

Supramolecular assemblies of phenolic metalloporphyrins: Structures and electrochemical studies

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ABSTRACT: The reactivity of two phenolic porphyrins bearing respectively catechol and gallol-derived *meso* substituents (5,10,15,20-tetrakis(3,4-dihydroxyphenyl)porphyrin and 5,10,15,20-tetrakis(3,4,5-trihydroxyphenyl)porphyrin) with trivalent metallic ions (Fe, Mn, In) was studied. Six supramolecular compounds were obtained and structurally characterized by single crystal X-ray diffraction. In each compound, the supramolecular assembly was based on the axial coordination of a phenolate function to the metallic ion lying in the porphyrinic core. A great diversity of supramolecular architectures was accessible through such simple arrangements, and objects ranging from dimers to one-dimensional polymers were isolated. Some of these assemblies were further investigated in solution by mass spectrometry and by UV-vis absorption spectroscopy. For the iron-based materials, the redox behavior was studied in solution through cyclic voltammetry experiments in inert conditions and under air.

KEYWORDS: supramolecular assembly, axial coordination, crystallography, structural studies, electrochemistry.

INTRODUCTION

Hybrid porphyrin and metal-based crystalline assemblies trigger interest in numerous areas such as materials chemistry [1–3], photophysics [4–6], sensor design [7–9] and catalyst development [10], the key point being that the structural control on a supramolecular level allows rationalization of the properties in such architectures. In our work on porphyrin-based porous metal-organic frameworks, we have aimed to develop coordination polymers with enough chemical stability to be considered for applications in catalysis [11–13] and electrocatalysis [14]. Given that the wide majority of

MOFs are built up using polycarboxylic acids such as terephthalic acid as organic linkers, it appears natural that TCPP (5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin)based MOFs have been the most studied examples [15]. Still, many such materials suffer from a lack of stability towards hydrolysis [16]. Therefore we recently focused on developing porphyrin-based hybrid frameworks built up from phenolate-cation rather than carboxylate-cations bonds. Interestingly, an unprecedented chemical stability was demonstrated for MOFs based on trioxobenzene ligands [17–19]. More specifically, we recently reported a particularly stable MOF, MIL-173, based on 5,10,15,20-tetrakis(3,4,5-trihydroxyphenyl)porphyrin (H₁₄TGP) and Zr^{4+} or RE³⁺ (RE: rare earth), which demonstrated catalytic activity for the aerobic oxidation of hydrocarbons [13]. In our quest to discover new coordination polymers based on oxyphenylporphyrins,

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we further explored the reactivity of both (H_{14} TGP) and 5,10,15,20-tetrakis(3,4-dihydroxyphenyl)porphyrin (H_{10} TCatP) with trivalent metals such as Fe, Mn and In.

It is of interest to consider the different possibilities of assembling porphyrinic ligands with metallic ions and specifically to differentiate two types of supramolecular structures based on whether they are built up from a unique building unit or two different components. In open-framework structures, external units are linked to the porphyrins or metalloporphyrins by coordination functions at the aryl meso positions. In this case the material is made up from two distinct building units: an inorganic one (metal site) and a ligand (porphyrin or metalloporphyrin), where each porphyrin is acting like a bridging unit between external inorganic units (Fig. 1, top). Another possibility to obtain supramolecular porphyrinic assemblies is through axial binding of one metalloporphyrin to the central metal ion of another; this way the resulting architecture consists of a supramolecular assembly of a single building unit (Fig. 1, bottom). Note that the dimensionality or the porosity of the resulting compound is not an inherent property of one or another type of coordination assemblies. In fact, discrete, 1D, 2D or 3D structures, as well as cage-like porous structures. can be obtained with either assembly mode, although better stability towards desolvation and the highest specific surface areas have always been achieved through the external coordination mode.

As stated earlier, the metal organic framework MIL-173 built up from H_{14} TGP and Zr or RE was first obtained in solvothermal conditions in a DMF/water mixture. When switching to lighter trivalent cations (Mn, Fe, In), formation of crystalline phases was again observed in solvothermal conditions but only using DMF/water mixtures with much higher water content, for both H_{10} TCatP and H_{14} TGP porphyrinic ligands. Unlike MIL-173, in the current study the observed coordination mode was through axial binding of one metalloporphyrin to another, and four distinct crystalline arrangements ranging from dimers to polymers were obtained. Herein we report the synthesis and structural characterizations in the solid state, and spectroscopic data in solution for self-assembled materials based on hydroxophenyl porphyrins. To the best of our knowledge, with the exception of 5,10,15,20-tetrakis(4hydroxyphenyl)porphyrin-manganese(III) [20]. no related structures have so far been reported. Nonetheless, phenolic porphyrins have been of interest in a number of studies regarding properties such as electrochemical behavior for catechol-functionalized porphyrins, [21, 22] supercapacitive catechol-porphyrin-derived materials [23], thin film assemblies of gallol-porphyrins [24] and other phenolic porphyrins have been studied for solar energy conversion [25]. In all these studies the exact structure of the molecular material is unknown; therefore our work paves a way to more precise knowledge about supramolecular arrangements of phenolic porphyrins, aiming to promote further fruitful studies in these fields.

