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A mesoporous NNN-pincer-based metal-organic framework scaffold for the preparation of noble-metal-free catalysts[†]

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Through topology-guided synthesis, a Zr-based mesoporous MOF was successfully constructed, adopting a β -cristobalite-type structure. The MOF is embedded with well-arranged terpyridine coordination sites for facile post-synthetic metalation, and can be effectively used as a general scaffold for the preparation of noble-metal-free catalysts. For instance, the scaffolded metal@MOF material exhibits highly efficient catalytic activity for alkene epoxidation and arene borylation.

As a burgeoning class of highly crystalline porous materials, metal-organic frameworks (MOFs) have attracted immense attention in the past two decades. The surge of interest in MOFs is mainly driven by their unique properties such as permanent porosity, structural diversity, and functional tunability.^{1,2} The exquisite assembly of a variety of inorganic metal clusters and organic linkers endows MOFs with enormous potential in various applications, especially in heterogeneous catalysis.³⁻⁷ MOFs have turned out to be a feasible platform to accommodate catalytically active sites for organic transformations. Due to the confinement effects of the framework, MOF-based heterogeneous catalysts exhibit a higher, if not, comparable activity and selectivity compared to their homogeneous counterparts. Moreover, the stability of the MOF increases the recyclability of the materials.^{8,9} General approaches towards introducing catalytic sites into the MOF scaffolds involve guest encapsulation, covalent grafting and linker functionalization.¹⁰⁻¹³ Although the linker design approach is often synthetically more demanding, it remains an attractive method owing to the resulting high loading of uniformly distributed catalytic sites on the scaffold.

Currently, organometallic complexes have gained prominence in accelerating organic reactions in homogeneous catalysis.¹⁴ They have also paved the way for building catalytically active MOFs.¹⁵

† Electronic supplementary information (ESI) available: Full experimental details, characterization and physical measurements (PDF). See DOI: 10.1039/c8cc09491h Through rational design of linkers, organometallic complexes with versatile chelating ligands have been embedded on MOFs *via* direct assembly or post-synthetic modification (PSM).^{16–20} However, there are fewer examples of MOFs constructed by pincer-containing linkers.^{21–24} Their ubiquity in MOFs was partially impeded by the harsh synthetic conditions in both ligand preparation and MOF synthesis. Considering their specific roles in catalysis, it remains an urgent task to introduce pincer complexes into the MOF template with the aim of expanding the scope of MOF-catalyzed transformations.

Classified as a neutral NNN-type pincer ligand, terpyridine and its derivatives possess superb coordination capability, which enables them to complex with redox-active metals under relatively mild conditions. In addition, their metal complexes have been widely utilized in organometallic catalysis, biomimetic oxidation and reduction reactions, *etc.*^{25–28} To date, most terpyridine-based MOFs adopt interpenetrating structures, which block their catalytic behaviours due to the low diffusion efficiency of substrates.^{29–32} Although the constraint can be released by synthesizing ultrathin 2D metal–organic layers (MOLs),^{33,34} a 3D mesoporous MOF to embody a terpyridine-based moiety for heterogeneous catalysis is still highly desirable.^{35–37}

Bearing all this in mind, we herein report a newly synthesized mesoporous MOF, namely PCN-308, which is built from zirconium clusters and terpyridine-based tritopic ligands, 4'-(4carboxyphenyl)-[2,2':6',2"-terpyridine]-5,5"-dicarboxylic acid (H₃TPY) (Fig. 1). PCN-308 is isostructural to PCN-777, a β -cristobalite network that requires six-connected D_{3d} nodes and trigonal-planar linkers to form super-tetrahedra in the zeotype framework.^{38,39} Although the three carboxylate groups in H3TPY cannot stay on the same plane in the ligand precursor, it is possible for them to fit into the faces of the super-tetrahedra in the β -cristobalite network, because the three nitrogen atoms at the terpyridine center can reduce the rotating steric hindrance during MOF synthesis. As a result, PCN-308 could be obtained through a one-pot solvothermal reaction between ZrOCl₂·8H₂O and H₃TPY under topological guidance. The powder X-ray diffraction (PXRD) patterns demonstrate the isostructural nature of PCN-308 (Fig. 2a). The corresponding structural model

