

A Functionalized Spiro[chlorin-porphyrin]-Type ‘Dimer’ Dizinc Complex from Rapid [4 + 2] Self-cycloaddition of a Conjugated [β,β' -Bis(methylene)porphyrinato]zinc

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Thermal extrusion of SO₂ from β,β' -sulfolenoporphyrins is an effective method for *in situ* generation of β,β' -bis(methylene)porphyrin which remained unobserved in typical synthetic applications but underwent quickly efficient [4 + 2]-cycloaddition reactions with dienophiles. We now report the thermal extrusion of SO₂ from the symmetrical (tetra- β,β' -sulfolenoporphyrinato)zinc **1**·**Zn** in the absence of a dienophile (*Scheme*). In the event, the thermally *in situ* generated conjugated diene underwent a [4 + 2] self-cycloaddition, to give the [spirobi[tri- β,β' -sulfolenoporphyrinato]]dizinc **4**·**2Zn**. This chiral (racemic) spirobiporphyrinoid dizinc complex represents the combination of the closely positioned and interacting chromophores of a (porphyrinato)zinc and of a (β -methylene- β,β' -dihydroporphyrinato)zinc. It carries six sulfoleno moieties that are still available for further SO₂ extrusion and cycloaddition reactions.

Introduction. – Natural porphyrinoids, such as hemes, chlorophylls, corrins, and corphins, are ubiquitous pigments and probably Nature’s most versatile cofactors [1][2]. Porphyrins and chlorins have obtained special attention also as catalysts (see, e.g., [3]), as mimics for artificial ‘photo-reaction centers’ [4], and as well-structured building blocks in multi-porphyrin assemblies [5][6].

For the purpose of the synthesis of suitably functionalized porphyrins and chlorins, β,β' -sulfolenopyrroles [7], β,β' -sulfolenoporphyrins [8][9], and β,β' -sulfolenochlorins [10][11] were designed and used as thermal precursors of reactive dienes (*Fig. 1*) (sulfolene = 2,5-dihydrothiophene 1,1-dioxide). We have introduced the symmetrical tetra- β,β' -sulfolenoporphyrin (= 5,11,17,23-tetrakis[3,5-bis(1,1-dimethylethyl)phenyl]-7,9,13,15,19,21-hexahydro-1*H*,3*H*,25*H*,27*H*-tetrathieno[3,4-*b*:3',4'-*g*:3'',4''-*l*:3''',4'''-*q*]-phorphine 2,2,8,8,14,14,20,20-octaoxide; **1**·**2H**) as a versatile building block that carries four reactive sulfone groups, and which was applied for the synthesis of porphyrins carrying up to four fullerene units [12][13]. More recently, the Zn^{II} complex **1**·**Zn** was also used to generate a new type of ‘blackened’ porphyrins, by attaching up to four conjugated benzoquinone units at the pyrrolic β -positions [14].

The mono- β,β' -sulfolenoporphyrin **2** was synthesized by *Gunter* and co-workers and was tested in thermal reactions in the presence or absence of a dienophile [8][15]: Thermolysis of **2** gave the spiro[chlorinporphyrin]-type dimer **3** by [4 + 2]-self-cycloaddition of the elusive β,β' -bis(methylene)porphyrin that was generated from **2** by

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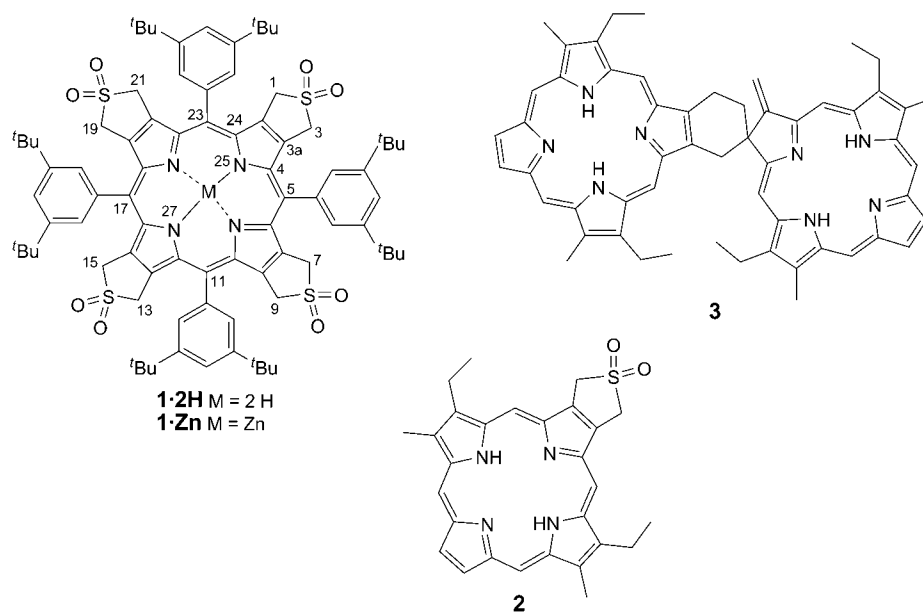


