Review

Metallophthalocyanines as Catalysts in Aerobic Oxidation

Carlos J. Pereira Monteiro [1,*] , Maria Amparo Ferreira Faustino [1] , Maria da Graça Pinho Morgado Silva Neves [1] , Mário M. Quialheiro Simões [1,*] and Enrico Sanjust [2,*]

[1] LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal; faustino@ua.pt (M.A.F.F.); gneves@ua.pt (M.d.G.P.M.S.N.)
[2] BBG-DiSB, Department of Biomedical Sciences, Cagliari State University, 09042 Monserrato, Italy
* Correspondence: cmonteiro@ua.pt (C.J.P.M.); msimoes@ua.pt (M.M.Q.S.); sanjust@unica.it (E.S.); Tel.: +351-234370360 (C.J.P.M. & M.M.Q.S.)

Abstract: The first remarkable property associated to metallophthalocyanines (MPcs) was their chemical "inertness", which made and make them very attractive as stable and durable industrial dyes. Nevertheless, their rich redox chemistry was also explored in the last decades, making available a solid and detailed knowledge background for further studies on the suitability of MPcs as redox catalysts. An overlook of MPcs and their catalytic activity with dioxygen as oxidants will be discussed here with a special emphasis on the last decade. The mini-review begins with a short introduction to phthalocyanines, from their structure to their main features, going then through the redox chemistry of metallophthalocyanines and their catalytic activity in aerobic oxidation reactions. The most significant systems described in the literature comprise the oxidation of organosulfur compounds such as thiols and thiophenes, the functionalization of alkyl arenes, alcohols, olefins, among other substrates.

Keywords: phthalocyanines; metallophthalocyanines; catalysis; oxidation; dioxygen; thiols; thiophenes; alkyl arenes; olefins; alcohols

1. General Introduction

After the casual discovery of phthalocyanines (Pcs) at the beginning of the 20th century [1], these macrocycles have been the subject of deep studies, mainly focused on their valuable dye properties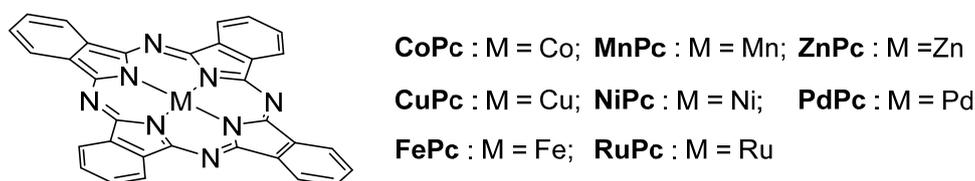 [2]. Along the first decades of 20th century, the importance of the coordination of Pcs with metal ions in their synthesis, and in the tuning of their chemical and dyeing properties was explored and emphasized [3,4]. In more recent years, the role of Pcs and their metal complexes (MPcs) as industrial dyes and pigments, was accompanied by an intensive search aiming to develop new fields of application [5,6]. In particular, a growing attention is focused on the redox catalytic properties of MPcs [7]. Although non-natural, Pcs show a noticeable resemblance to the structurally related macrocycle porphyrin, and also to other non-natural macrocycles such as porphyrazines and tetrabenzoporphyrins (Figure 1).

Like porphyrinoids, Pcs are aromatic macrocycles obeying the Hückel's rule (with 18 delocalized π electrons). However, the UV–Vis spectral patterns clearly reveal sharp differences that are reflected in the general chemical properties. Rather than from the benzocondensation, such differences mainly arise from the tetra-aza substitution of the four methinic bridges joining the pyrrolic-type rings in porphyrins. The four additional nitrogen atoms exert an electron-withdrawing effect, but also bear filled non-bonding orbitals, which are responsible for $n \rightarrow \pi$ transitions, increasing the width of the main absorption bands [8]. In fact, the Q bands of Pcs arise from a_{1u} to e_g transitions, whereas in porphyrins the corresponding bands are due to a_{2u} to e_g transitions [9].
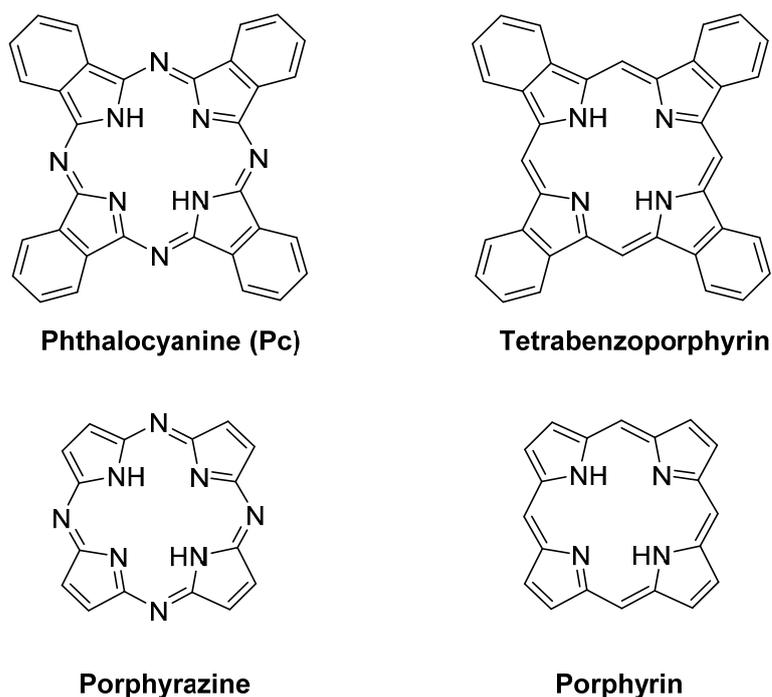
Figure 1. Chemical structures of tetrapyrrolic macrocycles: phthalocyanine, tetrabenzoporphyrin, porphyrazine, and porphyrin core.

Pcs show a high appetency to form the corresponding dianions upon deprotonation under suitable conditions, affording in the presence of the adequate metal ions the corresponding metal complexes MPcs (Figure 2).

CoPc : M = Co; **MnPc** : M = Mn; **ZnPc** : M = Zn

CuPc : M = Cu; **NiPc** : M = Ni;   **PdPc** : M = Pd

FePc : M = Fe; **RuPc** : M = Ru

Figure 2. Chemical structures of metallophthalocyanine complexes (MPcs) with different metals.

Such a tendency is so strong that very often the syntheses of Pcs is carried out in the presence of a suitable metal salt, thus giving directly the desired products in the form of the corresponding MPcs. Nearly all the elements of the periodic table are capable of forming complexes with Pcs, directly or, also, by metal-exchange reactions. With regard to such metal complexes, a further important difference between porphyrins and phthalocyanines is a consequence of the shorter bonds between the pyrrolic carbon atoms (from the isoindole units) and the nitrogen atoms of the aza bridges in phthalocyanines when compared with their porphyrin counterparts. So, the central cavity in a phthalocyanine ring is smaller than the corresponding one in porphyrins, and by consequence the central metal ions are forced to lower their spin. The more compact electron cloud of the coordinated metal ions in MPcs is also due to the stronger both σ donor and π acceptor character of Pcs when compared to identically substituted porphyrins. Therefore, in spite of the smaller space available, the metal ions fit better within a phthalocyanine rather than in the corresponding porphyrin, and thus in general they lean only slightly out of the phthalocyanine molecular plane [10,11].

An outstanding and well known feature of many Pcs and also of MPcs is their thermal stability that allows their purification by sublimation in high vacuum above 250 °C.

Thermal stability is paralleled by a noticeable chemical stability that is better defined as inertness for many Pcs and MPcs.

The four condensed benzene rings present in the isoindole units could undergo a number of electrophilic aromatic substitutions; however, a complex mixture of isomers, varying both in substitution degree and substituent positions, are usually formed, that could find application in industrial dyeing, whereas they are very tedious—if not impossible—to separate and purify for research purposes. To afford definite substitution products, the preferred routes start from the synthesis of properly substituted phthalonitriles. Once the derived Pcs are obtained, they could be further modified with the known organic synthesis tools [12]. However, unsymmetrically substituted phthalonitriles unavoidably afford isomeric mixtures of substituted Pcs.

Another noticeable feature of many MPcs is their very low solubility in many organic and aqueous solvents. Simple MPcs as well as the corresponding free-bases are completely water-insoluble, whilst slightly to moderately soluble in several organic solvents [13]; on the other hand, solubility in concentrated sulfuric acid is often high, owing to the protonation of the aza bridges between the isoindole rings. The introduction of alkyl or alkoxy substituents at the periphery of the Pc or MPc macrocycle causes a noticeable increase in the solubility of the substituted compounds in organic solvents. Under this context, the *t*-butyl substituents are bulky enough to prevent aggregation and stacking, and consequently are considered particularly suitable to improve the solubility of Pcs [12]. On the other hand, the introduction of very polar or ionizable substituents, such as $-SO_3^-$, $-N^+(CH_3)_3$, and pyridinium groups, affords water-soluble derivatives. Pcs and MPcs very often show a definite tendency to aggregate in solution, in particular in water or aqueous solvents, even when ionic substituents are present on the benzene rings. The aggregation state could be reliably estimated by means of spectroscopic techniques [9,14,15]. Aggregation could arise by simple stacking, driven by strong hydrophobic and π-interactions between the Pc rings, or also it depends on covalent interactions involving the central metal ions, linked each other by axial μ-oxo bridges. As expected, a decrease in the Pc concentration and an increase in the temperature milieu favor the presence of the monomeric form. MPcs facing to Pcs could form two additional, axial bonds with coordinating species and solvents, when the central metal ion prefers an octahedral coordination geometry. By consequence, MPcs that are insoluble or poorly soluble in "usual", non-coordinating solvents such as chloroaromatics are well soluble in coordinating solvents, such as pyridine (Py). As a well-known example, ZnPc is soluble in dichloromethane as its pyridine complex ($Zn(Py)_2Pc$), whereas it is quite insoluble in the absence of such a ligand [16]. Weakly coordinating solvents such as dimethylformamide (DMF), dimethylacetamide and dimethyl sulfoxide (DMSO) often represent a reasonable compromise as they dissolve many MPcs but are readily exchanged with stronger coordinating species when required. MPcs solutions in concentrated H_2SO_4 are useful for spectroscopic measurements as they contain protonated monomeric species, although their usefulness to determine other properties or find practical applications is negligible.

2. Metallophthalocyanines as Redox Catalysts: An Overview

As noted above, the first noteworthy property of MPcs was their chemical "inertness", which made and make them very attractive as stable and durable industrial dyes. However, their rich redox chemistry has only been explored in the last few decades [17].

In fact, MPcs are protected by their structure against the main threats jeopardizing redox-active metalloporphyrins, and that is the outstanding limitation towards an extensive use of the latter as industrial catalysts. First, the methinic bridges joining the pyrrole-type rings in porphyrins are the preferential targets of oxidative attack, leading initially to oxophlorins and later to macrocycle breaking and therefore to catalyst destruction [18]. Such methinic bridges are replaced in MPcs by aza bridges, which obviously are generally inert towards oxidative attacks. Second, the four condensed benzene rings protect the pyrrolic β-positions against any unwanted substitution reaction and prevent any possi-

bility of pyrrole ring cleavage. However, MPcs are not totally indestructible, and some reports exist, describing their degradation under relatively mild reaction conditions [19–21]. Nevertheless, in certain cases, the degradation products still show catalytic activity [22].

The Pc anions (Pc^{2-}) forming the various MPcs can be oxidized by one- or two-electron processes, leading, respectively, to radical anions $Pc^{\bullet-}$ or to a neutral species Pc. Conversely, reduction by one to four electrons affords, respectively, Pc^{3-}, Pc^{4-}, Pc^{5-}, and Pc^{6-}. Obviously, Pc^{3-} and Pc^{5-} have a radical character. Most of these oxidized or reduced species could be formed by means of electrochemical methods [17] and some are not found along the "normal" MPc chemistry. The central metal ion may be not involved in redox processes, as it can be anticipated for the majority of the main groups elements and for some transition metals such as Ni(II). However, in the case of most transition metals—they can show a rich redox chemistry while bound to the Pc ligand, which in turn is subject to its own redox changes.

A judicious choice of the peripheral substituents [12] in MPcs easily affords very soluble compounds, either in organic solvents or in water, suitable for electrochemical studies, or for several applications as redox catalysts. Moreover, the axial coordination to the central metal ions in the Pc inner core is responsible by further changes in their electrochemistry as well as in their redox properties, thus opening the way to a huge number of different redox-active species, that in principle could find application as redox catalysts. In this regard, MPcs show a large versatility, being able to work as photocatalysts, as electrocatalysts, and as "classical" catalysts, by activating oxidizing species such as O_2, H_2O_2, t-BuOOH, $KHSO_5$, and so on. MPc-mediated electrocatalysis and photocatalysis are out of the scope of the present minireview, whereas oxidative catalysis with oxygen will be reviewed and discussed in Section 3.

Stillman and Nyokong [16] have reviewed some general (and in particular spectroscopic) properties of nearly all phthalocyanine complexes with metals and also nonmetals, with additional focus on their redox properties, when the central metal is directly involved. Generally speaking, some MPcs, such as MnPcs, FePcs, or CoPcs, could directly interact, in their lower oxidation states, with dioxygen, forming adducts, more or less resembling the corresponding ferrohemoprotein-dioxygen adducts, such as oxyhemoglobins, oxymyoglobins, and also the ferroheme-containing cytochromes P-450 intermediate adducts with dioxygen. Some of these such adducts, which could be to a certain extent reversible, have been individualized; others should be transient species, more or less rapidly evolving to more stable products, where the oxidation state of the central metal ion has become higher. Comparative studies dealing with the ease of formation of such dioxygen adducts, and their tendency to undergo electroreduction, are those of Wang et al. [23] and of Shi and Zhang [24] that used Density Functional Theory to predict the electrocatalytic ability of some FePc and CoPc complexes in solution. Although specifically aimed to electrocatalysis, these studies are a suitable theoretical base to infer information about the catalytic redox properties of those phthalocyanines metal complexes and to extend the conclusions to similar ones.

As noted above, such adducts could arise from direct reaction of the corresponding MPcs, containing a proper divalent metal cation, with dioxygen. However, their similarity with ferroheme-dioxygen adducts is substantially low, as they are in fact superoxide complexes of the MPcs, where the oxidation number of the metal ions has increased to +3. Therefore, depending on the specific metal, on the peripheral substituents on the Pc macrocycle, and on the particular experimental conditions, they can act as one-electron oxidizers (where the oxidation number of the metal ion reverts to +2, whereas the superoxide more or less rapidly is degraded to H_2O_2). Alternatively, "direct" oxygenation of certain substrates could take place (vide infra).

MnPc and its substituted derivatives [25] can contain either Mn(II) and Mn(III); the very complex redox equilibria between the two oxidation states are highly sensitive to the presence of even traces of water. Additionally, reactions of Mn(II) derivatives with dioxygen (O_2) are very sensitive to the experimental conditions. In absolutely dry solvents such as

pyridine, Mn(II)Pc readily forms a monomeric adduct O_2-MnPc which has the electronic arrangement O_2^--Mn(III)Pc$^{\bullet+}$ corresponding to a superoxide adduct of Mn(III)Pc, which is the formal analogue of peroxidase Compound III (Figure 3) [26]. By contrast, when water traces are present, the reaction between dioxygen and Mn(II)Pc leads to a μ-oxo dimer PcMn(III)—O—Mn(III)Pc (Figure 3). With time, the μ-oxo dimer could also arise from the degradation of the Mn(III)-containing superoxide complex. Therefore, the superoxide adduct could well be the first, transitory reaction product, turning to further products under the influence of water traces. MnPcs, where eight electron-withdrawing substituents are present at the benzene rings, can exist as both stable Mn(II) and Mn(III) oxidation states, with no appreciable attitude to directly react with dioxygen. This feature opens the way to further studies, where the Mn(II)/Mn(III) complex couples could well exert interesting redox activities.
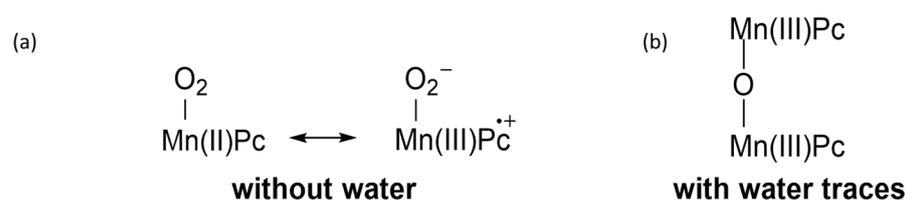
Figure 3. Electronic arrangements of Mn(II)Pc after reaction with dioxygen: (**a**) in the absence of water and (**b**) in the presence of water traces.

The experimental conditions have a great influence on the equilibria between Mn(II) and Mn(III) Pcs, as well as on their oxygenated derivatives; under certain conditions, the oxygenation to afford Mn(III)PcO$_2$ is reversible [27]. The peculiar catalytic properties of such superoxide adducts have been reported many years ago, as it catalyzes the di-oxygenation (with concomitant ring cleavage) of some indole derivatives [28]. Interestingly, the reaction is rather specific: 3-methyl-, 2,3-dimethyl-indole, and tryptophan are substrates, whereas plain indole, 1-methyl-, 2-methyl-, 1,2-dimethyl-, and 1,3-dimethyl-indole are not. In conclusion, a substituent must be present at the 3-position, whereas the 1-position must be unsubstituted, and the 2-position has not influence towards the susceptibility of the compound to the catalytic di-oxygenation reaction. When it happens, the di-oxygenation invariably affects the 2,3-bond, and in the case of the simplest substrate, 3-methyl-indole, the reaction product is 2-formamido-acetophenone. Although no detailed mechanism was proposed for the reaction, there is evidence that at the end of each catalytic cycle Mn(II)Pc must be obtained, which in turn reacts again with dioxygen to produce the reactive superoxide adduct.

The behaviour of the MnPcs to cycle between the two oxidation states of the central metal ion opened the way to a number of studies about the redox catalytic properties of the manganese complexes of variously substituted—and very often water-soluble—phthalocyanines. Moxon and colleagues [29] studied in detail the dioxygen adduct of symmetrical tetrasulfonated-Mn(II)Pc, and some of its changes upon pH variations. First of all, the solid adduct contains manganese(III) and superoxide. This arrangement changes upon dissolving the adduct in water, where it changes to a Mn(II) complex, binding dioxygen in a manner formally resembling oxymyoglobin and oxyhemoglobin. When pH is raised to >11, an intramolecular redox reaction takes place, and the Mn(III) adduct of superoxide is formed. At pH values > 14, the complex is reversibly destroyed with dioxygen evolution, but the process can be reversed by lowering the pH, for example to ∼3, where the Mn(II) is formed again, for which the authors have also claimed an H_2O_2-forming oxidase activity. These results form the background for further studies on the suitability of MnPcs as redox catalysts which be discussed in detail in Section 3.

