



Manganese chlorins immobilized on silica as oxidation reaction catalysts

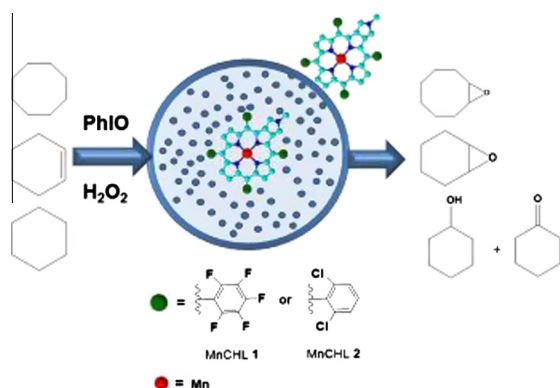


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GRAPHICAL ABSTRACT



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ABSTRACT

Synthetic strategies that comply with the principles of green chemistry represent a challenge: they will enable chemists to conduct reactions that maximize the yield of products with commercial interest while minimizing by-products formation. The search for catalysts that promote the selective oxidation of organic compounds under mild and environmentally friendly conditions constitutes one of the most important quests of organic chemistry. In this context, metalloporphyrins and analogues are excellent catalysts for oxidative transformations under mild conditions. In fact, their reduced derivatives chlorins are also able to catalyze organic compounds oxidation effectively, although they have been still little explored. In this study, we synthesized two chlorins through porphyrin cycloaddition reactions with 1,3-dipoles and prepared the corresponding manganese chlorins (MnChl) using adequate manganese(II) salts. These MnChl were posteriorly immobilized on silica by following the sol-gel process and the resulting solids were characterized by powder X-ray diffraction (PXRD), UVVIS spectroscopy, FTIR, XPS, and EDS. The catalytic activity of the immobilized MnChl was investigated in the oxidation of cyclooctene, cyclohexene and cyclohexane and the results were compared with the ones obtained under homogeneous conditions.

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1. Introduction

Hydrocarbons are abundant in nature and represent about 50% of the petrochemical industry input. Due to the low reactivity of these compounds their use *per se* is limited: they are mainly applied as solvents and fuels. Developing catalysts that can promote selective hydrocarbon oxidation has long been a goal in the field of organic synthesis [1,2]. In this sense, efficient and selective naturally occurring catalytic systems have frequently inspired the rational design of new catalytic systems [3].

In recent decades, researchers have faced the challenge to understand the role that different metal complexes play in biological processes, particularly in enzymatic reactions [4]. The past 30 years have witnessed many reports on synthetic porphyrins, especially their Fe(III) and Mn(III) complexes, being described as efficient and selective catalysts of a variety of hydrocarbon oxidations. Indeed, these metallocomplexes have been found to mimic the activity of the cytochrome P450 monooxygenase enzymes bearing Fe(III) porphyrin moieties in their active sites [5–8].

Porphyrins and their structural derivatives, like chlorins, participate in key biological processes [9–14]. Iron complexes such as heme constitute the prosthetic group of important classes of enzymes and of a wide variety of proteins [8]. Chlorophylls, involved in photosynthesis, are magnesium-substituted chlorin complexes [15]. These reduced derivatives are usually green, because the loss of a double bond at the β -pyrrolic position of the macrocycle alters the molecule symmetry, shifting the absorption towards the red region of the spectrum [16,17]. The spectral properties of chlorins (absorption in the 620–680 nm wavelength range) can contribute to their potential application in photodynamic therapy (PDT) [18,19].

Additionally, synthetic MnCHL x (where x = chlorin **1**, **2** or **3**) appear to be promising catalysts for oxidation reactions. In fact, these complexes have furnished moderate to good oxygenated products yields during cyclohexane oxyfunctionalization reactions [7]. Fe(III) and Mn(III) complexes of synthetic chlorins can also catalyze the oxidation of sulfides as efficiently as metalloporphyrins [20].

On the basis of the efficiency and selectivity of biological systems, researchers have devoted great efforts to develop synthetic metalloporphyrins for different purposes [11,21–26], namely to obtain (i) end products or synthetic precursors for the chemical/pharmaceutically industry (such as epoxides, alcohols, and acids), and (ii) compounds with pharmaceutical interest (such as isomers with specific pharmacological activity). In these processes, the desired catalytic selectivity towards certain products may require high degree of sophistication when modeling specific catalysts [23–27].

