Supporting Information for

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

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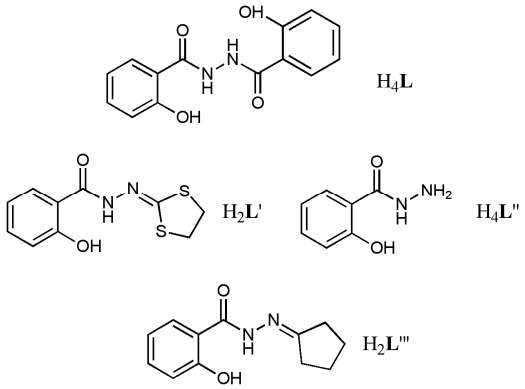
Experimental

Synthesis

H_2L' and **H_2L'''** were prepared using previously published procedures [1]. **H_4L''** was obtained commercially (Acros Organics) and was used as received.

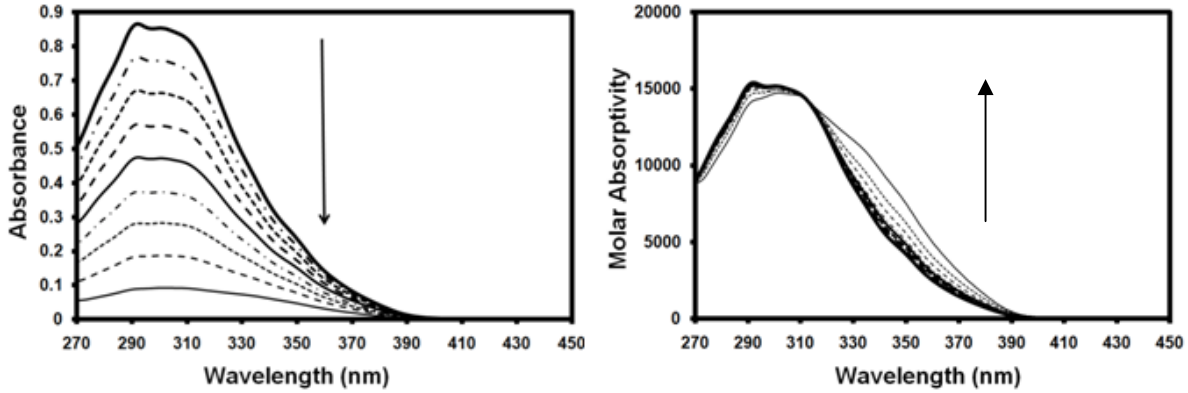
The studied molecules are depicted scheme SS1.



