Clean catalytic oxidation of 8-hydroxyquinoline to quinoline-5,8-dione with ^tBuOOH in the presence of covalently bound FePcS–SiO_2 catalysts

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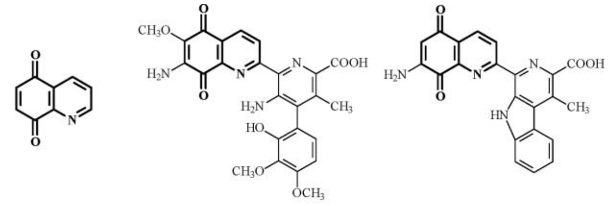
The clean catalytic oxidation of 8-hydroxyquinoline (8-HQ) with *tert*-butyl hydroperoxide to quinoline-5,8-dione (QD), a molecular framework fragment of antitumor compounds, over silica-supported iron tetrasulfophthalocyanine catalysts (FePcS) is reported. The pronounced influence of the FePcS state (monomer *vs.* dimer) and the support (amorphous SiO_2 *vs.* mesoporous MCM-41) on the catalytic activity and selectivity is revealed. Depending on the catalyst structure, turnover frequency values determined from the initial rates of 8-HQ consumption varied from 215 to 3570 h^{-1}.The effects of solvent, temperature, reagent concentrations and catalyst amounts on the substrate conversion and QD selectivity were studied to optimize the reaction conditions. With an optimal catalyst, the yield of the target product reached 66%. The truly heterogeneous nature of the catalysis was also demonstrated.

Introduction

Quinoline-5,8-dione (QD, Scheme 1) is a structural fragment of compounds that possess a wide spectrum of biological activity, and can be used as antitumor, antimalarial, antibacterial and antifungal drugs.[1–9] Aminoquinone antibiotics, such as streptonigrin (bruneomycin) and lavendamycin (Scheme 1), are known to be effective agents for the treatment of cancers.[8,10–13] A large number of studies have shown the crucial role of the quinoline-5,8-dione ring in the antitumor activity of these drugs.[1,14–17] Furthermore, QD has been used as a starting material in the synthesis of a series of antitumor agents developed by Bolognese and co-authors.[18–21]



Quinoline-5,8-dione (QD) Streptonigrin (bruneomycin) Lavendamycin

Scheme 1

Several approaches to the preparation of QD have been reported in the literature, emphasizing the synthetic interest in this transformation. The most effective procedure, suggested by Barret and Daudon, involves the stoichiometric oxidation of 5-hydroxyquinoline (5-HQ) and 5-/8-aminoquinoline by bis(trifluoroacetoxy)iodobenzene (2.2 equiv.), with a quinone yield of up to 88%.[22] However, the low active oxygen content in this oxidant (3.8%) leads to significant amounts of waste (the typical *E*-factor for these oxidation reactions is in the range 15–25). On the other hand, several methods for the preparation of QD based on the oxidation of 8-hydroxyquinoline (8-HQ) have been also reported.[23,24] The stoichiometric oxidation of 8-HQ to QD with $NaNO_2$, $Na_2S_2O_4$ or K_2CrO_4 is a multi-step process, producing the target product with a very low yield (16%).[23a] Potassium nitrosodisulfonate can also be applied for oxidation of 8-HQ.[23b,23c]

Substituted quinoline-5,8-quinones have been obtained by the photooxygenation of substituted 8-HQ in the presence of tetraphenylporphyrin in 50–82% yields.[23d] Sensitized photooxidation of 8-HQ or 5-HQ has afforded QD in 64–70% yields.[23e] So far, the only one-pot catalytic method for QD synthesis *via* 8-HQ oxidation has been published by Chauhan *et al.*[24] The authors used 5,10,15,20-tetraarylporphyriniron(III) chlorides as catalysts and hydrogen peroxide as the oxidant, the yield of QD being low to moderate (30%).

It has been shown that iron tetrasulfophthalocyanine (FePcS) covalently bound to silica supports provides efficient catalysts for the selective oxidation of aromatic compounds, especially for the oxidation of functionalized phenols and naphthols with ^tBuOOH to their corresponding quinones.[25–29] The efficiency of the iron porphyrins as catalysts in the oxidation of 8-HQ demonstrated by Chauhan *et al.*[24] has prompted us to suggest that iron phthalocyanines, having a similar structure, could also catalyze the oxidation of 8-HQ.

