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(54) Title: CONDUCTIVE ORGANOMETALLIC FRAMEWORK

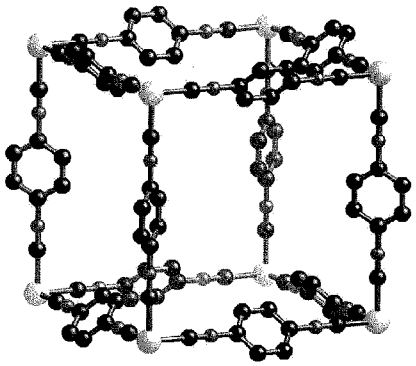


FIGURE 1

(57) Abstract: The disclosure provides organometallic frameworks, catalysts and sensors. In one aspect, the organometallic framework comprises di-isocyanide group.

CONDUCTIVE ORGANOMETALLIC FRAMEWORK

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority under 35 U.S.C. §119 from Provisional Application Serial No. 61/144,742, filed January 15, 2009, the disclosure of which is incorporated herein by reference.

TECHNICAL FIELD

[0002] The disclosure provides a conductive organometallic framework. The disclosure also provides sensors and catalysts comprising an organometallic framework of the disclosure.

BACKGROUND

[0003] Ligand-stabilized metal complexes (*i.e.*, organometallic complexes) are useful as catalysts, additives, stoichiometric reagents, monomers, solid state precursors, therapeutic reagents and drugs.

SUMMARY

[0004] The disclosure provides organometallic frameworks, compositions comprising such frameworks and uses of the frameworks for catalysis and gas sensing.

[0005] In one embodiment of the disclosure an organometallic framework is provided comprising at least two metal or metal ions linked by a linking ligand, wherein the linking ligand comprises at least one cyano group. In one embodiment, the linking ligand is a diisocyanide. In yet another embodiment, the organometallic framework comprises a general structure $(M\text{-}R_1\text{-}C\equiv N\text{-}R_2\text{-}N\equiv C\text{-}R_1\text{-}M)_n$ wherein R_1 can be absent (*e.g.*, $(M\text{-}C\equiv N\text{-}R_2\text{-}N\equiv C\text{-}M)_n$)and wherein when R_1 is present comprises an alkyl (*e.g.*, a lower alkyl) and R_2 is an an alkyl or cycloalkyl group comprising 1 to 20 carbon atoms, an aryl

group comprising 1 to 5 phenyl rings, a fused aromatic group comprising 2 to 6 rings or a porphine group comprising 20 to 80 carbon atoms, and n is 1 or more. In one embodiment, the backbone/cyano-substructure can be modified with an ancillary ligand system comprising organic substituents, and therefore provide an opportunity to modify the shape, electronic and chemical properties of the pores and structure of the organometallic framework. In one embodiment, the organometallic framework of the disclosure comprises a plurality of metal or metal ions separated by a diisocyanide to form a porous framework. In yet another embodiment, the porous organometallic framework of the disclosure comprises pores useful for catalysis. In yet another embodiment, the metals of the organometallic framework are homogeneous. In another embodiment, the diisocyanide linking ligands are homogeneous.

[0006] In one embodiment of the disclosure the framework comprises a network where the metal or metal ion is in the corner and a cyano-ligand is a bridge that connects between two metal-corners.

[0007] The details of one or more embodiments of the invention are set forth in the accompanying drawings and the description below. Other features, objects, and advantages of the invention will be apparent from the description and drawings, and from the claims.

DESCRIPTION OF DRAWINGS

[0008] Figure 1 depicts an example of a crystal structure of the organometallic framework.

[0009] Figure 2 shows X-ray powder diffraction of a framework of the disclosure.

[0010] Figure 3 shows an infrared spectrum of a framework of the disclosure.

DETAILED DESCRIPTION

[0011] 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 "a framework" includes a plurality of such frameworks and reference to "the metal ion" includes reference to one or more metal ions and so forth.

[0012] 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 to which this disclosure belongs. Although any methods and reagents similar or equivalent to those described herein can be used in the practice of the disclosed methods and compositions, the exemplary methods and materials are now described.

[0013] All publications mentioned herein 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.

[0014] The disclosure provides organometallic frameworks, compositions comprising such frameworks and uses of the frameworks for catalysis and gas sensing.

[0015] The disclosure provides organometallic frameworks comprising a plurality of metal or metal ions linked by a linking ligand that produces a pi-back

bonding (*i.e.*, pi-back donation) suitable for catalysis or as an electrically conductive material.

[0016] Pi-back bonding is a concept from chemistry, in which electrons move from an atomic orbital on one atom to a π* anti-bonding orbital on another atom or ligand. It is especially common in the organometallic chemistry of transition metals with multi-atomic ligands such as carbon monoxide, ethylene or the nitrosonium cation. Electrons from the metal are used to bond to the ligand, in the process relieving the metal of excess negative charge.

[0017] The electrons are taken from a d-orbital of the metal, and usually placed into an anti-bonding molecular orbital of the ligand, which causes the bond order of that ligand to decrease. This leads to a decrease in the vibrational frequency of the bond, which can be measured using IR spectroscopy. Although the bond-order within the ligand is decreased by this process, the metal-ligand bond order is increased.

