Electronic Supporting Information

Water Coordinated Zinc Dioxo-Chlorin and Porphyrin Self-assemblies as Chlorosomal Mimics: Variability of Supramolecular Interactions‡

Aldo Jesorka,[*a,b] Alfred R. Holzwarth,[*a] Andreas Eichhöfer,[c] Chilla Malla Reddy,[c,d] Yusuke Kinoshita,[e] Hitoshi Tamiaki,[*e] Martin Katterle,[a,f] Jean-Valère Naubron[g] and Teodor Silviu Balaban[*a,c,h] *

[a] *Max-Planck-Institut für Bioanorganische Chemie, P.O. Box 10 13 65, D-45413 Mülheim a.d. Ruhr, Germany. E-mail: holzwarth@mpi-muelheim.mpg.de, Fax: (+49) 208 3063951)*

[b] Present address: *Department of Chemistry and Bioscience, Chalmers University of Technology, Kemivägen 10, S-412 96 Gothenburg, Sweden. E-mail: aldo@chalmers.se;Fax: (+46) 31-772-3858*

[c] *Karlsruhe Institute of Technology, Institute for Nanotechnology, Karlsruhe, Germany*

[d] Present address: *Indian Institute of Science Education and Research, Kolkata, West Bengal, India*

[e] *Department of Bioscience and Biotechnology, Faculty of Science and Engineering, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan. E-mail: tamiaki@fc.ritsumei.ac.jp; FAX: (+81)77-561-2659*

[f] Present address: *Fraunhofer Institute for Biomedical Engineering, Potsdam, Germany*

[g] *Aix-Marseille Univ, CNRS FR 1739, Spectropôle, Campus Saint Jérôme, Avenue Escadrille Normandie Niemen, F-13397 Marseille, CEDEX 20, France.*

[h] Present address: *Aix-Marseille Univ, Institut des Sciences Moléculaires de Marseille, CNRS UMR 7313, Chirosciences, Campus Saint Jérôme, Avenue Escadrille Normandie Niemen, Case A62, F-13397 Marseille, CEDEX 20, France. E-mail*: ts.balaban@univ-amu.fr; *Fax : (+33)491-28-91-46*

---

‡ This work is dedicated to Professor Kurt Schaffner on the occasion of his 80th anniversary.

Materials and Methods. Melting points, which are uncorrected, were measured on a Reichert microscopic hot stage apparatus. Absorption spectra were measured on a Shimadzu UV2102PC spectrophotometer in 0.1 and 1 cm quartz cuvettes. FT-IR spectra were recorded in KBr pellets or in CaF_2 cells on Bruker IFS66, Bruker PMA 50 coupled to Vertex 70, and Perkin-Elmer 1600 spectrophotometers. Electronic CD spectra were recorded on AVIV 62ADS and JASCO 815 spectrometers. FAB HR-MS spectra were recorded as NBA matrix on a VG Instruments AUTOSPEC spectrometer. ^{1}H- and ^{13}C-NMR spectra were obtained on Bruker Avance DRX400 and DRX500 spectrometers and the chemical shifts are reported relative to the residual solvent peak taken for $CHCl_3$ at 7.24 ppm and for DMSO at 2.49 ppm. Column chromatoghraphy was performed on silica gel (Merck, 0.063-0.02 mm).

Azeotropic Drying Procedure. Sodium-lead alloy (1.0 g**)** and 30 mL anhydrous CCl_4 is placed in one end of a closed apparatus consisting of two 100 mL two-necked flasks connected by a 15 cm water cooled condenser as shown in Fig. S1. The CCl_4 is stirred at 60 °C for 2 hours under argon, then a saturated solution of the vacuum dried chlorin in anhydrous THF (1 mL) is placed into the flask at the opposite end of the condenser. Then 15 mL of the dry CCl_4 is distilled into the chlorin-containing flask and afterwards to nearly complete dryness back into the reservoir flask. This procedure is repeated three to four times. Using a syringe the water depleted chlorin can then be re-dissolved in a small amount of CH_2Cl_2 and removed from the apparatus.

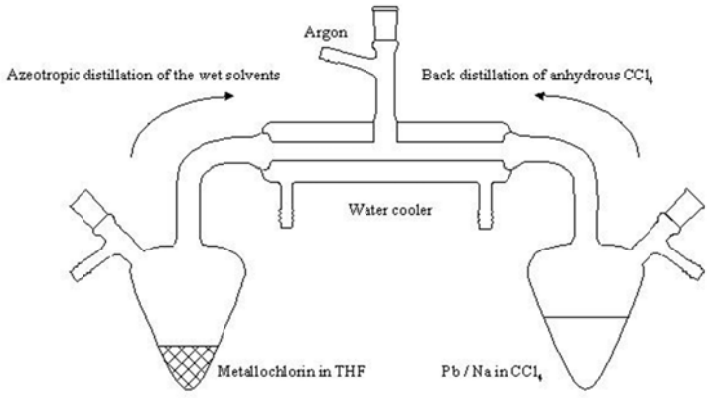

Fig. S1 Azeotropic drying of metallochlorins using a Pb/Na alloy.

3-Desvinyl-3-acetyl methyl pyropheophorbide *a* Zn complex (2). This compound was obtained by metallation with $Zn(OAc)_2$ of the free base obtained as described earlier.[S1]

Methyl pyropheophorbide-*a* (7). This compound was obtained from the green algae *Spirulina geitleri* in a comparable yield and the NMR spectra were identical to those reported earlier.[S2]

3-Desvinyl-3-formyl-methyl pyropheophorbide *a* (3-free base). This compound was prepared from **7** according to a modified literature procedure published earlier.[S3] Instead of running the reaction in THF or dioxane and slowly adding a sodium periodate solution in acetic acid, a phase transfer catalysis was applied from an ether / dilute acetic acid biphasic system. Higher yields and less by-products at comparable reaction times were obtained while facilitating the removal of the acetic acid. Analytical data of the compound are in agreement with the reported literature data.

