Phase engineering of metal-organic frameworks

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1 INTRODUCTION

Recently, phase engineering of nanomaterials (PEN) has emerged as an important strategy to modulate the atomic arrangement of nanomaterials, which can further tune their physicochemical properties and functions. Via PEN, a number of polymorphic nanomaterials, including metals and transition metal dichalcogenides, have exhibited outstanding performances in a wide range of promising applications. As a new kind of porous polymorphic materials, metal-organic frameworks (MOFs) have been extensively developed in the past decades. Constructed by metal ions/nodes with organic linkers, MOFs possess large surface area, tunable chemical compositions, and long-range ordered pore structures, making them excellent candidates for versatile applications including gas storage, separation, catalysis, drug delivery and optical device. Importantly, in addition to size, dimension and composition, the phase of MOFs, that is, the ordered arrangement of building blocks, is also a key parameter to tune the performances of MOFs. To date, considerable progress has been made in the phase-controlled synthesis and phase transformation of MOFs, which provides an effective strategy to tune the functional properties of nanomaterials by modulating the arrangement of atoms. In this review, we adopt “phase” instead of “topology” to describe the crystal structure of MOFs and summarize the recent advances in phase engineering of MOFs. The two main strategies used to control the phase of MOFs, that is, phase-controlled synthesis and phase transformation of MOFs, will be highlighted. The roles of various reaction parameters in controlling the crystal phase of MOFs are discussed. Then, the phase dependence of MOFs in various applications including luminescence, adsorption, and catalysis are introduced. Finally, some personal perspectives about the challenges and opportunities in this emerging field are presented.

KEYWORDS
crystal phase, metal-organic frameworks, phase engineering, phase transformation, phase-controlled synthesis
performances of MOFs in applications including luminescence, adsorption, and catalysis are introduced. Finally, personal perspectives are provided to discuss the challenges and opportunities for this emerging field. This review opens the way for the rational design and preparation of novel MOFs and MOF-based materials in versatile applications via PEN strategies.

2 | CRYSTAL PHASE OF MOFS

Different terminologies can be used to describe the structures of MOFs. The more frequently used term, “topology,” focuses on the connectivity of networks of MOFs [41,42] while phase emphasizes the packing mode of metal ions/nodes and linkers. To align with the terminology of PEN, in this review, we adopt “phase” to describe the ordered arrangements of metal nodes and linkers of MOFs. The unit cells of some representative phases of MOFs are shown in Figure 1. It is worth noticing that the abbreviations used in MOFs are sometimes different from those in other types of materials. For example, MOFs with face-centered cubic phase are denoted as “fcc” (Figure 1A), in which the metal nodes adopt a cubic close-packed fashion and are connected by 12 organic linkers. For metal nodes coordinated by 18 organic ligands, they often adopt a hexagonal close-packed (hcp, Figure 1B) fashion. Other commonly observed phases of MOFs including body-centered cubic (bcc, Figure 1C), primitive cubic (pcu, Figure 1D), reo (named after ReO₃, Figure 1E), dia (named after diamond, Figure 1F), scu (built from square planar and cubical nodes, Figure 1G), and cube-and-square (csq, Figure 1H) are also illustrated. In Table 1, detailed crystallographic information of MOFs discussed in this review are summarized, including linkers, metal clusters, phase, space group, and packing mode of metal clusters. Note that metal clusters with same packing mode can sometimes form different phases, which arises from different types of connectivity between metal clusters and linkers.

3 | PHASE ENGINEERING OF MOFS

3.1 | Direct phase-controlled synthesis of MOFs

In this section, direct synthesis strategies that can produce MOFs with different phases are introduced. The reported MOFs are categorized by the type of central metal, including Zr/Hf-MOFs, Mg-MOFs, Cu-MOFs, and In-MOFs.

3.1.1 | Zr/Hf-MOFs

The Zr/Hf-MOFs family is a representative example of polymeric MOFs [43,44]. Based on the types of the organic linker, Zr/Hf-MOFs with polymorphs can be further classified to ditopic carboxylate ligand- and tetra-carboxylate ligand-based Zr/Hf-MOFs.

