

Reversible Switching between Nonporous and Porous Phases of a New SIFSIX Coordination Network Induced by a Flexible Linker Ligand

Bai-Qiao Song, Qing-Yuan Yang, Shi-Qiang Wang, Matthias Vandichel, Amrit Kumar, Clare Crowley, Naveen Kumar, Cheng-Hua Deng, Victoria GasconPerez, Matteo Lusi, Hui Wu, Wei Zhou, and Michael J. Zaworotko*



Cite This: *J. Am. Chem. Soc.* 2020, 142, 6896–6901



Read Online

ACCESS |

Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: Closed-to-open structural transformations in flexible coordination networks are of potential utility in gas storage and separation. Herein, we report the first example of a flexible SiF_6^{2-} -pillared square grid material, $[\text{Cu}(\text{SiF}_6)(\text{L})_2]_n$ ($\text{L} = 1,4\text{-bis}(1\text{-imidazolyl})\text{benzene}$), **SIFSIX-23-Cu**. **SIFSIX-23-Cu** exhibits reversible switching between nonporous ($\beta 1$) and several porous (α , $\gamma 1$, $\gamma 2$, and $\gamma 3$) phases triggered by exposure to N_2 , CO_2 , or H_2O . In addition, heating $\beta 1$ to 433 K resulted in irreversible transformation to a closed polymorph, $\beta 2$. Single-crystal X-ray diffraction studies revealed that the phase transformations are enabled by rotation and geometrical contortion of L . Density functional theory calculations indicated that L exhibits a low barrier to rotation (as low as 8 kJmol^{-1}) and a rather flat energy surface. *In situ* neutron powder diffraction studies provided further insight into these sorbate-induced phase changes. **SIFSIX-23-Cu** combines stability in water for over a year, high CO_2 uptake (ca. 216 cm^3/g at 195 K), and good thermal stability.

Metal-organic materials (MOMs)¹ such as metal-organic frameworks (MOFs)² and porous coordination polymers (PCPs)³ offer potential solutions to the high-energy footprint, costs, and risks associated with storage or purification of gases and vapors.⁴ Whereas rigid microporous MOMs typically display type I isotherms, flexible MOMs (FMOMs)⁵ can exhibit stepped isotherms from structural contraction (expansion) under reduced (increased) pressure, i.e., breathing or swelling.⁶ FMOMs that exhibit stepped type F-IV isotherms, sudden switching from a nonporous (closed) activated phase to a porous (open) phase, are of particular interest for pressure swing adsorption (PSA) gas storage,⁷ as negligible adsorbate is present at low pressure.⁸ Closed-to-open transformations might also facilitate gas separation if adsorbates selectively induce transformations.⁹ Thus far, only ca. 150 FMOMs of the >20 000 porous MOMs reported are known to be flexible,^{5b,10} and just a handful exhibit type F-IV isotherms with saturated uptake of >200 cm^3/g .¹¹ None of these high-uptake FMOMs are sustained by inorganic linker ligands, a matter we address herein.

The “pillared sheet” platform of materials comprised of cationic square grid lattice (sql) sheets and hexafluorosilicate (SiF_6^{2-} , “SIFSIX”) pillars¹² exhibit benchmark performance with respect to separation of industrial gases such as CO_2 , SO_2 , and small-molecule hydrocarbons.¹³ Whereas modeling studies indicate that rotation of pyrazine rings in SIFSIX-3-M ($\text{M} = \text{Ni, Fe}$) can cause inflections in Xe adsorption isotherms, the framework remains rigid.¹⁴ SIFSIX nets can also transform into nonporous sql or sql-c* nets under humid conditions.¹⁵ Herein, we introduce the first flexible SIFSIX net, $[\text{Cu}(\text{SiF}_6)(\text{L})_2]_n$

($\text{L} = 1,4\text{-bis}(1\text{-imidazolyl})\text{benzene}$), **SIFSIX-23-Cu** (Figure 1).

Layering 1:1 MeOH/ H_2O onto CuSiF_6 in H_2O followed by further layering of a solution of L in MeOH afforded purple, needle-shaped crystals of **SIFSIX-23-Cu**· $x\text{MeOH}\cdot y\text{H}_2\text{O}$ (see

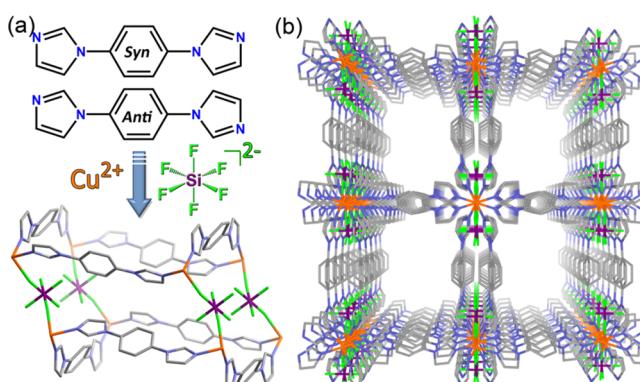


Figure 1. (a) Self-assembly strategy used to design **SIFSIX-23-Cu**. (b) 1D channels along the a -axis in the as-synthesized form, **SIFSIX-23-Cu- α** .

