Development of Novel Hydroporphyrins for Light Harvesting and Sensitising NIR Lanthanide Luminescence

RUISHENG XIONG
Chlorins, as the core structures of chlorophylls, have been extensively studied for harvesting solar energy, fluorescent imaging and photodynamic therapy against cancer. This thesis is concerned with design and synthesis of novel chlorins as antennae for harvesting light and sensitising near infrared lanthanide luminescence.

In the first part, a series of chlorin monomers, dimers and polymers were synthesised and their photophysical properties were characterised. The chlorin monomers were substituted with five-membered heterocycles, such as thiophenes and furans. These heterocycles function as auxochromes analogous to the natural ones in chlorophylls, and extend chlorin absorption and emission strongly to the red (up to $\lambda_{em} = 680 \text{ nm}$). A borylation method was developed to prepare borylated chlorins, which gave access to directly linked chlorin dimers through Suzuki coupling reaction. Different regioisomers of chlorin dimer were prepared, including $\beta$-meso homodimers, meso-meso homodimers and heterodimers. The dimerisation resulted in red-shifted absorption and emission. Chlorin polymerisations were performed both electrochemically and chemically. Bis-thienylchlorins yielded chlorin films and an organic solvent soluble copolymer with hexylthiophene, respectively. These polymers from both polymerisations have red absorptions beyond 700 nm, and might be used as light-harvesting antennae.

In the second part, chlorins were used as chromophores to sensitise near infrared lanthanide luminescence. Two types of chlorin-lanthanide dyads were prepared through lanthanide coordination with cyclen derivatives and dipicolinic acids (DPA). The cyclen-based dyads were poorly soluble in water, thus their near infrared emissions were not observed. The other type of complexes was fully soluble in $\text{H}_2\text{O}$ and THF. Both Nd and Yb emission were recorded even upon excitation into the Q bands of chlorins. In the dyads with free base chlorins, the singlet state of chlorins might be involved in the sensitisation of lanthanide luminescence. These DPA-based dyads presented two-color emission based on one chlorin and two-color excitation based on one lanthanide ion. These dyads would enable in theory 4-color imaging.

In the last part, a microwave-assisted two-step synthesis was described to prepare dipyrromethanes, which are the key intermediates in the chlorin synthesis. This mild method took advantage of the nucleophilicity of pyrrole and the electrophilicity of $N,N$-dimethylaminomethyl pyrroles. The usually used acid catalysis is detrimental to many functionalities, thus our methods enable the synthesis of dipyrromethanes with acid sensitive groups or a formyl group.

**Keywords:** chlorin, hydroporphyrin, chlorophyll analogues, light harvesting, lanthanide luminescence

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Chem Is Try
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


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Contributions

Paper I. Performed a half of the synthetic work and contributed to the photophysical studies. Contributed to the electrochemical measurements. Co-wrote the supplementary information.

Paper II. Performed the majority of the synthetic work and contributed to the electrochemical measurements. Co-wrote the supplementary information.

Paper III. Performed all of the synthetic work and co-wrote the supplementary information.

Paper IV. Performed all the synthetic work and contributed to the photophysical studies. Co-wrote the supplementary information.

Paper V. Performed the majority of the synthetic work and co-wrote the supplementary information.
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Abbreviations

Abbreviations are used in agreement with standards of the subject. Non-standard abbreviations that appear in this thesis are listed here.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>B$_2$pin$_2$</td>
<td>Bis(pinacolato)diboron</td>
</tr>
<tr>
<td>BODIPY</td>
<td>Boron-dipyrromethene</td>
</tr>
<tr>
<td>CuAAC</td>
<td>Cu catalysed alkyne-azide cyclisation</td>
</tr>
<tr>
<td>DDQ</td>
<td>2,3-dichloro-5,6-dicyano-p-benzoquinone</td>
</tr>
<tr>
<td>DPA</td>
<td>2,6-pyridinedicarboxylic acid</td>
</tr>
<tr>
<td>Fc</td>
<td>Ferrocene</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorine-doped tin oxide</td>
</tr>
<tr>
<td>HATU</td>
<td>1-[bis (dimethylamino) methylene]-1H-1,2,3-triazolo [4,5-b] pyridinium3-oxid hexafluorophosphate</td>
</tr>
<tr>
<td>HBpin</td>
<td>Pinacolborane</td>
</tr>
<tr>
<td>I$_B$/I$_Q$</td>
<td>The ratio of the peak intensity of the Soret band and the Q$_y$ band</td>
</tr>
<tr>
<td>Ln</td>
<td>Lanthanide</td>
</tr>
<tr>
<td>Mw</td>
<td>Weight average molecular weight</td>
</tr>
<tr>
<td>NIR</td>
<td>Near infrared</td>
</tr>
<tr>
<td>µw</td>
<td>Microwave</td>
</tr>
<tr>
<td>PCC</td>
<td>Pyridinium chlorochromate</td>
</tr>
<tr>
<td>PIDA</td>
<td>Diacetoxyiodobenzene</td>
</tr>
<tr>
<td>PIFA</td>
<td>Bis(trifluoroacetoxy)iodobenzene</td>
</tr>
<tr>
<td>Φ</td>
<td>Quantum yield</td>
</tr>
<tr>
<td>RP-HPLC</td>
<td>Reverse phase high-performance liquid chromatography</td>
</tr>
<tr>
<td>r.t.</td>
<td>Room temperature</td>
</tr>
<tr>
<td>TBTA</td>
<td>Tris(benzyltriazolylmethyl)amine</td>
</tr>
<tr>
<td>TBAF</td>
<td>Tris[(1-benzyl- 1H-1,2,3- triazol-4- yl)methyl]amine</td>
</tr>
<tr>
<td>TIPS</td>
<td>Trisopropylsilyl</td>
</tr>
<tr>
<td>TMPi</td>
<td>2,2,6,6-tetramethylpiperidine</td>
</tr>
<tr>
<td>TPP</td>
<td>meso-tetraphenylporphyrin</td>
</tr>
</tbody>
</table>
1. Introduction

Tetrapyrroles are among the most important natural products on Earth. They have been termed the pigments of life, since they keep our lives sustainable on this planet.\cite{2} The most biologically relevant tetrapyrroles are chlorophylls and heme, based on hydroporphyrins and porphyrins respectively, which are responsible for photosynthesis in plants and transporting oxygen to tissues in our bodies, respectively.\cite{3} As shown in Fig. I-1, photosynthesis transforms light energy into chemical energy and releases oxygen to the atmosphere. After food consumption, carbohydrates are oxidized back into CO$_2$ and H$_2$O by the O$_2$ delivered by hemoproteins.

![Figure I-1. Representation of tetrapyrroles in photosynthesis and cellular oxidation.](image)

Chlorophylls are the light harvesting antennae in photosynthesis because of their strong absorption of solar energy. Further tuning, e.g., interaction with proteins and combination with other chlorophyll variants provides a broad absorption range.\cite{4} In order to better harvest solar energy, both natural chlorophylls and synthetic chlorins have been extensively investigated.\cite{5} Due to their sharp absorption and narrow emission in the red or near infrared, chemists and biologists have also employed them as fluorescent imaging probes and photosensitisers in the photodynamic therapy of cancer.\cite{6} In this thesis, we focus on the development of novel chlorins for light harvesting and as photosensitisers for luminescence imaging.

1.1 Chlorins

Chlorin is the cyclic core structure of chlorophyll, which is a porphyrin hydrogenated on C-17 and C-18. A further reduction between C-7 and C-8 of ring B affords bacteriochlorin, with two pyrrolic rings located diagonally.
Both chlorins and bacteriochlorins are aromatic. Hydrogenation of porphyrin does not affect its aromaticity, which leaves the same 18 $\pi$-electron system.

According to Hückel’s rule, an aromatic compound has $4n+2$ $\pi$ electrons delocalised in its conjugated system. Different pathways can be drawn to illustrate the $\pi$-electrons delocalization in porphyrins. An [18]-anulene model is frequently used to describe porphyrin aromaticity, proposed by Rabinnovitch in 1944.[7] In this inner-outer-inner-outer pathway, as highlighted in the macrocycles shown in Scheme I-1, all the three tetrapyrroles are viewed as a conjugated 18-membered ring with 18-$\pi$ electrons, i.e., [18]-diazaanulene.

NMR is one of the most important tools to observe aromaticity by the chemical shifts due to the shielding of induced ring current. In chlorins, the aromaticity is confirmed by $^1$H NMR spectra. The inner N-Hs are well shielded by the ring current, so their chemical shifts are found at $< 0$ ppm, –1.5 ppm in CD$_2$Cl$_2$ for tetraphenylchlorin, while the peripheral protons are shifted downfield due to the deshielding effect. The resonance of $\beta$-protons is usually around $> 8$ ppm, and meso C-H signals are found at high frequency, often seen at $> 9$ ppm.[8]

It is noteworthy that the lone electron pairs of all N atoms are not involved in the delocalized system, and the double bonds of C7-C8 and C17-C18 are semi-isolated from the aromatic pathway. Although the aromaticity is untouched after hydrogenation, significant differences are observed in the electronic absorption spectra as a consequence of the double bond reduction.

1.1.1 Absorption
Chlorins are strongly colored compounds, which absorb intensively in the blue and red region, thus most often appear green in solution. The blue absorption is called the B band, or Soret band, while the red absorption is denoted as the Q band (vide infra), which is much stronger than that in an analogous porphyrin. The absorption is a combination of different electronic transitions in porphyrin, which can be rationalised by Gouterman’s four orbitals representation (two HOMOs and two LUMOs).[9] Structural modifica-
tions, e.g. reduction, affect the macrocycle symmetry, thus change the relative energy levels and intensities of these transitions, which give rise to the differences in absorption spectra.

Figure I-2. Absorption spectra of different chlorophylls in diethyl ether.

Figure I-3. Spectroscopic axes of chlorin.

Figure I-4. Four orbital representation of porphyrin and chlorin. [10]
A simplified diagram of two HOMOs (a_{1u} and a_{2u}) and two LUMOs (e_{gx} and e_{gy}) is shown in Fig. I-4. In porphyrins with D_{4h} symmetry, such as metallopophyrin and porphyrin dianions, the two HOMOs and two LUMOs are degenerate. The excitations a_{1u} \rightarrow e_{gy} and a_{2u} \rightarrow e_{gx} are x-polarized, which require similar energy to y-polarized transitions from a_{1u} \rightarrow e_{gx} and a_{2u} \rightarrow e_{gy}. Since the x and y axes are degenerate, this gives rise to highly allowed B transitions and Q transitions with almost zero-probability. For the less symmetric free base porphyrin, x- and y-polarized transitions are not degenerate any more. Configuration interaction and splitting between electronic states result in four transitions in two pairs, B_x/B_y with high energy and high intensity, and Q_x/Q_y with low energy and low intensity.

Reduction of porphyrin to form a chlorin decreases the symmetry, diminishing the degeneracy of the spectroscopically polarised transitions. The energy of a_{1u} and e_{gy} orbitals are considerably increased since a large amount of electron density are located in the saturated \(\beta,\beta\)-carbons (C-17 and C-18),\(^{[10]}\) while e_{gx} orbital is almost isoenergetic. The lowered energy gap results in a strong red-shift (~100 nm) in the Q_y absorption compared to porphyrin. Besides, the intensity of the Q_y band is increased substantially. This is attributed to symmetry allowed Q_y transition because of the changes in configuration interactions and transition dipoles during the orbitals splitting. For the x-polarised transitions, Q_x have the same energy and thus the spectral positions and intensities remain almost unchanged.

The characteristic Q_y bands in chlorins are sensitive and dependent on the chlorin substitution pattern.\(^{[8b, 11]}\) Extention of the macrocycle conjugation with functional groups shifts the Q_y absorption to longer wavelengths. These substituent effects are commonly seen in chlorophylls (Scheme I-3). The Q_y maxima in the absorption spectra of chlorophylls range from 626 nm to 707 nm when varying formyl and vinyl groups around the macrocycle. Compared to chlorophyll a, a dramatic bathochromic shift of the Q_y band was observed in formylated chlorophylls (d and f), while 7-CHO in chlorophyll b shift the Q_y absorption towards the blue significantly.\(^{[11c]}\) This can be rationalised with the 4-orbital model. In all cases, the formyl group stabilises the HOMO and the LUMO. When it resides in 2 or 3 positions, the effect is larger on the LUMO than on the HOMO.\(^{[11f]}\) In contrast, for 7-CHO, the shift is more profound on the HOMO while only a slight effect is observed on the LUMO.
The effect is remarkable in synthetic chlorins with few substituents, which lack interference from undesired functional groups. Apart from formyl groups, incorporation of other groups also engender similar red shifts in the Qy absorption in the following order, vinyl < ethynyl < acetyl < formyl.\textsuperscript{[11c]} Meso-substitution (5,10,15,20) has a smaller influence on the HOMO-LUMO energy gap than β substitution (2,3,12,13), and a consequently smaller red shift. On average, adding an aryl group in a meso position gives a 3 nm redshift in the Qy band vs 8 nm in β positions.\textsuperscript{[11d]} Concomitantly, the relative intensity of the Qy (Ib/IQy) band decreases in meso-substituted chlorins whereas the intensity increases as Qy band moves to the red in β position. The ratio of the peak intensity of the Soret band and the Qy band (Ib/IQ) can be used to evaluate the variation of Qy intensities in chlorophylls, particularly when accurate measurement of extinction coefficients is not possible.

