Supporting Information for

Morphological Diversity of Mn(III) Metalloporphyrin-Based Nanoand Microsize CPAs Assembled via Kinetic and Thermodynamic Controls and Their Application in Heterogeneous Catalysis

by

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I. Instrumentations

NMR spectra were recorded on a Varian AS400 (399.937 MHz for ¹H and 100.573 MHz for ¹³C) spectrometer. ¹H chemical shifts are referenced to the proton resonance resulting from protic residue in deuterated solvent and ¹³C chemical shift recorded downfield in ppm relative to the carbon resonance of the deuterated solvents. Absorbance and emission spectra were obtained using an Agilent UV-Vis-NIR spectrophotometer using quartz cells. All scanning electron microscopy (SEM) images were obtained using a JEOL JSM-7001F. Energy dispersive X-ray spectroscopy (EDX) was obtained using a Horiba EMAX Gatan at the Korea Basic Science Institute (KBSI) Seoul Center. Matrix-Assisted Laser-Desorption-Ionization Time-of-flight Mass Spectra (MALDI-TOF) were obtained on a Bruker Daltonics LRF20 MALDI-TOF Mass Spectrometer at the Industry-Academic Cooperation Foundation, Yonsei University. Powder X-ray diffraction measurements were recorded with a Rigaku

D/MAX Ultima III using nickel-filtered Cu K_{α} radiation ($\lambda = 1.5418$ Å) over a range of 2° < $2\theta < 40^{\circ}$ and X'celerator detector operating at 40 kV and 30 mA. Thermo Gravimetric Analyzer (TGA) measurements were carried out using a Scinco TGA N-1000 in a nitrogen atmosphere at a heating rate of 10 °C/min in the temperature range of 25~900 °C for particles. Gas Chromatography was recorded using a Hewlett Packard HP 6890 series. Ultrapure grade (99.999%) N₂ gas was used for the gas sorption experiments. The N₂ adsorption/desorption analysis was performed on a Belsorp-miniII at 77 K (BEL Japan). The samples were prepared by emerging in CHCl₃ for 48 h followed by drying at room temperature for 2 h under high vacuum before measurements. Infrared spectra were obtained from KBr pellets with a Bomen MB-104 spectrometer.

II. Materials and Synthesis

 $\{5,15$ -Bis(4-carboxyphenyl)-10,20-bis[2,6-diethoxyphenyl]porphyrinato} manganese(III) chloride L6, $\{5,15$ -bis(4-carboxyethylphenyl)-10,20-bis[2,6-diethoxyphenyl] porphyrinato}manganese(III) chloride L7 and 2-(*tert*-butylsulfonyl)iodosylbenzene were synthesized by according to previously reported procedures.¹ All other chemicals were obtained from commercial sources and used without further purification. All of the reactions and manipulations of the porphyrin building blocks were carried out under N₂ with the use of standard inert-atmosphere and Schlenk techniques unless otherwise noted. Solvent used in inert-atmosphere reactions were dried and degassed using standard procedures. Flash column chromatography was carried out with 230-400 mesh silica gel from Merk using wet-packing method. All deuterated solvents were purchased from Cambridge Isotope Laboratory.



Scheme S1. Synthesis of metalloporphyrins.

5,15-Bis(4-carboxyethylphenyl)-10,20-bis[2,6-diethoxyphenyl]porphyrin (L4). ¹H NMR (CDCl₃): δ 8.82 (d, ³*J*_{H-H} = 4.7 Hz, 4H), 8.72 (d, ³*J*_{H-H} = 4.7 Hz, 4H), 8.42 (d, ³*J*_{H-H} = 7.8 Hz, 4H), 8.32 (d, ³*J*_{H-H} = 7.8 Hz, 4H), 7.68 (t, ³*J*_{H-H} = 8.6 Hz 2H), 6.98 (d, ³*J*_{H-H} = 8.6 Hz, 4H), 4.57 (q, ³*J*_{H-H} = 7.0 Hz, 4H), 3.88 (q, ³*J*_{H-H} = 7.0 Hz 8H), 1.55 (t, ³*J*_{H-H} = 7.0 Hz 6H), 0.60 (t, ³*J*_{H-H} = 7.0 Hz 12H). ¹³C NMR (CDCl₃): δ 167.223, 160.083, 147.574, 134.826, 130.258, 129.784, 127.940, 117.691, 113.407, 105.626, 77.439, 77.077, 76.770, 76.453, 64.436, 61.476, 14.745, 14,611, 1.268. MS (MALDI-TOF): *m/z* = 934.360 for M⁺; Calcd 935.07.

