Regioselective reaction of 5,15-disubstituted porphyrins with organolithium reagents—synthetic access to 5,10,15-trisubstituted porphyrins and directly meso-meso-linked bisporphyrins

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The reaction of organolithium reagents with 5,15-disubstituted porphyrins, followed by hydrolysis of the intermediate anion to give a porphodimethene and oxidation with DDQ allows the facile preparation of 5,10,15-tri- and 5,10,15,20-tetrasubstituted porphyrins with mixed meso substituent types. Easily available 5,15-disubstituted porphyrins react almost quantitatively with sterically undemanding organolithium reagents (PhLi, BuLi) to give the respective 5,10,15-trisubstituted porphyrins (A_2B-type). When bulkier reagents are used (*e.g.* Bu^s or Bu^t) the number and yield of side products increases considerably. Thus, the regioselectivity of the nucleophilic attack (meso *versus* β) depends on the steric hindrance of the LiR reagents. The 5,10,15-trisubstituted porphyrins can in turn be used for another cycle of nucleophilic attack, hydrolysis, and oxidation giving rise to 5,10,15,20-tetrasubstituted porphyrins of the A_2B_2- or A_2BC-types. In contrast, reaction of 5,15-disubstituted porphyrins with LiR and direct oxidation of the intermediate anion without a hydrolysis step gives directly linked (5,5′) bisporphyrins allowing the preparation of bisporphyrins with mixed meso substituent pattern. In addition, the crystal structures of two 5,10,15-trisubstituted porphyrins (**25**, **28**) are reported. Both compounds exhibit moderately nonplanar macrocycles as a result of the sterically hindered meso substituents.

Introduction

Functionalization of porphyrins *via* organometallic coupling reactions has enjoyed considerable success recently.[1] For example, Heck and Suzuki coupling reactions allowed the synthesis of various meso and β-substituted porphyrins.[2] Considerable progress has also been made in the development of syntheses for directly linked bisporphyrins[3,4] and oligo/polyporphyrins[5] as novel (opto)electronic materials.[6] Nevertheless, the increasing demand for functionalized porphyrins, especially in the context of technical and medicinal applications,[7] requires short synthetic routes with as few steps as possible, high yields and preferably a wide substrate tolerance. Utilizing organolithium reagents we have shown that a wide range of meso substituted and functionalized porphyrins and porphodimethenes is accessible without having to prepare activated or prefunctionalized porphyrins.[8]

Initially we used octaethylporphyrin derivatives, *e.g.* **1** for our investigation.[8a] The method developed utilized a reaction sequence consisting of treatment of the porphyrin with RLi, hydrolysis with water to yield a porphodimethene, followed by oxidation with DDQ to give the desired porphyrin. For example, reaction of **1** with BuLi under the conditions described gave the respective 5-butylporphyrin **2** in quantitative yield. This method was equally successful with alkyl- and aryllithium reagents (*e.g.* **1** + PhLi ⟶ **3**) and could be used for the modification of both metallo porphyrins and free base porphyrins. Thus, reaction of 2,3,7,8,12,13,17,18-octaethylporphyrin **4** with either BuLi or PhLi, followed by hydrolysis and oxidation, gave the porphyrins **5** and **6**, respectively. The studies performed so far, indicate that this is a general method that can be used for the synthesis of any meso substituted porphyrin, provided the required LiR reagent can be prepared.

Next we turned our attention to the investigation of 5,10,15,20-tetrasubstituted porphyrins, *e.g.* the tetraalkylporphyrin **7**. Reaction with BuLi gives the porphodimethene (5,15-dihydroporphyrin) **10** as the sole product, that upon oxidation with DDQ can be converted into **11**, a 5,5[1]-didehydroporphodimethene with an exocyclic double bond.[8a,b] The reactivity of these porphyrins is strongly governed by the central metal and the meso substituents. For example, Callot and coworkers showed that tetraphenylporphyrin **8** reacts with alkyllithium reagents to give a variety of phlorins (5,22-dihydroporphyrins) (**12**) and porphodimethenes (5,10-dihydroporphyrins) (**13**).[9] In addition, C_b–C_b addition reactions to yield chlorins (**14**–**16**) were observed with both free base tetraphenylporphyrin **8**[9b] and the corresponding zinc(II) complex **9**.[8b]

In order to expand the synthetic utility of organolithium reagents for the synthesis of novel porphyrins and hydroporphyrins we have now utilized 5,15-disubstituted porphyrins as starting materials. Using compounds like **17**–**19**, *i.e.* porphyrins with both free meso and β positions, we intended to investigate the regioselectivity of this reaction. Provided that preferential attack of RLi occurs at the meso position, this would give a convenient entry into 5,10,15-tri- and 5,10,15,20-tetrasubstituted porphyrins. Porphyrins of this type are useful precursors for further transformations and are accessible only with difficulty *via* established routes.[10]

Results and discussion

The 5,15-disubstituted porphyrins **17**–**19** were chosen as starting materials as they are easily prepared in one step and acceptable yields from dipyrromethane and the appropriate aldehyde.[11] In addition, a quick investigation of the regioselectivity of the meso *versus* β attack should be possible. First we used sterically undemanding organolithium reagents. For example, reaction of the diphenylporphyrin **18** with either PhLi or BuLi yielded a brown reaction mixture, that after hydrolysis and oxidation turned deep red. After flash chromatographic separation the trisubstituted porphyrins **20** or **23** were obtained in almost quantitative yield. Similar reaction products (**21** or

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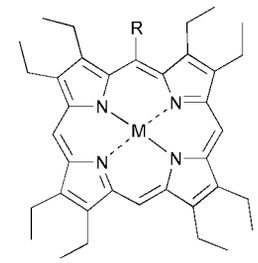
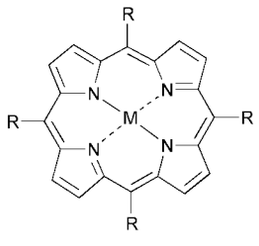
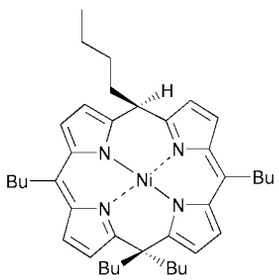


1 M = Ni^{II}, R = H
2 M = Ni^{II}, R = Bu
3 M = Ni^{II}, R = Ph
4 M = 2H, R = H
5 M = 2H, R = Bu
6 M = 2H, R = Ph



7 M = Ni^{II}, R = Bu
8 M = 2H, R = Ph
9 M = Zn^{II}, R = Ph



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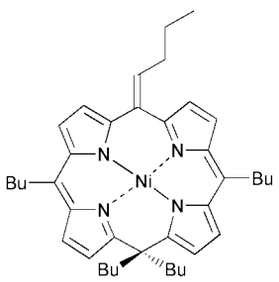

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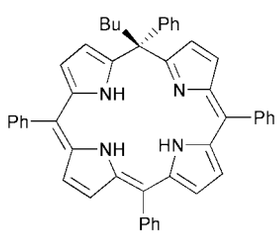

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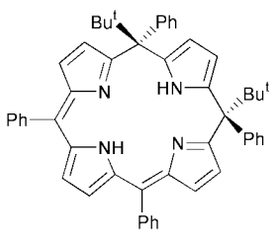

