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Note

Synthesis of pure iron(II) mesotetraphenylchlorin complexes via a versatile general method of iron insertion into chlorins

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ABSTRACT

An original synthesis of pure (tetraphenylchlorinato)iron(III) chloride (**1**) is reported. Insertion of iron is achieved using 1.2 equivalents of cadmium acetate in DMF at 110 °C, followed by a transmetallation reaction (in situ) using 8 equivalents of iron(II) chloride tetrahydrate in acetone at 60 °C. The ^{1}H NMR shifts at 25 °C of the pyrrole protons varied from 60 to 100 ppm. The absence of the signal at 80 ppm related to undesired (tetraphenylporphirinato)iron(III) chloride is a purity criterion and shows the importance of the method used.

Reaction of (tetraphenylchlorinato)iron(III) chloride (**1**) with four equivalents of *tert*-butyl isocyanide, 2,6-xylyl isocyanide and dimethylphenylphosphine in the presence of zinc amalgam in dichloromethane (DCM) afforded pure Fe^{II}(TPC)(*t*-BuNC)$_2$ (**2**), Fe^{II}(TPC)(2,6-xylylNC)$_2$ (**3**) and Fe^{II}(TPC)[P(Me)$_2$Ph]$_2$ (**4**) respectively.

1. Introduction

Investigations of the structural and spectroscopic properties of model compounds such as iron(III) chlorins and isobacteriochlorins [1–19] have been useful in understanding the active site of numerous heme enzymes such as heme d found in a terminal oxidase complex [20–23] or a catalase, hydroxyperoxidase II [24], all from *Escherichia coli*. In sulfmyoglobin, a nonfunctional form of myoglobin, the porphyrin macrocycle has been reduced to a chlorin by addition of a sulfur atom to a pyrrole ring [25]. Various hemoproteins such as myoglobins [26,27], horseradish peroxidase and cytochrome *b***5** [27] have also been reconstituted with iron chlorin prosthetic groups. A chlorin is a hydroporphyrin with one reduced pyrrole double bond. There are currently not enough results available of the physical properties of iron chlorins to explain their biological properties and their electronic ground state is still problematic [28]. In contrast, much more information is available with iron porphyrins [29].

Several considerations have prompted us to investigate iron chlorin models. A deeper understanding of the electronic ground state will require precise structural and spectroscopic features for the prosthetic group. The study of the binding of small ligands such as isocyanides and phosphorus derivatives to heme proteins is part of our long-term goal to establish correlations between the chemical and the electronic structures of heme derivatives [30,31].

Studies of the electronic structures with simple iron chlorins which might serve as models for naturally occurring iron chlorin proteins have been more limited due to the synthetic difficulty of preparing pure compounds due to the oxygen sensitivity of reduced macrocycle [4–16]. For the preparation of iron(III) derivatives as models for hemoproteins, the key step is the obtention of pure Fe(TPC)Cl (**1**). Our work was focused on finding optimal conditions allowing the production of pure Fe(TPC)Cl. This purity was then tested by preparing the first iron(II) diamagnetic complexes of TPC.

2. Experimental

2.1. General procedures and materials

As a precaution against the formation of the μ-*oxo* dimer [Fe(TPC)]$_2$O [10,40], all reactions were carried out in dried solvents in Schlenk tubes under an Argon atmosphere. Solvents were distilled from appropriate drying agents and stored under argon. The mesotetraphenylchlorin (TPC) was prepared by literature methods [41]. *tert*-Butyl isocyanide, 2,6-xylyl isocyanide and P(Me)$_2$Ph are commercially available.

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2.2. Physical measurements

UV–Vis spectra were recorded on an Uvikon 941 spectrophotometer in dichloromethane. ^{1}H NMR spectra were recorded on a Bruker AC 300P spectrometer in CD_2Cl_2 or $CDCl_3$ at 300 MHz. Tetramethylsilane was used as the internal reference. Mass spectrometry was performed by the Centre Régional de Mesures Physiques de l'Ouest, CRMPO, Rennes, France.

