Synthesis, crystallographic characterization and homogeneous catalytic activity of novel unsymmetric porphyrins†


Unsymmetric porphyrins, containing both pentafluorophenyl (PFPP = A) and 3,4-dimethoxyphenyl (DMP = B) substituents at the meso positions, were prepared using Lindsey’s methodology. The isomeric trans-A2B2 (P1) and cis-A3B2 (P2) porphyrins together with the tris(pentafluorophenyl)porphyrin A3B (P3) were isolated using chromatography. The porphyrins were characterized by UV-VIS, 1H NMR spectroscopy, mass spectrometry, elemental analysis (C, H, N) and cyclic voltammetry (CV), and their molecular structures were confirmed by single crystal XRD. Their manganese complexes, MnP1, MnP2 and MnP3, were also synthesized and used as catalysts in cyclooctene and cyclohexane oxidation reactions under homogeneous conditions. The catalytic studies were supported by electrochemical measurements and showed that the number of electron-withdrawing substituents on the porphyrins rings influences the catalytic activity. These porphyrins may be used as precursors for the design of new materials, such as Polymers of Intrinsic Microporosity (PIMs).

Introduction

Porphyrins are macrocyclic compounds with a large extended conjugated π-system and they are often called “the pigments of life”, as they play an important role in many biological systems. These compounds and their metallated complexes exhibit unique properties and can be synthesized through various methodologies. The macrocycles also show great flexibility towards structural modification which make them very interesting molecules in a number of different fields.

Metalloporphyrins, especially those containing Fe(III) and Mn(III) cations, have been extensively used as catalysts in oxidation reactions of a range of organic compounds using different oxidants. Studies have shown that the introduction of electron-withdrawing and/or bulky substituents at the ortho position of the meso-phenyl porphyrins (so called second generation porphyrins) can enhance their catalytic activity in oxidation reactions. This performance stems from the electronic effects that the substituents exert on the porphyrin ring, which enhances the electrophilicity of the active catalytic species (metal-oxo porphyrin) and also protects the ring, to some extent, against auto oxidative destruction. In this context, the free base ligand [5,10,15,20-tetrakis(pentafluorophenyl)porphyrin], [H2(TPFPP)], represents an important compound. The fluorine atoms on the phenyl ring at the four meso positions increases the stability and catalytic activity. In addition, the fluorine at para positions can be readily substituted by nucleophiles, which makes this compound a versatile platform for the design of new materials. Several materials have been recently prepared, which utilize the [H2(TPFPP)] porphyrin in a heterogeneous catalytic system. McKeown and co-workers used [H2(TPFPP)] porphyrin as a monomer in a polymerization reaction with 5,5′,6,6′-tetrahydroxy-3,3′,3′,5′-tetramethyl-1,1′-spirobisdihane (biscatecho) to prepare a porphyrin network PIM (so called polymer of intrinsic microporosity). The high surface area (up to 1000 m2 g−1) and the chemical stability of this material encourages the synthesis of new network PIMs and their application in heterogeneous oxidation catalysis.

Meso substituted A2B2 trans-porphyrins bearing different functional groups are useful building blocks for the design and synthesis of new materials with a wide range of applications, such as biomimetic systems and molecular materials. The trans pattern of substitution in these kinds of porphyrins can be used to achieve new materials with well-defined structures. For example, the same polymerization reaction previously used to synthesize the porphyrin network PIM, could be employed utilizing one meso–trans A2B2 porphyrin as a preformed monomer in order to achieve new soluble ladder PIMs. Moreover,
transition metal ions may also be coordinated to the porphyrin units for future investigation in catalytic membranes. Thus, we undertook the synthesis of a group of new unsymmetric porphyrins with either pentafluorophenyl \( (\text{PFP} = A) \) or 3,4-dimethoxyphenyl \( (\text{DMP} = B) \) at the four meso positions.

### Experimental

#### Materials

All chemicals used in this study were purchased from Sigma-Aldrich, Merck or Fluka and were of analytical grade. Iodosylbenzene (PhIO) was synthesized according to the literature. The solid was carefully dried under reduced pressure and kept at 5 °C; its purity was assessed by iodometric titration.

