Title: VERY LOW DENSITY METAL ORGANIC FRAMEWORKS WITH LARGE PORE VOLUMES

Abstract: The disclosure provides for metal organic frameworks (MOFs) which comprise a plurality of repeating magnesium-based SBUs that are linked together by BTB-based linking ligands. The disclosure further provides for the use of these MOFs in a variety of applications, including for gas separation, gas storage, catalysis, and water storage.
VERY LOW DENSITY METAL ORGANIC FRAMEWORKS WITH LARGE PORE VOLUMES

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority under 35 U.S.C. §119 from Provisional Application Serial No. 61/980,507, filed April 16, 2014, the disclosure of which is incorporated herein by reference.

TECHNICAL FIELD

[0002] The disclosure provides for metal organic frameworks (MOFs) which comprise a plurality of magnesium-based SBUs that are linked together by a plurality of BTB-based linking ligands. The disclosure further provides for the use of these MOFs in variety of applications, including for gas separation, gas storage, catalysis, and water storage.

BACKGROUND

[0003] Metal-organic frameworks (MOFs) are porous crystalline materials that are constructed by linking metal clusters called Secondary Binding Units (SBUs) and organic linking ligands. MOFs have high surface area and high porosity which enable them to be utilized in diverse fields, such as gas storage, catalysis, and sensors.

SUMMARY

[0004] The disclosure provides for MOFs that comprise a plurality of repeating magnesium-based SBUs that are linked together by 1,3,5-Tris (4-carboxyphenyl) benzene (BTB)-based linking ligands, including close analogs thereof. The MOFs disclosed herein have a very open structure where the magnesium-based SBUs are coordinated to BTB-based linking ligands and solvent molecules. The MOFs disclosed herein are characterized by having a large pore volume and extremely low density. The disclosure further provides for the use of the MOFs disclosed herein in various devices and applications including devices and/or methods for separating gases, storing gases, and catalysis.

[0005] In a particular embodiment, the disclosure provides for a metal organic framework (MOF) which comprises a plurality of repeating magnesium-based SBUs that are linked together by linking ligands which comprise the structure of Formula I:
wherein, $A^1 - A^3$ are independently a C or N; $R^1 - R^{12}$ are independently selected from H, D, FG, optionally substituted (C1-C12) alkyl, optionally substituted hetero- (C1-C12) alkyl, optionally substituted (C1-C12) alkenyl, optionally substituted hetero- (C1-C12) alkenyl, optionally substituted (C1-C12) alkynyl, optionally substituted hetero- (C1-C12) alkynyl, optionally substituted (C1-C12) cycloalkyl, optionally substituted (C1-C12) cycloalkenyl, optionally substituted aryl, optionally substituted heterocycle, optionally substituted mixed ring system, $-C(R^{13})_3$, $-CH(R^{13})_2$, $-CH_2R^{13}$, $-C(R^{14})_3$, $-CH(R^{14})_2$, $-CH_2R^{14}$, $-OC(R^{11})_3$, $OCH(R^{13})_2$, $-OCH2R^{13}$, $-OC(R^{14})_3$, $-OCH(R^{14})_2$, $OCH_2R^{14}$, wherein $R^1 - R^{12}$ when directly adjacent can be linked together to form one or more optionally substituted rings selected from the group comprising cycloalkyl, cycloalkenyl, heterocycle, aryl, and mixed ring system; $R^{13}$ is selected from FG, optionally substituted (C1-C12) alkyl, optionally substituted hetero- (C1-C12) alkyl, optionally substituted (C1-C12) alkenyl, optionally substituted hetero- (C1-C12) alkenyl, optionally substituted (C1-C12) alkynyl, optionally substituted hetero- (C1-C12) alkynyl, optionally substituted hetero- (C1-C12) alkenyl, hemiacetal, hemiketal, acetal, ketal, and orthoester; $R^{14}$ is selected from one or more optionally substituted rings selected from cycloalkyl, aryl and heterocycle, wherein the MOF crystalizes in the monoclinic space group of P2i/n, C2/c or C2/m and/or the MOF has a topology of point symbol $(6.8.10)_4$ $(6.82)_6$ $(6^2.86.10^6.12)$. In a further embodiment, $R^1 - R^{12}$ are independently selected from:
and M is an alkaline metal species, an alkaline-earth metal species, or transition metal species that has a formal charge of +1 and that can be coordinated by one or more neutral or charged ligands. In yet a further embodiment, the linking ligands comprise the structure of:
In a particular embodiment, a MOF disclosed herein is multivariate by comprising two or more linking ligands which comprise the structure of Formula I:

\[
\text{Formula (I)}
\]

wherein,

\(A^1 - A^3\) are independently a C or N;
R₁−R₁² are independently selected from H, D, FG, optionally substituted (C₁-C₁₂) alkyl, optionally substituted hetero- (C₁-C₁₂) alkyl, optionally substituted (C₁-C₁₂) alkenyl, optionally substituted hetero- (C₁-C₁₂) alkenyl, optionally substituted (C₁-C₁₂) alkynyl, optionally substituted hetero- (C₁-C₁₂) alkynyl, optionally substituted (C₁-C₁₂) cycloalkyl, optionally substituted (C₁-C₁₂) cycloalkenyl, optionally substituted aryl, optionally substituted heterocycle, optionally substituted mixed ring system, −C(R₁³)₃, −CH(R₁³)₂, −CH₂R₁³, −C(R₁³)₂, −CH₂R₁⁴, −OC(R₁³)₃, OCH(R₁³)₂, −OCH₂R₁³, −OC(R₁³)₂, OCH₂R₁⁴, wherein R₁−R₁² when directly adjacent can be linked together to form one or more optionally substituted rings selected from the group comprising cycloalkyl, cycloalkenyl, heterocycle, aryl, and mixed ring system; R₃ is selected from FG, optionally substituted (C₁-C₁₂) alkyl, optionally substituted hetero- (C₁-C₁₂) alkyl, optionally substituted (C₁-C₁₂) alkenyl, optionally substituted hetero- (C₁-C₁₂) alkenyl, optionally substituted (C₁-C₁₂) alkynyl, optionally substituted hetero- (C₁-C₁₂) alkynyl, hemiacetal, hemiketal, acetal, ketal, and orthoester; R₄ is selected from one or more optionally substituted rings selected from cycloalkyl, aryl and heterocycle; wherein the MOF comprises two or more linking ligands which have different structures and wherein the MOF crystallizes in the monoclinic space group of P2₁/n, C2/c or C2/m and/or the MOF has a topology of point symbol (6.8.10)₄(6.8₂)₆(6₃.8⁵.10₆.12). In a further embodiment, the two or more linking ligands are selected from:
comprises an equimolar ratio of the two or more differently functionalized linking ligands. In yet another embodiment, the MOF comprises 3 to 13 differently functionalized linking ligands. In a further embodiment, a MOF disclosed herein has a surface area of at least 3000 m²/g, at least 3500 m²/g, or at least 4500 m²/g. [0007] In a particular embodiment, the disclosure also provides that a MOF disclosed herein can be activated by removing guest molecules via calcination or by treatment with supercritical CO₂.
In a further embodiment, a MOF disclosed herein is characterized by having a high density of open metal sites. In yet a further embodiment, a MOF disclosed herein is reacted with a post framework reactant that adds at least one effect to the MOF selected from: modulating the gas storage ability of the MOF; modulating the sorption properties of the MOF; modulating the pore size of the MOF; modulating the catalytic activity of the MOF; modulating the conductivity of the MOF; and modulating the sensitivity of the MOF to the presence of an analyte of interest.

[0008] In a certain embodiment, the disclosure further provides for a gas separation and/or gas storage device comprising a MOF disclosed herein. In a further embodiment, the gas storage device is a gas tank. In yet a further embodiment, the gas tank is configured to be used in a vehicle. In another embodiment, a gas separation device includes purifiers, filters, scrubbers, pressure swing adsorption devices, molecular sieves, hollow fiber membranes, ceramic membranes, cryogenic air separation devices, and hybrid gas separation devices.

[0009] In a particular embodiment, the disclosure provides a method of separating and/or storing one or more gases from a gas mixture comprising contacting the gas mixture with a MOF or a device disclosed herein. In a further embodiment, the gas mixture comprises carbon dioxide and the gas that is separated and/or stored is carbon dioxide. In an alternate embodiment, the gas mixture comprises a natural gas stream and the gases that are separated from the natural gas stream are acid gases and/or water vapor.

**DESCRIPTION OF DRAWINGS**

[0010] **Figure 1** provides a representation of the Mg-BTB phase 1 crystal structure, where carbon and oxygen are represented by spheres while magnesium atoms are represented by polyhedra. Mg-BTB phase 1 crystallizes in the monoclinic space group P21/n, with lattice parameters a = 26.95 Å, b = 36.03 Å, c = 29.30 Å, α = 90°, β = 108.19°, and γ = 90°.