5,15-Bis(4-carboxyphenyl)-10,20-bis[2,6-diethoxyphenyl]porphyrin (L5). ¹H NMR (DMSO): δ 8.71 (m, 8H), 8.20 (d, ³*J*_{H-H} = 7.0 Hz, 4H), 8.02 (d, ³*J*_{H-H} = 7.0 Hz, 4H), 7.71 (t, ³*J*_{H-H} = 8.6 Hz, 2H), 7.09 (d, ³*J*_{H-H} = 8.6 Hz, 4H), 3.88 (q, ³*J*_{H-H} = 7.0 Hz, 8H), 0.47 (t, ³*J*_{H-H} = 7.0 Hz, 12H). ¹³C NMR (DMSO): δ 168.379, 159.725, 139.869, 135.004, 128.532, 125.574, 119.727, 118.387, 113.869, 106.119, 67.684, 64.278, 55.591, 46.026, 31.078, 14.865, 10.204. MS (MALDI-TOF): *m*/*z* = 878.191 for M⁺; Calcd 878.97.



Fig. S1 ¹H NMR spectra of **L4** (in CDCl₃) and **L5** (in DMSO-*d*₆). ***** represents protic residues in deuterated solvent.

{5,15-Bis(4-carboxyphenyl)-10,20-bis[2,6-diethoxyphenyl]porphyrinato}-manganese(III) chloride (L6). MS (MALDI-TOF): m/z = 931.298 for [M-Cl]⁺; Calcd 931.89.

{5,15-Bis(4-carboxyethylphenyl)-10,20-bis[2,6-diethoxyphenyl]porphyrinato}manganese(III) chloride (L7). MS (MALDI-TOF): m/z= 987.311 for [M-Cl]⁺; Calcd 987.95.

Preparation of Microsphere. To a solution of **L6** (1.9 mg, 2.0 μ mol) in anhydrous *N*,*N*-dimethylformamide (DMF, 0.4 mL) was added a solution of Co(OAc)₂·4H₂O (1.0 mg, 4.0 μ mol) in anhydrous DMF (0.1 mL) at a 4 mL vial equipped with a stirbar. The resulting mixture was heated at 90 °C and vigorously stirred for 30 min. After cooling to room temperature, the particles were collected by centrifugation, and washed several times with DMF.

Preparation of Apple. To a solution of **L6** (1.9 mg, 2.0 μ mol) in anhydrous *N*,*N*-dimethylformamide (DMF, 0.4 mL) was added a solution of Co(OAc)₂·4H₂O (1.0 mg, 4.0 μ mol) in anhydrous DMF (0.1 mL) at a 4 mL vial equipped with a stirbar. The resulting mixture was heated at 90 °C and vigorously stirred for 45 min. After cooling to room temperature, the particles were collected by centrifugation, and washed several times with DMF.

Preparation of Donut. To a solution of **L6** (1.9 mg, 2.0 μ mol) in anhydrous *N*,*N*-dimethylformamide (DMF, 0.4 mL) was added a solution of Co(OAc)₂·4H₂O (1.0 mg, 4.0 μ mol) in anhydrous DMF (0.1 mL) at a 4 mL vial equipped with a stirbar. The resulting mixture was heated at 90 °C and vigorously stirred for 60 min. After cooling to room temperature, the particles were collected by centrifugation, and washed several times with DMF.

Preparation of Rubber band. To a solution of **L6** (1.9 mg, 2.0 μ mol) in anhydrous *N*,*N*-dimethylformamide (DMF, 0.4 mL) was added a solution of Co(OAc)₂·4H₂O (1.0 mg, 4.0 μ mol) in anhydrous DMF (0.1 mL) at a 4 mL vial equipped with a stirbar. The resulting

mixture was heated at 90 °C and vigorously stirred for 90 min. After cooling to room temperature, the particles were collected by centrifugation, and washed several times with DMF.

