

Bottom-up Approach to Engineer Two Covalent-Porphyrinic Frameworks as Effective Catalyst for Selective Oxidation

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S1. Crystal data and structure refinements for THCPP.

Single-crystal X-ray data collections and structure determinations: The determination of the unit cell and data collection for the crystal of compound THCPP sealed capillaries was performed using an Oxford Xcalibur Gemini Ultra diffract meter with an Atlas detector. The data were collected using graphite monochromated-enhanced ultra-Cu radiation ($\lambda=1.54178 \text{ \AA}$) at 293 K. The data sets were corrected by empirical absorption correction by using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm.¹ The structure of THCPP was solved by direct methods and refined by full-matrix least-squares methods with the SHELX-97 program package.² The solvent molecules in compounds THCPP were highly disordered; the SQUEEZE subroutine of the PLATON software suite was used to remove the scattering from the highly disordered guest molecules.³ The resulting new file was used to further refine the structures. The H atoms on C atoms were generated geometrically. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: CCDC 955396, this data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

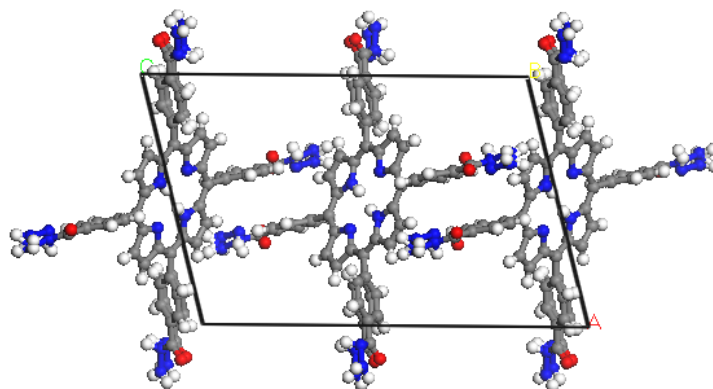


Figure S1. The THCPP network viewed along the crystallographic b-axis.

Section 2. Synthetic procedures

The 5, 10, 15, 20-tetrakis (4-carboxyphenyl) porphyrin was synthesized by the modified Lindsey method.⁴

5, 10, 15, 20-tetrakis (4-carboxyphenyl) porphyrin Synthesis. Thus, 1.22 g of 4-carbomethoxybenzaldehyde and 0.50g of distilled pyrrole were added to 750 mL of dry CH_2Cl_2 for 30 min. Then, BF_3 etherate (92 μL) was added via syringe, and the reaction mixture was protected from light. After stirring at room temperature for 1 h, 1.37 g of p-chloranil was added in the solid form and the solution was stirred overnight. The solution was concentrated to a small volume using a rotary evaporator. To this solution, silica gel (60-200 mesh) was added and the slurry was evaporated to give a dry black powder, which was loaded on a silica column using CHCl_3 . First CHCl_3 fraction removed any poly (pyrrole) impurity and the porphyrin was eluted with 2-4% acetone in CHCl_3 . It was then further purified by recrystallization from a 1:4 CHCl_3 /methanol mixture (v/v). Yield: 0.55 g (35 %). ^1H NMR (300 MHz, CDCl_3) δ 9.08-8.64 (m, 8H), 8.62-8.37 (m, 8H), 8.39-8.13 (m, 8H), 4.34-3.88 (m, 12H), -2.79 (s, 2H).

The meso-Tetra (4-hydrazidocarbonylphenyl)porphyrin (THCPP) was synthesized as follows: 0.2g 5, 10, 15, 20-tetrakis (4-carboxyphenyl) porphyrin were added to 30 mL of DMF. Then, 10 mL hydrazine hydrate was added and then refluxed for 6 h. After the reaction mixture was allowed to cool to room temperature, 100 mL water was poured into mixture. The product obtained was filtered and washed with water for several times. Yield: 0.15 g (72 %). ^1H NMR (300 MHz, CDCl_3) δ 8.82 (m, 8H), 8.40-8.47 (m, 8H), 8.26-8.31 (m, 8H), 4.09 (m, 12H), -2.81 (s, 2H).

meso-Tetra (4-hydrazidocarbonylphenyl)porphyrin -Mn(III) (Mn-THCPP). A solution of THCPP 0.4 g and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ 0.24 g in 50 mL of DMF was refluxed for 12 h. After the mixture was cooled to room temperature, 500 mL of H_2O was added. The resultant precipitate was filtered and washed with 200 mL of H_2O for three times. The obtained solid was dissolved in CHCl_3 , followed by washing three times with water. The organic layer was dried over anhydrous magnesium sulfate and evaporated to afford quantitative green crystals.

