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(54) **PROCESS FOR THE ALKOXYLATION OF  
MONOOLS IN THE PRESENCE OF  
METALLO-ORGANIC FRAMEWORK  
MATERIALS**

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(57) **ABSTRACT**

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The present invention relates to a process for the alkoxylation of a monool with at least one alkoxyating agent to an alkoxyated alcohol wherein a catalyst is employed which comprises a metallo-organic framework material of metal ions and at least bidentate coordinately bound organic ligands.

**PROCESS FOR THE ALKOXYLATION OF  
MONOOLS IN THE PRESENCE OF  
METALLO-ORGANIC FRAMEWORK MATERIALS**

**[0001]** The present invention relates to a process for the alkoxylation of monools in the presence of catalyst systems comprising a porous metallo-organic framework material of metal ions and a coordinately bound organic ligand which is at least bidentate. The invention further encompasses the use of polyoxyalkylene alcohols obtained in the process according to the present invention as tensides and flotation oils.

**[0002]** Polyoxyalkylene alcohols can be prepared e.g. by way of base or acid catalyzed polyaddition of alkaline oxides to polyfunctional organic compounds (starters). Suitable starters are e.g. water, alcohols, acids or amines or mixtures thereof which are selected according to the alcohol to be prepared. The drawback of the known preparation methods is that several elaborate purifying steps are necessary in order to separate the catalyst residue from the reaction product. Furthermore, the processes known in the art result in a mixture of various alkoxylation products, ranging from mono- to polyalkoxylated alcohols.

**[0003]** One object of the invention is to provide a process for the preparation of polyoxyalkylene alcohols from monools which does not show the drawbacks of the processes known in the art. In particular, the thus-obtained polyoxyalkylene alcohols should have a low impurity content, without requiring elaborate purifying steps of the starting materials and/or intermediate products. The process should furthermore not require elaborate purification steps in order to separate the catalyst from the reaction product(s). In particular, the process should give defined alkoxylation products with a defined alkoxylation range.

**[0004]** These objects are solved by a process for the alkoxylation of a monool with at least one alkoxyating agent to a polyoxyalkylene alcohol wherein a catalyst is employed which comprises a metallo-organic framework material of metal ions and at least bidentate coordinately bound organic ligands.

**[0005]** The present invention is drawn towards the alkoxylation of monools which are reacted with an alkoxyating agent, in general an alkylene oxide. Examples for monools which lend themselves for an alkoxylation according to the present invention are known to the person skilled in the art. Examples include monools of linear and branched alkyl groups having 1 to 30, preferably 1 to 20, in particular 1 to 15 carbon atoms, which alkyl groups may carry one or more aryl substituents, of homo- and polynuclear aromatic groups having 4 to 30, preferably 4 to 20, in particular 1 to 10 carbon atoms, which aromatic groups may carry one or more alkyl substituents, and of linear and branched alkenyl groups having 2 to 30, preferably 2 to 20, in particular 2 to 15 carbon atoms and which alkenyl groups may carry one or more aryl substituents. The alkyl, alkenyl and aryl groups may contain one or more hetero atoms in their carbon skeleton, and all said groups may carry one or more substituents other than those named. Examples for hetero atoms include N, O and S. Examples for substituents include halides and pseudohalides.

**[0006]** Preferred alcohols should be liquid at room temperature.

**[0007]** Examples for preferred alcohols include Propylheptanol, Tridecanol H und Tridecanol N.

**[0008]** The alkoxyating agent is in general selected from epoxides having two to 30 carbon atoms and mixtures of two or more thereof. Preferably a linear or branched, cyclic or non-cyclic alkylene oxide having two to 24 C-atoms optionally carrying one or more substituents from the group consisting of aromatic groups, halides, hydroxyl groups, silyl groups, non-cyclic ether and ammonium groups is employed.

**[0009]** For the preferred group of alkylene oxides, the following are cited by way of example: ethylene oxide, 1,2-epoxypropane, 1,2-epoxy-2-methylpropane, 1,2-epoxybutane, 2,3-epoxybutane, 1,2-epoxy-3-methylbutane, 1,2-epoxypentane, 1,2-epoxy-3-methylpentane, 1,2-epoxyhexane, 1,2-epoxyheptane, 1,2-epoxyoctane, 1,2-epoxynonane, 1,2-epoxydecane, 1,2-epoxyundecane, 1,2-epoxydodecane, 1,2-epoxycyclopentane, 1,2-epoxycyclohexane, (2,3-epoxypropyl)benzene, vinyloxirane, 3-phenoxy-1,2-epoxypropane, 2,3-epoxymethyl ether, 2,3-epoxyethyl ether, 2,3-epoxyl isopropyl ether, 2,3-epoxyl-1-propanol, (3,4-epoxybutyl)stearate, 4,5-epoxypentylacetate, 2,3-epoxy propane methacrylate, 2,3-epoxy propane acrylat, glycidylbutyrate, methylglycidate, ethyl-2,3-epoxybutanoate, 4-(trimethylsilyl)butane-1,2-epoxide, 4-(triethylsilyl)butane- 1,2-epoxide, 3-(perfluoromethyl)propane oxide, 3-(perfluoroethyl)propane oxide, 3-(perfluorobutyl)propane oxide, 4-(2,3-epoxypropyl)morpholine, 1-(oxirane-2-ylmethyl)pyrrolidin-2-one, styrene oxide, vinyl oxirane, aliphatic 1,2-alkylene oxides having 5 to 24 C-atoms, cyclopentane oxide, cyclohexane oxide, cyclododecatriane-(1,5,9)-monoxide and mixtures of two or more of the compounds cited.

**[0010]** Particularly preferred in the context of the present invention are ethylene oxide, propylene oxide, 1,2-epoxybutane, 2,3-epoxybutane, 1,2-epoxy-2-methylpropane, styrene oxide, vinyloxirane and any mixtures of two or more of the compounds cited. The most preferred epoxides are ethylene oxide, propylene oxide and mixtures of ethylene oxide with propylene oxide.

**[0011]** The process of preparing an epoxide by epoxidation is hereinafter described in detail by way of example, referring to propylene oxide.

**[0012]** Propylene oxide can be obtained by reacting propylene with oxygen; hydrogen and oxygen; hydrogen peroxide; organic hydroperoxides; or halohydrines, preferably by reacting propylene with hydrogen peroxide, more preferred by reacting propylene with hydrogen peroxide in the presence of a catalyst comprising a zeolitic material, particularly by reacting propylene with hydrogen peroxide in the presence of a catalyst comprising a titanium-containing zeolitic material having CS-1-structure.

**[0013]** It is particularly suitable to use hydrogen peroxide for the epoxidation.

**[0014]** The epoxidation is in principle known from e.g. DE 100 55 652.3 and further patent applications of the present applicant, such as DE 100 32 885.7, DE 100 32 884.9, DE 100 15 246.5, DE 199 36 547.4, DE 199 26 725.1, DE 198 47 629.9, DE 198 35 907.1, DE 197 23 950.1, the content of which fully encompassed in the present application.



[0015] The alkoxylation agent obtained in the epoxidation step may be directly used without further treatment. It is, however, also possible within the present invention that the alkoxylation agent is treated beforehand, e.g. purified. As the purification method, mention can be made of a fine distillation. Suitable processes are e.g. disclosed in EP-B 0 557 116.