Received: February 3, 2020

Published: March 27, 2020



Supporting Information (SI)), SIFSIX-23-Cu- α . Cu(II) cations are octahedrally coordinated to four equatorial L ligands (two L(*syn*) and two L(*anti*)), while SIFSIX anions occupy the axial sites to afford a noninterpenetrated pcu topology framework (Figure 1a). The CuL₂ sql net undulates due to out-of-plane protrusion of “V”-shaped L(*syn*) linker ligands. The pillars adopt a *cis*-bridging mode, unlike other coordination networks involving SIFSIX anions (Figures S1 and S2).^{12,13,16} SIFSIX-23-Cu- α possesses a 1D channel of diameter $5.4 \times 4.0 \text{ \AA}^2$ along the *a*-axis (Figure 1b) with a calculated accessible void volume of 41.8% (Figure S3).

We found that desolvation induces SIFSIX-23-Cu- α to undergo multiple phase transformations to SIFSIX-23-Cu- γ_1 , - γ_2 , - γ_3 , and a solvent-free closed form, SIFSIX-23-Cu- β_1 (Figures 2a and S4, Table S1). Whereas the space group and

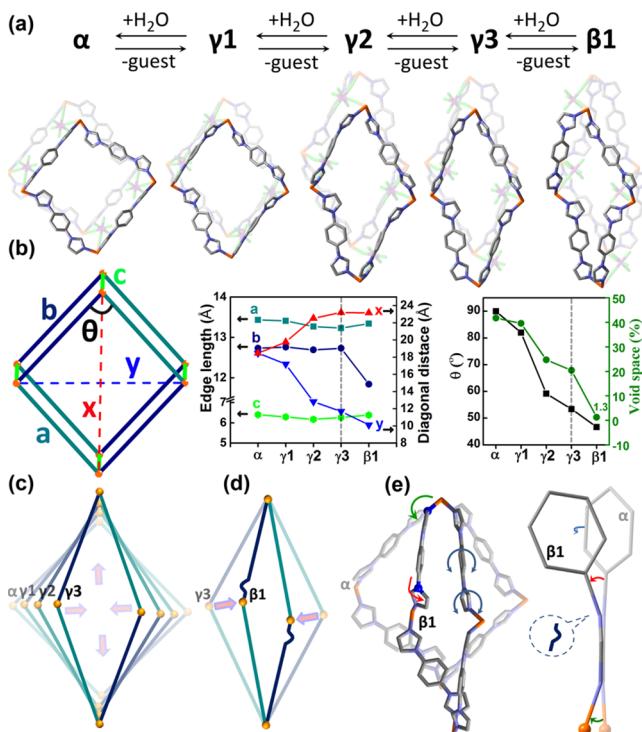


Figure 2. (a) Guest-induced reversible structural transformations occur between the α , γ_1 , γ_2 , γ_3 , and β_1 phases. (b) A parallelogram defines the structural parameters of each phase. Deformation of the parallelogram during the α to γ_3 (c) and the γ_3 to β_1 (d), transformations. (e) Overlapping parallelograms of the α and β_1 phases highlight structural distortions.

unit cell parameters vary, the connectivity of the SIFSIX-23-Cu network is preserved even with extreme deformation (Figure 2b, Table S2). The α to γ_3 transformation caused the parallelogram of the sql net to undergo hinge-like motion with negligible change in edge length ($\Delta d_{\max} = 0.2 \text{ \AA}$) but a decrease in $\angle \text{Cu}-\text{Cu}-\text{Cu}$ from 90° (α) to 53.4° (γ_3) (Figure 2b and c). Concomitantly, one diagonal of the parallelogram reduced from 18.46 \AA (α) to 11.67 \AA (γ_3), whereas the other expanded from 18.46 \AA (α) to 23.19 \AA (γ_3). An overall reduction in guest-accessible volume from 41.8% (α) to 20.4% (γ_3) was calculated by PLATON.¹⁷ Removal of solvent from γ_3 afforded SIFSIX-23-Cu- β_1 , a nonporous phase (Figures 2b and S5 and S6) with 34.5% volume reduction vs the α phase. The transformation from γ_3 to β_1 differs from the other phase changes (Figure 2b and d). FMOMs rarely exhibit such

extreme structural changes.¹¹ β_1 reverted to α after immersion in MeOH, EtOH, or CH₃CN (Figure S7).

Structural analysis of the SIFSIX-23-Cu phases (Figures 2e and S8–S11, Table S2 and S3)¹⁸ reveals hinge-like motion in the α to γ_1 transformation that originates from rotation of imidazolyl rings and reorientation of phenyl rings. Indeed, rotation of L is a feature of each transformation (Figure S8). In the γ_1 to β_1 transformation, the coordinated N atom acts as a hinge or “kneecap” at which the Cu-imidazolyl junction bends (Figure S9). For the γ_3 to β_1 transformation, one imidazolyl ring of L(*syn*) bends at the N(1)_{imidazolyl} atom to subtend an angle of 16.9° between the C_{phenyl}–N_{imidazolyl} bond and the imidazolyl plane (Figure S10), enabling shrinkage of the Cu–L(*syn*)–Cu edge in β_1 . These structural changes are mainly associated with L(*syn*) (Figure S11). C–H···F hydrogen bonds between SIFSIX anions and CH moieties of aromatic groups (Table S4) are often present in SIFSIX coordination networks (Figure S12).¹³ Density functional theory (DFT) calculations indicated that L exhibits a low rotational barrier (<8 kJ/mol) and a rather flat energy surface with minima corresponding to L(*syn*) and L(*anti*). A Cambridge Structural Database (CSD)²⁰ survey revealed that dihedral angles between phenyl and imidazolyl rings are consistent with those in L(*syn*) and L(*anti*) (Figures S13–S15). The energy difference of L(*syn*) calculated before and after bending from γ_3 to β_1 is also small (<16 kJ/mol) (Figure S16). The nature of L helps to explain the “softness” of SIFSIX-23-Cu.²¹

