An efficient synthesis of highly functionalized asymmetric porphyrins with organolithium reagents

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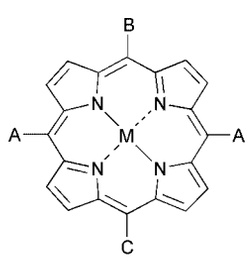
Received (in Cambridge, UK) 2nd January 2001, Accepted 26th February 2001
First published as an Advance Article on the web 3rd April 2001

Functionalized tri- (A_2B-type) and tetra- (A_2BC-type) meso-substituted asymmetric porphyrins bearing highly reactive centers like -NH_2, -OH, -C≡CH, -CHO in substituents at the meso positions were synthesized in good yields *via* the reaction of 5,15-diphenylporphyrin with corresponding functionalized organolithium reagents. Through further transformation other functional groups like carboxylate, iodophenyl, thiocarboxylate, tertiary amines and quaternary ammonium salts are easily available. Such porphyrins serve as precursors for highly complex tetrapyrrolic systems. As examples, several novel porphyrins with potentially useful chemical and physical properties such as amphiphilicity, water solubility, and electrochemical redox activity were synthesized. In contrast to existing methods such compounds are now accessible regioselectively *via* one-step or two-step reactions in high yields. In addition, protocols were developed to prepare porphyrins with meso-aryl substituents bearing functional groups at the *para*, *meta*, or *ortho* position. Thus, starting materials for various specifically superstructured tetrapyrroles are available *via* rational syntheses.

Introduction

Tetrapyrroles have broad technical applications in the area of catalysis,[1] nonlinear optics,[2] molecular recognition,[3] photosensitizers,[4] and medicinal applications (photodynamic therapy) – (PDT). Further development of these applications requires asymmetric and highly functionalized compounds. For these, novel and efficient synthetic methods, preferentially *via* a simple modification of easily accessible symmetric porphyrins, have to be developed. Thus, functionalized asymmetric porphyrin precursors like **1** (A = solubility-enhancing groups; B, C = functional groups) are key intermediates for the required compounds. Despite many efforts and the theoretical utility of porphyrin for both S_E and S_N reactions, only a few efficient functionalization reactions have been described.[5,6] In particular, the direct, regioselective introduction of functional groups has been rather limited up to now.



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In general, there are several synthetic avenues to functionalized, asymmetric porphyrins: a) mixed condensations, followed by laborious chromatographic separation; b) multi-step total synthesis by 2 + 2 or 3 + 1 condensation;[7] c) direct introduction of functional groups into easily synthesized symmetric porphyrins to yield the desired target compounds. Due to the difficult work-up and unsatisfactory yields of a) and the limited applicability of b),[7b] route c) offers potential for further development. Known functionalization reactions include Vilsmeier formylation, sulfonation, nitration, and halogenation reactions.[8,9] However, while the latter offers potential for metal-assisted C–C coupling reactions, many of these modification reactions require harsh conditions and/or use of metalloporphyrins, resulting in unsatisfactory yields and low tolerance towards functional groups.

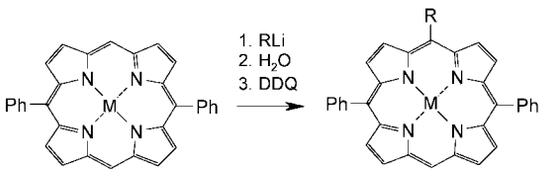
We are involved in a programme aimed at the development of highly efficient methods for the functionalization and modification of porphyrins. Two years ago, we found that porphyrins readily undergo meso substitution reactions with organolithium reagents[10] and since then have developed this reaction to a generally applicable method for the preparative synthesis of functionalized asymmetric porphyrin precursors.[11,12] In order to show that this method allows the preparation of porphyrins with complex functional groups suitable for further transformations, we have now undertaken a study of the reactivity of 5,15-disubstituted porphyrins with more complex reagents and report several simple and efficient applications of this methodology leading to the synthesis of highly functionalized porphyrins, and demonstrate their active chemical properties in coupling reactions.