3-Desvinyl-3-formyl - methyl pyropheophorbide *a* Zn complex (3). The free base **3** (165 mg, 0.25 mmol) was dissolved in methanol (20 mL). Solid zinc(II)-acetate 100 mg (0.54 mmol) was added and the mixture was stirred for 1 hour in an aluminum foil covered flask. The clear green solution was diluted with 150 mL of brine and extracted three times with diethyl ether (50 mL). The combined extracts were washed three times with water (100 mL), dried over sodium sulfate and the solvent was evaporated under reduced pressure. The residue was chromatographed on silica gel using diethyl ether as eluent to obtain 149 mg of **3**. (97%). M.p.: 175-178 °C. ^{1}H-NMR (500 MHz, $CDCl_3$): 10.81 (s, 1H, 3-CHO), 9.56 (s, 1H, 10-H), 9.16 (s, 1H, 5-H), 8.52 (s, 1H, 20-H), 5.15 (2d, J = 19.8 Hz, 2H, 13^2-CH_2), 4.40 (dq, $J_{17,\,18}$ = 2.0 Hz, $J_{18,\,18Me}$ = 7.2 Hz, 1H, 18-H), 4.16 (m, 1H, 17-H), 3.52 (s, 3H, O-Me), 3.45 (q, J = 7.0 Hz, 2H, 8^2 -CH_2), 3.41 (s, 3H, 12-Me), 3.34 (s, 3H, 2-Me), 2.97 (s, 3H, 7-Me), 2.42 (m, 2H, 17^{1A} -H, 17^{2A} -H), 2.12 (m, 2H, 17^{1B} -H, 17^{2B} -H), 1.81 (d, J = 7.3 Hz, 3H, 18-Me), 1.51 (t, J = 7.2 Hz, 3H, 8^2-Me). ^{13}C-NMR (133 MHz, $CDCl_3$): 196.6, 188.2, 173.3, 166.5, 160.8, 157.7, 150.5, 149.6, 148.8, 146.6, 145.5, 144.2,

143.4, 135.8, 135.1, 132.6 (2 C), 105.6, 105.1, 102.0, 93.57, 51.6, 51.1, 48.2, 48.0, 30.5, 29.4, 23.7, 19.2, 17.3, 12.6, 11.3, 10.7. UV/Vis (λ_{max}/nm, A_{rel}, CH_2Cl_2): 390 (0.5), 418 (0.7), 445 (0.99), 540 (0.04), 584 (0.07), 642 (0.14), 679 (1.0). HR-MS, *m/z*: calculated for $C_{33}H_{32}N_4O_4Zn$: 612.1716, found: 612.1740.

13^1-Deoxo-13^1-hydroxy-13^2-demethoxycarbonylmethylpheophorbide *a* (8a, 8b). Reduction of **7** (274 mg, 0.5 mmol) dissolved in 25 ml dry THF was performed by adding 19.0 mg (0.50 mmol) $NaBH_4$ suspended in 100 ml ethanol. After stirring for 1 h under argon, the light green mixture was poured into 100 ml 5% aqueous NH_4Cl and thoroughly extracted three times with 50 mL portions of diethyl ether. The combined extracts were washed once with 50 mL brine, then three times with water. After drying over sodium sulphate the solvents were removed in vacuum. A first chromatographic purification was performed on silica gel (3 x 60 cm) eluted with diethyl ether followed by HPLC-separation of the 13^1-epimers which resulted in 100 mg (0.18 mmol, 36%) **8a** und 150 mg (0.27 mmol, 55%) **8b**. UV/Vis (λ_{max}/nm, A_{rel}, CH_2Cl_2): 400 (1.0), 503 (0.14), 595 (0.07), 652 (0.25).

(13^1*R*)-13^1-Deoxo-13^1-hydroxy-13^2-demethoxycarbonylmethylpheophorbide *a* (8a): M.p.: 222-226 °C. ^{1}H-NMR (270 MHz, $CDCl_3$): 9.85 (s, 1H, 10-H), 9.62 (s, 1H, 5-H), 8.89 (s, 1H, 20-H), 8.21 (dd, $J_{3\text{-}1,\ 3\text{-}2A}$ = 17.8 Hz, $J_{3\text{-}1,\ 3\text{-}2B}$ = 11.5 Hz, 1H, 3^1-H), 6.51 (d, J = 5.7 Hz, 1H, 13^1-H), 6.33 (dd, $J_{3\text{-}2A,\ 3\text{-}2B}$ = 1.6 Hz, $J_{3\text{-}2A,\ 3\text{-}1}$ = 17.8 Hz, 1H, 3^{2A}-H), 6.16 (dd, $J_{3\text{-}2B,\ 3\text{-}2A}$ = 1.6 Hz, $J_{3\text{-}2B,\ 3\text{-}1}$ = 11.5 Hz, 1H, 3^{2B}-H), 5.38 (dd, $J_{13\text{-}2A,\ 13\text{-}2B}$ = 16.4 Hz, $J_{13\text{-}2A,\ 13\text{-}1}$ = 6.4 Hz, 1H, 13^{2A}-H), 4.64 (dq, $J_{17,\ 18}$ = 2.0 Hz, $J_{18,\ 18Me}$ = 7.2 Hz, 1H, 18-H), 4.59 (dd, $J_{13\text{-}2A,\ 13\text{-}2B}$ = 16.4 Hz, $J_{13\text{-}2B,\ 13\text{-}1}$= 1.1 Hz, 1H, 13^{2B}-H), 4.44 (m, 1H, 17-H), 3.82 (q, J = 7.6 Hz, 2H, 8^2-CH_2), 3.59 (s, 3H), 3.55 (s, 3H), 3.54 (s, 3H), 3.39 (s, 3H), 2.71 (m, 1H, 17^{1A}-H), 2.55 (m, 1H, 17^{2A}-H), 2.31 (m, 1H, 17^{1B}-H), 2.20 (m, 1H, 17^{2B}-H), 1.83 (d, J = 7.2 Hz, 3H, 18-Me), 1.74 (t, J = 7.6 Hz, 3H, 8^1-Me), -1.38 (s, br, 1H, NH), -3.22 (s, br, 1H, NH). ^{13}C-NMR (89 MHz, $CDCl_3$): 173.8, 166.7, 161.6, 150.7, 150.5, 143.3, 142.0 (2C), 140.3, 137.9, 136.2, 134.2, 132.4, 130.1, 128.9, 127.7, 121.4, 109.1, 99.5, 98.2, 93.1, 69.5, 52.9, 51.6, 49.3, 48.2, 30.8, 29.3, 23.9, 19.7, 17.7, 12.3, 11.7, 11.5. HR-

