

## Resonance Raman Spectroscopy of Fe<sup>II</sup>Fe<sup>III</sup> and Fe<sup>III</sup>Fe<sup>III</sup> Model Complexes Containing an Unsymmetrical Dinucleating Ligand: A Biomimetic Redox Pair for Uteroferrin

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Neste trabalho, investigamos os perfis de excitação Raman do complexo [Fe<sup>II</sup>Fe<sup>III</sup>(bpbpmp)(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>](ClO<sub>4</sub>) (**1**) e de sua inédita forma oxidada, [Fe<sup>III</sup>Fe<sup>III</sup>(bpbpmp)(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**2**), sendo bpbpmp a molécula 2-bis[[(2-piridilmetil)-aminometil]-6-[(2-hidroxibenzil)(2-piridilmetil)]-aminometil]-4-metilfenol. No complexo **1**, o modo vibracional mais intensificado no espectro Raman é o correspondente ao  $\nu(\text{Fe}-\text{O}_{\text{phen\_terminal}})$ , observado em 608 cm<sup>-1</sup>. Já no complexo **2**, passa a ser o  $\nu(\text{CO}_{\text{phen\_terminal}})$ , observado em 1276 cm<sup>-1</sup>. Estas diferenças são devidas às mudanças na estrutura eletrônica do esqueleto dinuclear unido por ponte fenolato, a qual é capaz de deslocalizar carga eletrônica entre os dois centros metálicos.

Raman excitation profiles for the complex [Fe<sup>II</sup>Fe<sup>III</sup>(bpbpmp)(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>](ClO<sub>4</sub>) (**1**), and its oxidized form, the new compound [Fe<sup>III</sup>Fe<sup>III</sup>(bpbpmp)(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**2**), are reported. H<sub>2</sub>bpbpmp is the proligand 2-bis[[(2-pyridylmethyl)-aminomethyl]-6-[(2-hydroxybenzyl)(2-pyridylmethyl)]-aminomethyl]-4-methylphenol. For compound **1**, the most enhanced vibrational mode in the Raman spectra is the  $\nu(\text{Fe}-\text{O}_{\text{phen\_terminal}})$ , observed at 608 cm<sup>-1</sup>. For compound **2**, the  $\nu(\text{CO}_{\text{phen\_terminal}})$ , which corresponds to the band at 1276 cm<sup>-1</sup>, becomes the most enhanced one. These differences are ascribed to the changes in the electronic structure of the dinuclear phenolate bridged core upon oxidation. The phenolate bridge allows charge density transmission between the metal centers.

**Keywords:** Resonance Raman spectroscopy, purple acid phosphatase, biomimetic analogue, mixed-valence, unsymmetrical ligand

## Introduction

Purple acid phosphatases (PAP's) constitute a class of metalloenzymes that have been isolated from animals, plants and fungi. They contain a dinuclear core Fe<sup>III</sup>M<sup>II</sup> (M = Fe, Mn or Zn) in their active sites, which are able to catalyze the hydrolysis of a variety of phosphoric acid esters and anhydrides within the pH range 4-7.<sup>1-3</sup>

In particular, the core Fe<sup>II</sup>Fe<sup>III</sup> is present in uteroferrin, a PAP from porcine uterus that is involved in the hydrolysis of orthophosphate monoesters and the regulation of the levels of phosphate at pH 4.9-6.0.<sup>1,4</sup> The reduced form of

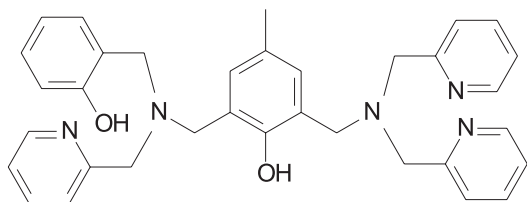
the enzyme is pink ( $\lambda_{\text{max}}=505\text{-}510\text{ nm}$ ,  $\epsilon \approx 4000\text{ L mol}^{-1}\text{ cm}^{-1}/\text{Fe}_2$ ), and is active for hydrolysis, while the purple form, Fe<sup>III</sup>Fe<sup>III</sup> ( $\lambda_{\text{max}}=550\text{-}570\text{ nm}$ ,  $\epsilon \approx 4000\text{ L mol}^{-1}\text{ cm}^{-1}/\text{Fe}_2$ ) is inactive.<sup>4</sup> The similarity between the molar absorptivities of these two forms comes from the fact that the reduced iron is not part of the chromophoric group (tyrosinate-Fe<sup>II</sup>).<sup>3</sup>

