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Assembly of Metal−Organic Frameworks of SiF_6^{2-} in Situ Formed from Borosilicate Glass

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Supporting Information

ABSTRACT: The SiF_6^{2-} anions are in situ formed in the reactions of MF_2 (M = Cu^{2+}, Zn^{2+}, Ni^{2+}, and Co^{2+}) salts and nitrogen-containing ligands in borosilicate glass tubes under solvothermal conditions and then used to further construct a family of metal−organic frameworks (MOFs). This in situ reaction demonstrates a new and facile strategy for the fabrication of MOFs based on SiF_6^{2-}.

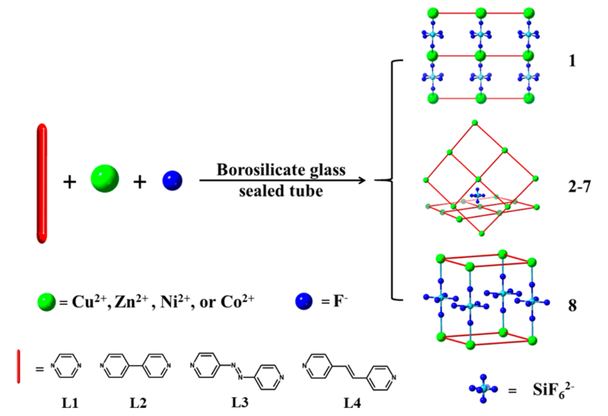
Metal−organic frameworks (MOFs) or porous coordination polymers are some of the most burgeoning porous materials and have attracted extensive research attention of scientists.[1] MOFs are constructed by metal ions or cluster and organic ligands and show a variety of potential applications including gas storage and separation,[2] catalysis,[3] drug delivery,[4] chemical sensing,[5] heavy-metal removal,[6] and water harvesting.[7] In recent years, a subclass of MOFs, called "SIFSIX", have emerged with exceptional uptake and selectivity toward carbon dioxide and hydrocarbons,[8] although the first one was synthesized around 24 years ago.[9] In these MOFs, metal ions coordinate to organic linkers to form a two-dimensional grid; then the grids are pillared with SiF_6^{2-} anions to form a porous three-dimensional framework.

Several synthetic approaches have been explored and reported for construction of the "SIFSIX" series MOFs. These MOFs are commonly synthesized using solvothermal and slow diffusion routes. For example, $[Fe(SIFSIX)(pyrazine)_2]_n$ was synthesized by the solvothermal reaction of $FeSiF_6{\cdot}6H_2O$ with pyrazine in methanol.[10] SIFSIX-3-Cu ($[Cu(SIFSIX)(pyrazine)_2]_n$) was prepared successfully by layering a methanol solution of pyrazine in a glass tube onto a methanol solution of $CuSiF_6{\cdot}xH_2O$ at room temperature.[8c] There is also a reported solvent-free method to obtain SIFSIX-3-Ni ($[Ni(SIFSIX)(pyrazine)_2]_n$).[11] This facile methodology is based on the mechanical mixing of both the organic and inorganic solid precursors, i.e., pyrazine and $NiSiF_6$. Interestingly, an industrial spray-drying technique has also recently been developed as a new synthetic route for preparing the "SIFSIX" MOF.[12] All of these reactions use hexafluorosilicates as reactants, but some metal hexafluorosilicates may not be commercially available or are too expensive.

