Supporting Information for

Structural, Magnetic and Optical Properties of a Fe\textsuperscript{II} Dimer Bridged by the Meridional Planar Divergent $N,N'$-\textit{bis}(salicyl)hydrazide and its Photo- and Electro-Chemistry in Solution

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Experimental

Synthesis

\textbf{H}_2\textbf{L}' and \textbf{H}_2\textbf{L}''' were prepared using previously published procedures [1]. \textbf{H}_4\textbf{L}''' was obtained commercially (Acros Organics) and was used as received. The studied molecules are depicted scheme SS1.

\textbf{UV-Visible measurements}

Similar behaviour as \textbf{H}_4\textbf{L} is observed in the case of the compound \textbf{H}_2\textbf{L}' for the evolution vs. the concentration (Figure S1), the addition of base (Figure S2) and acid (figure S3). Although the components of the measured absorption band are less well resolved (see later discussion).
**S1:** Absorption spectra (left) and molar absorptivity (right) of $H_2L'$ for different concentrations: $5.6 \times 10^{-5}$ M, $5.0 \times 10^{-5}$ M, $4.4 \times 10^{-5}$ M, $3.7 \times 10^{-5}$ M, $3.1 \times 10^{-5}$ M, $2.5 \times 10^{-5}$ M, $1.9 \times 10^{-5}$ M, $1.3 \times 10^{-5}$ M and $6.3 \times 10^{-6}$ M

(The arrow indicates the sense of the absorbance changes with decrease of the concentration)

**S2:** Absorbance changes resulting from the addition of triethylamine

Left: $H_2L'$ ($5 \times 10^{-5}$ M) with triethylamine concentrations equal to $0$ M, $5 \times 10^{-5}$ M, $1 \times 10^{-4}$ M, $2 \times 10^{-4}$ M, $3 \times 10^{-4}$ M, $5 \times 10^{-3}$ M, $1 \times 10^{-2}$ M and $1.5 \times 10^{-2}$ M

Right: $H_4L''$ ($5 \times 10^{-5}$ M) with triethylamine concentrations equal to $0$ M, $5 \times 10^{-5}$ M, $1 \times 10^{-4}$ M, $1.5 \times 10^{-4}$ M, $6 \times 10^{-3}$ M, $1.8 \times 10^{-2}$ M and $3.7 \times 10^{-2}$ M

(The arrows indicate the sense of the absorbance changes due to addition of triethylamine)
These results indicate that the spectroscopic changes reflect the protonation states of the molecules. Each molecule possesses a phenol and hydrazide or hydrazone functions which can play the role of acid groups [2-4]. In the case of $H_4L$, aggregation phenomenon is excluded considering DOSY NMR measurement depicted on Figure S4 (see the text of the article for the hydrodynamic volume data).
Thus, for both the present and previously studied systems [2,3], a basic understanding can be gained of their spectroscopic characteristics. In the selected wavelength range, electronic absorption spectra are a convolution of several transitions involving the functions Ph-OH, Ph-CO-NH-N=Р and Ph-CO-NH-. The nature (electron donor or not) of R has a strong influence on their absorbance properties within the molecule and on the overlapping of signals. An example of spectral changes can be seen when the electron donor group of H2L' is exchanged by a group with lower electron donor character (Figure S5). Two bands are observed which can correspond to a splitting of the broad signal of H2L' and can be assigned to transitions involving the overall function R’-CO-NH-N=R [2, 3].

![Absorbance spectra of H2L (dotted line) and H2L'' (thin line), both at 5 10⁻⁵ M](image)

Other transitions are present under the two broad bands. Indeed, the overall signal corresponds to the convolution involving the acid-base equilibria of the CO-NH-N=R ↔ CO-N'-N=R and Ph-OH ↔ Ph-O'. For these reactions, intramolecular hydrogen bonding, which could influence the absorbance properties, have to be taken into account. From different studies [2,3], several types of hydrogen bonds could be considered as depicted on scheme SS2.