Resonance Raman (RR) spectroscopy is a powerful tool in the investigation of molecular electronic excited states, since it allows the determination of the chromophoric group responsible for the electronic transition. In this way, electronic structure details can be accessed through this technique. It is worth to mention that it has been employed to investigate the nature of electronic transitions in a large range of systems, such as

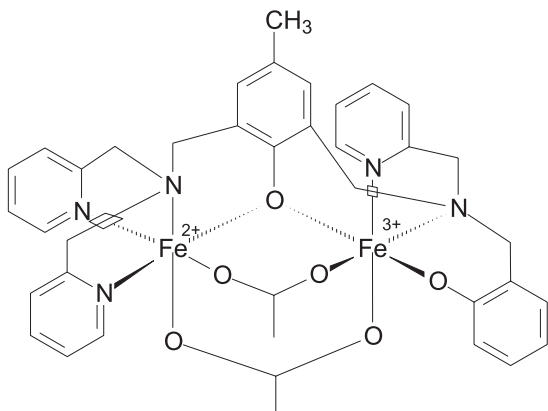
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inorganic coordination compounds,<sup>5</sup> metal-containing proteins<sup>6-8</sup> and their biomimetic analogues.<sup>9-18</sup> PAP's and related systems have also been studied by this technique,<sup>19-25</sup> aiming to characterize the chromophoric moiety for improved understanding of their electronic structure. The visible chromophore in the PAP enzyme has been associated with a tyrosinate to Fe<sup>III</sup> charge-transfer transition.<sup>2,4</sup> Resonance Raman studies on PAP's, using visible excitation, confirm the presence of tyrosinate ring modes.<sup>26</sup>

In a previous work,<sup>27</sup> a RR study of two isomeric dinuclear bis- $\mu$ -alkoxo complexes containing two Fe<sup>III</sup> centers, [Fe<sub>2</sub>(bbpnoI)<sub>2</sub>], revealed that the electronic coupling between the two centers is significantly increased in the *cis-cis* rather than in the *cis-trans* form. The mixed-valence Fe<sup>II</sup>Fe<sup>III</sup>,<sup>28</sup> Mn<sup>II</sup>Fe<sup>III</sup><sup>29</sup> and Mn<sup>II</sup>Mn<sup>III</sup><sup>30</sup> complexes containing the M<sup>II</sup>( $\mu$ -C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>M<sup>III</sup> moiety with H<sub>2</sub>bpbpmp have already been described in the literature. The molecular structures of H<sub>2</sub>bpbpmp and of its Fe<sup>II</sup>Fe<sup>III</sup> coordination compound (supposing the same structure of the Mn<sup>II</sup>Fe<sup>III</sup> complex<sup>29</sup>) are represented in Figures 1 and 2, respectively.



**Figure 1.** Representation of the molecular structure of H<sub>2</sub>bpbpmp.



**Figure 2.** Proposed molecular structure for compound 1.

In this work, we report a detailed RR study of two coordination compounds, aiming to analyze the effect of a mixed-valence core that may exhibit distinct reactivities as a function of the oxidation state, as well as to identify the changes in the electronic structure pertinent to the Fe<sup>III</sup>Fe<sup>X</sup> (X=II,III) core. The Fe<sup>III</sup>Fe<sup>III</sup> complex is still

unknown in the literature. It is important to notice that such complexes, which contain a terminal Fe<sup>III</sup>-O<sub>phenolate</sub> bond with the unsymmetrical proligand H<sub>2</sub>bpbpmp, have been proposed as structural and functional models for utero-porcine PAP.<sup>28</sup> Another goal is to corroborate previous results of a theoretical paper<sup>31</sup> concerning the force field parameters that reflect in the vibrational wavenumbers.

## Experimental

### Syntheses

**CAUTION!** Perchlorate salts of metal complexes are potentially explosive and therefore should be prepared in small quantities with the proper care.