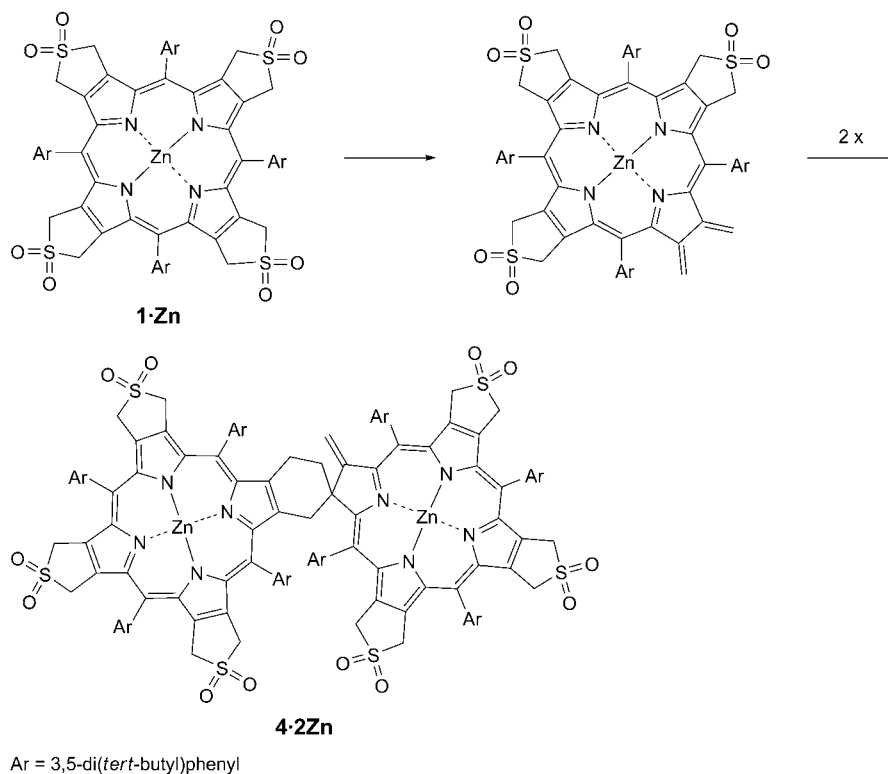
Fig. 1. Porphyrins **1·2H**, **1·Zn** (systematic atom numbering), and **2**, and spiro 'dimer' **3**

SO₂ loss. We have used the symmetrical tetra-β,β'-sulfolenoporphyrin **1·2H**, as well as several of its metal complexes (e.g., **1·Zn**) [12], as building blocks for the assembly of multi-modular porphyrinoid arrays [13]. To explore the reactivity of sterically hindered **1**, we have also set out on an investigation of the thermally accessible β,β'-bis(methylene)porphyrin itself, that could be generated by thermolysis of **1·Zn**. However, in the absence of an added dienophile, the thermally *in situ* generated (apparently strongly hindered) β,β'-bis(methylene)porphyrin derivatives did not accumulate in solution, and they 'dimerized' to a spiro[chlorin-porphyrin]-type compound, which carried six sulfoleno units ready for selective further transformations.

Results and Discussion. – *Preparation of Spiro[chlorin-porphyrin]-Type 'Dimer' Complex 4·2Zn.* Upon heating a solution of (tetra-β,β'-sulfolenoporphyrinato)zinc **1·Zn** in 1,2-dichlorobenzene at 140° for 2 h, ca. 30% of the starting material decomposed to give a major new compound, according to TLC analysis (*Scheme*). Separation of the mixture by prep. TLC allowed the recovery of 71% of **1·Zn** and yielded a major nonpolar green product, **4·2Zn**, isolated in ca. 17% yield (i.e., 59% based on the conversion of **1·Zn**). Several more polar fractions that may represent higher oligomers were not analyzed further.

The UV/VIS spectrum of the new green product **4·2Zn** exhibited distinctive features of a porphyrinoid compound. However, it displayed a split *Soret* band with two almost equally intense absorptions with maxima at 425 and 440 nm, which reflect the two interacting tetrapyrrole chromophores (*Fig. 2* and *Table 1*). Weaker absorption bands with maxima at 553 and 646 nm were also observed, which are characteristic for

Scheme. Synthesis of the Spiro[chlorin-porphyrin]-Type ‘Dimer’ complex **4·2Zn** via the [$\beta_4\beta'$ -Bis(methylene)porphyrinato]zinc, an Unobserved Reactive Intermediate Generated from **1·Zn** by Thermolytic SO_2 Extrusion



the superposition of chromophores of a porphyrinatozinc (e.g., **1·Zn**) and of a chlorinatozinc [16][17], respectively. Upon excitation at 553 or 647 nm, the solution of **4·2Zn** in CH_2Cl_2 exhibited strong fluorescence emission at 652 and 713 nm (Fig. 3).

