

A new Organopalladium compound containing four Iron (III) Porphyrins for the selective oxidation of alkanes/alkenes by *t*-BuOOH

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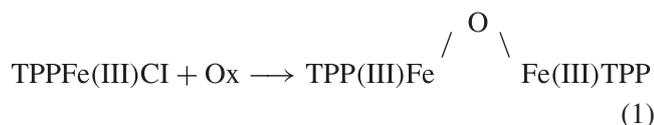
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Abstract. Two iron(III) tetraphenyl porphyrin catalytic units are connected by an azo-link to form the dimeric compound **A**. The compound **A** was then reacted with Pd²⁺ to make a tetrameric iron(III) porphyrin complex **B** with all four iron(III) catalytic sites open to the substrates and reactants. Both the compounds were characterized spectroscopically and the results of homogeneous oxidation of some alkanes and alkenes with *t*-BuOOH in presence of catalytic quantities of **A** and **B** have indicated remarkable improvement in selectivity and efficiency of **A** over the monomeric catalyst and **B** over **A**.

Keywords. Iron(III) porphyrin; catalysis; *t*-BuOOH; cycloalkenes/alkanes.

1. Introduction

The importance of metalloporphyrin-catalysed oxidation reactions in biology and their potential as industrial catalysts have led to a considerable volume of work in these reactions.¹ The properties of such catalysts are tuned by attaching different substituents to the macro cycle.² Such catalysts are then successfully used for selective oxidation reactions of various organic substrates by peracids and hydroperoxides.³ Mechanistic studies have shown that the epoxidation of alkenes by hydroperoxides, hydrogen peroxides and *m*-CPBA passes through higher valent metal-oxo intermediates.⁴ It has been observed that these monomeric catalysts were degraded by the formation of μ -oxo dimer (eq. 1).⁵



In order to avoid this, attempts have been made to anchor monomers into solid supports or to make covalent linkages.^{6,7} In such studies, instead of using tetraphenyl porphyrin, the tetrapyrrolyl porphyrins were used in the development of a series of interesting catalyst frameworks.^{8,9} In this process of modification, including ours, the materials were found to be amorphous in nature.¹⁰ Attempts were also made to make the materials crystalline in order to improve their catalytic efficiency.¹¹ In order to stop two catalytic units to destroy each other by μ -oxo-dimerization, we thought of a very simple compound depicted in scheme 1. The

plan is based on the known rich chemistry of cyclopladated azobenzene compounds.¹² Thus, the most easily available and degradable compound TPPFeCl was selected for the present study. Two such units are planned to couple by an azo-linkage to get compound **A**. Compound **A** is thus nothing but a *p*-substituted azobenzene, which on reaction with Na₂PdCl₄ should give **B**. Herein we report the synthesis, spectroscopic characterization and the remarkable improvement of the catalytic ability of **A** and **B** with respect to the monomer which is TPP(*p*-NO₂)FeCl.

