Supporting Information for

Immobilization of Porphyrinic Mn(III) Catalyst on a New Class of Silica Support Comprising Three-Dimensionally Interconnected Network with Two Different Sizes of Pores

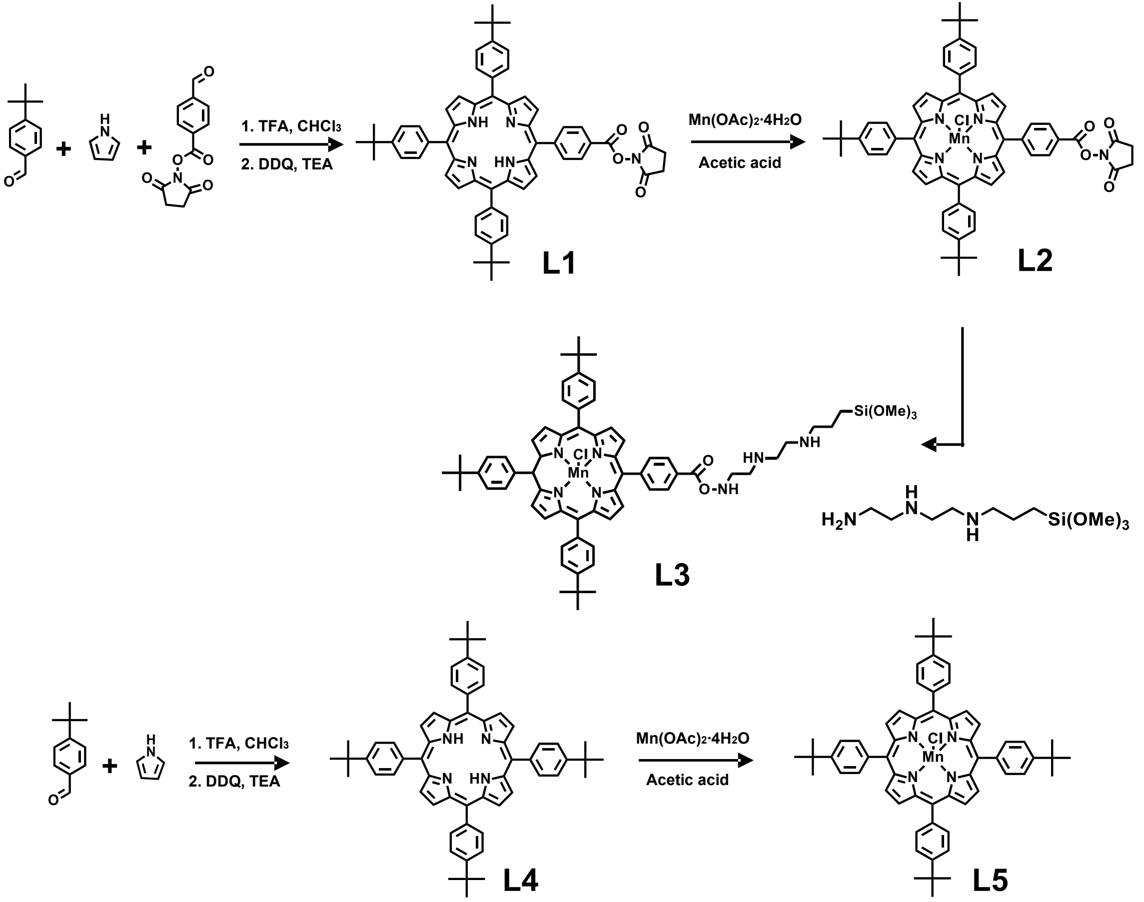
Dae Yong Shin,[a] Jong Ho Yoon,[a] Sung Hwan Kim,[a] Hionsuck Baik[b] and Suk Joong Lee*[a]

[a] *Department of Chemistry, Research Institute for Natural Sciences, Korea University, Seoul 136-701, Republic of Korea. Tel: (+82-2)3290-3145; E-mail: slee1@korea.ac.kr.*
[b]*Seoul Center Korea Basic Science Institute (KBSI), Seoul 02841, Republic of Korea.*