EXPERIMENTAL

Synthesis

General methods. All reagents were purchased from Sigma–Aldrich[®] and used without further purification. ¹H NMR spectroscopy was performed on an AVS 300 Bruker spectrometer at the Centre Commun de RMN at the University of Claude Bernard Lyon 1.

Synthesis of porphyrins

5,10,15,20-*tetrakis*(3,4,5-*trihydroxyphenyl*)*porphyrin* ($H_{14}TGP$). ($H_{14}TGP$) was synthesized as previously



Fig. 1. Schematic representation of two possible types of coordination compounds built up from a porphyrin and a metallic center. Top: assemblies through external coordination based on two building units. Down: assemblies through axial ligation based on one building unit

reported [24]. The porphyrin is isolated in solid state as a protonated product with bromide counter-ions. The overall yield of the synthesis was 15%. NMR ¹H (DMSO-d₆, 300 MHz) δ /ppm: -0.11 (s, 4H, NH), 7.61 (s, 8H, phenyl H), 8.58 (s, 8H, porphyrin β –H), 9.72 (broad s, 12H, OH); ESI-MS (m/z): 807.2 [M–H]⁺ 887.1 [M–2H– Br]⁺ UV-vis (DMF) λ_{max} /nm: 430 (Soret), 522, 560, 598, 655 (Q bands).

5,10,15,20-tetrakis(3,4-dihydroxyphenyl)por**phyrin** ($H_{10}TCatP$). The synthesis of $H_{10}TCatP$ was inspired by previously reported procedures [22, 23] and can be achieved from demethylation of either 5,10,15,20-tetrakis(3-methoxy-4-hydroxyphenyl) porphyrin or 5,10,15,20-tetrakis(3,4-dimethoxyphenyl) porphyrin by boron tribromide in anhydrous conditions. In a typical procedure, (0.925 g, 1.16 mmol) of 5,10,15,20-tetrakis(3-methoxy-4-hydroxyphenyl)porphyrin was dissolved in anhydrous dichloromethane (100 mL) in a round bottom flask and an inert atmosphere was established. Then boron tribromide (20.0 mL of 1M solution, 20.0 mmol) was slowly added at -70 °C and the reaction mixture was maintained at this temperature for 1 h. Then the reaction was left to reach room temperature and allowed to proceed for 20 h. Then the reaction was quenched by adding ice-cooled water. Saturated NaHCO₃ solution was added to the greenish reaction mixture followed by ethyl acetate, and the organic layer was separated and dried with anhydrous sodium sulfate. The solid obtained from evaporating the organic layer was washed with dichloromethane. The purple colored product was obtained *via* filtration (560 mg, 0.755 mmol, 65% yield). NMR ¹H (DMSO-d₆, 300 MHz) δ /ppm: -2.91 (s, 2H, NH), 7.18 (d, 4H, phenyl H, J = 7.9 Hz), 7.46 (d, 4H, phenyl H, J = 8.5 Hz), 7.59 (s, 4H, phenyl H), 8.90 (s, 8H, porphyrin β –H), 9.40 (d, 8H, OH, J =10.4 Hz); ESI-MS (m/z): 743.2 [M–H]⁺ 372.1 [M–2H]²⁺ UV-vis (DMF); λ_{max}/nm: 427 (Soret), 520 561, 596, 654 (Q bands).

Synthesis of supramolecular compounds

Compound 1 [FeH₇CatP]₂·xH₂O. 5,10,15,20-tetrakis-(3,4-dihydroxyphenyl)porphyrin (H₁₀TCatP) (40 mg, 0.05 mmol) was dissolved in a 5 mL mixture of H₂O/ DMF (v/v = 4:1) in a 12 mL glass vial. To the resultant mixture, FeCl₃·6H₂O (30 mg 0.11 mmol) was added and the mixture was sonicated for 5 min at room temperature. Afterwards, the suspension was heated at 120 °C for 48 h, where the temperature was increased over 4 h and then cooled down to room temperature over 4 h. The solid was recovered by vacuum filtration, washed thoroughly with deionized water until the washed solution was colorless. After drying, compound **1** was obtained as a dark crystalline solid in 82.5% yield based on the chemical formula (33 mg of product).

Compound 2 [*FeH*₇*CatP*]₄·*xH*₂*O*. 5,10,15,20-tetrakis-(3,4-dihydroxyphenyl)porphyrin ($H_{10}TCatP$) (40 mg,

0.05 mmol) was combined with pyrocatechol (200 mg, 1.82 mmol) in a 5 ml mixture of H_2O/DMF (v/v = 4:1) in a 12 mL glass vial. A FeCl₃·6H₂O (30 mg 0.11 mmol) was added and then the mixture was sonicated for 5 min at room temperature. Afterwards, the suspension was heated at 120 °C for 48 h, where the temperature was increased over 4 h and then cooled down to room temperature over 4 h. The solid was recovered by filtration, washed thoroughly with deionized water until the washed solution was colorless. After drying, the MOF was obtained as a dark crystalline solid in a 90% vield (36 mg of product).

