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J. Am. Chem. Soc., Just Accepted Manuscript • Publication Date (Web): 24 Nov 2017 Downloaded from http://pubs.acs.org on November 24, 2017

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# Systematic Engineering of Single Substitution in Zirconium Metal-Organic Frameworks towards High-Performance Catalysis

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ABSTRACT: Zirconium-based metal-organic frameworks (Zr-MOFs) exhibit great structural tunability and outstanding chemical stability, rendering them promising candidates for a wide range of practical applications. In this work, we synthesized a series of isostructural PCN-224 analogues functionalized by ethyl, bromo, chloro, and fluoro groups on the porphyrin unit, which allowed us to explicitly study the effects of electron-donating and electron-withdrawing substituents on catalytic performance in MOFs. Owing to the different electronic properties of ethyl, bromo, chloro, and fluoro substitutes, the molecular-level control over the chemical environment surrounding a catalytic center could be readily achieved in our MOFs. To investigate the effects of these substitutes on catalytic activity and selectivity, the oxidation of 3-methyl pentane to corresponding alcohols and ketones was utilized as a model reaction. Within these five analogues of PCN-224, an extremely high turnover number of 7680 and turnover frequency of 10240 h<sup>-</sup> was achieved by simply altering the substitutes on porphyrin rings. Moreover, a remarkable 99% selectivity of the tertiary alcohol over the five other possible byproducts are realized. We demonstrate that this strategy can be used to efficiently screen a suitable peripheral environment around catalytic cores in MOFs for catalysis.

## INTRODUCTION

In nature, enzymes adopt different three-dimensional structures and employ a series of organic and inorganic cofactors to assist in catalysis. The high activity, selectivity, and stability of the enzymes can be precisely tailored through noncovalent interactions around catalytic centers. Inspirited by the precision of the tailoring specific feature in enzymes, this principle has been successfully applied to a vast variety of supramolecular,<sup>1</sup> macromolecular,<sup>2</sup> biomimetic<sup>3</sup> and heterogeneous systems.<sup>4</sup> From the viewpoint of biomimetic chemistry, a highly efficient catalyst could be developed by the introduction of bioinspired concepts. These concepts mainly focus on confined chemical environment, hydrophobic binding cavities,<sup>5</sup> hydrogen bond donors,<sup>6</sup> synthesis of natural products,<sup>7</sup> and activation of small molecules.<sup>8</sup> Although there have been many artificial material platforms with intensive cavity or pores developed for heterogeneous catalysis, none of the materials yet reported equal or improve upon the outstanding activity and selectivity in enzyme catalysis.<sup>9</sup> For example, porous materials such as zeolites allow the tailoring of pore geometries and dimensions for size- and shape-selective catalysis.<sup>10</sup> However, the limited tunability in components and structures of zeolites has hindered the functionalization of the interior surface.11

Metal-organic frameworks (MOFs) are a class of organicinorganic hybrids constructed by metal-containing nodes and organic linkers.<sup>12</sup> The topologies, structures, pore environments and functionalities of MOFs are tunable through the judicious selection of metal-containing centers and organic bridging ligands. Theoretically, the combinations of various metals, render ACS Paragon Plus Environment

linkers and metals or metal clusters for the construction of new MOFs are unlimited.<sup>13</sup> Owing to the specific features, which include hybrid compositions, large surface areas, tunable pore sizes, adjustable functionality, and diverse structures, MOFs have attracted great attention and have been successfully applied to a wide range of research fields, such as gas adsorption,<sup>14</sup> light emitting,<sup>15</sup> chemical sensing,<sup>16</sup> ion conduction,<sup>1</sup> and heterogeneous catalysis.<sup>18</sup> Compared with traditional heterogeneous catalysts, the pore environment of MOFs can be well-determined and fine-tuned for the accommodation of a specific guest molecules.<sup>19</sup> In addition, various organic, and organometallic catalytic centers, as well as nanoparticles can be immobilized into MOFs by direct-synthesis or postsynthesis, forming well-defined active sites in the periodically ordered structures.<sup>20</sup> However, most MOFs are constructed by the combination of soft acids (low-oxidative transition metal ions) and hard bases (carboxylates), and consequently have relatively weak chemical stabilities, greatly limiting their application scope for heterogeneous catalysis.

To improve the stability of MOFs and gain in-depth insight into their catalytic activities, synthetic strategies to create chemically stable MOFs must first be employed. We are particularly focused on the Zr-polycarboxylate-based MOFs because of their high chemical stability and facile structural tunability. Previously, a series of zirconium-porphryinic MOFs have been reported by our group including PCN-222, (PCN stands for porous coordination network), PCN-223,<sup>22b</sup> and PCN-224,<sup>22c</sup> which possess extraordinary stability. The porphyrin center can be metalated with almost any transitional metals, rendering them versatile platforms for catalytic appli-

cations. Moreover, the structure of these MOFs can be readily tuned by adjusting the synthetic conditions.