MS, *m/z*: calculated for $C_{34}H_{39}N_4O_3$: 551.3022, found: 551.3008. NOE (400 MHz, $CDCl_3$; *NOE*-Experiment): 6.49 (13^1-H): 5.36 (st, 13^{2A}-H); 5.36 (13^{2A}-H): 6.50 (st, 13^1-H), 4.58 (st, 13^{2B}-H); 4.58 (13^{2B}-H): 5.36 (st, 13^{2A}-H), 4.43 (w, 17-H); 4.43 (17-H): 4.58 (st, 13^{2A}-H), 1.83 (st, 18-Me).

(13^1S)- 13^1-Deoxo-13^1-hydroxy-13^2-demethoxycarbonylmethylpheophorbide *a* (8b): M.p.: 184 -188 °C. ^{1}H-NMR (270 MHz, $CDCl_3$): 9.86 (s, 1H, 10-H), 9.62 (s, 1H, 5-H), 8.89 (s, 1H, 20-H), 8.21 (dd, $J_{3\text{-}1,\ 3\text{-}2A}$ = 17.8 Hz, $J_{3\text{-}1,\ 3\text{-}2B}$ = 11.5 Hz, 1H, 3^1-H), 6.47 (d, J = 5.7 Hz, 1H, 13^1-H), 6.32 (dd, $J_{3\text{-}2A,\ 3\text{-}2B}$ = 1.6 Hz, $J_{3\text{-}2A,\ 3\text{-}1}$ = 17.8 Hz, 1H, 3^{2A}-H), 6.16 (dd, $J_{3\text{-}2B,\ 3\text{-}2A}$ = 1.6 Hz, $J_{3\text{-}2B,\ 3\text{-}1}$ = 11.5 Hz, 1H, 3^{2B}-H), 5.25 (dd, $J_{13\text{-}2A,\ 13\text{-}2B.}$= 16.4 Hz, $J_{13\text{-}2B,\ 13\text{-}1}$= 6.4 Hz, 1H, 13^{2B}-H), 4.69 (dd, $J_{13\text{-}2A,\ 13\text{-}2B}$ = 16.4 Hz, $J_{13\text{-}2A,\ 13\text{-}1}$ = 1.1 Hz, 1H, 13^{2A}-H), 4.62 (dq, $J_{17,\ 18}$ = 2.0 Hz, $J_{18,\ 18Me}$ = 7.2 Hz, 1H, 18-H), 4.41 (m, 1H, 17-H), 3.82 (q, J = 7.5 Hz, 2H, 8^2-CH_2), 3.59 (s, 3H), 3.55 (s, 3H), 3.54 (s, 3H), 3.39 (s, 3H), 2.73 (m, 1H, 17^{1A}-H), 2.54 (m, 1H, 17^{2A}-H), 2.37 (m, 1H, 17^{1B}-H), 2.19 (m, 1H, 17^{2B}-H), 1.83 (d, J = 7.24 Hz, 3H, 18-Me), 1.74 (t, J = 7.6 Hz, 3H, 8^1-Me), -1.39 (s, br, 1H, NH), -3.24 (s, br, 1H, NH). ^{13}C-NMR (68 MHz, $CDCl_3$): 173.8, 166.6, 161.6, 150.6, 150.5, 143.2, 142.0 (2C), 140.4, 137.9, 136.2, 134.2, 132.4, 130.1, 128.8, 127.8, 121.4, 109.2, 99.4, 98.2, 93.0, 69.8, 52.9, 51.4, 49.3, 48.6, 30.8, 29.3, 23.9, 19.7, 17.7, 12.3, 11.6, 11.5. HR-MS, *m/z*: calculated for $C_{34}H_{39}N_4O_3$: 551.3022, found: 551.3007. NOE (400 MHz, $CDCl_3$; *NOE*-Experiment): 6.43 (13^1-H): 5.23 (st, 13^{2B}-H); 5.23 (13^{2B}-H): 6.43 (st, 13^1-H), 4.70 (st, 13^{2A}-H), 4.41 (w, 17-H); 4.69 (13^{2A}-H): 5.23 (st, 13^{2B}-H); 4.40 (17-H): 5.24 (st, 13^{2B}-H), 1.83 (st, 18-Me).