Central metallation blue shifts the Qy absorption. In unsubstituted chlorins, zinc chelation gives ~29 nm of blue shift compared to the free base chlorin; the biggest blue shift (46 nm) was found in palladated chlorins.\textsuperscript{[8b]}

### 1.1.2 Synthesis

Naturally occurring chlorins are fully β-substituted. Spectral modulations for specific applications are limited. Chlorins with tunable photophysical properties and amenable to further functionalisations are nevertheless highly desirable. Chlorins are usually prepared by the modification of natural chlorophylls, the functionalisation of porphyrins\textsuperscript{[12]} or \textit{de novo} synthesis.\textsuperscript{[5]}

Earlier approaches mainly relied on the peripheral functionalities including vinyl and formyl groups in the C-3 or C-7 positions, the C-17-ester moiety and the isocycle. One example\textsuperscript{[13]} is the modification of pheophorbide
through Diels-Alder reaction with one of the pyrrolic double bonds (Scheme I-3).

Scheme I-3. Modification of pheophorbide a.

This strategy is also well adapted for the transformation of porphyrins to chlorins through various cycloadditions, in addition to the Diels-Alder reaction. As mentioned above, two diagonal double bonds are semi-isolated from the macrocyclic conjugation, and are referred to as ‘cryptoolefinic’. Therefore, powerful reactions, such as diimide reduction and OsO₄ oxidation, can engage chlorins (Scheme I-4). These are the most established syntheses of chlorins. Accessible porphyrins, such as tetraphenyl porphyrin (TPP) can yield chlorins. The drawback is the adventitious dehydrogenation back to porphyrin. Dihydroxylchlorin can be further modified with its diol handles, e.g., by oxidation with DDQ to afford a porphyrin dione. The breaking of the β,β'-bond enables ring contraction or expansion. A twisted bacteriochlorin was recently prepared through this ‘breaking and mending’ strategy.

Scheme I-4. Semi-synthesis of chlorins from porphyrin.

Another way to access chlorins is through de novo synthesis. Through pre-macrocylic functionalisation it can also introduce substituents into β positions. Most synthetic chlorins bear a gem-dialkyl group (particularly gem-dimethyl) in the pyrroline ring to circumvent adventitious oxidation, instead of a trans-dialkyl group, which is present in the chlorophylls. The
chlorin precursor (e.g., tetrahydrodipyrrin) with the gem-dimethyl group is synthetically available (Scheme I-5).

Scheme I-5. Tetrahydrodipyrrin synthesis.\[^{19}\]

The first de novo synthesised chlorin was reported by Battersby and coworkers.\[^{20}\] This landmark synthesis condensed a Western Half (dihydrodipyrrin/tetrahydrodipyrrin) and an Eastern Half. The macrocyclisation was performed under photochemical or thermal conditions. In addition to the ‘2+2’, a ‘3+1’ approach was also introduced to construct the macrocycle, as seen in Montforts’ effort\[^{21}\] to chlorin synthesis.

Scheme I-6. Lindsey’s method of de novo chlorin synthesis.

Lindsey and co-workers\[^{22}\] have extensively investigated the thermal cyclisation step of the 2+2 condensation, which was widely applied to prepare synthetic chlorins. The nucleophilicity and electrophilicity of the two moieties could be adjusted. Condensation under acidic conditions affords a linear tetrahydrobiladiene intermediate, where reduction of acyl dipyrromethane to carbinol is necessary for the acid-catalysed condensation. The Zn-templated oxidative cyclisation requires a dilute solution. Several metal ions can replace Zn\(^{II}\) to mediate the cyclisation, but Zn(OAc)\(_2\) is the most effective.\[^{11a}\] This method is greatly facilitated by the efficient synthesis of dipyrromethanes.\[^{23}\] In turn, it gives access to a variety of chlorins substituted at C-5 and/or C-10. In parallel, the Western half synthesis has been refined giving access to multigram quantities.\[^{24}\] Bromination of Western half or Eastern half affords β-bromochlorins (2-, 3-, 12- or 13-position) as single regioisomers.\[^{25}\] These bromides can be utilized in formylation, acetylation, vinylation and alkynylation through Pd coupling to introduce various auxo-
chromes.\textsuperscript{[26]} Post-macro cyclic bromination can be selective for the C-15 position, which is essential to build isocyclic ring. Bromination can also be directed to the 7- or 8-position.\textsuperscript{[27]} This method is versatile and has been widely used in \textit{de novo} chlorin synthesis,\textsuperscript{[5]} however its yield is somewhat low.

Jacobi and coworkers\textsuperscript{[28]} described a chlorin synthesis (Scheme I-8), based on the MacDonald\textsuperscript{[29]} 2+2 porphyrin synthesis. It highlighted a diformyl-dipyrrolic unit and a dipyrromethane-dicarboxylic acid, akin to MacDonald synthesis of porphyrin. The mild condensation proceeded in 5\% TFA in CH\textsubscript{2}Cl\textsubscript{2} at room temperature with up to 87\% isolated yield. The high yield is ascribed to the adjusted oxidation state in the precursors, which do not require subsequent air oxidation in Lindsey’s procedure. In follow-up studies,\textsuperscript{[30]} various substituents were introduced into the dihydrodipyrrin meso-position, which are less accessible by other methods. The reactivities of both units have been modified to access chlorins without requiring symmetrically substituted dipyrromethanes. However, the photophysically interesting substituents along the y-axis (2,3,12,13) are still limited to alkyl chains in chlorins. Recently, Lindsey et al. has reported diversely substituted bacteriochlorins bearing akyl, aryl and carboethoxyl groups based on this strategy.\textsuperscript{[31]}

\textit{Scheme I-7.} Jacobi’s \textit{de novo} chlorin synthesis.

1.2 Chlorins in light harvesting

Chlorophylls [from the Greek \textit{χλωρός}, chloros (green) and \textit{φυλλον}, phyllom (leaf)], are the chief pigments responsible for the light harvesting in plant photosynthesis. As discussed above, their individual absorptions are narrow and do not cover the whole visible spectrum, which is not favorable for harvesting light. In photosynthetic systems, nature develops its own way to get broader absorption. Interactions with proteins can significantly shift the absorption bands (by hundreds of cm\textsuperscript{-1}).\textsuperscript{[4]} The absorptions of chlorophyll \textit{a} and \textit{b} are distinct and complementary to each other. Thus, combining different pigments enables covering a broader absorption range. There are a lot of pigments in Nature. With various combinations of different pigments, a series of useful absorptions is realised in photosynthesis.\textsuperscript{[4]}

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To mimic and investigate Nature’s photosynthetic edifices, synthetic chlorins, including chlorin-based dyads, have been prepared. These dyads include chlorin-porphyrin dyads, chlorin-BODIPY dyads and bis-chlorins. Installing a BODIPY through a phenylacetylene or an amide link into chlorins supplements the absorption in the green region, which is missing in the natural light harvesting. The energy transfer is quite efficient from BODIPY to chlorin, up to 97%. In addition, chlorins were also linked to perylene and terrylene to pursue panchromatic absorption. Bis-chlorins have been obtained from chlorophyll derivatives through McMurry homocoupling. Significant red shift and a hyperchromic effect were observed after dimerisation in directly linked chlorin dimers, consistent with their extended conjugation. Ethylene linked dimers connected at their meso-positions experienced air oxidation to the corresponding chlorin-porphyrin and porphyrin-porphyrin dimers, which might be possible to circumvent by introduction of gem-dimethyl groups to the pyrroline ring. The absorption spectra of Chlorin-porphyrin dyads is superimposable to a chlorin spectrum and a porphyrin spectrum with a slightly hypochromic effect in the Q-band.

1.3 Chlorins in NIR imaging

Fluorescence imaging is widely used in the life sciences, because of its non-invasiveness and high resolution. NIR imaging is preferred since the biological samples are relatively transparent in this region and NIR light can penetrate further.

Chlorins (Φ ~ 0.2) and bacteriochlorins (Φ ~ 0.15) are fluorescent in the red or near infrared region. Due to their unique photophysical properties, e.g. tunable red absorption and narrow Q-band, (bacterio)chlorins have been utilised for NIR imaging. There are different ways to adapt (bacterio)chlorins to NIR imaging.

Bioconjugatable bacteriochlorins with tunable NIR absorption have been prepared for bioorthogonal labeling. Bacteriochlorins equipped with a phosphine ligand underwent Staudinger ligation with an azide containing peptide smoothly. A bacteriochlorin probe with a N-hydroxysuccinimide has been used for in vivo imaging with single excitation and two-color NIR imaging.

Chlorin based dyads have also gained attention in imaging. A BODIPY-chlorin dyad displayed efficient energy transfer from BODIPY to chlorin. These dyads had large Stokes shifts over 140 nm. Chlorins were also adapted as energy donors in red absorbing and NIR emitting dyads, such as chlorin-bacteriochlorin dyads. In these dyads, the Stokes shifts are large (up to 143 nm) and the NIR emission wavelength can be tuned with different auxochromes.
Another way is using chlorins as antennae to sensitize NIR emitting lanthanides (Ln).[44] Chlorin-Ln dyads take advantage of the tunable red absorption of chlorins and the characteristic Ln luminescence emission. Ln luminescence is particularly interesting for bio-imaging due to its long lifetime (µs-ms) and insensitivity of its position to surrounding media. Chlorins have been reported to sensitize NIR emitting Yb and Nd. The combination of the narrow bands of chlorins absorption and Ln emission would allow distinguishing based on both excitation and emission.[45]

1.3.1 NIR Ln luminescence

Most trivalent Ln ions are luminescent, spanning the entire UV-Vis-NIR spectral range.[46] Ln luminescence lifetimes are long (up to ms), due to the forbidden 4f-4f transitions, which give rise to the luminescence emission. Since 4f electrons are well shielded, the Ln spectroscopic properties are insensitive to the coordinating environment changes. As a consequence, Ln emission spectra are narrow and characteristic of the ion with little overlap with each other.[47]

Though NIR Ln luminescence has been used in various applications,[48] the emission of Nd\textsuperscript{III} and Yb\textsuperscript{III} are faint, because of their low intrinsic quantum yields.[49] Direct excitation of Ln\textsuperscript{III} ions is also inefficient, due to their weak absorptions (ε < 10 M\textsuperscript{-1} cm\textsuperscript{-1}).[50] Thus, indirect excitation methods are needed to populate the Ln\textsuperscript{III} excited states. One approach is to sensitize Ln\textsuperscript{III} ions through energy transfer from organic chromophores, discovered by Weissman in 1942.[51] This is called luminescence sensitisation or the antenna effect.[47] The energy transfer from the excited organic chromophore, also known as the antenna, to Ln\textsuperscript{III} ions is a very complex process, simplified in Fig. I-5. Both the singlet and the triplet states can be involved in the energy transfer.[50] The ideal energy gap between the Ln and the antenna triplet should be between 2000 and 4000 cm\textsuperscript{-1} to get efficient energy transfer and avoid energy back transfer.[46]
1.4 Aim of this work

A series of novel chlorins and chlorin-based dyads were designed and synthesised. The photophysical properties of these chlorins and dyads were evaluated with the aim of using them for light harvesting and for sensitising lanthanide luminescence.

For better light harvesting, the peripheral substituents (C-3, C-10, C-13 and C-15) in chlorins were replaced with 5-membered heterocycles such as furan and thiophene, instead of classical auxochromes, i.e. formyl and vinyl groups. The hypothesis was that 5-membered heterocycles are sufficiently small to be coplanar with the chlorin, especially in the β positions along the Qy spectroscopic axis. The extended conjugations through these positions were expected to shift chlorin absorptions bathochromically. Furthermore, chlorin dimers and polymers were prepared to study the effect of dimerisation and polymerisation, which have been well studied in porphyrin arrays.

