Electronic Supporting Information

Boosting Selective Oxidation of Cyclohexane over a Metal-Organic Framework by Hydrophobicity Engineering of Pore Walls

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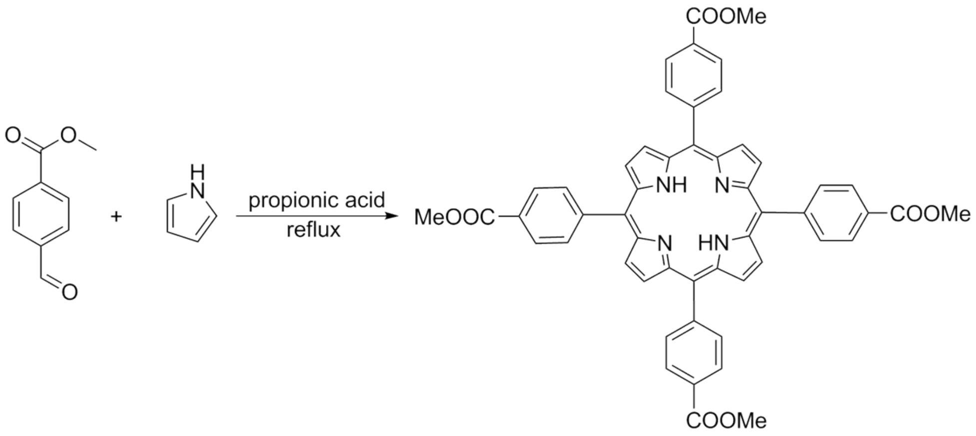
1. Materials and Instrumentation

All chemicals were purchased from commercial sources without further treatment unless otherwise mentioned. N,N-dimethylformamide (DMF, Sinopharm Chemical Reagent Co., Ltd., AR), benzoic acid (Energy Chemical, 99%), acetone (Energy Chemical), iron(II) chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$, Energy Chemical), zirconium (IV) chloride ($ZrCl_4$, Aladdin Industrial Inc., 98%), trifluoroacetic acid (Energy Chemical, 98%), perfluoropropionic acid (Energy Chemical, 98%), heptafluorobutyric acid (Energy Chemical, 98%), pyrrole (Energy Chemical, 99%), propionic acid (Aladdin Industrial Inc., 98%), methyl *p*-formylbenzoate, (Energy Chemical, 98%), N,N-diethylformamide (DEF, Aladdin Industrial Inc., 98%).

Powder X-ray diffraction (XRD) patterns were measured on a Japan Rigaku SmartLab rotation anode X-ray diffractometer or Holland X'Pert PRO fixed anode X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 1.54178 Å). Fluorine atoms in modified PCN-222 samples were analyzed by ^{19}F nuclear magnetic resonance spectrometer (^{19}F NMR, Bruker Avance III 400) by treating PCN-222(Fe)-F_n with H_2SO_4/DMSO-d_6. The transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) images were acquired on a JEOL JEM-2100F field-emission transmission electron microscope. Nitrogen adsorption-desorption isotherms were measured using a Micrometritics ASAP 2020 system at 77 K. Water sorption was measured on a BEL sorp-max machine, BEL, Japan at 298 K. The air-dried samples were further activated in vacuum at 120 ^oC for 12 h before water sorption measurement. Water contact angle measurement was carried out on OCA 40 optical contact angle meter at ambient conditions. Diffuse reflectance infrared spectra (DRIFTS) were recorded on a Nicolet™ iS™ 50 FTIR spectrometer equipped with an MCT detector. Samples prepared in atmosphere and the spectra were collected in a KBr mixture under N_2 purge with KBr utilized as the background. Catalytic oxidation reaction products were analyzed and identified by gas chromatography (GC, Shimadzu 2010 Plus with a 0.25 mm × 30 m Rtx-5 capillary column). Additional GC-MS analysis was performed on an Agilent Technologies 7890B GC system equipped with an Agilent Technologies 5977B MSD Mass Spectrometer.

