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Phthalocyanine metal complexes: Versatile catalysts for selective oxidation and bleaching

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ABSTRACT

Iron and other metal phthalocyanine complexes can mediate both selective oxidation and bleaching reactions depending on the choice of oxidant. Olefins, phenols, condensed aromatics can efficiently be oxidized to valuable products by ^{t}BuOOH. The use of H_2O_2 leads to a different kind of reactivity providing efficient systems for catalytic degradation of recalcitrant pollutants and bleaching. The discovery of remarkable catalytic properties of μ-nitrido diiron phthalocyanine complexes exemplified by mild catalytic oxidation of methane in water at near-ambient conditions is of especial significance. This emerging type of oxidation catalysts has a great potential for the development. In this context, a combinatorial approach might be particularly fruitful. First, different macrocyclic ligands can be used, e.g. phthalocyanines, porphyrins, porphyrazines, corroles, corrolazines, etc. to produce either symmetrical dimers with the same ligand or unsymmetrical dimers having two different macrocyclic ligands. Secondly, a number of transition metals (Fe, Mn, Ru, Cr, V, Ti, etc.) can be used for the preparation of homoleptic or heteroleptic dimers having the same or different metals. Finally, several single bridging atoms can be used including O, N, C. The great variability of possible metal, ligand, bridging atom combinations might provide a large variety of complexes with different and tunable catalytic properties.

1. Introduction

The development of clean oxidation processes is an important topic in current chemistry and industry. Enzymes, natural catalysts, are capable of performing very difficult chemical reactions, e.g. oxidation of inactivated C–H bonds, even in methane, under very mild physiological conditions. Mimicking active sites of enzymes in order to reproduce their catalytic activity is therefore a fruitful approach for development of catalysts which could operate under mild conditions in a clean fashion. However, the accessibility of the catalysts in terms of their price and availability at a large scale plays also an important role for economical viability of the processes. Available and cheap phthalocyanine metal complexes (MPc) are very attractive from this point of view. In addition, their macrocyclic structure resembles that of porphyrin complexes widely used by nature in the active sites of oxygenase enzymes suggesting their potential as catalysts for oxidation (Fig. 1).

Indeed, MPc complexes have been used for catalytic oxidation of alkanes [1–3], olefins [4,5], aromatic [6–12] and other compounds [13–19]. However, in contrast to well-documented porphyrin chemistry with established mechanisms and active species identified and characterized by different spectroscopic techniques, catalytic chemistry of MPc is not yet well developed. There is a stark contrast between state of the art of porphyrin and phthalocyanine oxidation chemistry.

Therefore, we develop new catalytic methods (homogeneous and heterogeneous) for oxidation based on phthalocyanine complexes and we try to investigate the mechanisms and active species involved in these oxidations. The appropriate choice of oxidant and change of the structure of these catalysts (metal, electron-withdrawing or donating substituents, support, etc.) allow tuning catalytic properties of the systems. In this manuscript we summarize our recent studies on MPc as catalysts for oxidation and bleaching, overview the catalytic properties of N-bridged diiron phthalocyanines and discuss the perspectives for further development of these emerging catalysts which are especially suitable for the combinatorial approach.

2. Experimental

Catalytic bleaching: UV–vis spectra of solutions and kinetic traces were recorded on a Perkin-Elmer Lambda 35 spectrophotometer. Metal tetrasulfophthalocyanine complexes were prepared as described before [20]. Experiments on bleaching of morin were carried out as described previously for terpyridine manganese complexes [21]. In a typical experiment, UV–vis cell was filled up

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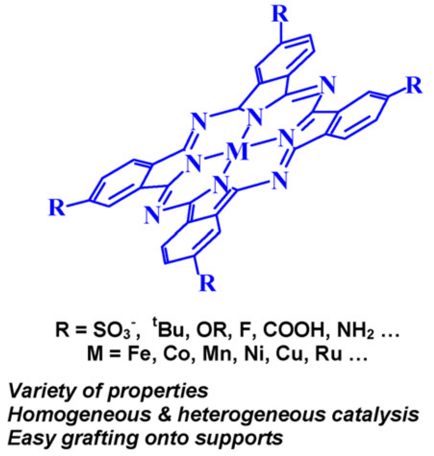


Fig. 1. Metallophthalocyanine complexes as potential catalysts for oxidation.

with 1 ml of 50 mM carbonate buffer solution (pH 10.0) containing 160 μM morin, 10 mM hydrogen peroxide and 0.3–2 μM catalyst. Bleaching of morin was followed as the decrease in absorbance at 410 nm.

3. Results and discussion

3.1. MPc complexes as catalysts for oxidation

Although homogeneous MPc can be successfully employed in catalytic reactions, heterogeneous catalysts provide significant advantages in easier separation of catalysts from reaction products and, in some cases, re-use of the same catalyst in the successive oxidations either in batch or continuous operation mode. Heterogeneous MPc catalysts can be prepared by different methods. MPc have been incorporated in zeolites [2]. An interesting approach was developed by Parton et al. [3,22]. They embedded MPc–zeolite material into polydimethylsiloxane membranes and achieved an efficient oxidation of alkanes. Supported MPc have been prepared by physical adsorption on mesoporous silicas [23–25], activated carbon [26] and by sol–gel processing [27]. Covalent anchoring of MPc on organic copolymers [28] and silica [29,30] is an alternative approach. We used the covalent approach for fixation of tetrasulfonated metallophthalocyanines (MPcS) onto amino-modified SiO_2 [11,17,31,32] or TiO_2 [33]. Depending on the experimental conditions FePcS can be fixed onto SiO_2 and other supports either in monomeric or μ-oxo dimeric form [11,31]. Noteworthy, the dimeric supported catalysts exhibit better catalytic properties in selective oxidation. The possible reasons for this will be discussed below. The immobilization of MPc on chitosan aerogel microspheres afforded oxidation catalysts containing basic sites that could be advantageous for some reactions [34]. The structures of supported catalysts are schematically presented in Fig. 2.

These supported catalysts were shown to be efficient in the allylic and propargylic oxidations of olefins [16,33–35] and alkynes [14], phenols [32,36–38] and aromatic compounds [10,17,32]. Importantly, only 0.5–1 mol.% amounts of catalyst are usually needed for these reactions. In the case of difficult substrates increased amount of catalyst (2 mol.%) can be used in order to improve the product yield. The most representative examples of the selective oxidation mediated by supported MPcS catalysts are listed in Tables 1–4. In general, several variable parameters can be tuned in order to obtain the best yield and, in certain cases, to change a selectivity. The most important variables are the nature and amount of oxidant, the nature and amount of the catalyst, the properties of the support, the reaction temperature and the solvent. These trends will be illustrated by selected examples.