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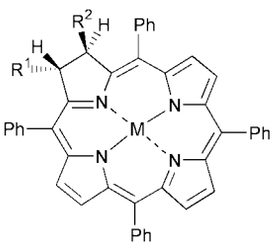
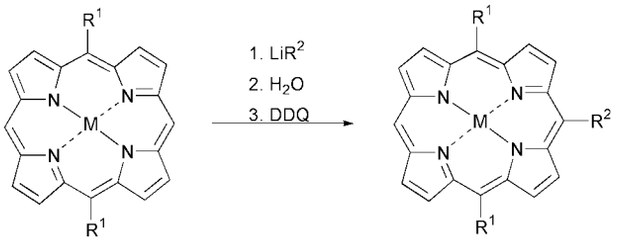


14 M = 2H, R^1 = Bu, R^2 = H
15 M = Zn^{II}, R^1 = Bu, R^2 = H
16 M = Zn^{II}, R^1 = R^2 = Bu



17 M = 2H, R^1 = Bu
18 M = Ni^{II}, R^1 = Ph
19 M = 2H, R^1 = Ph

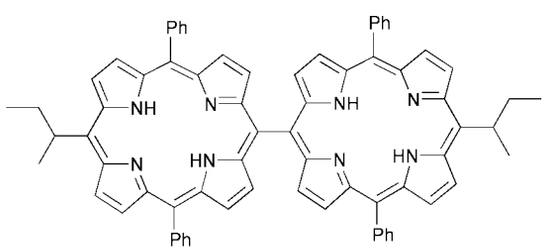
20 M = Ni^{II}, R^1 = R^2 = Ph
21 M = 2H, R^1 = R^2 = Ph
22 M = 2H, R^1 = Bu, R^2 = Ph
23 M = Ni^{II}, R^1 = Ph, R^2 = Bu
24 M = 2H, R^1 = Ph, R^2 = Bu
25 M = 2H, R^1 = Ph, R^2 = Pr^i
26 M = Ni^{II}, R^1 = Ph, R^2 = Pr^i
27 M = 2H, R^1 = Ph, R^2 = Bu^s
28 M = Ni^{II}, R^1 = Ph, R^2 = Bu^s
29 M = Ni^{II}, R^1 = Ph, R^2 = Bu^t

Scheme 1

24) were observed when the respective free base **19** was used as starting material. Alternatively, compounds like **22** could be prepared from the meso-alkylporphyrin **17**.[4] No β-substituted reaction products (either porphyrins or chlorins) were isolated from any of these reactions.

A different reactivity was observed upon reaction of either **18** or **19** with sterically more demanding LiR reagents (R = Pr^i, Bu^s, Bu^t). In general, an increasing number of reaction products was observed depending on the steric bulk of RLi. Using the nickel(II) complexes as starting material the desired trisubstituted porphyrins **26**, **28**, and **29** were obtained in acceptable yields ranging from 50 to 65%. Nevertheless, the formation of several side products (mainly green, brown, or blue) was observed. In contrast, the reactivity of the free bases with sterically demanding nucleophiles is much higher. For example, the reaction of **19** with Bu^tLi gave more than 20 different red, green, and blue products (by TLC). Attempts to separate this mixture by flash chromatography resulted in decomposition to even more products and we were unable to isolate the desired free base. Only the reaction of **18** with Pr^iLi or Bu^sLi gave the free bases **25** and **27** in 30 and 15% yield, respectively. Variation of the reaction conditions (temperature, solvents, and concentration of RLi) did not result in a significantly improved yield or a diminished number of side products.

Depending on the substitution pattern of the porphyrin or the steric hindrance of RLi, phlorins, chlorins, 5,10- and 5,15-dihydroporphyrins have been identified as possible products from the reaction of organolithium reagents with porphyrins.[8a,b,9] Based upon the blue color observed for several side products, irreversible ring-opening to linear tetrapyrroles can also occur and a further novel product was obtained from the reaction of **18** with Bu^sLi. As described the trisubstituted porphyrin **27** is formed in low yield. In addition, the directly meso–meso linked dimer **30** was isolated in 30% yield. TLC

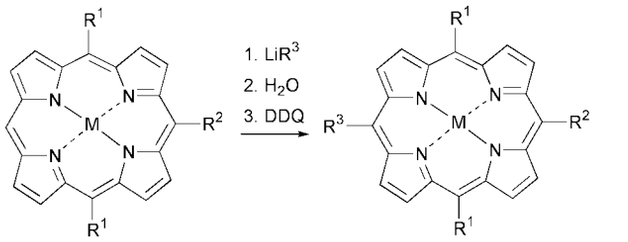


30

and spectroscopic analysis indicates that formation of the bisporphyrin occurs rapidly before the hydrolysis step.

5,10,15-Trisubstituted porphyrins **31** were subjected to the same reaction conditions as described above. For simple reagents like BuLi or PhLi excellent transformations to give 5,10,15,20-tetrasubstituted porphyrins of the A_2B_2- or A_2BC-types were observed. For example, **21** was converted to **32** with BuLi in 88% yield, and **20** gave **33** in 93% yield. Similar results were obtained with reagents like PhLi or other 5,10,15-trisubstituted porphyrins and the order of introduction of the different meso substituents is unimportant for the overall yield. Again, complete regioselectivity for the meso position was observed.

Utilization of sterically hindered nucleophiles gave similar results as described for 5,15-disubstituted porphyrins. Here, even use of Pr^iLi and reaction with the free base **25** gave a complex reaction mixture of numerous compounds that could



31

32 M = 2H, $R^1 = R^2$ = Ph, R^3 = Bu
33 M = Ni^{II}, $R^1 = R^2$ = Ph, R^3 = Bu
34 M = Ni^{II}, R^1 = Ph, R^2 = Bu^t, R^3 = Bu^s

Scheme 2

not be separated chromatographically. Thus, the reaction of 5,10,15-trisubstituted porphyrins is even more susceptible to the steric demand of the reagent than 5,15-disubstituted porphyrins. Again, the nickel(II) complexes were more suitable for transformations with hindered reagents. For example, reaction of **29** with Bu^sLi gave the tetrasubstituted porphyrin **34** in 55% yield. Presumably the different reactivity of free bases and nickel(II) complexes is the result of different intermediates that are formed as the primary product of the nucleophilic attack. Reaction of free bases with RLi proceeds through phlorins,[9] while nickel(II) complexes initially form porphodimethenes.[4] For rhodium porphyrins a phlorin has also been postulated as an intermediate.[12] As steric interactions in porphodimethenes are diminished this might be an explanation for the higher yields observed for the reaction of sterically hindered nucleophiles with nickel(II) complexes compared to free bases.

Thus, it is possible to prepare 5,10,15,20-tetrasubstituted porphyrins by successive use of two cycles of the LiR reaction. As compounds like **31** are notoriously difficult to prepare or require laborious chromatographic work-up of so-called mixed condensations this method presents a considerable improvement over existing methods.[10] However, as we have shown that similar products (including those with residues containing functional groups) can easily be prepared in a one-pot reaction using first an attack of RLi followed by reaction of the intermediate *in situ* with RI,[8c] no further experiments were undertaken in this area.