![Potential intramolecular hydrogen bonds occurring in studied (salicyl)hydrazine derivatives.](image)
Focusing on these collected data, it is possible to underline two points: Firstly, for the same concentration, the second band occurring into H₄L spectrum is more prominent compared to the first one, than what in observed in the case of H₂L’. Secondly, with two equivalents of triethylamine, this second band develops more for H₄L compared to H₂L’ or H₄L”'. The origin of this behaviour could simply be attributed to the two equivalent acid functions present in the H₄L molecule. Thus, higher signal can be expected. But, a second hypothesis, based on the difference of the acidity power of the molecules, could also be pointed out. All the investigations performed in this study would be in agreement with the second approach (see discussion below and electrochemical section). In the case of H₂L’, the combination of the hydrazone and hydrazide function would confer a greater acidity to the N-H proton than this of H₄L (scheme SS3). This effect can be supported considering the electronic delocalizations effect which stabilize the N⁺ state [2,3]. In these conditions, this proton would be more acid in the case of H₂L’.

SS 3: The circle indicates the more acid proton in the case of:
(1) H₂L’ or H₄L”’ and (2) H₄L

This last hypothesis would allow us to explain the observed results. In the case of H₂L’, some electronic transitions are related to the acid-base reaction involving the hydrazide/hydrazone part which are often overlap with the Ph-OH/PhO⁻ group [2,3]. If the NH proton are acid and more than in the case of Ph-OH, then the molecule could be mainly in the case B and C of the scheme 2. In this context, the proportion of PH-O⁻ is small. For H₄L, the opposite behaviour would be the origin of the observed property because of the lack of hydrazide/hydrazone part. The NH proton, which is less acid, leads the stabilisation of the Ph-O⁻ group and even increases the acidity of the phenol function. Then, the case A of the scheme 2 can exist and the proportion of Ph-O⁻ would be more important. One can notice that the enol equilibrium is not involved in the reasoning. Because it is common to all molecules, one can assume that it brings equivalent effect, therefore it is not a pertinent parameter.

When a base is added to a solution of H₂L’, the predominant reaction would be the exchange of the proton from NH function. More this process evolves and more Ph-OH would be involves via equilibrium and hydrogen bond. Then, only after removing a significant part of
NH protons, the Ph-OH protons would be affected. In the case of H₄L, less quantity of base will be necessary because the main protons source is the Ph-OH function. Regarding the addition of HCl acid, the difference between H₄L and H₂L' are lower than in the precedent case. In the case of addition of HCl acid, all the basic functions can react. H₂L' has three basic sites which are the N' ↔ C-O', Ph-O' and a third which corresponds to the protonation of N=C. The electronic transition should again overlap with the other processes to form the broad band at short wavelengths. The molecule H₄L has both Ph-O' and N- functions then the necessary amount of acid should be higher for H₂L' than for H₄L.

**Electrochemical measurements**

Cyclic voltammograms for the compounds H₄L, H₂L' and H₄L'' are given in Figure S6. All show a quasi reversible reduction step but only H₂L' and H₄L'' show oxidation processes (irreversible).

![Cyclic voltammograms of A) H₄L, B) H₂L' and C) H₄L'': C = 5mM, Pt working electrode, Pt pseudo reference electrode, TBA PF₆ = 150 mM, v = 0.1 V.s⁻¹](image)

This behaviour is consistent with the electronic distribution on the hydrazone function which only occurs on molecules H₂L' and H₄L''. The reduction step corresponds to proton reduction as it can be deduced from a comparison involving carbon and platinum electrodes [5] (Figure S7).
S7: Cyclic voltammograms of $H_4L$ (5 mM) recorded with carbon (thick line) and platinum (thin line) electrodes. 
DMF, TBAPF$_6 = 150$ mM, $v = 0.1$ V.s$^{-1}$.

Cyclic voltammetry as a function of concentration provided a satisfyingly linear current-concentration relation (Figure S8) for both $H_4L$ and $H_2L^-$.

S8: Cyclic voltammograms of A) $H_4L$ and B) $H_2L^-$ for different concentrations: 1, 1.95, 2.85, 3.72, 4.54 and 5 mM. C) Cyclic voltammogram of $H_4L$ for 1 mM and 5 mM with ferrocene to calibrate the potentials. DMF, Pt working electrode, Pt pseudo reference electrode, TBAPF$_6 = 150$ mM, $v = 0.1$V.s$^{-1}$, (insert: $I_p$ vs. $C$)
Further studies involving changing the scan rate (Figure S9) provided a good linear plot of $I_p$ vs. $v^{1/2}$, again consistent with $H_4L$ displaying no abnormal properties.

