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NH₃/H₂O-mediated proton conductivity and photocatalytic behaviour of Fe(II)-hydroxyphosphonoacetate and M(II)-substituted derivatives

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Synthesis redesign and derivatisation of Fe(II)-hydroxyphosphonoacetate, incorporating different ammonia loads and M(II) isomorphic substitutions (M = Mn, Co and Zn), have been implemented. The NH₃ adsorption led to materials with enhanced proton conductivity, up to $\sim 10^{-3}$ S cm⁻¹, although it caused a progressive amorphization. The Pair Distribution Function (PDF) analysis for this material confirmed the loss of crystallinity but the local order appeared to be maintained. The parent compound was shown to be an efficient photocatalyst for phenol, 4-chlorophenol and methylene blue even under mild conditions, with TOC removal of 75 - 90% at 50 - 150 min of reaction. The M(II)-substituted derivatives displayed similar behaviour in properties, and therefore their multifunctional character, as the parent compound, although with slightly reduced capabilities.

Introduction

Among the multitude of organic ligands, (poly)phosphonic acids have received intense attention in the last 20 years.^{1,2} There are several reasons for this: (a) the double deprotonation capability can create the mono-, or the di-anion (depending on pH) species, each one possessing different metal coordination behavior.³ (b) Phosphonates show high affinity for virtually all metal ions (from “small” monocations, such as Li⁺, to “large” trivalent lanthanides), with enhanced bridging capabilities.⁴ (c) The strong metal-oxygen and P-C bonds are resistant to thermal⁵ or oxidative/hydrolytic cleavage.⁶ In the rich phosphonate linker “toolbox”, one can single out phosphonates that contain one, two, three, four (or even more) phosphonate moieties,^{1,2,7} but also ligands that contain one (or more) phosphonate groups and additional functional moieties. These can be one or more amines,⁸ carboxylates,⁹ sulfonates,¹⁰ pyridines,¹¹ pyrazoles,¹² imidazoles,¹³ hydroxyls,¹⁴ etc. A recent

review presents all these “mixed” phosphonate ligands and their coordination chemistry in the construction of metal-organic materials.¹⁵

The linker R,S 2-hydroxyphosphonoacetic acid (HPAA) has been explored as a multifunctional linker in the construction of structurally diverse compounds.¹⁶⁻¹⁹ Its important structural features include a bis-acidic phosphonic moiety, a mono-acidic carboxylic group and a hydroxyl group. In the compounds reported, HPAA has a preferred (but not exclusive) coordination chemistry, which involves formation of two chelating rings (a 5-membered one utilizing a carboxylate and the hydroxyl oxygens, and a 6-membered one from a phosphonate oxygen and a second carboxylate oxygen). This coordination mode of HPAA is shown in Figure 1. Certain metal derivatives of HPAA have been investigated for potential applications as corrosion inhibitors,²⁰⁻²³ proton conductors²⁴⁻²⁵ and catalysts.²⁶

Figure 1. A common coordination mode of HPAA.

On the other hand, coordination polymers doped or incorporating more than one metal centres have attracted much attention since the combination of different metal ions in the solid may enhance their particular activity for certain

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Electronic Supplementary Information (ESI) available: Fig. S1: XRPD patterns for Fe-NH₃-xh and Fe_{0.41}Zn_{0.59}-NH₃-xh and Fe_{0.71}Zn_{0.29}-NH₃-xh derivatives; Fig. S2-S3: Rietveld plots for M-HPAA and Fe_{0.71}Zn_{0.29}-HPAA; Fig. S4: XRD pattern of Fe-HPAA/Zn-HPAA mixture and Fe_{0.71}Zn_{0.29}-HPAA; Fig. S5: Rietveld plots for Fe-NH₃-xh; Fig. S6: X-ray PDF analysis; Fig. S7-S8: Nyquist plots for Fe-NH₃-xh and Fe_{0.71}Zn_{0.29}-NH₃-xh; Fig. S9-11: Particle size distribution for Fe-NH₃-xh and Fe_{0.71}Zn_{0.29}-NH₃-xh; Fig. S12: Time evolution of Fe, P and Zn leached for the photocatalytic reactions; Fig. S13: Mössbauer absorption spectra for Fe-HPAA solids; Fig. S14: Time evolution of TOC removal in different cycles; Fig. S15: XRPD patterns for Fe-HPAA before and after photocatalytic test. Table S1: Elemental analysis and stoichiometries for Fe-NH₃-xh and Fe_{0.71}Zn_{0.29}-NH₃-xh compounds; Table S2: Crystallographic data for M-HPAA and Fe_{0.71}Zn_{0.29}-HPAA; Table S3: Chemical composition for Fe_{0.41}M_{0.59}-HPAA; Table S4: Fe(II)/Fe(III) ratio obtained by XPS. See DOI: 10.1039/x0xx00000x

