, chlorobenzene, diethylformamide, dimethyl sulfoxide, water, hydrogen peroxide, methylamine, sodium hydroxide solution, N-methylpyrrolidone ether, acetonitrile, benzyl chloride, triethylamine, ethylene glycol and mixtures thereof. Further metal ions, at least bidentate organic compounds and solvents for the preparation of MOFs are described, inter alia, in US-A 5,648,508 or DE-A 101 11 230.

The pore size of the metal-organic framework can be controlled by selection of the appropriate ligand and/or the at least bidentate organic compound. In general, the larger the organic compound, the larger the pore size. The pore size is preferably from 0.2 nm to 30 nm, particularly preferably in the range from 0.3 nm to 3 nm, based on the crystalline material.

Examples of metal-organic frameworks are given below. In addition to the designation of the framework, the metal and the at least bidentate ligand, the solvent and the cell parameters (angles α, β and γ and the dimensions A, B and C in Å) are also indicated. The latter were determined by X-ray diffraction.

MOF-n	**Constituents molar ratio M+L**	**Solvents**	**α**	**β**	**γ**	**a**	**b**	**c**	**Space group**
MOF-0	$Zn(NO_3)_2{\cdot}6H_2O$ H_3(BTC)	ethanol	90	90	120	16.711	16.711	14.189	P6(3)/ Mcm
MOF-2	$Zn(NO_3)_2{\cdot}6H_2O$ (0.246 mmol) H_2(BDC) 0.241 mmol)	DMF toluene	90	102.8	90	6.718	15.49	12.43	P2(1)/n
MOF-3	$Zn(NO_3)_2{\cdot}6H_2O$ (1.89 mmol) H_2(BDC) (1.93 mmol)	DMF MeOH	99.72	111.11	108.4	9.726	9.911	10.45	P-1
MOF-4	$Zn(NO_3)_2{\cdot}6H_2O$ (1.00 mmol) H_3(BTC) (0.5 mmol)	ethanol	90	90	90	14.728	14.728	14.728	P2(1)3
MOF-5	$Zn(NO_3)_2{\cdot}6H_2O$ (2.22 mmol) H_2(BDC) (2.17 mmol)	DMF chloro-benzene	90	90	90	25.669	25.669	25.669	Fm-3m

MOF-38	$Zn(NO_3)_2{\cdot}6H_2O$ (0.27 mmol) $H_3(BTC)$ (0.15 mmol)	DMF chloro-benzene	90	90	90	20.657	20.657	17.84	I4cm

MOF-31 $Zn(ADC)_2$	$Zn(NO_3)_2{\cdot}6H_2O$ 0.4 mmol $H_2(ADC)$ 0.8 mmol	ethanol	90	90	90	10.821	10.821	10.821	Pn(-3)m
MOF-12 $Zn_2(ATC)$	$Zn(NO_3)_2{\cdot}6H_2O$ 0.3 mmol $H_4(ATC)$ 0.15 mmol	ethanol	90	90	90	15.745	16.907	18.167	Pbca
MOF-20 ZnNDC	$Zn(NO_3)_2{\cdot}6H_2O$ 0.37 mmol H_2NDC 0.36 mmol	DMF chloro-benzene	90	92.13	90	8.13	16.444	12.807	P2(1)/c
MOF-37	$Zn(NO_3)_2{\cdot}6H_2O$ 0.2 mmol H_2NDC 0.2 mmol	DEF chloro-benzene	72.38	83.16	84.33	9.952	11.576	15.556	P-1
MOF-8 Tb_2 (ADC)	$Tb(NO_3)_3{\cdot}5H_2O$ 0.10 mmol H_2ADC 0.20 mmol	DMSO MeOH	90	115.7	90	19.83	9.822	19.183	C2/c
MOF-9 Tb_2 (ADC)	$Tb(NO_3)_3{\cdot}5H_2O$ 0.08 mmol H_2ADB 0.12 mmol	DMSO	90	102.09	90	27.056	16.795	28.139	C2/c
MOF-6	$Tb(NO_3)_3{\cdot}5H_2O$ 0.30 mmol H_2 (BDC) 0.30 mmol	DMF MeOH	90	91.28	90	17.599	19.996	10.545	P21/c
MOF-7	$Tb(NO_3)_3{\cdot}5H_2O$ 0.15 mmol $H_2(BDC)$ 0.15 mmol	H_2O	102.3	91.12	101.5	6.142	10.069	10.096	P-1
MOF-69A	$Zn(NO_3)_2{\cdot}6H_2O$ 0.083 mmol 4,4'BPDC 0.041 mmol	DEF H_2O_2 $MeNH_2$	90	111.6	90	23.12	20.92	12	C2/c
MOF-69B	$Zn(NO_3)_2{\cdot}6H_2O$ 0.083 mmol 2,6-NCD 0.041 mmol	DEF H_2O_2 $MeNH_2$	90	95.3	90	20.17	18.55	12.16	C2/c
MOF-11 $Cu_2(ATC)$	$Cu(NO_3)_2{\cdot}2.5H_2O$ 0.47 mmol H_2ATC 0.22 mmol	H_2O	90	93.86	90	12.987	11.22	11.336	C2/c
MOF-11			90	90	90	8.4671	8.4671	14.44	P42/

