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# Alternative synthetic approaches for metal–organic frameworks: transformation from solid matters†

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Developing economic and sustainable synthetic strategies for metal–organic frameworks (MOFs) is imperative for promoting MOF materials into large scale industrial use. Very recently, an alternative strategy for MOF synthesis by using solvent-insoluble “solid matters” as cation reservoirs and/or templates has been developed to accomplish this goal, in which the solid matters often refer to metals, metal oxides, hydroxides, carbonates, and so forth, but excluding the soluble metal salts which have been prevalently used in MOF synthesis. Although most of the pioneering activities in this field have just started in the past 5 years, remarkable achievements have been made covering the synthesis, functionalization, positioning, and applications. A great number of MOFs in powder form, thin-films, or membranes, have been prepared through such solid-to-MOF transformations. This field is rapidly developing and expanding, and the number of related scientific publications has strikingly increased over the last few years. The aim of this review is to summarise the latest developments, highlight the present state-of-the-art, and also provide an overview for future research directions.

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## 1 Introduction

Metal–organic frameworks (MOFs), as an emerging class of porous materials, show enormous application potential in a wide array of technological fields such as gas storage, membrane separation,

chemical sensing, controlled release, and heterogeneous catalysis.<sup>1–8</sup> From the view point of a supramolecular architecture, in particular, MOF solids are built by chemical coordination between metal ions (or clusters) and polytopic organic linkers into periodic porous frameworks.<sup>1</sup> Regarding their general synthetic methods, most MOFs are obtained prevalently from homogeneous solution reactions between soluble metal salts and organic ingredients in one or mixed polar solvents (e.g., water, alcohol, or other organic solvents).<sup>9</sup> Alternatively, in recent years, metal salt-free procedures have also been developed for the MOF synthesis using solid matters or electrodes as new

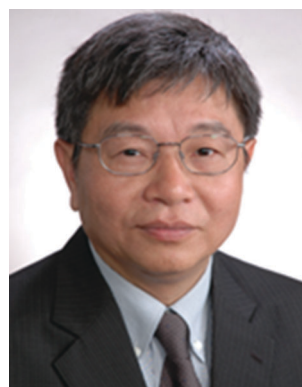
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sources of metal components.<sup>5,10</sup> In a typical electrochemical synthesis, for example, metal ions needed for the formation of MOFs are supplied continuously by the dissolution of anodic metals in an electrochemical cell containing desired organic linkers and electrolytes. Several archetypical Zn<sup>II</sup>, Cu<sup>II</sup>, and Al<sup>III</sup> based MOFs have been synthesised successfully.<sup>11</sup> Only a handful of MOFs have been prepared with this redox method so far, although the commercial production of HKUST-1 (Basolite<sup>®</sup> C 300) from sacrificial copper electrodes as a Cu<sup>II</sup> ion source has been achieved by BASF.

In contrast, a wealth of MOFs have been successfully produced from solid matters (*e.g.*, metals, metal oxides, hydroxides, carbonates, *etc.*), which appears to be a more general and powerful strategy. What is more, solid matters could provide a template role for directing the growth of MOFs. Therefore, in this review, we mainly focus on the recent progress in the use of solvent-insoluble solid matters for the synthesis of MOFs. Herein, we define the solid matters rather broadly as the solvent-insoluble metal precursors and the insolubility means the solid matters hardly release metal cations in the solvents without additional chemical reactions.