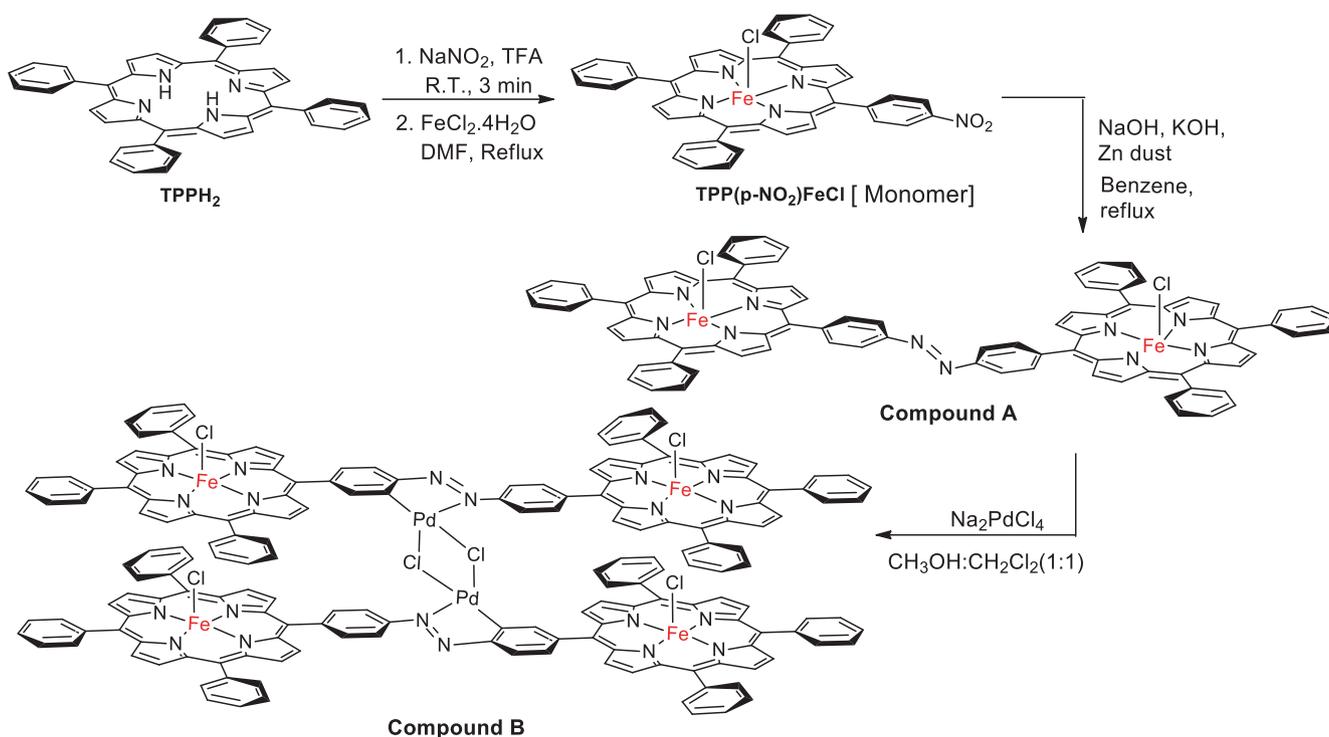
2. Experimental

2.1 Materials and synthesis

m-Cresol was distilled under argon before use. Other organic solvents for reactions were distilled over appropriate drying reagents under argon or obtained as dehydrated reagents from Merck (India) Chemicals. Deuterated solvents for NMR, pyrrole, *p*-nitrobenzaldehyde, *tert*-butyl hydroperoxide (*t*-BuOOH) and olefines were obtained from Sigma-Aldrich Chemical Pvt. Ltd (U.S.A.). Ferrous chloride tetrahydrate was obtained from LobaChemie. SnCl₂·2H₂O, acetic anhydride and hydrochloric acid were obtained from Qualigens Chemicals. Isoquinoline, ethanol and *m*-cresol were obtained from Spectrochemicals.

2.1a Synthesis of 5-(4-nitro phenyl),10,15,20 triphenylporphyrin: Sodium nitrite (20 mg, 0.29 mmol) to a solution of tetra phenyl porphyrin (TPPH₂) (100 mg,

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Scheme 1. The synthetic route and the possible structures of the two new catalysts compound A and compound B.

0.163 mmol) in TFA (10 mL) was added. The reaction mixture was stirred for 3 min at room temperature and was quenched by adding 100 mL of ice cold water. The reaction mixture was extracted with dichloromethane (6×25 mL) and the organic layer was washed first with saturated aqueous sodium bicarbonate and then with water and finally dried over anhydrous sodium sulphate. The dried solution was passed through a silica gel column. The desired compound 5-(4-nitrophenyl)-10,15,20-triphenyl porphyrin was eluted in 1:1 dichloromethane-hexane mixture. The solution was then evaporated to dryness under vacuum and the yield was 65 mg (59%) yield. This compound has following spectroscopic features: UV-Visible (CH₂Cl₂)λ^{max}/nm (ε/M⁻¹cm⁻¹): 418 (4.69×10⁵), 515 (2.65×10⁴), 550 (1.36×10⁴), 590 (1.24×10⁴), 645 (9.35×10³); ¹HNMR (300MHz, CDCl₃): δ -2.79 (s, 2H, NH pyrrole), 7.76-7.78 (t, 9H, m-&p-phenyl), 8.20-8.23 (m, 6H, o-phenyl), 8.39-8.42 (d, 2H, m-nitrophenyl), 8.63-8.66 (d, 2H, o-nitrophenyl), 8.73-8.75 (s, 2H, β pyrrole), 8.86-8.90 (s, 6H, β pyrrole); FTIR (KBr, cm⁻¹): ν 3442 (w), 1515 (s), 1343 (s). The compound was finally characterized by ESI-MS: C₄₄H₂₉N₅O₂[M](m/z) = 660.2370 ([M+H]⁺, observed), 660.2394 (calculated).

2.1b Synthesis of 5-(4-nitro phenyl),10,15,20 triphenylporphyrin iron(III) chloride: In a solution of 5-(4-nitro phenyl), 10,15,20 triphenylporphyrin (100 mg) in dimethyl formamide (100 mL) was added 2,4,

