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A Heck-Type Coupling for the Synthesis of Novel Bridged Metallochlorin–Fullerene C_{60} Dyads

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A short and convenient synthesis of metallochlorin–C_{60} dyads based on a Heck-type hetero coupling at the 3^2 position of a chlorin is described. *p*-Bromobenzaldehyde was treated with Zn-metalated 13^2-demethoxycarbonylmethylpheophorbide *a*, using a palladium acetate/LiCl catalyst mixture under phase-transfer conditions in DMF at 70 °C. The resulting asymmetric olefin was obtained in a high *trans*/*cis* ratio. The desired *trans* isomer was separated and subsequently transformed into a donor–acceptor dyad by a 1,3-dipolar cycloaddition to C_{60} in the presence of sarcosine in refluxing toluene. The resulting dyads are expected to undergo efficient photoinduced electron transfer and can potentially be utilized in solar energy conversion devices.

Introduction

There is a continuing interest in the synthesis of electron transfer (ET) dyads for the study of photoinduced electron transfer (PET) in artificial photosynthesis. Donor–acceptor systems featuring ultrafast and highly unidirectional photoinduced ET are desired to mimic the function of reaction center (RC) complexes of higher plants or phototrophic bacteria.[1] In recent years a large variety of such donor–acceptor compounds, known as ET dyads, have been synthesized by many groups. In most of them, porphyrins act as the primary electron donor, with covalently attached quinone derivatives as the electron acceptor.[2] More recently, fullerenes, and especially the most common species C_{60}, have become extraordinarily attractive as electron acceptors for designing new supramolecular RC equivalents[3] as they feature high chemical stability and remarkable photophysical properties such as, for example, an extremely small reorganization energy. This trend has also been stimulated by the recent development of powerful synthetic methods for the controlled functionalization of the fullerene surface.[4] It has since been shown in several investigations that C_{60} acts as a highly effective primary electron acceptor in such donor–acceptor assemblies, with lifetimes of the charge-separated state ranging up to microseconds or even seconds.[5]

A large variety of functional porphyrin derivatives and their photophysical investigations have been published in the literature.[6] Despite their potentially very attractive properties, natural tetrapyrrole derivatives, especially metallochlorins, have less often been the target of synthetic efforts.[7] The photophysical and chemical behavior of natural and semi-synthetic chlorophyll derivatives differ greatly from their symmetric porphyrin counterparts.[8] They show, for example, much stronger and bathochromically shifted Q_y-bands and lend themselves more readily to tuning of their redox and light-absorbing properties by selective modification of their molecular periphery.[9] Besides their function for biomimetic RC models, such molecules have also found another important application in photodynamic therapy, where long-wavelength-absorbing tetrapyrroles are meeting with growing interest.[7a]

Our aim is to investigate the photophysical behavior of bridged natural chlorin-based ET-compounds with C_{60} as the electron-acceptor moiety. Recently, a small number of fullerene-based donor–acceptor models have been reported in which C_{60} is covalently linked to different positions of natural tetrapyrrole derivatives.[10] Since the coupling of complex organic groups to chlorins often involves sophisticated synthetic strategies and lengthy product separation procedures under strict light and oxygen exclusion, the development of novel methods for specific coupling with high yields are required.[11]

Over the last few years palladium(0)-catalyzed coupling reactions have been developed to functionalize halogenated porphyrins or to construct large arrays of covalently linked porphyrins.[12] Some impressive examples have been described in the field of porphyrin chemistry using this powerful coupling strategy.[13] In contrast, only a few examples are known where halogenated chlorins and vinyl-substi-

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tuted coupling reagents have been employed for this reaction type.[14] These factors prompted us to develop a short and effective synthesis of chlorin–fullerene dyads starting from a chlorin building block, using Heck-type conditions, which effectively avoids undesired side-chain modification.

The Heck reaction has been shown many times to be very useful for the preparation of disubstituted olefins, thus opening-up an opportunity to extend a conjugated aromatic system via an olefinic bridge.[15] In this palladium-catalyzed reaction, a carbon–carbon bond is formed from a vinyl functionality, which is available in the 3-position of the naturally occurring Chl *a*, and an aryl halide. The reaction is readily adaptable for chlorins, which often carry multiple sensitive functional groups. Also, in contrast to other coupling methods, such as the McMurry reaction, which require nickel or copper complexes of the chlorin, zinc-centered metallochlorins can be employed directly.[16] This avoids a subsequent demetalation step, which requires harsh conditions and often results in unsatisfactory yields and generally low tolerance towards functional groups.[17] Consequently, the direct metallochlorin functionalization approach presented here greatly simplifies the modification of chlorins towards the construction of complex ET dyads and RC models.

Results and Discussion

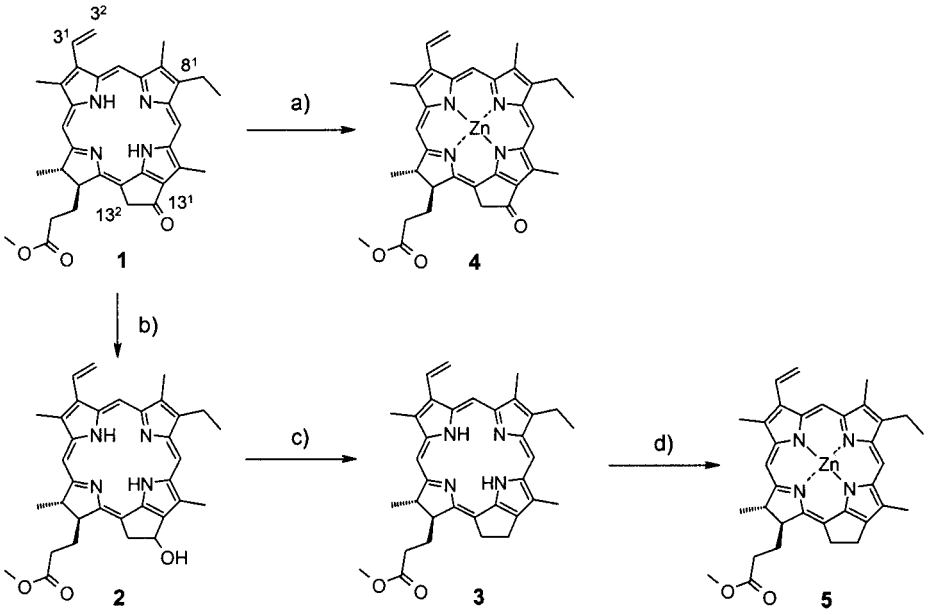
The synthesis of starting material **5** was achieved by consecutive reduction of the 13^1-keto group of methyl ester **1** with sodium borohydride in methanol (91% yield), followed by reduction of the corresponding 13^1-alcohol **2** with sodium borohydride in DCM/TFA at 0 °C to give compound **3** (95% yield; Scheme 1).

The diastereotopic protons in the ^{1}H NMR spectrum of the isocyclic ring of compound **3** were initially reported to appear as a complex multiplet.[18] To be able to exactly characterize the new compounds a detailed assignment of the coupling constants and chemical shifts of this ABXY spin system has been made. This was achieved by performing a spin-system simulation and a spectral fit. A partial structure of the chlorin, with the assigned protons of the isocyclic ring system, is shown in Figure 1, together with the measured and simulated spectra.

The simulated spectrum is in excellent agreement with the measured spectrum, in which partial overlap of the signal groups at δ_H = 3.95 ppm with the quartet of the 8^1-CH_2 group is observed. The assignment of the relative configuration was carried out based on NOE measurements on a structurally similar chlorin.[19] The magnitude of the coupling constants is in agreement with the data from this report. The full set of six coupling constants was only determined for compound **3**; however, the respective values for the other compounds deviate only minimally.

The free base chlorin **1** was directly converted into its zinc complex **4** by treatment with methanol/zinc(II) acetate; it was obtained in nearly quantitative yield. This metalation step is necessary to avoid palladium insertion during the following coupling step.

The synthesis of **5** has been described earlier using a one-step reaction from **1**, but with much lower yields.[9] The metalation of **3** was subsequently performed to yield the corresponding zinc complex **5** in a nearly quantitative amount.



