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Porphyrinic Coordination Polymer-Type Materials as Heterogeneous Catalysts in Catechol Oxidation

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Abstract

Coordination Polymer-type materials obtained from the reaction of 5,10,15,20-tetrakis[2,3,5,6-tetrafluoro-4-(4-pyridylsulfanyl)phenyl]porphyrin (H_2P1) and 5,10,15,20-tetrakis(4-pyridyl)porphyrin (H_2P2) with copper(II) and zinc(II) acetate are reported. Materials show catalytic activity for the oxidation of catechol comparable to that of the copper Porphyrin-Metal Organic Framework belonging to the same family of compounds previously reported by us. The ability of the porphyrin's tetrapyrrolic core to accommodate metal ions of varying charges seems to modulate the catalytic activity.

Keywords: porphyrin; heterogeneous catalysis; catechol oxidation; copper; zinc.

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1. Introduction

Coordination polymers (CPs) are materials composed of metal ions linked by organic ligands forming coordination-based extended arrays which could span from linear (one-dimensional – 1D) to framework-type networks (threedimensional – 3D) [1-3]. Porphyrins are one of such linkers that can act as attractive building blocks in the design of CPs due to their striking features, particularly good thermal stability, planar and rigid structure and potential application in catalysis [4-6], photosensitizers [7-10], sensors [11-14], among several others [15]. We note that in recent years, CPs have been extensively reported. Contrasting with the rich porphyrin chemistry developed in recent decades [16-18], the sub-field of porphyrin-based CPs remains comparatively less explored.

Robson and co-workers [19] reported the first study on the coordination ability of the *meso*-pyridyl groups with metal ions by self-assembly. This original report remains one of the most envisioning ones related to the birth of the CPs field showing both the advantages of the design of such compounds, as well as the various limitations which one can find when preparing such compounds. Since then, many CPs based on pyridyl moieties were reported [20-21], mainly on the 5,10,15,20-tetrakis(4-pyridyl)porphyrin [22-23]. Ma and co-workers showed, for example, that it is possible to *in situ* metallate the porphyrin core during the crystallization step [24].

The free-base porphyrin 5,10,15,20-tetrakis(4-pyridyl)porphyrin, in the presence of different metal ions (e.g., Ag(I) [22], Co(II) [25], Fe (II) [26], Zn(II) [27], Mn(III) [28] and Cu(II) [29]), is able to form CPs. In addition, the intrinsic coordination possibility of some metal cations being included in the porphyrin core further enables the design of novel metal-dependent heterogeneous catalysts. Suslick and co-workers showed, for the first time, that a porphyrinbased CP can be used as an effective heterogeneous catalyst [30]: PIZA-3, a microporous solid [5,10,15,20-tetrakis(4based on the carboxyphenyl)porphyrinate] organic linker connected by trinuclear manganese clusters, represents a significant advance in the development of porphyrin-MOF for heterogeneous catalysis displaying high selectivity to the epoxidation of cyclopentene (23% epoxide), cyclohexene (23% epoxide), cyclooctene (74%

epoxide), and limonene (20% epoxide). This material also displayed high robustness to autoxidation and recovery/reusability capabilities.



Scheme 1. Schematic representation of the free-base porphyrins, its copper and zinc derivatives and porphyrin-CP compounds.

We have recently reported the synthesis, characterization and catalytic activity of a novel copper-porphyrin-CP by the reaction of 5,10,15,20-tetrakis[2,3,5,6-tetrafluoro-4-(4-pyridylsulfanyl)phenyl]porphyrin with an excess of copper(II) acetate, where the S-pyridyl groups on the periphery of the fluorinated porphyrinic core was responsible for the formation of the hybrid material itself (**CuP1S** of this work) [31]. Presently we focus on the preparation, characterization and catalytic activity of a comprehensive series of CP-type compounds constructed in a similar fashion from the pyridyl and S-pyridyl

porphyrins which react with copper(II) or zinc(II) cations (Scheme 1). Compounds were effectively used as heterogeneous catalysts, with the derived results being compared to the previous ones reported for discrete copper complexes and copper-CP-based compounds [31].