Different from common soluble metal salts in homogeneous solution, metal ions within solvent-insoluble solid matters are constrained and would be released in a more controllable way from spatiotemporal views. The released cations would further coordinate with nearby organic ligands available and self-assemble to MOFs. At a fundamental level, MOF products are thermodynamically more stable than solid matters in the presence of ligands (minimization of the Gibbs free energy of the system<sup>12</sup>), which contributes to the main driving force for the metal liberation and the subsequent chemical conversion. Based on the most current processes reported in the literature, the following eight salient features could be summarised to describe this alternative route for MOF synthesis. In particular, the first three points highlight the green chemistry and sustainability of this strategy, and the last five emphasise the technical advantages of this type of synthesis. (i) Economy of raw materials: solid matters are usually inexpensive feedstocks from large-scale industrial production, ceramic materials, or even natural minerals which are more readily available than metal salts (which are commonly produced from immersing metals in an acid bath (HCl, HNO<sub>3</sub>, *etc.*)). (ii) Free of anion impurity: since no exotic metal salt source is used, undesired salt anions such as NO<sub>3</sub><sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, and Cl<sup>-</sup> are avoided during the synthesis that minimises unwanted waste, whereas acidic side-products are inherently present in the conventional MOFs. In addition, the nitrate metal salts are potentially explosive and the chloride metal salts are corrosive. (iii) Ecological advantage: environmentally more benign processes of solid into MOF transformation are realised, due to their fast kinetics and free or minimal use of problematic solvents (*e.g.*, *N*-methylpyrrolidine (NMP), dimethyl sulfoxide (DMSO), and dimethylformamide (DMF), which are commonly used in conventional MOF synthesis). For instance, copper hydroxide can be rapidly converted to HKUST-1 just within 5 min at room-temperature in aqueous ethanolic solution.<sup>13</sup> Helms *et al.* have reported a series of minute-MOFs prepared from divalent metal

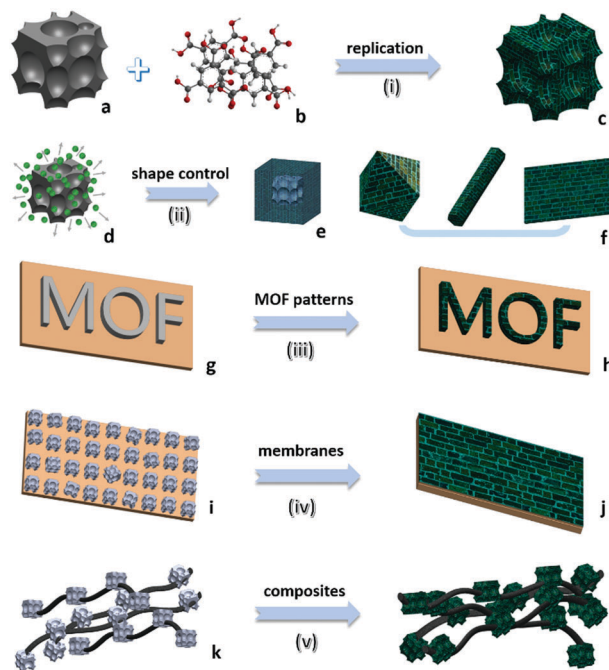


Fig. 1 Conceptual illustrations summarising various approaches used in conversion of solid matters to MOFs: (a) solid matters, (b) organic ligands, (c) replicated MOFs, (d) solid matters with releasing metal ions (small green spheres), (e) core-shell structured solid@MOF, (f) shape-controlled MOFs, (g) solid matter patterns on substrates, (h) MOF assembly on substrates, (i) pre-allocation of solid matters on substrates, (j) MOF membranes or films on the substrate, (k) pristine solid matter composites, and (l) MOF-containing composites.

oxides as precursors.<sup>14</sup> And it was reported that only one second of reaction time is required for the full conversion of V<sub>2</sub>O<sub>5</sub> to a vanadium-based MOF.<sup>15</sup> Importantly, the extremely fast transformation at room temperature did not compromise the high crystallinity. (iv) Morphological architectures (Fig. 1c): under sophisticated control, the morphology of the precursor phase (*viz.*, solid matters) can be replicated to the derived MOF. Because metal-based solid precursors can be pre-shaped into desirable structures *facilely via* well-established synthetic techniques of nanomaterials, morphological architectures of MOF materials can also be engineered accordingly. (v) Tuning the size and shape of MOFs (Fig. 1f): controlled release of metal ions from solid matters actually exerts additional influence on the crystallisation of MOFs. By employing solid precursors, metal ions in the solution become significantly scarce and relatively localised in the early stage of the reaction, which enables the kinetic control over the nucleation and growth of MOFs, yielding them with unusual properties and structures that are sought after. (vi) Pattern formation (Fig. 1h): MOF positioning is essential for device fabrication.<sup>16</sup> By applying self-templating solid matters (Fig. 1g), the location, crystal size, orientation, and overall patterns of MOFs can be controlled precisely. Moreover, such site-designation or assembly can lead to higher order architectures (*e.g.*, 3-dimensional (3D) superstructures) of MOFs. (vii) Fabrication of MOF films (Fig. 1j): solid matters can be easily fixed on a specific substrate. With the assistance of solid matters as both nucleation











