



(51) International Patent Classification:

B01J 20/22 (2006.01) F24F 3/14 (2006.01)

(21) International Application Number:

PCT/US2024/025444

(22) International Filing Date:

19 April 2024 (19.04.2024)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

63/509,196 20 June 2023 (20.06.2023) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA,

NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report (Rule 48.2(g))

(54) Title: SORBENTS FOR THE TUNABLE CAPTURE AND RELEASE OF WATER AND RELATED METHODS

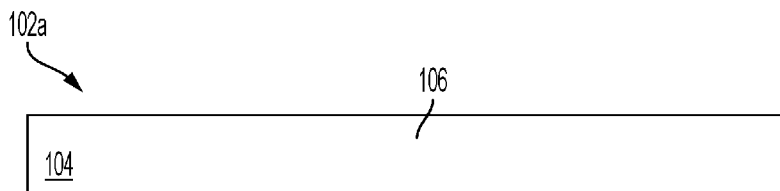


FIG. 1A

(57) Abstract: Compositions, articles, and methods related to sorbents for the tunable capture and release of a target species (e.g., water) are generally described.



– 1 –

SORBENTS FOR THE TUNABLE CAPTURE AND RELEASE OF WATER AND RELATED METHODS

RELATED APPLICATIONS

5 This application claims priority under 35 U.S.C. § 119(e) to U.S. Provisional Patent Application No. 63/509,196, filed June 20, 2023, and entitled “SORBENTS FOR THE TUNABLE CAPTURE AND RELEASE OF WATER,” which is incorporated herein by reference in its entirety for all purposes.

GOVERNMENT SPONSORSHIP

10 This invention was made with government support under DMR2105495 awarded by the National Science Foundation. The government has certain rights in the invention.

TECHNICAL FIELD

15 Compositions, articles, and methods related to sorbents for the tunable capture and release of a target species (e.g., water) are generally described.

BACKGROUND

20 Materials capable of selective uptake and release of atmospheric water can facilitate diverse applications ranging from harvesting of water in desert air and direct humidity control to the development of thermal batteries and more efficient air conditioning. Designing ideal water sorbents for each of these applications necessitates optimization of several key parameters including stability over cycling, working capacity, and relative humidity of pore condensation. Identifying a material possessing
25 all these properties, while also derived from readily accessible feedstocks to facilitate large-scale deployment, remains an even greater challenge.

SUMMARY

30 Compositions, articles, and methods related to sorbents for the tunable capture and release of a target species (e.g., water) are generally described.

– 2 –

This Summary introduces a selection of concepts in simplified form that are described further below in the Detailed Description. This Summary neither identifies key or essential features, nor limits the scope, of the claimed subject matter.

According to certain embodiments, a composition is described. In some
 5 embodiments, the composition comprises a metal-organic framework of the form $[(M_xZn_{1-x})_5(X_y(OAc)_{1-y})_4(\text{ligand})_3]$, wherein: M is a divalent metal cation; X is a monovalent anion; OAc is acetate; ligand is a dianionic nitrogen-containing heterocyclic compound; x is greater than 0 and less than 1; and y is: (i) greater than 0 and less than or equal to 0.2; or (ii) greater than or equal to 0.4 and less than 1.

10 In some embodiments, a composition is described, the composition comprising a metal-organic framework of the form $[(Zn)_5(X_y(OAc)_{1-y})_4(\text{ligand})_3]$, wherein: X is a monovalent anion; OAc is acetate; ligand is a dianionic nitrogen-containing heterocyclic compound; and y is greater than or equal to 0.8 and less than 1.

According to some embodiments, a method is described. In certain
 15 embodiments, the method comprises exposing a composition to a target species such that the metal-organic framework adsorbs the target species. In some embodiments, the composition comprises a metal-organic framework of the form $[(M_xZn_{1-x})_5(X_y(OAc)_{1-y})_4(\text{ligand})_3]$, wherein: M is a divalent metal cation; X is a monovalent anion; OAc is acetate; ligand is a dianionic nitrogen-containing heterocyclic compound; x is greater
 20 than 0 and less than 1; and y is: (i) greater than 0 and less than or equal to 0.2; or (ii) greater than or equal to 0.4 and less than 1. In certain embodiments, the composition comprises a metal-organic framework of the form $[(Zn)_5(X_y(OAc)_{1-y})_4(\text{ligand})_3]$, wherein: X is a monovalent anion; OAc is acetate; ligand is a dianionic nitrogen-containing heterocyclic compound; and y is greater than or equal to 0.8 and less than 1.

25 In certain embodiments, a method is described, the method comprising exposing a compound of the form MX^1_2 to a first metal-organic framework of the form $[Zn_5X^2_4(\text{ligand})_3]$, thereby forming a second metal-organic framework of the form $[(M_xZn_{1-x})_5(X^1_yX^2_{1-y})_4(\text{ligand})_3]$, wherein: M is a divalent metal cation; X^1 and X^2 are different, and each of X^1 and X^2 is a monovalent anion; ligand is a dianionic nitrogen-
 30 containing heterocyclic compound; and x is less than y.

– 3 –

One aspect of the disclosure herein is a metal-organic framework (MOF) comprising $M_5X_4(\text{bibta})_3$, in which:

- a. M is a cation such as Zn, Co, or Ni;
- b. X is a common anion such as Cl or OAc; and
- 5 c. bibta comprises 1H,1H'-5,5'-bibenzo[d][1,2,3]triazole.

In one embodiment of the disclosed MOF, the MOF comprises $(\text{Ni}_x\text{Zn}_{1-x})_5(\text{Cl}_y\text{OAc}_{1-y})_4(\text{bibta})_3$, wherein x is 0.22-0.74 and y is 0.41-0.95.

In one embodiment of the disclosed MOF, the MOF comprises $\text{Ni}_{3.5}\text{Zn}_{1.5}(\text{OAc})_{3.8}\text{Cl}_{0.2}(\text{bibta})_3$.

- 10 In one embodiment of the disclosed MOF, the MOF has a relative humidity at half-capacity (α) of 27-70%.

In one embodiment of the disclosed MOF, the MOF has water uptake capacity above 0.65 g H₂O/g MOF.

- 15 One aspect of the disclosure herein is a method of producing the disclosed MOF, the method comprising:

- a. reacting 1H,1H'-5,5'-bibenzo[d][1,2,3]triazole (bibta) with $\text{Zn}(\text{OAc})_2$ to produce $\text{Zn}_5(\text{OAc})_4(\text{bibta})_3$;
- b. reacting $\text{Zn}_5(\text{OAc})_4(\text{bibta})_3$ with: (i) $\text{Ni}(\text{OAc})_2$; or (ii) NiCl_2 and LiOAc to produce $(\text{Ni}_x\text{Zn}_{1-x})_5(\text{Cl}_y\text{OAc}_{1-y})_4(\text{bibta})_3$.

- 20 One aspect of the disclosure is a method of harvesting atmospheric water, the method comprising interacting atmospheric air with the disclosed MOF.

One aspect of the disclosure is a method of humidity control, the method comprising interacting atmospheric air with the disclosed MOF.

- 25 The following Detailed Description references the accompanying drawings which form a part this application, and which show, by way of illustration, specific example implementations. Other implementations may be made without departing from the scope of the disclosure. Other advantages and novel features of the present disclosure will become apparent from the following Detailed Description of various non-limiting embodiments of the disclosure when considered in conjunction with the accompanying figures. In cases where the present specification and a document incorporated by
- 30

– 4 –

reference include conflicting and/or inconsistent disclosure, the present specification shall control.

BRIEF DESCRIPTION OF THE DRAWINGS

5 Non-limiting embodiments of the present disclosure will be described by way of example with reference to the accompanying figures, which are schematic and are not intended to be drawn to scale unless otherwise indicated. In the figures, each identical or nearly identical component illustrated is typically represented by a single numeral. For purposes of clarity, not every component is labeled in every figure, nor is every
10 component of each embodiment of the disclosure shown where illustration is not necessary to allow those of ordinary skill in the art to understand the disclosure. In the figures:

FIG. 1A shows a cross-sectional schematic diagram of a composition comprising a metal-organic framework in the form of a film, in accordance with certain
15 embodiments.

FIG. 1B shows a cross-sectional schematic diagram of a composition comprising a metal-organic framework in the form of a plurality of particles, in accordance with certain embodiments.

FIG. 2 shows a cross-sectional schematic diagram of an article comprising a
20 composition, in accordance with certain embodiments.

FIG. 3A shows a model unit cell of $M'M_4X_4(\text{bibta})_3$, in accordance with certain embodiments.

FIG. 3B shows a structure and synthetic schematic of an organic linker, in accordance with certain embodiments.

25 FIG. 3C shows a Kuratowski-cluster secondary building unit (SBU) and a summary of synthetic modifications, in accordance with certain embodiments.

FIG. 4 shows a synthesis of CFA-1 and conditions for post-synthetic modification, in accordance with certain embodiments.

30 FIG. 5A shows nitrogen adsorption isotherms measured at 77 K, in accordance with certain embodiments.

– 5 –

FIG. 5B shows powder X-ray diffraction (PXRD) data for nickel-incorporated MOFs, in accordance with certain embodiments.

FIG. 6 shows water adsorption isotherms at 25 °C, in accordance with certain embodiments.

5 FIG. 7 shows synthesized MOFs and water sorption properties, in accordance with certain embodiments.

FIG. 8A shows nitrogen adsorption isotherms of CFA-1 before and after water sorption, in accordance with certain embodiments.

FIG. 8B shows nitrogen adsorption isotherms of Ni(60%)-CFA-1
10 $[(\text{Ni}_{0.6}\text{Zn}_{0.4})_5(\text{Cl}_{0.95}\text{OAc}_{0.05})_4(\text{bibta})_3]$ before and after water sorption, in accordance with certain embodiments.

FIG. 9 shows cycling data for Ni(60%)-CFA-1
 $(((\text{Ni}_{0.6}\text{Zn}_{0.4})_5(\text{Cl}_{0.95}\text{OAc}_{0.05})_4(\text{bibta})_3))$, in accordance with certain embodiments.

FIG. 10A shows diffuse reflectance infrared Fourier transform spectroscopy
15 (DRIFTS) studies of water dosing in Ni(60%)-CFA-1
 $[(\text{Ni}_{0.6}\text{Zn}_{0.4})_5(\text{Cl}_{0.95}\text{OAc}_{0.05})_4(\text{bibta})_3]$, in accordance with certain embodiments.

FIG. 10B shows exothermicity of binding as a function of water adsorbed in Ni(60%)-CFA-1 $[(\text{Ni}_{0.6}\text{Zn}_{0.4})_5(\text{Cl}_{0.95}\text{OAc}_{0.05})_4(\text{bibta})_3]$, in accordance with certain
20 embodiments.

FIG. 11 shows a comparison of MOFs with reversible water sorption below $\alpha = 30$, in accordance with certain embodiments.

FIG. 12 shows a view of $\text{M}'\text{M}_4\text{X}_4(\text{bibta})_3$ down the c-axis shown in FIG. 1, in accordance with certain embodiments.

FIG. 13 shows a plot of values for x and y for $[(\text{Ni}_x\text{Zn}_{1-x})_5(\text{Cl}_y\text{OAc}_{1-y})_4(\text{bibta})_3]$,
25 wherein the phase space is α (the relative humidity for pore condensation), the circles represent experimentally measured values, and the solid lines are best fits, in accordance with certain embodiments.

FIG. 14 shows DRIFTS studies of water dosing in $(\text{Zn})_5(\text{OAc})_4(\text{bibta})_3$, in accordance with certain embodiments.

– 6 –

FIG. 15 shows integrated difference spectra for Ni(60%)-CFA-1 $[(\text{Ni}_{0.6}\text{Zn}_{0.4})_5(\text{Cl}_{0.95}\text{OAc}_{0.05})_4(\text{bibta})_3]$ and $(\text{Zn})_5(\text{OAc})_4(\text{bibta})_3$, in accordance with certain embodiments.

FIG. 16 shows the isosteric enthalpy for adsorption of water in Ni(60%)-CFA-1 $[(\text{Ni}_{0.6}\text{Zn}_{0.4})_5(\text{Cl}_{0.95}\text{OAc}_{0.05})_4(\text{bibta})_3]$, in accordance with certain embodiments.

FIG. 17A shows cycling data for $[\text{Ni}_{0.74}\text{Zn}_{0.26})_5(\text{Cl}_{0.92}\text{OAc}_{0.08})_4(\text{bibta})_3]$ between 0 and 35% relative humidity at 25 °C over 450 cycles, with reactivation at 70 °C after 113 cycles, in accordance with certain embodiments.

FIG. 17B shows a magnification of the first five cycles shown in FIG. 17A, in accordance with certain embodiments.

FIG. 17C shows the working capacity over the 450 cycles shown in FIG. 17A along with a linear fit, in accordance with certain embodiments.

DETAILED DESCRIPTION

Compositions, articles, and methods related to sorbents for the tunable capture and release of a target species (e.g., water) are generally described. According to some embodiments, a composition comprises a metal-organic framework that efficiently adsorbs and/or desorbs water across a range of relative humidities. In certain embodiments, the metal-organic framework is a modified version of a zinc metal-organic framework scaffold of the form $[\text{Zn}_5(\text{X}')_4(\text{ligand})_3]$, wherein X' is an auxiliary (e.g., non-structural) ligand, such as acetate, and ligand is a structural ligand, such as a nitrogen-containing heterocyclic compound. According to some embodiments, the metal-organic framework is configured such that at least a portion of the auxiliary ligands (e.g., acetate) have been exchanged with a different auxiliary ligand (e.g., chloride) and/or at least a portion of the zinc atoms have been exchanged with a different metal atom (e.g., nickel and/or cobalt). Controlling the identity of the auxiliary (e.g., non-structural) ligands and/or the identity of the metal atoms modulates the water uptake capacity and/or the relative humidity at half-capacity of the metal-organic framework, thereby facilitating the use of a single metal-organic framework platform for a diverse range of water sorption and/or desorption applications.

– 7 –

According to certain embodiments, the metal-organic framework is of the form $[(M_xZn_{1-x})_5(X^1_yX^2_{1-y})_4(\text{ligand})_3]$, wherein: M is a divalent metal cation (e.g., nickel and/or cobalt); X^1 and X^2 are different; each of X^1 and X^2 is a monovalent anion (e.g., X^1 is chloride and X^2 is acetate); ligand is a dianionic nitrogen-containing heterocyclic compound; x is greater than 1 and less than 0; and y is greater than 1 and less than 0. In some embodiments, the metal-organic framework is capable of adsorbing and/or desorbing water with an advantageously high uptake capacity (e.g., greater than or equal to 0.7 g H₂O per gram of metal-organic framework) over a range of relative humidities, including low relative humidities (e.g., less than or equal to 30% RH). In accordance with certain embodiments, the metal-organic framework is hydrolytically stable and capable of extended adsorption-desorption cycling without a substantial reduction in water uptake capacity (e.g., a less than or equal to 5% decrease in water uptake capacity after at least 100 adsorption-desorption cycles). In certain embodiments, a composition comprising the metal-organic framework (e.g. in the form of a film, in the form of a plurality of particles), and/or an article comprising the composition disposed on a substrate, is used for adsorption and/or desorption of a target species. The target species (e.g., water) may, in some embodiments, be present in atmospheric air.

According to some embodiments, a method of synthesizing the metal-organic framework is described, the method comprising exposing a compound of the form $MX^{1/2}$ to a first metal-organic framework of the form $[Zn_5X^2_4(\text{ligand})_3]$, thereby forming a second metal-organic framework of the form $[(M_xZn_{1-x})_5(X^1_yX^2_{1-y})_4(\text{ligand})_3]$, wherein: M is a divalent metal cation (e.g., nickel and/or cobalt); X^1 and X^2 are different; each of X^1 and X^2 is a monovalent anion (e.g., X^1 is chloride and X^2 is acetate); ligand is a dianionic nitrogen-containing heterocyclic compound; x is greater than 1 and less than 0; and y is greater than 1 and less than 0. In some embodiments, the second metal-organic framework is synthesized such that the value of x is less than the value of y. In accordance with certain embodiments, the values of x and y can be controlled and/or fine-tuned based on the amount of starting materials employed in the synthesis of the metal-organic framework.

In certain embodiments, a method of adsorbing a target species (e.g., water) is described. In certain embodiments, the method comprises exposing a composition

– 8 –

comprising a metal-organic framework (e.g., a metal-organic framework of the form $[(M_xZn_{1-x})_5(X^1_yX^2_{1-y})_4(\text{ligand})_3]$) to the target species, thereby adsorbing the target species. The target species may adsorb into one or more pores of the metal-organic framework and/or may coordinate with one or more open coordination sites on one or more metals of the metal-organic framework, in accordance with certain embodiments. In some embodiments, a method of desorbing a target species from the metal-organic framework is described. In certain embodiments, for example, the target species desorbs from the metal-organic framework based on a change in relative humidity without subjecting the metal-organic framework to drastic changes in temperature and/or pressure. According to some embodiments, a method adsorbing and desorbing a target species over a number of cycles (e.g., at least 10 cycles) is described.

According to some embodiments, the composition comprises a metal-organic framework. As used herein, the term "metal-organic framework" is given its ordinary meaning in the art and refers to a one-, two-, or three-dimensional coordination polymer including metal ions and ligands which function as organic structural units, wherein at least a portion of the metal ions are each chemically bonded to at least one bi-, tri- or poly-dentate organic structural ligand. The metal ions, in addition to being coordinated with at least one ligand, may also be bound to one or more auxiliary (e.g., nonstructural) ligands, in accordance with certain embodiments.

The metal-organic framework may have any of a variety of suitable morphologies and may comprise any of a variety of suitable components. In some embodiments, the metal-organic framework comprises one or more structural motifs. For example, in some embodiments, the metal-organic framework comprises a plurality of metal ions that are linked together by a plurality of bridging ligands (e.g., structural ligands), thereby resulting in an ordered morphology. The ordered morphology may, in some embodiments, comprise features suitable for adsorption of a target species (e.g., water), such as a plurality pores into which the target species can be adsorbed into and/or one or more metals comprising one or more open coordination sites to which the target species can interact.

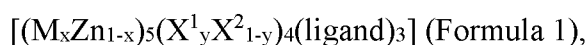
According to some embodiments, each metal ion of the plurality of metal ions is coordinated to at least one ligand of the plurality of ligands, wherein each ligand

– 9 –

comprises a nitrogen-containing heterocyclic compound. In certain embodiments, each metal ion of the plurality of metal ions is coordinated to at least two ligands of the plurality of ligands, wherein each ligand comprises a nitrogen-containing heterocyclic compound. In some embodiments, each metal ion of the plurality of metal ions is
 5 coordinated with at least three ligands of the plurality of ligands, wherein each ligand comprises a nitrogen-containing heterocyclic compound. According to some embodiments, each metal ion of the plurality of metal ions is coordinated to the at least one nitrogen-containing heterocyclic compound by a metal-nitrogen interaction (e.g., a metal-nitrogen covalent bond).

10 In certain embodiments, at least some of the metal ions of the plurality of metal ions are coordinated to at least one auxiliary ligand (e.g., non-structural ligand), which may be bridging or terminal.

The metal-organic framework may be of any of a variety of suitable forms. In some embodiments, for example, the metal-organic framework is of the form shown in
 15 Formula 1:



wherein: M is a divalent metal cation; X^1 and X^2 are different; each of X^1 and X^2 is a monovalent anion; and ligand is a dianionic nitrogen-containing heterocyclic compound.

20 The value of x in Formula 1 may be any of a variety of suitable values. In some embodiments, for example, x in Formula 1 is greater than 0, greater than or equal to 0.1, greater than or equal to 0.2, greater than or equal to 0.3, greater than or equal to 0.4, greater than or equal to 0.5, greater than or equal to 0.6, greater than or equal to 0.7, greater than or equal to 0.8, or greater than or equal to 0.9. In some embodiments, x in
 25 Formula 1 is less than 1, less than or equal to 0.9, less than or equal to 0.8, less than or equal to 0.7, less than or equal to 0.6, less than or equal to 0.5, less than or equal to 0.4, less than or equal to 0.3, less than or equal to 0.2, or less than or equal to 0.1.

Combinations of the above recited ranges are possible (e.g., x in Formula 1 is greater than 0 and less than 1, x in Formula 1 is greater than or equal to 0.6 and less than or
 30 equal to 0.7). Other ranges are also possible. In certain non-limiting embodiments, x in Formula 1 is greater than or equal to 0.6 and less than 1. In some embodiments, the

value of x can be controlled and/or fine-tuned based on the amount of starting materials employed in the synthesis of the metal-organic framework, as described herein in greater detail.

According to certain embodiments, the value of x is determined by inductively coupled plasma mass spectrometry (ICP-MS).

The value of y in Formula 1 may be any of a variety of suitable values. In some embodiments, for example, y in Formula 1 is greater than 0, greater than or equal to 0.1, greater than or equal to 0.2, greater than or equal to 0.3, greater than or equal to 0.4, greater than or equal to 0.5, greater than or equal to 0.6, greater than or equal to 0.7, greater than or equal to 0.8, or greater than or equal to 0.9. In some embodiments, y in Formula 1 is less than 1, less than or equal to 0.9, less than or equal to 0.8, less than or equal to 0.7, less than or equal to 0.6, less than or equal to 0.5, less than or equal to 0.4, less than or equal to 0.3, less than or equal to 0.2, or less than or equal to 0.1. Combinations of the above recited ranges are possible (e.g., y in Formula 1 is greater than 0 and less than 1, y in Formula 1 is greater than or equal to 0.4 and less than or equal to 0.5). Other ranges are also possible. In some non-limiting embodiments, y in Formula 1 is greater than or equal to 0.8 and less than 1. In some embodiments, the value of y can be controlled and/or fine-tuned based on the amount of starting materials employed in the synthesis of the metal-organic framework, as described herein in greater detail.

According to certain embodiments, the value of y is determined by nuclear magnetic resonance (NMR) spectroscopy.

In some embodiments, the value of x in Formula 1 is less than the value of y in Formula 1.

As described herein, M in Formula 1 may be any of a variety of suitable divalent metal cations. In certain embodiments, for example, M in Formula 1 is a divalent nickel (Ni) cation, a divalent cobalt (Co) cation, or a divalent zinc (Zn) cation. Combinations of divalent metal cations are also possible for M in Formula 1. Other divalent metal cations are also possible for M in Formula 1.

As described herein, X¹ in Formula 1 may be any of a variety of suitable monovalent anions. In some embodiments, X¹ is a halogen. For example, in certain

embodiments, X^1 is chloride (Cl^-), fluoride (F^-), bromide (Br^-), and/or iodide (I^-).

According to some embodiments, X^1 is acetate (OAc or CH_3COO^-). In certain embodiments, X^1 is a carboxylate (e.g., propionate, butyrate, formate, lactate, and the like). In some embodiments, X^1 is hydroxide (OH^-). Combinations of monovalent anions for X^1 in Formula 1 are also possible. Other monovalent anions for X^1 in Formula 1 are also possible.

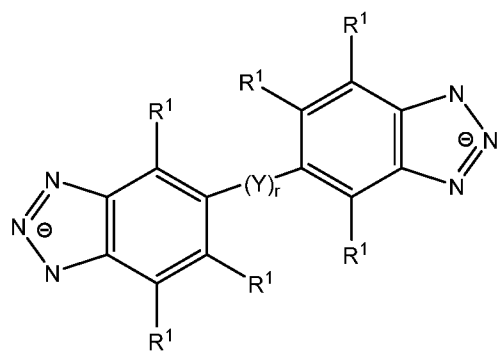
As described herein, X^2 in Formula 1 may be any of a variety of suitable monovalent anions. In certain embodiments, X^2 is OAc . In some embodiments, X^2 is a halogen (e.g., Cl^- , F^- , Br^- , and/or I^-). In certain embodiments, X^2 is a carboxylate (e.g., propionate, butyrate, formate, lactate, and the like). In some embodiments, X^2 is OH^- . Combinations of monovalent anions for X^2 in Formula 1 are also possible. Other monovalent anions for X^2 in Formula 1 are also possible.

As described herein, ligand in Formula 1 may be any of a variety of suitable dianionic nitrogen-containing heterocyclic compounds. In certain embodiments, the dianionic nitrogen-containing heterocyclic compound comprises at least one azolate group. As used herein, the term “azolate group” refers to a negatively-charged five-membered heterocyclic compound containing at least two non-carbon atoms, at least one of which is a nitrogen atom. Examples of azolate groups include, but are not limited to, imidazolate groups, triazolate groups, tetrazolate groups, pyrazolate groups, thiazolate groups, oxadiazolate groups, and/or purinate groups. In some embodiments, the dianionic nitrogen-containing heterocyclic compound comprises at least two azolate groups. In certain embodiments, the dianionic nitrogen-containing heterocyclic compound comprises at least two different azolate groups. In other embodiments, the dianionic nitrogen-containing heterocyclic compound comprises at least two identical azolate groups.

The dianionic nitrogen-containing heterocyclic compound may comprise the at least two azolate groups arranged about any of a variety of suitable organic cores. In some embodiments, the organic core is at least partially aromatic. For example, in some embodiments, the organic core comprises at least one aromatic moiety. Generally, the organic core comprises a rigid structure formed from one or more fused aryl and/or heteroaryl rings.

