# **Supporting Information**

# Systematically Engineering of Single Substitution in Zirconium Metal–Organic Framework towards High-Performance Catalysis

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#### Section 1. Methods

<sup>1</sup>H-NMR spectra were measured on Mercury NMR spectrometer, where chemical shifts ( $\delta$  in ppm) were determined with a residual proton of the solvent as standard. 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. 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 Micromeritics 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 chromatograph-mass spectrometry (GC-MS).

#### Section 2. Materials and Synthetic Procedures

The commercial chemicals are purchased unless mentioned otherwise. 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. 3,4-Difluoro-1*H*-pyrrole, 3-methyl pentane, and benzoic acid was 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).



β-Octaethyl-meso-tetrakis(*p*-4-methoxycarbonylphenyl)porphyrin (Et-TCPPOOMe). A solution of methyl 4-formylbenzoate (1.64 g, 10 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> 500 mL was charged in a two-necked round bottom flask under nitrogen atmosphere followed by the addition of 3,4-diethyl pyrrole (1.23 g, 10 mmol). After bubbling with N<sub>2</sub> for 30 min, the solution was cooled down to 0 °C, BF<sub>3</sub>OEt<sub>2</sub> 0.15 mL was add in one portion and the mixture was stirred overnight at room temperature. After that, 3,4-dicholoro-5,6-dicyano-1,4-benzoquinone (DDQ, 1 g, 4.4 mmol) were added and reflux another 2 h to complete the reaction. The solvent was evaporated followed by separation on silica chromatography using CH<sub>2</sub>Cl<sub>2</sub> as eluent. Et-TCPPOOMe was obtained as purple powder after evaporation in 36% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.62 (d, 8H), 8.40 (d, 8H), 4.12 (s, 12H), 2.18 (b, 16H), 0.78 (b, 24H). MALDI-TOF HRMS for C<sub>66</sub>H<sub>66</sub>N<sub>4</sub>O<sub>8</sub> [M<sup>+</sup>] calcd. 1042.49, found 1042.5031.

 $[\beta$ -Octaethyl-meso-tetrakis(*p*-4-methoxycarbonylphenyl)porphyrin]-Fe (III) chloride (Fe-Et-TCPPOOMe). The obtained Et-TCPPOOMe was stirred in 20 ml DMF solution of FeCl<sub>2</sub>•4H<sub>2</sub>O (2.0 g), and then heated at

100 °C overnight. After cooled to room temperature, the solution was poured into 100 mL water. The mixture was extracted with ethyl acetate (50 ml×3), and the combined organic solution was washed with brine (50 ml×3) and water (50 ml×2). The solution was dried over anhydrous MgSO<sub>4</sub>, filtered and the solvent was evaporated to give the final product as brown powder in 96% yield. MALDI-TOF HRMS for  $C_{68}H_{68}ClFeN_4O_8$  [M<sup>+</sup>] calcd 1159.41, found 1159.5124.



[ $\beta$ -Octaethyl-meso-tetrakis(p-4-carboxyphenyl)porphyrin]-Fe (III) chloride (Fe-Et-TCPP). The Fe-Et-TCPPOOMe (1.16 g, 1 mmol) was added into a 90 mL mixture of THF: MeOH: H<sub>2</sub>O = 1:1:1, to which 1.4 g NaOH was added and heated to reflux overnight. After cooling to RT, the mixture was filtered to obtain green solid. The solid was then stirred in 50 mL water and acidified with 20% HCl. After heating and stirring the mixture for 2 h, green solid was collected by filtration, washed with water and dried in vacuum to give 0.76g (0.83mmol) pure compound Fe-Et-TCPP (yield. 92%). MALDI-TOF HRMS for C<sub>68</sub>H<sub>56</sub>ClFeN<sub>4</sub>O<sub>8</sub> [M<sup>+</sup>] calcd 1075.31, found 1075.3264.



