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Communication

A low-temperature synthesis-induced defect formation strategy for stable hierarchical porous metal–organic frameworks

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ABSTRACT

A stable hierarchical porous metal–organic framework PCN-56 with abundant Lewis acid sites (denoted as Defective-PCN-56) was synthesized by the low-temperature synthesis-induced defect formation method. The existence of mesopore in structure was confirmed by N₂ sorption isotherm and the successful encapsulation of large dye molecules. The Defective-PCN-56 has higher loading capacity toward anti-cancer drug Doxo compared with that of “nearly ideal-crystal” (denoted as Ideal-PCN-56) synthesized at high temperature, showing potential application as drug carrier. The low-temperature synthesis-induced defect formation strategy presented here provides a new and facile way to synthesize stable MOFs with the combination of intrinsic micropore and additional mesopore as well as abundant Lewis acid sites.

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Metal–organic frameworks (MOFs) have attracted much attention due to their porosity, tailorability and diverse functionality [1–3]. The pore size of MOFs, as a window for accepting guest molecules, plays an important role in realizing the functionalization of materials. Compared with the majority of ones so far are restricted to microporous regime in the field of MOFs, mesoporous MOFs have more advantages such as higher load on guest molecules, unrestricted diffusion of guest molecule, and better size-exclusion effect [4], which enable them to adsorb larger guest molecules [5] and enhance the interactions between the guest molecules and framework of MOFs [6].

In the past few years, some mesoporous MOFs have been reported [7–12]. The classical synthesis methods can be summarized as follows: a) Increasing the length of ligands; b) Designing a reasonable ratio of metal to ligand; c) Ligand exchange; d) Adding soft/hard-template; e) Adding a long-chain monocarboxylic acid as modulators to induce defects. However, these methods usually resort to tedious synthesis procedures and the obtained materials sometimes suffer from low structural stability, being difficult to apply in large-scale production.

As two contradictory attributes, the pore size enlargement and structural stability have been rarely achieved together. Jiang's

group [9] used long-chain monocarboxylic acid as competitive reagent to create defects in MOFs, and successfully synthesized stable mesoporous materials. This study inspires us to ponder over the question that besides the induction of defects using competitive reagents for creating mesoporous structure, can the defects and mesopore be realized by simply controlling the synthesis condition? If it is possible, the synthesis expense including the raw material and time, would be greatly reduced, and the large-scale production could achieve. Therefore, we attempted to synthesize stable mesoporous MOFs by control of the synthesis condition without any modulator [13,14].

Zirconium-based MOFs attract our interest due to their excellent thermal and chemical stability. In the actual synthesized MOF materials, the structures always contain a considerable density of defects [15–22]. The existence of defects provides not only exposed metal sites (Lewis acid sites), but also can free up a larger pore space to generate hierarchical pore structure.

In this work, we choose 12-linked Zr-MOF with *fcu* topology as a prototype to create hierarchical micro-mesoporous materials with existence of abundant Lewis acid sites (Fig. 1). A series of isostructural Zr-MOF including UiO-66 [23], DUT-52 [24], UiO-67 [23], and PCN-56 [25], with the linkers elongating from BDC to 2,6-NDC, BPDC and TPDC-2CH₃, were synthesized. It is found that defects can be induced in all those four structures at the low synthesis temperature 60 °C. However, only the organic linker longer than BPDC can generate significant amount of mesopore in structure, which was confirmed by N₂ sorption isotherm and the

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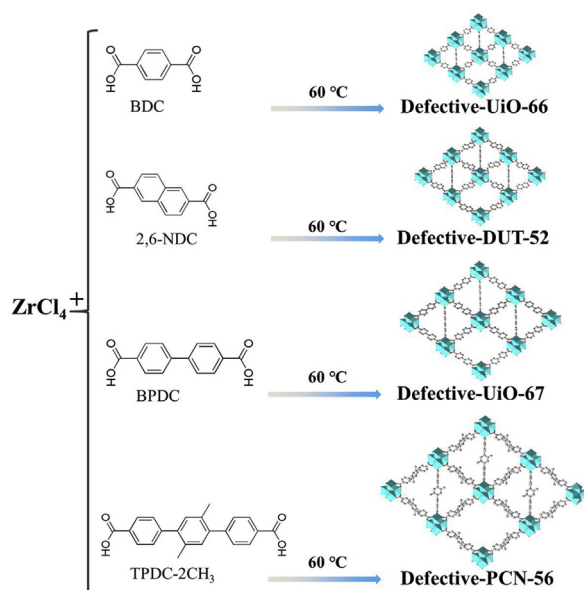


Fig. 1. The synthetic route for Defective-UiO-66, DUT-52, UiO-67, and PCN-56.

successful encapsulation of large dye molecules. The Defective-PCN-56 has higher loading capacity toward anti-cancer drug Doxo compared with that of “nearly ideal-crystal” (denoted as Ideal-PCN-56) synthesized at high temperature, showing potential application as drug carrier.

