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Structure–Property Relationships for Self-Assembled Zinc Chlorin Light-Harvesting Dye Aggregates

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Abstract: A series of zinc 3^1-hydroxymethyl chlorins **10a–e** and zinc 3^1-hydroxyethyl chlorins **17** with varied structural features were synthesized by modifying naturally occurring chlorophyll *a*. Solvent-, temperature-, and concentration-dependent UV/Vis and CD spectroscopic methods as well as microscopic investigations were performed to explore the importance of particular functional groups and steric effects on the self-assembly behavior of these zinc chlorins. Semisynthetic zinc chlorins **10a–e** possess the three functional units relevant for self-assembly found in their natural bacteriochlorophyll (BChl) counterparts, namely, the 3^1-OH group, a central metal ion, and the 13^1 C=O moiety along the Q_y axis, and they contain various 17^2-substituents. Depending on whether the zinc chlorins have 17^2-hydrophobic or hydrophilic side chains, they self-assemble in nonpolar organic solvents or in aqueous media, respectively. Zinc chlorins possessing at least two long side chains provide soluble self-aggregates that are stable in solution for a prolonged time, thus facilitating elucidation of their properties by optical spectroscopy. The morphology of the zinc chlorin aggregates was elucidated by atomic force microscopy (AFM) studies, revealing well-defined nanoscale rod structures for zinc chlorin **10b** with a height of about 6 nm. It is worth noting that this size is in good accordance with a tubular arrangement of the dyes similar to that observed in their natural BChl counterparts in the light-harvesting chlorosomes of green bacteria. Furthermore, for the epimeric 3^1-hydroxyethyl zinc chlorins **17** with hydrophobic side chains, the influence of the chirality center at the 3^1-position on the aggregation behavior was studied in detail by UV/Vis and CD spectroscopy. Unlike zinc chlorins **10**, the 3^1-hydroxyethyl zinc chlorins **17** formed only small oligomers and not higher rod aggregate structures, which can be attributed to the steric effect imposed by the additional methyl group at the 3^1-position.

Keywords: aggregation · dyes/pigments · light harvesting · self-assembly · zinc chlorins

Introduction

Progressive global warming caused mainly by burning fossil fuels is one of the major problems of the present time.[1] A way out from this detrimental problem is the utilization of renewable energy resources, particularly solar light, in a sustainable way.[2] For the exploration of this possibility, natural light-harvesting (LH) systems can serve as archetypes because nature satisfies its whole energy demand by using sunlight with the help of LH systems. A most fascinating example of such natural light-harvesting systems can be found in the chlorosomes of green phototrophic bacteria (e.g., *Chloroflexus aurantiacus*), which are constructed from the rod-type self-assemblies of bacteriochlorophylls (BChls) and are enveloped in a lipid monolayer.[3] In contrast with other bacterial and plant antenna systems, the chlorosomes are protein-free and their structure and function rely on the self-assembly of BChls *c*, *d*, and *e*, controlled and determined only by pigment–pigment interactions instead of protein–pigment interactions.[4] The construction of protein-free pigment aggregates allows the implementation of close packing of the units and facilitates very efficient light harvesting.[5] The efficient light harvesting by chlorosomal antennae enables such organisms to inhabit depths of up to 2300 m under the water surface where light is extremely scarce.[6] The intriguing architectural principle for the supramolecular organization of dyes in chlorosomes can be mimicked by using semisynthetic molecules that are preprogrammed for self-assembly. Thus, for the better understanding of chlorosomal light-harvesting systems, Tamiaki et al. developed zinc chlorin **2**,

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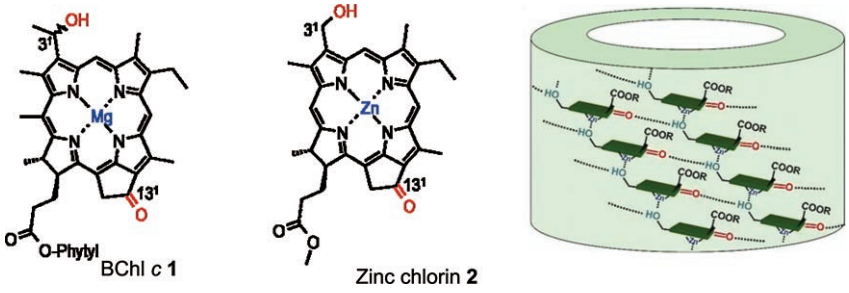
which is a model compound for the naturally occurring BChl *c* **1** (see Scheme 1).[7a] Like BChls, zinc chlorin **2** forms extended dye aggregates in nonpolar solvents, such as *n*-hexane or *n*-heptane.[7b,c] Intensive investigations of dye aggregates of BChl *c* **1** and zinc chlorin **2** revealed almost identical spectral and photophysical properties compared to those of the natural chlorosomal self-assemblies, which confirmed the suitability of zinc chlorin dyes for the imitation of chlorosomal antennae systems.[8] The major advantage of the zinc chlorin model compounds over the native bacteriochlorophylls lies in their easy semisynthetic accessibility from Chl *a* and their higher chemical stability.



Scheme 1. Structures of naturally occurring bacteriochlorophyll *c* **1** and zinc chlorin model compound **2**, and a model showing the three noncovalent interactions involved in the formation of supramolecular rod aggregates (right).

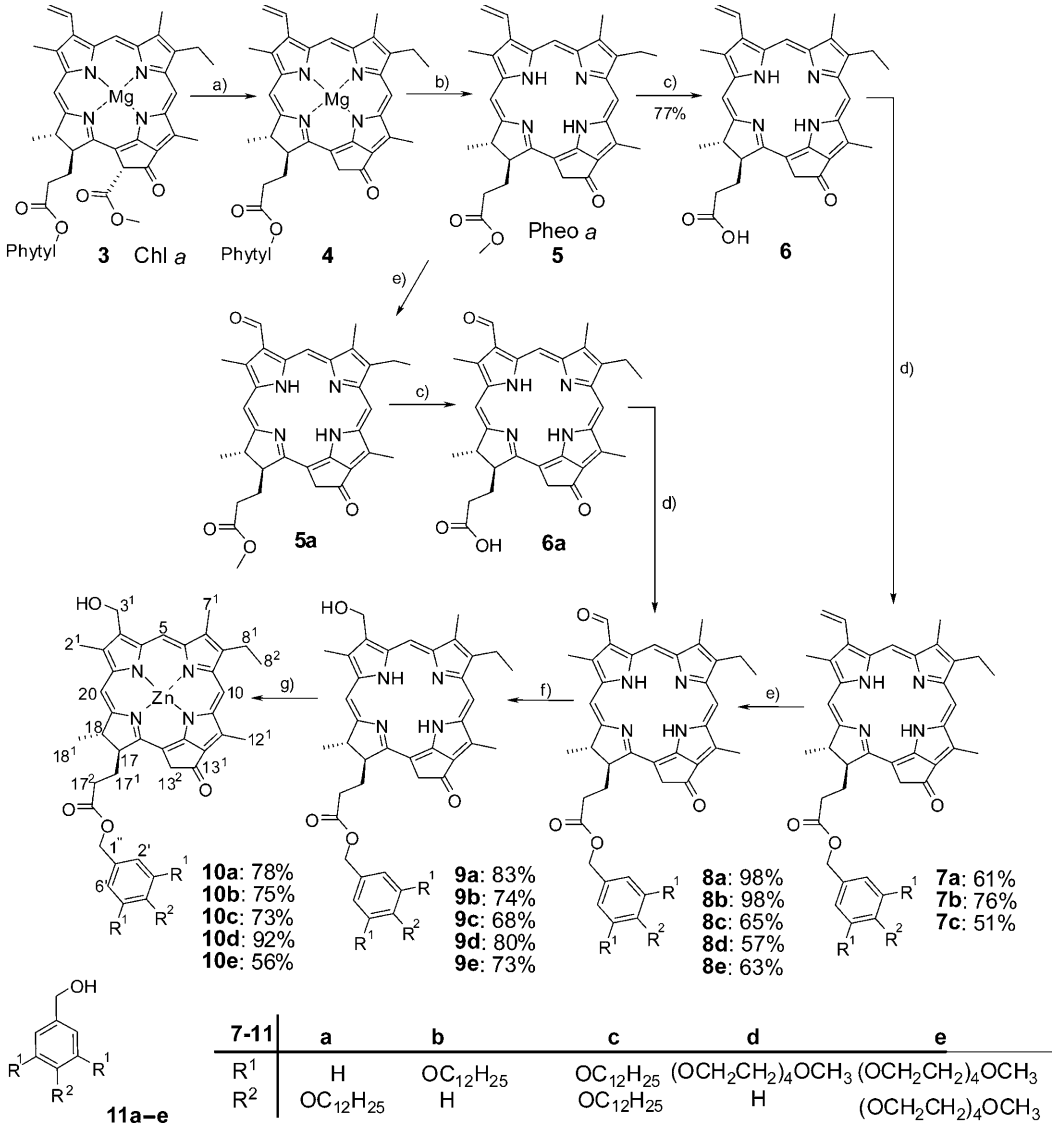
Although the self-aggregation of BChl *c*, *d*, and *e* is well known, as mentioned above, the exact structure of chlorosomal aggregates has been a matter of controversial discussion for a long time.[3i,7a,9] However, the common feature for all of the proposed structural models is the fact that the formation of the aggregates of BChl *c* is achieved by self-assembly that involves three noncovalent interactions (Scheme 1, right):[7a,10] 1) π–π interactions between the tetrapyrrole rings; 2) coordination between the central metal ion and the oxygen atom of the 3^1-hydroxy group, which creates a slipped arrangement of chromophores in the π stacks; and 3) hydrogen bonding between the 3^1-hydroxy and 13^1-keto groups, which assemble the chromophores into rod-shaped supramolecular structures. These interactions promote excitonic coupling among the most closely packed and well-ordered molecules resulting in excitonically coupled J-aggregates.[11]

Although the in vitro aggregates of **1** and **2** possess similar spectral properties to naturally occurring chlorosomal aggregates, they are of poor solubility in nonpolar solvents and thus prone to agglomeration,[12] consequently, only restricted information from spectroscopic investigations can be deduced. Balaban and co-workers have recently addressed this problem by preparing related porphyrin assemblies and they obtained microcrystalline structures that were characterized by X-ray diffraction and electron microscopy,[13] whereas we have focused our work on zinc chlorin model compounds that afford well-defined self-assembled aggregates with good solubility and lasting stability in solution to facilitate spectroscopic and microscopic investigations. Thus, we have synthesized zinc chlorins **10a–c**, which have one to three dodecyl chains at the 17^2 position,[14] as well as zinc chlorins **10d,e**, which contain hydrophilic polyethylene glycol chains (see Scheme 2), and thoroughly investigated their self-aggregation properties in nonpolar organic solvents and aqueous media, respectively.

Bacteriochlorophylls *c*, *d*, and *e* in the chlorosomes of green bacteria occur as diastereomeric mixtures, to be more specific, these are epimers because they only vary in the chirality at the 3^1 carbon center and the configurations at positions 17 and 18 are fixed.[15a] Depending on the type of bacteria and the light conditions under which they prevail, the epimeric ratio varies. Generally, the proportion of the *R* epimer outweighs that of the *S* epimer, for example, in *Chloroflexus aurantiacus* the proportion of the *R* epimer is about 67%, whereas in *Chlorobium tepidium* it is 85–90%.[15] The physiological relevance of 3^1S and 3^1R configured bacteriochlorophyll in chlorosomes is still unclear.[15a,16] Previous studies indicated that the aggregate structures of the 3^1S and 3^1R stereoisomers of the bacteriochlorophylls differ in size, and for the construction of chlorosomal light-harvesting systems both epimers are needed.[15a] In contrast to the natural bacteriochlorophyll, zinc chlorin model compound **2** lacks the methyl group at the 3^1 position. Thus, to have a better understanding of the influence of this additional chirality center on self-assembly, we have synthesized epimeric zinc chlorins (3^1S)-**17** and (3^1R)-**17** with two dodecyl alkyl chains analogous to **10b** at the 17^2 position to achieve enhanced solubility in nonpolar solvents such as *n*-hexane or *n*-heptane. The self-assembly of the epimerically pure zinc chlorins (3^1S)-**17** and (3^1R)-**17**, and mixtures with different percentages of *S* and *R* epimers have been studied in nonpolar solvents by UV/Vis and CD spectroscopies. Herein, we provide the synthetic and characterization details of zinc chlorins **10a–e** and **17** and report in-depth investigations of self-assembly of these dyes into soluble biomimetic light-harvesting aggregates that aim to contribute to the structural elucidation of chlorosomal antennae and to a better understanding of the structure–property relationships of these highly efficient light-harvesting systems.

Results and Discussion

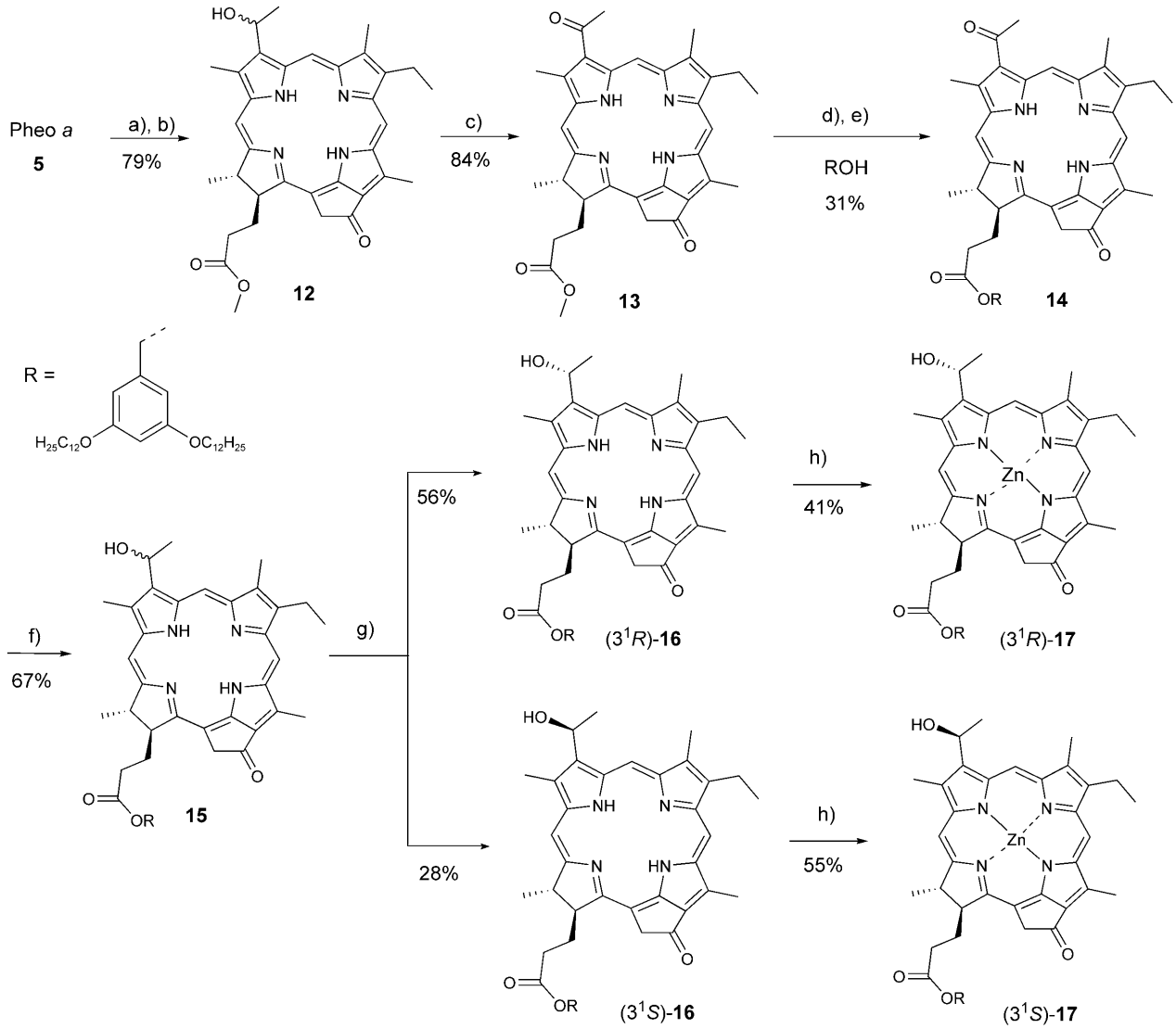
Synthesis of zinc chlorins 10a–c with 17^2-dodecyl chains and 10d,e with 17^2-oligoethylene glycol chains: Zinc chlorins **10a–e** were synthesized from Chl *a*, which was extracted from cyanobacteria *Spirulina platensis*[17] according to the route outlined in Scheme 2. Chl *a* was converted into pheophorbide *a* according to a literature procedure,[17] and the



Scheme 2. Synthesis of zinc chlorins **10 a**–**e**: a) Collidin, 170 °C, 6 h; b) concd H_2SO_4, MeOH, RT, 12 h; c) concd HCl, RT, 6 h; d) appropriate benzyl alcohol **11a**–**e**, DCC, DMAP, DPTS, Hünigs base, CH_2Cl_2, RT, 3–4 h; e) OsO_4, $NaIO_4$, AcOH, THF/H_2O, RT, 5 h; f) $BH_3(t\text{Bu})NH_2$, THF, RT, 2–4 h; g) $Zn(OAc)_2$, MeOH, THF, RT, 3 h.

latter was further hydrolyzed with concentrated hydrochloric acid in a yield of 77%. This was followed by esterification of **6** with the respective dodecyloxybenzyl alcohols **11a**–**c** and in the case of **6a** also with tetraethyleneoxybenzyl alcohols **11d**,**e** in the presence of dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), 4-(dimethylamino)pyridinium-*p*-toluenesulfonate (DPTS), and Hünigs base (*N*-ethyldiisopropylamine) in dry dichloromethane,[18] leading to the corresponding esters **7a**–**c** in yields of 51–76% and **8d**,**e** in yields of 57–63%. Subsequently, the 3^1-vinyl group of **7a**–**c** was transformed into the corresponding diol with osmium tetroxide, followed by oxidative cleavage by sodium periodate to afford the respective formyl derivatives **8a**–**c** in yields of 65–98%. Selective reduction of the formyl groups of **8a**–**e** to the corresponding alcohols **9a**–**e** was carried out with borane-*tert*-butylamine complex with a yield of 68–83%. Finally, the metalation step with methanolic zinc acetate in tetrahydrofuran (THF) afforded the zinc chlorins **10a**–**e** as turquoise green solids with yields of 56–92%. The intermediates and final products were purified by silica gel column chromatography, and subsequently by HPLC and characterized by ^{1}H NMR spectroscopy and high-resolution mass spectrometry (HRMS).

