Acid–base and spectroscopic properties of a novel supramolecular porphyrin bonded to four pentacyanoferrate(II) groups

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Abstract

The synthesis and characterization of a new supermolecular porphyrin obtained by the coordination of four pentacyanoferrate(II) groups to the pyridyl N-atoms of meso-(3-pyridyl)porphyrin are reported. The redox potential and the 57Fe Mössbauer isomeric shift indicated that the pyridylporphyrin behaves as an electron-withdrawing group. The binding of pentacyanoferrate(II) groups induced a remarkable increase in the basicity of the porphyrin ring, in contrast to the [Ru(bipy)2Cl]2+ groups. In the presence of Ni(II) ions, the pentacyanoferrateporphyrin complex precipitated forming a Prussian blue type material. The voltammograms of a carbon paste electrode of this material exhibited two broad redox waves around 0.43 and 0.63 V ascribed to two distinct iron sites, as confirmed by 57Fe Mössbauer spectroscopy.

Keywords: Supramolecular chemistry; Ferrate complexes; Cyano complexes; Porphyrin complexes

1. Introduction

Supramolecular systems can be conveniently assembled by means of the metal–ligand coordination chemistry approach. In our laboratory, multibridging complexes such as tris-bipyrazine ruthenium(II), meso-tetra(pyridyl)porphyrins and μ-oxo-ruthenium acetate clusters and terminal metal complexes such as [Ru(edta)]2−, [Ru(NH3)3]2+, [Fe(CN)5]3−, [Ru(bipy)2Cl]+ and μ-O–Ru3(CH3COO)6(py)2]+ have been employed successfully in the synthesis of many interesting supermolecules [1–22]. Among them, the pentacyanoferrate(II) derivatives have been pursued with great interest, envisaging the development of electrochemically, photoelectrochemically and/or electrocatalytically active materials by coordinative self-assembly. For example, a heptanuclear supermolecule constituted by a [Ru4(bpz)3]2+ complex coordinated to six [Fe(CN)5]3− species has been prepared and characterized spectroscopic and electrochemically [1]. Borcasly et al. [23] has shown that this compound forms Prussian blue films exhibiting photoelectrochemical properties. Ruthenium acetate clusters have also been coordinated to pentacyanoferrate groups through pyrazine bridges and immobilized onto nickel electrode surfaces as the corresponding Prussian blue type material [11].

In this article we report the synthesis, acid–base, spectroscopic and electrochemical properties of a novel supermolecule, here denoted H2(3-PCFP), obtained by coordination of 5,10,15,20-(3-pyridyl)porphyrin to four [Fe(CN)5]3− groups (Fig. 1). This type of molecule is particularly interesting, since it combines the characteristics and properties of porphyrins and cyanoiron species, allowing the preparation of new supramolecular interfaces based on Prussian blue type materials. Accordingly, the spectroscopic and electrochemical properties of the material obtained by reacting the new supermolecular porphyrin species with Ni(II) ions are also reported in this work.
The negative charges on the pentacyanoferrate groups were omitted.

2. Experimental

2.1. Synthesis

\[ \text{Na}_3\text{[Fe(CN)\textsubscript{6}]\textsubscript{3}(NH\textsubscript{3})\textsubscript{3}]:3H\textsubscript{2}O \] was prepared by the reaction of \( \text{Na}_3\text{[Fe(CN)\textsubscript{6}]\textsubscript{3}(NO)\textsubscript{3}:2H\textsubscript{2}O \) with concentrated NH\textsubscript{3}:H\textsubscript{2}O solution, as described in the literature [24].

\[ [\text{N}(\text{C}_4\text{H}_9\text{)}_4]\text{[Fe(CN)\textsubscript{5}(NH\textsubscript{3})]\textsubscript{3}(NH\textsubscript{3})\textsubscript{3}] \] complex was prepared inside a glove box, under a nitrogen atmosphere, according to the following procedure. Typically, four drops of 0.1 M solution of NH\textsubscript{3}:H\textsubscript{2}O, were added to 320 mg of \( [\text{N}(\text{C}_4\text{H}_9\text{)}_4]\text{[Fe(CN)\textsubscript{5}(NH\textsubscript{3})]\textsubscript{3}(NH\textsubscript{3})\textsubscript{3}]:3H\textsubscript{2}O \) in order to form a slurry. The mixture was kept at 0 °C, by using an ice/water bath, and then 2 ml of concentrated HCl was rapidly added. Immediately, \( [\text{Fe(CN)}\textsubscript{3}(\text{CN})\textsubscript{2}(\text{NH}\textsubscript{3})\textsubscript{3}\text{]} \) species precipitated out [25] as a faint yellow (almost white) solid. This was rapidly filtered in order to remove as much as possible of the NaCl and excess of HCl in solution. Then, the solid was dissolved in about 3 ml of \( [\text{N}(\text{C}_4\text{H}_9\text{)}_4]\text{OH} \) 20% solution (0.77 M) and immediately used for the preparation of the pentacyanoferrateporphyrin, as described below.

