

SYNTHESIS, COORDINATION CHEMISTRY, AND PHOTOPHYSICAL PROPERTIES  
OF THE 2-CHLOROETHOXY-IRON(III)(ETHYLTHIO) PORPHYRAZINEDaniela PIETRANGELI,<sup>a</sup> Giampaolo RICCIARDI,<sup>b</sup> Antonio SANTAGATA<sup>a</sup><sup>a</sup> CNR-IMIP, U.O.S. Potenza, c.da Santa Loja - Zona Industriale, 85050 Tito Scalo (PZ) - Italy<sup>b</sup> Dipartimento di Scienze, Università della Basilicata, Viale dell'Ateneo Lucano 10, 85100 Potenza

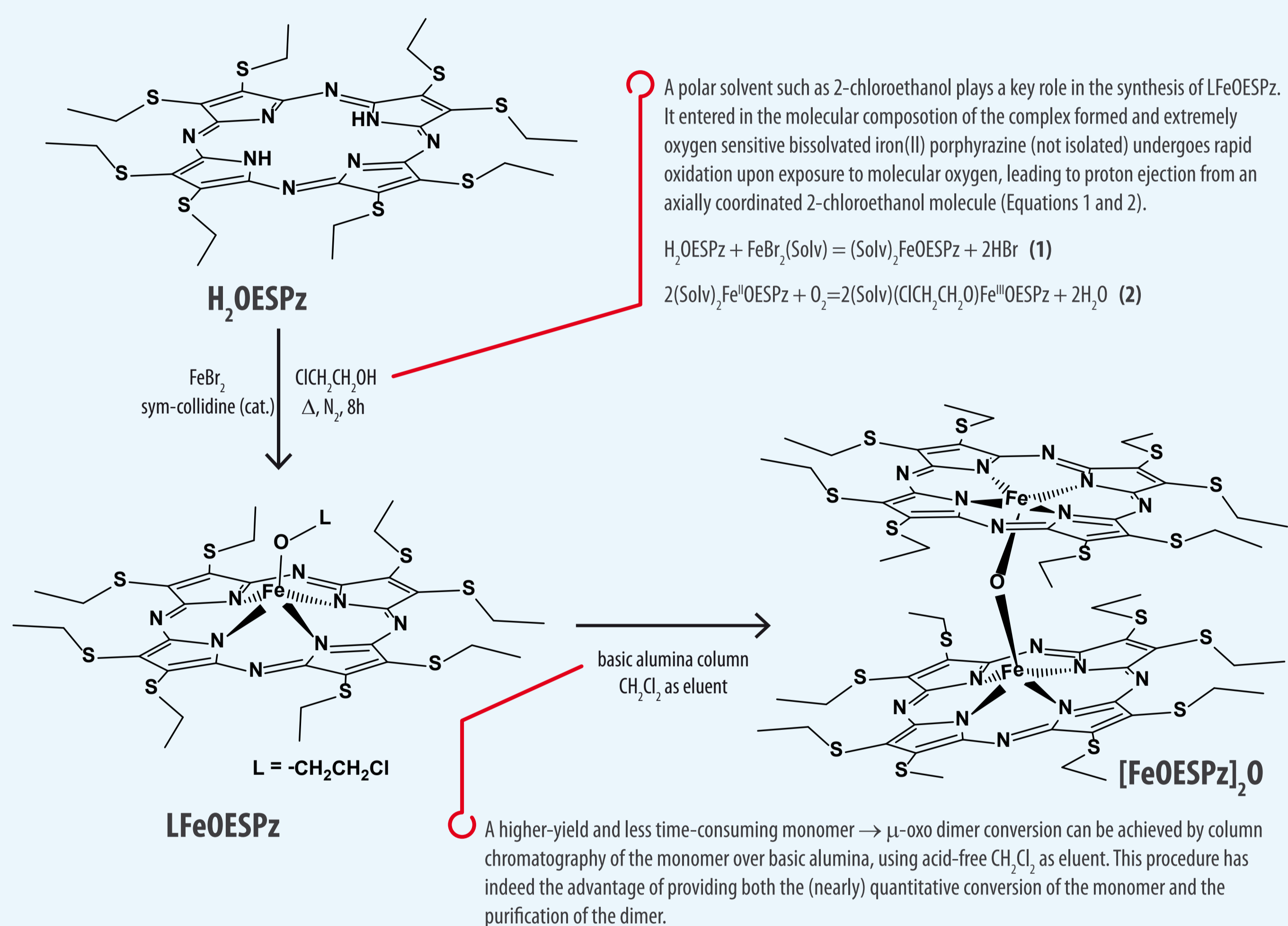
## HIGHLIGHT

Most of the promising properties of iron porphyrines rely on the quite peculiar electronic structure of the porphyrine ring and its impact on the metal-ligand interaction. The basic porphyrine (Pz) macrocycle is composed of four pyrrole rings bridged by nitrogen atoms, the most relevant electronic effect of which is to induce a significant stabilization of the lowest oxidation states, i.e. 2+ vs 3+, of the coordinated iron ion. As a matter of fact in FePzs the formal Fe<sup>II</sup>/Fe<sup>III</sup> redox potential shifts anodically by more than 400 mV (vs SCE) relative to nominally planar iron porphyrins, such as ClFeTPP (TPP=5,10,15,20-tetraphenylporphyrin), and approaches to electron deficient iron porphyrins. This makes FePzs systems also of potential interest