



UNIONE EUROPEA

Fondo Sociale Europeo

UNIVERSITÀ DEGLI STUDI DI TORINO

DIPARTIMENTO DI CHIMICA

DOTTORATO DI RICERCA IN SCIENZE CHIMICHE E DEI MATERIALI

CICLO: 37°

TITOLO DELLA TESI: Metal porphyrinate-based crystalline materials with Non Linear Optical properties for the development of biosensors and smart materials.

TESI PRESENTATA DA: Alma Cioci

SUPERVISORE: Domenica Marabello

COORDINATORE DEL DOTTORATO: Bartolomeo Civalleri

ANNI ACCADEMICI: 2022-2023-2024

SETTORE SCIENTIFICO-DISCIPLINARE DI AFFERENZA*: CHEM-03/A

(*N.B. Nel caso di più settori disciplinari interessati, deve essere indicato quello più presente nella trattazione della tesi).

Progetto svolto grazie al sostegno finanziario del **Programma Operativo Nazionale Ricerca e Innovazione 2014-2020 (CCI2014IT16M2OP005)**, risorse FSE REACT-EU, Azione IV.4 “Dottorati e contratti di ricerca su tematiche dell’Innovazione”



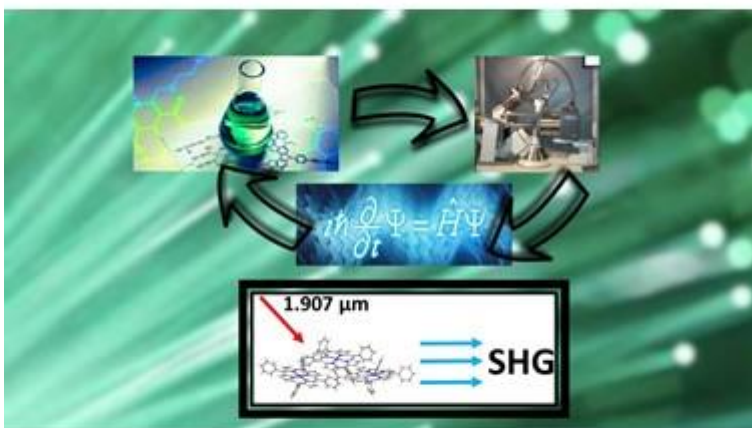


Università degli Studi di Torino

Doctoral School of the University of Torino

PhD Programme in Chemical and Materials Sciences XXXVII Cycle

**Metal porphyrinate-based crystalline materials with
Non Linear Optical properties for the development
of biosensors and smart materials.**



Alma Cioci

Supervisor:

Prof. Domenica Marabello



Università degli Studi di Torino

Doctoral School of the University of Torino

PhD Programme in Chemical and Materials Sciences XXXVII cycle

Metal porphyrinate-based crystalline materials with NLO properties for the development of biosensors and smart materials.

Candidate: **Alma Cioci**

Supervisor: Prof. **Domenica Marabello**

Jury Members: Prof. **Silvia Casassa**
Università degli Studi di Torino
Dipartimento di Chimica
Prof. **Marco Milanese**
Università del Piemonte Orientale
Dipartimento di Scienze e Innovazione Tecnologica
Prof. **Leonardo Mortati**
Istituto Nazionale di Ricerca Metrologica
Division of Advanced Materials and Life Sciences

Head of the Doctoral School: Prof. Alberto Rizzuti

PhD Programme Coordinator: Prof. Bartolomeo Civalieri

Torino, 14/04/2025

Table of Contents

1. INTRODUCTION	10
1.1. Metal Porphyrinates.....	11
1.2. Second Harmonic Generation (SHG) microscopy	13
1.3. The challenge: Development of Metal Porphyrinates-Based Materials for biosensors and SHG-based devices for optoelectronics	15
1.4. A Multidisciplinary Approach for the study of the SHG properties	15
2. METHODS	21
2.1. Synthesis.....	21
2.2. Spectroscopic and Magnetic Characterization	22
2.3. Structural Characterization	32
2.4. Non Linear Optical Characterization: The Kurtz and Perry method	36
2.5. Theoretical background and computational methods for the calculation of Non Linear Optical properties.....	39
3. RESULTS.....	56
3.1. Tetraphenylporphyrin (TPP) based crystalline materials	56
3.2. Tetrakis-nitro-phenylporphyrin (TNPP) based crystalline materials	58
4. Co-TPP: synthesis, characterization and SHG behavior	60
4.1. Synthesis of Cobalt(II) 5,10,15,20-tetraphenilporphyrinate (Co-TPP)	60
4.2. Characterization of Co-TPP.....	60
4.3. SHG behavior and further characterizations of Co-TPP.....	63
4.4. Theoretical study of Co-TPP	69
5. The isomorphous compounds Ni-TPP and Cu-TPP: synthesis, characterization and SHG behavior.....	80
5.1. Synthesis of Nickel(II)- and Copper(II)-5,10,15,20- tetraphenylporphyrinate (Ni-TPP and Cu-TPP)	80
5.2. Characterization of Ni-TPP and Cu-TPP.....	80

5.3.	SHG behavior and further characterizations of Ni-TPP and Cu-TPP.	81
5.4.	Theoretical study of Ni-TPP and Cu-TPP.	86
6.	Three centrosymmetric crystalline derivatives of Zn-TPP: synthesis, characterization and SHG behavior.....	100
6.1.	Synthesis of Zn(III) 5,10,15,20-tetraphenylporphyrinate (Zn-TPP, Zn-TPP-DMF and Zn-TPP-DMF(DCM))	100
6.2.	Characterization of Zn-TPP, Zn-TPP-DMF and Zn-TPP-DMF(DCM))	100
6.3.	SHG behavior and further characterizations of Zn-TPP, Zn-TPP-DMF and Zn-TPP-DMF(DCM)).....	108
6.4.	Theoretical study of Zn-TPP, Zn-TPP-DMF and Zn-TPP-DMF(DCM))	114
7.	New crystalline materials based on Co (II) Tetrakis-nitro-phenylporphyrin (Co-TNPP) and Zn(II)Tetrakis-nitro-phenylporphyrin (Zn-TNPP): synthesis, characterization and SHG behavior.....	139
7.1.	Synthesis of Co-TNPP and Zn-TNPP	139
7.2.	Characterization of Co-TNPP and Zn-TNPP.....	139
7.3.	SHG behavior of Co-TNPP and Zn-TNPP	146
8.	APPLICATIONS	147
8.1.	Cobalt-tetraphenylporphyrinate-chitosan microspheres for multi-theranostic applications	147
8.1.1	Experimental	148
8.1.2	Results and Discussion	150
8.1.3	Conclusions.....	163
8.2.	Applications in Optoelectronic Devices: Cu-TPP films grown on ceramic and ITO-coated glasses	164
8.2.1	Experimental	164
8.2.2	Results and discussion	165
8.2.2	Conclusions.....	180
9.	CONCLUSIONS.....	184
10.	APPENDIX.....	192
10.1.	Tables	192

1. INTRODUCTION

This doctoral thesis aims to investigate the innovative potential of metal porphyrinates in applications based on Second Harmonic Generation (SHG), a specific nonlinear optical (NLO) property. It will extensively examine the latest developments in the use of these compounds by means of an in-depth review of up-to-date scientific literature, while also providing a detailed account of their synthesis, characterization, and specific applications in biological imaging through a multidisciplinary approach. The primary focus will be the study of solid-state metal porphyrinates, whose use in SHG-applications represents an unexplored area of research.

This introduction, which is divided into 10 Sections, will begin with an overview of the main features of metal porphyrinates, delving into their biological roots and illustrating their current applications in bioimaging (Section 1.1). Then it will proceed to discuss the most salient characteristics of SHG microscopy (Section 1.2), before sketching out the challenge of developing solid-state metal porphyrinates for SHG microscopy (1.3). Last, will be considered and thoroughly analyzed the multidisciplinary approach adopted for the study of the SHG properties of the solid-state metal porphyrinates (1.4).

Chapter 2 will focus on the research methods we opted for, describing the process of synthesis (2.1), spectroscopic and magnetic characterization (2.2), structural characterization (2.3), and NLO characterization from both an experimental (2.4) and theoretical (2.5) and point of view of the materials sought.

Chapter 3 offers a sum of the results obtained via the previously discussed methods. Subsequently, Chapters from 4 to 7 will show the results obtained via the previously discussed methods, with regard to the synthesis, characterization and SHG behavior of each porphyrinate: Co-TPP (Chapter 4), the two isomorphous compounds Ni-TPP and Cu-TPP (Chapter 5), the three crystalline materials based on Zn-TPP (Chapter 6) and the two complexes Co-TNPP and Zn-TNPP.

Finally, two potential applications of these materials will be expounded in Chapter 8, which is divided into two Sections: Section 8.1, regarding the field

of bio-devices; and Section 8.2, concerning the sphere of optoelectronic devices.

1.1. Metal Porphyrinates.

Metal porphyrinates represent a class of organometallic compounds known for their molecular structure based on the porphyrin core (Figure 1.1.1a), within which a metal atom is incorporated. The porphyrin core, composed of four pyrrolic rings linked by methylene bridges, coordinates a metal ion after losing the two internal hydrogen atoms: the porphyrin core acquires two negative charges, which attract the two positive charges of the metal ion, and the internal nitrogen atoms act as donor atoms (Figure 1.1.1b). These porphyrin derivatives have attracted increasing scientific interest due to their unique properties and the numerous applications that stem from them.

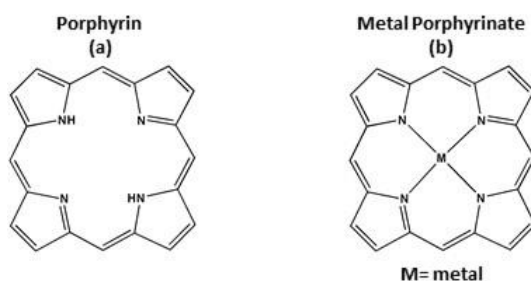


Figure 1.1.1 Scheme of the porphyrin core (a) and the metal porphyrinate (b).

Moreover, metal porphyrinates play a pivotal role in natural contexts, since many living organisms, including photosynthetic ones such as plants and bacteria, make use of metal porphyrinates to perform key biological processes. Notably, the ability to coordinate metals makes porphyrinates essential for crucial biological functions (Figure 1.1.2), as clearly exemplified by the transport of oxygen in the hemoglobin molecule. In the past few years, this has spurred innovative research aimed at shedding light on the presence and function of metal porphyrinates in various natural contexts^{1,2}.

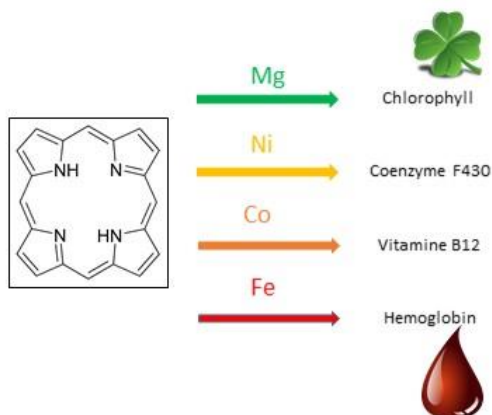


Figure 1.1.2 Some example of metal porphyrinates in nature³.

Alongside their biological implications, metal porphyrinates have attracted significant interest within the scientific community due to their numerous application in a wide range of fields: their chemical versatility allows for the synthesis of several derivatives with unique optical, electronic, and catalytic properties^{4,5}. Of particular relevance for this thesis work is the use of metal porphyrinates in bioimaging (Figure 1.1.3), where their fluorescence properties and low toxicological impact qualifies them as promising contrast agents for the analysis of biological samples^{6,7}.

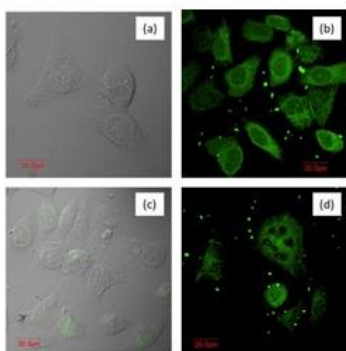


Figure 1.1.3 Example of bioimaging based on (5,10,15,20-tetrakis(4-methoxyphenyl)porphyrin) used as a biosensor: control cells (a), cells incubated with the porphyrin-based biosensor (b); cells incubated with a different biosensor (Phorbol 12-myristate 13-acetate) (c); and cells incubated with both the porphyrin and the different biosensor together (d)⁸.

1.2. Second Harmonic Generation (SHG) microscopy

Over the course of the past decade, traditional NLO spectroscopy methods have been fruitfully integrated and complemented with the microscopy techniques customarily used by biologists. Techniques such as Second Harmonic Generation (SHG), Third Harmonic Generation (THG), Coherent Anti-Stokes Raman Scattering (CARS), and Multiphoton Excitation (MPE), which have long been used by chemists, are now also being applied to the optical imaging of cells and tissues⁹.

Significant emphasis has been placed on the development of these methods not only as tools for basic scientific research, but also as potential diagnostic instruments for clinical applications, thanks to the sub-micrometric resolution provided by optical wavelengths. By contrast, other clinical tomographic techniques such as computed tomography (CT), magnetic resonance imaging (MRI), and positron emission tomography (PET) are limited to resolutions of around 1 millimeter. The sub-micrometric resolution offered exclusively by new microscopy methods is particularly relevant given the dimensional scale of cells and tissues, which feature structures that range from approximately 50 nanometers for organelles to tens of microns for whole cells. It is worth noting, in fact, that alterations on these scales in the three-dimensional tissue environment are strongly associated with a number of diseases⁹.

Historically, cellular-level clinical imaging has been performed primarily by pathologists on ex vivo biopsies removed by operating doctors. Although histology remains the standard, its accuracy depends on the pathologist's experience and interpretive skills. Additionally, histological samples are fixed and cut into thin sections (approximately 5-10 microns), making spatial correlation challenging. There is a significant potential role for quantitative optical microscopy approaches that address the shortcomings of both non-invasive imaging (lack of resolution/specificity) and traditional histology (subjectivity)^{10,11}.

SHG signals arise from induced polarization rather than absorption, resulting in a significant reduction in photo-bleaching and photo-toxicity compared to other fluorescence-based imaging methods. Additionally, since the fundamental laser wavelengths are typically in the near-infrared (NIR) spectral range (700-1000 nm), SHG microscopy can achieve high-resolution imaging at depths of several hundred microns.

Currently, SHG microscopy primarily leverages the intrinsic emission properties of tissues, such as collagen, to generate the SHG signal. Collagen is a highly nonlinear protein that produces a SHG signal when illuminated by a suitable laser. This makes SHG microscopy particularly useful for analyzing

the structure of collagen, as well as other nonlinear biological structures present in tissues (Figure 1.2.1).^{12,13}

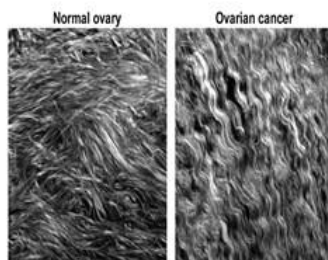


Figure 1.2.1 Representative single optical sections (field size = 170 μm) of the collagen fibers in normal human ovary (left) and malignant ovary (right), in which striking differences in collagen morphology are revealed by SHG.

SHG microscopy has been used for many different purposes, including the investigation of cell-cell interactions, the analysis of cell morphology, and even the real-time recording of electrochemical activity waves (action potentials) in neurons. However, to date, only contrast agents with modest NLO properties have been employed.^{14,15,16} For in vivo applications in large animals, new contrast agents and optimizations would be necessary to enhance SHG signal acquisition¹⁷, which underscores the interest in researching new biosensors with improved properties.

The optical linearity of inorganic compounds does not prove as satisfying as that of their organic counterpart, since the SHG efficiencies exhibited by the latter appear to be a thousand times as high as those shown by the former¹⁸. However, organic NLO crystals have often turned out to be fragile, difficult to grow, as well as sometimes too chemically unstable for practical applications. On the other hand, as highlighted, porphyrins stand out for their stability from both a chemical and a physical point of view, and have been widely studied as suitable biosensors due to their fluorescence properties^{19,20,21,22}, therefore they are potentially interesting as new contrast agents for SHG microscopy.

1.3. The challenge: Development of Metal Porphyrinates-Based Materials for biosensors and SHG-based devices for optoelectronics

The challenge of developing metal porphyrinate-based materials for SHG applications represents an exciting and strategic perspective in the field of NLO research. As shown in the previous paragraphs, these materials are highly versatile for various applications (Section 1.1), including the proposed use in SHG-based bioimaging (Section 1.3).

In the wake of these remarkable findings, most recent studies have emphasized how metal porphyrinates, either considered in solution, may constitute a viable option for SHG-based bioimaging applications, highlighting interesting NLO properties. Among these, some metal porphyrinates exhibit THG^{23,24,25,26,27}, in solution or encapsulated in polymers²⁸, and in this form they have recently been proposed and studied for bioimaging^{29,30}. Notably, the prominent π electron delocalization of the porphyrin ligand has the potential to significantly enhance the hyperpolarizability, a property which is strongly correlated with the SHG, by inserting a coordinated metal into the center of the porphyrin structure³¹.

This doctoral project focuses on the study of metal porphyrinates in the solid state, to fully exploit their potential in advanced imaging applications. The objective is to identify which metal porphyrinate-based crystalline solids exhibit the best responses in terms of NLO. Besides, we also expect to highlight the connection between the intrinsic nature of these materials and the properties detected, in order to understand the phenomena at play and become better able to provide clear guidelines for synthesizing and functionalizing materials with improved performance.

1.4. A Multidisciplinary Approach for the study of the SHG properties

To determine which porphyrin-based materials exhibited the best NLO properties, porphyrins of various alkaline earth and transition metals were synthesized.

Two different porphyrin ligands were tested: tetra-phenylporphyrin (H_2TPP) and tetrakis-nitro-phenylporphyrin (H_2TNPP). Specifically, H_2TPP derivatives appeared to be particularly suitable for our study because of their availability,

their ease of synthesis, and their ability to crystallize effectively. The effect of electron-withdrawing and/or electron-donating substituents on the porphyrin can affect NLO properties³¹, therefore, among the many available options, H₂TNPP was chosen, which is a tetraphenylporphyrin with electron-withdrawing nitro groups on the phenyl rings.

We mainly focused on transition metals (Mn, Fe, Co, Ni, Cu, and Zn), which could positively contribute to improvement of the hyperpolarizability, although some alkaline earth metals were tested as well (Mg and Ca). All the metals considered are available as divalent metal acetates, which is useful for the synthesis methods used in this work (Section 2.1).

The obtained metal porphyrinates were characterized using various analytical techniques: electronic and magnetic properties were studied through electronic spectroscopy (UV-VIS) and magnetic susceptibility measurements, while the purity of synthesized compounds was checked by Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy (Section 2.2).

A fundamental requirement for a material to be effectively used as a biosensor for SHG microscopy is the presence of a non-zero NLO coefficient. Such characteristic is ensured, in the case of a crystalline material, by the absence of the center of inversion in its crystal structure³². This can be verified by means of single-crystal X-ray diffraction, which allows for a complete determination of the crystal structure. Moreover, the crystal structure of every synthesized compounds was checked by powder X-ray diffraction (XRPD) (Section 2.3).

SHG measurements were conducted using the Kurtz and Perry method, which is accredited for these measurements (Sections 2.4).

The structural data obtained from single-crystal X-ray diffraction were used for theoretical calculations, specifically employing the Density Functional Theory (DFT) method. Properties such as the electric dipole moment, the polarizability and the hyperpolarizability were computed. Once hyperpolarizability has been computed, the second-order optical susceptibility can be derived, whose magnitude is related to the experimental value of SHG. Computational results can be compared to experimental measurements of Second Harmonic emission on powders (Section 2.5).

For potential applications of these materials in the field of bio-devices, we propose it is necessary to cover the nanoparticles with a suitable bio-compatible material, which can be further functionalized in order to drive them toward cancer cells. On the other hands, there are possible side effects of porphyrins in the biological applications³³, such as the potential coloration of the patient's epidermis and other cases of photosensitivity, and for this

reason a suitable carrier to introduce porphyrins inside human body is an interesting investigation proposal. This issue will be deeply explored in chapter 8.

References

- 1** Ladner, R. C.; Heidner, E. J.; Perutz, M. F. The Structure of Horse Methaemoglobin at 2.0 Å Resolution. *J. Mol. Biol.* 1977, 114, 385–414. DOI: 10.1016/0022-2836(77)90256-x.
- 2** Geno, M. K.; Halpern, J. Why Does Nature Not Use the Porphyrin Ligand in Vitamin B12? *J. Am. Chem. Soc.* 1987, 109, 1238–1240. DOI: 10.1021/ja00238a039.
- 3** <https://www.missionescienza.it/porifina-anello-della-vita/>
- 4** H. Lee, K.I. Hong, W.D. Jang Design and applications of molecular probes containing porphyrin derivatives *Coord. Chem. Rev.*, 354 (2018), pp. 46-73
- 5** A. Mahmood, J.Y. Hu, B. Xiao, A. Tang, X. Wang, E. Zhou Recent progress in porphyrin-based materials for organic solar cells *J. Mater. Chem. A*, 6 (2018), pp. 16769
- 6** A. Khadria, J. Fleischhauer, I. Boczarow, J.D. Wilkinson, M.M. Kohl, H.L. Anderson Porphyrin dyes for nonlinear optical imaging of live cells *iScience*, 4 (2018), pp. 153-163
- 7** J.E. Reeve, H.A. Collins, K.D. Mey, M.M. Kohl, K.J. Thorley, O. Paulsen, K. Clays, H.L. Anderson Amphiphilic porphyrins for second harmonic generation imaging *J. Am. Chem. Soc.*, 131 (8) (2009), pp. 2758-2759
- 8** Chandra, S., Mende, C., Bahadur, D., Hildebrandt, A., & Lang, H. (2015). Fabrication of a porphyrin-based electrochemical biosensor for detection of nitric oxide released by cancer cells. *Journal of Solid State Electrochemistry*, 19, 169-177.
- 9** Therien, M. J. (2009). How to improve your image. *Nature*, 458(7239), 716-717.
- 10** Boyd, R. W. (2003). *Nonlinear Optics*. San Diego: Academic Press.
- 11** Huang, X., El-Sayed, I. H., Qian, W., & El-Sayed, M. A. (2006). Cancer cell imaging and photothermal therapy in the near-infrared region by using gold nanorods. *Journal of the American Chemical Society*, 128(6), 2115-2120.
- 12** Jin, Y. (2012). *Adv. Mater.* 24, 5153–5165.
- 13** Liu, X., Guo, Q. & Qiu, J. (2017). *Adv. Mater.* 29, 1605886
- 14** Campagnola, P. J. & Loew, L. M. (2003). *Nat. Biotechnol.* 21, 1356–1360

-
- 15** Campagnola, P. (2011). Second harmonic generation imaging microscopy: applications to diseases diagnostics. *Analytical chemistry*, 83(9), 3224-3231.
- 16** Campagnola, P. J., & Loew, L. M. (2003). Second-harmonic imaging microscopy for visualizing biomolecular arrays in cells, tissues and organisms. *Nature biotechnology*, 21(11), 1356-1360.
- 17** Pantazis, P., Maloney, J., Wu, D. & Fraser, S. E. (2010). *Proc. Natl Acad. Sci. USA*, 107, 14535–14540.
- 18** Tam et al., 1989
- 19** G. Pandey, R. Chaudhari, B. Joshi, S. Choudhary, J. Kaur, A. Joshi Fluorescent biocompatible platinum-porphyrin-doped polymeric hybrid particles for oxygen and glucose biosensing *Sci. Rep.*, 9 (2019), pp. 5029-5040
- 20** K. Norvaisa, M. Kielmann, M.O. Senge Porphyrins as Colorimetric and photometric biosensors in modern bioanalytical systems *ChemBioChem*, 21 (2020), pp. 1-16
- 21** M. Imran, M. Ramzan, A.K. Qureshi, M.A. Khan, M. Tariq Emerging applications of porphyrins and metalloporphyrins in biomedicine and diagnostic magnetic resonance imaging *Biosensors*, 8 (2018), pp. 95-111
- 22** S. Chandra, C. Mende, D. Bahadur, A. Hildebrandt, H. Lang Fabrication of a porphyrin-based electrochemical biosensor for detection of nitric oxide released by cancer cells *J. Solid State Electrochem.*, 19 (2015), pp. 169-177
- 23** M. O. Senge, M. Fazekas, E. G. A. Notaras, W. J. Blau, M. Zawadzka, O. B. Locos and E. M. Ni Mhuircheartaigh, Nonlinear Optical Properties of Porphyrins, *Adv. Mater.* 19 (2007) 2737–2774.
- 24** F. Tessore, A. Orbelli Biroli, G. Di Carlo and M. Pizzotti, Porphyrins for Second Order Nonlinear Optics (NLO): An Intriguing History, *Inorganics* 6 (2018) 81.
- 25** K. S. Suslick, C. T. Chen, G. R. Meredith, L. T. Cheng, Push-pull porphyrins as nonlinear optical materials, *J. Am. Chem. Soc.* 114 (1992) 6928-6930.
- 26** X. Liu, D. Wang, H. Gao, Z. Yang, Y. Xing, H. Cao, W. He, H. Wang, J. Gu, H. Hu, Nonlinear optical properties of symmetrical and asymmetrical porphyrin derivatives with click chemistry modification, *Dyes and Pigments* 134 (2016), 155-163.
- 27** X. Liu, D. Wang, H. Gao, Z. Yang, Y. Xing, H. Cao, W. He, H. Wang, J. Gu, H. Hu, Nonlinear optical properties of symmetrical and asymmetrical

porphyrin derivatives with click chemistry modification, *Dyes and Pigments* 134 (2016), 155-163.

28 K. Sendhil, C. Vijayan, M.P. Kothiyal, Nonlinear optical properties of a porphyrin derivative incorporated in Nafion polymer, *Optical Materials* 27 (2005) 1606–1609.

29 A. Khadria, J. Fleischhauer, I. Boczarow, J. D. Wilkinson, M. M. Kohl and H. L. Anderson, Porphyrin Dyes for Nonlinear Optical Imaging of Live Cells, *iScience* 4 (2018) 153–163.

30 J.E. Reeve, H.A. Collins, K.D. Mey, M.M. Kohl, K.J.Thorley, O. Paulsen, K. Clays, H.L. Anderson, Amphiphilic Porphyrins for Second Harmonic Generation Imaging, *J. Am. Chem. Soc.* 131 8 (2009) 2758–2759.

31 X. Liu, D. Wang, H. Gao, Z. Yang, Y. Xing, H. Cao, W. He, H. Wang, J. Gu, H. Hu, Nonlinear optical properties of symmetrical and asymmetrical porphyrin derivatives with click chemistry modification, *Dyes and Pigments* 134 (2016) 155-163.

32 Marabello, D., Antoniotti, P., Benzi, P., Canepa, C., Mortati, L., & Sassi, M. P. (2017). *Acta Crystallographica Section B: Structural Science, Crystal Engineering and Materials*

33 Kakoullis L, Louppides S, Papachristodoulou E, Panos G. Porphyrins and photosensitivity: pathophysiology for the clinician. *Postgrad Med.* 2018 Nov;130(8):673-686. doi: 10.1080/00325481.2018.1533380. Epub 2018 Oct 23. PMID: 30296862.

2. METHODS

2.1. Synthesis

All the porphyrins employed were purchased from Porphychem, while all the metal acetates and the solvents from Sigma Aldrich and Alpha Aesar. All the chemicals were used without further purification. The complexation of the tetraphenylporphyrin (Figure 2.1.1) was carried out in boiling N, N-dimethylformamide (DMF), where the porphyrin and the metal acetate had been dissolved, for about three hours. DMF creates a basic environment, promoting the deprotonation of the porphyrin, and, being a high-boiling liquid, the reaction occurs at a temperature that promotes cation complexation. The basic environment subtracts the two protons from the porphyrin, which acquires two negative charges that are neutralized by the metal ion upon insertion into the ring.

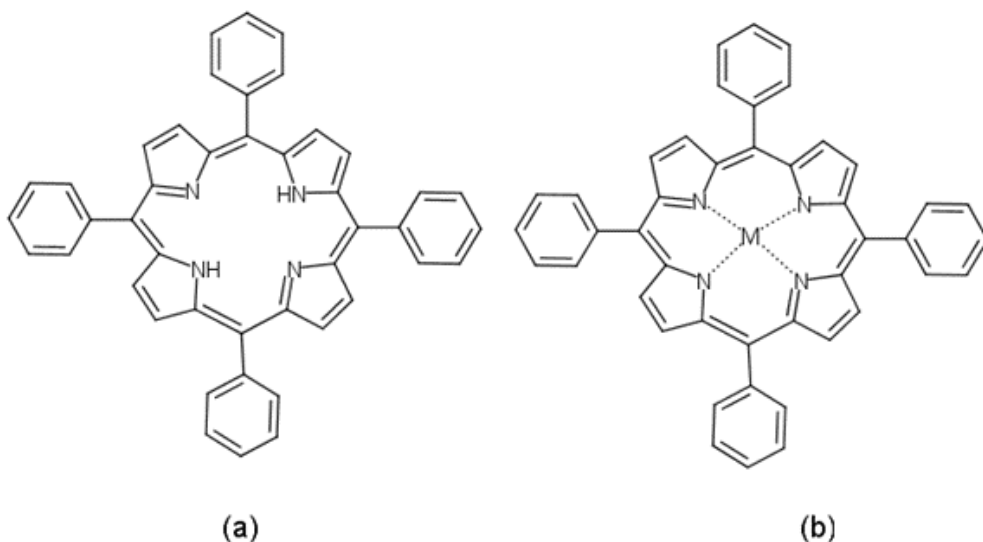
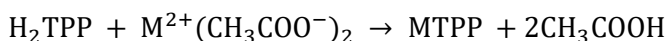


Figure 2.1.1 tetraphenylporphyrin protonated (a) or complexed (b)

The obtained product was precipitated adding water, filtered and air-dried. To obtain a single crystal suitable for X-ray diffraction, various crystallization attempts were conducted by varying the solvent, the temperature, and the evaporation rate. The synthesis of each complex will be fully described in the following chapters (Section 3.2-3.5).

2.2. Spectroscopic and Magnetic Characterization

For the characterization of the metal porphyrinates under study, UV-Visible absorption spectra were recorded with a Cary 60 spectrophotometer, using solutions in dichloromethane at two different concentrations (0.01 M and 0.002 M, Fig. 2.2.1).



Figure 2.2.1 Solutions of Cu porphyrinate in dichloromethane at two different concentrations

To understand the need for these different concentrations, consider the simple four-orbital model by Martin Gouterman (Fig. 2.2.2), which provides a theoretical framework to understand the electronic transitions observed for this class of molecules¹.

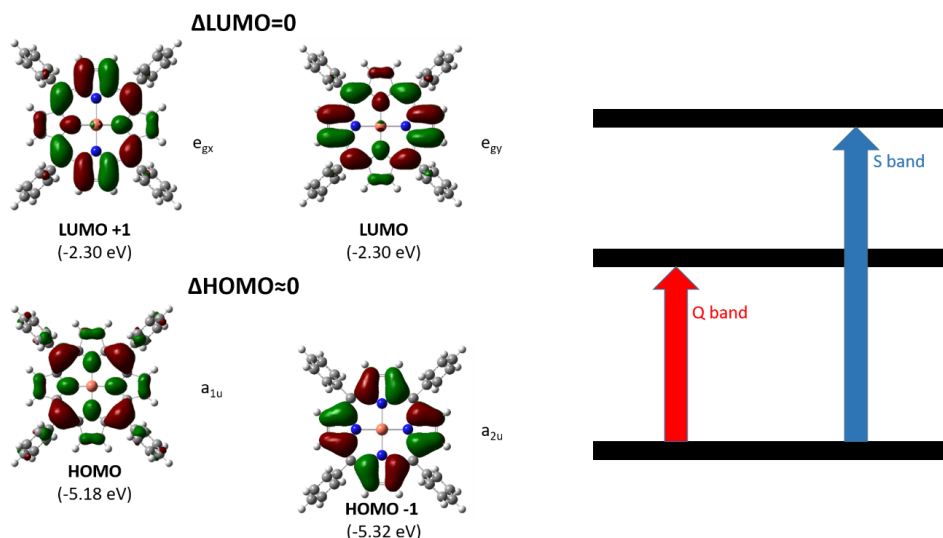


Figure 2.2.2 Representation of M. Gouterman's four orbitals model for Cu-TPP. Molecular orbitals shape was obtained by the GAUSSIAN16 program and its corresponding GaussView 6.0

The electronic absorption spectrum of a metal porphyrinate is characterized by a strong transition around 400 nm, known as the "S band," and a weaker transition around 550 nm, known as the "Q band". As shown in Figure 2.2.2, according to Gouterman's model, the S band is associated with the allowed transition between the four molecular orbitals, while the Q band is related to the symmetry-forbidden transition.²

Figure 2.2.3 a) shows the well-known electronic spectrum of tetra-phenylporphyrin, H_2TPP , recorded in dichloromethane^{3,4,5}. The S band is at 414 nm, and the Q bands are at 515, 549, 589, and 648 nm. It is known that the splitting of the Q bands in the free porphyrin is due to the C_{2h} symmetry of the molecule. In metal porphyrinates, due to metal coordination and the resulting appearance of a quadruple rotation axis that increases symmetry, this splitting is not observed, resulting in a single Q band (Fig. 2.2.3 b)³.

Thanks to this difference between the free base and the complex, UV-Visible spectroscopy in solution is a method to verify the insertion of the metal cation into the ring.

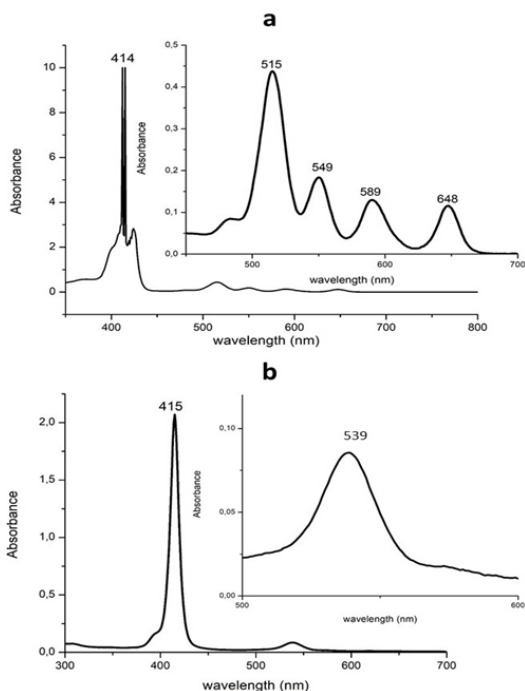


Figure 2.2.3 (a) UV-Vis spectrum of H_2TPP in dichloromethane solution between 350 and 800 nm. The inset shows the Q-band region between 450 and 700 nm in detail. (b) UV-Vis spectrum of $Cu-TPP$ in dichloromethane solution between 300 and 700 nm, with an inset showing the Q region between 500 and 600 nm in detail.

Since in this thesis the SHG properties of the porphyrinates are studied in solid state, the electronic spectrum derived from the diffuse reflectance of metal porphyrinate powders was also analyzed (Fig. 2.2.4). For this purpose, an Agilent Cary 100 spectrophotometer equipped with an integrating sphere was used.



Figure 2.2.4 Sample holder of the Agilent Cary 100 spectrophotometer filled with zinc porphyrinate

Figure 2.2.5 shows the UV-Vis spectrum of the Cu-TPP obtained from its powders as an example, compared with the free base H_2TPP . The y-axis of the figure represents the magnitude $F(R)$. The spectrum was originally recorded as a percentage of reflectance, which is negative relative to the reference. $F(R)$ is directly proportional to the Kubelka-Munk function and is the inverse of $1 - \text{reflectance}$. This quantity is commonly reported for such measurements as it is easily comparable to absorbance data in solution.

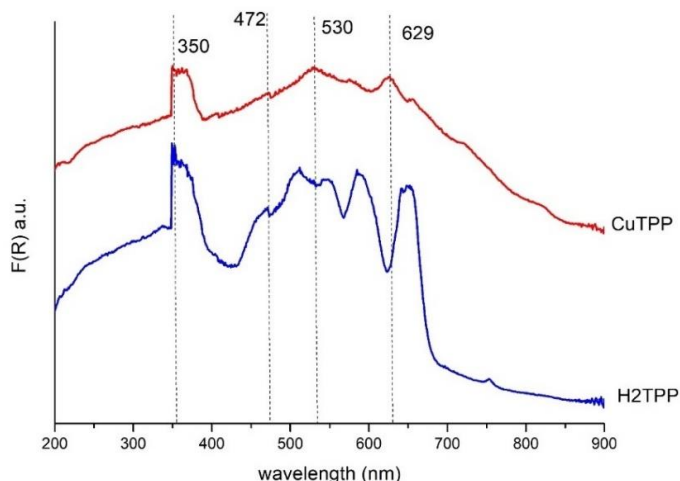


Figure 2.2.5 Comparison of the spectra of tetra-phenylporphyrin and copper tetra-phenylporphyrinate, both measured in the solid state

For the Cu-TPP complex compared with the free base H₂TPP, a simplification was also observed in the solid state spectrum, attributable to the increase in symmetry previously mentioned. Additionally, instead of a single very intense S band, we recorded two peaks, at 350 and 472 nm, as intense as the other bands. This splitting is generally attributed to the interaction between two or more molecules in the aggregate, leading to two or more excitonic transitions (electron transitions from the valence band to the conduction band upon interaction with sufficiently energetic photons) with high transition moments^{6,7,8}.

A useful technique we used to check the complexation and the purity of these materials in solid state is ATR-FTIR. The positions and assignments of the principal bands are reported in Tables 2.2.1, and Figs. 2.2.6 show the theoretical spectra compared to the experimental ones for Ni-TPP.

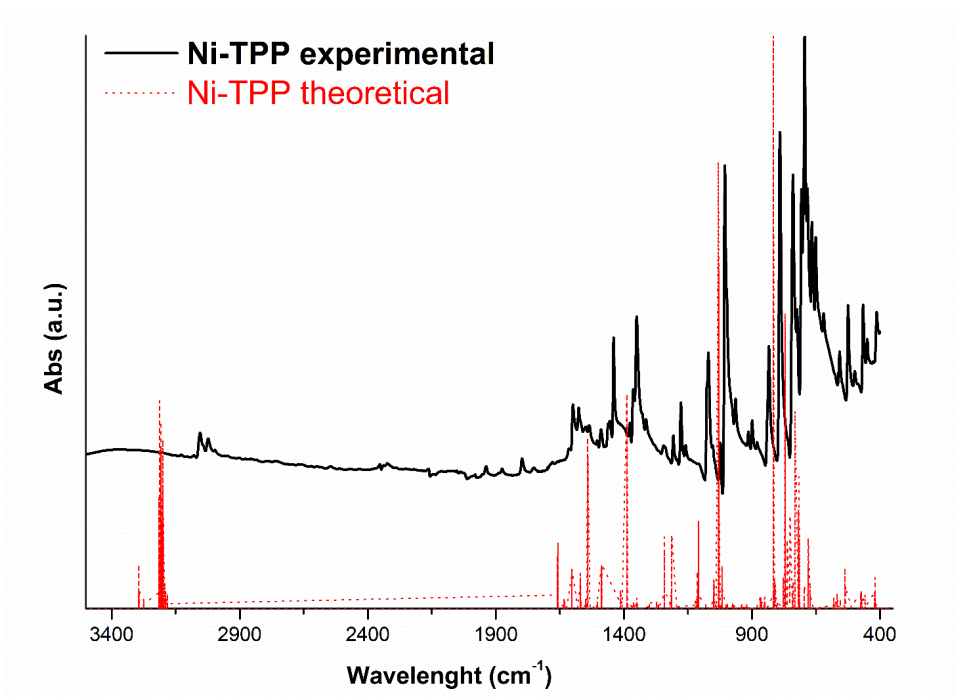


Figure 2.2.6 ATR-FTIR spectrum of Ni-TPP (black line) compared with theoretical data (red dotted line).

Table 2.2.1 Assignment of principal vibrational band, ATR-FTIR compared with B3LYP/6-31G(d), for Ni-TPP.

Ni-TPP		
ATR-FTIR (cm ⁻¹)	B3LYP/6-31G(d) (cm ⁻¹)	Assignment
413-466	418.65 – 474.87	<i>In-plane rotational motion of the pyrrole rings</i>
517-557	510.75 – 581.01	<i>Out-of-plane skeletal deformation of the phenyl groups</i>
650-695	634.8 – 653.20	<i>Expansion of the phenyl groups</i>
710 -725	714.90 – 742.60	<i>Wagging of the H atoms of the phenyl groups</i>
740 -834	751.87 – 817.08	<i>Wagging of H atoms on the phenyl groups and macrocycle, including twisting of the macrocycle</i>
1006	1016.90 – 1017.78	<i>In-plane bending deformation of the phenyl groups</i>
1077	1070.19 – 1070.80	<i>Rocking of the H atoms on the C atoms on the ring</i>
1350	1344.25 – 1350.96	<i>In-plane structural deformation of the pyrrole group</i>
1440	1412.73 - 1412.72	<i>Rocking of the H atoms on the phenyl rings and symmetric C-C-C bond stretching</i>
3027 - 3052	3181.79 – 3215.81	<i>C-H stretching of phenyl</i>

In Figure 2.2.7 are reported the ATR-FTIR spectra of H_2TNPP and $Co-TNPP$ between 2500 and 4200 cm^{-1} . The N-H bond stretching and bending frequencies of H_2TNPP are located at about 3300 cm^{-1} . When a metal ion (such as Co) is inserted into the porphyrin ring, the N-H bond vibration frequency of the free base porphyrins disappears and this constitutes a clear indicator of the formation of the metal porphyrin complex.

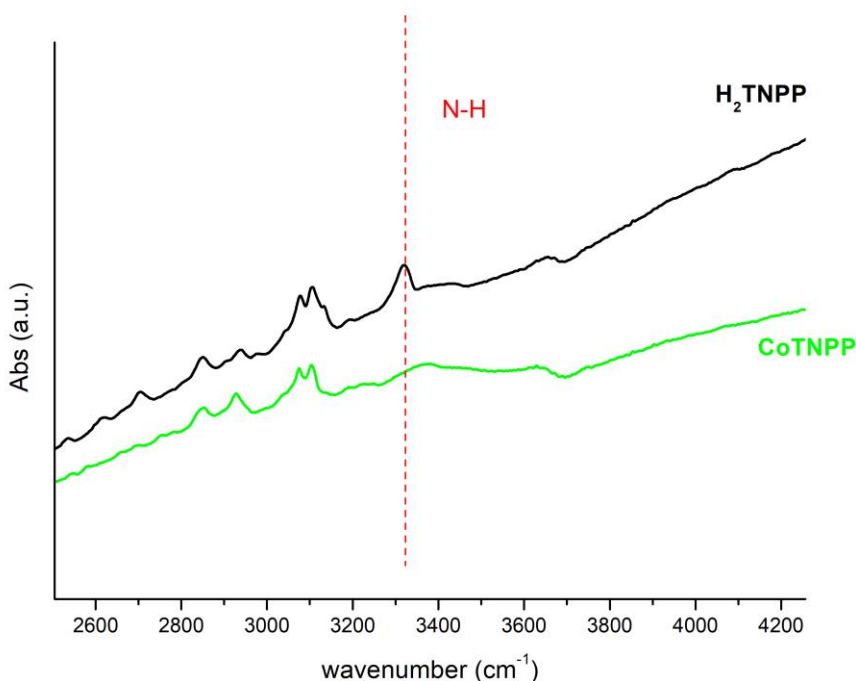


Figure 2.2.7 ATR-FTIR spectrum of the free base H_2TNPP (black line) compared with the complex $Co-TNPP$ (green line). The N-H bond vibration frequency at about 3300 cm^{-1} (red dotted line) disappears in the $Co-TNPP$ and this confirm the formation of the metal porphyrin complex.

In a transition metal complex, valence electrons can occupy the d orbitals of the central metal, and their distribution can lead to variable electronic configurations. These different configurations affect the complex's total spin. Variations in the spin multiplicity can influence the electromagnetic properties, making it crucial to determine the spin multiplicity of the crystalline solids in question. The spin multiplicity can be determined by measuring the magnetic susceptibility.

The magnetic susceptibility of porphyrinates was measured using a Johnson Matthey magnetic balance, employing the Evans method⁹. This balance (see fig 2.2.8) operates by keeping the sample stationary while the magnets move. A pair of magnets is positioned at the opposite ends of a beam, which maintains the system at equilibrium. The introduction of the sample between the poles of the two magnets causes a deviation of the beam, which is recorded by some phototransistors. A current pass through a coil mounted between the poles of a second pair of magnets, generating a force that restores the system's equilibrium. At equilibrium, the current in the coil is proportional to the force exerted by the sample and can be measured as a voltage drop.

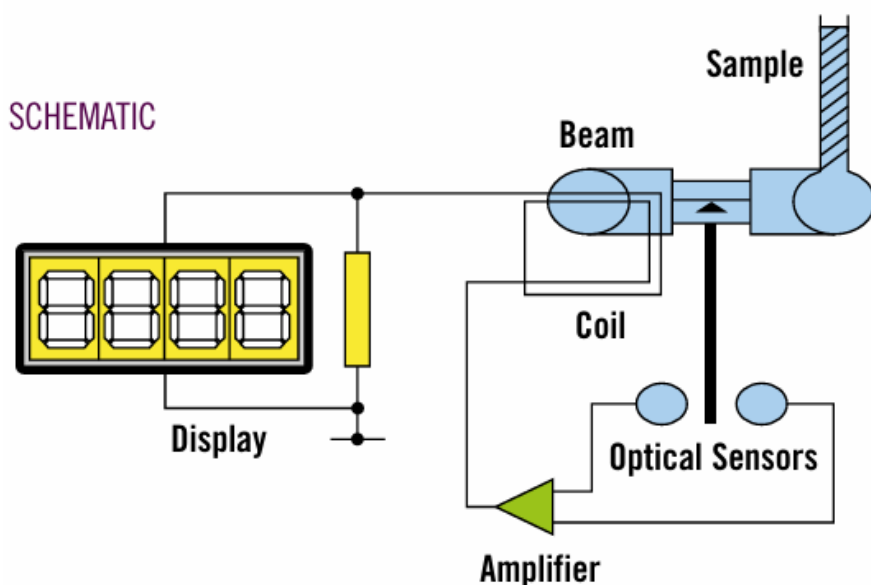


Figure 2.2.8 Operation diagram of the Johnson Matthey magnetic balance¹⁰

Equation 2.2.1 provides the general expression for susceptibility in units denominated *cgs*.

$$\chi_g = \frac{l}{m} (C * (R - R_0) + \chi_{vair} * A) \quad (\text{eq.2.2.1})$$

where:

C = constant of proportionality

R = reading obtained for tube plus sample

R_0 = empty tube reading

l = sample length (cm)

m = sample mass (g)

A = cross sectional area of the tube (cm²)

χ_{vair} = volume susceptibility of the displaced air

For powdered samples, such as those studied here, the correction term for the air susceptibility ($\chi_{vair} * A$) can be ignored. Regarding the value of the constant, $C=1/10^9$, so that:

$$\chi_g = \frac{l*(R-R_0)}{10^9*m} \quad (\text{eq. 2.2.2})$$

χ_g is negative for diamagnetic compounds and positive for paramagnetic compounds. Multiplying the value of χ_g by the molecular weight of the compound yields χ_m . For a diamagnetic compound, this value should be further multiplied by an appropriate correction factor to obtain χ_a .

At this point, it is possible to obtain the magnetic moment μ_{exp} :

$$(\mu_{\text{exp}})^2 = \frac{3*K*T*\chi_a}{N*B^2} \quad (\text{eq. 2.2.3})$$

Where:

K = Boltzmann's constant

T = absolute temperature

N = Avogadro's number

So that:

$$\mu_{\text{eff}} = 2.828 * \sqrt{T * \chi_a} \quad (\text{eq. 2.2.4 a})$$

The number of unpaired electrons, or spin multiplicity, can be directly determined from the magnetic moment using the following formula:

$$\mu_{\text{eff}} = \sqrt{n(n + 2)} \quad (\text{eq. 2.2.4 b})$$

Where n is the number of unpaired electrons.

2.3. Structural Characterization

The crystallization process requires the overcoming of an activation free energy that depends on the temperature, the solvent type, and the rate of the process. To obtain single crystals of metal porphyrinates, crystallizations were attempted under various temperature conditions (263.15K, 287.15K, 298.15K, 373.15K), various solvents (benzene, toluene, ethyl ether, benzaldehyde, dichloromethane, tetrahydrofuran, methanol, ethanol, n-butyl acetate, isobutyl acetate, dichloromethane, pyridine, dimethylformamide, acetic anhydride, dimethyl sulfoxide), and the kinetics of the process were monitored (control of the solvent evaporation). Sometimes, the solvent coordinates to the metal of the porphyrinate or is incorporated into the crystal structure, resulting in a solid with a composition different from pure porphyrinate and potentially different optical properties.

Crystal symmetry plays a crucial role in the understanding of chemical and physical properties of crystalline solids. X-ray diffraction on single crystals (XRD) is the main technique for the structural determination, providing comprehensive information about the unit cell, crystal symmetries, and atomic positions relative to the unit cell, from which bond distances, angles, and crystal packing can be derived. Since SHG properties are strongly correlated with the spatial symmetry of crystalline solids, the crystal structure determination with XRD is essential for the present project.

X-ray data collection was performed using the Atlas S2 Rigaku-Oxford Diffraction Gemini R-Ultra diffractometer, equipped with Cu-K α radiation (wavelength 1.5418 Å) and capable of operating at room or low temperature (100 K) for specific samples (Fig. 2.3.1). The acquired data were analyzed using the CrysAlisPro software package¹¹ for the integration, SHELXT¹² for resolution, SHELXL¹³ for refinement and Olex2¹⁴ for graphic representation. Although hydrogen atoms were found in the difference Fourier maps for each structure, they were calculated and refined with riding coordinates and fixed U_{iso} at 1.2 times of the U_{eq} of the connected C atoms.

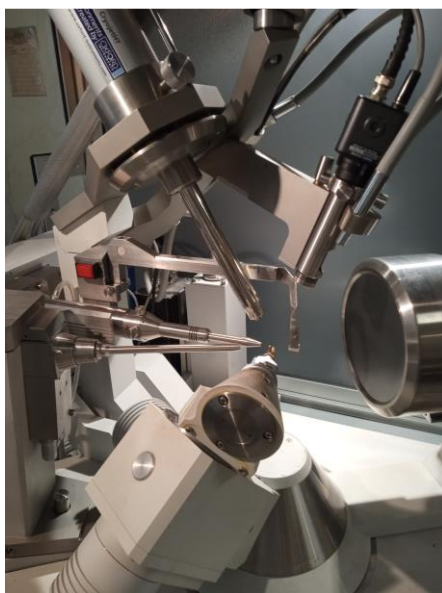


Figure 2.3.1 View of the central part of the diffractometer Atlas S2 Rigaku-Oxford Diffraction Gemini R-Ultra.

To identify the powders of the synthesized compounds and verify that they match the structure obtained from XRD, the X-ray powder diffraction (XRPD) technique was used. XRPD patterns can be considered as a "fingerprint" of the examined structure.

Given the small amount of synthesized sample for each compound, the XRPD patterns were acquired using the same Gemini diffractometer used for XRD data collection, since it allows to analyze very low quantities of sample. To collect the XRPD pattern with the Gemini diffractometer, each powder is mixed with paraffin oil and shaped into an agglomerate of approximately 0.45 mm in diameter, which is smaller than the X-ray beam diameter. The

agglomerate is then attached to a glass capillary, which is subsequently mounted on the goniometer head. Figure 2.3.2 shows a sample of powder mounted on the goniometer head, ready for analysis.

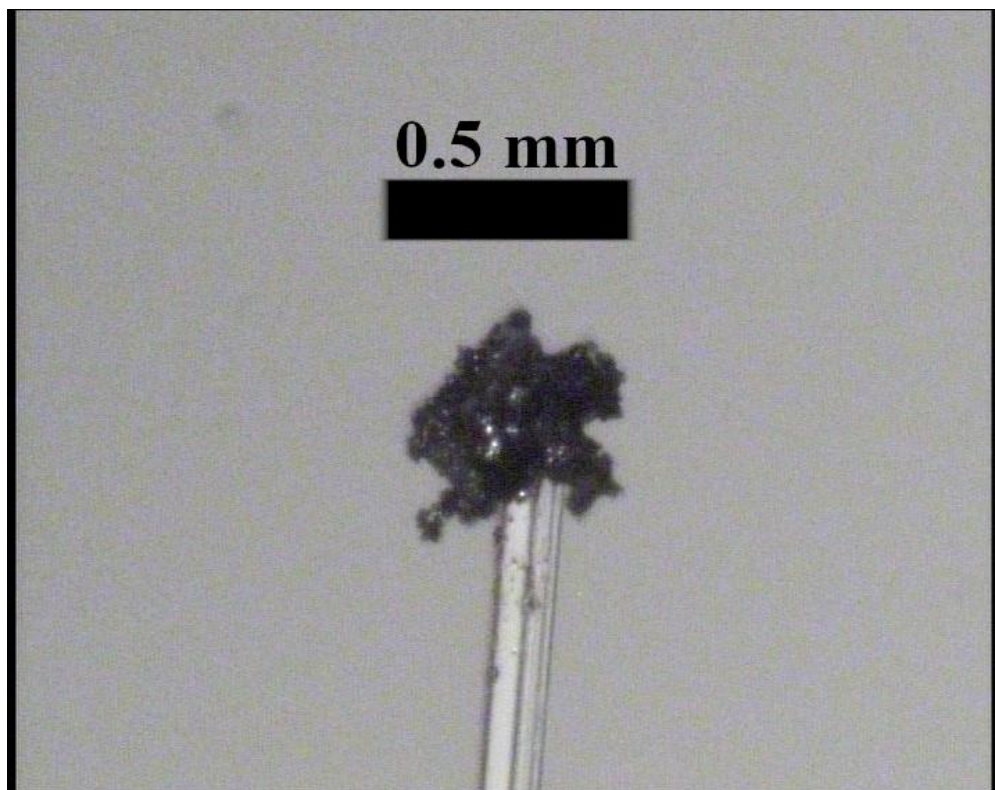


Figure 2.3.2 Sample of powder mounted on the goniometer head of the Atlas S2 Rigaku-Oxford Diffraction Gemini R-Ultra.

Figure 2.3.3 shows the powder patterns of two synthesized samples of zinc tetraphenylporphyrinate (black and green lines), compared to the powder pattern calculated from the XRD structure. While the black line pattern confirms the presence of the pure compound, the green line pattern shows additional peaks due to the presence of another crystalline compound.

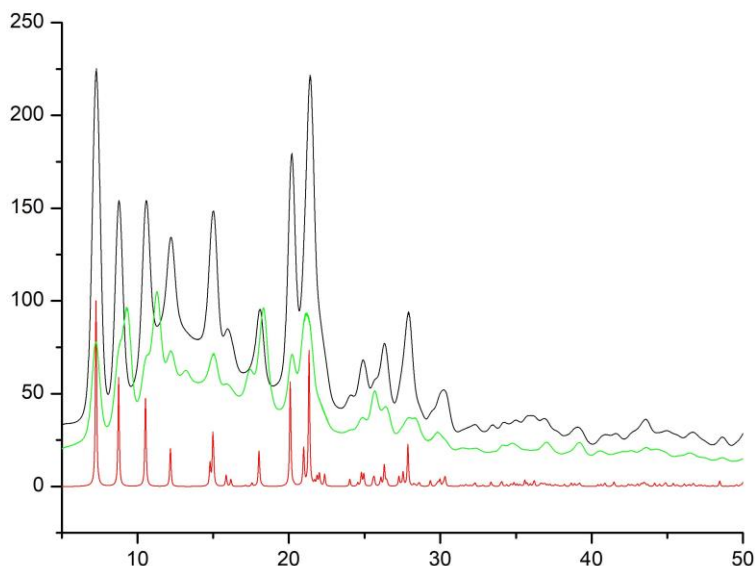


Figure 2.3.3 Powder pattern powder patterns of two synthesized samples of zinc tetraphenylporphyrinate (black and green lines), compared to the powder pattern calculated from the XRD structure (red line).

Since the Gemini diffractometer is equipped with an area detector, it collects the whole diffraction circles of the powder diffraction image, and the intensity of each diffraction peak of the powder pattern is calculated mediating the intensities of all point of the corresponding circle (Figure 2.3.4). This allows the collection of reproducible diffractograms also for poorly-ground powders, as well as powders characterized by preferred orientation, which turns out to be particularly important when it comes to porphyrinates whose powders are sometimes difficult to grind, due to agglomerates that may form during the process.