Ditopic carboxylate ligand-based Zr/Hf-MOFs

Zr-based UiO (University of Oslo) MOFs with the fcc structure were first reported by Cavka et al. in 2008 [45]. By using the ditopic carboxylate ligands, including 1,4-benzenedicarboxylate (BDC), 4,4’-biphenyldicarboxylate (BPDC), and aminotriphenyldicarboxylate (TPDC), as the linker, UiO-66, UiO-67, and UiO-68 with fcc phase were obtained, respectively. While UiO MOFs normally crystallize into a fcc phase [34], non-fcc phase UiO MOFs, such as reo [46], hcp [38], and lns [39], have been synthesized by adjusting the reaction conditions. It is worth noting that the modulator acids play key roles in the synthesis of MOFs with novel phase. For example, using formic acid as the modulator can greatly increase the concentration of missing-cluster defects in MOFs. These cluster vacancies were formed along <100> directions of the fcc matrix, leading to the formation of the reo UiO-66(Hf) (Figure 2A) [46]. In the mid-2010s, Lin’s group synthesized a series of Zr/Hf-based hexagonal UiO MOFs with non-fcc phase by using TPDC and quaterphenyldicarboxylate (QPDC) as linkers in the
| MOF       | Phase | Linkers | Cluster | Space group | Packing mode of cluster | Reference |
|-----------|-------|---------|---------|-------------|-------------------------|-----------|
| UiO-66(Zr) | fcu   | H$_2$BDC | Z$_6$(µ$_3$-O)$_4$(µ$_3$-OH)$_4$ | Fm-3 m | Cubic Close Packing | [45,85] |
|           | hcp   | H$_2$BDC | Z$_{12}$(µ$_5$-O)$_4$(µ$_3$-OH)$_6$ | P6(3)/mmc | Hexagonal Close Packing | [51,52,57,59] |
| UiO-66(Hf) | fcu   | H$_2$BDC | H$_6$(µ$_3$-O)$_4$(µ$_3$-OH)$_4$ | Fm-3 m | Cubic Close Packing | [39] |
|           | fcu   | H$_2$F$_2$BDC | H$_6$(µ$_3$-O)$_4$(µ$_3$-OH)$_4$ | Fm-3 m | Cubic Close Packing | — |
|           | hcp   | H$_2$BDC | [H$_6$(µ$_3$-O)$_4$(µ$_3$-OH)$_4$]$_2$(µ$_2$-OH)$_6$ | P6(3)/mmc | Hexagonal Close Packing | — |
|           | hcp   | H$_2$F$_2$BDC | [H$_6$(µ$_3$-O)$_4$(µ$_3$-OH)$_4$]$_2$(µ$_2$-OH)$_6$ | P6(3)/mmc | Hexagonal Close Packing | — |
|           | hns   | H$_2$F$_2$BDC | [H$_6$(µ$_3$-O)$_4$(µ$_3$-OH)$_4$]$_2$(µ$_2$-OH)$_6$ | P6/mmm | Primitive Hexagonal Packing | — |
|           | hxl   | H$_2$F$_2$BDC | [H$_6$(µ$_3$-O)$_4$(µ$_3$-OH)$_4$]$_2$(µ$_2$-OH)$_6$ | P6/mmm | Primitive Hexagonal Packing | — |
| UiO-67(Zr) | fcu   | H$_2$BPDC | Z$_6$(µ$_3$-O)$_4$(µ$_3$-OH)$_4$ | Fm-3 m | Cubic Close Packing | [45] |
|           | hcp   | H$_2$BPDC | Z$_{12}$(µ$_5$-O)$_4$(µ$_3$-OH)$_6$ | P6(3)/mmc | Hexagonal Close Packing | [50] |
| UiO-67(Hf) | fcu   | H$_2$BPDC | H$_6$(µ$_3$-O)$_4$(µ$_3$-OH)$_4$ | Fm-3 m | Cubic Close Packing | [38] |
|           | hcp   | H$_2$BPDC | H$_{12}$(µ$_5$-O)$_8$(µ$_3$-OH)$_8$ | P6(3)/mmc | Hexagonal Close Packing | [50] |
|           | hcp   | H$_2$BPDC | H$_{12}$(µ$_5$-O)$_8$(µ$_3$-OH)$_8$ | P6(3)/mmc | Hexagonal Close Packing | [50] |
|           | hns   | H$_2$BPDC | [H$_6$(µ$_3$-O)$_4$(µ$_3$-OH)$_4$]$_2$(µ$_2$-OH)$_6$ | P6/mmm | Primitive Hexagonal Packing | [38,39] |
|           | hxl   | H$_2$BPDC | [H$_6$(µ$_3$-O)$_4$(µ$_3$-OH)$_4$]$_2$(µ$_2$-OH)$_6$ | P6/mmm | Primitive Hexagonal Packing | [38] |
| Zr$_{12}$-BPYDC | hcp | H$_2$BPYDC | Z$_{12}$(µ$_5$-O)$_4$(µ$_3$-OH)$_6$ | P6(3)/mmc | Hexagonal Close Packing | [50] |
| Hf$_{12}$-BPYDC | hcp | H$_2$BPYDC | H$_{12}$(µ$_5$-O)$_8$(µ$_3$-OH)$_8$ | P6(3)/mmc | Hexagonal Close Packing | [50] |
| UiO-68(Zr) | fcu   | H$_2$TPDC | Z$_6$(µ$_3$-O)$_4$(µ$_3$-OH)$_4$ | Fm-3 m | Cubic Close Packing | [45] |
|           | hcp   | H$_2$TPDC | Z$_{12}$(µ$_5$-O)$_4$(µ$_3$-OH)$_6$ | P6(3)/mmc | Hexagonal Close Packing | [56] |
| UiO (Zr)  | fcu   | H$_2$DCDPA | Z$_6$(µ$_3$-O)$_4$(µ$_3$-OH)$_4$ | Fm-3 m | Cubic Close Packing | [58] |
|           | hcp   | H$_2$DCDPA | Z$_{12}$(µ$_5$-O)$_8$(µ$_3$-OH)$_8$ | P6(3)/mmc | Hexagonal Close Packing | — |
| MOL(Zr)   | hxl   | H$_2$DCDPA | Z$_6$(µ$_3$-O)$_4$(µ$_3$-OH)$_4$ | P6/mmm | Primitive Hexagonal Packing | — |
| EHU-30    | hex   | H$_2$BDC | Z$_6$(µ$_3$-O)$_4$(µ$_3$-OH)$_4$ | P6/mmc | Primitive Hexagonal Packing | [53,85] |
| CAU-38(Ce/Zr) | bcu | H$_2$PZDC | CeZ$_5$(µ$_3$-O)$_4$(µ$_3$-OH)$_4$ | Pnmm | Body-centered Orthorhombic Packing | [55] |
| DUT-67    | reo   | H$_2$TDC | Z$_6$(µ$_3$-O)$_8$(µ$_3$-OH)$_2$ | Fm-3 m | — | [54] |
| DUT-69    | bct   | H$_2$TDC | Z$_6$(µ$_3$-O)$_4$(µ$_3$-OH)$_4$ | P2$_1$2$_1$2$_1$ | Primitive Orthorhombic Packing | — |
| MOF-545   | csq   | H$_4$TCPP | Z$_6$(µ$_3$-O)$_8$ | P6/mmm | Primitive Hexagonal Packing | [61] |

