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SYNTHESIS OF BENZOPORPHYRINS WITH ONE OR TWO MESO-SUBSTITUTENTS VIA SUBSTITUTION REACTIONS

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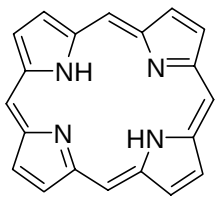
Abstract – Reaction of either free base benzoporphyrin, its zinc(II) complex or β-bicyclo(2,2,2)octeno appended precursor porphyrins with LiR reagents gave an entry into mono- and soluble di-meso-substituted benzoporphyrins.

Benzoporphyrins (**2**) with their annulated benzene rings are the connecting link between porphyrins (**1**) and the phthalocyanines (**3**).[1] However, compared to the latter much less is known about their chemistry and synthesis. While the extended π-system results in lower redox potentials their UV/VIS spectroscopic characteristics are similar to those of chlorins.[2] Their photophysical properties make them a potentially very useful class of compounds, notably in areas such as nonlinear optics, conducting materials or photodynamic therapy.[3] While much progress has been made with the development of new syntheses for (S_4) symmetric benzoporphyrins, much less effort has been put into the development of reactions aimed at the functionalization of benzoporphyrins. Significant progress with the use of benzoporphyrins in technical applications is still limited due to the extremely low solubility of the parent benzoporphyrin.



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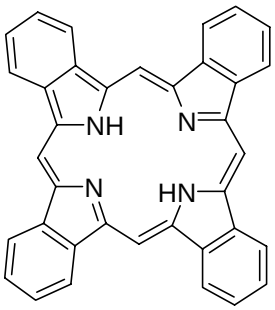

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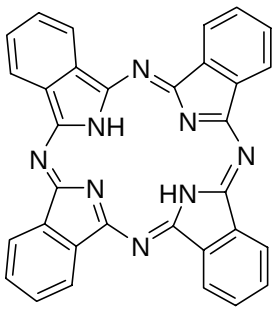


3

Many attempts have been made to develop template syntheses and to use solubility enhancing groups.[3-5] For example, much attention has focused on the use of condensation reactions for the preparation of meso-substituted benzoporphyrins.[6] However, these reactions are cumbersome, required high temperatures, and gave either regioisomeric mixtures or led to the formation of benzoporphyrins with

various degrees of meso-substitution. Significant advances have been made in the development of tetrabenzoporphyrin syntheses and core-modified analogs by using Ono's strategy of first preparing soluble precursors followed by a retro-Diels-Alder reaction[7] and a related concept by Vinogradov and coworkers involving aromatization of non-aromatically fused porphyrin precursors during the condensation reaction to yield various types of benzoporphyrin derivatives.[8] However, at present no method exists for the selective modification of individual meso positions in order to circumvent the laborious workup of regioisomeric mixtures or to access functionalized benzoporphyrins directly.

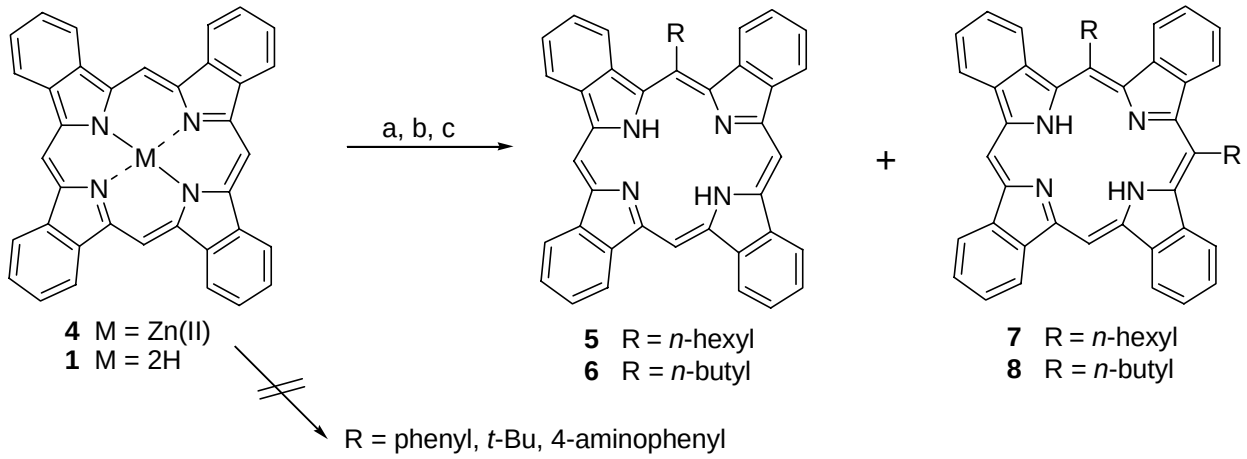
In contrast, many such methods exist for standard porphyrins.[9] These include transition metal catalyzed C-C coupling reactions and the use of organolithium reagents for the direct substitution of unactivated porphyrins. The latter method[10] was developed by us and applied successfully to the functionalization of unsubstituted porphyrin (porphin (**1**)) recently.[11] The difficulties in handling porphyrin due to its low solubility are akin to those encountered with benzoporphyrin and thus we surmised that the substitution of **3** with RLi might be a possible way to gain access to better soluble derivatives of benzoporphyrin.