Tetrabutylammonium \( \mu\text{-}\{\text{meso}-\text{tetra}(3\text{-pyridyl})\text{porphyrin}\}\text{-tetrakis-pentacyanoferrate(II), (TBA)}\textsubscript{2}H\textsubscript{2}(3\text{-PCFP}) \), was obtained by the reaction of 0.25 mmol of H\textsubscript{2}(3-TPyP) with an excess (about twice the stoichiometry) of the \( [\text{N}(\text{C}_4\text{H}_9\text{)}_4]\text{[Fe(CN)\textsubscript{5}(NH\textsubscript{3})]\textsubscript{3}(NH\textsubscript{3})\textsubscript{3}] \) aqueous solution. The pyridylporphyrin was precipitated out as a dark green solid, which was isolated by filtration. 257 mg of this product was obtained after drying overnight under vacuum. If the synthesis is carried out using stoichiometric amounts of the reagents, the products seem to incorporate significant amounts of unreacted H\textsubscript{2}(3-TPyP) and do not yield stable aqueous solutions. For practical reasons, it was found convenient to use an excess of the amminepentacyanoferrate(II) complex, even if it remains as a mixture in the product, since this species is required to prevent the dissociation and subsequent precipitation of the pyridylporphyrin, as detailed in the discussion section. In fact, the amminepentacyanoferrate(II) complex can be conveniently employed as stabilizer, considering that its properties are well known [26], and do not complicate the interpretation of the experimental results.

The Prussian blue type material, H\textsubscript{2}(3-PCFP)/Ni(II) was prepared by the drop wise addition of a 0.2 M NiCl\textsubscript{2} solution into a 0.02 M H\textsubscript{2}(3-PCFP) aqueous solution. The process can be monitored by the associated color changes and the UV–Vis spectra. In the presence of nickel ions, as a dark precipitate is formed, the porphyrin absorption bands rapidly decrease while the solution changes from a greenish color (due to the protonated free base porphyrin ring) to yellow, reflecting the excess of the \( [\text{Fe(CN)}\textsubscript{3}(\text{CN})\textsubscript{2}(\text{NH}\textsubscript{3})\textsubscript{3}\text{]} \) species employed as stabilizer. The addition of the NiCl\textsubscript{2} solution was stopped when the greenish color of the H\textsubscript{2}(3-PCFP) complex could not be perceived in the supernatant solution. It was observed that up to this point, the reaction proceeds in a rather selective way, i.e. the precipitation of the Prussian blue material derived from the amminepentacyanoferrate(II) complex is practically negligible, as shown by Mössbauer spectroscopy. The product was filtered off, washed with water and kept in a dessicator under vacuum.

Carbon paste electrodes containing the H\textsubscript{2}(3-PCFP)/Ni(II) material were prepared by grinding carefully 5 mg of the finely divided solid with 10 mg of graphite powder and 0.02 ml of mineral oil, as described in the literature [27]. The addition of small amounts of KNO\textsubscript{3} (up to 1 mg) was found to improve the electrochemical response. The paste was gently pressed into a 3-mm diameter and 4 mm deep cylindrical cavity with a coiled platinum wire inside, for the electrical contact.

2.2. Instrumentation

The UV–Vis spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer. The solid samples spectra were recorded on a Guided Wave 260
fiber optics spectrophotometer, using a Wand bundle probe in reflectance mode.

The infrared spectra of the samples as KBr pellets were obtained in a Midac FTIR spectrophotometer. The corresponding Raman spectra of the solid sample were recorded on a model 3000 Renishaw Raman microscope system.

The $^{57}$Fe Mössbauer spectra of the solid samples, diluted in borax, were recorded on a Wissel instrument at room temperature, using a $^{57}$Co(Rh) source. Isomer shift data were given against a metallic iron reference.

