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Synthesis of Porphyrin–Fullerene Dyads and Their Spectroscopic Properties

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Porphyrin–fullerene dyads with different linkages between the two subunits were synthesized for mimicking photosynthesis. NMR spectra and quantum mechanical calculations show special structural features that should influence light-induced electron transfer of the photosynthetic process. Starting point of the synthetic routes is a deuterioporphyrin dimethyl ester prepared from the readily accessible blood pigment heme.

Introduction

The most important biological process on the earth is photosynthesis producing chemical energy and organic matter from carbon dioxide and water by sun light as the source of energy.[1] The primary step of photosynthesis consists in light-induced electron transfer from a chlorin donor to a quinone acceptor arranged in the photosynthetic reaction centre.[2] For investigating and mimicking this process numerous artificial photosynthetic systems were designed from porphyrin donor and quinone acceptor subunits.[3] Since its discovery, fullerene C_{60} in particular became attractive as an acceptor subunit for dyads or more complex systems in which light-induced electron transfer proceeds from porphyrinoid donors to fullerenes.[4] The advantage of fullerene over quinone acceptors consists in their abilities to take up six electrons with low reorganization energy, λ, for the electron-transfer process.

In the work presented here our aim was to achieve facile access to porphyrin–fullerene dyads from readily available deuterioporphyrin dimethyl ester as a starting material.[5] For attaching fullerene C_{60} subunits to the porphyrin moieties, cycloaddition reactions were applied, thus giving porphyrin fullerene dyads of different constitutional and spatial arrangements.

Results and Discussion

Our first synthetic approach starts from deuterioporphyrin dimethyl ester (**1**), which is easily available from the red blood pigment heme.[5,6] Complexation of the porphyrin core with zinc(II) acetylacetonate and hydrolysis of the propionic acid ester functionalities yielded zinc(II) deuterioporphyrin **2**. The central zinc ion protects the inner core of the macrotetracycle and mimics the magnesium ion of natural chlorophyll photosynthetic pigments. The formation of the 17-membered bis(lactone) of **4** could be achieved very easily and with quite good yield relative to other macrolactonizations by treating the activated carboxylic acid **2** with sulfoleno bis(alcohol) **3**.[7] The facile formation of the macrocyclic lactone ring could be expected owing to the conformational restrictions of the porphyrin and the bis(alcohol). Porphyrin bis(lactone) **4** underwent a Diels–Alder reaction with fullerene C_{60} to yield porphyrin–fullerene dyad **5a**. The yield of 39% for the Diels–Alder reaction, which is initiated by sulfur extrusion from the sulfoleno moiety of **4**, is in the same range as that of [4+2] cycloadditions with fullerenes as diene components reported to date.[8,9] Dyad **5a** was separated from unreacted C_{60} by chromatography. Upon treatment with hydrochloric acid followed by column chromatography, zinc dyad **5a** was transformed into metal-free dyad **5b**. The structures of both dyads **5a**, **5b** were established by ^{1}H NMR spectroscopic data and mass spectrometry, which showed the complete set of proton signals and molecular masses of 1370 and 1308 Da, respectively. The UV/Vis absorption spectra of dyads **5a**, **5b** agree with the superposition of the single spectra of fullerene C_{60} and the corresponding porphyrins. The missing spectral perturbation indicates that there is no interaction and a great distance between the porphyrin and fullerene moieties. The greater separation distances between the porphyrin and the fullerene part differ significantly from previously reported porphyrin fullerene dyads with lactone spacers[10] and were confirmed by AM1 calculations.

The luminescence spectrum (Figure 1) of porphyrin–fullerene dyad **5a** and that of porphyrin **4** were compared after

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excitation at the wavelength of the Soret band (405 and 403 nm, respectively). Whereas **4** shows a strong luminescence, it was quenched significantly for **5a** by the fullerene acceptor. Quenching was independent of the concentration of dyad **5a**, which indicates an intramolecular transfer of energy and/or an electron from the porphyrin donor to the fullerene acceptor (Scheme 1).

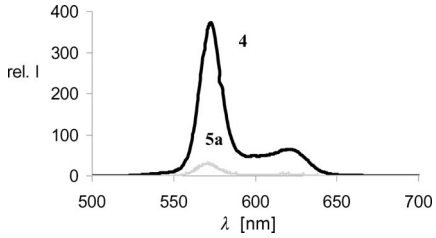
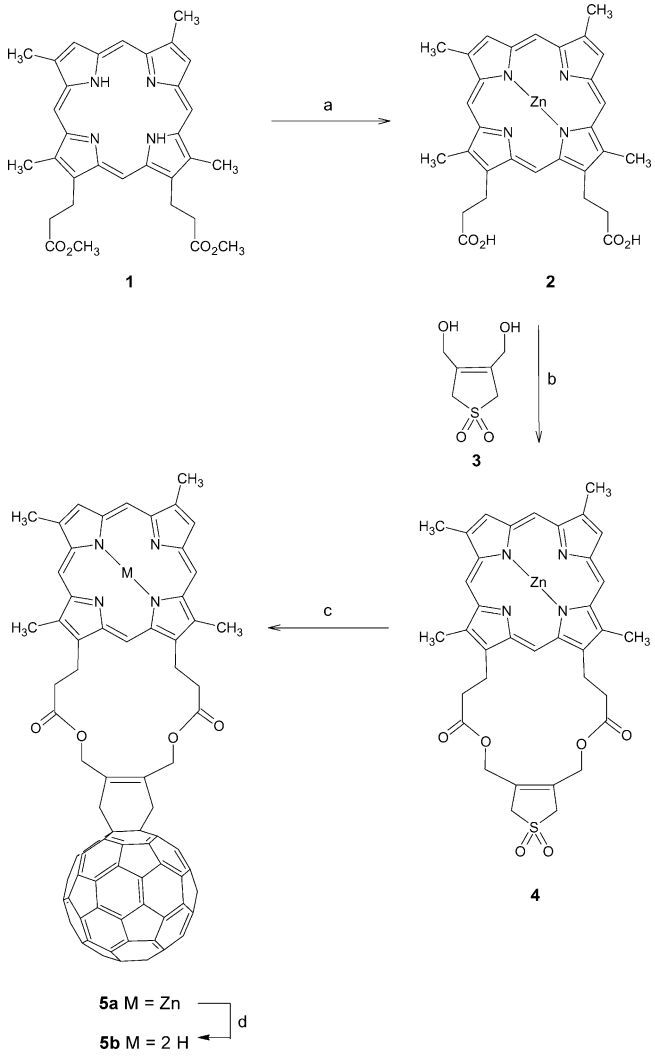


Figure 1. Luminescence spectra of **4** (solid line) and **5a** (dotted line) in CH_2Cl_2 after excitation at the individual Soret bands.



