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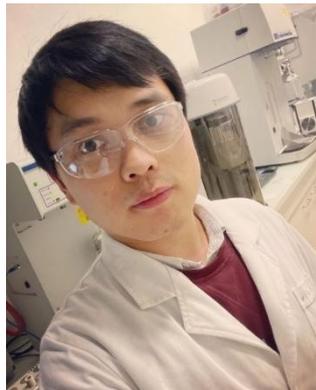
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Metal-Organic Frameworks: from ambient green synthesis to applications

Shan Dai,¹ Antoine Tissot,*¹ and Christian Serre*¹

¹Institut des Matériaux Poreux de Paris, UMR 8004 Ecole Normale Supérieure, ESPCI Paris, CNRS, PSL University, 75005, Paris, France



Shan Dai obtained his bachelor's degree in chemical engineering in 2015 and joined the “ENS-ECNU Joint Training PhD Program” at East China Normal University. He started his PhD from 2017 in École Normale Supérieure (ENS). His research interests deal with the environmentally friendly synthesis and the design of chemically robust MOFs and their composites for energy/ environment-related applications.



Antoine Tissot is a CNRS researcher at the Porous Materials Institute of Paris. Following his PhD in coordination chemistry dedicated to the study of molecular spin crossover nanocrystals at University Paris-Sud, he stayed at University of Geneva in the Physical Chemistry department as a postdoctoral researcher where he studied photophysics of coordination compounds. He was then recruited as CNRS researcher in the Institut Lavoisier de Versailles in 2014 and moved to the newly created Porous Materials Institute of Paris in September 2016. He is currently working on the synthesis and functionalization of Metal Organic Frameworks for applications in sensing and catalysis.



Christian Serre is a CNRS research director. He was previously the group leader of the Porous Solids team from Institut Lavoisier de Versailles, France. Christian then created in 2016 a new research institute fully dedicated to porous materials

(IMAP) at the Ecole Normale Supérieure and ESPCI Paris within PSL university. His research interests lie in the discovery of new robust functional Metal-Organic Frameworks and related composites in a view of potential applications in health, energy, and environment.

Abstract: Studies of the room temperature synthesis of Metal-Organic Frameworks (MOFs) are still scarce and mainly focused on divalent metals based MOFs. The development of room temperature synthesis of more chemically robust MOFs is still challenging and therefore lacks of exploration. Here, we review the development of ambient conditions synthesis of MOFs, from the properties of the sole MOF to their related composites. Low temperature green synthesis can not only meet the standards of sustainable chemistry, but also help to achieve a series of property enhancements, including their applications in catalysis, biomedicine, and sensing. Finally, perspectives associated to the synthesis strategies and applications of room temperature methods are discussed.

Keywords : Metal-Organic Frameworks, MOFs, room temperature synthesis, green synthesis, MOF applications

▪ Introduction

Metal-Organic Frameworks (MOFs) have emerged as a promising class of porous materials due to their long-range ordered structure, high specific surface area, tunable composition, as well as almost infinite structural diversity.^[1] All these features make these solids very promising for various applications, including catalysis,^[2] separation,^[3] conductive devices^[4] sensing,^[5] and bio-applications.^[6] In the 1990s, researchers realized the discrete inorganic materials can be interconnected by the organic ligands to form ordered structures.^[7] At the same time, a unique class of crystalline porous materials, namely Metal-Organic Frameworks (MOFs), was defined. Their sometimes extremely high surface area associated with their large chemical and structural diversity makes them appealing and competitive to traditional porous solids (e.g., zeolites, carbons) for a large range of applications, such as gas adsorption/ separation in the early stage.^[8] In particular, the high degree tunability of both the constitutive secondary building units (SBU)^[9] and organic ligands has opened up a rather unique opportunity in the field of porous to tune their properties. In this direction, the efforts have been dedicated to boldly combine almost all kinds of metal cations with varying organic linkers. According to the Cambridge Structural Database (CSD), there are more than 100,000 entries based on the CSD (~10% of the CSD).^[10] Accordingly, the number of relevant publications expanded rapidly in the past two decades (See Figure 1).

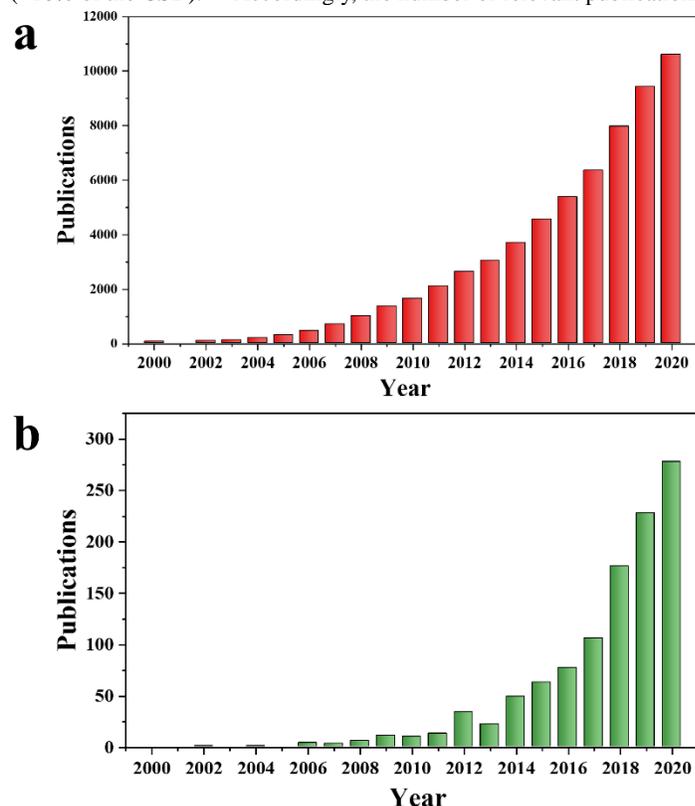


Figure 1. The number of publications of MOF in last two decades, from 2000 to 2020. a) the terms “MOF” or “Metal-Organic Frameworks” b) the terms of “metal-organic frameworks” and “green synthesis” were used to search in Web of Science.

The synthesis of MOFs is often at the origin of many novel properties for various applications. Of these, the most typical preparation route for MOFs is solvothermal/ hydrothermal synthesis, where the metal precursors and organic linkers are mixed and sealed in a Teflon autoclave containing certain solvents (e.g., N,N-dimethylformamide (DMF), N,N-diethylformamide (DEF), sometimes H₂O).^[11] The synthesis temperature is generally between 100 °C and 220 °C. The microwave-assisted hydro/solvothermal synthesis is another method, which is usually used to rapidly rise the temperature of the reaction in order to accelerate the kinetic of crystallisation. As such, microwave-assisted synthesis often combine high efficiency and effective production of nanocrystals due to the shortened synthesis duration.^[12] However, it should be noted that these synthesis methods still requires high temperature combined with autogenous pressure, which therefore limit their upscaling and eventually industrialization.^[13]

Recently, exciting advances have been achieved in the synthesis of MOFs,^[14] including the concept of “green synthesis” that has been applied to prepare MOFs.^[15] Publications grew more significantly in very recent 5 years (see Figure 1b). Depending on the targeted structures and properties, MOFs can be alternatively prepared by using many distinct and “relatively green” approaches, such as electrochemical,^[16] slow diffusion,^[17] spray-drying,^[18] pump flow,^[19] and mechanochemical^[20] syntheses. However, all these methods are associated with a specific energy cost, which, from a sustainable chemistry point of view, has to be taken into account prior to their future industrial production. Additionally, these methods might also hinder the incorporation of temperature sensitive compounds into core-shell structures.^[21]

Room temperature synthesis (RTS) of MOFs refers to the synthesis in ambient conditions without an external heating procedure. The RTS includes stepwise and direct methods. The former one represents the strategies with multiple steps, including the pre-treatment of organic ligands or inorganic metal cations, and the pre-synthesis of inorganic sub-units (e.g., Fe oxotrimer, Ti oxoclusters, Zr₆ oxoclusters).^[22] This step allows the subsequent ambient construction of the overall MOF. The direct RTS corresponds to a one-pot one-step synthesis without any additional treatment. This method is more interesting compared to stepwise synthesis in terms of synthetic complexity and overall preparation cost. Great progresses have been realized in the field of divalent metals based MOFs RTS within the last years. However, the RTS for high valence MOFs is still challenging due to the higher activation energy needed, which may request external heating to make the reaction start. In all these syntheses, the “space-time yield (SPY)” is rarely calculated regardless of its importance for real applications.

In this review, we summarize the development and the progress of room temperature synthesis methods of MOFs as a function of the charge of the metal cation. We emphasize the importance of RTS of more chemically robust high valence MOFs, such as tri or tetra-valent metals based carboxylate MOFs. The RTS allows a safer and greener synthesis that may be suitable for industrial applications. Additionally, the ambient synthesis that is compatible with the encapsulation of temperature sensitive compounds, could also lead to some property enhancements (e.g., catalysis, gas sorption, biomedicine). We finally discuss the future of the ambient synthesis of chemically robust MOFs and hope this will promote not only novel green synthesis routes but also new applications based on this strategy.