– 12 –

In some embodiments, the dianionic nitrogen-containing heterocyclic compound comprises the structure:



wherein:

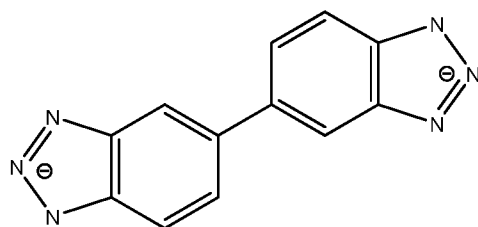
5 each R^1 is the same or different and is selected from the group consisting of hydrogen, $-C_1-C_{10}$ alkyl, $-C_2-C_{10}$ alkenyl, $-C_3-C_{10}$ alkynyl, a halogen, $-N(R^2)_2$, and $-OR^2$,

each R^2 is the same or different and is selected from the group consisting of hydrogen, $-C_1-C_{10}$ alkyl, $-C_2-C_{10}$ alkenyl, and $-C_3-C_{10}$ alkynyl,

10 each Y is independently alkylene, heteroalkylene, arylene, heteroarylene, $-O-$, $-C(=O)-$, $-S-$, and

r is 0, 1, 2, or 3.

In some embodiments, the nitrogen-containing heterocyclic compound comprises the structure:



15

According to certain non-limiting embodiments, ligand in Formula 1 is 5,5'-bibenzotriazolate. Other ligands for Formula 1 are also possible.

20 According to some embodiments, the ligand is at least partially hydrophilic. In some embodiments, employing an at least partially hydrophilic ligand advantageously provides a metal-organic framework comprising a plurality of at least partially hydrophilic pores that are suitable for adsorption of water, as described herein in greater detail.

– 13 –

According to some embodiments, a method of synthesizing a metal-organic framework (e.g., a metal-organic framework of the form shown in Formula 1) is described.

In certain embodiments, the method comprises exposing a compound of the form
5 MX^1_2 to a metal-organic framework (e.g., a first metal-organic framework) of the form $[\text{Zn}_5\text{X}^2_4(\text{ligand})_3]$, wherein: M is a divalent metal cation; X^1 and X^2 are different; each of X^1 and X^2 is a monovalent anion; and ligand is a dianionic nitrogen-containing heterocyclic compound.

According to some embodiments, exposing the compound of the form MX^1_2 to
10 the metal-organic framework of the form $[\text{Zn}_5\text{X}^2_4(\text{ligand})_3]$ is performed in solution. In certain embodiments, for example, the compound of the form MX^1_2 and the metal-organic framework of the form $[\text{Zn}_5\text{X}^2_4(\text{ligand})_3]$ are dissolved in a solvent and reacted in solution. In some embodiments, the solution is stirred (e.g. sonicated or stirred with a stir bar) to facilitate the reaction in solution. Advantageously, stirring the solution may
15 homogeneously distribute M and/or X^1 throughout the resulting material, in accordance with certain embodiments. The solvent may be any of a variety of suitable solvents. In some embodiments, for example, the solvent is an organic solvent. Suitable organic solvents include N,N-dimethylformamide (DMF), N,N-diethylformamide, N-methylformamide (NMF), methanol, and/or combinations thereof. Other solvents are
20 also possible.

Exposing the compound of the form MX^1_2 to the metal-organic framework of the form $[\text{Zn}_5\text{X}^2_4(\text{ligand})_3]$ (e.g., in solution) may be performed for any of a variety of suitable durations. In certain embodiments, for example, exposing the compound of the form MX^1_2 to the metal-organic framework of the form $[\text{Zn}_5\text{X}^2_4(\text{ligand})_3]$ is performed
25 for at least 1 hour, at least 6 hours, at least 12 hours, at least 24 hours, at least 36 hours, at least 48 hours, at least 60 hours, at least 72 hours, at least 84 hours, at least 96 hours, or at least 108 hours. In some embodiments, exposing the compound of the form MX^1_2 to the metal-organic framework of the form $[\text{Zn}_5\text{X}^2_4(\text{ligand})_3]$ is performed for less than or equal to 120 hours, less than or equal to 108 hours, less than or equal to 96 hours, less
30 than or equal to 84 hours, less than or equal to 72 hours, less than or equal to 60 hours, less than or equal to 48 hours, less than or equal to 36 hours, less than or equal to 24

hours, less than or equal to 12 hours, or less than or equal to 6 hours. Combinations of the above recited ranges are possible (e.g., exposing the compound of the form $\text{MX}^{1/2}_2$ to the metal-organic framework of the form $[\text{Zn}_5\text{X}^{2/4}(\text{ligand})_3]$ is performed for at least 1 hour and less than or equal to 120 hours, exposing the compound of the form $\text{MX}^{1/2}_2$ to the metal-organic framework of the form $[\text{Zn}_5\text{X}^{2/4}(\text{ligand})_3]$ is performed for at least 48 hours and less than or equal to 60 hours). Other ranges are also possible. In some embodiments, the duration of the exposing step affects the value of x and/or the value of y in the metal-organic framework of the form $[(\text{M}_x\text{Zn}_{1-x})_5(\text{X}^{1/4}_y\text{X}^{2/4}_{1-y})_4(\text{ligand})_3]$.

Exposing the compound of the form $\text{MX}^{1/2}_2$ to the metal-organic framework of the form $[\text{Zn}_5\text{X}^{2/4}(\text{ligand})_3]$ (e.g., in solution) may be performed at any of a variety of suitable temperatures. In some embodiments, for example, exposing the compound of the form $\text{MX}^{1/2}_2$ to the metal-organic framework of the form $[\text{Zn}_5\text{X}^{2/4}(\text{ligand})_3]$ is performed at room temperature (e.g., 20-22 °C). In certain embodiments, exposing the compound of the form $\text{MX}^{1/2}_2$ to the metal-organic framework of the form $[\text{Zn}_5\text{X}^{2/4}(\text{ligand})_3]$ is performed at a temperature greater than or equal to 20 °C, greater than or equal to 30 °C, greater than or equal to 40 °C, greater than or equal to 50 °C, greater than or equal to 60 °C, greater than or equal to 70 °C, greater than or equal to 80 °C, or greater than or equal to 90 °C. In some embodiments, exposing the compound of the form $\text{MX}^{1/2}_2$ to the metal-organic framework of the form $[\text{Zn}_5\text{X}^{2/4}(\text{ligand})_3]$ is performed at a temperature less than or equal to 100 °C, less than or equal to 90 °C, less than or equal to 80 °C, less than or equal to 70 °C, less than or equal to 60 °C, less than or equal to 50 °C, less than or equal to 40 °C, or less than or equal to 30 °C.

Combinations of the above recited ranges are possible (e.g., exposing the compound of the form $\text{MX}^{1/2}_2$ to the metal-organic framework of the form $[\text{Zn}_5\text{X}^{2/4}(\text{ligand})_3]$ is performed at a temperature greater than or equal to 20 °C and less than or equal to 100 °C, exposing the compound of the form $\text{MX}^{1/2}_2$ to the metal-organic framework of the form $[\text{Zn}_5\text{X}^{2/4}(\text{ligand})_3]$ is performed at a temperature greater than or equal to 60 °C and less than or equal to 70 °C). Other ranges are also possible. In some embodiments, the temperature at which the exposing step is performed affects the value of x and/or the value of y in the metal-organic framework of the form $[(\text{M}_x\text{Zn}_{1-x})_5(\text{X}^{1/4}_y\text{X}^{2/4}_{1-y})_4(\text{ligand})_3]$.

– 15 –

According to certain embodiments, as a result of exposing the compound of the form MX^{1_2} to the metal-organic framework of the form $[Zn_5X^{2_4}(\text{ligand})_3]$, a metal-organic framework (e.g., a second metal-organic framework) of the form $[(M_xZn_{1-x})_5(X^1_yX^{2_{1-y}})_4(\text{ligand})_3]$ (e.g., a metal-organic framework of the form shown in Formula 1) is formed, wherein: M is a divalent metal cation; X^1 and X^2 are different; each of X^1 and X^2 is a monovalent anion; and ligand is a dianionic nitrogen-containing heterocyclic compound.

In some embodiments, exposing the compound of the form MX^{1_2} to the metal-organic framework of the form $[Zn_5X^{2_4}(\text{ligand})_3]$ to form the metal-organic framework of the form $[(M_xZn_{1-x})_5(X^1_yX^{2_{1-y}})_4(\text{ligand})_3]$ is performed such that x (e.g., in the metal-organic framework of the form $[(M_xZn_{1-x})_5(X^1_yX^{2_{1-y}})_4(\text{ligand})_3]$) is greater than 0 (e.g., greater than or equal to 0.6, greater than or equal to 0.7, greater than or equal to 0.8, greater than or equal to 0.9) and less than 1, as described herein in greater detail with respect to Formula 1. In some embodiments, the value of x can be controlled and/or fine-tuned based on the amount of the compound of the form MX^{1_2} and/or the amount of the metal-organic framework of the form $[Zn_5X^{2_4}(\text{ligand})_3]$ used in the synthesis. For example, in certain embodiments, using an excess of the compound of the form MX^{1_2} relative to the amount of the metal-organic framework of the form $[Zn_5X^{2_4}(\text{ligand})_3]$ can result in a higher value of x.

In certain embodiments, exposing the compound of the form MX^{1_2} to the metal-organic framework of the form $[Zn_5X^{2_4}(\text{ligand})_3]$ to form the metal-organic framework of the form $[(M_xZn_{1-x})_5(X^1_yX^{2_{1-y}})_4(\text{ligand})_3]$ is performed such that y (e.g., in the metal-organic framework of the form $[(M_xZn_{1-x})_5(X^1_yX^{2_{1-y}})_4(\text{ligand})_3]$) is greater than 0 (e.g., greater than or equal to 0.8, greater than or equal to 0.9) and less than 1, as described herein in greater detail with respect to Formula 1. In some embodiments, the value of y can be controlled and/or fine-tuned based on the amount of the compound of the form MX^{1_2} and/or the amount of the metal-organic framework of the form $[Zn_5X^{2_4}(\text{ligand})_3]$ used in the synthesis. For example, in certain embodiments, using an excess of the compound of the form MX^{1_2} relative to the amount of the metal-organic framework of the form $[Zn_5X^{2_4}(\text{ligand})_3]$ can result in a higher value of y.

In some embodiments, exposing the compound of the form MX_2 to the metal-organic framework of the form $[Zn_5X_4(\text{ligand})_3]$ to form the metal-organic framework of the form $[(M_xZn_{1-x})_5(X^1_yX^{2_{1-y}})_4(\text{ligand})_3]$ is performed such that the value of x (e.g., in the metal-organic framework of the form $[(M_xZn_{1-x})_5(X^1_yX^{2_{1-y}})_4(\text{ligand})_3]$) is less than
 5 the value of y (e.g., in the metal-organic framework of the form $[(M_xZn_{1-x})_5(X^1_yX^{2_{1-y}})_4(\text{ligand})_3]$), as described herein in greater detail with respect to Formula 1.

In certain embodiments, M (e.g., in the compound of the form MX_2 , in the metal-organic framework of the form $[(M_xZn_{1-x})_5(X^1_yX^{2_{1-y}})_4(\text{ligand})_3]$) is any of a variety of suitable divalent metal cations as described herein in greater detail with respect to
 10 Formula 1. For example, in some embodiments, M (e.g., in the compound of the form MX_2 , in the metal-organic framework of the form $[(M_xZn_{1-x})_5(X^1_yX^{2_{1-y}})_4(\text{ligand})_3]$) is a divalent Ni cation, a divalent Co cation, a divalent Zn cation, or combinations thereof.

According to some embodiments, X^1 (e.g., in the compound of the form MX_2 , in the metal-organic framework of the form $[(M_xZn_{1-x})_5(X^1_yX^{2_{1-y}})_4(\text{ligand})_3]$) is any of a
 15 variety of suitable monovalent anions as described herein in greater detail with respect to Formula 1. In certain embodiments, for example, X^1 (e.g., in the compound of the form MX_2 , in the metal-organic framework of the form $[(M_xZn_{1-x})_5(X^1_yX^{2_{1-y}})_4(\text{ligand})_3]$) is a halogen (e.g., Cl^-).

The compound of the form MX_2 may be any of a variety of suitable compounds.
 20 In certain embodiments, for example, the compound of the form MX_2 is $NiCl_2$, NiF_2 , $NiBr_2$, NiI_2 , $Ni(OAc)_2$, $CoCl_2$, CoF_2 , $CoBr_2$, CoI_2 , $Co(OAc)_2$, $ZnCl_2$, ZnF_2 , $ZnBr_2$, ZnI_2 , $Zn(OAc)_2$ and/or combinations thereof. Other compounds of the form MX_2 are also possible.

In certain embodiments, X^2 (e.g., in the metal-organic framework of the form $[Zn_5X_4(\text{ligand})_3]$, in the metal-organic framework of the form $[(M_xZn_{1-x})_5(X^1_yX^{2_{1-y}})_4(\text{ligand})_3]$) is any of a variety of suitable monovalent anions as described herein in
 25 greater detail with respect to Formula 1. In certain embodiments, for example, X^2 (e.g., in the metal-organic framework of the form $[Zn_5X_4(\text{ligand})_3]$, in the metal-organic framework of the form $[(M_xZn_{1-x})_5(X^1_yX^{2_{1-y}})_4(\text{ligand})_3]$) is OAc.

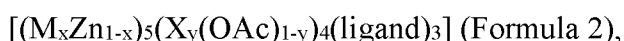
– 17 –

According to certain embodiments, the metal-organic framework of the form $[Zn_5X^2_4(\text{ligand})_3]$ is synthesized by reacting a compound of the form $Zn(X^2)_2$ with a suitable nitrogen-containing heterocyclic compound.

In certain embodiments, the method comprises exposing a compound of the form MX^1_2 and a compound of the form $M'X^2$ to a metal-organic framework (e.g., a first metal-organic framework) of the form $[Zn_5X^2_4(\text{ligand})_3]$, thereby forming a metal-organic framework (e.g., a second metal-organic framework) of the form $[(M_xZn_{1-x})_5(X^1_yX^{2}_{1-y})_4(\text{ligand})_3]$ (e.g., a metal-organic framework of the form shown in Formula 1), wherein: M is a divalent metal cation; M' is monovalent metal cation; X^1 and X^2 are different; each of X^1 and X^2 is a monovalent anion; and ligand is a dianionic nitrogen-containing heterocyclic compound.

The compound of the form $M'X^2$ may be any of a variety of suitable compounds. In certain embodiments, for example, the compound of the form $M'X^2$ is LiCl, LiF, LiBr, LiI, LiOAc, NaCl, NaF, NaBr, NaI, NaOAc, and/or combinations thereof. Other compounds of the form $M'X^2$ are also possible.

According to certain embodiments, the metal-organic framework is of the form shown in Formula 2:



wherein: M is a divalent metal cation; X is a monovalent anion; and ligand is a dianionic nitrogen-containing heterocyclic compound.

In certain embodiments, x in Formula 2 is any of a variety of suitable values as described herein in greater detail with respect to Formula 1. For example, in some embodiments, x in Formula 2 is greater than 0 and less than 1. Other ranges are also possible. In some non-limiting embodiments, x in Formula 2 is greater than or equal to 0.23, greater than or equal to 0.45, greater than or equal to 0.6, greater than or equal to 0.61, greater than or equal to 0.67, greater than or equal to 0.74, or greater than or equal to 0.79. As described herein, the value of x may be determined by ICP-MS, in accordance with certain embodiments.

The value of y in Formula 2 may be any of a variety of suitable values. In some embodiments, y in Formula 2 is greater than 0, greater than or equal to 0.05, greater than or equal to 0.1, or greater than or equal to 0.15. In certain embodiments, y in Formula 2

is less than or equal to 0.2, less than or equal to 0.15, less than or equal to 0.1, or less than or equal to 0.05. Combinations of the above recited ranges are possible (e.g., y in Formula 2 is greater than 0 and less than or equal to 0.2, y in Formula 2 is greater than or equal to 0.1 and less than or equal to 0.15). Other ranges are also possible. According to
5 certain non-limiting embodiments, y in Formula 2 is less than or equal to 0.04.

In certain embodiments, y in Formula 2 is greater than or equal to 0.4, greater than or equal to 0.5, greater than or equal to 0.6, greater than or equal to 0.7, greater than or equal to 0.8, or greater than or equal to 0.9. In some embodiments, y in Formula 2 is less than 1, less than or equal to 0.9, less than or equal to 0.8, less than or equal to 0.7,
10 less than or equal to 0.6, or less than or equal to 0.5. Combinations of the above recited ranges are possible (e.g., y in Formula 2 is greater than or equal to 0.4 and less than 1, y in Formula 2 is greater than or equal to 0.7 and less than or equal to 0.8). Other ranges are also possible. According to some non-limiting embodiments, y in Formula 2 is greater than or equal to 0.91, greater than or equal to 0.92, or greater than or equal to
15 0.95.

As described herein in greater detail, the value of y may be determined by NMR spectroscopy, in accordance with certain embodiments.

In certain embodiments, M in Formula 2 is any of a variety of suitable divalent metal cations as described herein in greater detail with respect to Formula 1. For
20 example, in some embodiments, M in Formula 2 is a divalent Ni cation, a divalent Co cation, a divalent Zn cation, or combinations thereof.

According to certain embodiments, X in Formula 2 is any of a variety of suitable monovalent anions as described herein in greater detail with respect to X¹ in Formula 1. In some embodiments, for example, X in Formula 2 is a halogen (e.g., Cl⁻).

25 In some embodiments, ligand in Formula 2 is any of a variety of suitable dianionic nitrogen-containing heterocyclic compounds as described herein in greater detail with respect to Formula 1. For example, in certain embodiments, ligand in Formula 2 is 5,5'-bibenzotriazolate.

According to some non-limiting embodiments, the metal-organic framework is of
30 the form shown in Formula 2, wherein: x is greater than or equal to 0.6 (e.g., greater than or equal to 0.7, greater than or equal to 0.8, greater than or equal to 0.9, etc.); y is less

than or equal to 0.1 (e.g., less than or equal to 0.05, etc.); M is selected from the group consisting of a divalent Ni cation and a divalent Co cation; and X is Cl⁻.

In other non-limiting embodiments, the metal-organic framework is of the form shown in Formula 2, wherein: x is greater than or equal to 0.6 (e.g., greater than or equal to 0.7, greater than or equal to 0.8, greater than or equal to 0.9, etc.); y is greater than or equal to 0.8 (e.g., greater than or equal to 0.9, etc.); M is selected from the group consisting of a divalent Ni cation and a divalent Co cation; and X is Cl⁻.

According to certain embodiments, the metal-organic framework is of the form shown in Formula 3:

10
$$[(Zn)_5(X)_y(OAc)_{1-y})_4(ligand)_3] \text{ (Formula 3),}$$

wherein: X is a monovalent anion; and ligand is a dianionic nitrogen-containing heterocyclic compound.

The value of y in Formula 3 may be any of a variety of suitable values. In certain embodiments, for example, y in Formula 3 is greater than or equal to 0.8, greater than or equal to 0.85, greater than or equal to 0.9, or greater than or equal to 0.95. In some embodiments, y in Formula 3 is less than 1, less than or equal to 0.95, less than or equal to 0.9, or less than or equal to 0.85. Combinations of the above recited ranges are possible (e.g., y in Formula 3 is greater than or equal to 0.8 and less than 1, y in Formula 3 is greater than or equal to 0.9 and less than or equal to 0.95). Other ranges are also possible. According to some non-limiting embodiments, y in Formula 3 is greater than or equal to 0.84. As described herein in greater detail, the value of y may be determined by NMR spectroscopy, in accordance with certain embodiments.

According to certain embodiments, X in Formula 3 is any of a variety of suitable monovalent anions as described herein in greater detail with respect to X¹ in Formula 1. In some embodiments, for example, X in Formula 3 is a halogen (e.g., Cl⁻).

In some embodiments, ligand in Formula 3 is any of a variety of suitable dianionic nitrogen-containing heterocyclic compounds as described herein in greater detail with respect to Formula 1. For example, in certain embodiments, ligand in Formula 3 is 5,5'-bibenzotriazolate.

According to some non-limiting embodiments, the metal-organic framework is of the form shown in Formula 3, wherein: y is greater than or equal to 0.8 (e.g., greater

– 20 –

than or equal to 0.85, greater than or equal to 0.9, greater than or equal to 0.95, etc.); and X is a halogen (e.g., Cl⁻).

According to certain embodiments, the metal-organic framework comprises a plurality of pores. Advantageously, the plurality of pores of the metal-organic framework may, at least in part, provide a material with a desirable surface area, in accordance with certain embodiments. The metal-organic framework may have any of a variety of suitable Brunauer–Emmett–Teller (BET) surface areas. In some embodiments, for example, the metal-organic framework has a BET surface area greater than or equal to 1800 m²/g, greater than or equal to 1900 m²/g, greater than or equal to 2000 m²/g, greater than or equal to 2100 m²/g, or greater than or equal to 2200 m²/g. In certain embodiments, the metal-organic framework has a BET surface area less than or equal to 2300 m²/g, less than or equal to 2200 m²/g, less than or equal to 2100 m²/g, less than or equal to 2000 m²/g, or less than or equal to 1900 m²/g. Combinations of the above recited ranges are possible (e.g., the metal-organic framework has a BET surface area greater than or equal to 1800 m²/g and less than or equal to 2300 m²/g, the metal-organic framework has a BET surface area greater than or equal to 2000 m²/g and less than or equal to 2100 m²/g). Other ranges are also possible.

According to certain embodiments, the BET surface area of the metal-organic framework is determined by measuring a nitrogen (N₂) adsorption isotherm of the metal-organic framework at 77 K.

The metal-organic framework may have any of a variety of suitable pore volumes. In certain embodiments, for example, the metal-organic framework has a pore volume greater than or equal to 0.8 cm³/g, greater than or equal to 0.82 cm³/g, greater than or equal to 0.84 cm³/g, greater than or equal to 0.86 cm³/g, or greater than or equal to 0.88 cm³/g. In some embodiments, the metal-organic framework has a pore volume less than or equal to 0.9 cm³/g, less than or equal to 0.88 cm³/g, less than or equal to 0.86 cm³/g, less than or equal to 0.84 cm³/g, or less than or equal to 0.82 cm³/g. Combinations of the above recited ranges are possible (e.g., the metal-organic framework has a pore volume greater than or equal to 0.8 cm³/g and less than or equal to 0.9 cm³/g, the metal-organic framework has a pore volume greater than or equal to 0.84 cm³/g and less than or equal to 0.86 cm³/g). Other ranges are also possible.

According to certain embodiments, the pore volume of the metal-organic framework is determined by measuring a nitrogen (N₂) adsorption isotherm of the metal-organic framework at 77 K.

The composition may comprise the metal-organic framework in any of a variety of suitable amounts. In some embodiments, for example, the composition comprises the metal-organic framework in an amount greater than or equal to 50 weight percent (wt.%), greater than or equal to 60 wt.%, greater than or equal to 70 wt.%, greater than or equal to 80 wt.%, greater than or equal to 90 wt.%, or greater than or equal to 99 wt.% versus a total weight of the composition. In certain embodiments, the composition comprises the metal-organic framework in an amount less than or equal to 100 wt.%, less than or equal to 99 wt.%, less than or equal to 90 wt.%, less than or equal to 80 wt.%, less than or equal to 70 wt.%, or less than or equal to 60 wt.% versus a total weight of the composition. Combinations of the above recited ranges are possible (e.g., the composition comprises the metal-organic framework in an amount greater than or equal to 50 wt.% and less than or equal to 100 wt.% versus a total weight of the composition, the composition comprises the metal-organic framework in an amount greater than or equal to 90 wt.% and less than or equal to 99 wt.% versus a total weight of the composition). Other ranges are also possible.

In certain embodiments, the composition comprises the metal-organic framework and one or more additives. Suitable additives include, for example, a desiccant, a polymer binder, and/or a thermally-conductive additive. Other additives are also possible.

The composition may comprise the one or more additives in any of a variety of suitable amounts. In some embodiments, for example, the composition comprises the one or more additives in an amount greater than or equal to 0 wt.%, greater than or equal to 1 wt.%, greater than or equal to 10 wt.%, greater than or equal to 20 wt.%, greater than or equal to 30 wt.%, or greater than or equal to 40 wt.% versus a total weight of the composition. In some embodiments, the composition comprises the one or more additives in amount less than or equal to 50 wt.%, less than or equal to 40 wt.%, less than or equal to 30 wt.%, less than or equal to 20 wt.%, less than or equal to 10 wt.%, or less than or equal to 1 wt.% versus a total weight of the composition. Combinations of

– 22 –

the above recited ranges are possible (e.g., the composition comprises the one or more additives in an amount greater than or equal to 0 wt.% and less than or equal to 50 wt.% versus a total weight of the composition, the composition comprises the one or more additives in an amount greater than or equal to 1 wt.% and less than or equal to 10 wt.% versus a total weight of the composition). Other ranges are also possible.

The composition may be in any of a variety of suitable forms. In some embodiments, for example, the composition is in the form of a film (e.g., a thin film). FIG. 1A shows a cross-sectional schematic diagram of composition 102a comprising a metal-organic framework 106 in the form of film 104, in accordance with certain embodiments.

In certain embodiments, the composition is in the form of a plurality of particles. FIG. 1B shows a cross-sectional schematic diagram of composition 102b comprising metal-organic framework 106 in the form of plurality of particles 108 (e.g., particles 108a and 108b), in accordance with certain embodiments. According to some embodiments, the plurality of particles is a plurality of crystalline particles.

