# Manganese(III) porphyrin covalently bound to sol-gel derived silica (Mn(III) porphyrinosilica): a reusable and green heterogeneous photocatalyst for oxidative decarboxylation of $\alpha$ -arylacetic acids with H<sub>2</sub>O<sub>2</sub>

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Manganese(III) (5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin)chloride, Mn<sup>III</sup>(TDCPP)CI, was chemically (covalently) bound to a silica matrix by a sol-gel method and used as a new reusable heterogeneous photocatalyt for the selective and efficient oxidative decarboxylation of  $\alpha$ -arylacetic acids with H<sub>2</sub>O<sub>2</sub> as a mild and clean oxidant at room temperature. The activity of this heterogeneous photocatalytic system is higher than that of a corresponding homogeneous systems and the catalyst can be reused several times without loss of its activity and selectivity.

Keywords: manganese(III) porphyrinosilica, α-arylacetic acids, photocatalyst, oxidative decarboxylation, hydrogen peroxide

Metalloporphyrins (MPs) have been widely used as active homogeneous catalysts in the oxidation of organic substrates in recent years (for a recent review see ref.1 and references cited therein).<sup>2,3</sup> They are model systems for studying the mechanism of mild oxidation of organic compounds in the liquid phase by biocatalysts such as monooxygenase cytochrome P-450.<sup>4</sup> Furthermore, the photoredox chemistry of MPs in the presence of organic compounds, which resulted in reduction of the former and oxidation of the latter, have been extensively studied.<sup>5</sup> It is well known that the photocatalytic efficiency of MPs is comparable to that of the TiO<sub>2</sub> semiconductor and new oxidation catalysts based on photoexcited MPs have been developed in homogeneous solutions.<sup>6,7</sup> However, it is difficult to separate these expensive and valuable complexes from the reaction mixture mainly due to their high solubility in polar media which impedes their ready recovery and reuse. For this reason, heterogenisation of MPs for catalytic purposes has attracted particular attention,<sup>8-10</sup> since the solid supports: (i) make the handling and recycling of the system easier; (ii) allow a freer choice of the reaction medium; (iii) can sometimes control the efficiency and selectivity of the photocatalytic processes; (iv) stabilise unhindered MPs against intermolecular self-oxidation or µ-oxo-dimerization; and (iv) minimise the problem of industrial waste treatment and disposal. A variety of solids such as molecular sieves,11 silica,12 zeolites,<sup>13</sup> clays,<sup>14</sup> as well as organic polymers<sup>15,16</sup> and resins<sup>17</sup> have been tested as the support of MPs. Among them, sol-gel derived silica provides a good host matrix for the immobilisation of enzymes and MPs due to its inertnes and stability even under drastic conditions.<sup>18,19</sup> In this context, metalloporphyrinosilicas in which the MP molecules were covalently bound to silica, have been prepared by the sol-gel process as a new class of hybrid organic-inorganic materials.<sup>20-</sup>

One of the best known chemical reactions of carboxylic acids and their derivatives is decarboxylation. Among the various carboxylic acids, oxidative decarboxylation of arylacetic acids has been given considerable attention due to its importance in biology and medicine.<sup>26–29</sup> As an example, most non-steroidal anti-inflammatory drugs (NSAIDs) such as Ketoprofen, Indomethacin and Ibuprofen, have an  $\alpha$ -arylacetic acid or  $\alpha$ -arylpropionic acid structure. It seems that these drugs are metabolised *in vivo* through an oxidative decarboxylation pathway. Study of the mode of metabolism of NSAIDs is one of the main reasons for the attention to decarboxylation of arylacetic acids. A variety of stoichiometric methods has been reported for the oxidative decarboxylation of arylacetic acids

to their corresponding aldehydes and ketones.<sup>30–35</sup> Photodecarboxylation of these acids has also been reported in the presence of various electron acceptors or photosensetizers.<sup>36–42</sup> Most of reported methods produce a large amount of metalcontaining waste, for example Cr, Mn and Hg derivatives and thus cause environmental problems. Therefore, the development of catalytic methods involving clean oxidants to carry out selective oxidative decarboxylation of arylacetic acids is still an active area of research.

