

# Access to functionalized quinones *via* the aromatic oxidation of phenols bearing an alcohol or olefinic function catalyzed by supported iron phthalocyanine†

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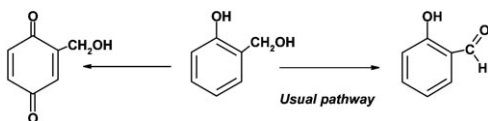
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The controlled oxidation at only one position of compounds with several oxidizable sites, while keeping the other sites intact, has been demonstrated for phenols bearing alcohol or olefinic functional groups. Iron tetrasulfophthalocyanine supported on silica was found to be an efficient catalyst for the preparation of functionalized quinones under mild conditions, with *tert*-butylhydroperoxide as the oxidant. A novel rapid and mild one-pot procedure for the covalent grafting of iron tetrasulfophthalocyanine onto silica has been developed. The supported catalyst was characterized by chemical analysis, a specific surface study, UV-vis spectroscopy and XPS. A non-radical mechanism for this unusual selective oxidation has been revealed by <sup>18</sup>O labelling experiments.

## Introduction

Quinones bearing different functional groups are powerful intermediates in organic synthesis, and they also frequently occur within the molecular frameworks of natural products.<sup>1</sup> Besides their reactive carbonyl and olefinic functional groups, the presence of other functionalities enhances their versatility as building blocks for the synthesis of elaborate structures, *e.g.* pharmaceuticals. Functionalised quinones can be prepared using different synthetic strategies,<sup>2</sup> but the selective oxidation of readily available phenols is the most direct and logical approach. Therefore, the search for selective methods to undertake this transformation is of great interest. In this respect, the selective oxidation of substrates with several oxidizable sites at only one position, keeping the other sites intact, is a key issue. For example, in the case of phenols bearing an alcohol function, especially in the benzylic position, its oxidation to an aldehyde group often prevails over aromatic oxidation. For example, 2-hydroxybenzyl alcohol (**2-HBA**) is usually oxidized to salicylaldehyde (**SA**) over noble metal catalysts.<sup>3</sup>



To the best of our knowledge, the stoichiometric oxidation of **2-HBA** to 2-hydroxymethyl-1,4-benzoquinone (**2-HQ**) by polymer-supported hypervalent iodine reagents (32% yield)

represents the only example of this aromatic oxidation.<sup>4</sup> Stoichiometric oxidation of the less easily available and more easily oxidized *para*-methoxyphenol derivative with hypervalent iodine oxidants to **2-HQ** (94% yield) has also been published.<sup>5</sup> Although not readily available at the large scale, hypervalent iodine compounds are popular and efficient oxidants for the stoichiometric oxidation of functionalized aromatic compounds.<sup>6</sup> Notably, an excess of oxidant is usually employed. Furthermore, a very low active oxygen content in these oxidants (only 3.8% for Dess–Martin periodinane and [bis(trifluoroacetoxy)iodo]benzene) leads to significant amounts of waste when they used as oxidants. The *E*-factor (waste/product ratio) for these oxidations is typically 15–25. Another serious drawback of Dess–Martin periodinane is its instability and explosion risk. Alternatively, **2-HQ** was obtained electrochemically from 2,5-dimethoxyphenylmethanol, but the yield was only about 30%.<sup>7</sup>

Consequently, the quest for selective aromatic oxidation methods that use clean oxidants, such as dioxygen or peroxides, and heterogeneous catalysts still remain an important challenge. Transition metal complexes immobilized on solid supports are especially attractive because they can provide selective oxidation and allow their easy separation from the reaction mixture.

In the present work, we describe the preparation of iron tetrasulfophthalocyanine (FePcS)-supported catalysts using a novel one-pot approach and the utilisation of this catalyst for the selective aromatic oxidation of functionalized phenols to their corresponding quinones.

## Experimental

### General

Solvents and chemicals were obtained from Sigma-Aldrich and used without further purification unless indicated. Deuterated acetonitrile-*d*<sub>3</sub> (99.8%), methylene chloride-*d*<sub>2</sub> (99.6%),

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acetone- $d_6$  (99.8%), methanol- $d_4$  (100%) and DMSO- $d_6$  (99.8%) were available from Euriso-top.  $^{18}\text{O}_2$  (98.5 atom.%) was also purchased from Euriso-top.

