New Heck-Type Coupling Reactions of Natural Tetrapyrroles − Synthesis of Porphyrinoligomers Bridged by Divinyl- and Trivinylbenzene

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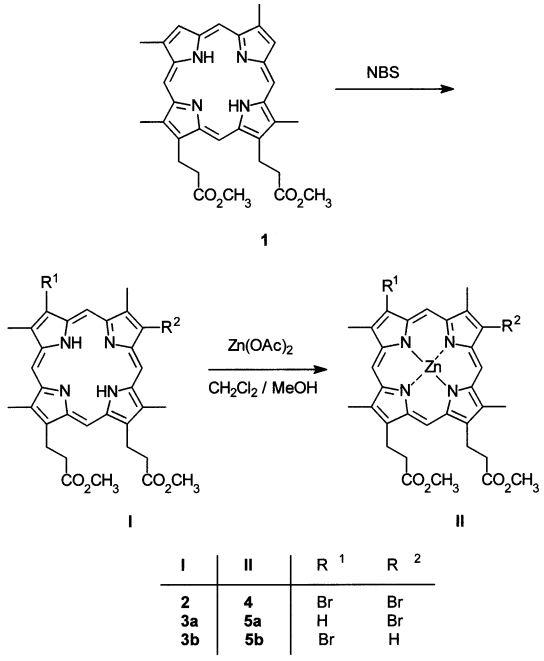
Using palladium(0)-catalyzed coupling reactions we were able to synthesize mono-, di-, and trimeric porphyrins linked by di- and trivinylbenzenes. The reactions were carried out with palladium(II) acetate in DMF under phase-transfer conditions. These coupling conditions are new in the field of porphyrin chemistry and proved to be a useful tool in the synthesis of C–C linked oligomeric porphyrins, as these compounds can be obtained in a simple one pot reaction with good yields.

The development of new strategies in the synthesis of oligomeric porphyrins, especially those linked by C−C bonds, has attracted considerable interest recently[1][2][3][4]. This is due to the possibilities that it offers for gaining an insight into the mechanisms of photosynthesis[5][6][7][8], which demands the construction of large arrays of covalent linked porphyrins. Another application is the possible use of these compounds in photodynamic therapy (PDT)[9]. In this field of research C−C linked porphyrin-oligomers in particular have been shown to be efficient photosensitizers in vivo[9][10][11]. This is particularly true for those possessing a substitution pattern related to that of the natural tetrapyrroles (e.g. hemato- or protoporphyrin[10][11]).

In particular, palladium(0)-catalyzed coupling reactions have been shown to be very powerful in the functionalization and linking of porphyrins[3][12][13][14]. Recent publications have described some impressive examples using this strategy, utilizing synthetic tetraphenyl-substituted porphyrin precursors which were linked by ethinyl and butadiinyl units to give up to pentameric units via Heck-type reactions[1]. In contrast only very few examples exploiting the natural tetrapyrrole derivatives are known[3][15]. Although these substances are much more interesting, due to their similarity to systems found in nature, they are more difficult to handle due to the additional functional groups which can lead to undesirable side reactions. Here we report on the reaction of brominated natural porphyrin-derivatives with multiple vinyl-substituted benzene derivatives to form C−C linked monomeric, dimeric, and trimeric porphyrin systems. Our studies have focused on the tetrapyrroles derived from porphyrins with a natural substitution pattern[16][17][18] which is favorable, or even essential, for applications in biological systems (e.g. PDT).

The halogenation of the deuteroporphyrin dimethyl ester **1** attracted our attention when looking for suitable porphyrin starting materials for palladium-catalyzed coupling reactions proceeding from natural tetrapyrroles. This compound is relatively easy to obtain from heme, the inexpensive natural porphyrin source. Among the various methods known for the halogenation of deuteroporphyrin dimethyl ester **1**[19][20][21], bromination with NBS in an inert solvent was found to be a particularly versatile and mild method. According to the work of Bonnett et al.[22], by controlling the stoichiometric amount NBS added this method allows either the dibromination at C-3 and C-8, or the monobromination at C-3 or C-8. Using 2.1 equivalents of NBS in the reaction with **1** in trichloromethane we obtained, after crystallization from dichloromethane/petroleum ether (2:1), the 3,8-dibromoporphyrin dimethyl ester **2**.

Scheme 1. Bromination of deuteroporphyrin-IX dimethyl ester **1**



1 **I** **II**

I	II	R 1	R 2
2	**4**	Br	Br
3a	**5a**	H	Br
3b	**5b**	Br	H

  1434−193X/98/0606−1193 $ 17.50+.50/0

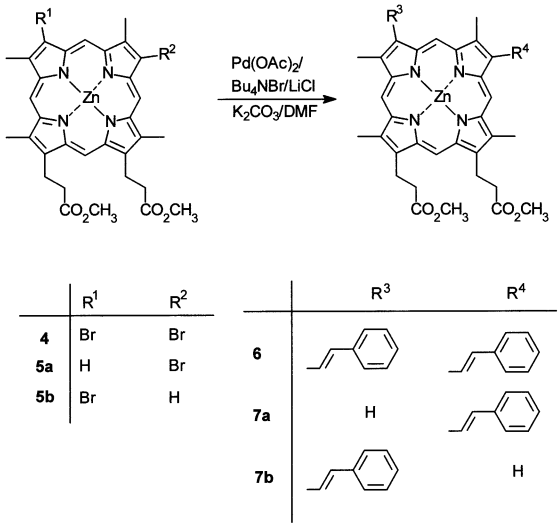
The monobrominated regioisomers **3a** and **3b** were formed by the reaction of **1** with one equivalent of NBS. Fortunately, we were able to separate the pure monobrominated regioisomers **3a** and **3b** by repeated crystallization from dichloromethane/hexane (5:1). In addition to a mixture of the regioisomers we also obtained some fractions with regioisomerically pure bromodeuteroporphyrin **3a** and **3b**[29]. The metallation that followed was carried out with zinc(II) acetate in a mixture of dichloromethane/methanol (1:1) to yield the corresponding porphyrin−zinc complexes **4** and **5a**, **b**.

Preliminary studies showed that the coupling reaction of zinc(II)−3,8-dibromodeuteroporphyrin dimethyl ester **4**[23] with styrene proceeds very well under phase transfer conditions[24] using 5 mol-% palladium(II) acetate in DMF as a catalyst. The resulting zinc(II)−3,8-distyryldeuteroporphyrin dimethyl ester **6** was separated in a yield of 87% (the *trans*-configured product was formed exclusively). Such reaction conditions have been extensively applied, with excellent results, in the Heck-type coupling reactions of several aryl halides[26][27][28]. Surprisingly they have not yet been applied to porphyrins. The styryl-coupling product **6** has already been described by Smith et al.[25], who prepared **6**, in a yield of 44%, by reacting zinc(II)−3,8-bis(chloromercurio)deuteroporphyrin-IX dimethyl ester with an excess of styrene in the presence of a ten-fold quantity of $LiPdCl_3$. Comparing this procedure with that of the phase transfer method shows the efficiency of the latter in the palladium catalyzed C−C bond formation of porphyrins. The yield is twice as high, and the amount of catalyst required is much less. Moreover, the use of toxic mercurioorganyls is avoided. The corresponding reaction of the monobrominated porphyrin **5** with styrene yielded the styrylporphyrin **7** (84%), which has not previously been reported in the literature.

The Pd^0-catalyzed C−C-coupling reactions allow the use of porphyrin−zinc complexes. This is a notable advantage since the demetallation to the free bases can be achieved very easily. Other methods (e.g. the McMurry reaction) are unfavorable in this respect because they require nickel or copper complexes, from which the metals are difficult to remove. The zinc−porphyrin complexes we used are readily demetallated by stirring a solution of the porphyrin complex in dichloromethane with dilute HCl. This procedure is described for the compounds **6-Zn** and **7-Zn** in the Experimental Section.

