Tutor



Treball Final de Grau

Functionalized porphyrins for visible-light photoredox catalysis

Porfirines funcionalitzades per a la catàlisi fotoredox amb llum visible

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Agrair als meus pares i al meu germà, que han estat un suport incondicional al llarg d'aquest camí. Sense la seva confiança, paciència i amor, no hauria estat possible arribar fins aquí.

Agrair la guia i suport del meu tutor, l'Albert Moyano, per la seva orientació i consells al llarg d'aquest projecte. Els seus coneixements i dedicació han estat fonamentals per dur a terme aquest treball.

Finalment, voldria agrair al Dr. Bart Limburg la realització dels estudis fotofísics per a la caracterització dels estats excitats singlet i triplet de la *meso*-tetrabenzoïlporfirina.

REPORT

IDENTIFICATION AND REFLECTION ON THE SUSTAINABLE DEVELOPMENT GOALS (SDG)

This bachelor's Thesis, entitled "Functionalized porphyrins for visible-light photoredox catalysis", aims to break new ground in the quest for sustainable chemistry, including most of the Sustainable Development Goals (SDGs), with a main focus on enabling the development of energy-efficient chemical processes while leaving behind a reduced ecological footprint for the traditional approaches to material synthesis.

One of the key considerations is Sustainable Development Goal 7: Affordable and Clean Energy. The use of visible light to catalyze chemical reactions represents a change in direction for renewable and sustainable energy modes within chemical synthesis. In so doing, this research takes an active stand in promoting greener production processes, emphasizing energy efficiency by way of reduced dependence on fossil fuels or high-energy inputs.

This certainly has strong relevance to SDG 9—Industry, Innovation, and Infrastructure—since it enables technological innovation with regard to chemical catalysis. The design and synthesis of functionalized porphyrins lead to a new class of catalysts that might change industrial practices. Such catalysts serve for building sustainable industrial infrastructures by allowing more efficient and environmentally friendly chemical transformations. This research has the potential to branch out into applied applications in pharmaceutical synthesis and materials manufacturing, in consequence ensuring a positive impact on society in the long term.

Sustainable Development Goal 12, which deals with Responsible Consumption and Production, is of high relevance to the present study. The purpose of this bachelor's Thesis is to reduce waste generation and diminish dependency on harmful reagents often associated with traditional catalytic methods. The project should contribute to the sustainable handling of resources, developing catalytic systems based on abundant, nontoxic materials that contribute to the lessening of chemical pollution, which is one of the most important problems in today's industries.

On top of its direct scientific contributions, the project carries the potential for broad societal applications. If taken further, new catalytic systems could permit basic transformations in industrial practices around chemical manufacturing and steer them toward a low-carbon, more sustainable economic model. This will not only promote environmental benefits but also advance economic and social resilience through the development of greener technologies.

While the project inherently involves the use of resources in its development phase, the potential gains far outweigh these initial inputs. The ability of the catalysts to increase energy efficiency and reduce dependence on harmful chemicals ensures that they fall under sustainable principles. Future efforts in scaling up these systems with low environmental impact are intended to ensure that long-term applications remain in line with the SDGs.

In summary, this study epitomizes the significant contribution that pioneering chemistry can make to overcome the challenges associated with global sustainability. This project, by developing cleaner energy alternatives, encouraging industrial innovation, and promoting responsible production practices, is a good example of what scholarly research can do to advance toward a sustainable and just future.

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1. SUMMARY

Visible light photocatalysis, particularly in the context of its applications in organic synthesis, has undergone a remarkable development over the past decade. The design of innovative organophotocatalysts with optimized and well-planned properties, while reducing or eliminating the use of scarce and potentially toxic transition metals, is considered a key direction in this field for the coming years. Although free-base porphyrins have been identified as a promising class of easily accessible and tuneable organic photoredox catalysts, a systematic analysis of how the electronic nature and position of substituents influence the redox potentials of these compounds, both in the ground and excited states, is still lacking. In our research group, we recently synthesized a series of *meso*-tetraarylporphyrin derivatives functionalized with benzoyl groups in various positions and determined their redox potentials both in the ground state and the singlet excited state. These results demonstrated that the presence of a single benzoyl substituent at a *meso* position enhances the facility of reduction in both the ground and the excited state. Building on these findings, this bachelor's Thesis aimed to study some *meso*-tetrabenzoylporphyrin derivatives to confirm the effect of these groups on both the ground-state and the excited-state redox properties of the porphyrins. After synthesizing these compounds, studies of their photophysical properties and redox potentials were conducted. These studies confirmed that the introduction of four benzoyl groups at the *meso* positions predictably and controllably modifies the redox behaviour of this promising class of organic photosensitzers. Finally, an initial analysis of their photocatalytic capacity was performed, validating the potential of these compounds as visible light-photoredox catalysts for future applications.

Keywords: photoredox catalysis, porphyrins, redox potential, substituent effects

2. RESUM

La fotocatàlisi amb llum visible, especialment en el context de les seves aplicacions en síntesi orgànica, ha experimentat un notable desenvolupament durant l'última dècada. El desenvolupament de fotocatalitzadors orgànics innovadors amb propietats optimitzades i planificades, alhora que redueix o elimina l'ús de metalls de transició escassos i potencialment tòxics, es considera una direcció clau en aquest camp per als propers anys. Malgrat que les porfirines de base lliure han estat identificades com una classe prometedora de catalitzadors orgànics fotoredox de fàcil obtenció i ajustament, encara no es disposa d'una anàlisi sistemàtica sobre com la naturalesa electrònica i la posició dels substituents influeixen en els potencials redox d'aquests compostos, tant en l'estat fonamental com en l'excitat. En el nostre grup de recerca, s'ha sintetitzat recentment un conjunt de derivats de *meso*-tetraarilporfirina monofuncionalitzats amb grups benzoïl en diverses posicions, i s'han avaluat els seus potencials redox en l'estat fonamental i en l'estat singlet excitat. Els resultats preliminars han demostrat que la presència d'un substituent benzoïl en posició *meso* afavoreix la reducció en l'estat fonamental i en l'estat excitat. Basant-nos en aquests descobriments, aquest Treball Final de Grau ha tingut com a objectiu estudiar alguns derivats de *meso*-tetrabenzoïl porfirina per confirmar l'efecte d'aquests grups sobre les propietats redox de la porfirina. Després de sintetitzar aquests compostos, s'han dut a terme estudis de les seves propietats fotofísiques i dels potencials redox, els quals han corroborat que la introducció de quarte grups benzoïl a les posicions *meso* modifica de manera previsible i controlada el comportament redox d'aquesta classe de fotosensibilitzants orgànics. Finalment, també s'ha realitzat una anàlisi inicial de la seva capacitat fotocatalítica, confirmant el potencial d'aquests compostos com a catalitzadors fotoredox en aplicacions futures.