[0016] According to the present invention the alkoxylation reaction is carried out in the presence of a catalyst system which comprises a so called metallo-organic framework material.

[0017] Metal-organic framework materials are known as such. They are described in, for example, U.S. Pat. No. 5,648,508, EP-A-0 709 253, M. O'Keeffe et al., *J. Sol. State Chm.*, 152 (2000) p. 3-20, H. Li et al., *Nature* 402 (1999) p. 276 seq., M. Eddaoudi et al., *Topics in Catalysis* 9 (1999) p. 105-111, B. Chen. Et al., *Science* 291 (2001) p. 1021-23. An inexpensive way for the preparation of said materials is disclosed in DE 101 11 230.0. The preparation of isoreticular MoF's is disclosed in WO 02/088148. The content of the above-mentioned publications and applications to which reference is made herein, is fully incorporated in present application.

[0018] The metal-organic framework materials, as used in the present invention, comprise pores, particularly micro- and/or mesopores. Micropores are defined as pores having a diameter of 2 nm or below and mesopores as being pores having a diameter in the range of above 2 nm to 50 nm, respectively, according to the definition given in *Pure Applied Chem.* 45, p. 71 seq., particularly on p. 79 (1976). The presence of the micro- and/or mesopores can be monitored by sorption measurements for determining the capacity of the metal-organic framework materials to take up nitrogen at 77 K according to DIN 66131 and/or DIN 66134. The specific surface areas cited in the context of the present invention are always determined according to DIN 66131 and/or DIN 66134.

[0019] For example, a type-I-form of the isothermal curve indicates the presence of micropores [see, for example, paragraph 4 of M. Eddaoudi et al., *Topics in Catalysis* 9 (1999)]. In a preferred embodiment, the specific surface area, as calculated according to the Langmuir model (DIN 66131, 66134) preferably is above 5 m<sup>2</sup>/g, further preferred above 10 m<sup>2</sup>/g, more preferably above 50 m<sup>2</sup>/g, particularly preferred above 500 m<sup>2</sup>/g and may increase to values of 3000 m<sup>2</sup>/g.

[0020] The metal ions forming the metal-organic framework material employed according to the present invention are preferably selected from the groups Ia, IIa, IIIa, IVa to VIIa and Ib to VIb of the periodic system of the elements. Among these metals, particular reference is made to Mg, Ca, Sr, Ba, Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, 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, more preferably Zn, Cu, Ni, Pd, Pt, Ru, Rh and Co. With respect to the metal ions of the aforementioned elements, particular reference is made to: Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Sc<sup>3+</sup>, Y<sup>3+</sup>, Ti<sup>4+</sup>, Zr<sup>4+</sup>, Hf<sup>4+</sup>, V<sup>4+</sup>, V<sup>3+</sup>, V<sup>2+</sup>, Nb<sup>3+</sup>, Ta<sup>3+</sup>, Cr<sup>3+</sup>, Mo<sup>3+</sup>, W<sup>3+</sup>, Mn<sup>3+</sup>, Mn<sup>2+</sup>, Re<sup>3+</sup>, Re<sup>2+</sup>, Fe<sup>3+</sup>, Fe<sup>2+</sup>, Ru<sup>3+</sup>, Ru<sup>2+</sup>, Os<sup>3+</sup>, Os<sup>2+</sup>, Co<sup>3+</sup>, Co<sup>2+</sup>, Rh<sup>2+</sup>, Rh<sup>+</sup>, Ir<sup>2+</sup>, Ir<sup>+</sup>, Ni<sup>2+</sup>, Ni<sup>+</sup>, Pd<sup>2+</sup>, Pd<sup>+</sup>, Pt<sup>2+</sup>, Pt<sup>+</sup>, Cu<sup>+</sup>, Cu<sup>2+</sup>, Ag<sup>+</sup>, Au<sup>+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, Al<sup>3+</sup>, Ga<sup>3+</sup>, In<sup>3+</sup>, Tl<sup>3+</sup>, Si<sup>4+</sup>, Si<sup>2+</sup>, Ge<sup>4+</sup>, Ge<sup>2+</sup>, Sn<sup>4+</sup>, Sn<sup>2+</sup>, Pb<sup>4+</sup>, Pb<sup>2+</sup>, As<sup>5+</sup>, As<sup>3+</sup>, As<sup>+</sup>, Sb<sup>5+</sup>, Sb<sup>3+</sup>, Sb<sup>+</sup>, Bi<sup>3+</sup> and Bi<sup>+</sup>.

[0021] With regard to the preferred metal ions and further details regarding the same, we particularly refer to: EP-A 0 790 253, particularly p. 10, 1. 8-30, section "The Metal Ions", which section is incorporated herein by reference.

[0022] In addition to the metal salts disclosed in EP-A 0 790 253 and U.S. Pat. No. 5,648,508, other metallic compounds can be used, such as sulfates, phosphates and other complex counter-ion metal salts of the main- and subgroup metals of the periodic system of the elements. Metal oxides, mixed oxides and mixtures of metal oxides and/or mixed oxides with or without a defined stoichiometry are preferred. All of the above mentioned metal compounds can be soluble or insoluble and they may be used as starting material either in form of a powder or as a shaped body or as any combination thereof.

[0023] The at least bidentate organic ligands present in the metal-organic framework material are capable of coordinating to the metal ion. Such ligands are known to the person skilled in the art. The at least bidentate organic ligand, is preferably selected from:

[0024] i) alkyl groups having from 1 to 10 carbon atoms,

[0025] ii) aryl groups having from 1 to 5 phenyl rings,

[0026] iii) alkyl and aryl amines carrying one or more alkyl groups having from 1 to 10 carbon atoms and/or one or more aryl groups having from 1 to 5 phenyl rings,

[0027] which are covalently substituted by at least one functional group X which can coordinately bind to the metal ion and which is selected from the group consisting of CO<sub>2</sub>H, CS<sub>2</sub>H, NO<sub>2</sub>, SO<sub>3</sub>H, Si(OH)<sub>3</sub>, Ge(OH)<sub>3</sub>, Sn(OH)<sub>3</sub>, Si(SH)<sub>4</sub>, Ge(SH)<sub>4</sub>, Sn(SH)<sub>3</sub>, PO<sub>3</sub>H, AsO<sub>3</sub>H, AsO<sub>4</sub>H, P(SH)<sub>3</sub>, As(SH)<sub>3</sub>, CH(RSH)<sub>2</sub>, C(RSH)<sub>3</sub>, CH(RNH<sub>2</sub>)<sub>2</sub>, C(RNH<sub>2</sub>)<sub>3</sub>, CH(ROH)<sub>2</sub>, C(ROH)<sub>3</sub>, CH(RCN)<sub>2</sub>, C(RCN)<sub>3</sub>, wherein R is an alkyl group having from 1 to 5 carbon atoms, or an aryl group consisting of 1 to 2 phenyl rings, and CH(SH)<sub>2</sub>, C(SH)<sub>3</sub>, CH(NH<sub>2</sub>)<sub>2</sub>, C(NH<sub>2</sub>)<sub>2</sub>, CH(OH)<sub>2</sub>, C(OH)<sub>3</sub>, CH(CN)<sub>2</sub> and C(CN)<sub>3</sub>. WO 02/088148 discloses bidentate organic ligand from the group of aromatic compounds which can carry one or more substituents. The content of WO 02/088148, pages 8-14 is herein fully incorporated by reference.