2. Experimental

All chemicals were purchased from Aldrich, Sigma or Merck and were of analytical grade. Catechol was recrystallized from hot toluene and kept in the dark. The synthesis and characterization of the free-base porphyrins was performed as described in the literature [32]. H_2P1 was obtained by structural modification of 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin with 4-mercaptopyridine [32].

CuP1, CuP2, ZnP1 and ZnP2 (Scheme 1) were obtained from the corresponding free-base porphyrin. The metalation reactions were performed with copper acetate or zinc acetate in CHCl₃/MeOH (7:3) or dimethylformamide (DMF) using a stoichiometric ratio of 1:1 (Metal:Porphyrin). After 24 h under magnetic stirring and reflux temperature with CHCl₃/MeOH (7:3) or 120 °C with DMF, the solvent was removed under reduced pressure and the desired metalloporphyrins were purified column chromatography by using dichloromethane/methanol (7:3 v:v) as eluent to remove any remaining freebase porphyrin. Complexes were characterized by UV-Vis, ATR-FTIR, electron paramagnetic resonance (EPR) spectroscopies and mass spectrometry.

CuP1: HRMS ESI(+): m/z: calcd for $C_{64}H_{25}F_{16}N_8S_4Cu$: 1400.0126 [M+H]⁺; found: 1400.0122; UV-Vis (DMF) λ_{max} , nm (log ϵ): 413 (4.68), 538 (3.73) and 570 (3.32).

ZnP1: HRMS ESI(+): m/z: calcd for C₆₄H₂₅F₁₆N₈S₄Zn: 1401.0120 [M+H]⁺; found: 1401.0107; UV-Vis (DMF) λ_{max} , nm (log ε): 415 (5.41) and 552 (4.21).

CuP2: HRMS ESI(+): m/z: calcd for C₄₀H₂₅N₈Cu: 680.1498 [M+H]⁺; found: 680.1490; UV-Vis (DMF) λ_{max} , nm (log ϵ): 412 (5.19) and 537 (3.73).

ZnP2: HRMS ESI(+): m/z: calcd for C₄₀H₂₅N₈Zn: 681.1494 [M+H]⁺, found: 681.1488; UV-Vis (CHCl₃) λ_{max} , nm (log ϵ): 415 (4.90) and 540 (3.40). (see Supporting information - SI).

2.1. Synthesis of ZnCuP1S, CuZnP1S, ZnCuP2S, and CuZnP2S

Solids were prepared by reacting **CuP1**, **ZnP1**, **ZnP2** or **CuP2** with copper(II) or zinc(II) acetate in DMF under magnetic stirring at ambient temperature until the total consumption of the starting porphyrin (48 or 72 h). **ZnCuP1S** was obtained by reacting **CuP1** with 9 equiv. of zinc(II) acetate [31] (Scheme 1). **CuZnP1S** was obtained by the reaction of **ZnP1** with 9 equiv. of copper(II) acetate salt at ambient temperature. Procedures to isolate **ZnCuP2S** and **CuZnP2S** were similar.

At the end of the reactions, the precipitation of the desired solids **ZnCuP1S**, **CuZnP1S**, **ZnCuP2S**, and **CuZnP2S** was observed. Solids were washed with different solvents (DMF, THF, H₂O, methanol and acetone) to remove any contamination from the starting metalloporphyrins or metal salts, dried under vacuum and characterized with a wide array of solid state techniques (PXRD, ATR-FTIR, EPR, UV-Vis, and fluorescence in the solid state).

2.2. Synthesis of the porphyrinic materials **ZnP1S** and **ZnP2S**

Zinc acetate (10 equiv.) was added to a solution of H₂P1 or H₂P2 (1 equiv.) in DMF or CHCl₃/CH₃OH 7:3 (10 mL) respectively, and the mixture was magnetically stirred at 120 °C (for DMF) or maintained under reflux for 48 h (for CHCl₃/CH₃OH). Purple precipitates were collected and sequentially washed with water and organic solvents to remove free/unreacted zinc acetate or porphyrin. Solids were dried under vacuum and characterized by PXRD, ATR-FTIR, EPR, UV-Vis, and fluorescence in the solid state.

