

Single-Crystal to Single-Crystal Mechanical Contraction of Metal–Organic Frameworks through Stereoselective Postsynthetic Bromination

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Supporting Information

ABSTRACT: The properties of metal–organic frameworks (MOFs) can be tuned by postsynthetic modification (PSM) to introduce specific functionalities after their synthesis. Typically, PSM is carried out on pendant functional groups or through metal/ligand exchange, preserving the structure of the MOF. We report herein the bromination of integral alkyne units in a pair of Zr⁴⁺ and Hf⁴⁺ MOFs, which proceeds stereoselectively in a single-crystal to single-crystal manner. The chemical and mechanical changes in the MOFs are extensively characterized, including the crystal structures of the postsynthetically brominated materials, which show a mechanical contraction of up to 3.7% in volume. The combination of stability and chemical reactivity in these MOFs leads to the possibility of tuning mechanical properties by chemical transformation while also opening up new routes to internal pore functionalization.

Metal–organic frameworks (MOFs),¹ porous coordination networks of metal clusters connected by organic linkers, have received widespread interest for use in a number of applications including, but not limited to, gas capture and sequestration,² catalysis,³ and drug delivery.⁴ Drawbacks associated with MOFs include their relatively low chemical and thermal stabilities,⁵ although recent findings suggest that Zr⁴⁺ linked MOFs,⁶ in particular those where Zr₆O₄(OH)₄ clusters link dicarboxylate struts into the UiO-66 isorecticular series,^{6d} exhibit dramatically improved chemical⁷ and mechanical⁸ stabilities. Postsynthetic modification (PSM), where the preformed MOF undergoes further chemical transformation(s) while retaining its crystalline structure, allows incorporation of additional functionality.⁹ PSM of Zr-MOFs has typically been achieved through ligand metalation,¹⁰ metal ion/ligand exchange,^{10c,11} and/or direct chemical transformations on the MOF itself.¹² Postsynthetic bromination of MOFs has been demonstrated as an attractive route for functionalization but, like the majority of covalent modifications, occurs mainly on pendant moieties.¹³ There are only a limited number of examples where PSM has been carried out on integral ligand sites that result in a change in length and/or geometry of the linker,^{14,15} and as far as we are aware, none in a single-crystal to single-crystal (SCSC) fashion to allow full structural characterization.¹⁶ Herein, we describe the synthesis and stereoselective postsynthetic bromination of two MOFs, [Zr₆O₄(OH)₄(edb)₆]_n (**1**) and [Hf₆O₄(OH)₄(edb)₆]_n (**2**), which are isostructural and contain

4,4'-ethynylendibenzoate (edb²⁻) organic linking units (Figure 1). The combined chemical and mechanical stabilities of the

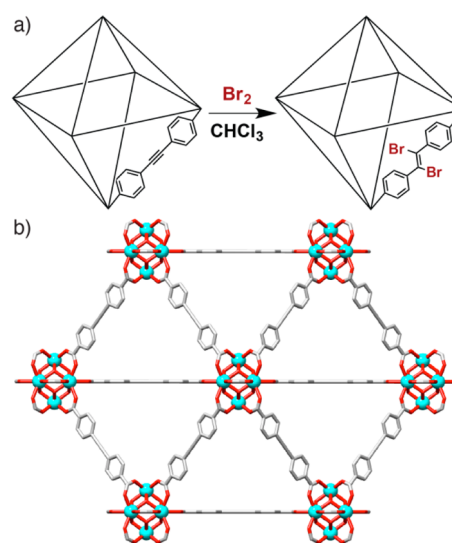


Figure 1. (a) Schematic of postsynthetic bromination, transforming the bound edb²⁻ ligand to edb-Br₂²⁻. (b) Packing diagram derived from our determination of the crystal structure of (**1**), which is isostructural with (**2**).

MOFs facilitate their quantitative, stereoselective bromination in a SCSC manner, resulting in incorporation of new functionality and permitting crystallographic characterization of the significant mechanical contraction, which the transformation induces.