Adducts arising from Fe(II)Pcs and O_2 must exist as reactive intermediates, very quickly evolving to stable products, namely the μ-oxo dimer of the type PcFe(III)–O–Fe(III)Pc. In relation to such a reactivity of the primary adduct, different FePcs under
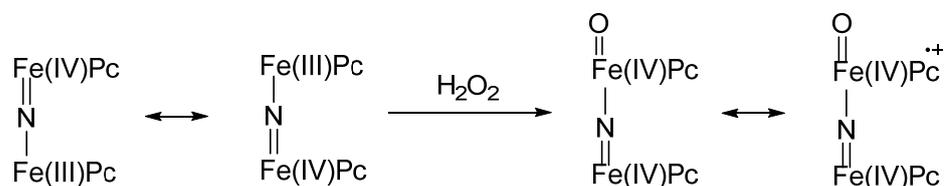
different experimental conditions could participate as catalysts in a wide variety of aerobic oxidation or oxygenation reactions. Many years ago, Ercolani and colleagues [30], working on unsubstituted Fe(II)Pc, found that the putative O_2-Fe(II)Pc complex, under suitable experimental conditions (toluene solution, high oxygen pressure), was able to catalyze the oxygenation of triphenylphosphine to the corresponding *P*-oxide. During the reaction, the insoluble Fe(III)-containing μ-oxo dimer slowly precipitated, with concomitant exhaustion of the catalysis. In the presence of two equivalents of pyridine, which promoted the formation of the soluble and catalytically very active Fe(II)(Py)$_2$Pc complex, the efficiency increased, and for this reaction the authors proposed the formation of the transient ferryl species O=Fe(IV)(Py)Pc. However, also this complex slightly decomposed with formation of the μ-oxo dimer, but the excess of pyridine prevented the formation of the latter and consequent catalyst inactivation. Interestingly, under the same experimental conditions, both Mn(II)Pc and Co(II)Pc were found to be quite inactive, despite their ability to form dioxygen adducts.

Additionally, rather complicated is the chemistry of the CoPcs with O_2, which in some cases requires the presence of H_2O_2 to afford the adduct formation [31]; the formation of a transient $O_2{}^-$-Co(III)Pc adduct has been suggested for other "autoxidation" reactions [32]; the behavior of non-supported Co(II)Pcs to readily form Co(III) μ-peroxo dimers is a well-established fact, which can be prevented by proper axial coordination [33]. As a consequence of a mono-axial coordination, the O_2-CoPc adducts become more efficient as oxidants. Of particular interest is the catalytic activity of Co(II)Pcs in aerobic oxidation of thiols to the corresponding disulfides, whose mechanism has been fully elucidated by Pan and coworkers (see Figure 16, as an example) [34]. The Co(II)Pc catalyst forms a ternary, bis-axial (octahedral) complex with the thiolate ion and dioxygen (the latter in the superoxide form, whereas the cobalt ion is in its +3 oxidation state). Then, a one-electron transfer to the cobalt(III) ion takes place, affording a thiyl radical RS$^\bullet$ whereas the metal is reduced back to Co(II). This causes the release of superoxide anion, which in turns reacts very rapidly with another thiolate ion, leading finally to disulfide and H_2O_2 as the reaction products.

As noted above, another crucial feature of MPcs containing redox-active metal ions such as Fe, Co, Mn, Ru, and others, is their ability, in particular when in their +3 oxidation state, to react with peroxo compounds or other oxygen donors such as iodosobenzene and iodibenzene derivatives [35]. More frequently, H_2O_2 and its alky or acyl derivatives have been explored for their ability to form peroxo complexes or hypervalent derivatives of MPcs (Figure 4). In principle, some compounds should be formed upon reaction of a suitable M(III)Pc with a generic hydroperoxide R–O–OH: (1) a Compound zero analogue, RO–O–M(III)Pc; (2) a Compound I analogue O=M(V)Pc $\leftrightarrow$ μ O=M(IV)Pc$^{\bullet+}$ $\leftrightarrow$ μ O$^\bullet$–M(IV)Pc; (3) a Compound II analogue O=M(IV)Pc $\leftrightarrow$ μ O$^\bullet$–M(III)Pc. As noted above, the electron-withdrawing effect of the phthalocyanine ring is, generally speaking, stronger than that observed for its porphyrin counterpart, and as a consequence the above reported compounds are more reactive but also more unstable [17]. This explains why until now only a few examples have been isolated and characterized, such as the inert O=V(IV)Pc [36,37] and O=Nb(IV)Pc [38], contrarily to that observed in the case of the corresponding metalloporphyrin compounds [39–44]. Apart from the formal resemblance between the porphyrin and Pc series, some substantial differences can be observed between the two families of redox-active metal complexes [7]. In fact, several different mechanisms can operate, as a function of the particular MPc catalyst, of the chosen oxidant, and of the particular substrate to be oxidized. The system Fe(III)Pc-BuOOH could operate with a one-electron mechanism—starting from the homolytic scission of the peroxo bridge O–O—when oxidizing phenols to quinones, although it oxidizes to quinones some other substrates such as anthracene and xanthene with a two-electron mechanism (as a consequence of a heterolytic scission releasing OH$^-$ and affording a very reactive hypervalent intermediate), as shown by the absence of oxidative coupling products, that are typical for one-electron (radical) mechanisms. On the other hand, the significant incorporation of ^{18}O from $^{18}O_2$ along

the oxidation of alkynes is a convincing proof of the radical mechanism. The reasons for such varying behavior of this and other MPc catalysts is still unknown. The propensity of Fe(III)Pc complexes to remain in the +3 oxidation state of the Compound 0 analogues has been assessed and discussed many years ago [45] and confirmed more recently [46]. In fact, the anionic form of such complexes, $^-$O–O–Fe(III)Pc, is an effective nucleophile acting as an epoxidizing agent towards electron-deficient double bonds, incorporated into an aromatic ring, for example in polychlorophenols [47].

Figure 4. Complexes or hypervalent derivatives of MPcs formed upon reaction of a suitable M(III)Pc with a generic hydroperoxide R–O–OH.

An outstanding feature of some MPcs is their high tendency to form μ-bridged dimers, where the two metal ions are linked together by –O– (oxo), –N= (nitrido) or also =C= (carbido) bridges [48]. Among these, diiron-oxo-bridged phthalocyanines have been deeply studied, mainly due to the easily preparation [7], as well as other binuclear complexes, containing different metal ions such as Ru, Cr, Mn, in different combinations (homo- or hetero-metallic) eventually hosted in the same Pc or in different Pcs (homo- or hetero-leptic complexes) [49]. In fact, when such a complex is treated with a peroxo compound, a Compound 0 analogue, involving only one Fe(III), is formed. This evolves preferentially to a Compound I analogue, as the formal positive charge arising on the involved Fe ion is efficiently delocalized, through the μ-oxo bridge, on the other Fe ion. In this way, a O=Fe(IV)Pc–O–Fe(IV)Pc is formed, lacking both the radical cation character and the positive charge, inherent to the Compound I analogue arising from the monometallic counterpart [46]. As a consequence, the hypervalent oxo compound deriving from the binuclear complex represents the optimal balance between stability against auto-destruction and effectiveness of oxidation catalysis. In other words, the two-electron oxidation mechanism arising from the heterolytic cleavage of the –O–O– peroxo bridge in the binuclear complex affords selective oxidation pathways for many to-be-oxidized substrates, in contrast with the mononuclear counterpart, where the homolytic cleavage leads to radical mechanism with concomitant oxidant wasting and catalyst consumption. Unluckily, along the catalysis the binuclear complex could gradually decompose into the mononuclear species, therefore lowering the overall catalytic efficiency [46,50]. The immobilization of the binuclear complexes on to suitable insoluble supports could obviate to this drawback, when a reaction medium is chosen, unable to dissolve the formed mononuclear species.

The things go quite differently in the case of binuclear complexes where the two metal ions are linked by a nitrido bridge. In fact, these compounds, whose importance in catalysis of recalcitrant substrates oxidations is steadily increasing, show some useful features such as their noticeable operational stability along the catalytic cycle, and high effectiveness as oxidants for their hypervalent oxygenated derivatives (Figure 5). In fact, a nitrido-diiron-phthalocyanine in its resting state is a mixed-valence compound showing a formal oxidation number of +3.5, PcFe(III)–N=Fe(IV)Pc ↔ μ PcFe(IV)=N–Fe(III)Pc. Upon reaction with H_2O_2, a ultra-high valent peroxo species arises: O=Fe(IV)Pc–N=Fe(IV)Pc ↔ μ O=Fe(IV)Pc$^{+\bullet}$–N=Fe(IV)Pc, passing through a peroxo complex, formally analogous to Compound 0, such as the ultra-high valent complex is the formal analogue of Compound I [46]. With time, the unprecedented, exceptional oxidizing catalytic power of μ-nitrido-bridged diiron complexes has been further explored, and such compounds are among the most promising oxidation and oxygenation catalysts for many practical applications, such as organic synthetic chemistry and degradation of recalcitrant pollutants. Outstanding examples are the controlled oxidation of methane at nearly ambient temperature and neutral

pH [51] and the oxidative hydroxylation and dehalogenation of perfluoroaromatics [52], for which the reaction mechanism has been elucidated [53].

Figure 5. Nitrido-diiron-phthalocyanine with mixed valence state and ultra-high valent peroxo species formed after reaction with oxygen peroxide.

In the next sections, special attention will be given to recent research concerning the catalytic activity of MPcs in the presence of O_2 towards different substrates like thiophene and other mercaptans, alkyl arenes, alcohols, and olefins.

3. Metallophthalocyanines and Their Catalytic Activity with Dioxygen as Oxidant

3.1. Thiols and Thiophenes

High activity, robustness, and the relative facile functionalization and immobilization of MPc in solid supports made these macrocycles excellent candidates for large scale industrial process catalysts. A paradigmatic example is the Merox® Process (Mercaptan Oxidation) [54], an industrially important worldwide process used on the desulfurization of different petroleum fractions from various thiols. This process, also known as "sweetening" in the petroleum refining industry, typically comprises the use of catalysts based on Co(II)Pcs or other MPcs (e.g., Fe, Mn, Mo, or V) to oxidize the foul-smelling and corrosive mercaptans (thiols) into innocuous disulfides with dioxygen (Equation (1)). The MPc catalysts can be used either as a suspension in alkaline medium (sulfonated MPc) or supported on a composite (e.g., MPc catalysts impregnated on charcoal granulates as a solid support).

$$2NaSR \ + \ 1/2\,O_2 + H_2O \ \xrightarrow{\text{MPc}} \ RSSR \ + \ 2NaOH \tag{1}$$
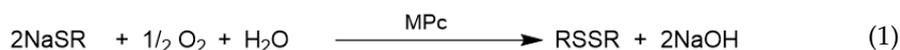
Under the context of catalytic oxidative desulfurization (ODS), Zhou and coworkers [55] compared the efficiency of the three Fe(III) phthalocyanine catalysts, **Fe(III)Pc(NO$_2$)$_4$**, **Fe(III)Pc(NO$_2$)$_3$NH$_2$** and **Fe(III)Pc(NH$_2$)$_4$**, bearing nitro and amine substituents (Figure 6) for the direct oxidation of dibenzothiophene (DBT), a well-known recalcitrant organosulfur compound. In the catalytic assays, the oxidation of DBT with dioxygen was performed in decalin as model fuel, under water-free conditions. The authors found that the catalytic activity of the Fe(III) Pcs decreases in the order **Fe(III)Pc(NO$_2$)$_4$** > **Fe(III)Pc(NO$_2$)$_3$NH$_2$** > **Fe(III)Pc(NH$_2$)$_4$**, indicating that the presence of the electron-donating group has a negative effect on the catalytic performance. The aerobic oxidation of DBT into the corresponding sulfone in the presence of **Fe(III)Pc(NO$_2$)$_4$** (1 wt%) at 100 °C and at O_2 initial pressure of 0.3 MPa exhibited the highest conversion (98.7%) after 2 h of reaction, whereas the conversion of DBT catalyzed by **Fe(III)Pc(NO$_2$)$_3$NH$_2$** and **Fe(III)Pc(NH$_2$)$_4$** was 87.8 and 64.1%, respectively. The **Fe(III)Pc(NO$_2$)$_4$** efficiency was maintained after five runs (98.4%) and the inferior performance of **Fe(III)Pc(NH$_2$)$_4$** was associated to its decomposition during the oxidation reactions (23.9% in the fifth run). However, when the catalyst **Fe(III)Pc(NO$_2$)$_3$NH$_3$$^+$** was immobilized on resin D-113 (a microporous week acid polyacrylic cationic exchange resin), Figure 6, its activity was raised to the level of the best non-immobilized catalyst **FePc(NO$_2$)$_4$**.

Figure 6. Molecular structure of the free Fe(III)Pc(NO$_2$)$_4$, Fe(III)Pc(NH$_2$)$_4$, Fe(III)Pc(NO$_2$)$_3$NH$_2$, and supported Fe(III)Pc(NO$_2$)$_3$NH$_3$$^+$@D-113 Resin Fe(III)Pcs catalysts.
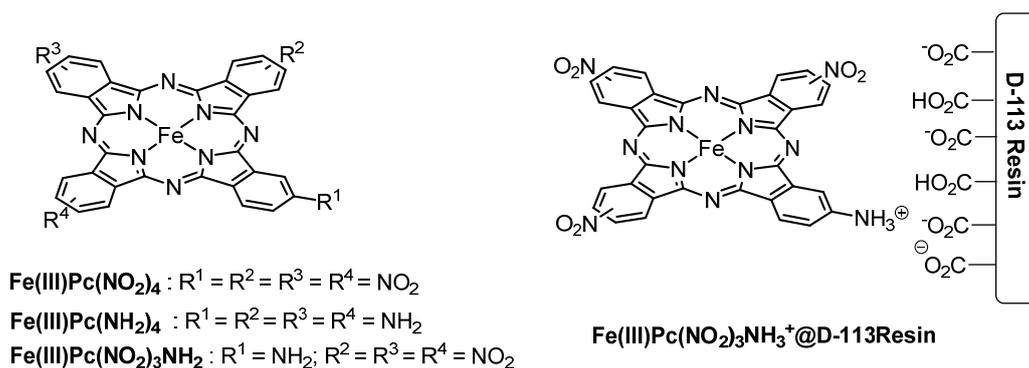
Chen and coworkers [56] selected **Fe(III)Pc(NO$_2$)$_3$NH$_2$** to be covalently immobilized onto Carbon Fiber (Single-Walled Nanotubes, SWNT) and evaluated the catalytic efficiency of this heterogeneous catalytic system in the direct oxidation of DBT in tridecane with O$_2$. The grafting of **Fe(III)Pc(NO$_2$)$_3$NH$_2$** in SWNT (Figure 7) was performed using isoamyl nitrite as oxidizing agent in DMSO according with a modified literature method [57] that gave rise to a final load of 0.23 wt% of the Fe(III)Pc based on the iron content determined by atomic absorption spectroscopy.
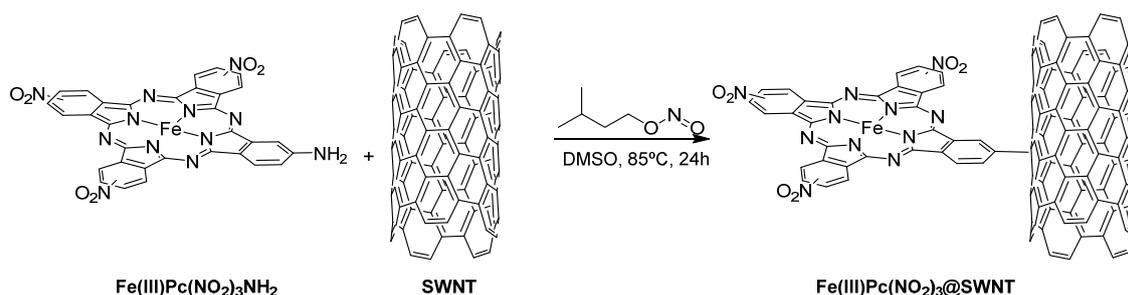
Figure 7. Synthetic route for the preparation of the MPc covalently supported on carbon fiber, **Fe(III)Pc(NO$_2$)$_3$@SWNT** (Adapted from [56]).

The new **Fe(III)Pc(NO$_2$)$_3$@SWNT** catalytic system exhibited a good catalytic performance with a conversion of DBT reaching 92% (vs. ~85% for FePc(NO$_2$)$_4$ and ~80% for **Fe(III)Pc(NO$_2$)$_3$NH$_2$**) at 130 °C, 10 g/L of catalyst, under an initial O$_2$ pressure of 0.2 MPa and after 3 h of reaction. The assays concerning the recyclability and reusability of the catalytic material showed a moderate decrease in DBT conversion from 92% (first cycle) into 78% (fourth cycle). In the catalytic oxidation of DBT to DBTO$_2$ with O$_2$ as oxidant, mediated by **Fe(III)Pc(NO$_2$)$_3$@SWNT**, the authors proposed the free radical high valent iron-oxo mechanism summarized in Figure 8; this proposal was supported by the absence of oxidized products (only traces of DBTO$_2$ were detected) in reactions performed in the presence of a radical inhibitor, hydroquinone.
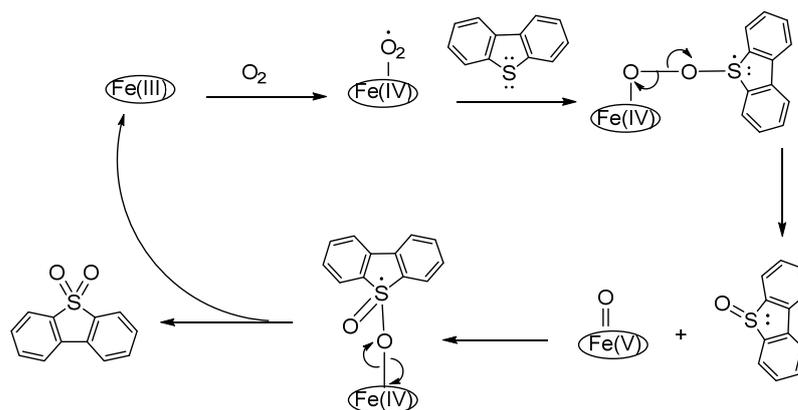
Figure 8. Proposed mechanism for DBT oxidation using Fe(III)Pc(NO$_2$)$_3$@SWCNT as catalyst (Adapted form [56]).

Dibenzothiophene was also selected by Zhang and coworkers [58] as model compound to compare the catalytic activity of four cobalt phthalocyanines with 4, 8, 12, and 16 chlorine atoms present in the Co(II)Pc periphery. The results obtained in the presence of air, at room temperature, and using the 1-propylpyridinium tetrafluoroborate ((ProPy)(BF$_4$)) ionic liquid as solvent showed that the catalytic activity increases in proportion to the number of chlorine atoms: **Co(II)Pc(Cl)$_4$** < **Co(II)Pc(Cl)$_8$** < **Co(II)Pc(Cl)$_{12}$** < **Co(II)Pc(Cl)$_{16}$**. The 90.4% removal of DBT from the octane model fuel (vs. 18% for CoPc(Cl)$_4$) in the presence of the most active catalyst **CoPc(Cl)$_{16}$** (Figure 9), after 2 h of reaction, merits to be emphasized since the reactions were performed at room temperature and at atmospheric pressure. These results indicated that the presence of electron-withdrawing group substituents has a positive impact on the Co(II)Pc catalytic performance. The study showed also that **CoPc(Cl)$_{16}$**/(PorPy)(BF$_4$) was able to be used five times without loss of activity (90.2% of DBT removal in the fifth run). The removal of other organosulfur compounds, namely thiophene (T), methylthiophene (MT), benzothiophene (BT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT) by **Co(II)Pc(Cl)$_{16}$** with air was also studied and the removal ratio decreases in the order T (100.0%) > DBT (90.4%) > BT (89.1%) > MT (81.9%) > 4,6-DMDBT (80%) at room temperature after 2 h. Another significant achievement for this desulfurization system was the decrease observed in the sulfur content from 1000 ppm to 30 ppm in the oxidation assays performed with CoPc(Cl)$_{16}$ in a real matrix (gasoline).
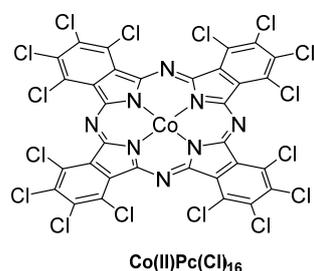
Co(II)Pc(Cl)$_{16}$

Figure 9. Example of a perchlorinated cobalt phthalocyanine, **Co(II)Pc(Cl)$_{16}$**, used by Zhang and coworkers for the desulfurization of model fuels and gasoline.

