Synthesis and Crystal Structure of a Meso-Meso Directly Linked Bisporphyrin

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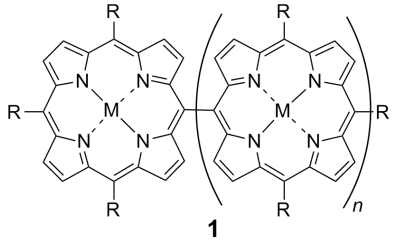
We report the synthesis and characterization of a meso-meso directly linked bisporphyrin **6** bearing both alkyl and aryl residues. Its oxidative fusing results in the corresponding meso-meso β-β,β-β-linked bisporphyrin. The first crystal structure analysis of a meso-meso directly linked porphyrin dimer (**6**) has shown the inequivalency of the two porphyrin units with regard to the macrocycle conformation. Quite distinct mixings of distortion modes were observed for the two aromatic macrocycles.

Key words: Porphyrins, Conformational Analysis, Bisporphyrins, Tetrapyrroles, Crystal Structure

Introduction

Directly linked oligoporphyrins **1** have attracted considerable interest in recent years [1, 2]. This is mainly related to the preparation of polymers and of the ability of the meso-meso-linked dimers to be oxidatively fused to yield meso-meso, and $2 \times \beta$-β-fused systems **2** (linked in the 2, 5, and 7 positions) [3]. Synthetically the meso-meso linked bisporphyrins **1** (n = 1) can be prepared either through treatment of porphyrins with free meso positions with $AgPF_6$ [3a], total synthesis [4], $AgPF_6 + I_2$ [5], electrochemically [6], or Ullmann homocoupling [7]. Our approach to these systems involved the reaction of a precursor porphyrin with RLi, *in situ* oxidation of the anion to the radical anion, followed by radical dimerization [8].

Surprisingly, despite the ongoing interest in these systems, only a few crystal structures of meso-meso-linked trisporphyrins have been reported [2b, 9]. This is related to the low solubility of some of these compounds. Likewise, only limited studies on the preparation of unsymmetrical systems thereof or porphyrin arrays amenable to further functionalization have been published. In the context of our interest in the preparation of near-IR absorbers for applications in photodynamic therapy (PDT) [10] we have begun to explore the chemistry of these compounds with the goal in mind to make unsymmetrical and amphiphilic systems for use in preclinical studies [11 – 13].



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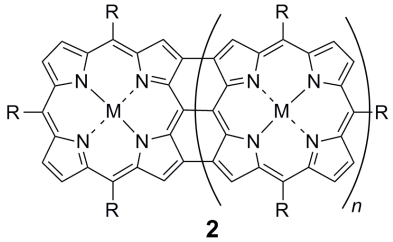

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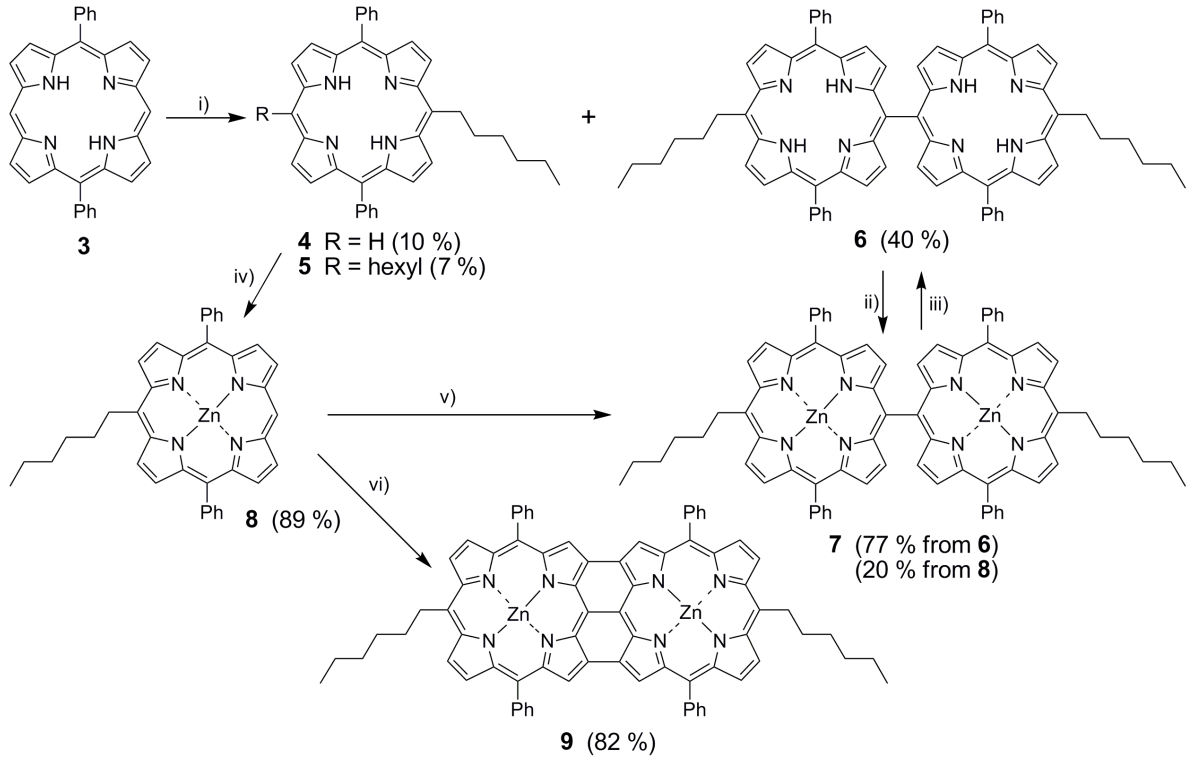
Results and Discussion