I. Equipment

NMR spectra were recorded on a Varian AS400 (399.937 MHz for ^{1}H and 100.573 MHz for ^{13}C) and Bruker 500 MHz Ascend spectrometer. All gas chromatography (GC) analyses using an Agilent Technologies 6890N Network GC system (Agilent Technologies, Inc., Santa Clara, CA, USA) equipped with an FID. Scanning electron microscopy (SEM) images were collected on a JSM-7001F (JEOL, Japan) microscope. Samples were activated and coated with Pt using a Sputter Coater 108 Auto (Cressington, Watford, UK) before imaging. All transmission electron microscopy (TEM) images, electron diffraction and diffraction contrast images of the crystals were obtained at 200 keV with LaB6 filament, using a Tecnai G2 F20 S-Twin and recorded with an 2K by 2K pixel resolution Veleta TEM camera (Olympus) on Cu TEM grids. Powder X-ray diffraction measurements were recorded with a Rigaku D/MAX Ultima III using nickel-filtered Cu Kα radiation ($\lambda = 1.5418$ Å) over a range of $2° < 2\theta < 40°$ and X'celerator detector operating at 40 kV and 30 mA. SEM/EDX experiments were carried out using a Hitachi SU-70 SEM equipped with a silicon drift EDX detector (50 mm^2, Horiba, Japan). The accelerating beam voltage was fixed to 15 kV. N_2 adsorption and desorption isotherms were measured on a BELSORP–mini II (MicrotracBEL Corp., Japan) instrument at 77 K. DFT pore size distributions were obtained from the desorption branch of the resulting isotherms. Before each run, samples were activated at 80 °C for 3 h under high vacuum on a BELSORP Prep II (MicrotracBEL Corp., Japan) or critical point dry on a SAMDRI-PVT-3D (Tousimis, USA). Around 50–80 mg of sample was used in each measurement. UV-Vis spectroscopies were performed on Agilent 8453 Spectrophotometer using quartz cells. Manganese contents were measured using inductively coupled plasma-atomic emission spectroscopy (ICP-AES, OPTIMA 8300, Perkin-Elmer(USA)), which were compared to the ICP standard solutions. 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.

Scheme S1. Synthesis of porphyrins.



II. General materials and synthesis

All reagents and solvents were purchased from commercial sources and were used without further purification, unless otherwise indicated. All of the reactions and manipulations were carried out under air atmosphere unless otherwise noted. Distilled solvents used in inert-atmosphere reactions were dried using standard procedures. All Flash column chromatography was carried out using silica gel 60 (230–400 mesh, Merck, Germany) using wet-packing method and TLC was performed on pre-coated silica gel plates (0.25 mm thick, 60 F254, Merck, Germany) and observed under UV light. All deuterated solvents were purchased from Cambridge Isotope Laboratories and Aldrich. 4-(Succinimidyloxycarbonyl)benzaldehyde was synthesized to modified literature procedures.[1]

5,10,15-Tri(4-*tert*-butylphenyl)-20-[4-(succinimidyloxycarbonyl)phenyl]porphyrin (L1).[2] 4-(succinimidyloxycarbonyl)benzaldehyde (247 mg, 1 mmol), 4-*tert*-butylbenzaldehyde (487 mg, 3 mmol), and distilled pyrrole (0.28 mL, 4 mmol) were dissolved in distilled $CHCl_3$ (400 mL) in a 1 L Schlenk flask equipped with a magnetic stirbar. This solution was degassed with N_2 for 10 min before

