Abstract: An imidazolate framework material comprises a general structure, M⁺⁻IM-M⁻⁻⁻⁻⁻⁻⁻⁺⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻~-~-~-~

B01J 23/10 (2006.01)
LANTHANIDE IMIDAZOLATE METAL ORGANIC FRAMEWORK MATERIAL

FIELD OF THE INVENTION

[0001] This invention relates to metal organic frameworks, their synthesis and their use.

BACKGROUND OF THE INVENTION

[0002] Metal organic frameworks (MOFs) are crystalline compounds consisting of metal ions or clusters coordinated to often rigid organic molecules to form one-, two-, or three-dimensional structures that can be porous. In some cases, guest molecules can stably enter the pores, thus MOF crystals can be used for the storage of gases such as hydrogen and carbon dioxide. Further, since some guest molecules can enter more easily than others, and the pores can be functionalized to change their chemical properties, this can be used as the basis for separation methodologies. For example, MOFs can be used to make highly selective and permeable membranes to separate small gas molecules (e.g., CO\textsubscript{2} from CH\textsubscript{4}) or liquid molecules (e.g., hydrocarbons, alcohols, water). Additional applications of MOFs are in catalysis, in drug delivery, and as sensors.

[0003] Zeolitic imidazolate frameworks or ZIFs are a subset of metal-organic frameworks and have properties similar to inorganic zeolitic materials. ZIFs are based on [M(IM)\textsubscript{4}] tetrahedral bonds in which IM is an imidazolate type linking moiety and M is a transition metal. These materials are generally referred to as zeolitic imidazolate frameworks or ZIFs since the angle formed by imidazolates (IMs) when bridging transition metals is similar to the 145° angle of the Si-O-Si bond in zeolites. ZIF counterparts of a large number of known zeolitic structures have been produced. In addition, porous framework types, hitherto unknown to zeolites, have also been produced. Discussion of this research can be found in, for example, the following publications from Yaghi and his co-workers: "Exceptional Chemical and Thermal Stability of Zeolitic Imidazolate Frameworks", Proceedings of the National Academy of Sciences of U.S.A., Vol. 103, 2006, pp. 10186-91, "Zeolite A Imidazolate Frameworks", Nature Materials, Vol. 6, 2007, pp. 501-6, "High-Throughput Synthesis of Zeolitic Imidazolate Frameworks and Application to CO\textsubscript{2} Capture", Science, Vol. 319, 2008, pp. 939-43, "Colossal Cages in Zeolitic Imidazolate Frameworks as

[0004] Much of this work on ZIF structures is summarized in U.S. Patent Application Publication No. 2007/0202038, the entire contents of which are incorporated herein by reference. In particular, the '038 publication discloses a zeolitic framework, comprising the general structure: M-L-M, wherein M comprises a transition metal and L is a linking moiety comprising a structure selected from the group consisting of I, II, III, or any combination thereof:
wherein A1, A2, A3, A4, A5, A6, and A7 can be either C or N, wherein R5-R8 are present when A1 and A4 comprise C, wherein R1, R4 or R9 comprise a non-sterically hindering group that does not interfere with M, wherein R2, R3, R5, R6, R7, R8, R10, R11, and R12 are each individually an alkyl, halo-, cyano-, nitro-, wherein M1, M2, M3, M4, M5, and M6 each comprise a transition metal, wherein when the linking moiety comprises structure III, R10, R11, and R12 are each individually electron withdrawing groups.

In a more recent work by Ni et al., the structure and synthesis of mixed-valence ZIFs are disclosed in U.S. Patent Application Publication No. 2010/0307336. Specifically, the authors disclose in the '336 publication a porous crystalline material having a tetrahedral framework comprising a general structure, M1-M-M2, wherein M1 comprises a metal having a first valency, wherein M2 comprises a metal having a second valency different from said first valency, and wherein IM is imidazolate or a substituted imidazolate linking moiety. Such materials can sometimes be described as iso-structural to known ZIF materials. In some embodiments, M1 may comprise a monovalent metal and M2 may comprise a trivalent metal.

ZIFs and other metal organic framework materials (MOFs) based on the imidazolate ligand have emerged as an attractive new platform for active materials for gas absorption, sensing (J. Am. Chem. Soc., 2010, 132 (23), pp 7832-7833), separation (J. Am. Chem. Soc., 2010, 132 (50), pp 17704-17706), and catalysis (e.g., ACS Catal., 2011, 1 (2), pp 120-127, ACS Catal., 2012, 2 (1), pp 180-183). In addition, in J. Inorg. Chem, 2011, 50, pp 12396-98, Norman et al. disclose strontium and barium imidazolate complexes which, under atomic layer deposition conditions using ozone as a reagent, can be used to deposit crystalline metal-containing films useful...
in the fabrication of dynamic random access memory (DRAM) and other electronic devices.

