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(54) Titre : METHODES POUR ENTREPOSER, ABSORBER ET RELACHER DES GAZ PAR DE NOUVEAUX  
ELEMENTS DE STRUCTURE  
(54) Title: METHOD OF STORING, UPTAKING, RELEASING OF GASES BY NOVEL FRAMEWORK MATERIALS

(57) Abrégé/Abstract:

The present invention relates to a method of using a metallo-organic framework material comprising pores and at least one metal ion and at least one at least bidentate organic compound, which is bound, preferably coordinately bound to said metal ion for uptaking, or storing, or releasing, or uptaking and storing, or uptaking and releasing, or storing and releasing or uptaking, storing and releasing at least one gas as well as a fuel cell comprising said material for the purposes outlined above.

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### **Abstract**

The present invention relates to a method of using a metallo-organic framework material comprising pores and at least one metal ion and at least one at least bidentate organic compound, which is bound, preferably coordinately bound to said metal ion for uptaking, or storing, or releasing, or uptaking and storing, or uptaking and releasing, or storing and releasing or uptaking, storing and releasing at least one gas as well as a fuel cell comprising said material for the purposes outlined above.

**Method of storing, uptaking, releasing of gases by  
Novel Framework Materials**

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The present invention relates to the technical field of storing gas including methane and hydrogen, in particular to the fuel cell technology. In particular, it relates to a method of using a metallo-organic framework material comprising pores and  
10 at least one metal ion and at least one at least bidentate organic compound, which is bound, preferably coordinately bound to said metal ion for uptaking, or storing, or releasing, or uptaking and storing, or uptaking and releasing, or storing and releasing or uptaking, storing and releasing at least one gas and an apparatus comprising the material defined above.

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Fuel cell technology is regarded as one of the core technologies of the 21<sup>st</sup> century, e.g. in relation to stationary applications, such as power plants, mobile applications such as cars, busses and trucks and portable applications, such as cellular phones and laptops and in so called APUs, such as the power supply in power  
20 plants. The reason therefor lies in the increased efficiency of fuel cells compared to normal combustion engines. Furthermore, the fuel cell produces significantly less emissions. An overview of the current developments in fuel cell technology may be found in Hynek et al. "Int. J. Hydrogen Energy", 22, no. 6, pp. 601 – 610 (1997), J.A. Kerres "Journal of Membrane Science", 185, 2001, p. 3 – 27 and a  
25 further review article by G. March in "Materials Today", 4, No.2 (2001), p. 20 – 24.

The use of metallo-organic complexe for storing gaseous C1 to C4 carbohydrates is disclosed in EP-A 0 727 608. However, the complexes disclosed therein are

- 2 -

difficult to synthesize. Furthermore, their storing capacity is low, if not too low to be industrially applicable.

Another attempt to provide materials useful for storing gases is the use of alkali-doped or undoped carbon nanotubes. An overview of the present status of research regarding this approach may be found in Yang, "Carbon" 38 (2000), pp. 623 – 641 and Cheng et al. "Science" 286, pp. 1127 – 1129.

10 In view of the above recited prior art, an object of the invention is to be seen in the provision of new materials which are particularly useful for storing and/or retaining and/or releasing gases.

This object is solved by and the present invention relates to a method for uptaking, or storing, or releasing, or uptaking and storing, or uptaking and releasing, or storing and releasing or uptaking, storing and releasing at least one gas, said method being characterized in that the gas is uptaken, or stored, or released, or uptaken and stored, or uptaken and released, or stored and released or uptaken, stored and released by an agent comprising a metallo-organic framework material comprising pores and at least one metal ion and at least one at least bidentate organic compound, which is bound, preferably coordinately bound, to  
20 said metal ion, wherein the gas is selected from the group consisting of hydrogen, a hydrogen containing gas mixture, a hydrogen generating substance, a hydrogen delivering substance, a gas mixture comprising at least one hydrogen generating substance and a gas mixture comprising at least one hydrogen delivering substance.

