Flexible Coordination Network Exhibiting Water Vapor–Induced Reversible Switching between Closed and Open Phases

Mohana Shivanna,§ Andrey A. Bezrukov,§ Victoria Gascón-Pérez, Ken-ichi Otake, Suresh Sanda, Daniel J. O’Hearn, Qing-Yuan Yang, Susumu Kitagawa,* and Michael J. Zaworotko*

ACCESS

ABSTRACT: That physisorbents can reduce the energy footprint of water vapor capture and release has attracted interest because of potential applications such as moisture harvesting, dehumidification, and heat pumps. In this context, sorbents exhibiting an S-shaped single-step water sorption isotherm are desirable, most of which are structurally rigid sorbents that undergo pore-filling at low relative humidity (RH), ideally below 30% RH. Here, we report that a new one-dimensional (1D) coordination network, [Cu(HQS)(TMBP)] (H₂HQS = 8-hydroxyquinoline-5-sulfonic acid and TMBP = 4,4′-trimethylenedipyridine), exhibits at least five phases: two as-synthesized open phases, α ⊃ H₂O and β ⊃ MeOH; an activated closed phase (γ); CO₂ (δ ⊃ CO₂) and C₆H₆ (ε ⊃ C₆H₆) loaded phases. The γ phase underwent a reversible structural transformation to α ⊃ H₂O with a stepped sorption profile (Type F-IV) when exposed to water vapor at <30% RH at 300 K. The hydrolytic stability of [Cu(HQS)(TMBP)] was confirmed by powder X-ray diffraction (PXRD) after immersion in boiling water for 6 months. Temperature-humidity swing cycling measurements demonstrated that working capacity is retained for >100 cycles and only mild heating (<323 K) is required for regeneration. Unexpectedly, the kinetics of loading and unloading of [Cu(HQS)(TMBP)] compares favorably with well-studied rigid water sorbents such as Al-fumarate, MOF-303, and CAU-10-H. Furthermore, a polymer composite of [Cu(HQS)(TMBP)] was prepared and its water sorption retained its stepped profile and uptake capacity over multiple cycles.

KEYWORDS: sorbents, structural flexibility, water sorption properties, atmospheric water harvesting, metal–organic frameworks, composites, stepped isotherm

INTRODUCTION

The emergence of a new generation of porous physisorbents for gas/vapor capture and storage has captured the imagination of materials chemists as exemplified by the emergence of porous liquids§ and various classes of porous crystalline solids. In this context, water vapor capture and storage are at the forefront as more than 70% of humanity is currently suffering from lack of ready access to clean water. Furthermore, the situation is deteriorating due to water pollution, climate change, and population growth. In addition, whereas desalination of seawater can be implemented, it is energy-intensive and economically viable only in coastal areas due to added transportation costs. Atmospheric water harvesting (AWH) is a promising alternative technology. There are three primary approaches to AWH: (a) fog collection by means of large nets is inexpensive and low-maintenance but requires fog formation and is therefore usually restricted to mountainous or coastal areas; (b) cooling air below its dew point is energy-intensive and economically infeasible under dry conditions; (c) AWH via adsorption of atmospheric water vapor by a porous desiccant§ and release by applying a temperature and/or humidity swing process offers an energy-efficient approach that can in principle be implemented even in the most arid locations. Physisorbents also offer potential to provide more energy-efficient solutions for related applications such as indoor humidity control, natural gas dehydration, thermal battery management, and temperature regulation using adsorption-based heat pumps and chillers. In this regard, traditional desiccants such as zeolites are highly effective at water vapor capture, even at low relative humidity (RH), and can offer high uptake capacity, but their strong hydrophilicity typically requires high regeneration temperatures (Figure 1a). Porous physisorbents that exhibit S-shaped or stepped water sorption isotherms below 30% RH are more desirable as they can offer both high working capacity (Figure 1b) and low regeneration energy. Unfortunately, such water vapor isotherms remain rare amongst traditional desiccants.