Paraules clau: catàlisis fotoredox, porfirines, potencials redox, efecte dels substituents

3. INTRODUCTION

3.1. PHOTOCHEMISTRY

A photochemical reaction occurs when ultraviolet or visible radiation is absorbed by a specific region of a molecule, known as the chromophore. This absorption promotes the substrate from its electronic ground state to an excited state with higher energy, enabling it to undergo a range of physical and chemical processes. While some of these processes, such as those studied in molecular spectroscopy, do not alter or consume the substrate, they are crucial for understanding molecular behaviour. In other cases, the energy of the excited state can drive chemical transformations, including elimination, cleavage, rearrangement, isomerization, cyclization, addition, or electron transfer reactions. Photochemical reactions encompass a variety of mechanisms, including direct excitation, photosensitization, photocatalysis, photoinduced electron transfer (PET), and photoredox catalysis.^[1]

3.1.1. Visible light photocatalysts

Visible light photocatalysts (PCs) are photoactive molecules that are catalytically introduced into reaction mixtures to transform visible light energy into chemical energy. When a photon of visible light is absorbed, the photocatalyst (PC) transitions to its electronically excited state (*PC). In this excited state, *PC facilitates the generation of reactive intermediates by participating in either photoinduced single electron transfer (SET) or photoinduced energy transfer (PET) processes with appropriate organic substrates or reagents. These interactions drive the desired chemical transformation. ^[2]

3.1.2 Photoredox catalysis

Essentially, photoredox catalysis is a branch of photochemistry that is based on photoinduced single electron transfer (SET) where the photocatalysts can return to their singlet ground state through two distinct quenching cycles, each involving two consecutive singleelectron transfer (SET) reactions: the oxidative quenching cycle and the reductive quenching cycle.^[2]

In the **oxidative quenching cycle**, the excited photocatalyst initially acts as a reductant by donating an electron to an electronaccepting species, resulting in the formation of the radical cation of the photocatalyst. This species is subsequently regenerated to its ground state by accepting an electron from a single-electron donor molecule.

In contrast, the **reductive quenching cycle** involves the excited photocatalyst functioning as an oxidant by accepting an electron from a donor species, transforming himself into a radical anion. The photocatalyst is then restored to its ground state when an electron-accepting species removes an electron from the radical anion.

These two mechanisms are illustrated in Figure 1.



Figure 1. Reductive and oxidative quenching cycles in photoredox catalysis. [PC] = Photocatalyst, [S] = excited singlet state, [T] = triplet state, A = acceptor, D = donor

Photoredox catalysis is categorized into three types of reactions:

- In **net oxidative reactions**, a stoichiometric amount of an oxidizing agent is required to complete the catalytic cycle. During the process, the substrate is oxidized by the photocatalyst, which itself is initially reduced (acting as an oxidant). The photocatalyst is then regenerated to its ground state by the oxidizing agent. Common oxidizing agents include molecular oxygen (O₂) and quinones.
- Similarly, in net reductive reactions, a reducing agent is necessary to restore the photocatalyst to its ground state. These
 stoichiometric agents play a critical role in maintaining the catalytic cycle's continuity.
- In redox neutral reactions, the substrates are both oxidized and reduced during the cycle, with no overall net change in the oxidation state.

3.2. PORPHYRINS

3.2.1. General background

Porphyrins are molecules composed of four pyrrole units linked by four methine bridges, forming a square planar macrocyclic structure. The porphyrin core contains a circuit of 18 delocalized π -electrons, adhering to Hückel's rule of aromaticity (4n + 2 π -electrons), which classifies it as an aromatic system. The simplest form of porphyrin, known as porphine, is unsubstituted.

A variety of functional groups can be attached to the porphine macrocycle at the *meso-* or β -positions, leading to the synthesis of a broad range of porphyrin derivatives. Additionally, free-base porphyrins can coordinate with a wide array of metal ions at the center of the macrocycle, resulting in metalloporphyrins (Figure 2).^[3]



Figure 2. a) porphine, b) β-substituted porphyrin c) meso-substituted porphyrin and d) metalloporphyrin

Porphyrins and their derivatives are highly versatile molecules and belong to an essential class of organic chromophores. Due to their unique properties, they have been utilized in a wide range of applications. Compared to individual porphyrin monomers, porphyrin-based compounds offer significant functional advantages, enhancing their properties and broadening their potential uses.

3.2.2. Porphyrins as photocatalysts

Under visible light irradiation, porphyrins can absorb photons and, in their excited state, transfer energy (photosensitization) or electrons (photoredox catalysis). Numerous studies have highlighted the use of metalloporphyrins as models for artificial photosynthesis, enzyme mimics, and catalysts in chemical reactions. These applications have included aliphatic C–H hydroxylation, a reaction naturally catalyzed by the heme-containing enzyme cytochrome P450. Other notable reactions facilitated by metalloporphyrins include amination, alkylation, olefin epoxidation, cyclopropanation, olefination, oxidative amine coupling, the oxidative Mannich reaction, Diels–Alder reactions, and various functional group transformations.