CPF-1 and Mn-CPF-1. An Dioxane/Mesitylene (3/1, 1mL) mixture of THCPP (0.024 mmol, 20.3mg) and terephthalaldehyde (0.06 mmol, 6.3 mg) in the presence of acetic acid catalyst (3M, 0.1 mL) in a Pyrex tube (10 mL) was degassed by three freeze-pump-thaw cycles. The tube was sealed off by flame and heated at 120 °C for 3 days. The precipitate was collected via centrifuge, washed with THF for 6 times, and washed with acetone 3 times. The powder was dried at 120 °C under vacuum overnight to give the corresponding CPF-1 in isolated yields of 60 %. Mn-CPF-1 was obtained with Mn-HTCPP as raw material instead of THCPP.

CPF-2 and Mn-CPF-2. In the typical synthesis, a Pyrex tube is charged with THCPP (0.024 mmol, 20.3mg), corresponding squaraine (0.06 mmol, 6.8 mg), Dioxane/Mesitylene (3/1) 2 mL. This mixture was sonicated for 10 min in order to get a homogeneous dispersion. The tube was then flash frozen at 77 K (liquid N₂ bath) and degassed by three freeze-pump-thaw cycles. The tube was sealed off and then heated at 120 °C for 3 days. The precipitate was collected via centrifuge, washed with THF for 6 times, and washed with acetone 3 times. The powder was dried at 120 °C under vacuum overnight to give the corresponding CPF-2 in isolated yields of 55 %. Mn-CPF-2 was obtained when Mn-HTCPP was used as raw material instead of THCPP.