Compound **3** [*In*(H_7TCatP)]_n· xH_2O . 5,10,15,20-tetrakis-(3,4-dihydroxyphenyl)porphyrin ($H_{10}TCatP$) (40 mg, 0.05 mmol) was combined with pyrocatechol (500 mg, 4.5 mmol) and InCl₃· $6H_2O$ (70 mg, 0.2 mmol) in a 5 ml mixture of H_2O/DMF (v/v = 4:1) in a 20 mL Teflon reactor that was inserted into an autoclave. The reaction mixture was heated at 160 °C for 48 h with 6 h heating and cooling time. The solid was recovered by filtration under vacuum. Due to the presence of indium hydroxide as impurity the final yield was not determined for this solid.

Compound 4 $[Mn(H_{11}TGP)]_n \cdot xH_2O.$ 5,10,15,20tetrakis(3,4,5-trihydroxyphenyl)porphyrin (H₁₄TGP) (40 mg, 0.05 mmol) was combined with MnCl₂·4H₂O (30 mg, 0.15 mmol) in a 4 mL mixture of H₂O/DMF (v/v = 4:1) in a 8 mL glass vial. The mixture was sonicated for 5 min and was heated at 120 °C for 48 h with 3 h heating and cooling time. The solid was recovered by filtration, washed with deionized water then ethanol. The compound was obtained as a dark crystalline solid in a 58% yield (25 mg of product).

Compound 5 $[Fe(H_{11}TGP)]_n \cdot xH_2O.$ 5,10,15,20tetrakis(3,4,5-trihydroxyphenyl)porphyrin (H₁₄TGP) (40 mg, 0.05 mmol) was combined with FeCl₂·4H₂O (30 mg, 0.15 mmol) in a 4 mL mixture of H₂O/DMF (v/v = 4:1) in a 8 mL glass vial. The mixture was sonicated for 5 min and was heated at 120 °C for 48 h with 3 h heating and cooling time. The solid was recovered by filtration, washed with deionized water then ethanol. The compound was obtained as a dark crystalline solid in a 62% yield (27 mg of product).

Compound 6 $[In(H_{11}TGP)]_n \cdot xH_2O.$ 5,10,15,20tetrakis(3,4,5-trihydroxyphenyl)porphyrin (H₁₄TGP) (40 mg, 0.05 mmol) was combined with InCl₃ (39.8 mg, 0.18 mmol) in a 5 mL mixture of H₂O/DMF (v/v = 4.5:0.5) in a 20 mL Teflon reactor that was inserted into an autoclave. The mixture was heated at 120 °C for 48 h with 6 h heating and cooling time. The solid was recovered by filtration under vacuum.

Single crystal diffraction

For compounds 1, 2, 3 and 6, suitable crystals were selected and mounted on a Geminini Oxford Diffractometer equipped with an Atlas CCD detector and using Mo radiation ($\lambda = 0.71069$ Å) for 1, 2 and 3

and using Cu radiation ($\lambda = 1.54056$ Å) for compound 6. Intensities were collected at room temperature for compounds 1 and 2 and at 100K for compound 3, by means of the CrysalisPro software [26]. Reflection indexing, unit-cell parameters refinement, Lorentzpolarization correction, peak integration and background determination were carried out with the CrysalisPro software [26]. An analytical absorption correction was applied using the modeled faces of the crystals. All the structures were solved by direct methods using SIR97 [27] and the least-squares refinement on F² was achieved with the CRYSTALS software [28]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C---H in the range 0.93-0.98 Å and $O_{---}H = 0.82$ Å) and $U_{iso}(H)$ (in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints. Residual electronic density between the metalloporphyrins was located but could not be modelled. The contribution of the disordered solvent molecules was removed using the SQUEEZE algorithm [29].

Crystal data of compound 5 was analyzed at room temperature using a Bruker-Nonius Kappa CCD diffractometer working at the Mo K α radiation. The Bruker AXS "Collect" suite was used to integrate and scale intensities, and a semi-empirical absorption correction (SADABS) was applied on the basis of multiple scans of equivalent reflections. For compound 4, only microcrystals could be obtained. Data were thus collected on the CRISTAL beamline at Synchroton Soleil, using a set-up adapted for small crystals at 100 (2) K on an Xcalibur, Atlas four-circle diffractometer and equipped with a CCD plate detector. Data reduction was performed using CrysAlis. An empirical absorption correction was applied using spherical harmonics on the basis of multiple scans of equivalent reflections, implemented in SCALE3 ABSPACK scaling algorithm. Both structures of 4 and 5 were solved by direct methods using SHELXS-97 and refined with the full-matrix least-squares routine SHELXL [30]. Free solvent molecules were discarded using the SQUEEZE procedure [29]. Non H-atoms were refined anisotropically, whereas H atoms were added as rigid bodies. In compound 5, Fe cations were found disordered over two positions related by an inversion center.

Powder diffraction

Powder X-Ray diffraction (PXRD) for compounds 1, 2, 3, and 6 was performed on a PANanlytical XpertPro MRD diffractometer with Cu K α 1 radiation (λ = 1.540598 Å) used with 40 kV and 30 mA settings in θ/θ mode, reflection geometry. PXRD data of compounds 4 and 5 were collected at 293 K on a Siemens D5000 diffractometer using CuK α radiation (λ = 1.5418 Å). The patterns were scanned over the angular range 5–30° (2 theta) with a step length of 0.02° (2 theta).