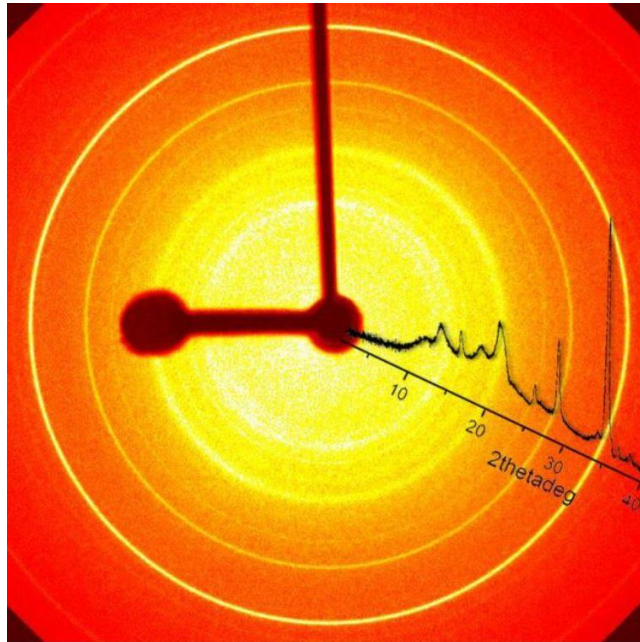


Figure 2.3.4 Diffraction image obtained with the Atlas S2 Rigaku-Oxford Diffraction Gemini R-Ultra. The various families of planes will simultaneously produce different diffraction cones and the intersection of these diffraction cones with a flat photographic plate results in a series of concentric diffraction rings.

2.4. Non Linear Optical Characterization: The Kurtz and Perry method

The theoretical foundation for second harmonic generation was developed in the 1960s and 1970s, when theoretical physicists began exploring the effects of optical nonlinearities in materials.

A key development is attributed to Robert W. Boyd, an American theoretical physicist. He provided a theoretical framework for understanding how materials can respond nonlinearly to intense electric fields of light. This included the idea that the material's polarization, which is proportional to the electric field of the light, could contain nonlinear components. In particular, he predicted the possibility of generating frequency components different from the frequency of the incident light, such as second harmonic generation¹⁵.

In 1961, the experimental discovery of the predicted second harmonic generation was made by Peter Franken and his team, who published a paper titled "Generation of Optical Harmonics" in the journal "Physical Review Letters".¹⁶ The experiment hinged on the use of a ruby laser emitting light in the visible region with a wavelength of 694.3 nanometers. When passing through a quartz crystal, a nonlinear material, the laser beam generated a radiation in ultraviolet region, i.e. with a frequency twice as high as that of the incident light. In this way, the second harmonic was observed and the theory confirmed.

Franken and colleagues' paper marked a turning point in the understanding and application of nonlinear optical properties, paving the way for further research and development. Second harmonic generation became a topic of great interest, leading to more experimental and theoretical studies in the 1980s.

Over the course of that decade, research on second harmonic generation played a central role in the development of advanced nonlinear microscopy techniques, as the ability to obtain high-resolution images without damaging biological samples made this technique immediately attractive to the scientific community. Since then, as described in Section 1.2, second harmonic generation has played a crucial role in the development of advanced imaging tools, allowing us to gain deeper insight into the complexity of microscopic structures.

The Kurtz and Perry method is a technique used to experimentally measure the NLO properties of powdered materials¹⁷. This technique was proposed in 1968, since previous methods required a single crystal with excellent optical properties for the materials under analysis. This technique served as a quick and simple method for evaluating NLO properties in powders and is still recognized today as the "standard" method to measure the SHG.



Figure 2.4.1 Apparatus used for the study of the second-harmonic generations in powders.

The setup used in this work is shown in Figure 2.4.1. This apparatus consists of a laser whose beam is focused in an area of approximately 0.2 mm of the powder under examination. The light emitted by the sample passes through a series of filters that remove the wavelengths other than the second harmonic. The second harmonic is detected by a photomultiplier, which converts the optical signal into an electrical one.

Before analyzing a sample, a reference system is measured, which in our case is sucrose. To maximize the amount of SHG radiation reaching the detector, an elliptical mirror is placed between the laser and the sample.

The laser used is a pulsed Nd:YAG laser (10 Hz) with a fundamental wavelength of 1.064 μm , shifted to 1.907 μm through stimulated Raman scattering in a high-pressure hydrogen cell.

The powder under analysis is firstly ground in an agate mortar and then sealed in a capillary tube, which is finally exposed to the laser beam.

The sample's response in terms of second harmonic emission is measured against the sucrose standard.

All porphyrin samples reported in this thesis were ground in an agate mortar for the same duration to achieve similarly sized solid particles, since particle size can severely influence the intensity of the second harmonic emission.

2.5. Theoretical background and computational methods for the calculation of Non Linear Optical properties

All electromagnetic phenomena are governed by Maxwell's equations:

$$\nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t}, \quad (\text{eq. 2.5.1})$$

$$\nabla \times \mathbf{B} = \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t} + \frac{4\pi}{c} \mathbf{J}, \quad (\text{eq. 2.5.2})$$

$$\nabla \cdot \mathbf{E} = 4\pi \rho, \quad (\text{eq. 2.5.3})$$

$$\nabla \cdot \mathbf{B} = 0, \quad (\text{eq. 2.5.4})$$

where $\mathbf{E}$ is the electric field, $\mathbf{B}$ is the magnetic field, and c is the speed of electromagnetic radiation in a vacuum. These equations also include the terms $\mathbf{J}$ and ρ , which are the current density and charge density, respectively. They are related by the charge conservation law:

$$\nabla \cdot \mathbf{J} + \frac{\partial \rho}{\partial t} = 0, \quad (\text{eq.2.5.5})$$

They can be expressed through the following multipole expansions:

$$\mathbf{J} = \mathbf{J}_0 + \frac{\partial \mathbf{P}}{\partial t} + c \nabla \times \mathbf{M} + \frac{\partial}{\partial t} (\nabla \mathbf{Q}) + \dots, \quad (\text{eq. 2.5.6})$$

$$\rho = \rho_0 - \nabla \cdot \mathbf{P} - \nabla \cdot (\nabla \mathbf{Q}) + \dots, \quad (\text{eq. 2.5.7})$$

where $\mathbf{P}$, $\mathbf{M}$, and $\mathbf{Q}$ respectively represent the electric polarization, the magnetization, and quadrupole moment. The equation for current density can be modified as follows:

$$\mathbf{J} = \mathbf{J}_{DC} + \frac{\partial \mathbf{P}^*}{\partial t}, \quad (\text{eq. 2.5.8})$$

where J_{DC} is the displacement current required to maintain consistency with the charge continuity equation, and $\mathbf{P}^*$ is the nonlocal polarization, which, for the purpose of this discussion, can be approximated by $\mathbf{P}$, i.e. the local electric polarization. Substituting into Maxwell's equations, we obtain:

$$\nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t}, \quad (\text{eq. 2.5.9})$$

$$\nabla \times \mathbf{B} = \frac{1}{c} \frac{\partial}{\partial t} (\mathbf{E} + 4\pi \mathbf{P}) + \frac{4\pi}{c} \mathbf{J}_{\text{dc}} \quad (\text{eq. 2.5.10})$$

$$\nabla(\mathbf{E} + 4\pi \mathbf{P}) = 0 \quad (\text{eq. 2.5.11})$$

$$\nabla \mathbf{B} = 0 \quad (\text{eq. 2.5.12})$$

where $\mathbf{P}$ is the only time-dependent term. In general, $\mathbf{P}$ is a function of $\mathbf{E}$, and this function fully describes the material's response to an electromagnetic field (constitutive equation).

If it were possible to simply write this equation with appropriate boundary conditions and solve it, all optical phenomena would be predictable and known. Unfortunately, this is rarely feasible, and approximations are often necessary.

In the case of a linear response, the polarization can be expressed as follows:

$$\mathbf{P}(\mathbf{r}, t) = \int_{-\infty}^{\infty} \chi^{(1)}(\mathbf{r} - \mathbf{r}', t - t') \mathbf{E}(\mathbf{r}', t') d\mathbf{r}' dt', \quad (\text{eq. 2.5.13})$$

Where $\chi^{(1)}$ is the electric susceptibility, a quantity that describes the material's response to the application of an electric field. Specifically, this is the first-order or linear susceptibility.

If $\mathbf{E}$ is a plane, monochromatic wave:

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}(\mathbf{k}, \omega) \exp(i(\mathbf{k}\mathbf{r} - \omega t)), \quad (\text{eq. 2.5.14})$$

Therefore, the Fourier transform of Equation 2.4.13 leads to the relationship:

$$\mathbf{P}(\mathbf{r}, t) = \mathbf{P}(\mathbf{k}, \omega) = \chi^{(1)}(\mathbf{k}, \omega) \mathbf{E}(\mathbf{k}, \omega) \quad (\text{eq. 2.5.15})$$

$$\chi^{(1)}(\mathbf{k}, \omega) = \int_{-\infty}^{\infty} \chi^{(1)}(\mathbf{r}, t) \exp(-i\mathbf{k}\mathbf{r} + i\omega t) d\mathbf{r} dt \quad (\text{eq. 2.5.16})$$

Within the electric dipole approximation, applicable when the dimensions of the dipole are much smaller than the distance between the charges, the electric susceptibility does not depend on the specific position within the field, i.e., $\chi^{(1)}$ does not depend on $\mathbf{r}$, and consequently, neither does it depend on $\mathbf{k}$. The same applies to the dielectric constant ε , which is related to $\chi^{(1)}$ by the equation:

$$\varepsilon(\mathbf{k}, \omega) = 1 + 4\pi\chi^{(1)}(\mathbf{k}, \omega), \quad (\text{eq. 2.5.17})$$

Moving on to the nonlinear case, if the electric field $\mathbf{E}$ is sufficiently weak, the polarization can be expressed as a function of $\mathbf{E}$ through a power series expansion:

$$\begin{aligned} \mathbf{P}(\mathbf{r}, t) = & \int_{-\infty}^{\infty} \chi^{(1)}(\mathbf{r} - \mathbf{r}', t - t') \mathbf{E}(\mathbf{r}, t') d\mathbf{r}' dt + \int_{-\infty}^{\infty} \chi^{(2)}(\mathbf{r} - \\ & \mathbf{r}_1, t - t_1; \mathbf{r} - \mathbf{r}_2, t - t_2) \mathbf{E}(\mathbf{r}_1, t_1) \times \mathbf{E}(\mathbf{r}_2, t_2) d\mathbf{r}_1 dt_1 d\mathbf{r}_2 dt_2 + \\ & \dots, \end{aligned} \quad (\text{eq. 2.5.18})$$

where $\chi^{(2)}$ is the second-order susceptibility, or nonlinear susceptibility. If $\mathbf{E}$ is a set of plane, monochromatic waves:

$$\mathbf{E}(\mathbf{r}, t) = \sum_i \mathbf{E}(\mathbf{k}_i, \omega), \quad (\text{eq. 2.5.19})$$

The equation 2.58 can therefore be transformed using the Fourier transform:

$$\mathbf{P}(\mathbf{r}, t) = \mathbf{P}^{(1)}(\mathbf{k}, \omega) + \mathbf{P}^{(2)}(\mathbf{k}, \omega) + \cdots, \quad (\text{eq. 2.5.20})$$

Where:

$$\mathbf{P}^{(1)}(\mathbf{k}, \omega) = \chi^{(1)}(\mathbf{k}, \omega) \mathbf{E}(\mathbf{k}, \omega), \quad (\text{eq. 2.5.21})$$

and:

$$\mathbf{P}^{(2)}(\mathbf{k}, \omega) = \chi^{(2)}(\mathbf{k} = \mathbf{k}_i + \mathbf{k}_j, \omega = \omega_i + \omega_j) \mathbf{E}(\mathbf{k}_i, \omega_i) \mathbf{E}(\mathbf{k}_j, \omega_j), \quad (\text{eq. 2.5.22})$$

so that:

$$\begin{aligned} \chi^{(2)}(\mathbf{k} = \mathbf{k}_1 + \mathbf{k}_2, \omega = \omega_1 + \omega_2) = \\ \int_{-\infty}^{\infty} \chi^{(2)}(\mathbf{r} - \mathbf{r}_1, t - t_1, \mathbf{r} - \mathbf{r}_2, t - t_2) \times \exp -i(\mathbf{k}_1(\mathbf{r} - \mathbf{r}_1) - \\ \omega_1(t - t_1) + \mathbf{k}_2(\mathbf{r} - \mathbf{r}_2) - \omega_2(t - t_2)) d\mathbf{r}_1 dt_1 d\mathbf{r}_2 dt_2, \end{aligned} \quad (\text{eq. 2.5.23})$$

Again, within the electric dipole approximation, the susceptibility does not depend on the specific position of the charges within the field, i.e., $\chi^{(2)}$ does not depend on $\mathbf{r}$, and, consequently, neither does it depend on $\mathbf{k}$.

Both linear and nonlinear susceptibilities characterize the optical properties of a medium. If the susceptibilities of order n are known for a given medium, then the nonlinear optical effects of order n in the medium can be predicted from Maxwell's equations. Susceptibilities are related to the microscopic structure of the medium and can only be accurately evaluated through quantum-mechanical calculations.¹⁵⁸

Overall, nonlinear optics deals with interactions between an electric field and matter, which (matter) generates a new electric field with different frequency, phase, or other physical properties.

From the equations shown for the first- and second-order susceptibilities ($\chi^{(1)}$ and $\chi^{(2)}$) were defined (eq 2.4.16 and 2.4.23), it clearly follows that susceptibility is the constant that associates an electric field ($\mathbf{E}$) to the response of a medium in terms of polarization ($\mathbf{P}$), i.e. the movement induced in the electric charges of the medium by the interaction with the electric field.

In general, one can write:

$$\mathbf{P} = \varepsilon_0 \chi \mathbf{E} \quad (\text{eq. 2.5.24})$$

Where ε_0 is the dielectric constant in vacuum, χ is the susceptibility tensor and $\mathbf{E}$ an applied electric field. Using the perturbation theory, the above equation can be expressed as a power series such that:

$$P_i = \varepsilon_0 \sum_j \chi_{ij}^{(1)} E_j + \varepsilon_0 \sum_{jk} \chi_{ijk}^{(2)} E_j E_k + \dots \quad (\text{eq. 2.5.25})$$

The terms $\chi_{ijk}^{(2)}$, the coefficients of the second-order susceptibility, are of particular interest for the project since, for a material to exhibit second harmonic generation and thus be used in microscopy based on this emission, the tensor $\chi^{(2)}$ must not equal zero.

The SHG tensor possesses in principle 27 independent components. However, this number can be reduced to 18 due to physical considerations, such as the symmetry of the electric field: $E_K E_J = E_J E_K$. To simplify the notation, the Voigt notation can be adopted for the two last indices, allowing the SHG tensor to be expressed as a second-order matrix $d_{i\alpha}$ with $i = 1, 2, 3$ and $\alpha = 1, 2, 3, 4, 5, 6$. By assuming a dispersionless medium, the number of independent components can then be brought down to 10. Additionally, the crystal symmetry may impose further constraints. In particular, for centrosymmetric compounds, no second-order response is expected, as all components of the SHG tensor vanish. Therefore, second-order nonlinear optical phenomena are, in theory, only possible in non-centrosymmetric materials¹⁸.

To calculate the optical susceptibility of a material using a computational approach, another optical property of the system, called hyperpolarizability

(β) , must be determined. To understand what this involves, consider the dipole moment vector:

$$\mu_i = - \left. \frac{\partial W(\mathbf{E})}{\partial (E_i)} \right|_{E=0} \quad (\text{eq. 2.5.26})$$

where $i=x,y,z$. Since the electric field is assumed to be static, $E=0$, the hyperpolarizability we will henceforth be referred to as the static hyperpolarizability.

When a molecule is subjected to an electric field of strength E_i , its dipole moment can be expressed as a Taylor expansion:

$$\mu_i = \mu_i^0 + \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \cdots \quad (\text{eq. 2.5.27})$$

Where μ , α , and β represent the dipole moment of the unperturbed molecule, the linear polarizability, and the hyperpolarizability, respectively. Using computational chemistry programs, it is possible to calculate these properties as derivatives (with sign changes) of the dipole moment with respect to the applied electric field:

$$\beta_{ijk} = - \left. \frac{\partial^3 W(\mathbf{E})}{\partial E_i \partial E_j \partial E_k} \right|_{E=0} \quad (\text{eq. 2.5.28})$$

Static hyperpolarizability is anisotropic, meaning it takes on different values along different directions in a crystalline solid. The total intrinsic hyperpolarizability is defined as follows:

$$\beta_{TOT} = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2} \quad (\text{eq. 2.5.29})$$

where

$$\beta_j = \frac{1}{3} \sum_{i=1}^3 (\beta_{jii} + \beta_{iji} + \beta_{iij}) \quad (\text{eq. 2.5.30})$$

where $i,j=x,y,z$.

The hyperpolarizability is indeed described by a tensor of dimension $3 \times 3 \times 3$, and in the case of static (frequency-independent) hyperpolarizability, the three indices are interchangeable, reducing the number of independent components from 27 to 10. Specifically, we have the following equalities:

- β_{xxx}
- $\beta_{xxy} = \beta_{yyx} = \beta_{xyx}$
- $\beta_{yxy} = \beta_{yyx} = \beta_{xyy}$
- β_{yyy}
- $\beta_{xxz} = \beta_{xzx} = \beta_{zxx}$
- β_{yxz}
- $\beta_{yyz} = \beta_{yzy} = \beta_{zyy}$
- $\beta_{zzx} = \beta_{zzx} = \beta_{xzz}$
- $\beta_{zyz} = \beta_{zzy} = \beta_{yzz}$
- β_{zzz}

The components are all independent and non-zero when a crystalline system has triclinic symmetry; however, in cases of higher symmetry, the number of components is further reduced. In fact, each medium exhibits a certain degree of symmetry and belongs to a specific spatial group, with a group of symmetry operator $\mathbf{S}$ under which the medium is invariant and, therefore, $\chi^{(2)}$ (and so β) remains unchanged. Another immediate consequence of this is that $\chi^{(2)}=0$ with the inversion symmetry.

From the value of the total intrinsic hyperpolarizability, it is possible to determine the optical susceptibility $\chi^{(2)}$ of the second order. To do this, consider again equations 2.4.16 and 2.4.23, which relate the susceptibility $\chi^{(n)}$, the electric field $\mathbf{E}$, and the polarization $\mathbf{P}$. To account for nonlinear effects, it is possible to write a series expansion with respect to the electric field:

$$\mathbf{P} = \chi^{(1)} \mathbf{E} + \chi^{(2)} \mathbf{E} + \dots \quad (\text{eq. 2.5.31})$$

Taking the vectorial nature of the electric field into account:

$$P_I = \sum_J \chi_{IJ}^{(1)} E_J + \frac{1}{2} \sum_{J,K} \chi_{IJK}^{(2)} E_J E_K + \dots \quad (\text{eq. 2.5.32})$$

Where the indices I, J, K run along the macroscopic axes of the material. In the context of a system composed of molecules, where each molecule contributes to the susceptibility tensor, the macroscopic susceptibilities $\chi^{(1)}$ and $\chi^{(2)}$ are related to the corresponding microscopic quantities α and β by a field factor F and the number of particles per cubic meter N . These relationships are expressed by the following equations:

$$\chi_{IJ}^{(1)} = N \sum_{ij} f_I \langle \cos \theta_{Ii} \rangle f_J \langle \cos \theta_{Ji} \rangle \alpha_{ij} \quad (\text{eq. 2.5.33})$$

$$\chi_{IJK}^{(2)} = N \sum_{ijk} f_I \langle \cos \theta_{Ii} \rangle f_J \langle \cos \theta_{Ji} \rangle f_K \langle \cos \theta_{Kk} \rangle \beta_{ij} \quad (\text{eq 2.5.34})$$

The indices i, k, j refer to the molecular axes, and the angle $\theta_{I,i}$ is the angle between the macroscopic axis I and the microscopic axis i . Regarding the field factor, it is essentially a correction for the difference between the applied field that the free molecule would experience and the electric field within the material. Considering the average quantity defined as the total intrinsic hyperpolarizability, we can write:

$$\chi^{(2)} = \beta_{TOT} N F \quad (\text{eq. 2.5.35})$$

The value of the field factor F depends on the crystal symmetry and is related to the refractive index, generally varying between 1 and 2. For the purposes of this thesis, whose computational investigation methodologies have been standardized by several previous studies,²²⁻²⁹ it was decided to set the field factor F in equation 2.4.33 equal to 1, as the focus of this thesis is to evaluate the trend of the ratio $\chi^{(2)} / \chi_{\text{sucrose}}^{(2)}$ related to the experimental SHG data.¹⁹ The formula thus simplifies to:

$$\chi^{(2)} = \beta_{TOT} N \quad (\text{eq. 2.5.36})$$

Where $N = n_{\text{AVOGADRO}}/V_{\text{molar}}$. The molar volume, like the hyperpolarizability, is calculated using an ab initio approach^{20,21}.

Among the various methodologies available to theoretical chemists, the density functional theory (DFT) method has been selected. This choice was primarily influenced by the results obtained by other research groups, who were the first to investigate the nonlinear optical properties of organic and metal-organic systems.^{20,21} Moreover, this choice is also supported by the results of an extensive study conducted by our research group over the past few years^{22,23,24,25,26,27}.

The focus of this study was on the NLO behavior of various metal-organic compounds based on sugars, particularly solid crystalline materials with Metal-Organic Framework (MOF) structures. These MOFs represent an ideal category of compounds for designing functional materials with physical properties dependent on crystal symmetry, including NLO properties.

The study included both experimental measurements and parallel computational calculations. Therefore, all methods employed were standardized based on comparisons between experimental and theoretical results, in terms of both structural parameters and NLO responses."

The computational approaches chosen for this thesis are the Density Functional Theory (DFT) and the Time Dependent Density Functional Theory (TD DFT).

DFT is based on the Hohenberg–Kohn theorems, which state that the electron density of a quantum system completely determines the properties of the system itself.

The DFT approach has proven a reliable tool for determining the equilibrium geometries of metal-organic compounds and for calculating NLO responses. This method relies on the description of the electronic density (ρ), which is experimentally measurable, and does not require the computation of complex wavefunctions that ab initio methods hinge upon. Instead, it uses mathematical functionals related to system properties, offering an excellent balance between accuracy and computational efficiency.

The choice to use DFT is also based on its computational speed, which falls between semi-empirical calculations and ab initio methods. Finally, DFT

requires minimal preliminary assumptions, such as the presence of nuclei and electrons with specific masses and charges, which makes it particularly flexible.

In TD DFT, an electronic density that varies over time is used to describe the system. The method maps an interacting many-body system onto an equivalent non-interacting system. To do so, a Kohn-Sham potential must be determined, reproducing the time-dependent electron density of the interacting system. The non-interacting system is governed by the time-dependent Kohn-Sham equation:

$$i\hbar \frac{\partial}{\partial t} \psi_i(\mathbf{r}, t) = \left[\frac{-\hbar^2}{2m} \nabla^2 + v_{eff}(\mathbf{r}, t) \right] \psi_i(\mathbf{r}, t) \quad (\text{eq. 2.5.38})$$

where $v_{eff}(\mathbf{r}, t)$ is the effective potential, including external, Hartree, and exchange-correlation contributions. The exchange-correlation potential depends on the time-dependent electron density and, in principle, its temporal history.

TD DFT is particularly useful for calculating electronic excitation energies. By using linear response theory, the excitation energies can be obtained by solving an eigenvalue problem derived from the Casida²⁸ equations, which describe the coupled electronic transitions in the system.

In the context of the DFT study of the NLO properties of organometallic complexes, selecting the appropriate density functional is crucial for obtaining accurate and efficient results. Among the many functionals available, the B3LYP functional has been chosen for this study^{29,30} for a variety of reasons.

Firstly, previous studies³¹ have shown that the B3LYP functional provides reliable estimates of the NLO properties of organometallic complexes while maintaining an acceptable computational burden. Its efficiency is particularly advantageous when analyzing large structures that serve as models for experimentally relevant complexes^{3,32}.

Calculations performed with the B3LYP functional have shown good agreement with the results obtained using more complex and computationally demanding theoretical levels, such as SAOP, GRACLB, and BLYP, which were compared in a previous study⁶, or CAM-B3LYP, taken into consideration by our group.

In conclusion, the choice of the B3LYP functional has proven a good compromise²²⁻²⁹ between accuracy and computational effort for calculating the NLO properties studied in this thesis.

Similar considerations apply to the basis set used, 6-31G(d)³³, which was evaluated against more expensive alternatives. For instance, larger basis sets such as 6-311G(d), 6-31G(d,p), and aug-cc-pVTZ, were tested, along with GRIM2 and GRIM3, which were considered primarily to account for London dispersion forces. However, not only did these not yield better results, but they also moved the geometric data further from the experimentally obtained values. Therefore, after carefully considering both accuracy and computational costs, we opted for the Pople basis set used in our previous work.²¹⁻²⁶

This basis set was used in conjunction with the LANL2DZ³⁴ basis set and associated pseudopotential for electron-rich atoms such as Co, Cu, Ni, and Zn. The use of pseudopotentials is common in computational chemistry, especially in DFT calculations. Pseudopotentials simplify computations by removing highly localized electrons in the inner atomic layers, thereby reducing the computational load. This approach allows to focus on valence electrons, which are primarily involved in chemical interactions and properties. The use of pseudopotentials is well-established in computational chemistry, and the selected one has yielded good results in previous studies²¹⁻²⁶.

The computational study was conducted using the Gaussian16 program.³⁵ This program is suitable for studying molecular clusters, which were selected based on their crystal structure to be representative of the material in its nanoparticle form. The data obtained in this way not only strike a reasonable balance between accuracy and computational demands compared to more intensive periodic simulations, but also account for the finite size of the crystals. Previous studies²²⁻²⁹ has highlighted how this method provides results comparable to the experimental values of second-harmonic emission intensity measured from powders using the Kurtz and Perry method.

The first step in calculating properties such as dipole moment, polarizability, and hyperpolarizability, is to determine the equilibrium geometry. Given the structural geometry identified experimentally through single-crystal X-ray diffraction, as described in section 2.3, the corresponding low-energy configuration can be determined using Gaussian16. This geometry optimization was carried out using gradient-based techniques without symmetry constraints. Each optimized structure was then characterized as an energy minimum by calculating its analytical frequencies.

As mentioned earlier, for the theoretical study of nanoparticles using Gaussian16, a preliminary choice of the molecular cluster is required. For a

molecular crystal based on metal porphyrin, this involves a structural fragment containing more than one porphyrin ring. Clusters were obtained using graphics programs such as Moldraw and Olex2 (Fig.2.5.1).

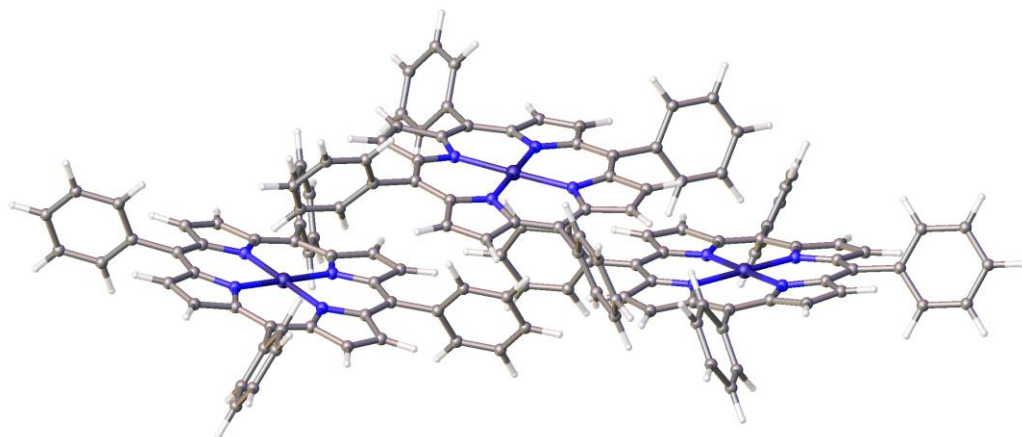


Figure 2.5.1 Molecular Cluster of Cobalt Tetraphenylporphyrin Containing Three Tetraphenylporphyrin Molecules.

The stationary points obtained were characterized as energy minima through vibrational frequency calculations. Finally, it was verified that the computational data at the considered theory level best reproduced the X-ray diffraction structural data (which will be analyzed on a case-by-case basis in Chapter 3). In conjunction with the vibrational frequency calculations, the program also calculated the intrinsic properties of interest discussed in the previous Section:

- **Dipole moment**
- **Polarizability**
- **Hyperpolarizability**

As defined in the dedicated section, hyperpolarizability is a property related to second harmonic emission, and specifically, *intrinsic total*

hyperpolarizability means we are considering the average of the tensor components provided as output by the Gaussian16 program, according to Equations 2.4.27 and 2.4.28. From the hyperpolarizability, it is possible to derive the second-order optical susceptibility coefficient, as defined in Equation 2.4.34. As mentioned in the previous Section, this value is of particular interest in that a second-order optical susceptibility coefficient different from zero is the sine qua non of second harmonic emission.

In addition to the calculation of hyperpolarizability, equation 2.4.34 requires the calculation of the molar volume. To do so, molar volumes were also computed using Gaussian16, specifically employing Monte Carlo numerical integration methods. As such methods entail a high degree of error, a strict convergence in the SCF procedure and a higher point density for more accurate integration were used to calculate the molar volume more quantitatively. For each nanoparticle, ten different volume calculations were averaged over geometries optimized at the B3LYP theory level with the options scf=tight, volume=tight, and iop(6/45=500,6/46=1).

At this point, it is appropriate to analyze the units of measurement used. Molar volumes provided by the program in $\text{bohr}^3\text{mol}^{-1}$ can be converted to $\text{m}^3\text{mol}^{-1}$ using the conversion factor 0.089239×10^{-6} . The tensor components of hyperpolarizability are computed both in atomic units (a.u.) and in $10^{-30} \text{ cm}^5\text{esu}^{-1}$. The value expressed in atomic units is then multiplied by the conversion factor 3.6213×10^{-42} to be transformed into m^4V^{-1} . By including these converted units in Equation 2.4.34, we obtain the second-order susceptibility coefficient expressed in $\text{m}^{-12}\text{V}^{-1}$, i.e., pmV^{-1} .

$$\chi^{(2)} = \beta_{TOT}N = \beta_{TOT} \frac{n_{AVOGADRO}}{V_{molar}} = \text{m}^4\text{V}^{-1} \frac{\text{mol}^{-1}}{\text{m}^3\text{mol}^{-1}} = \text{m}^{-12}\text{V}^{-1}$$

(eq. 2.5.39)

As previously stated, in addition to the absolute value of the second-order susceptibility coefficient, we also considered its relative value, $\chi^{(2)} / \chi_{\text{sucrose}}^{(2)}$. For this reason, concurrently, the computational work performed on the clusters of the compounds under investigation was also carried out on a suitably sized sucrose cluster²²⁻²⁹.

References

- 1** Gouterman, M. Study of the effects of substitution on the absorption spectra of porphin. *The Journal of Chemical Physics* 1959, 30 (5), 1139-1161. DOI: 10.1063/1.1730148
- 2** Zhang, A.; Kwan, L.; Stillman, M. J. The spectroscopic impact of interactions with the four Gouterman orbitals from peripheral decoration of porphyrins with simple electron withdrawing and donating groups. *Organic & Biomolecular Chemistry* 2017, 15 (43), 9081-9094. DOI:10.1039/C7OB01960B
- 3** Giovannetti, R., The use of spectrophotometry UV-Vis for the study of porphyrins. In *Macro to nano spectroscopy*, Uddin, J., Ed. InTech: 2012; pp 87-108.
- 4** Horváth, O.; Huszánk, R.; Valicsek, Z.; Lendvay, G. Photophysics and photochemistry of kinetically labile, water-soluble porphyrin complexes. *Coord. Chem. Rev.* 2006, 250 (13), 1792-1803. DOI: 10.1016/j.ccr.2006.02.014
- 5** Goldoni, A. Porphyrins: fascinating molecules with biological significance. *ELETTRA highlights* 2002, 2001, 64-65.
- 6** Davydov, A. S., *Theory of molecular excitons*. Springer: New York, NY, 1971; p 313.
- 7** El-Nahass, M. M.; Zeyada, H. M.; Aziz, M. S.; Makhoulf, M. M. Optical absorption of tetraphenylporphyrin thin films in UV-vis-NIR region. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 2005, 61 (13), 3026-3031. DOI: 10.1016/j.saa.2004.11.022
- 8** McRae, E. G.; Kasha, M. Enhancement of phosphorescence ability upon aggregation of dye molecules. *The Journal of Chemical Physics* 1958, 28 (4), 721-722. DOI: 10.1063/1.1744225
- 9** MAGNETIC SUSCEPTIBILITY BALANCE INSTRUCTION MANUAL MSB MK1, JOHNSON MATTEY
- 10** https://faculty.uca.edu/patrickd/chem3150/MSB1_Brochure.pdf
- 11** CrysAlisPro (2014). Agilent technologies, version 1.171.37.31 (release 14-01-2014 CrysAlis171. NET, compiled Jan 14 2014,18:38:05.
- 12** Sheldrick, G. M. (2015). SHELXT—Integrated space-group and crystal-structure determination. *Acta Crystallographica Section A: Foundations and Advances*, 71(1), 3-8.

-
- 13** Sheldrick, G. M. (2015). Crystal structure refinement with SHELXL. *Acta Crystallographica Section C: Structural Chemistry*, 71(1), 3-8.
- 14** Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A., & Puschmann, H. (2009). OLEX2: a complete structure solution, refinement and analysis program. *Journal of applied crystallography*, 42(2), 339-341.
- 15** Boyd, R. *Nonlinear Optics*, 3rd ed.; Academic Press: Philadelphia, 2008, ISBN: 978-0-12-369470-6
- 16** Franken, E. P., Hill, A. E., Peters, C. W., & Weinreich, G. (1961). Generation of optical harmonics. *Physical review letters*, 7(4), 118.
- 17** Kurtz, S. K., & Perry, T. T. (1968). A powder technique for the evaluation of nonlinear optical materials. *Journal of applied physics*, 39(8), 3798-3813.
- 18** Trinquet, V., Naccarato, F., Brunin, G., Petretto, G., Wirtz, L., Hautier, G., & Rignanese, G. M. (2024). Second-harmonic generation tensors from high-throughput density-functional perturbation theory. *Scientific Data*, 11(1), 757.
- 19** Marabello, D., Antoniotti, P., Benzi, P., Canepa, C., Cariati, E., Cioci, A., & Presti, L. L. (2022). Second Harmonic Generation Behavior of Two New d-Ribose/d-Fructose and Metal Halogenide-Based Coordination Compounds and Comparison to d-Fructose and d-Galactose Analogues: An Experimental and Theoretical Approach. *Crystal Growth & Design*, 22(10), 5923-5934.
- 20** Suponitsky, K. Y., Tafur, S., & Masunov, A. E. (2008). Applicability of hybrid density functional theory methods to calculation of molecular hyperpolarizability. *The Journal of chemical physics*, 129(4).
- 21** Kanis, D. R., Ratner, M. A., & Marks, T. J. (1994). Design and construction of molecular assemblies with large second-order optical nonlinearities. Quantum chemical aspects. *Chemical Reviews*, 94(1), 195-242.
- 22** Marabello, D., Antoniotti, P., Benzi, P., Canepa, C., Diana, E., Operti, L., ... & Sassi, M. P. (2015). Non-linear optical properties of β -D-fructopyranose calcium chloride MOFs: an experimental and theoretical approach. *Journal of Materials Science*, 50, 4330-4341.
- 23** Marabello, D., Antoniotti, P., Benzi, P., Canepa, C., Mortati, L., & Sassi, M. P. (2017). Synthesis, structure and non-linear optical properties of new isostructural β -D-fructopyranose alkaline halide metal-organic frameworks: A theoretical and an experimental study. *Acta Crystallographica Section B: Structural Science, Crystal Engineering and Materials*, 73(4), 737-743.
- 24** Marabello, D., Antoniotti, P., Benzi, P., Cariati, E., Lo Presti, L., & Canepa, C. (2019). Developing new SrI2 and β -D-fructopyranose-based metal-organic

frameworks with nonlinear optical properties. *Acta Crystallographica Section B: Structural Science, Crystal Engineering and Materials*, 75(2), 210-218.

25 Marabello, D., Antoniotti, P., Benzi, P., Beccari, F., Canepa, C., Cariati, E., ... & Lo Presti, L. (2021). Crystal structure or chemical composition of salt-sugar-based metal-organic frameworks: what are the nonlinear optical properties due to?. *Acta Crystallographica Section B: Structural Science, Crystal Engineering and Materials*, 77(4), 506-514.

26 Marabello, D., Benzi, P., Beccari, F., Canepa, C., Cariati, E., Cioci, A., ... & Antoniotti, P. (2020). Synthesis and Characterization of New Lithium and Boron Based Metal Organic Frameworks with NLO Properties for Application in Neutron Capture Therapy. *Processes*, 8(5), 558.

27 Marabello, D., Antoniotti, P., Benzi, P., Canepa, C., Cariati, E., Cioci, A., & Presti, L. L. (2022). Second Harmonic Generation Behavior of Two New d-Ribose/d-Fructose and Metal Halogenide-Based Coordination Compounds and Comparison to d-Fructose and d-Galactose Analogues: An Experimental and Theoretical Approach. *Crystal Growth & Design*, 22(10), 5923-5934.

28 M.E. Casida, in: *Recent advances in density functional methods*, Vol. 1, ed. D.P. Chong (World Scientific, Singapore, 1995).

29 A.D. Becke, Density-functional exchange-energy approximation with correct asymptotic behavior, *Phys. Review A* 38(6) (1988) 3098-3100.

30 A.D. Becke, Density-functional exchange-energy approximation with correct asymptotic behavior, *Phys. Review A* 38(6) (1988) 3098-3100.

31 Kulasekera, E., Petrie, S., Stranger, R., & Humphrey, M. G. (2014). DFT calculation of static first hyperpolarizabilities and linear optical properties of metal alkynyl complexes. *Organometallics*, 33(10), 2434-2447.

32 Marabello, D., Antoniotti, P., Benzi, P., Cariati, E., Lo Presti, L., & Canepa, C. (2019). Developing new SrI2 and β -D-fructopyranose-based metal-organic frameworks with nonlinear optical properties. *Acta Crystallographica Section B: Structural Science, Crystal Engineering and Materials*, 75(2), 210-218.

33 W.J. Hehre, L. Radom, P.vR Schleyer, J.A. Pople, *Ab initio Molecular Orbital Theory*, Wiley: New York (1986).

34 W.R. Wadt, P.J. Hay, *Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg*, *J. Chem. Phys.* 82 (1985) 270-283

35 Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Caricato, M., Hratchian, X., Li, H. P., Izmaylov, A. F., Bloino, J., Zheng, G., Sonnenberg, J. L., Hada, M., Ehara, M., Toyota, K., Fukuda, M.,

Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, J. A., Peralta, J. E. Jr, Ogliaro, F., Bearpark, M., Heyd, J. J., Brothers, E., Kudin, K. N., Staroverov, V. N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J. C.,

3.RESULTS

3.1. Tetraphenylporphyrin (TPP) based crystalline materials

Table 3.1.1 reports the metals used to synthesize the tetraphenylporphyrinates (first column), the complexes obtained and confirmed by spectroscopies (second column), and the tetraphenylporphyrinates for which the XRD structure was determined (third column); structures that have never been determined are indicated in bold.

Table 3.1.1 Metals used to synthesize the tetraphenylporphyrinates (first column), complexes obtained (second column), and XRD structures determined (third column). Structures that have never been determined are indicated in bold. Instead, the XRD structures of Co-TPP, Ni-TPP, Cu-TPP and Zn-TPP are already present in literature (CCDC: 2130188, 2130189, 1882098, 904978), but they were re-determined to obtain more accurate atom coordinates.

	Complexes obtained	XRD Structures
Na		
Mg	Mg(C ₄₄ H ₃₀ N ₄)	
Ca		
Fe	Fe(C ₄₄ H ₃₀ N ₄)	
Mn	Mn(C ₄₄ H ₃₀ N ₄)	
Co	Co(C ₄₄ H ₃₀ N ₄)	Co-TPP
Ni	Ni(C ₄₄ H ₃₀ N ₄)	Ni-TPP
Cu	Cu(C ₄₄ H ₃₀ N ₄)	Cu-TPP
Zn	Zn(C ₄₄ H ₃₀ N ₄)	Zn-TPP
	Zn(C ₄₄ H ₃₀ N ₄)	Zn-TPP_tricli
	Zn(C ₄₄ H ₃₀ N ₄)(C ₃ H ₇ NO)	Zn-TPP-DMF
		Zn-TPP-DMF(DCM)

In figures 3.1.1 and 3.1.2 are reported the molecular schemes of all the tetraphenylporphyrinates whose XRD structure was determined, for which was possible to perform the theoretical calculations.

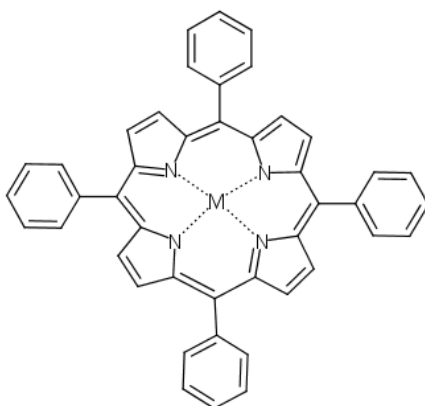


Figure 3.1.1 Scheme of Metal (II) 5,10,15,20-tetraphenylporphyrinate (Co-TPP, Ni-TPP, Cu-TPP, Zn-TPP).

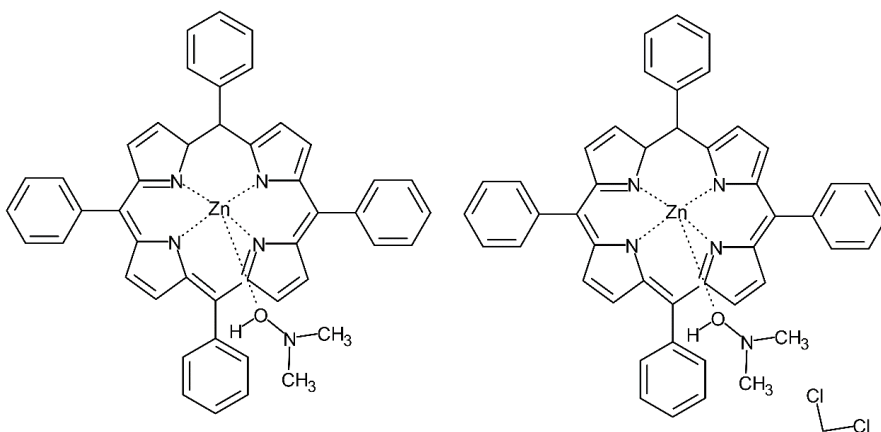


Figure 3.1.2 Structure of the Zinc (III) 5,10,15,20-tetraphenylporphyrinate (Zn-TPP-DMF) and the Zinc (III) 5,10,15,20-tetraphenylporphyrinate (Zn-TPP-DMF(DCM)).

3.2. Tetrakis-nitro-phenylporphyrin (TNPP) based crystalline materials

Table 3.2.1 reports the metals used to synthesize the tetrakis-nitro-phenylporphyrinates (first column), the complexes obtained and confirmed by spectroscopies (second column), and the tetrakis-nitro-phenylporphyrinates for which the XRD structure was determined (third column). All the structures have never been determined.

Table 3.2.1 Metals used to synthesize the tetrakis-nitro-phenylporphyrinates (first column), complexes obtained (second column), and XRD structures determined (third column). All the structures have never been determined.

	Complexes obtained	XRD structures
Na		
Mg		
Ca		
Fe		
Mn		
Co	$\text{Co}[(\text{C}_{44}\text{H}_{26}\text{N}_8\text{O}_8)] \cdot \text{C}_6\text{H}_5\text{CH}_3$ $\text{Co}[(\text{C}_{44}\text{H}_{26}\text{N}_8\text{O}_8)] \cdot \text{CHCl}_3$ $\text{Co}[(\text{C}_{44}\text{H}_{26}\text{N}_8\text{O}_8)] \cdot \text{C}_7\text{H}_6\text{O}$	Co-TNPP(tolu) Co-TNPP(cf) Co-TNPP(benz)
Ni	$\text{Ni}(\text{C}_{44}\text{H}_{26}\text{N}_8\text{O}_8)$	
Cu	$\text{Cu}(\text{C}_{44}\text{H}_{26}\text{N}_8\text{O}_8)$	
Zn	$[\text{Zn}(\text{C}_{44}\text{H}_{26}\text{N}_8\text{O}_8)] \cdot \text{CH}_2\text{Cl}_2$	Zn-TNPP(DCM)

The Schemes of the Co-TNPP(tolu) and Zn-TNPP(DCM) are reported in figure 3.2.1.

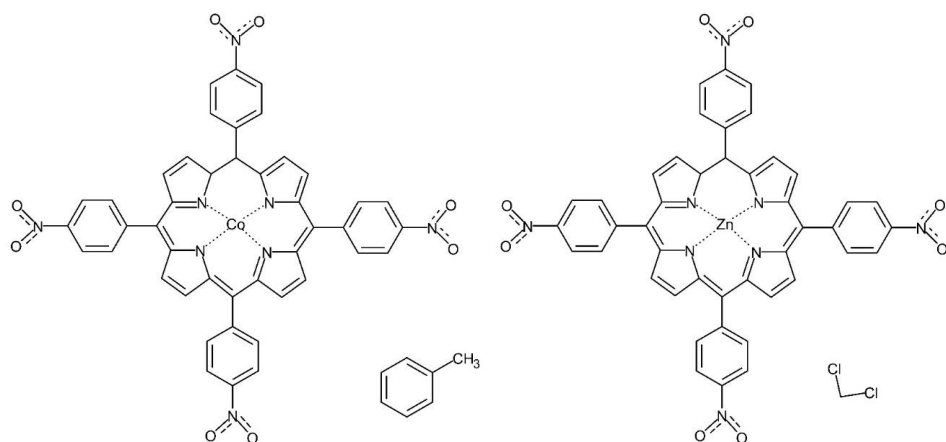


Figure 3.2.1 Scheme of Cobalt (II) 5,10,15,20-tetrakis(4- nitro-phenyl)porphyrin (Co-TNPP(tolu)) and Zink (II) 5,10,15,20-tetrakis(4- nitro-phenyl)porphyrin (Zn-TNPP(DCM)).

4. Co-TPP: synthesis, characterization and SHG behavior

4.1. Synthesis of Cobalt(II) 5,10,15,20-tetraphenylporphyrinate (Co-TPP)

All solvents and raw materials were used as received from commercial suppliers (Sigma-Aldrich, Alfa Aesar, Porphyrchem) without further purification. Co-TTP was synthesized according to the method described in Section 2.1.

The complexation of the tetraphenylporphyrin was carried out in boiling N, N-dimethylformamide (DMF), where 0.16 mmol of H₂TPP had been dissolved with 0.80 mmol of (CH₃COO)₂Co·4H₂O. The solution boiled 2.5 hours under reflux. The obtained Co-TPP was precipitated adding water, filtered and air-dried. The powder obtained was purified by dissolution in dichloromethane and re-crystallization through partial evaporation of the solvent. The crystalline powder was filtered and then washed with few drops of dichloromethane. The purity of the compound was checked through absorption and vibrational- spectroscopies, and powder X-ray diffraction (XRPD).

4.2. Characterization of Co-TPP

The UV-Vis spectrum of Co-TPP in dichloromethane solution, compared to H₂TTP, is shown in figure 4.2.1 (red and black line, respectively). On the right it is reported the area between 450 and 750 nm (Q bands) while on the left the area between 300 and 600 nm (S bands). From the two picture it is possible to ascertain that the complexation of the product is complete.

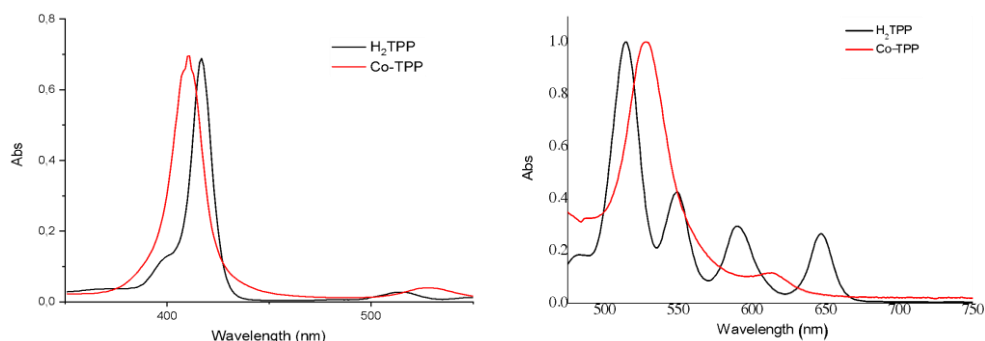


Figure 4.2.1 Absorption spectra (S bands on the left, Q bands on the right) in dichloromethane of H₂TPP (black) and the Co-TPP (red) complexes.

The crystal suitable for XRD was obtained by slow evaporation of the dichloromethane solution. Details on crystal data, data collection and least-squares refinements are reported in the Table 10.1.1 of the Appendix, while in the Table 10.1.2 are listed the relevant bonds.

The Co-TPP compound crystallize in the acentric $\bar{1}42d$ arrangement. The asymmetric unit of the Co-TPP is composed of a pyrrole ring with a branching phenyl ring and a quarter of metal atom connected to the nitrogen. The whole molecule is generated applying the $\bar{4}$ axis almost perpendicular to the mean plane of porphyrin ring and passing through the metal atom (Figure 4.2.2). The porphyrinate core is not planar but shows a *ruffled out-of-plane* conformation. In Figure 4.2.3 are reported the two perpendicular views of the S₄ ruffled porphyrinate core, where it is possible to observe the marked displacements of individual atoms with respect to the mean plane of the porphyrinate (root mean-square deviations = 0.249 Å). In the crystal structure, the molecules arranged around a 4 axis form rows along the [001] direction (Figure 4.2.4).

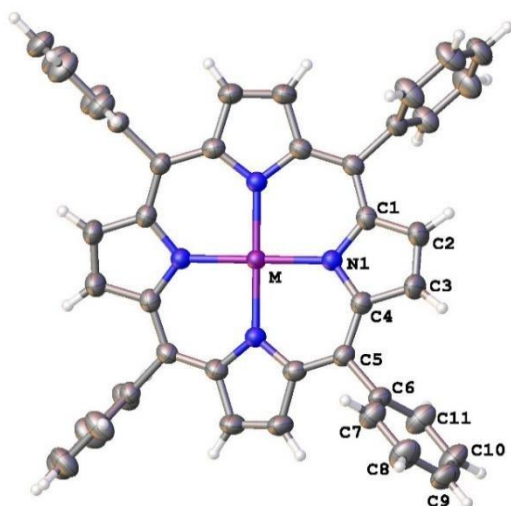


Figure 4.2.2 View of the molecule of Co-TPP perpendicular to the porphyrinate ring. The fragment with the non-hydrogen atom labelled composes the asymmetric unit.

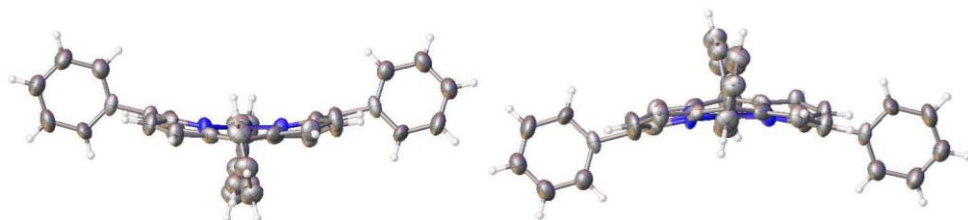


Figure 4.2.3 Two perpendicular views of the S4 ruffled porphyrinate core of the Co-TPP complex.

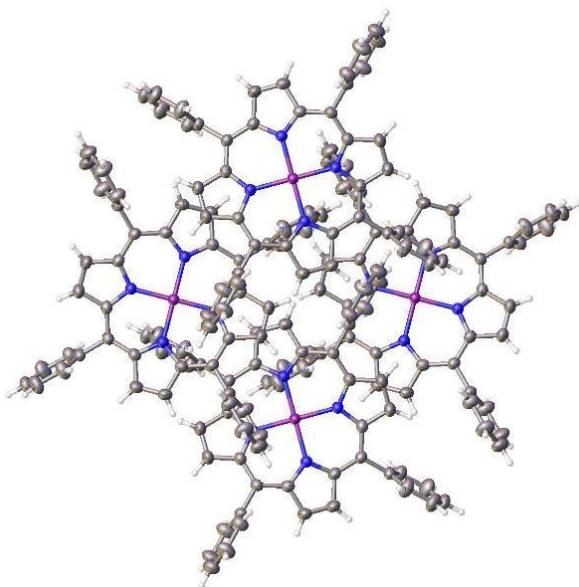


Figure 4.2.4 Row of Co-TTP molecules that are arranged around the 4 axis: view perpendicular to the [001] direction

4.3. SHG behavior and further characterizations of Co-TTP

Powders of Co-TTP and sucrose were ground separately in an agate mortar for the same length of time, and thus limiting differences on the SHG response by virtue of the crystal dimension. In order to measure the SHG efficiency, the ground powders were sealed into capillary tubes and irradiated with the 1.907 μm radiation. The initial efficiency of the Co-TTP sample was of the same order of that of the sucrose; however, quite surprisingly, it gradually increased under laser irradiation and then reached a plateau at a value about fifty times the initial one within few minutes. By visually analyzing the powders in the capillaries, a darker spot was observed in correspondence of the point where the laser hit the samples. By repeating the measurement on the same spot, a stable SHG about fifty times as high as that of the sucrose was measured; however, by moving the capillary on the not-irradiated powder, an upward trend identical to that shown before the irradiation was observed.

SHG measurements, carried out at regular intervals on one sample after irradiation, have shown that the enhanced SHG property is conserved over time.

Even though the H_2TTP crystallizes in the centrosymmetric $P\bar{1}$ space group,¹ and for this reason no SHG property is expected, its SHG behavior was

anyway analyzed in the same conditions for comparison. For the H₂TPP the SHG signal remained null, also after several minutes under irradiation.

For Co-TPP, to explain the peculiar enhancement of the SHG signal, at first we suspected the occurrence of a photo-degradation phenomenon. The UV-Vis absorption spectra before and after irradiation for Co-TPP are reported in figure 4.3.1.

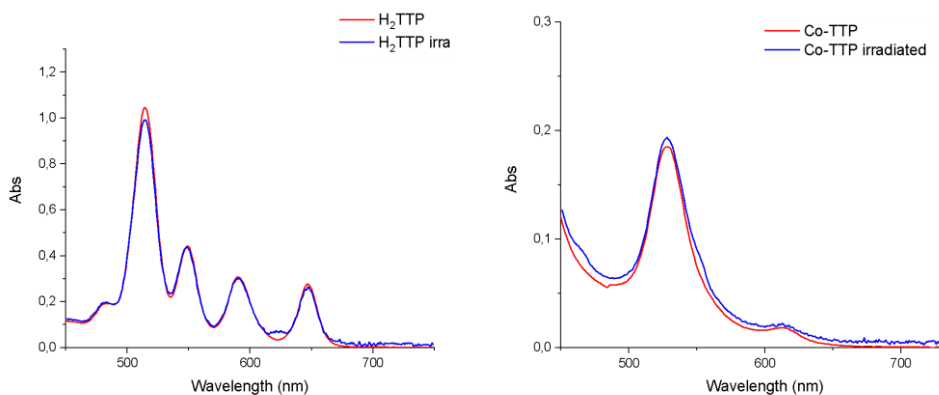


Figure 4.3.1 Absorption spectra (Q bands) in dichloromethane of H₂TPP and Co-TPP complexes before (red) and after (blue) irradiation with the 1.907 μ m Raman Shifted radiation of a Nd:YAG pulsed laser.

No changes in the spectra are observed after irradiation, which ruled out our initial hypothesis.

