



A. Fidalgo-Marijuan<sup>a</sup>, G. Barandika<sup>b</sup>, B. Bazán<sup>a</sup>, M. K. Urtiaga<sup>a</sup>, M. I. Arriortua<sup>a</sup>

<sup>a</sup>Department of Mineralogy and Petrology, University of the Basque Country (UPV/EHU), Apdo. 644, 48080 Bilbao (Spain)

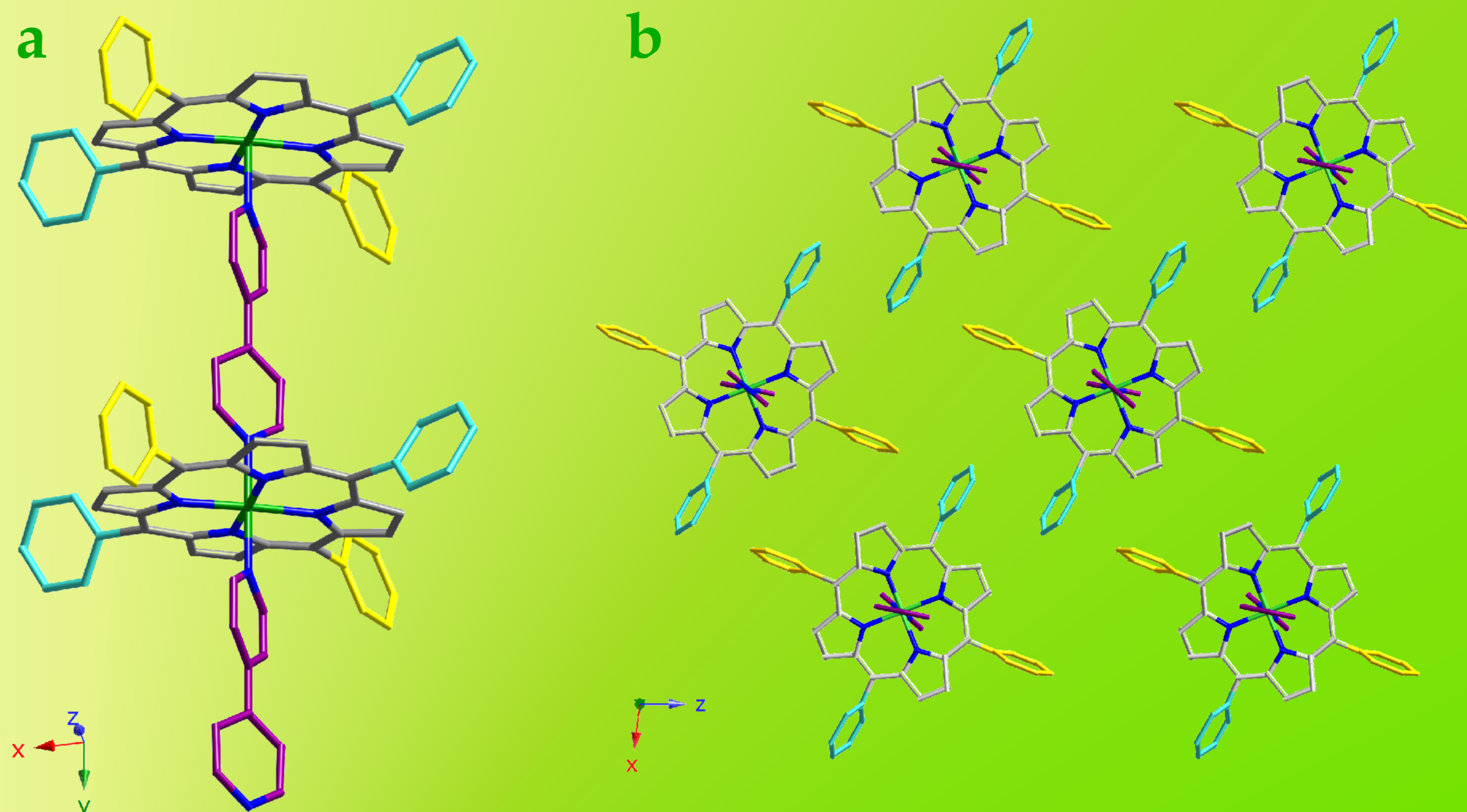
<sup>b</sup>Department of Inorganic Chemistry, University of the Basque Country (UPV/EHU), Paseo de la Universidad 7, 01006 Vitoria-Gasteiz (Spain)

## Introduction

Iron metalloporphyrins are paradigmatic examples of nanodevices used by natural systems like haemoglobin or cytochromes in oxygen transport, electron transfer and catalysis.<sup>1</sup> Therefore, they can be thought to be developed as MOFs for several applications, and the UV-Vis spectra of metalloporphyrins is a powerful tool to understand their electronic behaviour analyzing the typical Soret and Q bands.