Each particle of the plurality of particles may have any of a variety of suitable shapes. In some embodiments, for example, as shown in FIG. 1B, each particle of the plurality of particles has a substantially spherical shape. In other embodiments, one or more particles of the plurality of particles have an angular shape, a cylindrical shape, a cubic shape, an elliptical shape, and/or the like.

In certain embodiments, the plurality of particles comprise a plurality of microparticles. The term “microparticle” is used herein in a manner consistent with its ordinary meaning in the art. Microparticles are particles having a maximum characteristic dimension (e.g., a maximum diameter) from 1 micrometer to 100 micrometers. The maximum characteristic dimension of a particle generally refers to the longest dimension from a first surface of the particle to a second surface of the particle that is substantially opposite the first surface. As one illustrative example, referring to FIG. 1B, particle 108b has maximum characteristic dimension 112a. According to some embodiments, the maximum characteristic dimension of the microparticle is from 1 micrometer to 10 micrometers, 10 micrometers to 20 micrometers, 20 micrometers to 30 micrometers, 30 micrometers to 50 micrometers, 50 micrometers to 70 micrometers, or

70 micrometers to 100 micrometers. Combinations of the above recited ranges are possible (e.g., 30 micrometers to 70 micrometers, or 20 micrometers to 100 micrometers). Other ranges are also possible. The maximum characteristic dimension of the microparticle may be determined by electron microscopy techniques (e.g., scanning
5 electron microscopy).

In certain embodiments, the plurality of particles comprise a plurality of nanoparticles. The term “nanoparticle” is used herein in a manner consistent with its ordinary meaning in the art. Nanoparticles are particles having a maximum characteristic dimension from 1 nanometer to 1 micrometer. According to some
10 embodiments, the maximum characteristic dimension of the nanoparticle is from 1 nanometer to 100 nanometers, 100 nanometers to 200 nanometers, 200 nanometers to 300 nanometers, 300 nanometers to 500 nanometers, 500 nanometers to 700 nanometers, or 700 nanometers to 1 micrometer. Combinations of the above recited ranges are possible (e.g., 300 nanometers to 700 nanometers, or 200 nanometers to 1 micrometer).
15 Other ranges are also possible. The maximum characteristic dimension of the nanoparticle may be determined by electron microscopy techniques (e.g., scanning electron microscopy).

According to some embodiments, the plurality of particles comprises a combination of particles having different maximum characteristic dimensions.
20 According to some embodiments, for example, the plurality of particles comprises at least one microparticle and at least one nanoparticle.

According to some embodiments, an article is described. FIG. 2 shows a cross-sectional schematic diagram of article 202 comprising composition 102c, in accordance with certain embodiments. In certain embodiments, composition 102c comprises metal-
25 organic framework 106. Composition 102c may be disposed on surface 208 of substrate 204 such that composition 102c coats surface 208 of substrate 204, in accordance with some embodiments.

The substrate may comprise any of a variety of suitable materials. In some embodiments, the substrate comprises a plurality of pores. In certain embodiments, the
30 substrate comprises a filter and/or a membrane. In some embodiments, the substrate comprises a polymer and/or a metal.

According to certain embodiments, a method of adsorbing a target species is described.

In some embodiments, the method comprises exposing a composition to a target species such that at least a portion of the composition adsorbs the target species. In
5 certain embodiments, for example, the composition comprises a metal-organic framework, at least a portion of which adsorbs the target species. In certain embodiments, the metal-organic framework adsorbs the target species such that the target species is incorporated into one or more pores of the metal-organic framework. In some embodiments, the metal-organic framework adsorbs the target species such that the
10 target species interacts with one or more open coordination sites on one or more metals in the metal-organic framework. In certain embodiments, the interaction between the target species and the one or more open coordination sites on the one or more metals in the metal-organic framework is a metal-ligand bond, a covalent bond, an ionic bond, a hydrogen bond, an acid-base interaction, a dipole-dipole interaction, or a van der Waals
15 interaction. In some embodiments, the interaction between the target species and the one or more open coordination sites on the one or more metals in the metal-organic framework is an interaction between water and nickel.

According to some embodiments, exposing the composition to the target species comprises flowing the target species over the composition. Referring, for example, to
20 FIG. 1A, exposing composition 102a to the target species comprises flowing the target species over film 104 comprising composition 102a such that the target species is exposed to composition 102a, in accordance with certain embodiments. In certain embodiments, referring to FIG. 1B, exposing composition 102b to the target species comprises flowing the target species over plurality of particles 108 comprising
25 composition 102b such that the target species is exposed to composition 102b. In some embodiments, referring to FIG. 2A, exposing composition 102c to the target species comprises flowing the target species over article 202 comprising composition 102c such that the target species is exposed to composition 102c.

In some embodiments, exposing the composition to the target species comprises
30 mixing the composition with the target species. Referring, for example, to FIG. 1A, exposing composition 102a to the target species comprises mixing film 104 comprising

– 25 –

composition 102a with the target species. In certain embodiments, referring to FIG. 1B, exposing composition 102b to the target species comprises mixing plurality of particles 108 comprising composition 102b with the target species. In some embodiments, referring to FIG. 1C, exposing composition 102c to the target species comprising mixing
5 article 202 comprising composition 102c with the target species.

According to certain embodiments, exposing the composition to the target species comprises configuring the composition in an environment such that the composition is exposed to atmospheric air, which may, in some embodiments, comprise the target species. Referring, for example, to FIG. 1A, exposing composition 102a to the
10 target species comprises configuring film 104 in an environment such that composition 102a is exposed to atmospheric air. In some embodiments, referring to FIG. 1B, exposing composition 102b to the target species comprises configuring plurality of particles 108 in an environment such that compositions 102b is exposed to atmospheric air. In certain embodiments, referring to FIG. 1C, exposing composition 102c to the
15 target species comprises configuring article 202 comprising composition 102c in an environment such that compositions 102c is exposed to atmospheric air.

The target species may be or comprise any of a variety of suitable target species. According to some embodiments, the target species is a gas and/or a liquid. In certain embodiments, the target species is water. In some embodiments, the target species is
20 water vapor (e.g., present in atmospheric air). In certain embodiments, the target species is liquid water. Other target species are also possible.

According to some embodiments, exposing the composition to the target species comprises exposing the composition to a mixture of species comprising the target species. Advantageously, the composition may selectively adsorb the target species from
25 the mixture of species, in accordance with certain embodiments. In certain embodiments, the mixture of species comprises a gaseous target species (e.g., water vapor) and one or more additional gases. For example, in some embodiments, the mixture of species comprises nitrogen (N₂), oxygen (O₂), argon (Ar), and the like. In some embodiments, the target species is water vapor present in atmospheric air.
30 According to some embodiments, the mixture of species comprises a liquid target species (e.g., liquid water) and one or more additional liquids. In certain embodiments,

– 26 –

for example, the mixture of species comprises one or more organic solvents. In certain embodiments, the target species is liquid water present in a mixture of organic solvents. Other species for the mixture of species are also possible.

According to some embodiment wherein the target species is a gas, the mixture
5 of species comprising the target species may have any of a variety of suitable relative humidities. As used herein, the term “relative humidity” is given its ordinary meaning in the art and refers to a ratio of the water vapor pressure of a gas at a given temperature to the saturation water vapor pressure of the gas at the given temperature, expressed as a percentage. In certain embodiments, the mixture of species comprising the target species
10 has a relative humidity greater than or equal to 10% RH, greater than or equal to 20% RH, greater than or equal to 30% RH, greater than or equal to 40% RH, greater than or equal to 50% RH, greater than or equal to 60% RH, or greater than or equal to 70% RH. In some embodiments, the mixture of species comprising the target species has a relative humidity less than or equal to 80% RH, less than or equal to 70% RH, less than or equal
15 to 60% RH, less than or equal to 50% RH, less than or equal to 40% RH, less than or equal to 30% RH, or less than or equal to 20% RH. Combinations of the above recited ranges are possible (e.g., the mixture of species comprising the target species has a relative humidity greater than or equal to 10% RH and less than or equal to 80% RH, the mixture of species comprising the target species has a relative humidity greater than or
20 equal to 40% RH and less than or equal to 50% RH). Other ranges are also possible. In some non-limiting embodiments, the target species is water vapor, the mixture of species is atmospheric air comprising water vapor, and the atmospheric air has a relative humidity greater than or equal to 10% RH and less than or equal to 80% RH.

According to some embodiments, the relative humidity of the mixture of species
25 comprising the target species is measured by a hygrometer.

In certain embodiments wherein the target species is a liquid, the mixture of species comprising the target species may have any of a variety of suitable equilibrium relative humidities. As used herein, the term “equilibrium relative humidity” is given its ordinary meaning in the art and refers to the relative humidity of a gas surrounding a
30 material (e.g., one or more liquids), wherein the gas and the material are in thermodynamic equilibrium. In some embodiments, the mixture of species comprising

– 27 –

the target species has an equilibrium relative humidity greater than or equal to 10% ERH, greater than or equal to 20% ERH, greater than or equal to 30% ERH, greater than or equal to 40% ERH, greater than or equal to 50% ERH, greater than or equal to 60% ERH, or greater than or equal to 70% ERH. In certain embodiments, the mixture of
5 species comprising the target species has an equilibrium relative humidity less than or equal to 80% ERH, less than or equal to 70% ERH, less than or equal to 60% ERH, less than or equal to 50% ERH, less than or equal to 40% ERH, less than or equal to 30% ERH, or less than or equal to 20% ERH. Combinations of the above recited ranges are possible (e.g., the mixture of species comprising the target species has an equilibrium
10 relative humidity greater than or equal to 10% ERH and less than or equal to 80% ERH, the mixture of species comprising the target species has an equilibrium relative humidity greater than or equal to 40% ERH and less than or equal to 50% ERH). Other ranges are also possible. In some non-limiting embodiments, the target species is liquid water, the mixture of species is a mixture of liquids comprising liquid water, and the mixture of
15 liquids has an equilibrium relative humidity greater than or equal to 10% RH and less than or equal to 80% RH.

According to some embodiments, the equilibrium relative humidity of the mixture of species comprising the target species is measured by a hygrometer.

As described herein, the target species may be water, in accordance with certain
20 embodiments. The metal-organic framework may have any of a variety of suitable water uptake capacities. According to some embodiments, the water uptake capacity of the metal-organic framework is measured in grams of water per gram of metal-organic framework (i.e., g H₂O / g MOF, or g/g as used herein). In certain embodiments, the water uptake capacity of the metal-organic framework is greater than or equal to 0.65
25 g/g, greater than or equal to 0.70 g/g, greater than or equal to 0.75 g/g, greater than or equal to 0.8 g/g, or greater than or equal to 0.85 g/g. In some embodiments, the water uptake capacity of the metal-organic framework is less than or equal to 0.9 g/g, less than or equal to 0.85 g/g, less than or equal to 0.8 g/g, less than or equal to 0.75 g/g, or less than or equal to 0.7 g/g. Combinations of the above recited ranges are possible (e.g., the
30 water uptake capacity of the metal-organic framework is greater than or equal to 0.65 g/g and less than or equal to 0.9 g/g, the water uptake capacity of the metal-organic

framework is greater than or equal to 0.75 g/g and less than or equal to 0.8 g/g). Other ranges are also possible.

According to some embodiments, the water uptake capacity of the metal-organic framework is determined by measuring a water adsorption isotherm of the metal-organic framework. In certain embodiments, the water adsorption isotherm of the metal-organic framework is measured at room temperature (e.g., 20-22 °C).

According to certain embodiments wherein the target species is a gas, the metal-organic framework may have any of a variety of suitable relative humidities at half-capacity (α RH%). In certain embodiments, the value of the relative humidity at half-capacity is the value at which pore condensation occurs in the metal-organic framework. In some embodiments, the relative humidity at half-capacity depends on the pore size of the metal-organic framework, the pore hydrophilicity of the metal-organic framework, and/or the number of metals with open coordination sites in the metal-organic framework. According to certain embodiments, the metal-organic framework has an α greater than or equal to 20% RH, greater than or equal to 30% RH, greater than or equal to 40% RH, greater than or equal to 50% RH, or greater than or equal to 60% RH. In some embodiments, the metal-organic framework has an α less than or equal to 70% RH, less than or equal to 60% RH, less than or equal to 50% RH, less than or equal to 40% RH, or less than or equal to 30% RH. Combinations of the above recited ranges are possible (e.g., the metal-organic framework has an α greater than or equal to 20% RH and less than or equal to 70% RH, the metal-organic framework has an α greater than or equal to 40% RH and less than or equal to 50% RH). Other combinations are also possible.

According to certain embodiments wherein the target species is a liquid, the metal-organic framework may have any of a variety of suitable equilibrium relative humidities at half-capacity (α ERH%). In certain embodiments, the value of the equilibrium relative humidity at half-capacity is the value at which pore condensation occurs in the metal-organic framework. In some embodiments, the equilibrium relative humidity at half-capacity depends on the pore size of the metal-organic framework, the pore hydrophilicity of the metal-organic framework, and/or the number of metals with open coordination sites in the metal-organic framework. According to certain

embodiments, the metal-organic framework has an α greater than or equal to 20% ERH, greater than or equal to 30% ERH, greater than or equal to 40% ERH, greater than or equal to 50% ERH, or greater than or equal to 60% ERH. In some embodiments, the metal-organic framework has an α less than or equal to 70% ERH, less than or equal to 60% ERH, less than or equal to 50% ERH, less than or equal to 40% ERH, or less than or equal to 30% ERH. Combinations of the above recited ranges are possible (e.g., the metal-organic framework has an α greater than or equal to 20% ERH and less than or equal to 70% ERH, the metal-organic framework has an α greater than or equal to 40% ERH and less than or equal to 50% ERH). Other combinations are also possible.

In some embodiments, a method of desorbing a target species is described. According to some embodiments, the method comprises desorbing at least a portion of the target species from the composition. In certain embodiments, for example, the composition comprises a metal-organic framework and an adsorbed target species, at least a portion of which desorbs from the metal-organic framework. In some embodiments, the target species desorbs from one or more pores of the metal-organic framework. In certain embodiments, the target species desorbs from one or more coordination sites on one or more metals in the metal-organic framework.

In certain embodiments wherein the target species is a gas, the method comprises decreasing the relative humidity of the gas, thereby desorbing the target species from the composition (e.g., the metal-organic framework). According to some embodiments, decreasing the relative humidity of the gas comprises decreasing the pressure of the gas (and/or the composition comprising the adsorbed gas). The pressure of the gas may be decreased by any of a variety of suitable percentages. In some embodiments, for example, the pressure of the gas is decreased by at least 1%, at least 5%, at least 10%, at least 20%, at least 30%, at least 40%, at least 50%, at least 60%, at least 70%, at least 80%, or at least 90%. In certain embodiments, the pressure of the gas is decreased by less than or equal to 100%, less than or equal to 90%, less than or equal to 80%, less than or equal to 70%, less than or equal to 60%, less than or equal to 50%, less than or equal to 40%, less than or equal to 30%, less than or equal to 20%, less than or equal to 10%, or less than or equal to 5%. Combinations of the above recited ranges are possible (e.g., the pressure of the gas is decreased by at least 1% and less than or equal to 100%,

– 30 –

the pressure of the gas is decreased by at least 40% and less than or equal to 60%). Other ranges are also possible. In some embodiments, decreasing the relative humidity of the gas comprises increasing the temperature of the gas (and/or the composition comprising the adsorbed gas). The temperature of the gas may be increased by any of a variety of suitable percentages. In some embodiments, for example, the temperature of the gas is increased by at least 1%, at least 5%, at least 10%, at least 20%, at least 30%, at least 40%, at least 50%, at least 60%, at least 70%, at least 80% or at least 90%. In certain embodiments, the temperature of the gas is increased by less than or equal to 100%, less than or equal to 90%, less than or equal to 80%, less than or equal to 70%, less than or equal to 60%, less than or equal to 50%, less than or equal to 40%, less than or equal to 30%, less than or equal to 20%, less than or equal to 10%, or less than or equal to 5%. Combinations of the above recited ranges are possible (e.g., the temperature of the gas is increased by at least 1% and less than or equal to 90%, the temperature of the gas is increased by at least 40% and less than or equal to 60%). Other ranges are also possible.

In certain embodiments wherein the target species is a liquid, the method comprises decreasing the equilibrium relative humidity of the liquid (and/or the composition comprising the adsorbed liquid), thereby desorbing the target species from the composition (e.g., the metal-organic framework). In certain embodiments, decreasing the equilibrium relative humidity of the liquid comprises decreasing the pressure of the liquid (and/or the composition comprising the adsorbed liquid). The pressure of the liquid may be decreased by any of a variety of suitable percentages. In some embodiments, for example, the pressure of the liquid is decreased by at least 1%, at least 5%, at least 10%, at least 20%, at least 30%, at least 40%, at least 50%, at least 60%, at least 70%, at least 80%, or at least 90%. In certain embodiments, the pressure of the liquid is decreased by less than or equal to 100%, less than or equal to 90%, less than or equal to 80%, less than or equal to 70%, less than or equal to 60%, less than or equal to 50%, less than or equal to 40%, less than or equal to 30%, less than or equal to 20%, less than or equal to 10%, or less than or equal to 5%. Combinations of the above recited ranges are possible (e.g., the pressure of the liquid is decreased by at least 1% and less than or equal to 100%, the pressure of the liquid is decreased by at least 40%

and less than or equal to 60%). Other ranges are also possible. In some embodiments, decreasing the equilibrium relative humidity of the liquid comprises increasing the temperature of the liquid (and/or the composition comprising the adsorbed liquid). The temperature of the liquid may be increased by any of a variety of suitable percentages.

5 In some embodiments, for example, the temperature of the liquid is increased by at least 1%, at least 5%, at least 10%, at least 20%, at least 30%, at least 40%, at least 50%, at least 60%, at least 70%, at least 80%, or at least 90%. In certain embodiments, the temperature of the liquid is increased by less than or equal to 100%, less than or equal to 90%, less than or equal to 80%, less than or equal to 70%, less than or equal to 60%, less
10 than or equal to 50%, less than or equal to 40%, less than or equal to 30%, less than or equal to 20%, less than or equal to 10%, or less than or equal to 5%. Combinations of the above recited ranges are possible (e.g., the temperature of the liquid is increased by at least 1% and less than or equal to 90%, the temperature of the liquid is increased by at least 40% and less than or equal to 60%). Other ranges are also possible.

15 According to certain embodiments, the composition (e.g., metal-organic framework) advantageously desorbs the target species without subjecting the composition (and/or the target species) to drastic changes (e.g., increases or decreases) in temperature and/or pressure. For example, in certain non-limiting embodiments, the composition may be configured to: (i) adsorb the target species at a first temperature
20 greater than or equal to 20 °C and less than or equal to 30 °C (e.g., 25 °C); and (ii) desorb the target species at a second temperature greater than or equal to 40 °C and less than or equal to 50 °C (e.g., 45 °C).

According to certain embodiments, the surface area of the metal-organic framework changes (e.g., decreases) after adsorbing and desorbing the target species
25 (e.g., water). In some embodiments, the change in the surface area of the metal-organic framework after adsorbing and desorbing the target species is advantageously small. For example, in certain embodiments, the surface area of the metal-organic framework decreases by less than or equal to 30%, less than or equal to 20%, less than or equal to 10%, less than or equal to 5%, or less than or equal to 1% after adsorbing and desorbing
30 the target species. In some embodiments, the surface area of the metal-organic framework decreases by greater than or equal to 0.1%, greater than or equal to 1%,

– 32 –

greater than or equal to 5%, greater than or equal to 10%, or greater than or equal to 20% after adsorbing and desorbing the target species. Combinations of the above recited ranges are possible (e.g., the surface area of the metal-organic framework decreases by less than or equal to 30% and greater than or equal to 0.01% after adsorbing and
5 desorbing the target species, the surface area of the metal-organic framework decreases by less than or equal to 10% and greater than or equal to 5% after adsorbing and desorbing the target species). Other ranges are also possible.

In some embodiments, the composition is used for multiple adsorption and/or desorption cycles. For example, in certain embodiments, a method comprises adsorbing
10 and desorbing a target species multiple times. The method may comprise adsorbing and desorbing the target species any of a variety of suitable number of times. In certain embodiments, for example, the method comprises adsorbing and desorbing the target species at least 10 times, at least 50 times, greater than or equal to 100 times, at least 150 times, at least 200 times, at least 250 times, at least 300 times, at least 350 times, at least
15 400 times, at least 450 times, at least 500 times, or at least 750 times. In some embodiments, the method comprises adsorbing and desorbing the target species less than or equal to 1000 times, less than or equal to 750 times, less than or equal to 500 times, less than or equal to 450 times, less than or equal to 400 times, less than or equal to 350 times, less than or equal to 300 times, less than or equal to 250 times, less than or equal
20 to 200 times, less than or equal to 150 times, less than or equal to 100 times, or less than or equal to 50 times. Combinations of the above recited ranges are possible (e.g., the method comprises adsorbing and desorbing the target species greater than or equal to 10 times and less than or equal to 1000 times, the method comprises adsorbing and desorbing the target species greater than or equal to 300 times and less than or equal to
25 350 times). Other ranges are also possible.

As described herein, the target species may be water, in accordance with certain embodiments. Advantageously, the water uptake capacity of the metal-organic framework is substantially retained after multiple adsorption and/or desorption cycles, in accordance with certain embodiments. The water uptake capacity of the metal-organic
30 framework may decrease by any of a variety of suitable amounts after adsorbing and desorbing the target species any of a variety of suitable number of times. In certain

– 33 –

embodiments, for example, the water uptake capacity of the metal-organic framework decreases by less than or equal to 30%, less than or equal to 20%, less than or equal to 10%, or less than or equal to 5% after adsorbing and desorbing the target species at least 10 times (e.g., at least 50 times, greater than or equal to 100 times, at least 150 times, at least 200 times, at least 250 times, at least 300 times, at least 350 times, at least 400 times, at least 450 times, at least 500 times, at least 750 times, etc.). In certain embodiments, the water uptake capacity of the metal-organic framework decreases by greater than or equal to 1%, greater than or equal to 5%, greater than or equal to 10%, or greater than or equal to 20% after adsorbing and desorbing the target species at least 10 times (e.g., at least 50 times, greater than or equal to 100 times, at least 150 times, at least 200 times, at least 250 times, at least 300 times, at least 350 times, at least 400 times, at least 450 times, at least 500 times, at least 750 times, etc.). Combinations of the above recited ranges are possible (e.g., the water uptake capacity of the metal-organic framework decreases by less than or equal to 30% and greater than or equal to 1% after adsorbing and desorbing the target species at least 10 times, the water uptake capacity of the metal-organic framework decreases by less than or equal to 10% and greater than or equal to 5% after adsorbing and desorbing the target species at least 10 times). Other ranges are also possible.

The compositions, articles, and methods described herein may be used in any of a variety of suitable applications. In some embodiments, for example, the compositions and/or articles described herein are used in a method of harvesting atmospheric water. In certain embodiments, the compositions and/or articles described herein are used in a method of humidity control. Other applications are also possible.

The following application is incorporated herein by reference, in its entirety, for all purposes: U.S. Provisional Patent Application No. 63/509,196, filed June 20, 2023, and entitled “SORBENTS FOR THE TUNABLE CAPTURE AND RELEASE OF WATER”.

Definitions of specific functional groups and chemical terms are described in more detail below. For purposes of this description, the chemical elements are identified in accordance with the Periodic Table of the Elements, CAS version, Handbook of Chemistry and Physics, 75th Ed., inside cover, and specific functional groups are

generally defined as described therein. Additionally, general principles of organic chemistry, as well as specific functional moieties and reactivity, are described in Organic Chemistry, Thomas Sorrell, University Science Books, Sausalito: 1999, the entire contents of which are incorporated herein by reference.

5 It will be appreciated that the compounds, as described herein, may be substituted with any number of substituents or functional moieties. In general, the term “substituted” whether preceded by the term “optionally” or not, and substituents contained in formulas of this invention, refer to the replacement of hydrogen radicals in a given structure with the radical of a specified substituent (e.g., a substituent which upon
10 substitution results in a stable compound, such as a compound which does not spontaneously undergo transformation such as by rearrangement, cyclization, elimination, or other reaction). When more than one position in any given structure may be substituted with more than one substituent selected from a specified group, the substituent may be either the same or different at every position. As used herein, the
15 term “substituted” is contemplated to include all permissible substituents of organic compounds, and includes any of the substituents described herein that results in the formation of a stable compounds. In a broad aspect, the permissible substituents include acyclic and cyclic, branched and unbranched, carbocyclic and heterocyclic, aromatic and nonaromatic substituents of organic compounds. For purposes of this description,
20 heteroatoms such as nitrogen may have hydrogen substituents and/or any permissible substituents of organic compounds described herein which satisfy the valencies of the heteroatoms and results in the formation of a stable moiety. Furthermore, this description is not intended to be limited in any manner by the permissible substituents of organic compounds. Combinations of substituents and variables envisioned by this
25 description are preferably those that result in the formation of stable compounds. The term “stable”, as used herein, preferably refers to compounds which possess stability sufficient to allow manufacture and which maintain the integrity of the compound for a sufficient period of time to be detected and preferably for a sufficient period of time to be useful for the purposes detailed herein.