(Continues)
| MOF      | Phase | Linkers | Cluster | Space group | Packing mode of cluster | Reference       |
|----------|-------|---------|---------|-------------|-------------------------|-----------------|
| MOF-525  | ftw   | H₄TCPP  | Z₈₆(µ₃-O)₄(µ₃-OH)₄ | Pm-3 m      | Primitive Cubic Packing | [61,88]         |
| NU-902   | scu   | H₄TCPP  | Z₆₆(µ₃-O)₄(µ₃-OH)₄ | P4/mmm      | Primitive Cubic Packing | [62]            |
| PCN-221  | ftw   | H₄TCPP  | Z₆₆(µ₃-O)₄(µ₃-OH)₄ | Pm-3 m      | Primitive Cubic Packing | [63]            |
| PCN-222  | csq   | H₄TCPP  | Z₆₆(µ₃-OH)₄     | P6/mmm      | Primitive Hexagonal Packing | [64]           |
| PCN-223  | shp   | H₄TCPP  | Z₆₆(µ₃-O)₄(µ₃-OH)₄ | P6/mmm      | Primitive Hexagonal Packing | [65,88]         |
| PCN-224  | she   | H₄TCPP  | Z₆₆(µ₃-O)₄(µ₃-OH)₄ | I-₃ m       | —                        | [66]            |
| PCN-225  | sqc   | H₄TCPP  | Z₆₆(µ₃-O)₄(µ₃-OH)₄ | I₄(1)/amd   | Body-centered Tetragonal Packing | [67]          |
| NU-1000  | csq   | H₄TBAPy | Z₆₆(µ₃-OH)₄(µ₃-O)₄(OH)₄(OH)₂₄ | P₆/mmm      | Primitive Hexagonal Packing | [73,99]        |
| NU-901   | scu   | H₄TBAPy | Z₆₆(µ₃-OH)₄(µ₃-O)₄(OH)₄(OH)₂₄ | P₄/mmm      | Primitive Tetragonal Packing | [74,99]        |
| NU-906   | scu   | H₄TCPB-Br₂| Z₆₆(µ₃-O)₄(µ₃-OH)₄ | P₄/mmm      | Primitive Tetragonal Packing | [75,76]        |
| NU-1008  | csq   | H₄TCPB-Br₂| Z₆₆(µ₃-O)₄(µ₃-OH)₄ | P₆/mmm      | Primitive Hexagonal Packing |                |
| NU-500   | —     | H₄TCPB-Br₂| Z₆₆(µ₃-O)₄(µ₃-OH)₄ | C₂/m        | —                        | [76]            |
| NU-600   | she   | H₄TCPB-Br₂| Z₆₆(µ₃-O)₄(µ₃-OH)₄ | Pm-3 m      | Primitive Cubic Packing |                |
| [Mg₃(BTDC)₃(DMF)₄]·DMF | peu | H₂BTDC  | Mg₃(RCOO)₆    | P-1         | Triclinic Packing       | [79]            |
| [Mg₃(BTDC)₃(DMF)₄] | xsb | H₂BTDC  | Mg₃(RCOO)₆    | C₂/c        | —                        |                |
| NTU-51   | sql   | H₂fip   | Cu-based     | P₄/nmm      | Primitive Tetragonal Packing | [82]          |
| NTU-52   | dia   | H₂fip   | Cu-based     | I₄₁₂₂      | Diamond Packing         |                |
| ZMOF     | rho   | 4.5-1mDC| In-based     | I₃m-3       | Body-centered Cubic Packing | [83]           |
| sod      |        | 4.5-1mDC| In-based     | Fd₃c        | Face-centered Cubic Packing |                |
| PCN-250  | soc   | H₂ABTC  | Fe₃µ₃-oxo    | P-43n       | Primitive Cubic Packing | [40]            |
| PCN-250′ | soc   | H₂ABTC  | Fe₃µ₃-oxo    | C₂/c        | Base-centered Monoclinic Packing |                |
| PCN-250” | soc   | H₂ABTC  | Fe₃µ₃-oxo    | R-₃c        | Primitive Hexagonal Packing |                |
| bio-MOF-100 | dia-c | H₂BPDC  | Z₈₆(AD)₂O₁₆ | Cc          | Diamond Packing Packing | [93]            |
|         | lcs   | H₂BPDC  | Z₈₆(AD)₂O₁₆ | Iₐ-₃d       | —                        |                |

*The deformable property of the topology leads to the fact that one topology may have more than one type of packing mode for metal clusters.
presence of acetic acid as the modulator. Their crystal phases were first recognized as the fcu phase with structural distortions and later proved to be hcp phase by Dai et al. in 2017.

Prior to Dai et al., in the same year, Cliffe et al. found that hcp UiO-67(Hf) could be synthesized at high temperature (≥ 130 °C) with a high concentration of formic acid as the modulator (Figure 2A). Compared with fcu UiO-67(Hf), the ligand:metal ratio in hcp UiO-67(Hf) increased from the 12:2 (typical ratio in fcu phase) to 18:2, resulting in the transformation from the 12-connected Hf₆(µ₃-O)₄(µ₃-OH)₄ metal node to the 18-connected [Hf₆(µ₃-O)₄(µ₃-OH)₄]₂(µ₂-OH)₆ dimer via sharing six µ₂-OH bridges. The formation of the hcp phase UiO-67(Hf) may result from the low solubility of BPDC linker in the mixture of formic acid/N,N-dimethylformamide (DMF) and the condensation of the hafnium oxide nodes. In 2018, Ermer et al. reported the synthesis of UiO-66(Zr) with hcp phase by using acetic acid as the modulator and ionic liquid di-(tributyl-ethoxymethyl-phosphonium)terephthalate ([PBuMEE]₂[BDC]) as both the solvent and the linker precursor. By comparing different acid modulators including formic acid, acetic acid, and benzoic acid, they found that only acetic acid can lead to the formation of hcp UiO-66(Zr). Importantly, owing to the addition of [PBuMEE]₂[BDC], almost all undesired impurities in obtained hcp UiO-66(Zr) could be removed easily by simply washing the product with water. In contrast, for hcp UiO-66(Zr) obtained with H₂BDC, Na₂BDC, or 1-ethyl-3-methylimidazolium terephthalate ([EMIM][ HBDC]) as linker, the unreacted linkers remain as impurity in the product due to their low solubility in water. As a result, the sample needs to be extracted by DMF and then washed by ethanol. In another work, UiO-66(Zr) with different phases were synthesized by adding hydrochloric acid (HCl) with different concentrations. Specifically, at low HCl content (25 vol% and lower), UiO-66(Zr) with conventional fcu phase formed, whereas the increasing concentration of HCl to 50 vol% leads to the formation of hcp UiO-66(Zr). In addition, the EHU-30 (EHU: Euskal Herriko Unibertsitatea), reported as the first polymorph of UiO-66, has been synthesized by using highly concentrated methacrylic acid as the modulator. The methacrylic acid can not only slow down the nucleation and crystal growth but also act as a template to direct the framework structure. As a result, each secondary building unit [Zr₆(µ₃-O)₄(µ₃-OH)₄(µ-COO)]₁₂ is linked to eight surrounding clusters by 12 phenyl linkers, leading to the hex (primitive hexagonal lattice) phase instead of the fcu phase.

Other than UiO MOFs, other kinds of Zr- or Hf-based MOFs with different phases could also be synthesized by using acid modulators. For instance, Bon et al. reported the phase-controlled synthesis of Zr-MOFs by using 2,5-thiophenedicarboxylic acid (H₂TDC)
as linkers and acetic acid as modulators. When the amount of acetic acid (Ac) was ~120 molar equivalents of precursors, the 8-connected reo DUT-67(Zr) (DUT: Dresden University of Technology) (with a composition of \([\text{Zr}_6\text{O}_8\text{(OH)}_2\text{(TDC)}_4(\text{CH}_3\text{COO})_2])\) and reo DUT-67(Hf) (with a composition of \([\text{H}_6\text{O}_7\text{(OH)}_2\text{(TDC)}_4(\text{CH}_3\text{COO})_2])\) adopting primitive cubic packing were synthesized. Meanwhile, if the amount of acetic acid declined to 50 molar equivalents of precursors, the 10-connected body-centered tetragonal (bct) packing DUT-69(Zr) (with a composition of \([\text{Zr}_6\text{O}_8\text{(OH)}_2\text{(TDC)}_4(\text{Ac})_2])\) and bct DUT-69(Hf) (with a composition of \([\text{H}_6\text{O}_7\text{(OH)}_2\text{(TDC)}_4(\text{Ac})_2])\) were obtained. In another work, systematic investigations of the chemical system Ce\(^{4+}\)/Zr\(^{4+}\)/1-H-Pyrazole-3,5-dicarboxylic acid (H\(_2\)PZDC)/formic acid suggested that not only formic acid/metal ratio but also the ratio of metal precursor of Ce\(^{4+}\)/Zr\(^{4+}\) are important factors for the formation of MOFs with different phases. Specifically, at molar ratios of formic acid/metal of 175:2 and Ce/Zr ratio \(\sim 0.8\), the reo UiO-66(Ce/Zr) (PZDC) structure was formed. The increasing Ce\(^{4+}\)/Zr\(^{4+}\) ratio leads to the formation of the mixture of reo UiO-66(Ce/Zr) (PZDC) and reo DUT-67(Ce/Zr) (PZDC). At Ce/Zr ratio > 1.8:0.2, pure reo DUT-67(Ce) (PZDC) was formed. In another separate experiment, when the formic acid/metal ratio was fixed to 175:2 and the Ce\(^{4+}\)/Zr\(^{4+}\) ratio was varied (from 0.2 to 1.8:0.2), the as-obtained reo DUT-67(Ce/Zr) (PZDC) with tunable Ce/Zr ratios can be obtained. Further increasing the molar ratio of formic acid/metal to 350:2 at Ce\(^{4+}\)/Zr\(^{4+}\) ratios between 0.4:1.6 and 1.4:0.6 led to the formation of CAU-38(Ce/Zr) PZDC with bct phase.