**5,10,15,20-Tetrakis(4-methoxycarbonylphenyl)porphyrin (TCPPOOMe).** To refluxed propionic acid (100 mL) in a 500 mL three necked flask were added pyrrole (3.0, 0.043 mol) and methyl 4-formylbenzoate (6.9 g, 0.042 mol), and the solution was refluxed for 12 h in darkness. After the reaction mixture was cooled to room temperature, crystals were collected by filtration to afford purple crystals (2.2 g, 2.24 mmol, 23.2% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.81 (s, 8H), 8.43 (d, 8H), 8.28 (d, 8H), 4.11 (s, 12H), -2.83 (s, 2H). MALDI-TOF HRMS for C<sub>52</sub>H<sub>38</sub>N<sub>4</sub>O<sub>8</sub> [M<sup>+</sup>] calcd 846.27, found 846.2764.

[5,10,15,20-Tetrakis(4-methoxycarbonylphenyl)porphyrinato]-Fe(III) Chloride (Fe-TCPPOOMe). A solution of TCPPOOMe 0.854 g (1.0 mmol) and FeCl<sub>2</sub>•4H<sub>2</sub>O (2.5 g, 12.8 mmol) in 30 mL of DMF was refluxed for 6 h. After the mixture was cooled to room temperature, 150 mL of H<sub>2</sub>O was added. The resultant precipitate was filtered and washed with 50 mL of H<sub>2</sub>O for three times. The obtained solid was dissolved in CHCl<sub>3</sub>, followed by washing three times with 1 M HCl and twice with water. The organic layer was dried over anhydrous MgSO<sub>4</sub> and evaporated to afford quantitative dark brown crystals. MALDI-TOF HRMS for C<sub>52</sub>H<sub>36</sub>ClFeN<sub>4</sub>O<sub>8</sub> [M<sup>+</sup>] calcd 935.16, found 935.1642.

[5,10,15,20-Tetrakis(4-carboxyphenyl)porphyrinato]-Fe(III) Chloride. The obtained ester (0.75 g) was stirred in THF (25 mL) and MeOH (25 mL) mixed solvent, to which a solution of KOH (2.63 g, 46.95 mmol) in H<sub>2</sub>O (25 mL) was added. This mixture was refluxed for 12 h. After cooling down to room temperature, THF and MeOH were evaporated. Additional water was added to the resulting water phase and the mixture was heated until the solid was fully dissolved, then the homogeneous solution was acidified with 1M HCl until no further precipitate was detected. The brown solid was collected by filtration, washed with water and dried in vacuum. MALDI-TOF HRMS for  $C_{48}H_{28}CIFeN_4O_8$  [M<sup>+</sup>] calcd 879.09, found 879.1012.



*β*-Octabromo-meso-tetrakis(*p*-4-methoxycarbonylphenyl)porphyrin (Br-TCPPOOMe). The synthetic procedure for Fe-Br-TCPP followed previous report with slight modification.<sup>S1</sup> TCPPOOMe (400 mg, 0.47 mmol) was dissolved in 150 mL of chloroform followed by the addition of Cu(OAc)<sub>2</sub>•H<sub>2</sub>O (760 mg, 3.81 mmol, 8 equiv). The reaction mixture was stirred at reflux for 30 min. After complete conversion to copper porphyrin as detected by TLC, 4 mL liquid Br<sub>2</sub> was added to the reaction mixture directly. The solution was continually stirred for about 24 h at room temperature. Aqueous solution of sodium thiosulfate was added to quench the reaction. After removal of the excessive bromine, the reaction mixture was stirred for about 12 h for demetallization. The organic layer was separated and washed with aqueous and a solution of sodium bicarbonate and water, and dried over anhydrous MgSO<sub>4</sub>. The organic mixture was rotary-evaporated to give a solid. The crude product was purified by column chromatography on silica gel using chloroform/ethyl acetate 60:1 as eluent to give Br-TCPPOOMe (490 mg, 70% yield).