In organic synthesis, free-base porphyrins are primarily employed as photosensitizers for generating singlet oxygen. Upon light absorption, porphyrins are excited to a singlet state, which readily undergoes intersystem crossing (ISC) to form a triplet state. This triplet state facilitates the production of singlet oxygen through energy transfer or generates reactive oxygen species via electron transfer. Using this approach, compounds such as olefins, aromatic compounds, amines, enamines, and aldehydes have been

oxidized. For instance, Nagata and co-workers demonstrated the photooxidation of alcohols to aldehydes through photoinduced electron transfer from a porphyrin (free base or zinc) to a quinone. Additionally, free-base porphyrins have been shown to catalyze the photooxidative hydroxylation of arylboronic acids. However, in this case, a zirconium-organic framework incorporating substituted porphyrin groups proved to be more efficient. This reaction is thought to proceed via a reductive quenching mechanism.^[4]

Although porphyrins constitute a promising, easily accessible, and tunable class of organic photoredox catalysts, a systematic study on the effect of the electronic nature and of the position of the substituents on both the ground-state and the excited-state redox potentials of these compounds is still lacking, and our research group has recently prepared a set of known functionalized porphyrin derivatives containing different substituents either in one of the *meso* positions or at a β-pyrrole carbon, and determined their ground-and (singlet) excited-state redox potentials. While the estimated singlet excited-state energies are essentially unaffected by the introduction of substituents, the redox potentials (both in the ground- and in the singlet excited-state) depend on the electron-withdrawing or electron-donating nature of the substituents. Thus, the presence of groups with electron-withdrawing resonance effects results in an enhancement of the reduction facility of the photocatalyst, both in the ground and in the excited state.^[5]

In the Master's Thesis of Alexandra Millheim, four new prophyrins with a benzoyl radical in different positions (compounds **1** to **4**) were synthesized to ascertain the effect of the position of the carbonyl group in the facility of reduction the excited estate (Figure 3). It was found that the reduction facility of the porphyrin increases with the proximity of the substituent to the porphine core, reaching a maximum when the benzoyl substituent is introduced at a *meso* position (i.e., in compound **4**).^[6]



Figure 3. Benzoyl-monosubstituted porphyrins studied in the Master's Thesis of Alexandra Millheim

4.OBJECTIVES

In the light of these results, we decided to perform a similar study in a set of *meso*-tetrabenzoyl porphyrin derivatives (**5-8**, Figure 4), having different substituents at the *para* position of the benzoyl moiety. In this way, we wanted to confirm that the presence of several carbonyl substituents increased the facility of reduction in the excited state, and to explore the effect of the substituent on the photophysical properties of the porphyrin.

A subsequent objective was that of applying the porphyrins as visible-light photocatalysts in a benchmark photoredox reaction to test their behaviour.



Figure 4 Four meso-(benzoyl)substituted porphyrins, objective molecules of this Bachelor's Thesis

5.SYNTHESIS OF MESO-TETRABENZOYLPORPHYRINS

Compound **5** was originally synthesized by Lindsey through an acid-catalyzed condensation of pyrrole with phenylglyoxal hydrate, using $BF_3 \cdot OEt_2$ as the acid catalyst, followed by oxidation with DDQ and purification via chromatography (Scheme 1, conditions **A**). Following the same procedure, we successfully obtained the desired compound; however, the yield (7.2%) was lower than the 12% previously reported.^[7]

We attempted to synthesize compound **5** under alternative conditions (**B**), substituting $BF_3 \cdot OEt_2$ with trifluoroacetic acid (TFA) as the acid catalyst. Despite the change in catalyst, the yield remained the same at 7.2%.



Scheme 1. Synthesis of meso-tetrabenzoylporphyrins

Starting with 4-fluorophenylglyoxal hydrate and employing conditions **A**, porphyrin **7** was successfully synthesized with a yield of 8.7%.

Unfortunately, we were unable to obtain *meso*-tetra(4-methoxybenzoyl)porphyrin (8) using 4-methoxyphenylglyoxal hydrate as the starting material. Attempts were made under both conditions **A** and **B**, but neither approach resulted in the formation of porphyrin 8.

Finally, the Ni complex **6** was synthesized (78% yield) from the free-base porphyrin **5** (Scheme 2) under the same conditions previously reported for the preparation of NiTPP starting from TPPH₂ (TPPH₂ = *meso*-tetraphenylporphyrin).^[8]



Scheme 2. Synthesis of Ni complex 6

6. PHOTOPHYSICAL AND ELECTROCHEMICAL PROPERTIES OF MESO-TETRABENZOYLPORPHYRINS

6.1. CYCLIC VOLTAMMETRY

The effectiveness of a photosensitizer in catalytic processes is heavily influenced by its photophysical and electrochemical properties, both in its ground state and when excited. To estimate how well a photosensitizer might perform, researchers often measure its ground-state redox potential, with cyclic voltammetry being the most commonly used technique for this purpose. These measurements help to predict how the photosensitizer will interact with other components in a photoredox reaction.

Depending on the specific compound, cyclic voltammograms can appear as either reversible or irreversible patterns. The groundstate oxidation and reduction potentials are typically abbreviated as E_{ox} or E(PS⁺/PS)), and E_{red} or E(PS/PS⁻), respectively. These values represent the initial single-electron oxidation and reduction events of the photosensitizer. An example of reversible and irreversible cyclic voltammograms is illustrated in Figure 5.^[9]



Figure 5. Reversible wave cyclic voltamperograms (left) and irreversible cyclic voltamperograms (right) [9]

To characterize a reversible redox wave, the oxidation (E_{ox}) and reduction (E_{red}) potentials are averaged to determine the halfwave potential ($E_{1/2}$). This is expressed by Equation 1, where E_{pc} and E_{pa} represent the cathodic and anodic peak potentials, respectively:

$$E_{1/2} = \frac{1}{2} \left(E_{pc} + E_{Pa} \right)$$
 Equation 1

The measurements of $E_{1/2}$ can be influenced by several factors, including the choice of reference electrode and the supporting electrolyte. In this case, the reference electrode used was Ag/AgCl. To compare results with the saturated calomel electrode (SCE), the potential difference between the two electrodes—tabulated in the literature as $\Delta E = E(SCE) - E(Ag/AgCl) = +0.05$ V/was added to each $E_{1/2}$ value. The supporting electrolyte, tetrabutylammonium perchlorate (TBAP), can also affect redox potentials, as its composition and concentration influence the system. So, the final equation to calculate $E_{1/2}$ is:

$$E_{1/2} = \frac{1}{2} \left(E_{pc} + E_{Pa} \right) + 0.05$$
 Equation 2

As described above, we were able to synthesize *meso*-tetrabenzoylporphyrin **5**, the corresponding Ni(II) complex **6**, and the *meso*-tetra(*p*-fluorobenzoyl)porphyrin **7**. On the other hand, our attempts to synthesize the tetra(*p*-metoxybenzoyl) derivative **8** were unsuccessful.

