

Supporting Information

Mimics of the self-assembling chlorosomal bacteriochlorophylls: Regio- and stereo-selective synthesis and stereoanalysis of acyl-(1-hydroxyalkyl)-porphyrins

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Materials and Methods. General Remarks

Solvents were dried by prolonged heating under reflux as follows: dichloromethane over calcium hydride, toluene and tetrahydrofuran over sodium benzophenone ketyl, *n*-heptane over sodium metal, and were freshly distilled under nitrogen prior to use. The solvents for chromatography were degassed by sonicating shortly before use. All reactions flasks and chromatography columns were protected from ambient light with aluminium foil. Reactions were performed under nitrogen or argon atmosphere. Routine NMR spectra were recorded at 300 MHz (for ^1H) with a Bruker DPX 300 Avance spectrometer. NMR measurements on Mosher's esters were performed at 400 MHz on a JEOL AL-A400 instrument. Chemical shifts are given in ppm relative to the signal of CHCl_3 , which was taken as $\delta = 7.26$ (for ^1H) and 77.00 (for ^{13}C). Coupling constants are given in Hz. UV/Vis spectra were measured with a Varian Cary 500 equipped with a Peltier variable temperature unit. Fluorescence spectra were measured on a Varian Eclipse fluorimeter. Circular dichroism spectra were measured on a JASCO J-810 spectrometer equipped with a JASCO Julabo FP 35 thermostat which maintained the temperature at 20.0 ± 0.2 °C. The CD spectrometer was purged with nitrogen before recording each spectrum which was baseline subtracted. The baseline was always measured from the same solvent(s) and in the same cuvette as the samples. MALDI-ToF spectra were obtained on Voyager Instrument from Applied Biosystems with 1,8,9-anthracenetriol (dithranol) as matrix. HR-FAB-MS results were recorded using 3-nitrobenzylalcohol (NBA) as a matrix on a Finnigan MAT 90 spectrometer. Column chromatography was performed with Merck silica gel 0.040 – 0.063 mm. Retention factors are given for silica gel TLC plates (Macherey Nagel silica gel Polygram SIL 6/UV₂₅₄) using dichloromethane (0.2% ethyl alcohol as stabilizing agent) unless otherwise specified.

Experimental Procedures

Diacetylation of 1-Cu with acetic anhydride

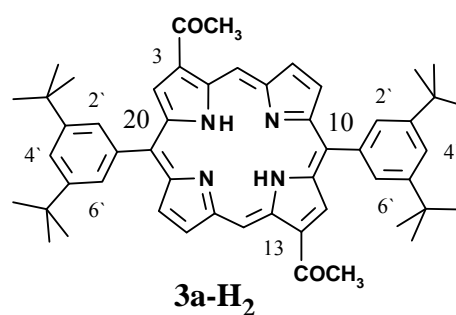
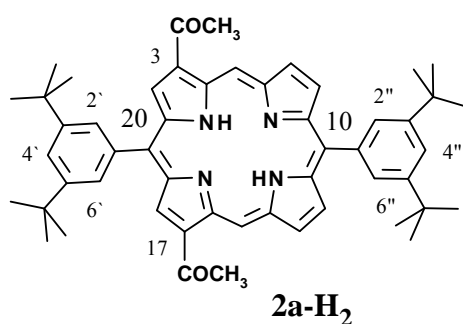
*3,17-Diacetyl-10,20-bis(3,5-di-*t*-butylphenyl)porphyrinato copper (2a-Cu)* and

*3,13-diacetyl-10,20-bis(3,5-di-*t*-butylphenyl)porphyrinato copper (3a-Cu)*

Diacetylation of the copper porphyrin **1-Cu** (400 mg, 0.53 mmol) was performed by dissolving it in carbon disulfide (160 mL) in a 1L three-necked flask equipped with a rubber septum, a reflux condenser and thermometer under argon and then adding at 0-3 °C acetic anhydride (141 mL, 1.5 mol) followed by addition of tin tetrachloride via syringe (34.8 g, 15.6 mL, 134 mmol). After stirring at 0-2°C for 30 min the reaction mixture was diluted with 300 mL CS₂ and ice cold water (100 mL) was added dropwise within 35 min and stirred afterwards for another 40 min. After extraction into dichloromethane and washing with brine twice, the mixture was washed with aqueous sodium hydrogen carbonate and then again with brine. The organic layers were dried on sodium sulfate and after removal of the solvents in vacuum the mixture was chromatographed on silica gel eluted with dichloromethane. The fraction containing an almost equimolar mixture of the two isomeric diacetylated copper porphyrins weighed 154.8 mg (35 % yield). Over different runs yields over 27% were consistently obtained.

*3,17-Diacetyl-10,20-bis(3,5-di-*t*-butylphenyl)-21,23H-porphyrin (2a-H₂)*

*3,13-Diacetyl-10,20-bis(3,5-di-*t*-butylphenyl)-21,23H-porphyrin (3a-H₂)*



The above mixture of copper porphyrins **2a-Cu** and **3a-Cu** (53 mg) was demetallated using a 10 mL degassed mixture of trifluoroacetic and sulfuric acids (1:1 v/v) by stirring for 1.5 h at room temperature. The work-up consisted in carefully pouring on ice and extraction into dichloromethane, washing with brine, neutralization with aqueous sodium hydrogen carbonate and again washing with brine. After drying on sodium sulfate and evaporation to dryness a reddish-purple solid 47.2 mg (96 % yield) was obtained. Demetallation yields over different runs and scales (up to 1.5 g) gave consistently yields above 86%. Careful column chromatography on silica gel of the above mixture after eluting with dichloromethane until the reddish isomer **2a-H₂** is separated was followed closely by a second greenish fraction of the compound **3a-H₂**. For separating a 600 mg equimolar mixture of **2a-H₂** and **3a-H₂** a 4 cm diameter column of 250 cm height filled up to 160 cm with silica gel was eluted with dichloromethane. Preparative HPLC separation could be performed on a VARIAN ProStar station equipped with a VARIAN Dynamax® 100 Å column (Φ = 2.5 mm) filled with a normal silica phase and eluted isocratically with 4 mL/min dichloromethane/*n*-hexane (1:1, v/v). UV-Detection was set at 430 nm and baseline separation could be obtained by injecting 200 μ L of a saturated solution in the same eluent (dissolution occurs after short sonication) of the isomeric mixture. The 3,17 diacetyl isomer **2a-H₂** elutes at 42 min while the 3,13-diacetyl isomer **3a-H₂** elutes at 46 min. With larger injection volumes (500 μ L) the peaks are still well

separated but slightly delayed (48 and 55 min, respectively). With overlapping injections it was possible to separate ca. 80 mg isomeric mixture in 6 hrs. For this reason, normal column chromatography is preferable for separations on a larger scale (up to 1 g).

3,17-Diacetyl-10,20-bis(3,5-di-*t*-butylphenyl)-21,23H-porphyrin (2a-H₂).

$R_f = 0.54$

¹H-NMR (CDCl₃): δ (ppm) = 11.30 (s, 2H, 5,15-H), 9.54 (s, 2H, 2,18-H), 9.40 (d, ³J = 4.8 Hz, 2H, 7,13-H), 9.02 (d, ³J = 4.8 Hz, 2H, 8,12-H), 8.19 and 8.09 (two d, ⁴J = 1.8 Hz, 2H each, 2',6'- and 2'',6''-H), 7.93 and 7.85 (two t, ⁴J = 1.8 Hz, 1H each, 4'- and 4''-H), 3.20 (s, 6H, CO-CH₃), 1.63 and 1.57 (two s, 18 H each, C(CH₃)₃), 2.32 (s, 2H, NH).

¹³C-NMR (CDCl₃): δ (ppm) = 29.9 (CO-CH₃), 31.7 (C(CH₃)₃), 35.09 and 35.18 (C(CH₃)₃), 107.1 (5,15-C), 120.4, 121.4, 121.6 (10,20-C), 124.4, 130.0 (2',6'-C), 131.1, 132.0, 134.2, 136.8, 139.67, 139.70, 149.4, 149.6, 196.8 (CO-CH₃).

MALDI-MS: 771.4. HR-FAB-MS: 771.4650 [M+H]⁺; Calc. for C₅₂H₅₉N₄O₂ = 771.4638.

UV/Vis (CH₂Cl₂): λ_{\max} (nm) 275(sh) 430, 528, 568, 603, 661.

Crystallization of 2a-H₂: A concentrated solution of **2a-H₂** in CH₂Cl₂ was diluted hundred fold with *n*-hexane in a centrifuge bottle and then centrifuged. After decantation, the supernatant was left in the refrigerator at -18°C for 20 months. During this time, small crystals appeared which were left to grow until suitable for conventional X-ray crystallography. Single-crystal X-ray diffraction data of **2a-H₂** were collected using graphite-monochromatized MoK α radiation ($\lambda = 0.71073$ Å) on a STOE IPDS II (Imaging Plate Diffraction System) at 190 K. The structures were solved with the direct methods program SHELXS^[1] of the SHELXTL PC suite programs, and were refined with the use of the full-matrix least-squares program SHELXL.^[1] Molecular diagrams were prepared using Diamond 2.1.^[2]

2a-H₂·0.5 *n*-Hexane: dark ruby red distorted hexagonal plates, 0.75 x 0.5 x 0.175 mm, $M_r = 814.15$, triclinic, space group $P\bar{1}$ (No. 1), $a = 9.914(2)$, $b = 13.760(3)$, $c = 18.584(4)$ Å, $\alpha = 69.15(3)$, $\beta = 81.49(3)$, $\gamma = 80.49(3)$, $V = 2325.6(8)$ Å³, $Z = 2$, $D_c = 1.153$ g/cm⁻³, $\mu = 0.070$ mm⁻¹ giving a final R_1 value of 0.0785 for 719 parameters and 8269 unique reflections with $I \geq 2\sigma(I)$ and wR_2 of 0.2124 for all 12628 reflections ($R_{\text{int}} = 0.0474$). A disorder has been modelled for the hexane solvent molecule (C94-C96 and symmetry equivalent positions).

CCDC-714094 contains 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].

^[1] 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.

^[2] K. Brandenburg, DIAMOND version 2.1d, Visual Crystal Structure Information System, Bonn, 2000.

*3,13-Diacetyl-10,20-bis(3,5-di-*t*-butylphenyl)-21,23H-porphyrin (3a-H₂)* $R_f = 0.52$

¹H-NMR (CDCl₃): δ (ppm) = 11.42 (s, 2H, 5,15-H), 9.56 (s, 2H, 2,12-H), 9.56 (d, ³J = 4.8 Hz, 2H, 7,17-H), 9.21 (d, ³J = 4.8 Hz, 2H, 8,18-H), 8.17 (d, ⁴J = 1.8 Hz, 4H, 2',6'-H), 7.92 (t, ⁴J = 1.8 Hz, 2H, 4'-H), 3.20 (s, 6H, CO-CH₃), 1.64 (s, 36H, C(CH₃)₃), -2.72 (s, 2H, NH).

¹³C-NMR (CDCl₃): δ (ppm) = 29.9 (CO-CH₃), 31.8 (C(CH₃)₃), 35.16 (C(CH₃)₃), 107.7 (5,15-C), 121.5 (10,20-C), 122.11 (4'-C), 129.1 (8,18-C), 130.7 (2',6'-C), 138.9, 139.7, 140.2, 140.9, 149.5, 150.1 (2,12-C), 151.4, 197.4 (CO-CH₃).

MALDI-MS: 772.5. [M+2H]⁺; calc. for C₅₂H₆₀N₄O₂ = 772.5. Base Peak at 770.6, calc. for C₅₂H₅₈N₄O₂ = 770.5

UV/Vis (CH₂Cl₂): λ_{\max} (nm) 286(sh), 434, 526, 566, 610, 668.

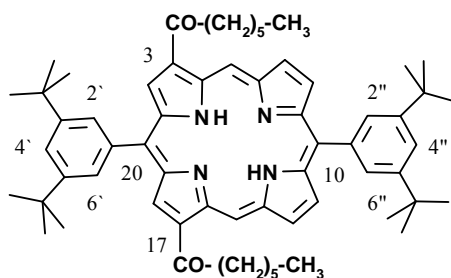
Friedel-Crafts diacetylation of 1-Cu with various acyl chlorides. General Procedure for obtaining preferentially 3,17-diacyl Cu porphyrins 2x-Cu, x = a, b, c. Demetallation to the corresponding free bases 2x-H₂, x = a, b, c.

Diacylation of the copper porphyrin **1-Cu** (300 mg, 0.40 mmol) was performed by dissolving it in carbon disulfide (10 mL) in a 100 mL three-necked flask equipped with a rubber septum, nitrogen bubbler and thermometer then adding at 2-4°C the corresponding acyl chlorides (3.5 equivalents, 1.4 mol) and then the reaction mixture was allowed to stir for 2-3 min followed by addition in one shot of anhydrous aluminium chloride (240 mg, 1.80 mmol, 4.5 equivalents). After stirring at 2-4 °C for 4-6 min ice cold water (10 mL) was added to the reaction mixture and stirred afterwards for another hour. After extraction into dichloromethane and washing with brine twice, the mixture was washed with aqueous sodium hydrogen carbonate and then again with brine. The organic layers were dried over sodium sulfate and after removal of the solvents in vacuum these gave the crude 3,17-diacyl porphyrins. When the reaction period was prolonged from more than 6 min, some 3,13-diacyl isomers were also obtained in 2-5% yields. In more dilute CS₂ solutions the diacylation proceeds more slowly and the 3,17-isomers can be isolated free of the 3,13-isomers. For obtaining the 3,13-isomers, the diacylation reaction needs to be performed on a larger scale and with a more mild Lewis acid, e.g. using 1.0 g of **1-Cu** in 25 mL CS₂, 7.34 g (8.10 mL, 20 eq) palmitoyl chloride and 22.27 g (10.05 mL, 64 eq) SnCl₄ (replacing AlCl₃) and stirring at 4 °C for 100 min under argon.

The above crude products of the corresponding longer chain copper porphyrins (**2b-Cu**, **2c-Cu**) were demetallated by using a 10 mL degassed mixture of trifluoroacetic and sulfuric acids (1:1 v/v) by stirring for at least one hour at room temperature. The work-up consisted in pouring on ice and extraction into dichloromethane, washing with brine, neutralization with aqueous sodium hydrogen carbonate and again washing with brine. After drying on sodium sulfate and evaporation to dryness the crude solid products were obtained. Demetallation yields were consistently in the range of 60-80%. Subsequent careful column chromatography on silica gel eluted first with dichloromethane : *n*-hexane (1:1, v/v) gave the corresponding monoacylated products as the firstly eluted fractions and as the second fractions the pure 3,17-diacyl isomers which were obtained in isolated yields as follows: **2a-H₂** – 35 %, **2b-H₂** – 68 %, and **2c-H₂** – 79 %. While **3b-H₂** could only be obtained in small amounts and not free from **2b-H₂**, **3c-H₂** was obtained pure after trituration with methanol. On a larger scale, 775 mg of dipalmitoyl isomers **2c-H₂** and **3c-H₂** were dissolved in 25 mL dichloromethane and 75 mL methanol were used to precipitate selectively the more insoluble 3,13-isomer (**3c-H₂**) which was filtered on a Hirsch funnel and was washed with methanol leaving 437 mg of pure compound which can thus be isolated without column chromatography. The filtrate, after evaporation gave 321 mg of an enriched mixture in **2c-H₂**

which, in turn, could be obtained pure after chromatography on silica gel eluted with a mixture of *n*-hexane-dichloromethane (3:1, v/v).

3,17-Diheptanoyl-10,20-bis(3,5-di-*t*-butylphenyl)-21,23H-porphyrin (2b-H₂)



2b-H₂

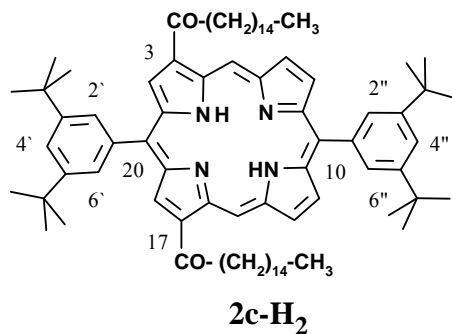
$R_f = 0.63$ (CH₂Cl₂ : *n*-hexane, 1:1, v/v).

