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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 iolet 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;

¹H NMR (CDCl₃): δ (ppm) –2.90 (2H, N-H), 7.87 (8H, J = 8.3 Hz,), 8.04 (8H, J = 8.3 Hz, 8.82 (8H,);

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

UV-Vis (λ; nm; CHCl₃): 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 MnC14H₂O (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%.

 $MS: \ m/z \ (C_{44}H_{24}Br_4ClMnN_4): calcd, \ 1017.86; \ found, 1017.46;$

IR (KBr): 1608, 1516cm⁻¹ (C=C), 1348 cm⁻¹ (C-N), 1010.9 cm⁻¹ (δ Mn-N), 808 cm⁻¹ (aromatics), 475 cm⁻¹1(C-Br); UV-Vis (λ ; nm; CHCl₃): 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 FeC14H₂O (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%.

 $MS: \ m/z \ (C_{44}H_{24}Br_4ClFeN_4): calcd, \ 1018.77; \ found, 1018.41;$

IR (KBr): 1594, 1481cm⁻¹ (C=C), 1331cm⁻¹(C-N), 1002 cm⁻¹ (δFe-N), 805 cm⁻¹ (aromatics), 461 cm⁻¹ (C-Br); UV-Vis (λ; nm; CHCl₃): 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)PPMnCl (204 mg, 0.20 1, 0.80 mmol), 4-phenyldiboronic acid (132.8)mg, 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-phenyldiboronic 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 $\{C_{56}H_{32}CIMnN_4\}_n$ (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 $\{C_{56}H_{32}CIFeN_4\}_n$ (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 \times 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



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

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



Fig. S6. UV-Vis spectra of MnP-CMP (black curve; powder sample) and T(p-Br)PPMnC1 (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 $(CH_3CH_2)_4NBr \ CH_2Cl_2$ solution (black curve); (b) Cyclic voltammogram of T(p-Br)PPMnCl in CH_2Cl_2 and 0.1 mol/L (CH_3CH_2)_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



Fig. S9. Thermogravimetric analysis curve of Mn(III)P-CMP.

9. Effect of amount of catalyst on cyclohexane oxidation



Fig. S10 Yields of alcohol and ketone in the reaction of cyclohexane catalyzed by different amounts of MnP-CMP; Catalyst: MnP-CMP, T = 150 °C, Vair = 1000 mL/min, P = 0.8 MPa, cyclohexane: 200 mL (1.85 mol).

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 $Mn^{3+}/cyclohexane = 1/340000$ to $Mn^{3+}/cyclohexane = 1/168000$ 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 $Mn^{3+}/cyclohexane=1/168000$ (molar ratio) in about 12 mg Mn(III)P-CMP.

10. The SEM images of the catalysts used



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



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).