UV-vis measurements

UV-vis absorption spectra were recorded with a Perkin Elmer Lambda 1050 spectrophotometer with a 3D WB detector module with DMF solutions of compounds 1-5 with a concentration range of 4.10^{-4} to 4.10^{-5} mol·L⁻¹.

Mass spectrometry

Mass spectrometry was performed on a Bruker MicrOTOFQ II in electrospray ionization mode (ESI) at the Centre Commun de Spectrométrie de Masse at the University Claude Bernard Lyon 1.

Electrochemistry

Solvents and reagents were available commercially and were used without further purification. Electrochemical measurements were performed using an Origalys allin-one potentiostat and a standard three-electrode setup with a glassy carbon electrode GCE (diameter: 3 mm), platinum wire auxiliary electrode and a SCE (Saturated Calomel Electrode) as reference electrode. DMF solution concentrations of the compound during the study were between 1.0 to 2.0 mM and *n*-Bu₄NPF₆ 0.1 M was used as supporting electrolyte. The voltage scan rate ranged from 0.1 to 0.5 V · s⁻¹. Considering these experimental conditions, the ferrocene/ferricinium couple, used as internal reference for potential measurements, was located at $E_{1/2} = 0.445$ V.

RESULTS AND DISCUSSION

Synthesis and structure analysis

Reactions with porphyrins bearing catechol coordinating functions ($H_{10}TCatP$) were attempted with Fe³⁺ and In³⁺ salts in DMF/water solvent mixtures at 120 °C, both with and without the addition of pyrocatechol. Small monotopic ligands such as pyrocatechol can be used in the synthesis of coordination assemblies as coordination modulators. In fact, they can be seen as competing additives that would slow down the reaction between the metal ions and the multitopic ligands and therefore favor single crystal growth or preferential growth orientations allowing to tune crystal morphology. This approach proved to be effective in the synthesis of crystalline carboxylate-based MOFs [31-34]. In the present case, single crystals were obtained both with and without the addition of pyrocatechol, but the crystal structures differed. In fact, reacting only the porphyrin with an excess of iron salt led to the crystallization of iron-porphyrin dimers (compound 1) while the same reaction in the presence of an excess of pyrocatechol resulted in the formation of tetrameric metalloporphyrin assemblies (compound 2, see below). When In^{3+} was used instead of Fe³⁺ in the presence of pyrocatechol



Scheme 1. Chemical structures of the phenolic porphyrins H₁₀TCatP (left) and H₁₄TGP (right) used in this work



Fig. 2. PXRD patterns for compounds 1 (a), 2 (b), 4 (c) and 5 (d). Black: calculated pattern from single crystal structure; grey: experimental pattern

a polymeric phase was obtained instead of discrete assemblies (compound **3**).

Similar reaction conditions (solvents, temperature) were applied to H_{14} TGP, this time employing pyrogallol as a modulator. Using both Mn^{2+} and Fe^{2+} salts as reactants, almost identical polymeric chains based on M^{3+} were obtained (compounds **4** and **5** respectively). Finally, a similar structure (compound **6**) was obtained when using InCl₃ as a precursor.

In case of In-based compounds (**3** and **6**), very low yields were obtained, along with co-crystallization of $In(OH)_3$, and the synthesis was poorly repeatable, hence precluding their full characterization. On the opposite, all iron and manganese-containing solids (**1**, **2**, **4** and **5**) were obtained in a pure form as confirmed by powder X-Ray diffraction of the

bulk samples (Fig. 2) and on a scale that allowed further investigations of their spectroscopic and redox properties (see below).

Structures of compounds **1–6** were solved from single crystal X-ray diffraction. These solids all contain solvent molecules which were discarded using the SQUEEZE procedure [29]. The cif files for the structures of compounds **1–6** can be obtained from the Cambridge Structural Database with reference numbers respectively: CCDC 1886722, CCDC 1886720, CCDC 1886719, CCDC 1886617, CCDC 1886616 and CCDC 1886721.

All solids present common features, notably the same stoichiometry, namely one M^{3+} cation for one porphyrin core, corresponding to the formula $M(H_7TCatP) \cdot xH_2O$ (compounds 1–3) and $M(H_{11}TGP) \cdot xH_2O$ (compounds 4–6), whatever the metal: ligand ratio used in the course



Fig. 3. The metallo(III) porphyrins in compounds 1 (top) to 6 (bottom), with the mean plane defined by the four nitrogen atoms shown in green. For compounds 2 and 3, the two crystallographically independent molecules are pictured

of the synthesis. The metallic ion was exclusively inserted inside the porphyrinic core and the supramolecular architectures were built through axial coordination of a phenolate substituent of one metalloporphyrin to the metallic center of another. The exact position of the cation depends on the nature of M (Fig. 3). For the solids built up from Fe (compounds 1, 2 and 5), the cation lies slightly outside of the porphyrinic ring (distances from the mean plane defined by the four N atoms are equal to 0.3977 (9) (1), 0.3879 (3) and 0.4258 (3) (2), and 0.320 (2) Å (5)). Its coordination is completed by a phenolate group arising from a neighboring molecule, leading to a square pyramidal coordination environment. In compound 4, the Mn ion adopts the same coordination geometry, although lying that time almost perfectly in the porphyrinic plane (distance from the mean plane defined by the four N atoms is equal to 0.0889(4) Å). In all cases, M-O and M-N bond distances are in the expected range, and in accordance with a +3 oxidation state, as confirmed by bond valence calculations (see Table 1 for bond distances and bond valence calculations). One can also mention the presence of another oxygen atom occupying