Synthesis of epimeric zinc chlorins with 3^1R and 3^1S configurations: The synthetic route to the epimeric zinc chlorins **17** is shown in Scheme 3. Starting from Pheo *a* (**5**), 3^1-hydroxyethyl Pheo *a* **12** was synthesized in two steps according to a known literature method.[16a,19] The 3^1-vinyl group of the Pheo *a* was subjected to bromination with 38% HBr in acetic acid, followed by substitution of the bromine atom with a hydroxyl group. In the subsequent step, the hydroxy



Scheme 3. Synthesis of zinc chlorins ($3^1R/S$)-**17**: a) 38% HBr/AcOH, RT, 12 h; b) MeOH, concd HCl, RT, 0.5 h; c) tetrapropylammonium perruthenate (TPAP), *N*-methylmorpholine-*N*-oxide (NMO), CH_2Cl_2, RT, 2 h; d) concd HCl, RT, 3 h; e) **11b**, DCC, DMAP, DPTS, Hünigs base, CH_2Cl_2, RT, 2.5 h; f) $NaBH_4$, EtOH, THF, RT, 1.5 h; g) separation of the epimers by HPLC with a chiral column (reprosil 100 chiral-NR) with *n*-hexane/CH_2Cl_2 (1:1) as eluent; h) $Zn(OAc)_2$, MeOH, THF, 1 h.

group was oxidized into the corresponding ketone **13** with tetrapropylammonium perruthenate and *N*-methylmorpholine-*N*-oxide in a yield of 84%.[20] Next, the 17^2-propionate ester was hydrolyzed into the corresponding carboxylic acid with concentrated HCl, and the resulting acid was esterified with 3,5-bis(dodecyloxy)benzyl alcohol **11b** as described before to afford the corresponding ester **14** in a yield of 31%. The $3^1R/S$ diastereomers of hydroxyethyl derivative **15** were obtained by the reduction of ketone compound **14** with sodium borohydride in dry ethanol in a yield of 67%. The diastereomers were separated by semipreparative HPLC using a chiral column in normal phase, and the integration of the HPLC chromatogram showed >99 and >95% diastereomeric purity for 3^1S-**16** and 3^1R-**16**, respectively. The separation of the diastereomers was followed by the metalation of 3^1R-**16** and 3^1S-**16** with a saturated solution of methanolic zinc acetate in THF as the solvent to afford the diastereomeric zinc chlorins 3^1R-**17** and 3^1S-**17**, which were again purified by semipreparative HPLC using a chiral column in normal phase. The intermediate products **12–15** were purified by HPLC with a reverse-phase column and characterized by ^{1}H NMR spectroscopy and HRMS. The configurations of 3^1R-**17** and 3^1S-**17** were assigned by comparing the HPLC retention times and significant ^{1}H NMR chemical shifts of these diastereomers with those of similar compounds reported in the literature (for details see the Supporting Information).[15b,16a,c,21]

Optical properties of zinc chlorins 10a–c and spectroscopic studies of their aggregation: The optical properties of monomers and aggregates of zinc chlorins **10a–c** have been characterized by UV/Vis and CD spectroscopies. For this pur-

pose, monomer stock solutions of the respective zinc chlorin were prepared in THF and subsequently added to nonpolar solvents, such as *n*-hexane or *n*-heptane, to prepare aggregate solutions containing 1 vol% THF.

The formation of aggregates can be visually observed by the instantaneous color change of turquoise-blue monomer solutions to a pale-green color in the aggregate solutions (Figure S2 in the Supporting Information). Compared with the absorption bands of the monomeric zinc chlorins, aggregates of these dyes show redshifted absorption maxima due to J-type excitonic coupling between the S_0-S_1 transition dipole moments of the chlorin Q_y bands.[11] Therefore, the aggregation properties of zinc chlorin dyes can be conveniently assessed by UV/Vis spectroscopy as the aggregate Q_y band shows a large bathochromic shift (about 100 nm), compared to that of the corresponding monomers. As can be seen in Figure 1, the maxima of the Q_y absorption bands of

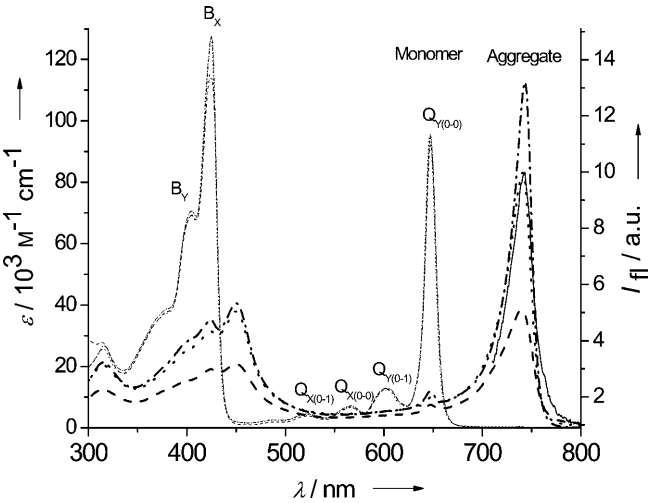


Figure 1. UV/Vis spectra of the zinc chlorin monomer **10a–c** in THF (λ_{Qy}=647 nm) and their aggregates (λ_{Qy}=740–743 nm) in *n*-heptane/THF (100:1) at RT (*c* for **10a**=1.2×10^{-5} M (– – –); *c* for **10b**=1.6×10^{-5} M (•••••); *c* for **10c**=2.8×10^{-5} M (–•–•). Thin lines refer to the monomers whereas thick lines are for the aggregates. Fluorescence emission spectrum (λ_{ex}=690 nm) of the aggregates of **10b** (——) in *n*-heptane/THF 100:1 is also shown; I_{fl}=fluorescence intensity.

the monomers of **10a–c** in THF appear at 648 nm, whereas for the corresponding aggregates in *n*-heptane/THF (100:1) the Q_y-band maxima occur at 741–743 nm for this series of compounds. Owing to precipitation from the aggregate solution, the absorption coefficient (ε) for **10a** aggregates appears to be too small.

The fluorescence emission spectrum of **10b** aggregates reveals a small Stokes shift of about 1 nm. The bathochromic shift of the Q_y band and the small Stokes shift are characteristic for the formation of J-aggregates.[11]

The long-term stability of the aggregates of **10a–c** was investigated by recording time-dependent UV/Vis spectra. A decrease in the absorbance of the aggregate solutions over a period of two days at room temperature indicates precipitation from the solution. Unlike the known literature model compound **2**, zinc chlorins **10b** and **10c** with two and three alkyl chains, respectively, form soluble aggregates that are stable for a long time in nonpolar solvents, which is evident by the almost unchanged absorption over two days (Figure S3 in the Supporting Information). In contrast, aggregates of **10a** show uncontrolled agglomeration over the course of a few hours, which leads to a decrease in absorption of the Q_y aggregate band and finally to precipitation. Based on these observations, it can be concluded that at least two alkyl chains at the 17^2 position are necessary for properly soluble and persistent aggregates of zinc chlorins in nonpolar solvents.

For further characterization of the self-assembly of chlorins **10b** and **10c**, the aggregation process was investigated by temperature-dependent UV/Vis spectroscopy in the temperature range between 15 and 95 °C. For this purpose, the zinc chlorins were dissolved in di-*n*-butyl ether (20%), followed by the addition of the nonpolar solvent *n*-heptane (80%) to initiate self-assembly. Prior to each measurement, the solutions were allowed to equilibrate for 1.5 h at the measuring temperature to ensure a stationary state. As shown in Figure 2a for zinc chlorin **10c**, with increasing temperature the Q_y band of the aggregates at 741–742 nm decreases and the monomer band at 648 nm increases. These spectral changes reveal that the aggregates dissociate at higher temperature. Upon cooling to the initial temperature of 15 °C, the Q_y band was completely recovered, which is indicative of the reversibility of the aggregation process. Similar observations were made for dye **10b**[14] (Figure S4 and S5 in the Supporting Information). Another remarkable feature of both dyes is that no precipitation was observed upon heating and cooling processes, proving the thermodynamic stability of the aggregates unlike many other self-organized dye aggregates[22] and model compound **2**.

Although, the aggregates of **10b** and **10c** in solution show similar properties, they can be distinguished by their distinct melting temperatures. The plot of normalized absorption at 741 nm of the Q_y band of the aggregates versus temperature provides sigmoidal curves (Figure 2b for **10c**), which can be approximated with the Boltzmann function [Eq. (1)],[23]

$$A = \frac{A_{agg}-A_{mon}}{1+e^{\frac{T-T_m}{\Delta T}}}+A_{mon} \quad (1)$$

in which A is the total absorption and can be expressed as a linear combination of absorption for the monomer and aggregates [Eq. (2)].

$$A = A_{agg}\alpha_{agg}+A_{mon}(1-\alpha_{agg}) \quad (2)$$

The term α_{agg} in Equation (2) is the normalized fraction of aggregated molecules, which can be related to the melting temperature T_m [Eq. (3)] at which $\alpha=0.5$ and ΔT are related to the width of the curve.

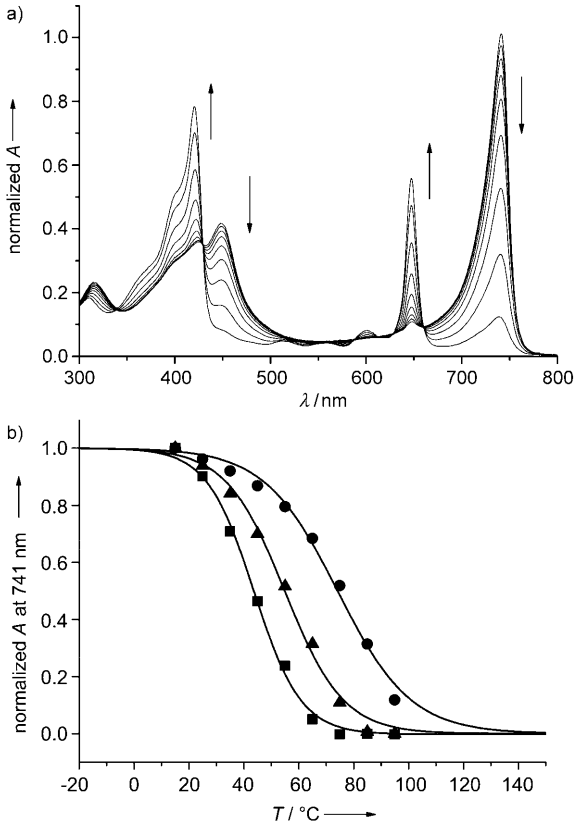


Figure 2. a) Temperature-dependent UV/Vis spectra of **10c** in *n*-heptane/di-*n*-butyl ether (4:1) at a concentration of 9.6×10^{-6} M. The initial temperature of 15 °C was increased successively in 10 °C steps up to 95 °C and at each temperature the solution was allowed to equilibrate prior to measurement; arrows indicate changes upon increasing temperature. b) Data points for the decrease of normalized absorption of the Q_y aggregate band at 741 nm at three different concentrations of solvents with increasing temperature and fitted curves with the Boltzmann function. The melting temperatures were obtained from fitted curves and are 74 °C at $c=9.6\times10^{-5}$ M (●), 55 °C at $c=5.8\times10^{-5}$ M (▲), and 44 °C at $c=2.9\times10^{-5}$ M (■). The UV/Vis spectra at concentrations of 5.8×10^{-5} M and 2.9×10^{-5} M are shown in Figure S6 in the Supporting Information.

$$\alpha_{agg}=\frac{1}{1+e^{\frac{T-T_m}{\Delta T}}} \quad (3)$$

Curve fitting with the Boltzmann function provided a concentration-dependent melting temperature in the range of 44 to 74 °C for the zinc chlorin **10c** (Figure 2b), whereas for **10b** melting temperatures of 60 and 74 °C at concentrations of 3.1×10^{-6} and 1.1×10^{-5} M, respectively, were observed (Figure S4, inset in the Supporting Information). A comparison of the melting temperatures of zinc chlorins **10b** and **10c** (60 and 44 °C, respectively) at very similar concentrations (3×10^{-6} M) of solutions reveals a higher thermodynamic stability for the aggregates of **10b**.

The dissociation of aggregates takes place not only at increasing temperature, but also in the presence of coordinating or polar solvents. Thus, the addition of 20–30% dichloromethane to the aggregate solution of **10c** in *n*-heptane led to a pronounced decrease of the aggregate band at 737 nm and the monomer band at 650 nm increased concomitantly. In addition to that, the maximum of the Q_y band shifted from 737 to 723 nm upon increasing the dichloromethane content, which suggested that the π–π interactions are disturbed by the solvent molecules that strongly interact with π systems, leading to dissociation of the aggregates (Figure S7 in the Supporting Information).

Further insight into the aggregation process for zinc chlorins **10b** and **10c** was obtained by temperature-dependent CD spectroscopy between 15 and 95 °C in *n*-heptane/di-*n*-butyl ether (4:1). The CD spectra (Figure 3) show a bisignate signal in the region of Q_y aggregate band as a result of an induced CD effect through excitonic coupling of the transition dipole moments[24] of chiral zinc chlorins. With increasing temperature the intensity of the CD signals decreases, which indicates the dissociation of aggregates. The observed exciton couplet reversibly arises (aggregate formation) and disappears (aggregate dissociation) upon changes to the temperature, validating the reversibility of the self-assembly process, hereby the signals do not undergo any time-dependent change at a particular temperature.