Cu_2(ATC) dehydr.									mmc
MOF-14 Cu_3 (BTB)	$Cu(NO_3)_2 \cdot 2.5H_2O$ 0.28 mmol H_3BTB 0.052 mmol	H_2O DMF EtOH	90	90	90	26.946	26.946	26.946	Im-3
MOF-32 Cd(ATC)	$Cd(NO_3)_2 \cdot 4H_2O$ 0.24 mmol H_4ATC 0.10 mmol	H_2O NaOH	90	90	90	13.468	13.468	13.468	P(-4)3m
MOF-33 Zn_2 (ATB)	$ZnCl_2$ 0.15 mmol H_4ATB 0.02 mmol	H_2O DMF EtOH	90	90	90	19.561	15.255	23.404	Imma
MOF-34 Ni(ATC)	$Ni(NO_3)_2 \cdot 6H_2O$ 0.24 mmol H_4ATC 0.10 mmol	H_2O NaOH	90	90	90	10.066	11.163	19.201	$P2_12_12_1$
MOF-36 Zn_2 (MTB)	$Zn(NO_3)_2 \cdot 4H_2O$ 0.20 mmol H_4MTB 0.04 mmol	H_2O DMF	90	90	90	15.745	16.907	18.167	Pbca
MOF-39 Zn_3O(HBTB)	$Zn(NO_3)_2$ $4H_2O$ 0.27 mmol H_3BTB 0.07 mmol	H_2O DMF EtOH	90	90	90	17.158	21.591	25.308	Pnma
NO305	$FeCl_2 \cdot 4H_2O$ 5.03 mmol formic acid 86.90 mmol	DMF	90	90	120	8.2692	8.2692	63.566	R-3c
NO306A	$FeCl_2 \cdot 4H_2O$ 5.03 mmol formic acid. 86.90 mmol	DEF	90	90	90	9.9364	18.374	18.374	Pbcn
NO29 MOF-0 similar	$Mn(Ac)_2 \cdot 4H_2O$ 0.46 mmol H_3BTC 0.69 mmol	DMF	120	90	90	14.16	33.521	33.521	P-1
BPR48 A2	$Zn(NO_3)_2$ $6H_2O$ 0.012 mmol H_2BDC 0.012 mmol	DMSO toluene	90	90	90	14.5	17.04	18.02	Pbca
BPR69 B1	$Cd(NO_3)_2$ $4H_2O$ 0.0212 mmol H_2BDC 0.0428 mmol	DMSO	90	98.76	90	14.16	15.72	17.66	Cc
BPR92 A2	$Co(NO_3)_2 \cdot 6H_2O$ 0.018 mmol	NMP	106.3	107.63	107.2	7.5308	10.942	11.025	P1

	H_2BDC 0.018 mmol								
BPR95 C5	$Cd(NO_3)_2$ $4H_2O$ 0.012 mmol H_2BDC 0.36 mmol	NMP	90	112.8	90	14.460	11.085	15.829	P2(1)/n
Cu $C_6H_4O_6$	$Cu(NO_3)_2{\cdot}2.5H_2O$ 0.370 mmol $H_2BDC(OH)_2$ 0.37 mmol	DMF chloro- benzene	90	105.29	90	15.259	14.816	14.13	P2(1)/c
M(BTC) MOF-0 similar	$Co(SO_4)$ H_2O 0.055 mmol H_3BTC 0.037 mmol	DMF	like MOF-0						
$Tb(C_6H_4O_6)$	$Tb(NO_3)_3{\cdot}5H_2O$ 0.370 mmol $H_2(C_6H_4O_6)$ 0.56 mmol	DMF chloro- benzene	104.6	107.9	97.147	10.491	10.981	12.541	P-1
Zn (C_2O_4)	$ZnCl_2$ 0.370 mmol oxalic acid 0.37 mmol	DMF chloro- benzene	90	120	90	9.4168	9.4168	8.464	P(-3)1m
Co(CHO)	$Co(NO_3)_2{\cdot}5H_2O$ 0.043 mmol formic acid 1.60 mmol	DMF	90	91.32	90	11.328	10.049	14.854	P2(1)/n
Cd(CHO)	$Cd(NO_3)_2{\cdot}4H_2O$ 0.185 mmol formic acid 0.185 mmol	DMF	90	120	90	8.5168	8.5168	22.674	R-3c
$Cu(C_3H_2O_4)$	$Cu(NO_3)_2{\cdot}2.5H_2O$ 0.043 mmol malonic acid 0.192 mmol	DMF	90	90	90	8.366	8.366	11.919	P43
Zn_6 $(NDC)_5$ MOF-48	$Zn(NO_3)_2{\cdot}6H_2O$ 0.097 mmol 14 NDC 0.069 mmol	DMF chloro- benzene H_2O_2	90	95.902	90	19.504	16.482	14.64	C2/m
MOF-47	$Zn(NO_3)_2$ $6H_2O$ 0.185 mmol $H_2(BDC[CH_3]_4)$ 0.185 mmol	DMF chloro- benzene H_2O_2	90	92.55	90	11.303	16.029	17.535	P2(1)/c
MO25	$Cu(NO_3)_2{\cdot}2.5H_2O$ 0.084 mmol BPhDC 0.085 mmol	DMF	90	112.0	90	23.880	16.834	18.389	P2(1)/c
Cu-Thio	$Cu(NO_3)_2{\cdot}2.5H_2O$ 0.084 mmol	DEF	90	113.6	90	15.474 7	14.514	14.032	P2(1)/c