Besides using acid as a modulator to tune the phase of MOFs, the addition of water in the reaction mixture may also promote the formation of MOFs with novel phase. For instance, Ji et al. found that hcp UiO-68(Zr) can be obtained by adding a suitable concentration of water to the reaction mixture.[56] Recently, Firth et al. systematically demonstrated that the amount of water and acid in the reaction mixture play equally crucial roles in synthesizing UiO family MOFs with different phases. [56] The reports suggest that the addition of modulator acid or water and the regulation of their relative concentrations could be promising strategies to directly synthesize MOFs with different phases.

Different from adding water or modulator acid into reaction mixture, Li et al. introduced a self-assembly strategy induced by salting-in species to synthesize Zr- or Hf-based UiO-66 with hcp or fcu phase in an aqueous solution.[59] According to the Hofmeister effect, the solubility of ligands (H\(_4\)BDC for UiO-66) in aqueous media could be enhanced with the use of salting-in ions. The hcp UiO-66(Zr) could be obtained by using salting-in ions with very limited solubilization capacity, like NO\(_3^-\), I\(^-\), ClO\(_4^-\), SCN\(^-\), and guanidinium (Gdm\(^+\)). When L-arginine, an extended and stronger salting-in ion, was used, the solubility of ligand (BDC) in aqueous solution was greatly increased, and the formation of the fcu phase instead of ligand-deficient hcp phase was observed. Similar to the synthesis of UiO-66(Zr), UiO-66(Hf) with hcp and fcu phase could also be synthesized using NaI and L-arginine as the mediator, respectively (Figure 2B).

**Tetra-carboxylate ligand-based Zr/Hf-MOFs**

Due to the abundant coordination sites in tetra-carboxylate ligands and the variable connectivity and symmetry of the Zr-based clusters, the combination of tetratopic carboxylic linkers and Zr-based inorganic units gives rise to multiple kinds of Zr-MOFs. 2,3,5,6-tetakis(4-carboxyphenyl) pyrazine (TCPP) is one of the most popular tetracarboxylic linkers or a zirconium acetate was formed when the amount of water or acetic acid was increased, respectively. Recently, Hu et al. found that not only the phase but also the morphology of UiO MOFs could be tuned by the addition of water or modulator acid.[58] fcu UiO(Zr) MOF with octahedral morphology was synthesized by using 4,4’-(9,10-anthracenediyl)di benzoic acid (H\(_2\)DCDA) as the linker and ZrCl\(_4\) as the metal precursor in a mixture of DMF and acetic acid. If acetic acid was changed to trifluoroacetic acid, the shape of fcu UiO(Zr) became hexagonal nanoplate. In addition, changing the solution to a mixture of water and trifluoroacetic acid could produce hxl MOL (metal-organic layers). In another separate experiment, when water was added to the reaction mixture with a volume ratio of acetic acid/water of 2:1, the hcp phase UiO(Zr) with hexagonal nanoplate morphology instead of octahedral fcu UiO(Zr) could be obtained. These reports suggest that the addition of modulator acid or water and the regulation of their relative concentrations could be promising strategies to directly synthesize MOFs with different phases.

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starting precursors (i.e., metal salts), and their concentrations and mutual ratios, various porphyrinic Zr-MOFs with different packing phases could be obtained. The first example of TCPP-based Zr-MOFs was reported by Morris et al. in 2012. In this work, the authors synthesized two kinds of Zr-MOF crystals with different phases, namely MOF-545 and MOF-525. They used zirconyl chloride octahydrate as the metal precursor and formic acid as the modulator to prepare MOF-545 crystal in a DMF solution. The MOF-545 is constructed by Zr$_6$($\mu_3$-O)$_8$ node and each node connects with eight ligands, which features a (4,8)-connected csq phase. In addition, there were triangular-shaped and hexagonal-shaped one-dimensional (1D) channels in the structure of MOF-545, with cavity diameters of 8 Å and 36 Å, respectively. By increasing the reaction temperature, decreasing the ratio of Zr precursor/H$_4$TCPP, and adding acetic acid as modulator rather than formic acid, MOF-525 with a (4,12)-connected ftw structure was prepared. Different from the 1D channel structures observed in MOF-545, MOF-525, cubic cage composed of eight corner-sharing Zr$_6$($\mu_3$-O)$_4$($\mu_3$-OH)$_4$ clusters and six face-sharing porphyrin units with an edge length of 20 Å was observed. Using the same substrate identities as this work, NU-902 was obtained by Deria et al. at a lower synthesis temperature using benzoic acid as a modulator. The structure of NU-902 is built by 8-connected Zr$_6$($\mu_3$-O)$_8$ nodes and features a new (4,8)-connected scu structure.