[0028] Particularly to be mentioned are substituted and unsubstituted aliphatic α, ω-dicarboxylic acids, substituted or unsubstituted, mono- or polynuclear aromatic di-, tri- and tetracarboxylic acids and substituted or unsubstituted, aromatic di-, tri- and tetracarboxylic acids, having one or more nuclei, and carrying at least one hetero atom

[0029] Preferred ligands are selected from 1,3,5-benzene tricarboxylic acid (BCT), NDC (naphthalene dicarboxylate), BDC (benzene dicarboxylate), BTC (benzene tricarboxylate), BTB (benzene tribenzoate), and DHBC (2,5-dihydroxyterephthalic acid).

[0030] DHBC is the most preferred ligand. Besides the at least bidentate organic ligand, the framework material as used in accordance with the present invention may also comprise one or more monodentate ligands, which are preferably selected from the following monodentate substances and/or derivatives thereof:



- [0031] a. alkyl amines and their corresponding alkyl ammonium salts, containing linear, branched, or cyclic aliphatic groups, having from 1 to 20 carbon atoms (and their corresponding ammonium salts);
- [0032] b. aryl amines and their corresponding aryl ammonium salts having from 1 to 5 phenyl rings;
- [0033] c. alkyl phosphonium salts, containing linear, branched, or cyclic aliphatic groups, having from 1 to 20 carbon atoms;
- [0034] d. aryl phosphonium salts, having from 1 to 5 phenyl rings;
- [0035] e. alkyl organic acids and the corresponding alkyl organic anions (and salts) containing linear, branched, or cyclic aliphatic groups, having from 1 to 20 carbon atoms;
- [0036] f. aryl organic acids and their corresponding aryl organic anions and salts, having from 1 to 5 phenyl rings;
- [0037] g. aliphatic alcohols, containing linear, branched, or cyclic aliphatic groups, having from 1 to 20 carbon atoms;
- [0038] h. aryl alcohols having from 1 to 5 phenyl rings;
- [0039] i. inorganic anions from the group consisting of:
- [0040] sulfate, nitrate, nitrite, sulfite, bisulfite, phosphate, hydrogen phosphate, dihydrogen phosphate, diphosphate, triphosphate, phosphite, phosphite, chloride, chlorate, bromide, bromate, iodide, iodate, carbonate, bicarbonate, and the corresponding acids and salts of the aforementioned inorganic anions,
- [0041] j. ammonia, carbon dioxide, methane, oxygen, ethylene, hexane, benzene, toluene, xylene, chlorobenzene, nitrobenzene, naphthalene, thiophene, pyridine, acetone, 1-2-dichloroethane, methylenechloride, tetrahydrofuran, ethanolamine, triethylamine and trifluoromethylsulfonic acid.
- [0042] Further details regarding the at least bidentate organic ligand and the mono-dentate substances, from which the ligands of the framework material as used in the present application are derived, may be deduced from EP-A 0 790 253, whose respective content is incorporated into the present application by reference.

[0043] Within the present application, framework materials of the kind described herein, which comprise  $Zn^{2+}$  as a metal ion and ligands derived from terephthalic acid as the bidentate ligand, are particularly preferred.

[0044] Further metal ions, at least bidentate and monodentate organic ligands which are useful for the preparation of the framework materials used in the present invention as well as processes for their preparation are particularly disclosed in EP-A 0 790 253, U.S. Pat. No. 5,648,508 and DE 10111230.0.

[0045] As solvents, which are particularly useful for the preparation of MOF-5, in addition to the solvents disclosed in the above-referenced literature dimethyl formamide, diethyl formamide and N-methylpyrrolidone, alone, in combination with each other or in combination with other solvents may be used. Within the preparation of the framework materials, particularly within the preparation of MOF-5, the solvents and mother liquors can be recycled after crystallization.

[0046] The pore sizes of the metal-organic framework can be adjusted by selecting suitable bidentate ligands (=linkers). Generally, the larger the linker, the larger the pore size. Any pore size that is still supported by the metal-organic framework in the absence of a host and at temperatures of at least 200° C. is conceivable. Pore sizes ranging from 0.2 nm to 30 nm are preferred, with pore sizes ranging from 0.3 nm to 3 nm being particularly preferred.

[0047] In the following, examples of metal-organic framework materials (MOFs) are given to illustrate the general concept given above. These specific examples, however, are not intended to limit the scope of the present invention.

[0048] By way of example, a list of metal-organic framework materials already synthesized and characterized is given below. This also includes novel isorecticular metal organic framework materials (IR-MOFs), which may be used in the context of the present application. Such materials having the same framework topology while displaying different pore sizes and crystal densities are described, for example in M. Eddouadi et al., *Science* 295 (2002) 469, whose respective content is incorporated into the present application by reference.

[0049] The solvents used are of particular importance for the synthesis of these materials and are therefore mentioned in the table. The values for the cell parameters (angles  $\Delta$ ,  $E$  and  $\Theta$  as well as the spacings  $a$ ,  $b$  and  $c$ , given in Angstrom) have been obtained by x-ray diffraction and represent the space group given in the table as well.

MOF-n	Ingredients molar ratios M + L	Solvents	$\alpha$	$\beta$	$\gamma$	a	b	c	Space Group
MOF-0	$Zn(NO_3)_2 \cdot 6H_2O$	Ethanol	90	90	120	16.711	16.711	14.189	P6(3)/ Mcm
MOF-2	$H_3(BTC)$ $Zn(NO_3)_2 \cdot 6H_2O$ (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