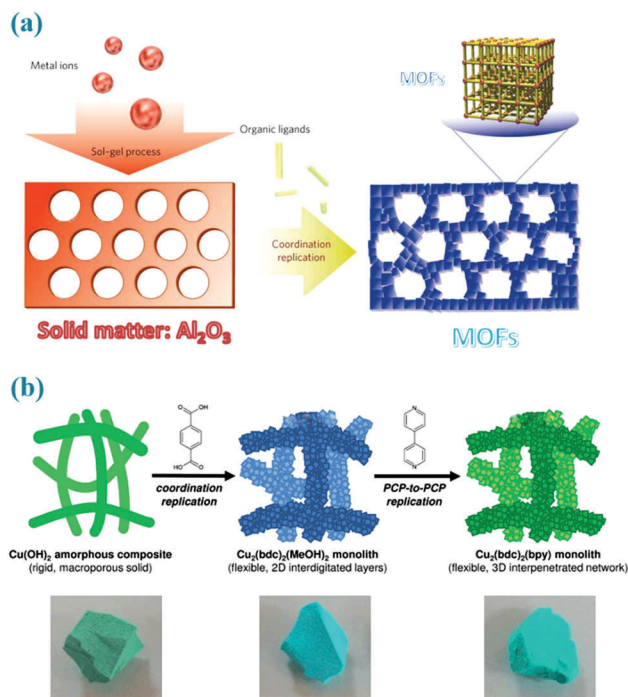


Fig. 4 (a) Coordination replication of  $\text{Al}_2\text{O}_3$  with honeycomb patterns to a more stable aluminium naphthalene dicarboxylate framework. Reprinted from ref. 61 with permission from Nature Publishing Group. (b) Two step coordination replication of the  $\text{Cu}(\text{OH})_2$ -polyacrylamide composite to 2D layered frameworks and 3D networks. Reprinted from ref. 45 with permission from the Royal Society of Chemistry.

mesoporous  $\text{SiO}_2$  monoliths, traits vital for industrial prospects. Sometimes, organic or inorganic binders could also be added to help shaping MOFs into technically relevant extrudates. For example,  $\text{Cu}(\text{OH})_2$  extrudates with 20 wt% kaolinite as a binder underwent transformation into HKUST-1 in the presence of an ethanolic  $\text{H}_3\text{BTC}$  solution.<sup>13</sup>

Overall, there are several factors that should be taken care in order to guarantee the perfect replication. The most important factor is the spatiotemporal synchronisation of the precursor dissolution and the MOF crystallisation. If the dissolution kinetics of the sacrificial phase is higher than the kinetics of MOF crystallisation, it is necessary to either apply polymer coating layers (as a barrier) on the solid matters or use solvent with high viscosity (e.g., octanol<sup>28</sup>) to slow down the out-diffusion of metal cations at solid-liquid interfaces. Secondly, it should be noted that the parent solid matter phase is required to possess huge porosity (e.g., containing mesopores or macropores) in order to facilitate the diffusion and transportation of organic ligands in the entire solid and fulfil the coordination replication.<sup>45</sup> Or else, only partial replication would be obtained, producing core-shell structures. Thirdly, the parent solid matters for coordination replication are generally micro-sized particles, and the daughter MOF phases in meso-structures usually comprise numerous polycrystalline grains (<100 nm) due to the heterogeneous nucleation. This is the reason why the surfaces of the generated MOFs are rather rough. On the other hand, it is difficult for nanoscale solid matters to