The same reaction conditions also proved to be extremely useful for the formation of porphyrin oligomers. Therefore, we chose multiple vinyl-substituted benzene derivatives to act as linking units between the porphyrin moieties using the synthetic strategy described above. Divinylbenzenes could be prepared from the corresponding benzenedialdehydes by a Wittig reaction in a straightforward manner. In the case of 1,4- and 1,3-divinylbenzene, the simple one-pot reaction according to Bigot[30], and starting with the dialdehydes, proved to be very suitable. In constrast, this method was unsuitable for the preparation of the 1,2-divinylbenzene isomer. Classical Wittig conditions were used in this case. For the preparation of 1,3,5-trivinylbenzene the

Scheme 2. Heck-coupling reaction of styrene with brominated porphyrins



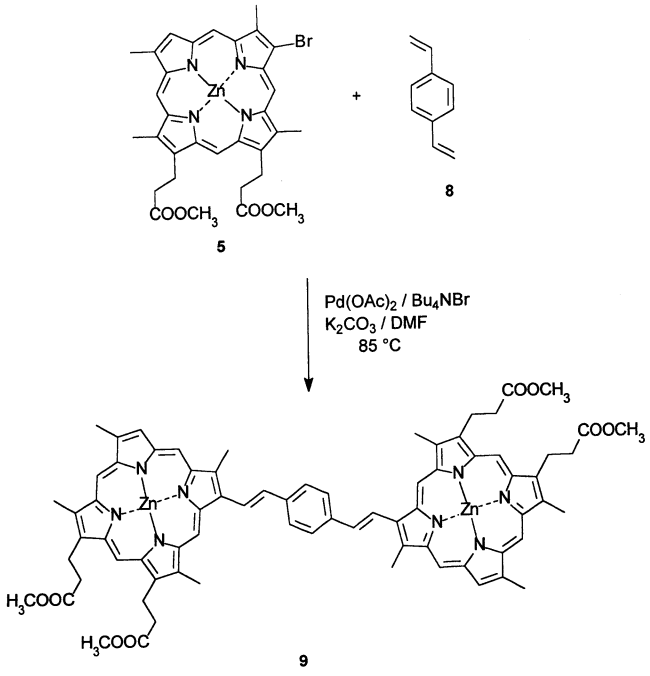
	R^1	R^2
4	Br	Br
5a	H	Br
5b	Br	H

	R^3	R^4
6		
7a	H	
7b		H

Stille coupling of 1,3,5-tribromobenzene with vinyltributylstannane appeared to be a more convenient way when compared with the Wittig pathway, as the required trialdehyde was not commercially available.

The coupling reaction of 1,4-divinylbenzene **8** with a twofold equivalent of **5** resulted in the formation of the novel dimeric porphyrin **9**[31]. The reaction was carried out under similar conditions to those described above (10 mol-% palladium acetate; 85°C; 8 h). **9** was separated in a yield of 76% from the 1,4-divinylbenzene substituted porphyrin monomer after chromatography on silica gel.

Scheme 3. Porphyrin dimer resulting from the Heck-coupling of 1,4-divinylbenzene with **5**

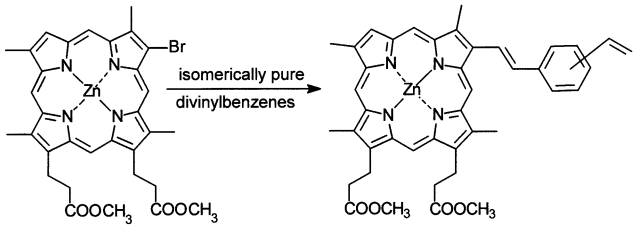


The structure of **9** was confirmed by FAB-MS and NMR spectroscopy. The NMR spectrum in [D_6]DMSO shows a

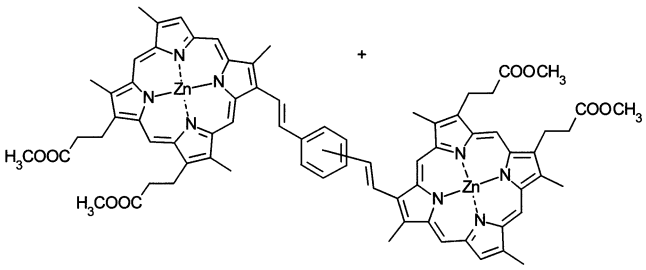
characteristic AB-system at δ = 8.01 (with J = 16.3 Hz) which belongs to both vinyl groups tied up with *trans*-configuration to the porpyhrin core. A H,H-COSY experiment localized the corresponding protons in a multiplet at δ = 9.17−9.23, overlaped by two β-pyrrolic protons. The UV/Vis spectra of **9** exhibit a red-shifted soret band when compared to compound **5**, which probably reveals an unhindered conjugation between the porphyrin and divinylbenzene units[32].

The reaction was carried out under similar conditions with 1,3- and 1,2-divinylbenzene. Although the reaction proceeds well to form the dimeric porphyrins **13** and **14** in these cases the yields are somewhat lower (about 50%). As by-products the divinylbenzene-substituted porphyrin monomers **11** and **12** are formed. The product mixture could be separated readily by chromatography on silica gel. The structure of both the monomeric and dimeric compounds was also confirmed by FAB-MS and NMR spectroscopy (including H,H-COSY) . Apparently different UV/Vis spectra are achieved from **13** and **14** compared to dimer **9**. The 1,3-divinylbenzene-bridged dimer **13** shows a spectrum which is almost identical to that for the monomeric compound **11,** indicating that there is no electronic interaction between the two porphyrin moieties. In contrast to this observation, the red-shifted, and significantly different spectrum of the 1,2-divinylbenzene-bridged dimer **14**, reveals the interaction between the two π systems which can be explained by a partly coplanar arrangement of the porphyrin macrocycles.

Scheme 4. Porphyrin dimers resulting from the Heck-coupling of isomeric divinylbenzenes



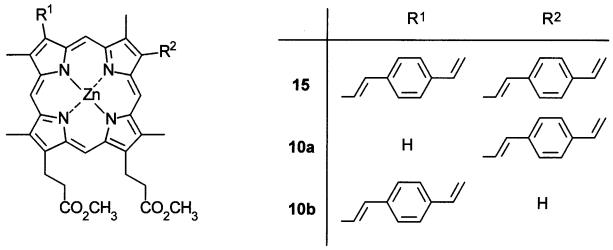
	isomer	yield
10	para	22 %
11	meta	31 %
12	ortho	32 %



	isomer	yield
9	para	73 %
13	meta	51 %
14	ortho	48 %

By use of an excess of divinylbenzene the predominate formation of substituted porphyrin monomers could also be achieved. The reaction of dibromoporphyrin **4** with 2.4-equivalents of 1,4-divinylbenzene resulted in the formation of the 1,4-divinylbenzene-substituted porphyrin **15**. The pure compound **15** was obtained by means of the general phase-transfer coupling conditions followed by the separation of oligomeric by-products by chromatography on silica gel. Under similar conditions the mono-1,4-divinylbenzene substitued porphyrin **10** was formed from the monobrominated porphyrin **5**. Both compounds are versatile porphyrin-building blocks, e. g. as starting materials for the formation of higher oligomers.

Scheme 5. 1,4-Divinylbenzene-substituted porphyrin-building blocks for the formation of porphyrinoligomers



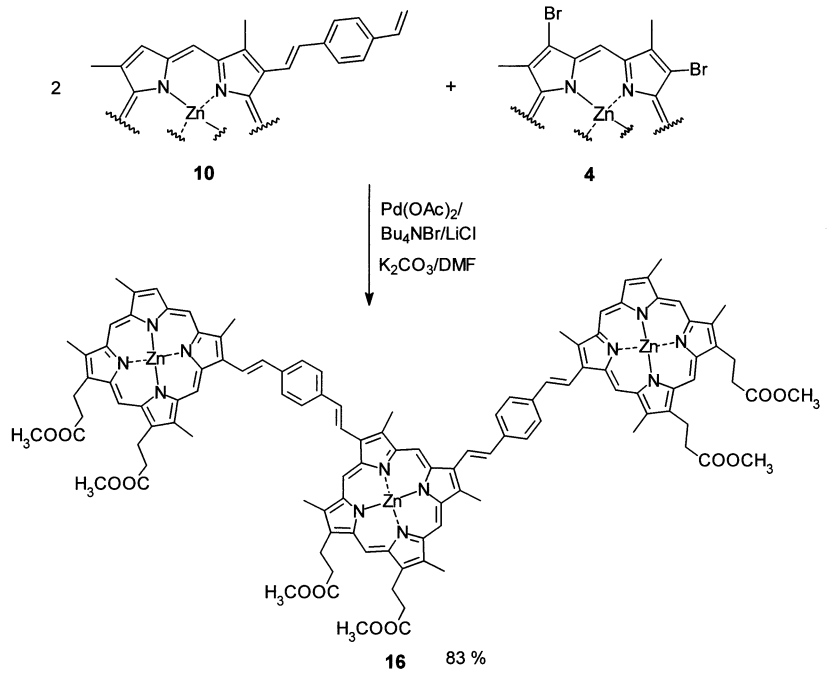
One example using this building block strategy is the formation of the porphyrin trimer **16**. This large porphyrin array was obtained by the coupling reaction of a new palladium(0)-catalyzed step, with two equivalents of compound **10** and one equivalent of dibromoporphyrin **4**. The dark green porphyrin trimer **16** was characterized by NMR spectroscopy and mass spectrometry. In contrast to the dimeric porphyrins described above, the FAB-MS spectra of the trimeric compounds showed no significant ion-molecule signal. However, this problem could be overcome with MALDI-MS spectroscopy[33] which gave very satisfactory spectra. The UV/Vis spectra are red shifted compared with the dimer **9**, illustrating the extended delocalisation over the entire π system. The construction of the identical product **16** was also achieved by the coupling of one equivalent porphyrin **15** with two equivalents of bromoporphyrin **5**.

