[Electronic Supporting Information to accompany]

Synthesis of catalytically active porous organic polymers with metalloporphyrin struts.

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I. Materials. 5-Pentafluorophenyl dipyrromethane,[S1] and tetrakis(4-aminophenyl)methane (**1**)[S3] were synthesized according to published procedures. 4-Methylphthalic acid (Sigma-Aldrich), benzoyl peroxide (Sigma-Aldrich), *N*-bromosuccinimide (Acros), 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ, Acros), $BF_3{\cdot}Et_2O$ (Sigma-Aldrich), tetrakis(pentafluorophenyl)porphyrin (Frontier Scientific, Inc.), $FeCl_2$ (Sigma-Aldrich), $MnCl_2{\cdot}4H_2O$ (Sigma-Aldrich), $BF_3{\cdot}Et_2O$ (Sigma-Aldrich), and silica gel (Sorbent Technologies, 60 Å, 40-63 μm) were obtained from commercial sources and used as received. Solvents were obtained from Sigma-Aldrich and used as received. 4Å molecular sieves (Grace Davison) were activated at 300 °C. Anhydrous DMF was obtained from a two-column Dow-Grubbs purification system installed by Glass Contours (now SG Water USA, Nashua, NH). The collected solvent was degassed with 3 freeze-pump-thaw cycles and stored in a Strauss flask before use. All deuterated solvents were purchased either from Cambridge Isotope Laboratories or Sigma-Aldrich and used as received. Microwaved reactions were carried out using a Biotage Initiator microwave reactor (Biotage, LLC, Charlotte, NC, USA).

II. Characterization. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 500 (499.37 MHz for ^{1}H, 125.76 MHz for ^{13}C) spectrometer. ^{1}H and ^{13}C chemical shifts are referenced to the residual proton resonance of solvent on the δ scale. ^{19}F NMR spectra were recorded on Varian Mercury 400 (376.31 MHz for ^{19}F) spectrometer and referenced to an external $CFCl_3$ standard. Matrix-Assisted Laser-Desorption-Ionization Time-of-flight (MALDI-ToF) mass spectra were obtained on a Bruker Autoflex III Smartbeam MALDI-TOF mass spectrometer in positive ionization mode with 2-hydroxy-1-naphthoic acid as a matrix.

Gas chromatography flame ionization detection (GC-FID) was performed using an HP 5890 instrument equipped with an HP-5 capillary column (50 m × 0.320 mm × 0.25 μm film thickness) and an FID detector. Product concentration was calculated from calibration curves that were established relative to an internal standard. In the case of the epoxidation of styrene, peaks from styrene oxide and phenylacetaldehyde (a thermally rearranged product of styrene oxide, known to occur under GC conditions) were combined.

GC-MS analysis was carried out on a computer-interfaced Agilent Technologies 6890 Network instrument equipped with an Agilent 5973 Network mass-selective detector. The column used was a 30-m HP-5 capillary column (30 m × 0.320 mm × 0.25 μm film thickness. Flow rate = 0.9 mL/min.

Elemental analyses were provided by Atlantic Microlab, Inc. (Norcross, GA). Thermogravimetric analysis (TGA) experiments were performed on a Mettler Toledo TGA/SDTA851 interfaced with a PC using Star software. Samples were heated at a rate of 10 ºC/min under a nitrogen atmosphere. Samples for scanning electron microscopy (SEM) were sputtered with a layer of Os (5-nm thickness) prior to taking images on a Hitachi S-4800 SEM with a 15.0 kV accelerating voltage.

Gas adsorption/desorption isotherms were measured volumetrically at 273 K in the range $8.0 \times 10^{-6} \leq P/Po \leq 1$ using a Quadrasorb *SI* instrument (Quantachrome Instruments) equipped with the ASWin software package. Ultra-high purity CO_2 (99.999%) was purchased from Airgas, Inc. and used as received. The samples were outgassed at 120 °C on a Masterprep Degasser (Quantachrome Instruments) for 24 h. Surface area was calculated by applying non-local density functional theory (NLDFT) in the range of $0.005 \leq P/P_o \leq 1.0$.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was conducted on a Varian Vista MPX ICP-OES instrument that is equipped to cover the spectral range from 175 to 785 nm. Samples (1-2 mg) were digested in conc H_2SO_4:30% aq H_2O_2 (3:1 v/v) and heated at 120 °C until the solution became clear and colorless and no further vapor was produced. An aliquot of this concentrated acid solution was diluted to 5% with deionized H_2O and analyzed for Fe (238.204 nm) or Mn (257.610 nm) content against standardized solutions.

Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku XDS 2000 diffractometer using nickel-filtered Cu Kα radiation (λ = 1.5418 Å) over a range of $5° < 2\theta < 40°$ in 0.1° steps with a 1-s counting time per step. Simulations were made based on the single-crystal data using the Mercury software. The powder samples were mounted on clear cellophane tape and PXRD data were collected immediately after mounting.

III. Synthesis

2-(*Tert*-butylsulfonyl)iodosylbenzene. A published procedure[S2] was modified to produce the title compound in good yield and purity. As shown below, the key modification was the use of a higher H_2O_2/iodobenzene ratio (24.8 instead of the 2.8 ratio used in the original procedure).