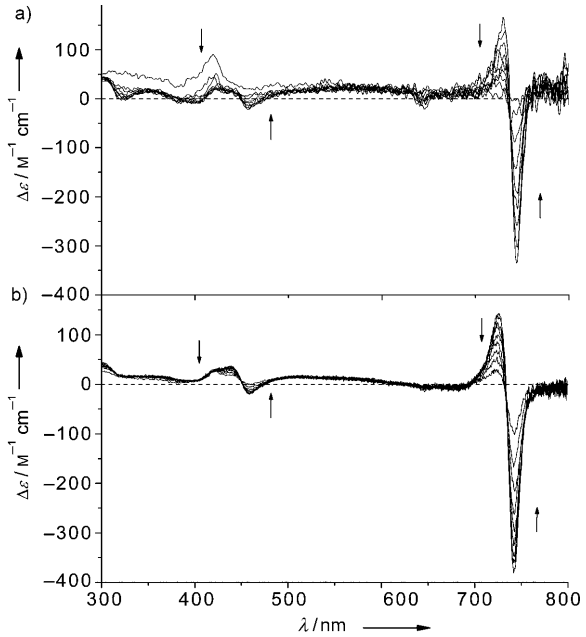


Figure 3. Temperature-dependent CD spectra of a) **10b** in *n*-heptane/di-*n*-butyl ether (4:1) at a concentration of 1.1×10^{-5} M and b) **10c** in *n*-heptane/di-*n*-butyl ether (4:1) at a concentration of 3.1×10^{-6} M. The initial temperature of 15 °C was increased successively in 10 °C steps up to 95 °C and at each temperature the solution was allowed to equilibrate prior to measurement; arrows indicate changes upon increasing temperature. The anisotropy factor calculated at 15 °C for **10b** is $g_{726}=2.51\times10^{-3}$ and for **10c** is $g_{730}=2.46\times10^{-3}$.

Surprisingly, different CD exciton couplets of isolated chlorosomes and in vitro BChl *c* aggregates were reported in the literature.[17a,25] Griebenow and co-workers have classified the observed CD spectra into three different types: in type I the sign of the CD curve changes from positive at

smaller wavelengths to negative at longer wavelengths [+/−], type II is the opposite of type I [−/+], and also the so-called mixed type [−/+/−].[26a] In a theoretical approach by the groups of Holzwarth and Knoester, it has been proposed that different types of CD spectra are the result of a "size effect".[26b,c] According to Holzwarth et al., type II converts to a mixed type at an aggregate length of over 30 molecules of BChl *c*.[26b] Interestingly, zinc chlorins **10b**,**c** show type I CD spectra and exhibit exciton couplets, which have close spectral resemblance to that of zinc chlorin model compound **2**.

Spectroscopic properties of the zinc chlorins 10d and 10e: The aggregation studies for zinc chlorins **10d**,**e** were performed in aqueous media because these dyes possess 17^2-hydrophilic side chains. For this purpose, monomer stock solutions of **10d**,**e** were prepared in THF and subsequently added to ultrapure water Milli-Q to prepare aggregate solutions in water containing 1 vol% THF. The formation of aggregates of **10d** was evident by an immediate color change from turquoise-blue monomer solutions to the pale-green color of aggregate solutions and the redshift of the Q_y aggregate band from 648 (in THF) to 733 nm (in water/THF 100:1) (Figure 4a), indicating self-assembly of this dye. The Q_y aggregate band showed a further bathochromic shift of up to 747 nm within 24 h, which was, however, accompanied by the formation of some precipitate. Also in the case of **10e**, which has three tetraethylene glycol side chains, no long-lasting solubility of the aggregates in water could be achieved. In fact, a slight shift of the Q_y aggregate band from 736 to 734 nm was observed after 24 h (Figure 4b), which can be attributed to the additional hydrophilic side chain in **10e**, which has a higher spatial demand leading to destabilization of the aggregates. The solubility properties of zinc chlorins **10d**,**e** in water/methanol were also examined, and a similar spectral pattern to that obtained in water/THF were observed.

With zinc chlorin **10d**, the formation of aggregates in water with a Q_y-band shift of 733 to 747 nm (Figure 4a), which lies in the same range as for chlorosomal aggregates, is achieved. Further evidence for the formation of J-aggregates of **10d** in water is provided by CD spectroscopy, as a bisignate CD couplet, similar to that of **10b**, is observed. The positive and negative peak values appear in the higher wavelength region at $\lambda = 742$ nm ($\Delta\varepsilon = 362\,\text{M}^{-1}\text{cm}^{-1}$) and $\lambda = 753$ nm ($\Delta\varepsilon = -544\,\text{M}^{-1}\text{cm}^{-1}$), whereas at the lower-wavelength region positive and negative peak values occur at $\lambda = 443$ nm ($\Delta\varepsilon = 54\,\text{M}^{-1}\text{cm}^{-1}$) and $\lambda = 466$ nm ($\Delta\varepsilon = -29\,\text{M}^{-1}\text{cm}^{-1}$).

Previously, work on the water solubility of chlorosome analogue aggregates was reported by Tamiaki's group in which the self-aggregates of BChl *c* or zinc chlorin model compound **2** were embedded in silicate capsules in which alkoxysilanes imitate the hydrophobic microenvironment of chlorosomes.[27] In another approach to attain water solubility, amphiphilic zinc chlorins with polyethylene glycol chains ($O(CH_2CH_2O)_nH$) or ($O(CH_2CH_2O)_nCOCH_3$) in the 17^2 position were employed. These chlorins showed smaller bathochromic shifts of the Q_y band in water/THF (100:1) in the range of 675 to 729 nm,[28] which was attributed to the formation of dimers or higher aggregates, unlike in the case of **10d** for which a significantly stronger redshift of up to 747 nm indicates extended chlorosomal-type aggregates.

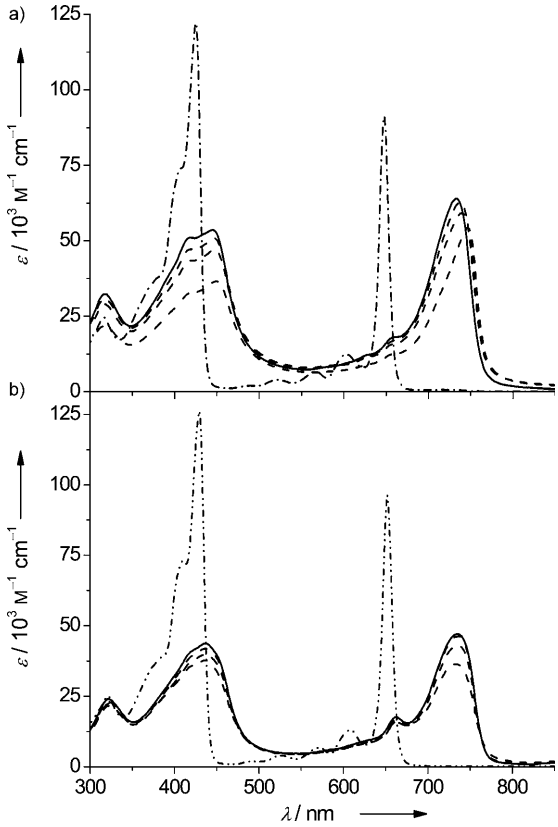


Figure 4. UV/Vis spectra of zinc chlorins a) **10d** at $c = 5.8\times10^{-6}$ M and b) **10e** at $c = 1.4\times10^{-5}$ M. Monomers (–•–•) in THF and aggregates (—— and ----- lines) in water with THF (100:1). Dashed lines refer to the aggregate spectra in a time course of 24 h. Decrease in the intensity of aggregate bands and the concomitant increase in the baseline are indicative of precipitation of the zinc chlorins.

Spectroscopic studies on aggregation properties of epimeric zinc chlorins (3^1R)-17 and (3^1S)-17: To explore the impact of the 3^1 chirality center on self-assembly of zinc chlorins, the aggregation behavior of $3^1R/S$-**17** was studied in detail by UV/Vis spectroscopy. Samples were prepared as before by dissolving (3^1R)-**17** and (3^1S)-**17** in THF to obtain monomer stock solutions, followed by the addition of a nonpolar solvent such as *n*-heptane (*n*-heptane/THF 100:1) to initiate aggregate formation. In the case of aggregates of epimerically pure (3^1S)-**17** (Figure 5b), a bathochromic shift of the absorption maxima of the Q_y band was observed from 648 (monomer) to 711 nm (aggregates), whereas the Q_y band for the aggregates of (3^1R)-**17** epimer shifted from 648 to 705 nm (Figure 6b). In solutions of both epimers, a significant proportion of monomers prevailed even after two to three days. This is in contrast with zinc chlorins **10b**,**c** for

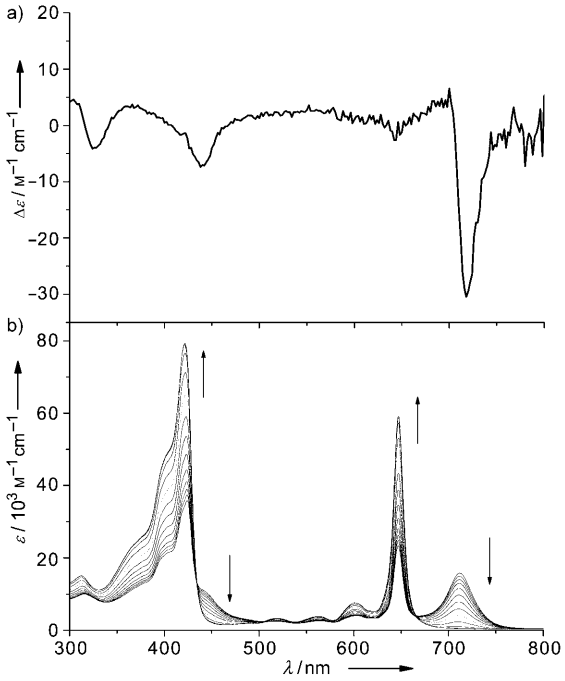


Figure 5. Spectroscopic investigation of zinc chlorin epimer (3^1S)-**17** in *n*-heptane/THF (100:1) at $c = 1.7 \times 10^{-5}$ M. a) CD spectrum at 20 °C. b) UV/Vis spectra in the temperature range of 20–80 °C measured at 5 °C intervals starting from 20 °C; the sample was allowed to equilibrate for 45 min prior to each measurement; arrows indicate changes upon increasing temperature.

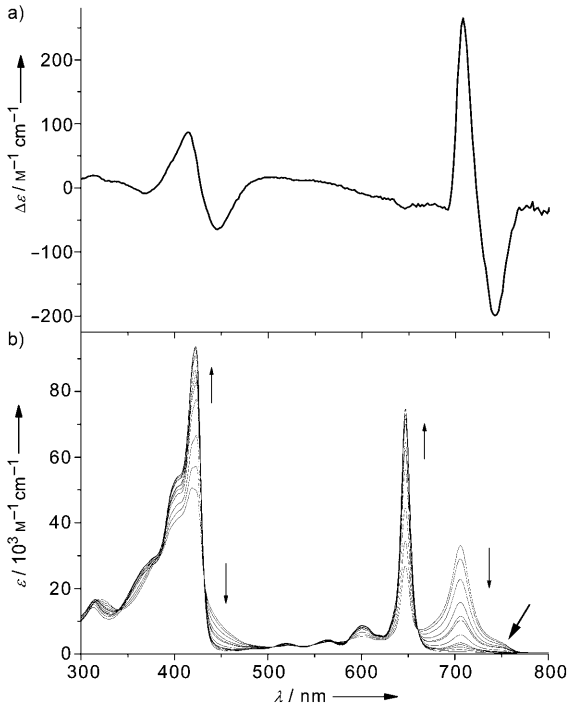


Figure 6. Spectroscopic investigation of the zinc chlorin epimer (3^1R)-**17** in *n*-heptane/THF (100:1) at $c = 1.7 \times 10^{-5}$ M. a) CD spectrum at 20 °C. b) UV/Vis spectra in the temperature range of 20–80 °C measured at 5 °C intervals starting from 20 °C, the sample was allowed to equilibrate for 45 min prior to each measurement; arrows indicate changes upon increasing temperature.

which, under comparable conditions, monomers could barely be observed. Additionally, the bathochromic shift of the Q_y band for (3^1R)-**17** and (3^1S)-**17** is less pronounced than the shift observed in the case of **10b**,**c** (up to 742 nm) without the 3^1-methyl group. These results indicate that (3^1R)-**17** and (3^1S)-**17** may form dimers or smaller oligomers rather than extended aggregates like rods, as in the case of **10b**,**c**. Noteworthy, however, is the fact that the UV/Vis spectra of the (3^1R)-**17** epimer shows a shoulder at about 747 nm (Figure 6b, bold arrow), where the absorption maxima for the extended rod aggregates of **10b**,**c** also appear.

The stability of the aggregates of zinc chlorins (3^1R)-**17** and (3^1S)-**17** was explored by temperature-dependent UV/Vis measurements in the range of 15 to 80 °C. With increasing temperature, the monomer bands of the zinc chlorins at 648 nm increased, whereas the aggregate bands at 711 and 705 nm for (3^1S)-**17** and (3^1R)-**17**, respectively, decreased, which is indicative of the dissociation of aggregates at higher temperatures. Upon cooling the aggregate solutions, the aggregate bands were completely recovered for both epimers, which confirmed that the aggregation was reversible.

Curve fitting with the Boltzmann function[23] provided a melting temperature of 49 °C for aggregates of (3^1S)-**17**, whereas a significantly lower melting temperature of 22 °C was obtained for the aggregates of (3^1R)-**17**, revealing a higher stability for the (3^1S)-**17** aggregates despite their less-defined J-aggregate spectra. Also, the CD spectra for the aggregates of (3^1R)-**17** and (3^1S)-**17** show distinct differences.

Thus, the amplitude of the CD signals for (3^1R)-**17** are not only higher in magnitude than those of (3^1S)-**17**, but also show a well-defined bisignate shape similar to **10b,c** (type I according to Griebenow et al.[26a]). The negative CD signal for the (3^1R)-**17** (742 nm) is also shifted more bathochromically compared with that of the (3^1S)-**17** stereoisomer (718 nm). Notably, in such partially self-assembled systems, a variety of aggregates with different size and geometry may prevail, which can exhibit quite distinct CD spectra. For this reason, UV/Vis and CD spectra do not always properly match together in such a situation. Thus, in the case of (3^1R)-**17** we attribute the intense bisignated CD signal (Figure 6a) at long wavelengths to a small fraction of extended chlorosomal-type J-aggregates that appeared as a shoulder in the UV/Vis spectra (Figure 6b, bold arrow).

In addition to investigations on the self-assembly of pure (3^1R)-**17** and (3^1S)-**17** epimers, we have also studied the mixtures of these epimers by UV/Vis spectroscopy. For this purpose, stock solutions of the epimers in THF were mixed in respective ratios and added to *n*-hexane for the formation of aggregates. To achieve the highest possible amount of aggregates compared with monomers, solutions containing only 0.5 vol% THF were used. To make the different shifts and forms of aggregation bands intelligible, the absorption spectra (Figure 7) are normalized. The higher the percentage of (3^1S)-**17**, the further the main aggregate Q_y band was bathochromically shifted.

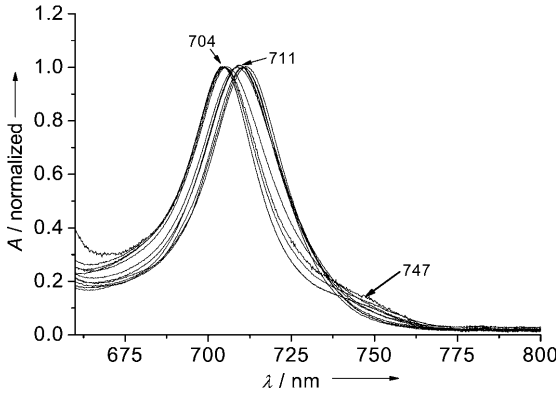


Figure 7. Normalized UV/Vis spectra (for clarity only the higher wavelength region is shown) of zinc chlorin Q_y band of (3^1R)-**17** and (3^1S)-**17** and their mixture in *n*-hexane with 0.5% THF ($c_{S\text{-}17}=c_{R\text{-}17}=9.6\times10^{-6}$ M). The spectra, from left to right, are for 100:0 *R*/*S* to 0:100 *R*/*S* with 10% incremental increases of the *S* epimer. The absorption maxima for pure (3^1R)-**17** and (3^1S)-**17** occur at 704 and 711 nm, respectively.

In several previous publications it was reported that the aggregation modes of 3^1R and 3^1S epimers of bacteriochlorophylls are quite distinct.[15c,16a–d] As in the case of the present zinc chlorin **17** epimers, earlier studies on BChl *c* and *e* revealed a larger bathochromic shift for the aggregate band of *S* epimers.[15c,16c,29] Compared with earlier studies on BChl *c* and *e*, a more pronounced bathochromic shift for the Q_y aggregate band for (3^1S)-**17** was observed. Thus, for aggregate bands of 3^1R-BChl *c* and 3^1S-BChl *c*, absorption maxima at 703 and 750 nm, respectively, were observed in concentrated dichloromethane.[15c]

For the epimers of BChl *e* in cyclohexane, the 3^1R-BChl exhibited the Q_y absorption maximum at 706 nm and the *S* epimer at 717 nm.[16c] Two previous independent studies showed that the addition of small amounts of the corresponding *S* epimers to solutions of *R* epimers of BChl *c* and *e* afforded aggregates with further bathochromically displaced Q_y absorption bands than those observed in the case of pure *R* epimers.[16c,d] These observations were considered to be supportive for the bacteriochlorophyll "double-tube" model, in which the outer layer is formed preferentially by *R* epimers and the inner tube by *S* epimers. However, our mixing experiments with the epimeric zinc chlorins (3^1R)-**17** and (3^1S)-**17** did not show such an effect.