Here, we wish to report on the oxidative decarboxylation of various arylacetic acids with  $H_2O_2$  over a Mn(III) porphyrin covalently bound to sol-gel derived silica as a reusable heterogeneous photocatalyst which resulted in the formation of the corresponding aldehydes and ketones in high yields. To the best of our knowledge, this is the first report of photocatalytic decarboxylation of arylacetic acids with  $H_2O_2$  in the presence of an MP covalently bonded to silica as the heterogeneous photocatalyst.

# Experimental

### Materials and methods

All chemicals were used as received from different commercial sources (Merck, Aldrich, Fluka) without further purification. UV-Vis spectra were recorded on a SINCO S-2100 UV-Vis spectrophotometer. Photocatalytic reactions were performed with an Osram 400W high-pressure mercury lamp equipped with a cool water circulating filter to absorb the near IR and a 320 nm cut-off filter in order to avoid direct photolysis of organic substrates. The distance between the light source and reaction vessel was 20 cm. The total incident light flux was  $6.88 \times 10^{-4}$  Einstein cm<sup>-2</sup> min<sup>-1</sup> as determined by ferrioxalate actinometry. GC-MS analyses of organic products of acids were carried out on a Shimadzu QP5050 GC-MS instrument. Quantitative analysis to determine the GC-yields has been carried out with calibration curves obtained with authentic samples. Identification of the GC-MS spectrometric features was achieved with the use of the Wilev library. All library-matched species exhibited the degree of match better than 95%. The <sup>1</sup>H NMR spectra were recorded on a Bruker 300 MHz spectrometer in CDCl<sub>3</sub>. Elemental analysis was performed using a Carlo Erba 1106 instrument. Mass spectra of porphyrins and metaloporphyrins were measured on a Finnigan Mat 251 mass spectrometer using the fast atom bombardment (FAB) method.

Preparation of 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin,  $H_2(TDC)PP$ :<sup>43</sup> This porphyrin was prepared by adding aldehyde (10 mmol) and pyrrole (10 mmol) to dry CH<sub>2</sub>Cl<sub>2</sub> (500 mL) in a 1000 mL three-necked flask. The solution was stirred magnetically at room temperature under a nitrogen atmosphere. After purging the solution for 5 min, the appropriate amount of BF<sub>3</sub> etherate (1.32 mL of a 2.5 M solution in CH<sub>2</sub>Cl<sub>2</sub>, 3.3 mmol), was added. The reaction vessel was shielded from ambient lighting. A sample of *p*-chloranil (1.84 g, 7.5 mmol) in powder form was added at once and the flask

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was immersed in a water bath preheated to 45 °C. The solution was refluxed for 1 hour and then concentrated by rotary evaporation to a volume of approximately 100 mL. The solution WAS poured into a 250 mL, round-bottomed flask containing 10 g of Florisil and the resulting slurry was evaporated to dryness. The powder was poured on top of a column (2 cm diameter) packed with a bed of Florisil, 25 cm in height. Flash chromatography with CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (9:1) eluted both porphyrin and polypyrrylmethenes. The eluant was concentrated, diethyl ether was added, and the solution was slowly concentrated again. Filtration afforded crystals of the porphyrin in 22% overall yield. Anal. Calcd for C<sub>44</sub>H<sub>22</sub>N<sub>4</sub>Cl<sub>8</sub>: C, 59.3; H, 2.5; N, 6.3. Found: C, 59.3; H, 2.5; N, 6.3%. MS (FAB), [M+H]<sup>+</sup>, m/z 887–905; UV-Vis (CHCl<sub>3</sub>; log  $\varepsilon$ ): 418 nm (100%), 512 (4.5), 588 (4.1), 611 (3.0), 657 (3.1); <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 8.62 (s, 8H), 7.68 (m, 12H), –2.59 (s, 2H).