▪ M(II) MOFs

Early-stage MOFs were primarily composed of divalent transition metals (Zn²⁺ or Cu²⁺) and polycarboxylate linkers. Divalent MOFs nowadays includes almost all divalent metal cations, such as Ca²⁺, Mg²⁺, Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺ and Ba²⁺.^[23] The typical ligands are based on carboxylates, phosphonates, or N donating linkers. All these options result in a wide range of structure types and porosities, from the micro to mesoscale and with possible functional groups on the organic spacers. The SBUs for M(II)-MOFs contains widely single metal cations, bi/ tri/ tetra-nuclear oxoclusters, and chains (illustrated in Figure 2).^[24] Great efforts were dedicated not only to develop novel M(II)-MOFs but also in to optimize ambient synthesis of these MOFs. For example, in 2008, the rapid, simple, and high-yield room temperature syntheses of various divalent MOFs, including MOF-5, MOF-74/ CPO-27, MOF-177, and Cu-BTC (or HKUST-1) was reported. The extension to a few new structures was also demonstrated by the authors. These examples demonstrated for the first time that heating is not necessary to produce highly crystalline MOFs.^[25] Subsequently, further optimizations of the ambient synthesis of M(II)-carboxylate MOFs were reported, including efficient ultrasonic synthesis,^[26] aqueous solution-based synthesis with high space-time yield^[27], nanosized MOFs preparation,^[28] mixed divalent metals MOF synthesis^[29] and even mechanochemical syntheses without solvents.^[30] Remarkably, the syntheses of M(II)-carboxylate benchmarks have been optimized and some of them even meet the industry need.^[31] However, the metal–ligand bonds in these MOFs are prone to rapid hydrolysis, often making them not suitable for most practical applications. Moreover, the quality of these room temperature prepared MOFs has been questioned in terms of textural properties.^[32]

Alternatively, using divalent metals and nitrogen containing ligands, such as triazole, tetrazole, imidazole, and pyrazole can lead to more chemically robust MOFs based on M(II)-N bonds.^[33] One typical example is the Zeolitic imidazolate framework (ZIF) series of MOFs. The first example of such structure was reported by Chen’s group in 2005 that obtained a MOF with a unique cage-like structure with a large cavity size of 1 nm and a window size of 3.3Å.^[34] Polymorphic structures with imidazolate and Zn(II) subsequently experienced a fast expansion mainly due to their easy crystallization and improved chemical stability and functionality.^[35] Afterwards, the corresponding efficient room temperature synthesis with high crystal quality and different crystal sizes using organic solvents,^[36] aqueous solution,^[37] or even using mechanochemistry,^[38] were reported.^[39] These novel environment-friendly ambient synthesis routes immediately attracted intensive research interest, which subsequently made them

the most used synthesis approaches for the synthesis of the ZIF series of MOFs.

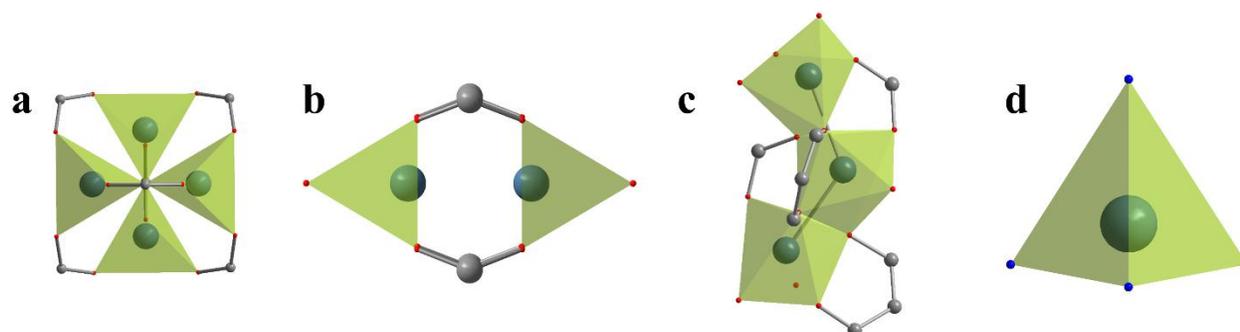


Figure 2. Graphical illustration of common SBUs obtained with divalent MOFs, a) $Zn_4O(CO_2)_6$ oxocluster, b) $Cu_2(CO_2)_4$, c) $Ni_3O_3(CO_2)_3$ chain, d) Zn(II) cation.

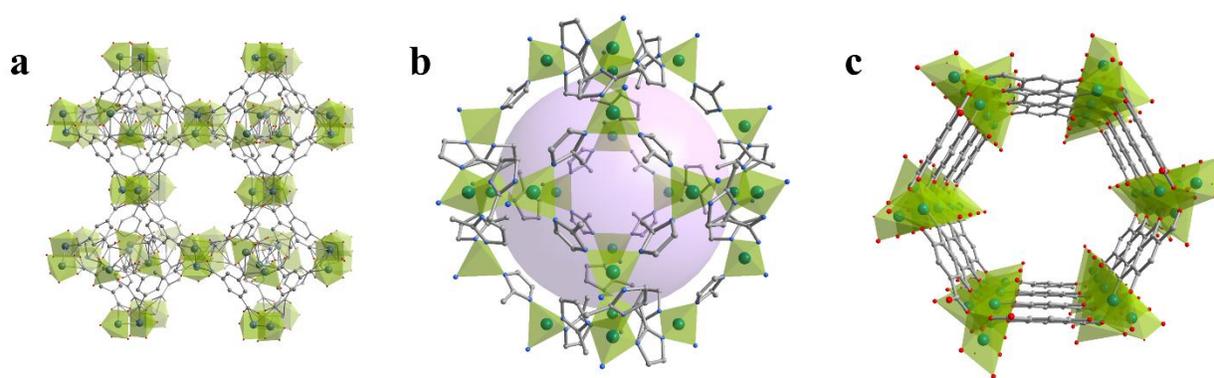


Figure 3. Typical divalent MOFs structures. a) HKUST-1, b) ZIF-8, c) MOF-74/CPO-27. Inorganic node polyhedra in light green with oxygen in red, nitrogen in blue and carbon atoms in grey.

It should be pointed out that even though MAF/ ZIF (MAF stands for Metal Azolate Framework) series of MOFs show improved chemical stability, some of them are still suffering from degradation in pure aqueous solution or slightly acidic conditions.^[40] The use of organic linkers bearing pyrazole groups with a higher pKa (= 19.8) has been applied to prepare even more robust M(II)-N based MOFs, which can be stable not only in boiling aqueous solutions but within a large range of pH, from 2 to 14, for two weeks.^[41] However, the vast majority of divalent MOFs still suffers from degradation in aqueous solution or sometimes even under humid air, which is a clear disadvantage in a view of practical applications.

Table 1. Ambient synthesis examples for M(II) based MOFs.

Materials	Method ^a	SBU	Solvents	Synthesis duration (h)	RTS _{surface} area/ OS _{surface} area (m ² /g)	Ref
MOF-5	Solution	Zn ₄	DMF	2.5	3909/ 2500-3000 ^[42]	[25]
HKUST-1	Solution	Cu ₂	DMF, EtOH, H ₂ O	23	-	[25]
MOF-177	Solution	Zn ₄	DMF	3	4944/ 4500 ^[43]	[25]
MOF-74	Solution	Ni ₃ chain	DMF	18	1187/ 816 ^[44]	[25]

ZIF-8	Solution	Zn atom	MeOH /DMF	1 /18	962 /1947 ^[35a]	[36]
HKUST-1	Mechanochemical	Cu ₂	-	0.42	758/ 1781 ^[44]	[30]
Cu ₃ (BTB) ₂	Mechanochemical	Cu ₂	-	0.42	628/ 1781 ^[44]	[30]
Cu ₂ (ndc) ₂ (dabco)	Solution	Cu ₂	DMF	24	143	[45]
MOF-74	Solution	Cu ₃ chain	MeOH	0.17	1013/ 816 ^[44]	[46]
Zn ₂ (X) ₂ (DABCO)	Solution	Zn/ Ni/ Co/ Cu atom	MeOH/ DMF	4	2113/ 2104	[47]
Ni ₂ Co ₁ _{1-x} Fe _x	Solution	-	DMF	1	130	[29]
HKUST	Ultrasonic	Cu ₂	DMF	0.08-1	1100/ 1781 ^[44]	[26]
HKUST-1(Cu, Zn), MOF-5 (Cu, Zn)	Salinization	Cu ₂ , Zn ₄ ,	H ₂ O	0.08-2	1721, 687/ 1781 ^[44]	[48]
HKUST-1	Solution	Cu ₂	H ₂ O	1	1749/ 1781 ^[44]	[27a]
HKUST-1	Solution	Cu ₂	DMSO, MeOH	0.17	-	[27b]
HE-MOF	Ultrasonic	Mn/ Fe/ Co/ Ni/ Cu atom	DMF, H ₂ O, EtOH	1	165	[49]
ZIF-8, ZIF-4	Mechanochemical	Zn atom	-	0.5-1	-	[38]
MOF-74	Solution	Zn ₃ , Co ₃ , Mn ₃ , Mg ₃ , Ni ₃ chain	DMF	20	402-1007/ 816 ^[44]	[28]
ZIF-67	Additive	Co atom	H ₂ O	0.17	868/ 316 ^[50]	[51]

ZIF-93	Additive	Zn atom	H ₂ O	18	604/ 94 ^[52]	[53]
ZIF-8	Solution	Zn atom	MeOH	2-24h	600/ 1947 ^[35a]	[54]
ZIF-8	Additive	Zn atom	MeOH	0.017	1566/ 1947 ^[35a]	[55]
ZIF-61	Additive	Zn atom	MeOH	0.017	-	[55]
ZIF-90	Additive	Zn atom	MeOH	0.017	-	[55]

a: Solution refers to the conventional synthesis that needs solvents. Salinization refers to the synthesis that needs pre-salinization of the organic ligands. Additive represent the using of additional agents in the solution synthesis.

*: OS represents the original synthesis, including solvothermal/ hydrothermal synthesis.