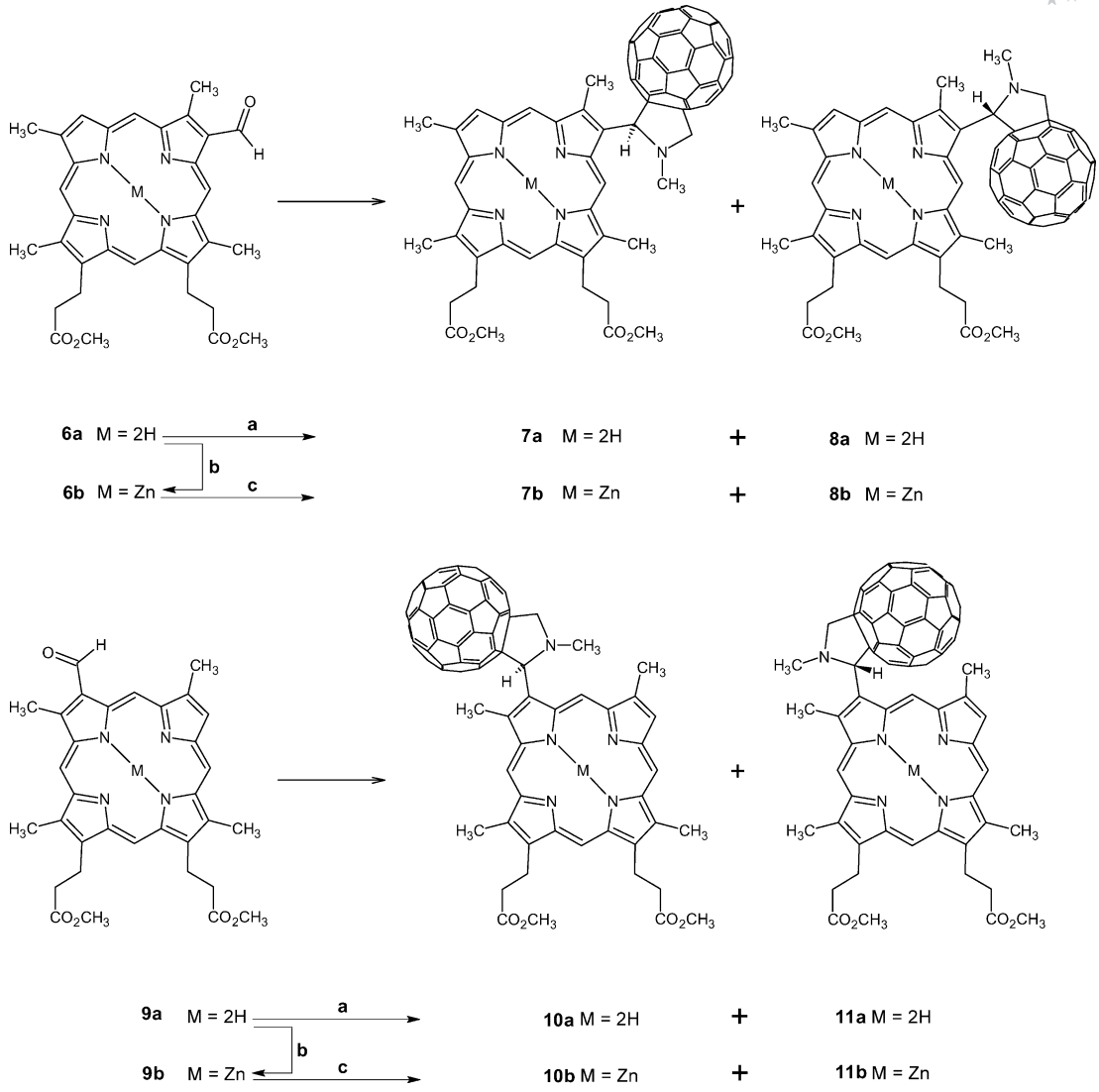
Scheme 1. Synthesis of a porphyrin–fullerene dyad. Reagents and conditions: (a) i) $Zn(acac)_2$, Ar, THF, reflux (93.6%); ii) KOH, THF, reflux (90.9%); (b) *n*-propyl phosphonic acid anhydride in ethyl acetate, DMPA, NEt_3, sulfoleno bis(alcohol) **3**, Ar, CH_2Cl_2, room temperature (39%); (c) fullerene C_{60}, trichlorobenzene, 200 °C (41%); (d) HCl, CH_2Cl_2 (84%).

The second route to porphyrin fullerene dyads **7**, **8**, **10** and **11** (Scheme 2) makes use of azomethine ylide [3+2] cycloaddition reactions of the porphyrin moieties to fullerene C_{60}.[11] As a starting material for the coupling of fullerene C_{60} with deuterioporphyrin dimethyl ester (**1**) and its zinc complex we used the 3- or 8-formyl deuterioporphyrin dimethyl esters **6a**, **6b**, **9a** and **9b**, which could be readily obtained from **1** by direct formylation and chromatographic separation of the constitutional isomers **6a** and **9a** and subsequent complexation with zinc(II).[6] The coupling reaction was performed by heating formyl porphyrins **6a**,**b** and **9a**,**b** with C_{60} and *N*-methylglycine in refluxing toluene. Together with the formyl functionalities of the porphyrins, and after decarboxylation, *N*-methylglycine forms azomethine ylides, which undergo cycloaddition reactions with the fullerene. All dyads were formed in excellent yields ranging from 61 to 72%. The mass spectra of all dyads confirmed the molecular mass of 1313 Da for metal free dyads **7a**, **8a**, **10a** and **11a** and 1375 Da (^{64}Zn) for zinc-containing dyads **7b**, **8b**, **10b** and **11b** with the characteristic isotope pattern for zinc.