[0011] **Figure 2** provides a representation of the Mg-BTB phase 2 crystal structures, where carbon and oxygen are represented by spheres while magnesium atoms are represented by polyhedra. Mg-BTB
phase 2 crystallizes in the monoclinic space group C2/c, with lattice parameters \(a = 46.25 \text{ Å}, b = 35.37 \text{ Å}, c = 34.35 \text{ Å}, a = 90^\circ, \beta = 98.79^\circ,\) and \(\gamma = 90^\circ\).

[0012] **Figure 3** provides a representation of the Mg-BTB phase 3 crystal structure, where carbon and oxygen are represented by spheres while magnesium atoms are represented by polyhedra. Mg-BTB phase 3 crystallizes in the monoclinic space group C2/m, with lattice parameters \(a = 32.60 \text{ Å}, b = 39.51 \text{ Å}, c = 27.66 \text{ Å}, a = 90^\circ, \beta = 124.51^\circ,\) and \(\gamma = 90^\circ\).

[0013] **Figure 4** illustrates two types of SBUs for a framework having the chemical formula of \([\text{Mg}_5\text{BTB}_3\text{DEF}]^+\). The di-atomic SBU is only coordinated to three carboxylates; the charges are not compensated. Carbon and oxygen are represented by black and dark gray spheres, respectively, while magnesium atoms are represented by polyhedra.

[0014] **Figure 5** illustrates that the three phases are polymorphs, in that they have the same topology but different cell volumes.

[0015] **Figure 6** provides a space filing model for the P2i/n polymorph. The surface area for the P2i/n polymorph is \(-3000 \text{ m}^2/\text{g}\).

[0016] **Figure 7** provides a space filing model for the C2/c polymorph. The surface area for the C2/c polymorph is \(-3500 \text{ m}^2/\text{g}\).

[0017] **Figure 8** provides a space filing model for the C2/m polymorph. The surface area for the C2/m polymorph is \(-4000 \text{ m}^2/\text{g}\).

**DETAILED DESCRIPTION**

[0018] As used herein and in the appended claims, the singular forms "a," "and," and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "an organic linking ligand" includes a plurality of such linking ligands and reference to "the metal ion" includes reference to one or more metal ions and equivalents thereof known to those skilled in the art, and so forth.

[0019] Also, the use of "or" means "and/or" unless stated otherwise. Similarly, "comprise," "comprises," "comprising" "include," "includes," and "including" are interchangeable and not intended to be limiting.
[0020] It is to be further understood that where descriptions of various embodiments use the term "comprising," those skilled in the art would understand that in some specific instances, an embodiment can be alternatively described using language "consisting essentially of" or "consisting of."

[0021] All publications mentioned throughout the disclosure are incorporated herein by reference in full for the purpose of describing and disclosing the methodologies, which are described in the publications, which might be used in connection with the description herein. The publications discussed above and throughout the text are provided solely for their disclosure prior to the filing date of the present application. Nothing herein is to be construed as an admission that the inventors are not entitled to antedate such disclosure by virtue of prior disclosure. Moreover, with respect to similar or identical terms found in the incorporated references and terms expressly defined in this disclosure, the term definitions provided in this disclosure will control in all respects.

[0022] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood to one of ordinary skill in the art. Although there are many methods and reagents similar or equivalent to those described herein, the exemplary methods and materials are presented herein.

[0023] The term "alkenyl", refers to an organic group that is comprised of carbon and hydrogen atoms that contains at least one double covalent bond between two carbons. Typically, an "alkenyl" as used in this disclosure, refers to organic group that contains 1 to 30 carbon atoms, unless stated otherwise. While a Ci-alkenyl can form a double bond to a carbon of a parent chain, an alkenyl group of three or more carbons can contain more than one double bond. It certain instances the alkenyl group will be conjugated, in other cases an alkenyl group will not be conjugated, and yet other cases the alkenyl group may have stretches of conjugation and stretches of nonconjugation. Additionally, if there is more than 1 carbon, the carbons may be connected in a linear manner, or alternatively if there are more than 3 carbons then the carbons may also be linked in a branched fashion so that the parent chain contains one
or more secondary, tertiary, or quaternary carbons. An alkenyl may be substituted or unsubstituted, unless stated otherwise.

[0024] The term "alkyl", refers to an organic group that is comprised of carbon and hydrogen atoms that contain single covalent bonds between carbons. Typically, an "alkyl" as used in this disclosure, refers to an organic group that contains 1 to 30 carbon atoms, unless stated otherwise. Where if there is more than 1 carbon, the carbons may be connected in a linear manner, or alternatively if there are more than 2 carbons then the carbons may also be linked in a branched fashion so that the parent chain contains one or more secondary, tertiary, or quaternary carbons. An alkyl may be substituted or unsubstituted, unless stated otherwise.

[0025] The term "alkynyl", refers to an organic group that is comprised of carbon and hydrogen atoms that contains a triple covalent bond between two carbons. Typically, an "alkynyl" as used in this disclosure, refers to organic group that contains 1 to 30 carbon atoms, unless stated otherwise. While a cis-alkynyl can form a triple bond to a carbon of a parent chain, an alkynyl group of three or more carbons can contain more than one triple bond. Where if there is more than 1 carbon, the carbons may be connected in a linear manner, or alternatively if there are more than 4 carbons then the carbons may also be linked in a branched fashion so that the parent chain contains one or more secondary, tertiary, or quaternary carbons. An alkynyl may be substituted or unsubstituted, unless stated otherwise.

[0026] The term "aryl", as used in this disclosure, refers to a conjugated planar ring system with delocalized pi electron clouds that contain only carbon as ring atoms. An "aryl" for the purposes of this disclosure encompass from 1 to 12 aryl rings wherein when the aryl is greater than 1 ring the aryl rings are joined so that they are linked, fused, or a combination thereof. An aryl may be substituted or unsubstituted, or in the case of more than one aryl ring, one or more rings may be unsubstituted, one or more rings may be substituted, or a combination thereof.

[0027] A "BTB-based linking ligand" as used herein refers to an organic structure that comprises a 1,3,5-tris (4-
carboxyphenyl) benzene (BTB) core structure which may be further substituted with one or more substituents, including ring structures arising from adjacent positions on the BTB-aryl rings. Additionally, for purposes of this disclosure, a "BTB-based linking ligand" also encompasses substitution of one or more carbon atoms of the central aryl ring with nitrogen atoms. A "BTB-based linking ligand" would include (4,4',4''-s-triazine-2,4,6-triyl-tribenzoate) (TATB), for example. While the various BTB based linking ligands depicted herein (e.g., Formula 1) are shown with carboxylic acid based linking clusters, it would be understood by one of skill in the art that these carboxylic acid groups undergo condensation to form one or more bonds to magnesium of the SBUs in order to link the SBUs together in the framework. For example, the carboxylic acid groups could be understood as having the generalized structure of: \[ \text{ when they condense with one or more magnesium ions to make a MOF of the disclosure.} \]

[0028] The term "cycloalkenyl", as used in this disclosure, refers to an alkene that contains at least 3 carbon atoms but no more than 12 carbon atoms connected so that it forms a ring. A "cycloalkenyl" for the purposes of this disclosure encompass from 1 to 12 cycloalkenyl rings, wherein when the cycloalkenyl is greater than 1 ring, then the cycloalkenyl rings are joined so that they are linked, fused, or a combination thereof. A cycloalkenyl may be substituted or unsubstituted, or in the case of more than one cycloalkenyl ring, one or more rings may be unsubstituted, one or more rings may be substituted, or a combination thereof.

[0029] The term "cycloalkyl", as used in this disclosure, refers to an alkyl that contains at least 3 carbon atoms but no more than 12 carbon atoms connected so that it forms a ring. A "cycloalkyl" for the purposes of this disclosure encompass from 1 to 12 cycloalkyl rings, wherein when the cycloalkyl is greater than 1 ring, then the cycloalkyl rings are joined so that they are linked, fused, or a combination thereof. A cycloalkyl may be substituted or unsubstituted, or in the case of more than one
cycloalkyl ring, one or more rings may be unsubstituted, one or more rings may be substituted, or a combination thereof.  

[0030] The term "framework" as used herein, refers to a highly ordered structure comprised of secondary building units (SBUs) that can be linked together in defined, repeated and controllable manner, such that the resulting structure is characterized as being porous, periodic and crystalline. Typically, "frameworks" are two dimensional (2D) or three dimensional (3D) structures. Examples of "frameworks" include, but are not limited to, "metal-organic frameworks" or "MOFs", "zeolitic imidazolate frameworks" or "ZIFs", or "covalent organic frameworks" or "COFs". While MOFs and ZIFs comprise SBUs of metals or metal ions linked together by forming covalent bonds with linking clusters on organic linking moieties, COFs are comprised of SBUs of organic linking moieties that are linked together by forming covalent bonds via linking clusters. As used herein, "framework" does not refer to coordination complexes or metal complexes. Coordination complexes or metal complexes are comprised of a relatively few number of centrally coordinated metal ions (i.e., less than 4 central ions) that are coordinately bonded to molecules or ions, also known as ligands or complexing agents. By contrast, "frameworks" are highly ordered and extended structures that are not based upon a centrally coordinated ion, but involve many repeated secondary building units (SBUs) linked together. Accordingly, "frameworks" are orders of magnitude much larger than coordination complexes and have different structural and chemical properties due to the framework's open and ordered structure. 