The present invention further relates to a device for uptaking, or storing, or releasing, or uptaking and storing, or uptaking and releasing, or storing and releasing, or uptaking, storing and releasing at least one gas, accomodating a metallo-organic framework material and according to the method defined

- 3 -

hereinabove, wherein the gas is selected from the group consisting of hydrogen, a hydrogen containing gas mixture, a hydrogen generating substance, a hydrogen delivering substance, a gas mixture comprising at least one hydrogen generating substance and a gas mixture comprising at least one delivering substance, and wherein the device further includes

a container accomodating the metallo-organic framework material;

an entrance/exit opening for allowing the at least one gas to enter or exit the device;

10 a gas-tight maintaining mechanism capable of maintaining the gas under pressure inside the container. Preferably, the device is a fuel cell.

The present invention still further relates to a use of an agent comprising a metallo-organic framework material comprising pores and at least one metal ion and at least one at least bidentate organic compound, which is bound, preferably coordinately bound to said metal ion for uptaking, or storing, or releasing, or uptaking and storing, or uptaking and releasing, or storing and releasing or uptaking, storing and releasing at least one gas in stationary, mobile and mobile portable applications, preferably in power plants, cars, trucks, busses, cell phones, laptops, wherein the gas is selected from the group consisting of hydrogen, a hydrogen containing gas mixture, a hydrogen generating substance, a hydrogen delivering substance, a gas mixture comprising at least one hydrogen generating substance and a gas mixture comprising at least one hydrogen delivering substance.

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It further relates to the use of the device described herein for supplying power to power plants, cars, trucks, busses, cell phones, laptops.

The metallo-organic pore containing framework material, which in turn comprises a metal ion and an at least bidentate organic compound, said bidentate organic compound being bound, preferably coordinately bound to the metal ion. Such materials are known as such

- 4 -

and described in e.g. US 5,648,508, EP-A-0 709 253, J. Sol. State Chem., 152 (2000) p. 3-20, Nature 402 (1999), p. 276 seq., Topics in Catalysis 9 (1999), p. 105-111, Science 291 (2001), p. 1021-23. An inexpensive way for their preparation is the subject of DE 10111230.0.