$^1\text{H}$  NMR spectra were obtained using an AM 250 Bruker spectrometer. Nitrogen sorption isotherm analysis was performed using a Catasorb apparatus. Diffuse reflectance UV-vis spectra of solid catalysts were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. The complex loading of the supported catalyst was determined by iron analysis using the inductively coupled plasma mass spectrometry method.

The oxidation products were identified by NMR and GC-MS methods. The quantitative GC analyses were not reproducible because of the instability of the substrates and/or reaction products under GC conditions. Therefore, conversions and product yields were determined by  $^1\text{H}$  NMR using biphenyl as the internal standard, as indicated in Figure S1 (ESI $^\dagger$ ) for the case of the oxidation of 2-hydroxybenzyl alcohol. Similar procedures were used for the other substrates.

The reaction products were identified by GC-MS (Hewlett-Packard 5973/6890 system; electron impact ionization at 70 eV, He carrier gas, 30 m  $\times$  0.25 mm cross-linked 5% PHME siloxane (0.25  $\mu\text{m}$  coating) capillary column, HP-5MS).

The degradation products of the aromatic rings were analyzed by GC-MS (capillary column VF5-MS, 100% dimethylpolysiloxane, 30 m  $\times$  0.25 mm, 0.25  $\mu\text{m}$  coating) using trimethylsulfonium hydroxide as the derivatization agent.<sup>8</sup> A trimethylsulfonium hydroxide solution (MeOH, 0.1 M) was prepared from trimethylsulfonium iodide and  $\text{Ag}_2\text{O}$  according to ref. 8. The reaction mixture (100  $\mu\text{L}$ ) was mixed with 40  $\mu\text{L}$  of a 0.1 M  $\text{Me}_3\text{SOH}$  solution at room temperature and immediately injected. Volatile methylated derivatives of compounds with phenolic and carboxylic groups were formed under the analysis conditions (the injector temperature was 220  $^\circ\text{C}$ ), and were analyzed by GC-MS. A control injection of the initial reaction mixture exhibited only the signals of methylated **2-HBA**. Analysis of the reaction mixture after 30 min and 2 h showed the presence of methylated derivatives of catechol, salicylic acid, maleic acid, succinic acid, hydroxysuccinic acid and acetic acid. Identification of the products was performed using authentic samples and the library of mass-spectra, NIST 02.

## Materials

Amino-modified silica was prepared using Degussa Aerosil 200 amorphous silica according to a published procedure,<sup>9</sup> and had a BET surface area of 185  $\text{m}^2 \text{g}^{-1}$  with 0.5 mmol  $\text{NH}_2$  group  $\text{g}^{-1}$  (chemical analysis). The sodium salt of iron tetrasulfophthalocyanine was prepared using a modified procedure of Weber and Busch.<sup>10</sup> The replacement of the sodium ion with tetrabutylammonium cation was performed as follows. Four equivalents of  $(\text{Bu}_4\text{N})\text{OH}$  (3.4 mL of a 40% aqueous solution) were added to a solution of FePcS (1.5 g, 1.3 mmol) in 50 mL water. The tetrabutylammonium salt of FePcS was extracted with  $\text{CH}_2\text{Cl}_2$  (5  $\times$  100 mL). The organic fraction was dried, the solvent removed and the product dried overnight in a vacuum at 50  $^\circ\text{C}$ .

## Preparation of supported catalyst

A solution of triphenylphosphine oxide (620 mg, 2.25 mmol) in 10 mL  $\text{CH}_2\text{Cl}_2$  was de-gassed and triflate anhydride (176.5  $\mu\text{L}$ , 1 mmol) added under argon. The solution thus obtained was stirred at room temperature for 15 min and a solution of iron tetrasulfophthalocyanine (tetrabutylammonium salt, 486 mg, 0.25 mmol) in 20 mL  $\text{CH}_2\text{Cl}_2$  was added. The resulting solution was stirred at 20  $^\circ\text{C}$  for 30 min. This solution was added dropwise to a suspension of the silica modified with 3-aminopropyltriethoxysilane (4.85 g) containing triethylamine (190  $\mu\text{L}$ , 1.38 mmol) at 0  $^\circ\text{C}$ . The resulting mixture was allowed to warm to 20  $^\circ\text{C}$  and stirred at this temperature for 1 h. The blue solid was isolated by filtration, washed with ethanol and water, and dried at 50  $^\circ\text{C}$  for 24 h.