	thiophene dicarboxylic acid 0.085 mmol								
ClBDC1	$Cu(NO_3)_2 \cdot 2.5H_2O$0.084 mmol $H_2(BDCCl_2)$ 0.085 mmol	DMF	90	105.6	90	14.911	15.622	18.413	C2/c
MOF-101	$Cu(NO_3)_2 \cdot 2.5H_2O$ 0.084 mmol BrBDC 0.085 mmol	DMF	90	90	90	21.607	20.607	20.073	Fm3m
$Zn_3(BTC)_2$	$ZnCl_2$ 0.033 mmol H_3BTC 0.033 mmol	DMF EtOH Base added	90	90	90	26.572	26.572	26.572	Fm-3m
MOF-j	$Co(CH_3CO_2)_2 \cdot 4H_2O$ (1.65 mmol) $H_3(BZC)$ (0.95 mmol)	H_2O	90	112.0	90	17.482	12.963	6.559	C2
MOF-n	$Zn(NO_3)_2 \cdot 6H_2O$ H_3 (BTC)	ethanol	90	90	120	16.711	16.711	14.189	P6(3)/mcm
PbBDC	$Pb(NO_3)_2$ (0.181 mmol) $H_2(BDC)$ (0.181 mmol)	DMF ethanol	90	102.7	90	8.3639	17.991	9.9617	P2(1)/n
Znhex	$Zn(NO_3)_2 \cdot 6H_2O$ (0.171 mmol) H_3BTB (0.114 mmol)	DMF p-xylene ethanol	90	90	120	37.1165	37.117	30.019	P3(1)c
AS16	$FeBr_2$ 0.927 mmol $H_2(BDC)$ 0.927 mmol	DMF anhydr.	90	90.13	90	7.2595	8.7894	19.484	P2(1)c
AS27-2	$FeBr_2$ 0.927 mmol $H_3(BDC)$ 0.464 mmol	DMF anhydr.	90	90	90	26.735	26.735	26.735	Fm3m
AS32	$FeCl_3$ 1.23 mmol $H_2(BDC)$ 1.23 mmol	DMF anhydr. ethanol	90	90	120	12.535	12.535	18.479	P6(2)c
AS54-3	$FeBr_2$ 0.927 BPDC 0.927 mmol	DMF anhydr. n-propanol	90	109.98	90	12.019	15.286	14.399	C2
AS61-4	$FeBr_2$ 0.927 mmol m-BDC 0.927 mmol	anhydrous pyridine	90	90	120	13.017	13.017	14.896	P6(2)c
AS68-7	$FeBr_2$ 0.927 mmol m-BDC	DMF anhydr. pyridine	90	90	90	18.3407	10.036	18.039	$Pca2_1$