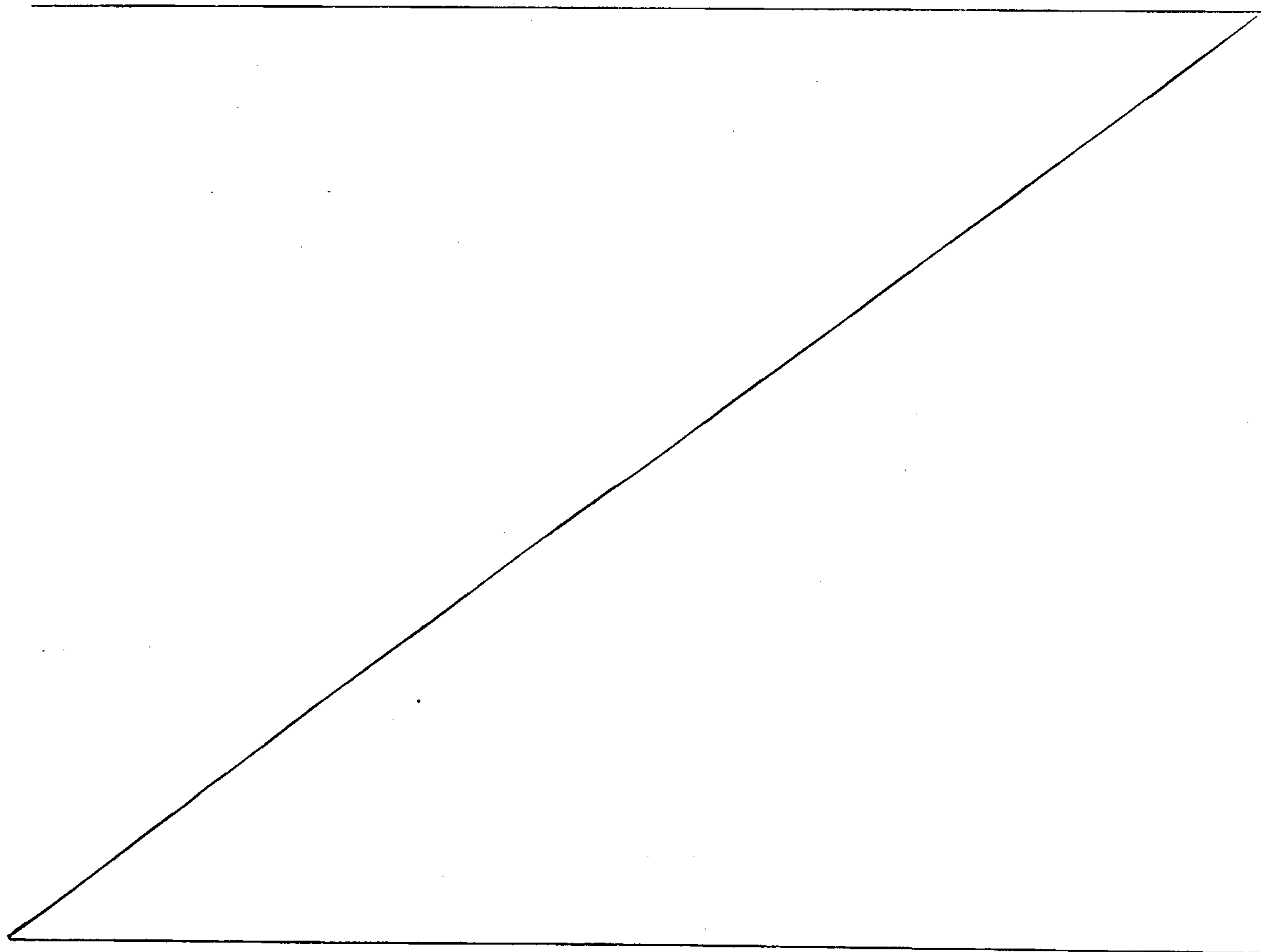
The metallo-organic framework materials, as used in the present invention, comprise pores, particularly micro- and/or mesopores, wherein micropores are defined as being pores having a diameter of 2 nm or below and mesopores being pores having a diameter in the range of above 2 nm to 50 nm, respectively, according to the definition in Pure Applied Chem. 45, p. 71 seq., particularly p. 79 (1976). The presence of the micro- and/or mesopores may be monitored by sorption measurements for determining the capacity of the metallo-organic framework materials to take up nitrogen at 77 K according to DIN 66131, 66134. A type-I-form of the isothermal curve indicates the presence of micropores. In a preferred embodiment, the specific surface areas, as calculated according to the Langmuir model are preferably above 5 m<sup>2</sup>/g, more preferable above 20 m<sup>2</sup>/g, even more preferably above 50 m<sup>2</sup>/g, particularly above 500 m<sup>2</sup>/g and may increase into the region of to above 2000 m<sup>2</sup>/g.

As the metal component within the framework material as used according to the present invention, particularly to be mentioned are metal ions of elements of groups Ia, IIa, IIIa, IVa to VIIIa and Ib to VIb of the periodic system; among those particularly to be mentioned are 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. As metal ions of these elements, particularly to be mentioned are: 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>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>2+</sup>, Cu<sup>+</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> and Bi<sup>5+</sup>, Bi<sup>3+</sup>, Bi<sup>+</sup>.

- 4a -

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, l. 8-30, section "The Metal Ions". As the at least bidentate organic compound, which is capable to coordinate with the metal ion, in principle all compounds which are suitable for this purpose and which fulfill the above requirements of being at least bidentate, may be used. The organic compound must have at least two centers, which are capable to coordinate with the metal ions of a metal salt, particularly with the metals of the aforementioned groups. With regard to the at least bidentate organic compound, specific mention is to be made of compounds having

- i) an alkyl group substructure, having from 1 to 10 carbon atoms,
- 10 ii) an aryl group substructure, having from 1 to 5 phenyl rings,
- iii) an alkyl or aryl amine substructure, consisting of alkyl groups having from 1 to 10 carbon atoms or aryl groups having from 1 to 5 phenyl rings,



- 5 -

said substructures having bound thereto at least one at least bidentate functional group "X", which is covalently bound to the substructure of said compound, and wherein X 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>,  
 5 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>.