Metal–organic materials (MOMs),§ also known as porous coordination polymers (PCPs) or metal–organic frameworks (MOFs), crystalline materials formed by the assembly of metal ions/clusters and organic linkers, are...
promising candidates for AWH because their pore size/chemistry can be fine-tuned to optimize water sorption properties. Rigid MOF sorbents, as exemplified by MOF-801,13−14 UiO-66,14 CAU-10-H,15,16 MOF-303,17−18 Cr-socMOF-1,19 Co,Cl2BTDD,20 and Al-fumarate,21 have been studied with respect to their water sorption properties and offer desirable S-shaped isotherms22−25 thanks to a pore-filling mechanism. Alternatively, S-shaped or stepped isotherms can result from structural flexibility induced by exposure to gases or vapors.26 Flexible MOFs, also known as soft PCPs, undergo structural changes, sometimes dramatic, in response to external stimuli.26−31 Flexible sorbents that switch between closed and open phases are of special interest as they offer high working capacities and could find utility in gas and vapor storage applications.32,33 With respect to water sorption applications, such sorbents remain understudied.34,35 In this work, we report that a flexible 1D coordination network, [Cu(HQS)·(TMBP)]·guest (guest = H2O, MeOH), transforms to a closed phase, γ, when activated by heat (Figure 1d). We herein report characterization of five crystal forms of [Cu(HQS)·(TMBP)] and the water sorption performance of γ and its polymer composite.

 EXPERIMENTAL SECTION

All reagents were purchased in high-purity grade and used as received. More details are provided in the Supporting Information (SI).

Preparation of [Cu(HQS)(TMBP)]·nH2O, α ⊃ H2O. In a typical reaction, a solution of water (2 mL) containing Cu(NO3)2·3H2O (48 mg, 0.20 mmol) was layered over a 5:2 solution of EtOH and water (7 mL) containing 8-hydroxyquinoline-S-sulfonic acid (H2HQS; 22.5 mg, 0.100 mmol) and 4,4′-trimethylenedipyridine (TMBP; 60 mg, 0.30 mmol). Then the reaction vessel was transferred into an oven and heated at 333 K for one day, at which point green single crystals were harvested from the wall and bottom of the vessel. A higher yield of crystals was obtained after standing for 2−3 days.

Preparation of [Cu(HQS)(TMBP)]·nMeOH, β ⊃ MeOH. A solution of Cu(NO3)2·3H2O in 2 mL of water was layered over a MeOH (5 mL) solution of H2HQS and TMBP. The procedure, including reaction conditions and concentrations, was the same as above.

Preparation of [Cu(HQS)(TMBP)], γ, α ⊃ H2O was activated at 353 K under vacuum for several hours to transform into γ. Similarly, β ⊃ MeOH was activated at 353 K under vacuum to afford γ.

Preparation of [Cu(HQS)(TMBP)]−Polymer Composite. A powdered sample of [Cu(HQS)(TMBP)]·(0.55 g), HYCAR 26410 polymer binder (0.5 g), isopropanol (3.85 g), and water (9.7 g) were mixed in a beaker and stirred using a mechanical mixer. The resulting slurry was placed on a Teflon plate and heated in an oven at 393 K for 1 h.

 RESULTS AND DISCUSSION

Synthesis and Structural Characterization. Dark green single crystals of α ⊃ H2O were isolated as described above (Figure S1). Single-crystal X-ray diffraction (SCXRD) analysis revealed that α ⊃ H2O had crystallized in the triclinic space group P1 (Table S1). Square pyramidal Cu cations coordinate to an axial sulfonate oxygen atom, whereas the equatorial positions are occupied by an HQS ligand (oxygen of oxo moiety and nitrogen of pyridine moiety) and two nitrogen atoms of two different TMBP ligands (Figure 2a). Adjacent Cu cations are connected by TMBP linker ligands to form cavities linked by HQS anions to generate a 1D coordination polymer

Figure 1. Illustration of water vapor sorption profiles and structural transformations in [Cu(HQS)(TMBP)]·H2HQS = 8-hydroxyquinoline-S-sulfonic acid and TMBP = 4,4′-trimethylenedipyridine). (a) Rigid sorbents typically exhibit strongly hydrophilic (red), moderately hydrophilic (green), or strongly hydrophobic (blue) isotherms. (b) Stepped sorption profiles are desirable because they can offer high working capacity. (c) Organic linkers and Cu cations form the one-dimensional (1D) coordination network [Cu(HQS)(TMBP)], which undergoes reversible transformation between its α and γ phases. (d) α phase is composed of Cu II and water, whereas β phase is composed of Cu II and MeOH.