Jain and coworkers [59] reported the preparation of the hybrid material **Co(II)Pc(SO$_2$Cl)$_3$ SO$_2$NH@CF**, obtained from poultry waste chicken feathers (**CF**) enriched with NH$_2$ functionalities (**NH$_2$@CF**) and the tetrasulfonylchloride cobalt(II) phthalocyanine (**Co(II)Pc(SO$_2$Cl)$_4$**), that was further evaluated as catalyst in the aerobic oxidation of a series of aliphatic and aromatic mercaptans under non alkaline conditions (Figure 10; Table 1).
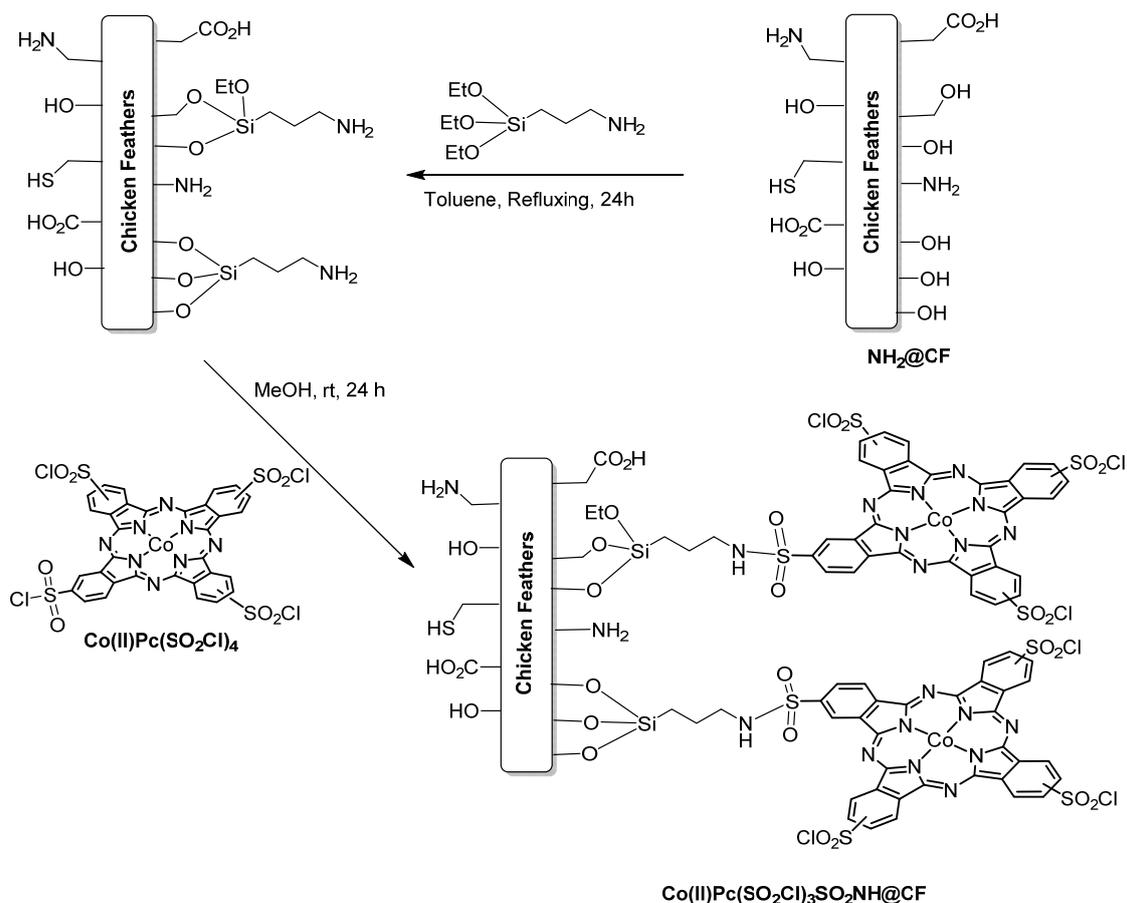
Figure 10. Schematic representation for the synthesis of the **Co(II)Pc(SO₂Cl)₃SO₂NH@CF** heterogeneous catalyst (adapted from [59]).

The amino functionalities were introduced by reacting the powered poultry waste chicken feathers with 3-aminopropyltriethoxysilane (**APTES**) that, after reaction with the **Co(II)Pc(SO₂Cl)₄** bearing sulfonyl chloride substituents, afforded the desired catalyst material. The authors verified that this material is able to selectively oxidize thiols to the corresponding disulfides (no evidence for the formation of the corresponding sulphonic acids) in yields ranging from 68–96%, using O_2 atmosphere and ultrasonic irradiation at room temperature in DMF and in the absence of bases (Equation (2)).

$$2RSH \ + \ 1/2 \ O_2 \ \xrightarrow{\text{catalyst}} \ RS{-}SR + H_2O \tag{2}$$

The results showed that the aromatic mercaptans were, in general, less reactive than the aliphatic ones and, among the aliphatic series, the reaction time was higher for those with longer chains. The study showed also that the immobilized catalyst presents a significantly higher catalytic activity towards thiophenol than the homogeneous counterpart (96 vs. 80% after 35 min) which was attributed to the synergistic effect of the support matrix. In addition, the authors demonstrated that the heterogeneous catalyst was easily recovered and recycled for five runs without loss of activity, since no leaching of the active Co(II)Pc catalyst was detected during the reactions.

The influence of fluorine atoms on the catalytic activity of CoPcs, towards mercaptans aerobic oxidation into disulfides in alkaline medium, was evaluated by Reid and Barat [60] in 2016. The experimental and kinetic studies were carried out in THF using 2-mercaptoethanol (2-ME) and 4-fluorobenzenethiol (4-FBT) as sulfur model substrates and the cobalt(II) phthalocyanines **Co(II)PcF₁₆** and **Co(II)PcF₆₄** as the fluorinated homogeneous catalysts at 22 °C. The non-fluorinated **Co(II)Pc** was used for comparison (Figure 11). The best performance, in

terms of kinetic parameters and catalyst stability, was found for the fluorinated **Co(II)PcF$_{64}$** showing the fastest conversion, followed by **Co(II)PcF$_{16}$**, and then by the non-substituted **Co(II)Pc**, thus confirming the positive effect driven by a higher Lewis acidity imposed by the fluorine atoms. The authors highlighted that the catalyst protection, imposed by the peripheral bulky isopropyl groups in the perfluorinated **Co(II)PcF$_{64}$** catalyst, is also an important feature for its higher catalytic activity and stability.

Table 1. Some of the results obtained for mercaptan aerobic oxidation mediated by **Co(II)Pc(SO$_2$Cl)$_3$SO$_2$NH@CF** as catalyst at room temperature (adapted from [59]).

Entry	Mercaptan	Dissulfide	Time (min)	Conv. (%)	Yield (%)
1			30	98.5	96
2			35	97	92
3			45	96	93
4			55	96	93
5			65	91	89
6			120	72	68
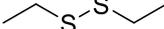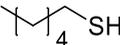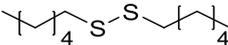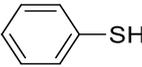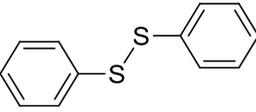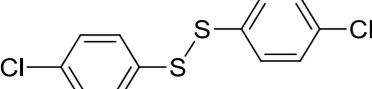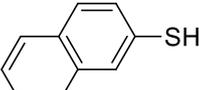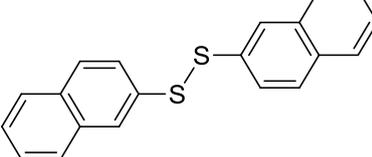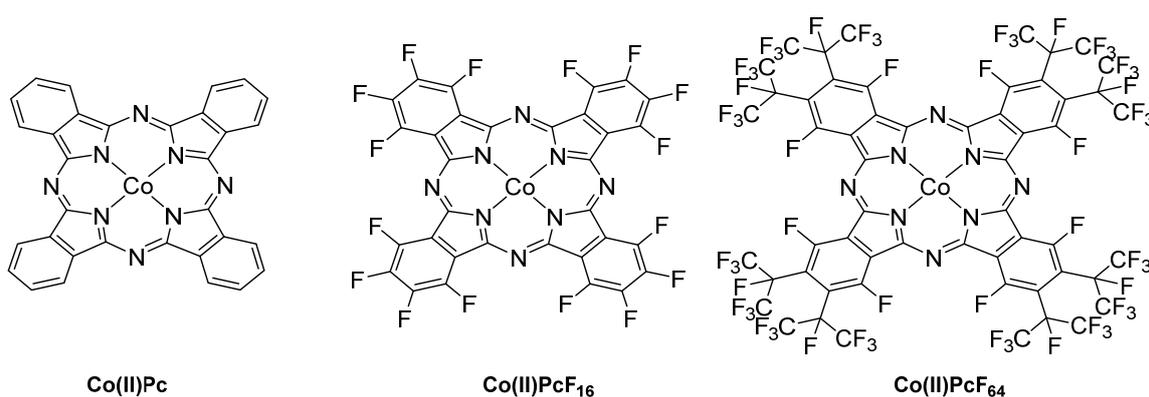
Figure 11. Structures of cobalt(II) phthalocyanine and its fluorinated derivatives used by Reid and Barat [60].

Vashurin and coworkers [61] compared the catalytic activity of several cobalt(II) phthalocyanines **Co(II)Pc(XC$_6$H$_4$CO$_2$H)$_4$R$_4$** (Figure 12) on the oxidation of sodium *N,N*-diethyldithiocarbamate (DTC) at pH 11 and 25 °C (Equation (3)).

$$2 \quad \underset{Et}{\overset{Et}{>}}N-C\underset{SNa}{\overset{S}{<}} + 1/2\ O_2 + H_2O \xrightarrow{\text{Catalyst}} \underset{Et}{\overset{Et}{>}}N-C\underset{S-S}{\overset{S\quad S}{<}}C-N\underset{Et}{\overset{Et}{<}} + 2\ NaOH \qquad (3)$$

The kinetic studies of the difunctional CoPcs, (a) bearing nitro groups combined with 4-amino, 4-hydroxyl and 4-sulfanyl benzoic acid substituents (**Co(II)Pc(XC$_6$H$_4$CO$_2$H)$_4$(NO$_2$)$_4$**, **X=O,S,NH**), or (b) containing just the 4-substituted benzoic acid as substituents (**Co(II)Pc (XC$_6$H$_4$CO$_2$H)$_4$(XABz)$_4$, X=O,S,NH**) for DTC oxidation revealed a structure-activity relationship. The differences observed on the catalytic activity were attributed to the nature of the heteroatom (NH; S; O) on the phthalocyanine peripheral substituents. The introduction of electron-acceptor groups in the periphery of the phthalocyanine molecule led to an increase in catalytic activity.

Figure 12. Structures of cobalt(II) complexes with tetrasubstituted phthalocyanines bearing nitro groups and benzoic acid groups.

Following an analogous approach, the same research group [62] prepared the sulfonated water soluble complexes **Co(II)PcS$_4$(NO$_2$)$_4$** or **Co(II)PcS$_8$** and **Cu(II)PcS$_4$(NO$_2$)$_4$** or **Cu(II)PcS$_8$** (Figure 13) and evaluated their catalytic activity, with O$_2$ as oxidant, and sodium *N,N*-diethyldithiocarbamate (DTC) as substrate (Equation (3)). The highest activity was achieved for Co(II) complexes, particularly the octasulfonic phthalocyanine **Co(II)PcS$_8$**, that was the most active catalyst. The authors explained this difference with sterical effects of peripheral substituents and aggregation phenomena. The octasulfonated bulky substituents present in both peripheric positions of **Co(II)PcS$_8$** reduces the aggregation that will be higher on the tetrasulfonated counterpart (**Co(II)PcS$_4$(NO$_2$)$_4$**).

Figure 13. Structures of Co(II) and Cu(II) complexes of tetrasubstituted phthalocyanines bearing nitro and sulfonic acid groups (adapted from [62]).

In 2017, Kimura and coworkers [63] reported the synthetic access to the two 3D network polymers **Zn(II)PcPoly1,2** and **Co(II)PcPoly1,2** (Figure 14) containing Zn(II) or Co(II) phthalocyanines interconnected with twisted 9,9′-spirobifluorene linkers and evaluated their catalytical performance in the aerobic oxidation of thiols. The results obtained in the polymers characterization were compared with those obtained from **M(II)Pc-dimer1** and **M(II)Pc-dimer2** used as prototypes of component units of **M(II)Pc** network (Figure 15).

Zn(II)PcPoly-1, M = Zn(II)
Co(II)PcPoly-1, M = Co(II)

Zn(II)PcPoly-2, M = Zn(II)
Co(II)PcPoly-2, M = Co(II)
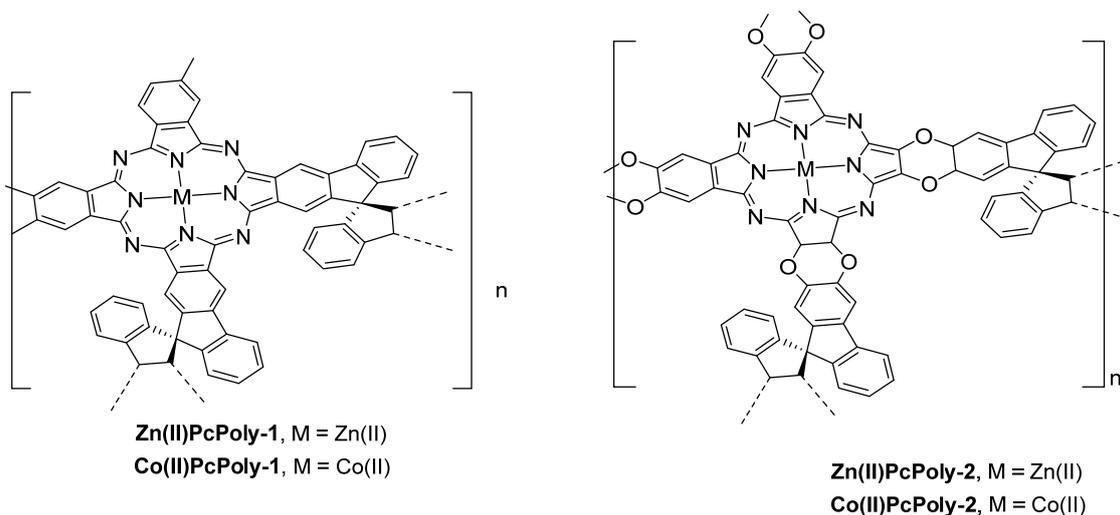
Figure 14. Structures of Zn(II) and Co(II) phthalocyanines network polymers, prepared by Kimura and coworkers (adapted form [63]).

Zn(II)Pc-dimer-1, M = Zn(II)
Co(II)Pc-dimer-1, M = Co(II)

Zn(II)Pc-dimer-2, M = Zn(II)
Co(II)Pc-dimer-2, M = Co(II)
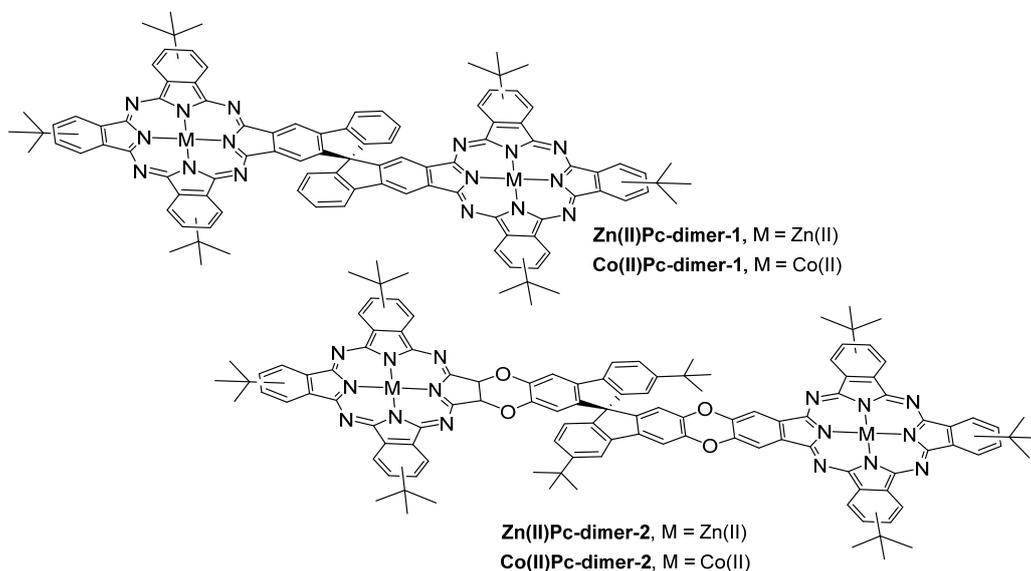
Figure 15. Structures of Zn(II) and Co((II) phthalocyanine dimers **M(II)Pc-dimer-1** and **M(II)Pc-dimer-2** connected with twisted linkers (adapted from [63]).

For instance, from XRD and N_2 adsorption and desorption techniques it was disclosed that the condensation of the twisted 9,9′-spirobifluorene linkers in the presence of zinc or cobalt ions established smaller cavities in the new polymeric materials, that showed to be important on their catalytic activities towards RSH oxidations. Although both polymers exhibited catalytic activity for RSH oxidations, the catalytic activity of polymer **M(II)PcPoly-1**, containing rigid and small cavities, was higher than that of **M(II)PcPoly-2** having larger cavities. This higher catalytic activity was associated to an easier substrate dif-

fusion in **M(II)PcPoly-1** when compared with **M(II)PcPoly-2**. It would be also interesting and insightful to compare the catalytic activities of polymer networks **M(II)PcPoly-1** and **M(II)PcPoly-2** with the corresponding **M(II)Pc-dimer-1** and **M(II)Pc-dimer-2**, however the authors did not accomplish further comparative studies.

Kang and coworkers [64] reported that the **Fe(II)Pc** (Figure 2) under optimized conditions (THF, room temperature, atmospheric O_2) is able to oxidize efficiently a series of thiols to the corresponding disulfides (Equation (2)). Under the context of the oxidation of thiols to disulfides, the results showed that the efficiency was not affected by the presence of electron-donating or electron-deficient substituents either in benzyl (Table 2, Entries 1, 2 and 3) or in aromatic mercaptans (Table 2, Entries 4, 5 and 6). Moreover, excellent conversions were obtained with mercaptans bearing bulky substituents (Table 2, entry 7) and with aliphatic mercaptans (Table 2, entry 8).

Table 2. Examples and scope of aerobic oxidation of thiols using **Fe(II)Pc** as catalyst [64].