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Particularly to be mentioned are substituted or unsubstituted, mono- or polynu-  
 clear aromatic di-, tri- and tetracarboxylic acids and substituted or unsubstituted,  
 aromatic, at least one hetero atom comprising aromatic di-, tri- and tetracarboxylic  
 acids, which have one or more nuclei.

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A preferred ligand is terephthalic acid, particularly preferred metal ions are Co<sup>2+</sup>  
 and Zn<sup>2+</sup>.

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Besides the at least bidentate organic compound, the framework material as used  
 in accordance with the present invention may also comprise one or more mono-  
 dentate ligands, which are preferably derived from the following mono-dentate  
 substances:

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- a. alkyl amines and their corresponding alkyl ammonium salts, containing  
 linear, branched, or cyclic aliphatic groups, having from 1 to 20 carbon at-  
 oms (and their corresponding ammonium salts);
- b. aryl amines and their corresponding aryl ammonium salts having from 1 to  
 5 phenyl rings;

- 6 -

- c. alkyl phosphonium salts, containing linear, branched, or cyclic aliphatic groups, having from 1 to 20 carbon atoms;
- d. aryl phosphonium salts, having from 1 to 5 phenyl rings;
- 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;
- f. aryl organic acids and their corresponding aryl organic anions and salts, having from 1 to 5 phenyl rings;
- g. aliphatic alcohols, containing linear, branched, or cyclic aliphatic groups, having from 1 to 20 carbon atoms;
- 10 h. aryl alcohols having from 1 to 5 phenyl rings;
- i. inorganic anions from the group consisting of:  
sulfate, nitrate, nitrite, sulfite, bisulfite, phosphate, hydrogen phosphate, dihydrogen phosphate, diphosphate, triphosphate, phosphite, chloride, chlorate, bromide, bromate, iodide, iodate, carbonate, bicarbonate, and the corresponding acids and salts of the aforementioned inorganic anions,
- 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.

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Further details regarding the at least bidentate organic compounds 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.

By way of example, a list of metal-organic framework materials already synthesized and characterized is given below. This also includes novel isoreticular metal organic framework materials (IR-MOFs), which may be used in the framework 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.

- 7 -

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  $\alpha$ ,  $\beta$  and  $\gamma$  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.

- 8 -

MOF-n	Ingredients molar ratios M+L	Solvent s	$\alpha$	$\beta$	$\gamma$	a	b	c	Space Group
MOF-0	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
MOF-2	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O (0.246 mmol) H <sub>2</sub> (BDC) 0.241 mmol)	DMF toluene	90	102.8	90	6.718	15.49	12.43	P2(1)/n
MOF-3	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O (1.89 mmol) H <sub>2</sub> (BDC) (1.93mmol)	DMF MeOH	99.72	111.11	108.4	9.726	9.911	10.45	P-1
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 chloro- benzene	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 chloro- benzene	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 chloro- benzene	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 chloro- benzene	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

- 9 -

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
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

- 10 -

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	PI
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
Cu C <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 chloro- benzene	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 chloro- benzene	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 chloro- benzene	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 chloro- benzene H <sub>2</sub> O <sub>2</sub>	90	95.902	90	19.504	16.482	14.64	C2/m

- 11 -

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 chloro- benzene 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> O 0.084 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

- 12 -

AS54-3	FeBr <sub>2</sub> 0.927 BPDC 0.927 mmol	DMF anhydr. n-pro- panol	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 chloro- benzene	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
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 chloro- benzene	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 chloro- benzene	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	metha- nol/ 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

