

Catalytic activity of nitro- and carboxy-substituted iron porphyrins in hydrocarbon oxidation

Homogeneous solution and supported systems

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Abstract

A series of iron(III)porphyrins containing NO₂-substituents in the meso-*ortho*-phenyl or COOH-substituents in the meso-*para*-phenyl rings (FeP) have been used to catalyse hydrocarbon oxidation by iodosylbenzene. The FeP series were efficient and selective catalysts for alkene epoxidation and alkane hydroxylation. The most promising iron porphyrin, 5,10,15-tri(2-nitrophenyl)20-mono-(4-carboxyphenyl)porphyrin iron(III) chloride, Fe(TNMCPP)Cl, was covalently bound to aminopropylated silica (APS) through covalent binding between –COOH groups in the FeP (after activation by reaction with SOCl₂) and –NH₂ groups on the functionalised silica resulting in the anchored catalyst Si–NH–(TNMCPP)FeCl. This system proved to be a highly efficient catalyst for alkene epoxidation. The same iron porphyrin was also supported on APS through electrostatic binding, resulting the heterogeneous catalyst Si–NH₃⁺–(TNMCPP)FeCl. The iron centres are in different surroundings on the two supports as demonstrated by EPR, UV/VIS and oxidation reactions results. The Si–NH₃⁺–(TNMCPP)FeCl is not a good catalyst for hydrocarbon oxidation, which can be attributed to the higher polarity of this support and the bis-axial coordination by the free –NH₂ groups of the support with the iron centre. Both effects are unfavourable for the interaction between the non-polar substrates and the catalyst. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Metalloporphyrins; Porphyrin; Iron porphyrin; Catalysis; Supported catalysts

1. Introduction

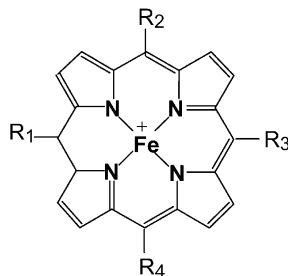
Over the last 20 years, metalloporphyrins have been successfully used as models for the cytochrome P-450 enzyme, with respect to the oxidation of organic compounds such as hydrocarbons [1–3]. Development in this area is based on different strategies with the aim of designing selective, stable and high turnover cat-

alytic systems [4]. These strategies involve synthesis of structured metalloporphyrins, use of efficient and clean oxidants and the search for methods to reproduce the enzyme environment responsible for the high rates and selectivities of the natural systems. First, second and third generations of homogeneous metalloporphyrin catalysts have been synthesised by substitution of the hydrogen atoms on the periphery of the porphyrin ring by electron withdrawing groups, which confers both stability and catalytic efficiency to these systems [1,5–10]. Current interest in this area is directed towards developing oxidation catalysts that

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Fe(TNPP)Cl	$R_1=R_2=R_3=R_4=o\text{-NO}_2\text{Ph}$
Fe(TNM CPP)Cl	$R_1=R_2=R_3=o\text{-NO}_2\text{Ph}, R_4=p\text{-COOHPh}$
Fe(DND CPP)Cl	$R_1=R_2(\text{or } R_3)=o\text{-NO}_2\text{Ph}, R_3(\text{or } R_2)=R_4=p\text{-COOHPh}$
Fe(MNT CPP)Cl	$R_1=o\text{-NO}_2\text{Ph}, R_2=R_3=R_4=p\text{-COOHPh}$
Fe(TCPP)Cl	$R_1=R_2=R_3=R_4=p\text{-COOHPh}$

Fig. 1. Nitro- and carboxy-substituted iron(III)porphyrins.

combine the versatility of homogeneous metalloporphyrins with the advantages of heterogeneous systems. To this end, metalloporphyrins have been chemically and physically anchored on a wide variety of solid supports and the chemistry of the resulting materials compared with those of homogeneous counterparts [11].

Supported metalloporphyrins matrices present advantages such as prevention of catalyst intermolecular self-oxidation, dimerisation of sterically unhindered metalloporphyrins and easy recovery and reuse of the catalyst. Furthermore, heterogeneous catalysts have become an important and attractive target to 'clean technology' since they present the possibility of replacing the traditional stoichiometric processes in industry, and therefore help to minimise the problem of industrial waste treatment and disposal [12].