6-collidine (100 μL, 97.7 mg,) and mixture was allowed to reflux under argon. Solid FeCl₂·4H₂O (310 mg, 1.559 mmol) was added to the refluxing reaction mixture. The refluxing was continued for 1 hr, then again FeCl₂·4H₂O (310 mg, 1.559 mmol) was added to the reaction mixture and reaction was continued for another 2 h. The reaction mixture was then brought to room temperature. Dichloromethane was added to the reaction mixture and the contents were slowly poured to a 500 mL separating flask containing 250 mL of distilled water. The organic layer was taken immediately without any shaking then this organic layer was washed with distilled water (6×250 mL). The organic layer was dried over anhydrous Na₂SO₄ for overnight and was decanted and was evaporated to dryness under reduced pressure. The crude solid was purified by silica gel column chromatography and the desired compound was eluted from column by using 3% methanol in dichloromethane. The characteristic spectroscopic features: UV-visible (CH₂Cl₂)λ^{max} (nm): 378 (1.09×10⁵), 416 (ε = 2.03×10⁵), 510 (2.55×10⁴); FTIR (KBr, cm⁻¹): ν 3442 (w), 1519 (s), 1335 (s), 998 (s, Fe-N stretch). This compound was characterized by following: ESI-MS: C₄₄H₂₇N₅O₂FeCl [M] (m/z) = 713.1441 ([M-Cl]⁺, observed), 713.1514 (calculated).

2.1c Synthesis of 4,4'-bis[5-(10,15,20-triphenyl)porphyrinyl] azobenzene iron(III) chloride: A solution of 1 g of NaOH in 1 mL of water and 50 mg of 5-(4-nitro

phenyl),10,15,20 triphenylporphyrin iron(III)chloride in 8 mL of benzene were heated to 80°C. The solution was stirred vigorously, and KOH (2 g) and zinc powder (0.5 g) were added to it. After the mixture was stirred for 10 h, zinc powder (0.5 g) was added again. The reaction mixture was then heated to 90°C and was stirred for 10 h. This hot solution was filtered and solid was washed with 5 mL of methanol. Air was passed through this solution for 5 h. The resultant solution was neutralized by HCl solution (1 N) and filtered. An excess of dichloromethane (50 mL) was added and the organic layer was separated and dried by Na₂SO₄. The solvent was evaporated to dryness and to this residue dichloromethane added again and solvent was removed under vacuum and powder solid product was collected. The product was purified by silica gel column chromatography and the desired compound was eluted by 10% methanol-dichloromethane mixture. The characteristic spectroscopic features of the compound: UV-Visible (CH₂Cl₂)λ^{max}/nm (ε/M⁻¹cm⁻¹): 416 (3.37×10⁵), 511 (3.95×10⁴); FTIR (KBr, cm⁻¹): ν 3442 (w), 1628 (s, -N=N- stretch), 999 (s, Fe-N stretch). It was characterized by: ESI-MS: C₈₈H₅₄N₁₀Fe₂Cl₂ [M] m/z = 681.1540 ([M-2Cl]²⁺ (observed), 681.1614 (calculated).

2.1d Synthesis of 4,4'-bis[5-(10,15,20-triphenyl)porphyrinyl]azobenzene iron(III) chloride coordinated to palladium(II): A solution of Na₂PdCl₄ (7.5 mg, 0.02 mmol) in 5 mL of methanol was added to a solution of 4,4'-bis[5-(10,15,20-triphenyl)porphyrinyl] azobenzene iron(III) chloride (30 mg, 0.02 mmol) in 5 mL of dichloromethane. The solution was stirred for 30 min at room temperature, and the precipitated compound was filtered by G-4 and was thoroughly washed with water and then with methanol. The solid residue (yield = 22 mg, 66%) was collected and was dried under vacuum. This product has following characteristic spectroscopic features: UV-Visible (CH₂Cl₂)λ^{max}/nm (ε/M⁻¹cm⁻¹): 378 (2.33×10⁵), 418 (ε = 4.22×10⁵), 510 (5.99×10⁴); FTIR (KBr, cm⁻¹): ν 3430 (w), 1597 (s, -N=N- stretch), 999 (s, Fe-N stretch), 726 (orthometallation), 555 (ν Pd-C) and 460 (ν Pd-N); and fragmented ESI-MS: [C₈₈H₅₃N₁₀Fe₂Pd]²⁺ m/z = 733.1933 (observed), 733.6094 (calculated).

2.2 Characterization and catalytic experiments

2.2a Characterization techniques: UV-Visible spectra were recorded by Agilent Technologies UV 8453 model. Fourier transformed infrared spectra (FTIR) were recorded on KBr pellets using Agilent Technologies Cary 660 model. Elemental analysis (C, H, N) was measured by Perkin Elmer instrument series II CHNS/O Analyser

2400 model while Cl analysis is performed by gravimetric method using AgNO₃.