While all the examples highlight the importance of topological structures in metal mediated reactions, precise control over the periphery of an active site remains synthetically challenging in non-biological systems. As in enzymes, the strategic placement of substituents around a catalytic center can lead to remarkable increases in activity, selectivity, and stability.3d-3f Herein we rationally designed and synthesized four new isostructural MOFs of PCN-224(Fe), namely Et-PCN-224(Fe), Br-PCN-224(Fe), Cl-PCN-224(Fe), and F-PCN-224(Fe). In these MOFs, the  $\beta$ -position of iron porphyrin is functionalized by substituents with different electronic properties to tune the periphery of the active iron sites. The effects of local substituent groups on catalyst activity, selectivity and stability have been investigated with the oxidation of 3methyl-pentane as the model reaction. An outstanding catalytic activity and distinguished selectivity (> 99%) can be achieved by simply altering the  $\beta$ -substituent groups. Among all these networks, Br-PCN-224(Fe) exhibits the highest total turnover number (TON) and turnover frequency (TOF) values as high as 7680 and 10240  $h^{-1}$ , respectively. Moreover, owing to the high chemical stability of Br-PCN-224(Fe), it can be recycled more than five times without significant loss of catalytic activity and selectivity. This strategy enables the systematic development of various tailor-made MOFs with tunable electronic properties as highly efficient catalysts.

### **EXPERIMENTAL SECTION**

**General Information.** The commercial chemicals used in this study were purchased unless otherwise specified. Pyrrole, trifluoroacetic acid (TFA), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), 4-carboxybenzaldehyde, 3,4-diethyl pyrrole and boron trifluoride diethyl etherate (BF<sub>3</sub>•Et<sub>2</sub>O) were purchased from Sigma-Aldrich Corporation. Benzoic acid, 3-methyl pentane, and 3,4-difluoro-1H-pyrrole were purchased from Ark Pharm, Inc. Iron(II) chloride (FeCl<sub>2</sub>), iodosobenzene (PhIO), bromine, and N-chlorosuccinimide (NCS), were purchased from Tokyo Chemical Industry Co., Ltd. (TCI). The MOF powder precipitates were collected by centrifugation and washed with anhydrous N, N-dimethylformamide (DMF) three times and acetone twice.

**Instrumentation.** Powder X-ray diffraction (PXRD) experiments were carried out on a BRUKER D8-Focus Bragg–Brentano X-ray powder diffractometer equipped with a Cu sealed tube ( $\lambda = 1.54178$  Å) at 40 kV and 40 mA. NMR data were collected on a Mercury 400 NMR spectrometer. Fourier transform infrared (FT-IR) spectra were recorded on an IR Affinity-1 instrument. Thermogravimetric analysis (TGA) data were obtained on a TGA-50 (SHIMADZU) thermogravimetric analyzer with a heating rate of 10 °C min<sup>-1</sup> under air atmosphere. N<sub>2</sub> adsorption–desorption isotherms were measured using a Micrometritics ASAP 2420 system at 77 K. The UV–vis absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer. The morphologies of the MOF sample were observed by using a SU8020 Scanning Electron Microscope (SEM, Hitachi, Japan). Elemental analysis (EA) was performed by vario EL cube Elementar. Inductively Coupled Plasma-Optical Emission spectroscopic (ICP-OES) data were collected on a Thermo iCAP-6300 Spectrometer. The conversions of the reactants and the yields of products were measured by Shimadzu QP2100 plus gas chromatographmass spectrometry (GC-MS).

**Synthesis of Ligands.** The synthesis routes and details of TCPP(Fe) (TCPP = tetrakis(4-carboxyphenyl)-porphyrin), Et-TCPP(Fe), Br-TCPP(Fe), Cl-TCPP(Fe), and F-TCPP(Fe) ligands are described in the Supporting Information Section 2.

Synthesis of PCN-224(Fe) Framework.  $ZrCl_4$  (30 mg), TCPP(Fe) (10 mg, 0.17 mmol), benzoic acid (400 mg) and DMF (2.0 mL), were ultrasonically dissolved in a 4 mL Pyrex vial. The mixture was heated to 120 °C for 2 days. After cooling down to room temperature, the resulting precipitate was collected by centrifugation. The brown crystalline powder was successively washed with DMF (3×3 mL) and anhydrous acetone (3×3 mL). The washed powders were exposed to a vacuum at 120 °C for another 2 h, yielding 10 mg (70%) of PCN-224(Fe) frameworks as dark red crystalline powder.