Porphyrins have been used to sensitise lanthanides since the 1970’s. Chlorins, as tunable and red absorbing dyes, have gained attention in lanthanide luminescence only recently. We have prepared two sets of chlorin-Ln dyads to investigate their potential as red absorbing and NIR emitting probes. In these series, the metallation states of the chlorins, the linker lengths, the linker positions and the lanthanide chelating ligands were varied to get a better sensitisation effect and minimise Ln luminescence quenching by inner-sphere OH/NH/CH oscillators.
2. Developing novel chlorins for light harvesting (Papers I & II)

The peripheral substitution pattern is an influential parameter of chlorin absorption spectra, as seen in chlorophylls. Formyl and vinyl groups are commonly used for natural spectral tuning. $Q_y$-band shifted from $\lambda_{\text{max}} = 665$ nm in chlorophyll $a$ to $\lambda_{\text{max}} = 707$ nm in chlorophyll $f$ by replacing the methyl group with a formyl group in the C-2 position. Switching these two substituents in the C-2 and C-7 positions resulted in a red shift of 55 nm in the $Q_y$-band maxima from chlorophyll $b$ to chlorophyll $f$. Since both type and position of chlorin substituents are crucial, a number of other auxochromes have been investigated widely in the last decade, such as ketones, alkynes and esters, in order to further understand their effect. Extended conjugated fragments were also exploited for intensive absorption in light harvesting. Although these groups offered chlorins with finely tuned absorption, further functionalisation without sacrificing their auxochromic behavior was limited.

Thiophene and furan were employed as reactive handles in porphyrin polymers$^{[53]}$ and linkers in porphyrin-sensitised solar cells.$^{[54]}$ Imahori et al.$^{[53]}$ observed an extended conjugation in meso-furyl porphyrin polymers but not in meso-thienyl porphyrin polymers. This was attributed to the steric bulk of thiophene, which is repulsed by the neighbouring $\beta$-protons. As the $\beta$ positions are less crowded, we proposed that thiophene in the $\beta$-position would adopt a more planar conformation with the tetrapyrrole macrocycle than the one accessible in the meso-position. The extended $\pi$-conjugation would yield a bathochromic shift of chlorin absorption, allowing furan and thiophene to be potential auxochromes for chlorins. By installing a third functional group such as an aldehyde into these five-membered heterocycles, further transformations would be possible without diminishing the extended conjugation.

Apart from substituent effects, dimerisation of photosensitisers also plays a significant role in photosynthetic light harvesting. A lot of effort has been made to access various porphyrin dimers and oligomers.$^{[55]}$ In porphyrin arrays, the linkers have contributed to the inter-porphyrin energy transfer. Directly linked porphyrin dimers and oligomers are very promising in molecular photonics.

Chlorins resemble natural photosynthetic pigments more than porphyrins. They absorb much stronger in the red than porphyrins. Therefore, chlorin dimers are preferred to porphyrin dimers for harvesting sunlight. Bis-
chlorins via different linkers, e.g. amide bond, ethynyl and diphenylethynyl groups, have been well reported as model compounds to investigate the photosynthetic mechanism.\textsuperscript{[5]} Since the electronic coupling is expected to be sensitive to the length and site of linker attachment in each pigment, directly linked chlorin dimers were deemed to be interesting.

With these in mind, we designed and synthesised a series of chlorins substituted with furans and thiophenes. Their formylated analogues were also prepared. Directly linked chlorin dimers were also accessed from the corresponding bromochlorins, with different regioisomers and metallation states. Polymerisation of \textit{bis}-thienylchlorins were performed both electrochemically and chemically. The photophysical and electrochemical properties of monomers, dimers and polymers were investigated.

2.1 Heterocyclic auxochrome substituted chlorins

2.1.1 Synthesis

10-thienyl chlorins were prepared through condensation of Western half (\textit{II}-1 or \textit{II}-1-\textit{Br}) with \textit{meso}-thienyl substituted Eastern half (\textit{II}-2-S) under the standard Lindsey conditions.\textsuperscript{[11a]} Acidic bromination of \textit{Chl10}\textsuperscript{S}, followed by Suzuki coupling with \textit{II}-3-S afforded the \textit{bis-meso} \textit{Chl10}\textsuperscript{S}15\textsuperscript{S}, while \textit{Chl3}\textsuperscript{Br}10\textsuperscript{S} was obtained through Suzuki coupling of \textit{Chl3}\textsuperscript{Br}10\textsuperscript{S} and \textit{II}-3-S with quantitative conversion. To our delight, thiophene was compatible with the chlorin synthesis and the acidic bromination occurred in the chlorin macrocycle rather than in the electron-rich thiophene.
Scheme II-1. Synthesis of β- and/or meso-thienylchlorins.

Chl3S15S and Chl3S13S were both synthesised via double coupling of II-3-S with the corresponding dibromochlorins Chl3Br15Br, Chl3Br13Br in good yields (Schemes II-1 and II-2). The latter is a known compound, and was prepared according to reported procedures.\textsuperscript{[56]} Chl3Br15Br was built through regio-selective bromination of Chl3Br in CH2Cl2/TFA, as described above.

Scheme II-2. Synthesis of mono- and di-β-substituted chlorins.
Under the same coupling conditions, a series of monosubstituted chlorins bearing thiophene and furan groups were acquired in moderate to excellent yields. Suzuki coupling with formylthiophene gave somewhat higher yield in the 13-position, while with formylfuran, the 3-position functionalisation was higher yielding. Furan pendent chlorins in either the 3- or the 13 positions were unstable.

Since the heterocycles were robust in both pre- and post-macrocyclisation functionalisation, the installation of two different heterocyclic substituents to chlorins along the y axis become possible by incorporating one heterocycle before chlorin formation and the other after. \( \text{Chl}^{3s}13^{s\text{-CHO}} \) was one example of these asymmetrically disubstituted chlorins, as shown in Scheme II-3. Pre-functionalised Western Half II-1-3S coupled with bromo-Eastern Half II-2-Br yielded the crucial intermediate \( \text{Chl}^{3s}13^{s\text{Br}} \), following Suzuki coupling of II-1-3^{s\text{Br}}-NTs with II-3-S and de-tosylation of II-1-3^{s\text{S}}-NTs. The coupling between \( \text{Chl}^{3s}13^{s\text{Br}} \) and II-3-S-CHO was straightforward under standard Suzuki conditions affording the product in a good yield.
2.1.2 Photophysical characterisation

The UV-Vis absorption spectra of heterocycle-substituted chlorins were recorded in CH₂Cl₂ (Table II-1 and Figure II-1). Both Soret bands and Qₓ bands had shifted considerably to the red compared to unsubstituted chlorin. A β-thienyl group resulted in a 10 nm red-shift of the Qₓ maximum (vs λ_max = 634 nm in toluene for unsubstituted free base chlorin), in contrast to around 6 nm red-shift in the meso-position, i.e 10- or 15-position. The larger effect on the photophysical properties of the β-substitution over the meso one is ascribed to their lying along the spectroscopic axis. A S-CHO group in the 3- or 13-position shifts the absorption maximum bathochromically by ~20 nm. A similar effect was observed in Chl₁₃⁰-CHO (25 nm). The asymmetric substitution with S-CHO and S in Chl₃S₁₃S-CHO extended its absorption up to 668 nm. These shifts are comparable to those caused by established auxochromes, e.g. vinyl, formyl and acetyl groups in the β-positions. For instance, placing 3-vinyl or 3-alkynyln groups in ZnChl resulted in 18 and 25 nm red shift in the Qₓ-absorption maxima. [11d]

Table II-1. Photophysical properties of the substituted chlorins in CH₂Cl₂.

<table>
<thead>
<tr>
<th>Entry</th>
<th>λₓ, λᵧ/nm</th>
<th>Iₓ/Iᵧ</th>
<th>Δν/ cm⁻¹ (nm)</th>
<th>λ_em/nm</th>
<th>Φᵦ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chl₃S</td>
<td>404, 644</td>
<td>3.43</td>
<td>143 (6)</td>
<td>650</td>
<td>0.22</td>
</tr>
<tr>
<td>Chl₃S-CHO</td>
<td>416, 653</td>
<td>2.72</td>
<td>299 (13)</td>
<td>666</td>
<td>0.25</td>
</tr>
<tr>
<td>Chl₁₀S-CHO</td>
<td>418, 659</td>
<td>2.53</td>
<td>114 (5)</td>
<td>664</td>
<td>0.25</td>
</tr>
<tr>
<td>Chl₁₀S</td>
<td>407, 639</td>
<td>4.14</td>
<td>74 (3)</td>
<td>642</td>
<td>0.11</td>
</tr>
<tr>
<td>Chl₁₁S</td>
<td>405, 644</td>
<td>3.28</td>
<td>191 (8)</td>
<td>652</td>
<td>0.23</td>
</tr>
<tr>
<td>Chl₁₁S-CHO</td>
<td>410, 655</td>
<td>2.15</td>
<td>230 (10)</td>
<td>665</td>
<td>0.30</td>
</tr>
<tr>
<td>Chl₁₁S₀-CHO</td>
<td>420, 660</td>
<td>2.32</td>
<td>159 (7)</td>
<td>667</td>
<td>0.21</td>
</tr>
<tr>
<td>Chl₃S₁₀S</td>
<td>417, 651</td>
<td>4.02</td>
<td>137 (5)</td>
<td>656</td>
<td>0.15</td>
</tr>
<tr>
<td>Chl₃S₁₃S</td>
<td>416, 656</td>
<td>2.91</td>
<td>229 (10)</td>
<td>666</td>
<td>0.25</td>
</tr>
<tr>
<td>Chl₃S₁₅S</td>
<td>409, 650</td>
<td>3.40</td>
<td>164 (7)</td>
<td>657</td>
<td>0.19</td>
</tr>
<tr>
<td>Chl₁₀S₁₅S</td>
<td>411, 645</td>
<td>4.14</td>
<td>96 (4)</td>
<td>649</td>
<td>0.13</td>
</tr>
<tr>
<td>Chl₃S₁₃S-CHO</td>
<td>420, 668</td>
<td>2.14</td>
<td>264 (12)</td>
<td>680</td>
<td>0.34</td>
</tr>
</tbody>
</table>

Φᵦ Determined using tetraphenylporphyrin in toluene as the reference. [57]

A larger red shift in the absorption spectra was observed in formylfuryl chlorins than in their formylthienyl analogues. This was explained by DFT calculations, which showed that furanylchlorins have smaller dihedral angles and
HOMO-LUMO gaps than thiophene-bearing chlorins. Thus the former have a more extended conjugation, over the furylformyl substituent. The absorption and emission properties are not strongly affected by the solvents at room temperature. In toluene, the largest red-shift ($\Delta \lambda = 8$ nm) of Soret bands were found for both \textit{Chl3$^{O-CHO}$} and \textit{Chl3$^{S-CHO}$}, compared to that in MeOH and MeCN respectively, while $Q_y$ bands shifted 4 nm to the red. Only slight changes were observed in the excitation and emission spectra.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{spectra.png}
\caption{Normalised absorption (top) and fluorescence emission (bottom) spectra of selected heterocycle-bearing chlorins in CH$_2$Cl$_2$ at room temperature.}
\end{figure}

The fluorescence spectra were recorded by excitation into the chlorin Soret bands. The emissions consisted of a major band with a small satellite. The small Stokes shifts, 74-299 cm$^{-1}$ (3-13 nm), are comparable to those observed in unsubstituted chlorins. The order of emission bands mainly keeps
the same as the $Q_y$ bands. However, the order is reversed between chlorins with O-CHO and S-CHO substituents in the same $\beta$ positions. Larger Stokes shifts were observed in formylthienyl chlorins than the ones with formylfuranyl substituents (Table II-1). This was ascribed to that thienylchlorins were twisted in ground state and adopt a relatively planar conformation after excitation. Excitation maxima of both Chl3$^{S-CHO}$ and Chl3$^{O-CHO}$ are observed at 651 nm in frozen THF at 77 K. The difference between the excitation and emission maxima of Chl3$^{S-CHO}$ decreased to 6 nm (93 cm$^{-1}$, from 279 cm$^{-1}$), versus 2 nm (47 cm$^{-1}$, from 115 cm$^{-1}$) for Chl3$^{O-CHO}$. The decrease of $\Delta\lambda$ is due to the smaller conformational changes, in accordance to that freezing with liquid nitrogen would afford similar conformations. This is also in line with less pronounced effect found in Chl3$^{O-CHO}$, since the furan and the chlorin are more coplanar.

The fluorescence quantum yields were ranging from 0.11 to 0.34, which are typical for free base chlorins. The highest quantum yield value was found in Chl3$^{13S-CHO}$. Its photophysical properties are quite exciting considering its intense red absorption ($\lambda_{max} = 668$ nm, $I_B/I_Q = 2.14$) and far-red emission ($\lambda_{em} = 680$ nm), although it requires multi-steps synthesis. It is noteworthy that a single S-CHO or O-CHO in either the 3- or the 13-position provided emission maxima up to ~665nm.