Scheme 1. Synthesis of starting materials for Heck-coupling reactions by sodium borohydride reduction and metalation of a demethoxycarbonylpheophorbide methyl ester. In the structure of **1** the important atom positions are labeled. Reagents and reaction conditions: a) zinc acetate, methanol, room temp.; b) sodium borohydride, methanol, room temp.; c) sodium borohydride, TFA, DCM, 0 °C; d) zinc acetate, methanol, room temp.

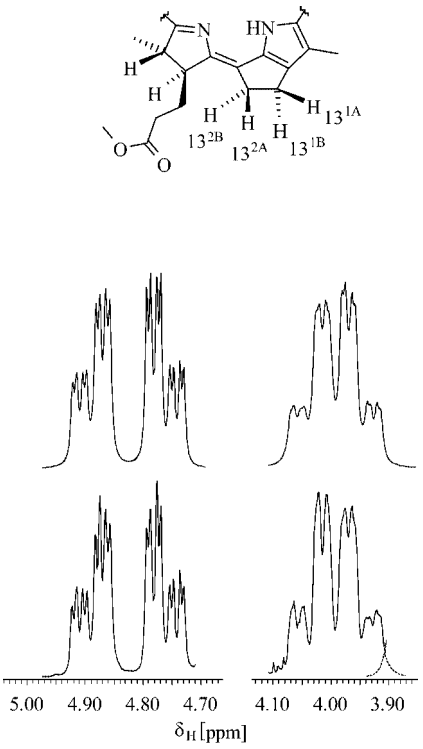


Figure 1. Simulated (upper row) and measured (at 400 MHz; lower row) ^{1}H NMR peak groups of the 13^1- (left group) and 13^2-protons (right group) of compound **3**. The signal on the right-hand side overlaps partially with the 8^1-CH_2 quadruplet (depicted by dotted lines at around δ = 3.91 ppm). The top drawing shows the partial structure with the assignment of the protons.

Heck Coupling of the Chlorin to the Bridging Molecule

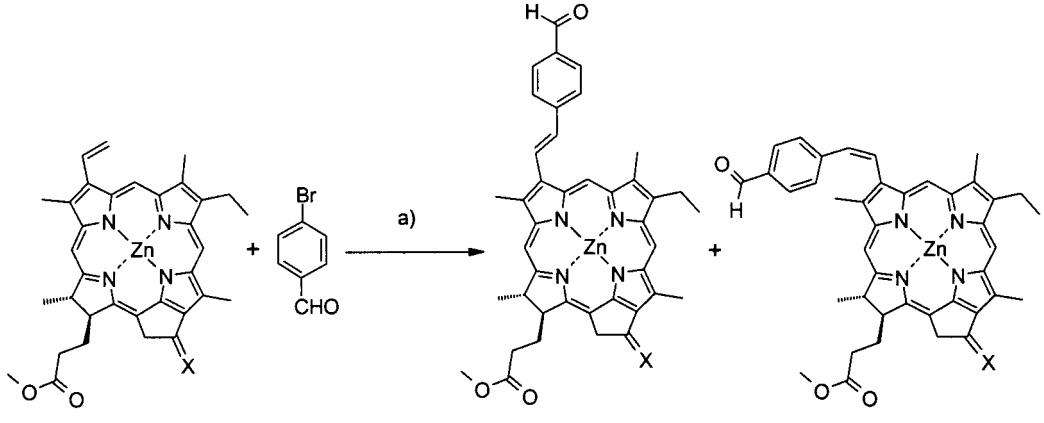
The coupling reaction of the zinc–chlorin complex **4** proceeds well under phase-transfer conditions with 4-bromobenzaldehyde in the presence of 5 mol-% palladium(II) acetate catalyst in DMF for 48 h at 70 °C. The 3^2-*trans*-configured product **6** is formed predominantly (68%) over the 3^2-*cis* product **7** (22%; Scheme 2). Both isomers could be easily separated from the remaining starting material by column chromatography on silica gel using 9:1 pentane/diethyl ether with 0.1% pyridine as eluent.

Conversion of the *cis* product **7** into the *trans* isomer by treatment with iodine was unsuccessful due to the strong oxidizing power of iodine, which results in the destruction of the chlorin system to give several unidentified porphyrin products. However, the unconverted starting material **5** could be easily recovered and used in subsequent coupling reactions.

An extensive study of the coupling conditions using other catalyst mixtures in order to increase the yield and the *trans*/*cis* ratio gave no further improvement. Only decreasing the reaction temperature to 70 °C provided an improved *trans*/*cis* ratio, albeit with slightly lower overall yield. Under otherwise identical reaction conditions, the coupling products **6** and **7** were isolated with yields of 75% and 8%, respectively. The same reaction parameters were used for the coupling of **5** with 4-bromobenzaldehyde. After workup and chromatography on silica gel yields of 66% and 11% were obtained for **8** and **9**, respectively.

The ^{1}H NMR spectrum of **6** in $CDCl_3$ (0.1% [D_4]methanol) shows a typical AB system at δ = 8.36 ppm (J = 16.4 Hz), for the *trans*-configured vinyl protons close to the chlorin core in the 3^1 position, and δ = 7.40 ppm, which can be assigned to the proton at the 3^2 position. The *cis*-configured vinyl protons appear at δ = 6.63 and 5.98 ppm. These signals are not well resolved and appear as a singlet.

The ^{1}H NMR spectra of **8** and **9** have the same characteristic features of *trans*- and *cis*-olefin products. The spectrum of **8** in $CDCl_3$ (0.1% CD_3OD) shows doublets with J

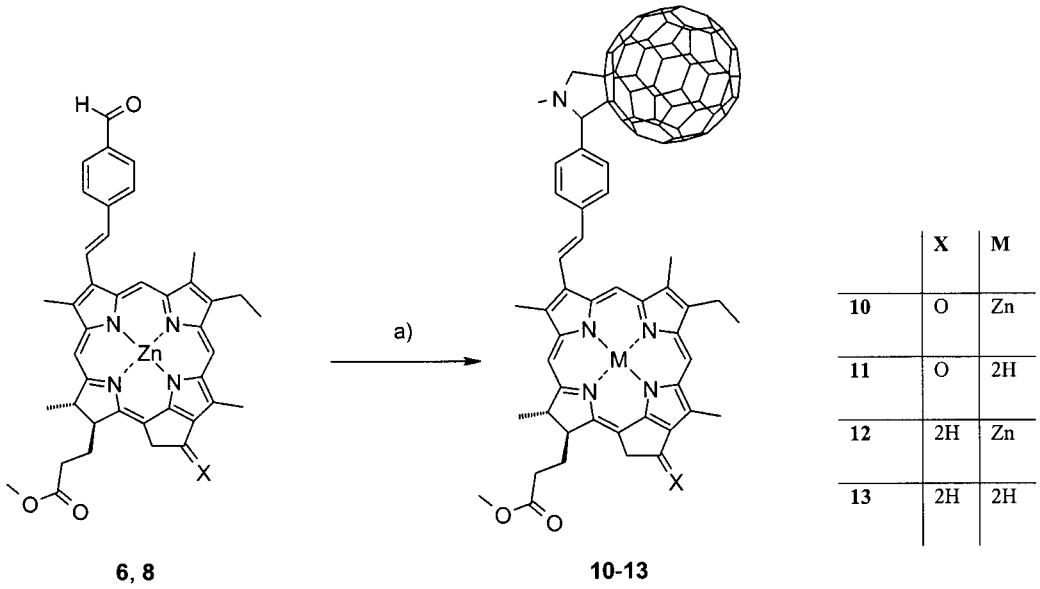


4: X = O
5: X = 2H

6: X = O
8: X = 2H

7: X = O
9: X = 2H

Scheme 2. Heck coupling of the zinc–chlorin complexes **4** and **5** with 4-bromobenzaldehyde under phase-transfer conditions. Reagents and reaction conditions: a) palladium acetate, tetra-*n*-butylammonium bromide, lithium chloride, potassium carbonate, DMF, 70 °C.



	X	M
10	O	Zn
11	O	2H
12	2H	Zn
13	2H	2H

Scheme 3. New fullerene–chlorin ET dyads obtained by Prato's method. Reagents and reaction conditions: a) fullerene C_{60}, sarcosine, toluene, reflux, 6 h.