Synthesis of Et-PCN-224(Fe) Framework.  $ZrCl_4$  (30 mg), Et-TPPC(Fe) (12.5 mg, 0.17 mmol), benzoic acid (350 mg) and DMF (2.0 mL), were ultrasonically dissolved in a 4 mL Pyrex vial. The mixture was heated to 120 °C for 2 days. After cooling to room temperature, the resulting precipitate was collected by centrifugation. The brown crystalline powder was successively washed with DMF (3×3 mL) and anhydrous acetone (3×3 mL). The washed powders were exposed to a vacuum at 120 °C for another 2 h, yielding 8.3 mg (64%) of Et-PCN-224(Fe) frameworks as dark red crystalline powder.

Synthesis of Br-PCN-224(Fe) Framework.  $ZrCl_4$  (30 mg), Br-TPPC(Fe) (16.8 mg, 0.17 mmol), benzoic acid (400 mg) and DMF (2.0 mL), were ultrasonically dissolved in a 4 mL Pyrex vial. The mixture was heated to 120 °C for 2 days. After cooling to room temperature, the resulting precipitate was collected by centrifugation. The brown crystalline powder was successively washed with DMF (3×3 mL) and anhydrous acetone (3×3 mL). The washed powders were exposed to a vacuum at 120 °C for another 2 h, yielding 10.5 mg (61%) of Br-PCN-224(Fe) frameworks as brown crystalline powder.

Synthesis of Cl-PCN-224(Fe) Framework.  $ZrCl_4$  (30 mg), Cl-TCPP(Fe) (13.1 mg, 0.17 mmol), benzoic acid (400 mg) and DMF (2.0 mL), were ultrasonically dissolved in a 4 mL Pyrex vial. The mixture was heated to 120 °C for 2 days. After cooling to room temperature, the resulting precipitate was collected by centrifugation. The brown crystalline powder was successively washed with DMF (3×3 mL) and anhydrous acetone (3×3 mL). The washed powders were exposed to a vacuum at 120 °C for another 2 h, yielding 8.9 mg (66%) of Cl-PCN-224(Fe) frameworks as brown crystalline powder.

Synthesis of F-PCN-224(Fe) Framework.  $ZrCl_4$  (30 mg), Cl-TCPP(Fe) (11.6 mg, 0.17 mmol), benzoic acid (400 mg) and DMF (2.0 mL), were ultrasonically dissolved in a 4 mL Pyrex vial. The mixture was heated to 120 °C for 2 days. After cooling to room temperature, the resulting precipitate was collected by centrifugation. The brown crystalline powder.

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**Figure 1.** (a) Assembly of  $D_{3d}$  and  $D_{4h}$  nodes into (4,6)-connected **she** topological network. The Zr<sub>6</sub> cluster and TCPP(Fe) ligand can be viewed as 6- and 4-connected node, respectively. (b) View down the tetragonal channels of R-PCN-224(Fe) (black, carbon; purple, iron; blue, nitrogen; hydrogen and chloride, omitted). The yellow spheres represent Et, Br, Cl, or F. (c) Chemical structures of Et-TCPP(Fe), Br-TCPP(Fe), Cl-TCPP(Fe), and F-TCPP(Fe) linkers used in this work.

was successively washed with DMF ( $3 \times 3$  mL) and anhydrous acetone ( $3 \times 3$  mL). The washed powders were exposed to a vacuum at 120 °C for another 2 h, yielding 8.0 mg (67%) of F-PCN-224(Fe) frameworks as purple crystalline powder.

Gas Adsorption of R-PCN-224(Fe) Frameworks. Before gas sorption experiment, as-synthesized R-PCN-224(Fe) samples (100 mg) was washed twice with DMF and acetone twice, respectively. Fresh acetone was subsequently added, and the sample was soaked for 24 h to exchange and remove the nonvolatile solvates (DMF). After the removal of acetone by decanting, the samples were activated by drying under vacuum, then dried again by using the "outgas" function of the adsorption instrument for 8 h at 120 °C prior to gas adsorption/desorption measurement. Then, all the N<sub>2</sub> uptake measurements were conducted at 77 K for each sample.