30 As used herein, “alkyl” refers to a radical of a straight-chain or branched saturated hydrocarbon group having from 1 to 10 carbon atoms (“C₁-C₁₀ alkyl”). In

some embodiments, an alkyl group has 1 to 9 carbon atoms (“C₁-C₉ alkyl”). In some embodiments, an alkyl group has 1 to 8 carbon atoms (“C₁-C₈ alkyl”). In some embodiments, an alkyl group has 1 to 7 carbon atoms (“C₁-C₇ alkyl”). In some embodiments, an alkyl group has 1 to 6 carbon atoms (“C₁-C₆ alkyl”). In some
5 embodiments, an alkyl group has 1 to 5 carbon atoms (“C₁-C₅ alkyl”). In some embodiments, an alkyl group has 1 to 4 carbon atoms (“C₁-C₄ alkyl”). In some embodiments, an alkyl group has 1 to 3 carbon atoms (“C₁-C₃ alkyl”). In some embodiments, an alkyl group has 1 to 2 carbon atoms (“C₁-C₂ alkyl”). In some
10 embodiments, an alkyl group has 1 carbon atom (“C₁ alkyl”). In some embodiments, an alkyl group has 2 to 6 carbon atoms (“C₂-C₆ alkyl”). Examples of C₁-C₆ alkyl groups include methyl (C₁), ethyl (C₂), n-propyl (C₃), isopropyl (C₃), n-butyl (C₄), tert-butyl (C₄), sec-butyl (C₄), iso-butyl (C₄), n-pentyl (C₅), 3-pentanyl (C₅), amyl (C₅), neopentyl (C₅), 3-methyl-2-butanyl (C₅), tertiary amyl (C₅), and n-hexyl (C₆). Additional examples of alkyl groups include n-heptyl (C₇), n-octyl (C₈), and the like. Unless otherwise
15 specified, each instance of an alkyl group is independently unsubstituted (an “unsubstituted alkyl”) or substituted (a “substituted alkyl”) with one or more substituents. In certain embodiments, the alkyl group is an unsubstituted C₁-C₁₀ alkyl (e.g., -CH₃). In certain embodiments, the alkyl group is a substituted C₁-C₁₀ alkyl.

As used herein, the term “alkenyl” includes a radical of a straight-chain or
20 branched saturated hydrocarbon group having from 2 to 10 carbon atoms, and also includes at least one carbon-carbon double bond. It will be understood that in certain embodiments, alkenyl may be advantageously of limited length, including C₂-C₁₀, C₂-C₉, C₂-C₈, C₂-C₇, C₂-C₆, C₂-C₅, C₂-C₄, and C₂-C₃.

As used herein, the term “alkynyl” includes a radical of a straight-chain or
25 branched saturated hydrocarbon group having from 3 to 10 carbon atoms, and also includes at least one carbon-carbon triple bond. It will be understood that in certain embodiments, alkynyl may be advantageously of limited length, including C₃-C₁₀, C₃-C₉, C₃-C₈, C₃-C₇, C₃-C₆, C₃-C₅, and C₃-C₄.

As used herein, the term “heteroalkyl” refers to an alkyl group as described
30 herein in which one or more carbon atoms is replaced by a heteroatom. Suitable heteroatoms include oxygen, sulfur, nitrogen, phosphorus, and the like. Examples of

heteroalkyl groups include, but are not limited to, alkoxy, alkoxyalkyl, amino, thioester, poly(ethylene glycol), and alkyl-substituted amino.

As used herein, the term “aryl” refers to aromatic carbocyclic groups, optionally substituted, having a single ring (e.g., phenyl), multiple rings (e.g., biphenyl), or multiple
5 fused rings in which at least one is aromatic (e.g., 1,2,3,4-tetrahydronaphthyl, naphthyl, anthryl, or phenanthryl). That is, at least one ring may have a conjugated pi electron system, while other, adjoining rings can be cycloalkyls, cycloalkenyls, cycloalkynyls, aryls and/or heterocycllys.

As used herein, the term “heteroaryl” refers to aryl groups comprising at least one
10 heteroatom as a ring atom. Suitable heteroatoms include oxygen, sulfur, nitrogen, phosphorus, and the like.

It should be understood that affixing the suffix “-ene” to a group indicates the group is a divalent moiety. For example, alkylene is the divalent moiety of alkyl (e.g., an acyclic carbon or a saturated acyclic carbon chain represented by the formula $-C_nH_{2n}-$),
15 alkenylene is the divalent moiety of alkenyl (e.g., an acyclic carbon chain which contains a carbon-to-carbon double bond represented by the formula $-C_nH_{2n-2}-$), and alkynylene is the divalent moiety of alkynyl (e.g., an acyclic carbon chain which contains a carbon-to-carbon triple bond represented by the formula $-C_nH_{2n-4}-$). Affixing the suffice “-yne” to a group indicates the group is trivalent moiety (e.g., alkylyne is the trivalent moiety of
20 alkyl, alkenylyne is the trivalent moiety of alkenyl, and alkynylyne is the trivalent moiety of alkynyl).

As used herein, the term “halogen” refers to fluorine (fluoro, $-F$), chlorine (chloro, $-Cl$), bromine (bromo, $-Br$), or iodine (iodo, $-I$).

The following examples are intended to illustrate certain embodiments of the
25 present disclosure, but do not exemplify the full scope of the disclosure.

EXAMPLE 1

Described herein are a class of materials that can be readily tailored to a range of water sorption applications, employing a material derived from earth abundant metals
30 and a simple organic molecule accessed in a single step from a common industrial monomer.

– 37 –

Given their microporosity and modular, designable structures, metal-organic frameworks (MOFs) have become a privileged class of water sorbents. The hydrophobicity of common MOF linkers combined with the size of common MOF pores facilitates extremely steep water uptake at the humidity of pore condensation, resulting in high working capacities. Further, the ability to introduce water-binding functionality within the MOF structure via the incorporation of specific open metal sites or linker modifications enables rational tuning of the interactions between the material and water. With this designability, however, often comes significant costs: the design of bespoke linkers generally requires challenging, multi-step syntheses that render the final materials very expensive relative to the proposed large-scale applications. Further, such multi-step synthesis of intricate linkers often generates significant waste, diminishing potential environmental benefits of employing MOF sorbents.

To address these challenges, it was envisioned that the MOF CFA-1 ($[\text{Zn}_5(\text{OAc})_4(\text{bibta})_3]$, $\text{H}_2\text{-bibta} = 1\text{H}, 1\text{H}'\text{-}5,5'\text{-bibenzo}[d][1,2,3]\text{triazole}$)—a material derived from widely produced 3,3'-diaminobenzidine (FIG. 3B) and known to undergo efficient metal and anion exchange—could serve as a cost-effective platform for the synthesis of a range of materials possessing diverse pore environments to modify sorption properties. Straightforward modulation of this structure provides access to a range of materials with practically useful working capacities and varied relative humidities of pore condensation. Counterion or metal exchange provides access to a range of materials of the form “ $\text{M}_5\text{X}_4(\text{bibta})_3$ ” where M is a cation such as zinc (Zn), cobalt (Co), and/or nickel (Ni) and X is a common anion such as chloride (Cl) and/or acetate (OAc) (FIGS. 3A and 3C). Despite a surprising lack of long-term stability for M = zinc, exchanging this metal for nickel provided access to water-stable structures capable of extended cycling (<2% reduction in working capacity over 80 cycles). Sequential metal and anion exchange provided efficient access to $\text{Ni}_{3.5}\text{Zn}_{1.5}(\text{OAc})_{3.8}\text{Cl}_{0.2}(\text{bibta})_3$, a novel MOF with excellent water sorption properties.

The parent MOF structure, CFA-1, was readily synthesized based on a previously reported procedure (FIG. 4). Subsequent cation exchange to replace the zinc atom in CFA-1 with other metal ions afforded a range of different nickel- and cobalt-incorporated MOFs (structures denoted $(\text{Zn}_{1-x}\text{M}_x)_5(\text{OAc}_{1-y}\text{Cl}_y)_4(\text{bibta})_3$). Detailed

studies into the thermodynamics of nickel exchange enabled development of a qualitatively predictive model to access a desired final metal incorporation as a function of nickel concentration and temperature. To evaluate the effect of the counterion on water sorption properties in the absence of changes to metal identity, conditions to exchange chloride with acetate for zinc-based CFA-1 (stirring with zinc chloride in *N,N*-dimethylformamide) and exchange acetate with chloride into nickel chloride-exchanged CFA-1 (stirring with lithium acetate in methanol) were developed.

In all cases, the isolated structures maintained the long-range order of the parent CFA-1 based on powder X-ray diffraction (PXRD) (FIG. 5B) and possessed similar porosity based on Brunauer-Emmett-Teller (BET) analysis of nitrogen adsorption isotherms (FIG. 5A). Studies into the morphology of the resulting structures by scanning electron microscopy (SEM) showed some reduction in particle size after extended stirring, a property that is possibly advantageous for increasing the rate of adsorption/desorption cycles.

Water adsorption isotherms were measured at 298 K for each of the synthesized materials. A clear trend was observed between nickel incorporation and the relative humidity at half-capacity (α), with water uptake at lower humidities observed at higher nickel incorporations. Overall, α values ranging from 27-70% relative humidity could be accessed (FIGS. 6-7), affording materials with water uptake values optimized for distinct applications ranging from atmospheric water harvesting to indoor humidity control. The counterion bound to the metal was further found to significantly impact α , with a reduction from 70 to 46% observed when exchanging chloride for acetate. In all cases, water uptake capacities above 0.65 g H₂O/g MOF were observed for the initial isotherm, illustrating the potential practical utility of these materials.

Contrary to expectations based on the reported properties of structurally related azolate MOFs, the synthesized CFA-1 derivatives containing only zinc were unstable to water adsorption/desorption cycles. For both parent CFA-1 and the zinc chloride-exchanged material, significant reductions in surface area (up to 40%) and water capacity (up to 30%) were observed following the initial water isotherm (FIG. 8A).

Exchange from zinc to nickel afforded MOFs with significantly improved water stability. CFA-1 exchanged with nickel chloride to afford 60% and 74% nickel-

– 39 –

exchanged MOFs showed <1% reduction in surface area following water adsorption/desorption (FIG. 8B). This facilitated extended cycling of [Ni(60%),Cl(95%)] CFA-1, which showed less than 2% reduction in working capacity after 80 cycles between 0 and 35% relative humidity (FIG. 9). The combination of long-term stability, high uptake capacity, practically useful humidity of uptake, and facile synthesis from inexpensive precursors renders this MOF and related structures particularly promising for large scale application.

To provide insight into the nature of water binding to the nickel-exchanged framework, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were conducted in which an inert gas with a controlled relative humidity was flowed over a sample of activated MOF. The spectra for Ni(60%)-CFA-1 shows a strong interaction with water at relative humidities below the alpha value; the appearance of a sharp feature at approximately $3,600\text{ cm}^{-1}$ is consistent with a well-defined water molecule directly bound to a nickel site prior to pore filling at higher relative humidity (FIG. 10A). Subsequent variable temperature water isotherms for this material further supported the importance of an initial interaction between water and an open nickel site, with significantly more exothermic binding at water loadings below 1 mol water/mol nickel (FIG. 10B). Taken together, these experiments support the role of discrete interactions between water and nickel facilitating water uptake at lower relative humidities for nickel-exchanged CFA-1.

Developing materials with the required pore structure and environment to facilitate water uptake at a useful relative humidity with long-term aqueous stability remains a significant challenge. Here, this task was accomplished while employing a material that is readily synthesized from an inexpensive, industrially produced monomer and earth-abundant metals. Metal exchange of the parent zinc CFA-1 structure—which possessed unpredicted water instability—provides access to a range of stable structures with practically useful relative humidities of uptake (27–35%), high water adsorption capacities (up to $0.78\text{ g H}_2\text{O/g MOF}$) and long-term stability to adsorption/desorption cycles (1.9% loss in capacity over 80 cycles). These structures compare favorably to existing MOFs with uptake humidities below 30% relative humidity (FIG. 11) and are derived from precursors that are much more accessible for large-scale deployment. The

– 40 –

predictable effect of metal and anion incorporation on relative humidity of uptake provides a straightforward approach to tune material properties for diverse applications. As a whole, these cation-exchanged CFA-1 derivatives present significant advantages over conventional state-of-the-art materials for reversible water sorption.

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EXAMPLE 2

Materials capable of selectively adsorbing or releasing water can enable valuable applications ranging from efficient humidity and temperature control to the direct atmospheric capture of potable water. Despite recent progress in employing metal-organic frameworks (MOFs) as privileged water sorbents, developing a readily accessible, water-stable MOF platform that can be systematically modified for high water uptake at low relative humidity remains a significant challenge. Reported herein is the development of a tunable MOF that efficiently captures atmospheric water (up to 0.78 g water/g MOF) across a range of uptake humidity (27–45%) employing a readily accessible Zn bibenzotriazolate MOF, CFA-1 ($[\text{Zn}_5(\text{OAc})_4(\text{bibta})_3]$, $\text{H}_2\text{bibta} = 1\text{H}, 1\text{H}'$ -5,5'-bibenzo[d][1,2,3]triazole), as a base for subsequent diversification. Controlling the metal identity (zinc, nickel) and coordinating nonstructural anion (acetate, chloride) via postsynthetic exchange modulates the relative humidity of uptake, facilitating the use of a single MOF scaffold for a diverse range of potential water sorption applications.

Further presented herein is a fundamental theory dictating how continuous variation of the pore environment affects the relative humidity of uptake. Exchange of substituents preserves capacity for water sorption, increases hydrolytic stability (with 5.7% loss in working capacity over 450 water adsorption-desorption cycles for the nickel-chloride-rich framework), and enables continuous modulation for the relative humidity of pore condensation. This combination of stability and tunability within a synthetically accessible framework renders Ni-incorporated $\text{M}_5\text{X}_4\text{bibta}_3$ promising materials for practical water sorption applications.

The use of reticular chemical principles within MOF syntheses has enabled the creation of tailored materials with enhanced properties and performance, expanding the range of applications of MOFs. An increasing number of studies have broadly investigated the use of MOFs for water adsorption, leveraging their tunable

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microporosity, steep water uptake due to uniform pore size, and the presence of potential binding groups, to facilitate atmospheric water harvesting, desiccation, moisture control, and refrigeration. As a result, MOFs have emerged as promising candidates for addressing challenges related to water management and environmental sustainability.

5 Designing ideal water sorbent materials for a given application necessitates optimization of several key parameters, including stability over cycling, relative humidity of pore condensation, working capacity, kinetics of cycling, environmental impact of the material and its synthesis, and costs associated with MOF synthesis and use. Considering these requirements in mind, advancements in reticular chemical
10 methods have led to the development of stable and porous frameworks with high water uptake. Furthermore, several research studies have demonstrated the importance of altering the hydrophilicity of the pore interior to effectively modulate the specific relative humidity (RH) at which pore condensation occurs (the relative humidity at half-capacity is denoted as α). This hydrophilicity can be modified through various
15 approaches, including ligand functionalization, cation/anion exchange, and, more recently, by varying the incorporation of organic linkers in multivariate MOFs. These variations have enabled shifts in the relative humidity for pore condensation up to 30% relative humidity. It was envisioned that systematically modifying a single, synthetically accessible MOF scaffold derived from inexpensive feedstocks could provide an ideal
20 approach to practically valuable MOF water sorption, enabling large-scale deployment of materials tailored to specific applications. The key to addressing this challenge has been identifying a MOF that could be synthesized from inexpensive precursors and capable of undergoing efficient modification to afford a range of diverse derivatives.

 The Zn bibenzotriazolate MOF CFA-1 ($[\text{Zn}_5(\text{OAc})_4(\text{bibta})_3]$, $\text{H}_2\text{bibta} = 1\text{H}, 1\text{H}'$ -
25 5,5'-bibenzo[d]-[1,2,3]triazole)—a material known to undergo efficient metal and anion exchange to provide access to a range of pore environments—appears suited to serve as a convenient platform for the synthesis of a range of materials with tunable water sorption properties. Further, the H_2bibta linker is derived from an industrially produced monomer already generated on a multiton scale annually, ensuring that any developed
30 materials could be efficiently and economically scaled up (FIG. 3B). Additionally, given that H_2bibta is a triazolate-based linker, it should form robust chemical bonds with

late transition metals, giving rise to hydrolytically stable MOFs, which is an essential parameter for practical water adsorption applications. Here, methods of accessing highly porous, hydrolytically stable, and scalable $M'M_4X_4\text{bibta}_3$ ($M' = \text{Zn}$; $M = \text{Zn}, \text{Ni}$; $X = \text{Cl}, \text{OAc}$) frameworks (FIGS. 3A, 3C, and 12) are reported. It has also been demonstrated that these materials capture water vapor at a broad range of uptake humidities (27-64% RH) with high water uptake capacities (up to 0.78 g H_2O /g MOF). Exchanging the majority of accessible zinc atoms provides efficient access to $[\text{Ni}(74\%), \text{Cl}(92\%)]$, a particularly valuable sorbent with a capacity of 0.78 g/g, uptake humidity of 27%, and hydrolytic stability over 450 water adsorption-desorption cycles.

$\text{Zn}_5(\text{OAc})_4(\text{bibta})_3$ (CFA-1; $\text{bibta}^{2-} = 5,5'$ -bibenzotriazolate, $\text{OAc} = \text{acetate}$) was synthesized by solvothermal synthesis in both *N,N*-dimethylformamide (DMF) and *N*-methylformamide (NMF). These materials display similar crystallinity, porosity (N_2 BET surface areas of 2,171 and 2,180 m^2/g and pore volumes of 0.84 and 0.85 cm^3/g , respectively; theoretical 2,140 m^2/g and 0.88 cm^3/g), and water sorption behavior (relative humidity at half-capacity, $\alpha = 50$ and 51%, respectively). However, there are slight differences in the morphology of the materials, which have downstream impacts on the water sorption properties. The altitude of the triangular crystal face in the *a-b* plane is approximately 4 times larger in the NMF crystallites ($23.00 \pm 2.30 \mu\text{m}$) compared to the DMF crystallites ($6.29 \pm 1.17 \mu\text{m}$). It was found that the larger NMF-derived crystals are more hydrolytically stable than the DMF-derived crystals, potentially due to improved response to the stress caused by surface tension during water desorption, although the effect of synthesis conditions on water stability remains under investigation. After one water adsorption-desorption cycle, the DMF-derived material's surface area drops to 905 m^2/g , whereas that of the NMF-derived material only decreases to 1,318 m^2/g . Due to the diminished water degradation of the NMF-derived materials, all subsequent experiments were prepared using the NMF procedure.

Similar to the postsynthetic metal exchange of Zn to Co, proof of concept exchange of Zn to Ni, and control over the relative humidity for pore condensation in MFU-4l by postsynthetic exchange of Zn to Co, it was recognized that detailed control of exchange of the Zn sites in CFA-1, as well as exchange of the nonstructural anion sites, could give rise to tunable water sorption. By performing the exchange at variable

– 43 –

temperature with varying concentrations of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in DMF, the nickel and chloride extent of exchange was precisely controlled while maintaining crystallinity and porosity (FIGS. 5A-5B). The resultant materials were isolated with a nickel loading ranging from 23 to 74% and a chloride loading ranging from 41 to 95%. The exchange

5 thermodynamics of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ at $\Delta H^\circ = 10.1 \pm 1.8$ kcal/mol and $\Delta S^\circ = 29.2 \pm 3.8$ cal/mol $\cdot$ K were estimated. It is noted that the assumption that activity coefficients are unity in the calculation of thermodynamic parameters is not strictly valid, leading to some nonlinear deviations from ideality when the concentration of nickel in solution is changed. Regardless, it was found that the thermodynamic parameters offer a

10 qualitatively useful guide for the determination of synthetic conditions to achieve a particular extent of exchange.

There may be significant diffusion limitation during postsynthetic exchanges that must be avoided. Exchange in the absence of stirring leads to materials with water isotherms containing two steps of pore condensation, consistent with the inhomogeneous

15 distribution of nickel within the material. As such, it is important that postsynthetic exchanges are done with stirring.

By performing multiple postsynthetic metal exchanges onto the same sample, the maximal conversion of metal exchange was determined to be 80%. This extent of exchange is consistent with complete exchange of the tetrahedral sites with no exchange

20 of the central octahedral site. This observation is consistent with the maximum extent of postsynthetic metal exchange of cobalt into CFA-1. As the extent of nickel exchange increases, the extent of chloride also increases (with a sigmoidal functional form). The nonlinear increase of chloride content with nickel content suggests a more complicated equilibrium in which there is a distribution of chloride and acetate over the nickel and

25 zinc centers. This nonlinearity highlights the importance of independent synthetic control over the metal and nonstructural anion content, to affect any resultant properties of the material. To this point, new postsynthetic exchange methodologies were developed using ZnCl_2 , LiOAc , as well as Ni(OAc)_2 as exchange partners, to increase chloride content or acetate content independently.

30 The exchange with ZnCl_2 was performed at 80 °C with a large excess of ZnCl_2 to drive the reaction forward ($K_{\text{eq}} < 1$). A material with the composition

– 44 –

(Zn)₅(OAc_{0.16},Cl_{0.84})₄(bibta)₃ was isolated with no loss in crystallinity, a N₂ BET surface area of 2,145 m²/g, and a pore volume of 0.86 cm³/g. To generate an acetate-rich Ni-bearing framework, two different methodologies were applied. First, the parent CFA-1 was subjected to an exchange with Ni(OAc)₂, in a fashion similar to the exchange with
 5 NiCl₂. This exchange is successful at low conversions, allowing for the isolation of (Zn_{0.78},Ni_{0.22})₅(OAc)₄(bibta)₃ (also referred here as [NiOAc-low], the full naming convention is listed in FIG. 7). However, when they are allowed to run at higher conversions in concentrated solutions of Ni(OAc)₂ in DMF, exchanges with the metal salts have a tendency to form gels. To circumvent this issue, sequential exchanges were
 10 performed with NiCl₂ followed by LiOAc, such that there would never be a simultaneous high concentration of both nickel and acetate in the same reaction vessel. Utilizing this procedure, (Zn_{0.33},Ni_{0.67})₅(OAc_{0.96},Cl_{0.04})₄(bibta)₃ was isolated. Importantly, no incorporation of lithium by inductively coupled plasma mass spectrometry (ICP-MS) was found.

15 The metal content during postsynthetic metal exchanges was analyzed by ICP-MS. The nonstructural ion content was analyzed by digestion followed by NMR spectroscopy. The ratio of acetate against bibta was recorded, and the fractional occupation was taken as 1 – (OAc/12)/(bibta/18). In all cases, the isolated structures maintained long-range order based on powder X-ray diffraction (PXRD) (FIG. 5B) and
 20 possessed porosity based on Brunauer–Emmett–Teller (BET) analysis of nitrogen adsorption isotherms at 77 K (FIG. 5A).

Water vapor adsorption isotherms measured at 298 K for each of the (Zn_{1-x},Ni_x)₅(OAc_{1-y},Cl_y)₄(bibta)₃ display Heaviside stepfunction or sigmoidal behavior, with pore condensation occurring between 27 and 70% relative humidity (FIG. 6). For
 25 the parent (Zn)₅(OAc)₄(bibta)₃ material, the relative humidity at half-capacity, α , occurs at 50% relative humidity, with a maximum capacity of 0.66 g/g. The parent material does not exhibit stable cycling behavior, with a decrease to 0.46 g/g of maximum capacity during the second cycle and a reduction in the BET surface area from 2182 to 1315 m²/g after water vapor exposure. Upon exchange of acetate with chloride,
 30 (Zn)₅(OAc_{0.16},Cl_{0.84})₄(bibta)₃ exhibits a shift in pore condensation to higher values, with α at 64% and the same maximum capacity of 0.66 g/g. This chloride exchanged zinc

framework also exhibits poor hydrolytic stability, with a decrease in maximum capacity to 0.57 g/g during the second cycle and a diminished BET surface area of 1853 m²/g. The poor stability of the zinc frameworks is attributed to the comparatively more labile Zn-triazolate bonds.

5 Upon exchange to 23% nickel, [Ni(23%),Cl(41%)] displays a decrease in the relative humidity of pore condensation, α , at 45% relative humidity and retention of maximum capacity at 0.66 g/g. Exchanging to 45% nickel, [Ni(45%),Cl(76%)] displayed an even lower α of 32% with a maximum capacity of 0.79 g/g. Exchanging to 61% nickel, [Ni(61%),Cl(91%)] displayed a α of 29% and a maximum capacity of 0.78
10 g/g. Exchanging to 74% nickel, [Ni(74%),Cl(92%)] displayed α of 27% and maximum capacity of 0.78 g/g. Additionally, an enhancement in hydrolytic stability is observed upon metal exchange, which is confirmed by the maintenance of total water uptake during the second cycling water adsorption experiments. The porosity of the materials remains intact, as confirmed by BET surface area analysis after activating the exposed
15 water materials at room temperature under dynamic vacuum (FIG. 7).

