Tunable Flexibility and Porosity of the Metal–Organic Framework DUT-49 through Postsynthetic Metal Exchange

Bikash Garai, Volodymyr Bon, Simon Krause, Friedrich Schwotzer, Martin Gerlach, Irena Senkovska, and Stefan Kaskel*

ABSTRACT: As a prominent and representative example of flexible metal–organic frameworks (MOFs), DUT-49(Cu) has gained attention due to the unique phenomenon of negative gas adsorption (NGA), originating from an unprecedented structural contraction during the gas adsorption. Herein, postsynthetic metal exchange is demonstrated to afford DUT-49 frameworks with a wide variety of metal cations, e.g., Mn²⁺, Fe²⁺, Ni²⁺, Zn²⁺, Cu²⁺, and Cd²⁺. The single-crystal-to-single-crystal conversion allowed characterization of the new MOFs by single crystal X-ray diffraction, indicating identical structure and topology compared with that of previously explored DUT-49(Cu) framework. This approach is proven successful in achieving Mn–Mn and Cd–Cd dimers, which are rare examples of M–M paddle-wheel SBUs. The relative stability and flexibility of the resulted frameworks are observed to be highly sensitive to the metal ion of the framework, following the trends predicted by the Irving–Williams series. DUT-49(Ni) was recognized as a second material from the DUT-49 series showing adsorption-induced transitions. A sequential increase in framework flexibility from rigid to flexible and from flexible to NGA has been achieved through selective incorporation of metal centers into the structure. Finally, heterometallic structures are formed by selective and controlled exchange of metal ions to finely tune the flexibility and NGA phenomenon of the framework.

INTRODUCTION

Metal–organic frameworks (MOFs) are an advanced class of porous materials that are formed by the coordination between metal nodes and organic spacers using modular building principle.1 The available scope to tune and achieve high porosity and desired functionality for intended applications renders them among the most intensively investigated materials in the past 2 decades.2 Recently flexible MOFs showed various advantages over rigid homologues in gas storage3 and separation and sensing applications.4 The structural transitions for such flexible frameworks involve swelling,5 breathing,6 linker rotation,7 and frameworks displacement in the case of interpenetrated structures.8 Collectively, these phenomena are responsible for showing modular porosities for the same framework, depending on the interaction with the adsorbent and other stimuli.9 The archetypical example of breathable MOFs is the MIL-53(M) family. Here, the nature and degree of flexibility of the structure can be varied by changing the metal ion (M)9 or adding functionality on the terephthalate linker.10

A fascinating property of some MOFs allows tuning of their existing structure through postsynthetic modification (PSM). Such modifications involve the exchange of constituents and their chemical modifications11 from the framework. Notably, the structure and/or property of the framework differs significantly from their pristine form.12 PSM is thus beneficial for synthesizing some rare structures and topologies that were otherwise not possible to achieve from de novo synthesis.13

In the case of DUT-49 framework, an unprecedented adsorption-induced pore contraction amplitude has been observed leading to the large shrinkage of its crystal lattice [cell length from 46.588 to 36.160 Å and volume from 101 117 to 47 281 Å³].14 This structural transition of the highly porous open pore phase into less porous contracted pore phase results in the release of excess adsorbate molecules from the pores, which is reproducibly observed in the volumetric physisorption experiments. This unique observation of negative gas adsorption (NGA) is associated with the distinctive structural feature of the DUT-49 framework. DUT-49 is constructed from a tetratopic linker, 9,9′-([1,1′-biphenyl]-4,4′-diyl)bis(9H-carbazole-3,6-dicarboxylic acid) (H₂BBCDC) which is defined by two carbazole 3,6-dicarboxylate moieties connected through a biphenyl spacer.15 The carbazole moieties forming 12 connected cuboctahedral cavities are then linked through the spacer (Figure 1a) in the three-dimensional network. These biphenyl spacers form additional octahedral and tetrahedral cavities, which undergo...
Taking into consideration the importance of the structural feature of the DUT-49 framework for observing NGA, paddle-wheel SBU is the only metal cluster that can maintain the same topology. Of the several bivalent metal ions of the periodic table, Cu has been known to form paddle-wheel motif easily, due to the favorable d–d interaction, although reports are there that describe the M–M paddle-wheel involving other metal ions such as Zn, Fe, Co, Ni, etc. but with limited instances. Herein, we present postsynthetic metal exchange as an efficient route to exchange the metal centers of the paddle-wheel to synthesize DUT-49(M) frameworks (M = Mn, Fe, Ni, Zn, Cd). This allows for synthesizing a series of the framework with different metal ions, which are otherwise unattainable from direct synthesis. The presence of large sized pores allows easy diffusion to achieve a complete exchange of all the metal ions from each crystal. The postsynthetically metal substituted frameworks display varying amount of flexibility and thereby NGA phenomenon.