Figure 2. Crystal structures of the as-synthesized (α, β) and activated (γ) phases. (a) In α, HQS coordinates to metal centers in parallel but oriented in opposite directions and, when connected by TMBP linkers, formed a 1D coordination with water channels. (b) In β, metal cations coordinate to MeOH and TMBP linkers to form a 1D structure that packs to form channels occupied by MeOH. (c) γ is the phase obtained upon activation; the TMBP linkers are squeezed, resulting in reduced guest accessible space.
revealed that with the same connectivity as synthesis afforded a different phase, of cavities. The use of MeOH/water as the solvent system for (Figure 2a). Four independent water molecules were found to Figure 3. 

PXRD data of a sample of upon activation. We collected high-resolution synchrotron structure by Rietveld refinement (Figure S12). network connectivity of the as-synthesized phases, but its void space was reduced to 7.5% of unit cell volume (Figure S13). The experimental and calculated PXRD patterns of γ match well (Figure S4).

Gas Sorption and In Situ PXRD Studies. Motivated by the structural flexibility that accompanied loss of guest molecules, we collected the CO₂ and C₂H₄ sorption isotherms of [Cu(HQS)(TMBP)] at 195 K (Figure 3a), following activation of α ⊃ H₂O at 353 K under vacuum for 12 h. A stepped isotherm was obtained for CO₂ (Figure 3a). In the low-pressure region from P/P₀ = 0.1 to 0.7, the uptake reached 30 cm³/g before the step to an uptake of 110 cm³/g at P/P₀ = 1. CO₂ desorption does not match adsorption because of hysteresis, the reverse step being at P/P₀ = 0.2. For C₂H₄ (Figure 3c), gradual uptake from 0 to 10 cm³/g occurred before a step at P/P₀ = 0.65 (gate-opening pressure) that resulted in an uptake of 110 cm³/g at P/P₀ = 1. C₂H₄ desorption also exhibited hysteresis.

To gain insight into the structural transformations associated with the stepped sorption isotherms, we conducted in situ coincident PXRD measurements with CO₂ and C₂H₄ at 195 K (Figure 3b,d). Representative PXRD patterns corresponding to points on the adsorption and desorption profiles were plotted. CO₂ sorption revealed that, from points 1 to 16, γ remained present as the experimental PXRD pattern matched its calculated PXRD pattern (Figure 3b). Increasing pressure afforded new PXRD peaks, which we attribute to a structural transformation from γ to a CO₂-loaded phase (δ ⊃ CO₂). δ ⊃ CO₂ remained present after further increases in pressure (17 to 19) and pressure reduction (23 to 31). Further reduction in pressure resulted in transformation back to γ (34 and 37). With respect to in situ C₂H₄ sorption (Figure 3d), the PXRD data revealed that γ reversibly transformed to a C₂H₄-loaded (Figure 2a). Four independent water molecules were found to be present in the channels that result from eclipsed alignment of cavities. The use of MeOH/water as the solvent system for synthesis afforded a different phase, β ⊃ MeOH. SCXRD revealed that β ⊃ MeOH had also crystallized in P1 (Table S1) with the same connectivity as α ⊃ H₂O, except that one MeOH coordinates to what is now an octahedral Cu cation (Figure 2b). The α and β phases exhibit accessible void spaces of 16.0 and 18.3% of unit cell volume, respectively (Figures S2 and S3). Phase purity of the as-synthesized phases was confirmed by powder X-ray diffraction (PXRD, Figure S4). Dehydration of α ⊃ H₂O and desolvation of β ⊃ MeOH by heating at 353 K in vacuo resulted in transformation to a closed phase, γ (Figures 1d, S4 and S5). We also observed that β ⊃ MeOH transformed to α ⊃ H₂O when heated at 353 K in ambient air (Figure S4). [Cu(HQS)(TMBP)] retained crystallinity after soaking in water at RT or in boiling water for at least 6 months (Figure S6). Thermogravimetric analysis (TGA) indicated that both α ⊃ H₂O and β ⊃ MeOH are thermally stable in N₂ flow to 503 K with ~7.5% weight loss corresponding to 4 H₂O or 3 MeOH molecules per formula unit, respectively (Figures S10 and S11). Cu-based MOFs such as HKUST-1 are known to suffer from poor hydrolytic stability. We attribute the excellent thermal and hydrolytic stability of [Cu(HQS)(TMBP)] to two factors: (i) chelation by HQS linkers and (ii) that Cu cations are not exposed to the pore surface in both the α and γ phases. Single crystals of α ⊃ H₂O and β ⊃ MeOH converted to microcrystalline powders of γ upon activation. We collected high-resolution synchrotron PXRD data of a sample of γ and determined its crystal structure by Rietveld refinement (Figure S12). γ retained the network connectivity of the as-synthesized phases, but its void space was reduced to 7.5% of unit cell volume (Figure S13). The experimental and calculated PXRD patterns of γ match well (Figure S4).
phase (\(\epsilon \supseteq C_2H_2\)). From points 1 to 34, \(\gamma\) was unchanged. Increasing pressure to point 43 (adsorption) afforded \(\epsilon \supseteq C_2H_2\) as indicated by PXRD. This phase remained until pressure was decreased at point 59, below which desorption occurred. The PXRD pattern at point 67 corresponds to \(\gamma\). Both the CO\(_2\) and C\(_2\)H\(_2\) pure gas isotherms exhibit large hysteresis, which is undesirable from a practical gas storage perspective.

