Furan- and Thiophene-Based Auxochromes Red-shift Chlorin Absorptions and Enable Oxidative Chlorin Polymerizations

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Abstract: The de novo syntheses of chemically stable chlorins with five-membered heterocyclic (furan, thiophene, formylfuran and formylthiophene) substituents in selected meso- and β-positions are reported. Heterocycle incorporation in the 3- and 13-positions shifted the chlorin absorption and emission to the red (up to $\lambda_{em} = 680$ nm), thus these readily incorporated substituents function analogously to auxochromes present in chlorophylls, for example, formyl and vinyl groups. Photophysical, theoretical and X-ray crystallographic experiments revealed small but significant differences between the behavior of the furan- and the thiophene-based auxochromes. Four regioisomeric bis-thienylchlorins (3,10;3,13,3,15 and 10,15) were oxidatively electropolymerized; the chlorin monomer geometry had a profound impact on the polymerization efficiency and the electrochemical properties of the resulting material. Chemical copolymerization of 3,13-bis-thienylchlorin with 3-hexylthiophene yielded an organic-soluble red-emitting polymer.

Introduction

For efficient solar energy conversion light-harvesting materials that can tap into large portions of the electromagnetic spectrum, and, in particular, can utilize red and near infrared light, are essential.[1] To illustrate the benefits of such pan-chromatic materials, it has been suggested that extending the photosynthetically useful spectral range from 400–700 nm to 400–750 nm would increase the usable photon flux by 19%.[1b,2] Porphyrin polymers are increasingly investigated for this purpose because of their attractive charge-transport properties and intense absorptions.[2] Applications of these versatile materials as semiconductors,[3a] as stimuli-responsive materials[4] and as catalysts[5] are also actively pursued. A variety of transformations have been successfully applied to the polymerization of diverse porphyrin monomers, such as metal-catalyzed cross-couplings, chemical oxidations, and oxidative and reductive electropolymerizations.[3a,b,6]

The light-harvesting and charge-transport properties of the polymers are governed by the monomers and the nature of the formed connection. Polymer length, porosity and solubility are additional tunable factors. All these parameters have been investigated to some extent, with the exception of the building blocks—these have almost exclusively been porphyrins, with non-ideal photophysical properties as a consequence, that is, negligible absorption outside of the blue. Monomeric panchromatic or "black" porphyrins and phthalocyanines have recently been obtained,[7] but are not readily polymerized due to the lack of suitable functionalities. Conjugated or fused porphyrin oligomers with red-shifted absorptions are known, however, their syntheses are demanding.[8] Chlorins share the carbon framework with porphyrins, with one of the pyrrolic double bonds removed. Consequently, chlorins have characteristic intense red absorptions in addition to the Soret band, which suggests that their polymers have potential as light-harvesting materials for the under-utilized low energy-part of the solar spectrum.

The UV/Vis absorption spectra of chlorins are sensitive to the type and position of the peripheral substituents. A striking example of spectral tuning is seen in chlorophylls (Figure 1). Vinyl and formyl groups positioned along the spectroscopic axes (i.e., the 2,3-, 7,8- and 12,13-positions, Figure 1, top) move the Qy-band from $\lambda_{abs} = 652$ nm (in MeOH)[9] in Chlb to $\lambda_{abs} = 707$ nm (in MeOH)[10] in what is the most red-shifted naturally-occurring chlorophyll, Chlb. Several other auxochromes, such as alkynes, ketones, cyclic esters and amides, as well as extended conjugated fragments have been extensively investigated for the past $\approx$ 10 years.[11] In addition to a deepened understanding of tetrapyrrole photophysics, these studies have provided intensely absorbing chromophores for photodynamic therapy and fluorescence imaging.[12] A limitation of these groups is that while some offer possibilities for functionalization (e.g., by traditional carbonyl chemistry), most conceivable...
transformations are detrimental to their abilities as auxochromes.