$BF_3{\cdot}O(Et)_2$ (0.38 mL, 3 mmol) was added, and the resulting mixture was stirred for 2 h at room temperature under N_2. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 681 mg, 3 mmol) was added and the resulting solution was stirred for an additional 1 h. TEA (0.42 mL, 3 mmol) was added and the resulting mixture was stirred for an additional 15 min. The reaction mixture was evaporated to dryness using a rotary evaporator to yield a dark residue, which was purified by silica-gel column chromatography (CH_2Cl_2/Hex/EtOAc 6:3:0.4 v/v) to afford pure **L1** as a dark purple solid (65 mg, 7 % yield). ^{1}H NMR ($CDCl_3$): δ 8.94 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H), 8.90 (s, 4H), 8.75 (d, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H), 8.55 (d, $^3J_{H\text{-}H}$ = 7.3 Hz, 2H), 8.40 (d, $^3J_{H\text{-}H}$ = 7.3 Hz, 2H), 8.16 (d, $^3J_{H\text{-}H}$ = 6.4 Hz, 6H), 7.78 (d, $^3J_{H\text{-}H}$ = 6.4 Hz, 6H), 1.62 (s, 27H), 1.25 (s, 4H), -2.75 (s, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 169.63, 162.37, 150.82, 149.76, 146.57, 139.23, 139.18, 135.17, 134.89, 134.68, 129.15, 124.48, 123.90, 123.84, 121.22, 120.86, 117.45, 99.94, 35.13, 31.91, 26.00, 25.07. MS (MALDI-TOF): *m/z* = 924.12 for M^+; Calcd 924.14.

[5,10,15-Tri(4-*tert*-butylphenyl)-20-[4-(succinimidyloxycarbonyl)phenyl]porphyrinato]-manganese(III)-chloride (L2). To a solution of free-base porphyrin (50 mg, 0.054 mmol) in $CHCl_3$ (6.5 mL) and acetic acid (2 mL) in a 25 mL Schlenk flask equipped with a magnetic stir bar and a water-cooled reflux condenser was added 1.2 equivalents of $Mn(OAc)_2$. The mixture was allowed to reflux under air overnight. Three equivalents of NaCl were then added and the resulting mixture was refluxed for 1 h. After cooling, hexane (30 mL) was added to precipitate a green solid that was filtered and washed with water (10 mL). The solid was dried and further purified by column chromatography ($CHCl_3$/MeOH (95.5:0.5 v/v)) to afford pure **L2** (39 mg, 72% yield) as a green solid. MS (MALDI-TOF): *m/z* 977.10 (calculated *m/z* 977.06 for $[M\text{-}Cl]^+$).

[5,10,15-Tri(4-tert-butylphenyl)-20-[4-[(3-trimethoxysilylpropyl)ethylenediamine]ethylaminocarbonyl)phenyl]porphyrinato]manganese(III)-chloride (L3). To a solution of (3-trimethoxysilylpropyl)diethylenetriamine (26.5 mg, 0.1 mmol) in distilled $CHCl_3$ (1 mL) was added a solution of Mn-porphyrin (10 mg, 0.01 mmol) in $CHCl_3$ (3 mL) dropwise. The resulting mixture was stirred for 1 h at room temperature under N_2. The volatiles were removed to dryness under reduced pressure and CH_2Cl_2 (5 mL) was added. The insolubles were removed by filtration and hexane was added to precipitate **L3**, which was collected by filtration as a green solid (11 mg, 91 % yield). MS (MALDI-TOF): m/z 1141.79 (calculated m/z 1142.10 for $[M\text{-}Cl]^+$).

Synthesis of 5,10,15,20-Tetrakis(4-*tert*-butylphenyl)porphyrin (L4). 4-*tert*-butylbenzaldehyde (643 mg, 4 mmol), and distilled pyrrole (0.28 mL, 4 mmol) were dissolved in distilled $CHCl_3$ (400 mL) in a 1 L Schlenk flask equipped with a magnetic stirbar. This solution was degassed with N_2 for 10 min before $BF_3{\cdot}O(Et)_2$ (0.38 mL, 3 mmol) was added, and the resulting mixture was stirred for 2 h at room temperature under N_2. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 681 mg, 3 mmol) was added and the resulting solution was stirred for an additional 1 h. TEA (0.42 mL, 3 mmol) was added and the resulting mixture was stirred for an additional 15 min. The reaction mixture was evaporated to dryness using a rotary evaporator to yield a dark residue, which was purified by silica-gel column chromatography (CH_2Cl_2/Hex/EtOAc 6:3:0.4 v/v) to afford pure **L4** as a dark purple solid (125 mg, 12 % yield). ^1H NMR ($CDCl_3$): δ 8.88 (s, 8H), 8.16 (d, $^3J_{H\text{-}H}$ = 8.1 Hz, 8H), 7.77 (d, $^3J_{H\text{-}H}$ = 8.3 Hz, 8H), 1.62 (s, 36H), -2.72 (bs, 2H,) ^{13}C NMR ($CDCl_3$): δ 150.4, 139.3, 134.5, 123.6, 120.1, 34.9, 31.7. MS (MALDI-TOF): *m/z* = 846.6 for M^+; Calcd 846.6.

