



TITLE:

Concluding remarks: current and next generation MOFs

AUTHOR(S):

Yao, Ming-Shui; Otake, Ken-ichi; Xue, Zi-Qian;
Kitagawa, Susumu

CITATION:

Yao, Ming-Shui ...[et al]. Concluding remarks: current and next generation MOFs. Faraday Discussions 2021, 231: 397-417

ISSUE DATE:

2021-10-01

URL:

<http://hdl.handle.net/2433/277067>

RIGHT:

This is an accepted manuscript of the article which has been published in final form at <https://doi.org/10.1039/D1FD00058F>. The full-text file will be made open to the public on 09 September 2022 in accordance with publisher's 'Terms and Conditions for Self-Archiving'; This is not the published version. Please cite only the published version. この論文は出版社版ではありません。引用の際には出版社版をご確認ご利用ください。

ARTICLE

Current and Next Generation MOFs

Ming-Shui Yao,^a Ken-ichi Otake,^a Zi-Qian Xue^a and Susumu Kitagawa^{*a}

Received 00th January 20xx,
 Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

This paper describes the content of my "closing remarks" talk at the Faraday Discussions meeting on MOFs for energy and the environment (online, 23-25 June 2021). The panel consisted of sessions on the design of MOFs and MOF hybrids (synthetic chemistry), their applications (e.g., capture, storage, separation, electrical devices, photocatalysis), advanced characterization (e.g., transmission electron microscopy, solid-state nuclear magnetic resonance), theory & modeling, and commercialization. MOF chemistry is undergoing a significant evolution from simply network chemistry to the chemistry of synergistic integration with heterogeneous materials involving other disciplines (we call it the fourth generation type). As reflected in the papers of the invited speakers and discussions with the participants, the present and future of this field will be described in detail.

1. Introduction

Coordination polymers (CPs) are coordination compounds with repeating coordination entities extending in one, two, or three dimensions. When CPs have a network structure with potential voids, they are called porous coordination polymers (PCPs) or metal-organic frameworks (MOFs).¹ For the sake of consistency, we will refer to these porous materials as MOFs in the concluding remarks. In the more than 20 years of the history of MOFs, a large number of publications on the structure and function of MOFs have been published worldwide.²⁻⁸

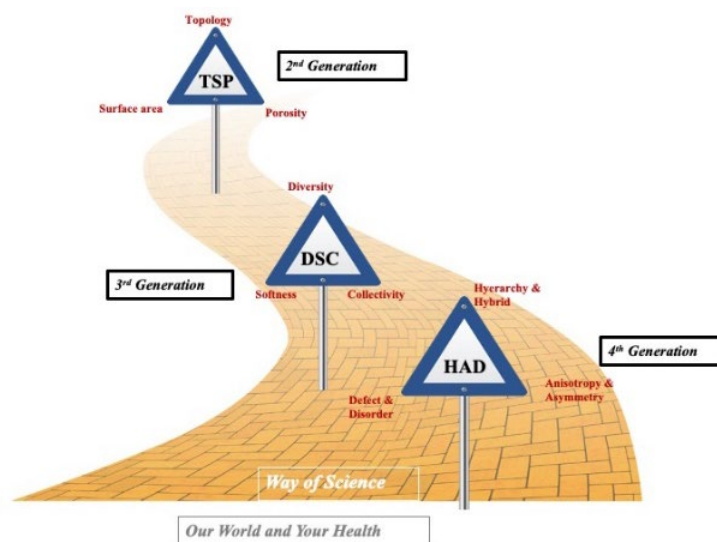


Figure 1. Development of MOF chemistry. Modified with permission from ref⁹. Copyright 2017 The Royal Society of Chemistry.

The design and synthesis of the porous network have evolved dramatically from basic science to application and industrialization. Faraday Discussion 2020, entitled Cooperative Phenomena in Framework Materials, was held last year. The subject was the cooperativity of structures and functions of MOFs and related materials, whose contents and discussions have already been published.¹⁰ The arguments here have been carried over to Faraday Discussion 2021. A central theme is "MOFs for energy and environment," an essential point of view in considering MOFs as materials that contribute to solving current social and

^aInstitute for Integrated Cell-Material Sciences (WPI-iCeMS), Kyoto University Institute for Advanced Study, Kyoto University, Yoshida Ushinomiya-cho, Sakyo-ku, Kyoto 606-8501 (Japan), E-mail: kitagawa@icems.kyoto-u.ac.jp.

environmental issues. Four session titles set for this symposium are convenient for an overview of current MOF chemistry; (1) Fundamental Studies and design of MOFs, (2) Application and development, (3) Theory and modeling, (4) Commercialization and applications.

On the other hand, different conceptual perspectives on MOF chemistry are needed when looking into the future. One of the authors listed and foresaw the attributes of future MOFs as the fourth generation type (Figure 1).⁹ When discussing the topics as the session titles, it is essential first to overview the MOF materials' chemical evolution.

These concluding remarks begin by describing the historical background of MOFs, followed by the current status and prospects. MOF materials have evolved through stages that can be categorized as follows. The first generation is the synthesis of coordination networks. The second generation is the construction of robust porous structures as well as zeolites and activated carbons. The third generation is flexible structures, so-called soft porous crystals.¹¹ The fourth generation is exactly the next one. The 4th generation will be the one with the attributes abbreviated as HAD. They are (1) Hybrid and Hierarchy, (2) Anisotropy and Asymmetry, and (3) Defect and Disorder.^{12, 13} Therefore, the concluding remarks are reorganized concerning the HAD attributes. In addition to the results presented here, were also summarized and organized the important results of MOF chemistry to date along with the attributes of 4th generation MOFs.

2. Development of MOF Chemistry

Since the advent of MOFs, researchers worldwide have been striving to develop MOF materials with new structures and functions. The followings are some of the essential points to keep in mind for the 4th generation MOF. In particular, they are MOFs with asymmetry or anisotropy in their networks, MOF crystals with size-dependent properties, and hybrid Systems such as MOF₁-on-MOF₂ and MOF on X (other materials). The invited speakers presented several topics. All the topical trends are essential for the development of the next generation MOF chemistry.

2-1. Synthesis of MOF network and control of crystal size, morphology, and phase transform

The design of the organic ligands that create porous networks is fundamental. The topological structure, the nature of the coordination sites, the interaction properties of the ligand itself (hydrogen bonding, interaction, polarity, etc.), and the structural flexibility are essential for the ligand design. In the future, organic ligands with unique geometric structures and functional groups will be synthesized in various ways. There was also a presentation related to this research at this symposium.¹⁴

2-2. Adding Asymmetry: Chiral MOF

The introduction of chirality into the network holds excellent promise for recognizing and selective separation of optically active species, creating chiral catalytic MOFs, and realizing dielectric properties. The most direct way to achieve this is to use chiral ligands.¹⁵ Furthermore, MOF synthesis using anisotropic templates is expected to be developed in the future.

2-3. Preparation of crystal morphology

Research on combining MOFs with different structures was realized in 2009 by epitaxial growth of two types of crystals (MOF-on-MOF structure).^{16, 17} Since then, various combinations of other MOFs and complex crystals with different morphologies have been synthesized even for the same MOF.

The morphology control is attractive even in one kind of MOF. For example, hollow MOF crystals could be used for a variety of applications.¹⁸

2-4. Downsizing leads to new properties

Here, the reason why the mesoscopic regime is essential for MOF chemistry needs to be stated. The mesoscopic regime (tens to hundreds of nm) is greater than the nanoscopic one (1-10 nm), which nanoscience and technology have extensively explored. On the other hand, it is smaller than the bulk size of more than one micron, consisting of a vast number of molecules. Between these two well-traveled lands, there is the vast unexplored land of the mesoscopic regime. Although molecular, atomic, and ionic interactions occurring in nano-space are an exciting subject of research, they are generally elementary processes. Nonlinear, weakly-cooperative events, which present challenging problems and can be the seeds for tomorrow's technology, occur in the mesoscopic field. In particular, a mesoscopic scale MOF crystal has thousands of pores, not so large, but a sufficient number of pores could show a unique property. Here are several examples of how different size crystals have other functions. The first discovery was the shape memory effect that appears in a mesoscopic scale crystal (Figure 2a).¹⁹ Figure 2b is another example of the difference in adsorption function between thin film and bulk.²⁰ Figure 2d is spatially-controlled anchoring of the flexible MOFs on the surface. This induces distinct structural responsiveness different from the bulk powder.²¹ Figure 2c is an example of negative expansion appearing differently depending on size.²² In this Faraday Discussion, size and morphology dependence of conductivity and guest transport was introduced (see section 4-4).²³

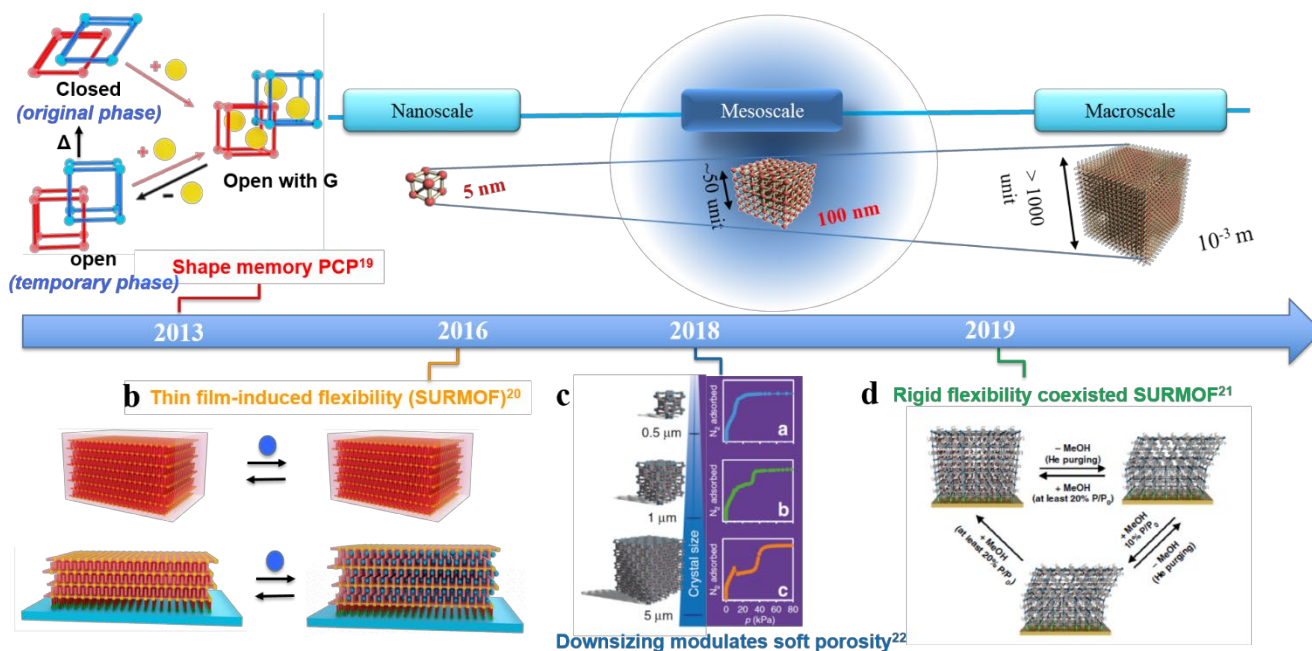


Figure 2 Downsizing leads to new properties. (a) Shape memory PCP.¹⁹ (b) Thin film-induced flexibility.²⁰ (c) Downsizing modulates soft porosity. Reproduced with permission from ref²². Copyright 2018, Springer Nature Limited. (d) Rigid flexibility coexisted SURMOF. Reproduced with permission from ref²¹. Copyright 2019, Springer Nature Limited.