2.2b General procedure for the oxidation of alkenes/alkane: The oxidations of cycloalkenes/alkane (400 mM) were carried out at room temperature in a 4 mL screw-capped vial fitted with PTFE septa. In all the experiments the iron(III) porphyrin catalyst in mM conc. were taken in 2.0 mL dichloromethane under argon. The oxidation reactions were initiated by adding the oxidants (10mM) at the end to the vial. This was followed by stirring the reaction mixture with a small magnetic bar and the reactions were carried out under argon. After the reaction was over, 2 μL dodecane was added to this reaction mixture as an internal standard. An aliquot (~1μL) was withdrawn after regular intervals using a microlitre syringe from the reaction mixture for analysis. At the end of the reaction the solid particles (catalyst) were separated by filtration and the product analysis for cycloalkenes/alkane oxidation was performed using Perkin-Elmer AutoSystemXL gas chromatography equipped with flame ionization detector (FID) and carbowax capillary column of 30 m length. Tetraphenyl porphyrin is synthesized according to the procedure reported in the literature.

3. Result and Discussion

The TPP(p-NO₂) was prepared by controlled reaction of NaNO₂ with TPPH₂. The iron insertion to this was done by conventional treatment of this porphyrin with FeCl₂·4H₂O in DMF to evolve TPP(p-NO₂)FeCl. The 4,4'-bis[5-(10,15,20-triphenyl)porphyrinyl] azobenzene iron(III) chloride (Compound A) was synthesized from 5-(4-nitro phenyl),10,15,20 triphenylporphyrin by reacting it with zinc dust and KOH in benzene (scheme 1). The dimer has soret band very similar to that of 5-(4-nitro phenyl),10,15,20 triphenylporphyrin iron(III) chloride monomer. The two iron porphyrin units are connected by azo linkage and this has changed the extinction coefficient per iron from 2.03×10⁵ in monomer to 1.68×10⁵ M⁻¹ cm⁻¹ in dimer (Supporting information: figures S1–S2). The ESI-Mass of the monomer gives parent ion peak at 713.1441 (figure S3) which indicates that chloride ion is dissociated which is common in iron(III) porphyrin compounds.¹³ The dimer exhibited a parent ion peak at m/z = 681.1540 (C₈₈H₅₄N₁₀Fe₂Cl₂ [M-2Cl]²⁺ = 681.1614) (Mass spectra, figure S5) due to dissociation of chloride ions. This can be rationalized by the generation of two positive charges on dissociation of two chloride ions from the dimer.¹⁴ The 4,4'-bis[5-(10,15,20-triphenyl)porphyrinyl]

nyl] azobenzene iron(III) chloride coordinated to Pd(II) complex (Compound **B**) was synthesized by reacting Compound **A** and Na_2PdCl_4 in 50% dichloromethane in methanol (scheme 1). The MALDI-TOF mass spectra show the major peak at 733.1512 (figure S6). This is due to the fragment containing iron(III) porphyrin dimer with one Pd only with all chlorides detached from the metal ions (Fe^{3+} and Pd^{2+}). The loss of one mass unit in this spectrum also signifies the formation of a C-Pd linkage as expected.¹⁵ In order to reinforce our analysis and observation the Cope compound ($\text{AzoBz}_2\text{Pd}_2\text{Cl}_2$) was prepared.^{12,16} The ESI-Mass of this compound showed the parent ion peak at ~ 365 , which is along the line of our expectation (figure S7).¹⁷

The FT-IR of compound **A** shows a characteristic -N=N- azo stretching frequency¹⁸ at 1628 cm^{-1} and that for the Fe-N stretching frequency at 999 cm^{-1} . Compound **A** forms azobenzene type of complex as shown in **B**, where the frequency of -N=N- was shifted to 1597 cm^{-1} . Similar shift is observed in case of cyclopalladated azobenzene complexes.¹⁹ The compound **B** exhibited other important IR peaks at 555 cm^{-1} (ν Pd-C), 726 cm^{-1} (orthometallation) and 460 cm^{-1} (ν Pd-N).²⁰ Elemental analysis of both **A** and **B** shows the content of C, H, N to be 74.47, 4.08, 10.39% and 67.02, 3.53, 8.49, respectively (theoretical values, for $\text{C}_{88}\text{H}_{54}\text{N}_{10}\text{Fe}_2\text{Cl}_2$: C 73.70%, H, 3.80%, N 9.77% and for $\text{C}_{176}\text{H}_{106}\text{N}_{20}\text{Fe}_4\text{Pd}_2\text{Cl}_6$: C 67.07%, H 3.45%, N 8.89%). In both these molecules the percentage of chloride is most important and this is done gravimetrically. The content of chloride ion in compound **A** and **B** was observed to be 5.02% and 6.95% (calculated values: 4.94% and 6.75%), respectively. In electronic absorption spectra, the extinction coefficients per iron for **A** and **B** are changed as expected, because the azo bond is coordinated to Pd (figure S9). These data and the known azobenzene chemistry of palladium support the most rational structure of Pd tetramer to be like that given in scheme 1.²¹

In order to demonstrate the catalytic activity of the iron(III)porphyrin monomer, dimer and tetramer the oxidation of norbornene by *t*-BuOOH in dichloromethane was undertaken and the results are summarized in table 1.