Preparation of 5,10,15,20-tetrakis(2,6-dichlorophenyl-3-sulfonylphenyl) porphyrin,  $H_2TDC(SO_3H)PP$ <sup>:44</sup> 5,10,15,20-tetrakis(2,6dichlorophenyl)porphyrin (100 mg, 0.11 mmol) was stirred with neat chlorosulfonic acid (6 mL, 90 mmol) at 100 °C for 3 h. After cooling the solution to room temperature, ice/water was added slowly (30– 40 g) to give a green crystalline precipitate of diprotonated 5,10,15,20tetrakis(2,6-dichlorophenyl-3-sulfonylphenyl)porphyrin. The required compound was extracted immediately into chloroform, which was then dried (MgSO<sub>4</sub>) and evaporated to give the solid H<sub>2</sub>TDC(SO<sub>3</sub>H) PP (115 mg, 89%). Anal. Calcd for C<sub>44</sub>H<sub>18</sub>N<sub>4</sub>O<sub>8</sub>Cl<sub>12</sub>S<sub>4</sub>: C, 41.1; H, 1.4; N, 4.4. Found: C, 40.6; H, 1.7; N, 4.1%. MS (FAB), [M+H]<sup>+</sup>, *m/z* 1279; UV-Vis (CHCl<sub>3</sub>; log  $\varepsilon$ ): 422 (100%), 514 (6.2), 548 (2.9), 592 (1.7), 658 nm (1.6); <sup>1</sup>H-nmr (CDCl<sub>3</sub>),  $\varepsilon$ : 8.65 (s, 8H), 8.60 (d, 4H), 8.05 (d, 4H), -2.40 (s, 2H).

Metallation of  $H_2(TDC)PP$  and  $H_2TDC(SO_2Cl)PP$ <sup>45</sup> The porphyrin (100 mg) was added to a 25 mL flask containing N,N-dimethylformamide (10 mL), 1 minute was allowed for complete solution to occur, and then a stoichiometric amount of manganese(II) chloride (0.5 g) was added and reaction was allowed to proceed under reflux on a hot plate. After a few minutes completion of the reaction was checked by the loss of the free porphyrin red fluorescence under long wave UV light or spectrophotometrically by withdrawing a small aliquot. The reaction vessel was removed from the hot plate and cooled in an ice-water bath for 15 minute. Chilled distilled water (1 L) was then added and the resulting partially crystalline precipitate was filtered in a Buchner funnel until the filtrate was clear. The filtered material was washed with water and then air dried. MnTDCPPCl (Yield: 98%): UV-Vis  $[CH_3OH, \{\lambda(\epsilon \text{ mol}^{-1} \ 1 \ cm^{-1})\}] = 372, 398$ (shoulder), 466 (7.9 ×10<sup>4</sup>, Soret band), 506 (1.1×10<sup>4</sup>), 576, 616 nm. MnTDC(SO<sub>3</sub>H)PPC1 (Yield: 93%): UV-Vis [CH<sub>3</sub>OH,{ $\lambda(\epsilon mol^{-1} l)$  $(cm^{-1})$ ] = 372, 398 (shoulder), 466 (7.9×10<sup>4</sup>, Soret band), 506  $(1.1 \times 10^4)$ , 576, 616 nm. Then, MnTDC(SO<sub>3</sub>H)PPCl was converted into MnTDC(SO<sub>2</sub>Cl)PPCl byreaction with 10 mL thionyl chloride at reflux overnight and the latter complex was purified in a silica column using dichloromethane as eluent. MnTDC(SO<sub>2</sub>Cl)PPCl (Yield: 85%); UV-Vis [CH<sub>2</sub>Cl<sub>2</sub>, { $\lambda(\epsilon \text{ mol}^{-1} 1 \text{ cm}^{-1})$ }] = 378, 400 (shoulder) 480 (9.8 × 10<sup>3</sup>, Soret band), 580 nm.