the second axial position in compounds 4 and 5, but at a distance too long (>2.5 Å) to correspond to an anionic ligand; hence, this oxygen arises from a neutral phenolic group, again in line with the bond valence calculations (see Table 1). When increasing the size of the cation (In), a truly octahedral coordination is sometimes observed. This is the case for compound **6**, as well as for half of the porphyrins in compound **3** (see Fig. 3 and Table 1). Here again, In-N and In-O bond distances are in agreement with those found in the literature for indium porphyrin, although bond valence calculations overestimate the charge of the cation. With a single exception (half of the molecules are fully planar in compound 3), the porphyrin cores present nonplanar deformations (Fig. 3). In catecholate-based compounds, porphyrins display a mainly saddle type deformation, with a more marked deformation in Fe-based (compounds 1 and 2) than In-based (compound 3) solids. For the gallate-based porphyrinic assemblies, only a wave-type deformation is observed (compounds 4-6). In compounds 2-6, C-O bond distances typical of the phenolic moieties are observed (1.34–1.40 Å), confirming that catechol

Compound	Distances M–N (Å) Bond valence				Distances M–O (Å) Bond valence		Total bond valence for M ⁿ⁺
1 (Fe)	2.034 (5) 0.6	2.039 (4) 0.6	2.059 (4) 0.6	2.061 (5) 0.5	1.882 (4) 0.7	>3	3.1
2 (Fe)	2.053 (2) 0.6	2.053 (2) 0.6	2.057 (2) 0.6	2.059 (2) 0.6	1.875 (2) 0.7	>3	3.1
	2.035 (2) 0.6	2.047 (2) 0.6	2.050 (2) 0.6	2.052 (2) 0.6	1.916 (1) 0.7	>3	3.1
3 (In)	2.109 (4) 0.8	2.109 (4) 0.8	2.117 (4) 0.8	2.117 (4) 0.8	2.255 (3) 0.4	2.255 (3) 0.4	4.0
	2.119 (4) 0.8	2.124 (4) 0.8	2.131 (4) 0.8	2.144 (4) 0.7	2.095 (4) 0.6	>3	3.6
4 (Mn)	1.998 (3) 0.7	1.998 (3) 0.7	2.003 (3) 0.7	2.011 (3) 0.7	2.159 (3) 0.3	2.528 (3) 0.1	3.3
5 (Fe)	2.026 (3) 0.6	2.033 (3) 0.6	2.039 (3) 0.6	2.047 (3) 0.6	2.023 (4) 0.5	2.660 (4) 0.1	3.1
6 (In)	2.081 (8) 0.9	2.081 (8) 0.9	2.114 (8) 0.8	2.114 (8) 0.8	2.416 (8) 0.3	2.416 (8) 0.3	3.8

Table 1. M–N and M–O bond lengths and corresponding bond valences (calculated from [35])

and gallol functionalities are not oxidized into quinone during the course of synthesis. For compound **1**, shorter C–O bond distances (1.25–1.27 Å) occur in one fourth of the catechol substituents, suggesting a partial oxidation. Nevertheless, such an oxidized compound was not detected by mass spectrometry (see below).

Although the way the metalloporphyrins interact with each other in the solid state through M–O bonds strongly depends on the nature of the cation and functional groups (catechol vs. gallol), as well as on the conditions of crystallization, again common features can be found. Note here that only anionic O atoms giving rise to short M–O distances (<2.5 Å) are taken into account. All structures built up from H₇TCatP are made of the same centrosymmetric dimer, constructed from doubly connected porphyrins (pictured in blue and pink in Fig. 4). In compound 1, these dimers remain isolated from each other (Figs 4-1), whereas in compound 2, both metalloporphyrins from one dimer connect to a new molecule (green and yellow) through a phenolate group, defining a tetramer (Figs 4-2). Eventually, when moving to compound 4, thanks to the octahedral coordination of In inserted in these extra porphyrins, they bind again to another dimer, giving rise to a chainlike coordination polymer (Figs 4–3). For the H₁₁TGPbased solids, all compounds crystalize in the same unit cell and define very similar chain-like motifs built up from a single type of metalloporphyrin, reminiscent of those observed with the related ether-functionalized 5,10,15,20-tetrakis(3,4,5-trimethoxyphenyl)porphyrinmagnesium and zinc [36]. Depending on the nature of the cation, these metalloporphyrins are either singly (compound 4) or doubly (compound 6) connected (Fig. 5). The case of compound 5 is more complex: the iron cation is disordered over two positions lying on both sides of the porphyrinic core. Hence, depending on the sequence of occupied positions, an infinite variety of motifs is defined, ranging from isolated dimers (similar to compound 1), oligomers of various lengths, to infinite chains (identical to compound 4).