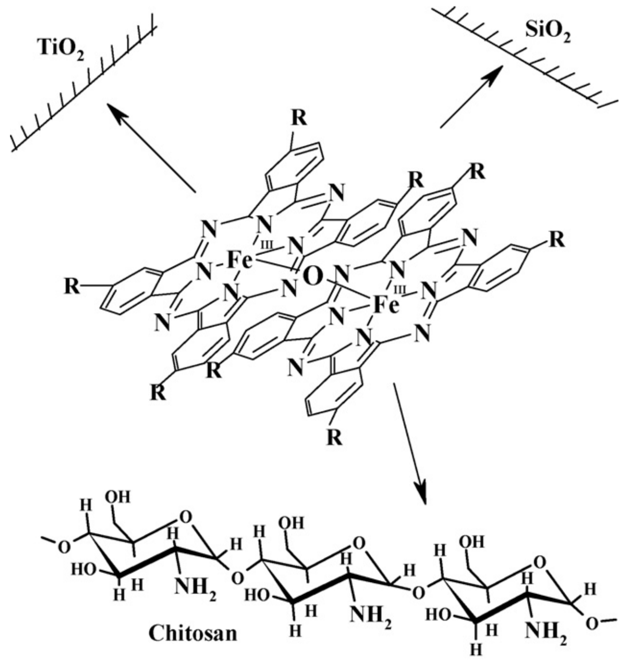


Fig. 2. Schematic representation of the heterogeneous FePcS catalysts supported onto SiO_2 [11,17,31,32], TiO_2 [33] and chitosan [34].

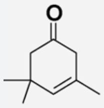
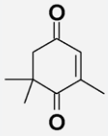
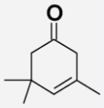
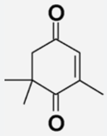
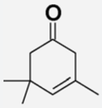
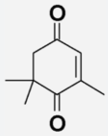
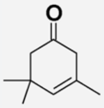
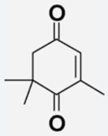
The selectivity of the oxidation of olefins can be changed depending on the oxidant used. For example, epoxides were obtained in good yields (74–90%) when molecular oxygen was used as oxidant in combination with isobutyric aldehyde (Table 1, entries 1–3). In the presence of ${}^{t}BuOOH$, 2-cyclohexen-1-one was obtained in the oxidation of cyclohexene with 57% yield along with only trace amount of epoxide (Table 1, entry 4). The FePcS-SiO_2–${}^{t}BuOOH$ system was successfully employed for propargylic oxidation closely related to allylic one [14]. Selective oxidation of alkynes at α-position keeping intact triple bond provided α,β-acetylenic ketones, highly valuable precursors in the preparation of fine chemicals, in high yields (62–84%, Table 1, entries 5–9). The influence of support was shown in the aerobic oxidation of β-isophorone (β-IP) to ketoisophorone (KIP) which is important intermediate for the preparation of flavours and fragrances [33,34]. A regular FePcS-SiO_2 catalyst provided a 38% yield of KIP (Table 1, entry 10) while the same FePcS complex grafted onto TiO_2 was more efficient giving a 57% KIP yield. It should be noted that TiO_2 was not an innocent support in this case. Although the mechanism of this cooperative effect is not yet clear, the combination of two catalytic sites in FePcS-TiO_2 resulted in more selective oxidation of β-IP to KIP [33]. Materials combining oxidation and basic sites were prepared by supporting of MPc onto chitosan, a polysaccharide containing free amino groups [34]. In this case CoPcS-chitosan exhibited better catalytic properties in the oxidation of β-IP to KIP than FePcS-chitosan catalyst (Table 1, entries 12 and 13).

Oxidation of aromatic compounds leads to quinones which are used for the preparation of vitamins and drugs. In particular, vitamin K_3 (2-methyl-1,4-naphthoquinone, 2MQ) can be obtained by oxidation of 2-methylnaphthalene (2MN). Industrially, vitamin K_3 is produced by stoichiometric oxidation of 2MN by CrO_3–H_2SO_4 with moderate 40–50% yields [39]. Along with 2MQ numerous 2MN oxidation products are usually formed [38] thus explaining why only moderate 2MQ yields can be obtained. In search for the cleaner oxidation method we found that FePcS-SiO_2–${}^{t}BuOOH$ oxidation system was capable of oxidizing this demanding substrate with

34% yield of 2MQ (Table 2, entry 1). Importantly, FePcS-SiO_2 catalyst supported in μ-oxo dimer form was more active and selective than homogeneous and monomeric supported catalyst (Table 2, entry 1 vs. entries 3 and 4). MnPcS-SiO_2 and CoPcS-SiO_2 were less active in the oxidation of 2MN (Table 2, entries 5 and 6). μ-Oxo dimeric FePcS grafted onto mesoporous MCM-41 material showed lower conversion and selectivity in 2MQ compared with the catalyst grafted onto regular amorphous SiO_2 (Table 2, entry 2 vs. entry 1). This decrease in selectivity could be explained by the increased residence time of substrate in porous system that should favour over-oxidation reactions. Less demanding aromatic oxidations of anthracene and xanthene resulted in 90% and 99% yields of anthraquinone and xanthone, respectively (Table 2, entries 8 and 9).

The same trends have been observed in the oxidation of 2,3,6-trimethylphenol (TMP) to 2,3,5-trimethylbenzoquinone (TMQ), precursor of vitamin E (Table 3). Although the catalytic activity was almost the same, the selectivity of SiO_2-supported dimeric catalyst (77% TMQ yield) was much higher than that of homogeneous FePcS and monomeric supported catalyst, 47% and 42% TMQ yield, respectively (Table 3, entries 1, 4, and 5). Again, SiO_2 support was superior than mesoporous MCM-41 in case of monomeric (42% vs. 21% yield, Table 3, entries 5 and 3) and dimeric catalyst (77% vs. 24% yield, Table 3, entries 4 and 2) suggesting easier over-oxidation in mesopores. Interestingly, manganese supported catalysts showed the opposite behaviour: MnPcS-MCM-41 provided 47% yield of TMQ vs. only 22% in the case of MnPc-SiO_2 catalyst (Table 3, entries 6 and 7).

Table 1
Oxidations of olefins mediated by heterogeneous MPc catalysts.

