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(54) Title: METAL ORGANIC FRAMEWORK ODOR SEQUESTRATION AND FRAGRANCE DELIVERY

(57) Abstract: The present invention is directed to methods for controlling or eliminating malodor by contacting a malodor molecule with a metal-organic framework ("MOF") comprising a plurality of metal ions bound to a plurality of organic polydentate bridging ligands. The present invention is also directed to methods for delivering to an environment fragrance compositions which have been incorporated into a MOF comprised of a plurality of metal ions bound to a plurality of organic polydentate bridging ligands.

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Metal Organic Framework Odor Sequestration and Fragrance Delivery

[0001] This application claims priority from US Provisional Application 60/718,485, filed September 19, 2005.

Field of Invention

[0002] The present invention relates to novel methods for sequestration of malodor molecules in metal-organic frameworks (MOFs). Also described are novel methods for controlled release of fragrance compositions from MOFs.

Statement of Federally-Sponsored Research

[0003] Not applicable.

Background of the Invention

[0004] Throughout the centuries, there has been a need for odor control – particularly, the elimination of malodor. Malodors are lower molecular weight volatile organic compounds which stimulate an aversive reaction in most humans. In part, this reaction has evolved as a warning mechanism to avoid dangerous or unhealthy situations (*e.g.*, unhygienic areas or decayed food). In the Middle Ages, for example, malodor control was accomplished by burning incense. Masking malodor with heavy doses of fragrance was commonly used by the French nobility prior to the Revolution of 1789. This remains one of the most common methods of malodor control and is exemplified in the deocologne product category for personal care. Malodor control is a problem in many industrial settings – from meat rendering plants to neighborhood hair salons. The multitude of chemicals available to control malodor – including Metazene® (Pestco) and Meelium® (Prentiss), activated charcoal, zinc ricinoleate, zeolites and cyclodextrins – reflects the fact that no one chemical or malodor control method can adequately address every malodor situation. Thus, there remains a long-felt but unmet need for a flexible chemical platform to control malodor with customized molecules. This need is met by the methods of the present invention.

[0005] In personal care applications, fragrance is most commonly delivered in a hydroalcoholic form, as perfume, cologne, or aftershave. In the household, industrial and environmental markets, fragrance is commonly delivered through aerosol sprays, electric air fresheners (commonly known as plug-ins), fragranced gels, cellulose pads, liquids with wicks and/or fragranced candles. In these and other applications, there has long-existed a desire to control fragrance release and thereby prolong the life of the fragrance. There is also a need in certain circumstances to protect fragrance chemicals from incompatibilities caused by hostile chemical/physical environments. Again, no one technology can address all of these needs. Through the design of fragrance release molecules with customized scaffolding, the present invention meets the needs for methods of controlling fragrance release and protecting fragrance.

[0006] Zeolites are microporous solid structures whose stable and rigid porous frameworks permit the selective and reversible inclusion of molecules. More particularly, they are framework silicates consisting of interlocking tetrahedrons of SiO_4 and AlO_4. In order to be a zeolite the ratio (Si +Al)/O must equal 1/2. *See, e.g.*, A. Dyer, *An Introduction to Zeolite Molecular Sieves*

(1988); R.M. Barrer, *Hydrothermal Chemistry of Zeolites* (1982). *See also,* J.M. Newsam, "The Zeolite Cage Structure," *Science*, 231:1093 (1986).

[0007] Zeolites are synthesized by mixing an alkali metal hydroxide with aqueous solutions of silicate and aluminate anions to form a hydrated aluminosilicate gel which is then heated up to 200°C under pressure. Industrial applications of zeolites include ion-exchange, separation, and catalysis. *See*, U.S. Patent Nos. 4,310,440, 4,440,871, and 4,500,651. (The disclosures of all cited published patent applications and granted patents are incorporated in their entirety by reference.)

[0008] Porous frameworks with properties similar to those of zeolites have been synthesized from sulfides and selenides. *See*, U.S. Patent No. 4,880,761.

[0009] Cyclodextrins are produced from starch by the enzyme cyclodextrin glycosyltransferase (CGTase). Structurally, cyclodextrins consist of 6, 7, or 8 (α, β and γ, respectively) d-glucopyranosyl units connected by alpha-(1,4) glycosidic linkages. The most stable three-dimensional molecular configuration for these non-reducing cyclic oligosaccharides takes the form of a toroid.

