

# Communication

# A Flexible Metal-Organic Framework with 4-Connected Zr6 Nodes

 Yuanyuan Zhang, Xuan Zhang, Jiafei Lyu, Ken-ichi Otake, Xingjie Wang, Louis R. Redfern, Christos D. Malliakas, Zhanyong Li, Timur Islamoglu, Bo Wang, and Omar K. Farha
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topology with diamond-shaped channels along the *a* axis (Figure 1). The 4-connected Zr6 node resembles a distorted paddlewheel structure where each pair of the carboxylate groups are on two of the adjacent edges of the Zr<sub>6</sub> octahedron (Scheme 1, center). The as-synthesized NU-1400 from DEF (NU-1400-AS-DEF) also has four formate groups on each Zr6 node, as confirmed by the <sup>1</sup>H NMR spectrum of NU-1400 digested in a solution of NaOD/D2O (Figure S2). The remaining coordination sphere of each Zr ion is further fulfilled by hydroxy/water groups, as evidenced by the O-H stretching at 3650 cm<sup>-1</sup> in its diffuse reflectance infrared Fourier transform spectrum (DRIFTS) (Figure S3). Upon solvent exchange with acetone and subsequent thermal activation (NU-1400-TA), the porosity of the material was evaluated by argon sorption measurement at 87 K which showed type I adsorption isotherm (Figure 2a). BET area and the total pore volume were calculated to be 560 m<sup>2</sup>/g and 0.23 cm<sup>3</sup>/g respectively. Pore size distribution based on DFT analysis indicates pore diameters of 5 Å and 8 Å (Figure 2b), in line with the pores along the *b* and *c* axis (Figure S4).

Thermogravimetric analysis and powder X-ray diffraction (PXRD) indicated that **NU-1400** did not decompose until 450 °C under air (Figure S5–S7). The chemical stability of **NU-1400-TA** was tested by soaking in hot water and solutions of pH = 1 and pH = 12 for 24 h, where the crystallinity and porosity were maintained as evidenced by PXRD (Figure 2c) and Ar sorption (Figure S8). These results demonstrated that the thermal and chemical stability are not compromised by the low connectivity of the Zr<sub>6</sub> nodes in **NU-1400**.



**Figure 1.** Structure of **NU-1400.** a) The construction of **NU-1400.** b) The framework topology of the *lvt* net (C, grey; O, red; Zr, green).

One notable feature in the PXRD pattern of bulk NU-1400-AS-DEF is the peak shift compared to the simulated pattern from single crystal data (Figure 2d), indicative of guest-dependent structural changes. The more distinct shifts in NU-1400-TA prompted us to obtain a crystal structure of NU-1400 after supercritical CO<sub>2</sub> activation (NU-1400-SA, a = 25.385(3) Å, b = 30.661(3) Å and c = 8.2771(9) Å at 200 K; Figure 3; Table S1), which matched well with the Le Bail fitting results of NU-1400-TA (Figure S10). This entails a 51% decrease in the *c* axis and a 43% decrease in the unit cell volume as compared to NU-1400-AS-DEF, suggesting much narrower channels in the activated samples (Figure S11). This is not surprising given the computational prediction by Smit that *lvt* net is inclined to be flexible<sup>40</sup> and the resemblance of the structure of NU-1400 to a foldable wine rack with diamond-shaped channels along the *a* axis.<sup>41</sup>

The flexibility of **NU-1400** was further probed by variable temperature (300, 250 and 200 K) single crystal X-ray diffraction studies using the same **NU-1400-AS-DEF** crystal. A contraction in the *c* axis of ~ 0.51 Å is accompanied by an elongation in the *b* axis of ~ 0.15 Å as the temperature decreases from 300 to 200 K, resulting in an overall unit cell volume shrinkage of 334 Å<sup>3</sup> (Table S2). This is further confirmed in variable temperature PXRD measurements, where a continuous expansion along the *c* axis was observed as the temperature increases from 200 to 400 K (Figure S12).



**Figure 2.** Structural characterization and stability of **NU-1400**. a) Ar sorption profile of **NU-1400-TA**. b) Pore size distribution of **NU-1400-TA** based on Ar-87 K isotherm adsorption branch using DFT model. c) PXRD patterns of **NU-1400-TA** after immersing in 0.1 M HCl solution, 0.01 M NaOH solution and 90 °C water for 24 h. d) Experimental and simulated PXRD patterns of **NU-1400-AS-DEF**, **NU-1400-SA** and **NU-1400-TA**.

Given the differences between the PXRD pattern of NU-1400-AS-DEF and the simulated one from the single crystal data (Figure 2d), we suspect the degree of solvation and the guest solvent molecules must also affect the flexibility of the MOF structure. To confirm our hypothesis, single crystal X-ray diffraction data were collected after soaking the single crystals of NU-1400-AS-DEF in water or ethanol (NU-1400water and NU-1400-EtOH) (Figure 3a; Table S1). X-ray quality crystals of NU-1400-DMF were independently synthesized using DMF as the solvent, where the resulting framework exhibits an isomorphous structure (see SI). Structural analysis on these four samples indicates that there is a monotonic increase in the length of the b axis and decrease in the c axis in the order of DMF, DEF, water and ethanol (Figure 3b,3c). Commensurate with these changes is the acute angle of the diamond-shaped channels, decreasing from 71.8° in DMF to 47.1° in ethanol (Figure 3d). The unit cell volume changes from 12401 Å<sup>3</sup> in DMF to 9379 Å<sup>3</sup> in ethanol, corresponding to a  $\sim$  32% decrease (Figure 3d).