Entry	Substrate (conversion, %)	Product (yield, %)	catalyst	Oxidant, conditions	Ref.
1	Cyclooctene (96%)	Cyclooctene oxide (90%)	FePc*-SiO_2[a]	O_2 + IBA[b] MeCN, 25 °C, 7 h	[16]
2	Cyclohexene (91%)	Cyclohexene oxide (78%) 2-Cyclohexene-1-ol (1%) 2-Cyclohexen-1-one (7%)	FePc*-SiO_2[a]	O_2 + IBA MeCN, 25 °C, 9 h	[16]
3	Styrene (90%)	Styrene oxide (74%) Benzaldehyde (18%)	FePc*-SiO_2[a]	O_2 + IBA MeCN, 25 °C, 5 h	[16]
4	Cyclohexene	Cyclohexene oxide (2%) 2-Cyclohexene-1-ol (5%) 2-Cyclohexen-1-one (57%)	FePcS-SiO_2	^{t}BuOOH MeCN, 40 °C, 24 h	[35]
5	$C_3H_7C\equiv CC_3H_7$ (80%)	$C_3H_7C\equiv CC(O)C_2H_5$ (71%)	FePcS-SiO_2	^{t}BuOOH BuOH, 40 °C, 24 h	[14]
6	$C_3H_7C\equiv CC_3H_7$ (79%)	$C_3H_7C\equiv CC(O)C_2H_5$ (70%)	$FePcCl_{16}$-SiO_2	^{t}BuOOH BuOH, 40 °C, 24 h	[14]
7	$PhC\equiv CC_2H_5$ (75%)	$PhC\equiv CC(O)CH_3$ (62%)	FePcS-SiO_2	^{t}BuOOH BuOH, 40 °C, 24 h	[14]
8	$PhC\equiv CC_2H_5$ (86%)	$PhC\equiv CC(O)CH_3$ (80%)	$FePcCl_{16}$-SiO_2	^{t}BuOOH BuOH, 40 °C, 24 h	[14]
9	$HC\equiv CC(OH)C_5H_{11}$ (84%)	$HC\equiv CC(O)C_5H_{11}$ (84%)	FePcS-SiO_2	^{t}BuOOH BuOH, 40 °C, 24 h	[14]
10	 (92 %)	 (38 %)	FePcS-SiO_2	O_2 DMSO, 60 °C, 24 h	[33]
11	 (99 %)	 (57 %)	FePcS-TiO_2	O_2 DMSO, 60 °C, 24 h	[33]
12	 (48 %)	 (17 %)	FePcS-chitosan	O_2 MeCN, 80 °C, 24 h	[34]
13	 (85 %)	 (39 %)	CoPcS-chitosan	O_2 MeCN, 80 °C, 24 h	[34]

[a] Pc* = 2(3),9(10),16(17),23(24)-tetra[1,5-di(3-triethoxysilyl)-(propyl)biuryl]phthalocyanine.
[b] IBA, isobutyric aldehyde.

Table 2
Oxidations of condensed aromatics mediated by heterogeneous MPc catalysts[a].

Entry	Substrate (conversion, %)	Product (yield, %)	Catalyst	Oxidant, conditions	Ref.
1	2MN (90%)	2MQ (34%) 6MQ (9%)	FePcS-SiO_2	^{t}BuOOH MeCN, 40 °C, 7h	[32]
2	2MN (81%)	2MQ (24%) 6MQ (11%)	FePcS-MCM-41	^{t}BuOOH MeCN, 40 °C, 24h	[32]
3	2MN (58%)	2MQ (11%) 6MQ (3%)	m-FePcS-SiO_2	^{t}BuOOH MeCN, 40 °C, 24h	[32]
4	2MN (64%)	2MQ (11%) 6MQ (6%)	Homogene-ous FePcS	^{t}BuOOH MeCN, 40 °C, 24h	[32]
5	2MN (49%)	2MQ (14%) 6MQ (6%)	MnPcS-SiO_2	^{t}BuOOH MeCN, 40 °C, 24h	[32]
6	2MN (16%)	2MQ (traces)	CoPcS-SiO_2	^{t}BuOOH BuOH, 40 °C, 24h	[32]
7	2,3-Dimethyl-naphthalene (88%)	2,3-Dimethyl-1,4-naphthoquinone (33%)	FePcS-SiO_2	^{t}BuOOH MeCN, 40 °C, 24h	[17]
8	Anthracene (100%)	Anthraquinone (90%)	FePcS-SiO_2	^{t}BuOOH $CHCl_2CH_3$, 40 °C, 24h	[10]
9	Xanthene (100%)	Xanthone (99%)	FePcS-SiO_2	^{t}BuOOH MeCN, 40 °C, 7h	[10]

[a] 2-MN, 2-methylnaphthalene; 2MQ, 2-methyl-1,4-naphthoquinone; 6MQ, 2-methyl-1,4-naphthoquinone.

Table 3
Oxidations of 2,3,6-trimethylphenol to 2,3,5-trimethylbenzoquinone mediated by heterogeneous MPc catalysts [32].

Entry	Catalyst	Conversion of substrate, %	Product yield, %
1	Homogeneous FePcS	96	47
2	FePcS-MCM-41	98	24
3	m-FePcS-MCM-41	98	21
4	FePcS-SiO_2	96	77
5	m-FePcS-SiO_2	95	42
6	MnPcS-SiO_2	65	22
7	MnPcS-MCM-41	94	47

Reaction conditions: ^{t}BuOOH, CH_2ClCH_2Cl, 30 °C, 2 h.

Oxidation of substrates having several oxidizable positions selectively on desired position keeping other sites intact is a significant synthetic challenge. A case example is the oxidation of functionalized phenols to quinones bearing different functional groups which are powerful intermediates in organic synthesis. In addition, they show biological activity since such quinone fragments often occur within the molecular frameworks of natural products. Although functionalized quinones can be prepared using multistep synthetic strategies, the selective aromatic oxidation of readily available phenols is the most direct approach [36]. FePcS-SiO_2 catalyst in combination with ^{t}BuOOH was found to be quite selective in aromatic oxidation of phenols containing easily oxidizable groups. Among them are alcohol groups, double and triple bonds, benzylic positions (Table 4). The presence of these functionalities enhances the versatility of these building blocks for the synthesis of elaborated structures. Product yields are generally in the range of 40–60%. Catalyst loading is generally 1 mol.%, but 0.5 mol.% catalyst has also been used effectively. Significantly those quinones bearing double and triple bonds have been obtained for the first time (Table 4, entries 5 and 6). The preparation of quinoline-5,8-dione by direct oxidation of 8-hydroxyquinoline with 61% yield (Table 4, entry 9) is another important example since some catalysts were inactive owing to coordination of metal center with quinoline nitrogen atom. The observed high selectivity of aromatic oxidation vs. oxidation of substituents can be explained by the coordination of phenolic group to iron phthalocyanine followed by interaction with ^{t}BuOOH and by two successive one electron oxidations. Such a mechanism was proposed for oxidation of alkyl-substituted phenols and naphthols on the basis of $^{18}O_2$ labelling experiments, EPR spectroscopy with spin traps, kinetic studies and complete analysis of all reaction products [12]. It should be noted that in order to get the optimal yield of quinones the solvent dependence should be studied since the selectivity of phenol oxidation depends on the solvent nature. In practice, acetonitrile, acetone and dichloroethane are among the best solvents for these reactions.