[0031] The term "functional group" or "FG" refers to specific groups of atoms within molecules that are responsible for the characteristic chemical reactions of those molecules. While the same functional group will undergo the same or similar chemical reaction(s) regardless of the size of the molecule it is a part of, its relative reactivity can be modified by nearby functional groups. The atoms of functional groups are linked to each other and to the rest of the molecule by covalent bonds. Examples of FGs that can be used in this disclosure, include, but are not limited to, substituted or unsubstituted alkyls, substituted or
unsubstituted alkenyls, substituted or unsubstituted alkynyls, substituted or unsubstituted aryls, substituted or unsubstituted hetero-alkyls, substituted or unsubstituted hetero-alkenyls, substituted or unsubstituted hetero-alkynyls, substituted or unsubstituted cycloalkyls, substituted or unsubstituted cycloalkenyls, substituted or unsubstituted hetero-aryls, substituted or unsubstituted heterocycles, halos, hydroxyls, anhydrides, carboxyls, carboxylates, aldehydes, haloformyls, esters, hydroperoxy, peroxy, ethers, orthoesters, carboxamides, amines, imines, imides, azides, azos, cyanates, isocyanates, nitrates, nitriles, isonitriles, nitrosos, nitros, nitrosooxy, pyridyls, sulfoxyls, sulfides, disulfides, sulfinyls, sulfos, thiocyanates, isothiocyanates, carbonothioyls, phosphinyls, phosphonos, phosphates, Si (OH)₉, Ge(OH)₉, Sn (OH)₉, Si(SH)₉, Ge(SH)₉, AsO₂H, AsO₃H, P(SH)₉, As(SH)₉, S₂O₃H, Si (OH)₉, Ge(OH)₉, Sn(OH)₉, Si(SH)₉, Ge(SH)₉, Sn(SH)₉, AsO₂H, AsO₃H, P(SH)₉, and As(SH)₉. In a particular embodiment, a functional group or "FG" is selected from the group comprising: halos, ethers, hydroxyls, aldehydes, ketones, carboxyls, esters, amines, imines, nitriles, azides, amides, nitriles, isocyanos, nitros, nitrosos, sulfoxyls, sulfides, sulfinyls, sulfonyls, phosphinyls, and phosphates.

[0032] The term "hetero-" when used as a prefix, such as, hetero-alkyl, hetero-alkenyl, hetero-alkyny, or hetero-hydrocarbon, for the purpose of this disclosure refers to the specified hydrocarbon having one or more carbon atoms replaced by non-carbon atoms as part of the parent chain. Examples of such non-carbon atoms include, but are not limited to, N, O, S, Si, Al, B, and P. If there is more than one non-carbon atom in the hetero-based parent chain then this atom may be the same element or may be a combination of different elements, such as N and O.

[0033] The term "heterocycle", as used in this disclosure, refers to ring structures that contain at least 1 noncarbon ring atom. A "heterocycle" for the purposes of this disclosure encompass from 1 to 12 heterocycle rings wherein when the heterocycle is greater than 1 ring the heterocycle rings are joined so that they are linked, fused, or a combination thereof. A heterocycle may be a heteroaryl or nonaromatic, or in the case of more than one
heterocycle ring, one or more rings may be nonaromatic, one or more rings may be hetero-aryls, or a combination thereof. A heterocycle may be substituted or unsubstituted, or in the case of more than one heterocycle ring one or more rings may be unsubstituted, one or more rings may be substituted, or a combination thereof. Typically, the noncarbon ring atom is N, O, S, Si, Al, B, or P. In case where there is more than one noncarbon ring atom, these noncarbon ring atoms can either be the same element, or combination of different elements, such as N and 0. Examples of heterocycles include, but are not limited to: a monocyclic heterocycle such as, aziridine, oxirane, thiirane, azetidine, oxetane, thietane, pyrrolidine, pyrroline, imidazolidine, pyrazolidine, pyrazoline, dioxolane, sulfolane 2,3-dihydrofuran, 2,5-dihydrofuran, tetrahydrofuran, thiophene, piperidine, 1,2,3,6-tetrahydro-pyridine, piperazine, morpholine, thiomorpholine, pyran, thiopyran, 2,3-dihydropyran, tetrahydropyran, 1,4-dihydropyridine, 1,4-dioxane, 1,3-dioxane, dioxane, homopiperidine, 2,3,4,7-tetrahydro-1H-azepine homopiperazine, 1,3-dioxepane, 4,7-dihydro-1,3-dioxepin, and hexamethylene oxide; and polycyclic heterocycles such as, indole, indoline, isoindoline, quinoline, tetrahydroquinoline, isoquinoline, tetrahydroisoquinoline, 1,4-benzodioxan, coumarin, dihydrocoumarin, benzofuran, 2,3-dihydrobenzofuran, isobenzofuran, chromene, chroman, isochroman, xanthene, phenoxathiin, thianthrene, indolizine, isoindole, indazole, purine, phthalazine, naphthyridine, quinoxaline, quinazoline, cinnoline, pteridine, phenanthridine, perimidine, phenanthroline, phenazine, phenothiazine, phenoxyzine, 1,2-benzisoxazole, benzothiophene, benzoazole, benzthiazole, benzimidazole, benztriazole, thioxanthine, carbazole, carboline, acridine, pyrrolizidine, and quinolizidine. In addition to the polycyclic heterocycles described above, heterocycle includes polycyclic heterocycles wherein the ring fusion between two or more rings includes more than one bond common to both rings and more than two atoms common to both rings. Examples of such bridged heterocycles include quinclidine, diazabicyclo [2.2.1]heptane and 7-oxabicyclo [2.2.1]heptane.

[0034] The terms "heterocyclic group", "heterocyclic moiety", "heterocyclic", or "heterocyclo" used alone or as a suffix or
prefix, refers to a heterocycle that has had one or more hydrogens
removed therefrom.

[0035] The term "hydrocarbons" refers to groups of atoms that contain only carbon and hydrogen. Examples of hydrocarbons that can be used in this disclosure include, but are not limited to, alkanes, alkenes, alkynes, arenes, and benzyls.

[0036] A "magnesium-based SBU" refers to the aggregation of magnesium metal ions, including any complexes which contain magnesium metal ions, as well as any corresponding metal salt counter-anions, into M-O-C clusters. The magnesium-based SBUs are sufficiently rigid because the magnesium metal ions are locked into their positions by the carboxylate ions of the BTB-based linking ligands.

[0037] The term "mixed ring system" refers to optionally substituted ring structures that contain at least two rings, and wherein the rings are joined together by linking, fusing, or a combination thereof. A mixed ring system comprises a combination of different ring types, including cycloalkyl, cycloalkenyl, aryl, and heterocycle.

[0038] The term "substituent" refers to an atom or group of atoms substituted in place of a hydrogen atom. For purposes of this disclosure, a substituent would include deuterium atoms.

[0039] The term "substituted" with respect to hydrocarbons, heterocycles, and the like, refers to structures wherein the parent chain contains one or more substituents.

[0040] The term "unsubstituted" with respect to hydrocarbons, heterocycles, and the like, refers to structures wherein the parent chain contains no substituents.

[0041] As used herein, a wavy line intersecting another line that is connected to an atom indicates that this atom is covalently bonded to another entity that is present but not being depicted in the structure. A wavy line that does not intersect a line but is connected to an atom indicates that this atom is interacting with another atom by a bond or some other type of identifiable association.

[0042] Metal-organic frameworks (MOFs) are porous crystalline materials that are constructed by the linkage of inorganic metal
clusters called secondary building units (SBUs) with organic linkers. These materials have very large surface areas and pore volumes. Therefore, MOFs are ideally suited for use in gas sorption and/or gas separation.

[0043] The disclosure provides for innovative highly porous MOFs which employ magnesium as a metal center linked by BTB-based linking ligands. For a metal, magnesium has a very low atomic mass and is relatively inexpensive and generally nontoxic. BTB-based ligands have high connectivities and are readily available from multiple vendors. The MOFs of the disclosure have a very open structure where the magnesium-based SBUs are coordinated to BTB-based linking ligands and solvent molecules. The MOFs of the disclosure have a surface area of at least 3000 m²/g⁻¹, and are generally in the range between 3000 to 4000 m²/g⁻¹. Further, the MOFs disclosed herein are characterized by having a very low bulk density and a large pore volume. Accordingly, in direct comparison to other MOFs taught in the art which employ BTB-based linking ligands and transition metals, the MOFs of the disclosure have much lower densities (i.e., \(<<0.427 \text{ g/cm}^3\)) and provide for larger void volumes by being comprised of magnesium. Additionally, MOFs of the disclosure have a large density of open metal sites not seen in other MOFs which employ BTB-based linking ligands (e.g., MOF-177 and variants).

