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FULL PAPER

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Solvent effects on catalytic activity of manganese porphyrins with cationic, anionic and uncharged *meso* substituents: Indirect evidence on the nature of active oxidant species

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Oxidation of cyclohexene and styrene with sodium periodate and tetra-n-butylammonium periodate (TBAP) catalyzed by MnT(3-MePy)P(OAc), MnT(4-SO_3)PP(OAc) and MnTPP(OAc) has been studied in water, methanol, acetonitrile and dichloromethane as solvents. The results show significant dependence of the product distribution on the type of solvent and the electronic nature of the aryl substituents introduced at the porphyrin periphery. While the oxidation of cyclohexene and styrene in the presence of MnT(3-MePy)P(OAc) and MnTPP(OAc) in water (also in methanol) gave the corresponding epoxides as nearly the sole product, performing the reactions in the presence of MnT(4-SO_3)PP(OAc) yielded the products of allylic oxidation, cyclohexene-2-ol and cyclohexene-2-one and acetophenone as the major products. In the case of styrene, performing the reaction in the presence of MnT(4-SO_3)PP(OAc), MnT(3-MePy)P(OAc) and MnTPP(OAc) in acetonitrile gave a mixture of styrene oxide and acetophenone as the products. Under the same conditions, the oxidation of cyclohexene afforded cyclohexene oxide as approximately the exclusive product. Furthermore, the oxidation of olefins in dichloromethane gave the corresponding epoxide as the exclusive products. The product distributions observed in the protic and aprotic solvents were used to provide indirect evidence on the relative contribution and reactivity of high valent manganese oxo and periodato Mn(III) porphyrin species to the oxidation reactions.

KEYWORDS
allylic oxidation of cyclohexene, oxidation of alkenes, manganese(III)porphyrins, solvent effects, Substituent effects

1 | INTRODUCTION

Biological oxidations including oxygenations of organic substrates catalyzed by cytochrome P-450, oxidations by peroxidases, oxidative halogenations by chloroperoxidases and hydrogen peroxide dismutation by catalase are the main reactions catalyzed by heme enzymes.[1] The catalytic oxidation of organic compounds with different terminal oxidants in the presence of metalloporphyrins has been the subject of extensive experimental and theoretical investigations since the late 1980,s.[1,2] The catalytic performance of metalloporphyrins is influenced by parameters such as the stereoelectronic properties of substituents at the porphyrin periphery and the type of metal center, axial base, solvent and terminal oxidant.[1e, 3] It is generally accepted[4] that electron-deficient metalloporphyrins are more efficient catalysts than the electron-rich ones in the oxidation of organic compounds with different terminal oxidants. However, there are many reports showing that electron-rich metalloporphyrins can have comparable or higher catalytic activity than the electron-deficient ones.[5] We have previously reported the oxidation of alkenes with tetra-n-butylammonium periodate (TBAP) in dichloromethane catalyzed by a series of manganese(III) and iron(III) porphyrins.[5d, e] According to the previous studies[3d, 5d, e] the catalytic performance of Mn(III) meso-tetra(aryl)porphyrins only weakly correlates with the electronic properties of the meso substituents. It is noteworthy that in manganese and iron porphyrin catalyzed oxidation of olefins with TBAP in dichloromethane, low valent periodato manganese(III) and iron(III) porphyrin species were found as the dominant active oxidant species. Furthermore, the formation of multiple active oxidants was evident for both heme and non-heme manganese catalysts in reaction with various terminal oxidants.[3e, f, 5b–f, 6] In a recent work,[1e] we have reported the catalytic activity of a series of water soluble and insoluble iron(III) and Mn(III) meso-tetra(aryl) porphyrins in the oxidation of alkenes with sodium periodate in water. The results were in good agreement with the higher catalytic activity of the electron-deficient iron and manganese porphyrins. As shown by Mohajer et al., using water-saturated dichloromethane as the solvent, significantly increases the catalytic activity of electron-deficient manganese porphyrins with little or no effect on that of the electron-rich ones.[5f] In the present work, the catalytic activity of two water soluble cationic and anionic manganese porphyrins and MnTPP(OAc) in the oxidation of alkenes with sodium periodate or TBAP was studied in water, methanol, acetonitrile and dichloromethane (Figure 1). In this study, the effects of solvent on the product distribution and total conversion were used to provide indirect evidence on the nature of the active oxidant involved in the oxidation reactions. It is noteworthy that due to the high reactivity of high valent manganese oxo porphyrin intermediates at room temperature, most of these species have been characterized by low temperature UV–vis spectroscopy or competitive oxidation of the *cis-* and *trans* isomers of sterically hindered olefins such as stilbene and octene.[3c–f, 5b–e, 6a] Furthermore, due to the environmental problems associated with the use of halogenated solvents,[7] oxidation of olefins in environmentally preferable solvents[8] is of great interest in the field of biomimetic catalysis.