We will develop the chemistry of dynamic pores by understanding and controlling the critical interactions of molecular complexes at the mesoscale with porous materials. We will realize this by creating a case of fourth-generation of porous materials by interdisciplinary approaches.

2-5. Phase control; melting

An epoch-making discovery in the chemistry of MOF crystals was the melting phenomenon.^{24,25,26} Previously, MOF crystals were thought to decompose and break down upon heating. Still, it has been demonstrated that they melt to give a liquid phase and that some of them undergo a reversible phase transition to a glassy phase or a single crystal phase upon cooling (the upper part of Figure 3).²⁴⁻²⁸ The melting of MOFs has various applications,²⁹⁻³¹ including the creation of membranes.³¹

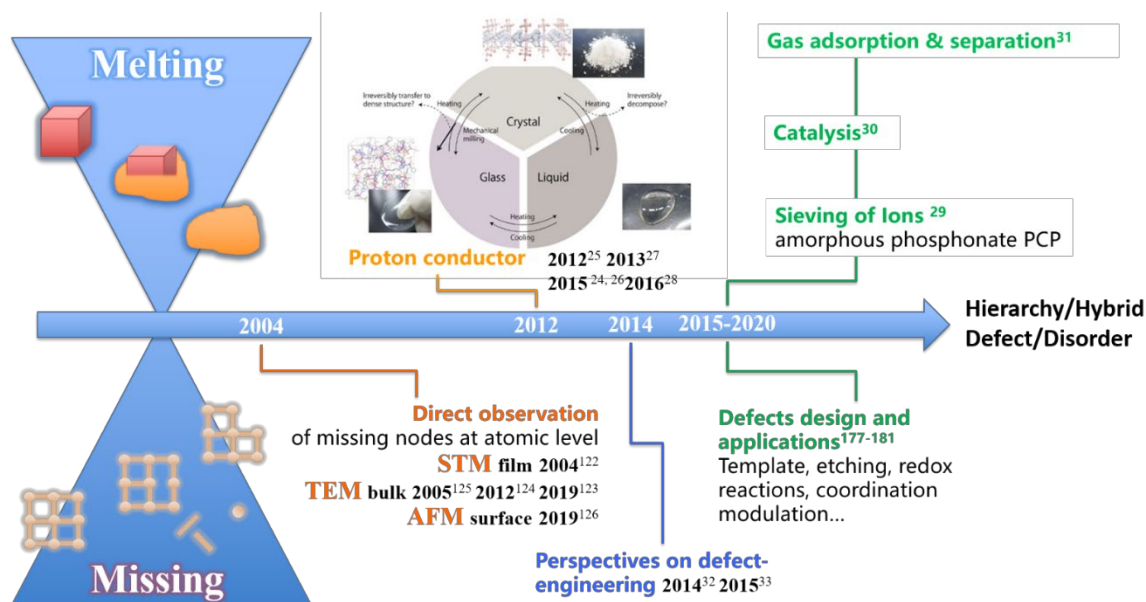


Figure 3 Melting and missing: a timeline of defected MOF chemistry. The figure for the proton conductor was reproduced with permission from ref²⁵. Copyright 2012, American Chemical Society.

2-6. Defects and disorder: Missing broadens MOF science

Another exciting development is the emergence of considering the imperfections of MOF crystals and exploiting them more aggressively. There exist no perfect crystals, and there are more or fewer defects and disorders. Since the advent of MOFs, researchers have focused on reducing crystal defects and disorders to maximize the accommodative properties of their porous structure. In doing so, researchers realized that they could control the defect or disorder and pull out the function. This is a significant property from the viewpoint of its application to their catalysts and physical properties. Controlling defects and disorders in MOF crystals is considered an important area of chemistry comparable to the framework's design (the lower part of Figure 3).^{32, 33}

3. MOF composites and hybrids.

Twelve years ago, the author first synthesized a core-shell crystal using the epitaxial growth of two crystals, one with small pores and the other with large pores. As shown in Figure 4, the outer one was size-selective, and the inner one was capable of massive storage.

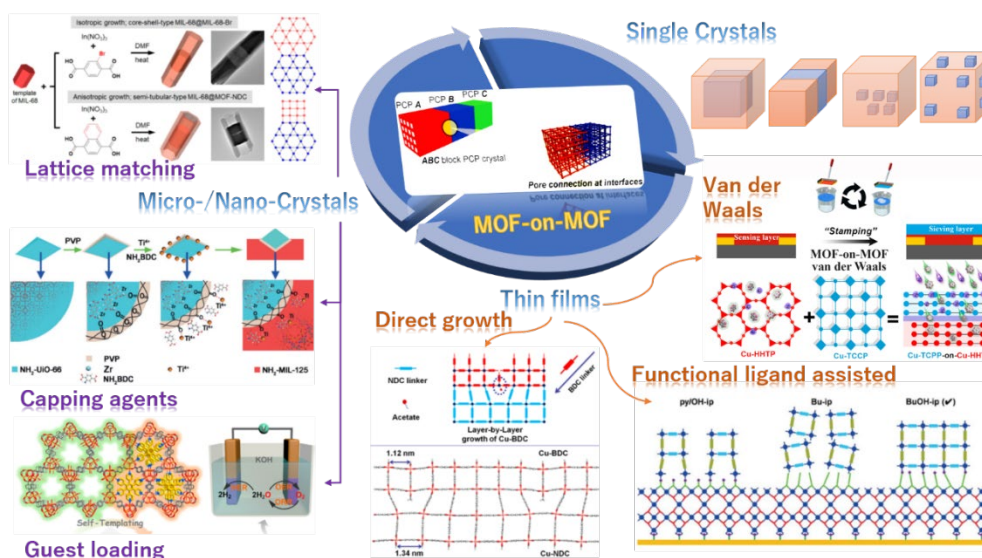


Figure 4. MOF-on-MOF single crystals, micro-/nano-crystals, and thin films. Reproduced with permission.³⁴ Copyright 2016, American Chemical Society. Reproduced with permission.³⁵ Copyright 2017, Wiley-VCH. Reproduced with permission.³⁶ Copyright 2019, American Chemical Society. Reproduced with permission.³⁷ Copyright 2014, American Chemical Society. Reproduced with permission.³⁸ Copyright 2020, Wiley-VCH. Reproduced with permission.³⁹ Copyright 2018, The Royal Society of Chemistry. Reproduced with permission.⁴⁰ Copyright 2021, Wiley-VCH.

Nowadays, a wide variety of MOF crystal composites have been synthesized, as shown in Figure 5. The numerous possible applications show that the development of MOF chemistry is progressing rapidly.

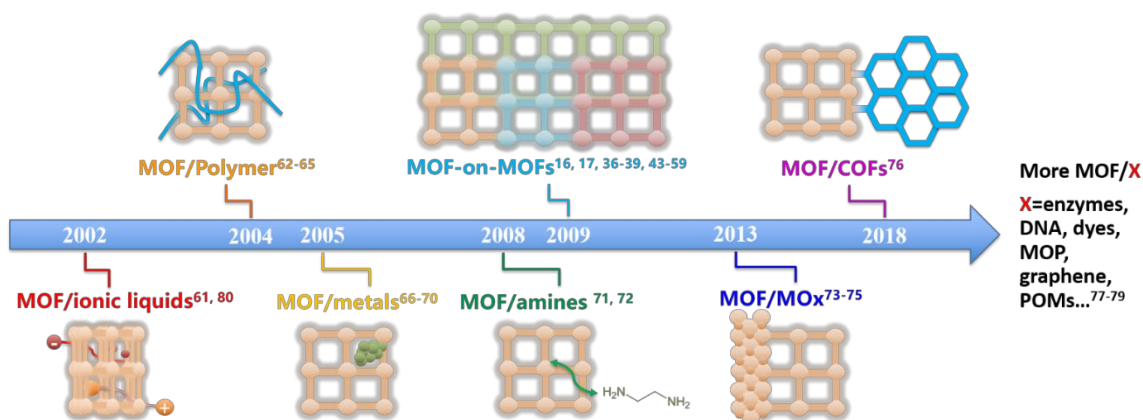


Figure 5. The timeline and schematic illustration of various MOF/X hybrids.

The most exciting and applicable materials using MOFs are hybrid systems with other materials. There has been a great deal of progress in the past decade, and many new hybrid materials have been published. These include hybrids with organic polymers, composites with metals, hybrids with metal oxides, and COFs.⁴⁰ In this Faraday Discussion, graphitic carbon nitride/MOF⁴¹ and nanoclusters/MOF⁴² were discussed.

The application of the hybrid systems is closely related to the central theme of this Faraday Discussion, “energy and environment.” This field will develop more and more rapidly and will have a significant ripple effect on other areas. In hybrid systems, the interface between different materials plays a crucial role. In other words, there are great expectations for the deepening and development of interface science. For this purpose, new observation tools and methods are indispensable. There are still some challenging issues for researchers who want to develop the chemistry of MOFs.