[0018] In one embodiment of the disclosure an organometallic framework is provided comprising at least two metal or metal ions linked by a linking ligand, wherein the linking ligand comprises at least one cyano group. In one embodiment, the linking ligand is a diisocyanide. In yet another embodiment, the organometallic framework comprises a general structure $(M\text{-}R_1\text{-}C\equiv N\text{-}R_2\text{-}N\equiv C\text{-}R_1\text{-}M)_n$ wherein R_1 can be absent (*e.g.*, $(M\text{-}C\equiv N\text{-}R_2\text{-}N\equiv C\text{-}M)_n$)and wherein when R_1 is present R_1 comprises an alkyl (*e.g.*, a lower alkyl) and R_2 is an alkyl or cycloalkyl group comprising 1 to 20 carbon atoms, an aryl group comprising 1 to 5 phenyl rings, a fused aromatic group comprising 2 to 6 rings or a porphine group comprising 20 to 80 carbon atoms or a heteroaryl, and n is 1 or more.

[0019] In one embodiment, the organometallic framework of the disclosure comprises a plurality of metal or metal ions (M) separated by a linking ligand comprising $(-R_1-C\equiv N-R_2-N\equiv C-R_1-)_n$ wherein R_1 can be present or absent (*e.g.*, $-C\equiv N-R_2-N\equiv C-)_n$ and wherein when R_1 is present R_1 comprises an alkyl (*e.g.*, a lower alkyl) and R_2 is an alkyl or cycloalkyl group comprising 1 to 20 carbon atoms, an aryl group comprising 1 to 5 phenyl rings, a fused aromatic group comprising 2 to 6 rings or a porphine group comprising 20 to 80 carbon atoms, and n is 1 or more to form a porous framework. Such a porous organometallic framework of the disclosure comprises pores useful for catalysis. In yet another embodiment, the metals of the organometallic framework are homogeneous. In another embodiment, the linking ligands are homogeneous.

[0020] In one embodiment, the organometallic framework of the disclosure comprises a plurality of metal or metal ions separated by a diisocyanide to form a porous framework. In yet another embodiment, the porous organometallic framework of the disclosure comprises pores useful for catalysis. In yet another embodiment, the metals of the organometallic framework are homogeneous. In another embodiment, the diisocyanide linking ligands are homogeneous.

[0021] In the embodiment where the organometallic frameworks of the disclosure comprises a diisocyanide, the framework comprises a pi-back bonding, also called π back donation, suitable for catalysis or as an electrical conductive material.

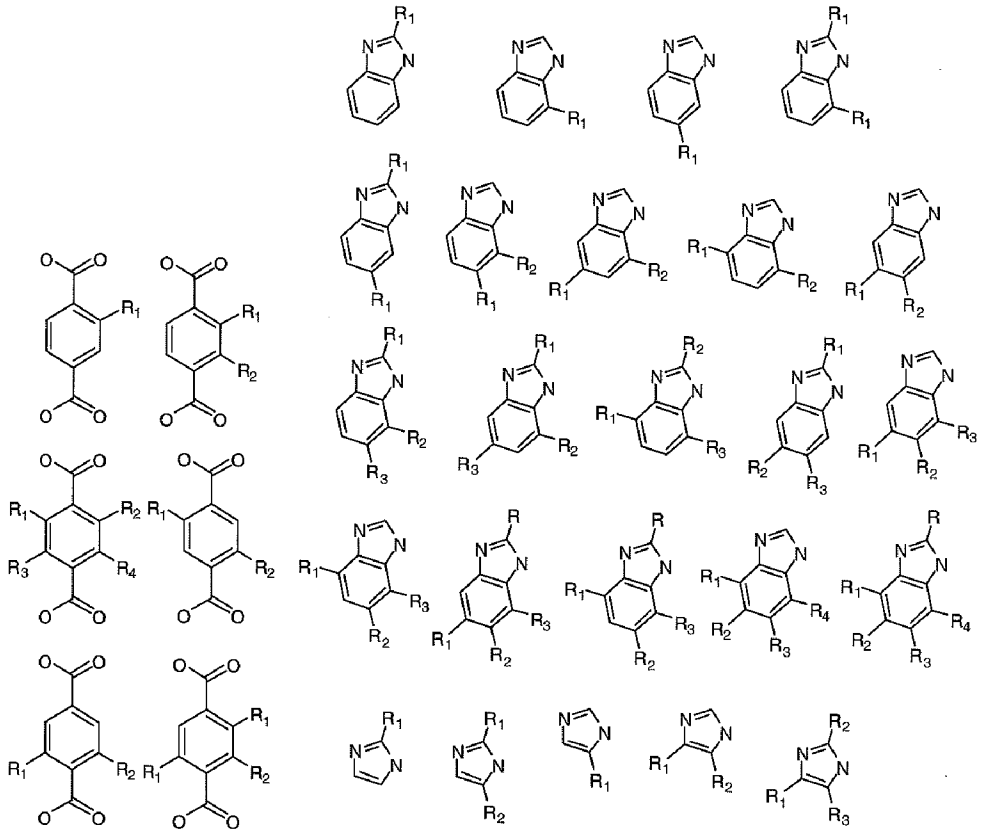
[0022] A "linking moiety" or "linking ligand" refers to a mono-dentate or polydentate compound that bind a transition metal or a plurality of transition metals, respectively. Generally a linking moiety comprises a substructure covalently linked to an alkyl or cycloalkyl

group, comprising 1 to 20 carbon atoms, an aryl group comprising 1 to 5 phenyl rings, or an alkyl or aryl amine comprising alkyl or cycloalkyl groups having from 1 to 20 carbon atoms or aryl groups comprising 1 to 5 phenyl rings, and in which a linking cluster (*e.g.*, a multidentate function groups) are covalently bound to the substructure. A cycloalkyl or aryl linked to a substructure may comprise 1 to 5 rings that comprise either of all carbon or a mixture of carbon with nitrogen, oxygen, sulfur, boron, phosphorus, silicon and/or aluminum atoms making up the ring. The substructure comprises at least one cyano group (*e.g.*, the linking ligand can be a diisocyanide).