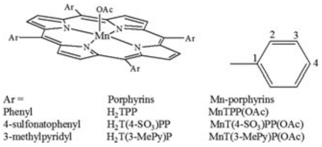


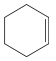
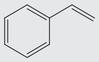
FIGURE 1 Porphyrins and manganese porphyrins used in this study

2 | RESULTS AND DISCUSSION

2.1 | Oxidation of alkenes catalyzed by MnT(4-SO$_3$)PP(OAc)

Oxidation of cyclohexene with TBAP in the presence of MnT(4-SO$_3$)PP(OAc) and imidazole (ImH) in water and methanol gave products derived from allylic oxidation as the major products and cyclohexene epoxide as the minor one (Table 1). The presence of ImH was found to play crucial roles in the stabilization and reactivity of high valent manganese(IV and V)–oxo porphyrin intermediates (Figure 2) as well as the low valent periodato manganese(III) species. These roles were attributed to the ability of ImH to form σ and π bonds with the manganese center and hydrogen bonds with the leaving group (here, IO_3^-) and the coordinated ImH. Also, the latter can stabilize a high valent manganese(IV and V)–oxo porphyrin intermediate by hydrogen bond formation with its oxygen atom.[3d, 9c] As was found in previous studies,[3d, 5c–e] performing the reaction in dichloromethane yields cyclohexene oxide as the sole product. In manganese porphyrin catalyzed oxidation of organic compounds, high valent manganese(IV)-oxo porphyrin π cation radical and low valent (oxidant)Mn(III)-porphyrin species are usually invoked as the active oxidants.[3a, 9] The use of protic solvents such as water and different alcohols has been found to facilitate the formation of high valent manganese

TABLE 1 Oxidation of olefins with periodate catalyzed by MnT(4-SO$_3$)PP(OAc) in water, methanol and dichloromethane at room temperature for a reaction time of 4 hr

	Conversion (Yield of epoxide) [Epoxide selectivity] (%)^b		
Olefins	water	CH_3OH	CH_2Cl_2
	96^c (trace)[0]^d	75 (4)[5]^d	20 (20)[100]
	37(17)[45]^e	45(<1)[0]	13(13)[100]

MnT(4-SO$_3$)PP(OAc):ImH:olefin:oxidant (TBAP and sodium periodate for the reaction performed in organic solvents and water, respectively) were used in a 1:20:85:170 molar ratio. [b] All reactions were repeated at least three times and the average values with an error of ca 5–10% are reported. [c] The use of ImH in 1:30 molar ratio relative to the catalyst led to a conversion of 100%. [d]Cyclohexene-2-ol and cyclohexen-2-one were obtained as the major products. [e] Acetophenone was the major product.

