Metallophthalocyanines Linked to Organic Copolymers as Efficient Oxidative Supported Catalysts

Muriel Sanchez,[a] Nicolas Chap,[a] Jean-Bernard Cazaux,[b] and Bernard Meunier*[a]

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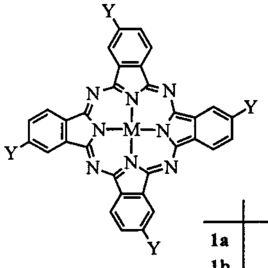
The covalent anchoring of metallo(chlorosulfonyl)phthalocyanines **1** onto the acrylic copolymers **2** and **3** has been achieved. When using H_2O_2 or $KHSO_5$ as oxidant, these supported catalysts are able to oxidize a poorly biodegradable molecule such as 2,4,6-trichlorophenol or a tannin model such as 3,5-di-*tert*-butylcatechol. The influence of the spacer and the nature of the reaction medium on the catalytic activities have been studied, as well as the recycling of these supported metallophthalocyanine catalysts.

Introduction

Metallophthalocyanines (e.g., **1** and **4**, Scheme 1) have attracted considerable interest because of their structural similarity to metalloporphyrin complexes found at the active sites of metalloenzymes.[1] These phthalocyanine complexes are often more easily prepared than synthetic metalloporphyrins, and exhibit interesting properties in areas such as sensitizers[1,2] (e.g., in photodynamic cancer therapy), catalysts[1,3] (e.g., for thiol oxidation in gasoline fractions), electrocatalysts[1,4] (e.g., for O_2 reduction in fuel cells), sensors[1][3c,5] (e.g., NO_x and O_2 gas sensors) or nonlinear optical devices.[1,6]



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	Y	M
1a	SO_2Cl	Fe
1b	SO_2Cl	Co
4a	$SO_3^-Na^+$	Mn
4b	$SO_3^-Na^+$	Fe
4c	$SO_3^-Na^+$	Co

Scheme 1. Structure of the metallo[2,9,16,23-tetrakis(chlorosulfonyl) and -tetrasulfo]phthalocyanines **1** and **4**

In the field of bio-inspired oxidations, it has been shown in our laboratory that water-soluble metallo(sulfo)phthalocyanines **4** (Scheme 1) can be used as oxidation catalysts with H_2O_2 or $KHSO_5$.[7] Highly reactive metal−peroxo (e.g., $Fe^{III}-OOY$) and metal−oxo ($Fe^{IV}=O$) species are probably involved in the catalytic oxidations of poorly biodegradable molecules such as polychlorinated phenols, catechols, and polycondensed aromatics.[7] One limitation of these catalysts is the formation in solution of inactive aggregates and dimers of the metallophthalocyanine complexes, which significantly affects their catalytic properties. This aggregation phenomenon is usually depicted as a coplanar association of the aromatic rings driven by enhanced van der Waals forces and dimer formation through μ-oxo bridges.[7a,8] In solution, the monomerization of water-soluble metallophthalocyanines can be achieved by adding an organic co-solvent[7a] or a detergent.[9] Another strategy used to obtain a monomolecular dispersion of these macrocyclic complexes is based upon their heterogenization on the surface of a support. Several types of carrier have been used for this task, such as charcoal,[10] organic polymers,[11] silica,[12] zeolites,[13] and clays.[14] Among the advantages of using supported catalysts is the easy separation of the catalysts from products and the subsequent possible recycling of the catalyst.[15]

Recently, we have described the covalent attachment of the chlorosulfonyl-substituted iron-phthalocyanine **1a** (Scheme 1) to functionalized 3-aminopropyl-silica via a sulfonamide linkage.[16] This supported catalyst, when using hydrogen peroxide as oxidant, is able to degrade a recalcitrant pollutant. However, the efficiency of this catalytic system was lower than that obtained under homogeneous conditions. This probably results from diffusion-limitation effects inherent to the use of silica as support, despite the fact that mineral supports have a better reputation of chemical stability compared to organic polymers in catalytic oxidations with supported catalysts.[17]

Here, we report the preparation of new organic polymers-supported metallophthalocyanines, and their efficiency as oxidation catalysts.

Results and Discussion

Preparation of the Supported Catalysts

We have previously shown that a sulfonamide linkage used to immobilize an iron-phthalocyanine onto modified

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[a] Laboratoire de Chimie de Coordination du CNRS,
205 route de Narbonne, 31077 Toulouse cedex 4, France
E-mail: bmeunier@lcc-toulouse.fr
[b] EXPANSIA,
Route d'Avignon, BP N 6, 30390 Aramon, France

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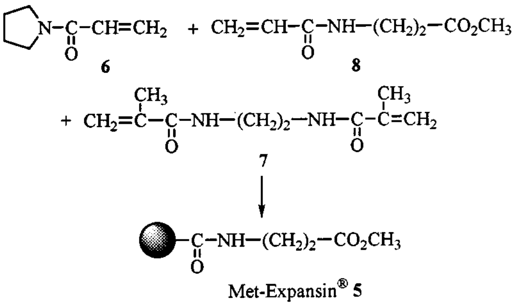
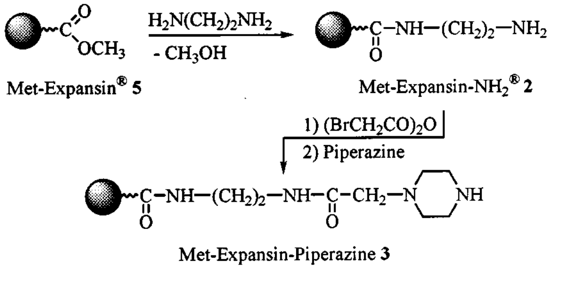
silica is stable under oxidative conditions.[15] Therefore, we decided to use the same type of linkage for the attachment of chlorosulfonyl-substituted phthalocyanine complexes **1** onto organic supports. The organic supports used were the acrylic copolymers Met-Expansin-NH$_2$® (**2**) and Met-Expansin-Piperazine (**3**), which both possess an amino-functionalized pendant arm and were prepared from Met-Expansin® (**5**) by EXPANSIA. These resins were synthesized from the polymerization of the monomer *N*-acryloylpyrrolidine (**6**), the cross-linking agent *N*,*N*′-bis(methacryloyl)-1,2-diaminoethane (**7**), and *N*-acryloyl-β-alanine methyl ester (**8**) as functionalizing agent (Patent EP 79842, 1982) (Scheme 2).