Apart from synthesizing novel suitable and resistant porphyrin ligands that can catalyze oxidation reactions after metallation, another strategy usually considered is the immobilization of the porphyrin complexes on rigid and inert inorganic supports, to obtain suitable catalysts for the oxidation of distinct hydrocarbons [28–32].

Catalyst immobilization (i) prevents the common catalytic species deactivation reactions that take place in homogeneous medium, avoiding catalytic efficiency loss and complex deactivation by self-oxidation [33], and (ii) offers the extra bonus of catalyst recovery from the reaction medium and reuse [30,31,33–37].

Silica is generally the support of choice when investigating the immobilization of metalloporphyrins and their analogues; silica is inexpensive and inert, and has high functionalization capacity [35,38]. Silica gel is an inorganic solid containing siloxane (Si–O–Si) and silanol groups (Si–OH) [37]. Immobilizing porphyrin complexes on solids such as silica gel inhibits dimer

formation, because the matrix reduces the interactions among the molecules fixed on the support surface [30,34,38,39]. The sol–gel process usually furnishes the silica under mild conditions; it is a very promising method to obtain high-purity solids that are suitable to immobilize different complexes, including metallochlorins and metalloporphyrins (MP) [33,35].

In this context, we report here the immobilization of two easily accessible manganese chlorins (MnCHL) (Fig. 1) on silica obtained by the sol–gel process. We tested the efficiency of the resulting solids as catalysts under heterogeneous conditions in cyclooctene and cyclohexene epoxidation and in cyclohexane hydroxylation. The oxidative processes were performed using iodosylbenzene (PhIO) and hydrogen peroxide (for cyclooctene) as oxidant and for comparison the efficiency of the non-immobilized were also evaluated.

2. Experimental

All the chemicals were purchased from Aldrich, Sigma, or Merck, and were of analytical grade. Iodosylbenzene (PhIO) was synthesized by hydrolysis of iodosylbenzenediacetate [40]; its purity was determined by iodometric titration [41]. The obtained solid was carefully dried under reduced pressure and kept at 5 °C.

2.1. Synthesis of manganese chlorins (MnCHL1 and MnCHL2)

The manganese chlorins (MnCHL1 and MnCHL2) were prepared in three steps, according to the literature [7,42–45]: (i) synthesis of the two free-base porphyrins 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin [H₂(TPFP)] (**1**) and 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin [H₂(TDCPP)] (**2**); (ii) synthesis of the respective chlorins (CHL1 and CHL2) by 1,3-dipolar cycloaddition reaction between **1** and **2** with azomethine ylide generated from *N*-methylglycine and paraformaldehyde; and (iii) metallation of the free-base chlorins (CHL1 and CHL2) using manganese(II) chloride in acetic acid or dimethylformamide (DMF) obtaining (Mn(II)CHL1 and Mn(III)CHL2, (Fig. 1)). The compounds were characterized by ¹H and ¹⁹F NMR, UVVIS spectroscopy, and mass spectrometry; the analytical data are in accordance with the literature [7,43,44].

2.2. Synthesis of manganese chlorin (MnCHL3)

The metallation of the free-base chlorin CHL1 was also done by a modification of the conventional method of Kobayashi [46] using acetic acid as solvent, manganese(II) acetate under reflux and magnetic stirring for 6 h. After the metallation process, the solvent was removed under vacuum giving rise to a solid that was washed thoroughly with water to remove the excess of metal salt. The complex produced was dissolved in a small amount of methanol and by standing at ambient temperature for two days small green crystals in needle form (MnCHL3) were obtained.

2.3. Structure determination by single crystal X-ray diffraction

X-ray data for a single crystal of MnCHL3 with approximate dimensions 0.111 mm × 0.144 mm × 0.560 mm were collected on an Bruker D8 Venture Photon 100 by using graphite-monochromated Cu K α radiation (λ = 1.5418 Å) at 100(2) K. Accurate unit cell dimensions and orientation matrices were determined by least-squares refinement of the reflections obtained by θ – X scans. The data were indexed and scaled with the ApexII Suite [47]. Bruker Saint and Bruker Sadabs were used to integrate and scaling of data, respectively. The structure was solved and refined using the

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