MOF-on-MOFs' molecule-level hybridizations were realized by direct growth for lattice matching cases⁴³ or assisted by capping agents for MOFs with great lattice and topology mismatch.^{40, 44} Post-synthetic methods^{36, 45-47} and the van der Waals integration method³⁸ were also employed to chemically and physically form a secondary MOF, respectively. The obtained MOF-on-MOFs with precise heterocompositions or heterostructures (single crystal,^{16, 17} micro-/nano-crystals,⁴⁸ and thin films⁴⁹⁻⁵¹) were experimentally observed to show multifunctions that single MOF cannot achieve,^{48, 52-59} such as photo-assisted flexibility,⁴⁷ guest transport modulation,⁶⁰ photocatalysis,³⁵ thermal catalyzes, highly sensitive and selective chemiresistors,³⁸ *etc.*

The MOFs with foreign components (marked as X), that is, MOF/X, started with ionic liquid as counterions,⁶¹ and then extended to various materials such as polymers,⁶²⁻⁶⁵ metal,⁶⁶⁻⁷⁰ amines,^{71, 72} metal oxides,⁷³⁻⁷⁵ COF,⁷⁶ enzymes,⁷⁷ carbons,⁷⁸ polyoxometalates (POMs),⁷⁹ *etc.*⁸⁰ Among them, various MOF/X based on covalent modification^{76, 81-86} or non-covalent interaction (*e.g.*, hydrogen bonds,⁸⁷⁻⁸⁹ coordination bonds,^{65, 73} π interactions,⁹⁰ electrostatic,⁸⁰ van der Waals forces^{89, 91})^{63, 92, 93} have been developed to facilitate the molecule-level hybridizations.

With a late start but fantastic upswing, the controlled syntheses of hollow or hierarchical structures endow molecule level frameworks of MOFs with meso- and macro-scale properties, which significantly promotes the mass transport, porosity, multi-active components/sites, and its compatibility with foreign components and complicated working conditions.^{40, 94-96} The synthetic methods include but not limited to soft/hard template,⁹⁷ interfaces,⁹⁸ etching,⁹⁹ “Modular programming”¹⁰⁰ and van der Waals attractions.¹⁰¹

4. Electronic and Photo-physical / -chemical Properties

The development of MOFs that effectively use renewable energy and contribute to a sustainable society and environment is significant, and this research must be pursued with increasing vigor. Now, in the development of MOF chemistry and storage, separation, and other functions, the development of physicochemical functions is significant. It is a MOF material in which charge, spin, and light play a leading role.

4-1 Photochemistry and physics

The physicochemical study of MOFs using light was discussed at this Faraday Discussion. Here is a summary of it. There were engaging presentations on charge transfer efficiency, reduction by electron transfer, and other aspects of catalysis, energy storage, and restitution.

As MOFs are a class of porous crystalline materials constructed by organic linkers with metal ions or clusters, the photoactive MOFs can be designed by incorporating light-harvesting organic linkers, metal clusters, or guests. Most MOFs are prepared by aromatic organic linkers, which can absorb UV or visible light to lead to $n-\pi^*$ - or $\pi-\pi^*$ -based transitions, thus exhibiting potential photoactive. The absorbance range of MOFs can be further altered by utilizing a conjugated aromatic system or introducing the functional group to the linkers of MOFs, which provides the possibility to regulate their photoactivity. Remarkably, the ordered arrangement of organic linkers and metal clusters in porous crystalline MOFs will effectively inhibit aggregation-caused fluorescence quenching. Additionally, metallo-ligands such as metalloporphyrin and metallopolyridyl can be incorporated into MOFs serve as photosensitisers or photocatalysts. So, MOFs provide a promising platform to explore attractive materials with luminescence and photocatalytic properties.

Due to the structural characteristics of MOFs, the ligand field transitions, metal-ligand charge-transfer transitions, and intra-ligand transitions endow MOFs with various electronic states and luminescence properties.¹⁰² The luminescence properties of MOFs can arise from ligand-centered emission, metal-centered emissions, the metal-ligand charge-transfer or/and host-guest interaction (Figure 6). Ligand-centered emission can occur in d^{10} metal ions such as Zn^{II} and Cd^{II} based MOFs with no d-d transition and redox in these metals.¹⁰³ Integrating photoactive organic linkers including spiropyran and metalloporphyrin into a Zn-based MOF, photochromic behavior can be observed.¹⁰⁴ Lanthanide-based MOFs (Ln-MOFs) typically show metal-centered emissions resulting from the shielding of the 4f orbitals by the $5p^66s^2$ shells.¹⁰⁵ Furthermore, the porous nature of MOFs allows introducing guests into the pore of MOFs. The host-guest interaction in MOFs may enhance the guest emission and prevent aggregation-induced emission quenching, which makes it possible to create multiple-emission luminescent materials.¹⁰⁶

Photocatalysis is one of the most promising applications for MOFs. MOFs' chemical and structural tunability allows them to modify their electronic structure and photophysical properties at molecular/ atomic - levels by accurately designing the inorganic cluster or organic linker. In particular, the structural constituent with different functions can be integrated into MOFs to achieve effective synergy. The organic linker can capture light to form a photo-induced electron, which metal nodes can utilize in MOF to convert the reactant caught in the pore of MOF. This provides a promising platform to construct efficient photocatalysts and insight into the structure-performance relationship.¹⁰⁷ The function of photoactive MOFs can be further regulated by hybridizing with guest molecular, complex, nanoparticles, polymer, or additional crystalline porous materials, which provides an opportunity to achieve enhanced or new functions such as dye degradation and premium artificial photosynthesis.^{41, 108}

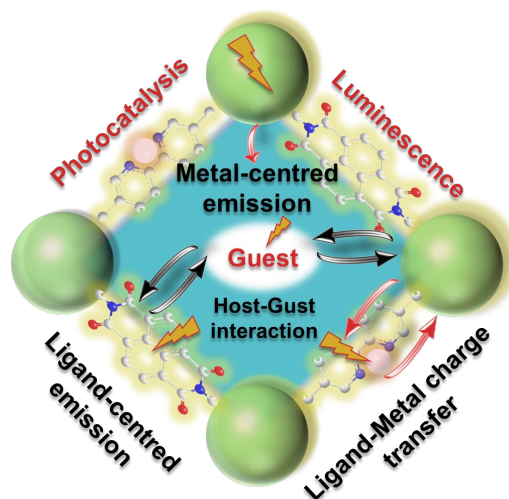


Figure 6. Scheme of the possible absorption and emission processes of light in photoactive MOFs.

4-2 Electrically conductive MOFs

Since its emergence, MOF has been considered to be an insulator compound. However, many MOFs have been synthesized in the past decade, ranging from semiconductors to metallic conductivity.^{96, 109, 110}

This MOF semiconductor/conductor is a promising material, which will be used in an increasing variety of applications in the future by making thinner films, creating intrinsic two-dimensional MOFs, and hybridizing with other materials at the molecule level.^{111, 112}

4-3 Electric conductivity and Photo-physical / -chemical Properties

In the last decade, the newly emerging electrically conductive metal-organic frameworks (cMOFs),¹¹²⁻¹¹⁴ constructed by organic ligands and metal nodes with effective band/hopping transport pathways,^{115, 116} have been intensively studied and successfully applied as binder-free active materials in electrical devices.^{56, 80, 117-119} Compared with organic semiconductors, cMOFs have additional metal ions for connecting organic molecules, affording well-ordered arrays that provide electrical conduction according to the band structure and active sites for electrical applications.^{9, 40} In addition to high conductivity, recently, there has been growing interest in MOF transport, which includes electron, proton, anion/cation conduction, and neutral molecules.^{28, 96, 120, 121}

4-4 Mass / Charge Transport: Morphology vs. Conductivity

To make the function of electrically conductive MOFs even more unique, their porous function must also be exploited. In other words, electrical conductivity generated by the incorporation of guest molecules into the pores of MOFs and their interaction with the MOF framework and electrical conductivity are related to the diffusion of guest molecules.

As a typical example, one of the representative cMOFs, Ni-HITP (HITP = 2,3,6,7,10,11-hexamino-triphenylene) with 1D channels along the c axis, is clearly present showed the transport facilitated sample morphology had a more significant impact on the measured electrode performance than bulk electrical conductivity.²³

5. Advanced Characterization

In the hybrid system described earlier, the interface between different materials plays a crucial role. In other words, there are great expectations for the deepening and development of interface science. For this purpose, new observation tools and methods

are indispensable. TEM and AFM are specific and powerful tools in the observation of MOF. In 2004, a single-phase copper-based MOF film was observed using STM,¹²² and later, the bulk and surface structure of MOF was observed using TEM¹²³⁻¹²⁵ and AFM,¹²⁶ respectively.

5-1. 3D Electron diffraction (3DED)

The electron diffraction method, which is one of the topics of this Faraday Discussion, has recently made significant progress. This is good news for MOF science. In particular, it is beautiful to obtain structural information for crystals smaller than a micron quickly.

As presented in this Faraday discussion,¹²⁷ three-dimensional electron diffraction (3DED) has been steadily developed as a powerful technique for solving the crystal structure of nano-sized crystals that are too small for SCXRD analyses.¹²⁸⁻¹³⁰ Compared to X-rays, electrons can generate diffraction patterns with much higher signal-to-noise ratios even when crystals are only a few hundred nanometers or less in size. Various practical 3DED techniques have been developed, including microcrystal electron diffraction (MicroED),¹²⁹ automated diffraction tomography (ADT),¹³¹ and continuous electron diffraction (cRED).¹³⁰ At this meeting, the effect of merging the dataset was discussed to improve the data quality of 3DED. It was demonstrated that the data completeness of 3DED data could be improved mainly by merging data obtained from a series of individual crystals, which results in an enhancement in the accuracy of the structural model.¹²⁷ This finding will provide complementary solutions for the typical drawback of the 3DED method, *i.e.*, low completeness and difficulty in solving low-symmetry systems. As a piece of intriguing news, Rigaku Corporation, a leading company producing X-ray analysis instruments, and JEOL Ltd., a leading company producing electron microscopes and other analytical instruments, have announced their joint project to launch an integrated electron diffraction platform.¹³² Soon, 3DED may become an easily accessible tool for many researchers who works on nanocrystals.