Scheme 2. Synthesis of Met-Expansin® (**5**)

The polyacrylamide **5** can be treated with ethylenediamine to afford **2** (Patent EP 81408, 1982) (Scheme 3). This resin contains 0.56 mmol-equiv. of NH$_2$ per gram of dry material that can be used to covalently anchor the metallo(chlorosulfonyl)phthalocyanines **1**. A spacer can also be used to increase the distance between the catalyst and the polymer surface. This modification of the tether helps to increase the solvent, substrate, and oxidant access, similar to homogeneous reaction conditions. Copolymer **3** was prepared by treating **2** with bromoacetic anhydride, followed by the addition of piperazine (Patent Fr. Dem. 9904135, 1999). It contains 0.5 mmol-equiv. of terminal NH functions per gram of dry resin.



Scheme 3. Synthesis of Met-Expansin-NH$_2$® (**2**) and Met-Expansin-Piperazine (**3**)

The two organic copolymers **2** and **3** are insoluble in organic solvents and in aqueous media; however, these resins swell in protic solvents to form gels. This property is certainly important for the preparation of supported catalysts, because the surface area of the carrier is considerably increased making the active catalytic centers more accessible.

The immobilization of the chlorosulfonyl derivatives **1** of the iron- and cobalt-phthalocyanines was achieved by heating a mixture of resin and complex in pyridine to reflux. The supported catalysts FePc-SO$_2$NH-Met-Expansin (**9**) (20.0 µmol of iron per gram of dry resin), FePc-SO$_2$N(pip)-Met-Expansin (**10a**) (26.5 µmol Fe/g), and CoPc-SO$_2$N-(pip)-Met-Expansin (**10b**) (42.0 µmol Co/g) were thus obtained from the polyacrylamides **2** and **3** (Scheme 4).

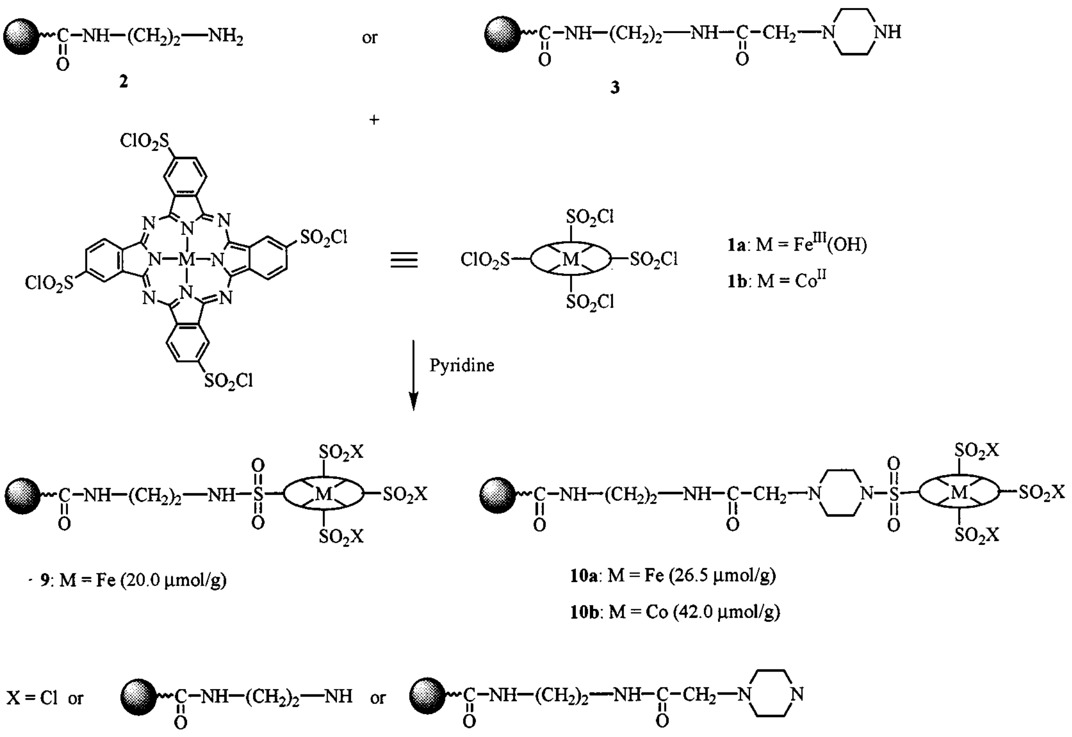
After filtration, the loading of the supports was indirectly calculated by determining the amount of **1** remaining in solution by UV/Vis spectroscopy. No release of metallophthalocyanine was observed after several washings with water, dimethylformamide, and ethanol. The green color of these modified polymers obtained after the washing procedures strongly suggested that the metallophthalocyanine complexes were attached in monomeric form (µ-oxo-metallophthalocyanine dimers and aggregates are generally blue).[7a] It is important to note that no desorption of the metallophthalocyanine catalysts was detected under oxidative conditions (e.g., after addition of H$_2$O$_2$ or KHSO$_5$) according to UV/Visible measurements.