**Water Vapor Sorption.** The presence of water molecules in \(\alpha \supseteq H_2O\) and its structural transformation upon water removal prompted us to study the water vapor sorption properties of [Cu(HQS)(TMBP)] at 300 K. Interestingly, \(\gamma\) exhibited a single-step adsorption profile (Type F-IV) at low RH with relatively small hysteresis. Whereas negligible uptake was observed up to 10% RH, uptake increased to 12 wt % at 30% RH followed by a gradual increase to 15 wt % at 90% RH. The desorption profile revealed the relatively small hysteresis.

![Figure 4](image-url)
complete desorption occurring by 6% RH (Figure 4a). Water sorption isotherms measured at 283, 293, 303, and 313 revealed gate-opening pressures of 10, 10, 12, and 15% RH, respectively (Figure 4b). The gate-closing pressures were observed to be similar for each temperature except for the isotherm measured at 283 K. No difference in water sorption observed to be similar for each temperature except for the revealed gate-opening pressures of 10, 10, 12, and 15% RH, resulted in slow adsorption kinetics in comparison to its more slow the kinetics of adsorption/desorption in a structurally Intuitively, one might expect that phase changes would also precluding a direct comparison. That the structural trans- (TMBP) was determined to be \( 110.7 \) to \( 115.8 ^\circ \)). The metal-to-metal distances within and between 1D chains are shorter than those in the \( \alpha \) phases, \( 7.503(119) \), and \( 4.682(134) \) Å, respectively. These results indicate that \( \gamma \) underwent large distortions following guest removal. The low-angle PXRD peaks and corresponding lattice planes most impacted by the phase transformation between the \( \alpha \) and \( \gamma \) forms are illustrated in Figures S41 and S42, respectively.

**CONCLUSIONS**

A new flexible coordination network, \([\text{Cu(HQ5)(TMBP)}]\), was found to exhibit switching between closed and open phases with multiple sorbates including water vapor. Sorption of water vapor at 300 K induced structural transformation with a single-step isotherm at low RH and small hysteresis, whereas sorption of gases (\( \text{CO}_2, \text{C}_2\text{H}_2 \)) at 195 K induced stepped isotherms with large hysteresis. The hydrolytic stability of \([\text{Cu(HQ5)(TMBP)}]\) is high, being unaffected after soaking in boiling water for \( >6 \) months and following multiple water vapor adsorption/desorption cycles. Interestingly, the kinetics of water loading and unloading compare favorably with leading rigid water sorbents such as MOF-303, Al-fumarate, and CAU-10-H. Furthermore, \([\text{Cu(HQ5)(TMBP)}]\) can be formulated into a polymer composite, and its characteristic single-step water vapor sorption isotherm was retained. Overall, this work reveals that flexible 1D coordination polymers can offer optimal kinetics and thermodynamics for water sorption and could be further explored as candidates in the context of AWH and related applications.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.2c10002.
Material synthesis and characterization methods, crystallographic parameters and crystal structure figures for all phases, PXRD patterns, TGA, SEM images, water vapor sorption isotherms and kinetic plots, sorption cycling plots (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**