[0010] The use of zeolites and cyclodextrins to trap malodor and or provide a delivery vehicle for aroma chemicals are well-known in the art. With respect to cyclodextrins, *see*, *e.g.*, US Patent Nos. 5,733,272, 6,103,678, 5,860,391, 6,100,233, and 5,714,445. With respect to zeolites, *see, e.g.*, US Patent Nos. 6,376,741 and 6,803,033. However, neither zeolites nor cyclodextrins can be rationally designed in shape, size, and reactivity to achieve specific guest/host relationships.

[0011] Early generation metal-organic frameworks were formed by linkages between a metal ion and an organic ligand around a templating agent. These structures, however, were not porous and, consequently, were unable to adsorb molecules or ions. One obstacle in creating porous metal-organic solids was the interaction between the templating agent and framework. Difficulties often arose when attempting to remove the templating agent from the solid without altering or destroying the framework.

[0012] A second barrier to creating porous MOFs was presented by interpenetration of frameworks. As the number of interpenetrating frameworks increased, the metal-organic solid became more densely packed, causing channels and pores in the material to become smaller. Ultimately, this resulted in loss of the desired porosity.

[0013] Porous metal-organic frameworks and their use in gas storage, particularly methane, have been reported in the literature. For example, selective binding and removal of guest molecules from metal organic frameworks was described by Yaghi *et al.* in *Nature*, Vol. 378, No. 6558, pp. 703-6 (1995). The building blocks of MOFs are organic molecules which bind to metal ions forming layers of the metal-organic compounds. Guest molecules are then selectively bound within the channels created by these layers. *See also*, “Metal-organic frameworks: a new class of porous materials,” *Microporous and Mesoporous Materials,* Vol. 73, pp. 3–14 (2004).

[0014] In August 1996, Yaghi presented synthetic strategies for preparing MOFs by linking transition metal complexes to 1,3,5-benzenetricarboxylic acid and utilizing hydrogen-binding interactions. Abstracts of Papers, 212th ACS National Meeting (1996).

[0015] Formation of MOFs by linking zinc metal complexes with a different organic ligand, 1,4-benzenedicarboxylate ("BDC"), is reported by Yaghi *et al.* *See*, *JACS*, Vol. 20, No. 33, pp. 8571-8572 (1998). The resulting crystalline compound (ZnBDC, also known as MOF-5) is reported to be stable when fully desolvated and when heated up to 300°C. *Nature,* Vol. 402, No. 6759, pp. 276-279 (1999).

[0016] U.S. Patent No. 5,648,508 (issued to Yaghi in July 1997) teaches crystalline, microporous metal-organic frameworks prepared in solution using mild reaction conditions from a metal or metalloid ion with a ligand containing multidentate functional groups in the presence of a templating agent. More particularly, Yaghi teaches that the metal ions is selected from the following: 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. Industrial uses for the microporous materials disclosed in the '508 Patent are taught to include catalysis, gas purification, separation, filtration, ion-exchange, and removal of impurities and contaminants from industrial streams.

[0017] Further characterization of zinc benzenedi- and -tricarboxylato MOFs is reported by Yaghi *et al.* in *JACS*, Vol. 122, No. 7, pp. 1391-1397 (2000). The evacuated form of MOF-5 is reported to have a free pore volume of 55-60%. *Id.*

[0018] The combination of $Cu(NO3)_2$ and adamantane tetracarboxylate to form an MOF was reported by Yaghi. Abstracts of Papers, 220th ACS National Meeting (August 2000.)

[0019] Reversible sorption of gases and organic solvents in a highly porous (16.4 Å in diameter), structurally-stable network created with MOFs was reported by Yaghi *et al.* *Science* Vol. 291, No. 5506, pp. 1021-1023 (2001).

[0020] Zinc-carboxylate polyamine metal organic dendrimer frameworks are reported by Yaghi *et al.* in JACS, Vol. 123, No. 46, pp. 11482-11483 (2001). Like MOFs, these metal organic dendrimer frameworks have three-dimensional porosity.

[0021] Yaghi *et al.* have reported isoreticular MOFs having an open space representing greater than 90% of the crystal volume and homogeneous periodic pores ranging in size from 3.8 Å to 28.8 Å in diameter. Abstracts of Papers, 223rd ACS National Meeting (April 2002).

[0022] US Patent Application Publication No. 2003/148165, now US Patent 6,929,679 (Mueller), teaches a method of uptake, storage and/or release of a gas by 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, to the metal ion.