2.3. Synthesis of the porphyrinic materials **CuP1S** and **CuP2S**

CuP1S and **CuP2S** were prepared according to previously reported procedures by our research group [31].

2.4. Catalysis

The catalytic activity of metalloporphyrins was evaluated by oxidizing catechol in a phosphate buffer (pH = 8.0) while in the presence of air, with or without the addition of aqueous hydrogen peroxide. Reactions were carried out in the dark for different reaction times (between 15 min and 24 h) under

constant magnetic stirring and in a thermostatic bath (30 °C). The progress of the catalytic reactions was monitored by UV-Vis spectroscopy. The kinetics of the oxidation of catechol was determined by the reduction of the band at 508 nm (the nitrite method)[33]. For all reactions involving H_2O_2 a molar ratio of 1:1000:100 (catalyst: H_2O_2 :catechol) was used. The reactions were also conducted in the absence of hydrogen peroxide, the procedure being similar to that described above.

2.5. Characterization Techniques

Mass spectra were acquired on a LTQ OrbitrapTM XL hybrid mass spectrometer (Thermo Fischer Scientific, Bremen, Germany) controlled by LTQ Tune Plus 2.5.5 and Xcalibur 2.1.0. The capillary voltage of the electrospray ionization source (ESI) was set to 3.0 kV. The capillary temperature was 275 °C. The sheath gas was at 65 (arbitrary units as provided by the software settings). The capillary voltage was 42936 V and the tube lens voltage 1720 V.

Electronic spectra (UV-Vis) were obtained on a Shimadzu UV-2501PC spectrophotometer, in the 350-800 nm range. For the diffuse reflectance characterization an UV-VIS Jasco V560 spectrophotometer was employed.

Attenuated Total Reflectance Transmission Fourier Transform Infrared (ATR-FTIR) spectra were registered on a FT Mattson 7000 Galaxy series spectrophotometer in the 400-4000 cm⁻¹ range. Spectra were collected with a resolution of 4 cm⁻¹ and accumulation of 32 scans.

Powder X-ray diffraction (PXRD) measurements were collected on selforiented solids placed on neutral glass sample holders. Routine PXRD data for all prepared materials were collected at ambient temperature on a Empyrean PANalytical diffractometer (Cu K $\alpha_{1,2}$ X-radiation, $\lambda_1 = 1.540598$ Å; $\lambda_2 = 1.544426$ Å), equipped with an PIXcel 1D detector and a flat-plate sample holder in a Bragg-Brentano para-focusing optics configuration (45 kV, 40 mA). Intensity data were collected by the step-counting method (step 0.01°), in continuous mode, in the *ca*. $3.5 \le 2\theta^\circ \le 50^\circ$ range.

Electron paramagnetic resonance (EPR) measurements were collected on an EPR BRUKER EMX microX spectrometer (frequency X, band 9.5 GHz) at both ambient temperature and 77 K (using liquid N₂), in the perpendicular microwave polarization X-band.

Fluorescence spectra were recorded using a fibre optic system connected to a Horiba Jobin Yvon Fluoro Max-3 spectrofluorimeter while exciting at appropriate λ (nm) of the solid compounds.

3. Results and Discussion

3.1. Materials characterization

All the prepared solids were obtained under similar conditions. Syntheses were carried out starting from the free-base H_2P1 or H_2P2 porphyrins which reacted with copper(II) or zinc(II) acetate in DMF at ambient temperature or 120 °C. CP-type materials were formed by coordination between the porphyrinic precursor (either free or metallated) and Zn(II) or Cu(II) metal nodes. All materials were extensively characterized by PXRD, FTIR, EPR, UV-Vis, and fluorescence in the solid state.