For comparison, the silica-supported catalysts FePc-SO$_2$NH-Silica (**11**) (42.0 µmol Fe/g) and FePc-SO$_2$N(pip)-Silica (**12**) (40.0 µmol Fe/g) were also prepared. The grafted polymer **11** comes from the direct fixation of **1** onto a commercially available modified silica featuring primary amine linkers, whereas **12** contains the piperazine spacer introduced by the same procedure used for the preparation of **3** from **2** (Scheme 5).

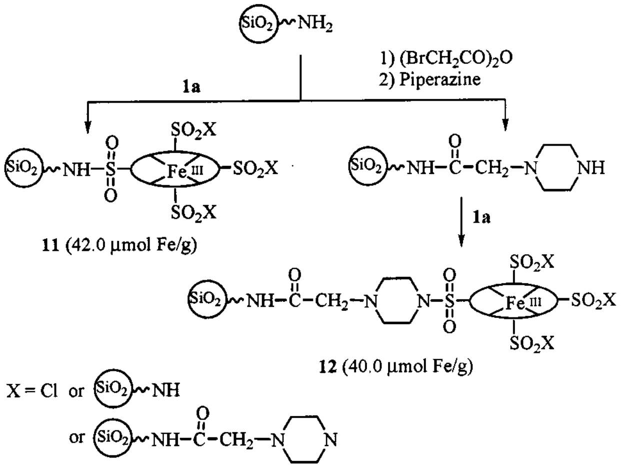
Catalytic Activities of the Grafted Complexes 9−11 for the H$_2$O$_2$ Oxidation of a Chlorinated Pollutant

2,4,6-Trichlorophenol (TCP) is produced by paper mills during the oxidative chlorine degradation of lignin in white paper manufacturing.[18] Due to its slow biodegradation by aerobic or anaerobic microorganisms and its resistance to oxidative or reductive chemical treatments, this substrate is extremely persistent in the environment. Thus, TCP is commonly used as a pollutant model. It has been shown that ligninase (a peroxidase isolated from the white-rot fungus *Phanerochaete chrysosporium*) is able to degrade TCP by an oxidative pathway, although the conversion is slow.[18b] Synthetic metalloporphyrins, which are efficient peroxidase models, are able to oxidize TCP to the corresponding quinone, but are unable to cleave the aromatic ring of TCP.[19] Using either soluble metallophthalocyanines, or the corresponding immobilized catalysts onto a support (silica or Amberlite), with H$_2$O$_2$ as a "green" oxidant, TCP has been converted in two classes of compounds: aromatic ring cleavage products (C$_4$ diacids, with chloromaleic acid being the major product) and oxidative coupling products (Scheme 6).[7,20]

Under the same experimental conditions [1 mM TCP solution in a mixture of 50 mM phosphate buffer (pH = 7)/acetone (80:20), 6 mM H$_2$O$_2$, and 2 mol-% of catalyst], however, the reaction was markedly faster with the iron-tetrasulfophthalocyanine catalyst **4b** under homogeneous condi-



Scheme 4. Immobilization of the metallophthalocyanines **1** onto **2** and **3**



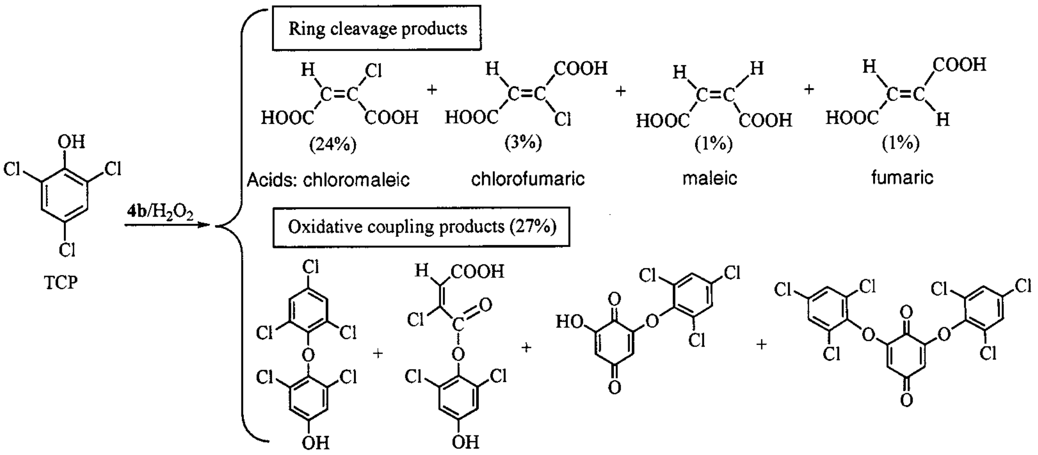
Scheme 5. Immobilization of the metallophthalocyanines **1** onto silica

tions, compared to the iron complex **11** grafted onto silica modified with primary amine linkers. Indeed, full conversion of TCP was achieved within 45 min with **4b** (Run 2, Table 1), while it took 1 h for the supported catalyst **11** to oxidize only 52% of TCP (Run 3).