## Typical procedure for the oxidation of phenols

To a 0.02 M solution of substrate (20  $\mu\text{mol}$ ) and a 0.0096 M solution of biphenyl (internal standard) in 1 mL deuterated solvent was added FePcS-SiO<sub>2</sub>, containing 0.2  $\mu\text{mol}$  of the complex (1 mol%). The reaction was started by the addition of a 70% aqueous  $^t\text{BuOOH}$  solution (20  $\mu\text{L}$ , 140  $\mu\text{mol}$ ) and was run, under stirring, for 2 h at 30  $^\circ\text{C}$ . The catalyst-substrate-oxidant ratio was 1 : 100 : 700. After the reaction, the catalyst was separated by filtration and the reaction mixture analyzed by  $^1\text{H}$  NMR. Product yields and conversions were determined by the integration of the corresponding proton signals relative to the internal standard signals (ESI $^\dagger$ ).

## $^{18}\text{O}_2$ experiments

Labelling experiments were performed under an atmosphere containing 20.4%  $^{18}\text{O}_2$  (99.6%  $^{18}\text{O}$  enrichment) and 79.2% Ar. The reaction flask contained 0.02 mmol substrate and 0.47 mmol  $^{18}\text{O}_2$  (23.5-fold excess of substrate). The isotopic compositions of the products and gas phase were determined by GC-MS. Each sample was analyzed three times and the  $m/z$  peak intensities of each peak were obtained by integrating all scans of that peak.<sup>11</sup>

The  $^{18}\text{O}$  content in 2-hydroxymethyl-1,4-benzoquinone could not be directly measured by the relative intensities of 138  $[\text{M}^+]$  and 140  $[\text{M} + 2]^+$  peaks since the authentic **2-HQ** sample exhibited a significant and varying  $m/z = 140$  signal (15–25% with respect to peak  $m/z = 138$ ). We propose that **2-HQ** could be partially reduced to 2-hydroxymethyl-1,4-hydrobenzoquinone under the conditions of MS analysis (electron impact ionization at 70 eV). Indeed, the relative intensity of peak  $m/z = 140$  increased along with the decreasing amount of sample injected. Taking into account that the  $^{18}\text{O}$  content in quinone should be the same as that in hydroquinone, we determined the  $^{18}\text{O}$  content in hydroquinone after treating the reaction mixture with triphenylphosphine. This procedure was highly reproducible, and the  $^{18}\text{O}$  content in hydroquinone obtained from the labelling experiments in the presence of  $^{18}\text{O}_2$  was found to be  $6.2 \pm 0.3\%$ .

## Results and discussion

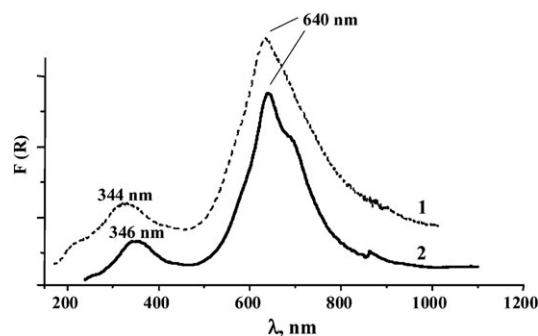
In the course of developing accessible and economically viable supported catalysts, we have recently shown that iron

phthalocyanines covalently supported on silica are efficient catalysts in the selective oxidation of 2,3,6-trimethylphenol<sup>12</sup> and alkynes<sup>13</sup> by <sup>t</sup>BuOOH. These supported catalysts are usually prepared by the reaction of a sulfonyl chloride derivative of iron tetrasulfophthalocyanine, FePc(SO<sub>2</sub>Cl)<sub>4</sub>, with amino-modified silica in pyridine. However, sulfonyl chlorides have some disadvantages, and they can be difficult to handle and not amenable to long-term storage.<sup>14</sup> In addition, the materials prepared by this method contained different species grafted onto the silica surface.<sup>9,12a</sup> We therefore searched for a more convenient method to graft the iron tetrasulfophthalocyanine (FePcS) onto the silica support.