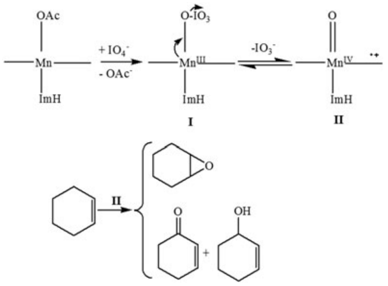


FIGURE 2 The formation of active oxidants (I and II) and competition between epoxidation and allylic oxidation of cyclohexene

oxo species[3d, 5f, 9, 10] which can oxidize alkenes to the corresponding epoxide or the allylic products. Hydrogen bonds formed between the leaving group (IO_3^-) and hydrogen bond donors such as water, methanol and ImH facilitate departure of the leaving group and the formation of high valent manganese(IV)-oxo porphyrin π cation radical species (Figure 2, species II). Also, these hydrogen bonds will stabilize species II and shift the equilibrium towards the formation of this species. The observed product distribution arises from the competition between the allylic C-H bond and the C=C double bond (Figure 2) for the active oxidant that also depends on the structure of the alkene.[11] While epoxidation of alkenes can proceed with the involvement of either a low valent periodato manganese(III) species (species I, Figure 2) or a high valent manganese oxo one (species II), the latter is necessary for the allylic oxidation (Figure 3) Accordingly, the exclusive formation of the allylic products in the oxidation of cyclohexene in water (Table 1), provides strong indirect evidence for the intermediacy of species II as the active oxidant in this reaction. Also, nearly the same product distribution was observed for the reaction performed in methanol. Oxidation of styrene in water gave nearly equal amounts of styrene oxide and acetophenone. It should be noted that the use of dichloromethane as the solvent led to the formation of styrene oxide as the sole product, consistent with the intermediacy of a periodato Mn(III)porphyrin intermediate as the main active oxidant.[3d–f]

Also, the higher reactivity of cyclohexene versus styrene demonstrates higher reactivity of the allylic CH bond of cyclohexene relative to the double bond of styrene towards oxidation with the active oxidants in water. It is observed that the product selectivity of the reaction catalyzed by MnT(4-SO_3)PP(OAc) depends strongly on the type of solvent, so that the change of solvent from dichloromethane to protic ones (water or methanol) in the case of cyclohexene leads to formation of the allylic oxidation products as exclusive product and significant decrease in the epoxide selectivity in the case of styrene.

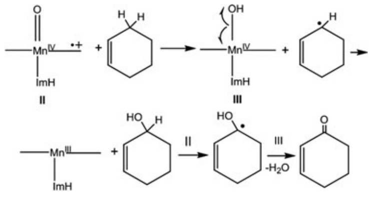
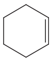
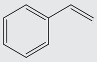


FIGURE 3 Oxidation of cyclohexene at the allylic CH bond with the species II

2.2 | Oxidation of alkenes in the presence of MnT(3-MePy)P(OAc)

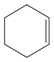
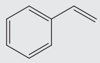
Oxidation of cyclohexene and styrene with sodium periodate catalyzed by MnT(3-MePy)P(OAc) led to the formation of the corresponding epoxides as nearly the sole product in water (Table 2). The use of methanol as solvent, again afforded cyclohexene oxide as the dominant product, but in the case of styrene, gave a mixture of approximately equal amounts of styrene oxide and acetophenone. In comparison with MnT(4-SO_3)PP(OAc), the catalyst showed a high selectivity towards the formation of the epoxide products. The use of acetonitrile as the solvent (Table 3) led to a higher selectivity for the epoxide in the case of cyclohexene. As was mentioned above, the presence of high valent metal oxo species is needed for the formation of allylic products. The substitution of 4-sulfonatophenyl group with the weaker electron-releasing 3-methylpyridyl substituent at the *meso* positions, can shift the equilibrium between species I and II (Figure 2) toward the former. This in turn shifts the reaction toward the formation of cyclohexe oxide.