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MOF-n	Ingredients molar ratios M + L	Solvents	$\alpha$	$\beta$	$\gamma$	a	b	c	Space Group
MOF-4	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O (1.00 mmol) H <sub>3</sub> (BTC) (0.5 mmol)	Ethanol	90	90	90	14.728	14.728	14.728	P2(1)3
MOF-5	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O (2.22 mmol) H <sub>2</sub> (BDC) (2.17 mmol)	DMF Chlorobezene	90	90	90	25.669	25.669	25.669	Fm-3m
MOF-38	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O (0.27 mmol) H <sub>3</sub> (BTC) (0.15 mmol)	DMF Chlorobenzene	90	90	90	20.657	20.657	17.84	I4cm
MOF-31 Zn(ADC) <sub>2</sub>	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O 0.4 mmol H <sub>2</sub> (ADC) 0.8 mmol	Ethanol	90	90	90	10.821	10.821	10.821	Pn(-3)m
MOF-12 Zn <sub>2</sub> (ATC)	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O 0.3 mmol H <sub>4</sub> (ATC) 0.15 mmol	Ethanol	90	90	90	15.745	16.907	18.167	Pbca
MOF-20 ZnNDC	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O 0.37 mmol H <sub>2</sub> NDC 0.36 mmol	DMF Chlorobenzene	90	92.13	90	8.13	16.444	12.807	P2(1)/c
MOF-37	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O 0.2 mmol H <sub>2</sub> NDC 0.2 mmol	DEF ChloroBenzene	72.38	83.16	84.33	9.952	11.576	15.556	P-1
MOF-8 Tb <sub>2</sub> (ADC)	Tb(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O 0.10 mmol H <sub>2</sub> ADC 0.20 mmol	DMSO MeOH	90	115.7	90	19.83	9.822	19.183	C2/c
MOF-9 Tb <sub>2</sub> (ADC)	Tb(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O 0.08 mmol H <sub>2</sub> ADB 0.12 mmol	DMSO	90	102.09	90	27.056	16.795	28.139	C2/c
MOF-6	Tb(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O 0.30 mmol H <sub>2</sub> (BDC) 0.30 mmol	DMF MeOH	90	91.28	90	17.599	19.996	10.545	P21/c
MOF-7	Tb(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O 0.15 mmol H <sub>2</sub> (BDC) 0.15 mmol	H <sub>2</sub> O	102.3	91.12	101.5	6.142	10.069	10.096	P-1
MOF-69A	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O 0.083 mmol 4,4'BPDC 0.041 mmol	DEF H <sub>2</sub> O <sub>2</sub> MeNH <sub>2</sub>	90	111.6	90	23.12	20.92	12	C2/c
MOF-69B	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O 0.083 mmol 2,6-NCD 0.041 mmol	DEF H <sub>2</sub> O <sub>2</sub> MeNH <sub>2</sub>	90	95.3	90	20.17	18.55	12.16	C2/c
MOF-11 Cu <sub>2</sub> (ATC)	Cu(NO <sub>3</sub> ) <sub>2</sub> ·2.5H <sub>2</sub> O 0.47 mmol H <sub>2</sub> ATC 0.22 mmol	H <sub>2</sub> O	90	93.86	90	12.987	11.22	11.336	C2/c
MOF-11 Cu <sub>2</sub> (ATC) dehydr.			90	90	90	8.4671	8.4671	14.44	P42/ mmc
MOF-14 Cu <sub>3</sub> (BTB)	Cu(NO <sub>3</sub> ) <sub>2</sub> ·2.5H <sub>2</sub> O 0.28 mmol H <sub>3</sub> BTB 0.052 mmol	H <sub>2</sub> O DMF EtOH	90	90	90	26.946	26.946	26.946	Im-3
MOF-32 Cd(ATC)	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 0.24 mmol H <sub>4</sub> ATC 0.10 mmol	H <sub>2</sub> O NaOH	90	90	90	13.468	13.468	13.468	P(-4)3m
MOF-33 Zn <sub>2</sub> (ATB)	ZnCl <sub>2</sub> 0.15 mmol H <sub>4</sub> ATB 0.02 mmol	H <sub>2</sub> O DMF EtOH	90	90	90	19.561	15.255	23.404	Imma

-continued

MOF-n	Ingredients molar ratios M + L	Solvents	$\alpha$	$\beta$	$\gamma$	a	b	c	Space Group
MOF-34 Ni(ATC)	Ni(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O 0.24 mmol H <sub>4</sub> ATC 0.10 mmol	H <sub>2</sub> O NaOH	90	90	90	10.066	11.163	19.201	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
MOF-36 Zn <sub>2</sub> (MTB)	Zn(NO <sub>3</sub> ) <sub>2</sub> .4H <sub>2</sub> O 0.20 mmol H <sub>4</sub> MTB 0.04 mmol	H <sub>2</sub> O DMF	90	90	90	15.745	16.907	18.167	Pbca
MOF-39 Zn <sub>3</sub> O(HBTB)	Zn(NO <sub>3</sub> ) <sub>2</sub> .4H <sub>2</sub> O 0.27 mmol H <sub>3</sub> BTB 0.07 mmol	H <sub>2</sub> O DMF EtOH	90	90	90	17.158	21.591	25.308	Pnma
NO305	FeCl <sub>2</sub> .4H <sub>2</sub> O 5.03 mmol formic acid 86.90 mmol	DMF	90	90	120	8.2692	8.2692	63.566	R-3c
NO306A	FeCl <sub>2</sub> .4H <sub>2</sub> O 5.03 mmol formic acid 86.90 mmol	DEF	90	90	90	9.9364	18.374	18.374	Pbcn
NO29 MOF-0 like	Mn(Ac) <sub>2</sub> .4H <sub>2</sub> O 0.46 mmol H <sub>3</sub> BTC 0.69 mmol	DMF	120	90	90	14.16	33.521	33.521	P-1
BPR48 A2	Zn(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O 0.012 mmol H <sub>2</sub> BDC 0.012 mmol	DMSO Toluene	90	90	90	14.5	17.04	18.02	Pbca
BPR69 B1	Cd(NO <sub>3</sub> ) <sub>2</sub> .4H <sub>2</sub> O 0.0212 mmol H <sub>2</sub> BDC 0.0428 mmol	DMSO	90	98.76	90	14.16	15.72	17.66	Cc
BPR92 A2	Co(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O 0.018 mmol H <sub>2</sub> BDC 0.018 mmol	NMP	106.3	107.63	107.2	7.5308	10.942	11.025	P1
BPR95 C5	Cd(NO <sub>3</sub> ) <sub>2</sub> .4H <sub>2</sub> O 0.012 mmol H <sub>2</sub> BDC 0.36 mmol	NMP	90	112.8	90	14.460	11.085	15.829	P2(1)/n
CuC <sub>6</sub> H <sub>4</sub> O <sub>6</sub>	Cu(NO <sub>3</sub> ) <sub>2</sub> .2.5H <sub>2</sub> O 0.370 mmol H <sub>2</sub> BDC(OH) <sub>2</sub> 0.37 mmol	DMF Chlorobenzene	90	105.29	90	15.259	14.816	14.13	P2(1)/c
M(BTC) MOF-0like	Co(SO <sub>4</sub> ) H <sub>2</sub> O 0.055 mmol H <sub>3</sub> BTC 0.037 mmol	DMF	Same as MOF-0						
Tb(C <sub>6</sub> H <sub>4</sub> O <sub>6</sub> )	Tb(NO <sub>3</sub> ) <sub>3</sub> .5H <sub>2</sub> O 0.370 mmol H <sub>2</sub> (C <sub>6</sub> H <sub>4</sub> O <sub>6</sub> ) 0.56 mmol	DMF chlorobenzene	104.6	107.9	97.147	10.491	10.981	12.541	P-1
Zn(C <sub>2</sub> O <sub>4</sub> )	ZnCl <sub>2</sub> 0.370 mmol oxalic acid 0.37 mmol	DMF chlorobenzene	90	120	90	9.4168	9.4168	8.464	P(-3)1m
Co(CHO)	Co(NO <sub>3</sub> ) <sub>2</sub> .5H <sub>2</sub> O 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 <sub>3</sub> ) <sub>2</sub> .4H <sub>2</sub> O 0.185 mmol formic acid 0.185 mmol	DMF	90	120	90	8.5168	8.5168	22.674	R-3c
Cu(C <sub>3</sub> H <sub>2</sub> O <sub>4</sub> )	Cu(NO <sub>3</sub> ) <sub>2</sub> .2.5H <sub>2</sub> O 0.043 mmol malonic acid 0.192 mmol	DMF	90	90	90	8.366	8.366	11.919	P43
Zn <sub>6</sub> (NDC) <sub>5</sub> MOF-48	Zn(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O 0.097 mmol 14 NDC 0.069 mmol	DMF chlorobenzene H <sub>2</sub> O <sub>2</sub>	90	95.902	90	19.504	16.482	14.64	C2/m