▪ M(III) MOFs

In this section, we only focus on the M(III)-carboxylate MOFs due to their higher thermal/ chemical stability compared to most divalent MOFs. Trivalent MOFs can be prepared using several transition metal cations including Al³⁺, Fe³⁺, Cr³⁺, V³⁺, Ga³⁺, Sc³⁺, In³⁺, Bi³⁺^[56] and even lanthanide metal cations^[57] combined with most of the conventional di, tri, and other multitopic linkers as organic ligands. Férey and Serre, that pioneers the discovery of trivalent MOFs, developed many well-known benchmark MOFs structures in the MIL-n series : MIL-53,^[58] MIL-101,^[59] MIL-100,^[60] MIL-88,^[61] MIL-127,^[62] etc. So far, two main SBUs constitute the majority of trivalent MOFs.^[63] The first one is the ‘chain’ SBU built from μ_2 -hydroxo corner-sharing M(III)O₆ octahedra (Figure 4a). The second is the M(III) trinuclear unit with a formula of M₃(μ_2 -O)(OH)(H₂O)₂(COO)₆ (Figure 4b), where the hydroxide groups can be replaced by other anionic species (e.g., F⁻, Cl⁻...) depending on the synthesis conditions. The typical synthesis route for trivalent MOFs is the solvothermal synthesis in polar solvents (e.g. water, DMF, alcohols). The large number of available M(III) salts is of great interest to optimize the MOF synthesis in order to meet the demand of the industry. For instance, the first commercially available MOF, Basolite A520,^[64] an analogue of MIL-53-Al solid, was synthesized in water using mild conditions.^[64] The RTS of trivalent MOFs has experienced long-time efforts with limited promising results. For example, Sánchez-Sánchez et al. reported a simple two-steps route for Al-chain based MIL-53-Al (Figure 4c) and its amino- and nitro- functionalized derivatives.^[65] This synthesis method relied on the use of disodium terephthalate as linker salt in sole water due to the poor solubility of terephthalic acid in water (illustrated in Figure 5). The use of linker salt completely changed the solubility of the linker and therefore the kinetics of MOF formation. Several techniques, such as PXRD, 77K nitrogen sorption isotherms and SEM were applied to confirm the quality of the resulting nanocrystals, which was comparable to those synthesized in DMF at high temperature. However, the protonated linker filled up the pores forcing the use of calcination to active MOFs, which is not a friendly method from green chemistry point of view. Apart from the RTS for the MOFs based on inorganic chains, strategies were also reported to deal with aforementioned trimer oxoclusters. MIL-100 is the benchmark ‘trimer’ trivalent carboxylate MOF and is built with M(III) oxotrimers and BTC linkers.^[66] It presents two types of cavities (2.9 nm and 2.5 nm) with a zeolite-like structure (Figure 4d). MIL-100 can be prepared with Cr(III),^[67] Fe(III),^[66] Al(III)^[68] and its synthesis was recently extended to metal(IV) cations such as Ti(IV),^[69] and larger tritopic linkers.^[70] Li and his team reported a RTS strategy by using iron powder and oxidizing radical as starting materials to accelerate the crystallization of MIL-100(Fe) without HF addition.^[71] First, the iron powder was dispersed in aqueous HNO₃ solution under sonication and the BTC linker was mixed in the aqueous solution with *p*-Benzoquinone to form a deprotonated linker. Then, these batches were mixed together under stirring at room temperature for 12 h. The obtained MIL-100(Fe) showed comparable surface area with the conventional synthesis, which indicated its high quality. However, the relatively low product yield, as well as the generated explosive gas (H₂), prevents the use of this synthesis strategy for industry.

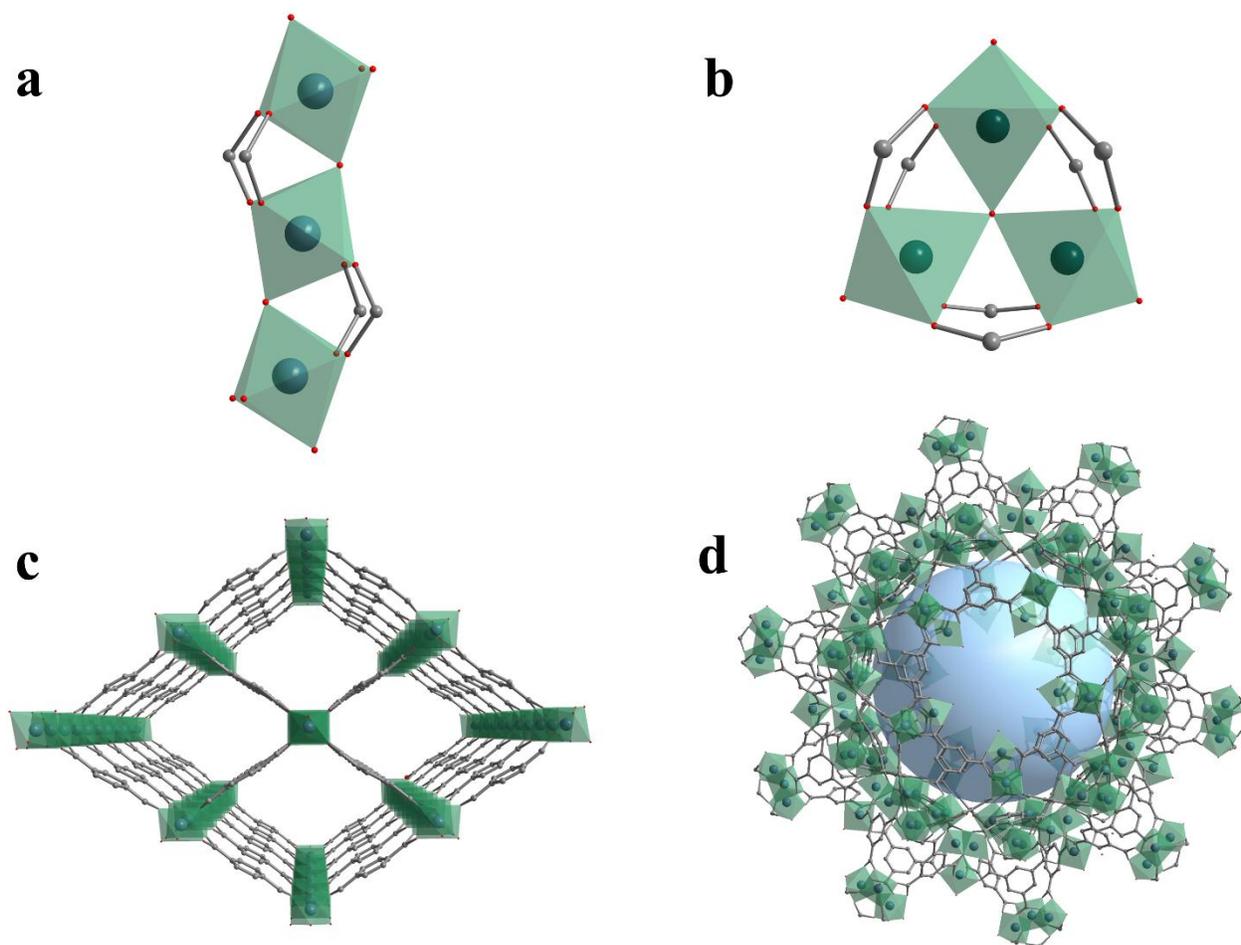
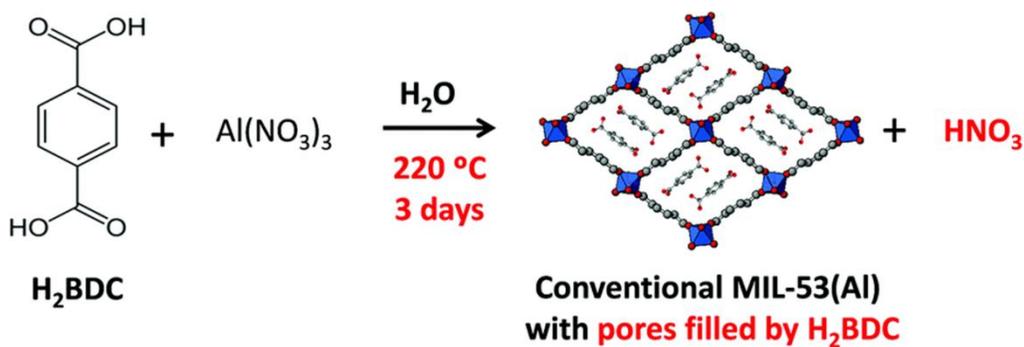


Figure 4. Archetypal SBUs observed in the M(III)-MOFs a) MO_6 chain, and b) M_3 oxo-trimer. c) Structure scheme of MIL-53, d) Structure scheme of MIL-100. Inorganic node polyhedra in green with oxygen atoms in red and carbon atoms in grey.

More recently, $\text{Fe}(\text{NO}_3)_3$ was directly used as starting metal salt and simply combined with BTC in water. After 48 h stirred at room temperature, an orange solution was obtained. The product was filtered and washed with water to yield an orange-brown solid. No further treatment was needed and therefore, the MOF nanoparticles obtained could be used as such. This is the first example that used directly Fe(III) salt and BTC in a pure aqueous solution to synthesize MIL-100(Fe). The resulting MIL-100 showed high quality, including porosity ($\sim 1800 \text{ m}^2/\text{g}$, BET model), crystallinity, and connectivity. More importantly, the MIL-100 owned a reasonable particle size distribution together with a mean size at around 60 nm, which is very suitable for nanomedicine that rely on bio-compatible nano-MOFs.^[72]

Conventional method



Room temperature method

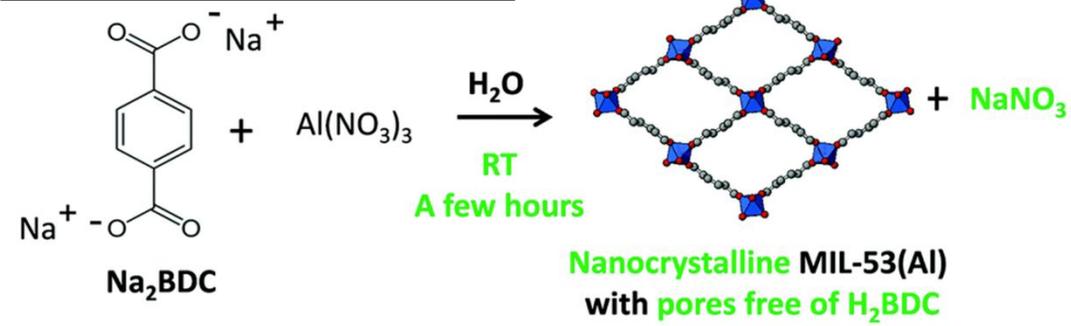


Figure 5. General reaction for the preparation of MIL-53(Al) by conventional (top) and the room temperature green synthesis methods. Produced with permission, RSC 2015.^[65]

Metal(III) oxo-trimers show more diverse structural complexity due to their higher degree of connectivity than metal(III) chains. MIL-88A is a prototypical breathing MOF with trivalent oxo-trimers as SBU. Serre et al reported in 2004 the ambient synthesis in methanol of this MOF relying on preformed trimeric Fe acetate SBU and in 2010 its ambient green synthesis conditions based on various metal sources.^[73] Very recently, Avci-Camur et al. reported RTS of MIL-88A in an aqueous solution through the assistance of acetylacetonate anions. However, the low product yield (25%) makes it hard to prepare at a large scale though it can be alternatively improved to 60% by heating the slurry at 90 °C.^[74]

Apart from the common SBUs observed in the abovementioned examples, more recently, a trivalent Bi(III) phenolate-based MOFs, bismuth ellagate (SU-101), was reported (see Figure 6).^[75] The overall framework is stable in a wide range of pH values. The synthesis was performed through a simple and green pathway, where only water and 6% of acetic acid (by volume) were used as solvent under ambient conditions. High-quality crystals were collected accordingly with a high product yield of 76%. Even though the space-time yield is still not high, only 5 kg m⁻³ day⁻¹, which is significantly lower than many other examples,^[76] one should note the simplicity of the synthesis procedure, carried out at atmospheric pressure and room temperature. To be noted, a very time-consuming synthesis at room temperature could also be problematic due to the many associated costs for an industrial production.

