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Flexible Metal–Organic Frameworks: Recent Advances and Potential Applications

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Flexible metal–organic frameworks (MOFs) receive much attention owing to their attractive properties that originate from their flexibility and dynamic behavior, and show great potential applications in many fields. Here, recent progress in the discovery, understanding, and property investigations of flexible MOFs are reviewed, and the examples of their potential applications in storage and separation, sensing, and guest capture and release are presented to highlight the developing trends in flexible MOFs.

1. Introduction

Metal–organic frameworks (MOFs) (also known as porous coordination polymers (PCPs)) have become a hot topic in both chemistry and material community in the last decade.[1–4] The blooming development of MOFs should be attributed to their inorganic–organic hybrid nature, which can deliver the unique structures and properties desired by chemists.[5,6] From the foundation of this concept in 1990s, MOFs have been considered as a new kind of porous material, and are frequently compared with other inorganic porous materials to emphasize their advantages. Among the various particular characteristics of MOFs, the flexibility of the framework and the thus-initiated dynamic behavior have attracted much attention. Compared with the non-flexible scaffold of inorganic porous materials, such as zeolites, MOFs can be structurally flexible owing to many factors, such as the nature of the organic ligands, the moderate metal–ligand interactions, the versatile configuration of metal ions/clusters, and the movement of interpenetrated subnets.[7] Generally, the term "flexible MOFs" has been used to describe MOFs with structural transformability of

considerable amplitude upon stimuli, considering the pioneering concept of "soft porous crystals (SPC)" proposed by Kitagawa and co-workers.[8] Then, "dynamic behavior" has been used to describe the transformation process between the multistable states of flexible MOFs. Based on the different structures of flexible MOFs, multitudinous dynamic behaviors, for example, the expansion/shrinkage of the framework,[9–11] the opening/closing of pores,[12,13] or the reversible change of the physicochemical properties,[14,15] have been realized. More importantly, these fascinating characteristics of flexible MOFs have great potential in storage, separation, sensing, and many other applications, which makes them more interesting in the classes of MOFs.[16]

However, it should be noted that, although thousands of MOFs have been reported, the ones with a flexible nature and dynamic properties are quite limited. Also, though strategies and methods for the targeted construction and investigation of the properties of MOFs have been well developed during the wide exploration, the rational construction of flexible MOFs is still a great challenge. This should be due to the fact that the successful introduction of flexible factors into a MOF and the realization of the anticipated dynamic properties are somewhat random. Thanks to the unremitting investigation of chemists and fast-developed characterization methods, more progress has been made in the understanding of the flexibility and dynamic behaviors of MOFs, as well as in the exploration of their potential applications as materials; furthermore, methods for the tuning of the flexibility have also been reported in recent years. The remarkable progress in this topic has been reviewed during the last five years,[16–18] and a comprehensive review was given by Fisher and co-workers recently.[19] Besides the well-summarized achievements and related mechanisms in the construction of flexible MOFs, discussions on their applications were also carried out briefly therein for the purpose of enlightening further research.

Here, the progress in the discovery and understanding of flexible MOFs is summarized, followed by the introduction of the most-recent advances of flexible MOFs. We will focus on flexible MOFs in terms of their potential applications in different fields. The examples will be classified and presented depending on the potential applications of the MOFs to outline the critical features that are desired for the targeted performances and the advantages of flexible MOFs. Finally, a summary and outlook of the future development of this field is given.

2. Discovery and Understanding of Flexible MOFs

The rational construction of flexible MOFs is relatively more difficult compared with that of non-flexible ones due to the

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uncertainty of the self-assembly process and the unmanageable nature of the flexible factors. On the other hand, appropriate characterization methods are also necessary for the determination of the flexibility of a MOF. Though numerous MOFs are potentially flexible, only a small number have been investigated and reported to have flexible properties, and only several readily available systems have been systematically investigated, such as the MIL (Materiaux Institute Lavoisier) series.[20] In spite of the limited examples available, researchers have classified the reported results in order to clarify the mechanisms of the flexibility. Also, new technologies and theories have been employed and developed to satisfy the requirements of investigation. In the following sections, we will review the understanding and tuning of the flexibility of MOFs based on recently reported examples. Then, recent advances in the characterization of flexibility will be introduced.

2.1. Understanding and Tuning of the Flexibility in MOFs

Though flexible MOFs show distinct structures depending on the different metal centers/clusters and ligands involved, their flexibility and dynamical behaviors can be simplified in several ways for ease of understanding, since general mechanisms can be found behind the various apparent phenomena. In one of the comprehensive reviews presented by Férey and Cerre,[16] the breathing effect, which is applicable to a considerable proportion of flexible MOFs, was concluded based on the well-studied examples of non-interpenetrated solids to determine that the inorganic part is often associated with a rigid behavior and the flexibility of MOFs is mainly determined by the organic linkers. Structurally, free space to accommodate the modified steric hindrance of the flexible part and non-rigid areas were pointed out to be necessary factors to generate breathing of a framework. In the cases of interpenetrated frameworks, interactions between the individual networks as well as host–guest interactions should also be considered, which could determine the displacement of subnets. Relative studies have been reviewed and discussed by Kitagawa and co-workers.[17] More generally, Jenkins and co-workers categorized flexible MOFs according to the dimensionality of rigid motifs.[21] Based on sufficient examples with confirmed structures under multiple states, the flexibility of MOFs has mainly been attributed to a conformation change of the flexible organic linkers. More importantly, in spite of the relative limited latitude of deformation, the twisting, bending, and tilting of rigid linkers could also contribute to the flexibility of the framework, when combined with the adaption of inorganic parts. More recently, flexibility originating from the changed coordination environment of metal ions,[22,23] and the deformed configuration/connectivity of secondary building units (SBUs) containing metal ions[24] in response to the removal/binding of coordinative molecules/ions have also been reported, indicating the vast potential and important role of the inorganic components.

Besides the necessary structure foundation of MOFs to realize flexibility, chemical or physical stimuli have been required to trigger the dynamic behaviors. In the early stage of research, most dynamic behaviors were related to the presence/removal of guest molecules.[25] The inherent interactions between the guest and the host framework have been illuminated through extensive studies of MIL-53, MIL-88, and paddle-wheel-based MOFs, which has been utilized for the separation and controllable-release applications of the materials.[16] Recently, photoresponsive flexible MOFs were reported, which could be utilized for sensing and targeted encapsulation applications.[26–28] On the other hand, the thermal responsive rotation of aromatic rings or the movement of dangling side chains of the organic ligands, which can affect the conformation of the linker and the resulting framework dynamic behavior,[20,29–32] have promoted the investigation of thermosensitive flexible MOFs. Some newly discovered examples of flexible MOFs based on above mentioned mechanisms have been summarized and reviewed in the articles of Fischer and co-workers[19] and Coudert.[33]