Acetic anhydride (165 mL, 1.75 mol) was placed in a 500-mL round-bottom flask equipped with a magnetic stir bar and cooled to 0 °C with an ice bath. H_2O_2 (39 mL of a 30 wt% solution in H_2O, 0.38 mol H_2O_2, 1.68 mol H_2O) was slowly added to the acetic anhydride and the solution was allowed to slowly warm up to room temperature and stirred for 24 h. ***Warning: Potential explosion hazard (see note below)***. 2-(*Tert*-butylsulfonyl)iodobenzene (5 g, 15.4 mmol) was added to this in situ-generated peracetic acid solution and stirred at room temperature for 4 hours. The solvent was distilled off under vacuum, care was taken to never heat the reaction mixture above ~40 °C. The crude intermediate 2-(*tert*-butylsulfonyl)diacetoxyiodobenzene was obtained as a white powder. Any large chunks were crushed into a fine powder and placed into a 250-mL Erlenmeyer flask equipped with a stir bar. While stirring vigorously, an aliquot (50 mL) of 3N NaOH (aq) was added dropwise to the flask and the white solid began to turn bright yellow. The reaction was stirred for an additional 20 minutes after addition of NaOH, then filtered to collect the product. The solid was washed on the filter paper with H_2O (300 mL), then Et_2O (200 mL). The yellow solid was dried under vacuum to obtain 3.56 g of the product (68% yield). Characterization was consistent with previously reported data for this compound.

Warning note added in proof. Although the aforementioned synthesis had been performed about a dozen times previously at Northwestern University without incident, a researcher in our laboratory very recently suffered serious injury from an explosion while repeating it using a more concentrated solution of H_2O_2 (35 mL of a 35 wt% solution in H_2O, 0.41 mol H_2O_2, 1.43 mol H_2O). While we do not know with any certainty what caused the explosion, we suspect that diacetyl peroxide, a side product in this synthesis, was a culprit. In the published procedure and in our aforementioned modified synthesis, combining aqueous H_2O_2 with acetic anhydride should form peracetic acid. For both of these cases, the water component of the aqueous H_2O_2 solution—in 94% and 96% molar ratio to the acetic anhydride, respectively—should serve to hydrolyze most of the excess acetic anhydride. We speculate that if some acetic anhydride remained after conversion of the majority of acetate equivalents to peracetic acid (the desired intermediate oxidant) or acetic acid (side product), the anhydride could have combined with peracetic acid to form diacetyl peroxide, which is known to be a shock-sensitive explosive. If our reasoning is correct, the amount of diacetyl peroxide that potentially can form is much greater in the reaction where the 35 wt% solution H_2O_2 was used.[S6] Upon concentrating the product in this reaction and drying, enough of the explosive diacetyl peroxide remains behind in the solid product to trigger the explosion that injured the researcher when this person attempted to break up the product with a spatula.

While the above "explanation" and discussion are speculative, especially because we do not know what the margin of error is with regard to water and hydrogen peroxide concentrations versus acetic anhydride concentration, it is sobering for us to realize that even with the 30 wt% hydrogen peroxide, some diacetyl peroxide could have been generated. As such we are stopping all synthetic work using the aforementioned procedure. At least until the cause of the explosion can be determined, we strongly encourage researchers to consider using alternative, non-peroxide routes to iodobenzene diacetate, 2-(*tert*-butylsulfonyl)iodosylbenzene,[S7] and related compounds. More generally, we recommend that the reagent combination of aqueous H_2O_2 and acetic anhydride either be avoided or used with great cares, despite the fact that, until now, this has been a commonly used reagent combination in oxidation chemistry. As always, prudence should be exercised in working with hypervalent iodine compounds such as iodobenzene diacetate, iodosylbenzene, and their derivatives, many of which have been known to detonate upon heating.[S8]

Dimethyl 4-methylphthalate. In a 500-mL round-bottom flask equipped with a magnetic stir bar, 4-methylphthalic acid (15.03 g, 83.4 mmol) was first dissolved in methanol (175 mL). Concentrated sulfuric acid (20mL) was then slowly added to the stirring solution. The solution was refluxed for 2 days before being cooled down and diluted with water (150 mL) before being extracted into diethyl ether (3 × 200 mL). The combined organic phase was washed with 0.1 M aqueous KOH (200 mL) and saturated brine (200 mL) before being dried over Na_2SO_4. Removal of solvent gave the product as a colorless oil (14.97 g, 86 % yield). ^{1}H NMR ($CDCl_3$): 7.65 (d, 1 H, J = 9.9 Hz), 7.45 (s, 1 H), 7.30 (d, 1 H, J = 5.0 Hz), 3.88 (s, 3 H), 3.86 (s, 3 H), 2.39 (s, 3 H). ^{13}C NMR ($CDCl_3$): See Fig. S1. GC-MS (EI): *m/z* 208.2 (Calcd *m/z* 208.1 for M^+).

Dimethyl 4-(dibromomethyl)phthalate. In a 250-mL round-bottom flask equipped with a magnetic stir bar, dimethyl 4-methylphthalate (14.5, 69.6 mmol) was dissolved in CCl_4 (150 mL) and treated with *N*-bromosuccinimide (26.03 g, 2.1 equiv) and benzoyl peroxide (190 mg). The solution then refluxed overnight, after which the solids were filtered off. The solvent was removed from the filtrate and the residue was purified by flash column chromatography (silica gel (7 cm × 20 cm column), 20 vol% ethyl acetate in hexanes). The solvent was removed from the eluted product to give the product as a colorless oil (24.89 g, 97 % yield). ^{1}H NMR ($CDCl_3$): 7.90 (s, 1 H), 7.73 (m, 2 H), 6.63 (s, 1 H), 3.92 (s, 3 H), 3.90 (s, 3 H). ^{13}C NMR ($CDCl_3$): See Fig. S2. GC-MS (EI): *m/z* 363.8 (Calcd *m/z* 363.9 for M^+).