The oxidative properties of the metallophthalocyanines immobilized onto the organic polymers **2** and **3** were also investigated. First, we checked that the TCP substrate was not oxidized by H_2O_2 and the support material alone, in the absence of metallophthalocyanine catalyst (Run 1). In addition, this control experiment confirmed that there is no physisorption of the substrate onto the surface of the support. In the presence of phosphate buffer, but without any organic co-solvent, the supported iron catalysts **9** and **10a** with H_2O_2 were able to degrade 85% (Run 4) and 62% (Run 10) of the TCP, respectively, within 1 h. The presence of an organic co-solvent such as ethanol or acetone, which allowed a better solubilization of the poorly water-soluble TCP substrate, improved the degradation process up to full conversion of TCP within 1 h (Runs 5, 6, 11, and 12). Also, with acetone as co-solvent, the degradation of TCP was complete after 20 min with **9** and after 25 min with **10a**. The turnover rates (based on the first 30 min of the reaction) of these two supported catalysts are 150 and 120 cycles per hour, respectively. These results are of great interest, since the catalytic activities of these new supported metallophthalocyanines are comparable to those observed under homogeneous conditions.

The recycling of **10a**, a key point for supported catalysts, was then investigated. After a first catalytic oxidation, a second portion of pollutant and oxidant was added to the reaction mixture. In this second run, 91% of TCP was converted in 15 min (Run 13) indicating that the catalytic activity of the metallophthalocyanine remained intact.

For comparison, the catalytic activity of the supported cobalt complex **10b** was also checked (Runs 14−17). The full conversion of TCP could be achieved in 30 min with 4 mol-% of **10b** and with 20% of acetone in the reaction mixture (Run 17). Although the results obtained with this supported catalyst are less impressive than with the corresponding iron(III) complex, they are also of potential commercial interest. Indeed, the (chlorosulfonyl)phthalocyanine **1b** used for the immobilization on the organic copolymer was synthesized from the readily available sulfo precursor



Scheme 6. Degradation products of 2,4,6-trichlorophenol by the catalytic metallophthalocyanine/H_2O_2 systems

Table 1. Oxidation of 2,4,6-trichlorophenol (TCP) catalyzed by the metallophthalocyanines/H_2O_2 systems

Run	Catalyst	Cat./TCP [mol-%]	Solvent	TCP conversion (%) 1:2 h	1 h	2 h	T.O.[a] [h^{-1}]
1	–	–	PB[b]	7	–	–	–
2	**4b**	2	PB/acetone	94	100		94
3	**11**	2	PB/acetone	39	52	69	39
4	**9**	2	PB	74	85	88	74
5	**9**	2	PB/EtOH	84	100		84
6	**9**	2	PB/acetone	100			> 100
7	**9**	2	H_2O/NaOH	43	55	56	43
8	**9**	3	H_2O/NaOH	53	65	79	35
9[c]	**9**	3	H_2O/NaOH	71	89	93	47
10	**10a**	2	PB	–	62	67	< 62
11	**10a**	2	PB/EtOH	99	100		99
12	**10a**	2	PB/acetone	100			> 100
13	**10a**	2	PB/acetone	100			> 100
				91[d] (15 min)			> 100
14	**10b**	2	PB	38	46	44	38
15	**10b**	4	PB	47	57	58	23.5
16	**10b**	4	PB/EtOH	67	94	100	33.5
17	**10b**	4	PB/acetone	100			50
18	**12**	2	PB/acetone	91	100		91
19	**12**	2	H_2O/NaOH	9	11	12	9

[a] T.O.: Turn over numbers calculated after 30 min of reaction. – [b] PB: Phosphate buffer (pH = 7). – [c] Sequential addition of H_2O_2: 4 × 1 aliquot every 10 min. – [d] Recycling of the supported catalyst: after 15 min of a first oxidation reaction, new portions of TCP and H_2O_2 were added in the same batch.

4c, which is widely used in the industrial mercaptan oxidation process (Merox) for the treatment of petroleum distillates.[3]

The covalent attachment of the metallophthalocyanines **1** onto the organic copolymers **2** and **3** proved to be suitable for the preparation of active systems for the catalytic oxidative degradation of recalcitrant pollutants such as 2,4,6-trichlorophenol. The different properties (flexibility, swelling, etc.) of these carriers make them excellent candidates for catalytic supports.

It should be noted that the behavior of **9** and **10a** are almost identical, with **9** being only slightly more efficient than the corresponding piperazine-containing polymer. These organic copolymers **2** and **3** are relatively flexible, consequently the role of an additional spacer to increase the distance between the catalyst and the support is rather limited. In contrast, with a more rigid carrier material like silica, this modification could notably change the catalytic properties of a metallophthalocyanine complex covalently linked to silica. In order to verify this hypothesis, we determined the oxidative properties of the silica-supported iron complex **12**, which features the same piperazine spacer as in **10a**.

Influence of the Piperazine Spacer

In order to determine the influence of the spacer, we compared the oxidative properties of **12** (containing 40.0 µmol of iron per gram of resin) to those of **11** with the same catalyst loading (42.0 µmol/g). In the oxidative degradation of TCP with H_2O_2, the catalytic activity of the supported catalyst containing the piperazine spacer was 3 times higher after 30 min (Runs 3 and 18, Table 1). In addition, for the first time, it was possible to achieve a full conversion of TCP in 1 h with a metallophthalocyanine grafted onto modified silica (Run 18). *This result strongly indicates that when anchoring a large catalyst molecule like a metallophthalocyanine (a macrocyclic molecule with a diameter of ca. 25 Å) onto a rigid support such as silica, it is necessary to introduce a long spacer between the catalyst and the surface of the support.* Without this modification, the oxidative activities of the corresponding supported catalysts are reduced. These results provide further motivation to use the flexible organic copolymers **2** and **3** as supports in catalytic oxidations.