¹H-NMR (CDCl₃): δ (ppm) = 11, 34 (s, 2H, 5,15-H), 9.59 (s, 2H, 2,18-H), 9.42 (d, ³J = 4.5 Hz, 2H, 7,13-H), 9.05 (d, ³J = 4.5 Hz, 2H, 8,12-H), 8.23 and 8.12 (two d, ⁴J = 1.8 Hz, 2H each, 2', 6'- and 2'', 6''-H), 7.97 and 7.87 (two t, ⁴J = 1.2 Hz, 1H each, 4'- and 4''-H), 3.61 (t, 4H, CO-CH₂-CH₂-CH₂-CH₂-CH₂-CH₃), 2.17 (m, 4H, CO-CH₂-CH₂-CH₂-CH₂-CH₂-CH₃), 1.68-1.44(m, 12H, CO-CH₂-CH₂-CH₂-CH₂-CH₂-CH₃) 1.68 and 1.61 (two s, 18 H each, C(CH₃)₃), 0.99 (t, 6H, CH₃), -2.31 (broad s, 2H, NH).

¹³C-NMR (CDCl₃): δ (ppm) = 14.15 (CO-(CH₂)₅-CH₃), 22.69, 24.84, 31.76 (C(CH₃)₃), 35.10 and 35.20 (C(CH₃)₃), 42.02 (CO-CH₂-(CH₂)₄-CH₃), 107.11, 120.34, 121.34, 121.52, 124.28, 128.39, 130.01, 131.19, 131.93, 134.13, 135.94, 136.72, 139.70, 149.36 and 149.56 (3', 5' and 3'', 5''-C), 200.46 (CO-(CH₂)₅-CH₃).

MALDI-MS: 913.2

HR-FAB-MS: [M+H]⁺ 913.6345; calc. for C₆₂H₈₁N₄O₂ = 913.6359.

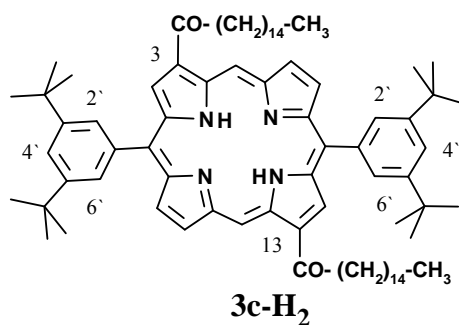
3,17-Dipalmitoyl-10,20-bis(3,5-di-*t*-butylphenyl)-21,23H-porphyrin (2c-H₂)

$R_f = 0.92$ (CH₂Cl₂ : *n*-hexane, 1:1, v/v).

¹H-NMR (CDCl₃): δ (ppm) = 11.34 (s, 2H, 5,15-H), 9.59 (s, 2H, 2,18-H), 9.42 (d, ³J = 4.5 Hz, 2H, 7,13-H), 9.05 (d, ³J = 4.5 Hz, 2H, 8,12-H), 8.23 and 8.12 (two d, ⁴J = 1.5 and 1.8 Hz, 2H each, 2',6'- and 2'',6''-H), 7.97 and 7.87 (two t, ⁴J = 1.8 Hz, 1H each, 4'- and 4''-H), 3.61 (t, ³J = 7.5 Hz, 4H, CO-CH₂-(CH₂)₁₃-CH₃), 2.19 (m, 4H, CO-CH₂-CH₂-(CH₂)₁₂-CH₃), 1.21-1.39 (broad m 48H, CO-CH₂-CH₂-(CH₂)₁₂-CH₃), 1.68 and 1.60 (two s, 18 H each, C(CH₃)₃), 0.90 (t, 6H, CH₃), -2.33 (s, 2H, NH).

¹³C-NMR (CDCl₃): δ (ppm) = 14.12, 22.67, 25.14, 29.35, 29.63, 29.65, 29.68, 29.70 (several C), 31.74 (C(CH₃)₃), 31.74, 31.76, 31.91, 35.09 and 35.19 (C(CH₃)₃), 42.38, 107.07, 119.88, 120.31, 129.99, 131.84, 134.13, 139.66, 139.78, 149.34 and 149.54 (3',5'- and 3'',5''-C), 200.17 (CO-(CH₂)₁₄-CH₃).

MALDI-MS: [M+H]⁺ 1163.5; calc. for C₈₀H₁₁₅N₄O₂ = 1163.9020

3,13-Dipalmitoyl-10,20-bis(3,5-di-*t*-butylphenyl)-21,23H-porphyrin (3c-H₂)

$R_f = 0.90$ (CH₂Cl₂ : *n*-hexane, 1:1, v/v).

¹H-NMR (CDCl₃): δ (ppm) = 11.38 (s, 2H, 5,15-H), 9.48 (s, 2H, 2,12-H), 9.51 (d, ³J = 4.8 Hz, 2H, 7,17-H), 9.17 (d, ³J = 4.8 Hz, 2H, 8,18-H), 8.13 (d, ⁴J = 1.8 Hz, 4H, 2',6'-H), 7.87 (t, ⁴J = 1.8 Hz, 2H, 4'-H), 3.48-3.53 (m, 4H, CO-CH₂-(CH₂)₁₃-CH₃), 1.55 (s, 36H, C(CH₃)₃), 1.24 (broad s, 28H CO-CH₂-(CH₂)₁₃-CH₃), 0.83-0.91 (m, 6H, CO-CH₂-(CH₂)₁₃-CH₃), -2.71 (s, 2H, NH).

¹³C-NMR (CDCl₃): δ (ppm) = 14.13, 22.69, 25.29, 29.36, 29.65, 29.70 (several C), 31.77 (C(CH₃)₃), 31.92, 35.15 (C(CH₃)₃), 42.11, 107.64 (5,15-C), 121.40, (10,20-C), 122.05 (4'-C), 128.95, 130.46, 130.74 (2',6'-C), 138.94, 139.79, 140.07, 140.28, 140.71, 149.46, 150.24 151.40, 200.44 (CO-(CH₂)₁₄-CH₃).

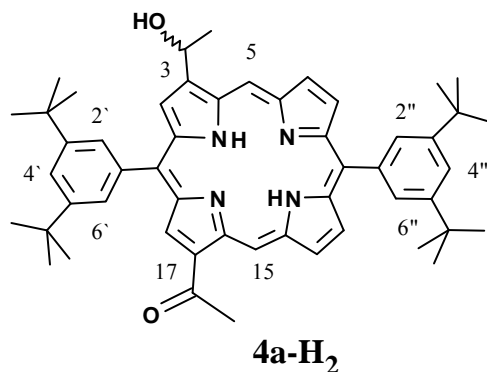
MALDI-MS: [M+H]⁺ 1163.5; calc. for C₈₀H₁₁₅N₄O₂ = 1163.9020.

Monoreduction of diacylporphyrins to acyl-hydroxyalkylporphyrins. General Procedure.

Monoreduction of the corresponding diacyl compounds (on a ~100 mg scale, 1 eq) was effected by dissolving them in 25 mL dichloromethane and 5 mL methanol and adding rapidly sodium borohydride (2 eq). After stirring for 15-150 min at room temperature the mixture was washed with brine and the organic layer was dried on anhydrous sodium sulfate and chromatographed on silica gel eluted with dichloromethane. Recovered starting material (16-47%) was eluted as the first fraction. The second band contained the monoreduced products (38-70%) and a final band with lower R_f consists of a mixture of the racemic and *meso*-dihydroxyalkyl porphyrins. The latter could be separated on a second column, however the reactions were usually quenched when TLC control showed the formation of the diols. In the case of **3c-H₂** chloroform was used in place of dichloromethane.

Table S1. Monoreduction with NaBH₄ of diacyl-10,20-bis-(3,5-di-tert-butylphenyl)-porphyrins to the corresponding (1-hydroxyalkyl)-acyl porphyrin free bases.

Comp. No.	Diacylporphyrin	Reaction time (min)	Product No.	Yield
2a-H₂	3,17-diacetyl	90	4a-H₂	70 %
2b-H₂	3,17-diheptanoyl	20	4b-H₂	38 %
2c-H₂	3,17-palmitoyl	40	4c-H₂	41 %
3a-H₂	3,13-diacetyl	120	5a-H₂	36 %
3c-H₂	3,13-dipalmitoyl	70	5c-H₂	44 %

(rac)-17-Acetyl-3-(1-hydroxyethyl)-10,20-bis(3,5-di-*t*-butylphenyl)-21,23H-porphyrin (**4a-H₂**)

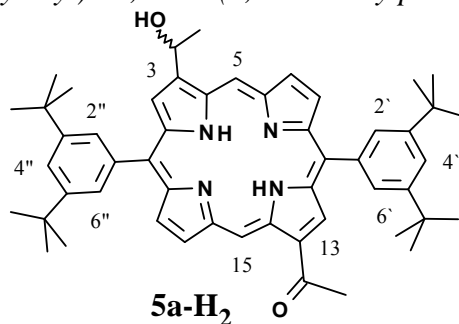
$R_f = 0.28$.

¹H-NMR (CDCl₃): δ (ppm) = 11.40 (s, 1H, 5-H), 10.38 (s, 1H, 15-H), 9.51 (s, 1H, 2-H), 9.51 (d, ³J = 4.8 Hz, 1H, 7-H), 9.29 (d, ³J = 4.5 Hz, 1H, 13-H), 9.11 (d, ³J = 4.8 Hz, 1H, 8-H), 9.11, (s, 1H, 18-H), 9.11 (d, ³J = 4.5 Hz, 1H, 12-H), 8.14 (d, ⁴J = 1.8 Hz, 2H, 2',6',-H), 8.10 (d, ⁴J = 1.8 Hz, 2H, 2'',6'',-H), 7.88 (t, ⁴J = 1.8 Hz, 1H, 4'-H), 7.84 (t, ⁴J = 1.8 Hz, 1H, 4''-H), 6.74 (q, ³J = 6.3 Hz, 1H, CH₃-CH-OH), 3.17 (s, 3H, CO-CH₃), 2.64 (broad s, 1H, CH₃-CH-OH), 2.31 (d, ³J = 6.3 Hz, 3H, CH₃-CH-OH), 1.61 and 1.57 (two s, 18 H each, C(CH₃)₃), -2.63 (broad s, 1H, NH), -2.89 (broad s, 1H, NH).

¹³C-NMR (CDCl₃): δ (ppm) = 25.88 (CO-CH₃), 29.93 (HO-CH-CH₃), 31.75 (C(CH₃)₃), 35.09 and 35.14 (C(CH₃)₃), 65.52 (HO-CH-CH₃), 121.26 (10,20-C), 122.06 (4'-C), 130.06, 130.79, 139.98, 140.06, 149.25, 149.34, 197.42 (CO-CH₃).

MALDI-MS: 772.1.

HR-FAB-MS: 773.4811 [M+H]⁺; calc. for C₅₂H₆₁N₄O₂ = 773.4795.

(rac)-13-Acetyl-3-(1-hydroxyethyl)-10,20-bis(3,5-di-*t*-butylphenyl)-21,23H-porphyrin (**5a-H₂**)

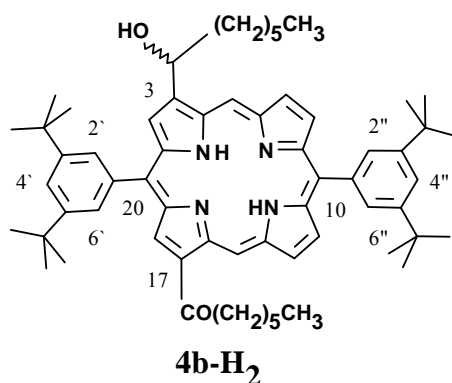
$R_f = 0.28$

¹H-NMR (CDCl₃): δ (ppm) = 11.40 (s, 1H, 5-H), 10.44 (s, 1H, 15-H), 9.51 (s, 1H, 2-H), 9.51 (d, ³J = 4.5 Hz, 1H, 7-H), 9.41 (d, ³J = 4.8 Hz, 1H, 17-H), 9.17 (d, ³J = 4.8 Hz, 1H, 8-H), 9.10 (d, ³J = 4.8 Hz, 1H, 18-H), 8.88, (s, 1H, 12-H), 8.14 (d, ⁴J = 1.8 Hz, 2H, 2',6',-H), 8.08 (m, 2H, non-equivalent 2'',6'',-H), 7.88 (t, ⁴J = 1.8 Hz, 1H, 4'-H), 7.84 (t, ⁴J = 1.8 Hz, 1H, 4''-H), 6.61 (q, ³J ~ 6 Hz, 1H, CH₃-CH-OH), 3.16 (s, 3H, CO-CH₃), 2.54 (broad s, 1H, CH₃-CH-OH), 2.25 (d, ³J = 6.3 Hz, 3H, CH₃-CH-OH), 1.60, 1.59, 1.57 and 1.57 (four s, 9 H each, C(CH₃)₃), -2.78 (broad s, 1H, NH).

¹³C-NMR (CDCl₃): δ (ppm) = 13.70, 25.72, 29.69, 29.93 (CO-CH₃), 31.77 (C(CH₃)₃), 35.10, 35.11 and 35.14 (C(CH₃)₃), 65.59 (HO-CH-CH₃), 102.67, 107.53 (5,15-C), 121.18 and 121.35 (10,20-C), 122.42 (4'-C), 128.32, 128.36, 130.67 (2',6'-C), 139.45, 139.980, 140.04, 149.26 and 149.36 (3',5'- and 3'',5''-C), 150.97 (2,12-C), 197.47 (CO-CH₃)

MALDI-MS: 772.8.

HR-FAB-MS: 773.4800 [M+H]⁺; calc. for C₅₂H₆₁N₄O₂ = 773.4795.

(rac)-17-Heptanoyl-3-(1-hydroxyheptyl)-10,20-bis(3,5-di-*t*-butylphenyl)-21,23H-porphyrin**(4b-H₂)** $R_f = 0.63$ (CH₂Cl₂ : *n*-hexane, 1:1, v/v).

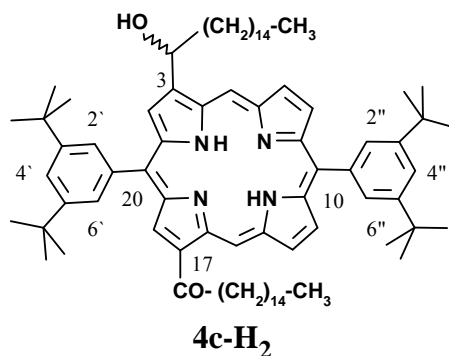
¹H-NMR (CDCl₃): δ (ppm) = 11.43 (s, 1H, 5-H), 10.36 (s, 1H, 15-H), 9.53 (s, 1H, 2-H), 9.51 (d, ³J = 4.8 Hz, 1H, 7-H), 9.30 (d, ³J = 4.5 Hz, 1H, 13-H), 9.13 (overlapped d, 1H, 8-H), 9.12, (s, 1H, 18-H), 9.03 (d, ³J = 4.5 Hz, 1H, 12-H), 8.11-8.17 (m, 4H, 2',6'-H and, 2'',6'' -H), 7.89 (t, ⁴J = 1.8 Hz, 1H, 4'-H), 7.85 (t, ⁴J = 1.8 Hz, 1H, 4''-H), 6.74 (q, ³J = 6.6 Hz, 1H, CH₃-CH₂-CH₂-CH₂-CH₂-CH₂-OH), 3.55 (t = 7.2 Hz, 2H, CO-CH₂ (CH₂)₄-CH₃), 2.63-2.60 (broad m, 4H, HO-CH-CH₂-CH₂-(CH₂)₃-CH₃), 2.13 (q, 2H, CO-CH₂-(CH₂)₃-CH₂-CH₃), 1.62 and 1.58 (two s, 18 H each, C(CH₃)₃), 1.26-1.55 (broad m, 12H, CO-CH₂-CH₂-CH₂-CH₂-CH₂-CH₃ & HO-CH-(CH₂)₂-CH₂-CH₂-CH₂-CH₃), 0.95 (t, 6.9 Hz, 3H, CO-CH₂-(CH₂)₄-CH₃), 0.87 (t, 6.9 Hz, 3H, HO-CH-(CH₂)₅-CH₃), -2.63 (broad s, 1H, NH), -2.89 (broad s, 1H, NH).