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Fig. 1 (a) Trigonal-planar organic linker TPY and six-connected D_{3d} -symmetric Zr₆ antiprismatic clusters. (b) The β -Cristobalite network of PCN-308 simulated based on the reported PCN-777 structure. The yellow sphere represents the void space.

of PCN-308 was simulated based on the reported PCN-777 structure using Material Studio 6.0.⁴⁰ In PCN-308, the six-connected antiprismatic Zr_6 clusters adopt a D_{3d} -symmetry, alternately connected by six carboxylate groups of organic linkers and terminal OH/H₂O moieties. The overall structure of PCN-308 is built by the assembly of super-tetrahedra cages in a staggered configuration, which are constructed from four Zr_6 units as vertexes linked by the trigonal planar organic linkers capping the faces. Finally, a mesoporous cage is formed with a diameter of 3.5 nm.

PCN-308 was activated with supercritical CO₂ and the porosity was determined by N₂ adsorption at 77 K. PCN-308 has a total N₂ uptake of 1525 cm³ g⁻¹ at 1 bar. The experimental Brunauer–Emmett–Teller (BET) surface area is 1962 m² g⁻¹. A steep increase at $P/P_0 = 0.4$ on the adsorption branch of the N₂ isotherm corresponds to the mesoporous cage of 3.5 nm in PCN-308. The pore volume is 2.85 cm³ g⁻¹ (Fig. 2b and Table S1, ESI[†]).

Facilitated by the strong interaction between the highly charged Zr_6 clusters and ligand carboxylates, PCN-308 remained intact in aqueous solution. The almost unchanged PXRD profile and N_2 isotherm of the sample after water treatment in comparison with those of the pristine PCN-308 indicate its excellent aqueous stability (Fig. S9 and S10, ESI†). However, it failed to survive in acidic aqueous solutions. The moderate chemical stability might be ascribed to the high hydrophilicity of the terpyridine-based backbones, which succumb to the attack of the proton. The thermal stability of PCN-308 was tested by thermal gravimetric

analysis (TGA), revealing that the decomposition temperature of PCN-308 is around 490 $^\circ C$ (Fig. S11, ESI†).

Fe@PCN-308 was prepared by treating the as-synthesized PCN-308 in an acetonitrile solution of $Fe(ClO_4)_2 \cdot 6H_2O$ (2.5 equiv.). After being stirred at room temperature for three hours, the white powder turned purple, demonstrating the formation of the Fe-terpyridine complex. Scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) showed the uniform distribution of iron within the MOF and the experimental atomic ratio of Fe: Zr was 0.81:3 (1:3 in theory), affording an 81% loading rate of cobalt relative to the terpyridine linker (Table S2, ESI⁺). The metalation yield was further tested by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), which showed a similar 79% loading rate of the digested Fe@PCN-308. The X-ray photoelectron spectroscopy (XPS) spectrum shows no satellite features of the Fe element, indicating the low oxidation state as well as low-spin nature of Fe(II) complexed with terpyridine (Fig. 3a and Fig. S22, ESI⁺). Similarly, post-synthetic metalation (PSM) of PCN-308 with 2.5 equiv. of Co(OAc)₂ in toluene afforded Co@PCN-308 as an orange solid. SEM-EDS revealed an 82% loading rate of Co relative to the linker, which also matched with the one afforded by ICP-OES (84%) (Table S3, ESI[†]). The XPS spectrum displays typical satellite features of $Co(\pi)$ (Fig. 3b and Fig. S23, ESI⁺). The structural integrity of the metalated samples is further confirmed by the PXRD analysis, where the PXRD profiles remain almost intact compared with that of the pristine PCN-308 (Fig. S13, ESI⁺). Moreover, owing to the presence of the coordinated metal centers and counterions, N2 isotherm measurements also show reasonable reduction in the BET surface areas, 1244 $m^2 g^{-1}$ and 1209 m² g⁻¹ for Fe@PCN-308 and Co@PCN-308, respectively (Fig. S16, ESI[†]).