[0044] Further, the magnesium-based SBUs disclosed herein are coordinated to a large number of solvent molecules which may be removed by using activation procedures, such as calcination or supercritical \(\text{CO}_2\), resulting in a high density of open metal sites. The open metal sites are highly reactive for the selective adsorption of high density gases, such as those gases characterized by comprising double or triple bonds (e.g., \(\text{CO}_2\), \(\text{CO}\), \(\text{N}_2\), \(\text{SO}_2\), \(\text{SO}_3\), \(\text{NO}_2\), ethylene, propene, and acetylene). In a particular embodiment, MOFs disclosed herein selectively bind \(\text{CO}_2\) with a high affinity. Moreover, MOFs with open metal sites can improve the separation of (quadru) polar/nonpolar gas pairs such as \(\text{CO}_2/\text{CH}_4\). Thus, MOFs of the disclosure are ideally suited for gas separation applications. Further, MOFs comprising open metal sites have found use in catalytic fields by facilitating the oxidation of molecules.
Depending upon the synthesis conditions various polymorphic MOF structures (e.g., Mg-BTB phase 1, Mg-BTB phase 2, and Mg-BTB phase 3) can be crystalized using the same reactants and solvents but which have different atomic properties (e.g., lattice parameters and space groups). In a particular embodiment, a MOF of the disclosure crystalizes in a monoclinic space group of C2/c, P2\(_1\)/n, or C2/m.

The disclosure also provides for a MOF of the disclosure being multivariate by being comprised of magnesium-based SBUs linked together by two or more functionalized BTB-based linking ligands having different structures. The material properties of these multivariate MOFs can readily be modified by changing the ratio between multiple types of differently functionalized BTB-based linking ligands. In yet another embodiment, the disclosure provides for MOFs of the disclosure which comprise magnesium-based SBUs that are linked by two or more types of differently functionalized BTB-based linking ligands, wherein the different types of functional groups on the BTB-based linking ligands modify the chemical and physical properties of a MOF of the disclosure. The structural tunability of the MOFs disclosed herein allows for an extremely high level of optimization for various applications such as gas separation, gas storage, water storage and release, or catalysis.

Provided herein is a versatile synthetic routes to efficiently prepare BTB derivatives with various functional groups. It should be understood that for MOFs disclosed herein which comprise multiple types of differently functionalized organic linking ligands, these linking ligands can originate from (1) organic linking ligands that are differentially functionalized pre-synthesis (i.e., constructing the framework with organic linking ligands that differ by the number and/or type of functional groups); (2) organic linking ligands that functional groups are modified post synthesis of the framework by reacting the functional group with a post framework reactant; (3) organic linking ligands that functional group(s) are protected with a suitable protecting group which can then be removed post synthesis of the framework, wherein the de-protected functional groups may be modified by
reacting with a post framework reactant; and (4) organic linking ligands that comprise functional groups which are protected with one type of protecting group while other functional groups are protected with a different type of protecting group, such that the protecting groups can be differentially removed post synthesis of the framework by using different reaction conditions. Using such a strategy, one can selectively de-protect certain functional groups while leaving other functional groups protected, so that the newly de-protected groups may be modified by reacting with a post framework reactant. The remaining protected functional groups may then be de-protected and be modified if so desired by reacting with a post framework reactant, etc.

[0048] In certain embodiments, one can prepare various functionalized BTB-based linking ligands as described herein and then react the functionalized BTB-based linking ligands with magnesium salts (e.g., MgCl2 or MgNO3-6H2O) in a suitable solvent (e.g., a polar aprotic solvent) at an elevated temperature for a sufficient period of time.

[0049] In a particular embodiment, the disclosure provides for MOFs that comprise a plurality of repeating magnesium based SBUs that are linked together by BTB-based linking ligands, wherein the linking ligands comprise the structure of Formula I:

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\[
\text{Formula (I)}
\]
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wherein,

\(A^1 - A^3\) are independently a C-H or N;
R¹-R¹² are independently selected from H, D, FG, optionally substituted (C₁-C₁₂) alkyl, optionally substituted hetero- (C₁-C₁₂) alkyl, optionally substituted (C₁-C₁₂) alkenyl, optionally substituted hetero- (C₁-C₁₂) alkenyl, optionally substituted (C₁-C₁₂) alkynyl, optionally substituted hetero- (C₁-C₁₂) alkynyl, optionally substituted (C₁-C₁₂) cycloalkyl, optionally substituted (C₁-C₁₂) cycloalkenyl, optionally substituted aryl, optionally substituted heterocycle, optionally substituted mixed ring system, -C(R¹³)₃, -CH(R¹³)₂, -CH₂R¹³, -C(R¹⁴)₃, -CH(R¹⁴)₂, -CH₂R¹⁴, -OC(R¹³)₃, OCH(R¹³)₂, -OCH₂R¹³, -OC(R¹⁴)₃, -OCH(R¹⁴)₂, OCH₂R¹⁴, wherein R¹⁻R¹² when adjacent can be linked together to form one or more optionally substituted rings selected from the group comprising cycloalkyl, cycloalkenyl, heterocycle, aryl, and mixed ring system;

R¹³ is selected from FG, optionally substituted (C₁-C₁₂) alkyl, optionally substituted hetero- (C₁-C₁₂) alkyl, optionally substituted (C₁-C₁₂) alkenyl, optionally substituted hetero- (C₁-C₁₂) alkenyl, optionally substituted (C₁-C₁₂) alkynyl, optionally substituted hetero- (C₁-C₁₂) alkynyl, hemiacetal, hemiketal, acetal, ketal, and orthoester; and

R¹⁴ is selected from one or more substituted or unsubstituted rings selected from cycloalkyl, aryl and heterocycle. In a particular embodiment, when A¹⁻A³ are C then at least one of R¹⁻R¹² are not H. In another embodiment, the MOF is multivariate by being comprised of at least two, three, four, five or six linking ligands of Formula I, wherein the linking ligands do not have the same structure.

[0050] In another embodiment, the disclosure provides for a MOF that comprises a plurality of repeating magnesium based SBUs that are linked together by BTB-based linking ligands, wherein the linking ligands comprise the structure of Formula I:
wherein,

$A^1 - A^3$ are independently a C-H or N;

$R^1 - R^{12}$ are independently selected from:

- $\text{H}$, $\text{D}$, $\text{Me}$, $\text{Et}$, $\text{Pr}$, $\text{Bu}$, $\text{Cy}$, $\text{Ph}$, $\text{Bz}$
- $\text{F}$, $\text{Cl}$, $\text{Br}$, $\text{I}$
- $\text{CN}$, $\text{NO}_2$
- $\text{CO}_2\text{H}$, $\text{CO}_2\text{Me}$, $\text{CONH}_2$, $\text{CONHMe}$
- $\text{OH}$, $\text{N}_2\text{H}$, $\text{N}_2\text{H}_2$, $\text{NH}_2$
- $\text{N}_2\text{H}_3$
M is an alkaline metal species, an alkaline-earth metal species, or a transition metal species that has a formal charge of +1 and that can be coordinated by one or more neutral or charged ligands.

[0051] In another embodiment, a MOF of the disclosure comprises a plurality of repeating magnesium-based SBUs that are linked together by BTB-based linking ligands, wherein the linking ligands are selected from:
It is yet further contemplated by this disclosure that to enhance chemoselectivity it may be desirable to protect one or more functional groups that would generate unfavorable products upon a chemical reaction desired for another functional group, and then deprotect this protected group after the desired reaction is completed. Employing such a protection/deprotection strategy could be used for one or more functional groups of any organic linking.
ligand described herein, including any structures depicted herein. Accordingly, hydroxyl groups may further comprise a hydroxyl protecting group, amine groups may further comprise an amine protecting group, and carbonyl groups may further comprise a carbonyl protecting group, unless stated otherwise herein.