In the present work, we report the oxidation of 8-HQ to QD in the presence of FePcS catalysts that were supported on silica in monomer or dimer forms (Fig. 1) using environmentally friendly and economically attractive ^tBuOOH and H_2O_2 oxidants. The effects of the structure of the active site and the nature of the support on the catalytic activity and selectivity have been

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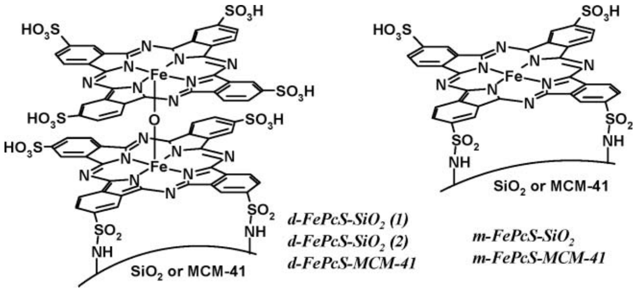


Fig. 1 A schematic representation of FePcS supported on silica and MCM-41 in monomer and dimer forms.

studied, and the reaction conditions optimized. The nature of the catalysis in this system has also been studied.

Results and discussion

Catalyst preparation and characterization

It is known that iron phthalocyanine complexes can exist in monomeric or μ-oxo-dimeric forms, depending on the conditions of their synthesis (solvent, concentration, *etc.*).[30]

Catalysts supported on amino-modified SiO_2 containing FePcS preferably exist in the μ-oxo-dimeric form (d-FePcS–SiO_2, samples **1** and **2**) and were prepared by two different methods. Catalyst **1** was synthesized by the reaction of a sulfonyl chloride derivative of iron tetrasulfophthalocyanine, $FePc(SO_2Cl)_4$, with amino-modified silica in pyridine at 80 °C by following a protocol described elsewhere.[25] In the second approach, FePcS anchoring was carried out under milder conditions. Sulfonate groups of a tetrabutylammonium salt of iron tetrasulfophthalocyanine, $FePcS(Bu_4N)_4$, activated with triphenylphosphine ditriflate, rapidly reacted with the amino groups of amino-modified SiO_2 in CH_2Cl_2 at 25 °C to form covalent sulfonamide bonds.[29] By following this procedure, we prepared **2**. The immobilization of FePcS on the mesostructured silicate MCM-41 was performed in the same way as for **1**. In order to prepare m-FePcS–SiO_2 and m-FePcS–MCM-41, catalysts containing monomeric forms of FePcS, a solution of $FePc(SO_2Cl)_4$ in pyridine was stirred for 18 h to transform the μ-oxo-dimeric species to a dipyridine mononuclear complex, which was then added to a suspension of amino-modified silica or MCM-41.[25] A sample of the mesoporous mesophase iron silicate Fe-MMM-2 was prepared for comparison.[31] The physicochemical characteristics of the Fe-containing catalysts prepared and used in this work are given in Table 1. The iron content in the supported FePcS catalysts was typically 0.2–0.3 wt%.

Diffuse reflectance UV-vis spectra of the supported FePcS catalysts are presented in Fig. 2A. The spectra of d-FePcS–SiO_2 (**1** and **2**) and d-FePcS–MCM-41 show an intensive Q band with a maximum at 630–640 nm, indicating a dimeric FePcS complex as the major species.[25] The bands below 500 nm correspond to metal to Pc ligand charge transfer. Upon dimerization, a more sensitive π–π* transition of the phthalocyanine ligand (Q band, between 600 and 700 nm) is blue-shifted with respect to that of the monomeric form. A shoulder at 690 nm, indicative of mononuclear species, suggests that a small amount of FePcS is present in the monomer form (Fig. 2A).[25]

Table 1 Physicochemical properties of the Fe-containing catalysts studied

Sample	Fe (wt%)	S^a/m² g⁻¹	$V_{Me}{}^b$/cm³ g⁻¹	$d_{Me}{}^c$/nm
d-FePcS–SiO_2 (**1**)	0.3	185	—[d]	—[d]
d-FePcS–SiO_2 (**2**)	0.2	185	—	—
m-FePcS–SiO_2	0.2	185	—	—
d-FePcS–MCM-41	0.2	860	1.3	3.9
m-FePcS–MCM-41	0.2	712	0.98	3.6
Fe-MMM-2	1.8	951	0.49	3.0

[a] BET surface area. [b] Specific mesopore volume. [c] Average mesopore diameter. [d] Non-porous material.