The parent MOFs, (**1**)¹⁷ and (**2**), were synthesized by an amino acid modulated protocol, with 4–5 equiv of L-proline and one of HCl added to a solvothermal synthesis of 4,4'-ethynylendibenzoic acid (edb-H₂)¹⁸ and MCl₄ (M = Zr, Hf) in *N,N'*-dimethylformamide (DMF), yielding single crystals of both MOFs (Figure 1b). Typically, large equivalents of benzoic or acetic acid have been used to promote crystallization of Zr MOFs,¹⁹ but we have found amino acids to be highly efficient modulators in low concentrations (see Supporting Information (SI), Section S2). Incorporation of alkyne functionalities into MOFs has been highlighted as a route to achieve stimuli responsive materials,²⁰ and both structures show large atomic displacement parameters for the carbon atoms at the center of

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the edb^{2-} ligands, suggesting the unsaturated triple bond imparts the MOFs with a degree of flexibility^{6e} as well as potential reactivity. The well-documented stability^{7,8} of UiO type MOFs led us to the realization that bromination of edb^{2-} to edb-Br_2^{2-} should be possible within the MOF cavity.

Brominations of both (1) and (2) were initially attempted (see SI, Section S3) on bulk microcrystalline powder samples, with the materials suspended in CHCl_3 , exposed to bromine, and left to stand in the dark for 48 h. After workup, the extent of chemical transformation in the brominated materials, (1- Br_2) and (2- Br_2), was analyzed by a number of techniques, which are detailed below for the Zr-MOF (1- Br_2) but also replicated for the Hf analogue (2- Br_2) (see SI). Powder X-ray diffraction (PXRD; see SI, Section S4) shows that (1) remains crystalline after postsynthetic bromination, with a small shift of the peaks of (1- Br_2) toward higher 2θ angles when compared with (1), associated with an overall decrease in size of the unit cell.

From the thermogravimetric analysis (TGA) profiles (Figure 2a), excluding initial solvent loss from the MOF pores (<200

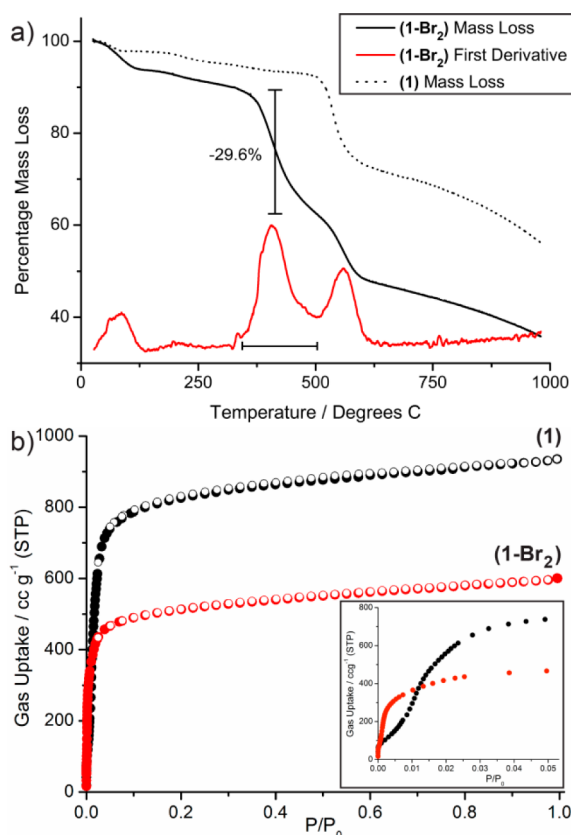


Figure 2. Transformation of (1) to (1- Br_2) is evident from (a) their TGA profiles, with a 29.6% mass loss in (1- Br_2) correlating very closely to its theoretical Br content, and (b) the decrease in N₂ uptake at 77 K by (1- Br_2) as the MOF contracts (adsorption, filled circles; desorption, empty circles). Analogous results are observed for the transformation of (2) to (2- Br_2) (see SI, Sections S5 and S6).