Variable-temperature PXRD studies of the α to β_1 transformation (Figures 3a and S17) revealed a new phase at

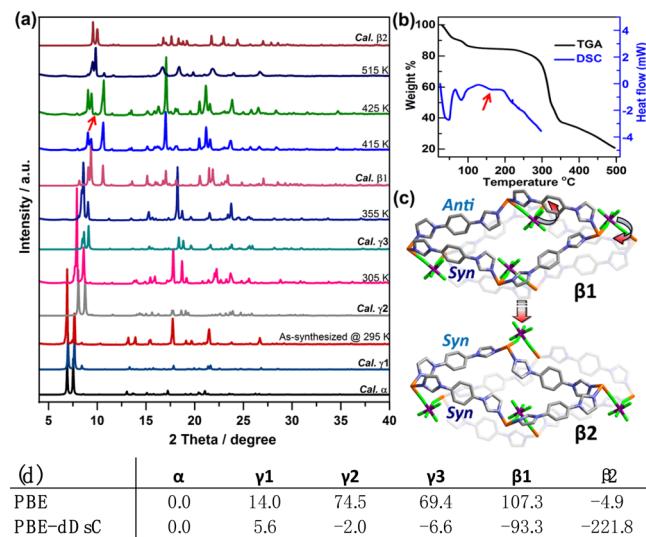


Figure 3. (a) VT-PXRD of SIFSIX-23-Cu from 295 to 515 K. (b) TGA and DSC of SIFSIX-23-Cu. (c) Structural changes in the β_1 to β_2 transformation. (d) Relative energies of the structurally characterized phases (kJ/mol, PBE and PBE-dDsC).

425 K as also suggested by DSC (Figure 3b). That no weight loss was seen in the corresponding TGA curve indicates that this was a temperature-controlled rather than guest-controlled transformation. Heating β_1 or any of the α phases at 433 K afforded single crystals of SIFSIX-23-Cu- β_2 . Single-crystal X-ray diffraction (SCXRD) characterization revealed that β_2 exhibits a slightly smaller cell volume than that of β_1 . The connectivity is unchanged if *anti*-to-*syn* switching of L(*anti*)

and swing motion of SIFSIX anions (Figure 3c) had occurred. That β_2 is more stable than β_1 is supported by its higher density, structural parameters which suggest less strain (Figure S11) and lack of reversibility after immersion in water, MeOH, EtOH, or CH₃CN (Figure S18) and periodic DFT calculations (PBE and PBE-dDsC). The DFT calculations revealed that small global energy differences between the α to γ_3 phases (Figure 3d) are consistent with the reversibility of the structural transformations (Table S5, Figure S19). The energy difference between β_1 and γ_3 is 86.7 kJ/mol, a value that can be offset by adsorption. The β_2 phase was determined to be relatively more stable (-222 kJ/mol vs α).

Since the closed-to-open transformation from β_1 to α was induced by solvent, we anticipated that gases might also trigger switching. The CO₂ isotherm of β_1 at 195 K indeed displayed switching with two steps (Figure 4a). The first step at ca. 2.4 mmHg (adsorbed CO₂ = 84 cm³/g) gave a micropore volume of 0.16 cm³/g, close to that estimated from the crystal structure of γ_3 (0.15 cm³/g). The second step occurred after saturation (ca. 216 cm³/g) with a micropore volume of 0.40 cc/g, in good agreement with the structure of α (0.40 cm³/g). The Langmuir surface areas for the phases in the first and second steps