17^3-Demethoxy-13^1-deoxo-13^1-hydroxy-13^2-demethoxycarbonylmethylpheophorbide *a* (9a, 9b). The epimeric mixture of **8a** and **8b** (150 mg, 0.27 mmol) was dissolved in anhydrous toluene and was stirred under argon for 20 min at -78 °C (dry ice / acetone bath). Then 0.3 ml (0.3 mmol) 1M DIBAL solution in toluene was added with a syringe through a rubber septum and stirring was continued for 10 min at -78 °C. To the cold solution, 100 mL water was added dropwise over a period of 10 min. The solidified mixture was brought to room temperature and carefully stirred with diethyl ether. Shaking was avoided in order not to cause excessive foaming. Water was added three times and the phases were carefully separated. The solvents were

removed on a rotary evaporator by heating at 60 °C in vacuum. Column chromatography on silica gel (3 x 90 cm) eluted with diethyl ether / ethyl acetate [10:1 v/v], provided a 13^1-epimeric mixture of **9a** and **9b** which could be further separated by reverse phase HPLC [mobile phase: methanol/water 95:5 (v/v)] affording 51 mg (0.10 mmol, 36%) **9a** and 70 mg (0.13 mmol, 49%) **9b**. UV/Vis (λ_{max}/nm, A_{rel}, CH_2Cl_2): 399 (1.0), 500 (0.15), 596 (0.06), 652 (0.27). HR-MS of the epimeric mixture, *m*/*z*: calculated for $C_{33}H_{36}N_4O_2$: 520.2838, found: 520.2840.

(13^1*R*)-17^3-Demethoxy-13^1-deoxo-13^1-hydroxy-13^2-demethoxycarbonylmethyl-pheophorbide *a* (9a): M.p.: 190-198°C. ^{1}H-NMR (400 MHz, $CDCl_3$): 9.85 (s, 1H, 10-H), 9.60 (s, 1H, 5-H), 9.55 (s, 1H, CHO), 8.88 (s, 1H, 20-H), 8.17 (dd, $J_{3\text{-}1,\ 3\text{-}2A}$ = 17.6 Hz, $J_{3\text{-}1,\ 3\text{-}2B}$ = 11.2 Hz, 1H, 3^1-H), 6.43 (d, J = 5.5 Hz, 1H, 13^1-H), 6.33 (dd, $J_{3\text{-}2A,\ 3\text{-}2B}$ = 1.4 Hz, $J_{3\text{-}2A,\ 3\text{-}1}$ = 17.8 Hz, 1H, 3^{2A}-H), 6.13 (dd, $J_{3\text{-}2B,\ 3\text{-}2A}$ = 1.4 Hz, $J_{3\text{-}2B,\ 3\text{-}1}$ = 11.3 Hz, 1H, 3^{2B}-H), 5.24 (dd, $J_{13\text{-}2A,\ 13\text{-}2B}$ = 16.3 Hz, $J_{13\text{-}2A,\ 13\text{-}1}$ = 6.2 Hz, 1H, 13^{2A}-H), 4.55 (dq, $J_{17,\ 18}$ = 1.9 Hz, $J_{18,\ 18Me}$ = 7.1 Hz, 1H, 18-H), 4.48 (dd, $J_{13\text{-}2A,\ 13\text{-}2B}$ = 16.3 Hz, $J_{13\text{-}2B,\ 13\text{-}1}$= 1.1 Hz, 1H, 13^{2B}-H), 4.41 (m, 1H, 17-H), 3.82 (q, J = 7.6 Hz, 2H, 8^2-CH_2), 3.53 (s, 3H), 3.43 (s, 3H), 3.37 (s, 3H), 2.58 (m, 1H, 17^{1A}-H), 2.52 (m, 1H, 17^{2A}-H), 2.31 (m, 1H, 17^{1B}-H), 2.12 (m, 1H, 17^{2B}-H), 1.81 (d, J = 7.1 Hz, 3H, 18-Me), 1.76 (t, J = 7.6 Hz, 3H, 8^1-Me), -1.40 (s, br, 1H, NH), -3.22 (s, br, 1H, NH). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 201.62, 166.5, 161.3, 150.7, 150.5, 143.3, 141.9 (2C), 140.3, 137.9, 136.2, 134.2, 132.4, 130.0, 128.9, 127.8, 121.5, 109.0, 99.6, 98.2, 93.0, 69.4, 52.6, 49.4, 48.0, 40.3, 26.1, 23.8, 19.7, 17.7, 12.3, 11.6, 11.5.

(13^1*S*)-17^3-Demethoxy-13^1-deoxo-13^1-hydroxy-13^2-demethoxycarbonylmethyl-pheophorbide *a* (9b): M.p.: 171-176 °C. ^{1}H-NMR (500 MHz, $CDCl_3$): 9.83 (s, 1H, 10-H), 9.61 (s, 1H, 5-H), 9.28 (s, 1H, CHO), 8.84 (s, 1H, 20-H), 8.17 (dd, $J_{3\text{-}1,\ 3\text{-}2A}$ = 17.6 Hz, $J_{3\text{-}1,\ 3\text{-}2B}$ = 11.0 Hz, 1H, 3^1-H), 6.21 (dd, $J_{3\text{-}2A,\ 3\text{-}2B}$ = 1.6 Hz, $J_{3\text{-}2A,\ 3\text{-}1}$ = 17.6 Hz, 1H, 3^{2A}-H), 6.25 (d, J = 5.5 Hz, 1H, 13^1-H), 6.16 (dd, $J_{3\text{-}2B,\ 3\text{-}2A}$ = 1.6 Hz, $J_{3\text{-}2B,\ 3\text{-}1}$ = 11.0 Hz, 1H, 3^{2B}-H), 4.90 (dd, $J_{13\text{-}2A,\ 13\text{-}2B.}$= 16.2 Hz, $J_{13\text{-}2B,\ 13\text{-}1}$= 6.3 Hz, 1H, 13^{2B}-H), 4.44 (dq, $J_{17,\ 18}$ = 2.1 Hz, $J_{18,\ 18Me}$ = 7.1 Hz, 1H, 18-H), 4.34 (dd, $J_{13\text{-}2A,\ 13\text{-}2B}$ = 16.4 Hz, $J_{13\text{-}2A,\ 13\text{-}1}$ = 1.0 Hz, 1H, 13^{2A}-H),, 4.10 (m, 1H, 17-H), 3.82 (q, J = 7.6 Hz, 2H, 8^2-CH_2), 3.52 (s, 3H), 3.48 (s, 3H), 3.37 (s, 3H), 2.32 (m, 2H, 17^{1A}-H, 17^{2A}-H), 2.05