Furthermore, it was previously reported that a methyl group at the 3^1 position suppresses aggregation, whereas an additional methyl group at this position (tertiary alcohol) has no further influence.[30] Thus, our observation that the 3^1 methyl group in zinc chlorin **17** has a strong influence on the aggregation behavior is in accordance with previous studies.

Microscopic characterization of aggregates of zinc chlorins: Followed by spectroscopic investigations, structural properties of the zinc chlorin aggregates were elucidated by atomic force microscopy (AFM). AFM measurements under ambient conditions allowed the visualization of the self-assembled rod aggregates of zinc chlorin **10b**.[14] Tapping-mode AFM images of an aggregate solution of **10b** (Figure 8) on a highly ordered pyrolytic graphite (HOPG) surface exhibited

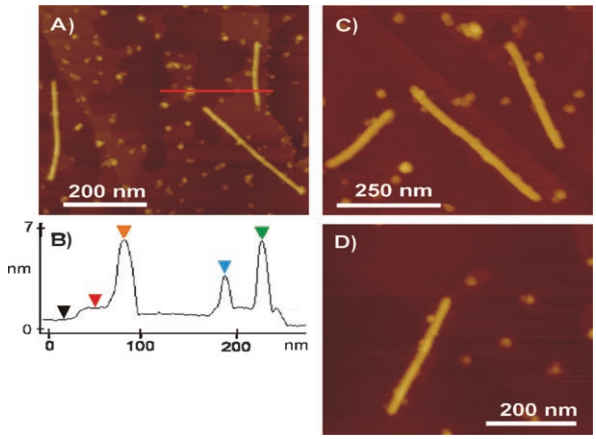


Figure 8. Tapping-mode AFM images of aggregates of zinc chlorin **10b** on HOPG. Different areas and enlargements of the sample are displayed in A), C), and D); B) shows the height profile along the red line in A). The sample was prepared by spin-coating of a solution of **10b** in *n*-hexane/THF (100:1) on HOPG and measured in air.

isolated rod aggregates with contour lengths of (300±97) nm and heights of (5.8±0.4) nm (vertical distance between the black and green triangle in Figure 8B) were in quite good agreement with the electron microscopy data for the chlorosomal (*C. aurantiacus*)[31] BChl *c* rod aggregates and also with the tubular model by Holzwarth.[32]

Besides rod-aggregates, globular structures with average heights of (3.1±0.6) and (5.6±0.7) nm (vertical distance between the black and blue and black and orange triangles, respectively, in Figure 8B) can also be seen, which are either formed by degradation of rods during the spin-coating process or they co-exist in solution with the rod-aggregates. An argument in favor of the first interpretation is the fact that the number of extended rod-aggregates diminishes over time. This indicates a low stability of these rod aggregates on the HOPG surface in air and suggests that evaporation of residual solvent molecules from the inner core of a tubular assembly destabilizes the rod architecture.

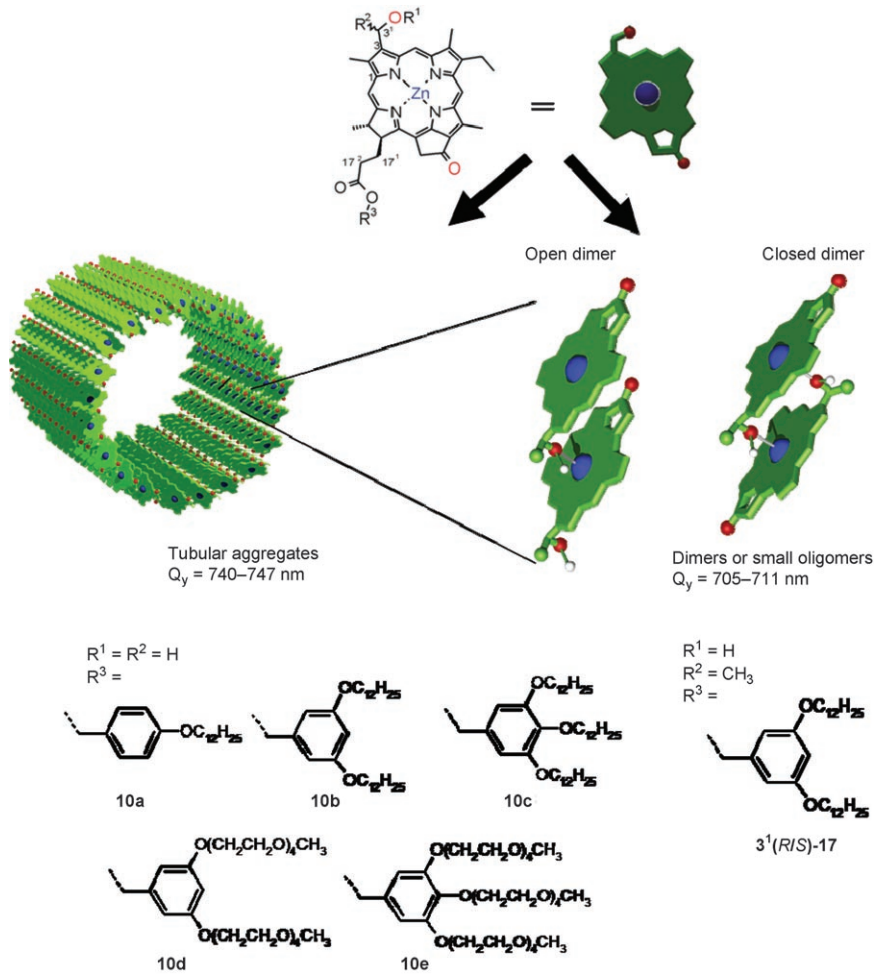
Conclusions

With the newly synthesized zinc chlorins it was possible to build model systems of natural light-harvesting BChl aggregates that are, in contrast to literature reported for zinc chlorin **2** aggregates, characterized by a proficient and durable solubility. This favorable property allowed thorough spectroscopic and microscopic investigations for the elucidation of the aggregate structural and optical features. To achieve solubility in nonpolar organic solvents, zinc chlorins with one (**10a**), two (**10b**), and three (**10c**) dodecyl side chains were synthesized, thereby a durable solubility of the

self-assembled aggregates was obtained with two or more side chains (**10b**,**c**). UV/Vis and CD spectroscopic studies have shown that the formation of the self-assemblies of **10b**,**c** is reversible. Moreover, based on the congruent position of aggregate Q_y bands (λ_{max} = 741–743 nm) in UV/Vis spectra and similar bisignate signals in the CD spectra of the zinc chlorins **10b**,**c** aggregates and natural BChl *c* aggregates, it could be concluded that the short-range arrangement of these aggregate structures is quite similar. AFM of **10b** aggregates provided direct evidence for the rod-shaped structure of the aggregates of this class of substances. To achieve water-soluble zinc chlorin aggregates, hydrophilic tetraethylene glycol side chains were introduced at the 17^2 position of the chlorin unit (**10d**,**e**), and they indeed self-assemble with similar spectral properties as the natural BChl *c* counterparts.

To relate these results to the natural BChl *c* aggregate structures and to investigate the influence of the chiral center at the 3^1 position on aggregation, epimeric zinc chlorins (3^1S)-**17** and (3^1R)-**17** were synthesized and isolated as pure stereoisomers. Spectroscopic studies revealed a strong influence of the methyl group at the 3^1 position on aggregation, leading to a decreased aggregation propensity of both diastereomers compared with **10b**,**c**. These observations suggest the formation of open or closed dimers, or other small oligomers of **17**. An additional Q_y band at 747 nm was only detected for (3^1R)-**17**, which can be ascribed to the formation of extended rod-shaped aggregates, as observed for the chlorosomal light-harvesting systems. Scheme 4 summarizes the structure–property relationships for the semisynthetic zinc chlorins **10a**–**e** and **17** investigated in this work.

To conclude, zinc chlorins with dodecyl side chains **10b**,**c** or containing polyethylene glycols **10d**,**e** form higher aggregates with nanorod shapes. In contrast, the aggregation propensity of zinc chlorins (3^1S)-**17** and (3^1R)-**17** with a methyl group at the 3^1 stereogenic center is strongly reduced, as evident from the less-pronounced aggregation and the smaller bathochromic shift of their Q_y aggregate bands. These relationships between molecular structure and self-assembly capability toward functional J-aggregates reveal a prominent influence of the 3^1-methyl group.



Scheme 4. Schematic illustration of the self-assembled aggregate structures and assignment of the zinc chlorins to the respective aggregate structures.

Experimental Section

General procedures

Acidic ester hydrolysis: Pheo *a* or its derivatives were dissolved in small amounts of THF and subsequently concentrated hydrochloric acid (5–10 mL) was added. After stirring for 5–6 h at RT under an argon atmosphere, the reaction mixture was poured into saturated aqueous $NaHCO_3$ solution and solid $NaHCO_3$ was added to adjust the pH to 6–7. The resulting carboxylic acids were extracted with CH_2Cl_2 and the solution was dried with sodium sulfate. After removal of the drying agent by filtration, the solvent was removed by rotary evaporation and the crude product was purified by column chromatography with mixtures of CH_2Cl_2/methanol as the eluent. The analytical data for the chlorin carboxylic acids obtained are in accordance with those reported in literature.[33]

Esterification of chlorin carboxylic acids: The free carboxylic acids at the 17^2 position of the chlorins were esterified with the respective alcohols by using dried coupling reagents. Chlorin carboxylic acids were dissolved in as small amounts of dry CH_2Cl_2 as possible and vacuum-dried coupling reagents DCC, DMAP, and DPTS were added in the presence of Hünigs base. After stirring at RT for 6 h in the dark, the resulting 17^2 esters were purified by silica gel column chromatography.

Oxidation reaction: The 3^1-vinyl group of chlorins was converted into the corresponding diol with a catalytic amount of OsO_4, followed by oxidative cleavage of the diol by sodium periodate ($NaIO_4$).[34] The respective 3^1-vinyl chlorin was first dissolved in THF, followed by the addition of

small amounts of a 1:1 mixture of water and acetic acid and then a catalytic amount of osmium tetroxide (1–2 small crystals; due to the toxicity of osmium tetroxide, weighing was avoided) was added. Subsequently, the reaction mixture was stirred at RT under an argon atmosphere, and the reaction was monitored by thin-layer chromatography. When significant amounts of diol intermediate were formed after 1–1.5 h, a saturated aqueous sodium periodate solution was added dropwise by a syringe pump (5–10 mL h^{-1}) within 2–4 h. Thereby a color change from olive green to the grey diol intermediate and then finally to brown 3^1-aldehyde was observed. Afterwards, water (100 mL) and diethyl ether (100 mL) were added and the acetic acid was neutralized with saturated aqueous $NaHCO_3$ solution. The product was extracted with diethyl ether (3× 100 mL) and washed several times with water (50 mL), and finally dried over sodium sulfate. After filtration to remove the drying agent the solvent was removed with a rotary evaporator.

Reduction reaction: The 3^1-formyl group of chlorins was selectively reduced to the corresponding primary alcohol with 10 equiv of borane-*tert*-butylamine complex (BH_3(*t*Bu)NH_2) reagent.[17a] The respective 3^1-formyl chlorin was dissolved in THF, followed by the addition of the boron reagent and the mixture was stirred at RT under an argon atmosphere. The color of the reaction mixture changed from dark brown to olive green, which indicated the formation of the chlorin with a 3^1-alcohol functionality. Diethyl ether (100 mL) and water (50 mL) were added to the reaction mixture and the amine complex was neutralized with saturated ammonium chloride aqueous solution (20 mL). The organic phases were washed several times with water and dried over sodium sulfate. The desiccant was filtered off and the solvent was removed under vacuum to give the 3^1-hydroxymethyl chlorin derivatives.

Metalation reaction: The metalation of chlorins was carried out in THF and with a saturated solution of zinc acetate in methanol and by stirring for 2–3 h at RT under an argon atmosphere. The incorporation of zinc ion into the chlorin center leads to a color change from olive green to turquoise blue. To terminate the reaction, water (100 mL) and diethyl ether (100 mL) were added. After adding a saturated aqueous $NaHCO_3$ solution (100 mL) for the neutralization of the acetate, the mixture was washed with water at least four times to remove the excess amount of zinc acetate. The organic phase was dried over sodium sulfate, the desiccant was filtered off and the solvent was then removed with a rotary evaporator to afford the zinc chlorins.

13^2-Demethoxycarbonylpheophorbide *a* methyl ester (Pheo *a*): The starting material for all the newly synthesized zinc chlorins was Pheo *a*, which was synthesized from natural chlorophyll *a* according to a known literature procedure.[17b,35] The provision of chlorophyll *a* was made by Soxhlet-extraction of dried algae *Spirulina platensis*. The extraction was performed with 800 g of algae and extracted for 2–3 d with acetone (1.5–2 L). After removal of acetone with a rotary evaporator, a dark green oily residue was obtained, which was heated at reflux with collidin (200 mL) for 6 h, afterwards collidin was removed under vacuum (30 mbar) and the residue was immediately cooled to room temperature. Subsequently, the residue was dissolved in methanol (200 mL) and cooled to 5 °C and 20 % sulfuric acid (150 mL) was added. After stirring for 12 h at RT, diethyl ether (500 mL) was added and the pH of the aqueous phase was adjusted to 6–7 by careful addition of saturated sodium hydrogen carbonate solution. The product was repeatedly extracted with diethyl ether and the combined organic phases were washed with water. The organic layer was dried over sodium sulfate, filtered, and the solvent was removed with a rotary evaporator. The crude product obtained was purified on a silica gel column using *n*-pentane as the eluent to remove the carotenoids and plant oils. Diethyl ether was used as the eluent to obtain the desired Pheo *a*. The latter has the tendency to aggregate on the column, thus the aggregated portions were collected from the column with the help of a spatula and washed with diethyl ether and after filtration the solvent was removed under vacuum. Starting from 800 g of *Spirulina platensis*, 3–4 g of Pheo *a* was obtained, which was then characterized by NMR and UV/Vis spectroscopies and mass spectrometry.[17b]

13^2-Demethoxycarbonylpheophorbide *a* (4′-dodecyloxy)benzyl ester 7a: According to the general procedure for esterification, the 17^2-carboxylic acid derivative of chlorin **6** (498 mg, 0.93 mol) was dissolved in dry CH_2Cl_2 (7 mL), followed by the addition of 4-(dodecyloxy)benzyl alcohol **11a** (545 mg, 1.87 mmol), DCC (1.53 g, 7.42 mmol), DMAP (568 mg, 4.65 mmol), and DPTS (1.37 g, 4.65 mmol). After stirring for 10 min at RT, Hünigs base (242 mg, 1.87 mmol) was added to the reaction mixture. It was further stirred for 3.5 h and was then directly subjected to column chromatography on silica gel with *n*-pentane/diethyl ether (1:1) as the eluent mixture. The olive-green solid obtained following purification by column chromatography was subjected to further purification by semipreparative HPLC (451 mg, 0.56 mmol, 61 %). M.p. 38–43 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.42 (s, 1H; 10-H), 9.32 (s, 1H; 5-H), 8.53 (s, 1H; 20-H), 7.96 (dd, $^3J_{trans}$ = 17.6 Hz, $^3J_{cis}$ = 11.6 Hz, 1H; 3^1-H), 7.14 (m, 2H; 6′-H, 2′-H), 6.76 (m, 2H; 3′-H, 5′-H), 6.25 (dd, $^3J_{trans}$ = 17.8 Hz, 2H, J = 1.5 Hz, 1H; 3^2-H), 6.15 (dd, $^3J_{cis}$ = 11.5 Hz, ^2J = 1.5 Hz, 1H; 3-H), 5.25 (d, ^2J = 19.8 Hz, 1H; 13^2-H), 5.06 (d, ^2J = 19.8 Hz, 1H; 13^2-H), 5.01 (d, ^2J = 12.0 Hz, 1H; 1″-H), 4.95 (d, ^2J = 12.0 Hz, 1H; 1″-H), 4.47 (dq, ^3J = 7.3, 2.0 Hz, 1H; 18-H), 4.27 (td, ^3J = 8.7, 2.1 Hz, 1H; 17-H), 3.87 (t, ^3J = 6.6, 2H; OCH_2), 3.64 (s, 3H; 12^1-H), 3.66–3.60 (m, 2H; 8^1-H), 3.39 (s, 3H; 2^1-H), 3.19 (s, 3H; 7^1-H), 2.75–2.54 and 2.35–2.26 (m, 4H; 17^1-H, 17^2-H), 1.79 (d, ^3J = 7.3 Hz, 3H; 18^1-H), 1.74–1.66 (m, 5H; CH_2, 8^2-H), 1.39–1.26 (m, 18H; 9×CH_2), 0.89 (t, ^3J = 6.7 Hz, 3H; OCH_3), 0.38 (s, 1H; NH), −1.75 ppm (s, 1H; NH); HRMS (ESI): *m*/*z* calcd for $C_{52}H_{64}N_4O_4Na$ $[M+Na]^+$: 831.4825; found: 831.4819.