Parallel to the work of Morris et al., PCN-222 with the same structure as MOF-545 was reported by Feng et al. at nearly the same time. Different from the reaction condition of MOF-545, ZrCl$_4$ was used as the metal precursor with benzoic acid as modulator to synthesize PCN-222 in a N,N-diethylformamide (DEF) solution. Following this work, PCN-225 with the rarely reported (4,8)-connected sqc phase was obtained by using both benzoic acid and acetic acid as modulators. The structure of PCN-225 possesses two types of pores: the small quadrangle-shaped cavity with a size of 15 Å and the big pear-like one of 22 Å. By choosing acetic acid as the only modulator, a novel Zr-MOF was explored, denoted as PCN-221. Like MOF-525, PCN-221 also crystallizes via the primitive cubic packing in the ftw phase. However, in PCN-221, each TCPP$^{-}$ organic ligand is combined with four novel Zr$_8$ cubic units instead of the classical Zr$_6$ octahedron. In addition, the structure of PCN-221 features cubic and distorted octahedral cavities with diameters of 20 Å and 11 Å, respectively. When the solvent is changed from DEF to DMF, PCN-223 and PCN-224 could be obtained by applying acetic acid and benzoic acid as the modulators, respectively. The phase of PCN-223 is hexagonal packing with another (4,12)-connected shp structure. In PCN-223, each Zr$_6$($\mu_3$-O)$_4$($\mu_3$-OH)$_4$ unit connects with twelve porphyrinic linkers, which forms uniform triangular 1D cavities of 12 Å along the c axis. As for PCN-224, there are three-dimensional (3D) channels with a diameter of 19 Å in its (4,6)-connected she structure. Importantly, the ratio of ZrCl$_4$/H$_4$TCPP was varied while the reaction temperature (120°C) was kept constant in synthesizing PCN-222 series.

Recently, some reports aimed to understand the correlation between experimental parameters and the structure of Zr-TCPP MOFs by controlling reaction variables. For example, Gong et al. analyzed the effect of reaction temperature on the phase structure of porphyrinic Zr-MOFs while keeping other variables constant (Figure 3). The synthesis at room temperature resulted in products with a mixed phase consisting of MOF-525 and PCN-224 with ftw and she structures, respectively, while a mixture of csq PCN-222, shp PCN-223, and scu NU-902 was obtained when the temperature was raised.
to 145°C. At the same temperature, the csq PCN-222 would dominate in the product when the reaction time was further increased to 7 days, indicating that MOF-525 and PCN-224 were the kinetically preferred products while PCN-222 was the thermodynamically preferred product. In another example, Shaikh et al. investigated the effect of the modulator on the synthesis of Zr-TCPP MOFs. Using strong acids such as difluorooacetic acid, formic acid, and nitrobenzoic acid as a modulator facilitated the formation of PCN-222. PCN-223 tended to form by employing less acidic modulators, like glacial acetic acid, propionic acid, and 4-chlorobenzonic acid, while employing weak acids such as 4-methoxybenzoic acid, decanoic acid, myristic acid, and stearic acid as a modulator led to the formation of MOF-525. The function of modulators could arise from the induction of different kinds of defect sites in Zr-based MOFs. The authors proposed that strong acidic modulators (difluoroacetic acid and formic acid) and sterically demanding modulators (myristic acid and stearic acid) would produce missing cluster defects, while the less acidic modulators (propionic acid) mainly generated missing linker defects. Therefore, the modulator acidity could be the key in determining the defect structures and thus phases of MOFs.

Besides TCPP, 1,3,6,8-tetrakis(p-benzoate)pyrene (TBAPy) and 1,4-dibromo-2,3,5,6-tetrakis(4-carboxyphenyl)benzene (TCPB-Br₂) are the other two kinds of tetratopic carboxylate ligands used in phase-controlled synthesis of Zr-MOFs. In the case of TBAPy₄⁻, ligand, NU-901 and NU-1000, two Zr-MOFs with identical building blocks but different phases, have been successfully reported. csq NU-1000 was prepared by Mondloch et al. by using ZrCl₄ as the metal precursor and benzoic acid as a modulator. The csq NU-1000 possesses mesoporous 31 Å hexagonal-shaped cavities and microporous 12 Å triangular-shaped cavities. When the modulator was changed to 4-amino-benzoic acidic, NU-901 with pure scu phase was obtained. The scu NU-901 features a diamond channel of 29 Å in length and 12 Å in width. The TCPB-Br₂ is another representative flexible linker and its conformation could be tuned to synthesize Zr-MOFs with different phases. For example, Lyu et al. reported that scu-NU-906 and csq-NU-1008 could be built from the Zr₆ nodes and H₂TCPB-Br₂ linker when benzoic acid and formic acid were used as modulators in DMF, respectively. Then, Chen et al. reported the preparation of scu-NU-906 and csq-NU-1008 by using different modulators or solvents. As shown in Figure 3C, when the solvent and modulator were changed to DEF and formic acid, respectively, the NU-1008 was synthesized. However, when choosing DMF as the solvent and acetic acid as the modulator, the NU-906 was obtained. Furthermore, the evolution from 8-connected Zr₆ nodes to 6-connected Zr₆ nodes would be observed when DMF was replaced with DEF, resulting in the formation of she-NU-600. Note that in this experiment changing merely the solvent could result in the phase-controlled synthesis of MOFs. The authors proposed that the stronger basicity of DEF than DMF would increase the deprotonation rate of TCPB-Br₂₄⁻ linker, leading to a fast nucleation and slow growth process to form the lower 6-connected Zr₆ nodes. Interestingly, after the modulator was altered from acetic acid to formic acid, the NU-500 with 5-connected Zr₆ nodes was formed. The stronger competition of formate with TCPB-Br₂₄⁻ linker led to a lower coordination of NU-500 node.

Compared to the many reports about the phase-controlled synthesis of Zr/Hf-MOFs, reports of other kinds of MOFs with different phases are relatively limited. This may be explained by the high oxidation state of Zr/Hf(IV) in Zr/Hf-MOFs compared with M(I), M(II), and M(III) in M-MOFs (M stands for metal) and tunable connection number of Zr₆/Hf₆ cluster without altering the robust [Zr₆/Hf₆(μ₃-O)(μ₂-OH)]₄ core. In the following parts, Mg-MOFs, Cu-MOFs, and In-MOFs with different phases prepared by direct synthesis methods are briefly discussed.

### 3.1.2 Mg-MOFs

In Mg-MOFs, the trinuclear carboxylate unit Mg₃(RCOO)₆ is a common 6-connected node, which is often organized in a 3D network with the pcu phase. It has been reported that the Mg₃(RCOO)₆ building units can be linked by the linear 2,2’-bithiophen-5,5’-dicarboxylate (H₂BTDC) ligand to synthesize three 2D MOFs with different structures via a temperature-controlled crystallization process. As a result, the [Mg₃(BTDC)₃(DMF)₄]·DMF with a common pcu (low-temperature phase) and [Mg₃(BTDC)₃(DMF)₄]·DMF with a rare sxb (six-coordinated net, b type) (high-temperature phase) have been prepared by tuning the orientation of btcd²⁻ anions under different reaction temperatures. Specifically, the [Mg₃(BTDC)₃(DMF)₄]·DMF and [Mg₃(BTDC)₃(DMF)₄]·DMF feature the parallel and semi-parallel arrangement of the btcd²⁻ linkers, respectively.