	1.204 mmol								
Zn(ADC)	$Zn(NO_3)_2 \cdot 6H_2O$ 0.37 mmol H_2(ADC) 0.36 mmol	DMF chloro-benzene	90	99.85	90	16.764	9.349	9.635	C2/c
MOF-12 Zn_2 (ATC)	$Zn(NO_3)_2 \cdot 6H_2O$ 0.30 mmol H_4(ATC) 0.15 mmol	ethanol	90	90	90	15.745	16.907	18.167	Pbca
MOF-20 ZnNDC	$Zn(NO_3)_2 \cdot 6H_2O$ 0.37 mmol H_2NDC 0.36 mmol	DMF chloro-benzene	90	92.13	90	8.13	16.444	12.807	P2(1)/c
MOF-37	$Zn(NO_3)_2 \cdot 6H_2O$ 0.20 mmol H_2NDC 0.20 mmol	DEF chloro-benzene	72.38	83.16	84.33	9.952	11.576	15.556	P-1
Zn(NDC) (DMSO)	$Zn(NO_3)_2 \cdot 6H_2O$ H_2NDC	DMSO	68.08	75.33	88.31	8.631	10.207	13.114	P-1
Zn(NDC)	$Zn(NO_3)_2 \cdot 6H_2O$ H_2NDC		90	99.2	90	19.289	17.628	15.052	C2/c
Zn(HPDC)	$Zn(NO_3)_2 \cdot 4H_2O$ 0.23 mmol H_2(HPDC) 0.05 mmol	DMF H_2O	107.9	105.06	94.4	8.326	12.085	13.767	P-1
Co(HPDC)	$Co(NO_3)_2 \cdot 6H_2O$ 0.21 mmol H_2 (HPDC) 0.06 mmol	DMF H_2O/ ethanol	90	97.69	90	29.677	9.63	7.981	C2/c
Zn_3(PDC)2.5	$Zn(NO_3)_2 \cdot 4H_2O$ 0.17 mmol H_2(HPDC) 0.05 mmol	DMF/ CIBz H_20/ TEA	79.34	80.8	85.83	8.564	14.046	26.428	P-1
Cd_2 (TPDC)2	$Cd(NO_3)_2 \cdot 4H_2O$ 0.06 mmol H_2(HPDC) 0.06 mmol	methanol/ CHP H_2O	70.59	72.75	87.14	10.102	14.412	14.964	P-1
Tb(PDC)1.5	$Tb(NO_3)_3 \cdot 5H_2O$ 0.21 mmol H_2(PDC) 0.034 mmol	DMF H_2O/ ethanol	109.8	103.61	100.14	9.829	12.11	14.628	P-1

ZnDBP	$Zn(NO_3)_2 \cdot 6H_2O$ 0.05 mmol dibenzyl phosphate 0.10 mmol	MeOH	90	93.67	90	9.254	10.762	27.93	P2/n
Zn_3(BPDC)	$ZnBr_2$ 0.021 mmol 4,4'BPDC	DMF	90	102.76	90	11.49	14.79	19.18	P21/n

	0.005 mmol								
CdBDC	$Cd(NO_3)_2 \cdot 4H_2O$ 0.100 mmol H_2(BDC) 0.401 mmol	DMF Na_2SiO_3 (aq)	90	95.85	90	11.2	11.11	16.71	P21/n
Cd-mBDC	$Cd(NO_3)_2 \cdot 4H_2O$ 0.009 mmol H_2(mBDC) 0.018 mmol	DMF $MeNH_2$	90	101.1	90	13.69	18.25	14.91	C2/c
Zn_4OBNDC	$Zn(NO_3)_2 \cdot 6H_2O$ 0.041 mmol BNDC	DEF $MeNH_2$ H_2O_2	90	90	90	22.35	26.05	59.56	Fmmm
Eu(TCA)	$Eu(NO_3)_3 \cdot 6H_2O$ 0.14 mmol TCA 0.026 mmol	DMF chloro-benzene	90	90	90	23.325	23.325	23.325	Pm-3n
Tb(TCA)	$Tb(NO_3)_3 \cdot 6H_2O$ 0.069 mmol TCA 0.026 mmol	DMF chloro-benzene	90	90	90	23.272	23.272	23.372	Pm-3n
Formate	$Ce(NO_3)_3 \cdot 6H_2O$ 0.138 mmol formic acid 0.43 mmol	H_2O ethanol	90	90	120	10.668	10.667	4.107	R-3m
	$FeCl_2 \cdot 4H_2O$ 5.03 mmol formic acid 86.90 mmol	DMF	90	90	120	8.2692	8.2692	63.566	R-3c
	$FeCl_2 \cdot 4H_2O$ 5.03 mmol formic acid 86.90 mmol	DEF	90	90	90	9.9364	18.374	18.374	Pbcn
	$FeCl_2 \cdot 4H_2O$ 5.03 mmol formic acid 86.90 mmol	DEF	90	90	90	8.335	8.335	13.34	P-31c
NO330	$FeCl_2 \cdot 4H_2O$ 0.50 mmol formic acid 8.69 mmol	form-amide	90	90	90	8.7749	11.655	8.3297	Pnna
NO332	$FeCl_2 \cdot 4H_2O$ 0.50 mmol formic acid 8.69 mmol	DIP	90	90	90	10.0313	18.808	18.355	Pbcn

