Supporting Information

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Adaptive organic nanoparticles of a Teflon coated iron (III) porphyrin catalytically activate dioxygen for cyclohexene oxidation

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Background

5,10,15,20-tetrakis-(2,3,4,5,6-pentafluorophenyl)porphyrinato iron(III) chloride, [Fe(III)TPPF$_{20}$]Cl is found to be catalytically active for the oxidation of olefins using synthetic oxygen sources, but not with the molecular oxygen, in solution phase reactions.[1] Gray et al. reported significantly different oxidation chemistry for a derivative of [Fe(III)TPPF$_{20}$]Cl wherein the eight β pyrrole positions are also halogenated.[2] The difference in the catalytic oxidation of perhalogenated porphyrins arises from both distortions in the otherwise planar macrocycles and electronic effects. When the β positions of [Fe(III)TPPF$_{20}$]Cl are chlorinated the catalytic oxidation of ethylbenzene using oxygen at 100 °C is increased, but not the stability towards the oxidative degradation of the catalyst. Stability increases when the catalyst is linked to polystyrene.[3] The catalytic activity of the metalloporphyrin is affected by the nature of the counter ion and the solvent in which the porphyrin is dissolved.[4] Fe(III)TPPF$_{20}$ was reported to be inactive for olefinic epoxidation when dissolved in acetonitrile but becomes active when methanol or another alcohol is added to the aprotic solvent.[1]

Experimental Section

Materials and instrumentation

5,10,15,20-tetrakis-(2,3,4,5,6-pentafluorophenyl)porphyrinato iron(III) chloride, [Fe(III)TPPF$_{20}$]Cl, cyclohexeneoxide (98%), 2-cyclohexene-1-ol (95%), 2-cyclohexene-1-one (95%), triethylene glycol monomethyl ether (PEG$_{164}$), tetrahydrofuran (THF, 99.9% anhydrous), methanol (99.9% anhydrous), N,N-dimethylformamide (DMF, 99.8%), and N,N-diisopropylethylamine (DIEPA, 99.5%) were purchased from Aldrich Chemical Co. HPLC grade dichloromethane, 30% H_2O_2, toluene and cyclohexene were purchased from Fisher Scientific Co. HPLC grade acetonitrile was purchased from J.T baker, and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-decanethiol (≥ 99.0%) was purchased from Fluka. Nanopure water was obtained by using Barnstead Nanopure water system. D_2O (99.6%) was obtained from Cambridge Isotope laboratories Inc. The oxidation products of cyclohexene were analyzed using an Agilent 5975 series GC-MS with a HP-5 column (HP-5MS 30 m x 0.250 mm, 0.25 micron nominal, 5% phenyl methyl siloxane). Electronic spectra were taken on Cary Bio-3 UV-visible spectrophotometer. A Precision Detector PD2000DLS Cool-Batch dynamic light scattering (DLS) instrument was used in batch mode at 25 ^{o}C to determine particle size. A Fisher SF15 sonicator was used for nanoparticle preparation. A Jeol 2100 was used to carry out Electron Microscopy studies.

Preparation of catalyst Fe(III)TPPF$_{84}$

Similar to our previous report,[5] 27.08 mg (56.4 µmol, 6 equivalents), of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-decanethiol were mixed in 2 mL DMF and 500 µL (0.37 g, 2.9 mmol) DIPEA was added under a nitrogen atmosphere. The solution was stirred at room temperature for 15 min. and then 10 mg (9.4 µmol) of [Fe(III)TPPF$_{20}$]Cl was added and the solution was further stirred at room temperature for 2 h. The product was then precipitated, filtered, and washed with distilled water and CH_2Cl_2. The precipitates were dried under vacuum, to yield 83% (22.67 mg, 7.8 μmol) of the product.

Preparation of the nanoparticles of Fe(III)TPPF$_{84}$ porphyrin

For the preparation of Nanoparticles of Fe(III)TPPF$_{84}$ we use our previously reported method.[6] A 0.4 mL portion of 1 mM stock solution of metalloporphyrin in THF was mixed with 0.2 mL PEG$_{164}$ in a 10.0 mL vial. 5.0 mL nanopure water was then added to this mixture while sonicating over a time period of 60 seconds and then the solution was further sonicated for another 2-3 minutes. The pH of the nanopure water was adjusted to 6.5-7.0, because the formation of the nanoaggregates, their size, stability, and their catalytic activity is highly pH dependent. The prepared nanoparticles are stable and are stored in refrigerator at ca. 4 ^{o}C.

Transmission Electron Microscopy (TEM):

ONP of Fe(III)TPPF$_{84}$ and Fe(III)TPPF$_{20}$ were dispersed onto carbon coated gold and copper grids (TED Pella and Electron Microscopy Sciences, respectively). The samples were imaged at 200KV using a Jeol 2100. Energy Dispersion Analysis was carried out to ensure that the ONP contained iron metal.

Reaction Details: Oxidation of cyclohexene by air/H_2O_2/Pure O_2

Solution phase catalysis

A 1 mM stock solution of Fe(III)TPPF$_{84}$ was prepared in THF. For reactions using the O_2 in air or with H_2O_2 as oxidant, 9 mL screw capped vials were used. 400 μL (0.4 μmol) of the porphyrin solution were mixed with 2.5 mL of methanol: acetonitrile (1:3) to make the final concentration of 0.13 mM. 25 μL of cyclohexene was added, the vial was tightly capped, and the reaction mixture stirred for 24 h. Here the 6 mL air in the vial contains ca. 1.3 mL O_2 (53 μmol), porphyrin: substrate: O_2 in air = 1:600:1400 equivalents. The same conditions were used for the reactions using H_2O_2 oxidant, but 40 µL (10.7 µmol) of 30% H_2O_2 were added. The ratio of the porphyrin: substrate: H_2O_2 = 1: 600: 1000 equivalents. For the reaction using O_2 as oxidant, 400 µL (0.4 µmol) of porphyrin solution were mixed with 2.5 mL of methanol: acetonitrile (1:3) and 200 µL of cyclohexene in a 25 mL pear-shaped flask fitted to a 125 mL separatory funnel filled with O_2 at 1 atm (filled by flushing the vessel three times with O_2, 5.3 mmol), and then O_2 was added by opening the stopcock. The ratio of the porphyrin: substrate: O_2 = 1: 4800: 13000 equivalents. The reactions were run for ca. 24 h. After 24 h reactions were quenchend by placing the vials in ice bath. For oxygen reactions, the pear shaped flask was cooled in an ice bath for about 30 minutes with the stopcock to the separatory funnel open, and the separatory funnel heated with hot air to condense all volatile organic species. 20 µL (1.88×10^{-4} moles) of toluene was then added to the condensate as an internal standard, and 4 µL of this solution was then diluted with 1 mL CH_2Cl_2. 2 µL of this diluted sample was then injected into the GC-MS for the analysis of the oxidation products of cyclohexene. All reactions were stirred using a magnetic stirring bar and were run a minimum of four times and the reported data represents the average of these reactions.