In addition to the experimental research on flexible MOFs, theoretical calculations and molecular modeling methods have been developed as powerful tools for better understanding or even predication of the behavior of flexible MOFs.[34] For the identification and predication of the flexibility of MOFs, Coudert and co-workers elucidated the relationship between the anisotropic elastic properties of MOFs and their flexibility.[35,36] By calculating and comparing the single-crystal elastic constants (Young's modulus, linear compressibility, shear modulus, and Poisson's ratio) of MOFs with distinct flexibilities confirmed by experimental results using ab initio quantum mechanical calculations in the density functional theory approach with localized basis sets, it was found that the high anisotropy of Young's modulus and shear modulus indicates the structure flexibility, and the anticipated flexible behavior under mechanical stimuli from the calculation results fit the experimental results well. Recently, the flexibility of CAU-13 and NOTT-300, two MOFs revealing a similar structure to flexible MIL-53(Al) but no obvious flexible behavior, were investigated using this method.[37] The conditions required for the triggering of mechanically induced breathing behaviors were predicted, which could guide the further experimental verifications. Furthermore, the possibility of structure transformation under a certain temperature, along with the equilibrium vapor pressures required as a trigger to rationalize the structure transformation of flexible MOFs triggered by adsorption/desorption of guest molecules or varied temperature, have been estimated by a thermodynamic analysis of equilibrium states,[38,39] This method could also help in the rationalization of unique flexible behaviors, like xenon adsorption in MIL-53,[40,41] which seems abnormal based on traditional considerations. On the other hand, Neimark, Coudert et al. proposed a stress-based model, in which the adsorption-induced stress was considered as the trigger of the structure transformation.[42] Combined with the analysis of the elastic constants of flexible MOFs, this model has been utilized to shed light on the mechanism and dynamics of structural transformations of MIL-53 on the unit cell or even crystal level.[43,44] Then, the possibility of phase coexistence in the process of structure transformation was predicated, which could help in the understanding and utilization of the shape change of flexible MOF crystals. For a better understanding of the performances of the MIL-53 family on the CO_2 separation and capture from a CO_2/CH_4 mixture, the evolution of structural transitions upon the adsorption of gas mixtures has
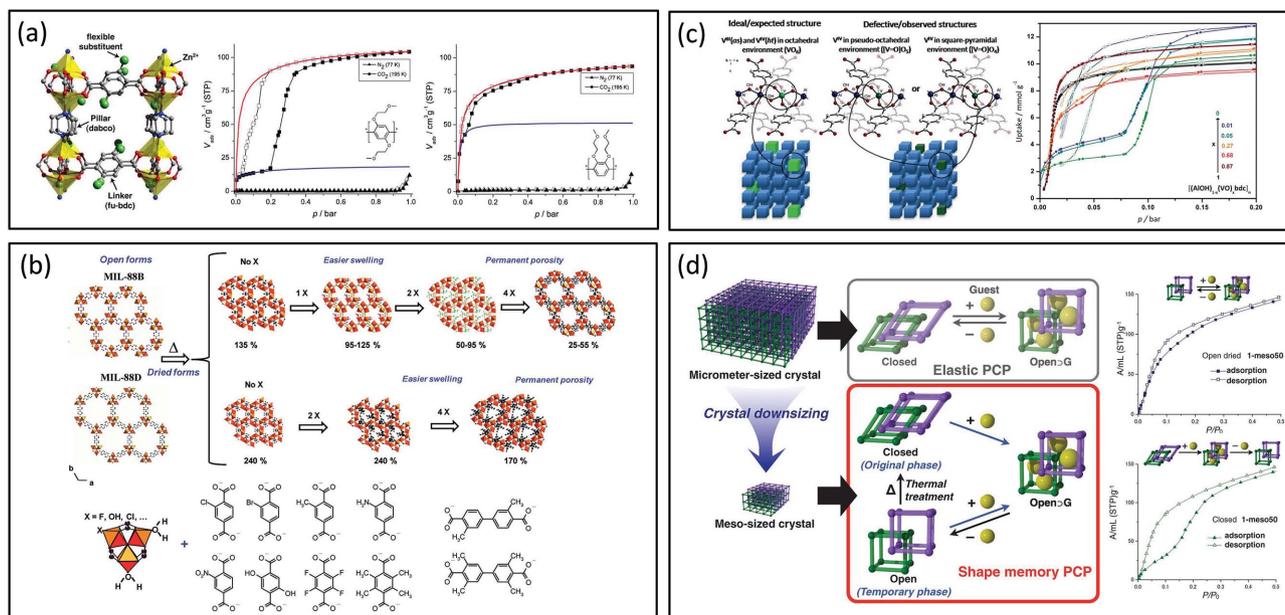
Figure 1. Examples of tuning of the flexibility of MOFs by different methods: a) introducing flexible side chains. Reproduced with permission.[29] Copyright 2012, American Chemical Society; b) modulation the host–guest interactions via linker functionalization. Reproduced with permission.[20] Copyright 2011, American Chemical Society; c) a mixed metal method. Reproduced with permission.[55] Copyright 2013, Wiley-VCH; d) modulation of the size of the crystal. Reproduced with permission.[56] Copyright 2013, American Association for the Advancement of Science.

been investigated using a method combining ideal adsorbed solution theory (IAST) and an osmotic ensemble framework, which is the so-called osmotic framework adsorbed solution theory (OFAST).[45–47] With this method, the flexible behavior of MIL-53 in full pressure, temperature, and component space can be predicted, which might be utilized for the optimization of the conditions for CO_2 separation. Besides the flexible behavior of the framework structure, the diffusion and arrangement of guest molecules in the pores/channels of flexible MOFs is another hot topic for theoretical investigations, since guest related applications, for example, drug delivery and guest capture/release, deeply rely on the understanding of these phenomena. A series of work by Maurin and co-workers focused on the behaviors of different guests, such as H_2S,[48] H_2O,[49] xylene isomers,[50] CO_2/CH_4 mixtures,[51] and light hydrocarbons,[52] in the MIL family of MOFs. Combining the experimental results and molecular dynamics (MD) simulations, the state of guest molecules in the channels of MOFs could be revealed, which helped in determining the critical host–guest interaction factors and the conditions for desired applications. It should be noted that most of the theoretical investigations mentioned above were performed with MIL-family MOFs as models, owing to their widely investigated properties suitable for the validation of methods/models. Though the methods/models could be utilized to explain or predict the flexible behaviors of some MIL MOFs, there are still many cases that could not be applied, like the breaking/recovery of bonds and the transformation of SBUs. A comprehensive theory that could provide predicting and full understanding of the flexibility of MOFs is still absent.

In contrast to the unpredictable direct construction of flexible MOFs, the modification and tuning of the flexible behavior is more reliable for targeted construction, based on the identification of the roles of different components as contributions

of systematic investigations. From the discovered examples of flexible MOFs mentioned above, it could be determined that the organic ligand could be a critical factor that determines the behaviors of the MOFs in most mechanisms. It should be noted that although ligands with fully flexible backbones (for example, alkyl chains) seem to benefit the realization of flexibility owing to their versatile configurations,[53] reported examples were quite rare. This might be caused by the self-assembly nature of the construction process of MOFs, which is mainly determined by thermodynamics. In this regard, a fully flexible ligand should be present in the configuration with a relatively low energy, and it is difficult to transform to another stable state to exhibit flexibility. However, the attachment of flexible side chains on the rigid linkers has been proved to be a simple method to generate and tune the flexibility of MOFs (**Figure 1**a) since the presence of the flexible behavior of the side chains in the designable pore space defined by the rigid linkers is more promising.[29] Besides that, the modulation of host–guest interactions via functionalization of organic linkers of inherently flexible MOFs is also an efficient method for the tuning of the dynamic behavior (Figure 1b), which could affect directly the primary origin of flexibility.[20] As another important component of MOFs, the nature of metal centers is also crucial. It has been reported that distinct flexible behaviors could he achieved in isostructural MOFs with different metal centers. Then, modulation of the dynamic behavior could be realized through a mixed-metal method (Figure 1c).[54,55] More recently, Kitagawa and co-workers reported a unique example of flexible MOFs whose dynamic behavior is affected by the size of the crystal, which is the so called "shape-memory effect" (Figure 1d).[56] By downsizing the crystal of the flexible MOF, the "open" state of the MOF could be maintained, and the gate-opening behavior caused by the phase change between "closed"

and "open" states diminished. This discovery further extended the possible methods for the tuning of flexibility. The discovery of the tuning of flexibility in the MOFs mentioned above indicates the diversity of methods for function-targeted modulation of flexible MOFs.