Synthesis of 5,10,15,20-Tetrakis(4-*tert*-butylphenyl)porphyrinato manganese(III)-chloride (L5). To a solution of free-base porphyrin (45.3 mg, 0.054 mmol) in $CHCl_3$ (6.5 mL) and acetic acid (2 mL) in a 25 mL Schlenk flask equipped with a magnetic stir bar and a water-cooled reflux condenser was added 1.2 equivalents of $Mn(OAc)_2$. The mixture was allowed to reflux under air overnight. Three equivalents of NaCl were then added and the resulting mixture was refluxed for 1 h. After cooling, hexane (30 mL) was added to precipitate a green solid that was filtered and washed with water (10 mL). The solid was dried and further purified by column chromatography ($CHCl_3$/MeOH (95.5:0.5 v/v)) to afford pure **L5** (40.5 mg, 81 % yield) as a green solid. MS (MALDI-TOF): *m/z* 892.08 (calculated *m/z* 891.92 for $[M-Cl]^+$).

Synthesis of SBA-15.[3] 1.0 g of Pluronic P123 and 3.84 g of KCl were dissolved in 60 mL of 1 M HCl in H_2O at room temperature until the solution became transparent, then 0.84 mL trimethylbenzene (TMB) was added. After stirring for 2 h, 2.28 g of tetraethyl orthosilicate (TEOS) was added dropwise and the resulting solution was stirred vigorously for 10 min. Then the mixture was kept under static conditions at 35 °C for 24 h, followed by another 24 h at 100 °C. The resultant precipitates were filtered, washed, and dried at 60 °C in vacuum. The collected solid was calcined at 500 °C for 6 h with a heating rate of 1 °C/min.

Synthesis of pSBA-15.[4] 0.45 g of CTAB and 0.1 g of NaOH were dissolved in 50 mL deionized water, and the mixtures were vigorously stirred at 40 °C for 24 h. After the mixtures were cooled to the room temperature, 1 g of SBA-15 was added to this solution and stirred for 4 h. Then the mixtures were transferred to an opened round-bottomed flask with a reflux condenser attached and heated to 100 °C for 48 h for hydrothermal reaction. The gray powder was recovered by filtration and extensively washed with deionized water. After drying at 100 °C for 12 h, the samples were calcined in a flowing air at 550 °C for 5 h.

Immobilization of Mn(III)-Porphyrin (1) on silica support. 0.2 g of freshly prepared SBA-15 (or pSBA-15) was added to a solution of **L3** (0.2 mmol) in dry $CHCl_3$ (50 mL). The mixture was refluxed for 24 h. The resulting solids were collected by centrifuge, washed repeatedly with CH_2Cl_2 until supernatant became clear solution, and dried under vacuum.

General procedure for Catalysis. In a 4 mL vial, **1** or **2** (0.08 μmol), substrate (16.0 μmol), and toluene (internal standard, 0.1 μmol) were dissolved in dichloromethane (1 mL). After shaking for 10 minute, the oxidant, 2-(tert-butylsulfonyl)iodosylbenzene (24 mg, 80 μmol), was added slowly to start the oxidation reaction. After shaking for 2 hours, Samples were passed through alumina plug (150 mg) with CH_2Cl_2 eluent (5 mL). The resulting solution was analyzed by GC-FID.

III. Additional data

Table S1 Surface areas and mean pore sizes of the series of MPSMs obtained during the pseudomorphic transformation of SBA-15 to pSBA-15 over time.