\(^1\)H and \(^{13}\)C NMR spectra were recorded on Bruker Advance 300 MHz spectrometers, using deuterated chloroform as solvent. Chemical shifts are reported in ppm (δ) and coupling constants (J) are given in Hz. The multiplicities of the signals in the \(^1\)H NMR spectra are abbreviated by s (singlet), d (doublet), q (quartet) and m (multiplet). Mass spectra were acquired on a Bruker Ultraflex MALDI-TOF or Thermo Electron MAT900 mass spectrometers (MALDI or EI). Electronic spectra (UV-VIS) were obtained from dichloromethane solutions on a Hewlett-Packard HP 8452A diode array spectrophotometer in the 200–800 nm range. Analysis were accomplished with a 1 cm path length cell. Fourier Transform Infrared (FTIR) spectra were measured on a Biorad 3500 GX spectrophotometer in the 400–1500 cm\(^{-1}\) range with a spectral resolution of 4 cm\(^{-1}\). Elemental analyses were obtained from dichloromethane solutions on a Perkin Elmer 2400 elemental analyzer.

#### Preparation of free base porphyrins P1, P2 and P3, and their manganese complexes MnP1, MnP2 and MnP3

The free base porphyrins were synthesized by Lindsey methodology using 5-(3,4-dimethoxyphenyl)dipyromethane (1.2 g; 4.57 mmol) and pentafluorobenzaldehyde (0.9 g, 4.57 mmol) dissolved in dry CH\(_2\)Cl\(_2\) (460 mL) followed by the addition of TFA (0.6 mL; 8.13 mmol). The solution was stirred under N\(_2\) atmosphere at room temperature for 50 min. Then, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1.34 g, 5.90 mmol) was added and the resultant solution was stirred further for 1 h. The resulting crude product was purified over two successive chromatography columns (silica, 6 cm diameter x 30 cm height, CH\(_2\)Cl\(_2\)) where it was possible to isolate the three porphyrins: P1 (R\(_i\) = 0.75), P2 (R\(_i\) = 0.61) and P3 (R\(_i\) = 0.84).

**Porphyrin P1.** Purple solid (0.134 g; 6.4% yield). Elemental analysis (\%) calcd. for C\(_{46}\)H\(_{19}\)F\(_{15}\)N\(_4\)O\(_2\): C 58.49, H 2.03, N 5.93; found: C 57.60, H 1.84, N 5.68; \(^{13}\)C NMR data (125 MHz, CDCl\(_3\)) \(\delta\) ppm: 149.1, 148.1, 134.6, 132.7, 120.3, 117.1, 111.8, 111.2, 108.5, 107.1, 56.0, 55.9, 43.6. LRMS (EI): m/z 282.1 (M\(^+\)).

**Porphyrin P2.** Purple solid (0.055 g, 2.6% yield). Elemental analysis (\%) calcd. for C\(_{46}\)H\(_{19}\)F\(_{15}\)N\(_4\)O\(_2\): C 58.49, H 2.03, N 5.93; found: C 57.60, H 1.84, N 5.68; \(^{13}\)C NMR data (125 MHz, CDCl\(_3\)) \(\delta\) ppm: 149.1, 148.1, 134.6, 132.7, 120.3, 117.1, 111.8, 111.2, 108.5, 107.1, 56.0, 55.9, 43.6. LRMS (EI): m/z 282.1 (M\(^+\)).

**Porphyrin P3.** Purple solid (0.134 g, 6.4% yield). Elemental analysis (\%) calcd. for C\(_{46}\)H\(_{19}\)F\(_{15}\)N\(_4\)O\(_2\): C 58.49, H 2.03, N 5.93; found: C 57.60, H 1.84, N 5.68; \(^{13}\)C NMR data (125 MHz, CDCl\(_3\)) \(\delta\) ppm: 149.1, 148.1, 134.6, 132.7, 120.3, 117.1, 111.8, 111.2, 108.5, 107.1, 56.0, 55.9, 43.6. LRMS (EI): m/z 282.1 (M\(^+\)).
were added in the reaction and the oxidant PhIO (catalyst/PhIO at a molar ratio of 1 : 10) in a solvent mixture (ACN : DCM, 5:1, v/v) and the substrates were purged with argon for 15 min. The catalysts (MnP$_1$, MnP$_2$ and MnP$_3$) and the substrates were purged with argon for 15 min. Then, the mixture of solvents (ACN : DCM, 1 : 1) was added to the reaction flask, followed by addition of the substrates (Z)-cyclooctene or cyclohexane. The molar ratio (catalyst/PhIO/substrate) used was 1 : 10 : 1000 which was calculated based on the molecular mass of the metalloporphyrins (about 0.5 mg of metalloporphyrins were used for each reaction). The oxidation reactions were performed under magnetic stirring for 1 h, at room temperature, in the absence of light. After 1 h, the excess of iodosylbenzene was consumed by addition of sodium sulfite and the reaction mixture was transferred to a volumetric flask (2 mL). The resulting solution containing the reaction products was analyzed by gas chromatography using bromobenzene or 1-pentanol as internal standards. The products from the oxidation reactions were quantified with an Agilent 6890 gas chromatograph (flame ionization detector) equipped with a 30 m long DB-WAX capillary column with 0.25 mm internal diameter (J&W Scientific). Product yields were based on the quantity of PhIO added to each reaction.