NO333	$FeCl_2 \cdot 4H_2O$ 0.50 mmol formic acid 8.69 mmol	DBF	90	90	90	45.275 4	23.861	12.441	Cmcm
NO335	$FeCl_2 \cdot 4H_2O$ 0.50 mmol formic acid 8.69 mmol	CHF	90	91.372	90	11.596 4	10.187	14.945	P21/n
NO336	$FeCl_2 \cdot 4H_2O$ 0.50 mmol formic acid 8.69 mmol	MFA	90	90	90	11.794 5	48.843	8.4136	Pbcm
NO13	$Mn(Ac)_2 \cdot 4H_2O$ 0.46 mmol benzoic acid 0.92 mmol bipyridine 0.46 mmol	ethanol	90	90	90	18.66	11.762	9.418	Pbcn
NO29 MOF-0 similar	$Mn(Ac)_2 \cdot 4H_2O$ 0.46 mmol H_3BTC 0.69 mmol	DMF	120	90	90	14.16	33.521	33.521	P-1
$Mn(hfac)_2$ $(O_2CC_6H_5)$	$Mn(Ac)_2 \cdot 4H_2O$ 0.46 mmol Hfac 0.92 mmol bipyridine 0.46 mmol	ether	90	95.32	90	9.572	17.162	14.041	C2/c
BPR43G2	$Zn(NO_3)_2 \cdot 6H_2O$ 0.0288 mmol H_2BDC 0.0072 mmol	DMF CH_3CN	90	91.37	90	17.96	6.38	7.19	C2/c
BPR48A2	$Zn(NO_3)_2$ $6H_2O$ 0.012 mmol H_2BDC 0.012 mmol	DMSO toluene	90	90	90	14.5	17.04	18.02	Pbca
BPR49B1	$Zn(NO_3)_2$ $6H_2O$ 0.024 mmol H_2BDC 0.048 mmol	DMSO methanol	90	91.172	90	33.181	9.824	17.884	C2/c
BPR56E1	$Zn(NO_3)_2$ $6H_2O$ 0.012 mmol H_2BDC 0.024 mmol	DMSO n-propanol	90	90.096	90	14.587 3	14.153	17.183	P2(1)/n
BPR68D10	$Zn(NO_3)_2$ $6H_2O$ 0.0016 mmol H_3BTC 0.0064 mmol	DMSO benzene	90	95.316	90	10.062 7	10.17	16.413	P2(1)/c
BPR69B1	$Cd(NO_3)_2$ $4H_2O$ 0.0212 mmol H_2BDC	DMSO	90	98.76	90	14.16	15.72	17.66	Cc

	0.0428 mmol								
BPR73E4	$Cd(NO_3)_2$ $4H_2O$ 0.006 mmol H_2BDC 0.003 mmol	DMSO toluene	90	92.324	90	8.7231	7.0568	18.438	P2(1)/n
BPR76D5	$Zn(NO_3)_2$ $6H_2O$ 0.0009 mmol H_2BzPDC 0.0036 mmol	DMSO	90	104.17	90	14.4191	6.2599	7.0611	Pc
BPR80B5	$Cd(NO_3)_2{\cdot}4H_2O$ 0.018 mmol H_2BDC 0.036 mmol	DMF	90	115.11	90	28.049	9.184	17.837	C2/c
BPR80H5	$Cd(NO_3)_2$ $4H_2O$ 0.027 mmol H_2BDC 0.027 mmol	DMF	90	119.06	90	11.4746	6.2151	17.268	P2/c
BPR82C6	$Cd(NO_3)_2$ $4H_2O$ 0.0068 mmol H_2BDC 0.202 mmol	DMF	90	90	90	9.7721	21.142	27.77	Fdd2
BPR86C3	$Co(NO_3)_2$ $6H_2O$ 0.0025 mmol H_2BDC 0.075 mmol	DMF	90	90	90	18.3449	10.031	17.983	Pca2(1)
BPR86H6	$Cd(NO_3)_2{\cdot}6H_2O$ 0.010 mmol H_2BDC 0.010 mmol	DMF	80.98	89.69	83.41 2	9.8752	10.263	15.362	P-1
	$Co(NO_3)_2$ $6H_2O$	NMP	106.3	107.63	107.2	7.5308	10.942	11.025	P1
BPR95A2	$Zn(NO_3)_2$ $6H_2O$ 0.012 mmol H_2BDC 0.012 mmol	NMP	90	102.9	90	7.4502	13.767	12.713	P2(1)/c
$CuC_6F_4O_4$	$Cu(NO_3)_2{\cdot}2.5H_2O$ 0.370 mmol $H_2BDC(OH)_2$ 0.37 mmol	DMF chloro-benzene	90	98.834	90	10.9675	24.43	22.553	P2(1)/n
Fe Formic	$FeCl_2{\cdot}4H_2O$ 0.370 mmol formic acid 0.37 mmol	DMF	90	91.543	90	11.495	9.963	14.48	P2(1)/n
Mg Formic	$Mg(NO_3)_2{\cdot}6H_2O$ 0.370 mmol formic acid 0.37 mmol	DMF	90	91.359	90	11.383	9.932	14.656	P2(1)/n
$MgC_6H_4O_6$	$Mg(NO_3)_2{\cdot}6H_2O$	DMF	90	96.624	90	17.245	9.943	9.273	C2/c