Catalytic Oxidation of TCP in Pure Aqueous Medium (without Buffer)

The experiments described above for the degradation of TCP were carried out in phosphate buffer (pH = 7) medium. Under homogeneous conditions it has been shown that this pH value is optimal for a good catalytic activity. This can be explained by the fact that the first step of TCP degradation is a one-electron oxidation of the phenolate anion [7a] (pK_a value of TCP: 6.2).[21] However, since the final aim of this work is the decontamination of industrial waste waters, the presence of phosphate ions is ecologically not appropriate.

With this in mind, we tried to degrade TCP in a pure aqueous medium, using the most active polyacrylamide- and silica-supported catalysts **9** and **12**. The pH value of the reaction mixture was adjusted to 7 with sodium hydroxide in order to have only the more oxidizable phenolate form of the substrate in solution. With a 2 mol-% ratio catalyst/TCP, the supported catalyst **9** and H_2O_2 are able to oxidize 55% of the starting TCP after 1 h (Run 7, Table 1), whereas, under the same conditions, the iron-phthalocyanine grafted onto the modified piperazine-silica **12** converted only 11% of TCP (Run 19). Since the tetrasulfophthalocyanine **4b** is totally inactive in a purely aqueous medium under homogeneous conditions,[22] these results were encouraging. The ratio catalyst/substrate was raised to 3 mol-% for **9** and the conversion of TCP increased to 65% after 1 h and to 79% after 2 h (Run 8). With a sequential addition of the oxidant in 4 aliquots, every 10 min, a quasi-complete degradation of TCP can be achieved in a purely aqueous medium within 2 h (Run 9). The sequential addition of H_2O_2 disfavors its consumption by a disproportionation reaction (leading to water and molecular oxygen) induced by the catalase-like reactivity of the metallophthalocyanine complex.[7a]

Catalytic Degradation of TCP with $KHSO_5$ as Oxidant

Potassium monopersulfate ($KHSO_5$) is an oxygen atom donor that has been shown to be highly efficient for the activation of metallophthalocyanines and metalloporphyrins.[7,19] It is commercially available as the triple salt $2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$, and is a classic reagent in Baeyer−Villiger oxidations.[23] An initial control experiment was made to ensure that TCP was not oxidized by $KHSO_5$ without catalyst (Run 1, Table 2) and that there was no leaching of the iron-phthalocyanine under these new oxidation conditions [8 mg of **9** suspended in 8 mL of a phosphate buffer (pH =7) with 5 equiv. of $KHSO_5$].

In a purely aqueous medium, the degradation of TCP by the catalytic **9** (2 mol-%)/$KHSO_5$ system is very fast (79% in 5 min, Run 2, Table 2). However, the conversion of TCP reached a plateau after 10 min and a bleaching of the supported catalyst was observed. The pH measurement of the solution gave a value of 2.5, which was attributed to the intrinsic acidity of $KHSO_5$. At such a low pH value, the supported catalyst is probably decomposed. In contrast, when the reaction mixture was buffered at pH = 7 using a phosphate buffer, the conversion of TCP was complete in 5 min (Run 3). Under these conditions, the turnover rate of this supported iron-(sulfonamido)phthalocyanine was 10 catalytic cycles per minute (based on the first five minutes of the reaction). With the catalytic **9**/$KHSO_5$ system, the turnover rate can be increased up to 16 cycles/min using 1 mol-% of catalyst (Run 4). In contrast, with only 0.1 mol-% of catalyst, the degradation of TCP was incomplete after 1 h (Run 5).

We also checked the possibility of recycling this supported catalyst under these strong oxidation conditions. After a first catalytic reaction, new portions of substrate and oxidant were added every 5 min (Run 6). The results were very surprising: the catalytic system was still efficient after the addition of 3 new portions of pollutant and had retained its initial catalytic activity.

We have established that the activation of metallophthalocyanines anchored onto **2** and **3** with either hydrogen peroxide or potassium monopersulfate as oxidants is an efficient method for the oxidative degradation of a notable pollutant such as TCP. Moreover, NMR studies carried out after the catalytic oxidation of TCP with H_2O_2 (as well as with $KHSO_5$) have shown the formation of ring cleavage products, which are biodegradable. For example, for the H_2O_2 oxidation of TCP catalyzed by **10a**, we observed the formation of 12% of chloromaleic acid, 3% of chlorofumaric acid, 4% of maleic acid, 3% of fumaric acid and 6% of coupling products. Thus, these catalytic systems might be useful for the oxidative treatment of industrial waste waters. However, these bio-inspired supported oxidative catalysts might also be useful as bleaching agents in a new generation of washing powders, able to operate at room temperature.

H_2O_2 Oxidative Degradation of 3,5-Di-*tert*-butylcatechol Catalyzed by 9

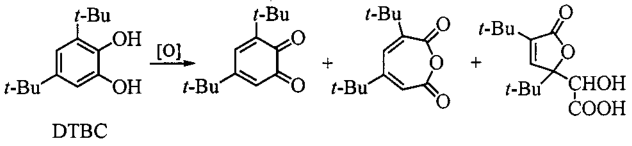
Catechol and its derivatives are often used as substrates for the evaluation of bleaching agents since they are considered good models of stains (catechols are the most common structure encountered in condensed tannins, which are among the main stains).[24] Under homogeneous conditions, the iron-sulfophthalocyanine **4b** in conjunction with an oxidant was able to degrade several catechols such as catechol itself, as well as its 3-methyl, 3-methoxy, 3,5-di-

Table 2. $KHSO_5$ oxidation of 2,4,6-trichlorophenol (TCP) catalyzed by **9**

Run	Cat./TCP [mol-%]	Solvent	TCP conversion (%) 5 min	10 min	15 min	30 min	60 min	T.O.[a] [min^{-1}]
1	–	PB[b]	–	–	–	0	–	–
2	2	H_2O[c]	79	88	89	92	92	7.9
3	2	PB	100					10
4	1	PB	81	96				16.2
5	0.1	PB	36	45	53	66	72	72
6[d]	2	PB	61					6.1
			97					9.7
			94					9.4
			87					8.7