HPL Chromatography, Spectroscopic Analysis and Configuration of Porphyrin–Fullerene Dyads

The ^1H NMR spectra of the dyads in $CDCl_3$–deuteriopyridine revealed that each of the [3+2] cycloadducts form two pairs of diastereomeric enantiomers as a result of the chiral centre of the pyrrolidine ring and because of a chiral axis (atropisomerism) arising from hindered rotation between the porphyrin moiety and the fullerene ball. The occurrence of arene fullerene atropisomers[12] and of atropisomeric chlorophyll-based fullerene dyads[13] similar to the dyads described here is a stereochemical feature of these systems. In case of the enantiomerically pure chlorophyll starting compound, which was attached to the fullerene, four enantiomerically pure diastereomers were formed, whereas with the achiral formyl porphyrins each diastereomer **7a**, **8a**, **7b**, **8b**, **10a**, **11a**, **10b** and **11b** is racemic. A complete assignment of the ^1H NMR spectroscopic signals of all the pairs of diastereomers **7a/8a**, **7b/8b**, **10a/11a** and **10b/11b** was obtained by HH ROESY (rotating frame Overhauser enhancement spectroscopy) experiments. The results are summarized in Table S1 (see Supporting Information).

Analysis of the ^1H NMR spectra of the products from each reaction showed very strong differences in the chemical shifts for the pairs of formed diastereomers. For instance, the 5-C*H* resonance of diastereomer **11b** is markedly shifted downfield to δ = 12.12 ppm. The significant downfield shift originates from the deshielding effect of the C_{60} moiety and indicates (Scheme 3) that in diastereomer **11b** the fullerene ball is located close to the 5-methine region of the porphyrin macrotetracycle. A significant deshielding effect of the fullerene subunit on the 2-CH_3 signal (δ =

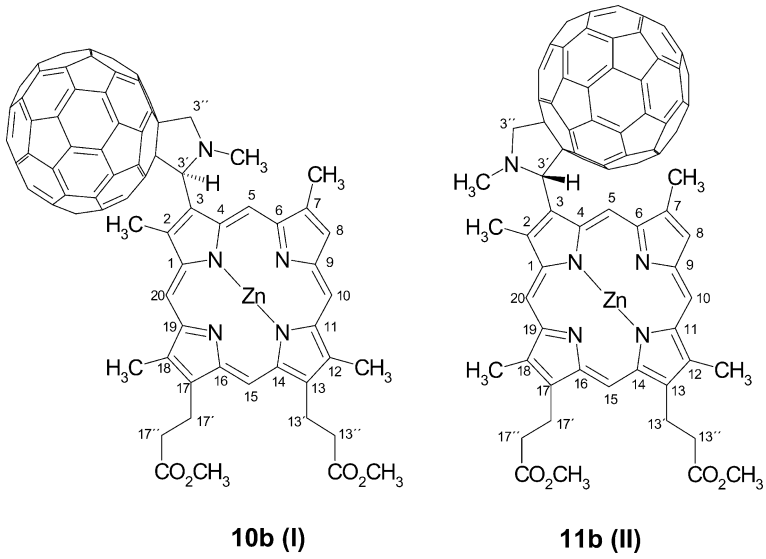


Scheme 2. Synthesis of porphyrin–fullerene dyads. Reagents and conditions: (a) sarcosine, fullerene C_{60}, Ar, toluene, reflux (**7a**, **8a**: 72%; **10a**, **11a**: 61%); (b) zinc(II) acetylacetonate, Ar, THF, reflux (**6c**, 91.1%; **9c**, 92.3%); (c) sarcosine, fullerene C_{60}, Ar, toluene, reflux (**7b**, **8b** 62%; **10b**, **11b**: 62%).

4.31 ppm) is also observed for diastereomer **10b**, whereas diastereomer **11b** shows with the 2-CH_3 chemical shift (δ = 3.78 ppm) a very similar value to that of Zn–deuteroporphyrin dimethyl ester (δ = 3.68 ppm). Weaker but nevertheless significant differences in the chemical shifts occur for the NCH_3- and 3′-*H*-resonances owing to the deshielding influence of the porphyrin macrocycle on these protons. In diastereomer **10b**, in which the NCH_3 group and the 3′-H proton come close to the aromatic porphyrin ring, the NCH_3 signal (δ = 3.29 ppm) and the 3′-H signal (δ = 7.16 ppm) are shifted downfield relative to the corresponding signals (NCH_3, δ = 3.16 ppm; 3′-H, δ = 6.58 ppm) of diastereomer **11b**. These observations establish clearly that the fullerene ball is very close to the β positions of the pyrrole ring A in diastereomer **10b** and close to the methine region for **11b**. Identical effects as discussed for the **10b/11b** pair were also found for diastereomers **7a/8a**, **10a/11a** and **7b/8b**, which thus undoubtedly reveals the stereostructures of these dyads.

The HH ROESY experiments furnished an independent confirmation of these findings by observing Overhauser effects between the 5-methine hydrogen atoms and the *N*-methyl groups in **10a** and **10b**, as well as between the 10-methine hydrogen atoms and the *N*-methyl groups of **7a** and **7b**. For diastereomers **8a** and **8b**, corresponding Overhauser effects between *N*-methyl and methyl groups at C-7 were found. The intensity of the signals in the ^{1}H NMR spectra gave information regarding the ratio of the diastereomers in each of the pairs, namely, **7a/8a**, 1:1.7; **7b/8b**, 1:1.4; **10a/11a**, 1:2.1 and **10b/11b**, 1:1.36 (Figure 2).

In the case of dyads **7a**, **8a** and **10a**, **11a**, HPLC was performed, which confirmed the NMR spectroscopic results. By chromatography on the achiral stationary phase Nucleosil 50–10, separation of the diastereomeric mixtures could not be observed. The chromatograms show only single peaks for the diastereomeric mixtures of **7a**, **8a** and **10a**, **11a** (Figure 3a). However, separations were possible by chromatography on the homochiral stationary phase Nu-



Scheme 3. Structures of diastereomeric porphyrin–fullerene dyads **10b** (I) and **11b** (II).