In a previous paper [13], we reported the synthesis, purification and characterisation of anionic tetraarylporphyrins bearing carboxy- and nitro-substituents on the phenyl rings (Fig. 1). These porphyrins associate carboxyl groups which can be ionised resulting water soluble compounds and *ortho*-nitro groups. These groups reduce electron density in the porphyrin ring and provide steric hindrance, thereby improving the stability of the metalloporphyrin catalysts in oxidation reactions [14,15]. Moreover, after chemical activation, both substituents can act as linkers to attach these porphyrins to other materials. For example, by amidation

the carboxyl-substituted porphyrins can be anchored to solid supports [11].

In this report, we have analysed the oxidation of hydrocarbons by iodobenzene, catalysed by a series of nitro- and carboxy-substituted iron(III) porphyrins in homogeneous solution and covalently bound to aminopropylsilica. The effect of the *ortho*-nitro and *para*-carboxy groups on the catalytic efficiency will be discussed. The ability of the carboxy groups as a linker was explored by covalently attaching the iron porphyrin bearing three nitro- and one carboxy-substituents, Fe(TNM CPP)Cl, onto the aminopropylated silica. The same compound was grafted onto this silica by either electrostatic interactions or by covalently attachment and the catalytic efficiencies were compared. The Fe(TNM CPP)Cl was selected in the series due to the possibility to anchor this iron porphyrin by only one link (via a COOH group), and the presence of three *ortho*-nitro groups which could offer steric protection to the self-oxidation of catalyst.

2. Experimental

2.1. Materials

All compounds used in this study were commercially available from Aldrich or Sigma and

of analytical grade purity unless otherwise stated. Dichloroethane and dichloromethane was distilled and stored on 4 Å molecular sieves. Acetonitrile and methanol were stored on 3 Å molecular sieves. Iodosylbenzene (PhIO) was prepared by the hydrolysis of iodosylbenzene diacetate following the method of Sharefkin and Saltzmann [16] and the purity was shown to be 96% by iodometric titration. The synthesis and purification of the porphyrins and the corresponding iron porphyrins was as described previously [13]. The alkenes (cyclohexene and Z-cyclooctene) were purified by passing them through a short activated alumina column (Merck) immediately before use. Aminopropyl modified silica with 9% functionalisation was purchased from Aldrich and used without further treatment.

2.2. Preparation of supported iron porphyrins (FeP)

2.2.1. Fe(TNMCPP)Cl covalently bound on to amino-modified silica

In order to anchor the Fe(TNMCPP)Cl onto the aminopropylsilica (APS), the carboxy-substituent was first activated through the acid chloride method [17]. The Fe(TNMCPP)Cl (10 mg, 11.3 mmol) was suspended in thionyl chloride, SOCl₂ (15 ml) and the mixture was refluxed for 3 h, after which the excess of SOCl₂ was removed by distillation. The remaining FeP was dissolved in dichloromethane (15 ml) and APS (1.0 g) was added. The suspension was magnetically stirred and maintained at the reflux temperature of the solvent (ca. 40°C) for 3 h, and subsequently cooled to room temperature. The resulting solid, Si–NH–(TNMCPP)FeCl, was washed with dichloromethane (24 h) and methanol (24 h) using a Soxhlet apparatus and dried under vacuum. The porphyrin loading was obtained using UV/VIS spectroscopy to measure the amount of iron porphyrin in the combined washings.

2.2.2. Fe(TNMCPP)Cl electrostatically bound on to amino-modified silica

Ionic immobilisation of Fe(TNMCPP)Cl on to APS was achieved by heating Fe(TNMCPP)Cl (10 mg, 11.3 mmol) with the APS (1.0 g) in dichloromethane at 40°C for 3 h. The resulting solid, Si–NH₃⁺–(TNMCPP)FeCl, was washed with dichloromethane (24 h) and then methanol (24 h)

using a Soxhlet apparatus and dried under vacuum. The porphyrin loading was obtained using UV/VIS spectroscopy to measure the amount of iron porphyrin in the combined washings.

2.2.3. Capping procedure

After anchoring the iron porphyrins, the free –NH₂ groups on the surface of the silica were protected by refluxing the supported catalyst (ca. 100 mg) with distilled acetic anhydride (15 ml) for 21 h [18]. The resulting solids were washed with deionised water until neutral pH, and subsequently washed with dichloromethane and then methanol using a Soxhlet apparatus and dried under vacuum. The porphyrin loading was obtained using UV/VIS spectroscopy to measure the amount of iron porphyrin in the combined washings.