Scheme 1 outlines our initial syntheses. In line with earlier results 5,15-diphenylporphyrin [14] was treated with 6 equiv. of *n*-hexyl lithium followed by direct addition of DDQ without a hydrolysis step and gave the meso-meso-linked dimer **6** as the main product in 40 % yield. Formation of this compound was accompanied by the generation of small amounts of the mono- (**4**) [15] and dihexylated (**5**) side products. The dimer **6** could easily be converted through standard reactions into the zinc(II) complex **7**. The UV/Vis spectrum of this dimer exhibits the characteristic split Soret band



Scheme 1. Synthesis of meso-meso-linked bisporphyrins. i) *n*-HexLi, DDQ, THF, −78 °C; ii) $Zn(OAc)_2$, CH_3OH, CH_2Cl_2, 20 °C; iii) $Sc(OTf)_3$, DDQ, toluene, Δ; iv) ZnO, TFA, CH_2Cl_2; v) $Sc(OTf)_3$, DDQ, toluene, Δ; vi) $Sc(OTf)_3$, DDQ, toluene, 20 °C.

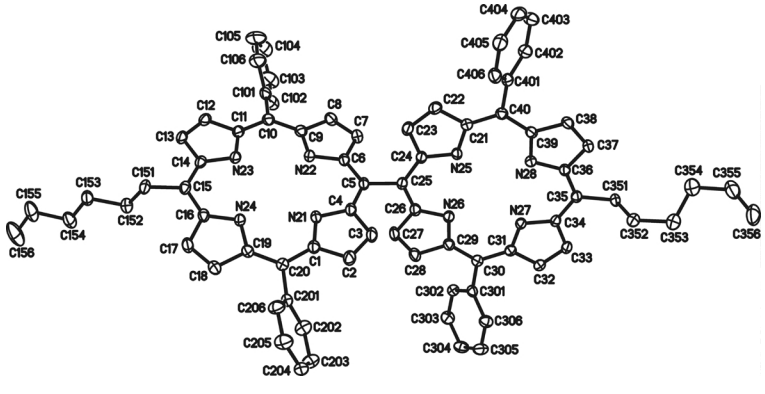


Fig. 1. View of the molecular structure of **6** in the crystal. Displacement ellipsoids are drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.

(422 and 455 nm) and Q-bands at 568 and 608 nm in CH_2Cl_2. As shown by the crystal structure of the free base (*vide supra*) the two porphyrin rings lie almost orthogonal to each other, which results in a weak ground state interaction between the two chromophores [16].