The electrochemistry (cyclic and differential pulse voltammetry) was carried out in aqueous solution, using a computer driven PAR model 283 potentiostat/galvanostat and model 270/250 Research Electrochemistry Software version 4.30. A conventional cell, consisting of a working glassy carbon or carbon paste electrode, Ag/AgCl (KCl 1.0 M, $E = 0.222$ V vs. SHE) reference and a coiled platinum wire auxiliary electrode, was employed. The spectroelectrochemistry data were collected using a mini-electrochemical cell mounted inside a quartz cuvette, constituted by a gold minigrid working electrode, Ag/AgCl (KCl 1.0 M) reference and coiled platinum wire auxiliary electrodes.

3. Results and discussion

Contrary to any expectation, the coordination of pentacyanoferate groups to meso-tetra(pyridyl)porphyrins, $\text{H}_2(\text{TPyP})$, is far from trivial. From the difficulties encountered in this work, mostly imposed by solubility problems, it became evident the reason why it has never been carried out before. Pentacyanoferate complexes are very soluble in water, but almost insoluble in organic solvents. In contrast, $\text{H}_2(\text{TPyP})$’s are insoluble in aqueous solution and in the majority of organic solvents. A possible synthetic route would be by employing strong acids, in order to make $\text{H}_2(\text{TPyP})$ soluble in water, since the protonation of the pyridyl groups and the inner ring N-atoms, imparts a $6+$ charge to the molecule. Unfortunately, however, the protonation of the pyridyl N-atoms prevents their binding to the $[\text{Fe(CN)}_3]^{3-}$ ions. For this reason, the use of acids was unsuccessful and the search of a convenient solvent or mixture of solvents was exhaustively pursued, instead.

After many attempts, a suitable experimental condition for the reaction of $\text{H}_2(\text{TPyP})$ and $[\text{N(C}_2\text{H}_3)_4]_2[\text{Fe(CN)}_3]^{3-}$ was achieved by using a mixture of CF$_3$CH$_2$OH and water, as described in the experimental section. While both reactants are moderately soluble in this solvent, the (TBA)$_{12}[\text{H}_2(\text{3-PCFP})]$ product is very soluble. This favorable condition requires the previous exchange of the Na$^+$ cation associated with the starting Na$_2\text{Fe(II)(CN)}_3(\text{NH}_3)$ complex by N(C$_4$H$_9$)$_4$$^+$, in order to increase its solubility in the mixed solvent. The use of an inert atmosphere is necessary also, since the redox potentials of the pentacyanoiron(I) complexes are dramatically lowered in organic solvents [28], turning them rather sensitive to dioxygen. In addition, the corresponding Fe(III) species is more inert to substitution and can give rise to mixed valence products in the presence of the cyanocorone(II) complexes.

While a suitable experimental condition has been obtained for the synthesis of the $\text{H}_2(3\text{-TPyP})$ derivative, our efforts to investigate the corresponding $\text{H}_2(4\text{-TPyP})$ supermolecular porphyrin derivative remain unsuccessful up to the present time. Unfortunately, the meso-tetra(4-pyridyl)porphyrin species is much less soluble in the mixed solvents employed. The binding of the $[\text{Fe(CN)}_3]^{3-}$ groups requires an intractable huge excess of the pentacyanoferate(II) complex, both in the synthetic procedure and as stabilizer in order to prevent the dissociation of the supermolecular species and consequent precipitation of pyridylporphyrin.