The structure of the new compound **4·2Zn** was deduced from spectroscopic analysis as that of a dizinc complex of a spiro[chlorin-porphyrin]-type ‘dimer’. A FAB-MS of **4·2Zn** showed quasimolecular-ion peaks at m/z 2842.4–2848.4, corresponding to a molecular formula $\text{C}_{168}\text{H}_{200}\text{N}_8\text{O}_{12}\text{S}_6\text{Zn}_2$ (calc. 2841.22). The signals displayed an isotopic distribution characteristic of the presence of two zinc centers. The base peak was observed at m/z 2458–2463, due to loss of six SO_2 groups. Smaller signals were also found at m/z 2778–2784, from loss of one SO_2 unit. Further fragmentation into the two porphyrinoid ‘monomers’ was not indicated by the MS. The ^1H -NMR spectrum (500 MHz) of **4·2Zn** exhibited the pattern of an unsymmetric and complex compound. Signal assignments (Table 2, Fig. 4 and 5, a) were achieved with the help of extensive analyses by ^1H , ^1H -COSY, ROESY (Fig. 5, b and c), HSQC, and HMQC experiments. The H-atoms of the three CH_2 groups of the cyclohexene ‘bridge’ between the porphyrin and chlorin moieties could all be assigned individually: The ‘isolated’

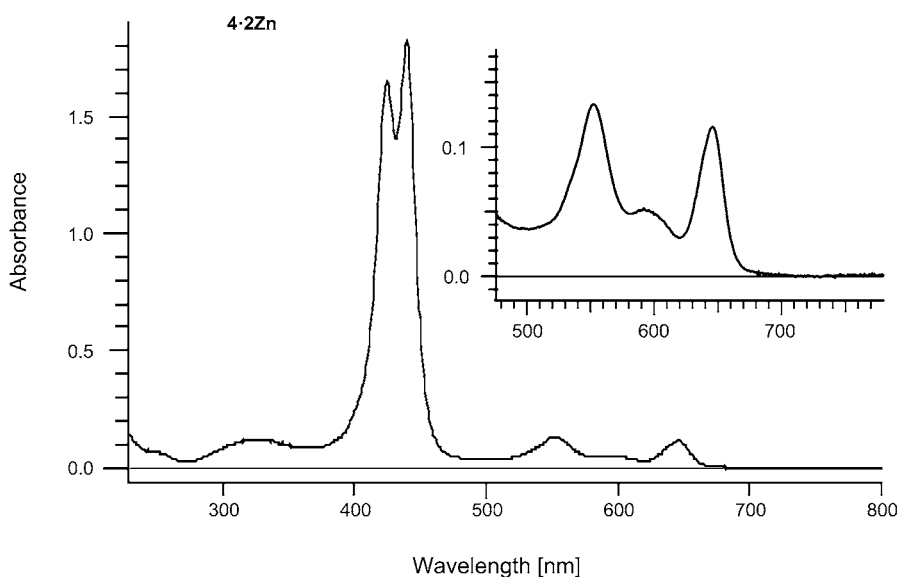


Fig. 2. UV/VIS Spectrum of spiro 'dimer' **4·2Zn** in CH_2Cl_2 ($c = 7.03 \cdot 10^{-6}$ M, CH_2Cl_2)

Table 1. Pertinent Values from Absorption Spectra (CH_2Cl_2 ; λ in nm) of the 'Monomer' **1·Zn** and the Spiro[chlorin-porphyrin]-Type 'Dimer' **4·2Zn**

	1·Zn	4·2Zn
Chlorin-type and Q bands	590, 549.5	646 ^a), 598, 553
Soret bands	424	440 ^a), 425
Other bands	326	325, 250

^a) Chlorin-type bands.

$\text{CH}_2(21)$ group appeared as an *AB* system at $\delta(\text{H})$ 2.82 and 4.20; the CH_2CH_2 group exhibited *m* at $\delta(\text{H})$ 1.92 and 2.08 ($\text{CH}_2(31)$), and at 2.78 and 2.94 ($\text{CH}_2(32)$). The exocyclic $\text{CH}_2(31')=\text{group}$ at the chlorin moiety gave rise to two *s* at $\delta(\text{H})$ 4.92 and 5.46, which coupled with a C-atom at $\delta(\text{C})$ 115.1. The signals of the 16 ^tBu groups appeared as 13 resolved signals at high field ($\delta(\text{H})$ 0.2–1.5). Likewise, the *meso*-aryl H-atoms were distributed between $\delta(\text{H})$ 6.15 and 7.95, with distinctive upfield shifts for most H-atoms of four aryl groups that were deduced to be near the linker site of the 'dimer'. The H-atoms of all of these four aryl groups showed strong intra-group NOE's, allowing for their assignment to a particular aromatic substituent. The 3,5-di(*tert*-butyl)phenyl group assigned as that at the 20-position of the porphyrin moiety had most strongly shifted signals and showed two high-field *s* at $\delta(\text{H})$ 0.21 (Me(2052)) and 0.54 (Me(2032)) for the ^tBu groups, and three low-field resonances at 7.24 (H–C(206)), 6.15 (H–C(204)), and 7.75 (H–C(202)) for the aromatic H-atoms in *ortho*, *para*, and *ortho* position, respectively. Likewise, the corresponding aromatic group assigned as that at the 20'-position of the chlorin moiety also had some very strongly upfield-shifted signals