**Results and discussion**

**Porphyrin synthesis**

It was anticipated that the porphyrin meso trans-A$_2$B$_2$(P1) would be synthesized using Lindsey’s methodology, between 5-(3,4-dimethoxyphenyl)dipropylene and pentafuorobenzaldehyde (Scheme 1). Analysis of the crude product mixture revealed that the desired porphyrin P1 was prepared along with the cis-A$_3$B$_1$ isomer P2 and the tris-pentafluorophenylporphyrin A$_3$B$_3$ (P3) (Scheme 1). The formation of P2 and P3 is probably associated with scrambling of the phenyl substituents due to acidolysis and recombination of dipropyrrenes. The yield for the desired porphyrin (P1) was low (6.4%), but respectable in comparison with that of the isomeric unsymmetric porphyrin 5,15-bis(3,5-dimethoxyphenyl)-10,20-bis(pentafluorophenyl) (3.8%), prepared using the mixed aldehyde methodology.

**Catalytic studies of MnP1, MnP2 and MnP3 using (Z)-cyclooctene and cyclohexane as substrates**

The catalytic activity and efficiency of the new metalloporphyrins was tested in the oxidation reactions of (Z)-cyclooctene (previously purified on alumina column) and cyclohexane with iodosylbenzene (PhIO). Furthermore, the two associated symmetric metalloporphyrins, 5,10,15,20-tetakis(pentafluorophenyl)porphyrin manganese(ii), MnTPFP, and 5,10,15,20-tetrakis(3,4-dimethoxyphenyl)porphyrin manganese(ii), MnTDMP, were also used as catalysts for comparison.

The catalytic reactions were performed in a 1.5 mL glass flask equipped with a magnetic stirrer, in a dark chamber. The solvent mixture (acetonitrile/dichloromethane, ACN : DCM, 1 : 1, v/v) and the substrates were purged with argon for 15 min. The catalysts (MnP$_1$, MnP$_2$, MnP$_3$, MnTPFP and MnTDMP) and the oxidant PhIO (catalyst/PhIO at a molar ratio of 1 : 10) were added in the reaction flask and they were also purged with argon for 15 min.
The $^1$H NMR spectroscopy was fundamental for differentiation between the trans-$A_B$$_2$ (P1) and cis-$A_B$$_2$ (P2) isomers (Table 1 and ESI: Fig. S3–S5†). The $D_{2h}$ symmetry of trans-$A_B$$_2$ molecule (P1) gives specific signal patterns with two doublets for the β-pyrole protons at 9.0 and 8.8 ppm, while the lower symmetry in the cis-$A_B$$_2$ (P2) compared to the trans P1 isomer gives rise to two singlets at 8.9 and 8.8 ppm and two doublets at 9.0 and 8.7 ppm. In the tris-$A_B$ (P3) the β-pyrole protons are split up into two doublets at 9.0 and 8.8 ppm and one multiplet at 8.9 ppm. These results are in agreement with the basic patterns of splitting of the β-pyrole protons in unsymmetric porphyrins as reported for Meng and co-workers.29

The UV-VIS spectra of the porphyrin macrocycle are consistent with the $D_{2h}$ micro-symmetry according to the Four-Orbital Model developed by Gouterman (ESI: Fig. 6†).30 The spectra of the free base porphyrins shows an intense absorption near 400 nm (Soret band) and four less intense bands (Q bands) labeled as IV, III, II and I, between 450 and 700 nm. In general, electron-donating substituents lead to red shifts for both the Soret and Q bands.30–35 The electronic coupling between electron-donating groups and the porphyrin core in P1–P3 decreases the HOMO–LUMO energy gaps and causes a red shift in its spectra compared to the free base porphyrin H$_2$TPFP (ESI: Fig. 6†).