(m, 1H, 17^{1B}-H), 1.96 (m, 1H, 17^{2B}-H), 1.68 (d, J = 7.24 Hz, 3H, 18-Me), 1.67 (t, J = 7.6 Hz, 3H, 8^{1}-Me), -1.47 (s, br, 1H, NH), -3.24 (s, br, 1H, NH). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 201.7, 166.5, 161.3, 150.6, 150.5, 143.2, 141.9 (2C), 140.3, 137.8, 136.2, 134.1, 132.3, 129.9, 128.8, 127.8, 121.4, 109.1, 99.4, 98.1, 92.9, 69.5, 52.4, 49.2, 48.4, 40.1, 26.1, 23.7, 19.6, 17.7, 12.3, 11.5, 11.4.

17^{3}-Demethoxy-13^{2}-demethoxycarbonylmethylpheophorbide *a* (10). A mixture of epimers **9a** and **9b** (155 mg, 0.3 mmol) was dissolved in dry dichloromethane under argon in the presence of activated molecular sieves (4 Å) and then 58 mg (0.5 mmol) *N*-methylmorpholine-*N*-oxide were added. After stirring for 10 min, 2 mg (0.006 mmol) tetra-*n*-propylammoniumperruthenate was added as catalyst and the reaction mixture was stirred for 45 min at room temperature. Completion of the reaction could be followed by TLC. The reaction mixture was extracted three times with 50 ml diethyl ether portions. The combined ethereal extracts were washed once with 25 ml of 5% aqueous Na_2SO_3 followed by five times washing with 100 ml water portions. After drying over $NaSO_4$ and removal of the solvent in vacuum, the residue was chromatographed on silica gel (3 x 60 cm) affording 141 mg (0.27 mmol, 91%) **10** as a grey-brown solid. M.p.: 248-252°C. ^{1}H-NMR (400 MHz, $CDCl_3$): 9.67 (s, 1H, CHO), 9.46 (s, 1H, 10-H), 9.35 (s, 1H, 5-H), 8.52 (s, 1H, 20-H), 7.98 (dd, $J_{3\text{-}1,\ 3\text{-}2A}$ = 17.6 Hz, $J_{3\text{-}1,\ 3\text{-}2B}$ = 11.2 Hz, 1H, 3^{1}-H), 6.26 (dd, $J_{3\text{-}2A,\ 3\text{-}2B}$ = 1.4 Hz, $J_{3\text{-}2A,\ 3\text{-}1}$ = 17.8 Hz, 1H, 3^{2A}-H), 6.15 (dd, $J_{3\text{-}2B,\ 3\text{-}2A}$ = 1.4 Hz, $J_{3\text{-}2B,\ 3\text{-}1}$ = 11.3 Hz, 1H, 3^{2B}-H), 5.16 (2d, J = 20.8 Hz, 2H, 13^{2}-CH_2), 4.42 (dq, $J_{17,\ 18}$ = 1.9 Hz, $J_{18,\ 18Me}$ = 7.1 Hz, 1H, 18-H), 4.29 (m, 1H, 17-H), 3.63 (s, 3H), 3.46 (q, J = 7.6 Hz, 2H, 8^{2}-CH_2), 3.38 (s, 3H), 3.21 (s, 3H), 2.65 (m, 1H, 17^{1A}-H, 17^{2A}-H), 2.31 (m, 1H, 17^{1B}-H, 17^{2B}-H), 1.78 (d, J = 7.0 Hz, 3H, 18-Me), 1.67 (t, J = 7.6 Hz, 3H, 8^{1}-Me), -0.14 (s, br, 1H, NH), -2.20 (s, br, 1H, NH). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 201.3, 196.1, 171.3, 160.0, 155.3, 150.8, 148.9 145.0, 141.6, 137.8, 136.2, 136.1, 135.9, 131.6, 130.5, 129.2, 128.4, 122.6, 106.0, 104.2, 97.2, 92.9, 51.4, 50.0, 48.0, 40.4, 26.7, 23.1, 19.5, 17.4, 12.1, 12.0, 11.2. UV/Vis (λ_{max}/nm, A_{rel}): 414 (1.0), 508 (0.1), 540 (0.1), 612 (0.09), 668 (0.4). HR-MS, *m*/*z*: calculated for $C_{33}H_{34}N_4O_2$: 518.2683, found: 518.2666.