2.2. Characterization of Flexibility in MOFs

For most flexible MOFs, the discovery of the flexibility is originated from the observation of unique physicochemical properties distinct from that of the non-flexible ones, for example, the gate-opening or multistep features of gas-sorption isotherms or the change of color/shape/emission under certain conditions. However, though the significantly changed properties of the material under stimuli indicate the possibility, proper technologies are required for the investigation and identification of the structure flexibility in MOFs due to their unique dynamic behaviors.

Among the various technologies available for the structure determination of MOFs, single-crystal X-ray diffraction (SCXRD) has been the most important and straightforward one since the structure could be determined at the atomic level, taking the advantages of the crystalline nature of these materials. Specific to the flexible MOFs, the structure determination of the targeted state of flexible MOFs by this method is feasible, but with the additional requirement of the sample and the testing conditions. The successful capture of the targeted state of the MOFs requires the retention of crystallinity, long-range order, as well as a relatively stable state and dimension of the crystal sample. On the other hand, if the targeted state could not be retained under common conditions, the trigger factor of the dynamic behaviors should be introduced in an appropriate way, which is a so-called in situ measurement. Recent advantages of the applications of SCXRD on structural transformations of porous coordination polymers, including examples of flexible MOFs, have been reviewed by Zhang et al.[57]

For microcrystalline samples, the investigations are mainly performed by way of powder X-ray diffraction (PXRD). The obvious structure change of MOFs accompanying the flexible behavior can be identified by the position and intensity change of the reflection peaks. Though the determination of the precise structure of a sample by PXRD is much more difficult compared with that by the SCXRD method, the results are intuitive for comparison purposes, and time-resolved measurements[58] are simpler with this method. In recent years, the in situ neutron diffraction method has also been developed for the determination of adsorption sites through the location of adsorbates, which is beyond the limit of X-ray diffraction.[59,60]

Except for the methods mentioned above, which are suitable for crystalline samples only, spectroscopy methods such as solid-state nuclear magnetic resonance (SSNMR),[61] X-ray absorption spectroscopy (X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS)),[62,63] Raman spectroscopy,[62] IR spectroscopy,[63] and dielectric relaxation spectroscopy[64] have been shown to be powerful technologies for structure determination and mechanism investigation of flexible MOFs. Recently, Mazaj et al. reported an example of comprehensive applications of spectroscopy methods for the investigation of the dynamic behavior of a Ca MOF.[63] To confirm the occurrence of a structure change upon the removal of solvent molecules of Ca(BDC) (DMF)(H$_2$O) (Ca-BDC) (BDC = 1,4-benzenedicarboxylate anion and DMF = N,N-dimethylformamide) with topology of MIL-53 evidenced by the varied PXRD patterns, elemental analyses and inductive-coupled plasma atomic emission spectrometry (ICP-AES) analyses were performed on the samples to confirm the components of the two stable phases. Then, the FTIR spectra, ^{1}H–^{13}C cross-polarization–magic-angle spinning (CP–MAS), ^{1}H combined rotation and multiple pulse spectroscopy (CRAMPS), and 2D ^{1}H–^{1}H homonuclear NMR spectroscopy were performed to investigate the coordination states of the BDC ligands and the solvent molecules, and the coordination environment of Ca^{2+} in the two samples was confirmed by X-ray absorption spectroscopy. The complementary spectroscopic investigations of the samples provided a good insight of the change of structure upon thermal treatment, and a mechanism for the dynamic behaviors was successfully clarified. These results indicate the importance of spectroscopy methods in the research of flexible MOFs. On the other hand, it also reflects the fact that the investigation and confirmation of the structures and properties of a flexible MOF could be an exhausting and time-consuming process, owing to the complexity of the mechanism and apparent behaviors, and the conclusion should be drawn very carefully.

3. Potential Applications of Flexible MOFs

As mentioned in the introduction, flexible MOFs with unique dynamic behaviors could show potential applications in many fields. Although the practical applications of flexible MOFs in industry still have a long way to go, they are still attractive and promising. In the following sections, selected examples will be introduced to highlight the most-recent advantages of flexible MOFs with potential applications in storage and separation, sensing, and guest capture and release. It should be noted that only examples in which the properties are directly related to the flexible nature of the MOF are included.

3.1. Storage and Separation

According to the porous nature of MOFs that is accessible to guest molecules, the storage and separation properties have been the most-interesting applications of these materials.[3,4,65] Compared with non-flexible MOFs, the guest-responsive dynamic behavior of flexible MOFs caused by host–guest interactions could be a unique advantage for storage and separation. In this field, two conditions should be distinguished: i) the storage/separation performance is enhanced by the flexible nature of the MOFs in response to the targeted molecules, and ii) the performances could be modulated by other factors that could affect the dynamic behavior and the correlated storage/ separation performances of the host framework. In the first situation, enhanced interactions between the targeted molecules and the host framework are desired, while a tuning of the performance of the materials could be readily achieved in the second situation.
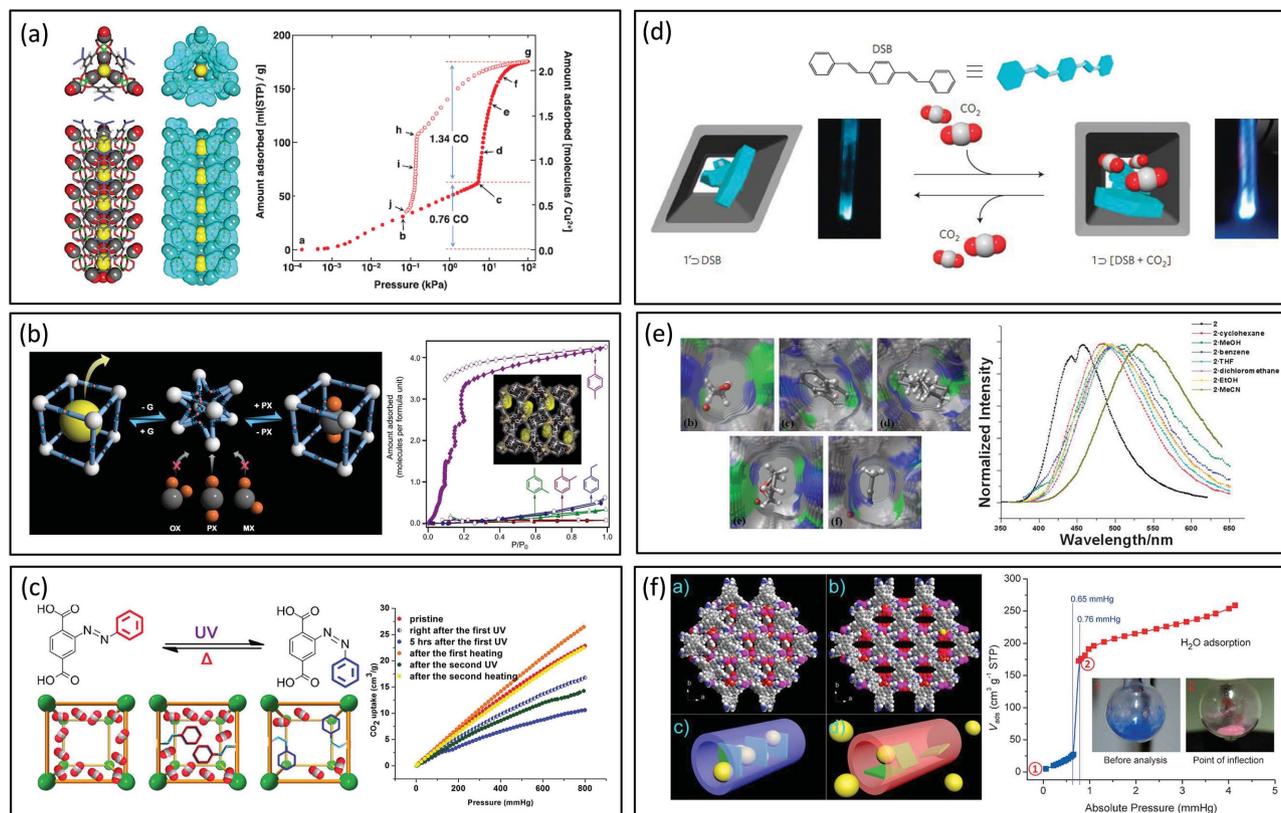
Figure 2. Examples of the storage/separation and sensing applications of flexible MOFs: a) the selective adsorption of CO in [Cu(aip)(H$_2$O)]. Reproduced with permission.[66] Copyright 2014, American Association for the Advancement of Science; b) the selective adsorption of p-xylene form isomers in [Zn$_4$O(L)$_3$]$_n$. Reproduced with permission.[67] Copyright 2014, Nature Publishing Group; c) the modulation of CO$_2$ adsorption in PCN-123 via the photoresponsive behavior of the linker. Reproduced with permission.[26] Copyright 2012, American Chemical Society; d) the sensing of CO$_2$ via monitoring of the configuration-related fluorescence emission of DSB in a flexible MOF. Reproduced with permission.[73] Copyright 2011, Nature Publishing Group; e) the guest-response structure change and fluorescent sensing of volatile-organic-solvents properties of [(CuCN)$_3$L]$_n$. Reproduced with permission.[74] Copyright 2013, Royal Society of Chemistry; f) the change of structure and color of [Co$_{1.5}$(tipb)(SO$_4$)(pta)$_{0.5}$] in the presence of H$_2$O. Reproduced with permission.[22] Copyright 2013, Wiley-VCH.