### Experimental Section

**General Methods.** All the chemicals were purchased from commercial sources and used after proper purification. Extent of postsynthetic metal exchanges was quantified using the ICP-OES technique. The crystallinity and phase purity of the MOFs were determined by recording powder X-ray diffraction (PXRD) patterns. PXRD patterns were recorded in the 2θ range of 2°–70° in transmission geometry with a STOE STADI P diffractometer operated at 40 kV and 30 mA with monochromatic Cu Kα1 (λ = 0.15405 nm) radiation. The MOFs were activated using supercritical carbon dioxide in a Jumbo Critical Point Dryer 13200J AB (SPI Supplies). Porosity of the activated MOFs was determined by measuring the N2 physisorption isotherm at 77 K using a volumetric BELSORP-max device.

**Single Crystal X-ray Diffraction.** A suitably sized cubic crystal of the DUT-49(M) MOF from NMP was brought into a borosilicate glass capillary (d = 0.3 mm) with a small amount of the mother liquor. The data sets were collected at BESSY MX BL14.3 beamline of Helmholtz-Zentrum Berlin für Materialien und Energie. Mono- chromic X-ray radiation with a wavelength of λ = 0.089499 nm (E = 13.85 keV) was used in experiments. All data sets were collected at room temperature. The crystal symmetry and scan range were determined in each particular case using the iMosflm program. The φ-scans with oscillation range of 1° were used for data collection. For each data set, 60 images were collected to reach the maximal completeness. The data sets were processed in the automatic regime using XDSAPP 2.0 software. Crystal structures were solved by direct methods and refined by full matrix least-squares on F2 using the SHELX-2018/3 program package. All non-hydrogen atoms were refined in anisotropic approximation. Hydrogen atoms were refined in geometrically calculated positions using the "riding model" with Uiso(H) = 1.2Ueq(C). The large pores, high crystal symmetry, and room temperature data collection led to disorder of solvent molecules within the pores of the frameworks. The SQUEEZE routine in PLATON was used to generate the reflection intensities with subtracted solvent contribution.

**DUT-49(Mn)**. C_{40}H_{20}Mn_2N_2O_{10}, FW = 798.46, cubic, FM3m, a = 47.080(5) Å, Z = 24, d_{calc} = 0.305 g cm⁻³, 4197 reflections, R int = 0.0218, R1 = 0.0619, wR2 = 0.2344, S = 1.106.

**DUT-49(Fe)**. C_{40}H_{20}Fe_2N_2O_{10}, FW = 800.28, cubic, FM3m, a = 46.890(5) Å, Z = 24, d_{calc} = 0.309 g cm⁻³, 3994 reflections, R int = 0.0296, R1 = 0.0929, wR2 = 0.3261, S = 1.442.

**DUT-49(Cu)**. C_{40}H_{20}Cu_2N_2O_{10}, FW = 806.00, cubic, FM3m, a = 46.820(5) Å, Z = 24, d_{calc} = 0.313 g cm⁻³, 4007 reflections, R int = 0.0461, R1 = 0.0911, wR2 = 0.3246, S = 1.002.

---

Figure 1. (a) Topological representation of DUT-49 framework composed of interconnected cuboctahedral cavities. Blue spheres represent the paddle-wheel SBUs, and the stick lines represent the linkers. (b) Schematics for postsynthetic exchange of different metal ions to the SBU leading to DUT-49(M) MOFs. "a" is the length of M–O.carboxylate bond and "b" is the M–M distance.
**RESULTS AND DISCUSSION**

In contrast to previous reports for synthesis of DUT-49(Cu), direct synthesis of DUT-49 framework with other bivalent metal nodes remained inefficient and sometimes not possible. Thus, several efforts for the synthesis of M\(^{2+}\) based DUT-49(M) frameworks in pure phase (M = Mn, Fe, Ni, Zn, Cd) were unsuccessful, despite following different synthetic routes. Fortunately, DUT-49(Co) could be readily synthesized with good yield and phase purity from the solvothermal reaction between H\(_4\)BBCDC linker and Co(NO\(_3\))\(_2\)-6H\(_2\)O in N-methyl-2-pyrrolidone (NMP) solvent. Taking DUT-49(Co) crystals as the starting point, we attempted the synthesis of other DUT-49(M) frameworks following the postsynthetic metal exchange approach. An efficient substitution of the Co metal centers with incoming bivalent metal ion was obtained by varying appropriate conditions. To achieve the metal exchange, the as-synthesized cubic crystals of DUT-49(Co) were first washed with fresh NMP to remove any residual reactants and then dipped into the solution of corresponding metal salts (nitrates of Mn, Ni, Cu, Zn, Cd, and FeSO\(_4\)) (Figure 1b; section S3, Supporting Information). On the basis of the kinetics of the exchange process, the crystals are then removed from the exchange media and washed again with fresh solvent. The exchange of metal ion in the framework is also clearly visible from the change in color of the crystals, where the bluish color for DUT-49(Co) changes into light pink (Mn), colorless to brown (Fe), green/yellow (Ni), blue (Cu), and colorless (Zn and Cd), as characteristic color of the incoming metal ion (Figure 2a). The release of Co(II) ions into the solution establishes an efficient tool to visually monitor the kinetics of the metal exchange process. It is observed that the exchange process to replace Co(II) from the framework was completed within 3 h by Cu(II) and within 24 h for Mn(II), Fe(II), Zn(II), and Ni(II). However, Cd(II) being bulkier in size has a slower reaction, and its complete exchange to substitute Co(II) from the DUT-49 framework takes around 3 days. Notably, aerial contact of DUT-49(Fe) crystals causes a color change from colorless to brown owing to the aerial oxidation of Fe(II) from the crystal surface.\(^{34}\)

