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Enhanced Gas Sorption Properties and Unique Behavior toward Liquid Water in a Pillared-Paddlewheel Metal–Organic Framework Transmetalated with Ni(II)

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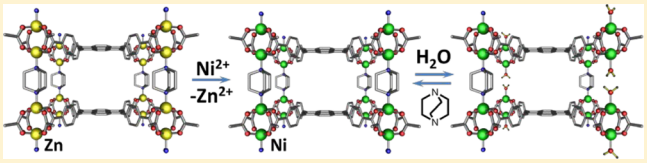
Supporting Information

ABSTRACT: The synthesis of a permanently porous pillared-paddlewheel metal–organic framework (MOF) was achieved through transmetalation of Zn(II) with Ni(II). The MOF can be treated with liquid water, leading to the reversible displacement of 50% of its pillars by water molecules and resulting in a most unusual crystalline and permanently porous structure.



INTRODUCTION

Metal–organic frameworks (MOFs) are hybrid crystalline materials featuring metal-based nodes connected by organic linkers. Their high tunability coupled by unrivaled porosity has led to their proof-of-concept use in applications such as gas storage[1−6] and separation,[7−10] catalysis,[11−13] sensing,[14] and light harvesting.[15−18] One particularly promising and extensively studied class of MOFs are pillared-paddlewheel materials, which are composed of two-dimensional (2D) sheets featuring binuclear metal centers linked by carboxylate-based ligands, which can be assembled into three-dimensional (3D) structures through pillaring with a ditopic nitrogen donor linker.[19,20] As mixed-linker MOFs, these materials offer ample opportunities for functional-group incorporation;[21,22] moreover, extension of the nitrogen donor pillar can potentially yield MOFs with ultralarge cavities and great porosity.[23] Nevertheless, activation of pillared-paddlewheel MOFs remains a challenge, as the relatively weakly bound pillars are prone to displacement by other small coordinating molecules (such as water in air), and the networks may suffer from irreversible collapse.[24] As a result, the apparent surface areas and pore volumes reported for such materials often lie well below the theoretically predicted values.

It has been recently reported that incorporation of nickel-based paddlewheel structural building units leads to a significant enhancement of the gas sorption properties of MOFs, most likely due to the increased thermodynamic stability of such structures owed to the position of Ni(II) in the Irving–Williams series.[25] Lah and co-workers demonstrated that utilization of Ni(II) nodes in a paddlewheel-based MOF of ith-d topology yields a structure that can be treated by heat and vacuum to achieve a Brunauer–Emmett–Teller (BET) area of 5590 m^2/g, which, to our knowledge, is a record value for MOFs activated without resorting to supercritical CO_2 drying.[26] Such high apparent surface areas are accessible even when Ni(II) is used in substoichiometric quantities (e.g., as a dopant).[27] Moreover, Tan et al. and Liang et al. exposed a series of isostructural $M_2(bdc)_2(dabco)$ pillared-paddlewheel MOFs to water vapor and found that the Ni(II) congener displays the highest stability toward linker displacement by water (M = Co(II), Ni(II), Cu(II) or Zn(II); bdc = benzene-1,4-dicarboxylate; dabco = 1,4-diazabicyclo[2.2.2]octane).[28,29] We reasoned that employing Ni(II) as a node would provide us with tetracarboxylate pillared-paddlewheel MOFs capable of displaying (i) permanent porosity, which would allow their consideration for applications requiring gas sorption, and (ii) framework stability in the presence of water, which would render them more suitable for use in industrial settings. In this paper, we report the effects of transmetalation from Zn(II) to Ni(II) on these aspects in a pillared-paddlewheel MOF structure.