[0007] To date, however, most imidazolate framework materials that have been reported have a net divalent metal charge (whether all metals are 2+ valent or there is a combination of 1+ and 3+ valent metals). There is, therefore, interest in producing imidazolate framework materials with a wider range of metal valencies, for example, only trivalent metals.

SUMMARY OF THE INVENTION

[0008] According to one aspect of the invention, an imidazolate framework material has now been synthesized wherein the composition comprises the general structure, M\(^i\)-IM-M\(^{2}\), wherein IM is an imidazolate or a substituted imidazolate linking moiety, wherein M\(^1\) and M\(^2\) comprise the same or different metal cations, wherein at least one of\(^{1+}\) and M\(^2\) comprises a trivalent metal cation and wherein neither M\(^1\) nor M\(^2\) comprises a monovalent cation.

[0009] In a further aspect, the invention resides in an imidazolate framework material comprising a general structure, M\(^i\)IM-M\(^{2}\), wherein IM is a dicyanoimidazolate or a hydrolyzed or substituted dicyanoimidazolate linking moiety, wherein M\(^1\) and M\(^2\) comprise the same or different metal cations, wherein at least one of M\(^1\) and M\(^2\) comprises a trivalent metal cation and wherein neither M\(^1\) nor M\(^2\) comprises a monovalent cation.

[0010] In certain embodiments, at least one of M\(^1\) and M\(^2\) comprises a trivalent lanthanide cation.

[0011] In certain embodiments, M\(^1\) and M\(^2\) are both trivalent metal cations, for example the same trivalent metal cation, especially the same lanthanide cation.

[0012] In yet a further aspect, the invention resides in an imidazolate framework material comprising a general structure, M\(^i\)IM-M\(^{2}\), wherein IM is an imidazolate or a substituted imidazolate linking moiety, wherein M\(^1\) and M\(^2\) comprise the same or different metal cations, wherein at least one of M\(^1\) and M\(^2\) comprises a trivalent metal cation selected from the group consisting of aluminum, gallium, indium, iron, niobium, scandium, yttrium, and combinations thereof and wherein neither M\(^1\) nor M\(^2\) comprises a monovalent cation.
In still yet a further aspect, the invention resides in an imidazolate framework material comprising a general structure, M^IM-M^2, wherein IM is a dicyanoimidazolate or a hydrolyzed or substituted dicyanoimidazolate linking moiety, wherein M^1 and M^2 comprise the same or different metal cations, wherein at least one of M^1 and M^2 comprises a trivalent metal cation selected from the group consisting of aluminum, gallium, indium, iron, niobium, scandium, yttrium, and combinations thereof and wherein neither M^1 nor M^2 comprises a monovalent cation.

In certain embodiments, each of M^1 and M^2 is a trivalent metal cation, for example the same trivalent metal cation selected from the group consisting of aluminum, gallium, indium, iron, niobium, scandium, yttrium, and combinations thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGs. 1(a-g) show X-ray diffraction patterns for the product of Example 1 and certain precursor and comparison materials.

FIG. 2 shows a scanning electron micrograph (SEM) image of the product of Example 1.

FIGs. 3(a-k) show X-ray diffraction patterns for the product of Example 2 at various temperatures from 30°C to 500°C.

FIG. 4 shows the result of TGA analysis of the product of Example 2.

FIGs. 5(a-c) show X-ray diffraction patterns for the product of Example 3 and certain precursor materials.

FIG. 6 shows an SEM image of the product of Example 3.

FIGS. 7 and 8 show 13C NMR spectra of the product of Example 3.

FIGs. 9(a-g) show X-ray diffraction patterns for the products of Example 2 to 8.

FIG. 10 shows 27Al NMR spectrum of the product of Example 6.

DETAILED DESCRIPTION OF THE EMBODIMENTS

Disclosed herein are novel imidazolate framework materials having one or more trivalent metal cations, especially lanthanide cations and, in certain embodiments, dicyanoimidazole linking moieties. In particular, it has been found that using dicyanoimidazole as a linking agent can facilitate the direct synthesis of lanthanide and...
other trivalent metal imidazolate framework materials which, to date, has proven elusive with other linking agents.

[0025] In particular, the present imidazolate framework materials can advantageously have a framework comprising a general structure, $M^\text{IM}M^2$, wherein IM is an imidazolate or a substituted imidazolate linking moiety, wherein $M^1$ and $M^2$ comprise the same or different metal cations, wherein at least one of $M^1$ and $M^2$ comprises a trivalent metal cation and wherein neither $M^1$ nor $M^2$ comprises a monovalent cation. Desirably, each of $M^1$ and $M^2$ can comprise a trivalent metal cation and, in certain embodiments, the same trivalent metal cation.