In this work, we have characterised the UV-Vis spectrum of  $[(\text{FeTPPbipy})]_n$  (TPP= *meso*-tetraphenylporphyrin, bipy= 4,4'-bipyridine) neutral radical from both experimental and theoretical points of view. The later has been carried out by means of Time Dependent-Density Functional Theory (TD-DFT) calculations.<sup>2</sup>

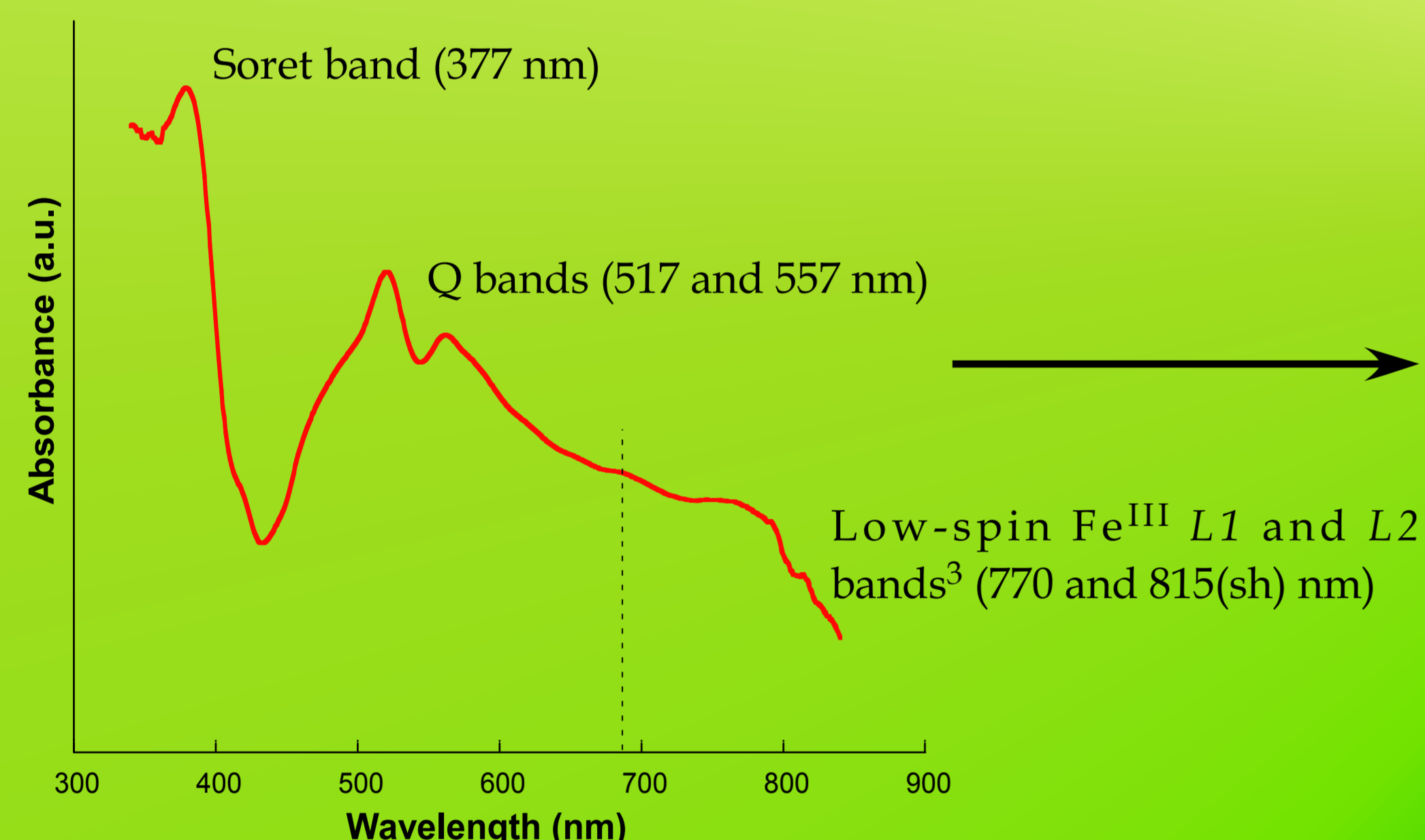
The interest of this compound lies on the presence of an unpaired electron per metallic centre that is delocalised on the phenyl groups of TPP. Moreover, the  $\pi$ -stacking of the crystal structure, is the crucial point on the behaviour of this compound.



