‖ **Porphyrinoids**

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 (furane, thiophene, formylfurane 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 crys-tallographic experiments revealed small but significant differences between the behavior of the furan- and the thiophene-based auxochromes. Four regioisomeric bis-thienyl-chlorins (3,10; 3,13, 3,15 and 10,15) were oxidatively electro-polymerized; the chlorin monomer geometry had a profound impact on the polymerization efficiency and the electro-chemical properties of the resulting material. Chemical co-polymerization of 3,13-bis-thienylchlorin with 3-hexylthio-phene 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-chromic materials, it has been suggested that extending the photosyn-thetically 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 pur-pose because of their attractive charge-transport properties and intense absorptions.[3] Applications of these versatile mate-rials as semiconductors,[3a] as stimuli-responsive materials[4] and as catalysts[5] are also actively pursued. A variety of transforma-tions 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, d, 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 build-ing blocks—these have almost exclusively been porphyrins, with non-ideal photophysical properties as a consequence, that is, negligible absorption outside of the blue. Monomeric panchromic 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 por-phyrin oligomers with red-shifted absorptions are known, how-ever, their syntheses are demanding.[8] Chlorins share the carbon framework with porphyrins, with one of the pyrrolic double bonds removed. Consequently, chlorins have character-istic intense red absorptions in addition to the Soret band, which suggests that their polymers have potential as light-har-vesting 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 Q_y-band from $\lambda_{abs} = 652$ nm (in MeOH)[9] in Chl *b* to $\lambda_{abs} = 707$ nm (in MeOH)[10] in what is the most red-shifted naturally-occurring chlorophyll, Chl *f*. Several other auxochromes, such as alkynes, ketones, cyclic esters and amides, as well as extend-ed conjugated fragments have been extensively investigated for the past ≈10 years.[11] In addition to a deepened under-standing of tetrapyrrole photophysics, these studies have pro-vided intensely absorbing chromophores for photodynamic therapy and fluorescence imaging.[12] A limitation of these groups is that while some offer possibilities for functionaliza-tion (e.g., by traditional carbonyl chemistry), most conceivable

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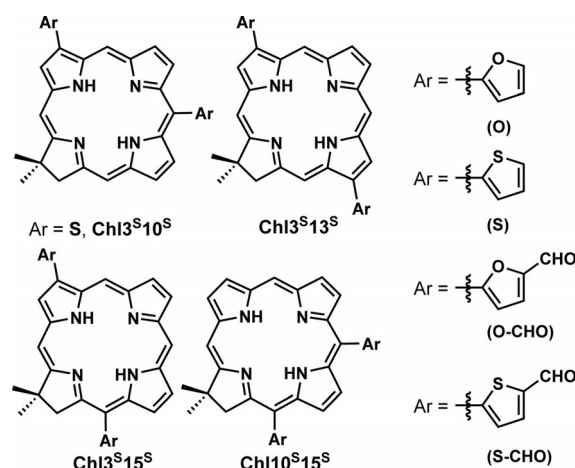*eszter.borbas@kemi.uu.se*
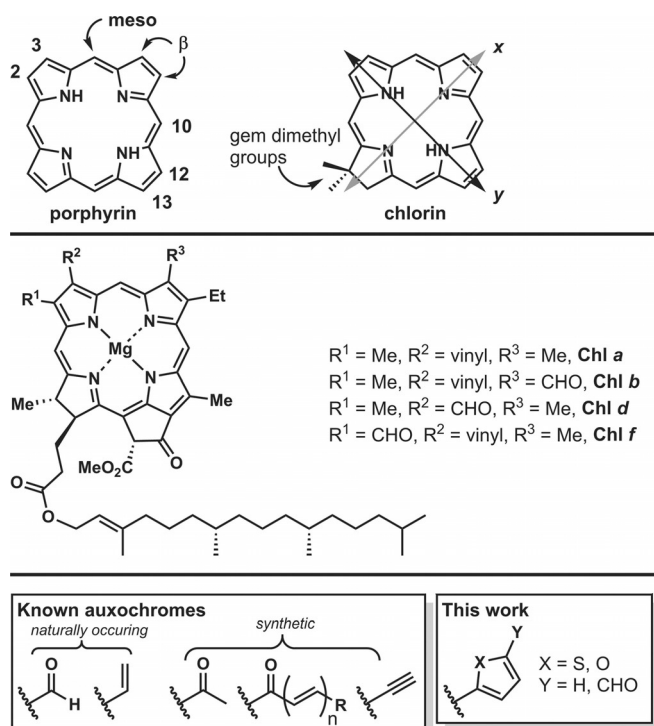
Figure 1. Comparison of chlorins and porphyrins, numbering, and spectroscopic axes (top), chlorophylls *a*, *b*, *d* and *f* (middle), and established naturally-occurring and synthetic auxochromes, and the auxochromes investigated here (bottom).