Next we attempted the preparation of the respective triply linked dimer **9**. Reaction of **6** with 5 equiv. of DDQ and 5 equiv. of $Sc(OTf)_3$ at 50 °C gave no fused product, and raising the temperature resulted in the formation of small amounts of the demetallated compound **6**. Similarly, an increase of $Sc(OTf)_3$ to 7 equiv. and heating to reflux resulted only in the formation of the singly linked free base **7**. As an alternative route we prepared the zinc(II) complex **8** from **4**. Reaction with 5 equiv. of $Sc(OTf)_3$ and 5 equiv. DDQ in toluene at 50 °C gave only the meso-meso-linked dimer **7** in 20 % yield. Surprisingly, performing the same reaction at room temperature for 18 h resulted in the formation

of the desired triply linked bisporphyrin **9** in very good yield. Although identification proved to be difficult due to solubility and stability issues, its formation could clearly be proven by mass spectrometry and UV/Vis spectroscopy. The absorption spectrum is very similar to those of related systems in the literature [17] and exhibits two strong Soret-like bands at 426 and 576 nm and a long wavelength absorption at 1135 nm in THF.

For compound **6** we were able to grow crystals suitable for X-ray crystallographic structure analysis. The structure is shown in Fig. 1 and presents the first structure of a meso-meso directly linked bisporphyrin [9a]. The meso-meso single bond linkage is clearly indicated by the C5–C25 bond length of 1.503(3) Å. The two tetrapyrrole rings are twisted against each other by 69.1(2)°. This value is similar to that found for the phenyl twist angle in various meso-tetraarylporphyrins [18]. The dihedral twist is clearly illustrated in the packing diagram shown in Fig. 2. Note, that the twist angle is different from the one in a related meso-β-linked porphyrin, 2-(5,10,15-triphenylporphyrin-20-yl)-5,10,15,20-tetraphenylporphyrin, where an angle of 106° was observed [19].

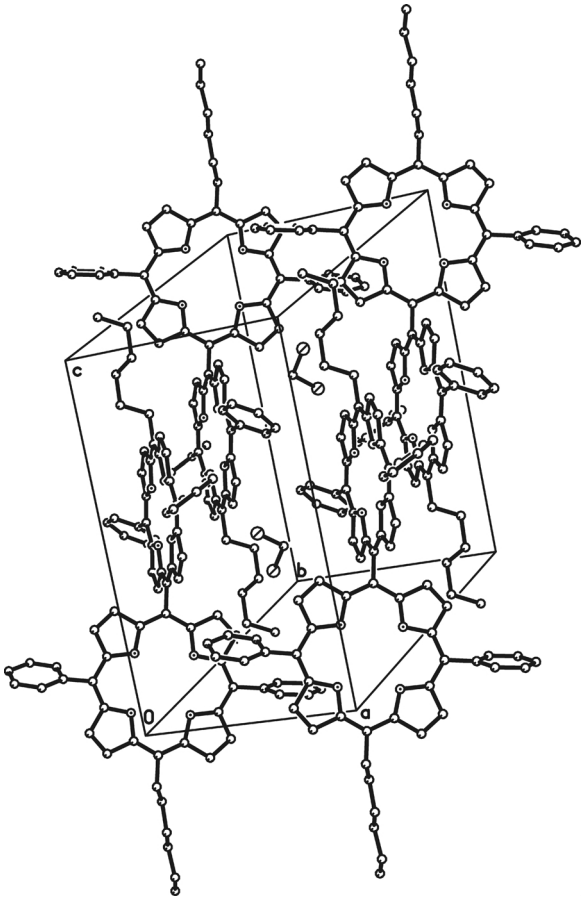


Fig. 2. View of the crystal structure of **6**. Hydrogen atoms have been omitted for clarity.

The compound crystallized as a dichloromethane solvate (Fig. 2). Interestingly the compound does not crystallize with an inversion center. The first obvious difference is the conformation of the two hexyl side chains, one of which shows a more folded arrangement. The packing of the molecules is characterized by very weak π-π interactions between neighboring ring II units. The mean plane separation is 3.34 Å, with a slip angle of 47.3° and a center-to-center separation of 4.924 Å. The methylene chloride solvate molecules are located in the voids between these units. The shortest intermolecular contact is Cl1S···H405 (2.903 Å).