Nanoparticle catalysis

For reactions using 21% O_2 in air or with H_2O_2 as oxidant, 2.5 mL of the porphyrin ONP stock solution (70 µM, 1.75×10^{-7} moles of porphyrin) were mixed in a 9 mL screw capped vial (ca. 6.5 mL air) with 25 µL of cyclohexene. 40 µL (10.7 µmol) of 30% H_2O_2 was added slowly to the reaction mixture over the course of 40 min. The ratio of the porphyrin: substrate: H_2O_2 = 1: 1400: 2200 equivalents while for O_2 in air as oxidant, porphyrin: substrate: O_2 in air= 1: 600: 1500. The reaction mixture was then stirred for ca. 24 h. After the reaction the vials were cooled in an ice bath for 30 min to condense the volatile species. The 2.6 mL reaction mixture was then extracted thoroughly once with 2.8 mL CH_2Cl_2 and the layers were allowed to separate. The water fraction and some of the organic fraction was then removed to leave a total volume of 2.0 mL (assures the same volume for every assay). 20 μL of toluene (1.88 x 10^{-4} moles) was then added to the 2.0 mL extraction as an internal standard, whereupon 4.0 μL of this solution was diluted into 1.0 mL CH_2Cl_2 and 2.0 μL of this solution was then injected into the GC-MS for the analysis. The same reaction conditions described above were used for the reactions using O_2 as oxidant. The ratio of porphyrin: substrate: O_2 = 1: 11300: 29000 equivalents. The 2.7 mL reaction volume was then extracted once with 8.0 mL CH_2Cl_2 and the layers were allowed to separate. The water fraction and some of the organic fraction was then removed to leave a final volume of 6.0 mL (assures the same volume for every assay). 20 μL of toluene was then added to this extraction as an internal standard, and 4 μL of this solution was then diluted with 1 mL CH_2Cl_2. 2 μL of this diluted sample was then injected into GC-MS for analysis.

Controls for Fe(III)TPPF$_{84}$ in solution: Control experiments in the absence of porphyrin; O_2 does not react with cyclohexene, nor does the porphyrin oxidize cyclohexene without O_2. The amount of cyclohexene recovered in these control reactions after the reaction were over was 185 μL (an average of three experiments). A variety of oxidizing agents such as organic peroxides-t-BuOOH, H_2O_2, iodosylbenzene, persulfates, $KHSO_5$ have been used in metalloporphyrin oxidation reactions but are generally ineffective with the ONP. [7]

Controls for Fe(III)TPPF$_{84}$ ONP: Reactions under elevated temperature and pressure gives no oxidation products, because it increases porphyrin decomposition. The control experiments here also in the absence of ONP, molecular oxygen (O_2), and cyclohexene yield no oxidation products. The other control experiment with ONP (20± 6 nm) of non-fluorinated dodecanethiol iron(III) porphyrin also gives no oxidation product for cyclohexene.

Table S1. Fe(III)TPPF$_{84}$ catalysis of cyclohexene oxidation

Solution^{A} or ONP^{B}	Conditions	% epoxide	% enol	% enone	TON	Comments
Solution and 15-20 nm ONP	21 % O_2 in 6.5 mL air	-----	------	-----	-----	no reaction, almost no decomposition of porphyrin
	H_2O_2, 1 atm	-----	------	-----	----	porphyrin decomposes in 15-20 min
15-20 nm ONP	125 mL O_2, 1 atm,40 ^{o}C or 50 ^{o}C	-----	------	-----	----	24 h, no porphyrin left

Table S1. ^{A}Solution Reactions: 0.4 mL (4 x 10^{-7} mol of porphyrin) of 1 mM catalyst was mixed 2.5 mL of methanol: acetonitrile (1:3) and 0.025mL of cyclohexene to a final concentration of 0.13 mM. For 21 % O_2 in 6.5 mL air as oxidant; porphyrin: cyclohexene: O_2 in air = 1: 600: 1400. While for the reactions using 40μL (H_2O_2 oxidant; porphyrin: cyclohexene: H_2O_2 = 1: 600: 1000. ^{B}ONP Reactions: 15-20 nm diameter ONP suspension (2.5 mL, 70 μM, 1.75 x 10^{-7} mol of porphyrin) mixed with cyclohexene (25 μL). For 21 % O_2 in 6.5 mL air as oxidant; porphyrin: cyclohexene: O_2 in air = 1: 600: 1500 while for the reactions using H_2O_2 oxidant; porphyrin: substrate: H_2O_2 = 1: 1400: 2200.