13^2, 17^3-Didemethoxycarbonylmethylpheophorbide *a* (11). The compound **10** (155 mg, 0.3 mmol) was dissolved in 50 ml benzene and heated to 55 °C. Wilkinson's decarbonylation reagent $(PPh_3)_3RhCl$, 180 mg, 0.3 mmol) was added as a solid in small portions of ca. 5 mg after which the mixture was heated to reflux. After cooling the room temperature the mixture was filtered, concentrated on a rotary evaporator and the very nonpolar residue was taken in 5 mL THF and chromatographed on silica gel (3 x 100 cm) eluted with diethyl ether. The main fraction consisted of 142 mg (0.29 mmol, 97%) **11** as grey-brown solid. M.p. 192-195°C. ^{1}H-NMR (400 MHz, $CDCl_3$): 9.35 (s, 1H, 10-H), 9.24 (s, 1H, 5-H), 8.54 (s, 1H, 20-H), 7.91 (dd, $J_{3\text{-}1,\ 3\text{-}2A}$ = 17.6 Hz, $J_{3\text{-}1,\ 3\text{-}2B}$ = 11.2 Hz, 1H, 3^1-H), 6.22 (dd, $J_{3\text{-}2A,\ 3\text{-}2B}$ = 1.4 Hz, $J_{3\text{-}2A,\ 3\text{-}1}$ = 17.8 Hz, 1H, 3^{2A}-H), 6.11 (dd, $J_{3\text{-}2B,\ 3\text{-}2A}$ = 1.4 Hz, $J_{3\text{-}2B,\ 3\text{-}1}$ = 11.3 Hz, 1H, 3^{2B}-H), 5.14 (2d, J = 19.7 Hz, 2H, 13^2-CH_2), 4.48 (dq, $J_{17,\ 18}$ = 2.0 Hz, $J_{18,\ 18Me}$ = 7.1 Hz, 1H, 18-H), 4.17 (m, 1H, 17-H), 3.60 (s, 3H), 3.57 (q, J = 7.6 Hz, 2H, 8^2-CH_2), 3.36 (s, 3H), 3.14 (s, 3H), 2.37 (m, 1H, 17^{1A}-H), 2.04 (m, 1H, 17^{1B}-H), 1.82 (d, J = 7.0 Hz, 3H, 18-Me), 1.67 (t, J = 7.6 Hz, 3H, 8^1-Me), 1.05 (t, J = 7.4 Hz, 3H, 17^1-Me), -0.23 (s, br, 1H, NH), -2.11 (s, br, 1H, NH). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 196.4, 172.0, 161.9, 154.9, 150.5, 149.0, 144.7, 141.4, 137.9, 136.1, 135.8, 135.6, 131.4, 130.2, 129.2, 128.5, 122.3, 105.8, 103.8, 96.9, 93.0, 54.0, 49.7, 48.1, 27.5, 23.2, 19.3, 17.4, 12.0, 11.9, 11.1, 10.7. UV/Vis (λ_{max}/nm, A_{rel}): 403 (0.87), 414 (1.0), 510 (0.12), 540 (0.11), 612 (0.1), 669 (0.43). HR-MS, *m*/*z*: calculated for $C_{32}H_{34}N_4O$: 490.2733, found: 490.2736.

3-Devinyl-3-formyl-13^2, 17^2-didemethoxycarbonylmethylphäophorbid *a* (12). A solution of **11** (245 mg, 0.5 mmol) in 25 mL THF was acidified with 2 mL glacial acetic acid and 2 mg of OsO_4 catalyst (0.008 mmol, usually one crystal of 1-2 mm) was added. Argon was bubbled and the mixture was protected from light with aluminium foil and stirred under agron for 15 min at room temperature. Then using a peristaltic pump, 5 mL of a saturated aqueous $NaIO_4$ solution was added at a rate of 2 ml/h. After completion of addition, the reaction mixture was further stirred at room temperature for 1 h. TLC control showed only traces of the intermediate 3^1,3^2-

diol. The work-up consisted in dilution of the reaction mixture with 100 mL diethyl ether, washing with brine (100 mL) and successively three times with 50 mL saturated aqueous sodium bicarbonate and finally three times with 50 mL water. After drying over sodium sulphate, the solvents were evaporated. The red-brownish residue was taken in 5 mL THF and chromatographed on silicagel (3 x 60 cm) eluted with diethyl ether to yield 150 mg (0.30 mmol, 61%) **12** as a grey-brown solid. M.p.: 248-252°C. ^{1}H-NMR (400 MHz, $CDCl_3$): 11.49 (s, 3H, 3-CHO), 10.19 (s, 1H, 10-H), 9.50 (s, 1H, 5-H), 8.80 (s, 1H, 20-H), 5.20 (2d, J = 19.7 Hz, 2H, 13^2-CH_2), 4.55 (dq, $J_{17,\ 18}$ = 2.0 Hz, $J_{18,\ 18Me}$ = 7.1 Hz, 1H, 18-H), 4.26 (m, 1H, 17-H), 3.73 (s, 3H), 3.66 (s, 3H), 3.62 (q, J = 7.6 Hz, 2H, 8^2-CH_2), 3.24 (s, 3H), 2.39 (m, 1H, 17^{1A}-H), 2.04 (m, 1H, 17^{1B}-H), 1.82 (d, J = 7.0 Hz, 3H, 18-Me), 1.67 (t, J = 7.6 Hz, 3H, 8^1-Me), 1.02 (t, J = 7.4 Hz, 3H, 17^1-Me), -0.19 (s, br, 1H, NH), -2.10 (s, br, 1H, NH). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 196.2, 188.4.0, 171.0, 163.0, 155.0, 152.2, 148.8, 145.4, 144.8, 140.6, 137.6, 134.6, 131.2, 130.8, 129.3, 128.8, 107.0, 103.2, 99.8, 94.9, 54.6, 49.2, 48.3, 28.0, 23.5, 19.4, 17.3, 12.1, 11.3, 11.2, 10.7. UV/Vis (λ_{max}/nm, A_{rel}, CH_2Cl_2): 389 (096), 430 (1.0), 524 (0.18), 558 (0.19), 640 (0.13), 661 (0.14), 699 (0.8). HR-MS, *m*/*z*: calculated for $C_{31}H_{32}N_4O_2$: 492.2525, found: 492.2510.