XRD patterns of the materials recorded before, during, and after the exchange does not show any distinct change (Figure S8, Supporting Information), confirming the retention of structural integrity of the framework throughout the whole process. Retention of the initial framework structure after the metal exchange is evidenced from XRD patterns obtained after the exchange with new metal ion (Figure 2b). This observation also establishes the nature of the conversion as single-crystal-to-single-crystal transformation, which makes it possible to

---

**Figure 2.** (a) Optical microscopic images of the DUT-49(M) crystals showing different color originating from different metal centers (scale bar, 100 μm). (b) XRD patterns of the as-synthesized crystals showing isostructural character for all the MOFs. (c) Efficiency and competitive kinetics for exchange of few metal ions to DUT-49(Co).
determine the structure of the final material through single crystal X-ray diffraction. Single crystal X-ray diffraction at room temperature shows similar lattice geometry for all the DUT-49(M) frameworks except for the slight difference in the M–M distance of the paddle-wheel and unit cell parameters. Like the previous instances of DUT-49(Cu), all of the new DUT-49(M) frameworks crystallize in the cubic \textit{Fm\textbar{3}m} space group (cell parameter: 46.080–47.420 Å). However, on the basis of the atomic size and interaction between the metal ion and carboxylate, the M–O and M–M distances vary, as presented in Figure 1b. This variation in M–O distance supports the complex formation ability of transition metal ions as proposed in the Irving–Williams series. On the other hand, the M–M distance in the paddle-wheel defines the possibility toward formation of $\delta$-bonding between the two metal ions and is also different for each of the cases. Both of M–O$_{substitution}$ and M–M distances attain the minima of 1.964 and 2.634 Å, respectively, for the case of Cu.

Notably, synthesis of these MOFs through postsynthetic metal exchange made it possible to analyze the structural features of very rare Mn–Mn and Cd–Cd paddle-wheel containing MOFs, which are very hard and rare to obtain in direct synthesis methods.

The exchange of metal nodes in DUT-49(Co) framework is further confirmed and quantified using ICP-OES, where it shows a 100% exchange of Co (Table S3, Supporting Information) with the targeted metal ion that can be achieved under suitable condition (0.2 M solution for Ni(II) and Cd(II) and 0.1 M solution for other metal ions; section S3, Supporting Information). A detailed investigation toward the competitive nature of the metal exchange among DUT-49(Co), DUT-49(Ni), DUT-49(Zn), DUT-49(Cu) from equimolar concentration (0.1 M) of the incoming metal salt shows that exchange of Co by Ni in DUT-49(Co) is feasible to an extent of 46%, while the reverse exchange is possible by an extent of 94%. In contrast, treatment of Zn(II) to DUT-49(Co) leads to a complete (100%) substitution of Co centers with Zn, against 31% efficiency for the reverse exchange. Interestingly, it is possible to totally replace the newly exchanged Ni(II) centers of the partially Ni exchanged DUT-49(Co) using Zn(II), while Ni exchange to DUT-49(Zn) was only possible reaching 10%. However, Cu is found to be capable of completely replacing any other metal ion from the framework. Analysis of a full study with all seven metal ions is presented in the Supporting Information (section S4). Most importantly, no other metal ion is able to replace any content of Cu centers from the DUT-49(Cu) framework. This established the most thermodynamic stability of the DUT-49(Cu) framework among other frameworks. Therefore, of the different metal SBUs contained in DUT-49 framework, DUT-49(Co) is the most susceptible toward metal-ion exchange while DUT-49(Cu) is the most reluctant one. The relative positions of the other two candidates in this study are intermediate with a sequential change as displayed in Figure 2c. These findings are in good agreement with previous reports on relative stabilities of M–M paddle-wheel SBUs, where it was observed that the Cu–Cu paddle-wheel is the thermodynamically stable SBU. The shortest distance between the two Cu atoms from the paddle-wheel SBU (indicating the strongest M–M interaction), as observed from the crystal structure analysis, is the possible reason behind its reluctance against substitution with any other metal ions.