View of the 1D coordination network extending along the [010] direction (a) and connection between chains through strong *edge-to-face* (between turquoise and yellow rings) and *face-to-face* (between turquoise rings)  $\pi$ -stacking (b). Colour codes: green=Fe; blue=N; grey, yellow and turquoise=C(porphyrin); purple=C(bipy).

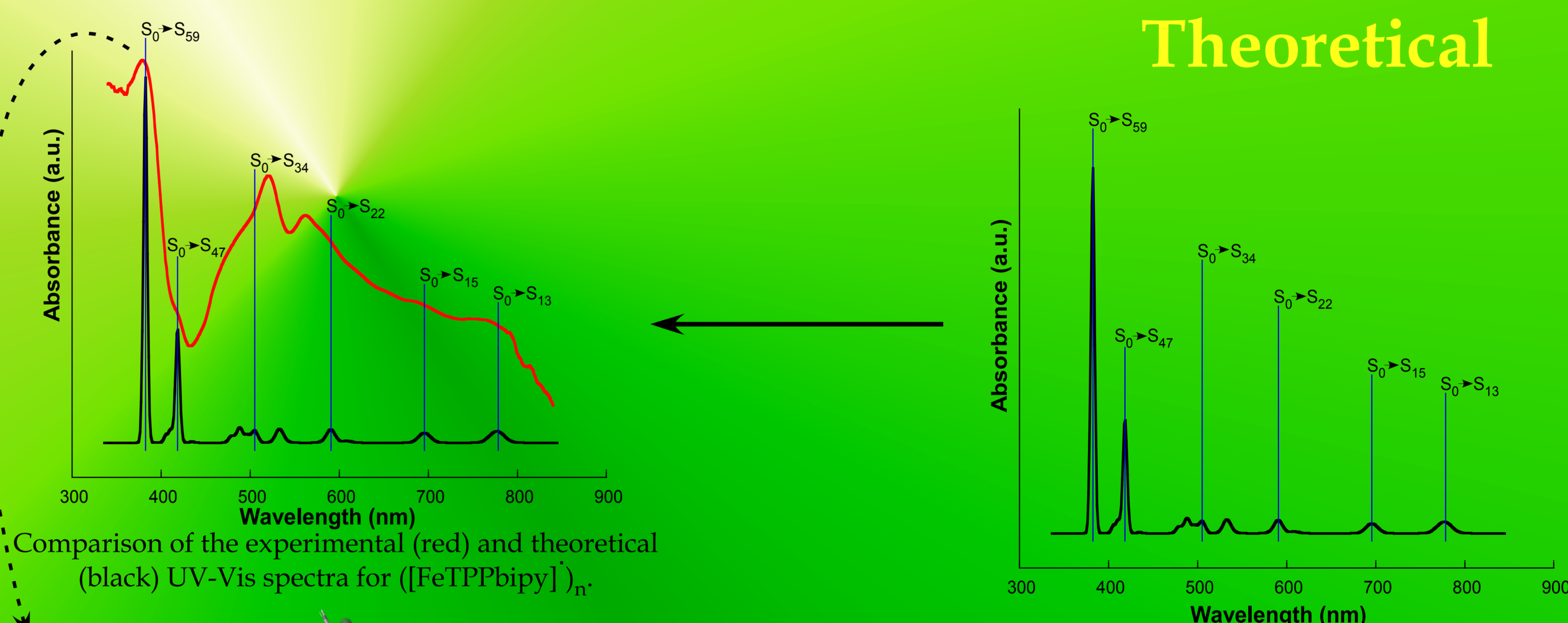
## UV-Vis absorption

### Experimental



A weak and broad band at 690 nm is in accordance with the presence of a porphyrinic radical.<sup>4</sup>