SS1: Molecules investigated in this work

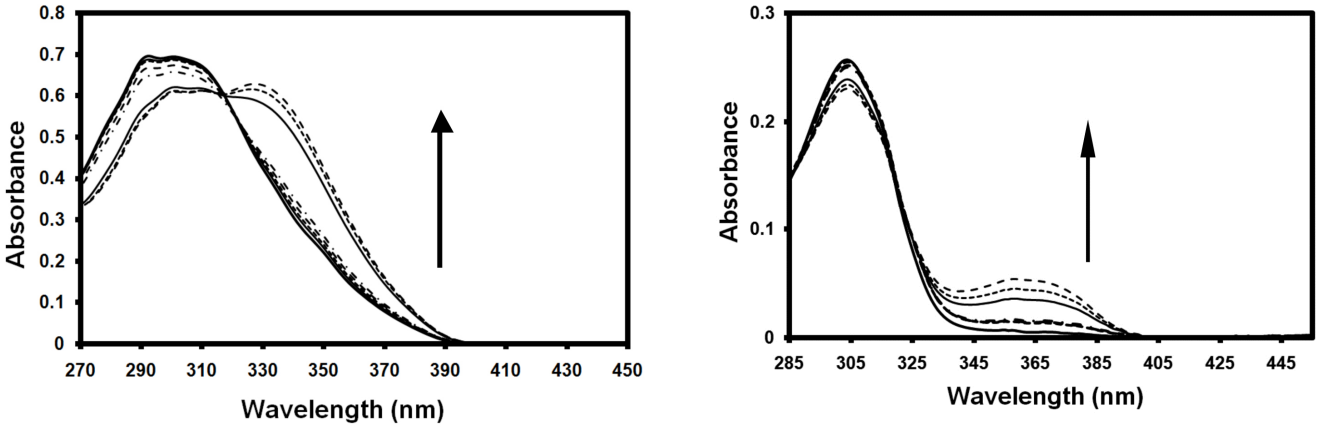
UV-Visible measurements

Similar behaviour as H_4L is observed in the case of the compound $H_2L^{'}$ for the evolution vs. he 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 10^{-5} M, 5.0 10^{-5} M, 4.4 10^{-5} M, 3.7 10^{-5} M, 3.1 10^{-5} M, 2.5 10^{-5} M, 1.9 10^{-5} M, 1.3 10^{-5} M and 6.3 10^{-6} M*

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

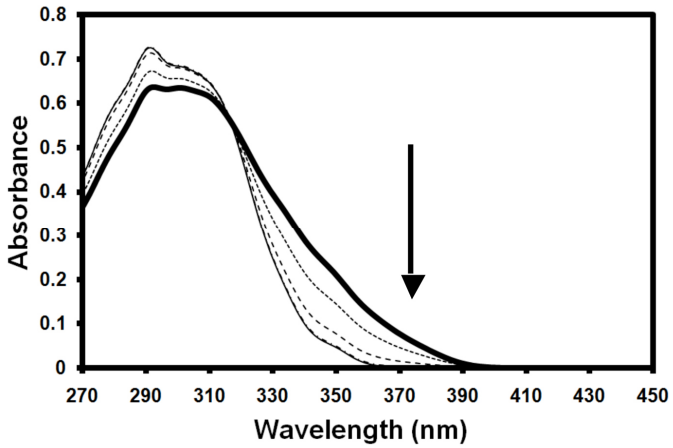


S2: *Absorbance changes resulting from the addition of triethylamine*

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

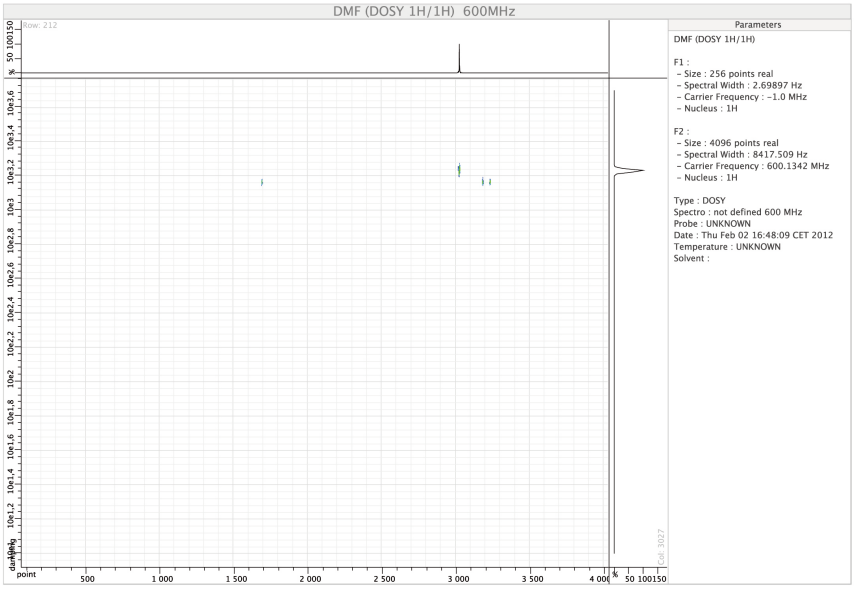
Right: H_4L'' (5 10^{-5} M) with triethylamine concentrations equal to 0 M, 5 10^{-5} M, 1 10^{-4} M, 1.5 10^{-4} M, 6 10^{-3} M, 1.8 10^{-2} M and 3.7 10^{-2} M