Due to their limited availability tri-meso substituted porphyrins have not been studied much with regard to their molecular structure and conformation.[13] So far, only one study has addressed conformational aspects of these interesting molecules.[14] Structural analysis of 5-nitro-10,20-diphenylporphyrin and (5-bromo-10,20-diphenylporphyrinato)nickel(II) showed the free base macrocycle to be ruffled while the nickel(II) complex exhibited a planar conformation. We were able to crystallize the free base **25** and the nickel(II) complex **28**, both containing one secondary alkyl residue in a meso position (Fig. 1).

A detailed conformational analysis (Fig. 2) showed that both compounds have ruffled macrocycles. Ruffling is characterized by rotation of the pyrrole rings against the C_b–C_b vector and significant displacements of the meso carbon atoms (C_m) from the mean plane of the molecule.[13] With average displacements of the C_m positions of 0.22 Å in **25** and 0.35 Å in **28** the molecules exhibit moderate ruffling. The degree of ruffling and thus the overall conformation is asymmetric. In addition, the overall distortion mode has some contribution from saddle distortion, too, as evidenced by the out-of-plane tilting of some pyrrole rings in both structures. The contribution from saddle distortion is larger in the nickel(II) complex **28**. The overall measure of nonplanarity (Δ24 = 0.11 to 0.2 Å) is much less compared to highly substituted porphyrins but the local steric influence of the meso substituents is indicated by the difference in individual C_a–C_m–C_a angles (Table 1). Substituted meso positions generally exhibit widened C_a–C_m–C_a angles.[15] The average Ni–N bond length in **28** is 1.951(5) Å. This is only

Table 1 Selected bond lengths, angles, and conformational parameters for the porphyrins studied

		28	
Compound	**25**	Molecule 1	Molecule 2
Bond lengths/Å			
Ni–N21	—	1.951(5)	1.951(5)
Ni–N22	—	1.940(5)	1.937(5)
Ni–N23	—	1.949(5)	1.951(5)
Ni–N24	—	1.953(5)	1.957(5)
Bond angles/degrees			
C4–C5–C6	123.9(2)	120.8(6)	121.8(6)
C9–C10–C11	125.0(2)	121.8(6)	122.4(6)
C14–C15–C16	127.5(2)	124.4(6)	124.2(6)
C19–C20–C1	124.9(2)	122.3(6)	122.6(6)
Conformational parameters/Å			
Core size ⊗ [a]	2.058	1.948	1.949
Core elongation Ξ [b]	0.007	−0.004	−0.008
Δ24 [c]	0.11	0.20	0.18
δC5 [d]	0.30	0.41	0.44
δC10 [d]	0.22	0.34	0.28
δC15 [d]	0.21	0.33	0.34
δC20 [d]	0.14	0.34	0.27
δC_m [e]	0.22	0.36	0.33
δC_b [e]	0.08	0.21	0.17
δNi [d]	—	0.007	0

[a] The core size is defined as the geometrical center of the four nitrogen atoms. [b] The core elongation parameter is defined as the difference between the vector lengths (|N21 − N22| + |N23 − N24|)/2 − (|N22 − N23| + |N21 − N24|)/2. [c] Deviation of the 24 macrocycle atoms from their least squares plane. [d] Deviation from the 4N-plane. [e] Average deviation from the 4N-plane.

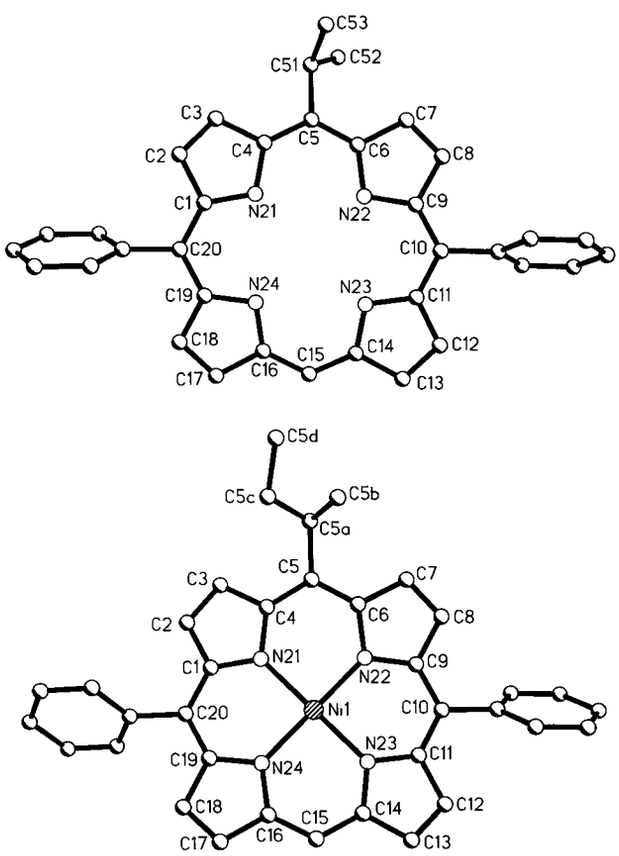


Fig. 1 View of the molecular structure and numbering scheme of **25** (top) and **28** (bottom, only one of the two crystallographically independent molecules shown). Hydrogen atoms and disordered positions have been omitted for clarity.

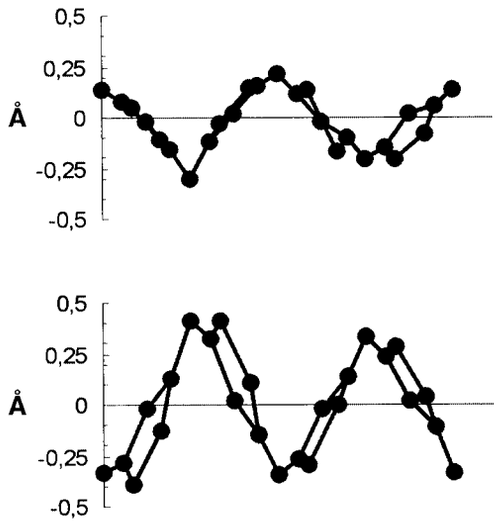
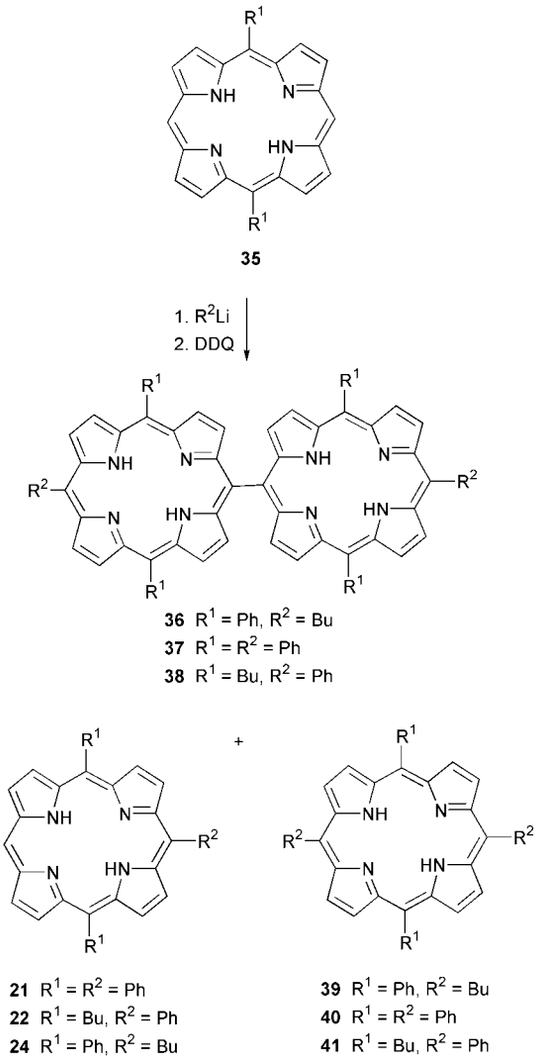