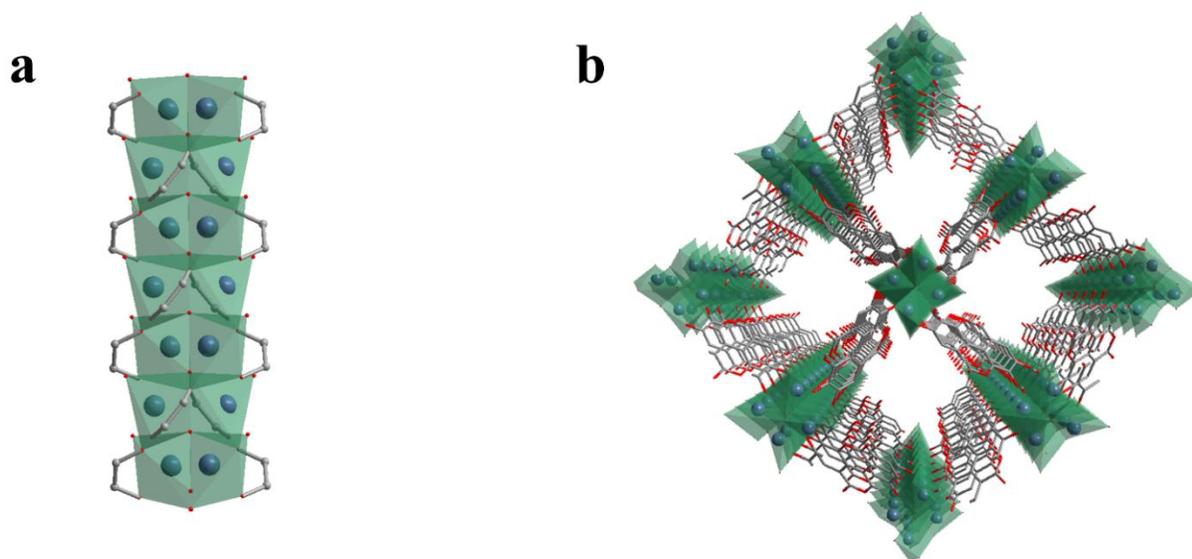


Figure 6. a) binuclear rod-like SBU (Bi_2O), b) the structure of SU-101 as viewed down the c -axis. Inorganic node polyhedra in green with oxygen in red, linker molecules in grey.

Table 2. Ambient synthesis examples for M(III) based MOFs.

Materials	Method	SBU	Modulator	Solvents	Synthesis duration (h)	$\frac{\text{RTS}_{\text{surface area}}}{\text{OS}_{\text{surface area}}}$ (m^2/g)	Ref
SU-101	One-step	Bi_2O	Acetic acid	H_2O	48	412	[75]
MIL-53(Al)	One-step	AlO_6	-	H_2O	24	1144/ 1140 ^[77]	[65]
MIL-100(Fe)	Two-steps	Fe_3 trimer	-	H_2O	12	2482/ 1800 ^[78]	[71]
MIL-100(Fe)	One-step	Fe_3 trimer	-	H_2O	48	1800/ 1800 ^[78]	[72a]
MIL-100(Fe)	Two-steps	Fe_3 trimer	-	Ethanol H_2O	0.08-72	356-1410/ 1800 ^[78]	[79]
MIL-53(Al)- NH_2	Two-steps	AlO_6	-	H_2O	14	518/ 1347 ^[80]	[81]
MIL-88A	One-step	Fe_3 trimer	-	H_2O	72	-	[74]
MIL-88A	One-step	Fe_3 trimer	-	EtOH H_2O	24	-	[82]

*: OS represents the original synthesis, including solvothermal/ hydrothermal synthesis.

In summary, the room temperature synthesis of crystalline trivalent MOFs is still at its early stage in contrast to divalent ones, mainly due to the higher reactivity of M(III) cations. The appearance of more general and easier synthetic approaches is still required. Besides, the excellent chemical/ thermal stability of trivalent MOFs can allow their doping with several metal cations. Recent publications have demonstrated that these heterometallic MOFs are of importance for emerging applications.^[83] Room-temperature synthesis might facilitate the integration of metals cations with various valences into MOFs structures by preventing their oxidation/ reduction that may occur using higher temperature syntheses. The relevant ambient syntheses of trivalent MOFs are listed in Table 2.

▪ M(IV) MOFs

Tetravalent-metal carboxylate based MOFs are another important subclass of MOFs, usually showing a high chemical/ thermal robustness in comparison to other MOFs.^[84] According to Pearson acid-base theory (HSAB), the hard Lewis acids (e.g., metal with high oxidation state) can bond strongly with hard Lewis bases (e.g., carboxylate, phosphonate,^[85] etc.), which thus makes the M(IV)-MOFs robust enough even in some very harsh conditions (boiling water, aqua regia, ammonia vapor).^[84a, 86] Typically, the M(IV) elements in the MOFs chemistry include all the group four elements, which is the second group of transition metals in the periodic table and some lanthanides and actinides. Zr(IV)-MOFs are the most explored tetravalent MOFs due to their appealing properties, including low toxicity, high abundance, excellent stability and their relatively easier crystallisation. For instance, UiO-66 (UiO= University of Oslo) is a benchmark Zr-MOF constructed from Zr(IV) hexanuclear oxoclusters (Figure 7b) connected through 12 terephthalate ligands (typically called 12-connected Zr₆ based phase).^[87] Since the report of UiO-66 in 2008, many promising applications based on this MOF or its analogues have been reported.^[88] This work has also inspired many following discoveries of other Zr-MOFs.^[89] The synthesis of Zr-MOFs was at that time still very challenging due to the high reactivity of Zr(IV) cations with organic linkers, which formed immediately poorly crystalline solids once mixed in solution. In 2011, Schaate et al. reported that the use of monocarboxylic acids (e.g., formic acid, acetic acid), employed as a modulator, enable a certain control of the kinetics of coordination between metal and di, tri, or polytopic ligands through competitive effect.^[90] The modulated synthesis of Zr-MOFs led to the rapid discovery of series of Zr-MOFs, in which Zr₆ oxocluster is the most common SBU. As this oxocluster can connect different carboxylate ligands regardless of their difference in topic, size, angle, or functional group, many MOF topologies were obtained.^[91] So far, there are Zr₆ based structures with 12-connected,^[92] 10-connected,^[92] 9-connected,^[93] 8-connected,^[86] 6-connected^[94] and 4-connected oxoclusters.^[95] The careful control over the synthesis conditions have also allowed the generation of Zr-MOFs with novel SBUs, such as the ZrO₇ chain found in the MIL-140 series (Figure 7a)^[96] or more recently Zr₁₂ oxoclusters (Figure 7c).^[97]

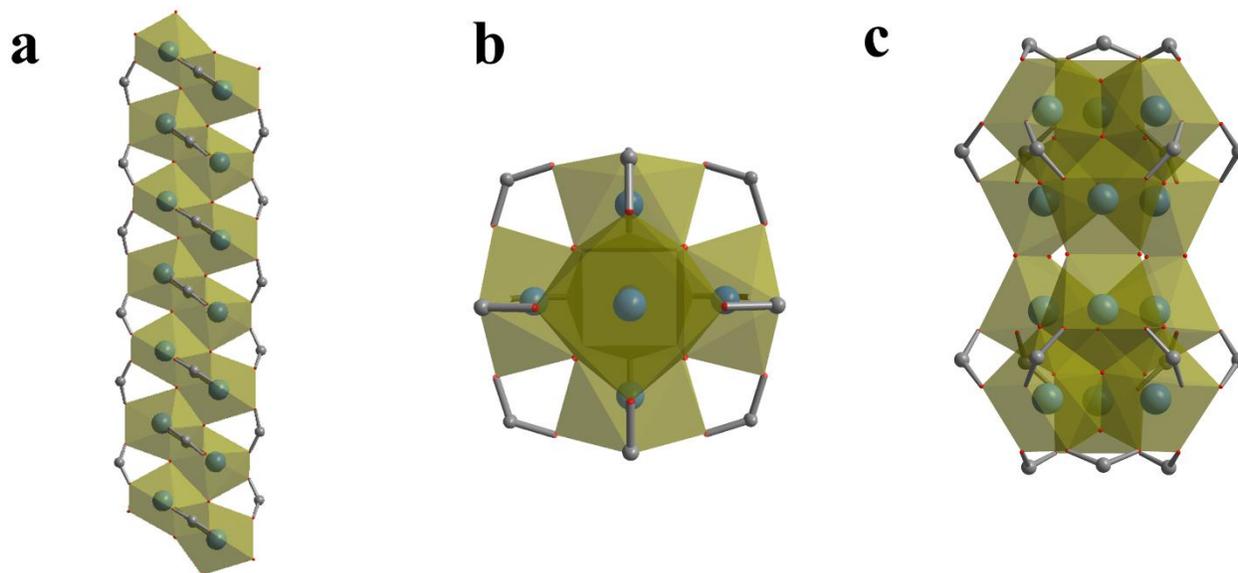


Figure 7. Graphical illustration of common SBUs within Zr(IV)-MOFs, a) ZrO_7 chain, b) Zr_6 oxoclusters, c) Zr_{12} oxoclusters.

The RTS of Zr-MOFs is complex for many reasons: 1) the high acidity of the solution, which makes difficult the deprotonation of the ligands before the formation of coordination bonds, 2) the exchange reaction between the modulator and organic ligand that needs to be controlled, possibly through heating steps, 3) to the fact that the activation energy for MOF nucleation and growth should be lowered if one wants to work at RT 4) the tendency to form poorly crystalline products. As tetravalent MOFs are relatively recent in comparison to their di/ tri-valent counterparts, the corresponding ambient routes are thus still scarce. In the following, we present several recent strategies that have been successfully applied so far to prepare such materials.