Table 1 below summarizes the ground-state E_{1/2} values (in V) obtained for four newly synthesized benzoyl-substituted porphyrins **5-7**, as determined by cyclic voltammetry, using dichloromethane as the solvent, and referred to the standard calomel electrode (SCE).

The results align with expectations: the introduction of four benzoyl groups in the *meso* position facilitates the reduction of the species compared both to compound **4** and to $TPPH_2$ (-0.76 V for compound **5** compared to -0.97 V for compound **4** and -1.21 V for $TPPH_2$)...It can be observed that the incorporation of a metal such as nickel (Ni) increases the absolute value of the first reduction potential (-0.76 V for **5** and -0.86 V for **6**). On the other hand, the presence of an electron-withdrawing group like fluorine (F) in the *para* position of the benzoyl group lowers the reduction potential (-0.76 V for **5** and -0.71 V for **7**).

What can be confirmed, moreover, is that the species containing four benzoyl groups do not undergo oxidation below *ca.* +2.2 V (we did not observe any oxidation wave both for **5** and for **7** even when using DMF as the solvent), indicating that it is not a good reducing agent. Although the only compound that undergoes oxidation is the Ni(II) complex **6**, it exhibits a more positive reduction potential for the radical cation (+1.38 V compared to +1.32 V for compound **4** and +1.09 V for TPPH₂).

Porphyrin	Experimental ground-state redox half-wave potentials (V vs. SCE, dichloromethane)			
	[PC/PC ²⁻]	[PC/PC-]	[PC ^{.+} /PC]	[PC ²⁺ /PC ⁺]
TPPH ₂	-1.63	-1.21	+1.09	+1.28
4	-1.17	-0.97	+1.32	+1.62
5	-0.95	-0.76	_ a	_a
6	-1.48	-0.86	+1.38	_a
7	-1.41	-0.71	_a	_a

Table 1. Ground-state redox potentials (E_{1/2}) of the three new porphyrins, with porphyrin **4** and TPPH₂ as a reference ^a Oxidation not observed

6.2. EXCITED-STATE REDOX POTENTIALS

The redox properties of a photosensitizer (PS) in its excited state determine its ability to act as a photoreductant or photooxidant. These properties are represented by the excited-state reduction potential ($*E_{red}(*PS/PS^-)$) and the excited-state oxidation potential ($*E_{ox}(PS^{*}/*PS)$), which correspond to the one-electron redox reactions of the photoexcited PS (*PS) These potentials, as shown in Equations 3 and 4, are typically calculated rather than directly measured, using the excited-state energy ($E_{0,0}S^1$) and the ground-state redox potentials according to Equations 3 and 4.

*
$$Ered[*PC/PC \cdot -] = Ered[PC/PC \cdot -] + E0,0$$
 (Photooxidant) Equation 3
* $Eox[PC \cdot +/*PC] = Eox[PC \cdot +/*PC] - E0,0$ (Photoreductant) Equation 4

In these calculations, factors such as entropy changes between the ground and excited states and the Coulombic effects of charge separation in different solvents are generally omitted. While some uncertainty exists in predicting E_{0,0}S¹ and the excited-state redox potentials, these estimates are still valuable for understanding the thermodynamic behavior of PSs in their excited states. Direct measurement of *E_{red} and of *E_{ox} is less common but can be achieved using phase-modulated voltammetry, an electrochemical technique that measures redox potentials under light irradiation.

In this study, the excited singlet state energy ($E^{S1}_{0,0}$) was determined using both UV-VIS absorption and fluorescence spectra. The Stokes shift, defined as the difference between the wavelength of light absorbed by a molecule during excitation and the wavelength of light emitted during fluorescence, has been measured. It should be noted here that although the excited triplet state energy ($E^{T1}_{0,0}$) should have been used to obtain the real redox potentials, their experimental determination is very difficult (cryogenic conditions are required), so that the values derived from the singlet excited-state energies are commonly used, especially to detect substituent effects.

The spectra were normalized using the lowest-energy Q band from the absorption spectrum and the Q(0,0)-peak of the emission spectrum (highest energy band). The intersection points of these normalized spectra provided the corresponding intersection wavelength. Using this wavelength, Planck's equation was applied to calculate the energy in joules (J). Dividing this energy by the electron charge allowed the determination of the singlet excited-state potential (in volts, V; Table 2).

Figure 6 illustrates the normalized absorption and emission spectra for *meso*-tetrabenzoylporphyrin nickel **6**, which were used to estimate the energy of the singlet excited state. Notably, this porphyrin exhibits a relatively large Stokes shift, whereas the Stokes shifts for the other porphyrins studied, particularly those without metal centers, are significantly smaller (see Appendix 4).



Figure 6. Normalized absorption and emission spectra of compound 6

Porphyrin	Less energetic absorption Q band (nm)	More energetic emision Q (0,0) band (nm)	Intersection wavelength (nm)	Singlet excited state energies (E ^{S1} 0,0), V
5	640	642	641	1.93
6	562	652	609	2.04
7	640	642	641	1.93

Table 2. Photophysical data for porphyrins 5-7

As observed, the free-base benzoyl-substituted porphyrins (compounds **5** and **7**) exhibit the same normalized intersection wavelength (641 nm), corresponding to an identical singlet excited-state energy of 1.93 V. These two compounds display a very small Stokes shift (2–3 nm). In contrast, the Ni complex (compound **6**) behaves quite differently from the other porphyrins. It shows a slightly

lower intersection wavelength (609 nm), indicating a higher singlet excited-state energy (by 0.11 V) and a significantly larger Stokes shift (90 nm).