°C), it can be seen that (1) exhibits typical thermal behavior for Zr-MOFs, with the large mass loss around 500 °C attributed to combustion of the ligand.^{6d} However, (1- Br_2) displays a two-step profile, with the initial mass loss between 350 and 500 °C accounting for 29.6% of the mass of the desolvated material; the bromine content of fully desolvated (1- Br_2) is calculated to be 29.8%. This very close correlation, alongside elemental analysis

data (measured Br content 26.2%), suggests quantitative bromination of (1) has been achieved, and although this apparent debromination step occurs around 350 °C, the underlying thermal stability appears to be unaltered. N₂ adsorption isotherms collected at 77 K (Figure 2b) show a dramatic decrease in surface area, from 3280 m² g⁻¹ for (1), to 2000 m² g⁻¹ for (1- Br_2). The higher mass of (1- Br_2) cannot fully account for this decrease in gravimetric surface area and, in concert with calculated pore size distributions showing a reduction in the major pore diameter from 12.5 to 11 Å (see SI, Section S6), suggests that the transformation from alkyne to dibromoalkene units has been successful, resulting in a mechanical contraction of the ligand and thus the MOF.

Comparison of the Raman spectra of (1) with (1- Br_2) (Figure 3a) provides striking evidence that quantitative bromination has

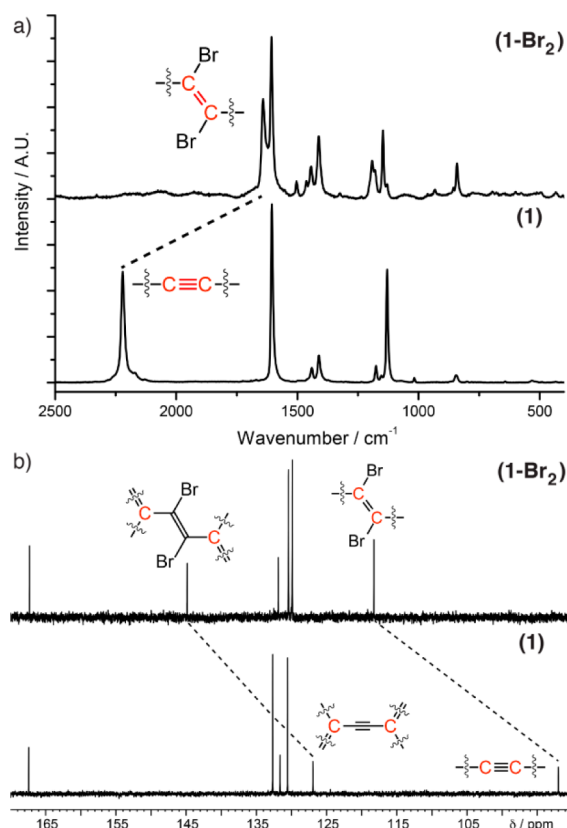


Figure 3. Spectroscopic evidence of the transformation of (1) to (1- Br_2) is found in (a) the Raman spectra of both, showing loss of an alkyne stretch at 2225 cm⁻¹ and appearance of an alkene stretch at 1640 cm⁻¹, and (b) ¹³C NMR spectra of digested MOF samples (DMSO-*d*₆/D₂SO₄, 293 K), which exhibit characteristic shifts of resonances associated with the functional groups. Analogous results are observed for the transformation of (2) to (2- Br_2) (see SI, Sections S7 and S8).

occurred, due to the complete disappearance of the stretch at 2225 cm⁻¹, which is typical of alkyne units conjugated with aromatic rings. The appearance of a peak at 1640 cm⁻¹ in (1- Br_2) corresponds to the stretching of the newly formed dibromoalkene moiety.¹⁴

The presence of two doublets in the ¹H NMR spectra (see SI, Section S8) of acid-digested samples of both (1) and (1- Br_2), whose splitting and chemical shifts were observed to change, indicates the presence of a different, single species in each. While this suggests a quantitative transformation, the presence of only aromatic protons provides limited information. The presence of