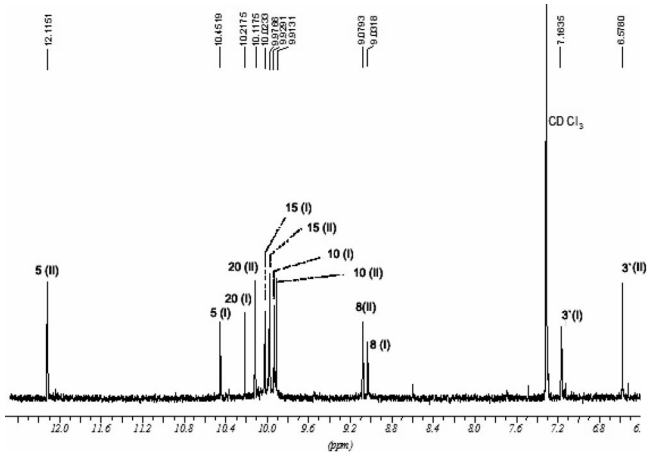


Figure 2. Part of the ^{1}H NMR spectrum of diastereomeric porphyrin–fullerene dyads **10b** (I) and **11b** (II).

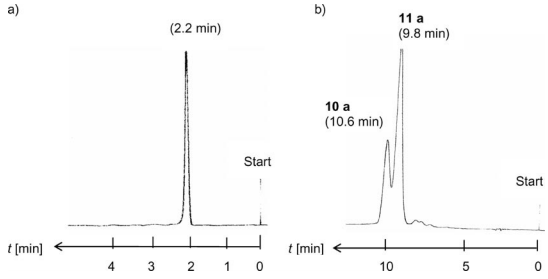


Figure 3. (a) HPLC of a diastereomeric mixture of **10a**/**11a**. HPLC conditions: Nucleosil 50–10; CH_2Cl_2/MeOH/*n*-heptane, 19:1:1; 1 mL/min; UV detection (405 nm). (b) HPLC of a diastereomeric mixture of **10a**/**11a**. HPLC conditions: Nucleosil-Chiral-2; *n*-heptane/1,4 dioxane, 70:30; 1 mL/min; UV detection (405 nm).

cleosil-Chiral-2 with *n*-heptane/1.4 dioxane (70:30) as eluent. For instance, the chromatogram (Figure 3b) of **10a**, **11a** shows two peaks in a 1:1.95 ratio for the diastereomers, which is in agreement with the ratio of isomers determined by ^{1}H NMR spectroscopy. Attempts to perform possible further separation of each diastereomer on the homochiral phase into their enantiomers by variation of the eluent system could not be achieved.

Theoretical Calculations

The preferred conformations of porphyrin–fullerene dyad **5a** were calculated by semiempirical PM3 method. The completely stretched conformation of **5a**/st (Figure 4a)

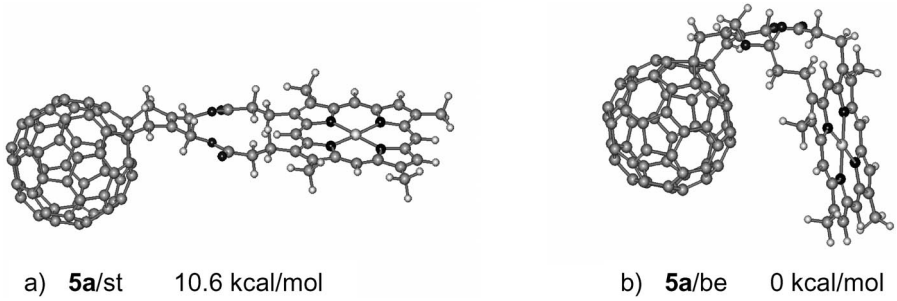


Figure 4. Calculated conformations of porphyrin–fullerene dyad **5a** (ball-and-stick representation).

is 10.6 kcal/mol higher in energy than the energetically favoured conformation of **5a**/be (Figure 4b). This conformation shows a bent structure with a distance of ca. 10 Å between the centre of the fullerene part and the central metal ion of the porphyrin moiety and ca. 6.3 Å between the fullerene periphery and the metal ion. Though attractive interactions between the two subunits for several porphyrin–fullerene dyads were observed,[14] the long distance between the fullerene part and the porphyrin subunit of dyad **5a** does not indicate any such attractive force. The preferred bent shape of **5a** is a consequence of the geometry of the spacer back bone, which shows a zigzag conformation with a minimum of energetically unfavoured *gauche* interactions.

The relative stabilities of the formed atropisomeric porphyrin–fullerene dyads **7**, **8** and **10**, **11** as well as the activation barrier for interconverting both isomers from one into the other was calculated by an AM1 calculation. Therefore, the substitution patterns of the dyads were simplified for the calculations by detaching all the substituents at the porphyrin chromophore with exception of the methyl groups around the fullerene porphyrin part of the whole molecule (Figure 5). Structure **B** with the fullerene moiety orientated to the methine region of the porphyrin was calculated to be 32 kcal/mol higher in energy than that of dyad **A**, in which the fullerene is located at the β-pyrrolic part of the macrotetracycle. The activation barrier for the interconversion of the isomers was calculated as $\Delta E^{\#}$ = 100 kcal/mol and shows clearly that configurationally very stable atropisomers exist.

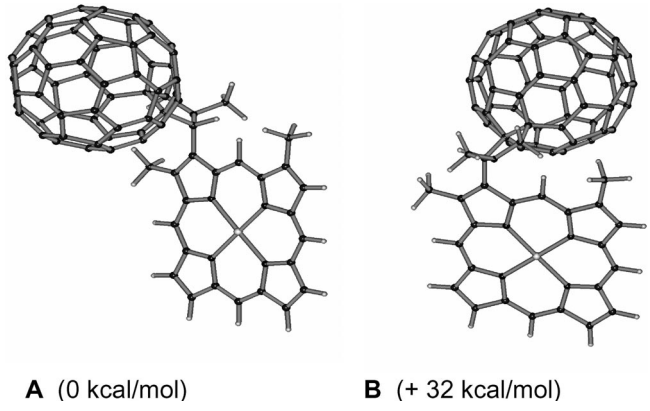


Figure 5. Calculated conformations/configurations of porphyrin–fullerene dyad atropisomers **A** and **B** (ball-and-stick representation).

Experimental Section

General Remarks: Starting materials were either prepared according to literature procedures or purchased from Fluka, Merck, Acros Organics or Sigma Aldrich and used without further purification. All solvents were purified and dried by standard methods. All reactions were carried out under an atmosphere of argon. ^{1}H NMR spectra were recorded with a Bruker DPX-200 AVANCE spectrometer; all chemical shifts were referenced to TMS lock signal. MS were obtained with a Finnigan MAT 8200 spectrometer [EI (70 eV) and ESI]. IR spectra were recorded with a Perkin–Elmer Paragon 500 FTIR spectrometer. UV/Vis spectra were obtained with a Varian Cary 50 spectrophotometer. HPLC were run with a Knauer 64 pump, Knauer spectral photometer, Nucleosil 50–10 (Knauer), Nucleosil-Chiral-2 (Machery-Nagel). Column chromatographic separations were performed on silica gel (32–63 μm, 60 Å, ICN) or aluminium oxide (activity grade II-III, neutral, ICN). Melting points are not corrected.