In situ reactions have been extensively investigated under solvothermal conditions, which is a useful strategy for the discovery of new organic reactions and construction of metal−organic assemblies, especially those inaccessible or not easily obtainable by conventional methods.[13] However, to our knowledge, most of such reactions are in situ metal/ligand reactions and rarely involve in situ anion reactions.[14]

Herein, we report a new strategy to preparing MOFs containing SiF_6^{2-} anions (Scheme 1), in which SiF_6^{2-} is in situ formed by reacting MF_2 (M = Cu^{2+}, Zn^{2+}, Ni^{2+}, and Co^{2+}) with SiO_2 of borosilicate glass tubes under solvothermal conditions. By using this serendipitous discovery, we have successfully obtained seven two-dimensional (4,4) square lattice (sql) MOFs and a three-dimensional "SIFSIX" MOF with four types of nitrogen-containing ligands [Scheme 1; L1 = pyrazine, L2 = 4,4′-bipyridine, L3 = (*E*)-1,2-di(pyridin-4-yl)diazene, L4 = (*E*)-1,2-di(pyridin-4-yl)ethene] and metal fluorides MF_2 (M = Cu^{2+}, Zn^{2+}, Ni^{2+}, and Co^{2+}). These SiF_6^{2-}-based MOFs are formulated as $[Cu(L1)_2(H_2O)_2(SiF_6)]$ (denoted as **1**), $[M(L2)_2(H_2O)_2]{\cdot}SiF_6$ (M = Co^{2+}, Ni^{2+}, Zn^{2+}, and Cu^{2+}, denoted as **2**−**5**, respectively), $[Cu(L3)_2(H_2O)_2]{\cdot}SiF_6$ (denoted as **6**), $[Cu(L4)_2(H_2O)_2]{\cdot}SiF_6$ (denoted as **7**), and $[Cu(L4)_2(SiF_6)]$ (denoted as **8**). The successful syntheses of these SiF_6^{2-}-based MOFs are manifested by single-crystal X-ray diffraction analysis, powder X-ray diffraction (PXRD), IR spectrometry, and energy-dispersive spectrometry (EDS), suggesting that this in situ reaction is a facile and economical strategy for the construction of SiF_6^{2-}-containing MOFs.

Scheme 1. Self-Assembly of Compounds 1−8



Nitrogen-containing ligands of L1−L4 mixed with metal fluorides (CuF_2, ZnF_2, NiF_2, and CoF_2) were sealed into borosilicate glass tubes to yield single crystals of compounds

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1−8 under solvothermal conditions [see the Supporting Information (SI) for details]. We found that the molar ratios between metal salts and ligands in the reactions are important. The ratio for metal/ligand of 2:1 obtained the purer and higher-yielded products. In addition, the presence of water also played a vital role in this process. Compound **1** was synthesized in methanol, while compounds **2−8** were yielded in water/methanol or water/ethanol solvents (for details, see the SI). The compounds **2−8** cannot be obtained in the absence of water in reaction solvents. Notably, there is no danger of implosion in this process because a very small amount of glass is reacted with MF_2.

For comparison, the reaction of CuF_2 with L1 in a Teflon-lined stainless-steel autoclave that does not contain any silicon was conducted as a blank experiment under the same conditions. The PXRD study (Figure S2) indicates that compound **1** containing L1 and SiF_6^{2-} cannot be obtained in this way. Furthermore, the characterized peaks of hexafluorosilicates could not be found in the IR spectrum of the product synthesized using a Teflon-lined stainless-steel autoclave (Figure S3). These results suggest that the silicon of SiF_6^{2-} originates from the borosilicate glass tubes.

Single-crystal structures of compounds **1−8** were successfully refined and determined, and summaries of the crystal data of the compounds are listed in Tables S1−S8. A search of the CCDC database found that this is the first time that compounds **1−3** and **7** are reported, while compounds **4−6** and **8** were reported previously.[8a,e,15]

The light-blue needle crystals (Figure 1a) of **1** crystallize in monoclinic space group *I*2/*m*. As shown in Figure 1b, the copper(II) center in **1** adopts a distorted octahedral coordination geometry and coordinates with two nitrogen atoms of L1 (Cu−N 2.038 Å), two oxygen atoms of water (Cu−O 1.956 Å), and two fluorine atoms of silicon hexafluoride anions (Cu−F 2.377 Å). The pyrazine ligands bridge the copper(II) centers to produce one-dimensional chains. The SiF_6^{2-} linkers serve as bridging ligands to link the pyrazine−Cu coordination chain and create a two-dimensional sheet (Figure 1c). The sheets pack together to form a supramolecular three-dimensional structure (Figure 1d). Compound **1** is a polymorph of a previously reported coordination polymer, which crystallizes in a monoclinic space group *C*2/*m*.[8j]