[0053] Examples of hydroxyl protecting groups include, but are not limited to, methyl, tert-butyl, allyl, propargyl, p-chlorophenyl, p-methoxyphenyl, p-nitrophenyl, 2,4-dinitrophenyl, 2,3,5, 6-tetrafluoro-4-(trifluoromethyl) phenyl, methoxymethyl, methylthiomethyl, (phenyldimethylsilyl)methoxymethyl, benzylxoxymethyl, p-methoxy-benzylxoxymethyl, p-nitrobenzylxoxymethyl, o-nitrobenzylxoxymethyl, (4-methoxyphenoxy) methyl, guaiacolmethyl, tert-butoxymethyl, 4-pentenyloxymethyl, tert-butyldimethylsiloxymethyl, thexyldimethylsiloxymethyl, tert-butyldiphenylxiloxymethyl, 2-methoxyethoxymethyl, 2,2,2-trichloroethoxymethyl, bis(2-chloroethoxy)methyl, 2-(trimethylsilyl) ethoxyethyl, menthoxymethyl, 1-ethoxyethyl, 1-(2-chloroethoxy) ethyl, 1-[2-(trimethylsilyl) ethoxy]ethyl, 1-methyl-1-ethoxyethyl, 1-methyl-1-benzylxoxymethyl, 1-methyl-1-benzyloxy-2-fluoroethyl, 1-methyl-1-phenoxyethyl, 2,2,2-trichloroethyl, 1-dianisyl-2, 2,2-trichloroethyl, 1,1,1,3,3,3-hexafluoro-2-phenylisopropyl, 2-trimethylsilyl ethyl, 2-(benzylthio) ethyl, 2-(phenylelenyl) ethyl, tetrahydropyranyl, 3-bromotetrahydropyranyl, tetrahydrothiopyranyl, 1-methoxycyclohexyl, 4-methoxytetrahydropyranyl, 4-methoxytetrahydrothiopyranyl, 4-methoxytetrahydroxypyran, S,S-dioxide, 1-[(2-chloro-4-methyl) phenyl]-4-methoxyperipendin-4-yl, 1-(2-fluorophenyl)-4-methoxyperipendin-4-yl, 1,4-dioxan-2-yl, tetrahydrofuranyl and the like; Benzy1, 2-nitrobenzyl, 2-trifluoromethylbenzyl, 4-methoxybenzyl, 4-nitrobenzyl, 4-chlorobenzyl, 4-bromobenzyl, 4-cyanobenzyl, 4-phenylbenzyl, 4-acylaminobenzyl, 4-azidobenzyl, 4-(methylsulfinyl) benzyl, 2,4-dimethoxybenzyl, 4-azido-3-chlorobenzyl, 3,4-dimethoxybenzyl, 2,6-dichlorobenzyl, 2,6-difluorobenzyl, 1-pyrenylmethyl, diphenylmethyl, 4,4'-dinitrobenzhydryl, 5-benzosuberyl, triphenylmethyl (trityl), .alpha.-naphthylidiphenylmethyl, (4-methoxyphenyl)-diphenylmethyl, di-(p-methoxyphenyl)-phenylmethyl,
tri- (p-methoxyphenyl)methyl, 4- (4' -bromophenacyloxy) -phenyldiphenylmethyl, 4,4',4' '-tris (4,5- dichlorophthalimidophenyl)methyl, 4,4',4' '-tris (leuvulinoxyloxyphenyl)methyl, 4,4' '-dimethoxy-3 '-(N- (imidazolylmethyl))trityl, 4,4' '-dimethoxy-3'- (N- (imidazolylethyl) carbamoyl) trityl, 1,1-bis (4-methoxyphenyl) -1'-pyrenylmethyl, 4-(1 7-tetrabenzo [a,c,g,I]fluorenethyl) -4,4' -dimethoxytrityl, 9-anthryl, 9- (9-phenyl) xantheryl, 9- (9-phenyl-10-oxo)anthryl and the like; Trimethylsilyl, triethylsilyl, triisopropylsilyl, dimethylisopropylsilyl, diethylisopropylsilyl, dimethylhexyisilyl, tert-butyldimethylsilyl, tert-butyldiphenylsilyl, triphenylsilyl, tri-p-xlylsilyl, triphenylsilyl, diphenylmethyisilyl, di-tert-butyldimethylsilyl, tris (trimethylsilyl)silyl, (2-hydroxystyryl) dimethylsilyl, (2-hydroxystyryl) diisopropylsilyl, tert-butylmethoxyphenylsilyl, tert-butoxydiphenylsilyl and the like; --C(0)R, where R is selected from the group consisting of alkyl, substituted alkyl, aryl and more specifically R = hydrogen, methyl, ethyl, tert-butyl, adamantyl, crotyl, chloromethyl, dichloromethyl, trichloromethyl, trifluoromethyl, methoxymethyl, triphenylmethoxymethyl, phenoxyethyl, 4-chloro phenoxymethyl, phenethyl, diphenylmethoxymethyl, 4-methoxy crotyl, 3-phenylpropyl, 4-pentenyl, 4-oxopentyl, 4,4- (ethylenedithio) pentyl, 5- [3-bis (4-methoxyphenyl) hydroxymethylphenoxy] -4-oxopentyl, phenyl, 4- methyl phenyl, 4-nitrophenyl, 4-fluorophenyl, 4-chlorophenyl, 4-methoxyphenyl, 4-phenylphenyl, 2,4,6-trimethylphenyl, a-naphthyl, benzoyl and the like; --C(0)OR, where R is selected from the group consisting of alkyl, substituted alkyl, aryl and more specifically R = methyl, methoxymethyl, 9-fluorenethyl, ethyl, 2,2,2-trichloromethyl, 1,1-dimethyl-2, 2,2-trichloroethyl, 2-(trimethylsilyl) ethyl, 2- (phenylsulfonyl) ethyl, isobutyl, tert-butyl, vinyl, allyl, 4-nitrophenyl, benzyl, 2-nitrobenzyl, 4-nitrobenzyl, 4-methoxybenzyl, 2,4-dimethoxybenzyl, 3,4- dimethoxybenzyl, 2- (methylthiomethoxy) ethyl, 2-dansenylethyl, 2- (4-nitrophenyl) ethyl, 2- (2,4-dinitrophenyl) ethyl, 2-cyano-l-phenylethyl, thiobenzyl, 4-ethoxy-l-naphthyl and the like.
Examples of carbonyl protecting groups include, but are not limited to, dimethyl acetal, 1,3-dioxane, 1,3-dioxolane, S,S'-dimethylthioacetal, 1,3-dithiane, 1,3-dithiolane, 1,3-oxathiolane, methyl ester, t-Butyl ester, allyl ester, 1,1-dimethylallyl ester, 2,2,2-trifluoroethyl ester, phenyl ester, benzyl ester, 4-methoxybenzyl ester, silyl ester, ortho ester, 9-fluorenylmethyl esters, 2-(trimethylsilyl) ethoxymethyl ester, 2-(trimethylsilyl) ethyl ester, halo esters, o-nitrobenzyl ester, and OBO ester.

Examples of amine protecting groups include, but are not limited to, methyl carbonate, 9-fluorenylmethyl carbamate (Fmoc), 2,2,2-trichloroethyl carbamate (Troc), t-butyl carbamate (Boc), 2-(trimethylsilyl) ethyl carbamate (Teoc), allyl carbamate (Alloc), benzyl carbamate (Cbz), trifluoroacetamide, benzylamine, allylamine, and tritylamine.

All the aforementioned linking ligands that possess appropriate reactive functionalities can be chemically transformed by a suitable reactant post-synthesis of the framework to add further functionalities to the framework. By modifying the organic links within the framework post-synthetically, access to functional groups that were previously inaccessible or accessible only through great difficulty and/or cost is possible and facile.

In a particular embodiment, the disclosure provides for a MOF disclosed herein which comprises a plurality of repeating magnesium based SBUs that are linked together by a BTB-based linking ligands, wherein the MOF comprises at least two (e.g., 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, or 13) BTB-based linking moieties which have a different structure. In a further embodiment, a MOF disclosed herein comprises at least 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 or 13 linking ligands that are selected from:
The MOFs of the disclosure may be generated by first utilizing a plurality of BTB-based linking ligands having different functional groups, wherein at least one of the functional groups may be modified, substituted, or eliminated with a different functional group post-synthesis of the framework. In other words, at least one BTB-based linking ligand comprises a functional group that may be reacted with a post framework reactant to further increase the diversity of the functional groups of the MOFs disclosed herein. In a particular embodiment, the MOF disclosed herein comprises multiple types of differently functionalized BTB-based linking ligands wherein one or more types of the linking ligands can undergo post-synthetic modification with post framework reactant so as to further functionalize the framework.

In a further embodiment, the MOFs of the disclosure may be further modified by reacting with one or more post framework reactants that may or may not have denticity. In another embodiment, a MOF as-synthesized is reacted with at least one, at least two, or at least three post framework reactants. In yet another embodiment, a MOF as-synthesized is reacted with at least two post framework reactants. In a further embodiment, a MOF as-synthesized is reacted with at least one post framework reactant that will result in adding denticity to the framework.

The disclosure provides that a MOF disclosed herein can be modified by a post framework reactant by using chemical reactions that modify, substitute, or eliminate a functional group post-synthesis. These chemical reactions may use one or more similar or divergent chemical reaction mechanisms depending on the
type of functional group and/or post framework reactant used in the reaction. Examples of chemical reaction include, but are not limited to, radical-based, unimolecular nucleophilic substitution (SN1), bimolecular nucleophilic substitution (SN2), unimolecular elimination (E1), bimolecular elimination (E2), ElcB elimination, nucleophilic aromatic substitution (SnAr), nucleophilic internal substitution (SNi), nucleophilic addition, electrophilic addition, oxidation, reduction, cyclo addition, ring closing metathesis (RCM), pericylic, electrocylic, rearrangement, carbene, carbenoid, cross coupling, and degradation. Other agents can be added to increase the rate of the reactions disclosed herein, including adding catalysts, bases, and acids.

[0061] In another embodiment, a post framework reactant adds at least one effect to a MOF of the disclosure including, but not limited to, modulating the gas storage ability of the MOF; modulating the sorption properties of the MOF; modulating the pore size of the MOF; modulating the catalytic activity of the MOF; modulating the conductivity of the MOF; and modulating the sensitivity of the MOF to the presence of an analyte of interest.

In a further embodiment, a post framework reactant adds at least two effects to the MOF of the disclosure including, but not limited to, modulating the gas storage ability of the MOF; modulating the sorption properties of the MOF; modulating the pore size of the MOF; modulating the catalytic activity of the MOF; modulating the conductivity of the MOF; and modulating the sensitivity of the MOF to the presence of an analyte of interest.