Time (h)	**Surface area (m^2/g)**	**Mean pore size (nm)**
0	767	10.03
2	866	5.87
6	921	4.68
12	1006	3.02
24	1225	2.82
36	1372	2.53
48	1468	2.41

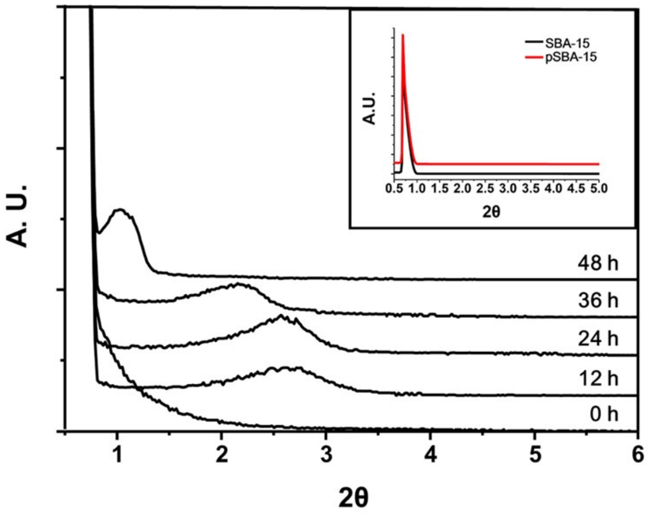


Fig. S1 PXRD of the series of MPSMs obtained during the during the pseudomorphic transformation of SBA-15 to pSBA-15 over time. Inset: PXRDs of SBA-15 and pSBA-15.

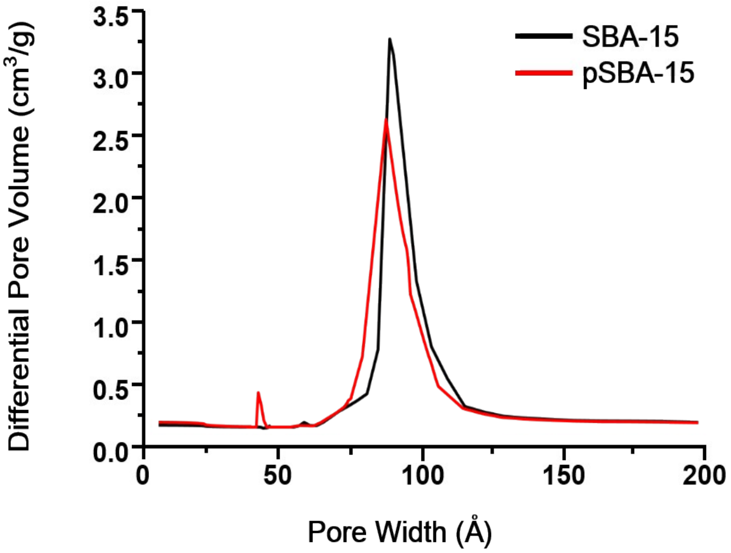


Fig. S2 Pore size distributions of MPSMs (SBA-15 and pSBA-15).

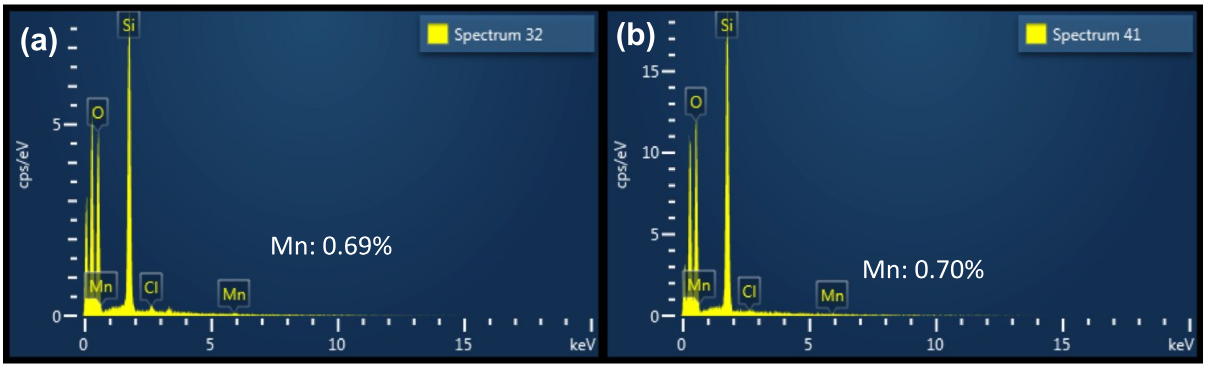


Fig. S3 EDX analysis of (a) **1** and (b) **2**.