[β-Octabromo-meso-tetrakis(p-4-methoxycarbonylphenyl)porphyrin]-Fe (III) chloride (Fe-Br-TCPPOOMe). A solution of Br-TCPPOOMe 1.47 g (1.0 mmol) and FeCl<sub>2</sub>•4H<sub>2</sub>O (2.5 g, 12.8 mmol) in 50 mL of DMF was refluxed for 6 h. After the mixture was cooled to room temperature, 150 mL of H<sub>2</sub>O was added. The resultant precipitate was filtered and washed with 50 mL of H<sub>2</sub>O for three times. The crude product was purified by column chromatography on silica gel using chloroform/ethyl acetate 60:1 as eluent to give Br-TCPPOOMe (2.20 g, 87% yield). MALDI-TOF HRMS for  $C_{52}H_{28}Br_8ClFeN_4O_8$  [M<sup>+</sup>] calcd 1558.44, found 1558.5382.



[ $\beta$ -Octabromo-meso-tetrakis(p-4-carboxyphenyl)porphyrin]-Fe (III) chloride (Fe-Br-TCPP). Fe-Br-TCPPOOMe (300 mg, 0.2 mmol) was dissolved in 50 mL of THF and 30 mL of a 2 M aqueous solution of potassium hydroxide was added. The solution was stirred in a sealed flask at room temperature for 3 days. The aqueous phase was collected and the pH lowered, using a 1M solution of hydrochloric acid, until precipitation of the porphyrin. The precipitate was washed with water and dried under vacuum to give Fe-Br-TCPP (250 mg, 86.7% yield). MALDI-TOF HRMS for C<sub>48</sub>H<sub>20</sub>Br<sub>8</sub>ClFeN<sub>4</sub>O<sub>8</sub> [M<sup>+</sup>] calcd 1502.38, found 1502.4213.



[\$-Octachloro-meso-tetrakis(p-4-methoxycarbonylphenyl)porphyrin]-Fe (III) chloride (Fe-Cl-TCPPOOMe).

The synthesis for Fe-CI-TCPP followed previous reports with slight modification.<sup>S2, S3</sup> Fe-TCPPOOMe (400 mg, 0.43 mmol) was dissolved in 50 mL of dichlorobenzene followed by addition of N-chlorosuccinimide (2g, 15 mmol). The reaction mixture was stirred at 140 °C overnight. Aqueous solution of sodium thiosulfate was added to quench the reaction. After removal of the excessive bromine, the reaction mixture was washed by H<sub>2</sub>O several times. The organic layer was separated and washed with aqueous and a solution of sodium bicarbonate and water, and dried over anhydrous MgSO<sub>4</sub>. The organic mixture was evaporated to give a solid. The crude product was purified by column chromatography on silica gel using chloroform/ethyl acetate 60:1 as eluent to give Fe-CI-TCPPOOMe (384 mg, 74% yield). MALDI-TOF HRMS for C<sub>52</sub>H<sub>28</sub>Cl<sub>9</sub>FeN<sub>4</sub>O<sub>8</sub> [M<sup>+</sup>] calcd. 1206.85, found 1206.2565.



[\beta-Octabromo-meso-tetrakis(p-4-carboxyphenyl)porphyrin]-Fe (III) chloride (Fe-Cl-TCPP).

Fe-Cl-TCPPOOMe (302 mg, 0.25 mmol) was dissolved in 5 mL of THF and 3 mL of a 2 M aqueous solution of potassium hydroxide was added. The solution was stirred in a sealed flask at room temperature for 3 days. The aqueous phase was collected and the pH lowered, using a 1M solution of hydrochloric acid, until precipitation of the porphyrin. The precipitate was washed with water and dried under vacuum to give Fe-Cl-TCPP (238 mg, 82.7% yield). MALDI-TOF HRMS for  $C_{48}H_{20}Cl_9FeN_4O_8$  [M<sup>+</sup>] calcd. 1150.78, found 1151.0343.