Furthermore, it is well established that the relative intensity of the four Q bands is dependent on the substituent groups at the macrocycle periphery. According to the relative intensities, the four visible Q bands are classified as etio, rhodo, oxorhodo, and phyllo.30–36 The porphyrins P1–P3 give a phyllo spectra (with intensities IV > II > III > I), which is in agreement with meso-phenylporphyrins spectra. The reduction in the intensities of bands III and I observed in the spectrum of the porphyrin P3 may be attributed to the restricted rotation of the phenyl groups resulting from steric interaction of the ortho-fluorine substituent and the β-pyrole hydrogens.36

The metalation process of the free base porphyrins P1, P2 and P3 with manganese(II) acetate was monitored by recording the electronic spectra at different reaction times. The bathochromic shift observed in the Soret band is characteristic of Mn(II) porphyrins, which confirms the formation of MnP1, MnP2 and MnP3 (ESI: Fig. S7†). These new metalloporphyrins were also characterized by solid state EPR (ESI: Fig. S8†) and no signal was observed at room temperature or 77 K, in agreement with presence of Mn(II) in the porphyrin core.35,36 Indeed, the Mn(II) ions have four unpaired d electrons with $S = 2$, typically featuring a pronounced Jahn–Teller distortion which results in substantial spin–orbit coupling.36 Thereby, the coupling and rapid spin relaxation process results in absence of signal in mononuclear Mn(II) EPR spectra even at 77 K (under perpendicular microwave polarization).35,36

Furthermore, the EPR confirms that the excess of manganese(II) acetate, which shows a signal in g = 2 (ESI: Fig. S8†), was removed during the purification of the new metalloporphyrins (through column and washing with warm water).

### Table 1

| $^1$H Chemical shift data (δ, ppm) for trans-$A_B$$_2$ (P1), cis-$A_B$$_2$ (P2) and tris-$A_B$ (P3) in CDC$_3$. Multiplicity and integration in parentheses |
|---|---|---|---|
| **H-β-pyrrolic** | **ArH** | **-OCH$_3$** | **NH** |
| Trans-$A_B$$_2$ (P1) | 9.04–9.03 (d, 4H) 8.82–8.81 (d, 4H) | 7.80–7.78 (m, 4H) 7.32–7.30 (m, 4H) | 4.22 (s, 6H) 4.03 (s, 6H) | –2.78 (s, 2H) |
| Cis-$A_B$$_2$ (P2) | 9.04–9.03 (d, 2H) 8.95 (s, 2H) 8.87 (s, 2H) 9.04–9.03 (d, 2H) | 7.80–7.76 (m, 4H) 7.31–7.29 (m, 4H) | 4.21 (s, 6H) 4.03 (s, 6H) | –2.70 (s, 2H) |
| Tris-$A_B$ (P3) | 9.06–9.05 (d, 2H) 8.9 (m, 4H) 8.83–8.82 (d, 2H) | 7.79–7.77 (m, 2H) 7.32–7.30 (m, 2H) | 4.22 (s, 3H) 4.03 (s, 3H) | –2.79 (s, 2H) |
Table 2  Selected crystallographic and geometric parameters for the crystal structure of P1, P2 and P3