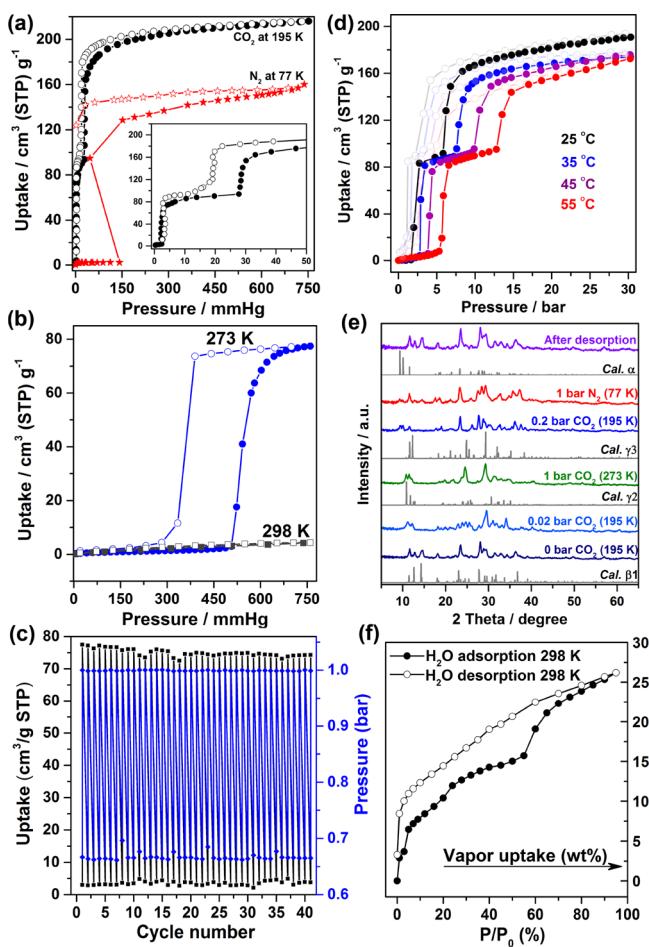


Figure 4. (a) Gas sorption isotherms of β_1 at 195 K (CO₂) and 77 K (N₂). (b) CO₂ sorption isotherms of β_1 at 273 and 298 K. (c) Adsorption/desorption cycles of β_1 at 273 K. (d) High-pressure CO₂ sorption isotherms at 25 to 55 °C. (e) In situ NPD patterns at various conditions. At 77 K, 1 bar N₂ trace β_1 is present because of large sample size (>1 g) and slow kinetics; equilibrium took >24 h. (f) Water sorption isotherm of β_1 at 298 K.

calculated from the CO₂ isotherm at 195 K are 451 and 941 m² g⁻¹, respectively (Figures S20 and S21). β_1 also displayed gate opening for N₂ at 77 K with an onset pressure of 142 mmHg and saturated uptake of 160 cm³/g at 738 mmHg (Figure 4a). In contrast, the N₂ (77 K) and CO₂ (195 K) isotherms for β_2 revealed no uptake (Figure S22).

In situ neutron powder diffraction (NPD) data were collected under various conditions to further study these switching events (Figure 4e). The diffraction pattern obtained at 0 bar matched that calculated for β_1 . For $P = 0.02$ bar at 195 K (the first step), the NPD pattern resembled that calculated for γ_3 . For $P = 0.2$ bar (the second step), the NPD pattern matched that calculated for α . The α phase reverted to β_1 at $P = 0$ bar and 298 K. NPD data of samples collected at 77 K under 1 bar N₂ validated the formation of α . The saturated uptake of N₂ was lower than that calculated from the pore volume based on the CO₂ sorption data (258 cm³/g), perhaps because at 77 K sorbate–sorbent interactions are strong enough to hinder diffusion.²² This guest-dependent switching behavior suggests that structural transformations are driven by host–guest interactions.

The low-pressure CO₂ sorption isotherms at near ambient temperature revealed no switching behavior induced by CO₂ at 298 K below 1 bar (Figures 4b and S23). However, β_1 exhibited a single step type F-IV isotherm at 273 K with a gate-opening pressure of 505 mmHg and saturated uptake of 77 cm³/g at 759 mmHg. The corresponding desorption isotherm displayed hysteresis. The calculated micropore volume of 0.15 cm³/g agrees with that calculated from the crystal structure of γ_3 (0.15 cm³/g). In situ NPD data collected at 273 K and 1 bar CO₂ showed a similar NPD pattern to that obtained at 195 K for 0.02 bar CO₂, i.e., the γ_3 phase (Figure 4e). That this phase switching is reversible was demonstrated by 41 cycles of CO₂ adsorption/desorption (Figures 4c and S24–S26). PXRD confirmed structural integrity (Figure S27). CO₂ triggered closed to open switching with an onset gate-opening pressure of <1 bar at 273 K observed in the ELM family of materials and zeolitic imidazolate frameworks (ZIFs).^{8b,23}

High-pressure CO₂ sorption on β_1 (Figure 4d) resembled the isotherm obtained at 195 K. The onset gate-opening pressures for the first and second step at 298 K are around 2 and 5.8 bar, respectively. Interestingly, even at 55 °C CO₂ triggers gate-opening with a threshold pressure of ca. 5.3 bar, a pressure suitable for high-temperature gas sorption and separation. CO₂-induced closed-to-open switching from β_1 to α at high pressure was found to be reversible (Figures S28–S30).

SIFSIX-23-Cu- β_1 also underwent closed-to-open switching induced by water vapor at 298 K (Figure 4f). The steep water uptake (2.8%) at low humidity matches the SCXRD results, which indicate that β_1 can capture one water molecule without a structural change. β_1 sequentially formed γ_3 , γ_2 , and γ_1 under atmospheric humidity (Figures S31 and S32) whereas water immersion caused β_1 to revert to α (Figures S7). SIFSIX-23-Cu- α retained single-crystallinity after immersion in water for one year (Figures 5 and S33 and S34). This strong hydrolytic stability contrasts with that of other SIFSIX materials.¹⁵

In summary, the new pillared square grid coordination network SIFSIX-23-Cu exhibits an uncommon *cis*-bridging coordination mode of SIFSIX anions and is to our knowledge the first hybrid coordination network that undergoes reversible guest-induced closed-to-open transformations. It is also one of