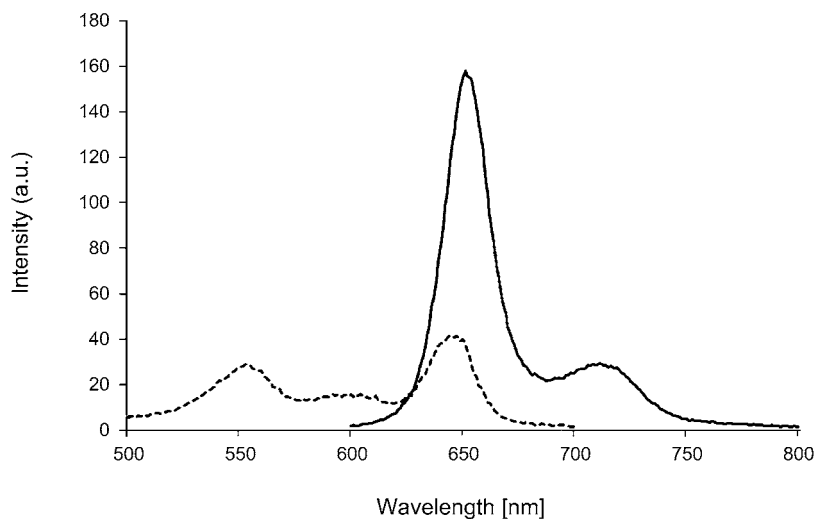


Fig. 3. Fluorescence emission (—; λ_{exc} at 552 nm) and excitation (---; λ_{em} at 712 nm) spectra of spiro 'dimer' **4·2Zn** ($c = 7.03 \cdot 10^{-6}$ M, CH_2Cl_2)

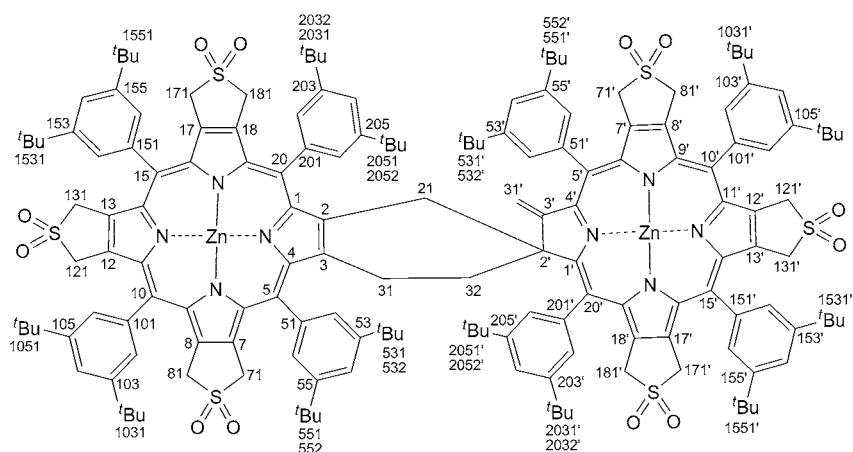


Fig. 4. Arbitrary atom numbering used for the spiro[chlorin-porphyrin]-type 'dimer' complex **4·2Zn**

and showed two high-field *s* at $\delta(\text{H})$ 0.31 (Me(2052')) and 1.20 (Me(2032')) for the 'Bu groups, and three low-field resonances, at $\delta(\text{H})$ 7.03 (H–C(202')), 7.28 (H–C(204')), and 7.85 (H–C(206')) for the aromatic H-atoms in *ortho*, *para*, and *ortho* positions (Fig. 5,a).

Compared to the position of the signals of the corresponding H-atoms in the porphyrinatozinc **1·Zn**, the signals of **4·2Zn** were shifted upfield by up to 1.29 or 1.19 ppm, as a consequence of the local shielding effect of nearby aromatic groups (Fig. 6). Four other aryl groups, which were assigned to the outer part of the spiro

Table 2. Pertinent ^1H - and ^{13}C -NMR Data (CDCl_3 ; 500 and 125 Mz, resp.) of **4•2Zn**^a). See Fig. 4 for arbitrary atom numbering.