RESULTS AND DISCUSSION

In analogy to the reaction sequences developed for the functionalization of β-substituted porphyrins[12] we first attempted the reaction of (benzoporphyrinato)zinc(II) (**4**) with standard organolithium reagents (Scheme 1). Sterically hindered reagents such as *t*-BuLi gave no reaction, even at elevated reaction temperatures (–100 to 40 °C). This is similar to the reactivity of 2,3,7,8,12,13,17,18-octaethylporphyrin (OEP).[10] However, in contrast to OEP no reaction took place using PhLi either. Even more reactive lithio aryl reagents such as *p*-aminophenyllithium gave no reaction. Thus, the reactivity of benzoporphyrin with LiR reagents is much lower than that of OEP or meso-substituted porphyrins.

Substitution only occurred when using alkyllithium reagents but even then required higher reaction temperatures (–30 °C) than those utilized for OEP (–100 to –40 °C).[11] For example, reaction with 5 equivalents of hexyllithium at –30 ° resulted in a color change to purple, which changed to brown within a few seconds. Addition of water did not give any further change in color but addition of DDQ for oxidation of the intermediary anionic hydroporphyrin species gave a green product mixture. The mixture was identified to consist of three products: free base benzoporphyrin (**1**) (32 %), 5-hexyl-benzoporphyrin (**5**) (38 %), and 5,10-dihexyl-benzoporphyrin (**7**) (9 %). A demetallation of zinc(II)porphyrins has also been observed for the OEP series under similar reaction conditions and may be explained with a relithiation and subsequent hydrolysis. The maximum achievable conversion was about 65 %. This required use of 8 equivalents of hexyllithium and gave 14 % of the disubstituted product (**7**), 46 % of the monosubstituted derivative (**5**) and 6 % recovered starting material. A fourth product was obtained in minor amounts (3 %) and tentatively identified as the dihexylated 5,15-regioisomer. Other modifications of the reaction conditions (increase in T, concentration, etc.) gave similar results. A comparable product