in electrocatalysis [1]. Owing to the presence of aza bridges, Pzs are much stronger  $\sigma$ -donors than porphyrins. This has a significant impact on the pattern of the frontier Fe-d based molecular orbitals (MOs) and the related properties of monomeric iron(III) porphyrines, but also on the physical and chemical properties of the iron(III) porphyrine  $\mu$ -oxo dimers, [FePz]<sub>2</sub>O.

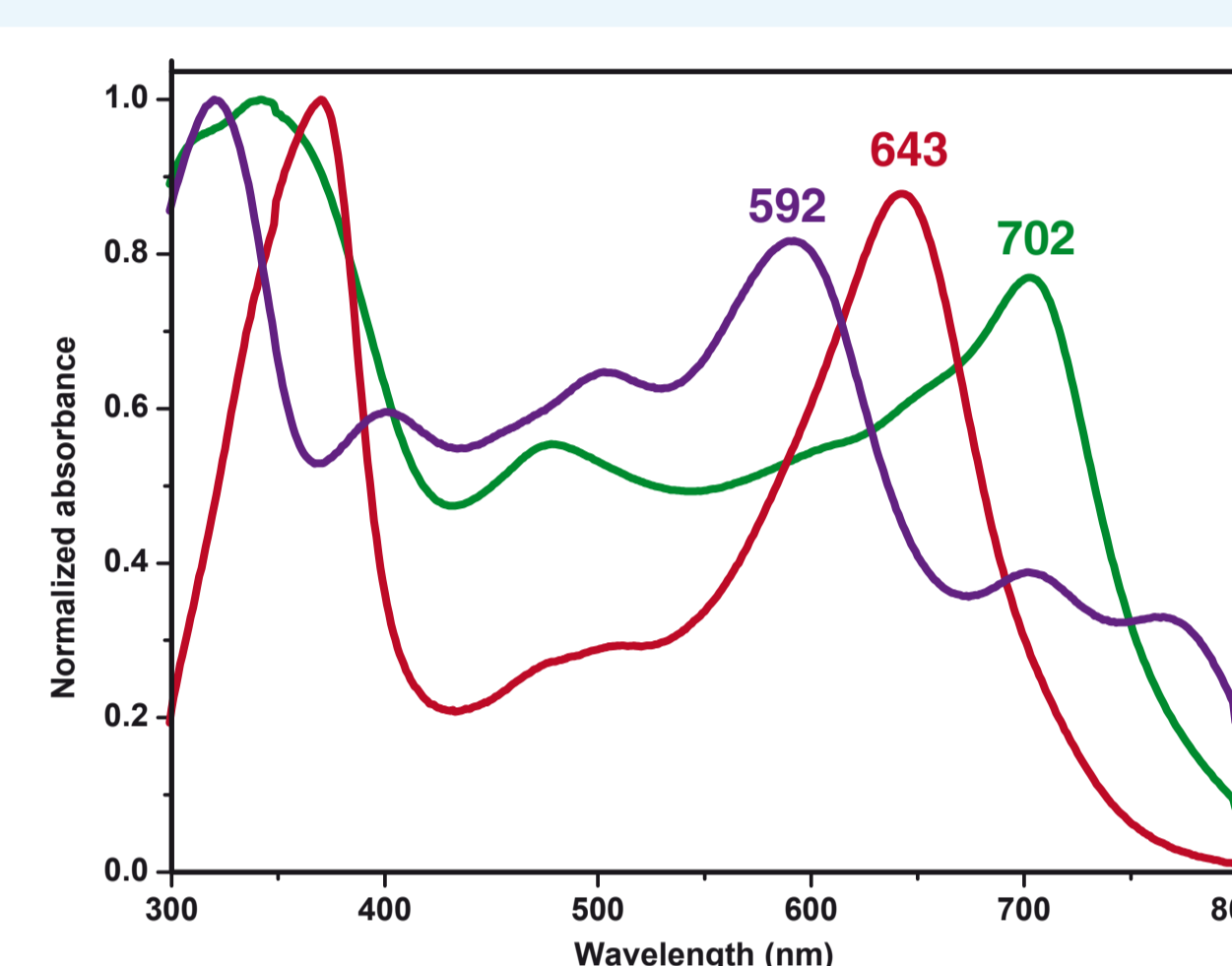
It is the aim of this contribution to deepen the knowledge of the fundamental properties of iron porphyrines and the modifications induced by peripheral heteroatom-containing chemical functions, by focusing on the iron(III)-2-chloroethoxy-2,3,7,8,12,13,17,18-octakis(ethylthio)porphyrine, ClCH<sub>2</sub>CH<sub>2</sub>OFe<sup>III</sup>OESPz (abbreviated as LFeOESPz) and the corresponding  $\mu$ -oxo dimer. A brief overview will be provided here on the adopted synthetic route, and on the electronic and coordination chemistry properties of these complexes in media of different polarity. The role of the metal- and ligand-centered excited states in determining the photo-physical behavior of the monomer, will be investigated through preliminary steady-state and time-resolved UV-visible absorption spectroscopy studies.