[0026] In one embodiment, at least one of, and desirably each of, $M^1$ and $M^2$ can comprise a trivalent lanthanide cation and, in certain embodiments, the same trivalent lanthanide cation.

[0027] As used herein, the term "lanthanide" is used to denote any of the fifteen metallic chemical elements with atomic numbers 57 through 71, from lanthanum through lutetium. In particular, the lanthanides include lanthanum, cerium, praseodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium.

[0028] Lanthanide imidazolate framework materials are of potential importance since lanthanides can have powerful Lewis acids and the nitrogen-lanthanide connectivity in such materials could be a potential source of Frustrated Lewis Pairs (FLPs), which in turn could activate a variety of small molecules (e.g., *J. Am. Chem. Soc.*, 2009, **131** (10), 3476-3477, *Chem. Rev.*, 2010, **110**, 4023-4078). Thus, lanthanide imidazolate framework materials have potential utility in certain catalytic applications, such as hydrogenation, hydroformylation, and CH-activation, and additionally or alternatively as sorption media. Further additionally or alternatively, lanthanide imidazolate framework materials can be attractive as volatile metal containing precursors for vapor deposition processes, including chemical vapor deposition (CVD), atomic layer deposition (ALD), plasma-enhanced ALD (PEALD), pulsed CVD, and/or plasma enhanced CVD (PECVD) for fabricating conformal lanthanide metal containing films on substrates, such as: silicon, metal, metal nitride, metal silicon nitride, metal oxide, and other metal-containing layers.
In other embodiments, at least one of, and desirably each of, M₁ and M₂ can comprise a trivalent metal cation selected from the group consisting of aluminum, gallium, indium, iron, niobium, scandium, and yttrium cations, and combinations thereof. In certain embodiments, M₁ and M₂ can consist of the same trivalent metal cation selected from the group consisting of aluminum, gallium, indium, iron, niobium, scandium, and yttrium cations, and combinations thereof. Again, imidazolate framework materials containing these trivalent metal cations can have potential utility in catalytic and/or sorptive applications, as well as potentially in volatile metal containing precursors for the vapor deposition of trivalent metal containing films on substrates.

In certain embodiments, linking moiety IM employed in the present imidazolate framework materials can comprise a dicyanoimidazolate or a hydrolyzed or substituted dicyanoimidazolate and can desirably be derived from 4,5-dicyanoimidazole or a substituted 4,5 dicyanoimidazole having formula (IV) below and/or its partially hydrolyzed form having formula V below and/or its fully hydrolyzed form having formula VI:
wherein \( R^1 \) can be any non-sterically hindering group that does not detrimentally interfere with \( M^1 \) or \( M^2 \) in the ZIF composition. In one embodiment, \( R^1 \) can be hydrogen.

[0031] The imidazolate framework materials disclosed herein may have tetrahedral framework structures characteristic of zeolitic materials. The framework types of the zeolitic imidazolate framework (ZIF) materials are denoted herein by a code consisting of three upper-case letters, in a similar manner to that used in the zeolite literature. It should be pointed out that a system of three-lower-case-letter symbols was introduced by O'Keeffe and Yaghi for the designation of the framework types of metal-organic frameworks (MOFs), meta-organic polyhedra (MOPs), zeolitic imidazolate frameworks (ZIFs), and covalent-organic frameworks (COFs). General information about the latter can be found, for example, in the publication by O'Keeffe and Yaghi et al, "Reticular Chemistry: Occurrence and Taxonomy of Nets and Grammar for the Design of Frameworks", Accounts of Chemical Research, Vol. 38, 2005, pp. 176-82, and at http://rcsr.anu.edu.auhome, the Reticular Chemistry Structure Resource (RCSR) website. For the purpose of uniformity, all framework type codes used herein are typically expressed in upper-case letters.