Considering the high surface area and structural flexibility for the DUT-49(Cu) MOF, the metal exchanged MOFs were subjected to solvent removal through supercritical CO$_2$ activation, the mildest activation process known so far. However, under the experimental condition of the activation procedure, DUT-49(Cu) retains its structure and the other materials tend to lose their crystallinity and amorphize at the end of the procedure. The experimental setup of the procedure limits the in situ monitoring of the activation procedure; thus it is not possible to determine whether the frameworks collapse during the exchange with liquid CO$_2$, during the introduction of the supercritical state, or upon release of supercritical CO$_2$ from the pores. To address and prevent the possible framework collapse during the exchange of solvent media with liquid CO$_2$, various solvents such as acetone, ethanol, and amyl acetate are tested (Figures S7 and S11, Supporting Information). However, in no case, DUT-49(M) [M = Mn, Fe, Co, and Cd] MOFs are able to retain their crystallinity after the activation procedure (Figure S6, Supporting Information). This amorphization of Mn, Fe, Co, Zn, and Cd containing DUT-49 frameworks restricts these materials to show the expected porosity, as observed for the DUT-49(Cu) framework.

The reduced porosity is evidenced from the drop of total N$_2$ uptake in their adsorption isotherms and the corresponding surface area values (Figure 3a). The collapse of the framework structure during the activation process arises from the inherent soft nature of the paddle-wheel SBUs in DUT-49 (Co, Zn, Mn, Fe, Cd) frameworks from the increased M–M distance, weakening the M–M interaction in between them. During the removal of solvent from the axial sites of metal centers, the paddle-wheel cluster undergoes additional deformation which adds to the activation stress for the MOFs. This makes the structures unstable during or after the solvent removal to create large voids in the highly porous MOFs. Similar instability of the paddle-wheel SBU has already been observed for other Zn based MOFs such as Zn-HKUST-1, where several attempts have failed to achieve permanent porosity for the framework. However, the Cu-exchanged crystals of the DUT-49(M) framework can sustain the activation procedure, showing similar crystallinity after activation as that of pristine DUT-49(Cu) synthesized from direct solvothermal conditions (Figure S9, Supporting Information). Moreover, these Cu exchanged frameworks show comparable total N$_2$ uptake, flexibility, and NGA steps as that of directly synthesized materials (Figure 3b). However, because of the difference in the crystal size (~0.8 mm for Cu exchanged crystals over ~0.1 mm for direct synthesized), a difference was observed in the total uptake as well as in the NGA step. It is noteworthy that in previous attempts, it was not possible to obtain large sized (>100 μm) single crystal for DUT-49(Cu) from direct synthesis. Thus, the approach of metal exchange is beneficial to increase the crystal size, allowing a broader aspect for analysis based on crystal size. The transition pressure ($p_{\textsf{NGA}}$) of DUT-49(Cu) shifts from a pressure of 8.9 to 9.9 kPa for the larger sized crystals that are achievable only from the exchange pathway. This completes the scope of crystal size effect for DUT-49 framework on its flexibility. The stability of the Cu exchanged framework possibly originates from the shortest Cu–Cu distance, as observed in its crystal structure, that makes the framework stable during the solvent removal process. The role of M–M distance in stabilizing the framework is further confirmed from the case of DUT-
49(Ni). In this case, the Ni–Ni distance in the SBU is 2.720 Å, which is very close to that Cu (2.634 Å). This indicates a possible stability for the system, which is exactly observed after the supercritical activation. Similar to DUT-49(Cu), DUT-49(Ni) is also capable of withstanding the activation stress and producing highly crystalline activated MOF (Figure S6d, Supporting Information). Moreover, DUT-49(Ni) shows higher uptake in its N₂ adsorption isotherm as compared to other metal containing DUT-49 frameworks (Figure 3a). DUT-49(Ni) also shows a hysteresis loop in the adsorption isotherm, similar to that of DUT-49(Cu) which accounts for the flexibility of the framework (Figure S13, Supporting Information). However, no NGA is observed for this case, highlighting the role of metal centers for observing flexibility and NGA phenomenon.

Since only the Cu–Cu paddle-wheel containing framework of DUT-49 MOF is found to be stable against the activation-induced stress, we synthesized mixed-metal MOFs with controllable Cu content in the DUT-49(M) [M = Mn, Fe, Co, Ni, Zn, Cd] with Cu(II) and subjected these solids to supercritical activation procedure using the same procedure after exchanging the solvent with acetone. For carrying out such controlled metal exchange, a certain amount of the respective MOF crystals (inside NMP solvent) is taken into a glass vial and spread onto its bottom surface, and then a calculated amount of Cu(II) solution is added. Additional amount of fresh solvent was added on top of the crystals beforehand for creating a longer path distance for the incoming Cu(II) solution, thereby reducing its rate of diffusion and making a uniform concentration throughout the whole solvent front (Figure S1, Supporting Information). Likewise, no change in the crystallinity is observed after the heterometallic framework formation, and interestingly the materials are capable of retaining their crystalline structure after the supercritical CO₂ activation process (Figure 4a), as that of DUT-49(Cu). A detailed investigation is performed with two different Cu loadings (50% and 70% relative to total amount of metal ion in the crystals, as measured from the metal solution concentration and SEM-EDX) with DUT-49(Co) and DUT-49(Zn) as the basic framework, to obtain DUT-49(0.5Cu0.5), DUT-49(Co0.7Cu0.3), DUT-49(Zn0.7Cu0.3), and DUT-49-

---

**Figure 3.** (a) N₂ adsorption isotherm at 77 K for DUT-49(M) frameworks. (b) N₂ adsorption isotherm (77 K) for few Cu exchanged DUT-49(M) framework showing flexibility and negative gas adsorption feature (magnified range in the inset). Filled and empty circles represent adsorption and desorption, respectively.