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MOF-n	Ingredients molar ratios M + L	Solvents	$\alpha$	$\beta$	$\gamma$	a	b	c	Space Group
MOF-47	Zn(NO <sub>3</sub> ) <sub>2</sub> 6H <sub>2</sub> O 0.185 mmol H <sub>2</sub> (BDC[CH <sub>3</sub> ] <sub>4</sub> ) 0.185 mmol	DMF Chlorobenzene H <sub>2</sub> O <sub>2</sub>	90	92.55	90	11.303	16.029	17.535	P2(1)/c
MO25	Cu(NO <sub>3</sub> ) <sub>2</sub> ·2.5H <sub>2</sub> O 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 <sub>3</sub> ) <sub>2</sub> ·2.5H <sub>2</sub> O 0.084 mmol thiophene dicarboxylic 0.085 mmol	DEF	90	113.6	90	15.4747	14.514	14.032	P2(1)/c
CIBDC1	Cu(NO <sub>3</sub> ) <sub>2</sub> ·2.5H <sub>2</sub> O0.0 84 mmol H <sub>2</sub> (BDCCl <sub>2</sub> ) 0.085 mmol	DMF	90	105.6	90	14.911	15.622	18.413	C2/c
MOF-101	Cu(NO <sub>3</sub> ) <sub>2</sub> ·2.5H <sub>2</sub> O 0.084 mmol BrBDC 0.085 mmol	DMF	90	90	90	21.607	20.607	20.073	Fm3m
Zn <sub>3</sub> (BTC) <sub>2</sub>	ZnCl <sub>2</sub> 0.033 mmol H <sub>3</sub> BTC 0.033 mmol	DMF EtOH Base Added	90	90	90	26.572	26.572	26.572	Fm-3m
MOF-j	Co(CH <sub>3</sub> CO <sub>2</sub> ) <sub>2</sub> ·4H <sub>2</sub> O (1.65 mmol) H <sub>3</sub> (BZC) (0.95 mmol)	H <sub>2</sub> O	90	112.0	90	17.482	12.963	6.559	C2
MOF-n	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O H <sub>3</sub> (BTC)	ethanol	90	90	120	16.711	16.711	14.189	P6(3)/mcm
PbBDC	Pb(NO <sub>3</sub> ) <sub>2</sub> (0.181 mmol) H <sub>2</sub> (BDC) (0.181 mmol)	DMF Ethanol	90	102.7	90	8.3639	17.991	9.9617	P2(1)/n
Znhex	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O (0.171 mmol) H <sub>3</sub> BTB (0.114 mmol)	DMF p-xylene ethanol	90	90	120	37.1165	37.117	30.019	P3(1)c
AS16	FeBr <sub>2</sub> 0.927 mmol H <sub>2</sub> (BDC) 0.927 mmol	DMF anhydr.	90	90.13	90	7.2595	8.7894	19.484	P2(1)c
AS27-2	FeBr <sub>2</sub> 0.927 mmol H <sub>3</sub> (BDC) 0.464 mmol	DMF anhydr.	90	90	90	26.735	26.735	26.735	Fm3m
AS32	FeCl <sub>3</sub> 1.23 mmol H <sub>2</sub> (BDC) 1.23 mmol	DMF anhydr. Ethanol	90	90	120	12.535	12.535	18.479	P6(2)c
AS54-3	FeBr <sub>2</sub> 0.927 BPDC 0.927 mmol	DMF anhydr. n- propanol	90	109.98	90	12.019	15.286	14.399	C2
AS61-4	FeBr <sub>2</sub> 0.927 mmol m-BDC 0.927 mmol	Pyridine anhydr.	90	90	120	13.017	13.017	14.896	P6(2)c
AS68-7	FeBr <sub>2</sub> 0.927 mmol m-BDC 1.204 mmol	DMF anhydr. Pyridine	90	90	90	18.3407	10.036	18.039	Pca2 <sub>1</sub>
Zn(ADC)	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O 0.37 mmol H <sub>2</sub> (ADC) 0.36 mmol	DMF Chlorobenzene	90	99.85	90	16.764	9.349	9.635	C2/c
MOF-12 Zn <sub>2</sub> (ATC)	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O 0.30 mmol H <sub>4</sub> (ATC) 0.15 mmol	Ethanol	90	90	90	15.745	16.907	18.167	Pbca

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MOF-n	Ingredients molar ratios M + L	Solvents	$\alpha$	$\beta$	$\gamma$	a	b	c	Space Group
MOF-20 ZnNDC	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O 0.37 mmol H <sub>2</sub> NDC 0.36 mmol	DMF Chlorobenzene	90	92.13	90	8.13	16.444	12.807	P2(1)/c
MOF-37	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O 0.20 mmol H <sub>2</sub> NDC 0.20 mmol	DEF Chlorobenzene	72.38	83.16	84.33	9.952	11.576	15.556	P-1
Zn(NDC) (DMSO)	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O H <sub>2</sub> NDC	DMSO	68.08	75.33	88.31	8.631	10.207	13.114	P-1
Zn(NDC)	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O H <sub>2</sub> NDC		90	99.2	90	19.289	17.628	15.052	C2/c
Zn(HPDC)	Zn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 0.23 mmol H <sub>2</sub> (HPDC) 0.05 mmol	DMF H <sub>2</sub> O	107.9	105.06	94.4	8.326	12.085	13.767	P-1
Co(HPDC)	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O 0.21 mmol H <sub>2</sub> (HPDC) 0.06 mmol	DMF H <sub>2</sub> O/ ethanol	90	97.69	90	29.677	9.63	7.981	C2/c
Zn <sub>3</sub> (PDC)2.5	Zn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 0.17 mmol H <sub>2</sub> (HPDC) 0.05 mmol	DMF/ CIBz H <sub>2</sub> O/ TEA	79.34	80.8	85.83	8.564	14.046	26.428	P-1
Cd <sub>2</sub> (TPDC)2	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 0.06 mmol H <sub>2</sub> (HPDC) 0.06 mmol	Methanol/ CHP H <sub>2</sub> O	70.59	72.75	87.14	10.102	14.412	14.964	P-1
Tb(PDC)1.5	Tb(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O 0.21 mmol H <sub>2</sub> (PDC) 0.034 mmol	DMF H <sub>2</sub> O/ ethanol	109.8	103.61	100.14	9.829	12.11	14.628	P-1
ZnDBP	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O 0.05 mmol dibenzylphosphate 0.10 mmol	MeOH	90	93.67	90	9.254	10.762	27.93	P2/n
Zn <sub>3</sub> (BPDC)	ZnBr <sub>2</sub> 0.021 mmol 4,4'BPDC 0.005 mmol	DMF	90	102.76	90	11.49	14.79	19.18	P21/n
CdBDC	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 0.100 mmol H <sub>2</sub> (BDC) 0.401 mmol	DMF Na <sub>2</sub> SiO <sub>3</sub> (aq)	90	95.85	90	11.2	11.11	16.71	P21/n
Cd-mBDC	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 0.009 mmol H <sub>2</sub> (mBDC) 0.018 mmol	DMF MeNH <sub>2</sub>	90	101.1	90	13.69	18.25	14.91	C2/c
Zn <sub>4</sub> OBNDC	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O 0.041 mmol BNDC	DEF MeNH <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	90	90	90	22.35	26.05	59.56	Fmmm
Eu(TCA)	Eu(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O 0.14 mmol TCA 0.026 mmol	DMF Chlorobenzene	90	90	90	23.325	23.325	23.325	Pm-3n
Tb(TCA)	Tb(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O 0.069 mmol TCA 0.026 mmol	DMF Chlorobenzene	90	90	90	23.272	23.272	23.372	Pm-3n
Formate	Ce(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O 0.138 mmol Formaic acid 0.43 mmol	H <sub>2</sub> O Ethanol	90	90	120	10.668	10.667	4.107	R-3m
	FeCl <sub>2</sub> ·4H <sub>2</sub> O 5.03 mmol Formic acid 86.90 mmol	DMF	90	90	120	8.2692	8.2692	63.566	R-3c
	FeCl <sub>2</sub> ·4H <sub>2</sub> O 5.03 mmol Formic acid 86.90 mmol	DEF	90	90	90	9.9364	18.374	18.374	Pbcn