The protection of free –NH₂ groups on the surface of the silica was also performed by simple washing of the supported systems (ca. 50 mg) with HCl solution (0.10 mol l⁻¹) followed by deionised water until neutral pH. The resulting solid was washed with dichloromethane (24 h) and then methanol (24 h) using a Soxhlet apparatus and dried under vacuum. The porphyrin loadings were obtained using UV/VIS spectroscopy to measure the amount of iron porphyrin in the combined washings.

2.2.4. Leaching procedure

The stability of the supported systems against leaching was investigated by heating (40°C) 10 mg of the supported catalysts with 3 ml of solution 8.3 mmol l⁻¹ of 4-dimethyl-amino-pyridine in dichloromethane for 3 h. The resulting solids, Si–NH–(TNMCPP)FeCl and Si–NH₃⁺–(TNMCPP)FeCl, were washed with dichloromethane (24 h) and then methanol (24 h) using a Soxhlet apparatus. The amount of porphyrins leached from the supports were measured in the combined washings by UV/VIS spectroscopy.

2.3. Alkene and alkane oxidations

In a typical oxidation reaction, the supported (ca. 20 mg, 0.25 μmol) or unsupported iron(III)porphyrin (0.25 μmol) was stirred with the substrate (500 μmol) in dichloroethane (1.5 cm³) and the reaction was initiated by the addition of iodosylbenzene (25 μmol). The reactions were monitored by removing 1.0 μl samples

for GC analysis. All reactions were carried out at room temperature with magnetic stirring. Reactions in the absence of dioxygen were carried out in a flask sealed with an open top screw cap containing a silicone teflon faced septum. The solid metalloporphyrin and iodosylbenzene were thoroughly flushed with argon prior to addition of substrate and dichloroethane which had previously been thoroughly flushed with argon. For reactions using methanol as solvent the formaldehyde yield was colorimetrically quantified at the end of reaction using the Nash test [19].

2.4. Instrumentation

UV/VIS spectra were obtained with a Hewlett-Packard 8452, diode array spectrometer. The spectra were recorded in 2 mm path length quartz cells (Hellma). A suspension of either the supported catalyst or a mixture of the supported catalysts and the support itself in CCl_4 was used to measure the Soret band of the immobilised systems.

The EPR spectra of supported iron porphyrins at 3 K were obtained with a Varian E-109 spectrometer, operating in the X band frequency (9 GHz) with a gain of 10^3 and 20 mW of microwave power and amplitude modulation of 4 gauss at liquid helium temperature. For the experiments in the presence of NO, the EPR tube containing ca. 100 mg of solid was flushed with N_2 for 1 h. Afterwards, the N_2 was removed with a syringe and the tube atmosphere was saturated with NO (generated from the reaction between Cu^0 and HNO_3) and the EPR spectra was recorded.

The GC analysis was performed on a Varian 3400 CX chromatograph with a hydrogen flame ionisation detector using a DB-wax (1 μm thickness) megabore column (30 m \times 0.538 mm). Nitrogen was used as the carrier gas. The results were recorded and processed on a Varian workstation.

3. Results and discussion

3.1. Alkene epoxidation by iodosylbenzene catalysed by iron(III)porphyrins in homogeneous solution

The efficiency and the stability of the investigated iron porphyrins as catalysts for epoxidation both in solution and supported on silica were examined

Table 1
Epoxidation of cyclooctene by iodosylbenzene catalysed by nitro- and carboxy-substituted iron porphyrins in homogeneous solutions

Entry	Catalyst	Epoxyde yield (%) ^a
1	Fe(TNPP)Cl	96 (91) ^b
2	Fe(TNMCPP)Cl	95 (72)
3	Fe(DNDCPP)Cl	90 (61)
4	Fe(MNTCPP)Cl	68 (38)
5	Fe(TCPP)Cl	13 (13)

^a Based on the starting PhIO, after constant yield.

^b The values in parenthesis are the yields for reactions in the presence of methanol. Reaction conditions: molar ratio of FeP:PhIO:substrate:methanol = 1:100:2000:2000 in dichloroethane.

using cyclooctene as the substrate. The reactions were carried out in dichloroethane using a catalyst:oxidant:substrate ratio of 1:100:2000. Table 1 shows the epoxide yields from homogeneous reactions in the presence and absence of methanol. This second solvent was used in order to solubilize the porphyrins bearing more COOH groups.