A centrally linked trimeric porphyrin **17** was formed by the coupling reaction of **5** with 1,3,5-trivinylbenzene. The trimer **17** was prepared under similar coupling conditions to those described above, using three equivalents of the porphyrin **5** and one equivalent of the benzene derivative.

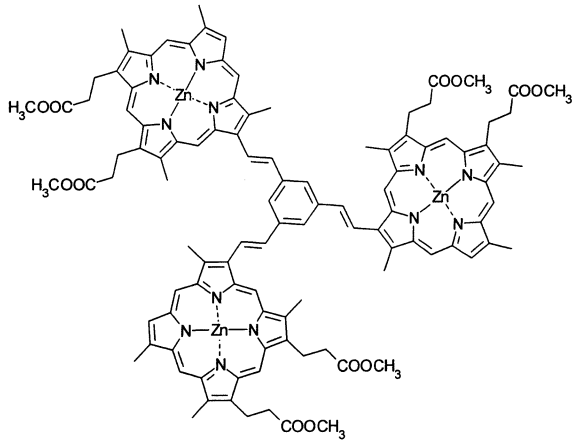
The structure of the dark purple trimer **17** was confirmed by NMR spectroscopy and MALDI-MS. The UV/Vis spectra of **17** expose a less red-shifted soret band when compared with **9** (the maximum is located between that of **5** and that of the porphyrin dimer **9**). These findings indicate that there is less conjugation between the porphyrin and the benzene core, possibly due to the sterical demands of the neighbouring porphyrins which prevent a planar arrangement.

The synthetic strategy described here is very flexible and suitable for the synthesis of a great variety of porphyrin oligomers. The yields achieved are very good compared to those for other syntheses in this field. The use of various

Scheme 6. Sequential Heck-coupling with 1,4-divinylbenzene to gain porphyrin trimers



Scheme 7. Porphyrin trimer from Heck-coupling of **5** with 1,3,5-trivinylbenzene



different building blocks enables the preparation of a variety of other porphyrin oligomers. Further research on the applications of palladium(0)-catalyzed coupling reactions on derivatives of natural tetrapyrroles is currently being carried out.

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Experimental Section

General: ^{1}H and ^{13}C NMR: Bruker AMX (300 MHz) respectively (ARX 200 MHz), $CDCl_3$, int. standard: TMS. − FAB-MS: Finnigan MAT 8230; Xe, 8 keV. − MALDI-MS: Kratos Kompact MALDI 2 − UV/Vis: UV - Vis SCANNING Spektrometer 2101 PC der Fa. Shimadzu − Elemental Analysis: Perkin Elmer Analysator 2400. − Melting Point: Büchi SMP 20 (uncorrected) − Column chromatography: Merck silica gel 60 (70−230 mesh). − All solvents are purified and dried in accordance with common procedures.

3(8)-Bromodeuteroporphyrin-IX Dimethyl Ester (**3a**, **b**): NBS (1.304 g, 7.3 mmol) was added to deuteroporphyrin dimethyl ester (**1**) (4.0 g, 7.4 mmol) in ethanol-free chloroform (300−400 ml) under an inert gas atmosphere (N_2) and the solution was heated 1 h at 70°C. After cooling the reaction mixture to room temp. the organic layer was washed with water (2 × 200 ml) and brine (100 ml), dried (Na_2SO_4), filtered, and concentrated in vacuo. The raw material was purified by repeated crystallisation from CH_2Cl_2/petroleum ether (2:1). The purity of the obtained fractions was proven by ^{1}H-NMR spectroscopy. The fractionated crystallization step gave a 1.43 g (32%) overall yield of regioisomer pure fractions [3-bromodeuteroporphyrin-IX dimethyl ester (**3a**) and 8-bromodeuteroporphyrin-IX dimethyl ester (**3b**)] and a 1.30 g (29%) yield in fractions as a mixture of regioisomers **3a** and **3b**.

Pure Regioisomer Fraction: M. p. 227°C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = −3.86 (s, 2 H, NH), 3.22 (t, 4 H, J = 7.59 Hz, 13^2/17^2-CH_2), 3.50 (s, 6 H, OCH_3), 3.62−3.71 (m, 12 H, CH_3), 4.28 (t, 2 H, 13^1/17^1-CH_2), 4.38 (t, 2 H, 13^1/17^1-CH_2), 8.99 (s, 1 H, $CH_{\beta\text{-pyr}}$), 9.78, 9.86, 9.90, 10.01 (s, 4 H, CH_{meso}). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.85, 12.99, 13.56, 14.04 (q, $CH_{3,\ pyr}$), 21.94, 22.26 (t, 13^1/17^1-CH_2), 37.09, 37.41 (t, 13^2/17^2-CH_2), 52.20 (q, OCH_3), 96.32, 97.35, 97.44, 100.18 (d, CH_{meso}), 121.84 (s, C−Br), 126.46 (d, $CH_{\beta\text{-pyr}}$), 134.88, 137.30, 139.58, 140.70, 141.14, 147.07, 150.24, 152.34 (s, C_{ring}), 173.83, 174.15 (s, CO_2CH_3).

Mixture of Regioisomers: M. p. 224°C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = −3.92 (s, 2 H, NH), 3.17 (t, 4 H, J = 7.55 Hz, 13^2/17^2-CH_2), 3.46−3.51 (s, 7 H, OCH_3), 3.60−3.72 (m, 11 H, CH_3), 4.24−4.40 (t, 4 H, 13^1/17^1-CH_2), 8.97, 9.02 (s, 1 H, $CH_{\beta\text{-pyr}}$), 9.70, 9.75, 9.84, 9.85, 9.88, 9.99, 10.03 (s, 4 H, CH_{meso}). − ^{13}C NMR

(50 MHz, $CDCl_3$): δ = 10.04, 11.50, 11.71, 12.10, 13.36, 13.90 (q, $CH_{3,pyr}$), 21.84, 22.22 (t, $13^1/17^1$-CH_2), 37.05, 37.39 (t, $13^2/17^2$-CH_2), 52.18 (q, OCH_3), 96.00, 96.71, 97.05, 97.96, 99.52, 99.86 (d, CH_{meso}), 121.47, 121.65 (s, C−Br), 126.07, 126.49 (d, $CH_{β\text{-}pyr}$), 134.26, 134.61, 135.70, 136.06, 136.35, 135.66, 136.98, 137.19, 137.53, 137.92, 139.32, 139.52, 140.07, 140.37, 140.49, 140.49, 141.14 (s, C_{ring}), 173.91, 174.13 (s, CO_2CH_3). − UV/Vis: $λ_{max}$ (lg ε) = 401 nm (4.997), 499 (4.144), 535 (4.069), 566 (3.937), 620 (3.452). − FAB-MS (nitrobenzyl alcohol): *m/z* (%): 618 (100) [M^+, ^{81}Br], 616 (100) [M^+, ^{79}Br], 545 (35) [M^+ − Br]. − $C_{32}H_{33}N_4O_4Br$ (617.54): calcd. C 62.2, H 5.40, N 9.1; C 62.14, H 5.22, N 8.91.