Since the Co-TPP shows the SHG peculiar property in the solid state, we recorded the UV-VIS spectra (Figure 4.3.2) on powdered material too. Again, for comparison, we perform the same experiment on powdered H₂TPP. About H₂TPP, as expected, no changes due to irradiation were observed in either the number or in the wavelength of the bands, which agrees with the SHG experimental measurements. Instead, for Co-TPP the UV-Vis spectra of the solid sample before and after irradiation show some differences: in the irradiated sample, a new peak was detected in the range 612-619 nm, while the non-irradiated sample in the same range exhibit only a slight shoulder. Moreover, the band between 700-780 nm splits into two peaks at 727 and 748 nm.

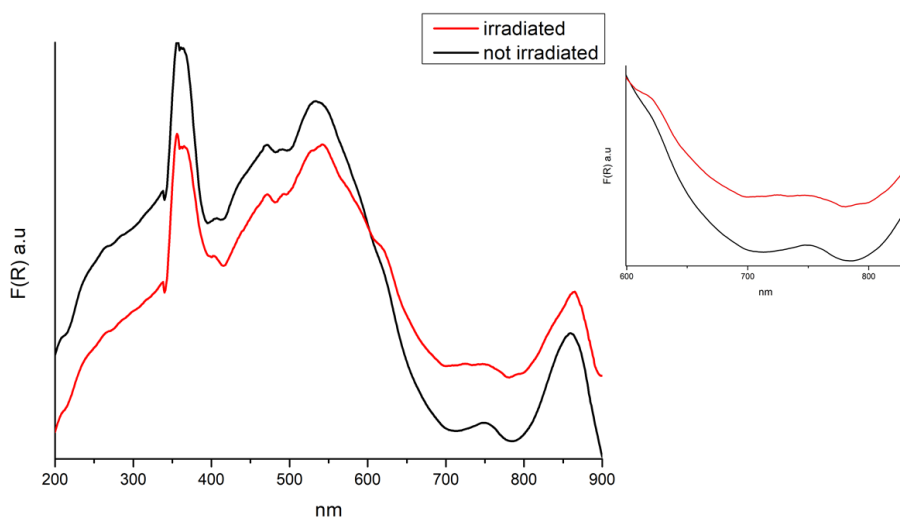
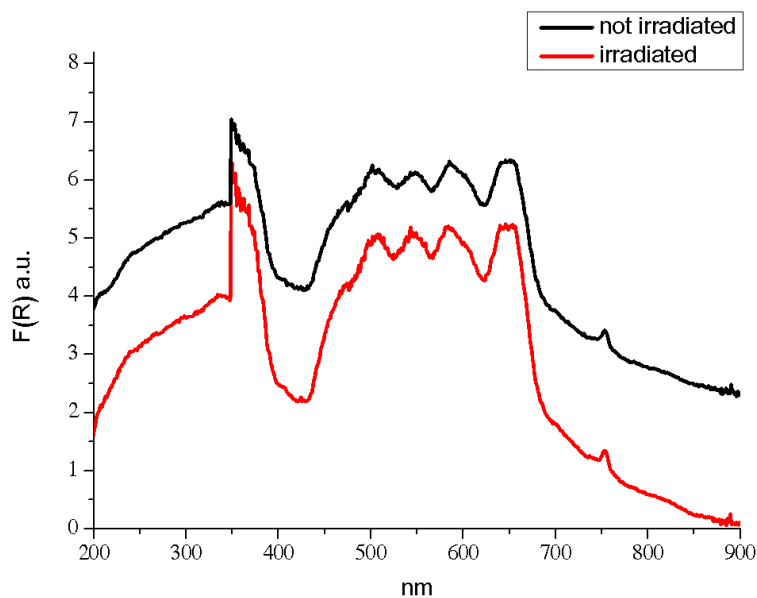
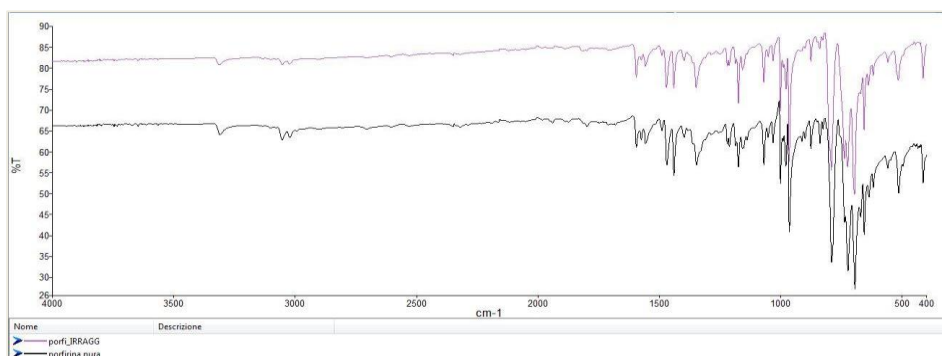
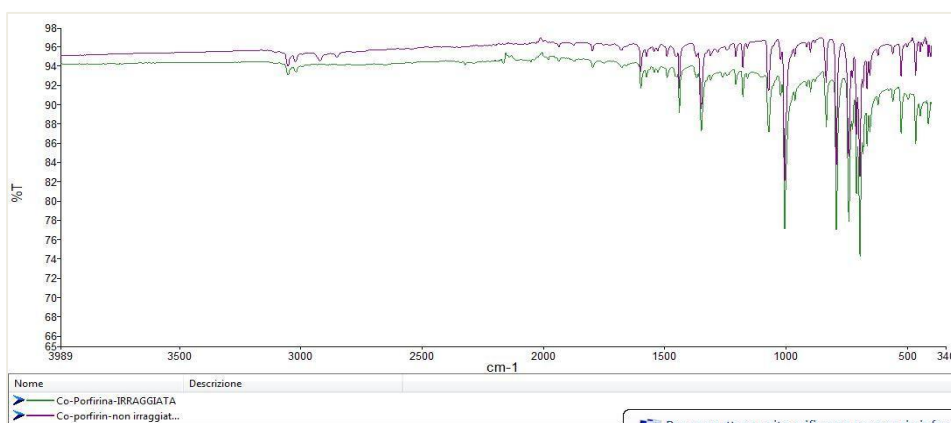


Figure 4.3.2 UV-Vis absorption spectra of solid H_2TPP (left) and of solid $Co-TPP$ (right) before and after irradiation.

About the ATR-FTIR (Fig. 4.3.3), no significant changes are detected before and after radiation, both for H₂TPP (as expected) and for Co-TPP. Once again, it was confirmed that no degradation occurred during irradiation.



a)



b)

Figure 4.3.3 FIR spectra of H₂TPP (a) and Co-TPP (b), before (red line) and after (green line) irradiation with the 1.907 μ m Raman Shifted radiation of a Nd:YAG pulsed laser.

After that, we considered the hypothesis of a possible phase transition or partial amorphization of the powders under the laser beam. Figure 4.3.4 reports the XRPD patterns of the Co-TPP before and after irradiation. Whereas the formation of a different crystalline phase after irradiation would cause a change in both the position and the intensity of the peaks, the

amorphization process is expected to reduce the intensities and contemporary to enhance the lengths of the peaks. In each powder sample, an equal amount of ZnO as standard was mixed and the patterns were scaled on its higher intense peak: an eventual lowering of the intensity of the peaks of the Co-TPP complex with respect to the ZnO would indicate a decrease in the crystalline amount in the powders.

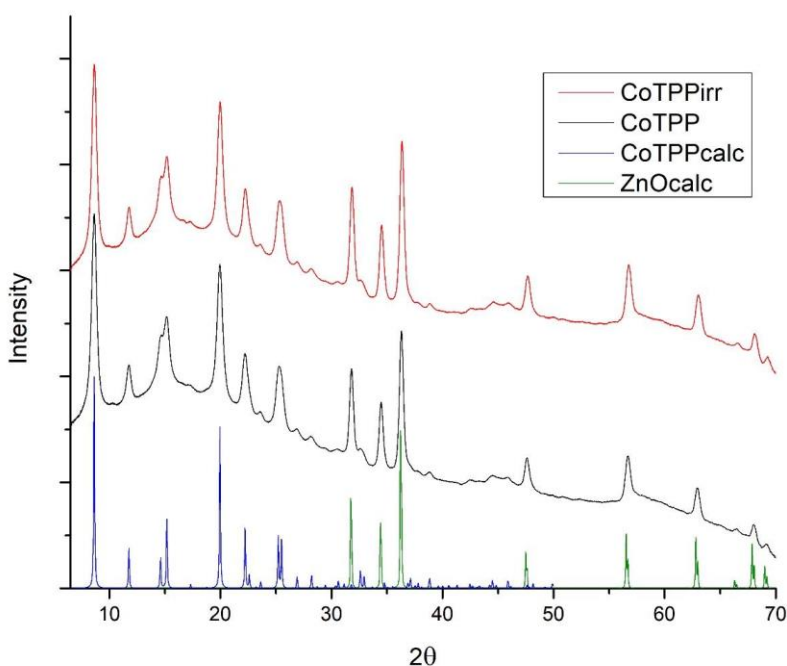


Figure 4.3.4 XRPD patterns of cobalt-porphyrinate powders before (Co-TPP) and after (Co-TPPirr) irradiation with the Nd:YAG pulsed laser, mixed with those of ZnO, compared to the XRPD patterns calculated from the XRD structure (Co-TPPcalc), and to the ZnO pattern calculated for the P63mc structure from the ICSD databank (ZnOcalc). The Co-TPP powder patterns are scaled on the peaks' intensity of ZnO.

Figure 4.3.4 shows that no structural modifications or amorphization occur after irradiation in Co-TPP, since the peaks' position are the same and the relative intensities with respect to ZnO remain unaltered. These results indicate also a strong chemical and structural stability of the Co-TPP to the irradiation with the laser beam.

In order to further investigate the possibility of an imperceptible variation in the structure, we tried to irradiate also a single crystal of Co-TPP: unfortunately, it blew up as soon as it was hit by the beam, splitting into several crystalline fragments.

In conclusion, the spectroscopic and XRPD analyses suggest that the cause of the remarkable increase in the SH signal may be due to changes in the electronic and/or spin state induced by the laser beam. In order to investigate this matter, we decided to perform the magnetic susceptibility measurements on Co-TPP.

The magnetic susceptibility of three different Co-TPP samples were measured with the Evans Balance, before and after irradiation and their magnetic moments were determined. The results of the measurements on the non-irradiated samples are consistent with the literature data, which attribute a low spin state to Co-TPP. Coherently, the measured magnetic moment lying between 2.0 and 2.8 BM. Instead, the irradiated Co-TPP samples show much higher magnetic moments, ranging from 5.3 to 8.2 BM. These correspond to 3-6 unpaired electrons. Therefore, these results show that during the irradiation a change of the spin state of the samples takes place and they are excited to a high spin state or higher spin states.

In order to investigate on the persistence of the magnetic behavior, six different measurements were carried out on one of the irradiated samples at intervals of one-week. No changes in the magnetic behavior was observed even in the last measurement.

In order to confirm the Evans balance results, we also performed EPR analysis. In Figure 4.3.5, are reported the EPR spectra recorded at 77 K of Co-TPP before and after irradiation.

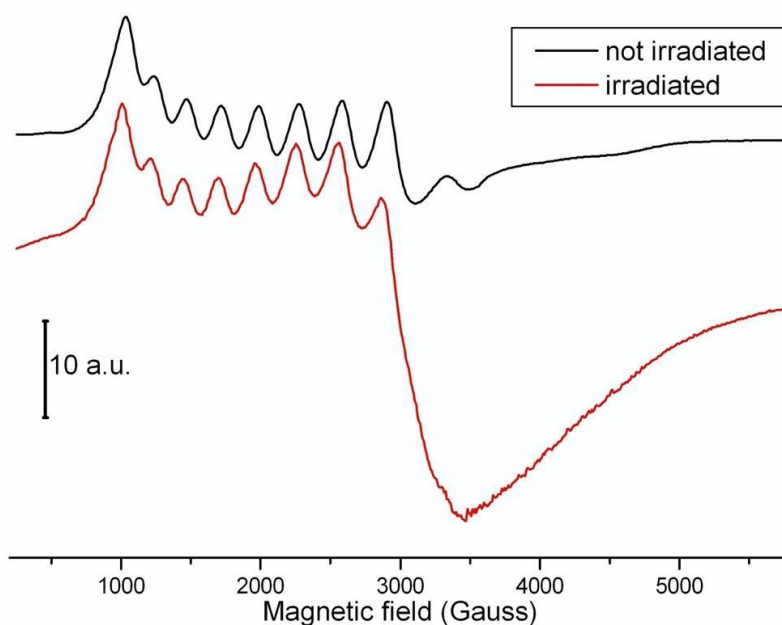


Figure 4.3.5 EPR spectra of Co-TPP at 77 K before and after irradiation

The spectrum before irradiation is comparable with previous data reported in literature and consistent with a Co(II) low-spin system ($S = 1/2$ and $I = 7/2$). Spectral simulation with the Bruker Anisotropic SpinFit software confirms for Co-TPP before irradiation an axial symmetry with a slight rhombic distortion ($g_{\perp} = 3.34$; $g_{\parallel} = 1.83$). After irradiation, this pattern is partially substituted by a very large isotropic signal, centered at $g = 2.40$, indicating a partial, but evident, modification of the Co-TPP properties. Unfortunately, the absence of a hyperfine structure or other specific features in the EPR signal of the irradiated sample does not allow to attribute these changes with certainty, but they are probably related to the modification in the spin state of the system, in agreement to the results of the magnetic susceptibility measurements.

4.4. Theoretical study of Co-TPP

Finally, we performed theoretical calculations, as described in Section 2.4.1. These calculations were carried out on the premise that the experimental SHG measurements refer to nanoparticle-sized crystalline powders. To better simulate the effects of this, two fragments were selected starting from the X-ray structures. These models allowed us to account for the structural

distortion that the surface forces can induce at the nanoscale level. The fragments of Co-TPP are composed of two or three rings cut from the crystallographic structural data of Co-TPP, in order to evaluate the effect of the fragment size on the hyperpolarizability and optical susceptibility. With regard to the H₂TPP, similar calculations were performed on a fragment composed of two rings selected from the crystal structure provided by the Cambridge Crystal Structural Database CSD². Fig. 4.4.1 shows the two and three ring fragments of Co-TPP and the two rings fragment of H₂TPP. Since sucrose is the reference compound for the SHG measurements, such calculations were carried out on a model of sucrose as well, composed of four sucrose units selected from the crystal structure downloaded from the CSD³.

For Co-TPP, calculations were performed on the lowest spin state, which is the doublet, basing on experimental data⁴.

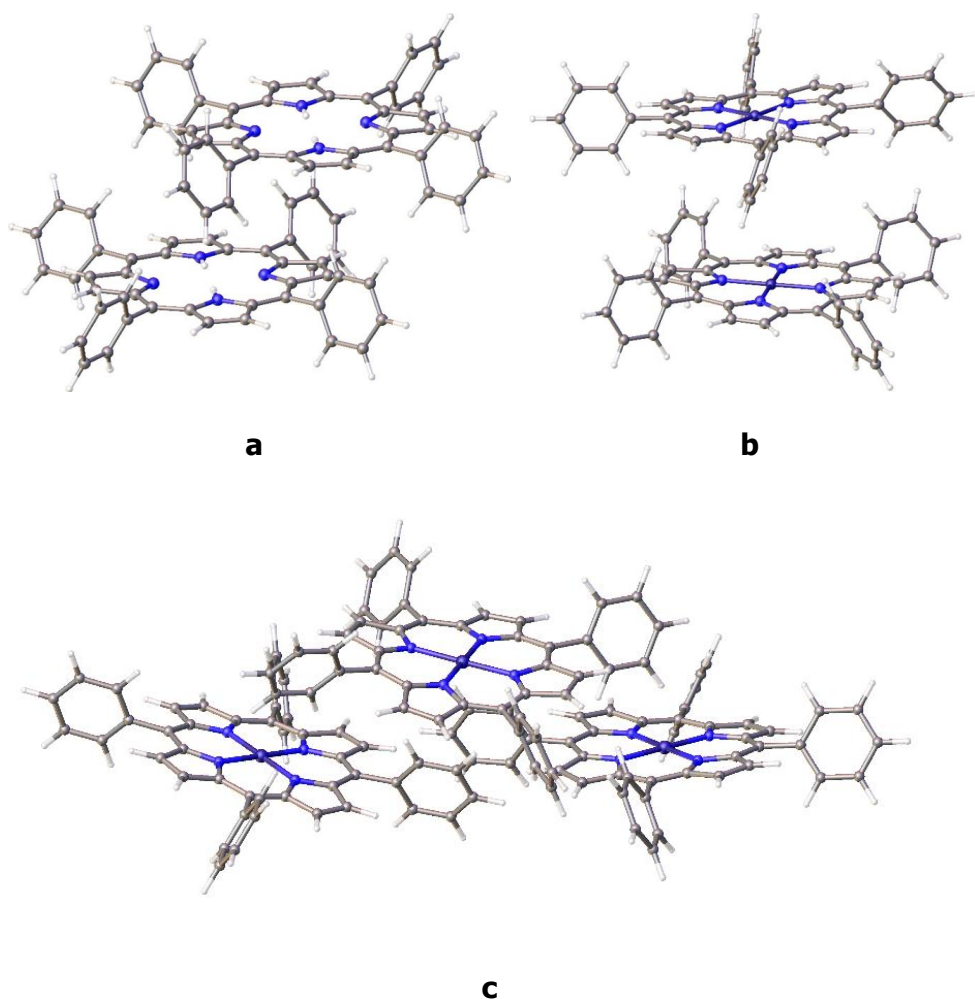


Figure 4.4.1 Fragments H2TPP (a) and Co-TPP (b) composed of two porphyrins rings and fragment of Co-TPP composed of three rings (c) selected from the X-ray structure.

Tables 4.4.1 and 4.4.2 show the most relevant geometrical parameters compared with the corresponding X-ray data. The bond differences in the fragments of the Co-TPP complexes are small and range from 0.046 Å for the two rings fragment to a maximum of 0.1 Å for the three rings (a); while, for the two ring and three ring fragments (a), the bond angles appear to comply with the experimental data.

Table 4.4.1 Relevant distances (Å) around the metal atom for Co-TPP from X-ray data and B3LYP/6-31G(d) calculations. All theoretical distances are averaged for the chemically equivalent bonds of the fragments.

	Co-TPP	Co-TPP	Co-TPP
	XRD	2 rings	3 rings
Co-N1	1.949(2)	1.995	2.051
Co-N1 ⁱⁱ	1.949(2)	1.993	2.051
Co-N1 ⁱⁱⁱ	1.949(2)	1.993	2.051
Co-N1 ^{iv}	1.949(2)	1.994	2.051

i1-X,1-Y,-Z; ii-3/2-Y,1/2+X,-1/2-Z; iii-2-X,-1-Y,+Z; iv-1/2+Y,-3/2-X,-1/2-Z

Table 4.4.2 Relevant bond angles (degree) around the metal atom for Co-TPP from X-ray data and B3LYP/6-31G(d) calculations. All theoretical angles are averaged for the chemically equivalent bonds of the fragments.

	Co-TPP	Co-TPP	Co-TPP
	XRD	2 rings	3 rings
N1 ¹ -Co1-N1 ²	178.75(12)	179.28	178.90
N1 ² -Co1-N1	90.006(2)	89.93	90.19
N1 ¹ -Co1-N1 ³	90.007(1)	90.05	90.19
N1 ³ -Co1-N1	178.75(12)	179.40	178.89
N1 ¹ -Co1-N1	90.007(2)	89.99	89.82
N1 ² -Co1-N1 ³	90.007(2)	90.03	89.82

1-3/2-Y,1/2+X,-1/2-Z; 2-1/2+Y,-3/2-X,-1/2-Z; 3-2-X,-1-Y,+Z

Table 4.4.3 illustrates the root mean-square deviations (RMSD) of the atomic positions, calculated with the Olex2 software, with respect to the mean plane of the porphyrin ring (which includes all the N atoms and all C atoms except for those of the phenyl rings) in the optimized fragments, obtained from XRD data. RMSD is close to the experimental values when it comes to H₂TPP, while the calculations provide a more planar structure for Co-TPP. On the other hand, the calculated Co-N bond distances found in Co-TPP are longer than the experimental ones (Table 4.4.3). These results confirm that the Co-N

bond distances have a great effect on the conformation of the porphyrin core, a conclusion that was similarly reached by Madura et al. in 1976⁵, who observed that the greater the length of the Co-N bond the greater the core ruffled.

Table 4.4.3 Root mean square deviations RMSD (Å) of the atomic positions with respect to the mean plane of the porphyrin ring for H2TPP and Co-TPP fragments.

	H₂TPP	Co-TPP	Co-TPP
	2 rings	2 rings	3 rings
B3LYP ^a	0.060 - 0.047	0.094 - 0.105	0.095 - 0.145 - 0.133
XRD	0.069 ²⁹	0.245	0.245

^a The values correspond to the deviation from the root mean square of the different rings.

Table 4.4.4 shows the computed values of the dipole moment μ , the mean polarizability α , an estimate of the intrinsic molecular hyperpolarizability β , second order susceptibilities $\chi^{(2)}$, and second order susceptibilities ratios with respect to sucrose values.

All Co-TPP fragments including porphyrin exhibit rather high polarizability values, but very low hyperpolarizability and optical susceptibility; besides, all values are of the same order of magnitude, while the ratios of optical susceptibility to sucrose are all extremely low. These results prove that both the porphyrin and the Co-TPP are characterized by low SHG, which accords with the experimental SHG efficiencies detected with the Nd:YAG pulsed laser at the beginning of the irradiation process. All components of hyperpolarizabilities tensor (Beta components) are reported in Table 4.4.5.

Considering the results obtained with the magnetic balance, i.e., the measured magnetic moment lying between 2.0 and 2.8 BM for the ground state, and the irradiated Co-TPP samples instead show much higher magnetic moments, ranging from 5.3 to 8.2 BM, we performed geometry optimizations at the B3LYP/6-31G(d) level on the two-ring fragment in different spin-excited states. We tested fragments in which the spin state increases from a doublet (one unpaired electron per Co, ground state) to a sextet (five unpaired electrons per Co) in order to evaluate the variation of the hyperpolarizability (β) as a function of the number of unpaired electrons of the system. The main geometrical parameters are shown in the Tables 4.4.6 and 4.4.7, and

the values of the dipole moment, polarizability and hyperpolarizability as a function of the number of unpaired electrons are shown in the Table 4.4.8. All components of beta tensor are reported in Table 4.4.9.

Table 4.4.4 Computed dipole moments μ (Debye), mean polarizabilities α (a.u.), first static hyperpolarizabilities β_{tot} (10^{-30} cm⁵esu⁻¹), second order susceptibilities $\chi^{(2)}$ (pmV⁻¹), second order susceptibilities ratios with respect to sucrose values.

	H₂TPP	Co-TPP 2 rings	Co-TPP 3 rings
μ	0.000	0.517	0.708
$\langle\alpha\rangle$	1214.6	1232.8	1888.8
β_{tot}	0.0	2.3	2.6
$\chi^{(2)}$	0.0	0.4	0.3
$\chi^{(2)} / \chi^{(2)}_{sucrose}$	0.0	0.2	0.2

Table 4.4.5 Beta components for Co-TPP (ground state)

	2 rings	3 rings
β_{xxx}	-150.788	155.616
$\beta_{xxy}=yxx=xyx$	116.901	-127.175
$\beta_{xyx}=yyx=xyy$	407.730	-945.065
β_{yyy}	-128.040	529.722
$\beta_{xxz}=xzx=zxz$	-593.711	120.406
β_{yxz}	-879.531	-333.259
$\beta_{yyz}=zyy=zyy$	466.532	648.583
$\beta_{zxx}=zzx=xzz$	250.368	166.661
$\beta_{zyz}=zzz=zyz$	135.733	-676.815
β_{zzz}	188.019	-806.463

Table 4.4.6 Relevant distances (Å) around the metal atom for Co-TPP of the two and three ring fragment spin excited states calculated at the B3LYP/6-31G(d) level, the number of unpaired electrons in the fragment is given in brackets . All theoretical distances are averaged for the chemically equivalent bonds of the fragments.

	2rings (6)	2rings (8)	2rings (10)	3rings (15)
Co-N1	2.049	2.051	2.060	2.060
Co-N1 ⁱⁱ	2.050	2.058	2.062	2.064
Co-N1 ⁱⁱⁱ	2.051	2.050	2.061	2,059
Co-N1 ^{iv}	2.052	2.058	2.061	2.065

i1-X,1-Y,-Z; ii-3/2-Y,1/2+X,-1/2-Z; iii-2-X,-1-Y,+Z; iv-1/2+Y,-3/2-X,-1/2-Z

Table 4.4.7 Relevant bond angles (degree) around the metal atom of the two and three ring fragment spin excited states calculated at the B3LYP/6-31G(d) level, the number of unpaired electrons in the fragment is given in brackets. All theoretical angles are averaged for the chemically equivalent bonds of the fragments.

	2rings (6)	2rings (8)	2rings (10)	3rings (15)
N1 ¹ -Co1-N1 ²	179.30	178.90	179.50	178.90
N1 ² -Co1-N1	90.05	89.85	90.00	90.01
N1 ¹ -Co1-N1 ³	89.88	90.10	89.94	90.07
N1 ³ -Co1-N1	179.50	179.8	178.99	178.65
N1 ¹ -Co1-N1	90.00	90.00	90.00	89.88
N1 ² -Co1-N1 ³	90.08	89.95	89.90	90.07

1-3/2-Y,1/2+X,-1/2-Z; 2-1/2+Y,-3/2-X,-1/2-Z; 3-2-X,-1-Y,+Z

Table 4.4.8 Computed dipole moments μ (Debye), mean polarizabilities α (a.u.), first static hyperpolarizabilities β_{tot} (10^{-30} cm⁵esu⁻¹) computed on optimized geometries of fragments with several excited spin states.

Unpaired electrons in the fragment of Co-TPP	6^a	8^a	10^a	15^b
μ	0.631	0.125	0.408	0.722
$\langle\alpha\rangle$	1259.7	1272.5	1332.9	2059.3
β_{tot}	2.7	11.1	17.9	18.9

^a Two ring fragment. ^b Three ring fragment

Data in Table 4.4.8 show that both the dipole moment and the polarizability values have small changes as a function of the spin state, while the hyperpolarizability changes by an order of magnitude from 2, 3 to 4, 5 unpaired electrons per Co. This result is in agreement with the experimental data of the magnetic balance, in which the irradiated sample has a high SHG emission and a rather high magnetic moment compatible with excited spin states.

Table 4.4.9 Beta components for Co-TPP (excited state)

Unpaired electrons in the fragment	6^a	8^a	10^a	15^b
β_{xxx}	649.466	933.068	136.530	786.401
$\beta_{xxy=yyx=xyx}$	-154.415	-313.040	-986.602	462.214
$\beta_{yxy=yyx=xyy}$	-516.215	-160.149	237.217	-100.273
β_{yyy}	554.860	-162.987	507.037	-255.348
$\beta_{xxz=xzx=zxz}$	107.406	401.558	395.952	2206.81
β_{yxz}	849.374	-860.066	134.211	-587.304
$\beta_{yyz=zyz=zyy}$	-162.991	-680.222	750.362	-120.586
$\beta_{zxx=zzx=xzz}$	-503.349	-452.656	-219.113	-220.752
$\beta_{zyz=zzz=yzz}$	-134.311	-216.021	110.094	110.167
β_{zzz}	-598.520	701.568	1589.95	-2707.04

^a Two ring fragment. ^b Three ring fragment

TDDFT calculations performed on the three-ring fragment, in the ground state yielded a UV spectrum that generally accords with the peak positions of the experimental spectrum (see Table 4.4.10). Differences are observed because of the presence of electronic transitions at wavelengths between 597 and 599 nm with a change in the spin state of the system from three to four unpaired electrons and with zero oscillator strength. Only a slight shoulder appears in the experimental spectrum of the non-irradiated sample, occurring at the same wavelengths. It is interesting to note that the experimental spectrum of the irradiated sample exhibits a more intense peak at the same wavelengths. Furthermore, a splitting of the band between 700 and 780 nm is observed in the theoretical TDDFT spectrum, which features two different ranges of electronic transitions 708 -712 nm and 777-780 both with spin state change and zero oscillator strength.

Table 4.4.10 Theoretical and experimental electronic transitions (nm), the width of the bands in brackets.

	Experimental	Theoretical
S bands	353 (348-398)	374 (369-398)
	536	(418-493)
	(712-782)	(701-712)
Q bands		522 (521-523)
	619	(597-599)
	(712-782)	(701-712)
		(777-780)
	(784-895)	(900-908)

References

- 1** S.J. Silvers, A. Tulinsky, The crystal and molecular structure of triclinic tetraphenylporphyrin, *J. Am. Chem. Soc.* 89 (1967) 3331–3337.
- 2** S.J. Silvers, A. Tulinsky, The crystal and molecular structure of triclinic tetraphenylporphyrin, *J. Am. Chem. Soc.* 89 (1967) 3331–3337.
- 3** Brown, G.M., Levy, H. A. (1973). *Acta Crystallographica* B29, 790-797.
- 4** M.-S. Liao, S. Scheiner, Electronic structure and bonding in metal porphyrins,
metal=Fe,Co,Ni,Cu,Zn, *J. Chem. Phys.* 117 (2002) 205-218.
- 5** P. Madura, W.R. Scheidt, Stereochemistry of Low-Spin Cobalt Porphyrins. *Inorg. Chem.* 15(12) (1976) 3182-3184.

5. The isomorphic compounds Ni-TPP and Cu-TPP: synthesis, characterization and SHG behavior

5.1. Synthesis of Nickel(II)- and Copper(II)-5,10,15,20-tetraphenylporphyrinate (Ni-TPP and Cu-TPP)

Ni-TPP and Cu-TPP were synthesized as the Co-TPP, except for the reflux time of Ni-TPP, which was about 5 hours. Purification and crystallization processes were also the same as those used for Co-TPP; for the detailed processes we remand to section 3.2.1.

5.2. Characterization of Ni-TPP and Cu-TPP

The absorption UV-Vis spectra of the Cu/Ni-TPP in dichloromethane solution, compared to the H₂TPP one, is shown in figure 5.2.1. Both figures exhibit a black line corresponding to the free base H₂TPP, a red line describing to the Cu complex, and a blue one referring to the Ni complex. The spectra confirm that the complexation of both products is complete.

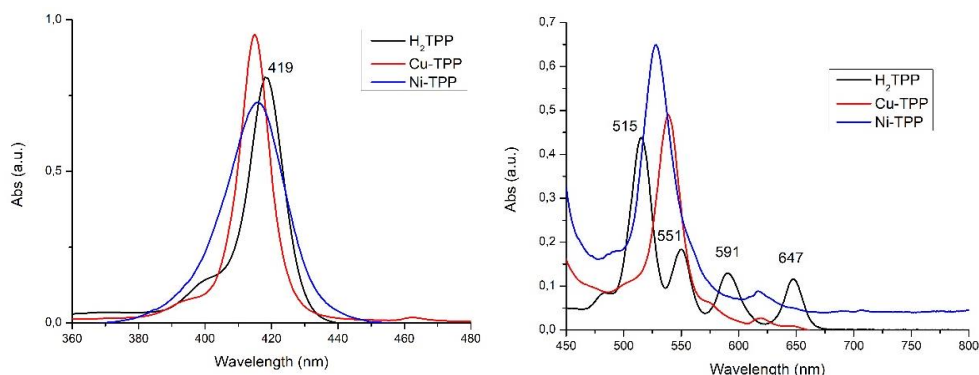


Figure 5.2.1 Absorption spectra (S bands on the left, Q bands on the right) in dichloromethane of H₂TPP (black) and the Cu/Ni-TPP (red/blue) complexes.

Details on crystal data, data collection, and least-squares refinements are reported in Appendix (table 10.1.3), and also relevant bond angles are listed in Appendix (table 10.1.4).

The Ni-TPP and Cu-TPP compounds, as the Co-TPP, crystallize in the same acentric $I\bar{4}2d$ arrangement. Since the two compounds are perfectly isomorphic with the Co-TPP, for the description of the structures see section 3.2.2.

5.3. SHG behavior and further characterizations of Ni-TPP and Cu-TPP.

Powders of Ni-TPP and Cu-TPP were ground separately in an agate mortar, and were sealed into different capillaries. They were irradiated with the same 1.907 μm pulsed laser radiation, as for Co-TPP, and the SHG efficiency was measured with respect to the sucrose. As already observed for Co-TPP, the initial efficiency of the two samples was similar to that of the sucrose, but after a few seconds under laser irradiation it gradually increased, reaching a plateau at approximately fifty times for Ni-TPP and ten times for Cu-TPP of the initial value. Thus, the final intensity of Ni-TPP is similar to Co-TPP, while that of Cu-TPP is one fifth lower. By visually analyzing the powders in the capillaries of both Ni-TPP and Cu-TPP, again a darker spot was observed in correspondence of the point where the laser hit the samples. By repeating the measurement at the same spot, the SH intensity in both compounds exhibits the value of the plateau, and it remains stable for a long time (it has been regularly checked for two months). However, by moving the capillary to the not-irradiated powder, the same SHG increase of the SHG intensity was observed under irradiation, as observed for Co-TPP. Furthermore, we noticed that the powders blew up into the capillary during the laser irradiation, especially for the Ni-TPP compound.

In order to exclude the possibility of a photo-degradation process, we performed the UV–VIS absorption spectra in the solid state, before and after irradiation (Figure 5.3.1). Contrary to the Co-TPP, no significant changes occur in either the number or the wavelength of the bands after irradiation. Moreover, in both compounds the darker color of the irradiated area tends to disappear after a few seconds. Thus, effectively a variation of the UV-VIS spectra should not be expected.

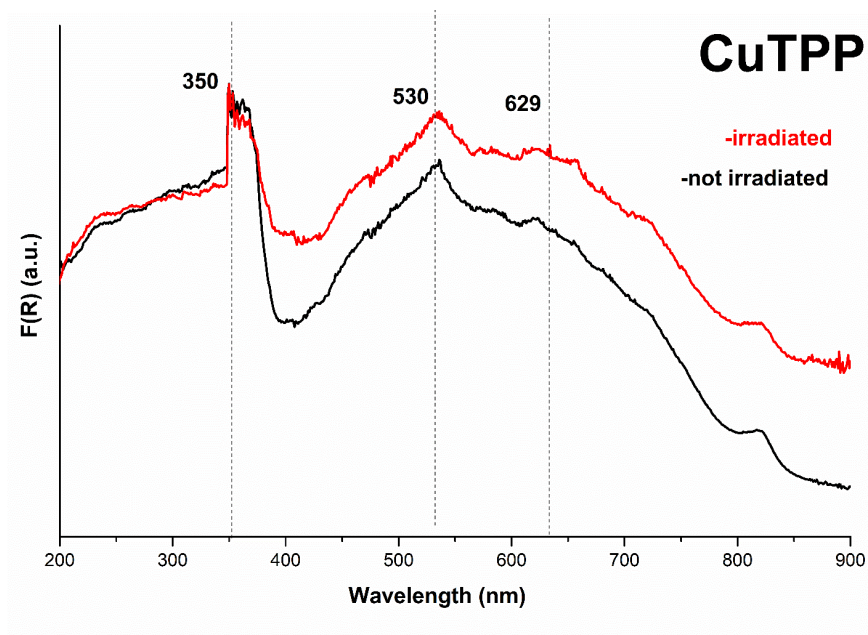
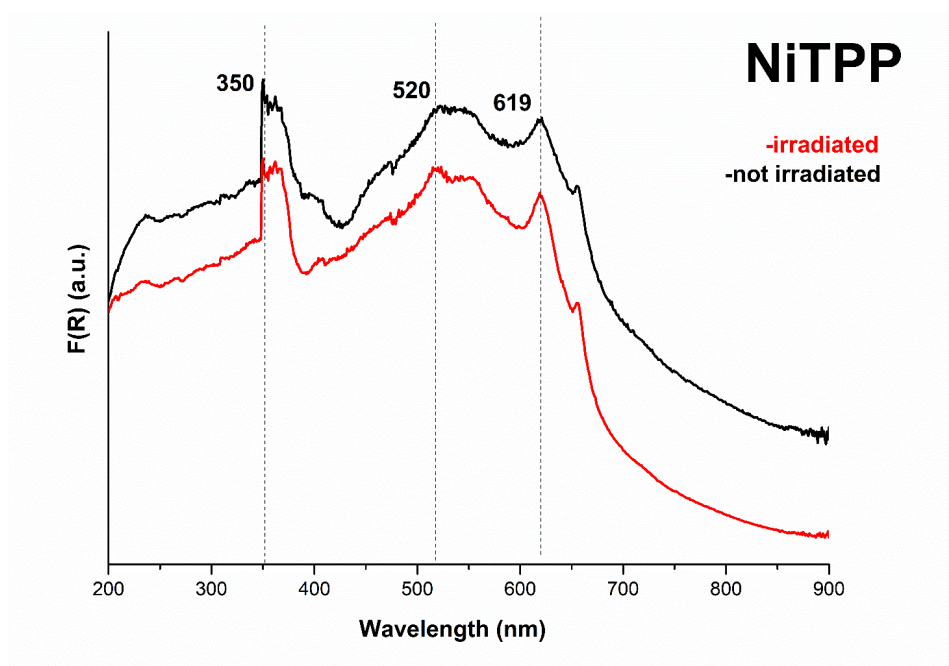


Figure 5.3.1 UV-Vis absorption spectra of solid Ni-TPP and Cu-TPP before and after irradiation

The ATR-FTIR spectra of Cu/Ni-TPP, both before and after irradiation, are shown in figure 5.3.2. Also in this case, no significant changes occur in either the number or the positions of the bands after irradiation.

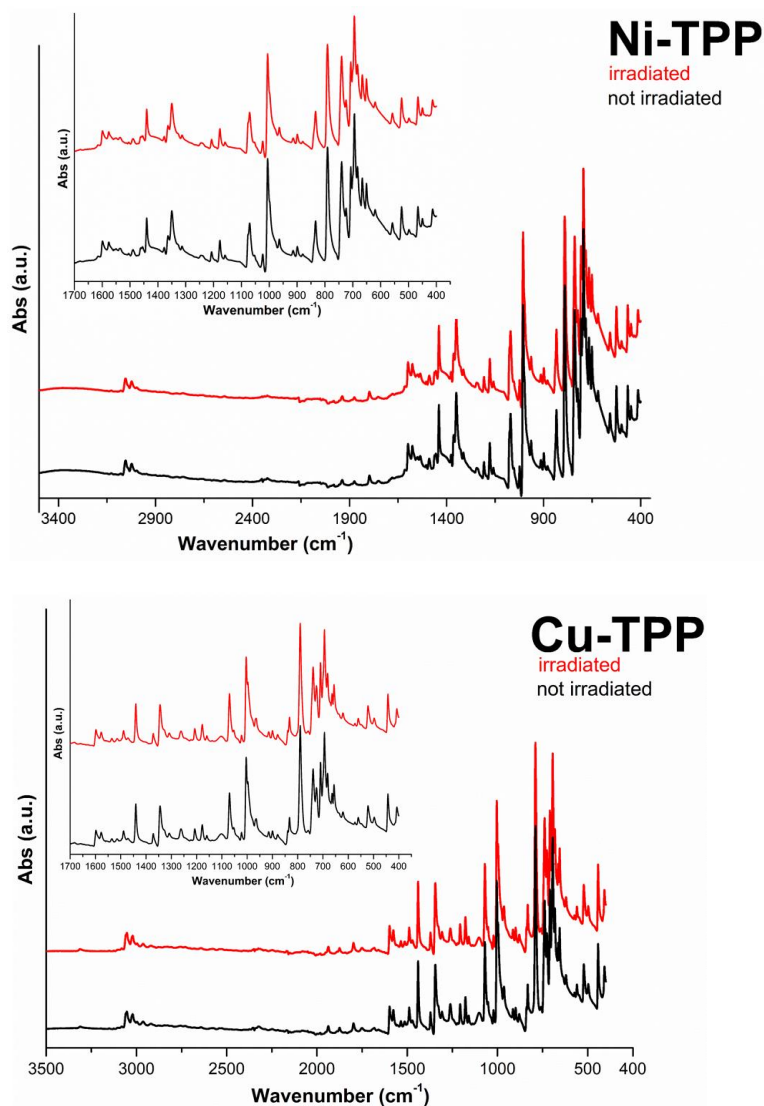


Figure 5.3.2 ATR-FTIR spectra of Ni-TPP before (back) and after (red) irradiation with the 1.907 μm Raman Shifted radiation of a Nd:YAG pulsed laser. The details high-right reported is the 1700-400 zone of the same spectra.

Since the photo-degradation phenomenon was ruled out by the spectroscopic characterization, we considered a possible phase transition or a partial amorphization of the powders under the laser beam. Figure 5.3.3 illustrates the XRPD patterns of the powders both before and after irradiation, compared to the XRPD patterns calculated from the XRD structures; in each powder sample, an equal amount of ZnO as standard was mixed, and the patterns were scaled on its highest peak. Figure 5.3.3 shows that no differences between the patterns before and after irradiation is observed, leading to the conclusion that no structural modifications or partial amorphization of the samples occurred, as already observed for the Co-TPP sample.

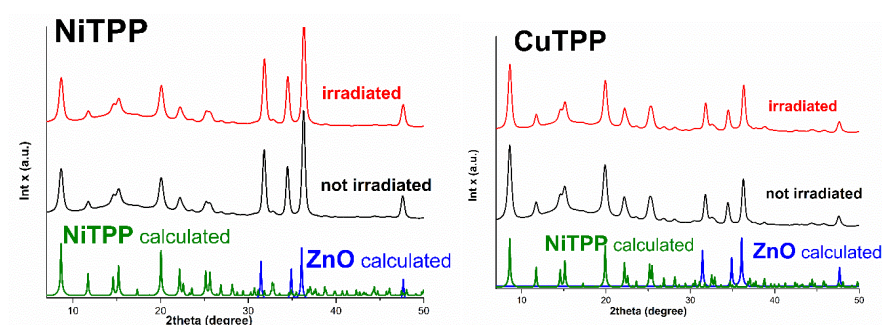


Figure 5.3.3 XRPD patterns of powders of Ni/Cu-porphyrinates, mixed with an equal amount of powders of ZnO, both before and after irradiation with the Nd:YAG pulsed laser. The XRPD patterns calculated from the XRD structures of the porphyrinates and ZnO (P63mc structure from the ICSD databank) were reported for comparison. The patterns of the Ni/Cu-TPP powders are scaled on the peaks' intensity of ZnO.

The magnetic moments of Ni and Cu-TPP were determined with the Evans balance, before and after irradiation. For the Ni-TPP compound, the results of the measurements on the non-irradiated samples are consistent with the literature data, which attribute a singlet spin state (diamagnetic condition). Instead, the irradiated Ni-TPP samples exhibit a significant increase in the magnetic moments, reaching values that vary between 5.16 and 6.28 Bohr Magnetons (BM). This behavior is similar to what was observed for the Co-TPP compound. As for the Co-TPP, measurements carried out at regular time intervals have shown that the magnetic property is conserved over time, together with the higher value of the SH intensity. These results prove that for Ni-TPP, during the laser irradiation of the samples, a change of the spin state takes place, *i.e.* it was excited into a high spin or higher state, and this condition is maintained over time.

The behavior of Cu-TPP is different: no changes in the magnetic moment were observed after irradiation. In fact, the values remain between 2.75 and 2.05 BM for every samples. This is consistent with the reported data¹, which attributed a doublet spin state to Cu-TPP. These results led us to hypothesize that the enhancement of the SH signal is not necessarily connected to an increase in the magnetic moment.

The EPR spectrum of Cu-TPP, recorded at room temperature (RT), is reported in Figure 3.3.4. It showed the typical axial pattern of a Cu(II) ion complexed in a square planar geometry with dx^2-y^2 ground state. The spectral parameters, obtained by a simulation of the experimental spectrum, are $g_{\parallel} = 2.19$; $g_{\perp} = 2.05$ $A_{\parallel} = 208$ Gs; $A_{\perp} = 38$ Gs in agreement with the literature. Moreover, no spectral changes were observed after irradiation, in accordance with the unchanged values of the magnetic moment obtained with the magnetic balance.

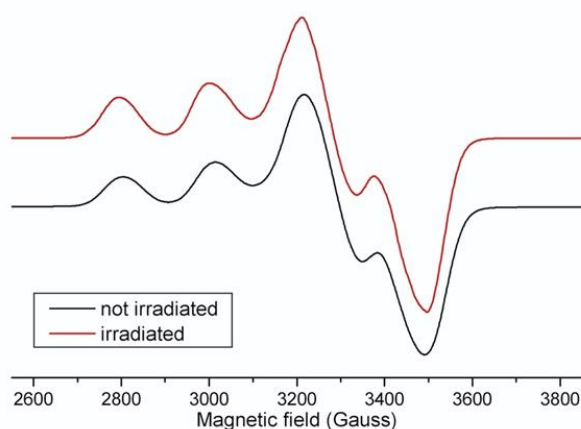


Figure 5.3.4 EPR spectra at RT of Cu-TPP before and after irradiation

The EPR spectrum of Ni-TPP, both before and after irradiation, do not reveal any signal, as expected for a diamagnetic system. In this case, however, it should be noted that the increase in the value of the magnetic moment observed at the magnetic balance does not give rise to transitions observable at the EPR. To deeply explore this phenomena, the spectra of this compounds were recorded also at 77K, providing identical results.

5.4. Theoretical study of Ni-TTP and Cu-TTP.

The fragments of both Ni-TTP and Cu-TTP are composed of two rings cut from the crystallographic structure (Figure 5.4.1).

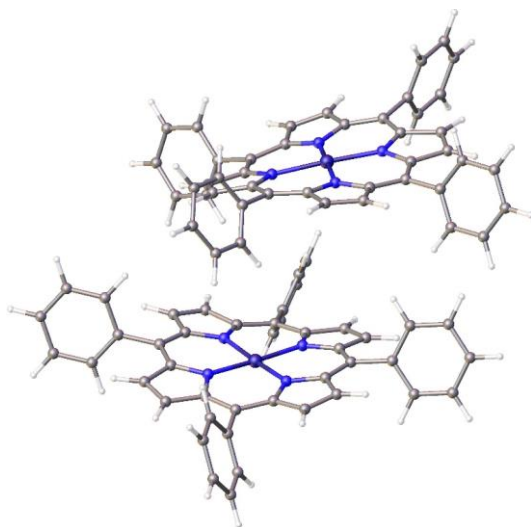


Figure 5.4.1 Fragment of M-TTP (M=Ni, Cu) composed of two porphyrinate rings selected from the X-ray structures.

For both fragments, calculations were performed on the spin state (singlet for Ni-TTP and doublet for Cu-TTP), suggested by experimental data.^{2,3}

Since sucrose is the reference compound for the SHG measurements, the same type of calculations was carried out also on a model of sucrose, composed of four sucrose units selected from the crystal structure downloaded from the Cambridge Structural Databank³.

In Tables 5.4.1 and 5.4.2 are reported the theoretical geometrical parameters around the metal atom, compared to the corresponding XRD parameters. The bond differences between the XRD structures and the theoretically optimized geometries appear to be small and ranging from 0.03 Å for the Ni-N bond in Ni-TTP to a maximum of 0.06 Å for the Cu-N bond in Cu-TTP. As for the bond angles, for Ni-TTP they are very similar to the experimental data, and the largest difference amounts to about 0.12° for the angle between N-Ni-N, while Cu-TTP seems to exhibit a more varied array of differences which are greater than 1° for N-Cu-N angles.

Table 5.4.1 Relevant distances (Å) around the metal atom for Ni-TPP and Cu-TPP from X-ray data and B3LYP/6–31G(d) calculations. All theoretical distances are averaged for the chemically equivalent bonds of the fragments.

	Ni-TPP (XRD)	Ni-TPP (B3LYP)	Cu-TPP (XRD)	Cu-TPP (B3LYP)
M-N1	1.93(1)	1.961	1.970(6)	2.027
M-N1¹	1.93(1)	1.961	1.970(6)	2.030
M-N1²	1.93(1)	1.961	1.970(6)	2.030
M-N1³	1.93(1)	1.962	1.970(6)	2.027

Table 5.4.2 Relevant bond angles (degree) around the metal atom for Ni-TPP and Cu-TPP from X-ray data and B3LYP/6–31G(d) calculations. All theoretical angles are averaged for the chemically equivalent bonds of the fragments.

	Ni-TPP (XRD)	Ni-TPP (B3LYP)	Cu-TPP (XRD)	Cu-TPP (B3LYP)
N1¹-M-N1²	179.7(7)	179.67	178.4(5)	179.70
N1²-M-N1	90.000(5)	90.00	90.011(7)	90.06
N1¹-M-N1³	90.000(3)	90.03	90.011(9)	89.98
N1³-M-N1	179.7(7)	179.82	178.4(5)	179.61
N1¹-M-N1	90.000(6)	90.00	90.011(9)	89.87
N1²-M-N1³	90.001(4)	90.00	90.010(7)	90.16

Table 5.4.3 describes the root mean-square deviations (RMSD), calculated with the Olex2 software, both in the optimized fragments and obtained from XRD structure. As shown, the RMSD for Ni-TPP is very close to the experimental value, while the calculation for Cu-TPP provides a little more planar structure. Effectively, in the Ni-TPP theoretical geometry the Ni-N bond distances are very close to the experimental data (see Table 5.4.1) and thus the calculated Ni-TPP molecules show substantially ruffled porphyrin cores. Instead, in Cu-TPP the calculated Cu-N bond distances are slightly longer than the experimental ones (see Table 5.4.2) and the porphyrin cores result more planar. These results are consistent with what has already been

observed for the Co-TPP, i.e. the greater is the length of the M-N bond the greater is the deviation from planarity of the porphyrin core.

Table 5.4.3 Root mean square deviations RMSD ($\text{\AA}$) of the atomic positions with respect to the mean plane of the porphyrin ring for Ni-TPP and Cu-TPP fragments. For the B3LYP geometries the values of both porphyrinate molecules are reported.

	Ni-TPP	Cu-TPP
B3LYP	0.243 - 0.246	0.156 - 0.155
XRD	0.272	0.229

Table 5.4.4 shows the computed values of the dipole moment μ , the mean polarizability α , an estimate of the intrinsic molecular hyperpolarizability β , second order susceptibilities $\chi^{(2)}$ and second order susceptibilities ratios with respect to sucrose values, computed as described in Section 2.4.1.

Both M-TPP fragments exhibit rather high polarizability values, but very low hyperpolarizability and optical susceptibility, as already observed for Co-TPP in our previous work. In particular, Ni-TPP shows near-zero values for dipole moment, hyperpolarizability and optical susceptibility, while the optical susceptibility value of Cu-TPP amounts to 0.1 with respect to the standard. However, all optical susceptibility ratios with respect to sucrose appear to be extremely low. These results are in agreement with the experimental SHG efficiencies of Ni-TPP and Cu-TPP at the beginning of the irradiation with the Nd:YAG pulsed laser.

All components of tensor are reported in Table 5.4.5.

Table 5.4.4 Computed dipole moments μ (Debye), mean polarizabilities $\langle\alpha\rangle$ (a.u.), first static hyperpolarizabilities β_{tot} (10^{-30} cm⁵ esu⁻¹), second order susceptibilities $\chi^{(2)}$ (pm V⁻¹), second order susceptibilities ratios with respect to sucrose values.

	Ni-TPP	Cu-TPP
μ	0.0208	0.5012
$\langle\alpha\rangle$	1238	1253
β_{tot}	0.2	1.3
$\chi^{(2)}$	0.0(4)	0.2
$\chi^{(2)}/\chi^{(2)}_{\text{sucrose}}$	0.0(2)	0.1

Table 5.4.5 Beta components for Ni-TPP and Cu-TPP (ground state)

	Ni-TPP	Cu-TPP
β_{xxx}	11.8374	-65.7589
$\beta_{\text{xyx}}=\beta_{\text{yxx}}=\beta_{\text{xyx}}$	-24.8827	-54.0824
$\beta_{\text{yxy}}=\beta_{\text{yyx}}=\beta_{\text{xyy}}$	-37.4573	-3.48700
β_{yyy}	70.1384	10.3399
$\beta_{\text{xxz}}=\beta_{\text{xzx}}=\beta_{\text{zxx}}$	109.204	101.454
β_{yxz}	58.1210	119.885
$\beta_{\text{yyz}}=\beta_{\text{zyy}}=\beta_{\text{zyy}}$	-69.5178	-57.8297
$\beta_{\text{zxx}}=\beta_{\text{zzx}}=\beta_{\text{xzz}}$	28.9269	44.1615
$\beta_{\text{zyz}}=\beta_{\text{zzy}}=\beta_{\text{yzz}}$	-51.5354	38.0680
β_{zzz}	-18.6868	87.5578

Considering the results obtained using the magnetic balance and the magnetic moments of the irradiated Ni-TPP, we performed geometry optimizations at the B3LYP/6-31G(d) in different spin excited states on the same fragment showed in fig 5.4.1. Thus, we were able to assess the variation of the hyperpolarizability (β) as a function of the number of unpaired electrons of the system. The main geometrical parameters are shown in Tables 5.4.6 and 5.4.7, and the values of the dipole moment, polarizability and hyperpolarizability as a function of the number of unpaired electrons are

shown in Table 5.4.8. All components of hyperpolarizability tensor are reported in Table 5.4.9. The geometrical parameters of the excited spin states are very similar to the geometry of the ground state, in agreement with the experimental XRPD data, which do not detect any structural changes in the irradiated sample. Instead, the polarizability values show small changes as a function of the spin state, and the dipole moments changes by an order of magnitude ranging from 0 to 2 or 4 unpaired electrons. In contrast, as observed for Co-TPP, both the dipole moment and the polarizability values slightly change as a function of the spin state. Furthermore, the hyperpolarizability changes by an order of magnitude from 0 to 2, and increases by a further order of magnitude from 2 to 4 unpaired electrons. This is consistent with our previous observations in Co-TPP, while the hyperpolarizability changes by an order of magnitude from 2-3 to 4-5 unpaired electrons. These results also accord with the experimental data of the magnetic balance, in which the irradiated sample exhibits a high SHG emission and a rather high magnetic moment, compatibly to the excited spin states.

Table 5.4.6 Relevant distances ($\text{\AA}$) around the metal atom for Ni-TPP in different spin excited states, calculated at the B3LYP/6-31G(d) level. The number of unpaired electrons in the fragments is given in columns. All theoretical distances are averaged for the chemically equivalent bonds of the fragments.

Ni-TPP	XRD	0	2	4
M-N1¹	1.93(1)	1.961	1,961	2,012
M-N1²	1.93(1)	1.961	1,961	2,008
M-N1ⁱ	1.93(1)	1.961	1,961	2,010
M-N1³	1.93(1)	1.962	1,961	2,007

Table 5.4.7 Relevant bond angles (degree) around the metal atom for Ni-TPP in different spin excited states calculated at the B3LYP/6–31G(d) level. The number of unpaired electrons in the fragments is given in columns. All theoretical angles are averaged for the chemically equivalent bonds of the fragments.

Ni-TPP	XRD	0	2	4
N1¹-M1-N1²	179.7(7)	179,73	179,73	179,49
N1²-M1-N1	90.000(5)	90,01	89,98	90,04
N1¹-M1-N1³	90.000(3)	89,98	90,01	89,95
N1³-M1-N1	179.7(7)	179,74	179,74	179,69
N1¹-M1-N1	90.000(6)	90,03	89,98	89,94
N1²-M1-N1³	90.001(4)	89,98	90,06	90,06

Table 5.4.8 Dipole moments μ (Debye), mean polarizabilities $\langle\alpha\rangle$ (a.u.), first static hyperpolarizabilities β_{tot} (10^{-30} cm⁵esu⁻¹) computed for Ni-TPP on optimized geometries of fragments with several excited spin states (0 unpaired electrons, 2 unpaired electrons and 4 unpaired electrons).

	0	2	4
μ	0.0208	0.4382	0.3479
$\langle\alpha\rangle$	1239	1230	1263
β_{tot}	0.2	3.1	24.5
$\chi^{(2)}$	0.0(4)	0,6	4,7
$\chi^{(2)}/\chi^{(2)}_{\text{sucrose}}$	0.0(2)	0,4	3,4

Table 5.4.9 Beta components for Ni-TPP (2 and 4 unpaired electrons)

	2	4
β_{xxx}	216.075	1097.46
$\beta_{xxy}=yxx=xyx$	12.9862	-614.001
$\beta_{xyx}=yyx=xyy$	7.34749	386.429
β_{yyy}	-193.025	-661.731
$\beta_{xxz}=xzx=zzx$	2.82739	682.311
β_{yxz}	58.4794	543.411
$\beta_{yyz}=zyy=zyy$	49.7973	-627.944
$\beta_{zxx}=zzx=xzz$	37.1088	197.434
$\beta_{zyz}=zzz=zzz$	-61.3044	-921.458
β_{zzz}	-1.12843	-661.651

TDDFT calculations were performed on both Ni-TPP and Cu-TPP in the ground state, in order to calculate the UV-Vis spectra to compare with the experimental ones recorded in the solid state. As shown in Tables 5.4.10 and 5.4.11, the theoretical and experimental UV-Vis spectra are in good agreement.

