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Synthesis of Directly meso-meso Linked Bisporphyrins Using Organolithium Reagents

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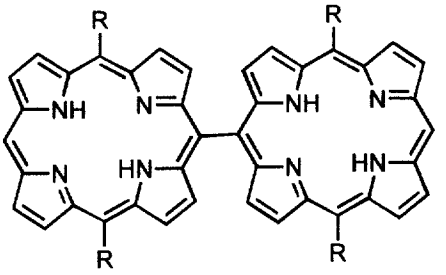
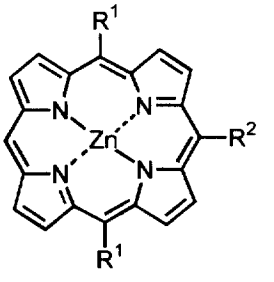
Abstract: Reaction of easily available 5,15-disubstituted free base porphyrins with organolithium reagents under anhydrous conditions affords 5,10,15-trisubstituted porphyrin anions that, upon oxidation with DDQ (2,3-dichloro-5,6-dicyano-*p*-quinone), give directly linked (5,5') bisporphyrins in good yields. This method allows the facile preparation of bisporphyrins with mixed meso substituent pattern. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Directly (5,5') linked bisporphyrins are attracting interest as multichromophoric model systems for the study of electron transfer reactions related to photosynthesis. The direct meso-meso connection in systems like **1** results in interesting electronic properties, e.g., a large exciton splitting of the Soret absorption band.[1] During the last few years several approaches have been described to prepare such meso-meso linked bisporphyrins. Coupling of 5,15-disubstituted 10-formylporphyrins with dipyrromethanes gave a 5,5'-linked bis- and trisporphyrin in very low yields.[2] A more facile method utilized the Ag(I) promoted oxidative coupling of (5,15-diarylporphyrinato)zinc(II) for the preparation of mixtures of dimers, trimers, and tetramers in low yield.[1] Utilization of different central metals later afforded the regioselective preparation of both meso-meso and meso-β linked bisporphyrins in low yields.[3] Synthetically satisfactory yields were obtained only when (5,10,15-triarylporphyrinato)zinc(II) was used as starting material preventing trimer formation.[4] A quite different multi step approach utilized a 2+2 MacDonald condensation of a dipyrromethane with a 1,1,2,2-tetra(5-formyl-2-pyrrolyl)ethene followed by oxidation for the construction of a meso unsubstituted bisporphyrin.[5]



1



2 R^2 = H
3 R^2 = Ar

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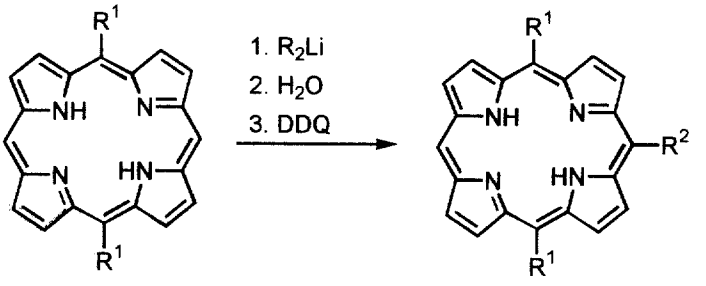
Recently, we reported on the reaction of porphyrins with organolithium reagents that allowed the convenient and often quantitative preparation of porphyrins with various types and numbers of meso substituents.[6] This method utilized a reaction sequence consisting of treatment of the porphyrin with RLi, hydrolysis with H_2O to yield a porphodimethene, followed by oxidation with DDQ to the meso substituted porphyrin. During more detailed mechanistic investigations of this reaction we found that simple omission of the hydrolysis step allows the facile preparation of 5,5'-linked bisporphyrins in good yields.

Initially we were interested to compare the relative reactivity of porphyrins with both free meso and β positions with RLi. As starting material we chose 5,15-disubstituted free base porphyrins (**4,5**) that are easily prepared via reaction of dipyrromethane with the respective alkyl or arylaldehydes.[7] When these porphyrins (either as free bases of nickel(II) complexes) were subjected to the standard reaction sequence, including the hydrolysis step, almost quantitative formation of the respective 5,10,15-trisubstituted porphyrins **6-9** was observed. As long as at least one free meso position was present in the starting material, no evidence for attack of the organolithium reagent at the β positions was found.