[0032] Zeolitic forms of the imidazolate framework materials disclosed herein can include such structures iso-structural to known zeolites and related minerals, as well as structures unique to the field of ZIFs, for example, those identified in U.S. Patent Application Publication Nos. 2007/0202038 and 2010/0307336, including ABW, ACO, AEI, AEL, AEN, AET, AFG, AFI, AFN, AFO, AFR, AFS, AFT, AFX, AFY, AHT, ANA, APC, APD, AST, ASV, ATN, ATO, ATS, ATT, ATV, AWO, AWY, BCT, BEA, BEC, BIK, BOG, BPH, BRE, CAG, CAN, CAS, CDO, CFI, CGF, CGS, CHA, CHI, CLO, CON, CRB, CZP, DAC, DDR, DFO, DFT, DIA, DOH, DON, EAB, EDI, EMT, EON, EPI, ERI, ESV, ETR, EUO, EZT, FAR, FAU, FER, FRA, FRL, GIS, GIU, GME, GON, GOO, HEU, HFR, IHW, ISV, ITE, ITH, ITW, IWR, IWV, IWW, JBW, KFI, LAU, LCS, LEV, LIO, LIT, LOS, LOV, LTA, LTL, LTN, MAR, MAZ, MEI, MEL, MEP, MER, MFI, MFS, MON, MOR, MOZ, MSE, MSO, MTF, MTN, MTT, MTW, MWW, NAB, NAT, NES, NON, NPO, NSI, OBW, OFF, OSI, OSO, OWE, PAR, PAU, PHI, PON, POZ, RHO, RON, RRO, RSN, RTE, RTH, RUT, RWR, RWY, SAO, SAS, SAT, SAV, SBE, SBS, SBT, SFE, SFF, SFH, SFN, SFO, SGT, SIV,
SOD, SOS, SSY, STF, STI, STT, SZR, TER, THO, TON, TSC, TUN, UEI, UFT, UOZ, USI, UTL, VET, VFI, VNI, VSV, WEI, WEN, YUG, ..., the relatively weaker base, imidazolate, to react with electrophilic metal cations, such as lanthanide (+3) cations. Such structures can include a tetrahedral framework type selected from the group consisting of CRB, DFT, CAG, SOD, MER, RHO, ANA, LTA, DIA, ZNI, GME, LCS, FRL, GIS, POZ, MOZ, and combinations thereof.

[0033] In some embodiments, the trivalent metal(s) in the imidazolate framework materials disclosed herein may be at least partially octahedrally coordinated. For example, the ratio of the degree of octahedral coordination to tetrahedral coordination, if any, may exceed about 5:1, even exceeding about 10:1 in some cases. In addition, the imidazolate framework materials disclosed herein can potentially exhibit no significant mesoporosity but can still tend to have relatively high BET surface area values, such as in excess of about 100 m²/g, which is unusual for high atomic weight materials, such as lanthanides.

[0034] The present imidazolate framework materials can be synthesized, e.g., by contacting a solution of the dicyanoimidazole linking agent and a solution of a salt of the or each metal M¹ or M² in the same or different polar aprotic organic solvents at a temperature from about 25°C to about 240°C until crystals of the desired imidazolate framework material are formed. When the crystallization step is completed, normally in about 30 minutes to about 168 hours, the resultant crystalline product can be recovered.

[0035] The organic solvent used in the synthesis can advantageously be polar and aprotic, and it typically comprises or is an amide (e.g., N,N-dimethylformamide, N,N-dimethylacetamide, 1,3-diisopropylcarbodiimide, or the like, or a combination thereof), a sulfoxide (e.g., dimethylsulfoxide), a phosphoramidate (e.g., hexamethylphosphoramide), an ether (e.g., dimethyl ether, diethyl ether, methylethyl ether, or the like, or combinations thereof), or a combination thereof.

[0036] In some cases, the synthesis may be assisted by the addition to the reaction mixture of an organic base, such as piperazine and/or 1,4-dimethylpiperazine. While not wishing the be bound be any theory of operation, it is believed that the organic base may activate the relatively weaker base, imidazolate, to react with electrophilic metal cations, such as lanthanide (+3) cations.
If desired, the synthesis can be conducted in the presence of template, which can typically comprise or be a neutral organic compound, such as an ether, ketone, ester, amine, nitrile, nitro compound, phosphine, hydrocarbon, halide, or the like, or combination thereof.

In its as-synthesized form, the crystalline product may contain guest species, typically solvent and/or template molecules, within its framework structure. In most cases, the guest species can be removed, *e.g.*, by evacuation at a pressure less than ~50 mTorr at a temperature of about 70°C to about 300°C, and/or by exchange with an organic solvent of small molecular size (*e.g.*, acetonitrile), followed by evacuation such as described above. In the case of ZIF materials, the removal of guest species may result in internal pore volume that can be used to adsorb various gases, such as carbon dioxide, carbon monoxide, hydrocarbons, hydrogen, nitrogen, oxygen, noble gases, amines, and the like, as well as combinations thereof. The size and shape of the pores in the final ZIF material can be controlled by the choice of imidazolate linking moiety, solvent, and template, *inter alia*. As a result, these materials show significant potential as catalysts and in the storage/separation of gases.

Additionally or alternatively, the invention can be described by one or more of the following embodiments.

**Embodiment 1.** An imidazolate framework material comprising a general structure, M^IM-M^2, wherein IM is an imidazolate or a substituted imidazolate linking moiety, wherein M^1 and M^2 comprise the same or different metal cations, wherein at least one of M^1 and M^2 comprises a trivalent metal cation and wherein neither M^1 nor M^2 comprises a monovalent cation.

**Embodiment 2.** The material of embodiment 1, wherein M^1 and M^2 are both trivalent metal cations, and/or wherein M^1 and M^2 are the same trivalent metal cation.