= 16.3 Hz at δ = 8.29 (3^1 proton) and 7.17 ppm (3^2 proton). The doublets of the vicinal protons of **9** are observed at δ = 6.61 and 6.01 ppm, with a coupling constant of 5.0 Hz.

Prato's method was employed to couple C_{60} with chlorin aldehyde derivatives **6** and **8** (Scheme 3).[20] Thus, the reaction of **6** with C_{60} and *N*-methylglycine in refluxing toluene for 6 h gave metalated compound **10** in 40% yield and the free base **12** in 42% yield. The first purification step was done by GPC and further purification by preparative HPLC. The individual diastereomers of the zinc complex could be separated readily by preparative reversed-phase HPLC, but no effort was made to assign the absolute configuration. The zinc–chlorin–fullerene dyads underwent ready demetalation upon stirring in a dilute solution of HCl in methanol or TFA in DCM to give the corresponding free-base dyads **11** and **13** (94% and 100% yield, respectively). We note that the demetalation leads to considerable decomposition of the chlorin unit. Therefore the most effective procedure is to use the free-base forms of **6** and **8**, which are obtained by demetalation with TFA in DCM in 100% yield, for the final C_{60}-coupling step. Attempts to separate the diastereomers after demetalation failed.

The structures of dyads **10**–**13** were confirmed by ^{1}H and ^{13}C NMR spectroscopy, FAB mass spectrometry, and elemental analysis.

The electronic absorption spectra of dyads **10** and **11** as well as the chlorins **4** and **6** were measured in benzene (Figure 2).

The pronounced bathochromic shift of the major absorption bands of the dyads, especially in the Q_y region, is typical of tetrapyrroles with extended aromatic systems and is due to the increased electron delocalization over the entire π-system. Coupling of the *p*-benzaldehyde moiety to the chlorin leads to a bathochromic shift of 13 nm in the Q_y band (from 657 nm in **4** to 670 nm in **6**; see Figure 2 inset).

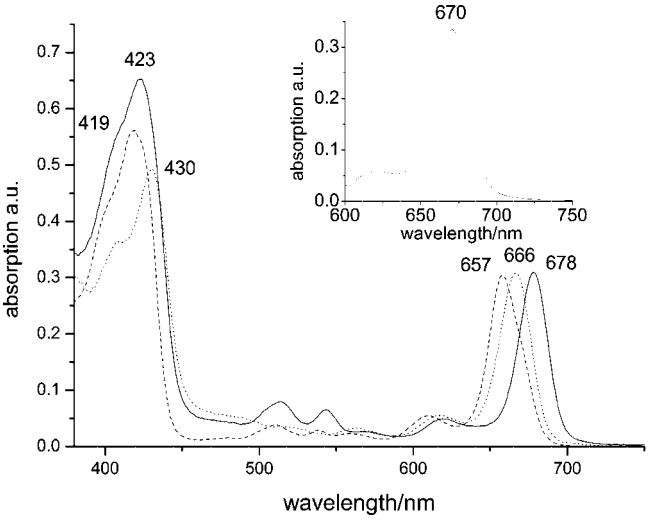
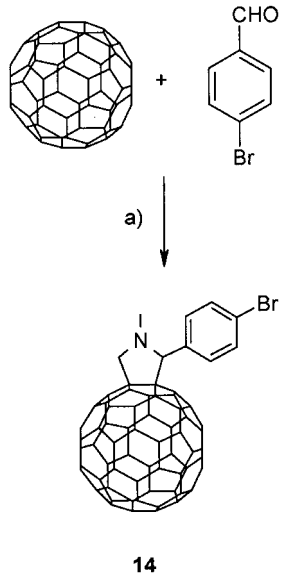


Figure 2. Electronic absorption spectra of dyad **10** (dotted line), dyad **11** (solid line), and chlorin **4** (dashed line) in benzene. The inset shows the Q_y band of compound **6** in benzene.

The subsequent attachment of C_{60} to **6** results in a hypsochromic shift of 4 nm (from 670 nm in **6** to 666 nm in **10**; Figure 2). This can be explained by the replacement of the aldehyde group by the five-membered ring in compound **10**; it is clearly the additional aromatic system that leads to the observed bathochromic shift. Furthermore, preliminary results show that all reported dyads undergo efficient photoinduced ET.[10b]

We envision that the reported coupling methodology will provide an excellent means of improving the preparation of ET dyads. In particular, it will allow us to achieve greater versatility towards other vinyl-substituted (bacterio)-chlorins.

In an attempt to further optimize the reaction sequence, we synthesized the aryl halide fullerene adduct **14**, in 33% yield, by refluxing 4-bromobenzaldehyde with sarcosine for 6 h in toluene and subsequent purification by chromatography on silica gel with $CHCl_3$/toluene (1:1). The resulting building block can be prepared on a larger scale, thus simplifying the reaction sequence and minimizing the reaction steps that involve the sensitive chlorin system (Scheme 4).



Scheme 4. Preparation of the fullerene building block for the Heck coupling reaction. Reagents and reaction conditions: a) sarcosine, toluene, reflux, 6 h; yield: 33%.

The building block **14** was coupled under phase-transfer conditions with the zinc-chlorin complex **4** in the presence of 10 mol-% palladium acetate as catalyst in DMF for 48 h at 90 °C. However, under these conditions we obtained only a yield of 10% of compound **6**. The main components in the reaction mixture were the unreacted starting materials **4** and **14**. The reason for the low yield might be the absence of the electron-withdrawing aldehyde group in the *para* position to the bromo group, or the size of the fullerene derivative, which sterically hinders the *syn*-insertion of the vinyl component into the catalytically active organopalladium species.

Concluding Remarks

A short and high-yield reaction sequence based on a Heck-type hetero-coupling of a semi-synthetic chlorin building block with an attached bridging aromatic aldehyde, followed by cycloaddition of this moiety to sarcosine/fullerene C_{60}, leads to novel covalently linked chlorin/C_{60} dyads. The reported reaction sequence has been optimized with respect to the Heck reaction conditions, leading to the finding that the reaction temperature provides the main control over the *cis*/*trans* ratio of the coupling product. Attempted simplification by an alternative preparation of a C_{60}-containing Heck precursor to be reacted directly with the chlorin moiety proved inferior due to severe limitations in the yield of the coupling. Studies are under way to investigate the suitability of these dyads for PET in artificial solar energy conversion devices.

Experimental Section

General: Melting points, which are uncorrected, were measured on a Reichert microscope hot-stage apparatus. Electronic absorption: Unicam UV2 spectrophotometer. Elemental Analysis: VarioEL 3. FAB-MS: Finnigan MAT 311A or 8230; Xe, 70 eV. ^1H and ^{13}C NMR: Bruker DRX-500 (500 MHz) and DRX-400 (400 MHz), respectively. The chemical shifts are reported relative to $CHCl_3$ at δ = 7.260 ppm. Win1D (analysis of the experimentally obtained spectrum and choice of starting parameters) and WinDAISY (simulation and iteration) (Bruker Inc.) were used for the spin-system analysis. Column Chromatography: Merck silica gel 60 (0.063–0.200 mm). All solvents for reactions were purified and dried in accordance with common procedures, UV/Vis measurements were performed in analytical grade solvents (UVASOL Merck). Analytical high-performance liquid chromatography (HPLC) was performed on a Shimadzu instrument equipped with a diode array wavelength detector and a C-18 reverse-phase cartridge (reverse phase, 250 × 7.8 mm, 5 μm particle size). A Gilson–Abimed chromatograph with a Nucleosil C-18 column from Macherey–Nagel (reverse phase, 250 × 20 mm, 7 μm particle size) and Shimadzu SPD10AV variable wavelength detector were used for preparative HPLC. All experiments were performed under argon and protected from the light.