applications.^{27–31} For instance, a partial isomorphous substitution of Fe^{2+} in the structure of a $\text{Fe}(\text{BDC})$ -based MOF catalyst ($\text{BDC}=\text{terephthalic acid}$) was revealed as a strong impact-causing factor as regards the efficiency of phenol degradation.³² Proton transport in phosphonate-based, and in general, coordination polymers arises as a direct result of their acidic nature and the possibility of create extended H-bonding networks into the frameworks with the participation of guest molecules, mainly H_2O . Moreover, by appropriate synthesis and post-synthesis modifications, proton-conducting performance can be conveniently enhanced upon incorporating other strong hydrogen bond-forming species, such as NH_3 , imidazole, H_2SO_4 , H_3PO_4 , etc., in view of possible practical applications of this class of proton-conductive materials to Fuel Cells.³³

On this basis, we focus on the compound $\text{Fe}(\text{II})$ -hydroxyphosphonoacetate, as a starting material to prepare new proton-conducting and photo-catalytically active derivatives, as well establishing useful correlations among properties and materials composition.

Experimental

Materials

Hydrated metal (II) sulfates $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ and hydrogen peroxide (33%, v/v) were purchased from Prolabo. $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and granular iron (10–40 mesh) from Panreac; methylene blue (MB) from BDH Laboratory; phenol and 4-chlorophenol from Sigma-Aldrich and (50%, v/v) R,S -2-hydroxyphosphonoacetic acid [HPAA: $\text{H}_2\text{O}_3\text{PCH}(\text{OH})\text{CO}_2\text{H}$] from BioLab.

Synthesis

Preparation of $\text{Fe}[\text{HO}_3\text{PCH}(\text{OH})\text{CO}_2] \cdot 2.5\text{H}_2\text{O}$ (Fe-HPAA). A mixture of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (13.9 g; 50 mmol) and granular iron (2.5 g; 89.5 mmol) was added to a HPAA aqueous solution (11.2 mL; 50 mmol of HPAA and 150 mL of DI water). The mixed solution was stirred under reflux for 1 day. The final pH value of this reaction mixture was ranging from 1.0 to 1.3. The solid product after refluxing was filtered, washed with deionized water and dried at 60 °C overnight. Unreacted iron was removed from the solid product by using a magnet and sieving. The yield of the reaction was 70% based on the iron salt. Elemental analysis; calc.: 9.42% C, 3.16% H. Found: 9.01% C, 2.94% H.

Preparation of $\text{Zn}[\text{HO}_3\text{PCH}(\text{OH})\text{CO}_2] \cdot 2.5\text{H}_2\text{O}$ (Zn-HPAA). 2.4 mL of HPAA stock solution (0.01 mmol) was reacted with 1.79 g $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ (0.01 mmol) in 30 mL of DI water. The mixed solution was stirred under reflux for 1 day. The solid was filtered, washed with deionized water and dried at 60 °C overnight. The yield of the reaction was 70% based on the zinc salt. Elemental analysis; calc.: 9.08% C, 3.05% H. Found: 8.87% C, 2.73 % H.

Preparation of $\text{Fe}_x\text{M}_{1-x}[\text{HO}_3\text{PCH}(\text{OH})\text{CO}_2] \cdot 2.5\text{H}_2\text{O}$ ($\text{Fe}_x\text{M}_{1-x}$ -HPAA, $\text{M} = \text{Mn}^{2+}, \text{Co}^{2+}, \text{Zn}^{2+}$). Solid solutions were synthesized following the procedure described above for Fe-HPAA but varying the $\text{Fe}^{2+}/\text{M}^{2+}$ molar ratios of the corresponding sulfate

salts and maintaining fixed the amount of granular iron (2.5 g; 89.5 mmol).