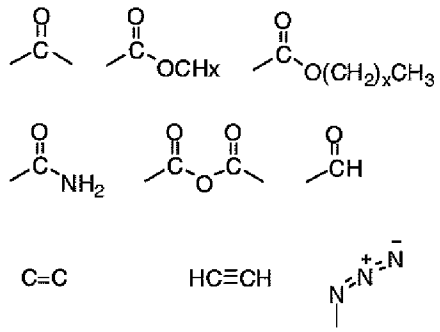
[0023] For example, an organometallic framework of the disclosure can comprise the general structure M-L-M, wherein L is linking moiety comprising a cyano group (*e.g.*, a cyano-linking group substructure) such as, for example, a diisocyanide substructure and M is a transition metal. The substructure may further comprising additional modifying groups useful for modifying pore size or specificity. For example, useful diisocyanides include those selected from 1,3-diisocyanopropane, 1,4-diisocyanobutane, 2,5-dimethyl-2,5-diisocyanohexane, cis-1-isocyano-4(2-isocyanopropyl)cyclohexane, 2,4-diisocyanopentane, 2-alkyl-1,3-diisocyanopropane, 1-isocyanobenzylisocyanamide, 1,2-diisocyanobenzene, 1,4-diisocyanocyclohexane, 1,8-diisocyanonaphthalene, 1,8-diisocyanofluorene, m-isocyanophenyl sulfone, 1,3-diisocyano-2,2,4,4,-tetramethylcyclobutane, 1,3-diisocyano-2-hydroxy propane, 2,4-diisocyanobutane sulfonic acid, 1, 4-diisocyanobenzene, α,α'-diisocyano-m-xylene and any combination thereof.

[0024] As used herein, a line in a chemical formula with an atom on one end and nothing on the other end means that the formula refers to a chemical fragment that is bonded to another entity on the end without an atom attached. Sometimes for emphasis, a wavy line will intersect the line.

[0025] In one aspect, the linking moiety substructure comprises a cyano- group modified to include additional groups selected from any of the following:



wherein R_1, R_2, R_3, R_4 = NH_2, CN, OH, =O, =S, SH, P, Br, CL, I, F,



wherein X=1, 2, or 3. Such additional groups can be used to modify and tune the pore sizes and 3D structure of the framework. Typically, the framework comprises a network where the metal or metal ion is in the corner and a cyano-ligand is a bridge that connects between two metal-corners. For example, isocyanides have similarity in chemistry with carbonyl ligands and many of the organometallic catalysts in use are based on metal-carbonyls, thus the organometallic framework of the disclosure can be used as a heterogenous organometallic catalyst for various catalyses.

[0026] Any number of metal or metal ions can be used in the organometallic framework. For example, the metal or metal ion can comprise a member selected from the group consisting of of Ti, V^{-}, V, Cr, Cr^{2+}, Mn^{-}, Mn, Mn^{+}, Fe^{2-}, Fe, Fe^{2+}, Fe^{3+}, Co^{-}, Co, Co^{2+}, Co^{3+}, Ni, Ni^{2+}, Cu, Cu^{+}, Cu^{2+}, Zn, Zn^{2+}, Zr, Nb, Nb^{-}, Mo, Mo^{2+}, Ru, Ru^{2+}, Ru^{3+}, Rh, Rh^{2+}, Rh^{3+}, Pd, Pd^{2+}, Ag, Ag^{+}, Cd, Cd^{2+}, Hf, Ta^{-}, Ta, W, W^{2+}, Re, Re^{+}, Os, Os^{+}, Os^{2+}, Os^{3+}, Os^{4+}, Ir, Ir^{2+}, Pt, Pt^{2+}, Au, Au^{+}, Au^{3+}; along with the corresponding metal salt counteranion. For example, in a specific embodiment described below, the metal is rhodium and the diisocyanide is 1,4-diisocyanobenzene.

[0027] A named R group will generally have the structure which is recognized in the art as corresponding to R groups having that name. These definitions are

intended to supplement and illustrate, not preclude, the definitions known to those of skill in the art.

[0028] The term "alkyl" is used herein to refer to a branched or unbranched, saturated or unsaturated, monovalent hydrocarbon radical. When the alkyl group has from 1-6 carbon atoms, it is referred to as a "lower alkyl." Suitable alkyl include, for example, methyl, ethyl, n-propyl, 1-propyl, 2-propenyl (or allyl), n-butyl, t-butyl, i-butyl (or 2-methylpropyl), and the like. As used herein, the term encompasses "substituted alkyls."

[0029] "Substituted alkyl" refers to alkyl as just described including one or more functional groups such as lower alkyl, aryl, acyl, halogen (*e.g.*, alkylhalos), hydroxy, amino, alkoxy, alkylamino, acylamino, acyloxy, aryloxy, aryloxyalkyl, mercapto, both saturated and unsaturated cyclic hydrocarbons, heterocycles and the like. These groups may be attached to any carbon of the alkyl moiety.