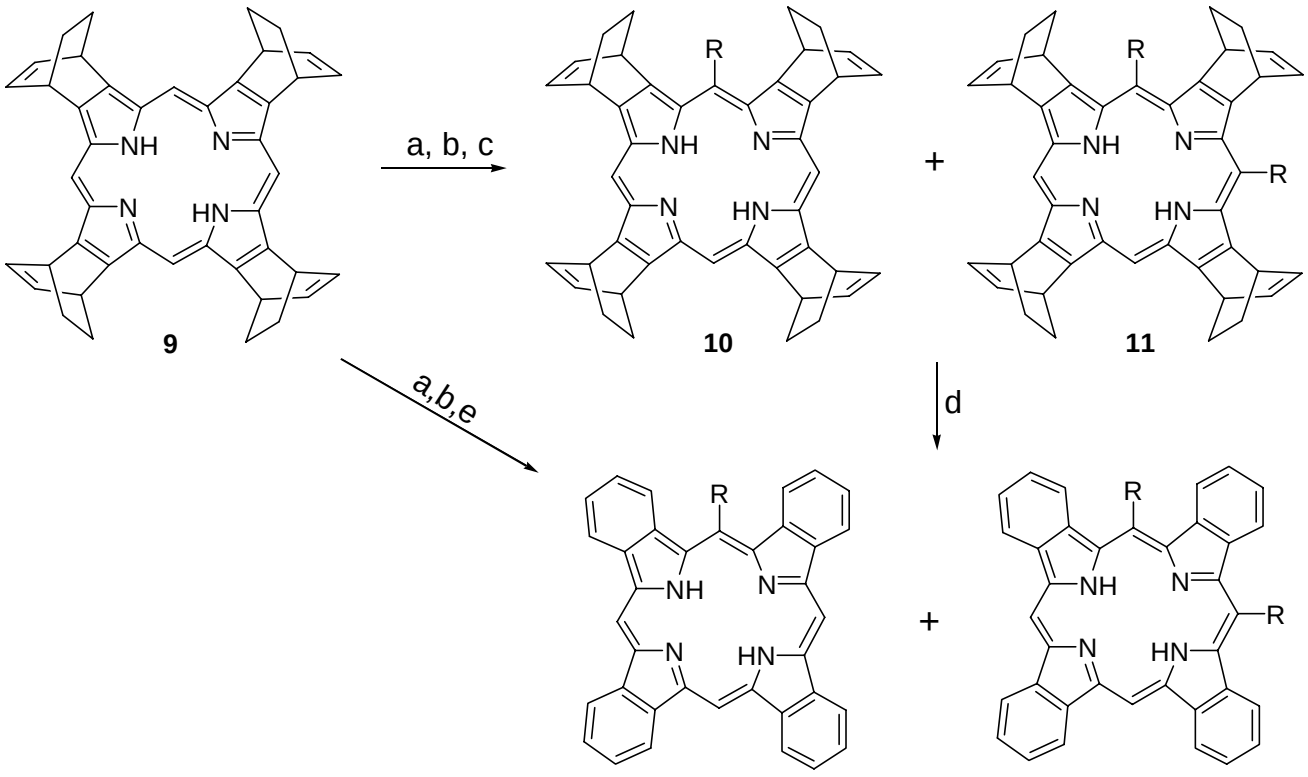
distribution was obtained using butyllithium: 10 % **1**, 42 % **6**, and 13 % **8**. Direct use of the free base (**1**) gave similar products but slightly lower yields, due to the even lower solubility of (**1**).



Scheme 1. Reactions of (tetrabenzoporphyrinato)zinc(II). a) LiR[1], THF, –30 to –80 °C; b) H_2O, 10 min; c) DDQ, 1 h.

While these reactions showed that benzoporphyrin could be directly substituted with highly reactive RLi reagents, this procedure has some limitations. Only the disubstituted products (**7**) and (**8**) are soluble in dichloromethane or acetic acid ethyl ester and can be purified with ease. Separation of the mono-substituted derivatives is still difficult; acceptable solubility was only found in THF/pyridine (99:1, v/v). Additionally, the low reactivity of benzoporphyrin towards LiR mandates using an excess of LiR, which, together with its lower oxidation potential compared to OEP leads to the additional formation of the disubstituted species.

Anticipating a better control over the reaction we then prepared soluble Ono–type benzoporphyrin precursors with masked isoindene units (**9**).[7] For compound (**9**) we expected a reactivity very similar to that of OEP as the electronic effect of the substitutents should be very similar and – based on spectroscopic data – both free bases have a similar macrocycle conformation. Surprisingly, reaction of the porphyrin with *n*BuLi gave a mixture of the mono- (**10**) and disubstituted products (**11**) based on NMR and MS spectral evidence (Scheme 2). Despite many attempts, we were unable to separate the two compounds. However, retro-Diels-Alder reaction on the TLC plate (using a hot air blow dryer) indicated that the two products are more easily separated on the benzoporphyrin stage. Thus, the reaction flask was purged with Ar, followed by addition of DDQ and heating at 200 °C for an hour. After workup 7 % of the dibutylated benzoporphyrin (**8**) and 43 % of the monosubstituted derivative (**6**) were isolated. Variation of the reaction conditions did not allow a complete suppression of the formation of the disubstituted product. Although involving more synthetic steps (preparation of (**9**)) this method is superior to the direct alkylation of benzoporphyrin, as the separation of **1** (not formed here) from **6** is notoriously difficult.