Michael J. Zaworotko — Department of Chemical Sciences, Bernal Institute, University of Limerick, Limerick V94 T9PX, Republic of Ireland; Email: Michael.Zaworotko@ul.ie

Susumu Kitagawa — Institute for Integrated Cell-Material Sciences, Kyoto University Institute for Advanced Study, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan; Email: kitagawa@icems.kyoto-u.ac.jp

**Authors**

Mohana Shivanna — Department of Chemical Sciences, Bernal Institute, University of Limerick, Limerick V94 T9PX, Republic of Ireland

Andrey A. Bezrukov — Department of Chemical Sciences, Bernal Institute, University of Limerick, Limerick V94 T9PX, Republic of Ireland

Victoria Gascon-Pérez — Department of Chemical Sciences, Bernal Institute, University of Limerick, Limerick V94 T9PX, Republic of Ireland

Ken-ichi Otake — Institute for Integrated Cell-Material Sciences, Kyoto University Institute for Advanced Study, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

Suresh Sanad — Department of Chemical Sciences, Bernal Institute, University of Limerick, Limerick V94 T9PX, Republic of Ireland

Daniel J. O’Hearn — Department of Chemical Sciences, Bernal Institute, University of Limerick, Limerick V94 T9PX, Republic of Ireland

Qing-Yuan Yang — Department of Chemical Sciences, Bernal Institute, University of Limerick, Limerick V94 T9PX, Republic of Ireland

Complete contact information is available at: https://pubs.acs.org/10.1021/acsami.2c10002

**Author Contributions**

$M.S.$ and A.A.B. contributed equally.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

M.J.Z. thanks the Science Foundation Ireland (16/1A/4624), the Irish Research Council (IRCLA/2019/167), and the European Research Council (ADG 885695). S.K. and K.O. gratefully acknowledge a KAKENHI Grant-in-Aid for Scientific Research (S) (JP18H05262, JP22H05005), and (C) (22K05128) from the Japan Society for the Promotion of Science (JSPS) for supporting this research. We thank the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal Nos. 2020A0649, 2021A1104, 2021A1682) for support of synchrotron XRD measurements. We also thank Dr. Naveen Kumar for synthesis of Al-fumarate and CAU-10-H and Dr. Kawaguchi of JASRI for experimental help at SPring-8.

**REFERENCES**

(1) Girin, N.; Del Pópolo, M. G.; Melaugh, G.; Greenaway, R. L.; Rätzke, K.; Koschine, T.; Pison, L.; Gomes, M. F. C.; Cooper, A. I.; James, S. L. Liquids with Permanent Porosity. Nature 2015, 527, 216–220.

(2) O’Hearn, D. J.; Bajpai, A.; Zaworotko, M. J. The “Chemistree” of Porous Coordination Networks: Taxonomic Classification of Porous Solids to Guide Crystal Engineering Studies. Small 2021, 17, No. 2006351.

(3) Mekonnen, M. M.; Hoekstra, A. Y. Four Billion People Facing Severe Water Scarcity. Sci. Adv. 2016, 2, No. e1500323.

(4) Hanikl, N.; Prévet, M. S.; Yaghi, O. M. MOF Water Harvesters. Nat. Nanotechnol. 2020, 15, 348–355.

(5) Gong, W.; Xie, H.; Idreess, K. B.; Son, F. A.; Chen, Z.; Sha, F.; Liu, Y.; Cui, Y.; Farha, O. K. Water Sorption Evolution Enabled by Reticular Construction of Zirconium Metal–Organic Frameworks Based on a Unique [2.2.]Paracyclophane Scaffold. J. Am. Chem. Soc. 2022, 144, 1826–1834.

(6) Llewellyn, P. L.; Schuetz, F.; Grillet, Y.; Rouquerol, F.; Rouquerol, J.; Unger, K. Water Sorption on Mesoporous Alumino-silicate MCM-41. Langmuir 1995, 11, 574–577.

(7) Lee, J. W.; Lee, J. W.; Shim, W. G.; Suh, S. H.; Moon, H. Adsorption of Chlorinated Volatile Organic Compounds on MCM-48. J. Chem. Eng. Data 2003, 48, 381–387.