[a] T.O.: Turn over numbers calculated after 5 min. – [b] PB: Phosphate buffer (pH = 7). – [c] Pure aqueous media (pH = 2.5). – [d] Recycling of the supported catalyst: after 5 min of a first oxidation reaction with 3.75 equiv. of $KHSO_5$, new portions of TCP and $KHSO_5$ were added every 5 min in the same batch.

tert-butyl, and tetrachloro derivatives.[25] The degradation products from 3,5-di-*tert*-butylcatechol (DTBC) were identified by ^1H NMR as 3,5-di-*tert*-butyl-1,2-benzoquinone, 3,5-di-*tert*-butylmuconic anhydride, and 3,5-di-*tert*-butyl-5-(carboxyhydroxymethyl)-2-furanone (Scheme 7).



Scheme 7. Degradation products of 3,5-di-*tert*-butylcatechol catalyzed by the iron-tetrasulfophthalocyanine **4b**

When H_2O_2 was used as oxidant, the noncatalyzed reaction with DTBC was negligible (Run 1, Table 3). The oxidative properties of the **9**/H_2O_2 system were used for the catalytic degradation of DTBC. We first noted that the substrate was not physisorbed on the surface of the support. Three reaction media were then checked for the degradation of DTBC at room temperature: borate buffer (pH = 9)/CH_3CN (50:50, v/v), phosphate buffer (pH = 7)/CH_3CN (50:50, v/v) and H_2O/CH_3CN (50:50, v/v). The presence of acetonitrile is necessary as organic co-solvent for a good solubility of DTBC. With 2 mol-% of catalyst, the results for the degradation of DTBC are quite similar in the three different reaction media (Runs 2–4, Table 3). The most interesting results were obtained without buffering the reaction solution (which can be considered as an advantage), and as a result, attempts were made to optimize this reaction. By increasing the catalyst/substrate ratio to 3 mol-%, full conversion of DTBC was achieved in 1 h (Run 5, Table 3). ^1H NMR studies carried out after the catalytic oxidation of DTBC in a water/acetonitrile mixture revealed the formation of 3,5-di-*tert*-butyl-1,2-benzoquinone (50% yield, no other products could be detected).

The recycling capacity of **9** was also studied in the degradation of DTBC. In this case, this supported catalyst also showed excellent behavior without loss of its oxidative properties, as expected for an efficient long-life catalyst. In fact, after having converted 82% of DTBC in a first catalytic oxidation, the same system was still able to degrade 4 new portions of substrate (Run 6, Table 3). However, for an application in washing powders, it would be accurate and realistic to work with a water-soluble catechol such as 3,4-dihydroxybenzoic acid, current work is underway in this direction.

Table 3. H_2O_2 oxidation of 3,5-di-*tert*-butylcatechol (DTBC) catalyzed by **9**

Run	Solvent	pH	Cat./DTBC [mol-%]	TCP conversion (%) 10 min	20 min	30 min	45 min	60 min	T.O.[a] [h^{-1}]
1[b]	H_2O/CH_3CN	5.5	–	–	–	1	–	2	–
2	BB/CH_3CN[c]	9	2	23	36	61	68	78	61
3	PB/CH_3CN[d]	7	2	41	49	55	60	62	55
4	H_2O/CH_3CN	5.5	2	29	45	61	71	81	61
5	H_2O/CH_3CN	5.5	3	39	71	84	90	97	56
6[e]	H_2O/CH_3CN	5.5	3			82			55
						74			49
						70			47
						55	71	78	37

[a] T.O.: Turn over numbers calculated after 30 min. – [b] Control reaction without catalyst. – [c] BB: Borate buffer (pH = 9). – [d] PB: Phosphate buffer (pH = 7). – [e] Recycling of the supported catalyst: after 30 min of a first oxidation reaction, new portions of TCP and $KHSO_5$ were added every 30 min in the same batch.

Conclusion

The covalent anchoring of metallophthalocyanines onto the acrylic copolymers Met-Expansin-NH_2® (**2**) and Met-Expansin-Piperazine (**3**) allowed the fixation of these macrocyclic complexes in a monomolecular dispersion, resistant to oxidative conditions. These bio-inspired supported catalysts, when activated with H_2O_2 (the "green" oxidant) or $KHSO_5$ were able to fully degrade a recalcitrant pollutant such as 2,4,6-trichlorophenol. The organic carriers proved flexible enough as to eliminate the need to introduce an additional piperazine spacer between catalyst and support as observed with modified silica. Furthermore, it has been possible to use these polyacrylamide-supported catalysts in a purely aqueous medium, whilst retaining a good catalytic activity of the metallophthalocyanine complex.

These new efficient supported catalysts could easily be used for the oxidative treatment of waste water or industrial effluents. Another possible field of application could also be related to the development of bleaching agents operating at room temperature, since such catalytic systems are able to oxidize a tannin model such as 3,5-di-*tert*-butylcatechol.