**Embodiment 3.** The material of embodiment 1 or embodiment 2, wherein at least one of M^1 and M^2 comprises a lanthanide cation.

**Embodiment 4.** The material of any one of the previous embodiments, wherein IM is a dicyanoimidazolate or a hydrolyzed or substituted dicyanoimidazolate linking moiety.

**Embodiment 5.** The material of any one of the previous embodiments, wherein at least one of M^1 and M^2 comprises a trivalent metal cation selected from the
group consisting of aluminum, gallium, indium, iron, niobium, scandium, yttrium, and combinations thereof.

[0045] The invention will now be more particularly described with reference to the following non-limiting Examples and the accompanying drawings.

EXAMPLES

Example 1: Synthesis of Gadolinium Imidazolate Framework Material

[0046] Gd(NO$_3$)$_3$.6H$_2$O (-452 mg, -1 mmol) was loaded in a -50 mL beaker and dissolved in -10 mL of N,N-dimethyl formamide (DMF). 4,5-dicyanoimidazole (-545 mg, -5 mmol) and piperazine (-5 mmol, -430 mg) were dissolved in -10 mL DMF in another -25 mL beaker. The two solutions were mixed and heated in an autoclave reactor at -140°C for -24 hours. A solid grey colored precipitate was formed that was washed with additional -20 mL of DMF followed by -30 mL of acetonitrile. The material was subjected to solvent exchange in a scintillation vial 3 times with another 3x~10 mL of acetonitrile. The solid residue was dried under vacuum overnight (about 8-16 hours) and analyzed by SEM and powder x-ray diffraction.

[0047] The powder XRD data of the precursors and product are shown in FIG. 1 and demonstrate the formation of a new material appearing markedly different than all of the starting materials. In FIG. 1, pattern (a) shows the XRD data for piperazine (crushed), pattern (c) shows the XRD data for 4,5-dicyanoimidazole (crushed), pattern (d) shows the XRD data for gadolinium (III) nitrate hexahydrate (crushed), pattern (e) shows the XRD data for the dried gadolinium imidazolate framework product (crushed), pattern (f) shows the XRD data for a dried and crushed gadolinium imidazolate framework product produced in a repeat experiment.

[0048] Also shown in FIG. 1 are the XRD data for crushed zinc phthalocyanine (pattern b) and for the dried and crushed gadolinium imidazolate framework product after treatment with a solution of zinc phthalocyanine in DMF (pattern g). The similarity of the patterns (e), (f), and (g) suggests the treatment resulted in no incorporation of the phthalocyanine ligand in the imidazolate framework.

[0049] The SEM analysis (FIG. 2) showed that the product had a high degree of porosity and was composed of two kinds of materials. This was confirmed by solid state $^{13}$C MAS NMR where the presence of both piperazine and 4,5-dicyanoimidazole was detected. Vibrational spectroscopic data (TR and Raman) confirmed the presence
of nitrile groups along with piperazine. Elemental Analysis confirmed the presence of gadolinium.

[0050] BET measurement showed that the product had a surface area of ~120 m²/g.

Example 2: Synthesis of Gadolinium Imidazolate Framework Material

[0051] The synthesis of Example 1 was repeated but with the 4,5-dicyanoimidazole being dissolved in 1,4-dimethyl piperazine and the molar ratio of 4,5-dicyanoimidazole: 1,4 dimethylpiperazine: Gd(N03)3.6H20 being ~3:~3:~1.

[0052] After solvent exchange with 3x~1.0 mL of acetonitrile, the solid residue was dried under vacuum overnight (for about 8-16 hours) at ~30°C and analyzed by XRD. The results are shown in FIG. 3(a). The product was then heated in flowing nitrogen to ~500°C and XRD data were taken at ~50°C and subsequently at every ~50°C interval as the temperature was increased to ~500°C. The results are shown in FIG. 3(b) to FIG. 3(k) and show the product to exhibit high stability at least until about 400°C.

[0053] A further sample of the vacuum dried residue was subjected to thermogravimetric analysis (TGA) by heating in air for ~600°C at ~3°C/minute heating rate. The results are shown in FIG. 4 and not only confirm the high thermal stability of the material but also show that part of the product seems to have sublimed and collected in the exhaust line during the TGA experiment, thereby preventing a reliable determination of the ligand:Gd³⁺ molar ratio.

Example 3; Synthesis of Lanthanum Tmidazolate Framework Material

[0054] About 3.54 grams of 4,5-dicyanoimidazole (~30 mmol), about 3.42 grams of 1,4-(1imethylpiperazine (~30 mmol), and about 4.33 grams (~10 mmol) of lanthanum nitrate (La(N03)3.6H20) were dissolved in N,N-dimethyl formamide (DMF) were assembled in a ~25cc Parr reactor and were kept at a temperature of ~140°C for ~3 days. A solid white colored precipitate was formed that was filtered and washed with ~25 mL of N,N-dimethyl-formamide, followed by -25 mL of acetonitrile. Vacuum drying of the precipitate for ~3 hours at ~100°C yielded about 6 grams of a solid product which was then analyzed by XRD and SEM.