Scheme 2. Reactions of the benzoporphyrin precursor **9**. a) LiR[1], THF, –30 to –80 °C; b) H_2O, 10 min; c) air, 18 h; d) DDQ, 1 h; e) DDQ, 200 °C, 1 h.

An added benefit of using **9** was the ability to prepare meso-arylated derivatives. Reaction of **9** with PhLi followed by hydrolysis, addition of DDQ and *in situ* retro-Diels-Alder reaction gave 52 % of **12** and 8 % of **13**. meso-Phenylbenzoporphyrins have been studied for a long time but in most cases only UV/VIS and MS spectral data were available due to their difficult purification.[6] The present method gave convenient access to the individual compounds and thus allowed detailed spectroscopic characterizations. The solubility of the mono-phenylbenzoporphyrin (**12**) is still low, but, e.g., ^{1}H NMR spectral data could be obtained easily for the highly soluble dication in solutions containing TFA. For example, the respective spectrum of [**12**]$^{2+}$ gave clearly resolved signals for the meso protons (10.97 and 11.09 ppm) and the expected pattern of 3 signals for the phenyl rings and 6 signals for the annulated benzene rings.

In summary, despite its low solubility, benzoporphyrin can be substituted directly with reactive RLi reagents to the monosubstituted products in about 40 to 50 % yield accompanied by ~10 % of the disubstituted product. Disubstitution may be the result of the low solubility of both the unsubstituted and mono-substituted benzoporphyrins. The anionic species formed is better soluble and thus can easier undergo a second substitution. The observation of the predominant formation of the 5,10-regioisomer is in line with results for other porphyrinic systems and can be explained with the structure of the intermediary anions.[10] Likewise, the "precursor" porphyrin (**9**) presents a facile starting material for the

preparation of meso-arylated benzoporphyrins. As we have already shown that octaethylporphyrin can react with a broad range of other organolithium reagents including those containing functional groups,[12] both (**1**) and (**9**) can be used for the preparation of other meso-substituted benzoporphyrins.

EXPERIMENTAL

General procedures. General experimental conditions and instrumentations were as described before.[10] (Tetrabenzoporphyrinato)zinc(II) (**4**)[4a] and 2,3:7,8:12,13:17,18-tetrakis{bicyclo(2,2,2)octeno}porphyrin (diastereoisomeric mixture) (**9**)[7] were synthesized according to literature procedures.

Reaction of benzoporphyrin with hexyllithium: (Benzoporphyrinato)zinc(II) (**4**) (100 mg, 0.17 mmol) was suspended in 150 mL of THF and cooled to -30 °C. After addition of 0.6 mL of hexyllithium (1.5 M, 0.9 mmol) the green-blue reaction mixture turned first purple then brown. After stirring for 30 min water (1 mL) was added without change in color. The cold bath was removed and 9 mL of a 0.6 M solution of DDQ was added after 10 min, resulting in a color change to green. Polar impurities were removed *via* chromatography on silica with THF/pyridine (9:1, v/v). TLC showed three green product fractions. A first silica gel column (*n*-hexane/acetic acid ethyl ester (99:1, v/v) resulted in isolation of 10 mg of blue crystals of dihexylated benzoporphyrin (**7**) after recrystallization from dichloromethane/*n*-hexane (9 %). Purification of the second and third fraction was achieved with another silica gel column (THF/pyridine, 99:1, v/v). The second TLC fraction consisted of 38 mg (38 %) of **5** while the third fraction was identified as demetallated benzoporphyrin (**1**) (27 mg, 32 %). Use of eight equivalents of hexyllithium resulted in a different product composition (**7**: 14 %, **5**: 46 %, **1**: 6 %).