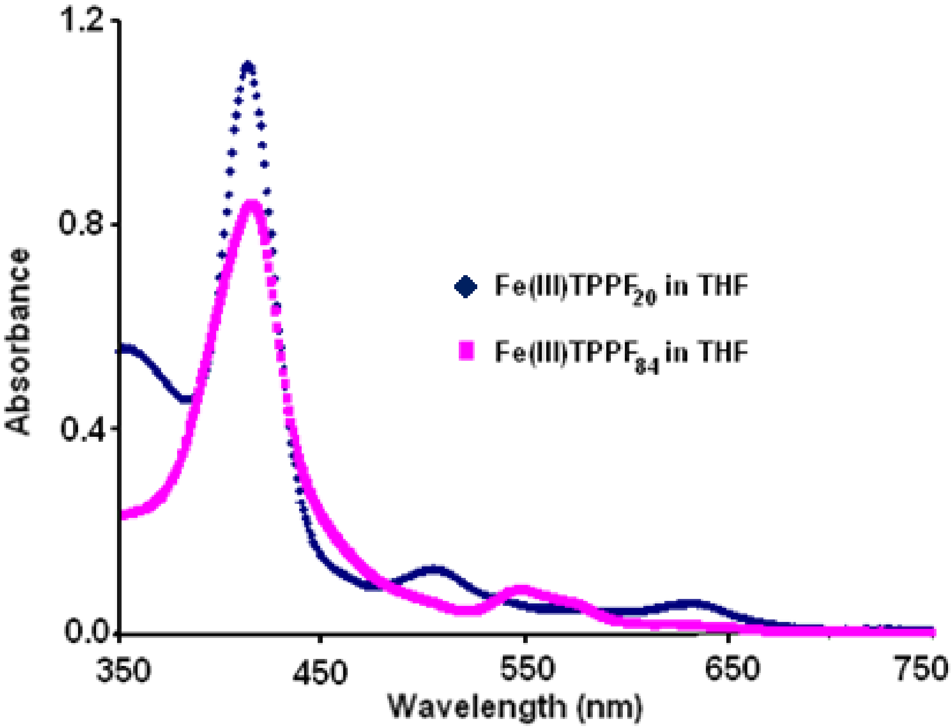
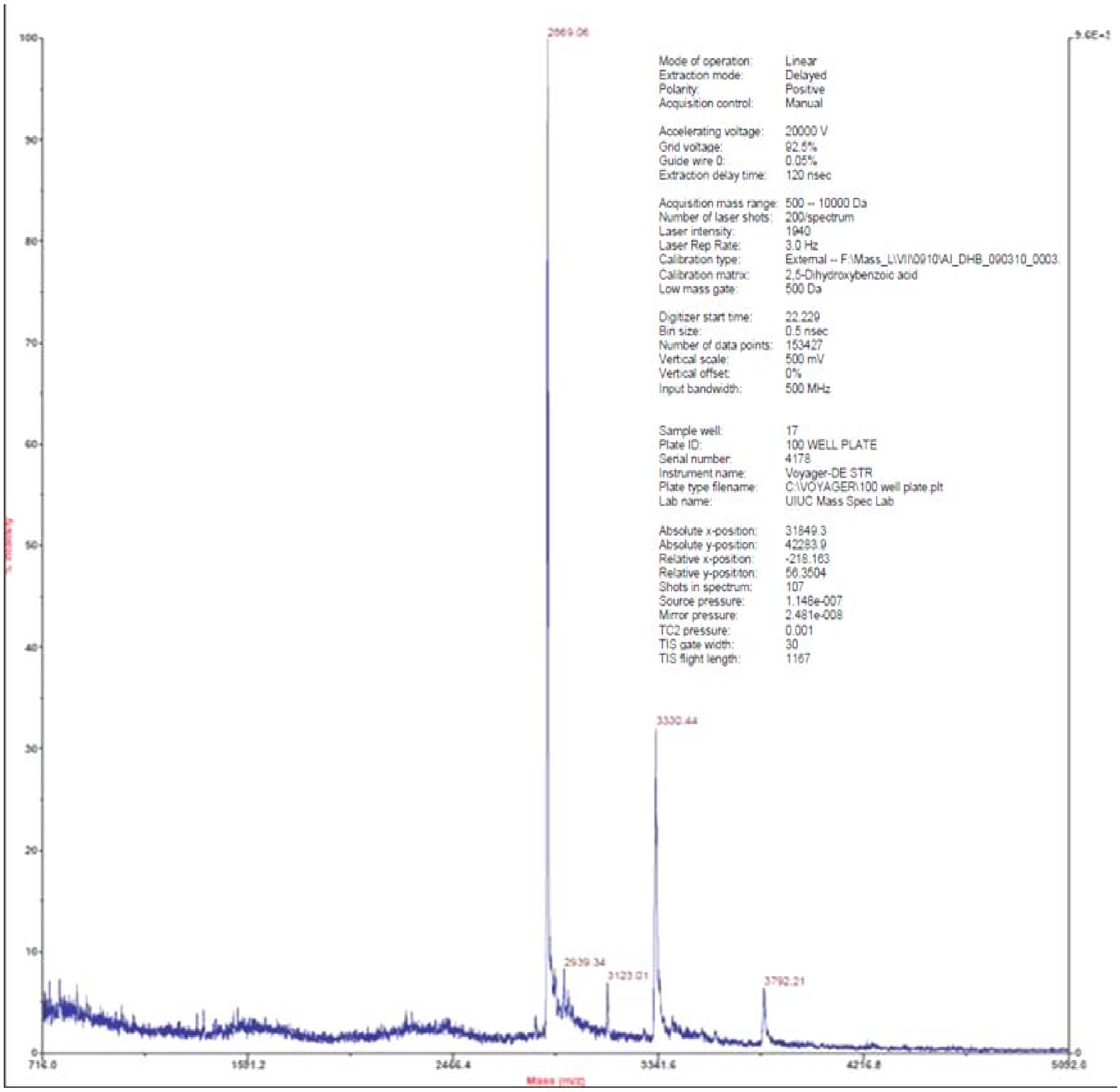


Figure S1: UV-visible spectra of Fe(III)TPPF$_{20}$ and Fe(III)TPPF$_{84}$ in THF. The B (Soret) bands for both Fe(III)TPPF$_{20}$ and Fe(III)TPPF$_{84}$ in THF appears at the same wavelength while the Q-bands for Fe(III)TPPF$_{84}$ are shifted towards the red, which is due to the replacement of an electron withdrawing F-atom on the para position by an electron donating S-atom. There also may be some aggregation of the highly fluorous compound in this solvent, see below.



Mode of operation: Linear
Extraction mode: Delayed
Polarity: Positive
Acquisition control: Manual

Accelerating voltage: 20000 V
Grid voltage: 92.5%
Guide wire 0: 0.05%
Extraction delay time: 120 nsec

Acquisition mass range: 500 -- 10000 Da
Number of laser shots: 200/spectrum
Laser intensity: 1940
Laser Rep Rate: 3.0 Hz
Calibration type: External -- F:\Mass_L\VI\0910\AI_DHB_090310_0003.
Calibration matrix: 2,5-Dihydroxybenzoic acid
Low mass gate: 500 Da

Digitizer start time: 22.229
Bin size: 0.5 nsec
Number of data points: 153427
Vertical scale: 500 mV
Vertical offset: 0%
Input bandwidth: 500 MHz

Sample well: 17
Plate ID: 100 WELL PLATE
Serial number: 4178
Instrument name: Voyager-DE STR
Plate type filename: C:\VOYAGER\100 well plate.plt
Lab name: UIUC Mass Spec Lab

Absolute x-position: 31849.3
Absolute y-position: 42283.9
Relative x-position: -218.163
Relative y-position: 56.3504
Shots in spectrum: 107
Source pressure: 1.148e-007
Mirror pressure: 2.481e-008
TC2 pressure: 0.001
TIS gate width: 30
TIS flight length: 1167

Figure S2: MALDI spectrum of Fe(III)TPPF$_{84}$ porphyrin. The major peak at 2869.06 corresponds to the four substitutions while the peak at 3300.44 corresponds to the five substitutions. The matrix used for MALDI is 2,5- dihydroxybenzoic acid.