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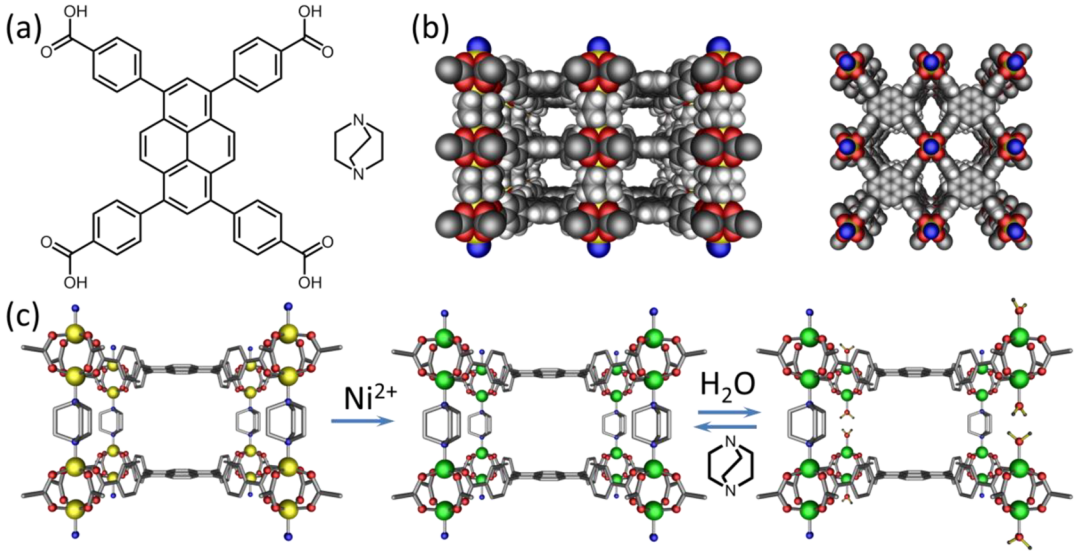
Scheme 1. (a) Structures of TBAPy (left) and dabco (right); (b) Crystal Structure of NU-505-Zn Viewed along the *a*-axis (left) and *c*-axis (right); and (c) Transmetalation of NU-505-Zn with Ni(II), Followed by Water Treatment and Reinsertion of dabco Pillars[a]



[a]Note that the displacement of the pillars occurs in columns, rather than randomly. See text for the description of how the structure of water-treated sample has been inferred.

EXPERIMENTAL SECTION

Instrumentation. ^{1}H NMR spectra were collected on a Bruker Avance III 500 MHz spectrometer. Powder X-ray diffraction (PXRD) patterns for capillary-encapsulated samples were obtained at room temperature with a Bruker MX IμS microsource (Cu Kα radiation) and ApexII CCD detector. Samples were mounted in capillaries with supernatant liquid; capillaries were sealed with wax and placed on goniometer heads for mounting on the diffractometer. The PXRD data were collected with an area detector as rotation frames over 180° in φ at 2θ values of 12° and 24° and exposed for 10 min for each frame. At a distance of 150 mm, the detector area covers 24° in 2θ. Overlapping sections of data were matched and the resulting pattern integrated using the Bruker APEX2 phase ID program. Powder-pattern data were treated for amorphous background scatter. The single-crystal data were collected on a Bruker APEX2 V2.1-4 CCDC diffractometer with Cu Kα radiation (λ = 1.54184 Å) at 100 K. Inductively coupled plasma−optical emission spectroscopy (ICP-OES) was conducted on a Varian Vista-MDX model ICP-OES spectrometer (Varian, Walnut Creek, CA) equipped with a CCD detector and argon plasma to cover the 175−785 nm spectral range. MOFs were evacuated with supercritical CO_2 in a Tousimis Samdri PVT-30 critical point dryer and stored in a glovebox after activation under an argon atmosphere. N_2 sorption isotherms were collected on a Tristar III 3020 and on an ASAP 2020 MP (Micromeritics). Thermal activation to 100 °C was performed on an ASAP 2020 (Micromeritics).