More striking differences between the two porphyrin units were found upon an analysis of their conformation. The average deviation from planarity, *i. e.* $\Delta 24$, was found to be 0.094 Å for macrocycle 1 and 0.047 Å for macrocycle 2. A more detailed inspection using a normal structural decomposition (NDS) [20] analysis revealed significant differences in the distortion modes and types of the two porphyrin macrocycles. Porphyrin unit 1 has about equal contributions from *sad* and *ruf* out-of-plane distortion and also exhibits *wav(x)* distortion. In contrast, porphyrin unit 2 has smaller contributions from these distortion types but has a significant *wav(y)* contribution. With regard to the in-plane distortions the main differences are larger *B*2*g* contributions in unit 2 and larger *A*2*g* contributions in unit 1 (Fig. 3). Such large difference

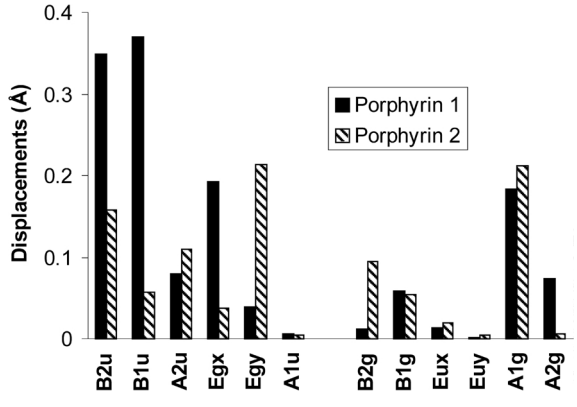


Fig. 3. Graphical representation of the displacements along the lowest-frequency coordinates that best simulate the two porphyrin units in molecule **6**. Signs have been omitted for ease of comparison.

in the type and composition of the distortion modes are rare in bisporphyrins and are probably due to an interplay of packing forces and to the mix of aryl- and alkyl-substituent types [21].

Experimental Section

For general conditions and instrumentation see reference [22].

*5,15-Dihexyl-10,20-diphenylporphyrin (**5**)*

5,15-diphenylporphyrin **3** (150 mg, 0.324 mmol) was dissolved in 80 mL of dry THF under an argon atmosphere, and the reaction mixture was cooled to −78 °C. *n*-HexLi (1.4 mL, 3.245 mmol) was added dropwise over 15 min *via* syringe. The cold bath was removed and stirring continued for 1.5 h at r. t. Next 0.5 mL of H_2O was added and stirring continued for 15 min. Then DDQ (730 mg, 3.245 mmol) in 10 mL of THF was added and the reaction mixture stirred for an additional hour. The reaction mixture was filtered through silica gel, followed by evaporation of the solvent. The residue was purified by column chromatography (*n*-hexane : ethyl acetate = 100 : 1, v/v). The first fraction was 5,15-dihexyl-10,20-diphenylporphyrin (**5**) (14 mg, 0.022 mmol, 7 %) as purple crystals, the second fraction contained 5-hexyl-10,20-diphenylporphyrin (**4**) (17 mg, 0.031 mmol, 10 %) [15] as purple crystals, and the third fraction the directly linked dimer **6** (70 mg, 0.064 mmol, 40 %) as purple crystals. **5**: M. p. > 300 °C. R_f = 0.5 (*n*-hexane : ethyl acetate = 1 : 1, v/v). – UV/Vis (CH_2Cl_2): $\lambda_{max}(\log\varepsilon)$ = 419 (5.71), 518 (4.31), 554 (4.09), 598 (3.86), 656 nm (3.93). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = −2.66 (s, 2H, N*H*), 0.95 (t, *J* = 7.01 Hz, 3H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.41 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.51 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.82 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 2.51 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 4.97 (t, *J* = 7.16 Hz, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 7.81 (s, 6H, Ar-*H*), 8.20 (s, 4H, Ar-*H*), 8.89 (d, *J* = 5.26 Hz, 4H, H_β), 9.46 (d, *J* = 4.68 Hz, 2H, H_β), 9.62 ppm (d, *J* = 4.68 Hz, 2H, H_β). – ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.9, 22.5, 29.5, 30.0, 31.7, 35.1, 35.4, 38.5, 38.6, 111.1, 112.6, 119.9, 121.1, 121.2, 126.3, 126.4, 126.5, 126.6, 126.7, 127.6, 127.8, 134.3, 134.5, 141.1, 141.8 ppm. – HRMS ((+)-ES): *m*/*z* = 631.3801 (calcd. 631.3808 for $C_{44}H_{47}N_4$, $[M+H]^+$).