The monomer shows $\sim 7\%$ conversion of norbornene to 2,3-exoepoxy norbornane. The dimeric iron(III) porphyrin (compound **A**) gives higher conversion up to 46% with 99% selectivity while tetrameric iron(III) porphyrin (compound **B**) gives highest conversion up to 95% with 99% selectivity. This result indicates that **B** is the most efficient catalyst for the selective oxidation of norbornene. In selecting the best reaction condition, the range of substrate concentration has also been optimized. The catalytic oxidation of some other cycloalkenes and cyclohexane by *t*-BuOOH has now been studied in presence of catalytic quantities of **A** and the results are shown in table 2.

Cyclohexene was oxidized to cyclohexene-1-one and cyclohexene-1-ol with 72% and 23% respectively (table 2, entry No. 2). Cyclooctene have better conversion to cyclooctene epoxide with 34% yield with respect to monomer. Cyclohexane has been oxidized to cyclohexan-1-one and cyclohexan-1-ol with 50% selectivity. Cyclooctane has been oxidized to cyclooctane 1-one (15%) and cyclooctane 1-ol (13%) with 52% selectivity. Styrene has been oxidized to styrene epoxide (56%) with 72 % selectivity.

In presence of Compound **B**, the oxidation of *cis*-2,3-norbornene was increased significantly from 7% for monomeric catalyst to 95% for the tetrameric one at room temperature. The oxidation of norbornene with comparable concentration of Pd^{2+} (table 1, entry no. 7 and 8) shows that Pd^{2+} is acting simply as a linker and has almost no catalytic role in **B**. For comparative study the oxidation of other cycloalkenes and cyclohexane were performed and the results are summarized in table 3.

It was observed that norbornene and cyclooctene give stereospecific epoxide products with 95% and 82%

Table 1. Oxidation of norbornene to 2,3-exoepoxy norbornane with *t*-BuOOH in CH_2Cl_2 at $25 \pm 2^\circ\text{C}^a$.

| Entry | Substrate conc. (mM) | Time (h) | Catalysts Conc. (mM) | Catalysts | Yield (%) ^b |
|-------|----------------------|----------|----------------------|----------------------------|------------------------|
| 1 | 200 | 24 | 0.313 | Monomer | 4 |
| 2 | 400 | 24 | 0.313 | Monomer | 7 |
| 3 | 200 | 24 | 0.328 | Compound A | 28 |
| 4 | 400 | 24 | 0.328 | Compound A | 46 |
| 5 | 200 | 24 | 0.317 | Compound B | 72 |
| 6 | 400 | 24 | 0.317 | Compound B | 95 |
| 7 | 200 | 24 | 0.317 | Na_2PdCl_4 | <1 |
| 8 | 400 | 24 | 0.317 | Na_2PdCl_4 | <1 |

[a] Solvent (2 mL), Oxidant(*t*-BuOOH) = 10 mM and dodecane (5mM) used as internal standard kept in Teflon-lined screw-cap vial and was sealed under dry argon atmosphere. The mixture was stirred at room temperature for 24h. [b] conversion in [%] was determined by GC. The yields are w.r.t. oxidant and average of duplicate sets.

Table 2. Compound **A** catalyzed oxidation of alkenes/alkanes^a.

| Entry | Reactant | Product | Yield ^b (%) | Selectivity ^c (%) |
|-------|-------------|--|------------------------|------------------------------|
| 1 | Norbornene | 2,3-exoepoxy norbornane | 46 | 99 |
| 2 | Cyclohexene | Cyclohexen1-one (72%) + Cyclohexene1-ol (23%) | 99 | 75 |
| 3 | Cyclooctene | Cyclooctane oxide | 34 | 99 |
| 4 | Cyclohexane | Cyclohexan1-one and cyclohexan1-ol | 10 | 50 ^d |
| 5 | Cyclooctane | Cyclooctan 1-one (15%) and Cyclooctan 1-ol (13%) | 28 | 52 ^e |
| 6 | Styrene | Styrene epoxide (56%) | 78 | 72 ^f |

[a] Catalyst **A** = 0.328 mM, Oxidant (*t*-BuOOH) = 10 mM, Substrate Conc. = 400 mM, dichloromethane (2.0 mL) and dodecane (5mM) were taken in a teflon-lined screw cap vial and it was sealed under dry argon atmosphere. The mixture was stirred at room temperature for 24 h. [b] conversion [%] and [c] selectivity [%] were determined by GC. The yields are w.r.t. oxidant and average of duplicate sets. [d] cyclohexane 1-one (5%) and cyclohexan-1-ol (5%). [e] cyclooctan-1-one (15%) and cyclooctan-1-ol (13%). [f] The by-products were benzaldehyde [12%] and benzeneacetaldehyde [10%].