13^1-Hydroxy-13^1-deoxo-13^2-demethoxycarbonylmethylpheophorbide *a* (2):[10] Compound **1** (250 mg, 0.46 mmol) was dissolved in THF (20 mL) and a solution of $NaBH_4$ (19.0 mg, 0.5 mmol) in ethanol (150 mL) was added dropwise with a syringe. After completion of the reaction (TLC and visible spectrum), the reaction mixture was diluted with diethyl ether (100 mL) and the remaining $NaBH_4$ was quenched by adding 5% NH_4Cl solution (100 mL). The green organic layer was washed with water (2 × 200 mL) and brine (100 mL), dried (Na_2SO_4), and filtered. The solvent was removed by evaporation with a Büchi evaporator under reduced pressure. The raw material was purified by flash chromatography on silica, eluting with diethyl ether. The major product **2** (228 mg, 91%) was isolated as a mixture of isomers. The analytical data are in agreement with literature data.[10] HR-MS: calcd. for $C_{34}H_{39}N_4O_3$ 551.3022; found 551.3008. UV/Vis: λ_{max} (A_{rel}) = 400 nm (1.0), 503 (0.14), 595 (0.07), 652 (0.25). M.p. 198–202 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.83, 9.81 (s, 2 H, 10-H), 9.56, 9.51 (s, 2 H, 5-H), 8.89, 8.78 (s, 2 H, 20-H), 8.20–8.13 (m, 4 H, 3^1-H), 6.36 (br. s, 2 H, 13^1-H), 6.33–6.28, 6.14–6.11 (m, 4 H, 3^2-H), 5.32–5.25, 5.19–5.10 (m, 2 H, 13^2-H), 4.63–4.56 (m, 2 H, 18-H), 4.47–4.42 (m, 2 H, 13^2-H), 4.37–4.29 (m, 2 H, 17-H), 3.84–3.78 (m, 4 H, 8^2-H), 3.58, 3.55 (s, 6 H), 3.53, 3.50 (s, 6 H), 3.45, 3.41 (s, 6 H), 3.38, 3.34 (s, 6 H), 2.71–2.68 (m, 2 H, 17^1-H), 2.54–2.51 (m, 2 H, 17^2-H), 2.29–2.28 (m, 2 H, 17^1-H), 2.19–2.15 (m, 2 H, 17^2-H), 1.86–1.82 (m, 6 H, 18-Me), 1.77–1.70 (m, 6 H, 8^1-Me), –1.38 (br. s, 2 H, NH), –3.22 (br. s, 2 H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.8, 173.7, 166.6 (2 C), 161.66 (2 C), 150.46 (2 C), 143.2, 143.2, 142.06 (2 C), 140.36 (2 C), 137.96 (2 C), 136.2, 134.2, 132.3, 130.9, 128.86 (2 C), 127.76 (2 C), 125.5, 121.36 (2 C), 109.2, 109.1, 99.4, 99.3, 98.1, 98.1, 93.1, 93.0, 69.6, 69.3, 65.5, 52.9, 52.8, 51.5, 51.4, 49.3, 48.5, 30.8, 30.6, 30.3, 29.7, 29.3, 23.8, 19.7, 19.2, 17.7, 13.7, 12.3, 11.5, 11.5, 11.4 ppm.

13^2-Demethoxycarbonyl-13^1-deoxomethylpheophorbide *a* (3): Compound **2** (200 mg, 0.36 mmol) was dissolved in degassed trifluoroacetic acid (15 mL), and the dark-blue solution was cooled to –5 °C in an ethanol/dry ice bath. Then, solid sodium borohydride (0.2 g, 0.6 mmol) was carefully added in small portions under a stream of argon. The cooling bath was warmed up to room temperature, and the reaction mixture was stirred overnight. The mixture was diluted with diethyl ether, rinsed with saturated aqueous sodium hydrogen carbonate, then dried, evaporated, and purified by flash chromatography on silica, eluting with diethyl ether, to give the dark-green chlorin **3**. The desired chlorin **3** was isolated with a yield of 193 mg (95%). $C_{34}H_{38}N_4O_2$ (534.71): calcd. C 76.37, H 7.16, N 10.48; found C 74.91, H 8.18, N 10.62. FAB-MS (nitrobenzyl alcohol): *m/z* (%) = 535 (61) $[M + H]^+$. UV/Vis: λ_{max} (A_{rel}) = 401 nm (1), 503 (0.19), 595 (0.02), 648 (0.25). M.p. 231–236 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.01 (s, 1 H, 10-H), 9.64 (s, 1 H, 5-H), 9.04 (s, 1 H, 20-H), 8.30 (dd, $J_{3\text{-}1,3\text{-}2A}$ = 17.5, $J_{3\text{-}1,3\text{-}2B}$ = 10.5 Hz, 1 H, 3^1-H), 6.40 (dd, $J_{3\text{-}2A,3\text{-}2B}$ = 1.6, $J_{3\text{-}2A,3\text{-}1}$ = 17.8 Hz, 1 H, 3^{2A}-H), 6.19 (dd, $J_{3\text{-}2B,3\text{-}2A}$ = 1.6, $J_{3\text{-}2B,3\text{-}1}$ = 11.5 Hz, 1 H, 3^{2B}-H), 4.92 (ddd*, 1 H, 13^{1A}-H), 4.81 (ddd*, 1 H, 13^{1B}-H), 4.73 (m, $J_{17,18}$ = 2.0, $J_{18,18Me}$ = 7.2 Hz, 1 H, 18-H), 4.52 (m, 1 H, 17-H), 4.05 (ddd*, 1 H, 13^{2A}-H), 4.00 (ddd*, 1 H, 13^{2B}-H), 3.92 (q, J = 7.6 Hz, 2 H, 8^2-CH_2), 3.65 (s, 3 H), 3.64 (s, 3 H), 3.51 (s, 3 H), 3.48 (s, 3 H), 2.82 (m, 1 H, 17^{1A}-H), 2.64 (m, 1 H, 17^{2A}-H), 2.36 (m, 1 H, 17^{1B}-H), 2.27 (m, 1 H, 17^{2B}-H), 1.94 (d, J = 7.2 Hz, 3 H, 18-Me), 1.87 (t, J = 7.6 Hz, 3 H, 8^1-Me), –1.55 (br. s, 1 H, NH), –3.30 (br. s, 1 H, NH) ppm. (The signals labeled with an asterisk were determined with a spin-system simulation, see Figure 1). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 173.9, 165.0, 162.5, 150.9, 149.3, 144.4, 143.7, 142.5, 141.9, 136.6, 136.2, 133.3, 131.1, 130.2, 127.6, 125.2, 121.0, 111.9, 98.3, 97.3, 93.2, 53.4, 51.5, 49.1, 36.3, 30.7, 29.0, 24.4, 24.0, 19.7, 17.7, 12.3, 11.7, 11.5 ppm.

Zinc Complex of 13^2-Demethoxycarbonylmethylpheophorbide *a* (4): The metalation of free base chlorin **1** (400 mg, 0.73 mol) was carried out in a solution of zinc acetate (0.25 g, 1.4 mmol) in MeOH (100 mL) and stirred for 2 h at room temperature. After completion (TLC), the dark-green mixture was diluted with diethyl ether (200 mL). The organic layer was subsequently washed with saturated sodium hydrogen carbonate solution (2 × 100 mL) and brine (100 mL), dried, evaporated, and purified by flash chromatography on silica, eluting with diethyl ether to give **4** (450 mg, 100%). FAB-MS (nitrobenzyl alcohol): *m/z* (%) = 613 (28) $[M + H]^+$ $C_{34}H_{34}N_4O_3Zn$ (612.05): calcd. C 66.72, H 5.60, N 9.15; found C 65.46, H 6.19, N 9.24. UV/Vis: λ_{max} (A_{rel}) = 307 nm (0.79), 428 (1), 570 (0.09), 609 (0.16), 656 (0.88). M.p. 205–209 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.98 (s, 1 H, 10-H), 8.88 (s, 1 H, 5-H), 8.34 (s, 1 H, 20-H), 7.84 (dd, $J_{3\text{-}1,3\text{-}2A}$ = 17.7, $J_{3\text{-}1,3\text{-}2B}$ = 11.4 Hz, 1 H, 3^1-H), 6.11 (dd, $J_{3\text{-}2B,3\text{-}2A}$ = 1.5, $J_{3\text{-}2B,3\text{-}1}$ = 11.5, 1 H, 3^{2A}-H), 6.01 (dd, $J_{3\text{-}2B,3\text{-}2A}$ = 1.5, $J_{3\text{-}2B,3\text{-}1}$ = 11.4 Hz, 1 H, 3^{2B}-H), 4.62 (2d, J = 19.2 Hz, 2 H, 13^2-CH_2), 4.36 (m, $J_{17,18}$ = 1.9, $J_{18,18Me}$ = 7.1 Hz, 1 H, 18-H), 4.10 (m, 1 H, 17-H), 3.38 (s, 3 H), 3.33 (q, J = 7 Hz, 2 H, 8^2-CH_2), 3.30 (s, 3 H), 2.95 (s, 3 H), 2.41 (m, 1 H, 17^{1A}-H, 17^{2A}-H), 2.19 (m, 1 H, 17^{1B}-H, 17^{2B}-H), 1.83 (d, J = 7.3 Hz, 3 H, 18-Me), 1.49 (t, J = 7.2 Hz, 3 H, 8^1-Me) ppm.