Figure 2. The bis-thienylchlorins studied in this work and the designations of the heterocycle substituents.

transformations are detrimental to their abilities as auxochromes.

Chlorins extracted from natural sources (e.g., chlorophylls) and those prepared from porphyrins by reduction[13] or dihydroxylation[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.[15] *gem*-Dialkyl groups can be installed by, for example, Claisen rearrangement starting from β-1-hydroxyethyl porphyrins, which in turn are available from vinyl- or acetylporphyrins.[16] A Ni[II]-chlorin carrying electropolymerizable pyrrole groups was prepared this way.[17] Polymerization on an electrode surface yielded immobilized coenzyme mimics. Electropolymerization did not alter the chlorin properties, presumably due to the relatively long macrocycle-anchoring group distance (>8 atoms).[17a] *gem*-Dialkyl-stabilized chlorins are also accessible by total synthesis.[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-,[12b] surface attachment-[19] and solubilizing groups,[20] auxochromes,[11e,i, 21] metal chelates[22] and even other tetrapyrroles.[23]

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 hydroporphyrins (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 dihydrodipyrrin (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.[11h,18e] 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[S]13[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.[24] The successful synthesis of these heterocycle-functionalized chlorins shows that chlorins with thiophene or furan pendent 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
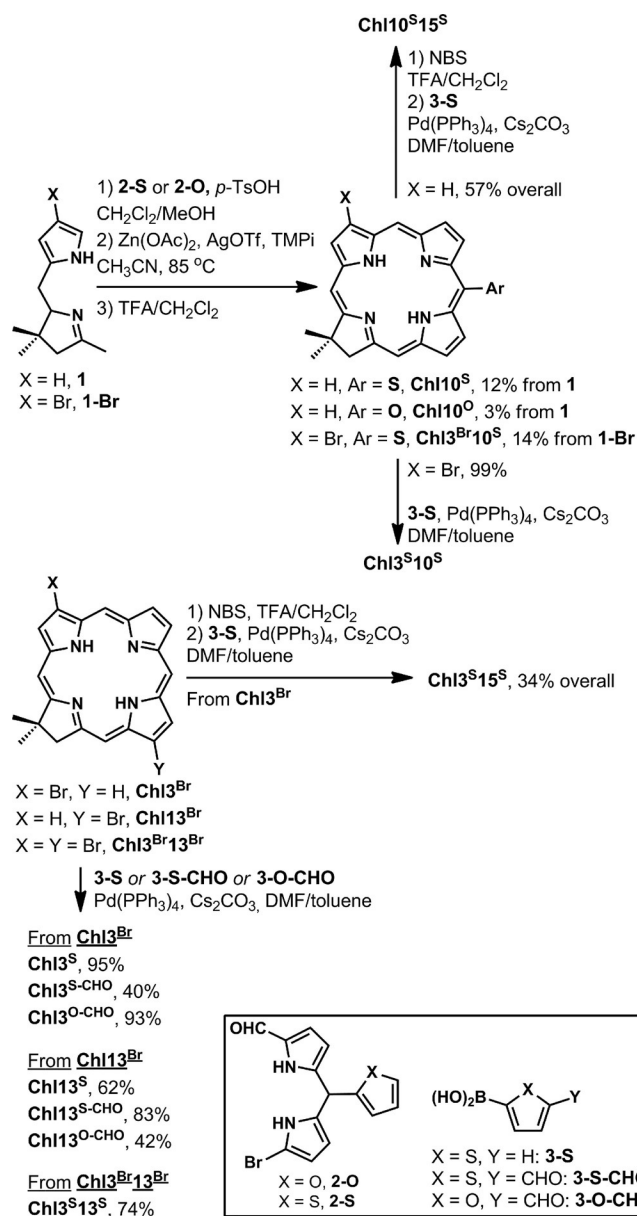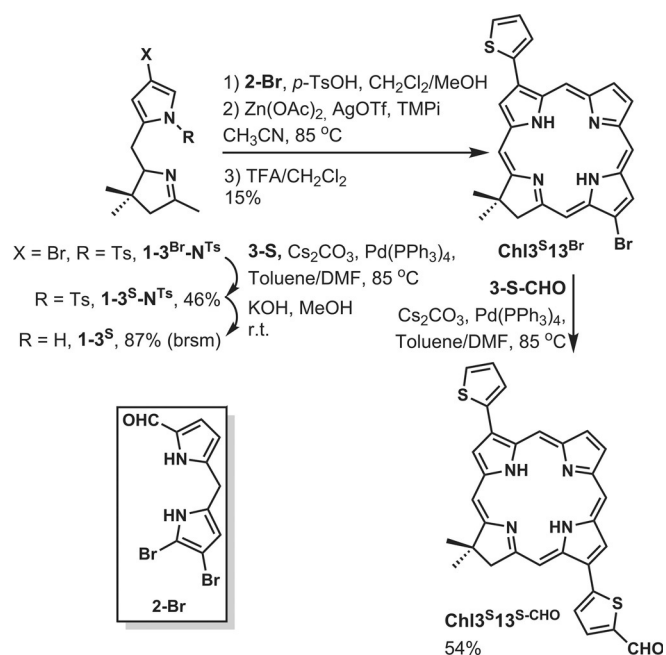
Scheme 1. Synthesis of the monosubstituted chlorins and chlorins carrying two identical substituents.