Notably, there is minimal adsorption-desorption hysteresis for all the water isotherms, similar to adsorption in related azolate frameworks. Minimal hysteretic loops in chemically similar materials has been ascribed to fast pore water dynamics (i.e., facile reorientation of water within the pores), potentially driven by a large number of
20 framework hydrogen-bond acceptors. The lack of a large hysteresis loop (and potentially the cause of fast water dynamics in related materials) concurrent with sharp water uptake may also be due to the capillary condensation occurring in a pore with a diameter slightly larger than the critical diameter for hysteresis at the measured temperature. The critical pore diameter for capillary condensation is well-approximated
25 by the scaling relation, $D_c \approx 4\sigma T_c / (T_c - T)$, where σ is the sorbate diameter, T_c is the critical temperature (374 °C for water), and T is the temperature for which the isotherm is measured. Above the critical pore diameter (or equivalently below the critical temperature for capillary condensation, T_c^{cap} , for a given pore diameter), capillary condensation should be accompanied by adsorption-desorption hysteresis, and the size of
30 the hysteresis loop should increase with increasing pore diameter. For pores just above the critical pore diameter, hysteretic loops may be small, and the uptake may remain

sharp. For water at 25 °C, the critical pore diameter is approximately 20 Å, slightly larger than the diameter of the largest cavity in (Zn)₅(OAc)₄(bibta)₃.

Qualitatively, it was observed that upon exchange of acetate to chloride, from (Zn)₅(OAc)₄(bibta)₃ to (Zn)₅(OAc_{0.16},Cl_{0.84})₄(bibta)₃, there is an increase in α , and upon exchange of Zn to Ni, as from (Zn_{0.77},Ni_{0.23})₅(OAc_{0.59},Cl_{0.41})₄(bibta)₃ to (Zn_{0.26},Ni_{0.74})₅(OAc_{0.08},Cl_{0.92})₄(bibta)₃, there is a decrease in α . There are multiple factors that can control whether a substitution will increase or decrease α , including modulation of pore size, modulation of pore hydrophobicity, or a change in the number of open metal sites that can coordinate water. The uptake behavior at low relative humidity for nickel-rich frameworks suggests that the four-coordinate nickel sites can bind 1-2 equivalents of water, while the zinc sites cannot (evidence for coordination of equivalents of water to the nickel sites is supported by the distinctive colorimetric change of the nickel-rich frameworks from red to green upon exposure to humidity). The additional waters bound to the nickel may seed the capillary condensation at lower relative humidity as they increase pore hydrophilicity. It is likely that the acetate causes the pores to be more hydrophilic than chloride due to additional hydrogen-bonding interactions of the acetate.

To quantify the effect of pore modulation on the relative humidity for capillary condensation, a thermodynamic model analogous to the Ostwald–Freundlich equation (also referred to as the Kelvin equation) was developed that describes the Gibbs free energy of binding water at the solid support-pore liquid interface (relative to the bulk liquid). Within this model, the mechanism for water adsorption may be considered capillary condensation. For the (Zn_{1-x},Ni_x)₅(OAc_{1-y},Cl_y)₄(bibta)₃ series, in which two sites can be continuously varied between two components, the model states,

$$\ln \alpha = c_1 + c_2 x' + c_3 y$$

where:

$$(x' = \frac{5}{4}x),$$

$$c_1 = \frac{2V}{ArkT} (\Delta G_{Zn} + \Delta G_{OAc} + \Delta G_{backbone}),$$

$$c_2 = \frac{2V}{ArkT} (\Delta G_{Ni} - \Delta G_{Zn}),$$

$$c_3 = \frac{2V}{ArkT} (\Delta G_{Cl} - \Delta G_{OAc}), \text{ and}$$

– 47 –

$\frac{2V}{ArkT}$ is a constant determined by the volume of a molecule of water, the projected surface area of a molecule of water on the MOF-pore water interface, the radius of the MOF pore, the Boltzmann constant, and temperature. Specifically, constants c_2 and c_3 encode the relative difference in Gibbs free energy of binding water to one component over the other. Approximation of the prefactor $\frac{2V}{ArkT}$ (using the kinetic diameter of water) may be used to estimate ΔG for binding water to one component over the other component (order of magnitude approximation, $\Delta G \approx 10$ kJ/mol). More quantitatively, the ratio $\frac{c_2}{c_3} = \frac{(\Delta G_{Ni} - \Delta G_{Zn})}{(\Delta G_{Cl} - \Delta G_{OAc})}$ is a physically meaningful parameter that does not depend on the prefactor. This ratio expresses the relative importance of substitution at each site.

10 Fitting the data, it was found that $\frac{c_2}{c_3} = -3.5$; thus, modulation of the cation from zinc to nickel affects the strength of binding water 3.5 times more than modulation of the anion from acetate to chloride (FIG. 13).

Infrared spectroscopy was used to characterize the nature of the water-framework interactions as a function of the relative humidity. Infrared spectra were recorded in

15 diffuse reflectance geometry with an inert gas carrying a controlled relative humidity flowing over the sample. The parent $Zn_5(OAc)_4(bibta)_3$ displays minimal interaction with water below the critical pressure for pore condensation (50%). The difference spectra can be fit to a broad feature that grows in a $3,385\text{ cm}^{-1}$ and a shoulder that maintains nearly constant intensity at $3,112\text{ cm}^{-1}$ (FIG. 14). The spectra for the nickel-

20 rich $(Zn_{0.40}, Ni_{0.60})_5(OAc_{0.05}, Cl_{0.95})_4(bibta)_3$ displays strong interaction with water below the critical pressure for pore condensation (27%), with a sharp feature at approximately $3,600\text{ cm}^{-1}$ (FIG. 10A). The difference spectra can be deconvoluted in three Gaussian peaks at $3,024$, $3,295$, and $3,521\text{ cm}^{-1}$. It is likely that the sharp feature around $3,600\text{ cm}^{-1}$ corresponds to water that is bound directly to nickel ions, which was not removed

25 by the initial activation at room temperature under a stream of inert gas.

By integrating the entire difference spectra, the quantity of water in the pores at each relative humidity was estimated, similar to a water isotherm (however, the extinction coefficients for the pore water are not necessarily identical), with spectral resolution (FIG. 15). The integrated difference spectra confirm the presence of water in

30 the Ni-rich material at relative humidity below the critical pressure for pore

condensation. These observations of direct water-nickel interactions are consistent with the increase in the maximum capacity for water sorption that is observed upon exchange of zinc to nickel, as there are additional binding pockets for the water to fill. An alternative possible explanation for the difference in maximum capacity could be that the Zn-rich frameworks immediately undergo partial decomposition upon initial exposure to humidity, decreasing the maximum capacity.

By performing variable temperature water isotherms for [Ni(60%),Cl(95%)] at 15, 25, and 35 °C, the isosteric enthalpy of adsorption, $-\Delta H$, of water to the frameworks was calculated (FIG. 16). Up to a loading of 1 mol of water per mol of Ni, $-\Delta H$ is approximately 52 kJ/mol. Above this loading, the isosteric enthalpy of adsorption decreases within the range of 38 to 45 kJ/mol. The increased interaction strength at the lowest loading is attributed to coordination of the waters to the nickel sites, whereas the lower interaction strength at higher loadings is attributed to water molecular binding to other waters within a hydrogen bonding network. This result agrees with the picture put forth by infrared spectroscopy. Outstandingly, the calculated isosteric enthalpy of adsorption is close to the enthalpy of vaporization for pure water (44 kJ/mol, 25 °C).

Extended cycling experiments confirmed significant differences in durability and recyclability among the various material compositions described above. Cycling of (Zn)₅(OAc)₄(bibta)₃ at 25 °C from 0 to 63% relative humidity revealed a significant loss of 12% in the maximum amount of water uptake over just 17 cycles. In contrast, cycling of (Zn_{0.40},Ni_{0.60})₅(OAc_{0.05},Cl_{0.95})₄(bibta)₃ at 25 °C from 0 to 35% relative humidity reveals minimal loss (1.9%) in working capacity for over 80 cycles. The feasibility of using [Ni(60%),Cl(95%)] for potable water production in arid regions was assessed by subjecting the MOF to a cycle of simulated desert day and night conditions. The daytime conditions included a temperature of 45 °C and a relative humidity of 5%, while the nighttime conditions were set at 25 °C and a relative humidity of 35%. Notably, the kinetics for desorption are dramatically improved upon elevation to 45 °C. The study showed that the MOF initially had a deliverable water capacity of 0.6 g/g. Comparatively, an extended cycling experiment for a similar high-loading Ni-based exchanged material, (Zn_{0.26},Ni_{0.74})₅(OAc_{0.08},Cl_{0.92})₄(bibta)₃, at 25 °C, with relative humidity ranging from 0 to 35%, showed only a minimal loss (5.7%) in working

capacity after more than 450 cycles (FIGS. 17A-17C). The higher stability of the nickel rich materials is attributed to the more kinetically inert Ni-triazolate bonds as compared to the Zn-triazolate bonds. An additional remarkable feature of these materials is their ability to release adsorbed water molecules at room temperature simply by reducing the relative humidity without requiring any heating to elevated temperatures. This portends a cost-effective and energy-efficient recycling process.

In comparison to other strategies, the incorporation of uniformly distributed strongly adsorbing Ni sites into this material offers additional advantages by enhancing the stability and overall capacity of the material while also allowing for flexibility in adjusting the operational relative humidity range. Further, the water adsorption uptake of $(\text{Zn}_{0.40}, \text{Ni}_{0.60})_5(\text{OAc}_{0.05}, \text{Cl}_{0.95})_4(\text{bibta})_3$ and $(\text{Zn}_{0.26}, \text{Ni}_{0.74})_5(\text{OAc}_{0.08}, \text{Cl}_{0.92})_4(\text{bibta})_3$ was evaluated in comparison with the-best performing materials for water capture with α below 30% RH (FIG. 11). The results demonstrated that these materials ranked among the top adsorbents in terms of their high adsorption capacity at low humidity levels. Critically, this low humidity regime between 10 and 30% relative humidity is useful for atmospheric water harvesting. Sorbents have a higher efficiency than dew plates, fog nets, and membranes systems for water harvesting in the regime of $\sim 20\text{--}30^\circ\text{C}$ at 20–30% relative humidity, as well as higher efficiency than both dew plates and fog nets in the 10–20% relative humidity at the same temperature range. The capability of modulating the relative humidity for pore condensation of $\text{M}_5\text{X}_4(\text{bibta})_3$ also offers the possibility for designing a multistage dehumidification system. Given the relatively fast kinetics for sorption, minimal hysteresis, and high capacity, a multistage desiccant wheel system is envisioned in which each stage in the system uptakes water at a progressively lower relative humidity.

In summary, the systematic synthetic modifications of the $(\text{Zn}_{1-x}, \text{Ni}_x)_5(\text{OAc}_{1-y}, \text{Cl}_y)_4(\text{bibta})_3$ MOF platform advance the fundamental knowledge of water adsorption in confined space. Moreover, they introduce a promising class of new adsorbent compositions characterized by their high water capacity, particularly at low relative humidity levels ($<30\%$). These synthetically scalable adsorbents further exhibit remarkable long-term stability, emphasizing their potential for practical applications.

The approach presented in this study offers the opportunity to extend its findings to incorporate various hydrophobic and hydrophilic anions. The introduction of nickel as a modulating cation enables the adjustment of the relative humidity range in which water uptake occurs and enhances the hydrolytic stability of the new MOFs. As described, the particular platform involving bibta ligands holds potential for a wide range of water sorption applications. By expanding the understanding of water confinement and leveraging the ability to tailor material properties, this research opens new avenues for the development of advanced materials with enhanced water sorption capacities.

Unless otherwise noted, all materials were acquired from commercial sources and used without further purification: N,N-dimethylformamide (Millipore Sigma, 98%), N-methylformamide (Millipore Sigma, 99%), methanol (Millipore Sigma, 99.8%), zinc acetate dihydrate (Sigma Aldrich, 99%), nickel chloride hexahydrate (Millipore Sigma, 99.9%), nickel acetate (Strem, 98%), [1,1'-biphenyl]-3,3',4,4'-tetraamine (AmBeed, 98%).

Powder X-ray diffraction (PXRD) patterns were recorded using A Bruker Advance II diffractometer with $\theta/2\theta$ reflection geometry and Ni-filtered Cu K α radiation ($K_{\alpha 1} = 1.5406 \text{ \AA}$, $K_{\alpha 2} = 1.5444 \text{ \AA}$, $K_{\alpha 2}/K_{\alpha 1} = 0.5$). The tube voltage and current were set at 40 kV and 40 mA, respectively. Thin layers of the samples were placed on zero-background silicon crystal plates before PXRD measurements.

Elemental analyses were carried out at Robertson Microlit Laboratories in Ledgewood, New Jersey. Measurements were performed in duplicate.

The number of water molecules in the formula unit was calculated by performing a regression on the following three equations. The chlorine percentage was taken from the NMR digestion experiments and the nickel content was taken from the ICP-MS experiments. Given that there are three dependent variables (C, H, N) and only one independent variable (H₂O), each equation was solved separately, and the average value was used for the number of water molecules.

$$1) \text{ Carbon Content} = (12.01 * (36 + 4 * 2 * (1 - \text{Cl}\%))) / \text{Total}$$

$$2) \text{ Hydrogen Content} = (1.01 * (18 + 4 * 3 * (1 - \text{Cl}\%)) + 1.05 * 2 * [\text{H}_2\text{O}\#]) /$$

Total

– 51 –

$$3) \text{ Nitrogen Content} = (14.04 * 18) / \text{Total}$$

$$4) \text{ Other} = (34.45 * (4 * \text{Cl}\%) + 58.69 * (5 * \text{Ni}\%) + 16.00 * (2 * 4 * (1 - \text{Cl}\%)) + 65.38 * (5 * (1 - \text{Ni}\%))) / \text{Total}$$

$$\text{Total} = \text{Carbon Content} + \text{Hydrogen Content} + \text{Nitrogen Content} + \text{Other}$$

5 Nitrogen adsorption isotherms were measured by a volumetric method using a Micromeritics ASAP 2020 Plus gas sorption analyzer. Typical samples of 30-60 mg were loaded into a pre-weighed analysis tube and capped with a Micromeritics TranSeal. The tube was activated at 150 °C on the degas port of the gas sorption analyzer for 24 hours and cooled to room temperature. The tube was then reweighed to determine the
10 mass of the sample and the pre-weighed tube. Free space correction measurements were performed using ultra-high purity He gas (UHP grade 5, 99.999% pure). Nitrogen isotherms were measured using UHP grade nitrogen. All nitrogen analyses were performed using a liquid nitrogen bath at 77 K. Oil-free vacuum pumps were used to prevent contamination of sample or feed gases.

15 Water vapor adsorption isotherms were measured by a volumetric method using a Micromeritics ASAP 2020 gas sorption analyzer with a vapor dose option and a heated manifold. To prepare for the analysis, a sample tube equipped with a Micromeritics TranSeal was weighed after being dried in an oven. Then, a typical 50 mg of MOF, pre-activated at 150°C to remove any residual solvent, was loaded into the pre-weighed
20 analysis tube. Finally, the tube containing the sample was transferred to the analysis port of the gas sorption analyzer. For free space correction measurements, ultra-high purity He gas was used. Milli-Q water was used for measuring water vapor adsorption isotherms, which was degassed on the ASAP 2020 manifold prior to measurement. The water analyses were conducted using water baths held at a constant temperature with a
25 recirculating chiller, and the manifold was kept 10 °C above the temperature of the sample water bath. The vapor dosing tube was also held 15°C above the temperature of the sample water bath. Oil-free vacuum pumps were employed to prevent any contamination of sample or feed gases.

Variable-temperature water vapor adsorption isotherms and water cycling
30 experiments were conducted using a gravimetric method with a Hiden Analytical XEMIS microbalance equipped with a vapor dose option and a heated manifold. A

– 52 –

typical sample of MOF weighing approximately 5 mg was loaded into the microbalance basket and subjected to external furnace activation at 150°C. The water analyses were carried out using a programmable water bath with a recirculating chiller, and oil-free vacuum pumps were utilized to avoid any sample or feed gas contamination.

5 Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were performed using a Bruker Tensor 37 IR spectrometer equipped with a liquid nitrogen cooled mercury cadmium telluride detector and a Pike DiffusIR™ accessory. Samples were loaded under air and diluted with KBr in a ratio of about 1:25-100 (MOF:KBr). The sample was activated under a constant flow of 500 sccm argon or
10 dry air. Dosing was performed by mixing a flow of inert gas with a flow of inert gas passed through a fritted bubbler filled with water. The relative humidity of the outflow was measured during the experiment to confirm that the fritted bubbler fully saturated the gas stream with water.

 Scanning electron microscopy (SEM) was conducted on a Zeiss Merlin high-
15 resolution scanning electron microscope with an InLens detector at a voltage of 1–3 V and current of 100–150 pA.

¹H NMR spectroscopy was conducted on a Bruker Avance-III HD Nanobay spectrometer (400 MHz) or Bruker Avance Neo spectrometer (400 MHz). ¹H NMR spectra are internally referenced to the residual solvent signal at $\delta = 2.50$ (DMSO-*d*₆).
20 MOF samples were digested prior to ¹H NMR analysis by sonicating in trifluoroacetic acid, heating to 60 °C until complete dissolution (2-18 hours), then diluting with DMSO-*d*₆ (4:1 TFA:DMSO-*d*₆).

 Inductively coupled plasma mass spectrometry (ICP-MS) data was collected using an Agilent 7900 ICP-MS spectrometer. Calibration standards were prepared for
25 ICP-MS analysis using analytical standard solutions purchased from VWR Chemicals BDH Aristar Plus and an aqueous 2% HNO₃ solution (prepared from EMD Millipore OmniTrace HNO₃ and ultrafiltered water). Digestion of samples was performed in concentrated HNO₃ (67-70%, OmniTrace Ultra, EMD Millipore).

 5,5'-bibenzotriazole (H₂bibta) was synthesized according to the following
30 procedure: A 250 mL round-bottom flask equipped with a stir bar under an atmosphere of air was charged with 3,3'-diaminobenzidine (2.0 g, 9.34 mmol, 1 equiv.) followed by

– 53 –

acetic acid (26 mL) and water (2 mL). The solution was cooled to 0 °C under vigorous stirring, then a solution of NaNO₂ (1.42 g, 20.55 mmol, 2.2 equiv.) in water (2.2 mL) was added dropwise over 5 minutes. The mixture was stirred at 0 °C for an additional hour. The resulting tan precipitate was filtered off and washed with 1 M HCl (50 mL),
5 water (50 mL), and methanol (5 × 50 mL). The solid was dried under vacuum to afford a tan solid (1.95 g, 88% yield).

Zn₅(OAc)₄(bibta)₃ was synthesized according to the following procedure: A suspension of 5,5'-bibenzotriazole (H₂bibta, 2 g, 8.47 mmol, 1 equiv.) in *N*-methylformamide (800 mL) was sonicated for 10 minutes to afford a yellow/orange
10 solution. To this solution was added zinc acetate dihydrate (7.8 g, 35.5 mmol, 4.2 equiv.), and the resulting suspension was sonicated for five minutes to afford a light tan suspension. The jar was placed in an oven preheated to 90 °C and left for 3 days. The solution was allowed to cool to room temperature, then decanted. The solid was suspended in *N,N*-dimethylformamide (30 mL), left overnight, then decanted, repeating
15 this process a total of three times. After completing the washes with DMF, the solid was resuspended in 30 mL methanol, left overnight, then decanted, repeating this process a total of three times. The solid was dried under vacuum at 150 °C overnight to afford a light tan powder (2.64 g, 76% yield).

An alternative preparation of Zn₅(OAc)₄(bibta)₃ was developed employing DMF:
20 In a screw top 250 mL media bottle 0.740 g of Zn(OAc)₂·2H₂O (3.39 mmol, 4 equiv.) was dissolved in 80 mL of DMF, 4mL of acetic acid. The mixture was sonicated to ensure complete dissolution of the solids. H₂bibta (0.2 g, 0.84 mmol, 1 eq) was added and the bottle was tightly sealed and heated to preheated oven 120 °C for 48 hours. The precipitated light brown powder was washed with DMF three times. After completing
25 the washes with DMF, the solid was resuspended in methanol, left overnight, then decanted, repeating this process a total of three times. The solid was dried under vacuum at 150 °C overnight to afford a light tan powder.

ZnCl₂ exchange was performed by stirring CFA-1 in a solution of zinc chloride in DMF at 80 °C.

30 Synthesis of (Zn)₅(OAc_{0.16},Cl_{0.84})₄(bibta)₃: To a solution of ZnCl₂ (1.09 g, 8 mmol) in *N,N*-dimethylformamide (20 mL) was added CFA-1 (Zn₅(OAc)₄(bibta)₃, 100

mg, 80 μ mol). The resulting suspension was stirred at 80 °C for 18 hours, then filtered (fine glass frit), washing extensively with N,N-dimethylformamide. The solid was suspended in N,N-dimethylformamide (30 mL), stirred at 80 °C for 3 hours, then filtered, washing extensively with N,N-dimethylformamide. The solid was suspended in 30 mL of DMF, left overnight, then decanted, repeating this process a total of three times. After completing the washes with DMF, the solid was resuspended in 30 mL methanol, left overnight, then decanted, repeating this process a total of three times. The solid was dried under vacuum at 150 °C overnight.

NiCl₂ exchange was performed by stirring CFA-1 in a solution of nickel chloride hexahydrate in DMF at 40-80 °C.

(Zn_{0.77},Ni_{0.23})₅(OAc_{0.59},Cl_{0.41})₄(bibta)₃: To a solution of NiCl₂ • 6 H₂O (46.0 mg, 0.11 mmol) in N,N-dimethylformamide (20 mL) was added CFA-1 (Zn₅(OAc)₄(bibta)₃, 100 mg, 80 μ mol). The resulting suspension was stirred at 40 °C for 4 days, then filtered (fine glass frit), washing extensively with N,N-dimethylformamide. The solid was suspended in 30 mL of DMF, left overnight, then decanted, repeating this process a total of three times. After completing the washes with DMF, the solid was resuspended in 30 mL methanol, left overnight, then decanted, repeating this process a total of three times. The solid was dried under vacuum at 150 °C overnight.

(Zn_{0.55},Ni_{0.45})₅(OAc_{0.24},Cl_{0.76})₄(bibta)₃: To a solution of NiCl₂ • 6 H₂O (200.7 mg, 0.84 mmol) in N,N-dimethylformamide (20 mL) was added CFA-1 (Zn₅(OAc)₄(bibta)₃, 100 mg, 80 μ mol). The resulting suspension was stirred at 40 °C for 4 days, then filtered (fine glass frit), washing extensively with N,N-dimethylformamide. The solid was suspended in 30 mL of DMF, left overnight, then decanted, repeating this process a total of three times. After completing the washes with DMF, the solid was resuspended in 30 mL methanol, left overnight, then decanted, repeating this process a total of three times. The solid was dried under vacuum at 150 °C overnight.

(Zn_{0.40},Ni_{0.60})₅(OAc_{0.05},Cl_{0.95})₄(bibta)₃: To a solution of NiCl₂ • 6 H₂O (9.4 g, 39.5 mmol) in N,N-dimethylformamide (200 mL) was added CFA-1 (Zn₅(OAc)₄(bibta)₃, 1.0 g, 0.80 mmol). The resulting suspension was stirred at 80 °C for 18 hours, then filtered (fine glass frit), washing extensively with N,N-dimethylformamide. The solid was suspended in 30 mL of DMF, left overnight, then decanted, repeating this process a total

of three times. After completing the washes with DMF, the solid was resuspended in 30 mL methanol, left overnight, then decanted, repeating this process a total of three times. The solid was dried under vacuum at 150 °C overnight.

(Zn_{0.39},Ni_{0.61})₅(OAc_{0.09},Cl_{0.91})₄(bibta)₃: To a solution of NiCl₂ • 6 H₂O (790.7 mg, 3.33 mmol) in N,N-dimethylformamide (20 mL) was added CFA-1 (Zn₅(OAc)₄(bibta)₃, 100 mg, 80 μmol). The resulting suspension was stirred at 40 °C for 4 days, then filtered (fine glass frit), washing extensively with N,N-dimethylformamide. The solid was suspended in 30 mL of DMF, left overnight, then decanted, repeating this process a total of three times. After completing the washes with DMF, the solid was resuspended in 30 mL methanol, left overnight, then decanted, repeating this process a total of three times. The solid was dried under vacuum at 150 °C overnight.

(Zn_{0.26},Ni_{0.74})₅(OAc_{0.08},Cl_{0.92})₄(bibta)₃: To a solution of NiCl₂ • 6 H₂O (790.7 mg, 3.33 mmol) in N,N-dimethylformamide (20 mL) was added CFA-1 (Zn₅(OAc)₄(bibta)₃, 100 mg, 80 μmol). The resulting suspension was stirred at 80 °C for 3 days, then filtered (fine glass frit), washing extensively with N,N-dimethylformamide. The solid was suspended in 30 mL of DMF, left overnight, then decanted, repeating this process a total of three times. After completing the washes with DMF, the solid was resuspended in 30 mL of methanol, left overnight, then decanted, repeating this process a total of three times. The solid was dried under vacuum at 150 °C overnight.

Ni(OAc)₂ exchange was performed by stirring CFA-1 in a solution of nickel acetate in DMF at 80 °C.

(Zn_{0.78},Ni_{0.22})₅(OAc)₄(bibta)₃: To a solution of Ni(OAc)₂ • 4 H₂O (500 mg, 2.0 mmol) in N,N-dimethylformamide (50 mL) was added CFA-1 (Zn₅(OAc)₄(bibta)₃, 100 mg, 80 μmol). The resulting suspension was stirred at 80 °C for 3 days, then filtered (fine glass frit), washing extensively with N,N-dimethylformamide. The solid was suspended in 30 mL of DMF, left overnight, then decanted, repeating this process a total of three times. After completing the washes with DMF, the solid was resuspended in 30 mL of methanol, left overnight, then decanted, repeating this process a total of three times. The solid was dried under vacuum at 150 °C overnight.