Table 3. Compound **B** catalyzed oxidation of alkenes/alkanes^a.

| Entry | Reactant | Product | Yield ^b (%) | Selectivity ^c (%) |
|-------|-------------|--|------------------------|------------------------------|
| 1 | Norbornene | 2,3-exoepoxy norbornane | 95 | 99 |
| 2 | Cyclohexene | Cyclohexen1-one (70) + Cyclohexe 1-ol (26) | 99 | 73 |
| 3 | Cyclooctene | Cyclooctane oxide | 82 | 99 |
| 4 | Cyclohexane | Cyclohexan1-one and Cyclohexan1-ol | 18 | 60 ^d |
| 5 | Cyclooctane | Cyclooctan 1-one and Cyclooctan 1-ol | 42 | 55 ^e |
| 6 | Styrene | Styrene epoxide (77%) | 99 | 77 ^f |

[a] Catalyst **B** (0.317 mM), Oxidant *t*-BuOOH (10 mM), Substrate Conc. (400 mM), dichloromethane (2.0 mL) and dodecane (5mM) were taken in a screw-capped vial and it was sealed under dry argon atmosphere. The mixture was stirred at room temperature for 24h. [b] conversion [%] and [c] selectivity [%] were determined by GC. The yields are w.r.t. oxidant and average of duplicate sets. [d] cyclohexane1-one (11%) and cyclohexan-1-ol (7%). [e] cyclooctan-1-one (23%) and cyclooctan-1-ol (19%). [f] The by-products were benzaldehyde [9%] and benzeneacetaldehyde [13%].

yields, respectively. Styrene was oxidized to styrene epoxide (77%) with 77% selectivity.

The time bound plot for exo-2,3-epoxy norbornane formation (figure 1) indicates that there is no co-operativity of four iron(III) catalytic sites for the substrate binding and in their subsequently oxidation reaction.

In these reactions the stability of the catalyst **A** and **B** were also checked under the oxidizing conditions. Thus after the completion of the first reaction, new batches (aliquot) of oxidants were added to the same pot and the product yields were measured. The UV-Visible spectrum before and after the reaction did not show any observable change. The recovered catalyst also did not show any degradation of original catalyst or transformation to C-Pd bond oxidation product on TLC. The process of oxidation in a separate set of similar experiment was repeated for 3 times for **A** and 5 times for **B** (table S1 in Supporting Information). The yields of product and the reaction time remained almost unchanged, which indicates that the catalysts were stable under the reaction conditions, unlike the monomeric one, which gets decayed substantially even after the first cycle. The complex **B** is more stable over **A** due to the formation of strong C-Pd bond and azo N-Pd bond

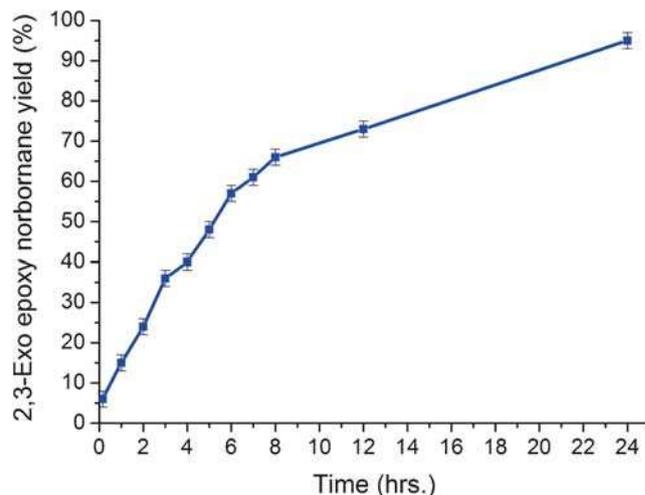
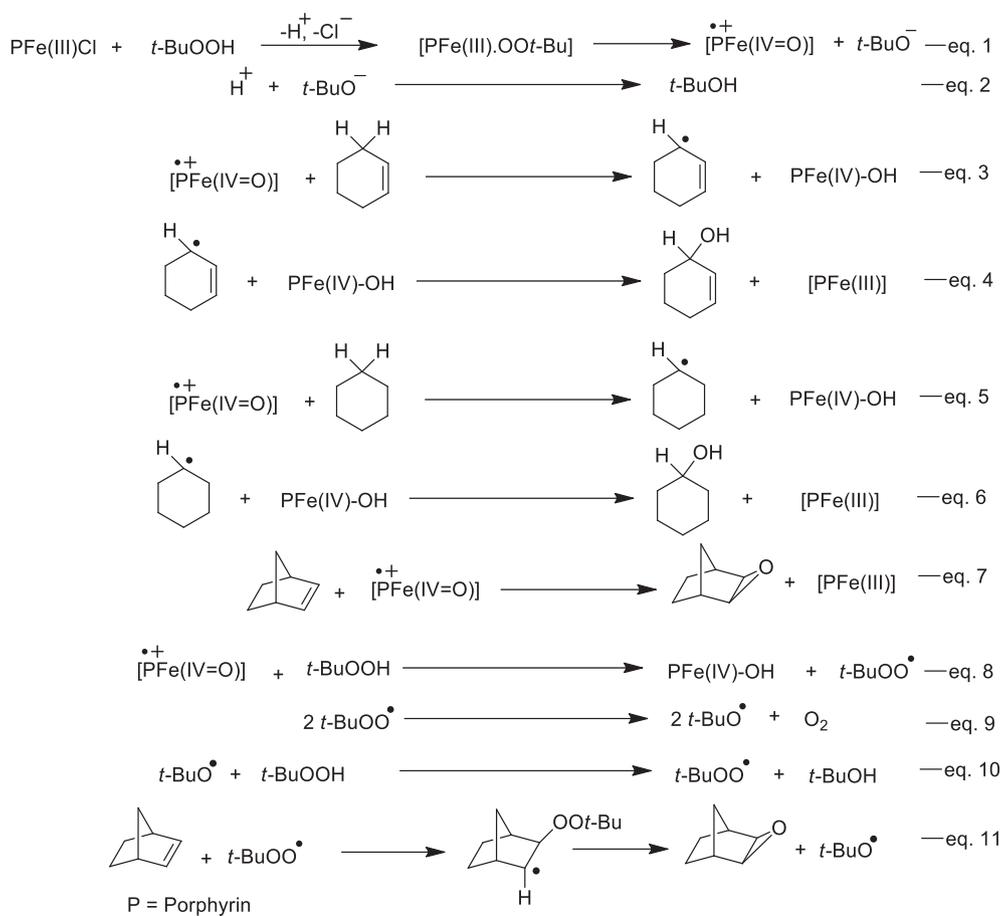


