Crystal Engineering

Reversible Switching between Highly Porous and Nonporous Phases of an Interpenetrated Diamondoid Coordination Network That Exhibits Gate-Opening at Methane Storage Pressures

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Abstract: Herein, we report that a new flexible coordination network, NiL$_2$ ($L=4$-(4-pyridyl)biphenyl-4-carboxylic acid), with diamondoid topology switches between non-porous (closed) and several porous (open) phases at specific CO$_2$ and CH$_4$ pressures. These phases are manifested by multi-step low-pressure isotherms for CO$_2$ or a single-step high-pressure isotherm for CH$_4$. The potential methane working capacity of NiL$_2$ approaches that of compressed natural gas but at much lower pressures. The guest-induced phase transitions of NiL$_2$ were studied by single-crystal XRD, in situ variable pressure powder XRD, synchrotron powder XRD, pressure-gradient differential scanning calorimetry (P-DSC), and molecular modeling. The detailed structural information provides insight into the extreme flexibility of NiL$_2$. Specifically, the extended linker ligand, L, undergoes ligand contortion and interactions between interpenetrated networks or sorbate–sorbent interactions enable the observed switching.

Crystalline solids are generally regarded as being rigid. However, porous materials such as zeolites$^{[1]}$ and porous coordination networks$^{[2]}$ can exhibit guest-induced structural transformations when exposed to appropriate stimuli. The degree of flexibility exhibited by such materials can be extreme in porous coordination networks, which are also known as porous coordination polymers (PCPs),$^{[3]}$ metal–organic materials (MOMs),$^{[3]}$ or metal–organic frameworks (MOFs).$^{[4]}$ Flexible microporous materials$^{[5–9]}$ challenge classical sorption classifications because they necessarily change their pore geometry as a consequence of a structural change. For example, whereas type-I (Langmuir) adsorption isotherms (Scheme 1a) are characteristic of rigid microporous materials, flexible microporous materials tend to exhibit “stepped” or “S-shaped” isotherm profiles caused by breathing$^{[6a]}$ or swelling.$^{[6b]}$ When the material becomes porous after activation, the pressure at which the step occurs coincides with a structural transformation between less open and more open phases through a gradual (Scheme 1b, type F-I)$^{[6c]}$ or sudden opening (Scheme 1c, type F-II).$^{[6d]}$ Transformation from a non-porous (closed) activated phase to a porous (open) phase can also occur gradually (Scheme 1d, type F-III) or suddenly (Scheme 1e, type F-IV).$^{[7]}$ Type F-IV

Scheme 1. Proposed classification of isotherm profiles for flexible microporous materials: Type I = rigid microporous material, Type F-I = flexible microporous material (gradual opening from small pore to large pore), Type F-II = flexible microporous material (sudden opening from small pore to larger pore), Type F-III = flexible microporous material (gradual opening from non-porous to porous), and Type F-IV = flexible microporous material (sudden opening from non-porous to porous). Type F-V depicts a shape memory effect$^{[8–11]}$ and is not relevant for this study.

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isotherms are desirable for pressure swing gas storage, including adsorbed natural gas (ANG) storage.[74] This is because type I, I-F, I-II and F-III isotherms (Scheme 1a–d) retain adsorbed gas at low pressures, thereby reducing working capacity. Unfortunately, whereas there are now circa 100 flexible metal-organic materials, [59] FMOMS, only 2 FMOMS[7a,d] exhibit F-IV isotherms and high uptake (> 250 cc/cc). Kasel’s group reported [Ni(2,6-n-dc)(dabco)], also termed DUT-8(Ni),[74] and Co(bdp) (bdp$^{2-} = 1,4$-benzenedi-pyrazolate) was reported by Long’s group.[74] The latter is of special interest because it undergoes a structural phase transformation in response to CH$_4$ pressures between 5–35 atm.[74] Herein, we introduce a new porous material that exhibits a type F-IV isotherm and high uptake, NiL$_2$ (L = 4-(4-Pyridyl)-biphenyl-4-carboxylic acid).