Chlorins extracted from natural sources (e.g., chlorophylls) and those prepared from porphyrins by reduction\(^\text{[13]}\) or dihydroxylation\(^\text{[14]}\) are prone to decomposition. This instability could explain the scarcity of reports on chlorin polymerization. The chlorin redox state can be locked-in by placing geminal dialkyl groups in the pyrroline ring.\(^\text{[15]}\) Gem-Dialkyl groups can be installed by, for example, Claisen rearrangement starting from \(\beta\)-1-hydroxyethyl porphyrins, which in turn are available from vinyl- or acetylporphyrins.\(^\text{[16]}\) An \(\mathrm{Ni}^{II}\)-chlorin carrying electropolymerizable pyrrole groups was prepared this way.\(^\text{[17]}\) Polymerization on an electrode surface yielded immobilized coenzyme mimics. Electropolymerization did not alter the chlorin properties, presumably due to the relatively long macrocycle-anchor group distance (> 8 atoms).\(^\text{[17a]}\) Gem-Dialkyl-stabilized chlorins are also accessible by total synthesis.\(^\text{[15b, 18]}\) Of the currently existing methods, the one developed by Lindsey is amenable to the introduction of a variety of peripheral substituents, for example, bioconjugatable-\(^\text{[12d]}\) surface attachment,\(^\text{[19]}\) and solubilizing groups\(^\text{[20]}\), auxochromes,\(^\text{[16a, 21]}\) metal chelates\(^\text{[22]}\) and even other tetrapyrroles.\(^\text{[21]}\)

We hypothesized that five-membered aromatic heterocycles would be sufficiently small to adopt co-planar conformations with the macrocycle, thus extending conjugation and red-shifting the chlorin absorption and emission (Figure 2). The advantage of using these substituents is their ease of installation and robustness under a range of conditions. Furthermore, the bis-thienylchlorin could be incorporated into polymers by electrochemical or chemical means. The results presented here establish furans and thiophenes as powerful auxochromes for hydrophyrins (chlorins), and bis-thienylchlorins as viable monomers to access red-absorbing polymers.

**Results and Discussion**

**Synthesis**

The chlorins were prepared using the Lindsey method (Schemes 1 and 2). This is a two-step one-pot protocol consisting of an initial acid-catalyzed condensation of a dihydrodipyrpin (Western half, e.g., 1) and a 1-bromo-9-formyl dipyrromethane (Eastern half, e.g., 2-S), followed by Zn\(^{II}\)-mediated, intramolecular oxidative cyclization under high-dilution conditions.\(^\text{[11h, 18]}\) The Zn-chelates formed in the macrocyclization can be difficult to purify and are poor substrates for subsequent transformations; thus they were demetallated in situ. The furan- and thiophene-based heterocycles were introduced pre-macrocyclization into the 10-position and the 3-position in Chl3\(^{35}\)S, Chl3\(^{35}\)S-CHO. Post-macrocyclization installation via Suzuki coupling between the appropriate bromochlorin and the heterocycle boronic acid derivative was also possible. The bromochlorins themselves were available either from brominated precursors (e.g., 1-Br), or through chlorin bromination under acidic conditions, which is known to be selective for the most electron rich and not sterically hindered 15-position.\(^\text{[24]}\) The successful synthesis of these heterocycle-functionalized chlorins shows that chlorins with thiophene or furan pendant groups undergo halogenation in the tetrapyrrole, and that electron-rich heterocycles are compatible with the oxidizing macrocyclization conditions.