The syntheses of the unsymmetrical proligand 2-bis[[(2-pyridylmethyl)-aminomethyl]-6-(2-hydroxybenzyl)(2-pyridylmethyl)-aminomethyl]-4-methylphenol, H<sub>2</sub>bpbpmp, and the complex [Fe<sup>II</sup>Fe<sup>III</sup>(bpbpmp)(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>](ClO<sub>4</sub>) (1), were already reported.<sup>28</sup> The oxidized form, the new compound [Fe<sup>III</sup>Fe<sup>III</sup>(bpbpmp)(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (2), was synthesized by reacting Fe<sup>III</sup> ions with the proligand, as follows: in a methanolic solution (50 mL) of Fe(ClO<sub>4</sub>)<sub>3</sub>·9H<sub>2</sub>O (2.13 mmol, Aldrich), H<sub>2</sub>bpbpmp (1 mmol) was added under magnetic stirring and ambient conditions. Then, sodium acetate trihydrate (4.25 mmol, Aldrich) was added and the resulting solution was heated at 40 °C for ten minutes. The dark-blue precipitate was filtered off and recrystallized from methanol/isopropanol (1:1), forming blue single-crystals. Yield 50% (0.56 g). Anal. Calc. for Fe<sub>2</sub>C<sub>38</sub>H<sub>39</sub>N<sub>5</sub>O<sub>6</sub>·2ClO<sub>4</sub>·3MeOH·3H<sub>2</sub>O: C, 43.87; H, 4.57; N, 6.24. Found C, 44.30; H, 4.58; N, 6.24%. All solvents and reagents employed were of analytical grade.

### Spectroscopic measurements

Raman spectra were obtained with a Renishaw Raman System 3000, using the 632.8 nm exciting line of a Helium-Neon laser (Spectra-Physics Model 127). The samples were finely ground and slightly pressed over glass slides. The spectral slit was set to 4 cm<sup>-1</sup>.

Resonance Raman (RR) spectra were obtained with a Jobin-Yvon U-1000 using the exciting lines of either Ar<sup>+</sup> and Kr<sup>+</sup> lasers (Coherent Innova 90) and photon-counting detection (EG & G PAR). The samples were prepared by dilution in KNO<sub>3</sub> (internal standard) in a 1:50 proportion (m/m). The finely ground mixture was placed in a rotating cell to avoid local heating. Laser power was adjusted in the

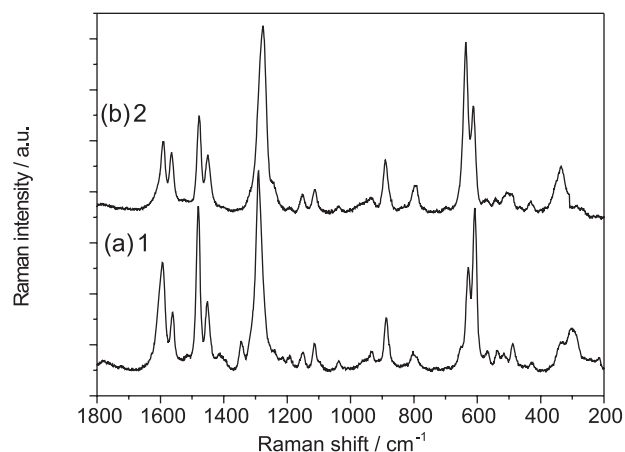
range of 50-100 mW. The spectral slit was set to 4 cm<sup>-1</sup>. Raman excitation profiles (REP) were constructed by plotting relative Raman intensities versus exciting wavelength. These relative Raman intensities were computed from the ratio of peak heights to the 1050 cm<sup>-1</sup> band of the internal standard.

In order to allow comparison between REP and optical spectra, these have been plotted together with the respective REP's. The optical spectra of the samples were obtained as diffuse reflectance spectra, using the integrating sphere attachment in the Perkin-Elmer Lambda-19. The samples were dispersed in MgO, which also served as reference.

## Results and Discussion

### Raman spectroscopy

The Raman spectra of the pure compounds [Fe<sup>II</sup>Fe<sup>III</sup>(bpbmp)(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>][ClO<sub>4</sub>] (**1**) and [Fe<sup>III</sup>Fe<sup>III</sup>(bpbmp)(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>][ClO<sub>4</sub>] (**2**), acquired near the resonance region in the Renishaw spectrometer, are displayed in Figure 3.