Results and discussion

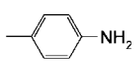
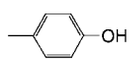
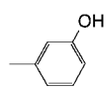
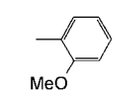
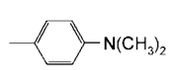
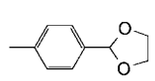
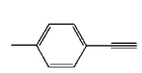
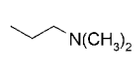
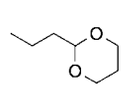
The overall reaction of RLi with porphyrins is a nucleophilic substitution like the Ziegler alkylation[13] and proceeds *via* initial reaction of the organic nucleophile with a meso carbon yielding an anionic species, which is hydrolyzed to a dihydroporphyrin or can be used as an *in situ* nucleophile for the reaction with alkyl iodides, allowing the introduction of two different substituents in a one-pot reaction.[11] Subsequent oxidation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) yields meso-substituted porphyrins.[12]

5,15-Diphenylporphyrin **2** (Scheme 1) is an easily synthesized symmetric porphyrin[14] with two free meso positions, in which new functionalized substituents from organolithium reagents and alkyl iodides can be selectively introduced without attack at β positions.[11,15] Alternatively, repetition of the addition–oxidation sequence of RLi with a tri-meso-substituted porphyrin allows the synthesis of bifunctionalized asymmetric

 DOI: 10.1039/b100012h



2 M = 2H
3 M = Ni

	R	M	Yield
4		2H	82
5		2H	75
6		2H	30
7		2H	83
8		2H	78
9		2H	86
10		2H	85
11		2H	75
12		Ni	73

Scheme 1

porphyrins by introducing a second functional group without formation of regioisomers as is observed in similar reactions with octaethylporphyrin.[10,16] Thus, at first we used 5,15-diphenylporphyrin **2** and its nickel(II) complex **3** for the preparation of various monofunctionalized porphyrins.

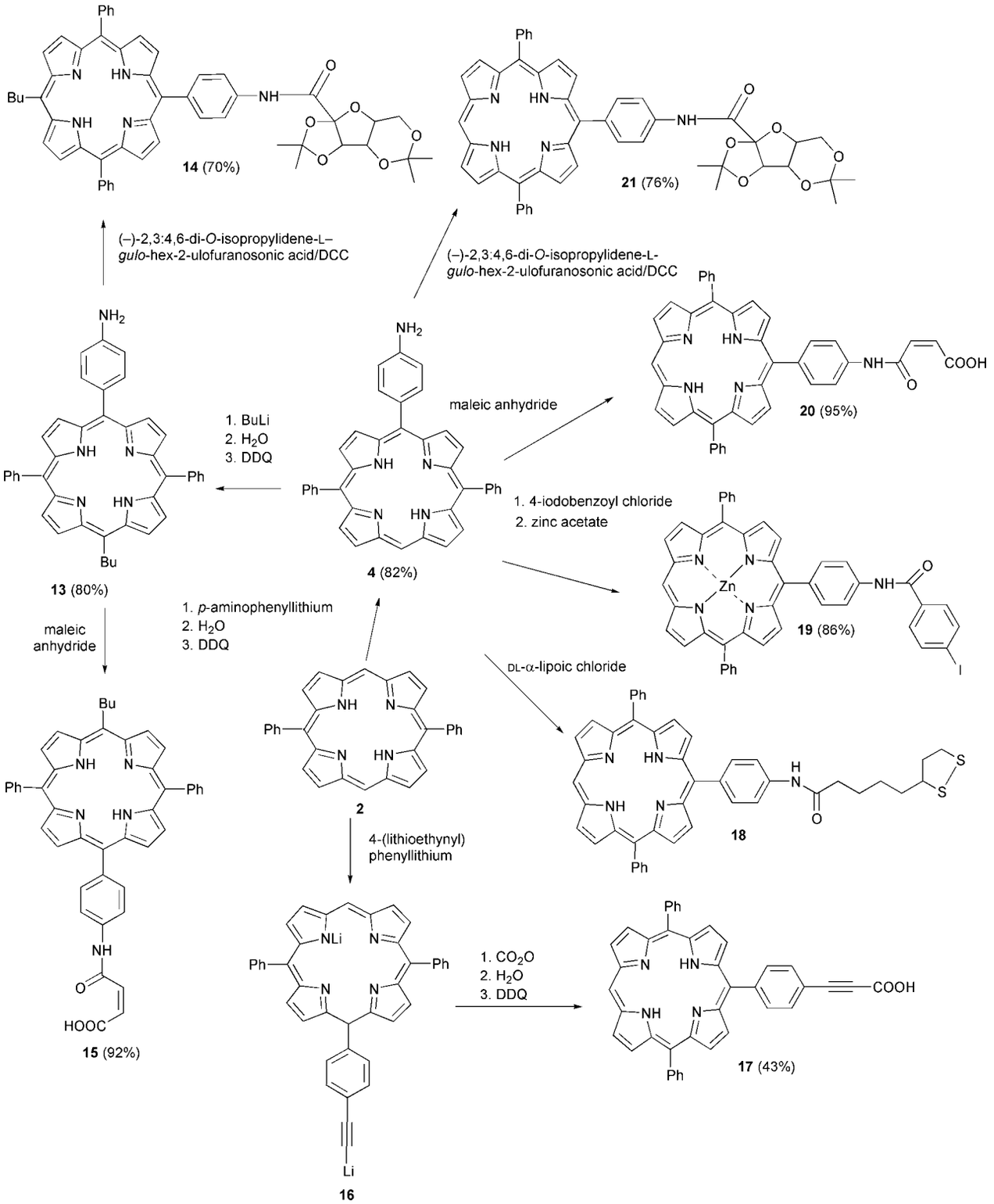
The porphyrins **4**–**12** were synthesized through the reaction of organolithium reagents with 5,15-diphenylporphyrin **2** and its nickel(II) complex **3** in good yields (≈80%) except for **6**. In order to achieve high yields in the synthesis shown in Scheme 1, more equivalents (10–15) of organolithium reagents were used than in our earlier reports on the case of RLi for porphyrin modification.[10–12] Under these reaction conditions no ring-opened products were observed. The larger excess of organolithium reagent led to a higher concentration of LiOH in the reaction mixture after hydrolysis with water, thus requiring more DDQ (10–15 equivalents to porphyrin), which is unstable in strongly basic media. The excess of hydrolyzed organolithium reagents can be removed either through distillation under high vacuum at 50–80 °C or by chromatographic separation eluting with an excess of *n*-hexane. The functionalized target porphyrins are much more polar than 5,15-diphenylporphyrin and thus product and educt can be separated easily from each other. In general, the reaction of 5,15-diphenylporphyrin **2** with aryllithium reagents requires a reaction temperature of 0–50 °C. Thus, some aryllithium reagents with highly functional groups like carboxylic acid ester or aldehyde, which are stable only at low temperatures (<−50 °C),[17] could not be employed in this synthesis. Test experiments recovered only starting material. Lithium reagents such as *o*-amino- or *o*-hydroxyphenyllithium or 2-pyridyllithium showed no reactivity against 5,15-diphenylporphyrin at various temperatures, while the porphyrin **6** with a *m*-hydroxyphenyl substituent at the 5-position was synthesized in yields of only 30%. However, if the functional groups are protected, *e.g.*, by using *o*-methoxyphenyllithium as reagent, the corresponding porphyrins could be prepared in good yields (for example, porphyrin **7**, 83%).