(The arrows indicate the sense of the absorbance changes due to addition of triethylamine)



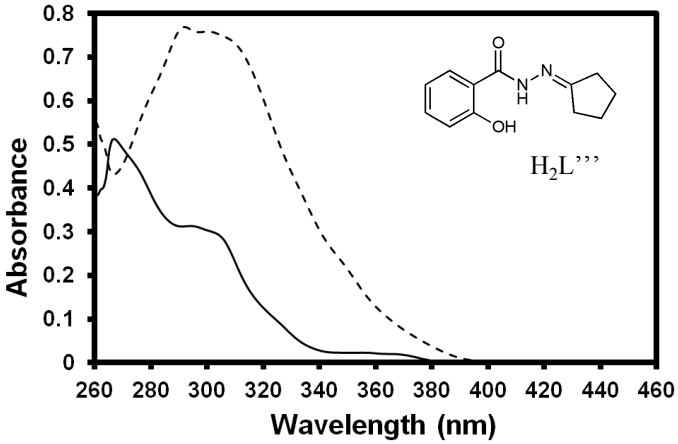
S3: *Absorbance changes due to the addition of HCl*
$H_2L^{'}$ (5 10^{-5} M) with HCl concentrations of 0 M, 5 10^{-5} M, 1 10^{-4} M, 1.5 10^{-4} M, 2 10^{-4} M
(The arrows indicate the sense of the absorbance changes due to addition of HCl)

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).



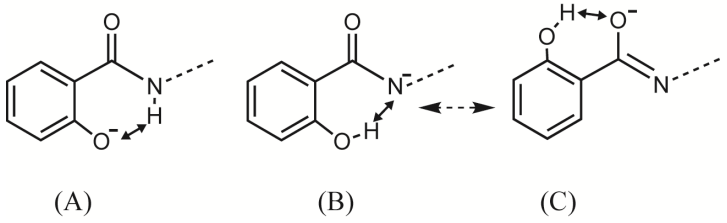
S4: *DOSY-NMR of 1 mM H_4L in DMF*

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=R 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 H_2L' is exchange 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 H_2L' and can be assigned to transition involving the overall function R'-CO-NH-N=R [2, 3].



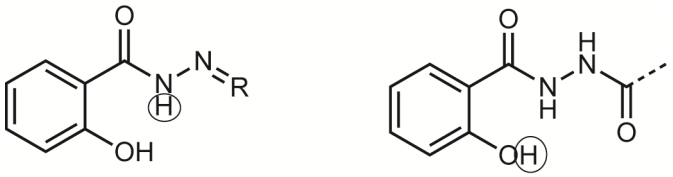
S5: *Absorbance spectra of H_2L' (dotted line) and H_2L''' (thin line), both at 5 10^{-5} M*

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-N**H**-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.



SS 2: *Potential intramolecular hydrogen bonds occurring in studied (salicyl)hydrazine derivatives.*

Focusing on these collected data, it is possible to underline two points: Firstly, for the same concentration, the second band occurring into H_4L spectrum is more prominent compared to the first one, than what in observed in the case of H_2L'. Secondly, with two equivalents of triethylamine, this second band develops more for H_4L compared to H_2L' or H_4L''. The origin of this behaviour could simply be attributed to the two equivalent acid functions present in the H_4L 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 H_2L', the combination of the hydrazone and hydrazide function would confer a greater acidity to the N-H proton than this of H_4L (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 H_2L'.