Preparation of NH_3 -loaded derivatives ($\text{Fe-NH}_3\text{-xh}$ and $\text{Fe}_x\text{Zn}_{1-x}\text{-NH}_3\text{-xh}$). These derivatives were prepared as elsewhere described by exposure of samples to ammonia vapours from a 14% NH_3 aqueous solution in a closed container for several hours (1–72 hours).^{34,35} Elemental analysis for NH_3 -loaded are given as Supplementary Information (SI) in Table S1 and their X-ray powder diffraction (XRPD) patterns are shown in Figure S1.

Chemical and Physical Characterization. Elemental analyses (C, N and H) were performed with a Perkin-Elmer 240 analyzer. TG-DTA analysis were recorded on an SDT-Q600 (TA instruments). The temperature varied from RT to 900 °C with a heating rate of 10 °C·min⁻¹. Measurements were carried out on samples in open platinum crucibles under a flow of air.

X-ray diffraction characterization. Solids were characterized by laboratory X-ray powder diffraction. XRPD patterns were collected using an Empyrean PANalytical diffractometer (Cu $\text{K}\alpha_{1,2}$) equipped with a PIXcel 1D detector in a Bragg-Brentano configuration, between 4° and 90° (2 θ), with a step size of 0.026° and a counting time of ~24 s/step.

Rietveld analysis, patterns were collected on a D8 ADVANCE (Bruker AXS) diffractometer equipped with a Johansson Ge (111) primary monochromator, using monochromatic Mo radiation, $\lambda = 0.7093 \text{ \AA}$, in transmission geometry (θ/θ). The X-ray tube was operating at 50 kV and 50 mA. Powder patterns were collected between 2.3 and 35° (2 θ), with a 0.02° step size and an equivalent counting time of ~1536 s/step. For $\text{Fe}_x\text{Zn}_{1-x}$ -HPAA solid solution crystal structures were refined by the Rietveld method³⁶ using the crystal structures of $\text{Fe}[\text{HO}_3\text{PCH}(\text{OH})\text{CO}_2] \cdot 2\text{H}_2\text{O}$ (CCDC n° 285711) and $\text{Zn}[\text{HO}_3\text{PCH}(\text{OH})\text{CO}_2] \cdot 2\text{H}_2\text{O}$ (CCDC n° 285713) as starting models and the GSAS package.³⁷ The following soft constraints were used to maintain chemically reasonable geometries for the phosphonate, chain and carboxylic groups: PO_3C_1 tetrahedron/ P-O [1.53(1) Å], P-C_1 [1.80(1) Å], $\text{O}\cdots\text{O}$ [2.55(2) Å], $\text{O}\cdots\text{C}_1$ [2.73(2) Å], $\text{C}_1\text{OH-C}_2\text{OO}$ group/ $\text{C}_1\text{-C}_2$ [1.50(1) Å], $\text{C}_2\text{-O}_{\text{carb}}$ [1.23(1) Å], $\text{C}_1\cdots\text{OH}$ [1.40(1) Å], $\text{P}\cdots\text{OH}$ [2.68(2) Å], $\text{C}_2\cdots\text{OH}$ [2.40(2) Å], $\text{O}_{\text{carb}}\cdots\text{O}_{\text{carb}}$ [2.21(2) Å] and $\text{C}_1\cdots\text{O}_{\text{carb}}$ [2.36(2) Å]. Hydrogen atoms were not included in the refinements. Crystallographic data are presented in Table S2 and the final Rietveld plots are given in Figure S2–S3.

Amorphous content (A) of NH_3 -loaded Fe^{2+} monometallic samples was determined from Rietveld analysis, using 33% w/w of TiO_2 as internal standard (NIST 674B) and the following equation:

$$A (\%) = \frac{1 - W_s/R_s}{100 - W_s} \cdot 10^4$$

where W_s is the weighted concentration of the internal standard and R_s stands for the Rietveld analysed concentration of the internal standard.³⁸

XPS characterization. The surface composition and chemical environment were carried out by X-ray photoelectron spectroscopy. Analyses were performed on a Physical Electronics ESCA 5701 spectrometer.