Using the measured values of the singlet excited states, we were able to calculate the ground-state and excited-state redox potentials for the benzoyl-substituted porphyrins 5–7. These values, along with those for TPPH₂ and 5-(benzoyl)-10,15,20-triphenylporphyrin, 4, (used as a reference), are presented in Table 3.

Porphyrin	Ground-state redox potentials (V vs. SCE)		(Singlet) excited-state redox potentials (V vs. SCE)	
	[PC/PC-]	[PC·*/PC]	[*PC/PC]	[PC */*PC]
TPPH ₂	-1.21	+1.09	+0.70	-0.82
4	-0.97	+1.32	+0.94	-0.59
5	-0.76	-	+1.17	-
6	-0.86	+1.38	+1.18	-0.66
7	-0.71	-	+1.22	-

Table 3. Ground-state and singlet excited-state redox potentials of the three porphyrins 5-7

Examining the values shown in Table 3, it is evident that the introduction of four benzoyl groups at the *meso*-positions of the porphine core significantly enhances the ease of reduction both in the ground and in the excited state. Additionally, the presence of an electron-withdrawing group such as fluorine further increases this value. This compound (7) exhibits an excited-state reduction half-wave potential of +1.22 V ([*PC/PC-]), suggesting that it should function efficiently as a photooxidant in a reductive quenching cycle.

6.3. STUDY OF THE PHOTOPHYSICAL PROPERTIES OF MESO-TETRABENZOYL PORPHYRIN 5

The singlet and triplet states of porphyrin 5 were characterized under the guidance of Dr. Bart Limburg.

The normalized absorption (red) and emission (blue) spectra for porphyrin 5 are shown in Figure 7.



Figure 7. Normalized excitation and emission of porphyrin 5

Transient absorption spectroscopy (TAS) is an extension of traditional absorption spectroscopy. TAS measures the absorption of a sample both before and after it is irradiated with a laser of a specific wavelength, allowing the dynamics of the excited state to be studied. The difference in absorption is calculated as follows:

$\Delta A = A_{(before)} - A_{(after)} = -\log\left(\frac{I_2}{I_1}\right)$	Equation 5
$A_{(before \ laser)} = -\log\left(\frac{I_1}{I_0}\right)$	Eqution 6
where I_0 would be the 'blank'	
$A_{(after \ laser)} = -\log(\frac{I_2}{I_0})$	Equation 7
where I_0 is the same as before	

In effect, this means we take the 'before laser' as a blank for the 'after laser', and by doing so, we remove the need to measure a blank.

In porphyrins, TAS is particularly useful for studying the triplet state. This technique is employed because the relaxation from the triplet state to the ground state does not emit photons and, therefore, cannot be detected by fluorescence emission techniques.

Figures 8 and 9 illustrate the TAS measurement results. A delay time of 100 ns after the laser irradiation was used, to ensure conversion by intersystem crossing of the excited singlet state to the triplet state. The data show a negative value for Δ Absorption at a wavelength of 416 nm because, upon laser irradiation, photons are excited, reducing the number of molecules remaining in the ground state compared to the initial condition. The result is negative, therefore, because the triplet state absorbs less light at this particular wavelength than the ground state. In contrast, a positive signal is observed at 440 nm, corresponding to an absorbance peak of the triplet excited state, as the ground state does not absorb at this wavelength (see Figure 7 and Appendix 4 [the normal UV-vis spectrum]). The kinetic traces of the Δ A signal at the 416 nm and 440 nm decay with similar time-constants characteristic of a single long-lived triplet state ($\tau = 41.8 \ \mu$ s).



Figure 8. Decays of meso-tetrabenzoylporphyrin.

Figure 9. TAS spectrum of meso-tetrabenzoylporphyrin

Time-correlated single photon counting (TCSPC) was utilized to analyze the relaxation dynamics of molecules transitioning from the singlet excited state to a lower energy state (either to the triplet state through intersystem crossing, or back to the ground state through internal conversion or fluorescence). The number of photons counted at each timepoint is proportional to the concentration of singlet excited state present at that time, and therefore the decay is exponential. Figure 10 presents the TCSPC results for porphyrin **5**, revealing two distinct relaxation rates. This indicates the presence of two different species in the singlet excited state, that have different lifetimes.



Figure 10. TCSPC spectrum of meso-tetrabenzoylporphyrin

Equation 8

The decay of the singlet excited state (S1) over time can be expressed mathematically as:

$$\frac{d[S_1]}{dt} = k_d[S_1]$$

This equation means that the rate of change in the concentration of S_1 is proportional to the amount of S_1 present, with k_d being the decay rate constant.

Solving this gives:

$$[S_1] \propto counts = Ae^{-k_d t} = Ae^{-\frac{t}{\tau}}$$
 Equation 9

A is an arbitrary constant that just depends on how long we've run the experiment (A = total number of photons counted at t= 0). τ =1/kd is the lifetime of the excited state, meaning the average time the system stays in the excited state before relaxing. Using a logarithmic scale for the counts, a linear correlation with slope -1/ τ should have been obtained in Figure 10.

In some systems, like porphyrin 5, you might observe two distinct relaxation processes with different lifetimes (T1 and T2). This is called biexponential decay, and it's expressed as

$$counts = Ae^{-\frac{t}{\tau_1}} + Be^{-\frac{t}{\tau_1}}$$
 Equation 10

- A and B are constants reflecting the contribution of each decay process at t=0.
- The presence of two terms indicates two species or pathways relaxing from the excited state, each with its own characteristic lifetime (r1 and r2).

In experiments like TCSPC, this biexponential behavior would show up as a curve that initially decays rapidly (dominated by the shorter lifetime, τ1), followed by a slower decay (dominated by the longer lifetime, τ2).

6. PRELIMINARY STUDY OF THE PHOTOCATALYTIC BEHAVIOR OF THE *MESO*-TETRABENZOYL-SUBSTITUTED PORPHYRINS 5-8

By analyzing the redox potential values presented in the previous section, it is clear that porphyrins with four benzoyl groups should act as highly effective photooxidants within a reductive quenching cycle. However, since time was limited in this Thesis's work, only a reaction was tested at one wavelength, 427 nm, using Kessil lamps.