As an example of the first situation, Matsuda, Kitagawa and co-workers recently reported a self-accelerating CO sorption of a flexible MOF [Cu(aip)(H$_2$O)](solvent)$_n$ (aip = 5-azidoisophthalate) (**Figure 2**a).[66] The original complex (PCP 1) reveals kagomé-type layers composed of binuclear Cu paddlewheel units bridged with aip ligands, which could undergo a structure change upon the removal of axial H$_2$O molecules to result in a dry state (PCP 2) with reduced porosity and narrowed channels. The easy recovery of PCP 1 from the dry state under humidity indicates that the structure transformation is reversible. More importantly, a selective adsorption of CO at 120 K is observed with PCP 2 compared with that of N$_2$, in spite of the similarity of the structures and physicochemical properties of these two gases. A detailed structure investigation using Rietveld analysis with synchrotron XRPD data in a CO atmosphere indicates that a Cu^{2+}–CO bond is formed when the accessible channels in the PCP 2 are filled with CO, and a global structure transformation is induced to expand the squeezed channels to provide extra space for additional CO molecules to be adsorbed. Besides the remarkable adsorption performances in a pure CO atmosphere, PCP 2 also reveals high adsorption selectivity of CO even in CO mixtures with N$_2$. The high performance of this material makes it applicable for the storage of CO, as well as

the separation of CO and N$_2$. This example presents well the unique variable pore structure/surface characters feature of flexible MOFs, which could benefit targeted storage and separation applications.

Based on a similar guest-selective mechanism, the successful separation of p-xylene over its congener C$_8$-alkyl aromatic isomers using a flexible MOF has been reported by Ghosh and co-workers (Figure 2b).[67] The reported porous MOF, {[Zn$_4$O(L)$_3$(DMF)$_2$]·xG}$_n$ (1⊃G) (G represents guest solvent molecules), constructed based on dicarboxylate ligands with a flexible ether backbone, could be transformed to a squeezed framework [Zn$_4$O(L)$_3$]$_n$ (**1**) by removing the coordinated and guest solvent molecules. A careful examination on the structure of **1** shows that the pore diameter in the framework (about 0.6 nm) is close to the diameter of xylenes, then systematic investigations were performed aimed at the separation of xylenes with comparable sizes. Exciting results were obtained in that p-xylene could be selectively adsorbed in the framework of **1** compared with its o-, m-isomers and ethylbenzene, which have similar dimensions, and framework expansion back was observed in the case of p-xylene adsorption. The p-xylene-targeted gate opening is mainly attributed to the delicate differences between the dimensions of the tested isomeric guests

and the restricted flexibility of the framework, which would not let the bigger isomers enter the porous. These results indicate the potential application of flexible MOFs in the separation of similar organic molecules.

Examples of the second situation have been reported for flexible MOFs with photoresponsive dynamic behaviors. Zhou and co-workers reported a photoactive flexible MOF with tunable CO_2 adsorption performance (Figure 2c).[26] Utilizing azobenzene-functionalized terephthalic acid as a linker, PCN-123 with MOF-5-like rigid framework and photoactive side chains was obtained. Through the control of the *trans* and *cis* configuration of the azobenzene motif upon photochemical or thermal treatment, the pore structure could be regulated, which affects the CO_2 uptake of the resulting material significantly. Shortly after that, Uemura, Kitagawa and co-workers reported another example of a photoactive flexible MOF.[27] Different from that reported by Zhou, a MOF with guest-determined flexible framework was selected as the host, and azobenzene was introduced as a guest to modulate the pore structure upon UV irradiation or heating, owing to its different configurations under different conditions, and a dramatic difference between the gas-sorption behaviors could be observed with the same sample under different states. Similar tuning of the CO_2 adsorption properties has also been reported by Pu, Guo and co-workers in a MOF based on a photoactive diarylethene linker, in which local framework movement due to the configuration change of the ligand under irradiation was proposed for the dynamic CO_2 release behavior.[28] These examples indicate that the tuning of sorption behaviors could be achieved more readily in targeted designed flexible MOFs compared with that in the non-flexible ones.

From the first two examples mentioned above, it is obvious that the selective guest-responsive dynamic behavior could be the main advantage of flexible MOFs for storage and separation applications. Though the mechanisms of the remarkable performances of flexible MOFs are accessible based on detailed investigations, and the design of performance-targeted functional motifs can be improved, it is still difficult to realize a straightforward "design-construction" process. This should be attributed to the indeterminate assembly of targeted flexible MOFs, which is even more complex with the disturbance of the interactions introduced by the predesigned functional motifs. However, utilizing flexible MOFs as fillers of mixed matrix membranes (MMMs) for CO_2 capture and CO_2/CH_4 separation, taking their advantages of variable pore structures, has been proved to be a successful example of targeted application of these materials. Though MOFs have been widely used as fillers of MMMs,[68,69] the introduction of flexible MOFs was pioneered by Gascon and co-workers.[70] In this first study, micrometer-sized NH_2-MIL-53(Al) particles were used to fabricate nanocomposite membranes with PSF Udel P-3500, and the MMMs obtained revealed a boosted CO_2/CH_4 selectivity with increased pressure, which is unique compared with the behaviors of inorganic membranes and desired for high-pressure applications. This remarkable character is attributed to the narrow pore (np) to large pore (lp) transition of NH_2-MIL-53(Al) particles at 5 bar CO_2, which fill the gaps between the polymer chains due to high CO_2 loading and substantially contribute to the total flux through the membrane to benefit the selectivity.