Recently, Caddick and co-workers published a direct synthesis of sulfonamides using the activating agent triphenylphosphine ditriflate.<sup>15</sup> We have applied this approach to develop a novel mild grafting method (Fig. 1).

In the first step, sulfonate groups of the complex were activated at 20 °C by treatment with reagent **1**, easily prepared from triphenylphosphine oxide and triflate anhydride. The addition of activated complex **2** to the silica, modified with 3-aminopropyltriethoxysilane, rapidly resulted in the formation of the blue supported material. Careful washing with water and organic solvents didn't result in any appreciable leaching of the complex into solution, suggesting the expected covalent grafting of the complex onto the silica surface *via* sulfonamide bonds. XPS spectra, recorded from 0 to 1000 eV, indicated that the amino-modified silica contained the N1s signal at 399.2 eV, and the neat FePcS had a N1s signal at 398.9 eV. The XPS spectrum of the FePcS-SiO<sub>2</sub> supported catalyst, along with the main peak at 399.0 eV, showed the appearance of a new signal at 401.6 eV, also indicating the formation of a covalent sulfonamide bond. Nitrogen sorption isotherm analysis showed a specific surface area of 185 m<sup>2</sup> g<sup>-1</sup>. The homogeneity of the FePcS distribution on the surface can be estimated from the broadness of the Q band in the diffuse reflectance UV-vis (DR UV-vis) spectrum.<sup>16</sup> The full width at half maximum of the 640 nm band was *ca.* 130 nm for the supported catalyst prepared by this novel method compared to *ca.* 180 nm for the supported catalyst prepared by the conventional method<sup>9</sup> (Fig. 2), suggesting a more uniform FePcS distribution in the former case. The complex loading, determined by iron analysis using the inductively coupled plasma-mass spectrometry method, was typically 38–43 μmol g<sup>-1</sup>.

Using the FePcS-SiO<sub>2</sub> supported catalyst in combination with <sup>t</sup>BuOOH, we first investigated the oxidation of **2-HBA** in different solvents (Table 1). Conversions and product yields

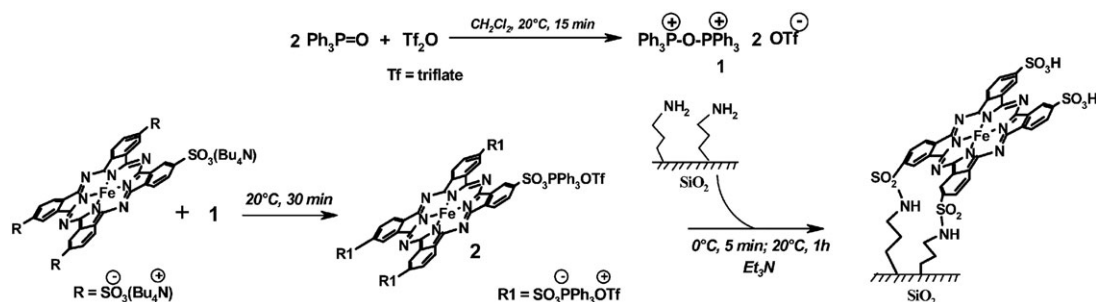


**Fig. 2** DR UV-vis spectra of the (1) FePcS-SiO<sub>2</sub> prepared by the conventional sulfonyl chloride method and (2) the FePcS-SiO<sub>2</sub> grafted by the novel method.

were determined by NMR using biphenyl as an internal standard, since quantitative GC analyses were not reproducible because of the instability of the substrates and/or reaction products under GC conditions. The heterogeneous reactions were performed in deuterated solvents and analyzed after separation of the catalyst by filtration at the end of the reaction. We performed several experiments with reaction times of 0.5, 1, 1.5, 2 and 3 h. The best selectivity for quinone was obtained after 2 h. Subsequent experiments were therefore performed with a 2 h reaction time. In the absence of catalyst, the conversion of **2-HBA** was less than 6% and no **2-HQ** was formed.