All studied FeP, except Fe(TCPP)Cl, are good catalysts for cyclooctene epoxidation (Table 1). The catalytic efficiency decreases with the number of nitro group substituents confirming that in the *ortho* positions these groups exert a beneficial effect on catalytic activity. As an electron withdrawing group they activate the catalytic species by improving the electrophilicity of this species and as a bulky group they improve the catalyst stability by protecting them from self oxidation. The protecting effect could be confirmed by the complete recovery of the catalyst bearing four to two nitro groups after oxidation reaction and low recovery (about 15%) of the catalyst which has only one *ortho*-nitro-substituent, Fe(MNTCPP)Cl.

Fig. 2 shows that a constant epoxide yield was rapidly reached for the more nitro-substituted catalysts. However, it took about 6 h for the catalyst containing only one nitro group to attain a constant yield due to its lower solubility in dichloroethane. The same effect was observed with the Fe(TCPP)Cl, which is insoluble in dichloroethane. When the oxidation reactions were carried out in methanol, which can better solubilize these two iron porphyrins and the PhIO, both the epoxide yields and catalyst recovery were lower due to the higher solubility of the oxidant. In these cases, methanol could also act as a substrate,

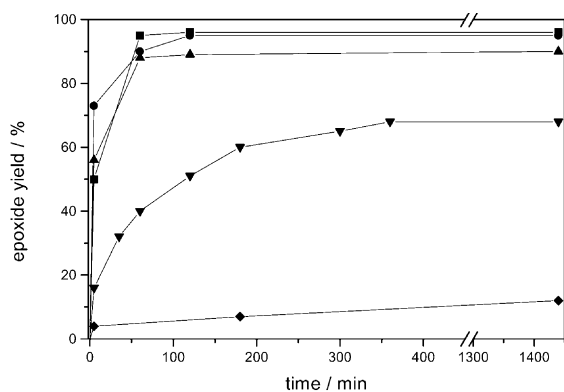


Fig. 2. A comparison of the epoxidation rates for cyclooctene by PhIO catalysed by: (■) Fe(TNPP)Cl; (●) Fe(TNM CPP)Cl; (▲) Fe(DNDCPP)Cl; (▼) Fe(MNTCPP)Cl; (◆) Fe(TCPP)Cl in dichloroethane.

leading to formaldehyde production. However, the quantification of formaldehyde by UV/VIS (Nash method [19]) gave only 8% of this product indicating that this side reaction is not predominant.

The oxidation of cyclohexene catalysed by this series of FeP was also investigated and the results are shown in Table 2. It is observed that almost all catalysts gave good yields of epoxy cyclohexane (entries 1–4, Table 2) which is consistent with high-valent iron–oxo porphyrin as the oxidizing species [20–24]. These catalysts also gave significant yields of two allylic oxidation products, cyclohex-2-en-1-ol and cyclohex-2-en-1-one with total yields consistently greater than 100%. Carrying out the reactions under argon atmosphere reduced the yield of the allylic products and in particular that of the ketone (entry 3, Table 2). The same effect was observed with other halogenated metalloporphyrins which led to oxidation

yields higher than 100% for reactions developed in air [20,25,26], and can be attributed to the well documented mechanism of autoxidation involving dioxygen trapping of cyclohexyl radicals [27,28].

3.2. The synthesis of the supported iron porphyrins

The Fe(TNM CPP)Cl was selected for studies with the support since it has just one COOH group which may react with the NH₂ group from APS. In this system the porphyrin is attached by just one point yet retains the steric hindrance offered by the three NO₂ groups substituents at the *ortho*-position of the *meso*-phenyl groups.

The covalent immobilisation of Fe(TNM CPP)Cl on aminopropylated silica was carried out through peptide bond formation in two steps. Initially, the acylating agent was formed by reaction of the COOH group of porphyrin with thionyl chloride, followed by treatment of the product with the aminopropylated silica as shown in Fig. 3A. The attachment of a leaving group to the acyl carbon of the COOH is necessary to enable attack by the amino group of the silica surface, and since ordinary carboxylic acids simply form salts with amines at ambient temperature; the transformation of these salts into the amide requires heating to high temperature [17]. For comparison, the Fe(TNM CPP)Cl was allowed to react with the amino functionalised support without previous activation of COOH group. This reaction resulted in a system having the iron porphyrin anchored by ionic interaction between the COO⁻ and NH₃⁺, which are formed due to the abstraction of the acid proton of the porphyrin by the basic NH₂ group of the support (Fig. 3B).