[0030] The term "aryl" is used herein to refer to an aromatic substituent which may be a single aromatic ring or multiple aromatic rings which are fused together, linked covalently, or linked to a common group such as a methylene or ethylene moiety. The common linking group may also be a carbonyl as in benzophenone. The aromatic ring(s) may include substituted or unsubstituted phenyl, naphthyl, biphenyl, diphenylmethyl and benzophenone among others.

[0031] "Substituted aryl" refers to aryl as just described including one or more functional groups such as lower alkyl, acyl, halogen, alkylhalos, hydroxy, amino, alkoxy, alkylamino, acylamino, acyloxy, mercapto and both saturated and unsaturated cyclic hydrocarbons which are fused to the aromatic ring(s), linked covalently or

linked to a common group such as a methylene or ethylene moiety.

[0032] The term "acyl" is used to describe a ketone substituent, --C(O)R, where R is alkyl or substituted alkyl, aryl or substituted aryl as defined herein.

[0033] The term "amino" is used herein to refer to the group --NRR', where R and R' may independently be hydrogen, lower alkyl, substituted lower alkyl, aryl, substituted aryl or acyl. When an amino group is bonded to a metal through the nitrogen atom, it is referred to as an "amido" bond.

[0034] The term "alkoxy" is used herein to refer to the --OR group, where R is an alkyl, substituted lower alkyl, aryl, substituted aryl, wherein the substituted alkyl, aryl, and substituted aryl groups are as described herein. Suitable alkoxy radicals include, for example, methoxy, ethoxy, phenoxy, substituted phenoxy, benzyloxy, phenethyloxy, t-butoxy, etc.

[0035] As used herein, the term "mercapto" defines moieties of the general structure R--S--R' wherein R and R' are the same or different and are alkyl, aryl or heterocyclic as described herein.

[0036] The term "saturated cyclic hydrocarbon" denotes groups such as the cyclopropyl, cyclobutyl, cyclopentyl, etc., and substituted analogues of these structures.

[0037] The term "unsaturated cyclic hydrocarbon" is used to describe a monovalent nonaromatic group with at least one double bond, such as cyclopentene, cyclohexene, etc. and substituted analogues thereof.

[0038] The term "heteroaryl" as used herein refers to aromatic rings in which one or more carbon atoms of the aromatic ring(s) are substituted by a heteroatom such as nitrogen, oxygen or sulfur. Heteroaryl refers to structures which may be a single aromatic ring, multiple

aromatic ring(s), or one or more aromatic rings coupled to one or more nonaromatic ring(s). In structures having multiple rings, the rings can be fused together, linked covalently, or linked to a common group such as a methylene or ethylene moiety. The common linking group may also be a carbonyl as in phenyl pyridyl ketone. As used herein, rings such as thiophene, pyridine, isoxazole, phthalimide, pyrazole, indole, furan, etc. or benzo-fused analogues of these rings are defined by the term "heteroaryl."

[0039] "Heteroarylalkyl" defines a subset of "alkyl" wherein the heteroaryl group is attached through an alkyl group as defined herein.

[0040] "Substituted heteroaryl" refers to heteroaryl as just described wherein the heteroaryl nucleus is substituted with one or more functional groups such as lower alkyl, acyl, halogen, alkylhalos (*e.g.*, CF_3), hydroxy, amino, alkoxy, alkylamino, acylamino, acyloxy, mercapto, etc. Thus, substituted analogues of heteroaromatic rings such as thiophene, pyridine, isoxazole, phthalimide, pyrazole, indole, furan, etc. or benzo-fused analogues of these rings are defined by the term "substituted heteroaryl."

[0041] "Substituted heteroarylalkyl" refers to a subset of "substituted alkyls" as described above in which an alkyl group, as defined herein, links the heteroaryl group to the nucleus.

[0042] The term "heterocyclic" is used herein to describe a monovalent saturated or unsaturated nonaromatic group having a single ring or multiple condensed rings from 1-12 carbon atoms and from 1-4 heteroatoms selected from nitrogen, phosphorous sulfur or oxygen within the ring. Such heterocycles are, for

example, tetrahydrofuran, morpholine, piperidine, pyrrolidine, etc.

[0043] The term "substituted heterocyclic" as used herein describes a subset of "heterocyclics" wherein the heterocycle nucleus is substituted with one or more functional groups such as alkyl, acyl, halogen, alkylhalos, hydroxy, amino, alkoxy, alkylamino, acylamino, acyloxy, mercapto, etc.

[0044] As used herein, the term "catalyst" refers to a compound which speeds a chemical reaction or causes it to occur. The catalysts of the disclosure are formally organometallic compounds.

[0045] Heterogeneous catalysis refers to the process wherein the catalyst is in a different phase relative to the reactants. Typically in heterogeneous catalysis one or more of the reactants must diffuse to the catalyst surface and adsorb onto it. After reaction, the products must desorb from the surface and diffuse away from the solid surface. Porous frameworks, for example, have found utility as catalysts because their surface areas may be in excess of 1000 m^2/g, which increases the probability that a reactant molecule in solution will come in contact with the catalyst surface and adsorb. If diffusion rates are not taken into account, the reaction rates for various reactions on surfaces depend solely on the rate constants and reactant concentrations. Accordingly, catalysis may be heterogeneous or homogeneous. It will be appreciated by those skilled in the art of catalysis that the aforementioned process conditions may vary depending on the particular reaction, the desired product, the equipment used, and the like.

[0046] Classically, compounds having bonds between one or more metal atoms and one or more carbon atoms of an organic group are defined as "organometallic compounds".