Zinc Complex of 13^2-Demethoxycarbonyl-13^1-deoxomethylpheophorbide *a* (5) : The metalation of **3** (200 mg, 0.37 mol) was carried out in a solution of zinc acetate (0.10 g, 0.56 mmol) in MeOH (50 mL) and stirred for 2 h at room temperature. After completion (TLC), the dark-green mixture was diluted with diethyl ether (100 mL) and the organic layer was subsequently rinsed with saturated sodium hydrogen carbonate solution (2 × 50 mL) and brine (100 mL), dried, evaporated, and purified by flash chromatography on silica, eluting with diethyl ether to give **5** (220 mg, 100%). FAB-MS (nitrobenzyl alcohol): *m/z* (%) = 599 (28) $[M + H]^+$ $C_{34}H_{36}N_4O_2Zn$ (598.06): calcd. C 68.28, H 6.07, N 9.37; found C 66.96, H 6.85, N 9.49. UV/Vis: λ_{max} (A_{rel}) = 410 nm (1), 513 (0.03), 581 (0.03), 623 (0.25). M.p. > 330 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.24 (s, 1 H, 10-H), 8.85 (s, 1 H, 5-H), 8.70 (s, 1 H, 20-H), 8.05 (dd, $J_{3\text{-}1,3\text{-}2A}$ = 17.4, $J_{3\text{-}1,3\text{-}2B}$ = 10.4 Hz, 1 H, 3^1-H), 6.19 (dd, $J_{3\text{-}2A,3\text{-}2B}$ = 1.5, $J_{3\text{-}2A,3\text{-}1}$ = 17.7 Hz, 1 H, 3^{2A}-H), 6.01 (dd, $J_{3\text{-}2B,3\text{-}2A}$ = 1.5, $J_{3\text{-}2B,3\text{-}1}$ = 11.5 Hz, 1 H, 3^{2B}-H), 4.62–4.54 (br. m, 3 H, 13^{1A}-H, 13^{1B}-H, 18-H), 4.35 (m, 1 H, 17-H), 3.80 (m, 1 H, 13^{2A}-H), 3.78 (m, 1 H, 13^{2B}-H), 3.47 (s, 3 H), 3.64 (s, 3 H), 3.34 (q, J = 7.6 Hz, 2 H, 82-H) 3.22 (s, 3 H), 3.00 (s, 3 H), 2.73 (m, 1 H, 17^{1A}-H), 2.51 (m, 1 H, 17^{2A}-H), 2.34 (m, 1 H, 17^{1B}-H), 2.21 (m, 1 H, 17^{2B}-H), 1.96 (d, J = 7.2 Hz, 3 H, 18-Me), 1.53 (t, J = 7.6 Hz, 3 H, 8^1-Me) ppm.

Zinc Complexes of (*E*/*Z*)-3^2-(4-Formylphenyl)-13^2-demethoxycarbonylmethylpheophorbide *a* (6/7): The reaction was carried out with **4** (60 mg, 0.1 mmol), K_2CO_3 (30 mg, 0.2 mmol), tetra-*n*-butylammonium bromide (16 mg, 0.05 mmol), LiCl (9 mg, 0.05 mmol), palladium acetate (23 mg, 10 mol-%), 4-bromobenzaldehyde (18 mg, 0.09 mmol), and anhydrous dimethylformamide (40 mL). The mixture was heated at 70 °C under argon for 48 h. The reaction was then cooled down to room temperature, dichloromethane (100 mL) was added, and the organic layer was subsequently rinsed with saturated sodium hydrogen carbonate solution (2 × 50 mL) and brine (100 mL), dried, evaporated, and purified by flash chromatography on silica, eluting with 8:2 diethyl ether/pentane and 0.1% pyridine. The faster running blue-green material was the starting material **4**, and the major product was a bright-green material which was identified by NMR spectroscopy as the *trans* product **6**. The slower running blue band was also collected, and the material was identified as the *cis*-configured zinc–chlorin complex **7**. The major product **6** was isolated as a green solid (44 mg, 68%) and the *cis* product **7** was also isolated (14 mg, 22%).

6: $C_{41}H_{38}N_4O_4Zn$ (716.15): calcd. C 68.76, H 5.35, N 7.82; found C 67.7, H 5.90, N 8.17. FAB-MS (nitrobenzyl alcohol): *m/z* (%) = 716 (10) $[M + H]^+$. UV/Vis: λ_{max} (A_{rel}) = 388 nm (0.82), 435 (1), 579 (0.12), 622 (0.22), 673 (0.89). M.p. 267 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.1 (s, 1 H, CHO), 9.28 (s, 1 H, 10-H), 9.10 (s, 1 H, 5-H) 8.44 (s, 1 H, 20-H), 8.36 (d, $J_{3\text{-}1,3\text{-}2}$ = 16.4 Hz, 1 H, 3^1-H), 8.00, 7.90 (2d, AA′BB′ J = 8.4 Hz, 4 H, Ar-H), 7.4 (d, $J_{3\text{-}1,3\text{-}2}$ = 16.4 Hz, 1 H, 3^2-H), 4.83 (2d, J = 17.4 Hz, 2 H, 13^2-CH_2), 4.42 (m, 1 H, 18-H), 4.29 (m, 1 H, 17-H), 3.58 (q, J = 7.7 Hz, 2 H, 8^2-CH_2), 3.47 (s, 3 H), 3.43 (s, 3 H), 3.36 (s, 3 H), 2.55 (br. m, 2 H, 17^{1A}-H, 17^{2A}-H), 2.24 (br. m, 2 H, 17^{1B}-H, 17^{2B}-H), 1.82 (d, J = 7.3 Hz, 3 H, 18-Me), 1.60 (t, J = 7.6 Hz, 3 H, 8^1-Me) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.5, 191.6, 173.4, 168.1, 161.1, 156.4, 153.4, 150.5, 147.4, 146.8, 145.1, 143.9, 143.8, 136.1, 135.5, 135.0, 134.8, 133.5, 133.4, 131.8, 130.4 (2 C), 127.0 (2 C), 125.0, 106.4, 105.5, 98.8, 92.6, 51.6, 50.6, 48.6, 47.8, 30.6, 29.5, 23.5, 19.3, 17.3, 12.8, 12.5, 10.9 ppm.

7: $C_{41}H_{38}N_4O_4Zn$ (716.15): calcd. C 68.76, H 5.35, N 7.82; found C 67.59, H 6.05, N 8.03. FAB-MS (nitrobenzyl alcohol): *m/z* (%) = 716 (10) $[M + H]^+$. UV/Vis: λ_{max} (A_{rel}) = 307 nm (0.79), 428 (1), 570 (0.09), 609 (0.16), 656 (0.88). M.p. 243 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.91 (s, 1 H, CHO), 9.36 (s, 1 H, 10-H), 9.00 (s, 1 H, 5-H) 8.45 (s, 1 H, 20-H), 7.80, 7.74 (2d, AA′BB′ J = 8.4 Hz, 4 H, Ar-H), 6.63 (s, 1 H, 3^2-H), 5.98 (s, 1 H, 3^1-H), 4.65 (2d, J = 17.4 Hz, 2 H, 13^2-CH_2), 4.42 (m, 1 H, 18-H), 4.29 (m, 1 H, 17-H), 3.65 (q, J = 7.7 Hz, 2 H, 8^2-CH_2), 3.36 (s, 3 H), 3.33 (s, 3 H), 3.11 (s, 3 H), 2.45 (br. m, 2 H, 17^{1A}-H, 17^{2A}-H), 2.24 (br. m, 2 H, 17^{1B}-H, 17^{2B}-H), 1.80 (d, J = 7.3 Hz, 3 H, 18-Me), 1.61 (t, J = 7.6 Hz, 3 H, 8^1-Me) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ =

196.8, 191.2, 174.0, 169.2, 161.6, 155.4, 152.4, 150.5, 147.4, 146.8, 145.1, 143.9, 143.8, 136.1, 135.5, 135.0, 134.8, 133.5, 133.4, 131.8, 130.4 (2 C), 127.0 (2 C), 125.0, 106.4, 105.5, 98.8, 92.6, 51.6, 50.6, 48.6, 47.8, 30.6, 29.5, 23.5, 19.3, 17.3, 12.8, 12.5, 10.9 ppm.