The covalent anchoring process led to a brown dark solid catalyst, Si–NH–(TNM CPP)FeCl, with 12 μmol

Table 2

Oxidation of cyclohexene by iodosylbenzene catalysed by the nitro- and carboxy-substituted iron porphyrins in homogeneous solution

Entry	FeP	Epoxide (%) ^a	Cyclohex-2-en-1-ol (%) ^a	Cyclohex-2-en-1-one (%) ^a
1	Fe (TNPP)Cl	80	36	66
2	Fe(TNM CPP)Cl	80	29	49
3	Fe(TNM CPP)Cl ^b	80	15	18
4	Fe(DNDCPP)Cl	77	29	54
5	Fe(MNTCPP)Cl	28	38	64
6	Fe(TCPP)Cl	15	46	66

^a Based in iodosylbenzene, after constant yield (24 h).

^b Reaction carried out in argon atmosphere.

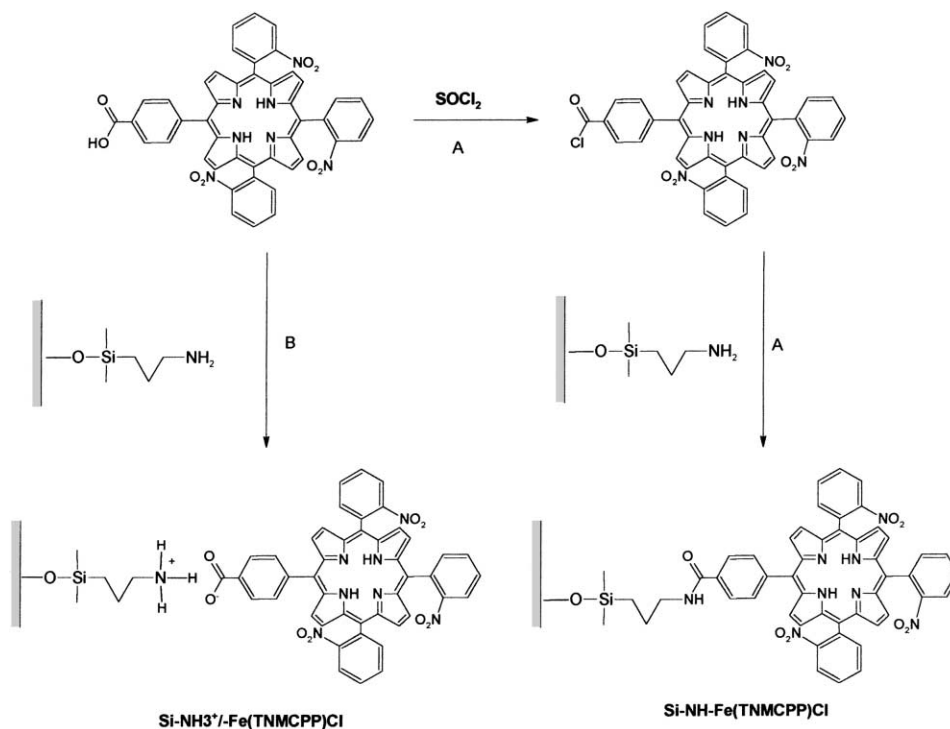


Fig. 3. Schematic steps to anchor Fe(TNMCPP)Cl on to aminopropylated silica. (A) by pre-activation of COOH group; (B) without pre-activation of COOH group.

of iron porphyrin per gram of support and the ionic anchoring process led to a green dark solid catalyst, Si-NH₃⁺-(TNMCPP)FeCl, with 11 μmol of iron porphyrin/g of support.

Attempts to confirm the formation of peptide bond in these systems by infrared spectroscopy were unsuccessful due to the presence of broad absorption bands associated with the Si-O-Si and Si-OH groups. However, the different modes of attachment in both catalysts was proven indirectly by the total leaching from each material after treatment with a strong base, 4-dimethyl-amine-pyridine, which led to 78% of Fe(TNMCPP)Cl leaching from the Si-NH₃⁺-(TNMCPP)FeCl and just 8% from the Si-NH-(TNMCPP)FeCl. The 8% of catalyst leached from this last support probably corresponds to the ionic anchored iron porphyrin as a result of incomplete COOH pre-acylation.