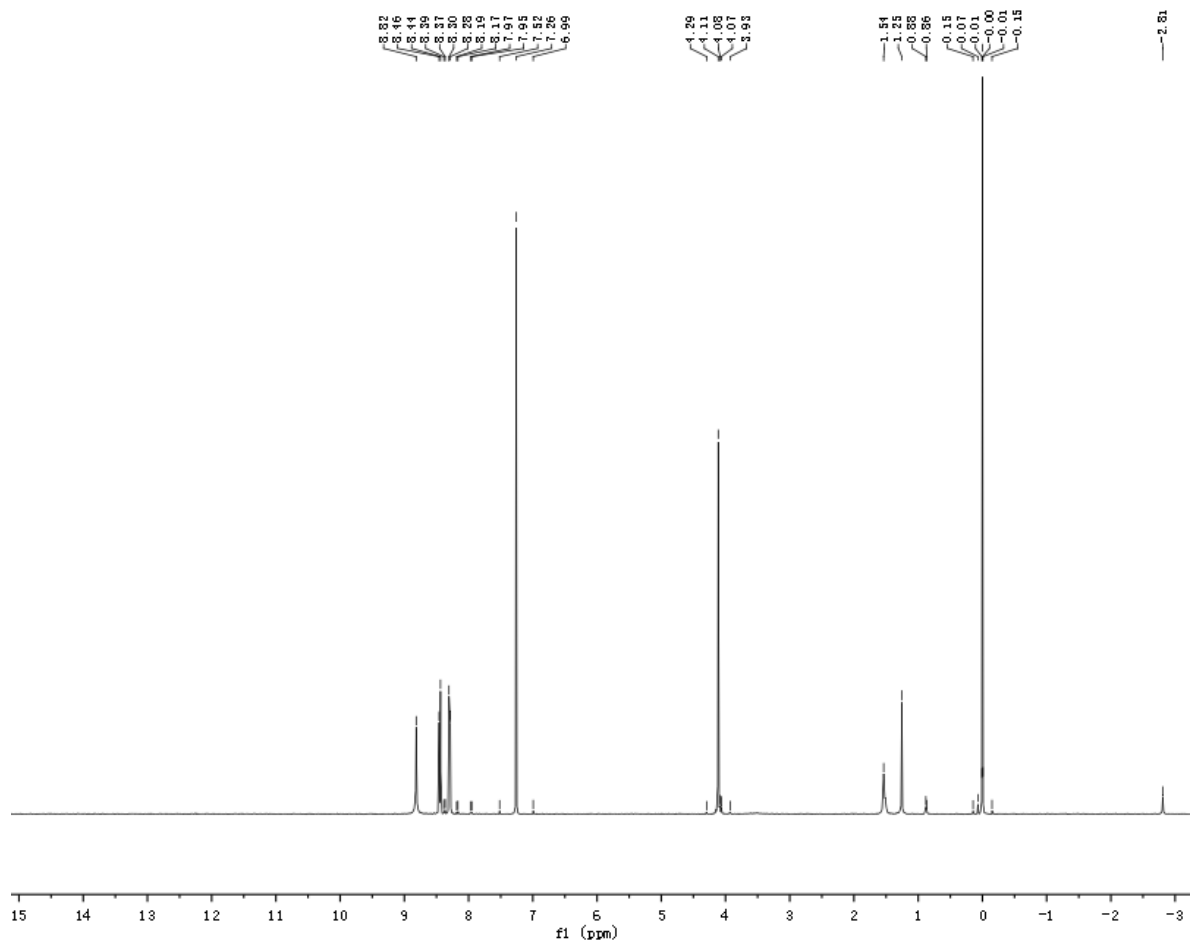
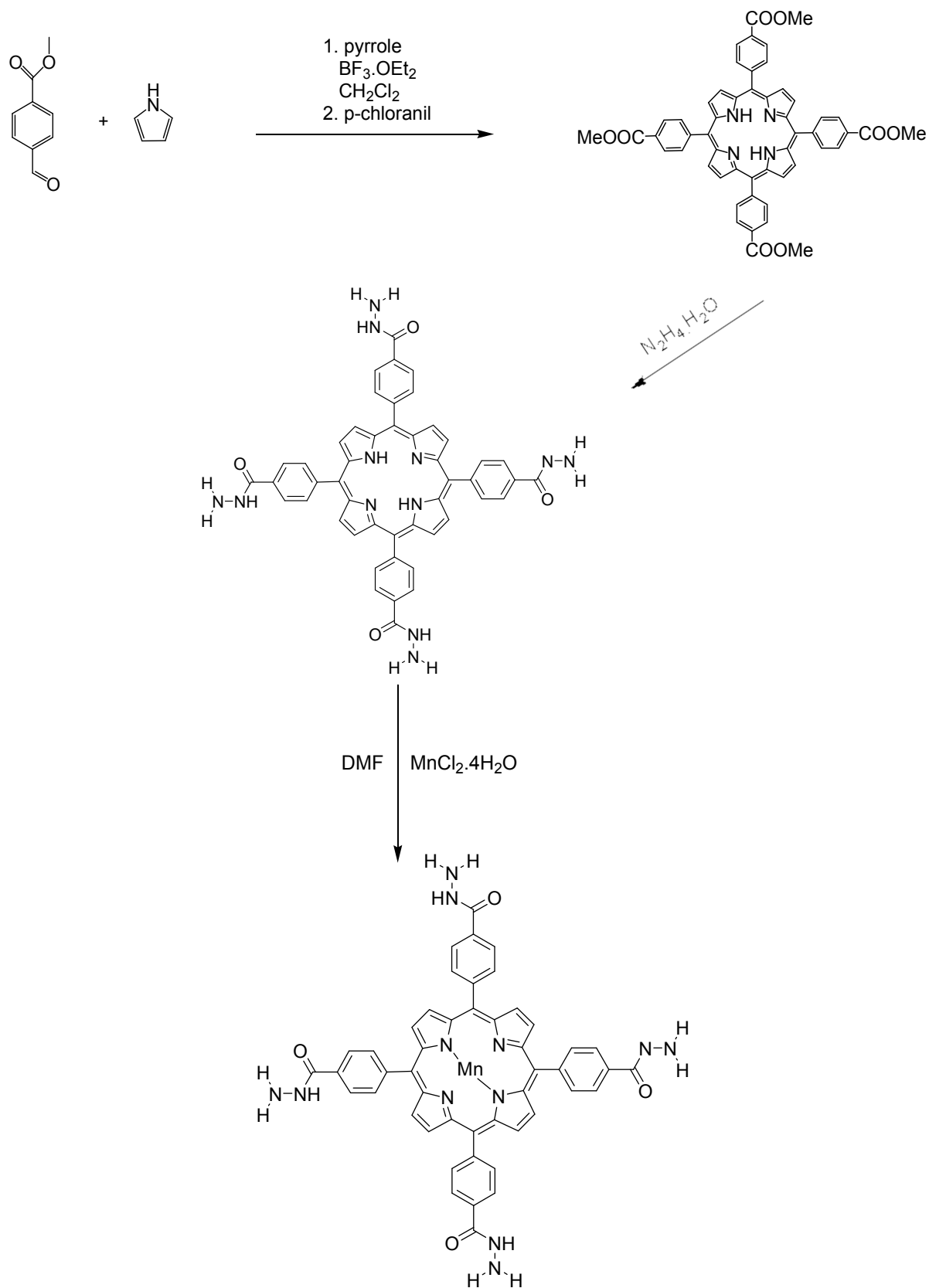