FePcS-SiO<sub>2</sub> supported catalyst provided selective aromatic oxidation of the phenol moiety bearing the benzylic alcohol to **2-HQ** in the majority of solvents, **SA** being a minor product (2–4%). In DMSO, the selectivity was switched in favour of conventional oxidation of the benzylic alcohol group, although the yields were low. With 1 mol% of catalyst, 91% conversion and 57% selectivity for **2-HQ** were obtained using acetone as the solvent, thus demonstrating a promising selectivity in this demanding oxidation.

Special attention has been paid to the analysis of the side products in the oxidation of **2-HBA**. Along with **SA** (4%), we have also found 2-hydroxymethyl-1,4-hydrobenzoquinone (~1%), 2,5-dihydroxybenzaldehyde (~4%), salicylic acid (<1%) and catechol (~4%) as minor reaction products. The side products of **2-HBA** oxidation were further studied by GC-MS using trimethylsulfonium hydroxide<sup>8</sup> to obtain, *in situ*, volatile compounds with methylated carboxylic and phenolic groups. We have identified maleic acid, succinic acid,



**Fig. 1** Covalent grafting of iron tetrasulfophthalocyanine onto silica and a schematic representation of the supported catalyst.

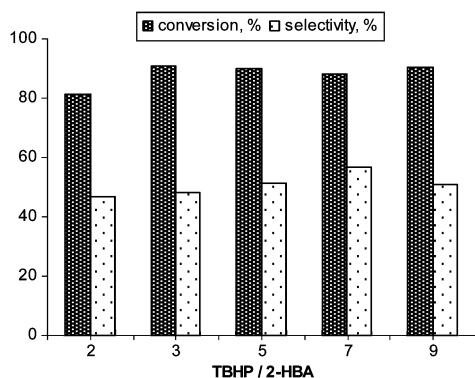
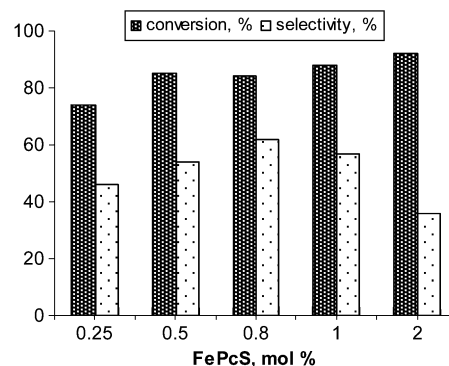
**Table 1** Solvent dependence of the oxidation of 2-hydroxybenzyl alcohol (**2-HBA**) by <sup>t</sup>BuOOH, catalyzed by FePcS-SiO<sub>2</sub><sup>a</sup>

Solvent	Conversion (%)	<b>2-HQ</b> selectivity (%)	SA selectivity (%)
CD <sub>2</sub> Cl <sub>2</sub>	100	47	2
CD <sub>3</sub> CN	94	48	3
Acetone- <i>d</i> <sub>6</sub>	91	57	4
CD <sub>3</sub> OD	86	29	4
DMSO- <i>d</i> <sub>6</sub>	92	14	25

<sup>a</sup> The reactions were carried out at 30 °C for 2 h.

hydroxysuccinic acid, acetic acid, acetaldehyde and formaldehyde. This result strongly suggests that the main side pathway is the cleavage of the aromatic ring rather than the formation of coupling products. These products of aromatic ring cleavage can be formed *via* the further oxidation of quinones. It should be mentioned that the catalytic system FePcS-H<sub>2</sub>O<sub>2</sub> was very efficient in the oxidative degradation of chlorinated phenols to give the products of aromatic ring cleavage.<sup>17</sup> The use of <sup>t</sup>BuOOH instead of H<sub>2</sub>O<sub>2</sub> allows selective oxidation to quinones and limits degradation of the aromatic ring.