<table>
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<th>P1</th>
<th>P2</th>
<th>P3</th>
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<tr>
<td>Empirical formula</td>
<td>C_{56}H_{69}Cl_{2}F_{10}N_{4}O_{4}</td>
<td>C_{56}H_{69}Cl_{2}F_{10}N_{4}O_{4}</td>
<td>C_{54}H_{62}F_{12}N_{2}O_{3}</td>
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<tr>
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<td>1153.48</td>
<td>975.68</td>
</tr>
<tr>
<td>Temperature/K</td>
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<td>200</td>
<td>120</td>
</tr>
<tr>
<td>Crystal system</td>
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<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2_1/c</td>
<td>P2_1/c</td>
<td>Cc</td>
</tr>
<tr>
<td>a/Å</td>
<td>13.948(3)</td>
<td>12.0821(2)</td>
<td>11.5360(2)</td>
</tr>
<tr>
<td>b/Å</td>
<td>15.6771(17)</td>
<td>17.9808(2)</td>
<td>15.0809(3)</td>
</tr>
<tr>
<td>c/Å</td>
<td>11.2006(16)</td>
<td>22.7546(3)</td>
<td>109.177(18)</td>
</tr>
<tr>
<td>β/°</td>
<td>109.177(18)</td>
<td>96.0320(10)</td>
<td>49.1957(12)</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>2313.2(7)</td>
<td>4915.97(12)</td>
<td>4398.56(16)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>4</td>
<td>4</td>
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<tr>
<td>2θ range for data collection/°</td>
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<td>8341</td>
<td>39 378</td>
<td>35 755</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>2340 [R_{int} = 0.0857, R_{sigma} = 0.0726]</td>
<td>5127 [R_{int} = 0.0661, R_{sigma} = 0.0289]</td>
<td>7617 [R_{int} = 0.0660, R_{sigma} = 0.0400]</td>
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<tr>
<td>Final R indexes [I &gt; 2σ(I)]</td>
<td>R_1 = 0.0725, wR_2 = 0.1897</td>
<td>R_1 = 0.0659, wR_2 = 0.1874</td>
<td>R_1 = 0.1043, wR_2 = 0.2897</td>
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<td>Final R indexes [all data]</td>
<td>R_1 = 0.1160, wR_2 = 0.2565</td>
<td>R_1 = 0.0708, wR_2 = 0.1943</td>
<td>R_1 = 0.1079, wR_2 = 0.3001</td>
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<td>CCDC deposition number</td>
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Demonstrates a much larger deviation of planarity compared to P1 and P2, with a maximum deviation from planarity of 0.351 Å. The two PFP substituents both exhibit significant disorder that could be modelled over two positions but still demonstrate a large amount of libration as shown on the thermal ellipsoids. The disorder appears to coincide with the presence of small voids around the PFP substituents, that when combined account for 5.7% (251 Å³) of the unit cell, as calculated by PLATON VOID.40

Further analysis with PLATON SQUEEZE40 calculated a residual electron count of 47 e⁻ that corresponds to another possible 0.6 molecules of methanol per molecule of P3. However, their scattering contribution to the overall structure refinement was not removed. The dihedral angle between the substituted phenyl groups varies from 68.4° to 86.3°, with the maximum dihedral angles observed for the two disordered PFP rings. The macrocycles within the crystal structure of P3 are arranged in a slip-stacked formation (Fig. 1f), which is arranged via a number of O⋯H, C⋯H, F⋯H, F⋯F, F⋯N, F⋯C and N⋯H close interactions and, as expected, a large number of the intermolecular interactions observed involve fluorine.

**Cyclic voltammetry of H₂P**

Fig. 2 shows the cyclic voltammograms (CV) of the free base porphyrins in CH₂Cl₂ solutions. H₂Ps showed two quasi-reversible oxidations and two quasi-reversible reductions. The oxidations exhibited E_{1/2} potentials that are referred to the SHE as follows: +1.671 V and +1.836 V for P1, +1.632 V and +1.866 V for P2 and +1.829 V and +2.023 V for P3. Reductions were observed at E_{1/2} = -0.942 V and -0.536 V for P1, -0.972 V and -0.608 V for P2 and -0.853 V and -0.447 V for P3.

These values clearly show a similar redox behavior for P1 and P2, which is expected since they have the same substituents, and differ only on their geometric configuration, cis or trans, thus offering the same overall outcome to the electronic density of the porphyrin. In contrast, the unsymmetric porphyrin P3 exhibited a significant resistance to oxidation, in agreement with the O⋯H close contacts generated by the association between the methoxy substituents of each porphyrin (Fig. S12-ESI†).
with the presence of a higher number of fluoro-atoms, which causes a strong inductive electron withdrawing effect. The mean potential difference between the two oxidations and between the two reductions for H$_2$Ps are 0.198 V and 0.392 V, respectively. This result is in accordance with analogue cases in the literature for successive mono-electronic ring-centered processes, explained by the formation of porphyrin π-cation/anion radicals and dications/dianions as depicted in Scheme 2.\textsuperscript{44,45} Furthermore, the potential difference between the first oxidation and the first reduction, $\Delta E_{1/2(oxi-red)}$ is a good estimate of the band gap between the frontier orbitals HOMO and LUMO. It was found the following order of decreasing $\Delta E_{1/2(oxi-red)}$: P$_3$ (2.276 V) > P$_2$ (2.240 V) > P$_1$ (2.207 V), in accordance with the higher resistance of P$_3$ towards oxidation. The values for P$_3$ are slightly higher than the 2.23 V observed for the meso-tetraphenylporphyrin [H$_4$(TPP)].\textsuperscript{43} and lower than 2.34 V for 5,10,15,20-tetrakis[pentafluorophenyl]porphyrin [H$_4$(TPFPP)]. All electrochemical data are collected in Table 3.