(8) Perry, J. J., IV; Perman, J. A.; Zaworotko, M. J. Design and Synthesis of Metal-Organic Frameworks Using Metal-Organic Polyhedra as Supermolecular Building Blocks. Chem. Soc. Rev. 2009, 38, 1400–1417.

(9) Kitagawa, S.; Kitaura, R.; Noro, S.-I. Functional Porous Coordination Polymers. Angew. Chem., Int. Ed. 2004, 43, 2334–2375.

(10) Batten, S. R.; Neville, S. M.; Turner, D. R. Coordination Polymers: Design, Analysis and Application Introduction, RSC Publishing: Cambridge, UK, 2009, pp. 9–13.

(11) Li, H.; Eddaudou, M.; O’Keeffe, M.; Yaghi, O. M. Design and Synthesis of an Exceptionally Stable and Highly Porous Metal-Organic Framework. Nature 1999, 402, 276.

(12) Schroder, M. Functional Metal-Organic Frameworks: Gas Storage, Separation and Catalysis. In Functional Metal-Organic Frameworks: Gas Storage, Separation and Catalysis, Schroder, M., Ed.; Topics in Current Chemistry, 2010; Vol. 293, pp 1–262.

(13) Xu, W.; Yaghi, O. M. Metal–Organic Frameworks for Water Harvesting from Air, Anywhere, Anytime. ACS Cent. Sci. 2020, 6, 1348–1354.

(14) Furukawa, H.; Gándara, F.; Zhang, Y.-B.; Jiang, J.; Queen, W. L.; Hudson, M. R.; Yaghi, O. M. Water Adsorption in Porous Metal–Organic Frameworks and Related Materials. J. Am. Chem. Soc. 2014, 136, 4369–4381.

(15) Fröhlich, D.; Pantatossaki, E.; Kolokathis, P. D.; Markey, K.; Reinsch, H.; Baumgartner, M.; van der Veen, M. A.; De Vos, D. E.; Stock, N.; Papadopoulos, G. K.; Henninger, S. K.; Janiak, C. Water Adsorption Behaviour of CAU-10-H: A Thorough Investigation of Its Structure–Property Relationships. J. Mater. Chem. A 2016, 4, 11859–11869.

(16) Cadiau, A.; Lee, J. S.; Damasceno Borges, D.; Fabry, P.; Devic, T.; Wharmby, M. T.; Martinau, C.; Foucher, D.; Taulelle, F.; Jun, C.-H.; Hwang, Y. K.; Stock, N.; De Lange, M. F.; Kapteijn, F.; Gascon, J.; Maurin, G.; Chang, J.-S.; Serre, C. Design of Hydrophilic Metal Organic Framework Water Adsorbents for Heat Reallocation. Adv. Mater. 2015, 27, 4775–4780.

(17) Hanikel, N.; Pei, X.; Chheda, S.; Luu, H.; Jeong, W.; Sauer, J.; Gagliardi, L.; Yaghi Omar, M. Evolution of Water Structures in Metal-Organic Framework Water Adsorbents for Heat Reallocation. J. Mater. Chem. A 2015, 3, 5270–5277.

(18) Hanikel, N.; Prévet, M. S.; Fatheieh, F.; Kapustin, E. A.; Luu, H.; Wang, H.; Diercks, N. J.; Glover, T. G.; Yaghi, O. M. Rapid Cycling and Exceptional Yield in a Metal-Organic Framework Water Harvester. ACS Cent. Sci. 2019, 5, 1699–1706.

(19) Abtab, S. M. T.; Alezi, D.; Bhatt, P. M.; Shikrenko, A.; Belmabkhout, Y.; Aaggarwal, H.; Wesselkifi, J.; Alsdun, N.; Samin, U.;
Hedhili, M. N.; Eddaoudi, M. Reticular Chemistry in Action: A Hydrolytically Stable MOF Capturing Twice Its Weight in Adsorbed Water. *Chem. 2018*, *4*, 94–105.

(20) Rieth, A. J.; Yang, S.; Wang, E. N.; Dincă, M. Record Atmospheric Fresh Water Capture and Heat Transfer with a Material Operating at the Water Uptake Reversibility Limit. *ACS Cent. Sci. 2017*, *3*, 668–672.

(21) Jeremias, F.; Fröhlich, D.; Janiak, C.; Henninger, S. K. Advancement of Sorption-Based Heat Transformation by a Metal Coating of Highly-Stable, Hydrophilic Aluminium Fumarate Mof. *RSC Adv. 2014*, *4*, 24073–24082.