X-ray crystallographic analysis supported the above explanation. The dihedral angle of Chl3$^{13SBr}$ is 22.8(11)$^\circ$ (24.2(5)$^\circ$) between the least squares plane (l.s.pl.) of the thiophene and the adjacent pyrrole ring. In contrast, meso-thiophene substituted chlorin has a much larger dihedral angle, l.s.pl. (56.6(3)$^\circ$ and 52.9(3)$^\circ$). It demonstrated that the $\beta$-thiophene, at least in the 3-position, could experience less twist with the chlorin than the meso-one.

![Figure II-2. Single-crystal X-ray structure of Chl3$^{13SBr}$ (left) and Chl10$^{3SBr}$ (right) in different views.](image)
2.1.3 Electrochemical characterisation

Cyclic voltammograms were measured in anhydrous CH\textsubscript{2}Cl\textsubscript{2}, using a three-electrode setup with a glassy carbon working electrode, and NBu\textsubscript{4}PF\textsubscript{6} as supporting electrolyte. The redox properties of the chlorins are summarised in Table II-2.

\textit{Table II-2.} Cyclic voltammetry data for chlorin dimers and the unsubstituted chlorin reference compound.\textsuperscript{a} Potentials are given versus Fc\textsuperscript{+/0}.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reduction E\textsubscript{red} [V]</th>
<th>Oxidation E\textsubscript{ox} [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chl1\textsuperscript{3}S</td>
<td>-2.06\textsuperscript{b}, -1.69\textsuperscript{b}</td>
<td>0.42, 0.93</td>
</tr>
<tr>
<td>Chl10\textsuperscript{S}</td>
<td>-2.11, -1.67\textsuperscript{b}</td>
<td>0.43, 0.93</td>
</tr>
<tr>
<td>Chl10\textsuperscript{O}</td>
<td>-2.14, -1.67\textsuperscript{b}</td>
<td>0.43, 0.83, 1.05</td>
</tr>
<tr>
<td>Chl13\textsuperscript{S}</td>
<td>-2.05\textsuperscript{b}, -1.69</td>
<td>0.39, 0.87</td>
</tr>
<tr>
<td>Chl3\textsuperscript{S}10\textsuperscript{S}</td>
<td>-2.06, -1.67\textsuperscript{b}</td>
<td>0.37, 0.86</td>
</tr>
<tr>
<td>Chl3\textsuperscript{S}13\textsuperscript{S}</td>
<td>-2.14, -1.67\textsuperscript{b}</td>
<td>0.44, 0.82</td>
</tr>
<tr>
<td>Chl3\textsuperscript{S}15\textsuperscript{S}</td>
<td>-2.09, -1.66\textsuperscript{b}</td>
<td>0.40, 0.84</td>
</tr>
<tr>
<td>Chl10\textsuperscript{S}15\textsuperscript{S}</td>
<td>-2.20, -1.70\textsuperscript{b}</td>
<td>0.41, 0.83</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Conditions: Measured with [analyte] = for 1 mM in CH\textsubscript{2}Cl\textsubscript{2} with 0.1 M NBu\textsubscript{4}PF\textsubscript{6} on glassy C-electrode; n = 100 mV s\textsuperscript{-1}. \textsuperscript{b} Reversible peak, the reported value is E\textsubscript{1/2} = (E\textsubscript{pa} + E\textsubscript{pc})/2.

In all chlorins, two reduction peaks were observed. One is reversible (-1.66 V to -1.70 V), and the other is quasi-reversible (-2.06 V to -2.20 V). Both of them are typically chlorin-based, while two oxidation peaks were shown in contrast to one in unsubstituted chlorin. The quasi-reversible peak (0.37 V to 0.44 V) originates from the chlorin, whereas the irreversible one (0.82-0.93 V) is assigned to the oxidation of the thiophene.
2.2 Polymerisation of bis-thienyl chlorins

During the cyclic voltammetry measurements, increased current was observed after repeated oxidative scans of bis-thienylchlorins. This is indicative of deposition of chlorin polymers on the working electrode.

Electropolymerisation was attempted with different bis-thiophene chlorin regioisomers. Instead of glassy carbon, fluorine doped tin oxide glass (FTO) was used as working electrode in the polymerisation. The polymerisation was performed by repeated cycling between oxidative (ca. 1.0 V) and reductive potentials (-0.5 to -0.2 V). After thorough polymer deposition, the homogeneous chlorin films p-Chl3S13S, p-Chl3S15S, p-Chl3S10S and p-Chl10S15S were obtained, as shown by scanning electron microscopy (SEM) analysis.

During the polymerisation, faster deposition and considerable current increases were found in more linear Chl3S13S and Chl3S15S, while Chl3S10S and Chl10S15S deposited slowly concomitant with a moderate current increase after 45 and 80 rounds of analysis, respectively. p-Chl3S13S and p-Chl3S15S showed a persistent oxidative peak, at +0.04 V and +0.01 V respectively, presumably due to tin metallation of chlorins.[58] A rapid decomposition was observed in p-Chl3S10S when reductive potentials were applied as we can see a substantial current decrease within the first 5 scans (Film S1 vs Film S5). This is in contrast to p-Chl10S15S which displayed a good bipolar conduction activity from -0.56 to +0.37 V.

After polymerisation, both B-bands (410-420 nm) and Q-bands (650-680 nm) of chlorin absorption have been broadened, except in the case of p-Chl3S10S. We were not able to record the absorption of p-Chl3S10S, presumably due to its low concentration of deposited chlorin. Similar low concentration was seen in p-Chl10S15S, as indicated by its low absorbance.
Emission was not observed in these chlorin polymers, probably because of their self-quenching due to the short inter-chlorin distance.

Figure II-4. Cyclic voltammograms of chlorin polymers. Polymerisation was performed on fluorine doped tin oxide glass (FTO), which was used as the working electrode in a three-electrode setup. The initial scan is highlighted in blue. The films were investigated at 100 mV s⁻¹ using different potential windows (blue dashed line).

Oxidation of a mixture of Chl₃S₁₃₅ and 3-hexylthiophene (1:20) with FeCl₃ yielded an organic soluble chlorin polymer p-Chl₃S₁₃S. The non-controlled radical polymerisation protocol was not optimised. The polymerisation was confirmed by ¹H-NMR and gel permeation chromatography analysis (GPC). The NMR integration of proton signals of the chlorin unit (-2 ppm, 4.6 ppm, >10 ppm) and regio-irregular hexylthiophene (e.g. 2-3 ppm) revealed a ~4% incorporation of chlorins. GPC showed a polydispersity index of 2.62, weight average molecular weight (Mw) of 5299 g/mol and number average molecular weight of 2020 g/mol for the polymer, which has an expected Mw of 3865 g/mol. Compared to polymer films, p-Chl₃S₁₃S-Hex₅ has less broadened absorption bands, and is much more emissive (λₘₐₓ = 681 nm), due to the diminished self-quenching.
2.3 Dimerisation of chlorins

Although bis-chlorins with various linkers have been extensively studied, only one example of directly meso-meso linked chlorin dimer was reported. This was prepared by oxidation of chlorin monomer with PIFA and PIDA. Moreover, as peripheral substituents are pertinent to chlorin photophysics, it is essential to selectively access different chlorin regioisomers. The work in this section was carried out to study the photophysical properties of various directly linked chlorin dimers.

Reactions of our chlorins (e.g. zinctated Chl10Mes) with PIFA and PIDA under the reported conditions did not afford any of the desired compounds. This is probably because chlorins are more prone to be oxidised than porphyrins, which results in extensive decomposition. An alternative approach was necessary in order to prepare different bis-chlorin regioisomers. Suzuki-Miyaura coupling, due to its mild conditions, was employed in this work to connect two chlorin species directly.

2.3.1 Synthesis

The regioselective bromination of chlorins is well established. Different regioisomers of bromochlorins are synthetically accessible. Starting from 15-bromochlorins, prepared with NBS under acidic bromination conditions, Miyaura borylation with HBpin afforded Chl15Bpin and Chl10Ph15Bpin in excellent yields. The boron source is crucial. Initial attempts with B2Pin2 were fruitless. Further optimisation found that the borylation was complete in one hour. The reaction is robust and can be scaled up to 100 mg of Chl10Ph15Bpin without lowering the yield. However, β-substituted borylation was not successful under the same condition. Treating Chl3Br and Chl13Br with HBpin only gave the debrominated product. Iridium-catalysed C-H borylation was also attempted in order to functionalise Chl10Mes, but did not yield any expected product.

![Scheme II-4](image-url)

Chl_{15}^{Bpin} underwent Suzuki coupling smoothly with Chl_{3}^{Br} and Chl_{13}^{Br}, affording the $\beta$-meso linked dimers Chl_{2,15} and Chl_{13,15} in moderate isolated yields, 52% and 32% respectively.

Scheme II-5. Synthesis of $\beta$-meso linked chlorin dimers.

Preparation of meso-meso linked dimer was more challenging, and initially gave less than 5% of the expected product along with a large amount of de-brominated and de-borylated compounds. In the hetero-coupling of Chl_{10}^{Ph15}^{Bpin} with Chl_{10}^{Mes15}^{Br} and Chl_{10}^{PhNO215}^{Br}, the homo-dimer Chl_{15}^{Ph15}^{Ph} was isolated, which is ascribed to the slow formation of the C_{15}-C_{15} bond because of the steric hindrance of the four methyl groups. Further optimisation with increased reaction concentration resulted in 32% of isolated yield for Chl_{15,15}, whilst varying the base (K_{2}CO_{3} and K_{3}PO_{4}) or the Pd source [Pd(Ph)_{2}Cl_{2} and Pd_{2}(dba)_{3}] did not yield any obvious improvement. The hetero-dimers Chl_{15}^{Ph,15}^{Mes} and Chl_{15}^{Ph,10}^{PhNO2} were also obtained under these optimised conditions in modest yields.
Metallated chlorin dimers were also prepared. Exposure to a 10-fold excess of Zn(OAc)$_2$ in CHCl$_3$ and MeOH at r.t. gave quantitative conversion of Chl$_{23,15}$ to bis-Zn-chelate Chl$_{23,15}$-Zn$_2$. Microwave heating Chl$_{215,15}$ with a large excess of Pd(acac)$_2$ in pyridine afforded the Pd chelate Chl$_{215,15}$-Pd$_2$. We tried to prepare Chl$_{23Zn,15}$ through mono-zincation of Chl$_{23,15}$ or Suzuki coupling of Chl$_{15Br}$ and Chl$_{3 Br}$ Zn, neither of which was successful.

2.3.2 NMR characterisation

The NMR spectra were in accordance with the expected chlorin dimer structures. It is interesting to note the shielding of CH$_3$ and CH$_2$ resonances due to the chlorin ring current in the $^1$H NMR spectra. In meso-meso dimer Chl$_{15,15}$, these signals were found at 1.82-1.85 ppm and 3.80-3.82 ppm respectively, significantly upfield shifted from those in the monomeric analogue Chl$_{15Ph}$(2.06 and 4.84 ppm, respectively). The effect is less obvious for the resonances of the β-meso linked dimer.
Scheme II-7. Atropisomerisation of chlorin dimers.

Directly linked bis-porphyrins are axially chiral, and have previously been separated with chiral HPLC.\textsuperscript{[62]} Chl$_{15,15}$ was expected to be as stable as its porphyrin analogues. Variable temperature NMR was employed to evaluate the interconversion of the atropisomers of Chl$_{13,15}$ and Chl$_{15,15}$ upon heating. The slight differences in the signals were explained by the worsened shimming at high temperature. The less sterically hindered $\beta$-meso linked dimer Chl$_{3,15}$ seemed to rotate to some extent at increased temperature. However, only small changes of the CH$_2$ ABq-signal ($\Delta\delta = -0.02$ ppm) were observed upon heating to 90 °C. The lack of coalescence of these proton signals indicated that there is no racemisation at the coupling temperature. Thus asymmetric synthesis of enantiopure chlorin dimers may be possible with chiral ligand.

Figure II-5. The CH$_2$ ABq-signal of chlorin dimers at r.t. and at 90 °C in toluene-$d_8$.