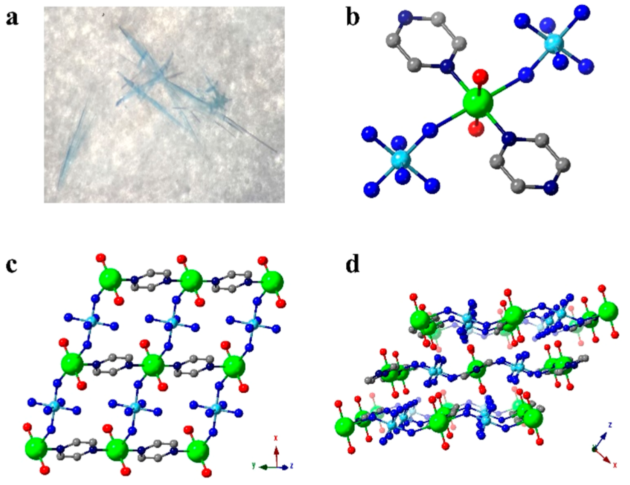

Figure 1. Photograph of single crystals of compound **1** (a). Crystal structures of compound **1**: coordination environment around the copper(II) center (b), two-dimensional grid (c), and three-dimensional supramolecular structure viewed along [011] (d). Color codes: F, bright blue; Cu, green; Si, cyan; O, red; C, gray; N, blue. Hydrogen atoms were omitted for clarity.

PXRD was used to characterize the crystallinity and purity of a bulky sample of **1**. The PXRD pattern is in good agreement with the pattern simulated from the single-crystal structure (Figure 2a). The presence of SiF_6^{2-} in the composite was also confirmed by IR (Figure 2b). There are two characteristic bands of SiF_6^{2-} in the IR spectrum of **1**. One very strong peak observed at 742.0 cm^{-1} was assigned to the ν_3 [ν_{as}(Si−F)] asymmetric stretching mode, and the other strong feature peak located at 482.6 cm^{-1} corresponded to the ν_4 [δ_{as}(F−Si−F)] asymmetric bending mode.[16] The same conclusion can also be drawn from the EDS mapping of different elements in **1** (Figure 2c,d), in which the mapping exhibited the distribution of silicon in the sample. Therefore, both IR and EDS results validated that SiF_6^{2-} is successfully formed in the in situ reaction between F^- and SiO_2 of borosilicate glass.

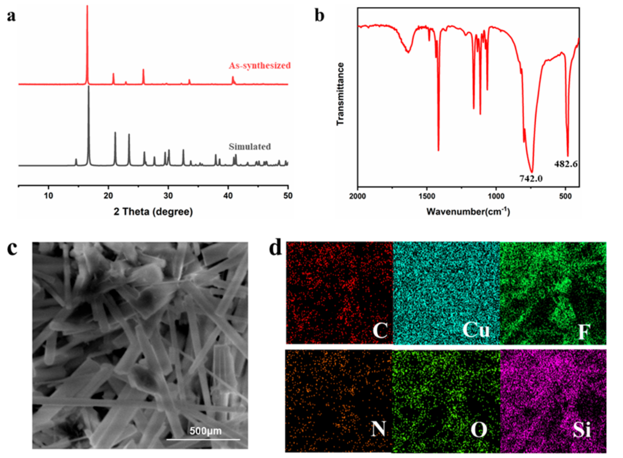

Figure 2. PXRD patterns for simulated (black line) and as-synthesized (red line) samples (a), IR spectrum (b), scanning electron microscopy image (c), and the corresponding elemental mapping (d) of compound **1**.