(1) (2)

SS 3: *The circle indicates the more acid proton in the case of: (1) H_2L' or H_4L'' and (2) H_4L*

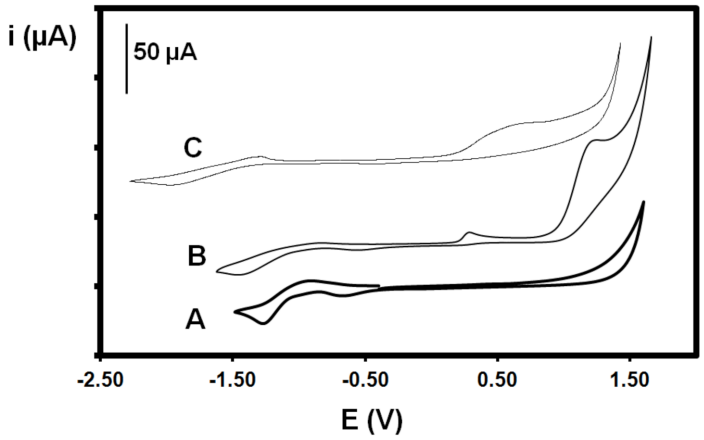
This last hypothesis would allow us to explain the observed results. In the case of H_2L', some electronic transitions are related to the acid-base reaction involving the hydrazide/hydrazone part which are often overlap with the Ph-OH/PhO^- group [2,3]. If the N**H** proton are acid and more than in the case of Ph-O**H**, then the molecule could be mainly in the case B and C of the scheme 2. In this context, the proportion of $PH\text{-}O^-$ is small. For H_4L, 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 $Ph\text{-}O^-$ group and even increases the acidity of the phenol function. Then, the case A of the scheme 2 can exist and the proportion of $Ph\text{-}O^-$ 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 H_2L', 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 H_4L, 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 H_4L and H_2L' are lower than in the precedent case. In the case of addition of HCl acid, all the basic functions can react. H_2L' has three basic sites which are the $N^- \leftrightarrow C\text{-}O^-$, $Ph\text{-}O^-$ 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 H_4L has both $Ph\text{-}O^-$ and N- functions then the necessary amount of acid should be higher for H_2L' than for H_4L.

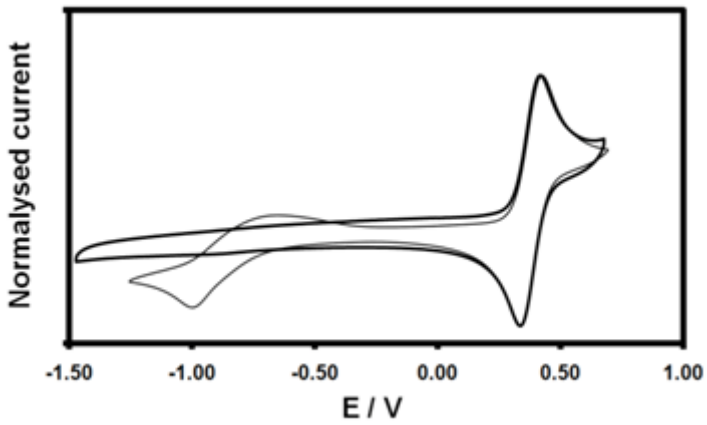
Electrochemical measurements

Cyclic voltammograms for the compounds H_4L, H_2L' and H_4L'' are given in Figure S6. All show a quasi reversible reduction step but only H_2L' and H_4L'' show oxidation processes (irreversible).