¹³C-NMR (CDCl₃): δ (ppm) = 14.07, 14.14 (CH₂-CH₃), 22.61, 22.64, 25.25, 26.29, 29.34, 31.76 (C(CH₃)₃), 31.84, 35.09 and 35.14 (C(CH₃)₃), 39.93, 42.09 (CO-CH₂-(CH₂)₄), 69.59 (HO-CH-(CH₂)₅-CH₃), 102.37, 107.62, 120.60, 121.23, 121.98, 126.57, 128.39, 129.00, 129.32, 130.08, 130.83, 130.86, 131.42, 133.83, 134.40, 138.30, 139.9, 140.12, 144.92, 149.23, 149.28, 149.32, 200.46 (CO-(CH₂)₅-CH₃).

MALDI-MS: 913.2

HR-FAB-MS: [M+H]⁺ 913.6345; calc. for C₆₂H₈₁N₄O₂ = 913.6359.

(rac)-3-(1-hydroxyhexadecyl)-17-palmitoyl-10,20-bis(3,5-di-*t*-butylphenyl)-21,23*H*-porphyrin
(**4c-H₂**)



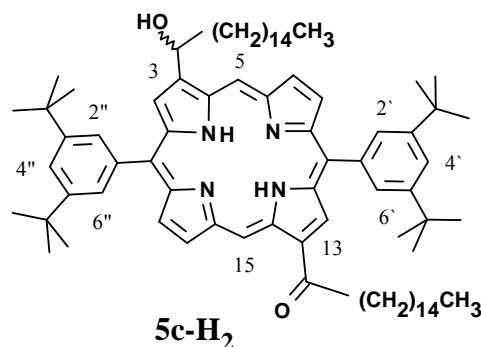
$R_f = 0.76$ (CH₂Cl₂ : *n*-hexane, 1:1, v/v).

¹H-NMR (CDCl₃): δ (ppm) = 11.43 (s, 1H, 5-H), 10.36 (s, 1H, 15-H), 9.52 (s, 1H, 2-H), 9.51 (d, ³J = 4.5 Hz, 1H, 7-H), 9.30 (d, ³J = 4.5 Hz, 1H, 13-H), 9.13 (overlapped d, 1H, 8-H), 9.12 (s, 1H, 18-H), 9.03 (d, ³J = 4.8 Hz, 1H, 12-H), 8.11-8.18 (m, 4H, 2',6'-H and 2'',6''-H), 7.89 (t, ⁴J = 1.8 Hz, 1H, 4''-H), 7.84 (t, ⁴J = 1.8 Hz, 1H, 4'-H), 6.51 (q, ³J = 6.3 Hz, 1H, CH₃-(CH₂)₁₄-CH₂-OH), 3.56 (t = 6.3 Hz, 2H, CO-CH₂-(CH₂)₁₃-CH₃), 2.53-2.63 (broad m, 4H, HO-CH-CH₂-CH₂-(CH₂)₁₂-CH₃), 2.12 (q, 2H, CO-CH₂-(CH₂)₁₂-CH₂-CH₃), 1.61 and 1.57 (two s, 18 H each, C(CH₃)₃), 1.20-1.25 (broad d, 46H, CO-CH₂-(CH₂)₁₂-CH₂-CH₃ and HOCH-(CH₂)₂-(CH₂)₁₀-CH₂-CH₃), 0.83-0.89 (m, 6H, CO-(CH₂)₁₄-CH₃ and CH₃-(CH₂)₁₄-CH-OH), -2.67 and 2.92 (two broad s, 2H, NH),

¹³C-NMR (CDCl₃): δ (ppm) = 14.12, 14.14, 22.67, 22.69, 25.29, 29.33, 29.36, 29.65, 29.71, 31.77 (C(CH₃)₃), 31.89, 31.92, 35.10 and 35.15 (C(CH₃)₃), 39.93, 42.10, 69.56 (HO-CH-(CH₂)₁₄-CH₃), 102.37, 107.62, 120.59, 121.22, 121.97, 126.56, 129.31, 130.11, 130.91, 131.41, 133.85, 134.42, 138.35, 139.21, 140.03, 140.13, 144.92, 149.23, 149.28, 149.31, 200.47 (CO-(CH₂)₁₄-CH₃).

MALDI-MS: 1164.5

(rac)-3-(1-hydroxyhexadecyl)-13-palmitoyl-10,20-bis(3,5-di-*t*-butylphenyl)-21,23*H*-porphyrin
(**5c-H₂**)



$R_f = 0.57$ (CHCl₃); on the same TLC the starting material **3c-H₂** has $R_f = 0.75$ and the meso- and (*rac*)-diols have $R_f = 0.17$ and 0.13 (not assigned).

¹H-NMR (CDCl₃): δ (ppm) = 11.41 (s, 1H, 5-H), 10.42 (s, 1H, 15-H), 9.52 (s, 1H, 2-H), 9.50 (d, ³J = 4.8 Hz, 1H, 7-H), 9.42 (d, ³J = 5.1 Hz, 1H, 17-H), 9.18 (d, ³J = 5.1 Hz, 1H, 8-H), 9.11 (d, ³J = 4.8 Hz, 1H, 18-H), 8.88 (s, 1H, 12-H), 8.09 – 8.16 (m, 4H, 2',6'-H and non-equivalent 2'',6''-H), 7.88 (t, ⁴J = 1.8 Hz, 1H, 4'-H), 7.84 (t, ⁴J = 1.8 Hz, 1H, 4''-H), 6.37 (q, ³J = 6.3 Hz, 1H, CH₃-(CH₂)₁₅-CH-OH), 3.54 (t, ³J = 7.2 Hz, 2H, CO-CH₂-(CH₂)₁₄-CH₃), 2.17 (broad s, 1H, HO-CH-(CH₂)₁₄-CH₂-CH₃), 2.10 (q, ³J = 7.5 Hz, 2H, HO-CH-CH₂-(CH₂)₁₅-

CH₃), 1.61 and 1.57 (two s, 18 H each, C(CH₃)₃), 0.83-0.89 (two overlapped t, 6H, CO-CH₂-(CH₂)₁₄-CH₃ and HO-CH-(CH₂)₁₅-CH₃), -2.76 and -2.79 (two s, 2H, NH).

¹³C-NMR_(CDCl₃): δ (ppm) = 14.11, 25.30, 26.43, 29.32, 29.35, 29.61, 29.64, 29.70, 29.75, 31.76 (C(CH₃)₃), 31.89, 31.91, 35.10 and 35.14 (C(CH₃)₃), 39.80, 42.09, 69.78 (HO-CH-(CH₂)₁₄-CH₃), 107.56, 120.23, 121.16, 121.30, 122.38, 129.17, 129.65, 130.14, 130.30, 130.72, 139.27, 140.02, 149.22, 149.23, 149.34, 149.87, 200.46 (CO-(CH₂)₁₄-CH₃).

Analytical and Preparative Chiral HPLC Separations

Analytical chiral HPLC experiments were performed on a screening unit composed of a Merck D-7000 system manager, Merck-Lachrom L-7100 pump, Merck-Lachrom L-7360 oven, Merck-Lachrom L-7400 UV-detector. Hexane, 2-propanol and ethanol were of HPLC grade, and were degassed and filtered on a 0.45 μm membrane before use. Chiralcel OD-H, OJ, OC, OG, OB-H, Chiralpak AS and AD from Chiral Technology Europa (Illkirch, France), Whelk-O1 (*S,S*) and ULMO (*S,S*) columns from Regis (Morton Grove, USA) were used for the screening. For the analytical separations, the flow-rate was 1 mL/min and the columns were thermostated at 25°C. Preparative HPLC separations were performed on a ULMO (*S,S*) columns from Regis using a Varian ProStar station equipped with two Rainin 210 pumps. For UV-Vis detection either a ProStar 345 dual wavelength detector or a 335 diode array detector were used.

Retention times *R_t* in minutes, retention factors $k_i = (R_{t_i} - R_{t_0})/R_{t_0}$ and enantioselectivity $\alpha = k_2/k_1$ are given. *R_{t0}* was determined by injection of 1,3,5-tri-*tert*-butyl benzene.

Table S2. Chiral HPLC separation for compound **4a**

The sample was dissolved ethanol, injected on the chiral column, and detected with an UV detector at 420 nm.

Column	Mobile Phase	<i>t</i> ₁	<i>k</i> ₁	<i>t</i> ₂	<i>k</i> ₂	α	<i>R_s</i>
Chiralpak AS	Hexane / Isopropanol 99/1	15.38	3.96			1	0
Chiralcel OD-H	Hexane / Isopropanol 99/1	29.88	7.95	38.49	10.52	1.32	1.31
	Hexane / Ethanol 98/2	13.02	3.13			1	0
Chiralcel OJ	Hexane / Isopropanol 99/1	16.71	3.99			1	0
Chiralcel OC	Hexane / Isopropanol 80/20	3.28	0.12			1	0
Chiralcel OG	Hexane / Isopropanol 80/20	4.53	0.51			1	0
Chiralcel OB-H	Hexane / Isopropanol 99/1	18.52	4.54			1	0
ULMO (<i>S,S</i>)	Hexane / Isopropanol 80/20	13.85	3.84	24.41	7.54	1.96	6.67
	Ethanol	12.21	3.27	16.36	4.72	1.44	3.01
Chiralpak AD	Hexane / Isopropanol 99/1	11.32	2.72	19.05	5.27	1.93	1.89
Whelk-O1 (<i>S,S</i>)	Hexane / Isopropanol 80/20	37.43	11.43	40.68	12.51	1.09	0.91
	Ethanol	13.63	3.53			1	0

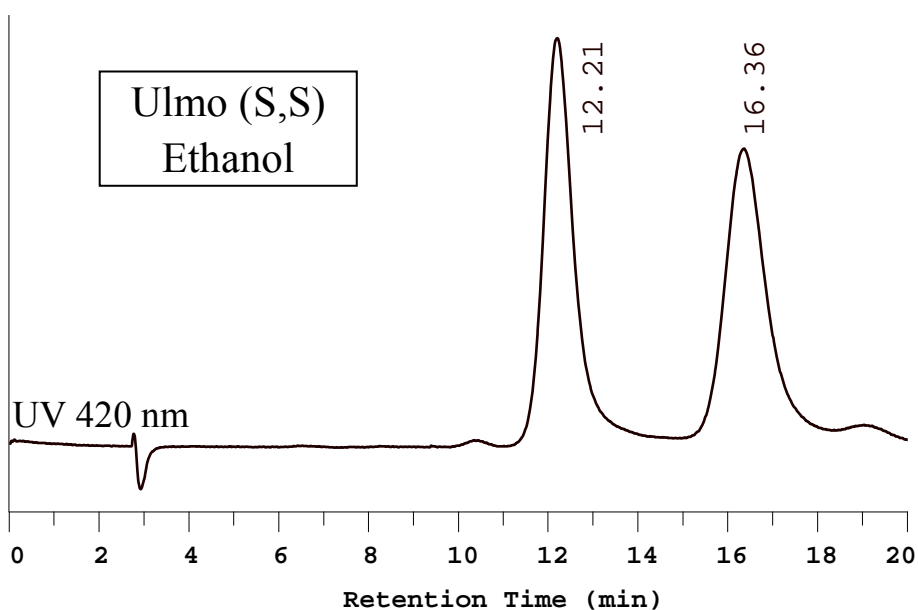


Figure S1. Typical Chromatogram for the separation of (*rac*)-**4a**

Table S3. Chiral HPLC separation for compound **5a**.

The sample was dissolved ethanol, injected on the chiral column, and detected with an UV detector at 420 nm.

Column	Mobile Phase	t_1	k_1	t_2	k_2	α	R_s
Chiralcel OD-H	Hexane / Isopropanol 95/5	6.08	0.99	7.84	1.57	1.58	0.85
ULMO (S,S)	Hexane / Isopropanol 80/20	18.91	5.20	20.05	5.57	1.07	<0.5
	Ethanol	17.25	5.03	19.56	5.84	1.16	1.19
Whelk-O1 (S,S)	Hexane / Isopropanol 90/10	25.91	7.61	36.15	11.01	1.45	4.13

N.B. The elution order is reversed on the ULMO (S,S) and Whelk-O1 (S,S) columns.

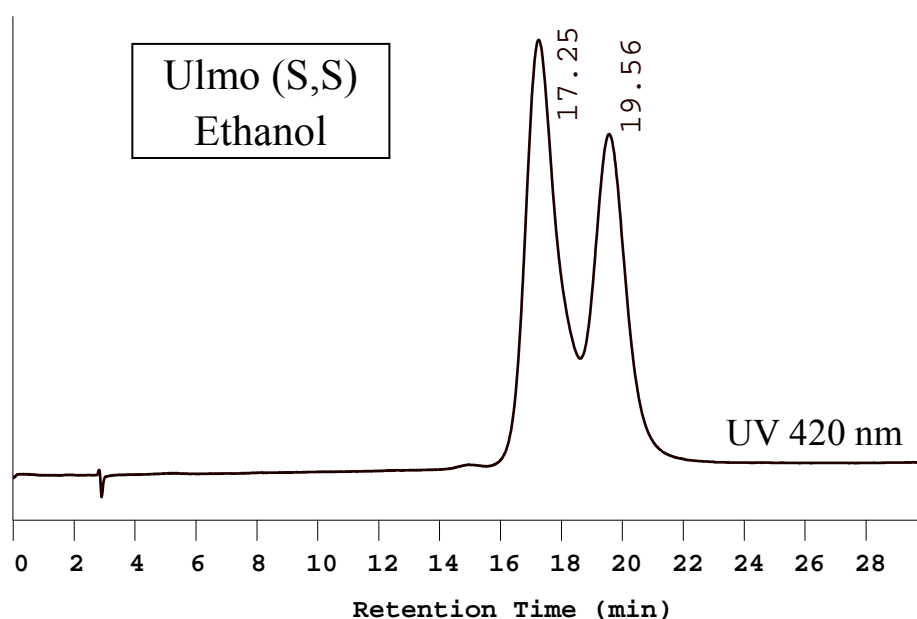


Figure S2. Typical chromatogram for the separation of (*rac*)-**5a**

Stereoselective reductions of **2a-H₂** - Selected Examples

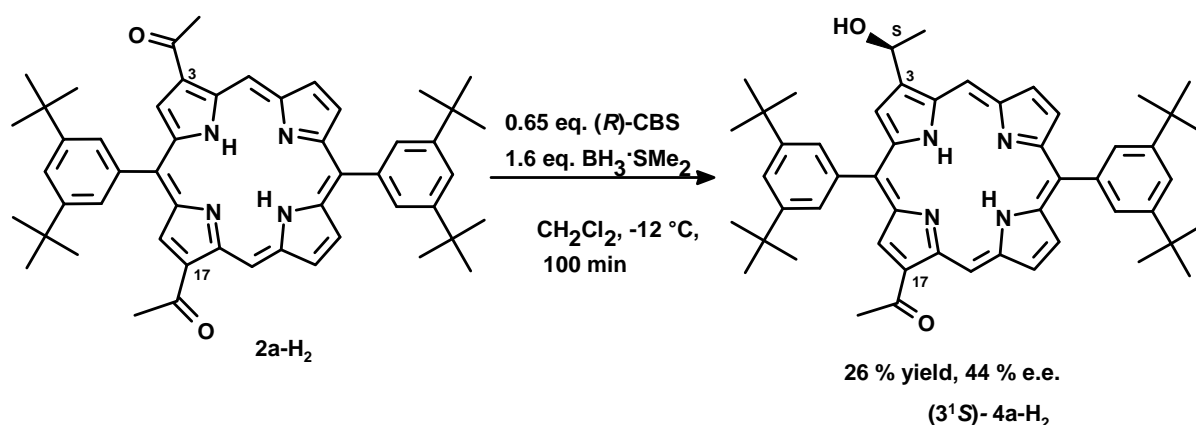
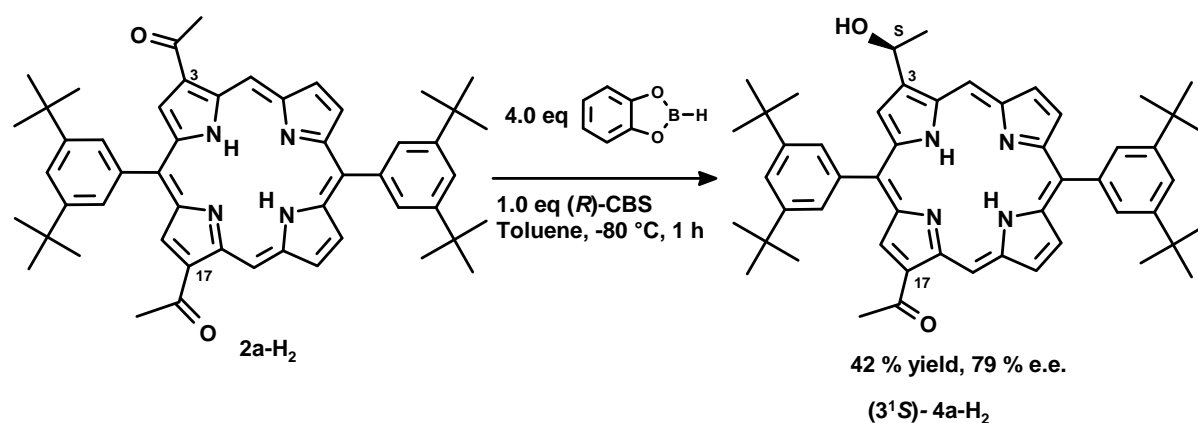