For the purposes of this application, "organometallic" is defined to include all ancillary ligand stabilized metallic complexes regardless of presence or absence of a metal-carbon bond.

[0047] The organometallic frameworks of the disclosure are suitable catalyst materials due to their pore size and/or modification that render the designable for specific catalytic reactions. For example, the framework comprising a cyano- substructure modified with a particular R-group as described above can used to link metal or metal ions, wherein the pores of the framework comprise R-groups that extend into the pores rendering them size or charge designed for a particular substrate.

[0048] The disclosure further provides sensors comprising an organometallic framework of the disclosure. Such sensors include, for example, a porous sensor material comprising a framework having a metal or metal ion linked to at least one other metal ion wherein the linking ligand provides pi-back bonding, wherein the framework is disposed between conductive leads and undergoes a change in resistance when the porous material adsorbs or absorbs an analyte. The change in the electrical resistance between the leads can be related to the sorption of an analyte to the porous sensor material. The materials of the disclosure are particularly suited to electrical conductivity measurements due to the pi-back bonding caused by the linking ligands of the disclosure. For example, such a sensor will comprise a material having the general structure In yet another embodiment, the organometallic framework comprises a general structure $(M\text{-}R_1\text{-}C{\equiv}N\text{-}R_2\text{-}N{\equiv}C\text{-}R_1\text{-}M)_n$ wherein R_1 can be absent (*e.g.*, $(M\text{-}C{\equiv}N\text{-}R_2\text{-}N{\equiv}C\text{-}M)_n$)and wherein when R_1 is present R_1 comprises an alkyl (*e.g.*, a lower alkyl) and R_2 is an alkyl or cycloalkyl group comprising 1 to 20 carbon

atoms, an aryl group comprising 1 to 5 phenyl rings, a fused aromatic group comprising 2 to 6 rings or a porphine group comprising 20 to 80 carbon atoms, and n is 1 or more.

[0049] Another type of sensor includes, for example, a crystalline colloidal array (CCA) as disclosed in U.S. Pat. No. 5,854,078 (the disclosure of which is incorporated herein by reference). Such sensors undergo a volume change in response to a specific analyte species. As the sensors are modulated in size the lattice spacing of the CCA embedded therein can change as well. The light diffraction, therefore, indicates the presence or absence of the analyte that causes the sensing material to change. Yet another type of sensor includes those wherein the sensors produce a spectral recognition patterns when an analyte is present. In this embodiment the sensor material changes in optical properties, whether by density or through a change in excitation or absorbance wavelengths.

[0050] Any number of sensor combinations comprising a porous framework of the disclosure or any number of transduction modalities can be used. For example, each individual sensor can provide a signal (*e.g.*, a transduced signal indicative of the presence of an analyte) or a plurality of signals from an array of sensors can be used to identify an analyte of interest in a fluid. The signal transduction mechanism through which the analyte or molecule produces a signal is potentially quite broad. These include arrays of surface acoustic wave devices, quartz crystal micro-balances, dye-coated fiber optics, resistometric, electrochemical, and others modalities readily identifiable to those skilled in the art. Accordingly, transduction mechanisms include, for example optical, electrical, and/or resonance.

[0051] The diversity of the sensors of the disclosure comprising a metal and a ligand having a cyano group (*e.g.*, a diisocyanide ligand) that are useful in obtaining libraries for various catalytic process or sensor systems.

[0052] In one embodiment, the disclosure provides a sensing platform based on using a sensitive layer made from organometallic framework of the disclosure. The framework is a porous nanostructure that readily adsorb/desorb an analyte which can be sensed via various transducing methods.

[0053] The organometallic framework of the disclosure has the properties that the pores can be tuned to match the prerequisites for a given analyte or substrate based upon modification of the R groups of the ligand. Tuneable properties include, but are not limited to, pore size, pore volume, polarity, magnetic properties, chemical environment (*e.g.*, functional groups, metal coordination sites), and geometry of binding sites (*e.g.*, introducing pockets for the analyte and the like).

[0054] An organometallic material of the disclosure can be used as a sensing material either alone or as a combination with inorganic materials, organic materials, electrical conductive materials (*e.g.*, inorganic conductors or organic conductors), polymers (*e.g.*, conductive or non-conductive polymers). For example, an organometallic framework of the disclosure can be used in conductometric sensor wherein transducers such as interdigtial electrode transducers can be used or optical transducers such as those comprising an optical path with a source and detector separated by the sensing material of the disclosure are used to sense an analyte.

[0055] The disclosure provides a class of porous frameworks that are based on the metal-carbon bond to exploit its application in heterogeneous organometallic catalysis (C-C coupling reactions, hydrogenation, carbonylation, polymerization, and the like, as well as gas sensing.

[0056] A two-dimensional rhodium-based conductive coordination polymer has been developed that shows electrical conductivity. Furthermore a molybdenum and 1,4-diisocyanobenzene has been generated. The organometallic framework is based on a network where the metal (or metal ion) is at the corner, and a diisocyanide ligand is a bridge that connects between two metal-corners. Isocyanides have much similarity in chemistry with a carbonyl ligand, and many of the organometallic catalysts used today are based on metal-carbonyls. Thus the organometallic framework can be used as a heterogeneous organometallic catalyst for various catalyses.

[0057] Metal-isocyanide bonds carry out pi-back-bonding; hence when the isocyanide is connected to a delocalized system the electronic communication from the metal-link-metal is possible. This phenomenon causes an electric conductivity which is useful in gas sensors.