Porphyrin 2: Deuterioporphyrin dimethyl ester (**1**; 250 mg, 0.47 mmol) and zinc(II) acetylacetonate (610 mg, 2.35 mmol) were dissolved in THF (8 mL) and heated at reflux under an atmosphere of argon for 24 h. The dark-red solution was mixed with CH_2Cl_2 (20 mL) and washed with brine (3×). The solution was filtered over aluminium oxide (act. II–III, neutral). Evaporation of the solvent yielded zinc(II) porphyrin dimethyl ester. Yield: 263.0 mg (0.44 mmol, 93.6%). The porphyrin dimethyl ester (200 mg, 0.33 mmol) was dissolved in THF (30 mL). KOH (5 N, 30 mL) was added, and the mixture was heated at reflux under an atmosphere of argon for 24 h. After cooling the mixture and removal of THF, buffer solution (pH = 4; 30 mL) was added, and the pH was adjusted at 2 to 3 with HCl (5 N). The dark-red solution was cooled in an ice bath and filtered through a blue ribbon filter. Product **2** was yielded as a red solid. Yield: 170.0 mg (0.30 mmol, 90.9%). M.p. 270–273 °C. R_f = 0.18 (silica gel; CH_2Cl_2/MeOH, 10:1). ^{1}H NMR (360 MHz, [D_6]DMSO, 25 °C, TMS): δ = 3.19 (m, 4 H, CH_2CH_2), 3.33 (s, 3 H, CH_3), 3.61 (s, 3 H, CH_3), 3.64 (s, 3 H, CH_3), 3.71 (s, 3 H, CH_3), 3.74 (s, 3 H, CH_3), 4.23–4.48 (m, 4 H, CH_2CH_2), 9.32 (s, 2 H, 3-, 8-CH), 10.23–10.35 (m, 4 H, CH-methine), 12.33 (s, 2 H, OH) ppm. IR (KBr): $\tilde{\nu}$ = 2914, 2854, 1694 cm^{-1}. UV/Vis ($CHCl_3$): λ (ε, L mol^{-1} cm^{-1}) = 323 (28357), 401 (224454), 532 (18648), 567 (18744) nm. MS (ESI, methanol, pos., neg., direct inlet): *m*/*z* = 572 [M]$^+$, 571[M – H]$^-$.

Porphyrin 4: Porphyrin **2** (52.5 mg, 91.5 μmol), sulfoleno bis(alcohol) **3**[7] (17.5 mg, 98.2 μmol) and dimethylaminopyridine (1.0 mg, 18.2 μmol) were dissolved under an atmosphere of argon in dry THF (40 mL). Triethylamine (1.7 mL) was added, and the mixture was cooled to 0 °C. At this temperature, *n*-propylphosphonic acid anhydride in ethyl acetate [50:50 (v/v), 1 mL, 1.70 mmol] was added over 60 min, and the solution was stirred for another 90 min. Stirring was continued for 19 h at room temperature. To complete the reaction, the solution was stirred for 45 min at 35 °C. After addition of CH_2Cl_2 (30 mL), the mixture was washed with water (2×) and saturated sodium hydrogen carbonate (1×), and the organic phase was filtered through cotton wool. The solvent was evaporated, and the residue was chromatographed on silica gel (CH_2Cl_2/MeOH, 19:1). Adduct **4** was obtained as a dark-red solid. Yield: 25.4 mg (35.5 μmol, 39.0%). M.p. 191 °C. R_f = 0.85 (silica gel; CH_2Cl_2/MeOH, 19:1). ^{1}H NMR [200 MHz, $CDCl_3$/[D_5]pyridine (10 μL), 25 °C, TMS]: δ = 3.56, 3.59, 3.77, 3.82 (4 s, each 3 H, 7-, 2-, 12-, 18-CH_3), 4.29 (m, 2 H, -CH_2-), 4.40 (m, 2 H, -CH_2- α to carbonyl), 5.10 (m, 2 H, -CH_2- β to carbonyl), 5.25 (m, 2 H, -CH_2-), 8.87 (s, 1 H, 8-H), 8.95 (s, 1 H, 3-H), 9.93 (s, 1 H, 5-H), 9.97 (s, 1 H, 10-H), 10.09 (s, 1 H, 20-H), 10.40 (s, 1 H, 15-H) ppm. IR (KBr): $\tilde{\nu}$ = 2918, 2853, 1736, 1318, 1151, 1120 cm^{-1}. UV/Vis ($CHCl_3$): λ (ε, L mol^{-1} cm^{-1}) = 403 (177133), 533 (10142), 569 (9528) nm. MS (ESI, methanol, pos., neg., direct inlet): *m*/*z* = 737 [M + Na]$^+$, 749 [M + Cl]$^-$.

Porphyrin–Fullerene 5a: Porphyrin **4** (14.9 mg, 20.8 μmol) and fullerene C_{60} (45.0 mg, 62.5 μmol) were dissolved under an atmosphere of argon in dry trichlorobenzene (2.5 mL) and treated in an ultrasonic bath for 10 min. The dark-red solution was stirred under an atmosphere of argon at 200 °C for 60 min. The solvent was evaporated in vacuo by using a kugelrohr at 40–50 °C, and the