Thus, the aforementioned examples illustrate how the appropriate change of the structure of the supported catalyst and reaction conditions leads to tuning the catalytic activity.

3.2. MPc complexes as bleaching catalysts

When water soluble iron phthalocyanines were used in combination with H_2O_2 different catalytic activity was observed. FePcS was very efficient for oxidative degradation of 2,4,6-trichlorophenol (TCP) [6–9]. Degradation of chlorinated aromatics is an important topic because these recalcitrant compounds are priority pollutants. FePcS–H_2O_2 system was able to cleave aromatic cycle of TCP to form chloromaleic and oxalic acids with traces of chlorofumaric, maleic and fumaric acids. The formation of CO_x (14% yield) and the release of more than 2 Cl^- anions per TCP molecule indicated a partial mineralization of TCP [6–9]. The key steps of proposed mechanism of the cleavage of aromatic cycle involve a putative nucleophilic iron (III) peroxo complex, $PcSFe^{III}OO^-$ (Fig. 3). This nucleophilic species was proposed to be able to epoxidize electron-deficient double bonds of the intermediate quinones and to attack their carbonyl positions to perform the aromatic C–C cleavage via a Grob-type fragmentation (Fig. 3) [7–9]. No evidence was obtained for formation of hydroxyl radicals from peroxides in the presence of FePcS [7,12]. The photochemical version of FePcS–H_2O_2 system was used for oxidative degradation of several dyes, such as rhodamine B, sulforhodamine B, crystal violet, acridine orange and orange II [40,41]. FePcS in combination with H_2O_2 was applied for catalytic degradation of several chelating agents in diluted aqueous solutions such as ethylenediamine tetraacetic acid (EDTA), nitriloacetic acid, β-alanine diacetic acid, and others [42]. Due to poor biodegradability, these chelating agents are accumulating in natural waters thus posing environmental problems.

Aforementioned examples prompted us to propose that MPc could be possible bleach catalysts for detergent applications. The use of catalysts might help to shift from current stoichiometric

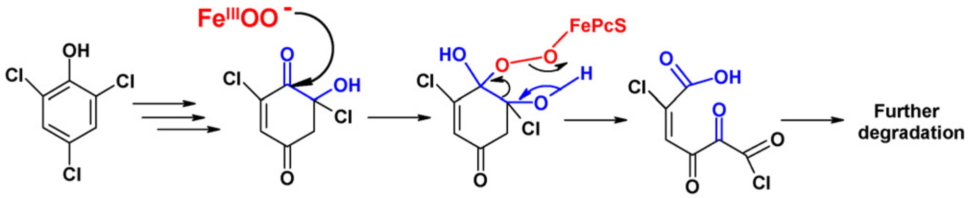
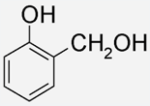
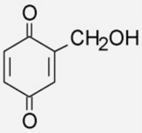
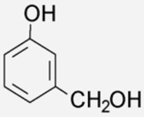
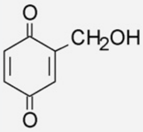
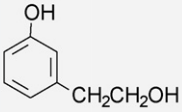
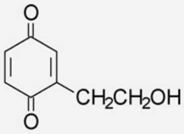
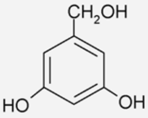
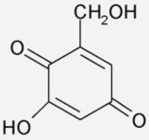
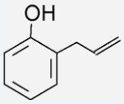
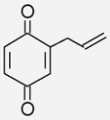
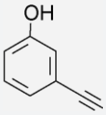
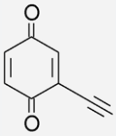
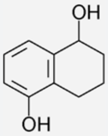
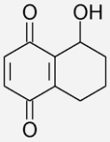
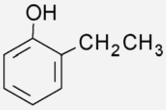
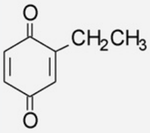
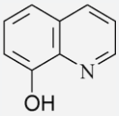
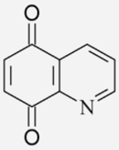
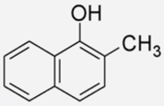
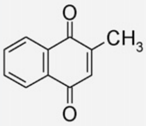


Fig. 3. Key step of proposed mechanism of aromatic cycle cleavage by FePcS–H_2O_2 system.

Table 4
Oxidations of functionalized phenols mediated by heterogeneous FePcS catalysts.

Entry	Substrate	Product	Conversion, % (reaction time, h)	Yield, %	Ref.
1[a]			91 (2)	52	[36]
2[a]			100 (2.5)	53	[36]
3[a]			100 (1.5)	56	[36]
4[a]			84 (2)	46	[36]
5[b]			98 (2)	47	[36]
6[a]			32 (2)	17	[37]
7[a]			100 (0.5)	40	[37]
8[a]			92 (2)	43	[37]
9[a]			84 (2)	61	[37]
10[c]			96 (1)	57	[38]

[a] Conditions: FePcS-SiO_2, ^tBuOOH, acetone, 30 °C.
[b] The same conditions, but in MeCN.
[c] Dichloroethane, 80 °C.

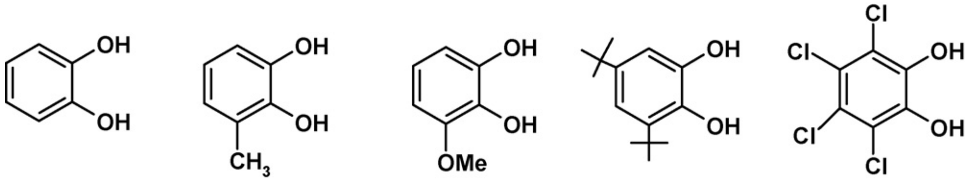


Fig. 4. Catechols: models of tannins.