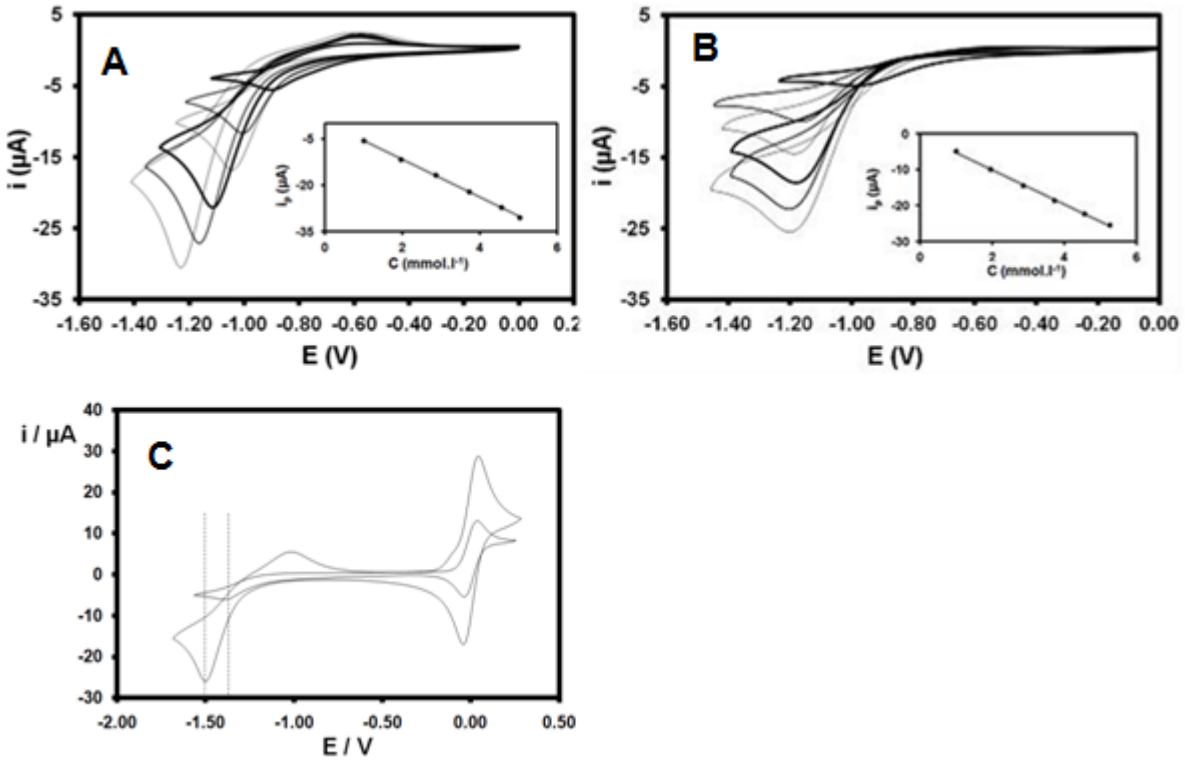
S 6: *Cyclic voltammograms of A) H_4L, B) H_2L' and C) H_4L'' : C = 5mM, Pt working electrode, Pt pseudo reference electrode, $TBAPF_6$ = 150 mM, v = 0.1 $V.s^{-1}$*

This behaviour is consistent with the electronic distribution on the hydrazone function which only occurs on molecules H_2L' and H_4L''. The reduction step corresponds to proton reduction as it can be deduced from a comparison involving carbon and platinum electrodes [5] (Figure S7).



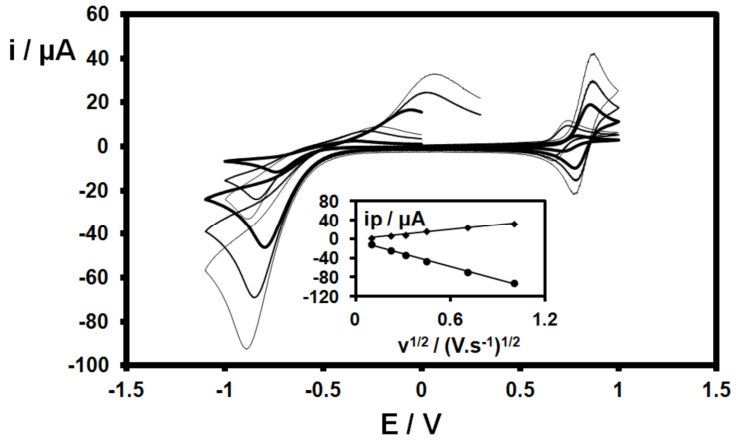
S 7: *Cyclic voltammograms of H_4L (5 mM) recorded with carbon (thick line) and platinum (thin line) electrodes. DMF, $TBAPF_6$ = 150 mM, v = 0.1 $V.s^{-1}$.*