Catalytic Oxidation Procedure of 3-Methyl Pentane in presence of PhIO. General catalytic conditions to determine different products are as follows: Under argon atmosphere, 3methyl pentane (0.37 mL, 3.0 mmol) in different solvents (1.0 mL) were added to a 20 mL Schlenk flask containing R-PCN-224(Fe) frameworks. In a separate vial, 6.6 mg of PhIO (0.03 mmol) was combined with 1.0 mL of solvents to form a partially dissolved slurry. The approximate molar ratio of alkane/PhIO/Fe is 1000/10/1. Two slurries were combined and stirred vigorously at different temperatures. After different reaction times, the reactions were stopped, the framework was filtrated and washed with THF ( $3 \times 2$  mL), and the resulting products were analyzed by GC-MS using *n*-dodecane as an internal standard. Each reaction was run in triplicate to obtain standard deviations. The yield of each product was calculated based on the amount of PhIO.

Catalytic Oxidation Procedure of 3-Methyl Pentane under O<sub>2</sub> or Air Atmosphere. General catalytic conditions to determine different products are as follows: 3-Methyl pentane (0.37 mL, 3.0 mmol) in different solvents (1.0 mL) were added to a 20 mL Schlenk flask containing R-PCN-224(Fe) frameworks. This slurry was stirred vigorously at different temperatures under O<sub>2</sub> or air atmosphere. The approximate molar ratio of alkane/Fe is 1000/1. After different reaction times, the reaction was stopped, the framework was removed by filtration and washed with THF (3×2 mL), and the resulting products were analyzed by GC-MS using *n*-dodecane as an internal standard. The isolated yields of products were given in Table S3. Each reaction was run in triplicate to obtain standard deviations.

**Turnover Number (TON) and Turnover Frequency (TOF) Studies of Br-PCN-224(Fe) Framework.** TON and TOF values were calculated with 5 mol% Br-PCN-224(Fe) for the oxidation reaction using 400 mmol of 3-methyl pentane with  $O_2$  (1 atm) as oxidant. After different reaction times, the yield of each product was measured by GC-MS using *n*-dodecane as an internal standard.

**Recycle use of Br-PCN-224(Fe) Framework.** Br-PCN-224(Fe) was recovered via centrifugation, washed with THF and a mixture of hexane/ $CH_2Cl_2$  (5% by volume) to remove any products in the framework and dried under vacuum at

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### **RESULTS AND DISCUSSION**

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PCN-224 is consisted of Zr<sub>6</sub> clusters and linked by the square planar TCPP ligand in space group of Im-3m.<sup>22c</sup> The Zr<sub>6</sub> cluster are connected to six TCPP ligands forming a she type of network (Figure 1a). Different from the 12-connected Zr<sub>6</sub> clusters in UiO-66 and 8-connected Zr<sub>6</sub> clusters in PCN-222, only six edges of the Zr<sub>6</sub> octahedron are bridged by carboxylates from TCPP ligands in PCN-224.22 Owing to the active metal sites within the metallized TCPP ligand, many PCN-224(M) networks have been employed as a functionally versatile metal-organic framework exhibiting remarkable performance in heterogeneous catalysis, including CO<sub>2</sub>/propylene oxide coupling reaction,<sup>22c</sup> C–H bond insertion reaction,<sup>23a</sup> and electrochemical water oxidation.<sup>23b</sup> All the previous reports emphasized on the effects of different metal centers within porphyrin ring on catalytic performance. However, functionalized analogues of this material are also uniquely suited for exploring outer coordination sphere effects on metal site reactivity. With this in mind, we sought to uncover the effects of peripheral chemical environment on the catalytic behavior of exposed iron sites in functionalized PCN-224(Fe) analogues.

Synthesis and Characterization of Functionalized Derivatives of PCN-224(Fe). In this work, we synthesized four isostructural derivatives of PCN-224(Fe), abbreviated Et-PCN-224(Fe), Br-PCN-224(Fe), Cl-PCN-224(Fe), and F-PCN-224(Fe), in which the central porphyrin ring is substituted with ethyl, bromo, chloro, and fluoro groups at  $\beta$  positions, respectively (Figure 1b and c). All the four frameworks were synthesized under solvothermal conditions in DMF at 120 °C. The four Et-PCN-224(Fe), Br-PCN-224(Fe), Cl-PCN-224(Fe), and F-PCN-224(Fe) frameworks were obtained as brown or purple crystalline powders in 64%, 61%, 66%, and 67% yield, respectively. The thermal gravimetric analysis (TGA) curve of the respective air-dried samples display a gradual weight loss up to 370 °C, indicating that the solvated molecules are evacuated slowly upon heating (Figures S1-S4). Notably, Et-PCN-224(Fe), Br-PCN-224(Fe), Cl-PCN-224(Fe), and F-PCN-224(Fe) exhibit different electronic absorption spectra with maximum adsorption at 580 nm, 603 nm, 614 nm, and 627 nm, respectively (Figure S5). In addition, the X-Ray photoelectron spectroscopy reveals that all the oxidation states of irons in the four R-PCN-224(Fe) networks are +3 (Figures S6-S10). Therefore, the electronic properties of these R-PCN-224(Fe) frameworks can be precisely tuned while retaining flexibility in designing compositions, components, and functions, and further implementing adjustment of catalytic activity and selectivity.

