

# Crystal structure and characterization of a new $\mu$ -oxo bridged iron porphyrin



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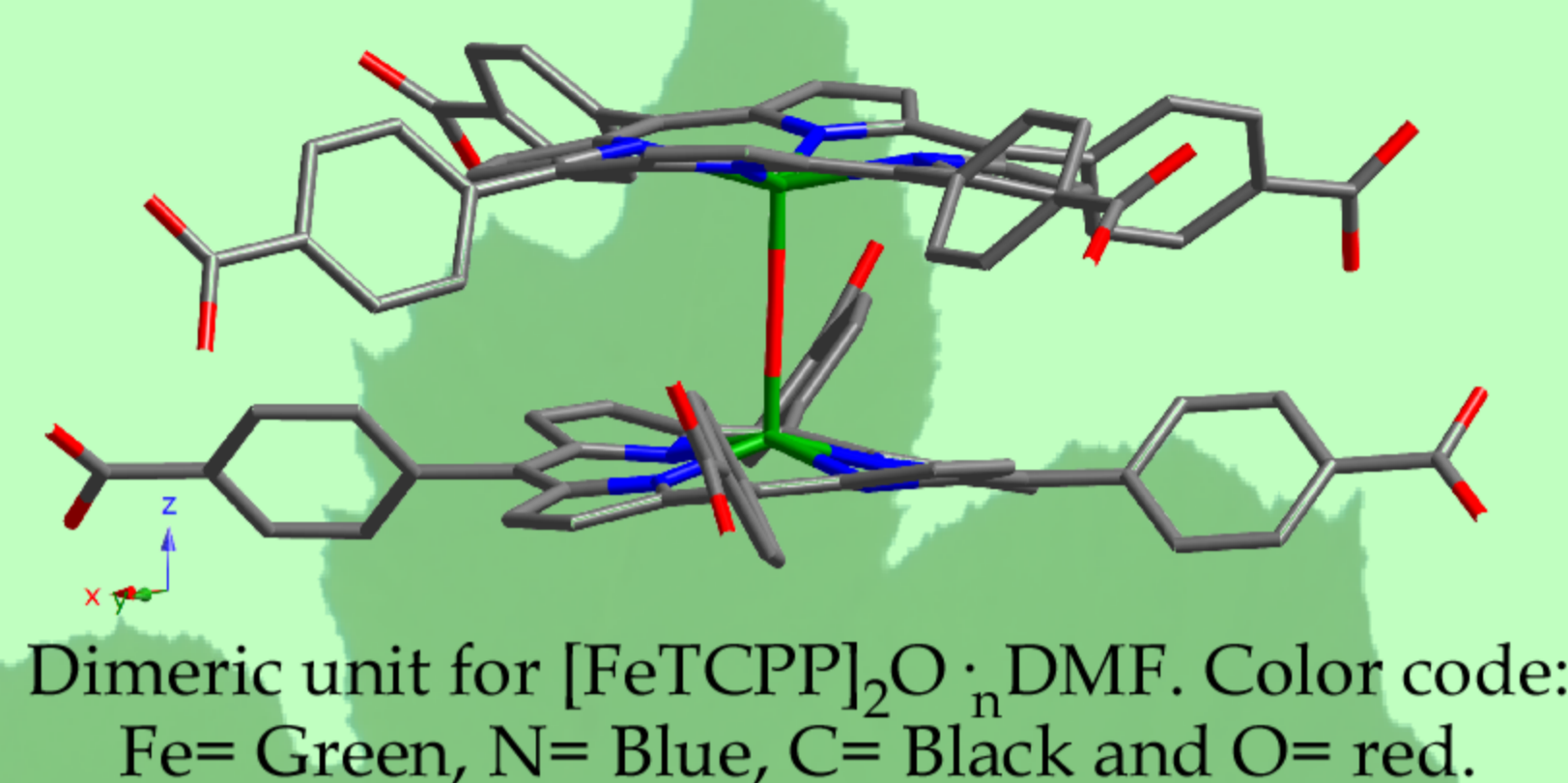
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## Introduction

Metalloporphyrin systems are one of the cornerstones on which the existence of life is based, as major biochemical, enzymatic and photochemical functions depend on the special properties of the tetrapyrrolic macrocycle [1]. Supramolecular entities based on self-assembly of those macrocycles are paradigmatic examples of the great efficiency of the nanodevices used by natural systems in photosynthesis, oxygen transport, electron transfer and catalysis [2], and our group is working with different combinations of metalloporphyrins in order to obtain new compounds that are able to mimicking the functions of those complexes [3,4].