2. Experimental Section



Synthesis of 5,10,15,20-Tetrakis(4-methoxycarbonylphenyl)porphyrin (TPPCOOMe): The synthetic procedure for TPPCOOMe was carried out by one step as follows.[S1] Typically, 6 g pyrrole, 200 mL propionic acid and 13.8 g methyl *p*-formylbenzoate were mixed in a 500-mL three necked flask, and the solution was refluxed at 140 °C for 12 h. After the solution was cooled down to room temperature, dark purple crystals were harvested by filtration with 150 mL ethanol and ethyl acetate washed, then dried in the vacuum oven at 60 °C for 12 h.

Synthesis of [5,10,15,20-Tetrakis(4-methoxycarbonylphenyl)porphyrinato]-Fe(III) Chloride (Fe-TCPPCl): The Fe-TCPPCl ligand was prepared according to the previous work as follows.[S1] A solution of TPPCOOMe (0.854 g, 1.0 mmol) and $FeCl_2 \cdot 4H_2O$ (2.5 g, 12.8 mmol) in 100 mL of DMF was refluxed for 6 h. After the mixture was cooled down to room temperature, 150 mL H_2O was added. The resultant precipitate was filtered and washed with 50 mL H_2O for two times. The obtained solid was dissolved in $CHCl_3$, 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.

Synthesis of PCN-222(Fe): PCN-222(Fe) was prepared based on the reported procedure.[S1] Typically, zirconium (IV) chloride (70 mg), Fe-TCPPCl (50 mg), benzoic acid (2.7 g) in 8 mL of DEF were ultrasonically dissolved in a 20 mL Teflon-lined autoclave and heated in a 120 °C oven for 48 h. Dark brown power was obtained by filtration and washed by 30 mL DMF and 20 mL acetone activated by drying for 6 h. Prior to further use, 60 mg of PCN-222(Fe) was stirred in 60 mL DMF in the presence or absence of 8 M HCl (1.5 mL) at 120 °C overnight to remove unreacted starting materials and trapped benzoic acid. The purple powder was harvested by filtration and washing with 30 mL DMF and 20 mL acetone. The sample was transferred to a 30 mL centrifuge tube and soaked in 20 mL fresh acetone for 24 h to exchange and remove the nonvolatile solvates (DMF). After the removal of acetone by filtration, the sample was activated by drying under vacuum for 12 h, then was dried again by using the ‘outgas’ function of the surface area analyzer for 12 h at 120 °C prior to gas adsorption/desorption measurement.

Synthesis of PCN-222(Fe)-F$_n$: PCN-222(Fe)-F$_n$ were synthesized by microwave reaction (CEM Discover SP). Typically, 60 mg of PCN-222(Fe), 0.24 mmol perfluoroalkyl acid and 2.4 mL DMF were mixed in a 10 mL microwave vial and reacted at 60 °C for 24 h by microwave treatment. After cooling to room temperature, all samples were washed by hot DMF, acetone and further activated by soaking in acetone for one day. Dark brown powder was harvested by centrifugation, washing with 60 mL DMF, 40 mL acetone and 30 mL aether, finally drying in air.[S2]

Solution-Phase Cyclohexane Adsorption Studies: In a 20 mL vial, 25 mg of PCN-222(Fe) or PCN-222(Fe)-F_n was immersed in 1 mL acetonitrile solution of cyclohexane (1 M) and the mixture was stirred at 25 ^{o}C for 4 h. The concentration of cyclohexane in the supernatant was analyzed by GC with 1,4-chlorobenzene as an internal standard.[S3] And the cyclohexane adsorption capacity was determined by the following equation：

$$q_t = \frac{(C_i - C_f)V}{m}$$

Where q_t is the amount of cyclohexane adsorbed at time t (mol/mol framework); C_i is the initial concentration of the adsorbate (mol/L); C_f is the final concentration after adsorption (mol/L); V is the volume of solution initially added to the framework (L); and m is the amount of adsorbent added (mol).