**Figure 4.** Heterometallic MOFs from partial Cu exchange to DUT-49(M) frameworks: (a) XRD patterns recorded after supercritical CO₂ activation, showing retention of the framework; (b) elemental mapping showing the Zn and Cu ion distribution along the crystal surface, scale bar = 25 μm; (c) N₂ adsorption isotherm of partially Cu exchanged DUT-49(Zn) frameworks, controlling the flexibility and NGA by controlling the amount of Cu in the heterometallic MOFs. Filled and empty circles represent adsorption and desorption, respectively.
(Zn₈Cu₁₀) as the heterometallic frameworks. Observation under optical microscope showed that the outer surface of the crystals retains a bluish color, corresponding to the presence of Cu(II).

There exist three different possibilities⁴¹ for the exchange of Cu to the bulk phase of DUT-49(Co/Zn) crystals. The first possibility is the nonhomogeneous substitution from different crystals, forming a physical mixture of individual metal containing MOFs. This has been strongly reduced by slowing the diffusion and occasional stirring of the crystals during the exchange. The second possibility is the substitution of Co/Zn from some areas of the MOF crystals forming different M−M SBUs within a single MOF crystal. This possibility is also known for formation of core−shell structures; however, the large sized pores facilitate easy diffusion of the metal ions into the core of the crystal, and hence no distinct core−shell formation was observed here. This has been confirmed from the elemental mapping showing homogeneous distribution of both of the metal ions throughout the crystal surface (Figure S13). The third possible state is the substitution of one Co/Zn from each of the affected SBU forming heterobimetallic SBU containing MOF. The second and third possibilities are believed to occur during the partial Cu exchange to the MOFs. Observation of homogeneous blue color for the crystal faces of all the crystals eliminates the possibility for obtaining a physical mixture of individual MOFs. Further, the location of the newly added Cu sites is established through SEM-EDX mapping analysis of the crystals.⁴² Analysis of DUT-49(Zn₀.₅Cu₀.₅) showed uniform distribution of both Zn and Cu atoms throughout the whole surface of the individual crystal (Figure 4b). These findings confirm the uniform distribution of the Cu−Cu SBU along with the other SBUs in the partially Cu exchanged frameworks.

The advantage of Cu doping inside these heterobimetallic MOFs becomes prominent when the crystals are subjected to supercritical CO₂ activation from acetone solvent. All of the MOFs remain crystalline, and no change in their XRD pattern is detected. Also, no observable difference in the XRD patterns is recorded for the activated materials when the crystals contain different Cu content (Figure S10, Supporting Information). The N₂ adsorption isotherm for these MOFs reveals their flexibility and permanent porosity (Figure 4c). As the Cu content in DUT-49(Co₁−ₓCuₓ) crystals is increased from 0% to 50% to 70%, the total uptake volume at ~100 kPa also increases from 9.4 to 11.96 to 47.27 mmol g⁻¹. Similar nonlinear increment is also observed for sequential Cu doping to DUT-49(Zn) where the total uptake at ~100 kPa varies from 11.92 to 23.17 to 43.39 mmol g⁻¹ (Table S5, Supporting Information). This nonlinear boost in the total uptake is possibly because of the distribution of the Cu throughout the whole crystal, instead of the localized substitution. This is also an indication of the formation of heterobimetallic SBUs, proposed as a third possibility during the metal exchange. Thus, formation of Cu−Zn SBU along with Cu−Cu SBU prevents the linear increment in the uptake value, as predicted otherwise for the formation of only Cu−Cu SBU during the metal exchange. However, these results imply that using this postsynthetic metal exchange in single crystal to single crystal manners can produce heterobimetallic MOFs. These heterobimetallic DUT-49 frameworks are capable of preserving and tuning the porosity and flexibility of the framework, based on the Cu content inside them.

The signature for the flexibility of DUT-49 framework is also achieved for these heterometallic MOFs, as seen from their N₂ adsorption isotherm. All of these MOFs show characteristic flexibility and NGA steps in the adsorption isotherm. The amount of the gas evolved during this step (ΔνNGA) is related to the amount of Cu in the structure. Thus, for the DUT-49(ZnₓCu₁−ₓ) crystals, ΔνNGA values increased from 0 to 1.08 to 3.31 and finally to 2.81 mmol g⁻¹. Also notably, the ΔνNGA value is lowered for the heterometallic MOFs, potentially indicating the effect of particle downsizing for the heterometallic MOFs. This could be originated from the distribution of Cu throughout the crystal, which causes the formation of small sized domains inside the crystals protected through the propagation of Cu centers. Thus, neighboring Cu SBUs are responsible for bringing in stability to the DUT-49(M) MOFs and restoring their flexible character.