TABLE 2 Oxidation of olefins with periodate catalyzed by MnT(3-MePy)P(OAc) in water, methanol and dichloromethane at room temperature for a reaction time of 4 hr

	Conversion (Yield of epoxide) [Epoxide selectivity] (%)^b		
Olefins	**water**	**CH_3OH**	**CH_2Cl_2**
	100^c (93) [93]^c	100 (95) [95]^c	~10 (~10) [100]
	100 (94) [94]^d	95 (53) [56]^d	~5 (~5) [100]

MnT(3-MePy)P(OAc):ImH:olefin:oxidant (sodium periodate or TBAP were used in water, methanol and dichloromethane, respectively) were used in a 1:30:85:170 molar ratio. [b] The average of three reactions. [c]Cyclohexene-2-ol and cyclohexen-2-one were obtained as the minor products. [d] Acetophenone was the other product.

TABLE 3 Oxidation of olefins with TBAP catalyzed by MnT(3-MePy)P(OAc), MnT(4-SO_3)PP(OAc) and MnTPP(OAc) in acetonitrile at room temperature for a reaction time of 4 hr

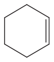
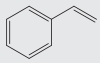
	Conversion (Yield of epoxide) [Epoxide selectivity] (%)		
Olefins	**Mn(3-MePy) P(OAc)**	**MnT(4-SO_3) PP(OAc)**	**MnTPP (OAc)**
	90^c (88) $[98]^b$	85 (80) $[91]^b$	78 (65) $[83]^b$
	67 (43) $[64]^c$	57 (45) $[79]^c$	60 (21) $[35]^c$

Catalyst:ImH:olefin:oxidant were used in a 1:30:85:170 molar ratio. [b]Cyclohexene-2-ol and cyclohexen-2-one were obtained as the minor products. [c] Acetophenone was the other product.

2.3 | Oxidation of alkenes catalyzed by MnTPP(OAc)

Oxidation of cyclohexene and styrene with periodate by using MnTPP(OAc) as the catalyst afforded the corresponding epoxides as the major product (Table 4). Although no allylic products were observed in the oxidation of cyclohexene in methanol, performing the reaction in water gave the allylic products with a yield of 10%. It is noteworthy that an epoxide selectivity of 100% was observed for the reaction performed in dichloromethane in the presence of different electron-rich and electron-deficient metalloporphyrins.[3d, 5d, e] The total conversions are also much higher than those obtained in dichloromethane. This finding suggests that a high valent manganese-oxo porphyrin species rather than a low valent periodato manganese(III) porphyrin is involved in the oxidation reactions conducted in water or methanol. The former has been considered as a stronger oxidant than the latter, due to the higher oxidation state of the metal center.[2a, 3e, f] On the other hand, the presence of the former led to the allylic oxidation of cyclohexene (Figure 3). It should be noted that the Mn(IV)/Mn(III) reduction potential of manganese porphyrins depends on the stereoelectronic properties of the *meso* and β substituents.[12] Accordingly, the oxidizability of species II formed from the manganese porphyrins is expected to decrease in the order MnT(3-MePy)P(OAc) > MnT(4-SO_3)PP(OAc) > MnTPP(OAc). However, the direction of equilibrium between species I and II (Figure 2) and consequently the extent of contribution of the two species in the catalytic cycle is determined by the nature of the *meso* substituents. Therefore, the formation of the allylic products upon the oxidation of cyclohexene in different solvents seems to be controlled by the relative oxidizability of high valent manganese-oxo species and the relative contribution of species I and II under the reaction conditions.

TABLE 4 Oxidation of olefins with periodate catalyzed by MnTPP(OAc) in water, methanol and dichloromethane at room temperature for a reaction time of 4 hr

	Conversion (Yield of epoxide) [Epoxide selectivity] (%)		
Olefins	**water**	**CH_3OH**	**CH_2Cl_2**
	100 (90) $[90]^b$	100 (100) [100]	45 (43) $[96]^b$
	85 (78) $[92]^c$	100 (89) $[89]^c$	54 (54) [100]

MnTPP(OAc):ImH:olefin:oxidant (sodium periodate and TBAP for the reactions in water and methanol, respectively) were used in a 1:20:85:170 molar ratio. [b] Cyclohexene-2-ol and cyclohexen-2-one were obtained as the major products. [c] Acetophenone was the other product.