- 13 -

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 chloro- benzene	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 chloro- benzene	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 Formic 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
	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
NO330	FeCl <sub>2</sub> ·4H <sub>2</sub> O 0.50 mmol Formic acid 8.69 mmol	form- amide	90	90	90	8.7749	11.655	8.3297	Pnna
NO332	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

- 14 -

NO333	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
NO335	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
NO336	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
NO13	Mn(Ac) <sub>2</sub> ·4H <sub>2</sub> O 0.46 mmol Bezoic acid 0.92 mmol Bipyridine 0.46 mmol	ethanol	90	90	90	18.66	11.762	9.418	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
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	ether	90	95.32	90	9.572	17.162	14.041	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	DMF CH <sub>3</sub> CN	90	91.37	90	17.96	6.38	7.19	C2/c
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 toluene	90	90	90	14.5	17.04	18.02	Pbca
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 methanol	90	91.172	90	33.181	9.824	17.884	C2/c
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 n-propanol	90	90.096	90	14.5873	14.153	17.183	P2(1)/n
BPR68D10	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O 0.0016 mmol H <sub>3</sub> BTC 0.0064 mmol	DMSO benzene	90	95.316	90	10.0627	10.17	16.413	P2(1)/c
BPR69B1	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

- 15 -

BPR73E4	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 0.006 mmol H <sub>2</sub> BDC 0.003 mmol	DMSO toluene	90	92.324	90	8.7231	7.0568	18.438	P2(1)/n
BPR76D5	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O 0.0009 mmol H <sub>2</sub> BzPDC 0.0036 mmol	DMSO	90	104.17	90	14.4191	6.2599	7.0611	Pc
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
	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	NMP	106.3	107.63	107.2	7.5308	10.942	11.025	P1
BPR95A2	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	90	102.9	90	7.4502	13.767	12.713	P2(1)/c
Cu <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
Zn C <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

- 16 -

MOF-49	ZnCl <sub>2</sub> 0.44 mmol m-BDC 0.261 mmol	DMF CH <sub>3</sub> CN	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 dicarbox- ylic 0.085 mmol	DMF	90	90	120	20.0652	20.065	20.747	R-3/m
MOF-107	Cu(NO <sub>3</sub> ) <sub>2</sub> ·2.5H <sub>2</sub> O 0.084 mmol thiophene dicarbox- ylic 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 dicarbox- ylic 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

- 17 -

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	Pnmm
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

- 18 -

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

	ADC	Acetylene dicarboxylic acid
	NDC	Naphtalene dicarboxylic acid
5	BDC	Benzene dicarboxylic acid
	ATC	Adamantane tetracarboxylic acid
	BTC	Benzene tricarboxylic acid
	BTB	Benzene tribenzoate
	MTB	Methane tetrabenzoate
10	ATB	Adamantane tetrabenzoate
	ADB	Adamantane dibenzoate

Particularly preferred are within the present application framework materials of  
 15 the kind described herein, which comprise Zn<sup>2+</sup> as a metal ion and ligands derived  
 from terephthalic acid as the bidentate compound, which are known as MOF-5 in  
 the literature.

Further metal ions and at least bidentate organic compounds and mono-dentate  
 20 substances, which are respectively 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, US 5,648,508 and DE 10111230.0.

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 are recycled after crystallization in order to save costs and materials.

The separation of the framework materials, particularly of MOF-5, from the mother liquor of the crystallization may be achieved by procedures known in the art such as solid-liquid separations, such as 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, spray-drying or spray granulation as well as by evaporation of the mother liquor at elevated temperature and/or in vacuo and concentrating of the solid.

The separated framework materials, particularly MOF-5, may be compounded, melted, extruded, co-extruded, pressed, spinned, foamed and granulated according to processes known within the processing of plastics, respectively. Generally the materials are used in the form of pellets or in film or sheet-like form for the purpose of this invention. However, the above methods allow to prepare various further and different geometries and shapes, which are necessary for the widespread application areas of said materials according to the present invention, particularly when used in mobile and mobile portable applications.