The light-yellow octahedral crystals (Figure S1a) of compound **2** obtained by reacting 4,4′-bipyridyl with CoF_2 under solvothermal conditions crystallize in the tetragonal space group *P*4/*ncc*. The cobalt(II) center is octahedrally coordinated to four nitrogen atoms of L2 in the equatorial plane and two oxygen atoms of water in the axial sites. All of the Co−N bond lengths are similar to each other with a distance of 2.158 Å, while the Co−O distance is 2.099 Å. The ligands link the cobalt(II) centers to form a two-dimensional (4,4) sql (Figure 3a). The grids with a size of 11.424 Å × 11.424 Å (Co−Co distance) are filled by free SiF_6^{2-} dianions having interactions with the coordinated H_2O molecules by hydrogen bonds (O⋯F 2.685 Å). A three-dimensional supramolecular structure is formed by perpendicular interpenetration (Figure 3b).

By replacing CoF_2 with NiF_2, ZnF_2, and CuF_2, we obtained compounds **3−5**, respectively. Compounds **3−5** have structures and coordination environments identical with those of compound **2** except of difference of the metal centers (Figure 3a), which are confirmed by single-crystal X-ray crystallographic analysis. Compound **3** is reported for the first

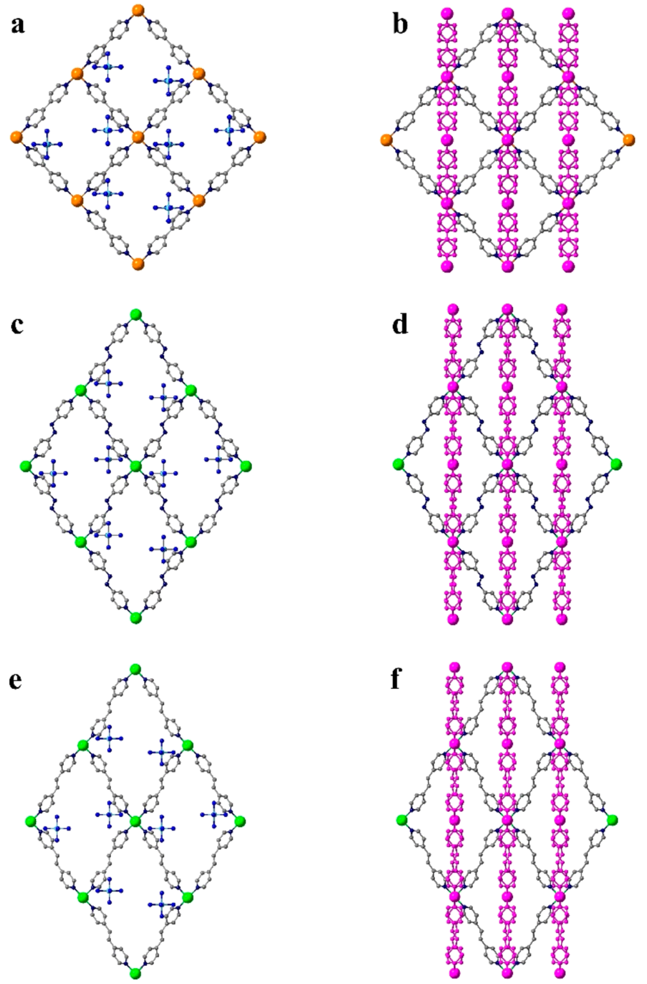

Figure 3. Views of the crystal structures of **2**−**5** (a and b), **6** (c and d), and **7** (e and f): two-dimensional grids and three-dimensional structures, respectively, formed by interpenetration. Color code: F, bright blue; Si, cyan; C, gray; N, blue; M (M = Co, Ni, Zn and Cu), orange; Cu, green. Hydrogen atoms were omitted for clarity. Purple nets (b, d, and f) represent the interpenetrated nets.

time, while both compounds **4** and **5** had been documented to be obtained by the reaction of $ZnSiF_6$ or copper(II) nitrate/$(NH_3)_2SiF_6$ and L2, respectively.[8a,15a] To further confirm formation of the SiF_6^{2-} anion in compounds **2**−**5**, IR and EDS studies were also used. As shown in Figures S4−S11, both the IR and EDS results proved that SiF_6^{2-} anions are present in compounds **2**−**5**, suggesting that SiF_6^{2-} is successfully generated in the in situ reactions for syntheses of the compounds.