Within the theoretical spectrum of Ni-TPP, some forbidden transitions ($f=0$) are detected in the range 711-718 nm, which can be associated to a change in the spin. As already reported, all these theoretical transitions occur at zero oscillator strength, although a lower intensity transition (722 nm) has been found in the experimental spectra, which is also visible both before and after laser radiation (see fig. 5.3.1). This is consistent with the results found for Co-TPP, previously discussed, which seem to imply that all these spin forbidden transitions can occur, as well as that they are permanent. Different is the situation for the Cu-TPP. As reported, this complex does not show any change of the magnetic moment or magnetic behavior, and thus we do not expect to come across any transitions associated with a change in the spin, which could suggest an excited state induced by the laser radiation. Within the theoretical spectra of Cu-TPP, we found forbidden transitions in the range 786-788 nm. These transitions are also present in the experimental spectra in the range 803- 837 nm (see fig. 5.3.1), with low intensity peaks, both before and after laser irradiation (821 nm).

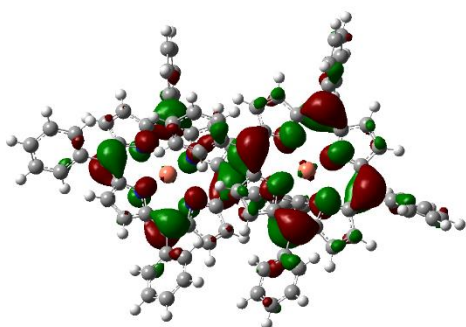
Table 5.4.10 Theoretical and experimental electronic transitions (nm) for Ni-TPP. The width of the bands is reported in parenthesis.

Ni-TPP	Experimental	Theoretical
Soret bands	358 (348-368)	375 (350-376)
	515	385 (380-399)
Q bands	519 (505-560)	523
	619	(592-601)
	655	644
	722	(711-718)

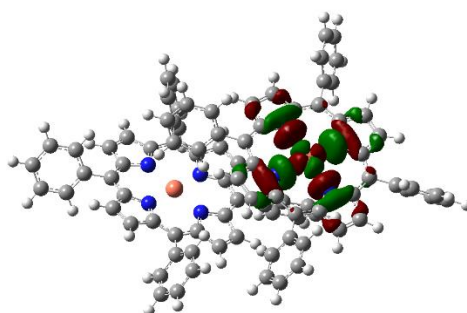
Table 5.4.11 Theoretical and experimental electronic transitions (nm) for Cu-TPP. The width of the bands is reported in parenthesis.

Cu-TPP	Experimental	Theoretical
Soret bands	349 (349-374)	377 (343-380)
	469 (457-476)	391 (385-404)
Q bands	533 (522-558)	522-539
	623 (604-638)	573-612
	657 (649-662)	668-740
	821 (803-837)	786-788

Figure 5.4.2 details the plot of the molecular orbitals⁴ that are mainly involved in the transition found at 788 nm. Oscillator strength equals zero ($f=0$) and the value of the operator S^2 amounts to 2.018, proving consistent with a doublet which is supposed to constitute the ground state of Cu-TPP. In this transition, the mainly involved orbitals are the 337B (starting MO) and the 339B (arriving MO). As we can clearly see, the starting molecular orbital is mainly constituted by π orbitals of the ligand, and the metal d orbitals significantly contributes to the arriving molecular orbital.



MO 337 B

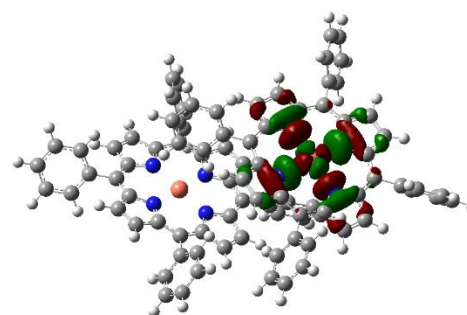
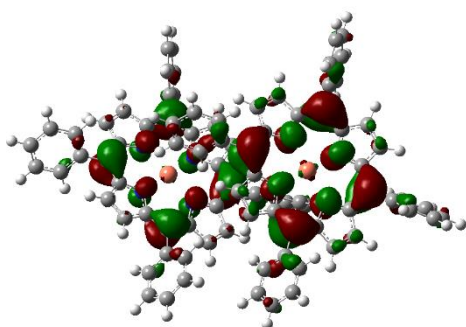


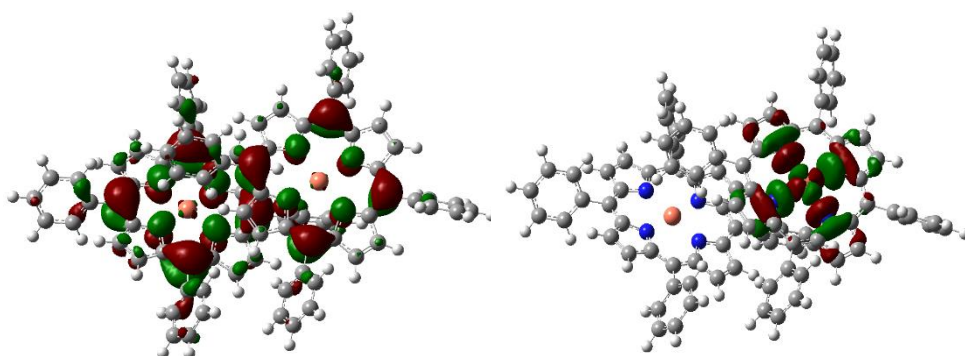
MO 339 B

Figure 5.4.2 Plot of the molecular orbitals (MO) principally involved in the forbidden transition found at 788 nm. The 337B is the starting MO, and the 339B is the arriving MO.

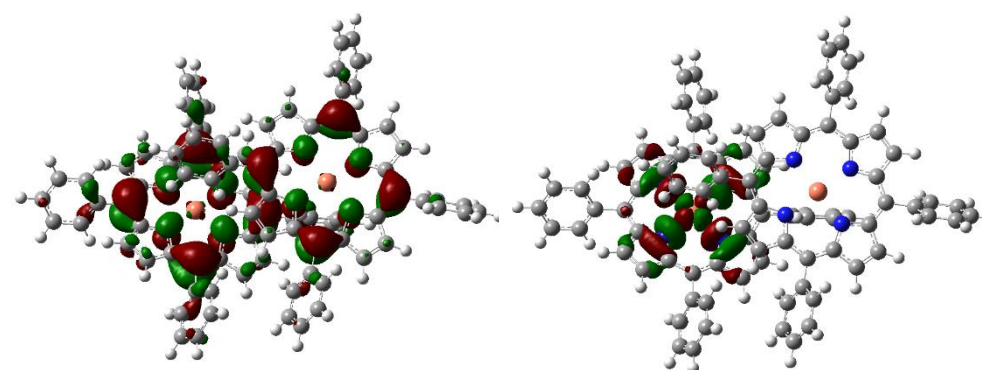
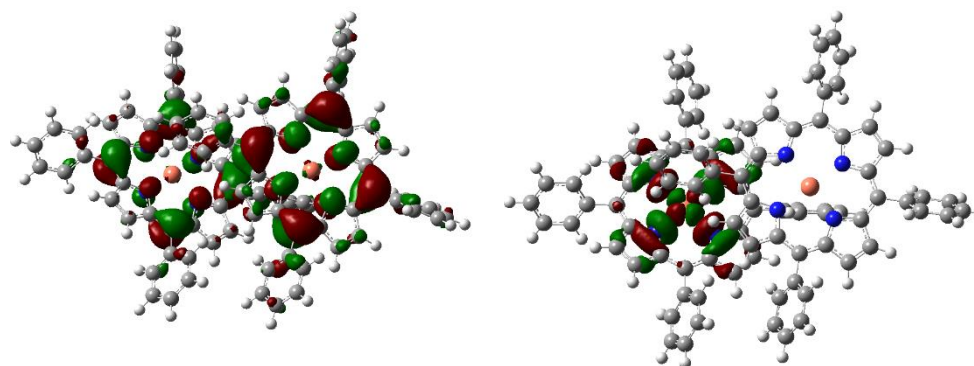
The plots of all the molecular orbitals mainly involved in the transitions at 788 nm are reported in the figure 5.4.3. By visualizing these plots, it is possible to see that all the forbidden transitions follow the same scheme showed in Figure 5.4.2. Therefore, all these transitions involve a change in the electronic distribution of the orbitals, which is consistent with the charge transfer that has been previously observed in metal porphyrinates.⁵

Excited State 1: 1.5734 eV (788.00 nm) $f=0.0000$ $\langle S^2 \rangle = 2.018$

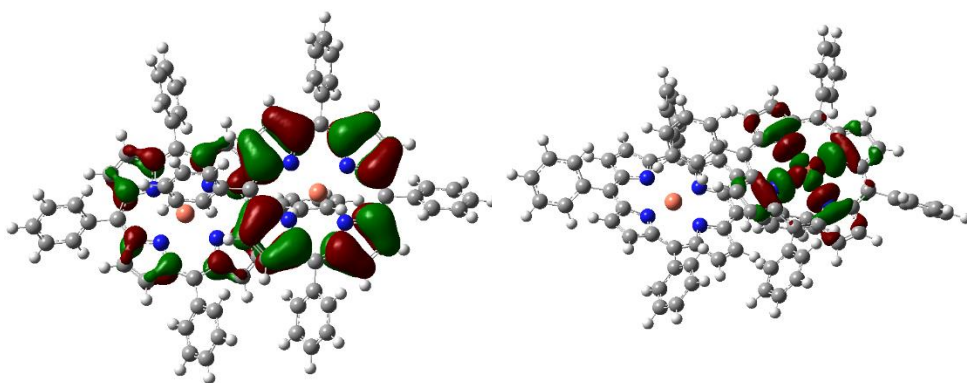




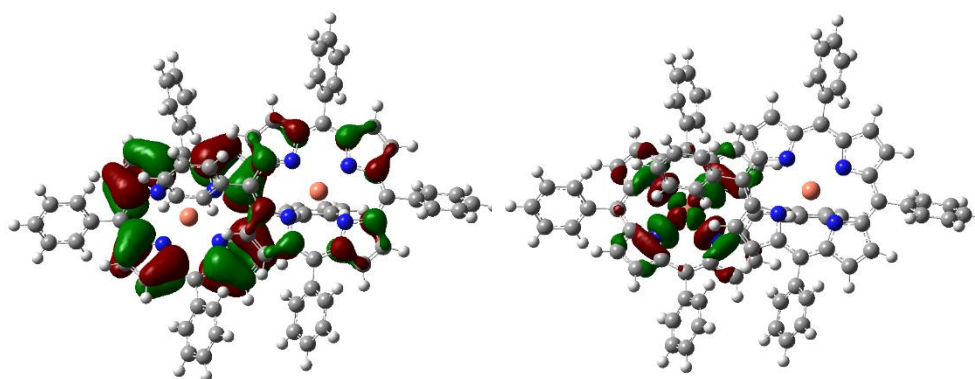
Excited State 2: 1.5766 eV (786.41 nm) $f=0.0000$ $\langle S^2 \rangle = 2.018$



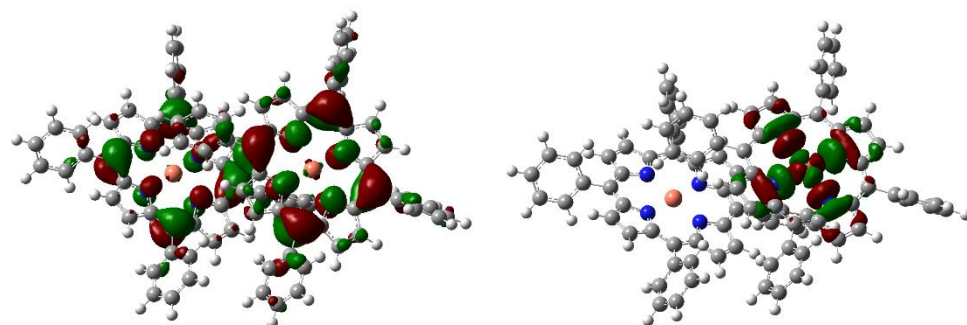
Excited State 7: 3.009-A 1.8543 eV 668.62 nm $f=0.0000$ $\langle S^2 \rangle = 2.013$

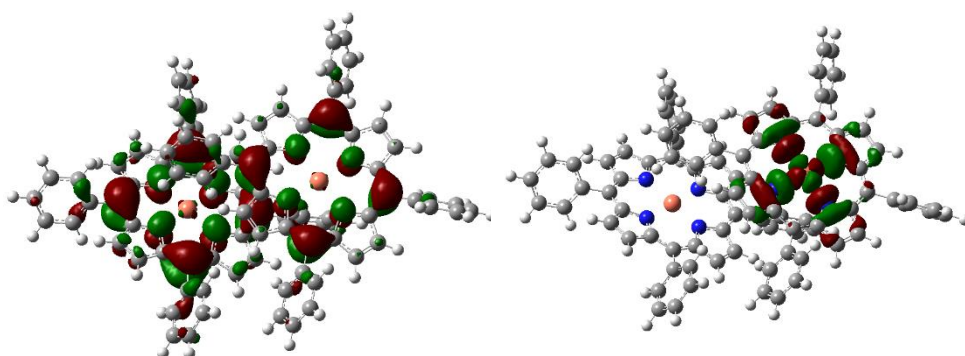


Excited State 8: 3.009-A 1.8574 eV 667.53 nm $f=0.0000$ $\langle S^2 \rangle = 2.013$

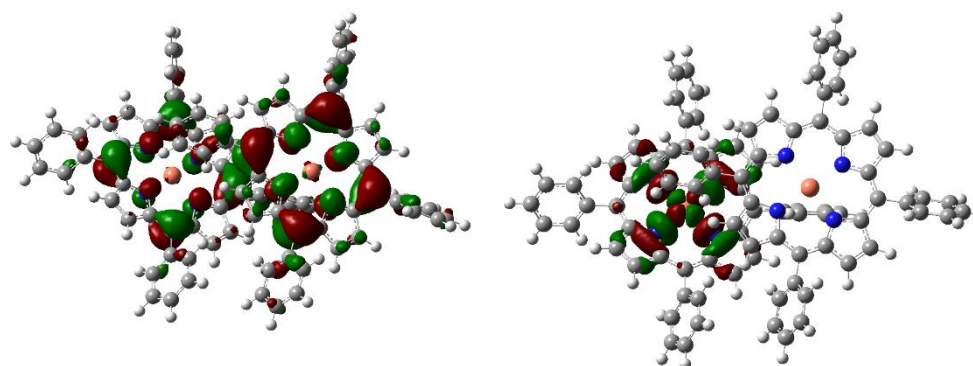


Excited State 13: 3.007-A 2.1552 eV 575.29 nm $f=0.0000$ $\langle S^2 \rangle = 2.010$





Excited State 14: 3.007-A 2.1631 eV 573.18 nm f=0.0000 $\langle S^2 \rangle = 2.010$



Excited State 23: 3.007-A 2.3656 eV 524.11 nm f=0.0000 $\langle S^2 \rangle = 2.010$

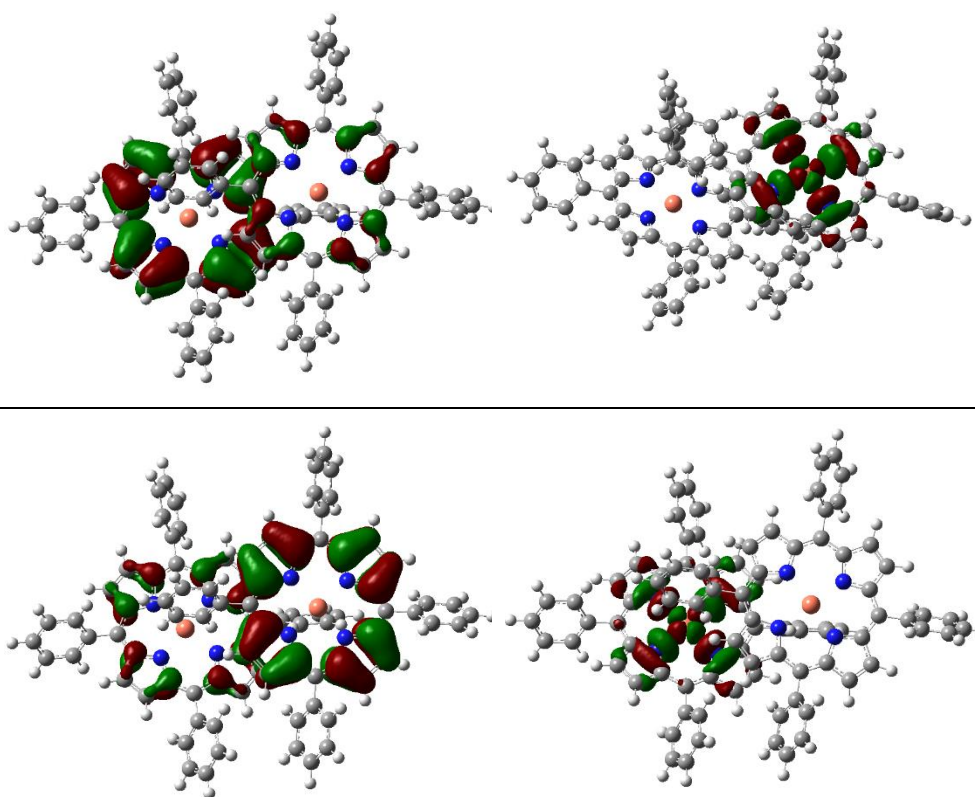


Figure 5.4.3 Plot of the molecular orbitals (MO) principally involved in the forbidden transition found at between 788 nm and 524 nm. On the right column the starting MO, in the left the arriving MO.

References

- 1** C. Calle, A. Schweiger, G. Mitrikas, Continuous-wave and pulse EPR study of the copper(II) complex of N-confused tetraphenylporphyrin: direct observation of a sigma metal-carbon bond, *Inorg. Chem.* 46 (2007) 1847–1855, <https://doi.org/10.1021/ic0621852>.
- 2** X. Liu, D. Wang, H. Gao, Z. Yang, Y. Xing, H. Cao, W. He, H. Wang, J. Gu, H. Hu, Nonlinear optical properties of symmetrical and asymmetrical porphyrin derivatives with click chemistry modification, *Dyes Pigm.* 134 (2016) 155–163.
- 3** M.S. Liao, S. Scheiner, Electronic structure and bonding in metal porphyrins, metal=Fe,Co,Ni,Cu,Zn, *J. Chem. Phys.* 117 (2002) 205–218
- 4** GaussView, Version 6, Roy Dennington, Todd Keith, and John Millam, SemichemInc., Shawnee Mission, KS, 2016.
- 5** Naumova, M. A., Paveliuc, G., Biednov, M., Kubicek, K., Kalinko, A., Meng, J., ... & Canton, S. E. (2024). Nonadiabatic Charge Transfer within Photoexcited Nickel Porphyrins. *The Journal of Physical Chemistry Letters*, 15, 3627-3638.

6. Three centrosymmetric crystalline derivatives of Zn-TPP: synthesis, characterization and SHG behavior

6.1. Synthesis of Zn(III) 5,10,15,20-tetraphenilporphyrinate (Zn-TPP, Zn-TPP-DMF and Zn-TPP-DMF(DCM))

The Zn-TPP was used as received from commercial suppliers (Porphychem) without further purification.

Zn-TTP-DMF and Zn-TPP-DCM(DMF) were synthesized as the Co-TPP, except for the reflux time, which was about 5 hours. For the detailed processes we remand to section 3.2.1.

The powder of Zn-TPP-DMF obtained was purified by dissolving the product in dimethylformamide (DMF) and re-crystallizing through partial evaporation of the solvent. The crystalline powder was filtered and then washed with a few drops of DMF. Dark purple crystals, suitable for the XRD analysis, were obtained by slow evaporation of a DMF solution in about a week. Regarding Zn-TPP-DMF(DCM), the powder obtained was purified by dissolving in dichloromethane (DCM) and re-crystallized through partial evaporation of the solvent. The crystalline powder was filtered and then washed with a few drops of DCM. Dark purple crystals, suitable for the XRD analysis, were obtained by slow evaporation of DCM in about two days.

6.2. Characterization of Zn-TPP, Zn-TPP-DMF and Zn-TPP-DMF(DCM))

The absorption UV-Vis spectrum of the Zn-TPP-DMF in dichloromethane solution, compared to the H₂TTP ones, is shown in figure 6.2.1 (red line) while the absorption UV-Vis spectrum of the Zn-TPP-DMF (DCM) in dichloromethane solution is represented by the blue line. In the right-hand graph are reported the Q-bands, while in the left-hand one the S-bands are shown. Comparing the H₂TPP ligand absorption spectra to the corresponding Zn-TPP-DMF and Zn-TPP-DMF(DCM) spectra we were able to ascertain that the complexation of the product is complete.

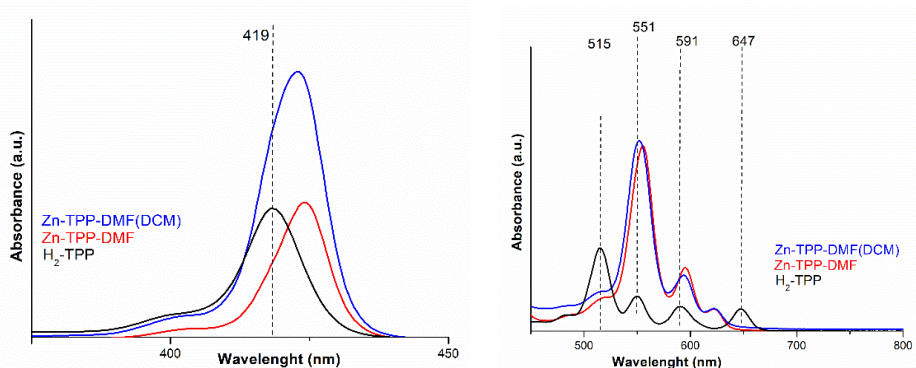


Figure 6.2.1 Absorption spectra (S bands on the left, Q bands on the right) in dichloromethane of H₂TPP (black), Zn-TPP-DMF (red) and Zn-TPP-DMF(DCM) (blue).

X-ray diffraction data were collected at 100 K for Zn-TPP-DMF and at room temperature for Zn-TPP-DMF(DCM). Details on crystal data, data collection, least-squares refinements are reported in the Appendix (table 10.1.5). In the same table are also reported the data for the already known structure of the Zn-TPP compound (CCDC 1882098).

Figure 6.2.2 shows the asymmetric unit of Zn-TPP compound. As reported²⁷, Zn-TPP crystallize in the centric $I4/m$ arrangement. The asymmetric unit of Zn-TPP is composed of a pyrrole ring connected to half a branching phenyl ring and half a metal atom connected to the nitrogen. The whole molecule is generated applying the $C4/m$ axis, perpendicular to the mean plane of porphyrin ring and passing through the metal atom. The mirror plane coincident with the mean plane is necessary to generate the missing parts of the phenyl groups. The porphyrinate core is planar (see fig 3.4.3, RMSD/A 0.000). Figure 6.2.3 illustrates the crystal packing along to the [001] direction, while figure 6.2.4 offers a view of the structure perpendicular to the **c** axis.

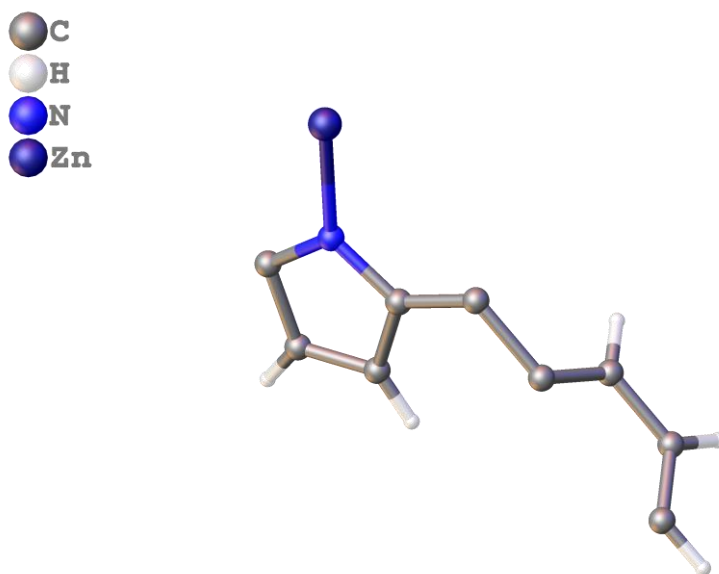


Figure 6.2.2 View of the asymmetric unit of the compounds Zn-TPP

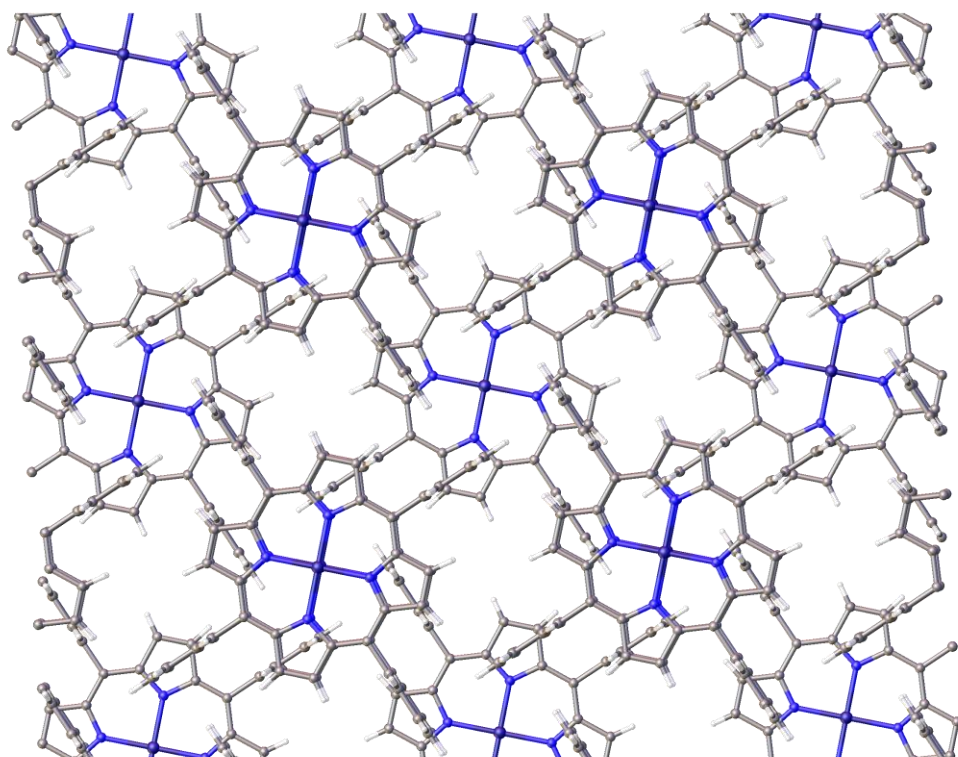


Figure 6.2.3 View of the structure of the Zn-TPP compound in the [001] plane.

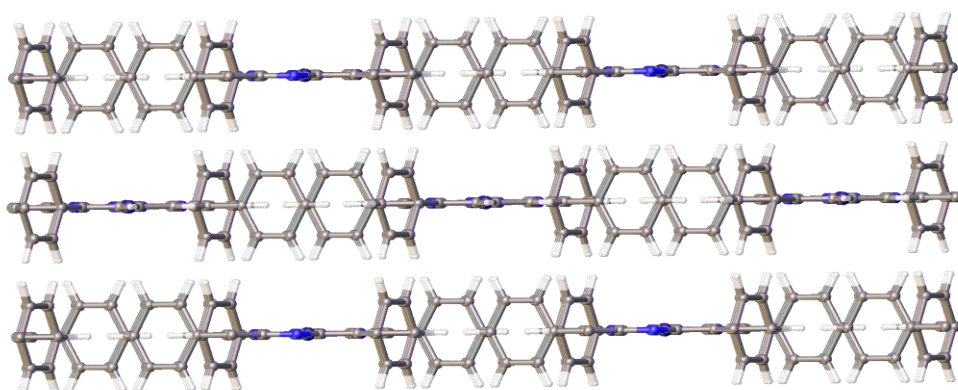


Figure 6.2.4 View of the structure of the Zn-TPP compound, perpendicular to the c axis.

The Zn-TPP-DMF compound crystallize in the centric $P2_1/c$ arrangement. The asymmetric unit of Zn-TPP-DMF (Figure 6.2.5) consists of a Zn-porphyrin ring

connected to a DMF molecule connected to the Zn. The porphyrinate core is not planar but shows a ruffled out-of-plane conformation (RMSD/A=0.219). Figure 6.2.6 offers a view of the structure along to the **a** axis, while Figure 6.2.7 shows the packing along the **b** axes.

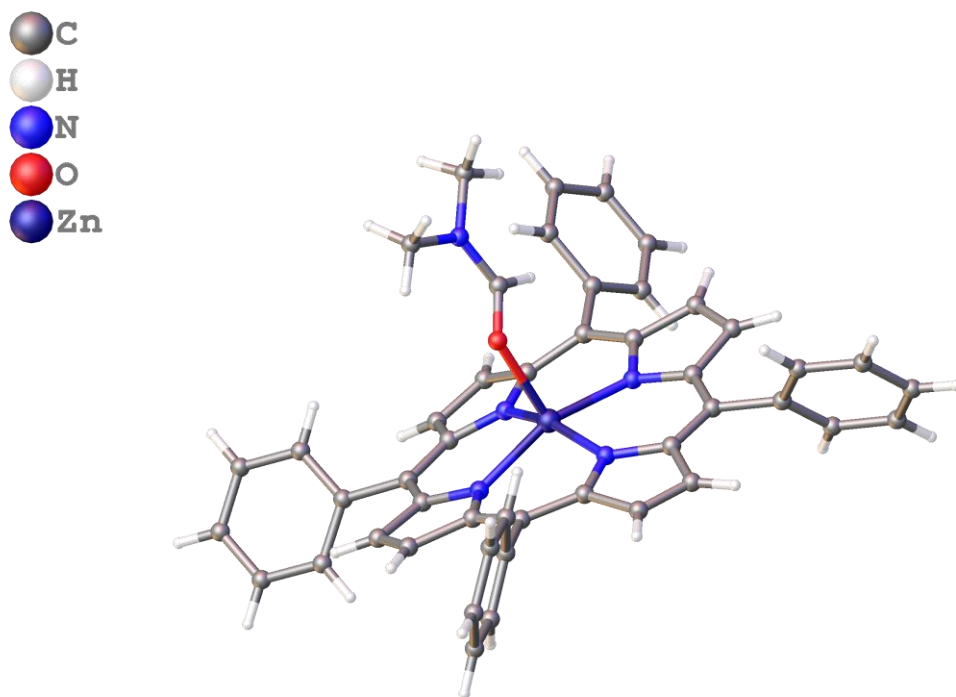


Figure 6.2.5 View of the asymmetric unit of the compounds Zn-TPP-DMF

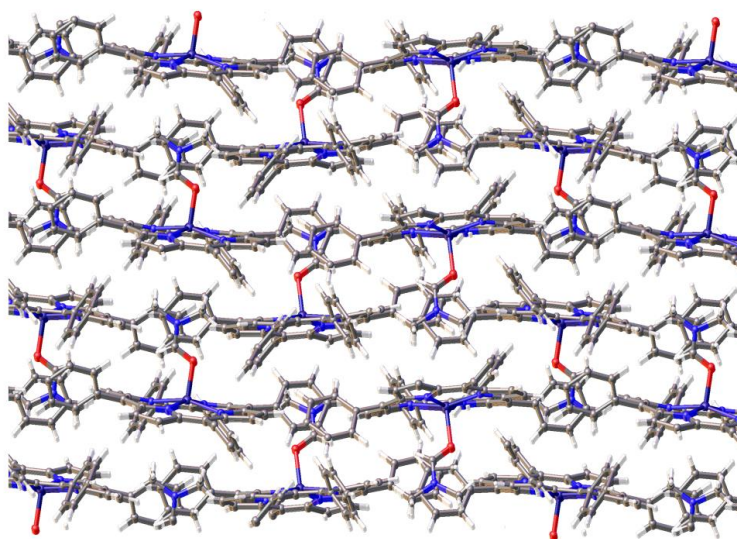


Figure 6.2.6 Crystal packing of Zn-TPP-DMF compound perpendicular to the a axis.

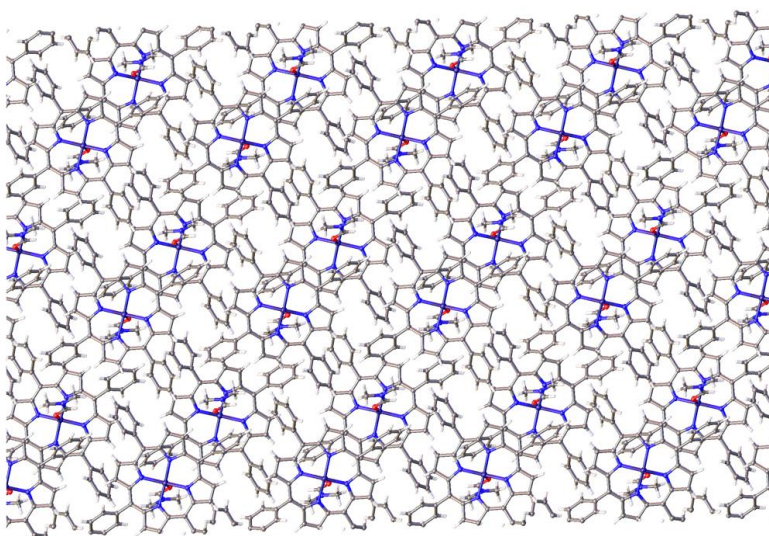


Figure 6.2.7 View of the crystal packing of Zn-TPP-DMF compound perpendicular to the b axis.

The Zn-TPP-DMF (DCM) compound crystallize in the centric $P\bar{1}$ arrangement. The asymmetric unit of Zn-TPP-DMF(DCM) (Figure 6.2.8) consists of one Zn atom inside a porphyrin ring with a DMF molecule connected to the Zn and a

co-crystallized molecule of dichloromethane (DCM). For this compound the porphyrinate core is almost planar ($\text{RMSD}/A=0.113$). Figure 6.2.9 offers a view of the structure along to the **b** axis, while Figure 6.2.10 shows the packing along the **c** axes.

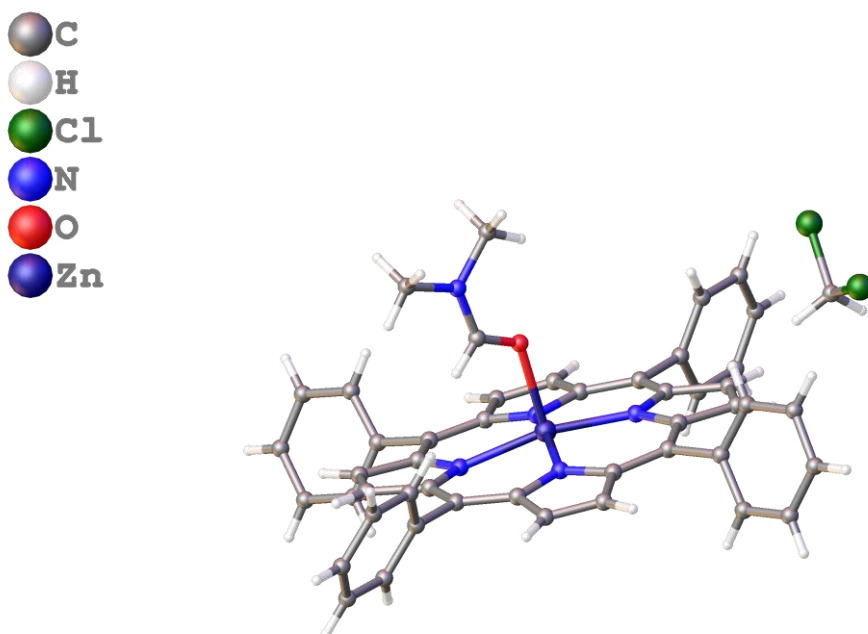


Figure 6.2.8 View of the asymmetric unit of the compounds Zn-TPP-DMF(DCM)

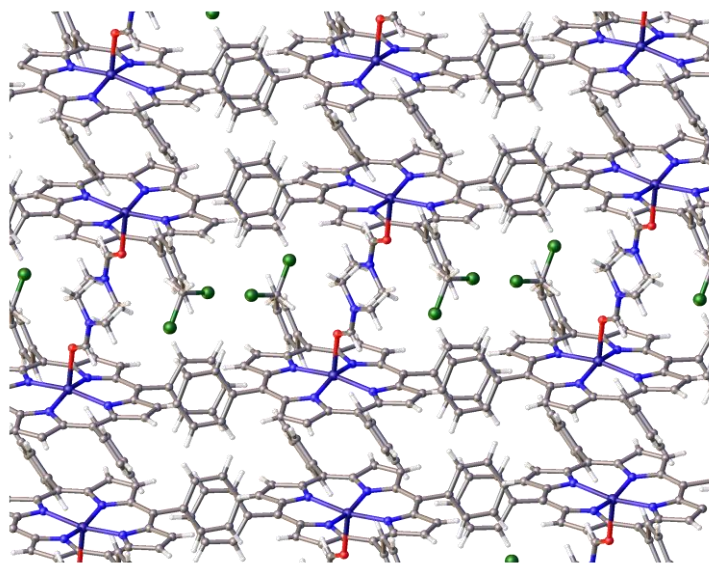


Figure 6.2.9 Crystal packing of the Zn-TPP-DMF(DCM) compound perpendicular to the b axis.

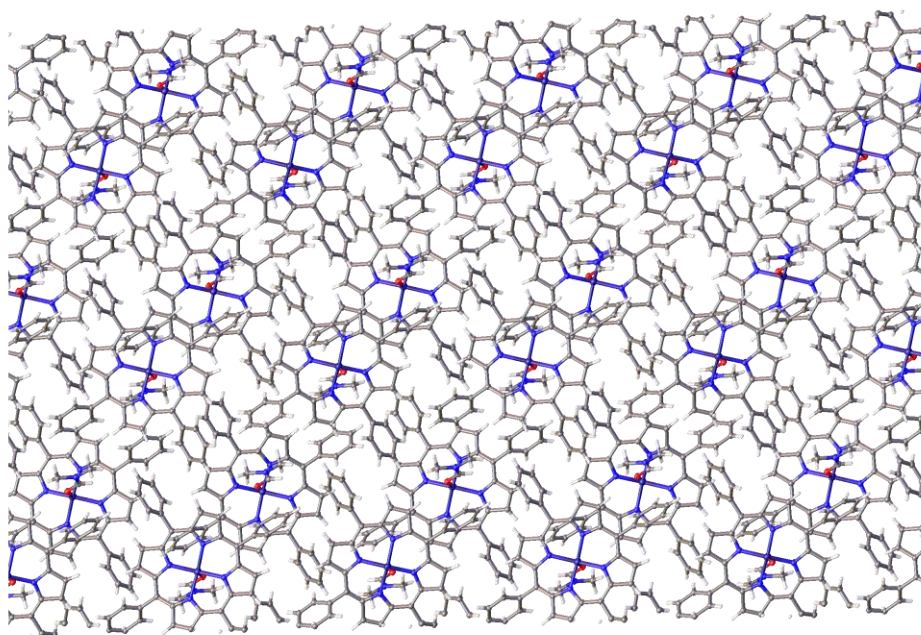


Figure 6.2.10 Crystal packing of the Zn-TPP-DMF compound perpendicular to the b axis.

6.3. SHG behavior and further characterizations of Zn-TPP, Zn-TPP-DMF and Zn-TPP-DMF(DCM))

Powders of Zn-TPP, Zn-TPP-DMF and Zn-TPP-DMF(DCM) were sealed into capillaries and irradiated with the 1.907 μm pulsed laser radiation in order to measure their SHG efficiency with respect to standard sucrose. Interestingly, the three compounds show different behaviors. In particular, despite its belonging to a centrosymmetric space group, the irradiated Zn-TPP displays a not null SHG signal, which gradually increases until it reaches a plateau at approximately 10 times the initial value, as already observed for Cu-TPP. Also in this case, by visually inspecting the powders in the capillary, a darker spot was observed in correspondence of the point of laser irradiation. By repeating the measurement at the same spot, the SH signal assumes the same value as the plateau and remains stable for at least two months (during this period the SH value was regularly checked). However, irradiating the sample in a not-irradiated portion, the increase of the signal was again observed.

Regarding Zn-TPP-DMF and Zn-TPP-DMF(DCM), a stable SHG signal close to that of standard sucrose is observed even after prolonged laser irradiation.

Because of the peculiarity of the results, for these three centrosymmetric compounds, we performed others measurements changing the wavelengths and the power of the lasers. Concerning the new measurements, the SHG efficiency of the powders of Zn-TPP, Zn-TPP-DMF and Zn-TPP-DMF(DCM) was measured in relation of a sucrose powder using an upright microscope (BX51WI, Olympus, Tokyo, Japan) combined with a microscope scanning unit (FluoView FV300, Olympus, Tokyo, Japan). The SHG signal was detected scanning the powder samples point-by-point with high resolution and excitation efficiency through an objective (UPLSAPO 20x objective NA = 0.75, Olympus), using as excitation source the output tuned at 930 nm with a pulse duration of about 2 ps and a repetition rate of 80 MHz of an Optical Parametric Oscillator (Levante Emerald OPO) (APE, Berlin, Germany). The OPO was pumped by a Yb-fiber-based laser (Emerald Engine HP, APE, Berlin, Germany) emitting at about 516 nm with a pulse duration of about 2 ps and a repetition rate of 80 MHz. The SHG signal was optically filtered in the range 330 – 480 nm (FF01-405/150 Semrock) and acquired in a back-scattering geometry (epi-detection), using one of the two PMT detectors placed inside the microscope scanning head. For all the powders the same excitation power and PMT gain and voltage were applied. The powders were placed on a microscope slide glass with on top a rectangular coverslip and measured through the microscope. The SHG efficiency was then extracted in relation to the sucrose one after the powders were optically activated. The obtained images were thresholded using the same threshold level and the average intensity of the foreground powder crystals was computed. The threshold value was subtracted from the average intensities and using these values, the SHG ratios were computed with respect to the sucrose one.

For all the three compounds, the signal remains null before the optical activation, and became larger after the activation, precisely $21 I/I_{\text{sucrose}}$ for Zn-TPP, $29 I/I_{\text{sucrose}}$ for the Zn-TPP-DMF and $39 I/I_{\text{sucrose}}$ for the Zn-TPP-DMF (DCM).

In Figures 6.3.1, 6.3.2, and 6.3.3 are reported the UV–VIS absorption spectra in the solid state of the three Zn-porphyrinates, before and after irradiation. No significant changes were detected either in the number or in the wavelength of the bands after the irradiation.

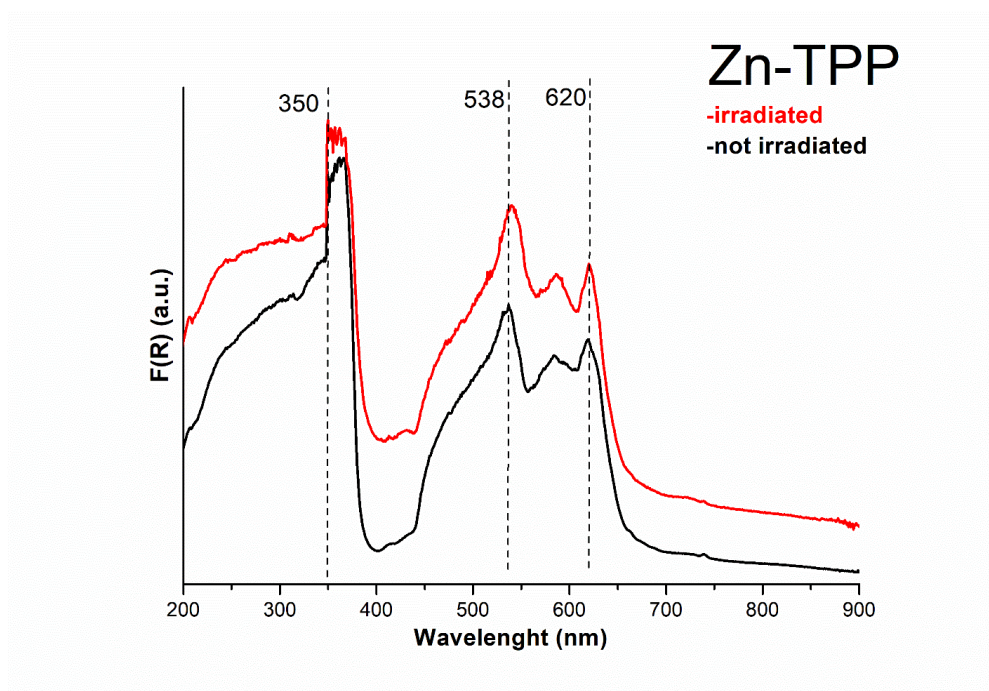


Figure 6.3.1 UV-Vis absorption spectra of solid Zn-TPP before and after irradiation

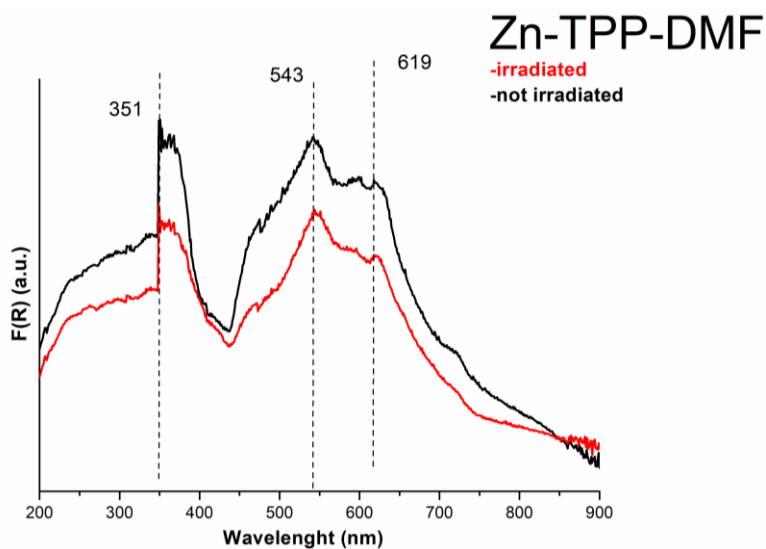


Figure 6.3.2 UV-Vis absorption spectra of solid Zn-TPP-DMF before and after irradiation

Zn-TPP-DMF(DCM)

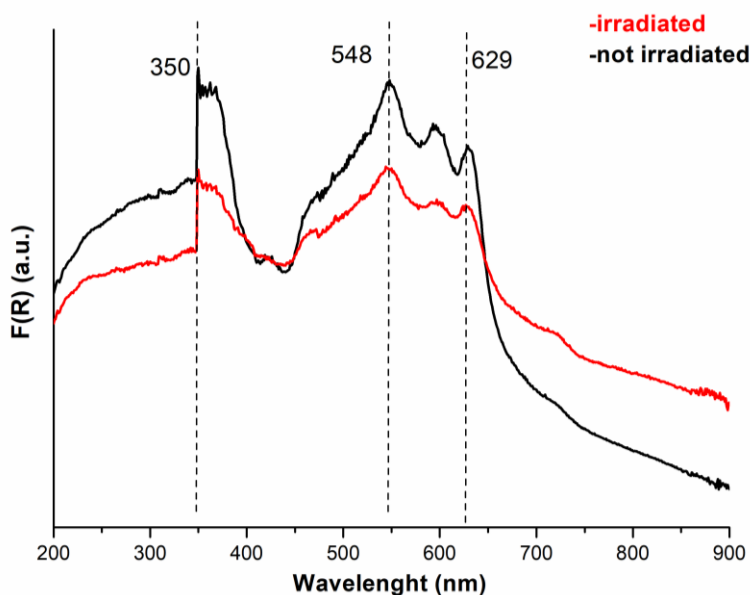


Figure 6.3.3 UV-Vis absorption spectra of solid Zn-TPP-DMF before and after irradiation

The ATR-FTIR spectra of powdered Zn-TPP, before and after irradiation, are reported in figures 6.3.4, 6.3.5, and 6.3.6. No changes are detectable in spectra, before and after irradiation.

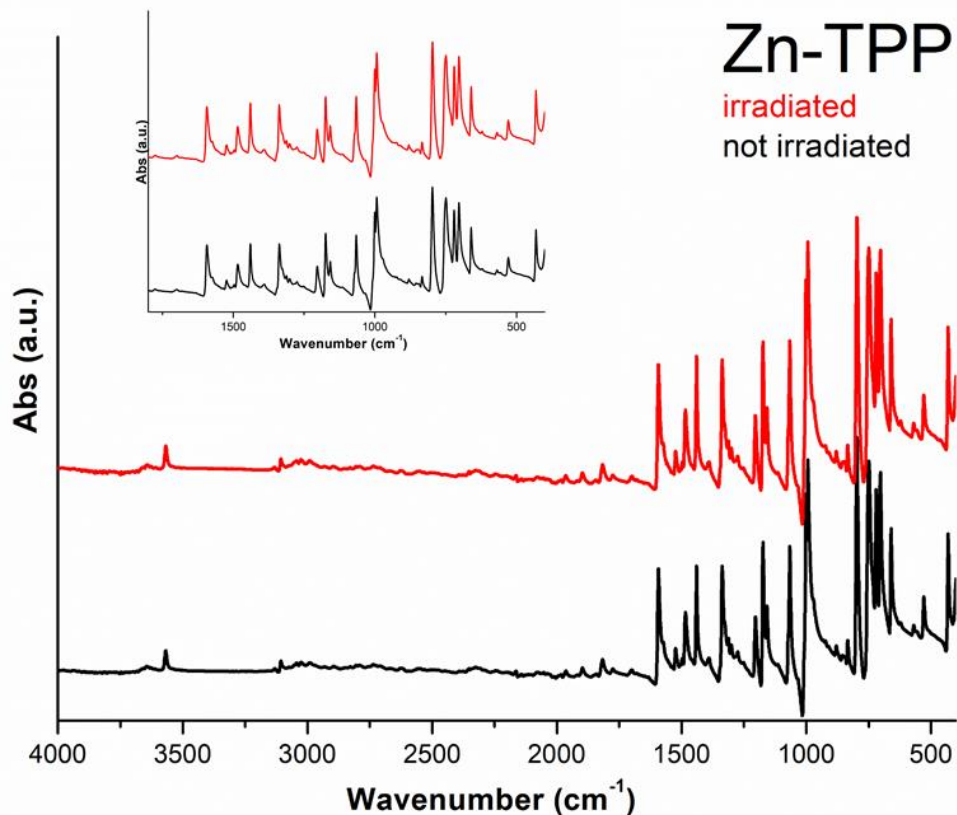


Figure 6.3.4 ATR-FTIR spectra of Zn-TPP before (back) and after (red) irradiation with the 1.907 μm Raman Shifted radiation of a Nd:YAG pulsed laser. The detail reported is the 1700-400 zone of the same spectra.

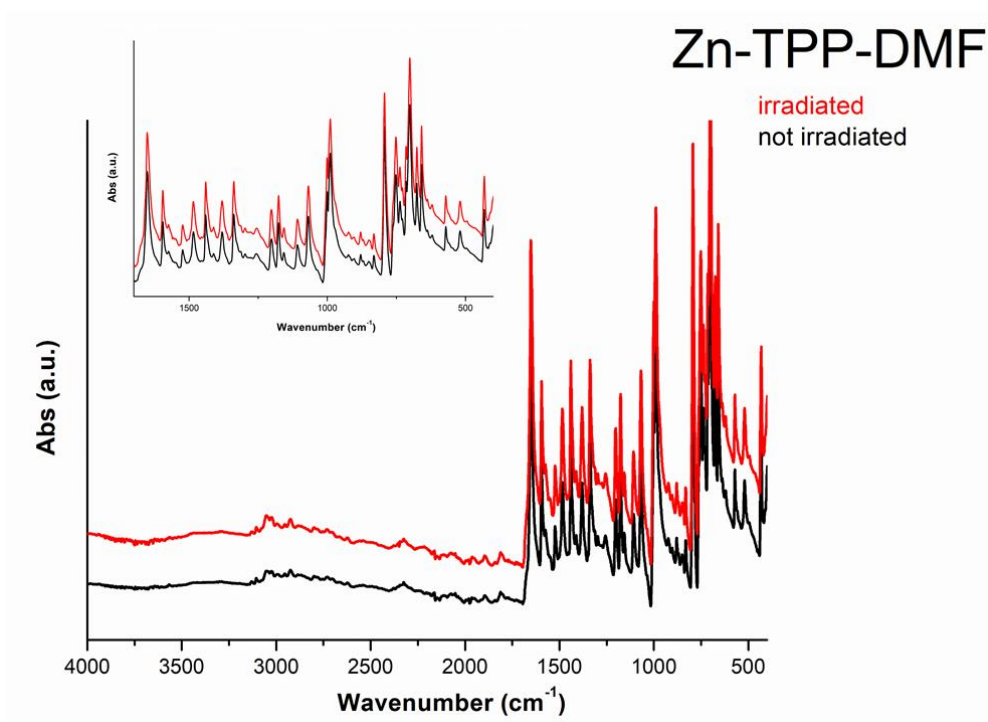


Figure 6.3.5 ATR-FTIR spectra of Zn-TPP-DMF before (back) and after (red) irradiation with the 1.907 μm Raman Shifted radiation of a Nd:YAG pulsed laser. The detail reported is the 1700-400 zone of the same spectra.

Zn-TPP-DMF(DCM)

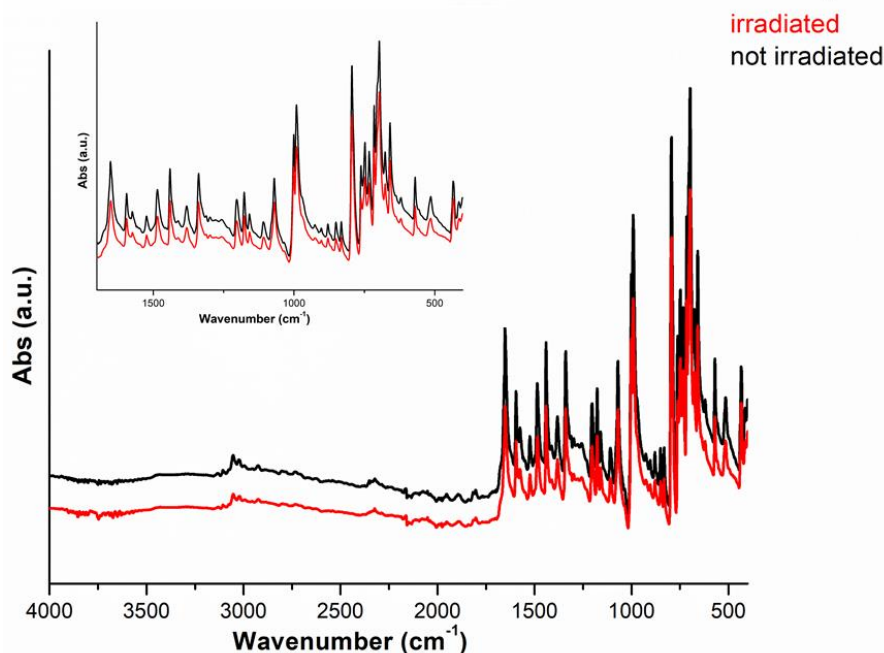


Figure 6.3.6 ATR-FTIR spectra of Zn-TPP-DMF (DCM) before (back) and after (red) irradiation with the 1.907 μm Raman Shifted radiation of a Nd:YAG pulsed laser. The detail reported is the 1700-400 zone of the same spectra.

About the magnetic moment measurements, no changes in the expected diamagnetic behavior of the complexes are observed before and after irradiation. These results confirm that the enhancement of the SH signal is not necessarily connected to an increase in the magnetic moment, in agreement with what was already observed for Cu-TPP.

6.4. Theoretical study of Zn-TPP, Zn-TPP-DMF and Zn-TPP-DMF(DCM))

In order to investigate the SHG behavior of the Zn-TPP, Zn-TPP-DMF and Zn-TPP-DMF (DCM), theoretical calculations were performed.