– 56 –

LiOAc exchange was performed by stirring Ni(70%)-CFA-1 in a solution of lithium acetate in methanol at room temperature based on a procedure employed for the synthesis of acetate-exchanged Co-MFU-4l.

(Zn_{0.30},Ni_{0.70})₅Cl₄(bibta)₃: To a solution of NiCl₂ • 4 H₂O (9.4 g) in N,N-dimethylformamide (200 mL) in a 500 mL round bottom flask equipped with a stir bar was added CFA-1 (1 g). The reaction mixture was stirred at 80 °C overnight. The reaction mixture was filtered, washing extensively with N,N-dimethylformamide. The resulting solid was suspended in 30 mL of N,N-dimethylformamide, left overnight, then decanted, repeating this process a total of three times. After completing the washes with N,N-dimethylformamide, the solid was resuspended in 30 mL methanol, left overnight, then decanted, repeating this process a total of three times. The solid was dried under vacuum at 150 °C overnight to afford a light orange powder.

(Zn_{0.33},Ni_{0.67})₅(OAc_{0.96},Cl_{0.04})₄(bibta)₃: To a solution of LiOAc (660 mg, 10 mmol) in methanol (20 mL) was added (Zn_{0.30},Ni_{0.70})₅Cl₄(bibta)₃ (100 mg, 87 μmol). The resulting suspension was stirred at room temperature for 1 day, then filtered (fine glass frit), washing extensively with methanol. The solid was suspended in 30 mL of methanol, left overnight, then decanted, repeating this process a total of three times. The solid was dried under vacuum at 150 °C overnight.

It should be understood that the subject matter defined in the appended claims is not necessarily limited to the specific implementations described above. The specific implementations described above are disclosed as examples only. While several embodiments of the present disclosure have been described and illustrated herein, those of ordinary skill in the art will readily envision a variety of other means and/or structures for performing the functions and/or obtaining the results and/or one or more of the advantages described herein, and each of such variations and/or modifications is deemed to be within the scope of the present disclosure. More generally, those skilled in the art will readily appreciate that all parameters, dimensions, materials, and configurations described herein are meant to be exemplary and that the actual parameters, dimensions, materials, and/or configurations will depend upon the specific application or applications for which the teachings of the present disclosure is/are used. Those skilled in the art will

recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the disclosure described herein. It is, therefore, to be understood that the foregoing embodiments are presented by way of example only and that, within the scope of the appended claims and equivalents thereto, the disclosure may be practiced otherwise than as specifically described and claimed. The present disclosure is directed to each individual feature, system, article, material, and/or method described herein. In addition, any combination of two or more such features, systems, articles, materials, and/or methods, if such features, systems, articles, materials, and/or methods are not mutually inconsistent, is included within the scope of the present disclosure.

The indefinite articles “a” and “an,” as used herein in the specification and in the claims, unless clearly indicated to the contrary, should be understood to mean “at least one.”

The phrase “and/or,” as used herein in the specification and in the claims, should be understood to mean “either or both” of the elements so conjoined, i.e., elements that are conjunctively present in some cases and disjunctively present in other cases. Other elements may optionally be present other than the elements specifically identified by the “and/or” clause, whether related or unrelated to those elements specifically identified unless clearly indicated to the contrary. Thus, as a non-limiting example, a reference to “A and/or B,” when used in conjunction with open-ended language such as “comprising” can refer, in one embodiment, to A without B (optionally including elements other than B); in another embodiment, to B without A (optionally including elements other than A); in yet another embodiment, to both A and B (optionally including other elements); etc.

As used herein in the specification and in the claims, “or” should be understood to have the same meaning as “and/or” as defined above. For example, when separating items in a list, “or” or “and/or” shall be interpreted as being inclusive, i.e., the inclusion of at least one, but also including more than one, of a number or list of elements, and, optionally, additional unlisted items. Only terms clearly indicated to the contrary, such as “only one of” or “exactly one of,” or, when used in the claims, “consisting of,” will refer to the inclusion of exactly one element of a number or list of elements. In general, the term “or” as used herein shall only be interpreted as indicating exclusive alternatives

(i.e. “one or the other but not both”) when preceded by terms of exclusivity, such as “either,” “one of,” “only one of,” or “exactly one of.” “Consisting essentially of,” when used in the claims, shall have its ordinary meaning as used in the field of patent law.

As used herein in the specification and in the claims, the phrase “at least one,” in reference to a list of one or more elements, should be understood to mean at least one element selected from any one or more of the elements in the list of elements, but not necessarily including at least one of each and every element specifically listed within the list of elements and not excluding any combinations of elements in the list of elements. This definition also allows that elements may optionally be present other than the elements specifically identified within the list of elements to which the phrase “at least one” refers, whether related or unrelated to those elements specifically identified. Thus, as a non-limiting example, “at least one of A and B” (or, equivalently, “at least one of A or B,” or, equivalently “at least one of A and/or B”) can refer, in one embodiment, to at least one, optionally including more than one, A, with no B present (and optionally including elements other than B); in another embodiment, to at least one, optionally including more than one, B, with no A present (and optionally including elements other than A); in yet another embodiment, to at least one, optionally including more than one, A, and at least one, optionally including more than one, B (and optionally including other elements); etc.

As used herein, “wt.%” is an abbreviation of weight percentage. As used herein, “at.%” is an abbreviation of atomic percentage.

Some embodiments may be embodied as a method, of which various examples have been described. The acts performed as part of the methods may be ordered in any suitable way. Accordingly, embodiments may be constructed in which acts are performed in an order different than illustrated, which may include different (e.g., more or less) acts than those that are described, and/or that may involve performing some acts simultaneously, even though the acts are shown as being performed sequentially in the embodiments specifically described above.

Use of ordinal terms such as “first,” “second,” “third,” etc., in the claims to modify a claim element does not by itself connote any priority, precedence, or order of one claim element over another or the temporal order in which acts of a method are

– 59 –

performed, but are used merely as labels to distinguish one claim element having a certain name from another element having a same name (but for use of the ordinal term) to distinguish the claim elements.

5 In the claims, as well as in the specification above, all transitional phrases such as “comprising,” “including,” “carrying,” “having,” “containing,” “involving,” “holding,” and the like are to be understood to be open-ended, i.e., to mean including but not limited to. Only the transitional phrases “consisting of” and “consisting essentially of” shall be closed or semi-closed transitional phrases, respectively, as set forth in the United States Patent Office Manual of Patent Examining Procedures, Section 2111.03.

– 60 –

CLAIMS

What is claimed is:

- 5 1. A composition, comprising:
a metal-organic framework of the form $[(M_xZn_{1-x})_5(X_y(OAc)_{1-y})_4(\text{ligand})_3]$,
wherein:
M is a divalent metal cation,
X is a monovalent anion,
10 OAc is acetate,
ligand is a dianionic nitrogen-containing heterocyclic compound,
x is greater than 0 and less than 1, and
y is: (i) greater than 0 and less than or equal to 0.2; or (ii) greater than or
equal to 0.4 and less than 1.
15
2. The composition of claim 1, wherein x is greater than or equal to 0.2, greater
than or equal to 0.4, greater than or equal to 0.6, or greater than or equal to 0.7.
3. The composition of any one of claims 1-2, wherein x is greater than or equal to
20 0.23, greater than or equal to 0.45, greater than or equal to 0.6, greater than or equal to
0.61, greater than or equal to 0.67, or greater than or equal to 0.74.
4. The composition of any one of claims 1-3, wherein M is selected from the group
consisting of a divalent Ni cation and a divalent Co cation.
25
5. The composition of any one of claims 1-4, wherein y is greater than or equal to
0.8 or greater than or equal to 0.9.
6. The composition of any one of claims 1-5, wherein y is greater than or equal to
30 0.91, greater than or equal to 0.92, or greater than or equal to 0.95.
7. The composition of any one of claims 1-4, wherein y is less than or equal to 0.1.

– 61 –

8. The composition of any one of claims 1-4 and 7, wherein y is less than or equal to 0.04.
- 5 9. The composition of any one of claims 1-8, wherein X is chloride.
10. The composition of any one of claims 1-5 and 9, wherein:
x is greater than or equal to 0.6,
M is selected from the group consisting of a Ni divalent cation and a Co divalent
10 cation,
y is greater than or equal to 0.8, and
X is chloride.
11. The composition of any one of claims 1-4 and 7-9, wherein:
15 x is greater than or equal to 0.6,
M is selected from the group consisting of a divalent Ni cation and a divalent Co
cation,
y is less than or equal to 0.1, and
X is chloride.
- 20 12. The composition of any one of claims 1-11, wherein ligand is 5,5'-
bibenzotriazole.
13. A composition, comprising:
25 a metal-organic framework of the form $[(\text{Zn})_5(\text{X}_y(\text{OAc})_{1-y})_4(\text{ligand})_3]$, wherein:
X is a monovalent anion,
OAc is acetate,
ligand is a dianionic nitrogen-containing heterocyclic compound, and
y is greater than or equal to 0.8 and less than 1.
- 30 14. The composition of claim 13, wherein y is greater than or equal to 0.84.

– 62 –

15. The composition of any one of claims 13-14, wherein X is chloride.
16. The composition of any one of claims 13-15, wherein ligand is 5,5'-bibenzotriazolate.
- 5 17. A method, comprising:
exposing the composition of any one of claims 1-16 to a target species such that the metal-organic framework adsorbs the target species.
- 10 18. The method of claim 17, wherein the target species is water.
19. The method of any one of claims 17-18, wherein a water uptake capacity of the metal-organic framework is greater than or equal to 0.65 g of H₂O per gram of the metal-organic framework.
- 15 20. The method of claim 19, wherein the water uptake capacity of the metal-organic framework is greater than or equal to 0.70 g of H₂O per gram of the metal-organic framework.
- 20 21. The method of any one of claims 17-20, wherein exposing the composition to the target species comprises exposing the composition to a mixture of species comprising the target species.
22. The method of claim 21, wherein the target species is a gas and the mixture of
25 species comprises one or more additional gases.
23. The method of claim 22, wherein the mixture of species has a relative humidity greater than or equal to 10% RH and less than or equal to 80% RH.
- 30 24. The method of claim 21, wherein the target species is a liquid and the mixture of species comprises one or more additional liquids.

– 63 –

25. The method of claim 24, wherein the mixture of species has an equilibrium relative humidity greater than or equal to 10% ERH and less than or equal to 80% ERH.
26. A method, comprising:
- 5 exposing a compound of the form MX^1_2 to a first metal-organic framework of the form $[\text{Zn}_5\text{X}^2_4(\text{ligand})_3]$, thereby forming a second metal-organic framework of the form $[(\text{M}_x\text{Zn}_{1-x})_5(\text{X}^1_y\text{X}^2_{1-y})_4(\text{ligand})_3]$, wherein:
- M is a divalent metal cation,
X¹ and X² are different, and each of X¹ and X² is a monovalent anion,
10 ligand is a dianionic nitrogen-containing heterocyclic compound, and
x is less than y.
27. The method of claim 26, wherein M is selected from the group consisting of a divalent Ni cation, a divalent Co cation, and a divalent Zn cation.
- 15 28. The method of any one of claims 26-27, wherein x is greater than or equal to 0.6 and less than 1.
29. The method of any one of claims 26-28, wherein y is greater than or equal to 0.8
20 and less than 1.
30. The method of any one of claims 26-29, wherein X¹ is Cl.
31. The method of any one of claims 26-30, wherein X² is acetate (OAc).
- 25 32. The method of any one of claims 26-31, wherein ligand is 5,5'-bibenzotriazole.