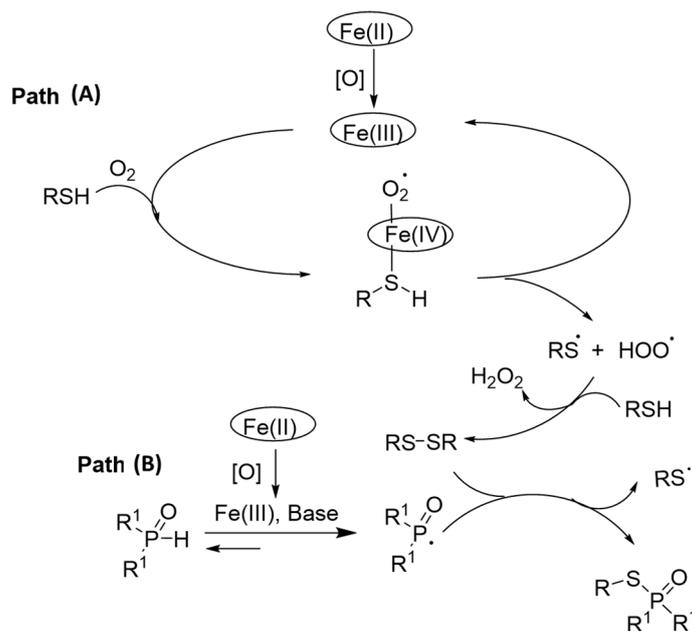| Entry	Mercaptan	Dissulfide	Conv. (%)	Yield (%)
1			-	99
2			98	-
3			97	-
4			99	99
5			91	-
6			98	-
7			99	-
8			99	-
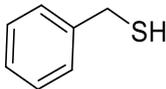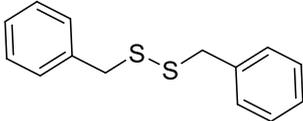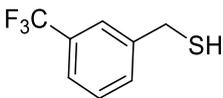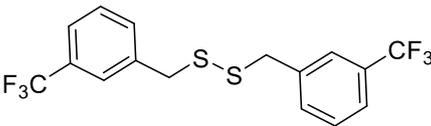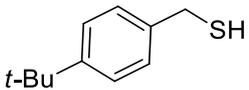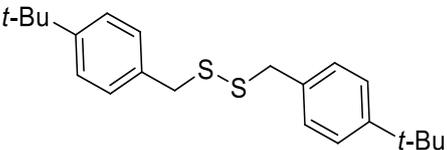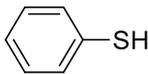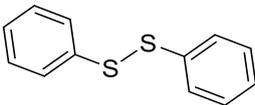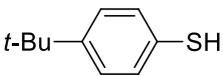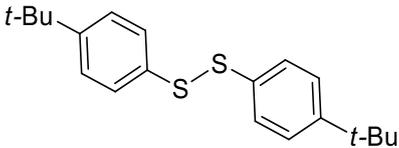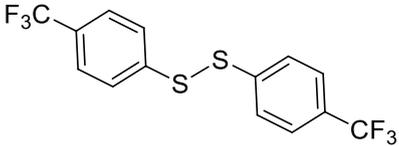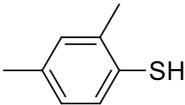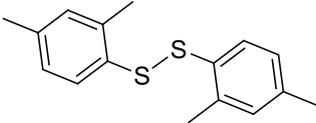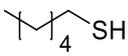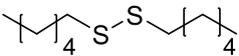
The same complex **Fe(II)Pc** have been also explored on cross-dehydrogenative coupling (CDC) with H-phosphonates and H-phoshine oxides (Equation (4)).

$$RSH \quad + \quad \underset{R^1}{\overset{\overset{\displaystyle O}{\parallel}}{\underset{\displaystyle H-P-R^1}{}}} \quad \xrightarrow[\text{THF, 60°C, 24h}]{\begin{array}{c}\text{Fe(II)Pc (3.0 mol\%)}\\\text{Base (1.0 equiv.)}\end{array}} \quad \underset{R^1}{\overset{\overset{\displaystyle O}{\parallel}}{\underset{\displaystyle R^\text{S}P-R^1}{}}} \tag{4}$$
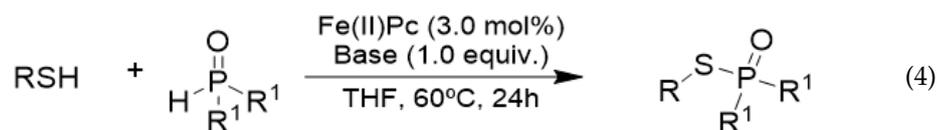
The cross-dehydrogenative coupling (CDC) of thiols with H-phosphonates (Equation (4)), mediated by the same catalyst, was performed at 60 °C in the presence of a base (e.g., NH$_3$; 1,8-diazabicyclo [5.4.0]undec-7-ene, DBU or diisopropylamine, DIPA). The best base for these cross-coupling reactions was DIPA (yields between 45 and 90%, Table 3) and the control experiments revealed that this oxidative coupling seems to follow the free radical pathway indicated in Figure 16 (Path A and B).

Table 3. Examples and scope of the **Fe(II)Pc** catalyzed cross-dehydrogenative coupling (CDC) reactions using DIPA as base [64].

| Entry	Mercaptan	H-Phosphonate/H-phosphine	Product	Isolated Yield (%)
1	PhSH	$H-P(=O)(OEt)_2$	PhS-P(=O)(OEt)$_2$	90
2	PhSH	$H-P(=O)(OMe)_2$	PhS-P(=O)(OMe)$_2$	73
3	PhSH	$H-P(=O)Ph_2$	PhS-P(=O)Ph$_2$	63
4	4-CH$_3$-C$_6$H$_4$-SH	$H-P(=O)(OEt)_2$	4-CH$_3$-C$_6$H$_4$-S-P(=O)(OEt)$_2$	88
5	4-F$_3$C-C$_6$H$_4$-SH	$H-P(=O)(OEt)_2$	4-F$_3$C-C$_6$H$_4$-S-P(=O)(OEt)$_2$	52
6	4-t-Bu-C$_6$H$_4$-SH	$H-P(=O)(OEt)_2$	4-t-Bu-C$_6$H$_4$-S-P(=O)(OEt)$_2$	57
7	2-CH$_3$-4-CH$_3$-C$_6$H$_3$-SH	$H-P(=O)(OEt)_2$	2-CH$_3$-4-CH$_3$-C$_6$H$_3$-S-P(=O)(OEt)$_2$	79
8	PhCH$_2$SH	$H-P(=O)(OEt)_2$	PhCH$_2$-S-P(=O)(OEt)$_2$	77
9	CH$_3$(CH$_2$)$_4$SH	$H-P(=O)(OEt)_2$	CH$_3$(CH$_2$)$_4$-S-P(=O)(OEt)$_2$	45
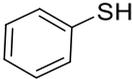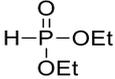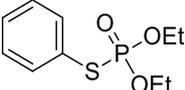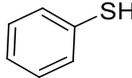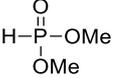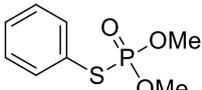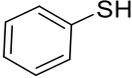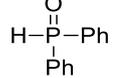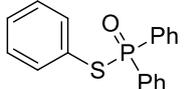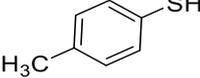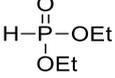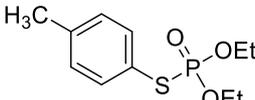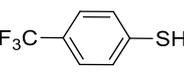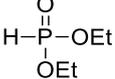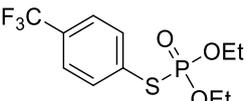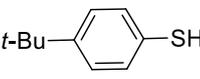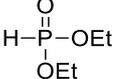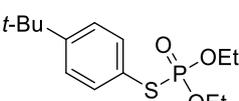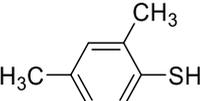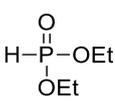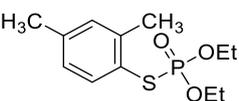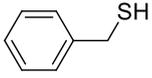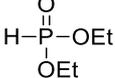
Figure 16. Proposed mechanism for cross-dehydrogenative coupling (CDC) of thiols with H-phosphonates and H-phoshine oxides (adapted from [64]).

Solid base catalysts obtained from the noncovalent attachment of the tetrasulfonated cobalt(II) phthalocyanine **Co(II)Pc(SO₃H)₄** to graphene oxide (GO) functionalized with different amines, namely propylamine (PA), butylamine (BA), ethylenediamine (EDA) and tetramethylenediamine (TMD) (Figure 17) were evaluated and compared in the oxidation of various thiols [65]. The catalytic performance in the oxidation of various thiols was evaluated in heptane without base addition. The catalytic efficiency was dependent on the functionalized amine GO (**Co(II)Pc@GOEDA** > **Co(II)Pc@GOTMD** > **Co(II)Pc@GOPA** > **Co(II)Pc@GOBA**) and the potentiality of the best material **Co(II)Pc@GOEDA** was investigated in the oxidation of thiols present in a real matrix like gasoline. The results were really promising with the removal of 96.6% of the thiols and after eight runs no significant change was observed in the **Co(II)Pc@GOEDA** activity used in real context.
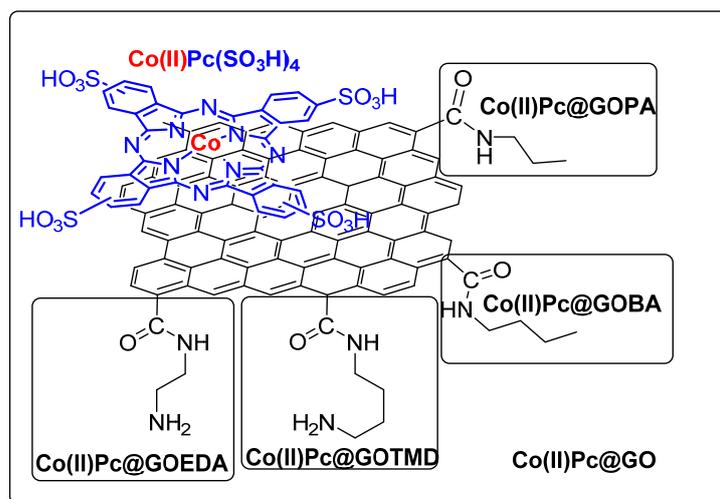
Figure 17. Schematic representation of Co(II) phthalocyanine **Co(II)Pc(SO₃H)₄** attached to graphene oxide (**GO**) functionalized with different amines: propylamine (**PA**), butylamine (**BA**), ethylenediamine (**EDA**) and tetramethylenediamine (**TMD**) (adapted from [65]).

Considering the importance of developing alternatives to the drastic conditions used in Merox® process (high pressure and temperature, presence of caustic soda), Omadoko and coworkers [66] found that Co(II) complex of the sodium salt of tetrasulfonated phthalocyanine (**Co(II)Pc(SO₃Na)₄**) (Figure 18) is able to fully oxidize ethanethiol to diethyl disulfide, under base free conditions, in O_2 saturated dimethylformamide (DMF) after 10 min at 40 °C with a turnover number (TON) of 72 and turnover frequency (TOF) of 8.1 min^{-1}.
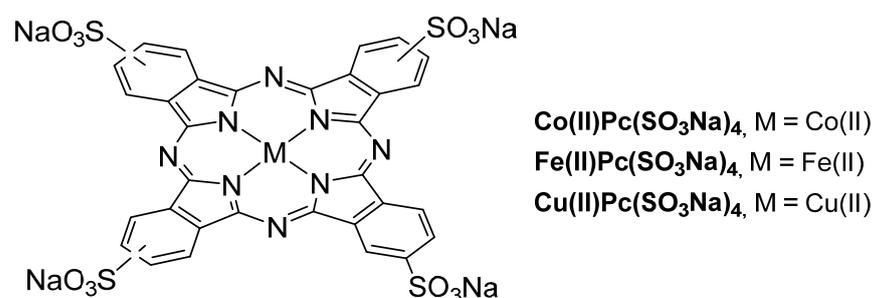
Figure 18. Structure of metallophthalocyanines **Co(II)Pc(SO₃Na)₄**, **Fe(II)Pc(SO₃Na)₄** and **Cu(II)Pc(SO₃Na)₄** used for ethanethiol oxidation. Adapted from [66].

In addition to **Co(II)Pc(SO₃Na)₄**, in this study the efficiency of the analogues **Fe(II)Pc(SO₃Na)₄** and **Cu(II)Pc(SO₃Na)₄** (Figure 18) and the non-substituted **Co(II)Pc** (Figure 2) were also evaluated. The results showed that **Cu(II)Pc(SO₃Na)₄** has no catalytic activity, while **Co(II)Pc(SO₃Na)₄**, had the highest turnover number (8.1 min^{-1}), followed by **Co(II)Pc** and **Fe(II)Pc(SO₃Na)₄**. These results demonstrated that the metal centers showed a higher impact on catalytic activity than peripheral substituents.

The monitorization of the reaction by UV-Vis spectroscopy suggested that the oxidation step occurs with both thiol units coordinated to the **M(II)Pc**, followed by the disulfide dissociation from the catalyst, mediated by DMF.

Another interesting contribution concerning the desulfurization of real fuel matrixes such as gasoline and diesel was reported in 2019 by Li and coworkers [67]. The authors found that the hybrid assembly constituted by the tetramer **(Co(II)Pc)₄** (Figure 19) and the polyoxometalate $(NH_4)_5H_6PV_8Mo_4O_{40}$ (**PMoV**) is an efficient hybrid to perform the oxidative desulfurization of model oils containing dibenzothiophene (DBT), 4,6-dimethyldibenzothiophene (4,6-DMDBT), benzothiophene (BT) and thiophene (T) to the sulphones under aerobic conditions. Conversions of almost 100% were found for DBT and 4,6-DMDBT and 97.6% for T with TOFs of 24.31, 48.89, 34.83, 23.77 h^{-1}, respectively. The solubility features of the hybrid assembly obtained by mixing both components, the **(Co(II)Pc)₄** and the polyoxometalate in THF showed to be dependent on the molar ratio used; a 1:7 ratio **(Co(II)Pc)₄:PMoV** gave rise to a solid insoluble in water and decaline **hybrid (I)**, while a ratio 4:1 **(Co(II)Pc)₄:PMoV** afforded a hybrid soluble in water **hybrid (II).** The efficiency of the **hybrid (I)** was maintained in the desulfurization of real matrix such as gasoline and diesel affording sulfur contents (2.73 and 8.01 ppm at 7 h, respectively) on line with the required European level of 10 ppm.
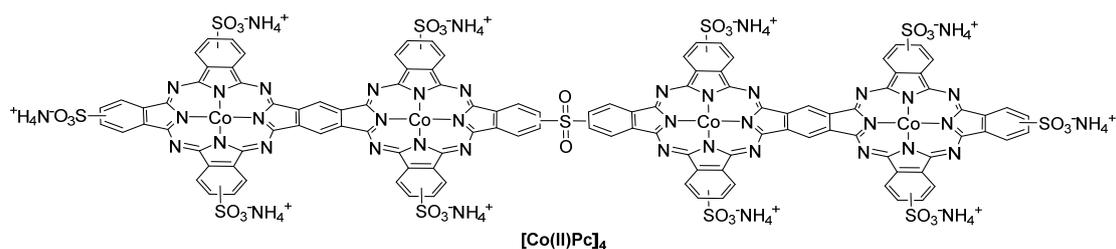
Figure 19. Co(II) phthalocyanine tetramer **(Co(II)Pc)₄** used for the preparation of organic-inorganic polyoxometalate (POM) **hybrids (I)** and **(II)** through controlling the molar ratio of precursors **((Co(II)Pc)₄:PMoV)** (adapted from [67]).

The stability of **hybrid (I)**, associated with the possibility of being reused, at least nine times in organic solvent or in aqueous solutions, without significant loss of activity and no leaching of active sites confirmed the heterogeneous features of the assembly. The authors pointed out that the collaboration of multiple active sites in one combined unit can achieve high efficiency in aerobic heterogeneous catalysis.

Under the context of thiol oxidation in fuels, Makarov, Wörhle, and coworkers [68] developed a catalyst with high catalytic activity and stability, based on a new binuclear Co(II) phthalocyanine **bisCo(II)Pc-2** with an extended π-system and functionalized with 2,6-dimethylphenoxy groups (Figure 20). For comparison, the study was extended to the mononuclear Co(II) phthalocyanine **Co(II)Pc-1** (Figure 20) also with electron donating phenoxy groups. The binuclear (**bisZn(II)Pc-2**) and mononuclear (**Zn(II)Pc-1**) Zn(II) phthalocyanine were also considered for these studies as redox-inactive complexes.

Co(II)Pc-1, M = Co(II)
Zn(II)Pc-1, M = Zn(II)

bisCo(II)Pc-2, M = Co(II)
bisZn(II)Pc-2, M = Zn(II)
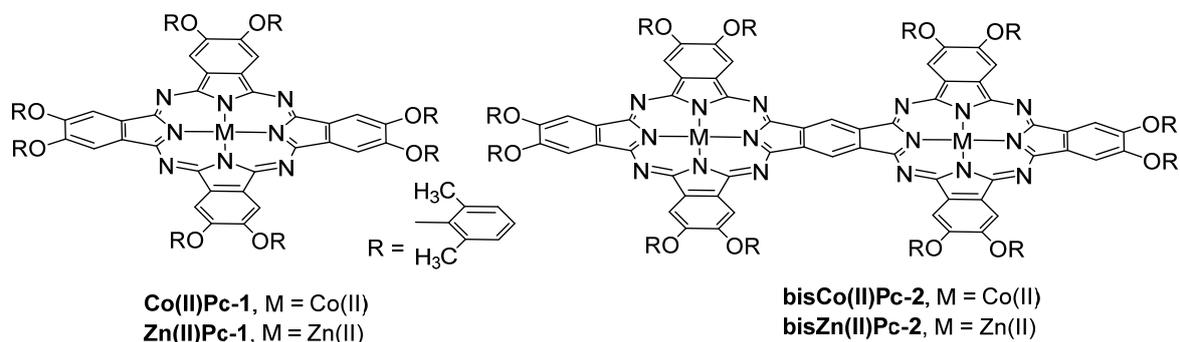
Figure 20. Structures of mononuclear Co(II) and Zn(II) phthalocyanines (**M(II)Pc-1**) and binuclear Co(II) and Zn(II) phthalocyanines (**bisM(II)Pc-2** (adapted from [68]).

The catalytic studies, using 2-mercaptoethanol (2-ME) as the substrate at 25 °C under O_2 demonstrated a remarkable increase in the efficiency of the oxidative process going from the mononuclear **Co(II)Pc-1** to the binuclear **bisCo(II)Pc-2** Co(II) phthalocyanine complexes; an extremely high value for TOF of ~9000 min^{-1} was provided by the binuclear complex **bisCo(II)Pc-2** versus 250 min^{-1} for the mononuclear **Co(II)Pc-1**. On the other hand, authors found negligible catalytic activities of **Zn(II)Pc-1** and **bisZn(II)Pc-2**. The result was expected since Zn(II) is a closed-shell transition metal. Considering the mechanism of thiol oxidation mediated by a mononuclear **Co(II)Pc-1** (Figure 20), an explanation for the high activity of the binuclear Co(II)-complex (**bisCo(II)Pc-2**) relies on a favorable electronic contact between the two cobalt centres through the extended π-electron system that facilitates the electron transfer from thiolate to oxygen.

3.2. Alkyl Arenes and Alcohols

The oxidation of alkyl arenes and alcohols to their corresponding carbonyl compounds is of significant importance in organic chemistry [69]. The manufacturing of bulk carbonyl compounds, such as benzoic acid, terephthalic acid, and isophthalic acid, comprises the aerobic oxidation of alkyl arenes and alcohols. These processes are usually conducted

under harsh reaction conditions: high temperatures (175–225 °C) and high air pressures (15–30 atm) in the presence of metal catalysts such as $Co(OAc)_2/Mn(OAc)_2$ and bromine, typically in the form of HBr, NaBr or tetrabromoethane in acetic acid [70].

Over the last years, research efforts have been devoted to the development of smooth oxidation reaction conditions. In this context, MPcs have emerged as an attractive and powerful alternative as efficient catalytic materials since they play a unique role in the catalytic activation of O_2 as was demonstrated above [7]. In addition, and as mentioned above, MPcs are remarkable versatile and robust compounds with improved thermal and chemical stability, which allied with the low cost and availability become their use very attractive [71].