*β*-Octafluoro-meso-tetrakis(*p*-4-methoxycarbonylphenyl)porphyrin (F-TCPPOOMe). A solution of methyl 4-formylbenzoate (1.64 g, 10 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> 500 mL was charged in a two-necked round bottom flask under nitrogen atmosphere followed by the addition of 3,4-difluoropyrrole (1.23 g, 10 mmol). After bubbling with N<sub>2</sub> for 30 min, the solution was cooled down to 0 °C, BF<sub>3</sub>OEt<sub>2</sub> 0.15 mL was add in one portion and the mixture was stirred overnight at room temperature. After that, 3,4-dicholoro-5,6-dicyano-1,4-benzoquinone (DDQ, 1 g, 4.4 mmol) were added and reflux another 2 h to complete the reaction. The solvent was evaporated followed by separation on silica chromatography using CH<sub>2</sub>Cl<sub>2</sub> as eluent. F-TCPPOOMe was obtained as purple powder after evaporation in 36% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.85 (s, 8H), 8.44 (d, 8H), 4.10 (s, 12H). MALDI-TOF HRMS for C<sub>52</sub>H<sub>30</sub>F<sub>8</sub>N<sub>4</sub>O<sub>8</sub> [M<sup>+</sup>] calcd. 990.19, found 990.15.

[β-Octafluoro-meso-tetrakis(p-4-methoxycarbonylphenyl)porphyrin] Fe(III) Chloride (Fe-F-TCPPOOMe).

A solution of TCPPOOMe 0.854 g (1.0 mmol) and FeCl<sub>2</sub>·4H<sub>2</sub>O (2.5 g, 12.8 mmol) in 100 mL of DMF was refluxed for 6 h. After the mixture was cooled to room temperature, 150 mL of H<sub>2</sub>O was added. The resultant precipitate was filtered and washed with 50 mL of H<sub>2</sub>O for two times. The obtained solid was dissolved in CHCl<sub>3</sub>, followed by washing three times with 1 M HCl and twice with water. The organic layer was dried over anhydrous magnesium sulfate and evaporated to afford quantitative dark brown crystals. MALDI-TOF HRMS for  $C_{52}H_{28}F_8N_4O_8$  [M<sup>+</sup>] calcd. 1079.08, found 1078.94.



[ $\beta$ -Octafluoro-meso-tetrakis(p-4-carbonylphenyl)porphyrin] Fe(III) Chloride (Fe-F-TCPP). The obtained ester (0.75 g) was stirred in THF (25 mL) and MeOH (25 mL) mixed solvent, to which a solution of KOH (2.63 g, 46.95 mmol) in H<sub>2</sub>O (25 mL) was introduced. This mixture was refluxed for 12 h. After cooling down to room temperature, THF and MeOH were evaporated. Additional water was added to the resulting water phase and the mixture was heated until the solid was fully dissolved, then the homogeneous solution was acidified with 1M HC1 until no further precipitate was detected. The brown solid was collected by filtration, washed with water and dried in vacuum. MALDI-TOF HRMS for C<sub>48</sub>H<sub>20</sub>ClF<sub>8</sub>FeN<sub>4</sub>O<sub>8</sub> [M<sup>+</sup>] calcd. 1023.02, found 1023.1427.