The UV/VIS analysis of the freshly prepared supported materials showed a single Soret band at 448 and 432 nm for Si-NH-(TNMCPP)FeCl

and Si-NH₃⁺-(TNMCPP)FeCl respectively, which are red shifted compared to Soret band of this iron(III)porphyrin in dichloroethane solution (422 nm). These spectra indicate that the Fe(TNMCPP)Cl is in different surroundings in both materials. The effect of changes in the porphyrin ring planarity lead to a destabilisation of the HOMO but not of the LUMO orbitals thus leading to the decrease in the HOMO-LUMO energy gap, responsible for the red shift of the Soret band. The increased red shift of the Soret band for Si-NH-(TNMCPP)FeCl can be related to the greater distortion of the hindered macrocycle due to the covalent attachment to the solid surface. In the ionic attached catalyst, Si-NH₃⁺-(TNMCPP)FeCl, this distortion is reduced. These effects have been reported for other distorted porphyrins ([29,30 and references 9,13,14] therein).

The EPR spectra of Si-NH-(TNMCPP)FeCl and Si-NH₃⁺-(TNMCPP)FeCl systems show three signals at $g = 6.0$, 4.3 and 2.0 corresponding to high spin Fe(III) ($S = 5/2$, $g = 6.0$ and 2.0) and high spin

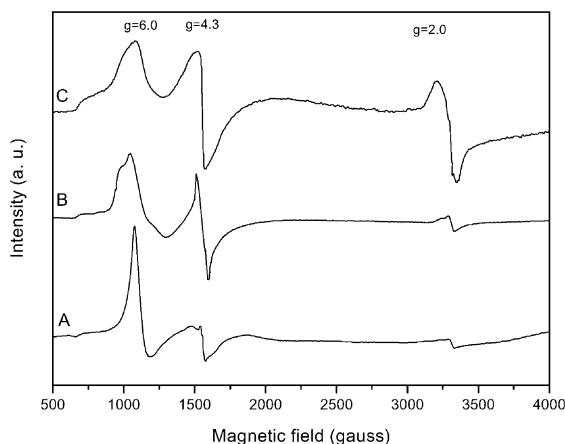


Fig. 4. EPR spectra of (A) Si–NH–(TNMCPP)FeCl (12 μ mol FeP/g of support); (B) Si–NH₃⁺–(TNMCPP)FeCl (11 μ mol FeP/g of support); (C) Si–NH–(TNMCPP)FeCl (12 μ mol of FeP/g of support) in the presence of NO. $T = 3$ K; $\nu = 9.270$ GHz, gain 1600 for A and B and 5000 for C.

Fe(III) with rhombic distortion ($g = 4.3$) (Fig. 4A and B).

The signal at $g = 6.0$ in the EPR spectrum of Si–NH–(TNMCPP)FeCl shows a well defined axial symmetry (Fig. 4A) which is expected for a complex with weak ligands in the fifth and sixth positions of the iron. The signal at $g = 4.3$ is composed of more than one line (Fig. 4A) indicating species with different rhombic distortions, which could be due to the presence of ionic anchored iron porphyrin as an impurity in this support. The $g = 4.3$ signal is more symmetrical for Si–NH₃⁺–(TNMCPP)FeCl (Fig. 4 B), as expected for species with axial rhombic distortion [31]. The broad lines in the low field region in the EPR spectrum of Si–NH₃⁺–(TNMCPP)FeCl are compatible with two species involving iron spin state $S = 5/2$: one axially symmetric and the other distorted. The asymmetry of these signals is clear evidence of the distortions of the porphyrin ligand in these solids, and the different profiles of these signals confirm the different surroundings of the iron centre in both catalysts.

The red shift of the Soret band in these catalysts could also be explained by the presence of iron(II) in mixture with iron(III). The iron(II) presence was confirmed by EPR spectrum of the Si–NH–(TNMCPP)FeCl in the presence of NO, which is a paramagnetic probe to detect iron(II) since this

ligand binds to the iron resulting in a paramagnetic centre ($S = 1/2$) with a $g = 2$ signal [32]. Fig. 4C show the EPR spectrum of Si–NH–(TNMCPP)FeCl, with a $g = 2$ signal, confirming the presence of Fe(II)–NO species. The reduction of iron(III) is probably provoked by the coordination of free NH₂ groups on the surface of the silica as observed with other iron porphyrins anchored onto silicas functionalised with nitrogen bases such as imidazole, pyridine and amine [25,33]. Stronger evidence of the different nature of both supported systems was provided by the results of the catalysis studies.