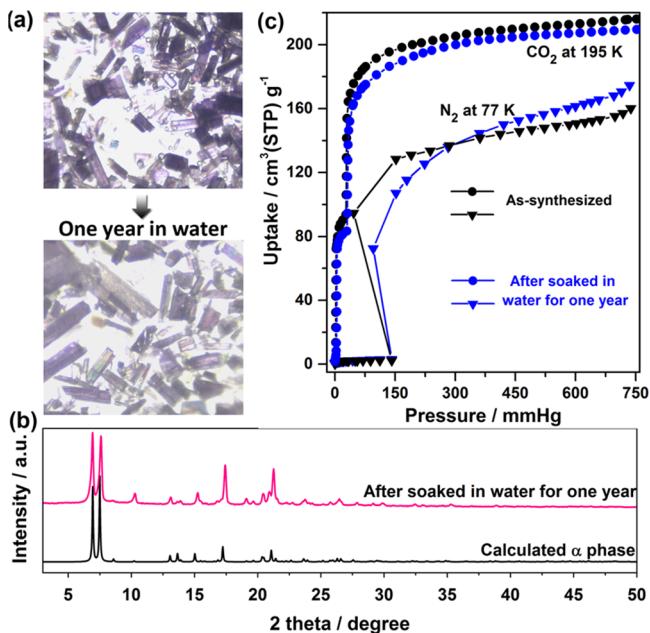


Figure 5. (a) As-synthesized crystals compared to those soaked in water for one year. (b) PXRD pattern of SIFSIX-3-Cu soaked in water for one year compared with that calculated for α . (c) The 195 K CO₂ and 77 K N₂ adsorption isotherms of samples before and after being soaked in water for one year.

the highest uptake materials with a type F-IV isotherm. We attribute these facile and reversible transformations to the low rotational barrier of L and the correspondingly flat energy surface.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.0c01314>.

Materials and methods, supporting figures, supporting tables, and supporting references ([PDF](#))
 Crystallographic information file ([CIF](#))
 Crystallographic information file ([CIF](#))

AUTHOR INFORMATION

Corresponding Author

Michael J. Zaworotko — Department of Chemical Sciences and Bernal Institute, University of Limerick, Limerick V94 T9PX, Republic of Ireland; orcid.org/0000-0002-1360-540X; Email: Michael.Zaworotko@ul.ie

Authors

Bai-Qiao Song — Department of Chemical Sciences and Bernal Institute, University of Limerick, Limerick V94 T9PX, Republic of Ireland

Qing-Yuan Yang — School of Chemical Engineering and Technology, Xi'an Jiaotong University, Xi'an 710049, China; orcid.org/0000-0002-1742-2088

Shi-Qiang Wang — Department of Chemical Sciences and Bernal Institute, University of Limerick, Limerick V94 T9PX, Republic of Ireland; orcid.org/0000-0003-1213-8317

Matthias Vandichel — Department of Chemical Sciences and Bernal Institute, University of Limerick, Limerick V94 T9PX, Republic of Ireland

Amrit Kumar — Department of Chemical Sciences and Bernal Institute, University of Limerick, Limerick V94 T9PX, Republic of Ireland

Clare Crowley — Department of Chemical Sciences and Bernal Institute, University of Limerick, Limerick V94 T9PX, Republic of Ireland

Naveen Kumar — Department of Chemical Sciences and Bernal Institute, University of Limerick, Limerick V94 T9PX, Republic of Ireland

Cheng-Hua Deng — Department of Chemical Sciences and Bernal Institute, University of Limerick, Limerick V94 T9PX, Republic of Ireland

Victoria GasconPerez — Department of Chemical Sciences and Bernal Institute, University of Limerick, Limerick V94 T9PX, Republic of Ireland

Matteo Lusi — Department of Chemical Sciences and Bernal Institute, University of Limerick, Limerick V94 T9PX, Republic of Ireland

Hui Wu — NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-6102, United States; orcid.org/0000-0003-0296-5204

Wei Zhou — NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-6102, United States; orcid.org/0000-0002-5461-3617

Complete contact information is available at:
<https://pubs.acs.org/10.1021/jacs.0c01314>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge Science Foundation Ireland (SFI Awards 13/RP/B2549 and 16/IA/4624) and the Irish Research Council (IRCLA/2019/167).

REFERENCES

- Perry, J. J., IV; Perman, J. A.; Zaworotko, M. J. Design and synthesis of metal–organic frameworks using metal–organic polyhedra as supramolecular building blocks. *Chem. Soc. Rev.* **2009**, *38*, 1400.
- (a) Furukawa, H.; Cordova, K. E.; O’Keeffe, M.; Yaghi, O. M. The Chemistry and Applications of Metal-Organic Frameworks. *Science* **2013**, *341*, 1230444. (b) Farrusseng, D. *Metal-Organic Frameworks: Applications from Catalysis to Gas Storage*; Wiley, 2011.
- (a) Kitagawa, S.; Kitaura, R.; Noro, S.-I. Functional Porous Coordination Polymers. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334. (b) Batten, S. R.; Neville, S. M.; Turner, D. R. *Coordination Polymers: Design, Analysis and Application*; The Royal Society of Chemistry: Cambridge, U.K., 2009.
- (a) Adil, K.; Belmabkhout, Y.; Pillai, R. S.; Cadiou, A.; Bhatt, P. M.; Assen, A. H.; Maurin, G.; Eddaoudi, M. Gas/vapour separation using ultra-microporous metal–organic frameworks: insights into the structure/separation relationship. *Chem. Soc. Rev.* **2017**, *46*, 3402. (b) Kitagawa, S. Porous Materials and the Age of Gas. *Angew. Chem., Int. Ed.* **2015**, *54*, 10686. (c) Lin, R.-B.; Xiang, S.; Xing, H.; Zhou, W.; Chen, B. Exploration of porous metal–organic frameworks for gas separation and purification. *Coord. Chem. Rev.* **2019**, *378*, 87.
- (a) Horike, S.; Shimomura, S.; Kitagawa, S. Soft porous crystals. *Nat. Chem.* **2009**, *1*, 695. (b) Schneemann, A.; Bon, V.; Schwedler, I.; Senkovska, I.; Kaskel, S.; Fischer, R. A. Flexible metal–organic

frameworks. *Chem. Soc. Rev.* **2014**, *43*, 6062. (c) Férey, G. Hybrid porous solids: past, present, future. *Chem. Soc. Rev.* **2008**, *37*, 191. (d) Murdock, C. R.; Hughes, B. C.; Lu, Z.; Jenkins, D. M. Approaches for synthesizing breathing MOFs by exploiting dimensional rigidity. *Coord. Chem. Rev.* **2014**, *258–259*, 119.