3-Devinyl-3-formyl-13^2-demethoxycarbonylpheophorbide *a* (4′-dodecyloxy) benzyl ester 8a: According to the general procedure for the oxidation reaction, the oxidative cleavage of the 3^1-vinyl group of chlorin **7a** was carried out by dissolving **7a** (253 mg, 0.31 mmol) in THF (40 mL), followed by the addition of water (0.5 mL) and concentrated acetic acid, and subsequently, a small crystal of osmium tetroxide was added. After stirring the reaction mixture for 2.5 h at RT, saturated aqueous $NaIO_4$ solution (6 mL h^{-1}) was added dropwise. The reaction mixture was extracted as described in the general procedure and subjected to silica gel column chromatography with a mixture of *n*-pentane/diethyl ether (3:2), and then further purified by semipreparative HPLC to obtain a brown solid (254 mg, 0.31 mmol, 98 %). Analytical HPLC: **8a** eluted after 8.1 min at a flow of 1 mL min^{-1} with a solvent mixture of methanol/CH_2Cl_2 (7:3). M.p. 43–52 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 11.53 (s, 1H; 3^1-H), 10.28 (s, 1H; 10-H), 9.59 (s, 1H; 5-H), 8.81 (s, 1H; 20-H), 7.12 (m, 2H; 6′-H, 2′-H), 6.75 (m, 2H; 3′-H, 5′-H), 5.31 (d, ^2J = 20.0 Hz, 1H; 13^1-H), 5.13 (d, ^2J = 20.0 Hz, 1H; 13^2-H), 4.99 (d, ^2J = 12.0 Hz, 1H; 1″-H), 4.92 (d, ^2J = 11.9 Hz, 1H; 1″-H), 4.55 (dq, ^3J = 7.3, 1.9 Hz, 1H; 18-H), 4.36 (td, ^3J = 8.6, 2.4 Hz, 1H; 17-H), 3.87 (t, ^3J = 6.6 Hz, 2H; OCH_2), 3.76 (s, 3H; 12^1-H), 3.74–3.68 (m, 5H; 8^1-H, 2^1-H), 3.30 (s, 3H; 7^1-H), 2.77–2.56 and 2.36–2.27 (m, 4H; 17^1-H, 17^2-H), 1.83 (d, ^3J = 7.3 Hz, 3H; 18^1-H), 1.73–1.68 (m, 5H; CH_2, 8^2-H), 1.41–1.24 (m, 18H; 9×CH_2), 0.87 (t, ^3J = 6.9 Hz, 6H; CH_3), −0.19 (s, 1H; NH), −2.1 ppm (s, 1H; NH); HRMS (ESI): *m*/*z* calcd for $C_{51}H_{63}N_4O_5$ $[M+H]^+$: 811.4798; found: 811.4793.

3-Devinyl-3-hydroxymethyl-13^2-demethoxycarbonylpheophorbide *a* (4′-dodecyloxy)benzyl ester 9a: Borane-*tert*-butylamine complex (261 mg, 3.00 mmol) was added to a solution of **8a** (250 mg, 0.30 mmol) in THF (40 mL), and stirred for 3 h at RT in the dark, and the reaction mixture was extracted as described in the general procedure for the reduction reaction. The resulting olive-grey solid was purified by semipreparative HPLC (203 mg, 0.25 mmol, 83 %). Analytical HPLC: Compound **9a** was eluted after 5.2 min at a flow of 1 mL min^{-1} with a solvent combination of methanol/CH_2Cl_2 (7:3). M.p. 60–64 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.53 (s, 1H; 10-H), 9.47 (s, 1H; 5-H), 8.57 (s, 1H; 20-H), 7.10 (m, 2H; 2′-H, 6′-H), 6.74 (m, 2H; 3′-H, 5′-H), 5.90 (s, 2H; 3^1-H), 5.23 (d, ^2J = 19.8 Hz, 1H; 13^2-H), 5.05 (d, ^2J = 19.8 Hz, 1H; 13^2-H), 4.97 (d, ^2J = 12.0 Hz, 1H; 1″-H), 4.90 (d, ^2J = 12.4 Hz, 1H; 1″-H), 4.47 (dq, ^3J = 7.3, 2.0 Hz, 1H; 18-H), 4.27 (td, ^3J = 6.3, 2.5 Hz, 1H; 17-H), 3.78 (t, ^3J = 6.6 Hz, 2H; OCH_2), 3.70 (q, ^3J = 7.6 Hz, 2H; 8^1-H), 3.66 (s, 3H; 12^1-H), 3.41 (s, 3H; 2^1-H), 3.26 (s, 3H; 7^1-H), 2.73–2.52 and 2.33–2.25 (m, 4H; 17^1-H, 17^2-H), 1.77 (d, ^3J = 7.3 Hz, 3H; 18^1-H), 1.71–1.68 (m, 5H; CH_2, 8^2-H), 1.41–1.24 (m, 18H; 9×CH_2), 0.87 (t, ^3J = 6.9 Hz, 3H; CH_3), 0.21 (s, 1H; NH), −1.83 ppm (s, 1H; NH); HRMS (ESI): *m*/*z* calcd for $C_{51}H_{64}N_4O_5Na$ $[M+Na]^+$: 835.4774; found: 835.4770.

3-Devinyl-3-hydroxymethyl-13^2-demethoxycarbonylpheophorbide *a* (4′-dodecyloxy)benzyl ester zinc complex 10a: According to the general procedure for metalation, 3^1-hydroxy chlorin **9a** (50 mg, 0.06 mmol) was dissolved in THF (5 mL), followed by the addition of a saturated solution of zinc acetate in methanol (10 mL) and the reaction mixture was stirred for 2 h at RT. The reaction mixture was extracted as described in the general procedure and the turquoise-colored product was purified by semi-preparative HPLC (41 mg, 0.05 mmol, 78 %). Analytical HPLC: **10a** eluted after 7.4 min at a flow of 1 mL min^{-1} with a solvent mixture of methanol/CH_2Cl_2 (9:1). M.p. 233 °C; ^{1}H NMR (400 MHz, $CDCl_3$, [D_5]pyridine, 25 °C): δ = 9.56 (s, 1H; 10-H), 9.37 (s, 1H; 5-H), 8.31 (s, 1H; 20-H), 7.12 (m, 2H; 2′-H, 6′-H), 6.76 (m, 2H; 3′-H; 5′-H), 5.85 (s, 2H; 3^1-H), 5.17 (d, ^2J = 19.7 Hz, 1H; 13^2-H), 5.02 (d, ^2J = 19.6 Hz, 1H; 13^2-H), 4.94 (d, ^2J = 11.9 Hz, 1H; 1″-H), 4.89 (d, ^2J = 11.9 Hz, 1H; 1″-H), 4.36 (dq, ^3J = 7.2, 1.9 Hz, 1H; 18-H), 4.19 (td, ^3J = 7.7, 2.1 Hz, 1H; 17-H), 3.87 (t, ^3J = 6.6 Hz, 2H; OCH_2), 3.74 (q, ^3J = 7.5 Hz, 2H; 8^1-H), 3.69 (s, 3H; 12^1-H), 3.30 (s, 3H; 2^1-H), 3.19 (s, 3H; 7^1-H), 2.62–2.24 and 1.94–1.88 (m, 4H; 17^1-H, 17^2-H), 1.74–1.68 (m, 8H; 18^1-H, 8^2-H, CH_2), 1.41–1.24 (m, 18H; 9×CH_2), 0.88 ppm (t, ^3J = 7.0 Hz, 3H; CH_3); HRMS (ESI): *m*/*z* calcd for $C_{51}H_{62}N_4O_5Zn$ [*M*]$^+$: 874.4011; found: 874.4004; UV/Vis (THF): λ_{max} (ε_{max}) = 648 nm (91 000 M^{-1} cm^{-1}).

13^2-Demethoxycarbonylpheophorbide *a* (3′,5′-bis-dodecyloxy)benzyl ester 7b: In dry CH_2Cl_2 (6 mL), 13^2-demethoxycarbonylpheophorbide *a* **5** (150 mg, 0.28 mmol) was dissolved, followed by the addition of 3,5-bis-(dodecyloxy)benzyl alcohol **11b** (200 mg, 0.42 mmol), DCC (289 mg, 1.40 mmol), DMAP (69.1 mg, 0.56 mmol), and DPTS (165 mg, 0.56 mmol). After 30 min of stirring at RT, Hünigs base (57.2 mg, 0.43 mmol) was added. The reaction was stirred for another 3 h, followed by the addition of water (100 mL) and a saturated solution of NH_4Cl (20 mL) to terminate the reaction. The product was extracted with CH_2Cl_2 (3×100 mL) and then washed with water. After removal of the solvent, the residue was loaded on a silica gel column and purified by using 1:1 *n*-pentane/diethyl ether as the eluent. It was further purified by semipreparative HPLC (212 mg, 0.21 mmol, 76 %). Analytical HPLC: The olive-grey chlorin **7b** was eluted after 21.9 min at a flow of 1 mL min^{-1} with a solvent mixture of methanol/CH_2Cl_2 (7:3). M.p. 51–55 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.46 (s, 1H; 10-H), 9.35 (s, 1H; 5-H), 8.54 (s, 1H; 20-H), 7.98 (dd, J_{trans} = 17.6 Hz, $^3J_{cis}$ = 11.6 Hz, 1H; 3^1-H), 6.39 (d, ^4J = 2.3 Hz, 2H; 6′-H, 2′-H), 6.34 (t, ^4J = 2.3 Hz, 1H; 4′-H), 6.26 (dd, $^3J_{trans}$ = 17.8 Hz, ^2J = 1.5 Hz, 1H; 3^2-H), 6.15 (dd, $^3J_{cis}$ = 11.6 Hz, ^2J = 1.5 Hz, 1H; 3^2-H), 5.24 (d, ^2J = 19.8 Hz, 1H; 13^2-H), 5.09 (d, ^2J = 19.8 Hz, 1H; 13^2-H), 5.01 (d, ^2J = 12.2 Hz, 1H; 1″-H), 4.95 (d, ^2J = 12.2 Hz, 1H; 1″-H), 4.48 (dq, ^3J = 7.3, 2.0 Hz, 1H; 18-H), 4.29 (td, ^3J = 8.7, 2.4 Hz, 1H; 17-H), 3.83 (t, ^3J = 5.3, 4H; OCH_2), 3.69–3.63 (q, ^3J = 6.7 Hz, 2H; 8^1-H), 3.65 (s, 3H; 12^1-H), 3.40 (s, 3H; 2^1-H), 3.21 (s, 3H; 7^1-H), 2.78–2.58 and 2.38–2.29 (m, 4H; 17^1-H, 17^2-H), 1.79 (d, ^3J = 7.3 Hz, 3H; 18^1-H), 1.71–1.64 (m, 7H; CH_2, 8^2-H), 1.37–1.22 (m, 36H; 18×CH_2), 0.88 (t, ^3J = 6.8 Hz, 6H; CH_3), 0.42 (s, 1H; NH), −1.72 ppm (s, 1H; NH); HRMS (ESI): *m*/*z* calcd for $C_{64}H_{88}N_4O_5Na$ [*M*+Na]$^+$: 1015.6650; found: 1015.6647.

3-Devinyl-3-formyl-13^2-demethoxycarbonylpheophorbide *a* (3′,5′-bis-dodecyloxy)benzyl ester 8b: Chlorin **7b** (100 mg, 0.10 mmol) was dissolved in THF (30 mL), and water (0.5 mL) and concentrated acetic acid (0.5 mL) were added. Subsequently, two small crystals of OsO_4 were added to the reaction mixture and stirred at RT for 1.5 h. Within another 2 h, a saturated solution of $NaIO_4$ was added dropwise (6 mL h^{-1}). The reaction mixture was extracted according to the general procedure for oxidation reaction. The brown solid was purified on a silica gel column by eluting with a mixture of *n*-pentane/diethyl ether (3:2), and also by semipreparative HPLC (98 mg, 0.1 mmol, 98 %). Analytical HPLC: **8b** was eluted after 15.4 min at a flow of 1 mL min^{-1} with methanol/CH_2Cl_2 (7:3). M.p. 54–58 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 11.53 (s, 1H; 3^1-H), 10.27 (s, 1H; 10-H), 9.58 (s, 1H; 5-H), 8.82 (s, 1H; 20-H), 6.37 (d, ^4J = 2.15 Hz, 2H; 6′-H, 2′-H), 6.34 (t, ^4J = 2.14 Hz, 1H; 4′-H), 5.33 (d, ^2J = 20.0 Hz, 1H; 13^2-H), 5.17 (d, ^2J = 20.0 Hz, 1H; 13^2-H), 5.00 (d, ^2J = 12.3 Hz, 1H; 1″-H), 4.91 (d, ^2J = 12.3 Hz, 1H; 1″-H), 4.56 (dq, ^3J = 7.3, 1.8 Hz, 1H; 18-H), 4.38 (td, ^3J = 8.5, 2.4 Hz, 1H; 17-H), 3.83 (t, ^3J = 6.7 Hz, 4H; OCH_2), 3.76 (s, 3H; 12^1-H), 3.73–3.68 (q, ^3J = 6.7 Hz, 2H; 8^1-H), 3.70 (s, 3H; 2^1-H), 3.30 (s, 3H; 7^1-H), 2.80–2.62 and 2.39–2.28 (m, 4H; 17^1-H, 17^2-H), 1.82 (d, ^3J = 7.3 Hz, 3H; 18^1-H), 1.72–1.65 (m, 7H; CH_2, 8^2-H), 1.34–1.17 (m, 36H; 18×CH_2), 0.87 (t, ^3J = 6.7 Hz, 6H; CH_3), −0.13 (s, 1H; NH), −2.10 ppm (s, 1H; NH); HRMS (ESI): *m*/*z* calcd for $C_{63}H_{87}N_4O_6$ [*M*+H]$^+$: 995.6625; found: 995.6619.

3-Devinyl-3-hydroxymethyl-13^2-demethoxycarbonylpheophorbide *a* (3′,5′-bis-dodecyloxy)benzyl ester 9b: According to the general procedure for the reduction reaction, chlorin **8b** (80.2 mg, 0.08 mmol) was dissolved in CH_2Cl_2 (10 mL), followed by the addition of borane-*tert*-butylamine complex (70.1 mg, 0.08 mmol) and the reaction mixture was stirred for 1 h at RT. The reaction mixture was extracted according to the general procedure and the olive-grey product **9b** was purified by column chromatography on silica gel column with a solvent mixture of CH_2Cl_2/methanol (9:1), and subsequently by semipreparative HPLC (yield: 59.1 mg, 0.06 mmol, 74 %). Analytical HPLC: **9b** eluted after 8.7 min at a flow of 1 mL min^{-1} with solvent mixture methanol/CH_2Cl_2 (7:3). M.p. 51–54 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.50 (s, 1H; 10-H), 9.45 (s, 1H; 5-H), 8.56 (s, 1H; 20-H), 6.34 (s, 3H; 2′-H, 4′-H, 6′-H), 5.89 (s, 2H; 3^1-H), 5.23 (d, ^2J = 19.8 Hz, 1H; 13^2-H), 5.05 (d, ^2J = 19.7 Hz, 1H; 13^2-H), 4.99 (d, ^2J = 12.4 Hz, 1H; 1″-H), 4.88 (d, ^2J = 12.4 Hz, 1H; 1″-H), 4.29 (dq, ^3J = 7.3, 2.0 Hz, 1H; 18-H), 4.29 (td, ^3J = 8.3, 2.3 Hz, 1H; 17-H), 3.84–3.78 (m, 4H; OCH_2), 3.72–3.66 (q, ^3J = 7.6 Hz, 2H; 8^1-H), 3.66 (s, 3H; 12^1-H), 3.40 (s, 3H; 2^1-H), 3.26 (s, 3H; 7^1-H), 2.73–2.53 and 2.37–2.26 (m, 4H; 17^1-H, 17^2-H), 1.77 (d, ^3J = 7.3 Hz, 3H; 18^1-H), 1.69–1.63 (m, 7H; CH_2, 8^2-H), 1.35–1.21 (m, 36H; 18×CH_2), 0.88 (t, ^3J = 7.1 Hz, 6H; CH_3), 0.24 (s, 1H; NH), −1.83 ppm (s, 1H; NH); HRMS (ESI): *m*/*z* calcd for $C_{63}H_{89}N_4O_6$ [*M*+H]$^+$: 997.6782; found: 997.6777.