Mossbauer spectroscopy. The Mossbauer spectra were recorded with the MS1104 Em spectrometer designed and built in Scientific Research Institute of Physics at Southern Federal University. Moving-source geometry is employed. The γ -ray source is ^{57}Co in a chromium matrix. Isomer shifts are calculated with respect to the metallic $\alpha\text{-Fe}$. Experimental spectra were fitted using UnivemMS software.³⁹

Particle size distribution. The particle size measurements were carried out in a Zetasizer Nano ZS from Malvern. As a general procedure, the particle suspensions were prepared at a concentration ~ 1 mg/mL in MilliQ water and they were sonicated in a water bath for 1 minute to get a homogeneous dispersion. The size was determined via Dynamic Light Scattering (DLS) using a 632.8 nm wavelength laser as the light source. Then, the measurement was performed measuring backscattered light at 173° in order to minimize multiple scattering and the results were averaged and presented in intensity (raw data). The samples were measured in 1 cm path-length disposable polystyrene cuvettes.

Pair Distribution Function (PDF). Synchrotron X-ray powder diffraction (SXRPD) data were collected in Debye-Scherrer (transmission) mode using the X-ray powder diffraction beamline BL04-MSPD at ALBA synchrotron (Barcelona, Spain).⁴⁰ The used wavelength was $0.4124(1)$ Å (30 keV) and it was selected with a double-crystal Si (111) monochromator and determined from a Si640d NIST standard ($a=5.43123$ Å) measurement. This diffractometer is equipped with a MYTHEN detector. The data acquisition time was 37 minutes per each individual pattern. Five patterns were collected for each sample and added in order to improve the signal-to-noise ratio. The glass capillaries, 0.7 mm of diameter, were rotated during data collection to improve diffracting particle statistics.

PDF experimental data were obtained using PDFgetX3⁴¹ with $Q_{\text{max}}=24$ Å⁻¹. PDFgui software⁴² was used to carry out the PDF fits. Final global optimized parameters were: scale factors, unit cell parameters, ADPs and atomic positions (in some selected cases that are described in the results section). Moreover, only for the low- r region fits, delta2 parameter (low- r correlated motion peak sharpening factor)^{43,44} was refined. The instrumental parameters were obtained by measuring a similar data set for crystalline nickel. Nickel PDF data analysis converged to $Q_{\text{damp}}=0.00273$ Å⁻¹ and $Q_{\text{broad}}=0.00738$ Å⁻¹.

It is worth noting that we do not report errors in the results as the standard deviations are not properly calculated by PDFgui. This is because the standard data reduction obtained by PDFgetX3⁴¹ does not include the dG column, standard deviations of G, which is needed to properly calculate the errors.

Photocatalytic experiments. The photocatalytic experiments were conducted on a Luzchem CCP-4 V photochemical reactor (Luzchem Research) provided with mechanical stirring, which was accordingly equipped with 14 UVA black lamps (Hitachi FL8BL-B, 8W) or 14 visible light lamps (Prilux, 8W). Prior to

photocatalytic experiments, the catalysts were pre-activated by irradiation with UVA light (6 lamps), for 30 min, in an aqueous suspension (780 mg/L, $V=0.9$ L) containing 50 mg/L of H_2O_2 . After pre-treatment, phenol or 4-chlorophenol were added to get a total concentration of 50 mg/L of the pollutant together with 500 mg/L of H_2O_2 . Photodegradation of methylene blue (MB) was carried out as indicated above but without pre-treatment and using 14 UVA lamps. Analyses were carried out with 8 mL filtered aliquots, extracted at different times. Total Organic Carbon (TOC) was determined using a Shimadzu TOC-V-CSH. H_2O_2 consumption was analysed by the Iodometric titration method. Fe^{2+} concentration in solution was monitored by ICP-MS using an Optima 7300 DV Perkin-Elmer spectrometer. Dissolved Cl^- from 4-chlorophenol photodegradation was analysed by ion chromatography using a Metrohm 883 Basic IC plus. The reaction intermediate products for phenol and 4-chlorophenol were analyzed with a HPLC-MS TSQ Quantum Access Max Thermo Electron device. Samples were prepared in 3:2 methanol/water mixtures with 5% ammonia (pH 10.0). The recyclability of the catalyst was studied by filtering the catalyst after the photocatalytic tests. The solid was suspended in 80 mL of 10^{-3} M solution of H_2SO_4 and stirred for 1 hour. The catalyst was filtered, washed with deionized water, dried at 60°C and used in a second cycle.