residue was chromatographed on silica gel first with toluene to elute unreacted fullerene and then with CH_2Cl_2/MeOH (19:1) to elute the fullerene porphyrin dyad **5a**. Adduct **5a** was obtained as a brown solid. Yield: 11.8 mg (8.6 μmol, 41.0%). M.p. >350 °C. R_f = 0.76 (silica gel; CH_2Cl_2/MeOH, 19:1). ^{1}H NMR [600 MHz, $CDCl_3$/[D_5]pyridine (10 μL), 25 °C, TMS]: δ = 3.54 (s, 3 H, 7-CH_3), 3.57 (s, 3 H, 2-CH_3), 3.76 (s, 3 H, 12-CH_3), 3.80 (s, 3 H, 18-CH_3), 3.99 (m, 4 H, -CH_2-), 4.20 (m, 4 H, -CH_2- at carbonyl), 5.10 (m, 4 H, -CH_2- at carbonyl), 5.25 (m, 4 H, -CH_2-), 8.84 (s, 1 H, 8-H), 8.93 (s, 1 H, 3-H), 9.91 (s, 1 H, 5-H), 9.94 (s, 1 H, 10-H), 10.07 (s, 1 H, 20-H), 10.37 (s, 1 H, 15-H) ppm. IR (KBr): $\tilde{\nu}$ = 2919, 2844, 1735, 527 cm^{-1}. UV/Vis ($CHCl_3$): λ (ε, L mol^{-1} cm^{-1}) = 257 (89106), 326 (41457), 405 (163203), 532 (11545), 567 (12070) nm. MS (ESI, methanol, +, neg., direct inlet): *m*/*z* = 1370 $[M]^+$, 1393 $[M + Na]^+$, 1370 $[M^-]^-$.

Porphyrin–Fullerene 5b: Porphyrin–fullerene **5a** (1 mg, 0.728 μmol) was dissolved in CH_2Cl_2 and extracted with HCl (2.5 N, 3×). The colour of the solution changed to red-brown. The organic phase was then washed with water and filtered through cotton wool. The solvent was evaporated in vacuo, and the residue was chromatographed on silica gel first with toluene and then with CH_2Cl_2/MeOH (19:1) to elute the fullerene porphyrin dyad **5b**. Adduct **5b** was obtained as a red-brown solid. Yield: 0.8 mg (0.611 μmol, 84.0%). M.p. >350 °C. R_f = 0.85 (silica gel; CH_2Cl_2/MeOH, 19:1). IR (KBr): $\tilde{\nu}$ = 3307, 2922, 2855, 1706, 527 cm^{-1}. UV/Vis (CH_2Cl_2): λ (ε, L mol^{-1} cm^{-1}) = 256 (65980), 330 (31292), 404 (83170), 499 (7617), 530 (4529), 570 (3911), 622 (1647) nm. MS (ESI; CH_2Cl_2/methanol, 1:100; pos.; neg.; direct inlet): *m*/*z* = 1308 $[M]^+$, 1331 $[M + Na]^+$, 1307 $[M]^-$.

Porphyrin–Fullerenes 7a and 8a: Porphyrin **6a** (2.1 mg, 3.67 μmol) and sarcosine (10 mg, 0.11 mmol) were dissolved in dry toluene (7 mL). A solution of fullerene C_{60} (5.0 mg, 6.9 μmol) in dry toluene (7 mL) was then added, and the mixture was heated at reflux under an atmosphere of argon for 21 h. After cooling the mixture, the solution was chromatographed directly on silica gel with toluene and then with CH_2Cl_2/methanol (19:1). Porphyrin–fullerene dyads **7a** and **8a** were obtained a brown solid. Yield: 3.5 mg (2.7 μmol, 72.0%). M.p. >350 °C. R_f = 0.85 (silica gel; CH_2Cl_2/methanol, 19:1). HPLC (Nucleosil 50–10; CH_2Cl_2/MeOH/*n*-heptane, 19:1:1; 1 mL/min; 405 nm): t_R = 2.2 min. HPLC (Nucleosil-Chiral-2; *n*-heptane/1,4 dioxane, 70:30; 1 mL/min; 405 nm): t_R = 10.7 (**8a**), 11.6 (**7a**) min; **7a/8a**, 1:2.38. ^{1}H NMR [600 MHz, $CDCl_3$/[D_5]pyridine (10 μL), 25 °C, TMS]: δ = **7a**: δ = –3.62 (s, 2 H, NH), 3.20 (s, 3 H, NCH_3), 3.25 (m, 4 H, -CH_2- α to carbonyl), 3.60 (s, 3 H, 18-CH_3), 3.49 (s, 3 H, 12-CH_3), 4.24 (s, 3 H, 7-CH_3), 4.38 (m, 4 H, -CH_2- β to carbonyl), 4.70 (AB system, 1 H, 8′′-CH_2- B), 5.36 (AB system, 1 H, 8′′-CH_2- A), 7.07 (s, 1 H, 8′-H), 9.10 (s, 1 H, 3-H), 10.07 (s, 1 H, 15-H), 10.16 (s, 1 H, 5-H), 10.09 (s, 1 H 20-H), 10.44 (s, 1 H, 10-H) ppm. **8a**: δ = –3.62 (s, 2 H, NH), 3.09 (s, 3 H, NCH_3), 3.25 (m, 4 H, -CH_2- α to carbonyl), 3.59 (s, 3 H, 18-CH_3), 3.78 (s, 3 H, 7-CH_3), 3.80 (s, 3 H, 12-CH_3), 4.38 (m, 4 H, -CH_2- β to carbonyl) 4.65 (AB system, 1 H, 8′′-CH_2- B), 5.50 (AB system, 1 H, 8′′-CH_2- A), 6.50 (s, 1 H, 8′-H), 9.09 (s, 1 H, 3-H), 10.06 (s, 1 H, 20-H), 10.07 (s, 1 H, 15-H), 10.07 (s, 1 H 15-H), 12.12 (s, 1 H, 10-H) ppm. IR (KBr): $\tilde{\nu}$ = 3307, 1735, 1433, 527 cm^{-1}. UV/Vis (CH_2Cl_2): λ (ε, L mol^{-1} cm^{-1}) = 255 (98329), 323 (40862), 406 (172605), 501 (12379), 535 (7649), 570 (6341), 626 (2919) nm. MS (ESI, acetonitrile, pos.): *m*/*z* = 1314 $[M + H]^+$.