5-2. Crystal surface Observation: HRTEM, STM, and AFM

To deepen the MOF science, seeking advanced characterization techniques are of great importance. In particular, structural characterization methods of nano-sized crystals, surface/interface, and defects of MOF have been desired in this field to pursue a deeper insight into their physicochemical properties.

To explore the surface chemistry of MOF science, a high-resolution transmission electron microscope (HRTEM), scanning tunneling microscopy (STM), and atomic force microscopy (AFM) are essential techniques. These techniques can enable the direct observation of crystal surfaces and the monitoring of crystal growth processes at the nanoscale.^{125, 133, 134}

Although these techniques can observe brilliant regular forms (Figure 7), there is an unavoidable drawback in the following porous materials: the inability to simplify phenomena involving the entry and exit of guest molecules. Due to this high vacuum observation condition, we could not track the adsorption and desorption of guest molecules, so we had to seek other methods. The direct observation of the changes in a MOF crystal under guest species is the specialty of AFM. AFM observed single layer growth of sub-micron MOF crystal in 2008.^{134, 135}

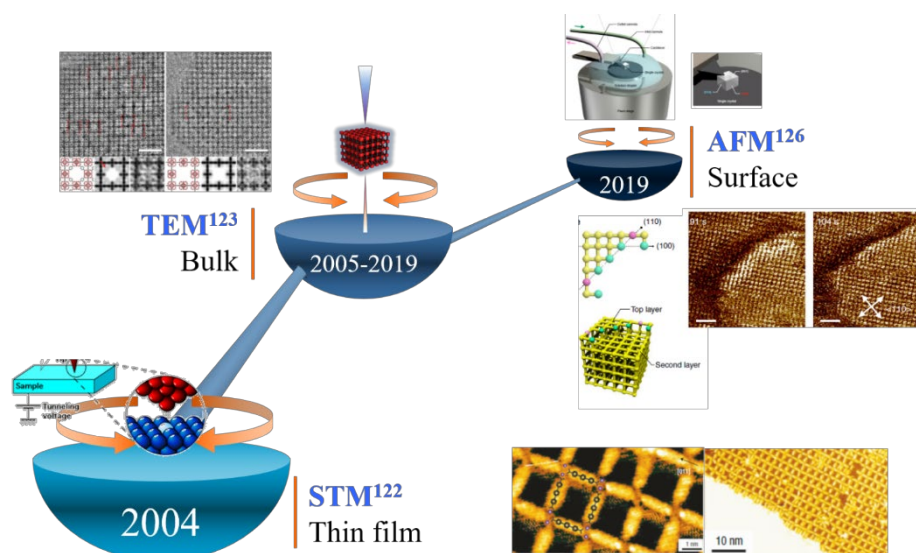


Figure 7 The timeline of the high-resolution technology for the direct observation of missing nodes at molecule level (STM, TEM, AFM). Reproduced with permission from ref ^{122, 123, 126}. Copyright 2004, 2019 Springer Nature Limited.

In this Faraday Discussions, crystal growth of the core and rotated epitaxial shell of a heterometallic MOF were revealed with AFM. In this case, the lattice structure of the substrate MOF and additional MOF growing on it are the same. Still, when the metal ions are different, they cannot grow epitaxially because of the slight difference in the metal-ligand bond distance. The in-plane

rotation epitaxy between the two crystals was first observed 12 years ago using synchrotron radiation X-ray diffraction,¹⁷ and, herein, through the use of in situ AFM, it is well consistent with the synchrotron XRD observation.¹³⁶

As an intriguing example, the surprising flexibility of crystal surfaces of a MOF was revealed using real-time in situ AFM.¹²⁶ The result demonstrated that the liquid-solid interface of MOF was more sensitive to the guest than the bulk phase.

5-3. Solid-state nuclear magnetic resonance (ssNMR) and nonlinear optics (NLO) method

There are other worth noting techniques for the advanced characterization of PCP/MOFs, such as solid-state nuclear magnetic resonance (ssNMR) and nonlinear optics (NLO) method. ssNMR is one of the most powerful methods for determining the framework structure and dynamics even when the target MOFs are non-crystalline. In addition, ssNMR can give valuable information for the dynamics of the guest molecule and the guest-framework interaction.¹³⁶ Continuous, systematic development of ssNMR will assist the further development of the PCP/MOF field. On the other hand, the NLO method is an emerging strategy for visualizing defects within MOF. NLO refers to a phenomenon in which a material responds nonlinearly to an electric field of light. NLO method has been proven to be a useful technique for visualizing inhomogeneities and defects within MOFs.¹³⁷ The utilization of these techniques will help further explore MOFs' otherwise elusive structural and phenomenological mysteries.

6. Theory and Modeling

Timeline of theoretical studies on MOF systems can be found in Figure 8.

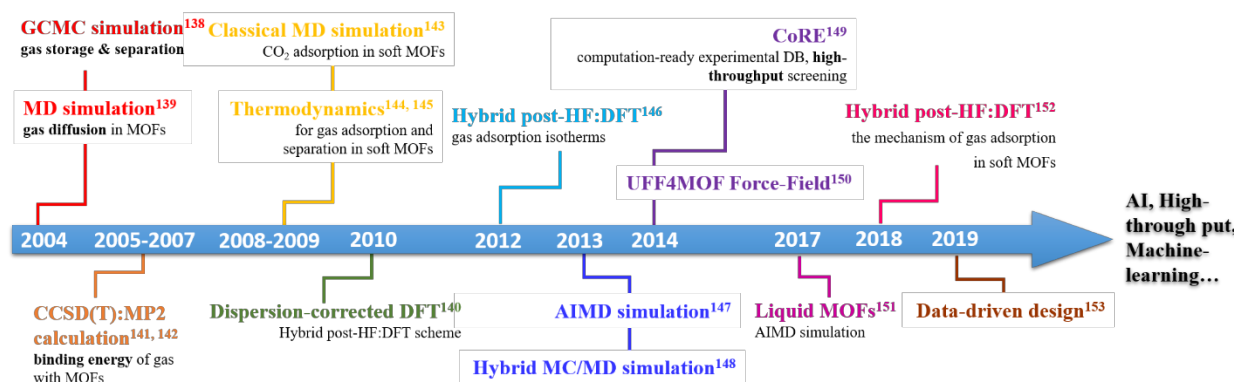


Figure 8 Timeline of theoretical studies on MOF systems. A lot of experimental data on MOFs has been published so far. It is essential to understand the results theoretically. It is also very promising to predict the structure and function. This is a theoretical treatment of MOFs and progress in computer science. We can see that GCMC¹³⁸ and MD simulation¹³⁹ and DFT calculation¹⁴⁰ are making significant progress.¹⁴¹⁻¹⁵³

The computational study can provide a deep understanding of the underlying physics for the observed physicochemical properties.¹⁵⁴ In particular, the porous properties of MOF, such as gas storage,^{155, 156} separation,^{157, 158} and transport properties,^{138, 159} have been intensively investigated to understand the origins of the phenomena. It is relatively easy to make a reasonable structural model for the calculation to benefit from their crystalline nature. Thus, the theoretical investigation in MOF could give accurate structural and chemical insights. In addition, computational screening techniques have been proven to be a powerful tool in predicting and discovering top-performing MOFs for a particular application.¹⁶⁰⁻¹⁶² Such computational screening methods have recently witnessed a rapid expansion due to several factors such as (1) the growth of the open public databases, (2) the advances in methods for hypothetical structural construction, and (3) the development of artificial intelligence techniques.¹⁶³⁻¹⁶⁵ In fact, machine learning techniques have now shown great promise in MOF science because it is not feasible to experimentally single out top-performing structures from the vast and ever-growing MOF library, which now exceeds >70,000 MOF structures. In this Faraday discussion, high-throughput computational screening of MOF in applying xenon/krypton separation,¹⁶⁵ methane storage,¹⁶⁶ and biogas purification¹⁶⁷ were discussed. They demonstrated that their methods provide the best candidates and a better comprehension of the structure-property relationships in the target application.

We also hope to progress soft porous crystals' theory and computer science that respond to guest molecules and physical stimuli.

7. Commercialization and Application

MOF science is now moving from the science phase to the business phase.^{168, 169} Due to the broad applicability and material designability, MOF materials have attracted great industrial attention in various fields, including gas storage, separation, water harvesting, direct CO/CO₂ reduction using H₂, antibiotic elimination from water, etc. So far, 24 start-ups in total relating to MOF

materials have already been launched worldwide (Table 1).¹⁶⁸ Still, there are several concerns to consider for the actual application of these materials.

Table 1 PCP/MOF start-ups around the world

<i>Company Name</i>	<i>Year founded</i>	<i>country</i>	<i>University</i>
<i>Framergy</i>	2011	US	Texas A&M University
<i>MOF Technologies</i> <i>Adsorbent Nanomaterials</i>	2012	UK	Queen's University Belfast
<i>NuMat Technologies</i>	2012	US	Northwestern University
<i>MOFapps</i>	2013	Norway	University of Oslo, Norway CNRS Lyon, France University of Catalonia, Spain University of Versailles, France
<i>Matrix Sensors</i>	2013	US	-
<i>Mosaic Materials</i>	2014	US	U.C. Berkeley
<i>MOF WORX</i>	2014	Australia	Commonwealth Scientific and Industrial Research Organisation (CSIRO)
<i>Immaterial</i>	2015	UK	Cambridge University
<i>Atomis</i>	2015	Japan	Kyoto University
<i>novaMOF</i>	2016	Swiss	ETH Zurich Paul Scherrer Institute
<i>ProfMOF</i>	2016	Norway	University of Oslo
<i>ACSYNAM</i>	2016	Canada	McGill University
<i>Tarsis Technology</i>	2016	UK	Cambridge University

Table 1 PCP/MOF start-ups around the world (continued)

<i>Company Name</i>	<i>Year founded</i>	<i>country</i>	<i>University</i>
<i>Flux Technology</i>	2016	US	U.C. Berkeley
<i>Transaera</i>	2017	US	MIT
<i>ZoraMat Solutions</i>	2017	Canada	The University of Calgary
<i>UniSieve</i>	2018	Swiss	ETH Zurich
<i>EnergyX</i>	2018	Puerto Rico	-
<i>Water Harvesting Inc.</i>	2018	US	U.C. Berkeley
<i>SyncMOF</i>	2019	Japan	Nagoya University
<i>LANTHA Sensors</i>	2019	US	The University of Texas

First of all, the production cost is a crucial matter from the industrial point of view. In this Faraday Discussion, a case of a complete assessment of large-scale production cost was discussed.¹⁷⁰ This estimation was based on the economically green and the ton-scale production of the prototypical MOF MIL-160(Al). This, for the first time, includes a complete economic analysis considering the investment in a production plant. The result showed that the production scale impacted the production cost significantly decreased when the manufacturing scale is larger. This study demonstrates the possibility for MOF to reach reasonable competitive prices, highlighting the potential to reach the market for large-scale applications.