### 3.1.3 Cu-MOFs

As for Cu-MOFs, Liu et al. reported that the reaction of copper nitrate and 5-(furan-2-yl)isophthalic acid (H₂fip) in a DMF/H₂O solution led to the formation of NTU-51 (NTU: Nanjing Tech University) with 2D planar sqa (square lattice) phase of the Cu-paddlewheel clusters by adding a trace amount of HNO₃, while the 3D diamond-like dia NTU-52 was obtained in absence of HNO₃. The carboxylate groups of the fip ligands around the Cu-paddlewheel clusters possessing different coordination orientations and different rotations of carboxylate groups caused the distinct structural difference.

### 3.1.4 In-MOFs

The phase tuning of the In-based zeolite-like MOFs (ZMOFs) was investigated by Shi et al. via tuning the concentration of structure-directing agents. The morphology and phase evolution from porous rho (rho topology) ZMOF particles to non-porous sphere-like sod (sodalite topology) ZMOF particles has been achieved by gradually increasing the concentration of hexamethylenetetramine, which performed as both structure-directing agent and space-filling species to fill the cages and channels and therefore form a non-porous structure.
3.2 Phase transformation in MOFs

Phase transformation is an important part of the phase engineering of MOFs and offers an alternative approach to tune the phase of MOFs. Although the research about the phase transformation is essential, it is still at the initial stage. Here, we summarized some representative factors that induce the phase transformation of MOFs, including modulator, solvent, mechanochemistry, and pressure.

3.2.1 Modulator

In MOFs synthesis, the modulator can not only be used to achieve the phase diversity of MOFs by direct synthesis from the precursors and linkers, but also be employed to induce the phase transformation. For example, the phase transformation from the kinetically stable \textit{hex} EHU-30 to the thermodynamically stable \textit{fcu} UiO-66 has been achieved under the mediation of acetic acid modulator and heating, which was based on a partial dissolution-recrystallization process driven by the realignment of linkers to release strain.\cite{85} Similar phase transformation mechanism was also observed in another work, where irreversible phase transformation from the microporous \textit{scu} NU-906 to the mesoporous \textit{csq} NU-1008 through dissolution-reprecipitation mechanism by soaking NU-906 in a solution of DMF/formic acid under heat treatment (Figure 4A).\cite{75} The formic acid facilitated the dissolution of NU-906 and also acted as a modulator, as a result, the intermediate solution containing Zr$_6$-clusters, TCPB-Br$_2$ linkers, formic acid and DMF was formed after the dissolution of NU-906 and led to the generation of NU-1008.

3.2.2 Solvent

The addition of solvent is also a useful strategy to induce phase transformation of MOFs. For instance, Chen et al. reported that the phase transformation from \textbf{fcu} UiO-66 to \textbf{hcp} UiO-66 can be achieved by adding a solution of acetic acid and water.\cite{57} Subsequently, by using different acetic acid/water ratio, the authors demonstrated that both acetic acid and water are crucial to this phase transformation. Notably, there was no \textbf{hcp} UiO-66 formed when heating the as-synthesized \textbf{fcu} UiO-66 in pure DI water even at 150$^\circ$C, indicating a good stability of \textbf{fcu} UiO-66 in pure water. In contrast, if the reaction mixture contains 25 vol$\%$ acetic acid and was kept undisturbed under 150$^\circ$C for 24 h, the \textbf{fcu}
UiO-66 would partially transform to hcp UiO-66. Such phase transformation from fcu UiO-66 to hcp UiO-66 could proceed further by simply increasing the acetic acid concentration to 75 vol%. However, if pure acetic acid was used to treat fcu UiO-66 at 150°C for 24 h, no hcp UiO-66 could be obtained. They proposed that acetic acid could break node-ligands bonds and form node-acetate bonds, whereas water could induce the formation of Zr$_{12}$O$_{22}$ cluster through the dimerization of the Zr$_6$O$_x$ node. In addition, compared with the directly synthesized one, the hcp UiO-66 converted from fcu UiO-66 showed more defect sites.

3.2.4 Pressure

Pressure is also an important parameter to induce the phase transformation of MOFs by distorting the porous structure or the framework of MOFs. The phase of MOFs may transform to an amorphous state under high pressure. For example, Chapman et al. reported that the volume of ZIF-8 framework was compressed quickly by 5% under hydrostatic pressure of 0.34 GPa. With the increase of pressure, the phenomenon of phase transformation from crystalline to amorphous phase was observed. However, Brunauer-Emmett-Teller (BET) test taken at different pressure-treated ZIF-8 samples suggested that the crystallinity of ZIF-8 was progressively eliminated with the increment of pressure from 0.9 GPa to 1.2 GPa. In addition, pressure could also induce the formation of a new high-pressure phase. PCN-250 with a sequential phase transformation under uniaxial mechanical pressure was reported. PCN-250 constructed by Fe$_3$µ$_3$-oxo clusters and 3,3',5,5'-azobenzenetetracarboxylate (ABTC) possess a soc (square-octahedron) net. In PCN-250, each cubic cage is composed of eight corner-sharing Fe-based clusters and six face-sharing ABTC ligands units. As shown in Figure 4C, when uniaxial pressure of 19 MPa was applied, PCN-250 underwent an irreversible phase and 1.26% contraction of framework could be observed. The PCN-250' (at 19 MPa) with metastable state could transform into a new phase PCN-250'' when the uniaxial pressure further increased to 150 MPa. Due to the high distortion caused by the flipping of ligands, all lattice angles in PCN-250’’ would no longer be 90° and the unit cell of PCN-250’’ could be converted to hexagonal lattices with higher symmetry.

3.2.5 Other methods

Besides aforementioned experimental approaches, other methods, like ligand exchange, can also be adopted to induce the phase transformation of MOFs. For example, the phase transformation from dia-c (2 fold dia$^{[91]}$) bio-MOF-100 to lcs$^{[92]}$ bio-MOF-100 has been investigated by Miera et al.$^{[93]}$ The dia-c-bio-MOF-100, built from zinc-adeninate (Zn$_6$(AD)$_2$O$_{16}$) building units connected by BPDC ligands, was soaked in iridium complexes (IrL) to perform the BPDC$^{2-}$ ligand exchange with IrL$^{2-}$ at room temperature. The phase transformation of bio-MOF-100 from the 2-fold interpenetrated dia-c to the non-interpenetrated lcs was realized via breaking and re-coordinating of metal-ligand bonds and reassembling the building units within the MOFs. Besides, reversible phase transformation between hcp and lxl UiO-67(Hf) has been reported (Figure 2A).$^{[38]}$ The phase of as-synthesized UiO-67(Hf) transformed from hcp to lxl by releasing the bpdc$^{2-}$ ligands under ambient conditions after several days. The obtained lxl UiO-67(Hf) is stable under ambient conditions for more than one year. However, if lxl UiO-67(Hf) is washed with DMF at 70°C, the lxl sheets can be re-connected by the bpdc$^{2-}$ ligands to form hcp phase UiO-67(Hf). Similar to hcp UiO-67(Hf), the lxl UiO-66(Hf) (F$_2$BDC) can also be converted to a layered lns phase by washing the as-synthesized samples with DMF or methanol.$^{[30]}$ Very recently, Zhou et al. reported a phase transformation from CuBDC to Cu$_2$BDC via a top-down molecular scalpel cleavage strategy.$^{[94]}$ The conventional CuBDC MOFs were chemically cleaved by ascorbic acid to form Cu$_2$BDC, possessing a different layered structure compared to that of CuBDC. The authors believe ascorbic acid could act as a molecular scalpel to cleave BDC linkers in CuBDC by regulating the chemical state and coordination number of Cu metal centers, leading to the formation of Cu$_2$BDC.