*Bis(5-hexyl-10,20-diphenylporphyrin-15-yl) (**6**)*

The compound was obtained from the reaction described for the preparation of **5** as purple crystals (70 mg, 0.064 mmol, 40 %). M. p. > 300 °C. R_f = 0.37 (*n*-hexane : ethyl acetate = 1 : 1, v/v). – UV/Vis (CH_2Cl_2): $\lambda_{max}(\log\varepsilon)$ = 418 (5.28), 448 (5.33), 523 (4.64), 558 (4.13), 598 nm (4.12). – ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = −2.15 (s, 4H, N*H*), 0.98 (t, *J* = 7.6 Hz, 6H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.44 (m, 4H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.53 (m, 4H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.88 (m, 4H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 2.63 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 5.14 (t, *J* = 7.16 Hz, 4H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 7.70 (s, 12H, Ar-*H*), 8.05 (d, *J* = 3.51, 4H, H_β), 8.22 (s, 8H, Ar-*H*), 8.55 (d, *J* = 4.68 Hz, 4H, H_β), 8.99 (d, *J* = 4.67 Hz, 4H, H_β), 9.60 ppm (d, *J* = 5.26 Hz, 4H, H_β). – ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.7, 22.6, 29.2, 30.1, 31.8, 35.5, 38.8, 52.8, 53.0, 53.4, 53.6, 116.5, 120.3, 121.8, 126.4, 127.4, 131.4, 134.2, 141.9 ppm. – HRMS ((+)-ES): *m*/*z* = 1091.5489 (calcd. 1091.5472 for $C_{76}H_{67}N_8$, $[M+H]^+$).

*Bis{(5-hexyl-10,20-diphenylporphyrin-15-ylato)zinc(II)} (**7**)*

Bis(5-hexyl-10,20-diphenylporphyrin-15-yl) (**6**) (85 mg, 0.0788 mmol) and zinc acetate dihydrate (205 mg, 0.934 mmol) in 20 mL dried CH_2Cl_2 were reacted at r. t. for 3 h. Purification of the product was carried out by recrystallization from CH_2Cl_2/MeOH to afford the desired compound (80 mg, 0.065 mmol, 77 %) as purple crystals. M. p. > 300 °C. R_f = 0.55 (*n*-hexane : CH_2Cl_2 = 1 : 2, v/v). – UV/Vis (CH_2Cl_2): $\lambda_{max}(\log\varepsilon)$ = 422 (5.19), 456 (5.21), 568 (4.51), 608 nm (4.01). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.99 (t, *J* = 7.60 Hz, 6H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.49 (m, 4H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.63 (m, 4H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.93 (m, 4H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 2.67 (m, 4H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 5.16 (t, *J* = 7.60 Hz, 4H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 7.70 (s, 12H, Ar-*H*), 8.1 (d, *J* = 3.51 Hz, 4H, H_β), 8.25 (m, 8H, Ar-*H*), 8.64 (d, *J* = 3.51 Hz, 4H, H_β), 9.08 (d, *J* = 3.5 Hz, 4H, H_β), 9.69 ppm (d, *J* = 4.1 Hz, 4H, H_β). – ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.7, 22.3, 29.2, 29.9, 31.5, 38.6, 120.8, 125.9, 126.9, 128.6, 131.4, 131.6, 133.2, 133.8, 142.3, 148.9, 149.6, 154.5 ppm. – HRMS ((+)-LD): *m*/*z* = 1214.3636 (calcd. 1214.3680 for $C_{76}H_{62}N_8Zn_2$, $[M]^+$).

Alternatively, this compound could be prepared in 20 % yield *via* reaction of porphyrin **8** with 5 eq. of DDQ and 5 eq. of $Sc(OTf)_3$ in dry toluene at 50 °C for 2 h.

*(5-Hexyl-10,20-diphenylporphyrinato)zinc(II) (**8**)*

The free base porphyrin **5** (90 mg, 0.2 mmol) was dissolved in 20 mL of dried dichloromethane and treated with zinc oxide (141.2 mg, 1.2 mmol). After the addition of 4 drops of TFA, the reaction mixture first turned green, and subsequent a color change back to red indicated completion of the reaction. The product was separated from ZnO and most of the TFA by filtration through a short silica column. Remaining traces of TFA were removed by washing with water. After drying with sodium sulfate, the solvent was removed *in vacuo*, and the product was purified by column