Proton Conductivity Studies. Impedance measurements of the powdered polycrystalline compounds were carried out on cylindrical pellets (~ 5 mm diameter; ~ 0.9 – 1.1 mm thickness) obtained by pressing ~ 30 – 40 mg of sample at 250 MPa for 1 min between porous C electrodes (Sigracet, GDL 10 BB, no Pt). Pellets were placed inside a temperature and humidity controlled chamber (Espec SH-222). Impedance data were collected using an AUTOLAB PGSTAT302N or HP4284A impedance analyser over the frequency range from 20 Hz to 1 MHz with an applied voltage of 0.35 or 0.5 V. All measurements were electronically controlled by the winDETA package of programs.⁴⁵ In order to equilibrate the water content, pellets were first preheated ($0.2^\circ\text{C}/\text{min}$) from 25 to 80°C at 95 %RH. Impedance spectra were recorded over upon cooling using stabilization times of 5 hours at different temperature intervals from 80 to 25°C . Water condensation on the sample was avoided by reducing first the relative humidity before decreasing temperature. The total pellet resistance (RT) was obtained from the intercept of the spike and/or the arc (low-frequency end) on the Z' axis from the Nyquist plots.

Results and discussion

Synthesis

In this work, we used a simplified synthesis procedure of that reported elsewhere²⁶, intended to remove accessory additives and shorten time of reaction (from 96h to 24h). Moreover, controlled crystallization was achieved by employing jointly $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and elemental iron as the iron sources. This method led to a slightly more hydrated solid, $\text{Fe}[\text{HO}_3\text{PCH}(\text{OH})\text{CO}_2] \cdot 2.5\text{H}_2\text{O}$, respect to the original dihydrate

compound. In addition, we took advantage of the existence of an isostructural series for divalent transition metals (Mn^{2+} to Zn^{2+}) with this ligand for preparing and extend the study to a number of bimetallic compounds, $\text{Fe}_x\text{M}_{1-x}\text{-HPAA}$ (Table S3). As illustrated for $\text{Fe}_x\text{Zn}_{1-x}\text{-HPAA}$ ($0.41 < x < 0.89$), the Rietveld analysis shows that the partial substitution of Fe^{2+} by Zn^{2+} lead to a reduction of the unit cell volume depending on the composition, compatible with the formation of a solid solution (Figure S3, Table S2). Furthermore, a simple verification can be carried out by comparing the XRD patterns of physical mixtures of single metal derivatives with those of the corresponding bimetallic compounds, since the latter does not exhibit a peak splitting in the 2θ range of $16\text{--}18^\circ$ (Figure S4).

Ammonia adsorption. In previous work, we demonstrated that the adsorption of ammonia is a simple way of tuning the proton conductivity properties of phosphonate-based coordination polymers by favouring the formation of extended H-bond networks together with water and remaining acidic groups.^{34,35} The incorporation of this basic guest molecule entails a progressive amorphisation of the solid, which depend on the exposure time of the sample to ammonia vapours, from ammonia aqueous solution. For $\text{Fe-NH}_3\text{-xh}$, the amorphous fraction was quantified by Rietveld analysis³⁶ (Table 1, Figure S5) showing that the incorporation of $1 - 1.75$ mol NH_3 per formula leads to the practical sample amorphisation. Maximum adsorption of NH_3 was not higher than 1.5 mol per formula for $\text{Fe}_x\text{Zn}_{1-x}\text{-NH}_3\text{-xh}$ materials (Table S1). From XPS analysis, the measured surface $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios appear to indicate that ammonia adsorption is not accompanied by iron oxidation (Table 1). It is noteworthy, that amorphisation does not caused any increase in the BET surface areas, which correspond to non-porous solids ($S_{\text{BET}} \sim 2 \text{ m}^2/\text{g}$).

In order to gather further structural information, we have undertaken a PDF study. This methodology provides information about local bonding environments of amorphous, nanoparticles and crystalline phases.⁴⁶ Figure 2 displays the PDF patterns for **Fe-NH₃-xh** samples, which confirm the loss of crystallinity with increasing ammonia content, since larger atomic order beyond $5 \text{ \AA}$ is not observed for the samples with the highest NH_3 loads (i.e. 72 h). However, local atomic order apparently remains (Figure 2).