### Section 3. Supporting Tables

Table S1. Unit cell parameters of Et-PCN-224(Fe), Br-PCN-224(Fe), Cl-PCN-224(Fe), and F-PCN-224(Fe),

	Et-PCN-224(Fe)	Br-PCN-224(Fe)	Cl-PCN-224(Fe)	F-PCN-224(Fe)	
Space group	Im-3m	Im-3m	Im-3m	Im-3m	
a, b, c / Å	38.643(5)	38.633(5)	38.586(2)	38.514(1)	
α, β, γ / Å	90	90	90	90	
$V/\text{\AA}^3$	571431(5)	57426(3)	57357(4)	57122(6)	
R <sub>exp</sub>	1.463	1.234	1.125	0.756	
R <sub>wp</sub>	2.432	2.134 2.342		1.534	
R <sub>p</sub>	<b>R</b> <sub>p</sub> 1.353 1.433 1		1.687	1.534	
Wavelength (Å)	Wavelength (Å)         0.727680         0.727680		0.727680	0.727680	
Temperature298 K298 K		298 K	298 K		

determined via Pawley fitting of powder X-ray diffraction data.

Table S2. N2 uptake, surface areas, pore sizes and pore volumes of Et-PCN-224(Fe), Br-PCN-224(Fe),

MOFs	$N_2$ uptake (cm <sup>3</sup> g <sup>-1</sup> )	$S_{\rm BET} ({ m m}^2{ m g}^{-1})$	Pore size (nm)	Pore volume (cm <sup><math>3</math></sup> g <sup><math>-1</math></sup> )
Et-PCN-224(Fe)	694	2287	1.9	1.34
Br-PCN-224(Fe)	651	2142	1.9	1.27
Cl-PCN-224(Fe)	689	2268	1.9	1.33
F-PCN-224(Fe)	716	2359	1.9	1.39

Cl-PCN-224(Fe), and F-PCN-224(Fe).

Table S3. Isolated yield of the products in oxygenation of 3-methyl pentane.<sup>a,b,c</sup>

	↓	ССС	+ \	↓ он +	ОН ✓ ↓ +	но个	$\downarrow$	н +	↓ ↓ ↓		
r		10		2°	30		diol		2-one	2,4-dion	e
Entry	Catalyst	Solvent	°C	Time	Oxidant		Alcoho	1	Diol	2-one	2,4-dione
				(11)		1°	2°	3°			
1	PCN-224(Fe)	CH <sub>2</sub> Cl <sub>2</sub>	25	2	PhIO	12	14	57	_	13	_
2	Et-PCN-224(Fe)	CH <sub>2</sub> Cl <sub>2</sub>	25	2	PhIO	24	11	52	-	6	-
3	Br-PCN-224(Fe)	CH <sub>2</sub> Cl <sub>2</sub>	25	2	PhIO	2	2	77	—	2	9
4	Cl-PCN-224(Fe)	$CH_2Cl_2$	25	2	PhIO	-	-	61	_	7	28
5	F-PCN-224(Fe)	$CH_2Cl_2$	25	2	PhIO	_	-	54	_	11	30
<sup>d</sup> 6	Br-PCN-224(Fe)	$CH_2Cl_2$	25	2	O <sub>2</sub>	-	-	90	-	7	-
7	Cl-PCN-224(Fe)	$CH_2Cl_2$	25	2	O <sub>2</sub>	_	_	68	-	10	15
8	Br-PCN-224(Fe)	C <sub>6</sub> H <sub>6</sub>	25	2	O <sub>2</sub>	-	-	98	-	-	-
9	Cl-PCN-224(Fe)	$C_6H_6$	25	2	$O_2$	-	-	80	-	5	7
10	Br-PCN-224(Fe)	$C_6H_6$	60	1	O <sub>2</sub>	-	-	99	-	-	-
<sup>e</sup> 11	Br-PCN-224(Fe)	$C_6H_6$	60	1	$O_2$	-	-	98	-	-	-
12	Br-PCN-224(Fe)	$C_6H_6$	25	16	air	_	_	98	_	_	_
13	Br-PCN-224(Fe)	C <sub>6</sub> H <sub>6</sub>	60	10	air	_	_	98	_	_	_
14	Cl-PCN-224(Fe)	$C_6H_6$	25	5	air	_	_	78	_	14	5
15	No catalyst	$CH_2Cl_2$	25	3	PhIO	5	10	60	_	18	_
16	No catalyst	$CH_2Cl_2$	25	3	$O_2$	_	_	_	_	_	-
17	No catalyst	$C_6H_6$	25	3	PhIO	3	11	60	_	16	-
18	No catalyst	C <sub>6</sub> H <sub>6</sub>	25	3	O <sub>2</sub>	_	_	_	-	-	_
19	Br-PCN-224	C <sub>6</sub> H <sub>6</sub>	25	2	O <sub>2</sub>	-	-	-	_	-	_
20	Br-PCN-224(Ni)	C <sub>6</sub> H <sub>6</sub>	25	2	O <sub>2</sub>	_	_	_	-	_	_
21	Br-TCPP(Fe)	C <sub>6</sub> H <sub>6</sub>	25	2	O <sub>2</sub>	_	_	72	-	-	-
<sup>e</sup> 22	<i>a</i> Br-PCN-224(Fe)	$C_6H_6$	25	2	O <sub>2</sub>	—	-	40	-	_	_