▪ **Stepwise room temperature synthesis**

In 2010, Guillerm et al. reported the synthesis of a UiO-type of MOF with *trans*, - *trans*-muconic acid as the organic ligand using pre-formed zirconium methacrylate oxoclusters as the starting material in DMF at room temperature.^[22b] This strategy is called “two-steps synthesis” (illustrated in Figure 8a) because the commercially unavailable Zr_6 oxoclusters should be pre-synthesized. However, it should be noted that the resulting Muconate-Zr MOF showed relatively low crystallinity even after 4 days of synthesis. Farha and his coworkers more recently used a similar two-steps synthesis to successfully prepare higher quality UiO-66 and its analogues (linker functionalized with $-NO_2$, $-OH$ and $-NH_2$) in DMF at room temperature. They also demonstrated that the defect content of the synthesized UiO-66 decreased when the reaction temperature was increased.^[98] Afterwards, the same group reported that the two-steps synthesis can be also used to synthesize an 8-connected Zr_6 -MOF, NU-901, at room temperature regardless the lower connectivity mode of the oxocluster.^[99] The works involving two-steps RTS are summarized in Table 3. Apart from the two-steps synthesis based on the performed Zr_6 oxoclusters, another two-steps strategy was also proposed recently by Pakamoré et al., where the 2-aminoterephthalic (ATA) acid was pre-treated with NaOH to form Na_2ATA salt at 60 °C. The Na_2ATA solution was then mixed with $ZrOCl_2 \cdot 8H_2O$ in the mixture of H_2O and acetic acid to efficiently form well-crystalline UiO-66- NH_2 (Figure 8b). Notably, authors alternatively used H_2O as solvent instead of the usual toxic and degradable DMF, which will hopefully pave the way towards more sustainable synthesis.^[100] Two-steps room temperature synthesis gives advances for applications, which are discussed in the following part. However, it hinders their use for industrial-level applications due to the relatively complex synthesis procedure. Furthermore, the use of highly toxic solvents, such as DMF and DEF, should be avoided as much as possible. Alternatively, green chemistry, as defined by IUPAC, points out that the chemicals should be non-hazardous to humans.^[101] Therefore, the use of greener solvents, such as H_2O , ethanol, acetone, ethyl acetate, that are commonly accepted in MOFs synthesis is recommended.^[15, 102]

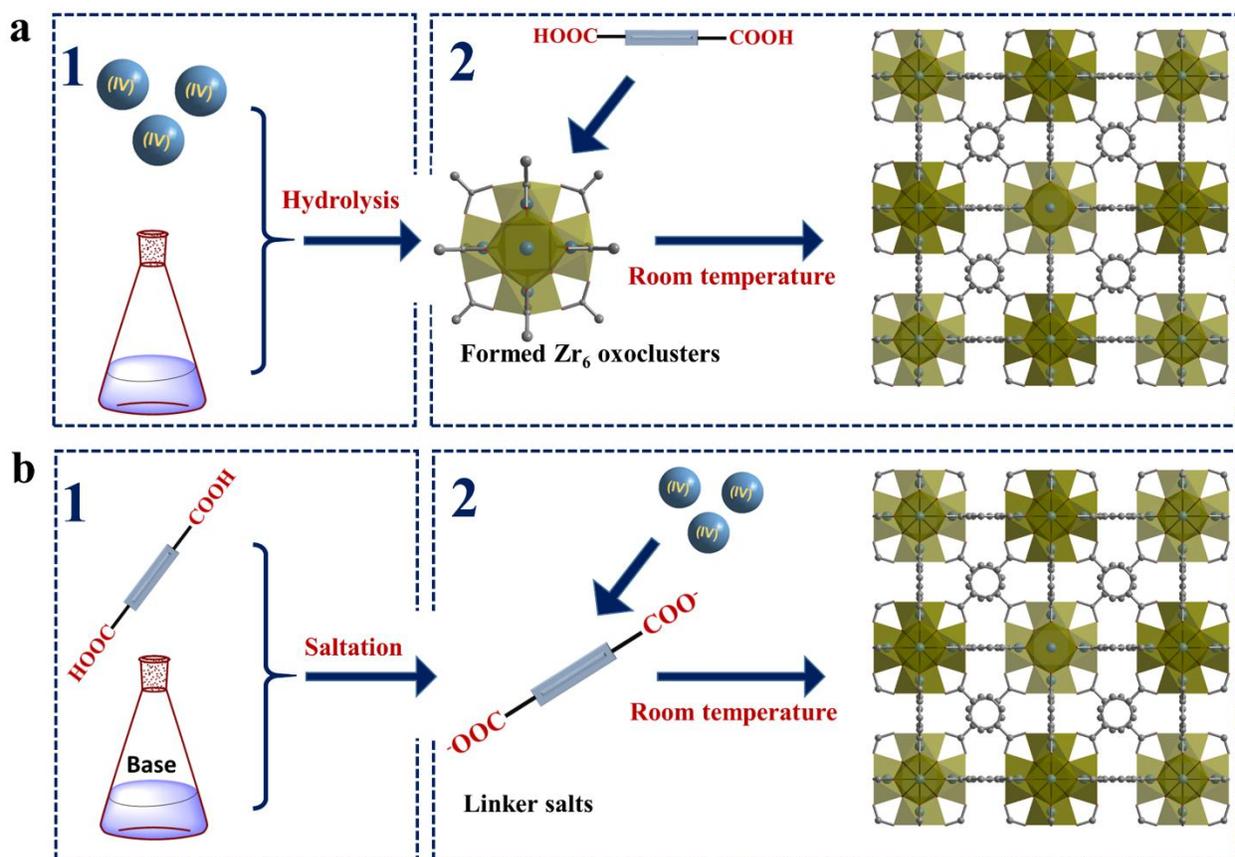


Figure 8. Two-steps room temperature synthetic approaches a) based on performed Zr_6 oxoclusters, b) based on the pre-treated

organic linker. the

- **Additives-assisted room temperature synthesis**

Additive-assisted RTS refers to the synthesis that requires additional species to facilitate the formation of the corresponding MOFs at room temperature. Often, these additives can effectively lower the activation energy of both the MOF nucleation and growth. The room temperature synthesis frequently needs long synthesis duration (>2 days), even when two-steps syntheses are used.^[22b, 98-99] In order to address this, Gu and his team proposed a salting-in species induced self-assembly (SSISA) strategy based on the Hofmeister effect to synthesize a series of MOFs with milder conditions.^[103] Taking advantage of SSISA strategy, they found that a series of pure Ce-UiO-66-X (-H, -CH₃, -Br, -NO₂) can be synthesized at room temperature within 10 min to 6h. Ce(IV)-MOFs are another class of tetravalent MOFs, showing many structural similarities to the well-known Zr-MOFs, in addition to their unique photo-redox properties.^[104] Hofmeister effect describes the influence of anions in the solubility of organic solutes. In that case, BDC was used as a model ligand due to its intensive use in MOFs chemistry. The salting-in ions (the left side in Figure 9a, NO₃⁻, ClO₄⁻, SCN⁻, I⁻) significantly enhance the solubility of BDC in aqueous solution, which therefore decreased the activation energy of MOF nucleation to allow the MOFs formation at room temperature (Figure 9b). However, these RT Ce-UiO-66-X neededs to be well-washed with DMF after the synthesis, particularly when using pristine BDC, probably due to the incomplete crystallization of MOFs in these conditions.

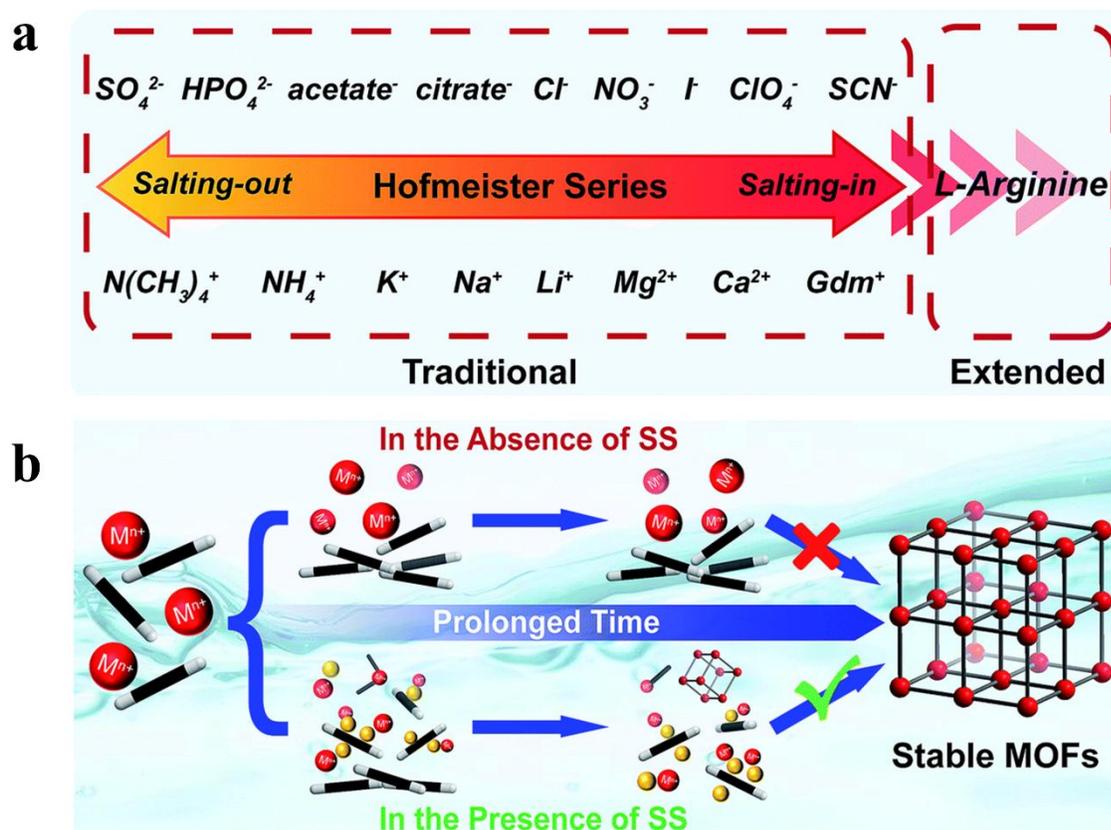


Figure 9. a) Illustration of Hofmeister effect, b) schematic illustration of the SSISA strategy based on Hofmeister effect, SS= Salting-in species. Reproduced with permission, RSC 2019.^[103]

This promising SSISA strategy could hopefully pave the way for realizing more general RTS. Nevertheless, the introduced additives may rise issues such as sample contamination and additional costs. As such, more straightforward synthetic methods are still desired.