[0023] US Patent Application Publication No. 2003/004364, now US Patent 6,930,193 (Yaghi), teaches isoreticular metal-organic frameworks (IRMOFs) consisting essentially of secondary building units (SBUs) and specific compounds for linking adjacent SBUs (comprising linear ditopic carboxylates having at least one phenyl group and at least one functional group attached to at least one phenyl group). The disclosed IRMOFs are taught to be adapted to store at least one gas (*e.g.*, methane).

[0024] In 2004, Yaghi reported MOFs containing octahedral zinc metal clusters and trigonal tricarboxylic acid ligands. Abstracts of Papers, 227th ACS National Meeting (March 28-April 1, 2004).

[0025] US Patent Application Publication 2004/0097724 (Mueller) describes a process for making organometallic, microporous frameworks by reaction of a metal salt in solution or suspension with a bidentate organic compound in the presence of at least one base and a solvent comprising at least one lactam and/or lactone.

[0026] US 2004/0225134 (Yaghi) teaches MOFs having a surface area greater than about 2,900 m^2/g where adjacent metal clusters are linked to charged multidentate ligands. A specific compound, MOF 177, is taught to have a high surface area (approx. 4,500 m^2/g) with ordered pore structure of a diameter sufficient to allow binding of large organic molecules such as petroleum fragments and drug molecules. The design, synthesis and properties of this compound are further described in *Nature*, Vol. 427, No. 6974, pp. 523-527 (2004).

[0027] Metal-organic polyhedra (truncated tetrahedral and heterocuboidal), whose pore size and functionality can be varied have been reported by Yaghi. *JACS*, Vol. 127, No. 19, pp. 7110-7118 (2005).

[0028] US Patent Application Publication 2005/0124819 (Yaghi) describes porous, polyhedral metal-organic framework compounds comprising metal clusters, with each cluster comprising two or more metal ions and a sufficient number of capping ligands to inhibit polymerization of the metal organic polyhedra. More specifically, metal clusters at one or more vertices of the polyhedron are connected by multidentate linking ligands forming a polyhedron.

[0029] US Patent Application Publication 2005/0154222 (Mueller) describes a process for preparing MOFs by reacting at least one metal salt with at least one at least bidentate compound where the bidentate compound comprises at least two carboxy groups and at least one additional group which is not a carboxy group and which is capable of forming a hydrogen bridge linkage. This publication teaches the use of the above-described MOF as a material for uptaking and/or storing and/or releasing a noble gas, carbon monoxide, carbon dioxide, nitrogen, a hydrocarbon, hydrogen, or a compound generating and/or delivering theses gases. Preferred gasses which are stored in and/or released from the MOF are propane, ethane, or methane, or hydrogen.

[0030] US Patent Application Publication 2005/0192175 (Yaghi) teaches specific types of isoreticular MOFs and their use in gas storage.

[0031] US Patent Application Publication 2006/0099398 (Mueller) describes a process for preparing a shaped body containing a metal organic framework. More particularly, the process involves converting an MOF-containing powder into a shaped body based on specific surface area per volume ratios of the shaped body to the starting MOF-containing powder. Potential applications of these MOFs are generally described to include use as catalysts, support for catalysts, sorption, storage of fluids, desiccants, ion exchanger materials, molecular sieves (separators), materials for chromatography, materials for the selective release and/or uptaking of molecules, “molecular recognition”, “nanotubes” and “nanoreactors.”

[0032] International Patent Application Publication WO 2005/087369 teaches a method for preparing a porous framework material with pores and pore walls throughout having pre-selected porosity and chemically binding organic, organometallic, or biological molecules to the pore walls of the porous framework material through chemical linkages. Among the disclosed applications are microelectronic packaging, electronic printing, chiral separation and catalysis, sensors, chromatography, bioassays, thermal and acoustical insulation.

[0033] The prior art has not suggested or taught the use of MOFs for odor control or delivery of fragrances. There has been and remains a need for efficient systems to counteract specific odors and to deliver specific fragrances. These needs are met by the novel uses for MOFs that are the subject of the present invention.

Summary of the Invention

[0034] The present invention relates to methods for sequestering malodor molecules in a metal-organic framework (“MOF”). The present invention also relates to methods for delivery of fragrance compounds from MOFs.

Detailed Description of the Invention

[0035] The present invention is directed to methods for controlling or eliminating malodor by contacting a malodor molecule with a metal-organic framework comprising a plurality of metal ions bound to a plurality of organic polydentate bridging ligands.

