Introduction

Metal–organic frameworks (MOFs), a class of crystalline porous materials constructed from metal nodes and organic ligands by coordination bonds, have found a wide range of applications such as gas storage and separation, catalysis, magnetism, drug delivery, small-molecule recognition and chemical sensing. This functional diversity is largely due to their versatile structural tunability where a variety of components can be combined to generate an almost indefinite number of novel materials. However, elucidating the parameters that dictate the MOF structures, including their topology and porosity, is non-trivial. Considering Zr₆ cluster-based MOFs as an example, although linkers of lower connectivity generally favor one particular topology, more topologies can be accessed from linkers with higher connectivity due to their tendency to undergo conformational changes, resulting in challenges in predicting MOF structures.

Since the first reports of Zr-MOFs with tetratopic linkers, several topologies have been observed, including ftw, csq, she, shp, scu, flu, ith, sqc and lvt which can be attributed to the linker conformation adjustments under different synthetic conditions. This conformational change can be induced by controlling one of the many factors, such as the modulating reagent, concentration, metal salt, temperature and solvent. For example, a csq-net MOF (NU-1000) is produced when using benzoic acid as the modulator whereas a scu-net MOF (NU-901) is obtained using 4-amino-benzoic acid with the same 1,3,6,8-tetrakis(p-benzoic acid)pyrene (TBApy) linker and Zr precursor. Using a tetrapodal linker with arms of a high degree of rotational freedom, such as tetraacarboxyphenylporphyrin (TCPP), multiple topologies have been observed. A similar phenomenon was also observed when we explored the isoreticular tetracarboxylate Zr-MOF csq-net NU-100X series for enzyme immobilization where MOFs with ftw topology were produced instead when using linkers with longer arms. Therefore, our group concluded that the torsion angle between the planar “backbone” (benzene, pyrene, porphyrin) and the arms (carboxylic acid) had a critical influence on the framework topology. Specifically, if the torsion angle was close to 60°, the csq topology was favored, whereas the ftw topology formed if the torsion angle was close to 0°.

In addition to using organic linkers with higher rotational freedom, installing functional groups to the organic linkers
affords another effective strategy to affect the linker conformation, thereby the material topology. For instance, Yaghi and co-workers successfully synthesized qom-net MOF-177 series with uncommon topologies (pyr and rtl) by introducing functional groups. Recently, Zhou and co-workers introduced steric hindrance into the biphenyl-3,3′,5,5′-tetra(phenyl-4-carboxylic acid) (TCPB) linker to affect linker conformation, which subsequently effect the topology of the resulting Zr-tetracarboxylate MOFs. However, accompanying the original structure were mixed phase materials that formed as byproducts, most likely due to the introduction of the bulky substituents. In high agreement with experimental results, computational studies compared the energy of MOFs with different substituents to demonstrate the influence of introduced steric hindrance on linker conformation and MOF topology. With these design rules and challenges in mind, we set out to tune the steric hindrance of the organic linkers in a stepwise fashion, aiming to achieve topology control in the resulting series of Zr-MOFs.

Results and discussion

Introduction of steric hindrance

In addition to the 1,2,4,5-tetrakis[4-carboxyphenyl]benzene (TCPB) linker (Fig. 1, L1), two more linkers were designed. A nitro group (Fig. 1, L2) and two bromo groups (Fig. 1, L3) were installed on the central benzene respectively to introduce steric hindrance to affect the rotational freedom of the peripheral benzoate arms and in turn control the topology of the resulting MOFs. To ensure consistency and to eliminate variability from factors such as solvent, temperature and modulator on the topology of the resulting MOFs, the syntheses with the three TCPB-based linkers were carried out under identical solvothermal conditions (ESI†).

Topology and porosity diversity of the as-synthesized MOFs

As previously reported by Stock and co-workers, Zr6 nodes and the L1 linker form NU-903 with an scu topology with characteristic diamond-shaped channels along the c axis (Fig. 1). NU-903 is isoreticular to TBApy-based NU-901 and TCPP-based NU-902.

The crystals of the resulting MOF with linker L2 are oval in shape (Fig. 3b). Single crystal X-ray diffraction analysis (Table S1, ESI†) revealed that NU-904 crystallized in the P21/m space group (a = 19.64 (1) Å, b = 12.63 (1) Å, c = 19.635 (4) Å and β = 119.994° (2) at 200 K) with the formula as Zr6(μ-O)4(μ-OH)4(HCOO)1.5(H2O)2.5(Oh)2.5(L2). The 3D structure consists of 8-connected Zr6 nodes and mononitro-substituted TCPB linkers, yielding a rare scu topology. The single crystal structure of NU-904 is characteristic of a reticular-merohedral twin structure in which three orientations stack together along the b axis, twisting 60° from each other (Fig. 2). The reticular twins of three scu net components gave rise to the overall 6-fold symmetry in the structure. Topologically, the average structure of the threefold twinned NU-904 is based on the highly connected 4,12-c shp net. Interestingly, the threefold twins of ordered 4,8-c scu structure led to a twinned 4,12-c rare shp structure (Fig. S17, ESI†). To the best of our knowledge, the inherent correlation between these two topological nets has not been realized until this work. As a result, the average structure is observed as triangular-shaped instead of the expected diamond-shaped channels in NU-903 (Fig. 2).