3.1. Properties in solution

The solutions of $\text{H}_2(3\text{-PCFP})$ were found to be stable for at least 30 minutes at room temperature. Because of the intrinsic lability of pentacyanoferate(II) complexes, after this period of time, $\text{H}_2(3\text{-TPyP})$ starts to precipitate releasing the dissociated $[\text{Fe(CN)}_3(\text{OH}_2)]^{5-}$ species into the solution. Consequently, this complex, which is also generated by the aquation of the $[\text{Fe(CN)}_3(\text{NH}_3)]^{3-}$ species, has a fundamental role in stabilizing the supermolecular species in solution. Conversely, the removal of the free pentacyanoferate ions by the addition of competing ligands such as isonicotinamide, promotes the complete dissociation of the supermolecular porphyrin species and formation of the corresponding $[\text{Fe(CN)}_3(\text{isonic})]^{3-}$ complex [29–31]. This species can be readily separated from the precipitated $\text{H}_2(3\text{-TPyP})$ by filtration and quantified based on the intensity of its characteristic Fe$^\text{II}(d\pi)\rightarrow py(p\pi^*)$ MLCT band. On the other hand, one can also evaluate spectrophotometrically the amount of pyridylporphyrin present in the $\text{H}_2(3\text{-PCFP})$ sample by dissolving the solid $\text{H}_2(3\text{-TPyP})$ residue with 1 M HCl solution and measuring the intensity of the Soret band at 434 nm. (TBA)$_{12}[\text{H}_2(3\text{-PCFP})]$ is a dark green solid, insoluble even in the most polar organic solvent such as methanol. But, it readily dissolves in water generating a dark green solution, which becomes red in the presence of a weak base such as NH$_4$OH. This color change is reversible, as confirmed upon the addition of some drops of 1 M HCl solution. This is evidence that the porphyrin moiety is in equilibrium with its protonated counterpart (Scheme 1), even at a pH as high as 6.

The UV–Vis spectrum pattern of a $\text{H}_2(3\text{-PCFP})$ aqueous solution above pH 7.1 is characteristic of a
free base porphyrin, exhibiting the Soret band at 413 nm and Q bands at 517, 550, 585 and 640 nm (Fig. 2). At pH 1, the Soret band is red shifted to 434 nm and a couple of Q bands appears at 594 and 646 nm, as expected for the protonated porphyrin species. The protonated H$_4$(3-TPyP) species exhibits those bands at 434, 584 and 632 nm, respectively. Nevertheless, the bands of the peripheral pentacyanoferrate complexes, including the Fe$^{III}$(dπ)$\rightarrow$pyP(π*) charge transfer band, were poorly discernible in the spectra. The MLCT band is expected around 440 nm (ε ≈ 1 × 10$^4$ M$^{-1}$ cm$^{-1}$) and probably, it is being masked by the very intense Soret band (ε ≈ 3 × 10$^5$ M$^{-1}$ cm$^{-1}$).

In fact, even the electrochemical oxidation of the peripheral complexes to the [Fe$^{III}$(CN)$_x$](pyP)$]^-2$ species (at 0.5 V, where pyP = pyridyl ligand bond to the porphyrin ring) did not change significantly the spectrum, confirming that the molar absorptivity of that charge transfer band is relatively weak in comparison with the Soret band. However, at 0.7 V, a decrease and broadening of the Soret band (Fig. 3) was noticeable. This is a clear indication that the porphyrin ring is being oxidized even at this low positive potential, suggesting that the electron density on the ring is higher than in conventional porphyrins. Generally, the oxidation of the (pyridyl)porphyrin ring is found around 0.9 V [32,33]. The pK$_a$ = 4.7 ± 0.1 of the H$_2$(3-PCFP) species was determined from the spectral changes as a function of the pH (Fig. 2), using the modified Henderson/Hasselbach relationship shown in Eq. (1). Each spectrum was registered soon after the homogenization of a mixture of 100 µl of a stock H$_2$(3-PCFP) aqueous solution and 4.00 ml of phosphate or acetate buffer at the desired pH.

$$\text{pH} = \frac{1}{n} \log \left( \frac{\text{abs}(x) - \text{abs}(\text{H}_2\text{P})}{\text{abs}(\text{H}_2\text{P}) - \text{abs}(x)} \right)$$

(1)

The protonation of a base depends on the energy and orbital overlap related to the non-bonding electron pair, as well as on the solvation and steric factors involved in the reaction. Electrostatic factors may also play a role, in association with the charge distribution effects over the molecule after protonation. It should be noted that the H$_2$(3-PCFP) species has a high negative charge (−12), implying in significant electrostatic repulsion, particularly at the periphery of the molecule.