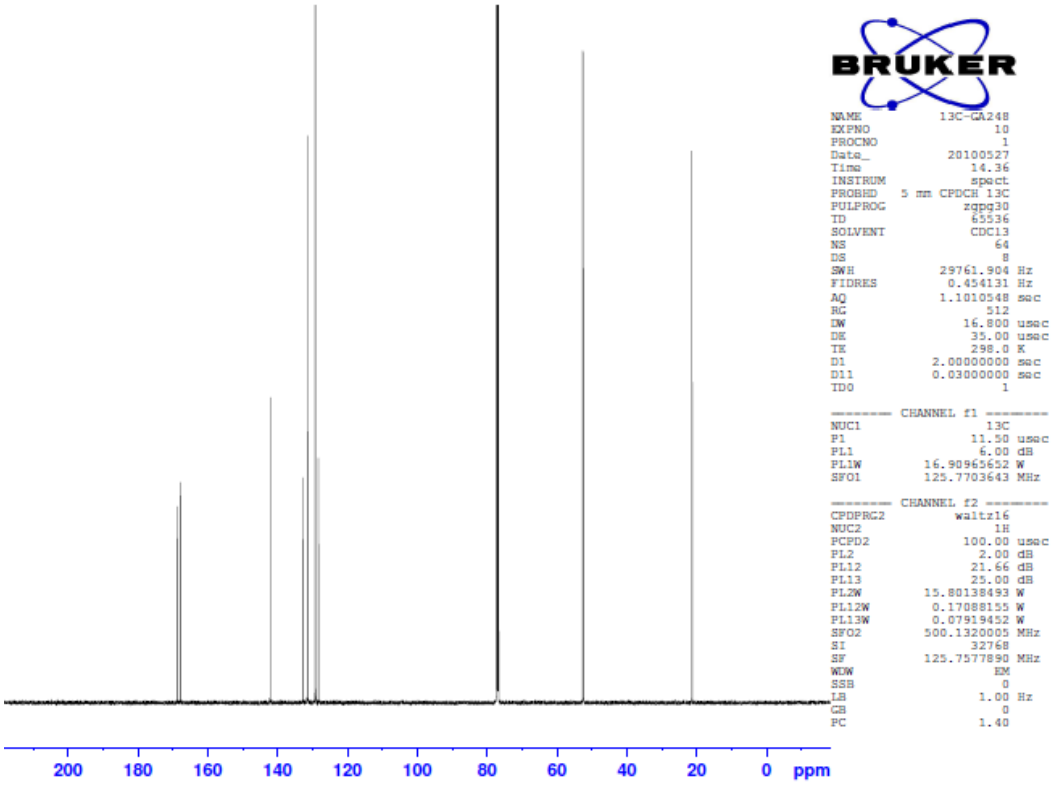

Fig. S1. ^{13}C NMR ($CDCl_3$) spectrum of dimethyl 4-methylphthalate.

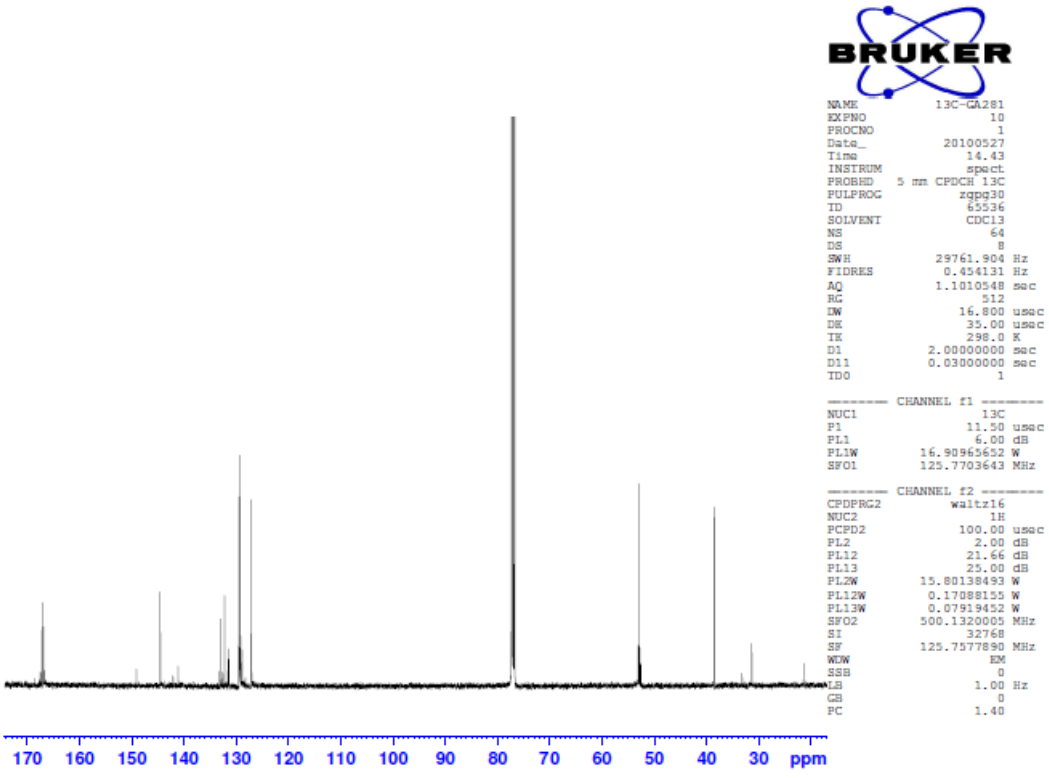

Fig. S2. ^{13}C NMR ($CDCl_3$) spectrum of dimethyl 4-(dibromomethyl)phthalate.