Powder X-ray diffraction (PXRD) studies revealed that the four R-PCN-224(Fe) networks have strong diffraction patterns and definite unit cells, which are consistent with that of the PCN-224(Fe) structure type (Figure 2a, and Table S1). As the four ethyl, bromo, chloro and fluoro substituents are different in sizes and weight, Brunauer–Emmett–Teller (BET) surface areas and pore sizes correspondingly deviate from those of PCN-224(Fe) (Figure 2b and Table S2). However, these differences are relatively minor, with only a ~10% deviation in BET surface area, pore size, and pore volume between PCN-224(Fe) and the most sterically crowded and heavy derivative, Br-PCN-224(Fe). With the same pore size of 1.9 nm, BET surface areas for Et-PCN-224(Fe), Br-PCN-224(Fe), Cl-PCN-224(Fe) and F-PCN-224(Fe) are 2287, 2142, 2268, and 2359 m<sup>2</sup> g<sup>-1</sup>, respectively. Interestingly, the four R-PCN-224(Fe) also showed high adsorption capacity of bulky 3methyl pentane at 298 K (Figure S11). These results suggest that large molecules could still be able to diffuse freely through the functionalized metalloporphyrin frameworks.



Figure 2. (a) Powder XRD patterns for PCN-224(Fe) (black curve), Et-PCN-224(Fe) (blue curve), Br-PCN-224(Fe) (green curve), Cl-PCN-224(Fe) (yellow curve), F-PCN-224(Fe) (red curve) and simulated result (grey curve). (b)  $N_2$  adsorption isotherm of PCN-224(Fe) (black curve), Et-PCN-224(Fe) (blue curve), Br-PCN-224(Fe) (green curve), Cl-PCN-224(Fe) (yellow curve), and F-PCN-224(Fe) (red curve) samples at 77 K.

Chemical Stability of R-PCN-224(Fe) Frameworks. Although all the  $\beta$ -positions are replaced with different functional groups, four of the PCN-224(Fe) derivatives still exhibited high chemical stability. To investigate the chemical stability of

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Figure 3. (a) PXRD patterns of Br-PCN-224(Fe) after treatment in different solutions for 24 h. (b) Residue weight percentage of Br-PCN-224(Fe) after treatment for 24 h in different solutions. (c) N<sub>2</sub> sorption isotherms for Br-PCN-224(Fe) after treatment for 24 h in different solutions (black curve, pristine sample; red curve, water treatment for 24 h; purple curve, pH = 1 solution treatment for 24 h; brown curve, 1M HCl solution treatment for 24 h; green curve, pH = 10 solution treatment for 24 h; blue curve, pH = 11 solution treatment for 24 h). adsorption  $(d)N_2$ of Br-PCN-224(Fe) for 24 different quantity after treatment h in solutions.

Et-PCN-224(Fe), Br-PCN-224(Fe), Cl-PCN-224(Fe), and F-PCN-224(Fe), we dispersed the four samples in different aqueous solutions over a wide pH range, including water, basic solutions with pH = 10 and 11, and acid solutions with pH = 0 and 1 (Figure 3, and Figures S12-S17). Take Br-PCN-224(Fe) as an example, after being soaked in these aqueous solutions for 24 h, its PXRD patterns are almost unchanged, which suggests maintenance of the crystallinity (Figure 3a). Figure 3b presents the residue weight percentage of the sample. In different aqueous solutions examined, Br<sub>8</sub>-PCN-224(Fe) exhibited almost no weight loss (<5 wt%). Even under the ultra-harsh conditions of an aqueous acid (pH = 0) and an aqueous base (pH = 11) solutions, the residual weight percentages were 96

and 95 wt%, respectively. To further confirm that all the networks were intact, we conducted N<sub>2</sub> sorption measurements after different treatments. N2 sorption measurement of Br-PCN-224(Fe) after solution treatments have minimal deviation from the pristine sample, which indicates the robustness of the framework under harsh chemical conditions, displaying similar stability as its counterpart PCN-224(Fe) (Figure 3c and d).<sup>22c</sup> In addition, we tested the stability of the four R-PCN-224(Fe) networks under O<sub>2</sub> atmosphere at 60 °C. Both of the PXRD and N<sub>2</sub> sorption analysis revealed that these MOFs are quite stable under highly oxidizing conditions (Figures S18 and S19). These porphyrin-based R-PCN-224(Fe) frameworks with functionalized linkers successfully realize the