**Figure 3.** Raman spectra of compounds (a) **1** and (b) **2** excited at 632.8 nm, near the resonance region.

Selected vibrational wavenumbers of the most prominent bands were picked up from the Raman spectra and presented in Table 1, that also contains a tentative assignment based on previous works on related systems.<sup>27,31</sup>

### Resonance Raman spectroscopy

Raman excitation profiles were constructed for the most prominent bands of compounds **1** and **2**, indicated in Figures 4 and 5, respectively. The optical spectra of compound **1** in the solid state ( $\lambda_{\text{max}} = \text{ca. } 570 \text{ nm}$ ) agrees

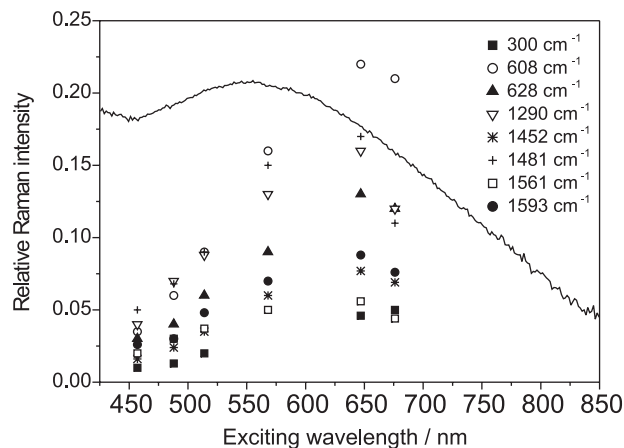
**Table 1.** Observed Raman wavenumbers (cm<sup>-1</sup>) for complexes **1** and **2**. Ring modes are indicated by Wilson vibration numbering

| 1        | 2        | assignment   |
|----------|----------|--|
| 300(w)   | —        | $\nu_s(\text{Fe-O}_{\text{phen\_bridge}}-\text{Fe})$           |
| 333(sh)  | 335(w)   | $\nu_s(\text{Fe-O}_{\text{phen\_bridge}}-\text{Fe})$           |
| 608(s)   | —        | $\nu(\text{Fe-O}_{\text{phen\_terminal}})$                     |
| —        | 612(m)   | 6b   |
| 628(m)   | —        | 6b   |
| —        | 636(s)   | $\nu(\text{Fe-O}_{\text{phen\_terminal}})$                     |
| 798(vw)  | 795(vw)  | $\nu_{\text{AS}}(\text{Fe-O}_{\text{phen\_bridge}}-\text{Fe})$ |
| 887(w)   | 890(w)   | 1  |
| 1114(w)  | 1112(w)  | 18a  |
| 1150(w)  | 1151(w)  | 15   |
| —        | 1243(sh) | $\nu(\text{CO})_{\text{phen\_bridge}}$                         |
| 1290(vs) | 1276(vs) | $\nu(\text{CO})_{\text{phen\_terminal}}$                       |
| 1344(w)  | —        | 14   |
| 1452(m)  | 1451(m)  | 19b  |
| 1481(s)  | 1478(m)  | 19a  |
| 1561(m)  | 1564(m)  | 8b   |
| 1593(s)  | 1591(m)  | 8a   |

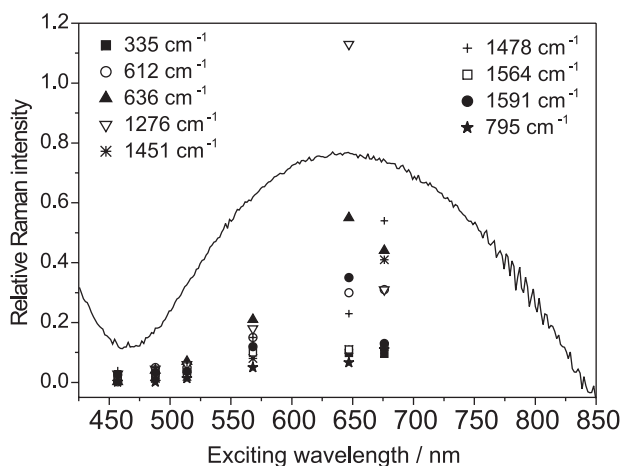
v=very weak, w=weak, m=medium, s=strong, vs=very strong, sh=shoulder, br=broad.

with that reported in CH<sub>3</sub>CN solution by Neves *et al.* ( $\lambda_{\text{max}} = 555 \text{ nm}$ ).<sup>28</sup> From the diffuse reflectance spectra, it is possible to observe that the REP is red-shifted relative to the optical spectrum for compound **1**, a behavior already noticed for this kind of substance (see 27 and references therein). The solid state optical spectra of compound **2** ( $\lambda_{\text{max}} = \text{ca. } 650 \text{ nm}$ ) also correlates well with that reported by de Brito<sup>32</sup> in CH<sub>3</sub>CN solution ( $\lambda_{\text{max}} = 618 \text{ nm}$ ), and there is no significant shift for the most enhanced vibrational modes.