<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>All the yield in this table is isolated yield. <sup>d</sup>The pressure of  $O_2$  and air is 1 atm. <sup>e</sup>The catalyst amount is 5 mol%.

Entry	Catalyst	Amount of Catalyst (mol%) Time (h)		Yield (%)	
1	Br-PCN-224(Fe)	10	2	>99	
2	Br-PCN-224(Fe)	5	3	>99	
3	Br-PCN-224(Fe)	1	6	>99	
4	Br-PCN-224(Fe)	0.1	14	>99	
5	Br-PCN-224(Fe)	0.01	35	>99	

Table S4. The effects of the amount of catalyst on the conversion and yield of oxidation of 2-methyl pentane.

Section 4. Supporting Figures.



Figure S1. The thermal gravimetric analysis (TGA) analysis result of Et-PCN-224(Fe).



Figure S2. The thermal gravimetric analysis (TGA) analysis result of Br-PCN-224(Fe).



Figure S3. The thermal gravimetric analysis (TGA) analysis result of Cl-PCN-224(Fe).



Figure S4. The thermal gravimetric analysis (TGA) analysis result of F-PCN-224(Fe).



Figure S5. UV spectra of Et-PCN-224(Fe), Br-PCN-224(Fe), Cl-PCN-224(Fe) and F-PCN-224(Fe) samples.



Figure S6. XPS spectra of Et-PCN-224(Fe) sample.



Figure S7. XPS spectra of Br-PCN-224(Fe) sample.



Figure S8. XPS spectra of Br-PCN-224(Fe) sample after the 1<sup>st</sup> cycle of catalysis.



Figure S9. XPS spectra of Cl-PCN-224(Fe) sample.



Figure S10. XPS spectra of F-PCN-224(Fe) sample.



**Figure S11.** 3-Methylpentane sorption isotherms of Et-PCN-224(Fe) (black curve), Br-PCN-224(Fe) (red curve), Cl-PCN-224(Fe) (blue curve), and F-PCN-224(Fe) (green curve) at 298 K.



**Figure S12.** PXRD patterns of Et-PCN-224(Fe) after treatment in different solutions after 24 h (black curve, pristine; red curve, water; blue curve, pH = 1 solution; green curve, 1 M HCl solution; purple curve, pH = 10 solution; brown curve, pH = 11 solution).



**Figure S13.** PXRD patterns of Cl-PCN-224(Fe) after treatment in different solutions after 24 h (black curve, pristine; red curve, water; blue curve, pH = 1 solution; green curve, 1 M HCl solution; purple curve, pH = 10 solution; brown curve, pH = 11 solution).



**Figure S14.** PXRD patterns of F-PCN-224(Fe) after treatment in different solutions after 24 h (black curve, pristine; red curve, water; blue curve, pH = 1 solution; green curve, 1 M HCl solution; purple curve, pH = 10 solution; brown curve, pH = 11 solution).



