



Hierarchical porous materials based on nanoscale metal-organic frameworks dominated with permanent interparticle porosity



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ABSTRACT

In order to extensively synthesize mesoporous metal-organic frameworks (mesoMOFs), we developed a strategy to construct permanent interparticle porosity based on nanoscale metal-organic frameworks (NMOFs). Using the strategy, we have attained a series of interparticle porosity dominated mesoMOFs (IPD-mesoMOFs) from six MOF-types with MIL-100, MIL-53, HKUST-1, DUT-5, DUT-4 and MIL-101(Cr) (termed as IPD-mesoMOF-1, -2, -3, -4, -5 and -6) structure, respectively. All members of this series are not only comparable to inorganic mesoporous materials to have the tunable mesopore apertures varying from a few nanometers to over a dozen nanometers, but also superior to the inorganic counterparts to remain hierarchical porosity with higher surface area (up to $2130 \text{ m}^2 \text{ g}^{-1}$), larger mesopore volume (the highest to $2.59 \text{ cm}^3 \text{ g}^{-1}$) and optional micro-porosity of diverse crystalline structures. The large mesopore apertures and rich carboxyl residues on the mesopore-walls also allow the IPD-mesoMOF series to accommodate large organic and inorganic molecules, especially to immobilize the bulky natural protein, such as, hemoglobin.

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1. Introduction

Metal-organic frameworks (MOFs) are highly porous materials [1–3]. Owing to high porosity, crystalline nano-sized space and excellent tunable functionality, they are potentially applied to gas storage [4], molecule separation [5], catalysis [6,7] and drug delivery [8,9]. However, most MOFs are still microporous that limits the application involving large organic, inorganic and biological molecules [10]. Very recently, a crystalline pore aperture in IRMOF-74 [11] comes to a climax of *ca.* 10 nm which robust architecture based on a very slender organic link benefits from the non-interpenetrating nature of MOF-74 architecture, setting an almost unduplicated record. Nevertheless, the reality is that only a minority of MOFs discovered so far are mesoporous and they almost all depend on the rigid slim organic links which, unlike IRMOF-74, unavoidably lead to framework instability and interpenetration [12]. Although in recent years, soft-templating method has led to several mesoporous MOFs (termed here as ST-mesoMOFs) [13–19], this method is obviously not so effective as it has been utilized extensively in the synthesis of mesoporous silica or metal oxides. The reason could be summarized as follows: (1) unlike the amorphous pore-wall nature of inorganic mesoporous materials

[20], the mesopore walls of some ST-mesoMOFs are based on the micron scale or nanoscale MOF (NMOF) single crystals, where the mesopores are the imprints inherited from the surfactant micelles mixed into the MOF single crystals. However, all crystalline substance has a tendency to expel the non-building blocks coming outside its crystal body that is why those ST-mesoMOFs only exhibit lower mesopore volume [17,18] (except a special example synthesized in an ionic liquid/ CO_2 /surfactant system [14]); (2) for some of the ST-mesoMOFs [13,15,16] with pore walls consisting of NMOF particles, the surfactant micelles must be sufficiently large to match with the size of NMOF particles. Otherwise, the surfactant cannot serve as the template, but as the filler in the micropores (as well as the interparticle pores) hard to be removed afterward; and (3) more important is that many MOFs have to be prepared hydrothermally (or solvothermally) at a temperature over $100 \text{ }^\circ\text{C}$. In such a synthesis condition, it is not feasible for most surfactants to form the supramolecular micelles. That is why merely a limited numbers of ST-mesoMOFs have been reported so far and they are mostly based on the MOF-type of HKUST-1 structure [13,15,17,18], which can be synthesized at a temperature below $100 \text{ }^\circ\text{C}$.

Since interparticle porosity in some NMOF samples [21–25] has not gotten as much attention as it should, we believe that permanent interparticle porosity can be created with many MOFs as long

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as they are prepared as NMOF particles. Sufficiently small NMOF particles should aggregate into monoliths [28] through coordination bonds between free metal coordination sites and organic residues on the surfaces and edges of NMOF particles in mutual contact, sustaining a permanent interparticle porosity. Thereby, to obtain the NMOF monoliths with mesoscopic interparticle porosity, we need only to prepare the NMOF particles within a size-confined nanoscale: assuming that these NMOFs were uniform rigid spheres with diameter ϕ_s and they could be closely packed into face-centred cubic (FCC) or hexagonal close packing (HCP) arrangements [26], forming tetrahedral and octahedral interparticle holes with diameter $\phi_{ht} \approx 0.225\phi_s$ and $\phi_{ho} \approx 0.414\phi_s$, respectively. Therefore, the interparticle porosity dominated mesoMOFs (IPD-mesoMOFs) with a pore diameter $2 \leq \phi_h \leq 50$ nm could be prepared by controlling the size of NMOF particles in the range from 5 to 222 nanometers. Thus, preparing NMOF particles (less than 222 nm) and making them closely packed should be the crucial criteria for generating IPD-mesoMOFs.