3 | EXPERIMENTAL

3.1 | Instrumental

^{1}H NMR spectra were obtained on a Bruker 250 MHz spectrometer. The absorption spectra were recorded on a GBC-916 UV–Vis spectrophotometer. All reactions were analyzed by a Varian CP-3800 gas chromatograph equipped with a HP-5 capillary column (phenylmethyl siloxane 30 m × 320 μm × 0.25 μm) and a flame-ionization detector.

3.2 | Preparation of porphyrins and manganese porphyrins

Meso-tetra(4-sulfonatophenyl) porphyrin, $H_2T(4\text{-}SO_3)PP$, *meso*-tetra(4-sulfonatophenyl)porphyrinatomanganese(III) acetate, MnT(4-SO_3)PP(OAc), *meso*-tetra(3-pyridyl)p, H_2T(3-Py)P, N-methylated meso-tetra(pyridyl)porphyrin, H_2T(3-MePy)P and *meso*-tetra(3-methylpyridyl)porphyrinatomanganese(III) acetate, MnT(3-MePy)P(OAc) were prepared and purified according to the literature.[13] More experimental details can be found in our previous works.[1f, g, 5d]

H_2TPP: ^{1}H NMR ($CDCl_3$, 400 MHz): −2.77 (2H, br, s, NH), 7.75–7.77 ($8H_m$ and $4H_{p,m}$), 8.21–8.24 ($8H_o$, d), 8.84 ($8H_\beta$, s); UV–Vis (λ/nm) in CH_2Cl_2: 417 (Soret), 512, 545, 586, 647. *Meso*-tetraphenylporphyrin, H_2TPP was synthesized and purified by Adler et al. method.[13c] $H_2T(4\text{-}SO_3)$PP was synthesized according to the literature as follows: 5,10,15,20-tetrakis(4-chlorosulphonylphenyl)porphyrin was prepared by dropwise addition of an excess amount of chlorosulfonic acid (200 μl, 2.7 mmol) to

H_2TPP (50 mg, 0.08 mmol) in dichloromethane (4 ml). The solution was magnetically stirred at room temperature for 4 hr. After the required time, the solution was cooled to 4 °C and 4 ml of cold distilled water was added to the mixture. The precipitate was filtered and the solid residue was washed with dichloromethane to remove the unreacted H_2TPP until the filtrate becomes colorless. The suspension of 5,10,15,20-tetrakis(4-chlorosulphonylphenyl)porphyrin in water was refluxed for 12 hr.[13e] Rotary evaporation of the solvent gave $H_2T(4\text{-}SO_3)PP$. The formation of tetrasulfonated salt of $H_2T(4\text{-}SO_3)PP$ was confirmed by ^1H NMR; dichloromethane extraction of $H_2T(4\text{-}SO_3)PP$ with tetra-n-butylammonium bromide from an alkaline aqueous solution led to the formation of $(n\text{-}Bu)_4H_2T(4\text{-}SO_3)PP$ that was used to prepare the ^1H NMR spectra in $CDCl_3$.

$H_2T(4\text{-}SO_3)PP$ (tetra-n-butylammonium salt), ^1H NMR ($CDCl_3$, 400 MHz): −2.85 (2H, br, s, NH), 8.15–8.17 ($8H_m$, d), 8.32–8.33 ($8H_o$, d), 8.82 ($8H_\beta$, s), the protons of tetra-n-butylammonium appear at δ 1.01, 1.42, 1.60 and 3.38 ppm; UV–Vis (λ/nm) in CH_2Cl_2: 418 (Soret), 512, 543, 582, 645.