Table. S4. Reductions of **2a-H₂** with CBS and borane dimethylsulfide

Substrate	Temp. (±2) °C	Conc. (mmol/l)	R-CBS (eq.)	BH ₃ ·SMe ₂ (eq.)	Reaction	Yield (3 ¹ S)4a-H ₂	e.r. (R : S)
2a-H₂	-12	20.0	0.65	1.6	Borane added during 20 min, then stirring for 80 min	26 %	28 : 72
	-15	26.0-14.5	1.0	2.0	Borane slowly added during 2 h	~40 %	30 : 70
	-15	17.0	1.0	2.0	Substrate added during 10 min then stirring for 1.5 h	38 %	32 : 68

Optimized stereoselective reduction of **2a** with the Corey-Bakshi-Shibata (CBS) reagent

In a reaction flask that has been stored overnight in an oven at 110 °C and which was heated with a heat gun while slowly purging with dry nitrogen, 3,17-diacetylporphyrin **2a-H₂** (10 mg, 13.0 μmol) was dissolved in 0.50 mL dry toluene, freshly distilled from sodium metal, and cooled to -80 (±5) °C. With a cannula a 1.0 mol/L solution of (*R*)-CBS in toluene (1.0 eq., 13 μL, 13.0 μmol, Aldrich) was added and shortly stirred before adding slowly, over 40 min, a 1.0 mol/L solution of catecholborane in THF (4.0 eq., 52 μL, 52 μmol, Aldrich). Because of the small reaction volume this corresponded to adding approximately one drop of the THF solution every five minutes. After stirring for another 20 min, the reaction course was monitored by TLC knowing that the *R_f* of **2a-H₂** in dry CH₂Cl₂ is 0.46, while for the ketol **4a-H₂** *R_f* = 0.25. The reaction was quenched by adding 1 mL of distilled water and stirring for 5 min at room temperature when a brief hydrogen evolution was observed. The organic layer was diluted to 20 mL with CH₂Cl₂ and washed successively twice with 5 mL brine and the 5 mL distilled water. After removal of the solvents on a rotary evaporator and drying in vacuum 11 mg crude product were obtained which were separated on a silica gel column (12 g, Φ = 1 cm) eluted with CH₂Cl₂. The product weighed 4.2 mg (5.43 μmol, 42 % yield). Chiral HPLC as described above showed an enantiomeric ratio (*R/S*) = 10.5 / 89.5 which corresponded to 79 % e.e. Further fractions from the silicagel column consisted in 4.5 mg recuperated **2a-H₂** and 1.3 mg diol.

**Table S5.** Reductions of **2a-H₂** with CBS and catecholborane.

Substrate	Temp. (± 3) °C	Solvent	Conc. (mmol/l)	<i>R</i> -CBS (eq.)	Catechol- borane (eq.)	Reaction time (h)	Yield (3' ^S)-4-H ₂	e.r. (<i>R</i> : <i>S</i>)
2a-H₂	-90	THF	22	1.0	6.0	1.5	< 20 %	36 : 64
	-90	CH ₂ Cl ₂	22	1.0	6.0	1.0	~ 25 %	22 : 78
	-90	Toluene	23	1.0	4.0	1.0	~ 25 %	11 : 89
	-80	Toluene	23	1.0	4.0	1.0	~ 42 %	10 : 90

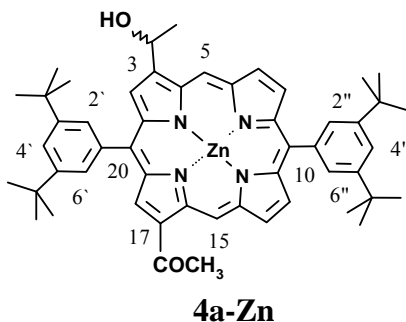
Table S6. Reductions of **2a-H₂** with 1.0 eq. (3'¹*R*) and (3'¹*S*) CBS performed in anhydrous toluene at -80 ± 3 °C and 4.0 eq. catecholborane and at a substrate concentration of 23.0 ± 0.5 mmol/L

Substrate	CBS (eq.)	Reaction time (min)	Yield	e.r. (<i>R</i> : <i>S</i>)
2a-H₂	1.0 (<i>R</i>)	60	~ 42 %	10 : 90
	1.0 (<i>S</i>)	50	~ 33 %	78 : 22
3a-H₂	1.0 (<i>R</i>)	60	~ 33 %	23 : 77
	1.0 (<i>S</i>)	50	~ 42 %	69 : 31

Zinc metalation of acyl-hydroxyalkylporphyrins. General Procedure.

Zinc insertion into the corresponding free bases (on a 50 to 100 mg scale) was effected by stirring overnight at room temperature in a 30 mL mixture of chloroform and methanol (3:1 v/v) with excess zinc acetate. The reaction mixture was diluted with dichloromethane, washed with aqueous sodium hydrogen carbonate and subsequently with brine. Column chromatography on silica gel eluted with 3% methanol in dichloromethane afforded the zinc-methanol monomeric adducts in yields exceeding 80%. The main eluted fraction was washed at least twice with brine in order to remove the residual methanol. After evaporation of the solvents, the residue was dissolved in a minimal amount of dry dichloromethane (1-2 mL) which was slowly added to ca. 60 mL dry *n*-hexane or *n*-heptane in a centrifuge bottle which could be closed with a screw cap. Centrifugation for 5 to 10 min at room temperature and 4000 rpm usually produced good pellets which after decantation of the supernatant were dried in vacuum (10^{-3} mbar) overnight. Samples prepared in this way could be reproducibly self-assembled in nonpolar solvents. In CDCl_3 or CD_2Cl_2 no interpretable ^1H -NMR spectra can be obtained in the absence of CD_3OD due to extensive aggregation.

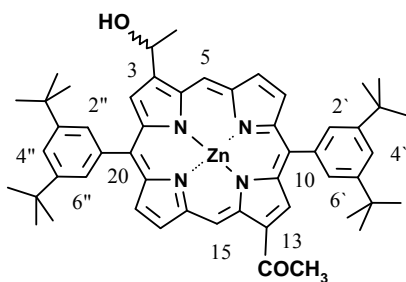
(*rac*)-17-Acetyl-3-(1-hydroxyethyl)-10,20-bis(3,5-di-*t*-butylphenyl)porphinato zinc (**4a-Zn**)



$R_f = 0.09$.

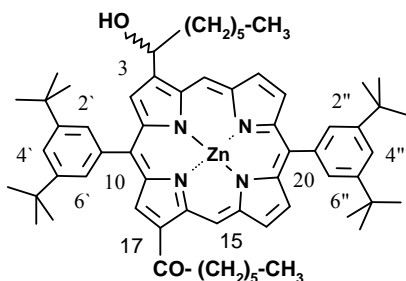
^1H -NMR ($\text{CDCl}_3:\text{CD}_3\text{OD}$, 9:1 v,v): δ (ppm) = 11.30 (s, 1H, 5-H), 10.30 (s, 1H, 15-H), 9.58 (s, 1H, 2-H), 9.47 (d, $^3J = 4.5$ Hz, 1H, 7- or 13-H), 9.37 (d, $^3J = 4.5$ Hz, 1H, 13- or 7-H), 9.12 and 9.11 (two overlapping d, $^3J \sim 4.2$ Hz, 2H, 12- and 8-H), 9.01 (s, 1H, 18-H), 8.15 and 8.11 (two t, $^4J = 1.8$ Hz, 2H, nonequivalent 2' or 6'-H and 2'' or 6''-H), 8.09 (dd, $^4J = 1.8$ Hz, 2H, nonequivalent 6' or 2'-H and 6'' or 2''-H), 7.87 and 7.84 (two t, $^4J = 1.8$ Hz, 2H, 4'- and 4''-H), 6.54 (q, $^3J \sim 6$ Hz, 1H, $\text{CH}_3\text{-CH-OH}$), 3.16 (s, 3H, CO-CH_3), 2.38 (broad s, 1H, $\text{CH}_3\text{-CH-OH}$), 2.24 (d, $^3J = 6.3$ Hz, 3H, $\text{CH}_3\text{-CH-OH}$), 1.60, 1.59, 1.57 and 1.57 (four s, 9 H each, nonequivalent $\text{C}(\text{CH}_3)_3$).

HR-FAB-MS: 834.3871; Calc. for $\text{C}_{52}\text{H}_{58}\text{N}_4\text{O}_2\text{Zn}$ = 834.3851.

(rac)-13-Acetyl-3-(1-hydroxyethyl)-10,20-bis(3,5-di-*t*-butylphenyl)porphinato zinc (**5a-Zn**)**5a-Zn** $R_f = 0.09$

$^1\text{H-NMR}$ ($\text{CDCl}_3:\text{CD}_3\text{OD}$, 9:1 v,v): δ (ppm) = 11.35 (s, 1H, 5-H), 10.37 (s, 1H, 15-H), 9.59 (s, 1H, 2-H), 9.47 (d, $^3J = 4.5$ Hz, 1H, 7-H), 9.38 (d, $^3J = 4.5$ Hz, 1H, 17-H), 9.17 (d, $^3J = 4.5$ Hz, 1H, 8-H), 9.10 (d, $^3J = 4.5$ Hz, 1H, 18-H), 8.90 (s, 1H, 12-H), 8.14 (d, $^4J \sim 1.5$ Hz, 2H, 2',6'-H), 8.05 (m, 2H, nonequivalent 2'',6''-H), 7.87 (t, $^4J = 1.8$ Hz, 1H, 4'-H), 7.84 (t, $^4J = 1.8$ Hz, 1H, 4''-H), 6.63 (m, $^3J \sim 6.3$ Hz, 1H, $\text{CH}_3\text{-CH-OH}$), 3.18 (s, 3H, CO-CH_3), ~ 2.5 (broad d, $\text{CH}_3\text{-CH-OH}$), 2.23 (d, $^3J = 6.6$ Hz, 3H, $\text{CH}_3\text{-CH-OH}$), 1.60, 1.57 and 1.53 (three s, 9, 9 and 18H respectively, nonequivalent $\text{C}(\text{CH}_3)_3$).

HR-FAB-MS: 834.3842; calc. For $\text{C}_{52}\text{H}_{58}\text{N}_4\text{O}_2\text{Zn} = 834.3851$.

(rac)-3-Heptanoyl-17-(1-hydroxyheptyl)-10,20-bis(3,5-di-*t*-butylphenyl)porphinato zinc (**4b-Zn**)**4b-Zn**

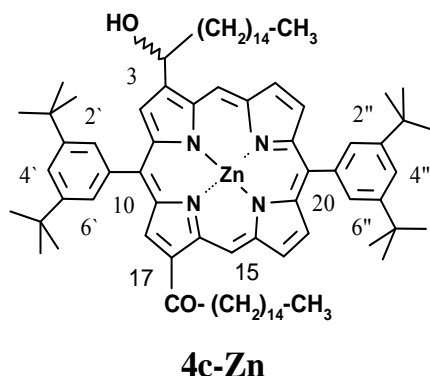
$R_f = 0.30$ (CH_2Cl_2 : *n*-hexane, 1:1, v/v).

$^1\text{H-NMR}$ ($\text{CDCl}_3:\text{CD}_3\text{OD}$, 9:1 v,v): δ (ppm) = 11.43 (s, 1H, 5-H), 10.36 (s, 1H, 15-H), 9.53 (s, 1H, 2-H), 9.51 (d, $^3J = 4.8$ Hz, 1H, 7-H), 9.30 (d, $^3J = 4.5$ Hz, 1H, 13-H), 9.13 (overlapped d, 1H, 8-H), 9.12 (s, 1H, 18-H), 9.03 (d, $^3J = 4.5$ Hz, 1H, 12-H), 8.11-8.17 (m, 4H, 2',6'-H and, 2'',6''-H), 7.89 (t, $^4J = 1.8$ Hz, 1H, 4'-H), 7.85 (t, $^4J = 1.8$ Hz, 1H, 4''-H), 6.74 (q, $^3J = 6.6$ Hz, 1H, $\text{CH}_3\text{-(CH}_2)_5\text{-CH-OH}$), 3.55 (t = 7.2 Hz, 2H, $\text{CO-CH}_2\text{-(CH}_2)_4\text{-CH}_3$), 2.63-2.60 (broad m, 4H, $\text{HO-CH-CH}_2\text{-CH}_2\text{-(CH}_2)_3\text{-CH}_3$), 2.13 (q, 2H, $\text{CO-CH}_2\text{-(CH}_2)_3\text{-CH}_2\text{-CH}_3$), 1.62 and 1.58 (two s, 18 H each, $\text{C}(\text{CH}_3)_3$), 1.26-1.55 (broad m, 12H, $\text{CO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$ & $\text{HO-CH-(CH}_2)_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$), 0.95 (t, 6.9 Hz, 3H, $\text{CO-CH}_2\text{-(CH}_2)_4\text{-CH}_3$), 0.87 (t, 6.9 Hz, 3H, $\text{HO-CH-(CH}_2)_5\text{-CH}_3$).

MALDI-MS: 974.1

HR-FAB-MS: $[\text{M}+\text{H}]^+$ 975.5484; calc. for $\text{C}_{62}\text{H}_{78}\text{N}_4\text{O}_2\text{Zn} = 975.5494$

(*rac*)-3-(1-Hydroxyhexadecyl)-17-palmitoyl-10,20-bis(3,5-di-*t*-butylphenyl)porphinato zinc
(**4c-Zn**)

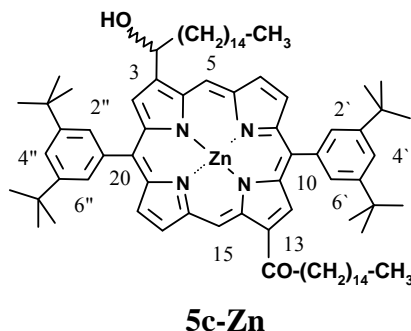


$R_f = 0.47$ ($\text{CH}_2\text{Cl}_2 : n\text{-hexane}$, 1:1, v/v); $R_f = 0.60$ (CH_2Cl_2 distilled from CaH_2 unstabilized); $R_f = 0.77$ (1% MeOH in CH_2Cl_2).

$^1\text{H-NMR}$ ($\text{CDCl}_3:\text{CD}_3\text{OD}$, 9:1 v,v): δ (ppm) = 11.16 (s, 1H, 5-H), 10.22 (s, 1H, 15-H), 9.52 (s, 1H, 2-H), 9.35 (d, $^3J = 4.8$ Hz, 1H, 7-H), 9.28 (d, $^3J = 4.5$ Hz, 1H, 13-H), 9.17 (d, $^3J = 4.8$ Hz, 1H, 8-H), 8.99 (d, $^3J = 4.5$ Hz, 1H, 12-H), 8.95, (s, 1H, 18-H), 8.03-8.09 (m, 4H, 2', 6'-H and 2'', 6''-H), 7.81 (t, $^4J = 1.5$ Hz, 1H, 4''-H), 7.77 (t, $^4J = 1.5$ Hz, 1H, 4'-H), 6.35 (q, $^3J = 6.6$ Hz, 1H, $\text{CH}_3(\text{CH}_2)_{14}\text{CH}_2\text{-OH}$), 3.51 (t, $^3J = 7.5$ Hz, 2H, $\text{CO-CH}_2\text{-(CH}_2)_{13}\text{-CH}_3$), 2.53-2.69 (broad m, 4H, $\text{HO-CH-CH}_2\text{-CH}_2\text{-(CH}_2)_{12}\text{-CH}_3$), 2.07 (q, 2H, $\text{CO-CH}_2\text{-(CH}_2)_{12}\text{-CH}_2\text{-CH}_3$), 1.56 and 1.52 (two s, 18 H each, $\text{C(CH}_3)_3$), 0.79-0.85 (m, 6H, $\text{CO-(CH}_2)_{14}\text{-CH}_3$ and $\text{CH}_3\text{-(CH}_2)_{14}\text{-CH-OH}$).