Materials. Dimethyl sulfoxide (Sigma, 99.5%), $Zn(NO_3)_2{\cdot}6H_2O$ (Fluka, 99%) $NiCl_2{\cdot}6H_2O$ (Sigma, 98%), 1,4-diazabicyclo[2.2.2]-octane (Sigma, 97%), ethanol (Sigma, 99.5%), *N*,*N*′-dimethylformamide (Macron, 99.8%), dimethyl sulfoxide−d_6(Cambridge, 99%), D_2SO_4 (Cambridge, 96%−98% solution in D_2O), Zn ICP standard (Fluka, 1000 mg/L in 2% w/w HNO_3), and Ni ICP standard (Fluka, 1002 mg/L in 2% w/w HNO_3) were used as received. H_4TBAPy was synthesized according to a previously published procedure.[30]

Synthesis of NU-505-Zn. Fifty milligrams (50 mg, 0.074 mmol) of H_4TBAPy, 44 mg (0.148 mmol) of $Zn(NO_3)_2{\cdot}6H_2O$, and 8 mL of *N*,*N*′-dimethylformamide (DMF) were added to an 8-dram vial and the solid was dissolved by sonication. A solution of 16.8 mg (0.148 mmol) dabco in 4 mL of DMF was added and the solution became cloudy. In a separate vial, eight drops of fuming HNO_3 (90%) were added to 10 mL of DMF. A small volume (0.85 mL) of that HNO_3 solution was added to the reaction mixture and the solution became clear again. The vial was incubated in a 60 °C oven for 30 min, and then the temperature was increased to 75 °C and kept for 3 days. After that time, bright yellow cubic microcrystals formed. Crystalline powder was collected by careful decantation of the mother solution and washed with fresh DMF several times to remove soluble impurities.

Transmetalation of NU-505-Zn to Ni. Sixty two milligrams (62 mg) of $NiCl_2{\cdot}6H_2O$ (0.26 mmol) were dissolved in 5 mL of dimethyl sulfoxide (DMSO) in a 2 dram vial. Thirty milligrams (30 mg) of NU-505-Zn (0.03 mmol) were added to the resulting solution. The reaction mixture was heated at 100 °C for 2 days, upon which ICP analysis indicated a >95% exchange of Zn to Ni.

NMR of MOFs. Approximately 1−5 mg of pillared-paddlewheel MOF crystals (filtered and washed with DMF) were placed in a 1.5-dram vial containing deuterated dimethyl sulfoxide (DMSO). Three drops of D_2SO_4 were added and the crystals were sonicated to achieve complete dissolution. The sample was then transferred to an NMR tube. The ^{1}H NMR spectra were obtained by locking to DMSO.

ICP of MOFs. MOF samples (1−3 mg) were digested in 1 mL of a mixture of 3:1 v/v concentrated H_2SO_4:H_2O_2 (30 wt % in H_2O) solution and heated in a Biotage (Uppsala, Sweden) SPX microwave reactor at 150 °C for 10 min, upon which the solution became clear and homogeneous. The acidic solution was diluted to 25 mL with ultrapure deionized H_2O and analyzed for Ni (216.555, 221.648, and 231.604 nm) and Zn (202.548, 206.200, and 334.502 nm) content as compared to standard solutions.

Water Treatment of MOFs. MOF samples (~40 mg) were immersed in ~5 mL of pure H_2O for 8 h at ambient temperature, after which they were resolvated in DMF and subjected to further characterization.

Supercritical CO_2 Activation of MOFs. Solvent exchange to ethanol was performed on the MOFs (~40 mg samples) over the course of three days. After that, supercritical CO_2 exchange was performed.[21,24,31] Activated samples were immediately transferred to an argon-filled glovebox; samples for sorption analysis were similarly prepared under inert conditions (argon atmosphere).

Reinsertion of dabco in Water-Treated NU-505-Ni. Thirty milligrams (30 mg) of water-treated NU-505-Ni (resolvated in DMF) were added to a DMF solution of excess dabco (20 mg in 5 mL of DMF) and placed in an oven at 100 °C overnight.