	$\delta(\text{H})$	$\delta(\text{C})$		$\delta(\text{H})$	$\delta(\text{C})$
C(2)			C(2')		54.3
CH ₂ (21)	2.82 (H _a), 4.20 (H _b)	41.8			
CH ₂ (31)	2.94 (H _a), 2.78 (H _b)	22.9	CH ₂ (31')	4.92 (H _a), 5.46 (H _b)	115.1
CH ₂ (32)	2.08 (H _a), 1.92 (H _b)	29.3			
C(4)			C(4')		153.3 ^b)
H–C(52)	7.95	126.8	H–C(52')	7.63	126
C(53)		150.7	C(53')		151.9
C(531)		35.4	C(531')		35.2
Me(532)	1.41	31.5	Me(532')	1.39	31.6
H–C(54)	7.84	122.3	H–C(54')	7.52	121.7
C(55)		149.7	C(55')		151
C(551)		35.4	C(551')		34.6
Me(552)	1.52	31.8	Me(552')	0.90	31.1
H–C(56)	7.64	126.9	H–C(56')	7.54	128.2
CH ₂ (71)	4.22 (H _a), 3.90 (H _b)	56.7	CH ₂ (71')	3.77	56.4
C(18)		137 ^b)	C(18')		
CH ₂ (181)	3.50 (H _a), 3.81 (H _b)	56.3	H–C(181')	3.33 (H _a), 3.86 (H _b)	56.3
H–C(202)	7.75	126.7	H–C(202')	7.03	130
C(203)		151	C(203')		150.9
C(2031)		34.6	C(2031')		34.1
Me(2032)	0.54	31.2	Me(2032')	1.20	31.6
H–C(204)	6.15	121.6	H–C(204')	7.28	121.7
C(205)		150.9	C(205')		151
C(2051)		33.9	C(2051')		35.2
Me(2052)	0.21	30.5	Me(2052')	0.31	30.6
H–C(206)	7.24	126.5	H–C(206')	7.85	126.2

^a) Signal assignments for selected H-atoms and their correlations with directly and indirectly bound C-atoms (from HSQC and HMBC spectra). ^b) Tentatively assigned signals.

'dimer', displayed signals with chemical shifts similar to those found in the porphyrin 'monomer' **1•Zn**. The unambiguous individual assignment of the signals of the core part of the spiro 'dimer' **4•2Zn** thus revealed intriguing shifts (mostly upfield) as the result of anisotropic fields associated with the ring currents of closely positioned porphyrinoid and 3,5-di(*tert*-butyl)phenyl moieties (Fig. 6). In contrast, most of the signals derived for H-atoms at the outer part of the spiro 'dimer' were overlapping and could not be assigned individually.

Discussion. – Several groups have used β,β' -sulfolenoporphyrins as effective thermal precursors of β,β' -bis(methylene)porphyrins [8–15]: Such reactive conjugated β,β' -diene derivatives of porphyrins have exhibited an excellent reactivity towards typical dienophiles. As they quickly underwent efficient [4 + 2] cycloaddition reactions, the β,β' -bis(methylene)porphyrin remained unobserved in the synthetic applications. When examining the behavior of the β,β' -bis(methylene)porphyrin (that was generated from the metal-free *meso*-unsubstituted sulfolenoporphyrin **2**) in the absence of an