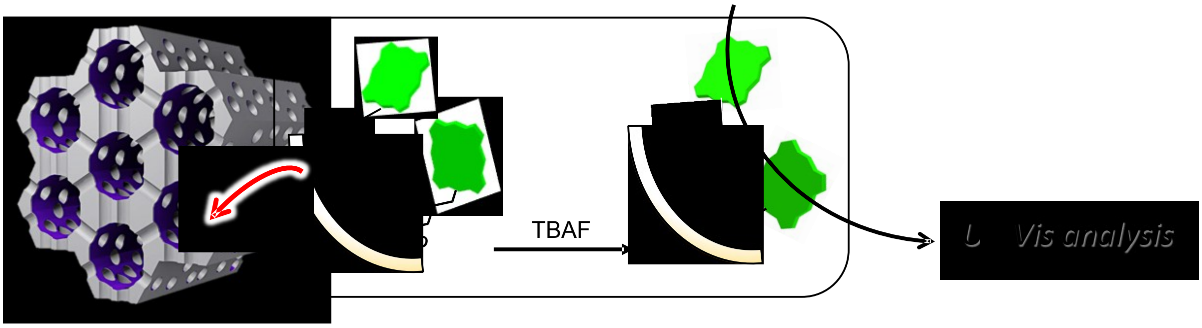


Fig. S4 Schematic representation of UV-Vis analysis of Mn(III)-porphyrin loaded MPSM after treating with TBAF.

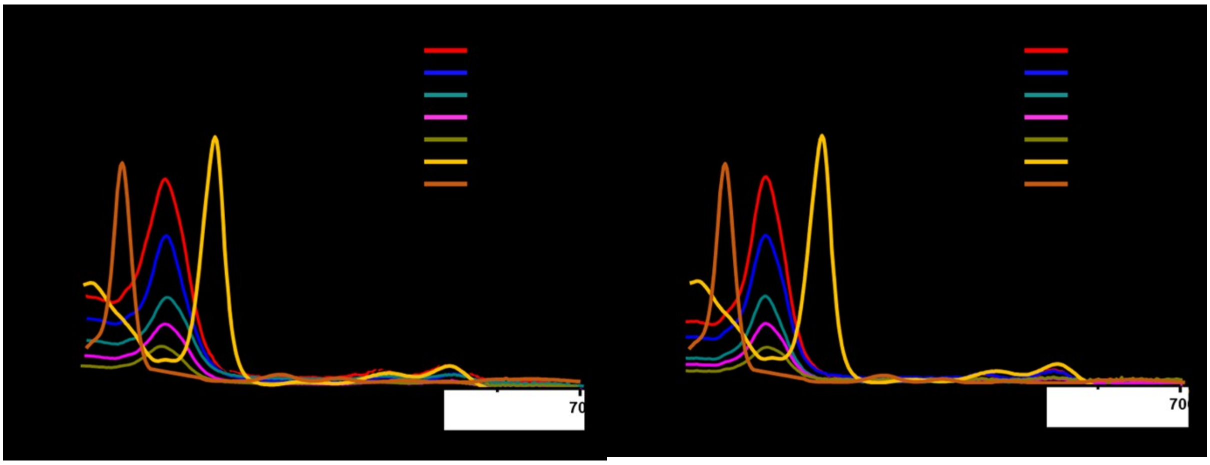


Fig. S5 Absorption spectra of (a) **1** and (b) **2** after treating with TBAF. Samples were prepared by 20 mg of MPSMs with various concentrations (from 0.1 mM to 8 mM) of **L3** in refluxing $CHCl_3$ (5.6 mL) for 24 h.

Table S2 Mn(III)-porphyrin loadings for MPSMs[a] calculated from UV-Vis analysis in Fig. S5.