The general pattern of the spectra is very similar to that exhibited by the bovine spleen purple acid phosphatase, as reported by Averill *et al.*,<sup>26</sup> what is a strong evidence of the similarity between the iron coordination environment in the complexes and the phosphatase active center. The enhanced bands can be assigned to the



**Figure 4.** Raman excitation profiles for compound **1**, together with the diffuse reflectance spectrum (solid line).



**Figure 5.** Raman excitation profiles for compound **2**, together with the diffuse reflectance spectrum (solid line).

phenolate internal ring, the terminal phenolate  $\nu(\text{C}-\text{O}_{\text{phen}})$ , and the  $\nu(\text{Fe}-\text{O}_{\text{phen\_terminal}})$  modes.

The comparison between the two Raman excitation profiles allows drawing the following conclusions. The  $\nu(\text{CO}_{\text{phen\_terminal}})$  mode is much more intensified in compound **2** than in **1**. As pointed out previously by Paes *et al.*,<sup>31</sup> the terminal phenolate oxygen bears a high electronic density in this kind of compound containing two phenolate rings. In compound **2**, the presence of two  $\text{Fe}^{\text{III}}$  atoms would imply in electronic states having altered charge distribution, compared to compound **1**. See, for instance, the case of the electronic ground state, which presents an expressive figure for the  $\Delta\nu = |\nu(\text{C}-\text{O}_{\text{phen\_terminal}}) (\mathbf{1}) - \nu(\text{C}-\text{O}_{\text{phen\_terminal}}) (\mathbf{2})| = 14 \text{ cm}^{-1}$ . This change in the charge distribution would also result in an increased dissimilarity between the fundamental and the excited electronic states, as the LUMO would then have the contribution from the two  $\text{Fe}^{\text{III}}$  atoms (since the bridge couples electronically the two  $\text{Fe}^{\text{III}}$  atoms). The net effect is to increase the transition dipole moment, thus leading to an enhanced tyrosinate-to- $\text{Fe}^{\text{III}}$  CT transition (as more charge will be displaced), which increases the molar absorptivity ( $\epsilon$ ) and thus the RR enhancement, as observed for compound **2**. The effective electronic coupling provided by the Fe-O-Fe bridge was reported in a previous work.<sup>27</sup> However, this should not be confused with the weak antiferromagnetic coupling exhibited by the phenoxo bridges, which is caused by the low electronic density on the oxygen bridge.<sup>31</sup>

Data for other iron complexes with phenolate ligands<sup>33</sup> show that tyrosinate-to- $\text{Fe}^{\text{III}}$  CT transition molar absorptivities are much higher than the phenolate(bridge)-to- $\text{Fe}^{\text{III}}$  analogs. As the RR intensification is proportional to the squared molar

absorptivities, most of the RR enhanced bands of compounds **1** and **2** can be safely assigned to terminal phenolates. In the low-frequency region, the bands at 300-335  $\text{cm}^{-1}$  range are tentatively assigned to  $\nu(\text{Fe}-\text{O}_{\text{phen\_bridge}})$ , although the correct normal mode description would be a kind of chelate ring breathing, as proposed previously.<sup>27</sup> The much smaller intensification observed for these low-frequency bands indicates that the  $\text{O}_{\text{phen\_bridge}}$ -to- $\text{Fe}^{\text{III}}$  CT transition is very weak, compared to the stronger tyrosinate-to- $\text{Fe}^{\text{III}}$  CT transition in the electronic spectra, which overlays the weaker one. This also reflects in the Raman spectra of **2**, as the shoulder at 1243  $\text{cm}^{-1}$  (assigned to  $\nu(\text{CO}_{\text{phen\_bridge}})$ ) is much less intense than the band at 1276  $\text{cm}^{-1}$ , assigned to  $\nu(\text{CO}_{\text{phen\_terminal}})$ . It is interesting to observe that no counterpart for this shoulder at 1243  $\text{cm}^{-1}$  could be safely assigned in the Raman spectrum of compound **1**, since in this compound there is only one vicinal  $\text{Fe}^{\text{III}}$  to enhance the  $\text{O}_{\text{phen\_bridge}}$ -to- $\text{Fe}^{\text{III}}$  CT transition.