Preparation of Nanosphere. To a solution of **L6** (1.9 mg, 2.0 μ mol) in anhydrous *N*,*N*-dimethylformamide (DMF, 0.4 mL) was added a solution of Co(OAc)₂·4H₂O (1.0 mg, 4.0 μ mol) in anhydrous DMF (0.1 mL) at a 4 mL vial equipped with a stirbar. The resulting mixture was heated at 90 °C and vigorously stirred for 300 min. After cooling to room temperature, the particles were collected by centrifugation, and washed several times with DMF.

Preparation of Microcube. To a solution of **L6** (1.9 mg, 2.0 μ mol) in anhydrous *N*,*N*-dimethylformamide (DMF, 0.4 mL) was added a solution of Co(OAc)₂·4H₂O (1.0 mg, 4.0 μ mol) in anhydrous DMF (0.1 mL) at a 4 mL vial equipped with a stirbar. The resulting mixture was heated at 90 °C and vigorously stirred for 450 min. After cooling to room temperature, the particles were collected by centrifugation, and washed several times with DMF.



Fig. S2 IR spectra of L6 and microsphere.

General reaction condition of olefin epoxidation. The catalyst was prepared by emerging in CH_2Cl_2 for 48 h followed by a brief drying to prevent decomposition of their framework. Dried CPAs (5.00 mg, 4.8 µmol) were dispersed to a solution of 2-(*tert*-butylsulfonyl) iodosylbenzene (17.01 mg, 50 µmol), olefin (35 µmol) and hexadecane (7.93 mg, 35 µmol) in dichloromethane (DCM, 1 mL). The reaction mixture was shaken at room temperature for 30 min. The adequate amount of solution was taken via syringe and filtered through a silica gel plug which was further washed with DCM. The conversions of substrates were determined by gas chromatography with hexadecane as an internal standard.

III. Additional SEM images and EDX data



Fig. S3 SEM images monitoring the process of conversion of amorphous microspheres into microcubes obtained by varying reaction periods; a) 30, b) 45, c) 60, d) 75, e) 90, f) 120, g) 200, h) 250, i) 300, j) 380, k) 420, and l) 450 min.



Fig. S4 EDX data of nano- and micro-sized CPAs obtained by varying reaction periods; a) 30 (microsphere), b) 45 (apple), c) 60 (donut), d) 300 (nanosphere), and e) ~450 min (microcube). Insets: SEM images of CPAs taken during the EDX analysis.



Fig. S5 SEM image of a set of various particles obtained from a reaction at 120 °C, showing microspheres, apples, donuts, rubber bands, stretched rubber bands, nanospheres and microcubes in a same reaction mixture.



IV. Powder X-Ray Diffraction (PXRD)

Fig. S6 The PXRD patterns of nano- and microsized CPAs obtained by varying reaction periods.

V. Thermogravimetric Analysis (TGA)



Fig. S7 TGA analysis of nano- and microsized CPAs obtained by varying reaction periods.

VI. Catalysis

Table S1 Investigation of the recyclability.^a



^a Reaction conditions; styrene: 35 μmol, oxidant: 50 μmol, catalyst: 5 mg, CH₂Cl₂: 1 mL, reaction time: 30 min, rt. ^b Oxidant: 2-(*tert*-butylsulfonyl)iodosylbenzene. ^c Conversion (%) determined by GC with hexadecane as an internal standard.



Fig. S8 SEM images of recovered microspheres and microcubes after the oxidation: Before (left) and after (right) the oxidation.



Fig. S9 The comparison of conversions(%) and catalytic stability of the microsphere, microcube and homogeneous catalyst {5,15-bis(4-carboxyethylphenyl)-10,20-bis[2,6-diethoxyphenyl]porphyrinato}manganese(III) chloride **L7** (molar ratio of styrene:oxidant: catalyst = 2000:1000:1, CH₂Cl₂ 6 mL). 2-(*t*-butylsulfonyl)iodosylbenzene was used as oxidant and the conversions of substrates were determined by gas chromatography with hexadecane as an internal standard.

VII. References

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