Crystallinity of the new materials and of the metalloporphyrins was assessed by means of PXRD. CuZnP1S and ZnCuP1S exhibit distinct PXRD patterns (Fig. 1) which are different from the previously reported CuP1 [31] and from **ZnP1**. From our previous studies with this type of materials, particularly in the self-assembly of supramolecular structures with porphyrin-type molecules, we know that the overall crystallinity is strongly affected by the need of the materials to retain the crystallisation solvent molecules. With porphyrin-type molecules, solvent molecules are easily removed from the compounds, even when crystals are being formed in the reaction medium. Moreover, also for the CuZnP1S and ZnCuP1S materials, the existence of the well-known paddlewheel motifs induces additional separation between the building units thus, expectedly, leading to the formation of channels that can be escape routes of any solvent molecule. So, for all these materials it is not surprising to observe the isolation of predominantly amorphous materials instead of very crystalline ones. In addition, the distribution of metals in the framework architecture is an additional source of disorder and, thus, a motor for the isolation of amorphous compounds. Goodwin and co-workers [34] reported, for example, that the metal cation or ligand positions are strongly correlated with amorphous compounds. Finally, it is important to note that the complexity of these building units can promote the self-assembly in the solid-state in semi-crystalline forms with very

different space groups, hence, when observed, the presence of distinct powder X-ray diffraction patterns.



Figure 1.

ZnP2 shows the expected PXRD pattern [35]. The reaction between **CuP2** or **ZnP2** and copper(II) or zinc (II) acetate leads to the isolation of microcrystalline powders that do not exhibit diffraction peaks corresponding to either the free salts or the metalloporphyrins (Fig. 2). Although the materials are (poorly) crystalline, it was not possible to unveil their crystal structure by means of X-ray crystallography as in our previous studies.



The ATR-FTIR of ZnP1 and ZnP1S, CuZnP1S and ZnCuP1S are depicted in Fig. 3. The typical symmetric and asymmetric stretching bands of the pyrrole ring of v NH, v CH of H₂P1 are observed in the range 700–1700 cm⁻¹. For H₂P1, the band at 3300 cm⁻¹, ascribed to NH stretching was also observed (Fig. 3a). It is noticeable the disappearance of NH vibrations, that suggests a complete metalation reaction. A strong band emerged near 1000 cm⁻¹, due to the metalloporphyrin skeletal ring, indicating the formation of Zn(II) porphyrin compound. The bands observed at ~1571 and ~1413 cm⁻¹ for **ZnP1S**, at 1571 and 1406 cm⁻¹ for ZnCuP1S and at 1546 and 1411 cm⁻¹ for CuZnP1S, are attributed to the $v_{as}(C=O)$ and $v_{s}(C=O)$ vibrational modes, respectively. We believe that these vibrations must arise from the presence of the typical paddle wheeled Cu(II) or Zn(II) acetate cluster, in a similar fashion to that reported for **CuP1S.** The difference between the bands for the asymmetric and symmetric stretching (Δv) for both materials suggests the presence of carboxylic groups linked via a µ2-syn,syn-bridge [31]. ZnP2S, ZnCuP1S and CuZnP1S exhibit the same vibrations at 1560 and 1400 cm⁻¹. The band at ~1720 cm⁻¹ may refer to C=O stretching from DMF molecules which seems to be present in all compounds.