3. Catalytic Activity Characterization

Assessment of the catalytic performance of PCN-222(Fe) and PCN-222(Fe)-F$_n$ for the cyclohexane oxidation: Typically, a mixture of 20 mg PCN-222(Fe) or PCN-222(Fe)-F$_{n,}$ 0.1 mmol cyclohexane, 2.5 mL CH_3CN and 25.6 mg $AgBF_4$ was laced in a necked round-bottomed flask (10 mL) with a O_2 balloon, refluxing for 24 h at 80 ^{o}C. For the catalytic recycling/durability experiments, PCN-222(Fe)-F$_7$ was separated by centrifugation after reaction, thoroughly washed by 10 mL acetonitrile and 10 mL acetone for 3 times. It was dried in a vacuum drying oven for 12 h for the next run. After the completion of the reaction, 30 μL of the resultant mixture was taken to a mixed solvent with 1 mL H_2O and 1 mL ethyl acetate. Upon the adequate shaking, the above mixture was allowed to be centrifuged and the reaction product was extracted to the upper layer of ethyl acetate. Then, 600 μL of sample in the upper solution was detected by GC.

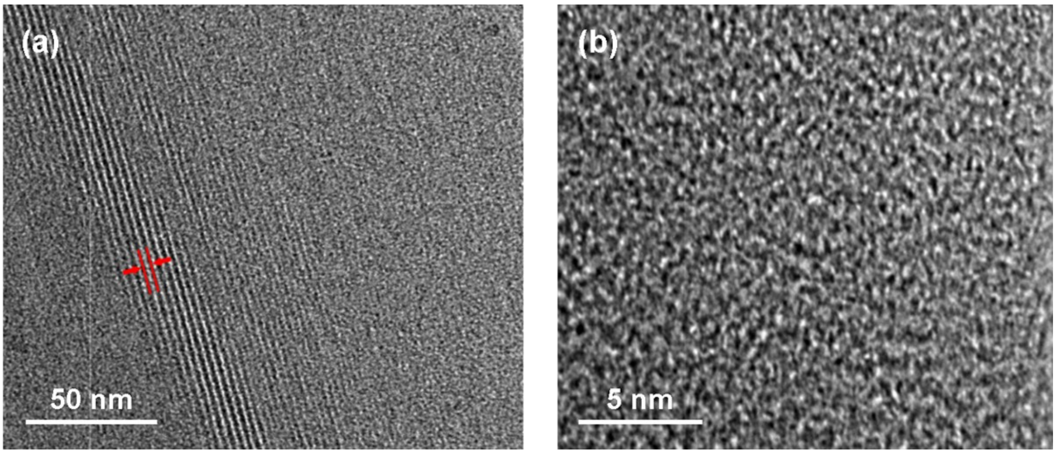


Fig. S1 (a) TEM and (b) HR-TEM images of PCN-222(Fe). The 1D channels in PCN-222 are observable in TEM image while unidentifiable in HR-TEM image, possibly due to the well-known MOF instability upon long-time exposure to electron beam during the HR-TEM observation. [S4]