**Figure S15.**  $N_2$  sorption isotherms of Et-PCN-224(Fe) after treatment in different solutions after 24 h (black curve, pristine; pink curve, water; blue curve, pH = 1 solution; green curve, 1 M HCl solution; red curve, pH = 10 solution; brown curve, pH = 11 solution).



**Figure S16.**  $N_2$  sorption isotherms of Cl-PCN-224(Fe) after treatment in different solutions after 24 h (black curve, pristine; pink curve, water; blue curve, pH = 1 solution; green curve, 1 M HCl solution; red curve, pH = 10 solution; brown curve, pH = 11 solution).



**Figure S17.** N<sub>2</sub> sorption isotherms of F-PCN-224(Fe) after treatment in different solutions after 24 h (black curve, pristine; pink curve, water; blue curve, pH = 1 solution; green curve, 1 M HCl solution; red curve, pH = 10 solution; brown curve, pH = 11 solution).



**Figure S18.** N<sub>2</sub> sorption isotherms of Et-PCN-224(Fe) (black curve), Br-PCN-224(Fe) (red curve), Cl-PCN-224(Fe) (blue curve), and F-PCN-224(Fe) (green curve) under O<sub>2</sub> atmosphere at 60 °C after 24 h.



**Figure S19.** N<sub>2</sub> sorption isotherms of Et-PCN-224(Fe) (red curve), Br-PCN-224(Fe) (blue curve), Cl-PCN-224(Fe) (green curve), and F-PCN-224(Fe) (black curve) under O<sub>2</sub> atmosphere at 60 °C after 24 h.



**Figure S20.** The time-dependent conversion plot (black curve) and time-dependent yield (red curve, tertiary alcohol; blue curve, other products) of oxidation of 3-methylpentane under O<sub>2</sub> atmosphere in presence of Br-PCN-224(Fe).



**Figure S21.** The time-dependent conversion plot (black curve) and time-dependent yield (red curve, tertiary alcohol; blue curve, other products) of oxidation of 3-methylpentane under the air in presence of Br-PCN-224(Fe).



**Figure S22.** The time-dependent conversion plot (black curve) and time-dependent yield (red curve, tertiary alcohol; green curve, secondary alcohol; blue curve, 2-noe; brown curve, 2,4-dione) of oxidation of 3-methylpentane under O<sub>2</sub> atmosphere in presence of Cl-PCN-224(Fe).



**Figure S23.** The time-dependent conversion plot (red curve) and time-dependent yield (red curve, tertiary alcohol; green curve, secondary alcohol; blue curve, 2-noe; brown curve, 2,4-dione) of oxidation of 3-methylpentane under the air in presence of Cl-PCN-224(Fe).



**Figure S24.** PXRD patterns of Br-PCN-224(Fe) after five cycles (black curve, 1<sup>st</sup> run; red curve, 2<sup>nd</sup> run; purple curve, 3<sup>rd</sup> run; green curve, 4<sup>th</sup> run; blue curve, 5<sup>th</sup> run).



**Figure S25.**  $N_2$  sorption isotherms of Br-PCN-224(Fe) after five cycles (black curve, 1<sup>st</sup> run; red curve, 2<sup>nd</sup> run; blue curve, 3<sup>rd</sup> run; green curve, 4<sup>th</sup> run; purple curve, 5<sup>th</sup> run).



**Figure S26.** Corresponding yield of 1 mol% Br-PCN-224(Fe) in the oxidation reaction of 3-methyl pentane over the five cycles.



**Figure S27.** Corresponding yield of 0.1 mol% Br-PCN-224(Fe) in the oxidation reaction of 3-methyl pentane over the five cycles.



**Figure S28.** Corresponding yield of 0.01 mol% Br-PCN-224(Fe) in the oxidation reaction of 3-methyl pentane over the five cycles.

## Section 5. Supporting References

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