More recently, a detailed investigation of the structure–performance relationships in CO_2/CH_4 separation over NH_2-MIL-53(Al)@ polyimide MMMs was performed by Rodenas, Gascon and co-workers.[71] The results show that the framework configuration of the flexible MOFs in the MMMs and the performance of the MMMs could be adjusted by controlling the membrane casting conditions: a higher percentage of np configurations could be achieved through a faster solvent-removal process to result in membranes with increased CO_2 permeability and separation factor. On the other hand, the "frozen" lp structure resulting from the penetrating polymer chain in the pores or the impeded framework flexibility by embedding could be detrimental for the MMM performance.[71] Based on these discoveries, MMMs with optimized CO_2/CH_4 separation performances can be rationally designed and fabricated.

3.2. Sensing

Compared with the extensively investigated applications of flexible MOFs in storage and separation, their investigations as sensors are relatively limited. Though the stimuli-responsive properties of most flexible MOFs meet the fundamental requirements for sensor applications, noteworthy changes of physicochemical properties upon the dynamic process are also necessary as signals for detection.

One of the ideal signals for detection is the fluorescence emission of the material, since changes of both the intensity and wavelength can be utilized for determination of the sensing performance. Several promising examples have been reported by Kitagawa and co-workers.[72,73] A flexible MOF, $[Zn_2(bdc)_2(dpNDI)]_n$ (bdc = 1,4-benzenedicarboxylate anion and dpNDI = N,N′-di(4-pyridyl)-1,4,5,8-naphthalenediimide), which was composed of a two-fold interpenetrated framework structure, reveals framework displacement and bending of the linker upon the accommodation of guest molecules. As a result, strong charge transfer induced by the host–guest interactions occurs, and the enhanced fluorescence emission of the MOF incorporating the guest could be utilized for the detection. More importantly, the emission wavelength shows obvious guest-dependent behavior, which could be used for distinguishing targeted volatile organic compounds (VOCs).[72] By introducing fluorescent distyrylbenzene (DSB) molecules into a flexible MOF $[Zn_2(terephthalate)_2(triethylenediamine)]_n$ as indicator, a sensor that could respond to CO_2 and C_2H_2 was obtained (Figure 2d).[73] The sensing of gas molecules was achieved based on the enhanced interactions between the gas molecules and the porous framework, which allows the selective entrance of targeted guest molecules. The changed pore structure upon gas sorption could regulate the configuration and the configuration-related emission property of the DSB indicator. Then, the presence of a targeted molecule could be detected by monitoring the fluorescence. More recently, the sensing of volatile organic solvents by a flexible MOF was reported by Li and co-workers (Figure 2e).[74] The two interpenetrated frameworks of $[(CuCN)_3L]_n$ (L = 2,6-bis((3,5-dimethyl-1*H*-pyrazol-4-yl)methyl) pyridine) show dynamic features toward guest molecules, and the guest-dependent luminescent variation makes it available for qualitative and quantitative detection applications.

The dramatic change of color is another property desired for sensing applications, which could allow for naked-eye identification without the requirement of additional equipment. We have reported an example of the sensing of coordinative molecules with a Co-based MOF (Figure 2f).[22] The Co MOF obtained under anhydrous reaction conditions, $[Co_{1.5}(tipb)(SO_4)(pta)_{0.5}]\cdot(DMF)_{1.75}$ (BP⊃DMF) (tibp = 1,3,5-tris(p-imidazolyl-phenyl)benzene, pta = terephthalic anions), could undergo a single-crystal to single-crystal (SC–SC) structure transformation under the presence of H_2O, to result in $[Co_{1.5}(tipb)(SO_4)(H_2O)_{3.6}]\cdot(pta)_{0.5}(solvent)_n$ (RP-H_2O). With the displacement of pta with H_2O, the (3,8)-connected self-penetrating topology network of BP transformed into a twofold interpenetrating (3,6)-connected **sit** net of RP. More importantly, a color change from blue to red could be observed accompanying the structure transformation, according to the changed coordination geometry of the Co^{2+} ions (tetrahedral to octahedral). The transformation is reversible and rapid under common conditions. Also, the water vapor pressure required for the triggering of the transformation falls in a narrow range (0.65–0.76 mm Hg at 273 K), which could benefit quantitative sensing and determination applications.

The expansion or shrinkage of crystals under a stimulus, though relatively difficult to be detected, could also be utilized as an output signal for sensing, especially in device forms in which minute but particular responses are desired.[75] For example, Zhang and co-workers reported a guest-triggered crystal-deformation behavior based on a flexible ultra-microporous framework.[76] Due to the confined pore space and the rotational flexibility of the ligand in guest-free $[Mn(pba)_2]$ (MCF-34, pba = 3-(pyridine-4-yl)benzoic carboxylate), it shows large and constant positive thermal expansion (PTE) and negative thermal expansion (NTE) coefficients in a wide temperature range (about 550 K). Also, no adsorption of N_2 or O_2 was observed even under low temperature. The established thermal-expansion character of the material makes it a good candidate as a temperature sensor through the detection of the shape change of the material. On the other hand, the thermal-expansion behavior of the guest-included MCF-34 was found to be guest dependent, which could be utilized for the modulation of the thermal-expansion properties of this material.

3.3. Guest Capture and Release

The controllable capture and release of guest molecules by flexible MOFs under an appropriate stimulus, which can be applied directly in drug delivery and the elimination of hazardous substances or used as a trigger for sensing, catalysis, and other applications, is another fascinating property worth investigating. This property could be achieved by the modulation of host–guest interactions or the state (open/closed) of the pore structure through an appropriate stimulus. Besides the widely investigated drug-delivery properties of flexible MOFs,[77,78] examples with diversiform guest molecules have been reported in recent years.

Cramb, Shimizu and co-workers reported the controllable mechanical capture and release of gas molecules in flexible barium 1,3,5-benzenetrisulphonate (**Figure 3**a).[79] It was observed that this compound could undergo SC–SC transformation upon the removal of solvent water molecules from the pores under heating, and the desolvated phase revealed a contracted framework, in which gas molecules of the external atmosphere could be trapped due to the significantly reduced pore aperture dimension. The release of trapped gas molecules could be realized readily in the presence of water, which could rehydrate and restore the framework structure. Though the limited pore volume of the material restricts the guest molecules available to be trapped, this investigation is still valuable and revelatory for further research since it proves that straightforward mechanical capture/release of small guest molecules can be achieved by utilizing the flexibility of MOFs. A similar guest capture and release function was also observed in the reversible transformation between BP and RP that we mentioned before (Figure 2f).[22] The dissociation/recovery of pta ligands in the channels of the compound defined the open and closed states of the channels, which determined the encapsulation/release of guest molecules. Taking advantage of the various conditions available for the structure transformation (in solvents and in air) and the trigger stimuli for encapsulation (removal of coordinative molecules by heating, vacuuming, or solvent soaking), the guests available to be loaded are widely extended, which promises various potential applications of this material.

On the other hand, Dalgarno, Thallapally and co-workers reported an ionic flexible MOF showing metal-ion-capture properties (Figure 3b).[23] The application of a flexible ligand and the presence of a trinuclear Mn_3 cluster resulted in the flexibility of the scaffold obtained in $[Mn_3(L)_2]^{-2}\cdot2[NH_2(CH_3)_2]^+\cdot9DMF$ and $[Mn_3(L)_2]^{-2}\cdot2[H_3O]^+\cdot12DMF$ (H_4L = tetrakis[4-(carboxyphenyl)-oxamethyl]methane acid). Both these two MOFs reveal a dynamic behavior in the presence of transition metal ions such as Cu^{2+}, Co^{2+}, and Ni^{2+} owing to the deformation of the trinuclear cluster and the coordination of additional metal ions, which could be utilized for the abatement of harmful metal ions. Compared with ionic non-flexible MOFs with similar properties based on the ion-exchange mechanism, this flexible MOF is attractive for the high capture selectivity originating from the coordination interaction of targeted ions and the framework.