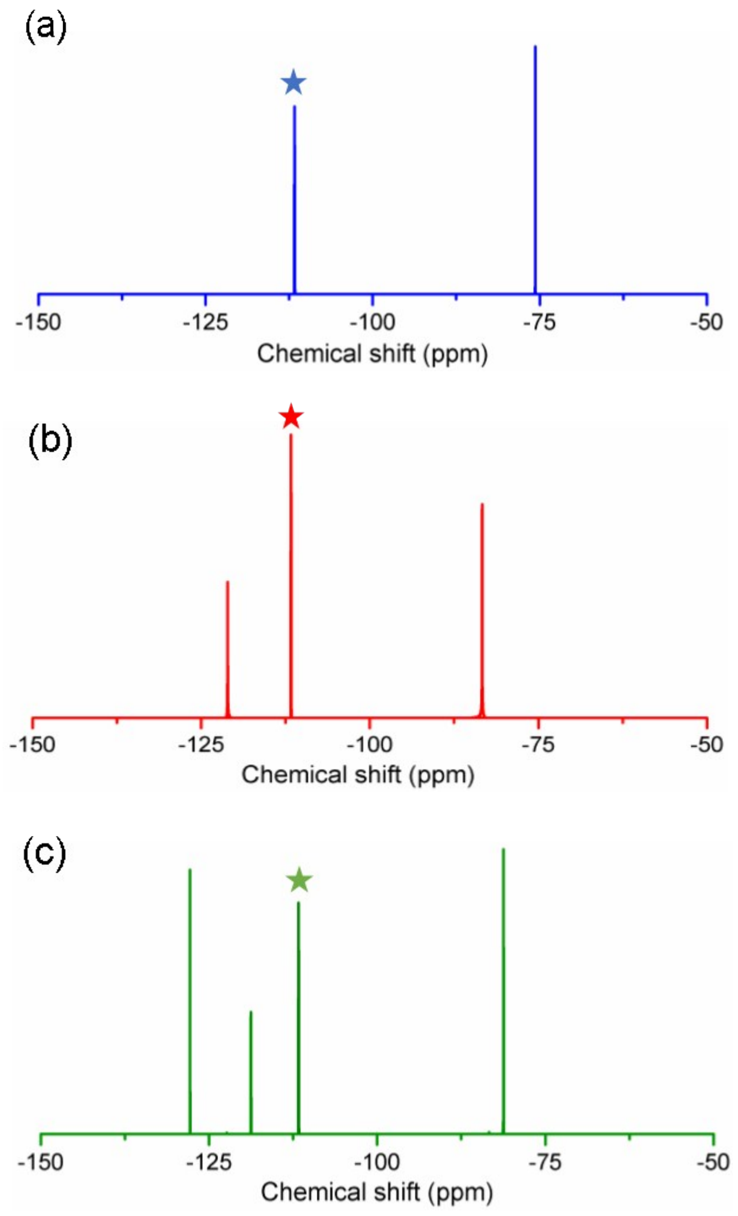


Fig. S2 ^{19}F NMR spectra for (a) PCN-222(Fe)-F_3, (b) PCN-222(Fe)-F_5 and (c) PCN-222(Fe)-F_7. The samples were dissolved in 10% H_2SO_4/DMSO-d_6 before ^{19}F NMR measurement with ^{19}F signal of 1-ethynyl-4-fluorobenzene as an internal standard (marked with the star symbol). The obtained ^{19}F signals indicate the successful grafting perfluorinated alkyls onto pore walls of PCN-222(Fe). The F contents: PCN-222-F_3 (8.1 wt%), PCN-222-F_5 (14.5 wt%) and PCN-222-F_7 (15.5 wt%), evaluated by ^{19}F NMR with 1-ethynyl-4-fluorobenzene as an internal standard.