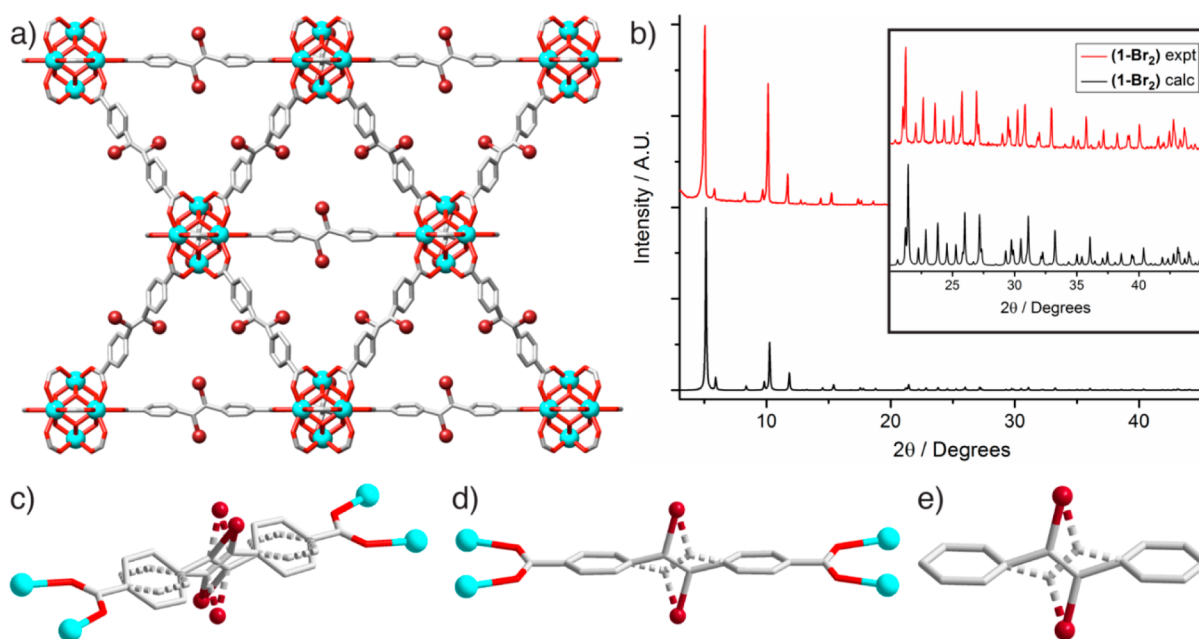


Figure 4. (a) Packing diagram of $(1-\text{Br}_2)$ derived from its crystal structure, with disorder omitted for clarity. (b) Stacked PXRD patterns show the bulk brominated sample of $(1-\text{Br}_2)$ closely matches the pattern calculated from the crystal structure, indicating quantitative bromination and excellent phase purity. (c) Positional disorder in the $\text{trans-edb-Br}_2^{2-}$ ligand is evident in $(1-\text{Br}_2)$. (d) The end-to-end disorder in the ligand is strikingly similar to that seen in (e) the crystal structure of $\text{trans-dibromostilbene}$ (CCDC deposition LAGKUZ).^{22a} Analogous results are derived from the crystal structure of $(2-\text{Br}_2)$ (see SI, Section S10).

only six resonances in the ^{13}C NMR spectrum of digested $(1-\text{Br}_2)$ (Figure 3b) is indicative that only one of the possible isomers of the dibromoalkene (*cis* and *trans*) has been obtained, i.e., the postsynthetic modification has occurred *stereoselectively*. Due to the geometrical constraints imposed on the edb^{2-} ligand bound within (1) , we hypothesize that sole generation of the *trans*-dibromoalkene occurs, yet NMR spectroscopic characterization is complicated by conflicting literature reports.²¹ The solution phase bromination of dimethyl 4,4'-ethynylendibenzoate (edb-Me_2) under similar reaction conditions results in the formation of two geometrical isomers, *cis*- and *trans*- $\text{edb-Me}_2\text{-Br}_2$, as evident from both ^1H and ^{13}C NMR spectra (see SI, Section S9), which show resonances for both isomers. There has been some conflicting evidence in the literature concerning the ^{13}C NMR chemical shifts of the resonances of dibromostilbene alkenyl carbon atoms; our results unambiguously show that the signals observed around $\delta = 118$ ppm correspond to the *trans* isomer, while those around $\delta = 124$ ppm correspond to the *cis* species. The geometrical constraints imposed within the MOFs ensure stereoselective addition, resulting exclusively in the *trans*-bromoalkene product.²²