bleach chemistry involving peroxides and activators to more economic and cleaner catalytic bleaching. The main classes of bleach catalysts and their possible modes of action have recently been reviewed [43]. Several manganese, iron, and in less extent copper and cobalt complexes have previously been tested as bleaching catalysts for laundry cleaning [21,43–46]. Among them are manganese terpyridine [21,43], 1,4,7-triazacyclononane [43,46], Schiff base [43], cross-bridged macrocyclic and polypyridineamine complexes [43] as well as iron complexes with Tris(pyridin-2ylmethyl)amine (TPA), pentadentate nitrogen-donor and macrocyclic tetraamidate (TAML) ligands [43,47]. Although careful mechanistic studies of catalytic bleaching are rare [48], mono- and binuclear high-valent oxo species, like $LMn^{V}{=}O$, $LMn^{IV}{=}O$ (L—ligand), have been proposed to be involved in these reactions. In the case of iron complexes, LFe^{III}-OOH and $LFe^{IV}{=}O$ were assumed to be active species. $[Mn^{IV}_2(\mu\text{-}O)_3(Me_3tacn)_2](PF_6)_2$ complex was employed in laundry detergents in 1994 but was withdrawn from the market after discovery that it provoked increased fabric- and dye-damage [43]. Nevertheless, the bleach catalyst concept is still attractive because if an efficient catalyst without side effects would be found it would be beneficial in several aspects. First, activation of peroxides by catalyst should allow performing the cleaning process at lower, even near-ambient temperatures providing significant saving of energy. Currently, high washing temperatures (70–90 °C, 40–60 °C in case of peracids) are necessary for good bleaching. Application of bleaching catalysts might decrease the temperature of bleaching processes and energy consumption. The replacement of bulk activators by small amount of the efficient catalyst will result in more compact and concentrated compositions that is also more energy efficient. In addition, significant decrease of the content of bulk chemicals would strongly reduce the environmental pollution. To achieve this challenging goal, several requirements for catalyst should be fulfilled. The future catalyst should be cost-efficient, hydrolytically stable, especially in alkaline aqueous media and selective, providing stain bleaching without oxidative damage to other dyes and textiles [43]. The catalyst should keep the performance under a wide variety of conditions and be safe for humans and the environment [43].

Metallophthalocyanine complexes meet at least some of these criteria. They are cheap, easily available in a large scale and currently used in many industrial applications. Their worldwide production is more than 80,000 t/year. Since MPc are perspective compounds for photodynamic therapy of cancers, intensive toxicological studies of them have been performed to show their good toxicological properties [49]. Taking into account the high bleaching activity of MPc towards phenols, these complexes might be perspective as bleach catalysts. Polyphenolic chromophores are very often the target of bleach processes in laundry. Intensely coloured polyphenolic compounds of fruits, tea, wine, etc. represent the most frequent and recalcitrant stains. The mechanism of bleaching of polyphenols was proposed to involve nucleophilic deprotonated hydrogen peroxide and peracids which attack chromophores to form epoxides, then diols thus leading to degradation of chromophore and increase of solubility in water. Several lines of evidence indicate a nucleophilic iron (III) peroxo complex, $PcSFe^{III}OO^-$ as the key active species in the oxidative degradation of chlorinated phenols. In order to evaluate MPc as bleaching catalysts we have studied the oxidation of catechol. Catechols can be considered as good models of tannins which are among the main stains (Fig. 4). A good bleaching catalyst should deeply oxidize catechol and tannins to colourless and water soluble products that necessitates several oxidation steps. We have shown that MPcS (M = Co, Fe, Mn) complexes were very efficient in the bleaching of five catechols using four oxidants: H_2O_2, $Na_2CO_3 \times 1.5\ H_2O_2$, $NaBO_3$ and $NaBO_3$ in combination with tetraacetylethylenediamine (TAED) [50]. The influence of these variables as the reaction temperature (20 °C, 40 °C) and pH (7, 9, 10, 10.5 and 11) on the rate of catechols oxidation was studied. Noteworthy, only 0.01–0.1 mol.% catalyst charge was sufficient to achieve a high substrate conversion to quinones. The further oxidative degradation of quinones to aromatic cycle cleavage products provided efficient bleaching of the reaction mixture within 2–5 min. The experiments in the presence of EtOH or mannitol showed no decrease of the bleaching rate suggesting that OH radicals were not involved in these oxidations. To further evidence the bleaching potential of MPc we have studied the oxidation of morin. Morin (2′,3,4′,5,7-pentahydroflavone) is a polyphenolic compound belonging to a group of flavonoid plant dyes present in tea, fruits and vegetables (Fig. 5). Morin can be considered as a simple, soluble model of a typical bleachable stain. First, several metal complexes (M = Fe, Mn, Co, Ni, V, Ru) on tetrasulfophthalocyanine and tetracarboxyphthalocyanine platforms were initially screened.

Bleaching experiments were carried out as described previously for terpyridine manganese complexes [21]. Because of very high bleaching activity of phthalocyanine catalysts, the experiments were performed at 25 °C with 0.3–2 μM catalyst compared with 40 °C and 2.5–10 μM catalyst in case of terpyridine manganese complexes. Bleaching of morin was followed as the decrease in absorbance at 410 nm (Fig. 6). Iron, cobalt and manganese complexes showed a high catalytic activity. Even with small catalyst amount (5–10 fold less than in experiments with terpyridine manganese complexes [21]) the bleaching of morin was completed within 1 min. Remarkably, turnover frequency of this oxidation achieved 800 catalytic cycles per minute. The catalytic activity of iron phthalocyanine complexes in the morin bleaching was at least 5 times higher than that of published manganese terpyridine complexes. Ongoing research suggests that appropriate modification of the catalytic system allows to improve bleaching properties and to use molecular oxygen as the terminal oxidant. Thus, the high bleaching capacity of MPc at ambient temperatures due to its ability to cleave aromatic cycles strongly suggest a possible use of these accessible and inexpensive catalysts in environmentally friendly bleaching processes.

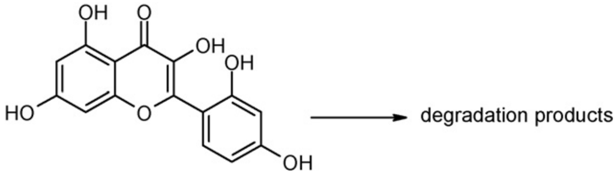


Fig. 5. Structure of morin (2′,3,4′,5,7-pentahydroflavone).

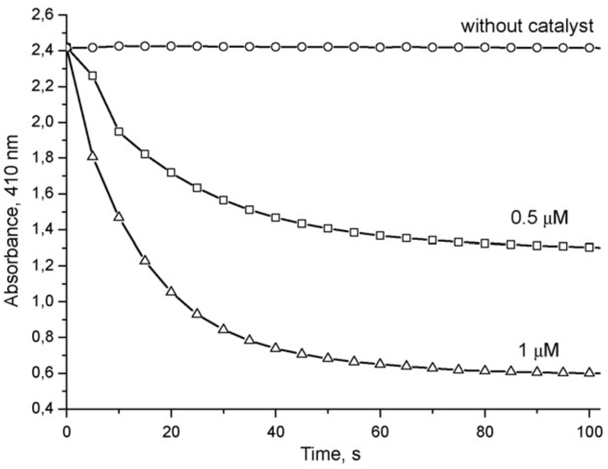


Fig. 6. Typical kinetic traces of morin oxidation. Conditions: [morin] = 160 μM, [H_2O_2] = 10 mM, 25 °C, pH 10.