Another important aspect to realize MOF materials in actual applications but often overlooked is the utilization of the macroscopic form of the materials. Most academic studies on MOFs are focused on their powdery form. However, powder samples are not suited for industrial use in most cases due to their dustiness and inevitable pressure drop in fluid flow applications. Pelletization is one of the most straightforward approaches and has been well studied. However, the high pressure required during the pelletization process sometimes alters or destroys the porosity of the MOF. Thus, sensible choices of mechanical conditions and appropriate binders are necessary. At the meeting, the investigation of monolithic form was discussed for its use in the gas separation process.¹⁷¹ In contrast to high-pressure pelletization, self-shaping methods can lead to a reduction in cost and the risk of MOF collapse. It was demonstrated that the monolithic form of MOF materials exhibits superior volumetric gas sorption performance compared to packed powder materials, keeping similar kinetics.

The development of green synthesis approaches is also essential when considering industrial scale-up. Typically, the MOF synthetic procedure involves non-negligible environmental and health risks. For example, the most common solvothermal synthetic methods for MOF often involve toxic and non-renewable solvents. Thus, attention is given to the development of greener and industrially acceptable synthetic procedures based on (i) safer solvent or reaction media such as water, (ii) sustainable metal ions, and (iii) biocompatible organic linkers (iv) minimization of harmful by-products.^{172, 173} A better understanding of the green processes involved in MOF fabrication should lead to improved sustainability of MOF application.

8. Conclusions

To date, the control of the size, shape, and structure of MOF crystals with variable metal nodes and organic ligands has been achieved by various synthetic methods. Toward multi-functions, the molecule-level control (e.g., ligand design, chirality),

mesoscopic scale control of defects and disorder across the crystal have been intensively studied and employed in the synthetic strategies. Challenging targets are hybridizations (e.g., MOF-on-MOF, MOF based composites with other organic and inorganic materials),^{40, 63} as well as the construction of asymmetric and anisotropic hierarchical structures,^{94, 95, 174} MOFs have now evolved from the chemistry of their network structure (reticular chemistry) to functional interface chemistry with various materials, ranging from the mesoscopic to the macroscopic regime.

Melting or missing are keywords for defected MOFs. In such an emerging area, the boosting developments on the increasing diversification of applications, defects induced functions, and stimuli-responsive flexible structures contribute to a growing acceptance of disorder and defects.^{32, 33, 175, 176} The direct observation of missing linkers or nodes of MOFs by STM (2004),¹²² TEM (2019),¹²³ and AFM (2019)¹²⁶ provided solid proof of the existence of defects on the dynamic surface and in the common frameworks. Targeting the defects control, various methods such as hard/soft template,¹⁷⁷ etching,¹⁷⁸ redox reactions,¹⁷⁹ coordination modulation¹⁸⁰ and electrochemical synthesis¹⁸¹ have been successfully developed. MOFs with too many defects and disorders that lost the long-range order can be treated as amorphous MOFs (*a*MOFs). Glassy MOFs are a sub-class of *a*MOFs that retain the crystalline MOFs' short-range order and connectivity, which was generally prepared by quenching high-temperature liquid MOFs, ball milling, pressurization, and heating (without melting).^{175, 176}

MOFs are well-designed, and a wide variety of porous structures have been synthesized, including thermodynamic stability, chemical resistance, processability, low cost, etc. MOFs are now at the stage of commercialization. One of the authors has always advocated that MOFs will contribute significantly to gas science and technology.^{12, 13} MOFs are expected to have unexpected applications such as drug delivery for our health, water purification, and harmful drug removal from polluted water. The theme, "MOF for energy and environment," in this Faraday Discussion is spot on now.

The development of the 4th generation MOF will contribute to the solution of current unsolved global problems and provide an important framework for scientific discovery and the creation of new concepts.

Author Contributions

SK set the conceptual content and overall section of the paper and finalised the manuscript; MY, ZX, and KO researched and wrote their respective parts of the article.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by a KAKENHI Grant-in-Aid for Scientific Research (S) (JP18H05262) and Early-Career Scientists (JP19K15584) from the Japan Society for the Promotion of Science (JSPS).

Notes and references

- 1 S. R. Batten, N. R. Champness, X.-M. Chen, J. Garcia-Martinez, S. Kitagawa, L. Öhrström, M. O'Keeffe, M. P. Suh and J. Reedijk, *Pure Appl. Chem.*, 2013, **85**, 1715-1724.
- 2 S. Kitagawa, R. Kitaura and S. i. Noro, *Angew. Chem. Int. Ed.*, 2004, **43**, 2334-2375.
- 3 G. Férey and C. Serre, *Chem. Soc. Rev.*, 2009, **38**, 1380-1399.
- 4 H. Furukawa, K. E. Cordova, M. O'Keeffe and O. M. Yaghi, *Science*, 2013, **341**, 1230444.
- 5 D. J. O'Hearn, A. Bajpai and M. J. Zaworotko, *Small*, 2021, **17**, 2006351.
- 6 P. Z. Moghadam, A. Li, S. B. Wiggin, A. Tao, A. G. Maloney, P. A. Wood, S. C. Ward and D. Fairen-Jimenez, *Chem. Mater.*, 2017, **29**, 2618-2625.
- 7 S. L. James, C. J. Adams, C. Bolm, D. Braga, P. Collier, T. Friščić, F. Grepioni, K. D. M. Harris, G. Hyett, W. Jones, A. Krebs, J. Mack, L. Maini, A. G. Orpen, I. P. Parkin, W. C. Shearouse, J. W. Steed and D. C. Waddell, *Chem. Soc. Rev.*, 2012, **41**, 413-447.
- 8 G. L. Smith, J. E. Eyley, X. Han, X. Zhang, J. Li, N. M. Jacques, H. G. W. Godfrey, S. P. Argent, L. J. McCormick McPherson, S. J. Teat, Y. Cheng, M. D. Frogley, G. Cinque, S. J. Day, C. C. Tang, T. L. Eason, S. Rudić, A. J. Ramirez-Cuesta, S. Yang and M. Schröder, *Nat. Mater.*, 2019, **18**, 1358-1365.
- 9 S. Kitagawa, *Faraday Discuss.*, 2017, **201**, 395-404.
- 10 F. Discussions, *Cooperative Phenomena in Framework Materials*, Royal Society of Chemistry, 2021.
- 11 S. Horike, S. Shimomura and S. Kitagawa, *Nat. Chem.*, 2009, **1**, 695-704.
- 12 S. Kitagawa, *Angew. Chem. Int. Ed.*, 2015, **54**, 10686-10687.
- 13 S. Kitagawa, *Acc. Chem. Res.*, 2017, **50**, 514-516.
- 14 R. Fucci and C. M. V. Velde, *Faraday Discuss.*, 2021, DOI: 10.1039/D1FD00026H.
- 15 W. Gong, Y. Liu and Y. Cui, *Faraday Discuss.*, 2021, DOI: 10.1039/D1FD00014D.
- 16 S. Furukawa, K. Hirai, Y. Takashima, K. Nakagawa, M. Kondo, T. Tsuruoka, O. Sakata and S. Kitagawa, *Chem. Commun.*, 2009, 5097-5099.