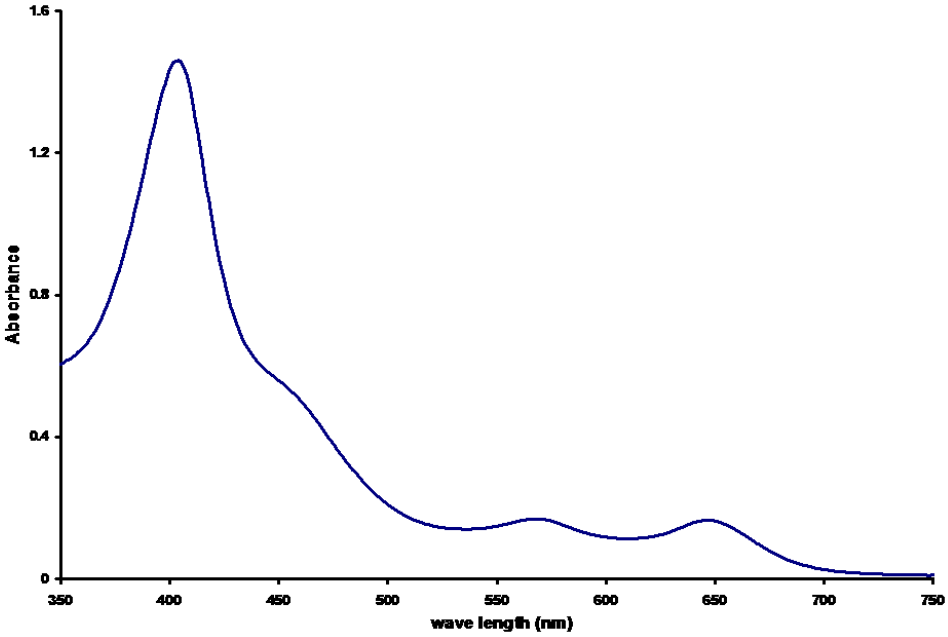


Figure S3: UV-visible spectra of nanoaggregates of Fe(III)TPPF$_{84}$ in THF/water mixed solvent system. The appearance of a shoulder on the red side of the Soret band indicative of J-aggregation of the porphyrin. Generally both types of aggregation J and H exist in the ONP.

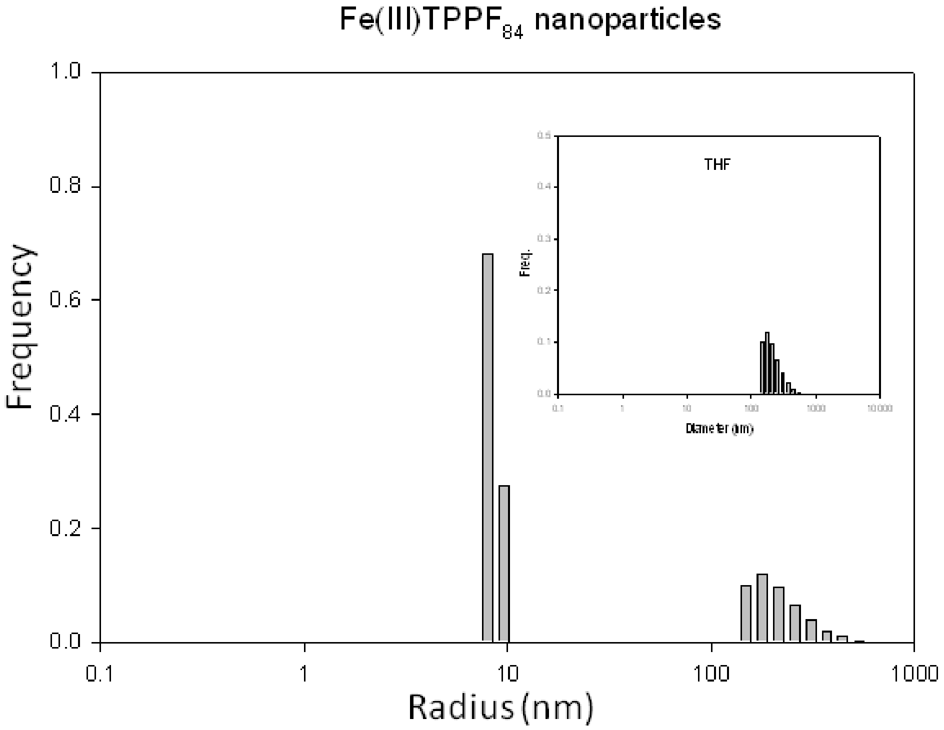


Figure S4: Typical dynamic light scattering data indicating the diameter of the catalytic nanoparticles, 15-20 nm. For miscible solvents, large solvent clusters are typically observed by DLS (4-5% of the total number of observed particles) at around 350-750 nm (inset).

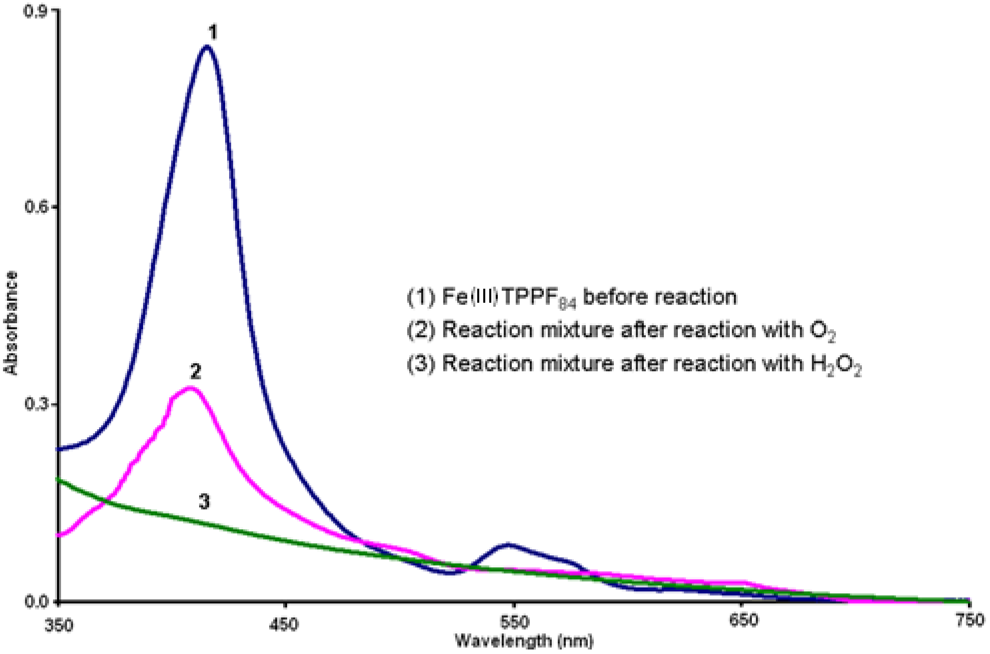


Figure S5: UV-visible spectra of (1) Fe(III)TPPF$_{84}$ in reaction mixture (solution phase) before reaction, (2) 36% left over Fe(III)TPPF$_{84}$ in reaction mixture after reaction with O_2, and (3) reaction mixture after reaction with H_2O_2 shows nearly complete decomposition of the metalloporphyrin.