The reaction of CuF_2 and L3 under similar solvothermal conditions yielded yellow rod crystals of compound **6**. The structure features rhombically distorted square-grid sheets that interpenetrate perpendicularly to form a three-dimensional framework (Figure 3c,d). This structure is similar to those of compounds **2**−**5** and identical with the compound obtained by the reaction of $CuSiF_6$ and L3 in the literature.[8e,15b,c] It is an interpenetrated 2D structure that has the same space group as compound **2**. When L3 was replaced with L4, we obtained a new compound. As shown in Figure 3e,f, the structures of **6** and **7** are alike. Similarly, IR and EDS also reveal that SiF_6^{2-} anions exist in compounds **6** and **7** (Figures S12−S15).

Interestingly, when ethanol was used as the solvent rather than methanol in the reaction of CuF_2 and L4, compound **8** as dark-purple crystals was obtained. Compound **8** features a "SIFSIX" MOF structure in the tetragonal space group *P*4/*nmm*, as shown in Figure S22. Four pyridyl nitrogen atoms of L4 and two fluoride atoms of the SiF_6^{2-} anions are coordinated to the octahedral coordination copper(II) center. L4 bridged copper(II) ions to form two-dimensional square lattices, which were further pillared by SiF_6^{2-} anions to give a three-dimensional structure without interpenetration.[8d]

The crystallinity and purity of compound **8** were checked by PXRD, as shown in Figure S23. The PXRD pattern is in good agreement with the simulated one from the single-crystal structure. The characteristic peaks of 746.3 and 483.1 cm^{-1} corresponding to ν_3 $[\nu_{as}(Si{-}F)]$ and ν_4 $[\delta_{as}(F{-}Si{-}F)]$, respectively, in the IR spectrum of **8** confirm the presence of SiF_6^{2-} (Figure S24). The same conclusion can also be obtained from the EDS mapping of different elements (Figure S25).

We speculate that the origin of SiF_6^{2-} is as follows: MF_2 hydrolyzes in solvent to form HF (eq 1), and then SiO_2 of borosilicate glass tubes could react with HF to produce H_2SiF_6 (eq 2). Acid−base neutralization reaction occurs between H_2SiF_6 and $M(OH)_2$ to produce $MSiF_6$ (eq 3). This mechanism is supported by previous reports,[14] in which SiF_6^{2-} can be yielded by reacting BF_4^- with SiO_2 and decomposing to form F^- under solvothermal conditions. Finally, $MSiF_6$ reacted with nitrogen-containing ligands to assemble the MOFs.

$$MF_2 + 2H_2O \rightarrow 2HF + M(OH)_2 \tag{1}$$

$$6HF + SiO_2 \leftrightarrows H_2SiF_6 + 2H_2O \tag{2}$$

$$H_2SiF_6 + M(OH)_2 \rightarrow MSiF_6 + 2H_2O \tag{3}$$

In summary, we developed a new method to fabricate MOFs with SiF_6^{2-} anions in situ formed from metal fluoride and borosilicate glass under solvothermal conditions. The successful synthesis demonstrates that the in situ method is a convenient and universal route to preparing "SIFSIX" MOFs. The application of this novel in situ approach to yield novel MOFs by employing other types of nitrogen-containing ligands is ongoing. We anticipate that further interesting and unprecedented "SIFSIX" MOFs will be produced by employing this approach.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b01732.

> Experimental procedures, crystal data, PXRD patterns, IR spectra, scanning electron microscopy images, elemental mappings, and photographs of the materials (PDF)

Accession Codes

CCDC 1911851−1911854 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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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. The Chemistry and Applications of Metal-Organic Frameworks. *Science* **2013**, *341*, 1230444.