MALDI-MS: 1226.5; calc. for $\text{C}_{80}\text{H}_{114}\text{N}_4\text{O}_2\text{Zn} = 1226.82$.

(*rac*)-3-(1-Hydroxyhexadecyl)-13-palmitoyl-10,20-bis(3,5-di-*t*-butylphenyl)porphinato zinc
(**5c-Zn**)



$R_f = 0.54$ (CH_2Cl_2 distilled from CaH_2 unstabilized); $R_f = 0.77$ (1% MeOH in CH_2Cl_2).

$^1\text{H-NMR}$ ($\text{CDCl}_3:\text{CD}_3\text{OD}$, 9:1 v,v): δ (ppm) = 11.13 (s, 1H, 5-H), 10.22 (s, 1H, 15-H), 9.51 (s, 1H, 2-H), 9.33 (d, $^3J = 4.5$ Hz, 1H, 7-H), 9.26 (d, $^3J = 4.5$ Hz, 1H, 17-H), 9.05 (d, $^3J = 4.5$ Hz, 1H, 8-H), 8.96 (d, $^3J = 4.5$ Hz, 1H, 18-H), 8.88 (s, 1H, 12-H), 8.08 (d, $^4J = 1.8$ Hz, 2H, 2', 6'-H), 8.01 (d, $^4J = 1.8$ Hz, 2H, non-equivalent 2'', 6''-H), 7.80 (t, $^4J = 1.8$ Hz, 1H, 4'-H), 7.75 (t, $^4J = 1.8$ Hz, 1H, 4''-H), 6.33 (q, $^3J = 6.6$ Hz, 1H, $\text{CH}_3\text{-(CH}_2)_{15}\text{-CH}_2\text{-OH}$), 3.51 (t, $^3J = 7.5$ Hz, 2H, $\text{CO-CH}_2\text{-(CH}_2)_{14}\text{-CH}_3$), 2.43 – 2.58 (broad m, 4H, $\text{CO-CH}_2\text{-(CH}_2)_{13}\text{-CH}_2\text{-CH}_3$ and $\text{HO-CH-(CH}_2)_{14}\text{-CH}_2\text{-CH}_3$), 2.13 (broad s, 1H, $\text{HO-CH-(CH}_2)_{14}\text{-CH}_2\text{-CH}_3$), 2.06 (quint, $^3J = 7.2$ Hz, 2H, $\text{HO-CH-CH}_2\text{-(CH}_2)_{14}\text{-CH}_2\text{-CH}_3$), 1.54 and 1.51 (two s, 18 H each, $\text{C(CH}_3)_3$), 0.77-0.83 (two overlapped t, 6H, $\text{CO-CH}_2\text{-(CH}_2)_{14}\text{-CH}_3$ and $\text{HO-CH-(CH}_2)_{15}\text{-CH}_3$).

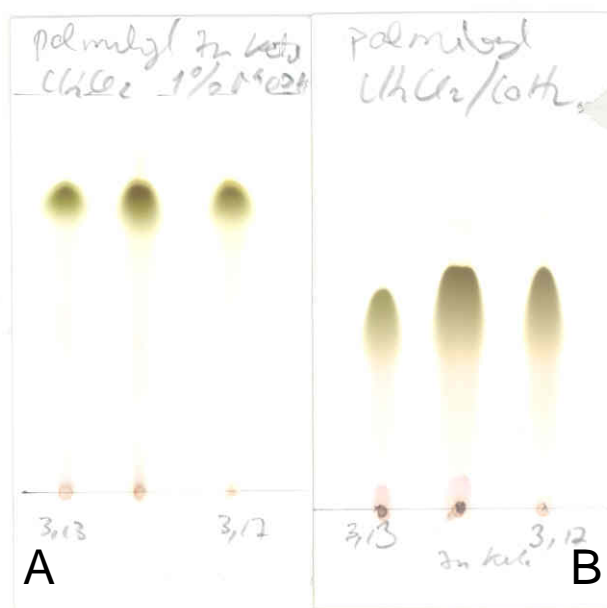
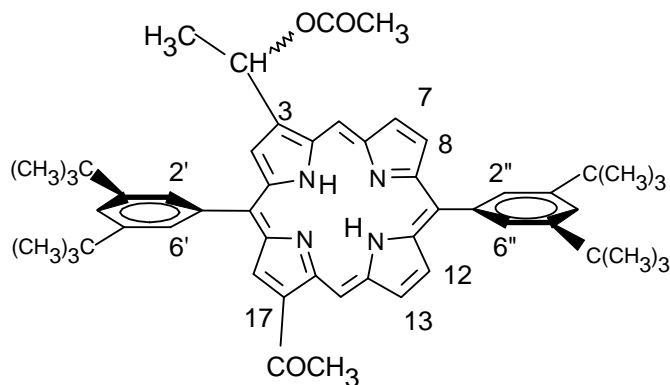


Figure S3. Typical TLC traces of the 3,17- and 3,13-Zn Ketols **4c-Zn** and **5c-Zn**. Polygram® SIL G/UV₂₅₄ from Macherey-Nagel were eluted (A) with 1% methanol in dichloromethane and (B) with dichloromethane distilled from CaH₂ (unstabilized with ethanol). Note the pronounced tailing in the latter case due to partial aggregation. Middle lane is the cross-spot.

(*rac*)-17-Acetyl-3-(1-acetoxyxyethyl)-10,20-bis(3,5-di-*t*-butylphenyl)-21,23H-porphyrin (**4aOAc-H₂**)



4aOAc-H₂

The free base **4a-H₂** (20 mg) dissolved in 10 mL dry THF was stirred for 3 hrs at room temperature together with 10 mL acetic anhydride and 10 mL dry pyridine. The reaction mixture was diluted with 50 mL dichloromethane and the organic phase was washed with water. After evaporation of the solvents, column chromatography on silica gel gave a pure **4aOAc-H₂** in quantitative yield (22 mg).

¹H-NMR (CDCl₃): δ (ppm) = 11.42 (s, 1H, 15-H), 10.27 (s, 1H, 5-H), 9.55 (s, 1H, 18-H), 9.51 (d, ³J = 4.2 Hz, 1H, 13-H), 9.30 (d, ³J = 4.5 Hz, 1H, 7-H), 9.17, (s, 1H, 2-H), 9.11 (d, ³J = 4.8 Hz, 1H, 12-H), 9.03 (d, ³J = 4.8 Hz, 1H, 8-H), 8.18 (two t, ⁴J = 1.8 Hz, 2H, non-eq. 2',6'-H), 8.11 (d, ⁴J = 1.8 Hz, 2H, 2'',6''-H), 7.90 (t, ⁴J = 1.8 Hz, 1H, 4'-H), 7.85 (t, ⁴J = 1.8 Hz, 1H, 4''-H), 7.79 (q, ³J = 6.6 Hz, 1H, CH₃-CH-OCOCH₃), 3.19 (s, 3H, CO-CH₃), 2.31 (d, ³J = 6.6 Hz, 3H, CH₃-CH-OCOCH₃), 2.27 (s, 3H, CH₃-OCO), 1.630 and 1.629 (two s, 9 H each, two non-eq. C(CH₃)₃), 1.58 (s, 18H, C(CH₃)₃), -2.63 and -2.85 (two broad s, 1H each, NH).

Microscale Oxidative Degradation Procedure. To a stirred two-phase mixture of 100 μL of CH_3CN , 100 μL of CCl_4 , and 200 μL of a 9.1 M sodium phosphate buffer (pH 6) in a 2.5 mL Wheaton screw-cap vial, ca. 1 mg of the faster eluting enantiomer of **4a-H₂** after *O*-acetylation in the first case, and of the slower eluting enantiomer in the second case, as well as the catalyst $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ (0.1 mg, 0.4 μmol) were added at room temperature. Over a period of 45 min, 25 mg (183 μmol) NaIO_4 were added in small portions, followed by stirring for another 1.5 h. To the resulting carboxylic acid, 700 μL H_2O were given and the mixture was stirred for a short period. The aqueous solution was washed three times with 300 μL CHCl_3 and then lyophilized. The residue was extracted with 1.5 mL dry MeOH, followed by separation of the insoluble inorganic salts by applying an ultrasonic bath for 1 h. After evaporation of the solvent and dissolution in CH_2Cl_2 , the mixture was filtered over a microfilter and the clear solution was analyzed by GC.

Capillary GC. GC-EI-MSD analyses were performed with a transfer-line temperature maintained at 280 $^\circ\text{C}$ resulting in a source temperature of 170 $^\circ\text{C}$ and an ionizing energy of 70 eV. Helium was used as the carrier gas with a column head pressure of 100 kPa. A CDX-B (J&W Scientific) column, 25 m \times 0.22 mm (i.d.) \times 0.25 μm with an on-column injector maintained at 210 $^\circ\text{C}$ was used for the enantiomeric separations of 2-acetoxypionic acid. Column temperature was programmed 5 min at 100 $^\circ\text{C}$, 5 $^\circ\text{C}/\text{min}$ to 150 $^\circ\text{C}$ for 5 min, 10 $^\circ\text{C}/\text{min}$, and finally held at 200 $^\circ\text{C}$ for 5 min.

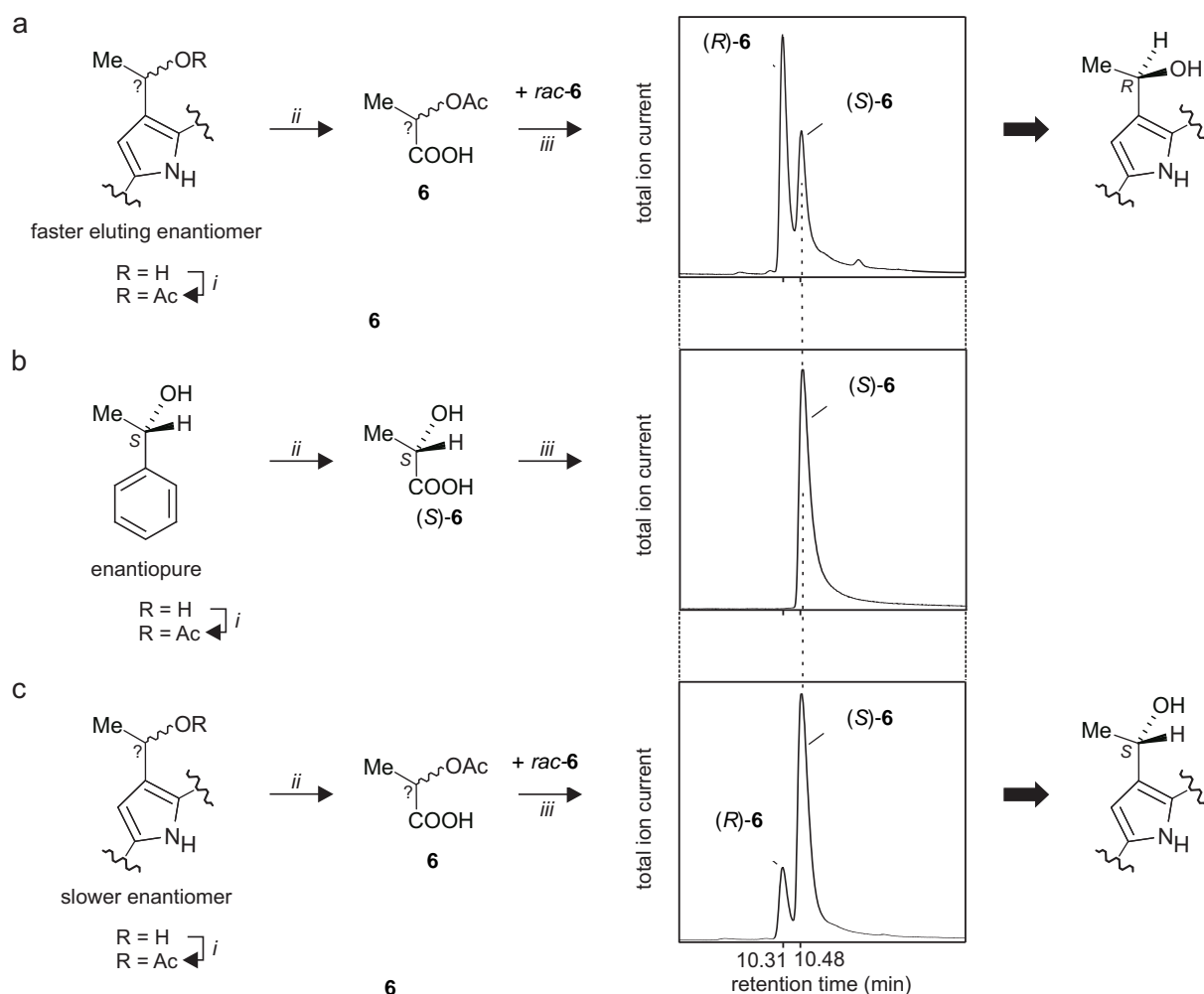


Figure S4. Further evidence for the enantiomeric assignment (see also Figure 5 of the main text) of the degradation product **6** of the faster eluting enantiomer of the *O*-acetylated **4aOAc-H₂** (a) and the more slowly eluting one (c) by co-elution experiments with racemic 2-acetoxypropionic acid in comparison with an enantiopure standard of (S)-**6** (b) prepared from (S)-1-phenylethanol by acetylation. (i) $AcCl$, NEt_3 ; (ii) $RuCl_3$, $NaIO_4$; (iii) GC analysis on a chiral CDX-B phase.

Materials and Methods for the preparation of Mosher's esters 7.

HPLC was performed with a Shimadzu LC-10AD liquid chromatograph equipped with a Shimadzu SPD-M10A diode-array detector. ^1H -NMR spectra in CDCl_3 (99.8 % CEA) were recorded at room temperature with a JEOL AL-A400 Fourier transform NMR spectrometer; tetramethylsilane (TMS) was used as an internal standard. All solvents were used without further purification except the dried pyridine which was used for the preparation of Mosher's esters.

Preparation of Mosher's ester 7a-H₂. To a dry pyridine solution (100 μl) of porphyrin **A2** or **B2**, and separately **B1** or **B2**, commercially available and optically active MTPA-Cl (α -methoxy- α -(trifluoromethyl)phenylacetyl chloride, 10 μl) was added in the dark. After stirring at room temperature ($\sim 26^\circ\text{C}$) for 90 min, *N,N*-dimethyl-1,3-propanediamine (15 μl) was added and stirred for 15 min. The reaction mixture was poured into aqueous 4 % NaHCO_3 , extracted with CH_2Cl_2 , washed with H_2O twice, dried over Na_2SO_4 and filtered. After evaporation, the residue was purified by HPLC to give the corresponding desired ester. The resulting diastereoisomeric MTPA esters were characterized by their ^1H -NMR spectra.

HPLC conditions: column, Cosmosil 5SL-II 4.6 mm ϕ x 150 mm (Nacalai Tesque); eluent, hexane : acetone = 97.5 : 2.5 (v/v) for analysis and hexane : acetone = 96.0 : 4.0 (v/v) for preparative runs; flow rate, 1.0 ml/min for both analysis and preparation. For the chemical shifts of samples **A2** and **B2** see the Main Text Chart 2 and Table S7. For verification, samples **B1** and **B2** were treated in the same manner and the chemical shifts are given in Table S8.