Fig. 2 Linear display of the skeletal deviations of the macrocycle atoms from the 4N-plane for compounds **25** and **28** (molecule 1). The *x*-axis (Å) is not to scale.

slightly shorter than that found in the triclinic A form of (2,3,7,8,12,13,17,18-octaethylporphyrinato)nickel(II) (1.958(2) Å),[16] but significantly longer compared to ruffled 5,10,15,20-tetraalkylporphyrins.[17] This indicates that the observed conformation is mainly the result of steric interactions and not due to a simple metal effect. As no multiple modifications have yet been described for 5,10,15-trisubstituted porphyrins the influence of packing forces cannot be completely ruled out. Nevertheless, the structural data listed in Table 1 fit into the concepts now established for sterically hindered porphyrins in all respects.[13] In addition, UV/VIS spectroscopy showed increasing bathochromic shifts of the absorption bands for porphyrins with sterically more demanding substituents. Red-shifted absorption bands are good indicators for nonplanar macrocycles in solution.[18] For example, the long wavelength absorption maxima for the nickel complexes **31** with R^2 = Bu, Pr^i, Bu^s, Bu^t are 556, 558, 560, and 581 nm, respectively. Relief of steric strain is only facilitated by out-of-plane distortions; as indicated by the small values for the core elongation factor Ξ,[13,19] no evidence for in-plane distortion was found.

Besides giving convenient access to tri- and tetra-meso-substituted porphyrins, the reaction of 5,15-disubstituted porphyrins with organolithium reagents has further synthetic potential. As outlined in a communication,[4] a simple switch of the reaction conditions leads to directly linked bisporphyrins. As described above, the reaction of porphyrins with LiR typically involves an intermediate hydrolysis step to hydrolyze excess organolithium reagent and to protonate the intermediary anion to a porphodimethene. Subsequent oxidation with DDQ then gives the desired meso substituted porphyrin. We found, that quite a different reactivity is observed upon reaction of 5,15-disubstituted free bases **35** (R^1 = Bu or Ph) with BuLi or PhLi followed by direct addition of the oxidant DDQ without the intermediary hydrolysis step.

This reaction sequence yielded the meso–meso linked bisporphyrins **36**–**38** directly in yields ranging from 55 to 78%. As side products tri- (**21**,**22**,**24**) and tetra-meso substituted (**39**–**41**) porphyrins were observed. This indicates that two competing reactions occur. Dimerization presumably proceeds *via* oxidation of the anion to give a π stabilized radical followed by radical dimerization. DDQ induced oxidative dimerizations are known[20] and related reactions have been described for other tetrapyrroles.[21] On the other hand, hydride abstraction to give the neutral porphyrins **21**, **22** or **24** (depending on the reagents) can occur, which then react with a second molecule RLi to give **39**–**41**. Other oxidants gave mixed results. With iodine the reaction with PhLi proceeded well with slightly improved yields,



Scheme 3

while reactions with BuLi and I_2 resulted in diminished yields (*ca.* 30%) and formation of several side products. UV light can be used to accelerate the reaction but has to be used with care. Normally the dimerization reaction is complete within 10–15 min. Illumination with a UV lamp leads to completion within 5 min. Longer exposure to UV light results in diminished yields and formation of side products. This method works well with free bases, but reaction of nickel(II) complexes under the same conditions resulted in formation of the tri- and tetrasubstituted porphyrins. While other syntheses of 5,5′-bisporphyrins[22] often suffer from low yields or laborious synthetic requirements, this new method gives good yields and allows the preparation of bisporphyrins with a mixed meso substitution pattern at C5, C15, and C20 in one step.

In conclusion, the reaction of 5,15-disubstituted and 5,10,15-trisubstituted porphyrins with sterically unhindered organolithium reagents proceeds regioselective at the meso positions. Only when sterically hindered reagents are used or when all meso positions are substituted does reaction at the β-positions become a competing reaction. Thus the reaction provides a convenient entry into tri- and tetrasubstituted porphyrins. In addition, simple variation of the reaction conditions provide a route to directly meso–meso linked bisporphyrins in high yield.

Experimental

General

All chemicals used were of analytical grade and purified before

use by distillation. The reactions of porphyrins with organolithium compounds were performed under a purified argon atmosphere by using modified Schlenk techniques and dried and degassed solvents. Melting points are uncorrected and were measured with a Reichert Thermovar apparatus. Neutral alumina (Alfa) (usually Brockmann Grade III, *i.e.* deactivated with 7.5% water) was used for column chromatography. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel or alumina 60 (neutral, fluorescence indicator F_{254}) precoated plates. Proton NMR spectra were recorded at a frequency of 250 MHz with a Bruker AC 250 instrument. All chemical shifts are given in ppm and have been converted to the δ scale and are referenced against the TMS signal as internal standard. *J* Values are given in Hz. Electronic absorption spectra were recorded with a Specord S10 (Carl Zeiss) spectrophotometer using dichloromethane as solvent. Mass spectra were obtained using a Varian MAT 711 mass spectrometer. Calculated mass for Ni complexes refers to ^{58}Ni. Elemental analyses were performed with a Perkin-Elmer 240 analyzer.

General procedure for the preparation of substituted porphyrins

A Schlenk flask was charged with 0.1 mmol of the porphyrin (*ca.* 50 mg) dissolved in 30–40 ml dry THF under an argon atmosphere. The solution was cooled to −70 °C for RLi (R = *n*-, sec-, iso-, or *tert*-butyl) or to 0 °C for reactions using phenyllithium. The organolithium reagent (0.6 mmol, 0.3 ml of a 2 M solution in cyclohexane) was added dropwise over 15 min. After removal of the cold bath the reaction mixture was stirred for another 15 min, followed by addition of 0.5 ml water in 5 ml THF. After stirring for 10 min, a solution of four equivalents of DDQ in methylene chloride (*ca.* 0.06 M) was added and the reaction mixture was stirred for another 60 min at room temperature. Subsequently, the mixture was filtered through neutral alumina and subjected to column chromatography on neutral alumina (Alfa) followed by recrystallization from CH_2Cl_2–methanol.

(5,10,15-Triphenylporphyrinato)nickel(II) 20. Chromatography eluting with ethyl acetate–*n*-hexane (1 : 150, v/v); yield 55 mg (92%) purple crystals (Found: C, 72.78; H, 3.96; N, 8.60. $C_{38}H_{24}N_4Ni$ requires C, 76.67; H, 4.06; N, 9.41%. $C_{38}H_{24}N_4Ni\cdot 0.5CH_2Cl_2$ requires C, 72.50; H, 3.95; N, 8.78%): mp 278 °C (CH_2Cl_2–CH_3OH); $\lambda_{max}(CH_2Cl_2)$/nm 406 (log ε/dm^3 mol^{-1} cm^{-1} 5.18), 520 (3.98), 554 (3.29); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) 7.55–7.65, 7.85–8.05 (15 H, each m, H_{Ph}), 8.75–8.78 (4 H, m, 4 × $H_{\beta\text{-pyrrole}}$), 8.85, 9.07 (4 H, each d, ^3J 5.0, 8 × $H_{\beta\text{-pyrrole}}$), 9.80 (1 H, s, H_{meso}); *m*/*z* (EI, 80 eV): 594.1387 (M^+, 100%. $C_{38}H_{24}N_4Ni$ requires 594.1354), 516 (19, $M^+ - C_6H_5$), 297 (14, M^{2+}).