(6) (a) Zhou, D.-D.; Chen, P.; Wang, C.; Wang, S.-S.; Du, Y.; Yan, H.; Ye, Z.-M.; He, C.-T.; Huang, R.-K.; Mo, Z.-W.; Huang, N.-Y.; Zhang, J.-P. Intermediate-sized molecular sieving of styrene from larger and smaller analogues. *Nat. Mater.* **2019**, *18*, 994. (b) Zhang, Y.; Zhang, X.; Lyu, J.; Otake, K.-i.; Wang, X.; Redfern, L. R.; Malliakas, C. D.; Li, Z.; Islamoglu, T.; Wang, B.; Farha, O. K. A Flexible Metal–Organic Framework with 4-Connected Zr₆ Nodes. *J. Am. Chem. Soc.* **2018**, *140*, 11179. (c) Rabone, J.; Yue, Y.-F.; Chong, S. Y.; Stylianou, K. C.; Bacsa, J.; Bradshaw, D.; Darling, G. R.; Berry, N. G.; Khimyak, Y. Z.; Ganin, A. Y.; Wiper, P.; Claridge, J. B.; Rosseinsky, M. J. An Adaptable Peptide-Based Porous Material. *Science* **2010**, *329*, 1053. (d) Katsoulidis, A. P.; Antypov, D.; Whitehead, G. F. S.; Carrington, E. J.; Adams, D. J.; Berry, N. G.; Darling, G. R.; Dyer, M. S.; Rosseinsky, M. J. Chemical control of structure and guest uptake by a conformationally mobile porous material. *Nature* **2019**, *565*, 213. (e) Carrington, E. J.; McAnally, C. A.; Fletcher, A. J.; Thompson, S. P.; Warren, M.; Brammer, L. Solvent-switchable continuous-breathing behaviour in a diamondoid metal–organic framework and its influence on CO₂ versus CH₄ selectivity. *Nat. Chem.* **2017**, *9*, 882. (f) Xiao, B.; Byrne, P. J.; Wheatley, P. S.; Wragg, D. S.; Zhao, X.; Fletcher, A. J.; Thomas, K. M.; Peters, L.; Evans, J. S. O.; Warren, J. E.; Zhou, W.; Morris, R. E. Chemically blockable transformation and ultraselective low-pressure gas adsorption in a non-porous metal organic framework. *Nat. Chem.* **2009**, *1*, 289. (g) Shivanna, M.; Yang, Q.-Y.; Bajpai, A.; Patyk-Kazmierczak, E.; Zaworotko, M. J. A dynamic and multi-responsive porous flexible metal–organic material. *Nat. Commun.* **2018**, *9*, 3080. (h) Serre, C.; Mellot-Draznieks, C.; Surblé, S.; Audebrand, N.; Filinchuk, Y.; Férey, G. Role of Solvent-Host Interactions That Lead to Very Large Swelling of Hybrid Frameworks. *Science* **2007**, *315*, 1828. (i) Serre, C.; Millange, F.; Thouvenot, C.; Noguès, M.; Marsolier, G.; Louër, D.; Férey, G. Very Large Breathing Effect in the First Nanoporous Chromium(III)-Based Solids: MIL-53 or Cr^{III}-(OH)_x{O₂C-C₆H₄-CO₂}·{HO₂C-C₆H₄-CO₂H}_x·H₂O_y. *J. Am. Chem. Soc.* **2002**, *124*, 13519.

(7) (a) Sakaida, S.; Otsubo, K.; Sakata, O.; Song, C.; Fujiwara, A.; Takata, M.; Kitagawa, H. Crystalline coordination framework endowed with dynamic gate-opening behaviour by being downsized to a thin film. *Nat. Chem.* **2016**, *8*, 377. (b) Jin, J.; Zhao, X.; Feng, P.; Bu, X. A Cooperative Pillar–Template Strategy as a Generalized Synthetic Method for Flexible Homochiral Porous Frameworks. *Angew. Chem.* **2018**, *130*, 3799. (c) Engel, E. R.; Jouaiti, A.; Bezuidenhout, C. X.; Hosseini, M. W.; Barbour, L. J. Activation-Dependent Breathing in a Flexible Metal–Organic Framework and the Effects of Repeated Sorption/Desorption Cycling. *Angew. Chem., Int. Ed.* **2017**, *56*, 8874. (d) Hazra, A.; van Heerden, D. P.; Sanyal, S.; Lama, P.; Esterhuyse, C.; Barbour, L. J. CO₂-induced single-crystal to single-crystal transformations of an interpenetrated flexible MOF explained by *in situ* crystallographic analysis and molecular modeling. *Chem. Sci.* **2019**, *10*, 10018.