Crystals of (1) and (2) were suspended in CHCl_3 and exposed to an excess of Br_2 for 4 days, before washing and resolating in DMF. The brominated MOFs $(1-\text{Br}_2)$ and $(2-\text{Br}_2)$ were examined by single crystal X-ray diffraction (Figure 4a) and found to retain the same $Fm\bar{3}m$ space group as their parent structures, with bromination resulting in a shortening of the unit cell edges from 30.2386(4) Å for (1) to 29.861(2) Å for $(1-\text{Br}_2)$. This mechanical contraction of the frameworks, a 3.7% decrease in unit cell volume, occurs without damaging the crystal and is a result of the edb^{2-} linker shortening on bromination to edb-Br_2^{2-} , which is evident when examining other crystallographic parameters such as solvent accessible void space (see SI, Section S10). Comparison of the calculated PXRD pattern from the crystal structure of $(1-\text{Br}_2)$ with the experimental pattern of the

bulk brominated material (Figure 4b) confirms that the stereoselective bromination proceeds quantitatively and produces phase pure material. The bent edb-Br_2^{2-} linkers lie disordered along the $[110]$ mirror plane and are geometrically frustrated as a result of the nonlinearity that originates from the sp^2 carbon atoms at their centers. The ligands adopt two different positions (Figure 4c), each of which has its own end-to-end orientational disorder (Figure 4d). Despite the disorder, it is clear that the bromination has proceeded stereoselectively to yield only *trans*- edb-Br_2^{2-} ; similar end-to-end disorder has previously been observed in the crystal structure of *trans*-dibromo-stilbene (Figure 4e).^{22a} The crystal structure of $(2-\text{Br}_2)$ is isostructural, with an unambiguously *trans*- edb-Br_2 linker and similar mechanical contraction (see SI, Section S10).

In conclusion, we have demonstrated a rare example of postsynthetic modification of an integral component of a MOF linker in a SCSC manner, stereoselectively and quantitatively brominating internal alkynes in the Zr- and Hf-MOFs (1) and (2) . The process has been extensively characterized both spectroscopically and structurally, as bromination results in both the chemical and mechanical transformation of the MOFs. This simple method of changing the hybridization of carbon atoms in MOF linkers should allow facile tuning of *mechanical* properties of MOFs through *chemical* introduction of flexibility. We are currently investigating further reactions across unsaturated bonds to introduce a variety of pore functionalities and geometries, while halogenation of alkynes may prove a useful strategy for irreversible chemisorptive capture of radioactive I_2 from nuclear energy processing and/or accidents.²³ Indeed, a sample of (1) exposed to I_2 vapors for 1 week in a proof-of-concept experiment showed 61% iodination of its edb^{2-} linkers, corresponding to 41% *w/w* irreversible trapping of I_2 (see SI, Section S11).