[0058] The organometallic frameworks of the disclosure can be used as catalysts and gas sensors for specific purposes by designing the framework with specific metals or metal ions and/or linking ligands having function groups useful for defining the pore size, charge and characteristics.

[0059] Advantages of the organometallic framework of the disclosures include the use as heterogeneous catalysts having high surface area thereby increasing the catalytic rate and the products are easily recovered. In

addition the gas-sensing embodiments provide for designing sensors with specificity suing appropriate metal and ligands.

[0060] The organometallic frameworks of the disclosure can be synthesized by mixing the solutions that contain the metal precursor and the ligand in an inert atmosphere. The preparation of the frameworks are typically carried out in a non-aqueous system. The solvent may be polar or nonpolar as the case may be. The solvent may be the templating agent or the optional ligand containing monodentate function group. Examples of solvents include n-alkanes, such as pentane, hexane, benzene, toluene, xylene, chlorobenzene, nitrobenzene, cyanobenzene, aniline, naphthalene, napthas, n-alcohols such as methanol, ethanol n-propanol, isopropanol, acetone, 1,2, dichloroethane, methylene chloride, chloroform, carbon tetrachloride, diethyl ether, 1,4 dioxane, tetrahydrofuran, dimethylformamide, dimethylsulfoxide, N-methlpyrollidone, dimethylacetamide, diethylformamide, thiophene, pyridine, ethanolamine, triethylamine, ethylenediamine, and the like. Those of skill in the art can readily determine an appropriate solvent based on the starting reactants and the choice of solvent is not belived to be critical in obtaining the organometallic framework materials of the disclosure.

[0061] The templating agents employed in the disclosure are added to the reaction mixture for the purpose of occupying the pores in the resulting crystalline organometallic framework materials. Examples of possible templating species are: (a) alkyl amines and their corresponding alkyl ammonium salts, containing linear, branched or cyclic aliphatic groups having from 1-20 carbon atoms; (b) aryl amines and their corresponding aryl ammonium salts having from 1 to 5

phenyl rings; (c) alkyl phosphonium salts, containing linear, branched or cyclic aliphatic groups having from 1 to 20 carbon atoms; (d) aryl phosphonium salts, having 1 to 5 phenyl rings; (e) alkyl organic acids and their corresponding salts, containing linear, branched or cyclic aliphatic groups, having from 1 to 20 carbon atoms; (f) aryl organic acids and their corresponding salts, having 1 to 5 phenyl rings; (g) aliphatic alcohols, containing linear, branched or cyclic aliphatic groups, having from 1 to 20 carbon atoms; and (h) aryl alcohols having from 1 to 5 phenyl rings.

[0062] The crystallization step is carried out by layering the metal precursor solution and the ligand solution to cause slow layer diffusion, using a temperature gradient or leaving the metal-ligand containing solution at room temperature or in isothermal oven for up to 200 C.

[0063] Figure 1 depicts an example of a crystal structure of the organometallic framework. Figure 2 shows X-ray powder diffraction of a framework of the disclosure. Figure 3 shows an infrared spectrum of a framework of the disclosure.

[0064] A number of embodiments of the invention have been described. Nevertheless, it will be understood that various modifications may be made without departing from the spirit and scope of the invention. Accordingly, other embodiments are within the scope of the following claims.

WHAT IS CLAIMED IS:

1. An organometallic framework comprising the general structure:

M-L-M, wherein L is a cyano- substructure and M is a transition metal.

2. The organometallic framework of claim 1, wherein the framework comprises a cage.

3. The organometallic framework of claim 2, wherein the cage comprises at least 4 metal atoms.

4. The organometallic framework of claim 2, wherein the cyano- substructure comprises a diisocyanide of the formula $(CN)_2R$ where R is an organic divalent group containing 2 to 20 carbon atoms.

5. The organometallic framework of claim 4, wherein R is selected from alkylene, arylene, alkarylene, cycloalkylene, alkylcyoalkylene or alkarylene.

6. The organometallic framework of claim 1, wherein cyano- substructure is a diisocyanide.

7. The organometallic framework of claim 6, wherein the diisocyanide is selected from the group consisting of 1,3-diisocyanopropane, 1,4-diisocyanobutane, 2,5-dimethyl-2,5-diisocyanohexane, cis-1-isocyano-4(2-isocyanopropyl)cyclohexane, 2,4-diisocyanopentane, 2-alkyl-1,3-diisocyanopropane, 1-isocyanobenzylisocyanamide, 1,2-diisocyanobenzene, 1,4-diisocyanocyclohexane, 1,8-diisocyanonaphthalene, 1,8-diisocyanofluorene, m-isocyanophenyl sulfone, 1,3-

diisocyano-2,2,4,4,-tetramethylcyclobutane, 1,3-diisocyano-2-hydroxy propane, 2,4-diisocyanobutane sulfonic acid, 1, 4-diisocyanobenzene, α,α'-diisocyano-m-xylene and any combination thereof.

8. The organometallic framework of claim 1, wherein the framework comprise different metals.

9. The organometallic framework of claim 6, wherein the framework comprises a heterogeneous combination of diisocyanide ligands.

10. The organometallic framework of claim 1, wherein the pi-back-bonding is delocalized between metal atoms.

11. The organometallic framework of claim 6, wherein the metal is rhodium and the diisocyanide is 1,4-diisocyanobenzene.

12. An organometallic framework comprising a metal bridging a plurality of organic links, each organic link comprising a cyano-group substructure covalently bound to (i) an alkyl or cycloalkyl group comprising 1 to 20 carbon atoms, (ii) an aryl group comprising 1 to 5 phenyl rings, and/or (iii) a fused aromatic group comprising 2 to 6 rings or a porphine group comprising 20 to 80 carbon atoms.