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MOF-n	Ingredients molar ratios M + L	Solvents	$\alpha$	$\beta$	$\gamma$	a	b	c	Space Group
NO330	FeCl <sub>2</sub> .4H <sub>2</sub> O 5.03 mmol Formic acid 86.90 mmol	DEF	90	90	90	8.335	8.335	13.34	P-31c
	FeCl <sub>2</sub> .4H <sub>2</sub> O 0.50 mmol Formic acid 8.69 mmol	formamide	90	90	90	8.7749	11.655	8.3297	Pnna
	FeCl <sub>2</sub> .4H <sub>2</sub> O 0.50 mmol Formic acid 8.69 mmol	DIP	90	90	90	10.0313	18.808	18.355	Pbcn
NO332	FeCl <sub>2</sub> .4H <sub>2</sub> O 0.50 mmol Formic acid 8.69 mmol	DBF	90	90	90	45.2754	23.861	12.441	Cmcm
NO333	FeCl <sub>2</sub> .4H <sub>2</sub> O 0.50 mmol Formic acid 8.69 mmol	CHF	90	91.372	90	11.5964	10.187	14.945	P21/n
NO335	FeCl <sub>2</sub> .4H <sub>2</sub> O 0.50 mmol Formic acid 8.69 mmol	MFA	90	90	90	11.7945	48.843	8.4136	Pbcm
NO336	FeCl <sub>2</sub> .4H <sub>2</sub> O 0.50 mmol Formic acid 8.69 mmol	Ethanol	90	90	90	18.66	11.762	9.418	Pbcn
NO13	Mn(Ac) <sub>2</sub> .4H <sub>2</sub> O 0.46 mmol Bezoic acid 0.92 mmol Bipyridine 0.46 mmol	DMF	120	90	90	14.16	33.521	33.521	P-1
NO29 MOF-0 Like	Mn(Ac) <sub>2</sub> .4H <sub>2</sub> O 0.46 mmol H <sub>3</sub> BTC 0.69 mmol	Ether	90	95.32	90	9.572	17.162	14.041	C2/c
Mn(hfac) <sub>2</sub> (O <sub>2</sub> CC <sub>6</sub> H <sub>5</sub> )	Mn(Ac) <sub>2</sub> .4H <sub>2</sub> O 0.46 mmol Hfac 0.92 mmol Bipyridine 0.46 mmol	DMF CH <sub>3</sub> CN	90	91.37	90	17.96	6.38	7.19	C2/c
BPR43G2	Zn(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O 0.0288 mmol H <sub>2</sub> BDC 0.0072 mmol	DMSO Toluene	90	90	90	14.5	17.04	18.02	Pbca
BPR48A2	Zn(NO <sub>3</sub> ) <sub>2</sub> 6H <sub>2</sub> O 0.012 mmol H <sub>2</sub> BDC 0.012 mmol	DMSO Methanol	90	91.172	90	33.181	9.824	17.884	C2/c
BPR49B1	Zn(NO <sub>3</sub> ) <sub>2</sub> 6H <sub>2</sub> O 0.024 mmol H <sub>2</sub> BDC 0.048 mmol	DMSO n- propanol	90	90.096	90	14.5873	14.153	17.183	P2(1)/n
BPR56E1	Zn(NO <sub>3</sub> ) <sub>2</sub> 6H <sub>2</sub> O 0.012 mmol H <sub>2</sub> BDC 0.024 mmol	DMSO Benzene	90	95.316	90	10.0627	10.17	16.413	P2(1)/c
BPR68D10	H <sub>3</sub> BTC 0.0064 mmol Cd(NO <sub>3</sub> ) <sub>2</sub> 4H <sub>2</sub> O 0.0212 mmol	DMSO	90	98.76	90	14.16	15.72	17.66	Cc
BPR69B1	H <sub>2</sub> BDC 0.0428 mmol Cd(NO <sub>3</sub> ) <sub>2</sub> 4H <sub>2</sub> O 0.006 mmol	DMSO Toluene	90	92.324	90	8.7231	7.0568	18.438	P2(1)/n
BPR73E4	H <sub>2</sub> BDC 0.003 mmol Zn(NO <sub>3</sub> ) <sub>2</sub> 6H <sub>2</sub> O 0.0009 mmol	DMSO	90	104.17	90	14.4191	6.2599	7.0611	Pc
BPR76D5	H <sub>2</sub> BzPDC 0.0036 mmol								

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MOF-n	Ingredients molar ratios M + L	Solvents	$\alpha$	$\beta$	$\gamma$	a	b	c	Space Group
BPR80B5	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 0.018 mmol H <sub>2</sub> BDC 0.036 mmol	DMF	90	115.11	90	28.049	9.184	17.837	C2/c
BPR80H5	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 0.027 mmol H <sub>2</sub> BDC 0.027 mmol	DMF	90	119.06	90	11.4746	6.2151	17.268	P2/c
BPR82C6	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 0.0068 mmol H <sub>2</sub> BDC 0.202 mmol	DMF	90	90	90	9.7721	21.142	27.77	Fdd2
BPR86C3	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O 0.0025 mmol H <sub>2</sub> BDC 0.075 mmol	DMF	90	90	90	18.3449	10.031	17.983	Pca2(1)
BPR86H6	Cd(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O 0.010 mmol H <sub>2</sub> BDC 0.010 mmol	DMF	80.98	89.69	83.412	9.8752	10.263	15.362	P-1
BPR95A2	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O 0.012 mmol H <sub>2</sub> BDC 0.012 mmol	NMP NMP	106.3 90	107.63 102.9	107.2 90	7.5308 7.4502	10.942 13.767	11.025 12.713	P-1 P2(1)/c
CuC <sub>6</sub> F <sub>4</sub> O <sub>4</sub>	Cu(NO <sub>3</sub> ) <sub>2</sub> ·2.5H <sub>2</sub> O 0.370 mmol H <sub>2</sub> BDC(OH) <sub>2</sub> 0.37 mmol	DMF Chloro- Benzene	90	98.834	90	10.9675	24.43	22.553	P2(1)/n
Fe Formic	FeCl <sub>2</sub> ·4H <sub>2</sub> O 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 <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O 0.370 mmol Formic acid 0.37 mmol	DMF	90	91.359	90	11.383	9.932	14.656	P2(1)/n
MgC <sub>6</sub> H <sub>4</sub> O <sub>6</sub>	Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O 0.370 mmol H <sub>2</sub> BDC(OH) <sub>2</sub> 0.37 mmol	DMF	90	96.624	90	17.245	9.943	9.273	C2/c
ZnC <sub>2</sub> H <sub>4</sub> BDC MOF-38	ZnCl <sub>2</sub> 0.44 mmol CBBDC 0.261 mmol	DMF	90	94.714	90	7.3386	16.834	12.52	P2(1)/n
MOF-49	ZnCl <sub>2</sub> 0.44 mmol m-BDC 0.261 mmol	DMF CH3CN	90	93.459	90	13.509	11.984	27.039	P2/c
MOF-26	Cu(NO <sub>3</sub> ) <sub>2</sub> ·5H <sub>2</sub> O 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 <sub>3</sub> ) <sub>2</sub> ·2.5H <sub>2</sub> O 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 <sub>3</sub> ) <sub>2</sub> ·2.5H <sub>2</sub> O 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 <sub>3</sub> ) <sub>2</sub> ·2.5H <sub>2</sub> O 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 <sub>3</sub> ) <sub>2</sub> ·2.5H <sub>2</sub> O 0.084 mmol thiophene dicarboxylic 0.085 mmol	DMF	90	90	120	20.0652	20.065	20.747	R-3/m