$H_2T(3\text{-}Py)P$ was synthesized and purified according to the Adler method with some modifications have been described in our previous work.[13g] $H_2T(3\text{-}MePy)$ P was prepared by refluxing $H_2T(3\text{-}Py)P$ with excess amounts of methyltosylate in dimethylformamide and purified according to the literature.[13h, i]

$H_2T(3\text{-}Py)P$. ^1H NMR ($CDCl_3$, 400 MHz): −2.83 (2H, br, s, NH), 7.77–7.80 ($4H_m$,dd), 9.46 ($4H_o$, br, s), 8.52–8.54 ($4H_o$, br, d), 9.07–9.08 ($4H_p$, dd), 8.87 ($8H_\beta$, s); UV–Vis (λ/nm) in CH_2Cl_2: 418 (Soret), 512, 547, 588, 646. $H_2T(3\text{-}MePy)P$: ^1H NMR (DMSO-d_6, 400 MHz): −3.124 (2H, br, s, NH), 8.626–8.661 ($4H_m$, dd), 10.007 ($4H_o$, adjacent to heteroatom, s), 9.323 ($4H_o$, d), 9.579–9.594 ($4H_p$, d), 9.266 ($8H_\beta$, s), 4.698 (12H, CH_3). UV–vis (λ/nm) in water: 415 (Soret), 512, 540, 577, 628.

The manganese complexes of H_2TPP, $H_2T(3\text{-}MePy)P$ and $H_2T(4\text{-}SO_3)PP$ were prepared by the method of Adler et al.[13j] MnTPP(OAc):UV–Vis (λ_{max}/nm) in CH_2Cl_2: 470 (Soret band), 575, 612; $MnT(4\text{-}SO_3)PP(OAc)$: UV–Vis ($\lambda_{max}$/nm) in H_2O: 465 (Soret band), 557, 592; MnT(3-MePy)P(OAc): UV–Vis (λ_{max}/nm) in H_2O: 459 (Soret band), 551.

3.3 | General oxidation procedure

In a typical reaction, metalloporphyrin, alkene, imidazole and oxidant were used in a molar ratio of 1:20 (or 30 in the case of water):85:170 which, with the exception of ImH, is the same as that previously optimized by Mohajer et al. for the reactions performed in dichloromethane, using water insoluble manganese porphyrins as the catalysts.[3d] However, in this study, a 1:20 (or 1:30 in water) molar ratio of metalloporphyrin to ImH was found to be the optimized one. TBAP and sodium periodate were used as oxidant for the oxidation reactions conducted in the organic solvents and water, respectively. Progress of the reactions was followed by GC. For the reactions in water, the organic compounds were extracted by dichloromethane. After drying the solution on anhydrous sodium sulfate, the mixture was passed through a short silicagel column to remove the catalyst and then analyzed by GC.

4 | CONCLUSION

Oxidation of cyclohexene and styrene with sodium periodate and TBAP catalyzed by MnT(3-MePy)P(OAc), $MnT(4\text{-}SO_3)PP(OAc)$ and MnTPP(OAc) was studied in different protic and aprotic solvents and found that: (*i*) oxidation of cyclohexene with sodium periodate catalyzed by $MnT(4\text{-}SO_3)PP(OAc)$ in water and methanol (using TBAP as the oxidant) afforded the products of allylic oxidation as nearly the sole product; (*ii*) performing the reaction in the presence of MnT(3-MePy)P(OAc) in methanol, water or acetonitrile gave cyclohexene oxide as nearly the exclusive product; (*iii*) the oxidation of styrene in water, catalyzed by $MnT(4\text{-}SO_3)PP(OAc)$ yielded styrene oxide as nearly the sole product, but the use of methanol or acetonitrile led to the formation of acetophenone in addition to styrene oxide. Also, the use of $MnT(4\text{-}SO_3)PP(OAc)$ as the catalyst gave nearly equal amounts of styrene oxide and acetophenone; (*iv*) oxidation of the alkenes in the presence of MnTPP(OAc) in water or methanol produced the corresponding epoxides as the major product. In other word, the product distribution is similar to that observed in dichloromethane as an aprotic solvent. The large differences between the product distribtion observed in the used solvents were attributed to the relative stability and contribution of high valent manganse oxo and periodato Mn(III) porphyrin species in the protic and aprotic solvents. On the other hand, the observed product distributions gave evidence on the nature of active oxidant species. Also, the formation of high valent manganese oxo porphyrin intermediates is probably governed by the electronic properties of the meso substituents.