3-Devinyl-3-hydroxymethyl-13^2-demethoxycarbonylpheophorbide *a* (3′,5′-bis-dodecyloxy)benzyl ester zinc complex 10b: According to the general procedure for metalation, chlorin **9b** (50 mg, 0.05 mmol) was dissolved in a small amount of THF followed by the addition of saturated solution of zinc acetate in methanol (12 mL) and was stirred at RT. The reaction mixture was extracted according to the general procedure with CH_2Cl_2 instead of diethyl ether and purified by column chromatography with an eluting solvent mixture of CH_2Cl_2/methanol (9:1), and further purified using semipreparative HPLC (40.3 mg, 0.04 mmol, 75 %). Analytical HPLC: **10b** was eluted after 6.1 min at a flow of 1 mL min^{-1} with solvent mixture of methanol/CH_2Cl_2 (7:3). M.p. 241 °C; ^{1}H NMR (400 MHz, [D_8]THF, 25 °C): δ = 9.62 (s, 1H; 10-H), 9.49 (s, 1H; 5-H), 8.49 (s, 1H; 20-H), 6.40 (d, ^4J = 2.3 Hz, 2H; 2′-H, 6′-H), 6.32 (t, ^4J = 2.2 Hz, 1H; 4′-H), 5.71 (d, ^3J = 5.8 Hz, 2H; 3^1-H), 5.11 (d, ^2J = 19.5 Hz, 1H; 13^2-H), 5.00–4.92 (m, 3H; 13^2-H, 1″-H), 4.53 (dq, ^3J = 7.2, 2.1 Hz, 1H; 18-H), 4.40 (t, ^3J = 5.8 Hz, 1H; 3^1-OH), 4.31 (td, ^3J = 8.3, 2.3 Hz, 1H; 17-H), 3.84 (m, 6H; OCH_2, 8^1-H), 3.61 (s, 3H; 12^1-H), 3.31 (s, 3H; 2^1-H), 3.29 (s, 3H; 7^1-H), 2.74–2.59 and 2.36–2.26 (m, 4H; 17^1-H, 17^2-H), 1.78 (d, ^3J = 7.3 Hz, 3H; 18^1-H), 1.71–1.63 (m, 7H; 8^2-H, CH_2), 1.40–1.22 (m, 36H; 18×CH_2), 0.88 ppm (t, ^3J = 6.9 Hz, 6H; CH_3); HRMS (ESI): *m*/*z* calcd for $C_{63}H_{86}N_4O_6Zn$ [*M*]$^+$: 1058.5839; found: 1058.5830; UV/Vis (THF): λ_{max} (ε_{max}) = 648 nm (90,000 M^{-1} cm^{-1}).

13^2-Demethoxycarbonylpheophorbide *a* (3′,4′,5′-tris-dodecyloxy)benzyl ester 7c: 3,4,5-Tris(dodecyloxy)benzyl alcohol **11c** (743 mg, 1.12 mmol), DCC (1.24 g, 5.99 mmol), DMAP (458 mg, 3.75 mmol), and DPTS (1.10 g, 3.75 mmol) were added to a solution of **6** (400 mg, 0.75 mmol) in dry CH_2Cl_2 (20 mL). After stirring for 5 min at RT, Hünigs base (194 mg, 1.5 mmol) was added and the reaction mixture was stirred for a further 4 h at RT. The reaction was terminated by the addition of water (100 mL) and a solution of NH_4Cl (20 mL), and the reaction mixture was extracted with diethyl ether (3×100 mL). The united organic phases were washed with water (100 mL) and dried over sodium sulfate. After removal of the desiccating agent, the olive-grey solid was purified by silica gel column chromatography with *n*-pentane/diethyl ether (3:2) as the eluent, and further purified by semipreparative HPLC (447 mg, 0.38 mmol, 51 %). Analytical HPLC: **7c** eluted after 6.7 min at a flow of 1 mL min^{-1} with a solvent mixture of methanol/CH_2Cl_2 (1:1). M.p. 59–64 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.49 (s, 1H; 10-H), 9.38 (s, 1H; 5-H), 8.54 (s, 1H; 20-H), 8.00 (dd, $^3J_{trans}$ = 17.8 Hz, $^3J_{cis}$ = 11.6 Hz, 1H; 3^1-H), 6.46 (s, 2H; 6′-H, 2′-H), 6.28 (dd, $^3J_{trans}$ = 17.9 Hz, ^2J = 1.5 Hz, 1H; 3^2-H), 6.17 (dd, $^3J_{cis}$ = 11.6 Hz, ^2J = 1.5 Hz, 1H; 3^2-H), 5.25 (d, ^2J = 19.8 Hz, 1H; 13^2-H), 5.09 (d, ^2J = 19.8 Hz, 1H; 13^2-H), 4.99 (d, ^2J = 12.0 Hz, 1H;

1″-H), 4.92 (d, ^2J=12.0 Hz, 1H; 1″-H), 4.47 (dq, ^3J=7.3, 2.0 Hz, 1H; 18-H), 4.29 (td, ^3J=8.5, 2.4 Hz, 1H; 17-H), 3.87 (t, ^3J=6.6 Hz, 6H; OCH_2), 3.71–3.65 (q, ^3J=7.7 Hz, 2H; 8^1-H), 3.67 (s, 3H; 12^1-H), 3.40 (s, 3H; 2^1-H), 3.23 (s, 3H; 7^1-H), 2.76–2.57 and 2.37–2.28 (m, 4H; 17^1-H, 17^2-H), 1.78 (d, ^3J=7.3 Hz, 3H; 18^1-H), 1.73–1.64 (m, 9H; CH_2, 8^2-H), 1.43–1.21 (m, 54H; 27×CH_2), 0.88 (m, 9H; CH_3), 0.45 (s, 1H; NH), −1.70 ppm (s, 1H; NH); HRMS (ESI): *m/z* calcd for $C_{76}H_{112}N_4O_6Na$ $[M+Na]^+$: 1199.8480; found: 1199.8471.

3-Devinyl-3-formyl-13²-demethoxycarbonylpheophorbide *a* (3′,4′,5′-tris-dodecyloxy)benzyl ester 8c: According to the general procedure for the oxidation reaction, chlorin derivative **7c** (300 mg, 0.26 mmol) was dissolved in THF (10 mL), followed by the addition of water (0.5 mL), concentrated acetic acid, and a small crystal of osmium tetroxide. The reaction mixture was stirred at RT for further 2 h, afterwards a saturated solution of $NaIO_4$ (7 mL h^{-1}) was added dropwise. Extraction of the reaction mixture was performed according to the general procedure and the resulting brown-colored formyl chlorin **8c** was purified by column chromatography with a mixture of *n*-pentane/diethyl ether (3:2), and was additionally purified by semipreparative HPLC (194 mg, 0.16 mmol, 65%). Analytical HPLC: **8c** eluted after 23.4 min at a flow of 1 mL min^{-1} with solvent mixture of methanol/CH_2Cl_2 (7:3). M.p. 132–138°C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ=11.57 (s, 1H; 3^1-H), 10.35 (s, 1H; 10-H), 9.65 (s, 1H; 5-H), 8.82 (s, 1H; 20-H), 6.46 (s, 2H; 6′-H, 2′-H), 5.34 (d, ^2J=20.0 Hz, 1H; 13^2-H), 5.17 (d, ^2J=20.0 Hz, 1H; 13^2-H), 4.99 (d, ^2J=12.0 Hz, 1H; 1″-H), 4.90 (d, ^2J=12.0 Hz, 1H; 1″-H), 4.56 (dq, ^3J=7.3, 1.9 Hz, 1H; 18-H), 4.38 (td, ^3J=9.0, 2.5 Hz, 1H; 17-H), 3.88–3.85 (t, ^3J=6.6 Hz, 6H; OCH_2), 3.78–3.72 (m, 8H; 8^1-H, 12^1-H, 2^1-H), 3.35 (s, 3H; 7^1-H), 2.80–2.91 and 2.40–2.28 (m, 4H; 17^1-H, 17^2-H), 1.81 (d, ^3J=7.3 Hz, 3H; 18^1-H), 1.75–1.61 (m, 9H; CH_2, 8^2-H), 1.40–1.21 (m, 54H; 27×CH_2), 0.88 (m, 9H; CH_3), −0.09 (s, 1H; NH), −2.03 ppm (s, 1H; NH); HRMS (ESI): *m/z* calcd for $C_{75}H_{111}N_4O_7$ $[M+H]^+$: 1179.8452; found: 1179.8446.

3-Devinyl-3-hydroxymethyl-13²-demethoxycarbonylpheophorbide *a* (3′,4′,5′-tris-dodecyloxy)benzyl ester 9c: Borane-*tert*-butylamine complex (110 mg, 1.27 mmol) was added to a solution of formyl chlorin **8c** (150 mg, 0.13 mmol) in CH_2Cl_2 (20 mL), and stirred for 1 h at RT. The reaction mixture was extracted as described in the general procedure for reduction. The olive-grey reduced product **9c** was purified by column chromatography by eluting with a mixture of diethyl ether/*n*-pentane (3:2), and was further purified by semipreparative HPLC (102 mg, 0.09 mmol, 68%). Analytical HPLC: **9c** was eluted after 6.8 min at a flow of 1 mL min^{-1} with a solvent mixture of methanol/CH_2Cl_2 (3:2). M.p. 104–106°C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25°C): δ=9.51 (s, 1H; 10-H), 9.46 (s, 1H; 5-H), 8.50 (s, 1H; 20-H), 6.25 (s, 2H; 6′-H, 2′-H), 5.90 (m, 2H; 3^1-H), 5.25 (d, ^2J=19.8 Hz, 1H; 13^2-H), 5.08 (d, ^2J=19.8 Hz, 1H; 13^2-H), 4.91 (d, ^2J=12.1 Hz, 1H; 1″-H), 4.67 (d, ^2J=12.3 Hz, 1H; 1″-H), 4.48 (dq, ^3J=7.3, 2.1 Hz, 1H; 18-H), 4.30 (td, ^3J=8.1, 2.4 Hz, 1H; 17-H), 3.84 (t, ^3J=6.6 Hz, 2H; OCH_2), 3.79–3.64 (m, 9H; 8^1-H, OCH_2, 12^1-H), 3.37 (s, 3H; 2^1-H), 3.26 (s, 3H; 7^1-H), 2.77–2.68 and 2.54–2.28 (m, 4H; 17^1-H, 17^2-H), 1.76 (d, ^3J=7.3 Hz, 3H; 18^1-H), 1.72–1.63 (m, 9H; CH_2, 8^2-H), 1.34–1.21 (m, 54H; 27×CH_2), 0.87 (m, 9H; CH_3), 0.34 (s, 1H; NH), −1.81 ppm (s, 1H; NH); HRMS (ESI): *m/z* calcd for $C_{75}H_{113}N_4O_7$ $[M+H]^+$: 1181.8608; found: 1181.8606.

3-Devinyl-3-hydroxymethyl-13²-demethoxycarbonylpheophorbide *a* (3′,4′,5′-tris-dodecyloxy)benzyl ester zinc complex 10c: According to the general procedure for metalation, 3^1-hydroxy chlorin **9c** (80.1 mg, 0.07 mmol) was dissolved in THF (3 mL) followed by the addition of a saturated solution of zinc acetate in methanol (12 mL). After 2 h reaction time, the mixture was worked up according to the general procedure, and the resulting turquoise product was purified by column chromatography by using *n*-pentane/diethyl ether (3:2), and further purified by semipreparative HPLC (62.2 mg, 0.05 mmol, 73%). Analytical HPLC: **10c** eluted after 9.8 min at a flow of 1 mL min^{-1} with solvent mixture of methanol/CH_2Cl_2 (7:3). M.p. 187–189°C; ^{1}H NMR (400 MHz, [D_5]pyridine, $CDCl_3$, 25°C): δ=9.62 (s, 1H; 10-H), 9.48 (s, 1H; 5-H), 8.36 (s, 1H; 20-H), 6.53 (s, 2H; 6′-H, 2′-H), 5.91 (s, 2H; 3^1-H), 5.23 (d, ^2J=19.6 Hz, 1H; 13^2-H), 5.08 (d, ^2J=19.7 Hz, 1H; 13^2-H), 5.02 (d, ^2J=12.0 Hz, 1H; 1″-H), 4.96 (d, ^2J=12.0 Hz, 1H; 1″-H), 4.42 (dq, ^3J=7.3, 2.2 Hz, 1H; 18-H), 4.23 (td, ^3J=7.9, 2.4 Hz, 1H; 17-H), 3.93 (m, 6H; OCH_2), 3.77 (q, ^3J=7.6 Hz, 2H; 8^1-H), 3.73 (s, 3H; 12^1-H), 3.32 (s, 3H; 2^1-H), 3.20 (s, 3H; 7^1-H), 2.69–2.60, 2.53–2.45, 2.39–2.29, and 2.12–2.04 (m, 4H; 17^1-H, 17^2-H), 1.79–1.71 (m, 12H; 18^1-H, CH_2, 8^2-H), 1.50–1.27 (m, 54H; 27×CH_2), 0.91 ppm (m, 9H; CH_3); HRMS (ESI): *m/z* calcd. for $C_{75}H_{110}N_4O_7Zn$ $[M+Na]^+$: 1265.7563; found: 1265.7558; UV/Vis (THF): λ_{max} (ε_{max})= 648 nm (92000 M^{-1} cm^{-1}).

3-Devinyl-3-hydroxymethyl-13²-demethoxycarbonylpheophorbide *a* methyl ester (5a): The synthesis was performed according to the literature and the analytical data are in accordance with those reported.[17a]

3-Devinyl-3-methoxymethyl-13²-demethoxycarbonylpheophorbide *a* methyl ester (6a): The synthesis was performed according to the literature and the analytical data are in accordance with those reported.[36]

3-Devinyl-3-formyl-13²-demethoxycarbonylpheophorbide *a* [3′,5′-bis-(2-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}ethoxy)]benzyl ester 8d: According to the general procedure for esterification, the acid of **6a** (90.3 mg, 0.17 mmol) was dissolved in dry CH_2Cl_2 (10 mL) and **11d** (233 mg, 0.45 mmol) was added, followed by the addition of DCC (277 mg, 1.34 mmol), DMAP (103 mg, 0.84 mmol), and DPTS (247 mg, 0.84 mmol). After stirring at RT for 5 min, Hünigs base (65.2 mg, 0.50 mmol) was added. The reaction mixture was stirred for a further 3 h and then treated with CH_2Cl_2 (100 mL) and a saturated solution of NH_4Cl (20 mL), then it was washed with water (50 mL) several times. Because of the highly polar ethyleneglycol side chains, the aqueous phase was re-extracted with CH_2Cl_2 (2×100). The combined organic phases were dried with Na_2SO_4, solvent was removed and the residue was purified by column chromatography with a mixture of CH_2Cl_2/ethanol (95:5) as the eluent, and was further purified by semipreparative HPLC (100 mg, 0.10 mmol, 57%). Analytical HPLC: **8d** eluted after 10.2 min at a flow of 1 mL min^{-1} with methanol as the solvent. M.p. 173°C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25°C): δ=11.55 (s, 1H; CHO), 10.31 (s, 1H; 10-H), 9.62 (s, 1H; 5-H), 8.84 (s, 1H; 20-H), 6.38 (s, 3H; 2′-H, 4′-H, 6′-H), 5.32 (d, ^2J=19.9 Hz, 1H; 13^2-H), 5.16 (d, ^2J=19.8 Hz, 1H; 13^2-H), 4.97 (d, ^2J=12.5 Hz, 1H; 1″-H), 4.88 (d, ^2J=12.4 Hz, 1H; 1″-H), 4.57 (dq, ^3J=7.3, 2.0 Hz, 1H; 18-H), 4.39 (td, ^3J=8.4, 2.2 Hz, 1H; 17-H), 4.01–3.98 (m, 4H; OCH_2), 3.77–3.70 (m, 13H; CH_2O, CH_2, 8^1-H, 12^1-H), 3.61 (s, 3H; 2^1-H), 3.65–3.48 (m, 20H; CH_2), 3.34 (s, 6H; CH_3), 3.32 (s, 3H; 7^1-H), 2.79–2.58 and 2.38–2.30 (m, 4H; 17^1-H, 17^2-H), 1.83 (d, ^3J=7.3 Hz, 3H; 18^1-H), 1.72 (t, ^3J=7.6 Hz, 3H; 8^2-H), overlap with TMS (1H; NH), −2.06 ppm (s, 1H; NH); HRMS (ESI): *m/z* calcd for $C_{57}H_{74}N_4O_{14}Na$: 1061.5098 $[M+Na]^+$; found: 1061.5094.