A solvothermal reaction of 4-(4-pyridyl)-biphenyl-4-carboxylic acid (HL) (Figure 1a) with Ni(NO$_3$)$_2$·6H$_2$O in DMF at 105°C afforded crystals of the expected[10] diamondoid (dia) network NiL$_2$, X-dia-1-Ni. L was prepared through serial Suzuki–Miyaura coupling reactions (Supporting Information, Figure S1). Characterization of single crystals as-synthesized X-dia-1-Ni, X-dia-1-Ni-a1, by single-crystal XRD (SC-XRD) revealed that it crystallizes in tetragonal space group $I_4/mcd$ with $a = b = 24.2018(6)$ Å, $c = 16.2670(8)$ Å, $V = 9528.0$ (7) Å$^3$. Ni$^{2+}$ cations are coordinated to four oxygen and two nitrogen atoms from four ligands and serve as 4-connected nodes. X-dia-1-Ni-a1 is a 6-fold interpenetrated dia net (Figure 1c), interpenetration being enabled by adamantanoid cages with Ni–Ni edges of 17.2 Å. The accessible void volume available in X-dia-1-Ni-a1 is 49% despite the high level of interpenetration thanks to rectangular channels along the c axis (Figure 1d). The bulk purity of X-dia-1-Ni-a1 was confirmed by PXRD experiments (Figure 1f).

X-dia-1-Ni-a1 underwent single-crystal-to-single-crystal (SCSC) transformations after exchange with CH$_2$Cl$_2$ or heating at 85°C for 24 h to less open phases, X-dia-1-Ni-a2 and X-dia-1-Ni-a3, respectively (Supporting Information, Figure S3). Whereas space group and connectivity are unchanged, reductions in cell volume (9528, 8637, and 7441 Å$^3$ for a1–a3, respectively), length of the a and b axis (24.20, 22.17, and 19.95 Å for a1–a3, respectively) and solvent-accessible void volume (49, 43, and 33% for a1–a3, respectively) accompanied the phase changes (Figure 1e and the Supporting Information, Figure S4). The adamantanoid cages exhibit Ni–Ni–Ni angles of 90°120°, 80°126°, and 71°132° for a1–a3, respectively. The breathing of the framework is accompanied by changes in N–Ni–N–C–Ni–C bond angles; 93.0°/101.5°, 90.7°/101.4°, and 88.0°/102.4° for a1–a3, respectively (Supporting Information, Table S3). L also undergoes conformational changes; the dihedral angle formed by the benzoate plane and the pyridine plane is perpendicular in a1 (89.4°) but parallel in a2, (6.1°) and a3 (1.8°).

Figure 1. a) Structure of 4-(4-pyridyl)-biphenyl-4-carboxylic acid (HL). b) Adamantanoid cage in NiL$_2$. c) 6-fold interpenetrated dia nets in NiL$_2$. d) Rectangular channels viewed along the c-axis. e) Single crystal structures of the porous (a1, a2, a3) and non-porous (c1) phases of X-dia-1-Ni. f) Crystal morphology and PXRD pattern of a1. g) Crystal morphology and synchrotron PXRD (λ = 0.8262 Å) pattern of c1.[75]
effect can be monitored by powder XRD (PXRD) (Supporting Information, Figure S5); the lowest angle reflection (200) shifts from $2\theta = 7.08^\circ$ in a1 to $2\theta = 8.94^\circ$ in a3.

Heating the a1–a3 phases in vacuo results in a color change from dark green to light green and SCXRD revealed that the light green phase, X-dia-1-Ni-c1, is a non-porous dia net (orthorhombic space group Pnn2). Crystal morphology changes accompany the structural transformation (Figures 1f,g) as monitored by thermal microscopy. The Ni$^{2+}$ cations of X-dia-1-Ni-c1 adopt an octahedral coordination geometry and serve as 4-connected nodes as in the open a1–a3 forms. The planarity of L as quantified by the N(pyridyl)–phenyl-centroid-C(carboxylate) angle is $174^\circ$ in a1, $176^\circ$ in a2, $177^\circ$ in a3 and, remarkably, $155^\circ$ in c1 (Figure 1c). The Ni–Ni edges of the adamantane cages decrease from 17.2 Å (a1) to 16.3 Å (c1). We attribute the existence of X-dia-1-Ni-c1 to the ability of L to contort and changes in the coordination geometry (Table S3). The crystallographic program PLATON[11] revealed that X-dia-1-Ni-c1 has only 2% solvent-accessible volume. Overall, X-dia-1-Ni-a1 undergoes a contraction of pore volume from 0.58 cm$^3$ g$^{-1}$ to 0.01 cm$^3$ g$^{-1}$ in X-dia-1-Ni-c1 (Figure 1c). Such extreme structural transformations between closed and open phases are unusual. We are aware of only four previously reported FMOMs[6b,7c,d,8d] that are known to exhibit such dramatic solvent or gas induced structural change (Supporting Information, Table S4).