[0062] In one embodiment, a post framework reactant has 1-20 carbons with functional groups including atoms such as N, S, and O.

[0063] In another embodiment, a post framework reactant is selected to modulate the size of pores of a MOF disclosed herein.

[0064] In another embodiment, a post framework reactant is selected to increase the hydrophobicity of a MOF disclosed herein.

[0065] In yet another embodiment, a post framework reactant is selected to modulate gas separation of a MOF disclosed herein. In a certain embodiment, a post framework reactant creates an electric dipole moment on the surface of a MOF of the disclosure when it chelates a metal ion.
In a further embodiment, a post framework reactant is selected to modulate the gas sorption properties of a MOF of the disclosure. In another embodiment, a post framework reactant is selected to promote or increase greenhouse gas (e.g., CO2) sorption of a MOF disclosed herein. In another embodiment, a post framework reactant is selected to promote or increase hydrocarbon gas sorption of a MOF of the disclosure.

In yet a further embodiment, a post framework reactant is selected to increase or add catalytic efficiency to a MOF disclosed herein.

In another embodiment, a post framework reactant is selected so that organometallic complexes can be tethered to a MOF of the disclosure. Such tethered organometallic complexes can be used, for example, as heterogeneous catalysts.

In a particular embodiment, a MOF of the disclosure can be used for a variety of applications, including for gas, liquid or vapor separation, gas storage, separation of bioproducts or compounds, or catalysis. In particular embodiment, the disclosure provides for MOFs that can be tuned to adsorb a specific gas or multiple gases from mixed gas stream. For example, a MOF disclosed herein that is comprised of multiple types of BTB-based linking ligands can provide functional groups that have differential binding/interaction characteristics for specific gas molecules. Further, by activating the MOFs by removing solvent molecules, reveals a large number and density of open magnesium metal sites, which are highly reactive for the selective adsorption of high density gases, such as CO2.

In one embodiment of the disclosure, a gas storage or gas separation material comprising a MOF of the disclosure is provided. Advantageously, a MOF of the disclosure includes a number of adsorption sites for storing and/or separating gas molecules. Suitable examples of such gases include, but are not limited to, gases comprising ammonia, argon, methane, propane, carbon dioxide, carbon monoxide, sulfur dioxide, hydrogen sulfide, phosphine, nitrous oxide, hydrogen, oxygen, nitrogen, fluorine, chlorine, helium, carbonyl sulfide, and combinations thereof. In a particularly useful variation a MOF disclosed herein is a hydrogen
storage material that is used separate hydrogen from a gaseous mixture. In another particularly useful variation, a MOF disclosed herein is a carbon dioxide storage material that may be used to separate carbon dioxide from a gaseous mixture. In yet another particularly useful variation, a MOF disclosed herein is a methane storage material that may be used to separate methane from a gaseous mixture.

[0071] The disclosure also provides an apparatus and method for separating one or more component gases from a multi-component gas using a separation system having a feed side and an effluent side separated by a MOF of the disclosure. The apparatus may comprise a column separation format.

[0072] "Natural gas" refers to a multi-component gas obtained from a crude oil well (associated gas) or from a subterranean gas-bearing formation (non-associated gas). The composition and pressure of natural gas can vary significantly. A typical natural gas stream contains methane as a significant component. The natural gas will also typically contain ethane, higher molecular weight hydrocarbons, one or more acid gases (such as carbon dioxide, hydrogen sulfide, carbonyl sulfide, carbon disulfide, and mercaptans), and minor amounts of contaminants such as water, nitrogen, iron sulfide, wax, and crude oil. A MOF of the disclosure can be used as an adsorbent for methane. In a certain embodiment, a MOF disclosed herein can be used to separate and/or store one or more gases from a natural gas stream. In another embodiment, a MOF disclosed herein can be used to separate and/or store methane from a natural gas stream. In yet another embodiment, a MOF disclosed herein can be used to separate and/or store methane from a town gas stream. In yet another embodiment, a MOF disclosed herein can be used to separate and/or store methane from a biogas stream. In a certain embodiment, a MOF disclosed herein can be used to separate and/or store methane from a syngas stream.

[0073] In a particular embodiment, a MOF disclosed herein is part of a device. In another embodiment, a gas separation device comprises a MOF of the disclosure. In a further embodiment, a gas separation device used to separate one or more component gases from
a multi-component gas mixture comprises a MOF disclosed herein. Examples of gas separation and/or gas storage devices include, but are not limited to, purifiers, filters, scrubbers, pressure swing adsorption devices, molecular sieves, hollow fiber membranes, ceramic membranes, cryogenic air separation devices, and hybrid gas separation devices. In a certain embodiment, a gas separation device used to separate carbon dioxide from a mixed gas stream comprises a MOF of the disclosure.

[0074] In a particular embodiment of the disclosure, a gas storage material comprises a MOF disclosed herein. A gas that may be stored or separated by the methods, compositions and systems of the disclosure includes gases such as ammonia, argon, methane, propane, carbon dioxide, carbon monoxide, sulfur dioxide, hydrogen sulfide, phosphine, nitrous oxide, hydrogen, oxygen, nitrogen, fluorine, chlorine, helium, carbonyl sulfide, and combinations thereof. In a particularly useful variation a gas storage material is a hydrogen storage material that is used to store hydrogen. In another particularly useful variation, a gas storage material is a methane storage material that may be used to store methane. In yet another particularly useful variation, a gas storage material is a carbon dioxide storage material that may be used to store carbon dioxide.

[0075] In a certain embodiment, a MOF of the disclosure can be used as heterogeneous catalyst. A MOF can be synthesized to have catalytic activity or be functionalized post synthetically with a post framework reactant to become catalytic. Catalytic activities would include, but are not limited to, hydrolysis reactions, oxidations, reductions, ring closure reactions, metathesis reactions, and isomerizations. As the MOFs of the disclosure can provide open magnesium metal sites, it would be expected that the MOFs of the disclosure could effectively oxidize various organic molecules.

[0076] The disclosure also provides methods for using a MOF disclosed herein. In a certain embodiment, a method to separate or store one or more gases comprises contacting one or more gases with a MOF of the disclosure. In a further embodiment, a method to separate or store one or more gases from a mixed gas mixture
comprises contacting the gas mixture with a MOF disclosed herein. In a certain embodiment, a method to separate or store one or more gases from a fuel gas stream comprises contacting the fuel gas stream with a MOF disclosed herein. In a further embodiment, a method to separate or store methane from a natural gas stream comprises contacting the natural gas stream with a MOF disclosed herein. In a certain embodiment, a method to separate or store one or more gases from flue-gas comprises contacting the flue-gas with a MOF disclosed herein.

**Sorption** is a general term that refers to a process resulting in the association of atoms or molecules with a target material. Sorption includes both adsorption and absorption. Absorption refers to a process in which atoms or molecules move into the bulk of a porous material, such as the absorption of water by a sponge. Adsorption refers to a process in which atoms or molecules move from a bulk phase (that is, solid, liquid, or gas) onto a solid or liquid surface. The term adsorption may be used in the context of solid surfaces in contact with liquids and gases. Molecules that have been adsorbed onto solid surfaces are referred to generically as adsorbates, and the surface to which they are adsorbed as the substrate or adsorbent. Adsorption is usually described through isotherms, that is, functions which connect the amount of adsorbate on the adsorbent, with its pressure (if gas) or concentration (if liquid). In general, desorption refers to the reverse of adsorption, and is a process in which molecules adsorbed on a surface are transferred back into a bulk phase. The MOFs of the disclosure can therefore be used as adsorbents for greenhouse or fuel energy gases. In a particular embodiment, an Absorbed Natural Gas tank comprises a MOF disclosed herein as an adsorbent for natural gas, methane or hydrogen. In a further embodiment, a vehicle comprises an Absorbed Natural Gas tank that comprises a MOF of the disclosure.

**MOFs** of the disclosure can be used as standard compounds for sorption instruments, and obtained results would be helpful to improve various industrial plants (i.e. separation or recovery of chemical substance).
In a variation of this embodiment, the gaseous storage site comprises a MOF with a pore which has been functionalized with a group having a desired size or charge. In a refinement, this activation involves removing one or more chemical ligands (guest molecules) from a MOF disclosed herein. Typically, such guest molecules include species such as water, solvent molecules contained within a MOF disclosed herein, and other chemical ligands having electron density available for attachment. In a particular embodiment, solvent molecules coordinated to magnesium ions of the SBUs may be removed, resulting in a high density of open metal sites.

A MOFs used in the embodiments of the disclosure include a plurality of pores for gas adsorption. In one variation, the plurality of pores has a unimodal size distribution. In another variation, the plurality of pores have a multimodal (e.g., bimodal) size distribution.

The following examples are intended to illustrate but not limit the disclosure. While they are typical of those that might be used, other procedures known to those skilled in the art may alternatively be used.