5,10,15-Triphenylporphyrin 21. Chromatography eluting with ethyl acetate–*n*-hexane (1 : 200, v/v); yield 48 mg (89%) purple crystals (Found: C, 81.02; H, 4.92; N, 9.94. $C_{38}H_{26}N_4$ requires C, 84.73; H, 4.87; N, 10.40%. $C_{38}H_{26}N_4\cdot 0.5CH_2Cl_2\cdot 0.5CH_3OH$ requires C, 81.45; H, 4.94; N, 9.81%): mp 300 °C (CH_2Cl_2–CH_3OH); $\lambda_{max}(CH_2Cl_2)$/nm 412 (log ε/dm^3 mol^{-1} cm^{-1} 5.20), 508 (3.78), 543 (3.00), 584 (3.14), 638 (2.37); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) −3.05 (2 H, s, 2 × N*H*), 7.65–7.80, 8.15–8.35 (15 H, each m, H_{Ph}), 8.82–8.90 (4 H, m, 4 × $H_{\beta\text{-pyrrole}}$), 9.05, 9.35 (4 H, each d, *J* 5.0, 8 × $H_{\beta\text{-pyrrole}}$), 10.25 (1 H, s, H_{meso}); *m*/*z* (EI, 80 eV): 538.2128 (M^+, 100%. $C_{38}H_{26}N_4$ requires 538.2157), 461 (3, $M^+ - C_6H_5$), 269 (16, M^{2+}).

5,15-Dibutyl-10-phenylporphyrin 22. Chromatography eluting with ethyl acetate–*n*-hexane (1 : 150, v/v); yield 43 mg (74%) purple crystals: mp 210 °C (CH_2Cl_2–CH_3OH); $\lambda_{max}(CH_2Cl_2)$/nm 413 (log ε/dm^3 mol^{-1} cm^{-1} 5.36), 511 (4.19), 550 (3.88), 591 (3.69), 648 (3.56); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) −2.75 (2 H, s, 2 × N*H*), 1.10 (6 H, t, ^3J 7.5, $CH_2CH_2CH_2CH_3$), 1.75–1.95 (4 H, m, $CH_2CH_2CH_2CH_3$), 2.45–2.65 (4 H, m, $CH_2CH_2CH_2CH_3$), 5.05 (4 H, t, ^3J 7.5, $CH_2CH_2CH_2CH_3$), 7.75–7.90, 8.20–8.40 (5 H, each m, H_{Ph}), 8.75–8.95, 9.25–9.35, 9.40–9.50, 9.55–9.65 (8 H, m, 8 × $H_{\beta\text{-pyrrole}}$), 10.15 (1 H, s, H_{meso}); *m*/*z* (EI, 80 eV): 498.2762 (M^+, 100%. $C_{34}H_{34}N_4$ requires 498.2784), 455 (66, $M^+ - CH_2CH_2CH_3$), 412 (13, $M^+ - 2 \times CH_2CH_2CH_3$), 249 (7, M^{2+}).

(10-Butyl-5,15-diphenylporphyrinato)nickel(II) 23. Chromatography eluting with ethyl acetate–*n*-hexane (1 : 100, v/v); yield 55 mg (95%) purple crystals (Found: C, 73.70; H, 4.92; N, 9.77. $C_{36}H_{28}N_4Ni$ requires C, 75.16; H, 4.91; N, 9.74%. $C_{36}H_{28}N_4Ni\cdot 0.5H_2O$ requires C, 73.87; H, 5.17; N, 9.57%): mp 230 °C (CH_2Cl_2–CH_3OH); $\lambda_{max}(CH_2Cl_2)$/nm 408 (log ε/dm^3 mol^{-1} cm^{-1} 5.16), 523 (4.00), 556 (3.17); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) 1.15 (3 H, t, ^3J 7.6, $CH_2CH_2CH_2CH_3$), 1.60–1.75 (2 H, m, $CH_2CH_2CH_2CH_3$), 2.25–2.45 (2 H, m, $CH_2CH_2CH_2CH_3$), 4.60 (2 H, t, ^3J 7.8, $CH_2CH_2CH_2CH_3$), 7.55–7.65, 7.95–8.05 (10 H, each m, H_{Ph}), 8.85 (4 H, m, 4 × $H_{\beta\text{-pyrrole}}$), 9.05, 9.35 (4 H, each d, *J* 4.9, 4 × $H_{\beta\text{-pyrrole}}$), 9.70 (1 H, s, H_{meso}); *m*/*z* (EI, 80 eV): 574.1642 (M^+, 98%. $C_{36}H_{28}N_4Ni$ requires 574.1667), 531 (100, $M^+ - CH_2CH_2CH_3$), 287 (4, M^{2+}).

10-Butyl-5,15-diphenylporphyrin 24. Chromatography eluting with ethyl acetate–*n*-hexane (1 : 150, v/v); yield 47 mg (94%) purple crystals (Found: C, 83.11; H, 5.64; N, 10.58. $C_{36}H_{30}N_4$ requires C, 83.37; H, 5.83; N, 10.80%): mp 250 °C (CH_2Cl_2–CH_3OH); $\lambda_{max}(CH_2Cl_2)$/nm 411 (log ε/dm^3 mol^{-1} cm^{-1} 5.12), 509 (3.84), 543 (3.27), 584 (3.35), 641 (3.07); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) −3.02 (2 H, s, 2 × N*H*), 1.15 (3 H, t, ^3J 7.5, $CH_2CH_2CH_2CH_3$), 1.78–1.90 (2 H, m, $CH_2CH_2CH_2CH_3$), 2.55–2.60 (2 H, m, $CH_2CH_2CH_2CH_3$), 5.05 (2 H, t, ^3J 7.8, $CH_2CH_2CH_2CH_3$), 7.75–7.85, 8.25–8.32 (10 H, each m, 10H, H_{Ph}), 8.95, 9.25, 9.55 (8 H, each d, *J* 4.9, 8 × $H_{\beta\text{-pyrrole}}$), 10.07 (1 H, s, H_{meso}); *m*/*z* (EI, 80 eV): 518.2441 (M^+, 61%. $C_{36}H_{30}N_4$ requires 518.2476), 475 (100, $M^+ - CH_2CH_2CH_3$), 259 (9, M^{2+}).