[0036] The present invention is also directed to methods for delivering to an environment fragrance compositions which have been incorporated into a metal-organic framework comprised of a plurality of metal ions bound to a plurality of organic polydentate bridging ligands.

[0037] Metal-Organic Framework

[0038] As used in the present invention, by MOF is meant a polyhedral, porous framework created by a plurality of metal ions bound to a plurality of organic polydentate bridging ligands.

[0039] In one embodiment, the plurality of metal ions comprising the MOF are selected from selected from the group consisting of Cu, Fe, Zn, Ag, Cd, Co, and Ni. Preferably, the plurality of metal ions are coordinately bound to the plurality of organic polydentate bridging ligands.

[0040] In another embodiment, the MOF is created by a plurality of metal clusters bound to a plurality of organic polydentate bridging ligands. In this embodiment, the metal clusters are comprised of two or more metal ions. The organic polydentate bridging ligands connect adjacent metal clusters into a polyhedron, with the metal clusters positioned at the vertices of the polyhedron.

[0041] In a further embodiment, the organic polydentate bridging ligands are composed of alkyl or aryl groups and two, three or four reactive sites.

[0042] MOFs useful in the present invention can be prepared according to the methodologies known to those of skill in the art including those described in the US Patent Application Publications and granted US patents incorporated herein by reference as well as the methods set out hereinbelow.

[0043] Many MOFs can be made easily by reacting metal salts with dicarboxylic acids in water, followed by separation and analytical confirmation of structure. Advances in x-ray crystallography have simplified characterization of these molecules.

[0044] In one aspect of the present invention, microwave radiation is used to produce increased yields of MOFs. This is described further in Example 1 below.

[0045] In a preferred aspect of the present invention – described in Example 2 below – MOFs are made in a solvent-free system.

[0046] As used in the present invention, the phrase "solvent-free system" is to be understood to mean combining the components in a neat form and subjecting them to mechanical forces. A preferred solvent-free system is mechanically grinding metal ions and organic polydentate binding ligands together according to the methodology discovered by James *et. al* and published in *Cryst. Eng. Comm.* Vol. 8, pp. 211-214 (2006).

[0047] Sequestration of Malodor Molecule in MOF

[0048] Malodor is a concept well-known to persons of skill in the art. As used in the present invention, by the term "malodor molecule" is meant a lower molecular weight volatile organic compound which stimulates an aversive reaction in humans. Non-limiting examples, of malodors include rotten eggs, the spray of a skunk, fecal odor, bad breath, and tobacco smoke. The chemistry of malodors is distinct from the chemistry of pleasant odors, malodors typically having sulfur, halogen, or amine groups.

[0049] As used in the present invention, by "sequestering" is meant entrapment or uptake and storage of a malodor molecule within a MOF.

[0050] Non-limiting examples of malodor molecules that may be sequestered within MOFs according to the method of the present invention include: Hydrogen sulfide; 2-Propanone; 1,2-Methyl propanal; 2-Propanol; Decane; 2-Butanol; Methyl benzene; 2-Methyl propanol; Ethyl benzene; 1,3-Dimethyl benzene; 2-Methoxy ethanol; 1-2-Dimethyl benzene; Dodecane; Pyridine; Cineole; Chloro benzene; 1-Ethyl,2-methyl benzene; 2-Methyl,1-propene; 1-Ethyl,2-methyl benzene; 1,2,3-Trimethyl benzene; Dodecane; 1-Ethyl-4(2)-methyl benzene; 8-Methyl heptadecane; Tritetracontane; Heptadecane; 1,3(1,4)-Dichloro benzene; Acetic acid; 1,2-Dichloro benzene; 2,3-Dihydro-5-methyl 1H-indene; 1H-Pyrrole; Camphor; Propanoic acid; Dimethyl propanedioic acid; Hexadecane; Butanoic acid; 1-Phenyl ethanone; 3-Methyl butanoic acid; Heptadecane; Pentanoic acid; Naphthalene; N,phenyl formamide; Cyclododecane; Phenol; 3-Methyl phenol; 1,4,6-Trimethyl naphthalene; 3-Ethyl phenol; 2,5-Dichloro phenol; 1H-Indole; Benzeneacetonitrile; 3-Methyl 1H-indole; 2-Heptadecanol.