(2) (a) Li, J.-R.; Sculley, J.; Zhou, H.-C. Metal−Organic Frameworks for Separations. *Chem. Rev.* **2012**, *112*, 869−932. (b) Li, B.; Wen, H.-M.; Zhou, W.; Xu, J. Q.; Chen, B. Porous Metal-Organic Frameworks: Promising Materials for Methane Storage. *Chem.* **2016**, *1*, 557−580. (c) Liao, P.-Q.; Huang, N.-Y.; Zhang, W.-X.; Zhang, J.-P.; Chen, X.-M. Controlling guest conformation for efficient purification of butadiene. *Science* **2017**, *356*, 1193−1196.

(3) (a) Liu, J.; Chen, L.; Cui, H.; Zhang, J.; Zhang, L.; Su, C.-Y. Applications of metal−organic frameworks in heterogeneous supramolecular catalysis. *Chem. Soc. Rev.* **2014**, *43*, 6011−6061. (b) Yang, Q.; Xu, Q.; Jiang, H.-L. Metal−organic frameworks meet metal nanoparticles: synergistic effect for enhanced catalysis. *Chem. Soc. Rev.* **2017**, *46*, 4774−4808. (c) Du, J.-J.; Zhang, X.; Zhou, X.-P.; Li, D. Robust heterometallic MOF catalysts for the cyanosilylation of aldehydes. *Inorg. Chem. Front.* **2018**, *5*, 2772−2776.

(4) Wu, M.-X.; Yang, Y.-W. Metal−Organic Framework (MOF)-Based Drug/Cargo Delivery and Cancer Therapy. *Adv. Mater.* **2017**, *29*, 1606134.

(5) (a) Lustig, W. P.; Mukherjee, S.; Rudd, N. D.; Desai, A. V.; Li, J.; Ghosh, S. K. Metal−organic frameworks: functional luminescent and photonic materials for sensing applications. *Chem. Soc. Rev.* **2017**, *46*, 3242−3285. (b) Wang, J.-H.; Li, M.; Li, D. A dynamic, luminescent and entangled MOF as a qualitative sensor for volatile organic solvents and a quantitative monitor for acetonitrile vapour. *Chem. Sci.* **2013**, *4*, 1793−1801. (c) Huang, R.-W.; Wei, Y.-S.; Dong, X.-Y.; Wu, X.-H.; Du, C.-X.; Zang, S.-Q.; Mak, T. C. W. Hypersensitive dual-function luminescence switching of a silver-chalcogenolate cluster-based metal−organic framework. *Nat. Chem.* **2017**, *9*, 689.

(6) (a) He, Y.; Hou, Y.-L.; Wong, Y.-L.; Xiao, R.; Li, M.-Q.; Hao, Z.; Huang, J.; Wang, L.; Zeller, M.; He, J.; Xu, Z. Improving stability against desolvation and mercury removal performance of Zr(iv)−carboxylate frameworks by using bulky sulfur functions. *J. Mater. Chem. A* **2018**, *6*, 1648−1654. (b) He, Y.; Huang, M.; Deng, X.; Shengxian, C.; Wong, Y.-L.; Hou, Y.-L.; He, J.; Zeller, M.; Xu, Z. Janus triple tripods build up a microporous manifold for $HgCl_2$ and I_2 uptake. *Chem. Commun.* **2019**, *55*, 5091−5094.

(7) Kim, H.; Yang, S.; Rao, S. R.; Narayanan, S.; Kapustin, E. A.; Furukawa, H.; Umans, A. S.; Yaghi, O. M.; Wang, E. N. Water harvesting from air with metal-organic frameworks powered by natural sunlight. *Science* **2017**, *356*, 430−434.