Table 1. Selectivity of	Oxygenation	of 3-Methyl	Pentane.	Dashes	Indicate	None	Observed;	Spaces	Indicate	Not	Deter
mined. <sup>a,b</sup>											

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1	PCN-224(Fe)	$CH_2Cl_2$	25	2	PhIO	14	15	58	_	13	_
2	Et-PCN-224(Fe)	$CH_2Cl_2$	25	2	PhIO	25	12	54	_	9	_
3	Br-PCN-224(Fe)	$CH_2Cl_2$	25	2	PhIO	4	5	78	-	3	10
4	Cl-PCN-224(Fe)	$CH_2Cl_2$	25	2	PhIO	_	-	62	-	9	29
5	F-PCN-224(Fe)	$CH_2Cl_2$	25	2	PhIO	_	_	55	_	12	33
°6	Br-PCN-224(Fe)	$CH_2Cl_2$	25	2	$O_2$	—	_	91	_	9	-
7	Cl-PCN-224(Fe)	$CH_2Cl_2$	25	2	$O_2$	_	_	71	_	11	18
8	Br-PCN-224(Fe)	$C_6H_6$	25	2	$O_2$	_	_	>99	_	_	-
9	Cl-PCN-224(Fe)	$C_6H_6$	25	2	$O_2$	_	_	82	_	8	10
10	Br-PCN-224(Fe)	$C_6H_6$	60	1	$O_2$	_	_	>99	—	-	—
<sup>d</sup> 11	Br-PCN-224(Fe)	$C_6H_6$	60	1	$O_2$	_	_	>99	_	_	-
12	Br-PCN-224(Fe)	$C_6H_6$	25	16	air	_	_	>99	_	_	-
13	Br-PCN-224(Fe)	$C_6H_6$	60	10	air	_	_	>99	_	_	-
14	Cl-PCN-224(Fe)	$C_6H_6$	25	5	air	_	_	80	_	15	5
15	No catalyst	$CH_2Cl_2$	25	3	PhIO	7	12	62	_	19	_
16	No catalyst	$CH_2Cl_2$	25	3	$O_2$	_	_	_	_	_	_
17	No catalyst	$C_6H_6$	25	3	PhIO	5	13	61	_	18	_
18	No catalyst	$C_6H_6$	25	3	$O_2$	_	_	_	_	_	_
19	Br-PCN-224	$C_6H_6$	25	2	$O_2$	_	_	_	_	_	_
20	Br-PCN-224(Ni)	C <sub>6</sub> H <sub>6</sub>	25	2	$O_2$	_	_	_	_	_	_
21	Br-TCPP(Fe)	$C_6H_6$	25	2	$O_2$	_	_	74	_	_	_
°22	<i>a</i> Br-PCN- 224(Fe)	$C_6H_6$	25	2	0 <sub>2</sub>	_	_	41	_	_	_

<sup>*a*</sup>The valence of iron in all the R-PCN-224(Fe) frameworks is +3. <sup>*b*</sup>The catalyst amount in the oxidation reaction is 10 mol%. <sup>*c*</sup>The pressure of  $O_2$  and air is 1 atm. <sup>*d*</sup>The catalyst amount is 5 mol%. <sup>*e*</sup>The *a*Br-PCN-224(Fe) is an amorphous and nonporous coordination network.

combination of porosity with high stability, and would be of great potential for applications in nanoscale chemistry. With the most important advantage of heterogeneous catalysis, which is that it is easy to separate the catalyst from the reaction mixture, catalyst efficiency could be maintained and contamination from catalyst decomposition could be avoided.

Influence of Different Substitutes on Selective Oxygenation of 3-Methyl Pentane. To investigate the effects of different substitutes on the oxidation performance, we employed four of the functionalized PCN-224 as heterogeneous catalysts for selective oxygen ation of 3-methyl pentane (Table 1). As shown in Table 1, we explored the effects of various factors on the catalytic performance, including solvents, amount of catalysts, oxidant sources, temperature, and reaction time. While the surface face areas, pore sizes, and unit cell parameters of the four R-PCN-224(Fe) frameworks are relatively similar, their catalytic activity and selectivity are dramatically different. At room temperature, the activity and selectivity of oxyfunctionalization of 3-methylpentane are similar for PCN- 224(Fe)/PhIO and Et-PCN-224(Fe)/PhIO pairs, respectively forming tertiary (58% and 54%), secondary (15% and 12%), and primary (14% and 25%) alcohols, plus a small quantity of ketones (13% and 9%) (Table 1, entries 1 and 2), suggesting the electron donating ethyl group contributes little for the oxidation catalysis. However, the Br-PCN-224(Fe)/PhIO counterpart exhibited higher selectivity towards tertiary alcohol (78%), together with generation of small amounts of secondary (5%), primary (4%) alcohols, 2-one (3%), and 2,4-dione (10%) (Table 1, entry 3). By contrast, when the substitutes were changed to chloro and fluoro, the yield of tertiary alcohol decreased, while the yield of overoxidized products significantly increased. The Cl-PCN-224(Fe)/PhIO couple produced tertiary alcohol (62%), 2-one (9%), and comparatively higher 2,4-dione (29%) (Table 1, entry 4). And in the F-PCN-224(Fe)/PhIO catalytic system, tertiary alcohol, 2-one and 2,4dione were generated in 55%, 12%, and 33% yield, respectively (Table 1, entry 5).