The PDF pattern of crystalline Fe-HPAA was fitted with the crystal structure of Fu et al.⁴⁷ as a starting point. The scale factor, cell parameters, ADPs and atomic positions, excluding that of the C atoms, were refined in the r -range from 1.4 to $50 \text{ \AA}$. The final fit is displayed in Figure S6 and the R_w and refined parameters values obtained are shown in Table 2. For Fe-NH₃-36h two r -regions were used to perform the PDF fits. Initially, a high r -range, from 10 to $50 \text{ \AA}$, was considered to study the crystalline region, for which scale factor, cell parameters, ADPs and atomic positions were refined (Table 2). For the second region, 1.4 to $10 \text{ \AA}$, the obtained parameters plus the $\Delta 2$ parameter were refined (excluding the atomic positions) in order to obtain the best PDF fit in this region. The same procedure was applied for Fe-NH₃-48h in the $10\text{--}50 \text{ \AA}$ region using the PDF fit of Fe-NH₃-36h as starting point. In the low r -

region, 1.4 to $10 \text{ \AA}$, only the scale factor and unit cell parameters were refined.

As can be seen in Table 2, the unit cell parameters, as determined in the high r -range, remain unchanged up to 48h of exposure to NH_3 indicating that the crystalline phase corresponds to an unreacted microcrystalline fraction of the solid. For the low r -range, the PDF fit to data diverges from the starting structural model as NH_3 content increases, as a result of the loss of short-range order ($>5 \text{ \AA}$). However, the first P-O, Fe-O, Fe-P distances at 1.55 , 2.14 and $3.29 \text{ \AA}$, respectively, are quite similar for all samples, which supports the idea that the local environment of iron was essentially preserved upon NH_3 adsorption.

Figure 2. (Top) Experimental synchrotron PDF patterns from 1.4 to 50 for the $\text{Fe-NH}_3\text{-xh}$ [0h (black), 36h (red), 48h (blue), 72h (green)]. (Bottom) Selected interatomic distances are highlighted.

Proton conductivity.

This study was undertaken to ascertain the effects of NH_3 adsorption on proton conductivity. From the Nyquist plots, (Figures S7-S8) the Arrhenius plots (Figure 3) were obtained, and the corresponding activation energies calculated (Table 3). A comparison of the $\text{NH}_3/\text{H}_2\text{O}$ content before and after impedance measurements (Tables 1 and 3) indicated that the overall composition of all materials was essentially maintained throughout the experiments. For Fe-NH₃-xh samples, a gradual enhancement of the proton conductivity with NH_3 content was observed, from $1.1 \cdot 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ (Fe-NH₃-0h) to $1.8 \cdot 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ (Fe-NH₃-72h) at 80°C and 95% RH, i.e. an increment of two orders of magnitude.

Table 1. Selected crystallographic details, amorphous percentage (A) and XPS Fe²⁺/Fe³⁺ analysis for **Fe-NH₃-xh** samples.

Sample*	0h	12h	24h	36h	48h	72h
NH ₃ /H ₂ O content (mol/formula)	0/2.5	0.2/2.5	0.4/2.5	0.75/3	1.25/3	1.75/3
Space group	P 2 ₁ /c	P 2 ₁ /c	P 2 ₁ /c	P 2 ₁ /c	P 2 ₁ /c	-
λ (Å)	0.7093	0.7093	0.7093	0.7093	0.7093	-
a (Å)	5.7459(3)	5.7446(3)	5.7456(3)	5.7457(3)	5.7432(4)	-
b (Å)	15.556(1)	15.5534(9)	15.556(1)	15.555(1)	15.551(1)	-
c (Å)	7.8824(5)	7.8801(5)	7.8810(5)	7.8805(5)	7.8781(7)	-
β (°)	109.647(3)	109.640(3)	109.634(4)	109.632(4)	109.635(6)	-
R _{wp}	0.1040	0.0932	0.0878	0.0778	0.0550	-
R _p	0.0784	0.0691	0.0654	0.0575	0.0392	-
A (%)	4.7	15.5	23.0	35.1	75.0	100.0
Fe ²⁺ /Fe ³⁺	1.34	1.26	1.27	1.37	1.38	1.97

*xh stand for hours of exposure to a 14% NH₃ solution

Table 2. Selected results from synchrotron PDF analysis of **Fe-NH₃-xh** samples.