The mild chlorin synthesis conditions enable the introduction of two non-identical heterocyclic substituents into the final product by installing one substituent before the macrocyclization, and the second after. An example for such a synthesis is shown in Scheme 2. Suzuki coupling between boronic esters and thiophenes or furans is possible. The results presented here establish furans and thiophenes as powerful auxochromes for hydrophyrins (chlorins), and bis-thienylchlorins as viable monomers to access red-absorbing polymers.
acid 3-S and 1-3′-N, followed by removal of the Ts protecting group yielded the thienyl-functionalized Western half 1-3′-Br. Macrocyclization with brominated Eastern half 2-Br, followed by demetallation with TFA in CHCl₃ afforded the brominated, thienyl-functionalized chlorin Chl3S. This species was readily coupled with boronic acid 3-S-CHO under standard Suzuki conditions, affording Chl3S-CHO in good yield after column chromatography on silica gel.

Photophysical characterization

The UV/Vis absorption and fluorescence emission spectra of the chlorins were recorded in CH₂Cl₂ (Table 1 and Figure 1). The absorption and emission properties of Chl3S-CHO and Chl3O-CHO were found to be essentially solvent independent (Table S1). The largest red-shifts in the Soret and Q band absorptions of Chl3 CHO were Δλ = 8 nm and 4 nm, respectively, upon going from MeOH to toluene. The situation was similar for Chl3O-CHO, and the absorption spectrum shifted to the red by Δλ = 8 nm (Soret) and 5 nm (Qₗ) upon replacing acetonitrile with toluene. Changes in the fluorescence excitation and emission maxima were even smaller (Table S1). The molar extinction coefficients (ε) could not be accurately determined due to the limited amount of material available. Therefore, absorption spectra were normalized to enable direct comparison of substituent effects on the B/Q-band ratio. A 2-thienyl group at the 3- or 13-positions red-shifts the absorption maximum by 10 nm compared to the unsubstituted free base chlorin (λ max = 634 nm in toluene), a 5-formyl-2-thienyl group in the same positions results in a 20 nm-red shift. The effect of 10-substitution is small (Δλ ≤ 6 nm red-shift for thiophene), comparable to the effect of a meso-Ph-group. These differences are in line with published data. [22a]

| Table 1. Photophysical properties of the substituted chlorins in CH₂Cl₂. |
|---|---|---|---|---|---|
| Entry | λₒ [nm] | λmax [nm] | Δε [cm⁻¹] | φ [Φ] |
| Chl3 | 404, 644 | 650 | 3.43 | 0.22 |
| Chl3CHO | 418, 659 | 664 | 2.53 | 0.25 |
| Chl3OCHO | 407, 639 | 642 | 4.14 | 0.11 |
| Chl3Br | 405, 644 | 652 | 3.28 | 0.23 |
| Chl3SCHO | 410, 655 | 665 | 2.15 | 0.30 |
| Chl3SCHO | 420, 660 | 667 | 2.32 | 0.21 |
| Chl3OCHO | 420, 660 | 657 | 2.32 | 0.21 |
| Chl10S | 411, 651 | 656 | 4.02 | 0.15 |
| Chl13S | 416, 656 | 666 | 2.91 | 0.25 |
| Chl13SCHO | 409, 650 | 657 | 3.40 | 0.19 |
| Chl10SCHO | 411, 645 | 649 | 4.14 | 0.13 |
| Chl13SCHO | 420, 668 | 680 | 2.14 | 0.34 |

[a] Determined using tetraphenylporphyrin in toluene as the reference.
with the fact that the 3- and the 13-positions lie along one of the spectroscopic axes of the chlorins (Figure 1), thus, their substitutions have a larger effect on the photophysical properties than a 10-substitution. The simultaneous 3-thienyl, 13-formylthienyl substitution (Chl3[13]-S-CHO) affords dramatically red-shifted absorption (to 668 nm), and a fluorescence emission with a maximum at 680 nm. The effect of the heterocycles is comparable to those of vinyl-, formyl- or acetyl auxochromes at the same positions. For example, 3-alkynyl or 3-vinyl groups shift the $Q_y$-absorption of ZnChl from 602 to 627 nm or 620 nm, respectively, while 13-acetylation results in $\lambda_{\text{max}} =$ 632 nm. Thus these established auxochromes can be replaced by, for example, thiophene, which is also a convenient synthetic handle for further functionalizations, such as modifications at their α-positions or oxidative radical-polymerization (vide infra).