Experimental Section

General Remarks: The conversions of 2,4,6-trichlorophenol (TCP) and 3,5-di-*tert*-butylcatechol (DTBC) were monitored by HPLC (Waters) equipped with a μ-Bondapak C18 column using a methanol/ammonium acetate buffer mixture [7:3, v/v; 50 mM acetate buffer (pH = 5) acidified to pH = 4 with acetic acid] with detection at 220 nm for TCP and a methanol/water mixture (8:2, v/v) with detection at 226 nm for DTBC. − The UV/Vis absorption spectra were recorded with a Hewlett Packard 8452A spectrophotometer. Met-Expansin-NH_2® (**2**) (0.56 mmol-equiv. NH_2/g) and Met-Expansin-Piperazine (**3**) (0.50 mmol-equiv. NH/g) copolymers were a gift from EXPANSIA. The 3-aminopropyl-functionalized silica gel (0.90 mmol-equiv. NH_2/g) was purchased from Aldrich.[26] The reactants bromoacetic acid, dicyclohexylcarbodiimide and piperazine are commercially available and were used without further purification. 2,4,6-Trichlorophenol was obtained from Janssen and 3,5-di-*tert*-butylcatechol from Aldrich. Hydrogen peroxide was supplied from Acros as a 35 wt-% aqueous solution. Curox® ($2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$) was a gift from Peroxid Chemie GmbH. All solvents used were of analytical grade and milliQ-water was always used to prepare aqueous solutions. Iron(III) and cobalt(II) tetrasulfophthalocyanines (**4b** and **4c**) were prepared according to previously published modifications[7a] of the method of Weber and Busch.[27]

Attachment of the Piperazine Linker on Silica: A solution of dicyclohexylcarbodiimide (0.56 g, 2.70 mmol) in CH_2Cl_2 (10 mL) was added dropwise at 0 °C to a solution of bromoacetic acid (0.75 g, 5.40 mmol) in CH_2Cl_2 (10 mL). The solution was allowed to warm to room temperature and stirred for 1 h. The dicyclohexylurea precipitate that formed was removed by filtration, the solid was washed three times with CH_2Cl_2 (3 × 20 mL), and the washings were combined. The bromoacetic anhydride solution thus obtained was directly added to the commercially available silica containing primary amine linkers (1.00 g, 0.90 mmol of NH_2 functions) and stirred for 12 h at room temperature. The modified silica was filtered, washed three times with CH_2Cl_2 (3 × 20 mL), and dried for 12 h at 50 °C. A suspension of the carrier containing CH_2Br end groups in DMF (5 mL) was added to a solution of piperazine (0.77 g, 9.00 mmol) in DMF (5 mL) and stirred 24 h at room temperature. The modified support thus obtained was isolated by filtration, washed three times with water (3 × 20 mL), ethanol (3 × 20 mL) and acetone (3 × 20 mL) prior to drying at 50 °C for 12 h. Yield: 0.78 g (78%).

General Procedure for the Immobilization of the Metallophthalocyanines: In a typical experiment, a suspension of the metallo(chlorosulfonyl)phthalocyanine **1a** or **1b** in pyridine (20 mL) and the carrier was heated at reflux for 24 h. The mixture was filtered and the solid obtained washed three times with a dimethylformamide/water mixture (80:20, v/v) (3 × 20 mL) and then ether (3 × 20 mL) prior to drying at 53 °C for 12 h. The supported metallo(sulfonamido)phthalocyanines were obtained as green powders. The contents of catalyst fixed onto the carriers were determined indirectly by calculating the amount of unchanged **1** using UV/Vis spectroscopy. The quantities used and yields obtained are given in Table 4.

Table 4. Quantities and yields for the preparation of the supported metallophthalocyanines

Product	1		Support		Loading	Yield
	mg	μmol	g	μmol (NH)	[μmol/g]	(%)
9	25.6	22.8	1.00	560	20.0	88
10a	50.0	44.5	1.00	500	26.5	60
10b	25.0	22.2	0.50	280	42.0	100
11	32.6	29.0	0.50	450	42.0	100
12	20.3	18.0	0.40	360	40.0	89

General Procedure for Catalytic TCP Degradation: In a typical experiment, for a catalyst/TCP ratio of 2 mol-%, 0.16 μmol of Fe^{III} or Co^{II} of the supported catalyst [i.e., 8.0 mg of **9** (loading 20.0 μmol/g), 6.0 mg of **10a** (loading 26.5 μmol/g), 3.8 mg of **10b** (loading 42.0 μmol/g), 3.8 mg of **11** (loading 42.0 μmol/g), 4.0 mg of **12** (loading 40.0 μmol/g)] and 40 μL of a 1.2 M aqueous solution of hydrogen peroxide (48.0 μmol) were added to a 1 mM TCP solution (8 mL, 8.0 μmol) in phosphate buffer 50 mM (pH = 7). The reaction mixture was stirred at room temperature and analyzed by HPLC. For the experiments carried out in the presence of an organic co-solvent, a 1 mM TCP solution was prepared in a mixture of 50 mM phosphate buffer/ethanol or acetone (80:20, v/v). Run 7 in Table 1 was carried out with a 1 mM TCP aqueous solution adjusted to pH = 7 with NaOH (final concentration of NaOH: 1 mM). When $KHSO_5$ was used as oxidant, a solution of Curox® (12.3 mg, 40.0 μmol) in water (100 μL) was added to the reaction mixture.