3-Devinyl-3-hydroxymethyl-13²-demethoxycarbonylpheophorbide *a* [3′,5′-bis-(2-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}ethoxy)]benzyl ester 9d: Borane-*tert*-butylamine complex (84.1 mg, 0.96 mmol) was added to a solution of **8d** (100 mg, 0.10 mmol) in dry CH_2Cl_2 (50 mL), and stirred for 1.5 h at RT. The reaction mixture was then diluted with CH_2Cl_2 (100 mL) and water (50 mL), and the neutralization of the amine complex was performed with a saturated aqueous solution of NH_4Cl (20 mL). The organic phase was washed several times with water (50 mL) and then dried over sodium sulfate. The desiccant was removed by filtration and the solvent was removed under vacuum. The olive-grey colored chlorin **9d** was further purified by semipreparative HPLC (80.0 mg, 0.07 mmol, 80%). Analytical HPLC: **9d** eluted after 5.6 min at a flow of 1 mL min^{-1} using methanol as solvent. M.p. 164°C; ^{1}H NMR (400 MHz, THF, 25°C): δ=9.72 (s, 1H; 10-H), 9.70 (s, 1H; 5-H), 8.82 (s, 1H; 20-H), 6.55 (d, ^4J=2.3 Hz, 2H; 2′-H, 6′-H), 6.51 (t, ^4J=2.3 Hz, 1H; 4′-H), 5.93 (d, ^3J=5.7 Hz, 2H; 3^1-H), 5.31 (d, ^2J=19.7 Hz, 1H; 13^2-H), 5.13 (d, ^2J=19.8 Hz, 1H; 13^2-H), 5.11 (d, ^2J=12.4 Hz, 1H; 1″-H), 5.03 (d, ^2J=12.4 Hz, 1H; 1″-H), 4.83 (t, ^3J=5.7 Hz, 1H; 3^1-OH), 4.68 (dq, ^3J=7.2, 1.9 Hz, 1H; 18-H), 4.46 (td, ^3J=9.1, 2.4 Hz, 1H; 17-H), 4.10–4.07 (m, 4H; OCH_2), 3.83 (q, ^3J=7.7 Hz, 2H; 8^1-H), 3.81–3.77 (m, 4H; CH_2O), 3.73 (s, 3H; 12^1-H), 3.71–3.69 (m, 8H; CH_2), 3.65–3.58 (m, 12H; CH_2), 3.53 (s, 3H; 2^1-H), 3.51–3.48 (m, 4H; CH_2), 3.37 (s, 3H; 7^1-H), 3.34 (m, 6H; CH_3), 2.90–2.73 and 2.54–2.35 (m, 4H; 17^1-H, 17^2-H), 1.90 (d, ^3J=7.2 Hz, 3H; 18^1-H), 1.81 (t, ^3J=7.6 Hz, 3H; 8^2-H), 0.42 (s, 1H; NH), −1.74 ppm (s, 1H; NH); HRMS (ESI): *m/z* calcd for $C_{57}H_{76}N_4O_{14}Na$: 1063.5255 $[M+Na]^+$; found: 1063.5250.

3-Devinyl-3-hydroxymethyl-13²-demethoxycarbonylpheophorbide *a* [3′,5′-bis-(2-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}ethoxy)]benzyl ester zinc

complex 10d: According to the general procedure for metalation, chlorin derivative **9d** (40 mg, 0.04 mmol) was dissolved in THF (10 mL), followed by the addition of a saturated solution of zinc acetate in methanol (10 mL), the reaction mixture was stirred for 3 h at RT and for additional 30 min at 40 °C . The reaction was then terminated by the addition of CH_2Cl_2 (100 mL), water (100 mL), and a saturated aqueous solution of $NaHCO_3$ (20 mL). The resulting turquoise zinc chlorin **10d** was then extracted several times with CH_2Cl_2 (150 mL), and the combined organic phases were dried over sodium sulfate, the desiccant was removed by filtration and the solvent was removed under vacuum. Zinc chlorin **10d** was further purified by semipreparative HPLC (39.0 mg, 0.04 mmol, 92 %). Analytical HPLC: **10d** was eluted after 4.0 min at a flow of 1 mL min^{-1} with methanol as the solvent. M.p. 231–234 °C; ^{1}H NMR (400 MHz, THF, 25 °C): δ = 9.71 (s, 1H; 10-H), 9.58 (s, 1H; 5-H), 8.58 (s, 1H; 20-H), 6.52 (d, ^4J = 2.3 Hz, 2H; 2′-H, 6′-H), 6.48 (t, ^4J = 2.3 Hz, 1H; 4′-H), 5.81 (d, ^3J = 6.1 Hz, 2H; 3^{1}H), 5.20 (d, ^2J = 19.6 Hz, 1H; 13^2-H), 5.04 (d, ^2J = 19.5 Hz, 1H; 13^2-H), 5.08 (d, ^2J = 12.4 Hz, 1H; 1″-H), 5.02 (d, ^2J = 12.3 Hz, 1H; 1″-H), 4.63 (dq, ^3J = 7.2, 2.1 Hz, 1H; 18-H), 4.50 (t, ^3J = 5.7 Hz, 1H; 3^1-OH), 4.41 (td, ^3J = 8.1, 1.9 Hz, 1H; 17-H), 4.07–4.05 (m, 4H; OCH_2), 3.89 (q, ^3J = 7.7 Hz, 2H; 8^1-H), 3.79–3.76 (m, 4H; CH_2O), 3.71 (s, 3H; 12^1-H), 3.68–3.66 (m, 12H; 6 × CH_2), 3.65–3.58 (m, 8H; 4 × CH_2), 3.50–3.47 (m, 4H; CH_2), 3.41 (s, 3H; 2^1-H), 3.38 (s, 3H; 7^1-H), 3.33 (m, 6H; CH_3), 2.83–2.68 and 2.50–2.36 (m, 4H; 17^1-H, 17^2-H), 1.88 (d, ^3J = 7.2 Hz, 3H; 18^1-H), 1.81 ppm (t, ^3J = 7.7 Hz, 3H; 8^2-H); HRMS (ESI): *m*/*z* calcd for $C_{57}H_{74}N_4O_{14}ZnNa$: 1125.4390 [*M*+Na]$^+$; found: 1125.4385; UV/Vis (THF): λ_{max} (ε_{max}) = 648 nm (91 000 M^{-1} cm^{-1}).

3-Devinyl-3-formyl-13^2-demethoxycarbonylpheophorbide *a* [3′,4′,5′-tris-(2-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}ethoxy)]benzyl ester 8e: According to the general procedure for esterification, chlorin derivative **6a** (80.1 mg, 0.15 mmol) was dissolved in dry CH_2Cl_2 (10 mL), followed by the addition of **11e** (218 mg, 0.30 mmol), DCC (247 mg, 1.20 mmol), DMAP (92.0 mg, 0.75 mmol), and DPTS (221 mg, 0.75 mmol). The reaction mixture was stirred for 10 min at RT, and subsequently, Hünigs base (62.0 mg, 0.48 mmol) was added. After stirring for 3 h, the reaction mixture was treated with CH_2Cl_2 (100 mL) and a saturated solution of NH_4Cl (20 mL), then washed with water (50 mL) several times. The aqueous phase was re-extracted with CH_2Cl_2 (2 × 100 mL). The combined organic phases were dried over Na_2SO_4 and the solvent was removed under vacuum. The resulting product was purified on a silica gel column with a mixture of CH_2Cl_2/methanol (98:2) as the eluent and further purified by semipreparative HPLC (118 mg, 0.09 mmol, 63 %). Analytical HPLC: **8e** was eluted after 8.5 min at a flow of 1 mL min^{-1} with methanol as the solvent. M.p. 88–92 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 11.56 (s, 1H; CHO), 10.36 (s, 1H; 10-H), 9.66 (s, 1H; 5-H), 8.87 (s, 1H; 20-H), 6.50 (s, 2H; 2′-H, 6′-H), 5.35 (d, ^2J = 20.0 Hz, 1H; 13^2-H), 5.18 (d, ^2J = 20.0 Hz, 1H; 13^2-H), 4.91 (d, ^2J = 12.3 Hz, 1H; 1″-H), 4.87 (d, ^2J = 12.1 Hz, 1H; 1″-H), 4.58 (q, ^3J = 7.4 Hz, 1H; 18-H), 4.39 (d, ^3J = 8.3 Hz, 1H; 17-H), 4.08–4.05 (m, 6H; OCH_2), 3.78–3.58 (m, 47H; CH_2, 8^1-H, 12^1-H, 2^1-H), 3.53–3.48 (m, 9H; CH_2), 3.35 (s, 3H; 7^1-H), 3.34 (s, 9H; CH_3), 2.80–2.60 and 2.38–2.30 (m, 4H; 17^1-H, 17^2-H), 1.83 (d, ^3J = 7.3 Hz, 3H; 18^1-H), 1.73 (t, ^3J = 7.6 Hz, 3H; 8^2-H), overlap with TMS signal (1H; NH), −2.05 ppm (s, 1H; NH); HRMS (ESI): *m*/*z* calcd for $C_{66}H_{92}N_4O_{19}Na$: 1267.6252 [*M*+Na]$^+$, found: 1267.6248.

3-Devinyl-3-hydroxymethyl-13^2-demethoxycarbonylpheophorbide *a* [3′,4′,5′-tris-(2-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}ethoxy)]benzyl ester 9e: Borane-*tert*-butylamine complex (82.3 mg, 0.95 mmol) was added to a solution of **8e** (118 mg, 0.09 mmol) in dry CH_2Cl_2 (20 mL), and stirred for 2 h at RT. The reaction mixture was then extracted with $CHCl_3$ (100 mL) and the amine complex was neutralized with a saturated aqueous solution of NH_4Cl. The organic phase was washed several times with water and then dried over sodium sulfate. The desiccant was filtered and the solvent was removed under vacuum. The olive-grey product **9e** was purified on a silica gel column, and then by semipreparative HPLC (86.0 mg, 0.07 mmol, 73 %). Analytical HPLC: **9e** was eluted after 5.2 min at a flow of 1 mL min^{-1} with methanol as the solvent. M.p. 119 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ = 9.58 (s, 1H; 10-H), 9.53 (s, 1H; 5-H), 8.57 (s, 1H; 20-H), 6.27 (s, 2H; 2′-H, 6′-H), 5.92 (m, 2H; 3^1-H), 5.27 (d, ^2J = 20.1 Hz, 1H; 13^2-H), 5.11 (d, ^2J = 19.8 Hz, 1H; 13^2-H), 4.85 (d, ^2J = 12.5 Hz, 1H; 1″-H), 4.61 (d, ^2J = 12.4 Hz, 1H; 1″-H), 4.51 (q, ^3J = 7.3 Hz, 1H; 18-H), 4.33 (d, ^3J = 7.8 Hz, 1H; 17-H), 4.04–3.87 (m, 6H; CH_2O), 3.74–3.47 (m, 47H; CH_2, 8^1-H, 12^1-H), 3.40 (s, 3H; 2^1-H), 3.35–3.33 (m, 9H; CH_3), 3.28 (s, 3H; 7^1-H), 2.54–2.26 (m, 4H; 17^1-H, 17^2-H), 1.80 (d, ^3J = 7.3 Hz, 3H; 18^1-H), 1.71 ppm (t, ^3J = 7.6 Hz, 3H; 8^2-H), overlap with TMS (1H; NH), −1.82 (s, 1H; NH); HRMS (ESI): *m*/*z* calcd for $C_{66}H_{94}N_4O_{19}$: 1269.6409 [*M*+Na]$^+$; found: 1269.6405.

3-Devinyl-3-hydroxymethyl-13^2-demethoxycarbonylpheophorbide *a* [3′,4′,5′-tris-(2-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}ethoxy)]benzyl ester zinc complex 10e: According to the general procedure for metalation, chlorin **9e** (76.1 mg, 0.06 mmol) was dissolved in THF (15 mL), followed by the addition of a saturated solution of zinc acetate in methanol (10 mL). The reaction mixture was stirred for 3 h at RT and for an additional 15 min at 40 °C. The reaction was terminated by the addition of CH_2Cl_2 (100 mL), water (100 mL), and an aqueous solution of $NaHCO_3$ (20 mL) and the turquoise zinc chlorin was extracted with CH_2Cl_2 (150 mL) several times. The combined organic phases were dried over sodium sulfate, the desiccant was filtered off and the solvent was removed under vacuum. The product was purified by semi-preparative HPLC (45.2 mg, 0.03 mmol, 56 %). Analytical HPLC: **10e** was eluted after 3.7 min at a flow of 1 mL min^{-1} with methanol as the solvent. M.p. 234–236 °C; ^{1}H NMR (400 MHz, $CDCl_3$, [D$_5$]pyridine, TMS, 25 °C): δ = 9.56 (s, 1H; 10-H), 9.35 (s, 1H; 5-H), 8.32 (s, 1H; 20-H), 6.44 (s, 2H; 2′-H, 6′-H), 5.83 (s, 2H; 3^1-H), 5.18 (d, ^2J = 19.7 Hz, 1H; 13^2-H), 5.04 (d, ^2J = 19.7 Hz, 1H; 13^2-H), 4.91 (d, ^2J = 12.1 Hz, 1H; 1″-H), 4.84 (d, ^2J = 12.3 Hz, 1H; 1″-H), 4.39 (dq, ^3J = 7.3, 2.1 Hz, 1H; 18-H), 4.20 (dt, ^3J = 7.8, 2.7 Hz, 1H; 17-H), 4.07–4.01 (m, 6H; OCH_2), 3.74–3.57 (m, 38H; CH_2, 8^1-H), 3.68 (s, 3H; 12^1-H), 3.52–3.48 (m, 6H; CH_2), 3.33 (m, 9H; CH_3), 3.30 (s, 3H; 2^1-H), 3.21 (s, 3H; 7^1-H), 3.02 (s, 1H; 3^1-OH), 2.61–2.56 and 2.44–2.25 and 2.03–1.96 (m, 4H; 17^1-H, 17^2-H), 1.72–1.68 ppm (m, 6H; 18^1-H, 8^2-H); HRMS (ESI): *m*/*z* calcd for $C_{66}H_{92}N_4O_{19}Zn$: 1308.5647 [*M*]$^+$; found: 1308.5643; UV/Vis (THF): λ_{max} (ε_{max}) = 647 nm (94 000 M^{-1} cm^{-1}).