### CONCLUSION

In summary, we have introduced and presented the concept of postsynthetic metal exchange to synthesize a series of DUT-49(M) framework, through single-crystal-to-single-crystal transformation. This metal exchange with 100% efficiency has allowed the incorporation of six different metal ions in the DUT-49 framework and formation of very rare structural motifs such as Mn−Mn and Cd−Cd paddle-wheel. The structural analysis provides insight into their relative stabilities and changes during the activation procedure. After supercritical CO₂ activation, the frameworks show varying degree of porosity: (a) Mn, Fe, Co, Zn, Cd paddle-wheel containing DUT-49 frameworks show no crystallinity and very low remaining porosity; (b) DUT-49(Ni) stays crystalline and shows moderate porosity and flexibility; (c) DUT-49(Cu) shows the highest porosity and flexibility with NGA. The flexibility and NGA feature of DUT-49 have been further improved and tuned by heterometallic framework formation.

### ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.9b04769.

Detailed experimental procedure, XRD patterns, single crystal X-ray diffraction data, estimation of metal ion exchange through ICP-OES, summary and comparison of BET surface area (PDF).

### AUTHOR INFORMATION

**Corresponding Author**

Stefan Kaskel − Technische Universität Dresden, Dresden, Germany; orcid.org/0000-0003-4572-0303; Email: stefan.kasel@chemie.tu-dresden.de

**Other Authors**

Bikash Garai − Technische Universität Dresden, Dresden, Germany; orcid.org/0000-0001-5945-9375

Volodymyr Bon − Technische Universität Dresden, Dresden, Germany; orcid.org/0000-0002-9851-5031

Simon Krause − Technische Universität Dresden, Dresden, Germany; orcid.org/0000-0001-9504-8514

Friedrich Schwotzer − Technische Universität Dresden, Dresden, Germany

894

https://dx.doi.org/10.1021/acs.chemmater.9b04769
Chem. Mater. 2020, 32, 889−896
The authors thank Helmholtz-Zentrum Berlin für Materialien und Energie (HZB) for the allocation of the synchrotron radiation beamtime on the MX BL14.3 beamline and travel grants.

**ABBREVIATIONS**

DUT, Dresden University of Technology; HKUST, Hong Kong University of Science and Technology; SBU, secondary building unit; ICP-OES, inductively coupled plasma optical emission spectroscopy; SEM, scanning electron microscopy; EDX, energy-dispersive X-ray

**REFERENCES**

1. Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O’Keeffe, M.; Yaghi, O. Modular Chemistry: Secondary Building Units as a Basis for the Design of Highly Porous and Robust Metal–Organic Carboxylate Frameworks. *Acc. Chem. Res.* 2001, 34, 319–330.

2. Li, B.; Wen, H.-M.; Cui, Y.; Zhou, W.; Qian, G.; Chen, B. Emerging Multifunctional Metal–Organic Framework Materials. *Adv. Mater.* 2016, 28, 8819–8860.

3. Mason, J. A.; Oktavianie, J.; Taylor, M. K.; Hudson, M. R.; Rodriguez, J.; Bachman, J. E.; Gonzalez, M. I.; Cervellino, A.; Guagliardi, A.; Brown, C. M.; et al. Methane Storage in Flexible Metal–Organic Frameworks with Intrinsic Thermal Management. *Nature* 2015, 527, 357–361.

4. Takashima, Y.; Martinez, V. M.; Furukawa, S.; Kondo, M.; Shimomura, S.; Uehara, H.; Nakahama, M.; Sugimoto, K.; Kitagawa, S. Molecular Decoding Using Luminescence from an Entangled Porous Framework. *Nat. Commun.* 2011, 2, 168.

5. Mellot-Draznieks, C.; Serre, C.; Sublè, S.; Audebrand, N.; Férey, G. Very Large Swelling in Hybrid Frameworks: A Combined Computational and Powder Diffraction Study. *J. Am. Chem. Soc.* 2005, 127, 16273–16278.

6. Serre, C.; Millange, F.; Thouvenot, C.; Nogues, M.; Marsolier, G.; Louër, D.; Férey, G. Very Large Breathing Effect in the First Nanoporous Iron(III)-Based Solids: MIL-53 or Cr III (OH)-[O 2 C–C 6 H 4 –CO 2 ]2 (HO 2 C–C 6 H 4 –CO 2 H)2 x H2 O. *J. Am. Chem. Soc.* 2012, 134, 13519–13526.

7. Fairen-Jiménez, D.; Moggach, S. A.; Wharmby, M. T.; Wright, P. A.; Parsons, S.; Düren, T. Opening the Gate: Framework Flexibility in ZIP-8 Explored by Experiments and Simulations. *J. Am. Chem. Soc.* 2011, 133, 8903–8902.

8. Schneemann, A.; Bon, V.; Schwedler, I.; Senkovska, I.; Kaskel, S.; Fischer, R. A. Flexible Metal–Organic Frameworks. *Chem. Soc. Rev.* 2014, 43, 6062–6096.