The purity of the c1 phase was confirmed by PXRD and synchrotron X-ray powder diffraction (SXRD) experiments. The SXRD pattern of X-dia-1-Ni-c1 exhibits a diagnostic peak at $2\theta = 5.58^\circ$ ($\lambda = 0.8269 \\AA$) (Figure 1g). Thermodgravimetric analysis of X-dia-1-Ni-c1 indicated no weight loss until decomposition at $330^\circ$C (Supporting Information, Figure S6). X-dia-1-Ni-c1 reverts to X-dia-1-Ni-a1 when soaked in DMF or toluene at room temperature for 1 min (Supporting Information, Figure S7).

CO$_2$, with its large quadrupolar moment ($13.4 \times 10^{-20}$ Cm$^2$) and small kinetic diameter (3.3 Å), was chosen to probe how pressure affects switching between the open (a1–a3) and closed (c1) phases. The low-pressure adsorption isotherm of X-dia-1-Ni for CO$_2$ at 195 K exhibits multiple steps and the surface area of the least-dense phase is 1641 m$^2$ g$^{-1}$ by Langmuir fitting (Figure 2a). There is strong hysteresis and clear steps are also present in the desorption isotherm. We conducted in situ PXRD and sorption coincident measurements[12] (Figure 2b) by placing X-dia-1-Ni-c1 on a copper plate under high vacuum before collecting PXRD data during CO$_2$ adsorption and desorption. The diagnostic low angle peak of the c1 phase (10.03$^\circ$, $\lambda = 1.54178 \AA$) gradually diminished as the diagnostic peaks of a3 (8.94$^\circ$) and a2 (7.93$^\circ$) appeared, indicative of gate opening (Supporting Information, Figure S8). The steep CO$_2$ uptake after 0.1 bar is consistent with transformation from c1 to an open phase. The PXRD pattern did not change markedly in the pressure range 0.2–0.4 bar, which is consistent with the plateau observed in the adsorption isotherm. When CO$_2$ pressure was increased to 0.42 bar, the diagnostic low angle peak of a1 (7.08$^\circ$) appeared. The steep CO$_2$ uptake around 0.45 bar is consistent with a structural change from a2 to a1 that is complete at 0.77 bar. The in situ PXRD patterns on desorption indicate reversible structural changes between open and closed phases (Supporting Information, Figure S9). X-dia-1-Ni exhibited no N$_2$ uptake at 1 bar and 77 K (Figure 2a).[13] Simulations predict N$_2$ adsorption for a1 (Figure 2a) and stepwise CO$_2$ adsorption at 195 K (Supporting Information, Figure S17). The four steps in the 195 K CO$_2$ sorption isotherm of X-dia-1-Ni can be attributed to structural transformations as the framework switches from c1 to a3, a2, and then a1. Structural transformations from a1 to a2, a3 and c1 occur during desorption.