(8) (a) Noro, S.-i.; Kitaura, R.; Kondo, M.; Kitagawa, S.; Ishii, T.; Matsuzaka, H.; Yamashita, M. Framework engineering by anions and porous functionalities of Cu(II)/4,4′-bpy coordination polymers. *J. Am. Chem. Soc.* **2002**, *124*, 2568−2583. (b) Nugent, P.; Belmabkhout, Y.; Burd, S. D.; Cairns, A. J.; Luebke, R.; Forrest, K.; Pham, T.; Ma, S.; Space, B.; Wojtas, L.; Eddaoudi, M.; Zaworotko, M. J. Porous materials with optimal adsorption thermodynamics and kinetics for CO_2 separation. *Nature* **2013**, *495*, 80. (c) Shekhah, O.; Belmabkhout, Y.; Chen, Z.; Guillerm, V.; Cairns, A.; Adil, K.; Eddaoudi, M. Made-to-order metal-organic frameworks for trace carbon dioxide removal and air capture. *Nat. Commun.* **2014**, *5*, 4228. (d) Burd, S. D.; Ma, S.; Perman, J. A.; Sikora, B. J.; Snurr, R. Q.; Thallapally, P. K.; Tian, J.; Wojtas, L.; Zaworotko, M. J. Highly selective carbon dioxide uptake by $[Cu(bpy\text{-}n)_2(SiF_6)]$ (bpy-1 = 4,4′-bipyridine; bpy-2 = 1,2-bis(4-pyridyl)ethene). *J. Am. Chem. Soc.* **2012**, *134*, 3663−3666. (e) O'Nolan, D.; Kumar, A.; Zaworotko, M. J. Water Vapor Sorption in Hybrid Pillared Square Grid Materials. *J. Am. Chem. Soc.* **2017**, *139*, 8508. (f) Li, B.; Cui, X.; O'Nolan, D.; Wen, H.-M.; Jiang, M.; Krishna, R.; Wu, H.; Lin, R.-B.; Chen, Y.-S.; Yuan, D.; Xing, H.; Zhou, W.; Ren, Q.; Qian, G.; Zaworotko, M. J.; Chen, B. An Ideal Molecular Sieve for Acetylene Removal from Ethylene with Record Selectivity and Productivity. *Adv. Mater.* **2017**, *29*, 1704210. (g) Chen, K.-J.; Yang, Q.-Y.; Sen, S.; Madden, D. G.; Kumar, A.; Pham, T.; Forrest, K. A.; Hosono, N.; Space, B.; Kitagawa, S.; Zaworotko, M. J. Efficient CO_2 Removal for Ultra-Pure CO Production by Two Hybrid Ultramicroporous Materials. *Angew. Chem., Int. Ed.* **2018**, *57*, 3332−3336. (h) Zhang, S. Y.; Jensen, S.; Tan, K.; Wojtas, L.; Roveto, M.; Cure, J.; Thonhauser, T.; Chabal, Y. J.; Zaworotko, M. J. Modulation of Water Vapor Sorption by a Fourth-Generation Metal-Organic Material with a Rigid Framework and Self-Switching Pores. *J. Am. Chem. Soc.* **2018**, *140*, 12545−12552. (i) Cui, X.; Chen, K.; Xing, H.; Yang, Q.; Krishna, R.; Bao, Z.; Wu, H.; Zhou, W.; Dong, X.; Han, Y.; Li, B.; Ren, Q.; Zaworotko, M. J.; Chen, B. Pore chemistry and size control in hybrid porous materials for acetylene capture from ethylene. *Science* **2016**, *353*, 141−144. (j) Uemura, K.; Maeda, A.; Maji, T. K.; Kanoo, P.; Kita, H. Syntheses, Crystal Structures and Adsorption Properties of Ultramicroporous Coordination Polymers Constructed from Hexafluorosilicate Ions and Pyrazine. *Eur. J. Inorg. Chem.* **2009**, *2009*, 2329−2337.

(9) Subramanian, S.; Zaworotko, M. J. Porous Solids by Design: $[Zn(4,4'\text{-}bpy)_2(SiF_6)]_n\cdot xDMF$, a Single Framework Octahedral Coordination Polymer with Large Square Channels. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2127−2129.