5-Hexyl-tetrabenzoporphyrin (5). mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$ + 10 % CF_3COOD, $SiMe_4$): δ=1.07 (m, 3H, $(CH_2)_5CH_3$), 1.58 (m, 2H, $(CH_2)_4CH_2CH_3$), 1.74 (m, 2H, $(CH_2)_3CH_2CH_2CH_3$), 2.19 (m, 2H, $CH_2CH_2CH_2(CH_2)_3$), 2.87 (m, 2H, $CH_2CH_2(CH_2)_4$), 5.49 (m, 2H, $CH_2(CH_2)_5$), 8.35, 8.49 (each m, 8H, 2^1,2^4,7^1,7^4,12^1,12^4,17^1,17^4-H_{benzo}), 9.33, 9.46, 9.52 (each m, 2H, 2H, 4H, 2^2,2^3,7^2,7^3,12^2,12^3,17^2,17^3-H_{benzo}), 10.84 (s, 1H, 15-H), 11.02 ppm (s, 2H, 10,20–H); MS (EI, 80 eV), *m/z* (%): 594 (100) [M^+], 523 (37) [M^+–C_5H_{11}], 297 (7) [M^{2+}]; UV/VIS (CH_2Cl_2): λ_{max} (log ε)=397 (4.13), 422 (4.78), 435 (4.82), 571 (3.50), 605 (4.10), 609 (4.09), 664 nm (3.76); HRMS [$C_{42}H_{34}N_4$]: calcd 594.2783, found 594.2758; [$C_{42}H_{34}N_4$, 594.76 g mol^{-1}]. Anal. Calcd for $C_{42}H_{34}N_4$ C 84.82, H 5.76, N 9.42. Found C 84.53, H 5.64, N 9.73.

5,10-Dihexyl-tetrabenzoporphyrin (7). mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$, $SiMe_4$): δ=–1.39 (s, 2H, N*H*), 0.86 (m, 6H, 2×$(CH_2)_5CH_3$), 1.33 (m, 4H, 2×$(CH_2)_4CH_2CH_3$), 1.40 (m, 4H, 2×$(CH_2)_3CH_2CH_2CH_3$), 1.80 (m, 2H, $CH_2CH_2CH_2(CH_2)_3$), 2.29 (m, 2H, $CH_2CH_2(CH_2)_4$), 5.31 (m, 2H, $CH_2(CH_2)_5$), 7.72, 8.00, 8.10 (each m, 4H, 2H, 2H, 2^1,2^4,7^1,7^4,12^1,12^4,17^1,17^4–H_{benzo}), 9.00, 9.20, 9.43 (each m, 2H, 4H, 2H, 2^2,2^3,7^2,7^3,12^2,12^3,17^2,17^3–H_{benzo}), 10.17 ppm (s, 2H, 15,20–H); MS (EI, 80 eV),

m/z (%): 679 (84) [M^++H], 678 (59) [M^+], 607 (26) [M^+–C_5H_{11}]; UV/VIS (CH_2Cl_2): λ_{max} (log ε)=397 (4.57), 422 (5.14), 435 (5.12), 528 (3.46), 568 (3.98), 608 (4.57), 665 nm (4.34); HRMS [$C_{48}H_{46}N_4$] calcd 678.3743, found 678.3722; [$C_{48}H_{46}N_4$, 678.92 g mol^{-1}]. Anal. Calcd for $C_{48}H_{46}N_4$ C 84.92, H 6.83, N 8.25. Found C 84.88, H 6.62, N 8.47.

Reaction of benzoporphyrin with butyllithium: The procedure followed the protocol given above for the hexylation reactions using 0.6 mL (2.5 M, 1.5 mmol) of butyllithium. Polar impurities were removed with an alumina column (THF/pyridine, 9:1, v/v) and TLC again indicated three product fractions. Chromatography on silica gel (*n*-hexane/acetic acid ethylester, 6:1, v/v) yielded the dibutylated compound (**8**) **(**14 mg blue crystals after recrystallization from CH_2Cl_2/*n*-hexane, 13 %). A second silica column (THF/pyridine, 99:1, v/v) separated the two remaining fractions yielding first 40 mg (42 %, blue crystals) of **6** followed by 9 mg (10 %, blue crystals) of **1**.