In this discussion only the acid/base properties of pyridylporphyrins and their derivatives are being considered, such that the orbital geometry of the donor orbital, and the steric contributions to the thermodynamics of the reaction should be similar and cancel out. In principle, the energy of the electron pair is the main factor influencing the basicity of the porphyrin inner ring N-atoms. Therefore, the electronic effect responsible for the increase of pK$_a$ should be transmitted through the bridging pyridyl groups. It is interesting, however, that the pyridyl N-atom in the bridging group is in meta position relative to the C−C bond connecting it to the porphyrin ring. Since there is a nodal plane in the pyridyl π-system exactly on the bridging carbon atom, the propagation of the π-resonance effects from...
the backbonding interactions involving the pentacyano-
ferrate(II) groups should be minored. This implies that the
coupling should be more effective in the case of the
H_{3}(TPyP) isomer; a fact which indeed has been
confirmed by the detection of a strong ruthenium(II)-
to-porphyrin charge-transfer band at 690 nm in the
spectrum of the [H_{4}(TPyP){Ru(bipy)2Cl}4]^{6+} species
[20], which is absent in the related [H_{4}(3-
TPyP){Ru(bipy)2Cl}4]^{6+} isomer. Unfortunately, the
analogous pentacyanoferriate(II) species has not been
worked out successfully, at the present time, preventing
any similar comparison.

To our surprise, the pK_{a} of the [H_{2}(4-
TPyP){Ru(bipy)2Cl}4]^{4+} species (pK_{a} = 2.0), was
comparable to that of the [H_{2}(3-TPyP){Ru(bipy)2Cl}4]^{4+}
isomer (pK_{a} = 2.2). We presume that, in spite of the
greater orbital expansion of the Ru(II) ions which turns
them more effective than the low spin Fe(II) ions in
promoting π-backbonding interactions to N-heterocyc-
lic ligands, the 2,2'-bipyridine ligands should be rever-
sing such a trend. In fact, 2,2'-bipyridine is a strong π
electron acceptor and a much weaker σ-donor. So, this
ligand competes for the electron density on the ruthe-
nium(II) ion decreasing its backbonding effect to the
bridging pyridylporphyrin group. In contrast, the cy-
nide ligand is a much better σ-donor than a π-electron
acceptor toward 3d metals. Accordingly, the cyamide
ligands can increase the electronic density on the Fe(II)
ion [35], and this effect, multiplied by the four penta-
cyanoiron(II) groups, is being transmitted through the
Fe^{II}-pyP σ and π bonds. In addition, the protonation
of the porphyrin center should also involve a synergistic
effect between the electron donor-acceptor interactions
with the pentacyanoiron(II) groups, stabilizing the
system in terms of charge distribution, and allowing a
reduction in the electrostatic repulsion between the
peripheral complexes. This would explain the opposite
behavior observed for the tetraruthenated porphyrins
species where the peripheral groups consists of cationic
species.

The H_{3}(3-PCFP) supermolecule was also character-
ized by ^{57}Fe Mössbauer spectroscopy. The correspond-
ing spectra exhibited a doublet with I.S. = −0.01 mm
s^{-1} and Q.S. = 0.64 mm s^{-1}, which are consistent with
a tetragonally distorted low spin iron(II) complex
coordinated to the pyridyl substituents of H_{2}(3-TPyP)
[36–40]. The isomeric shift is less positive than for the
[Fe^{III/II}(CN)_{5}(py)]^{3−} complex (0.004 mm s^{-1}) suggesting
that the electron density on the Fe(II) ion is smaller
when coordinated to H_{3}(3-TPyP), but not as small as in
the DMSO (−0.032 mm s^{-1}) or CO (−0.140 mm s^{-1})
complexes [36]. Both are well known straing π-acid
ligands.

The cyclic voltammograms of a 2 mM solution (Fig.
4) of H_{3}(3-PCFP) exhibited a reversible wave at 0.45 V,
which is 0.11 and 0.01 V more positive than the redox

density at 0.39 V was assigned to the contribution of the
[Fe(CN)_{3}(NH_{3})^{3−} species in solution.

3.2. Properties of the Prussian blue materials

As shown above, the chemistry of H_{3}(3-PCFP)
resembles that of conventional pentacyanoferriate
complexes. Consequently, one can expect that other char-
acteristic properties of those complexes should also be
preserved in the supermolecular species. For example, a
precipitate was immediately formed after the addition of
concentrated inorganic acids into an concentrated aq-
uous solution. In analogy with the conventional penta-
cyanoferriate complexes [25]. When the same experiment
was repeated using a mixture of H_{2}(3-TPyP) and
Na_{3}[Fe(CN)(NH_{3})], only a dark green solution was
obtained instead. These results clearly show that the
simple mixture of the negatively charged pentacyano-
ferriate and protonated pyridylporphyrin species does
not lead to the formation of any sparingly soluble
species. In conclusion, only the neutral species [H_{4}(3-
PCFP)] obtained by protonation of some of the cyano
ligands of the supermolecular porphyrin precipitated
out after addition of concentrated inorganic acids.