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MOF-n	Ingredients molar ratios M + L	Solvents	$\alpha$	$\beta$	$\gamma$	a	b	c	Space Group
MOF-107	Cu(NO <sub>3</sub> ) <sub>2</sub> ·2.5H <sub>2</sub> O 0.084 mmol thiophene dicarboxylic 0.085 mmol	DEF	104.8	97.075	95.206	11.032	18.067	18.452	P-1
MOF-108	Cu(NO <sub>3</sub> ) <sub>2</sub> ·2.5H <sub>2</sub> O 0.084 mmol thiophene dicarboxylic 0.085 mmol	DBF/ methanol	90	113.63	90	15.4747	14.514	14.032	C2/c
MOF-102	Cu(NO <sub>3</sub> ) <sub>2</sub> ·2.5H <sub>2</sub> O 0.084 mmol H <sub>2</sub> (BDCCl <sub>2</sub> ) 0.085 mmol	DMF	91.63	106.24	112.01	9.3845	10.794	10.831	P-1
Clbdc1	Cu(NO <sub>3</sub> ) <sub>2</sub> ·2.5H <sub>2</sub> O 0.084 mmol H <sub>2</sub> (BDCCl <sub>2</sub> ) 0.085 mmol	DEF	90	105.56	90	14.911	15.622	18.413	P-1
Cu(NMOP)	Cu(NO <sub>3</sub> ) <sub>2</sub> ·2.5H <sub>2</sub> O 0.084 mmol NBDC 0.085 mmol	DMF	90	102.37	90	14.9238	18.727	15.529	P2(1)/m
Tb(BTC)	Tb(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O 0.033 mmol H <sub>3</sub> BTC 0.033 mmol	DMF	90	106.02	90	18.6986	11.368	19.721	
Zn <sub>3</sub> (BTC) <sub>2</sub> Honk	ZnCl <sub>2</sub> 0.033 mmol H <sub>3</sub> BTC 0.033 mmol	DMF Ethanol	90	90	90	26.572	26.572	26.572	Fm-3m
Zn <sub>4</sub> O(NDC)	Zn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 0.066 mmol 14NDC 0.066 mmol	DMF ethanol	90	90	90	41.5594	18.818	17.574	aba2
CdTDC	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 0.014 mmol thiophene 0.040 mmol DABCO 0.020 mmol	DMF H <sub>2</sub> O	90	90	90	12.173	10.485	7.33	Pmma
IRMOF-2	Zn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 0.160 mmol o-Br-BDC 0.60 mmol	DEF	90	90	90	25.772	25.772	25.772	Fm-3m
IRMOF-3	Zn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 0.20 mmol H <sub>2</sub> N-BDC 0.60 mmol	DEF Ethanol	90	90	90	25.747	25.747	25.747	Fm-3m
IRMOF-4	Zn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 0.11 mmol [C <sub>3</sub> H <sub>7</sub> O] <sub>2</sub> -BDC 0.48 mmol	DEF	90	90	90	25.849	25.849	25.849	Fm-3m
IRMOF-5	Zn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 0.13 mmol [C <sub>5</sub> H <sub>11</sub> O] <sub>2</sub> -BDC 0.50 mmol	DEF	90	90	90	12.882	12.882	12.882	Pm-3m
IRMOF-6	Zn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 0.20 mmol [C <sub>2</sub> H <sub>4</sub> ]-BDC 0.60 mmol	DEF	90	90	90	25.842	25.842	25.842	Fm-3m
IRMOF-7	Zn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 0.07 mmol 1,4NDC 0.20 mmol	DEF	90	90	90	12.914	12.914	12.914	Pm-3m
IRMOF-8	Zn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 0.55 mmol 2,6NDC 0.42 mmol	DEF	90	90	90	30.092	30.092	30.092	Fm-3m
IRMOF-9	Zn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 0.05 mmol BPDC 0.42 mmol	DEF	90	90	90	17.147	23.322	25.255	Pnnm

-continued

MOF-n	Ingredients molar ratios M + L	Solvents	$\alpha$	$\beta$	$\gamma$	a	b	c	Space Group
IRMOF-10	Zn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 0.02 mmol BPDC 0.012 mmol	DEF	90	90	90	34.281	34.281	34.281	Fm-3m
IRMOF-11	Zn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 0.05 mmol HPDC 0.20 mmol	DEF	90	90	90	24.822	24.822	56.734	R-3m
IRMOF-12	Zn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 0.017 mmol HPDC 0.12 mmol	DEF	90	90	90	34.281	34.281	34.281	Fm-3m
IRMOF-13	Zn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 0.048 mmol PDC 0.31 mmol	DEF	90	90	90	24.822	24.822	56.734	R-3m
IRMOF-14	Zn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 0.17 mmol PDC 0.12 mmol	DEF	90	90	90	34.381	34.381	34.381	Fm-3m
IRMOF-15	Zn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 0.063 mmol TPDC 0.025 mmol	DEF	90	90	90	21.459	21.459	21.459	Im-3m
IRMOF-16	Zn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 0.0126 mmol TPDC 0.05 mmol	DEF NMP	90	90	90	21.49	21.49	21.49	Pm-3m
	FeBr <sub>2</sub> 0.927 mmol BDC 0.927 mmol FeCl <sub>3</sub> ·6H <sub>2</sub> O BDC 1.23 mmol Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O DHBC 0.185 mmol	DMF 1 Propanol DMF Ethanol DMF							
	Zn(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 0.20 mmol DHBC 0.10 mmol Mn(ClO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O DHBC 0.065 mmol Tb(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O DHBC 0.050 mmol	DMF i-Propanol DMF i-Propanol DMF i-Propanol	90	90	120	25.9	25.9	6.8	R-3

ADC Acetylene dicarboxylic acid  
NDC Naphtalene dicarboxylic acid  
BDC Benzene dicarboxylic acid  
ATC Adamantane tetracarboxylic acid  
BTC Benzene tricarboxylic acid  
BTB Benzene tribenzoate  
MTB Methane tetrabenzoate  
ATB Adamantane tetrabenzoate  
ADB Adamantane dibenzoate  
BPDC 4,4-Biphenyldicarboxylic acid  
DHBC 2,5-Dihydroxyterephthalic acid

[0050] Examples for the synthesis of these materials as such can, for example, be found in: J. Am. Chem. Soc. 123 (2001) pages 8241 seq. or in Acc. Chem. Res. 31 (1998) pages 474 seq., which are fully encompassed in the present application.