Small fragments of the three mentioned compounds were selected, starting with the X-ray structures. As shown in Figure 6.4.1, the Zn-TPP fragment is composed of two rings, while the Zn-TPP-DMF fragment consists of two rings and two DMF molecules (Figure 6.4.2), and the Zn-TPP-DMF(DCM) fragment

exhibits two rings, two DMF molecules, and two DCM molecules (Figure 6.4.3).

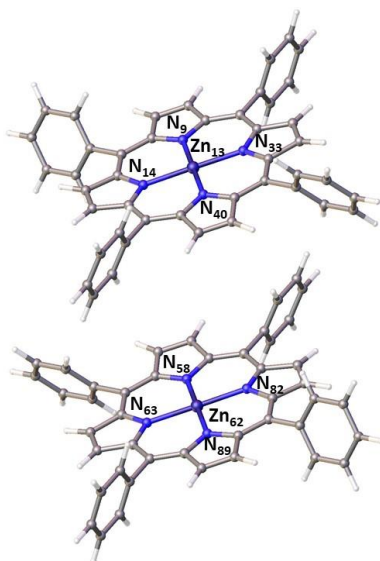


Figure 6.4.1 Fragment of Zn-TPP composed of two porphyrinate rings selected from the X-ray structures.

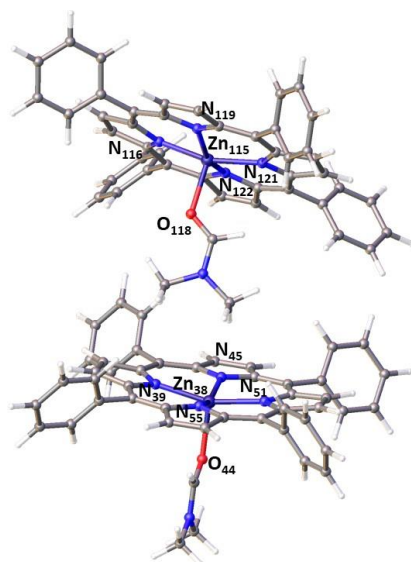


Figure 6.4.2 Fragment of Zn-TPP-DMF composed of two porphyrinate rings and two DMF molecules selected from the X-ray structures.

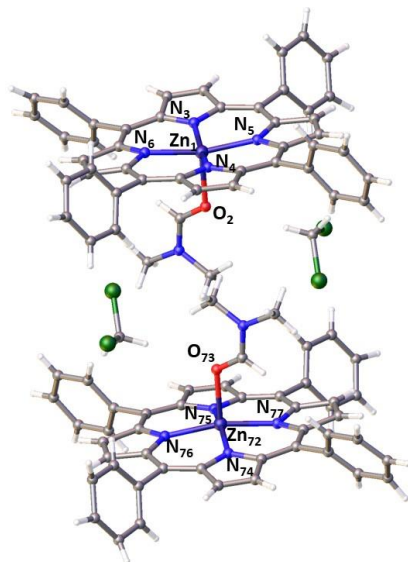


Figure 6.4.3 Fragment of Zn-TPP-DMF composed of two porphyrinate rings and two DMF molecules selected from the X-ray structures.

The same calculations were performed on a model of sucrose, which is the reference compound for the SHG measurements, composed of four sucrose units selected from the crystal structure downloaded from the Cambridge Structural Databank.

In table 6.4.1 and 6.4.2 are reported the theoretical geometrical parameters around the metal atom, compared to the corresponding XRD parameters. For the bond N-Zn all the differences are 0.000 Å. All the other bond lengths distances are reported in Table 10.1.6 in Appendix. Regarding the bond angles, all the N-Zn-N are reported in table 6.4.2. The differences ranges from a maximum to 0.03° to a minimum of 0.00° and the average amounts to 0.01°.

Table 6.4.1 Relevant distances (Å) around the metal atom for Zn-TPP calculated at the B3LYP/6–31G(d) level compared to the corresponding XRD parameters.

Zn-TPP	XRD	B3LYP
N₉Zn₁₃	2,069	2,069
N₁₄Zn₁₃	2,069	2,069
N₃₃Zn₁₃	2,069	2,069
N₄₀Zn₁₃	2,069	2,069
N₅₈Zn₆₂	2,069	2,069
N₆₃Zn₆₂	2,069	2,069
N₈₂Zn₆₂	2,069	2,069
N₈₉Zn₆₂	2,069	2,069

Table 6.4.2 Relevant bond angles (°) around the metal atom for Zn-TPP calculated at the B3LYP/6–31G(d) level compared to the corresponding XRD parameters.

Atom	XRD	B3LYP
N₉Zn₁₃N₁₄	89,97	89,96
N₉Zn₁₃N₃₃	90	90,01
N₁₄Zn₁₃N₄₀	90,07	90,08
N₃₃Zn₁₃N₄₀	89,97	89,96
N₅₈Zn₆₂N₆₃	89,97	89,96
N₅₈Zn₆₂N₈₂	90,07	90,08
N₆₃Zn₆₂N₈₉	90	90,01
N₈₂Zn₆₂N₈₉	89,97	89,97
N₉Zn₁₃N₄₀	179,16	179,14
N₁₄Zn₁₃N₃₃	179,14	179,12
N₅₈Zn₆₂N₈₉	179,16	179,14
N₆₃Zn₆₂N₈₂	179,14	179,11

Table 6.4.3 shows the root mean square (RMSD) for Zn-TPP, calculated with the Olex2 software, of the atomic positions of the porphyrinate ring with respect to the mean plane of the ring (that includes all N and C atoms, except those of the phenyl rings), both in the optimized fragments and as obtained from XRD structure. As we can see, the calculation provides a little less planar structure.

Table 6.4.3 Root mean square deviations RMSD (Å) of the atomic positions with respect to the mean plane of the porphyrin ring for Zn-TPP. For the B3LYP geometries the values of both porphyrinate molecules are reported.

Zn-TPP	
B3LYP	0.041 – 0.041
XRD	0.000

In table 6.4.4 and 6.4.5 are reported the theoretical geometrical parameters around the metal atom, compared to the corresponding XRD parameters. For the Zn-N bond we have a maximum difference value of 0.06 Å, a minimum of 0.01 Å and an average of 0.03 Å. The two differences between the Zn-O distances are 0.06 and 0.05 Å. About the bond angles (table 6.4.5), the differences range from a maximum to 9.36° to a minimum of 0.97° and the average is 3.88°.

Table 6.4.4 Relevant distances (Å) around the metal atom for Zn-TPP-DMF calculated at the B3LYP/6–31G(d) level compared to the corresponding XRD parameters.

Zn-TPP-DMF	XRD	B3LYP
N₃₉Zn₃₈	2.0917	2.0993
N₄₅Zn₃₈	2.0779	2.1035
N₅₁Zn₃₈	2.0664	2.1041
N₅₅Zn₃₈	2.0614	2.1181
N₁₁₆Zn₁₁₅5	2.0917	2.1138
N₁₁₉Zn₁₁₅	2.0779	2.0940
N₁₂₁Zn₁₁₅	2.0664	2.1142
N₁₂₂Zn₁₁₅	2.0614	2.1026
Zn₃₈O₄₄	2.1350	2.1990
Zn₁₁₅O₁₁₈	2.1350	2.1830

Table 6.4.5 Relevant bond angles (°) around the metal atom for Zn-TPP-DMF calculated at the B3LYP/6–31G(d) level compared to the corresponding XRD parameters.

Atom	XRD	B3LYP
N₂₃Zn₃₈N₁₂₁	156.49	159.72
N₄₅Zn₃₈N₅₅	161.46	159.43
N₁₁₆Zn₁₁₅N₁₂₁	159.46	157.40
N₁₁₉Zn₁₁₅N₁₂₂	161.46	153.42
N₂₃Zn₃₈N₄₅	83.02	88.40
N₃₉Zn₃₈N₁₁₉	87.29	88.72
N₃₉Zn₃₈N₁₂₂	87.42	90.12
N₅₁Zn₃₈N₁₁₆	84.78	94.14
N₄₀Zn₁₁₅N₁₁₆	93.50	85.01
N₅₁Zn₁₁₅N₁₂₁	94.94	87.86
N₅₅Zn₁₁₅N₁₁₆	91.88	88.33
N₁₁₆Zn₁₁₅N₁₁₉	87.34	88.66
N₂₃Zn₃₈N₁₁₆	157.04	158.01
N₂₃Zn₃₈N₁₂₁	156.49	158.87
N₃₉Zn₃₈N₅₁	159.46	160.44
N₄₅Zn₃₈N₅₅	161.46	158.42

Table 6.4.6 shows RMSD for Zn-TPP-DMF. The calculation provides a little more planar structure for the compound analyzed, as previously observed for Co-TPP and Cu-TPP.

Table 6.4.6 Root mean square deviations RMSD (Å) of the atomic positions with respect to the mean plane of the porphyrin ring for Zn-TPP-DMF. For the B3LYP geometries the values of both porphyrinate molecules are reported.

Zn-TPP-DMF	
B3LYP	0.143-0.138
XRD	0.219

In table 6.4.7 and 6.4.8 are reported the theoretical geometrical parameters around the metal atom, compared to the corresponding XRD parameters. For the Zn-N bond all differences are 0.04 Å. The differences between the Zn-O distances are both 0.06. Regarding the bond angles (table 6.4.8), the differences ranges from a maximum to 4.72° to a minimum of 0.02° and the average amounts to 2.03°.

Table 6.4.7 Relevant distances (Å) around the metal atom for Zn-TPP-DMF (DCM) calculated at the B3LYP/6-31G(d) level compared to the corresponding XRD parameters.

Zn-TPP-DMF (DCM)	XRD	B3LYP
N₃Zn₁	2.0657	2.1021
N₄Zn₁	2.0594	2.1006
N₅Zn₁	2.0542	2.0952
N₆Zn₁	2.0687	2.1055
N₇₄Zn₇₂	2.0657	2.102
N₇₅Zn₇₂	2.0594	2.1006
N₇₆Zn₇₂	2.0542	2.0952
N₇₇Zn₇₂	2.0687	2.1054
Zn₁O₂	2.1747	2.2388
Zn₇₂O₇₃	2.1747	2.2389

Table 6.4.8 Relevant bond angles (°) around the metal atom for Zn-TPP-DMF (DCM) calculated at the B3LYP/6–31G(d) level compared to the corresponding XRD parameters.

Atom	XRD	B3LYP
N₃Zn₁N₅	89.40	88.85
N₃Zn₁N₆	88.71	88.15
N₃Zn₁N₇	87.71	88.61
N₄Zn₁N₅	89.55	88.52
N₄Zn₁N₆	88.88	88.86
N₅Zn₁N₇₇	86.62	88.15
N₅Zn₁N₇₈	89.52	88.60
N₆Zn₇₂N₇₆	86.62	88.52
N₃Zn₁N₄	164.37	160.61
N₅Zn₁N₆	167.23	162.51
N₇₄Zn₇₂N₇₅	164.37	160.61
N₇₆Zn₇₂N₇₇	167.23	162.51

Table 6.4.9 shows the RMSD for Zn-TPP-DMF (DCM). Again, the calculation provides a little more planar structure.

Table 6.4.9 Root mean square deviations RMSD (Å) of the atomic positions with respect to the mean plane of the porphyrin ring for Zn-TPP-DMF (DCM). For the B3LYP geometries the values of both porphyrinate molecules are reported.

Zn-TPP-DMF (DCM)	
B3LYP	0.054 – 0.060
XRD	0.113

Table 6.4.10 shows the computed values of the dipole moment μ , the mean polarizability α , an estimate of the intrinsic molecular hyperpolarizability β ,

second-order susceptibilities $\chi^{(2)}$ and second-order susceptibilities ratios with respect to sucrose values, computed as described in Section 2.4.1.

The Zn-TPP and Zn-TPP-DMF (DCM) fragments are characterized by rather high polarizability values, but exhibit very low dipole moment and hyperpolarizability, while the value of the optical susceptibility is very close to zero. For Zn-TPP-DMF, we observed higher values of dipole and hyperpolarizability while, for Zn-TPP-DMF, the ratios of optical susceptibility with respect to sucrose is close to 1, i.e. susceptibility values is close to that of the sucrose. As already said in Section 3.4.3, the value of the initial efficiency of all the three samples fell within a 0-1 range (1 = sucrose standard), in accordance with the experimental SHG efficiencies detected at the beginning of the irradiation with the Nd:YAG pulsed laser.

Table 6.4.10 Ground state structure: Computed dipole moments μ (Debye), mean polarizabilities $\langle\alpha\rangle$ (a.u.), first static hyperpolarizabilities β_{tot} (10^{-30} cm⁵ esu⁻¹), second order susceptibilities $\chi^{(2)}$ (pm V⁻¹), second order susceptibilities ratios with respect to sucrose values. $I^{(2)}/I^{(2)}_{sucrose}$ value is referred to the standard SHG measurement, while $I^{(2)}/I^{(2)}_{sucrose_micro}$ to the SHG measurement performed using an upright microscope.

	Zn-TPP	Zn-TPP-DMF	Zn-TPP-DMF(DCM)
μ	0.001	13.937	0.004
$\langle\alpha\rangle$	1323.68	1342.18	1384.88
β_{tot}	0.01	3.33	0.01
$\chi^{(2)}$	0.0	0.5	0.0
$\chi^{(2)}/\chi^{(2)}_{sucrose}$	0.0	0.4	0.0
$I^{(2)}/I^{(2)}_{sucrose}$	1	1	1
$I^{(2)}/I^{(2)}_{sucrose_micro}$	//	//	//

In order to simulate a structure that could be compared to the experimental SHG efficiencies at the end of the irradiation with the Nd:YAG pulsed laser, we performed TD DFT optimization on excited states of the same three fragments of the compounds (see figs 6.4.1, 6.4.2 and 6.4.3).

First we performed a single point TD DFT calculation, on the ground states of the fragments. These calculations also allowed for the calculation of the

UV-VIS spectra to be compared with the experimental results (see section 3.4.3). As shown in Tables 6.4.11, 6.4.12 and 6.4.13, the theoretical and experimental UV-VIS spectra appear to be in good agreement.

About the Zn-TPP, between all the excited states available, we choose to optimize the Root 1, corresponding to the transition at 543.63 nm, that is a forbidden transition without change in the spin state ($f=0$, $S_2=0$). By visualizing the plots of the molecular orbitals involved in this transition we observed a possible charge transfer, as previously observed for Cu-TPP; this hypothesis must be confirmed after the optimization, by visualizing the plot of the molecular orbitals of the optimized structure (see at the end of this section). About the Zn-TPP-DMF, looking for similar condition, we optimized the Root 4, corresponding to the transition at 579.21 nm. Finally, for the Zn-TPP-DMF (DCM) we again choose the Root 4, corresponding to the transition at 553.45 nm.

Table 6.4.11 Theoretical and experimental electronic transitions (nm) for Zn-TPP. The width of the bands is reported in parenthesis.

Zn-TPP	Experimental	Theoretical
Soret bands	350 (350-368)	384 (377-387)
	475	(480-481)
Q bands	538	543 (542-544)
	587	616
	621	618
	724 (724-741)	766

Table 6.4.12 Theoretical and experimental electronic transitions (nm) for Zn-TPP-DMF. The width of the bands is reported in parenthesis.

Zn-TPP-DMF	Experimental	Theoretical
Soret bands	350 (350-375)	378 (378-410)
	475	439
Q bands	543	546
	599 (587-602)	558-560
	618 (618-633)	618-630
	720 (708-729)	812-821

Table 6.4.13 Theoretical and experimental electronic transitions (nm) for Zn-TPP-DMF(DCM). The width of the bands is reported in parenthesis.

Zn-TPP-DMF(DCM)	Experimental	Theoretical
Soret bands	350 (350-372)	376 (375-379)
	475	(405-477)
Q bands	548	553 (525-555)
	593 (593-604)	611-623
	629 (629-634)	611-623
	716 (716-729)	790

In table 6.4.14 and 6.4.15 are reported the theoretical geometrical parameters around the metal atom, for the excited state of the Zn-TPP fragment, compared to the corresponding XRD parameters. For the Zn-N bond all differences show a maximum 0.01 Å, a minimum of 0.00 Å and an average of 0.00 Å. Regarding the bond angles (table 3.4.15), the differences range from a maximum of 1.04° to a minimum of 0.00° and the average is 0.16°.

Table 6.4.14 Relevant distances (Å) around the metal atom for the excited state of Zn-TPP calculated at the TD B3LYP/6–31G(d) level compared to the corresponding XRD parameters.

Zn-TPP^{exc}	XRD	TD B3LYP
N₉Zn₁₃	2,069	2,069
N₁₄Zn₁₃	2,069	2,069
N₃₃Zn₁₃	2,069	2,069
N₄₀Zn₁₃	2,069	2,069
N₅₈Zn₆₂	2,069	2,084
N₆₃Zn₆₂	2,069	2,070
N₈₂Zn₆₂	2,069	2,083
N₈₉Zn₆₂	2,069	2,071

Table 6.4.15 Relevant bond angles (°) around the metal atom for excited state of Zn-TPP calculated at the TD B3LYP/6–31G(d) level compared to the corresponding XRD parameters.

Atom	XRD	TD B3LYP
N₉Zn₁₃N₁₄	89,97	89,96
N₉Zn₁₃N₃₃	90	90,00
N₁₄Zn₁₃N₄₀	90,07	90,08
N₃₃Zn₁₃N₄₀	89,97	89,97
N₅₈Zn₆₂N₆₃	89,97	89,92
N₅₈Zn₆₂N₈₂	90,07	90,16
N₆₃Zn₆₂N₈₉	90	90,04
N₈₂Zn₆₂N₈₉	89,97	89,94
N₉Zn₁₃N₄₀	179,16	179,15
N₁₄Zn₁₃N₃₃	179,14	179,12
N₅₈Zn₆₂N₈₉	179,16	178,36
N₆₃Zn₆₂N₈₂	179,14	178,10

Table 6.4.16 shows (RMSD) for the excited Zn-TPP. As for the ground state, the calculation provides a little less planar structure.

Table 6.4.16 Root mean square deviations RMSD (Å) of the atomic positions with respect to the mean plane of the porphyrin ring for Zn-TPP. For the TD B3LYP geometries, the values of both porphyrinate molecules are reported.

Zn-TPP	
B3LYP^{exc}	0.051 – 0.051
XRD	0.000

In table 6.4.17 and 6.4.18 are reported the theoretical geometrical parameters around the metal atom, for the excited state of the Zn-TPP-DMF fragment compared to the corresponding XRD parameters. For the Zn-N

bond, differences show a maximum 0.65 Å, a minimum of 0.12 Å and an average of 0.37 Å. Finally, the two Zn-O bond change of 0.63 and 0.29. Regarding the bond angles (table 6.4.18), the differences ranges from a maximum to 2.32° to a minimum of 0.25° and the average is 1.43°.

Table 6.4.17 Relevant distances (Å) around the metal atom for the excited Zn-TPP-DMF calculated at the TD B3LYP/6–31G(d) level compared to the corresponding XRD parameters.

Zn-TPP-DMF^{exc}	XRD	TD B3LYP
Zn₃₈O₄₄	21.354	21.983
Zn₁₁₅O₁₁₈	21.354	21.644
N₃₉Zn₃₈	20.917	21.034
N₄₅Zn₃₈	20.779	21.037
N₅₁Zn₃₈	20.664	20.995
N₅₅Zn₃₈	20.614	21.178
N₁₁₆Zn₁₁₅	20.917	21.089
N₁₁₉Zn₁₁₅	20.779	21.066
N₁₂₁Zn₁₁₅	20.664	21.310
N₁₂₂Zn₁₁₅	20.614	21.186

Table 6.4.18 Relevant bond angles (°) around the metal atom for the excited Zn-TPP-DMF calculated at the TD B3LYP/6–31G(d) level compared to the corresponding XRD parameters.

Atom	XRD	TD B3LYP
N₃₉Zn₃₈N₅₁	159.46	157.17
N₄₅Zn₃₈N₅₅	161.46	163.66
N₁₁₉Zn₁₁₅N₁₂₂	161.46	163.18
N₁₁₆Zn₁₁₅N₁₂₁	159.46	158.03
N₃₉Zn₃₈N₄₅	87.34	89.66
N₃₉Zn₃₈N₅₅	88.26	90.04
N₅₁Zn₃₈N₅₅	88.97	87.68
N₄₅Zn₃₈N₅₁	88.86	87.94
N₁₁₆Zn₁₁₅N₁₁₉	87.34	88.66
N₁₁₆Zn₁₁₅N₁₂₂	88.26	88.51
N₁₁₉Zn₁₁₅N₁₂₁	88.86	88.34
N₁₂₁Zn₁₁₅N₁₂₂	88.97	87.86

Table 6.4.19 shows RMSD for the excited Zn-TPP-DMF. Comparing the first ring of the fragment, as observed for the ground state, the calculation provides a little more planar structure, while the second ring value is very close to the experimental one.

Table 6.4.19 Root mean square deviations RMSD (Å) of the atomic positions with respect to the mean plane of the porphyrin ring for the excited Zn-TPP-DMF. For the TD B3LYP geometries, the values of both porphyrinate molecules are reported.

Zn-TPP-DMF^{exc}	
TD B3LYP	0.140-0.236
XRD	0.219

In table 6.4.20 and 3.4.21 are reported the theoretical geometrical parameters around the metal atom, for the excited state of the Zn-TPP-DMF (DCM) fragment compared to the corresponding XRD parameters. Regarding the Zn-N bonds, the minimum difference is 0.03 Å, the maximum 0.07 Å and the average amount to 0.04 Å. Finally, the two Zn-O bonds exhibit respectively a difference of 0.06 Å and 0.04 Å.

With regard to the bond angles (table 6.4.21), the differences range from a maximum to 6.68° to a minimum of 0.07° and the average is 2.09°.

Table 6.4.20 Relevant distances (Å) around the metal atom for the excited Zn-TPP-DMF (DCM) calculated at the B3LYP/6–31G(d) level compared to the corresponding XRD parameters.

Zn-TPP-DMF (DCM)^{exc}	XRD	TD B3LYP
Zn₁O₂	2,175	2,238
Zn₇₂O₇₃	2,175	2,220
N₃Zn₁	2,066	2,105
N₄Zn₁	2,059	2,101
N₅Zn₁	2,054	2,102
N₆Zn₁	2,069	2,095
N₇₄Zn₇₂	2,066	2,104
N₇₅Zn₇₂	2,059	2,103
N₇₆Zn₇₂	2,054	2,120
N₇₇Zn₇₂	2,069	2,109

Table 6.4.21 Relevant bond angles (°) around the metal atom for the excited Zn-TPP-DMF (DCM) calculated at the TD B3LYP/6–31G(d) level compared to the corresponding XRD parameters

Atom	XRD	TD B3LYP
N₃Zn₁N₄	164.37	162.5
N₅Zn₁N₆	167.23	160.55
N₇₄Zn₇₂N₇₅	164.37	159.68
N₇₆Zn₇₂N₇₇	167.23	163.23
N₃Zn₁N₅	89.4	88.52
N₃Zn₁N₆	88.71	88.15
N₄Zn₁N₅	87.71	91.51
N₄Zn₁N₆	89.55	91.34
N₄Zn₇₂N₇₅	88.88	88.59
N₇Zn₇₂N₇₆	89.4	88.04
N₇₅Zn₇₂N₇₆	88.71	88.95
N₇₅Zn₇₂N₇₇	89.55	88.57

Table 6.4.22 shows the RMSD for the excited Zn-TPP-DMF (DCM). It is possible to notice that the results of calculation are very close the experimental data; as observed for the ground state, it provides a little more planar structure.

Table 6.4.22 Root mean square deviations RMSD (Å) of the atomic positions with respect to the mean plane of the porphyrin ring for Zn-TPP-DMF (DCM). For the B3LYP geometries the values of both porphyrinate molecules are reported.

Zn-TPP-DMF (DCM)	
B3LYP	0.106 – 0.099
XRD	0.113

Table 6.4.23 shows the computed values of the dipole moment μ , the mean polarizability α , an estimate of the intrinsic molecular hyperpolarizability β , second order susceptibilities $\chi^{(2)}$ and second order susceptibilities ratios with respect to sucrose values, computed on the TD DFT optimized state. The label "micro" indicates the SHG measurements performed with the upright microscope.

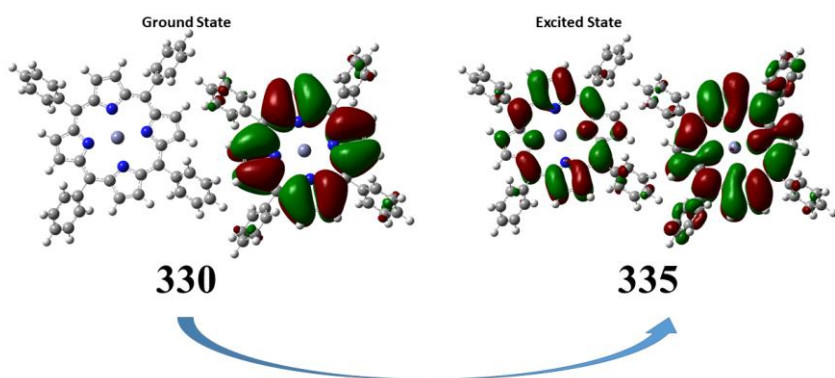
The Zn-TPP and Zn-TPP-DMF(DCM) fragments are characterized by rather high polarizability values, but exhibit very low dipole moment. On the other hands, as for the ground state (see table 6.4.10), Zn-TPP-DMF have higher dipole moment. About the hyperpolarizability and optical susceptibility values of the three compounds, we can notice a huge increase, in agreement with the experimental data provided by the measurements performed with the upright microscope. (see Section 3.4.3).

Table 6.4.23 Excited state structures: Computed dipole moments μ (Debye), mean polarizabilities $\langle\alpha\rangle$ (a.u.), first static hyperpolarizabilities β_{tot} (10^{-30} cm⁵ esu⁻¹), second order susceptibilities $\chi^{(2)}$ (pm V⁻¹), second order susceptibilities ratios with respect to sucrose values. $I^{(2)}/I^{(2)}_{\text{sucrose}}$ value is referred to the standard SHG measurement, while $I^{(2)}/I^{(2)}_{\text{sucrose_micro}}$ to the SHG measurement performed using an upright microscope.

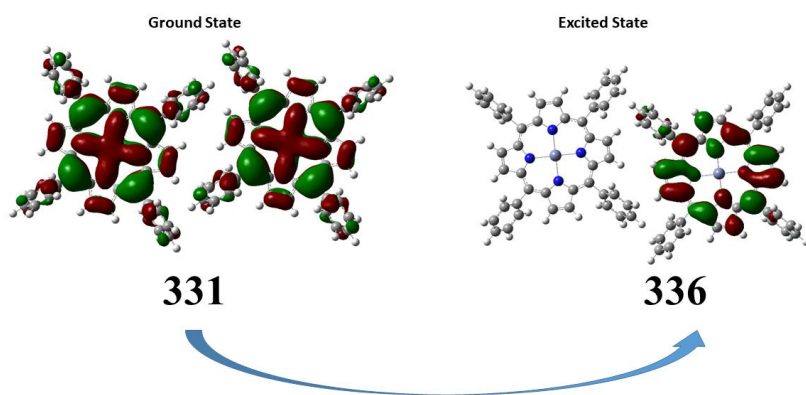
	Zn-TPP	Zn-TPP-DMF	Zn-TPP-DMF(DCM)
μ	0.031	14.096	0.228
$\langle\alpha\rangle$	1398.55	1398.81	1431.15
β_{tot}	481.8	957.7	73.1
$\chi^{(2)}$	88.7	154.7	11.1
$\chi^{(2)}/\chi^{(2)}_{\text{sucrose}}$	62.9	109.7	7.9
$I^{(2)}/I^{(2)}_{\text{sucrose}}$	15	1	1
$I^{(2)}/I^{(2)}_{\text{sucrose_micro}}$	21	29	39

Further consideration can be done focusing on the excited state chosen for optimization and second-order correction. About the Zn-TPP, the transition chosen (Root 1) remains a forbidden transition without change in the spin state ($f=0$, $S^2=0$). The main molecular orbitals involved in this transition are the 330/331/332 (starting MOs, ground state) and the 334/335/336 (arriving MOs, excited state), and they are shown in figure 6.4.4.

Zn-TPP



Zn-TPP



Zn-TPP

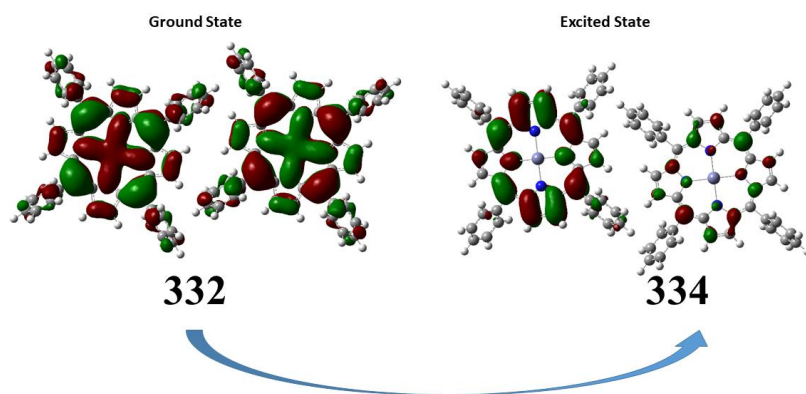
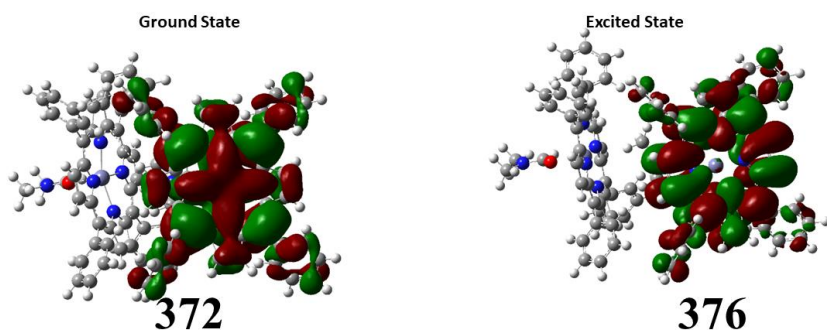


Figure 6.4.4 Plots of the molecular orbitals mainly involved in the excited State 1 of Zn-TPP: 543.63 nm (2.2807 eV), $f=0.0003$, $\langle S^2 \rangle=0.000$, Total Energy, $E(\text{TD-HF/TD-DFT}) = -3956.31958150$. Only transitions with a weight of at least 0.3 are reported.

About the Zn-TPP-DMF, the excited state chosen (Root 4), after the optimization, results to be a weakly allowed transition without change in the spin state ($f=0.04$, $S^2=0$). In this transition, the mainly involved orbitals are the 372/371 (starting MOs, ground state) and the 376/375 (arriving MOs, excited state), and they are shown in figures 6.4.5.

Zn-TPP-DMF



Zn-TPP-DMF

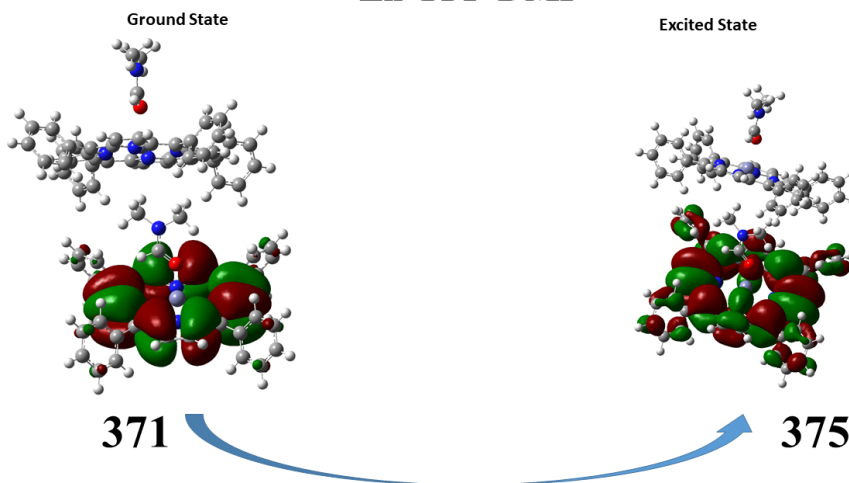
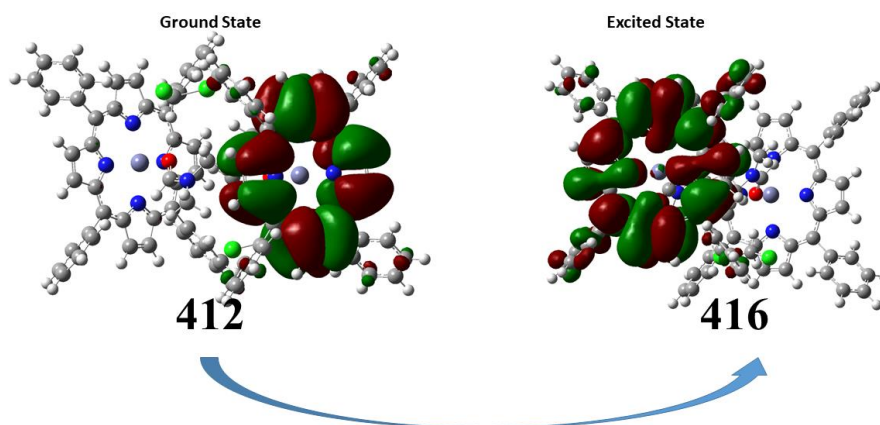


Figure 6.4.5 Plots of the molecular orbitals involved in the excited State 4 of Zn-TPP-DMF: 579.21 nm (2.1406 eV), $f=0.0447$, $\langle S^2 \rangle = 0.000$, Total Energy, $E(\text{TD-HF/TD-DFT}) = -4453.38432114$. All the transitions are reported (weight 0.4 and 0.6 respectively).

About the Zn-TPP-DMF (DCM), the excited state chosen (Root 4) is a weakly allowed transition without change in the spin state ($f=0.02$, $S^2=0$). In this transition, the mainly involved orbitals are the 412/413 (starting MOs, ground state) and the 416/418 (arriving MOs, excited state), and they are shown in figure 6.4.6.

Zn-TPP-DMF(DCM)



Zn-TPP-DMF (DCM)

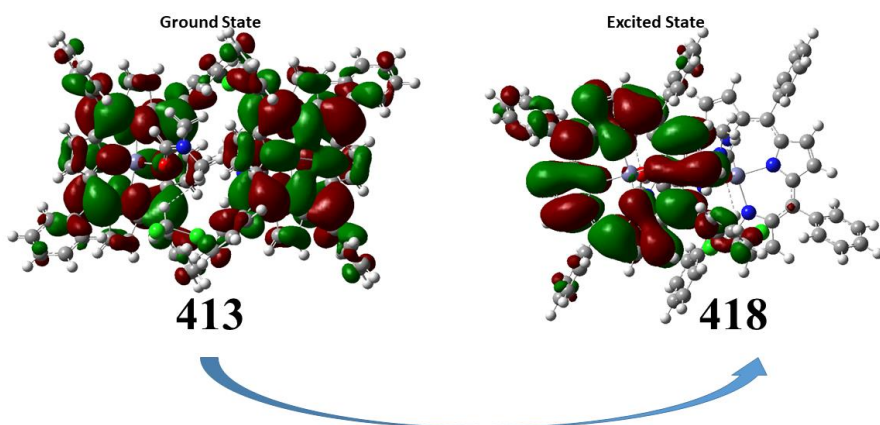


Figure 6.4.6 Plots of the molecular orbitals mainly involved in the excited State 4 of Zn-TPP-DMF (DCM): 553.45 nm (2.2402 eV), $f=0.0203$, $\langle S^2 \rangle=0.000$, Total Energy, $E(\text{TD-HF/TD-DFT}) = -6372.77769200$. Only transitions with a weight of at least 0.4 are reported.

Comparing the plots obtained for these three complexes with the ones obtained for the Cu-TPP (Fig 5.4.3), we can't see the same strong charge

transfer character previously observed. Further investigation about the MOs and their contribution to the transition are ongoing.

7.New crystalline materials based on Co (II) Tetrakis-nitro-phenylporphyrin (Co-TNPP) and Zn(II)Tetrakis-nitro-phenylporphyrin (Zn-TNPP): synthesis, characterization and SHG behavior

7.1. Synthesis of Co-TNPP and Zn-TNPP

The complexation of the TNPP was carried out in boiling N, N-dimethylformamide (DMF), where the 0.28 mmol of porphyrin and 0.45 mmol of Zinc/Cobalt acetate had been dissolved, for about half an hour. The Zn/Co-TNPP complexes obtained were precipitated adding water, filtered and air-dried.

The powder of Zn-TNPP was purified by dissolution in dichloromethane (DCM) and re-crystallization through partial evaporation of the solvent. The crystalline powder was filtered and washed with a few drops of DCM.

The powder of Co-TNPP was purified by dissolution in toluene and re-crystallization through partial evaporation of the solvent. The crystalline powder was filtered and washed with a few drops of toluene.

7.2. Characterization of Co-TNPP and Zn-TNPP

The purity of the compounds was checked by absorption spectroscopy.

Figure 7.2.1 reports the absorption UV-Vis spectrum of Co-TNPP, Zn-TNPP, and H₂TNPP for comparison, recorded in chloroform, which confirm the complexation for both compounds.

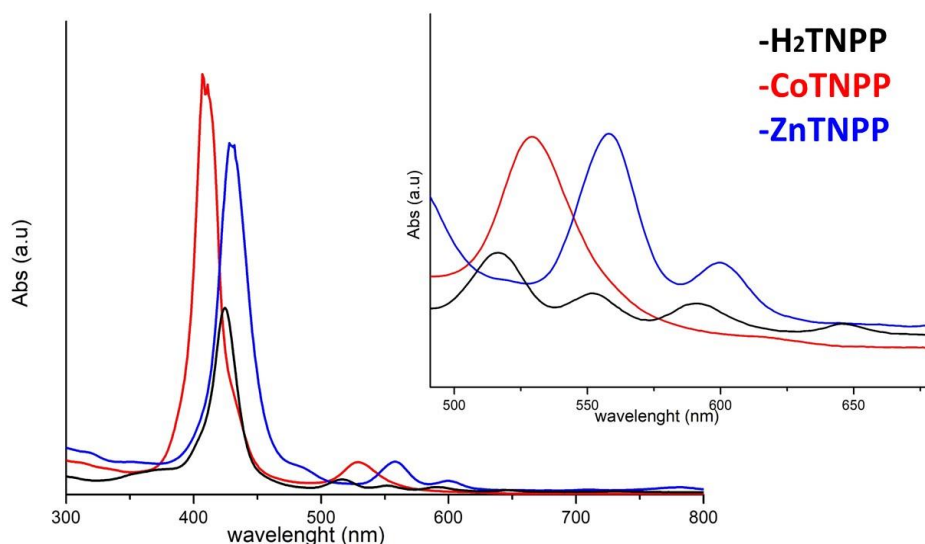


Figure 7.2.1 UV-Vis spectrum of the Co/Zn-TNPP, compared with the H₂TNPP spectrum. All the spectra were recorded in chloroform solution.

For both compounds, we obtained a single crystals suitable for the XRD analysis. X-ray diffraction data were collected at room temperature for Co-TNPP, and at 100 K for Zn-TNPP, since the resolution of the last compound from data at room temperature was not accurate. The crystallization solvent (toluene for Co-TNPP, and DCM for Zn-TNPP) was highly disordered, and cannot be resolved in the difference Fourier maps. Thus, the Olex option "solvent mask" was used for both compounds. Further details on crystal data, data collection, and least-squares refinements, are reported in the Appendix (Table 10.1.24).

Figure 7.2.2 shows the asymmetric unit of Co-TNPP compound, which is composed of half a molecule of Co-TNPP. Figure 7.2.3 illustrates how the Cobalt atom of a molecule is coordinated by one of the four nitro group of another molecule, resulting in a 3D structure (3D Metal Organic Framework). Figure 7.2.4 provides a view of the crystal packing of Co-TNPP. In addition, lists of bond length and bond angles for Co-TNPP are provided in Appendix (Tables 10.1.25 and 10.1.26).

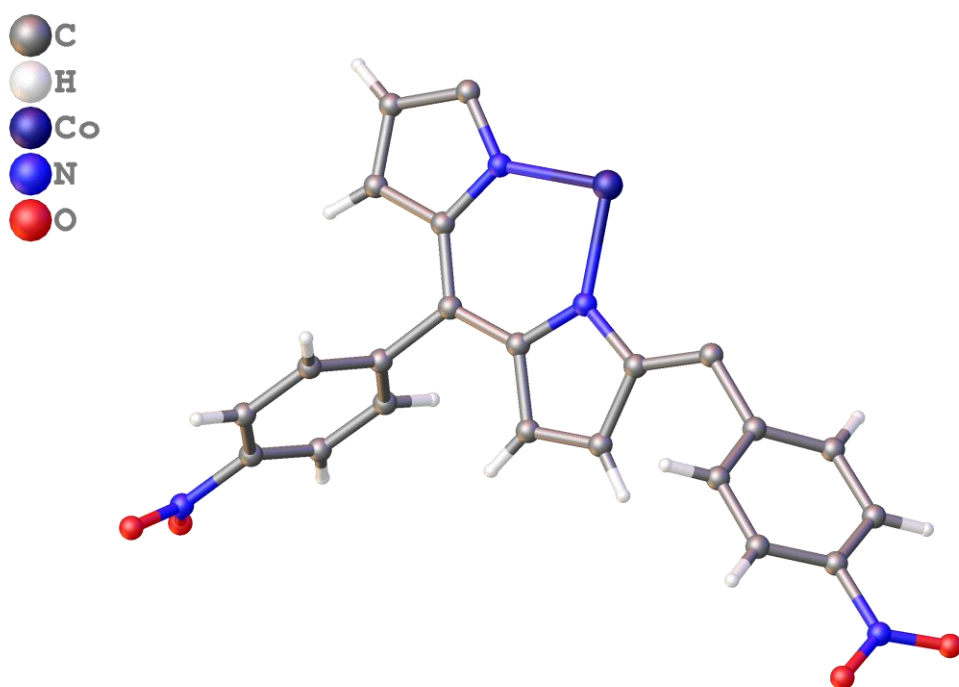


Figure 7.2.2 View of the asymmetric unit of the compounds Co-TNPP

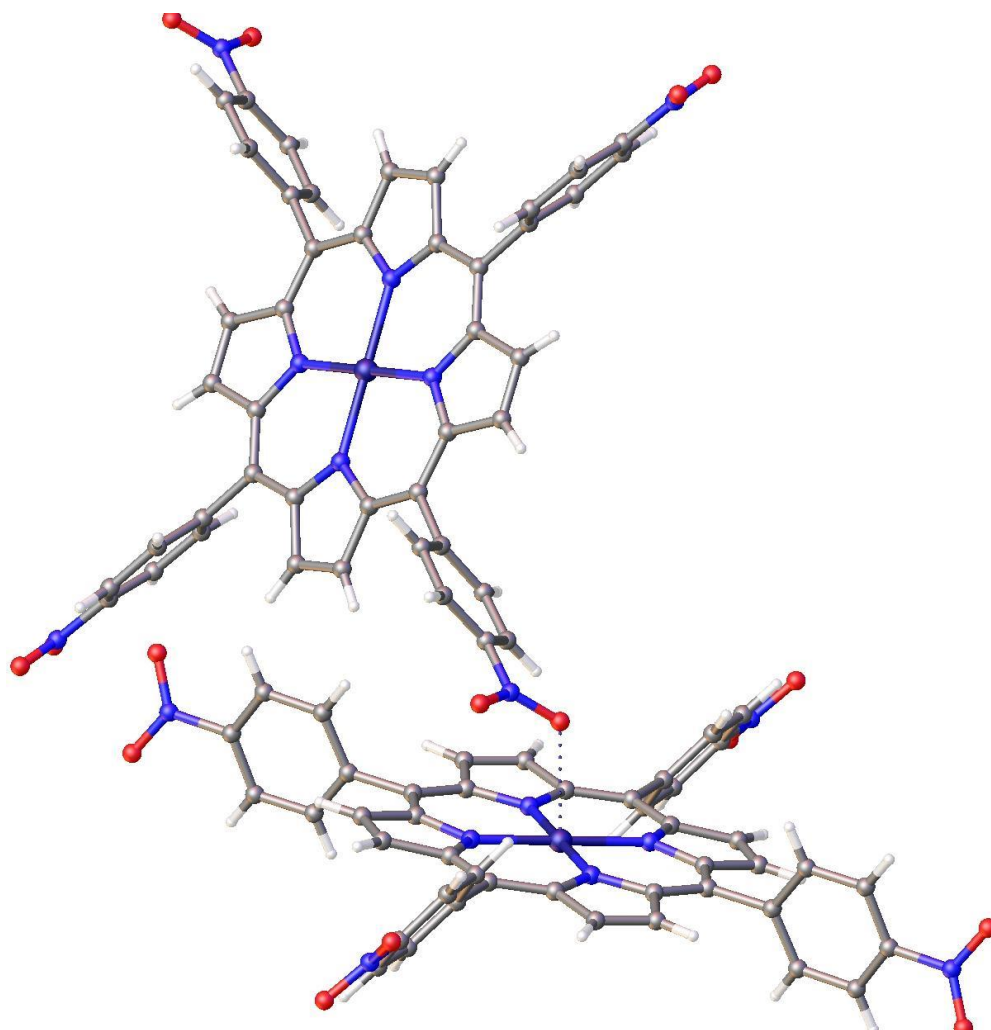


Figure 7.2.3 The Cobalt atom coordinated by a porphyrin ring also coordinates an O atom of an O-N-O group in another porphyrin ring.

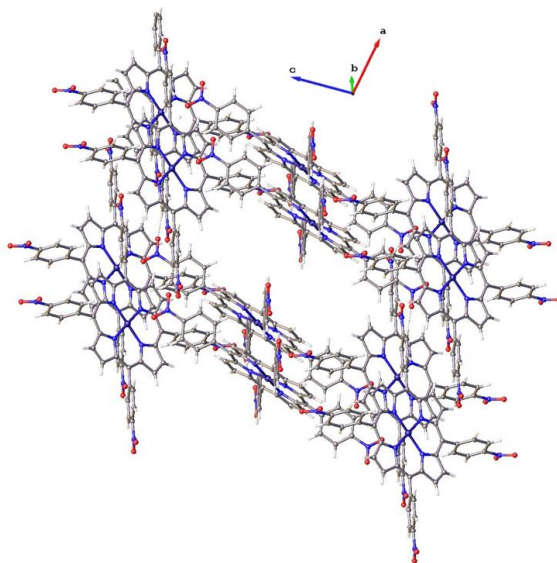


Figure 7.2.4 View of the crystal packing of Co-TNPP.

Figure 7.2.5 shows the asymmetric unit of Zn-TNPP, which is composed of the whole molecule. Figure 7.2.6 illustrates how the Zinc atom of a molecule is coordinated by one nitro group of another molecule, resulting in a 3D structure (3D Metal Organic Framework). Figure 7.2.7 provides a view of the crystal packing of Zn-TNPP. Lists of bond length and bond angles for Zn-TNPP are reported in Appendix (Tables 10.1.27 and 10.1.28).

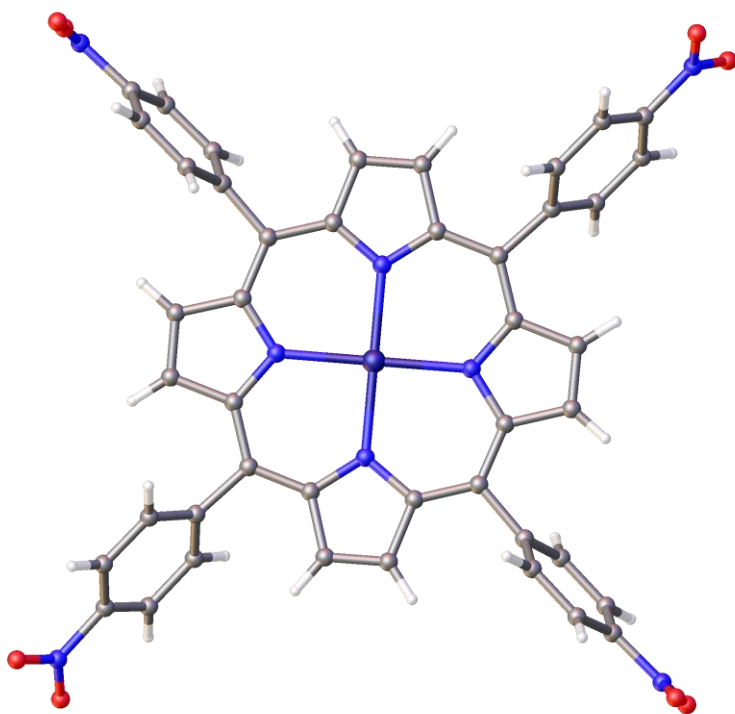
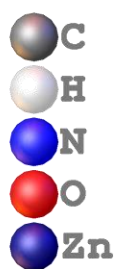


Figure 7.2.5 View of the asymmetric unit of the compounds Zn-TNPP (DCM)

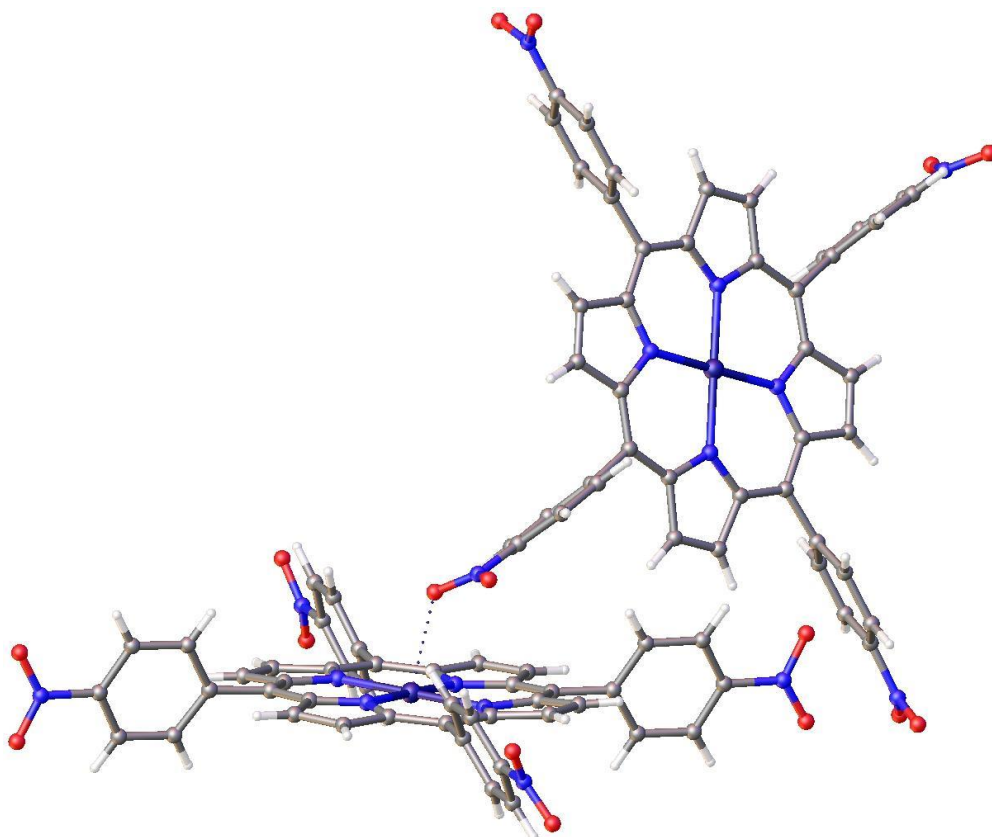


Figure 7.2.6 The Zinc atom coordinated by a porphyrin ring also coordinates an O atom of an O-N-O group in another porphyrin ring.

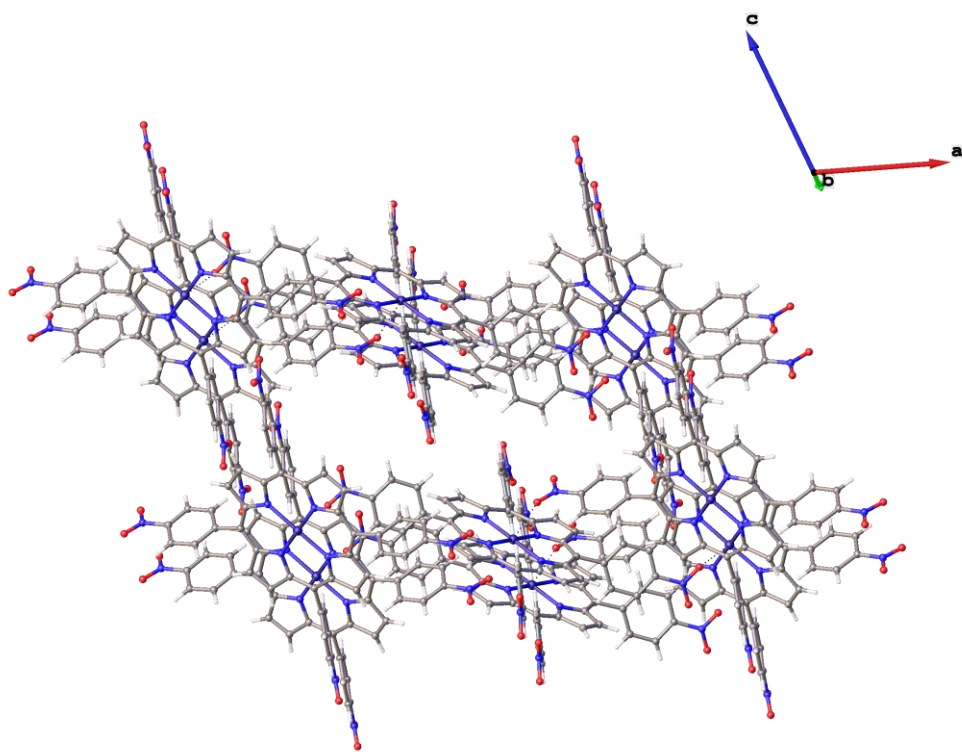


Figure 7.2.7 View of the crystal packing of Zn-TNPP (DCM) along the [010] crystallographic direction.

7.3. SHG behavior of Co-TNPP and Zn-TNPP

Co-TNPP shows, under laser irradiation, a non-null SHG signal, which gradually increases until it reaches a plateau at approximately fifty times the initial value, the same behavior observed in Co-, Cu-, and Ni-TPP.

Instead, Zn-TNPP produces a stable SHG signal close to that of standard sucrose, even after prolonged laser irradiation. Thus, it shows the same behavior already observed for Zn-TPP-DMF and Zn-TPP-DMF(DCM).

Further analyses and theoretical studies are underway, as for the compounds previously considered.

8.APPLICATIONS

8.1. Cobalt-tetraphenylporphirinate-chitosan microspheres for multi-theranostic applications

In Chapter 4, the SHG behavior of Co-5,10,15,20-tetraphenylporphyrinate (Co-TPP) in the solid state was analyzed, and a remarkable enhancement of the SHG emission was observed after a few minutes of irradiation of the powdered sample with a nanosecond Nd:YAG pulsed laser (1.907 μm). This behavior stimulated us to study this material for SHG biosensing. Furthermore, as a consequence of the irradiation, the magnetic moment of the powder increased by approximately three times, and the crystals blew up, scattering many crystalline fragments in the capillary. In other words, the CoTPP crystals were photoresponsive, i.e. they responded to an external laser light stimulus by an enhancement of the magnetic moment, and also by macroscopic mechanical motion (dynamic crystals)¹. Furthermore, to destroy cancer cells, the magnetic nanoparticles can also be mechanically activated under a low-frequency magnetic fields². The enhancement of the magnetic moment is of particular interest, since in anticancer therapy magnetic particles are studied for hyperthermia treatments, i.e. applying an alternating magnetic field to magnetic particles encapsulated in a cancer tissue, they can heat the tissue and kill the cancer cells³.

We propose the use of nanoparticles of Co-TPP for diagnosis, due their remarkable fluorescent and SHG properties, and for therapeutics, exploiting their magnetic and SHG-dynamic properties; thus, they can be employed for multi-theranostic purposes. However, for the biological applications, it is necessary to cover the nanoparticles with a suitable bio-compatible material, which can be further functionalized in order to drive them toward cancer cells. In this work, we experimented the coating of Co-TPP nanoparticles with a very cheap, bio-compatible, and non-toxic polysaccharide, the chitosan.