Preparation of Mn(III) porphyrinosilica: This material was prepared according to the reported method as follows:46 To a round bottom flask containing MnTDC(SO<sub>2</sub>Cl)PP (0.042 mmol), dry dichloromethane (8 mL) and pyridine (0.500 mmol) was added 3aminopropyltriethoxysilane (APTES, 0.017 mmol). The mixture was refluxed under an argon atmosphere for 6 h. Then, pyridine (0.5 mmol) as a template, tetraethoxysilane (TEOS, 3 mL), ethanol (3 mL) and water (0.5 mL) were added to the flask. The reaction vessel was open to air and left to stand for 9 days at room temperature. The resulting solid was washed with water (20 mL), methanol (10 mL), acetone (10 mL) and dichloromethane (10 mL), successively. The solid was ground and washed with dichloromethane (25 mL), methanol (25 mL) and acetonitrile (25 mL) in a Soxhlet extractor during 3, 2 and 2 days, respectively. UV/Vis spectroscopy of the combined washing liquids was performed to determine the amount of Mn(III) porphyrin that did not polymerise, which was less than 1%. The Mn (III) porphyrin loading onto silica was 18 wt.%. The solid material had the Soret band at 470 nm which has blue shifted when compared with Mn(III) porphyrin spectrum (Soret band at 480 nm). Finally, the Mn(III) porphyrinosilica without the template molecule was obtained through Soxhlet extraction in dichloromethane (50 mL) acidified with 10% HCl (5 mL) according to Scheme 1.

# Photocatalytic oxidative decarboxylation of $\alpha$ -arylacetic acids with $H_2O_2$ over Mn(III) porphyrinosilica

To a solution of α-arylacetic acid (1 mmol) in acetonitrile (20 mL) in a 50 mL Pyrex cell containing a Teflon-coated magnetic stirring bar, was added hydrogen peroxide (0.5 mL, 30%) and Mn(III) porphyrinosilica (0.1 g). The reaction mixture was then placed in a water bath with its temperature adjusted to  $25 \pm 2$  °C. It was irradiated with a high-pressure Mercury lamp (HPML,  $\lambda > 320$  nm) while every 2 h was added hydrogen peroxide (0.2 mL, 30%). The progress of reaction was followed by TLC and GC-MS. After an appropriate time, the irradiation was stopped and the Mn(III) porphyrinosilica photocatalyst was separated via filtration. The filtrate was concentrated and chromatographed on a silica-gel plate or column with n-hexane-EtOAc as the eluting solvent to give the pure product. The results are shown in Table 1. All products are commercially available and were identified by comparison of their physical and spectroscopic data (m.p., TLC, IR, GC-MS) with those of authentic samples. Decarboxylation of arylacetic acids was also investigated in the presence of homogeneous Mn(III) porphyrin (MnTDCPPCl, 0.025 mmol) in a similar manner above. After 24 h, the reaction mixture was analysed by GC-MS. The results obtained are compared with the heterogeneous system in Table 1.



Scheme 1 Preparation of Mn(III) porphyrinosilica.