As already mentioned, the catechol and gallol moieties are only partially deprotonated. For the structures built up from H_7TCatP (compounds 1–3), the aforementioned dimer involves oxygen atoms in *meta* position of the porphyrin ring, whereas the most acidic group, namely the oxygen atoms in para position, are deprotonated only in compounds 2 and 3 to further form the tetramer and chain-like motifs. Similarly, the most acidic proton in the gallol moieties is the one located in *para* position [37], and this is the first being deprotonated in previously reported MOFs [18, 19, 38]. In the present work, the deprotonation only occurred in the *meta* position. Hence, the protonation state in the final structure of compounds 1-6 is not governed by the relative values of the pKa, but more likely by an optimization of the molecular packing. Indeed, connection through the oxygen atoms in *para* position would lead to perpendicular porphyrin rings and thus very open structures, while the connection through the oxygen atoms in meta position affords closer contacts between adjacent porphyrins.

Characterizations in solution

As described above, compounds 1, 2, 4 and 5 were obtained in good yield as pure phase crystalline materials. It was nevertheless found that these solids could



Fig. 4. Assemblies of MH_7TCatP in compounds 1 (dimer), 2 (tetramer) and 3 (chain). Left: atomic structures (for the sake of clarity, H atoms are omitted, and only one position is shown for the disordered catechol groups). Right: corresponding coordination paths



Fig. 5. Chain-like assemblies of $MH_{11}TGP$ in compounds **4 to 6**. Left: atomic structures (for the sake of clarity, H atoms are omitted, and only one position is shown for the disordered cation in compound **5**). Right: corresponding coordination paths

redissolve in DMF. Unsurprisingly, discrete compounds 1 and 2 were more readily dissolved than the polymeric assemblies 4 and 5, however, with time all the above cited materials appear soluble in DMF. Discrete compounds 1 and 2 could be analyzed by mass spectrometry, whereas the polymeric compounds 4 and 5 did not give any usable spectra, presumably due to the difficulty of ionizing polymeric assemblies. The spectroscopic properties of all samples were assessed by UV-vis absorption and the redox properties of iron-containing architectures were evaluated by cyclic voltammetry.

Mass spectrometry

Discrete assemblies based on iron and catecholate porphyrin 1 and 2 could be analyzed by electrospray ionization mass spectrometry (MS). The data obtained for the tetrameric compound 2 display a distribution of mass to charge m/z signals corresponding to the parent doubly charged tetrameric molecular ion $([2 - H + Na)^{2+})$ at 1603 m/z, $[2]^{2+}$ at 1591.7 m/z) and additional signals corresponding to m/z of trimeric ([C132H83Fe3N12O24]2+ at 1194 m/z), dimeric ($[C_{88}H_{54}Fe_2N_8O_{16}]^{2+}$ at 1592.2 m/z and monomeric (m/z at 796.1) compounds (see ESI Sec. 2). Although it cannot be clearly concluded at the current stage whether these latter complexes are originating from the fragmentation of the tetramer during the electrospray or are already present in equilibrium in solution, this proves that the supramolecular assembly 2 observed in solid state does exist in DMF solution. Therefore, intermolecular interactions are strong enough to be at least partially preserved when the solid is dissolved even at high dilution. In case of compound 1, the observations were similar. At first sight, the main signals originated from the monomer and dimer singly charged molecular ions at 796.1 and 1592.2 m/z respectively. When the compound at 1592.2 m/z was selected for the MS/MS experiment, the resulting product ion corresponded as expected to the monomeric form with the signal at 796.1. More importantly, a closer look at the m/z region around the dimeric molecular ion revealed the presence of signals originating from the doubly charged tetrameric assembly at 1591.7 m/z as described previously. Therefore the MS analysis implies that when dissolved in DMF, compounds 1 and 2 are hardly distinguishable and a dynamic equilibrium between monomeric and oligomeric forms is established. Moreover, for both samples, signals corresponding to species with a loss of one or more Fe atoms are observed. Metalloporphyrins demetallation has already been observed to happen during the analysis and therefore cannot be considered representative of the sample. Further UV-vis data presented below indeed strongly support a quantitative metal insertion.

UV-vis spectroscopy

Catechol and gallol free-base porphyrins display similar features in their absorption spectra in DMF solution, with a Soret band at 427 and 430 nm respectively (Figs 6a and 6b). As reported before [22] this slightly red-shifted values of the Soret band wavelength (compared to the tetraphenyl porphyrin) is characteristic of the electrondonating effect of the hydroxo substituents on the phenyl rings [39]. In the visible region, as expected, 4 Q bands are distinguished at 520, 561, 596, 654 nm for $H_{10}TCatP$ and 516, 552, 592, 648 nm for $H_{14}TGP$.

The UV-vis absorption spectra of supramolecular compounds derived from iron and $H_{10}TCatP$ (1 and 2), and from $H_{14}TGP$ (5) are presented Fig. 6). For all of these iron containing compounds, very similar spectra are obtained. The reduction of the number of Q bands confirms the metal insertion into the porphyrin core and in each case, two Q bands are visible at 510 and 670 nm. The generally broad bands obtained for 1, 2 and 5 are indicative of supramolecular interactions in solution as bands broadening is commonly observed in case of porphyrin aggregation [40], supporting the presence of oligomers or polymers in solution as established by mass spectrometry.