9. Horcajada, P.; Serre, C.; Maurin, G.; Ramsayhe, N. A.; Balas, F.; Vallet-Regí, M.; Sebba, M.; Taulelle, F.; Férey, G. Flexible Porous Metal–Organic Frameworks for a Controlled Drug Delivery. *J. Am. Chem. Soc.* 2008, 130, 6774–6780.

10. Munn, A. S.; Pillai, R. S.; Biswas, S.; Stock, N.; Maurin, G.; Walton, R. I. The Flexibility of Modified-Linker MIL-53 Materials. *Dal. Trans.* 2016, 45, 4162–4168.

11. Yin, Z.; Wan, S.; Yang, J.; Kurmoo, M.; Zeng, M.-H. Recent Advances in Post-Synthetic Modification of Metal–Organic Frameworks: New Types and Tandem Reactions. *Coord. Chem. Rev.* 2019, 378, 500–512.

12. Tanabe, K. K.; Cohen, S. M. Postsynthetic Modification of Metal–Organic Frameworks—a Progress Report. *Chem. Soc. Rev.* 2011, 40, 498–519.

13. Brozek, C. K.; Dincă, M. Ti 3+ – V 2+ /3+ – Cr 2+ /3+ – Mn 2+ – Fe 2+ -Substituted MOF-5 and Redox Reactivity in Cr- and Fe-MOF-5. *J. Am. Chem. Soc.* 2013, 135, 12886–12891.

14. Krause, S.; Bon, V.; Senkovska, I.; Stoeck, U.; Wallacher, D.; Többens, D. M.; Zander, S.; Pillai, R. S.; Maurin, G.; Coudert, F. X.; et al. A Pressure-Amplifying Framework Material with Negative Gas Adsorption Transitions. *Nature* 2016, 532, 348–352.

15. Stoeck, U.; Krause, S.; Bon, V.; Senkovska, I.; Kaskel, S. A Highly Porous Metal–Organic Framework, Constructed from a Cuboctahedral Super-Molecular Building Block, with Exceptionally High Methane Uptake. *Chem. Commun.* 2012, 48, 10841.

16. Schaber, J.; Krause, S.; Paasch, S.; Senkovska, I.; Bon, V.; Többens, D. M.; Wallacher, D.; Kaskel, S.; Brunner, E. In Situ Monitoring of Unique Switching Transitions in the Pressure-Amplifying Flexible Framework Material DUT-49 by High-Pressure 129 Xe NMR Spectroscopy. *J. Phys. Chem. C* 2017, 121, 5185–5200.

17. Evans, J. D.; Becquet, L.; Coudert, F. X. Origins of Negative Gas Adsorption. *Chem. 2016, 1, 873–886.

18. Krause, S.; Evans, J. D.; Bon, V.; Senkovska, I.; Ehrlich, S.; Stoeck, U.; Yot, P. G.; Iacomì, P.; Plewellyn, P.; Maurin, G.; et al. Adsorption Contraction Mechanics: Understanding Breathing Enthalpies in Isoreticular Metal–Organic Frameworks. *J. Phys. Chem. C* 2018, 122, 19171–19179.

19. Krause, S.; Evans, J. D.; Bon, V.; Senkovska, I.; Iacomì, P.; Kolbe, F.; Ehrlich, S.; Troschke, E.; Getzschmann, J.; Többens, D. M.; et al. Towards General Network Architecture Design Criteria for Negative Gas Adsorption Transitions in Ultraporous Frameworks. *Nat. Commun.* 2019, 10, 3632.

20. Krause, S.; Bon, V.; Senkovska, I.; Többens, D. M.; Wallacher, D.; Pillai, R. S.; Maurin, G.; Kaskel, S. The Effect of Crystallite Size on Pressure Amplification in Switchable Porous Solids. *Nat. Commun.* 2018, 9, 1573.

21. Köberl, M.; Cokoja, M.; Herrmann, W. A.; Kühn, F. E. From Molecules to Materials: Molecular Paddle-Wheel Synths of Macromolecules, Cage Compounds and Metal–Organic Frameworks. *Dal. Trans.* 2011, 40, 6834–6859.

22. Ayappa, A. B.; Saha, S.; Garai, B.; Thote, J.; Kurungot, S.; Banerjee, R. A Distinctive PdCl2 -Mediated Transformation of Fe-Based Metalloalgs into Metal–Organic Frameworks. *Cyst. Growth Dev.* 2014, 14, 3434–3437.

23. Ehrlich, S.; Senkovska, I.; Bon, V.; Evans J. D.; Petkov, P.; Kruskaya, V.; Kataev, V.; Wulf, T.; Krylov, A.; Vyturin, A.; et al. Crystal Size versus Paddle Wheel Deformability: Selective Gated Adsorption Transitions of the Switchable Metal–Organic Frameworks DUT-8(Co) and DUT-8(Ni). *J. Mater. Chem. A* 2019, 7, 21459–21475.

24. Maniam, P.; Stock, N. Investigation of Porous Ni-Based Metal–Organic Frameworks Containing Paddle-Wheel Type Inorganic Building Units via High-Throughput Methods. *Inorg. Chem.* 2011, 50, 5085–5097.