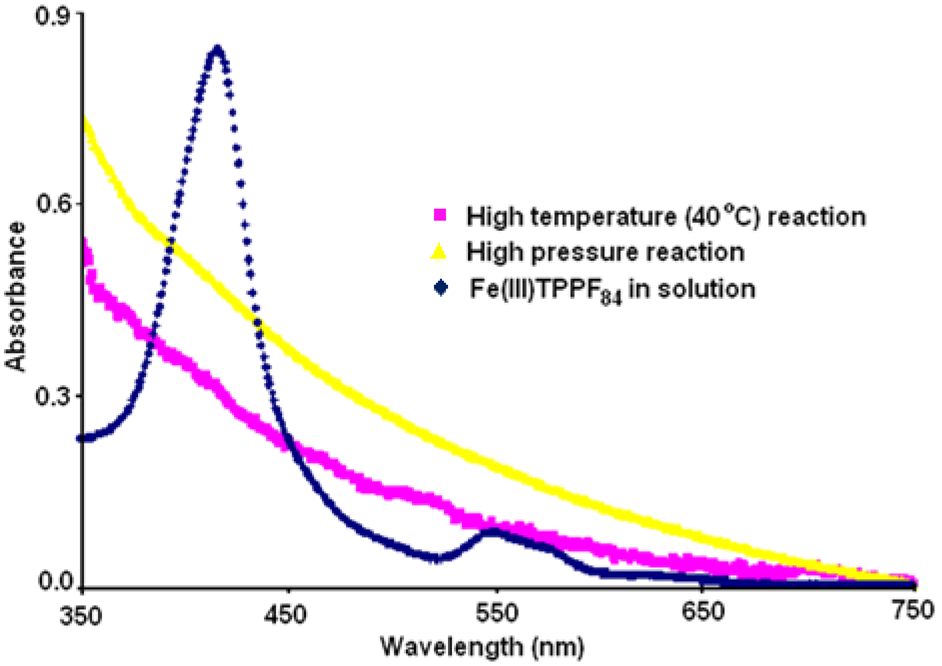


Figure S6: UV-visible spectra of Fe(III)TPPF$_{84}$ before reaction (solution phase) in blue, after reaction at elevated pressure (1.7 atm) in yellow, and after reaction at higher temperature (40 ^{o}C) in purple.

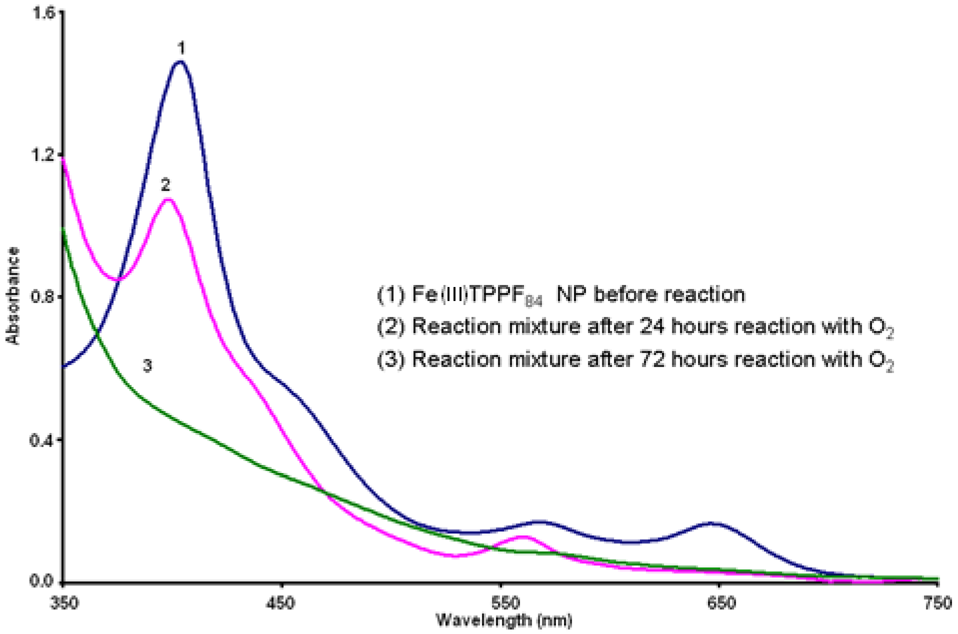


Figure S7: UV-visible spectra of (1) Fe(III)TPPF$_{84}$ ONP reaction mixture before reaction (2) Reaction mixture after 24 h reaction with O_2 shows ca. 26% porphyrin ONP left, and (3) reaction mixture after 72 h reaction with O_2 shows the complete decomposition of the porphyrin ONP in the reaction mixture.

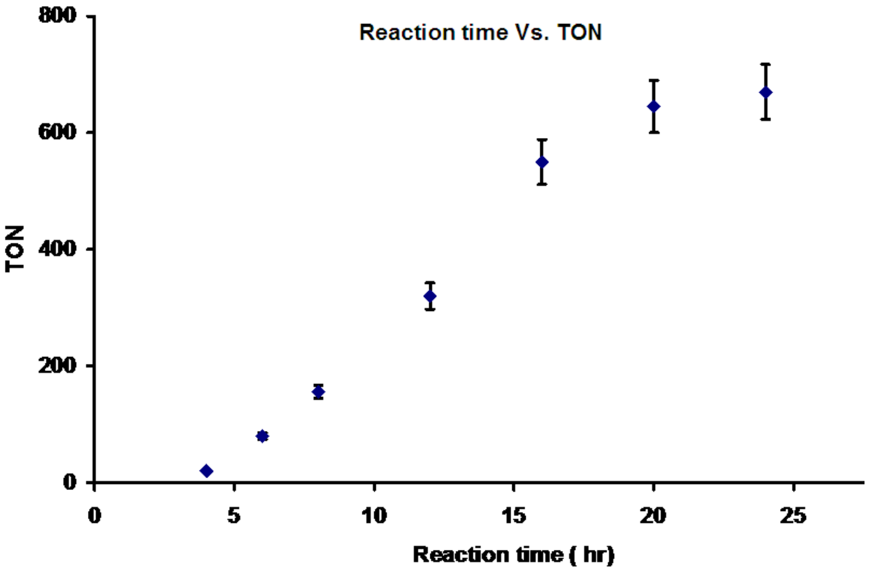


Figure S8: The reaction run time versus TON of product formation, where the error bars represent the average of four different experiments. The half life time ($t_{1/2}$) for the product formation is ca. 14 h. Note the 4-5 h lag phase.

GC of standard mixture solution of cyclohexene, cyclohexene oxide, cyclohex-2-en-1-ol, cyclohex-2-en-1-one, and toluene.