![Graph showing cyclic voltammograms](image)

**S 9**: Cyclic voltammograms of $H_4L$ (5 mM) for different scan rates: 0.01, 0.05, 0.1, 0.2, 0.5 and 1 V s$^{-1}$. Pt working electrode, TBAPF$_6$ = 150 mM (Insert: $I_p$ vs. $v^{1/2}$)

Hence, some interesting information can be reached considering Figures S8 and S10.

![Graph showing cyclic voltammograms](image)

**S 10**: A) $H_4L$ (thick line) and $H_2L'$ (thin line) 1 mM, $v$ = 0.02 V s$^{-1}$.  
B) $H_4L$ 1 mM (thick line) and $H_4L$ 1 mM with HCl 1 mM (thin line), $v$ = 0.1 V s$^{-1}$

Pt working electrode, TBAPF$_6$ = 150 mM, the potential of ferrocene is arbitrary fixed to 0 V.
The current intensity peaks related to H₄L and H₂L⁻ are similar and in comparison with an equivalent of HCl, it becomes possible to indicate that this signal would correspond to only one proton. From this result, it is possible to assume that, despite of the presence of two equivalents phenol functions on H₄L molecule, statically only one is engaged. This point allows us to rule out the hypothesis (assumed previously) related to the number of active acid functions.

However, H₄L does not seem present expected evolution when the potential parameter is considered (Figures S8C and S9). This kinetic behaviour is confirmed plotting Eₚ vs. Log(𝑣). The result is presented Figure S12 and indicates that kinetic limitation has influence on the proton potential reduction in a scan rate range of 0.002 V.s⁻¹ – 100 V.s⁻¹. Hence, there is not range of scan rate wherein the potential is independent of the scan rate. In the case of compounds H₂L' and H₂L'”, cyclic voltammograms (Figure S10A) and successive records show shape evolution consistent with kinetic limitations. Adsorption of ligands onto platinum electrode is probably the origin of the protons reduction kinetic limitation.

![Plot of $E_p$ vs. Log(𝑣) for H₄L: 1 mM (square) and 5 mM (cross). Arrows show measurements performed with both Pt electrode and Pt microelectrode at 1 V.s⁻¹ to indicate that resistance effect is not the only limitation.](image)

**S 12:** Plot of $E_p$ vs. Log(𝑣) for H₄L: 1 mM (square) and 5 mM (cross). Arrows show measurements performed with both Pt electrode and Pt microelectrode at 1 V.s⁻¹ to indicate that resistance effect is not the only limitation.

**EPR**

**EPR measurement:** EPR spectra were recorded on EMX Bruker spectrometer (operating at 10 GHz) equipped with an Oxford Instruments ESR 900 continuous-flow helium cryostat. The static field was controlled with a Hall probe, whereas the microwave frequency was simultaneously recorded with a frequency counter (HP-5350 B). Samples were illuminated with an Argon-Krypton laser (model stability 2018-RM from Spectra Physic) using the multiline mode (superposition of visible lines from the blue (457 nm) up to the green (574 nm)) directly in situ in the EPR cavity.
In this study, chemical physics properties comparisons have been performed between N,N’-bis(salicyl)hydrazine and related mono salicylic hydrazide derivatives. UV-Vis spectroscopy and electrochemistry studies allow us to point out acid-base differences despite apparent close chemical similarities. Although for each type of molecule, only one proton is involved in the acid-base equilibrium, the proton exchange site is different between N,N’-bis(salicyl)hydrazine and related mono salicylic hydrazide derivatives. In the first case, the Ph-OH group provides protons whereas in the second case, the NH group is engaged in the acid-base equilibrium. This observation can be understood assuming that acidic power of identical acid functions are affected because of the presence or not of the hydrazide/hydrazone combination within the molecules. Hence, a relative positioning acidic power can be proposed:
PhOH\(_{(H4L)}\) ≥ NH\(_{(H4L)}\) and NH\(_{(H2L')}\) > PhOH\(_{(H2L')}\)

**References**