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In the O<sub>2</sub> atmosphere, oxidation by Br-PCN-224(Fe) and Cl-PCN-224(Fe) gives higher selectivity toward the tertiary position with 91% and 71% yields, respectively (Table 1, entries 6 and 7). This discrepancy indicates that the oxidizing species in the O<sub>2</sub> reactions is different from that in the PhIO reactions. Interestingly, when the solvent was changed to the less polar C<sub>6</sub>H<sub>6</sub>, the selectivity of oxidation by Br-PCN-224(Fe) and Cl-PCN-224(Fe) increased greatly with 99% and 82% yields, respectively (Table 1, entries 8 and 9). Moreover, higher activity can be achieved as the reaction temperature was increased to 60 °C. Under these conditions, the Br-PCN-224(Fe)/O<sub>2</sub> oxidation system produces tertiary alcohol with 99% yield after 1 h, which suggests that the Br-PCN-224(Fe) framework exhibits higher activity at 60 °C (Table 1, entry 10). More importantly, we can lower the catalyst amount to 5 mol% while keeping the outstanding reactivity of the Br-PCN-224(Fe) catalyst (Table 1, entry 11).

15 Encouraged by the notable catalytic performance of the Br-16 PCN-224(Fe) catalyst under O<sub>2</sub> atmosphere, we attempted to 17 conduct the oxidation reaction in the air. Under such condi-18 tions, an excellent selectivity (>99%) of tertiary alcohol was 19 achieved after 16 h (Table 1, entry 12). Meanwhile, the oxida-20 tion reaction proceeds almost equivalently to produce tertiary alcohol at 60 °C after 10 h in the atmosphere (Table 1, entry 22 13). However, when the Cl-PCN-224(Fe) framework was em-23 ployed as a catalyst in air, the tertiary alcohol (80%) together 24 with while 2-one (15%) and 2,4-dione (5%) were obtained due 25 to the partly overoxidation of 3-methyl pentane (Table 1, entry 14). As control experiments, the oxidation reactions were fur-26 ther conducted without any catalyst using PhIO and O<sub>2</sub> as oxi-27 dants, respectively. In the presence of PhIO, the oxidation 28 reaction exhibited lower selectivity with tertiary alcohol (62%), 29 primary alcohol (7%), secondary alcohol (12%), and 2-one 30 (19%) formed (Table 1, entry 15). While no product was found in the O<sub>2</sub> atmosphere (Table 1, entry 16). Under similar 32 conditions, no significant difference in performance was ob-33 served in the benzene solution (Table 1, entries 17 and 18). 34 Furthermore, iron-free Br-PCN-224 and Br-PCN-224(Ni) 35 were proven to be noneffective on the oxidation reaction (Table 1, entries 19 and 20). Finally, the Br-TCPP(Fe) ligand and 36 amorphous aBr-PCN-224 were also employed as catalysts, 37 while a moderate yield (74%) and a low yield (41%) of ter-38 tiary alcohol were obtained (Table 1, entries 21 and 22), re-39 spectively, which highlighted the advantage of the high po-40 rosity found within MOFs.

To obtain the further insight of the Br-PCN-224(Fe) catalyst in the oxidation reaction, we evaluated the turnover number (TON) and turnover frequency (TOF) with 5 mol% Br-PCN-224(Fe) using 400 mmol 3-methyl pentane under an O2 atmosphere. Remarkably, for the oxidation reaction of 3-methyl pentane, the yield was 96% after 45 min; thus, the TON and TOF were calculated as 7680 and 10240  $h^{-1}$ , respectively. In addition, the time-dependent conversion and time-dependent yield of products were studied to get an insight into the reaction kinetic processes. We found that the Br-PCN-224(Fe) exhibited high catalytic selectivity toward the formation of tertiary alcohol under O<sub>2</sub> or air atmosphere (Figures S20 and S21). Interestingly, the Cl-PCN-224(Fe) catalytic system initially generated secondary and tertiary alcohols as main products. As reaction time was prolonged, the secondary alcohol was gradually consumed, producing the 2-one and 2,4-dione as final products (Figures S22 and S23). Finally, we investigated the possibility of iron leaching out from the four R-