Furthermore, H_{3}(3-PCFP) readily forms a precipitate
with transition metal ions (for example, Ni(II)) in
aqueous solution, generating a Prussian blue type
material. Interestingly, H_{3}(3-PCFP) was preferentially
incorporated in the solid in detriment of the pentacya-
noferriate species present in solution. Probably this
characteristic is a consequence of the lower solubility
and higher stability of that supramolecular material. In
fact, this solid is an inorganic polymer in which the porphyrin rings are surrounded/bonded to a Prussian blue type material.

The resonance Raman (rR) spectrum (\( \lambda_{exc} = 4880 \, \text{Å} \)) of a solid H\(_2\)(3-PCFP) sample is shown in Fig. 5A. As expected, the symmetric vibrational modes of the pyridylporphyrin center was intensified by the pre-resonance interaction with the spin and dipole moment allowed Soret transition, giving a spectrum with intense and well resolved peaks in the 300–1600 cm\(^{-1} \) range. In contrast to the parent pyridylporphyrin spectra, the rR spectrum of (TBA)\(_3\)[H\(_2\)(3-PCFP)] exhibited a very intense band at 1548 cm\(^{-1} \), which was tentatively assigned to the porphyrin ring vibrational modes \( v(C\sb{m}C) \), \( v(C–N) \), \( v(C\sb{p}C) \) and the pyridyl residue vibrational mode \( v(py) \). The contribution of the vibrational modes from the pyridyl groups was confirmed by Tosi et al. \[41\] to the combination modes involving the axial and equatorial C–N stretching normal modes, while the remaining bands were assigned to isotopic effects and hydrogen bonding sensitive vibrational modes.

In contrast with the rR spectra which exhibited almost exclusively pyridylporphyrin vibrational modes, the FTIR spectrum was dominated by intense \( v(C\sb{m}C) \) bands around 2000 cm\(^{-1} \). The frequency of the C–N stretching modes is sensitive to the oxidation state and coordination environment around the iron. Considering a complex with \( C\sb{4v} \) symmetry, three bands (2\( A\sb{1} + E \)) are expected in the 2000–2200 cm\(^{-1} \) range. However, up to seven bands can be observed in the spectrum of Na\(_2\)[Fe(CN)\(_5\)(NO)]·2H\(_2\)O species. Four of them were attributed by Tosi et al. \[41\] to the combination modes involving the axial and equatorial C–N stretching normal modes, while the remaining bands were assigned to isotopic effects and hydrogen bonding sensitive vibrational modes. A broad and intense band was observed at 2055 cm\(^{-1} \) in the H\(_2\)(3-PCFP) species (Fig. 5B), while in the Na\(_2\)[Fe(CN)\(_5\)(NH\(_3\))]·3H\(_2\)O complex it was found at 2043 cm\(^{-1} \). The shift to higher frequencies is consistent with the higher electron withdrawing capability of H\(_2\)(3-TPyP) ligand in comparison with NH\(_3\). That band was observed around 2060 cm\(^{-1} \) in the H\(_2\)(3-PCFP)/Ni(II) material. The shift to higher stretching frequencies is consistent with the presence of bridging cyanide ligand, i.e. Fe–CN–Ni bonds \[42\], which increases the force constant of the \( v(C\sb{m}C) \) vibrational normal modes.