Zinc Complexes of (*E*/*Z*)-3^2-(4-Formylphenyl)-13^2-demethoxycarbonyl-13^1-deoxomethylpheophorbide *a* (8/9): The reaction was carried out using **5** (60 mg, 0.1 mmol), K_2CO_3 (30 mg, 0.2 mmol), tetra-*n*-butylammonium bromide (16 mg, 0.05 mmol), LiCl (9 mg, 0.05 mmol), palladium acetate (23 mg, 10 mol-%), 4-bromobenzaldehyde (18 mg, 0.09 mmol), and anhydrous dimethylformamide (40 mL). The reaction mixture was heated at 70 °C under argon for 48 h. The mixture was cooled down to room temperature, then dichloromethane (100 mL) was added and the organic layer was rinsed with saturated sodium hydrogen carbonate solution (2 × 50 mL) and brine (100 mL), dried, the solvent evaporated, and the remaining solid purified by flash chromatography on silica, eluting with 8:2 diethyl ether/pentane and 0.1% pyridine. The faster running blue-green material was the starting material **5**, but the major product was a green material which was found by NMR spectroscopy to be the *trans* product **8**. The slower running blue band was also collected and this material was found to be the *cis*-configured zinc–chlorin complex **9**. Major product **8** could be isolated to give 41 mg (65%) of a green solid; the *cis* product **9** was isolated with a yield of 9.5 mg (11%).

8: $C_{41}H_{40}N_4O_3Zn$ (702.17): calcd. C 70.13, H 5.74, N 7.98; found C 69.87, H 6.67, N 8.19. FAB-MS (nitrobenzyl alcohol): *m*/*z* (%) = 701 (100) $[M - H]^+$. UV/Vis: λ_{max} (A_{rel}) = 420 nm (1), 523 (0.09), 598 (0.09), 647 (0.47). M.p. 234–236 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.98 (s, 1 H, CHO), 9.34 (s, 1 H, 10-H), 9.32 (s, 1 H, 5-H), 8.67 (s, 1 H, 20-H), 8.29 (d, $J_{3\text{-}1,3\text{-}2}$ = 16.3 Hz, 1 H, 3^1-H), 7.85, 7.67 (2d, AA′BB′ J = 7.8 Hz, 4 H, Ar-H), 7.17 (d, $J_{3\text{-}1,3\text{-}2}$ = 16.3 Hz, 1 H, 3^2-H), 4.68 (br. m, 1 H, 13^{1A}-H), 4.58 (br. m, 2 H, 13^{1B}-H, 18-H), 4.37 (m, 1 H, 17-H), 3.85 (br. m, 2 H, 13^{2A}-H, 13^{2B}-H), 3.70 (q, J = 7.6 Hz, 2 H, 82-H), 3.57 (s, 3 H), 3.35 (s, 3 H), 3.33 (s, 3 H), 3.24 (s, 3 H), 2.75 (m, 1 H, 17^{1A}-H), 2.59 (m, 1 H, 17^{2A}-H), 2.37 (m, 1 H, 17^{1B}-H), 2.27 (m, 1 H, 17^{2B}-H), 1.88 (d, J = 7.3 Hz, 3 H, 18-Me), 1.68 (t, J = 7.6 Hz, 3 H, 8^1-Me) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 191.6, 173.8, 162.3, 159.3, 158.8, 151.6, 148.9, 145.3, 144.8, 144.6, 144.3, 142.0, 141.0, 135.0, 134.9, 133.4, 131.4, 131.3, 130.2 (2 C), 129.8, 126.6 (2 C), 125.9, 119.9, 100.1, 100.0, 92.9, 52.1, 51.6, 47.8, 35.5, 30.6, 28.9, 24.2, 24.1, 19.5, 17.6, 12.9, 12.11, 11.1 ppm.

9: $C_{41}H_{40}N_4O_3Zn$ (702.17): calcd. C 70.13, H 5.74, N 7.98; found C 67.78, H 6.78, N 7.61. FAB-MS (nitrobenzyl alcohol): *m*/*z* (%) = 700 (100) $[M - H]^+$. UV/Vis: λ_{max} (A_{rel}) = 388 nm (0.67), 417 (1), 520 (0.08), 635 (0.35). M.p. 241–242 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.97 (s, 1 H, CHO), 9.54 (s, 1 H, 10-H), 9.48 (s, 1 H, 5-H), 8.76 (s, 1 H, 20-H), 7.85, 7.79 (2d, AA′BB′ J = 7.8 Hz, 4 H, Ar-H), 6.67 (d, $J_{3\text{-}1,3\text{-}2}$ = 5 Hz, 1 H, 3^2-H), 6.01 (d, $J_{3\text{-}1,3\text{-}2}$ = 5 Hz, 1 H, 3^2-H), 4.73 (br. m, 1 H, 13^{1A}-H), 4.58 (br. m, 2 H, 13^{1B}-H, 18-H), 4.42 (m, 1 H, 17-H), 3.93 (br. m, 2 H, 13^{2A}-H, 13^{2B}-H), 3.81 (q, J = 7.6 Hz, 2 H, 8^2-H), 3.54 (s, 3 H), 3.43 (s, 3 H), 3.21 (s, 3 H), 3.24 (s, 3 H), 2.70 (m, 1 H, 17^{1A}-H), 2.56 (m, 1 H, 17^{2A}-H), 2.38 (m, 1 H, 17^{1B}-H), 2.18 (m, 1 H, 17^{2B}-H), 1.85 (d, J = 7.3 Hz, 3 H, 18-Me), 1.68 (t, J = 7.6 Hz, 3 H, 8^1-Me) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 191.9, 173.8, 164.7, 156.4, 158.8, 151.6, 148.9, 145.3, 144.8, 144.6, 144.3, 142.0, 141.0, 135.0, 134.9, 133.4, 131.4, 131.3, 130.2 (2 C), 129.8, 126.6 (2 C), 125.9, 119.9, 100.1, 100.0, 92.9, 52.1, 51.6, 47.8, 35.5, 30.6, 28.9, 24.2, 24.1, 19.5, 17.6, 12.9, 12.11, 11.1 ppm.

Zinc Complex 10: Compound **6** (60 mg, 0.08 mmol) and *N*-methylglycine (sarcosine) (27 mg, 0.3 mmol) were added to a solution of fullerene C_{60} (60 mg, 0.08 mmol) in toluene (40 mL). The resulting solution was heated for six hours at reflux temperature, then the crude reaction mixture was filtered and the solvent removed in vacuo. The resulting solid was purified by flash chromatography on silica, eluting with toluene. The dark-green major band was collected and the solvent removed in vacuo. The material was subjected to HPLC purification (reversed phase, 250 × 20 mm, 7 μm, 100 Å, C-18 Macherey–Nagel) with MeOH/THF/CH_2Cl_2 (4:1:4; 4 mL min^{-1}) as eluent. After evaporation of the solvent, 46 mg (40%) of product **10a/b** was obtained as a dark-green powder (mixture of diastereomers **10a/b**, ratio 1:1). $C_{103}H_{43}N_5O_3Zn$ (1463.9): calcd. C 84.51, H 2.96, N 4.78; found C 84.56, H 2.53, N 5.33. FAB-MS (nitrobenzyl alcohol): *m*/*z* (%) = 1464 (1) $[M + H]^+$, 720 (100, $[C_{60}]^-$). UV/Vis (benzene): λ_{max} (A_{rel}) = 409 nm (0.75), 430 (1), 563 (0.10), 616 (0.14), 667 (0.65). M.p. > 330 °C. For ^{1}H and ^{13}C NMR measurements the diastereomers were separated by HPLC [eluent: MeOH/THF/CH_2Cl_2 (4:0.5:4.5); 10 mL min^{-1}].