Shaabani and coworkers [72] compared the efficiency of a series of MPc: **Co(II)Pc**, **Cu(II)Pc**, **Ni(II)Pc**, **Ru(II)Pc**, **Pd(II)Pc**, **Zn(II)Pc** (Figure 2), in the aerobic conversion of fluorene to 9-fluorenone and benzoin to benzil (Figure 21) in different ionic liquids (ILs). In both cases the best results were obtained with **Co(II)Pc** in the presence of 1-butyl-3-methylimidazolium bromide (bmim)Br but different temperatures were required; the optimal temperature for the oxidation of fluorenone was 100 °C (91% yield, 6 h of reaction) and for benzoin was 70 °C (92% yield, 1 h of reaction). The scope of this approach was extended to other primary and secondary benzylic hydrocarbons and alcohols affording the expected carbonyl products in excellent yields (between *ca.* 80 and 93%) confirming the versatility and the efficiency of the combination. under mild conditions. Interestingly, the oxidation of the primary alcohols gave rise to aldehydes and not to carboxylic acids. The study showed also that both the (bmim)Br and the **Co(II)Pc** could be reused at least six times in consecutive runs without affecting the yield of the products.
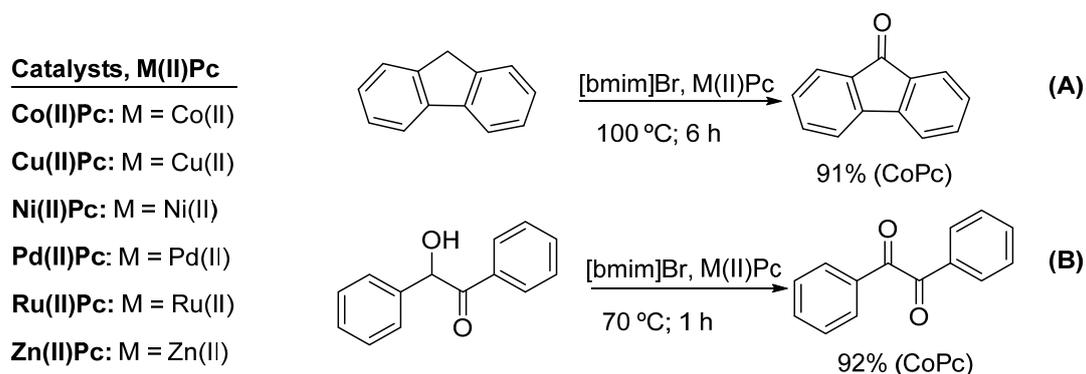
Figure 21. Metallophthalocyanine used for the aerobic oxidation of fluorene (**A**) and benzoin (**B**) in ionic liquids as solvent (adapted from [72]).

The authors suggest that the reaction occurs trough the removal of hydrogen from the carbon attached to the hydroxyl group in alcohols, and from the benzylic position in the alkyl arenes by the superoxocobalt(III) species as summarized in Figure 22.

The efficiency of the heterogeneous catalyst **Co(II)Pc(NH₂)₃NH@Cel** (Figure 23) obtained from cellulose and the cobalt(II) complex of the tetraaminophthalocyanine derivative **Co(II)Pc(NH₂)₄** was also considered by the same group [73] in the aerobic oxidation of alkyl arenes and alcohols.

The immobilization of **Co(II)Pc(NH₂)₄** via amino groups required the previous activation of the cellulose primary hydroxyl groups with tosyl chloride (TosCl) and a metallophthalocyanine loading of 0.36 wt% was attained. The oxidation of the alkyl arenes mediated by **Co(II)Pc(NH₂)₃NH@Cel** was performed in refluxing *o*-xylene under an O_2 atmosphere and in the presence of KOH and *N*-hydroxyphthalimide (NHPI). Under these conditions, the expected ketones were obtained in excellent yields (82 to 91%). The oxidation of aliphatic, aromatic and allylic primary and secondary alcohols was also performed in *o*-xylene but, in this case, at room temperature and in the absence of NHPI; the corresponding aldehydes and ketones were obtained in yields ranging from 78 to 90%. The

studies showed that the catalyst can be readily recovered from the reaction mixture and reused for several runs without a significant decrease in its catalytic activity.
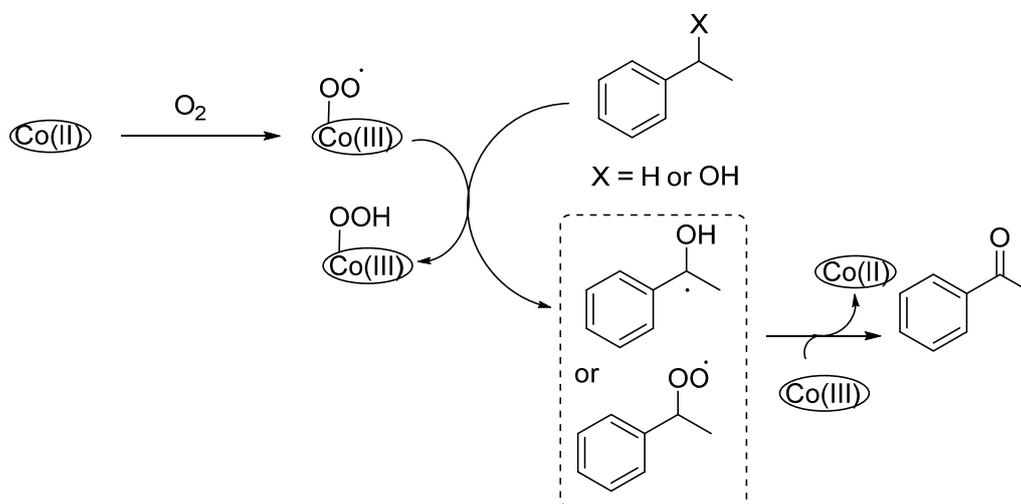

Figure 22. Proposed mechanism for akyl arenes and alcohols aerobic oxidation (adapted from [72]).
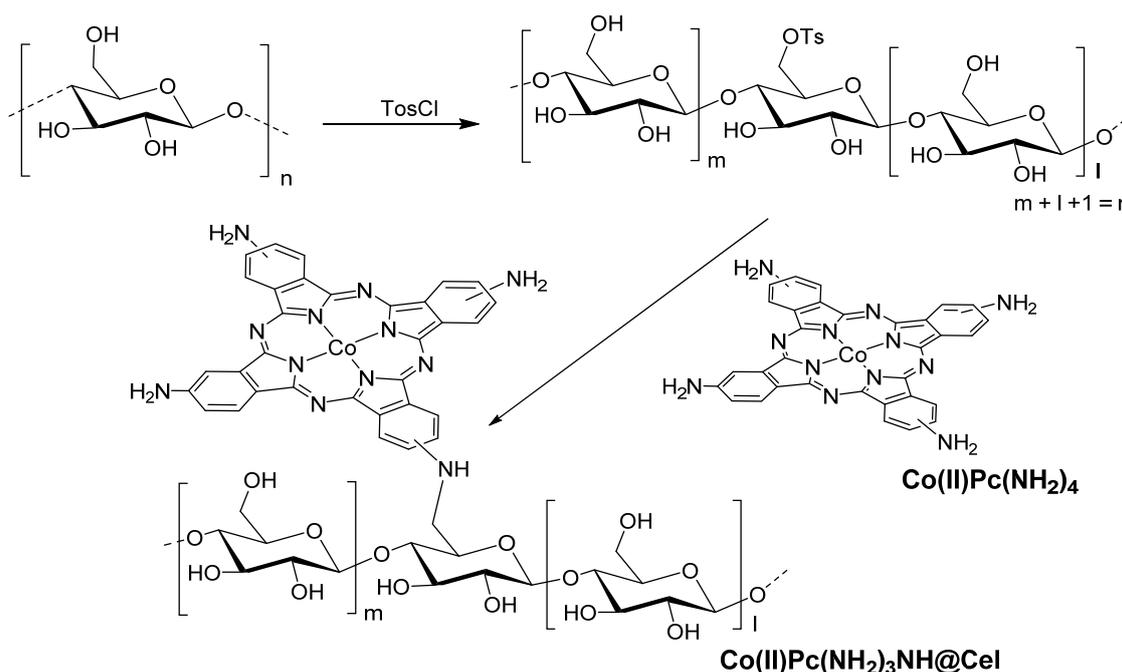

Figure 23. Synthetic methodology used to covalently graft the **Co(II)Pc(NH₂)₄** in tosyl chloride functionalized cellulose (adapted from [73]).

In the proposed mechanisms for such transformation (Figure 24) NHPI mediated the initial formation of radical (B) in the case of the alkyl arenes while in the case of the alcohols is the phthalocyanine superoxocobalt(III) intermediate (H) that is involved in the formation of radical (G). Then the benzylic radical (B) reacts with O_2 activated by CoPc affording the intermediate (C) that gave rise to the ketone after a hydrogen atom transfer and cleavage of the oxygen-oxygen bond. In the case of alcohols, the intermediates (G) and (I) formed give rise to the ketone (E) and H_2O_2.
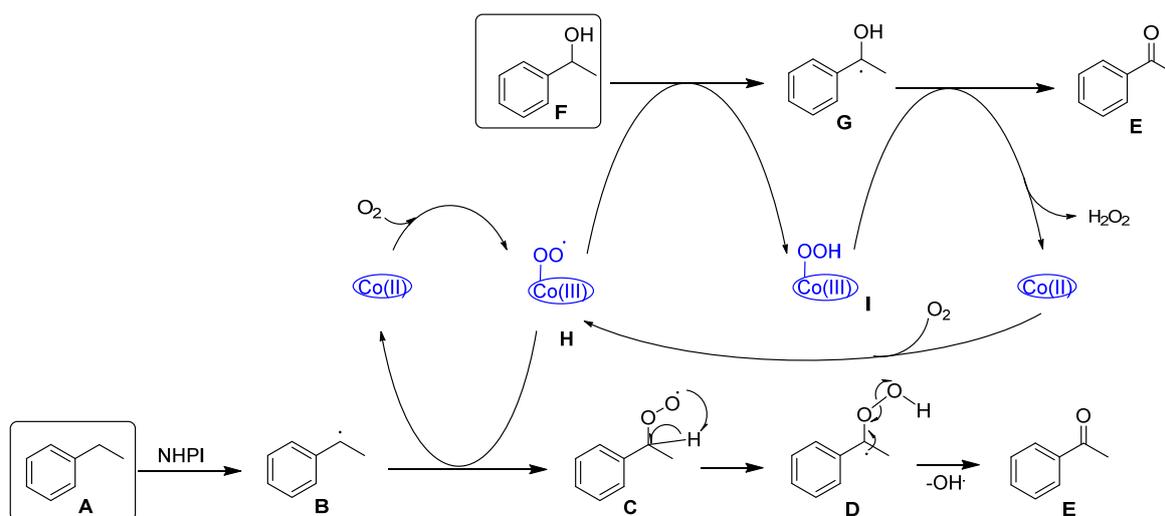
Figure 24. Proposed mechanism for akyl arenes and alcohols aerobic oxidation (adapted from [73]).

Shaabani group [74] evaluated the efficiency of the hybrid catalyst **Fe(II)Pc(NO$_2$)$_3$S@GO** (Figure 25) obtained from the iron phthalocyanine **Fe(II)Pc(NO$_2$)$_4$** and graphene oxide (GO) nanosheets in the aerobic oxidation of a series of alcohols. In the design of this heterogeneous catalyst the authors considered the nucleophilic substitution of one of the nitro groups in **Fe(II)Pc(NO$_2$)$_4$** by 3-(trimethoxysilyl)propane-1-thiol and then the covalent grafting of the resulting derivative to exfoliated graphene oxide sheets (GO) mediated by well-known hydroxyl–methoxysilane coupling reactions.

The catalyst containing 12% *w/w* of M(II)Pc immobilized in GO (**Fe(II)Pc(NO$_2$)$_3$S@GO**) was evaluated in the oxidation of benzyl alcohol into benzaldehyde (97% of conversion; selectivity > 99%) in water and at 60 °C throughout 3 h in the presence of 0.4 mmol% of the catalyst and 50 mmol% of K$_2$CO$_3$. High conversion (90–97%) and high selectivity (96–99%) towards the carbonyl compounds (aldehydes or ketones) were also attained when the scope of the reaction, under the same conditions, was extended to a variety of primary and secondary aliphatic and aromatic alcohols. Moreover, after six runs no significant loss of activity and selectivity was found for the **Fe(II)Pc(NO$_2$)$_3$S@GO** catalyst.
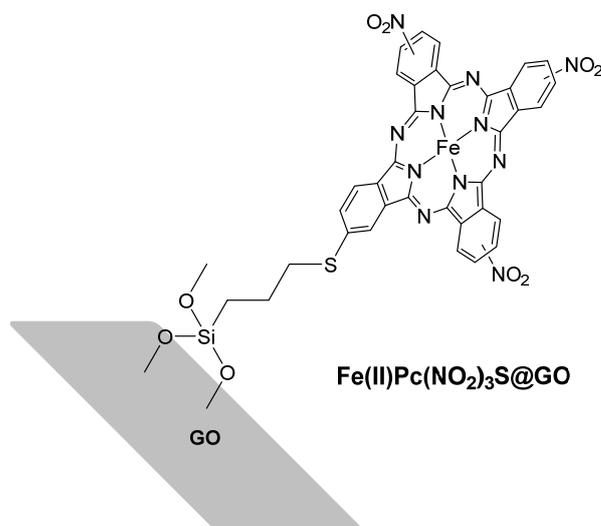
Figure 25. Schematic representation of the hybrid catalyst **Fe(II)Pc(NO$_2$)$_3$S@GO** obtained from the iron phthalocyanine FePc(NO$_2$)$_4$ and graphene oxide (GO) nanosheets (adapted from [74]).

Chauhan and Yan [75] reported the preparation and evaluation of an efficient catalyst, a copper tetrasulfonate phthalocyanine (tetrasodium salt) **Cu(II)Pc(SO₃Na)₄** immobilized through electrostatic interaction on a quaternary amine functionalized nanocrystalline cellulose (**NCCel**) (Figure 26).
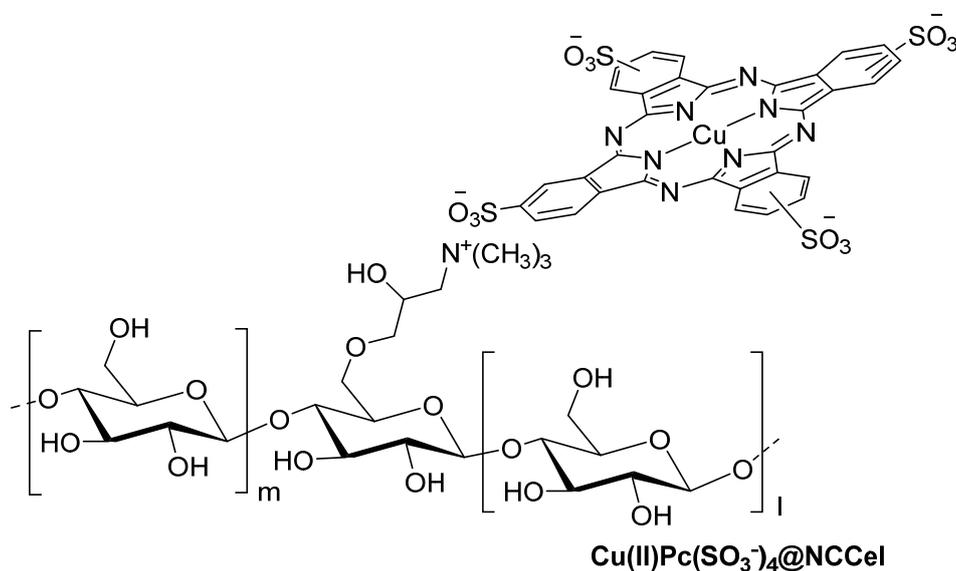
Figure 26. Graphical representation of the hybrid material **Cu(II)Pc(SO₃⁻)₄@NCCel** prepared trough electrostatic interaction of copper(II) tetrasulfonate phthalocyanine (tetrasodium salt) CuPc(SO₃Na)₄ on the quaternary amine functionalized nanocrystalline cellulose (NCC). (adapted from [75]).

The hybrid material **Cu(II)Pc(SO₃⁻)₄@NCCel** has been employed as catalyst in the aerobic oxidation of alcohols and alkyl arenes in water. Under optimal catalytic conditions (0.004 mol% Cu(II) content, at room temperature), conversions of 99% for benzyl alcohol and 92% for tetralin were attained with excellent selectivity in both cases (selectivity > 99%) for the expected carbonyl derivatives (benzaldehyde and tetralone). After 7 cycles, a minor decrease in product yield was observed, thus indicating high stability of the catalyst.

Jain and collaborators [76] selected polyaniline (PANI) to covalently graft the **Co(II)Pc (SO₂Cl)₄** catalyst through the activated sulfonyl chloride units (Figure 27) and the efficiency of the obtained hybrid **Co(II)Pc(SO₂Cl)₃SO₂@PANI** was assessed in the aerobic oxidation of alcohols.

The best performance for the oxidation of benzhydrol (diphenylmethanol), selected as the model substrate, was found in the assays taken in acetonitrile at 65 °C and in the presence isobutyraldehyde as sacrificial agent. After 3.5 h, benzophenone was obtained with the best yield (76%) and the best TOF (21.7 h⁻¹). This efficiency was maintained or even increased when the reaction scope was enlarged to the oxidation of a variety of primary and secondary alcohols (e.g., furfuryl alcohol, cyclohexanol, benzyl alcohol substituted with electron-donating or electron-withdrawing substituents, 1-phenylethanol, octan-1-ol), selectively affording the corresponding carbonyl compounds in good yields (72–88%) without any overoxidation product. The catalyst was found to be highly stable and could be reused for several runs (six times) without any significant loss in its catalytic activity.
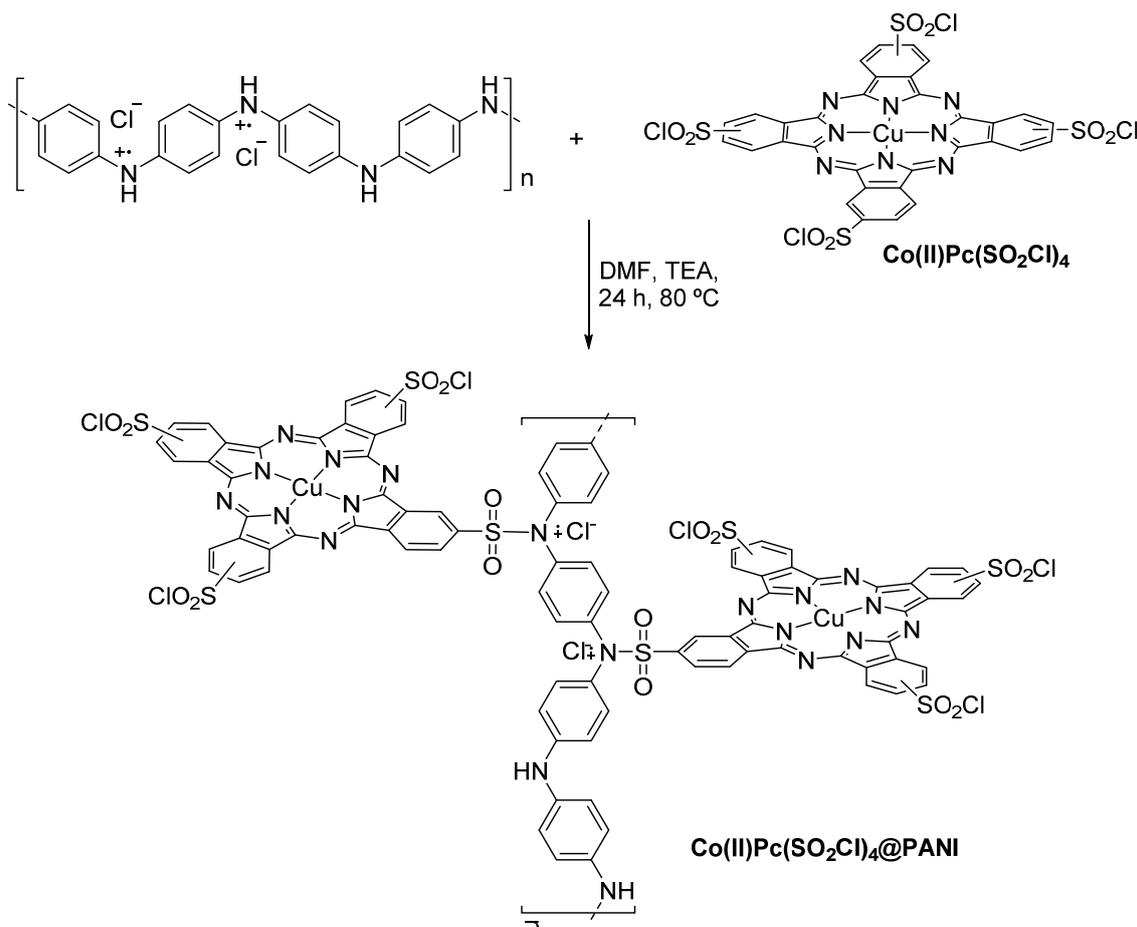
Figure 27. Structure and synthetic pathway to **Co(II)Pc(SO₂Cl)₃SO₂@PANI** adapted from [76]).