Abbreviations used: TPC = 7,8-dihydro-5,10,15,20-tetraphenylporphyrin dianion or mesotetraphenylchlorin, TPP = 5,10,15,20-tetraphenylporphyrin dianion or mesotetraphenylporphyrin, Fe(TPC)Cl = (7,8-dihydro-5,10,15,20-tetraphenylporphyrin) iron(III) chloride or (tetraphenylchlorinato) iron(III) chloride, Fe(TPP)Cl = (5,10,15,20-tetraphenylporphyrin) iron(III) Chloride or (tetraphenylporphyrinato)iron(III) chloride, Fe(TPC)(*t*-BuNC)**2** = (7,8-dihydro-5,10,15,20-tetraphenylporphyrin) iron(II) bis-(*tert*-butyl)isocyanide, Fe(TPC)(2,6-xylylNC)**2** = (7,8-dihydro-5,10,15,20-tetraphenylporphyrin) iron(II) bis-(2,6-xylyl)isocyanide, Fe(TPC)[P(Me)$_2$Ph]**2** = (7,8-dihydro-5,10,15,20-tetraphenylporphyrin) iron(II) bis-dimethylphenylphosphine, 2,6-xylylisocyanide = 2-isocyano-1,3-dimethylbenzene, P(Me)$_2$Ph = dimethylphenylphosphine.

2.3. Tetrakis(phenyl)-chlorinatoiron(III) chloride (**1**)

2.3.1. Fe^{III}(TPC)Cl (**1**)

0.5 g of TPC (0.81 mmol) and 0.26 of cadmium acetate dihydrate (0.97 mmol, 1.2 equiv.) were mixed in a Schlenk under argon atmosphere. 45 mL of distilled DMF were then introduced by a syringe. The mixture was heated and stirred at 110 °C for 20 min. The reaction was monitored by UV–Vis spectroscopy. DMF was evaporated under vacuum. In situ and under argon, 200 mg of solid sodium ascorbate, 1.29 g of iron(II) chloride tetrahydrate (6.48 mmol, 8 equiv.) and 50 mL of pure acetone (99%) was added by a syringe,. This mixture was heated at 60 °C for 2 h. The reaction was monitored by UV–Vis spectroscopy and TLC (eluent: pentane then chloroform). Acetone was evaporated under vacuum and the residue obtained was purified by column chromatography on neutral alumina, using a mixture of $CHCl_3$/CH_3OH (95/5) as eluent. Two drops of HCl (12 N) were added (to avoid the formation of the FeIII–μoxo dimer complex), and the sample was evaporated to dryness. 0.4 g was obtained. Yield = 80%. Dark green powder. UV–Vis λ_{max} (nm) (ε, 10^{-3} dm^3 M^{-1} cm^{-1}) (CH_2Cl_2): 385 (ε 74); 415 (ε 89); 600 (ε 16.4); 646 (ε 4.5); 740 (ε 4.9). FAB MS (*m*/*z*): [M]$^+$ 706.2.

2.4. Bis(tert-butyl isocyanide) tetrakis(phenyl)-chlorinatoiron(II) (**2**)

2.4.1. Fe^{II}(TPC)(t-BuNC)$_2$ (**2**)

A solution of Fe(TPC)Cl (0.1 g, 0.14 mmol) in 15 mL of dichloromethane was reduced under argon by Zn–Hg amalgam at room temperature. After a reaction time of 60 min, the solution was filtered and 4 equiv. of *tert*-Butyl isocyanide added by a syringe to the Fe(TPC) species. The solution was then stirred for 30 min. Hexane (40 mL) was added gradually and the solution set aside for crystallization. Fine crystals were collected by filtration after 3 days. Yield 0.1 g (85%). Dark red powder. UV–Vis ($CHCl_3$): λ_{max} (nm) 427 (ε 110 dm^3 mmol^{-1} cm^{-1}), 608 (ε 17). ^{1}H NMR (δ, CD_2Cl_2, ppm) 8.19 (2H, s, H$_{pyr}$); 8.18 (2H, d, H$_{pyr}$); 7.85 (2H, d, H$_{pyr}$); 7.95, 7.76 (8H, m, H$_o$); 7.6 (m, 12H, H$_{m+p}$); 4.02 (s, 4H, H$_{pyrroline}$); −0.07 (s, 18H, H$_{ligand}$).