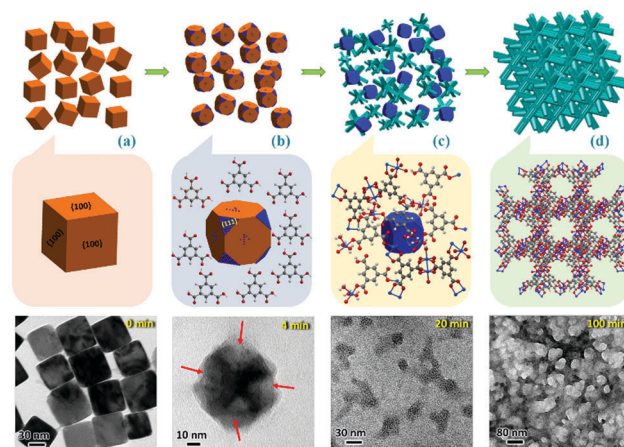


Fig. 5 Synthetic approach for HKUST-1 3D-nets prepared from  $\text{Cu}_2\text{O}$  nanocubes. (a) Synthesis of  $\text{Cu}_2\text{O}$ ; (b) oxidative dissolution of  $\text{Cu}^I$  to  $\text{Cu}^{II}$  ions (illustrated as blue colour) with the assistance of  $\text{H}_3\text{BTC}$ ; (c) nucleation-growth of HKUST-1 in growing domains and domain integration; and (d) total consumption of the  $\text{Cu}_2\text{O}$  phase and the formation of HKUST-1 3D-nets. Reprinted from ref. 44 with permission from the Royal Society of Chemistry.

maintain their original morphology owing to relatively easy release of metal ions. However, they could be used as solid precursors for the domain growth of 3D-networks of MOFs. In our recent study (Fig. 5), for example, uniform  $\text{Cu}_2\text{O}$  nanocubes (edge length of 60 nm) were used as a point source of copper ions to prepare 3D-networks of HKUST-1 with hierarchically arranged pore structures (e.g., micro-, meso-, and macropores).<sup>44</sup>

## 5 Shape and dimensional controls

To date, it remains difficult to control geometric shapes of MOF products by adjusting coordination behaviours of metals and ligands. In particular, low dimensional MOF morphologies (e.g., 1D fibres and 2D nanosheets) are difficult to prepare and thus they are seldom reported. The usage of solid matter as a metal ion source actually plays a kinetic role in adjusting the coordination behaviours of targeted MOFs. As shown in Fig. 6, recently, our group has reported a facile route at room temperature and ambient pressure for the preparation of copper-containing nanostructured MOFs with low dimensional shapes (i.e., fibres, rods, sheets and cuboids) using  $\text{Cu}_2\text{O}$  nanoparticles in spherical or cubic shape to provide required copper ions.<sup>47</sup> Interestingly, when the monovalent  $\text{Cu}_2\text{O}$  was replaced by divalent  $\text{CuO}$ , the product HKUST-1 only has an irregular shape which is totally different from  $\text{Cu}(\text{H}_3\text{BTC})\text{-1}$  by using  $\text{Cu}_2\text{O}$  as a parent solid (Fig. 6). It is inferred that the starting  $\text{Cu}^I$  solution is essential to promote the slow growth of low-dimensional MOFs. In this regard, the growth process is somewhat similar to the shape-controlled synthesis of gold nanoplates achieved by using a syringe pump to slowly deliver the precursor to the reaction system.<sup>63</sup>

## 6 Synthetic positioning and patterning

Currently, the grown MOFs are difficult to be positioned in a designated region with traditional methods due to the lack of







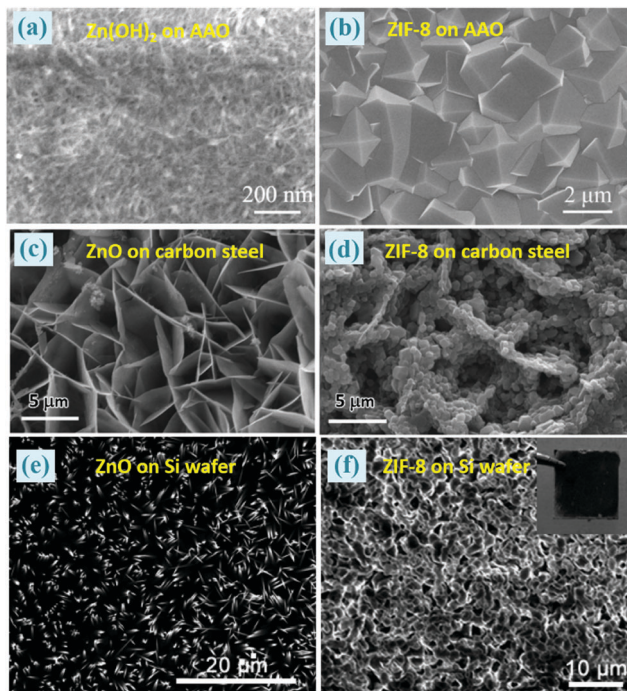


Fig. 8 (a–f) SEM images of ZIF-8 films coated on versatile substrates through the transformation of the corresponding ZnO films. Inset in (f): a photograph of the ZIF-8 film. Reprinted from ref. 38 and 56 with permission from the Royal Society of Chemistry and ref. 68 with permission from the American Chemical Society.