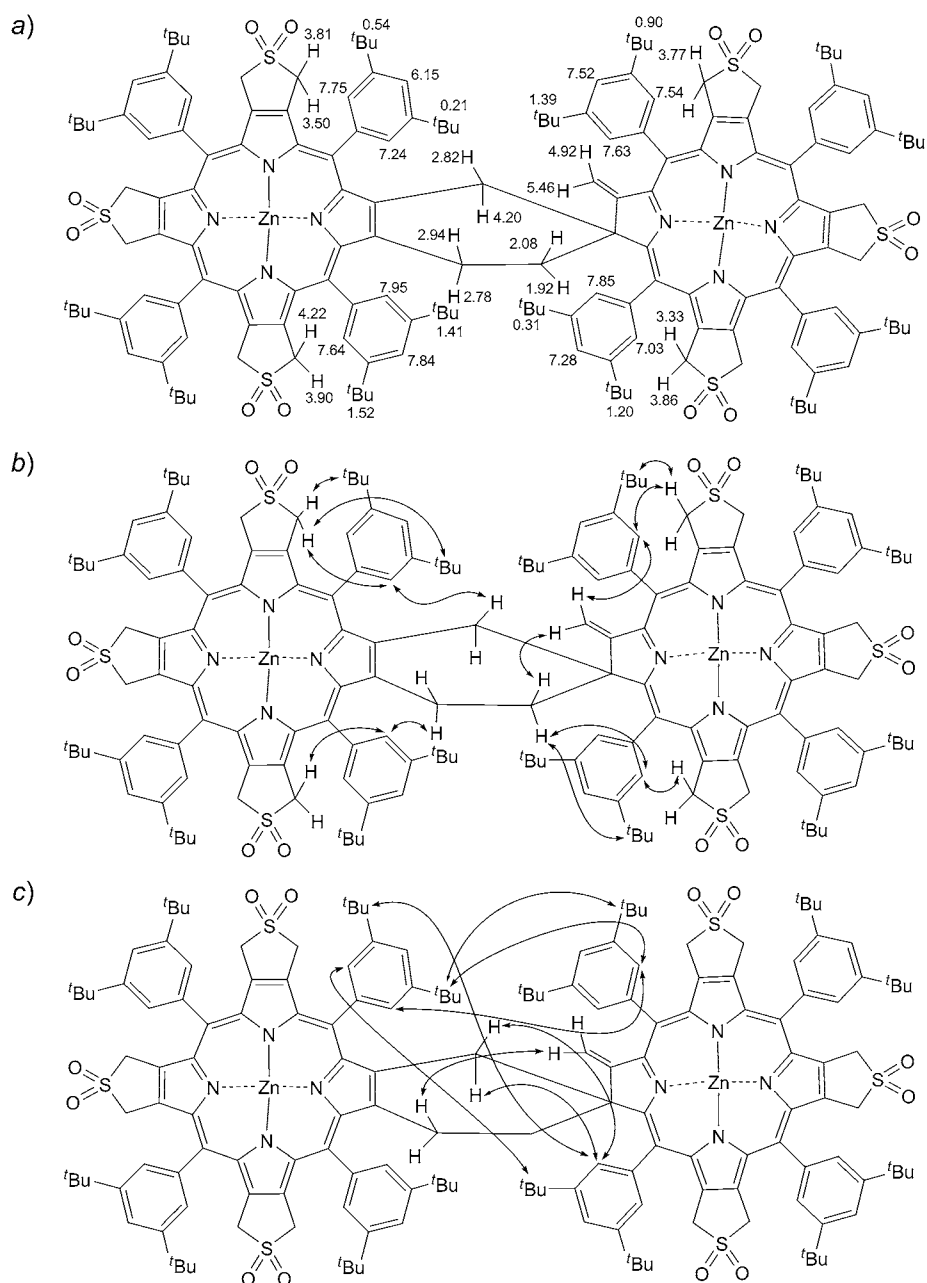


Fig. 5. a) $^1\text{H-NMR}$ Chemical shift assignments for the structural section of core part and b) ROESY ($\text{H} \leftrightarrow \text{H}$) correlations within the chromophore moieties and c) ROESY interchromophore correlations of $4 \cdot 2\text{Zn}$

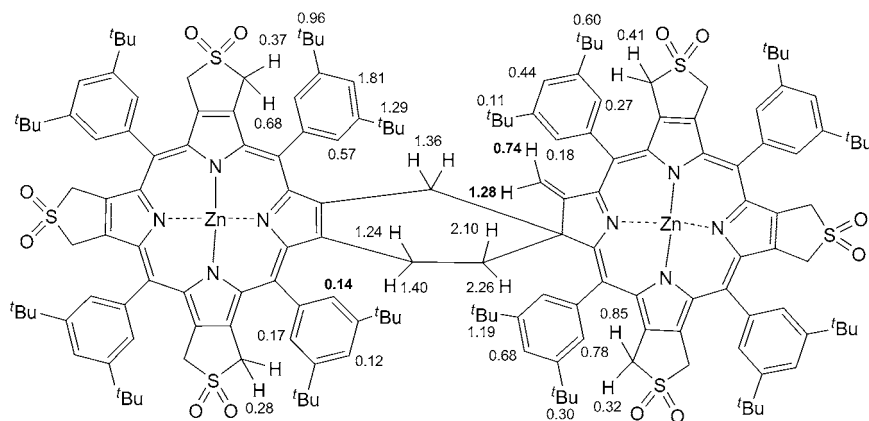


Fig. 6. $^1\text{H-NMR}$ Chemical-shift differences $\Delta\delta(\text{H})$ between of $\mathbf{4}\cdot\mathbf{2Zn}$ and $\mathbf{1}\cdot\mathbf{Zn}$. $\Delta\delta = \delta(\mathbf{4}\cdot\mathbf{2Zn}) - \delta(\mathbf{1}\cdot\mathbf{Zn})$ ($|\Delta\delta| > 0.1$ ppm); standard numbers indicate $\Delta\delta < 0$, and bold numbers indicate $\Delta\delta > 0$.

added dienophile, *Gunter* and co-workers obtained the corresponding *Diels–Alder* product **3** with another porphyrin's exocyclic $\text{CH}_2=$ [8][15].