The heterogeneous catalyst **Fe(II)Pc(CO₂H)₃CONH@NH₂SBA-15** (Figure 28), obtained by coupling the Fe(II) tetracarboxyphthalocyanine **Fe(II)Pc(CO₂H)₄** with amino-functionalized SBA-15 (**NH₂-SBA-15**), was developed by the Liu and Zhu research group [77] in order to evaluate its eficiency in toluene oxidation assisted by dioxygen and *N*-hydroxyphthalimide (NHPI). APTES was used to introduce the amino functions onto the support surface before the coupling with **Fe(II)Pc(CO₂H)₄**. Further insights on the relationship between catalytic selectivity and catalyst composition have been assessed by preparing catalysts with different amounts of **Fe(II)Pc(CO₂H)₄** supported on **NH₂-SBA-15**. The study disclosed that toluene conversion in the oxidative process mediated by the catalyst with the highest **Fe(II)Pc(CO₂H)₄** load (20 wt% on **Fe(II)Pc(CO₂H)₃CONH@NH₂SBA-15**) attained a maximum of 35.3% with a selectivity of 71.8% for benzoic acid, whereas with the catalyst with lower MPc content (11 wt%) the toluene conversion attained 23.7 with 56.4% selectivity for benzaldehyde. The authors stated that the catalytic system is suitable for oxidizing both electron-donating and electron-withdrawing substituted toluene derivatives and no significant loss of catalytic activity and selectivity was observed during the reusability and recyclability assays.
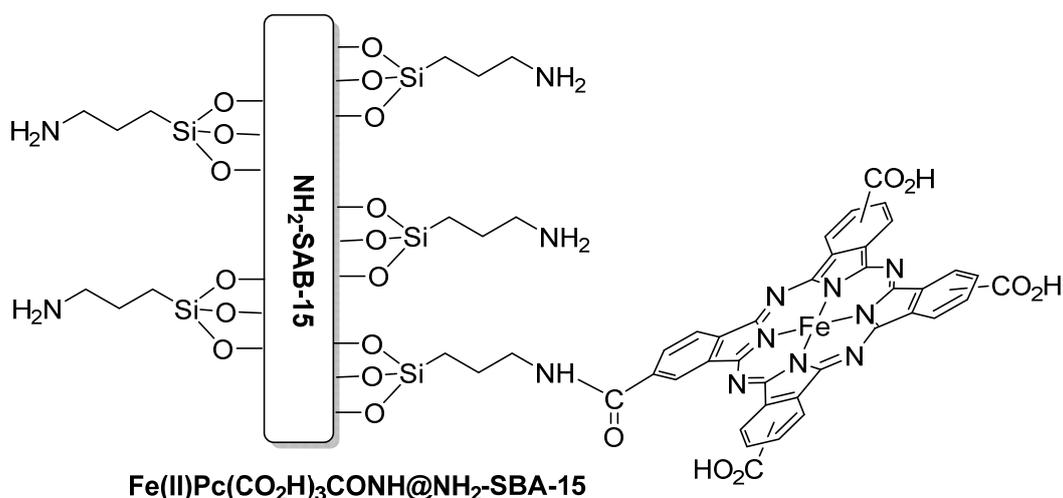
Figure 28. Schematic representation of iron(II) tetracarboxylphthalocyanine **Fe(II)Pc(CO$_2$H)$_4$** grafted onto amino-functionalized SBA-15 (**NH$_2$-SBA-15**) (adapted from [77]).

The importance of developing sustainable conditions to obtain the 2-nitro-4-methylsulf onylbenzoic acid (NMSBA), a key intermediate in the synthesis of the cornfield herbicide mesotrione, prompted Liu and Zhu [78] to evaluate the efficiency of the Fe(II) and Cu(II) complexes of phthalocyanine, **Fe(II)Pc** and **Cu(II)Pc** (Figure 2) in the aerobic oxidation of the precursor 2-nitro-4-methylsulfonyltoluene (NMST) (Figure 29).

The efficiency of the catalysts was evaluated first by using toluene derivatives with electron-withdrawing substituents in the presence of air or oxygen and the results showed that the highest yields were obtained under pure oxygen. The results showed that the catalytic activity in the oxidation of NMST was greatly affected by phthalocyanine metal ion, reaction time, reaction temperature, oxygen pressure and concentrations of phthalocyanine and NaOH. The best performance (NMSBA yield up to 53%; 89.3% of NMST conversion; 8 h of reaction) was found in the reactions carried out in methanol, at 55 °C, in the presence of the Fe(II) phthalocyanine (1.0×10^{-4} mol L^{-1}), O$_2$ atmosphere (2.0 MPa) and NaOH (0.6 mol L^{-1}). A plausible mechanism for this catalytic process was proposed, which involved deprotonation and radical pathways.
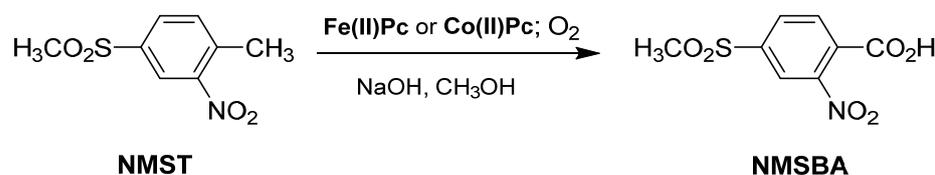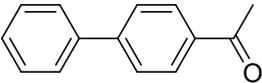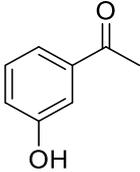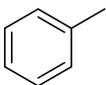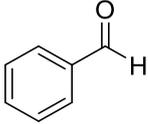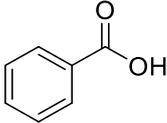

Figure 29. Cobalt(II) and iron(II) phthalocyanines used for the catalytic oxidation of 2-nitro-4-methylsulfonyltoluene (NMST) into the 2-nitro-4-methylsulfonylbenzoic acid (NMSBA) (adapted from [78]).

Chen and collaborators [79] found that the hybrid materials **M(II)Pc(SO$_3^-$)$_4$@-Zn$_2$Al-LDH** (M = Co(II), Cu(II), Mn(II), and Fe(II)), obtained from the coprecipitation method of the metal complexes of the anionic tetrasulfonic phthalocyanine M(II)Pc(SO$_3$H)$_4$ (Figure 17) with zinc and aluminum layered double hydroxides (LDHs) showed an excellent catalytic performance in the oxidation of different olefins in the presence of O$_2$/isobutyraldehyde, IBA [80] and are also efficient catalysts for the selective oxidation of ethylbenzene to acetophenone in the presence of O$_2$/NHPI (*N*-hydroxyphthalimide), using benzonitrile as solvent at 120 °C. The best results were observed for the hybrid M = Co(II) (90% of conversion and selectivity higher than 99%) with no appreciable reduction on its activity or selectivity even after five runs. Under the optimized reaction conditions, **M(II)Pc(SO$_3^-$)$_4$@-Zn$_2$Al-LDH** was also able

to catalyze the aerobic oxidation of other alkyl arenes (Table 4) and a series of controlled experiments suggested that a synergistic effect might exist between the basicity of the support and the activity of M(II)Pc during the oxidation.

Table 4. Catalytic oxidation of different substrates using **Co(II)Pc(SO$_3^-$)$_4$@-Zn$_2$Al-LDH** as catalyst [79] *.

| Entry	Substrate	Product	Conversion (%)	Selectivity (%)
1	R = OMe, Br, NO$_2$ or NH$_2$	R = OMe, Br, NO$_2$ or NH$_2$	92 (R = OMe) 76 (R = Br) 55 (R = NO$_2$) 0 (R = NH$_2$)	99 (R = OMe) 99 (R = Br) 99 (R = NO$_2$) - (R = NH$_2$)
2			82	99
3			80	99
4			79	99
5			90	99
6			86	99
7			0	-
8			48	15 85

* Reaction conditions: substrate 2 mmol; NHPI 0.4 mmol; CoPcTs-Zn$_2$Al-LDH 30mg; benzonitrile 6 mL; O$_2$ 10 mL/min; reaction time 12 h; temperature 20 °C.

Based on the obtained results a possible mechanism for the oxidation of ethylbenzene in the presence of O_2/NHPI has been proposed (Figure 30). It was suggested that phthalimido-*N*-oxyl radical (PINO) generated from NHPI through the catalytic action of **Co(II)Pc(SO$_3^-$)$_4$@-Zn$_2$Al-LDH**, or through autoxidation, promotes the formation of the benzylic radical that, after reaction with O_2, affords the acylperoxy radical. This acylperoxy radical can abstract hydrogen from ethylbenzene or NHPI leading to the hydroperoxide, which can be decomposed in acetophenone and 1-phenylethanol by **Co(II)Pc(SO$_3^-$)$_4$@-Zn$_2$Al-LDH**.
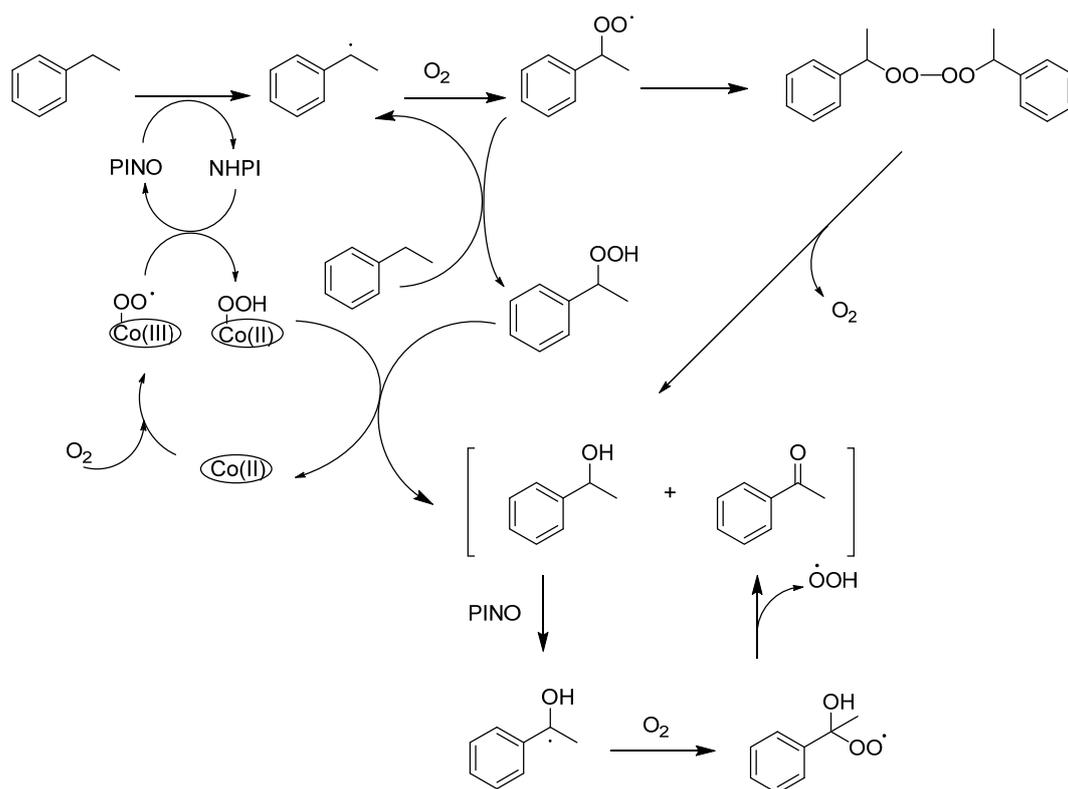

Figure 30. Proposed mechanism for ethylbenzene oxidation catalyzed by **Co(II)Pc(SO$_3^-$)$_4$@-Zn$_2$Al-LDH** in the presence of O_2/NHPI (adapted from [79]).

Shaabani, Amini and coworkers [81] studied the efficiency of the metal–organic framework (MOF)**MIL-101(Cr)-NH$_2$** decorated with a Co(II) phthalocyanine, **Co(II)Pc(CO$_2$H)$_4$** to catalyze the one-pot tandem oxidative A^3 coupling reactions of alcohols (through the aldehyde intermediates) with amines and alkynes (Figure 31). The covalent immobilization of **Co(II)Pc(CO$_2$H)$_4$** in **MIL-101(Cr)-NH$_2$** mediated by amide bonds was performed after activation of the carboxylic acid groups as acyl chlorides. An optimization of the reaction conditions using the tandem oxidative reaction between benzyl alcohol (**1**), piperidine (**3**), and phenylacetylene (**4**) (40 mg of **Co(II)Pc(CONH)$_4$@MIL-101**, 10 mol% of KOH, 80 °C, 8 h, and toluene as solvent) afforded the expected propargylamine (**5**) in 91% yield. The high efficiency of the approach was maintained when other benzyl alcohols (R = Cl; Me; MeO; NO$_2$), different secondary amines (morpholine or pyrrolidine), and another arylacetylene (R'' = Me) were used (yields between 83 and 93%). The reusability of **Co(II)Pc(CONH)$_4$@MIL-101** was investigated and the recycled catalyst was efficiently used in five consecutive cycles without significant loss of catalytic activity.
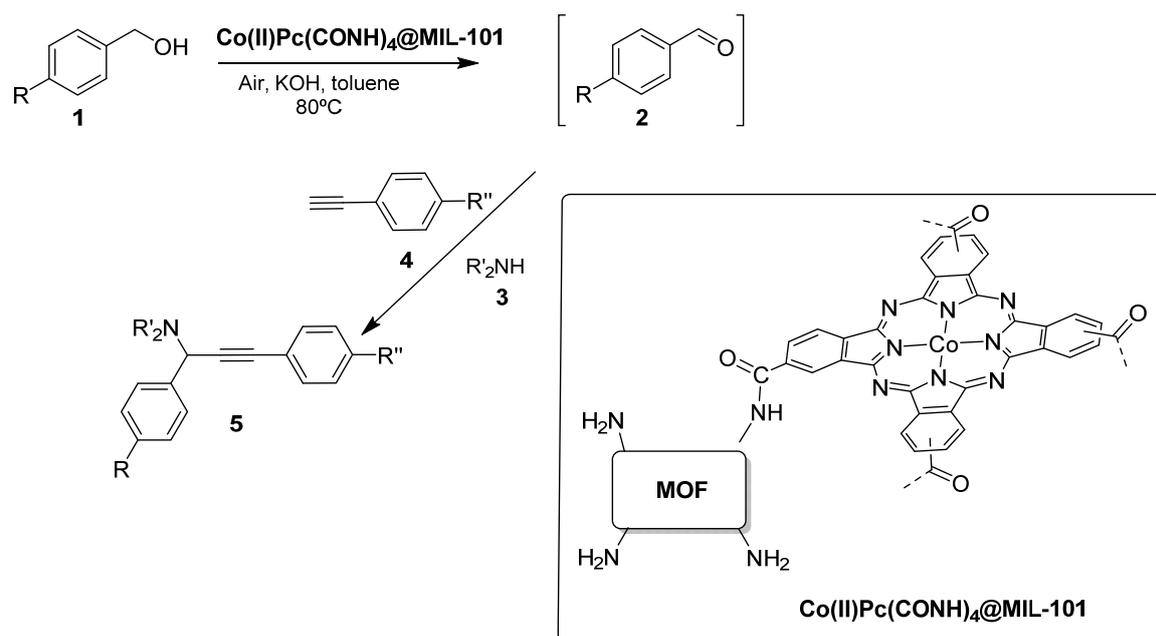
Figure 31. Synthesis of propargylamines via tandem oxidative A3 coupling reaction of benzyl alcohols using **Co(II)Pc(CONH)4@MIL-101** (adapted from [81]).

The possibility of NHPI to replace isobutyraldehyde, benzaldehyde, or *t*-butylhydroperoxide as co-oxidant in aerobic oxidation reactions catalyzed by MPc prompted Sun and collaborators [82] to test the Co(II) tetraamide phthalocyanine **Co(II)Pc(CONH₂)₄** (Figure 32) efficiency in the oxidation of hydrocarbons and alcohols with O_2, in the presence of NHPI. The optimization of the reaction parameters with α-methylstyrene (affording acetophenone by C-C double bond cleavage) allowed the establishment of a synergistic catalytic system based on NHPI (20 mol%) and **Co(II)Pc(CONH₂)₄** (8 mol%) to perform the aerobic oxidation of alcohols and α-alkylaryl groups in acetonitrile (15 mL) at 75 °C under O_2 (1 atm) for 24 h. This study reported also the use of the catalytic system in the oxidation of other substrates (alkyl arenes and alcohols) affording the carbonyl (or carboxylic) products with reasonable to very high yields.
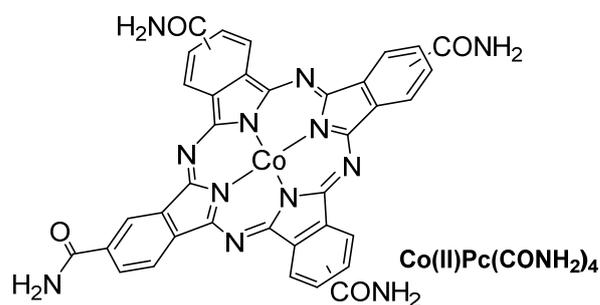

Figure 32. Co(II) tetraamide phthalocyanine **Co(II)Pc(CONH₂)₄** (adapted from [82]).
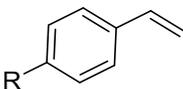
3.3. Olefins

The oxidation of olefins is of considerable interest in industrial organic synthesis, because derivatives containing an oxygen substituent are highly valuable as synthetic intermediates in bulk industrial processes or as crucial intermediates in the synthesis of fine chemicals. Selective oxidation of double bonds provides epoxides and diols, whereas the oxidation of allylic positions leads to the formation of allylic alcohols and ketones. Thus, the development of effective methods for the selective oxidation of olefins has drawn much attention over the years.