## RESULTS AND DISCUSSIONS

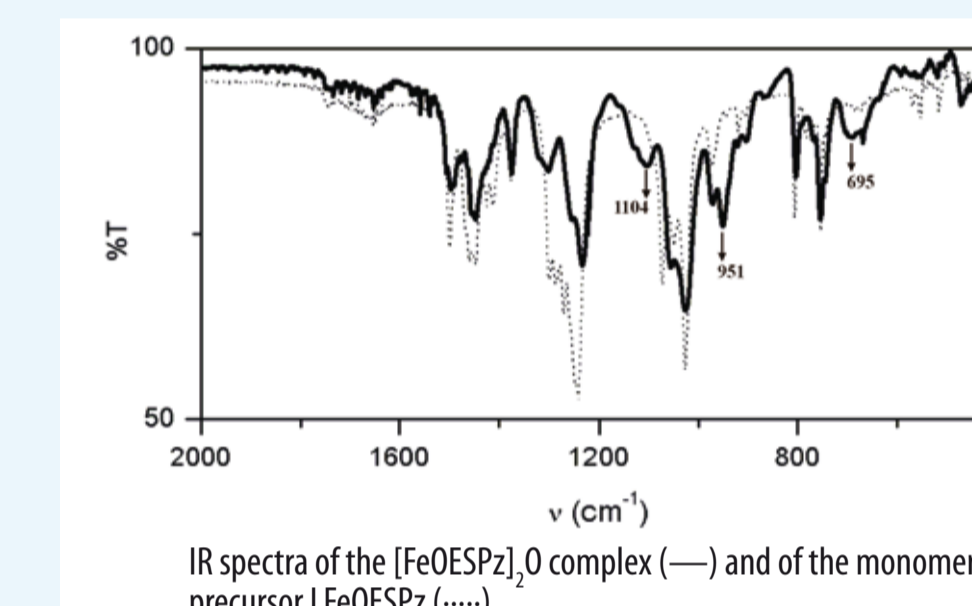
## Synthesis of LFeOESPz