2.3.3 Photophysical characterisation

The UV-Vis absorption spectra were recorded in CH$_2$Cl$_2$, and the data are summarised in Table II-3. The absorption spectra of the dimers were similar to that of the monomers. Significant changes were observed, even though they were small.
Table II-3. Photophysical properties of dimers and reference compounds.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{Soret}}, \lambda_Q$</th>
<th>$I_B/I_Q$</th>
<th>$\lambda_{\text{em}} (\lambda_{\text{exc}})$</th>
<th>$\Phi^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chl$_{23,15}$</td>
<td>391, 413, 642</td>
<td>2.1</td>
<td>646</td>
<td>0.19</td>
</tr>
<tr>
<td>Chl$_{213,15}$</td>
<td>392, 413, 642</td>
<td>2.0</td>
<td>645</td>
<td>0.16</td>
</tr>
<tr>
<td>Chl$_{215,15}$</td>
<td>413, 645</td>
<td>2.6</td>
<td>648</td>
<td>0.255</td>
</tr>
<tr>
<td>Chl$_{23,15}$-Zn$_2$</td>
<td>401, 615</td>
<td>2.6</td>
<td>619</td>
<td>0.11</td>
</tr>
<tr>
<td>Chl$_{215}^{\text{Ph}},15^{\text{Mes}}$</td>
<td>410, 421, 648</td>
<td>2.6</td>
<td>652</td>
<td>0.39</td>
</tr>
<tr>
<td>Chl$_{215}^{\text{Ph}},15^{\text{PhNO}_2}$</td>
<td>420, 650</td>
<td>2.9</td>
<td>654</td>
<td>n.d.</td>
</tr>
<tr>
<td>Chl$_{215}^{\text{Ph}},15^{\text{Ph}}$</td>
<td>411, 421, 649</td>
<td>2.9</td>
<td>653</td>
<td>0.28</td>
</tr>
<tr>
<td>Chl</td>
<td>389, 634\textsuperscript{d}</td>
<td>2.4\textsuperscript{d}</td>
<td>636\textsuperscript{d}</td>
<td>0.19\textsuperscript{d}</td>
</tr>
<tr>
<td>Chl$_{15}^{\text{Ph}}$-Pd\textsuperscript{b}</td>
<td>391, 587</td>
<td>1.9</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Chl$_{215,15}$-Pd$_2$\textsuperscript{b}</td>
<td>401, 601</td>
<td>1.5</td>
<td>608</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

\textsuperscript{a} In CH$_2$Cl$_2$. \textsuperscript{b} In THF. \textsuperscript{c} Using tetraphenyporphyrin in toluene as reference.\textsuperscript{[57]} \textsuperscript{d} From reference,\textsuperscript{[8b]} measured in toluene.

As shown in Fig II-6, Soret bands were split in both meso-meso and $\beta$-meso bis-chlorins. The split of the B-band was more significant in the $\beta$-meso linked bis-chlorins (Chl$_{23,15}$), than in the meso-meso linked Chl$_{215,15}$. The splits were ~10 nm in 10-substituted $\beta$-meso bis-chlorins, and up to 22 nm for the sparsely substituted chlorin dimer Chl$_{23,15}$. The $Q_y$ bands were slightly bathochromically shifted (8-11 nm) compared to the reference Chl. It is in line with the aryl substituent effect at C-15 postion. (Chl$_{15}^{\text{Ph}}$, 4 nm red-shift). The lower ratio of the intensity of the Soret band and the $Q_y$ band ($I_B/I_Q$) in the dimers than in the monomers (2.0-2.9 vs 2.4-5.6) suggests chlorin dimers have more relatively intense red absorption than the monomers. $\beta$-meso bis-chlorins have lower $I_B/I_Q$, i.e. stronger $Q_y$ bands compared to their Soret bands than their meso-meso analogues (2.6-2.9). Small Stokes shifts (3-4 nm) were seen in all dimers, as in the monomers. The fluorescence quantum yields of the meso-meso dimers (0.26-0.29) are a bit higher than those of the monomers (0.19), while it is almost the same in the monomers as in the $\beta$-meso dimers (0.16-0.19).
Both metallation with Zn$^{II}$ and Pd$^{II}$ caused the Q$_y$ bands to blue-shift. For the Pd-chelate, the phosphorescence was recorded at 77 K with excitation at 391 nm. Chl$_{15}$Ph-Pd was used as the reference compound. Compared to Chl$_{15}$Ph-Pd, which emits at 762 nm, the phosphorescence of Chl$_{15,15}$-Pd$_2$ has an emission maximum at 774 nm (Fig. II-7). The triplet lifetime of Chl$_{15,15}$-Pd$_2$ was 358 µs, comparable to that of Chl$_{15}$Ph-Pd (406 µs). The small difference implied that the dimerisation has limited effect of chlorin triplet state.

## 2.3 Electrochemical characterisation

Cyclic voltammetry measurements were performed to study the redox properties of chlorin dimers. Both β-meso and meso-meso linked free base dimers showed two reversible reduction peaks, in contrast to only one in the reference monomer Chl$_{15}$Ph. One irreversible oxidation peak was also seen.
As summarised in Table II-4, the dimerisation caused a slight shift of the first oxidation and reduction potentials in meso-meso dimer. Little effect was seen in β-meso dimerisation.

### 2.4 Conclusion

β- and meso-substituted chlorins with furans and thiophenes were prepared by Suzuki coupling of bromochlorins with the corresponding furyl or thienyl boronic acid, or from de novo synthesis with prefunctionalised Eastern Half or Western Half. Their red-shifted absorption and emission spectra relative to parent chlorins show that these small aromatic heterocycles are promising auxochromes, comparable to established ones. It is interesting to note that an increase in Stokes shift was observed in thienyl chlorins compared to the analogous furan substituted ones. This is tentatively assigned to the higher planarity of thienylchlorin in the excited state. Moreover, the heterocycles can be employed to extend the π-conjugation for further modification with their formyl handle to exploit lower wavelength solar energy.

A series of directly linked chlorin dimers were prepared through regio-specific Suzuki coupling reactions, including β-meso homodimers and meso-meso linked hetero-and homodimers with different substituents and metallation states. The dimerisation resulted in red shifted absorption and emission spectra. The photophysical properties depend on the linker position. β-meso dimers had stronger red absorption than meso-meso ones. Small differences were observed even between the 3,15-dimer and the 13,15-dimer. The extended strong red absorption of chlorin dimers can utilise a larger photon flux of solar energy, making them more interesting as light harvesting materials.
Chlorin polymers were accessed from both electrochemical and chemical polymerisation. Different peripheral substitution patterns resulted in dramatically different deposition efficiency and electrochemical properties of the chlorin film products. The 3,13-\textit{bis}-thienylchlorin copolymerised with hexylthiophene resulted in an organic soluble polymer. The chlorin polymers from both polymerisations have absorptions extended beyond 700 nm, while the soluble one is also strongly fluorescent. These materials have the potential to be used as panchromic light-harvesting antennae.
3. Synthesis and characterisation of chlorin-lanthanides dyads (Papers III & IV)

Chlorin-based dyads have been extensively investigated as light harvesting architectures. Various chlorin-organic fluorophore dyads, such as chlorin-porphyrin dyads, chlorin-bacteriochlorin dyads and chlorin-BODIPY dyads have been prepared to interrogate the energy transfer pathway in photosynthesis or explore their capacities for bio-imaging due to their red absorption and NIR emission.

Compared to organic fluorophores, lanthanide emissions are long-lived (up to ms) and the positions of their emission bands are insensitive to the environment. Since the emission originates from forbidden f-f transition, the excitation requires energy transfer from light harvesting antennae. Porphyrins are good antennae to sensitise NIR emitting lanthanides, due to their lower energy levels of the triplet states. Since porphyrins were employed by Horrocks and Gouterman to sensitise Yb emission, a lot of porphyrins have been exploited to sensitise and/or coordinate NIR lanthanide ions.

Chlorins with similar low-lying triplet state (10400–11700 cm\(^{-1}\)) to porphyrins are also promising chromophores to sensitise Nd and Yb, which have excited states at \(\sim11400\) cm\(^{-1}\) (\(^4\)F\(_{3/2}\)) and \(\sim10200\) cm\(^{-1}\) (\(^2\)F\(_{5/2}\)) respectively. With a reduced pyrrolic ring, chlorins photophysical properties are more characteristic than porphyrins, i.e., narrow absorption and tunable Qy bands. These properties could be valuable for applications requiring excitation-based discrimination between multiple species.

Very few chlorin-Ln dyads are available, except a ternary Yb-chlorophyll complex reported by Tamiaki’s group. One possible reason is that chlorin synthesis is more demanding than porphyrins. Ln\(^{III}\) ions can be directly linked to the chlorin macrocycle sandwich structures as seen in Ln-porphyrin dyads. However Ln coordination with chlorins is very challenging, an alternative way to prepare chlorin-Ln dyads is to graft chlorins or chlorin derivatives into known Ln coordination complexes. The lack of accessible chlorins (derivatives) for conjugations with Ln\(^{III}\) complexes greatly limited the preparation of these dyads.

Another challenge is the demanding lanthanide coordination environment. The coordination number of trivalent lanthanide ions is usually 8 or 9 in solution. Ln\(^{III}\) ions require a stable and saturated coordination sphere to minimise luminescence quenching. Polydentate ligands are commonly
used to bind Ln$^{III}$ ions in luminescent Ln probes. A successful approach is to install pendant arms into a small macrocycle, such as 1,4,7,10-tetraazacyclododecane (cyclen).$^{[69]}$ Another well described ligand to chelate Ln$^{III}$ ions is dipicolinic acid, which provides a 3:1 complex with Lns.$^{[70]}$ Porphyins, as cryptands, have been reported to coordinate Ln$^{III}$ ions, as mentioned above.

In this chapter, we adopted cyclen and DPA to coordinate lanthanides. Two series of Ln-chlorin complexes were designed and synthesised to study their photophysical properties. First, cyclen-coordinated lanthanides were connected to the \textit{meso}-position of chlorins through different linkers. The properties of the linker and chlorin metallation state were varied for further investigation of sensitization efficiency. In the second type, 3:1 homoleptic and 1:2:1 heteroleptic Ln complexes with DPA as coordination chelates were prepared. Both \textit{meso}- and β-positions in chlorins were used for attachment to lanthanide complexes. For both types of chlorin-Ln dyads, a detailed photophysical study of the dyads and the chlorin ligands were conducted.

\begin{center}
\textbf{Chart III-1.} Two types of chlorin-Ln dyads.
\end{center}
3.1 Cyclen-based Ln-chlorin dyads

3.1.1 Synthesis of cyclen-based Ln-chlorin dyads

The cyclen-based Ln-chlorin dyads were prepared with two different linkers, amides or triazoles. For the amide bond linked dyads, the starting point is a prefunctionalised amine-bearing cyclen (III-1), which was coupled to chlorin carboxylic acid. Ln metallation was the final step. The triazole is forged through Cu catalysed azide-alkyne cycloadditions (CuAAC) of Ln-cyclen complexes (Chart III-2) with complementary chlorins.

![Chart III-2. Cyclen derivatives and cyclen-based Ln complex building blocks.](image)

Initially, we followed a reported procedure[^44] to synthesise chlorin carboxylic acid for the coupling with the lanthanide-binding DO3A. Starting from t-butyl ester, III-4, demetallation with p-TsOH gave free base chlorin, followed by metallation with Pd\(\text{II}\), Ni\(\text{II}\) and Cu\(\text{II}\). Microwave heating[^71] with Pd(acac)$_2$ and Ni(OAc)$_2$$\cdot$4H$_2$O in pyridine afforded III-6Pd and III-6Ni respectively. Cupration is much more straightforward with Cu(OAc)$_2$, and was successful at ambient temperature. Deprotection of t-butyl ester with TFA/CH$_2$Cl$_2$ (even as little as 10% of TFA in CH$_2$Cl$_2$) resulted in a color change. UV-Vis spectrometry indicated demetallation of these chlorins, which was quite surprising. These metallated chorins were expected to be stable to moderately acidic conditions since the reported demetallation[^72] of these metal chelates of chlorins were conducted under harsher conditions such as heating in concentrated H$_2$SO$_4$/TFA.
Therefore, another way to cleave $t$-butyl esters was necessary. Thermolysis of III-6Ni was successful. This observation was suggested by the lack of color change in the reaction mixture, which indicated that the metal chelate was intact. Unfortunately, this approach did not work for the Pd and Cu analogues. However the carboxylic acid III-7 was robust under the metallating conditions, even under microwave irradiation. The cuprated chlorin III-8Cu was formed readily after 5 min stirring at room temperature, while the Ni and Pd complexation required microwave heating. Palladation required more demanding conditions, i.e. a 20-fold excess of Pd(acac)$_2$ and extended time of heating. Once the reaction was complete, the purification was straightforward via normal silica gel column chromatography giving the products in 83–85% yield.

Scheme III-1. Synthesis of metallated chlorin carboxylic acids.