chromatography (silica gel, dichloromethane), followed by recrystallization from CH_2Cl_2/MeOH to give purple crystals (109 mg, 0.178 mmol, 89 %). M. p. > 300 °C. R_f = 0.57 (CH_2Cl_2 : *n*-hexane = 2 : 1, v/v). – UV/Vis (CH_2Cl_2): $\lambda_{max}(\log\varepsilon)$ = 414 (4.84), 452 (3.42), 543 nm (3.44). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, J = 7.02 Hz, 3H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.44 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 1.55 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 1.88 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 2.62 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 5.13 (t, J = 7.16 Hz, 2H, $CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 7.83 (s, 6H, Ar-*H*), 8.26 (m, 4H, Ar-*H*), 9.07 (d, J = 5.26 Hz, 2H, H_β), 9.37 (d, J= 4.68 Hz, 2H, H_β), 9.66 (d, J = 4.68 Hz, 2H, H_β), 10.19 ppm (s, 1H, H_{meso}). – ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 13.7, 22.3, 29.9, 31.5, 35.4, 38.7, 104.6, 119.4, 121.6, 126.1, 128.3, 130.9, 131.6, 132.0, 133.8, 134.0, 142.3, 149.1, 149.2 ppm. – HRMS ((+)-ES): m/z = 609.1997 (calcd. 609.2006 for $C_{38}H_{33}N_4Zn$, $[M+H]^+$).

*Bis{(5-hexyl-10,20-diphenylporphyrin-13,15,17-triylato)-zinc(II)} (**9**)*

(5-Hexyl-10,20-diphenylporphyrinato)zinc(II) (**8**) (30.5 mg, 0.05 mmol) was dissolved in dry toluene (freshly distilled over CaH_2). The flask was degassed with argon and heated to 50 °C. Then DDQ (56.75 mg, 0.25 mmol) and $Sc(OTf)_3$ (123.04 mg, 0.25 mmol) in dry toluene were added, and stirring continued for 3 h. THF (15 mL) was added, and the reaction mixture was stirred for 60 min. The reaction mixture was filtered through silica gel and the solvent removed under reduced pressure. The residue was purified by column chromatography (CH_2Cl_2 : CH_3OH = 50 : 1, v/v) and gave purple crystals (25 mg, 0.020 mmol, 82 %). M. p. > 300 °C. R_f = 0.4 (CH_2Cl_2 : CH_3OH = 40 : 1, v/v). – UV/Vis (THF): $\lambda_{max}(\log\varepsilon)$ = 426 (3.88), 479 (3.59), 576 (3.90), 995 (3.03), 1135 nm (3.30). – ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.90 (t, J = 13.41 Hz, 3H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.58 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.84 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.98 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 2.07 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 3.98 (t, J = 6.06 Hz, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 7.00 (s, 4H, H_β), 7.56 (m, 20H, Ar-*H*), 7.74 (m, 4H, H_β), 8.23 (m, 4H, H_β) ppm. – HRMS ((+)-ES): m/z = 1210.3315 (calcd. 1210.3367 for $C_{76}H_{58}N_8Zn_2$, $[M+H]^+$).

*X-Ray structure determination of **6***

Growth and handling of crystals followed the concept developed by Hope [23]. Intensity data for the compound were collected with a Rigaku CCD system using graphite-monochromated MoK_α radiation (λ = 0.71073 Å). The intensities were corrected for Lorentz, polarization and absorption effects. Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed into geometrically calculated positions and refined using a ridging model. The structure was solved with Direct Methods using the SHELXTL PLUS program system and refined against $|F^2|$ with the program XL from SHELX-97 using all data [24].

Crystal structure data: $C_{76}H_{66}N_8{\cdot}CH_2Cl_2$, M = 1176.29, triclinic, space group $P\bar{1}$, a = 11.448(2), b = 15.175(2), c = 18.459(2) Å, α = 77.168(4), β = 86.858(5), γ = 82.364(4)°, V = 3098.0(7) Å^3, Z = 2, T = 98 K, μ(MoK_α) = 0.1 cm^{-1}; 23512 reflections measured, 10810 unique reflections (R_{int} = 0.0208), 9615 reflections with $I \geq 2.0\ \sigma(I)$, 805 refined parameters; refinement against $|F^2|$, $R1(I \geq 2.0\ \sigma(I))$ = 0.0582, *wR*2 (all data) = 0.1521, S = 1.034, $\Delta\rho_{fin}$ (max) = 0.793 e Å^{-3}. *Refinement:* Hydrogen atoms at N25 and N27 were located in difference maps and refined using the standard riding model. For N21, N22, N23, N24 hydrogen atoms with 50 % occupancy were added using the riding model. The methylene chloride of solvation is disordered, and the two Cl atoms were refined as disordered over two positions with free occupancy variables. Several atoms still show high librational movement.

CCDC 815159 (**6**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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