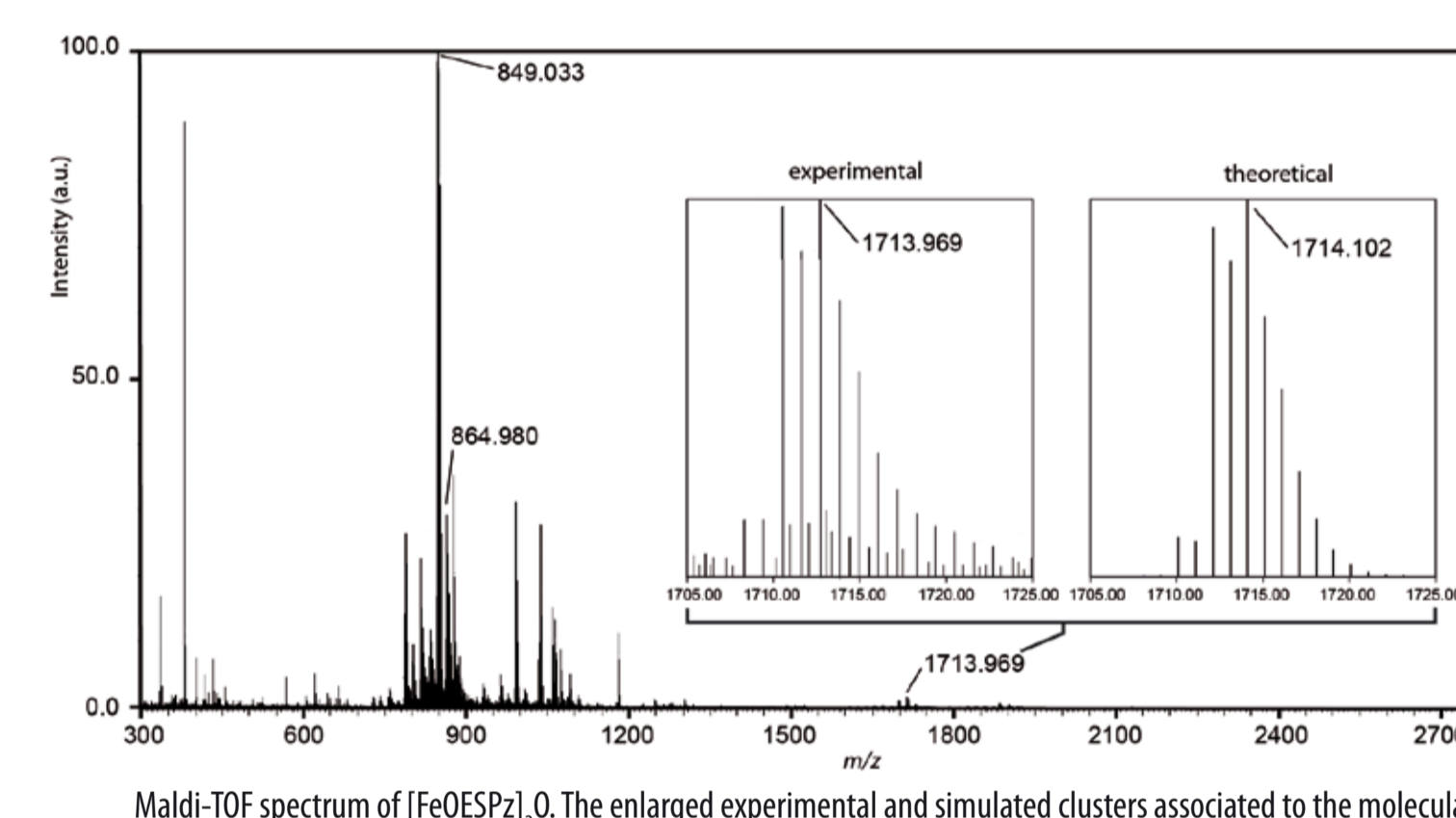
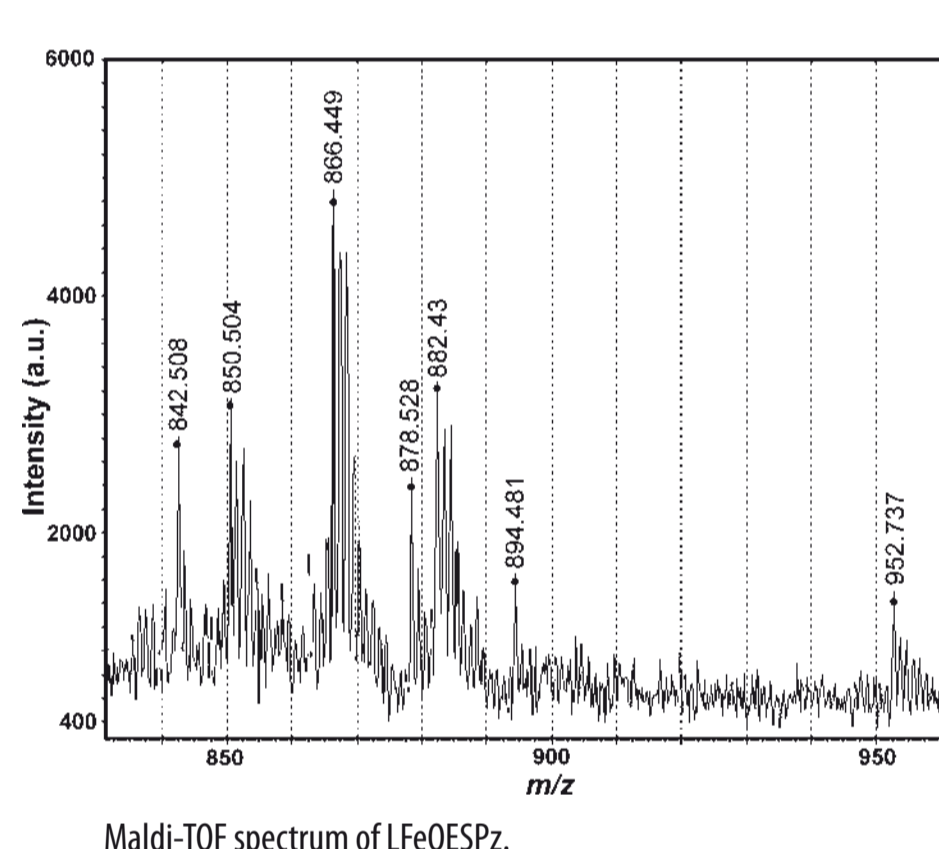
## Characterization