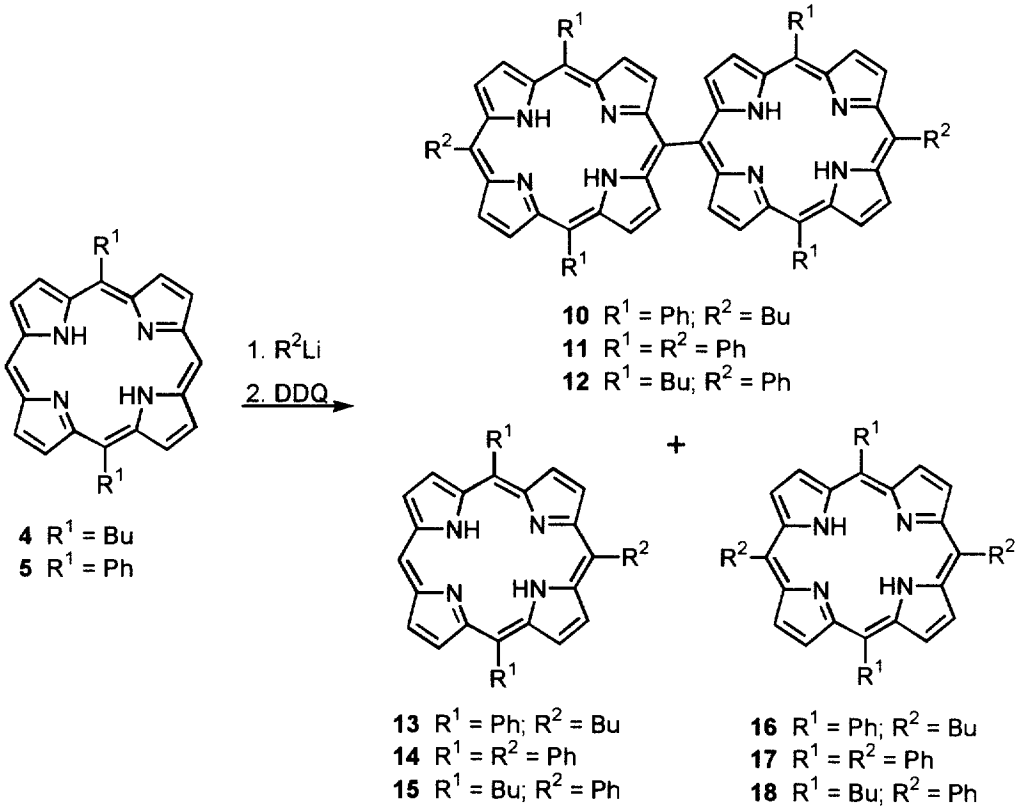
4 R^1 = Bu
5 R^1 = Ph

6 $R^1 = R^2$ = Bu
7 R^1 = Bu; R^2 = Ph
8 $R^1 = R^2$ = Ph
9 R^1 = Ph; R^2 = Bu

Quite a different reactivity was observed upon reaction of either **4** or **5** with PhLi or BuLi followed by direct addition of the oxidant DDQ without intermediary hydrolysis step. For example, reaction of **5** with BuLi followed by oxidation with DDQ gave the bisporphyrin **10** in 75 % yield.[8,9a] Similarly, **5** could be converted with PhLi to **11**[8,9b] and **4** with PhLi to **12**.[8,9c] In principle, all possible substituent combinations for R^1 and R^2 are accessible via this way. The mechanism for the dimerization presumably proceeds via oxidation of the anion to a π stabilized radical followed by radical dimerization. There is ample precedence that DDQ can induce oxidative dimerizations[10] and similar reactions have been described for oxophlorins[11a] and naphthochlorins.[11b] The spectroscopic properties of the dimers are similar to those obtained via other synthetic methods.[1-5]

5,10,15-Tri- (**13-15**) and 5,10,15,20-tetrasubstituted porphyrins (**16-18**) were observed as side products

from the dimerization reaction. This indicates that, alternatively to the oxidation to the radical, hydride abstraction to the neutral porphyrins **13-15** can occur, which can react with a second molecule RLi to yield **16-18**. When the solution with the initially formed anion from **5** was added dropwise to a solution of DDQ (the reverse order of our normal reaction giving mainly dimerization) transformation to a mixture of **14** (40 %) and **11** (60 %) was found. Under these conditions no tetrasubstituted porphyrins were formed. Use of the respective nickel(II) complexes of **4** or **5** for the coupling reaction resulted in the formation of the tri- and tetrasubstituted porphyrins **13-18**; no dimer formation was observed.