- **One-step synthesis**

Room temperature direct synthesis stands for the straightforward synthesis without additional additives, multiple steps, or dependence on any salts. In contrast with the above-mentioned strategy relying on additives, using a specific solvent, precursor or synthetic conditions can lead to tetravalent MOFs crystallization. For example, Sang et al. in 2017 reported that using ionic

liquids (ILs) as solvent, high-quality UiO-66 can be efficiently prepared in 0.5h at room temperature. In that case, the size of the UiO-66 particles can also be simply controlled from 30 nm to 80 nm by changing the anions and cations of ILs. In-situ small-angle X-ray scattering (SAXS), X-ray absorption fine structure (XAFS), and ^1H nuclear magnetic resonance (^1H NMR) spectroscopy were applied to dynamically follow the formation of MOF nanoparticles. First, the solvation effect of Zr(IV) precursor $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ causes hydrolysis and dehydration to yield polymeric hydroxide $\text{Zr}_4(\text{OH})_{12}$ (displayed in Figure 10i). Subsequently, the introduced ILs promote the coordination between the BDC and Zr(IV) through its stronger interaction with acetic acid, which accelerated both the formation of Zr_6 oxoclusters and MOF NPs (Figure 10ii, iii, iv). The resulting UiO-66 showed comparable BET surface area as the examples synthesized using solvothermal strategy, which indicates the excellent removal of the additives.^[105]

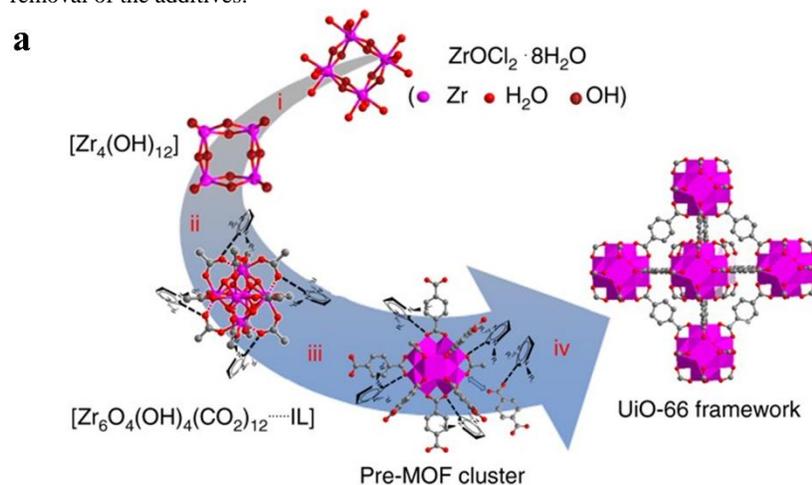


Figure 10. Schematic diagram of the UiO-66 formation in ionic liquid, (i) $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ hydrolysis to polymeric hydroxide $\text{Zr}_4(\text{OH})_{12}$, (ii) Complexation of zirconium by addition of acetic acid, (iii) IL-assisted linker exchange between acetic acid and BDC to produce pre-MOF oxocluster, (iv) UiO-66 framework formation. Produced with permission. Spring 2017.^[105]

Recently, Avci-Camur et al. showed that metal acetylacetonate complexes can serve as metal sources for the aqueous synthesis of MOFs with good yield (>85%).^[74] Interestingly, by using this approach, a series of UiO-type of MOFs including Fumarate-Zr, UiO-66-(OH)₂, and UiO-66-NH₂ can be facily prepared at room temperature in an aqueous solution without any additional additives or pre-treatment. Even though this synthesis took around 3 days, this example offered guidance for the following studies, where heating Zr(IV) precursors or ligands is not necessary. However, neither UiO-66-COOH nor UiO-66-(COOH)₂ were synthesized at room temperature and rising the temperature to 90 °C along with increasing reactants concentration were required. This work demonstrated the unique role of metal acetylacetonate complexes in synthesizing UiO-type of MOFs at room temperature. However, no further explanation on the role of acetylacetonate complexes was proposed, while this might be the key to understand the mechanism for future development.

Very recently, we reported the first versatile one-step synthesis at room temperature of tetravalent based MOFs in water using commercial reactants.^[106] As shown in Figure 11a, archetypical MOFs based on either 12-connected phases (MOF-801, UiO-66-NH₂, UiO-66-COOH) and 8-connected (DUT-67, PCN-222) Zr_6 oxoclusters were all simply synthesized at room temperature with the use of water/ ethanol. Furthermore, fumarate-Zr (or MOF-801) was used as a representative example to demonstrate that the synthesis can be performed with different Zr precursors (inorganic/ organic salts) and with several other tetravalent metal cations (Zr, Hf, Ce) and different type of modulators (acetic acid, formic acid). *In-situ* powder diffraction (Figure 11b) was considered to shed light on the nucleation/ growth process, revealing the importance of the concentration on the synthetic efficiency. In addition to the previously investigated synthetic factors, the critical role of the reactants concentration in lowering down the activation energy may guide the future RTS of tetravalent MOFs. This facile synthesis also allowed a modulator-induced size tuning from 220 nm to 45 nm, which will hopefully be useful for applications based on nano-MOFs. Finally, a 5 L pilot-scale system was used (Figure 11c) to evaluate its scalability. The space-time yield (STY) was also determined for the first time with this system, giving a value of 168 kg/ m³/ day. The N₂ isotherms, PXRD measurements, and pilot-scale system demonstrated the high quality of all the prepared MOFs obtained at high yield, which will hopefully pave the way for their future industrial production. To be noted, the low-temperature-induced defect (LTID) was observed among all the synthesized 12-connected MOFs, which made each Zr_6 oxoclusters linked to 8 ligands in average. The very high content of defect for *fcu* phases may also endow many possibilities to the applications that rely on coordination unsaturated sites.

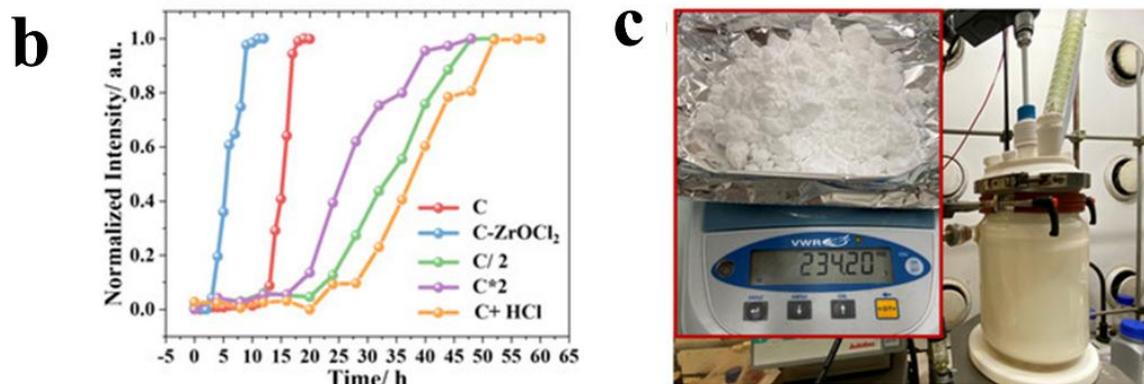
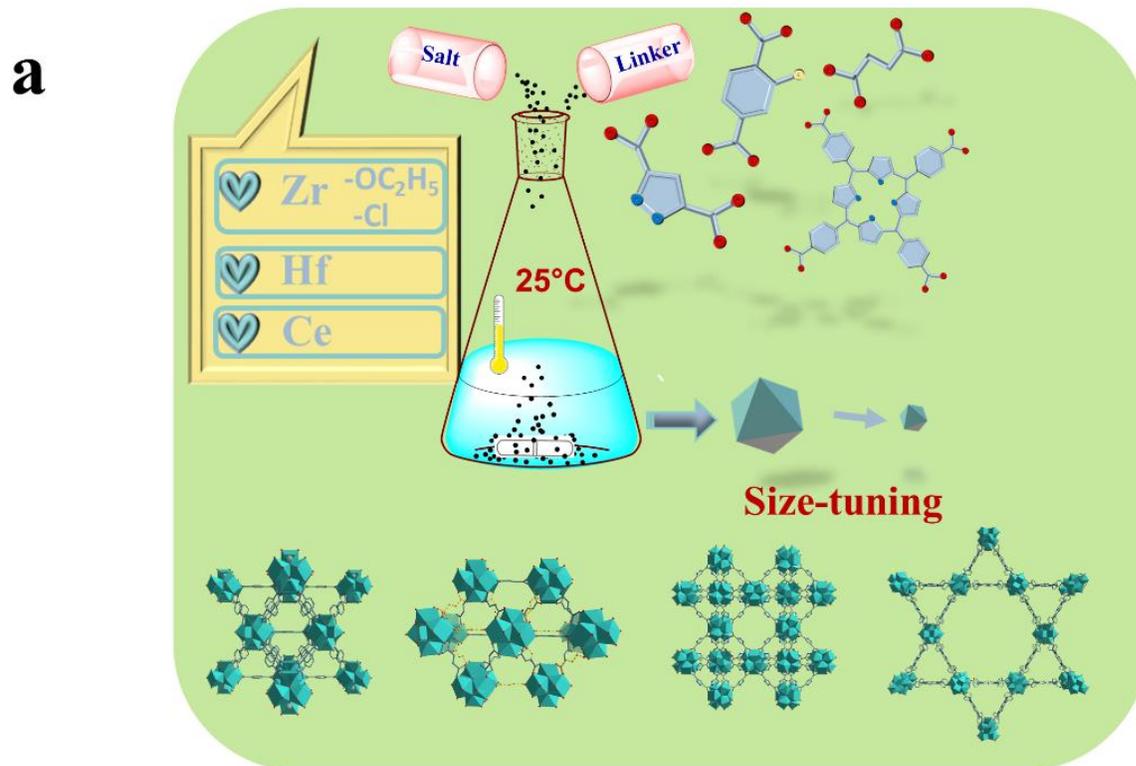


Figure 11. a) Schematic diagram of the room temperature one-step approach, b) plot of the synthesis time versus the intensities of the strongest (1, 1, 1) reflection of MOF-801 with varying precursors concentrations (the reactions were considered saturated when the intensities did not grow significantly), C represented the MOF-801 synthesized in 0.15 mmol/ mL precursors concentration, C*2 represented the 2 times multiple concentration, C/2 represented the 2 times divided concentration, C-ZrOCl₂ represented the MOF-801 synthesized with ZrOCl₂ in 0.15 mmol/ mL concentration, C+ HCl represented the MOF-801 synthesized in 0.15 mmol/ mL reactant with the presence 0.6 mmol/ L of HCl, c) 5L glass reactor laboratory pilot scale system for the upscaling synthesis of MOF-801, inserted picture: mass of product after synthesis, washing and drying. Produced with permission, Wiley 2021.