Scheme 2. Synthesis of asymmetrically substituted **Chl3^{S}13^{O-CHO}**.

Table 1. Photophysical properties of the substituted chlorins in CH$_2$Cl$_2$.
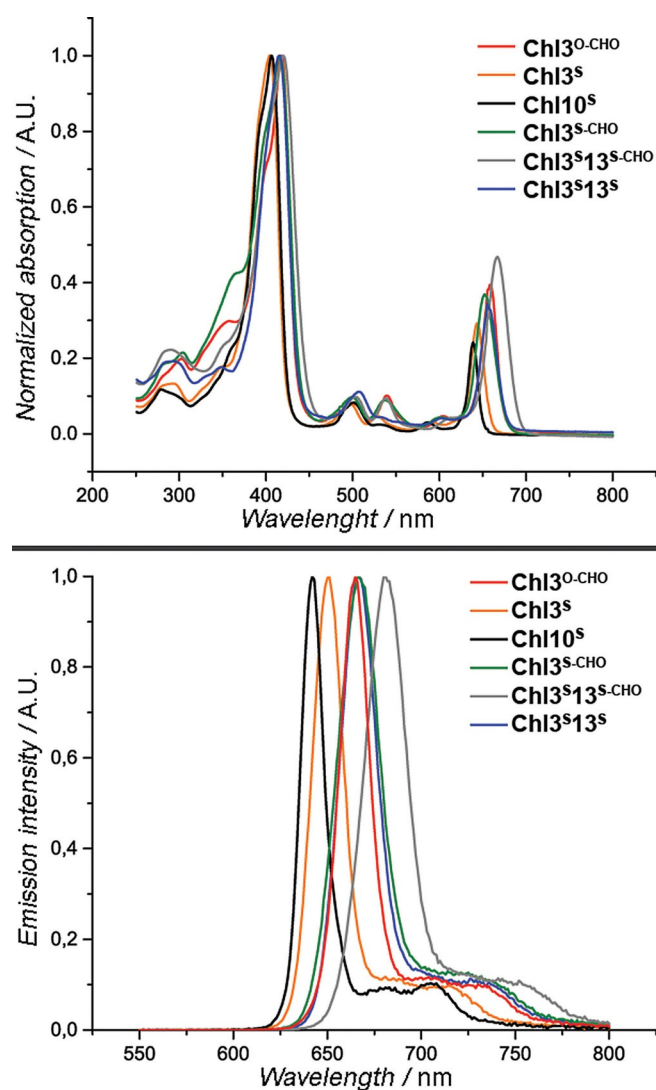
Entry	λ_B, λ_Q [nm]	I_B/I_Q	$\Delta\nu$ [cm^{-1}] ([nm])	λ_{em} [nm]	Φ[a]
Chl3^S	404, 644	3.43	143 (6)	650	0.22
Chl3^{S-CHO}	416, 653	2.72	299 (13)	666	0.25
Chl3^{O-CHO}	418, 659	2.53	114 (5)	664	0.25
Chl10^S	407, 639	4.14	74 (3)	642	0.11
Chl13^S	405, 644	3.28	191 (8)	652	0.23
Chl13^{S-CHO}	410, 655	2.15	230 (10)	665	0.30
Chl13^{O-CHO}	420, 660	2.32	159 (7)	667	0.21
Chl3^{S}10^S	417, 651	4.02	137 (5)	656	0.15
Chl3^{S}13^S	416, 656	2.91	229 (10)	666	0.25
Chl3^{S}15^S	409, 650	3.40	164 (7)	657	0.19
Chl10^{S}15^S	411, 645	4.14	96 (4)	649	0.13
Chl3^{S}13^{S-CHO}	420, 668	2.14	264 (12)	680	0.34