4 PHASE-DEPENDENT APPLICATIONS OF MOFS

As a kind of functional porous materials, the potential applications of MOFs have been widely studied. Via affecting the building block arrangement and the local chemical environment of MOFs, phase could alter the physicochemical properties and thus performances of MOFs in different applications. To date, studies of phase-dependent properties of MOFs are still limited. In this section, we summarized recent studies about the applications of MOFs with different phases in the fields of luminescence, absorption and catalysis.

4.1 Luminescence

The optical applications of MOFs have attracted much research attention in recent years owing to their fascinating
The luminescent properties of MOFs could be tuned by the flexible combination of diverse organic/inorganic components, as well as the voids in the MOFs. Notably, different phases of MOFs represent various node connectivity and symmetry of the linkers, which could also modify the luminescent performances of MOFs. For example, Deria et al. investigated the phase-dependent emissive properties of two Zr-based MOFs (scu NU-902 and ftw MOF-525). They found that the emissive spectral properties of MOFs are dependent on the phase of MOFs, which can affect the interchromophoric orientation and interactions and therefore cause the shift of spectra. Specifically, compared to the emission spectra of their free linker in dichloromethane solvent, those of scu NU-902 and ftw MOF-525 exhibited different extent of red shift. The spectra of scu NU-902 showed more red shift than ftw MOF-525. The fluorescence lifetime of scu NU-902 (~4.6 ns) was also found to be shorter than that of ftw MOF-525 (~5.6 ns).

In another work, Yu et al. reported that MOFs with the same chemical identities but different phases could affect the excited-state electronic structures. Specifically, they found that due to the different inter-linker distance, the scu NU-901 and csq NU-1000 demonstrated different excited-state properties. As shown in Figure 5A, femtosecond transient absorption (fs-TA) spectroscopy of scu NU-901 had an instantaneous S1 → S0 spectral evolution at 750 nm and gradually decreased by the occurrence of the broad induced absorption due to the formation of rapid excimer. However, the fs-TA of csq NU-1000 (Figure 5B) showed an obvious difference from that of scu NU-901, which only displayed a sharp induced absorption band at 740 nm. Moreover, theoretical calculations predicted that the csq NU-1000 had optically allowed charge-transfer states, but this state for NU-901 was forbidden.

4.2 Adsorption

MOFs are excellent adsorption materials for the removal of pollutants due to their generally high porosity and large surface area. Different phases of MOFs could exhibit different porosity and surface area, leading to differences in their adsorption capabilities. For instance, a recent report investigated the abilities of fcu UiO-66, defective fcu UiO-66 and hcp UiO-66 in the removal of perfluorooctanesulfonate (PFOS). The BET test results of the difference MOFs samples showed that defective fcu UiO-66 possess a much higher surface area (~1400 m²/g) than defect-free fcu UiO-66 (~1121 m²/g), while hcp UiO-66 exhibited the lowest surface area of ~687 m²/g, likely due to the cluster condensation in hcp UiO-66. The authors found that the PFOS adsorption capacity of MOFs showed a trend of defective fcu UiO-66 > hcp UiO-66 > defect-free fcu UiO 66. Although hcp UiO-66 possessed a relatively lower surface area than defect-free fcu UiO-66, it exhibited a better PFOS adsorption capacity, which may be attributed to additional small fraction of mesopores (>20 Å) in hcp UiO-66. In another report, Garibay et al. studied the capacity of carbon dioxide (CO₂) uptake of NU-901-act (act, HCl activated) and NU-1000-act. It was found that NU-1000-act showed enhanced CO₂ absorption performance compared to NU-901-act, especially at higher absolute CO₂ pressure, indicating that the
pore environment with NU-1000 phase is more accessible for CO₂ uptake.

Difference in pore structures of MOFs with different phases is also an important factor to determine their adsorption abilities. In the work reported by Chen et al., the adsorption abilities of she-NU-600, scc-NU-906, and esq-NU-1008 toward n-hexane and 2-chloroethyl ethyl sulfide (CEES) were studied. The NU-906 has micropores with a diameter of 10.9 Å, which showed steep uptake of n-hexane and could reach saturation at low pressure (Figure 5C). Meanwhile, both NU-600 and NU-1008 have hierarchically porous structures. NU-600 has micropores and mesopores with the diameter of 11.8 Å and 20.0 Å, respectively, while those of NU-1008 are 11.8 Å and 29.5 Å, respectively. Therefore, NU-600 and NU-1008 showed stepwise adsorption behaviors for n-hexane. Particularly, NU-1008 displayed three-step adsorption behavior toward n-hexane, and the adsorption of n-hexane into the larger hexagonal mesopores would cause the narrowing of the mesopores into micropores, leading to a sharp filling at the third step with the highest final uptake of 140.7 cm³/g. As for CEES adsorption, these MOFs also showed different behaviors under both dry and humid conditions (Figure 5D). Pore size was found to be the key factor in determining the CEES adsorption ability under dry conditions. NU-906 has the smallest pore diameter and showed the highest adsorption ability of CEES with a value of 13.3 mol/kg. NU-1008 has the same 8-connected Zr₆ nodes as NU-906 but a larger pore size and showed a lower CEES loading than NU-906. Under humid conditions, the NU-906 still had the highest CEES uptake ability among these three MOFs. But since the Zr₆ nodes could interact with water and result in a competing uptake of CEES, the NU-906 had a sharp decline of CEES adsorption abilities to 3.6 mol/kg. Compared with NU-906 and NU-1008, NU-600 had the lowest CEES loading under both dry and humid conditions.