Chitosan (CS) consists of β (1-4)-linked 2-amino-2-deoxy-D-glucose (D-glucosamine) and 2-acetamido-2-deoxy-D-glucosamine (N-acetyl-D-glucosamine) units, and it shows some structural similarities with cellulose^{4,5}. It is considered a versatile material for various biological applications, including the coating of solid nanoparticles that will be introduced into biological cells^{6,7}. In fact, chitosan nanospheres were proposed as drug delivery systems, since their surface can be easily functionalized^{8,9,10}.

Previously, my research group, in collaboration with the Universidad Autonoma de Mexico (UNAM), developed the synthesis of chitosan-based

nanospheres with Sr^{2+} ions encapsulated¹¹, to apply as SHG biosensors, and contemporary as carriers of ^{89}Sr radionuclide for radiopharmaceutical treatments in cancer therapy. The results encouraged us to attempt the encapsulation of porphyrinate-based particles into chitosan spheres, to allow the exploitation of the biosensing and therapeutic properties of the solid porphyrinates.

Thus, in this work we report the synthesis of new Co-TPP-chitosan based microspheres (Co-TPP-CS-MPs), characterized with X-ray powder diffraction (XRPD), Optical and Scanning Electron (SEM) Microscopy. Finally, their SHG behavior was investigated with a high resolution SHG microscope, in order to investigate their possible application as SHG biosensors, and for anticancer therapeutic purposes.

8.1.1 Experimental

For the chitosan microspheres (CS-MPs), all chemicals utilized were purchased from Sigma-Aldrich and used as received. The acetic acid was HPLC-grade, and the CS powder was medium-molecular weight, with a 75–85% degree of deacetylation. The polyvinylalcohol (PVA) has 99% degree of hydrolysis and a typical average molecular weight (Mw) of 89,000–98,000 g/mol.

Chitosan (CS) powder was dissolved in a 1% (w/v) acetic acid water solution, under magnetic stirring for 24 h at room temperature. A 2.5% w/v chitosan solution was obtained. PVA was dissolved in deionized water under magnetic stirring at 80 °C for two hours, to obtain a 10% w/v solution. The two hydrogels were then mixed at CS:PVA 3:1 volume ratio, and leaved under magnetic stirring at room temperature for about two hours. A homogeneous polymeric blend was obtained.

A solution containing SPAN 80 (1%) and polyisobutylene liquid or NF70 was stirred with an Ultra Turrex dispenser at 12,000 rpm. The CS/PVA polymeric blend was then added drop by drop. Finally, the crosslinker glutaraldehyde (GA, analytical grade, 50% w/v) was added, and the emulsion was subjected to magnetic stirring for 40 minutes. After the centrifugation of the emulsion, the polymeric hybrid CS/PVA/GA microspheres (CS-MPs) were collected at the bottom of the test tube, and were washed with two aliquots of hexane and two aliquots of water. The CS-MPs are conserved in water suspension, to avoid the agglomeration of particles.

For the Co-TPP-loaded chitsan-based microspheres (Co-TPP-CS-MPs), the powder of Co-TPP was ground in a TMAX-DSP-LT01 Planetary ball mill,

equipped with 50mL ZnO jars and ZnO balls of 4 mm diameter. The grinding parameters were: 60 minutes at 500 rpm, with 8-minutes cycles clockwise and counterclockwise, and 1 minute break.

The Co-TPP particles were encapsulated in the chitosan matrix, following the same procedure used to prepare the CS-MPs, except that the Co-TPP particles were suspended in the CS/PVA polymeric blend: different amounts (0.6% m/m, 1% m/m, 1.5% m/m and 3% m/m) of Co-TPP were alternatively added to the aqueous solution of PVA and sonicated until the suspension became homogeneous (20-30 minutes for the 0.6%, 1 h for 1% and 1.5% and 1.5 h for the 3%), and then the suspension was mixed with the CS solution to form the hydrogel.

The optical microscope used is an OMAX 40X-2500X Digital Lab Trinocular Compound LED Microscope, equipped with a 5MP Digital Camera.

Field-Emission Scanning Electron Microscopy (FESEM) and EDS were performed using a TESCAN S9000G FESEM 3010 microscope working at 30kV and equipped with a high-brightness Schottky emitter. For the microanalysis, the OXFORD Ultim Max-software Aztec was used. To average the measurements of the nanospheres, the program ImageJ was used¹².

The diffraction pattern was collected using a Bruker D8 Advance diffractometer, equipped with Ni-filtered Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). All patterns were recorded over the 2θ range 5° – 70° , with a scan rate of $0.4^\circ/\text{min}$.

The second harmonic generation (SHG) efficiency of the samples was assessed in comparison to sucrose powder, using an upright microscope (BX51WI, Olympus, Tokyo, Japan) paired with a scanning unit (FluoView FV300, Olympus, Tokyo, Japan). The SHG signal was detected by scanning the samples point by point with high resolution and excitation efficiency, through an objective lens (UPLSAPO 20x, NA = 0.75, Olympus). The excitation source was a pulse output tuned to 930 nm, with a duration of about 2 ps, and a repetition rate of 80 MHz, generated by an Optical Parametric Oscillator (Levante Emerald OPO) (APE, Berlin, Germany). The Oscillator was pumped by a Yb-fiber laser (Emerald Engine HP, APE, Berlin, Germany), emitting at approximately 516 nm, also with a pulse duration of around 2 ps and a repetition rate of 80 MHz.

The SHG signal, detected around 465 nm, was optically filtered within the range of 330 – 480 nm (using FF01-405/150 Semrock), and collected in a back-scattering configuration (epi-detection) via one of two PMT detectors located in the microscope scanning head. The same PMT gain, voltage, and offset settings were applied for all samples.

The Co-TPP powder was simply spread on the slide, while for the CS-MPs and the Co-TPP-CS-MPs a drop of the suspension was placed on a glass microscope slide, and allowed to dry. Before the samples were examined under the microscope, a rectangular coverslip was adhered to each slide to avoid the eventual dispersion of the samples. The samples were irradiated using the excitation pulse at 930 nm, and an average power over the sample of about 30 mW.

8.1.2 Results and Discussion

In order to obtain the polymeric hybrid CS/PVA/GA microspheres (CS-MSs), we used the o/w emulsion method already reported in our previous work¹¹. In addition, to prepare the o/w emulsion, we also tested the less dense oil NF70 as replacement for polyisobutylene liquid. Due to its lower density, the cosmetic NF70 oil facilitate the diffusion of glutaraldehyde into the microspheres, and improved the reaction yield. Furthermore, it is cheaper with respect to the polyisobutylene. Thanks to this exchange, the total mass of the product switched from a mode of 0.1 g to a mode of 2.5 g.

In Figure 8.1.1 are reported the images, obtained through the optical microscopy, of the CS-MSs synthesized with polyisobutylene oil with 1ml of GA (Figure 8.1.1 a), and those synthesized with NF70 with 1, 0.5, and 0.25 ml of GA (Figures 8.1.1 b, c, and d, respectively). Considering the same amount of GA (Figures 8.1.1 a and b), the microspheres produced with polyisobutylene are smaller and more homogeneous in size with respect to the microspheres produced with NF70; however, the larger size of the microspheres synthesized with NF70 suggested the possibility of an easier loading of the Co-TPP particles. Furthermore, with polyisobutylene the yield is very low, while with NF70 the yield is much more significant. For these reasons, we decided to proceed with the microspheres produced with NF70, optimizing the amount of GA used. Comparing the Figures 8.1.1 b, c, and d, it is clear that a good compromise between homogeneity of the size of the microspheres and their yield is obtained using 0.5 ml of GA (Figure 8.1.1 c).

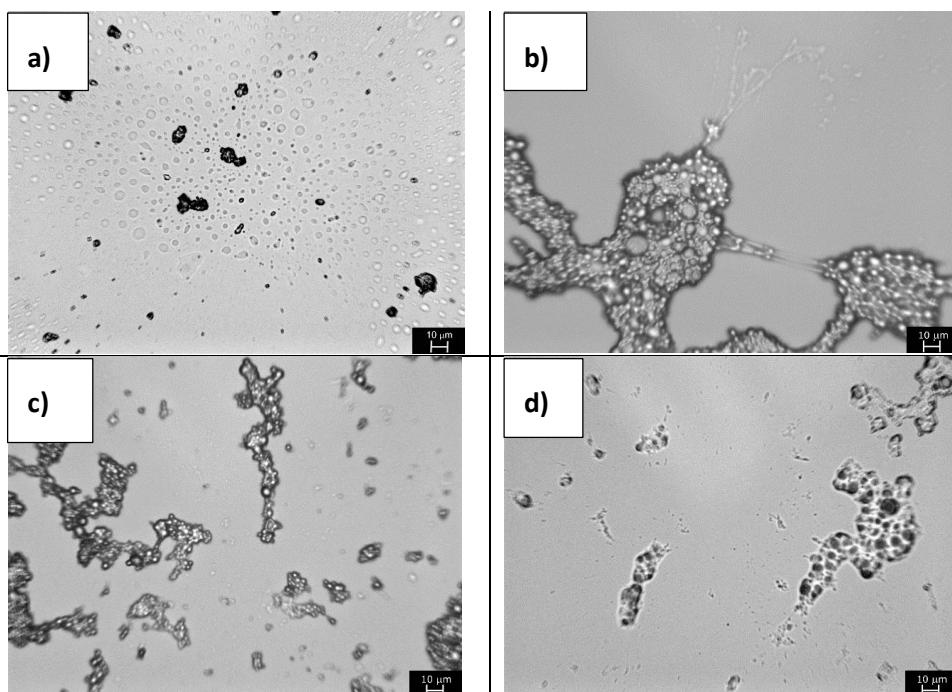


Figure 8.1.1 Optical microscopy images, at the magnifications of 40x, of CS-MPs synthesized with polyisobutylene (a), CS-MPs synthesized with NF 70 and 1 ml (b), 0.5 ml(c), or 0.25 ml (d) of GA

To prepare the Co-TPP-CS-MPs, the solid Co-TPP was vigorously ground with a planetary ball mill. In Figure 8.1.2 is reported a SEM image of the nanoparticles, in which were measured particles in the range $50 \div 150$ nm. In figure 8.1.3 the XRPD pattern of the Co-TPP nanoparticles is compared to the XRPD pattern calculated from the single crystal X-ray structure (CCDC 2130187), to confirm that the sample was not degraded during the high energy grinding. Even if the dimension of the nanoparticles is low, the XRPD pattern does not show enlarged peaks, which confirm the crystal structure remains unaltered after the grinding.

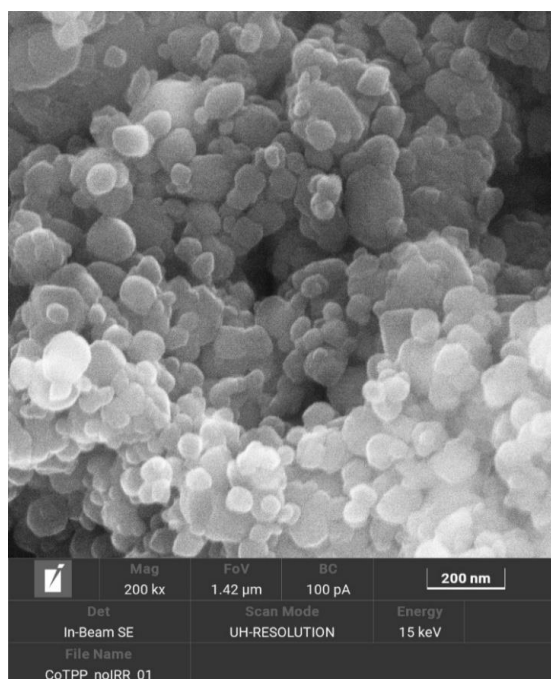


Figure 8.1.2 SEM image of Co-TPP nanoparticles.

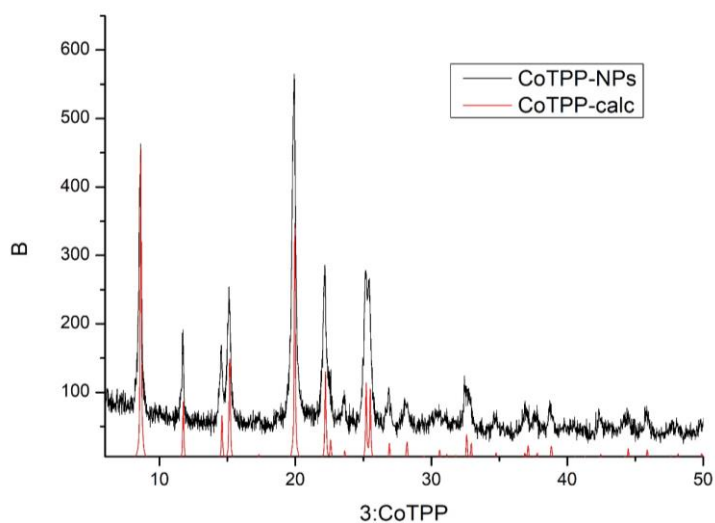


Figure 8.1.3 XRPD pattern of Co-TPP nanoparticles (black line), compared to the XRPD pattern calculated from the single crystal X-ray structure (red line).

Before proceeding with the encapsulation of the Co-TPP with chitosan, we checked its persistence both in the CS/PVA hydrogel and in the mineral oil used for the synthesis. In figure 8.1.4 are reported the images recorded with an Optical microscope of the CS/PVA hydrogel alone (a), the Co-TPP nanoparticles suspended in the CS/PVA hydrogel (b), in polyisobutylene liquid (c), and in NF70 (d). The pictures show that the Co-TPP nanoparticles were not dissolved by the CS/PVA hydrogel, nor in the mineral oils. Furthermore, the Co-TPP nanoparticles suspended in NF70 (d) are less agglomerated and well dispersed with respect to those dispersed in polyisobutylene (c).

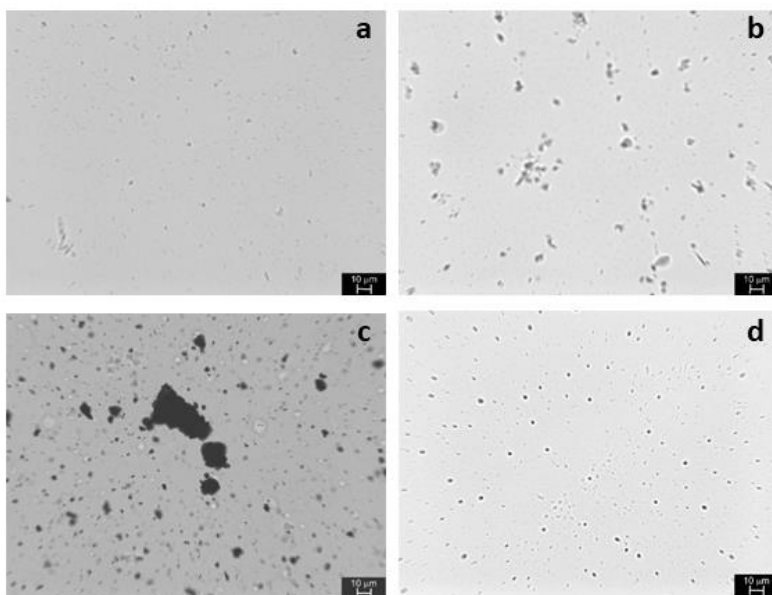


Figure 8.1.4 Optical microscopy images, at the magnification of 40x, of the CS/PVA hydrogel (a), the Co-TPP/CS/PVA suspension (b), the Co-TPP nanoparticles suspended in polyisobutylene (c), and in NF70 (d).

To encapsulate the Co-TPP into chitosan microspheres, a suspension of Co-TPP nanoparticles in an aqueous solution of polyvinylalcohol (PVA) was sonicated until became homogeneous. This suspension was used in place of the CS/PVA hydrogel used for the synthesis of the CS-MSs, and the same procedure was followed.

We performed TEM analysis in order to compare CS-MPs morphology and particle dimensions with Co-TPP-CS-MPs.

TEM images of CS-MPs confirm the morphology and dimension already obtained¹¹ (see Fig 8.1.5). For Co-TPP-CS-MPs we can see how the presence of metal-organic nanoparticles affects the morphology and the dimension. The nanosphere of CS-MPs shown in Figure 8.1.5 a is approximately 0.5 microns in diameter, while the one of Co-TPP-CS-MPs shown in Figure 4.1.5 b appear to be larger.

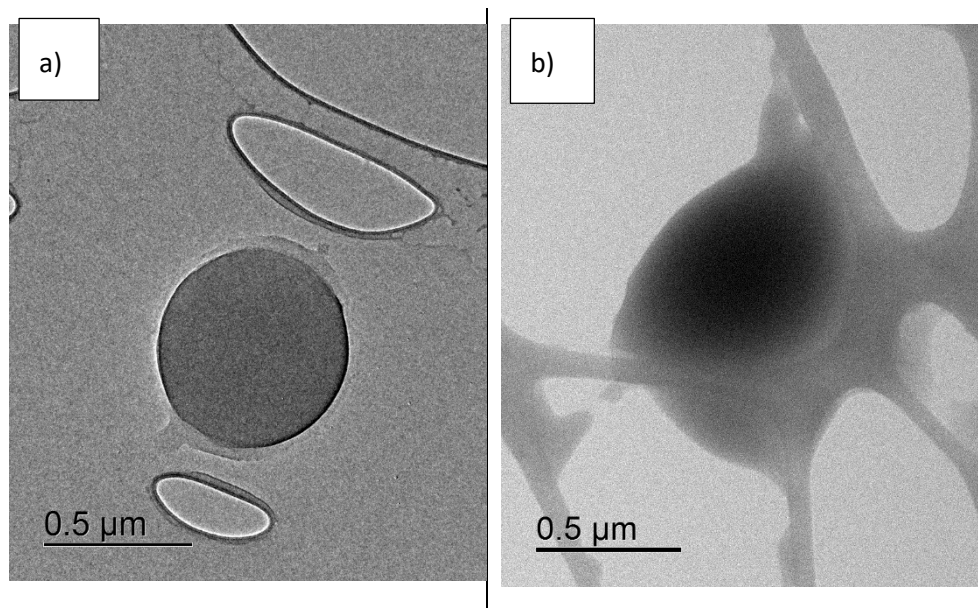


Figure 8.1.5 TEM images of a) CS-MPs and b) Co-TPP-CS-MPs nanoparticles.

In order to optimize the yield vs the microspheres features, different concentrations (1.0%, 1.5%, and 3.0% w/w) of Co-TPP nanoparticles were tested. The highest concentration (3.0% w/w) resulted in a small loss of Co-TPP during the hexane washing process, since the hexane used to wash the Co-TPP-CS-MPs was pink colored.

In figure 8.1.6, are reported the SEM images of the Co-TPP-CS-MPs obtained with the three Co-TPP concentrations tested. In the first sample, the dimensions there are many small spherical particles (1.5 μm) and some larger not spherical (5 μm). Comparing this results with the TEM (Fig 8.1.5), where the smaller particles where not loaded with Co-TPP, it is possible to hypnotize that not all the CS-MPs are converted in Co-TPP-CS-MPs during the Co-TPP loading, so the empty one are smaller.

In the other two samples, no differences in morphology and dimensions were observed.

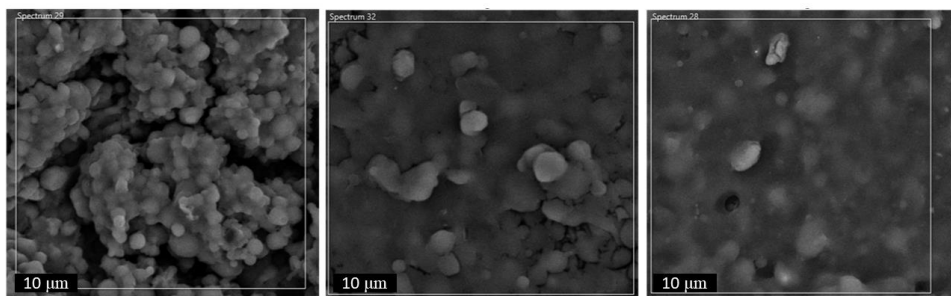


Figure 8.1.6 SEM microscopy images of the Co-TPP-CS-MPs synthesized with 1.0% (a), 1.5% (b), and 3.0% w/w of the Co-TPP nanoparticles.

In the sample with 1.0% w/w of Co-TPP, the SEM-EDS analysis evidence a non-homogeneous distribution of cobalt, in the range $0.0 \div 0.1\%$, close to the tool's detection limit. Instead, the sample with 1.5% w/w of Co-TPP, the distribution of cobalt is more uniform, with values that are around 0.2%. Also, in the sample with 3.0% w/w of Co-TPP the distribution of cobalt is not homogeneous: in most areas the concentration of Co is in the range $0.0 \div 0.2\%$, but there are bigger aggregates that contain a significantly larger amount of Co (around 5.1%), evidencing the non-homogeneity of the sample. Thus, we concluded that the sample with the best features is the one synthesized with 1.5% of Co-TPP.

SHG measurement were performed on the Co-TPP nanoparticles, on the CS-MPs, and on the Co-TPP-CS-MPs synthesized with 1.5% of Co-TPP nanoparticles.

The efficiencies of the samples were compared to sucrose.

In section 3.1 we described the peculiar behavior of the Co-TPP powder under irradiation with a 1907 nm pulsed laser: during laser irradiation, a gradual increase of the intensity of the SH signal was observed until, after a few minutes, it reached a plateau of about fifty times the initial value. After this activation of the powder, it was able to emit the SH light under irradiation for a long time, directly starting from the value of the plateau. For this reason, the Co-TPP is a good candidate for the production of SHG bio-sensors. Furthermore, the crystals of the powder during irradiation vigorously jumped

inside the capillary, i.e. they showed a prominent photodynamic property that should be exploited for an eventual therapy against cancer cells. However, in order to apply Co-TPP in bio-sensing we have to demonstrate that the synthesized Co-TPP-CS-MPs maintain the same features.

We irradiated the samples with a 930 nm pulsed laser, since for bio-sensing application the SHG response should be in the visible spectrum (in this case 465nm): the Co-TPP powder showed the same SHG behavior as with the 1907 nm radiation. In particular, the movement of the crystals was so vigorous that it was necessary to cover the powder with a coverslip, to avoid the loss of the sample.

The CS-MPs when irradiated show a significant SH emission, as expected, and the microspheres' shape is evident in the pictures (Fig 8.1.7 a). However, after a few seconds their SH emission suddenly disappears, probably because they are degraded by the laser energy, and the image goes completely dark (Fig 8.1.7 b). The Co-TPP-CS-MPs (Fig 8.1.7 c and d), instead, show a behavior similar to the Co-TPP powder (Fig 8.1.7 e and f), except for the signal propagates in all the sample more slowly, probably because there is a lower concentration of Co-TPP particles with respect to the Co-TPP powder, or also because the presence of the CS cover should limit the contact between the Co-TPP particles. In any case, after a longer time the SH intensity remains globally constant, except for the zones in which the Co-TPP particles move away.

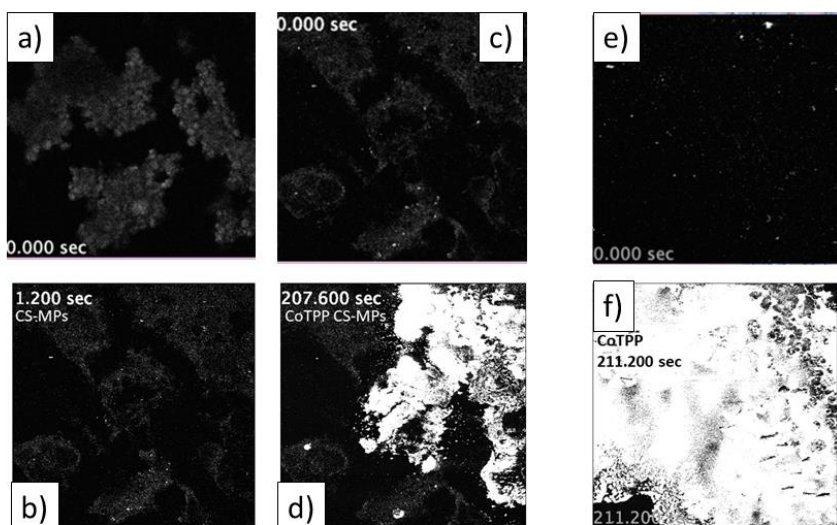


Figure 8.1.7 CS-MPs at the start of irradiation (a), CS-MPs at the end of irradiation (b), Co-TPP-CS-MPs at the start of irradiation (c) and Co-TPP-CS-MPs at the end of irradiation (d), Co-TPP at the start of irradiation (e) and Co-TPP at the end of irradiation (f). SHG signal at 930 nm with excitation power on the sample of about 33 mW (2 ps pulse 80 MHz).

To achieve a more accurate estimation of the SHG efficiency across various samples, the SHG signals produced by the samples were captured at 20 different excitation power levels. These SHG images were processed using a specialized algorithm, developed on the ImageJ¹² platform, to extract the average intensity of the foreground objects for each power level. A quadratic fit was performed on these average values ($y=bx^2+c$), yielding a parameter b that is proportional to the characteristic hyperpolarizability β of the materials, and thus represent the SHG efficiency of the material. In the Figures 8.1.8, 8.1.9, 8.1.10 and 8.1.11 are reported the intensity vs excitation power with quadratic fitting curve for b parameter extraction for sucrose and for each sample. In table 8.1.1 are reported the values of the parameters.

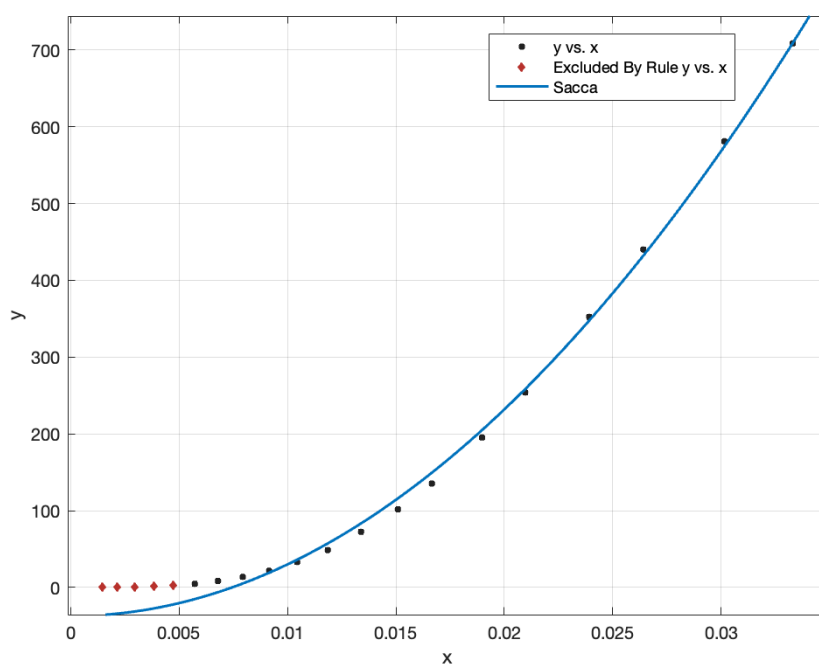


Figure 8.1.8 Sucrose SHG intensity vs excitation power with quadratic fitting curve for b parameter extraction

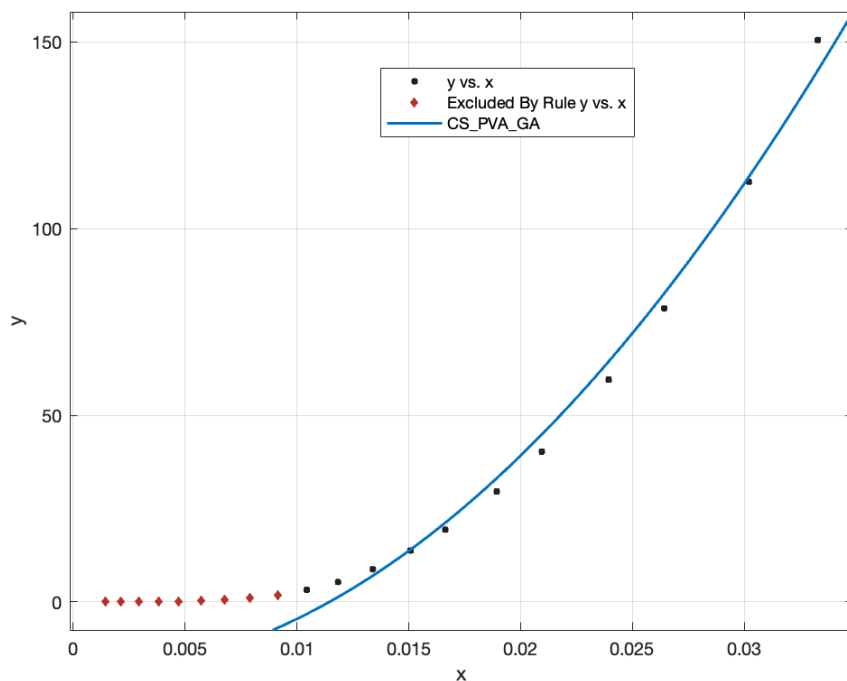


Figure 8.1.9 CS-MPs SHG intensity vs excitation power with quadratic fitting curve for b parameter extraction

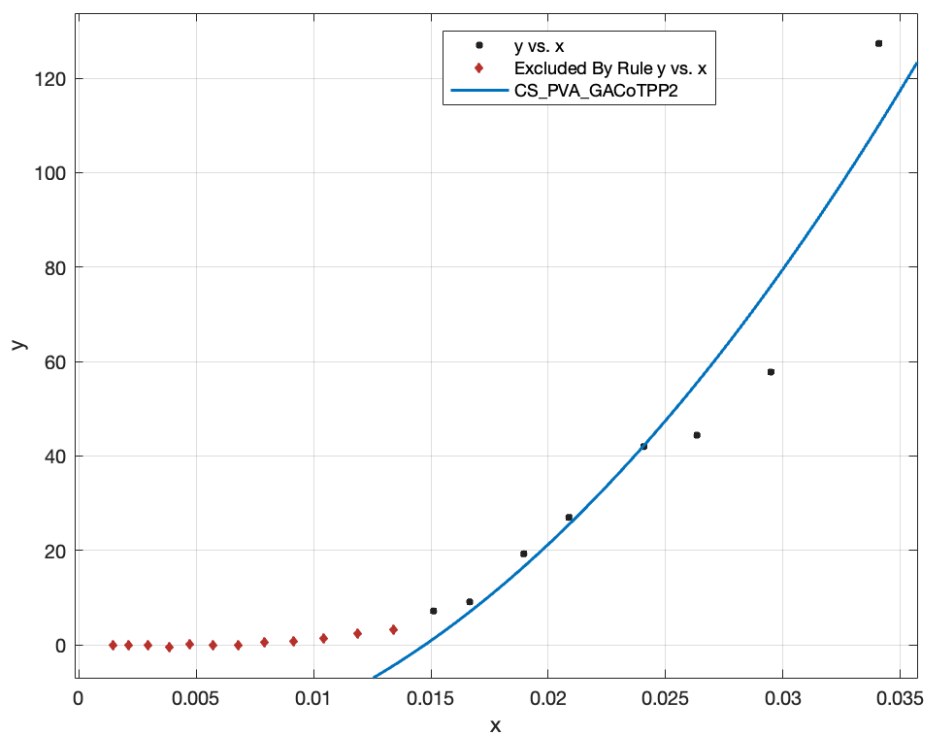


Figure 8.1.10 CS-Co-TPP MPs SHG intensity vs excitation power with quadratic fitting curve for b parameter extraction

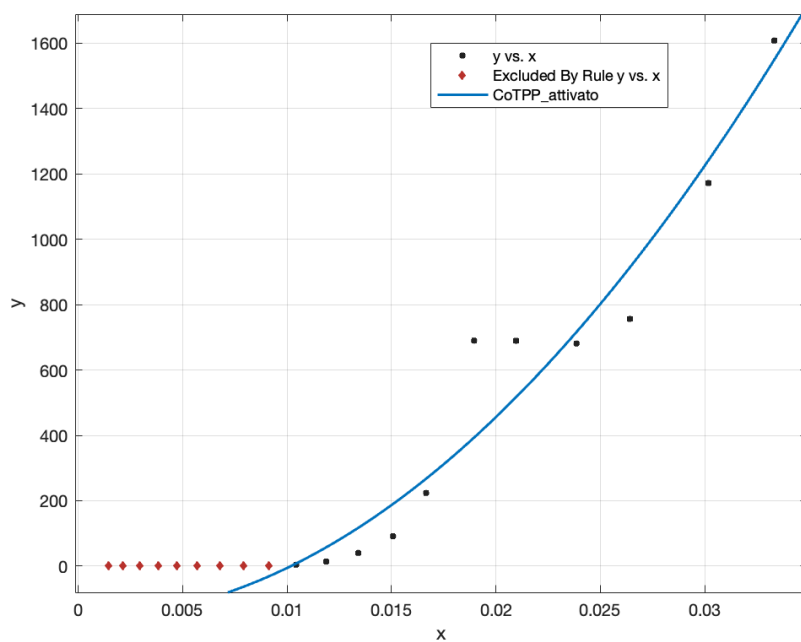


Figure 8.1.11 Co-TPP powder activated SHG intensity vs excitation power with quadratic fitting curve for b parameter extraction

Table 8.1.1 Values of the fitting parameters

Sucrose	value	lower	upper	R-square	SSE	adj-R-square
b	$6.73 \cdot 10^5$	$6.54 \cdot 10^5$	$6.92 \cdot 10^5$	0.99781	1554.5	0.99764
c	-37.214	-46.205	-28.223			
CS-MPs						
b	$1.46 \cdot 10^5$	$1.35 \cdot 10^5$	$1.56 \cdot 10^5$	0.97364	906.7	0.97217
c	-19.145	-24.91	-13.381			
Co-TPP-CS-MPs						
b	$1.16 \cdot 10^5$	$8.31 \cdot 10^4$	$1.50 \cdot 10^5$	0.92388	805.03	0.9112
c	-25.302	-46.989	-3.615			
Co-TPP NPs activated						
b	$1.54 \cdot 10^6$	$1.24 \cdot 10^6$	$1.84 \cdot 10^6$	0.9482	$2.2 \cdot 10^5$	0.94536
c	-159.612	-325.244	6.020			

The ratios of the related b parameters (Table 8.1.2) show that Co-TPP powder activated has higher SHG efficiency than sucrose, while the CS-MPs and non-activated Co-TPP-CS-MPs have similar values with the latter slightly lower. This difference could be related to a probable Co-TPP light absorbance or poor transparency.

Table 8.1.2. Ratios of the related b parameters.

$b_{sample}/b_{sucrose}$ values	Averaged	lower	upper
Sucrose	1.00	1.00	1.00
CoTPP	2.28	1.90	2.66
CS-MPs	0.22	0.21	0.23
CoTPP-CS-MPs	0.17	0.13	0.22

8.1.3 Conclusions

The solid Co-TPP was reduced to nanoparticle size of about 25 nm². Then, the Co-TPP nanoparticles were encapsulated into chitosan microspheres (CS-MPs) of approximately 0.7 μ m of diameter. TEM/SEM analyses were performed to verify the size, morphology and composition of the products. It was confirmed that chitosan microparticles with the Co-TPP nanoparticles encapsulated were obtained. To measure SHG response, samples of Co-TPP nanoparticles, CS-MPs and Co-TPP-CS-MPs were tested with Kurtz and Perry method using the upright microscope: Co-TPP nanoparticles showed the same SHG behavior already observed for Co-TPP powder. Also, the movement of the crystals was so vigorous that it was necessary the presence of the coverslip to avoid the loose of the sample. The CS-MPs showed an initial lower SH intensity with respect to sucrose, and after few seconds they seem to melt under the laser beam. The Co-TPP-CS-MPs showed an initial lower intensity of the SH response with respect to the CS-MPs, probably because the chitosan shell covers the signal; however, after a few seconds the emission enhanced and the MPs were destroyed, leaving on the slide a sort of blended material.

8.2. Applications in Optoelectronic Devices: Cu-TPP films grown on ceramic and ITO-coated glasses

Porphyrin-based compounds have received considerable attention as emitting dopant material^{13,14} for organic light-emitting diodes (OLEDs), a technology with potential advantages such as its low cost, efficiency, flexibility, and large-area emitting properties. Pd, Pt, and Ir porphyrins have been studied as emitters for OLED composites. More recently, Chernyadyev et al.¹⁵ have successfully demonstrated ternary composites of $\alpha,\beta,\gamma,\delta$ - copper(II) tetraphenylporphyrinate (Cu-TPP) with PVK poly(vinylcarbazole) (PVK) and 2-(4-biphenyl)-5-(4-*t*-butyl-phenyl)-1,3,4-oxadiazole (PBD) to be promising materials for the light-emitting layer in near-infrared OLEDs.

Nonetheless, despite the good balance of hole and electron mobilities reported for Cu-TPP solid layers,¹⁵ to the best of the authors' knowledge, no detailed studies have been conducted on this promising material in the form of films deposited on glass substrates through the simple layer-by-layer (LBL) deposition technique. Therefore, this research group, in collaboration with 2Dto3D, aimed to assess the prospects of using pure Cu-TPP LBL-deposited films. The optical properties of thin films of Cu-TPP were investigated using infrared and UV-Vis spectroscopies by comparing the starting material (Cu-TPP in powder form) with the films deposited on different substrates. Additionally, the structure and morphology of the films were analyzed using X-ray powder diffraction and scanning electron microscopy.

8.2.1 Experimental

The $\alpha,\beta,\gamma,\delta$ -tetraphenylporphyrin (H_2TPP) moiety was synthesized according to the method described in Section 2.1 and Cu-TPP was used as received from the supplier (CAS: 14172-91-9, >98%; PorphyChem, lot:293ESi19), without further purification.

Thin films of Cu-TPP were deposited on ceramic glass substrates or indium-tin-oxide (ITO)-coated glasses by LBL deposition, starting with a 0.005 M solution of Cu-TPP or H_2TPP in dichloromethane. Each layer was produced with 5 μ L of the solution. The solution was left to evaporate for a day at room temperature. Afterward, the samples were heated in an oven at 100 or 200 °C for 30 min.

The ceramic glass was composed of Si (31.55%), Al (9.82%), Zr (2.70%), Zn (2.53%), Ti (2.19%), Ba (between 1.49%), As (0.62%), K (0.35%), Mg (0.28%), Ca (0.04%), Fe (0.03%), and Sr (0.02%). The ITO-coated glass slides

were 20×20×1.1 mm, with 85% transmission, and sheet resistance of 5-6 Ω/sq .

8.2.2 Results and discussion

To determine the decomposition temperature of Cu-TPP, a thermogravimetry experiment was conducted under a nitrogen atmosphere up to a temperature of 900 °C. Then, the oxidation of the residues was conducted in air conditions. The thermogravimetric curve is reported in Figure 8.2.1.

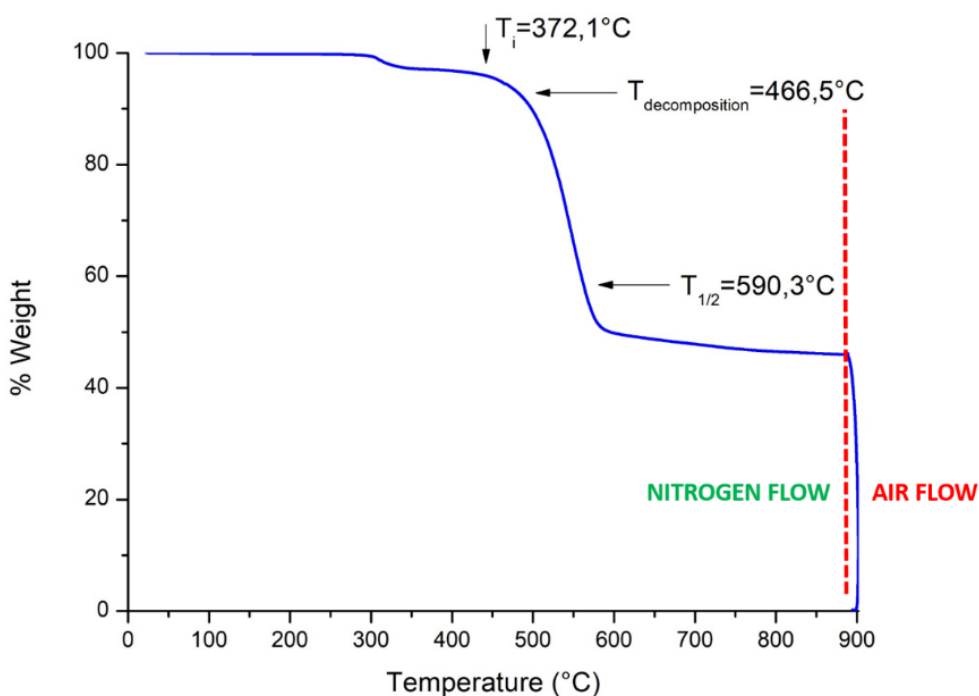


Figure 8.2.1 Thermogravimetric curve for Cu-TPP

The beginning of a weight loss was observed at $T_i = 372.1^\circ\text{C}$, and at $T_{1/2} = 536.8^\circ\text{C}$ the sample had (?) lost half of its initial weight. At temperatures lying between these two end values, decomposition of the samples occurred, and the decomposition temperature was determined as $T_{\text{decomposition}} = 466.5^\circ\text{C}$. The inorganic residue found at the end of the experiment was ground, analyzed by XRPD, and identified as CuO (see Fig 8.2.2)).

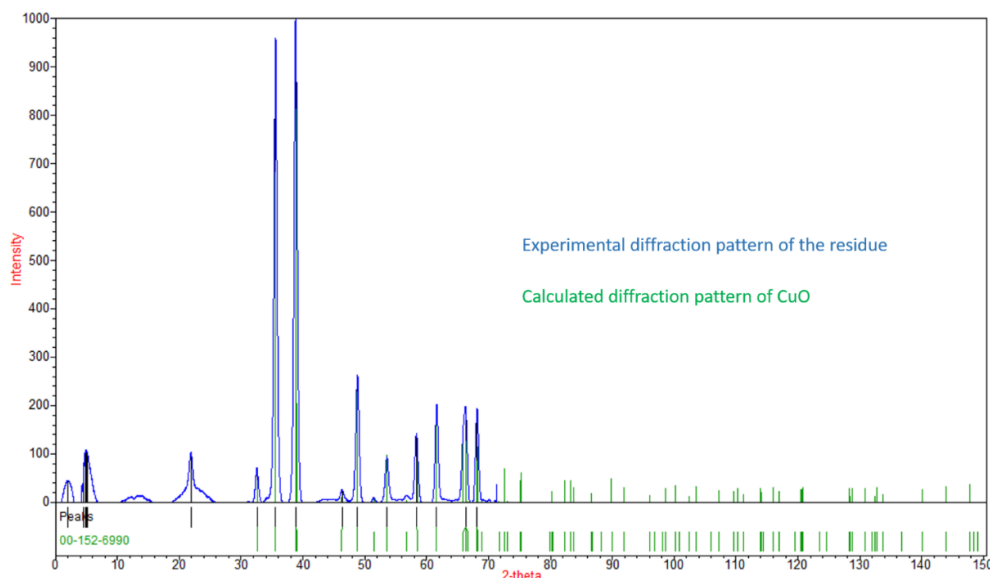


Figure 8.2.2 Experimental diffraction pattern of the residue of Cu-TPP compared to the calculated diffraction pattern of CuO using the QUALX program¹⁶.

Figure 8.2.3 depicts the UV-Vis spectra of one-, two-, and three-layer films of Cu-TPP deposited on ceramic glasses at room temperature (RT). The black line refers to the one-layer (1L) Cu-TPP film, the red line to the two-layer (2L) Cu-TPP film, and the blue line to the three-layer (3L) Cu-TPP film. It can be observed that the number of layers deposited increased the intensity of the bands ($1L < 2L < 3L$). It is also possible to notice that, as is the case with the powder (see Section 2.2), the S-band splits in the solid state. In the Cu-TPP 3L spectrum, the main peaks appeared at 342, 440 (split S-band), and 543 nm (Q-band); in Cu-TPP 2L, a slight shift was observed (351, 452, and 544 nm); and, in Cu-TPP 1L, the bands are located at 336, 442 and 547 nm, respectively.

The UV-Vis spectra of the Cu-TPP films deposited on the ceramic glasses and thermally treated for 30 minutes at 100 °C are shown in Figure 8.2.4. Again, it is possible to see that the number of layers deposited increased the intensity of the bands ($1L < 2L < 3L$), as expected. In particular, the bands of the 3L film were much more intense than those exhibited by 1L and 2L films. The main peaks in the Cu-TPP 3L spectrum occurred at 348, 461, and 542 nm, while in Cu-TPP 2L they occurred at 336, 451, and 544 nm; finally, in Cu-TPP 1L, they took place at 349 nm, 444, and 545 nm.

In Figure 8.2.5, the UV-Vis spectra of the Cu-TPP films deposited on ceramic glass after a 30-minute heating at 200 °C are reported. This time, the band located at lower wavelengths was practically undetectable in the three spectra, and, overall, the shape of the bands was different. The main peaks of the Cu-TPP 3L spectrum were detected at 468, and 554 nm; while in Cu-TPP 2L they were located at 468 and 552 nm; and at 490, and 560 nm, in Cu-TPP 1L.

Figure 8.2.6 shows the UV-Vis spectra of the H₂TPP deposited on ceramic glass. By comparing Figure 8.2.6 and Figure 4.2.1, it can be noticed that the shape of the Q-bands of the porphyrin film spectrum closely resembles the shape of the bands of the spectrum obtained from the porphyrin solution; however, the position of these bands (at 522, 560, 599, and 657 nm) is closer to those detected in the powder. As in the case of Cu-TPP, the S-band splits in the solid state.

Figure 8.2.7 shows the UV-Vis spectra of Cu-TPP films deposited on ITO-coated glass. The black line refers to unheated Cu-TPP, the red line to the Cu-TPP treated for 30 minutes at 100 °C, and the blue line to the Cu-TPP treated for 30 minutes at 200 °C. The UV band lies (only under RT conditions) at around 298 nm, and is redshifted when compared to the other Cu-TPP spectra. The Q-bands are found between 476 and 545 nm. All the mentioned bands are of the same order of magnitude. Figure 8.2.8 shows the UV-Vis spectrum of the H₂TPP deposited on ITO.

It can be observed, both for H₂TPP and Cu-TPP deposited on different substrates, that the S-band split is maintained in the solid state, both in the powder samples and in the films. Furthermore, unlike the powder samples and similarly to the solutions, the film appeared to feature Q-bands that were well apart from one another.

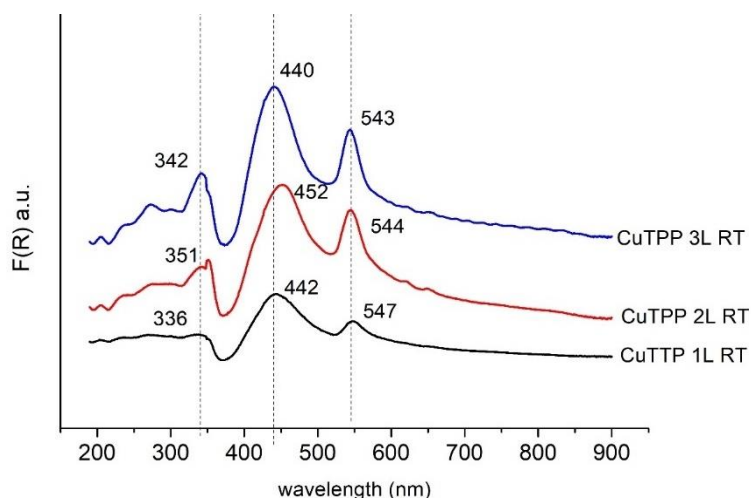


Figure 8.2.3 Comparison between the UV-Vis spectra of the Cu-TPP film deposited on a ceramic glass substrate between 200 and 900 nm. RT conditions. The thin films were deposited by the LBL technique. 1L, 2L, and 3L means 1-layer, 2-layers, and 3-layers film, respectively.

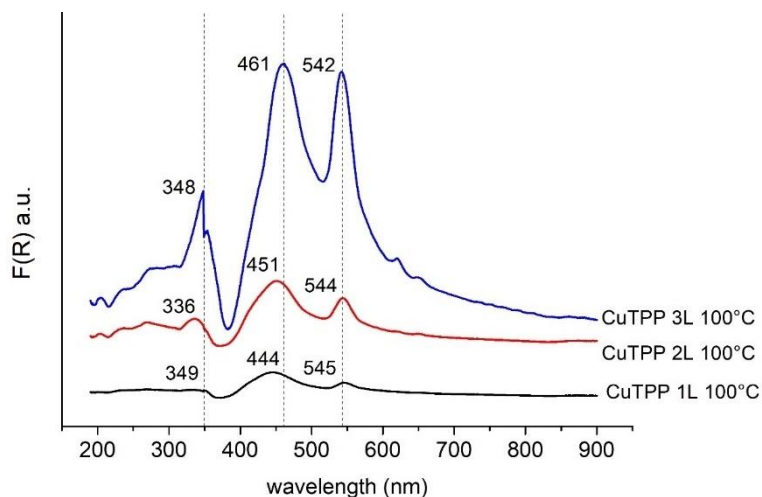


Figure 8.2.4 Comparison between the UV-Vis spectra of the Cu-TPP film deposited on a ceramic glass substrate and heated at 100 °C. The thin films were deposited by the LBL technique. 1L, 2L, and 3L means 1-layer, 2-layers, and 3-layers film, respectively.

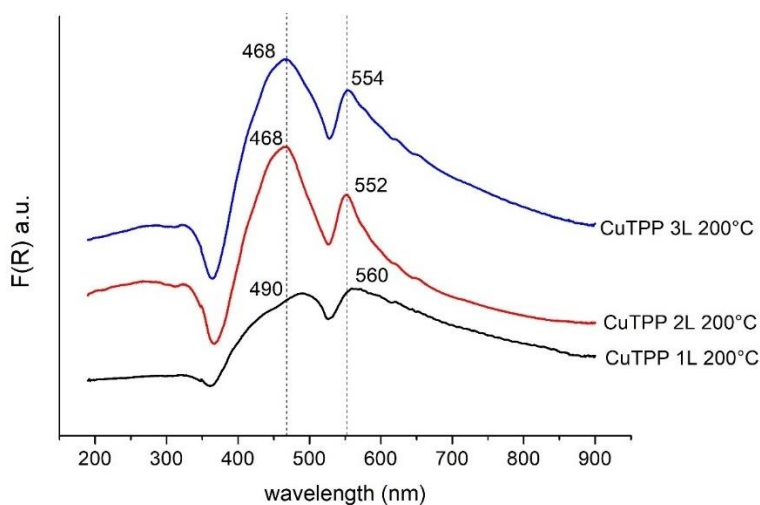


Figure 8.2.5 Comparison between the UV-Vis spectra of the Cu-TPP film deposited on a ceramic glass substrate and heated at 200 °C. The thin films were deposited by the LBL technique. 1L, 2L, and 3L means 1-layer, 2-layers, and 3-layers film, respectively.

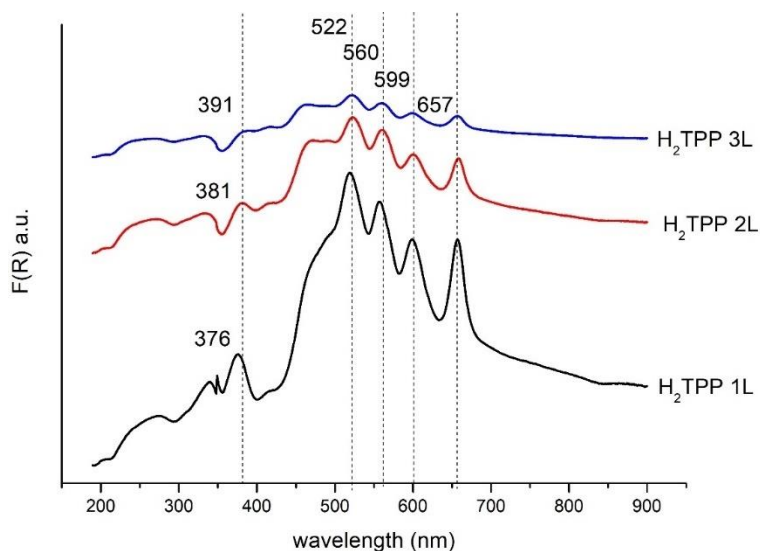


Figure 8.2.6. Comparison between the UV-Vis spectra of the H_2TPP film deposited on a ceramic glass substrate. The thin film was deposited by the LBL technique and 3L, 2L, 1L meaning, respectively, 1 Layer, 2 Layer, 3 Layer. RT conditions.

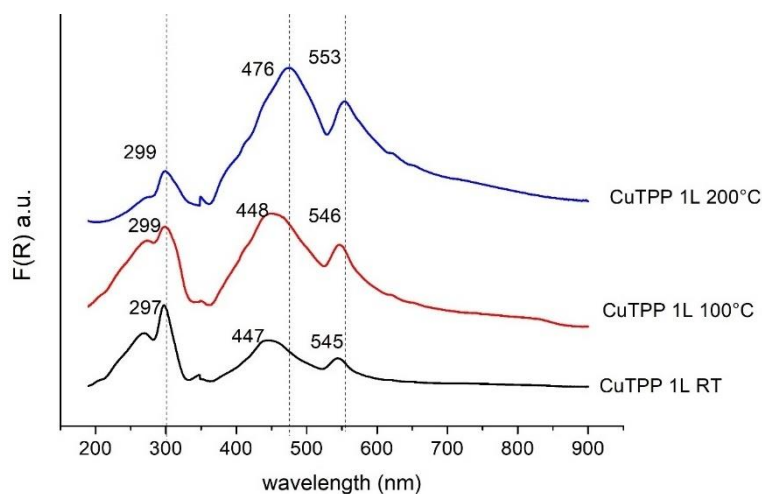


Figure 8.2.7. Comparison between the UV-Vis spectra of 1-layer $CuTPP$ films deposited on an ITO-coated glass substrate. RT, 100 and 200 °C indicate the annealing temperatures.

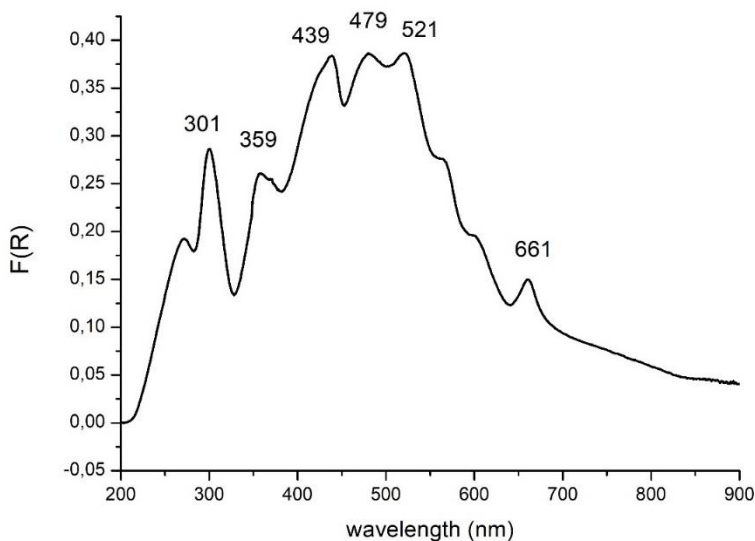


Figure 8.2.8. UV-Vis spectrum of an H_2TPP film deposited on an ITO-coated glass substrate.

The Cu-TTP structure (Tab 10.1.4 in Appendix) elucidated by single crystal X-ray powder diffraction was in good agreement with that previously reported.¹⁷

The XRPD pattern of the starting Cu-TTP powder is shown in Figure 8.2.9, in which the Miller indices for the main peaks have been indicated. The higher (o "higher"?) peaks, with indices (101) and (103), appeared at $2\theta = 8.6^\circ$ and $2\theta = 19.9^\circ$, respectively.

Figure 8.2.10 shows the XRPD pattern of the thin films of Cu-TTP deposited on ceramic glass at RT. It is worth noting that all peaks of the starting Cu-TTP phase have disappeared. This is a clear indication of the interaction between the Cu-TTP and the substrate, which would lead to a major change in the structure. In Cu-TTP 1L and Cu-TTP 3L films, only one peak at $2\theta = 7.2^\circ$ was observed, while Cu-TTP 2L also exhibited a small peak at $2\theta = 8.8^\circ$ and some broader peaks at ca. 14.1° , 17.1° , and 18.4° .