To explore this further, we selected a benchmark photochemical reaction where the catalyst operates within a reductive quenching cycle, with molecular oxygen acting as an external stoichiometric oxidant. This reaction, the Povarov-type addition of N,N-dimethylanilyne (9) to N-phenylmaleimide (10),^[8] was chosen based on conditions under which the synthesized *meso*-tetrabenzoylporphyrins could demonstrate enhanced effectiveness. The specific reaction is as follows (Scheme 3):



Scheme 3. Photochemical Povarov-type addition of N,N-dimethylanilyne (9) to N-phenylmaleimide (10)





Figure 11. Proposed mechanism of the photochemical Povarov-type addition

Mechanistically, it is proposed that the single electron transfer (SET) from the electron-rich amine system to photoexcited porphyrin *following reductive quenching pathway* leads to the generation of an α - aminoalkyl radical, which undergoes addition to the olefinic double bond and subsequent free radical cyclization. Most likely, the Lewis acidic additive BF₃ is accelerating this step by coordinating with the carbonyl group. The redox cycle of the photocatalyst is completed by the generation of peroxy radical O₂⁻⁻ by SET, which also helps in the rearomatization by abstraction a hydrogen atom of the radical cyclized intermediate, to furnish the tetrahydroquinoline **11**.

The experiment was conducted using all porphyrins 5–7, as well as TPPH₂ and NiTPP, to allow for a more comprehensive comparison. The % yield was estimated by the NMR of the crude reaction mixture, by integrations of the signals corresponding to the

N-Me peak both in **9** and in **11**, that appear in different regions of the spectrum. Uniform conditions were applied across all trials to ensure consistency and reliability in the results (Table 4).

Porphyrins as a photocatalysts (3 mol%)		
Porphyrin	Yield (%) NMR	
TPPH ₂	18	
NiTPP	25	
5	35	
6	33	
7	41	

Table 4. % Yield of the photocatalyzed Povarov addition with different porphyrins.

Based on the results, we can conclude that porphyrins with four benzoyl groups perform better than tetraphenylporphyrins. As *shown* in Table 4, the compound with the highest efficiency is the *meso*-tetra(*p*-fluorobenzoyl)porphyrin 7, that due to the fluorine atoms in the *para* position of the benzoyl groups is the one most easily reduced in the excited state (see Table 3).

7. EXPERIMENTAL SECTION

7.1. MATERIALS AND METHODS

Commercially obtained reagents, catalysts, and solvents were utilized without further purification unless stated otherwise. Dichloromethane, used for porphyrin synthesis, was distilled over calcium hydride before use. Deuterated solvents were sourced from Merck Life Science.

Thin-layer chromatography was conducted on silica gel plates (Merck 60 F254), with compounds visualized under UV light and/or treated with chemical stains such as potassium permanganate, p-anisaldehyde, or vanillin. Column chromatography was carried out under pressurized air using silica gel (Merck 60, particle size 0.040–0.063 mm) as the stationary phase and a combination of solvents (hexane, ethyl acetate, and dichloromethane) as eluents.

Proton nuclear magnetic resonance (¹H NMR) spectra were acquired using a 400 MHz Varian Mercury spectrometer (Agilent Technologies, Santa Clara, CA, USA). Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane (TMS, δ = 0.00 ppm), with coupling constants (J) provided in hertz (Hz). Spectra were recorded at ambient temperature, with signals described as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). Infrared (IR) spectra were obtained with a Nicolet 6700 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) using attenuated total reflectance (ATR) methods.

7.2. PHOTOPHYSICAL METHODS

UV-Vis spectra were obtained using a double-beam Cary 500-scan spectrophotometer (Varian) with 1 cm quartz cuvettes (QS Suprasil, Hellma, Hellma GmbH & Co. KG, Mülheim, Germany) for absorption measurements. All spectra were recorded in dichloromethane (DCM) freshly filtered through basic Al₂O₃ to remove potential traces of hydrochloric acid.

Fluorescence spectra were measured using a PTI Felix GX spectrofluorimeter, with recordings performed in an open window of 1.5 mm. The optical path length of the cuvettes was 1 cm. Stock solutions of the porphyrins were prepared at concentrations of 10⁻⁵ M and 10⁻⁶ M for absorption and emission measurements, respectively.

TAS and TCSPC spectrums were measured under the guidance of Dr. Bart Limburg. Time-correlated single photon counting (TCSPC) experiments and steady-state fluorimetry were performed on an Edinburgh Instruments FS-5 spectrofluorometer equipped with a SC-20 sample chamber. Samples were degassed through repeated freeze-pump-thaw cycles until no gas bubbles evolved upon

thawing and introduced into a 1 cm cuvette fitted with a septum (Hellma 117100F-10-40). Samples were thermostated and stirred at 20 °C. Excitation was performed at 450 nm or 446 nm using either a Xenon lamp (steady-state fluorimetry) or a laser diode (Edinburgh instruments EPL-450, TCSPC), respectively. Collected data were fitted and plotted using in-house written python scripts.

Transient absorption spectra and kinetics were measured using an Edinburgh Instruments LP980 spectrometer fitted with a PMT photodetector and a Andor Technology iStar 320 ICCD detector. Samples were pumped using an Amplitude Laser Surelite I-10 nanosecond laser fitted with an Amplitude Laser Horzion I OPO set to an excitation wavelength of 450 nm. Probe-light was supplied by a 150 W pulsed Xenon lamp, and the differential absorbance was calculated by the following formula: \DeltaA = -log(I_s/I_ref), where I_s is the light spectrum observed after the laser pulse, and I_ref is the light spectrum observed without laser pulse. Collected data were fitted and plotted using in-house written python scripts.

7.3. CYCLIC VOLTAMMETRY

Cyclic voltammetry (CV) measurements were performed using a computer-controlled potentiostat (Model Epsilon Eclipse, BASi). The setup consisted of an undivided electrochemical cell equipped with a glassy carbon working electrode (3 mm diameter), a platinum wire counter electrode, and a saturated Ag/AgCl reference electrode. All voltammograms were recorded at a sweep rate of 100 mV/s.