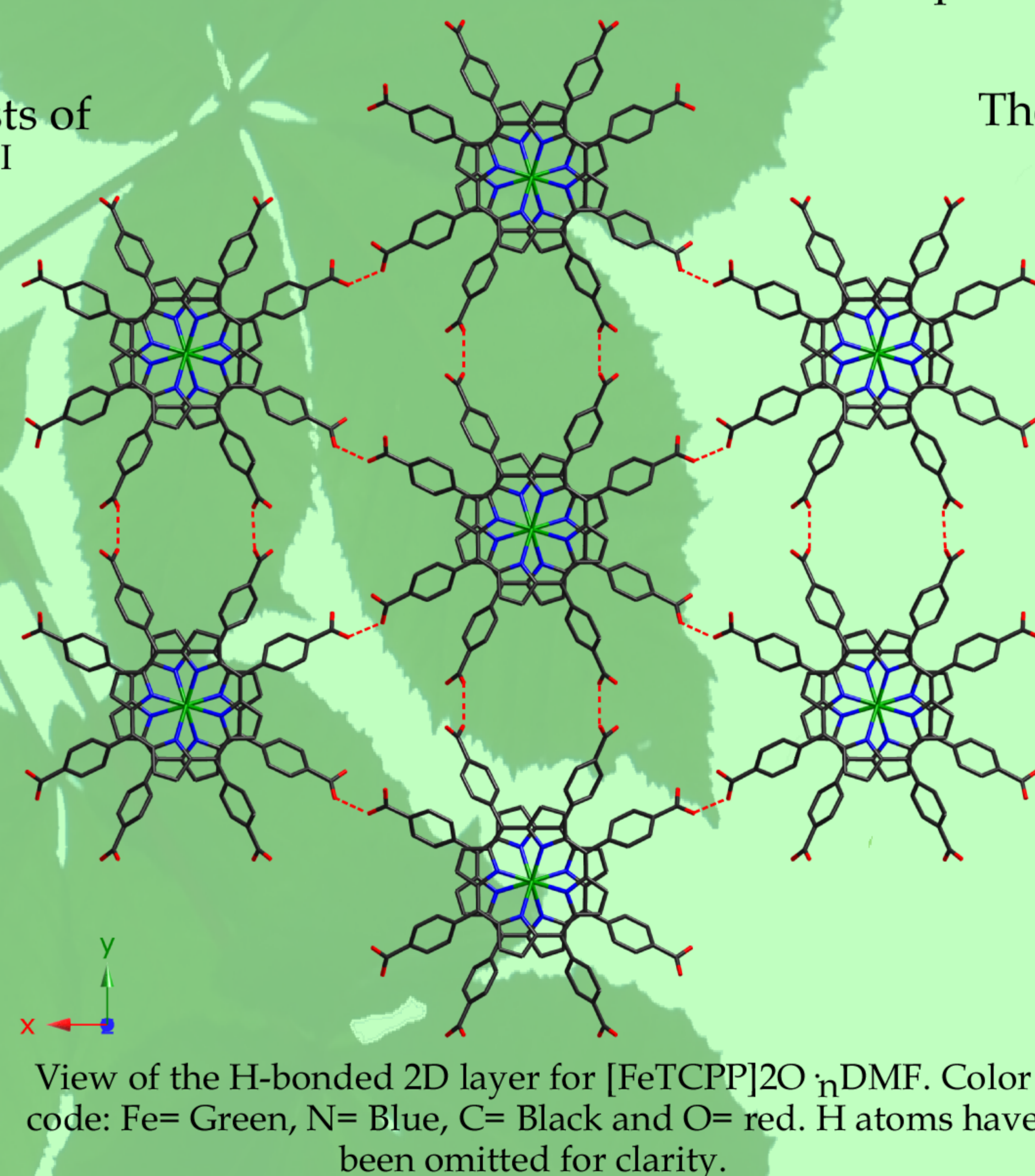
We present the characterization of the  $[\text{FeTCPP}]_2\text{O} \cdot n\text{DMF}$  (TCPP= meso-tetracarboxyphenylporphyrin, DMF= N,N'-dimethylformamide) compound. This is the first  $\mu$ -oxo bridged iron porphyrin with TCPP.