A unique example of the tuning of guest release in a flexible MOF was reported by Brown, Yaghi and co-workers (Figure 3c).[80] By introducing the photoactive azobenzene motif into the one-dimensional channels of a MOF with MOF-74-like structure, azo-IRMOF-74-III, the dimension of the channels could be readily modulated by controlling the *trans/cis* configuration of the motif. More importantly, a wagging movement of the azobenzene motif, caused by transformation between the *trans* and *cis* forms, could be activated by the irradiation of a 408 nm laser. This wagging movement could help to expel guest dye molecules from the channels, which was evidenced by the increased release rate under irradiation. Despite the limited enhanced release rate achieved, this work presents a successful example of performance-targeted construction of flexible MOFs and the utilizing of the dynamic feature.

4. Summary and Outlook

Recent advances of the research of flexible MOFs and their potential applications are summarized here. By reviewing the

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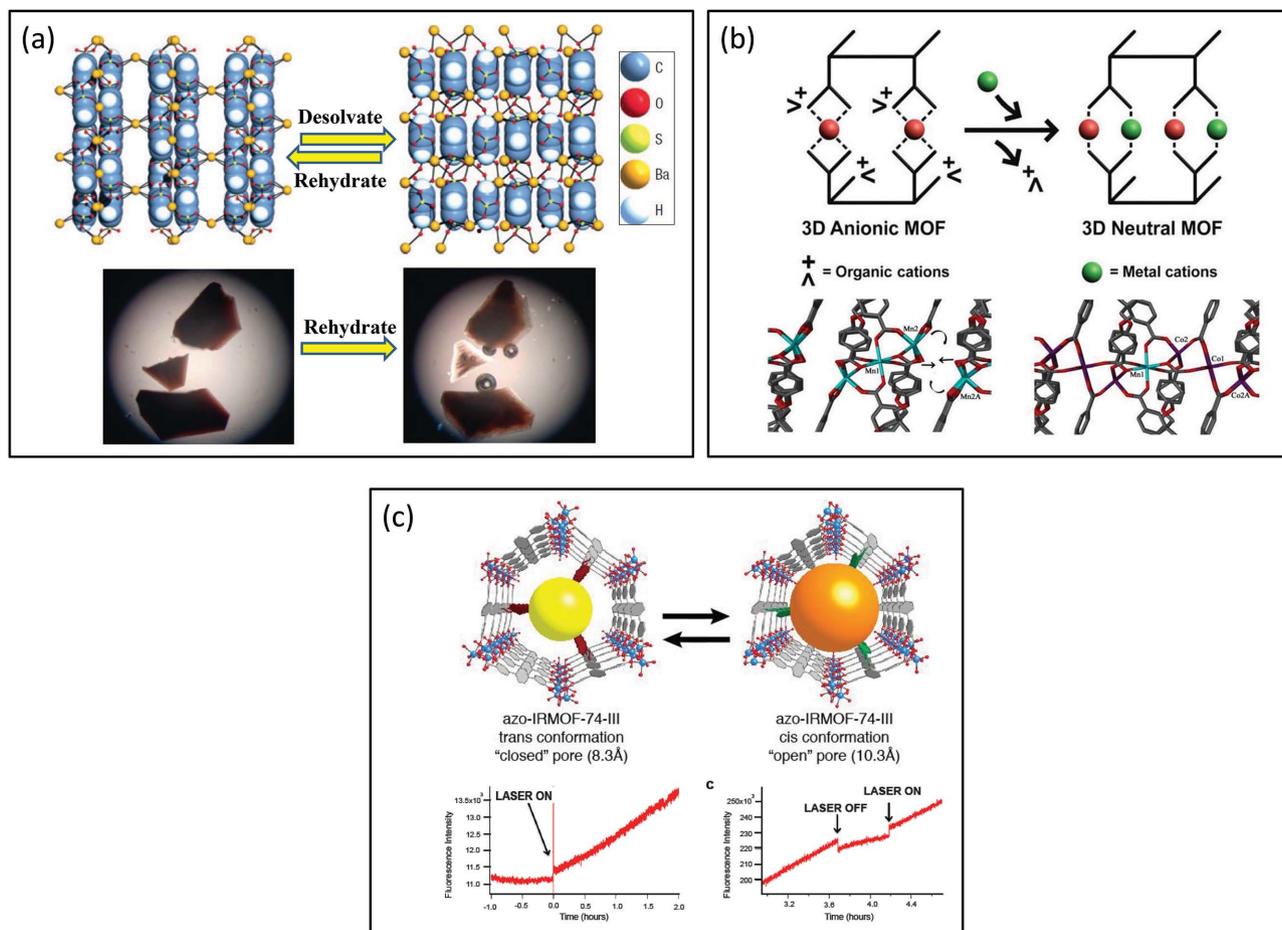www.advmat.de

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Figure 3. Examples of the guest capture and release applications of flexible MOFs: a) the capture and release of gases molecules via desolvation and rehydration of barium 1,3,5-benzenetrisulphonate. Reproduced with permission.[79] Copyright 2008, Nature Publishing Group; b) The selective capture of transition metal ions in a $[Mn_3(L)_2]^{-2}$ framework. Reproduced with permission.[23] Copyright 2012, American Chemical Society; c) The tuning of channel dimension and the guest-release rate in azo-IRMOF-74-III. Reproduced with permission.[80] Copyright 2013, Royal Society of Chemistry.

achievements in this field in recent years, it is found that the number of flexible MOFs reported is increasing, and the related characterization and property investigations reveal a more in-depth tendency. Also, the potential applications of these materials have been widely extended and even performance-targeted design and construction has emerged. Such progress should be attributed to both the quickly developing characterization and research technologies, based on which a better understanding of the mechanisms of the flexible behaviors of MOFs is realized, and the well-developed design and construction strategies that are also applicable in flexible MOFs.

Though remarkable progress has been achieved, there are still, however, many challenges in this field. As mentioned above, the identification and property investigations of flexible MOFs rely heavily on detailed characterizations and overall analysis of the results obtained by different methods, which are always time consuming. To achieve the goal more effectively, further development of the characterization methods, especially in situ methods, are urgently required. On the other hand, the development of specific theoretical guidance deserves more attention since it could not only help the identification but also the targeted construction of flexible MOFs with defined

functions. From the application perspective, it should be noted that, although the dynamic behaviors of flexible MOFs originate from the microscopic change of structure, most of their applications are based on their macroscopically apparent properties. Though the accurate control of the dynamic behaviors on the microscale is rather difficult, it has been found that controllable dynamic behaviors can be utilized for the regulation and transport of guest molecules. These behaviors are quite similar to that of some biomacromolecules, such as enzymes, with which the substrate could be modulated and transformed. Then, these properties of flexible MOFs might be applied for the mimicking of biomacromolecules: utilizing the variable pore structures, the configuration of the reactants/products may be regulated dynamically to give a desired compound, while the stimulus required for the realization of the dynamic behavior could provide the energy needed. In this way, a flexible MOF could be regarded as a nano machine and energy transducer for the modulation of substrate molecules, in which way the microscopic changes are utilized in a straightforward manner. Furthermore, despite the well-investigated pore-related properties and applications, examples of flexible MOFs with more-general responsive stimuli (temperature, magnetic, electricity, etc.) are

still limited. Since flexible MOF materials showing responsiveness to general responsive stimuli are more suitable for practical applications in devices, related research is more promising to the benefit of the application goal.