The solvent was dichloromethane (DCM), with tetrabutylammonium perchlorate (TBAP, 0.1 M) as the supporting electrolyte in 50 mL of solution.

Prior to CV measurements, the reaction mixtures were purged with argon to eliminate oxygen and ensure an inert environment. For the experiments and to assess the presence of potential catalytic currents, stock solutions of the synthesized porphyrins were prepared at a concentration of 5 mM.

7.4. SYNTHESIS OF PORPHYRINS

7.4.1. Synthesis of meso-tetrabenzoylporphyrin 5



In a 500mL roud-bottom flask, phenylglyoxal monohydrate (304 mg, 2.0 mmol) and freshly distilled pyrrole (139 µL, 2.0 mmol) in dry CH₂Cl₂ (200 mL, distilled from CaH₂) were added. We introduced 0.01 M BF₃·OEt₂ (0.083 mL, 0.66 mmol) to the reaction mixture, which was stirred continuously, 1h, until the aldehyde was fully consumed, as confirmed by TLC (silica, CH₂Cl₂). Subsequently, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone DDQ (341 mg, 1.5 mmol) was introduced, and the reaction was heated to 45 °C for 1 hour. After cooling to rt, the solution was concentrated under vacuum to a final volume of *ca.* 10 mL. The product was purified through column chromatography (silica gel, Cl₂CH₂), to separate the porphyrin-containing fraction from the polypyrrrole oligomers. The residue was re-purified by preparative thin-layer chromatography on silica gel using dichloromethane as eluent, affording 45 mg of porphyrin **5** (7.2% yield).



We tested an alternative synthesis method to produce compound **5** to evaluate whether the yield could be improved. A 200 mL reaction was set up with DCM and phenylglyoxal monohydrate (0.608 g, 4.0 mmol), and was purged with argon for 15 min. Then, freshly distilled pyrrole (0.28 mL, 4.0 mmol) was added dropwise. The resulting mixture was stirred for 5 min and trifluoroacetic acid (0.61 mL, 8 mmol) was added dropwise. At this point a change in colour was observed. After 3 h of stirring at rt, DDQ (0.61 g, 3.0 mmol) was added, and the resulting solution was stirred under reflux for 1 h. After cooling to rt, triethylamine (1.1 mL, 8 mmol) was added dropwise. The solvents were evaporated in vacuo, and the resulting residue was submitted to column chromatographic purification (silica gel, DCM gradient with ethyl acetate) affording **5** (53 mg, 7.1% yield).

- ¹H NMR (400 MHz, CDCl₃) δ -2.84 (s, 2 H), 7.43 (t, J= 7.6 Hz, 4 H). 7.62 (t, J= 7.2 Hz, 8 H), 7.93 (d, J=6.95 Hz, 8 H), 9.04 (s, 8 H)
- ¹³C NMR (101 MHz, CDCl₃) δ 198.2, 141.3, 134.1, 131.6, 131.2, 128.8, 118.5 ppm.
- **IR** (solid, $v(cm^{-1})$) = 1653 (CO)
- HRMS (ESI) m/z calculated for C₄₈H₃₁N₄O₄ [M+H]⁺, 727.2340; found , 727.2340. m/z C₉₆H₂₂N₈O₈ [2M+H]⁺, 1454.4654; found, 1454.4685.
- **UV-vis** [DCM, λ_{max} (log ϵ), C = 1x10⁻⁵ M]: 418 (5.21), 510 (4.00), 546 (3.06), 586 (3.32), 640 (2.89).

7.4.2. Synthesis of meso-tetrabenzoylporphyrin nickel 6



Ni(AcO)₂ (42 mg, 0.042 mmol) was added to a magnetically stirred solution of *meso*-tetrabenzoylporphyrin **5** (35 mg, 0.14 mmol) in 10 mL of DMF, that was subsequently heated at 153°C for 4 h. The solvent was evaporated under reduced pressure and the solid was washed with warm water and purified through column chromatography (silica gel, Cl₂CH₂), followed by preparative thin-layer chromatography on silica gel using dichloromethane, affording 28 mg of porphyrin **6** (74% yield).

- ¹H NMR (CDCl₃, 400 MHz) d= 7.27 (t. 4 H, PhH). 7.47 (t, 8 H, PhH), 7.63 (d, 8 H, PhH), 8.86 (s, 8 H, p-pyrrole)
- UV-vis [DCM, λmax (logε), C = 1x10⁻⁵ M]: 412 (6.14), 528 (3.93), 561 (3.82).
- **IR** (solid, $\nu(cm^{-1})$) = 1653 (CO)

7.4.3. Synthesis of meso-(4-fluorotetrabenzoyl) porphyrin 7



The procedure of the reaction is the same as in 7.4.1 but starting with 4-fluorophenylglyoxal monohydrate (304 mg, 2.0 mmol), that was combined with pyrrole (139 μ L, 2.0 mmol) and 0.01M BF₃·OEt₂ (0.83 mL, 0.66 mmol) with 200 mL of DCM as a solvent. The mixture was stirred at 45 °C for 1 hour, followed by oxidation with DDQ (341 mg, 1.5 mmol). The product was purified using column chromatography on alumina with dichloromethane as the eluent, followed by preparative thin-layer chromatography (silica, dichloromethane), obtaining 35 mg of porphyrin **7** with a 8.68% yield.

- ¹H NMR (400 MHz, CDCl₃) δ -2.84 (s, 2 H), 7.10 (t, J= 8 Hz, 4 H). 7.94 (m, 8 H), 9.04 (s, 8 H)
- **IR** (solid, $\nu(cm^{-1})$) = 1653 (CO)
- HRMS (ESI) m/z calculated for C₄₈H₂₇N₄O₄F₄ [M+H]⁺, 799.1962; found, 799.1963.
- **UV-vis** [DCM, λ_{max} (log ϵ), C = 1x10⁻⁵ M]: 418 (5.39), 510 (4.03), 546 (3.29), 586 (3.56), 640 (2.93).