3.3. Alkene epoxidation by iodosylbenzene catalysed by supported systems

Table 3 presents the results for the epoxidation of cyclooctene catalysed by the supported porphyrin systems. The covalently anchored iron porphyrin, Si–NH–(TNMCPP)FeCl, is as good a catalyst as the corresponding homogeneous system (Table 1). However, the ionic supported iron porphyrin, Si–NH₃⁺–(TNMCPP)FeCl, presents a very low activity (Table 3). These results clearly show that this iron porphyrin is in different surroundings in these systems, as indicated by UV/VIS and EPR data. The low epoxide yields observed with Si–NH₃⁺–(TNMCPP)FeCl can be attributed to the higher polarity of this catalyst which is unfavourable for the interaction with the non-polar substrate. Another reason is the inaccessibility of the catalytic site due to bis-coordination of the free amino groups to the iron centre. This effect was proven by the reaction using this solid catalyst after washing HCl, which protonates the free amino group avoiding its coordination with the iron. The epoxide yield of this reaction was

Table 3
Epoxidation of cyclooctene by iodosylbenzene catalysed by the supported Fe(TNMCPP)Cl systems

Entry	Catalyst	Epoxide yield (%) ^a
1	Si–NH–(TNMCPP)FeCl	93
2	Si–NH–(TNMCPP)FeCl ^b	96
3	Si–NH ₃ ⁺ –(TNMCPP)FeCl	26
4	Si–NH ₃ ⁺ –(TNMCPP)FeCl ^c	56

^a Based in PhIO after constant yield.

^b After capping procedure with acetic anhydride.

^c After treatment with HCl.

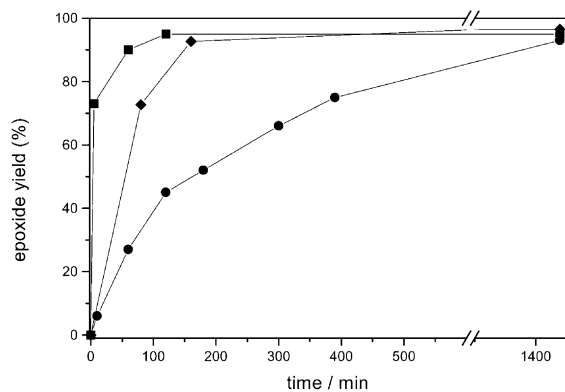


Fig. 5. A comparison of the epoxidation rates of cyclooctene by PhIO catalysed by (■) Fe(TNMCPP)Cl; (●) Si-NH-(TNMCPP)FeCl; (◆) Si-NH-(TNMCPP)FeCl after the capping procedure (with acetic anhydride), in dichloroethane.

duplicated (Table 3, entry 4). The bis-coordination of the iron is favoured in Si-NH₃⁺-(TNMCPP)FeCl, perhaps because the iron centre is not as close to the support as in the Si-NH-(TNMCPP)FeCl. For the Si-NH-(TNMCPP)FeCl the end capping procedure of the NH₂ group by acylation did not affect the epoxide yield (Table 2, entry 2), indicating that iron is not hexa-coordinated in this system. However, the reaction rate was significantly increased after the treatment with acetic anhydride (Fig. 5), becoming similar to that with homogeneous catalyst. This effect probably results from the change in surface's polarity by the acylation of the support. The surface polarity of a solid strongly affects its ability to adsorb compounds from the surrounding liquid [34]. The catalytic activity of the supported metalloporphyrin may depend upon the compatibility of the surface polarity with the substrates and products. Evans [18] has measured the polarities of different supports through the Reichardt dye method [34,35]. The polarities of aminopropylated silica before and after treatment with acetic anhydride were 0.69 and 0.61 respectively. Evans also observed a reduced induction period for the oxidation of ethylbenzene catalysed by FeTFPP¹ supported on 1,6-diaminehexylpropylsilica, after protection of the NH₂ groups by acylation. The decrease in polarity of the Si-NH-(TNMCPP)FeCl, resulting from the treatment of this support with acetic anhydride could

¹ TFPP is 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin.