4.3 | Catalysis

MOFs are also regarded as a promising group of catalysts for various kinds of catalytic reactions due to their large surface area, well-defined porous structures, versatile structural tunability, and abundant reactive sites. Notably, recent studies indicate that the phase of MOFs plays an important role in tuning their catalytic properties. MOFs with different phases and node-connectivity possess alien surface area, pore size and distribution, and density of active sites/defects, which could remarkably affect the mass transformation efficiency, substrate absorption capacity, and utilization of active sites, finally resulting in various catalytic performances. Chen et al. reported that, compared with fcu UiO-66, the hcp UiO-66 showed higher catalytic performance towards ring-opening epoxidation reactions with alcohols due to its high densities of defect sites. It was also pointed out that the node-bridging OH groups in hcp UiO-66 could be selectively removed during reaction and increased the overall density of active sites, leading to the enhanced catalytic activity. Liu et al. studied the catalytic performance of PCN-222(Cu) and PCN-224(Cu) towards the electrocatalytic CO₂ reduction reaction (CO₂RR) (Figure 5E). Due to the larger specific surface area and pore diameter, PCN-222(Cu) could facilitate more efficient mass transfer during the reaction, leading to improved activity and selectivity for CO₂ reduction to formic acid in the high potential range (−0.7 ~ −0.9 V vs. reversible hydrogen electrode (RHE)). However, compared to PCN-222(Cu), PCN-224(Cu) showed a greater heat of adsorption and better affinity for CO₂, promoting the uptake of CO₂ onto the active sites. As a result, PCN-224(Cu) revealed better catalytic activity in the low potential range (−0.4 ~ −0.6 V vs. RHE). Recently, the photocatalytic CO₂RR performances of three porphyrinic Zr-MOFs with different Zr₆-oxocluster connectivities, including PCN-222, PCN-223, and PCN-224, were investigated by Jin et al. Compared with 8-connected PCN-222 and 12-connected PCN-223, the 6-connected PCN-224 showed the highest formate yield rate, 45.2 µmol g⁻¹ h⁻¹. It is worth mentioning that theoretical calculation suggested that PCN-224 had the lowest CO₂ adsorption energy among the three samples, which possibly explained the improved photocatalytic CO₂RR performance of PCN-224.

5 | CONCLUSIONS AND PERSPECTIVES

In summary, we have provided a brief overview of recent advances in phase engineering of MOFs, including direct phase-controlled synthesis and phase transformation of MOFs, as well as the phase-dependent performances of MOFs in luminescence, absorption, and catalysis. To date, direct synthesis is the most common strategy to obtain MOFs with new phases. Among the various kinds of directly synthesized MOFs, Zr- and Hf- based MOFs show the most phase complexity owing to the variable connectivity and symmetry of the Zr- and Hf- based clusters. Compared to the direct synthesis, experimental approaches that can induce phase transformation of MOFs have less been explored, although a few factors such as solvent, pressure, modulator have been reported. With the successful preparations of MOFs with various phases, the role of phase in determining their performances in various applications has also been demonstrated. Although considerable progress in phase engineering of MOFs has been achieved, there are still some challenges. First, in-depth theoretical insights on the formation and transformation mechanisms of the unconventional phase in MOFs phases are still limited, compared with the relatively extensive experimental studies. Theoretical guidance is highly desired to accelerate the discovery and enable the rational design of MOFs with novel phases. In fact, it has been demonstrated that the computational approach is an efficient way to screen and generate possible MOF structures from given secondary building units and ligands. Second, the synthetic conditions of polymorphic MOFs are usually similar, making it difficult to obtain MOFs with high phase purity in a one-pot synthesis. The lack of methods to prepare MOFs that undergo different phases in high purity is hindering further investigations on the phase-dependent properties of MOFs. Last, investigations on the applications of MOFs with different phases still remain limited. It is believed that more phase-relevant physicochemical properties and applications of MOFs should be studied. In addition, methods to induce the phase transformation of MOFs are still lacking. One key challenge could be the identification of the factors to promote the kinetic control of MOF structures and suppress the thermodynamically unfavored
phase of MOFs could be obtained. For example, Mainland et al. found that the different phases of Zr-MOFs constructed by TCPP (FeIII) could affect the redox hopping conductivity of MOF-deposited electrodes.\cite{107} However, the phase-dependent performance of polymorphic Zr-MOFs (FeIII) as photoactive and/or redox-active species in photo- or electrochemical conversions has not been explored.

Despite the abovementioned challenges, there are also opportunities in engineering the phase of MOFs. First of all, apart from the reported methods to obtain MOFs with new phases, other synthetic methodologies should be developed, including but not limited to electrochemical method, photochemical method, microwave radiation-assisted method, magnetic field-assisted method, spray-drying, and flow synthesis. For example, compared with the conventional heating method, microwave radiation-assisted synthesis of MOFs is a more effective and faster heating approach, which can cause the crystallizations at the microwave-induced hot spots.\cite{108}

Second, defect engineering could be another effective strategy to obtain MOFs with novel structures. By incorporating ordered defects such as missing linker and/or node into MOFs, novel phases or mixed phases of MOFs may be produced.\cite{109} For example, using the formic acid as a modulator could introduce missing-cluster defects along the < 100 > directions in the fcu matrix of UiO-66(Hf), leading to the formation of reo UiO-66(Hf) instead of fcu UiO-66(Hf).\cite{110} More of such defect-induced phase transformation should be explored. Third, it has been reported that the rational design and synthesis of nanomaterials with heterophase structure will bring enhanced properties in specific applications due to the synergistic effects between different phases, as well as the presence of phase boundaries.\cite{7,110} Hence, developing methods to produce MOFs with well-defined heterophase is another promising research direction. Controllable phase distribution and/or composition of heterophased MOFs, may endow MOFs with intriguing physicochemical properties and broader applications. Fourth, due to the structural complexity and sensitivity of MOFs, advanced analytic technologies are crucial to characterize unconventional phases in MOFs. For instance, the recent development of low electron dose transmission electron microscopy and rotation electron diffraction allows direct and precise structure observation of MOFs.\cite{111,112} Moreover, advancements of in situ observation techniques could further deepen our understanding of the formation and transformation mechanisms of various phases in MOFs. Fifth, the applications of MOFs with unconventional phases can be further explored. Besides luminescence, adsorption, and catalysis, MOFs with unconventional phases may also exhibit enhanced performances in other emerging applications of MOFs, such as biomedicine,\cite{113} mechanical applications,\cite{114} and sensors.\cite{115} Sixth, the concept of PEN can be extended to MOF-based hybrid materials. For example, MOFs with different phases can be used as templates to grow other kinds of organic or inorganic nanomaterials. MOFs with different phases have different pore shape, size, and arrangement, which could be used to control the morphology, size, and even phase of the guest nanomaterials by adjusting the phase of host MOFs. Phase engineering of a rationally designed MOF-based hybrid could further improve their performances toward specific application. Last but not the least, the principles of phase engineering of MOFs can also be used to develop other materials with similar structure complexity such as covalent organic frameworks (COFs) and hydrogen-bonded organic frameworks (HOFs).

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**Conflict of Interest**

The authors declare no conflict of interest.

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