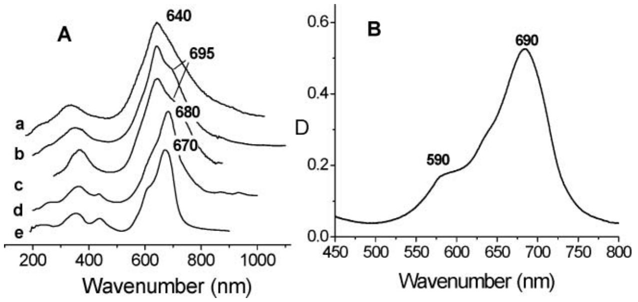
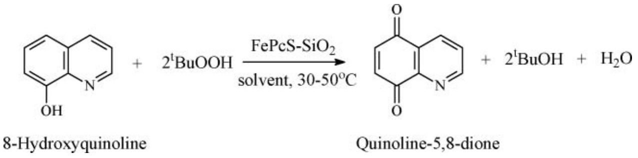


Fig. 2 (A) DR UV-vis spectra of (a) d-FePcS–SiO_2 (**1**), (b) d-FePcS–SiO_2 (**2**), (c) d-FePcS–MCM-41, (d) m-FePcS–MCM-41 and (e) m-FePcS–SiO_2. (B) The UV-vis spectrum of $FePcS(Bu_4N)_4$ (10^{-5} M) in acetone.

The broadness of the Q band in the UV-vis spectrum characterizes the homogeneity of the FePcS distribution on the surface.[29] The full width at half maximum of the 640 nm band is 160, 130 and 160 nm for **1**, **2** and d-FePcS–MCM-41, respectively. This result suggests a more homogeneous distribution of FePcS on the surface of the SiO_2 for **2** compared to **1** and d-FePcS–MCM-41. On the other hand, the DR UV-vis spectra of m-FePcS–SiO_2 and m-FePcS–MCM-41 exhibit a Q band at 670–680 nm, indicating a monomeric FePcS complex as the major supported species (Fig. 2A). Note that $FePcS(Bu_4N)_4$ in acetone also exists mainly in the monomeric form, as can be judged from the position of the Q band at 690 nm in the UV-vis spectrum (Fig. 2B).

Catalytic oxidation of 8-HQ

We examined the catalytic properties of the supported dimeric and monomeric iron phthalocyanines in the selective oxidation of 8-HQ with ^tBuOOH (Scheme 2) and compared them with those of homogeneous $FePcS(Bu_4N)_4$.



Scheme 2

Fig. 3 shows 8-HQ consumption and QD selectivity *vs.* time. No induction period was revealed for both substrate conversion and target product accumulation. One can see from Fig. 3A that m-FePcS–SiO_2, d-FePcS–MCM-41 and homogeneous

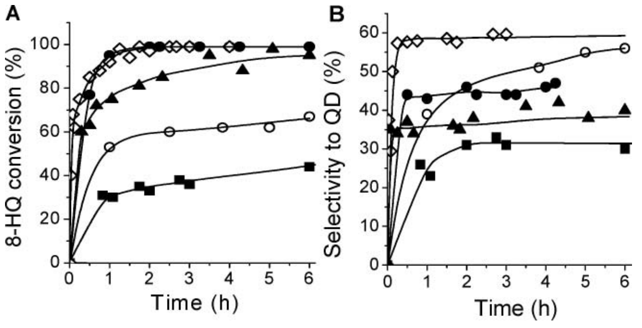


Fig. 3 Kinetic profiles of 8-HQ oxidation in the presence of d-FePcS–SiO_2 (**1**) (■), d-FePcS–SiO_2 (**2**) (○), d-FePcS–MCM-41 (●), m-FePcS–SiO_2 (◇) and m-FePcS(Bu_4N)$_4$ (▲). Reaction conditions: [8-HQ] = 0.1 M, catalyst 0.2 mol% Fe, [^{t}BuOOH] = 0.7 M, 30 °C, acetone.

m-FePcS(Bu_4N)$_4$ were significantly more active than both d-FePcS–SiO_2 samples. At the same time, **2** showed a higher activity than **1**.

The turnover frequency (TOF) values estimated from the initial rates of 8-HQ consumption were 215 and 470 h^{-1} for **1** and **2**, respectively. In turn, TOFs as high as 1400 h^{-1} were achieved with d-FePcS–MCM-41 and FePcS(Bu_4N)$_4$. The highest activity (TOF = 3570 h^{-1}) was found for m-FePcS–SiO_2. Thus, we may conclude that both the state of the FePcS complex and the porous structure of the support affect the catalytic activity. The higher catalytic activity of **2** in comparison to **1** results, most likely, from the more homogeneous FePcS distribution on the support (*vide supra*), which makes the majority of the iron centres accessible by reactants.