PCN-224(Fe) catalysts. After the catalytic reaction, the R-PCN-224(Fe) powder samples were separated by filtration. The X-Ray photoelectron spectroscopy (XPS) revealed that the valence of irons in all the residual samples is +3 (Figure S8). At the same time, the inductively coupled plasma mass spectrometry (ICP-MS) indicated that 0.02% of irons existing in the four filtrates, which could be ascribed to the possibility that an extremely small amount of irons leached out and formed iron nanoparticles or the iron porphyrin ligands dissociate from the frameworks. These results illustrates that the four R-PCN-224(Fe) frameworks have the similar stability in the catalytic process.

To the best of our knowledge, Br-PCN-224(Fe) exhibits the highest catalytic selectivity reported to date for the oxidation reaction of 3-methyl pentane under mild conditions. Among the proposed mechanisms, the outstanding activity and selectivity of the halogenated Br-PCN-224(Fe) framework as catalyst can be ascribed to the following factors: (i) The electronwithdrawing bromo substituent shifts the Fe<sup>111/11</sup> potential to more positive values, increasing the rate of the slow step in peroxide decomposition, which has been suggested by Lyons and Ellis.<sup>24a</sup> (ii) Electronic stabilization of  $Fe^{II}$  disfavors  $O_2$  binding.<sup>24b</sup> (iii) Halogenation helps stabilize the porphyrin against oxidative degradation.<sup>25</sup> (iv) The three-dimensional crystalline networks and excellent porosity contribute to the high activity. Although chloro and fluoro units are also typical electron withdrawing substituents, they are too strong for the Fe<sup>III/II</sup> potential shift, thus leading to overoxidation of 3-methyl pentane to ketones.



**Figure 4.** (a) Yields and (b) TON values of Br-PCN-224(Fe) in the oxidation reaction of 3-methyl pentane over the five cycles.

Upon completion of the oxidation of 3-methyl pentane, Br-PCN-224(Fe) framework could be easily recovered by centrifugal separation and reused at least in five cycles without significant loss of its original catalytic activity and selectivity. PXRD and N<sub>2</sub> sorption measurements showed that the crystallinity and porosity of Br-PCN-224(Fe) remained almost unchanged after five reaction cycles (Figures S24 and S25). Notably, after five cycles, the yield of tertiary alcohol remains 95% (Figure 4a). The Br-PCN-224(Fe) still exhibits TON and TOF values as high as 7132 and 9509 h<sup>-1</sup>, respectively (Figure 4b). We also performed the recycling experiments with lower catalyst loading (1, 0.1, and 0.01 mol%). As the catalyst amount decreasing, the reaction time was prolonged to complete the oxidation conversion (Table S4). In all three catalytic conditions, 1, 0.1, and 0.01 mol%, the Br-PCN-224 (Fe) exhibited excellent catalytic performance after five cycles. At five cycles, catalytic loading was maintained at 92%, 88%, and 81% for 1, 0.1 and 0.01 mol % respectively (Figures S26-S28).

## CONCLUSIONS AND OUTLOOK

In summary, four isoreticular analogues of the PCN-224(Fe) have been successfully developed. By insertion of ethyl, bromo, chloro, and fluoro units into the  $\beta$ -position of TCPP ligand, the four MOFs allow for a systematic single substitution study. Incorporation of simple substitution groups remarkably increases both the activity and selectivity of MOF-embedded iron sites for 3-methyl pentane oxidation catalysis without directly changing the topological structure, crystallinity, and porosity of the frameworks. Periphery modification of catalytic sites and single substitution engineering may prove to be highly effective on the control over catalytic performance in the context of many other MOFs. This study therefore introduces a new strategy for tuning the catalytic properties of MOFs and screening high-performance catalysts through modular chemistry.

## ASSOCIATED CONTENT

**Supporting Information**. Full details for ligand synthesis and sample characterization results are available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENT

The gas adsorption-desorption studies of this research was supported by the Center for Gas Separations Relevant to Clean Energy Technologies, an Energy Frontier Research Center funded by the US Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001015. Structural analyses were supported as part of the Hydrogen and Fuel Cell Program under Award Number DE-EE-0007049. We also acknowledge the financial supports from U.S. Department of Energy Office of Fossil Energy, National Energy Technology Laboratory (DE-FE0026472) and Qatar National Research Fund (NPRP9-377-1-080).

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