3-Devinyl-3-formyl-13^2, 17^2-didemethoxycarbonylmethylpheophorbide *a* Zn complex (4). Metallation of the free base **12** (245 mg, 0. 5 mmol) which was suspended in 25 ml methanol was effected with 200 mg (108 mmol) solid zinc acetate. Stirring for 2 h at room temperature under argon was followed by a typical work-up procedure consisting in diluting with 50 mL brine and extracted into 100 mL diethyl ether. The ethereal layer was washed twice with 50 mL saturated aqueous sodium hydrogen carbonate and then finally three times with water. Chromatography on silica gel (3 x 60 cm) eluted with diethyl ether afforded 273 mg (0.49 mmol, quantitative) **4** as a velvet green solid. M.p. 146-150 °C. ^{1}H-NMR (400 MHz, DMSO): 11.40 (s, 3H, 3-CHO), 10.12 (s, 1H, 10-H), 9.68 (s, 1H, 5-H), 8.82 (s, 1H, 20-H), 5.14 (2d, J = 19.8 Hz, 2H, 13^2-CH_2), 4.58 (dq, $J_{17,\ 18}$ = 2.0 Hz, $J_{18,\ 18Me}$ = 7.1 Hz, 1H, 18-H), 4.26 (m, 1H, 17-H), 3.78 (q, J = 7.6 Hz, 2H, 8^2-CH_2), 3.67 (s, 3H), 3.61 (s, 3H), 3.27 (s, 3H), 2.39 (m, 1H, 17^{1A}-

H), 2.05 (m, 1H, 17^{1B}-H), 1.80 (d, J = 7.0 Hz, 3H, 18-Me), 1.66 (t, J = 7.6 Hz, 3H, 8^{1}-Me), 0.96 (t, J = 7.4 Hz, 3H, 17^{1}-Me). UV/Vis (λ_{max}/nm, A_{rel}, CH_2Cl_2): 416 (0.65), 442 (1.0), 541 (0.18), 585 (0.18), 629 (0.25), 679 (1.0). HR-MS, *m*/*z*: calculated for $C_{31}H_{32}N_4O_2Zn$: 554.1660, found: 554.1662.

Crystallographic details. Crystals suitable for single crystal X-ray diffraction were taken directly from the solution of the compound and then selected in perfluoroalkylether oil. Single-crystal X-ray diffraction data of **2** were collected using graphite-monochromatised MoKα radiation (λ = 0.71073 Å) on a STOE IPDS II (Imaging Plate Diffraction System). Single-crystal X-ray diffraction data of **6** were collected using synchrotron radiation (λ = 0.80 Å) on a STOE IPDS II (Imaging Plate Diffraction System) at the ANKA synchrotron source in Karlsruhe. Raw intensity data were collected and treated with the STOE X-Area software Version 1.39. Data for all compounds were corrected for Lorentz and polarisation effects.

The structures were solved with the direct methods program SHELXS of the SHELXTL PC suite programs,[S4] and were refined with the use of the full-matrix least-squares program SHELXL. Atomic form factors for λ = 0.80000 Å (15.510 keV) were obtained by the method of Brennan and Cowan[S5] as implemented on http://skuld.bmsc.washington.edu /scatter/AS_periodic. html. Molecular diagrams were prepared using Diamond, Mercury and HyperChem.[S6]

In **2** all Zn, Cl, O, N and C atoms were with anisotropic displacement parameters. Cl2/Cl2A and O1/O1A were refined with split positions. The major part of the H atoms could be successfully located in the difference Fourier map while the rest were placed in fixed riding positions.

The tiny crystals of **6** diffracted only very weakly above 2Θ of 40° although measured with the high intensity beam at a synchrotron source. Already for reflections with a resolution smaller than *d* = 1.4 the mean I/σ ratio drops below 8 accompanied by an increase of the *R*(int) value

above 0.20. Below d = 1 the I/σ ratio amounts to less than 2 and R(int) values above 45 %. This might help to explain the relatively high R-values in the refinement.

Lattice solvent molecules (most probably heptane) were identified within the structure of **6** which were badly disordered and could not be adequately refined. The data were therefore corrected for these using the SQUEEZE option within the PLATON[S74] program package finding a total of 77 electrons (~1.3 C_7H_{16}) in a potential solvent accessible area of 303 $Å^3$.

In **6** all Zn, O and N atoms were refined with anisotropic displacement parameters. C atoms of three of the four tertiary butyl groups showed disorder which was modelled using partial-occupancy carbon atoms. These atoms were refined isotropically whereas all other C atoms were refined with anisotropic displacement parameters. H atoms of the water ligand (H3A, H3B) were refined with geometrical restraints (fixed bond lengths). All other H atoms were placed in fixed positions.

CCDC-853621 (**2**) and 853622 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; Email:deposit@ccdc.cam.ac.uk).