10a: ^{1}H NMR (500 MHz, $CDCl_3/CS_2$): δ = 9.26 (s, 1 H, 10-H), 9.11 (s, 1 H, 5-H), 8.38 (s, 1 H, 20-H), 8.29 (d, J = 16.5 Hz, 3^1-H), 7.94 (br. s, 2 H, Ar-H), 7.89 (m, 2 H, Ar-H), 7.47 (d, J = 16.5 Hz, 3^2-H), 5.05 (d, J = 19.4 Hz, 1 H, 13^2-CH$_2$), 4.99 (s, 2 H, 5′-H, 2′-H), 4.88 (d, J = 19.7 Hz, 1 H, 13^2-CH$_2$), 4.44 (m, 1 H, 18-H), 4.24 (m, 1 H, 2′-H), 4.18 (m, 1 H, 17-H), 3.51 (s, 3 H), 3.49 (s, 3 H), 3.44 (q, J = 7.24 Hz, 2 H, 8^2-CH$_2$), 3.33 (s, 3 H), 3.06 (s, 3 H), 2.89 (s, 3 H, 1′-*N*–Me), 2.57 (m, 1 H, 17^{1A}-H), 2.49 (m, 1 H, 17^{1B}-H),2.26 (m, 2 H, 17$^{2A/B}$-H), 1.80 (d, J = 7.24 Hz, 3 H, 18-Me), 1.57 (t, J = 7.5 Hz, 3 H, 8^1-Me) ppm. ^{13}C NMR (101 MHz, $CDCl_3/CS_2$): δ = 196.2, 173.4, 168.3, 156.1, 153.8, 152.8, 151.6 (2 C), 150.8, 147.2, 146.9, 143.8, 143.1, 138.3, 135.8, 135.1, 134.3, 133.2, 131.9, 130.0, 128.2, 126.6, 125.5, 121.6, 106.4, 105.5, 98.5, 92.5, 83.5, 77.2, 70.0, 51.6, 50.6, 48.8, 40.1, 30.3, 29.5, 21.1, 19.15, 17.2, 12.8, 12.3, 10.9 ppm.

10b: ^{1}H NMR (500 MHz, $CDCl_3/CS_2$): δ = 9.31 (s, 1 H, 10-H), 9.16 (s, 1 H, 5-H), 8.39 (s, 1 H, 20-H), 8.34 (d, J = 16.25 Hz, 3^1-H), 7.90 (br. s, 4 H, Ar-H), 7.49 (d, J = 16.25 Hz, 3^2-H), 5.05 (d, J = 19.4 Hz, 1 H, 13^2-CH$_2$), 4.98 (s, 2 H, 5′-H, 2′-H), 4.93 (d, J = 19.7 Hz, 1 H, 13^2-CH$_2$), 4.42 (m, 1 H, 18-H), 4.26 (m, 1 H, 2′-H), 4.19 (m, 1 H, 17-H), 3.60 (q, J = 7.24 Hz, 2 H, 8^2-CH$_2$), 3.56 (s, 3 H), 3.51 (s, 3 H), 3.35 (s, 3 H), 3.13 (s, 3 H), 2.88 (s, 3 H, 1′-*N*-Me), 2.58 (m, 1 H, 17^{1A}-H), 2.49 (m, 1 H, 17^{1B}-H),2.26 (m, 2 H, 17$^{2A/B}$-H), 1.80 (d, J = 7.24 Hz, 3 H, 18-Me), 1.61 (t, J = 7.5 Hz, 3 H, 8^1-Me) ppm. ^{13}C NMR (101 MHz, $CDCl_3/CS_2$): 196.3, 173.2, 168.1, 156.3, 153.4, 152.7, 151.3 (2 C), 150.4, 147.3, 146.6, 143.7, 143.5, 138.2, 137.5, 135.5, 135.4, 134.1, 133.1, 131.6, 129.1, 128.3, 126.3, 125.3, 125.1, 121.5, 106.2, 105.4, 98.2, 92.6, 83.7, 77.3, 70.4, 67.6, 51.7, 50.5, 48.7, 40.1, 30.3, 26.9, 21.1, 19.5, 17.2, 12.8, 12.3, 10.9 ppm.

Pheophorbide *a* Derivative 11: Trifluoroacetic acid (3 mL) was added to a solution of pure diastereomer **10a** (30 mg, 0.02 mmol) in CH_2Cl_2 (30 mL), and the mixture stirred at room temperature for 1 h under argon. The reaction was then quenched by slow addition of 5% $NaHCO_3$ solution. The organic phase was extracted with CH_2Cl_2 and washed with water. After standing over anhydrous Na_2SO_4, the organic extract was concentrated to dryness. The resulting solid was purified by flash chromatography on silica, eluting with toluene. After evaporation of the solvent, 28 mg (94%) of **11** was isolated as a brownish green powder. $C_{103}H_{45}N_5O_3$ (1399.9): calcd. C 88.33, H 3.24, N 5.00; found C 88.31, H 3.19, N 5.23. FAB-MS (nitrobenzyl alcohol): *m*/*z* (%) = 1400 (1) $[M + H]^+$, 720 (100) $[C_{60}]^-$. UV/Vis (benzene): λ_{max} (A_{rel}) = 421 nm (1), 514 (0.12), 544 (0.11), 619 (0.07), 679 (0.48). M.p. > 330 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.50 (s, 1 H, 10-H), 9.44 (s, 1 H,

5-H), 8.56 (s, 1 H, 20-H), 8.41 (d, J = 16.5 Hz, 3^1-H), 7.93 (m, 4 H, Ar-H), 7.63 (d, J = 16.5 Hz, 3^2-H), 5.25 (d, J = 19.7 Hz, 1 H, 13^2-CH_2), 5.08 (d, J = 19.7 Hz, 1 H, 13^2-CH_2), 4.99 (d, J = 9 Hz, 1 H, 5′-H), 4.98 (s, 1 H, 2′-H), 4.47 (m, 1 H, 18-H), 4.23 (m, 1 H, 17-H, 5′-H), 3.69 (q, J = 7.24 Hz, 2 H, 8^2-CH_2), 3.65 (s, 3 H), 3.59 (s, 3 H), 3.46 (s, 3 H), 3.23 (s, 3 H), 2.89 (s, 3 H, 1′-*N*-Me), 2.67 (m, 1 H, 17^{1A}-H), 2.55 (m, 1 H, 17^{1B}-H), 2.30 (m, 2 H, $17^{2A/B}$-H), 1.80 (d, J = 7.24 Hz, 3 H, 18-Me), 1.68 (t, J = 7.5 Hz, 3 H, 8^1-Me), 0.40 (br. s, 1 H, NH), –1.68 (s, 1 H, NH) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 206.3, 173.5, 169.2, 160.8, 153.5, 147.3, 147.2, 146.3, 146.1, 146.0, 145.9, 145.7, 145.4, 145.3, 145.2, 144.3, 143.1, 142.1, 142.6, 142.5, 142.2, 142.0, 141.9, 141.6, 141.5, 140.1, 138.1, 136.5, 135.8, 135.6, 130.2, 127.3, 125.5, 121.3, 116.1, 106.4, 104.2, 97.1, 92.6, 83.4, 70.2, 69.7, 51.8, 51.7, 50.0, 48.1, 34.2, 31.9, 31.0, 29.9, 27.2, 23.2, 21.2, 19.5, 19.4, 17.4, 12.6, 12.2, 11.44 ppm.