Table S7. ^1H -chemical shifts (δ in ppm) in CDCl_3 (TMS as an internal standard)

Proton	(S)-MTPA-ester		(R)-MTPA-ester		Δ^a	
	B2	A2	B2	A2	B2	A2
15-H	11.357	11.352	11.347	11.358	+0.010	-0.006
5-H	10.293	10.244	10.241	10.295	+0.052	-0.051
18-H	9.600	9.591	9.590	9.600	+0.010	-0.009
13-H	9.486	9.482	9.480	9.487	+0.006	-0.005
7-H	9.330	9.309	9.307	9.330	+0.023	-0.021
2-H	9.166	9.127	9.125	9.167	+0.041	-0.040
8-H	9.122	9.117	9.115	9.122	+0.007	-0.005
12-H	9.112	9.109	9.107	9.112	+0.005	-0.003
3 ¹ -H	7.982	7.938	7.939	7.980	+0.043	-0.042
MTPA-OCH ₃	3.391	3.565	3.566	3.391	-0.175	+0.174
17-CO-CH ₃	3.196	3.193	3.193	3.194	+0.003	-0.001
3 ¹ -CH ₃	2.330	2.424	2.424	2.330	-0.094	+0.094

^a $\Delta\delta = \delta[(S)\text{-MTPA ester}] - \delta[(R)\text{-MTPA ester}]$

Conclusion: A2 has 3¹-(R)-configuration & B2 has 3¹-(S)-configuration

Table S8. ^1H -chemical shifts for MTPA esters stemming from prophyrins **B1** and **B2** (δ in ppm) in CDCl_3 (TMS as an internal standard).

Proton	<i>(S)</i> -MTPA-ester		<i>(R)</i> -MTPA-ester		Δ^*	
	B2	B1	B2	B1	B2	B1
15-H	11.357	11.361	11.347	11.347	+0.010	+0.014
5-H	10.293	10.296	10.241	10.241	+0.052	+0.055
18-H	9.600	9.602	9.590	9.591	+0.010	+0.011
13-H	9.486	9.488	9.480	9.481	+0.006	+0.007
7-H	9.330	9.332	9.307	9.309	+0.023	+0.023
2-H	9.166	9.168	9.125	9.127	+0.041	+0.041
8-H	9.122	9.124	9.115	9.117	+0.007	+0.007
12-H	9.112	9.113	9.107	9.109	+0.005	+0.004
3 ¹ -H	7.982	7.981	7.939	7.940	+0.043	+0.041
MTPA-OCH ₃	3.391	3.391	3.566	3.566	-0.175	-0.175
17-CO-CH ₃	3.196	3.198	3.193	3.193	+0.003	+0.005
3 ¹ -CH ₃	2.330	2.331	2.424	2.425	-0.094	-0.094

* $\Delta = \delta [(S)\text{-MTPA ester}] - \delta [(R)\text{-MTPA ester}]$

Conclusion: both B1&B2 have 3¹-(S)-Configuration

Illustrative Spectra

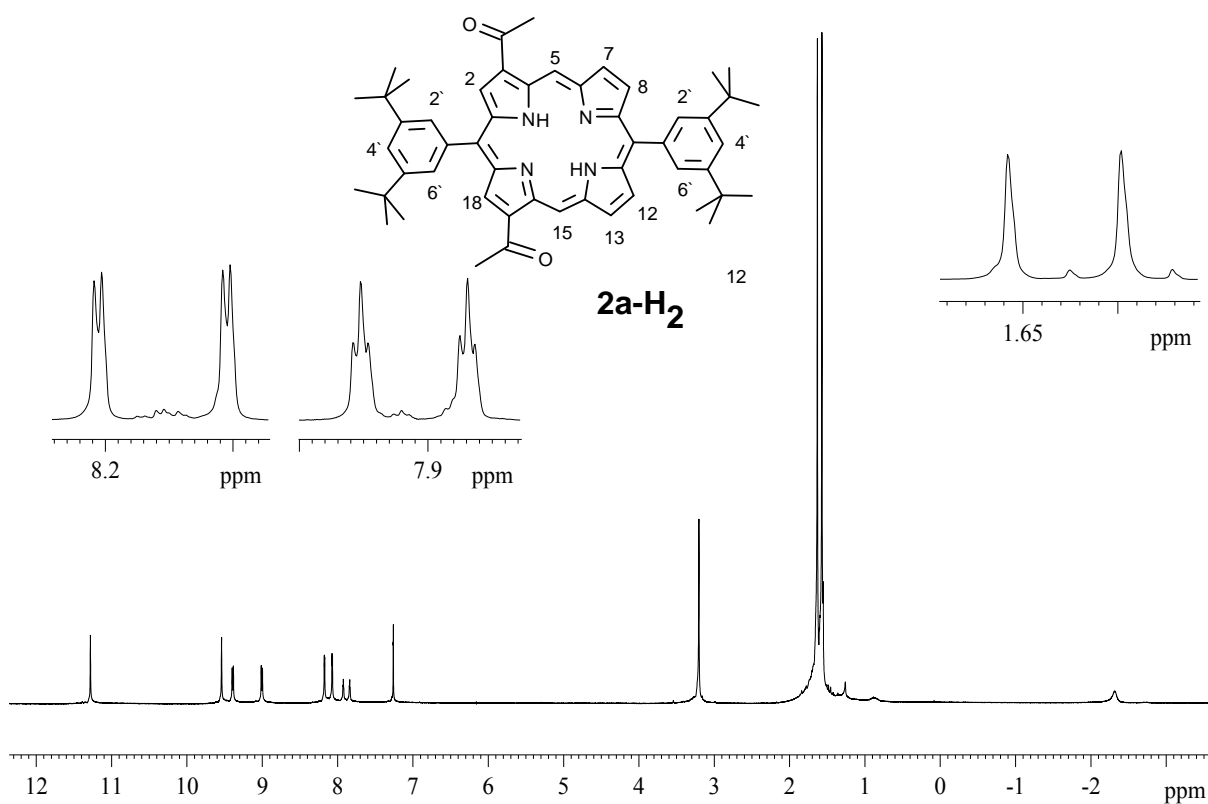


Figure S5. The full ¹H-NMR spectrum (300 MHz in CDCl₃) for 3,17-diacetyl-10,20-bis-(3,5-di-*tert*-butylphenyl)-21,23H-porphyrine (**2a-H₂**) shows two doublets for the 2' & 6' protons while the 4' protons show two triplets. Additionally, the four *t*-butyl groups are split into two different sharp singlets.

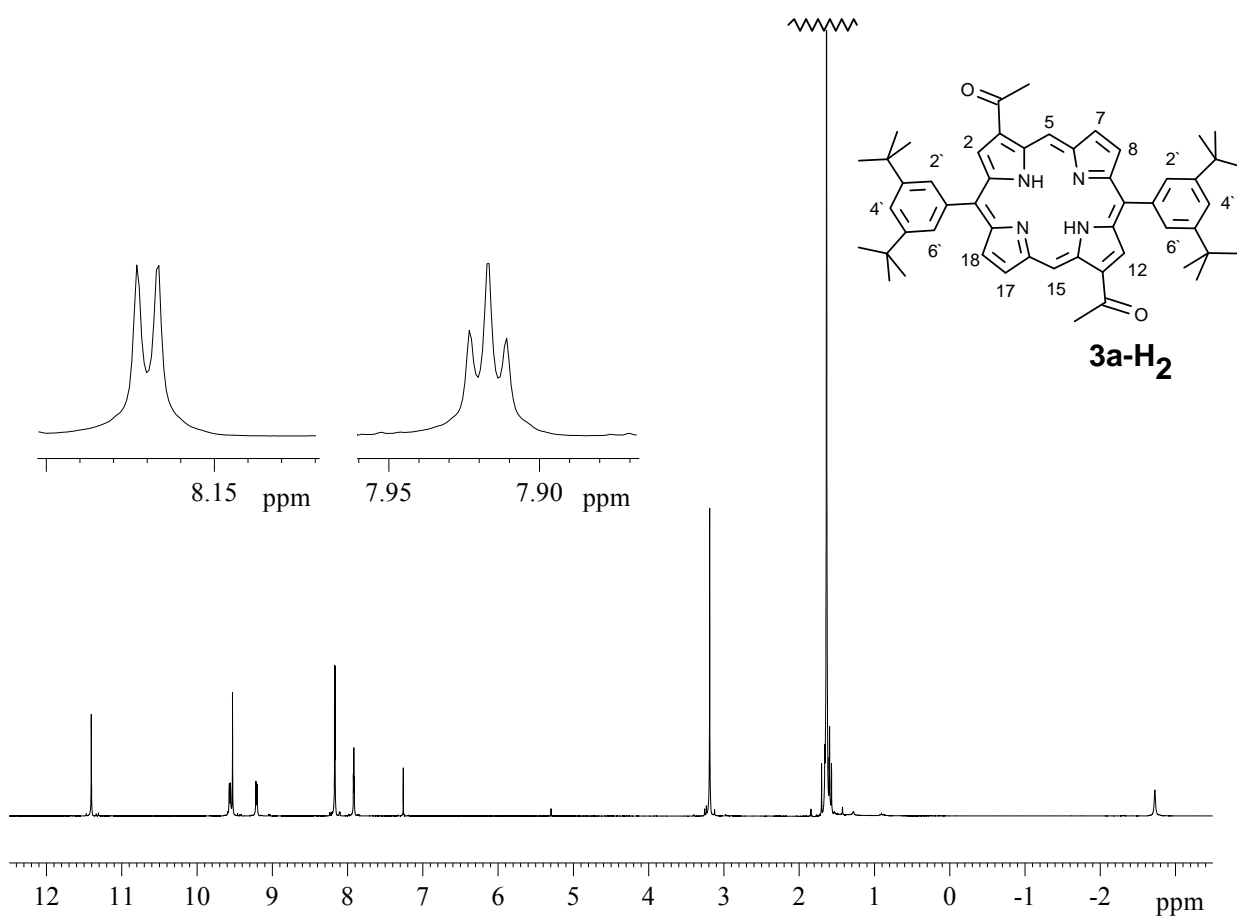


Figure S6. The full ^1H -NMR spectrum (300 MHz in CDCl_3) for 3,13-diacetyl-10,20-bis-(3,5-di-*t*-butylphenyl)-21,23H-porphin (**3a-H₂**) shows one doublet for the 2' and 6' protons while the 4' protons show a single triplet. Also the four *t*-butyl groups show a singlet indicating a symmetric structure.

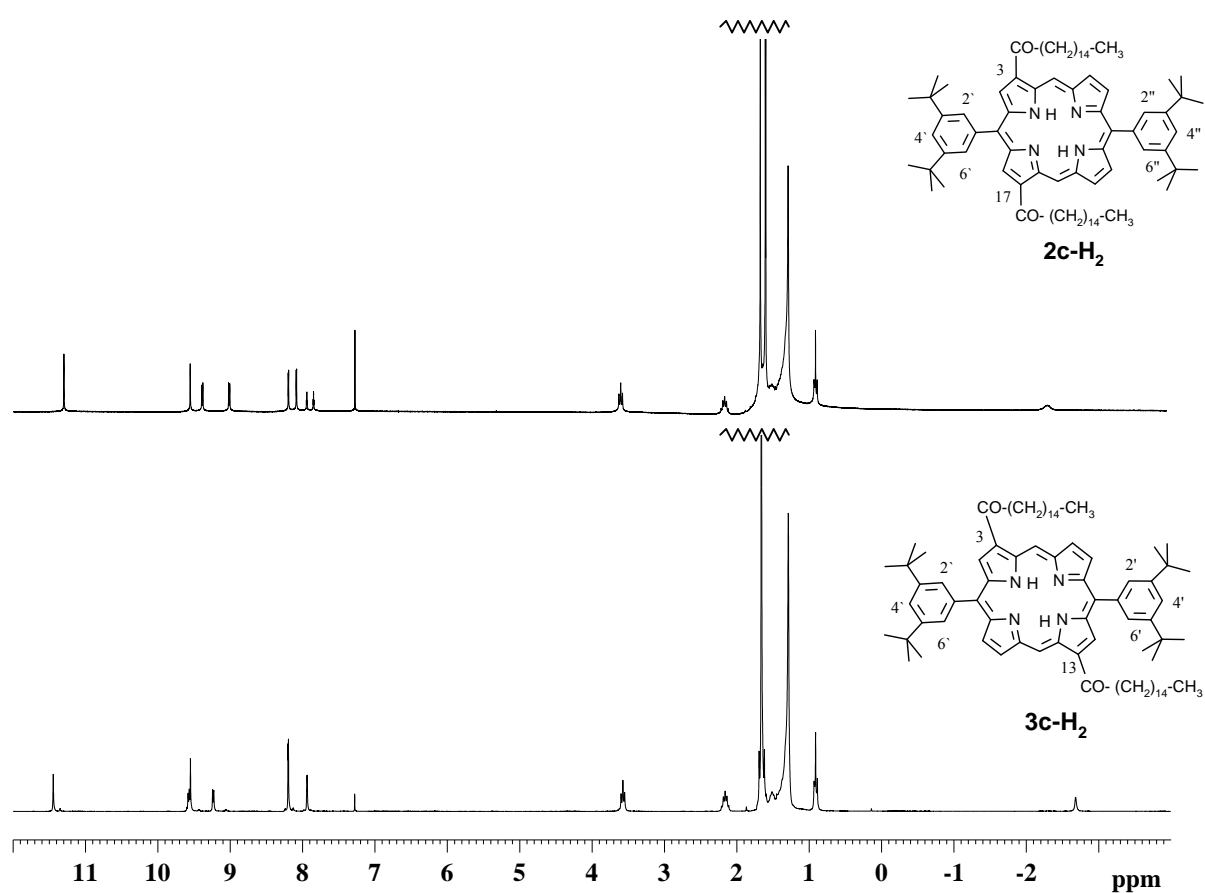


Figure S7. 300 MHz ¹H- NMR spectra of 3,17- (top trace) and 3,13- (bottom trace) dipalmitoyl substituted porphyrin free bases **2c-H₂** and **3c-H₂** in CDCl₃.

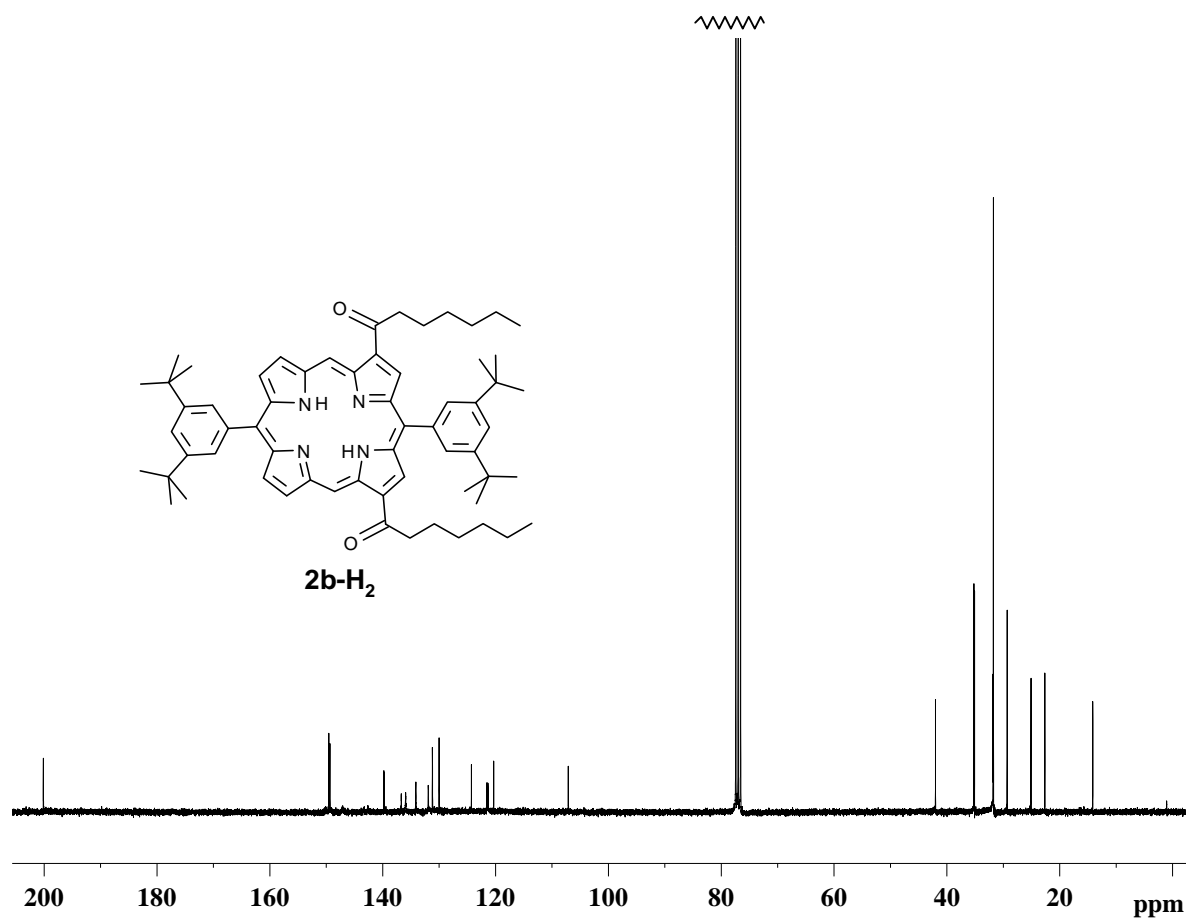


Figure S8. Representative 75 MHz ¹³C- NMR spectra of 3,17-diheptanoyl free base porphyrins **2b-H₂** in CDCl₃. For some assignments see SI-p. 8.