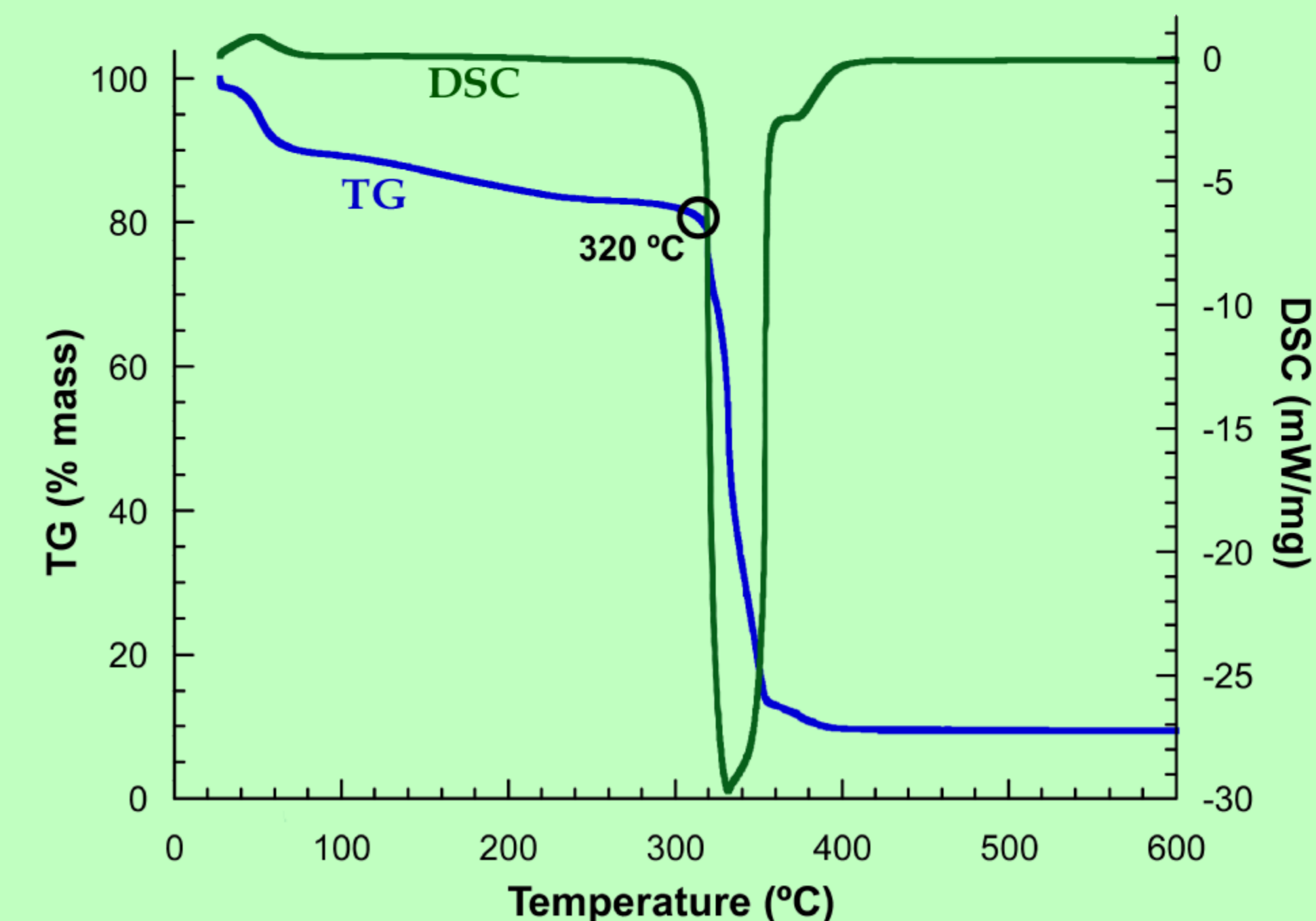
## Crystal Structure

Crystal structure of  $[\text{FeTCPP}]_2\text{O} \cdot n\text{DMF}$  consists of dimers formed by the union between two  $\text{Fe}^{\text{III}}$  porphyrins via an oxygen atom. The iron atom is on a square-based pyramid environment, and it is displaced from the mean plane of the porphyrin to the linking oxygen atom. Each dimer is surrounded by another six producing an H-bonded 2D layer on the (a,b) plane.