Considering that inexpensive and robust layered double hydroxides (LDHs) He, Xu and coworkers [80] extended the study of the hybrid materials **M(II)Pc(SO$_3^-$)$_4$@-Zn$_2$Al-LDH** based on the intercalation of the anionic **M(II)Pc(SO$_3$H)$_4$** coordinated with Co, Cu, Mn, and Fe into **Zn$_2$Al-LDH**. The catalytic activity of these hybrids (**M(II)Pc(SO$_3^-$)$_4$@-Zn$_2$Al-LDH**) was initially evaluated in the aerobic epoxidation of styrene in the presence of isobutyraldehyde (IBA). After a systematic evaluation of the reaction conditions, it was found that the hybrid based on the Co(II) complex also gave the highest yield of styrene oxide (Table 5), followed by Cu(II) > Mn(II) > Fe(II). The authors related this order with the redox potentials of the MPc and with the different accelerating activity in the production of the isobutyryl radical (Figure 33). Extra experiments allowed to conclude that the predominant pathway to the formation of styrene oxide (acylperoxy radical vs. peroxyacid) is radical (a) (Figure 33).
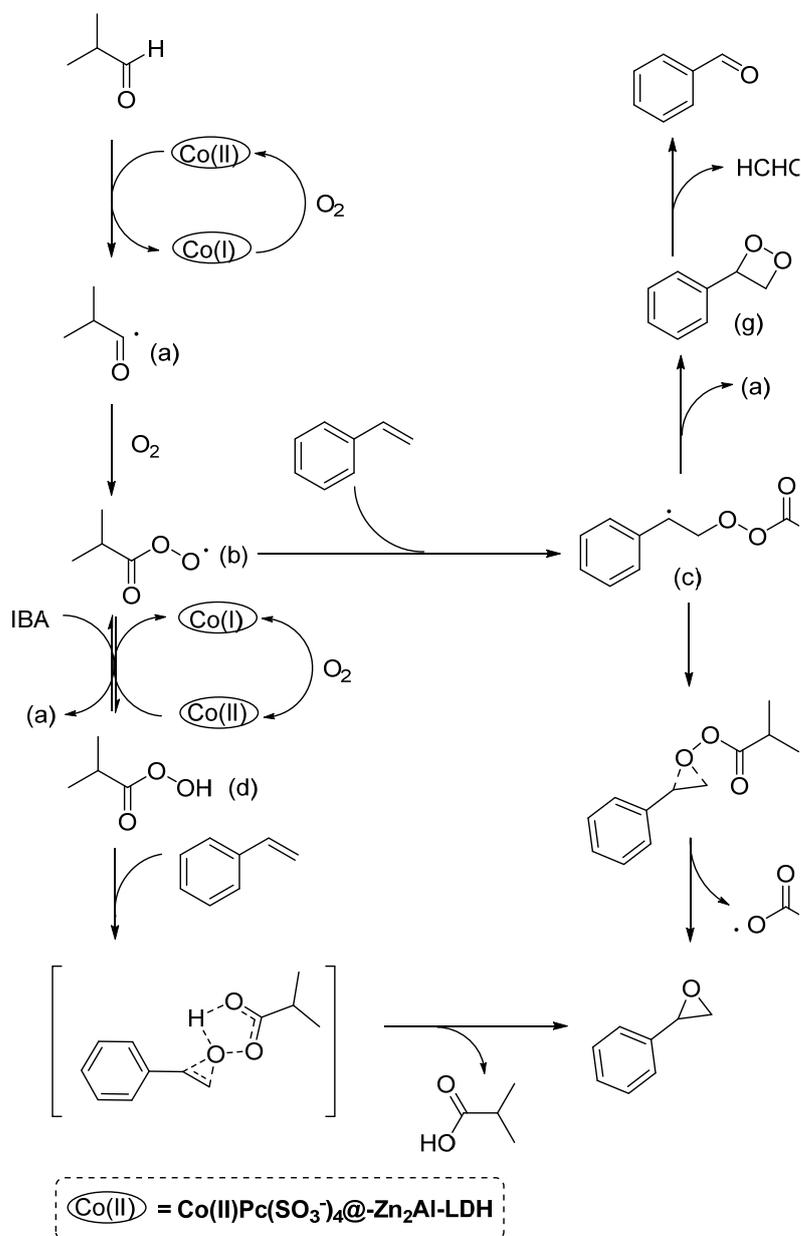
Figure 33. Proposed mechanism for the epoxidation of styrene over **Co(II)Pc(SO$_3^-$)$_4$@-Zn$_2$Al-LDH** in the presence O$_2$/IBA (adapted from [80]).

Table 5. Epoxidation of different olefins using **Co(II)Pc(SO$_3$$^-$)$_4$@-Zn$_2$Al-LDH** as catalyst [78] *.

Entry	Substrate	Product	Rection Time (h)	Conv. (%)	Yield (%)
1	R = H, CH$_3$ or F	R = H, CH$_3$ or F	1.5 1.5 2	100 (R = H) 100 (R = CH$_3$) 98 (R = F)	90 (R = H) 82 (R = CH$_3$) 85 (R = F)
2			2	100	81
3			2	98	89
4			2	98	99
5			2	99	99
6	n = 2 or 4	n = 2 or 4	2 4	98 (*n* = 2) 86 (*n* = 4)	99 (*n* = 2) 99 (*n* = 4)
7			2	100	82
8			2	99	90
9			4	58	98
10			1,5	100	99

* Reaction conditions: substrate 2 mmol; catalyst 6 mg; IBA 5 mmol; acetonitrile 8 mL; O$_2$ 15 mL/min; temperature 60 °C.

After the formation of isobutyryl radical (a) from isobutyraldehyde, mediated by **Co(II)Pc(SO$_3$$^-$)$_4$@-Zn$_2$Al-LDH** or through autoxidation, this species reacts with O$_2$ affording acylperoxy radical (b). This radical can then react with styrene, thus affording the epoxide or benzaldehyde, this one through the dioxetane intermediate (g). Additionally, radical (b) can abstract a hydrogen from IBA leading to the peroxyacid (d), that after reaction with styrene affords the epoxide. Other assays allowed to conclude that the active site for the epoxidation are the Co(II)Pc molecules in the interlayer of the hybrid and the basicity of the intercalated LDHs is an important feature to improve epoxide selectivity by restraining the transformation of radical (c) into the dioxetane (g) (Figure 33). These
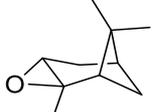
studies were extended to other olefins (Table 5), demonstrating that **Co(II)Pc(SO$_3^-$)$_4$@-Zn$_2$Al-LDH** in the presence of O$_2$/IBA is an excellent bifunctional catalyst to selectively epoxidize alkenes.

Inspired on Wacker-type processes, Knölker and Puls [83] reported a simple procedure for the oxidation of olefins into ketones under mild reaction conditions using an iron phthalocyanine complex. In the optimization of the reaction conditions using 2-vinylnaphthalene as model substrate (Figure 34), the authors found that the best achievements (2-acetonaphthone in 82% yield after 6 h of reaction) were obtained in reactions mediated by the already studied **Fe(II)PcF$_{16}$** (Figure 11). These reactions, in the presence of O$_2$ and using triethylsilane (Et$_3$SiH) as additive, were performed in ethanol, at room temperature. Reactions in solvents other than ethanol (methanol, isopropanol, 2,2,2-trifluoroethanol, dichloromethane, diethylether, tetrahydrofuran, diglyme, acetone, acetonitrile) gave lower yields.

The scope of this iron-catalyzed Wacker-type oxidation was evaluated using other substituted styrene derivatives, which provided the corresponding ketones in yields ranging from 65 to 95%, confirming the high functional group tolerance of this approach. However, the oxidation of aliphatic olefins was found to be more problematic, since the oxidation of octadec-1-ene with 10 mol% of **Fe(II)PcF$_{16}$,** 6 equiv. of PMHS (poly(methylhydrosiloxane)) in ethanol afforded octadecan-2-one in only 30% yield after four days of reaction at reflux.


Figure 34. Fe(II) complex of the hexadecafluorinated phthalocyanine (Fe(II)PcF$_{16}$) used as catalyst in the oxidation of 2-vinylnaphthalene as model substrate (adapted from [83]).

3.4. Miscellaneous Substrates

Recently, Castro at al [84] reported the preparation of a Pc coordination polymer, **Cu(II)Pc(SPyCu)$_4$**, and its corresponding homogeneous precursor **Cu(II)Pc(SPy)$_4$** (Figure 35), which were used as catalysts in the aerobic oxidation of 3,5-di-*tert*-butylcatechol (3,5-DTBC) into 3,5-di-*tert*-butyl-*o*-benzoquinone (3,5-DTBQ), using dioxygen from air, in the absence or in the presence of hydrogen peroxide. Parameters such as reaction time, pH, oxidant, and catalyst amount have been studied in the catechol oxidase-like activity of both systems. The best performance (82.2% conversion) of **Cu(II)Pc(SPyCu)$_4$** vs. **Cu(II)Pc(SPy)$_4$** was justified considering that the supramolecular structure is able to minimize the aggregation and the autooxidative degradation of the catalyst, both common in homogeneous catalysts based on Pcs. The turnover rate estimated for **Cu(II)Pc(SPyCu)$_4$** (27.5 h^{-1}) is almost seven times higher than that observed for **Cu(II)Pc(SPy)$_4$** (4.2 h^{-1}) in the presence of H$_2$O$_2$. The activity of the new material was maintained nearly unchanged during four catalytic cycles, an important feature for future applications.

An oxidative system based on heterogeneous *N*-heterocyclic carbene (NHC) catalysis, which is composed by a polystyrene-supported triazolium pre-catalyst (using DBU (50 mol%) as the optimal base to produce the carbene species), Fe(II) phthalocyanine (**Fe(II)Pc**, Figure 2) and air as the terminal oxidant was described by Massi and collaborators [85] for the selective conversion of 5-hydroxymethylfurfural (HMF) into the added-value 5-hydroxymethyl-2-furancarboxylic acid (HMFCA). The reported one-pot two-step procedure involves sequential oxidative esterification of HMF to produce a polyester oligomer, at room temperature, possessing both hydroxyl and carboxyl terminal groups. The **Fe(II)Pc** is able to mediate the aerobic oxidative esterification of HMF, the polyester being hydrolyzed in the presence of a ionic supported base to give HMFCA in 87% overall yield. The same strategy was adopted for the effective synthesis of ester and amide deriva-

tives of HMFCA by nucleophilic depolymerization of the oligomeric intermediate with methanol and butylamine, respectively. Moreover, the utilization of this oxidative system for the direct conversion of HMF and furfural into their corresponding ester, amide, and thioester derivatives was also reported.
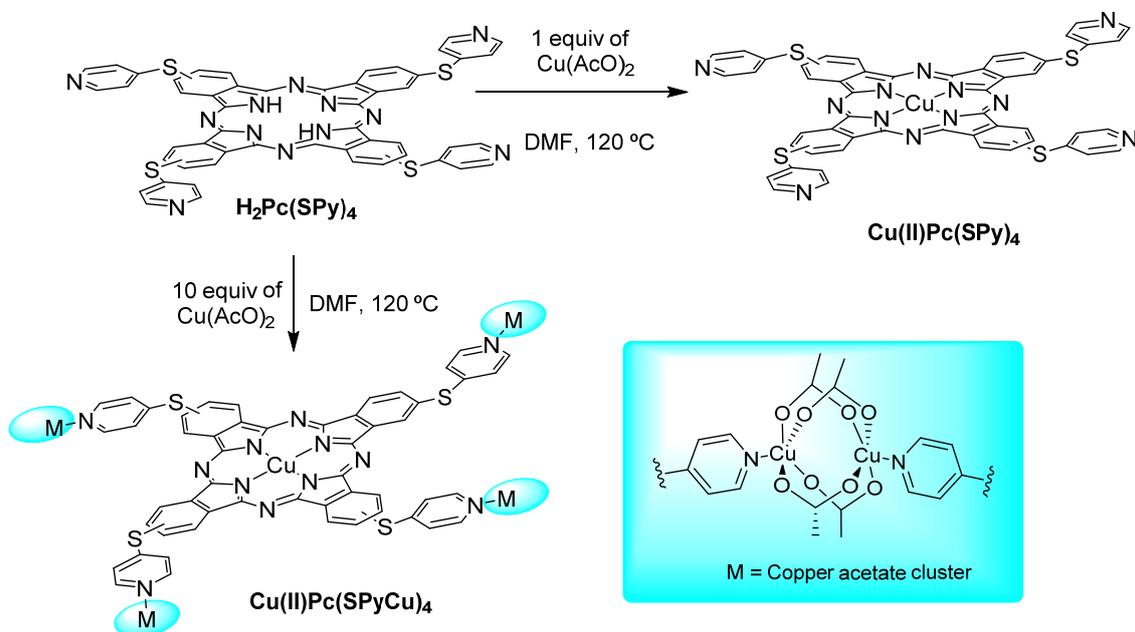
Figure 35. Schematic synthetic pathway to obtain the metallophthalocyanine **Cu(II)Pc(SPy)₄** and the **Cu(II)Pc(SPyCu)₄** polymeric material, starting from **H₂Pc(SPy)₄** (adapted from [84]).

4. Conclusions

Since the serendipitous discovery of Pcs, at the beginning of the 20th century, a growing attention has been devoted to the ubiquitous catalytic properties and applications of Pcs and Pcs coordinated with metal ions, MPcs. In fact, these old synthetic dyes have been very attractive in the view of academic research, but mainly for industrial purposes as these dyes are easily accessible on a large scale, are robust under harsh reaction conditions, show high activity and can be recovered and recycled.

In this mini-review, we have provided the progresses, mainly gathered in the last decade, made with Pc complexes with transition metals as catalysts in the aerobic oxidation of thiols and thiophenes, and on the production of added-value fine chemicals resulting from the oxidation of alkyl arenes, alcohols, and olefins, among others. The success and diversity of MPcs as catalysts over different substrates is mostly attributed to their high structural flexibility in terms of metals and electronic properties of the phthalocyanine ligands. For each substrate and each catalyst, a careful evaluation of the reaction conditions is required for the best achievements. Sustained research efforts on the synthesis, and new insights on the understanding of MPcs reaction mechanisms should provide a great variety of novel and featured MPcs complexes with diverse properties, paving the way for new applications as selective and environmentally friendly catalysts for oxidation reactions.

Author Contributions: Conceptualization: M.M.Q.S. and E.S.; writing—original draft preparation: C.J.P.M., M.M.Q.S. and E.S.; writing—review and editing: M.A.F.F., M.M.Q.S. and M.d.G.P.M.S.N.; supervision: M.M.Q.S. and M.d.G.P.M.S.N. All authors have read and agreed to the published version of the manuscript.

Institutional Review Board Statement: Not applicable.

References

1. Braun, A.; Tcherniac, J. Über die Produkte der Einwirkung von Acetanhydrid auf Phthalamid. *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 2709–2714. [CrossRef]
2. Linstead, R.P.; Lowe, A.R. Phthalocyanines part III Preliminary experiments on the preparation of phthalocyanines from phthalonitrile. *J. Chem. Soc.* **1934**, 1022–1027. [CrossRef]
3. Robertson, J.M.; Woodward, I. 37. An X-ray study of the phthalocyanines. Part III. Quantitative structure determination of nickel phthalocyanine. *J. Chem. Soc.* **1937**, *10*, 219–230. [CrossRef]
4. Moser, F.H.; Thomas, A.L. Phthalocyanine compounds. *J. Chem. Educ.* **1964**, *41*, 245. [CrossRef]
5. Claessens, C.G.; Hahn, U.; Torres, T. Phthalocyanines: From outstanding electronic properties to emerging applications. *Chem. Rec.* **2008**, *8*, 75–97. [CrossRef] [PubMed]
6. Gobo, N.R.S.; Brocksom, T.J.; de Oliveira, K.T. Soluble and Non-Aggregated Phthalocyanines: Synthesis, Mechanistic Aspects and Their Main Building Blocks. *Curr. Org. Synth.* **2017**, *14*, 1132–1155. [CrossRef]
7. Sorokin, A.B. Phthalocyanine Metal Complexes in Catalysis. *Chem. Rev.* **2013**, *113*, 8152–8191. [CrossRef] [PubMed]
8. Ferraudi, G.; Lappin, A.G. Review: Properties chemical reactivity of metallo phthalocyanine and tetramethylbenzoannulene complexes grafted into a polymer. *J. Coord. Chem.* **2014**, *67*, 3822–3839. [CrossRef]
9. Stillman, M.J.; Nyokong, T. Absorption and Magnetic Circular Dichroism Spectral Properties of Phthalocyanines Part 1: Complexes of the Dianion Pc(–2). In *Phthalocyanines-Properties and Applications*; Leznoff, C.C., Lever, A.B.P., Eds.; VCH Publishers, Inc.: New York, NY, USA, 1989; Volume 1, pp. 133–290.
10. Fitzgerald, J.P.; Haggerty, B.S.; Rheingold, A.L.; May, L.; Brewer, G.A. Iron Octaethyltetraazaporphyrins: Synthesis, Characterization, Coordination Chemistry, and Comparisons to Related Iron Porphyrins and Phthalocyanines. *Inorg. Chem.* **1992**, *31*, 2006–2013. [CrossRef]
11. Koczorowski, T.; Szczolko, W.; Goslinski, T. Physicochemical Properties and Catalytic Applications of Iron Porphyrazines and Phthalocyanines. In *Recent Progress in Organometallic Chemistry-IntechOpen*; Rahman, M.M., Asiri, A.M., Eds.; IntechOpen Limited: London, UK, 2017. [CrossRef]
12. Nemykin, V.N.; Lukyanets, E.A. Synthesis of substituted phthalocyanines. *Arkivoc* **2010**, *1*, 136–208. [CrossRef]
13. Ghani, F.; Kristen, J.; Riegler, H. Solubility Properties of Unsubstituted Metal Phthalocyanines in Different Types of Solvents. *J. Chem. Eng. Data* **2012**, *57*, 439–449. [CrossRef]
14. Boucher, L.J. Metal Complexes of Phthalocyanines. In *Coordination Chemistry of Macrocyclic Compounds*; Melson, G.A., Ed.; Springer: Boston, MA, USA, 1979; pp. 461–516. [CrossRef]
15. Kobak, R.Z.U.; Ari, M.U.; Tekin, A.; Gul, A. Aggregation behavior in unsymmetrically substituted metal-free phthalocyanines. *Chem. Phys.* **2015**, *448*, 91–97. [CrossRef]
16. Nyokong, T.; Gasyna, Z.; Stillman, M.J. Phthalocyanine. pi.-cation-radical species: Photochemical and electrochemical preparation of [ZnPc(-1).+ in solution. *Inorg. Chem.* **1987**, *26*, 548–553. [CrossRef]
17. Milaeva, E.R.; Speier, G.; Lever, A.B.P. *The Redox Chemistry of Metallophthalocyanines in Solution*; Wiley-VCH: New York, NY, USA, 1993; Volume 3, pp. 3–69.
18. Silva, A.M.S.; Neves, M.G.P.M.S.; Martins, R.R.L.; Cavaleiro, J.A.S.; Boschi, T.; Tagliatesta, P. Photo-oxygenation of meso-tetraphenylporphyrin derivatives: The influence of the substitution pattern and characterization of the reaction products. *J. Porphyr. Phthalocyanines* **1998**, *2*, 45–51. [CrossRef]
19. D'Alessandro, N.; Tonucci, L.; Dragani, L.K.; Morvillo, A.; Bressan, M. Fate of nickel and cobalt sulfophthalocyanines under oxidizing conditions: A spectroscopic investigation. *J. Porphyr. Phthalocyanines* **2003**, *7*, 484–492. [CrossRef]
20. D'Alessandro, N.; Tonucci, L.; Morvillo, A.; Dragani, L.K.; Di Deo, M.; Bressan, A. Thermal stability and photostability of water solutions of sulfophthalocyanines of Ru(II), Cu(II), Ni(II), Fe(III) and Co(II). *J. Organomet. Chem.* **2005**, *690*, 2133–2141. [CrossRef]
21. Jones, C.W. On the Stability and Recyclability of Supported Metal-Ligand Complex Catalysts: Myths, Misconceptions and Critical Research Needs. *Top. Catal.* **2010**, *53*, 942–952. [CrossRef]
22. Bressan, M.; Celli, N.; d'Alessandro, N.; Liberatore, L.; Morvillo, A.; Tonucci, L. Ruthenium sulfophthalocyanine catalyst for the oxidation of chlorinated olefins with hydrogen peroxide. *J. Organomet. Chem.* **2000**, *593*, 416–420. [CrossRef]
23. Wang, G.; Ramesh, N.; Hsu, A.; Chu, D.; Chen, R. Density functional theory study of the adsorption of oxygen molecule on iron phthalocyanine and cobalt phthalocyanine. *Mol. Simul.* **2008**, *34*, 1051–1056. [CrossRef]