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RESULTS AND DISCUSSION

We recently synthesized the pillared-paddlewheel MOF NU-505-Zn, consisting of two-dimensional (2D) sheets of the tetracarboxylate linkers TBAPy (1,3,6,8-tetrakis(p-benzoate)-pyrene) and dabco pillars. The structure was confirmed by single-crystal X-ray diffraction (XRD) studies (Scheme 1b). Geometrical analysis using Platon software confirmed the highly porous nature of the as-synthesized material (61% of the unit cell volume); however, attempts to desolvate the framework using commonly applied procedures (vacuum and thermal treatment) were unsuccessful. Therefore, we resorted to supercritical CO_2 drying.[2,24,31] With this method, NU-505-Zn exhibited high initial porosity, as evidenced by a pore volume of 0.63 cm^3/g and a BET area of 1600 m^2/g. Grand Canonical Monte Carlo (GCMC) simulations of N_2 sorption performed for this MOF resulted in a predicted pore volume of 1.02 cm^3/g and a predicted BET area of 2660 m^2/g. The fact that the experimental values are smaller indicates that complete activation was not achieved. Furthermore, we discovered that the evacuated MOF did not display *persistent* porosity.[32] When N_2 isotherms were collected 24 and 48 h after activation, the BET area decreased to 1370 m^2/g and then 1280 m^2/g, implying gradual structural collapse; after a week, almost all N_2 porosity was lost (see the Electronic Supporting Information (ESI)).

The lack of permanent long-term porosity in NU-505-Zn prompted us to consider it as a candidate for the transmetalation of the Zn(II) nodes with Ni(II), specifically to test the notion that the exchange could render the material persistently porous, as well as water-tolerant. Exposing NU-505-Zn to a concentrated $NiCl_2 \cdot 6H_2O$ solution in DMSO (4 mol equiv, with respect to Zn in the MOF) at 100 °C for 2 days led to a stark color change from light yellow to green and replacement of 94% of the Zn(II) ions with Ni(II), as indicated by inductively coupled plasma–atomic emission spectroscopy (ICP-AES). ^{1}H nuclear magnetic resonance (^{1}H NMR) spectroscopy performed on digested MOF crystals demonstrated that the TBAPy:dabco ratio in the transmetalated daughter material remained unchanged, with respect to the Zn(II) parent (i.e., no dabco leaching had occurred during the metal exchange process (ESI)). Moreover, PXRD measurements of NU-505-Ni showed preservation of the pillared-paddlewheel structure (Figure 1).

NU-505-Ni was activated via supercritical CO_2 drying and exhibits a pore volume of 0.83 cm^3/g and a BET area of 2110 m^2/g, thus approaching the values predicted by GCMC simulations (Figure 2). In contrast to NU-505-Zn, consecutive N_2 sorption measurements performed on NU-505-Ni up to 6 days after solvent evacuation revealed no change in the surface area (ESI). The material's surface area was unchanged, even after heating at 100 °C for 18 h, indicating a marked increase in the stability of the MOF realized by transmetalation to Ni(II). The combination of the robust Ni(II) centers with the basic dabco linkers (the pK_a of the monoprotonated conjugate-acid of dabco is 10.16) has markedly enhanced the stability of the structure.

To test the water stability of the material, we immersed the NU-505-Ni crystals in pure water. After exposure at room temperature for 8 h, the MOF crystals were resolvated in *N*,*N*-dimethylformamide (DMF). ^{1}H NMR spectroscopy of the resolvated material revealed, to our surprise, that the TBAPy:dabco ratio had changed from 1:1 to 1:0.5. In addition