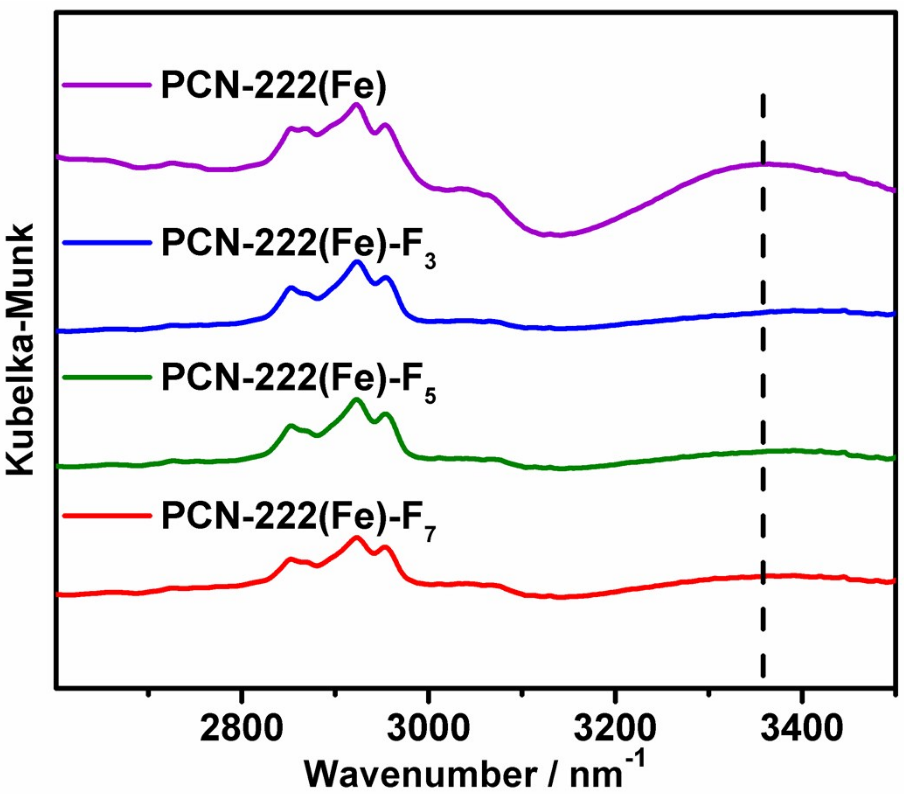


Fig. S3 DRIFTS curves for PCN-222(Fe), PCN-222(Fe)-F_3, PCN-222-F_5 and PCN-222-F_7. The peak at 3375 cm^{-1} assignable to the terminal -OH group of $Zr_6O_8(OH)_8$ nodes in PCN-222(Fe) almost disappears in PCN-222(Fe)-F_n, which supports the complete exchange replacement by perfluorocarboxylic acids.[S2]

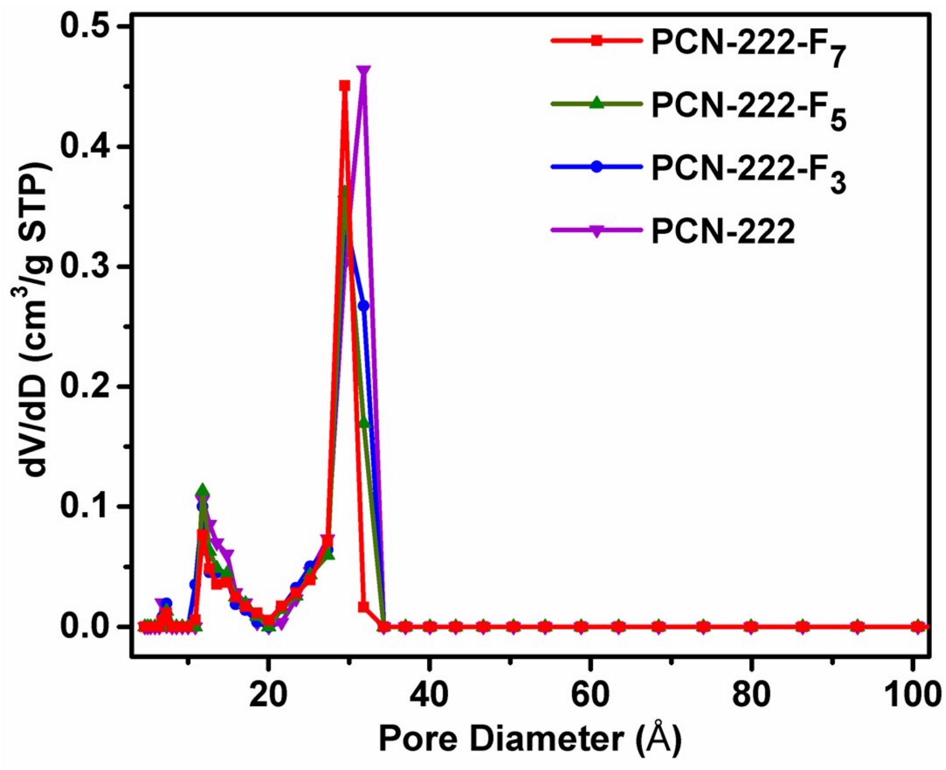


Fig. S4 Pore size distribution based on DFT method for PCN-222(Fe) and PCN-222(Fe)-F_n.