The functional groups introduced are highly reactive and easily employed in further coupling reactions. For example, it is known from the literature that amino and hydroxy groups like those in porphyrins **4** and **5** react as nucleophiles smoothly with carboxylic acid chloride, anhydride, and its activated ester [*N*,*N*′-dicyclohexylcarbodiimide (DCC), hydroxysuccinimide] as well as with many halogeno compounds.[18,19] After deprotection of the porphyrins **9** and **12** the corresponding aldehydes can be used as key intermediates for the synthesis of porphyrin dimers or oligomers undergoing acid-catalyzed condensation with pyrrole or dipyrromethane as well as with other bifunctional nucleophiles such as Wittig reagents.[20–22] Porphyrins **8** and **11** are good intermediates for the synthesis of cationic derivatives by treatment with iodomethane. Such compounds are widely used for investigating their interaction with proteins or used as an entry into water-soluble porphyrins.[23] Porphyrins **6** and **7** are very interesting starting materials for the synthesis of tetrapyrrole systems with modified spatial orientation and possessing special chelation abilities useful in molecular recognition and catalysis.[24,25] Other potential applications are the synthesis of 'picket-fence' and 'basket-handle' porphyrins.[26,27] In particular, porphyrin **10** will be a candidate for the rational synthesis of porphyrin-based materials such as porphyrin arrays or push-pull porphyrins *via* Glaser or Heck coupling.[28–30] Porphyrins bearing such functional groups have already found broad applications in the synthesis of superstructured materials or in the synthesis of phenyl-bridged porphyrinquinone systems *via* Dötz reaction.[31] However, up to now the synthesis of such porphyrins was quite laborious and hampered by the involved chromatographic work-up.[29,32]

Furthermore, the porphyrins **4**–**12** still possess a free meso position, where further functional groups can be inserted either by another reaction with RLi or other meso-selective reactions such as iodination with bis(trifluoroacetoxy)iodobenzene iodine[33–35] followed by oxidative coupling to give directly meso-meso-linked bisporphyrins[36] and can therefore be employed in the synthesis of bifunctionalized porphyrins of the A_2BC type (Scheme 2).