Selectivities of QD formation for the different catalysts were compared when their values achieved a constant level, after 1 or 2 hours depending on the catalyst, and increased in the order d-FePcS–SiO_2 (**1**) (30%) < FePcS(Bu_4N)$_4$ (37%) < d-FePcS–MCM-41 (47%) < d-FePcS–SiO_2 (**2**) (55%) < m-FePcS–SiO_2 (59%) (Fig. 3B). Hence, no general correlation between the catalytic activity and QD selectivity was revealed. Importantly, grafting FePcS onto silica allowed the attainment of a superior selectivity towards the target product compared to the homogeneous FePcS(Bu_4N)$_4$. In spite of the considerably different reaction rates, m-FePcS–SiO_2 and d-FePcS–SiO_2 (**2**) demonstrated a similar final selectivity to QD. However, the evolution of selectivity for d-FePcS–SiO_2 (**2**) was quite different to those of the other catalysts (Fig. 3B). The reason for this difference is not yet clear. The results obtained allow us to suggest that the structure of the FePcS complex strongly affects the activity of the catalyst, but not the selectivity. It is worth noting that d-FePcS grafted onto MCM-41 was more active but less selective than d-FePcS grafted on SiO_2 (**2**). Therefore, the use of a mesoporous support favours increasing the reaction rate but leads to a decreasing QD selectivity.

Importantly, the QD product was found to be stable under the reaction conditions used. After the addition of a 7-fold excess of ^{t}BuOOH to a mixture containing 0.05 mmol QD and 0.2 mol% of **2** in 1 mL of acetone, no conversion of QD was observed over 3 h. Hence, we may conclude that parallel pathways lead to the formation of the target and by-products.

To optimize the reaction conditions for QD production, we studied the effects of the reaction conditions (temperature, atmosphere, reagent concentrations, additives, *etc.*) on the oxidation of 8-HQ by ^{t}BuOOH over FePcS–SiO_2 (**1** and **2**). Firstly, we found that the reaction atmosphere (air or argon) does not affect the conversion of 8-HQ and the yield of the quinone. The addition of a typical chain radical inhibitor (ionol) to the reaction mixture showed no retarding effect on the reaction rate, indicating that the 8-HQ oxidation is not a chain radical process. This is consistent with the fact that the reaction rate is not influenced by the presence of O_2. Increasing the reaction temperature from 30 to 50 °C had no impact on the QD yield.

We found that the QD yield could be improved by decreasing the 8-HQ concentration (Fig. 4). The addition of the substrate in portions to the reaction mixture led to some decrease in the QD yield. The substrate conversion and quinone yield increased with increasing catalyst amount until a certain Fe/8-HQ ratio was reached; then the QD yield had a tendency to decrease. For **1** and [8-HQ] = 0.02 M, the optimal catalyst amount was 3.0 mol% Fe (Fig. 5A). Using this amount, 99% conversion of 8-HQ and 50% yield of QD were attained. Significantly, the optimal amount of **2** was lower (0.8 mol% Fe), and even at a higher 8-HQ initial concentration (0.1 M), a yield of QD as high as 56% was obtained with complete substrate conversion (Fig. 5B). Thus, comparing the QD yields at a similar substrate conversion (close to 100%), we may conclude that, irrespective of the reaction conditions employed, **2** was not only more active

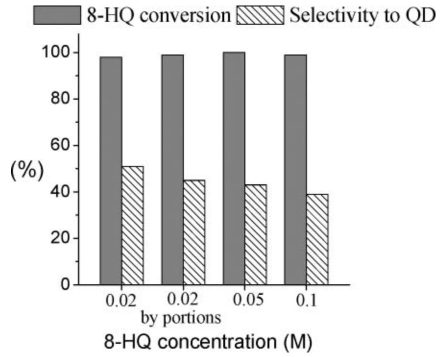


Fig. 4 The effect of 8-HQ concentration on the oxidation of 8-HQ over FePcS–SiO_2 (**1**). Reaction conditions: catalyst 3 mol% Fe, [^{t}BuOOH]/[8-HQ] = 7, 30 °C, acetone, 6 h.

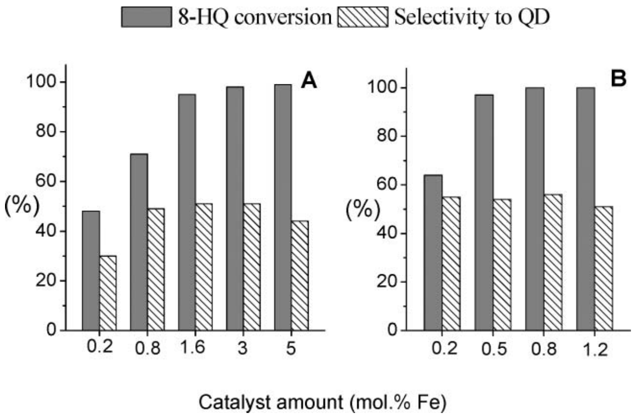


Fig. 5 The effect of catalyst amount on the oxidation of 8-HQ over FePcS–SiO_2. Reaction conditions: [^{t}BuOOH]/[8-HQ] = 7, 30 °C, acetone, 6 h, (A) catalyst **1**, [8-HQ] = 0.02 M and (B) catalyst **2**, [8-HQ] = 0.1 M.

but also more selective than **1**. This is in line with the results shown in Fig. 3.