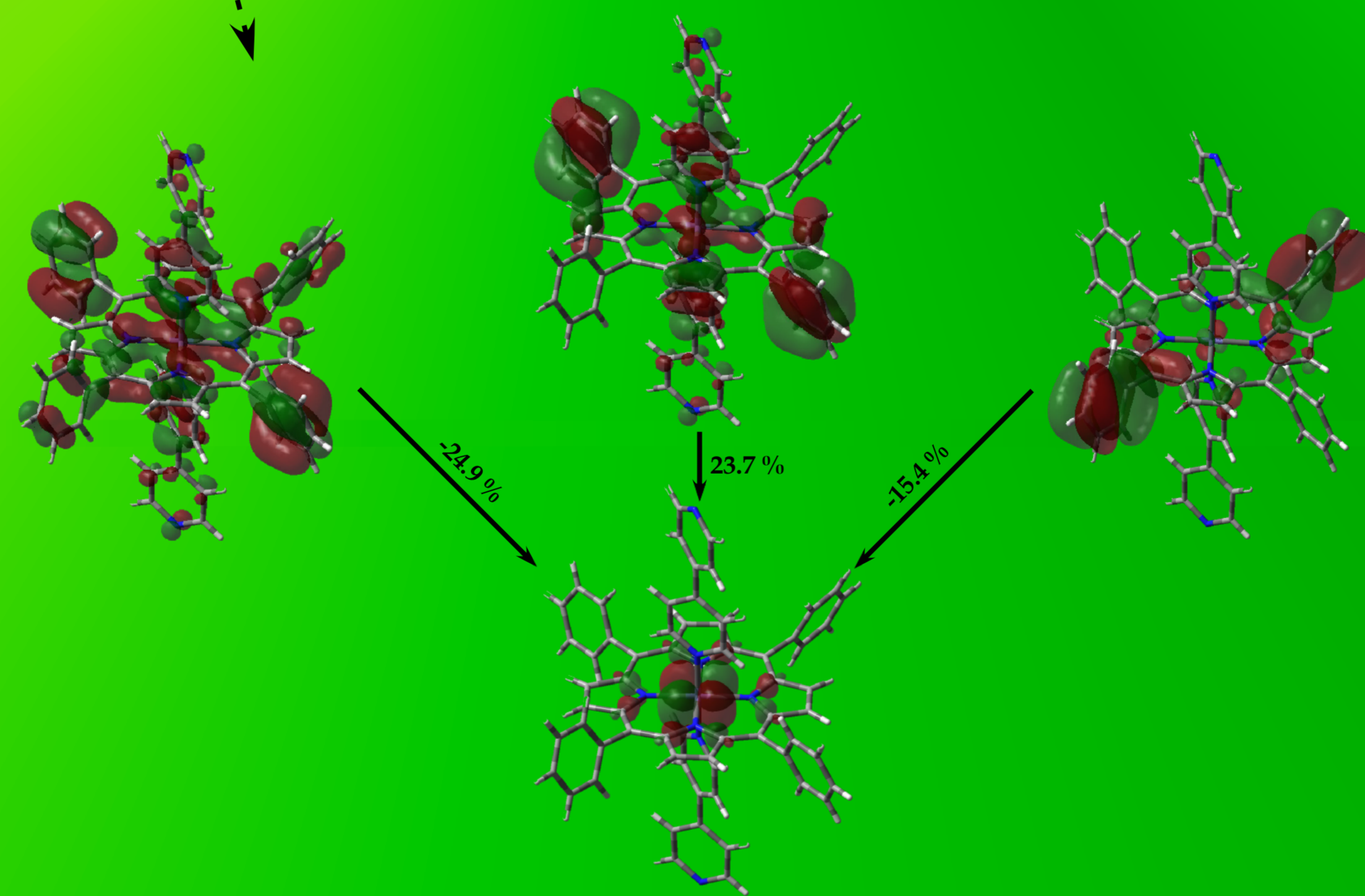
### Theoretical



Theoretical spectra and electronic transitions obtained by TD-DFT calculations (B3LYP, 6-31G) are in good concordance with the experimental.

## Conclusions

- The blue shifted Soret band indicates the presence of a radical specie.
- The  $\pi$ -stacking along the crystal structure is the responsible of the electron pairing.
- An important charge transfer takes place between the phenyl groups and the metal centre of the porphyrin.



The Soret transition ( $S_0 \rightarrow S_{59}$ ) represent an important charge transfer between the molecular orbitals of the phenyl rings and the metal centre.



Involved molecular orbitals in the *edge-to-face* and *face-to-face*  $\pi$ -stacking.

## Acknowledgements

This work has been financially supported by the Ministerio de Ciencia e Innovación (MAT2010-15375) and the Gobierno Vasco (Basque University System Research Groups, IT-177-07), which we gratefully acknowledge. SGIker (UPV/EHU) technical support (MEC, GV/EJ, European Social Fund) is gratefully acknowledged. A. Fidalgo-Marijuan thanks the UPV/EHU fellowships.

## References

- [1] S. Mohnani, D. Bonifazi, *Coord. Chem. Rev.*, **2010**, 254, 2342-2362.
- [2] D. Delaere, T. N. Minh, *Chem. Phys. Lett.*, **2003**, 376, 329-337.
- [3] E.-i. Ochiai, in *Bioinorganic Chemistry: An Introduction*, Allyn and Bacon, Inc., Boston, USA, 1977, ch. 5.
- [4] A. Ikezaki, H. Tukada and M. Nakamura, *Chem. Commun.*, **2008**, 2257.