After access of the chlorin acids, HATU mediated amide formation was employed to incorporate the chlorins into the cyclen-based lanthanides. The coupling products were isolated in good to excellent yields (65%–93%). In amino-functionalised cyclen, methyl esters were used instead of t-butyl esters, since the metalated chlorins would not survive the acidic deprotection of t-butyl esters. However, the hydrolysis of methyl esters turned out to be extremely difficult. Deprotection with 4 equiv. of NaOH upon heating at 60 °C was difficult to follow. RP-HPLC analysis and the crude $^1$H NMR spectrum indicated the presence of starting material and a couple of new species, after heating for a week. Thermolysis of III-9Ni-tBu with microwave heating at 225 °C in pyridine did not afford the triacid III-10Ni as expected, instead resulted in a large extent of decomposition.

Eventually, a single compound was obtained in all cases after treatment with a large excess of LiOH (10 eq.) and KOH (10 eq.), although the isolated yields were poor (20-26%). We were not able to characterise III-10Pd, III-10Ni and II-10Cu unambiguously by NMR spectroscopy due to the small quantities obtained and because II-10Cu was paramagnetic. Nevertheless, we managed to characterise them in an alternative way. III-10Cu was prepared separately from II-10 by treatment with 1 equiv. Cu(OAc)$_2$-H$_2$O, which resulted in an immediate color change. UV-Vis absorption spectrometry confirmed the cupration with the characteristic Q-band of Cu-chlorin ($\lambda_{\text{max}} = 596$ nm) and the Q-band of free base chlorin III-10 ($\lambda_{\text{max}} = 632$ nm).
disappeared instantaneously. This sample of III-10Cu was used as a reference for the RP-HPLC analysis of the hydrolysis of III-9Pd, III-9Ni and III-9Cu.

The lanthanide complexations were performed according to reported conditions,[73] i.e. treatment of the ligands with the corresponding LnCl₃ salts in refluxing MeOH. III-11NiLn precipitated out within minutes, however, III-11PdLn was quite apolar, and could be extracted with organic solvents during purification. Although III-11NiLn (minutes) and III-11PdLn (hours) were formed rapidly, the formation of III-11Ln and III-11CuLn progressed slowly, with only approximately 50% conversion after days, as shown by HPLC.

Besides the amide bond linker, chorins-Ln complexes were also prepared through CuAAC to study the effect of the linker length and rigidity. Synthesis of azide- and alkyne-functionalised chlorins is shown in Scheme III-3. Azido and alkynyl functional groups were installed into benzaldehydes respectively, which were used in Lindsey’s Eastern Half synthesis.[72b] Then condensation with western Half I-9 afforded the expected chlorins.[17]


Scheme III-5. CuAAC of alkynylchlorins and alkyne-bearing Ln-DO3A complexes.
Chlorins III-15a, b and d underwent CuAAC smoothly with complementary Ln complexes III-2Ln or III-3Ln to give the dyads with CuOAc/NaAsc as the Cu(I) source, with TBTA as ligand in DMSO.\(^{[74]}\) The reaction between III-15c and III-2Ln was not successful under either these conditions or those previously reported (CuI, piperidine/CH\(_3\)CN, \(\mu\)w)\(^{[75]}\) only returning starting materials. For efficient cyclisation, it is important to get a homogeneous solution. The purification of the products was straightforward. The residue obtained after removing solvent, was dissolved in methanol, and precipitated with diethyl ether. The dark green precipitate was separated by centrifugation. The procedure was repeated until a pure solid was obtained as shown by RP-HPLC.

3.1.2 Photophysical characterisation

All the chlorin-Ln dyads were subjected to photophysical characterisation with III-4–6 as the reference compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\lambda^B_{\text{max}}/\text{nm})</th>
<th>(\lambda^Q_{\text{max}}/\text{nm})</th>
<th>(I_B/I_Q^a)</th>
<th>(\Phi^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>III-5(2H)</td>
<td>408</td>
<td>632</td>
<td>3.9</td>
<td>0.23</td>
</tr>
<tr>
<td>III-6Ni</td>
<td>395</td>
<td>595</td>
<td>3.3</td>
<td>-</td>
</tr>
<tr>
<td>III-6Pd</td>
<td>390</td>
<td>583</td>
<td>2.5</td>
<td>0.05</td>
</tr>
<tr>
<td>III-4(Zn)</td>
<td>404</td>
<td>602</td>
<td>6.0</td>
<td>8.4</td>
</tr>
<tr>
<td>III-6Cu</td>
<td>397</td>
<td>596</td>
<td>5.4</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\)Calculated from the absorbance at a concentration of 1 \(\mu\)M. \(^b\)The quantum yields of these chlorins were calculated with TPP as reference.\(^{[57]}\)

As shown in Table III-1 and Fig III-1, metallation shifts the chlorins Q-bands dramatically to the blue region, from 632 nm (free base) to 583 nm (III-6Pd). The blue shifts of the B-bands are much smaller, from 408 nm to 390 nm. These hypsochromic shifts were consistent with the metallation effect of porphyrinoid compounds.\(^{19b}\) In addition, a slight increase of \(I_B/I_Q\) was observed in metallochlorins compared to the free base chlorin, in the order 2H \(\leq\) Ni \(<\) Pd \(<\) Zn \(<\) Cu.
The excitation and emission spectra of III-4–6 were recorded in methanol (Fig. III-2). The excitation spectra overlapped with the absorption spectra well. Free base chlorin III-5 and II-4 (Zn) were emissive, while III-6Ni and III-6Pd had week emission. The emission band of the Ni chlorin was broadened significantly, due to its low emission requiring high apertures of monochromators. This also precluded the accurate quantum yield measuring of Ni chlorin. It was expected that III-6Pd would have a low quantum yield because of the increased intersystem crossing. It is known that Cu quenches chlorin fluorescence, thus yielding a non-emissive III-6Cu. These small Stokes shifts and quantum yields are typical for both metallated and free base chlorin.\cite{8b}
Phosphorescence was recorded in frozen methanol at 77 K. The phosphorescence maximum of III-6Pd was observed at 762 nm. Its lifetime was 365 µs according to a monoexponential fit of the phosphorescent decay. This is in line with the low fluorescence quantum yield of palladated chlorin, since Pd would increase the intersystem crossing rate as it is a heavy atom. We were unable to observe the phosphorescence spectra of the other chlorins. This is limited by our instrument setup since their phosphorescence emission is more to the NIR.
After incorporation of chlorins to Ln-cyclen complexes, these Ln-chlorin dyads are no longer fully soluble either in water or organic solvents. Though the concentrations are not reliable, the absorption differences were highlighted in the normalised absorbances, which were recorded with their saturated solutions in water.
As shown in Fig III-4, Q-bands were similar for all of these dyads with different Ln ions and different linkers ($\lambda_{\text{max}} = 609$ nm), due to the same Zn-chlorin motif. The Soret bands varied a lot. **III-16Yb** showed similar B-band to the reference chlorin ($\lambda_{\text{max}} = 409$ nm). However, the complexes with the reversed type of linker presented a big difference. **III-18Nd** and **III-18Gd** displayed the maxima of the B-band at 349 nm, with a small shoulder at 409 nm. The **III-18Yb** spectrum consisted of a normal band around 409 nm and a broad band ($\lambda_{\text{max}} = 349$ nm) with somewhat lower intensity. These differences in absorption were probably explained by various aggregations of the complexes in solution, due to their poor solubilities. This was also indicated by the broadened and red-shifted bands. Therefore, the first type of linker could limit the aggregation to some extent.

![Figure III-5. Emission (dashed line) and excitation (solid line) spectra of triazole-linked complexes.](image)

These Zn-chlorin-Ln complexes displayed similar emission ($\lambda_{\text{max}} = 610$ nm) and excitation ($\lambda_{\text{max}} = 395$ nm) spectra to the chlorin reference. These spectra seemed to be less influenced by the aggregation regardless of the linker type and Ln$^{ll}$ ions (Fig. III-5). The quantum yields were calculated with TPP as reference. The values were 0.5% for **III-18Gd** and **III-18Yb** and 0.23% for **III-18Nd**. While **III-16Yb** was the lowest, 0.08%, behaving once more differently to others. It is ambiguous if the low quantum yield was correlated to the energy transfer to Ln due to the lack of evidence, since we were not able to record the NIR emission with our setup.
At last, we attempted to record the Ln emission of $\text{III-11Ln}$, $\text{III-11PdLn}$ and $\text{III-11NiLn}$ with the available setup. Unfortunately, we did not see the characteristic peaks of Yb (980 nm) and Nd (1064 nm), even in deuterated solvents and deoxygenated solutions. Although Yb and Nd sensitization by chlorins were reported in our previous work\textsuperscript{42}, the NIR emissions were excited by laser and were faint, which indicated the NIR emission was extremely weak.

### 3.2 DPA-linked Ln-chlorin dyads

The classic DPA framework is well adapted to coordinate Ln ions and provides 3:1 complexes.\textsuperscript{76} The full occupancy of Ln coordination sites excludes H$_2$O molecules, diminishing quenching by O-H oscillators. Besides, DPA-Ln complexes lack of C-H oscillators, unlike cyclen-Ln ones. These oscillators are detrimental to Ln luminescence,\textsuperscript{50} therefore DPA bound Ln-chlorin dyads are expected to afford better luminescent properties. Apart from being a chelating ligand, DPA is also a good chromophore.\textsuperscript{49} As mentioned above, chlorin photophysical properties are tunable with auxochromic substituents. Different substitution patterns of DPA in chlorins will vary the excited state levels of chlorins.

Another important issue to take into account was the solubility. The Ln-cyclen-chlorin complexes have poor the solubilities. This is presumably due to the hydrophobicities of chlorins. Dipicolinic acid is polar and water-soluble. Substituting chlorins with DPA would increase chlorins solubilities, and introduce negative charge to the chlorin-Ln dyads.

The third consideration was the linker length. Ln sensitization, through triplet state or singlet state, depends on the distance between Ln and the antenna.\textsuperscript{77} Ln-cyclen complexes were linked to the chlorin through either an amide bond or a triazole. The linkers are rather long, although the complexes might fold up to shorten the actual distance in solution. Excitation spectra were not recorded, so the sensitization process was ambiguous. In order to get higher energy transfer efficiency, the linker was shortened to the minimum, i.e. DPA directly linked to the chlorin.

#### 3.2.1 Ligand Synthesis

Initially, the 10-substituted DPA-chlorin was designed and we attempted its synthesis. Following Lindsey’s method,\textsuperscript{11a} meso-substituted Estern Half was required.

Starting from the dimethyl ester of dipicolinic acid, Fenton reaction afforded the carbinol III-21 in low yield.\(^{[78]}\) After PCC oxidation, the aldehyde III-22 was obtained, which was reacted with pyrrole to give meso-DPA substituted dipyrromethane III-23 in good yields. Vilsmeier reaction at 0 °C successfully installed one formyl group into the pyrrole ring.

Scheme III-7. Synthetic attempt of 10-DPA chlorin.

The bromination of formyldipyrromethane was straightforward. Treatment of III-24 with NBS in THF at -78 °C gave quantitative conversion by TLC. However the chlorin formation was unsuccessful under standard conditions, presumably due to the pyridine moiety. This route was then discontinued.
Instead of 10-DPA chlorin, another meso-substituted DPA-chlorin Chl15^{DPAMe} was synthesised, as shown in Scheme III-8. Suzuki coupling of bromochlorin Chl15^{Br} and DPA-Bpin offered the desired DPA-chlorin in moderate yield. Hydrolysis of the ester with 3 equiv. of NaOH (0.22 M) in THF was quantitative. β-substituted DPA-chlorin Chl3^{DPAMe} was prepared from Chl3^{Br} under similar conditions.

In addition to substituent patterns, the metallation states also play significant roles in chlorin photophysical properties. Pd chlorins have efficient populated triplet states. This is an advantage for Ln sensitisation, since the triplet state of the antennae is often important in the energy transfer process. Thus, the Pd chelates of chlorins Chl3^{DPAMe-Pd} and Chl15^{DPAMe-Pd} were also prepared, under similar microwave conditions. The solvent was changed from pyridine to benzonitrile. In pyridine, the DPA-chlorin underwent extensive decomposition, resulting in tedious purification. This may be assigned to the various extent of hydrolysis of dimethylester. In benzonitrile, full conversion was achieved with convenient chromatographic purification.
as a result. The hydrolysis of these palladated chlorins proceeded smoothly to furnish the ligands \textbf{Chl}_3^{\text{DPA}}\text{-Pd} and \textbf{Chl}_{15}^{\text{DPA}}\text{-Pd}.

Scheme III-10. Synthesis of 3-acetylated DPA-chlorins.