Figure S2. ¹H NMR spectrum of THCPP



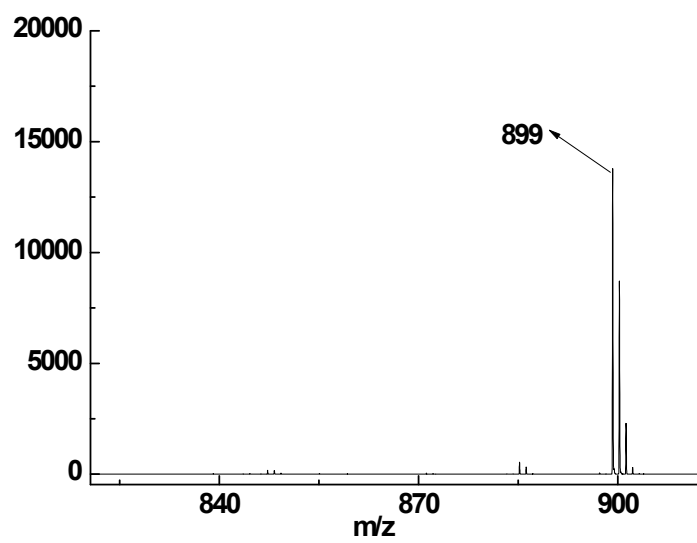


Figure S3. MALDI-MS spectra of the Mn-HTCPP.

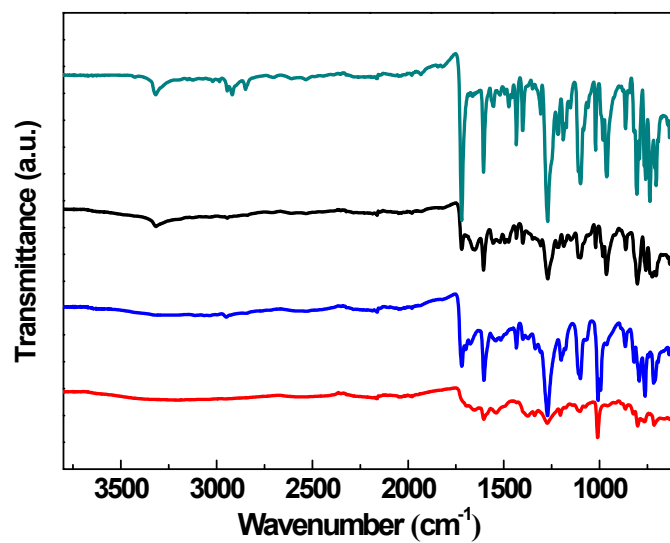


Figure S4. FT-IR spectra of HTCPP (green line), CPF-1 (black line) Mn-HTCPP (blue line) and Mn-CPF-1 (red line)