LFeOESPz shows a prominent feature in the visible, at ca. 592 nm, two distinct bands in the red region, at ca. 600 and 750 nm, and a broad envelope in the near-UV terminating with an intense absorption at 330 nm, commonly denoted the Soret band. (—) Solutions of the  $\mu$ -oxo dimer in weakly coordinating solvents, such as CH<sub>2</sub>Cl<sub>2</sub> or CHCl<sub>3</sub>, assume a typical gray-blue color. In these solvents the UV-vis spectrum of the complex is characterized by a quite intense absorption at ca. 700 nm (the Q-band), followed to the blue by a plateau, which ends up in the proximity of the rather broad Soret band peaking at ca. 355 nm. (—) Solutions of the  $\mu$ -oxo dimer in aliphatic alcohols, such as MeOH or EtOH, assume a bright blue color and the Q-band shifts by ca. 60 nm toward shorter wavelengths.



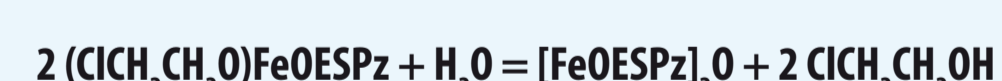
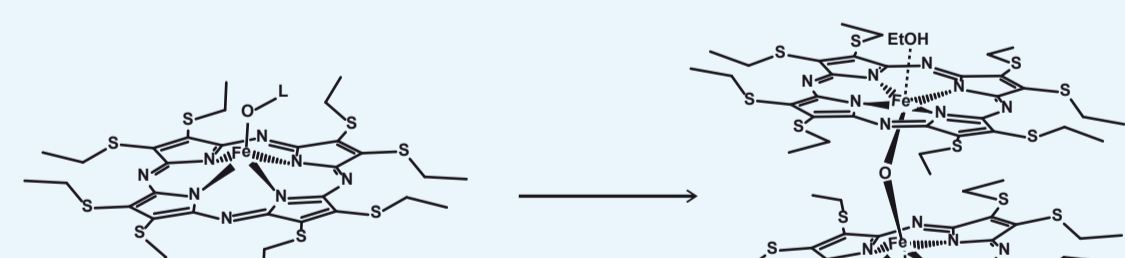
The IR spectrum of the  $\mu$ -oxo dimer differs significantly, in terms of number, energy, and relative intensity of the main peaks, from that of the monomer. Low-to-medium intensity peaks are found at ca. 695, 951, and 1104 cm<sup>-1</sup> in the IR spectrum of the dimer, which have no counterpart in the spectrum of the monomer. Comparison with previous IR studies on similar  $\mu$ -oxo dimers seems to suggest a possible assignment of the lowest-energy band to the asymmetric O—Fe—O stretching vibration. [3]



The MALDI-TOF MS spectrum of the complex shows, besides the molecular peak at  $m/z = 1713.97$  Da, intense peaks at  $m/z = 864.98$  and  $849.03$  Da, generated by the loss of a FeOESPz and a FeOESPz(O) fragment, respectively. This is consistent with the pronounced sensitivity of the complex to acidic media — so is the matrix used for laser desorption/ionization — and the related capability of the dimer to convert into the monomeric constituents.