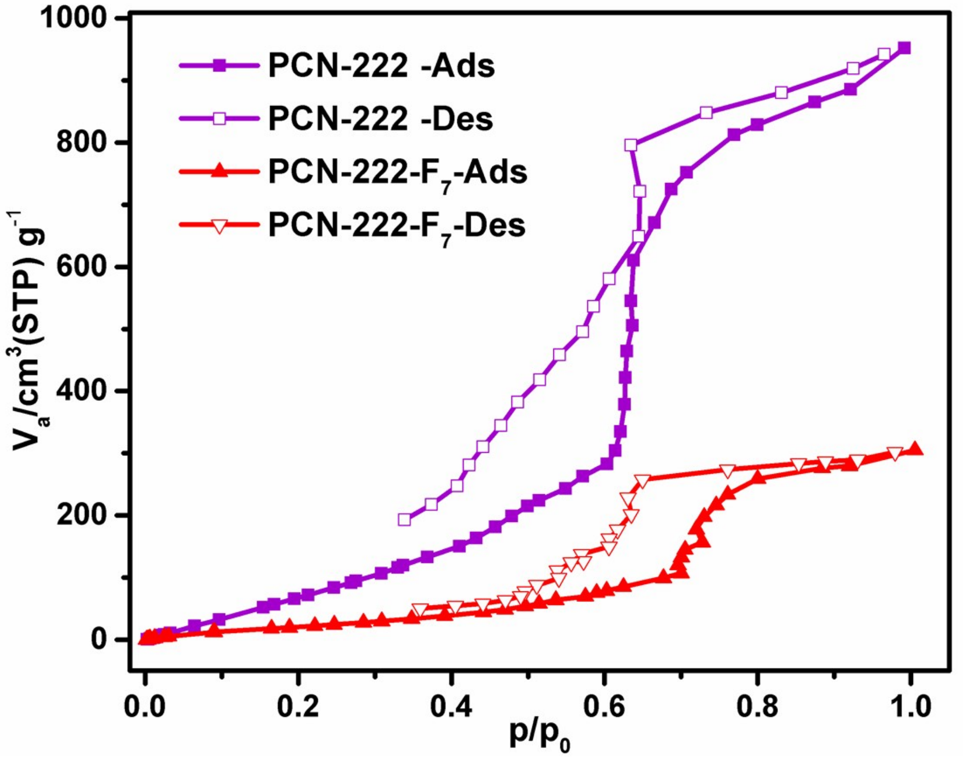
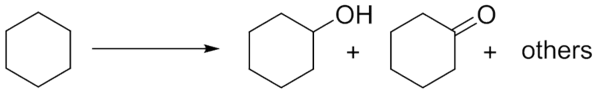


Fig. S5 Water adsorption isotherms for PCN-222 and PCN-222-F$_7$ at 298 K.

Table S1. The catalytic results of cyclohexane oxidation over PCN-222-F_7 in the presence of different amounts of $AgBF_4$.



Entry	m_{AgBF4} (mg)	Conv. (%)	Sel. of KA (%)	Yield of KA (%)	K/A
1	0	40.5	67.5	27.3	3/1
2	25.6	55.3	65.6	36.3	12.4/1

Reaction conditions: cyclohexane (0.1 mmol), PCN-222-F_7 (20 mg), CH_3CN (2.5 mL), TBHP (8 μL), 1 bar O_2, 80 °C, refluxing for 24 h, A indicates cyclohexanol, K indicates cyclohexanone.

Table S2. The catalytic activities of cyclohexane oxidation over different catalysts

Catalyst	Con. of KA oil (%)	Sel. of KA oil (%)	Ref.
$PCN-222(Fe)-F_7$	**50.2**	**90.1**	**This work**
Cr-MIL-101	36.0	83.0	S5a
Fe-MIL-101	38.0	49.0	
MIL-53(Cr)	23.3	84.6	S5b
MIL-53(Al)	8.7	71.5	
Au/MIL-101(Cr)	30.5	87.7	
Au/MIL-96(Al)	17.1	70.5	
Au/MIL-110(Al)	17.2	69.3	
Au/MIL-53(Cr)	31.3	81.9	
AuPd@MIL-101	41.5	84.4	S5c
NH_2-MIL-101(Cr)-Sal-Co	36.1	91.7	S5d
NH_2-MIL-101(Al)-Sal-Co	20.3	77.3	