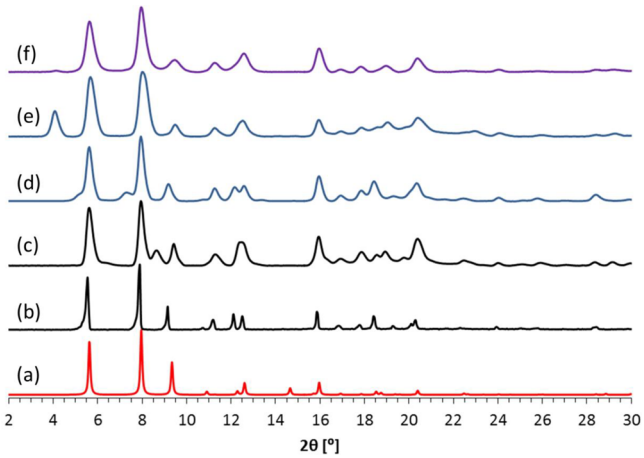

Figure 1. Powder X-ray diffraction (PXRD) patterns of (a) simulated NU-505-Zn, (b) experimentally obtained NU-505-Zn, (c) experimentally obtained NU-505-Ni, (d) NU-505-Zn treated with liquid water, (e) NU-505-Ni treated with liquid water, and (f) NU-505-Ni treated with liquid water after the reinsertion of dabco.

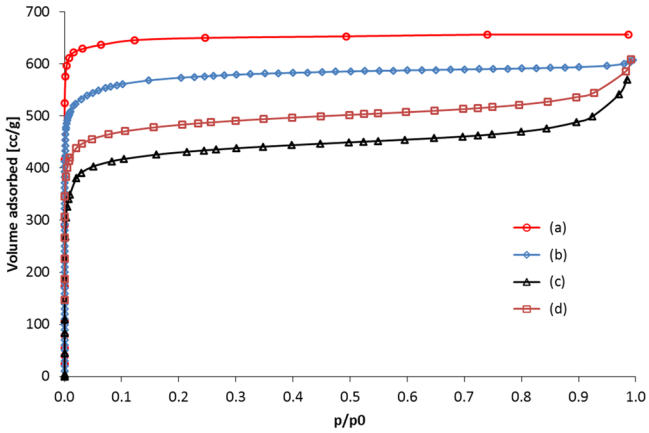

Figure 2. N_2 isotherms of (a) NU-505 generated by the GCMC simulations, (b) NU-505-Ni after supercritical CO_2 drying, followed by heating under vacuum to 100 °C for 24 h (BET area = 2110 m^2/g), (c) NU-505-Ni after water treatment and resolvation in DMF, followed by supercritical CO_2 drying and heating under vacuum to 100 °C for 24 h (BET area = 1630 m^2/g), and (d) NU-505-Ni after water treatment and resolvation in DMF, followed by reinsertion of dabco and supercritical CO_2 drying (BET area = 1910 m^2/g).

to the peaks observed for untreated NU-505-Ni, the PXRD pattern of the water-treated material displayed a new peak at 2θ = 4.08° (Figure 1). Together, these data are consistent with a structural transformation—albeit not so significant as to preclude the framework from being permanently porous upon activation. Unfortunately, the extensive postsynthesis treatment (transmetalation followed by water exposure) rendered the original crystals unsuitable for the collection of single-crystal quality data. Consequently, we relied on computational modeling to elucidate the structure of the new material. The experimentally obtained PXRD pattern of the water-treated NU-505-Ni material was used to index the unit cell and to obtain its symmetry group. Pawley fitting combined with molecular simulation was employed to refine *in silico* the coordinates of the structure against the PXRD data, starting from a known structure, using a procedure described previously (see ESI).[33] The resulting structure is a pillared-paddlewheel

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3D MOF in which, in ordered fashion, every other dabco pillar has been eliminated (Scheme 1). Given that the dabco loss occurs in water, we assume that the vacated site on Ni(II) is immediately filled with a ligated water molecule, and net substitution of dabco by two water molecules occurs. To be clear, however, the PXRD data alone are insufficient to establish that coordinated water molecules are present.

Supercritical CO_2 drying was performed and a N_2 adsorption isotherm was collected on this material to obtain a pore volume of 0.74 cm^3/g and a BET area of 1630 m^2/g (Figure 2). When a nitrogen isotherm was collected on the same sample 1 week after activation (ESI), the porosity was found to be unchanged. We additionally analyzed the various isotherms to obtain estimates of pore-size distributions (see the ESI for plots). Untreated NU-505-Ni yielded a single pore of effective diameter of 10 Å, while the version that was water-treated, supercritically dried, and then heated at 100 °C showed, in addition to the 10 Å pores, a set of pores of effective diameter of 15 Å, consistent with the alternating and periodic absence of dabco pillars.