 $\label{eq:table_$ 

	Ar	1	۸n(III)porphyrin-۹	SiO <sub>2</sub> Ar Ar		
	R	- COOH - (	$CH_3CN$ , hv, $H_2O_2$	, R.T. R (A) R (B)	H + Ar — COOH <b>(C)</b>	
Entry	Ar	R	Heterogeneous photocatalyst		Homogeneous photocatalyst	
			Time /h	Yield <sup>b,c</sup> /%	Time /h	Yield <sup>b</sup> /%
1	C <sub>6</sub> H <sub>5</sub>	Н	10	A: 100 (93)	24	<b>A</b> : 18; <b>B</b> : 1; <b>C</b> : 5
2	4-MeC <sub>6</sub> H₄	Н	10	A: 100 (95)	24	A: 9.5; B: 1.5; C: 2
3	3-MeC <sub>6</sub> H₄	Н	10	A: 100 (92)	24	A: 4.5; B: 1.5; C: 0.5
4	2-MeC <sub>6</sub> H <sub>4</sub>	Н	10	A: 100 (92)	24	A: 7; B: 1.5; C: 1
5	4-MeOC <sub>6</sub> H <sub>4</sub>	Н	10	A: 100 (96)	24	A: 20.5; B: 7.5; C: 3.5
6	2-MeOC <sub>6</sub> H <sub>4</sub>	Н	10	A: 100 (93)	24	<b>A</b> : 9.5; <b>B</b> : 2.2
7	2,4-(MeO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Н	10	<b>A</b> : 100 (95)	24	<b>A</b> : 27; <b>B</b> : 14
8	4-CIC <sub>6</sub> H <sub>4</sub>	Н	10	A: 100 (96)	24	A: 19; B: 2.2; C: 6.3
9	3-CIC <sub>6</sub> H <sub>4</sub>	Н	10	<b>A</b> : 100 (94)	24	A: 15; B: 2.2; C: 4.3
10	2-CIC <sub>6</sub> H <sub>4</sub>	Н	10	<b>A</b> : 100 (94)	24	A: 18.5; B: 2.2; C: 2.8
11	2,6-(CI) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	Н	10	<b>A</b> : 12.5	24	A: 8; B: 2.6; C: 0.6
12	4-FC <sub>6</sub> H <sub>4</sub>	Н	10	<b>A</b> : 32.5; <b>C</b> : 2	24	A: 22; B: 3.2; C: 6.5
13	$4-NO_2C_6H_4$	Н	10	<b>A</b> : 55; <b>C</b> : 45	24	A: 22.5; B: 3.2; C: 5.5
14	1-Naphthyl	Н	10	<b>C</b> : 100 (92)	24	<b>B</b> : 9.4; <b>C</b> : 15.5
15	C <sub>6</sub> H <sub>5</sub>	$C_2H_5$	10	<b>A</b> : 85 (79); <b>B</b> : 15	24	A: 3; B: 2.2; C: 6.3
16	$C_6H_5$	$C_6H_5$	10	<b>A</b> : 22; <b>B</b> : 10	24	<b>A</b> : 46.25; <b>B</b> : 2; <b>C</b> : 6.3

Conditions: substrate (1 mmol), oxidant (0.5 mL) in CH<sub>3</sub>CN (20 m), r.t. <sup>b</sup> GC-yields. <sup>c</sup> The numbers in parenthesis are isolated yield of products.

 Table 2
 Reusability of the Mn(III) porphyrinosilica

 photocatalyst.<sup>a</sup>
 Photocatalyst.<sup>a</sup>

Run	1	2	3	4
Yield (%) <sup>b,c</sup>	100 (93)	100 (91)	100 (92)	100 (91)
<sup>a</sup> Conditions	s: substrate	(1 mmol),	oxidant (0.5	mL) in CH₂CN

(20 m), r.t.

<sup>b</sup> GC-yields.

<sup>c</sup> The numbers in parenthesis are isolated yield of products.

# Reuseability of the photocatalyst

After the decarboxylation of phenylacetic acid, the reaction mixture was filtered and the heterogeneous photocatalyst was separated. The recovered catalyst was washed, dried and then reused for four further runs. The results presented in Table 2.

# **Results and discussion**

In initial experiments when a mixture of phenylacetic acid (1, 1 mmol), H<sub>2</sub>O<sub>2</sub> (0.5 mL) and manganese(III) porphyrinosilica (0.1 g) in acetonitrile solution (20 mL) was irradiated with a high pressure mercury lamp (HPML,  $\lambda > 320$  nm), benzaldehyde (2) was formed as the sole product in 100 % GC-yield (93 % isolated yield) after 10 h (Scheme 2).

Blank experiments showed that no decarboxylation occurs when Mn(III) porphyrinosilica or irradiation were omitted from the system. Also, the reaction did not take place when the metal-free porphyrin was used revealing that the Mn(III) ion in the Mn(III) porphyrinosilica plays an important role in the oxidation process.

To evaluate the scope and limitations of this method, the oxidative decarboxylation of various  $\alpha$ -arylacetic acids was studied under the same reaction conditions. The results are listed in Table 1. As can be seen, a variety of ring-substituted phenylacetic acids having various electron-donating and electron-withdrawing groups were converted into the corresponding aldehydes in moderate to excellent yields without over-oxidation to the carboxylic acids under the reaction