13. The organometallic framework of claim 12, wherein the organic link comprises a cycloalkyl or aryl substrature comprising 1 to 5 rings that comprise either all carbon or a mixture of carbon with nitrogen, oxygen,

sulfur, boron, phosphrous, silicon and aluminum atoms making up the ring.

14. The organometallic framework of any of claims 1-12, wherein the metal is selected from the group consisting of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Lr, Rf, Db, Sg, Bh, Hs, Mt, Ds, Rg and Uub.

15. An organometallic framework comprising a plurality of metal or metal ions linked to one another comprising a general structure:

$$-(M\text{-}R_1\text{-}C{\equiv}N\text{-}C\text{-}R_2C\text{-}N{\equiv}C\text{-}R_1)-_n$$

wherein M is the metal or metal ion, R_1 when present is an alkyl or substituted alkyl, R_2 is a an alkyl or cycloalkyl group comprising 1 to 20 carbon atoms, an aryl group comprising 1 to 5 phenyl rings, a fused aromatic group comprising 2 to 6 rings or a porphine group comprising 20 to 80 carbon atoms.

16. A sensor having a region of an organometallic framework of any one of claims 1-13 or 15.

17. A sensor having a region of an organometallic framework of claim 14.

18. A conductive electrical circuit comprising an organometallic framework of any one of claims 1-13 or 15.

18. A method for sensing a gas comprising measuring a change in the electrical conductivity of the sensor of claim 16 in the presence and absence of the gas, wherein a change is indicative of the presence of the gas.