[0055] The powder XRD data of the product are shown in FIG. 5 and demonstrate the formation of a new material appearing markedly different than all of the starting materials. In FIG. 5, pattern (a) shows the XRD data for lanthanum (III) nitrate hexahydrate (crushed), pattern (b) shows the XRD data for 4,5-dicyanoimidazole
(crushed), and pattern (c) shows the XRD data for the dried lanthanum imidazolate framework product (crushed).

[0056] The SEM image of the product is shown in FIG. 6 and suggests that the product is a single phase material with a high degree of porosity. This result suggests that, by substituting piperazine with 1,4-dimethyl piperazine as base, it was possible to reduce the level of coproduct coming from a second phase as seen in Example 1.

[0057] FIG. 7 provides a 125.53 MHz $^{13}$C Bloch decay magic-angle spinning NMR spectrum of the vacuum dried product acquired with a pulse delay of ~180 seconds using a ~5mm rotor spinning at ~8 kHz, in which asterisks indicate spinning sidebands. The peak centered at around 42 ppm indicates the presence of piperazine or piperazine-containing moiety. The rest of the peaks (around 117, 123, and 149 ppm) correspond to the dicyanoimidazolate moiety (diCNIm), with peaks around -102, 53, 59, 181, and 187 ppm being identified as spinning sidebands in the spectrum by asterisks. The spinning sidebands were confirmed by performing different spinning speed experiments. The SEM images that indicated different morphologies appear to be consistent with the NMR observation of the incorporation of the piperazine and the dicyanoimidazolate moieties.

[0058] FIG. 8 provides a 125.53 MHz $^{13}$C cross-polarization magic-angle spinning NMR spectrum of the vacuum dried product after heat treatment at ~140°C for ~12 hours. The spectrum was acquired with a 1H-$^{13}$C cross polarization contact time of ~2.5 ms using a ~1.6-mm rotor spinning at ~40 kHz and a pulse delay of ~60 seconds. The spectrum appeared to exhibit the dicyanoimidazolate structure and its hydrolyzed or substituted form. The absence of the piperazine (believed to be solid at room/ambient temperature) moiety was presumed to be due to the fact that, in this synthesis, the 1,4-dimethyl piperazine (believed to be liquid at room/ambient temperature) was used as a base.

Examples 4-7: Synthesis of Further Trivalent Metal Imidazolate Frameworks

[0059] Using the ~3:~3:~1 molar ratio of 4,5-dicyanoimidazole: 1,4 dimethylpiperazine: trivalent metal precursor in N,N-dimethylformamide as solvent, the process of Example 3 was repeated with the following trivalent metal precursors: Praseodymium nitrate ($\text{Pr(NO}_3\text{)3.6H}_2\text{O}$) - Example 4; Ytterbium nitrate
(Yb(N$_{3}$)$_{3}$)$_{3}$H$_{2}$O) - Example 5; Aluminum nitrate (Al(N$_{3}$)$_{3}$)$_{9}$H$_{2}$O) - Example 6; and Iron (III) nitrate (Fe(N$_{3}$)$_{3}$)$_{9}$H$_{2}$O) - Example 7.

The XRD data on the resultant products are shown in FIG. 9, in which pattern (b) provides the XRD pattern for the product of Example 4, pattern (c) provides the XRD pattern for the product of Example 5, pattern (f) provides the XRD pattern for the product of Example 6, and pattern (g) provides the XRD pattern for the product of Example 7. For comparison, patterns (a) and (e) provide the XRD patterns for the products of Examples 2 and 3, respectively. In addition, pattern (d) in FIG. 9 shows the XRD data for the product of Example 8, a repeat of Example 2 but with the solvent for the Gd(N$_{3}$)$_{3}$H$_{2}$O being diethylether instead of N,N-dimethylformamide. It may be seen that the change of solvent appeared to result in the imidazolate framework product of Example 8 having a different structure from the material of Example 2.

FIG. 10 provides a ~130.1 MHz $^{27}$Al Bloch decay magic-angle spinning NMR spectrum of the aluminum imidazolate framework product of Example 6 acquired with a pulse delay of ~0.3 seconds using ~4mm rotor spinning at ~12 kHz. The $^{27}$Al MAS NMR shows that ~93 mol% of the total aluminum appeared to be octahedrally coordinated and ~7 mol% appeared to be tetrahedrally coordinated (peak centered around 65 ppm). Asterisks in the figure were used to designate spinning sidebands.