FAB MS (*m*/*z*): [M−2*t*-BuNC]$^+$ 670. IR ν(CN) 2117 cm^{-1} (Nujol).

2.5. Bis(2.6-xylyl isoyanide) tetrakis(phenyl)-chlorinatoiron(II) (**3**)

2.5.1. Fe^{II}(TPC)(2,6-xylylNC)$_2$ (**3**)

A solution of Fe(TPC)Cl (0.1 g, 0.14 mmol) in 15 mL of dichloromethane was reduced under argon by Zn–Hg amalgam at room temperature. After a reaction time of 60 min, the solution was then filtered and 4 equiv. of 2,6-xylyl isocyanide added by a syringe to the Fe(TPC) species. The solution was then stirred for 30 min. Hexane (40 mL) was added gradually and the solution set aside for crystallization. Fine crystals were collected by filtration after 3 days. Yield 0.09 g (69%). Dark red powder. UV–Vis ($CHCl_3$): λ_{max} (nm) 427 (ε 80 dm^3 mmol^{-1} cm^{-1}), 610 (ε 11).

^{1}H NMR (δ, CD_2Cl_2, ppm) 8.29 (s, 2H, H$_{pyr}$); 8.27 (d, 2H, H$_{pyr}$); 7.85 (d, 2H, H$_{pyr}$); 7.99; 7.81 (m, 8H, H$_o$); 7.66 (m, 12H, H$_{m+p}$); 6.67 (t, 2H, H$_p$ ligand); 6.49 (d, 4H, H$_m$ ligand); 4.12 (s, 4H, H$_{pyrroline}$); 0.79 (s, 12H, CH_3 ligand). FAB MS (*m*/*z*): [M−2(2,6-xylylNC)]$^+$ 670. IR ν(CN) 2111 cm^{-1} (Nujol).

2.6. Bis(dimethylphenylphosphine) tetrakis(phenyl)-chlorinatoiron(II) (**4**)

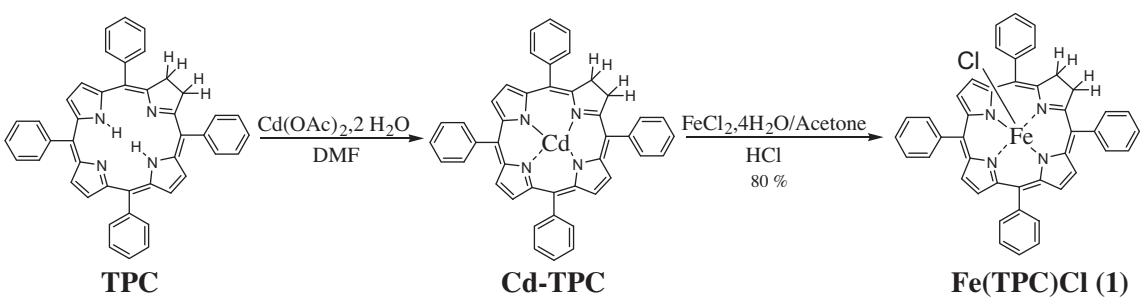
2.6.1. Fe^{II}(TPC)[P(Me)$_2$Ph]$_2$ (**4**)