■ ASSOCIATED CONTENT

S Supporting Information

All synthesis, postsynthetic modifications, and analytical data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b05434.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2013**, *341*, 6419.
- (2) (a) Barea, E.; Montoro, C.; Navarro, J. A. R. *Chem. Soc. Rev.* **2014**, *43*, 5419–5430. (b) Ma, S.; Zhou, H.-C. *Chem. Commun.* **2010**, *46*, 44–53. (c) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R. *Chem. Rev.* **2012**, *112*, 724–781.
- (3) (a) Gascon, J.; Corma, A.; Kapteijn, F.; Llabrés i Xamena, F. X. *ACS Catal.* **2014**, *4*, 361–378. (b) Lee, J.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. *Chem. Soc. Rev.* **2009**, *38*, 1450–1459. (c) Liu, J.; Chen, L.; Cui, H.; Zhang, J.; Zhang, L.; Su, C.-Y. *Chem. Soc. Rev.* **2014**, *43*, 6011–6061.
- (4) (a) Della Rocca, J.; Liu, D.; Lin, W. *Acc. Chem. Res.* **2011**, *44*, 957–968. (b) Horcajada, P.; Gref, R.; Baati, T.; Allan, P. K.; Maurin, G.; Couvreur, P.; Férey, G.; Morris, R. E.; Serre, C. *Chem. Rev.* **2012**, *112*, 1232–1268.
- (5) Kang, I. J.; Khan, N. A.; Haque, E.; Jhung, S. H. *Chem. - Eur. J.* **2011**, *17*, 6437–6442.
- (6) (a) Morris, W.; Voloskiy, B.; Demir, S.; Gándara, F.; McGrier, P. L.; Furukawa, H.; Cascio, D.; Stoddart, J. F.; Yaghi, O. M. *Inorg. Chem.* **2012**, *51*, 6443–6445. (b) Wang, T. C.; Bury, W.; Gómez-Gualdrón, D. A.; Vermeulen, N. A.; Mondloch, J. E.; Deria, P.; Zhang, K.; Moghadam, P. Z.; Sarjeant, A. A.; Snurr, R. Q.; Stoddart, J. F.; Hupp, J. T.; Farha, O. K. *J. Am. Chem. Soc.* **2015**, *137*, 3585–3591. (c) Furukawa, H.; Gándara, F.; Zhang, Y.-B.; Jiang, J.; Queen, W. L.; Hudson, M. R.; Yaghi, O. M. *J. Am. Chem. Soc.* **2014**, *136*, 4369–4381. (d) Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. P. *J. Am. Chem. Soc.* **2008**, *130*, 13850–13851. (e) Schaate, A.; Roy, P.; Preusse, T.; Lohmeier, S. J.; Godt, A.; Behrens, P. *Chem. - Eur. J.* **2011**, *17*, 9320–9325.
- (7) (a) Kandiah, M.; Nilsen, M. H.; Usseglio, S.; Jakobsen, S.; Olsbye, U.; Tilset, M.; Larabi, C.; Quadrelli, E. A.; Bonino, F.; Lillerud, K. P. *Chem. Mater.* **2010**, *22*, 6632–6640. (b) Mondloch, J. E.; Katz, M. J.; Planas, N.; Semrouni, D.; Gagliardi, L.; Hupp, J. T.; Farha, O. K. *Chem. Commun.* **2014**, *50*, 8944–8946.
- (8) (a) Van de Voorde, B.; Stassen, I.; Bueken, B.; Vermoortele, F.; De Vos, D.; Ameloot, R.; Tan, J.-C.; Bennett, T. D. *J. Mater. Chem. A* **2015**, *3*, 1737–1742. (b) Wu, H.; Yildirim, T.; Zhou, W. *J. Phys. Chem. Lett.* **2013**, *4*, 925–930.
- (9) Cohen, S. M. *Chem. Rev.* **2012**, *112*, 970–1000.
- (10) (a) Gonzalez, M. I.; Bloch, E. D.; Mason, J. A.; Teat, S. J.; Long, J. R. *Inorg. Chem.* **2015**, *54*, 2995–3005. (b) Manna, K.; Zhang, T.; Greene, F. X.; Lin, W. *J. Am. Chem. Soc.* **2015**, *137*, 2665–2673. (c) Fei, H.; Cohen, S. M. *J. Am. Chem. Soc.* **2015**, *137*, 2191–2194.
- (11) (a) Deria, P.; Bury, W.; Hod, I.; Kung, C.-W.; Karagiari, O.; Hupp, J. T.; Farha, O. K. *Inorg. Chem.* **2015**, *54*, 2185–2192. (b) Kim, M.; Cahill, J. F.; Fei, H.; Prather, K. A.; Cohen, S. M. *J. Am. Chem. Soc.* **2012**, *134*, 18082–18088. (c) Hong, D. H.; Suh, M. P. *Chem. - Eur. J.* **2014**, *20*, 426–434.