	0.370 mmol $H_2BDC(OH)_2$ 0.37 mmol								
Zn C_2H_4BDC MOF-38	$ZnCl_2$ 0.44 mmol CBBDC 0.261 mmol	DMF	90	94.714	90	7.3386	16.834	12.52	P2(1)/n
MOF-49	$ZnCl_2$ 0.44 mmol m-BDC 0.261 mmol	DMF CH_3CN	90	93.459	90	13.509	11.984	27.039	P2/c
MOF-26	$Cu(NO_3)_2{\cdot}5H_2O$ 0.084 mmol DCPE 0.085 mmol	DMF	90	95.607	90	20.8797	16.017	26.176	P2(1)/n

MOF-112	$Cu(NO_3)_2{\cdot}2.5H_2O$ 0.084 mmol *o*-Br-*m*-BDC 0.085 mmol	DMF ethanol	90	107.49	90	29.3241	21.297	18.069	C2/c
MOF-109	$Cu(NO_3)_2{\cdot}2.5H_2O$ 0.084 mmol KDB 0.085 mmol	DMF	90	111.98	90	23.8801	16.834	18.389	P2(1)/c
MOF-111	$Cu(NO_3)_2{\cdot}2.5H_2O$ 0.084 mmol o-BrBDC 0.085 mmol	DMF ethanol	90	102.16	90	10.6767	18.781	21.052	C2/c
MOF-110	$Cu(NO_3)_2{\cdot}2.5H_2O$ 0.084 mmol thiophene dicarboxylic acid 0.085 mmol	DMF	90	90	120	20.0652	20.065	20.747	R-3/m
MOF-107	$Cu(NO_3)_2{\cdot}2.5H_2O$ 0.084 mmol thiophene dicarboxylic acid. 0.085 mmol	DEF	104.8	97.075	95.206	11.032	18.067	18.452	P-1
MOF-108	Cu(NO3)2·2.5H2O 0.084 mmol thiophene dicarboxylic acid 0.085 mmol	DBF/ methanol	90	113.63	90	15.4747	14.514	14.032	C2/c
MOF-102	Cu(NO3)2·2.5H2O 0.084 mmol H2(BDCCl2) 0.085 mmol	DMF	91.63	106.24	112.01	9.3845	10.794	10.831	P-1
Clbdc1	Cu(NO3)2·2.5H2O 0.084 mmol H2(BDCCl2) 0.085 mmol	DEF	90	105.56	90	14.911	15.622	18.413	P-1
Cu(NMOP)	Cu(NO3)2·2.5H2O 0.084 mmol NBDC 0.085 mmol	DMF	90	102.37	90	14.9238	18.727	15.529	P2(1)/m

Tb(BTC)	Tb(NO3)3·5H2O 0.033 mmol H3BTC 0.033 mmol	DMF	90	106.02	90	18.6986	11.368	19.721	
Zn3(BTC)2 Honk	ZnCl2 0.033 mmol H3BTC 0.033 mmol	DMF ethanol	90	90	90	26.572	26.572	26.572	Fm-3m
Zn4O(NDC)	Zn(NO3)2·4H2O 0.066 mmol 14NDC 0.066 mmol	DMF ethanol	90	90	90	41.5594	18.818	17.574	aba2
CdTDC	Cd(NO3)2·4H2O 0.014 mmol thiophene 0.040 mmol DABCO 0.020 mmol	DMF H2O	90	90	90	12.173	10.485	7.33	Pmma
IRMOF-2	Zn(NO3)2·4H2O 0.160 mmol o-Br-BDC 0.60 mmol	DEF	90	90	90	25.772	25.772	25.772	Fm-3m
IRMOF-3	Zn(NO3)2·4H2O 0.20 mmol H2N-BDC 0.60 mmol	DEF ethanol	90	90	90	25.747	25.747	25.747	Fm-3m
IRMOF-4	Zn(NO3)2·4H2O 0.11 mmol [C3H7O]2-BDC 0.48 mmol	DEF	90	90	90	25.849	25.849	25.849	Fm-3m
IRMOF-5	Zn(NO3)2·4H2O 0.13 mmol [C5H11O]2-BDC 0.50 mmol	DEF	90	90	90	12.882	12.882	12.882	Pm-3m
IRMOF-6	Zn(NO3)2·4H2O 0.20 mmol [C2H4]-BDC 0.60 mmol	DEF	90	90	90	25.842	25.842	25.842	Fm-3m
IRMOF-7	Zn(NO3)2·4H2O 0.07 mmol 1,4NDC 0.20 mmol	DEF	90	90	90	12.914	12.914	12.914	Pm-3m
IRMOF-8	Zn(NO3)2·4H2O 0.55 mmol 2,6NDC 0.42 mmol	DEF	90	90	90	30.092	30.092	30.092	Fm-3m
IRMOF-9	Zn(NO3)2·4H2O 0.05 mmol BPDC 0.42 mmol	DEF	90	90	90	17.147	23.322	25.255	Pnnm
IRMOF-10	Zn(NO3)2·4H2O	DEF	90	90	90	34.281	34.281	34.281	Fm-3m