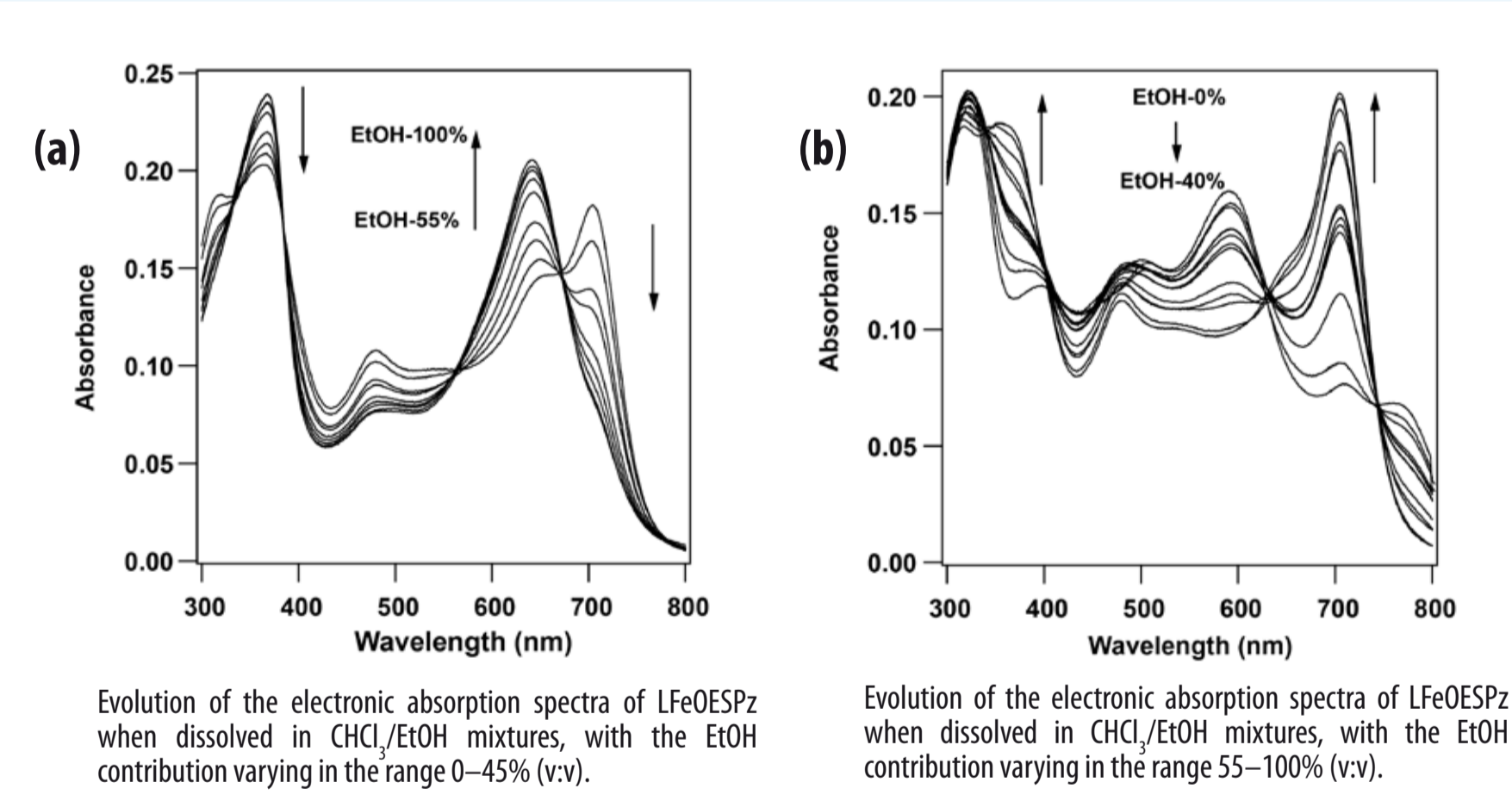
Formation and spectroscopic properties of [FeOESPz]<sub>2</sub>O

Color change is observed when LFeOESPz is dissolved in CH<sub>2</sub>Cl<sub>2</sub>/EtOH mixture of variable composition, in the presence of oxygen. Figure (a) and (b) display the evolution of the optical spectra of the monomer dissolved in CH<sub>2</sub>Cl<sub>2</sub> containing increasing percentages (v/v) of EtOH. As inferred from the spectra in figure (a), initially, the monomer converts into the  $\mu$ -oxo dimer. The degree of conversion is larger the larger is the EtOH content of the solution.