A solution of (TPC)FeCl (0.1 g, 0.14 mmol) in 15 mL of dichloromethane was reduced under argon by Zn–Hg amalgam at room temperature. After a reaction time of 60 min, the solution was then filtered and 4 equiv. of dimethylphenylphosphine added by a syringe to the Fe(TPC) species. The solution was then stirred for 30 min. Hexane (40 mL) was added gradually and the solution set aside for crystallization. Fine crystals were collected by filtration after 3 days. Yield: 0.094 g (70%). Dark red powder. UV–Vis (toluene): λ_{max} (nm) 370 (ε 13.7 dm^3 mmol^{-1} cm^{-1}), 444 (ε 62.4) 569 (ε 7.9), 609 (ε 17.1), 654 (ε 4.3). ^{1}H NMR (δ, $CDCl_3$, ppm, 298 K): Chlorin: 8.2 (s, 2H, H$_{pyrr}$); 7.8 (m, 4H, H$_o$); 7.6 (m, 20H, H$_{pyrr}$ + H$_{o,m,p}$); 4.35 (s, 4H, H$_{pyrroline}$). Ligand: 6.9 (t, 2H, H$_p$); 6.7 (t, 4H, H$_m$); 4.9 (t, 4H, Ho); −2.35 (s, 12H, CH_3). FAB MS (*m*/*z*): [M]$^+$ 946.3, [M−P(Me)$_2$Ph]$^+$ 808.3, [M−2P(Me)$_2$Ph] 670.3.

3. Results and discussion

3.1. Syntheses

The insertion of iron in the TPC was performed by a transmetallation reaction using the cadmium complex Cd–TPC as intermediate (Scheme 1).



Scheme 1. Synthesis strategy of Fe^{III}(TPC)Cl (**1**).

Table 1
Percentages of oxidized macrocycle using classical insertion methods.

$FeCl_2.4H_2O$	$FeBr_2$	Transmetallation via Cd
Yield = 75% FeTPPCl = more than 25%	Yield = 75% FeTPPCl = 10–20%	Yield = 80% FeTPPCl (not detected)

This method developed in our laboratory, is adapted from a procedure used by Scherz with bacteriochlorophyll a [32]. The procedure allows one to obtain a pure compound and overcomes the problem of oxidation of the TPC that gives non negligible amounts of Fe(TPP)Cl together with the desired product (**1**) [35].

Obviously, this reaction is the key-step to master, in order to prepare iron(II) and especially iron(III) complexes of sufficient purity for structural and spectroscopic studies.

Using classical methods of iron insertion such as $FeCl_2$ or $FeBr_2$ under reflux in DMF gave huge amounts of oxidized macrocycle (Table 1).

The Cadmium complex Cd–TPC is easily accessible with the method (acetate/DMF) and could be subject to transmetallation in good yields (80%) into other metal complexes under mild conditions. The ease of transmetallation of Cd(TPC) complexes is probably due to the large ionic radius of cadmium (r_M^i) Cd^{2+}(0.95 Å) with respect to that of Fe^{2+} (0.65 Å). In addition, it is well know that the cadmium does not completely fit into the core of the macrocycle and is found slightly displaced above its plane [33]. This explains the average stability of the cadmium complex which is demetallated at pH 6–7. Accordingly, these complexes were not isolated and the transmetallation is performed in situ.

Another important factor of the reaction is the use of acetone as solvent for the transmetallation together with the counteranion chloride. In fact, during the transmetallation, $CdCl_2$ and the Fe–TPC complex are in equilibrium with the starting materials and the driving force of the reaction is the very low solubility of $CdCl_2$ in acetone that shifts the equilibrium in the direction of formation of the products.

This procedure has proven its efficiency with other chlorins differently substituted on the meso positions of the phenyl groups.

The synthesis of symmetrical bis-isocyanides and bis-phosphine (**2**–**4**) complexes in the iron(II) state was *via* a variation of our method, previously reported for the synthesis of Fe(TPP)$(CNR)_2$ and Fe(TPP)$(phosphine)_2$ (Scheme 2) [36].

Starting from Fe(TPC)Cl, the reduction of Fe(III) to Fe(II) was carried out with zinc amalgam under argon. The compounds were obtained as crystalline solids in 70–80% yield and characterized by ^1H NMR. The stability of the reduced complexes was satisfactory at ambient temperature so that it was not necessary to add excess ligand in the solution to record NMR spectra. This result was expected since it was previously reported that the stability constants for ligand binding to metal complexes generally increase with increasing saturation of the macrocycle [37,38].