**EXAMPLES**

**X-ray diffraction analysis:** X-ray diffraction (SXRD) data are typically collected on a Bruker D8-Venture diffractometer equipped with Mo- (\( \lambda = 0.71073 \, \text{A} \)) and Cu-target (\( \lambda = 1.54184 \, \text{A} \)) micro-focus X-ray tubes and a PHOTON 100 CMOS detector, unless indicated otherwise. Additional data is collected using synchrotron radiation in the beamline 11.3.1 of the Advanced Light Source, LBNL.

**Powder X-ray diffraction patterns (PXRD)** are recorded using a Bruker D8 Advance diffractometer (Gobel-mirror monochromated Cu K\( \alpha \) radiation \( \lambda = 1.54056 \, \text{A} \)). Room-temperature neutron powder diffraction data are collected on the high-resolution neutron powder diffractometer, BT1, using a Ge(311) monochromator \( \lambda = 2.0781 \, \text{A} \) and a 60 minute collimator.

**Nuclear Magnetic Resonance (NMR) and Elemental Microanalysis (EA) analysis:** Solution \(^1\text{H}\) NMR spectra are acquired on a Bruker AVB-400 NMR spectrometer. EA are performed using a
Perkin Elmer 2400 Series II CHNS elemental analyzer. Attenuated total reflectance (ATR) FTIR spectra of neat samples are performed using a Bruker ALPHA Platinum ATR-FTIR Spectrometer equipped with a single reflection diamond ATR module.

[0085] **Thermal gravimetric analysis:** TGA curves are recorded on a TA Q500 thermal analysis system under air flow.

[0086] **Isotherm analysis:** Low-pressure gas (N₂ and Ar) adsorption isotherms are recorded using a Quantachrome Autosorb-1 volumetric gas adsorption analyzer. Liquid nitrogen and argon baths are used for the measurements at 77 and 87 K, respectively. Water isotherms are measured on a BEL Japan BELSORP-aqua3, and the water uptake in weight percent (wt%) unit is calculated as [(adsorbed amount of water) / (amount of adsorbent) x 100], consistent with the established procedures. Prior to the water adsorption measurements, water (analyte) are flash frozen under liquid nitrogen and then evacuated under dynamic vacuum at least five times to remove any gases in the water reservoir. The measurement temperature is controlled with a water circulator. Helium is used for the estimation of dead space for gas and water adsorption measurements. Ultra-high-purity grade N₂, Ar, and He gases (Praxair, 99.999% purity) are used throughout the experiments.

[0087] **Synthesis of Homotopically Functionalized BTB-based linking ligands:** The syntheses of the acid forms of BTB derivative organic linkers with various functional groups are all based on the palladium-catalyzed Suzuki-Miyaura cross-coupling reactions to produce their ester forms with further saponification and acidification. There are two routes to synthesize the ester form of organic linkers: (1) Synthesize different (4-(methoxycarbonyl)phenyl)boronic acids (or their pinacol esters) with desired functional group on them, and further coupling with 1,3,5-tribromobenzene; (2) synthesize the 1,3,5-tris (boronic pinacol ester) benzene, and coupling with different functionalized 4-bromobenzoate esters, which are more commercially available. For example, **Scheme 1** provides a reaction to synthesize the 1,3,5-tris (boronic pinacol ester) benzene 1 that can be coupled with any number of differently functionalized 4-bromobenzoate esters:
Scheme 1: General synthetic route to produce 1,3,5-tris (boronic pinacol ester) benzene 1.

Homotopically functionalized BTB linkers can be synthesized through a versatile route by coupling the 1,3,5-tris (boronic pinacol ester) benzene with methyl-4-bromobenzoate analogs bearing desired functionalities, which are further hydrolyzed and acidified to provide the acid forms of the linkers (see Scheme 2).

Scheme 2. General synthetic route to produce homotopically functionalized BTB linkers; \(-R = -\text{NH}_2, -\text{F}, -\text{Me}, -\text{OMe}, -\text{OBn}, -\text{NO}_2, \) and etc.
Additional homotopically functionalized BTB linkers can be synthesized by coupling the 1,3,5-tris (boronic pinacol ester)benzene with methyl-4-bromobenzoate analogs bearing desired functionalities, by following Scheme 3:

Scheme 3: Synthetic route to produce ester form of 1,3,5-tris (2'-nitro-4'-carboxyphenyl) benzene and 1,3,5-tris (2'-amino-4'-carboxyphenyl) benzene.

[0089] Heterotopically functionalized BTB linkers can be prepared by coupling sequentially of three different (4-(methoxycarbonyl)-phenyl)-boronic acids or esters onto a tribromobenzene or 1,3-dibromo-5-iodobenzene (see Scheme 4).
Scheme 4. Stepwise synthetic route of heterotopically functionalized BTB linkers (i.e.; \( R = H, R' = NH_2 \)).

[0090] **Synthesis of Mg-BTB MOFs.** Phase 1: of \( \text{MgNO}_3 \cdot 6\text{H}_2\text{O} \) (0.123 g) and benzenetribenzoic acid (\( \text{H}_3\text{BTB} \)) (0.042 g) were dissolved in diethylf ornamide (5 mL) in a 20 mL scintillation vial. The vial was placed in an oven and heated at 80 °C for 15 hours. White crystals
ranging between 0.01 and 1 mm in size were obtained. The crystals were characterized by using X-ray diffraction techniques. The same phase can be obtained by heating a mixture with the above composition at 60 °C for 72 hours or at 90 °C for 3 hours.

Phase 2: Mg(NO₃)₂·6H₂O (0.123 g) and H₂BTB (0.042g) were dissolved in diethylformamide (5 mL) in a 20 mL scintillation vial. The vial was placed in an oven and heated at 60 °C for 10 days. Alternatively, the vial can be heated at 85 °C for 18 hours. White crystals ranging between 0.01 and 1 mm in size were obtained. The crystals were characterized by using X-ray diffraction techniques. The same phase can be obtained by heating a mixture with the above composition at 90 °C for 48 hours or at 110 °C for 3 hours.

Phase 3: MgCl₂ (0.123 g) and 0.042g of H₂BTB (0.042g) were dissolved in 5 mL of diethylformamide (5 mL) in a 20 mL scintillation vial. The vial was placed in an oven and heated at 120 °C for 15 h. White crystals ranging between 0.01 and 1 mm in size were obtained. The crystals were characterized by using X-ray diffraction techniques. The same phase can be obtained by heating a mixture with the above composition at 100 °C for 72 hours or at 130 °C for 6 hours.

Synthesis of Multivariate Mg-BTB based MOFs: Generally, conditions used to produce Mg-BTB MOFs can be used to synthesize multivariate Mg-BTB based MOFs, except the initial reaction mixture comprises one or more functionalized BTB-base linkers, usually in equimolar amounts.

Structural characterization of the three crystal phases of Mg-BTB MOF (phase 1, phase 2, and phase 3 crystals): Depending upon the reaction conditions various polymorphs of Mg-BTB can be crystallized using the same reactants (see Table 1).

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>Space Group</th>
<th>Mg(NO₃)₂ (g)</th>
<th>MgCl₂ (g)</th>
<th>BTB (g)</th>
<th>DEF (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>C2/c</td>
<td>0.123</td>
<td>-</td>
<td>0.042</td>
<td>5</td>
</tr>
<tr>
<td>100</td>
<td>P2₁/n</td>
<td>0.123</td>
<td>-</td>
<td>0.042</td>
<td>5</td>
</tr>
<tr>
<td>120</td>
<td>C2/c</td>
<td>0.123</td>
<td>-</td>
<td>0.042</td>
<td>5</td>
</tr>
<tr>
<td>120</td>
<td>C2/m</td>
<td>-</td>
<td>0.04</td>
<td>0.042</td>
<td>5</td>
</tr>
</tbody>
</table>
These crystal phases of Mg-BTB, termed Mg-BTB phase 1, Mg-BTB phase 2, and Mg-BTB phase 3 herein, crystalize in different monoclinic space groups and have different lattice parameters (see TABLE 1 and TABLE 2). While the three crystal phases of Mg-MTB have the same topology of point symbol \((6.8.10)\), \((6^2.8^2.10)\), \((6^2.8^2.10^2.12)\), they have different cell volumes and surface area (see TABLE 2).