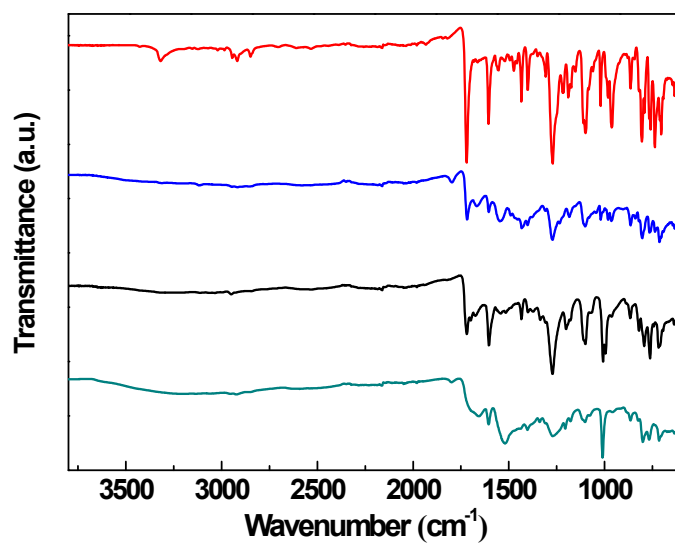
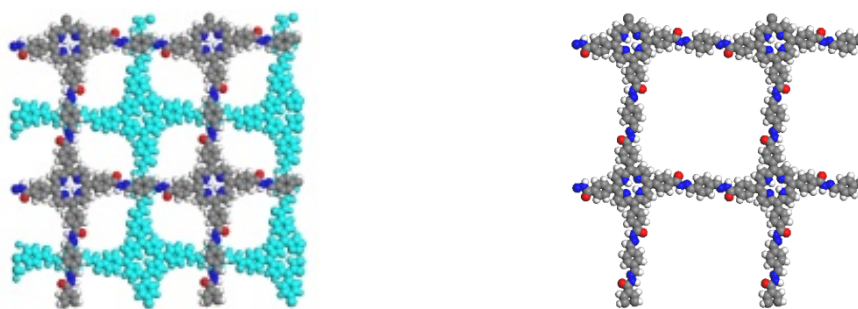


Figure S5. FT-IR spectra of HTCPP (red line), CPF-2 (blue line) Mn-HTCPP (black line) and Mn-CPF-2 (green line)



Unit cell parameters of AB stacking COF-1	Unit cell parameters of AA stacking COF-1
Space group: P4/mmm	Space group: P4/mmm
a=b= 30.1 Å c= 7.8 Å	a=b= 30.1 Å c= 3.4 Å
$\alpha=\beta=\gamma= 90^\circ$	$\alpha=\beta=\gamma= 90^\circ$

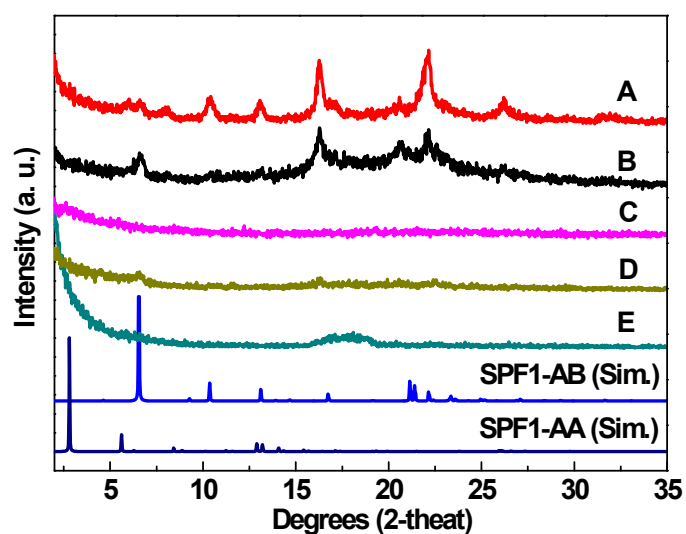
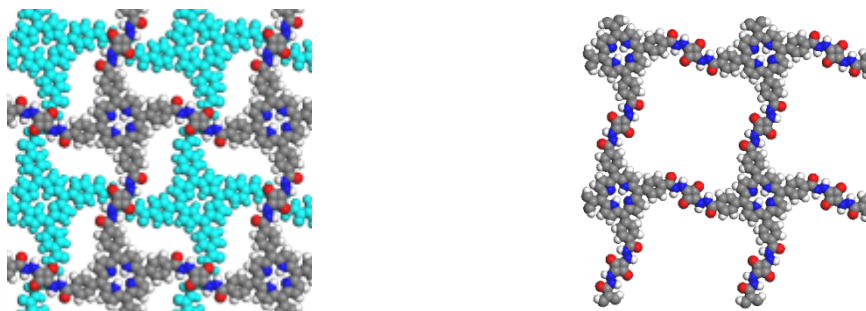