We expected that the bulky 3,5-di(*tert*-butyl)phenyl groups at the *meso*-positions of tetra- β,β' -sulfolenoporphyrin $\mathbf{1}\cdot\mathbf{Zn}$ would hinder this type of [4 + 2] cycloaddition reaction between two β,β' -bis(methylene)porphyrin derivatives, and thus improve their stability. However, the experiments reported here, and our further studies, confirmed the [4 + 2] self-cycloaddition of two β,β' -bis(methylene)porphyrin to be rapid in liquid solution, even when sterically hindered, and to result in congested unsymmetrical spiro[chlorin-porphyrin]-type 'dimers' efficiently. Thus, when the tetra- β,β' -sulfolenoporphyrinato)zinc $\mathbf{1}\cdot\mathbf{Zn}$ was thermolyzed to partial conversion, the dizinc complex $\mathbf{4}\cdot\mathbf{2Zn}$ of the hexa- β,β' -sulfolenospino[corin-porphyrin]-type 'dimer' ligand was obtained in good yield. Further direct thermolysis of $\mathbf{4}\cdot\mathbf{2Zn}$ in the absence of an added dienophile was not studied, as it was expected to yield complex higher oligomers. Unfortunately, attempts to separate the expected two enantiomers of the chiral spiro 'dimer' $\mathbf{4}\cdot\mathbf{2Zn}$ were unsuccessful.

The structure of the chiral spiro 'dimer' was deduced from analysis of an extensive set of spectral data, taken from UV/VIS, MS, and NMR spectra, in particular. The two porphyrinoid moieties of these spiro 'dimers' were found to be attached to each other by a short covalent link, which generated a sterically congested arrangement in its vicinity. As a result of this, significant anisotropic effects were observed for signals in the $^1\text{H-NMR}$ spectra that are assigned to close-by H-atoms (*Figs. 5* and *6*). The covalent link, a fused cyclohexene unit, presumably orients the mean planes of the two porphyrinoid moieties in an almost orthogonal fashion towards each other. As a consequence, one (or several) of the 3,5-di(*tert*-butyl)phenyl groups near the linker site may be positioned close to the other porphyrinoid moiety, experiencing significant anisotropic effects.

Spiro 'dimer' $\mathbf{4}\cdot\mathbf{2Zn}$ still carries six sulfoleno groups at six pairs of β,β' -positions of the two porphyrinoid moieties that (presumably) are accessible to typical dienophiles. Thus, these six functional groups that remain in the 'spiro dimer' are expected to offer

the opportunity for attachment of suitable dienophiles in further [4 + 2] cycloaddition reactions at the periphery of this spiro ‘dimer’. The excellent disposition of the dizinc complex **4·2Zn** for the generation of conjugated β,β' -bis(methylene)porphyrin derivatives in solution by SO₂ extrusion, as explored earlier with the ‘monomeric’ (tetra- β,β' -sulfolenoporphyrinato)zinc **1·Zn** [12–14], thus provides an excellent platform for synthetic investigations of subsequent cycloaddition reactions with dienophiles, such as C₆₀ or benzoquinone. Such follow-up transformations with C₆₀ and the formation of hexafullereno-fused spiro ‘dimers’ have been explored in our laboratory, due to be reported in a future manuscript.

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Experimental Part

General. The 1,2-dichlorobenzene (*Fluka*), CH₂Cl₂, petroleum ether (40–60°), MeOH, and toluene (*Acros*) were distilled before use. The 3-nitrobenzyl alcohol matrix (NOBA) was a reagent-grade chemical from *Fluka* and was used as received. Tetra- β,β' -sulfolenoporphyrins **1·2H** and **1·Zn** were synthesized as published [12]. Glassware for all reactions was oven-dried at 110° and cooled under N₂ flow prior to use. Reactions, workup, and chromatography were performed under protection from light (alumina foil). High vacuum: *ca.* 0.05 mbar. Column chromatography (CC): silica gel 60 (SiO₂; 230–400 mesh; *Fluka*). Prep. TLC: SiO₂, 60 plates (0.25 mm; *Merck*). UV/VIS Spectra: *U 3000* spectrometer (*Hitachi*); 1 mm or 10 mm quartz cells; λ_{\max} (log ϵ) in nm. Fluorescence spectra: *Varian Cary Eclipse*; excitation (λ_{exc}) and emission wavelengths (λ_{em} (rel. int.)) in nm. ¹H- and ¹³C-NMR Spectra: *Varian-500 spectrometer*; at 298 K in CDCl₃; δ in ppm rel. to CDCl₃ solvent (δ (H) 7.26 (CHCl₃) and δ (C) 77.2) as internal standard, *J* in Hz. FAB-MS: *Finnigan MAT-95*; positive-ion mode; NOBA matrix; *m/z* (rel. %).