Time	0h		36h		48h	
Region (Å)	1.4-10	10-50	1.4-10	10-50	1.4-10	10-50
Scale factor	0.3657	0.3334	0.3025	0.2252	0.1969	0.0777
a (Å)	5.7686	5.7584	5.7444	5.7586	5.6606	5.7567
b (Å)	15.6310	15.606	15.6919	15.6039	15.9319	15.6049
c (Å)	7.9111	7.8977	7.8142	7.8978	7.6593	7.8959
β (°)	110.31	109.707	109.8	109.686	110.477	109.683
ADP (Fe)	0.0081	0.0100	0.0099	0.0109	0.0099	0.0113
ADP (P)	0.0082	0.0111	0.0094	0.0112	0.0095	0.0102
ADP (O)	0.0233	0.0224	0.0083	0.0235	0.0083	0.0234
ADP (C)	0.0888	0.0306	0.0567	0.0432	0.0567	0.0437
Delta2	2.3634	-	2.2981	-	2.2981	-
Rw (%)	24.9	14.5	38.1	16.6	67.9	22.9

It is noteworthy that the latter sample exhibits a similar proton conductivity value to that of Fe_{0.71}Zn_{0.29}-NH₃-5h, which contains equivalent amounts of NH₃/H₂O. The solid solution compounds showed much higher NH₃ adsorption capability reaching to the maximum NH₃ content in much shorter exposure time. However, these materials became highly hygroscopic by increasing the concentration of the Zn²⁺ in the structure, which could be due to its higher affinity towards NH₃ and water.

Table 3. Proton conductivity (at 80 °C and 95% RH) and Ea values for selected materials.

Compound	x (h)	NH ₃ /H ₂ O content*	σ (S·cm ⁻¹)	E _a (eV)
Fe-NH ₃ -xh	0	0/2.5	1.1·10 ⁻⁵	0.31
	12	0.2/2.5	2.8·10 ⁻⁴	0.42
	24	0.4/3	3.5·10 ⁻⁴	0.41
	36	0.5/3	6.4·10 ⁻⁴	0.41
	42	0.75/3	8.1·10 ⁻⁴	0.43
	48	1/3	1.2·10 ⁻³	0.41
	72	1.2/3	1.8·10 ⁻³	0.42
Fe _{0.71} Zn _{0.29} -NH ₃ -xh	0	0/2.5	4.7·10 ⁻⁵	0.41
	1	0.5/3	1.9·10 ⁻⁴	0.37
	5	1.1/3	1.3·10 ⁻³	0.43
Fe _{0.41} Zn _{0.59} -NH ₃ -xh	0	0/3	9.8·10 ⁻⁶	0.44
	1	0.75/2.5	1.5·10 ⁻⁴	0.57

*After impedance measurements

As already observed for other coordination polymers^{34, 35, 48,49}, the increment in the proton conductivity values can be attributed to an enhancement of the H-bond network by the presence of NH₃. We highlight that all materials display similar particle sizes around 1 μ m and not significant changes occur upon impedance measurements (Figures S9-S11). The relatively low activation energy values calculated (Table 3) suggest that a Grotthuss-type proton transfer mechanism (E_a < 0.5 eV) mainly takes place in these materials.⁵⁰

Figure 3 Arrhenius plots for **Fe-HPAA_{xh}** (left) at different ammonia exposure times: 0h (black), 12h (purple), 24h (pink), 36h (red), 42h (orange), 48h (blue) and 72h (olive) and **Fe,Zn_{1-x}-HPAA_{xh}** (right): **Fe_{0.49}Zn_{0.51}-HPAA** (●), **Fe_{0.49}Zn_{0.51}-NH₃-1h** (○), **Fe_{0.71}Zn_{0.29}-HPAA** (▲), **Fe_{0.71}Zn_{0.29}-NH₃-1h** (△), **Fe_{0.71}Zn_{0.29}-NH₃-5h** (△).

Photocatalytic properties

In a previous work²⁶, we reported the photocatalytic properties of Fe-HPAA relative to phenol photodegradation in the presence of UVA light and H₂O₂. The photodegradation process can be explained in terms of a photo-Fenton reaction, in which, highly oxidant •OH radicals, formed by Fe²⁺/Fe³⁺ cycling reactions, act as the photoactive species.²⁶ Furthermore, it was realized that the overall photocatalytic activity results from a combined homogenous-heterogeneous action during reaction, as noted by a partial, low iron leaching and subsequent re-adsorption on the catalyst surface (Figure S12).