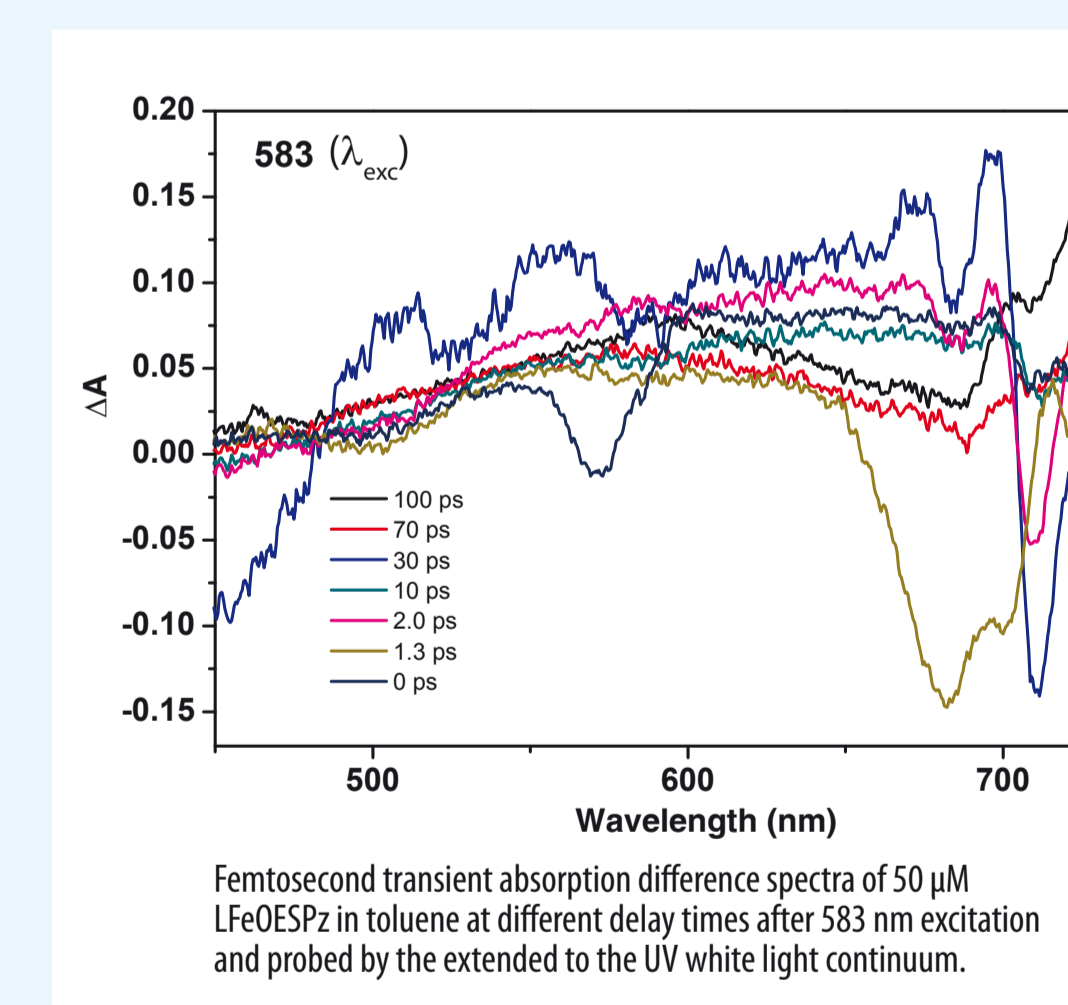
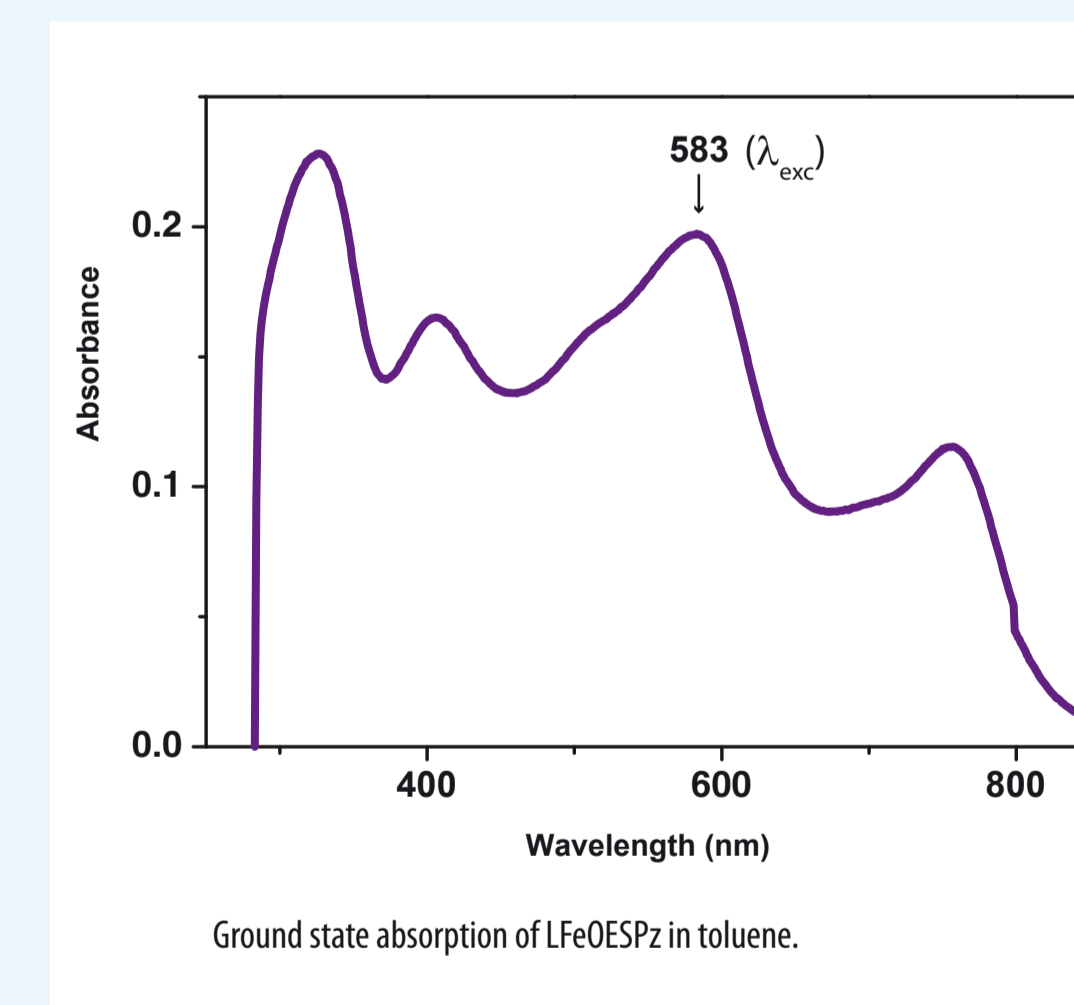