[0051] Additional non-limiting examples of malodor molecules that may be entrapped within MOFs according to the methods of the present invention include: Acetaldehyde; Methyl Mercaptan; Ethyl mercaptan; Ammonia; Methylamine; Dimethylamine; Trimethylamine; Ethylamine; Triethylamine; Butyl amine; Butyric acid; Dimethyl Sulfide; Dimethyl disulfide; Skatole.

[0052] Another aspect of the present invention is directed to reversible sequestration of malodor molecule. “Reversible sequestration” is achieved by heating the MOF to a temperature sufficient to allow the malodor molecule to be purged from the framework. In this manner, the malodor molecules are discharged from the pores and the MOF can be reused.

[0053] In one aspect of the present invention, the MOF is used as a household room deodorizer.

[0054] In another aspect of the present invention, the MOF is used an industrial or institutional deodorizer.

[0055] In a further aspect of the present invention, the MOF is applied to an absorbent article (*e.g.*, fabric or garment) for the purpose of odor control. In one embodiment of this aspect of the invention, MOFs are incorporated in absorbent articles worn by humans to control the odor from human bodily fluids. As used in the present invention, malodorous human bodily fluids are to be understood to include urine, menstrual fluid, perspiration, and diarrhea. Examples of such absorbent articles include sanitary napkins, pantiliners, disposable diapers, incontinence pads, tampons and the like. Relatedly, MOFs may be incorporated into baby changing pads.

[0056] Another embodiment within the scope of this aspect of the invention is the use of MOFs to absorb odor from carpets and rugs.

[0057] In a still further aspect of the present invention, the MOF is used in a litter box to absorb odor.

[0058] Some MOFs are not stable when exposed to water. Accordingly, essentially-anhydrous or anhydrous MOF odor control systems (with or without a desiccant) are within the scope of this aspect of the present invention.

[0059] As used in the present invention, "essentially anhydrous" is to be understood to mean that the MOF contains no more than about 3.0%, preferably no more than about 1%, and still more preferably less than about 0.1% of water.

[0060] Release of Fragrance Composition from MOF

[0061] Another aspect of the present invention relates to release of fragrance compounds into the environment.

[0062] For purposes of the present invention, the term "fragrance compound" is to be understood as a material which has the ability to form of a distinct aroma based on blending perfumery materials of defined quality in specified proportions.

[0063] Perfumery materials are well-known in the art and include essential oils, concretes and extracts and aroma-producing chemicals, which may be of natural or synthetic origin. Chemically, perfumery materials may be aliphatic and aromatic alcohols, aldehydes, ketones, aliphatic and aromatic esters, nitriles, ethers, lactones, heterocyclics or terpenes. They are obtained by techniques that are well-known to those of skill in the art – essential oils by steam distillation or crushing; concretes by extraction with volatile solvents; absolutes by extraction of concretes with alcohol.

[0064] Natural, botanical sources of perfumery ingredients useful in the present invention are often grouped into the following families: flowers and blossoms; leaves and twigs; roots, rhizomes and bulbs; seeds; fruits and fruit peels; woods; barks; resins and saps; lichens and mosses.

[0065] The fragrance family of flowers and blossoms are understood by those of skill in the art to include bergamot; clove; citrus including orange (neroli), lemon, lime, grapefruit, mandarin; geranium; jasmine; lavender; orchid; osmanthus or mimosa genera; plum, rose; tuberose; Ylang-ylang.

[0066] The fragrance family of leaves and twigs are understood to include citrus leaves; patchouli; rosemary; sage; thyme.

[0067] The fragrance family of roots, rhizomes and bulbs includes the rhizomes from iris and ginger, and roots of vetiver.

[0068] The fragrance family of seeds includes anise, caraway, cardamom, cocoa, coriander, cumin, mace, nutmeg, pepper, tonka bean, vanilla.

[0069] The fruit fragrance family includes apple, banana, cherry, melon, peach, pineapple, strawberry, citrus rinds including orange, lemon, lime, grapefruit, and mandarin.

[0070] The woods fragrance family includes agarwood, birch, cedar, juniper, pine, rosewood, and sandalwood.

[0071] The bark fragrance family includes cascarilla, cinnamon, and sassafras.

[0072] The fragrance family of resins and saps includes amber, copal, fir, frankincense, gum benzoin, labdanum, myrrh, peru balsam, and pine.

[0073] The fragrance family of lichens and mosses includes oakmoss and treemoss.