3-Devinyl-3^1-hydroxyethyl-13^2-demethoxycarbonylpheophorbide *a* methyl ester 12: The synthesis was performed according to the known literature methods developed by Tamiaki and Hynninen.[16a,19] Pheo *a* **5** (460 mg, 0.840 mmol) was dissolved in 38 % HBr in acetic acid (10 mL) and stirred at RT overnight. The reaction mixture was poured into ice water (100 mL) and extracted with $CHCl_3$ (4 × 100 mL). The combined organic phases were washed several times with a saturated solution of $NaHCO_3$ (100 mL) and water (2 × 100 mL) and dried over Na_2SO_4. After removal of the drying agent by filtration, solvent was removed under vacuum, the residue dissolved in methanol (60 mL), followed by addition of concentrated HCl (6 mL), and stirred for 30 min. Finally, the olive-green colored product was purified by column chromatography on a silica gel column with a mixture of CH_2Cl_2/methanol (9:1) as the eluent (377 mg, 0.67 mmol, 79 %). The analytical data were in accordance with those reported in the literature.[19]

3-Devinyl-3-acetyl-13^2-demethoxycarbonylpheophorbide *a* methyl ester 13: Compound **13** was synthesized from **12** according to a known literature method, and the analytical data are in accordance with those reported.[20]

3-Devinyl-3-acetyl-13^2-demethoxycarbonylpheophorbide *a* (3′,5′-bis-dodecyloxy) benzyl ester 14: Starting with 3-acetylchlorin **13** (115 mg, 0.20 mmol), the free carboxylic acid derivative was generated by adding concentrated hydrochloric acid (5–10 mL) and stirring for 5–6 h at RT. The reaction mixture was adjusted to pH 6–7 by careful addition of a saturated aqueous solution of $NaHCO_3$. The intermediate product was extracted with CH_2Cl_2 and dried over sodium sulfate. After removal of the drying agent, the solvent was removed, and the carboxylic acid was purified by column chromatography with a mixture of CH_2Cl_2/methanol (9:1) as the eluent (82.3 mg, 0.15 mmol, 73 %).

Because the acid was difficult to purify by HPLC, it was used for esterification without further characterization. For this purpose, the carboxylic acid (75.1 mg, 0.14 mmol) was dissolved in dry CH_2Cl_2 (15 mL), and **11b** (212 mg, 0.44 mmol) was added, followed by the addition of the vacuum-dried coupling reagents DCC (184 mg, 0.89 mmol), DMAP (67.0 mg, 0.55 mmol), and DPTS (161 mg, 0.55 mmol) and the reaction mixture was stirred for 2.5 h at RT. The reaction mixture was directly subjected

to purification by column chromatography with a mixture of diethyl ether/*n*-pentane (1:1) as the eluent. It was additionally purified by semipreparative HPLC (57.3 mg (0.06 mmol, 42%). Analytical HPLC: **14** was eluted after 15.59 min at a flow of 1 mL min^{-1} with a solvent mixture of methanol/CH_2Cl_2 (7:3). M.p. 64°C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ=10.01 (s, 1H; 5-H), 9.62 (s, 1H; 10-H), 8.76 (s, 1H; 20-H), 6.38 (d, ^4J=2.3 Hz, 2H; 2′-H, 6′-H), 6.34 (t, ^4J=2.2 Hz, 1H; 4′-H), 5.31 (d, ^2J=19.8 Hz, 1H; 13^2-H), 5.14 (d, ^2J=19.7 Hz, 1H; 13^2-H), 5.01 (d, ^2J=12.3 Hz, 1H; 1″-H), 4.93 (d, ^2J=12.3 Hz, 1H; 1″-H), 4.53 (dq, ^3J=7.2, 1.4 Hz, 1H; 18-H), 4.36 (d, ^3J=7.6 Hz, 1H; 17-H), 3.83 (t, ^3J=6.6 Hz, 4H; OCH_2), 3.74 (q, ^3J=7.7 Hz, 2H; 8^1-H), 3.72 (s, 3H; 12^1-H), 3.65 (s, 3H; 2^1-H), 3.30 (s, 3H; 7^1-H), 3.29 (s, 3H; 3^2-H), 2.79–2.59 and 2.37–2.31 (m, 4H; 17^1-H, 17^2-H), 1.81 (d, ^3J=7.3 Hz, 3H; 18^1-H), 1.74–1.66 (m, 7H; CH_2, 8^2-H), 1.35–1.22 (m, 36H; 18×CH_2), 0.87 (t, ^3J=6.9 Hz, 6H; CH_3), −0.06 (s, 1H; NH), −2.01 ppm (s, 1H; NH); HRMS (ESI): *m*/*z* calcd for $C_{64}H_{88}N_4O_6$ $[M]^+$: 1008.6703; found: 1008.6647 $[M]^+$ and 1009.6794 $[M+H]^+$.

3-Devinyl-(3^1*R*/*S*)-hydroxymethyl-13^2-demethoxycarbonylpheophorbide *a* (3′,5′- bis-dodecyloxy)benzyl ester 15: 3-Acetyl chlorin **14** (28.0 mg, 0.03 mmol) was dissolved in dry THF (2 mL) and dry ethanol (10 mL) was added. Subsequently, sodium borohydride (4.40 mg, 0.12 mmol) was added and was stirred for 70 min at RT. The reaction was terminated by the addition of water (15 mL) and the pH of the reaction mixture was adjusted to 6–7 with a saturated solution of NH_4Cl. The product was extracted with diethyl ether (3×100 mL) and the combined organic phases were dried over sodium sulfate. After filtration of the drying agent, the solvent was removed under vacuum and the olive-grey product was purified by column chromatography with a solvent mixture of diethyl ether/*n*-pentane (3:2), and additionally by semipreparative HPLC (19.1 mg, 0.02 mmol, 67%). Analytical HPLC: **15** was eluted after 7.0 min (21.1 min) with a flow of 1 mL min^{-1} with a solvent mixture of methanol/CH_2Cl_2 (8:2). ^{1}H NMR of (*R*/*S*)-diastereomer mixture (400 MHz, $CDCl_3$, 25°C): δ=9.70/9.65 (s, 1H; 5-H), 9.48/9.47 (s, 1H; 10-H), 8.51/8.49 (s, 1H; 20-H), 6.40 (q, ^3J=6.8, 1H; 3^1-H), 6.34–6.32 (m, 3H; 2′-H, 4′-H, 6′-H), 5.25/5.23 and 5.20/5.18 (d, ^2J=19.7 Hz, 1H; 13^2-H), 5.09/5.08 and 5.04/5.03 (d, ^2J=19.7 Hz, 1H; 13^2-H), 5.00 and 4.97 (d, ^2J=12.8 Hz, 1H; 1″-H), 4.90/4.88 and 4.87/4.85 (d, ^2J=12.4 Hz, 1H; 1″-H), 4.46 (q, ^3J=7.3 Hz, 1H; 18-H), 4.26 (m, 1H; 17-H), 3.84–3.79 (m, 4H; OCH_2), 3.69 (q, ^3J=6 Hz, 2H; 8^1-H), 3.64 (s, 3H; 12^1-H), 3.40/3.37 (s, 3H; 2^1-H), 3.25 (s, 3H; 7^1-H), 2.74–2.51 and 2.36–2.27 (m, 4H; 17^1-H, 17^2-H), 2.15/2.14 and 2.13/2.12 (d, ^3J=6.7 Hz, 3H; 3^2-H), 1.76 (t, ^3J=7.7 Hz, 3H; 8^2-H), 1.78–1.63 (m, 7H; 18^1-H, CH_2), 1.34–1.22 (m, 36H; 18×CH_2), 0.87 (t, ^3J=6.9 Hz, 6H; CH_3), (undefined broad signal, 1H; NH), −1.85 ppm (s, 1H; NH); HRMS (ESI): *m*/*z* calcd for $C_{64}H_{90}N_4O_6$ $[M]^+$: 1010.6860; found: 1010.6855 $[M]^+$ and 1011.6961 $[M+H]^+$.

The diastereoisomers were in a 1:1 ratio and they were successfully separated by HPLC using a semipreparative chiral column (reprosil 100 chiral-NR) with a solvent mixture of *n*-hexane/CH_2Cl_2 (1:1).

3-Devinyl-(3^1*S*)-hydroxymethyl-13^2-demethoxycarbonylpheophorbide *a* (3′,5′-bis-dodecyloxy)benzyl ester (3^1*S*)-16: Analytical HPLC on chiral column: (3^1*S*)-**16** was eluted after 17.7 min at a flow of 1 mL min^{-1} in eluting mixture of *n*-hexane/CH_2Cl_2 (1:1). The integration of the HPLC chromatogram showed almost 100% diastereomeric purity (4.01 mg, 0.004 mmol, 28%). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ=9.88 (s, 1H; 5-H), 9.68 (s, 1H; 10-H), 8.66 (s, 1H; 20-H), 6.48 (q, ^3J=6.6 Hz, 1H; 3^1-H), 6.35 (m, 3H; 2′-H, 4′-H, 6′-H), 5.29 (d, ^2J=19.8 Hz, 1H; 13^2-H), 5.12 (d, ^2J=19.8 Hz, 1H; 13^2-H), 4.98 (d, ^2J=12.4 Hz, 1H; 1″-H), 4.89 (d, ^2J=12.3 Hz, 1H; 1″-H), 4.53 (q, ^3J=7.2 Hz, 1H; 18-H), 4.34 (d, ^3J=8.08 Hz, 1H; 17-H), 3.82 (dt, ^3J=6.6 Hz, ^2J=2.2 Hz, 4H; OCH_2), 3.76 (q, ^3J=7.8 Hz, 2H; 8^1-H), 3.71 (s, 3H; 12^1-H), 3.44 (s, 3H; 2^1-H), 3.30 (s, 3H; 7^1-H), 2.80–2.57 and 2.39–2.31 (m, 4H; 17^1-H, 17^2-H), 2.16 (d, ^3J=6.7 Hz, 3H; 3^2-H), 1.81 (d, ^3J=7.3 Hz, 3H; 18^1-H), 1.73–1.66 (m, 7H; 8^2-H, CH_2), 1.39–1.23 (m, 36H; 18×CH_2), 0.87 (t, ^3J=6.7 Hz, 6H; CH_3), broad signal (1H; NH), −1.84 ppm (s, 1H; NH).

3-Devinyl-(3^1*R*)-hydroxymethyl-13^2-demethoxycarbonylpheophorbide *a* (3′,5′-bis-dodecyloxy)benzyl ester (3^1*R*)-16: Analytical HPLC on chiral column: (3^1*R*)-**16** was eluted after 19.7 min at a flow of 1 mL min^{-1} with solvent mixture *n*-hexane/CH_2Cl_2 (1:1). Integration of the HPLC chromatogram showed 95% diastereomeric purity (7.98 mg, 0.008 mmol, 56%). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ=9.87 (s, 1H; 5-H), 9.63 (s, 1H; 10-H), 8.60 (s, 1H; 20-H), 6.45 (m, 1H; 3^1-H), 6.32 (m, 3H; 2′-H, 4′-H, 6′-H), 5.27 (d, ^2J=20.0 Hz, 1H; 13^2-H), 5.12 (d, ^2J=20.0 Hz, 1H; 13^2-H), 4.98 (d, ^2J=12.4 Hz, 1H; 1″-H), 4.85 (d, ^2J=12.3 Hz, 1H; 1″-H), 4.53 (m, 1H; 18-H), 4.34 (m, 1H; 17-H), 3.82–3.74 (m, 6H; OCH_2, 8^1-H), 3.70 (s, 3H; 12^1-H), 3.41 (s, 3H; 2^1-H), 3.29 (s, 3H; 7^1-H), 2.78–2.53 and 2.39–2.30 (m, 4H; 17^1-H, 17^2-H), 2.17 (d, ^3J=6.5 Hz, 3H; 3^2-H), 1.79 (d, ^3J=7.2 Hz, 3H; 18^1-H), 1.73–1.65 (m, 7H; 8^2-H, CH_2), 1.34–1.23 (m, 36H; 18×CH_2), 0.87 (t, ^3J=6.8 Hz, 6H; CH_3), broad signal (1H; NH), −1.83 ppm (s, 1H; NH).

3-Devinyl-(3^1*S*)-hydroxymethyl-13^2-demethoxycarbonylpheophorbide *a* (3′,5′-bis-dodecyloxy)benzyl ester zinc complex (3^1*S*)-17: According to the general procedure for metalation, chlorin (3^1*S*)-**16** (3.98 mg, 0.004 mmol) was dissolved in THF (3.5 mL), followed by the addition of a saturated solution of zinc acetate in methanol (6 mL) and the mixture was stirred for 1 h at RT. After extraction according to the general procedure, the turquoise zinc chlorin (3^1*S*)-**17** was purified by semipreparative chiral HPLC column (2.98 mg, 0.002 mmol, 55%). Analytical HPLC: (3^1*S*)-**17** was eluted after 13.0 min at a flow of 1 mL min^{-1} with a solvent mixture of *n*-hexane/CH_2Cl_2/methanol (70:25:5). The integration of HPLC chromatogram showed 100% diastereomeric purity. M.p. 214°C; ^{1}H NMR: (400 MHz, [D$_8$]THF, 25°C): δ=9.70 (s, 1H; 5-H), 9.60 (s, 1H; 10-H), 8.45 (s, 1H; 20-H), 6.40 (d, ^4J=2.3 Hz, 2H; 2′-H, 6′-H), 6.32–6.30 (m, 1H; 4′-H), 6.29–6.28 (m, 1H; 3^1-H), 5.10 (d, ^2J=19.6 Hz, 1H; 13^2-H), 4.99–4.90 (m, 3H; 13^2-H, 1″-H), 4.52 (dq, ^3J=7.2, 2.2 Hz, 1H; 18-H), 4.30 (dt, ^3J=8.1, 2.6 Hz, 1H; 17-H), 3.86–3.76 (m, 6H; OCH_2, 8^1-H), 3.61 (s, 3H; 12^1-H), 3.34 (s, 3H; 2^1-H), 3.28 (s, 3H; 7^1-H), 2.68–2.61 and 2.31–2.26 (m, 4H; 17^1-H, 17^2-H), 2.00 (d, ^3J=6.6 Hz, 3H; 3^2-H), 1.78 (d, ^3J=7.3 Hz, 3H; 18^1-H), 1.73–1.63 (m, 7H; 8^2-H, CH_2), 1.41–1.27 (m, 36H; 18×CH_2), 0.88 ppm (t, ^3J=6.9 Hz, 6H; CH_3); HRMS (ESI): *m*/*z* calcd for $C_{64}H_{88}N_4O_6Zn$ $[M]^+$: 1072.5995; found: 1072.5990; UV/Vis (THF): λ_{max} (ε_{max})=648 nm (83700 M^{-1} cm^{-1}).

3-Devinyl-(3^1*R*)-hydroxymethyl-13^2-demethoxycarbonylpheophorbide *a* (3′,5′-bis-dodecyloxy)benzyl ester zinc complex (3^1*R*)-17: According to the general procedure of metalation, (3^1*R*)-**16** (8.001 mg, 0.008 mmol) was dissolved in THF (4 mL), followed by the addition of a saturated solution of zinc acetate in methanol (6 mL) and the reaction mixture was stirred for 1 h at RT. After extraction of the reaction mixture, the resulting zinc chlorin (3^1*R*)-**17** was purified by semipreparative chiral HPLC column (3.50 mg, 0.003 mmol, 41%). Analytical HPLC: (3^1*R*)-**17** was eluted after 13.8 min at a flow of 1 mL min^{-1} with a solvent mixture of *n*-hexane/CH_2Cl_2/methanol (70:25:5). The integration of HPLC chromatogram showed 100% diastereomeric purity. M.p. 209°C; ^{1}H NMR (400 MHz, [D$_8$]THF, 25°C): δ=9.75 (s, 1H; 5-H), 9.60 (s, 1H; 10-H), 8.44 (s, 1H; 20-H), 6.40 (d, ^4J=2.3 Hz, 2H; 2′-H, 6′-H), 6.32 (t, ^4J=2.3 Hz, 1H; 4′-H), 6.26 (dq, ^3J=6.7, 2.6 Hz, 1H; 3^1-H), 5.09 (d, ^2J=19.6 Hz, 1H; 13^2-H), 4.97–4.90 (m, 3H; 13^2-H, 1″-H), 4.53 (dq, ^3J=7.3, 2.0 Hz, 1H; 18-H), 4.29 (dt, ^3J=8.3, 2.7 Hz, 1H; 17-H), 3.86–3.76 (m, 6H; OCH_2, 8^1-H), 3.60 (s, 3H; 12^1-H), 3.31 (s, 3H; 2^1-H), 3.28 (s, 3H; 7^1-H), 2.73–2.59 and 2.35–2.27 (m, 4H; 17^1-H, 17^2-H), 2.01 (d, ^3J=6.6 Hz, 3H; 3^2-H), 1.77 (d, ^3J=7.3 Hz, 3H; 18^1-H), 1.69–1.63 (m, 7H; 8^2-H, CH_2), 1.38–1.27 (m, 36H; 18×CH_2), 0.88 ppm (t, ^3J=6.8 Hz, 6H; CH_3); HRMS (ESI): *m*/*z* calcd for $C_{64}H_{88}N_4O_6Zn$ $[M]^+$: 1072.5995; found: 1072.5990; UV/Vis (THF): λ_{max} (ε_{max})=648 nm (87600 M^{-1} cm^{-1}).

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