Figure S6. PXRD pattern of as-synthesized CPF-1 after reaction for 3 days in different conditions compared with staggered and eclipsed stacking models. A: Dioxane/Mesitylene (3/1) 1 mL, 0.1 mL 3M HOAc; B: Dioxane/Mesitylene (3/1) 1 mL, 0.1 mL 6M HOAc; C: Dioxane/Mesitylene (3/1) 2 mL, 0.2 mL 6M HOAc; D: Dioxane/Mesitylene (1/1) 1 mL, 0.1 mL 3M HOAc (Mn-HTCPP instead of HTPCP); E: Dioxane/Mesitylene (3/1) 2 mL, 0.2 mL 6M HOAc.



Unit cell parameters of AB stacking COF-2	Unit cell parameters of AA stacking COF-2
Space group: P4/mmm	Space group: P4/mmm
a=b= 27.3 Å c= 6.9 Å	a=b= 27.4 Å c= 3.4 Å
$\alpha=\beta=\gamma= 90^\circ$	$\alpha=\beta=\gamma= 90^\circ$

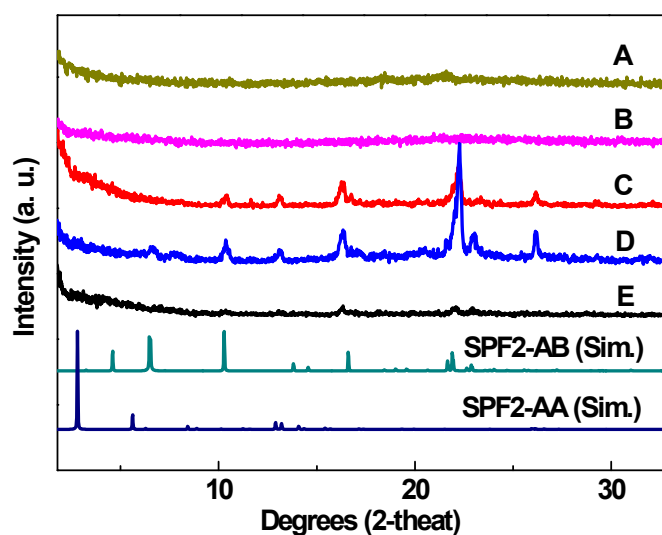


Figure S7. PXRD pattern of as-synthesized CPF-2 after reaction for 3 days in different conditions compared with staggered and eclipsed stacking models. A: Dioxane/Mesitylene (1/19) 2 mL; B: Dioxane/Mesitylene (3/1) 2 mL (Mn-HTCPP instead of HTCPP); C: Dioxane/Mesitylene (3/1) 1 mL; D: Dioxane/Mesitylene (3/1) 2 mL; E: Dioxane/Mesitylene (3/1) 3 mL.