[0074] In the past, certain families of fragrance materials were obtained from animals. The family of musks was derived from musk deer, muskrat, musk ox. The family of civet was obtained from various species of the family Viverridae, including civets, genets and linsangs. Castoreum was obtained from the North American beaver. Ambergris was obtained from the sperm whale. Today, synthetic perfumery ingredients are created through organic chemical processes to mimic these animal-derived materials.

[0075] Synthetic perfumery ingredients are also created to mimic fragrances derived from botanical sources, as well as to create fragrances not typically found in natural sources.

[0076] Each perfumery ingredient has a characteristic odor or “note”. Generally, these are classified into “top”, “middle” and “bottom” or “base”.

[0077] Top notes are scents that are perceived within the first few minutes of release of the fragrance composition from the skin or hair. They are lighter scents, usually lasting from about five to ten minutes. Representative top notes include those classified as “citrus” such as grapefruit, lemon, orange or bergamot, or those classified as “herbaceous” such as mint, rosemary, or sage.

[0078] Middle notes are the scents that emerge after the top notes evaporate. These notes form the "heart" or main body of a scent; they smooth or round out the initial sharpness caused by the top notes and last for up to one hour.

Typically, middle notes emerge fifteen minutes after release of the top note(s). Representative of middle notes are lavender, juniper or chamomile.

[0079] Base notes are usually not perceived until about one hour after the release of the fragrance composition, and may last for several hours. Representative base notes include woody or musk notes such as sandalwood, synthetic musk (civet) or vetiver.

[0080] Fragrance compositions are made up of "accords" – mixtures of two or more perfumery materials having a unified olfactory theme. A widely-utilized methodology for constructing fragrance compositions, well-known to those of skill in the art, is to combine accords starting with those of the lowest volatility ("base notes"), then adding ingredients of intermediate volatility or tenacity ("middle notes") and lastly adding the most volatile materials ("top notes").

[0081] A typical fragrance composition is comprised of about 25% top notes, about 25% middle notes and about 50% bottom notes. The individual perfumery materials and accords suitable for use in the delivery system of the present invention are catalogued and described in references and databases well-known to those of skill in the art including the following: S. Arctander, *Perfume and Flavor Chemicals, Volumes I & II* (1960, 1969; reprinted 2000); *Allured's Flavor and Fragrance Materials* (2005); the database maintained by the Research Institute for Fragrance Materials at www.rifm.org. Additional perfumery ingredients and fragrance compositions are described in US Patent No. 6,741,954, the disclosure of which is incorporated in its entirety.

[0082] Fragrance compositions within the scope of the present invention are comparatively small, volatile molecules, having molecular weights of from about 25 to about 450. In a preferred embodiment of the present invention, fragrance compositions to be incorporated in and delivered from MOFs are in a molecular weight size range of from about 35 to about 400.

[0083] Fragrances evolve based on vapor pressure and molecular weight via free evaporation. MOFs can be used to change the evolution of a fragrance. For example, top notes incorporated into an MOF can be held back; bottom notes in an MOF can pushed forward. Thus, the life cycle of a fragrance can be altered to create new fragrance effects that have heretofore not been possible.

[0084] As used in the present invention, by the phrase “controlled release” is meant delaying or accelerating the rate of evaporation of one or more accords making up the fragrance composition. This can be accomplished by rationally designing MOFs with specific pore size or groups that selectively bind to the fragrance composition.

[0085] Uptake of a fragrance composition into an MOF can be accomplished by purging an aroma gas into the MOF or by adding a liquid fragrance composition directly to the MOF.

[0086] It is also possible to utilize a fragrance composition as a solvent in the synthesis of the MOF, thus creating a guest/host complex in one step.

[0087] Release of a fragrance composition from a MOF can be accomplished by using an MOF in a sachet or similar porous enclosure.

[0088] In another aspect of the present invention, the MOF may be used in an air freshener to emit a fragrance composition into a desired area. Such an air freshener may use a fan or other source of forced air.

[0089] As discussed above, certain MOFs have been reported to have limited stability when exposed to water. Therefore, anhydrous or essentially-anhydrous MOFs may be designed for releasing fragrance.

[0090] Examples

[0091] The following examples are further illustrative of the present invention. The components and specific ingredients are presented as being typical, and various modifications can be derived in view of the foregoing disclosure within the scope of the invention.