(8) (a) Wharmby, M. T.; Henke, S.; Bennett, T. D.; Bajpe, S. R.; Schwedler, I.; Thompson, S. P.; Gozzo, F.; Simoncic, P.; Mellot-Draznieks, C.; Tao, H.; Yue, Y.; Cheetham, A. K. Extreme Flexibility in a Zeolitic Imidazolate Framework: Porous to Dense Phase Transition in Desolvated ZIF-4. *Angew. Chem., Int. Ed.* **2015**, *54*, 6447. (b) McGuirk, C. M.; Runčevski, T.; Oktawiec, J.; Turkiewicz, A.; Taylor, M. K.; Long, J. R. Influence of Metal Substitution on the Pressure-Induced Phase Change in Flexible Zeolitic Imidazolate Frameworks. *J. Am. Chem. Soc.* **2018**, *140*, 15924. (c) Kundu, T.; Wahiduzzaman, M.; Shah, B. B.; Maurin, G.; Zhao, D. Solvent-Induced Control over Breathing Behavior in Flexible Metal–Organic Frameworks for Natural-Gas Delivery. *Angew. Chem., Int. Ed.* **2019**, *58*, 8073. (d) Yang, H.; Guo, F.; Lama, P.; Gao, W.-Y.; Wu, H.; Barbour, L. J.; Zhou, W.; Zhang, J.; Aguila, B.; Ma, S. Visualizing

Structural Transformation and Guest Binding in a Flexible Metal–Organic Framework under High Pressure and Room Temperature. *ACS Cent. Sci.* **2018**, *4*, 1194.

(9) (a) Güçüyener, C.; van den Bergh, J.; Gascon, J.; Kapteijn, F. Ethane/Ethene Separation Turned on Its Head: Selective Ethane Adsorption on the Metal-Organic Framework ZIF-7 through a Gate-Opening Mechanism. *J. Am. Chem. Soc.* **2010**, *132*, 17704. (b) Nijem, N.; Wu, H.; Canepa, P.; Marti, A.; Balkus, K. J.; Thonhauser, T.; Li, J.; Chabal, Y. J. Tuning the Gate Opening Pressure of Metal–Organic Frameworks (MOFs) for the Selective Separation of Hydrocarbons. *J. Am. Chem. Soc.* **2012**, *134*, 15201. (c) Taylor, M. K.; Runčevski, T.; Oktawiec, J.; Bachman, J. E.; Siegelman, R. L.; Jiang, H.; Mason, J. A.; Tarver, J. D.; Long, J. R. Near-Perfect CO₂/CH₄ Selectivity Achieved through Reversible Guest Templating in the Flexible Metal–Organic Framework Co(bdp). *J. Am. Chem. Soc.* **2018**, *140*, 10324. (d) Wang, S.-Q.; Mukherjee, S.; Patyk-Kazmierczak, E.; Darwish, S.; Bajpai, A.; Yang, Q.-Y.; Zaworotko, M. J. Highly Selective, High-Capacity Separation of o-Xylene from C₈ Aromatics by a Switching Adsorbent Layered Material. *Angew. Chem.* **2019**, *131*, 6702.

(10) Moghadam, P. Z.; Li, A.; Wiggin, S. B.; Tao, A.; Maloney, A. G. P.; Wood, P. A.; Ward, S. C.; Fairén-Jimenez, D. Development of a Cambridge Structural Database Subset: A Collection of Metal–Organic Frameworks for Past, Present, and Future. *Chem. Mater.* **2017**, *29*, 2618.

(11) (a) Mason, J. A.; Oktawiec, J.; Taylor, M. K.; Hudson, M. R.; Rodriguez, J.; Bachman, J. E.; Gonzalez, M. I.; Cervellino, A.; Guagliardi, A.; Brown, C. M.; Llewellyn, P. L.; Masciocchi, N.; Long, J. R. Methane storage in flexible metal–organic frameworks with intrinsic thermal management. *Nature* **2015**, *527*, 357. (b) Klein, N.; Hoffmann, H. C.; Cadiau, A.; Getzschmann, J.; Lohe, M. R.; Paasch, S.; Heydenreich, T.; Adil, K.; Senkovska, I.; Brunner, E.; Kaskel, S. Structural flexibility and intrinsic dynamics in the M₂(2,6-ndc)₂-(dabco) (M = Ni, Cu, Co, Zn) metal–organic frameworks. *J. Mater. Chem.* **2012**, *22*, 10303. (c) Zhu, A.-X.; Yang, Q.-Y.; Kumar, A.; Crowley, C.; Mukherjee, S.; Chen, K.-J.; Wang, S.-Q.; O’Nolan, D.; Shivanna, M.; Zaworotko, M. J. Coordination Network That Reversibly Switches between Two Nonporous Polymorphs and a High Surface Area Porous Phase. *J. Am. Chem. Soc.* **2018**, *140*, 15572. (d) Yang, Q.-Y.; Lama, P.; Sen, S.; Lusi, M.; Chen, K.-J.; Gao, W.-Y.; Shivanna, M.; Pham, T.; Hosono, N.; Kusaka, S.; Perry, J. J., IV; Ma, S.; Space, B.; Barbour, L. J.; Kitagawa, S.; Zaworotko, M. J. Reversible Switching between Highly Porous and Nonporous Phases of an Interpenetrated Diamondoid Coordination Network That Exhibits Gate-Opening at Methane Storage Pressures. *Angew. Chem., Int. Ed.* **2018**, *57*, 5684. (e) Zhu, A.-X.; Yang, Q.-Y.; Mukherjee, S.; Kumar, A.; Deng, C.-H.; Bezrukov, A. A.; Shivanna, M.; Zaworotko, M. J. Tuning the Gate-Opening Pressure in a Switching pcu Coordination Network, X-pcu-5-Zn, by Pillar-Ligand Substitution. *Angew. Chem., Int. Ed.* **2019**, *58*, 18212. (f) Chen, L.; Mowat, J. P. S.; Fairén-Jimenez, D.; Morrison, C. A.; Thompson, S. P.; Wright, P. A.; Düren, T. Elucidating the Breathing of the Metal–Organic Framework MIL-53(Sc) with ab Initio Molecular Dynamics Simulations and in Situ X-ray Powder Diffraction Experiments. *J. Am. Chem. Soc.* **2013**, *135*, 15763. (g) Seo, J.; Matsuda, R.; Sakamoto, H.; Bonneau, C.; Kitagawa, S. A Pillared-Layer Coordination Polymer with a Rotatable Pillar Acting as a Molecular Gate for Guest Molecules. *J. Am. Chem. Soc.* **2009**, *131*, 12792.