[0051] The separation of the framework materials from the mother liquor of the crystallization can be achieved by procedures known in the art such as solid-liquid separations, centrifugation, extraction, filtration, membrane filtration, cross-flow filtration, flocculation using flocculation adjuvants (non-ionic, cationic and anionic adjuvants) or by the addition of pH shifting additives such as salts, acids or bases, by flotation, as well as by evaporation of the mother liquor at elevated temperature and/or in vacuo and concentrating of

the solid. The material obtained in this step is typically a fine powder and cannot be used for most practical applications, e.g., in catalysis, where shaped bodies are required.

[0052] The separated framework materials may be compounded, melted, extruded, co-extruded, pressed, spinned, foamed and granulated according to processes known within the processing of plastics, respectively.

[0053] One advantage of the process according to the present invention is that the polyoxyalkylene alcohols obtainable have a low, preferred degree of alkoxylation. The alcohols comprise generally 1 to 5 alkoxy units, preferably 1 to 3 alkoxy units, more preferably 1 or 2 alkoxy units, in particular 1 alkoxy unit.



[0054] The polyoxyalkylene alcohols which are obtainable according to the present invention lend themselves for a number of applications. Non-limiting examples include polyurethane-foams, lubricating liquids, hydraulic fluid, carrier liquid, tenside and flotation oil.

[0055] The invention is now illustrated by way of the following examples which are not intended to limit the scope of the present invention.

### EXAMPLES

#### Example 1 (Preparation of MOF-5)

[0056]

Starting Material	Molar Amount	Calculated	Experimental
terephthalic acid	12.3 mmol	2.04 g	2.34 g
Zinc nitrate-tetrahydrate	36.98 mmol	9.67 g	9.66 g
Diethylformamide (Merck)	2568.8 mmol	282.2 g	282.2 g

[0057] The above-mentioned amounts of the starting materials were dissolved in a beaker in the order diethylformamide, terephthalic acid and zinc nitride. The resulting solution was transferred into two autoclaves (250 ml) with teflon covered inner walls.

[0058] The crystallization occurred at 105° C. over 68 hours. Subsequently, the orange solvent, together with the red crystals, was transferred into a beaker, and the suspension is filtered under an N<sub>2</sub> atmosphere. The suspension was washed with 3 ml of chloroform before being activated in vacuo. There were obtained 2.3 g of product.

#### Example 2

[0059] 2,5-Dihydroxyterephthalic acid (19 mg, 0.10 mmol) and Zn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (53 mg, 0.20 mmol) were dissolved in a mixed solution of DMF (2.0 mL), PrOH (0.10 mL) and water (0.10 mL), which was placed in a pyrex tube (10 mm×70 mm). The tube was frozen and evacuated, and flame sealed under vacuum. The tube was heated to 105° C. at 2° C./min, held for 20 hours, then cooled to room temperature at 2° C./min. Yellow needle crystals were collected and washed with DMF (3×5 mL). Yield: 26 mg, 81% based on the 2,5-dihydroxyterephthalic acid.

#### Example 3 (Alkoxylation of i-Tridecanol N with Propylene Oxide)

[0060] i-Tridecanol N (4.8 g corresponding to 0.024 mole) and 0.8 g of the catalyst prepared according to Example 1 were given into an autoclave. Subsequently, the autoclave was filled with 12 g propylene oxide (0.207 mole). The reaction was carried out at 135° C., and in total 9.4 mole propylene oxide/mole starting alcohol were reacted to obtain 18.7 g of product.

#### Example 4 (Alkoxylation of 2-Propylheptanol with Ethylene Oxide)

[0061] 2-Propylheptanol (12.67 g corresponding to 0.08 mole) and 0.49 g of the catalyst prepared according to

Example 2 were given into an autoclave. Subsequently, the autoclave was filled with 7.05 g ethylene oxide (0.16 mole). The reaction was carried out at 135° C. over 10 h, before the autoclave was cooled to 50° C., at which temperature the reaction mixture was stirred for another 3 h. In total 3.74 mole ethylene oxide/mole starting alcohol were reacted, to obtain 27.98 g of product.

#### 1. A process, which comprises:

alkoxylating a monool with at least one alkoxylating agent to obtain a polyoxyalkylene alcohol in the presence of a catalyst which comprises a metallo-organic framework material of metal ions and at least bidentate coordinately bound organic ligands.

2. The process according to claim 1, wherein the metal ion is selected from the group consisting of any one elements of Groups 1 to 18, and combinations thereof of the periodic table of the elements.

3. The process according to claim 1, wherein the bidentate organic ligand is selected from the group consisting of a substituted aromatic mononuclear polycarboxylic acid, an unsubstituted aromatic mononuclear polycarboxylic acid, a substituted polynuclear aromatic polycarboxylic acid, an unsubstituted polynuclear aromatic polycarboxylic acid, a substituted aromatic mononuclear polycarboxylic acid comprising at least one heteroatom, an unsubstituted aromatic mononuclear polycarboxylic acid comprising at least one heteroatom, a substituted aromatic polynuclear polycarboxylic acid comprising at least one heteroatom, an unsubstituted aromatic polynuclear polycarboxylic acid comprising at least one heteroatom, and combinations thereof.

4. The process according to claim 3, wherein the bidentate organic ligand is terephthalic acid or a derivative thereof.

5. The process according to claim 1, wherein the metallo-organic framework material exhibits a specific surface area, as determined via adsorption, of >20 m<sup>2</sup>/g.

6. The process according to claim 1, wherein the alkoxylation agent is selected from the group consisting of a monofunctional epoxide having 2 to 30 carbon atoms, a multifunctional epoxide epoxides having 2 to 30 carbon atoms and mixtures thereof.

7. The process according to claim 6, wherein the epoxide is selected from the group consisting of ethylene oxide, propylene oxide, a butylene oxide and mixtures thereof.

8. (Cancelled).

9. A method of using an alcohol obtained by the process as claimed in claim 1, which comprises:

preparing a tenside, a flotation oil, a lubricating liquid, a hydraulic fluid, a carrier liquid or a polyurethane foam comprising the alcohol.

10. The method of using according to claim 9 where the alcohol is selected from monools of linear and branched alkyl groups having 1 to 30 carbon atoms, which alkyl groups may carry one or more aryl substituents, of homo- and polynuclear aromatic groups having 4 to 30 carbon atoms, which aromatic groups may carry one or more alkyl substituents, and of linear and branched alkenyl groups having 2 to 30 carbon atoms and which alkenyl groups may carry one or more aryl substituents.