The present method allows the convenient preparation of directly linked dimers with mixed meso substituent pattern. It circumvents the problems associated with oligomer formation using the oxidative Ag(I) coupling of 5,15-disubstituted porphyrins[1] and gives high yields comparable to those using 5,10,15-triarylporphyrins[4] while still using the more easily prepared 5,15-disubstituted porphyrins as starting material. Currently we are expanding this reaction to prepare functionalized bisporphyrins.

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References and Notes

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8. *General Procedure*: The 5,15-disubstituted porphyrin (0.11 mmol) was dissolved in 20 ml dry THF and a solution of 0.2 ml 2M butyl lithium (0.42 mmol) in cyclohexane was added at -70 °C 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.
9. a) *Bis(15-butyl-10,20-diphenylporphyrin-5-yl)* **10:** Chromatography eluting with ethyl acetate/n-hexane (1:100, v/v); yield 42 mg (75 %). ^{1}H NMR: (250 MHz) δ = -2.21 (*s*, 4H; NH), 1.23 (*t*, ^{3}J = 7.5 Hz, 6H, $CH_2CH_2CH_2C\underline{H}_3$), 1.75-1.94 (*m*, 4H, $CH_2CH_2C\underline{H}_2CH_3$), 2.45-2.65 (*m*, 4H, $CH_2C\underline{H}_2CH_2CH_3$), 5.04 (*t*, ^{3}J = 7.9 Hz, $C\underline{H}_2CH_2CH_2CH_3$), 7.64-7.75, 8.15-8.25 (each *m*, 20 H, H_{Ph}), 7.95, 8.50, 8.95, 9.65 ppm (each *d*, ^{3}J = 4.9 Hz, 16H, H_β); UV/vis (CH_2Cl_2): λ_{max} (lg ε) = 417 (5.14), 448 (5.13), 523 (4.51), 561 (4.14), 597 (4.15), 664 nm (4.07); MS (EI, 80 eV), m/z (%): 1035 (100) [M^+], 517 (14) [M^{2+}]; HRMS [$C_{72}H_{58}N_8$]: calc. 1034.4784, found 1034.4748; m.p. >300 °C. b) *Bis(10,15,20-triphenylporphyrin-5-yl)* **11:** Chromatography eluting with CH_2Cl_2/n-hexane (1:3, v/v); yield 46 mg (79 %). ^{1}H NMR: (250 MHz) δ = -2.25 (s, 4H; NH), 7.65-7.70, 7.75-7.82, 8.15-8.22, 8.35 (each *m*, 30 H, H_{Ph}), 8.05, 8.60 (each *d*, ^{3}J = 4.4 Hz, 8H, H_β), 8.80-8.95 ppm (*m*, 8H, H_β); UV/vis (CH_2Cl_2): λ_{max} (lg ε) = 415 (4.99), 449 (5.04), 524 (4.39), 561 (3.81), 595 (3.89), 651 nm (2.53); MS (EI, 80 eV), m/z (%): 1074 (100) [M^+], 537 (14) [M^{2+}]; HRMS [$C_{76}H_{50}N_8$]: calc. 1074.4158, found 1074.4116; m.p. >300 °C. c) *Bis(10,20-dibutyl-15-phenylporphyrin-5-yl)* **12:** Chromatography eluting with ethyl acetate/n-hexane (1:100, v/v); yield 30 mg (55 %). ^{1}H NMR: (250 MHz) δ = -2.20 (*s*, 4H; NH), 1.05 (*t*, ^{3}J = 7.5 Hz, 12H, $CH_2CH_2CH_2C\underline{H}_3$), 1.70-1.85 (*m*, 8H, $CH_2CH_2C\underline{H}_2CH_3$), 2.35-2.65 (*m*, 8H, $CH_2C\underline{H}_2CH_2CH_3$), 4.85 (*t*, ^{3}J = 8.1 Hz, 8H, $C\underline{H}_2CH_2CH_2CH_3$), 7.75-7.80, 8.23-8.35 (each *m*, 10 H, H_{Ph}), 8.02, 8.87, 9.23, 9.43 ppm (each *d*, ^{3}J = 4.7 Hz, 16H, H_β); UV/vis (CH_2Cl_2): λ_{max} (lg ε) = 411 (5.0), 451 (5.18), 526 (4.40), 562 (3.88), 6.01 (3.82), 660 nm (3.67); MS (EI, 80 eV), m/z (%): 994 (100) [M^+]; HRMS [$C_{68}H_{66}N_8$]: calc. 994.5410, found 994.5457; m.p. >300 °C.
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