Supporting Information

Synthesis of porous polymeric metalloporphyrins for highly efficient oxidation of cyclohexane in heterogeneous systems

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1. Synthesis of Mn(III)/Fe(III) 5, 10, 15, 20-Tetraksi (4'-bromophenyl) porphyrin ----(T(p-Br)PPMn/FeCl)

1.1 Synthesis of 5,10,15,20-Tetraksi (4'-bromophenyl) porphyrin

Fig. S1 Synthesis of 5,10,15,20-Tetraksi (4'-bromophenyl) porphyrin

A solution of p-bromobenzaldehyde (0.10 mol, 18.5 g) in propionic acid (120 mL) was heated up to reflux temperature (140 °C), and added with freshly distilled pyrrole (0.10 mol, 6.7 g), diluted with propionic acid (30 mL) in 10 min. The reaction mixture was stirred at 140 °C for 0.5h, cooled to room temperature and the precipitate was collected by filtration and washed with methanol for three times. The product was further purified by recrystallization from chloroform and methanol (15 mL: 60 mL) three times, dried in vacuum to give 5,10,15,20-Tetraksi (4'-bromophenyl) porphyrin as yellow crystalline powder (4.9 g) in 21.13% yield.

MS: m/z (C_{44}H_{26}Br_4N_4): calcd, 929.89; found, 929.66;

^1^H NMR (CDCl_3): δ (ppm) -2.90 (2H, N-H), 7.87 (8H, J = 8.3 Hz, 8H, J = 8.3 Hz, 8.82 (8H);

IR (KBr): 3315, 965 cm\(^{-1}\) (N-H), 3053, 3024 cm\(^{-1}\) (C-H), 1559, 1466 cm\(^{-1}\) (C=C), 1348 cm\(^{-1}\) (C=N), 796 cm\(^{-1}\) (aromatics), 475 cm\(^{-1}\) (C-Br);

UV-Vis (λ; nm; CHCl_3): 419, 520, 553, 590,645.

1.2 Synthesis of Mn(III)5,10,15,20-Tetraksi (4'-bromophenyl) porphyrin
Fig. S2 Synthesis of Mn(III)5,10,15,20-Tetraksi (4\'-bromophenyl) porphyrin

5,10,15,20-Tetraksi (4\'-bromophenyl) porphyrin (0.9303 g, 0.001 mol) in DMF (180 mL) in 250 mL flask was heated up to reflux temperature (150 °C), and MnCl\textsubscript{2}·4H\textsubscript{2}O (2-3 g) were added into flask and the mixture was stirred at 150 °C for 1.0 h, cooled to room temperature and poured into a large number of water, the precipitate was collected by filtration and washed with water until the filtrate being colorless. The crude product was further purified by aluminium oxide (100-200 mesh) chromatography (chloroform/acetone, 10:1) to give Mn(III)5,10,15,20-Tetraksi (4\'-bromophenyl) porphyrin (0.8161 g) in 87.23%.

MS: m/z (C\textsubscript{44}H\textsubscript{24}Br\textsubscript{4}ClMnN\textsubscript{4}) : calcd, 1017.86; found, 1017.46;
IR (KBr): 1608, 1516 cm\textsuperscript{-1} (C=C), 1348 cm\textsuperscript{-1} (C-N), 1010.9 cm\textsuperscript{-1} (δMn-N), 808 cm\textsuperscript{-1} (aromatics), 475 cm\textsuperscript{-1} (C-Br);
UV-Vis (λ; nm; CHCl\textsubscript{3}): 481, 583, 615.