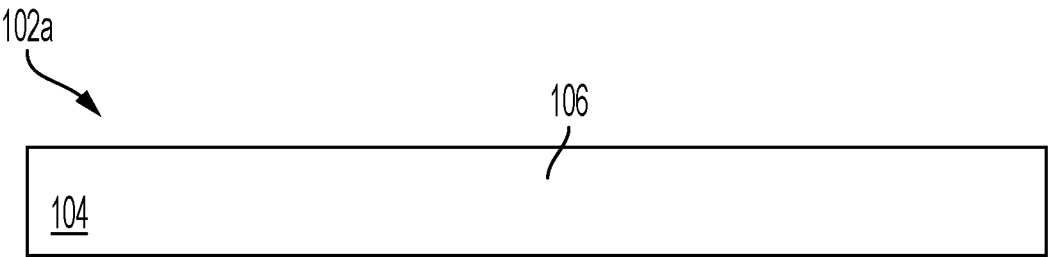


FIG. 1A

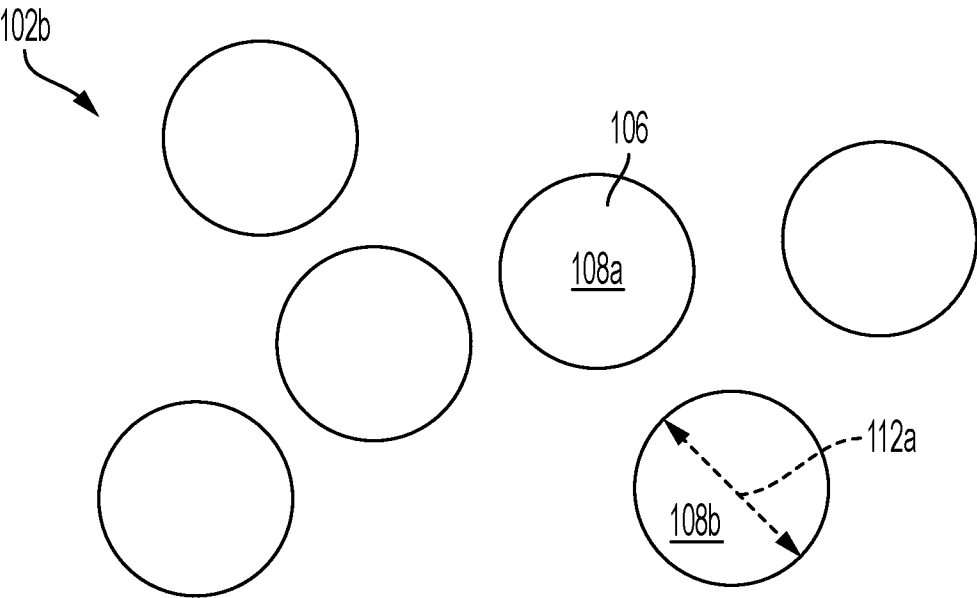


FIG. 1B

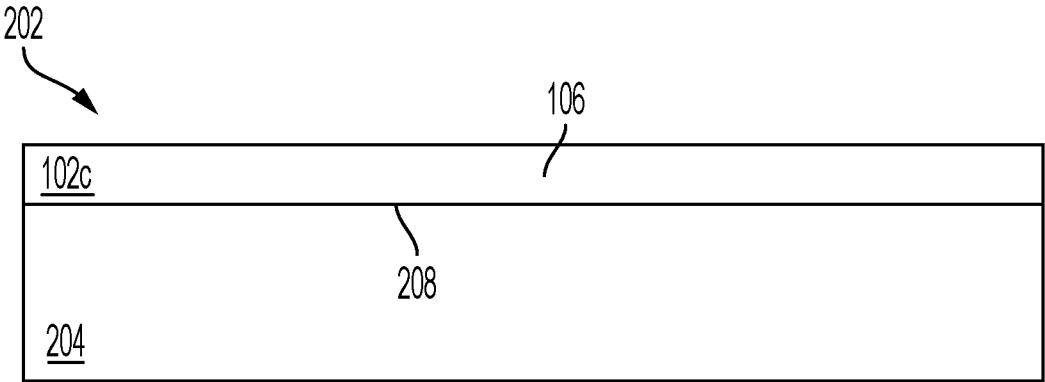


FIG. 2

3/20

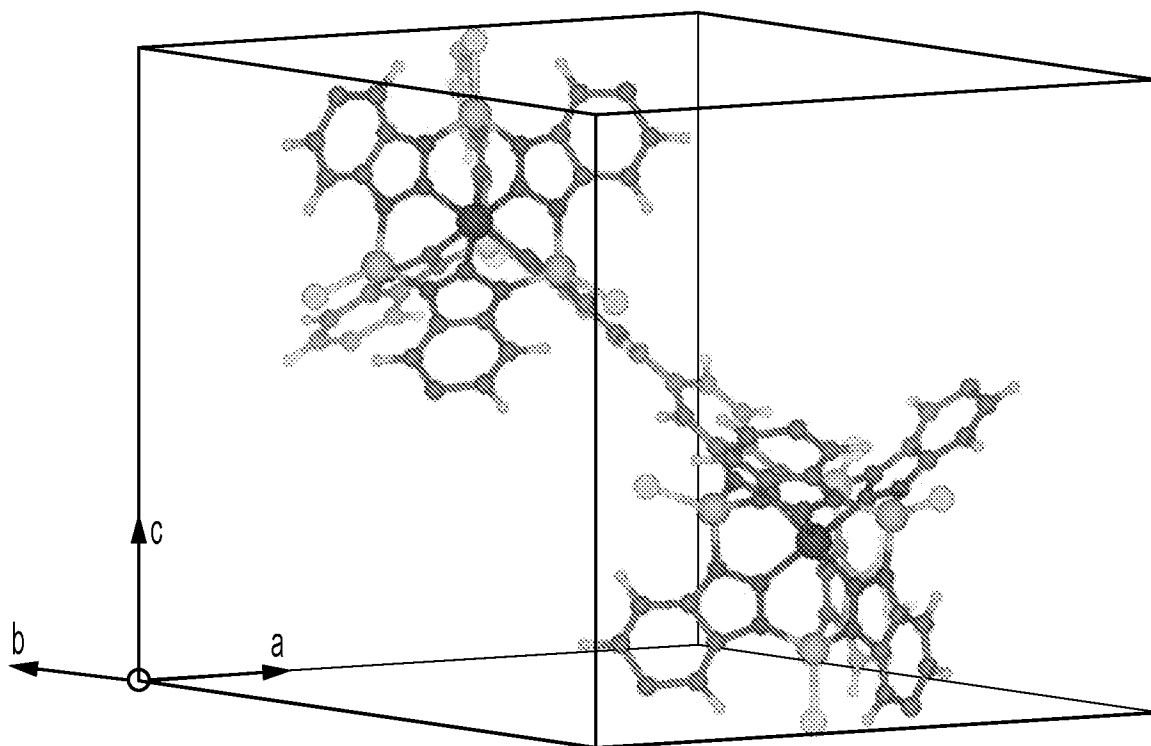


FIG. 3A

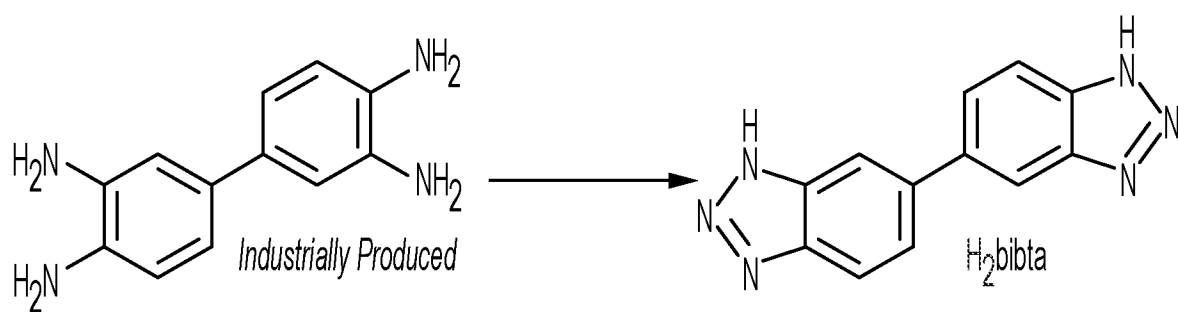


FIG. 3B

4/20

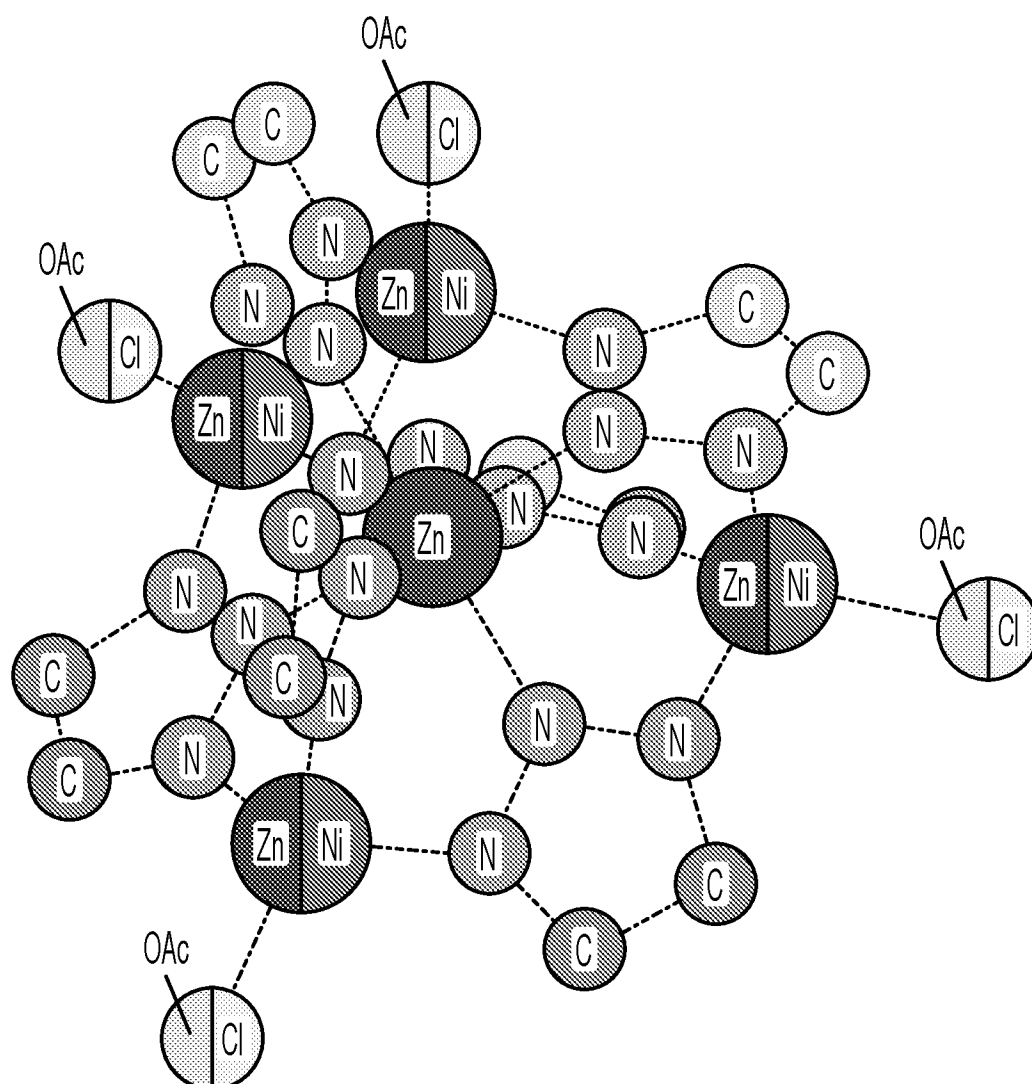


FIG. 3C

5/20

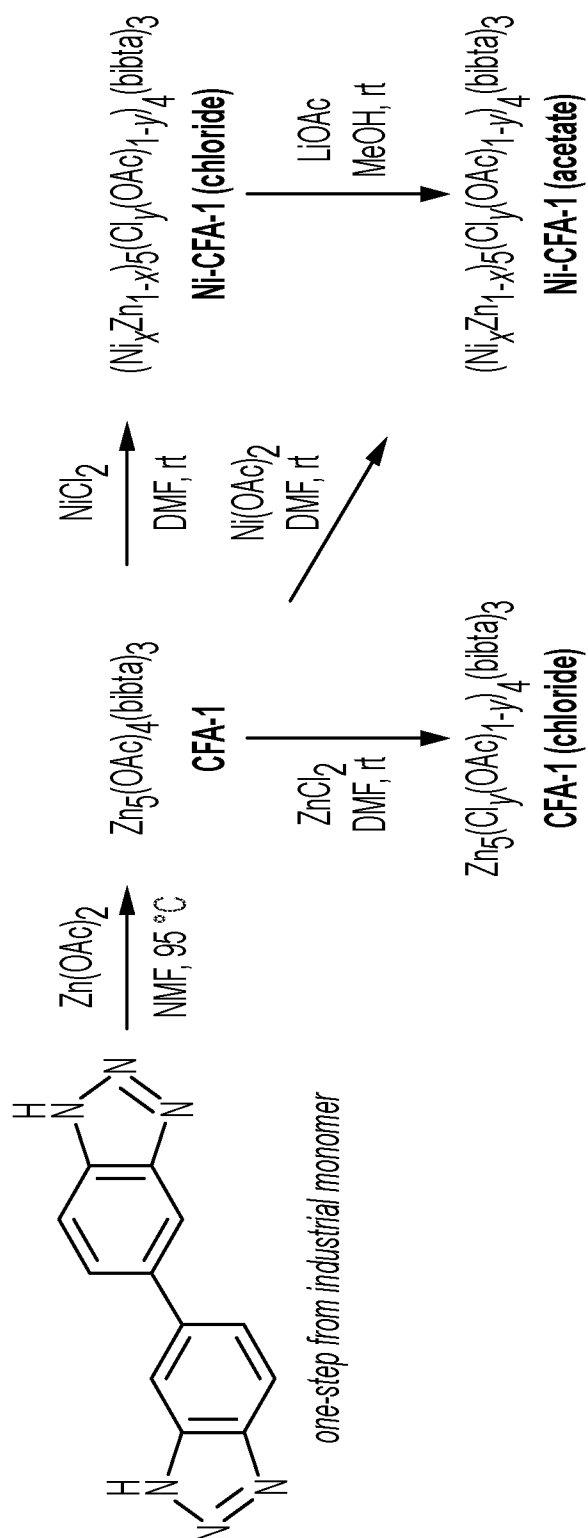


FIG. 4

6/20

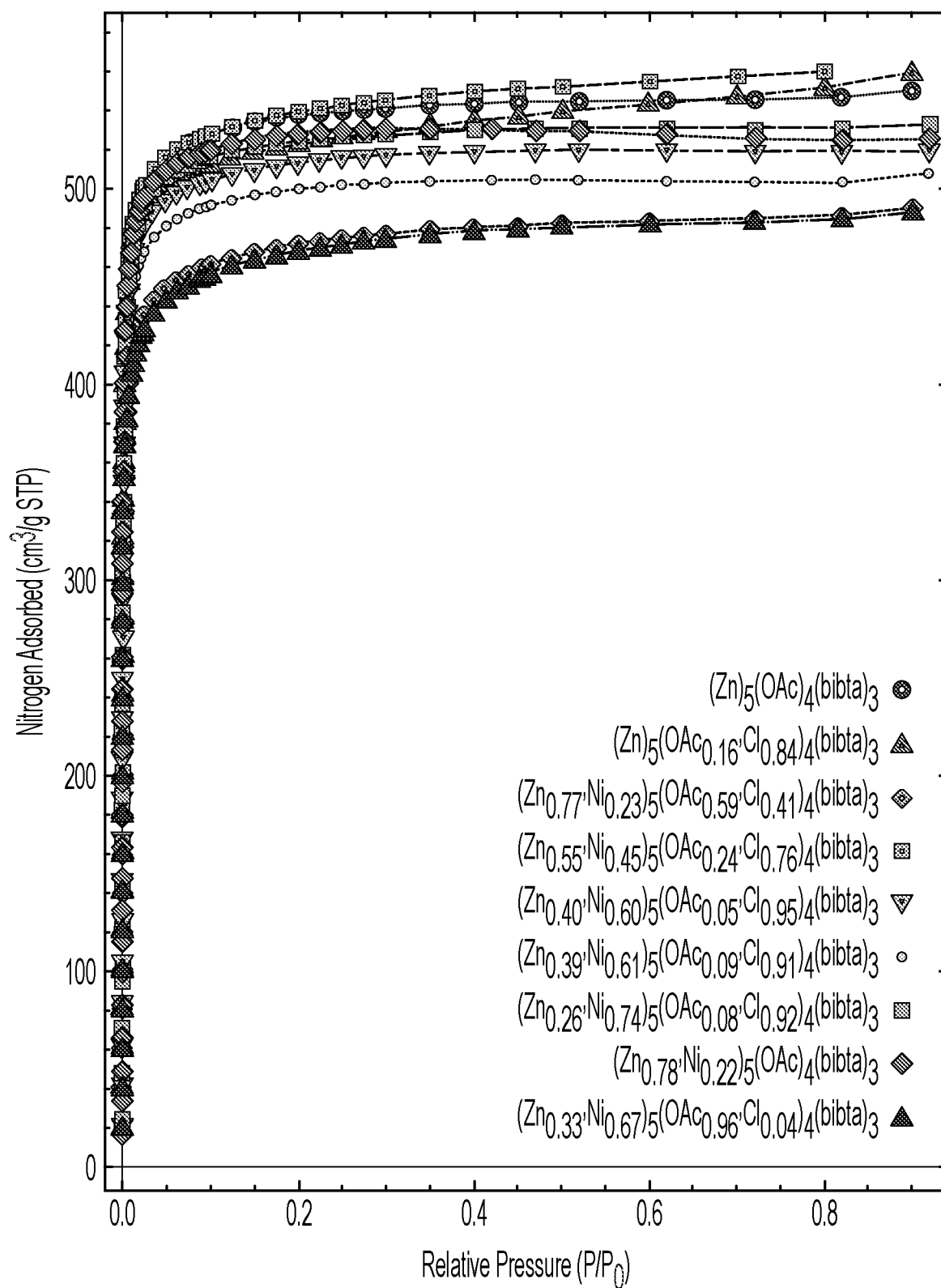


FIG. 5A

7/20

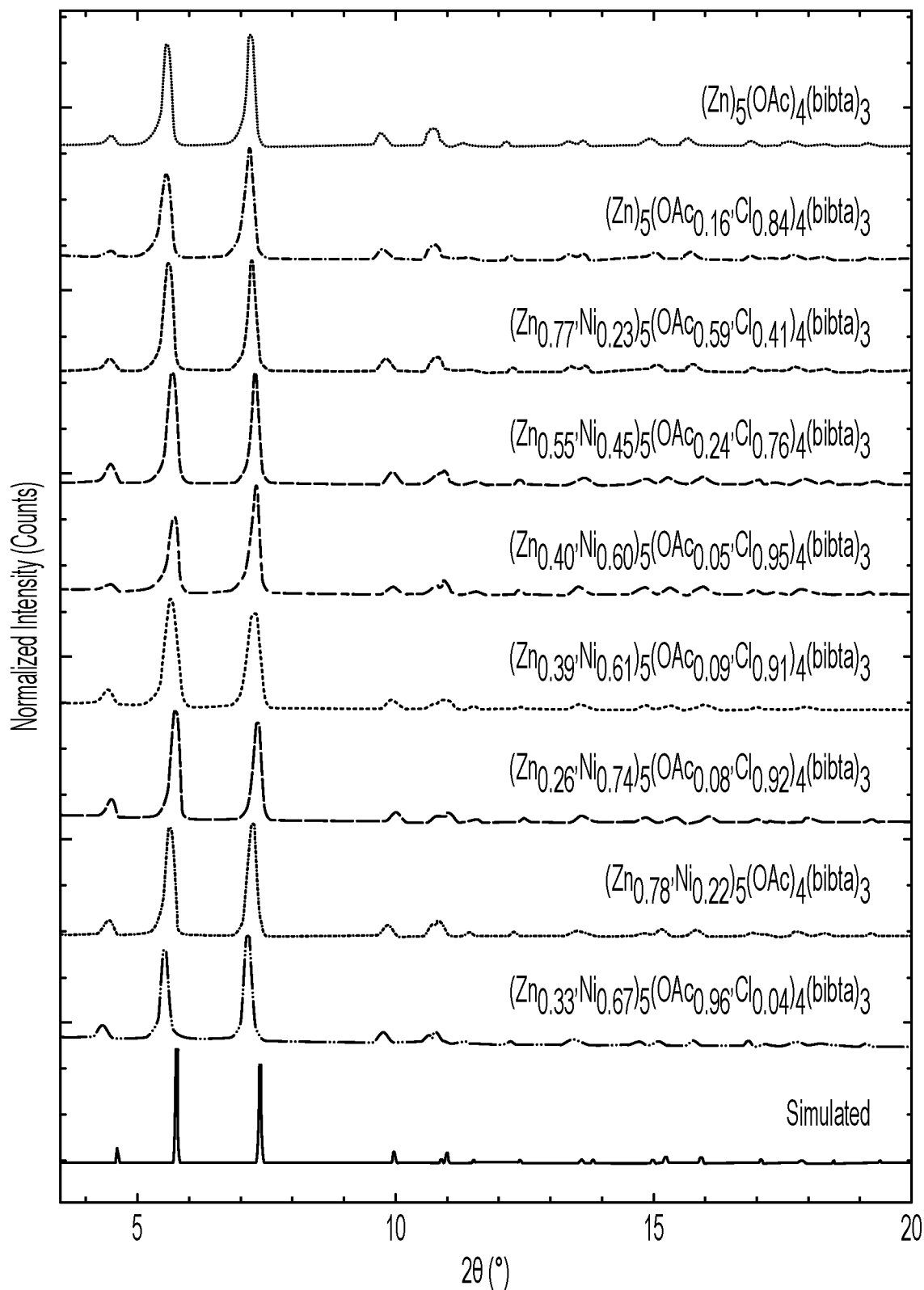


FIG. 5B

8/20

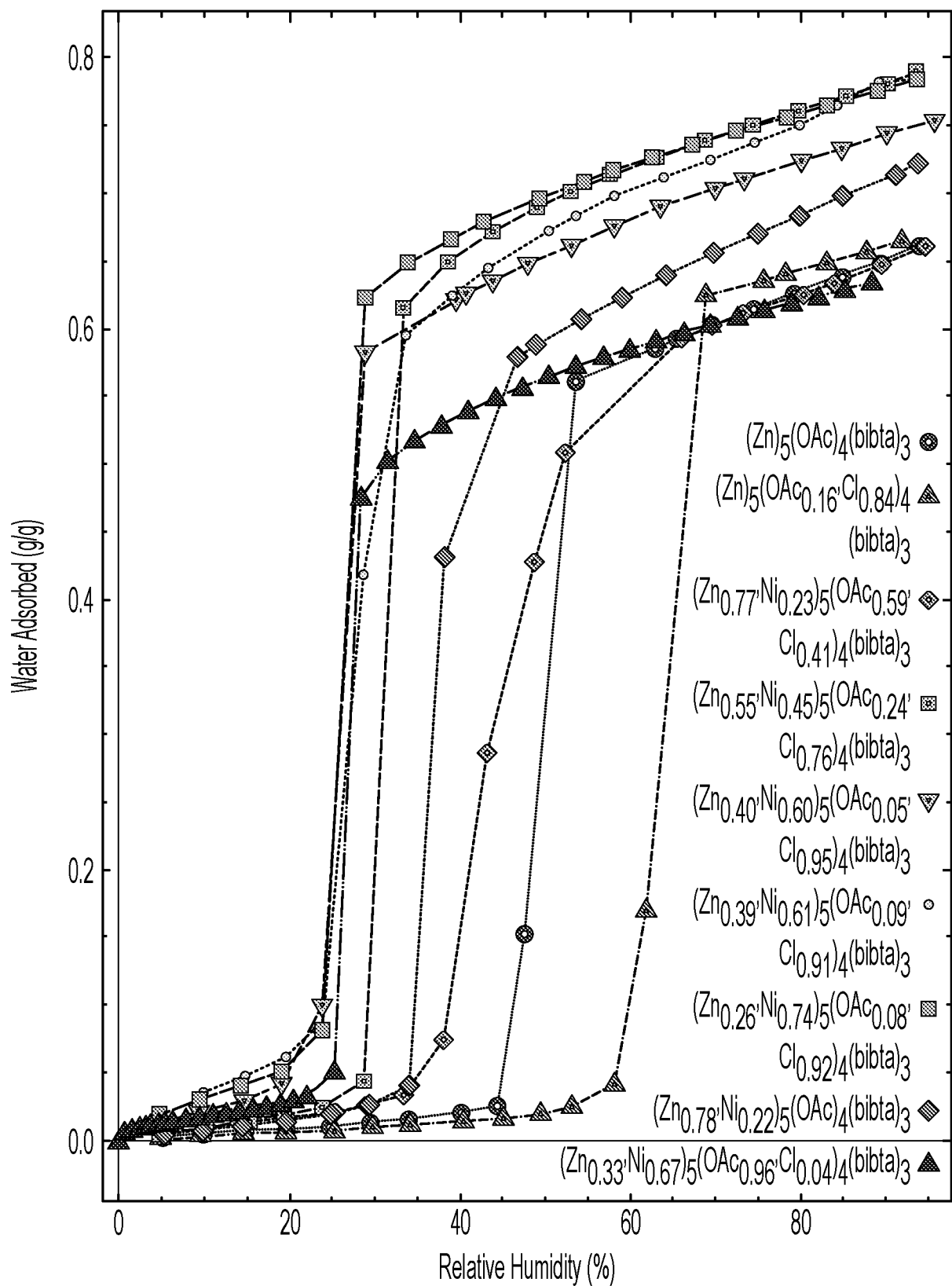


FIG. 6

shorthand name	formula unit	α (RH %)	surface area (first isotherm/ second isotherm) (m ² /g)		max measured water capacity (first isotherm/ second isotherm) (g/g)		note
			first isotherm	second isotherm	first isotherm	second isotherm	
CFA-1	(Zn) ₅ (OAc) ₄ (bibta) ₃	50	2182/1315		0.66/0.46		unstable, 30% decrease in capacity after 1 cycle
[ZnCl]	(Zn) ₅ (OAc) _{0.16} Cl _{0.84} (bibta) ₃	64	2145/1853		0.66/0.57		unstable, 14% decrease in capacity after 1 cycle
[Ni(23%), Cl(41%)]	(Zn _{0.77} Ni _{0.23}) ₅ (OAc) _{0.59} Cl _{0.41} (bibta) ₃	45	1900/1829		0.66/0.64		stable, minimal loss in capacity after 2 cycles
[Ni(45%), Cl(76%)]	(Zn _{0.55} Ni _{0.45}) ₅ (OAc) _{0.24} Cl _{0.76} (bibta) ₃	32	2187/2100		0.79/0.78		stable, minimal loss in capacity after 2 cycles
[Ni(60%), Cl(95%)]	(Zn _{0.40} Ni _{0.60}) ₅ (OAc) _{0.05} Cl _{0.95} (bibta) ₃	27	2099/1993		0.76/0.78		stable to >80 cycles, 1.9% decrease in capacity
[Ni(61%), Cl(91%)]	(Zn _{0.39} Ni _{0.61}) ₅ (OAc) _{0.09} Cl _{0.91} (bibta) ₃	29	2039/1857		0.78/0.75		stable, minimal loss in capacity after 2 cycles
[Ni(74%), Cl(92%)]	(Zn _{0.26} Ni _{0.74}) ₅ (OAc) _{0.08} Cl _{0.92} (bibta) ₃	27	2147/2007		0.78/0.78		stable to >450 cycles, 5.7% decrease in capacity
[NiOAc-low]	(Zn _{0.78} Ni _{0.22}) ₅ (OAc) ₄ (bibta) ₃	38	2156/1900		0.72/0.68		stable, minimal loss in capacity after 2 cycles
[NiOAc-high]	(Zn _{0.33} Ni _{0.67}) ₅ (OAc) _{0.96} Cl _{0.04} (bibta) ₃	27	1859/1741		0.63/0.60		stable, minimal loss in capacity after 2 cycles

FIG. 7

10/20

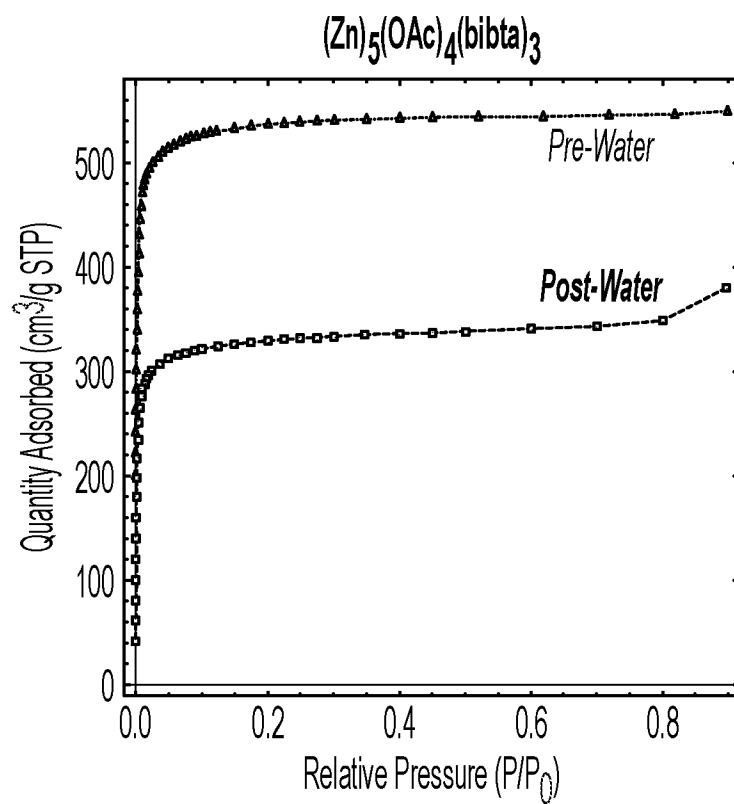


FIG. 8A

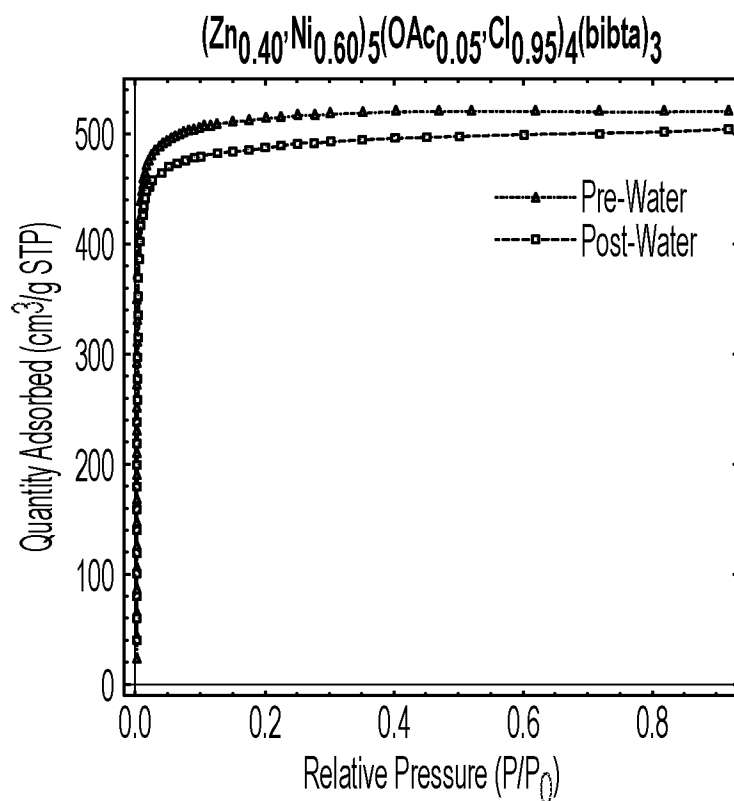


FIG. 8B

11/20

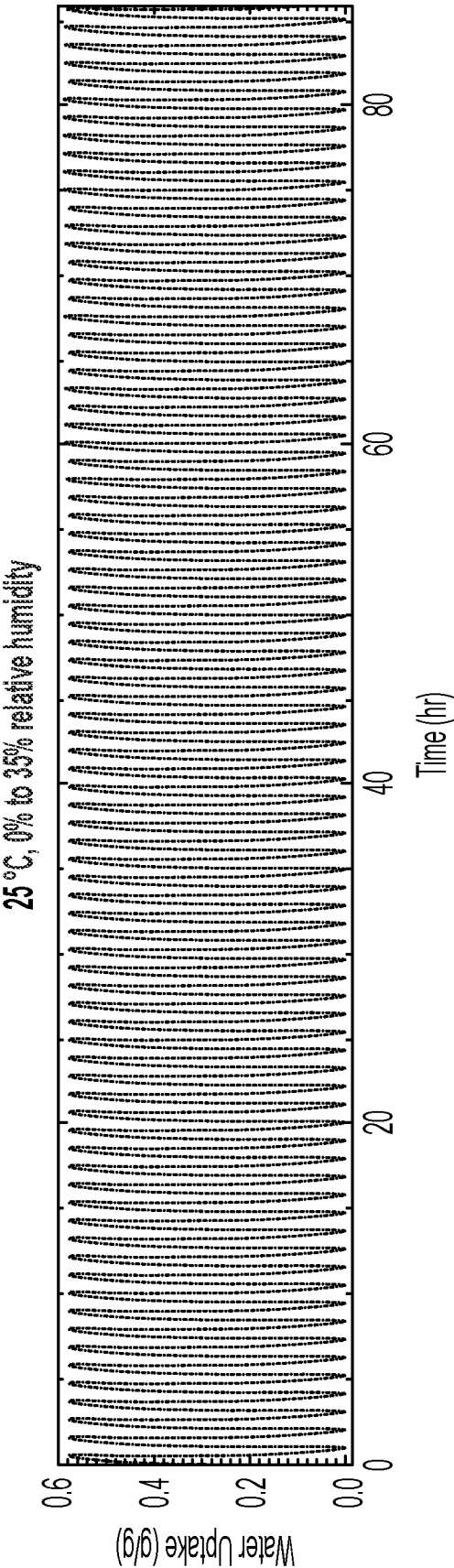


FIG. 9

12/20

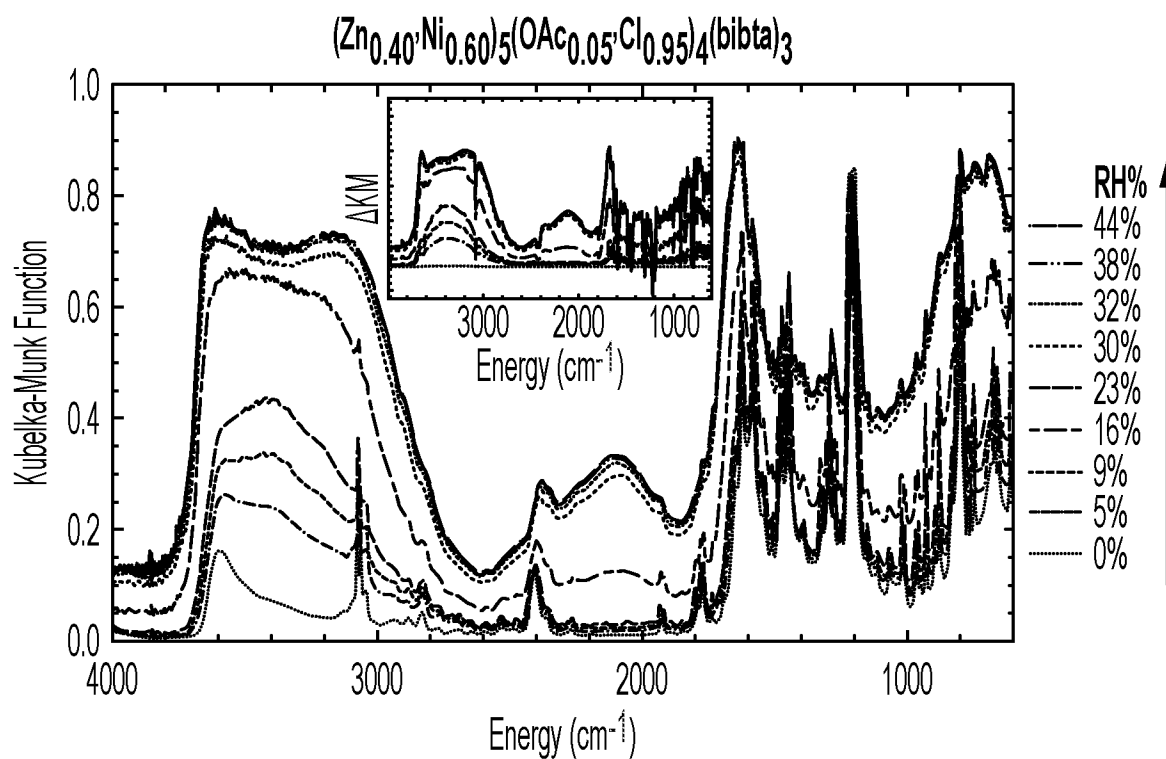


FIG. 10A

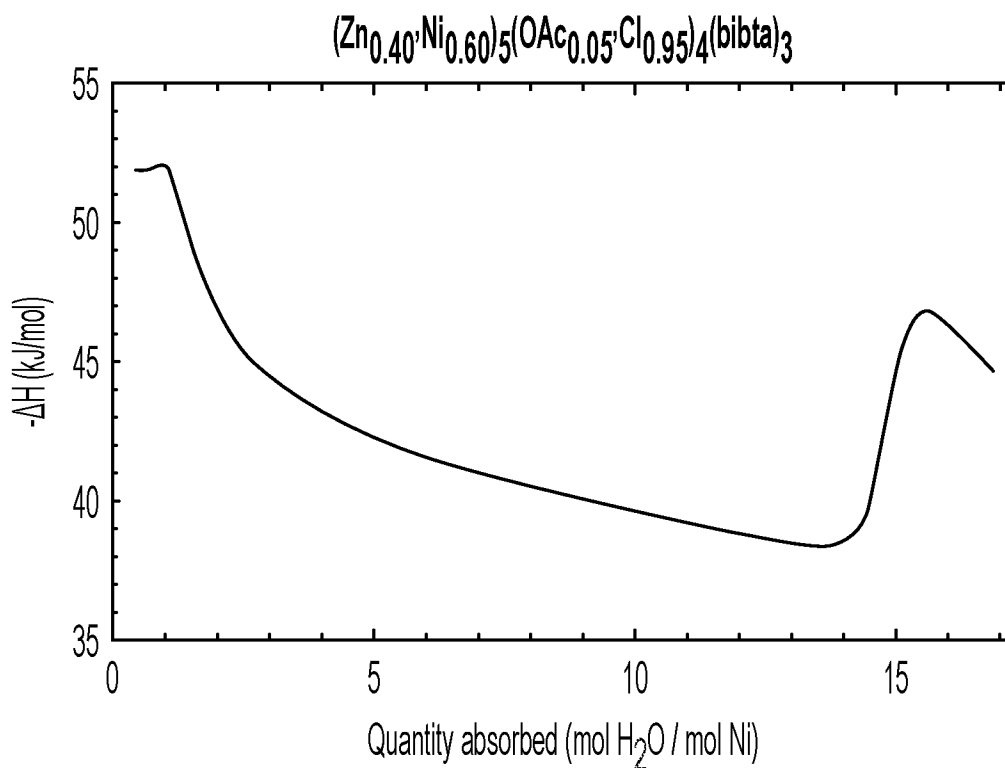


FIG. 10B

material	α (RH%)	capacity at 30% RH (g/g)	maximum gravimetric capacity (g/g)	crystal density (g/cm ³)	maximum volumetric capacity (cm ³ /cm ³)	note on stability
[Ni(74%), Cl(92%)] ^a	27	0.63	0.78	0.73	0.57	5.7% decrease in working capacity after 450 cycles (79 cycles/1% loss)
[Ni(60%), Cl(95%)] ^a	27	0.60	0.75	0.73	0.55	1.9% decrease in working capacity after 80 cycles (42 cycles/1% loss)
Ni ₂ Cl ₂ BTDD	29-32%	1.00	1.14	0.64	0.73	2% decrease in working capacity over 400 cycles (200 cycles/1% loss)
Co ₂ Cl ₂ BTDD	29	0.87	0.97	0.65	0.63	6.3% decrease in working capacity over 30 cycles (4.8 cycles/1% loss)
ZnMOF-PEP-1	30	0.62	0.83	0.81	0.67	two step sorption with ~0.62 g/g after first step. 6% decrease in working capacity over 500 cycles (83 cycles/1% loss)
Ni ₂ Br ₂ BTDD	24	0.66	0.76	0.76	0.58	<5% decrease in working capacity over 400 cycles (>80 cycles/1% loss)
MOF-LA2-1	26	0.61	0.68	0.85	0.58	6% decrease in working capacity over 150 cycles (25 cycles/1% loss)
Ti-MIL-125-NH ₂	23	0.52	0.68	0.54	0.37	No decrease in capacity after 10 cycles