The resonance Raman spectrum of the Prussian blue type material exhibited a good signal to noise ratio, enabling the calculation of the spectroscopic parameters from the theoretical fitting. The H\(_2\)(3-PCFP)/Ni(II) exhibited two doublets in the Mössbauer spectrum (Fig. 6). The signal at \( I.S. = 0.01 \, \text{mm} \, \text{s}^{-1} \) and \( Q.S. = 0.88 \, \text{mm} \, \text{s}^{-1} \) corresponds to about 2/3, while the one at \( I.S. = -0.08 \, \text{mm} \, \text{s}^{-1} \) and \( Q.S. = 1.81 \, \text{mm} \, \text{s}^{-1} \) corresponds to about 1/3 of the iron sites. This is a clear indication that there are two different chemical environments for the pentacyanoferrate(II) groups coordinated to the \textit{meso}-tetra-(3-PCFP) complex.
pyridyl)porphyrin, probably as a consequence of distinct interactions in volving Ni(II) ions, in the solid matrix. It is possible to infer by comparing the isomeric and quadrupole shifts that the electronic density on the I.S./C30/C10.08 mm s/C281 iron ions are smaller than on the I.S./C30/C0.01 mm s/C281 sites and are tetragonally more distorted. A similar behavior has also been reported for the analogous [FeII(CN)5(isonic)]27/C27 material and for [FeII(CN)4(bipy)]27/C27 films[42,43] grown onto a nickel electrode surface. No direct evidence of iron containing impurities could be found in the spectrum (Fig. 6), but a third minor signal (~3% of the total iron sites) at I.S. = 0.16 mm s\(^{-1}\) and Q.S. = 0.50 mm s\(^{-1}\) found in the fitting procedure was assigned to the [Fe(CN)5(NH3)]3\(^{3-}\) complex.

The absorption bands of the meso-3-pyridylporphyrin dominate the UV–Vis spectra of the H₂(3-PCFP)/Ni(II) samples, but the Soret band is broader and less intense. Interestingly, the formation of the solid increased its resistance to protonation by acids. As can be seen in Fig. 7 only a small amount of porphyrin ring was protonated even at pH 3, a pH much lower than the pKₐ = 4.7 of the H₂(3-PCFP) species in solution. We believe that only the porphyrin molecules that are in the outside boundary of the grains are effectively being protonated, while the solid matrix is inhibiting the reaction with the porphyrin molecules embedded in the bulk of the grains. At pH 1, the solid dissolved quite rapidly generating a dark green solution, showing that the protonation of the porphyrin ring destabilizes the lattice.

The electrochemical, catalytic and photochemical properties of Prussian blue type materials have been extensively explored in the last decades [44–47]. For example, Prussian blue films have been used to prepare cation selective modified electrodes [48]. The presence of channels with defined dimensions is responsible for the selectivity because large solvated ions will have more difficulty than smaller ones to diffuse through them and keep the electric charge balance during the electrochemical processes [49–58]. In the Prussian blue type materials, the migration of the solvated cation is known to control the electrochemical response.

The cyclic voltammograms of H₂(3-PCFP)/Ni(II) material in carbon paste electrodes exhibited a less intense wave at 0.43 V and a more intense one at 0.73 V, both reversible (Fig. 8). The presence of two redox processes in spite of the presence of only one redox species was observed previously even for solid materials obtained by the reaction of hexacyanoferrate with nickel(II) ions [42]. This electrochemical response was assigned to the presence of two different [FeIII/II(CN)₆] sites in the lattice, in which the complex is more or less paired with the electrolyte cation, such as K\(^{+}\). Similarly, one attributed the couple of waves observed in the voltammograms to the presence of two non-equivalent
Fe(III/II) redox pairs (Fig. 8), associated with two non-equivalent chemical environments around the pentacyanoferrate peripheral groups. In our case, however, those waves are broader suggesting the superposition of many redox processes with similar potentials. In addition, the voltammograms were only marginally sensitive to the supporting electrolyte, in contrast with other Prussian blue type materials, probably as a consequence of a lower degree of long range molecular order. However, one cannot rule out another possibility. The pore size in the new material may be sufficiently large to allow the diffusion of large hydrated cations without imposing significant resistance. The differential pulse voltammograms were also consistent with the presence of two main electrochemically active sites with a range of redox potentials (Fig. 8).

4. Concluding remarks

A new supermolecular pentacyanoferrate porphyrin was synthesized and characterized on the basis of spectroscopic and electrochemical methods. Interestingly, the pentacyanoferrate groups induced a significant increase in the basicity on the porphyrin ring in comparison with [Ru(bipy)2Cl]+ groups, as reflected in the pKa shift from about 2.2, in the ruthenium complex derivative, to 4.7 in the H3(3-PCFP). The new supermolecular porphyrin UV-Vis and rR spectra are dominated by the porphyrin absorptions band. Also, it forms very stable Prussian blue type material with Ni(II) in a rather selective way, as reflected by the exclusion of the pentacyanoferrate(II) species present in excess in solution. The voltammograms in carbon paste electrodes exhibited two broad redox pairs around 0.43 and 0.63 V, assigned to non-equivalent iron sites. This assignment was confirmed by Mössbauer spectroscopy.

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