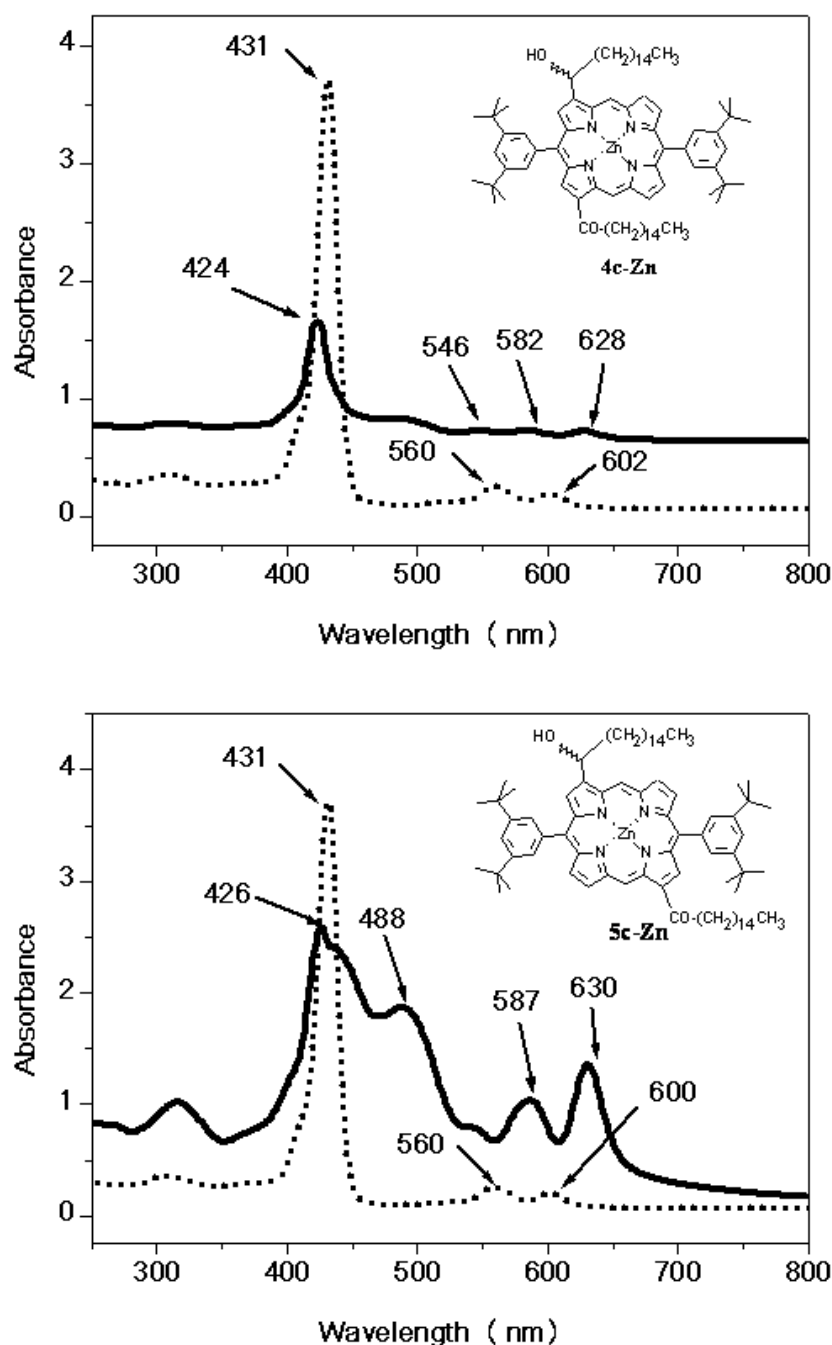


Figure S9. Self-assembled **4c-Zn** (upper part) and **5c-Zn** (lower part) in dry *n*-heptane at room temperature (thick solid traces) at the same concentration of 1.16×10^{-4} mM. The dotted traces are after addition of 0.05 mL of methanol and the same quantity of dry dichloromethane and two-fold dilution with *n*-heptane. Pathlength was 1 mm for all traces. Note that a linear arrangement of the hydroxyalkyl and acyl anchoring positions with a zinc atom (as in **5c-Zn**) is not a prerequisite for self-assembly to occur as demonstrated by **4c-Zn**. The self-assembly is however much more easily visualized by absorption spectra for **5c-Zn** than for **4c-Zn** due to the more extensive overlap of the porphyrin macrocycles.

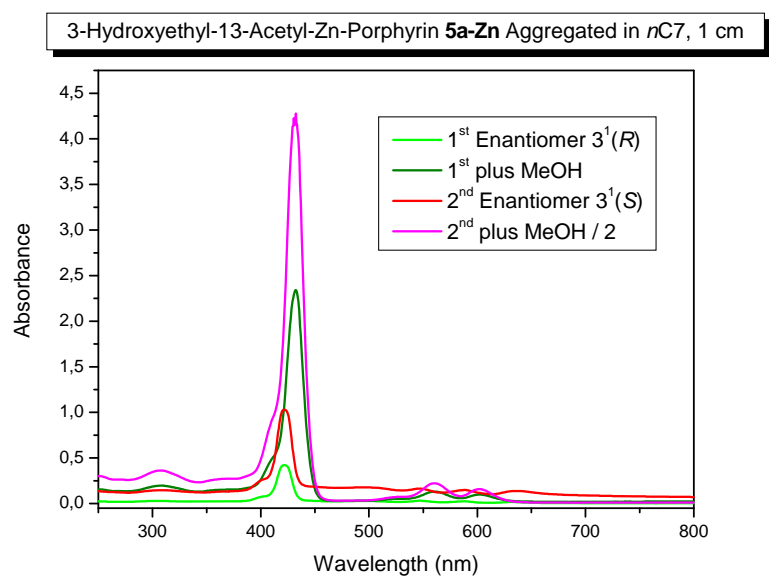


Figure S10. The separated enantiomers of **5a-Zn** self-assembled in *n*-heptane. Note the more intense monomer band in respect with the aggregate bands (green and red traces). Upon disassembly with methanol (olive and magenta traces) the Soret band shifts slightly to the red due to formation of the zinc-methanol monomeric adducts. Pathlength was 1 cm and the magenta trace was recorded after a twofold dilution with *n*-heptane.

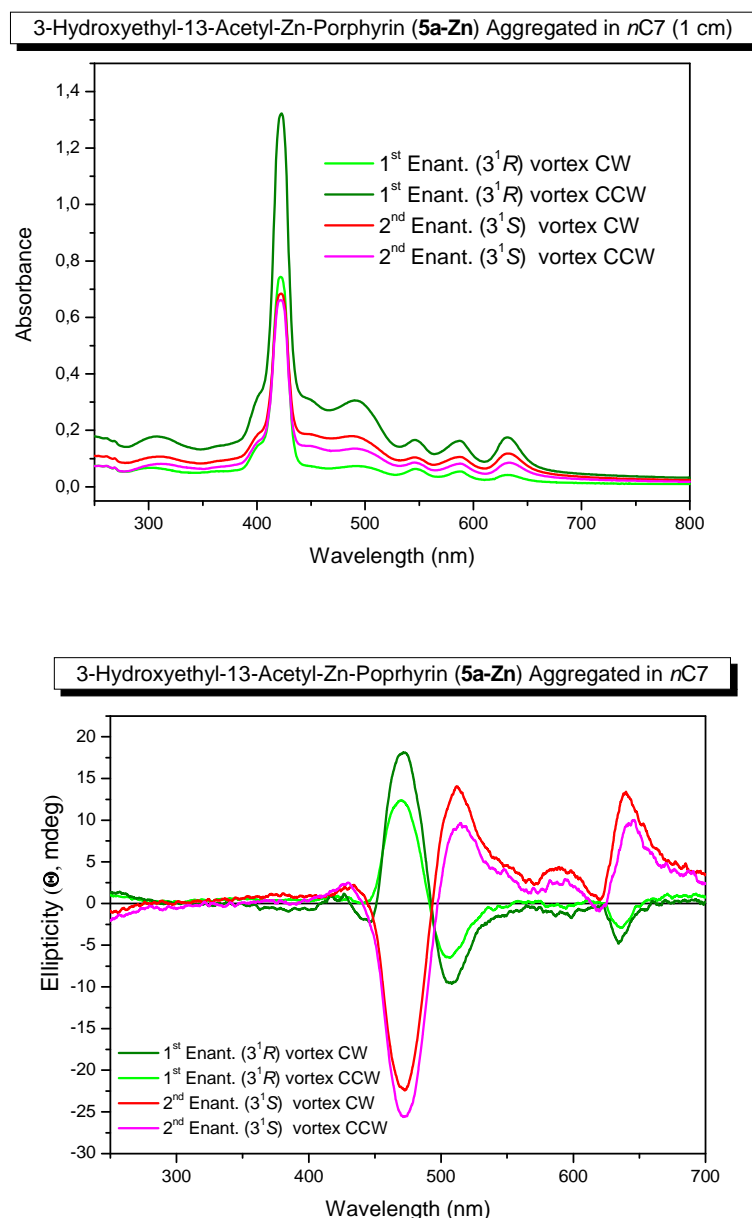


Figure S11. No drastic influences by shearing forces upon vortex stirring. Absorption (top graph) and CD (lower graph) spectra of **5a-Zn** self-assembled in *n*-heptane. Pathlength was 1 cm and the same cuvette was used for all measurements. Note the much more intense monomer Soret bands (422 nm) and lower aggregate bands (at ca. 500 nm and 639 nm) than for racemate samples (Fig. 8, main text). A concentrated stock solution (~50 μL) of **5a-Zn** (~0.6 mg) dissolved in dry dichloromethane (300 μL) was injected with a Hamilton microsyringe into a Hellma UV/CD cuvette with 1 cm pathlength containing 3.0 mL of dry *n*-heptane. Baseline correction was performed within the same cuvette with the same amount of dichloromethane in *n*-heptane. Vortex stirring was effected counterclockwise (CCW) for 3 min with a Vortex Genie-2 (Scientific Industries, Bohemia, NY 11716, USA) by pushing the cuvette bottom to the rotating touchpad. Clockwise (CW) stirring for 3 min was effected by using the same settings of the instrument (#9) which was turned upside down and by pushing the cuvette top (teflon cap) to the touch pad. Poor reproducibility and exact mirror imaging of CD traces is due to the different combination of centrifugal/gravitational shearing forces upon the aggregates when the vortex stirrer is in normal or upturned position. A thorough study of these observations is currently in progress and will be reported in due course.

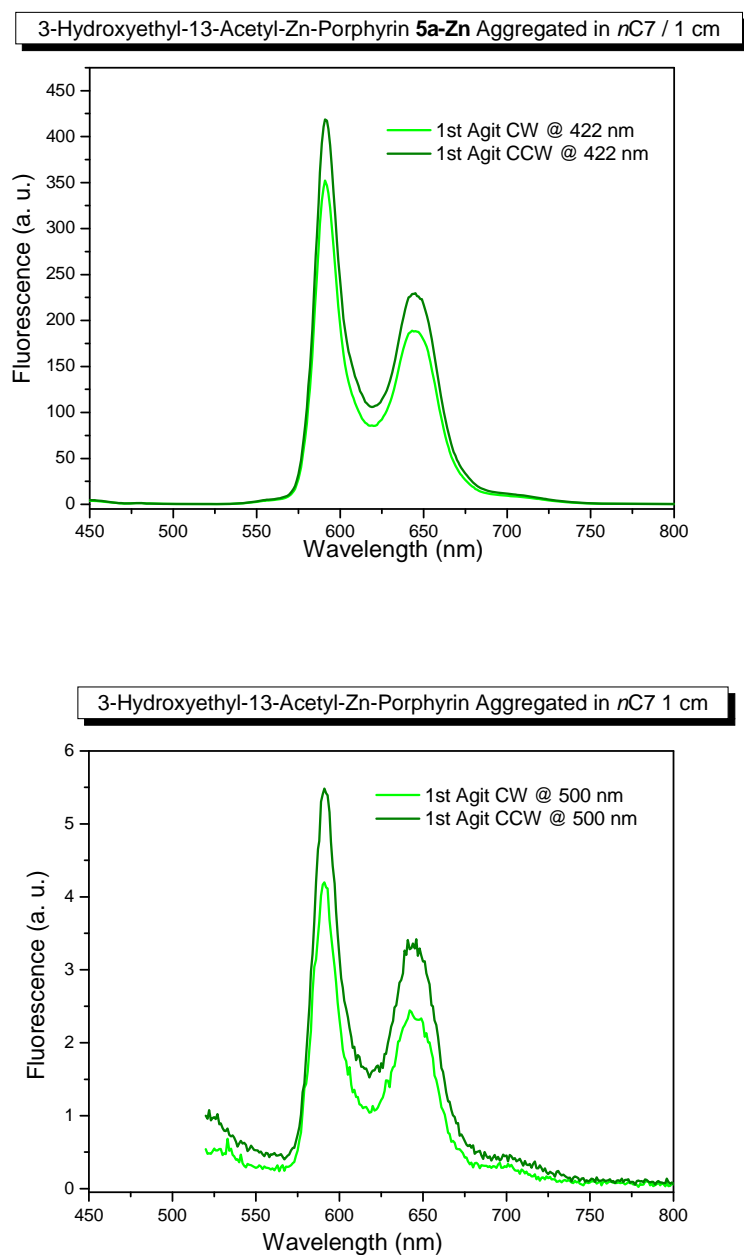


Figure S12. No drastic influences by shearing forces upon vortex stirring on the stationary fluorescence spectra. The 1st eluted enantiomer (3¹*R*) from the ULMO (*S,S*) column in the same cuvette as recorded in Figure S11 was excited at 422 nm in the Soret monomer band (top graph) and in the aggregate band at 500 nm (lower graph). The fluorescence intensity is about 80-fold more reduced in the latter case. Note the very marginal effect, and within the error limits of the measurement, of the vortexing sense upon the fluorescence intensity.

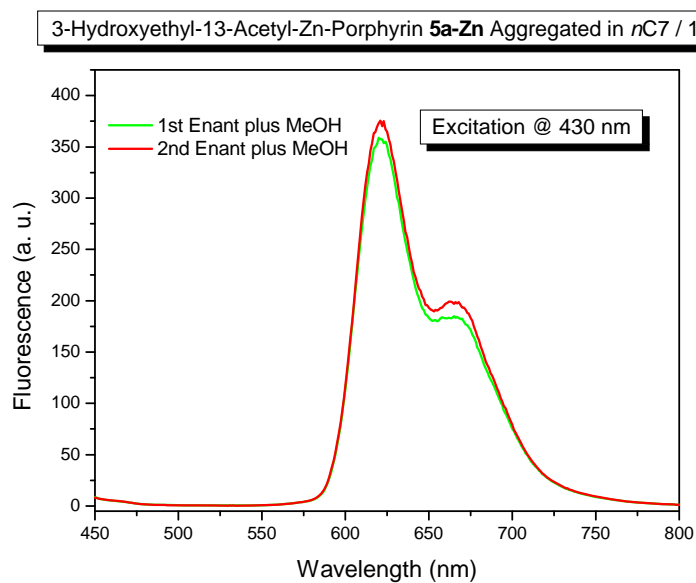


Figure S13. Fluorescence spectra of the Zn-methanol adducts of (3^1R)- and (3^1S)-**5a-Zn**. To the same cuvette in which the spectra in Figs. S11 and S12 were recorded two drops of methanol were added to ensure complete disassembly of the aggregates.