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



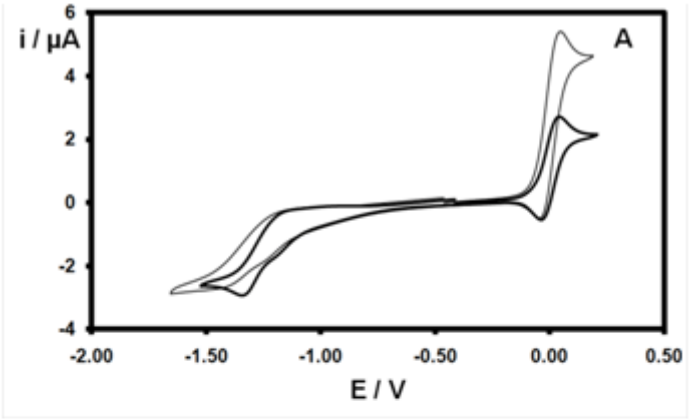
S 8: *Cyclic voltammograms of A) H_4L and B) H_2L' for different concentrations: 1, 1.95, 2.85, 3.72, 4.54 and 5 mM. C) Cyclic voltammogram of H_4L for 1 mM and 5 mM with ferrocene to calibrate the potentials. DMF, Pt working electrode, Pt pseudo reference electrode, $TBAPF_6$ = 150 mM, v = 0.1V.s-1, (insert: Ip vs. C)*

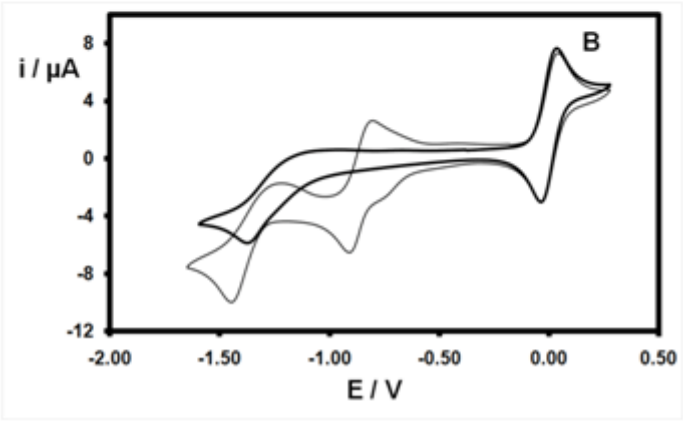
Further studies involving changing the scan rate (Figure S9) provided a good linear plot of I_p vs. $v^{1/2}$, again consistent with H_4L displaying no abnormal properties.



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: Ip vs. $v^{1/2}$)*

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

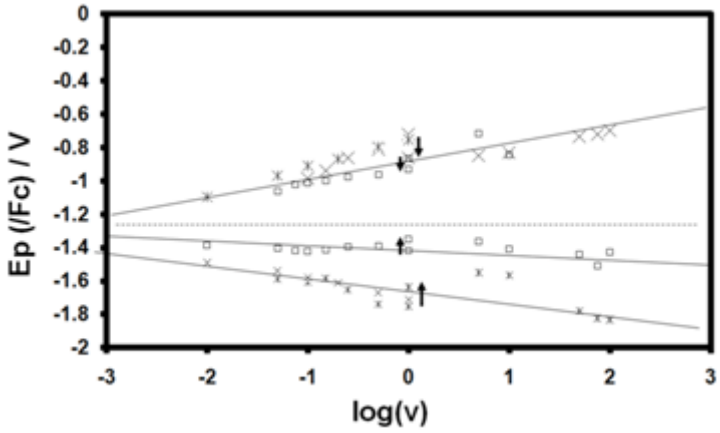




S 10: *A) H_4L (thick line) and H_2L' (thin line) 1 mM, v = 0.02 $V.s^{-1}$.*
B) H_4L 1 mM (thick line) and H_4L 1 mM with HCl 1 mM (thin line), v = 0.1 $V.s^{-1}$
Pt working electrode, $TBAPF_6$ = 150 mM, the potential of ferrocene is arbitrary fixed to 0 V.