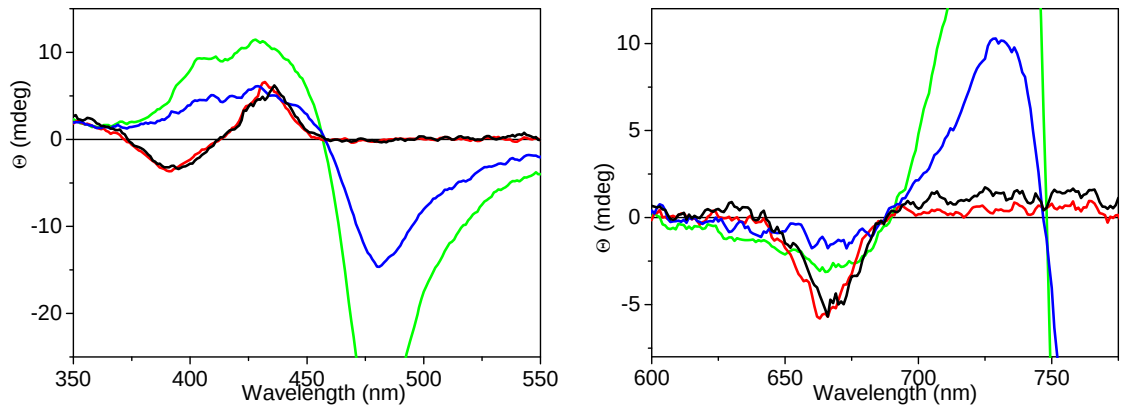

Fig. S2 Enlargements of the isosbestic points in the ECD spectra of **2**. Colours of traces are as in Fig. 3 in the main text.

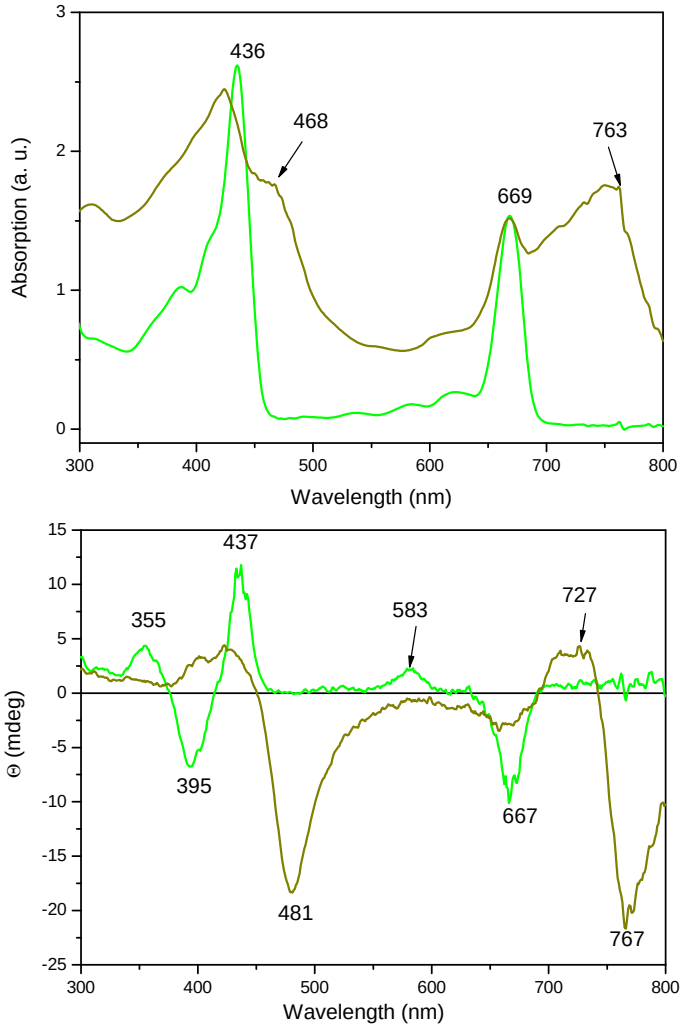

Fig. S3 Absorption and ECD spectra of a concentrated solution of **2** (4.0 mg dissolved in 450 µL dry CH_2Cl_2) out of which 10 µL were injected into 3 mL water saturated *n*-heptane in a quartz cuvette with 1 cm pathlength (gold traces) and briefly sonicated. Some green fluffs were present in suspension. The green traces are after addition of two drops of pyridine, removal of 1.5 mL solution and dilution with 1.5 mL *n*-heptane. The absorption spectra are scaled at the monomer Q_y maximum at 669 nm by multiplying the aggregate spectrum by a factor of 3.9.

References

S1 H. Tamiaki, S. Yagai and T. Miyatake, Synthetic zinc tetrapyrroles complexing with pyridine as a single axial ligand, *Bioorg. Med. Chem.*, 1998, **6**, 2172–2178.

S2 K. M. Smith, D. A. Goff and D. J. Simpson, *Meso* substitution of chlorophyll derivatives: direct route for transformation of bacteriopheophorbides *d* into bacteriopheophorbides *c*, *J. Am. Chem. Soc.*, 1985, **107**, 4946–4954.

S3 H. Tamiaki, M. Amakawa, Y. Shimono, R. Tanikaga, A. R. Holzwarth and K. Schaffner, Synthetic zinc and magnesium chlorin aggregates as models for supramolecular antenna complexes in chlorosomes of green photosynthetic bacteria, *Photochem. Photobiol.*, 1996, **63**, 92–99.

S4 G. M. Sheldrick, SHELXTL PC version 5.1 An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data, Bruker Analytical X-ray Systems, Karlsruhe, 2000.

S5 S. Brennan and P. L. Cowan, A suite of programs for calculating X-ray absorption reflection, and diffraction performance for a variety of materials at arbitrary wavelengths, *Rev. Sci. Instrum*., 1992, **63**, 850–853.

S6 Diamond Version 2.1d, K. Brandenburg, Crystal Impact GbR, 1996-2000.

S7 A. L. Spek, PLATON - A multipurpose crystallographic tool, *J. Appl. Cryst.*, 2003, **36**, 7–13.