The fluorescence spectrum in all cases consists of a $Q_y$-band and a low-intensity satellite (Figure 3). The Stokes shifts are small, 3–13 nm (74–299 cm$^{-1}$). The order of emission bands generally follows the same order as the $Q_y$ absorption bands. This order is reversed for Chl3[13]-S-CHO and Chl3[13]-S-CHO, and similarly for Chl3[13]-S-CHO and Chl13[13]-S-CHO. A formylfuryl substituent results in a larger red-shift in the absorption spectrum than a formylthienyl group in the same position. This is explained by the extension of the conjugation over the formylfuryl group (Figure S3), and the resulting decrease in the HOMO–LUMO gap, as shown by DFT calculations (Table S2). The calculated dihedral angles are smaller for the furan-appended chlorins than for the thiénylchlorins (Table S2), which is in line with extended conjugation for the former, but not the latter. The formylthienyl-substituted chlorins have larger Stokes shifts. One explanation for this may be that the twisted thiénylchlorins relax into a more co-planar conformation after excitation. An X-ray crystallographic analysis of Chl3[13]-S-CHO showed a dihedral angle of 22.8(11)$^\circ$ (24.2(5)$^\circ$) between the least squares plane (l.s.pl.) of the thienyl and the adjacent pyrrole ring, showing that such quite planar conformations are accessible for 3- and presumably 13-thiénylchlorins. In contrast, the same substituent in the meso-position (in Chl10[3]-S-CHO) shows significantly larger torsion of the chlorin and the thiophene l.s.pl. (56.6(3)$^\circ$ and 52.9(3)$^\circ$) (Figure 4).

It is interesting to note that Imahori and co-workers have observed an increased Stokes shift for poly-meso-furanyl-porphyrin but not for poly-meso-thiénylporphyrin. This was explained with the larger steric bulk of the thiényl group, which in the meso-position precludes co-planarization with the macrocycle. We propose that in the less crowded β-position the small furan can be co-planar, and the thiophene can become significantly co-planar in the excited state. Freezing THF-solutions of Chl3[13]-S-CHO and Chl3[13]-S-CHO at 77 K afforded excitation maxima at 651 nm for both species (Table S3). The difference between the excitation and emission maxima diminished to 2 nm (47 cm$^{-1}$, from 115 cm$^{-1}$) for Chl3[13]-S-CHO and to 6 nm (93 cm$^{-1}$, from 279 cm$^{-1}$) for Chl3[13]-S-CHO. These observations are consistent with freezing resulting in similar conformations for the two chlorins; hence the similar excitation maxima. The small difference between $\lambda_{\text{ex}}$ and $\lambda_{\text{em}}$ could be due to the lack of conformational changes for Chl3[13]-S-CHO in the solid state; this effect is less pronounced for Chl3[13]-S-CHO.

The fluorescence quantum yields were found to be typical of previously reported free base chlorins, with values ranging from 0.11 to 0.34. The photophysical properties of Chl3[13]-S-CHO are particularly appealing, combining intense red-shifted absorption and emission with the highest quantum yield in this series. The synthesis of this compound is however rather long. Therefore, we note that already the attachment of a single formylthienyl group to either the 3 or the 13-position affords emission above 660 nm.

**Electrochemistry**

The redox properties of the chlorins were studied by cyclic voltammetry (CV) in CH$_2$Cl$_2$ with NBut$_4$PF$_6$ as supporting electrolyte. The results of these investigations are summarized in Table 2. All chlorin derivatives show one reversible (–1.66 to

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**Figure 3.** Normalized absorption (top) and fluorescence emission (bottom) spectra of selected heterocycle-bearing chlorins in CH$_2$Cl$_2$ at room temperature. Emission spectra were recorded with excitation into the Soret band.
Chl3 shows an ambipolar conduction behavior [0.43, 0.83, 1.05] (b). Ellipsoids (Figure S4) with 0.1 Cyclic voltammetry of monomeric chlorins. The first quasi-reversible oxidation (0.37 to 0.44 V) is typically chlorin based,[11a] while the second oxidation is irreversible (0.83–0.86 V), and is assigned to thienyl oxidation.[15] Depending on the bis-thienylchlorin substitution pattern, we have observed different increased increments of current upon repeated oxidative scans, indicative of deposition of polymeric species on the glassy carbon (GC) working electrode.