Dimethyl 4-carboxaldehydephthalate. In a 250-mL round-bottom flask equipped with a magnetic stir bar, dimethyl 4-(dibromomethyl)phthalate (24.5 g, 67 mmol) was dissolved in acetonitrile (140 mL). A solution of $AgNO_3$ (34.03 g, 200 mmol) in water (28 mL) was added to the reaction, yielding copious amounts of a pale-green precipitate. The combined mixture was stirred and refluxed for 1 h before being cooled to room temperature. CH_2Cl_2 (200 mL) was added to the reaction flask and the combined mixture were filtered. The remaining solids were rinsed with CH_2Cl_2 and the combined organics was washed with water (60 mL) and dried over $MgSO_4$. The solvent was removed and the residue was purified by

flash column chromatography (silica gel (7 cm × 20 cm column), 20 vol% ethyl acetate in hexanes). The product was collected as the second fraction, which gave a colorless oil upon solvent removal (12.47 g, 84 % yield). ^{1}H NMR ($CDCl_3$): 10.07 (s, 1 H), 8.27 (s, 1 H), 8.05 (d, 1 H, J = 10.0 Hz), 7.81 (d, 1 H, J = 8.0 Hz), 3.93 (s, 6 H). ^{13}C NMR ($CDCl_3$): See Fig. S3. GC-MS(EI): *m/z* 222.1 (Calcd *m/z* 222.1 for M^+).

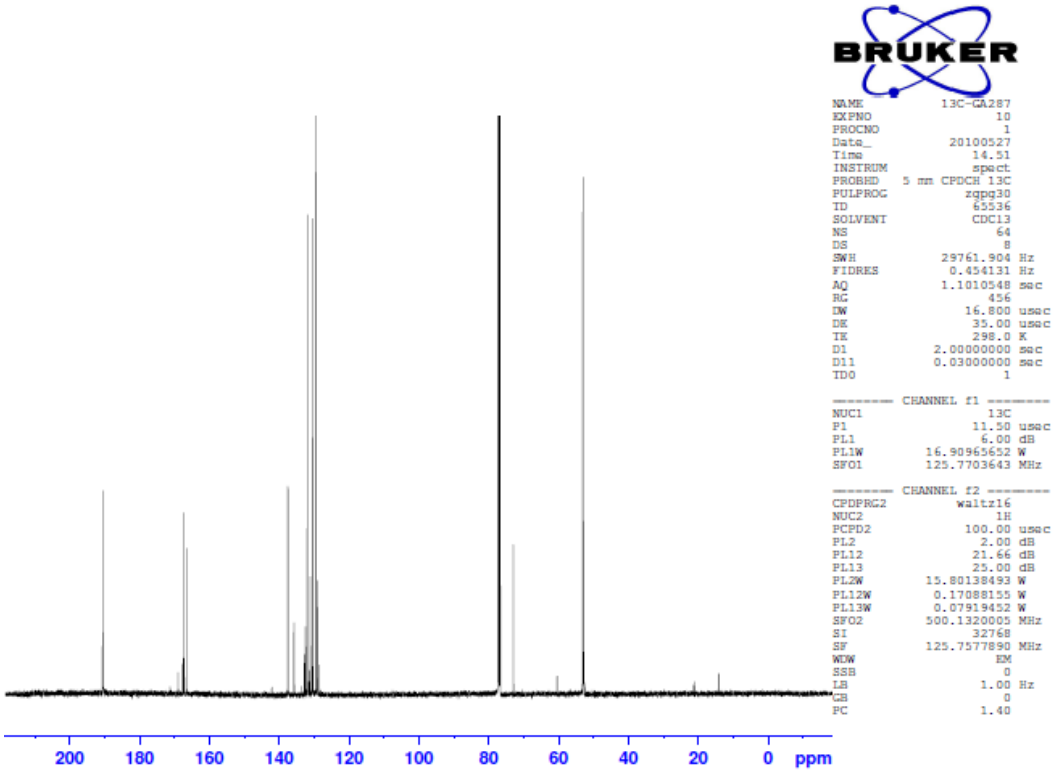

Fig. S3. ^{13}C NMR ($CDCl_3$) spectrum of dimethyl 4-carboxaldehydephthalate.

5,15-bis(dimethyl phthalate)-10,20-bis(pentafluorophenyl)porphyrin. In a 3-L round-bottom flask equipped with a magnetic stir bar, dimethyl 4-carboxaldehydephthalate (3.99 g, 18 mmol) and 5-pentafluorophenyl dipyrromethane (5.63 g, 18 mmol) were dissolved in chloroform (2.4 L). Activated 4 Å molecular sieve (10 g) was added and the solution was degassed by a bubbling stream of nitrogen for 20 minutes. $BF_3{\cdot}Et_2O$ (1.95 mL) was added via syringe under nitrogen and the reaction was capped with a septa and shielded from light before being stirred for 19 h. DDQ (12.24 g, 3 equiv) and pyridine (10 mL) were added to the reaction flask, and the combined mixture was stirred at room temperature for 5 more hour. To remove the DDQ residue and insoluble byproducts, the crude reaction mixture was then passed through a short silica plug (7 cm × 10 cm, pre-wetted with CH_2Cl_2, then eluted with 10 vol% ethyl acetate in CH_2Cl_2) and the fractions containing porphyrinic product (appears green and the porphyrin can be detected as a red-glow fluorescence using a long-wavelength hand-held UV lamp) were isolated. The solvent was removed from the combined organics and the remaining residue was redissolved in toluene (400 mL) before being refluxed in the presence of DDQ (4 g) for 5 h. After cooling down, most of the solvent was removed from the reaction mixture and the concentrated crude materials was again passed through a short silica plug (7 cm × 10 cm, pre-wetted with CH_2Cl_2, then eluted with 10 vol% ethyl acetate in CH_2Cl_2). The porphyrin-containing fractions were combined and repurified via flash column chromatography (7 cm × 20 cm, eluted with CH_2Cl_2, then 2 vol% ethyl acetate in CH_2Cl_2). The solvent was then removed from the porphyrin-containing fractions to give the product as purple solid (2.13 g, 23 % yield). ^{1}H NMR ($CDCl_3$): 8.88 (d, 8 H, J = 11.5 Hz), 8.60 (s, 2 H), 8.40 (d, 2 H, J = 7.5 Hz), 8.17 (d, 2 H, J = 8.0 Hz), 4.13 (s, 6 H), 3.99 (s, 6 H), -2.90 (s, 2H). ^{13}C NMR ($CDCl_3$): See Fig. S4. MALDI-ToF MS: *m/z* 1026.9 (Calcd *m/z* 1026.2 for M^+).