(22) Liu, X.; Wang, X.; Kapteijn, F. Water and Metal−Organic Frameworks: From Interaction toward Utilization. *Chem. Rev. 2020*, *120*, 8303–8377.

(23) Schlüsener, C.; Xhinovci, M.; Ernst, S.-J.; Schmitz, A.; Tannert, N.; Janiak, C. Solid-Solution Mixed-Linker Synthesis of Isoreticular Al-Based MOFs for an Easy Hydrophilicity Tuning in Water-Sorption Heat Transformations. *Chem. Mater. 2019*, *31*, 4051–4062.

(24) Rieth, A. J.; Yang, S.; Wang, E. N.; Dincă, M. Record Atmospheric Fresh Water Capture and Heat Transfer with a Material Operating at the Water Uptake Reversibility Limit. *ACS Cent. Sci. 2017*, *3*, 668–672.

(25) Krause, S.; Hosono, N.; Kitagawa, S. Chemistry of Soft Porous Crystals: Structural Dynamics and Gas Adsorption Properties. *Angew. Chem., Int. Ed. 2020*, *59*, 15325–15341.

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

(27) Elsaidi, S. K.; Mohamed, M. H.; Banerjee, D.; Thallapally, P. K. Flexibility in Metal−Organic Frameworks: A Fundamental Understanding. *Coord. Chem. Rev. 2018*, *358*, 125–152.

(28) Morris, R. E.; Brammer, L. Coordination Change, Lability and Hemilability in Metal-Organic Frameworks. *Chem. Soc. Rev. 2017*, *46*, 5444–5462.

(29) Férey, G.; Serre, C. Large Breathing Effects in Three-Dimensional Porous Hybrid Matter: Facts, Analyses, Rules and Consequences. *Chem. Soc. Rev. 2009*, *38*, 1380–1399.

(30) Horike, S.; Shimomura, S.; Kitagawa, S. Soft Porous Crystals. *Nat. Chem. 2009*, *1*, 695–704.

(31) 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. t.; Ma, S.; Space, B.; Barbour, L. J.; Kitagawa, S.; Zaworotko, M. J. Reversible Switching between Highly Porous and Nonporous Phases of an Interepenetrated Diamondoid Coordination Network That Exhibits Gate-Opening at Methane Storage Pressures. *Angew. Chem., Int. Ed. 2018*, *57*, 5684–5689.

(32) Mason, J. A.; Oktawiec, J.; Taylor, M. K.; Hudson, M. R.; Rodriguez, J.; Bachman, J. E.; Gonzalez, M. I.; Cervellino, A.; Giagliardi, 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*, 357–361.

(33) Bourrell, S.; Moulin, B.; Rivara, A.; Maurin, G.; Devautour-Vinot, S.; Serre, C.; Devic, T.; Horcajada, P.; Vimont, A.; Clet, G.; Daturi, M.; Lavalley, J.-C.; Loera-Serna, S.; Denoyel, R.; Llewellyn, P. L.; Férey, G. Explanation of the Adsorption of Polar Vapors in the Highly Flexible Metal Organic Framework MIL-53(Cr). *J. Am. Chem. Soc. 2010*, *132*, 9488–9498.

(34) Krause, S.; Bon, V.; Du, H.; Dunin-Borkowski, R. E.; Stoek, U.; Senkovska, I.; Kaskel, S. The Impact of Crystal Size and Temperature on the Adsorption-Induced Flexibility of the Zr-Based Metal−Organic Framework DUT-98. *Beilstein J. Nanotechnol. 2019*, *10*, 1737–1744.

(35) Hiraide, S.; Sakanaoka, Y.; Kajiro, H.; Kawaguchi, S.; Miyahara, M. T.; Tanaka, H. High-Throughput Gas Separation by Flexible Metal−Organic Frameworks with Fast Gating and Thermal Management Capabilities. *Nat. Commun. 2020*, *11*, No. 3867.

(36) Fröhlich, D.; Hügenell, P.; Reinsch, H. Investigating Water Vapour Sorption Kinetics of Aluminium MOFs by Powder X-Ray Diffraction. *CrystEngComm 2019*, *21*, 2551–2558.