**Figure 3.** Structural changes of **NU-1400** in different solvents from single crystal X-ray diffraction data. a) Structures of **NU-1400-AS-DMF**, **NU-1400-AS-DEF**, **NU-1400-water**, **NU-1400-EtOH** and **NU-1400-SA** viewed along *a* axis. b) Schematic representation of the changes of the diamond-shape channel. c) and d) Unit cell parameters and volume changes of **NU-1400** in different solvents obtained from single-crystal structure (200 K).

Theoretical predictions of the flexibility of MOFs are generally obtained by assuming both the linker and the node to be rigid bodies; therefore, flexible topologies must originate from the hinge-like motion of the joints between the two rigid components.<sup>40,42</sup> The reduction in the connectivity of the node and topicity of the linker allows for higher degrees of freedom and thereby more flexibility in compatible topologies. Analysis of the structural details of NU-1400 in different forms revealed that the deformation of the diamond-shaped channels is correlated to the bending of the carboxylate groups out of the plane of the adjacent phenyl ring and the simultaneous twisting of the carboxylate oxygen atoms around the phenyl-carboxy C-C bond (Figure 4a). This torsional angle increases as the pore contracts, indicating additional disruption of the conjugation between the carboxy group and the phenyl ring (Figure 4b). The out-of-plane bending of the phenyl-carboxy bond, however, first decreases as the pore contracted from NU-1400-AS-DMF to NU-1400-water, but then increases as the pore further contracts when soaked in ethanol (Figure 4b). A larger out-of-plane phenyl-carboxy bending angle would endow extra strain and be less energetically favorable owing to the rigidity of the TPDC linker. Therefore, we postulated that the less bent carboxy group in NU-1400-water indicates a stronger affinity of water to NU-1400, likely due to the unique polarity and hydrogen-bonding ability of water compared to other solvents tested in this study.5 Different from the classic paddlewheel structure, where the O-O axis of adjacent carboxylate groups are parallel to each other, there is a dihedral angle between the two adjacent carboxylate groups on the Zr<sub>6</sub> node in NU-1400 (Scheme 1, center). As a result, the carboxylate groups in NU-1400 have to both bend and twist to accommodate the hinge-like motion.



**Figure 4.** Origin of flexibility in **NU-1400**. a) Illustration of the main contributions to the pore deformation. b) Details of phenyl-carboxy bending angle and twisting angle changes in **NU-1400**.

Compared to the flexibility exhibited by NU-1400-AS-DEF in response to guest molecules and temperatures, NU-1400-TA was found to be more rigid. When immersed in different solvents at room temperature, NU-1400-TA maintains its contracted conformation showing little dependence on the solvent molecules (Figure S13). Variable temperature PXRD patterns of NU-1400-TA collected from 200 to 400 K also show the structural rigidity under different temperatures (Figure S14). However, the structure changes to an expanded conformation when heated in a mixture of DMF and formic acid (Figure S15), demonstrating that flexibility can be recovered in NU-1400-TA. Neverthe less, the more energy demanding structural expansion process<sup>5</sup> of NU-1400-TA offers a stable "closed pore" form of NU-1400 under ambient conditions in solutions.

Owing to the Lewis acidity of Zr (IV), a number of Zr-MOFs have been employed as catalysts in the hydrolysis of organophosphorus ester bonds of nerve agents and simulants<sup>43</sup>. We hypothesized that the variable pore sizes of different conformations of the flexible NU-1400 would make it promising for shape-selective catalysis.<sup>44</sup> To test this hypothesis, dimethyl 4-nitrophenyl phosphate (DMNP) was chosen as a substrate because it has a size (7.4 Å  $\times$  5.0 Å of the smallest cross section) larger than the window size of NU-1400-TA (Figure 5a,b). As a result, DMNP will have limited access to the pores of NU-1400-TA while a more expanded conformation can more readily accommodate it (Figure S16). The catalytic activity of NU-1400-TA was evaluated with 6 mol% of the MOF as a catalyst, and the DMNP conversion was monitored by in situ <sup>31</sup>P NMR measurements (Figure S17). The hydrolysis conversion profile of NU-1400-TA is shown in Figure 5c, and the halflife calculated based on the initial rate is about 80 min. In comparison, a more expanded form of NU-1400 showed higher catalytic activity with half-life of only 3 min, demonstrating that different configurations of the framework influence the accessibility of DMNP to the Zr-node active sites.



**Figure 5.** Hydrolysis of DMNP. a) Hydrolysis reaction of DMNP. b) Molecular size of DMNP. c) Hydrolysis profiles of DMNP with openpore form and narrow-pore form **NU-1400**.

In summary, a flexible Zr-MOF with 4 connected nodes has been reported, and the guest- and temperature-dependent structural dynamics have been studied by single-crystal X-ray diffraction. NU-1400 possesses one-dimensional diamond-shaped channels that exhibit variable opening configurations in a single-crystal to single-crystal fashion. Taking advantage of the structural flexibility, both contracted and expanded forms of NU-1400 were tested as the catalysts for the hydrolysis of a nerve-agent simulant, DMNP, illustrating the potential application as a Lewis acid catalyst with adjustable accessibility to the catalytic sites. The intriguingly responsive properties of NU-1400 towards different solvents make it a promising candidate for selective adsorption and separation of small molecules.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental details and characterization data (PDF) Crystallographic data (CIF)

# Corresponding Author

\*o-farha@northwestern.edu

Author Contributions

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## Notes

The authors declare no competing financial interests.

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