The EPR spectra of the metalloporphyrins and CP-type materials are depicted in Figs. 4 and S3 in the SI. The EPR spectra of ZnP1, ZnP2 and of **ZnP1S** and **ZnP2S** are similar, without EPR signals, attesting that the solids are not contaminated with any other paramagnetic species. The EPR spectrum of ZnCuP1S exhibits the characteristic anisotropic signal expected for Cu(II) in axial symmetry, showing the expected four lines with $g_{\parallel} > g_{\perp}$ and with a hyperfine splitting (A $_{//}$ = 234 G) higher than that of CuP1S and CuP1. The values of g_1 , $g_{//}$, and $A_{//}$ for **ZnCuP1S** and **CuP1** were distinct, showing that the presence of zinc(II) ions affects the metalloporphyrin core. CuZnP1S displayed an anisotropic signal with four characteristic lines of copper(II), axial symmetry in the region of g = 2.0, and different values of g// and $g\perp$. However, in this case, it also evidences a multiple-line pattern in the perpendicular spectrum region. This is typical of a superhyperfine interaction ($A_N = 17$ G) of the copper(II) ion unpaired electron with four magnetically equivalent ¹⁴N nuclei (I = 1) arising from pyridyl groups which should result in the expected deployment of each signal into nine lines. The CuP2 derivative CP-type materials (Fig. S3) also exhibit the characteristic anisotropic signal of copper(II), S = 3/2, in axial symmetry in the region of q = 2.0.

Nonomura and co-workers studied the EPR of Cu(II) complexes of porphyrins, chlorins and phthalocyanines, and showed a strict relationship between the values of $A_{//}$, $g_{//}$ and the degree of distortion in these compounds: a larger distortion is associated with greater values of $g_{//}$ and lower values of $A_{//}$. The patterns observed in EPR spectra indicate the presence of copper as linker in the solids (Table 1).

Compound	A _{//Cu}	g//	g⊥	
CuP1	218	2.193	2.057	
CuP1S	202	2.193	2.058	
ZnCuP1S	234	2.344	2.056	
CuZnP1S	128	2.331	2.048	
CuP2	199	2.189	2.073	
CuP2S	190	2.206	2.081	
ZnCuP2S	183	2.305	2.060	
CuZnP2S	176	2.264	2.067	

Table 1. Spin Hamiltonian Parameters obtained for the X-band EPR spectralsimulations of CuP and materials at 77 K.

The EPR parameters listed above were obtained by simulating the experimental spectrum for solid samples at 77 K. The Simfonia simulation pack software was employed. Hyperfine coupling constants are expressed in Gauss.

The UV-Vis spectra of the materials and of the precursor complexes are depicted in Figs. 5 and S4 (in the SI), revealing the typical UV-Vis features of porphyrins, namely the Soret (410-440 nm) and the Q-bands (500-650 nm) arising from π - π * transitions. The Soret bands are slightly blue-shifted (*ca.* 3-9 nm) when compared with those of the corresponding metalloporphyrins. On the other hand, the Q-bands are red-shifted (*ca.* 1-21 nm, depending on the porphyrin).

The solid-state interactions lead to broadening of the bands. The displacement observed for the Soret band of the materials may be caused by modifications of the metalloporphyrin molecular environment. The red-shift of the Q-bands indicates an increasing of π -conjugation and a HOMO–LUMO energy gap reduction caused by the change of local symmetry.



The fluorescent properties of the metalloporphyrins and of the materials were also studied in the solid state. As depicted in Fig. 6, with excitation at 420 nm H_2P1 emits strong fluorescence with peaks at 663 and 704 nm which correspond to the S1 \rightarrow S0 transitions of the porphyrins. **ZnP1** emits with a peak at 633 and a shoulder at 685 nm. The corresponding **ZnP1S** shows only a

broad emission band centred at 654 nm, suggesting that the linker cluster exerts to some extent influence on the fluorescence properties [36]. Generally, the porphyrin chromophore in the solid state can form aggregates that lead to fluorescence quenching. This behaviour was observed for H_2P2 (Fig. S5, see SI).

The coordination of zinc reduces the electron delocalization of the porphyrin molecules, which increases the lowest excited state energy level. As a consequence, the energy level difference of the S1 \rightarrow S0 transition was widened and a blue-shift for **ZnP1** and **ZnP1S** was observed.

For **CuP1**, **CuP2** and materials **CuP1S**, **CuP2S**, **ZnCuP1S** and **ZnCuP2S** no emission was observed, which is due to an open-shell configuration, attributed to the effect of the coordinated Cu(II) in the porphyrin core (see Fig. 6 and Fig. S5 in the SI). Copper porphyrins are non-luminescent due to the intersystem crossing transition from excited singlet to triplet states. For **CuZnP1S** and **CuZnP2S**, the presence of an open-shell copper(II) ion in the materials provides a local fluorescence quenching site, due to relaxation *via* d–d transitions [37].