3,8-Dibromodeuteroporphyrin-IX Dimethyl Ester (**2**): NBS (1.68 g, 9.45 mmol) was added to deuteroporphyrin dimethyl ester (**1**) (2.42 g, 4.5 mmol) in ethanol-free chloroform (150 ml) under an inert gas atmosphere (N_2) and the solution was heated for 1.5 h at 70°C. After cooling the reaction mixture to room temp. the organic layer was washed with water (2 × 150 ml) and brine (60 ml), dried (Na_2SO_4), filtered, and concentrated in vacuo. Crystallisation from CH_2Cl_2/petroleum ether (2:1) gives 2.55 g (81%) of **2**, red crystals, m. p. 277°C (ref.[18]: 278−279°C). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = −3.94 (s, 2 H, NH), 3.20 (t, 4 H, *J* = 7.69 Hz, $13^2/17^2$-CH_2), 3.46−3.56 (3s, 9 H, CH_3), 3.65 (s, 3 H, CH_3), 4.30−4.35 (2s, 6 H, CH_3), 4.33 (t, 4 H, *J* = 7.69 Hz, $13^1/17^1$-CH_2), 9.54, 9.56, 9.71, 9.76 (4s, 4 H, CH_{meso}). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.06, 14.62 (q, $CH_{3,\ pyr}$), 22.27 (t, $13^1/17^1$-CH_2), 36.02, (t, $13^2/17^2$-CH_2), 52.63 (q, OCH_3), 100.66, 100.97, 101.84 (d, CH_{meso}), 122.48, 122.69 (s, C−Br), 140.09, 140.55, 140.71, 141.06, 141.07, 141.89, 142.13, 142.26, 142.51, 143.54, 143.66 (s, C_{ring}), 173.51 (s, CO_2CH_3).

Zinc(II)-3(8)-bromodeuteroporphyrin-IX Dimethyl Ester (**5a**, **b**): The metallation of 3(8)-bromodeuteroporphyrin-IX dimethyl ester (**3a**, **b**) (1.0 g, 1.62 mmol) was carried out in a mixture of CH_2Cl_2/MeOH (1:1, 160 ml) and a zinc acetate × 2 H_2O (1.77 g, 8.09 mmol) solution in 15 ml of MeOH under an inert gas atmosphere (N_2). The mixture was stirred at room temp. (1−2 h, completion of metallation was controlled by TLC). After the addition of CH_2Cl_2 (80 ml) the organic layer was subsequently extracted with water (4 × 150 ml) and brine (1 × 50 ml), dried (Na_2SO_4), filtered, and evaporated. Further purification was not necessary. The zinc complex **5a**, **b** was obtained as bright red crystals, m. p. 230−231°C decomp., yield 1.08 g (98%) − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.95−3.20 (m, 10 H, $13^2/17^2$-CH_2, CH_3), 3.35−3.41 (m, 6 H, CH_3), 3.63, 3.67 (s, 6 H, OCH_3), 4.03−4.17 (t, 4 H, $13^1/17^1$-CH_2), 8.43, 8.58, 8.98, 9.05, 9.09 9.70, 9.75, 9.84, 9.85, 9.88, 9.99, 10.03 (s, 4 H, $H_{β\text{-}pyr}$, H_{meso}). − UV/Vis: $λ_{max}$ (lg ε) = 410 nm (5.517), 540 (4.297), 578 (4.151). − FAB-MS (nitrobenzyl alcohol): *m/z* (%): 680.07 (100) [M^+, ^{64}Zn, ^{81}Br].

Zinc(II)−3,8-Dibromodeuteroporphyrin-IX Dimethyl Ester (**4**): The metallation was carried out as described above starting from the 3,8-dibromodeuteroporphyrin-IX dimethyl ester (**1**) (2.55 g, 3.66 mmol), zinc acetate × 2 H_2O (4.02 g, 18.3 mmol) in a solvent mixture of CH_2Cl_2/MeOH (1:1, 160 ml) to give the zinc complex **4** as bright red cyrstals, m. p. 279−280°C, yield 2.66 g (96%). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.98−3.09 (m, 7 H, $13^2/17^2$-CH_2, CH_3), 3.19−3.26 (m, 6 H, CH_3), 3.38 (s, 3 H, CH_3), 3.64 (s, 6 H, CH_3), 9.93−4.25 (m, 4 H, $13^1/17^1$-CH_2), 8.48, 8.66, 8.89, 9.00 (4s, 4 H, H_{meso}).

General Procedure for the Synthesis of the Styrene and Styrene-Derivatives Functionalized Porphyrin Monomers: A solution of mono- or dibromodeuteroporphyrin-IX dimethyl ester−zinc(II) (0.3−0.5 mmol), K_2CO_3 (1.5−2.5 mmol), tetra-*n*-butylammonium bromide (0.3−0.5 mmol), LiCl (0.3−0.5 mmol), palladium(II) acetate (5−10 mol-%), and styrene derivative (0.4−1.2 mmol) in anhydrous DMF (10−20 ml) was heated at 90°C under an inert gas atmosphere (argon) for 8−15 h. After cooling the solution to room temp. CH_2Cl_2 (150 ml) was added and the organic layer was extracted with water (4 × 200 ml), dried (Na_2SO_4), filtered, and evaporated. The crude product was purified by chromatography on silica gel using an elution mixture of CH_2Cl_2/methanol (100:1).

Zinc(II)−(E,E)-3,8-Bis(α-styryl)deuteroporphyrin-IX Dimethyl Ester (**6**): The reaction was carried out with zinc(II)−3,8-dibromodeuteroporphyrin-IX dimethyl ester (**4**) (342 mg, 0.45 mmol), K_2CO_3 (311 mg, 2.25 mmol), tetra-*n*-butylammonium bromide (145 mg, 0.45 mmol), LiCl (19 mg, 0.45 mmol), $Pd(OAc)_2$ (5.1 mg, 5 mol-%), styrene (0.13 ml, 1.13 mmol), and 15 ml of DMF following the procedure described above. (reaction time 12 h). Chromatographic separation gave 316 mg (87%) of a green solid, m. p. 268−271°C decomp. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.29 (t, 4 H, *J* = 8.18 Hz, $13^2/17^2$-CH_2), 3.61−3.77 (m, 18 H, CH_3), 4.41 (t, 4 H, *J* = 8.18 Hz, $13^1/17^1$-CH_2), 7.49 (d, 2 H, *J* = 7.30 Hz, $CH_{aryl,\ para}$), 7.61 (dd, 4 H, *J* = 7.30, 7.34, $CH_{aryl,\ meta}$) 7.74 (d, 2 H, *J* = 16.32 Hz, AB-CH_{vinyl}), 7.97 (d, 4 H, *J* = 7.34 Hz, $CH_{aryl,\ ortho}$), 8.65 (d, 2 H, *J* = 16.32 Hz, AB-CH_{vinyl}), 10.03, 10.08, 10.20, 10.23 (s, 4 H, H_{meso}). − UV/Vis: $λ_{max}$ (lg ε) = 411 nm (5.227), 542 (3.701), 585 (4.038).

Zinc(II)−(E)-3(8)-α-Styryldeuteroporphyrin-IX Dimethyl Ester (**7**): The reaction was carried out with zinc(II)−3(8)-bromodeuteroporphyrin-IX dimethyl ester (**5**) (204 mg, 0.3 mmol), K_2CO_3 (208 mg, 1.5 mmol), tetra-*n*-butylammonium bromide (97 mg, 0.3 mmol), LiCl (13 mg, 0.3 mol), $Pd(OAc)_2$ (7 mg, 10 mol-%), styrene (0.042 ml, 0.38 mmol), and 10 ml of DMF following the procedure described above. (reaction time 8 h). Chromatographic separation gave 177 mg (84%, pure regioisomer) of a green solid, m. p. 248−251°C decomp. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.90−2.98 (m, 4 H, $13^2/17^2$-CH_2), 3.03, 3.07 (2s, 6 H, CH_3), 3.32, 3.36 (2s, 6 H, CH_3), 3.64, 3.68 (2s, 6 H, CH_3), 3.96 (t, 2 H, *J* = 7.37 Hz, $13^1/17^1$-CH_2), 4.11 (t, 2 H, *J* = 7.55 Hz, $13^1/17^1$-CH_2), 7.02 (d, 1 H, *J* = 15.93 Hz, AB-CH_{vinyl}), 7.39−7.42 (m, 3 H, CH_{aryl}), 7.58−7.60 (m, 1 H, CH_{aryl}) 7.64 (d, 1 H, *J* = 15.93 Hz, AB-CH_{vinyl}), 8.32 (s, 1 H, $H_{β\text{-}pyr}$), 8.40, 8.86, 8.89, 8.96 (s, 4 H, H_{meso}). − UV/Vis: $λ_{max}$ (lg ε) = 409 nm (5.198), 538 (3.670), 581 (4.015). − FAB-MS (nitrobenzyl alcohol): *m/z* (%): 702.23 (65) [M^+, ^{64}Zn]. − $C_{40}H_{38}N_4O_4Zn$ (704.15): calcd. C 68.23, H 5.44, N 7.96; C 67.78, H 5.28, N 7.88.