5-Butyl-tetrabenzoporphyrin (6): mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$ + 10 % CF_3COOD, $SiMe_4$): δ=1.00–1.75 (m, 5H, $CH_2CH_2CH_2CH_3$), 2.77 (m, 2H, $CH_2CH_2CH_2CH_3$), 5.45 (m, 2H, $CH_2CH_2CH_2CH_3$), 8.27, 8.43 (each m, 4H, 2^1,2^4,7^1,7^4,12^1,12^4,17^1,17^4–H_{benzo}), 9.31, 9.41, 9.50 (each m, 1H, 1H, 2H, 2^2,2^3,7^2,7^3,12^2,12^3,17^2,17^3–H_{benzo}), 10.78 (s, 1H, 15–H), 10.98 ppm (s, 2H, 10,20–H); MS (EI, 80 eV), *m/z* (%): 566 (21) [M^+], 523 (16) [M^+–C_3H_7], 283 (7) [M^{2+}], 261 (20) [M^{2+}–C_3H_7]; UV/VIS (CH_2Cl_2): λ_{max} (log ε)=398 (4.12), 421(4.73), 434 (4.79), 568 (3.49), 603 (4.08), 609 (4.09), 664 nm (3.77; HRMS [$C_{40}H_{30}N_4$]: calcd 566.24705, found 566.24701; [$C_{40}H_{30}N_4$, 566.70 g mol^{-1}]. Anal. Calcd for $C_{40}H_{30}N_4$ C 84.87, H 5.34, N 9.89. Found C 84.61, H 5.51, N 9.63.

5,10-Dibutyl-tetrabenzoporphyrin (8): mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$, $SiMe_4$): δ=–2.39–-2.10 (s, 2H, br, N*H*), 0.80–2.10 (m, 6H, $CH_2CH_2CH_2CH_2$), 5.31 (m, 2H, $CH_2CH_2CH_2CH_3$), 7.90–8.12 (m, 8H, 2^1,2^4,7^1,7^4,12^1,12^4,17^1,17^4–H_{benzo}), 8.92–9.40 (m, 8H, 2^2,2^3,7^2,7^3,12^2,12^3,17^2,17^3–H_{benzo}), 10.30 ppm (s, 2H, 15,20–H); MS (EI, 80 eV), *m/z* (%): 622 (15) [M^+], 537 (17) [M^{2+}–C_6H_{13}]; UV/VIS (CH_2Cl_2): λ_{max} (log ε)=406 (4.54), 435 (5.08), 447 (5.10), 574 (4.33), 621 (4.51), 679 nm (4.34); HRMS [$C_{44}H_{38}N_4$]: calcd 622.30965, found 622.30943; [$C_{44}H_{38}N_4$, 622.81 g mol^{-1}]. Anal. Calcd for $C_{44}H_{38}N_4$ C 84.85, H 6.15, N 9.00. Found C 84.71, H 6.30, N 9.13.

Reaction of compound (9) with butyllithium. As an alternative to the method described above 100 mg (0.16 mmol) of the norbornene precursor (**9**) were dissolved in 100 mL of THF and cooled to –80 °C. Subsequently 0.3 mL of butyllithium (2 M, 0.6 mmol) were added dropwise. After stirring for 5 to 20 min 7 mL of a 0.06 molar solution of DDQ in THF were added and the mixture warmed to rt. The flask was purged with argon and heated under vacuum for 1 h at 200 °C resulting in almost quantitative retro-Diels-Alder reaction. Chromatography on silica gel eluting with neat THF yielded a green fraction of the dibutylated porphyrin (**8**) (7 mg of blue crystals after recrystallization from CH_2Cl_2/*n*-hexane, 11

μmol, 7 %). Immediately after elution of this fraction the solvent used for chromatography was changed to THF/pyridine (99:1, v/v) and yielded a second fraction containing 39 mg (43 % in reference to **9**, blue crystals) of **6**.