10-Isopropyl-5,15-diphenylporphyrin 25. Chromatography eluting with ethyl acetate–*n*-hexane (1 : 100, v/v); yield 15 mg (30%) dark purple crystals (Found: C, 82.88; H, 5.62; N, 10.48. $C_{35}H_{28}N_4$ requires C, 83.30; H, 5.59; N, 11.10%): mp 270 °C (CH_2Cl_2–CH_3OH); $\lambda_{max}(CH_2Cl_2)$/nm 412 (log ε/dm^3 mol^{-1} cm^{-1} 5.11), 509 (3.95), 542 (3.89), 585 (3.61), 639 (3.49); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) −3.01 (2 H, s, 2 × N*H*), 2.48 (6 H, t, ^3J 7.3, $CH(CH_3)_2$), 5.76 (1 H, q, *J* 7.3, $CH(CH_3)_2$), 7.75–7.85, 8.25–8.32 (10 H, each m, H_{Ph}), 8.85–8.95 (4 H, m, 4 × $H_{\beta\text{-pyrrole}}$), 9.22, 9.65 (4 H, each d, *J* 4.8, 4 × $H_{\beta\text{-pyrrole}}$), 10.02 (1 H, s, H_{meso}); *m*/*z* (EI, 80 eV): 504.2354 (M^+, 100%. $C_{35}H_{28}N_4$ requires 504.2314), 489 (72, $M^+ - CH_3$), 252 (12, M^{2+}).

(10-Isopropyl-5,15-diphenylporphyrinato)nickel(II) 26. Chromatography eluting with ethyl acetate–*n*-hexane (1 : 100, v/v); yield 30 mg (52%) purple crystals (Found: C, 75.16; H, 4.91; N, 9.74. $C_{35}H_{26}N_4Ni$ requires C, 74.89; H, 4.67; N, 9.98%): mp 245 °C (CH_2Cl_2–CH_3OH); $\lambda_{max}(CH_2Cl_2)$/nm 410 (log ε/dm^3 mol^{-1} cm^{-1} 5.14), 527 (4.09), 558 (3.14); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) 2.30 (6 H, t, ^3J 7.3, $CH(CH_3)_2$), 5.15 (1 H, q, *J* 7.3, $CH(CH_3)_2$), 7.60–7.75, 7.85–8.05 (10 H, each m, H_{Ph}), 8.90 (4 H, d, *J* 4.8, 4 × $H_{\beta\text{-pyrrole}}$), 9.05, 9.45 (4 H, each d, *J* 4.8, 4 × $H_{\beta\text{-pyrrole}}$), 9.60 (1 H, s, H_{meso}); *m*/*z* (EI, 80 eV): 560.1553 (M^+, 100%. $C_{35}H_{26}N_4Ni$ requires 560.1510), 545 (45, $M^+ - CH_3$) 280 (6, M^{2+}).

10-(1-Methylpropyl)-5,15-diphenylporphyrin 27. Chromatography eluting with ethyl acetate–*n*-hexane (1 : 100, v/v); yield 8 mg (15%) purple crystals (Found: C, 82.18; H, 5.80; N, 10.04. $C_{36}H_{30}N_4$ requires C, 83.37; H, 5,83; N, 10.80%. $C_{36}H_{30}N_4\cdot 0.5H_2O$ requires C, 81.94; H, 5.92; N, 10.62%): mp 270 °C (CH_2Cl_2–CH_3OH); $\lambda_{max}(CH_2Cl_2)$/nm 410 (log ε/dm^3 mol^{-1} cm^{-1} 5.12), 448 (5.08), 524 (4.53), 558 (4.14), 598 (4.16), 664 (4.07);

δ_H (250 MHz; $CDCl_3$; $SiMe_4$) −3.05 (2 H, s, 2 × N*H*), 1.15 (3 H, t, ^3J 7.3, CH(CH_3)(CH_2CH_3)), 2.45 (3 H, d, ^3J 7.4, CH(CH_3)(CH_2CH_3)), 2.75–3.25 (2 H, m, CH(CH_3)(CH_2CH_3)), 5.45–5.55 (1 H, m, C*H*(CH_3)(CH_2CH_3)), 7.75–7.85, 8.15–8.35 (10 H, each m, H_{Ph}), 8.90, 9.30, 9.65 (8 H, each d, *J* 4.8, 4 × $H_{\beta\text{-pyrrole}}$), 10.20 (1 H, s, H_{meso}); *m*/*z* (EI, 80 eV): 518.2454 (M^+, 100%. $C_{36}H_{30}N_4$ requires 518.2470), 503 (4, $M^+ - CH_3$), 489 (62, $M^+ - CH_2CH_3$), 259 (12, M^{2+}).

[10-(1-Methylpropyl)-5,15-diphenylporphyrinato]nickel(II) 28. Chromatography eluting with ethyl acetate–*n*-hexane (1:100, v/v); yield 37 mg (65%) purple crystals (Found: C, 73.92; H, 4.77; N, 9.19. $C_{36}H_{28}N_4Ni{\cdot}\frac{1}{2}H_2O$ requires C, 73.87; H, 5.17; N, 9.57%): mp 220 °C (CH_2Cl_2–CH_3OH); λ_{max}(CH_2Cl_2)/nm 410 (log ε/dm^3 mol^{-1} cm^{-1} 5.24), 526 (4.15) 560 (3.29); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) 0.85 (3 H, t, ^3J 7.3, CH(CH_3)(CH_2CH_3)), 2.35 (3 H, d, *J* 7.4, CH(CH_3)(CH_2CH_3)), 2.55–2.80 (2 H, m, CH(CH_3)(CH_2CH_3)), 4.65–4.80 (1 H, m, C*H*(CH_3)(CH_2CH_3)), 7.60–7.75, 7.85–8.05 (10 H, each m, H_{Ph}), 8.75–8.85 (4 H, m, 4 × $H_{\beta\text{-pyrrole}}$), 9.05, 9.45 (4 H, each d, *J* 4.8, 4 × $H_{\beta\text{-pyrrole}}$), 9.60 (1 H, s, H_{meso}); *m*/*z* (EI, 80 eV): 574.1639 (M^+, 100%. $C_{36}H_{26}N_4Ni$ requires 574.1667), 559 (4, $M^+ - CH_3$), 545 (63, $M^+ - CH_2CH_3$), 287 (5, M^{2+}).

(5,15-Diphenyl-10-*tert*-butylporphyrinato)nickel(II) 29. Purification *via* column chromatography (hexane–ethyl acetate, 100:1, v/v) and recrystallization gave 30 mg bright purple crystals in 53% yield (Found: C, 74.78; H, 4.65; N, 9.45. $C_{36}H_{28}N_4Ni$ requires C, 75.16; H, 4.91; N, 9.74%): mp >300 °C (CH_2Cl_2–CH_3OH); λ_{max}(CH_2Cl_2)/nm 418 (log ε/dm^3 mol^{-1} cm^{-1} 5.17), 542 (4.05), 581 (3.25); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) 2.15 (9 H, s, C(CH_3)$_3$), 7.60–7.70, 7.80–7.95 (10 H, each m, H_{Ph}), 8.55–8.65 (4 H, m, 4 × $H_{\beta\text{-pyrrole}}$), 8.95 (2 H, d, *J* 4.8, 2 × $H_{\beta\text{-pyrrole}}$), 9.45–9.55 (3 H, m, 2 × $H_{\beta\text{-pyrrole}}$, H_{meso}); *m*/*z* (EI, 80 eV) 574.1661 (M^+, 100%. $C_{36}H_{28}N_4Ni$ requires 574.1667), 559 (93, $M^+ - CH_3$), 544 (9, $M^+ - 2CH_3$), 287 (5, M^{2+}).