One major difficulty may be encountered in preparing iron(II) complexes of chlorins. The oxidation of the chlorin ring to a porphyrin ring may occur, as previously reported with imidazole ligands [15]. This problem was solved by the iron insertion method presented above.

3.2. ^1H NMR spectroscopy

A representative ^1H NMR spectrum of [Fe(TPC)]Cl (**1**) is shown in Fig. 1. The non-equivalent pyrrole (pyr) proton resonances for (**1**) at 87, 77 and 68 ppm (298 K) are within the range of 50–100 ppm found for the pyrrole resonances in other high-spin chlorin complexes ($S = 5/2$) [11]. These values are much further downfield than the values of 10–40 ppm found for spin-admixed ($S = 3/2, 5/2$) complexes such as [Fe(TPP)]CF_3SO_3 and [Fe(TPP)]ClO_4 suggesting a pure high-spin state for our paramagnetic complex (**1**) [34].

The three pyrrole type resonances that are strongly shifted downfield are indicative of a strong sigma contact shift at these positions. This is in accordance with a half-filled $d_{x^2-y^2}$ electron of iron(III) and a delocalisation through the σ orbitals of the chlorin [35].

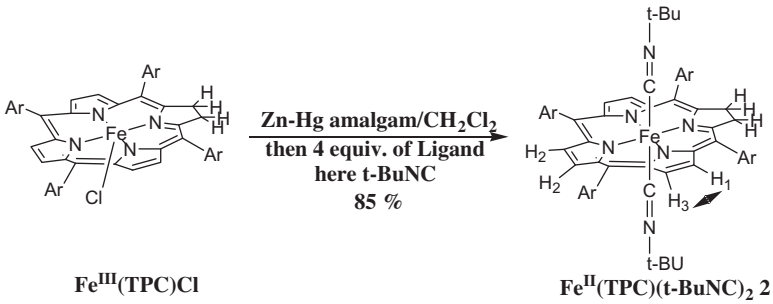
It is important to notice the absence of the shift at 80 ppm related to Fe(TPP)Cl, which was always present when classical means of iron insertion were used [35].

As a proof of high purity of (**1**), A representative ^1H NMR spectrum of Fe^{II}(TPC)$(t\text{-BuNC})_2$ (**2**) is shown in Fig. 2. The peaks for the phenyl protons of the chlorin ring are fully assigned by proton COSY experiments (Fig. 3). For isocyanide axial ligands, measurements of the relative intensities and relative line-widths fully determine the assignment. The shift of the isocyanide ligand is unchanged in the presence of excess ligand. Hence axial ligand dissociation is not expected to be significant at ambient temperature.

The ^1H NMR spectrum of Fe(TPC)$(t\text{-BuNC})_2$ (**2**) displays two groups of signals corresponding to the chlorin ring protons: 8.19, 8.18 and 7.85 (H_{pyr}); 7.80 (H_o); 7.56–7.6 (H_{m+p}); 4.02 ($H_{pyrroline}$) and to the ligand (−0.07 ppm). These chemical shifts are very similar to those found for Fe(TPC)$(PMe_2Ph)_2$ (**4**) and are as expected for diamagnetic iron(II) chlorin derivatives. The protons of the ligand are shifted to high field (*vs.* free ligand) due to the ring current shift of the macrocycle. Similar results were obtained with complex (**3**).

3.3. IR spectroscopy

In the IR spectrum of the new complex Fe^{II}(TPC)$(t\text{-BuNC})_2$ (**2**), The ν(C≡N) stretching frequency of CNR is decreased upon



Fe^{III}(TPC)Cl — Fe^{II}(TPC)(t-BuNC)$_2$ **2**

Scheme 2. Synthesis of Fe^{II} complexes.