[a] Determined using tetraphenylporphyrin in toluene as the reference.

acid **3-S** and **1-3^{Br}-N^{Ts}**, 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 CH$_2$Cl$_2$ afforded the brominated, thienyl-functionalized chlorin **Chl3^{S}13^{Br}**. This species was readily coupled with boronic acid **3^{S-CHO}** under standard Suzuki conditions, affording **Chl3^{S}13^{S-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 CH$_2$Cl$_2$ (Table 1 and Figure 1). The absorption and emission properties of **Chl3^{S-CHO}** and **Chl3^{O-CHO}** were found to be essentially solvent independent (Table S1). The largest red-shifts in the Soret and Q$_y$-band absorptions of **Chl3^{S-CHO}** were $\Delta\lambda = 8$ and 4 nm, respectively, upon going from MeOH to toluene. The situation was similar for **Chl3^{O-CHO}**, and the absorption spectrum shifted to the red by $\Delta\lambda = 8$ nm (Soret) and 5 nm (Q$_y$) 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.[22a] Therefore, absorption spectra were normalized to enable direct comparison of substituent effects on the B/Q-band ratio.[11b] 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 ($\lambda_{max} = 634$ nm in toluene[25]), a 5-formyl-2-thienyl group in the same positions results in a 20 nm-red shift. The effect of 10-substitution is small (≈ 6 nm red-shift for thiophene), comparable to the effect of a meso-Ph-group.[26] These differences are in line

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 ($\mathbf{Chl3^{S}13^{S\text{-}CHO}}$) 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.[11a] For example, 3-alkynyl or 3-vinyl-groups shift the Q_y-absorption of $\mathbf{ZnChl}$ from 602 to 627 nm or 620 nm, respectively, while 13-acetylation results in $\lambda_{max} = 632$ nm.[11a] 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 $\mathbf{Chl3^{O\text{-}CHO}}$ and $\mathbf{Chl3^{S\text{-}CHO}}$, and similarly for $\mathbf{Chl13^{O\text{-}CHO}}$ and $\mathbf{Chl13^{S\text{-}CHO}}$. A formylfuryl substituent results in a larger red-shift in the absorption spectrum than a formyl-thienyl 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 thienylchlorins (Table S2), which is in line with extended conjugation for the former, but not the latter. The formylthien-yl-substituted chlorins have larger Stokes shifts. One explanation for this may be that the twisted thienylchlorins relax into a more co-planar conformation after excitation. An X-ray crystallographic analysis of $\mathbf{Chl3^{S}13^{Br}}$ showed a dihedral angle of 22.8(11)° (24.2(5)°) 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-thienylchlorins. In contrast, the same substituent in the meso-position (in $\mathbf{Chl10^{S}3^{Br}}$) shows significantly larger torsion of the chlorin and the thiopehene l.s.pl. (56.6(3)° and 52.9(3)°) (Figure 4).

It is interesting to note that Imahori and co-workers have observed an increased Stokes shift for poly-meso-furyl-porphyrin but not for poly-meso-thienylporphyrin.[3b] This was explained with the larger steric bulk of the thienyl 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 $\mathbf{Chl3^{S\text{-}CHO}}$ and $\mathbf{Chl3^{O\text{-}CHO}}$ 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 $\mathbf{Chl3^{O\text{-}CHO}}$ and to 6 nm (93 cm^{-1}, from 279 cm^{-1}) for $\mathbf{Chl3^{S\text{-}CHO}}$. These observations are consistent with freezing resulting in similar conformations for the two chlorins; hence the similar excitation maxima. The small difference between λ_{ex} and λ_{em} could be due to the lack of conformational changes for $\mathbf{Chl3^{S\text{-}CHO}}$ in the solid state; this effect is less pronounced for $\mathbf{Chl3^{O\text{-}CHO}}$.