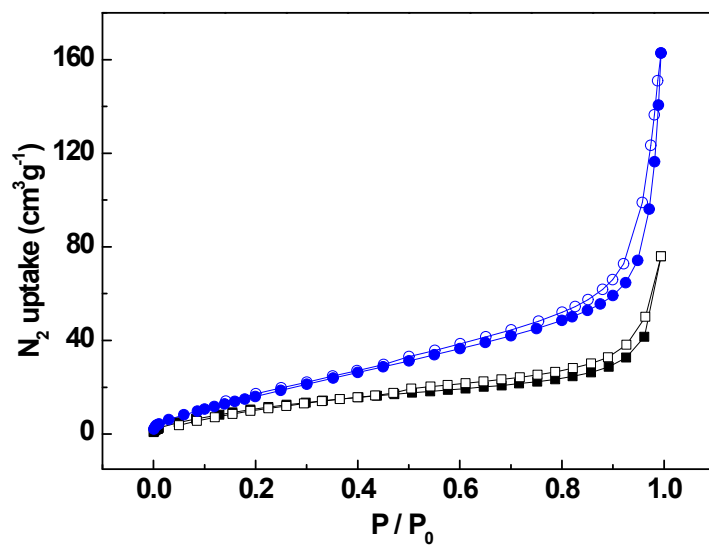


Figure S8. Representative N₂ adsorption (closed circles) and desorption (open circles) isotherms of CPF-1 (blue) and CPF-2 (black)

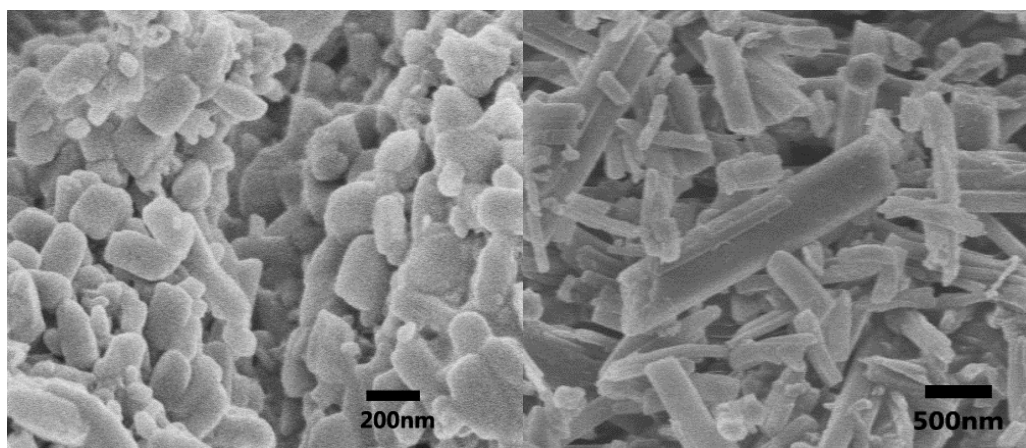


Figure S9. Scanning electron microscope image of CPF-1 (left) and CPF-2 (right)

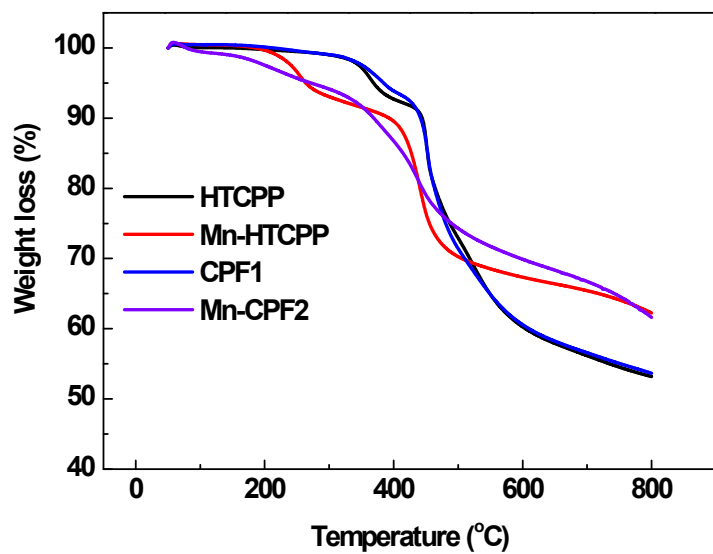


Figure S10. The TG curves of HTCPP (black line), Mn-HTCPP (red line), CPF-1 (blue line) and Mn-CPF-2 (purple line) under N₂ atmosphere.