- (12) (a) Phang, W. J.; Jo, H.; Lee, W. R.; Song, J. H.; Yoo, K.; Kim, B.; Hong, C. S. *Angew. Chem., Int. Ed.* **2015**, *54*, 5142–5146. (b) Zhang, Y.; Feng, X.; Li, H.; Chen, Y.; Zhao, J.; Wang, S.; Wang, L.; Wang, B. *Angew. Chem., Int. Ed.* **2015**, *54*, 4259–4263. (c) Morris, W.; Briley, W. E.; Auyeung, E.; Cabezas, M. D.; Mirkin, C. A. *J. Am. Chem. Soc.* **2014**, *136*, 7261–7264.
- (13) (a) Wang, Z.; Cohen, S. M. *Angew. Chem., Int. Ed.* **2008**, *47*, 4699–4702. (b) Prasad, T. K.; Suh, M. P. *Chem. - Eur. J.* **2012**, *18*, 8673–8680. (c) Hindelang, K.; Kronast, A.; Vagin, S. I.; Rieger, B. *Chem. - Eur. J.* **2013**, *19*, 8244–8252. (d) Sun, F.; Yin, Z.; Wang, Q.-Q.; Sun, D.; Zeng, M.-H.; Kurmoo, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 4538–4543.
- (14) Frahm, D.; Hoffmann, F.; Fröba, M. *Cryst. Growth Des.* **2014**, *14*, 1719–1725.
- (15) The bromination of an integral alkene unit in a Zn-MOF has been reported, but the high reaction temperature required had a detrimental effect on crystallinity and porosity, so no structural or mechanical information on the PSM process could be reported. See: Jones, S. C.; Bauer, C. A. *J. Am. Chem. Soc.* **2009**, *131*, 12516–12517.
- (16) Zhang, J.-P.; Liao, P.-Q.; Zhou, H.-L.; Lin, R.-B.; Chen, X.-M. *Chem. Soc. Rev.* **2014**, *43*, 5789–5814.
- (17) During the course of our study, the synthesis (modulated by 175 equivalents of acetic acid) and gas uptake properties of (1) were independently reported. See: Lv, X.-L.; Tong, M.; Huang, H.; Wang, B.; Gan, L.; Yang, Q.; Zhong, C.; Li, J.-R. *J. Solid State Chem.* **2015**, *223*, 104–108.
- (18) Gadzikwa, T.; Zeng, B.-S.; Hupp, J. T.; Nguyen, S. T. *Chem. Commun.* **2008**, 3672–3674.
- (19) (a) Katz, M. J.; Brown, Z. J.; Colon, Y. J.; Siu, P. W.; Scheidt, K. A.; Snurr, R. Q.; Hupp, J. T.; Farha, O. K. *Chem. Commun.* **2013**, *49*, 9449–9451. (b) Schaate, A.; Roy, P.; Godt, A.; Lippke, J.; Waltz, F.; Wiebcke, M.; Behrens, P. *Chem. - Eur. J.* **2011**, *17*, 6643–6651.
- (20) Coudert, F.-X. *Chem. Mater.* **2015**, *27*, 1905–1916.
- (21) (a) Schuh, K.; Glorius, F. *Synthesis* **2007**, 2297–2306. (b) Schreiner, P. R.; Prall, M.; Lutz, V. *Angew. Chem., Int. Ed.* **2003**, *42*, 5757–5760. (c) Bianchini, R.; Chiappe, C.; Lo Moro, G.; Lenoir, D.; Lemmen, P.; Goldberg, N. *Chem. - Eur. J.* **1999**, *5*, 1570–1580.
- (22) Stereoselective bromination of alkynes, using specialized reaction conditions or catalysts, is a topic of research. For examples, see: (a) Espenson, J. H.; Zhu, Z.; Zauche, T. H. *J. Org. Chem.* **1999**, *64*, 1191–1196. (b) Podgoršek, A.; Eissen, M.; Fleckenstein, J.; Stavber, S.; Zupan, M.; Iskra, J. *Green Chem.* **2009**, *11*, 120–126. (c) Ma, K.; Li, S.; Weiss, R. G. *Org. Lett.* **2008**, *10*, 4155–4158. (d) Yao, M.-L.; Kabalka, G. W.; Blevins, D. W.; Reddy, M. S.; Yong, L. *Tetrahedron* **2012**, *68*, 3738–3743.
- (23) Bennett, T. D.; Saines, P. J.; Keen, D. A.; Tan, J.-C.; Cheetham, A. K. *Chem. - Eur. J.* **2013**, *19*, 7049–7055.