In conclusion, based on the impressive achievements of the research of flexible MOFs in the current state, a brighter future can be expected.

Acknowledgements

[1] T. K. Maji, S. Kitagawa, *Pure Appl. Chem.* **2007**, *79*, 2155.
[2] G. Férey, *Chem. Soc. Rev.* **2008**, *37*, 191.
[3] J.-R. Li, R. J. Kuppler, H.-C. Zhou, *Chem. Soc. Rev.* **2009**, *38*, 1477.
[4] K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae, J. R. Long, *Chem. Rev.* **2012**, *112*, 724.
[5] H. Gliemann, C. Wöll, *Mater. Today* **2012**, *15*, 110.
[6] M. D. Allendorf, V. Stavila, *CrystEngComm* **2015**, *17*, 229.
[7] K. Uemura, R. Matsuda, S. Kitagawa, *J. Solid State Chem.* **2005**, *178*, 2420.
[8] S. Horike, S. Shimomura, S. Kitagawa, *Nat. Chem.* **2009**, *1*, 695.
[9] F. Salles, G. Maurin, C. Serre, P. L. Llewellyn, C. Knöefel, H. J. Choi, Y. Filinchuk, L. Oliviero, A. Vimont, J. R. Long, G. Férey, *J. Am. Chem. Soc.* **2010**, *132*, 13782.
[10] V. Colombo, C. Montoro, A. Maspero, G. Palmisano, N. Masciocchi, S. Galli, E. Barea, J. A. R. Navarro, *J. Am. Chem. Soc.* **2012**, *134*, 12830.
[11] Y.-X. Tan, F. Wang, Y. Kang, J. Zhang, *Chem. Commun.* **2011**, *47*, 770.
[12] J.-P. Zhang, X.-M. Chen, *J. Am. Chem. Soc.* **2008**, *130*, 6010.
[13] M. Handke, H. Weber, M. Lange, J. Möllmer, J. Lincke, R. Gläser, R. Staudt, H. Krautscheid, *Inorg. Chem.* **2014**, *53*, 7599.
[14] X.-N. Cheng, W.-X. Zhang, Y.-Y. Lin, Y.-Z. Zheng, X.-M. Chen, *Adv. Mater.* **2007**, *19*, 1494.
[15] X.-L. Qi, R.-B. Lin, Q. Chen, J.-B. Lin, J.-P. Zhang, X.-M. Chen, *Chem. Sci.* **2011**, *2*, 2214.
[16] G. Férey, C. Serre, *Chem. Soc. Rev.* **2009**, *38*, 1380.
[17] S. Furukawa, Y. Sakata, S. Kitagawa, *Chem. Lett.* **2013**, *42*, 570.
[18] M. E. Medina, A. E. Platero-Prats, N. Snejko, A. Rojas, A. Monge, F. Gándara, E. Gutiérrez-Puebla, M. A. Camblor, *Adv. Mater.* **2011**, *23*, 5283.
[19] A. Schneemann, V. Bon, I. Schwedler, I. Senkovska, S. Kaskel, R. A. Fischer, *Chem. Soc. Rev.* **2014**, *43*, 6062.
[20] P. Horcajada, F. Salles, S. Wuttke, T. Devic, D. Heurtaux, G. Maurin, A. Vimont, M. Daturi, O. David, E. Magnier, N. Stock, Y. Filinchuk, D. Popov, C. Riekel, G. Férey, C. Serre, *J. Am. Chem. Soc.* **2011**, *133*, 17839.
[21] C. R. Murdock, B. C. Hughes, Z. Lu, D. M. Jenkins, *Coord. Chem. Rev.* **2014**, *258*, 119.
[22] Q. Chen, Z. Chang, W.-C. Song, H. Song, H.-B. Song, T.-L. Hu, X.-H. Bu, *Angew. Chem., Int. Ed.* **2013**, *52*, 11550.
[23] J. Tian, L. V. Saraf, B. Schwenzer, S. M. Taylor, E. K. Brechin, J. Liu, S. J. Dalgarno, P. K. Thallapally, *J. Am. Chem. Soc.* **2012**, *134*, 9581.
[24] J. Seo, C. Bonneau, R. Matsuda, M. Takata, S. Kitagawa, *J. Am. Chem. Soc.* **2011**, *133*, 9005.
[25] S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem., Int. Ed.* **2004**, *43*, 2334.
[26] J. Park, D. Yuan, K. T. Pham, J.-R. Li, A. Yakovenko, H.-C. Zhou, *J. Am. Chem. Soc.* **2012**, *134*, 99.
[27] N. Yanai, T. Uemura, M. Inoue, R. Matsuda, T. Fukushima, M. Tsujimoto, S. Isoda, S. Kitagawa, *J. Am. Chem. Soc.* **2012**, *134*, 4501.
[28] F. Luo, C. B. Fan, M. B. Luo, X. L. Wu, Y. Zhu, S. Z. Pu, W.-Y. Xu, G.-C. Guo, *Angew. Chem., Int. Ed.* **2014**, *53*, 9298.
[29] S. Henke, A. Schneemann, A. Wütscher, R. A. Fischer, *J. Am. Chem. Soc.* **2012**, *134*, 9464.
[30] J.-P. Zhang, X.-M. Chen, *J. Am. Chem. Soc.* **2009**, *131*, 5516.
[31] S. Henke, R. A. Fischer, *J. Am. Chem. Soc.* **2011**, *133*, 2064.
[32] C. A. Fernandez, P. K. Thallapally, B. P. McGrail, *ChemPhysChem* **2012**, *13*, 3275.
[33] F.-X. Coudert, *Chem. Mater.* **2015**, *27*, 1905.
[34] F.-X. Coudert, A. Boutin, M. Jeffroy, C. Mellot-Draznieks, A. H. Fuchs, *ChemPhysChem* **2011**, *12*, 247.
[35] A. U. Ortiz, A. Boutin, A. H. Fuchs, F.-X. Coudert, *Phys. Rev. Lett.* **2012**, *109*, 195502.
[36] A. U. Ortiz, A. Boutin, A. H. Fuchs, F.-X. Coudert, *J. Chem. Phys.* **2013**, *138*, 174703.
[37] A. U. Ortiz, A. Boutin, F.-X. Coudert, *Chem. Commun.* **2014**, *50*, 5867.
[38] F.-X. Coudert, C. Mellot-Draznieks, A. H. Fuchs, A. Boutin, *J. Am. Chem. Soc.* **2009**, *131*, 3442.
[39] F.-X. Coudert, M. Jeffroy, A. H. Fuchs, C. Mellot-Draznieks, *J. Am. Chem. Soc.* **2008**, *130*, 14294.
[40] F.-X. Coudert, A. Boutin, A. H. Fuchs, A. V. Neimark, *J. Phys. Chem. Lett.* **2013**, *4*, 3198.
[41] A. Boutin, M.-A. Springuel-Huet, A. Nossov, A. Gédéon, T. Loiseau, C. Volkringer, G. Férey, F.-X. Coudert, A. H. Fuchs, *Angew. Chem., Int. Ed.* **2009**, *48*, 8314.
[42] A. V. Neimark, F.-X. Coudert, A. Boutin, A. H. Fuchs, *J. Phys. Chem. Lett.* **2010**, *1*, 445.
[43] C. Triguero, F.-X. Coudert, A. Boutin, A. H. Fuchs, A. V. Neimark, *J. Chem. Phys.* **2012**, *137*, 184702.
[44] C. Triguero, F.-X. Coudert, A. Boutin, A. H. Fuchs, A. V. Neimark, *J. Phys. Chem. Lett.* **2011**, *2*, 2033.
[45] F.-X. Coudert, C. Mellot-Draznieks, A. H. Fuchs, A. Boutin, *J. Am. Chem. Soc.* **2009**, *131*, 11329.
[46] A. U. Ortiz, M.-A. Springuel-Huet, F.-X. Coudert, A. H. Fuchs, A. Boutin, *Langmuir* **2012**, *28*, 494.
[47] F.-X. Coudert, *Phys. Chem. Chem. Phys.* **2010**, *12*, 10904.
[48] L. Hamon, H. Leclerc, A. Ghoufi, L. Oliviero, A. Travert, J.-C. Lavalley, T. Devic, C. Serre, G. Férey, G. De Weireld, A. Vimont, G. Maurin, *J. Phys. Chem. C* **2011**, *115*, 2047.
[49] F. Salles, S. Bourrelly, H. Jobic, T. Devic, V. Guillerm, P. Llewellyn, C. Serre, G. Férey, G. Maurin, *J. Phys. Chem. C* **2011**, *115*, 10764.
[50] S. Rives, H. Jobic, D. I. Kolokolov, A. A. Gabrienko, A. G. Stepanov, Y. Ke, B. Frick, T. Devic, G. Férey, G. Maurin, *J. Phys. Chem. C* **2013**, *117*, 6293.
[51] F. Salles, H. Jobic, T. Devic, V. Guillerm, C. Serre, M. M. Koza, G. Férey, G. Maurin, *J. Phys. Chem. C* **2013**, *117*, 11275.
[52] N. Rosenbach Jr., H. Jobic, A. Ghoufi, T. Devic, M. M. Koza, N. Ramsahye, C. J. Mota, C. Serre, G. Maurin, *J. Phys. Chem. C* **2014**, *118*, 14471.
[53] Z.-J. Lin, J. Lu, M. Hong, R. Cao, *Chem. Soc. Rev.* **2014**, *43*, 5867.
[54] M. I. Breeze, G. Clet, B. C. Campo, A. Vimont, M. Daturi, J.-M. Grenèche, A. J. Dent, F. Millange, R. I. Walton, *Inorg. Chem.* **2013**, *52*, 8171.