Based on the lower overall stability of NU-505-Zn compared to the Ni(II) analogue, we expected its ability to withstand exposure to liquid water to be limited. To test our hypothesis, we subjected NU-505-Zn to the same water treatment process as the Ni(II)-based material. As was the case with the Ni(II) analogue, the ^1H NMR spectrum of the water-treated Zn(II)-based material showed a decrease of the TBAPy:dabco ratio to 1:0.6. However, the PXRD pattern did not show an additional low-angle peak and, instead, remained largely unchanged, barring the presence of low-intensity shoulders around the main peaks at 2θ = 5.56° and 2θ = 7.90° (Figure 1). Furthermore, there was a marked decrease in the BET area of the material (1150 m^2/g, compared to 1600 m^2/g attainable for the pristine NU-505-Zn), suggesting a loss of structural integrity. Again, as in the case with the pristine NU-505-Zn, the porosity of the water-treated MOF material was observed to be nonpersistent, with 20% of porosity lost within 48 h of activation (ESI).

We next examined whether the displacement of dabco pillars by water could be reversed. We were pleased to see that, following the exposure of the water-treated NU-505-Ni to a concentrated dabco solution in DMF for 24 h, an increase of the TBAPy:dabco ratio from 1:0.5 to 1:1.1 was evidenced by ^1H NMR spectroscopy. The low-angle 2θ = 4.08° peak in the PXRD pattern disappeared and overall the pattern appeared identical to that of pristine NU-505-Ni MOF (Figure 1). The pore volume and the BET area of the supercritically dried material increased to 0.816 cm^3/g and 1910 m^2/g, respectively, thereby approaching the values obtained for the parent (Figure 2). Together, these characterization data provide persuasive evidence that the MOF structure was restored by exposure to a solution of dabco.

Our observations of the behavior of NU-505-Ni in the presence of water complement, the findings of Tan et al.[28] These researchers report the stability of the pillared-paddlewheel MOF $Ni_2(bdc)_2$ (dabco) toward water; however, the MOF was only exposed to low quantities of water vapor (with the partial pressure not exceeding 10 Torr) and it was determined that water condensation inside frameworks caused their decomposition due to reaction with water. In contrast, our findings demonstrate that exposure of NU-505-Ni to condensed water does not decompose the framework, but creates a new MOF that shows permanent and persistent porosity. The missing dabco pillars in the daughter product render it a particularly attractive candidate for applications such as synthesis of a well-defined, mixed-pillar MOF through post-synthesis pillaring by a different nitrogen-based pillar, or deployment as a dual-site catalyst upon removal of solvent molecules from the Ni_2 nodes that have been subjected to the displacement of dabco.

CONCLUSIONS

In conclusion, we have successfully employed transmetalation with Ni(II) on a pillared-paddlewheel metal−organic framework (MOF) to create an unusual material that, unlike its Zn(II)-based parent, exhibits a permanent high BET area. Treatment of this material NU-505-Ni with water leads to the displacement of 50% of the dabco pillars by water molecules. The water-treated material is crystalline and permanently porous toward N_2, and the missing dabco pillars can be reinstalled by exposure of the crystals to a concentrated dabco solution leading to complete restoration of the parent NU-505-Ni MOF properties. We hope that this unique way of producing pillared-paddlewheel MOFs with missing linkers leads to the creation of new MOFs displaying useful and unique behavior or properties.

ASSOCIATED CONTENT

Supporting Information

Single-crystal data for NU-505-Zn (CIF, CCDC 1009334); *in silico* generated CIF for water-treated NU-505-Ni; experimental details for N_2 sorption, ^1H NMR, simulation, and single-crystal data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

○These authors contributed equally.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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