Noteworthy, this reactivity can also be used for synthetic purposes. After initial screening of different MPc, the FePcS–H_2O_2 catalytic system was successfully applied for clean transformation of polysaccharides by oxidation (Fig. 7) [15,51]. Polysaccharides are by far the most abundant renewable raw materials already used in non-food applications in paper, textile, detergent, pharmaceutical and cosmetic industries on the scale of several million tons per year only in Europe. These inexpensive, non-toxic and already highly functionalized renewables could replace materials derived from fossil feedstock. However, to fulfill demands for tailored application profiles native polysaccharides should often be modified. Selective oxidation may provide industrially viable products for different applications. The FePcS–H_2O_2 system was used for clean modification of starch, cellulose and its derivatives, guar gum, inuline and offers an evident advantage over traditional oxidation methods involving NaOCl or $NaIO_4$ as terminal oxidants [15]. Only small amounts of water, H_2O_2 and a cheap and readily available on the industrial scale catalyst are used for clean one-step modification of polysaccharides without any production of waste/side products. The process can be performed in homogeneous conditions or using a suspension of polysaccharide in aqueous solution of catalyst. From practical point of view, the most interesting option is probably the dry oxidation method. By mixing solid polysaccharide, e.g. starch, with a small amount of aqueous solution of the catalyst, a homogeneous distribution of the catalyst in the solid substrate can be obtained. Addition of H_2O_2 leads to catalytic oxidation. Using very small amount of catalyst (0.00004 mol. equiv. to substrate) turnovers of more than 2000 has been attained. The efficiency of utilisation of H_2O_2 to form carbonyl and carboxyl groups reached 80%. During reaction the catalyst is bleached and colourless modified polysaccharide can be recovered. Depending on the application of modified polysaccharide, the trace amount of residual iron due to extremely low catalyst charge can be removed by washing with cold water or even can be left in the material. The products were characterized by carbonyl and carboxyl substitution degrees, ^{13}C NMR, TGA, SEM and SEC methods. The process is flexible to yield a controlled content of carboxyl and carbonyl groups, up to 30 COOH and 20 CHO groups per 100 anhydroglucose units, respectively, the former generate hydrophilic properties that are important for numerous technological applications, while the presence of carbonyl groups provides specific properties. The products obtained by this method do not contain any contamination and were successfully tested for the surface coating of paper, latex and paint preparation as well as in applications where the purity of product is an important issue, e.g. in cosmetic formulations. This method corresponds to all criteria of green chemistry: only small amounts of water, H_2O_2 and a cheap catalyst available at industrial scale are used for clean, one-step modification of polysaccharides without any production of waste/side products.

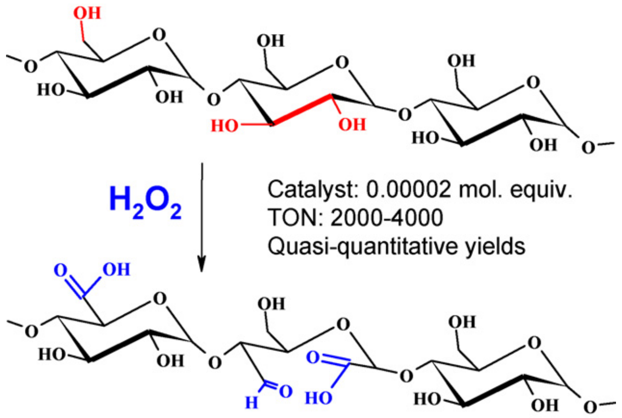


Fig. 7. Schematic representation of oxidation of starch.

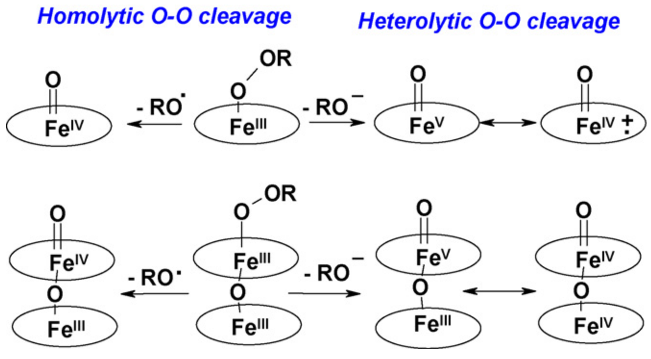


Fig. 8. Possible pathways for the formation of high-valent oxo species from mononuclear and binuclear iron complexes.

3.3. *Binuclear vs. mononuclear iron phthalocyanines: novel possibilities for oxidation*

μ-Oxo dimeric species are often considered as catalytically inactive forms. The observation of the superior catalytic properties of μ-oxo dimeric FePcS supported complex in selective oxidations is in a conflict with this dogma. Nevertheless, some rational explanations can be put forward to explain this fact. Iron complexes are believed to activate terminal oxidants (peroxides, peracids, etc.) to form high-valent oxo species (Fig. 8). It should be noted that the interaction of peroxides with iron complexes is an important subject of numerous studies and debates in the literature. Iron mononuclear complexes can initiate the formation of free radicals via homolytic cleavage of O–O peroxide bond resulting in free radical oxidation. Otherwise, high-valent iron oxo species, e.g. $LFe^{IV}{=}O$ and $L^{+\bullet}Fe^{IV}{=}O$ (L—ligand) are formed via heterolytic cleavage of O–O bond. In the latter case, these intermediates are oxidizing species. Although activation of peroxides by binuclear porphyrin-like complexes is not yet well studied one can propose the similar mechanism [32]. However, the heterolytic rather than homolytic O–O cleavage should be favoured in the case of binuclear LFe–O–FeL due to better delocalization of the charge at two iron atoms with respect to mononuclear scaffold (Fig. 8). A macrocyclic ligand can also play an important role for charge delocalization and serve as an “electron reservoir”. A high selectivity in the case of dimer can be explained by avoiding the formation of $OR^{\bullet}$ radical during formation of the active species which could provoke side reactions thus decreasing selectivity of oxidation. The difference in the intrinsic reactivity of the putative $LFe^{IV}{=}O$ and $LFe^{IV}–O–(L^{+\bullet})Fe^{IV}{=}O$ species could be also responsible for the difference in their catalytic properties. The difference in oxidation pathways (heterolytic vs. homolytic O–O peroxide cleavage) should depend on the properties of macrocyclic ligand L. In the case of ligands stabilizing lower oxidation states, e.g. phthalocyanines, the difference between mononuclear and binuclear complexes in generation of high-valent oxo species should be more pronounced. Several examples of high catalytic activity of μ-oxo dimeric complexes have been reported by us [11,17,31,32] and by other groups [52–55]. Our initial results on catalytic oxidation using supported μ-oxo diiron phthalocyanines prompted us to study this class of complexes more systematically.