[0092] Example 1 – Microwave Synthesis

[0093] One preferred MOF that may be used to sequester a malodor molecule or deliver a fragrance composition is $Cu_3(BTC)_2$ (Cu-MOF). A non-limiting exemplary method for preparing this MOF using microwave synthesis is as follows: $Cu(NO_3)_2{\cdot}3H_2O$ (1.45g, 6mmol) and H_3TC (0.84g, 4mmol) are heated in ethylene glycol (10mL) for 15 minutes in a microwave oven adapted with a reflux condenser producing a blue solid. The blue solid is collected by filtration, washed with methanol (100mL), and dried overnight at 90°C to yield of 1.15g (90%) of $Cu_3BTC_2(H_2O)_3$. It has pores of about 0.9 nm in diameter and is temperature-stable to about 200°C. This methodology is further described in *Science*, Vol. 283, p. 1148 (1999).

[0094] Example 2 – Solvent-Free Synthesis

[0095] Another preferred MOF that may be used to sequester a malodor molecule or deliver a fragrance composition is $Cu(INA)_2$ (Cu-MOF2). A non-limiting exemplary method for preparing this MOF using solvent-free synthesis is as follows: Cu(OAc)2·H_2O (0.60g, 3mmol) and HINA (0.74g, 6mmol) are ground together in a ball mill (Retsch Mixer Mill type MM200) for 30 minutes at 30 Hz. The resulting blue powder is collected and heated at 120°C under vacuum for 5 hours to yield $Cu(INA)_2$ quantitatively. It has pores of from about 0.2 nm to about 0.4 nm in diameter and is temperature-stable to about 200°C. This methodology is further described in *J. Solid State Chem.*, Vol. 158, p. 315 (2001).

[0096] Example 3 – Diffusion

[0097] Another preferred MOF that may be used to sequester a malodor molecule or deliver a fragrance composition is $Zn(INA)_2$ (Zn MOF). A non-limiting exemplary method for preparing this MOF using diffusion is as follows: A solution of $Zn(NO_3)_2.6H_2O$ (0.30g, 1mmol) in DMSO (7mL) is mixed with HINA (0.26g, 2mmol) in DMSO (10mL) and stirred for 30 minutes. A solution of triethylamine (9mmol) in ethanol (10mL) is slowly diffused into the solution. Crystals are obtained after a few days. They are collected by filtration, washed with ethanol (50mL) and ether (50mL) and dried under suction to give 0.11g (35%) of $Zn(INA)_2$.

[0098] Examples– Sequestration of Malodor and Fragrance Delivery

[0099] Butyraldehyde ($CH_3(CH_2)_2CHO$) and butyric acid ($CH_3(CH_2)_2COOH$) are two malodor molecules well-known to those in the art. Sequestration of these malodor molecules in MOFs according to the methods of the present invention is demonstrated by the following method.

[00100] Into an impermeable gas-collecting bag (available from a variety of sources, including SKC, Inc., Eighty Four, PA) a predetermined volume of the malodor molecule is introduced. In the present example, a gas collection bag (SKC Sample Bag, Catalogue N° 231-08A; Capacity 10 L) is partially-filled with two liters of air. To this bag is added 0.5 μL of butyraldehyde (commercially-available from a variety of chemical suppliers including Aldrich, Milwaukee, WI).

[00101] The malodor molecule (butyraldehyde in the present example) is then completely evaporated by warming. Thereafter, the gas collection bag is filled with more air until completely full. In the present example, the bag is filled to a volume of about 10 L.

[00102] A pre-weighed MOF powder sample is placed between two pieces of cotton in an Automated Thermal Desorption ("ATD") glass tube (PerkinElmer Life and Analytical Science, Shelton, CT).

Example	MOF	Weight
Example 4	Cu MOF(2)-13	0.02000 g
Example 5	Cu MOF(2)-1	0.02030 g
Example 6	Cu MOF(2)-3	0.02059 g
Example 7	Cu MOF(2)-4	0.02136 g
Example 8	Zn-MOF-9	0.01995 g
Example 9	Zn-MOF-10	0.02062 g
Example 10	Zn-MOF-15	0.02000 g

[00103] A separate ATD reference tube is connected to a pump through a plastic connection. Next, the ATD glass tube (containing the MOF) is connected to the ATD reference tube, again through a plastic connection. The ATD glass tube (containing the MOF) is connected to the gas-collecting bag (in which the malodor molecule is evaporated) through a plastic connection.

[00104] The pump draws air containing the evaporated malodor molecule through both the MOF and reference tubes. In the present example, over a period of from two to three minutes, approximately 150 to 250 ml of air (in which the malodor molecule is evaporated) is drawn through both tubes.