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 $\mathbf{Chl3^{S}13^{S\text{-}CHO}}$ 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_2Cl_2 with NBu_4PF_6 as supporting electrolyte. The results of these investigations are summarized in Table 2. All chlorin derivatives show one reversible (−1.66 to

Figure 3. Normalized absorption (top) and fluorescence emission (bottom) spectra of selected heterocycle-bearing chlorins in CH_2Cl_2 at room temperature. Emission spectra were recorded with excitation into the Soret band.
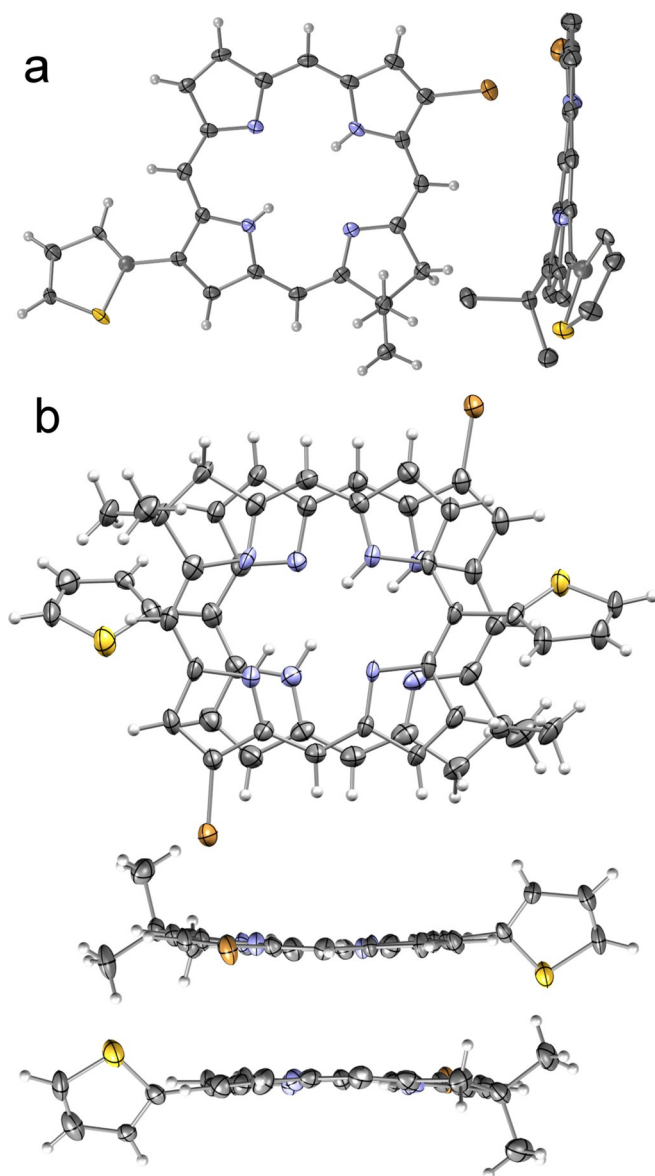
Figure 4. ORTEP representations of **Chl3^{S}13^{Br}** (a) and **Chl10^{S}3^{Br}** (b). Ellipsoids at 50 % probability level. For clarity only one of the disordered thienyl units in **Chl3^{S}13^{Br}** is shown. Solution and refinement parameters are found in the SI.

Table 2. Cyclic voltammetry of monomeric chlorins.		
Entry	Reduction E_{red} [V]	Oxidation E_{ox} [V]
Chl3^S	−2.06[b], −1.69[b]	0.42, 0.93
Chl10^S	−2.11, −1.67[b]	0.43, 0.93
Chl10^O	−2.14, −1.67[b]	0.43, 0.83, 1.05
Chl13^S	−2.05[b], −1.69	0.39, 0.87
Chl3^{S}10^S	−2.06, −1.67[b]	0.37, 0.86
Chl3^{S}13^S	−2.14, −1.67[b]	0.44, 0.82
Chl3^{S}15^S	−2.09, −1.66[b]	0.40, 0.84
Chl10^{S}15^S	−2.20, −1.70[b]	0.41, 0.83

[a] Conditions: Measured with [analyte] = for 1 mM in CH$_2$Cl$_2$ with 0.1 M NBu$_4$PF$_6$ on glassy C-electrode; n = 100 mV s^{-1}. Potentials are given versus Fc$^{+/0}$. [b] Reversible peak, the reported value is $E_{1/2}$ = (E_{pa} + E_{pc})/2.

−1.70 V) and one quasi-reversible reduction (−2.06 to −2.20 V, Figure 5). 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.[27] 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.