Figure 1. Plot of % yield of exo-2,3-epoxy norbornane vs time (h) for Catalyst **B** with *t*-BuOOH in dichloromethane. The error range is shown with each data point.

in the molecular frame. The structure provides rigidity to the complex **B** while compound **A** has flexible cis-trans orientation. This has indeed provided the remarkable improvement in selectivity and catalytic efficiency of catalyst **B** over catalyst **A**. Probable



Scheme 2. The probable scheme for the iron(III) porphyrin catalyzed oxidation reactions of cycloalkenes/alkanes by *t*-BuOOH.

pathway for the catalytic oxidation reaction is presented in scheme 2.

4. Conclusions

New iron(III) porphyrin catalysts have been prepared. These catalysts selectively oxidize several alkenes/alkanes. The tetrameric catalysts were highly efficient and non-degradable up to at least five cycles in one pot. The dimeric and tetrameric compounds are soluble in organic solvents. The spectroscopic methods are used to establish the structure of the catalysts. We could not get single crystals of any of these catalysts. The work is in progress, so that more accurate rationalization of the structure of the catalysts can be ascertained and whether more such catalysts with variable linkers can be prepared.

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Supplementary Information

Electronic spectra, ESI-Mass, Maldi TOF spectra and stability of the catalysts under oxidizing condition (table S1) are given in supporting information. Supplementary Information is available at www.ias.ac.in/chemsci.

References

- (a) Groves J T and Han Y-Z 1995 In *Cytochrome P 450: Structure, Mechanism and Biochemistry* P R Ortiz de Montellano (Ed.) 2nd edn. (New York: Plenum Press) p. 1; (b) Dolphin D and Traylor T G 1997 *Acc. Chem. Res.* **36** 251; (c) Traylor T G, Kim C, Richards J L, Xu F and Perrin C L 1995 *J. Am. Chem. Soc.* **117** 3468
- (a) Traylor P S, Dolphin D, and Traylor T G 1984 *J. Chem. Soc., Chem. Commun.* 279; (b) Traylor T G and Tsuchiya Shinji 1987 *Inorg. Chem.* **26** 1338; (c) Mclain J L, Lee J and Groves J T 2009 In *Biomimetic Oxidations by Transition Metal Complexes* B Meunier (Ed.) (London: Imperial College Press) p. 91; (d) Que L and Tolman W B 2008 *Nature* **455** 333; (e) Agarwala A and Bandyopadhyay D 2006 *Chem. Commun.* 4823
- (a) Traylor T G, Tsuchiya S, Byun Y S and Kim C 1993 *J. Am. Chem. Soc.* **115** 2775; (b) Traylor T G and Xu F