The standard conditions used for the oxidation of **2-HBA** employed the catalyst, substrate and oxidant in the molar ratio 1 : 100 : 700. We studied the influence of the different reaction parameters on the efficiency of **2-HBA** oxidation. In fact, the oxidation was still efficient with 5, 3 and even with 2 equivalents of oxidant with respect to the substrate, the selectivity for **2-HQ** being 52, 49 and 47%, respectively (Fig. 3). It should be noted that 2 equivalents of oxidant are necessary to convert a phenol to a quinone. Consequently, the yield of quinone based on the oxidant can be considered as rather reasonable, although the best selectivity, of 57%, has been achieved with 7 equivalents of <sup>t</sup>BuOOH, suggesting the participation of <sup>t</sup>BuOOH in the reaction steps leading to **2-HQ**. A decrease in selectivity of the oxidation in the presence of 9 equivalents of <sup>t</sup>BuOOH can be explained by over-oxidation reactions. The increase of initial **2-HBA** concentration from 0.02 to 0.06 M resulted in only a small decrease in **2-HQ** selectivity from 57 to 52%. However, further increasing the initial **2-HBA** concentration to 0.1 M resulted in only a 39% selectivity. Interesting results have been obtained when studying the influence of the







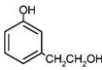
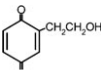


**Fig. 3** Dependence of the oxidation of **2-HBA** on the <sup>t</sup>BuOOH/**2-HBA** ratio. Reaction conditions: 0.02 M **2-HBA** solution in acetone-*d*<sub>6</sub> (1 mL), 1 mol% FePcS-SiO<sub>2</sub>, 30 °C, 2 h.**Fig. 4** Dependence of the oxidation of **2-HBA** on the catalyst amount. Reaction conditions: 0.02 M **2-HBA** solution in acetone-*d*<sub>6</sub> (1 mL), 0.14 M <sup>t</sup>BuOOH, 30 °C, 2 h.

amount of supported catalyst. Remarkably, the oxidation was still efficient with 0.25 mol% catalyst (Fig. 4). The best selectivity, of 62%, at 84% conversion was obtained using 0.8 mol% catalyst, indicating a good catalytic performance by FePcS-SiO<sub>2</sub>. When the catalyst amount increases from 0.25 to 0.5 and 0.8 mol%, the selectivity of oxidation also increases from 46 to 54 and 62%, respectively. Any further increase in the catalyst amount leads to a decrease in selectivity, 57 and 36% with 1 and 2 mol% catalyst, respectively, suggesting over-oxidation in the presence of a large amount of catalyst.

The recyclability of the heterogeneous catalyst was studied using 0.8 mol% FePcS-SiO<sub>2</sub>. After completing the first run, the catalyst was isolated by filtration, washed with MeCN and dried at 80 °C. On reuse, we observed a sharp decrease in its catalytic activity. In order to determine the possible leaching of the complex, the isolated solution was analyzed for Fe by inductively coupled plasma mass spectrometry. The residual iron content of the solution was below the detection limit (less than 1.5% of the supported complex), indicating the expected absence of complex leaching into solution; as expected since the complex was supported on the silica surface by covalent anchoring of the phthalocyanine ligand. Taking into account the formation of acids owing to over-oxidation processes, we propose that the catalytic sites could coordinate acid ligands and thus become deactivated. Indeed, when the oxidation of **2-HBA** was performed in the presence of oxalic acid, a significant decrease in catalytic activity was observed, strongly suggesting the inhibition of FePcS sites by acid over-oxidation products.

The oxidation of other alcohol-containing substrates, including 3,5-dihydroxybenzyl alcohol, containing two hydroxyl groups also provided quinones, with selectivity reaching 54% (Table 2). The scope of the reaction was further tested using 2-allylphenol, the substrate having an oxidizable double bond and a reactive benzylic/allylic position. Importantly, aromatic oxidation was the major pathway and 2-allyl-1,4-benzoquinone was obtained with 48% selectivity (Table 2). Only trace amounts of products arising from oxidation of the double bond were detected by GC-MS. Usually, in the presence of oxidants, allylphenols undergo epoxidation and cyclization reactions.<sup>18</sup> Previously, allylquinones have been prepared by the allylation of quinones with allyltin<sup>19</sup> and allylindium<sup>20</sup>