(12) Subramanian, S.; Zaworotko, M. J. Porous Solids by Design: [Zn(4,4'-bpy)₂(SiF₆)]_n·xDMF, a Single Framework Octahedral Coordination Polymer with Large Square Channels. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2127.

(13) (a) 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 CO₂ separation. *Nature* **2013**, *495*, 80. (b) 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. (c) Chen, K.-J.; Madden, D. G.; Mukherjee, S.; Pham, T.; Forrest, K. A.; Kumar, A.; Space, B.; Kong, J.; Zhang, Q.-Y.; Zaworotko, M. J. Synergistic sorbent separation for one-step ethylene purification from a four-component mixture. *Science* **2019**, *366*, 241.
- (d) Shekhar, 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. (e) Cui, X.; Yang, Q.; Yang, L.; Krishna, R.; Zhang, Z.; Bao, Z.; Wu, H.; Ren, Q.; Zhou, W.; Chen, B.; Xing, H. Ultrahigh and Selective SO₂ Uptake in Inorganic Anion-Pillared Hybrid Porous Materials. *Adv. Mater.* **2017**, *29*, 1606929.
- (14) Elsaidi, S. K.; Mohamed, M. H.; Simon, C. M.; Braun, E.; Pham, T.; Forrest, K. A.; 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 networks. *Chem. Sci.* **2017**, *8*, 2373.
- (15) O’Nolan, D.; Kumar, A.; Zaworotko, M. J. Water Vapor Sorption in Hybrid Pillared Square Grid Materials. *J. Am. Chem. Soc.* **2017**, *139*, 8508.
- (16) Wang, X.-F.; Du, C.-C.; Zhou, S.-B.; Wang, D.-Z. Six complexes based on bis(imidazole/benzimidazole-1-yl)pyridazine ligands: Syntheses, structures and properties. *J. Mol. Struct.* **2017**, *1128*, 103.
- (17) Spek, A. Structure validation in chemical crystallography. *Acta Crystallogr., Sect. D: Biol. Crystallogr.* **2009**, *65*, 148.
- (18) Zhang, J.-P.; Liao, P.-Q.; Zhou, H.-L.; Lin, R.-B.; Chen, X.-M. Single-crystal X-ray diffraction studies on structural transformations of porous coordination polymers. *Chem. Soc. Rev.* **2014**, *43*, 5789.
- (19) (a) Deria, P.; Gómez-Gualdrón, D. A.; Bury, W.; Schaeff, H. T.; Wang, T. C.; Thallapally, P. K.; Sarjeant, A. A.; Snurr, R. Q.; Hupp, J. T.; Farha, O. K. Ultraporous, Water Stable, and Breathing Zirconium-Based Metal–Organic Frameworks with ftw Topology. *J. Am. Chem. Soc.* **2015**, *137*, 13183. (b) Liu, D.; Liu, T.-F.; Chen, Y.-P.; Zou, L.; Feng, D.; Wang, K.; Zhang, Q.; Yuan, S.; Zhong, C.; Zhou, H.-C. A Reversible Crystallinity-Preserving Phase Transition in Metal–Organic Frameworks: Discovery, Mechanistic Studies, and Potential Applications. *J. Am. Chem. Soc.* **2015**, *137*, 7740.
- (20) Groom, C. R.; Bruno, I. J.; Lightfoot, M. P.; Ward, S. C. The Cambridge Structural Database. *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater.* **2016**, *72*, 171.
- (21) Gu, C.; Hosono, N.; Zheng, J.-J.; Sato, Y.; Kusaka, S.; Sakaki, S.; Kitagawa, S. Design and control of gas diffusion process in a nanoporous soft crystal. *Science* **2019**, *363*, 387.
- (22) Nugent, P. S.; Rhodus, V. L.; Pham, T.; Forrest, K.; Wojtas, L.; Space, B.; Zaworotko, M. J. A Robust Molecular Porous Material with High CO₂ Uptake and Selectivity. *J. Am. Chem. Soc.* **2013**, *135*, 10950.
- (23) Kondo, A.; Noguchi, H.; Ohnishi, S.; Kajiro, H.; Tohdoh, A.; Hattori, Y.; Xu, W.-C.; Tanaka, H.; Kanoh, H.; Kaneko, K. Novel Expansion/Shrinkage Modulation of 2D Layered MOF Triggered by Clathrate Formation with CO₂ Molecules. *Nano Lett.* **2006**, *6*, 2581.