FIG. 11

material	α (RH%)	capacity at 30% RH (g/g)	maximum gravimetric capacity (g/g)	crystal density (g/cm ³)	maximum volumetric capacity (cm ³ /cm ³)	note on stability
MOF-841	22	0.51	0.51	1.05	0.54	6% decrease in capacity after 5 cycles (0.83 cycles/1% loss)
MOF-303	15	0.36	0.48	1.16	0.56	~1% variation over 150 cycles (>150 cycles/1% loss)
Al fumarate	27	0.33	0.48	1.06	0.51	~12% decrease in isobaric capacity after 4500 cycles (375 cycles/1% loss)
MIP-200	18	0.39	0.45	1.17	0.53	two step sorption. 6% decrease in working capacity after 10 cycles, followed by no further loss over 40 cycles
Ni ₂ Cl ₂ BBTA	3	0.35	0.4	1.1	0.44	11% decrease in working capacity after 9 cycles (0.8 cycles/1% loss)
MOF-801-P	9	0.31	0.36	1.59	0.56	3.5% decrease is capacity after 5 cycles (1.4 cycles/1% loss)
EMM-8	16	0.29	0.35	1.50	0.53	3% decrease in working capacity after 30 cycles (10 cycles/1% loss)
CAU-10-H	18	0.26	0.32	1.15	0.39	no loss in capacity after 10,000 cycles
ALPO-78	18	0.26	0.32	1.70	0.54	no cycling data reported
α This work						

FIG. 11
CONTINUED

15/20

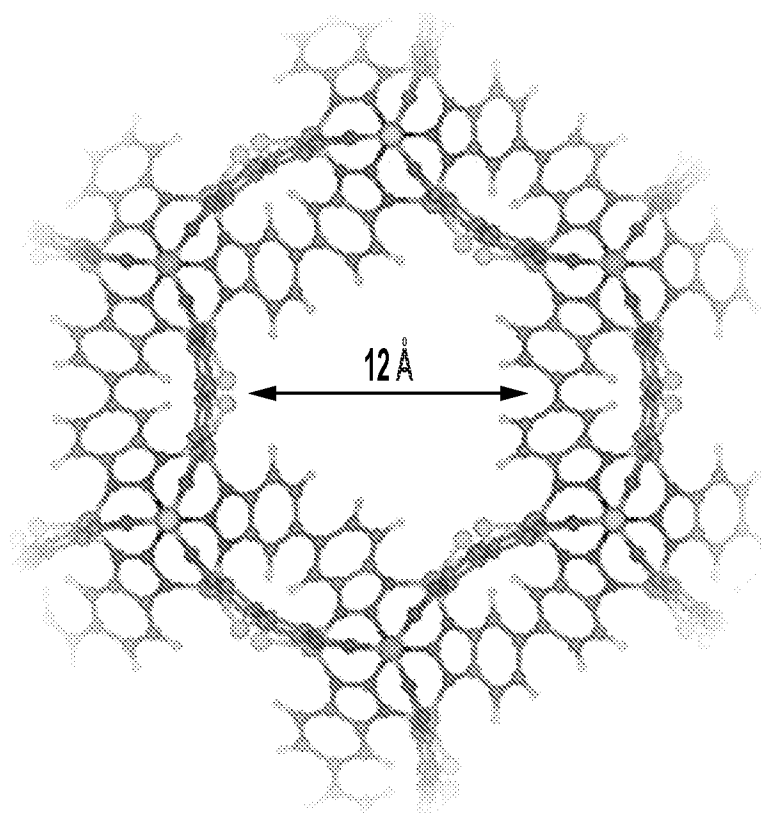


FIG. 12

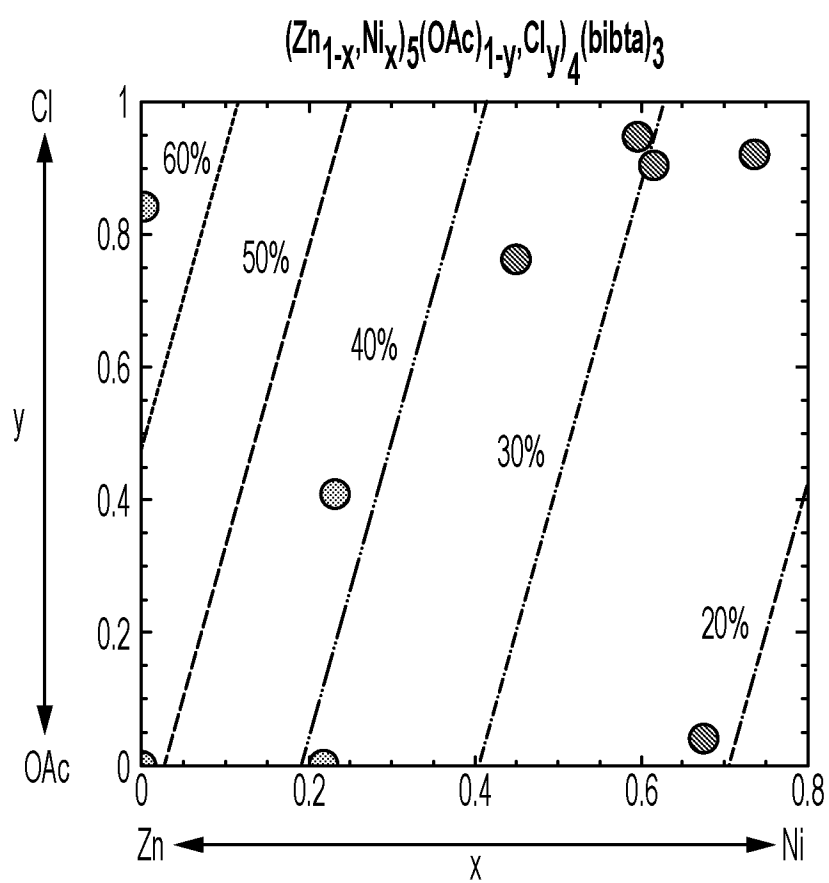


FIG. 13

16/20

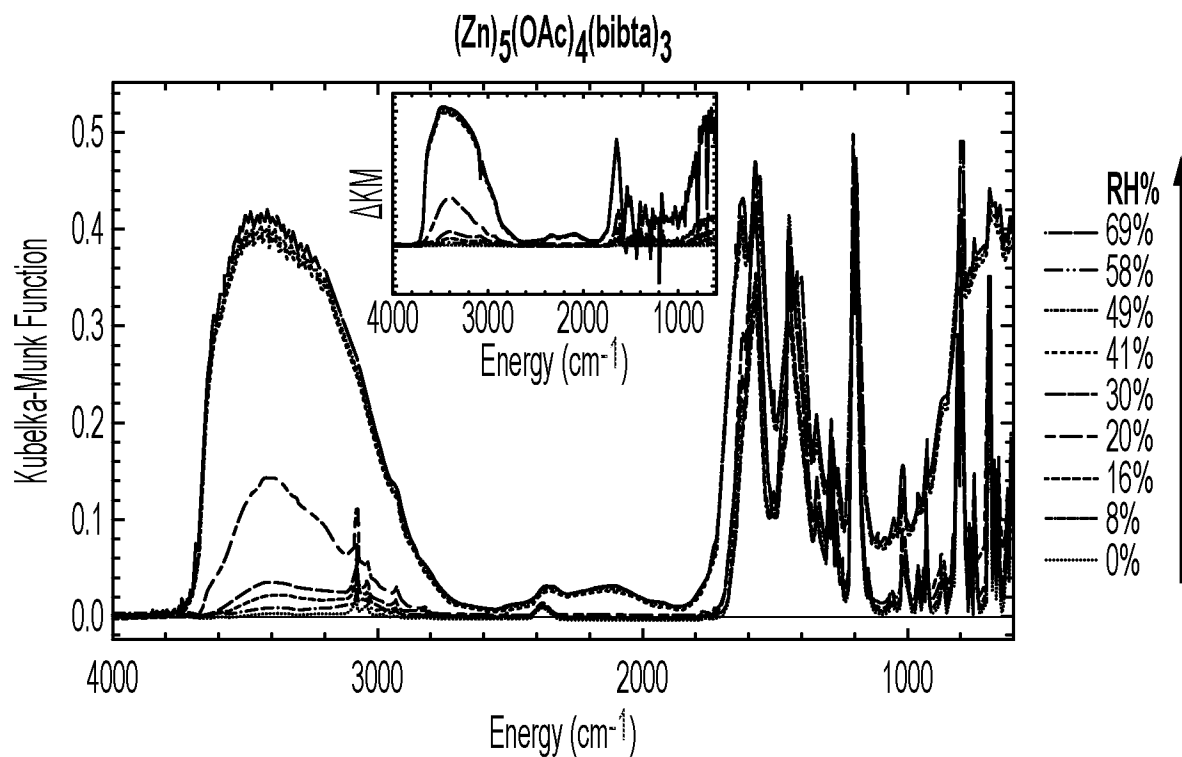


FIG. 14

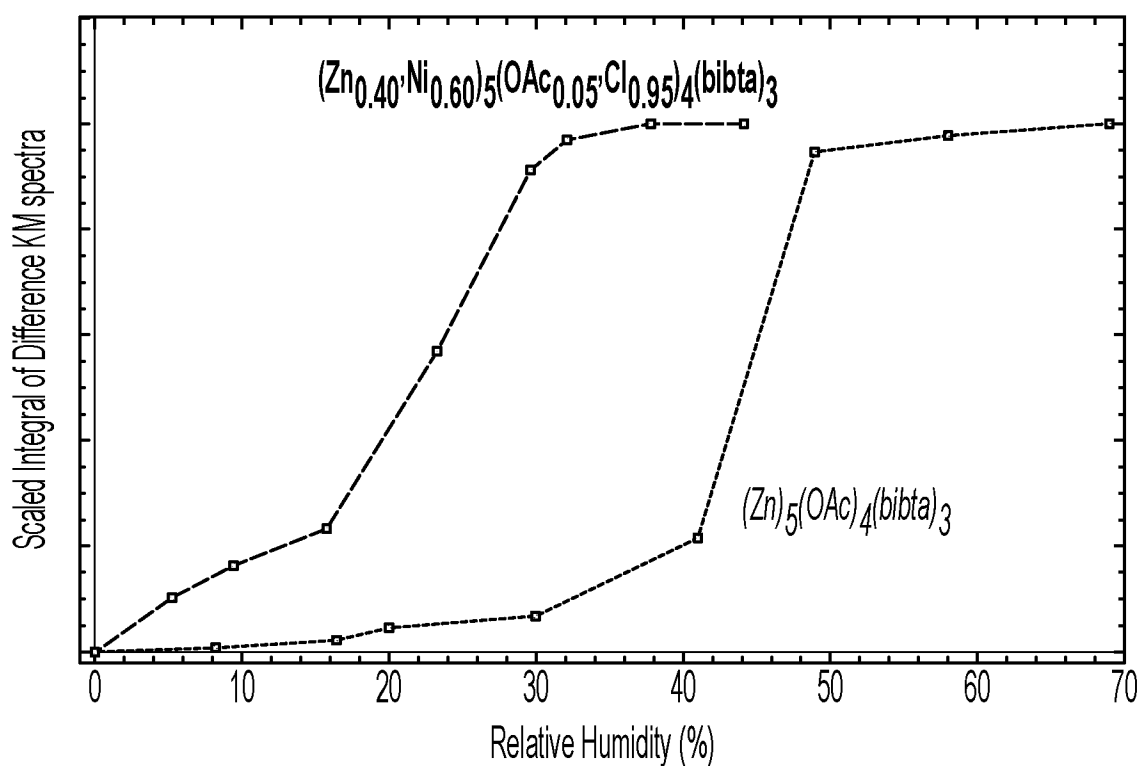


FIG. 15

17/20

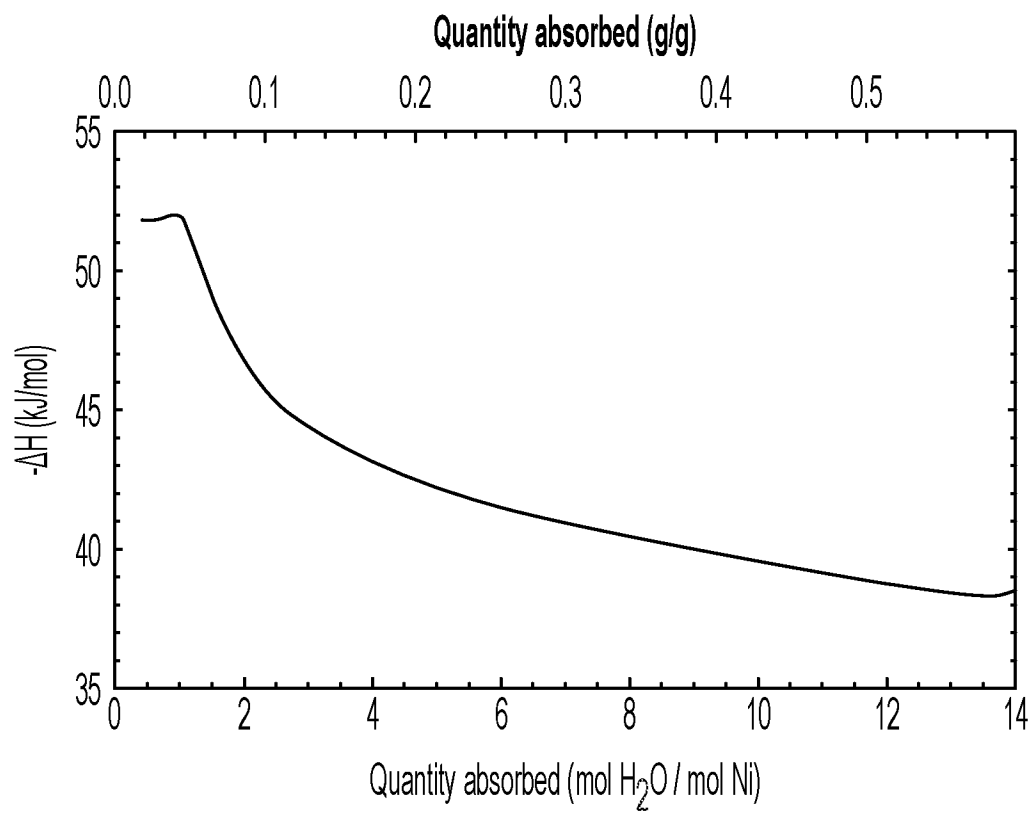


FIG. 16

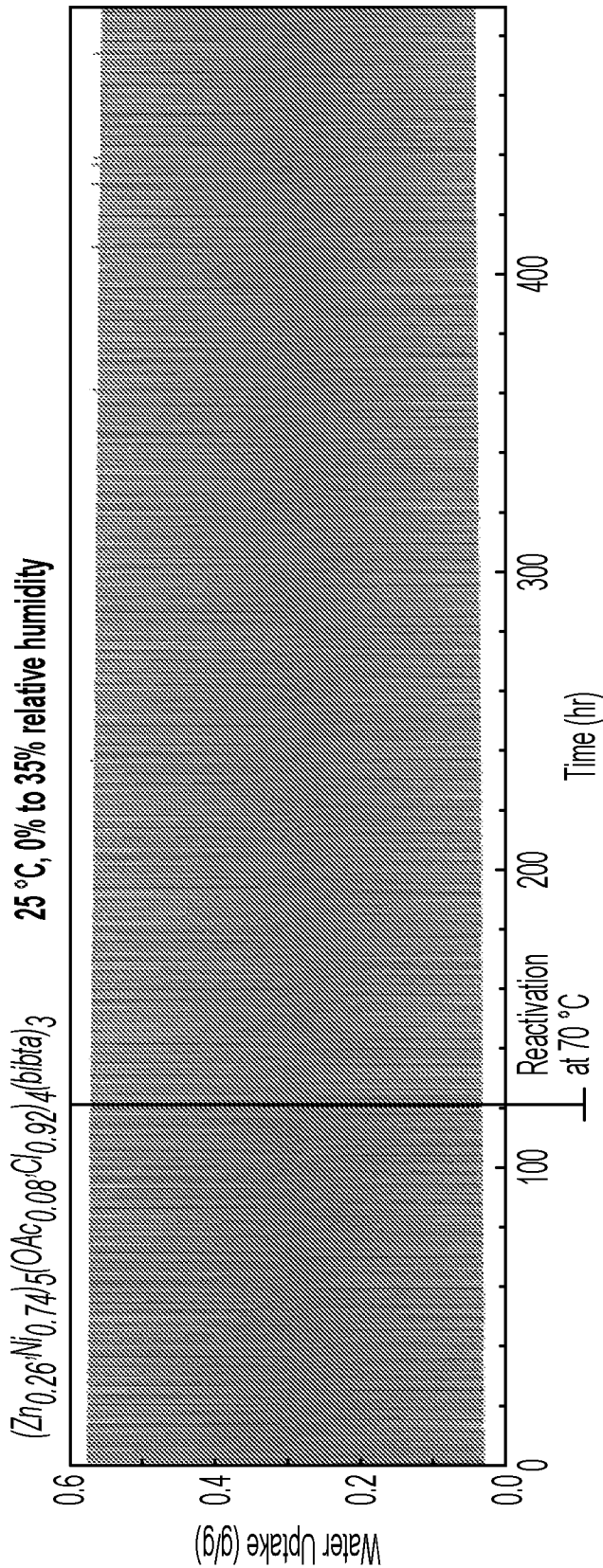


FIG. 17A

19/20

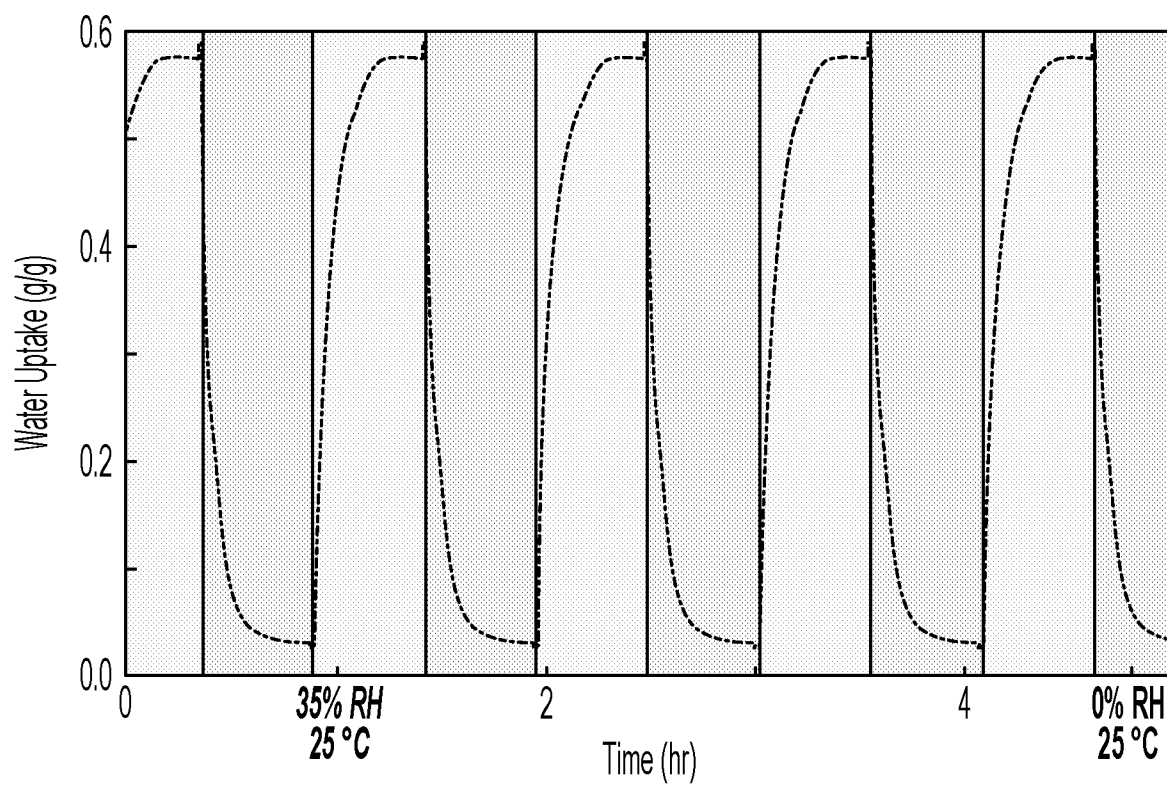


FIG. 17B

20/20

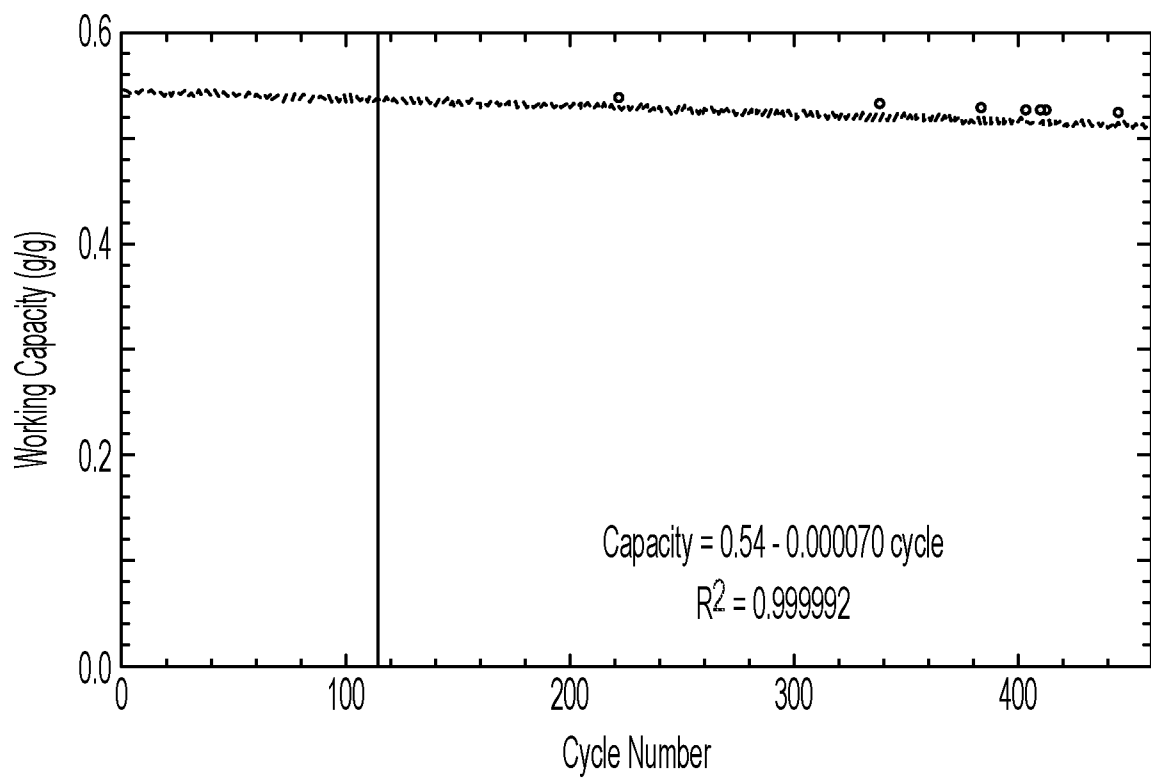


FIG. 17C