In compound **1**, an outstanding fact is that the most enhanced band in the REP is the one at 608  $\text{cm}^{-1}$ , assigned to the terminal  $\nu(\text{Fe}-\text{O}_{\text{phen\_terminal}})$  mode, whose frequency is in the region reported for other iron-phenolate complexes.<sup>34</sup> This assignment also corrects that of a previous work,<sup>29</sup> since it would not be expected that an asymmetric mode such as the  $\nu_{\text{AS}}(\text{Fe}-\text{O}_{\text{phen\_bridge}}-\text{Fe})$  would present such a high RR enhancement, at least for a Raman intensification mechanism based on the A-term Albrecht formalism.<sup>3</sup> The new proposed values for the  $\nu_{\text{AS}}(\text{Fe}-\text{O}_{\text{phen\_bridge}}-\text{Fe})$  (798 and 795  $\text{cm}^{-1}$  for complexes **1** and **2**, respectively) are consistent with the relative low RR enhancement exhibited by these bands (the 798  $\text{cm}^{-1}$  band is not represented in the REP due to its low intensity). The assignment for the  $\nu(\text{Fe}-\text{O}_{\text{phen\_terminal}})$  (608  $\text{cm}^{-1}$ ) and the 6b ring mode (628  $\text{cm}^{-1}$ ) is also based on the higher Raman intensification showed by the former one, since the molecular orbitals of the  $(\text{Fe}-\text{O}_{\text{phen\_terminal}})$  chemical bond should participate more effectively in the chromophoric group. The ring mode 6b is weakly coupled to the  $\nu(\text{Fe}-\text{O}_{\text{phen\_terminal}})$ ; therefore, it should exhibit only a slight enhancement. This weak enhancement of the ring mode is a behavior already noticed for the compound “*cis-cis*”- $[\text{Fe}_2(\text{bbpno})_2]$ .<sup>29</sup> However, for compound **2**, the Raman intensification pattern is just reversed (see the respective REP), *viz.*, the band at 612  $\text{cm}^{-1}$  is less intensified than the one at 636  $\text{cm}^{-1}$  (see Figure 5). This finding suggests *per se* that the vibrational assignment of this doublet should also be reversed, as shown in Table 1, that is, the band at lower wavenumber is now assigned to the

ring mode 6b and the other at higher wavenumber is assigned to the  $\nu(\text{Fe-O}_{\text{phen\_terminal}})$  mode. Besides, the change in the iron oxidation state should disturb the  $\nu(\text{Fe-O}_{\text{phen\_terminal}})$  mode in a higher extension than the ring  $\nu_{6b}$  ring mode, as evidenced by the  $\Delta\nu: |\nu_{6b}(\mathbf{1}) - \nu_{6b}(\mathbf{2})| = 16 \text{ cm}^{-1}$  versus  $|\nu(\text{Fe-O}_{\text{phen\_terminal}})(\mathbf{1}) - \nu(\text{Fe-O}_{\text{phen\_terminal}})(\mathbf{2})| = 28 \text{ cm}^{-1}$ . Also, this change in the iron oxidation state is expected to increase the wavenumber of the  $\nu(\text{Fe-O}_{\text{phen\_terminal}})$  mode in compound **2** due to the charge redistribution that reinforces the Fe-O<sub>phen\_terminal</sub> bonding by populating bonding orbitals. The charge probably came from the ring orbitals, since the 6b ring mode vibrational wavenumber decreases in compound **2** (as well as the other ring modes, in a general way). The fact that the change in oxidation state of the iron atom on the other side of the Fe-O-Fe bridge (coordinated to the pyridine ligands) disturbs the iron atom coordinated to the terminal phenolate just confirms the high degree of electronic delocalization on the bridge, also favored by the *trans* disposition of the terminal phenolate.

## Conclusions

The change in the oxidation state in a mixed valence bridged core affects the fundamental state as revealed by the shifting of the vibrational wavenumbers. This change also reflects in the electronic excited state as evidenced by the comparison between the REP's of compounds **1** and **2**. The phenolate bridge is able to transmit charge density between the two iron centers. Complexes **1** and **2** can be considered good models for the resonance Raman properties of PAP's in their reduced and oxidized forms, respectively.

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