With redox-active metal centers on the struts, Fe@PCN-308 was examined as a self-supporting catalyst for the epoxidation of olefins. At the outset, styrene was chosen as a model substrate to optimize the reaction conditions. Screening reactions were carried out which showed that 1.0 mol% of Fe@PCN-308 could catalyse the epoxidation of styrene in excellent yields with 1.5 equiv. of *tert*-butyl hydroperoxide (TBHP) as an oxidant and toluene as a solvent at room temperature. A control experiment was performed without a catalyst and it afforded merely 12% yield of the product, which was likely caused by the oxidation of TBHP (Table S4, entry 1, ESI⁺). The addition of non-metalated



Fig. 2 (a) PXRD comparison between as-synthesized PCN-308 (red) and PCN-777 (black). Inset shows the SEM image of PCN-308. (b) The N_2 isotherm uptake of PCN-308. Inset shows the DFT pore size distribution.



Fig. 3 The XPS spectra of (a) Fe@PCN-308 and (b) Co@PCN-308. Inset shows the color changes in PCN-308 after post-metalation.

PCN-308 into the solution similarly generated a low yield of the product (12%), excluding the influence of the Lewis acidity of the metal clusters on the reaction (Table S4, entry 8, ESI†). The recyclability of Fe@PCN-308 was also tested. The MOFs separated from the reaction could be reused four additional times without the loss of their catalytic activities. The PXRD patterns of the samples recovered from each recycle show no essential changes in the profiles from the pristine ones, suggesting the intact crystallinity of the MOFs under the catalytic conditions (Fig. S24 and S25, ESI†).

The universal capability of Fe@PCN-308 was further examined with various olefins under optimal conditions and the results are summarized in Table 1. All the olefins were converted to the corresponding epoxides in satisfactory yields with negligible byproducts. The efficient catalytic performance was ascribed to the high loading of the reactive catalytic centers as well as the mesoporous nature of the MOF structure, which guarantees the accessibility of the catalytic centers to the substrates. However, due to the relatively small apertures of the pores in the MOF, the steric hindrance of the substrates exerted a considerable effect on the epoxidation reactions. Olefins with small molecular size afforded nearly quantitative yields of the products within 6 hours whereas it took more reaction time for the large ones to convert to the corresponding epoxides to react completely. To be specific, in comparison with entries 6 and 8, the extra phenyl group in the stilbene remarkably impeded the reaction process, causing a 27%

Table 1	Epoxidation of selected olefins ^a				
R ₁ R ₂ TBHP, Toluene, rt. 0 R ₁ R ₂ R ₂ R ₁ R ₂					
Entry	Substrate	Time (h)	% conversions ^b		
1		6	>99		
2		6	>99		
3	\bigcirc	6	>99		
4		6	>99		
5		6	98		
6		6	97		
7		6	95		
8	Ph Ph	12	70		
9	Ph	12	61		
10		. 24	49		

^{*a*} Reaction conditions: To a 4 mL Pyrex vial were added olefins (0.2 mmol), catalyst (1 mol%), solvent (2 mL) and TBHP (2.0 equiv.) and the mixture was stirred at room temperature. ^{*b*} Conversions were determined by GC-analysis with mesitylene as an internal standard.

decrease in yield even with a longer reaction time. In addition, *trans*-stilbene afforded a lower yield than its *cis*-isomer due to the steric effect. On the other hand, the electronic effect of the olefins synergistically influences the epoxidation reaction, which could be demonstrated by the dramatic decrease in the yield of substrate 10.