Cyclic voltammery of MnP

The cyclic voltammograms (CV) of manganese(III) porphyrins showed irreversible oxidations starting at +1.8 V, which were assigned to the electrogenerated cation radicals and the dications of the macrocycle ring (Fig. 2). An irreversible reduction of MnP, probably related to the irreversible oxidations, was seen in the range of −0.35 V to −0.48 V along with quasi-reversible reduction processes between −0.926 V and −0.999 V to produce the monoanion radical and dianions of porphyrins, in that order. Anodic peak potentials of the quasi-reversible electron transfer centered in the manganese ion were observed at +0.440 V, +0.413 V and +0.558 V, for MnP$_1$, MnP$_2$ and MnP$_3$, respectively. The overall electron transfer sequence can be summarized in the following steps: [Mn$^{III}$P$^2+$] $\rightarrow$ [Mn$^{III}$P$^+$] $\rightarrow$ [Mn$^{III}$P] $\rightarrow$ [Mn$^{III}$P$^+$/C$_0^+$] $\rightarrow$ [Mn$^{III}$P$^+$$/C_0^+$].\textsuperscript{44,45}

Ucso$\acute{k}$i and co-workers\textsuperscript{46} reported the electrochemistry of the 5,10,15,20-tetrakis(1,3-benzodioxole)-Mn$^{III}$ porphyrin in dichloromethane and observed a $E_{1/2} = −0.61$ V vs. SHE for the Mn$^{III}$/Mn$^{II}$ couple. This result agrees with the donor character of the dioxole substituent, compared to the substrates reported in this work, making the oxidation of the manganese center an easier process in that case. Also for comparison, $E_{1/2}$ of Mn$^{III}$/ Mn$^{II}$/C$_0$/P$_3$) or one (MnP) were observed in acetonitrile at +0.05 and at +1.75 V vs. SHE, respectively.\textsuperscript{47}

Catalytic studies of MnP1, MnP2 and MnP3 using (Z)-cyclooctene and cyclohexane as substrates

The efficiency of the porphyrins MnP$_1$, MnP$_2$ and MnP$_3$ and the model compounds Mn$_{TPFP}$ and Mn$_{TDMP}$ as catalysts in homogeneous oxidation reactions was tested using the substrates (Z)-cyclooctene and cyclohexane and iodosylbenzene (PhIO) as an oxidant (Fig. 3). It has been previously shown that electron-withdrawing substituents at the ortho position of the meso-phenyl substituents in the porphyrin ring can enhance the catalytic activity of these compounds for oxidation reactions.\textsuperscript{6,7} Hence, Mn$_{TPFP}$ was used as a model catalyst because it is recognized as a highly efficient catalyst in homogeneous oxidation reactions for various substrates.\textsuperscript{48,49} Its enhanced performance can be attributed mainly to its greater stability under oxidative conditions, resulting from the electron-withdrawing nature of the PFP substituent, which protects, to some extent, the self-destruction of the porphyrin ring. On the other hand, Mn$_{TDMP}$ was used as an opposing model catalyst for comparison because it contains only the highly electron-donating DMP substituents.