(E,E)-3,8-Bis(α-styryl)deuteroporphyrin-IX Dimethyl Ester (**6-Zn**): The demetallation of the porphyrin−zinc complex **6** (241 mg, 0,3 mmol) was carried out in a CH_2Cl_2 solution (80 ml) which was vigorously stirred with a 4 N HCl solution (30 ml) for 0.5−1 h (TLC control). Then water was added (50 ml) and the organic layer was extracted with saturated $NaHCO_3$ solution (2 × 30 ml), water (1 × 30 ml), dried ($MgSO_4$), filtered, and evaporated under reduced pressure. The demetallated product was obtained as a dark purple solid, m. p. 262−265°C decomp. (ref.[22] 264−267°C), yield 216 mg (97%). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.26 (t, 4 H, *J* = 7.51 Hz, $13^2/17^2$-CH_2), 3.55−3.60 (m, 9 H, CH_3), 3.67 (s, 9 H, CH_3), 3.37 (t, 4 H, *J* = 7.51 Hz, $13^1/17^1$-CH_2), 7.48 (d, 2 H, *J* = 7.36 Hz, $CH_{aryl,\ para}$), 7.60 (dd, 4 H, *J* = 7.36, 6.98, $CH_{aryl,\ meta}$) 7.93 (d, 4 H, *J* = 6.98 Hz, $CH_{aryl,\ ortho}$), 8.51 (d, 2 H, *J* = 16.50 Hz, AB-CH_{vinyl}), 8.56 (d, 2 H, *J* = 16.50 Hz, AB-CH_{vinyl}), 9.94, 9.96, 10.03, 10.08 (s, 4 H, H_{meso}). − UV/Vis: $λ_{max}$ (lg ε) = 406 nm (5.243), 512 (4.354), 550 (4.396), 580 (4.207), 638 (4.146).

(E)-3(8)-α-Styryldeuteroporphyrin-IX Dimethyl Ester (**7-Zn**): The demetallation of compound **7** (140 mg, 0.2 mmol) follows the procedure desribed above. The reaction yielded 125 mg (98%, pure regioisomer) of a dark purple solid, m. p. 243−245°C decomp. −

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.24−3.32 (t, 4 H, *J* = 7.44 Hz, $13^2/17^2$-CH_2), 3.61−3.76 , 3.07 (m, 18 H, CH_3), 4.36−4.48 (m, 4 H, $13^1/17^1$-CH_2), 4.11 (t, 2 H, *J* = 7.55 Hz, $13^1/17^1$-CH_2), 7.02 (d, 1 H, *J* = 15.93 Hz, AB-CH_{vinyl}), 7.49 (d, 1 H, *J* = 7.43 Hz, $CH_{aryl,\ para}$), 7.62 (dd, 2 H, *J* = 7.43, 7.41, $CH_{aryl,\ meta}$) 7.72 (d, 1 H, *J* = 16.47 Hz, AB-CH_{vinyl}), 7.96 (d, 2 H, *J* = 7.41 Hz, $CH_{aryl,\ ortho}$), 8.64 (d, 1 H, *J* = 16.47 Hz, AB-CH_{vinyl}), 9.10 (s, 1 H, $CH_{β\text{-}pyr}$), 10.05, 10.12, 10.15, 10.27 (s, 4 H, CH_{meso}). − UV/Vis: $λ_{max}$ (lg ε) = 402 nm (5.213), 503 (4.245), 537 (4.316), 575 (4.189), 624 (4.022).

Synthesis of the Styrene Derivatives for the Heck-Coupling Reactions 1,4-Divinylbenzol (**8**)[27]: Methyltriphenylphosphonium bromide (15.72 g, 44 mmol), K_2CO_3 (7 g, 51 mmol), water (0.6 ml), and dioxane (40 ml) are added to terephthaldialdehyde (2.68 g, 20 mmol). The reaction mixture was heated to reflux for 15 h under an inert gas atmosphere (N_2). After cooling to room temp. CH_2Cl_2 (80 ml) was added and the organic layer was extracted with water (3 × 100 ml), dried (Na_2SO_4), filtered, and evaporated under reduced pressure. The crude product mixture was chromatographied on silica gel with petroleum ether to give 2.0 g (77%) of a colorless liquid. − ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ = 5.23 (dd, 2 H, *J* = 10.85 Hz, *J* = 0.88 Hz, H_A), 5.73 (dd, 2 H, *J* = 17.63 Hz, *J* = 0.88 Hz, H_B), 6.69 (dd, 2 H, *J* = 10.85 Hz, *J* = 17.63 Hz, H_X), 7.35 (s, 4 H, CH_{aryl}). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 114.29 (t, $CH_{2,\ vinyl}$), 126.69 (d, CH_{aryl}), 136.93 (d, CH_{vinyl}), 137.56 (s, C_{aryl}).

1,3-Divinylbenzol[34]: The reaction was carried out as described above, using isophthalaldehyde instead of terephthalaldehyde, to give 1.95 g (75%) of a colorless liquid. − ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ = 5.24 (dd, 2 H, *J* = 10.90 Hz, *J* = 0.82 Hz, H_A), 5.75 (dd, 2 H, *J* = 17.61 Hz, *J* = 0.82 Hz, H_B), 6.70 (dd, 2 H, *J* = 10.88 Hz, *J* = 17.61 Hz, H_X), 7.19−7.31 (m, 3 H, CH_{aryl}), 7.42 (s, 1 H, CH_{aryl}). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 114.53 (t, $CH_{2,\ vinyl}$), 124.70 (d, CH_{aryl}), 126.06 (d, 2 × CH_{aryl}), 129.15 (d, CH_{aryl}), 137.16 (d, CH_{vinyl}), 138.24 (s, C_{aryl}).

1,2-Divinylbenzol[29]: A 1.6 M butyllithium solution (7.5 ml, 17.2 mmol) was added to methyltriphenylphosphonium bromide (6.15 g, 17.2 mmol) in 40 ml of anhydrous diethyl ether under an inert gas atmosphere, and the mixture was stirred for 1 h at room temp. Then a solution of phthaldialdehyde (1.15 g, 8.6 mmol) in diethyl ether (20 ml) was added dropwise and the reaction mixture was stirred for 1 h. Diethyl ether (40 ml) was added and the organic layer was extracted with water (3 × 100 ml), dried (Na_2SO_4), filtered, and evaporated under reduced pressure. Chromatography of the crude product on silica gel using petroleum ether as eluent gives 0.41 g (37%) of a colorless liquid. − ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ = 5.35 (dd, 2 H, *J* = 10.98 Hz, *J* = 1.40 Hz, H_A), 5.54 (dd, 2 H, *J* = 17.42 Hz, *J* = 1.40 Hz, H_B), 7.01 (dd, 2 H, *J* = 10.98 Hz, *J* = 17.42 Hz, H_X), 7.31−7.22 (m, 2 H, CH_{aryl}), 7.50−7.43 (m, 2 H, CH_{aryl}). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 116.56 (t, $CH_{2,\ vinyl}$), 126.88 (d, CH_{aryl}), 128.44 (d, CH_{aryl}), 135.21 (d, CH_{vinyl}), 135.34 (s, C_{aryl}).