15,15′-Bis(1-methylpropyl)-10,10′,20,20′-tetraphenyl-5,5′-biporphyrin 30. This compound was obtained as one of the products from the reaction of **19** with Bu^{s}Li. Column chromatography on alumina with hexane–ethyl acetate (100:1, v/v) eluted first **27** and then **30**. Final yield of **30** after recrystallization was 15 mg (30%) of dark purple crystals (Found: C, 82.76; H, 5.38; N, 10.54. $C_{72}H_{58}N_8$ requires C, 83.53; H, 5.65; N, 10.82%. $C_{72}H_{58}N_8{\cdot}0.5H_2O$ requires C, 82.81; H, 5.69; N, 10.73%): mp >300 °C (CH_2Cl_2–CH_3OH); λ_{max}(CH_2Cl_2)/nm 406 (log ε/dm^3 mol^{-1} cm^{-1} 5.42), 446 (4.52), 506 (4.01), 530 (3.43), 582 (3.15); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) −2.25 (4 H, s. 4 × N*H*), 1.15 (6 H, t, ^3J 7.3, 2 × CH$CH_3CH_2CH_3$), 2.55 (6 H, d, *J* 7.4, 2 × CH$CH_3CH_2CH_3$), 2.75–3.25 (4 H, m, 2 × CHCH_3-CH_2CH_3), 5.40–5.55 (2 H, m, 2 × C*H*$CH_3CH_2CH_3$), 7.60–7.75, 8.25–8.45 (20 H, each m, H_{Ph}), 8.05, 8.50, 8.95, 9.75 (16 H, each d, ^3J 4.8, 16 × $H_{\beta\text{-pyrrole}}$); *m*/*z* (EI, 80 eV) 1034.4738 (M^+, 100%. $C_{72}H_{68}N_8$ requires 1034.4784), 1019 (10, $M^+ - CH_3$), 1005 (89, $M^+ - CH_2CH_3$), 517 (6, M^{2+}).

5-Butyl-10,15,20-triphenylporphyrin 32. Chromatography eluting with ethyl acetate–*n*-hexane (1:200, v/v); yield 52 mg (88%) purple crystals (Found: C, 79.49; H, 5.30; N, 8.80. $C_{42}H_{34}N_4{\cdot}\frac{1}{2}CH_2Cl_2$ requires C, 80.11; H, 5.54; N, 8.79%): mp >300 °C (CH_2Cl_2–CH_3OH); λ_{max}(CH_2Cl_2)/nm 417 (log ε/dm^3 mol^{-1} cm^{-1} 5.23), 515 (3.89), 551 (3.46), 593 (3.27), 648 (3.24); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) −2.75 (2 H, s, N*H*), 1.10 (3 H, t, ^3J 7.5, $CH_2CH_2CH_2CH_3$), 1.75–1.85 (2 H, m, CH_2CH_2-CH_2CH_3), 2.45–2.60 (2 H, m, $CH_2CH_2CH_2CH_3$), 5.05 (2 H, t, ^3J 7.5, $CH_2CH_2CH_2CH_3$), 7.60–7.75, 8.10–8.25 (10 H, each m, H_{Ph}), 8.75 (4 H, s, 4 × $H_{\beta\text{-pyrrole}}$), 8.90, 9.45 (4 H, each d, *J* 4.9, 4 × $H_{\beta\text{-pyrrole}}$); *m*/*z* (EI, 80 eV): 594.2743 (M^+, 100%. $C_{42}H_{34}N_4$ requires 594.2783), 551 (56, $M^+ - CH_2CH_2CH_3$), 297 (10, M^{2+}).

(5-Butyl-10,15,20-triphenylporphyrinato)nickel(II) 33. Chromatography eluting with ethyl acetate–*n*-hexane (1:200, v/v); yield 60 mg (93%) red–purple crystals (Found: C, 76.62; H, 4.98; N, 8.36. $C_{42}H_{32}N_4Ni$ requires C, 77.68; H, 4.66; N, 8.63%. $C_{42}H_{32}N_4Ni{\cdot}0.5H_2O$ requires C, 76.62; H, 4.75; N, 8.51%): mp >300 °C (CH_2Cl_2–CH_3OH); λ_{max}(CH_2Cl_2)/nm 415 (log ε/dm^3 mol^{-1} cm^{-1} 5.29), 529 (4.14), 556 (3.44); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) 1.05 (3 H, t, ^3J 7.5, $CH_2CH_2CH_2CH_3$), 1.55–1.65 (2 H, m, $CH_2CH_2CH_2CH_3$), 2.25–2.40 (2 H, m, CH_2CH_2-CH_2CH_3), 4.65 (2 H, t, ^3J 7.5, $CH_2CH_2CH_2CH_3$), 7.55–7.70, 7.95–8.05 (15 H, each m, H_{Ph}), 8.65 (4 H, s, 4 × $H_{\beta\text{-pyrrole}}$), 8.80, 9.35 (4 H, each d, *J* 4.8, 4 × $H_{\beta\text{-pyrrole}}$); *m*/*z* (EI, 80 eV): 650.1946 (M^+, 100%. $C_{42}H_{32}N_4Ni$ requires 650.1980), 607 (94, $M^+ - CH_2CH_2CH_3$), 325 (4, M^{2+}).

[5-(1-Methylpropyl)-10,20-diphenyl-15-*tert*-butylporphyrinato]nickel(II) 34. This compound was obtained from the reaction of **29** with Bu^{s}Li. Column chromatography on alumina with hexane–ethyl acetate (100:1, v/v) gave 35 mg (55%) of red–purple crystals after recrystallization (Found: C, 74.82; H, 5.56; N, 8.25. $C_{40}H_{36}N_4Ni$ requires C, 76.09; H, 5.75; N, 8.87%. $C_{40}H_{36}N_4Ni{\cdot}0.5H_2O$ requires C, 75.02; H, 5.82; N, 8.75%): mp 285 °C (CH_2Cl_2–CH_3OH); λ_{max}(CH_2Cl_2)/nm 424 (log ε/dm^3 mol^{-1} cm^{-1} 5.13), 551 (4.13), 580 (3.92); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) 0.85 (3 H, t, ^3J 7.3, $CHCH_3CH_2CH_3$), 2.15 (9 H, s, C(CH_3)$_3$), 2.25 (3 H, d, ^3J 7.4, $CHCH_3CH_2CH_3$), 2.45–2.70 (2 H, m, $CHCH_3CH_2CH_3$), 4.5 (1 H, m, C*H*CH_3CH_2-CH_3), 7.65–7.75, 7.85–8.05 (10 H, each m, H_{Ph}), 8.50–8.65 (4 H, m, 4 × $H_{\beta\text{-pyrrole}}$), 9.25, 9.45 (4 H, each d, ^3J 4.8, 4 × $H_{\beta\text{-pyrrole}}$); *m*/*z* (EI, 80 eV) 630.2290 (M^+, 100%. $C_{36}H_{30}N_4$ requires 630.2293), 615 (35, $M^+ - CH_3$), 601 (13, $M^+ - CH_2CH_3$), 315 (2, M^{2+}).

General procedure for directly linked bisporphyrins

The 5,15-disubstituted porphyrin (0.11 mmol) was dissolved in 20 ml dry THF and a solution of 0.2 ml 2 M organolithium reagent (approx. 0.42 mmol) in cyclohexane was added at −70 °C for BuLi and 0 °C for PhLi under stirring. After complete addition the cold bath was removed and stirring continued for an additional 15 min. Subsequently, a solution of 95 mg DDQ (0.42 mmol) in 5 ml dry THF was added resulting in a color change from dark blue to dark brown. Stirring was continued for 30 min, the solvent removed *in vacuo*, and the residue purified by chromatography on neutral alumina (Brockmann grade III) followed by recrystallization from CH_2Cl_2–CH_3OH.