	0.02 mmol BPDC 0.012 mmol								
IRMOF-11	Zn(NO3)2·4H2O 0.05 mmol HPDC 0.20 mmol	DEF	90	90	90	24.822	24.822	56.734	R-3m
IRMOF-12	Zn(NO3)2·4H2O 0.017 mmol HPDC 0.12 mmol	DEF	90	90	90	34.281	34.281	34.281	Fm-3m
IRMOF-13	$Zn(NO_3)_2·4H_2O$ 0.048 mmol PDC 0.31 mmol	DEF	90	90	90	24.822	24.822	56.734	R-3m
IRMOF-14	$Zn(NO_3)_2·4H_2O$ 0.17 mmol PDC 0.12 mmol	DEF	90	90	90	34.381	34.381	34.381	Fm-3m
IRMOF-15	$Zn(NO_3)_2·4H_2O$ 0.063 mmol TPDC 0.025 mmol	DEF	90	90	90	21.459	21.459	21.459	Im-3m
IRMOF-16	$Zn(NO_3)_2·4H_2O$ 0.0126 mmol TPDC 0.05 mmol	DEF NMP	90	90	90	21.49	21.49	21.49	Pm-3m

ADC acetylenedicarboxylic acid
NDC naphthalenedicarboxylic acid
BDC benzenedicarboxylic acid
ATC adamantanetetracarboxylic acid
BTC benzenetricarboxylic acid
BTB benzenetribenzoic acid
MTB methanetetrabenzoic acid
ATB adamantanetetrabenzoic acid
ADB adamantanedibenzoic acid

Further metal-organic frameworks are MOF-2 to 4, MOF-9, MOF-31 to 36, MOF-39, MOF-69 to 80, MOF103 to 106, MOF-122, MOF-125, MOF-150, MOF-177, MOF-178, MOF-235, MOF-236, MOF-500, MOF-501, MOF-502, MOF-505, IRMOF-1, IRMOF-61, IRMOP-13, IRMOP-51, MIL-17, MIL-45, MIL-47, MIL-53, MIL-59, MIL-60, MIL-61, MIL-

63, MIL-68, MIL-79, MIL-80, MIL-83, MIL-85, CPL-1 to 2, SZL-1, which are described in the literature.

Particularly preferred metal-organic frameworks are MIL-53, Zn-tBu-isophthalic acid, Al-BDC, MOF-5, MOF-177, MOF-505, IRMOF-8, IRMOF-11, Cu-BTC, Al-NDC, Al-aminoBDC, Cu-BDC-TEDA, Zn-BDC-TEDA, Al-BTC, Cu-BTC, Al-NDC, Mg-NDC, Al-fumarate, Zn-2-methylimidazolate, Zn-2-aminoimidazolate, Cu-biphenyldicarboxylate-TEDA, MOF-74, Cu-BPP, Sc-terephthalate. Greater preference is given to Sc-terephthalate, Al-BDC and Al-BTC. In particular, however, preference is given to Mg-formate, Mg-acetate and mixtures thereof because of their environmental friendliness. Aluminum-fumarate is particularly preferred.

The layer of the porous metal-organic framework preferably has a mass in the range from 0.1 g/m^2 to 100 g/m^2, more preferably from 1 g/m^2 to 80 g/m^2, even more preferably from 3 g/m^2 to 50 g/m^2.

Examples

The following examples indicate various methods of coating filter paper with aluminum-fumarate MOF by means of direct synthesis.

For all examples, two solutions were produced as described below:
Solution 1: Deionized water (72.7 g) was placed in a vessel and $Al_2(SO_4)_3x18H_2O$ (16.9 g, 25.5 mmol) was dissolved therein with stirring.
Solution 2: Deionized water (87.3 g) was placed in a vessel and NaOH (6.1 g, 152.7 mmol) was dissolved therein with stirring. Fumaric acid (5.9 g, 50.9 mmol) was subsequently added while stirring and the mixture was stirred until a clear solution was formed.

For example 1, filters from Macherey-Nagel (d = 150 mm) were used. Filter papers from Schleicher & Schuell (d = 90-110 mm) were used for example 2. The surface area of the untreated filter papers is ~1-2 m^2/g (specific surface area determined by the Langmuir method (LSA)). The surface areas of the coated papers were determined using a small sample of the filters (~ 100 mg).

In all examples, room temperature is 22°C.

Example 1: Coating of filter papers by spraying-on the solutions in a rotating spraying drum at room temperature

Experimental method:

The filter paper was fixed in the spraying drum by means of adhesive tape and sprayed with solution 1 by means of a pump having a spray head at room temperature and rotation of the drum. After brief drying or in the moist state, solution 2 was sprayed on at room temperature by means of the pump. The filter paper was subsequently dried at room temperature in a jet of compressed air in the rotating drum. Uniform coating with a few flakes at the edge was obtained. The increase in mass of the filters was 1.2-2.3 g. The dried papers were washed 4 times with 10 ml each time of H_2O on a suction filter under a slight water pump vacuum and dried again at room temperature. The filters obtained were activated at 150°C in a vacuum drying oven for 16 hours. XRD analysis of a selected sample displayed, in addition to Ibeta cellulose, a weak peak at 10 2-theta which can be assigned to the aluminum-fumarate MOF. The corresponding surface area was 51 m^2/g LSA.