Zinc Complex 12: Compound **8** (60 mg, 0.08 mmol) and *N*-methylglycine (sarcosine) (27 mg, 0.3 mmol) were added to a solution of fullerene C_{60} (60 mg, 0.08 mmol) in toluene (40 mL). The resulting solution was heated for six hours at reflux temperature. This crude reaction mixture was filtered and the solvent removed in vacuo. The resulting solid residue was purified by flash chromatography on silica, eluting with toluene. The dark-green major band was collected and the solvent removed in vacuo. The material was subjected to HPLC purification (reversed phase 250 × 20 mm, 7 μm, 100 Å, C-18 Macherey–Nagel) with MeOH/THF/CH_2Cl_2 (4:1:4; 4 mL min^{-1}) as eluent. After evaporation of the solvent, 46 mg (42%) of a mixture of both diastereomers **12a/b** (ratio 1:1) was isolated as a green powder. ^{1}H NMR spectroscopic data were only determined for one diastereomer (**12a**). $C_{103}H_{45}N_5O_2Zn$ (1449.9): calcd. C 85.33, H 3.13, N 4.83; found C 85.69, H 2.97, N 5.03 (**12a**); C 85.96, H 3.196, N 4.99 (**12b**). FAB-MS (nitrobenzyl alcohol): *m/z* (%) = 1449 (1) $[M]^+$, 720 (52) $[C_{60}]^-$, 729 (15) $[M - C_{60}]^+$. UV/Vis: λ_{max} (A_{rel}) = 408 nm (1), 518 (0.06), 595 (0.06), 637 (0.29). M.p. > 330 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.33 (s, 1 H, 10-H), 9.29 (s, 1 H, 5-H), 8.84 (s, 1 H, 20-H), 8.31 (d, J = 17 Hz, 1 H, 3^1-H), 7.85, 7.77 (2d, AA′BB′ J = 7.4 Hz, 4 H, Ar-H), 7.21 (d, J = 17 Hz, 1 H, 3^2-H), 4.99 (s, 2 H, 2′-H, 5′-H), 4.93 (br. m, 1 H, 13^{1A}-H), 4.58 (br. m, 2 H, 13^{1B}-H, 18-H), 4.39 (m, 1 H, 17-H), 4.26 (m, 1 H, 2′-H) 3.89 (br. m, 2 H, 13^{2A}-H, 13^{2B}-H), 3.81 (q, J = 7.6 Hz, 2 H, 8^2-CH_2), 3.52 (s, 3 H), 3.44 (s, 3 H), 3.25 (s, 3 H), 3.23 (s, 3 H), 2.91 (s, 3 H, 1′-NMe), 2.71 (m, 1 H, 17^{1A}-H), 2.58 (m, 1 H, 17^{2A}-H), 2.39 (m, 1 H, 17^{1B}-H), 2.21 (m, 1 H, 17^{2B}-H), 1.84 (d, J = 7.3 Hz, 3 H, 18-Me), 1.66 (t, J = 7.6 Hz, 3 H, 8^1-Me) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.8, 164.7, 156.4, 158.8, 155.5, 153.3, 152.3, 151.8, 151.6, 150.1, 148.9, 147.2, 146.1, 146.0, 145.9, 145.8, 145.5, 145.4, 145.3, 145.1, 144.8, 144.6, 144.5, 144.4, 144.3, 144.2, 142.6, 142.0, 141.9, 141.8, 141.6, 141.4, 141.0, 139.8, 139.4, 135.0, 134.9, 133.4, 131.4, 131.3, 130.2 (2 C), 129.8, 126.6 (2 C), 125.9, 119.9, 100.1, 100.0, 92.9, 82.2, 69.9, 68.8, 52.1, 51.6, 39.8, 47.8, 35.5, 30.6, 28.9, 24.2, 24.1, 19.5, 17.6, 12.9, 12.1, 11.1 ppm.

Pheophorbide *a* Derivative 13: Trifluoroacetic acid (3 mL) was added to a solution of **12** (30 mg, 0.02 mmol) in CH_2Cl_2 (30 mL) and the mixture was stirred for 1 h at room temperature under argon. The reaction was then quenched by slow addition of $NaHCO_3$ solution, and the organic phase was extracted with CH_2Cl_2 and washed with water. After standing over anhydrous Na_2SO_4, the organic extract was concentrated to dryness. The resulting mixture was purified by flash chromatography on silica, eluting with toluene. After evaporation of the solvent, 30 mg (100%) of **13** was isolated as a brownish green powder. $C_{103}H_{47}N_5O_2$ (1386.6): calcd. C 89.22, H 3.42, N 5.05; found C 89.45, H 3.62, N 5.02. FAB-MS (nitrobenzyl alcohol): *m/z* (%) = 1386 (2) $[M + H]^+$, 720 (45) $[C_{60}]^-$. UV/Vis: λ_{max} (A_{rel}) = 401 nm (1.0), 501 (0.14), 595 (0.02), 647 (0.24). M.p. > 330 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.49 (s, 1 H, 10-H), 9.35 (s, 1 H, 5-H), 8.97 (s, 1 H, 20-H), 8.44 (d, J = 17 Hz, 1 H, 3^1-H), 7.94, 7.90 (2d, AA′BB′ J = 7.4 Hz, 4 H, Ar-H), 7.43 (d, J = 17 Hz, 1 H, 3^2-H), 5.02 (s, 2 H, 2′-H, 5′-H), 4.99 (br. m, 1 H, 13^{1A}-H), 4.62 (br. m, 2 H, 13^{1B}-H, 18-H), 4.46 (m, 1 H, 17-H), 4.31 (m, 1 H, 2′-H) 3.91 (br. m, 2 H, 13^{2A}-H, 13^{2B}-H), 3.82 (q, J = 7.6 Hz, 2 H, 8^2-CH_2), 3.55 (s, 3 H), 3.44 (s, 3 H), 3.25 (s, 3 H), 3.23 (s, 3 H), 2.93 (s, 3 H, 1′-NMe), 2.69 (m, 1 H, 17^{1A}-H), 2.57 (m, 1 H, 17^{2A}-H), 2.37 (m, 1 H, 17^{1B}-H), 2.23 (m, 1 H, 17^{2B}-H), 1.82 (d, J = 7.3 Hz, 3 H, 18-Me), 1.69 (t, J = 7.6 Hz, 3 H, 8^1-Me), –0.02 (br. s, 1 H, NH), –1.68 (s, 1 H, NH) ppm.

2′-(4-Bromphenyl)[60]fullero[*c*]tetrahydropyrrole (14): 4-Bromobenzaldehyde (50 mg, 0.30 mmol) and *N*-methylglycine (sarcosine) (110 mg, 1.2 mmol) were added to a solution of C_{60} (200 mg, 0.30 mmol) in toluene (100 mL). The resulting solution was heated for six hours at reflux temperature. This crude reaction mixture was filtered and the solvent was removed in vacuo. The residue was purified by flash chromatography on silica, eluting with toluene/$CHCl_3$ (1:1). The brown major band was collected. After evaporation of the solvent, 88 mg (33%) of **14** was isolated as a brown powder. $C_{69}H_{10}BrN$ (932.76): calcd. C 88.85, H 1.08, N 1.50; found C 88.17, H 0.74, N 1.73. ESI-MS (CH_2Cl_2): *m/z* =933 $[M + H]^+$, 720 $[C_{60}]^-$. UV/Vis: λ_{max} (A_{rel}) = 246 nm (1), 311 (0.41), 419 (0.06). M.p. 168–173 °C. ^{1}H NMR (250 MHz, $CDCl_3/CS_2$, 1:1): δ = 7.67 (d, J = 7.5 Hz, 2 H, 2, 6-Ar-H), 7.53 (d, J = 7.5 Hz, 2 H, 3, 5-Ar-H), 4.97 (d, J = 9.5 Hz, 1 H, pyrrolidone-5′-H), 4.88 (s, 1 H, pyrrolidone-2′-H), 4.25 (d, J = 9.5 Hz, 1 H, pyrrolidone-5′-H), 2.78 (s, 3 H, pyrrolidone-1′-Me) ppm. ^{13}C NMR (63 MHz, $CDCl_3/CS_2$, 1:1): δ = 156.0, 153.7, 153.0, 152.7, 147.3, 146.5, 146.4, 146.2, 145.9, 145.7, 145.6, 145.5, 145.4, 144.7, 143.0, 142.7, 142.6, 142.3, 142.1, 142.0, 141.8, 140.2, 136.4, 136.1, 131.9, 130.9, 129.0, 128.3, 125.3, 122.7, 82.9, 70.0, 68.9, 67.6, 39 ppm.

Supporting Information (see footnote on the first page of this article): CHN analytical data of key compounds.

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