1,3,5-Trivinylbenzene[35]: A solution of 1,3,5-tribromobenzene (315 mg, 1 mmol), LiCl (25 mg, 0.6 mmol), tetrakistriphenylphosphanpalladium(0) (69 mg, 6 mol-%), and vinyltributylstannane (0.96 ml, 3.3 mmol) in 10 ml of anhydrous dioxane was heated at 100°C for 15 h. After cooling the reaction mixture to room temp. CH_2Cl_2 (75 ml) was added and the organic layer was extracted with water (4 × 50 ml), dried (Na_2SO_4), filtered, and evaporated under reduced pressure. The crude product was purified by chromatography on silica gel with petroleum ether as eluent. The product was obtained as a colorless liquid, yield 0.14 g (92%). − ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ = 5.28 (d, 3 H, *J* = 10.87 Hz, H_A), 5.88 (d, 3 H, *J* = 17.55 Hz, H_B), 6.72 (dd, 3 H, *J* = 10.87 Hz, *J* = 17.55 Hz, H_X), 7.34 (s, 3 H, CH_{aryl}). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 114.76 (t, $CH_{2,\ vinyl}$), 124.02 (d, CH_{aryl}), 137.00 (d, CH_{vinyl}), 138.43 (s, C_{aryl}).

General Procedure for the Synthesis of the Divinylbenzene-Linked Zinc(II)−Deuteroporphyrin-IX Dimethyl Ester Derivatives: A solution of zinc(II)−3(8)-bromodeuteroporphyrin-IX dimethyl ester (**5**) (306 mg, 0.45 mmol), K_2CO_3 (312 mg, 2.25 mmol), tetra-n-butylammonium bromide (145 mg, 0.45 mmol), LiCl (19 mg, 0.45 mmol), palladium(II) acetate (10 mg, 10 mol-%), and divinylbenzene (29 mg, 0.225 mmol) in 15 ml of anhydrous DMF was heated at 85°C for 8−15 h under an inert gas atmosphere. After cooling the solution to room temp. CH_2Cl_2 (150 ml) was added and the organic layer was extracted with water (4 × 200 ml), dried (Na_2SO_4), filtered, and evaporated. The crude product was purified by chromatography on silica gel using an elution mixture of CH_2Cl_2/methanol (100:1) and CH_2Cl_2/methanol (30:1) to remove monomeric components. The desired dimeric porphyrin was eluted with CH_2Cl_2/THF (30:1).

(E,E)-β,β′-Bis[zinc(II)−deuteroporphyrin-IX dimethyl ester-3(8)-yl]-1,4-divinylbenzene (**9**): The porphyrin dimer **9** was obtained from bromoporphyrin **5** and 1,4-divinylbenzene, following the general procedure described above, as a dark green solid; m. p. >300°C, yield 217 mg (73%, pure regioisomer). The divinylbenzene-substituted porphyrin **10** was also formed, yield 73 mg (22%). − ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 3.30−3.33 (m, 8 H, $13^2/17^2$-CH_2), 3.60−3.95 (m, 36 H, $CH_{3,\ pyr}$, $COOCH_3$), 4.38−4.40 (m, 8 H, $13^1/17^1$-CH_2), 8.01 (d, *J* = 16.3 Hz, 2 H, AB-CH_{vinyl}), 8.36−8.38 (m, 4 H, CH_{aryl}), 9.17−9.23 [m, 4 H, AB-CH_{vinyl}, 3(8)-$CH_{β\text{-}pyr}$], 10.09−10.13 (m, 4 H, CH_{meso}), 10.25 (s, 2 H, CH_{meso}), 10.48−10.50 (s, 2 H, CH_{meso}). − ^{13}C NMR (50 MHz, [D_6]DMSO): δ = 12.26, 12.37, 14.35, 14.53 (q, $CH_{3,\ pyr.}$), 22.37 (t, $13^1/17^1$-CH_2), 37.77, (t, $13^2/17^2$-CH_2), 52.28 (q, OCH_3), 97.38, 98.59, 98.94 (d, CH_{meso}), 123.49 (d, CH_{vinyl}), 128.30 (d, CH_{aryl}), 130.53 (d, $CH_{β\text{-}pyr.}$), 134.14 (d, CH_{vinyl}), 137.42, 138.05, 138.70, 140.05, 140.20, 141.92, 148.36, 148.55, 138.66, 148.90, 149. 21 (s, C_{ring}), 173.97 (s, CO_2CH_3). − UV/Vis (CH_2Cl_2): $λ_{max}$ (lg ε) = 595 (4.771), 549 (4.603), 413 (5.161), FAB-MS (nitrobenzyl alcohol): *m/z* (%): 1327.92 (4) [M^+, ^{64}Zn]. − $C_{74}H_{70}N_8O_8Zn_2$ (1330.18): calcd. C 66.82, H 5.30, N 8.42, found C 66.58, H 5.43, N 8.27.

Reaction of Zinc(II)−3(8)-Bromodeuteroporphyrin-IX Dimethyl Ester with 1,3-Divinylbenzene: The reaction of bromoporphyrin **5** with 1,3-divinylbenzene, following the general procedure described above, resulted in a mixture of the monomeric porphyrin **11** and the dimer **13**.

Zinc(II)−3(8)-[3-Vinyl-(E)-α-styryl]deuteroporphyrin-IX Dimethyl Ester (**11**): The porphyrin **11** was obtained as a green solid, m. p. 201−203 C decomp., yield 103 mg (31%, mixture of regioisomers). − ^{1}H NMR (200 MHz, $CDCl_3$, TMS): *δ* = 3.17 (t, 4 H, *J* = 7.51 Hz, $13^2/17^2$-CH_2), 3.42−3.64 (m, 18 H, $CH_{3,\ pyr}$), 4.18−4.29 (m, 4 H, $13^1/17^1$-CH_2), 5.42 (d, 1 H, *J* = 10.91 Hz, ABX-CH_{vinyl}), 5.98 (d, 1 H, *J* = 17.55 Hz, ABX-CH_{vinyl}), 6.94 (d, 1 H, *J* = 10.91 Hz, *J* = 17.55, ABX-CH_{vinyl}), 7.47−7.57 (m, 3 H, CH_{aryl}, AB-CH_{vinyl}), 7.82 (d, 1 H, *J* = 6.96 Hz, CH_{aryl}) 7.89 (s, 1 H, CH_{aryl}), 8.39, 8.45 (d, 1 H, *J* = 16.38 Hz, AB-CH_{vinyl}), 8.77, 8.74 [s, 1 H, 3(8)-$CH_{β\text{-}pyr}$], 9.40, 9.48, 9.52, 9.59, 9.61, 9.63, 9.69, 9.77 (s, 4 H, CH_{meso}). − UV/Vis (CH_2Cl_2): $λ_{max}$ (lg ε) = 404 (5.387), 535 (4.145), 572 (4.234). − FAB-MS (nitrobenzyl alcohol): *m/z* (%): 728.19 (23) [M^+, ^{64}Zn]. − $C_{42}H_{40}N_4O_4Zn$ (730.18): calcd. C 69.09, H 5.52, N 7.67, found C 68.94, H 5.44, N 7.83.

(E,E)-β,β′-Bis[zinc(II)−deuteroporphyrin-IX dimethyl ester-3(8)-yl]-1,3-divinylbenzene (**13**): The dimer **13** was obtained as a

dark green solid, m. p. >300°C, yield 152 mg (51%, mixture of regioisomers). – ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 3.24–3.42 (m, 8 H, 13^2/17^2-CH$_2$), 3.57–3.75 (m, 36 H, CH$_{3\ pyr}$, COOCH$_3$), 4.27–4.53 (m, 8 H, 13^1/17^1-CH$_2$), 7.80–7.88 (m, 1 H, CH$_{vinyl}$), 8.05 (d, 2 H, *J* = 16.52 Hz, CH$_{vinyl}$), 8.24 (d, 2 H, *J* = 8.35 Hz, CH$_{aryl}$), 9.34 (s, 1 H, CH$_{aryl}$), 9.22–9.34 [m, 4 H, CH$_{vinyl}$, 3(8)-CH$_{β\text{-}pyr}$], 10.12–10.17 (m, 4 H, CH$_{meso}$), 10.26 (s, 2 H, CH$_{meso}$), 10.49 (s, 2 H, H$_{meso}$). – ^{13}C NMR (50 MHz, [D$_6$]DMSO): δ = 12.31, 12.54, 14.28, 14.57 (q, CH$_{3,\ pyr}$), 22.36 (t, 13^1/17^1-CH$_2$), 37.78, (t, 13^2/17^2-CH$_2$), 52.28 (q, OCH$_3$), 97.64, 98.44, 98.95, 102.02 (d, CH$_{meso}$), 123.99 (d, CH$_{vinyl}$), 125.71, 126.37, 126.99 (d, CH$_{aryl}$), 130.47, 130.86 (d, CH$_{β\text{-}pyr}$), 134.55 (d, CH$_{vinyl}$), 137.68 (d, CH$_{aryl}$), 137.34, 138.10, 138.63, 139.50, 139.87, 140.06, 140.57, 141.29, 147.79, 148.31, 148.64, 148.95, 149.95 (s, C$_{ring}$), 173.98 (s, CO$_2$CH$_3$). – UV/Vis (CH$_2$Cl$_2$): λ$_{max}$ (lg ε) = 408 (5.421), 544 (4.216), 585 (4.234). – FAB-MS (nitrobenzyl alcohol): *m/z* (%): 1330.38 (2) [M$^+$]. – C$_{74}$H$_{70}$N$_8$O$_8$Zn$_2$ (1330.18): calcd. C 66.82, H 5.30, N 8.42, found C 66.58, H 5.23, N 8.27.