We now extend the study to include other known pollutants, such as 4-chlorophenol and the dye methylene blue, and investigating the photoactivity in the visible light range, as well as the effects of substituting partially Fe²⁺ by M²⁺ ions in the structure. Since the phosphonate ligand, as a part of the solid photocatalyst, is stable under UVA irradiation, TOC measurements were considered as a valid indicator of the catalyst photoactivity.²⁶

Regarding phenol photodegradation, mineralisation (or TOC removal) was found to be more efficient under UVA light at reaction times shorter than 120 min, but high mineralization degree (> 80%) were also reached by irradiation with visible

light beyond this time (Figure 4). Partial substitution of Fe²⁺ by Zn²⁺ (Co²⁺ or Mn²⁺, Figure 4) did not lead to a drastic reduction of the photocatalytic activity, indicating that the bimetallic compounds are also efficient photocatalysts, even under visible light. Mössbauer spectroscopy (Figure S13) revealed that the iron local environments correspond to Fe²⁺ in bulk samples, whether prepared under different experimental conditions, or corresponding to the spent catalyst, which indicates that the phosphonate ligand displays a strong trend to stabilise Fe²⁺ in these compounds, even though highly oxidant species, as OH radicals, were formed upon the photocatalytic reaction.

For 4-chlorophenol photodegradation, high mineralisation percentages (~90%) were reached at relatively short times of reaction (~50 min) under UVA light, but required about 150 min for attaining similar levels of TOC removal under visible light. Significantly, pollutant dechlorination was very fast, even using a visible light source, as it came to completion in less than 40 min of reaction Figure 4. After 5 min, phenol was identified by HPLC-MS at *m/z* = 94, while the aromatic ring oxidation could be detected after 10 min, by the presence of hydroquinone (*m/z* = 126) and catechol (*m/z* = 109) in solution.

For MB photodegradation, although mineralisation was negligible under visible light, the photocatalyst Fe-HPAA exhibited high efficiency (~75%) at about 30 min of reaction (Figure 4) by using UVA light. Like in phenol photodegradation, the bimetallic compounds were less efficient than Fe-HPAA at short times of reaction; nevertheless, a maximum TOC removal was reached at 150 min for both photocatalysts. Monitoring the metal ion and phosphorous concentration revealed low leaching from the catalysts (Figure S12) and, hence, under the photo-Fenton reaction conditions used, the stability can be considered acceptable. Catalyst recycling for phenol degradation under visible light, as a representative test of reusability (Figure S14), indicated that no significant loss of photocatalytic activity occurred after two cycles, in agreement with the previous stability analyses and further corroborated by comparing the PXRD patterns of the spent photocatalysts (Figure S15) and the original material.

Figure 4. Evolution with time of: (left) phenol removal with UVA light (Fe-HPAA, black square) or visible light [Fe-HPAA (orange squares), Fe_{0.71}Zn_{0.29}-HPAA (blue circles), Fe_{0.78}Co_{0.22}-HPAA (pink diamonds) and Fe_{0.8}Mn_{0.2}-HPAA (green triangles)]; (centre) 4-chlorophenol removal with Fe-HPAA, UVA light (black) or visible light (orange), Cl⁻ releasing measurements in the inset; and (right) MB removal in UVA light, with Fe-HPAA (black square) or Fe_{0.71}Zn_{0.29}-HPAA (blue circles).

Conclusions

In this work, we demonstrate that Fe(II)-hydroxyphosphonoacetate is an easy-to-prepare, multifunctional solid with interesting ammonia-tunable proton conductivity and Photo-Fenton catalytic properties, for pollutants removal from aqueous solutions, even in the presence of visible light. In addition, we show this compound to be amenable for obtaining a number of isostructural Fe(II)/M(II) bimetallic derivatives, whose high Fe(II)-content members (mol % > 50) essentially maintained the same functionalities as the parent compound and could be potential precursors of high temperature-synthesised bimetallic electrocatalysts.

Conflicts of interest

There are no conflicts to declare.

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TOC Graphics