15,15′-Dibutyl-10,10′,20,20′-tetraphenyl-5,5′-biporphyrin 36. Chromatography eluting with ethyl acetate–n-hexane (1:100, v/v); yield 42 mg (75%) purple crystals (Found: C, 82.17; H, 5.94; N, 10.40. $C_{72}H_{58}N_8$ requires C, 83.53; H, 5.65; N, 10.82%. $C_{72}H_{58}N_8{\cdot}1H_2O$ requires C, 82.10; H, 5.74; N, 10.64%): mp >300 °C (CH_2Cl_2–CH_3OH); λ_{max}(CH_2Cl_2)/nm 417 (log ε/dm^3 mol^{-1} cm^{-1} 5.14), 448 (5.13), 523 (4.51), 561 (4.14), 597 (4.15), 664 (4.07); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) −2.21 (4 H, s, 2 × N*H*), 1.23 (6 H, t, ^3J 7.5, 2 × $CH_2CH_2CH_2CH_3$), 1.75–1.94 (4 H, m, 2 × $CH_2CH_2CH_2CH_3$), 2.45–2.65 (4 H, m, 2 × CH_2-$CH_2CH_2CH_3$), 5.04 (4 H, t, ^3J 7.9, 2 × $CH_2CH_2CH_2CH_3$), 7.64–7.75 and 8.15–8.25 (20 H, each m, H_{Ph}), 7.95, 8.50, 8.95 and 9.65 (16 H, each d, *J* 4.9, 16 × $H_{\beta\text{-pyrrole}}$); *m*/*z* (EI, 80 eV) 1034.4748 (M^+, 100%. $C_{72}H_{58}N_8$ requires 1034.4784), 993 (21, $M^+ - CH_2CH_2CH_3$), 517 (14, M^{2+}).

5,5′,10,10′,20,20′-Hexaphenyl-5,5′-biporphyrin 37. Chromatography eluting with CH_2Cl_2–n-hexane (1:3, v/v); yield 46 mg (79%) purple crystals (Found: C, 84.36; H, 4.49; N, 10.03. $C_{76}H_{50}N_8$ requires C, 82.06; H, 6.68; N, 11.26%. $C_{76}H_{50}N_8{\cdot}\frac{1}{2}CH_3OH$ requires C, 84.20; H, 4.80; N, 10.27%): mp >300 °C (CH_2Cl_2–CH_3OH); λ_{max}(CH_2Cl_2)/nm 415 (log ε/dm^3 mol^{-1} cm^{-1}

4.99), 449 (5.04), 524 (4.39), 561 (3.81), 595 (3.89), 651 (2.53); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) −2.25 (4 H, s, 2 × N*H*), 7.65–7.70, 7.75–7.82, 8.15–8.22, 8.35 (30 H, each m, H_{Ph}), 8.05, 8.60 (8 H, each d, *J* 4.4, 8 × $H_{\beta\text{-pyrrole}}$), 8.80–8.95 (8 H, m, 8 × $H_{\beta\text{-pyrrole}}$); *m*/*z* (EI, 80 eV): 1074.4158 (M^+, 100%. $C_{76}H_{50}N_8$ requires 1074.4116), 537 (14, M^{2+}).

10,10′,20,20′-Tetrabutyl-15,15′-diphenyl-5,5′-biporphyrin 38. Chromatography eluting with ethyl acetate–*n*-hexane (1 : 100, v/v); yield 30 mg (55%) purple crystals (Found: C, 81.40; H, 6.66; N, 11.26. $C_{68}H_{66}N_8 \cdot \frac{1}{2}H_2O$ requires C, 81.32; H, 6.72; N, 11.16%): mp >300 °C (CH_2Cl_2–CH_3OH); $\lambda_{max}(CH_2Cl_2)$/nm 411 (log ε/dm^3 mol^{-1} cm^{-1} 5.0), 451 (5.18), 526 (4.40), 562 (3.88), 6.01 (3.82), 660 (3.67); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) −2.20 (4 H, s, 4 × N*H*), 1.05 (12 H, t, ^3J 7.5, 4 × $CH_2CH_2CH_2CH_3$), 1.70–1.85 (8 H, m, 4 × $CH_2CH_2CH_2CH_3$), 2.35–2.65 (8 H, m, 4 × $CH_2CH_2CH_2CH_3$), 4.85 (8 H, t, ^3J 8.1, 4 × $CH_2CH_2CH_2CH_3$), 7.75–7.80, 8.23–8.35 (10 H, each m, H_{Ph}), 8.02, 8.87, 9.23, 9.43 (16 H, each d, ^3J 4.7, 16 × $H_{\beta\text{-pyrrole}}$); *m*/*z* (EI, 80 eV): 994.5457 (M^+, 100%. $C_{68}H_{66}N_8$ requires 994.5410).

Crystal structure determinations

Suitable single crystals were immersed in hydrocarbon oil (Paraton N®), a single crystal selected, mounted on a glass fiber and placed in the low-temperature N_2 stream.[23] Intensity data were collected at 130 K using a Siemens P4 diffractometer equipped with a rotating anode and low temperature device using Cu-Kα radiation (λ = 1.54178 Å). The intensities were corrected for Lorentz, polarization and absorption effects (XABS2);[24] extinction effects were disregarded. The structures were solved *via* Direct Methods using the SHELXS program.[25] Refinements were carried out by full-matrix least squares on $|F^2|$ using SHELXL-97.[26]

Crystal data for compound 25. $C_{35}H_{28}N_4$, *M* = 504.61, monoclinic, *a* = 12.157(5), *b* = 18.255(10), *c* = 13.045(6) Å, β = 116.75(3)°, *U* = 2585(2) Å^3, *T* = 130 K, space group $P2_1/n$, *Z* = 4, μ(Cu-Kα) = 0.597 mm^{-1}, 3746 reflections measured, 3415 unique (R_{int} = 0.051), 2885 reflections with $I > 2.0\sigma(I)$, 354 parameters, Δ/ρ_{max} = 0.315 e Å^{-3}, R_1 [$I > 2\sigma(I)$] = 0.0418, R_1 (all data) = 0.0514, wR_2 (all data) = 0.1182.

Crystal data for compound 28. $C_{36}H_{28}N_4Ni$, *M* = 575.33, monoclinic, *a* = 12.738(6), *b* = 14.973(8), *c* = 28.374(15) Å, β = 93.06(4)°, *U* = 5404(5) Å^3, *T* = 130 K, space group $P2_1/n$, *Z* = 8 (2 indep. Molecules), μ(Cu-Kα) = 1.289 mm^{-1}, 7578 reflections measured, 7123 unique (R_{int} = 0.091), 4789 reflections with $I > 2.0\sigma(I)$, 570 parameters, Δ/ρ_{max} = 0.940 e Å^{-3}, R_1 [$I > 2\sigma(I)$] = 0.0786, R_1 (all data) = 0.1170, wR_2 (all data) = 0.2365. Disorder in the methyl-propyl side chain of one of the two independent molecules. All phenyl rings were refined as rigid hexagons with isotropic thermal parameters.

CCDC reference number 207/478. See http://www.rsc.org/suppdata/p1/b0/b005411i/ for crystallographic files in .cif format.

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