Reaction of Zinc(II)–3(8)-Bromodeuteroporphyrin-IX Dimethyl Ester with 1,2-Divinylbenzene: The reaction of the bromoporphyrin **5** with 1,2-divinylbenzene, following the general procedure described above, resulted in a mixture of the monomeric porphyrin **12** and the dimer **14**.

Zinc(II)–3(8)-[2-Vinyl-(E)-α-styryl]deuteroporphyrin-IX Dimethyl Ester (**12**): The porphyrin **12** was obtained as a green solid, m. p. 204°C decomp., yield 105 mg (32%, mixture of regioisomers). – ^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.02 (t, 4 H, *J* = 7.82 Hz, 13^2/17^2-CH$_2$), 3.14–3.26 (m, 9 H, CH$_{3,\ pyr}$), 3.41 (s, 3 H, CH$_{3,\ pyr}$), 3.65–3.67 (m, 6 H, COOCH$_3$), 4.05 (t, 4 H, *J* = 7.82 Hz, 13^1/17^1-CH$_2$), 5.57 (d, 1 H, *J* = 10.97 Hz, ABX-CH$_{vinyl}$), 5.92 (d, 1 H, *J* = 17.31 Hz, ABX-CH$_{vinyl}$), 7.42 (d, 1 H, *J* = 10.97 Hz, *J* = 17.31, ABX-CH$_{vinyl}$), 7.53 (d, 1 H, *J* = 7.39 Hz, CH$_{aryl}$), 7.61–7.76 (m, 2 H, CH$_{aryl}$, AB-CH$_{vinyl}$), 7.74 (d, 1 H, *J* = 7.68 Hz, CH$_{aryl}$), 7.85 (d, 1 H, *J* = 16.25 Hz, AB-CH$_{vinyl}$), 8.07 (d, 1 H, *J* = 7.68 Hz, CH$_{aryl}$), 8.38 [s, 1 H, 3(8)-CH$_{β\text{-}pyr}$], 8.84, 8.96, 9.00, 9.08 (s, 4 H, H$_{meso}$).– UV/Vis (CH$_2$Cl$_2$): λ$_{max}$ (lg ε) = 406 (5.183), 537 (4.062), 575 (4.177). – FAB-MS (nitrobenzyl alcohol): *m/z* (%): 728.12 (24) [M$^+$,^{64}Zn]. – C$_{42}$H$_{40}$N$_4$O$_4$Zn (730.18): calcd. C 69.09, H 5.52, N 7.67; found C 68.87, H 5.36, N 7.59.

(E,E)-β,β′-Bis[zinc(II)–deuteroporphyrin-IX dimethyl ester-3(8)-yl]-1,2-divinylbenzene (**14**): The dimer **14** was obtained as a dark green solid, m. p. > 300°C, yield 143 mg (48%, mixture of regioisomers). – ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 3.26–3.34 (m, 8 H, 13^2/17^2-CH$_2$), 3.47–3.70 (m, 36 H, CH$_{3,\ pyr}$, COOCH$_3$), 4.04–4.33 (m, 8 H, 13^1/17^1-CH$_2$), 7.69–7.80 (m, 2 H, CH$_{vinyl}$), 8.36–8.58 (m, 4 H, CH$_{aryl}$), 8.95–9.11 [m, 4 H, CH$_{vinyl}$, 3(8)-CH$_{β\text{-}pyr}$], 9.91–10.05 (m, 6 H, CH$_{meso}$), 10.37 (s, 2 H, CH$_{meso}$). – UV/Vis (CH$_2$Cl$_2$): λ$_{max}$ (lg ε) = 404 (5.254), 542 (4.140), 578 (4.243). – FAB-MS (nitrobenzyl alcohol): *m/z* (%): 1330.36 (5) [M$^+$, ^{64}Zn]. – C$_{74}$H$_{70}$N$_8$O$_8$Zn$_2$ (1330.18): calcd. C 66.82, H 5.30, N 8.42, found C 66.63, H 5.18, N 8.24.

Reaction with 1,4-Divinylbenzene to Form Monomeric Porphyrin-Building Blocks Zinc(II)–3,8-Bis(4-vinyl-(E)-α-styryl)deuteroporphyrin-IX Dimethyl Ester **(15):** The reaction was carried out with zinc(II)–3,8-dibromodeuteroporphyrin-IX dimethyl ester (**4**) (380 mg, 0.5 mmol), K$_2$CO$_3$ (345 mg, 2.5 mmol), tetra-*n*-butylammonium bromide (161 mg, 0.5 mmol), LiCl (21 mg, 0.5 mmol), Pd(OAc)$_2$ (11 mg, 10 mol-%), 1,4-divinylbenzene (156 mg, 1.2 mmol) and 20 ml of DMF following the procedure described above. (reaction time 15 h). Chromatographic separation gave 246 mg (57%) of a green solid, m. p. 213–215°C decomp. – ^{1}H NMR (200 MHz, CDCl$_3$, TMS): δ = 2.86–3.25 (m, 16 H, 13^2/17^2-CH$_2$, CH$_{3,\ pyr}$), 3.63–3.66 (m, 6 H, COOCH$_3$), 3.96–4.04 (m, 4 H, 13^1/17^1-CH$_2$), 5.44 (d, 2 H, *J* = 11.27 Hz, ABX-CH$_{vinyl}$), 5.99 (d, 2 H, *J* = 17.55 Hz, ABX-CH$_{vinyl}$), 6.95 (d, 2 H, *J* = 11.27 Hz, *J* = 17.55, ABX-CH$_{vinyl}$), 7.33 (d, 2 H, *J* = 15.97 Hz, AB-CH$_{vinyl}$), 7.70 (d, 4 H, *J* = 8.04 Hz, CH$_{aryl}$), 7.88 (d, 4 H, *J* = 8.04 Hz, CH$_{aryl}$), 8.04 (d, 1 H, *J* = 15.97 Hz, AB-CH$_{vinyl}$), 8.67, 8.76, 8.86, 8.95 (s, 4 H, CH$_{meso\text{-}pyr}$).– UV/Vis (CH$_2$Cl$_2$): λ$_{max}$ (lg ε) = 328 (4.498), 406 (5.305), 542 (4.189), 582 (4.365). – FAB-MS (nitrobenzyl alcohol): *m/z* (%):856.31 (4) [M$^+$]. – C$_{52}$H$_{48}$N$_4$O$_4$Zn (858.35): calcd. C 72.76, H 5.64, N 6.53, found C 72.45, H 5.48, N 6.31.