### Table 2. Cyclic Voltammetry of Monomeric Chlorins.

| Entry | Reduction $E_{pa}$ [V] | Oxidation $E_{pc}$ [V] |
|-------|------------------------|------------------------|
| Chl3 | $-2.06^{[a]}; -1.69^{[a]}$ | 0.42, 0.93 |
| Chl10 | $-2.11, -1.67^{[b]}$ | 0.43, 0.93 |
| Chl10$^0$ | $-2.14, -1.67^{[a]}$ | 0.43, 0.83, 1.05 |
| Chl13 | $-2.05^{[a]}; -1.69$ | 0.39, 0.87 |
| Chl3$^{10}$ | $-2.06, -1.67^{[a]}$ | 0.37, 0.86 |
| Chl3$^{13}$ | $-2.14, -1.67^{[a]}$ | 0.44, 0.82 |
| Chl3$^{15}$ | $-2.09, -1.66^{[a]}$ | 0.40, 0.84 |
| Chl10$^{15}$ | $-2.20, -1.70^{[a]}$ | 0.41, 0.83 |

[a] Conditions: Measured with [analyte] = for 1 mM in CH$_2$Cl$_2$ with 0.1 M NBut$_4$PF$_6$ on glassy C-electrode; $n = 100$ mVs$^{-1}$. Potentials are given versus Fe$^{3+/2-}$. [b] Reversible peak, the reported value is $E_{1/2} = (E_{pa} + E_{pc})/2$.

Polymerization

With these data in hand we attempted a controlled electropolymerization of bis-thienylchlorins Chl3$^{10}$, Chl3$^{13}$, Chl3$^{15}$ and Chl10$^{15}$ (Figure S4). We have carried out the polymerization on fluorine doped tin oxide (FTO) conductive glass substrates by repeated cycling between oxidative (ca. 1.00 V) and reductive potentials (−0.5 to −0.2 V), which gives rise to homogeneous polymer films in all cases (vide infra). The polymerization of Chl10$^{15}$ and Chl3$^{10}$ proceeded slowly showing only moderate current increases after 45 and 80 cycles, respectively. By contrast, chlorins Chl3$^{15}$ and Chl3$^{13}$ showed rapid polymer deposition concomitant with a substantial current increase. The cyclic voltammograms of p-Chl3$^{15}$ and p-Chl3$^{13}$ displayed persistent oxidative peaks at +0.04 V and 0.01 V, respectively, upon cycling to negative potentials. This could be attributed to formation of metallated tin chlorin.[26]

Although p-Chl3$^{10}$ shows an ambipolar conduction behavior we observe a rapid decomposition of the film with applied reductive potentials as observed by a significant current decrease within the first five scans (Film S1 vs. Film S5, Figure 5). This contrasts the behavior observed for p-Chl10$^{15}$, which exhibits good bipolar conduction behavior between −0.56 and +0.37 V. The polymer films on the FTO substrate had broad absorptions with bands around 410–420 nm and 650–680 nm (Figure S4) with the exception of p-Chl3$^{10}$ (which was probably not observed due to low concentrations, that is, thin films). The films were essentially non-emissive because of self-quenching due to the short intra-chlorin distances (Figures S6, S7).

Scanning electron microscopy (SEM) analysis of the films revealed a uniform film formation on the FTO substrate during the electropolymerization indicative of a controlled radical polymerization (Figure S9).