[55] O. Kozachuk, M. Meilikhov, K. Yusenko, A. Schneemann, B. Jee, A. V. Kuttatheyil, M. Bertmer, C. Sternemann, A. Pöppl, R. A. Fischer, *Eur. J. Inorg. Chem.* **2013**, *2013*, 4546.

[56] Y. Sakata, S. Furukawa, M. Kondo, K. Hirai, N. Horike, Y. Takashima, H. Uehara, N. Louvain, M. Meilikhov, T. Tsuruoka, S. Isoda, W. Kosaka, O. Sakata, S. Kitagawa, *Science* **2013**, *339*, 193.

[57] J.-P. Zhang, P.-Q. Liao, H.-L. Zhou, R.-B. Lin, X.-M. Chen, *Chem. Soc. Rev.* **2014**, *43*, 5789.

[58] R. I. Walton, A. S. Munn, N. Guillou, F. Millange, *Chem. Eur. J.* **2011**, *17*, 7069.

[59] E. J. Carrington, I. J. Vitórica-Yrezábal, L. Brammer, *Acta Crystallogr., Sect. B: Struct. Sci.* **2014**, *70*, 404.

[60] V. Bon, I. Senkovska, D. Wallacher, A. Heerwig, N. Klein, I. Zizak, R. Feyerherm, E. Dudzik, S. Kaskel, *Microporous Mesoporous Mater.* **2014**, *188*, 190.

[61] A. Sutrisno, Y. Huang, *Solid State Nucl. Magn. Reson.* **2013**, *49–50*, 1.

[62] Y. Chen, J. Zhang, J. Li, J. V. Lockard, *J. Phys. Chem. C* **2013**, *117*, 20068.

[63] M. Mazaj, G. Mali, M. Rangus, E. Žunkovič, V. Kaučič, N. Z. Logar, *J. Phys. Chem. C* **2013**, *117*, 7552.

[64] S. Devautour-Vinot, G. Maurin, C. Serre, P. Horcajada, D. Paula da Cunha, V. Guillerm, E. de Souza Costa, F. Taulelle, C. Martineau, *Chem. Mater.* **2012**, *24*, 2168.

[65] C. Janiak, *Chem. Commun.* **2013**, *49*, 6933.

[66] H. Sato, W. Kosaka, R. Matsuda, A. Hori, Y. Hijikata, R. V. Belosludov, S. Sakaki, M. Takata, S. Kitagawa, *Science* **2014**, *343*, 167.

[67] S. Mukherjee, B. Joarder, B. Manna, A. V. Desai, A. K. Chaudhari, S. K. Ghosh, *Sci. Rep.* **2014**, *4*, 5761.

[68] B. Seoane, J. Coronas, I. Gascon, M. E. Benavides, O. Karvan, J. Caro, F. Kapteijn, J. Gascon, *Chem. Soc. Rev.* **2015**, *44*, 2421.

[69] H. B. Tanh Jeazet, C. Staudt, C. Janiak, *Dalton Trans.* **2012**, *41*, 14003.

[70] B. Zornoza, A. Martinez-Joaristi, P. Serra-Crespo, C. Tellez, J. Coronas, J. Gascon, F. Kapteijn, *Chem. Commun.* **2011**, *47*, 9522.

[71] T. Rodenas, M. van Dalen, E. García-Pérez, P. Serra-Crespo, B. Zornoza, F. Kapteijn, J. Gascon, *Adv. Funct. Mater.* **2014**, *24*, 249.

[72] Y. Takashima, V. Martinez Martinez, S. Furukawa, M. Kondo, S. Shimomura, H. Uehara, M. Nakahama, K. Sugimoto, S. Kitagawa, *Nat. Commun.* **2011**, *2*, 168.

[73] N. Yanai, K. Kitayama, Y. Hijikata, H. Sato, R. Matsuda, Y. Kubota, M. Takata, M. Mizuno, T. Uemura, S. Kitagawa, *Nat. Mater.* **2011**, *10*, 787.

[74] J.-H. Wang, M. Li, D. Li, *Chem. Sci.* **2013**, *4*, 1793.

[75] P. Falcaro, R. Ricco, C. M. Doherty, K. Liang, A. J. Hill, M. J. Styles, *Chem. Soc. Rev.* **2014**, *43*, 5513.

[76] H.-L. Zhou, R.-B. Lin, C.-T. He, Y.-B. Zhang, N. Feng, Q. Wang, F. Deng, J.-P. Zhang, X.-M. Chen, *Nat. Commun.* **2013**, *4*, 2534.

[77] A. C. McKinlay, J. F. Eubank, S. Wuttke, B. Xiao, P. S. Wheadey, P. Bazin, J. C. Lavalley, M. Daturi, A. Vimont, G. De Weireld, P. Horcajada, C. Serre, R. E. Morris, *Chem. Mater.* **2013**, *25*, 1592.

[78] D. Cunha, M. Ben Yahia, S. Hall, S. R. Miller, H. Chevreau, E. Elkaïm, G. Maurin, P. Horcajada, C. Serre, *Chem. Mater.* **2013**, *25*, 2767.

[79] B. D. Chandler, G. D. Enright, K. A. Udachin, S. Pawsey, J. A. Ripmeester, D. T. Cramb, G. K. H. Shimizu, *Nat. Mater.* **2008**, *7*, 229.

[80] J. W. Brown, B. L. Henderson, M. D. Kiesz, A. C. Whalley, W. Morris, S. Grunder, H. Deng, H. Furukawa, J. I. Zink, J. F. Stoddart, O. M. Yaghi, *Chem. Sci.* **2013**, *4*, 2858.