Table 3. Ambient synthesis examples for M(IV) based MOFs.

Materials	Method ^a	Connectivity of Zr ₆	Modulator ^b	Solvents	Synthesis duration (h)	RTS _{surface} area/ ST _{surface} area (m ² /g)	Ref
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PCN-224	Two-steps	(4, 6)	AA	DMF	12	2164/ 2600 ^[107]	[108]
UiO-66	Two-steps	12	AA	DMF	18	1450/ 1105 ^[109]	[98]
UiO-66-NH₂	Two-steps	12	AA	DMF	18	1290/ 1123 ^[109]	[98]
UiO-66-OH	Two-steps	12	AA	DMF	18	1140/ 1000 ^[110]	[98]
UiO-66-NO₂	Two-steps	12	AA	DMF	18	960/ 792 ^[109]	[98]
NU-901	Two-steps	(4, 8)	AA	DMF	ON	2130/ 2276 ^[111]	[99]
UiO-66-NH₂	Two-steps	12	AA	H ₂ O	24	888/ 1123 ^[109]	[100]
UiO-66	OS-RD	12	AA	ILs	0.5	1519/ 1105 ^[109]	[105]
UiO-66-NH₂	Two-steps	12	AA	H ₂ O	0.17	717/ 1123 ^[109]	[112]
Muconate-Zr	Two-steps	12	AA	DMF	96	905	[22b]
UiO-66-(COOH)₂	Two-steps	12	TFA	H ₂ O	48	890/ 415 ^[113]	[114]
UIO-66-F₄	Two-steps	12	AA	H ₂ O	48	690/ 680 ^[115]	[114]
Ce-UiO-66	Additive	12	-	H ₂ O	6	968/ 1282 ^[104b]	[103]
Ce-UiO-66-NO₂	Additive	12	-	H ₂ O	0.08	-	[103]
Ce-UiO-66-Br	Additive	12	-	H ₂ O	0.08	-	[103]

Ce-UiO-66-CH₃	Additive	12	-	H ₂ O	0.08	-	[103]
Fumarate-Zr	OS-RD	12	AA	H ₂ O	72	1249/ 856 ^[116]	[74]
UiO-66-NH₂	OS-RD	12	AA	H ₂ O	72	1106/ 1123 ^[109]	[74]
UiO-66-(OH)₂	OS-RD	12	AA	H ₂ O	72	733/ 560 ^[110]	[74]
Fumarate-Zr	One-step	12	AA/ FA	H ₂ O	5	1035/ 856 ^[116]	[106]
Hf-MOF-801	One-step	12	AA/ FA	H ₂ O	12	737	[106]
Ce-MOF-801	One-step	12	AA/ FA	H ₂ O	1	781/ 732 ^[104b]	[106]
UiO-66-NH₂	One-step	12	AA/ FA	H ₂ O EtOH	12	1256/ 1123 ^[109]	[106]
UiO-66-COOH	One-step	12	AA/ FA	H ₂ O	72	1052/ 551 ^[117]	[106]
DUT-67	One-step	(2, 8)	FA	H ₂ O	48	1018/ 1057 ^[118]	[106]
PCN-222	One-step	(4, 8)	FA	H ₂ O EtOH	48	1394/ 1728 ^[119]	[106]

a: OS-RD indicates the direct one-step synthesis while having a reagent-dependent issue.

b: AA, FA represent acetic acid and formic acid, respectively, TFA refers to trifluoroacetic acid.

*: OS represents the original synthesis, including solvothermal/ hydrothermal synthesis.

Tetravalent MOFs have been extensively investigated in the past decade mainly due to their extraordinary chemical robustness. Apart from the interest in discovering new structures, the room temperature synthesis route of M(IV)-MOFs in green solvents offers potential promises for their next-step scale-up synthesis and commercialization. Furthermore, we are convinced that room-temperature synthesis of tetravalent MOFs can not only stimulate their broader fundamental study due to the simplified synthetic threshold, but also promote the exploration of derived new composites in a view of selected applications.

Applications of room temperature synthesis strategy

Compared to other porous solids like zeolites, which in most cases still need harsh hydrothermal synthesis conditions,^[120] MOFs can now be synthesized more and more frequently at room temperature. This is of interest not only to meet the requirements of sustainable chemistry and pave the way for their future industrial production but also to develop novel applications. In the following content, we will summarize the main progress in this topic.

- Incorporating temperature-sensitive species through bottle-around-ship

Incorporating guest moieties into MOFs can endow a great potential for several applications such as catalysis^[121] and bio-labeling. The properties of the resulting composites may outperform the one of each single component, particularly for catalysis applications. The concept of catalytically synergetic effect in MOF-based composites has been well-described and reviewed in many articles.^[122] The bottle-around-ship strategy represents the construction of a core-shell structure, where the core is preformed and then mixed with the MOF precursors solution, which subsequently allows the fabrication of a shell on the surface of the core materials. It enables the incorporation of active species regardless of the differences in size, shape, morphology, and even components between the core and shell.^[21] This strategy differs significantly from the conventional occupancy of MOFs cavity by active guests, which is called ship-in-a-bottle strategy.^[123] However, to successfully prepare core-shell composites, especially when dealing with small inorganic nanoparticles, relatively mild MOF synthesis conditions are requested due to the easy degradation of these temperature-sensitive guests.^[124]

In an early stage contribution, Lu et al. reported a versatile approach using ambient synthesis to fabricate a series of core-shell Au/ Pt NPs@ZIFs structures (Figure 12a).^[125] The subsequent catalytic/ photonic property enhancement was observed. Subsequent works using ZIF series prepared at room temperature led to even more exciting achievements.^[126] The ambient synthesis of chemically stable Zr-MOFs is also interesting for the construction of inorganic nanoparticles based core-shell architecture. For instance, a very recent paper from Jiang's group reported the successful fabrication of core-shell Pt NCs@PCN-224 through RTS (Figure 12b). The same fabrication while using the conventional solvothermal method led to core-shell structure too, but with a pronounced aggregation of Pt NPs, which is a drawback for catalytic applications.^[127] In addition to the small inorganic nanoparticles, another temperature-sensitive biomolecules have also been incorporated in MOFs using RTS (e.g., protein, Figure 12c).^[128] The formed protein@ZIF-8 showed a retained bioactivity even after being treated at 80 °C and boiled in DMF. Another study revealed the encapsulation of enzymes within ZIF-8 that led to not only stability improvement but also bioactivity enhancement.^[129]

These results illustrate the premises of core-shell composites in many applications regardless of their difficulty in synthesis.^[130] The RTS approach provides optimized synthetic parameters for this goal. Nevertheless, the most investigated MOFs so far are divalent MOFs, which are in most cases not robust enough against humidity or water for some applications. The recent developments of ambient synthesis strategies on more chemically robust tri/ tetra-valent MOFs may however pave the way for the future expansion of this field.