24. Shi, Z.; Zhang, J.J. Density functional theory study of transitional metal macrocyclic complexes' dioxygen-binding abilities and their catalytic activities toward oxygen reduction reaction. *J. Phys. Chem. C* **2007**, *111*, 7084–7090. [CrossRef]

25. Dolotova, O.V.; Bundina, N.I.; Kaliya, O.L.; Lukyanets, E.A. Manganese Phthalocyanine Coordination Chemistry: Recent Results and Present Status. *J. Porphyr. Phthalocyanines* **1997**, *1*, 355–366. [CrossRef]

26. Wariishi, H.; Gold, M.H. Lignin peroxidase compound III. Mechanism of formation and decomposition. *J. Biol. Chem.* **1990**, *265*, 2070–2077. [CrossRef]

27. Lever, A.B.P.; Wilshire, J.P.; Quan, S.K. Oxidation of manganese(II) phthalocyanine by molecular-oxygen. *Inorg. Chem.* **1981**, *20*, 761–768. [CrossRef]

28. Uchida, K.; Soma, M.; Naito, S.; Onishi, T.; Tamaru, K. Manganese phthalocyanine as a model of tryptophan-2,3-dioxygenase. *Chem. Lett.* **1978**, *7*, 471–474. [CrossRef]

29. Moxon, N.T.; Fielding, P.E.; Gregson, A.K. Manganese 4,4′,4″,4‴-tetrasulfonated phthalocyanine, its dioxygen adduct, and electron-spin-resonance evidence for intramolecular electron-transfer in solution. *J. Chem. Soc. Chem. Commun.* **1981**, 98–99. [CrossRef]

30. Ercolani, C.; Gardini, M.; Pennesi, G.; Rossi, G. Dioxygen Activation and Catalytic Oxidation of triphenylphosphine by iron phthalocyanine compounds. *J. Mol. Catal.* **1985**, *30*, 135–144. [CrossRef]

31. Kontarinis, D.; Paraskevas, S.M.; Paraskevas, M.S. Oxygen adducts of Co-phthalocyanine. *Synth. React. Inorg. Met. Org. Chem.* **2003**, *33*, 1381–1389. [CrossRef]

32. Hassanein, M.; Abdo, M.; Gerges, S.; El-Khalafy, S. Study of the oxidation of 2-aminophenol by molecular oxygen catalyzed by cobalt(II) phthalocyaninetetrasodiumsulfonate in water. *J. Mol. Catal. A Chem.* **2008**, *287*, 53–56. [CrossRef]

33. Schutten, J.H.; Piet, P.; German, A.L. Some observations on complexes of a cobalt phthalocyanine with poly(vinylamine) and their catalytic activity in the autoxidation of thiols. *Die Makromol. Chem.* **1979**, *180*, 2341–2350. [CrossRef]

34. Pan, Y.; Chen, W.X.; Lu, S.F.; Zhang, Y.F. Novel aqueous soluble cobalt phthalocyanine: Synthesis and catalytic activity on oxidation of 2-mercaptoethanol. *Dye. Pigment.* **2005**, *66*, 115–121. [CrossRef]

35. Geraskin, I.M.; Luedtke, M.W.; Neu, H.M.; Nemykin, V.N.; Zhdankin, V.V. Organic iodine(V) compounds as terminal oxidants in iron(III) phthalocyanine catalyzed oxidation of alcohols. *Tetrahedron Lett.* **2008**, *49*, 7410–7412. [CrossRef]

36. Kivits, P.; Debont, R.; Vanderveen, J. Vanadyl phthalocyanine: An organic material for optical data recording. *Appl. Phys. A* **1981**, *26*, 101–105. [CrossRef]

37. Ramadan, A.J.; Rochford, L.A.; Moffat, J.; Mulcahy, C.; Ryan, M.P.; Jones, T.S.; Heutz, S. The morphology and structure of vanadyl phthalocyanine thin films on lithium niobate single crystals. *J. Mater. Chem. C* **2016**, *4*, 348–351. [CrossRef]

38. Wong, E.W.Y.; Walsby, C.J.; Storr, T.; Leznoff, D.B. Phthalocyanine as a Chemically Inert, Redox-Active Ligand: Structural and Electronic Properties of a Nb(IV)-Oxo Complex Incorporating a Highly Reduced Phthalocyanine(4-) Anion. *Inorg. Chem.* **2010**, *49*, 3343–3350. [CrossRef]

39. Harris, D.L. High-valent intermediates of heme proteins and model compounds. *Curr. Opin. Chem. Biol.* **2001**, *5*, 724–735. [CrossRef]

40. Dolphin, D. The Electronic Configurations of Catalases and Peroxidases in their High Oxidation States: A Definitive Assessment. *Isr. J. Chem.* **1981**, *21*, 67–71. [CrossRef]

41. Jiang, G.; Chen, J.; Thu, H.Y.; Huang, J.S.; Zhu, N.; Che, C.M. Ruthenium porphyrin-catalyzed aerobic oxidation of terminal aryl alkenes to aldehydes by a tandem epoxidation-isomerization pathway. *Angew. Chem. Int. Ed.* **2008**, *47*, 6638–6642. [CrossRef]

42. Collman, J.P.; Barnes, C.E.; Brothers, P.J.; Collins, T.J.; Ozawa, T.; Gallucci, J.C.; Ibers, J.A. Oxidation of ruthenium(II) and ruthenium(III) porphyrins. Crystal structures of .mu.-oxo-bis[(p-methylphenoxo)(meso-tetraphenylporphyrinato)ruthenium(IV)] and ethoxo(meso-tetraphenylporphyrinato)(ethanol)ruthenium(III)-bisethanol. *J. Am. Chem. Soc.* **1984**, *106*, 5151–5163. [CrossRef]

43. Baek, H.K.; Vanwart, H.E. Elementary Steps in the Formation of Horseradish Peroxidase Compound I: Direct Observation of Compound 0, a New Intermediate with a Hyperporphyrin Spectrum. *Biochemistry* **1989**, *28*, 5714–5719. [CrossRef]

44. Zucca, P.; Neves, C.M.B.; Simoes, M.M.Q.; Neves, M.G.P.M.S.; Cocco, G.; Sanjust, E. Immobilized Lignin Peroxidase-Like Metalloporphyrins as Reusable Catalysts in Oxidative Bleaching of Industrial Dyes. *Molecules* **2016**, *21*, 964. [CrossRef]

45. Meunier, B.; Sorokin, A. Oxidation of pollutants catalyzed by metallophthalocyanines. *Acc. Chem. Res.* **1997**, *30*, 470–476. [CrossRef]

46. Sorokin, A.B.; Kudrik, E.V. Phthalocyanine metal complexes: Versatile catalysts for selective oxidation and bleaching. *Catal. Today* **2011**, *159*, 37–46. [CrossRef]

47. Sorokin, A.; Meunier, B. Oxidative Degradation of Polychlorinated Phenols Catalyzed by Metallosulfophthalocyanines. *Chem. Eur. J.* **1996**, *2*, 1308–1317. [CrossRef]

48. Floris, B.; Donzello, M.P.; Ercolani, C. Single-atom bridged dinuclear metal complexes with emphasis on phthalocyanine systems. In *The Porphyrin Handbook*; Kadish, K.M., Smith, K.M., Guilard, R., Eds.; Academic Press: San Diego, CA, USA, 2003; pp. 1–62.

49. Sorokin, A.B. Recent progress on exploring μ-oxo bridged binuclear porphyrinoid complexes in catalysis and material science. *Coord. Chem. Rev.* **2019**, *389*, 141–160. [CrossRef]

50. Sorokin, A.B.; Tuel, A. Metallophthalocyanine functionalized silicas: Catalysts for the selective oxidation of aromatic compounds. *Catal. Today* **2000**, *57*, 45–59. [CrossRef]

51. Sorokin, A.B.; Kudrik, E.V.; Bouchu, D. Bio-inspired oxidation of methane in water catalyzed by N-bridged diiron phthalocyanine complex. *Chem. Comm.* **2008**. [CrossRef]

52. Colomban, C.; Kudrik, E.V.; Afanasiev, P.; Sorokin, A.B. Degradation of chlorinated phenols in water in the presence of H2O2 and water-soluble mu-nitrido diiron phthalocyanine. *Catal. Today* **2014**, *235*, 14–19. [CrossRef]

53. Colomban, C.; Tobing, A.H.; Mukherjee, G.; Sastri, C.V.; Sorokin, A.B.; de Visser, S.P. Mechanism of Oxidative Activation of Fluorinated Aromatic Compounds by N-Bridged Diiron-Phthalocyanine: What Determines the Reactivity? *Chem. Eur. J.* **2019**, *25*, 14320–14331. [CrossRef]

54. Basu, B.; Satapathy, S.; Bhatnagar, A.K. Merox and Related Metal Phthalocyanine Catalyzed Oxidation Processes. *Catal. Rev. Sci. Eng.* **1993**, *35*, 571–609. [CrossRef]

55. Zhou, X.R.; Li, J.; Wang, X.N.; Jin, K.; Ma, W. Oxidative desulfurization of dibenzothiophene based on molecular oxygen and iron phthalocyanine. *Fuel Process. Technol.* **2009**, *90*, 317–323. [CrossRef]

56. Chen, S.C.; Lu, W.Y.; Yao, Y.Y.; Chen, H.X.; Chen, W.X. Oxidative desulfurization of dibenzothiophene with molecular oxygen catalyzed by carbon fiber-supported iron phthalocyanine. *React. Kinet. Mech. Catal.* **2014**, *111*, 535–547. [CrossRef]

57. Price, B.K.; Tour, J.M. Functionalization of Single-Walled Carbon Nanotubes "On Water". *J. Am. Chem. Soc.* **2006**, *128*, 12899–12904. [CrossRef] [PubMed]

58. Zhang, J.; Li, J.; Ren, T.; Hu, Y.; Ge, J.; Zhao, D. Oxidative desulfurization of dibenzothiophene based on air and cobalt phthalocyanine in an ionic liquid. *RSC Adv.* **2014**, *4*, 3206–3210. [CrossRef]

59. Chauhan, D.K.; Patnam, P.L.; Ganguly, S.K.; Jain, S.L. A two in one approach: Renewable support and enhanced catalysis for sweetening using chicken feather bound cobalt(II) phthalocyanine under alkali free environment. *RSC Adv.* **2016**, *6*, 51983–51988. [CrossRef]

60. Reid, N.; Barat, R. Impact of Fluorinated Cobalt(II) Phthalocyanine Catalysts on Aerobic Thiol Oxidation Kinetics. *Chem. Eng. Commun.* **2016**, *203*, 714–723. [CrossRef]

61. Vashurin, A.; Maizlish, V.; Kuzmin, I.; Znoyko, S.; Morozova, A.; Razumov, M.; Koifman, O. Symmetrical and difunctional substituted cobalt phthalocyanines with benzoic acids fragments: Synthesis and catalytic activity. *J. Porphyr. Phthalocyanines* **2017**, *21*, 37–47. [CrossRef]

62. Filippova, A.; Vashurin, A.; Znoyko, S.; Kuzmin, I.; Razumov, M.; Chernova, A.; Shaposhnikov, G.; Koifman, O. Novel Co(II) phthalocyanines of extended periphery and their water-soluble derivatives. Synthesis, spectral properties and catalytic activity. *J. Mol. Struct.* **2017**, *1149*, 17–26. [CrossRef]

63. Tamura, R.; Kawata, T.; Hattori, Y.; Kobayashi, N.; Kimura, M. Catalytic Oxidation of Thiols within Cavities of Phthalocyanine Network Polymers. *Macromolecules* **2017**, *50*, 7978–7983. [CrossRef]

64. Huang, H.; Ash, J.; Kang, J.Y. Base-controlled Fe(Pc)-catalyzed aerobic oxidation of thiols for the synthesis of S-S and S-P(O) bonds. *Org. Biomol. Chem.* **2018**, *16*, 4236–4242. [CrossRef]

65. Motahari, K.; Salabat, A.; Ahmadi, H. Co (II) phthalocyanine-amine functionalized graphene oxide as a solid base catalyst for the oxidation of thiols. *Fuller. Nanotub. Carbon Nanostruct.* **2018**, *26*, 342–350. [CrossRef]

66. Scott, D.W.; Myers, D.L.; Hill, H.; Omadoko, O. Sodium cobalt(II) tetrasulfophthalocyanine and catalytic oxidation of ethanethiol. *Fuel* **2019**, *242*, 573–579. [CrossRef]

67. Li, Y.; Zhang, H.Z.; Jiang, Y.; Shi, M.; Bawa, M.; Wang, X.H.; Zhu, S.Y. Assembly of metallophthalocyanine-polyoxometalate hybrid for highly efficient desulfurization of organic and inorganic sulfur under aerobic conditions. *Fuel* **2019**, *241*, 861–869. [CrossRef]

68. Makarov, S.G.; Ketkov, S.Y.; Wohrle, D. A planar binuclear cobalt(ii) phthalocyanine as a highly efficient catalyst for the oxidation of a mercaptan. *Chem. Comm.* **2020**, *56*, 5653–5656. [CrossRef] [PubMed]

69. Adolfsson, H. Transition Metal-Catalyzed Epoxidation of Alkenes. In *Modern Oxidation Methods*; Bäckvall, J.-E., Ed.; Wiley-VCH Verlag GmbH & Co.: Weinheim, Germany, 2004; pp. 21–49. [CrossRef]

70. Pernicone, N.; Cerboni, M.; Prelazzi, G.; Pinna, F.; Fagherazzi, G. An investigation on Pd/C industrial catalysts for the purification of terephthalic acid. *Catal. Today* **1998**, *44*, 129–135. [CrossRef]

71. Sorokin, A.B. Catalytic Transformations in the Presence of Metal Phthalocyanine Complexes and Their Analogs. In *Handbook of Porphyrin Science*; World Scientific: Singapore, 2016; pp. 193–322. [CrossRef]

72. Shaabani, A.; Farhangi, E.; Rahmati, A. Aerobic oxidation of alkyl arenes and alcohols using cobalt(II) phthalocyanine as a catalyst in 1-butyl-3-methyl-imidazolium bromide. *Appl. Catal. A Gen.* **2008**, *338*, 14–19. [CrossRef]

73. Shaabani, A.; Keshipour, S.; Hamidzad, M.; Shaabani, S. Cobalt(II) phthalocyanine covalently anchored to cellulose as a recoverable and efficient catalyst for the aerobic oxidation of alkyl arenes and alcohols. *J. Mol. Catal. A Chem.* **2014**, *395*, 494–499. [CrossRef]

74. Mahyari, M.; Shaabani, A. Graphene oxide-iron phthalocyanine catalyzed aerobic oxidation of alcohols. *Appl. Catal. A Gen.* **2014**, *469*, 524–531. [CrossRef]

75. Chauhan, P.; Yan, N. Nanocrystalline cellulose grafted phthalocyanine: A heterogeneous catalyst for selective aerobic oxidation of alcohols and alkyl arenes at room temperature in a green solvent. *RSC Adv.* **2015**, *5*, 37517–37520. [CrossRef]

76. Panwar, V.; Kumar, P.; Ray, S.S.; Jain, S.L. Organic inorganic hybrid cobalt phthalocyanine/polyaniline as efficient catalyst for aerobic oxidation of alcohols in liquid phase. *Tetrahedron Lett.* **2015**, *56*, 3948–3953. [CrossRef]

77. Huang, C.; Liu, R.; Yang, W.Y.; Zhang, C.T.; Zhu, H.J. Iron(II) phthalocyanine immobilized SBA-15 catalysts: Preparation, characterization and application for toluene selective aerobic oxidation. *Inorg. Chim. Acta* **2017**, *467*, 307–315. [CrossRef]

78. Huang, C.; Liu, R.; Zhang, C.T.; Cheng, Q.P.; Zhu, H.J. Iron(II) and copper(II) phthalocyanine-catalyzed synthesis of 2-nitro-4-methylsulfonylbenzoic acid under mild conditions. *J. Chem. Sci.* **2017**, *129*, 1587–1594. [CrossRef]

79. Zhou, W.; Dai, X.; Chen, Y.; Sun, F.A.; He, M.; Chen, Q. Synergistic Catalytic Oxidation of Ethylbenzene to Acetophenone by Metallophthalocyanine Intercalated Layered Double Hydroxide with Oxygen. *ChemistrySelect* **2018**, *3*, 566–572. [CrossRef]

80. Zhou, W.Y.; Zhou, J.C.; Chen, Y.; Cui, A.J.; Sun, F.A.; He, M.Y.; Xu, Z.X.; Chen, Q. Metallophthalocyanine intercalated layered double hydroxides as an efficient catalyst for the selective epoxidation of olefin with oxygen. *Appl. Catal. A Gen.* **2017**, *542*, 191–200. [CrossRef]

81. Shaabani, A.; Mohammadian, R.; Hashemzadeh, A.; Afshari, R.; Amini, M.M. Amine-functionalized MIL-101(Cr) embedded with Co(ii) phthalocyanine as a durable catalyst for one-pot tandem oxidative A(3) coupling reactions of alcohols. *New J. Chem.* **2018**, *42*, 4167–4174. [CrossRef]

82. Li, F.; Tang, S.; Tang, Z.L.; Ye, L.J.; Li, H.H.; Niu, F.F.; Sun, X.L. Synergistic Catalytic Effect of N-Hydroxyphthalimide/Cobalt Tetraamide Phthalocyanine and Its Application for Aerobic Oxidation of Hydrocarbons and Alcohols. *Catal. Lett.* **2020**. [CrossRef]

83. Puls, F.; Knolker, H.J. Conversion of Olefins into Ketones by an Iron-Catalyzed Wacker-type Oxidation Using Oxygen as the Sole Oxidant. *Angew. Chem. Int. Ed.* **2018**, *57*, 1222–1226. [CrossRef]

84. Castro, K.; Figueira, F.; Paz, F.A.A.; Tome, J.P.C.; da Silva, R.S.; Nakagaki, S.; Neves, M.G.P.M.S.; Cavaleiro, J.A.S.; Simoes, M.M.Q. Copper-phthalocyanine coordination polymer as a reusable catechol oxidase biomimetic catalyst. *Dalton Trans.* **2019**, *48*, 8144–8152. [CrossRef]

85. Brandolese, A.; Ragno, D.; Di Carmine, G.; Bernardi, T.; Bortolini, O.; Giovannini, P.P.; Pandoli, O.G.; Altomare, A.; Massi, A. Aerobic oxidation of 5-hydroxymethylfurfural to 5-hydroxymethyl-2-furancarboxylic acid and its derivatives by heterogeneous NHC-catalysis. *Org. Biomol. Chem.* **2018**, *16*, 8955–8964. [CrossRef] [PubMed]