- 1990 *J. Am. Chem. Soc.* **112** 178; (c) Bartoli J F, Barch K L, Palacio M, Battioni P and Mansuy D 2001 *Chem. Commun.* 1718; (d) Suzuki N, Higuchi T and Nagano T 2002 *J. Am. Chem. Soc.* **124** 9622; (e) Traylor T G, Fann W P and Bandyopadhyay D 1989 *J. Am. Chem. Soc.* **111** 8010
4. (a) Wadhvani P, Mukherjee M and Bandyopadhyay D 2001 *J. Am. Chem. Soc.* **123** 12430; (b) Derat E, Kumar Hirao H and Shaik S 2006 *J. Am. Chem. Soc.* **128** 473; (c) Alkordi M H, Liu Y, Larsen R W, Eubank J F and Eddaoudi M 2008 *J. Am. Chem. Soc.* **130** 12639; (d) Kamaraj K and Bandyopadhyay D 1997 *J. Am. Chem. Soc.* **119** 8099
5. Che C, Lo V K, Zhou C and Huang J 2011 *Chem. Soc. Rev.* **40** 1950
6. (a) Merlau ML, Mejia MP, Nguyen S T and Hupp J T 2001 *Angew. Chem. Int. Ed.* **40** 4239; (b) Sheng X, Guo H, Qin Y, Wang X and Wang F 2015 *RSC Adv.* **5** 31664; (c) Lu G, Yang H, Zhu Y, Huggins T, Ren Z J, Liu Z and Zhang W J 2015 *Mater. Chem. A* **3** 4954
7. (a) Hilal H S, Jondi W, Khalaf S, Keilani A, Suleiman M and Schreine A F 1996 *J. Mol. Catal. A: Chem.* **113** 35; (b) Vinodu M V and Padmanabhan M 2001 *Proc. Indian Acad. Sci. (J. Chem. Sci.)* **1131**
8. (a) Shultz A M, Farha O K, Hupp J T and Nguyen S T 2011 *Chem. Sci.* **2** 686; (b) Lee K Y, Lee YS, Kim S, Ha H M, Bae S, Huh S, Janga H G and Lee S J 2013 *Cryst. Eng. Comm.* **15** 9360
9. (a) Sigen A, Zhang Y, Li Z, Xia H, Xue M, Liu X and Mu Y 2014 *Chem. Commun.* **50** 8495; (b) Maeda C, Taniguchi T, Ogawa K and Ema T 2015 *Angew. Chem. Int. Ed.* **54** 134
10. (a) Singh M K and Bandyopadhyay D 2014 *J. Chem. Sci.* **126** 1707; (b) Liu X, Sigen A, Zhang Y, Luo X, Xia H, Li H and Mu Y 2014 *RSC. Adv.* **4** 6447
11. Chen X, Huang N, Gao J, Xu H, Xu F and Jiang D 2014 *Chem. Commun.* **50** 6161
12. Cope A C and Siekman R W 1965 *J. Am. Chem. Soc.* **87** 3272
13. The monomer ($C_{44}H_{27}N_2O_2FeCl = 748.45$) is supposed to give the parent ion peak at ~ 748 but we are getting it at ~ 713 which is the parent ion peak – one chloride ion (figure S3). The monomeric porphyrin (figure S4, $C_{44}H_{29}N_5O_2 [M] \sim 659$) gives the major peak at $[M+H]^+ = 660.2370$ as expected
14. On dissociation of the chloride ions from the dimer **A**, two +ve charges are generated in the molecule, so expectedly the parent ion peak should come at $(M-2Cl)/2$ which is clearly visible at 681.1540 (observed), 681.1614 (calculated). We also see the small peak for the dimer at 1361.2811
15. The tetramer **B** (Scheme 1) is a gigantic derivative of Cope compound
16. Mahapatra A K, Bandyopadhyay D, Bandyopadhyay P and Chakravorty A 1986 *Inorg. Chem.* **25** 2214
17. The crystal structure of well-known Cope compound (**I**) is given in figure S8. Our present compound **B** is nothing but a derivative of **I**. Thus we prepared **I** and took its ESI mass and have observed the major peak at ~ 365 (given in supporting information figure S7). The mass of **I** ($C_{24}H_{18}N_4Pd_2Cl_2$) is 645, but we get the major peak at ~ 365 ($C_{12}H_9N_2Pd + 2K^+$). In **I** the $C_{12}H_9N_2Pd$ fragment has no charge, so it picks up two K^+ from the K^+ -formate matrix used during performing the ESI-mass. Thus we conclude that similar thing happens in case of **B** and because it has already two charges on the iron centres, no additional charge (K^+) is required for the major peak (~ 733) to appear
18. Tsuchiya S 1999 *J. Am. Chem. Soc.* **121** 48
19. (a) Molnar S P and Orchin M J 1969 *Organometal. Chem.* **16** 196; (b) Balch A L and Petridis D 1969 *Inorg. Chem.* **8** 2247
20. Ahmed A H 2014 *Int. J. Chem. Tech. Res.* **6** 36
21. Sinha C R, Bandyopadhyay D and Chakravorty A 1988 *J. Chem. Soc. Chem. Comm.* 468