5,15-bis(phthalic acid)-10,20-bis(*p*-hydroxy-tetrafluorophenyl)porphyrin (2). The tetramethyl ester (1.2 g, 1.17 mmol) was dissolved in THF (30 mL) and combined with a solution of NaOH (5 g) in water (10 mL). The mixture was split into two 20-mL microwave vials and microwaved at 130 °C for 1 h. After cooling down, the THF was removed from each vial under reduced pressure and water (10 mL) was added to each vial. The resulting mixture was then further microwaved at 130 °C for 1 h. Concentrated HCl was slowly added dropwise to the cooled reaction mixture to precipitate the crude product. This solid was filtered, washed with water (100 mL), redissolved in a 1:1 v/v mixture of acetone and methanol (20 mL), then filtered again. The filtrate was evaporated to dryness to give the product as a dark purple solid (929 mg, 82 % yield). ^{1}H NMR (DMSO-d_6): 9.23 (s, 4 H), 8.92 (s, 4 H), 8.64 (s, 2 H), 8.49 (s, 2 H), 8.29 (s, 2 H), -3.06 (s, 2 H). The ^{13}C NMR spectrum of this compound couldn't be obtained due to low solubility. MALDI-ToF MS: *m/z* 966.8 (Calcd *m/z* 966.1 for M^+).

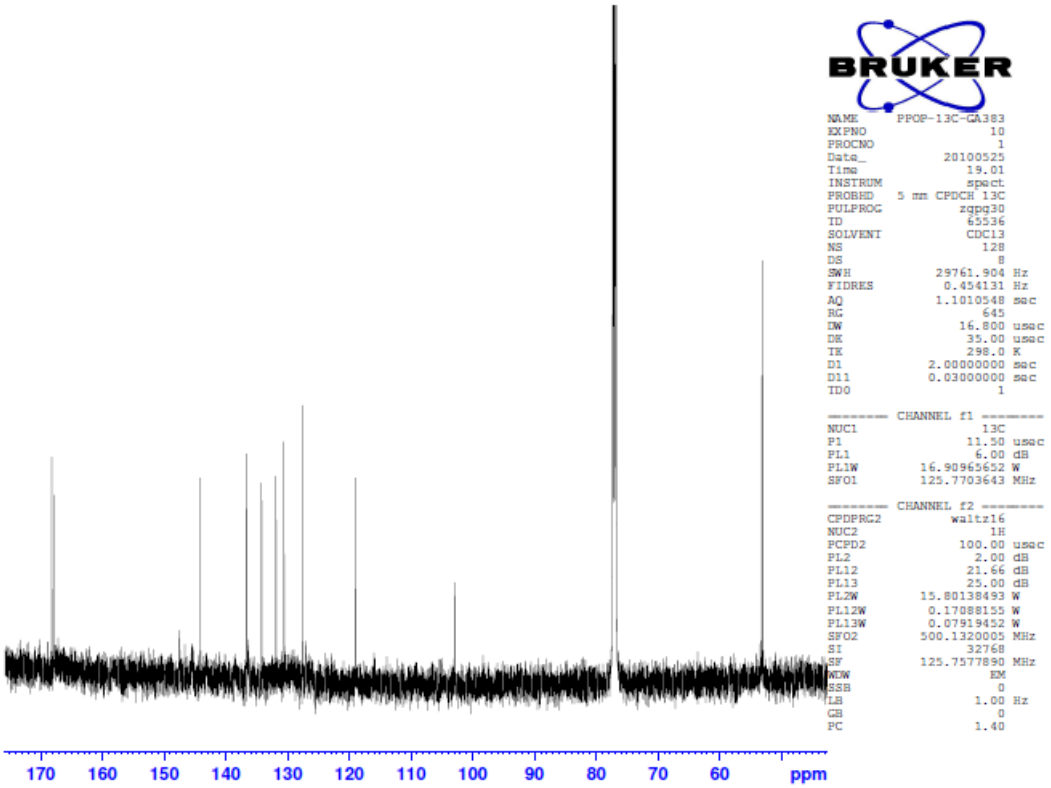

Fig. S4. ^{13}C NMR ($CDCl_3$) of 5,15-bis(dimethyl phthalate)-10,20-bis(pentafluorophenyl)porphyrin.