Figure 6.

3.2. Catalytic activity

We have recently reported that the CP-type materials obtained from the reaction of H_2P1 and H_2P2 with copper(II) acetate were able to act as biomimetic catalysts of catechol oxidase. **CuP1S** and **CuP2S** showed high heterogeneous catalytic activity in the oxidation of catechol into *ortho*-benzoquinone in the presence or absence of aqueous H_2O_2 (30% w/w) when compared to **CuP1** and **CuP2**, particularly **CuP1S** [31].

The conversion of catechol into *ortho*-benzoquinone was determined by the nitrite method. Results are summarized in Fig. 7 and all the assays were performed without hydrogen peroxide. Complexes **ZnP1** and **ZnP2** are inactive in catechol oxidation, with similar results being observed for non-catalysed reactions. **ZnCuP1S** showed a similar conversion rate to that obtained for **CuP1**, showing that the zinc clusters do not influence catechol conversion.

The heterogeneous catalytic systems using **ZnCuP1S** and **CuZnP1S** attain a maximum of 16-18% after 24 h when the experiments are performed without the addition of H₂O₂. It is known that the peripherally-coordinated copper centres linked to the pyridyl units have catalytic activity in the oxidation of catechol. The catalytic efficiency of **CuZnP1S** is, however, lower when compared to **CuP1S** (which affords total conversion at the same time of reaction (Fig. S6, SI) [31]). The catalytic activity of **CuP1S** was approximately 5 times higher than **CuZnP1S** or **ZnCuP1S** under the same experimental conditions (Fig. S6, SI) [31]. **ZnCuP2S** shows similar catalytic performance to **CuZnP2S**.



The catalytic reactions were also performed in the presence of hydrogen peroxide as oxidant. The collected data are summarized in Fig. 8 (and also Fig. S6, SI) and show that the catalytic activity is highly dependent on the reaction time. An increase in the reaction time from 1 to 6 h using **CuZnP1S** as catalyst leads to a remarkable increase in the total conversion from *ca*. 5 to 22%. The catalytic efficiency of the CP-type materials reported here follows the order **CuZnP1S** and **CuZnP2S** > **ZnCuP2S** > **ZnCuP1S**, with average conversions of 56%, 55%, 35%, and 25% after 24 h, respectively. We note that the reactivity order was not the same in the absence of hydrogen peroxide (**ZnCuP1S** > **CuZnP1S** > **CuZnP2S** = **ZnCuP2S**, Fig. 7).

Materials formed from **CuP1** were slightly more active. The difference in the tetrapodal linkers in terms of rigidity, such as observed for **CuP2S**, with a more rigid nature, is less effective than materials containing **CuP1**. The variation in the catalytic activity with changes in the electronic structure suggests that a synergism between the metalloporphyrin and the peripherally-coordinated metal centre may occur, rendering a strong effect on the affinity for the substrate.



Figure 8.

With the set of results obtained for **CuZnP1S** and for **CuZnP2S**, the positive contribution made by Cu(II) coordinated to the pyridyl groups seems clear. However, when comparing the catalytic activity of **CuP1S**, **CuZnP1S** and **ZnCuP1S**, one notices that the activity observed for **CuP1S** is not simply the

sum of that of the peripherally-coordinated copper cations and **CuP1**, suggesting that the good catalytic performance obtained previously for **CuP1S** is related to the structure of the catalyst itself. Similar behaviour was observed for **CuZnP2S** and **ZnCuP2S**. In fact, the appropriate network topology may increase the observed catalytic activity [38]. We further notice that the structure of the porphyrins also affects the crystal topology by changing the dihedral angles of the *meso*-aryl groups, according to Yamada [39].