(10) Elsaidi, S. H.; Mohamed, M.; Simon, C. M.; Braun, E. D.; Pham, T.; Forrest, K.; Xu, W.; Banerjee, D.; Space, B.; Zaworotko, M. J.; Thallapally, P. K. Effect of Ring Rotation upon Gas Adsorption in SIFSIX-3-M (M = Fe, Ni) Pillared Square Grid Network. *Chem. Sci.* **2017**, *8*, 2373−2380.

(11) Shekhah, O.; Belmabkhout, Y.; Adil, K.; Bhatt, P. M.; Cairns, A. J.; Eddaoudi, M. A facile solvent-free synthesis route for the assembly of a highly CO_2 selective and H_2S tolerant NiSIFSIX metal-organic framework. *Chem. Commun.* **2015**, *51*, 13595−13598.

(12) Guillerm, V.; Garzón-Tovar, L.; Yazdi, A.; Imaz, I.; Juanhuix, J.; Maspoch, D. Continuous One-Step Synthesis of Porous M-XF_6-Based Metal-Organic and Hydrogen-Bonded Frameworks. *Chem. - Eur. J.* **2017**, *23*, 6829−6835.

(13) Chen, X.-M.; Tong, M.-L. Solvothermal in Situ Metal/Ligand Reactions: A New Bridge between Coordination Chemistry and Organic Synthetic Chemistry. *Acc. Chem. Res.* **2007**, *40*, 162−170.

(14) (a) Chen, K.-J.; Perry, J. J., IV; Scott, H. S.; Yang, Q.-Y.; Zaworotko, M. J. Double-walled pyr topology networks from a novel fluoride-bridged heptanuclear metal cluster. *Chem. Sci.* **2015**, *6*, 4784−4789. (b) Li, J.; Luo, X.; Zhao, N.; Zhang, L.; Huo, Q.; Liu, Y. Two Finite Binuclear $[M_2(\mu_2\text{-}OH)(COO)_2]$ (M = Co, Ni) Based Highly Porous Metal−Organic Frameworks with High Performance for Gas Sorption and Separation. *Inorg. Chem.* **2017**, *56*, 4141−4147.

(15) (a) Gable, R. W.; Hoskins, B. F.; Robson, R. A new type of interpenetration involving enmeshed independent square grid sheets. The structure of diaquabis-(4,4′-bipyridine)zinc hexafluorosilicate. *J. Chem. Soc., Chem. Commun.* **1990**, 1677−1678. (b) Withersby, M. A.; Blake, A. J.; Champness, N. R.; Cooke, P. A.; Hubberstey, P.; Realf, A. L.; Teat, S. J.; Schröder, M. Engineering of co-ordination polymers of

trans-4,4′-azobis(pyridine) and trans-1,2-bis(pyridin-4-yl)ethene: a range of interpenetrated network motifs. *J. Chem. Soc., Dalton Trans.* **2000**, 3261−3268. (c) Sensharma, D.; Vaesen, S.; Healy, C.; Hartmann, J.; Kathalikkattil, A. C.; Wix, P.; Steuber, F.; Zhu, N.; Schmitt, W. CO_2 Adsorption in SIFSIX-14-Cu-i: High Performance, Inflected Isotherms, and Water-Triggered Release via Reversible Structural Transformation. *Eur. J. Inorg. Chem.* **2018**, *2018*, 1993−1997.

(16) Jalbout, A. F.; Ouasri, A.; Jeghnou, H.; Rhandour, A. Experimental and theoretical studies of monoalkylammonium hexafluorosilicate $[CH_3(CH_2)_nNH_3]_2SiF_6$ (n = 2, 3) and ethylammonium hexafluorosilicate $[(C_2H_5)_2NH_2]_2SiF_6$. *Vib. Spectrosc.* **2007**, *44*, 94−100.

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