## 8 Synthesising nanocomposites

Integration of MOFs with functional nanoparticles facilitates their wider applications, which can be realised by using solid matter/nanoparticle (NP) composites as the precursors. Compared with MOFs, metal oxides can more easily be deposited on metal NPs. For example,  $\text{Cu}_2\text{O}$  can be coated on various metal NPs (e.g., Au and Pd).<sup>73</sup> Then, the transformation of  $\text{Cu}_2\text{O}$  into Cu-based MOFs leads to the formation of well-defined yolk-shell structured NPs@Cu-MOFs.<sup>48</sup> An alumina coated gold nanorod can be used as a precursor to prepare a core-shell composite with an aluminium-based MOF coated on the surface of gold nanorods.<sup>74</sup> The oriented growth of Al-MOF on Ag NPs can be achieved by atomic layer deposition of alumina thin films (thickness from 0.1 to 3 nm) on Ag NPs and the subsequent transformation.<sup>75</sup> Similarly, binary metal oxide ( $\text{ZnSnO}_3$ ) can be translated to ZIF-8/ $\text{SnO}_2$  composites, since the ligands would preferentially react with  $\text{Zn}^{\text{II}}$  rather than  $\text{Sn}^{\text{IV}}$ .<sup>76</sup> Recently, Ni-rich Pt-Ni alloy nanoparticles were used to produce a (Pt-Ni)@(Ni-MOF-74) composite.<sup>21</sup> The MOF coating layer on the surface of Pt endows the hybrid with molecular sieve effects in several catalytic reactions.

Multifunctional (metal-oxide)@MOFs with core-shell or yolk-shell structures can be synthesised by using metal oxides as a template, in which if the diffusion rate of metal ions is larger than that of organic ligands, a yolk@shell product was obtained, whereas, core@shell one was obtained if the opposite happens.<sup>77</sup> The growth of MOFs was confined on the core surface because metal ions for constructing MOFs were provided solely

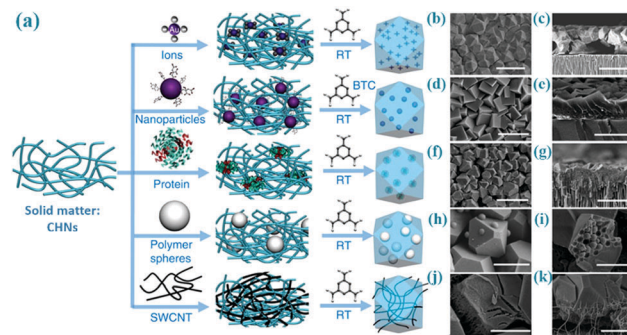


Fig. 9 (a) Functionalization of HKUST-1 membranes by using copper hydroxide nanostrands (CHNs) as a copper ion source; (b–k) SEM images of the resultant products combining HKUST-1 with various different components (e.g., small ions, polymer spheres, CNTs, inorganic nanoparticles and bioactive proteins, etc.). The scale bars are (b) 3  $\mu\text{m}$ ; (c) 4  $\mu\text{m}$ ; (d and e) 3  $\mu\text{m}$ ; (f) 5  $\mu\text{m}$ ; (g and h) 3  $\mu\text{m}$ ; (i) 5  $\mu\text{m}$ ; (j) 3  $\mu\text{m}$ ; (k) 2  $\mu\text{m}$ , respectively. Reprinted from ref. 79 with permission from Nature Publishing Group.