The molecule (Z)-cyclooctene is a useful diagnostic substrate as it is easily oxidized in the presence of metalloporphyrins, with (Z)-cycloocteneoxide usually being the sole product of reaction.\textsuperscript{18-20} The catalytic activity of the new manganese(II) porphyrins MnP$_1$, MnP$_2$ and MnP$_3$ using (Z)-cyclooctene as a substrate resulted in similar product yields. The new unsymmetric manganese(II) porphyrins also showed analogous catalytic activity to that observed for the completely symmetric porphyrin Mn$_{TPFP}$ (~86%) (Fig. 4). This result suggests that the presence of two (MnP$_1$ and MnP$_2$) or one (MnP$_3$) 3,4-dimethoxy groups...
in the structure of the new synthesized metalloporphyrins does not seem to interfere in their catalytic activity for the oxidation of (Z)-cyclooctene. However, the catalytic activity of the completely symmetric MnTDPMP was lower (~73%), which can be attributed to the absence of electron-withdrawing substituents in this porphyrin.50

Cyclohexane is a less reactive substrate than (Z)-cyclooctene in oxidation reactions and when metalloporphyrins are used as catalysts, both cyclohexanol and cyclohexanone are obtained as major products.10,48–50 The novel metalloporphyrins reported here have shown alcohol selectivity in the cyclohexane oxidation (Fig. 5), which is in agreement with reported results of homogeneous catalysis using other metalloporphyrins.48–50

For the cyclohexane reactions it was possible to observe a trend in the catalytic activity of the fluorine-substituted metalloporphyrins which increased with an increasing number of pentafluorophenyl substituents present in the porphyrin: MnP1 ~ MnP2 (~40% yield for alcohol) < MnP3 (~49%) < MnTPFPP (~54%). The low catalytic activity of the MnTDMPP (~14%) under the reaction conditions is associated with the absence of bulky or electron-withdrawing substituents at the ortho position of the meso-phenyl macrocycle, which is in agreement with results obtained previously using a similar porphyrin structure.50

The oxidation peak potentials (Epa) values of MnP1 (+0.440 V), MnP2 (+0.413 V) and MnP3 (0.558 V) (Table 3) correlates well with their increasing catalytic activity, in that order, towards the oxidation of cyclohexane (Fig. 5). The similarity of Epa for MnP1 and MnP2 agrees with the close yields (~40%) observed for the cyclohexanol production, while MnP3 showed a 49% yield for the alcohol. The higher reduction potential of MnP3 compared to the other metalloporphyrins herein reported means that the active intermediate containing the high valent manganese51–53 IV or V Mn=(O)P3 is a better oxidant agent due to the increased number of pentafluorophenyl groups in the porphyrin composition, thus, in the course of the reaction, it favors the oxygen transfer to the substrate. Furthermore, the pentafluorophenyl substituents protect the porphyrin from oxidative damage, increasing the turnover numbers and helps increase the yields of the oxidation reactions.

![Fig. 3](image-url) Structures of porphyrins MnP1, MnP2 and MnP3, and the model compounds MnTPFPP, MnTDMPP used as catalysts for (Z)-cyclooctene and cyclohexane oxidation reactions.

![Fig. 4](image-url) (Z)-Cyclooctene oxidation reaction using PhIO catalyzed by MnP1, MnP2, MnP3, MnTPFPP and MnTDMPP. Catalyst/PhIO/ Substrate molar ratio = 1 : 10 : 1000. The product yields were calculated based on the amount of PhIO used in the reactions. Results represent reactions performed in duplicate.
Conclusions

In this work the synthesis, characterization and crystal structure of three unsymmetrical free base porphyrins [P1, P2 and P3] are reported. The catalytic activity of the metallated unsymmetrical porphyrins MnP1, MnP2 and MnP3, together with the electrochemical studies, showed that the number of pentafluorophenyl groups on the metalloporphyrin structure (two or three) has a direct influence on their catalytic activity in homogeneous medium. The compound MnP3, which has three pentafluorophenyl in its structure, showed better catalytic results, similar to the MnTPFPP, and also higher reduction potential compared to the other metalloporphyrins herein reported. These porphyrins are interesting precursors for the design of well-defined new materials, with a focus towards the construction of PIMs that combine high surface area with recognized catalytic properties of metallated porphyrins.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors are grateful to Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) – Science without Borders, Fundação Araucária and Universidade Federal do Paraná (UFPR) for financial support and the authors thank the EPSRC (grant EP/N01331X/1) for funding. Kátia C. M. Westrup thanks Fundação Araucária and Capes for the postdoctoral scholarship (Convenio 396/2014 – Projeto 41060 – SIT 21045). The authors are also grateful to The University of Edinburgh and acknowledge beam line I19 of the Diamond Light Source (DLS), UK, for assistance in obtaining crystallographic data.

References