The diffraction pattern of the Cu-TTP 3L film annealed at 100°C , after the evaporation of the solvent, is shown in Figure 8.2.11. The pattern showed the same main peak at $2\theta = 7.2^\circ$ present in the non-heated Cu-TTP 3L sample, but also the three peaks at 2θ values of 14.1° , 17.1° , and 18.4° observed for the non-heated Cu-TTP 2L sample, albeit with different relative intensities.

Figure 8.2.12 shows the diffraction patterns of the Cu-TPP thin films annealed at 200 °C. Interestingly, the main peak at $2\theta = 7.2^\circ$ was present only in the Cu-TPP 2L and Cu-TPP 3L samples, while the peak at $2\theta = 18.4^\circ$ was present in the three samples.

Concerning the ITO-coated glass substrate, Figure 8.2.13 shows the diffraction pattern of the Cu-TPP 1L thin film at RT conditions and treated at 100 and 200 °C. The main peak at $2\theta = 7.2^\circ$ was clearly visible only in the film annealed at 200 °C, while at 100 °C it was barely visible, and it disappeared at room temperature. The peak at $2\theta = 18.4^\circ$ was observed for the films annealed at 100 and 200 °C, while another small peak at $2\theta = 11.2^\circ$ was only present in the latter sample. The differences evidenced for the Cu-TPP 1L samples deposited on ceramic glass and ITO-coated glass suggest that the interactions with these two types of substrates are very different.

Considering all the above-discussed X-ray powder patterns for Cu-TPP films, two peaks at $7.0\text{--}7.2^\circ$ and $18.3\text{--}18.4^\circ$ are most frequently observed, and their 2θ values are close to those of the most intense peaks of the starting Cu-TPP powder (8.6 and 20.0° , respectively).

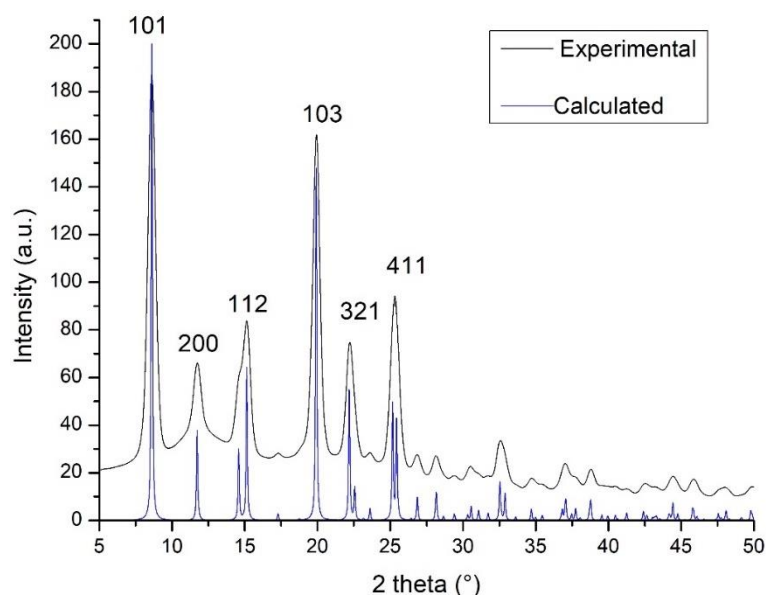


Figure 8.2.9. X-ray powder diffraction pattern of Cu-TPP in powder form.

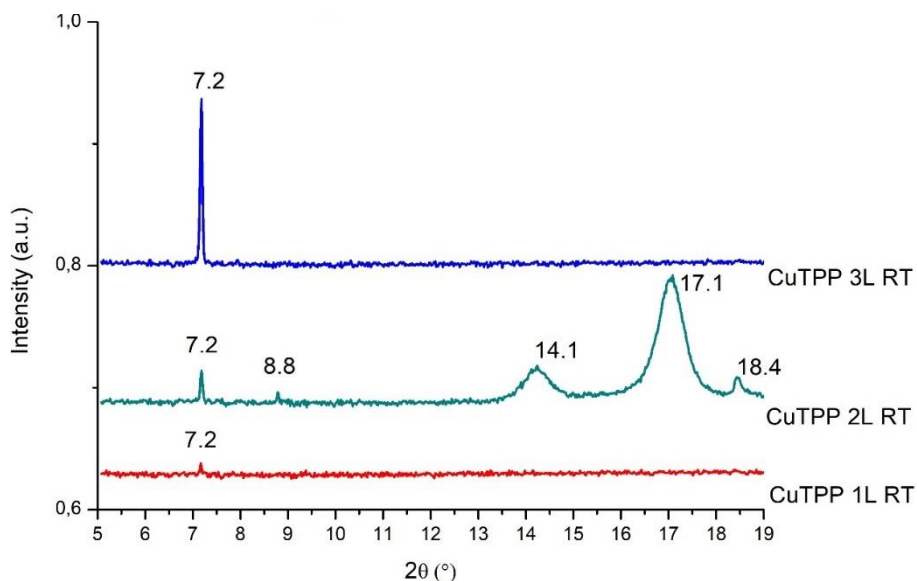


Figure 8.2.10. X-ray powder diffraction patterns of Cu-TPP thin films deposited on a ceramic glass substrate using the LBL technique. RT conditions. 1L, 2L, and 3L indicate the number of deposited layers.

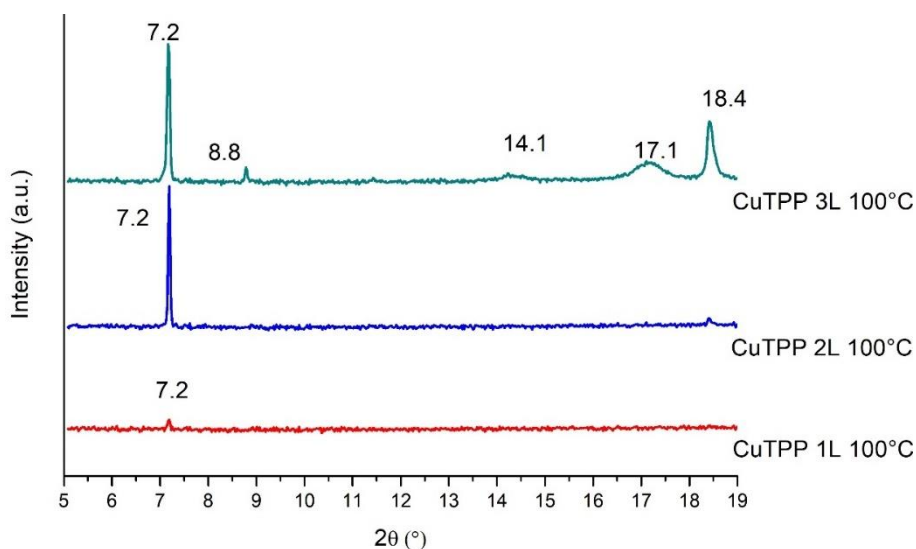


Figure 8.2.11. X-ray powder diffraction patterns of Cu-TPP thin films deposited on a ceramic glass substrate using the LBL technique and annealed at 100°C . 1L, 2L, and 3L indicate the number of deposited layers.

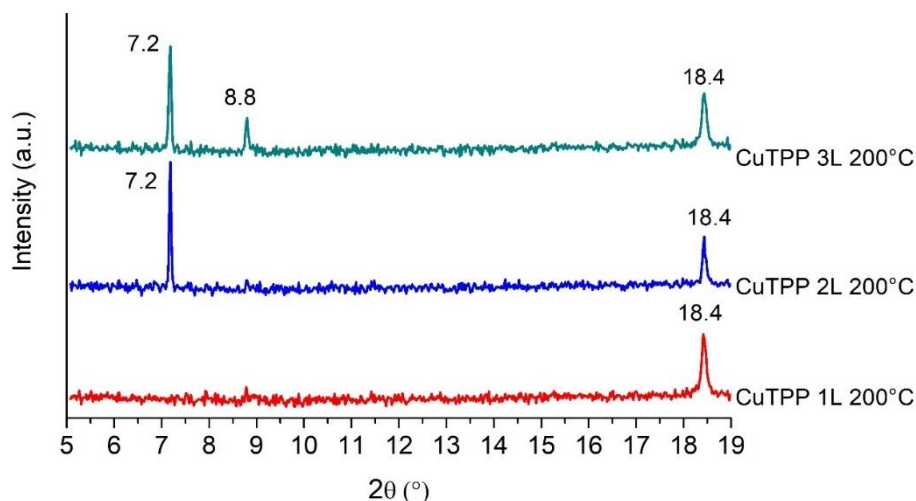


Figure 8.2.12. X-ray powder diffraction patterns of Cu-TPP thin films deposited on a ceramic glass substrate using the LBL technique and annealed at 200 °C. 1L, 2L, and 3L indicate the number of deposited layers.

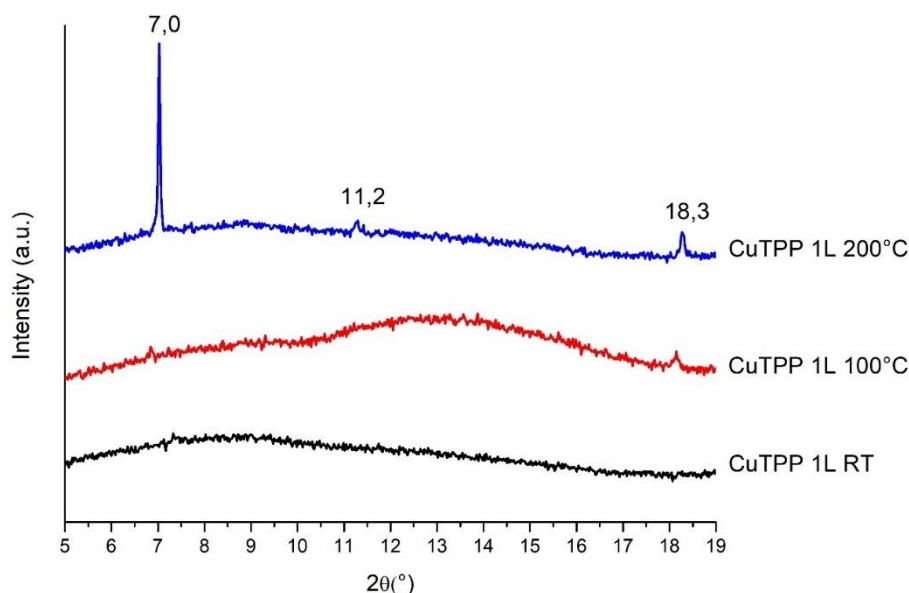


Figure 8.2.13. X-ray diffraction patterns of Cu-TPP thin film deposited on ITO-coated glass using the LBL technique, at RT and after annealing at 100 and 200 °C.

Figure 8.2.14 shows the SEM micrographs of Cu-TPP 1L on ITO-coated glass. The particles were similar to the octahedral nanostructures previously

reported¹⁸ for Zn-TTP and Cu-TTP prepared in CHCl_3 -i-PrOH. They were similarly dispersed on the film before (left-hand image) and after annealing at 200 °C (right-hand image). Pyramid-like formations appeared to be predominant, but the crystalline aggregates differed in both shape and size: the aggregates of the sample annealed at 200 °C were smaller. This was confirmed by an increase in the magnification (Figure 8.2.15 and Figure 8.2.16). Considering the pyramid-like aggregates, it is possible to notice that after annealing at 200 °C they were thinner. Figure 8.2.17 shows the edge of one of these aggregates: the two-dimensional preferential growth is particularly noticeable. Therefore, the annealing seems to favor the growth of two-dimensional aggregates on the surface of ITO-coated glass.

Images 8.2.18 and 8.2.19 shows the Energy Dispersive Spectroscopy (EDS) analysis of the Cu-TPP 1L film sample at RT and annealed at 200 °C. It can be observed that Cu is always present in the pyramid-like particles, while it is not detected among particles.

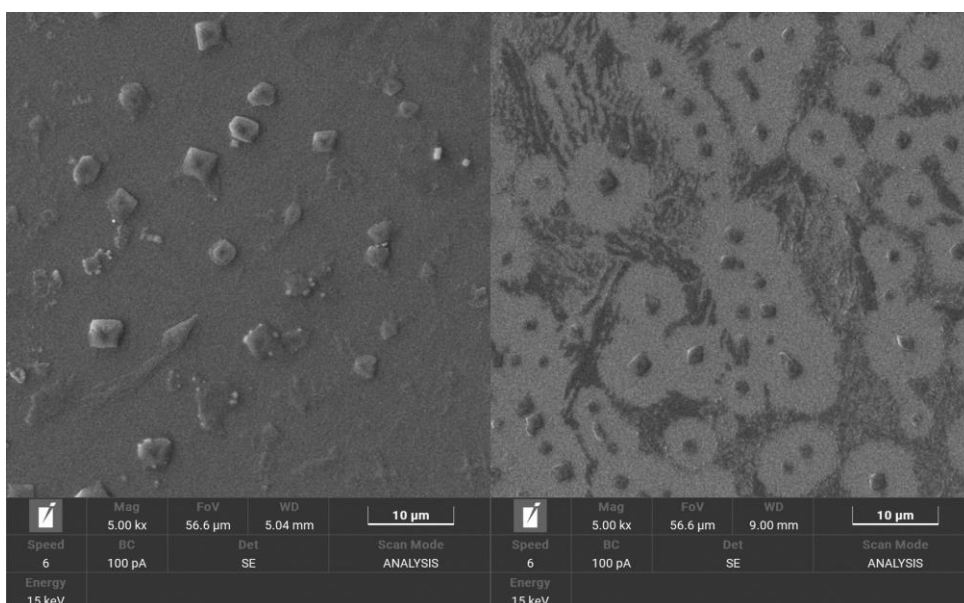
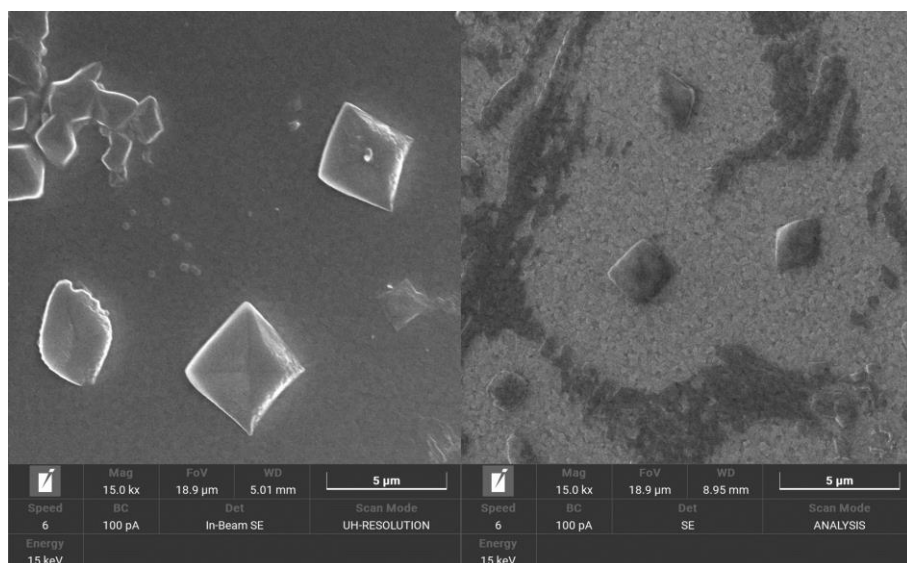


Figure 8.2.14 SEM images of Cu-TPP 1L films deposited on ITO-coated glass using the LBL technique at 5000× magnification. CuTTP 1L film before (left) and after annealing at 200 °C (right).



Figure

8.2.15 SEM images of aggregates in Cu-TTP 1L films deposited on ITO-coated glass using the LBL technique at 15000 $\times$ magnification. CuTTP 1L film before (left) and after annealing at 200 $^{\circ}$ C (right).

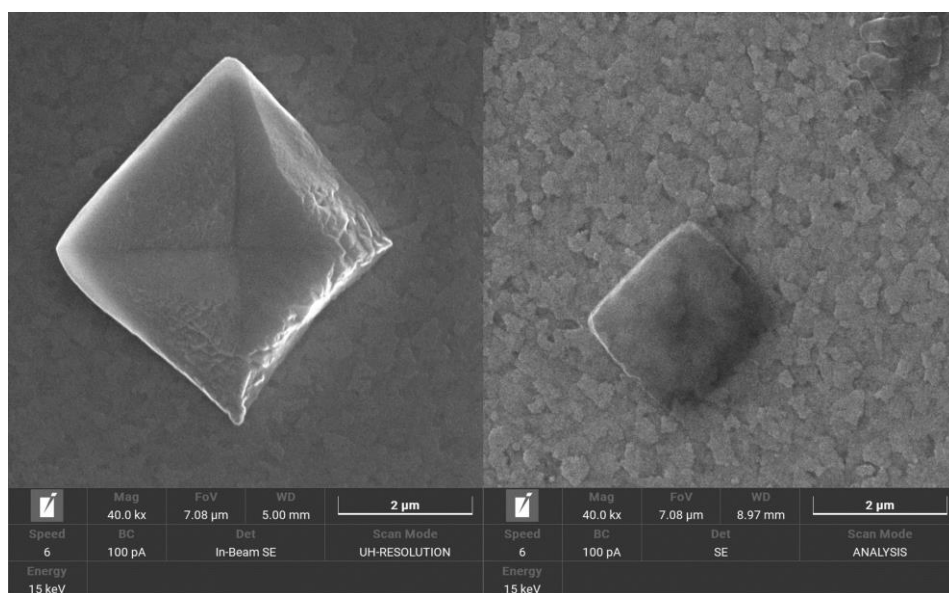


Figure 8.2.16 SEM images of aggregates of the Cu-TTP 1L films deposited on ITO-coated glass using the LBL technique at 40000 $\times$ magnification. CuTTP 1L film before (left) and after annealing at 200 $^{\circ}$ C (right).

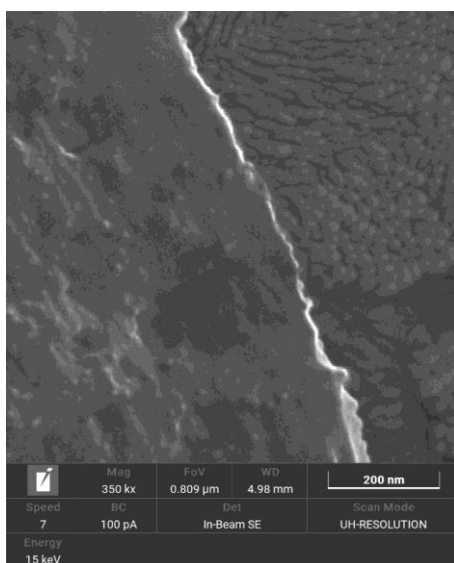


Figure 8.2.17 SEM micrograph of the edge of a small square-shaped particle of Cu-TPP 1L film deposited on ITO-coated glass and annealed at 200 °C.

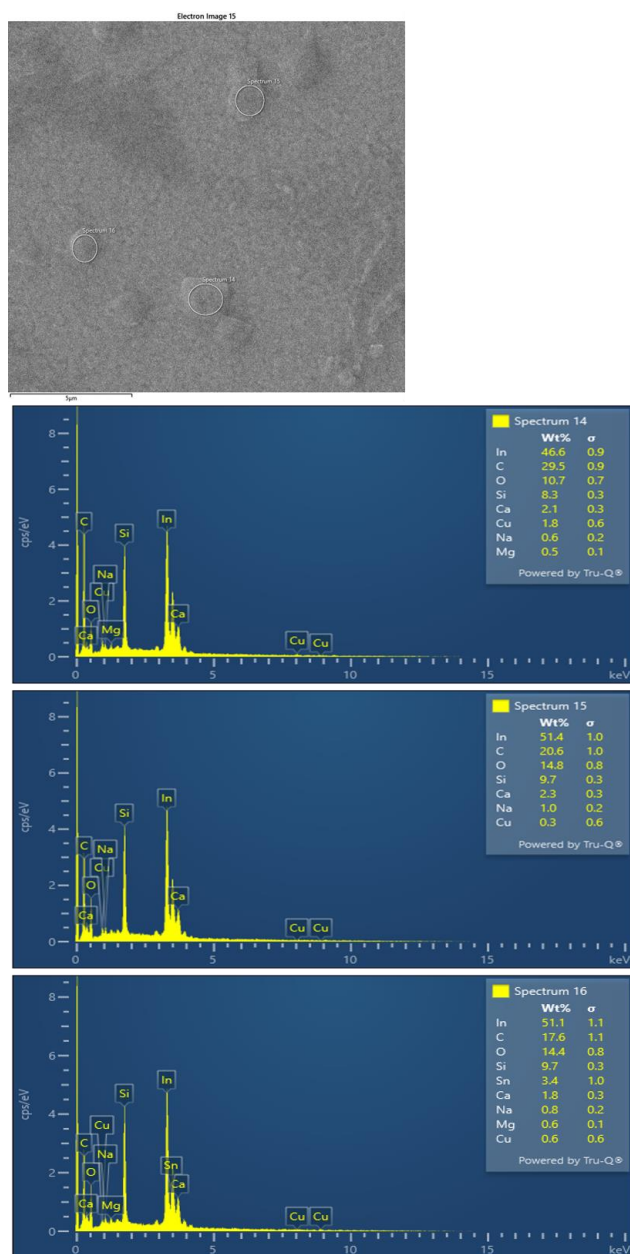


Figure 8.2.18 EDS analysis of Cu-TPP 1L film on ITO-coated glass after annealing at 200 °C

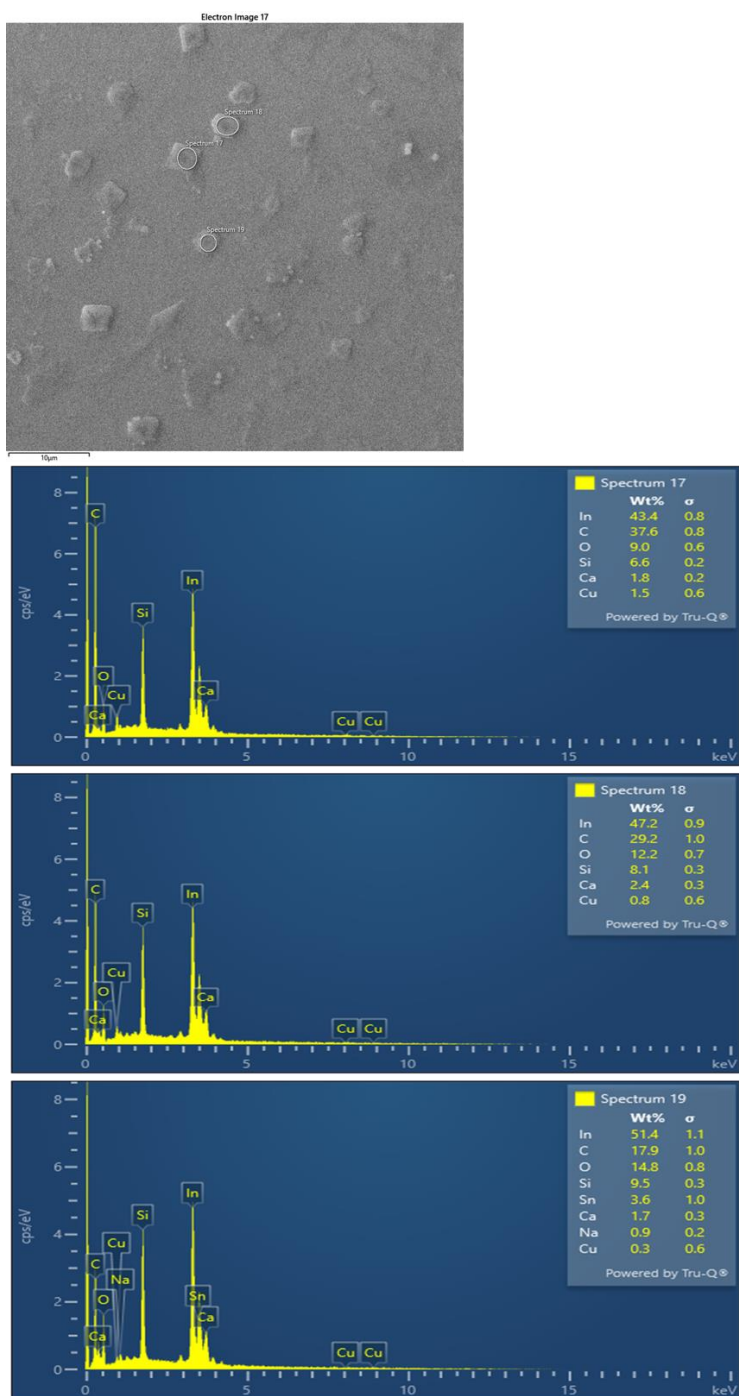


Figure 8.2.19 Figure 4.1.19 EDS analysis of Cu-TPP 1L film on ITO-coated glass before annealing at 200 °C (RT film).

8.2.2 Conclusions

The Cu-TPP compound was considered as an active material for the preparation of Organic Light-emitting Diodes (OLEDs). For this application, the compound was deposited as a thin film on a ceramic glass and on a ITO conductive glass. Various layer-by-layer deposition tests were carried out, and the UV-Vis absorption and ATR spectra and the SEM images were recorded. Unfortunately, the analysis evidences that the films do not have the necessary homogeneity for the creation of a prototype.

References

- 1** Naumov, P.; Karothu, D. P.; Ahmed, E.; Catalano, L.; Commins, P.; Mahmoud Halabi, J.; Al-Handawi, M. B.; Li, L. The Rise of the Dynamic Crystals. *J. Am. Chem. Soc.* **2020**, *142*, 13256– 13272, DOI: 10.1021/jacs.0c05440
- 2** S. Lopez, N. Hallali, Y. Lalatonne, A. Hillion, J. C. Antunes, N. Serhan, P. Clerc, D. Fourmy, L. Motte, J. Carrey, V. Gigoux, Magneto-mechanical destruction of cancer-associated fibroblasts using ultra-small iron oxide nanoparticles and low frequency rotating magnetic fields, *Nanoscale Adv.* 2021, 4(2):421–436. doi: 10.1039/d1na00474c
- 3** H. S. Huang, J. F. Hainfeld, Intravenous magnetic nanoparticle cancer Hyperthermia, *Int. J. Nanomedicine*, 2013:8 2521–2532, and references therein.
- 4** J. A. Benítez-Martínez, I. M. Garnica-Palafox, G. Vázquez-Victorio, M. Hautefeuille, F. M. Sánchez-Arévalo, Semi-interpenetrating polymeric networks based on poly(dimethylsiloxane)-chitosan-poly(vinyl alcohol) crosslinked with genipin with possible use in biomedical applications, *J. Mater. Sci.* 2009, 56(1), 1-20
- 5** I.M. Garnica-Palafox, F.M. Sánchez-Arévalo, Influence of natural and synthetic crosslinking reagents on the structural and mechanical properties of chitosan-based hybrid hydrogels, *Carbohydr. Polym.*, 2016, 151, 1073-1081
- 6** L. A. Frank, G. R. Onzi, A. S. Morawski, A. R. Pohlmann, S. S. Guterres, R. V. Contri, Chitosan as a coating material for nanoparticles intended for biomedical Applications, *React. Funct. Polym.* 147 (2020) 104459
- 7** Ji, J., Hao, S., Wu, D., Huang, R., & Xu, Y. (2011). Preparation, characterization and in vitro release of chitosan nanoparticles loaded with gentamicin and salicylic acid. *Carbohydrate polymers*, 85(4), 803-808.
- 8** R. Pandey, G. Mathur, Current Trends in Chitosan Functionalization Methods and Their Applications, *Starch* 2025, 77, 2300248-2300255
- 9** R. Wu, A. S. Abdulhameed, S. K. Yong, H. Li, Z. A. AlOthman, L. D. Wilson, A. H. Jawad, Functionalization of chitosan biopolymer with SiO₂ nanoparticles and benzaldehyde via hydrothermal process for acid red 88 dye adsorption: Box-Behnken design optimization, *Int. J. Biol. Macromol.* 247 (2023) 125806-125818

10 F. Tang, L. Zhang, J. Zhu, Z. Cheng, X. Zhu, Surface Functionalization of Chitosan Nanospheres via Surface-Initiated AGET ATRP Mediated by Iron Catalyst in the Presence of Limited Amounts of Air, *Ind. Eng. Chem. Res.*, 2009, 48(13), 6216–6223

11 A. Cioci, P. Benzi, C. Canepa, L. Mortati, A. Alvarez de la Paz, I. M. Garnica-Palafox, F. M. Sánchez-Arévalo, R. C. Dante, D. Marabello, Fructose-Based Metal–Organic Framework as a Means to Synthesize Sr-Loaded Chitosan Nanospheres with NLO

Properties for Theranostic Applications in Radiotherapy, *Inorganics* 2024, 12, 231.

12 Collins, T. J. ImageJ for microscopy. *Biotechniques* 2007, 43(S1), S25-S30.

13 Graham, K. R.; Yang, Y.; Sommer, J. R.; Shelton, A. H.; Schanze, K. S.; Xue, J.; Reynolds, J. R. Extended conjugation platinum(II) porphyrins for use in near-infrared emitting organic light emitting diodes. *Chem. Mater.* 2011, 23 (24), 5305-5312. DOI: 10.1021/cm202242x

14 Zhu, L.-J.; Wang, J.; Reng, T.-G.; Li, C.-Y.; Guo, D.-C.; Guo, C.-C. Effect of substituent groups of porphyrins on the electroluminescent properties of porphyrin-doped OLED devices. *J. Phys. Org. Chem.* 2010, 23 (3), 190-194. DOI: 10.1002/poc.1592

15 Chernyadyev, A. Y.; Aleksandrov, A. E.; Lypenko, D. A.; Tyurin, V. S.; Tameev, A. R.; Tsivadze, A. Y. Copper(II) meso-tetraphenyl- and meso-tetrafluorenyl porphyrinates as charge carrier transporting and electroluminescent compounds. *ACS Omega* 2022, 7 (10), 8613-8622. DOI: 10.1021/acsomega.1c06557

16 Altomare, A., Cuocci, C., Giovacazzo, C., Moliterni, A., & Rizzi, R. (2008). QUALX: a computer program for qualitative analysis using powder diffraction data. *Journal of Applied Crystallography*, 41(4), 815-817

17 Fleischer, E. B.; Miller, C. K.; Webb, L. E. Crystal and molecular structures of some metal tetraphenylporphines. *Journal of the American Chemical Society* **1964**, 86 (12), 2342-2347. DOI: 10.1021/ja01066a009

18 Cai, J.; Chen, H.; Huang, J.; Wang, J.; Tian, D.; Dong, H.; Jiang, L. Controlled self-assembly and photovoltaic characteristics of porphyrin derivatives on a silicon surface at solid–liquid interfaces. *Soft Matter* **2014**, 10 (15). DOI: 10.1039/c3sm53061b

9.CONCLUSIONS

The main purpose of this PhD work is to understand the origin of the SHG behavior of metal porphyrinate-based crystalline materials, in order to comprehend the relationship between the chemical composition, the structural and electronic characteristics, and the NLO properties, that should allow to drive the synthesis toward more SHG-efficient metal porphyrinates for the development of new bio-sensors. For this purpose, an experimental/computational method was experienced: old and new metal porphyrinate-based crystalline materials were synthesized, crystallized, and characterized with XRD and XRPD, UV-Vis, and IR spectra in solution and in solid state. Furthermore, Magnetic Susceptibility measurements were carried out, and the SHG efficiency was determined by the Kurtz–Perry powder technique. Finally, theoretical calculations were performed on fragments of the compounds, to calculate an intrinsic greatness related to the SHG behavior to be compared with the experimental results.

Most of the porphyrinates studied show a peculiar behavior when irradiated with an IR laser: the initial efficiency is of the same order of that of the sucrose, but after a few minutes of laser irradiation it gradually increases, reaching a plateau at a higher value of different order of magnitude (from 10 to 50 times). By visually analyzing the powders in the capillaries, a darker spot is observed in correspondence of the point where the laser hit the samples, and repeating the measurement on the same spot, the SHG value starts from the value of the plateau and remains stable. Furthermore, during the irradiation the powder vigorously scatters in any direction. In Table 9.1.1 are summarized the experimental SHG responses of the metal porphyrinates studied in this work.

Table 9.1.1. SHG responses, recorded with a Nd:YAG pulsed (10 Hz) laser at 1.907 μm with respect to the sucrose, of the metal porphyrinates studied in this work.

		Before irradiation	After irradiation
Co-TPP	$\text{Co}(\text{C}_{44}\text{H}_{30}\text{N}_4)$	≈ 1	50
Ni-TPP	$\text{Ni}(\text{C}_{44}\text{H}_{30}\text{N}_4)$	$\approx$	50
Cu-TPP	$\text{Cu}(\text{C}_{44}\text{H}_{30}\text{N}_4)$	≈ 1	10
Zn-TPP	$\text{Zn}(\text{C}_{44}\text{H}_{30}\text{N}_4)$	≈ 1	15
Zn-TPP-DMF	$\text{Zn}(\text{C}_{44}\text{H}_{30}\text{N}_4)(\text{C}_3\text{H}_7\text{NO})$	≈ 1	≈ 1
Zn-TPP-DMF(DCM)	$[\text{Zn}(\text{C}_{44}\text{H}_{30}\text{N}_4)(\text{C}_3\text{H}_7\text{NO})] \cdot \text{CH}_2\text{Cl}_2$	≈ 1	≈ 1
Zn-TNPP(DCM)	$[\text{Zn}(\text{C}_{44}\text{H}_{26}\text{N}_8\text{O}_8)] \cdot \text{CH}_2\text{Cl}_2$	≈ 1	≈ 1
Co-TNPP(tolu)	$\text{Co}[(\text{C}_{44}\text{H}_{26}\text{N}_8\text{O}_8)] \cdot \text{C}_6\text{H}_5\text{CH}_3$	≈ 1	50
H₂TPP	H_2TPP	≈ 0	≈ 0
Sucrose	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$	1	1

The enhancement of the SH intensity was not observed for all the metal porphyrinates, and only for some of them (Co-TPP, Ni-TPP and Co-TNPP) the enhancement value was 50 time the initial value, while for Cu-TPP and Zn-TPP the value was lower.

It is noteworthy that this peculiar behavior is observed also for Zn-TPP, which crystallizes in the centrosymmetric group $I4/m$, for which no SHG property is expected.

As explained in chapter 2.5, for centrosymmetric compounds no second-order response is expected, as all components of the SHG tensor vanish. Therefore, second-order nonlinear optical phenomena are, in theory, only possible in non-centrosymmetric materials. Some studies have attributed SHG observed in centrosymmetric crystals to an incorrect assignment of the centrosymmetric space group or to issues related to the stability of the refinement¹, but we excluded this possibility, checking ourselves by single

crystal X-ray diffraction and powder X-ray diffraction experiments. However, in recent years, a SHG signal was observed from a centrosymmetric Zn(II) complex, and it was hypothesized that residual non-centrosymmetry in the structure (defects, structural disorders, local imperfections) giving rise to polarizability leading to the strong SHG observed². Moreover, the SHG effect from centrosymmetric crystals with vicinal faces has been reported³, and there was a resurgence of interest in SHG from cubic centrosymmetric crystals^{4,5}. In the work of Sipe et al.⁶ it was showed that SHG measurements could be utilized to probe non-centrosymmetric surface structures which are clearly distinguishable from the bulk centrosymmetric structure.

For the free porphyrin, H₂TPP, that crystallizes in the centrosymmetric P-1 space group, the SHG signal remains null also after several minutes under irradiation, suggesting that the presence of the metal is strongly correlated to the observed enhancement of the SHG signal.

On the three centrosymmetric Zn-TPP complexes, additional SHG experiment using an upright microscope combined with a microscope scanning unit, equipped with a pulsed excitation source at 930 nm. Again, for all the three compounds the signal remains null for some seconds, and became higher after the activation, precisely 21 times the initial one for Zn-TPP, 29 for the Zn-TPP-DMF and 39 for the Zn-TPP-DMF (DCM). This behavior demonstrates that changing the wavelength of the excitation source, also the porphyrinates that do not emit at 1907 nm are able to generate a significant SHG signal.

In order to explain this peculiar phenomenon, it was hypothesized a possible photo-degradation process or a phase transition from crystalline to amorphous solid state. By comparing the XRPD patterns of all the porphyrinates, that are identical both before and after irradiation, the photo-degradation or phase transition processes were excluded. Since the structures of the three zinc porphyrinates are all centrosymmetric, it follows that the presence of the inversion center in all the structures is not relevant to the manifestation of the SHG property, as normally established for the SHG emitting solid materials.

It was also hypothesized that the enhancement of signal can be imputable to an electronic or spin transition that occurs when the metal porphyrinate was irradiated. To validate this hypothesis, Magnetic Susceptibility measurements were carried out. For Co-TPP and Ni-TPP a substantial change in the spin state of the samples occurs after irradiation. In particular, the magnetic moment of the Co-TPP powder goes from a low to a high spin state, while the Ni-TPP goes from a diamagnetic condition to a high spin state. Measurements carried out over several months, at regular time intervals, have shown that the magnetic property is conserved over time, as well as the higher value of the SHG intensity. On the other hand, for Cu-TPP, Zn-TPP,

Zn-TPP-DMF and Zn-TPP-DMF-DCM the magnetic moment does not change after the laser radiation.

Since experiments suggested a correlation between SHG behaviors and an electronic or spin transition occurred during the radiation with the laser, theoretical calculations on some of the compounds were performed in order to deeply explore the phenomena.

The calculations were performed on fragments selected from the X-ray structures, and the theoretical geometrical parameters were compared with the corresponding X-ray structural data, to validate the optimized model. Subsequently, the total dipole moment, the polarizability and the first order hyperpolarizability were calculated from the model. Considering the magnetic moment measurements, theoretical calculations on fragments of Co-TPP and Ni-TPP were performed in higher spin states in order to simulate their excited states. For the three Zn porphyrinates, that do not show a change in their magnetic moment after the laser irradiation, the excited states were studied by time dependent method (TD). In Table 9.1.2 are summarized the theoretical results for all the porphyrinates analyzed with the theoretical calculations. Both first and second series of SHG measurement are reported for the three Zn porphyrinates.

Table 9.1.2. Theoretical value of hyperpolarizability (Calc β_{tot}) and second order susceptibility ratio respect sucrose (Calc $\chi^{(2)}/\chi^{(2)}_{\text{sucrose}}$) for all the compounds on which theoretical calculations were performed; the experimental $I^{(2)}/I^{(2)}_{\text{sucrose}}$ values, both for the first (Exp 1) and the second (Exp 2) series of measurements, are reported for comparison. For Co-TPP and Ni-TPP the theoretical values are referred to fragments with higher spin multiplicities, while for Zn-TPP complexes are the results of the TD-DFT calculation.

Ground States				
	Calc	Calc	Exp 1	Exp 2
	β_{tot}	$\chi^{(2)}/\chi^{(2)}_{\text{sucrose}}$	$I^{(2)}/I^{(2)}_{\text{sucrose}}$	$I^{(2)}/I^{(2)}_{\text{sucrose}}$
Co-TPP	2.3	0.2	≈ 1	//
Ni-TPP	0.2	0.0	≈ 1	//
Cu-TPP	1.3	0.0	≈ 1	//
Zn-TPP	0.0	0.0	≈ 1	//
Zn-TPP-DMF	3.3	0.4	≈ 1	//
Zn-TPP-DMF-DCM	0.0	0.0	≈ 1	//
Excited States (different spin multiplicity)				
	Calc	Calc	Exp 1	Exp 2
	β_{tot}	$\chi^{(2)}/\chi^{(2)}_{\text{sucrose}}$	$I^{(2)}/I^{(2)}_{\text{sucrose}}$	$I^{(2)}/I^{(2)}_{\text{sucrose}}$
Co-TPP (10 unpaired e ⁻)	18.9	2.4	50	//
Ni-TPP (4 unpaired e ⁻)	24.5	3.4	10	//
Excited States (Time Dependent)				
Zn-TPP	481.8	62.9	15	21
Zn-TPP-DMF	957.7	109.7	1	29
Zn-TPP-DMF-DCM	73.1	7.9	1	39

For Co-TPP and Ni-TPP the theoretical values of hyperpolarizability and second order susceptibility of the excited states were obtained by the simulation of fragments with higher spin multiplicities. As highlighted in table 5.1.2, these optimizations, for both the complexes, yields higher hyperpolarizability and susceptibility values respect to the ones computed for the ground states, in agreement with experimental results. Also, both fragments re-optimized with higher spin multiplicities do not change significantly their geometry, compatibly with the XRPD data.

Regarding the three Zn porphyrinates, the properties of the excited states were obtained by TD calculations. These calculations provide an increase in the hyperpolarizability and susceptibility values for each complex in his excited state, in good agreement with the experimental data obtained with the microscope scanning unit (Exp 2). The fragments re-optimized at the TD level of theory do not change significantly their geometry, compatibly with the XRPD data.

During the last year of this PhD, new metal porphyrinates, with functionalized porphyrin ligands, were also synthesized, and for two of them (Co-TNPP and Zn-TNPP) the X-ray structure was obtained. Chemical and physical characterization and computational work are ongoing, in order to obtain, for the new materials, the same level of knowledge acquired for the other porphyrinates studied.

For some of the porphyrinates studied were performed also preliminary tests for possible applications. The Cu-TPP compound was considered as an active material for the preparation of Organic Light-emitting Diodes (OLEDs). For this application, the compound was deposited as a thin film on a ceramic glass and on a ITO conductive glass. Various layer-by-layer deposition tests were carried out, and the UV-Vis absorption and ATR spectra and the SEM images were recorded. Unfortunately, the analysis evidences that the films do not have the necessary homogeneity for the creation of a prototype.

The Co-TPP compound, instead, was considered as bio-material for multi-theranostic applications, i.e. as SHG bio-sensors and for therapeutic purposes in the anticancer field. For the second application, the photo-responsive property and the enhancement of the magnetic moment can be exploited. Thus, the solid Co-TPP was reduced to nanoparticle size of about 25 nm², and the Co-TPP nanoparticles were encapsulated into chitosan microspheres of approximately 0.7 μm of diameter. TEM/SEM analyses were performed to verify the size, morphology and composition of the products. It was confirmed that chitosan microparticles with the Co-TPP nanoparticles encapsulated were obtained. They were tested with Kurtz and Perry method using the upright microscope, and the Co-TPP-chitosan microparticles showed a good SHG

emission and a contemporary disruption due to the movement of the Co-TPP cores. Therefore, the Co-TPP-chitosan microparticles are very promising biosensors and contemporary can be used to destroy cancer cells, if suitably functionalized on the surface. Next step of this research will be the *in vitro* biological tests.

The enhancement of the magnetic moment is also of particular interest, since magnetic particles can heat the tissue under an alternating magnetic field, or can be mechanically activated under a low-frequency magnetic fields and kill the cancer cells. This possible application will be developed in a future research.

In conclusion, this thesis cannot be considered as the "final word" on the peculiar SHG behavior of porphyrinates, since the observation that by changing the wavelength and/or the power of the incident laser, big changes in the SHG responses were observed, opened new questions. Moreover, the application of porphyrinates as biosensors it appears very promising, and further investigations are ongoing.

References

- 1** Acta Crystallogr C Struct Chem 2021 Oct 1;77(Pt 10):586-590. doi: 10.1107/S2053229621009293. Epub 2021 Sep 22.
- 2** Sun, H., Weid, J., & Vittalb, J. J. Second harmonic generation from the 'centrosym-metric' crystals.
- 3** Verheijen, M. A., Van Hasselt, C. W., & Rasing, T. (1991). Optical second harmonic generation study of vicinal Si (111) surfaces. Surface science, 251, 467-471.
- 4** Wensheng, G., Guo, F., Wei, C., Liu, Q., Zhou, G., Wang, D., & Shao, Z. (2002). SHG from centrosymmetric supermolecular crystal. Science in China Series B: Chemistry, 45, 267-274.
- 5** Cazzanelli, M., Bianco, F., Ghulinyan, M., Pucker, G., Modotto, D., Wabnitz, S., ... & Pavesi, L. (2012). Second-order nonlinear silicon photonics. SPIE Newsroom.
- 6** Sipe, J. E., Moss, D. J., & Van Driel, H. M. (1987). Phenomenological theory of optical second-and third-harmonic generation from cubic centrosymmetric crystals. Physical Review B, 35(3), 1129.

10. APPENDIX

10.1. Tables

*Table 10.1.1 Crystal data and structure refinement for **Co-TPP***

Empirical formula	C ₄₄ H ₂₈ N ₄ Co
Formula weight	671.63
Temperature/K	293(2)
Crystal system	tetragonal
Space group	I $\bar{4}$ 2d
a/Å	15.0395(3)
b/Å	15.0395(3)
c/Å	13.9558(5)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	3156.63(15)
Z	4
ρ_{calc} /cm ³	1.413
μ /mm ⁻¹	0.584
F(000)	1388.0
Crystal size/mm ³	0.22 × 0.22 × 0.22
Radiation	Mo-K α (λ = 0.71073)
2 θ range/°	6.724 to 56.56
Index ranges	-20 ≤ h ≤ 20
Reflections collected	27771
Independent reflections	1963
R _{int}	0.0347
R _{sigma}	0.0111
Data/restraints/parameters	1963/0/111
Goodness-of-fit on F ²	1.112
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0314
Final R indexes [all data]	R ₁ = 0.0330

Largest diff. peak/hole/eÅ ⁻³	0.36/-0.13
Flack parameter	-0.022(5)

Table 10.1.2 Experimental bond lengths (Å) and angles (°) for *Co-TPP*.

Bond lengths (Å)		Bond angles(°)	
M-N1	1.949(2)	N1 ¹ -M1-N1 ²	178.75(12)
M-N1 ⁱⁱ	1.949(2)	N1 ² -M1-N1	90.006(2)
M-N1 ⁱⁱⁱ	1.949(2)	N1 ¹ -M1-N1 ³	90.007(1)
M-N1 ^{iv}	1.949(2)	N1 ³ -M1-N1	178.75(12)
N1-C1	1.375(3)	N1 ¹ -M1-N1	90.007(2)
N1-C4	1.381(3)	N1 ² -M1-N1 ³	90.007(2)
C1-C2	1.434(3)	C1-N1-M1	127.60(15)
C2-C3	1.349(4)	C4-N1-M1	127.24(15)
C3-C4	1.431(3)	C1-N1-C4	105.05(18)
C4-C5	1.388(3)	C4-C5-C1 ¹	122.3(2)
C1-C5 ⁱⁱ	1.388(3)		
C5-C6	1.494(3)		
C6-C7	1.379(4)		
C6-C11	1.381(4)		
C7-C8	1.386(4)		
C8-C9	1.380(5)		
C9-C10	1.372(5)		
C10-C11	1.386(4)		

i 1-3/2-Y, 1/2+X, -1/2-Z

ii 2-1/2+Y, -3/2-X, -1/2-Z

iii 3-2-X, -1-Y, +Z

*Table 10.1.3 Crystal data and structure refinement **Ni-TPP** and **Cu-TPP**.*

	Ni-TPP	Cu-TPP
Empirical formula	C ₄₄ H ₂₈ N ₄ Ni	C ₄₄ H ₂₈ N ₄ Cu
Formula weight	671.41	676.24
Temperature/K	293(2)	293(2)
Crystal system	tetragonal	tetragonal
Space group	I $\bar{4}$ 2d	I $\bar{4}$ 2d
a/Å	15.0800(2)	15.0627(5)
b/Å	15.0800(2)	15.0627(5)
c/Å	13.8780(3)	13.9877(8)
$\alpha/^\circ$	90	90
$\beta/^\circ$	90	90
$\gamma/^\circ$	90	90
Volume/Å ³	3155.95(11)	3173.6(3)
Z	4	4
$\rho_{\text{calc}}/\text{cm}^{-3}$	1.413	1.415
μ/mm^{-1}	1.195	1.278
F(000)	1392.0	1396.0
Crystal size/mm ³	0.12 × 0.08 × 0.08	0.30 × 0.30 × 0.30
Radiation/Å	Cu-K α (λ = 1.54184)	Cu-K α (λ = 1.54184)
2 θ range/ $^\circ$	8.66 to 88.966	8.626 to 88.832
Index ranges	-13 ≤ h ≤ 13	-12 ≤ h ≤ 13
Reflections collected	8110	4447
Independent reflections	629	631
R _{int}	0.0280	0.0535
R _{sigma}	0.0105	0.0316
Data/restraints/parameters	629/0/111	631/0/111
Goodness-of-fit on F ²	1.247	1.110
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0587	R ₁ = 0.0324
Final R indexes [all data]	R ₁ = 0.0588	R ₁ = 0.0390
Largest diff. peak/hole/eÅ ⁻³	0.24/-0.24	0.12/-0.19
Flack parameter	0.012(16)	0.06(3)

Table 10.1.4 Experimental bond lengths (Å) and angles (°) for *Ni-TPP* and *Cu-TPP*.

	Ni-TPP	Cu-TPP		Ni-TPP	Cu-TPP
M-N1	1.93(1)	1.970(6)	N1 ¹ -M1-N1 ²	179.7(7)	178.4(5)
M-N1 ⁱⁱ	1.93(1)	1.970(6)	N1 ² -M1-N1	90.000(5)	90.011(7)
M-N1 ⁱⁱⁱ	1.93(1)	1.970(6)	N1 ¹ -M1-N1 ³	90.000(3)	90.011(9)
M-N1 ^{iv}	1.93(1)	1.970(6)	N1 ³ -M1-N1	179.7(7)	178.4(5)
N1-C1	1.38(2)	1.383(8)	N1 ¹ -M1-N1	90.000(6)	90.011(9)
N1-C4	1.39(2)	1.376(9)	N1 ² -M1-N1 ³	90.001(4)	90.010(7)
C1-C2	1.42(2)	1.43(1)	C1-N1-M1	127.5(7)	126.8(5)
C2-C3	1.36(2)	1.35(1)	C4-N1-M1	125.8(7)	128.0(6)
C3-C4	1.48(2)	1.43(1)	C1-N1-C4	106.5(9)	105.1(6)
C4-C5	1.38(2)	1.38(1)	C4-C5-C1 ¹	118.5(11)	123.5(8)
C1-C5 ⁱⁱ	1.40(2)	1.40(1)	N1-C4-C5	129.3(11)	124.6(8)
C5-C6	1.46(2)	1.50(1)	N1-C1-C5 ¹	126.5(10)	125.4(8)
C6-C7	1.38(2)	1.36(1)	N1-C1-C2	110.5(10)	110.2(6)
C6-C11	1.37(2)	1.36(1)	N1-C4-C3	108.4(11)	110.6(8)
C7-C8	1.40(2)	1.40(1)	C1-C2-C3	107.7(11)	107.0(7)
C8-C9	1.37(2)	1.35(1)	C2-C3-C4	106.7(11)	107.0(8)
C9-C10	1.36(2)	1.35(1)	C3-C4-C5	122.1(13)	124.8(9)
C10-C11	1.39(2)	1.38(1)	C2-C1-C5 ¹	122.6(11)	124.1(9)
			C4-C5-C6	120.6(11)	119.6(8)
			C6-C5-C1 ¹	120.8(10)	116.9(8)
			C5-C6-C7	119.0(12)	121.1(9)
			C5-C6-C11	122.1(12)	120.6(9)
			C6-C7-C8	120.4(13)	120.9(9)
			C6-C11-C10	119.7(13)	120.2(9)
			C7-C8-C9	120.1(13)	120.0(9)
			C9-C10-C11	122.2(13)	121.6(9)
			C8-C9-C10	118.6(13)	119.1(9)
			C7-C6-C11	118.9(11)	118.3(8)

ii-3/2-Y,1/2+X,-1/2-Z; iii-2-X,-1-Y,+Z; iv-1/2+Y,-3/2-X,-1/2-Z

1-3/2-Y,1/2+X,-1/2-Z; 2-1/2+Y,-3/2-X,-1/2-Z; 3-2-X,-1-Y,+Z

Table 10.1.5 Crystal data and structure refinement for *Zn-TPP*, *Zn-TPP DMF* and *Zn-TPP DMF (DCM)*.

	Zn-TPP	Zn-TPP DMF	Zn-TPP DMF DCM
Empirical formula	C ₂₂ H ₁₄ N ₂ Zn _{0.5}	C ₄₇ H ₃₅ N ₅ OZn	C ₂₄ H _{18.5} ClN _{2.5} O _{0.5} Zn _{0.5}
Formula weight	339.04	751.17	418.05
Temperature/K	293(2)	172.9(8)	293(2)
Crystal system	tetragonal	monoclinic	triclinic
Space group	I4/m	P2 ₁ /c	P-1
a/Å	13.4206(9)	14.9527(5)	11.3499(4)
b/Å	13.4206(9)	8.9590(3)	12.6326(4)
c/Å	9.7210(16)	27.5364(11)	14.6881(3)
α/°	90.00	90	99.480(2)
β/°	90.00	102.205(4)	93.910(2)
γ/°	90.00	90	103.693(3)
Volume/Å ³	1750.9(3)	3605.4(2)	2005.50(11)
Z	4	4	4
ρ _{calc} /cm ³	1.286	1.384	1.385
μ/mm ⁻¹	0.738	1.299	2.421
F(000)	700.0	1560.0	864.0
Crystal size/mm ³	0.289 × 0.127 × 0.098	0.13 × 0.053 × 0.03	0.13 × 0.053 × 0.03
Radiation	Mo Kα (λ = 0.71073)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2θ range/°	7.98 to 57.22	6.048 to 133.75	7.332 to 124.512
Index ranges	-14 ≤ h ≤ 16, -15 ≤ k ≤ 17, -13 ≤ l ≤ 6	-17 ≤ h ≤ 14, -10 ≤ k ≤ 8, -32 ≤ l ≤ 32	-13 ≤ h ≤ 12, -13 ≤ k ≤ 14, -16 ≤ l ≤ 13
Reflections collected	2029	33915	11891
Independent reflections	1055	6382	6080
R _{int}	0.0317	0.1098	0.0219
R _{sigma}	0.0476	0.0732	0.0281
Data/restraints/parameters	1055/0/69	6382/0/489	6080/0/516
Goodness-of-fit on F ²	1.033	1.037	1.045
Final R indexes [I>=2σ (I)]	R ₁ = 0.0419, wR ₂ = 0.1022	R ₁ = 0.0509, wR ₂ = 0.1056	R ₁ = 0.0382, wR ₂ = 0.1048
Final R indexes [all data]	R ₁ = 0.0559, wR ₂ = 0.1098	R ₁ = 0.0854, wR ₂ = 0.1218	R ₁ = 0.0425, wR ₂ = 0.1094
Largest diff. peak/hole/eÅ ⁻³	0.30/-0.34	0.56/-0.31	0.55/-0.46

Tables 10.1.6, 10.1.7 and 10.1.8 illustrate all the bond lengths distances for the **Zn-TPP** fragment, compared to the corresponding XRD parameters. The bond differences between the XRD structures and the optimized geometries range, for the C-C bond, from a maximum of 0.15 Å to a minimum of 0.00 Å, with an averaged value of 0.04 Å. For the C-H value all the differences are 0.00 Å. The C-N differences are, again, 0.00 Å.

Table 10.1.6 Distances (Å) for all the C-C in the 2 rings fragment of Zn-TPP. First column distances are from X-ray data, and second column are from the optimized fragment at B3LYP/6-31G(d).