Empirical formula	$\text{C}_{96}\text{H}_{52}\text{Fe}_2\text{N}_8\text{O}_{17}$
Formula Weight	1701.16 g/mol
Crystal system	Monoclinic
Space Group	$C2/c$
a	39.3340(4) Å
b	19.8329(2) Å
c	16.0292(2) Å
$\beta$	98.418(1)°
Volume	12369.8(2) Å <sup>3</sup>
Z	4
Final R indexes	$R_1=0.0609$ , $wR_2=0.1869$

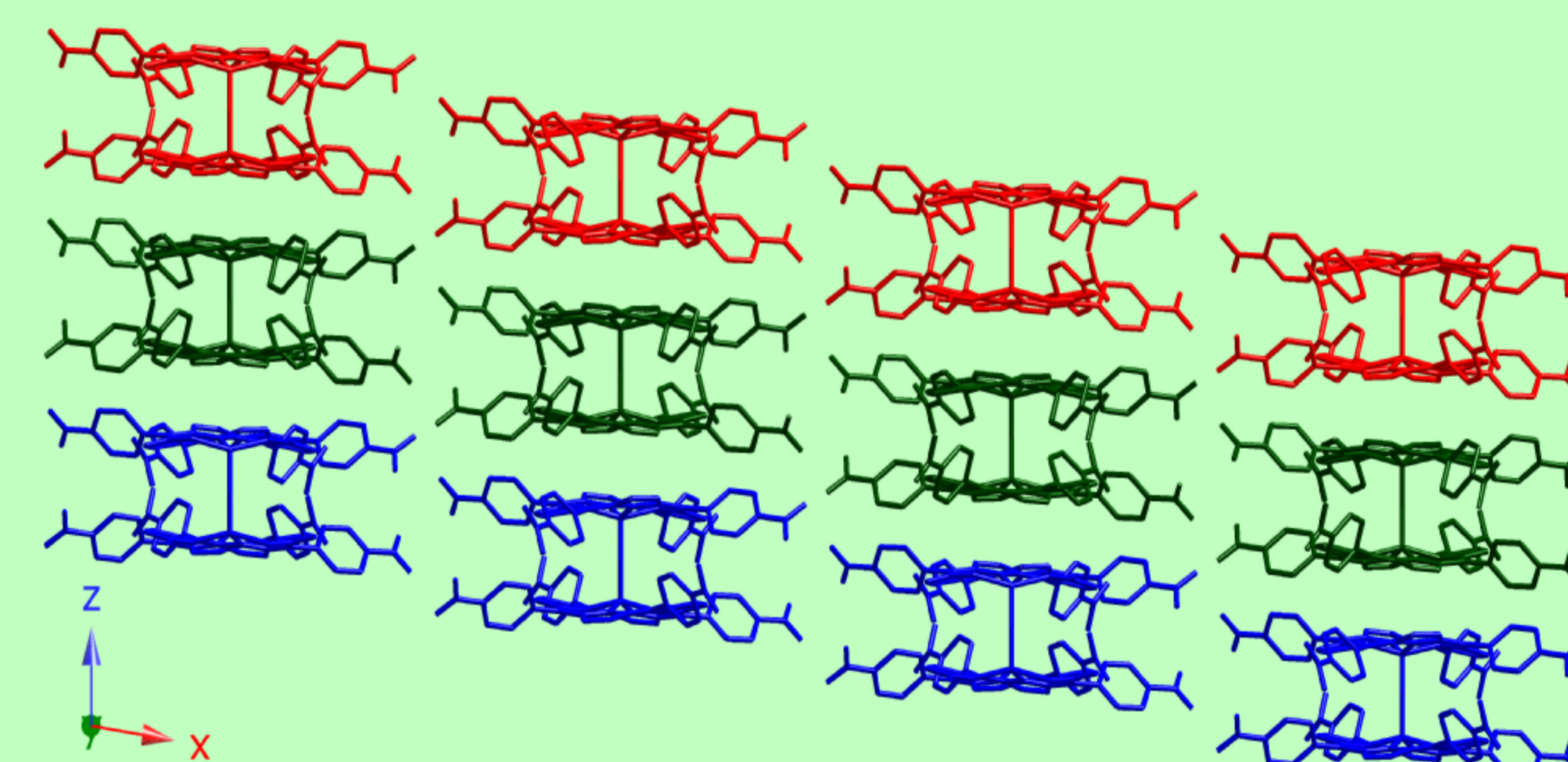


## Thermal Characterization



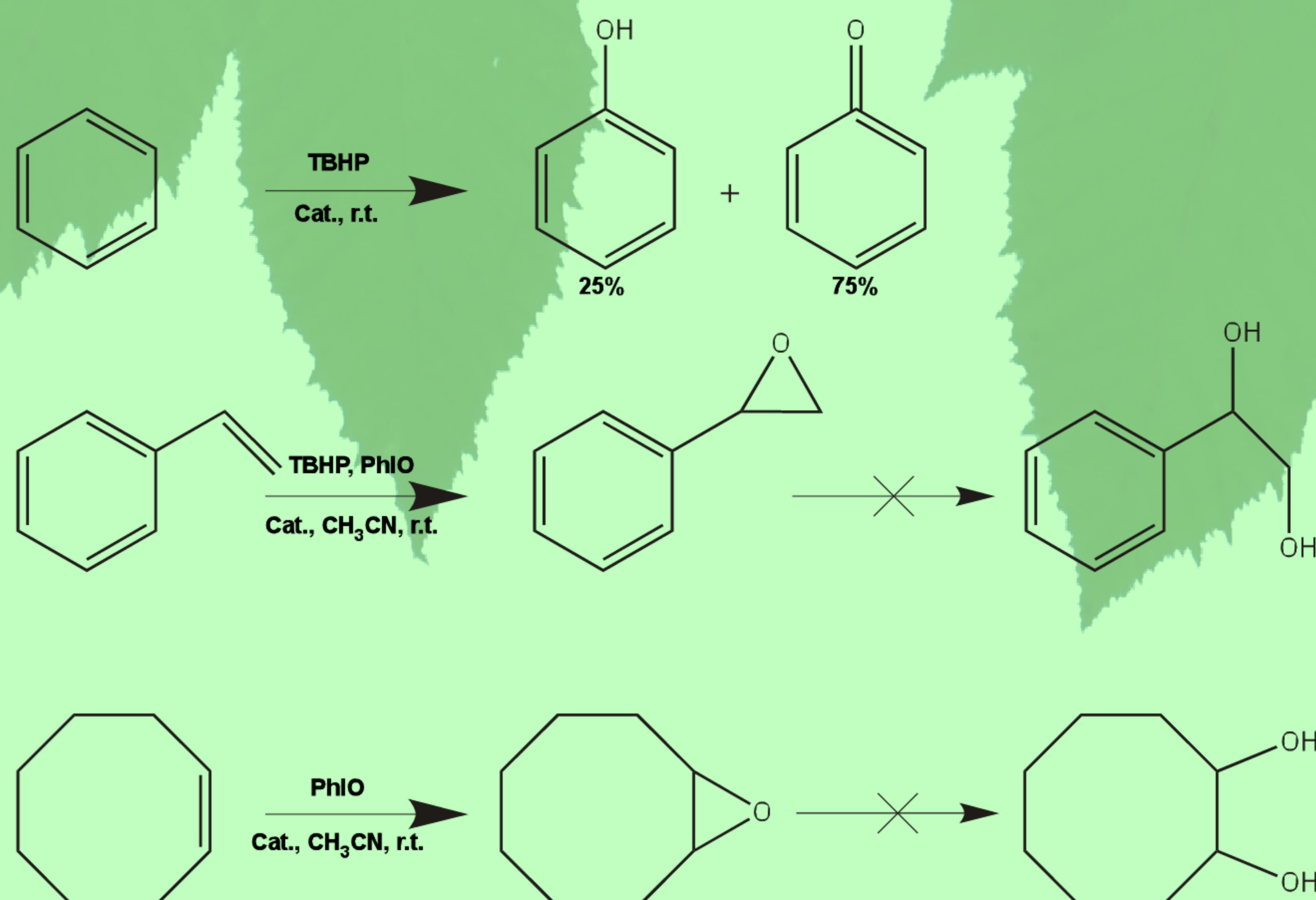
The thermogravimetric decomposition curve for  $[\text{FeTCPP}]_2\text{O} \cdot n\text{DMF}$  shows a continuous weight loss from r.t. to 320 °C associated with DMF molecules, and above this temperature an abrupt loss takes place related to the porphyrins.

These layers are stacked along the (001) direction, and sustained by  $\pi$ - $\pi$  interactions (3.5 ~ 3.9 Å) among the dimers of each layer. Crystallization DMF molecules are located in the voids generated between dimers (47% of the cell volume). Unfortunately, these molecules have not been localized in the structure refinement process.



## Catalytic Properties

$[\text{FeTCPP}]_2\text{O} \cdot n\text{DMF}$  compound has been successfully tested on the selective oxidation of aromatic alkanes and on the epoxidation of aromatic alkenes.



Oxidants: TBHP (tert-Butyl hydroperoxide) and PhIO (iodosylbenzene).  
Solvents: Tests were measured without any solvent or with  $\text{CH}_3\text{CN}$ .

## Conclusions

- $[\text{FeTCPP}]_2\text{O} \cdot n\text{DMF}$  is the first  $\mu$ -oxo bridged iron porphyrin with TCPP.
- The compound is stable up to 320 °C while losing crystallization DMF molecules.
- Catalytic tests show that this compound exhibits selectivity for the cyclohexane oxidation and formation of epoxides from styrene and cyclooctene.

## Acknowledgements

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