The stoichiometry of 8-HQ oxidation with ^{t}BuOOH to produce QD is 1 : 2. However, the selectivity to QD increased with increasing [^{t}BuOOH]/[8-HQ] ratio until it reached 7 (Fig. 6). The addition of ^{t}BuOOH in portions to the reaction mixture led to some decrease of QD yield (Fig. 6A). A further increase in the oxidant concentration resulted in a decay of the QD yield, which could be explained by the enhancing of over-oxidation reactions. Importantly, when using ^{t}BuOOH reactant in decane instead of ^{t}BuOOH in H_2O, we observed a decrease of both substrate conversion and product yield (Fig. 6B), which allows the suggestion that water can participate in the pathway leading to the formation of quinone according to mechanism proposed in our recent paper.[29b]

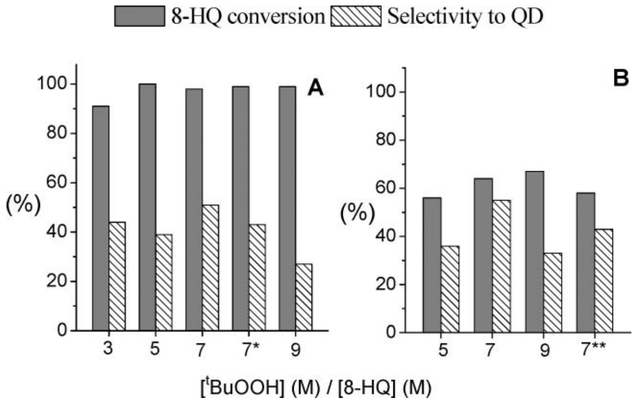


Fig. 6 The effect of [^{t}BuOOH]/[8-HQ] molar ratio on the oxidation of 8-HQ over FePcS–SiO_2. Reaction conditions: 30 °C, acetone, 6 h, (A) [8-HQ] = 0.02 M, catalyst **1** 3 mol% Fe and (B) [8-HQ] = 0.1 M, catalyst **2** 0.2 mol% Fe. * ^{t}BuOOH was added in portions. ** A ^{t}BuOOH solution in decane was used.

A study of 8-HQ oxidation in different solvents showed that the highest yields of QD were achieved in acetone, 1,2-dichloroethane and toluene (Fig. 7). Acetonitrile and ethyl acetate could also be considered suitable solvents. Importantly, some water should be present to reach higher QD yields. As was mentioned earlier, ^{t}BuOOH in water was a better choice than ^{t}BuOOH in decane. Furthermore, we found that at a fixed concentration of ^{t}BuOOH, the QD yield increased with increases in H_2O concentration until it reached a value of 0.3 M and then tended to decrease (**1**, Fig. 8A). When a more concentrated 8-HQ solution was used in the presence of **2**, the selectivity to QD also increased with the addition of supplementary water up to [H_2O] = 3 M (Fig. 8B). Meanwhile, as can be seen from Fig. 7B, an additional increase in the oxidant concentration also allowed an increase in QD yield.

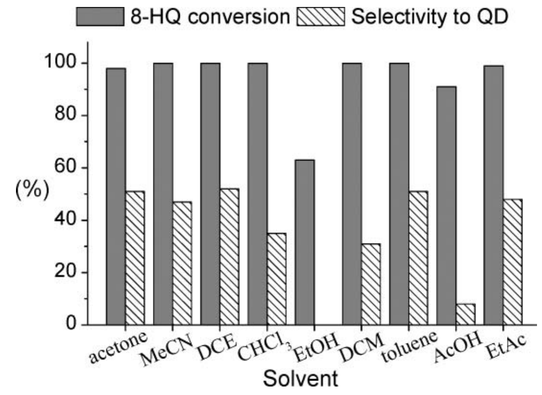


Fig. 7 The effect of solvent on the oxidation of 8-HQ over FePcS–SiO_2 (**1**). Reaction conditions: [8-HQ] = 0.02 M, catalyst 3 mol% Fe, [^{t}BuOOH] = 0.14 M, 6 h, 30 °C.