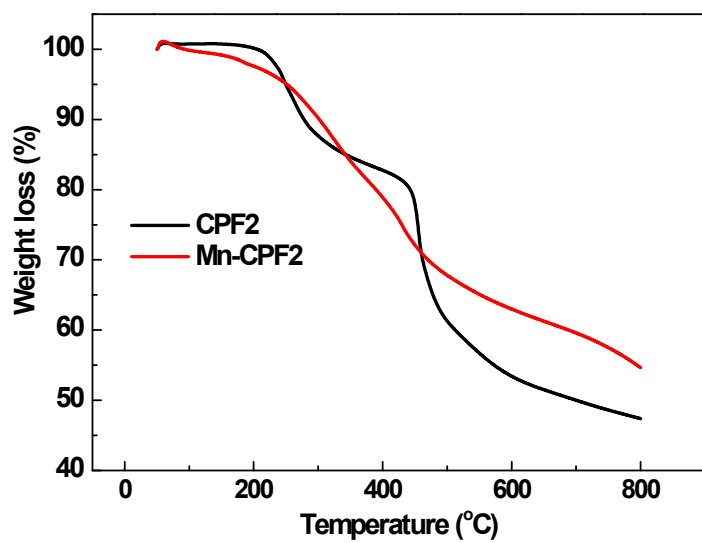


Figure S11. The TG curves of CPF-2 (black line) and Mn-CPF-2 (red line) under N₂ atmosphere.

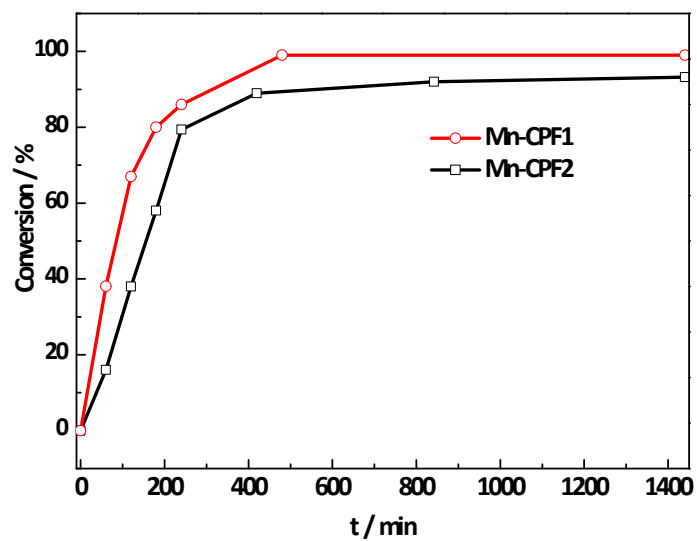


Figure S12. Traces of the styrene oxide conversion versus reaction time catalyzed by freshly prepared Mn-CPF-1 (red) and Mn-CPF-2 (black).

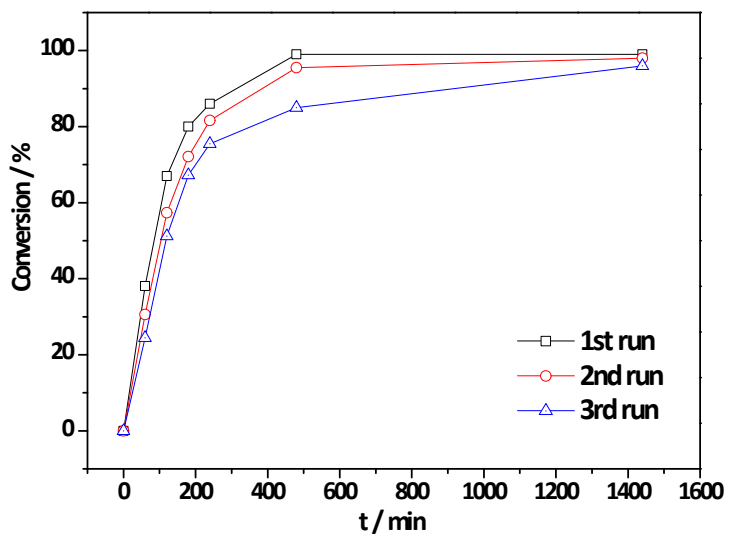


Figure S13. Traces of the styrene oxide conversion versus reaction time catalyzed by recycled catalyst.

References

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