The MOF synthesis with linker L3 yields hexagonal rod-shaped crystals (Fig. 3b). Single crystal X-ray diffraction analysis (Table S1, ESI†) revealed that NU-1008 crystallized in the hexagonal P63/mmc space group with the chemical formula as Zr6(μ-O)4(μ-OH)4(HCOO)(H2O)2(Oh)2(L3); the 3D structure consists of 8-connected Zr6 nodes and dibromo-substituted TCPB linkers in a csq topology. Isoreticular to NU-1000, there are two types of channels along the c axis, a 1 nm wide triangular channel and a 3 nm hexagonal channel (Fig. 1). The incorporation of the dibromo groups does not compromise the porosity of the material because the bromo groups reside in the window connecting the hierarchically triangular micropores and hexagonal mesopores. Therefore, the pore size distribution of NU-1008 is similar to NU-1000.

Characterization of as-synthesized MOFs

Due to the 8-connected Zr6 nodes present in all three MOFs, 1H NMR was employed to identify the coordinated species on the remaining accessible sites of the node. Upon digestion of the MOFs with a dilute NaOD solution, a peak was observed for all three materials around 8.37 ppm that is characteristic of
formate ligand. Quantifying the amounts of formate relative to the organic linker in the three samples gives ca. 2, 2 and 3 formate groups per Zr6 node in NU-903 (Fig. S4, ESI†), NU-904 (Fig. S5, ESI†) and NU-1008 (Fig. S6, ESI†), respectively. Diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) also confirms the presence of formate groups with the observed C–H stretching at 2745 cm\(^{-1}\). In addition, N=O stretching (1658 and 1373 cm\(^{-1}\)) and C–Br stretching (712 cm\(^{-1}\)) in the DRIFTS spectra of NU-904 and NU-1008 confirmed the presence of L2 and L3, respectively (Fig. S10–S12, ESI†).

The phase purity of the bulk materials was confirmed by PXRD (Fig. 3a). The particle morphology of NU-904 is oval-shaped and NU-1008 is hexagonal rod-shaped (Fig. 3b), as evidenced by the SEM images (Fig. S13, ESI†). Nitrogen sorption isotherms of three different MOFs were measured at 77 K; the type I isotherms of NU-903 and NU-904 are indicative of microporous structure of the MOFs, while the type IV isotherm of NU-1008 indicates the presence of both micropores and mesopores in the material. The BET areas were calculated to be 1140, 1410 and 1400 m\(^2\) g\(^{-1}\) for NU-903, NU-904 and NU-1008, respectively. DFT pore size distributions reveal micropores of 11 Å for NU-903, 10 Å for NU-904 and hierarchical micropores of 11 Å and mesopores of 29 Å for NU-1008 (Fig. 3c). The total pore volumes were 0.515, 0.613 and 0.819 cm\(^3\) g\(^{-1}\) for NU-903, NU-904 and NU-1008, respectively. The larger gravimetric pore volume and the type IV isotherm of NU-1008 is again consistent with a mesoporous structure. Thermogravimetric analysis (TGA) under air showed no sign of mass loss up to 400 °C (Fig. S7–S9, ESI†), demonstrating the high thermal stability of the three MOFs. In addition, all three materials showed good stability under acidic condition with treatment of 0.5 M HCl aqueous solution for 10 hours (Fig. S14, ESI†).

**Topology and porosity control through introduction of steric effect**

To investigate the influence of linker conformation on topology control, we performed a detailed analysis of linker conformation in the three crystal structures. In the scu-net NU-903 structure,\(^{45}\) the TCPB linker with no substituents adopts a \(C\sb{2h}\) symmetry with the \(C\sb{2}\) axis and the perpendicular \(s\sb{h}\) depicted in Fig. 4a. In the MOF structure, the two adjacent phenyl arms in the upper side rotate away from each other, whereas the lower ones rotate toward each other (Fig. 4a). In NU-904, the introduction of the mononitro group lowers the symmetry of the linker to \(C\sb{2}\) but the conformation of the peripheral phenyl arms was found to be similar to the non-substituted TCPB linker in NU-903 (Fig. 4b). As a result, each of the twinning portions that comprise this structure has the same scu topology as NU-903, even though the average structure of NU-904 has 1D triangular channels instead of the diamond-shaped channels with a typical scu topology. Notably, the mononitro group on the central benzene rotates ~32° to fit in the structure. In NU-1008 with dibromo-substituted TCPB, the linker adopts a \(C\sb{2v}\) symmetry due to the rotation of the upper and lower pair of phenyl arms toward each other (Fig. 4c) which directs the