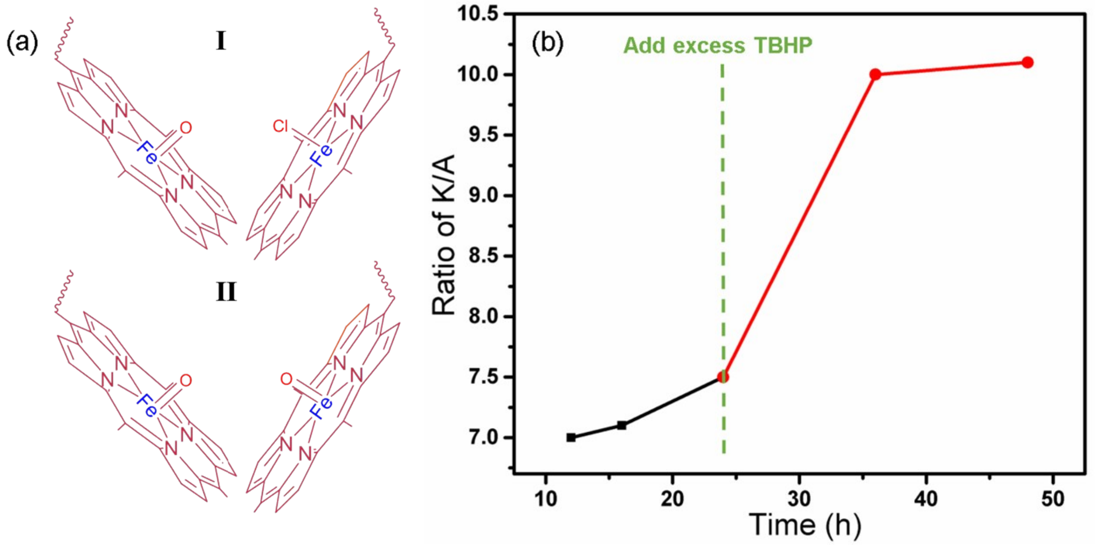


Fig. S6 (a) The formation of TCPP-Fe(IV)-oxo (I) before and (II) after introducing $AgBF_4$. (b) Ratio of K/A before and after adding excess 4 μL TBHP into the reaction system. A and K indicates cyclohexanol and cyclohexanone, respectively. Reaction conditions: cyclohexane (0.1 mmol), PCN-222-F_7 (20 mg), CH_3CN (2.5 mL), TBHP (8 μL), 1 bar O_2, 80 ^oC, refluxing for 24 h.

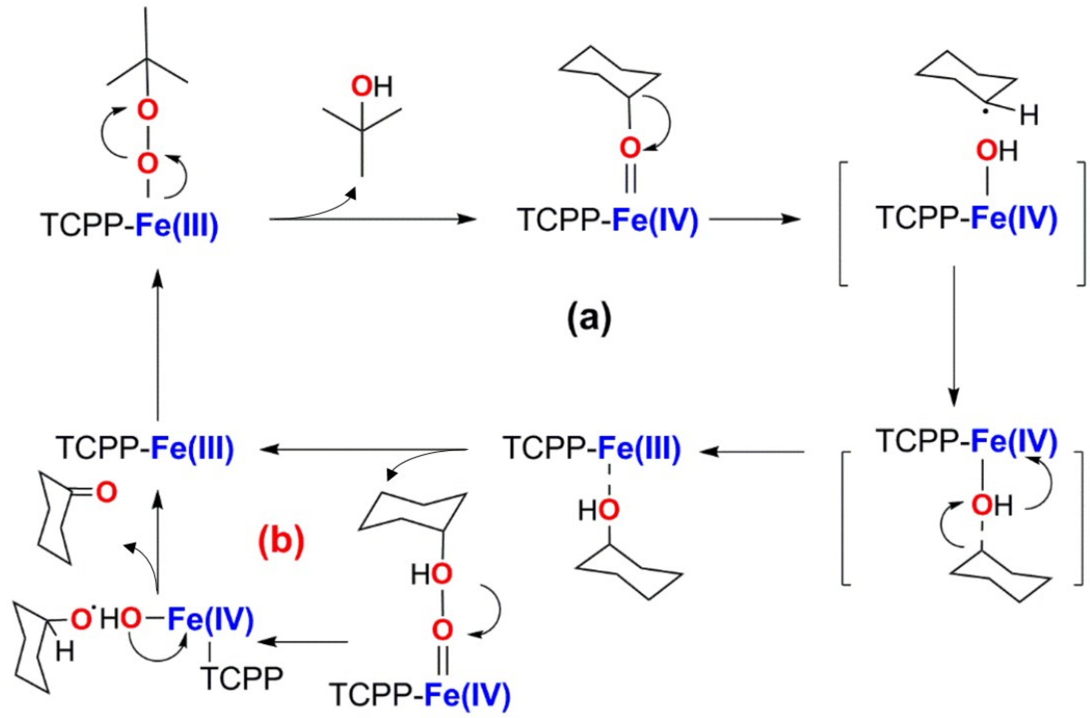


Fig. S7 Proposed catalytic mechanism toward the oxidation of cyclohexane.

References

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