The acetyl group is a well-known chlorin auxochrome. To further tune the excited energy levels of chlorins, 3-Ac chlorin was built by Stille coupling according to reported procedures.\cite{25} \textbf{III-3Ac15Br}, was obtained by acidic bromination with NBS. \textbf{Chl}_3^{\text{Ac}}_{15}\text{FB-Me} and \textbf{Chl}_3^{\text{Ac}}_{15}\text{Pd-Me} were prepared through the same synthetic route described for \textbf{Chl}_{15}^{\text{Br}}. The latter had a limited solubility, thus we were not able to perform its hydrolysis under our standard conditions.
3.2.2 Chlorin-Ln complex preparation

Homoleptic complexes were prepared by treatment of chlorin-DPA ligands with stoichiometric LnCl$_3$ solutions (3:1)[70] The formation of the complexes was confirmed by observation of characteristic NIR Ln luminescence (vide infra).

Homoleptic complexes were prepared by treatment of chlorin-DPA ligands with stoichiometric LnCl$_3$ solutions (3:1). The formation of the complexes was confirmed by observation of characteristic NIR Ln luminescence (vide infra).


Heteroleptic complexes were formed by mixing Ln(DPA)$_2$ with corresponding chlorin ligands (1:1). Ln(DPA)$_2$ were synthesised through reported procedure,[79] shown in Scheme III-12.

Scheme III-12. Preparation of heteroleptic chlorin-Ln dyads.
3.2.3 Photophysical characterisation

The chlorin ligands and Ln-chlorin dyads were subject to photophysical measurements. The mechanism of chlorin sensitising NIR luminescence of Ln ions was also investigated. Finally, the photostability of the Ln-chlorin dyads was studied.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_B$ (nm)</th>
<th>$I_B/I_Q$</th>
<th>$\lambda_Q$ (nm)</th>
<th>$\lambda_{em}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chl$_3^{DPA}$</td>
<td>404</td>
<td>2.76</td>
<td>644</td>
<td>651</td>
</tr>
<tr>
<td>Chl$_3^{DPA}$-Pd</td>
<td>390</td>
<td>1.74</td>
<td>600</td>
<td>613</td>
</tr>
<tr>
<td>Chl$_{15}^{DPA}$</td>
<td>393</td>
<td>3.25</td>
<td>639</td>
<td>639</td>
</tr>
<tr>
<td>Chl$_{15}^{DPA}$-Pd</td>
<td>391</td>
<td>1.69</td>
<td>589</td>
<td>596</td>
</tr>
<tr>
<td>Chl$_3^{Ac15}^{DPA}$</td>
<td>414</td>
<td>2.30</td>
<td>665</td>
<td>672</td>
</tr>
</tbody>
</table>

The absorption and emission spectra of the chlorin ligands were recorded in THF and H$_2$O, and the data are summarised in Table III-2. DPA in the 3- and 15-positions resulted in red-shifted Q$_y$ bands compared to unsubstituted free base chlorin ($\lambda_{max} = 634$ nm in toluene). The red shift of the Q$_y$ bands was larger in 3-substitution (10 nm) than that in 15-substituted compounds (5 nm). A 3-acetyl substitution of free base chorin ($\text{Chl}_3^{Ac15}^{DPA}$) extended the red absorption up to 665 nm. Considerable blue shifts (44-50 nm) were observed after palladation in these DPA-based chlorins. The metallated species had stronger Q$_y$ bands relative to the Soret bands than in the free base chlorins (Fig III-6). These observations are typical of chlorins as discussed before. The emission spectra of these chlorins were recorded by excitation into the corresponding Soret bands. The palladated chlorins had much weaker fluorescence emission than the free base ones. The normalised emission spectra are shown in Fig. III-6.
After complexation with Ln$^{III}$ ions, the absorption of the chlorins did not change. Only slight differences of absorbance were found in the dyads with the same chlorin ligand and different Ln ions. A dramatic decrease in the
fluorescence emission intensity of chlorins were seen when comparing the emission of \( \text{Gd(Chl}_3^{\text{DPA}}) \) and \( \text{Nd(Chl}_3^{\text{DPA}}) \) or \( \text{Yb(Chl}_3^{\text{DPA}}) \), specifically 29% and 40%, respectively. The emission spectra were recorded by excitation at 411 nm where all three dyads have almost same absorbance [0.65 for \( \text{Gd(Chl}_3^{\text{DPA}}) \) and \( \text{Yb(Chl}_3^{\text{DPA}}) \), 0.66 for \( \text{Nd(Chl}_3^{\text{DPA}}) \)]. The fluorescence intensity decrease in the Nd complex may be a result of energy transfer from the singlet state of the chlorin to the Nd\textsuperscript{III} ion. This is because Nd\textsuperscript{III} ion has several non-emissive states, some of which have energy overlap to the chlorin excited singlet state. The decrease in Yb complex is different since Yb\textsuperscript{III} ion has only one excited state, which is in energy way below the chlorin excited singlet state. The decrease of emission intensity in Yb complex can be rationalised by an electron exchange mechanism between the chlorin excited singlet state and the Yb\textsuperscript{III} ion. Yb\textsuperscript{III} ion was first reduced by the excited chlorin to generate a chlorin radical cation and an Yb\textsuperscript{II} ion, and then may be reformed by a back electron transfer from the Yb\textsuperscript{II} ion to the chlorin.\textsuperscript{[80]}

![Fluorescence emission spectra of Gd(Chl3\textsuperscript{DPA})3, Nd(Chl3\textsuperscript{DPA})3 and Yb(Chl3\textsuperscript{DPA})3 in THF and H2O (\( \lambda_{\text{ex}} = 411 \text{ nm} \)).](image)

The NIR emission and excitation spectra are shown in Fig III-8. The characteristic bands of Yb (~980 nm) and Nd (~880 nm and 1060 nm) were clearly observed in all dyads upon excitation into the Qy bands of chlorins. The excitation spectra resembled the corresponding chlorin absorption spectra very
well. One chlorin ligand can sensitise Yb and Nd ions simultaneously in the solution after mixing two dyads [Nd(Chl15^DPA-Pd)_3 and Yb(DPA)_2Chl15^DPA-Pd]. The emission spectrum is an overlay of an Yb spectrum and a Nd spectrum. One Ln ion can be sensitised by two chlorin ligands (Chl15^DPA and Chl15^DPA-Pd). This is unambiguously indicated by the excitation spectra, which is a superimposition of the separate excitation spectra of the two component dyads.

![Excitation and Emission Spectra](image)

**Figure III-8.** NIR emission and excitation spectra of Ln-chlorin dyads in THF and H_2O. Emission spectra were recorded with excitation into the Q band of corresponding chlorin ligands (λ_ex = 640 nm for Chl15^DPA and λ_ex = 590 nm for Chl15^DPA-Pd). Excitation spectra were recorded with emission at 980 nm for Yb and at 1060 nm for Nd.

Finally, the photostabilities of two Ln-chlorin dyads were measured with cyanine dye (DTDCI) as the reference compound. The red emissions were compared after 10 min of irradiation at the corresponding absorption maxima [390 nm for Nd(Chl15^DPA-Pd)_3 and Yb(Chl15^DPA-Pd)_3, 649 nm for cyanine]. After 1 h, only marginal decrease of emission intensity (17% and 20% respectively) were observed in Nd(Chl15^DPA-Pd)_3 and Yb(Chl15^DPA-Pd)_3, while cyanine extensively decomposed (75%). These Ln-chlorin dyads were not substantially photolabile.
3.3 Conclusion

Two sets of Ln-chlorin dyads were prepared with cyclen derivatives or dipicolinic acids as coordinating chelates. Chlorins were linked to the Ln moiety through different linkers. The photophysical properties of these Ln-chlorin dyads were studied. The linkers were found to be pivotal to the photophysics in these Ln-chlorin dyads.

Cyclen-based Ln-chlorin complexes were poorly soluble in H₂O and/or CH₃OH. Lack of observable NIR Ln emission in these complexes was probably due to the significant aggregation in solution. Incorporation of dipicolinic acid into Ln-chlorin dyads improved their solubilities dramatically. NIR emission of both Nd and Yb were observed in all DPA-based Ln-chlorin complexes upon excitation into the red absorption of chlorins. In addition, the singlet state was indicated to be involved in the energy transfer process in the Ln complexes with free base chlorins. Two-color NIR emission based on the same chlorin and two-color excitation based on the same Ln ion were also measured. With two chlorins and two Ln ions, multicomplex imaging with four colors would be possible.
4. Mild microwave-assisted synthesis of dipyrromethanes and their analogues (Paper V)

4.1 Introduction

_De novo_ chlorin synthesis relies on the condensation of two parts, either Western/Eastern Halves, or Northern/Southern Halves. Either approach has dipyrromethanes as essential building blocks. Dipyrromethane synthesis has been extensively studied, thus has facilitated chlorin synthesis.

Currently, dipyrromethane synthesis relies often on the acid-catalysed condensation of an aldehyde with pyrrole, or the acid-catalysed coupling of a pyrrole-2-carbinol with pyrrole. These procedures require an acid catalyst, which excludes acid sensitive substrates and limits their application. Furthermore, compounds with carbonyl groups are not compatible with these conditions. Protection with robust cyclic acetals might be an alternative way, but it entails extra protection and deprotection steps. Additional difficulties also exist, such as extensive side product formation (polymers and N-confused analogues) and tedious purifications. Other methods either are limited in scope or require harsh conditions (up to 24 h heating at 140 °C). Therefore, complementary synthetic methods to prepare dipyrromethanes are highly in demand for chlorins synthesis and other applications.

The electrophilicity of _N,N_-dimethylaminomethyl pyroles has been well-documented. The nucleophilicity of electron-rich pyroles, as indicated in the formation of porphyrins, are sufficient for this reaction. We proposed that substituting pyroles with _N,N_-dimethylaminomethyl pyroles would afford asymmetric dipyrromethanes without an acidic catalyst.
4.2 Synthesis

Starting from pyrroles or indoles, the dipyrromethane could be acquired in a two-step reaction in moderate to excellent overall yields, in the absence of any catalyst. The intermediate IV-2 was prepared by the Mannich reaction. The corresponding substrates were treated with Eschenmoser’s salt at ambient temperature in a CH₂Cl₂ solution. The reaction could be followed by TLC analysis. The N,N-dimethylaminomethylated pyrroles were not stable, and decomposed on silica gel during our attempts of purification by chromatography. After washing with an aqueous NaHCO₃ solution, the crude products were used for the next step directly. A suspension of IV-2 in pyrrole was heated to 150 ºC in the microwave reactor to give IV-3. These reactions were clean, thus purification of the products was straightforward. Evaporation of the excess pyrrole, followed by silica gel column chromatography provided the pure dipyrromethanes as single regioisomers. The yields were in the range of 42–82%, comparable to those of acid-catalysed conditions. A series of differently functionalised dipyrromethanes and indolodipyrromethanes were obtained under the above conditions. The structures and the yields are shown in Table IV-1 and Table IV-2.

![Scheme IV-1. The synthesis of the dipyrromethanes.](image)

4.3 Discussion on successful reactions

Both electron-rich and electron-poor pyrroles reacted with Eschenmoser’s salt smoothly under the mild conditions, although the latter needed higher reaction temperatures, longer reaction times, or a higher excess of Eschenmoser’s salt. The Mannich reaction of pyrroles has a large tolerance of functional groups, including for silyl, ester and 3-formyl groups. Primary screening indicated that an electron-withdrawing group on the 2-position (CHO, CO₂Me) was not tolerated.

This reaction was readily applied to indoles, affording the 3-alkylated indoles. Even for the slightly sterically hindered 2-methyl indole IV-1k, the yield (89%) was excellent. Both electron-withdrawing and electron-donating groups were tolerated in the phenyl ring. As expected, the electron-poor indole IV-1j necessitated longer time (ca. 26 h) for complete conversion.
The Mannich reaction of both pyrroles and indoles has excellent regioslectivity. As mentioned above, indoles were alkylated at the C-3 position, while pyrroles were functionalised at the most nucleophilic $\alpha$-positions except for N-TIPS pyrrole (IV-1e). This is consistent with the previous report$^{[85]}$ that $\alpha$-positions could be shielded by an N-TIPS group. $\beta$-substitution gave an N-confused dipyrromethane, which is relevant to N-confused porphyrin synthesis.$^{[86]}$ Besides, both alkylation of IV-1d and IV-1f only afforded a single regioisomer, as opposed to the Vilsmeier-Haack formylation of those substrates, which usually afforded mixtures of C-2 and C-5 formylated products.

From $^1$H NMR, another product species was observed (singlet in the $\delta = 4.45–4.73$ ppm region), for substrates with a free NH. This was tentatively assigned as a bis-C$_n$N-alkylated compound. The putative assignment was further supported by the peak at $\delta = 64–70$ ppm in the $^{13}$C NMR spectra. These are in accordance with a $\text{NCH}_2\text{N}$ signal. In addition, a decrease of the intensity of the corresponding NH proton signal was also observed.
Table IV-1. Synthesis of dipyrromethanes IV-3a–g.