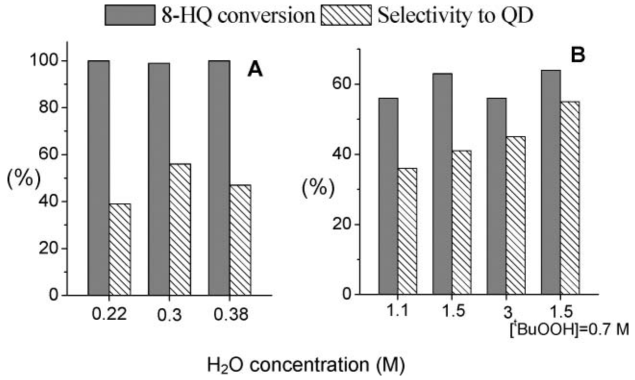


Fig. 8 The effect of H_2O concentration on the oxidation of 8-HQ over FePcS–SiO_2. Reaction conditions: [^{t}BuOOH]/[8-HQ] = 5, 30 °C, acetone, 6 h, (A) [8-HQ] = 0.02 M, catalyst **1** 3 mol% Fe and (B) [8-HQ] = 0.1 M, catalyst **2** 0.2 mol% Fe.

To summarize, the optimal reaction conditions for the production of QD from 8-HQ were established as follows: [8-HQ] = 0.02 M, [^{t}BuOOH] = 0.14 M, [H_2O] = 0.3 M, catalyst 0.8 mol% Fe, acetone, 30 °C. Table 2 presents the results of the catalytic tests performed using different grafted FePcS catalysts under these optimal conditions. For comparison, the data acquired in a blank experiment (without any catalyst) with homogeneous FePcS$(Bu_4N)_4$ and mesostructured iron silicate Fe-MMM-2 are also given.

The reaction barely occurs without catalyst; only 15% of 8-HQ was converted after 6 h, while no formation of QD was observed (Table 2, entry 7). One can see that the highest yield (66%) of QD was reached when using d-FePcS–SiO_2 (**2**) (Table 2, entry 2). The optimization of the reaction conditions allowed an increasing

Table 2 8-HQ oxidation in the presence of Fe-containing catalysts[a]

Entry	Catalyst	Time/h	8-HQ conversion (%)	QD yield (%)[b]
1	d-FePcS–SiO_2 (**1**)	6	59	31 (52)[c]
		24	73	51 (70)
2	d-FePcS–SiO_2 (**2**)	6	94	66 (70)[d]
3	m-FePcS–SiO_2	4	100	62 (62)
4	d-FePcS–MCM-41	2	100	40 (40)
5	m-FePcS–MCM-41	2	100	55 (55)
6	FePcS$(Bu_4N)_4$[e]	6	96	37 (39)
7	No catalyst	6	15	— (—)
8	d-FePcS–SiO_2 (**2**)[f]	4	25	— (—)
9	Fe-MMM-2	6	3	— (—)

[a] Reaction conditions [8-HQ] = 0.02 M, [^{t}BuOOH] = 0.14 M, [H_2O] = 0.3 M, catalyst amount 0.8 mol% Fe, acetone, 30 °C. [b] GC yield based on the initial substrate; GC yield based on the substrate consumed (selectivity) is given in parentheses. [c] The yield of the main identified by-product, 6,7-epoxy-6,7-dihydroxyquinoline-5,8-dione, was 9%. [d] The yield of 6,7-epoxy-6,7-dihydroxyquinoline-5,8-dione was 16%. [e] Homogeneous catalyst. [f] H_2O_2 was used instead of ^{t}BuOOH.

selectivity towards QD of up to 70% in the oxidation of 8-HQ over the dimeric d-FePcS–SiO_2 catalysts. The activity of **1** remained significantly lower, and 24 h were needed to obtain QD in a 51% yield (Table 2, compare entries 1 and 2). On the other hand, the alteration of the reaction conditions produced very little effect on the results acquired using monomeric m-FePcS–SiO_2, for which the QD yield reached 62% (Table 2, entry 3).

The FePcS complexes supported on MCM-41 provided a higher activity with respect to the same complexes anchored onto amorphous silica (Table 2, entries 4 and 5 *vs.* entries 2 and 3). In the former case, a complete substrate conversion was reached in 2 h, while 4 and 6 h were needed to obtain 100 and 94% conversion with m-FePcS–SiO_2 and d-FePcS–SiO_2 (**2**), respectively. However, both MCM-41 supported catalysts were less selective than the SiO_2 supported examples. Importantly, the majority of the supported FePcS catalysts demonstrated a superior catalytic performance in comparison to the homogeneous catalyst FePcS$(Bu_4N)_4$ (Table 2, entry 6).