3.4. N-bridged diiron phthalocyanines: powerful catalysts for oxidation

Another argument in favour of binuclear oxidation catalysts comes from nature. In nature, methane monooxygenase (MMO) enzymes exhibit the most striking example of catalytic activity of diiron sites oxidizing CH_4 to CH_3OH by O_2 at ambient conditions. The ability of diiron non-heme active site of soluble MMO to perform oxidation of one of the most inert organic substrates has initiated numerous studies directed on reproducing the same catalytic activity using synthetic binuclear non-heme complexes. Although significant advance in structural and spectroscopic MMO models has been achieved, no diiron non-heme complex able to perform the oxidation of CH_4 is yet available [56]. Considering other natural catalysts capable of oxidizing strong C–H bonds, cytochromes P-450, with mononuclear iron porphyrin active site and taking into account promising catalytic properties of macrocyclic dimers described above we have proposed a novel approach for the development of catalysts for oxidation on the basis of stable binuclear porphyrin-like complexes.

A single atom bridged dimers provide an additional option for modification of structure. Along with μ-oxo bridge, μ-nitrido and μ-carbido connecting groups can be used for the formation of binuclear metal complexes [57]. N-bridged diiron porphyrin [58] and phthalocyanine [59] complexes have been prepared a long time ago, but have never been evoked as catalysts. Unsubstituted $(FePc)_2N$ is insoluble in common organic solvents that complicates its investigation and use in catalysis. To overcome this drawback we have prepared μ-nitrido diiron tetra-tert-butylphthalocyanine $(FePc^tBu_4)_2N$ (Fig. 9) by the treatment of mononuclear $FePc^tBu_4$ with NaN_3 in refluxing xylene with 62% yield [60]. The distinctive feature of $(FePc^tBu_4)_2N$ is its high stability which is an important requirement for the development of the oxidation catalyst. The stability of the binuclear structure is provided by the bridging N atom as follows from 1s N XPS and ESI-MS data [60,61]. The 1s N XPS spectrum of $(FePc^tBu_4)_2N$ shows a strong signal at 398.7 eV from 16 nitrogen atoms of the phthalocyanine moieties and a small signal at much higher energy of 402.4 eV assigned to strongly bonded bridging nitrogen atom. ESI-MS spectrum of $(FePc^tBu_4)_2N$ exhibits a very strong molecular peak at $m/z = 1599.8$ with no fragmentation due to monomerization indicating the high stability of dimeric structure.

UV–vis and EPR data indicated a slow reaction between $(FePc^tBu_4)_2N$ and H_2O_2 to form hydroperoxo $(Pc^tBu_4)Fe^{IV}{=}N–Fe^{III}(Pc^tBu_4)–OOH$ complex. This complex undergoes heterolytic O–O cleavage to generate high-valent diiron oxo complex $(Pc^tBu_4)Fe^{IV}{=}N–Fe^{IV}(^{+}Pc^tBu_4){=}O$ (Fig. 9) as directly evidences by ESI-MS experiments with labelled $H_2{}^{18}O_2$ [60,61]. Such a highly electrophilic species should be a very powerful oxidant. This hypothesis was checked in the oxidation of methane.

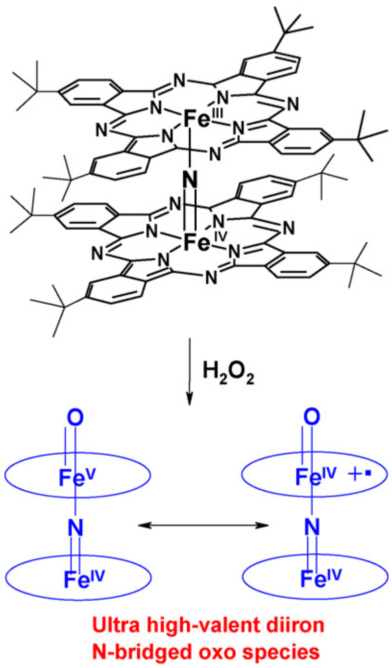


Fig. 9. Structure of μ-nitrido bridged diiron tetra-tert-butylphthalocyanine and formation of active species in the presence of hydrogen peroxide.

The low temperature oxidation of methane is a long standing fundamental and practical challenge. For a long time this approach has been associated with activation of CH_4 at transition metal centers like Pt, Pd, Ir, Hg, etc. in harsh conditions [62]. For instance, the most efficient so far Pt system operates at 220 °C in oleum converting CH_4 to CH_3OSO_3H [63]. A catalytic system for CH_4 oxidation at near-ambient conditions would be an important achievement.

Using labelled $^{13}CH_4$ we have unambiguously evidenced the formation of $^{13}CH_3OH$, $^{13}CH_2O$ and $H^{13}COOH$ in the supported $(FePc^tBu_4)_2N–H_2O_2$ system [60]. Formic acid was a main product because of easier oxidation of intermediate CH_3OH and CH_2O compared to CH_4. Remarkably, CH_4 was oxidized even at 25 °C in pure water although with a moderate TON of 13. The optimal reaction temperature was 40–60 °C to obtain TON ~ 26–29. Mechanistically, the heterolytic cleavage of O–O bond in $Fe^{IV}NFe^{III}OOH$ (Pc^tBu_4 ligands are omitted for clarity) with formation of formally $Fe^{IV}NFe^{V}{=}O$ active species should be favoured by protonation of peroxide oxygen and release of H_2O, better leaving group. Indeed, a significant improvement of the catalytic activity was observed in the presence of diluted H_2SO_4 [60,64]. When a new portion of H_2O_2 was added directly to the reaction mixture after completing the first reaction, practically the same catalytic activity was found in the second cycle indicating a high stability of the catalyst and even a possibility of recycling [60]. At optimal pH, the TON_{HCOOH} was increased by factor 10 to attain 220 [64]. The catalyst exhibits a very high performance which is far higher than that of the most published systems operating via CH_4 activation and comparable to the most efficient so far Periana's system based on Pt(II) complex in oleum at 220 °C [63]. The $(FePc^tBu_4)_2N–H_2O_2$ system was also efficient in oxidation of propane [61] and ethylene [64].