The equation describe how the formation of the  $\mu$ -oxo dimer is most likely allowed by the residual water present in EtOH.

In pure EtOH, the bis-solvated  $\mu$ -oxo dimer is the dominant species. As a matter of fact, the UV-vis spectrum of the monomer dissolved in EtOH (the final spectrum in figure b) and the UV-vis spectrum of the  $\mu$ -oxo dimer directly dissolved in EtOH, are identical, and so stay indefinitely. The larger polarity of EtOH, as compared to CH<sub>2</sub>Cl<sub>2</sub>, is thought to favor the conversion of the monomer into the  $\mu$ -oxo dimer in the former solvent.



## Preliminary ultrafast Pump-Probe measurements



Similar to other iron(III) tetrapyrroles, the investigated iron(III) porphyrine is not emitting upon excitation into the Q-band. The so excited  $^4(\pi, \pi^*)$  state decays radiationlessly to the quartet ground spin state through a very complex mechanism occurring in the sub-picosecond and picosecond time regime. The key steps of the mechanism involve several ligand-field (LF) excited states, and, most likely, excited states with charge transfer (CT) character. Kinetic and theoretical studies are in progress to better characterize the excited states in question and their role in the deactivation

## Conclusions

It is shown that reaction of octakis(ethylthio)-porphyrine with FeBr<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>/EtOH at 135 °C affords the 2-chloroethoxy-iron(III)-ethylthio-porphyrine, (ClCH<sub>2</sub>CH<sub>2</sub>O)Fe<sup>III</sup>OESPz, (LFe<sup>III</sup>OESPz) in good yield. The complex shows interesting spectroscopic and coordination properties, and easily converts into its  $\mu$ -oxo dimer derivative, [Fe<sup>III</sup>OESPz]<sub>2</sub>O. The basic properties of the latter have been characterized in some detail. The spectroscopic and coordination properties of the monomer and the  $\mu$ -oxo dimer have been discussed in the context of those shown by iron porphyrin analogs.

## References

- [1] Pietrangeli, D.; Rosa, A.; Ristori, S.; Salvati, A.; Altieri, S.; Ricciardi, G. *Coord. Chem. Rev.*, 2013, 257, 2213–2231.
- [2] Pietrangeli, D.; Rosa, A.; Pepe, A.; Ricciardi, G. *J. Porphyrin Phthalocyanines*, 2013, 17, 870–880.
- [3] Stuzhin PA, Ul-Haq A, Nefedov SE, Kumeev RS and Koifman OI. *Eur. J. Inorg. Chem.* 2011; 2567–2578.

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