The ^{1}H NMR study showed the presence of a by-product in the reaction mixture, which is tentatively identified as 6,7-epoxy-6,7-dihydroquinoline-5,8-dione on the basis of GC-MS data and its fragmentation pattern (see the Experimental section). In principle, quinoline-5,8-dione-*N*-oxide, which could be expected as the oxidation by-product, would have the same molecular ion ($m/z = 175$). However, the presence of the peak at $m/z = 106$ due to the loss of the OCC(O)CH fragment is only consistent with the 6,7-epoxy-6,7-dihydroquinoline-5,8-dione structure. The yield of the by-product, calculated by integration of the corresponding NMR signals, amounted to 5–16%, but we could not calculate the total balance of products because of the formation of tars.

We have found that iron silicate Fe-MMM-2, containing mostly site-isolated Fe ions,[31] showed no catalytic activity in 8-HQ oxidation with ^{t}BuOOH; only 3% substrate conversion was observed after 6 h (Table 2, entry 9). This indicates the crucial role of the FePcS complex in this specific oxidation reaction. When H_2O_2 was used as the oxidant instead of ^{t}BuOOH, the conversion of 8-HQ after 1 h was about 25%, but no QD was found in the reaction mixture (Table 2, entry 8). Furthermore, the phthalocyanine chromophore undergoes bleaching in the presence of H_2O_2.[32] Consequently, the combination of the FePcS catalyst and the alkyl hydroperoxide oxidant is essential for the selective oxidation of 8-HQ to QD.

In order to check for the possible contribution of a homogeneous catalytic reaction due to leached iron species into the overall oxidation process, we performed hot catalyst filtration experiments using **2** by following the methodology suggested by Sheldon and co-workers.[33] No further 8-HQ conversion and QD formation in the filtrate solution was found after separation of the solid catalyst (Fig. 9). This result clearly demonstrates that the catalysis is of a heterogeneous nature and is not due to iron species leached into solution from the catalyst surface.

We also studied the reusability of **2** under the optimal reaction conditions. Unfortunately, both the activity and selectivity decreased drastically in the second operation cycle. After 5 h, the conversion of 8-HQ was only 25% and the formation of QD was not observed. Although the phthalocyanine complex was much more stable in the presence of ^{t}BuOOH than in the presence of H_2O_2, a progressive oxidative degradation of the phthalocyanine ligand cannot be excluded, leading to a decrease of the activity and selectivity of the oxidation. Noteworthy, m-FePcS–SiO_2 was more amenable to recycling. In the second cycle, the conversion of 8-HQ was 66% and the selectivity of QD formation was 41%. Increasing the reaction time to 24 h allowed 90% conversion and 45% selectivity to QD to be achieved. However, good recyclability of the supported FePcS–SiO_2 catalysts remains a challenge.

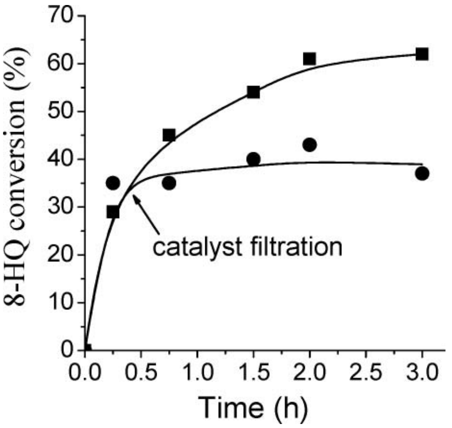


Fig. 9 The oxidation of 8-HQ with ^{t}BuOOH over FePcS–SiO_2 (**2**). Reaction conditions: [8-HQ] = 0.1 M, catalyst 0.2 mol% Fe, [^{t}BuOOH] = 0.7 M, 30 °C, acetone. (●) 8-HQ conversion after hot catalyst filtration.

Experimental

General

Catalysts and materials. Iron tetrasulfophthalocyanine, FePcS, was prepared according to a published procedure.[34] Covalently bound FePcS–SiO_2 and FePcS–MCM-41 materials were obtained by anchoring FePcS onto the surface of amino-modified non-porous SiO_2 (Aerosil, Degussa) and mesoporous MCM-41 (synthesized according to a published procedure[35]). Monomeric m-FePcS–SiO_2 and m-FePcS–MCM-41, and dimeric d-FePcS–MCM-41 and d-FePcS–SiO_2 (**1**) were prepared by following literature protocols,[25] dimeric d-FePcS–SiO_2 (**2**) was prepared as described previously.[29] Mesostructured iron silicate Fe-MMM-2 was prepared by a sol-mesophase route.[31] FePcS$(Bu_4N)_4$ was obtained by replacement of the sodium cation with tetrabutylammonium using tetrabutylammonium hydroxide.[29] 8-Hydroxyquinoline and *tert*-butyl hydroperoxide (70 wt% aqueous solution) were purchased from Aldrich. The other reactants were obtained commercially and used as received. The concentration of hydrogen peroxide (28–33 wt% aqueous solution) was determined iodometrically prior to use.