Concentration (mM)[b]	Time (h)	Silica amount (mg)	Mn(III)-porphyrin loading on **1**[c] (mmol/mg)	Mn(III)-porphyrin loading on **2**[c] (mmol/mg)
0.1	24	20	0.05×10^{-4}	0.06×10^{-4}
0.5	24	20	0.19×10^{-4}	0.21×10^{-4}
1	24	20	0.37×10^{-4}	0.38×10^{-4}
2	24	20	0.65×10^{-4}	0.66×10^{-4}

4	24	20	1.21×10^{-4}	1.24×10^{-4}
8	24	20	2.42×10^{-4}	2.44×10^{-4}

[a] Catalysts loading was quantified by treating with excess TBAF (Condition: MPSM 20 mg, TBAF 3.5 mL of 0.1 M in THF, reaction time 48 h, room temperature). [b] Solvent: $CHCl_3$ 5.6 mL. [c] Extinction coefficient for **1**: 4.6×10^5 $M^{-1}\cdot cm^{-1}$.

Table S3 Comparison of catalyst loadings on MPSMs obtained from ICP-AES, UV-Vis, and EDX analysis.

	ICP-AES	UV-Vis	EDX
1	1.19×10^{-4} mmol/mg 1.55×10^{-11} mol/cm^2 0.65 wt%	1.21×10^{-4} mmol/mg 1.57×10^{-11} mol/cm^2 0.66 wt%	1.20×10^{-4} mmol/mg 1.56×10^{-11} mol/cm^2 0.69 wt%
2	1.22×10^{-4} mmol/mg 8.31×10^{-12} mol/cm^2 0.67 wt%	1.24×10^{-4} mmol/mg 8.44×10^{-12} mol/cm^2 0.68 wt%	1.27×10^{-4} mmol/mg 8.65×10^{-12} mol/cm^2 0.70 wt%

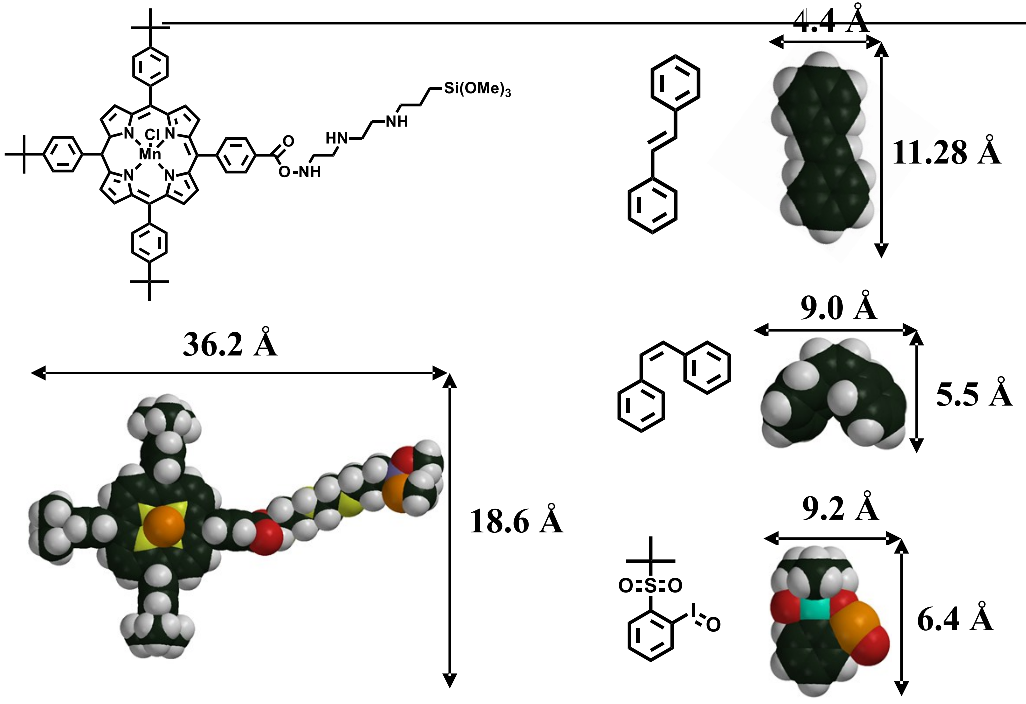


Fig. S6 Calculated sizes of selected molecules.