Natural gas (NG), is mainly comprised of CH$_4$ and increasingly utilised for vehicular applications thanks to its geological abundance and low carbon footprint.[15] Current storage technologies typically use cryogenic (liquefied NG at $-161^\circ$C, LNG) or high-pressure (compressed NG at 210–250 atm, CNG), conditions that are fraught with hazards and high costs. Adsorbed NG (ANG) using porous materials could mitigate these risks and costs. However, whereas over 20000 physisorbent materials exist (for example, activated carbons,[16] zeolites,[17] MOFs,[18,19] and molecular crystals),[20] none yet offer a volumetric working capacity that
suggests that no current class of rigid physisorbent is
is stabilized by interactions
are based
X-dia-1-Ni (Figure 4a) were calculated at the MP2/6-31G(d,p) level of theory. We indeed observed increases in pre-step adsorption
uptake before the step (Supporting Information, Figure S21). In situ variable CH$_4$ pressure PXRD studies were conducted at 298 K by loading activated X-dia-1-Ni into a capillary and exposing the sample to methane (Supporting Information, Figure S11). The kinetics of X-dia-1-Ni are too slow to observe phase changes; the mixed metal variant (X-dia-1-Ni$_{Co}$) is more readily observable. ARGentine isomorphic to X-dia-1-Ni and was formed under the same conditions. Under vacuum, the cl phase of X-dia-1-Ni$_{Co}$ is present, whereas from 25 bar to 50 bar the peaks of the a1 phase appear. At 50 bar, X-dia-1-Ni$_{Ni-Co}$ had fully transformed to its a1 phase. The a1 phase fully converts to the cl phase by around 5 bar. This phase change was also studied by P-DSC. An activated sample of X-dia-1-Ni was placed in a DSC sample chamber and exposed to CH$_4$ in the pressure range 1–50 bar at 298 K. An exothermic peak at 25 bar is consistent with the phase change observed by in situ PXRD. The total CH$_4$ uptake of X-dia-1-Ni at 25°C is 176 cm$^3$ g$^{-1}$ (150 cm$^3$ cm$^{-3}$) for adsorption at 35 bar and 222 cm$^3$ g$^{-1}$ (189 cm$^3$ cm$^{-3}$) at 65 bar. The potential working capacity, 147 cm$^3$ cm$^{-3}$ as calculated from the adsorption isotherm between 35 bar and 5 bar, approaches that of benchmark MOFs (Supporting Information, Table S5). However, hysteresis reduces the working capacity to 110 cm$^3$ cm$^{-3}$ (5–35 bar) and 149 cm$^3$ cm$^{-3}$ (5–65 bar), respectively. Approaches to controlling hysteresis are being investigated.

The mechanism of structural flexibility for FMOMs such as paddle-wheel-based pillared-layered frameworks (the prototype for which is DMOF-1) and trigonal prism-based networks such as MIL-88 are based upon hinge motion associated with carboxylate coordination. Structural characterization of the various phases of NiL$_2$ indicates a mechanism that largely relies upon ligand contortion. In addition, cl is stabilized by interactions between interpenetrated networks. We note that a similar dia network formed by a shorter linker ligand, 4-(4-pyridyl) benzoic acid, did not exhibit framework flexibility under the same conditions. We attribute this to the lesser ability of shorter ligands to undergo extreme contortions of the type observed for L. Therefore, the key to the phase changes observed for this prototypical dia network is the use of the extended “X-ligand”, L. The single point energies of L in cl (Figure 4c) and cl (Figure 4a) were calculated at the MP2/aug-cc-pVDZ level of theory. The energy difference calculated between the two conformations of the ligand is +165 kJ mol$^{-1}$ (Figure 4b). Ligands that can contort during structural transformation are rare and no others are yet known to induce framework switching between closed and open phase. Ligand contortion and framework strain might be expected to lead to poor recyclability and reduced performance. We indeed observed increases in pre-step adsorption at 298 K after four sorption/desorption cycles (Supporting Information, Figure S23b).

In summary, X-dia-1-Ni undergoes pressure- and solvent-induced SCSC transformations between closed and open phases. Four distinct phases of X-dia-1-Ni were isolated and studied by SC-XRD, PXRD, and SXRD to provide structural insight into how ligand contortion can enable structural flexibility. X-dia-1-Ni is only the second high-surface-area

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**Figure 3.** a) Total CH$_4$ uptake isotherm at 298 K for X-dia-1-Ni. b) Pressure-ramped DSC (CH$_4$, 298 K) for X-dia-1-Ni. c) The simulated CH$_4$ adsorption isotherms in the open (a1) and closed (cl) phases of X-dia-1-Ni at 298 K with the experimental adsorption isotherm. d) The modelled structure at CH$_4$ saturation in the open phase of X-dia-1-Ni. e) Switching between closed (left) and open (right) phases of X-dia-1-Ni under CH$_4$ pressure.
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Conflict of interest

The authors declare no conflict of interest.

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