Zinc(II)–3(8)-(4-Vinyl-(E)-α-styryl)deuteroporphyrin-IX Dimethyl Ester (**10**): The reaction was carried out with zinc(II)–3(8)-bromodeuteroporphyrin-IX dimethyl ester (**5**) (306 mg, 0.43 mmol), K$_2$CO$_3$ (297 mg, 2.15 mmol), tetra-*n*-butylammonium bromide (139 mg, 0.43 mmol), LiCl (18 mg, 0.43 mol), Pd(OAc)$_2$ (10 mg, 10 mol-%), 1,4-divinylbenzene (168 mg, 1.3 mmol), and 20 ml of DMF following the procedure described above. (reaction time 12 h). Chromatographic separation gave 209 mg (67%, pure regioisomer) of a green solid, m. p. 205–207°C decomp. – ^{1}H NMR (200 MHz, CDCl$_3$, TMS): δ = 3.01 (t, 4 H, *J* = 7.55 Hz, 13^2/17^2-CH$_2$), 3.19–3.28 (m, 6 H, CH$_{3,\ pyr}$), 3.43 (s, 3 H, CH$_{3,\ pyr}$), 3.60–3.66 (m, 9 H, CH$_{3,\ pyr}$, COOCH$_3$), 4.05 (t, 4 H, *J* = 7.55 Hz, 13^1/17^1-CH$_2$), 5.37 (d, 1 H, *J* = 11.25 Hz, ABX-CH$_{vinyl}$), 5.92 (d, 1 H, *J* = 17.83 Hz, ABX-CH$_{vinyl}$), 6.89 (d, 1 H, *J* = 11.25 Hz, *J* = 17.83, ABX-CH$_{vinyl}$), 7.38 (d, 1 H, *J* = 16.10 Hz, AB-CH$_{vinyl}$), 7.65 (d, 2 H, *J* = 8.23 Hz, CH$_{aryl}$), 7.87 (d, 2 H, *J* = 8.23 Hz, CH$_{aryl}$), 8.14 (d, 1 H, *J* = 16.10 Hz, AB-CH$_{vinyl}$), 8.44 [s, 1 H, 3(8)-CH$_{β\text{-}pyr}$], 8.99, 9.07, 9.10, 9.17 (s, 4 H, CH$_{meso}$). – ^{13}C NMR (50 MHz, CDCl$_3$): δ = 11.43, 11.62, 12.33, 13.26 (q, CH$_{3,\ pyr}$), 21.55 (t, 13^1/17^1-CH$_2$), 37.06, 37.20 (t, 13^2/17^2-CH$_2$), 52.11 (q, OCH$_3$), 95.01, 95.62, 96.09, 99.14 (d, CH$_{meso}$), 114.06 (t, CH$_{2,\ vinyl}$), 121.49, 121.84 (d, 2× CH$_{vinyl}$), 126.99, 127.19 (d, 2× CH$_{aryl}$) 128.20 (s, CH$_{β\text{-}pyr}$), 131.68 (d, CH$_{vinyl}$), 137.21 (d, CH$_{vinyl}$), 141.90, 143.55, 144.73, 144.95, 145.15, 145.37, 145.48, 145.61, 145.81, 145.91, 146.36, 146.49 (s, C$_{ring}$), 173.91, 174.01 (s, CO$_2$CH$_3$). – UV/Vis (CH$_2$Cl$_2$): λ$_{max}$ (lg ε) = 403 (5.447), 534 (4.180), 572 (4.294). – FAB-MS (nitrobenzyl alcohol): *m/z* (%): 728.22 (18) [M$^+$]. – C$_{42}$H$_{40}$N$_4$O$_4$Zn (730.18): calcd. C 69.09, H 5.52, N 7.67, found C 68.94, H 5.36, N 7.89.

Bis[(E)-4-{1-[zinc(II)–deuteroporphyrin-IX dimethyl ester-3(8)-yl]ethen-2-yl}-(E)-α-styryl]-3,8-zinc(II)–deuteroporphyrin-IX Dimethyl Ester **(16):** A solution of zinc(II)–3(8)-[4-vinyl-(*E*)-α-styryl]deuteroporphyrin-IX dimethyl ester (**10**) (140 mg, 0.19 mmol), zinc(II)–3,8-dibromodeuteroporphyrin-IX dimethyl ester (**4**) (70 mg, 0.09 mmol), K$_2$CO$_3$ (138 mg, 1 mmol), tetra-*n*-butylammonium bromide (64 mg, 0.2 mmol), LiCl (8 mg, 0.2 mmol), and palladium(II) acetate (4.5 mg, 0.02 mmol) in 10 ml of anhydrous DMF was heated at 85°C for 24 h under an inert gas atmosphere (argon). After cooling the solution to room temp. CH$_2$Cl$_2$ (100 ml) was added and the organic layer was extracted with water (4 × 150 ml), dried (Na$_2$SO$_4$), filtered, and evaporated. To remove the small amount of starting material the residue was heated twice [with 10 ml of CH$_2$Cl$_2$/hexane (3:1) with 1% methanol] to reflux and was decanted after cooling to room temp. The trimeric porphyrin **16** was obtained as a dark green solid, m. p. > 300°C, yield 154 mg (83%, pure regioismer). – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 3.20–3.40 (m, 12 H, 13^2/17^2-CH$_2$), 3.60–4.03 (m, 54 H, CH$_{3,\ pyr}$, COOCH$_3$), 4.22–4.63 (m, 12 H, 13^1/17^1-CH$_2$), 7.97–8.08 (m, 4 H, AB-CH$_{vinyl}$), 8.32–8.43 (m, 8 H, H$_{aryl}$), 9.13–9.28 [m, 6 H, AB-CH$_{vinyl}$, 3(8)-CH$_{β\text{-}pyr}$], 10.03–10.28 (m, 8 H, CH$_{meso}$), 10.40–10.55 (m, 4 H, CH$_{meso}$). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 12.33, 13.85, 14.33, 14.53 (q, CH$_{3,\ pyr}$), 21.83, 22.34 (t, 13^1/17^1-CH$_2$), 37.70, 37.79 (t, 13^2/17^2-CH$_2$), 52.29 (q, OCH$_3$), 98.41, 99.14 (d,

CH_{meso}), 123.37 (d, CH_{vinyl}), 128.30 (d, CH_{aryl}), 129.66 (d, $CH_{\beta\text{-pyr}}$), 130.51 (d, CH_{vinyl}), 137.09, 138.23, 138.37, 140.05, 148.34, 148.53, 148.65, 148.88, 149.17 (s, C_{ring}), 173.95 (s, CO_2CH_3).– UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 700 (3.668), 598 (4.517), 552 (4.391), 415 (5.462). – MALDI-MS [*t*-3-(3-indolyl)acrylic acid]: *m/z* (%): [2050.9] (100) [M^+, ^{64}Zn]. – $C_{116}H_{108}N_{12}O_{12}Zn_3$ (2058.34): calcd. C 67.7, H 5.3, N 8.2, found C 67.63, H 5.13, N 8.04.

(E,E,E)-β,β′,β″-Tri[zinc(II)–deuteroporphyrin-IX dimethyl ester-3(8)-yl]-1,3,5-trivinylbenzene (**17**): A solution of zinc(II)–3(8)-bromodeuteroporphyrin-IX dimethyl ester (**5**) (138 mg, 0.2 mmol), K_2CO_3 (138 mg, 1 mmol), tetra-*n*-butylammonium bromide (65 mg, 0.2 mmol), LiCl (9 mg, 0.2 mmol), palladium(II) acetate (5 mg, 10 mol-%), and 1,3,5-trivinylbenzene (10 mg, 0.067 mmol) in 10 ml of anhydrous DMF was heated at 90°C for 24 h under an inert gas atmosphere (argon). After cooling the solution to room temp. CH_2Cl_2 (100 ml) was added and the mixture was extracted with water (4 × 150 ml), dried (Na_2SO_4), filtered, and evaporated. The crude product was purified by chromatography on silica gel using an elution mixture of CH_2Cl_2/methanol (50:1) to remove the monomeric components. The desired trimeric porphyrin **17** was eluted with CH_2Cl_2/THF (50:1) as a deep purple solid, m.p. > 300°C, yield 73 mg (56%, pure regioisomer). – ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 3.23–3.43 (m, 12 H, $13^2/17^2$-CH_2), 3.51–4.10 (m, 54 H, $CH_{3,\ pyr}$, $OOCH_3$), 4.26–4.50 (m, 12 H, $13^1/17^1$-CH_2), 8.30 (d, 3 H, *J* = 16.5 Hz, -CH_{vinyl}), 8.98 (s, 3 H, CH_{aryl}), 9.27 (s, 3 H, $3^1/8^1$-$H_{\beta\text{-pyr}}$), 9.57 (d, 3 H, *J* = 16.5 Hz, AB-CH_{vinyl}), 10.11–10.16 (m, 6 H, H_{meso}), 10.32 (s, 3 H, H_{meso}), 10.65–10.69 (m, 3 H, H_{meso}). – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 589 (4.873), 547 (4.809), 510 (4.243), 413 (5.598). – MALDI-MS (gentisic acid): *m/z* (%): [1948.8] (100) [M^+, ^{64}Zn]. – $C_{108}H_{99}N_{12}O_{12}Zn_3$ (1953.19): calcd. C 66.41, H 5.11, N 8.61; found C 65.91, H 5.02, N 8.42.

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