As the gases to be retained and/or stored and/or released, particularly to be mentioned are hydrocarbons, alcohols, hydrogen, nitrogen, noble gases, CO, CO<sub>2</sub>,

- 20 -

natural gases, synthesis gas, compounds generating and/or delivering these gases and mixtures of two or more thereof. Particularly preferred are hydrogen, a hydrogen containing gas mixture, a hydrogen generating or delivering substance, a gas mixture comprising at least one hydrogen generating and/or delivering substance.

In a further embodiment the metallo-organic framework material is contacted with at least one capacity-enhancing agent selected from the group consisting of: solvents, complexes, metals, metal hydrides, alloys, and mixtures of two or more thereof, such as embodiments of the above derived from Pd, Pt, Ni, and Ru as the metal.

Furthermore, the present invention relates to a device for uptaking, or storing, or releasing, or uptaking and storing, or uptaking and releasing, or storing and releasing, or uptaking, storing and releasing at least one gas, accommodating a metallo-organic framework material, as defined herein.

Said device may include the following further components:  
a container accommodating the metallo-organic framework material;  
an entrance/exit opening for allowing the at least one gas to enter or exit the device;  
a gas-tight maintaining mechanism capable of maintaining the gas under pressure inside the container.

The invention further relates to a fuel cell accommodating the agent as described herein.

It also relates to a method of using an agent comprising the metallo-organic framework material described herein for uptaking, or storing, or releasing, or uptaking and storing, or uptaking and releasing, or storing and releasing or uptaking, storing and releasing at least one gas in stationary, mobile and mobile portable

- 21 -

applications, preferably in power plants, cars, trucks, busses, cell phones, laptops, and a method of using the device according to the present invention for supplying power to power plants, cars, trucks, busses, cell phones, laptops.

The invention is now further described by way of the following examples, which are, however, not meant to limit the scope of the present application.

### Examples

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

Starting Material	Molar Amount	Calculated	Experimental
terephthalic acid	12.3 mmol	2.04 g	2.04 g
zinc nitrate-tetra hydrate	36.98 mmol	9.67 g	9.68 g
diethylformamide (Merck)	2568.8 mmol	282.2 g	282.2 g

The above-mentioned amounts of the starting materials were dissolved in a beaker in the order diethylformamide, terephthalic acid and zinc nitrate. The resulting solution was introduced into two autoclaves (250 ml), having respectively inner walls which were covered by teflon.

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The crystallization occurred at 105° C within twenty hours. Subsequently, the orange solvent was decanted from the yellow crystals, said crystals were again covered by 20 ml dimethylformamide, the latter being again decanted. This procedure was repeated three

- 22 -

times. Subsequently, 20 ml chloroform were poured onto the solid, which was washed and decanted by said solvent two times.

The crystals (14.4 g), which were still moist, were introduced into a vacuum device and first at room temperature in vacuo ( $10^{-4}$  mbar), afterwards dried at 120°C.

Subsequently, the resulting product was characterized by X-ray powder diffraction and an adsorptive determination of micropores. The resulting product shows the X-ray diffractogramm which coincides with MOF-5.

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The determination of the sorption isotherm with argon (87K; Micromeritics ASAP 2010) shows an isotherm of type I, being typical for microporous materials, and having a specific surface area of 3020 m<sup>2</sup>/g, calculated according to Langmuir, and a micropore volume of 0.97 ml/g (at a relative pressure  $p/p^0 = 0,4$ ).

### Example 2

By using a magnetic suspension balance of the company Rubotherm Präzisionsmesstechnik GmbH, Bochum the storing capacity for hydrogen of the sample of Example 1 was  
20 determined as follows. The sample was weighed, introduced into the apparatus. After closing and evacuating the same to a pressure of  $10^{-5}$  mbar by way of a membrane prepump and a turbo molecular pump the sample was heated under vacuum at 100°C for 16 h.

After thermostabilizing the sample at a temperature of 30°C, hydrogen (purity 99,999 %; company Messer) was added at various pressures. The resulting sorption isotherm shows that at a hydrogen pressure of about 150 mbar the sample is capable of storing about 1 wt.-% hydrogen relative to the total weight of the activated sample. Under further increased pressure the storing capacity even increases.