- 17 S. Furukawa, K. Hirai, K. Nakagawa, Y. Takashima, R. Matsuda, T. Tsuruoka, M. Kondo, R. Haruki, D. Tanaka and H. Sakamoto, *Angew. Chem. Int. Ed.*, 2009, **48**, 1766-1770.
- 18 P. Chen, J. Chen, X. Hu and C. Wang, *Faraday Discuss.*, 2021, DOI: 10.1039/D1FD00016K.
- 19 Y. Sakata, S. Furukawa, M. Kondo, K. Hirai, N. Horike, Y. Takashima, H. Uehara, N. Louvain, M. Meilikhov and T. Tsuruoka, *Science*, 2013, **339**, 193-196.
- 20 S. Sakaida, K. Otsubo, O. Sakata, C. Song, A. Fujiwara, M. Takata and H. Kitagawa, *Nat. Chem.*, 2016, **8**, 377-383.
- 21 S. Wannapaiboon, A. Schneemann, I. Hante, M. Tu, K. Epp, A. L. Semrau, C. Sternemann, M. Paulus, S. J. Baxter, G. Kieslich and R. A. Fischer, *Nat. Commun.*, 2019, **10**, 346.
- 22 S. Krause, V. Bon, I. Senkowska, D. M. Töbrens, D. Wallacher, R. S. Pillai, G. Maurin and S. Kaskel, *Nat. Commun.*, 2018, **9**, 1573.
- 23 M. A. Borysiewicz, J.-H. Dou, I. Stassen and M. Dinca, *Faraday Discuss.*, 2021, DOI: 10.1039/d1fd00028d.
- 24 T. D. Bennett, J.-C. Tan, Y. Yue, E. Baxter, C. Ducati, N. J. Terrill, H. H. M. Yeung, Z. Zhou, W. Chen, S. Henke, A. K. Cheetham and G. N. Greaves, *Nat. Commun.*, 2015, **6**, 8079.
- 25 S. Horike, D. Umeyama, M. Inukai, T. Itakura and S. Kitagawa, *J. Am. Chem. Soc.*, 2012, **134**, 7612-7615.
- 26 D. Umeyama, S. Horike, M. Inukai, T. Itakura and S. Kitagawa, *J. Am. Chem. Soc.*, 2015, **137**, 864-870.
- 27 T. D. Bennett, Y. Yue, P. Li, A. Qiao, H. Tao, N. G. Greaves, T. Richards, G. I. Lampronti, S. A. Redfern and F. d. r. Blanc, *J. Am. Chem. Soc.*, 2016, **138**, 3484-3492.
- 28 S. Horike, D. Umeyama and S. Kitagawa, *Acc. Chem. Res.*, 2013, **46**, 2376-2384.
- 29 S. H. Park and S. J. Lee, *Adv. Funct. Mater.*, 2019, **29**, 1904016.
- 30 C. Liu, J. Wang, J. Wan, Y. Cheng, R. Huang, C. Zhang, W. Hu, G. Wei and C. Yu, *Angew. Chem. Int. Ed.*, 2020, **59**, 3630-3637.
- 31 Y. Wang, H. Jin, Q. Ma, K. Mo, H. Mao, A. Feldhoff, X. Cao, Y. Li, F. Pan and Z. Jiang, *Angew. Chem. Int. Ed.*, 2020, **59**, 4365-4369.
- 32 M. J. Cliffe, W. Wan, X. Zou, P. A. Chater, A. K. Kleppe, M. G. Tucker, H. Wilhelm, N. P. Funnell, F.-X. Coudert and A. L. Goodwin, *Nat. Commun.*, 2014, **5**, 4176.
- 33 Z. Fang, B. Bueken, D. E. De Vos and R. A. Fischer, *Angew. Chem. Int. Ed.*, 2015, **54**, 7234-7254.
- 34 S. Choi, T. Kim, H. Ji, H. J. Lee and M. Oh, *J. Am. Chem. Soc.*, 2016, **138**, 14434-14440.
- 35 Y. Gu, Y.-n. Wu, L. Li, W. Chen, F. Li and S. Kitagawa, *Angew. Chem. Int. Ed.*, 2017, **56**, 15658-15662.
- 36 Y.-S. Wei, M. Zhang, M. Kitta, Z. Liu, S. Horike and Q. Xu, *J. Am. Chem. Soc.*, 2019, **141**, 7906-7916.
- 37 Z. Wang, J. Liu, B. Lukose, Z. Gu, P. G. Weidler, H. Gliemann, T. Heine and C. Wöll, *Nano Lett.*, 2014, **14**, 1526-1529.
- 38 M. S. Yao, J. W. Xiu, Q. Q. Huang, W. H. Li, W. W. Wu, A. Q. Wu, L. A. Cao, W. H. Deng, G. E. Wang and G. Xu, *Angew. Chem. Int. Ed.*, 2019, **58**, 14915-14919.
- 39 Z. Wang, S. Wannapaiboon, K. Rodewald, M. Tu, B. Rieger and R. A. Fischer, *J. Mater. Chem. A*, 2018, **6**, 21295-21303.
- 40 H. Zhang, C. Gu, M.-S. Yao and S. Kitagawa, *Adv. Energy Mater.*, 2021, DOI: 10.1002/aenm.202100321.
- 41 H. V. Doan, H. T. Nguyen, V. P. Ting, S. Guan, J.-C. Eloi, S. R. Hall and X. N. Pham, *Faraday Discuss.*, 2021, DOI: 10.1039/D1FD00010A.
- 42 C. E. Pompe and P. Á. Szilágyi, *Faraday Discuss.*, 2021, DOI: 10.1039/D1FD00012H.
- 43 J. Ha and H. R. Moon, *CrystEngComm*, 2021, **23**, 2337-2354.
- 44 L. Heinke and C. Wöll, *Adv. Mater.*, 2019, **31**, 1806324.
- 45 X. Liu, Y. Li, Y. Ban, Y. Peng, H. Jin, H. Bux, L. Xu, J. Caro and W. Yang, *Chem. Commun.*, 2013, **49**, 9140-9142.
- 46 X. Song, T. K. Kim, H. Kim, D. Kim, S. Jeong, H. R. Moon and M. S. Lah, *Chem. Mater.*, 2012, **24**, 3065-3073.
- 47 D. Mutruc, A. Goulet - Hanssens, S. Fairman, S. Wahl, A. Zimathies, C. Knie and S. Hecht, *Angew. Chem. Int. Ed.*, 2019, **58**, 12862-12867.
- 48 H. J. Lee, Y. J. Cho, W. Cho and M. Oh, *Acs Nano*, 2013, **7**, 491-499.
- 49 O. Shekhah, H. Wang, D. Zacher, R. A. Fischer and C. Wöll, *Angew. Chem. Int. Ed.*, 2009, **48**, 5038-5041.
- 50 D. Zacher, K. Yussenko, A. Bétard, S. Henke, M. Molon, T. Ladnorg, O. Shekhah, B. Schüpbach, T. de los Arcos and M. Krasnopolski, *Chemistry—A European Journal*, 2011, **17**, 1448-1455.
- 51 O. Shekhah, K. Hirai, H. Wang, H. Uehara, M. Kondo, S. Diring, D. Zacher, R. A. Fischer, O. Sakata, S. Kitagawa, S. Furukawa and C. Woll, *Dalton Trans.*, 2011, **40**, 4954-4958.
- 52 K. Ikigaki, K. Okada, Y. Tokudome, T. Toyao, P. Falcaro, C. J. Doonan and M. Takahashi, *Angew. Chem. Int. Ed.*, 2019, **58**, 6886-6890.
- 53 B. Liu, M. Ma, D. Zacher, A. Bétard, K. Yussenko, N. Metzler-Nolte, C. Wöll and R. A. Fischer, *J. Am. Chem. Soc.*, 2011, **133**, 1734-1737.
- 54 B. Liu, M. Tu, D. Zacher and R. A. Fischer, *Adv. Funct. Mater.*, 2013, **23**, 3790-3798.
- 55 V. Chernikova, O. Shekhah, I. Spanopoulos, P. N. Trikalitis and M. Eddaoudi, *Chem. Commun.*, 2017, **53**, 6191-6194.
- 56 M.-S. Yao, W.-H. Li and G. Xu, *Coord. Chem. Rev.*, 2021, **426**, 213479.
- 57 K. Hirai, S. Furukawa, M. Kondo, H. Uehara, O. Sakata and S. Kitagawa, *Angew. Chem. Int. Ed.*, 2011, **50**, 8057-8061.
- 58 M. Pan, Y. X. Zhu, K. Wu, L. Chen, Y. J. Hou, S. Y. Yin, H. P. Wang, Y. N. Fan and C. Y. Su, *Angew. Chem. Int. Ed.*, 2017, **56**, 14582-14586.
- 59 Q. Zhang, Z. Yang, B. Chen and X. Liang, *Chem. Commun.*, 2019, **55**, 8450-8453.
- 60 T. Li, J. E. Sullivan and N. L. Rosi, *J. Am. Chem. Soc.*, 2013, **135**, 9984-9987.
- 61 K. Jin, X. Huang, L. Pang, J. Li, A. Appel and S. Wherland, *Chem. Commun.*, 2002, 2872-2873.
- 62 H. Yehia, T. J. Pisklak, J. P. Ferraris, K. J. Balkus and I. H. Musselman, *Abstr. Pap. Am. Chem. Soc.*, 2004, **227**, U351-U351.
- 63 M. Kalaj, K. C. Bentz, S. Ayala Jr, J. M. Palomba, K. S. Barcus, Y. Katayama and S. M. Cohen, *Chem. Rev.*, 2020, **120**, 8267-8302.
- 64 B. Le Ouay, M. Boudot, T. Kitao, T. Yanagida, S. Kitagawa and T. Uemura, *J. Am. Chem. Soc.*, 2016, **138**, 10088-10091.
- 65 A. Knebel, A. Bavykina, S. J. Datta, L. Sundermann, L. Garzon-Tovar, Y. Lebedev, S. Durini, R. Ahmad, S. M. Kozlov and G. Shterk, *Nat. Mater.*, 2020, **19**, 1346-1353.
- 66 S. Hermes, M. K. Schröter, R. Schmid, L. Khodeir, M. Muhler, A. Tissler, R. W. Fischer and R. A. Fischer, *Angew. Chem. Int. Ed.*, 2005, **44**, 6237-6241.
- 67 H.-L. Jiang, T. Akita, T. Ishida, M. Haruta and Q. Xu, *J. Am. Chem. Soc.*, 2011, **133**, 1304-1306.
- 68 G. Li, H. Kobayashi, J. M. Taylor, R. Ikeda, Y. Kubota, K. Kato, M. Takata, T. Yamamoto, S. Toh and S. Matsumura, *Nat. Mater.*, 2014, **13**, 802-806.
- 69 M. Zhao, K. Yuan, W. Yun, G. Li, J. Guo, G. Lin, W. Hu, H. Zhao and Z. Tang, *Nature*, 2016, **539**, 76-80.