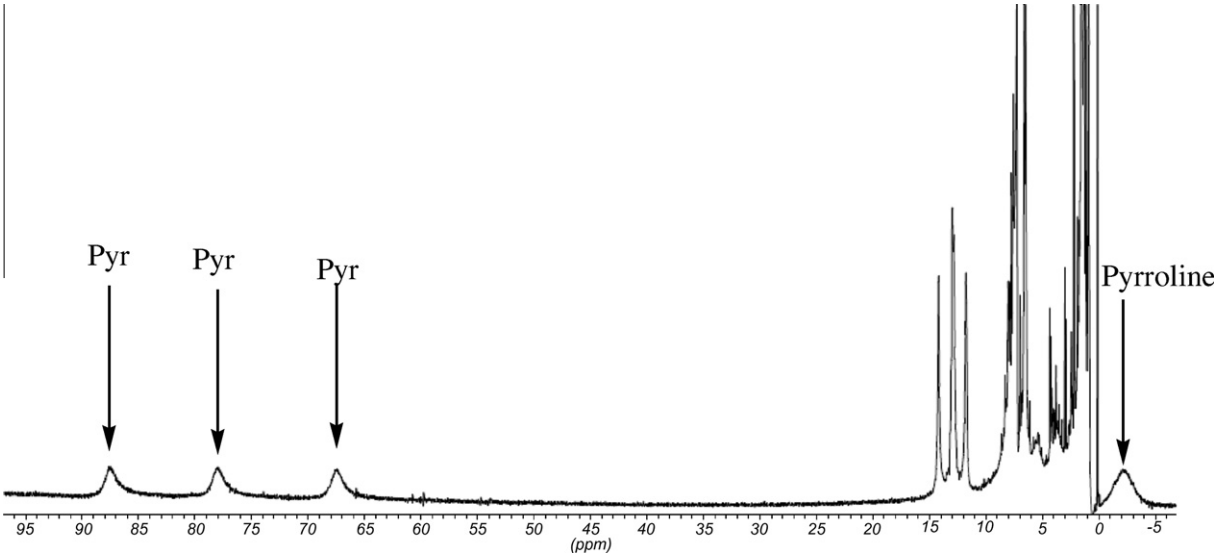


Fig. 1. ^{1}H NMR spectrun of Fe(TPC)Cl (**1**) in CD_2Cl_2 at 298 K.