Example 2: Coating of filter paper by simultaneous spraying-on of the solutions 1 and 2

Experimental method:

The filter paper was suspended and simultaneously sprayed with up to 1 ml of the two solutions (Eco-Spray sprayer and Desaga SG-1 sprayer). The treated filter paper was dried in air at room temperature while suspended. Homogeneous layers having a few small flakes were obtained. The increasing mass of the filters was 80-290 mg. The paper was subsequently washed 4 times with 10 ml each time of H_2O and dried at 100°C in a convection drying oven for 16 hours. 31-279 mg were then detected on the filter papers. This corresponds to from 4.9 to 42 g/m^2. XRD analysis of a selected sample displayed, in addition to Ibeta cellulose, a strong peak at 10 2-theta (crystallinity ~3000) which can be assigned to the aluminum-fumarate MOF.

Example 3: Coating of further support surfaces

10 × 10 cm pieces of a teatowel (90% cotton, 10% linen) **A**, a cotton glove **B**, cellulose cloths (Zewa®) **C**, bandaging waste (viscose) **D** and Basotect **E** (melamine resin foam) were treated in the same way as the filter paper in example 2. The mass taken up after spraying and drying was 770-500 mg. After washing of the samples A to D with water and subsequent drying at room temperature, coatings of 440-580 mg were obtained. This corresponds to from 4.4 to 5.8 g/m². Analysis of all samples displayed, in addition to the signals of the respective material, a peak at 10° (2-theta), which can be assigned to the aluminum-fumarate MOF. The surface areas of the treated materials were 17-22 m²/g LSA.

Claims

1. A process for coating at least part of a surface of a support with a porous metal-organic framework comprising at least one at least bidentate organic compound coordinated to at least one metal ion, which comprises the steps

   (a) spraying of the at least one part of the support surface with a first solution comprising the at least one metal ion;
   (b) spraying of the at least one part of the support surface with a second solution comprising the at least one at least bidentate organic compound,

   where step (b) is carried out before, after or simultaneously with step (a), to form a layer of the porous metal-organic framework.

2. The process according to claim 1, wherein the layer is dried.

3. The process according to claim 2, wherein the layer is dried at at least 150°C.

4. The process according to any of claims 1 to 3, wherein the spraying with the first, the second or with both solutions is carried out in a spraying drum.

5. The process according to any of claims 1 to 4, wherein the first, the second or both solutions are at room temperature.

6. The process according to any of claims 1 to 5, wherein the first, the second or both solutions are aqueous solutions.

7. The process according to any of claims 1 to 6, wherein the support surface is a fibrous or foam surface.

8. The process according to any of claims 1 to 7, wherein the at least one metal ion is selected from the group of metals consisting of Mg, Ca, Al and Zn.

9. The process according to any of claims 1 to 8, wherein the at least one at least bidentate organic compound is derived from a dicarboxylic, tricarboxylic or tetracarboxylic acid.

10. The process according to any of claims 1 to 9, wherein the layer of the porous metal-organic framework has a mass in the range from 0.1 g/m^2 to 100 g/m^2.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2011/055446

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07F; B01D69/-; B01D71/-; B01D39/-; B01J20/-

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNABS, EPODOC, WPI, CNKI, GOOGLE SCHOLAR: MOF?, metal 2d (organic w (framework? or skeleton)), bidentat+, membrane?, film?, layer?, coat???, spray???, support???, carrier?, load???

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CA2704521A1 (BLUECHER GMBH) 07 May 2009(07.05.2009) page 30 line 1 to page 33 line 15 of description	1-10
A	US2004/0081611A1 (BASF A.G. et al.) 29 Apr. 2004(29.04.2004) the whole document	1-10
A	CN101693168A (UNIV. DALIAN TECHNOLOGY) 14 Apr. 2010(14.04.2010) the whole document	1-10
A	CN101890305A (UNIV. DALIAN TECHNOLOGY) 24 Nov. 2010(24.11.2010) the whole document	1-10

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim (S) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&"document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
07 Mar. 2012(07.03.2012)	**12 Apr. 2012 (12.04.2012)**

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/IB2011/055446

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
CA2704521A1	07.05.2009	DE202008000810U1	29.01.2009
		DE102008005218A1	07.05.2009
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CN101693168A	14.04.2010	none	
CN101890305A	24.11.2010	none	

INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB2011/055446

A. CLASSIFICATION OF SUBJECT MATTER

C07F5/06 (2006.01) i

C07F3/06 (2006.01) i

C07F3/04 (2006.01) i

C07F3/02 (2006.01) i