On the other hand, the cobalt-metalated PCN-308 turned out to be a superior air-stable catalyst in the C-H borvlation of arenes. an important reaction that produces versatile aryl boronate esters in organic synthesis.⁴¹ With $B_2(pin)_2$ (pin = pinacolate) as the borylating agent, a broad range of arenes were investigated for the borylation reaction. Generally, the reactions were performed in sealed vials charged with reagents under the protection of N₂. LiOMe was added as an indispensable additive to accelerate the reaction.²⁶ With the addition of $B_2(Pin)_2$, the color of the reaction mixtures immediately changed from orange to deep purple, indicating the activation of the catalyst. The reactions were terminated by exposure to air and the obtained products were tested by GC analysis to afford conversions and yields. As shown in Table 2, 5 mol% of Co@PCN-308 revealed the highest yields in neat arenes at 100 °C for 48 h. Both benzene and toluene afforded monoborylated products under standard conditions, while for the latter, the borylation happened at both meta- and para-positions, affording the corresponding products in a 70:30 ratio (entries 1, 2). The heterogeneous catalyst was also active in borylating bulky arenes. The regioselectivity of the reaction favored the positions with less steric hindrance, which are analogous to those of the reported homogeneous systems (entries 3, 4).42 Heteroarenes, indole for example, could also be efficiently transferred into the borylated product with an yield of 88% (entry 5). Control experiments

Table 2 Borylation of neat arenes ^a						
Ar-H + $B = B$ f h						
Entry	Substrate	Product	% conversion ^b	% yield ^b		
1		BPin	98	83		
2 ^{<i>c</i>}		BPin Me	98	78 <i>o:m:p</i> 0:70:30		
3		BPin	92	72		
4	MeO	BPin MeO OMe	83	65		
5	T T T T T T T T T T T T T T T T T T T	H BPin	88	73		

^{*a*} Reaction conditions: arenes (5.7 mmol), B_2Pin_2 (0.38 mmol) and catalyst (5% mol) were sealed with a screw cap fitted with Teflon septa in a glove box. Samples were brought out of the glove box and heated for 48 h. ^{*b*} Determined by GC-analysis with mesitylene as the internal standard. ^{*c*} Product ratio was determined by ¹H NMR analysis.

with non-metalated PCN-308 as a catalyst showed no activity in the borylation reaction. The borylated products could also be obtained from the homogeneous catalytic counterpart, $[(CO_2Me)_3]$ tpy-Co(OAc)₂, under the same conditions. However, the yields were much lower, demonstrating the necessity of active site isolation in the MOF struts (Table S5, ESI†). Co@PCN-308 can be easily separated and recovered from the reaction system by filtration. Its structural integrity was evaluated by the PXRD patterns, which deviate slightly from that of the as-synthesized PCN-308 (Fig. S26, ESI†). The catalyst could also be reused for at least three cycles without remarkable loss of catalytic activity (Fig. S27, ESI†).

In summary, a tritopic terpyridine-based linker (H_3TPY) was judiciously designed and utilized to construct a mesoporous MOF, PCN-308, with predictable β -cristobalite topology. Due to the direct one-pot synthesis, the terpyridine-based chelating sites were evenly distributed on the scaffold, which could be easily accessed by post-synthetic metalation of redox-active metal ions under mild conditions. The scaffolded MOF materials, Fe@PCN-308 and Co@PCN-308, contained high loadings of catalytic centers and turned out to be efficient catalysts for alkene expoxidation and arene borylation, respectively. This work exemplified the introduction of terpyridine-based pincer complexes into 3D mesoporous MOF structures, providing a successful approach to utilize the MOF scaffold in the preparation of pincer-type heterogeneous catalysts.

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Conflicts of interest

There are no conflicts to declare.

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