25. Bhunia, M. K.; Hughes, J. T.; Mettger, J. C.; Navrotsky, A. Thermochemistry of Paddle Wheel MOFs: Cu-HKUST-1 and Zn-HKUST-1. *Langmuir* 2013, 29, 8140–8145.

26. Song, X.; Jeong, S.; Kim, D.; Lah, M. S. Transmetalations in Two Metal–Organic Frameworks with Different Framework Flex-
(27) Gerlach, M.; Mueller, U.; Weiss, M. S. The MX Beamlines BL14.1-3 at BESSY II. J. Large-Scale Res. Facil. 2016, 2, 1–6.
(28) Batye, T. G. G.; Kontogiannis, L.; Johnson, O.; Powell, H. R.; Leslie, A. G. W. IMOSFLM: A New Graphical Interface for Diffraction-Image Processing with MOSFLM. Acta Crystallogr., Sect. D: Biol. Crystallogr. 2011, 67, 271–281.
(29) Winn, M. D.; Ballard, C. C.; Cowtan, K. D.; Dodson, E. J.; Emsley, P.; Evans, P. R.; Keegan, R. M.; Krissinel, E. B.; Leslie, A. G. W.; McCoy, A.; et al. Overview of the CCP 4 Suite and Current Developments. Acta Crystallogr., Sect. D: Biol. Crystallogr. 2011, 67, 235–242.
(30) Sparta, K. M.; Krug, M.; Heinemann, U.; Mueller, U.; Weiss, M. S. XDSAPP2.0. J. Appl. Crystallogr. 2016, 49, 1085–1092.
(31) Sheldrick, G. M. A Short History of SHELX. Acta Crystallogr., Sect. A: Found. Crystallogr. 2008, 64, 112–122.
(32) Sheldrick, G. M. Crystal Structure Refinement with SHELXL. Acta Crystallogr., Sect. C: Struct. Chem. 2015, 71, 3–8.
(33) Spek, A. L. Structure Validation in Chemical Crystallography. Acta Crystallogr., Sect. D: Biol. Crystallogr. 2009, 65, 148–155.
(34) Kim, Y.; Das, S.; Bhattacharya, S.; Hong, S.; Kim, M. G.; Yoon, M.; Natarajan, S.; Kim, K. Metal-Ion Metathesis in Metal-Organic Frameworks: A Synthetic Route to New Metal-Organic Frameworks. Chem. - Eur. J. 2012, 18, 16642–16648.
(35) Deria, P.; Mondloch, J. E.; Karagiardhi, O.; Bury, W.; Hupp, J. T.; Farha, O. K. Beyond Post-Synthesis Modification: Evolution of Metal-Organic Frameworks via Building Block Replacement. Chem. Soc. Rev. 2014, 43, 5896–5912.
(36) Mondloch, J. E.; Karagiardhi, O.; Farha, O. K.; Hupp, J. T. Activation of Metal-Organic Framework Materials. CrystEngComm 2013, 15, 9258–9264.
(37) Grüninger, R.; Bon, V.; Müller, P.; Stoeck, U.; Krause, S.; Mueller, U.; Senkovska, I.; Kaskel, S. A New Metal-Organic Framework with Ultra-High Surface Area. Chem. Commun. 2014, 50, 3450–3452.
(38) Seo, J.; Bonneau, C.; Matsuda, R.; Takata, M.; Kitagawa, S. Soft Secondary Building Unit: Dynamic Bond Rearrangement on Multinuclear Core of Porous Coordination Polymers in Gas Media. J. Am. Chem. Soc. 2011, 133, 9005–9013.
(39) Bureekaew, S.; Amirjalayer, S.; Schmid, R. Orbital Directing Effects in Copper and Zinc Based Paddle-Wheel Metal Organic Frameworks: The Origin of Flexibility. J. Mater. Chem. 2012, 22, 10249–10254.
(40) Feldblyum, J. I.; Liu, M.; Gidley, D. W.; Matzger, A. J. Reconciling the Discrepancies between Crystallographic Porosity and Guest Access as Exemplified by Zn-HKUST-1. J. Am. Chem. Soc. 2011, 133, 18257–18263.
(41) Dolgopolova, E. A.; Brandt, A. J.; Ejegbavwo, O. A.; Duke, A. S.; Maddumapatabandi, T. D.; Galhenage, R. P.; Larson, B. W.; Reid, O. G.; Ammal, S. C.; Heyden, A.; et al. Electronic Properties of Bimetallic Metal–Organic Frameworks (MOFs): Tailoring the Density of Electronic States through MOF Modularity. J. Am. Chem. Soc. 2017, 139, 5201–5209.
(42) Zhu, J.; Chen, J.; Qiu, T.; Deng, M.; Zheng, Q.; Chen, Z.; Ling, Y.; Zhou, Y. Cobalt Substitution in a Flexible Metal–Organic Framework: Modulating a Soft Paddle-Wheel Unit for Tunable Gate-Opening Adsorption. Dalt. Trans. 2019, 48, 7100–7104.