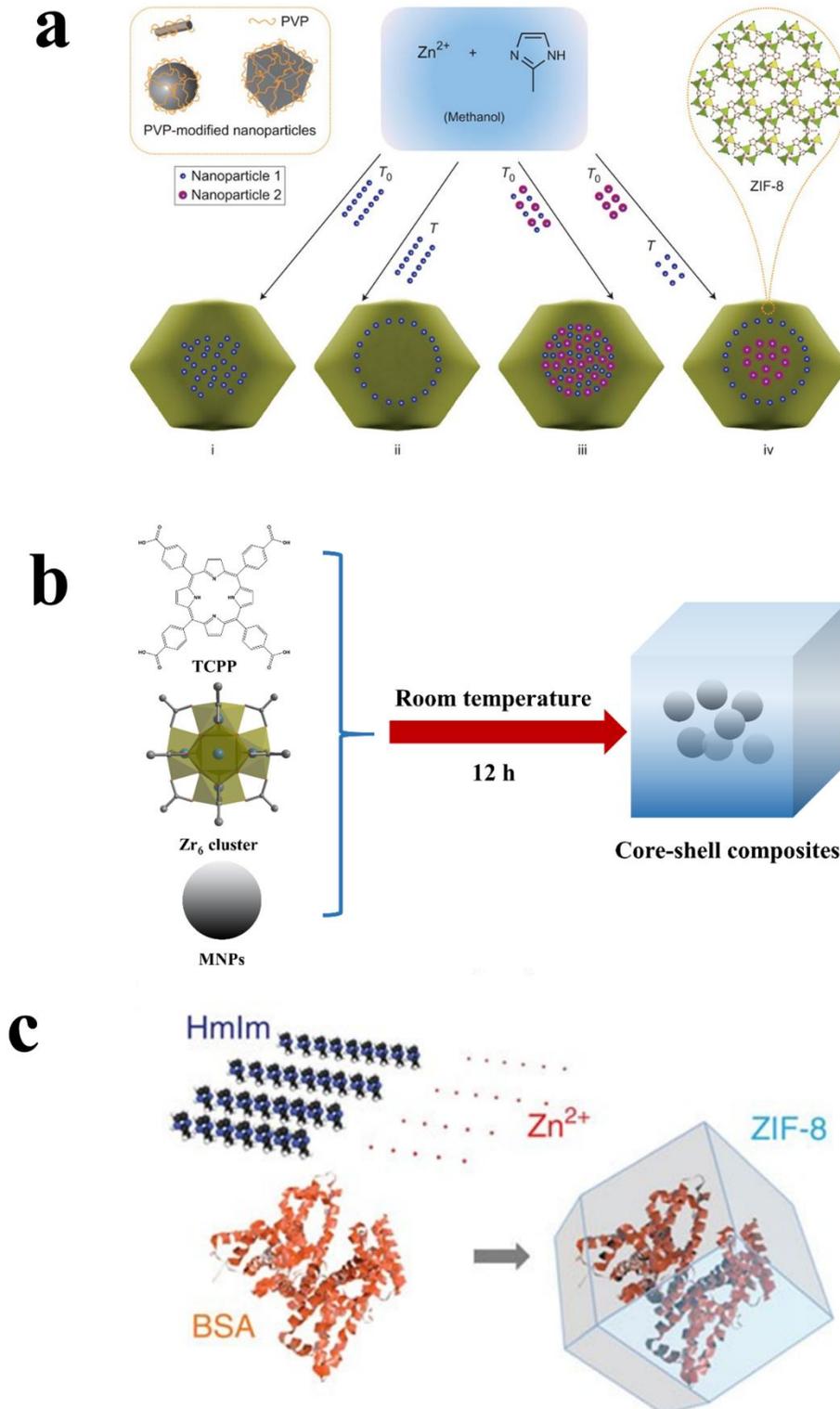


Figure 12. a) Scheme of the controlled encapsulation of inorganic nanoparticles in ZIF-8, the spatial distribution of incorporated PVP-modified nanoparticles within ZIF-8 crystals can also be controlled by their different addition sequence, b) Scheme of the strategy to form core-shell Pt NPs@PCN-224, c) Schematic proposing the fabrication of protein@ZIF-8 composite. Produced with permission, Springer 2012,^[125] Springer 2015.^[128]

- Room temperature assisted defect-engineered MOFs

Low-temperature synthesis method has been realized as a useful tool to manipulate the defect content in Zr-MOFs in 2010.^[22b] Farha and co-workers found similar results in the cases of 12-connected UiO-66 and 8-connected NU-901, both synthesized at room temperature.^[99, 131] It has been well-documented that the presence of defect sites in given MOF is of particular interest for their properties modulation, such as catalytic reactivity mainly due to the more exposed metal sites. Our recent findings revealed that RTS in the aqueous solution can effectively generate highly defective UiO-type MOFs. The synthesized fumarate-Zr displayed 8-fold connectivity for each Zr_6 instead of 12, which is among the most defective UiO-type of MOF. Consequently, the water vapor isotherm on the defective fumarate-Zr indicated the high adsorption capacity, as well as high affinity with H_2O of these very defective MOFs due to the increased Coulomb interaction from $-OH$ group at the defect sites.^[106] Kang et al. recently found that the rapid and ambient electrosynthesis of a Cu-carboxylate MOF (MFM-100) led to more defective MFM-100(c, d) (Figure 13c, d) than MFM-100 (a, b) from solvothermal batch (Figure 13a, b),^[132] making them more reactive for the selective oxidation of benzyl alcohol (Figure 13e). More importantly, the produced defective mesoporous MFM-100 can be reused for at least five cycles, indicating there is no much compromising in the MOF stability when defect are presents (Figure 13f). This example revealed the ambient synthesis can not only lead to a larger pore size material but also facilitate catalytic oxidation with excellent cycling performance.

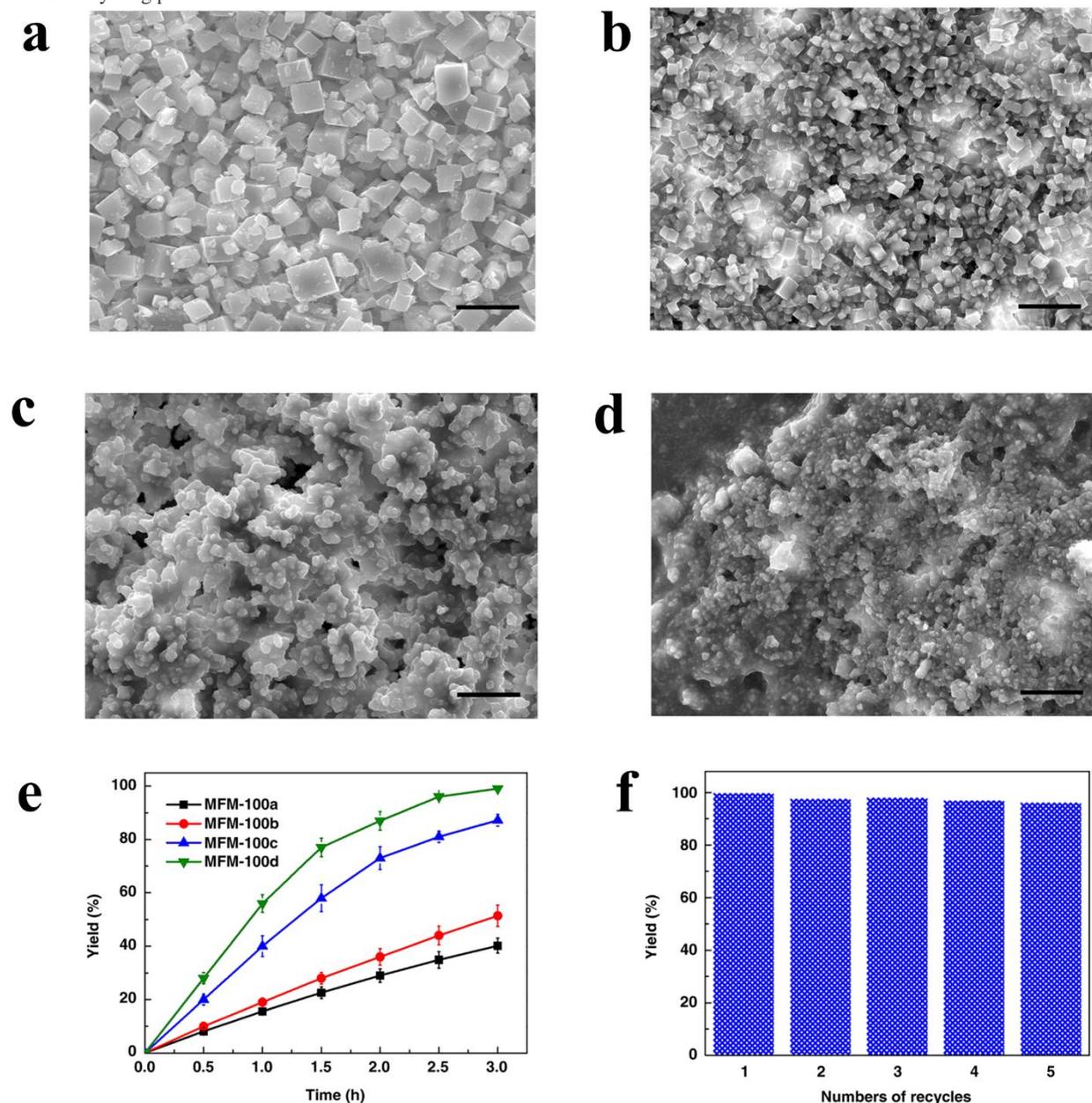


Figure 13. SEM images of a) MFM-100a, b) MFM-100b, c) MFM-100c, d) MFM-100d. e) Time-dependent yields of aldehydes

from selected substrates catalyzed over MFM-100. f) Reusability of MFM-100d. Produced with permission, Springer 2019.^[132]

RTS can be regarded as a useful platform to stretch the applications of the corresponding MOFs, such as the aforementioned ones. However, synthesizing MOFs in mild conditions has also been demonstrated as an interesting way to allow many *in-situ* techniques that are only operational in very mild conditions, such as *in-situ* Transmission electron microscopy,^[133] *in-situ* Static light scattering,^[134] and laboratory *in-situ* Powder X-ray diffraction.^[106] For instance, in order to get an insight on the crystallization process of any given MOF, *in-situ* PXRD is often the best technique. However, most of MOFs syntheses rely on solvothermal/ hydrothermal conditions to form crystals and can therefore only be studied using synchrotron-based X-Ray radiation combined with pressure-resistant systems. The ambient synthesis conditions can allow researchers to investigate the MOF synthesis kinetics using a laboratory X-ray diffractometer. From a fundamental understanding point of view, having an insight on nucleation and growth processes, as well as the existence of possible intermediates, is of critical importance, as it may lead to a better understanding of the synthesis processes and even to new synthetic concepts.

▪ Perspectives and conclusions

Developing the room temperature synthesis (RTS) under green conditions of a MOF of interest, has become nowadays pre-requisite in parallel to the investigation of its potential applications. In this review, we have summarized the development of MOFs RTS with a special emphasis on the most chemically stable MOFs. Even though some promising synthesis routes have been reported to date, many challenges still remain. In terms of sustainable synthesis, RTS is of interest when compared to the conventional heating methods. However the limited product yield, as well as the prolonged synthesis duration, still need to be circumvented prior to their utilization in industry. The space-time yield, although by far not the sole parameter to be considered to assess the technico-economic production of a solid, is still not taken into account systematically in most studies. Moreover, the use of highly toxic organic solvents or corrosive metal salts is still common, while it is not favorable for industrial applications. One can alternatively consider the use of greener organic solvents, such as ethanol, acetone, or ethyl acetate if the organic ligands are insoluble in pure water at room temperature. The extension of RTS to more chemically robust MOFs has been recently preliminary achieved, but the mechanism behind still needs further understanding, particularly for the nucleation-growth kinetics. Regarding the potential applications, the room temperature synthesis of divalent MOFs, particularly ZIFs, has already intensively been used for the incorporation of temperature-sensitive compounds. The room temperature efficient synthesis procedure and ideal crystallinity make especially ZIF-8 very suitable for achieving this goal. However, the ultra-small aperture size (3.4Å), limited chemical stability and deficient functions of ZIF-8 are in some cases important drawbacks for this MOF. The application of high-valence MOFs might hopefully address these limitations although their range of stability and properties often differs. Additionally, room temperature synthesis routes allow high throughput parametric investigation, possibly assisted by fluidics, which is more desired in the stage of materials optimization. Finally, we hope this review article will facilitate the development of new energy-saving green synthesis routes of MOFs, their potential applications, and even new concepts in a near future.

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