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**Fig. 3** Characterization of the three MOFs. (a) PXRD patterns; (b) optical images of the single crystals of NU-904 (left) and NU-1008 (right), the scale bars in the images are 100 μm; (c) N\(_2\) sorption isotherms and DFT pore size distribution of NU-903, NU-904 and NU-1008.
framework to csq topology over the scu-net MOF. In addition, to accommodate the dibromo groups in NU-1008, the dihedral angle between the arm benzene and central benzene in the csq-net NU-1008 is closer to 90° than the dihedral angle observed in scu-net NU-903 and NU-904 (Table S3, ESI†). Additionally, the angle between the arms (117°) in NU-1008 is larger than in scu-net NU-903 (115°) and NU-904 (108.5°).

The 8-connected Zr₆ cluster in the three MOFs can be regarded as a cubic shaped node and the linker as a rectangular plane. In NU-903, the non-substituted TCPB linker with C₂ᵥ symmetry can link the clusters in the same orientation (Fig. 1), giving the scu topology. In contrast, the Zr₆ clusters in NU-1008 undergo an orientation change to conform to the C₂ᵥ symmetry of dibromo TCPB linker, and form a different topology, csq. The topology change confirmed our hypothesis that the steric effect induced by linker functionalization can achieve the topology control of MOF materials.

Catalytic performance for CO₂ fixation under mild conditions
CO₂ is a well-established greenhouse gas that originates from the carbon footprint of human activities. In order to mitigate the adverse effect of CO₂ to the environment, considerable progress has been made in its capture and storage in recent years, and promising strategies for the consumption of CO₂ have received much attention. Rational utilization of CO₂ is of great significance for the deceleration of global warming and the development of sustainable energy. Chemical fixation of CO₂ with epoxides through a facile cycloaddition process, catalysed by acidic sites, is an attractive route to convert this greenhouse gas into highly demanded cyclic organic carbonates.

Owing to the presence of substrate accessible Lewis acidic sites, MOFs have been previously explored to catalyse the cycloaddition of CO₂ and epoxides. However, energy-demanding reaction conditions such as elevated temperatures and pressures are generally required for the efficient conversion of CO₂ into cyclic carbonates. Inspired by these reports, CO₂ fixation into styrene oxide was used as a model reaction to test the catalytic performance of MOFs reported in this study under mild conditions.

NU-903, NU-904 and NU-1008 were investigated for CO₂ fixation into styrene oxide under room temperature with 1 bar of CO₂. The styrene oxide (0.2 mmol), tetrabutylammonium bromide (6.5 mg, 0.02 mmol) pre-dissolved in 400 μL of acetonitrile and MOF material (4.0 mol%, 0.002 mmol) were added to an autoclave batch reactor, which had previously been dried for 6 h at 80 °C. The autoclave reactor was evacuated, purged with CO₂, and then placed under a constant pressure of CO₂ under 5 bar for 15 min to allow the system to equilibrate. The reaction was carried out at room temperature for 24 hours after the pressure was reduced to 1 bar of gauge pressure. After the reaction, the catalyst was separated by centrifugation and a small aliquot of the supernatant reaction mixture was taken to be analyzed by ¹H NMR to calculate the conversion (Fig. 5).

Fig. 4 Linker conformation in (a) NU-903, (b) NU-904 and (c) NU-1008.
A control experiment without any MOF catalyst exhibited negligible conversion of styrene oxide. However, vastly different CO\textsubscript{2} fixation activities were observed within the three MOF catalysts utilized in this report. Remarkably, full conversion of styrene oxide was observed with NU-1008 after 24 hours under mild conditions (room temperature, 1 bar of CO\textsubscript{2}). Previous reports using MOF catalysts for this reaction required elevated temperatures (~120 °C), pressures (10–20 bar) or longer reaction time (up to 56 hours) to afford similar or lower substrate conversions (Table S2, ESI†). Thus, NU-1008 stands out as a more environmentally friendly solid acid catalyst for the chemical fixation of CO\textsubscript{2} compared to others reported.

In comparison, NU-903 and NU-904 showed much lower conversion (Fig. 6a), despite the fact that they had similar CO\textsubscript{2} adsorption performance to NU-1008 (Fig. S15, ESI†). This significant difference is likely attributed to the aforementioned narrower pores and smaller pore volumes in NU-903 and NU-904 (around 10 Å, 0.50 cm\textsuperscript{3} g\textsuperscript{-1}) compared to the mesoporous channels in NU-1008 (around 30 Å, 0.82 cm\textsuperscript{3} g\textsuperscript{-1}). The mesoporous NU-903 and NU-904 most likely limited the diffusion of the sizeable substrate and product (Fig. 6b) and resulted in the lower conversion. The turnover numbers (TONs) in 24 hours were calculated to be 20.3, 22.8 and 99.4 for NU-903, NU-904 and NU-1008, respectively.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**