Kinetic, ^{18}O labelling and spectroscopic data for this catalytic system are consistent with oxo-transfer chemistry rather than free radical mechanism. The further evidence for involvement of high-valent diiron oxo species $(Pc^tBu_4)Fe^{IV}{=}N–Fe^{IV}(^{+}Pc^tBu_4){=}O$ was obtained in the study on oxidation of benzene [65]. We observed the formation of benzene epoxide in the course of oxidation of PhH to PhOH as well as NIH shift (migration of the

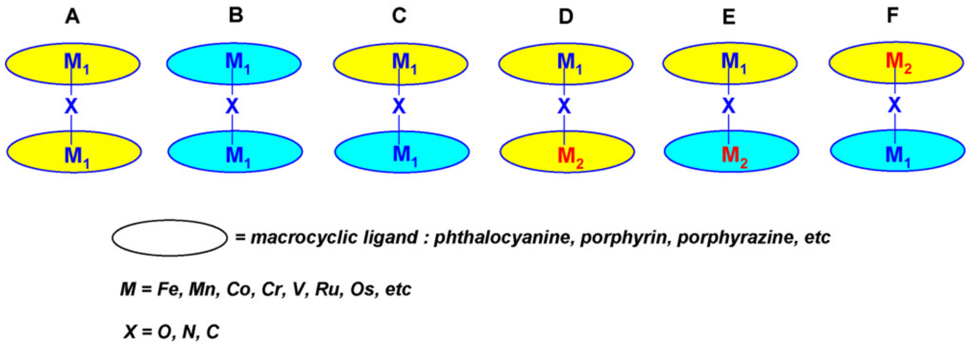


Fig. 10. Various possible structures of single atom bridged bimetallic macrocyclic complexes.

substituent from the site of hydroxylation to an adjacent carbon atom, the name NIH shift arised from the U.S. National Institutes of Health where this phenomenon was discovered [66]). Both phenomena, formation of benzene epoxide and NIH shift, are characteristic of biological oxidation mediated by cytochromes P-450 and toluene monooxygenases involving high-valent iron oxo complexes. The same mechanistic features of benzene oxidation by (FePc^{t}Bu$_4$)$_2$N–H$_2$O$_2$ system strongly support the oxo-transfer mechanism.

Unusual properties of Fe–N–Fe structural unit on the phthalocyanine platform were further demonstrated in the synthesis of μ-nitrido diiron (IV) phthalocyanine cation–radical complexes (X)PcFe^{IV}–N–Fe^{IV}Pc$^{+\bullet}$(X) (X = Cl, Br) as evidenced by UV–vis, EPR, ESI-MS, Mössbauer, XANES and EXAFS data [67]. Noteworthy, these diiron(IV) dihalogenated complexes are completely stable at ambient conditions which represent a rare case of stable Fe(IV) complexes. Fe K-edge EXAFS analysis of (X)PcFe^{IV}–N–Fe^{IV}Pc$^{+\bullet}$(X) showed bridging N atom at 1.69 Å distance. The distance between two equivalent hexacoordinated in-plane iron (IV) centers is 3.39 Å. Fe–X bond lengths are 2.33 Å and 2.54 Å for X = Cl, Br respectively. The use of (Cl)PcFe^{IV}–N–Fe^{IV}Pc$^{+\bullet}$(Cl) for catalytic oxidation of organic substrates has been shown for the first time [67].

A limited number of N-bridged binuclear phthalocyanine complexes have so far been prepared. In order to enlarge the choice of N-bridged complexes and to gain a deeper insight into this novel chemistry we have prepared a series of μ-nitrido diiron phthalocyanines with electron-withdrawing alkylsulfonyl substituents SO$_2$R [68,69]. ESI-MS, UV–vis, FTIR, EPR, XPS, Mössbauer techniques as well as Fe K-edge X-ray absorption spectroscopy (XANES, EXAFS) were used for complete characterization of these novel complexes. Interestingly, the change in the size of alkyl substituents R on the periphery of Pc ligand introduced the difference in the iron oxidation state. While the complexes with small R (Me, Et, n-hexyl) are neutral mixed-valence Fe$^{+3.5}$–N–Fe$^{+3.5}$ complexes, the dimers with bulky R (t-Bu, cyclohexyl, adamantly) are cationic Fe^{IV}–N–Fe^{IV} species. These complexes selectively catalyze benzylic oxidation of alkyl aromatic compounds [68].

3.5. *Metal–N–metal: a versatile platform*

Binuclear M–N–M (M = transition metal) complexes on macrocyclic porphyrin-like platform are emerging class of oxidation catalysts. This unusual structure provides unprecedented catalytic properties and reactivity. The most significant so far example is the mild oxidation of methane. We believe that this finding is a breakthrough in the oxidation field. Clean and practical character of this system coupled with real availability of the phthalocyanines suggests a high application potential of this approach. In addition, this system has a great potential for further development by modification of the structure (Fig. 10). Different macrocyclic ligands (phthalocyanines, porphyrins, porphyrazines, corroles, corrolazines, etc.) can be used to accommodate M–X–M structural unit with different transition metals in a variety of combinations. Several levels of structural variation can be envisaged:

(i) variation of macrocyclic ligand, e.g. introduction of different electron donating or electron-withdrawing substituents: homoleptic and heteroleptic arrangements;
(ii) variation of type of macrocyclic ligand (phthalocyanine, porphyrin, porphyrazine, etc.): homoleptic and heteroleptic arrangements;
(iii) variation of transition metal (Fe, Mn, Ru, Cr, V, Os, etc.): homometallic and heterometallic complexes;
(iv) variation of the single bridging atom (Fe^{III}–O–Fe^{III}, Fe^{III}–N–Fe^{IV}, Fe^{IV}–C–Fe^{IV} structural units for μ-oxo, μ-nitrido and μ-carbido dimers, respectively).

Provided that synthetic challenges will be overcome, a large library of localized and delocalized binuclear complexes can be prepared (Fig. 10). Tuning of aforementioned structural parameters should considerably affect the electronic structure and can therefore be used to tune catalytic properties. A wise modification of structure would lead to the improvement of the catalytic performance and would provide the tailored catalysts for the oxidation of compounds of different nature and many applications can be envisaged. These binuclear complexes show interesting electronic, magnetic and spectroscopic features. This makes these materials very attractive for different applications.

4. Conclusions

We have shown a large scope of application of MPc as oxidation catalysts. Many valuable products can be obtained in clean catalytic processes catalyzed by these accessible catalysts. Appropriate modification of the catalytic system changes the character of oxidation to enable catalytic bleaching reactions which are also important for many applications such as waste water treatment, pulp and paper bleaching. N-bridged diiron phthalocyanine complexes show a new unexpected reactivity and provide a novel promising approach in the field of oxidation. Binuclear N-bridged phthalocyanine and related complexes present a novel, largely unexplored field in the catalytic oxidation. These emerging catalysts are especially suitable for combinatorial approach. Several levels of variation of the structure can be envisaged to prepare a large library of symmetrical and unsymmetrical complexes for future systematic studies. Future studies will focus on these aspects. We feel that this chemistry shows great promise.

Acknowledgments

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