Polymerization

With these data in hand we attempted a controlled electropolymerization of bis-thienylchlorins **Chl3^{S}10^S**, **Chl3^{S}13^S**, **Chl3^{S}15^S** and **Chl10^{S}15^S** (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 homogenous polymer films in all cases (vide infra). The polymerization of **Chl10^{S}15^S** and **Chl3^{S}10^S** proceeded slowly showing only moderate current increases after 45 and 80 cycles, respectively. By contrast, chlorins **Chl3^{S}15^S** and **Chl3^{S}13^S** showed rapid polymer deposition concomitant with a substantial current increase. The cyclic voltammograms of *p*-**Chl3^{S}13^S** and *p*-**Chl3^{S}15^S** 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.[28] Although *p*-**Chl3^{S}10^S** 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^{S}15^S**, 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^{S}10^S** (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^{S}13^S-Hex^S**) was prepared by treating a 1:20 mixture of **Chl3^{S}13^S** 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
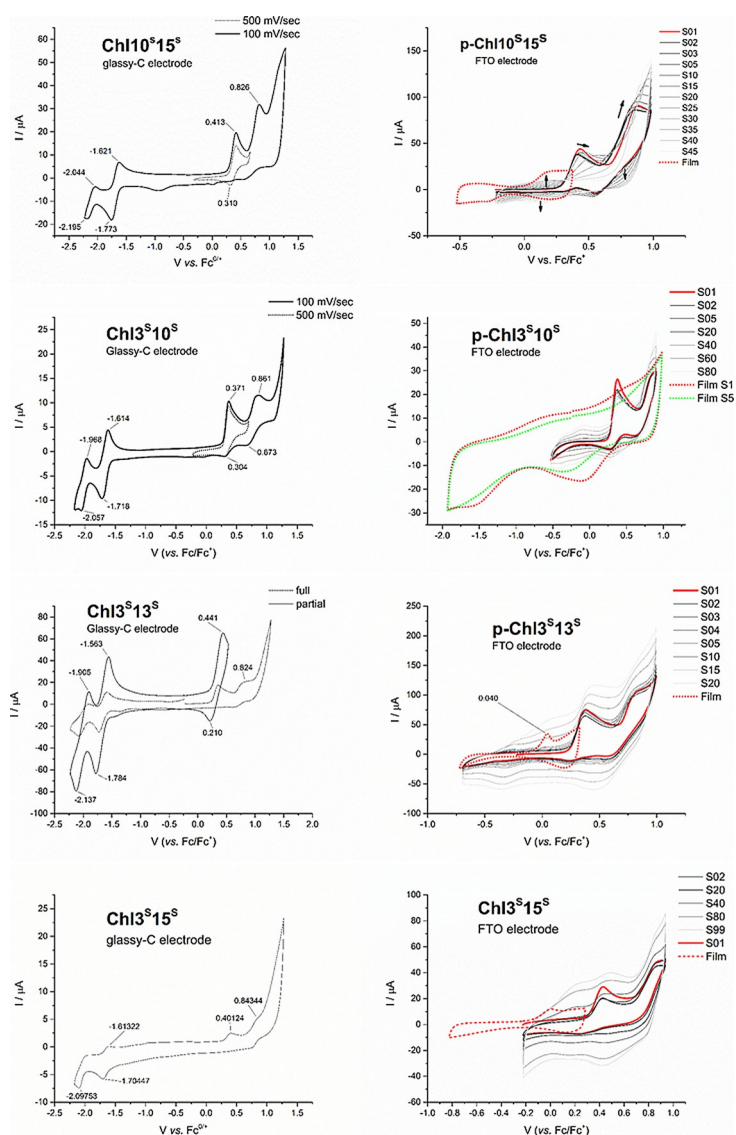
Figure 5. Cyclic voltammograms of the bis-thienylchlorin monomers (left), the electropolymerizations of the monomers, and the characterization of the polymer films (right). Monomers were recorded in dry, de-areated CH_2Cl_2 using a three-electrode setup with a GC working electrode. The potentials are referenced internally to the $Fc^{0/+}$ 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_2Cl_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).

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^{S}13^S-Hex^S** had slightly broadened Soret and Q-bands (Figure S5), and was much more fluorescent than the films ($\lambda_{max} = 681 \, nm$ in CH_2Cl_2, Figures S6–S8), which is consistent with the larger spacing between the chromophores.

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 thienyl 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 panchromic light harvesting in artificial photosynthesis, and as red emitters for sensing and imaging applications.

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