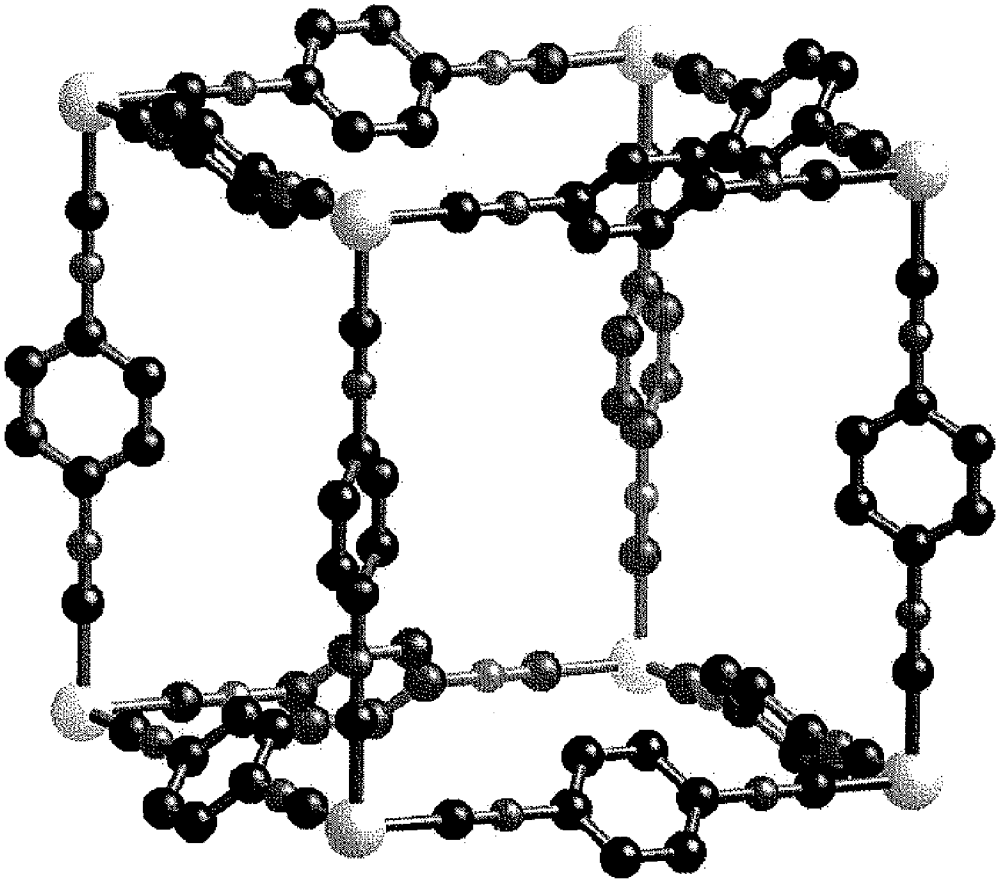


FIGURE 1

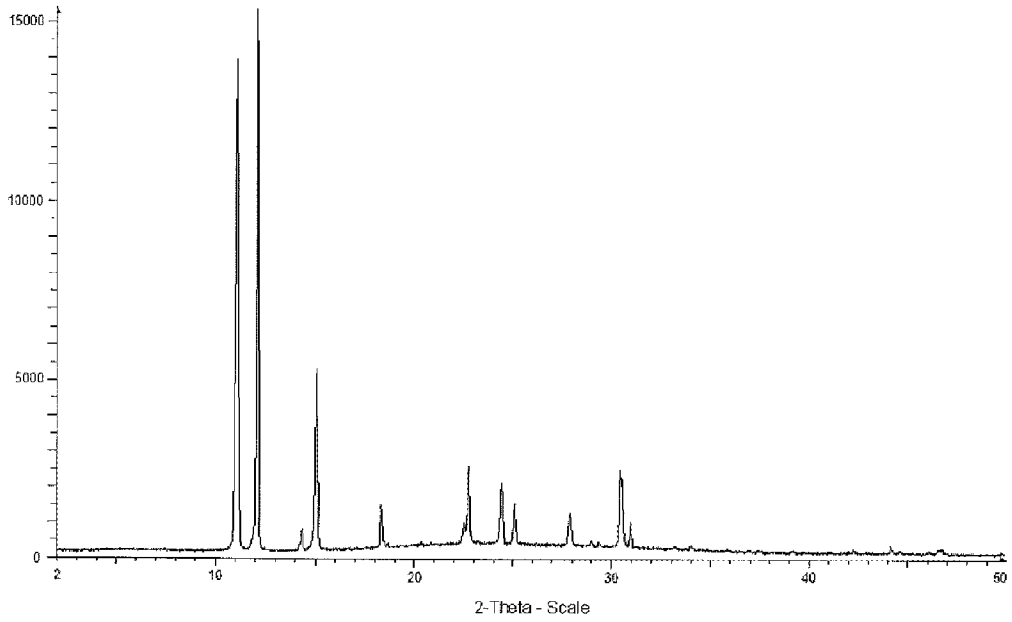


FIGURE 2

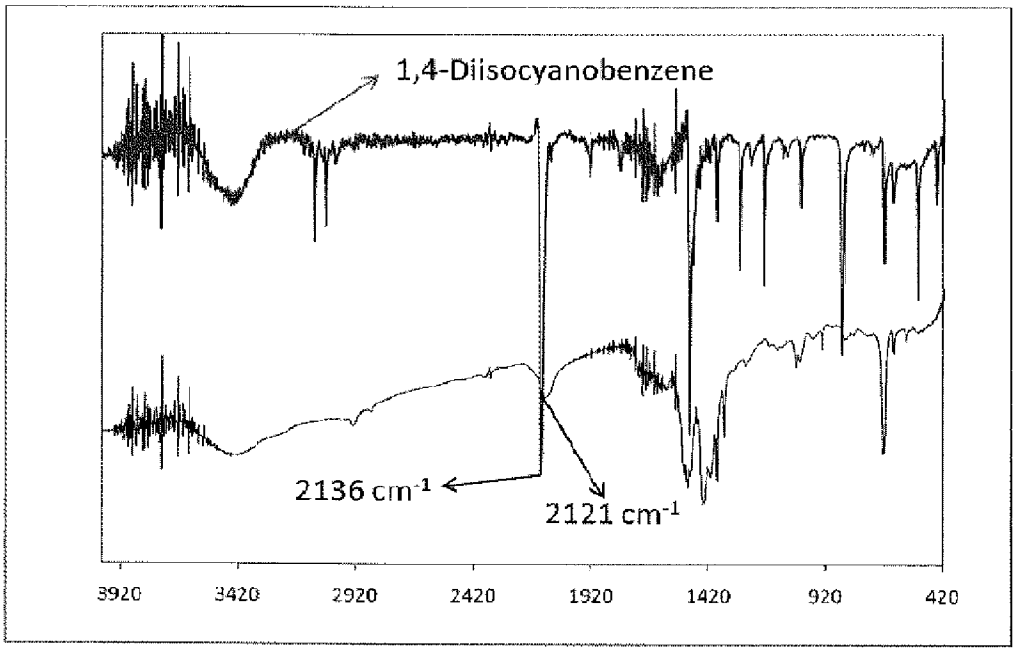


FIGURE 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/021201

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J31/16

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

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 practical, search terms used)
EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MÜLLER-BUSCHBAUM ET AL: "The first dinitrile frameworks of the rare earth elements: [LnCl3(1,4-Ph(CN)2] and [Ln2Cl6(1,4Ph(CN)2], Ln = Sm, Gd, Tb, Y;Access to novel metal-organic frameworks by solvent free synthesis in molten 1,4-benzodinitril" INORGANIC CHEMISTRY, vol. 47, no. 21, 10 August 2008 (2008-08-10), page 10141, XP002574067 chart 1, figures 4,5; table 1 ----- -/--	1-15

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* 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 document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or 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.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 March 2010	27/04/2010

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Klaes, Daphne

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/021201

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CIANI ET AL: "Nanoporous three-dimensional networks topologically related to cooperite from the self-assembly of copper(I)centres and the square-planar building block 1,2,4,5-tetracyanobenzene" NEW J.CHEM, vol. 23, no. 23, 31 December 1999 (1999-12-31), pages 397-401, XP002574068 figures 2,3,4	1-15
X	JACONSEN ET AL: "Synthesis and structural characterization of the one dimensional polymers [Rh2(OAc)4(NCPhCN)S, S = CH3COCH3, CH3OH, C2H5OH, C4H8O and C6H6" POLYHEDRON, vol. 17, no. 23-24, 31 December 1998 (1998-12-31), pages 4079-4089, XP009131207 abstract; figures 1-5	1-15
X	DE 10 2005 023856 A1 (BASF AG [DE]) 30 November 2006 (2006-11-30) paragraph [0147]; claim 11	1-19

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2010/021201

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		EP 1888817 A2	20-02-2008
		WO 2006125761 A2	30-11-2006
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		KR 20080021037 A	06-03-2008
		US 2008214806 A1	04-09-2008