Catalytic experiments and product analysis

Catalytic oxidations were performed in thermostated glass vessels at 30–50 °C under vigorous stirring (500 rpm). Typically, the reactions were initiated by adding 0.06–0.90 mmol of ^{t}BuOOH or 0.7 mmol of H_2O_2 to a mixture containing 0.02–0.10 mmol of substrate and 6–20 mg (0.04–1.00 μmol Fe) of supported FePcS catalyst or 100 μL of a 0.0016 M solution of FePcS$(Bu_4N)_4$ in acetone (0.16 μmol Fe) or 4.4 mg (1.6 μmol

Fe) of Fe-MMM-2 in 1 mL of acetone or another solvent. For recycling experiments, before their second use, the catalyst was filtered off, washed with acetone and methanol, and dried at 100 °C. The oxidation products were identified by GC-MS and ^{1}H NMR spectroscopy. The substrate conversions and product yields were quantified by GC using biphenyl as the internal standard, as well as by ^{1}H NMR spectroscopy. The experiments were performed at least in triplicate and were reproducible within 5%. The mass balances were in the range 80–85%. The remaining 15–20% was accounted for by tars.

Quinoline-5,8-dione. GC-MS (EI) m/z (relative int.): 159 (100, $[M]^+$), 131 (51, $[M-CO]^+$), 103 (72, $[M-CO]^+$), 77 (27, $[M-C_4H_2O]^+$), 76 (48, $[M-C_4H_3O]^+$), 50 (29).

^{1}H NMR δ_H (250 MHz; CD_3COCD_3): 7.15 (1H, d, J = 10.4 Hz, $H^{6(7)}$), 7.18 (1H, d, J = 10.4 Hz, $H^{7(6)}$), 7.86 (1H, dd, J_1 = 8.0 Hz, J_2 = 4.7 Hz, H^3), 8.41 (1H, dd, J_1 = 8.0 Hz, J_2 = 1.5 Hz, H^4), 9.02 (1H, dd, J_1 = 4.7 Hz, J_2 = 1.5 Hz, H^2).

6,7-Epoxy-6,7-dihydroquinoline-5,8-dione. GC-MS (EI) m/z (relative int.): 175 (100, $[M]^+$), 159 (9, $[M-O]^+$), 147 (12, $[M-CO]^+$), 131 (6, $[M-O\text{-}CO]^+$), 119 (52, $[M-2CO]^+$), 106 (40, $[M-C_3HO_2]^+$), 103 (16, $[M-O\text{-}2CO]^+$).

Instrumentation

GC analyses were performed using a Tsvet-500 gas chromatograph equipped with a flame ionization detector and DB-5MS capillary column (30 m × 0.25 mm). GC-MS analyses of organic products were carried out using a Saturn 2000 gas chromatograph equipped with a CP-3800 mass spectrometer (30 m × 0.32 mm WCOT fused silica CP-SIL 8 CB capillary column) and Hewlett Packard 5973/6890 mass spectrometer (30 m × 0.25 mm cross-linked 5% PHME siloxane (0.25 μm coating) capillary column HP-5MS). ^{1}H NMR spectra of the reaction products were run on an AM 250 Bruker instrument. DRS UV-vis and solution UV-vis spectra were run on a Shimadzu UV-vis 2501PC spectrophotometer and a Specord M40 spectrophotometer, respectively.

Conclusions

A clean and efficient procedure for the oxidation of 8-hydroxyquinoline to quinoline-5,8-dione with ^{t}BuOOH in the presence of iron phthalocyanine supported on silica has been presented. The catalysts with a dimeric active site, d-FePcS–SiO_2, demonstrated a higher selectivity than those with a monomeric active site, m-FePcS–SiO_2. Both mononuclear and dinuclear FePcS complexes supported on mesoporous MCM-41 showed a higher activity but a lower selectivity than the corresponding complexes supported on non-porous SiO_2. The crucial factors affecting QD yield were the procedure for grafting the FePcS complex onto the SiO_2, the nature of the solvent, the 8-HQ concentration, the ^{t}BuOOH/8-HQ ratio and the catalyst amount. Over the best catalyst (d-FePcS–SiO_2 prepared under mild conditions) and under the optimal reaction conditions, the selectivity to quinone attained 70% at a 94% substrate conversion. Although further work is still required to improve the product yield and catalyst recyclability, the results already achieved demonstrate a promising clean way for QD production by a heterogeneous oxidation process.

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