Porphyrin–Fullerenes 10a and 11a: Porphyrin **9a** (4.1 mg, 7.17 μmol) and sarcosine (19 mg, 0.22 mmol) were dissolved in dry toluene (10 mL). A solution of fullerene C_{60} (5.9 mg, 8.2 μmol) in dry toluene (10 mL) was then added, and the mixture was heated at reflux under an atmosphere of argon for 21 h. After cooling the mixture, the solution was chromatographed directly on silica gel with toluene and then with CH_2Cl_2/methanol (19:1). Porphyrin–fullerene dyads **10a** and **11a** were obtained as a brown solid. Yield: 3.5 mg (4.34 μmol, 61.0%). M.p. > 350 °C. R_f = 0.85 (silica gel; CH_2Cl_2/methanol, 19:1). HPLC (Nucleosil 50–10; CH_2Cl_2/MeOH/*n*-heptane, 19:1:1; 1 mL/min; 405 nm): t_R = 2.2 min. HPLC (Nucleosil-Chiral-2; *n*-heptane/1,4 dioxane, 70:30; 1 mL/min; 405 nm): t_R = 9.8 (**11a**), 10.6 (**10a**) min; **10a/11a**, 1:1.95. ^{1}H NMR [600 MHz, $CDCl_3$/[D_5]pyridine (10 μL), 25 °C, TMS]: **10a**: δ = –3.71 (s, 2 H, NH), 3.25 (s, 3 H, NCH_3), 3.26 (m, 4 H, -CH_2- α to carbonyl), 3.58 (s, 3 H, 12-CH_3), 3.62 (s, 3 H, 7-CH_3), 3.68 (s, 3 H, 18-CH_3), 4.29 (s, 3 H, 2 CH_3), 4.40 (m, 4 H, -CH_2- α to carbonyl), 4.71 (AB system, 1 H, 3′′-CH_2- B), 5.37 (AB system, 1 H, 3′′-CH_2- A), 7.07 (s, 1 H, 3′-H), 9.03 (s, 1 H, 8-H), 10.00 (s, 1 H, 10-H), 10.08 (s, 1 H, 5-H), 10.26 (s, 1 H 20-H), 10.50 (s, 1 H, 5-H) ppm. **11a**: δ = –3.67 (s, 2 H, NH), 3.12 (s, 3 H, NCH_3), 3.26 (m, 4 H, -CH_2- α to carbonyl), 3.58 (s, 3 H, 12-CH_3), 3.66 (s, 3 H, 18-CH_3), 3.91 (s, 3 H, 7-CH_3), 4.40 (m, 4 H, -CH_2- β to carbonyl) 4.65 (AB system, 1 H, 3′′-CH_2- B), 5.49 (AB system, 1 H, 3′′-CH_2- A), 6.51 (s, 1 H, 3′-H), 9.11 (s, 1 H, 8-H), 10.00 (s, 1 H, 10-H), 10.05 (s, 1 H, 15-H), 10.16 (s, 1 H 20-H), 12.17 (s, 1 H, 5-H) ppm. IR (KBr): $\tilde{\nu}$ = 3307, 1734, 1433, 526 cm^{-1}. UV/Vis (CH_2Cl_2): λ (ε, L mol^{-1} cm^{-1}) = 255 (105212), 323 (44081), 406 (184982), 501 (13781), 534 (8569), 570 (7244), 624 (3357) nm. MS (ESI; methanol/acetone, 10:1; pos.): *m*/*z* = 1314 $[M + H]^+$.

Porphyrin 6b: Porphyrin **6a** (7.5 mg, 13.0 μmol) and zinc(II) acetylacetonate (10.0 mg, 35.0 μmol) were dissolved in dry THF (10 mL), and the mixture was heated at reflux under an atmosphere of argon for 20 h. The solution was mixed with CH_2Cl_2 (20 mL) and washed with brine (3×). The combined organic phase was filtered through cotton wool. After evaporation of the solvent, the residue was chromatographed on aluminium oxide (act. II–III, neutral; CH_2Cl_2/methanol, 19:1). Yield: 7.6 mg (12.0 μmol, 91.1%). M.p. 255 °C. R_f = 0.76 (aluminium oxide, CH_2Cl_2). ^{1}H NMR [200 MHz, $CDCl_3$/[D_5]pyridine (20 μL), 25 °C, TMS]: δ = 3.24 (t, *J* = 6.71 Hz, 4 H, -CH_2- α to carbonyl), 3.57, 3.61, 3.68, 3.93 (4 s, CH_3), 4.35 (t, *J* = 6.71 Hz, 4 H, -CH_2- β to carbonyl), 9.04 (s, 1 H, 3-H), 9.86, 9.94, 10.01, 10.79 (4 s, each 1 H, 5-, 10-, 15-, 20-H), 11.57 (s, 1 H, formyl) ppm. IR (KBr): $\tilde{\nu}$ = 2951, 1735, 1661 cm^{-1}. UV/Vis (CH_2Cl_2): λ (ε, L mol^{-1} cm^{-1}) = 365 (23575), 416 (195749), 548 (9662), 592 (21449) nm. MS (EI, 402 °C): *m*/*z* (%) = 628 (100) $[M]^+$, 555 (50) $[M - CH_2CO_2CH_3]^+$, 482 (26) $[M - 2\ CH_2CO_2CH_3]^+$.

Porphyrin 9b: Porphyrin **9a** (7.5 mg, 13.0 μmol) and zinc(II) acetylacetonate (10.0 mg, 35.0 μmol) were dissolved in dry THF (10 mL), and the mixture was heated at reflux under an atmosphere of argon for 20 h. The solution was mixed with CH_2Cl_2 (20 mL) and washed with brine (3×). The combined organic phase was filtered through cotton wool. After evaporation of solvent, the residue was chromatographed on aluminium oxide (act. II-III, neutral; CH_2Cl_2/methanol, 19:1). Yield: 7.7 mg (12.0 μmol, 92.3%). M.p. 255 °C. R_f = 0.75 (aluminium oxide, CH_2Cl_2). ^{1}H NMR [200 MHz, $CDCl_3$/[D_5]pyridine (20 μL), 25 °C, TMS]: δ = 3.27 (t, *J* = 6.70 Hz, 4 H, -CH_2- α to carbonyl), 3.57, 3.63, 3.65, 3.75, 4.01 (5 s, 15 H, CH_3), 4.37 (t, *J* = 6.70 Hz, 4 H, -CH_2- β to carbonyl), 9.00 (s, 1 H, 8-H), 9.82, 9.90, 10.14, 10.86 (4 s, each 1 H, 5-, 10-, 15-, 20H), 11.63 (s, 1 H, formyl) ppm. IR (KBr): $\tilde{\nu}$ = 2951, 1735, 1663 cm^{-1}. UV/Vis (CH_2Cl_2): λ (ε, L mol^{-1} cm^{-1}) = 365 (22432), 416 (195689), 548 (9704), 593 (20994) nm. MS (EI, 420 °C): *m*/*z* (%) = 628 (100) $[M]^+$, 555 (50) $[M - CH_2CO_2CH_3]^+$, 482 (26) $[M - 2\ CH_2CO_2CH_3]^+$.