5,15-bis(phthalic anhydride)-10,20-bis(*p*-hydroxy-tetrafluorophenyl)porphyrin (3). The bis(phthalic acid)porphyrin **2** (900 mg, 0.93 mmol) was dissolved in acetic anhydride (20 mL) in a 20-mL microwave vial. This solution was microwaved at 100 °C for 1 h. The solvent was removed from the reaction mixture under high vacuum to give the product as a purple solid (865 mg, 99 % yield). ^{1}H NMR ($CDCl_3$): 8.89 (s, 4 H), 8.86 (s, 2 H), 8.81 (s, 4 H), 8.75 (t, 2 H), 8.45 (t, 2 H), -2.85 (s, 2H). ^{13}C NMR ($CDCl_3$): See Fig. S5. MALDI-ToF MS: *m/z* 931.2 (Calcd *m/z* 930.1 for M^+).

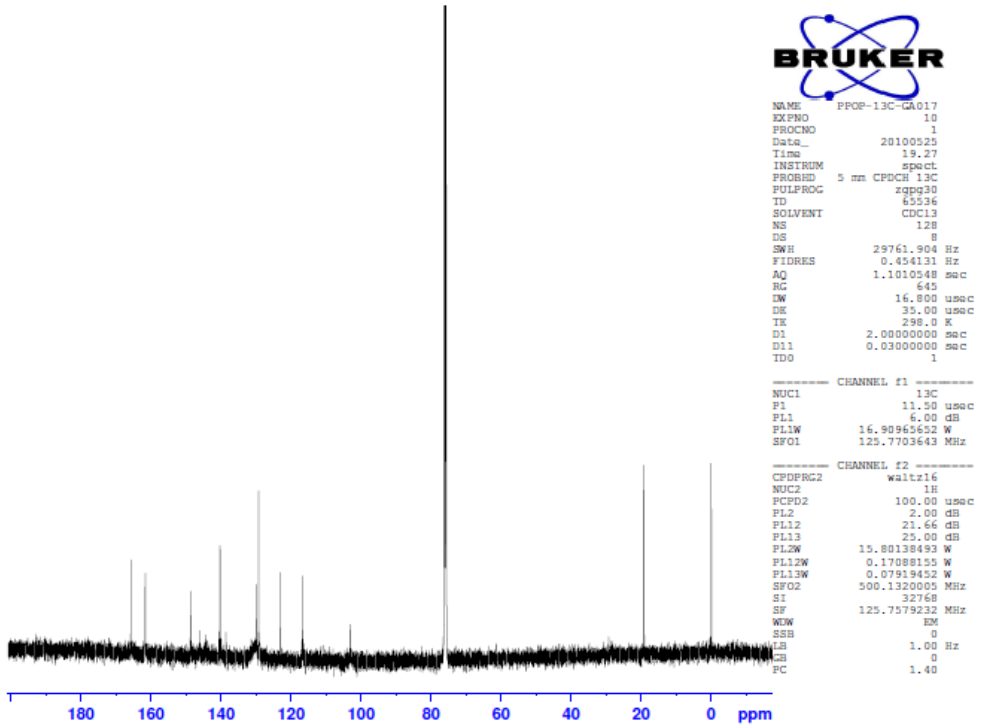

Fig. S5. ^{13}C NMR ($CDCl_3$) spectrum of **3.**

Fb-PPOP. In a 25-mL round-bottom flask equipped with a magnetic stir bar, the porphyrin **3** (200 mg, 0.22 mmol) was dissolved in propionic acid (8 mL) and heated to 150 °C. A solution of the tetraamine **1** (40 mg, 0.11 mmol) in propionic acid (3 mL) was slowly added dropwise and the solution refluxed for 2 days and then cooled to room temperature. The reaction mixture was filtered, washed with DMF and air dried on filter paper. Removal of solvent under vacuum at 120 °C gave a purple solid (160 mg, 70 % yield). Anal.: Calcd for $(C_{121}H_{52}F_{16}N_{12}O_{12})_n$: C, 66.92; H, 2.51; N, 7.74. Found: C, 62.23; H, 3.05; N, 7.55.

A potential concern in using porphyrin **3** in this reaction is the potential susceptibility of the *m*-fluoro group to undergo substitution by primary amines.[S4] However, this displacement from C_6F_5-substituted porphyrins has to be carried out in refluxing or microwave-irradiated DMF or NMP;[S4] in contrast, the ring-opening of anhydride by amine is know to occur readily at room temperature.[S5] In addition, because we carried out the PPOP synthesis in propionic acid, we expected very little amine will be available for fluoro displacement to make this a major concern. By FT-IR analysis, the formation of the diimide can be observed, indicating that the primary amines are largely reacting with the anhydride, as desired. Whether substitution at the fluoro group is occurring to a small degree is difficult to tell given the heterogeneous nature of our materials.

Fe-PPOP. In a 25-mL Schlenk flask equipped with a magnetic stir bar, **Fb-PPOP** (100 mg) and $FeCl_2$ (150 mg, 20 equiv to porphyrin) were placed under N_2 and dry DMF (10 mL) was added by syringe. The reaction mixture was heated at 120 °C for 2 days before being cooled to room temperature. The reaction flask was opened to air, LiCl (100 mg) was added, and the reaction mixture was stirred overnight. The solid product was filtered and washed with DMF (50 mL) and water (50 mL). Drying under vacuum at 120 °C gave a dark solid (103 mg). Anal.: Calcd for $(C_{121}H_{52}F_{16}N_{12}O_{12}Fe_2Cl_2)_n$: C, 61.83; H, 2.14; N, 7.15. Found: C, 56.15; H, 3.05; N, 7.37.