Reaction of compound (9) with phenyllithium. Compound (**6**) (100 mg, 0.16 mmol) was dissolved in 100 mL of THF and cooled to 0 °C. After addition of 0.5 mL of LiPh (1.8 M, 0.9 mmol in THF) the red brown suspension changed color to brown. After 15 min the mixture was warmed to 30 °C and stirred for another 15 min. After cooling to 0 °C 1 mL of water was added, resulting in a color change to green. The mixture was stirred for 18 h under air to complete oxidation and turned brown. The reaction flask war purged with Ar and heated under vacuum for 1 h at 200 °C. TLC control showed two green bands and a weak, brown residue at the starting line. Chromatography on neutral alumina (Brockmann grade III, CH_2Cl_2/*n*-hexane, 2:1, v/v) yielded first **13** (see below) followed by **12** (48 mg blue crystals, 52 % in relation to **9**).

5-Phenyl-tetrabenzoporphyrin (12). mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$ + 10 % CF_3COOD, $SiMe_4$): δ=7.57 (d, 2H, ^3J=4.1 Hz, H_{Ph}), 7.86 (t, 2H, ^3J=7.4 Hz, H_{Ph}), 8.03 (m, 2H, 2^3,2^4,7^1,7^2,12^3,12^4,17^1, 17^2-H_{benzo}), 8.12 (t, 1H, ^3J=7.6 Hz, H_{Ph}), 8.20, 8.39 (each m, 2H, 2H, 2^3,2^4,7^1,7^2,12^3,12^4,17^1,17^2-H_{benzo}), 8.49 (m, 4H, 2^2,7^3,12^2,17^3-H_{benzo}), 9.38 (m, 2H, 2^3,2^4,7^1,7^2,12^3,12^4,17^1,17^2-H_{benzo}), 9.62 (m, 4H, 2^1,7^4,12^1,17^4-H_{benzo}), 10.97 (s, 1H, 15–H), 11.09 ppm (s, 2H, 10,20–H); MS (EI, 80 eV), *m/z* (%): 586 (100) [M^+], 293 (14) [M^{2+}]; UV/VIS (CH_2Cl_2): λ_{max} (log ε)=389 (4.11), 420 (4.75), 433 (4.68), 558 (3.39), 599 (3.96), 608 (4.02), 664 nm (3.79); HRMS [$C_{42}H_{26}N_4$]: calcd 586.2157, found 586.2159; [$C_{42}H_{26}N_4$, 586.70 g mol^{-1}]. Anal. Calcd for $C_{42}H_{26}N_4$ C 85.98, H 4.47, N 9.55. Found C 86.16, H 4.78, N 9.87.

5,10-Diphenyl-tetrabenzoporphyrin (13). The first green fraction obtained during the synthesis was further purified by preparative HPLC (Nukleosil 50-5, CH_2Cl_2/*n*-hexane, 2:3, v/v) yielding 9 mg (0.013 mmol, 8 %) after recrystallization from CH_2Cl_2/CH_3OH. mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$ + 10 % CF_3COOD, $SiMe_4$): δ=7.37 (d, 4H, ^3J=4.0 Hz, H_{Ph}), 7.56 (m, 4H, H_{benzo}), 7.67 (t, 4H, ^3J=7.4 Hz, H_{Ph}), 7.89 (t, 2H, ^3J=7.5 Hz, H_{Ph}), 7.99 (m, 4H, H_{benzo}), 8.15 (d, 4H, ^3J=3.4 Hz, H_{benzo}), 9.56 (d, 4H, ^3J=3.8 Hz, H_{benzo}), 10.99 (s, 2H, 15,20–H); MS (EI, 80 eV), *m/z* (%): 662 (100) [M^+], 331 (19) [M^{2+}]; UV/VIS (CH_2Cl_2): λ_{max} (log ε)=395 (3.99), 424 (4.83), 438 (4.91), 569 (3.52), 602 (4.07), 610 (4.16), 666 nm (3.89); HRMS [$C_{48}H_{30}N_4$] calcd 662.2470, found 662.2459; [$C_{48}H_{30}N_4$, 662.79 g mol^{-1}]. Anal. Calcd for $C_{48}H_{30}N_4$ C 86.98, H 4.56, N 8.45. Found C 87.13, H 4.69, N 8.51.