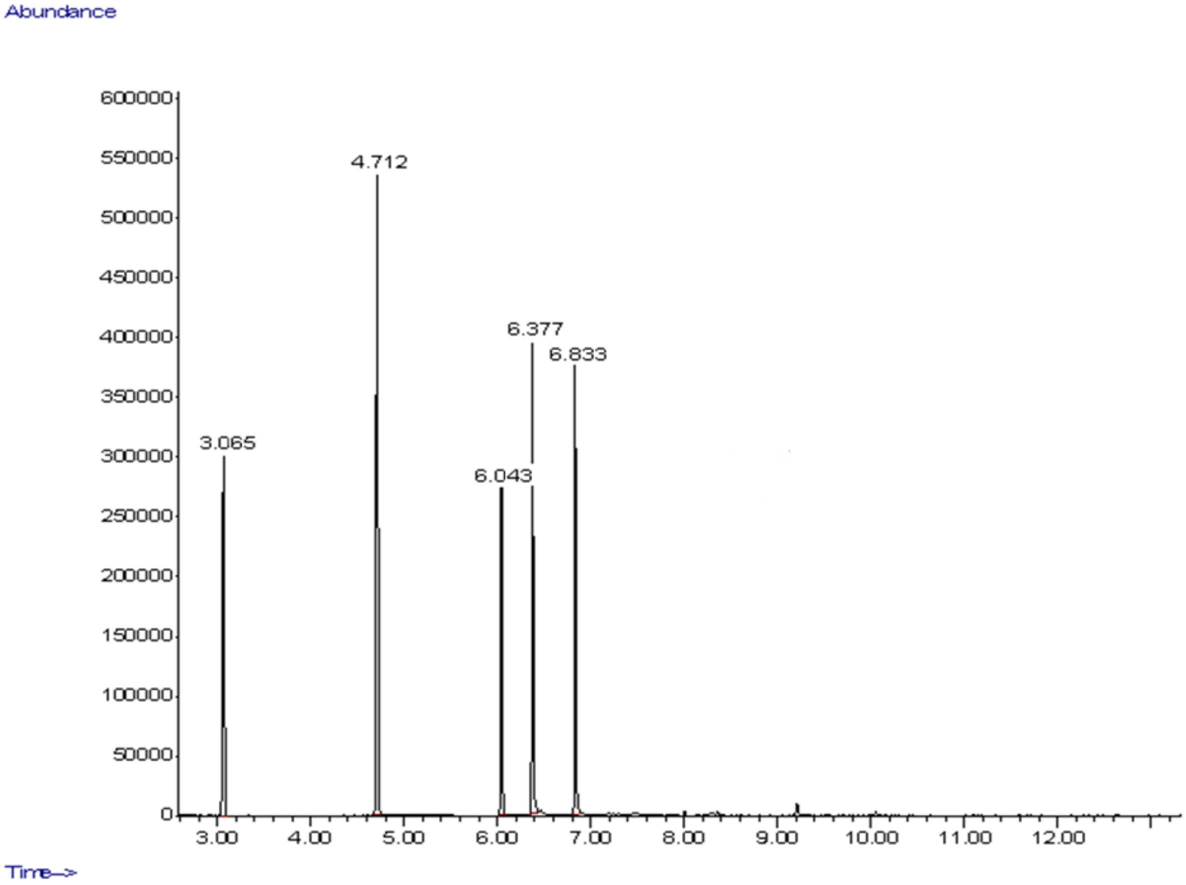


Figure S9: GC of standards: cyclohexene = 3.06 min, toluene = 4.71 min, cyclohexene oxide = 6.04 min, cyclohex-2-en-1-ol = 6.37 min, cyclohex-2-en-1-one = 6.83 min. Mass spectroscopy confirms the identity of each compound. The peak at 9.21 min is because of polysiloxanes from the column.

GC of Fe(III)TPPF$_{84}$ solution phase catalytic reaction using O$_2$ as oxidant

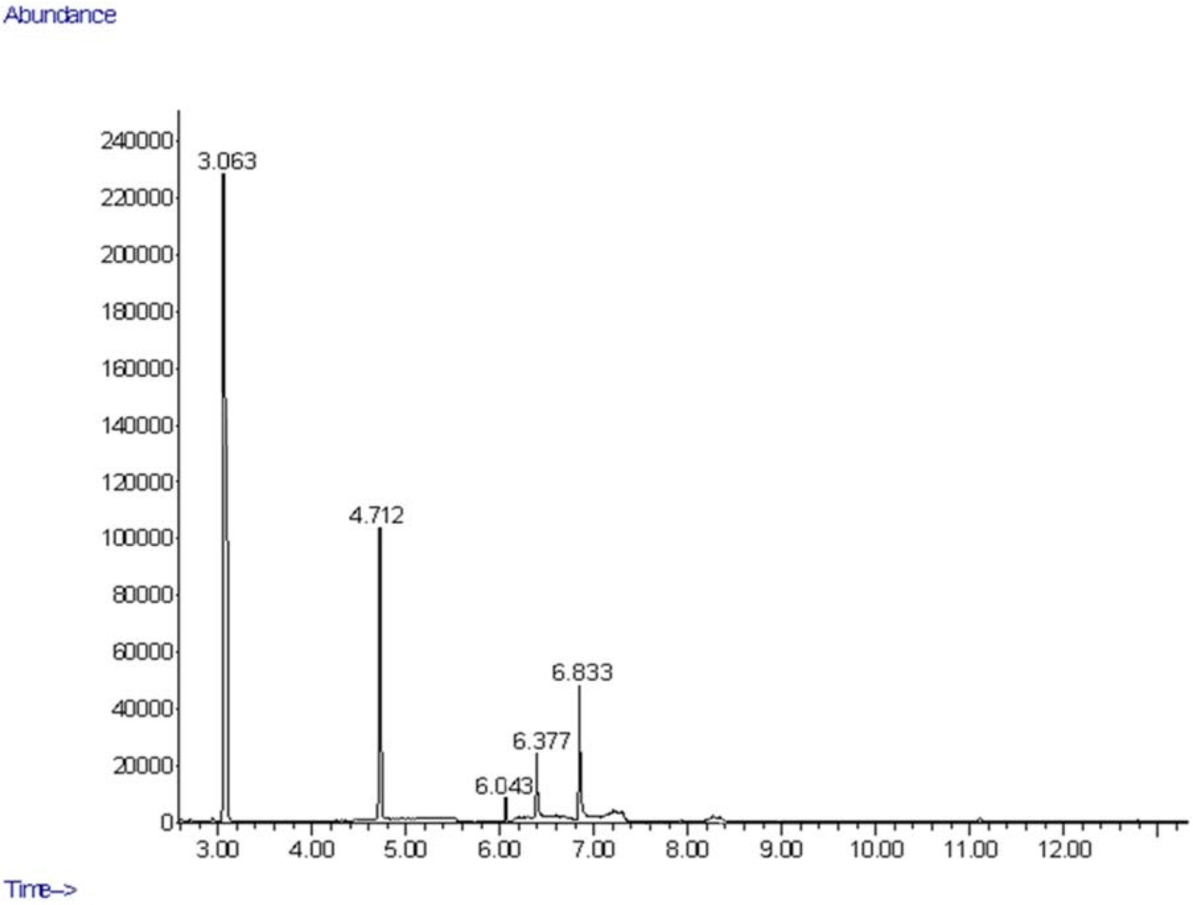


Figure S10: GC of a solution phase reaction using Fe(III)TPPF$_{84}$ catalyst. Retention time of cyclohexene = 3.06 min, toluene =4.71 min, cyclohexene oxide = 6.04 min, cyclohex-2-en-1-ol = 6.38 min, cyclohex-2-en-1-one = 6.83 min. Mass spectrometry confirms the identity of each compound.