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REFERENCES

[1] a) B. Meunier, *Chem. Rev.* **1992**, *92*, 1411. b) G. Huang, T. Su, K. Zeng, Y. Guo, S. Zhao, S. Wei, *Appl. Organometal. Chem.* **2018**, *32*, e4140. https://doi.org/10.1002/aoc.4140 c) Y. Li, B. Sun, Y. Zhou, W. Yang, *Appl. Organometal. Chem.* **2017**, 31. https://doi.org/10.1002/aoc.3578 d) M. Moghadam, I. Mohammadpoor-Baltork, S. Tangestaninejad, V. Mirkhani, A. R. Khosropour, S. Abdolmanaf Taghavi, *Appl. Organometal. Chem.* **2011**, *25*, 687. e) S. Zakavi, A. Hashemi amiri, F. Asadi, *Appl. Organometal. Chem.* **2018**, *32*. https://doi.org/10.1002/aoc.4117 f) S. Zakavi, S. Ebadi, M. Javanmard, *Appl. Organometal. Chem.* **2018**, 32. https://doi.org/10.1002/aoc.4175 g) A. Talaeizadeh, M. Tofighi, S. Zakavi, *Appl. Organometal. Chem.* **2018**, *32*, e3967, https://doi.org/10.1002/aoc.3967.

[2] a) J. T. Groves, T. E. Nemo, R. S. Myers, *J. Am. Chem. Soc.* **1979**, *101*, 1032. b) J. T. Groves, in *Cytochrome P450: Structure, Mechanism, and Biochemistry*, (Ed: P. R. O. de Montellano), Kluwer Academic/Plenum Publisher, New York **2005**. c) M. J. F. Calvete, M. Piñeiro, L. D. Dias, M.,. M. Pereira, *ChemCatChem* **2018**, https://doi.org/10.1002/cctc.201800587, *10*, 3615.

[3] a) W. Nam, *Acc. Chem. Res.* **2007**, *40*, 522. b) W. Nam, M. H. Lim, S. Oh, *Inorg. Chem.* **2000**, *39*, 5572. c) S. Rayati, S. Zakavi, H. Kalantari, *J. Porphyrin Phthalocyanines* **2011**, *15*, 131. d) D. Mohajer, G. Karimipour, M. Bagherzadeh, *New J. Chem.* **2004**, *28*, 740. e) R. Nasrollahi, S. Zakavi, *New J. Chem.* **2018**, *42*, 1806. f) R. Nasrollahi, S. Zakavi, *Eur. J. Inorg. Chem.* **2017**, *2017*, 2002.

[4] a) W. Nam, H. J. Choi, H. J. Han, S. H. Cho, H. J. Lee, S. Y. Han, *Chem. Commun.* **1999**, *387*. b) D. Mansuy, *Pure Appl. Chem.* **1994**, *66*, 737.

[5] a) J. Chen, C. M. Che, *Angew. Chem. Int. Ed.* **2004**, *43*, 4950. b) S. Zakavi, L. Ebrahimi, *Polyhedron* **2011**, *30*, 1732. c) S. Zakavi, F. Heidarizadi, S. Rayati, *Inorg. Chem. Commun.* **2011**, *14*, 1010. d) S. Zakavi, A. G. Mojarrad, S. Rayati, *J. Mol. Catal. A: Chem.* **2012**, *363*, 153. e) S. Zakavi, T. Mokary yazdeli, *J. Mol. Catal. A: Chem.* **2013**, *367*, 108. f) L. Mahmoudi, D. Mohajer, R. Kissnerb, W. H. Koppenol, *Dalton Trans.* **2011**, *40*, 8695.