Zn–Porphyrin–Fullerene Dyads 7b and 8b: Porphyrin **6b** (4.6 mg, 7.3 μmol) and sarcosine (19 mg, 0.21 mmol) were dissolved in dry

toluene (10 mL). A solution of fullerene C_{60} (5.9 mg, 8.2 μmol) in dry toluene (10 mL) was then added, and the mixture was heated at reflux under an atmosphere of argon for 21 h. After cooling the mixture, the solution was chromatographed directly on silica gel with toluene and then with CH_2Cl_2/methanol (19:1). Porphyrin–fullerene dyads **7b** and **8b** were obtained as a brown solid. Yield: 6.2 mg (4.5 μmol, 62.0%). M.p. >350 °C. R_f = 0.86 (silica gel; CH_2Cl_2/methanol, 19:1). ^{1}H NMR [600 MHz, $CDCl_3$/[D_5]pyridine (10 μL), 25 °C, TMS]: **7b**: δ = 3.26 (s, 3 H, NCH_3), 3.24 (m, 4 H, -CH_2- α to carbonyl), 3.50 (s, 3 H, 12-CH_3), 3.63 (s, 3 H, 18-CH_3), 3.73 (s, 3 H, 2-CH_3), 4.24 (s, 3 H, 7-CH_3), 4.41 (m, 4 H, -CH_2- β to carbonyl), 4.71 (AB system, 1 H, 8′′-CH_2- B), 5.38 (AB system, 1 H, 8′′-CH_2- A), 7.10 (s, 1 H, 8′-H), 9.07 (s, 1 H, 3-H), 9.95 (s, 1 H, 15-H), 10.07 (s, 1 H, 20-H), 10.09 (s, 1 H 5-H), 10.35 (s, 1 H, 10-H) ppm. **8b**: δ = 3.12 (s, 3 H, NCH_3), 3.26 (m, 4 H, -CH_2- α to carbonyl), 3.62 (s, 3 H, 18-CH_3), 3.77 (s, 3 H, 12-CH_3), 3.80 (s, 3 H, 7-CH_3), 4.40 (m, 4 H, -CH_2- β to carbonyl), 4.68 (AB system, 1 H, 8′′-CH_2- B), 5.51 (AB system, 1 H, 8′′-CH_2- A), 6.52 (s, 1 H, 8′-H), 9.05 (s, 1 H, 3-H), 9.93 (s, 1 H, 15-H), 10.00 (s, 1 H, 5-H), 10.03 (s, 1 H 20-H), 12.02 (s, 1 H, 10-H) ppm. IR (KBr): $\tilde{\nu}$ = 1735, 1433, 527 cm^{-1}. UV/Vis (CH_2Cl_2): λ (ε, L mol^{-1} cm^{-1}) = 255 (90689), 323 (41222), 407 (244229), 553 (13579), 572 (13191) nm. MS (ESI; methanol/acetone, 10:1; pos.; neg.; direct inlet): *m*/*z* = 1398 [M + Na]$^+$, 1375 [M]$^-$.

Zn–Porphyrin–Fullerene Dyads 10b and 11b: Porphyrin **9b** (4.6 mg, 7.3 μmol) and sarcosine (19 mg, 0.21 mmol) were dissolved in dry toluene (10 mL). A solution of fullerene C_{60} (5.9 mg, 8.2 μmol) in dry toluene (10 mL) was then added, and the mixture was heated at reflux under an atmosphere of argon for 21 h. After cooling the mixture, the solution was chromatographed directly on silica gel with toluene and then with CH_2Cl_2/methanol (19:1). Porphyrin–fullerene dyads **10b** and **11b** were obtained as a brown solid. Yield: 6.2 mg (4.5 μmol, 62.0%). M.p. > 350 °C. R_f = 0.86 (silica gel; CH_2Cl_2/methanol, 19:1). ^{1}H NMR [600 MHz, $CDCl_3$/[D_5]pyridine (10 μL), 25 °C, TMS]: **10b**: δ = 3.26 (s, 3 H, NCH_3), 3.24 (m, 4 H, -CH_2- α to carbonyl), 3.50 (s, 3 H, 12-CH_3), 3.63 (s, 3 H, 18-CH_3), 3.73 (s, 3 H, 2-CH_3), 4.24 (s, 3 H, 7-CH_3), 4.41 (m, 4 H, -CH_2- β to carbonyl) 4.71 (AB system, 1 H, 8′′-CH_2- B), 5.38 (AB system, 1 H, 8′′-CH_2- A), 7.10 (s, 1 H, 8′-H), 9.07 (s, 1 H, 3-H), 9.95 (s, 1 H, 15-H), 10.07 (s, 1 H, 20-H), 10.09 (s, 1 H 5-H), 10.35 (s, 1 H, 10-H) ppm. **11b**: δ = 3.12 (s, 3 H, NCH_3), 3.26 (m, 4 H, -CH_2- α to carbonyl), 3.62 (s, 3 H, 18-CH_3), 3.77 (s, 3 H, 12-CH_3), 3.80 (s, 3 H, 7-CH_3), 4.40 (m, 4 H, -CH_2- β to carbonyl), 4.68 (AB system, 1 H, 8′′-CH_2- B), 5.51 (AB system, 1 H, 8′′-CH_2- A), 6.52 (s, 1 H, 8′-H), 9.05 (s, 1 H, 3-H), 9.93 (s, 1 H, 15-H), 10.00 (s, 1 H, 5-H), 10.03 (s, 1 H 20-H), 12.02 (s, 1 H, 10-H) ppm. IR (KBr): $\tilde{\nu}$ = 1735, 1433, 527 cm^{-1}. UV/Vis (CH_2Cl_2): λ (ε, L mol^{-1} cm^{-1}) = 255 (90689), 323 (41222), 407 (244229), 553 (13579), 572 (13191) nm. MS (ESI; methanol/acetone, 10:1; pos.; neg., direct inlet): *m*/*z* = 1398 [M + Na]$^+$, 1375 [M]$^-$.

Supporting Information (see footnote on the first page of this article): Assignment of ^{1}H NMR signals of diastereomers **7a/8a**, **7b/8b**, **10a/11a** and **10b/11b**.

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