Mn-PPOP. In a 25-mL Schlenk flask equipped with a magnetic stir bar, **Fb-PPOP** (100 mg) and $MnCl_2{\cdot}4H_2O$ (150 mg, 20 equiv to porphyrin) was placed under N_2 and dry DMF (10 mL) was added by syringe. The reaction mixture was heated at 120 °C for 2 days before being cooled to room temperature. The reaction flask was opened to air, LiCl (100 mg) was added, and the reaction mixture was stirred overnight. The solid product was filtered and washed with DMF (50 mL) and water (50 mL). Drying under vacuum at 120 °C gave a dark solid (100 mg). Anal.: Calcd for $(C_{121}H_{52}F_{16}N_{12}O_{12}Mn_2Cl_2)_n$: C, 61.88; H, 2.15; N, 7.16. Found: C, 58.85; H, 3.22; N, 7.62.

A second potential side reaction that may slightly alter the structure/composition of the POP during metallation is the reaction of the PPOP with small amounts of dimethylamine, known to form in prolonged-reflux DMF, which may result in substitution of some small number of the *m*-F group on the porphyrin. While this is certainly possible, we have carried out a test reaction where a free-base porphyrin (tetrakis(2,3,5,6-tetrafluoro-4-hydroxyphenyl)porphyrin, see synthesis below) analogous to **3** is refluxed in DMF over the same period (2 days) used for metallation and found no change in the starting materials via ^{19}F NMR analysis (Figure S6). As such, the reaction of the secondary amine with the meta-F is unlikely to occur to a significant degree. We employed tetrakis(2,3,5,6-tetrafluoro-4-hydroxyphenyl)porphyrin in this reaction instead of the dianhydride monomer **3** due to its susceptibility to react with dimethylamine in the absence of the tetra(amine) co-monomer **1**.

Tetrakis(2,3,5,6-tetrafluoro-4-hydroxyphenyl)porphyrin. In a 2-mL microwave reaction vial were combined commercially available tetrakis(pentafluorophenyl)porphyrin (20 mg, 0.021 mmol), NaOH (700 mg, 17.5 mmol), and a 2/1 v/v mixture of DMSO:H_2O (3 mL). The reaction vial was crimped and microwaved at 130 ºC for 1 h. After being cooled to room temperature, the reaction mixture was neutralized with 0.1 M aqueous HCl and extracted with CH_2Cl_2 (5 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness to afford a solid purple powder which is used as isolated. MALDI-ToF MS: *m/z* 966.8 (Calcd *m/z* 966.1 for M^+). ^{19}F NMR (CD_3OD): see Figure S6.

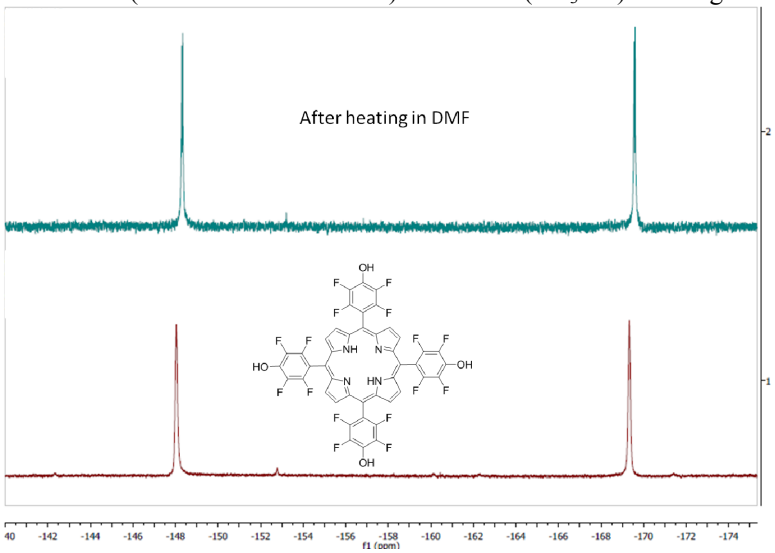

Fig. S6. ^{19}F NMR spectra of as-synthesized tetrakis(2,3,5,6-tetrafluoro-4-hydroxyphenyl)porphyrin in CD_3OD before (bottom), and after heating in DMF for 2 days at 120 °C (top).

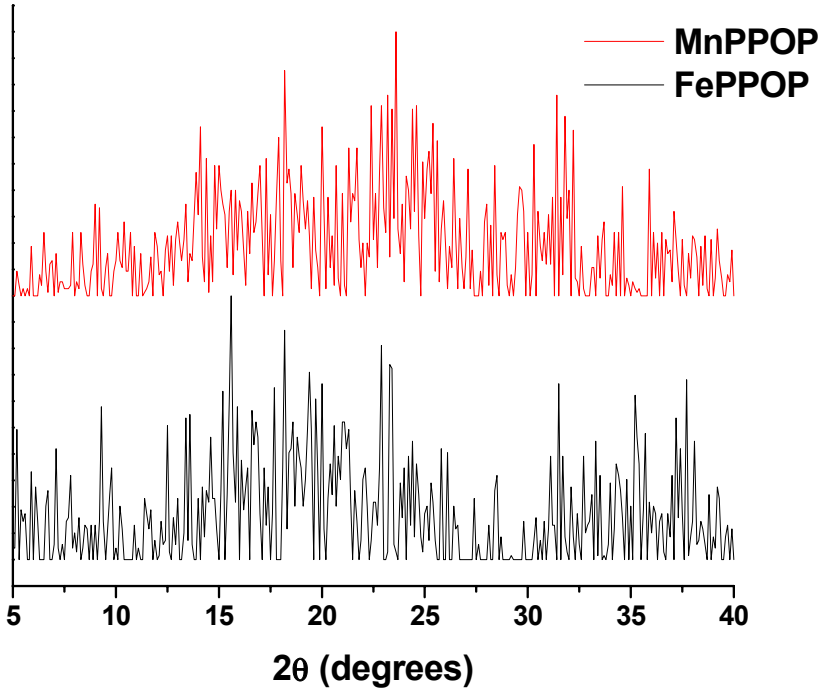

Fig. S7. PXRD patterns of activated (heated under vacuum at 120 °C for 24 h) samples of **Mn-PPOP** and **Fe-PPOP**. The observed patterns exhibit only noise, indicating that there was no formation of crystalline metal nanoparticles.