Kaiser and co-workers [40] prepared a series of mixed-ligand copper complexes able to mimic catechol oxidase and proposed that the electron density on the copper centre significantly increase the reactivity towards the oxidant used. In this work, the difference of the external metals clearly has a remarkable effect on the network architecture, which ultimately impacts the catalytic activity.

4. Conclusions

The synthesis and characterization of new solid materials, obtained from the porphyrins H₂P1 and H₂P2 with copper(II) or zinc(II) acetate is reported, as well as their copper and zinc MOF derivatives. These porphyrin-based insoluble materials evidenced only fair catalytic activity for the oxidation of catechol by oxygen from air, whereas with the addition of aqueous hydrogen peroxide good catalytic activity was registered for the oxidation of catechol, a substrate suitable to identify functional models of catechol oxidase. Results for **CuZnP1S** and for **CuZnP2S** seem to indicate that Cu(II) bound to the pyridyl groups has a key contribution in the catalytic system. The coordination of pyridyl units with metal clusters provide adequate catalysts towards catechol conversion, depending of the set metal cluster and porphyrin macrocycle. The ability of the porphyrin's tetrapyrrolic core to accommodate metal ions of varying charges seems to modulate the catalytic activity.

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FIGURE CAPTIONS

Figure 1. PXRD for (a) ZnP1, (b) ZnP1S, (c) ZnCuP1S and (d) CuZnP1S.

Figure 2. PXRD for (a) ZnP2, (b) ZnP2S, (c) ZnCuP2S and (d) CuZnP2S.

Figure 3. ATR-FTIR spectra of (a) H₂P1 (b) ZnP1S, (c) ZnCuP1S, (d) ZnP1 and (e) CuZnP1S.

Figure 4. EPR spectra of (a) ZnP1, (b) ZnP1S, (c) ZnCuP1S, (d) CuP1, (e) CuP1S and (f) CuZnP1S.

Figure 5. UV-Vis spectra in the solid state of (a) CuP1, (b) CuP1S, (c) ZnP1, (d) ZnP1S, (e) CuZnP1S and (f) ZnCuP1S.

Figure 6. Emission spectra in the solid state for (a) H_2P1 (b) ZnP1 (c) ZnP1S (d) ZnCuP1S (e) CuZnP1S (f) CuP1 and (g) CuP1S.

Figure 7. Catechol oxidation in the presence of air (without H_2O_2) catalyzed by CuZnP1S, ZnCuP1S, ZnP1, ZnP1S, CuZnP2S, ZnCuP2S, ZnP2 and ZnP2S in phosphate buffer (pH 8.0). Conversions were calculated based on the amount of substrate remaining. Results represent reactions performed in duplicate or triplicate. Under these conditions the conversion values were in the range of ± 2.0%. The formation of *ortho*-benzoquinone from catechol was confirmed by the appearance of its characteristic band at ca. 480 nm. Results for CuP1, CuP2, CuP1S and CuP2S from reference [31] are shown in the SI.

Figure 8. Catechol oxidation in the presence of 30% aqueous hydrogen peroxide (and air) catalyzed by **CuZnP1S**, **ZnCuP1S**, **ZnP1**, **ZnP1S**, **CuZnP2S**, **ZnCuP2S**, **ZnP2** and **ZnP2S** in phosphate buffer (pH 8.0). Reactions were carried out in the dark for different reaction times: (A) between 15 min and 60 min and (B) 3, 6 and 24 h. Conversions were calculated based on the amount of substrate remaining. Results represent reactions performed in duplicate or triplicate. Under these conditions the conversion values were in the range of ± 2.0%. The formation of *ortho*-benzoquinone from catechol was confirmed by the appearance of its characteristic band at ca. 480 nm. Results for **CuP1**, **CuP2**, **CuP1S** and **CuP2S** from reference [31] are shown in the SI.

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SYNOPSIS:

Coordination polymers (CPs) constructed from pyridyl or S-pyridyl porphyrins sa Acceretice containing copper or zinc clusters are reported. The metal cluster has a key contribution in catechol oxidation.