GC of Fe(III)TPPF$_{84}$ ONP catalytic reaction using O$_2$ as oxidant

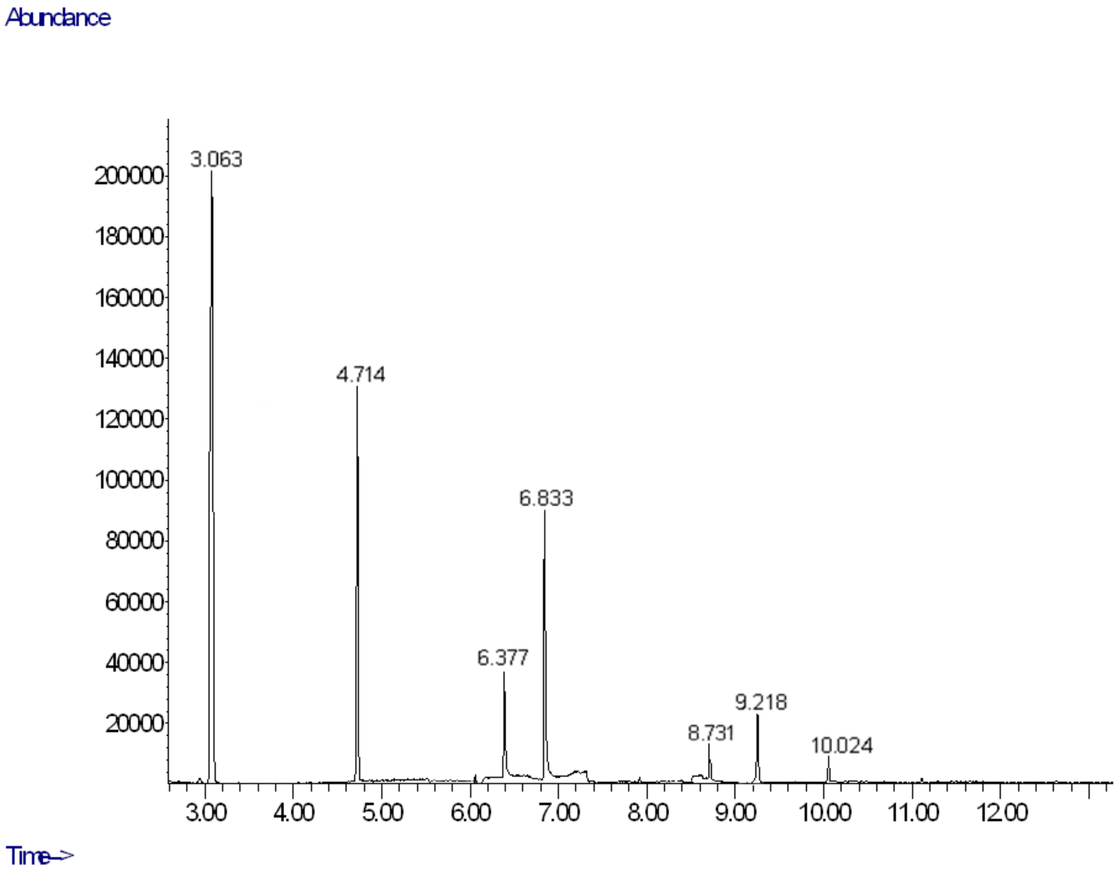


Figure S11: GC of a typical ONP catalytic reaction using Fe(III)TPPF$_{84}$ catalyst. Retention time of cyclohexene = 3.06 min, toluene =4.71 min, cyclohex-2-en-1-ol = 6.37 min, cyclohex-2-en-1-one = 6.83 min. Mass spectrometry confirms the identity of each compound. The peak at 8.73 min is the PEG from the ONP preparation. However the peaks at 9.21 min and 10.02 min are polysiloxane from column.

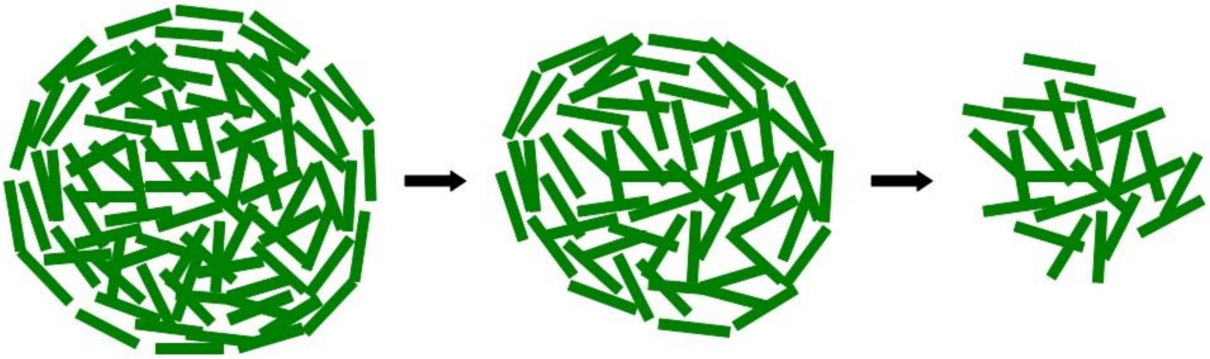


Figure S12. A schematic representation for the onion type mechanism and degradation of porphyrin ONP. The UV-vis changes which indicate the partition of the substrate into the ONP and wtaer. The diameter of the ONP increases with the binding of the substrate[8] and in this case not. The cartoon here represents the trends of decrease DLS shows that ONP decrease in size as the reaction progress.