While the present invention has been described and illustrated by reference to particular embodiments, those of ordinary skill in the art will appreciate that the invention lends itself to variations not necessarily illustrated herein. For this reason, then, reference should be made solely to the appended claims for purposes of determining the true scope of the present invention.
CLAIMS:

1. An imidazolate framework material comprising a general structure, M^IM-M^2, wherein IM is an imidazolate or a substituted imidazolate linking moiety, wherein M^1 and M^2 comprise the same or different metal cations, wherein at least one of M^1 and M^2 comprises a trivalent metal cation and wherein neither M^1 nor M^2 comprises a monovalent cation.

2. The material of claim 1, wherein M^1 and M^2 are both trivalent metal cations, and/or wherein M^1 and M^2 are the same trivalent metal cation.

3. The material of claim 1 or claim 2, wherein at least one of M^1 and M^2 comprises a lanthanide cation.

4. The material of any one of the previous claims, wherein IM is a dicyanoimidazolate or a hydrolyzed or substituted dicyanoimidazolate linking moiety.

5. The material of any one of the previous claims, wherein at least one of M^1 and M^2 comprises a trivalent metal cation selected from the group consisting of aluminum, gallium, indium, iron, niobium, scandium, yttrium, and combinations thereof.
26407-161; Gd-ZIF; [Dicyano Imidizole]; vac dry @ RT
oxid in air; O(600-3 degC/min)

FIG. 4
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07F5/00 B01J23/10 B01J31/18

ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07F B01J

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, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X,P</td>
<td>CN 104 672 260 A (FUZHOU UNIVERSITY, PEOP. REP. CHINA) 3 June 2015 (2015-06-03)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>M0F of (1-Methyl -3-hexyl -imi dazolium) Eu(DHBDC)2, composing a unit M1-M1-M2,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>with M1, M2 being Ln3+ Use as fluorescent probe material</td>
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</tbody>
</table>

Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

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

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

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

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

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

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

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

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

"Z" document member of the same patent family

Date of the actual completion of the international search

18 September 2015

Date of mailing of the international search report

05/10/2015

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV RIJWIJK
Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016

Authorized officer

Lange, Tim
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>&amp; DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; XI E, ZAI LAI ET AL: &quot;Fluorescent probe material made from rare earth metal organic framework compounds used for detecting barium ions and preparation thereof&quot;, XP002744463, retrieved from STN Database access number 2015:930987 abstract</td>
<td>1-3</td>
</tr>
<tr>
<td>X,P</td>
<td>ZHAO, SHU-NA ET AL: &quot;Lanthane de ion Codoped Emitters for Tailoring Emissivity Trajectory and Temperature Sensing&quot;, ADVANCED FUNCTIONAL MATERIALS, 25(9), 1463-1469 CODEN: AFMDC6; ISSN: 1616-301X, 27 January 2015 (2015-01-27), XP002744460, DOI: 10.1002/ADFM.201402061 MOFs [Ln ((L)2 (OH)) x H2O], [Ln ((L)2 (C02)) x (H2O)]2 with Ln = Y and codoped Ln-MOFs Eu_xTb(1-x) L: page 1464, left column, 2nd paragraph</td>
<td>1-5</td>
</tr>
<tr>
<td>X,P</td>
<td>MEYER, L. V. ET AL: &quot;A blue luminescent MOF as a rapid turn-off/tturn-on detector for H2O, O2 and CH2C12, MeCN: 3. infin. [Ce((Im)3ImH)]...cntdot. ImH&quot;, DALTON TRANSACTIONS, 44(9), 4070-4079 CODEN: DTARAF; ISSN: 1477-9226, 15 January 2015 (2015-01-15), XP002744461, DOI: 10.1039/C4DT03578J MOF of [Ce((Im)3ImH)] (compound 1, page 4077) and [Pr((Im)3 (ImH))] (page 4071, left column, last paragraph)</td>
<td>1-3</td>
</tr>
<tr>
<td>X,P</td>
<td>SHI, BINGBING ET AL: &quot;Two dimethyl phenyl imidazole di-carboxylate-based lanthane de metal-organic frameworks for luminescence sensing of benzaldehyde&quot;, DALTON TRANSACTIONS, 44(9), 4362-4369 CODEN: DTARAF; ISSN: 1477-9226, 8 January 2015 (2015-01-08), XP002744462, DOI: 10.1039/C4DT03326D [Eu(H2DMPhIDC)3 (H3DMPhIDC)] n (compound 1) and [Tb(H2DMPhIDC)3 (H3DMPhIDC)] n (compound 2) on page 4363</td>
<td>1-4</td>
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Form PCT/ISA/210 (continuation of second sheet) (April 2005)
<table>
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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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<tr>
<td>X</td>
<td>MEYER, LARISSA VALERIE ET AL: &quot;In si tu growth of luminescent MOF thin fi lms of Sr/Eu( I I )-imidazolate on functi onal ized nanostructured al umini na&quot;. CRYSTENGCOMM, vol. 15, no. 45, 29 August 2013 (2013-08-29) , pages 9382-9386, XP055212905, ISSN: 1466-8033, DOI: 10.1039/C3CE41087K Mono or bimetal l ic MOF of [Sr(I-x) Eu(x)Im2], x=0-l Use as luminescent materi al for surface modi fi cations</td>
<td>1-5</td>
</tr>
<tr>
<td>Y</td>
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<td>5</td>
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<tr>
<td>Category</td>
<td>Citation of document, with indication, where appropriate, of the relevant passages</td>
<td>Relevant to claim No.</td>
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<tr>
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<td>----------------------------------------------------------------------------------</td>
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<tr>
<td></td>
<td>MOFs [Sm₃ (Im)₉ (ImH)₂] x 2 ImH, [Eu(Im)₂ (ImH)₂] x [Pr(Im)₃ (ImH)] x ImH: Page 261, left col umn, bottom MOFs [Sm₃ (Im)₉ (ImH)₂] x 2 ImH, [Gd(Im)₆ (ImH)₁.₅] x 0.₅ ImH, [Dy(Im)₃] x ImH: Page 262</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MOF [Sr₁-xEux(Im)²] Eu(x) (Im)²] with x=0. 01-1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MOF of 2-(pyridine-3-yl)-1H-4,5-imidazole-di-carboxylic acid with Nd³⁺: compound 3 MOF features unit Nb- (substituted imidazole e)-Nb: figures 2-3</td>
<td></td>
</tr>
</tbody>
</table>