Example	MOF	Time	Volume Purged
11	Ex. 4	2 min	178 ml
12	Ex. 5	2 min	243 ml
13	Ex. 6	3 min	192 ml
14	Ex. 7	2 min	196 ml
15	Ex. 8	2 min	200 ml
16	Ex. 9	2 min	192 ml
17	Ex.10	2 min	202 ml

[00105] The contents of the MOF-containing ATD tube and the reference ATD tube are then analyzed by thermal desorption and gas chromatography / mass spectrometry (GC/MS), two techniques well-known to those of skill in the art. Results (based on changes in area under the GC peaks) are as follows:

Example	MOF	% Butyraldehyde Adsorbed
18	Ex. 4	33.1
19	Ex. 5	34.4
20	Ex. 7	40.0
21	Ex. 8	31.3
22	Ex. 9	27.6

Example	MOF	% Butyric Acid Adsorbed
23	Ex. 4	100
24	Ex. 5	100
25	Ex. 6	100
26	Ex. 7	100
27	Ex. 8	90.7
28	Ex. 9	98.4
29	Ex. 10	98.5

[00106] Delivery of fragrance compounds from MOFs may also be demonstrated through head space analysis using GC/MS according to techniques known to those of skill in the art. A pre-weighed sample of MOF in which a fragrance composition is incorporated is placed in a head space jar in which humidity and temperature are controlled. After a period of equilibration (*e.g.*, two hours), a head space sample is taken and analyzed by thermal desorption and GC/MS.

[00107] While the illustrative embodiments of the invention have been described with particularity, it will be understood that various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the spirit and scope of the invention. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the examples and descriptions set forth hereinabove but rather that the claims be construed as encompassing all the features of patentable novelty which reside in the present invention, including all features which would be treated as equivalents thereof by those skilled in the art to which the invention pertains.

Claims

1. A method for sequestering a malodor molecule by contacting the malodor molecule with a metal-organic framework comprised of a plurality of metal ions bound to a plurality of organic polydentate bridging ligands.

2. A method of Claim 1 where the plurality of metal ions are coordinately bound to the plurality of organic polydentate bridging ligands.

3. A method of Claim 2 where the plurality of metal ions are selected from the group consisting of Cu, Fe, Zn, Ag, Cd, Co, and Ni.

4. A method of Claim 2 where the plurality of metal ions is a cluster of at least two metal ions selected from the group consisting of Cu, Fe, Zn, Ag, Cd, Co, and Ni.

5. A method of Claim 1 where the metal-organic framework is synthesized in a solvent-free system.

6. A method for releasing a fragrance compound into an environment where the fragrance compound has been incorporated into a metal-organic framework comprising a plurality of metal ions bound to a plurality of organic polydentate bridging ligands.

7. A method of Claim 6 where the plurality of metal ions are coordinately bound to the plurality of organic polydentate bridging ligands.

8. A method of Claim 7 where the plurality of metal ions are selected from the group consisting of Cu, Fe, Zn, Ag, Cd, Co, and Ni.

9. A method of Claim 8 where the plurality of metal ions is a cluster of at least two metal ions selected from the group consisting of Cu, Fe, Zn, Ag, Cd, Co, and Ni.

10. A method of Claim 6 where the metal-organic framework is synthesized in a solvent-free system.

11. A method for reusing a metal-organic framework to sequester a malodor molecule comprising applying heat to the metal-organic framework at a temperature sufficient to release a malodor molecule previously sequestered in the framework.

12. A method of Claim 1 where the metal-organic framework is essentially-anhydrous.

13. A method of Claim 6 where the metal-organic framework is essentially-anhydrous.

14. A method of Claim 1 where the metal-organic framework is incorporated in an article for absorbing malodorous human bodily fluids.

15. A method of Claim 1 where the metal-organic framework retards the rate of evaporation of at least one accord.

16. A method of Claim 1 where the metal-organic framework accelerates the rate of evaporation of at least one accord.

17. A method of Claim 1 where the metal-organic framework is selected from the group consisting of $Cu_3BTC_2(H_2O)_3$, $Cu(INA)_2$, and $Zn(INA)_2$.

18. A method of Claim 6 where the metal-organic framework is selected from the group consisting of $Cu_3BTC_2(H_2O)_3$, $Cu(INA)_2$, and $Zn(INA)_2$.