The four compounds were synthesized by a reaction using the same metal-ligand molar ratio (2:1) in DMF at 60 °C. As mentioned in Fig. S1 (Supporting information), the experimental powder X-ray powder diffractor (PXRD) patterns match very well with the simulated ones, which means the pure phases of these four materials have been obtained. As shown in Fig. 2a, the N₂ sorption isotherms of UiO-66 and DUT-52 display much lower uptake (173 cm³/g and 326 cm³/g,

respectively) than those of the materials synthesized at higher temperature in previous report, indicating the existence of higher density of defect in structures [23,24]. However, pore size distributions show that the defect only causes very small amount of mesopore in structures (Table S1 in Supporting information). Elongation of ligands to BPDC, the N₂ sorption isotherm of obtained UiO-67 starts to show slight stepwise behaviors, and larger amount of mesopore was observed (uptake: 574 cm³/g, BET: 2501 m²/g, pore width: 0.6~2.5 nm) [23]. Further elongation of ligand to TPDC-2CH₃, the N₂ sorption isotherm of Defective-PCN-56 exhibits an obvious stepwise adsorption, which belongs to the type VI adsorption (adsorption capacity: 960.9 mmol/g; Langmuir surface area: 4182 m²/g). This is a characteristic feature of hierarchical porosity in MOFs materials. The pore size distribution indicates that a large proportion of pore in PCN-56 distributed in the mesoporous region from 2.0 nm to 3.9 nm under low-temperature synthetic conditions (Fig. 2b). Interestingly, increasing synthesis temperature to 90 °C results in the disappearance of stepwise adsorption behaviors. The adsorption capacity is 858.2 cm³/g (Langmuir surface area 3735 m²/g) and pore size distribution is around 0.63~1.85 nm, approaching the value reported before [26]. Therefore, the higher synthesis temperature can result in less defects in the obtained structure, while the lower synthesis temperature induced the missing of linker and generation of mesopore in structure. Accompanying with the existence of mesopore, structural defect causes abundant Lewis acid sites in material. Lewis acid sites can strongly polarize gas adsorbents, and thus are favorable to CO₂ uptakes as well as adsorption enthalpy (Q_{st}) [27]. From Figs. 2c and d, we can see that the Q_{st} for Defective-PCN-56 is 22.41 kJ/mol, which is larger than that of the Ideal-PCN-56 (Q_{st} = 19.69 kJ/mol). Furthermore, the thermogravimetric analyses (Fig. S2 in Supporting information) show that the defective-PCN-56 synthesized at 60 °C has lower weight loss than the Ideal-PCN-56 [13], indicating fewer organic components in Defective-PCN-56. Additional evidence came from FT-Infrared spectra (Fig. S3 in Supporting information)

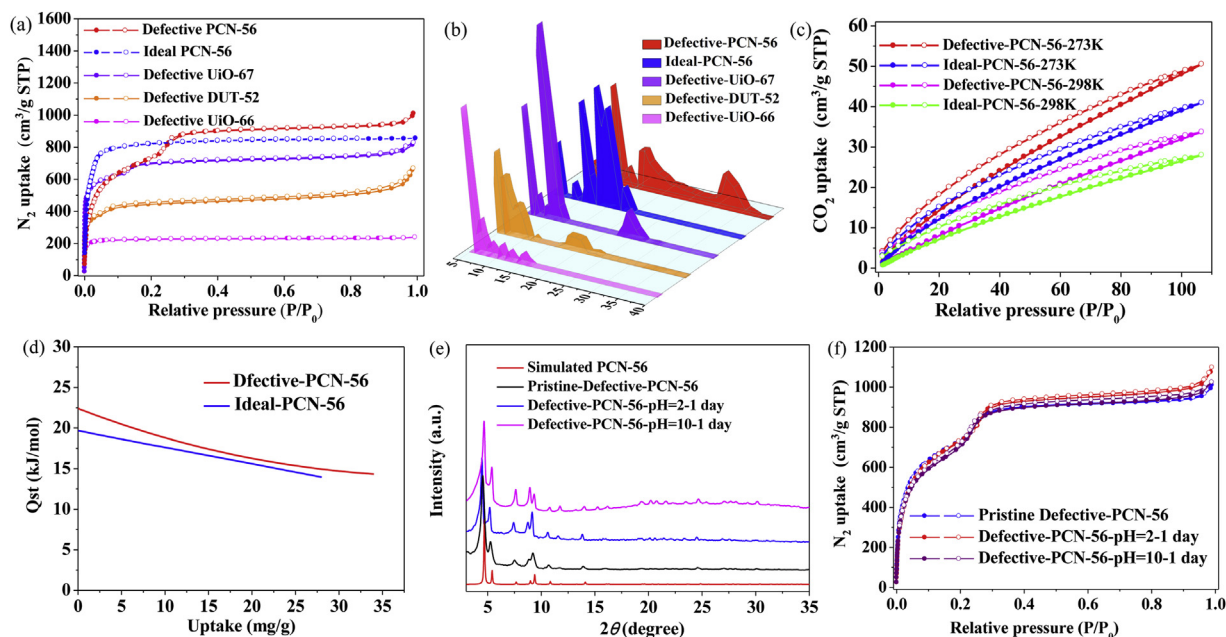


Fig. 2. (a) The N₂ sorption isotherms of Defective-UiO-66, DUT-52, UiO-67, and PCN-56 at 77 K; (b) The pore widths of Defective-UiO-66, DUT-52, UiO-67, PCN-56 and Ideal-PCN-56; (c) The CO₂ sorption isotherms of Defective-/Ideal-PCN-56 at 273 K and 298 K; (d) The CO₂ adsorption enthalpy of Defective-/Ideal-PCN-56; (e) The PXRD patterns of Defective-PCN-56 treated with pH 2 and pH 10 aqueous solution for 1 day; (f) The N₂ sorption isotherms at 77 K of Defective-PCN-56 after being treated with pH 2 and pH 10 aqueous solution for 1 day.

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