Atoms		XRD	B3LYP	Atoms		XRD	B3LYP	Atoms		XRD	B3LYP
C8	C10	1,402	1,405	C43	C52	1,379	1,361	C98	C104	1,340	1,446
C8	C33	1,442	1,396	C47	C166	1,380	1,450	C100	C110	1,343	1,418
C9	C15	1,401	1,404	C49	C56	1,384	1,411	C102	C108	1,382	1,365
C9	C29	1,440	1,500	C52	C150	1,362	1,414	C108	C162	1,376	1,450
C10	C14	1,402	1,396	C54	C57	1,382	1,500	C109	C118	1,378	1,416
C10	C17	1,497	1,396	C56	C150	1,368	1,449	C109	C152	1,381	1,423
C11	C20	1,400	1,397	C57	C147	1,358	1,449	C114	C123	1,379	1,493
C11	C35	1,442	1,412	C79	C81	1,402	1,365	C118	C153	1,380	1,442
C12	C21	1,405	1,414	C79	C104	1,442	1,404	C120	C127	1,384	1,446
C12	C24	1,438	1,450	C80	C86	1,401	1,404	C123	C168	1,362	1,368
C13	C15	1,401	1,450	C80	C100	1,440	1,396	C125	C128	1,382	1,425
C13	C41	1,437	1,414	C81	C85	1,402	1,397	C127	C168	1,368	1,492
C14	C22	1,436	1,362	C81	C88	1,497	1,396	C128	C175	1,358	1,445
C15	C19	1,502	1,449	C82	C91	1,400	1,396	C143	C145	1,397	1,441
C16	C21	1,400	1,363	C82	C106	1,442	1,447	C145	C147	1,363	1,371
C16	C39	1,446	1,450	C83	C92	1,405	1,415	C152	C186	1,390	1,406
C17	C43	1,383	1,414	C83	C95	1,438	1,363	C153	C185	1,400	1,406
C17	C49	1,379	1,499	C84	C86	1,401	1,451	C155	C159	1,383	1,395
C18	C20	1,401	1,414	C84	C112	1,437	1,417	C157	C159	1,369	1,397
C18	C27	1,440	1,405	C85	C93	1,436	1,494	C160	C164	1,383	1,397
C19	C31	1,388	1,405	C86	C90	1,502	1,424	C162	C164	1,369	1,395
C19	C155	1,384	1,396	C87	C92	1,400	1,406	C165	C179	1,387	1,407
C20	C26	1,504	1,396	C87	C110	1,446	1,406	C166	C178	1,400	1,407
C21	C38	1,499	1,397	C88	C114	1,383	1,395	C171	C173	1,397	1,395
C22	C41	1,346	1,396	C88	C120	1,379	1,397	C173	C175	1,363	1,397
C24	C35	1,354	1,500	C89	C91	1,401	1,397	C178	C179	1,400	1,397
C26	C54	1,386	1,414	C89	C98	1,440	1,395	C185	C186	1,400	1,395
C26	C143	1,383	1,404	C90	C102	1,388	1,494				
C27	C33	1,340	1,404	C90	C160	1,384	1,425				
C29	C39	1,343	1,396	C91	C97	1,504	1,406				
C31	C37	1,382	1,396	C92	C109	1,499	1,406				
C37	C157	1,376	1,397	C93	C112	1,346	1,395				
C38	C47	1,378	1,396	C95	C106	1,354	1,396				
C38	C165	1,381	1,450	C97	C125	1,386	1,397				
				C97	C171	1,383	1,395				

Table 10.1.7 Distances (Å) for all the C-H in the 2 rings fragment of Zn-TPP. First column distances are from X-ray data, and second column are from the optimized fragment at B3LYP/6–31G(d).

<i>Atoms</i>		<i>XRD</i>	<i>B3LYP</i>	<i>Atoms</i>		<i>XRD</i>	<i>B3LYP</i>
C1	H132	1,0866	1,0866	C61	H138	1,08	1,08
C3	H127	1,0866	1,0866	C65	H124	1,08	1,08
C4	H128	1,0869	1,0869	C66	H114	1,08	1,08
C5	H130	1,0867	1,0867	C70	H120	1,087	1,087
C6	H133	1,0869	1,0869	C71	H121	1,087	1,087
C11	H101	1,0802	1,0802	C72	H123	1,087	1,087
C12	H129	1,0803	1,0803	C73	H126	1,087	1,087
C16	H113	1,0802	1,0802	C74	H125	1,087	1,087
C17	H102	1,0803	1,0803	C77	H108	1,086	1,086
C21	H106	1,0865	1,0865	C78	H109	1,087	1,087
C22	H107	1,0869	1,0869	C79	H115	1,087	1,087
C23	H112	1,0863	1,0863	C80	H119	1,087	1,087
C24	H117	1,0868	1,0867	C81	H118	1,086	1,086
C25	H116	1,0866	1,0865	C84	H151	1,08	1,08
C28	H99	1,0865	1,0865	C85	H141	1,08	1,08
C29	H100	1,0869	1,0869	C91	H122	1,08	1,08
C30	H103	1,0867	1,0867	C92	H150	1,08	1,08
C31	H105	1,0869	1,0869	C94	H148	1,087	1,087
C32	H104	1,0865	1,0865	C95	H149	1,087	1,087
C35	H142	1,0802	1,0802	C96	H152	1,087	1,087
C36	H131	1,0803	1,0803	C97	H154	1,087	1,087
C42	H111	1,0803	1,0803	C98	H153	1,087	1,087
C43	H140	1,0802	1,0802				
C45	H136	1,0863	1,0863				
C46	H137	1,087	1,087				
C47	H143	1,0867	1,0867				
C48	H147	1,087	1,087				
C49	H146	1,0864	1,0864				
C50	H139	1,0863	1,0863				
C51	H135	1,0868	1,0867				
C52	H134	1,0866	1,0865				
C54	H144	1,0865	1,0865				
C55	H145	1,0869	1,0869				
C60	H110	1,0802	1,0802				

Table 10.1.8. Distances ($\text{\AA}$) for all the C-N in the 2 rings fragment of Zn-TPP. First column distances are from X-ray data, and second column are from the optimized fragment at B3LYP/6-31G(d).

<i>Atoms</i>		<i>XRD</i>	<i>B3LYP</i>
C8	N9	1,375	1,375
C10	N9	1,375	1,375
C15	N14	1,375	1,375
C18	N14	1,375	1,375
C34	N33	1,375	1,375
C37	N33	1,376	1,376
C39	N40	1,376	1,376
C41	N40	1,376	1,376
C57	N58	1,376	1,376
C59	N58	1,376	1,376
C64	N63	1,376	1,376
C67	N63	1,375	1,375
C83	N82	1,375	1,375
C86	N82	1,375	1,375
C88	N89	1,375	1,375
C90	N89	1,375	1,375

Tables 10.1.9, 10.1.10 and 10.1.11 illustrate all the bond lengths distances for the **Zn-TPP-DMF** fragment, compared to the corresponding XRD parameters. The bond differences between the XRD structures and the optimized geometries range, for the C-C bond, from a maximum of 0.15 Å to a minimum of 0.00 Å, with an averaged value of 0.05 Å. For the C-H value we have a maximum value of 0.17 Å, a minimum of 0.10 Å and an average of 0.14 Å. The C-N differences range from a maximum of 0.08 Å to a minimum of 0.00 Å with an average of 0.01 Å.

Table 10.1.9 Distances (Å) for all the C-C in the 2 rings fragment of Zn-TPP-DMF. First column distances are from X-ray data, and second column are from the optimized fragment at B3LYP/6-31G(d).

Atoms		XRD	B3LYP	Atoms		XRD	B3LYP	Atoms		XRD	B3LYP
C5	C7	1,382	1,405	C73	C74	1,488	1,449	C128	C129	1,439	1,450
C5	C64	1,401	1,396	C73	C85	1,406	1,414	C129	C130	1,404	1,414
C7	C9	1,381	1,405	C74	C75	1,396	1,498	C130	C131	1,502	1,362
C9	C11	1,384	1,498	C74	C83	1,395	1,415	C130	C134	1,422	1,450
C11	C65	1,382	1,396	C75	C77	1,379	1,405	C131	C132	1,391	1,413
C15	C17	1,382	1,397	C77	C79	1,373	1,405	C134	C135	1,443	1,414
C15	C131	1,401	1,397	C79	C81	1,384	1,396	C135	C137	1,347	1,497
C17	C19	1,381	1,413	C81	C83	1,378	1,396	C137	C139	1,440	1,450
C19	C21	1,384	1,414	C85	C86	1,442	1,397	C139	C140	1,410	1,450
C21	C132	1,382	1,449	C86	C88	1,336	1,396	C140	C141	1,488	1,362
C27	C46	1,344	1,413	C88	C90	1,445	1,448	C140	C152	1,406	1,414
C27	C56	1,444	1,362	C90	C91	1,395	1,364	C141	C142	1,396	1,498
C29	C30	1,392	1,498	C91	C92	1,500	1,448	C141	C150	1,395	1,450
C29	C36	1,406	1,414	C92	C93	1,385	1,449	C142	C144	1,379	1,450
C29	C57	1,487	1,405	C92	C101	1,394	1,414	C144	C146	1,373	1,362
C30	C32	1,385	1,405	C93	C95	1,388	1,363	C146	C148	1,384	1,405
C32	C34	1,371	1,396	C95	C97	1,373	1,449	C148	C150	1,378	1,405
C34	C35	1,382	1,397	C97	C99	1,376	1,415	C152	C153	1,442	1,396
C35	C36	1,376	1,397	C99	C101	1,388	1,498	C153	C155	1,336	1,397
C41	C46	1,436	1,396	C104	C120	1,344	1,414	C155	C157	1,445	1,396
C41	C91	1,413	1,450	C104	C123	1,444	1,405	C157	C158	1,395	1,396
C56	C57	1,412	1,414	C106	C107	1,392	1,405	C158	C159	1,500	1,405
C57	C58	1,405	1,362	C106	C113	1,406	1,396	C159	C160	1,385	1,405
C58	C59	1,447	1,449	C106	C124	1,487	1,397	C159	C168	1,394	1,396
C59	C61	1,349	1,498	C107	C109	1,385	1,396	C160	C162	1,388	1,397
C61	C62	1,439	1,415	C109	C111	1,371	1,396	C162	C164	1,373	1,397
C62	C63	1,404	1,405	C111	C112	1,382	1,497	C164	C166	1,376	1,396
C63	C64	1,502	1,405	C112	C113	1,376	1,414	C72	C73	1,410	1,362
C63	C67	1,422	1,396	C117	C120	1,436	1,405	C126	C128	1,349	1,396
C64	C65	1,391	1,397	C117	C158	1,413	1,405				
C67	C68	1,443	1,396	C123	C124	1,412	1,396				
C68	C70	1,347	1,396	C124	C125	1,405	1,397				
C70	C72	1,440	1,449	C125	C126	1,447	1,397				

Table 10.1.10 Distances (Å) for all the C-H in the 2 rings fragment of Zn-TPP-DMF. First column distances are from X-ray data, and second column are from the optimized fragment at B3LYP/6-31G(d).

<i>Atoms</i>	<i>XRD</i>	<i>B3LYP</i>	<i>Atoms</i>	<i>XRD</i>	<i>B3LYP</i>
C5 H6	0,949	1,086	C86 H87	0,951	1,097
C7 H8	0,950	1,087	C88 H89	0,951	1,097
C9 H10	0,951	1,087	C93 H94	0,949	1,096
C11 H12	0,951	1,087	C95 H96	0,950	1,096
C15 H16	0,949	1,087	C97 H98	0,949	1,093
C17 H18	0,950	1,080	C99 H100	0,950	1,090
C19 H20	0,951	1,080	C101 H102	0,950	1,095
C21 H22	0,951	1,098	C104 H105	0,951	1,095
C24 H25	0,949	1,090	C107 H108	0,950	1,099
C27 H28	0,951	1,096	C109 H110	0,951	1,081
C30 H31	0,950	1,096	C111 H13	0,950	1,081
C32 H33	0,951	1,087	C112 H3	0,950	1,086
C34 H2	0,950	1,087	C113 H114	0,951	1,087
C35 H1	0,950	1,087	C120 H103	0,951	1,087
C36 H37	0,951	1,087	C126 H127	0,949	1,087
C42 H43	0,949	1,087	C128 H14	0,951	1,086
C46 H26	0,951	1,080	C132 H133	0,950	1,087
C47 H48	0,979	1,080	C135 H136	0,949	1,087
C47 H49	0,980	1,086	C137 H138	0,951	1,087
C47 H50	0,980	1,087	C142 H143	0,950	1,087
C52 H53	0,980	1,087	C144 H145	0,949	1,086
C52 H54	0,981	1,087	C146 H147	0,951	1,080
C52 H178	0,920	1,087	C148 H149	0,950	1,080
C59 H60	0,949	1,080	C150 H151	0,950	1,080
C61 H4	0,951	1,080	C153 H154	0,951	1,080
C65 H66	0,950	1,087	C155 H156	0,951	1,080
C68 H69	0,949	1,087	C160 H161	0,949	1,080
C70 H71	0,951	1,087	C162 H163	0,950	1,086
C75 H76	0,950	1,087	C164 H165	0,949	1,087
C77 H78	0,949	1,086	C166 H167	0,950	1,087
C79 H80	0,951	1,080	C168 H169	0,950	1,087
C81 H82	0,950	1,080	C170 H172	0,920	1,086
C83 H84	0,950	1,093	C170 H173	0,980	1,086
			C170 H177	0,920	1,087
			C171 H174	0,920	1,087
			C171 H175	0,920	1,087
			C171 H176	0,980	1,086

Table 10.1.11 Distances ($\text{\AA}$) for all the C-H in the 2 rings fragment of Zn-TPP-DMF. First column distances are from X-ray data, and second column are from the optimized fragment at B3LYP/6-31G(d).

<i>Atoms</i>		<i>XRD</i>	<i>B3LYP</i>
C24	N23	1,323	1,374
C41	N39	1,372	1,374
C42	N40	1,323	1,345
C52	N40	1,449	1,373
C56	N39	1,367	1,373
C58	N45	1,364	1,373
C62	N45	1,373	1,373
C67	N51	1,367	1,375
C72	N51	1,373	1,375
C85	N55	1,361	1,340
C90	N55	1,371	1,373
C117	N116	1,372	1,373
C123	N116	1,367	1,371
C125	N119	1,364	1,371
C129	N119	1,373	1,372
C134	N121	1,367	1,372
C139	N121	1,373	1,372
C152	N122	1,361	1,372

Tables 10.1.12, 10.1.13 and 10.1.14 illustrate all the bond lengths distances for the **Zn-TPP-DMF (DCM)** fragment, compared to the corresponding XRD parameters. The bond differences between the XRD structures and the theoretically optimized geometries range, for the C-C bond, from a maximum of 0.04 Å to a minimum of 0.00 Å, with an averaged value of 0.01 Å. For the C-H value, we have a maximum of 0.17 Å, a minimum of 0.09 Å and an average of 0.14 Å. Considering the C-N, differences range from a maximum of 0.07 Å to a minimum of 0.00 Å with an average of 0.01 Å.

Table 10.1.12 Distances (Å) for all the C-C in the 2 rings fragment of Zn-TPP-DMF (DCM). First column distances are from X-ray data, and second column are from the optimized fragment at B3LYP/6-31G(d).

Atoms		XRD	B3LYP	Atoms		XRD	B3LYP	Atoms		XRD	B3LYP
C8	C10	1,402	1,415	C43	C52	1,379	1,396	C97	C125	1,386	1,405
C8	C33	1,442	1,449	C47	C166	1,380	1,396	C97	C171	1,383	1,405
C9	C15	1,401	1,414	C49	C56	1,384	1,396	C98	C104	1,340	1,363
C9	C29	1,440	1,450	C52	C150	1,362	1,396	C100	C110	1,343	1,361
C10	C14	1,402	1,412	C54	C57	1,382	1,396	C102	C108	1,382	1,396
C10	C17	1,497	1,500	C56	C150	1,368	1,397	C108	C162	1,376	1,396
C11	C20	1,400	1,414	C57	C147	1,358	1,396	C109	C118	1,378	1,404
C11	C35	1,442	1,449	C79	C81	1,402	1,415	C109	C152	1,381	1,404
C12	C21	1,405	1,414	C79	C104	1,442	1,449	C114	C123	1,379	1,396
C12	C24	1,438	1,449	C80	C86	1,401	1,414	C118	C153	1,380	1,396
C13	C15	1,401	1,414	C80	C100	1,440	1,450	C120	C127	1,384	1,396
C13	C41	1,437	1,450	C81	C85	1,402	1,412	C123	C168	1,362	1,396
C14	C22	1,436	1,450	C81	C88	1,497	1,500	C125	C128	1,382	1,396
C15	C19	1,502	1,500	C82	C91	1,400	1,414	C127	C168	1,368	1,397
C16	C21	1,400	1,411	C82	C106	1,442	1,449	C128	C175	1,358	1,396
C16	C39	1,446	1,450	C83	C92	1,405	1,414	C143	C145	1,397	1,396
C17	C43	1,383	1,404	C83	C95	1,438	1,449	C145	C147	1,363	1,397
C17	C49	1,379	1,405	C84	C86	1,401	1,414	C152	C186	1,390	1,396
C18	C20	1,401	1,413	C84	C112	1,437	1,450	C153	C185	1,400	1,397
C18	C27	1,440	1,449	C85	C93	1,436	1,450	C155	C159	1,383	1,396
C19	C31	1,388	1,404	C86	C90	1,502	1,500	C157	C159	1,369	1,397
C19	C155	1,384	1,404	C87	C92	1,400	1,411	C160	C164	1,383	1,396
C20	C26	1,504	1,499	C87	C110	1,446	1,450	C162	C164	1,369	1,397
C21	C38	1,499	1,500	C88	C114	1,383	1,404	C165	C179	1,387	1,396
C22	C41	1,346	1,362	C88	C120	1,379	1,405	C166	C178	1,400	1,397
C24	C35	1,354	1,365	C89	C91	1,401	1,413	C171	C173	1,397	1,396
C26	C54	1,386	1,405	C89	C98	1,440	1,449	C173	C175	1,363	1,397
C26	C143	1,383	1,405	C90	C102	1,388	1,404	C178	C179	1,400	1,396
C27	C33	1,340	1,363	C90	C160	1,384	1,404	C185	C186	1,400	1,396
C29	C39	1,343	1,361	C91	C97	1,504	1,499	C38	C165	1,381	1,404
C31	C37	1,382	1,396	C92	C109	1,499	1,500				
C37	C157	1,376	1,396	C93	C112	1,346	1,362				
C38	C47	1,378	1,404	C95	C106	1,354	1,365				

Table 10.1.13 Distances (Å) for all the C-H in the 2 rings fragment of Zn-TPP-DMF (DCM). First column distances are from X-ray data, and second column are from the optimized fragment at B3LYP/6-31G(d).

Atoms		XRD	B3LYP	Atoms		XRD	B3LYP
C22	H23	0,931	1,080	C98	H99	0,930	1,081
C24	H25	0,930	1,081	C100	H101	0,930	1,080
C27	H28	0,930	1,081	C102	H103	0,931	1,087
C29	H30	0,930	1,080	C104	H105	0,930	1,081
C31	H32	0,931	1,087	C106	H107	0,930	1,081
C33	H34	0,930	1,081	C108	H149	0,929	1,087
C35	H36	0,930	1,081	C110	H111	0,930	1,080
C37	H170	0,929	1,087	C112	H113	0,931	1,080
C39	H40	0,930	1,080	C114	H115	0,929	1,086
C41	H42	0,931	1,080	C116	H117	0,931	1,097
C43	H44	0,929	1,086	C118	H119	0,931	1,087
C45	H46	0,931	1,097	C120	H121	0,931	1,087
C47	H48	0,931	1,087	C123	H124	0,930	1,087
C49	H50	0,931	1,087	C125	H126	0,930	1,087
C52	H53	0,930	1,087	C127	H169	0,930	1,087
C54	H55	0,930	1,087	C128	H129	0,930	1,087
C56	H151	0,930	1,087	C130	H131	0,960	1,095
C57	H58	0,930	1,087	C130	H132	0,960	1,094
C59	H60	0,960	1,095	C130	H133	0,959	1,089
C59	H61	0,960	1,094	C134	H135	0,960	1,095
C59	H62	0,959	1,089	C134	H136	0,960	1,096
C63	H64	0,960	1,095	C134	H137	0,961	1,093
C63	H65	0,960	1,096	C139	H140	0,970	1,087
C63	H66	0,961	1,093	C139	H141	0,970	1,087
C68	H69	0,970	1,087	C143	H144	0,930	1,086
C68	H70	0,970	1,087	C145	H146	0,931	1,087
C93	H94	0,931	1,080	C147	H148	0,930	1,087
C95	H96	0,930	1,081	C150	H177	1,000	1,087
C166	H167	0,929	1,087	C152	H122	0,930	1,087
C168	H183	1,000	1,087	C153	H154	0,929	1,087
C171	H172	0,930	1,086	C155	H156	0,930	1,086
C173	H174	0,931	1,087	C157	H158	0,930	1,087
C175	H176	0,930	1,087	C159	H182	1,000	1,087
C178	H180	1,000	1,087	C160	H161	0,930	1,086
C179	H181	1,000	1,087	C162	H163	0,930	1,087
C185	H187	1,000	1,087	C164	H184	1,000	1,087
C186	H188	1,000	1,087	C165	H51	0,930	1,087

Table 10.1.14 Distances (Å) for all the C-N in the 2 rings fragment of Zn-TPP-DMF (DCM). First column distances are from X-ray data, and second column are from the optimized fragment at B3LYP/6–31G(d).

Atoms		XRD	B3LYP
C8	N4	1,370	1,372
C9	N3	1,370	1,372
C11	N5	1,371	1,373
C12	N5	1,376	1,373
C13	N6	1,374	1,374
C14	N6	1,372	1,374
C16	N3	1,368	1,373
C18	N4	1,376	1,373
C45	N7	1,309	1,337
C59	N7	1,442	1,372
C79	N75	1,370	1,372
C80	N74	1,370	1,373
C82	N76	1,371	1,373
C83	N76	1,376	1,374
C84	N77	1,374	1,374
C85	N77	1,372	1,373
C87	N74	1,368	1,373
C89	N75	1,376	1,337

Table 10.1.15, 10.1.16 and 10.1.17 illustrates all the bond lengths distances for the excited state of **Zn-TPP** fragment, optimized using TD DFT method, compared to the corresponding XRD parameters. The bond differences between the XRD structures and the theoretically optimized geometries range, for the C-C bond, from a maximum of 0.10 Å to a minimum of 0.00 Å, with an averaged value of 0.03 Å. For the C-H value, we have a maximum value of 0.01 Å, a minimum of 0.00 Å and an average of 0.00 Å. Considering the C-N, differences range from a maximum of 0.01 Å to a minimum of 0.00 Å, with an averaged value of 0.00 Å.

Table 10.1.15 Distances (Å) for all the C-C in the 2 rings fragment of the excited state of Zn-TPP. First column distances are from X-ray data, and second column are from the optimized TD B3LYP/6–31G(d).

Atoms		XRD	TD B3LYP	Atoms		XRD	TD B3LYP
C1	C2	1,404	1,404	C56	C57	1,412	1,406
C1	C6	1,396	1,396	C56	C86	1,412	1,407
C2	C3	1,404	1,404	C57	C61	1,447	1,395
C2	C7	1,500	1,499	C59	C60	1,447	1,397
C3	C4	1,396	1,396	C59	C75	1,412	1,397
C4	C5	1,396	1,396	C60	C61	1,362	1,396
C5	C6	1,396	1,396	C64	C65	1,447	1,447
C7	C8	1,411	1,411	C64	C68	1,411	1,364
C7	C37	1,411	1,412	C65	C66	1,362	1,445
C8	C12	1,447	1,447	C66	C67	1,448	1,414
C10	C11	1,447	1,447	C67	C75	1,412	1,421
C10	C26	1,411	1,411	C68	C69	1,500	1,495
C11	C12	1,362	1,362	C68	C90	1,411	1,441
C15	C16	1,447	1,447	C69	C70	1,404	1,443
C15	C19	1,412	1,362	C69	C74	1,404	1,422
C16	C17	1,362	1,447	C70	C71	1,396	1,368
C17	C18	1,447	1,412	C71	C72	1,396	1,492
C18	C26	1,412	1,412	C72	C73	1,396	1,415
C19	C20	1,498	1,498	C73	C74	1,396	1,407
C19	C41	1,412	1,447	C75	C76	1,499	1,406
C20	C21	1,405	1,447	C76	C77	1,405	1,395
C20	C25	1,404	1,412	C76	C81	1,404	1,397
C21	C22	1,395	1,362	C77	C78	1,396	1,397
C22	C23	1,397	1,499	C78	C79	1,397	1,395
C23	C24	1,397	1,412	C79	C80	1,397	1,490
C24	C25	1,396	1,405	C80	C81	1,396	1,416
C26	C27	1,499	1,404	C83	C84	1,447	1,407
C27	C28	1,404	1,396	C83	C87	1,412	1,407
C27	C32	1,404	1,397	C84	C85	1,362	1,394
C28	C29	1,396	1,397	C85	C86	1,447	1,398
C29	C30	1,396	1,396	C87	C88	1,411	1,397
C30	C31	1,396	1,500	C87	C93	1,499	1,395
C31	C32	1,396	1,411	C88	C92	1,447	1,405
C34	C35	1,448	1,404	C90	C91	1,447	1,405
C34	C38	1,412	1,404	C91	C92	1,362	1,395
C35	C36	1,362	1,396	C93	C94	1,404	1,397
C36	C37	1,447	1,396	C93	C98	1,404	1,396
C38	C39	1,412	1,396	C94	C95	1,396	1,396
C38	C44	1,499	1,396	C95	C96	1,396	1,445
C39	C43	1,447	1,404	C96	C97	1,396	1,364
C41	C42	1,447	1,405	C97	C98	1,396	1,447
C42	C43	1,362	1,396	C48	C49	1,396	1,448
C44	C45	1,404	1,397	C50	C51	1,397	1,443
C44	C49	1,405	1,397	C50	C55	1,397	1,368
C45	C46	1,396	1,395	C51	C52	1,396	1,423
C46	C47	1,397	1,447	C52	C53	1,404	1,441
C47	C48	1,397	1,362	C53	C54	1,405	1,423
C54	C55	1,395	1,415	C53	C56	1,498	1,492

Table 10.1.16 Distances (Å) for all the C-H in the 2 rings fragment of the excited state of Zn-TPP. First column distances are from X-ray data, and second column are from the optimized TD B3LYP/6-31G(d).

<i>Atoms</i>				<i>Atoms</i>			
		<i>XRD</i>	<i>TD B3LYP</i>			<i>XRD</i>	<i>TD B3LYP</i>
C1	H132	1,087	1,087	C51	H135	1,087	1,080
C3	H127	1,087	1,087	C52	H134	1,087	1,086
C4	H128	1,087	1,087	C54	H144	1,087	1,087
C5	H130	1,087	1,087	C55	H145	1,087	1,087
C6	H133	1,087	1,087	C60	H110	1,080	1,087
C11	H101	1,080	1,080	C61	H138	1,080	1,086
C12	H129	1,080	1,080	C65	H124	1,080	1,080
C16	H113	1,080	1,080	C66	H114	1,080	1,080
C17	H102	1,080	1,080	C70	H120	1,087	1,080
C21	H106	1,087	1,080	C71	H121	1,087	1,080
C22	H107	1,087	1,080	C72	H123	1,087	1,086
C23	H112	1,086	1,086	C73	H126	1,087	1,087
C24	H117	1,087	1,087	C74	H125	1,087	1,087
C25	H116	1,087	1,087	C77	H108	1,086	1,087
C28	H99	1,087	1,087	C78	H109	1,087	1,086
C29	H100	1,087	1,086	C79	H115	1,087	1,086
C30	H103	1,087	1,087	C80	H119	1,087	1,087
C31	H105	1,087	1,087	C81	H118	1,086	1,086
C32	H104	1,087	1,087	C84	H151	1,080	1,087
C35	H142	1,080	1,087	C85	H141	1,080	1,086
C36	H131	1,080	1,087	C91	H122	1,080	1,086
C42	H111	1,080	1,087	C92	H150	1,080	1,087
C43	H140	1,080	1,087	C94	H148	1,087	1,087
C45	H136	1,086	1,086	C95	H149	1,087	1,087
C46	H137	1,087	1,087	C96	H152	1,087	1,086
C47	H143	1,087	1,087	C97	H154	1,087	1,080
C48	H147	1,087	1,080	C98	H153	1,087	1,080
C49	H146	1,086	1,080	C50	H139	1,086	1,080

Table 10.1.17 Distances (Å) for all the C-N in the 2 rings fragment of the excited state of Zn-TPP. First column distances are from X-ray data, and second column are from the optimized TD B3LYP/6–31G(d).

<i>Atoms</i>		<i>XRD</i>	<i>B3LYP</i>
C8	N9	1,375	1,375
C10	N9	1,375	1,375
C15	N14	1,375	1,375
C18	N14	1,375	1,375
C34	N33	1,375	1,376
C37	N33	1,376	1,376
C39	N40	1,376	1,376
C41	N40	1,376	1,375
C57	N58	1,376	1,378
C59	N58	1,376	1,379
C64	N63	1,376	1,378
C67	N63	1,375	1,381
C83	N82	1,375	1,379
C86	N82	1,375	1,377
C88	N89	1,375	1,381
C90	N89	1,375	1,379

Table 10.1.18, 10.1.19 and 10.1.20 illustrates all the bond lengths distances for the excited state of **Zn-TPP-DMF** fragment, optimized using TD DFT method, compared to the corresponding XRD parameters. The bond differences between the XRD structures and the theoretically optimized geometries range, for the C-C bond, from a maximum of 0.55 Å to a minimum of 0.00 Å, with an averaged value of 0.05 Å. For the C-H value, we have a maximum value of 0.17 Å, a minimum of 0.10 Å and an average of 0.14 Å. Considering the C-N, differences range from a maximum of 0.08 Å to a minimum of 0.00 Å, with an averaged value of 0.01 Å.

Table 10.1.18 Distances (Å) for all the C-C in the 2 rings fragment of the excited state of Zn-TPP-DMF. First column distances are from X-ray data, and second column are from the optimized TD B3LYP/6-31G(d).

<i>XRD</i>	<i>TD B3LYP Atoms</i>		<i>TD B3LYP</i>	
C7	1,382	1,405	C91C92	1,395 1,397
C5C64	1,401	1,396	C92C93	1,500 1,396
C7C9	1,381	1,405	C92C101	1,385 1,442
C9C11	1,384	1,498	C93C95	1,394 1,426
C11C65	1,382	1,396	C95C97	1,388 1,370
C15C17	1,382	1,397	C97C99	1,373 1,443
C15C131	1,401	1,397	C99C101	1,376 1,426
C17C19	1,381	1,414	C104C120	1,388 1,489
C19C21	1,384	1,413	C104C123	1,344 1,416
C21C132	1,382	1,449	C106C107	1,444 1,408
C24C170	1,998	1,450	C106C113	1,392 1,407
C27C46	1,344	1,414	C106C124	1,406 1,395
C27C56	1,444	1,362	C107C109	1,487 1,398
C29C30	1,392	1,498	C109C111	1,385 1,397
C29C36	1,406	1,415	C111C112	1,371 1,395
C29C57	1,487	1,405	C112C113	1,382 1,416
C30C32	1,385	1,405	C117C120	1,376 1,489
C32C34	1,371	1,396	C117C158	1,436 1,449
C34C35	1,382	1,397	C123C124	1,413 1,449
C35C36	1,376	1,396	C124C125	1,412 1,415
C41C46	1,436	1,396	C125C126	1,405 1,363
C41C91	1,413	1,449	C126C128	1,447 1,427
C56C57	1,412	1,414	C128C129	1,349 1,489
C57C58	1,405	1,362	C129C130	1,439 1,440
C58C59	1,447	1,449	C130C131	1,404 1,441
C59C61	1,349	1,414	C130C134	1,502 1,428
C61C62	1,439	1,413	C131C132	1,422 1,371
C62C63	1,404	1,498	C134C135	1,391 1,489
C63C64	1,502	1,449	C135C137	1,443 1,416
C63C67	1,422	1,449	C137C139	1,347 1,408
C64C65	1,391	1,362	C139C140	1,440 1,408
C67C68	1,443	1,498	C140C141	1,410 1,395
C68C70	1,347	1,415	C140C152	1,488 1,398
C70C72	1,440	1,405	C141C142	1,406 1,397
C72C73	1,410	1,405	C141C150	1,396 1,395
C73C74	1,488	1,396	C142C144	1,395 1,408
C73C85	1,406	1,396	C144C146	1,379 1,408
C74C75	1,396	1,397	C146C148	1,373 1,395
C74C83	1,395	1,396	C148C150	1,384 1,397
C75C77	1,379	1,448	C152C153	1,378 1,397
C77C79	1,373	1,364	C153C155	1,442 1,394
C79C81	1,384	1,448	C155C157	1,336 1,448
C81C83	1,378	1,405	C157C158	1,445 1,363
C85C86	1,442	1,405	C158C159	1,395 1,449
C86C88	1,336	1,396	C159C160	1,500 1,408
C88C90	1,445	1,397	C159C168	1,385 1,408
C90C91	1,395	1,397	C160C162	1,394 1,395
C5C7	1,382	1,405	C162C164	1,388 1,397

Table 10.1.19 Distances (Å) for all the C-H in the 2 rings fragment of the excited state of Zn-TPP-DMF. First column distances are from X-ray data, and second column are from the optimized TD B3LYP/6–31G(d).

Atoms		XRD	TD B3LYP	Atoms		XRD	TD B3LYP
C5	H6	0,949	1,087	C88	H87	0,951	1,097
C7	H8	0,950	1,086	C93	H89	0,951	1,097
C9	H10	0,951	1,087	C95	H94	0,949	1,096
C11	H12	0,951	1,087	C97	H96	0,950	1,096
C15	H16	0,949	1,087	C99	H98	0,949	1,093
C17	H18	0,950	1,080	C101	H100	0,950	1,089
C19	H20	0,951	1,080	C104	H102	0,950	1,095
C21	H22	0,951	1,099	C107	H105	0,951	1,095
C24	H25	0,949	1,090	C109	H108	0,950	1,098
C27	H28	0,951	1,096	C111	H110	0,951	1,080
C30	H31	0,950	1,096	C112	H13	0,950	1,080
C32	H33	0,951	1,086	C113	H3	0,950	1,086
C34	H2	0,950	1,087	C120	H114	0,951	1,087
C35	H1	0,950	1,087	C126	H103	0,951	1,087
C36	H37	0,951	1,087	C128	H127	0,949	1,087
C42	H43	0,949	1,087	C132	H14	0,951	1,086
C46	H26	0,951	1,080	C135	H133	0,950	1,080
C47	H48	0,979	1,080	C137	H136	0,949	1,080
C47	H49	0,980	1,080	C142	H138	0,951	1,080
C47	H50	0,980	1,080	C144	H143	0,950	1,080
C52	H53	0,980	1,087	C146	H145	0,949	1,086
C52	H54	0,981	1,087	C148	H147	0,951	1,087
C52	H178	0,920	1,087	C150	H149	0,950	1,087
C59	H60	0,949	1,087	C153	H151	0,950	1,087
C61	H4	0,951	1,086	C155	H154	0,951	1,086
C65	H66	0,950	1,080	C160	H156	0,951	1,086
C68	H69	0,949	1,080	C162	H161	0,949	1,087
C70	H71	0,951	1,087	C164	H163	0,950	1,087

Table 10.1.20 Distances (Å) for all the C-N in the 2 rings fragment of the excited state of Zn-TPP. First column distances are from X-ray data, and second column are from the optimized TD B3LYP/6-31G(d).

<i>Atoms</i>		<i>XRD</i>	<i>B3LYP</i>
C24	N23	1,323	1,373
C41	N39	1,372	1,373
C42	N40	1,323	1,345
C52	N40	1,449	1,373
C56	N39	1,367	1,373
C58	N45	1,364	1,374
C62	N45	1,373	1,374
C67	N51	1,367	1,375
C72	N51	1,373	1,375
C85	N55	1,361	1,339
C90	N55	1,371	1,374
C117	N116	1,372	1,373
C123	N116	1,367	1,377
C125	N119	1,364	1,378
C129	N119	1,373	1,376
C134	N121	1,367	1,376

Table 10.1.21, 10.1.22 and 10.1.23 in Appendix illustrates all the the bond lengths distances for the excited state of **Zn-TPP-DMF (DCM)** fragment, optimized using TD DFT method, compared to the corresponding XRD parameters. The bond differences between the XRD structures and the theoretically optimized geometries range, for the C-C bond, from a maximum of 0.15 Å to a minimum of 0.00 Å, with an averaged value of 0.04 Å. For the C-H value we have a maximum value of 0.17 Å, a minimum of 0.08 Å and an average of 0.14 Å. Considering the C-N, differences we have a maximum of 0.11 Å, a minimum of 0.00 Å and an average of 0.01 Å.

Table 10.1.21 Distances (Å) for all the C-C in the 2 rings fragment of Zn-TPP-DMF (DCM). First column distances are from X-ray data, and second column are from the optimized fragment at B3LYP/6-31G(d).

Atoms		XRD	B3LYP	Atoms		XRD	B3LYP	Atoms		XRD	B3LYP
C8	C10	1,402	1,405	C49	C56	1,384	1,411	C102	C108	1,382	1,365
C8	C33	1,442	1,396	C52	C150	1,362	1,414	C108	C162	1,376	1,450
C9	C15	1,401	1,404	C54	C57	1,382	1,500	C109	C118	1,378	1,416
C9	C29	1,440	1,500	C56	C150	1,368	1,449	C109	C152	1,381	1,423
C10	C14	1,402	1,396	C57	C147	1,358	1,449	C114	C123	1,379	1,493
C10	C17	1,497	1,396	C79	C81	1,402	1,365	C118	C153	1,380	1,442
C11	C20	1,400	1,397	C79	C104	1,442	1,404	C120	C127	1,384	1,446
C11	C35	1,442	1,412	C80	C86	1,401	1,404	C123	C168	1,362	1,368
C12	C21	1,405	1,414	C80	C100	1,440	1,396	C125	C128	1,382	1,425
C12	C24	1,438	1,450	C81	C85	1,402	1,397	C127	C168	1,368	1,492
C13	C15	1,401	1,450	C81	C88	1,497	1,396	C128	C175	1,358	1,445
C13	C41	1,437	1,414	C82	C91	1,400	1,396	C143	C145	1,397	1,441
C14	C22	1,436	1,362	C82	C106	1,442	1,447	C145	C147	1,363	1,371
C15	C19	1,502	1,449	C83	C92	1,405	1,415	C152	C186	1,390	1,406
C16	C21	1,400	1,363	C83	C95	1,438	1,363	C153	C185	1,400	1,406
C16	C39	1,446	1,450	C84	C86	1,401	1,451	C155	C159	1,383	1,395
C17	C43	1,383	1,414	C84	C112	1,437	1,417	C157	C159	1,369	1,397
C17	C49	1,379	1,499	C85	C93	1,436	1,494	C160	C164	1,383	1,397
C18	C20	1,401	1,414	C86	C90	1,502	1,424	C162	C164	1,369	1,395
C18	C27	1,440	1,405	C87	C92	1,400	1,406	C165	C179	1,387	1,407
C19	C31	1,388	1,405	C87	C110	1,446	1,406	C166	C178	1,400	1,407
C19	C155	1,384	1,396	C88	C114	1,383	1,395	C171	C173	1,397	1,395
C20	C26	1,504	1,396	C88	C120	1,379	1,397	C173	C175	1,363	1,397
C21	C38	1,499	1,397	C89	C91	1,401	1,397	C178	C179	1,400	1,397
C22	C41	1,346	1,396	C89	C98	1,440	1,395	C185	C186	1,400	1,395
C24	C35	1,354	1,500	C90	C102	1,388	1,494	C102	C108	1,382	1,365
C26	C54	1,386	1,414	C90	C160	1,384	1,425	C108	C162	1,376	1,450
C26	C143	1,383	1,404	C91	C97	1,504	1,406				
C27	C33	1,340	1,404	C92	C109	1,499	1,406				
C29	C39	1,343	1,396	C93	C112	1,346	1,395				
C31	C37	1,382	1,396	C95	C106	1,354	1,396				
C37	C157	1,376	1,397	C97	C125	1,386	1,397				
C38	C47	1,378	1,396	C97	C171	1,383	1,395				
C38	C165	1,381	1,450	C98	C104	1,340	1,446				
C43	C52	1,379	1,361	C100	C110	1,343	1,418				

Table 10.1.22 Distances (Å) for all the C-H in the 2 rings fragment of the excited state of Zn-TPP-DMF (DCM). First column distances are from X-ray data, and second column are from the optimized TD B3LYP/6-31G(d).

Atoms		XRD	TD B3LYP	Atoms		XRD	TD B3LYP
C22	H23	0,931	1,087	C98	H99	0,930	1,081
C24	H25	0,930	1,086	C100	H101	0,930	1,081
C27	H28	0,930	1,087	C102	H103	0,931	1,087
C29	H30	0,930	1,087	C104	H105	0,930	1,087
C31	H32	0,931	1,087	C106	H107	0,930	1,087
C33	H34	0,930	1,080	C108	H149	0,929	1,087
C35	H36	0,930	1,080	C110	H111	0,930	1,087
C37	H170	0,929	1,081	C112	H113	0,931	1,087
C39	H40	0,930	1,081	C114	H115	0,929	1,087
C41	H42	0,931	1,087	C116	H117	0,931	1,097
C43	H44	0,929	1,087	C118	H119	0,931	1,095
C45	H46	0,931	1,087	C120	H121	0,931	1,094
C47	H48	0,931	1,087	C123	H124	0,930	1,089
C49	H50	0,931	1,086	C125	H126	0,930	1,080
C52	H53	0,930	1,087	C127	H169	0,930	1,080
C54	H55	0,930	1,087	C128	H129	0,930	1,086
C56	H151	0,930	1,087	C130	H131	0,960	1,087
C57	H58	0,930	1,087	C130	H132	0,960	1,087
C59	H60	0,960	1,086	C130	H133	0,959	1,087
C59	H61	0,960	1,097	C134	H135	0,960	1,086
C59	H62	0,959	1,095	C134	H136	0,960	1,087
C63	H64	0,960	1,096	C134	H137	0,961	1,087
C63	H65	0,960	1,093	C139	H140	0,970	1,087
C63	H66	0,961	1,095	C139	H141	0,970	1,087
C68	H69	0,970	1,094	C143	H144	0,930	1,086
C68	H70	0,970	1,089	C145	H146	0,931	1,080
C93	H94	0,931	1,080	C147	H148	0,930	1,080
C95	H96	0,930	1,080	C150	H177	1,000	1,080
C152	H163	0,930	1,087	C164	H184	1,000	1,086
C153	H184	1,000	1,086	C165	H51	0,930	1,086
C155	H51	0,930	1,086	C166	H167	0,929	1,087
C157	H167	0,929	1,087	C168	H183	1,000	1,087
C159	H183	1,000	1,087	C171	H172	0,930	1,087
C160	H172	0,930	1,087	C173	H174	0,931	1,086
C162	H174	0,931	1,086	C175	H176	0,930	1,095
C178	H180	1,000	1,096				
C179	H181	1,000	1,093				
C185	H187	1,000	1,087				
C186	H188	1,000	1,087				

Table 10.1.23 Distances (Å) for all the C-N in the 2 rings fragment of the excited state of Zn-TPP-DMF (DCM). First column distances are from X-ray data, and second column are from the optimized TD B3LYP/6-31G(d).

<i>Atoms</i>		<i>XRD</i>	<i>B3LYP</i>
C8	N4	1,370	1,374
C9	N3	1,370	1,374
C11	N5	1,371	1,372
C12	N5	1,376	1,373
C13	N6	1,374	1,337
C14	N6	1,372	1,372
C16	N3	1,368	1,373
C18	N4	1,376	1,373
C45	N7	1,309	1,373
C59	N7	1,442	1,336
C79	N75	1,370	1,379
C80	N74	1,370	1,375
C82	N76	1,371	1,379
C83	N76	1,376	1,376
C84	N77	1,374	1,378
C85	N77	1,372	1,375

Table 10.1.24 Crystal data and structure refinement for *Co-TNPP* and *Zn-TNPP*.

	Co-TNPP (tolu)	Zn-TNPP (DCM)
Empirical formula	C _{49.6} H _{30.4} CoN ₈ O ₈	C ₄₅ H ₂₅ Cl ₂ N ₈ O ₈ Zn
Formula weight	925.35	942.00
Temperature/K	293(2)	172.9(2)
Crystal system	monoclinic	monoclinic
Space group	C2/c	P2 ₁ /n
a/Å	23.2214(5)	21.3969(9)
b/Å	8.2116(2)	7.9907(3)
c/Å	21.3071(5)	26.5903(14)
α/°	90	90
β/°	92.893(2)	111.973(5)
γ/°	90	90
Volume/Å ³	4057.76(16)	4216.1(4)
Z	4	4
ρ _{calc} /cm ³	1.515	1.484
μ/mm ⁻¹	3.913	2.528
F(000)	1900.0	1916.0
Crystal size/mm ³	0.217 × 0.119 × 0.035	0.166 × 0.068 × 0.034
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2θ range for data	7.624 to 133.586	6.682 to 133.798
Index ranges	-27 ≤ h ≤ 26, -9 ≤ k ≤ 9, -23 ≤ l	-25 ≤ h ≤ 24, -8 ≤ k ≤ 7, -31 ≤ l
Reflections collected	22284	56888
Independent reflections	3519 [R _{int} = 0.0514, R _{sigma} =	7317 [R _{int} = 0.1337, R _{sigma} =
Data/restraints/parameter	3519/0/277	7317/0/550
Goodness-of-fit on F ²	1.057	1.019
Final R indexes [I > 2σ]	R ₁ = 0.0370, wR ₂ = 0.0966	R ₁ = 0.0569, wR ₂ = 0.1269
Final R indexes [all data]	R ₁ = 0.0436, wR ₂ = 0.1008	R ₁ = 0.0954, wR ₂ = 0.1436
Largest diff. peak/hole / e	0.19/-0.32	0.32/-0.35

Table 10.1.25 Bond Lengths for **Co-TNPP**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Co1	N2 ¹	1.9784(16)	C5	C6	1.389(3)
Co1	N2	1.9784(16)	C5	C4	1.384(3)
Co1	N1 ¹	1.9848(16)	C6	C7	1.421(3)
Co1	N1	1.9848(16)	C1	C10 ¹	1.389(3)
N2	C9	1.383(3)	C1	C2	1.446(3)
N2	C6	1.380(3)	C4	C3	1.434(3)
N1	C1	1.378(3)	C10	C1 ¹	1.389(3)
N1	C4	1.383(3)	C10	C17	1.493(3)
O004	Co1 ²	2.5431(18)	C14	C15	1.380(3)
O004	N3	1.240(3)	C14	C13	1.367(3)
O005	N3	1.215(3)	C17	C22	1.386(3)
N3	C14	1.476(3)	C17	C18	1.394(3)
N4	O008	1.216(3)	C16	C15	1.389(3)
N4	O00D	1.222(3)	C12	C13	1.388(3)
N4	C20	1.469(3)	C20	C19	1.377(4)
C9	C10	1.389(3)	C20	C21	1.375(3)
C9	C8	1.437(3)	C22	C21	1.388(3)
C11	C5	1.500(3)	C2	C3	1.341(3)
C11	C16	1.392(3)	C19	C18	1.383(3)
C11	C12	1.381(3)	C8	C7	1.345(3)

¹1/2-X,3/2-Y,1-Z; ²+X,1-Y, -1/2+Z

Table 10.1.26 Bond Angles for **Co-TNPP**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N2 ¹	Co1	N2	180.0	N1	C1	C10 ¹	125.90(17)
N2 ¹	Co1	N1 ¹	90.51(7)	N1	C1	C2	110.19(18)
N2	Co1	N1 ¹	89.49(7)	C10 ¹	C1	C2	123.90(19)
N2 ¹	Co1	N1	89.49(7)	N1	C4	C5	125.99(18)
N2	Co1	N1	90.51(7)	N1	C4	C3	110.16(18)
N1 ¹	Co1	N1	180.00(13)	C5	C4	C3	123.77(19)
C9	N2	Co1	127.87(13)	C9	C10	C1 ¹	122.75(19)
C6	N2	Co1	127.24(13)	C9	C10	C17	118.35(18)
C6	N2	C9	104.63(16)	C1 ¹	C10	C17	118.89(17)
C1	N1	Co1	127.87(13)	C15	C14	N3	118.9(2)
C1	N1	C4	105.21(16)	C13	C14	N3	118.4(2)
C4	N1	Co1	126.74(14)	C13	C14	C15	122.68(19)
N3	O004	Co1 ²	122.96(14)	C22	C17	C10	120.42(19)
O004	N3	C14	117.3(2)	C22	C17	C18	118.6(2)
O005	N3	O004	124.5(2)	C18	C17	C10	121.0(2)
O005	N3	C14	118.2(2)	C15	C16	C11	121.0(2)
O008	N4	O00D	123.4(2)	C11	C12	C13	120.9(2)
O008	N4	C20	118.6(2)	C19	C20	N4	119.2(2)
O00D	N4	C20	118.0(2)	C21	C20	N4	118.7(2)
N2	C9	C10	125.85(19)	C21	C20	C19	122.1(2)
N2	C9	C8	110.35(17)	C17	C22	C21	121.2(2)
C10	C9	C8	123.78(19)	C3	C2	C1	106.83(19)
C16	C11	C5	120.3(2)	C20	C19	C18	118.7(2)
C12	C11	C5	120.70(19)	C14	C15	C16	117.9(2)
C12	C11	C16	119.01(19)	C7	C8	C9	106.7(2)
C6	C5	C11	118.39(18)	C20	C21	C22	118.4(2)
C4	C5	C11	117.85(17)	C19	C18	C17	120.9(2)
C4	C5	C6	123.75(18)	C8	C7	C6	107.52(19)
N2	C6	C5	125.51(19)	C2	C3	C4	107.59(19)
N2	C6	C7	110.76(18)	C14	C13	C12	118.6(2)
C5	C6	C7	123.73(19)				

¹1/2-X, 3/2-Y, 1-Z; ²+X, 1-Y, -1/2+Z

*Table 10.1.27 Bond Lengths for **Zn-TNPP**.*

Atom	Atom	Lenath/Å	Atom	Atom	Lenath/Å
Zn1	O7 ¹	2.461(3)	C11	C12	1.439(5)
Zn1	N1	2.065(3)	C13	C12	1.357(5)
Zn1	N2	2.036(3)	C14	C13	1.440(5)
Zn1	N3	2.059(3)	C14	C15	1.402(5)
Zn1	N4	2.039(3)	C15	C33	1.496(6)
O1	N5	1.215(5)	C16	C15	1.408(5)
O2	N5	1.219(5)	C17	C16	1.437(5)
O3	N6	1.230(5)	C18	C17	1.348(6)
O4	N6	1.212(6)	C18	C19	1.438(5)
O5	N7	1.213(5)	C19	C20	1.398(5)
O6	N7	1.209(6)	C20	C1	1.398(5)
O7	Zn1 ²	2.461(3)	C20	C39	1.501(5)
O7	N8	1.235(5)	C21	C22	1.390(6)
O8	N8	1.206(5)	C22	C23	1.368(6)
N1	C1	1.374(5)	C24	C23	1.387(6)
N1	C4	1.364(5)	C24	C25	1.376(6)
N2	C6	1.363(5)	C25	C26	1.386(6)
N2	C9	1.370(5)	C26	C21	1.391(6)
N3	C11	1.366(5)	C27	C10	1.490(5)
N3	C14	1.369(5)	C27	C28	1.400(6)
N4	C16	1.365(5)	C27	C32	1.393(6)
N4	C19	1.376(4)	C28	C29	1.387(6)
N5	C24	1.471(5)	C30	C29	1.353(6)
N6	C30	1.478(5)	C30	C31	1.387(6)
N7	C36	1.475(6)	C32	C31	1.386(6)
N8	C42	1.479(5)	C34	C33	1.382(6)
C2	C1	1.437(5)	C34	C35	1.382(7)
C2	C3	1.344(5)	C36	C35	1.379(7)
C4	C3	1.444(5)	C37	C36	1.359(6)
C4	C5	1.401(5)	C37	C38	1.391(6)
C5	C6	1.404(5)	C38	C33	1.399(6)
C5	C21	1.501(6)	C39	C44	1.389(6)
C7	C6	1.447(5)	C40	C39	1.388(5)
C8	C7	1.351(6)	C40	C41	1.389(5)
C8	C9	1.434(6)	C42	C41	1.375(6)
C10	C9	1.410(5)	C42	C43	1.380(6)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C11	C10	1.401(5)	C44	C43	1.389(5)

$1/3-Z-X, 1/2+Y, 3/2-Z; 2/3-Z-X, -1/2+Y, 3/2-Z$

*Table 10.1.28 Bond Angles for **Zn-TNPP**.*

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Zn1	O7 ¹	83.27(11)	C13	C12	C11	106.9(3)
N2	Zn1	O7 ¹	95.02(12)	C12	C13	C14	106.8(3)
N2	Zn1	N1	89.47(12)	N3	C14	C13	109.7(3)
N2	Zn1	N3	90.37(12)	N3	C14	C15	125.5(3)
N2	Zn1	N4	179.69(16)	C15	C14	C13	124.8(3)
N3	Zn1	O7 ¹	97.70(11)	C14	C15	C16	125.1(3)
N3	Zn1	N1	179.03(13)	C14	C15	C33	118.6(3)
N4	Zn1	O7 ¹	85.29(11)	C16	C15	C33	116.3(3)
N4	Zn1	N1	90.56(12)	N4	C16	C15	125.7(3)
N4	Zn1	N3	89.59(12)	N4	C16	C17	109.7(3)
N8	O7	Zn1 ²	124.6(3)	C15	C16	C17	124.6(3)
C1	N1	Zn1	125.7(3)	C18	C17	C16	107.1(4)
C4	N1	Zn1	127.0(2)	C17	C18	C19	107.4(3)
C4	N1	C1	106.9(3)	N4	C19	C18	109.1(3)
C6	N2	Zn1	126.7(2)	N4	C19	C20	125.6(3)
C6	N2	C9	107.0(3)	C20	C19	C18	125.2(3)
C9	N2	Zn1	125.9(3)	C1	C20	C39	116.6(3)
C11	N3	Zn1	126.5(3)	C19	C20	C1	126.5(3)
C11	N3	C14	106.6(3)	C19	C20	C39	116.9(3)
C14	N3	Zn1	126.7(2)	C22	C21	C5	122.5(4)
C16	N4	Zn1	126.9(2)	C22	C21	C26	118.8(4)
C16	N4	C19	106.7(3)	C26	C21	C5	118.7(3)
C19	N4	Zn1	125.5(2)	C23	C22	C21	121.2(4)
O1	N5	O2	123.3(4)	C22	C23	C24	118.6(4)
O1	N5	C24	118.4(4)	C23	C24	N5	119.1(4)
O2	N5	C24	118.3(4)	C25	C24	N5	118.6(4)
O3	N6	C30	117.4(4)	C25	C24	C23	122.2(4)
O4	N6	O3	124.5(4)	C24	C25	C26	118.1(4)
O4	N6	C30	118.1(4)	C25	C26	C21	121.1(4)
O5	N7	C36	118.5(5)	C28	C27	C10	120.9(4)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O6	N7	O5	121.8(4)	C32	C27	C10	120.0(3)
O6	N7	C36	119.7(4)	C32	C27	C28	119.1(3)
O7	N8	C42	116.7(4)	C29	C28	C27	120.5(4)
O8	N8	O7	123.8(3)	C30	C29	C28	118.8(4)
O8	N8	C42	119.5(4)	C29	C30	N6	118.2(4)
N1	C1	C2	108.7(3)	C29	C30	C31	122.8(4)
N1	C1	C20	125.2(3)	C31	C30	N6	119.0(4)
C20	C1	C2	125.9(3)	C32	C31	C30	118.5(4)
C3	C2	C1	108.1(3)	C31	C32	C27	120.2(4)
C2	C3	C4	106.4(3)	C34	C33	C15	122.8(4)
N1	C4	C3	109.8(3)	C34	C33	C38	117.9(4)
N1	C4	C5	125.0(3)	C38	C33	C15	119.2(3)
C5	C4	C3	125.2(3)	C33	C34	C35	121.7(4)
C4	C5	C6	125.2(3)	C36	C35	C34	117.8(4)
C4	C5	C21	118.2(3)	C35	C36	N7	119.3(4)
C6	C5	C21	116.6(3)	C37	C36	N7	117.2(4)
N2	C6	C5	126.3(3)	C37	C36	C35	123.4(4)
N2	C6	C7	109.3(3)	C36	C37	C38	117.6(4)
C5	C6	C7	124.4(3)	C37	C38	C33	121.5(4)
C8	C7	C6	107.0(3)	C40	C39	C20	120.9(3)
C7	C8	C9	107.2(3)	C40	C39	C44	119.2(3)
N2	C9	C8	109.5(3)	C44	C39	C20	119.9(3)
N2	C9	C10	126.1(3)	C39	C40	C41	120.7(4)
C10	C9	C8	124.4(3)	C42	C41	C40	117.9(3)
C9	C10	C27	117.6(3)	C41	C42	N8	118.5(3)
C11	C10	C9	125.6(3)	C41	C42	C43	123.7(3)
C11	C10	C27	116.8(3)	C43	C42	N8	117.8(4)
N3	C11	C10	125.2(3)	C42	C43	C44	117.0(4)
N3	C11	C12	109.8(3)	C43	C44	C39	121.4(4)
C10	C11	C12	124.7(3)				

$1/3-2-X$, $1/2+Y$, $3/2-Z$; $2/3-2-X$, $-1/2+Y$, $3/2-Z$