Form PCT/ISA210 (continuation of second sheet) (April 2005)
<table>
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<tr>
<td>X</td>
<td>LI, XIA ET AL: &quot;Syntheses of Metal -2- (Pyridin-4-yl)-1H-imidazole-4,5-dicarboxylate Networks with Topology, Stability and Fluorescent Emission Properties&quot;, CRYSTAL GROWTH &amp; DESIGN, vol. 9, no. 8, 17 June 2009 (2009-06-17), pages 3423-3431, XP055212992, ISSN: 1528-7483, DOI: 10.1021/CG801321E MOFs with Fe3+, Eu3+, Tb3+, Y3+ and 2-(pyridin-4-yl)-1H-imidazole-4,5-dicarboxylic acid: page 3424 the framework material comprises the unit Metal - (substituted imidazole) -Metal: scheme 1 Use of MOFs for Gas storage: see title</td>
<td>1-5</td>
</tr>
<tr>
<td>Y</td>
<td></td>
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</table>
This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

   Impartial

   see FURTHER INFORMATION sheet PCT/ISA/210

2. ☑ Claims Nos.: because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☑ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:  

4. ☑ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:  

Remark on Protest

☒ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☒ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☒ No protest accompanied the payment of additional search fees.
Continuation of Page 11.2

Claims Nos.: 1-3 (partially)

The present application, claim 1 is lacking clarity and the claims are lacking support to such an extent that a meaningful search could not be performed beyond the scope as set forth by the examples of the described on.

Furthermore, present claims 1-4 relate to an extremely large number of possible compounds due to defining the scope of the claim by a vague structural unit "Ml-Im-M2", with "Im" being "a substituted imidazol ate", and thus in very general terms. In contrast to this, support and disclosure in the sense of Article 6 and 5 PCT can only be found for only a very small proportion of the claimed structural space, namely by examples, where "Im" represents "3,4-di cyanomethyl dazol e". The discrepancy between the scope of the claim on the one hand and the actual disclosed on the other hand constitutes a non-compliance with the substantial prerequisites to such an extent, that the search was performed taking into consideration this non-compliance (PCT Guidelines 9.19 and 9.23).

A further reason for focusing the search on the subject-matter of claims 4-5 is the fact that the initial phase of the search revealed a very large number of documents relevant to the issue of novelty. So many documents were retrieved that it is impossible to determine which parts of the claim 1-3 may be said to define subject-matter for which protection might legally be sought (Article 6 PCT).

The search of claims 1-5 thus was focused on and is only complete with respect to the subject-matter characterized by both features of claims 4 and 5.

It should be understood that any positive statement as to novelty and/or inventiveness step exclusively relates to said limited subject matter.

The applicant's attention is drawn to the fact that claims relating to inventiveness in respect of which an international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examination Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the applicant proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination on before the EPO (see EPO Guidelines C-IV, 7.2), should the problems which led to the Article 17(2) declaration be overcome.
<table>
<thead>
<tr>
<th>Patent document cited in search report</th>
<th>Publication date</th>
<th>Patent family member(s)</th>
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<td>CN 104672260</td>
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