1.3 Synthesis of Fe(III)5,10,15,20-Tetraksi (4\'-bromophenyl) porphyrin

Fig. S3 Synthesis of Fe(III)5,10,15,20-Tetraksi (4\'-bromophenyl) porphyrin

5,10,15,20-Tetraksi (4\'-bromophenyl) porphyrin (0.9303 g, 0.001 mol) in DMF (180 mL) in 250 mL flask was heated up to reflux temperature (150 °C), and FeCl\textsubscript{4}H\textsubscript{2}O (2-3 g) were added into flask and the mixture was stirred at 150 °C for 1.0 h, cooled to 80°C and 6mol/L of HCl solution was added in to mixture until the red solid on the flask was all dissolved. Then the mixture was cooled to room temperature, the precipitate was collected by filtration and washed with 6mol/L of HCl solution, water and ethanol until the filtrate being colorless. The crude product was further purified by aluminium oxide (100-200 mesh) chromatography (chloroform/acetone, 10:1) to give Fe(III)5,10,15,20-Tetraksi (4\'-bromophenyl) porphyrin (0.8161 g) in 85.45%.

MS: m/z (C\textsubscript{44}H\textsubscript{24}Br\textsubscript{4}ClFeN\textsubscript{4}) : calcd, 1018.77; found,1018.41;
IR (KBr): 1594, 1481 cm\textsuperscript{-1} (C=C), 1331 cm\textsuperscript{-1} (C-N), 1002 cm\textsuperscript{-1} (δFe-N), 805 cm\textsuperscript{-1} (aromatics), 461 cm\textsuperscript{-1} (C-Br);
UV-Vis (λ; nm; CHCl\textsubscript{3}): 378, 418, 510.
2. Synthesis of Fe and Mn porphyrin polymers

Mn(III)P-CMP was synthesized with the steps as follows: A mixture of T(p-Br)PMPnCl (204 mg, 0.20 mmol), 1, 4-phenyl diboronic acid (132.8 mg, 0.80 mmol), bis(tricyclohexylphosphine)palladium(0) (13.5 mg, 20 µmol), K2CO3 (221.0 mg, 1.6 mmol), 1, 4-dioxane (16 mL) and aqueous solution (4.0 mL) was added to a reaction flask, degassed by three freeze-pump-thaw cycles, purged with argon, and stirred at 125°C for 24 h. TLC method was used to detect excess 1, 4-phenyl diboronic acid. Finally, the mixture was allowed to cool at room temperature and poured into water. The precipitate was collected by filtration, thoroughly washed with THF, methanol and trichloromethane respectively, and then dried in vacuum. The solid was rigorously washed by Soxhlet extraction for 24 h with THF, methanol and trichloromethane respectively until the solvent in Soxhlet extractor did not exhibit porphyrin peaks in UV-Vis detection, and then dried in vacuum to give Mn(III)P-CMP as dark green solid particles in 91.12% yield. The synthesis method of Fe(III)P-CMP was the same as that of Mn(III)P-CMP, giving atrovirens solid particles in 90.36% yield.

Elemental analysis (%). For \{C56H32ClMnN4\}_n (Theoretical formula for an infinite polymer of Mn(III)P-CMP) C 79.01, H 3.76, Cl 4.17, Mn 6.47, N 6.58; Found: C 72.2, H 3.96, Cl 2.57, N 4.37, B 2.78, Br 9.01, Mn content by atomic absorption spectrometry: 4.98 wt%.

FeP-CMP was synthesized with the same steps to MnP-CMP with the yield of 90.36% at the same material ratio.

Elemental analysis (%). For \{C56H32ClFeN4\}_n (Theoretical formula for an infinite polymer of Fe(III)P-CMP) C 78.93, H 3.78, Cl 4.16, Fe 6.55, N 6.57; Found: C 71.53, H 3.80, Cl 2.31, N 5.14, B 2.38, Br 10.03, Fe content by atomic absorption spectrometry: 4.22 wt%.

3. The detailed procedure for the analysis (by GC, GC/MS) of the oxidation products

Fig. S4. The examples of chromatograms

Reaction products were identified by GC-MS (Shimadzu QP-5000 MS) (helium as the carrier gas). The samples were analyzed by GC using chlorobenzene as an internal standard. Chromatographic analyses were run on a Shimadzu GC-17A series gas chromatograph equipped with
a FID detector and a PEG-20000 (25 m × 0.25 mm) capillary column. The contents of adipic acid, ester and hyperoxide were measured by chemical titration.