<table>
<thead>
<tr>
<th>Pyrrole</th>
<th>Mannich product</th>
<th>Dipyrromethane</th>
<th>Yield&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Pyrrole" /></td>
<td><img src="image" alt="Mannich product" /></td>
<td><img src="image" alt="Dipyrromethane" /></td>
<td>64%</td>
</tr>
<tr>
<td>IV-1a</td>
<td>IV-2a</td>
<td>IV-3a</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Pyrrole" /></td>
<td><img src="image" alt="Mannich product" /></td>
<td><img src="image" alt="Dipyrromethane" /></td>
<td>82%</td>
</tr>
<tr>
<td>IV-1b</td>
<td>IV-2b</td>
<td>IV-3b</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Pyrrole" /></td>
<td><img src="image" alt="Mannich product" /></td>
<td><img src="image" alt="Dipyrromethane" /></td>
<td>10-13%</td>
</tr>
<tr>
<td>IV-1c</td>
<td>IV-2c</td>
<td>IV-3c</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Pyrrole" /></td>
<td><img src="image" alt="Mannich product" /></td>
<td><img src="image" alt="Dipyrromethane" /></td>
<td>42%</td>
</tr>
<tr>
<td>IV-1d</td>
<td>IV-2d&lt;sup&gt;a&lt;/sup&gt;</td>
<td>IV-3d</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Pyrrole" /></td>
<td><img src="image" alt="Mannich product" /></td>
<td><img src="image" alt="Dipyrromethane" /></td>
<td>54%&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>IV-1e</td>
<td>IV-2e</td>
<td>IV-3e</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Pyrrole" /></td>
<td><img src="image" alt="Mannich product" /></td>
<td><img src="image" alt="Dipyrromethane" /></td>
<td>52%</td>
</tr>
<tr>
<td>IV-1f</td>
<td>IV-2f&lt;sup&gt;a,b&lt;/sup&gt;</td>
<td>IV-3f</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Pyrrole" /></td>
<td><img src="image" alt="Mannich product" /></td>
<td><img src="image" alt="Dipyrromethane" /></td>
<td>6%</td>
</tr>
<tr>
<td>IV-1g</td>
<td>IV-2g&lt;sup&gt;a,c&lt;/sup&gt;</td>
<td>IV-3g</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> In MeCN;  
<sup>b</sup> conditions: 6 equiv. of Eschenmoser’s salt;  
<sup>c</sup> At 60 °C;  
<sup>d</sup> Overall yield for isolated products over two steps;  
<sup>e</sup> Reaction was run at 180 °C.
Initial attempts to react crude compounds IV-2 with excess pyrrole in the presence of Lewis or Bronsted acids did not yield any product, either at r.t. or upon heating. Fortunately, the reaction proceeded smoothly upon microwave heating with pyrrole as solvent, even without any additives. Preliminary screening showed that irradiation at 120-150 °C for 30 min led to complete conversion of the starting material to the product. Lowering the reaction temperature either required longer reaction times or just returned the starting material. Higher temperatures resulted in decomposition, except for compound IV-1e, which required 180 °C for reaction completion. The indole analogues were reactive under standard conditions. These reactions are quite robust, and are insensitive to moisture or air.

Table IV-2. Synthesis of indolo-dipyrrromethanes IV-3h–k.

<table>
<thead>
<tr>
<th>Indole</th>
<th>Mannich product(^{a})</th>
<th>Yield(^{b})</th>
<th>Indolo-Dipyrrromethane</th>
<th>Yield(^{c})</th>
</tr>
</thead>
<tbody>
<tr>
<td>III-1h</td>
<td>III-2h</td>
<td>92% (7.7:1(^{c}))</td>
<td>III-3h</td>
<td>77%</td>
</tr>
<tr>
<td>III-1i</td>
<td>III-1i</td>
<td>82% (2.8:1(^{c}))</td>
<td>III-3i</td>
<td>80%</td>
</tr>
<tr>
<td>III-1j</td>
<td>III-2j</td>
<td>53% (3:1(^{c}))</td>
<td>III-3j</td>
<td>81%</td>
</tr>
<tr>
<td>III-1k</td>
<td>III-2k</td>
<td>89% (3.2:1(^{c}))</td>
<td>III-3k</td>
<td>40%</td>
</tr>
</tbody>
</table>

\(^{a}\) In MeCN with 1.2 equiv of Eschenmoser’s salt; \(^{b}\) Yield of crude product; \(^{c}\) Ratio of C- and N-alkylated compounds; \(^{d}\) Isolated yield from IV-2.

The purification of the dipyrrromethanes was straightforward. The N-alkylation seemed not to be a problem, since the N-alkyl group was cleaved under the reaction conditions, thus the same product was formed. There were
two exceptions, IV-3c and IV-3g. In the case of IV-3c, the precursor IV-2c was not stable in solution and seemed to decompose during aqueous washing. This complicated the purification of IV-3c so much that we were unable to get the pure compound. For the reaction of IV-3g, the intermediate IV-2g is formed in low yield, as indicated by the crude $^1$H NMR spectrum, and the impure IV-2g resulted in the formation of a lot of impurities along with crude IV-3g, which also diminished the isolated yield.

4.4 Discussion on the unsuccessful substrates

Besides the pyrroles and indoles, we also intended to adopt the Mannich reaction to other heterocycles, such as furan, thiophene and imidazole. Unfortunately, treating furan and 3-methylthiophene with Eschenmoser’s salt did not yield any promising products. The reaction of the latter resulted in a complex mixture, which did not furnish any thienyldipyrromethane after heating in pyrrole.

Imidazole (IV-1l) underwent smooth alkylation with Eschenmoser’s salt, but a large part of IV-2l was lost during aqueous workup due to its high aqueous solubility. Both $^1$H NMR spectroscopy and ESI-HRMS analysis indicated several alkylated species in crude IV-2l, which is not surprising. Under the standard conditions, IV-2l afforded the dipyrromethane IV-3a as the single product in 38% overall yield (57% from IV-2l). Thus, IV-2l behaved as a “bis-activated methylene”, which allowed double substitution with pyrrole (Scheme IV-2).

4.5 Conclusion

We developed a mild two-step synthesis to prepare dipyrromethanes, N-confused dipyrromethanes and their indole analogues. Our procedure requires shorter reaction times and simpler purifications than the reported ones. The method excludes acid activation, thus is suitable to incorporate acid sensitive substituents and a formyl group to the dipyrromethanes without tedious protection and deprotection steps.
A limit of this approach is the resistance of pyrroles with electron withdrawing substituents to the Mannich reaction. Further work is needed to address this weakness and facilitate synthesis of porphyrins and chlorins.
Chlorins have very characteristic photophysical properties, featuring narrow, intense and tunable red absorption and emission. These lay the foundation for light harvesting and fluorescence imaging. This thesis provided a valuable series of novel chlorins to complement available ones. We have not yet investigated their light harvesting in photosynthesis and NIR bio-imaging, further work would be needed to realise these aims.

For better light harvesting, panchromatic antennae are sought after. In the first part, we presented a series of novel chlorin monomers, dimers and polymers, with bathochromically shifted absorption (beyond 700 nm). Small heterocycles were found to be as good auxochromes as natural ones, i.e., formyl and vinyl groups. Borylated chlorins were first prepared, as powerful intermediates not only in chlorin dimerisation but also in other functionalisations. However, a β-β chlorin dimer could not be accessed, and polymerisation conditions require further optimisation. Hopefully, future work will enable these materials to be panchromatic and be applied to exploit lower solar energy in photosynthesis.

In the second part, chlorins were demonstrated to sensitise Ln luminescence. NIR emissions were not observed in cyclen-based Ln-chlorin dyads, due to their poor solubilities and aggregation in solution. It is beneficial to increase dyad solubilities to maximise their NIR emission. Ln emissions in all DPA-based Ln-chlorin complexes were recorded with increased solubilities. These dyads presented two-color Ln emission based on one chlorin excitation and two-color excitation based on one Ln emission. These work represent a significant step forward in multiplex imaging, enabling four-color NIR imaging. These are the first excitation spectra recorded for chlorin-appended NIR-emitting Ln complexes. The sensitisation mechanism is studied, but further work is required to interrogate the energy transfer process.

In addition, a microwave-assisted synthesis was described to prepare dipyrromethanes, a key intermediate in the chlorin synthesis. This method is mild, features a two-step reaction, and does not require acid activation as traditional approaches. A limit of this approach is the resistance of electron withdrawing substituents in pyrroles. Further work is needed to address this weakness and facilitate chlorins synthesis, in turn to provide interesting chlorins for light harvesting and bio-imaging.
Svensk sammanfattning

Tetrapyrrol är kärnstrukturen hos många naturprodukter. De har även benämns *livets pigment* då dessa färgade substanser spelar en oerhört viktig roll i människans liv. Hemgruppen och klorofyll är ur ett biologiskt perspektiv, två av de mest betydelsefulla exemplen av tetrapyrroler. Hemgruppen finns i röda blodkroppar och medverkar i syretransport medan klorofyll är involverad i fotosyntesen, där solljus utnyttjas för att omvandla koldioxid och vatten till kolhydrater och syrgas. (Figur 1)

![Första figur](image1.png)

*Figur 1.* Representation av tetrapyrroler i fotosyntesen och cellulär oxidation.

Klorofylls cykliska kärnstruktur kallas klorin (Figur 2) och fungerar som ljussamlande antenner i fotosyntesen. Medan Naturen använder sig av formyl och vinylgrupper för att finskjustera de fotofysiska egenskaperna hos kloriner, har forskningen under det senaste decenniet undersökt i stor omfattning diverse auxokromer bland annat ketoner, alkyner och estrar. Studier rörande naturliga och syntetiska klorofyller har gett oss värdefulla information om hur fotosyntesen fungerar samt drivit utvecklingen av nya klorofyll-analoger.

![Andra figur](image2.png)

*Figur 2.* Struktur och nomenklatur av klorofyll *b* och klorin
I denna avhandling rör design, framställning och utvärdering av nya klorinanaloga (monomerer, dimerer och polymerer). I den första delen av avhandlingen har en serie furan- och tiofensubstituerade kloriner studerats. Då storleken på dessa heterocykliska fem-ringar är tillräckligt liten, befinner de i samma plan som klorin (speciellt i β-positionen i den spektroskopiska axeln Q_y). Resultatet blir en förlängd π-konjugering och i samband med detta sker det ett rödskift i absorption- och emissionspektra. Vi spekulerar att dessa små aromatiska heterocykler är lika, om inte bättre än de andra auxokromerna som finns beskrivna i litteraturen.


I den andra delen av avhandlingen har fokuset ställt på konceptet att utnyttja kloriner för att fotosensibilisera lantanoider. Kloriner erhåller small fluorescencemission i det röda eller nära det infraröda (NIR) våglängdsområdet, vilket gör de till utmärkta kandidater för luminiserande prober samt fotosensibilisatorer i fotodynamisk terapi mot cancer. Vi har tagit fram och studerat de fotofysiska egenskaperna hos olika cyklen- respektive dipikolinsyraseverader klorin-lantanoidkomplex. Olika parametrar såsom metalens oxidations tillstånd, länkavståndet, länkpositionerna och lantanoidkelaterande ligander undersökes för att optimera de fotofysiska egenskaperna.

Till skillnad från de cyklenbaserade klorin-lantanoidkomplex, där aggregering av komplexet var ett problem vid emissionsmätningarna, observerades emissionen av de mer vatten- och metanollösliga dipikolinysyrabaserade klorin-lantanoidkomplex. Olika parametrar såsom metalens oxidations tillstånd, länkavståndet, länkpositionerna och lantanoidkelaterande ligander undersökes för att optimera de fotofysiska egenskaperna.

Tillsammans med två lantanoidjoner kan leda till utvecklingen av ett multikomplex med fyra färger.
First of all, I would like to express my deepest gratitude to my advisor, Dr. Eszter Borbas. Thank you for giving me the opportunity to work in your group and guiding me on the research of life pigments. I am indebted to your help for my settlement. Your treatment of lunches and dinners are also appreciated. You are a very good adviser.

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黄枭，我们一起摘草莓、一起游泳，一起搬家，谢谢你和翠燕的关心和帮助！
家辉，谢谢你一直做我的瑞典语翻译专家，帮我搬家，还帮我翻译论文的瑞典语摘要。
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小娇姐，谢谢你过年请我们吃饭，给孩子买礼物！

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A doctoral dissertation from the Faculty of Science and Technology, Uppsala University, is usually a summary of a number of papers. A few copies of the complete dissertation are kept at major Swedish research libraries, while the summary alone is distributed internationally through the series Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology. (Prior to January, 2005, the series was published under the title “Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology”.)