7.5. GENERAL PROCEDURE OF THE SYNTHESIS OF TETRAHYDRO-1HPYRROLO[3,4-C]QUINOLINE-1,3(2H)-DIONE

A screw cap tube (10 mL) equipped with a magnetic stirring bar, was charged with a DMF solution (2.5 mL) of *N*-phenylmaleimide **10** (x mmol, 2.0 equiv), *N*,*N*-dimethylaniline (1.0 equiv) and photocatalyst (3 mol%). The tube was degassed and purged with oxygen three times. After that $BF_3 \cdot OEt_2$ (0.15 equiv) were added. The resultant reaction mixture was placed in front of a 427 nm Kessil lamp and was stirred at room temperature for 22 h.

When the irradiation was stopped, EtOAc (20 mL) was added, and the reaction mixture was washed with brine (10 mL), dried over Na₂SO₄, concentrated under a vacuum, and purified by silica gel column chromatography using 20% ethyl acetate in hexane to deliver the tetrahydro-1*H*-pyrrolo[3,4- c]quinoline-1,3(2*H*)-dione **11**. The crude product was analyzed by ¹H-NMR. The reaction was repeated irradiating at 427 nm for each photocatalyst. Kessil lamps were used that range from 44 to 52 W when used at 100% intensity. The set-up of the reaction is shown below (Figure 12).



Figure 12. Experimental set-up for the photoredox reactions

8. CONCLUSIONS

1) Three porphyrins have been prepared and characterized: *meso*-tetrabenzoylporphyrin, *meso*-tetra(4-fluorobenzoylporphyrin and *meso*-tetrabenzoylporphyrin nickel. The last two compounds were previously unknown.

2) The *meso*-tetra(4-metoxybenzoyl)porphyrin could not be synthesized by the acid-catalyzed condensation between pyrrole and 4-methoxyphenylglyoxal.

3) The ground-state and the singlet excited-state redox potentials of the synthesized porphyrins have been determined by cyclic voltammetry. A combination of UV-vis and fluorescence spectra has been used to estimate the energy of the singlet excited state.

4) The lifetimes of both the triplet and the singlet excited states of *meso*-tetrabenzoylporphyrin have been measured by transient absorption spectroscopy and by time-correlated single photon counting, respectively.

5) As predicted from its electronic characteristics, the *p*-fluorosubstituted *meso*-tetrabenzoylporphyrin is most easily reduced in both the ground and the excited state. This compound has in fact afforded the highest yield in a photochemical reaction operating by a reductive quenching cycle (Povarov-type photoaddition).

9. REFERENCES AND NOTES

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11. ACRONYMS

AcOEt: Ethyl Acetate aq.: Aqueous BP: Benzophenone cat.: Catalyst DCM: Dichloromethane DMF: N,N-Dimethylformamide DDQ: 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone equiv.: Equivalents ESI: Electrospray Ionization ET: Energy Transfer FG: Functional Group HOMO: Highest Occupied Molecular Orbital IR: Infrared IUPAC: International Union of Pure and Applied Chemistry LUMO: Lowest Unoccupied Molecular Orbital MS: Mass Spectroscopy NaOAc: Sodium Acetate NiTPP: 5,10,15,20-Tetraphenylporphyrin nickel NMR: Nuclear Magnetic Resonance PC: Photocatalyst TAS: Transient Absorption Spectroscopy TSCPC: Time-Correlated Single Photon Counting TLC: Thin Layer Chromatography TMS: Trimethylsilyl (or Tetramethylsilane) **TPPH₂:** 5,10,15,20-Tetraphenylporphyrin

UV-Vis: Ultraviolet-Visible

APPENDICES

APPENDIX 1: SYNTHESIS OF MESO-SUBSTITUTED PORPHYRINS

Meso-substituted porphyrins have garnered significant attention due to the relative ease of their synthesis. The first method for synthesizing these porphyrins was introduced in 1936 by Rothmund, involving a condensation and oxidation reaction between pyrrole and an aldehyde. ^[10] This initial method required high concentrations, elevated temperatures, and extended reaction times, yielding a modest 7.5–9%.^[11]

Subsequent advancements utilized organic acids such as propionic acid as both catalysts and reaction media. Conducting the oxidation step in open air and reducing the reaction time increased the yield to approximately 20%. Later, the Alder-Logo synthesis was refined by Lindsey and colleagues ^[7], who employed Lewis acids like boron trifluoride or strong organic acids such as trifluoroacetic acid in chlorinated solvents. These modifications significantly enhanced yields, reaching 30–40%, depending on the symmetry of the porphyrin.

These yields are considered relatively high, given the propensity of pyrroles to undergo self-polymerization, forming polypyrrole polymers. A schematic representation of the general reaction mechanism between pyrrole and aldehyde is provided in Figure 13. The reaction initially provides an octahydroporphyrin, that is subsequently oxidized *in situ* by a suitable oxidant (molecular oxygen, DDQ).



Figure 13. General mechanism of porphyrin synthesis with pyrrole and aldehyde, including a condensation and oxidation

APPENDIX 2: NMR SPECTRA

NMRs of meso-tetrabenzoylporphyrin (5)



¹³C-MNR







0.0 9.9 9.8 9.7 9.6 9.5 9.4 9.3 9.2 9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 f1 (ppm)

NMR of meso-tetra(p-fluorobenzoyl)porphyrin (7)

¹H-NMR



9.4 9.3 9.2 9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 f1 (ppm)

APPENDIX 3: CYCLIC VOLTAMMETRY

MESO-TETRABENZOYLPORPHYRIN (5)

Reduction



MESO-TETRABENZOYLPORPHYRIN NICKEL (6)

Oxidation



Reduction



MESO-TETRA(P-FLUOROBENZOYL)PORPHYRIN (7)



APPENDIX 4: UV-VIS AND FLUORESCENCE SPECTRA

MESO-TETRABENZOYLPORPHYRIN (5)

UV-vis



Fluorescence



Normalized absorption and emission



MESO-TETRABENZOYLPORPHYRIN NICKEL (6)

UV-vis



Fluorescence



Normalized absorption and emission



MESO-TETRA(P-FLUOROBENZOYL)PORPHYRIN (7)





Fluorescence



Normalized absorption and emission