**TABLE 2. Lattice properties of the three crystal phases of Mg-BTB MOF.**

<table>
<thead>
<tr>
<th></th>
<th>Mg–BTB phase 1</th>
<th>Mg–BTB phase 2</th>
<th>Mg–BTB phase 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>P21/n</td>
<td>C2/c</td>
<td>C2/m</td>
</tr>
<tr>
<td>Lattice parameter:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>26.9498 Å</td>
<td>46.2508 Å</td>
<td>32.6038 Å</td>
</tr>
<tr>
<td>b</td>
<td>36.028 Å</td>
<td>35.3727 Å</td>
<td>39.5115 Å</td>
</tr>
<tr>
<td>c</td>
<td>29.3005 Å</td>
<td>34.3478 Å</td>
<td>27.6578 Å</td>
</tr>
<tr>
<td>(\beta)</td>
<td>108.19°</td>
<td>98.79°</td>
<td>124.51°</td>
</tr>
<tr>
<td>Cell Volume</td>
<td>27022 Å³</td>
<td>55533 Å³</td>
<td>29359 Å³</td>
</tr>
<tr>
<td>Calc. Surface Area:</td>
<td>3000 m²/g</td>
<td>3500 m²/g</td>
<td>4000 m²/g</td>
</tr>
</tbody>
</table>

A number of embodiments have been described herein. Nevertheless, it will be understood that various modifications may be made without departing from the spirit and scope of this disclosure. Accordingly, other embodiments are within the scope of the following claims.
WHAT I S CLAIMED I S:

1. A metal organic framework (MOF) that comprises a plurality of repeating magnesium-based SBUs that are linked together by linking ligands which comprise the structure of Formula I:

\[
\text{Formula (I)}
\]

wherein,

- \( A^1-A^3 \) are independently a C or N;
- \( R^1-R^{12} \) are independently selected from H, D, FG, optionally substituted (C1-C12) alkyl, optionally substituted hetero-(C1-C12) alkyl, optionally substituted (C1-C12) alkenyl, optionally substituted hetero-(C1-C12) alkenyl, optionally substituted (C1-C12) alkynyl, optionally substituted hetero-(C1-C12) alkynyl, optionally substituted (C1-C12) cycloalkyl, optionally substituted (C1-C12) cycloalkenyl, optionally substituted aryl, optionally substituted heterocycle, optionally substituted mixed ring system, \(-C(R^{13})_3\), \(-CH(R^{13})_2\), \(-CH2R^{13}\), \(-C(R^{14})_3\), \(-CH(R^{14})_2\), \(-CH2R^{14}\), \(-OC(R^{15})_3\), \(-OCH(R^{13})_2\), \(-OCH_2R^{13}\), \(-OC(R^{14})_3\), \(-OCH(R^{14})_2\), \(-OCH_2R^{14}\), wherein \( R^1-R^{12} \) when directly adjacent can be linked together to form one or more optionally substituted rings selected from the group comprising cycloalkyl, cycloalkenyl, heterocycle, aryl, and mixed ring system;
- \( R^{13} \) is selected from FG, optionally substituted (C1-C12) alkyl, optionally substituted hetero-(C1-C12) alkyl, optionally substituted (C1-C12) alkenyl, optionally substituted hetero-(C1-C12) alkenyl, optionally substituted (C1-C12) alkynyl, optionally substituted hetero-(C1-C12) alkynyl, optionally substituted (C1-C12) cycloalkyl, optionally substituted (C1-C12) cycloalkenyl, optionally substituted aryl, optionally substituted heterocycle, optionally substituted mixed ring system.

\[
\text{Formula (I)}
\]
hetero-(C1- C12) alkynyl, hemiacetal, hemiketal, acetal, ketal, and orthoester;

R\textsuperscript{4} is selected from one or more optionally substituted rings selected from cycloalkyl, aryl and heterocycle,

wherein the MOF crystallizes in the monoclinic space group of P2\textsubscript{1}/n, C2/c or C2/m, and/or the MOF has a topology of point symbol (6.8.10) \textsuperscript{4} (6.8\textsuperscript{2}) \textsuperscript{6} (6\textsuperscript{2}.8\textsuperscript{6}.10\textsuperscript{6}.12) .

2. The MOF of claim 1, wherein the linking ligands comprise the structure of Formula I:

Formula I

wherein,

A\textsuperscript{1}-A\textsuperscript{3} are independently a C or N;

R\textsuperscript{1}-R\textsuperscript{12} are independently selected from:

- Acetic acid, propionic acid, butyric acid,
- F, Cl, Br, I, CN, NO\textsubscript{2},
- Acetamide, formamide,
- OH, N\textsubscript{2}, NH\textsubscript{2},
- Benzene, phenyl, toluene,
M is an alkaline metal species, an alkaline-earth metal species, or transition metal species that has a formal charge of +1 and that can be coordinated by one or more neutral or charged ligands.

3. The MOF of any preceding claim, wherein the linking ligands comprise the structure of:
4. The MOF of any preceding claim, wherein the MOF is multivariate by comprising two or more differently functionalized linking ligands comprising the structure of Formula I:

\[
\begin{align*}
\text{Formula (I)}
\end{align*}
\]

wherein,

- \( A^1 - A^3 \) are independently a C or N;
- \( R^1 - R^{12} \) are independently selected from H, D, FG, optionally substituted (C1-C12) alkyl, optionally substituted hetero- (C1-C12) alkyl, optionally substituted (C1-C12) alkenyl, optionally substituted hetero- (C1-C12) alkenyl, optionally substituted (C1-C12) alkynyl, optionally substituted hetero- (C1-C12) alkynyl, optionally substituted (C1-C12) cycloalkyl, optionally substituted (C1-C12) cycloalkenyl, optionally substituted aryl, optionally substituted heterocycle, optionally substituted mixed ring system, -C(R^3), -
CH(R^{13})_2, -CH2R^{13}, -C(R^{14})_3, -CH(R^{14})_2, -CH2R^{14}, -OC(R^{13})_3, OCH(R^{13})_2, -OCH_2R^{13}, -OC(R^{14})_3, -OCH(R^{14})_2, OCH_2R^{14}, wherein R^1-R^{12} when directly adjacent can be linked together to form one or more optionally substituted rings selected from the group comprising cycloalkyl, cycloalkenyl, heterocycle, aryl, and mixed ring system;

R^{13} is selected from FG, optionally substituted (C1-C12) alkyl, optionally substituted hetero- (C1-C12) alkyl, optionally substituted (C1-C12) alkenyl, optionally substituted hetero- (C1-C12) alkenyl, optionally substituted (C1-C12) alkynyl, optionally substituted hetero- (C1-C12) alkynyl, hemiacetal, hemiketal, acetal, ketal, and orthoester;

R^{14} is selected from one or more optionally substituted rings selected from cycloalkyl, aryl and heterocycle,

wherein the MOF crystallizes in the monoclinic space group of P21/n, C2/c or C2/m, and/or the MOF has a topology of point symbol (6.8.10)_4 (6.8^2)_6 (6^2.8^6.10^6.12).

5. The MOF of claim 4, wherein the two or more linking ligands are selected from:
6. The MOF of claim 4 or 5, wherein the MOF comprises an equimolar ratio of the two or more differently functionalized linking ligands.

7. The MOF of any one of claims 4 to 6, wherein the MOF comprises 3 to 13 differently functionalized linking ligands.
8. The MOF of any preceding claim, wherein the MOF has a surface area of at least 3000 m²/g.

9. The MOF of claim 8, wherein the MOF has a surface area of at least 3500 m²/g.

10. The MOF of claim 9, wherein the MOF has a surface area of at least 4500 m²/g.

11. The MOF of any one of the preceding claims, wherein the MOF has been activated by removing guest molecules via calcination or by treatment with supercritical CO₂.

12. The MOF of any one of the preceding claims, wherein the MOF is characterized by having a high density of open magnesium metal sites.

13. The MOF of any one of the preceding claims, wherein the MOF is reacted with a post framework reactant that adds at least one effect to the MOF selected from:
   - modulating the gas storage ability of the MOF;
   - modulating the sorption properties of the MOF;
   - modulating the pore size of the MOF; and
   - modulating the catalytic activity of the MOF;
   - modulating the conductivity of the MOF; and
   - modulating the sensitivity of the MOF to the presence of an analyte of interest.

14. A gas separation and/or gas storage device comprising a MOF of any one of the preceding claims.

15. The device of claim 14, wherein the gas storage device is a gas tank.

16. The device of claim 15, where in the gas tank is configured to be used in a vehicle
17. The device of claim 14, wherein the gas separation device is a purifier, filter, scrubber, pressure swing adsorption device, molecular sieve, hollow fiber membrane, ceramic membrane, cryogenic air separation device, and hybrid gas separation device.

18. A method of separating and/or storing one or more gases from a gas mixture comprising contacting the gas mixture with a MOF of any one of claims 1 to 13 or the device of claims 14 to 17.

19. The method of claim 18, wherein the gas mixture comprises carbon dioxide and the gas that is separated and/or stored is carbon dioxide.

20. The method of claim 18, wherein the gas mixture comprises a natural gas stream and the gases that are separated from the natural gas stream are acid gases and/or water vapor.
**INTERNATIONAL SEARCH REPORT**

**PCT/US2015/026109**

### A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J20/22 B01J20/28 B01D53/02 C07F3/02

ADD.

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

### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01J C07F B01D

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

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

EPO-Internal, WPI Data

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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<td>wo 2009/042802 AI (UNIV CALIFORNIA [US]; YAGHI OMAR M [US]; LI QIAOWEI [US]; FANG QIANRON) 2 April 2009 (2009-04-02)</td>
<td>1-3, 8-19</td>
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**Date of the actual completion of the international search**

22 June 2015

**Date of mailing of the international search report**

29/06/2015

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Authorized officer

Kl emps, Chri stian

Form PCT/ISA/210 (second sheet) (April 2005)
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<td>02-04-2009</td>
<td>EP 2190662 Al</td>
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