- 70 A. M. Abdel-Mageed, B. Rungtaweivoranit, M. Parlinska-Wojtan, X. Pei, O. M. Yaghi and R. J. Behm, *J. Am. Chem. Soc.*, 2019, **141**, 5201-5210.
- 71 Y. K. Hwang, D. Y. Hong, J. S. Chang, S. H. Jhung, Y. K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre and G. Férey, *Angew. Chem.*, 2008, **120**, 4212-4216.
- 72 E. J. Kim, R. L. Siegelman, H. Z. Jiang, A. C. Forse, J.-H. Lee, J. D. Martell, P. J. Milner, J. M. Falkowski, J. B. Neaton and J. A. Reimer, *Science*, 2020, **369**, 392-396.
- 73 M. S. Yao, W. X. Tang, G. E. Wang, B. Nath and G. Xu, *Adv. Mater.*, 2016, **28**, 5229-5234.
- 74 Z. Jiang, X. Xu, Y. Ma, H. S. Cho, D. Ding, C. Wang, J. Wu, P. Oleynikov, M. Jia and J. Cheng, *Nature*, 2020, **586**, 549-554.
- 75 W.-w. Zhan, Q. Kuang, J.-z. Zhou, X.-j. Kong, Z.-x. Xie and L.-s. Zheng, *J. Am. Chem. Soc.*, 2013, **135**, 1926-1933.
- 76 Y. Peng, M. Zhao, B. Chen, Z. Zhang, Y. Huang, F. Dai, Z. Lai, X. Cui, C. Tan and H. Zhang, *Adv. Mater.*, 2018, **30**, 1705454.
- 77 W.-H. Chen, M. Vázquez-González, A. Zoabi, R. Abu-Reziq and I. Willner, *Nat. Catal.*, 2018, **1**, 689-695.
- 78 M. Muschi, A. Lalitha, S. Sene, D. Aureau, M. Fregnaud, I. Esteve, L. Rivier, N. Ramsahye, S. Devautour-Vinot, C. Sicard, N. Menguy, C. Serre, G. Maurin and N. Steunou, *Angew. Chem. Int. Ed.*, 2020, **59**, 10353-10358.
- 79 T. Wei, M. Zhang, P. Wu, Y.-J. Tang, S.-L. Li, F.-C. Shen, X.-L. Wang, X.-P. Zhou and Y.-Q. Lan, *Nano Energy*, 2017, **34**, 205-214.
- 80 S. Bi, H. Banda, M. Chen, L. Niu, M. Chen, T. Wu, J. Wang, R. Wang, J. Feng and T. Chen, *Nat. Mater.*, 2020, **19**, 552-558.
- 81 J. Han, M. Zhang, G. Chen, Y. Zhang, Q. Wei, Y. Zhuo, G. Xie, R. Yuan and S. Chen, *J. Mater. Chem. B*, 2017, **5**, 8330-8336.
- 82 Z. Wang, S. Wang, A. Wang, X. Liu, J. Chen, Q. Zeng, L. Zhang, W. Liu and L. Zhang, *J. Mater. Chem. A*, 2018, **6**, 17227-17234.
- 83 Y. Lu, H. Zhang, J. Y. Chan, R. Ou, H. Zhu, M. Forsyth, E. M. Marijanovic, C. M. Doherty, P. J. Marriott and M. M. B. Holl, *Angew. Chem. Int. Ed.*, 2019, **58**, 16928-16935.
- 84 F. Li, D. Wang, Q.-J. Xing, G. Zhou, S.-S. Liu, Y. Li, L.-L. Zheng, P. Ye and J.-P. Zou, *Appl. Catal., B*, 2019, **243**, 621-628.
- 85 H. J. Peng, J. Raya, F. Richard, W. Baaziz, O. Ersen, A. Ciesielski and P. Samori, *Angew. Chem. Int. Ed.*, 2020, **59**, 19602-19609.
- 86 W. L. Xue, W. H. Deng, H. Chen, R. H. Liu, J. M. Taylor, Y. K. Li, L. Wang, Y. H. Deng, W. H. Li, Y. Y. Wen, G. E. Wang, C. Q. Wan and G. Xu, *Angew. Chem. Int. Ed. Engl.*, 2021, **60**, 1290-1297.
- 87 C. Ma and J. J. Urban, *Adv. Funct. Mater.*, 2019, **29**, 1903243.
- 88 A. K. Chaudhari, I. Han and J.-C. Tan, *Adv. Mater.*, 2015, **27**, 4438-4446.
- 89 N. Liédana, A. Galve, C. Rubio, C. Téllez and J. Coronas, *ACS Appl. Mater. Interfaces*, 2012, **4**, 5016-5021.
- 90 D. Wang, H. Wu, J. Zhou, P. Xu, C. Wang, R. Shi, H. Wang, H. Wang, Z. Guo and Q. Chen, *Adv. Sci.*, 2018, **5**, 1800287.
- 91 M. C. So, S. Jin, H.-J. Son, G. P. Wiederrecht, O. K. Farha and J. T. Hupp, *J. Am. Chem. Soc.*, 2013, **135**, 15698-15701.
- 92 K. T. Mahmudov, M. N. Kopylovich, M. F. C. Guedes da Silva and A. J. L. Pombeiro, *Coord. Chem. Rev.*, 2017, **345**, 54-72.
- 93 N. Hosono and T. Uemura, *Matter*, 2020, **3**, 652-663.
- 94 T. Qiu, S. Gao, Z. Liang, D. G. Wang, H. Tabassum, R. Zhong and R. Zou, *Angew. Chem. Int. Ed.*, 2021, **60**, 17314-17336.
- 95 L. Feng, K.-Y. Wang, J. Powell and H.-C. Zhou, *Matter*, 2019, **1**, 801-824.
- 96 J.-S. M. Lee, K.-i. Otake and S. Kitagawa, *Coord. Chem. Rev.*, 2020, **421**, 213447.
- 97 J. Reboul, S. Furukawa, N. Horike, M. Tsotsalas, K. Hirai, H. Uehara, M. Kondo, N. Louvain, O. Sakata and S. Kitagawa, *Nat. Mater.*, 2012, **11**, 717-723.
- 98 G.-Y. Jeong, R. Ricco, K. Liang, J. Ludwig, J.-O. Kim, P. Falcaro and D.-P. Kim, *Chem. Mater.*, 2015, **27**, 7903-7909.
- 99 W. Liu, J. Huang, Q. Yang, S. Wang, X. Sun, W. Zhang, J. Liu and F. Huo, *Angew. Chem. Int. Ed.*, 2017, **56**, 5512-5516.
- 100 L. Feng, X.-L. Lv, T.-H. Yan and H.-C. Zhou, *J. Am. Chem. Soc.*, 2019, **141**, 10342-10349.
- 101 N. Yanai and S. Granick, *Angew. Chem. Int. Ed.*, 2012, **51**, 5638-5641.
- 102 É. Whelan, F. W. Steuber, T. Gunnlaugsson and W. Schmitt, *Coord. Chem. Rev.*, 2021, **437**, 213757.
- 103 Y. Cui, Y. Yue, G. Qian and B. Chen, *Chem. Rev.*, 2012, **112**, 1126-1162.
- 104 C. R. Martin, K. C. Park, R. E. Corkill, P. Kittikhunnatham, G. A. Leith, A. Mathur, Sakiru L. Abiodun, A. B. Greytak and N. B. Shustova, *Faraday Discuss.*, 2021, DOI: 10.1039/D1FD00013F.
- 105 G.-X. Wen, Y.-P. Wu, W.-W. Dong, J. Zhao, D.-S. Li and J. Zhang, *Inorg. Chem.*, 2016, **55**, 10114-10117.
- 106 S. Xing and C. Janiak, *Chem. Commun.*, 2020, **56**, 12290-12306.
- 107 P. M. Stanley, M. Parkulab, B. Rieger, J. Warnan and R. A. Fischer, *Faraday Discuss.*, 2021, DOI: 10.1039/D1FD00009H.
- 108 T. Kajiwara, M. Fujii, M. Tsujimoto, K. Kobayashi, M. Higuchi, K. Tanaka and S. Kitagawa, *Angew. Chem.*, 2016, **128**, 2747-2750.
- 109 L. Sun, M. G. Campbell and M. Dincă, *Angew. Chem. Int. Ed.*, 2016, **55**, 3566-3579.
- 110 B. Zhu, D. Wen, Z. Liang and R. Zou, *Coord. Chem. Rev.*, 2021, **446**, 214119.
- 111 Z. Meng, R. M. Stolz, L. Mendecki and K. A. Mirica, *Chem. Rev.*, 2019, **119**, 478-598.
- 112 L. S. Xie, G. Skorupskii and M. Dinca, *Chem. Rev.*, 2020, **120**, 8536-8580.
- 113 S. Takaishi, M. Hosoda, T. Kajiwara, H. Miyasaka, M. Yamashita, Y. Nakanishi, Y. Kitagawa, K. Yamaguchi, A. Kobayashi and H. Kitagawa, *Inorg. Chem.*, 2009, **48**, 9048-9050.
- 114 J.-H. Dou, M. Q. Arguilla, Y. Luo, J. Li, W. Zhang, L. Sun, J. L. Mancuso, L. Yang, T. Chen and L. R. Parent, *Nat. Mater.*, 2021, **20**, 222-228.
- 115 X. Huang, P. Sheng, Z. Y. Tu, F. J. Zhang, J. H. Wang, H. Geng, Y. Zou, C. A. Di, Y. P. Yi, Y. M. Sun, W. Xu and D. B. Zhu, *Nat. Commun.*, 2015, **6**, 7408.
- 116 M. Hmadeh, Z. Lu, Z. Liu, F. Gándara, H. Furukawa, S. Wan, V. Augustyn, R. Chang, L. Liao, F. Zhou, E. Perre, V. Ozolins, K. Suenaga, X. Duan, B. Dunn, Y. Yamamoto, O. Terasaki and O. M. Yaghi, *Chem. Mater.*, 2012, **24**, 3511-3513.
- 117 X. Song, X. Wang, Y. Li, C. Zheng, B. Zhang, C. a. Di, F. Li, C. Jin, W. Mi and L. Chen, *Angew. Chem. Int. Ed.*, 2020, **59**, 1118-1123.
- 118 J. Liu, D. Yang, Y. Zhou, G. Zhang, G. Xing, Y. Liu, Y. Ma, O. Terasaki, S. Yang and L. Chen, *Angew. Chem. Int. Ed.*, 2021, **60**, 14473-14479.
- 119 R. Sakamoto, K. Takada, T. Pal, H. Maeda, T. Kambe and H. Nishihara, *Chem. Commun.*, 2017, **53**, 5781-5801.
- 120 S.-S. Bao, G. K. H. Shimizu and L.-M. Zheng, *Coord. Chem. Rev.*, 2019, **378**, 577-594.
- 121 D.-W. Lim and H. Kitagawa, *Chem. Rev.*, 2020, **120**, 8416-8467.
- 122 S. Stepanow, M. Lingenfelder, A. Dmitriev, H. Spillmann, E. Delvigne, N. Lin, X. Deng, C. Cai, J. V. Barth and K. Kern, *Nat. Mater.*, 2004, **3**, 229-233.