**Table 2** <sup>t</sup>BuOOH-catalyzed oxidation of phenols having an alcohol function by FePcS-SiO<sub>2</sub> in acetone

Substrate	Product	Conversion (%)	Selectivity (%)
		91 84 <sup>a</sup>	57 62 <sup>a</sup>
		100	53
		84	54
		100	56
		98 <sup>b</sup>	48

<sup>a</sup> With 0.8 mol% of catalyst. <sup>b</sup> Acetonitrile solvent.

reagents. To the best of our knowledge, no selective oxidation of alkenylphenols to quinones that retain the double bond have been published in the literature.

What mechanism is operating to provide such an unusual selectivity in the oxidation of functionalized quinones? When iron complexes in combination with hydroperoxide are involved in oxidation, iron complex-based oxo species or alkoxy- and/or peroxy-radicals might be responsible for this oxidation. To distinguish a “radical free” from a free radical mechanism, we studied the oxidation of **2-HBA** in the presence of <sup>18</sup>O<sub>2</sub>. If the radical mechanism is operating, significant <sup>18</sup>O incorporation in the oxidation products should be observed due to the reaction of intermediate phenoxy radicals with <sup>18</sup>O<sub>2</sub>, leading finally to a labelled quinone. Isotopic compositions of **2-HBA** and oxidation products, determined by GC-MS, were constant during the reaction course, indicating no oxygen exchange between <sup>18</sup>O<sub>2</sub> and the products. As expected, no <sup>18</sup>O incorporation was detected in **SA**. Importantly, 93.8 ± 0.3% 2-hydroxymethyl-1,4-benzoquinone contained no <sup>18</sup>O label. This low level of <sup>18</sup>O incorporation into **2-HQ** (6.2%) strongly suggests two-electron oxidation as a principal reaction pathway, probably *via* two closely associated one-electron transfers,<sup>21</sup> consistent with the involvement of iron phthalocyanine-centered species and not consistent with a radical pathway. In the latter case, alkoxy- and peroxy-radicals should easily generate a phenoxy radical from phenol, which should result in significant <sup>18</sup>O content developing in **2-HQ**. A two-electron oxidation pathway is also consistent with the high yield of quinones, while coupling products should be obtained if a one-electron pathway is operating.

Another piece of evidence in favor of a mechanism without significant free radical involvement was obtained by careful analysis of the gas phase during this oxidation. The isotopic composition of O<sub>2</sub> (99.6 ± 0.3% <sup>18</sup>O content) and the O<sub>2</sub>/Ar ratio (20.4 ± 0.2% oxygen) were constant during the oxidation (determined before the reaction and at reaction times of 1 and 2 h), indicating no appreciable O<sub>2</sub> formation from <sup>t</sup>BuOOH and no O<sub>2</sub> consumption during the oxidation. After a 2 h reaction time, we detected a trace amount of <sup>16/18</sup>O<sub>2</sub> (0.0022 mmol, 1.5% relative to total the <sup>t</sup>BuOOH amount), strongly suggesting only a very low level involvement of free radicals in this oxidation.

## Conclusion

In conclusion, a novel one-pot procedure for the covalent grafting of phthalocyanine complexes has been developed. This method is very convenient (very short reaction times, ambient temperature) and can be readily applied to other complexes, including those unstable under the high temperatures and/or acid conditions of the conventional sulfonyl chloride route. This supported catalyst exhibits unusual selectivity in the oxidation of model phenol substrates bearing alcohol groups, double bonds or activated benzylic/allylic positions, favoring aromatic oxidation to quinones rather than conventional oxidation of these easily oxidizable functionalities. It should be noted that the catalytic oxidation of aromatic compounds is a largely unexplored field compared to the oxidation of alkanes and epoxidation of olefins. The results obtained provide a basis for a new promising green route to valuable synthetic intermediates containing carbonyl groups, double bonds and alcohol function groups in adjacent positions. Such compounds might be useful building blocks for the synthesis of the elaborate structures found in pharmaceuticals.

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