Table 4

Hydroxylation of cyclohexane by iodosylbenzene catalysed by nitro- and carboxy-substituted iron porphyrins in homogeneous solution

Entry	FeP	Cyclohexanol (%) ^a
1	Fe (TNPP)Cl	12
2	Fe(TNMCPP)Cl	7
3	Fe(DNDCPP)Cl	4
4	Fe(MNTCPP)Cl	2
5	Fe(TCPP)Cl	0

^a Based on PhIO, after constant yield.

favour the interaction between the non-polar substrate with the anchored catalyst leading to higher oxidation rate after treatment.

3.4. Hydroxylation of cyclohexane and adamantane by PhIO catalysed by FeP in solution and supported on APS

The investigated nitro- and carboxy-substituted iron porphyrins were not good catalysts for the oxidation of inert alkanes such as cyclohexane under standard conditions (Table 4). However, it is possible to observe that the reactions with this substrate were selective for the alcohol and iron porphyrins bearing multiple nitro-substituents were more efficient. This is due to the effect both of the electron withdrawing substituents in activating the catalytic species which favours the attack to the inert substrate, and the steric protection offered by these groups against catalyst self oxidation. When the iron porphyrin:oxidant:substrate ratio were changed in order to diminish the competitive reactions

Table 5

Hydroxylation of cyclohexane by iodosylbenzene catalysed by Fe(TNMCPP)Cl in homogeneous and supported systems

Entry	FeP	FeP:PhIO: substrate ratio	Cyclohexanol yield (%) ^a
1	Fe(TNMCPP)Cl	1:100:2000 ^b	7
2	Fe(TNMCPP)Cl	1:100:27730 ^c	45
3	Fe(TNMCPP)Cl	1:20:2000	14
4	Fe(TNMCPP)Cl	1:20:27730	54
5	Si-NH-Fe(TNMCPP)Cl	1:100:27730	32

^a Based on PhIO, after constant yield (24 h).

^b Standard conditions.

^c Dichloroethane: cyclohexane (1:1) (1.5 cm³), in all cases no cyclohexanone was obtained.

Table 6
Yields from oxidation of adamantane^a by iodosylbenzene catalysed by FeP

FeP	Adamantan-1-ol (%) ^b	Adamantan-1-one (%) ^b	Adamantan-2-ol (%) ^b
Fe(TNPP)Cl	47	2	10
Fe(TNMCPP)Cl	49	2	10
Fe(DNDCCP)Cl	45	2	8
Fe(MNTCCP)Cl	18	2	4
Si–NH–Fe(TNMCPP)Cl	25	–	6

^a The solvent of these reaction was dichloroethane: benzene (1:1) (1.5 cm³).

^b Based on PhIO after constant yield (24 h).

(catalyst oxidation, iodosylbenzene catalysed decomposition), the cyclohexanol yields were significantly improved (Table 5) and became similar to those obtained with other iron porphyrin systems [20,25,36].

The catalytic activity of FeP for oxidation of adamantane was investigated in order to determine the relative reactivity of the tertiary and secondary C–H bonds which can lead to production of adamantan-1-ol, adamantan-2-ol and adamantan-2-one. The investigated iron porphyrins appeared as enzyme mimetics in the adamantane oxidation, since the observed products were mainly adamantan-1-ol and adamantan-2-ol with small amounts of the ketone (Table 6). The selectivity for the tertiary centre (yield of 1-ol versus 2-ol + 2-one, ca. 13:1) was predominant for all investigated compounds as expected for systems having a high-valent iron–oxo complex as the catalytic species [21,37,38]. The supported Fe(TNMCPP)Cl system was less efficient as a catalyst than the homogeneous analogue, probably due to the increased steric constraints around the iron–oxo centre at the active site on the support which did not favour the interaction with the substrate.

4. Conclusions

The results of this study have demonstrated the importance of bulk electron withdrawing substituents on the porphyrin ring to activate the catalytic species and to protect the catalyst against self oxidation. It was observed that the Fe(TNMCPP)Cl bearing three *ortho*-nitro groups presented the best catalytic profile, which was associated with the advantage that this iron porphyrin could be anchored to functionalised supports by covalent and ionic binding through COOH

group. The covalently anchored iron porphyrin was a much more efficient catalyst for alkene and alkane oxidation by iodosylbenzene than the ionic anchored catalyst. The higher polarity of the ionic supported iron porphyrin could be exploited for the catalytic oxidations of more polar substrates.

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