conditions (Table 1, entries 2-13). Phenylacetic acid (Table 1, entry 1) and acids having electron-donating groups e.g. -Me and -OMe on their aromatic ring, (Table 1, entries 2-11), were oxidised into the corresponding aldehydes in excellent isolated yields ( $\geq 90\%)$  while systems with electron-withdrawing substituents, e.g. -F and -NO2 (Table 1, entries 12-13) gave lower yields and increasing the irradiation time did not improve the yields. In contrast to ring-substituted phenylacetic acids, 1-naphthylacetic acid gave 1-naphthycarboxylic acid as the sole product in high yield (Table 1, entry 14). Under the same conditions, a secondary  $\alpha$ -aryl- and an  $\alpha$ , $\alpha$ -diaryl-carboxylic acid were also converted into ketone and alcohol in low to moderate yields (Table 1, entries 15-16). Note that sterically hindered arylacetic acids such as 2,6-dichlorophenylacetic acid (Table 1, entry 11) and diphenylacetic acid (Table 1, entry 16) have been decarboxylated with very low yields under the reaction conditions, confirming that steric effects play an important role in this photoreaction.

In all cases, results obtained over the heterogeneous photocatalytic system were compared with the homogeneouse system under similar conditions. As shown in Table 1, the oxidative decarboxylation of arylacetic acids in homogeneous solution leads to the formation of various products including aldehydes, ketones and acids while heterogeneous oxidation leads to the formation of aldehydes as the sole product. The results clearly indicate that the Mn(III) porphyrinosilica is much more active than the parent homogeneous system, so that it took shorter reaction times. Higher selectivity was observed for the heterogeneous system. As expected, the immobilisation of Mn(III) porphyrin on a solid matrix strongly affects the chemoselectivity of the oxidation process and increases both the photochemical efficiency and the stability of the Mn(III) porphyrin, mainly due to uniform dispersion and site isolation of the MP covalently bonded to the silica.

In order to establish the reusability and stability of the Mn(III) porphyrinosilica photocatalyst, it was separated from the reaction mixture after its first use in the decarboxylation of phenylacetic acid. The recovered catalyst was found to be reusable for four runs without significant loss in activity (Table 2). At the same time, the concentration of Mn in the filtrate was determined to be less than 0.1 % by ICP-AES. These observations confirm that the Mn(III) porphyrinosilica is stable under the reaction conditions and was not affected by the reactants. The high stability of Mn(III) porphyrin chemically bound to the sol-gel derived silica, prevents both fast oxidative degradation of the porphyrin ring and the formation of  $\mu$ -oxo-dimers.

Although the exact mechanism for this reaction over Mn(III) porphyrinosilica is not very clear, on the basis of the above observations and reported mechanisms in the literature,<sup>5,47</sup> a plausible mechanism is suggested. As shown in Scheme 3, catalytic reduction is initiated by coordinating the carboxyl group of the acid to Mn(III) of MP (**a**). One



Scheme 3 The proposed photocatalytic pathway for the oxidative decarboxylation of  $\alpha$ -arylacetic acids with H<sub>2</sub>O<sub>2</sub> over Mn(III) porphyrinosilica.

electron-transfer from the carboxylate ligand to the photoexcited Mn(III) porphyrin (**b**) resulted in solvent-caged manganese(II) porphyrin and the carboxyl radical (**c**). The carboxyl radical can be easily converted to a benzylic radical (**d**) by a rapid decarboxylation. The benzylic radical is then oxidised to the aldehyde probably by a high-valent metal-oxo porphyrin complex (**e**), formed by a hydrogen peroxide activation route. The use of  $H_2O_2$  as the oxygen donor appeared to be particularly interesting, as it is an inexpensive, readily available oxidant which gives  $H_2O$  as the only by-product. The low efficiency for the decarboxylation of bulky arylacetic acid such as aryl 2,6-dicholorophenylacetic acid and diphenylacetic acid confirms that the coordination of carboxyl group to MP is necessary for this conversion. It is possible that the steric hindrance between bulky groups on these acids and similar substituents on MP, prevents coordination of the carboxyl group of the acid to the MP.