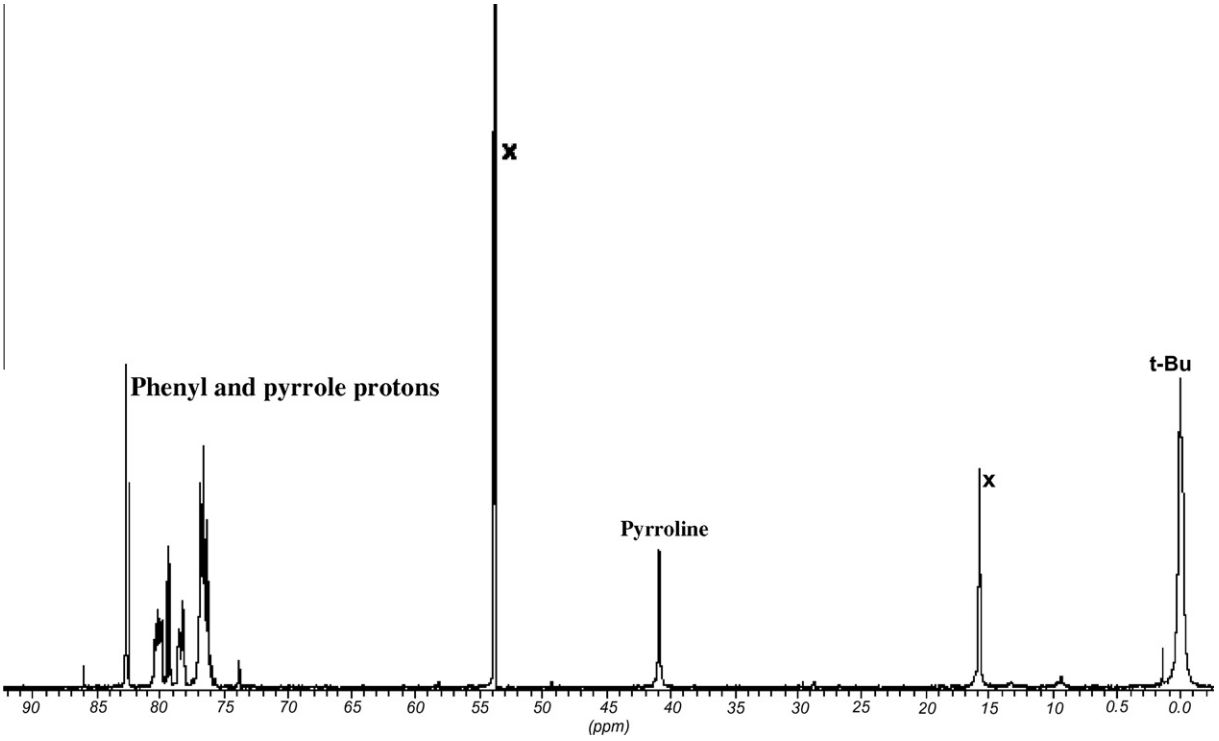


Fig. 2. ^{1}H NMR of Fe(TPC)(*t*-BuNC)$_2$ (**2**) in CD_2Cl_2 at 298 K.

coordination of the isocyanide to the metal, decreasing from 2130 cm^{-1} for the free ligand to 2117 cm^{-1} in (**2**.) This suggests that the observed isocyanide stretching frequency is influenced by the reduction of the porphyrin ring (*cis*-macrocycle influence). Thus, isocyanide ligands bonded to iron(II) chlorins (ν(C≡N) 2117 cm^{-1}) have lower CN stretching frequencies than their corresponding Fe(TPP)(*t*-BuNC)**$_2$** (ν(C≡N) 2129 cm^{-1}) [39]. As expected, the more electron donating the macrocycle the lower the (CN) frequency due to an increase in the π^* population of the CN bond of the iron(II) complex.

In summary, a simple and highly efficient synthesis of pure Fe^{III}-TPCCl (**1**) has been developed. The purity of this compound was unprecedented and allowed the synthesis of iron(II) complexes (**2**–**4**). This methodology will open a new perspective in the synthesis and correct characterization of highly pure iron(II) and iron(III) complexes of chlorins as models of hemoproteins.

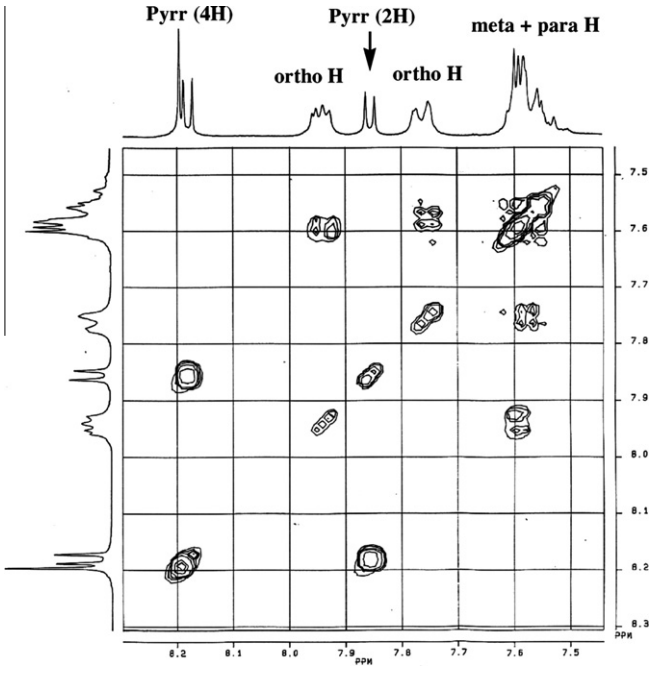


Fig. 3. Part of the COSY 2D spectrum of Fe(TPC)(*t*-BuNC)$_2$ (**2**) in CD_2Cl_2 at 298 K.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2013.01.012.

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