ACKNOWLEDGEMENTS

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REFERENCES

1. J. H. Helberger, *Ann. Phys.*, 1938, **536**, 197; 173.
2. D. W. Clack and N. S. Hush, *J. Am. Chem. Soc.*, 1965, **87**, 4238. J. R. Sams and T. B. Tsin, *Chem. Phys. Lett.*, 1974, **25**, 599. A. Vogler, B. Rethwisch, H. Kunkely, J. Hüttermann, and J. O. Besenhard, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 952. M. Yasuike, T. Yamaoka, O. Ohno, K. Ichimura, H. Morii, and M. Sakuragi, *Inorg. Chim. Acta*, 1991, **185**, 39. C. K. Chang and J. Fajer, *J. Am. Chem. Soc.*, 1980, **102**, 848.
3. S. A. Vinogradov and D. F. Wilson, *J. Chem. Soc., Perkin Trans. 2*, **1995**, 103. R. Bonnett, K. A. Mc Manus, and A. Kimberly, *J. Chem. Soc., Perkin Trans. 1*, **1996**, 2461. M. Brunel, F. Chaput, S. A. Vinogradov, B. Campagne, M. Canva, J. P. Boilot, and A. Brun, *Chem. Phys.*, 1997, **218**, 301.
4. a) A. Vogler and H. Kunkely, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 760. b) M. G. H. Vicente, A. C. Tome, A. Walter, and J. A. S. Cavaleiro, *Tetrahedron Lett.*, 1997, **38**, 3639. S. Ito, T. Murashima, H. Uno, and N. Ono, *Chem. Commun.*, **1998**, 1661.
5. R.-J. Cheng, Y. R. Chen, and C.-E. Chuang, *Heterocycles*, 1992, **34**, 1.
6. V. N. Kopranenkov, S. N. Dashkevich, V. N. Shevtsov, and K. Luk`yanets, *Khim. Geterotsikl. Soedin.*, **1984**, 61. K. Ichimura, M. Sakuragi, H. Morii, M. Yasuike, M. Fukui, and O. Ohno, *Inorg. Chim. Acta*, 1990, **176**, 31; 1991, **182**, 83; 1991, **186**, 95.
7. S. Ito, T. Murashima, H. Uno, and N. Ono, *Chem. Commun.*, **1998**, 1661. H. Uno, T. Ishikawa, T. Hoshi, and N. Ono, *Tetrahedron Lett.*, 2003; **44**, 5163. Y. Shimizu, Z. Shen, T. Okujima, H. Uno, and N. Ono, *Chem. Commun.*, **2004**, 374.
8. O. Finikova, A. Cheprakov, I. Beletskaya, and S. A. Vinogradov, *Chem. Commun.*, **2001**, 261.O. S. Finikova, A. V. Cheprakov, P. J. Carroll, and S. A. Vinogradov, *J. Org. Chem.*, 2003, **68**, 7517. O. Finikova, A. Glakin, V. Rozhkov, M. Cordero, C. Haegerhael, and S. A. Vinogradov, *J. Am. Chem. Soc.*, 2003, **125**, 4882. I. B. Rietveld, E. Kim, and S. A. Vinogradov, *Tetrahedron*, 2003, **59**, 3821. O. S. Finikova, A. V. Cheprakov, I. P. Beletskaya, P. J. Carroll, and S. A. Vinogradov, *J. Org. Chem.*, 2004, **69**, 522.
9. M. O. Senge and J. Richter, *J. Porphyrins Phthalocyanines*, 2004, **8**, 934.
10. W. W. Kalisch and M. O. Senge, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 1107. M. O. Senge, W. W. Kalisch, and I. Bischoff, *Chem. Eur. J.* 2000, **6**, 2721. X. Feng, I. Bischoff, and M. O. Senge, *J. Org. Chem.*, 2001, **66**, 8694. A. Wiehe, C. Ryppa, and M. O. Senge, *Org. Lett.*, 2002, **4**, 3807.
11. S. Hatscher and M. O. Senge, *Tetrahedron Lett.*, 2003, **44**, 157.
12. M. O. Senge and I. Bischoff, *Eur. J. Org. Chem.*, **2001**, 1735; *Tetrahedron Lett.*, 2004, **45**, 1647.