# Conclusions

In conclusion, a new and green method with high efficiency and selectivity has been presented for the oxidative decarboxylation of arylacetic acids by using  $H_2O_2$  as an inexpensive, readily available clean oxidant in the presence of Mn(III) porphyrin covalently bonded to silica as a heterogeneous photocatalyst. The activity of this heterogeneous photocatalytic system was higher than homogeneous system and can be reused several times, without loss of its activity and selectivity. This work should be of interest to organic and inorganic photochemists, and biologists.

Received 23 November 2010; accepted 30 January 2011 Paper 1000443 doi: 10.3184/174751911X12983110046865 Published online: 23 March 2011

## References

- 1 C.M. Che and J.S. Huang, Chem. Commun., 2009, 27, 3996.
- 2 J. Piera and J.E. Bäckvall, Angew. Chem. Int. Ed. Engl., 2008, 47, 3506.
- 3 S. Murahashi and D. Zhang, Chem. Soc. Rev., 2008, 37, 1490.
- 4 J.T. Groves, T.E. Nemo and R.S. Myers, J. Am. Chem. Soc., 1979, 101, 1032.
- 5 A. Maldotti, G. Varani, A. Malinari, P. Battioni and D. Mansuy, *Inorg. Chem.*, 1996, 35, 1126.
- 6 C. Bartocci, A. Maldotti, G. Varani, P. Battioni, V. Carassiti and D. Mansuy, *Inorg. Chem.*, 1991, **30**, 1255.
- 7 L. Weber, R. Hommel, J. Behling, G. Haufe and H. Hennig, J. Am. Chem. Soc., 1994, 116, 2400.
- 8 J.R. Lindsay-Smith, In: R.A Sheldon (ed.), Metalloporphyrins in catalytic oxidations, Marcel Dekker Inc., NewYork, 1994, Ch. 11.
- 9 A.W. Van der Made, J.W.H. Smeets, R.J.M. Nolte and W. Drenth, J. Chem. Soc., Chem. Commun., 1983, 1204.
- D. Mansuy and P. Battioni, *Metalloporphyrins in catalytic oxidations*, Marcel Dekker, New York, 1994.
- 11 Z. Li, C. Xia and X. Zhang, J. Mol. Catal. A: Chem., 2002, 185, 47.
- 12 F.S. Vinhado, C.M.C. Prado-Manso, H.C. Sacco and Y. Iamamoto, J. Mol. Catal. A.: Chem., 2001, 174, 279.
- 13 I.L. Viana Rosa, C.M.C. Prado-Manso, O.A. Serra and Y. Iamamoto, J. Mol. Catal. A.: Chem., 2000, 160, 199.
- 14 F. Bedioui, Coord. Chem. Rev., 1995, 144, 39.