In order to circumvent the self-quenching observed in the electropolymerized systems, an organic-soluble chlorin polymer (p-Chl3$^{15}$-Hex)$^3$ was prepared by treating a 1:20 mixture of Chl3$^{15}$ and 3-hexylthiophene with FeCl$_3$. $^1$H NMR analysis of the resulting co-polymer (Figure S1) showed unique broadened signals assigned to the macrocycle (4% incorporation; −2 ppm, 4.6 ppm, >10 ppm), along with typical resonance associated with regio-irregular hexylthiophene (e.g., 2–3 ppm). The polymer was analyzed by gel permeation chromatography, which yielded a weight average molecular weight ($M_w$) of 5299 g mol$^{-1}$, a number average molecular weight ($M_n$) of 2020 g mol$^{-1}$ and a polydispersity index (PDI) of 2.62 (Figure S2). The relatively large PDI is typical of non-controlled radical polymerization; we have not attempted to optimize this...
procedure yet. The $M_w$ value confirms the presence of high $M_w$ oligomers. A hexylthiophene 20-mer containing a single bis-thienylchlorin, which corresponds to an $\approx 4\%$ incorporation is expected to have a $M_w$ of 3865 g mol$^{-1}$. $p$-Chl3$^{13}$-Hex$^{2}$ had slightly broadened Soret and Q-bands (Figure S5), and was much more fluorescent than the films ($\lambda_{max} = 681$ nm in CH$_2$Cl$_2$. Figures S6–S8), which is consistent with the larger spacing between the chromophores.

**Figure 5.** Cyclic voltammograms of the bis-thienylchlorin monomers (left), the electropolymorizations of the monomers, and the characterization of the polymer films (right). Monomers were recorded in dry, de-areated CH$_2$Cl$_2$ using a three-electrode setup with a GC working electrode. The potentials are referenced internally to the Fc$^{2+}$/Fc$^{0}$ couple. Generally, a scan rate of 100 mV s$^{-1}$ was used; semi-reversible redox events were investigated at higher scan rates (500 mV s$^{-1}$, dotted lines). Polymerization 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 red, with subsequent scans going from black to light gray. After polymer deposition the films are thoroughly washed with CH$_2$Cl$_2$ and placed in pure electrolyte solution. The electrochemical response of the films was investigated at 100 mV s$^{-1}$ using different potential windows (red dotted line).

**Conclusion**

Chlorins functionalized with furans and thiophenes in the peripheral positions were prepared by de novo synthesis from substituted dihydrodipyrrins or dipyrromethanes, or by Suzuki coupling between furanyl/thienyl boronic acids and bromochlorins. The reported chlorins have red-shifted absorption and emission spectra compared to the parent macrocycles. In the case of furanyl and formylfuranyl substitution, the red-shift could be ascribed to the extension of the π-conjugation. An interesting increase in Stokes shift was noted for thiophene derivatives compared to those of furan-substituted chlorins, which was tentatively attributed to the adoption of a co-planar conformation of the thiynyl substituent and the chlorin in the excited state. However, further investigation of this hypothesis is necessary.

The bis-thienylchlorins participated in electrochemical polymerization affording thin films. An organic-soluble co-polymer with hexylthiophene was prepared by radical polymerization. The thienylchlorin regioisomers differed greatly in polymerization efficiency and the electrochemical properties of the resulting films, which underscores the impact of monomer structure. Both the films and the soluble polymer had absorptions extending beyond 700 nm, and substantial absorption over large portions of the visible spectrum. Additionally, the soluble polymer retained the chlorin monomer’s intense red emission. Taken together, our results showcase the utility of small heterocycles as chlorin auxochromes that are analogous to the well-established vinyl-, formyl- and acetyl groups with the benefit of undergoing straightforward chemical and electrochemical polymerization. These new materials are expected to be useful for panchromatic light harvesting in artificial photosynthesis, and as red emitters for sensing and imaging applications.

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