The examples of chromatograms as showed in Fig S4. (a) is cyclohexane; (b) is chlorobenzene; (c) is cyclohexanol and (d) is cyclohexanone. The more detailed GC analysis conditions: Column temperature 110°C; Sample injection temperature 200°C; Detector temperature 180°C. Column inlet pressure 0.02 MPa (N₂); Air pressure 0.12 MPa; Hydrogen pressure 0.06 MPa. Split ratio 1:80.

4. FT-IR spectra of MnP-CMP and T(p-Br)PPMnCl

![FT-IR spectra of MnP-CMP and T(p-Br)PPMnCl](image)

Fig. S5 FT-IR spectra of MnP-CMP and T(p-Br)PPMnCl

5. UV-Vis spectra of MnP-CMP and T(p-Br)PPMnCl

![UV-Vis spectra of MnP-CMP and T(p-Br)PPMnCl](image)

Fig. S6. UV-Vis spectra of MnP-CMP (black curve; powder sample) and T(p-Br)PPMnCl (red curve; CHCl₃ solution).
6. Cyclic voltammogram of MnP-CMP and T(p-Br)PPMnCl

Fig. S7. (a) Cyclic voltammogram of MnP-CMP on glassy carbon electrodes in 0.1 mol/L (CH₃CH₂)₄NBr CH₂Cl₂ solution (black curve); (b) Cyclic voltammogram of T(p-Br)PPMnCl in CH₂Cl₂ and 0.1 mol/L (CH₃CH₂)₄NBr (red curve); Scan rate is 50 mV/s.

7. Powder X-Ray Diffraction

Fig. S8. Powder X-Ray Diffraction pattern of Mn(III)P-CMP.

8. Thermogravimetric analysis
9. Effect of amount of catalyst on cyclohexane oxidation

![Graph showing yields of alcohol and ketone in the reaction of cyclohexane catalyzed by different amounts of MnP-CMP.]

The effects of amount of catalyst on the product selectivity in cyclohexane oxidation are shown in Fig. S10. When the amount of catalyst was Mn$^{3+}$/cyclohexane = 1/84000 (molar ratio) per 200 mL (1.85 mol) cyclohexane, the total yields of alcohol and ketone reached 14.3% at 0.5 h, increased rapidly at 2.0 h and reached the highest (17.9%). Because of the increased by-products, the content of alcohol and ketone decreased obviously. When the amount of catalyst was Mn$^{3+}$/cyclohexane = 1/680000 (molar ratio) per 200 mL (1.85 mol) cyclohexane, the reaction was relatively slow, and the
total yields of alcohol and ketone peaked at 18.5% after 5.0 h. When the amount of catalyst increased from Mn\(^{3+}/\text{cyclohexane} = 1/340000\) to Mn\(^{3+}/\text{cyclohexane} = 1/168000\) per 200 mL (1.85 mol) cyclohexane, the catalytic activity was not improved significantly, indicating that within a certain range, raising the catalyst/substrate ratio barely promoted the reaction. Therefore, the catalytic performance was optimized when Mn\(^{3+}/\text{cyclohexane} = 1/168000\) (molar ratio) in about 12 mg Mn(III)P-CMP.

10. The SEM images of the catalysts used

![SEM images of the catalysts](image)

Fig. S11. The SEM images of the catalysts used Mn(III)P-CMP(a) and Fe(III)P-CMP(b).

11. EDX test of Mn(III)P-CMP and Fe(III)P-CMP

![EDX test images](image)

Fig. S12 EDX test of Mn(III)P-CMP (a) and Fe(III)P-CMP (b)

12. Conversions and selectivities for a number of consecutive reuses of catalysts
Fig. S13. The conversion of cyclohexane for a number of consecutive reuses of catalysts 5 times (a);
Selectivity of alcohol and ketone for a number of consecutive reuses of catalysts 5 times (b).