through sacrificing the core material. A  $\text{ZnO}$ @ZIF-8 core-shell heterostructure could be prepared by partial conversion of ZnO on the surface region.<sup>27,28</sup> In another report, ZnO nanoparticles could be adsorbed on the surface of carbon nanotubes (CNTs), then the transformation of ZnO into ZIF-8 proceeded on the surface of CNTs, leading to the formation of a ZIF-8/CNT composite.<sup>78</sup> Likewise, MOF/polymer composites can be prepared by firstly mixing the solid matters and polymers followed by the conversion. For example, ZnO-to-ZIF chemical transformation can help to fabricate the ZIF/polymer composites with layered architectures.<sup>26</sup> Moreover, the included polymer in the MOF/polymer composites would increase their mechanical robustness, so the resultant MOFs are easily handled.<sup>45</sup>

Besides the fabrication of MOF films on substrates (Section 7), the solid-matter assisted method enables incorporation of other functional materials within the MOF thin films. As illustrated in Fig. 9, Peng *et al.* have explored a general  $\text{Cu}(\text{OH})_2$  assisted technique to confine diverse components (such as small ions, micrometre-sized particles, inorganic nanoparticles and bioactive proteins) in HKUST-1 thin films at room temperature.<sup>79</sup> Therefore, the resultant composite MOF films have dual merits from both the size-sieving effect of HKUST-1 and the original property of the encapsulated materials. For example, Au/HKUST-1 composite thin films can be explored as catalytic membrane reactors, which show the selective hydrogenation of *n*-hexene (26.3% conversion) and *cis*-stilbene (0%). Along these lines, the approach would provide virtually unlimited possibility for hybridisation of MOFs with any nanomaterials if their parent solid matters can be hybridised both chemically and structurally.

## 9 Conclusions and perspectives

As introduced in the foregoing examples of solid-to-MOF transformation, this methodology could be considered as one of the most versatile strategies in controlled synthesis and functionalization of MOFs with special architectures. Below are some urgent





issues and technical challenges which should be addressed in order to further develop this topical research.

(1) At the moment, solid precursors used in this strategy have been limited to less soluble solids, and they have so far been focused only on a few groups of inorganic substances, as discussed above. In fact, many others are still largely unexplored, especially those of mineral materials. Associated with this issue, furthermore, general criteria to efficiently distinguish and rapidly screen potential precursor matters for such MOF synthesis have not been established yet.

(2) Although our knowledge on the general synthesis of this strategy has been accumulated rapidly, our understanding of mechanistic aspects such as nucleation and crystal-growth processes of MOFs is still unclear. In principle, many *in situ* and *operando* evaluation tools established in nanoscience and nanotechnology research studies over the past few decades can be readily applied into these types of time-resolved dynamic investigations.

(3) The concentration gradient of metal ions caused by the solid matters in the solution phase could be used for adjusting the crystal growth rate of MOFs. Therefore, more effort should be made to understand the fundamental mechanism of solid-to-MOF transformation in order to grow MOFs into predesigned shape and architectures.

(4) The main kinetic issue involved in these transformative syntheses is the rate of solid matter dissolution and the rate of MOF formation. Thus, how to create a predictable and reproducible kinetics for the solid matter dissolution is critically important. However, most of the current investigations have mainly focused on MOF formation, but the fine control over the solid matter dissolution has not been achieved, particularly over complicated transformations involving multiple types of metal precursors and variable valence metal ions when additional redox reactions are involved.

(5) The solvent-free approach is generally considered “greener”. Unlike the solution approach, however, solid form of reactants limits intra- and inter-particle diffusions. Therefore, thorough mixing of solid reactants becomes a crucial synthetic parameter to such transformative reactions. Nevertheless, it should be noted that mixing of raw materials by hand-grinding in a mortar is less manageable, though it has been commonly adopted. Due to variations in experimental conditions (*e.g.*, the size of mortar and the force applied), such processes are insufficiently reproducible among the researchers.

(6) It remains a great challenge to confine the growth of MOFs inside a pore or a cavity (*e.g.*, with porous silica or carbon nanoshells). Since they can provide constraining metal ion sources, solid state metal sources can also be used for the confined construction of MOFs inside spaces of porous structures. Nonetheless, so far no such attempts have been reported in the literature.

With more research endeavours devoted, we believe that the above urgent issues and technical challenges could be addressed at both macroscopic and microscopic (molecular) levels in near future, not only to pursue fundamental interest in advanced synthesis but also to make this strategy more suitable for

sustainable large scale production and industrial applications of MOFs.

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