Fig. 6. Normalized UV-vis absorption spectra of free-base porphyrins and iron-based compounds 1, 2 and 5



Fig. 7. Normalized UV-vis spectra of **4** in the course of time (a) and upon addition of formic acid (b)

The case of compound 4 appeared to be more complex when the UV-vis spectrum was recorded in DMF solution. In fact, a fresh sample displayed a spectrum with two intense absorption bands at 430 and 476 nm along with three less intense bands at 520, 572 and 615 nm (Fig. 7a). Moreover, an evolution of the absorption spectrum was observed when the sample was left in DMF in aerobic conditions: the signal at 430 nm decreased, whereas the band at 476 nm became predominant. As the intense absorption band at 430 nm seemed quite surprising for a Mn(III) porphyrinic compound we first aimed to check whether this could be due to the presence of free-base porphyrin arising from a partial metal insertion in the bulk sample. To check this, formic acid was added to the DMF solution of the free base porphyrin and to a solution of 4. In the former case, no spectral changes were noticed (Fig. S14), while in the latter a sharp decrease of the absorption at 430 nm was observed, leading to a characteristic spectrum of Mn(III) porphyrin with an intense Soret band at 476 nm and two Q bands at 570 and 608 nm along with charge transfer bands at higher energies (430, 404, 385 and 345 nm) (see Fig. 7b). Given that the addition of formic acid did not induce any changes on the absorption of H₁₄TGP but dramatically modified the absorption properties of 4, it was concluded that the absorption signal at 430 nm did not originate from the presence of metalfree compound but is proper to the Mn-based compound 4. Given its pKa (3.75), formic acid is strong enough to protonate the phenolate function in 4, and then favor the decomplexation of the axial gallate ligand. For this reason we believe that the absorption observed at 430 nm originates from the particular coordination of Mn by the redox-active gallate ligand that might induce a charge transfer giving rise to this intense band. Considering this, the data in Fig. 7a indicate that in solution an equilibrium of this axial ligation is reached with time. Still, this axial ligation appears quite stable as diluting a solution of 4 by a factor 100 does not induce any immediate changes (Fig. S12). An absorption band at 430 nm in the case of Mn-porphyrins can also be attributed to the presence of reduced (Mn(II)) or oxidized (Mn(IV)) species. Although this hypothesis seemed very unlikely given that these species are expected to be unstable in air, we wanted to ensure that no redox reaction took place that could reduce a Mn(IV) compound to Mn(III), as formic acid could be oxidized into CO₂. For that purpose, formic acid was replaced by propionic acid, and the same observations were made (see Fig. S13). In light of these combined data we concluded that the absorption band at 430 nm originates from the charge transfer due to the particular axial coordination of the phenolate group to Mn(III).

Electrochemical studies

 H_7TCatP -based compounds **1** and **2** were dissolved in DMF and studied by cyclic voltammetry (CV) at variable scanning rates from $0.1V \cdot s^{-1}$ to $0.5V \cdot s^{-1}$ (all the data presented below are plotted at a $0.1V \cdot s^{-1}$ scanning rate unless specified) using an SCE reference electrode. Both compounds display a characteristic irreversible oxidation peak at 1.18 V associated to an irreversible reduction peak at 0.15 V in reverse voltage scan (Fig. S17). The pattern of these voltammograms corresponds to the well-known oxidation of the catechol moiety in a non-aqueous solvent [41–43] and was observed in case of the free-base $H_{10}CatP$ (see Fig. S17). For these two complexes, the voltammograms also remain similar in the reduction region, as shown in Fig. 8.

Indeed, both compounds display the following signals: a quasi-reversible electrochemical process centered around -0.5 V, a reversible reduction at -1.25 V and an irreversible reduction at -1.9 V. Therefore, **1** and **2** present the same redox properties and cannot be distinguished by cyclic voltammetry in solution, in line with the result of the mass spectrometry data. For this reason, only the data associated with compound **1** will be presented. Given the values of the redox potentials, the first redox process is assigned to the metal-centered redox process when the other two are assigned to the macrocyclecentered electrochemical reactions (see Fig. 8b). Quite



Fig. 8. Cyclic voltammetry at $0.1 \text{ V} \cdot \text{s}^{-1}$ in DMF at GC electrode for (a): **1** (black) and **2** (grey); (b): for **1** (black) and the corresponding free-base porphyrin (grey)

low potentials for [Fe(III) \rightarrow Fe(II)] redox processes are usually observed in the presence of an axial ligand that is strongly coordinated, stabilizing the trivalent state [44]. Therefore this observation corroborates what is observed by mass spectrometry, *i.e.* the retention of supramolecular architectures in solution through a strong M–O axial ligation and quite short bond length.

Then, we focused our attention on this metal-centered monoelectronic reduction (see the cathodic peak C1 on Fig. 8b). This process is not fully reversible since after the reduction, part of the Fe(II) entities undergo an oxidation at a much higher potential of 0.25 V (see A1 vs. A2, Fig. 9) which is itself related to the new reduction peak observed around -0.15 V (C2 on Fig. 9). This result indicates the presence of a general electrochemicalchemical-electrochemical (ECE) process as shown in the equations below, where the "FeIII is first reduced to the ^aFe^{II} complex and the later undergoes a chemical transformation into the **bFeII** complex which is oxidized at 0.25V. Although the exact nature of the ECE process was not elucidated in this case, one can stipulate that the probable change in the axial ligation of the generated Fe^{II} compound would be at least partly responsible for the irreversibility we observe here.