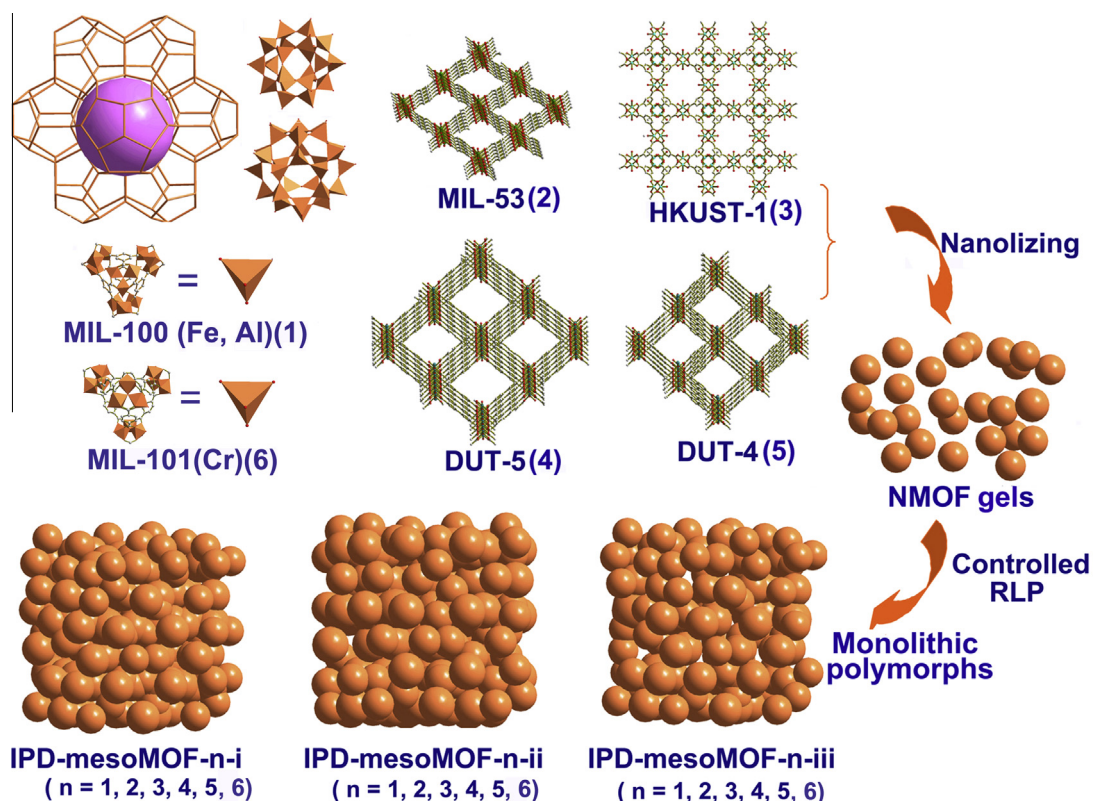
However, it is experimentally revealed that the size of NMOF particles is not as we have expected to be readily controlled and the interparticle interaction forces cannot hold the large (as large as 200 nm) NMOF particles into a stable monolith, sustaining the permanent interparticle porosity [27]. Thus, the interparticle-porosity-manipulation cannot be realized by controlling the size of the NMOF particles. It is also experimentally revealed that the NMOF particles are neither absolutely uniform nor rigid. Moreover, the interparticle forces make the sufficiently small NMOFs cohesive and the syneresis of liquid solvent as dried to gas leads the gelatinous NMOF solution to random loose packing (RLP) [28] or random close packing (RCP) [29] rather than the ordered FCC/HCP arrangements. Fortunately, the RCP and RLP arrangements of the sufficiently small NMOFs can be controlled by adding some of spherical organic compounds as interparticle-filler into the gelatinous NMOF solution to form monolithic polymorphs

dominated by the expected mesoporosity. Using the strategy, we have successfully attained a series of IPD-mesoMOFs based on the MOF-types of MIL-100(Fe, Al) [30,31], MIL-53(Al) [32], HKUST-1 [33], DUT-5, DUT-4 [34], and MIL-101(Cr) [35] structure (namely, IPD-mesoMOF-1, -2, -3, -4, -5 and -6) (Scheme 1), respectively.

2. Results and discussion

2.1. Synthesis and characterization of IPD-mesoMOFs

All members of the IPD-mesoMOFs are prepared solvothermally (except IPD-mesoMOF-3) in ethanol at a proper temperature for a certain reaction time (details see the experimental section). The IPD-mesoMOF-1(Fe)-i is the first IPD-mesoMOF obtained based on the NMOF formulated as $[\text{Fe}_3\text{O}(\text{BTC})_2(\text{OH})(\text{H}_2\text{O})_2]$. The SEM images show monoliths consisting of ca. 40 nm NMOF particles which are randomly close-packed and afford almost non-interparticle porosity [Fig. 1 (left: a)]. This result was further confirmed by nitrogen adsorption analysis that demonstrates a mixture of type I and IV isotherms with very small H4 hysteresis loop, giving rise to a mesopore volume only $0.14 \text{ cm}^3 \text{ g}^{-1}$ and Brunauer–Emmett–Teller (BET) surface area ca. $944 \text{ m}^2 \text{ g}^{-1}$ [Fig. 1 (right: black square)]. Small-angle X-ray scattering (SAXS) in the 2θ range of $0.5\text{--}3$ degree does not show any peak, indicative of disordering of the NMOF particles. Powder X-ray diffraction (PXRD) pattern in the 2θ range of $3\text{--}40^\circ$ shows broad peaks which is in agreement with that simulated from MIL-100 (Fe) structure with regard to whose large cubic crystal unit-cell (SI Fig. S1) [30]. By mixing a small amount of *t*-butanol into the ethanol solvent or by using *t*-butanol as the solvent, the different levels of RLP monolithic xerogels, termed as IPD-mesoMOF-1(Fe)-ii and -iii, were obtained. As uniformly aggregated NMOF particles, the



Scheme 1. Schematic diagram of the interparticle porosity generated from the controlled random loose packing NMOFs.

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