The current intensity peaks related to H_4L and $H_2L^{'}$ 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 H_4L 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, H_4L does not seem present expected evolution when the potential parameter is considered (Figures S8C and S9). This kinetic behaviour is confirmed plotting E_p 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 $H_2L^{'}$ and H_2L'', 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.



S 12: *Plot of E_p vs. Log(v) for H_4L : 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.

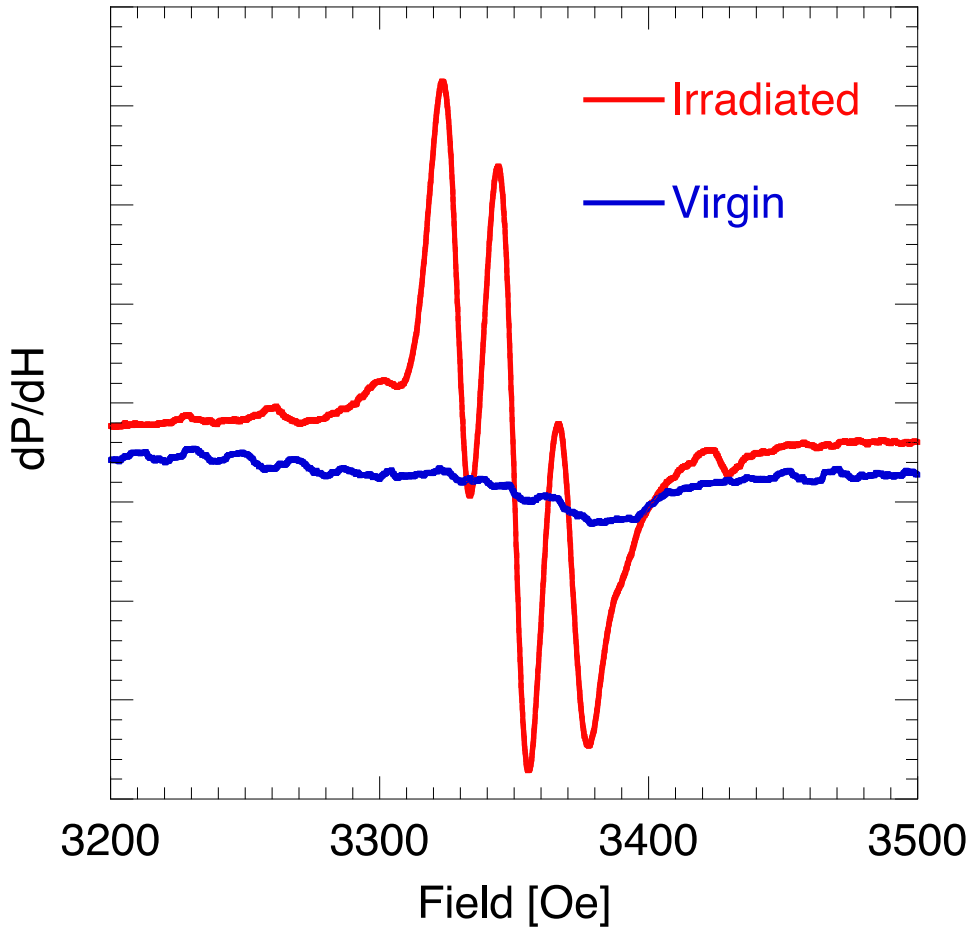


Fig S13: EPR spectra of the iron complex in DMF at 6 K: blue line before irradiation, red line after 3 hours of irradiation.

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:

$PhOH_{(H4L)} \geq NH_{(H4L)}$ and $NH_{(H2L')} > PhOH_{(H2L')}$

References

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