Example 3 (comparative)

By using the same experimental setup and the same procedure as in Example 2 the storing capacity for hydrogen of activated carbon (company CECA, AC 40; specific surface area according to Langmuir 2037 m<sup>2</sup>/g) was measured. The results show a significantly less capacity of activated carbon compared to MOF-5.

**WHAT IS CLAIMED IS:**

1. Method of uptaking, or storing, or releasing, or uptaking and storing, or uptaking and releasing, or storing and releasing or uptaking, storing and releasing at least one gas, said method being characterized in that the gas is uptaken, or stored, or released; or uptaken and stored; or uptaken and released, or stored and released or uptaken, stored and released by an agent comprising a metallo-organic framework material comprising pores, at least one metal ion and at least one at least bidentate organic compound, which is bound to said metal ion, wherein the gas is selected from the group consisting of hydrogen; a hydrogen containing gas mixture, a hydrogen generating substance, a hydrogen delivering substance, a gas mixture comprising at least one hydrogen generating substance and a gas mixture comprising at least one hydrogen delivering substance.  
10
2. Method according to claim 1, characterized in that the at least one bidentate organic compound is coordinately bound to the metal ion.
3. Method according to claim 1, characterized in that the metal ion is selected among ions of elements of groups Ia, IIa, IIIa, IVa to VIIIa and Ib to VIb of the periodic table of the elements.
4. Method according to claim 1, characterized in that the metallo-organic framework material is contacted with at least one capacity-enhancing agent selected from the group consisting of solvents, complexes, metals, metal hydrides, metal alloys, and mixtures of two or more thereof.  
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5. Method according to claim 1; characterized in that the bidentate organic compound is selected among substituted and unsubstituted aromatic polycarboxylic acids, which may comprise one or more nuclei; and substituted and unsubstituted

- 25 -

aromatic polycarboxylic acids, which comprise at least one hetero-atom and which may have one or more nuclei.

6. Method according to claim 1 characterized in that the metallo organic framework material comprising pores exhibits a BET specific surface area, as determined via adsorption according to DIN 66131, larger than 20 m<sup>2</sup>/g.

7. Device for uptaking, or storing, or releasing, or uptaking and storing, or uptaking and releasing, or storing and releasing, or uptaking, storing and releasing at least one gas, accomodating a metallo-organic framework material and according to the method defined in claim 1, wherein the gas is selected from the group consisting of hydrogen, a hydrogen containing gas mixture, a hydrogen generating substance, a hydrogen delivering substance, a gas mixture comprising at least one hydrogen generating substance and a gas mixture comprising at least one hydrogen delivering substance, and wherein the device further includes

10 a container accomodating the metallo-organic framework material;  
an entrance/exit opening for allowing the at least one gas to enter or exit the device;  
a gas-tight maintaining mechanism capable of maintaining the gas under pressure inside the container.

8. Use of an agent comprising a metallo-organic framework material comprising pores and at least one metal ion and at least one at least bidentate organic compound, which is bound to said metal ion as for uptaking, or storing, or releasing, or uptaking and storing, or uptaking and releasing, or storing and releasing or uptaking, storing and releasing at least one gas in stationary, mobile and mobile portable applications, wherein the gas is selected from the group consisting of hydrogen, a hydrogen containing gas mixture, a hydrogen generating substance, a hydrogen delivering substance, a gas mixture comprising at least one hydrogen

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- 26 -

generating substance and a gas mixture comprising at least one hydrogen delivering substance.

9. Use according to claim 8, characterized in that the at least one at least bidentate organic compound is coordinately bound to the metal ion.

10. Use according to claim 8 or 9, wherein the applications are selected from the group consisting of power plants, cars, trucks, busses, cell phones and laptops.

11. Use of a device as defined in claim 7 for supplying power to a device selected from the group consisting of power plants, cars, trucks, busses, cell phones and laptops.