- 123 L. Liu, Z. Chen, J. Wang, D. Zhang, Y. Zhu, S. Ling, K.-W. Huang, Y. Belmabkhout, K. Adil, Y. Zhang, B. Slater, M. Eddaoudi and Y. Han, *Nat. Chem.*, 2019, **11**, 622-628.
- 124 H. Deng, S. Grunder, K. E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gándara, A. C. Whalley, Z. Liu and S. Asahina, *Science*, 2012, **336**, 1018-1023.
- 125 O. I. Lebedev, F. Millange, C. Serre, G. Van Tendeloo and G. Férey, *Chem. Mater.*, 2005, **17**, 6525-6527.
- 126 N. Hosono, A. Terashima, S. Kusaka, R. Matsuda and S. Kitagawa, *Nat. Chem.*, 2019, **11**, 109-116.
- 127 M. Ge, T. Yang, Y. Wang, F. Carraro, W. Liang, C. Doonan, P. Falcaro, H. Zheng, X. Zou and Z. Huang, *Faraday Discuss.*, 2021, DOI: 10.1039/D1FD00020A.
- 128 Z. Huang, E. S. Grape, J. Li, A. K. Inge and X. Zou, *Coord. Chem. Rev.*, 2021, **427**, 213583.
- 129 B. L. Nannenga, D. Shi, A. G. Leslie and T. Gonen, *Nat. Methods*, 2014, **11**, 927-930.
- 130 D. Zhang, P. Oleynikov, S. Hovmöller and X. Zou, *Z. Kristallogr. Cryst. Mater.*, 2010, **225**, 94-102.
- 131 E. Mugnaioli, T. Gorelik and U. Kolb, *Ultramicroscopy*, 2009, **109**, 758-765.
- 132 J. Rigaku Co., Rigaku and JEOL launch a revolutionary electron diffraction platform Xtalab synergy-ED, <https://www.rigaku.com/press/tue-05252021-1200/192631151>).
- 133 R. Otero, F. Hümmlink, F. Sato, S. B. Legoas, P. Thstrup, E. Lægsgaard, I. Stensgaard, D. S. Galvão and F. Besenbacher, *Nat. Mater.*, 2004, **3**, 779-782.
- 134 M. Shoaee, M. W. Anderson and M. P. Atfield, *Angew. Chem. Int. Ed.*, 2008, **47**, 8525-8528.
- 135 N. S. John, C. Scherb, M. Shöäë, M. W. Anderson, M. P. Atfield and T. Bein, *Chem. Commun.*, 2009, 6294-6296.
- 136 F. I. Pambudi, M. W. Anderson and M. P. Atfield, *Faraday Discuss.*, 2021, DOI: 10.1039/D1FD00033K.
- 137 M. Wolf, K. Hirai, S. Toyouchi, E. Fron, W. Peeters, S. De Feyter and H. Uji-i, *Chem. Commun.*, 2020, **56**, 13331-13334.
- 138 A. I. Skoulidas, *J. Am. Chem. Soc.*, 2004, **126**, 1356-1357.
- 139 T. Düren, L. Sarkisov, O. M. Yaghi and R. Q. Snurr, *Langmuir*, 2004, **20**, 2683-2689.
- 140 L. Grajciar, O. Bludsky and P. Nachtigall, *J. Phys. Chem. Lett.*, 2010, **1**, 3354-3359.
- 141 T. Sagara, J. Klassen, J. Ortony and E. Ganz, *J. Chem. Phys.*, 2005, **123**, 014701.
- 142 T. B. Lee, D. Kim, D. H. Jung, S. B. Choi, J. H. Yoon, J. Kim, K. Choi and S.-H. Choi, *Catal. Today*, 2007, **120**, 330-335.
- 143 F. Salles, A. Ghoufi, G. Maurin, R. G. Bell, C. Mellot - Draznieks and G. Férey, *Angew. Chem. Int. Ed.*, 2008, **47**, 8487-8491.
- 144 F.-X. Coudert, M. Jeffroy, A. H. Fuchs, A. Boutin and C. Mellot-Draznieks, *J. Am. Chem. Soc.*, 2008, **130**, 14294-14302.
- 145 F.-X. Coudert, C. Mellot-Draznieks, A. H. Fuchs and A. Boutin, *J. Am. Chem. Soc.*, 2009, **131**, 11329-11331.
- 146 K. Sillar and J. Sauer, *J. Am. Chem. Soc.*, 2012, **134**, 18354-18365.
- 147 L. Chen, J. P. Mowat, D. Fairen-Jimenez, C. A. Morrison, S. P. Thompson, P. A. Wright and T. Düren, *J. Am. Chem. Soc.*, 2013, **135**, 15763-15773.
- 148 L. Zhang, Z. Hu and J. Jiang, *J. Am. Chem. Soc.*, 2013, **135**, 3722-3728.
- 149 Y. G. Chung, J. Camp, M. Haranczyk, B. J. Sikora, W. Bury, V. Krungleviciute, T. Yildirim, O. K. Farha, D. S. Sholl and R. Q. Snurr, *Chem. Mater.*, 2014, **26**, 6185-6192.
- 150 M. A. Addicoat, N. Vankova, I. F. Akter and T. Heine, *J. Chem. Theory Comput.*, 2014, **10**, 880-891.
- 151 R. Gaillac, P. Pullumbi, K. A. Beyer, K. W. Chapman, D. A. Keen, T. D. Bennett and F.-X. Coudert, *Nat. Mater.*, 2017, **16**, 1149-1154.
- 152 J.-J. Zheng, S. Kusaka, R. Matsuda, S. Kitagawa and S. Sakaki, *J. Am. Chem. Soc.*, 2018, **140**, 13958-13969.
- 153 P. G. Boyd, A. Chidambaram, E. García-Díez, C. P. Ireland, T. D. Daff, R. Bounds, A. Gładysiak, P. Schouwink, S. M. Moosavi, M. Maroto-Valer, J. A. Reimer, J. A. R. Navarro, T. K. Woo, S. Garcia, K. C. Stylianou and B. Smit, *Nature*, 2019, **576**, 253-256.
- 154 F.-X. Coudert and A. H. Fuchs, *Coord. Chem. Rev.*, 2016, **307**, 211-236.
- 155 M. Nagaoka, Y. Ohta and H. Hitomi, *Coord. Chem. Rev.*, 2007, **251**, 2522-2536.
- 156 S. S. Han, J. L. Mendoza-Cortés and W. A. Goddard III, *Chem. Soc. Rev.*, 2009, **38**, 1460-1476.
- 157 T. Düren, Y.-S. Bae and R. Q. Snurr, *Chem. Soc. Rev.*, 2009, **38**, 1237-1247.
- 158 R. Krishna and J. M. van Baten, *PCCP*, 2011, **13**, 10593-10616.
- 159 S. Keskin, J. Liu, R. B. Rankin, J. K. Johnson and D. S. Sholl, *Ind. Eng. Chem. Res.*, 2009, **48**, 2355-2371.
- 160 C. E. Wilmer, M. Leaf, C. Y. Lee, O. K. Farha, B. G. Hauser, J. T. Hupp and R. Q. Snurr, *Nat. Chem.*, 2012, **4**, 83-89.
- 161 Y. J. Colón and R. Q. Snurr, *Chem. Soc. Rev.*, 2014, **43**, 5735-5749.
- 162 S. O. Odoh, C. J. Cramer, D. G. Truhlar and L. Gagliardi, *Chem. Rev.*, 2015, **115**, 6051-6111.
- 163 Z. Shi, W. Yang, X. Deng, C. Cai, Y. Yan, H. Liang, Z. Liu and Z. Qiao, *Mol. Syst. Des. Eng.*, 2020, **5**, 725-742.
- 164 J. Schmidt, J. Shi, P. Borlido, L. Chen, S. Botti and M. A. Marques, *Chem. Mater.*, 2017, **29**, 5090-5103.
- 165 E. Ren and F.-X. Coudert, *Faraday Discuss.*, 2021, DOI: 10.1039/D1FD00024A.
- 166 M. Suyetin, *Faraday Discuss.*, 2021, DOI: 10.1039/D1FD00011J.
- 167 E. Besley and J. Glover, *Faraday Discuss.*, 2021, DOI: 10.1039/D1FD00005E.
- 168 Z. Chen, M. C. Wasson, R. J. Drout, L. Robison, K. B. Idrees, J. G. Knapp, F. A. Son, X. Zhang, W. Hierse, C. Kühn, S. Marx, B. Hernandez and O. K. Farha, *Faraday Discuss.*, 2021, **225**, 9-69.
- 169 T. Faust, *Nat. Chem.*, 2016, **8**, 990-991.
- 170 M. I. Severino, E. Gkaniatsou, F. Nouar, M. L. Pinto and C. Serre, *Faraday Discuss.*, 2021, DOI: 10.1039/D1FD00018G.
- 171 D. G. Madden, R. Babu, C. Çamur, N. Rampal, J. Silvestre-Albero, T. Curtin and D. Fairen-Jimenez, *Faraday Discuss.*, 2021, DOI: 10.1039/D1FD00017A.
- 172 S. Kumar, S. Jain, M. Nehra, N. Dilbaghi, G. Marrazza and K.-H. Kim, *Coord. Chem. Rev.*, 2020, **420**, 213407.
- 173 M. Bonneau, C. Lavenn, P. Ginet, K.-i. Otake and S. Kitagawa, *Green Chem.*, 2020, **22**, 718-724.
- 174 Z.-X. Cai, Z.-L. Wang, J. Kim and Y. Yamauchi, *Adv. Mater.*, 2019, **31**, 1804903.
- 175 T. D. Bennett and S. Horike, *Nat. Rev. Mater.*, 2018, **3**, 431-440.
- 176 S. Horike, S. S. Nagarkar, T. Ogawa and S. Kitagawa, *Angew. Chem. Int. Ed.*, 2020, **59**, 6652-6664.
- 177 H. Li, F. Meng, S. Zhang, L. Wang, M. Li, L. Ma, W. Zhang, W. Zhang, Z. Yang and T. Wu, *Angew. Chem. Int. Ed.*, 2020, **59**, 2457-2464.

ARTICLE

Journal Name

- 178 C. Avci, J. Ariñez-Soriano, A. Carné-Sánchez, V. Guillerm, C. Carbonell, I. Imaz and D. Maspoch, *Angew. Chem. Int. Ed.*, 2015, **54**, 14417-14421.
- 179 S. C. Qi, X. Y. Qian, Q. X. He, K. J. Miao, Y. Jiang, P. Tan, X. Q. Liu and L. B. Sun, *Angew. Chem. Int. Ed.*, 2019, **58**, 10104-10109.
- 180 Z. Xue, K. Liu, Q. Liu, Y. Li, M. Li, C.-Y. Su, N. Ogiwara, H. Kobayashi, H. Kitagawa and M. Liu, *Nat. Commun.*, 2019, **10**, 5048.
- 181 X. Kang, K. Lyu, L. Li, J. Li, L. Kimberley, B. Wang, L. Liu, Y. Cheng, M. D. Frogley and S. Rudić, *Nat. Commun.*, 2019, **10**, 4466.

For Table of Contents Use Only



The theme, "MOF for energy and environment," reflects the ongoing evolution of MOF from simply network chemistry to the chemistry of synergistic integration with heterogeneous materials involving other disciplines (the 4th generation type).