{ μ {5,5',11,11',17,17',22,24-Oktakis[3,5-bis(1,1-dimethylethyl)phenyl]-7,7',9,9',13,13',15,15',21,22-decahydro-19-methylenesprio[1H,3H,26H,28H-benzo[b]trithieno[3,4-g:3',4'-1:3'',4''-q]porphine-20(19H), 20'(19H)-[1H,3H,24H,26H]trithieno[3,4-b:3',4'-g:3'',4''-l]phorphine]- $\kappa\text{N}^{26},\kappa\text{N}^{27},\kappa\text{N}^{28},\kappa\text{N}^{29}:\kappa\text{N}^{24},\kappa\text{N}^{25},\kappa\text{N}^{26},\kappa\text{N}^{27}$ } 2,2,2',2',8,8,8',8',14,14,14',14'-dodecaoxidato(4-)}dizinc (**4·2Zn**). A deoxygenated soln. of (tetra- β,β' -sulfolenoporphyrinato)zinc **1·Zn** (22.5 mg, 15.13 μmol) in 1,2-dichlorobenzene (4.4 ml) was immersed in a pre-heated oil bath and heated under stirring at 140°. After 2 h, the mixture was removed from the oil bath and allowed to cool to r.t. under Ar. Upon cooling, the solvent was distilled at 55° under high vacuum, and the dry mixture was purified by prep. TLC (SiO₂, development with 0.6% MeOH/CH₂Cl₂). The separated bands were scratched off the TLC plate: The product **4·2Zn** (top green band) and the unreacted **1·Zn** (second red band) were each washed off the SiO₂ with 3–5% MeOH/CH₂Cl₂ (25 ml) and filtered through a cotton-stuffed pipette. The filtrates containing **4·2Zn** and **1·Zn** were each washed with sat. aq. NaHCO₃ soln. (3 \times 30 ml) and extracted with CH₂Cl₂ (50 ml), the extracts filtered through a plug of dried cotton, and the solvents evaporated. The dry residues were re-dissolved in CH₂Cl₂ the solns. transferred into small vials, and the solvents evaporated with a N₂ flow. The vial contents were dried at 50° under high vacuum for 12 h: 3.65 mg (17%) **4·2Zn** and 16.0 mg (71%) of unreacted **1·Zn**. **4·2Zn**: UV/VIS (*c* = 7.03 \cdot 10⁻⁶ M, CH₂Cl₂): 646 (4.22), 598 (sh, 3.84), 553 (4.28), 440 (5.41), 425 (5.37), 400 (sh, 4.53), 325 (br., 4.23), 250 (3.99) (*Fig. 2*). Fluorescence emission spectrum (λ_{exc} 552 nm, *c* = 7.03 \cdot 10⁻⁶ M, CH₂Cl₂): 652 (1.00), 713 (0.16); excitation spectrum (λ_{em} 712 nm): 553 (0.70), 647 (1.00) (*Fig. 3*). ¹H-NMR: 0.21, 0.31, 0.54, 0.90, 1.20, 1.25, 1.39, 1.41, 1.46, 1.48, 1.51, 1.52, 1.54 (144 H); 1.91–1.93 (*m*); 2.02–2.08 (*m*); 2.75–2.81 (*m*); 2.85 (*m*); 2.92–2.94 (*m*); 3.32–4.24 (*m*); 4.92 (*s*, 1 H); 5.46 (*s*, 1 H); 6.15 (*s*); 7.03 (*s*); 7.24 (*s*); 7.28 (*s*); 7.29 (*s*); 7.53 (*s*); 7.64–7.66 (br.); 7.76 (*s*); 7.78 (*s*); 7.79 (*s*); 7.82 (br.); 7.84 (*s*); 7.85 (*s*); 7.88 (*s*); 7.90 (*s*); 7.94 (br.). MS (C₁₆₈H₂₀₀N₈O₁₂S₆Zn₂; calc. 2841.219): 2850.4 (15), 2849.4 (19), 2848.4 (24), 2847.4 (31), 2846.4 (31), 2845.4 (33), 2844.4 (35), 2843.3 (34), 2842.4 (23, [M + H]⁺), 2841.4 (16), 2840.4 (9), 2839.4 (6), 2786.4 (7), 2785.4 (6), 2784.4 (8), 2783.4 (11), 2782.4 (10), 2781.3 (12), 2780.3 (12), 2779.3 (11, [M – SO₂ + H]⁺), 2778.4 (14), 2777.3 (9), 2776.4 (7), 2478.0 (43), 2477.0

(47), 2476.0 (54), 2475.0 (57), 2474.0 (53), 2473.0 (45), 2472.0 (44), 2471.0 (37), 2466.0 (38), 2465.0 (43), 2464.1 (62), 2463.1 (76), 2462.1 (85), 2461.1 (100), 2460.1 (97), 2459.1 (96, $[M - 6 \text{SO}_2 + \text{H}]^+$), 2458.1 (83), 2457.1 (66), 2456.1 (54), 2455.1 (39).

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