- 15 P.R. Cooke and J.R. Lindsay-Smith, J. Chem. Soc. Perkin Trans. I., 1994, 1913.
- 16 M.V. Vinodu and M. Padamanabhan. Proc. Indian Acad. Sci., 1998, 110, 461.
- 17 S. Campestrini and B. Meunier, Inorg. Chem., 1992, 31, 1999.
- 18 E.A. Vidoto, M.S.M. Moreira, F.D.S. Vinhado, K.J. Ciuffi, O. R. Nascimento and Y. Iamamoto J. Non-Cryst. Solids, 2002, 304, 151.
- 19 D.C. de Oliveira, H.C. Sacco, O.R. Nascimento, Y. Iamamoto and K.J. Ciuffi, J. Non-Cryst. Solids, 2001, 284, 27.
- 20 M.S. M. Moreira, P.R. Martins, R.B. Curi, O.R. Nascimento and Y. Iamamoto J. Mol. Catal. A: Chem., 2005, 233, 73.
- 21 J.C. Biazzotto, E.A. Vidoto, O.R. Nascimento, Y. Iamamoto and O.A. Serra, J. Non-Cryst. Solids, 2002, 304, 101.
- 22 K.J. Ciuffi, H.C. Sacco, J.B. Valim, C.M.C.P. Manso, O.A. Serra, O.R. Nascimento, E.A. Vidoto and Y. Iamamoto J. Non-Cryst. Solids, 1999, 247, 146.
- 23 D.C. de Oliveira, H.C. Sacco, O.R. Nascimento, Y. Iamamoto and K.J. Ciuffi, J. Non-Cryst. Solids, 2001, 284, 27.
- 24 G.S. Machado, K.A.D. de Freitas Castro, O.J. de Lima, E.J. Nassar, K.J. Ciuffi and S. Nakagaki, *Colloids Surf. A*, 2009, **349**, 162.
- 25 K. J. Ciuffi, H.C. Sacco, J.C. Biazzotto, E.A. Vidoto, O.R. Nascimento, C.A.P. Leite, O.A. Serra and Y. Iamamoto, J. Non-Cryst. Solids, 2000, 273, 100.
- 26 S. Encinas, M.A. Miranda, G. Marconi and S. Monti, *Photochem. Photobiol.*, 1998, **67**, 420.
- 27 L.L. Costanzo, G. De Guidi, G. Condorelli, A. Cambria and M. Farma, J. Photochem. Photobiol. B: Biol., 1989, 3, 223.
- 28 V. Mirkhani, S. Tangestaninejad, M. Moghadam and Z. Karimian, *Bioorg. Med. Chem. Lett.*, 2003, 13, 3433.
- 29 M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork, N. Sirjanian and P. Somayeh, *Bioorg. Med. Chem.*, 2009, 17, 3394.
- 30 O. Toussaini, P. Capdevielle and M. Maumy, *Tetrahedron*, 1984, 40, 3229.
- 31 M. Komuro, Y. Nagatsu, T. Higuchi and M. Hirobe, *Tetrahedron Lett.*, 1992, **33**, 4949.
- 32 A.R. Kore, A.D. Sagar and M.M. Salunkhe, Org. Prep. Proc. Int., 1995, 27, 373.
- 33 A.R. Kore and M.M. Salunkhe, Indian J. Chem., Sect. B: Org. Chem. Incl. Med. Chem., 1996, 35B, 151.
- 34 K. Mohri, J. Mamiya, Y. Kasahara, K. Isobe and Y. Tsuda, *Chem. Pharm. Bull.*, 1996, 44, 2218.
- 35 Y.I. Kim and Y.H. Kim, Tetrahedron Lett., 1998, 39, 639.
- 36 D. Budac and P. Wan, J. Photochem. Photobiol. A: Chem. 1992, 67, 135.
- 37 K. Isobe, K. Mohri, J. Taga, Y. Sasaki and Y. Tsuda, *Chem. Pharm. Bull.*, 1992, 40, 2188.
- 38 H. Koshima, K. Ding, I. Miyahara, K. Hirotsu, M. Kanzaki and T. Matsuura, J. Photochem. Photobiol. A: Chem., 1995, 87, 219.
- 39 A. Itoh, T. Kodama, S. Inagaki and Y. Masaki, Org. Lett., 2000, 2, 331.
- 40 M. Sobczak and P. Wagner, Org. Lett., 2002, 4, 379.
- 41 S. Farhadi, P. Zaringhadam and R. Zareisahamieh, Tetrahedron Lett., 2006,
- **47**, 1965.
- 42 M.H. Habibi and S. Farhadi, J. Chem. Res., 2004, 296.
- 43 J.S. Lindsey, I.C. Schreiman, H.C. Hsu, P.C. Kearney and A.M. Marguerettaz, J. Org. Chem., 1987, 52, 827.
- 44 A.M.A. Rocha Gonsalves, R.A.W. Johnstone, M.M. Pereira, A.M.P. Santana, A.C. Serra, A.J.F.N. Sobral and P.A. Stocks, *Heterocycles*, 1996, 43, 1423.
- 45 A.D. Adler, F.R. Longo, F. Kampas and J. Kim, *J. Inorg. Nucl. Chem.*, 1970, **32**, 2443.
- 46 K.J. Ciuffi, H.C. Sacco, J.C. Biazzoto, M.R.Zuccki, O.A. Serra, O.R. Nascimento, C.A.P. Leite and Y. Iamamoto, J. Non-Cryst. Solids., 2000, 273, 150.
- 47 P. Hanson, J.R.L. Smith and V.A. Osborne, J. Chem. Soc., Perkin Trans. 2, 1998, 2653.

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