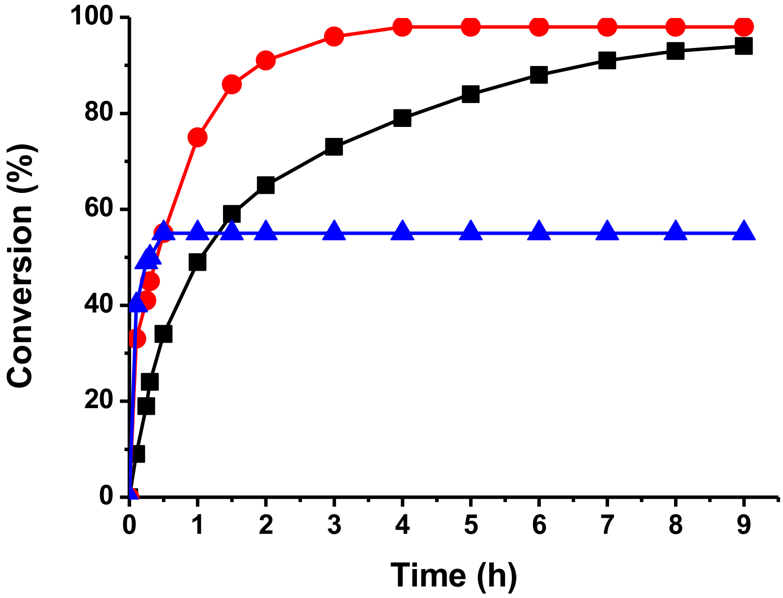


Fig. S7 Comparison of conversions and catalytic stabilities of the homogeneous catalyst [tetra-(4-*t*-butylphenyl)porphyrinato]manganese(III) chloride (**L4**) and the Mn(III)-porphyrin-loaded MPSMs, **1** and **2**, (molar ratio of styrene:oxidant:catalyst = 1000:1000:1). 2-*t*-butyl-sulfonyliodosylbenzene was used as an oxidant.

Table S4 Recyclability study of MPSMs.[a,b]

Cycles	Catalyst	Conversion (%)[c]	Yield (%)	TON	TOF (h^{-1})
1	**1**[d]	50 %	49 %	250	500
	2[d]	73 %	72 %	365	730
2	**1**	50 %	50 %	250	500
	2	72 %	72 %	360	720
3	**1**	51 %	50 %	255	510
	2	75 %	73 %	375	750
4	**1**	49 %	49 %	245	490
	2	72 %	71 %	360	720
5	**1**	49 %	48 %	245	490
	2	72 %	71 %	360	720

[a] Reaction conditions: olefin 0.16 mmol, oxidant 0.16 mmol, catalyst 1.6×10^{-4} mmol (1000:1000:1), CH_2Cl_2 1 mL, reaction time 1 h, room temperature. [b] Oxidant: 2-tert-butyl-sulfonyliodosylbenzene. [c] Determined by GC with toluene as an internal standard (200 equiv.). [d] Catalysts loading on the particles: 1.55×10^{-11} mol/cm^2 (**1**) and 8.31 $\times 10^{-12}$ mol/cm^2 (**2**).

IV. Reference

1. N. Zhan, G. Palui, J. P. Merkl and H. Mattoussi, *J. Am. Chem. Soc*. 2016, **138**, 3190-3201.
2. (a) J. Y. Kim, K. Y. Lee, S. Kim and S. J. Lee, *Bull. Korean Chem. Soc*. 2015, **36**, 1936-1939; (b) M. Wielopolski, G. de Miguel Rojas, C. van der Pol, L. Brinkhaus, G. Katsukis, M. R. Bryce, T. Clark and D. M. Guldi, *ACS Nano*. 2010, **4**, 6449-6462.
3. L. Wang, T. Qi, Y. Zhang and J. Chu, *Microporous Mesoporous Mater*. 2006, **91**, 156-160.
4. W. Zhu, X. Li, D. Wu, J. Yu, Y. Zhou, K. Wei and W. Ma, *Microporous Mesoporous Mater*. 2016, **222**, 192-201.