Fig. 9. Cyclic voltammetry of **1** at GC electrode at $0.1 \text{ V} \cdot \text{s}^{-1}$ in DMF under inert atmosphere. C1: first cathodic peak, A1 first anodic peak relating to the C1/A1 redox system; A2: second anodic peak, C2 second cathodic peak relating to the A2/C2 redox system



Fig. 10. Cyclic voltammetry of 1 at GC electrode at $0.1 \text{ V} \cdot \text{s}^{-1}$ in DMF, both under inert atmosphere (grey) and under air (black)

$^{\mathrm{a}}\mathrm{Fe}^{\mathrm{III}} + \mathrm{e}^{\mathrm{-}} \rightarrow ^{\mathrm{a}}\mathrm{Fe}^{\mathrm{II}}$	Electrochemical reduction $E = -0.5V$, C1 with redox system C1/A1
${}^{a}\mathrm{Fe}^{\mathrm{II}} \rightarrow {}^{b}\mathrm{Fe}^{\mathrm{II}}$	Chemical reaction
${}^{\mathrm{b}}\mathrm{Fe}^{\mathrm{II}} \rightarrow {}^{\mathrm{b}}\mathrm{Fe}^{\mathrm{III}}$	Electrochemical oxidation $E = 0.25V$, A2 with redox system C2/A2

When air was bubbled in the electrochemical cell, the reduction peak intensity at -0.5V rose by approximately a factor of 2.5 (Fig. 10) and the oxidation signal was lost, which points to a catalytic activation of oxygen reduction at the potential where Fe(III) is reduced to Fe(II). Given that oxygen reduction in DMF at the GC electrode occurs at -0.77V, compounds 1 and 2 are active electrocatalysts



Fig. 11. Cyclic voltammetry of **5** at GC electrode at 0. $1V \cdot s^{-1}$ in DMF. Left: under inert atmosphere. Right: under inert atmosphere (black) and under air (grey)

for oxygen reduction in DMF. Such catalytic activity is widely known for Fe-based metalloporphyrins [45]. Interestingly, the O_2^{\bullet} generated by the electroreduction catalysis process seems to react with the Fe^{II} compound to give a new entity, which is oxidized at 0.3V. This is not surprising as oxygen activation by iron porphyrins was often described as an irreversible process, for example leading to Fe-O-O-Fe dimers after oxygen binding to the metallic center [46]. Moreover, the cyclic voltammetry at 0.1 V \cdot s⁻¹ exhibits a continuous increase of all of the current density upon cycling; this is presumably due to an increase of the electrode conductivity originating from the deposition of a conductive material on the electrode surface, as visually observed during the experiment. The mechanism associated to the oxygen activation appears to be complex and is currently under investigation in our laboratory.

When the gallol-based polymeric compound **5** was studied by CV at a $0.1V \cdot s^{-1}$ scanning rate in DMF, two irreversible oxidation waves characteristic of gallol moiety oxidation in non-aqueous solvents were observed

at 0.98 V (Fig. S16) [47, 48]. In the reduction scan, two signals are observed: first an almost irreversible peak at -0.51 V ascribed to Fe(III) reduction and a second wave at -1.25 V (Fig. 11a). This second reduction is associated to a thin and intense oxidation peak at -1.18 V characteristic of a redissolution. As previously, we focused on the first reduction process; here, the system appears practically irreversible (Fig. S15). In the presence of atmospheric oxygen, a large reduction peak appears close to -0.51 V, characteristic of a catalytic oxygen activation (Fig. 11b), as observed for compounds 1-2. However, upon multiple cycling, the intensity of the oxidation peak at $0.1 \,\mathrm{V}\cdot\mathrm{s}^{-1}$ dramatically decreases, probably because of the deposition of an insulating film on the electrode surface. To summarize, the electrochemical behaviors in solution of all Fe-based compounds appear to be very similar under inert atmosphere. Under oxygen atmosphere, even if a catalytic activation of oxygen is observed for all compounds, this complicated mechanism seems to lead to opposite results upon multiple cycling, namely the deposition of a conducting film for compounds 1 and 2, and an insulating one for compound 5.

CONCLUSION

In conclusion, six new supramolecular assemblies based on phenolic porphyrins were synthesized and structurally characterized. Their arrangements in the solid state and their behaviors in solution were studied and redox active iron-based compounds were electrochemically investigated. By tuning synthesis conditions, the nature of the trivalent metallic cation and the number of hydroxo functionalities on the phenyl *meso* positions, a broad diversity of structural arrangements was obtained, even if all of them are based on one only metalloporphyrin as a building unit. We believe that coordination assemblies based on phenolic porphyrins should be further explored for a deeper understanding of the reactions mechanisms and physico-chemical (notably redox) behaviors of these non-innocent ligands.

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Supporting information

Single crystal X-Ray diffraction, mass spectrometry, UV-vis spectroscopy and electrochemistry for the examined compounds are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under numbers CCDC-1886722, CCDC-1886720, CCDC-1886719, CCDC-1886617, CCDC-1886616 and CCDC-1886721. Copies can be obtained on request, free of charge, *via* http://www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or email: deposit@ccdc.cam.ac.uk)

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