Transmission Electron Microscopy and Scanning Transmission Microscopy Studies

The specimens were examined in an FEI Tecnai F20 TEM/STEM (scanning transmission electron microscope) operated at 200 kV with an extraction voltage for the field emission gun of 3.9 eV. Additional equipment included a Gatan Imaging Filter (GIF) and an EDAX X-ray spectrometer consisting of an energy dispersive X-ray SiLi detector with a super-ultra-thin window (S-UTW). The point resolution of this microscope was about 0.235 nm at Scherzer focus and an information limit of ca. 0.14 nm could be achieved. For performing EDX analyses on nanometre-sized probes (1 nm² spot size) an extraction voltage of 4.5 keV was used in the STEM mode (Scanning TEM). An analytical double tilt holder (Philips) was used for the samples which were prepared by drop casting a suspension of the self-assemblies from dry dichloromethane onto carbon coated copper grids. High-resolution micrographs were taken with a 1K×1K CCD camera and analyzed with the software package from Digital Micrographs Version 3.5.2, Gatan Co. for performing fast Fourier Transformations (FFT).

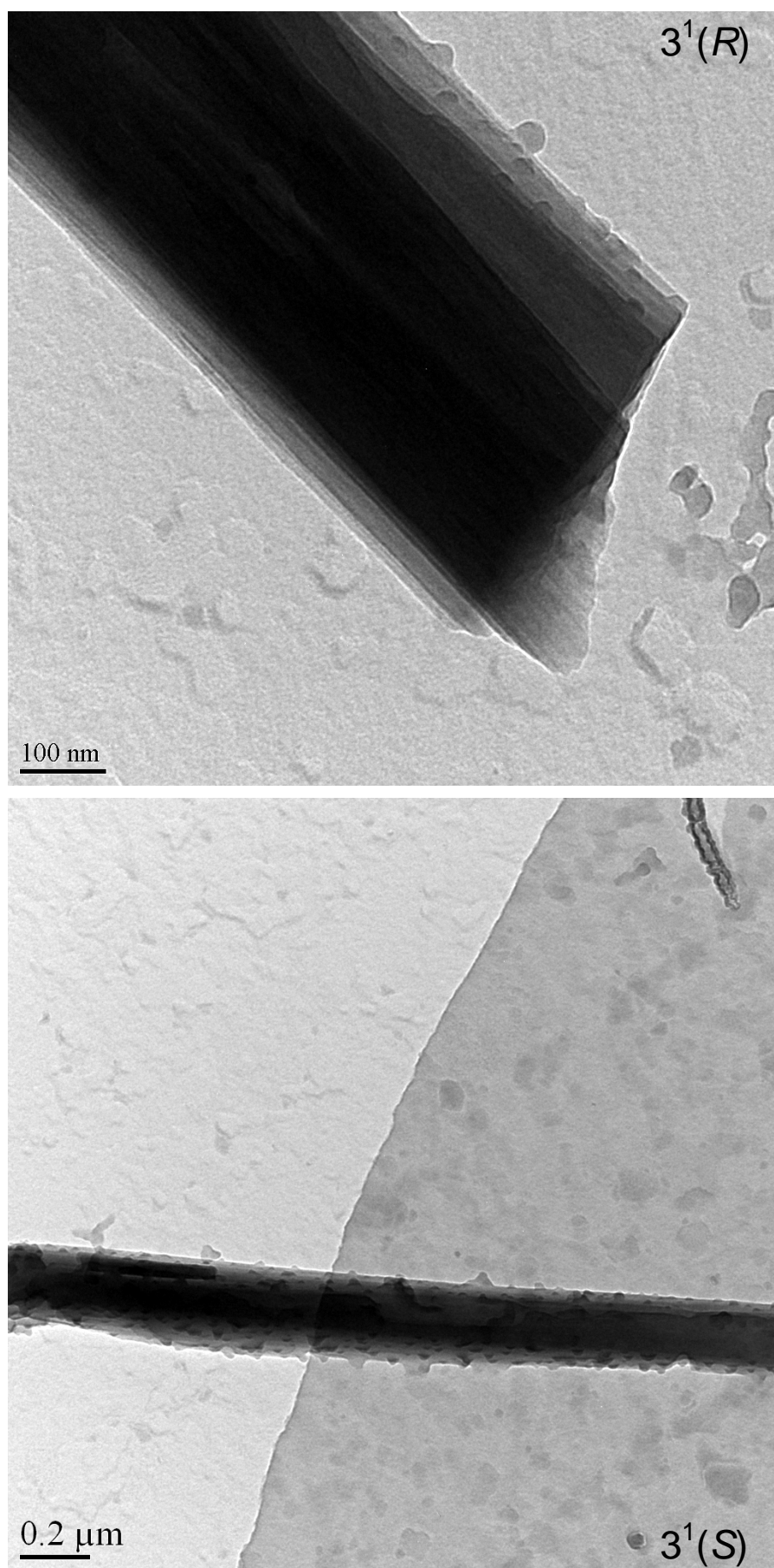


Figure S14. TEM bright-field micrograph showing individual nanorods of **4a-Zn**.

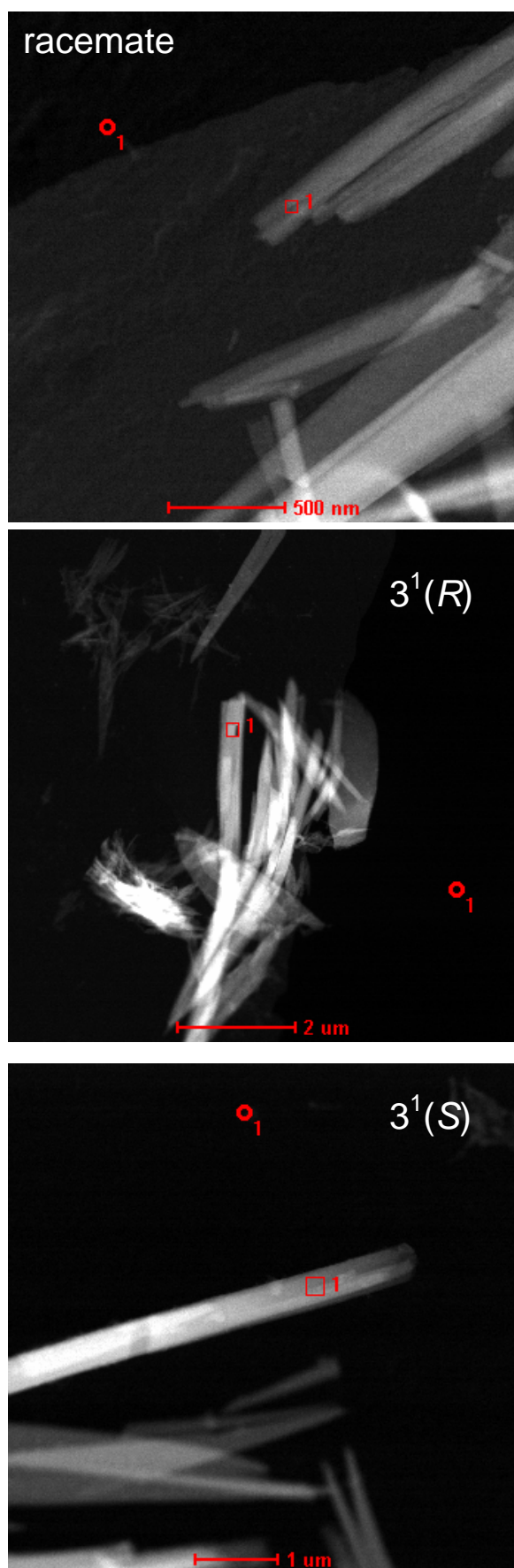


Figure S15

STEM (HAADF) micrograph: overview. The red square indicates the area for the EDX-analysis (Figure S15). The red circle area was used for background subtraction.

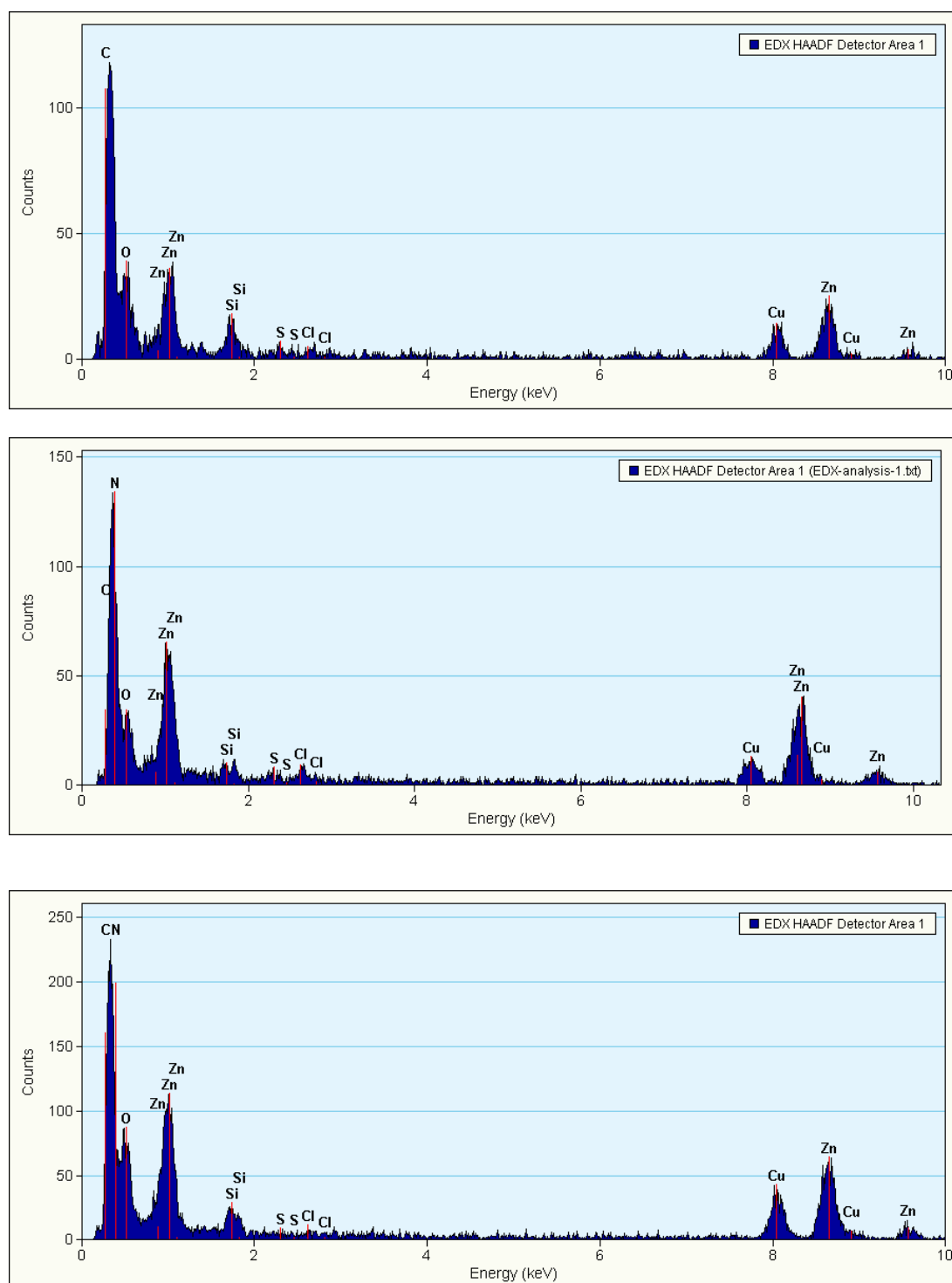


Figure S16. Corresponding EDX (energy-dispersive x-ray) spectra revealing the presence of Zn in the above shown nano-rods (Figure S14). The Cu signal is related to the copper grid used for the TEM investigation.

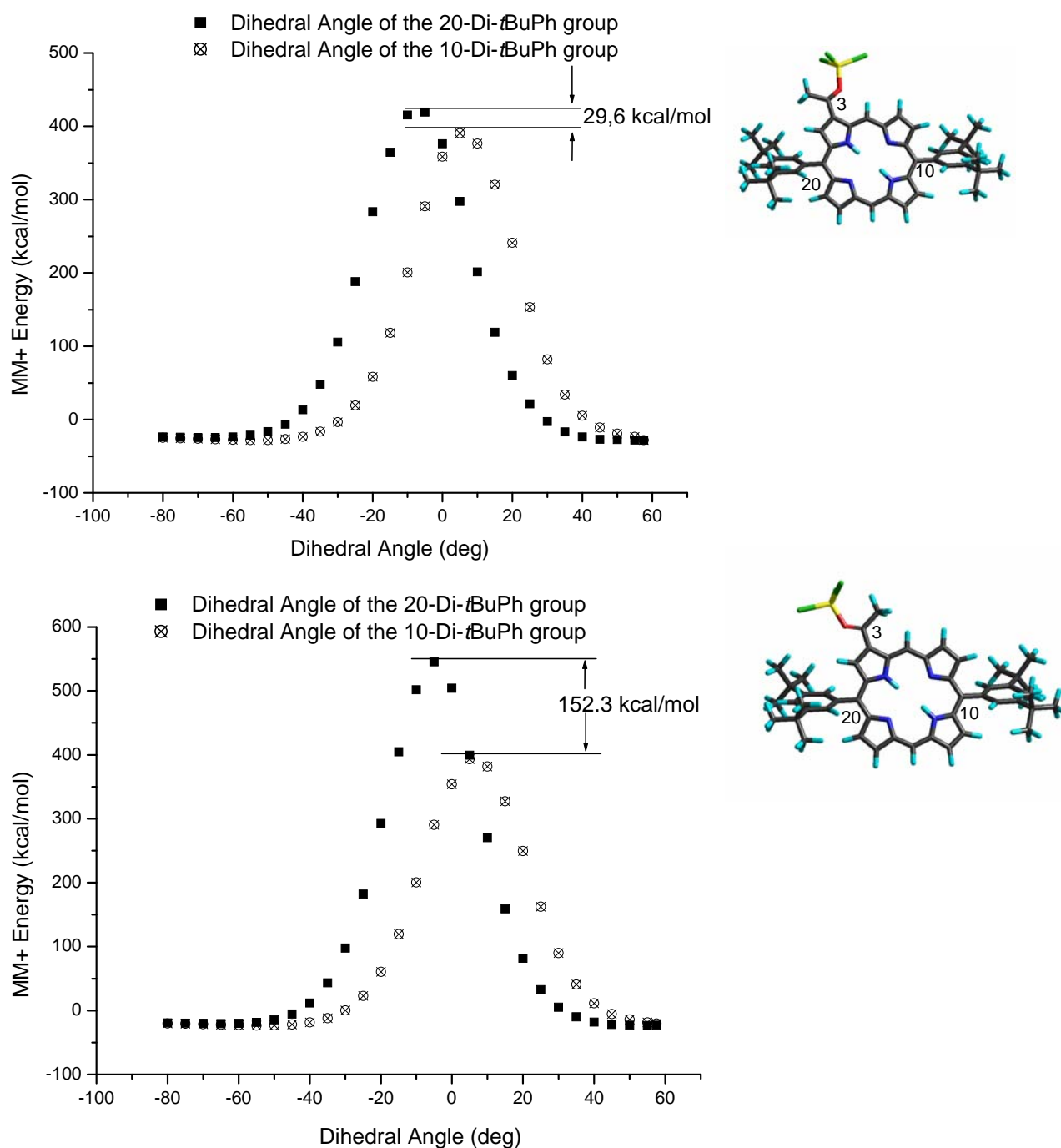


Figure S17. Conformational analyses by molecular mechanics (MM+ force field implemented in the HyperChem Program Package²³) of the 3-acetyl-10,20-bis-di-*tert*-butylphenyl porphyrin complexed by aluminium chloride. Instead of the copper complex the porphyrin free base was considered but this should not influence the rotation barriers of the 10- and 20- di-*tert*-butylphenyl groups. In the upper figure, the 3-acetyl group is pointing with the carbonyl group towards the 5-meso proton and this is the most stable conformation. In the lower figure, the acetyl group points towards the 20-di-*tert*-butylphenyl group, and this conformation is by 4.8 kcal/mol higher in energy. Upon rotation of the 20-di-*tert*-butylphenyl group, in both cases, a higher barrier is encountered as upon rotation of the unhindered 10-di-*tert*-butylphenyl group. The ca. 30 kcal/mol barrier indicates that the 20-di-*tert*-butylphenyl rotates much less frequently than the 10-di-*tert*-butylphenyl, explaining why the second acylation occurs in the 17 position.