For example, porphyrin **13** was prepared *via* the reaction with butyllithium and *p*-aminophenyllithium with an overall yield of 70%. Using **13** as starting material the porphyrins **14** and **15** were prepared in yields of 70 and 92%, respectively. Interestingly, the reaction of 5,15-diphenylporphyrin **2** with an RLi reagent prepared from *p*-bromophenylethyne and BuLi yielded the monoanionic lithiated porphyrin derivative **16** as an intermediate. This highly active nucleophile can be trapped with CO_2 to yield the porphyrin **17** in 43% yield (not optimized) and should prove to be useful in trapping reactions with other functionalized electrophiles such as aldehydes, esters with highly functional groups[37] or in coupling reactions with Pd/Cu catalysis.[38]

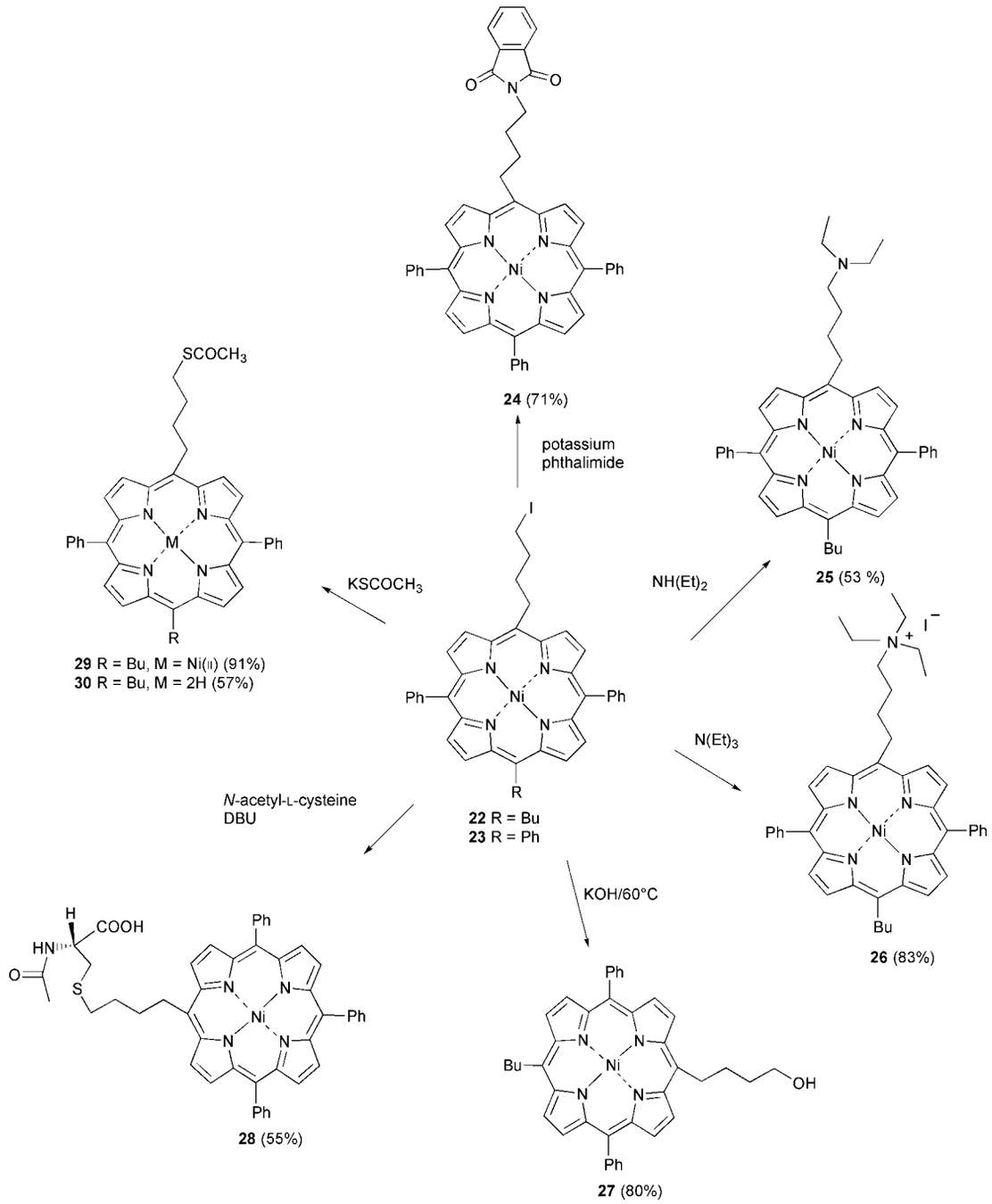
In order to test the chemical reactivity of the functionalized porphyrins synthesized, we subjected them to coupling reactions to obtain porphyrins suitable for the applications described in the Introduction. Porphyrin **4** with a free amino group at the phenyl substituent reacted smoothly and quantitatively with electrophiles like maleic anhydride to afford porphyrin **20** (95%), while reaction with *p*-iodobenzoyl chloride and subsequent introduction of zinc ion gave the porphyrin **19**