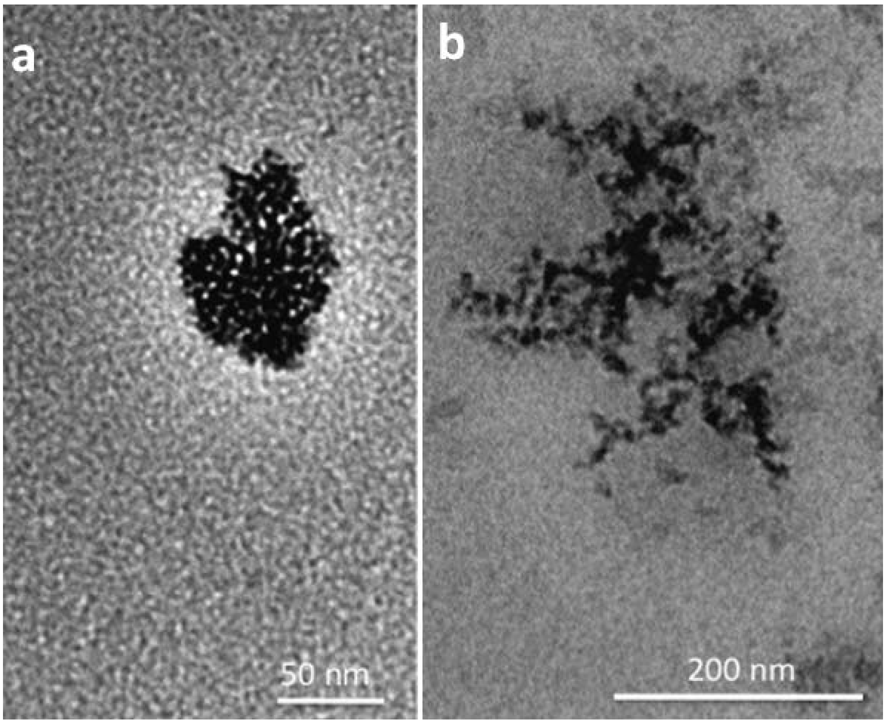


Figure S13: TEM images of ONP of Fe(III)TPPF$_{84}$ a) before reaction and b) after reaction. Before reaction the size of ONP on carbon coated gold and copper grid was found to be ca. 25 nm diameter which gets dispersed into their subdomains after reaction. EDAX shows that these are not nanoparticles of FeO.

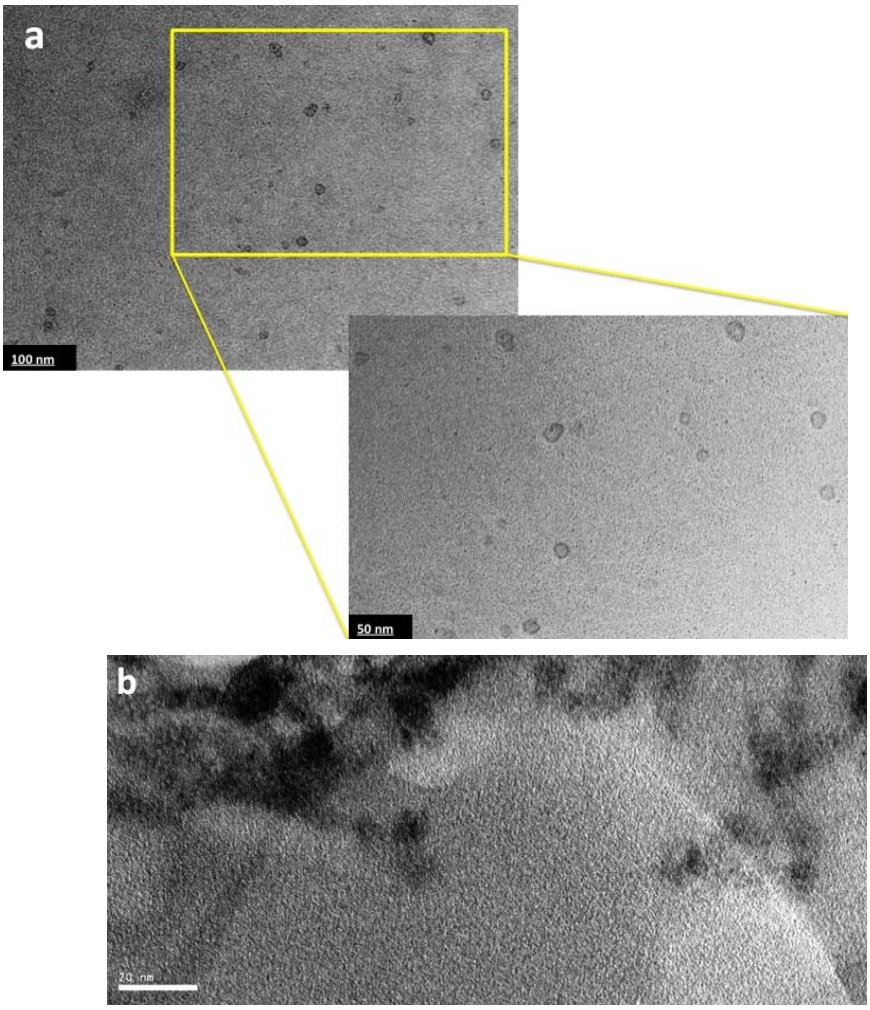


Figure S14: TEM images of ONP of Fe(III)TPPF$_{20}$ (a) before reaction and (b) after oxidation reaction. The size of ONP was found to be ca. 20 nm diameter before oxidation reaction and no ONP was observed after the reaction. These are also not the nanoparticles of FeO.

The standardized response of the GC (area) for each component in CH_2Cl_2 (2.0 mL total volume) is reported in Table S2.

Table S2: The standard response of GC area for each component

Compounds	Response Factor	Ratio to toluene	Volume used	Corrected area	Moles injected
Cyclohexene	1.30	1.76	20 µL	4040215	7.52×10^{-10}
Toluene	2.29	1	20 µL	6782091	7.17×10^{-10}
Cyclohexene oxide	1.00	2.29	20 µL	3109662	7.54×10^{-10}
Cyclohex-2-en-1-ol	1.21	1.90	20 µL	3877485	7.77×10^{-10}
Cyclohex-2-en-1-one	1.86	1.86	20 µL	4014942	7.88×10^{-10}

A response factor of 1.90 for the combined products was used to calculate the TON for all reactions. The TON for each reaction was calculated based on the corrected area for each peak using the internal standard (toluene) and the response factor obtained in GC-MS.

For O_2 reactions:

The 2.7 mL reaction mixture volume was extracted once with 8.0 mL CH_2Cl_2 and the layers were allowed to separate. The water fraction and some of the organic fraction was removed to leave a total volume of 6.0 mL of CH_2Cl_2 (this assures the same volume for every reaction assay). To this volume was added 20 µL toluene. 4.0 µL of the extract was diluted into 1.0 mL dichloromethane and then 2.0 µL of this solution is injected into the GC-MS.

TON = moles products/moles porphyrin = $5.31 \times 10^{-4} / 1.75 \times 10^{-7} = 3037$, Since the porphyrin slowly decomposes in the reaction mixture, TON is for reactions run until [porphyrin] < 0.2 µM, ca. 24 h.

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