IV. Catalytic reactions

Procedure for styrene epoxidation reaction. Stock solutions in acetonitrile were made of styrene (1.15 M) and biphenyl (internal standard, 0.06 M). 2-(*Tert*-butylsulfonyl)iodosylbenzene (1 g, ~5000 equiv) was regularly added to the solution in 15 portions over 500 minutes. After the oxidant addition, the resulting mixture was placed on a shaker (Thermolyne Maxi-Mix III) to mix the reaction. Aliquots (0.1 mL) were periodically taken and passed through a silica plug (0.5 cm × 3 cm) and eluted with methylene chloride (5 mL). Gas chromatography analysis of the eluted aliquot was carried out using the following method: initial temperature = 60 °C, initial time = 4 minutes, ramp = 10 °C/min, final temperature = 190 °C, final time =1 minute. Data are shown in Fig. 3.

After the reaction, the residual catalyst was washed with methanol and dried under vacuum before being analyzed by ICP-OES for metal content:

	Pristine	**After catalysis**
Fe-PPOP	3.6 wt% Fe	3.5 wt % Fe
Mn-PPOP	2.8 wt% Mn	2.4 wt% Mn

Procedure for recycling study. Into a 20-mL vial equipped with a Teflon-lined screw-cap were combined acetonitrile (8 mL), biphenyl stock (1 mL, 65 equiv), styrene stock (1 mL, 11,000 equiv), and **M-PPOP** catalyst (1 mg, 1 equiv). 2-(*Tert*-butylsulfonyl)iodosylbenzene (1 g, 5000 equiv) was added in 5 portions over 1 hour. The mixture was placed on a shaker and aliquots taken periodically as described above. After a cycle of catalysis, the **M-PPOP** solids were rinsed thoroughly with methanol, allowed to dry, then reused. Data are shown in Fig. 5.

Procedure for oxidation of cyclohexane. Into a 20-mL volumetric flask were combined cyclohexane, biphenyl, and CH_2Cl_2 to make a stock solution 1 M in cyclohexane and 0.06 M in biphenyl. Into a 4-mL vial equipped with a Teflon-lined screw-cap were combined this stock solution (0.5 mL, 800 equiv of cyclohexane to the metal) and **M-PPOP** catalyst (1 equiv of metal). 2-(*Tert*-butylsulfonyl)iodosylbenzene (200 mg, 100 equiv to the metal) was added to the solution in 1 portion and the mixture was placed on a shaker overnight. In the morning, an aliquot (0.1 mL) was taken and passed through a silica plug (0.5 cm × 3 cm) and eluted with methylene chloride (5 mL). Gas chromatography was carried out using the following method: initial temperature = 40 °C, initial time = 4 minutes, ramp = 10 °C/min, final temperature = 180 °C, final time =3 minutes. Data are shown in the text before the Conclusion section.

In a separate experiment, the aforementioned cyclohexane/biphenyl stock solution (10 mL, 16,000 equiv of cyclohexane to the metal) and **M-PPOP** catalyst (1 equiv of metal). 2-(*Tert*-butylsulfonyl)iodosylbenzene (350 mg, 1000 equiv to the metal) was added to the solution in 7 portion over 2 hours and the mixture was placed on a shaker. Aliquots (0.1 mL) were periodically taken and passed through a silica plug (0.5 cm × 3 cm) and eluted with methylene chloride (5 mL). Gas chromatography was carried out using the following method: initial temperature = 40 °C, initial time = 4 minutes, ramp = 10 °C/min, final temperature = 180 °C, final time =3 minutes. Data are shown in Fig. S8.

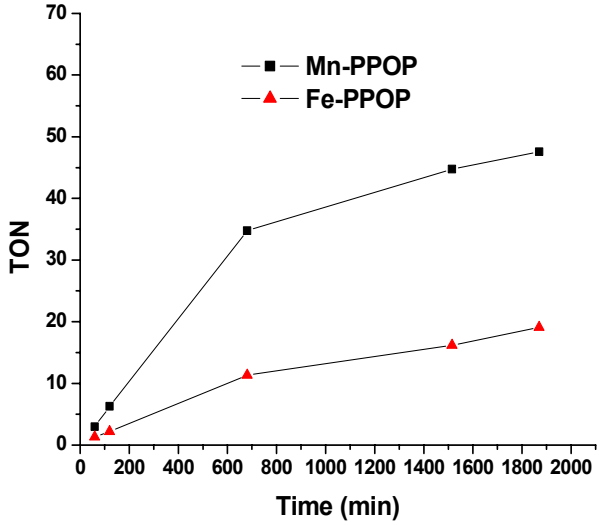

Fig. S8. Reaction profile of the oxidation of cyclohexane by 2-(*tert*-butylsulfonyl)iodosylbenzene, catalyzed by **M-PPOP**s (0.1 mol% catalyst).

VI. References

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