[6] a) M. Y. Hyun, Y. D. Jo, J. H. Lee, H. G. Lee, H. n. M. Park, I. H. Hwang, K. B. Kim, S. J. Lee, C. Kim, *Chem. Eur. J.* **2013**, *19*, 1810. b) Y. J. Song, S. H. Lee, H. M. Park, S. H. Kim, H. G. Goo, G. H. Eom, J. H. Lee, M. S. Lah, Y. Kim, S.-J. Kim, J. E. Lee, H.-I. Lee, C. Kim, *Chem. – Eur. J.* **2011**, *17*, 7336.

[7] F. M. Kerton, *Alternative Solvents for Green Chemistry*, RSC Publishing, Cambridge **2009**.

[8] C. Capello, U. Fischer, K. Hungerbühlera, *Green Chem.* **2007**, *9*, 927.

[9] a) W. J. Song, M. S. Seo, S. D. George, T. Ohta, R. Song, M. J. Kang, T. Tosha, T. Kitagawa, E. I. Solomon, W. Nam, *J. Am. Chem. Soc.* **2007**, *129*, 1268. b) D. Mohajer, M. Abbasi, *Eur. J. Inorg. Chem.* **2008**, *3218*. c) S. Zakavi, A. Abasi, A. R. Pourali, S. Talebzadeh, *Bull. Korean Chem. Soc.* **2012**, *33*, 35.

[10] L. Mahmoudi, D. Mohajer, R. Kissner, W. H. Koppenol, *Dalton Trans.* **2011**, *40*, 8695.

[11] a) E. Baciocchi, F. d'Acunzo, C. Galli, M. Ioele, *J. Chem. Soc., Chem. Commun.* **1995**, *429*. b) A. J. Appleton, S. Evans, J. R. Lindsay Smith, *J. Chem. Soc. Perkin Trans.* **1981**, *2*, 281.

[12] a) G. R. Friedermann, M. Halma, K. A. D. Castro, F. L. Benedito, F. G. Doro, S. M. Drechsel, A. S. Mangrich, M. D. Assis, S. Nakagaki, *Appl. Catal. A: Gen.* **2006**, *308*, 172. b) S. Reboucas, I. Spasojevic, I. Batinic-Haberle, *J. Biol. Inorg. Chem.* **2008**, *13*, 289.

[13] a) K. Kalyanasundaram, *Inorg. Chem.* **1984**, *23*, 2453. b) I. Mayer, A. L. B. Formiga, F. M. Engelmann, H. Winnischofer, P. V. Oliveira, D. M. Tomazela, M. N. Eberlin, H. E. Toma, K. Araki, *Inorg. Chim. Acta* **2005**, *358*, 2629. c) A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour, L. Korsakoff, *J. Org. Chem.* **1967**, *32*, 476. d) A. M, d.' A. R. Gonsalves, R. A. W. Johnstone, M. M. Pereira, A. M. P. d. SantAna, A. C. Serra, A. J. F. N. Sobral, P. A. Stocks, *Heterocycles* **1996**, *43*, 829. e) K. Hosomizu, M. Oodoi, T. Umeyama, Y. Matano, K. Yoshida, S. Isoda, M. Isosomppi, N. V. Tkachenko, H. Lemmetyinen, H. Imahori, *J. Phys. Chem. B* **2008**, *112*, 16517. f) B.-H. Ye, Y. Naruta, *Tetrahedron* **2003**, *59*, 3593. g) S. Zakavi, A. G. Mojarrad, T. Mokary yazdely, *Macroheterocycles* **2012**, *5*, 67. h) K. Kalyanasundaram, *Inorg. Chem.* **1984**, *23*, 2453. i) P. Hambright, T. Gore, M. Burton, *Inorg. Chem.* **1976**, *15*, 2314. j) A. D. Adler, F. R. Longo, F. Kampas, J. Kim, *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443.

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