^{1}H NMR Analysis of the Degradation Products of TCP by the Catalytic 10a/H_2O_2 System: The supported catalyst **10a** (loading 26.5 μmol/g) (60.0 mg, 1.6 μmol) and 400 μL of a 1.2 M aqueous solution of hydrogen peroxide (480.0 μmol) were added to a 1 mM TCP solution (80 mL, 80.0 μmol) in a 50 mM phosphate buffer (pH = 7)/ethanol (80:20, v/v) mixture. The reaction mixture was stirred for 1 h at room temperature. After filtration of the supported catalyst **10a** and several washings with acetonitrile, the reaction mixture was dried under vacuum. Then 7 mL of 1 M HCl, saturated with NaCl, was added to the dry residue and the organic products were extracted with diethyl ether (3 × 60 mL). After concentration of the ether extracts, the solid residue was dissolved in deuterated dimethyl sulfoxide ([D$_6$]DMSO) for NMR analysis. Then 5 μL of $CHCl_3$ (62.0 μmol) was added as an internal standard to quantify the oxidation products. − ^{1}H NMR ([D$_6$]DMSO): $\delta =$

6.39 (s, 2 H, maleic acid, 4%), 6.69 (s, 1 H, chloromaleic acid, 12%), 6.74 (s, 2 H, fumaric acid, 3%), 7.30 (s, 1 H, chlorofumaric acid, 3%), 7.80−8.10 (br, 2 H, coupling products, 6%). − It should be noted that these yields differ from one experiment to another, depending on the time the oxidation reaction was stopped.

General Procedure for Catalytic DTBC Degradation: In a typical experiment, for a catalyst/TCP ratio of 2 mol-%, 8.0 mg of the supported catalyst **9** (loading 20.0 μmol/g) (0.16 μmol) and 40 μL of a 1.2 M aqueous solution of hydrogen peroxide (48.0 μmol) were added to a 1 mM DTBC solution (8 mL, 8.0 μmol) in a 50 mM borate buffer (pH = 9)/acetonitrile (1:1, v/v) mixture or in 50 mM phosphate buffer (pH = 7)/acetonitrile (1:1, v/v) or in water/acetonitrile (1:1, v/v). The reaction mixture was stirred at room temperature and analyzed by HPLC.

^{1}H NMR Analysis of the Degradation Products of DTBC by the Catalytic 9/H_2O_2 System: The supported catalyst **9** (loading 20.0 μmol/g) (80.0 mg, 1.5 μmol) and 250 μL of a 1.2 M aqueous solution of hydrogen peroxide (300.0 μmol) were added to a 6.25 mM DTBC solution (8 mL, 50.0 μmol) in a water/acetonitrile (1:1, v/v) mixture. The reaction mixture was stirred for 45 min at room temperature. After filtration of the supported catalyst and several washings with acetonitrile, the reaction mixture was dried under vacuum. Then 7 mL of 1 M HCl, saturated with NaCl, was added to the dry residue and the organic products were extracted with diethyl ether (3 × 60 mL). After concentration of the ether extracts, the solid residue was dissolved in deuterated dimethyl sulfoxide ([D$_6$]DMSO) for NMR analysis. Then 2 μL of $CHCl_3$ (25.0 μmol) was added as an internal standard to quantify the oxidation products. − ^{1}H NMR ([D$_6$]DMSO): δ = 1.30 (s, 9 H, *t*Bu), 1.33 (s, 9 H, *t*Bu), 6.25 (d, *J* = 2.2 Hz, 1 H, HC=), 7.08 (d, *J* = 2.2 Hz, 1 H, HC=). − ^{13}C{^{1}H} NMR ([D$_6$]DMSO): δ = 27.7 (s, *C*H$_3$C), 29.1 (s, *C*H$_3$C), 35.1 (s, CH$_3$*C*), 35.8 (s, CH$_3$*C*), 121.9 (s, HC=), 133.5 (s, HC=), 149.0 (s, C=), 162.6 (s, C=), 180.0 (s, C=O), 180.6 (s, C=O).

Recycling of the Supported Catalysts in the Oxidative Degradation of TCP and DTBC

TCP Degradation by 10a and H_2O_2: The supported metallophthalocyanine **10a** [6.0 mg, loading 26.5 μmol/g (0.16 μmol of iron, 2 mol-%)] and 40 μL of a 1.2 M aqueous solution of H_2O_2 (48.0 μmol) were added to a 1 mM TCP solution (8 mL, 8.0 μmol) in a 50 mM phosphate buffer (pH = 7)/acetone (80:20, v/v) mixture. The oxidation reaction was stirred for 30 min at room temperature. A 0.16 M TCP solution (50 μL, 8.0 μmol) in acetone and 40 μL of a 1.2 M aqueous solution of H_2O_2 (48.0 μmol) were then added to the reaction mixture. The TCP conversion was monitored by HPLC analysis.

TCP Degradation by 9 and $KHSO_5$: The supported metallophthalocyanine **9** [(8.0 mg, loading 20.0 μmol/g (0.16 μmol of iron, 2 mol-%)] and 50 μL of a 0.8 M Curox® solution (40.0 μmol) in water were added to a 1 mM TCP solution (8 mL, 8.0 μmol) in 50 mM phosphate buffer (pH = 7). The oxidation reaction mixture was stirred for 5 min at room temperature. A 0.8 M TCP solution (10 μL, 8.0 μmol) in acetonitrile and 50 μL of a 0.8 M Curox® solution (40.0 μmol) were then added to the reaction mixture every 5 min. The TCP conversion was monitored by HPLC analysis.

DTBC Degradation by 9 and H_2O_2: The supported metallophthalocyanine **9** [(12.0 mg, loading 20.0 μmol/g (0.24 μmol of iron, 3 mol-%)] and 40 μL of a 1.2 M aqueous solution of H_2O_2 (48.0 μmol) were added to a 1 mM DTBC solution (8 mL, 8.0 μmol) in a water/acetonitrile (1:1, v/v) mixture. The oxidation reaction mixture was stirred for 30 min at room temperature. A 0.4 M DTBC solution (20 μL, 8.0 μmol) in acetonitrile and 40 μL of a 1.2 M aqueous solution of H_2O_2 (48.0 μmol) were then added to the reaction mixture every 30 min. The DTBC conversion was monitored by HPLC analysis.

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