Scheme 2

in a yield of 86%. Novel tetrapyrrole systems for photochemical studies can be synthesized directly *via* Heck coupling with the zinc(II) porphyrin **19**. Other transformations yielded functional groups like -COOH or -I. Under mild reaction conditions porphyrin **21** could be obtained by the reaction of porphyrin **4** with (−)-2,3:4,6-di-*O*-isopropylidene-L-*gulo*-hex-2-ulofuranosonic acid in the presence of DCC in 76% yield. In this context we report here several new porphyrins, which were obtained from the precursor compounds described above through reaction of the porphyrin anionic intermediate with alkyl iodides.[11] The results are shown in Scheme 3.

Porphyrins **22** and **23**[11] with an iodo group at the end of the *n*-butyl substituent also showed excellent reactivity against nucleophilic reagents. For example, the porphyrin **24** was synthesized through the reaction of **23** with potassium phthalimide in *N*,*N*-dimethylformamide (DMF) in a yield of 71%. Porphyrins **22** and **23,** like normal alkyl iodides, also showed good electrophilic properties in their reactions with secondary and tertiary amines. Thus, porphyrins **25** and **26** were obtained by substitution with diethylamine and triethylamine in 53 and 83% yield, respectively while the known compound **27** could be prepared *via* reaction with KOH. In polar aprotonic, strong basic media {1,8-diazobicyclo[5.4.0]undec-7-ene (DBU) in DMF} the iodo group can be substituted by excess of weak



Scheme 3

nucleophiles like *N*-acetyl-L-cysteine and the porphyrin **28** bearing an amino acid was synthesized in 55% yield. Compound **29** was prepared by reaction of **22** with potassium thioacetate in DMF in 91% yield. Porphyrin **30** was obtained by demetallation of **29** under mild conditions[39] with boron tribromide in a yield of 57%, while several polar, purple fractions were also detected on TLC. These possibly involve saponification of the thioester group and ring-opening reactions.

The synthesized porphyrins should be interesting as model compounds for many studies due to their special chemical and physical properties. For example, the porphyrins **20** and **21** bearing sugar or carboxy groups should show variable amphiphilicity in comparison with **14** and **15** with additional *n*-butyl substituents. Such compounds and also **27** are often used in membrane studies due to their special localization properties.[40] Porphyrins **18** and **29** and **30** can be easily bound to gold particles and layers for surface electrochemical studies.[41] In contrast to the easily synthesized tetra-aryl-substituted porphyrins conventionally used in gold surface studies, the fluorescence spectrum of the trisubstituted porphyrin **18** shows an interesting 'exciton splitting effect' between the neighboring porphyrins that indicates a crowded arrangement on the gold surface.[42] Porphyrin **24** is a reversible redox-system,[43] while cationic porphyrins such as **26** with amphiphilic properties can be used in the investigation of pigment–protein interactions in the biological environment.[23,44]

In conclusion, the present methodology, in conjunction with established techniques, should allow the synthesis of almost any desired meso-functionalized-porphyrin and more complicated macrocyclic systems with special chemical and physical properties in few steps and with high yields.

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. Mps 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 $SiMe_4$ (TMS) signal as internal standard. 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 reaction of porphyrins with organolithium reagents. A Schlenk flask was charged with 0.4 mmol of the porphyrin (≈200 mg) dissolved in 80 ml of dry THF under an argon atmosphere. The porphyrin solution was cooled to −40 °C and added to a solution of 4–6 mmol organolithium reagent in a Schlenk flask at 0–40 °C. RLi reagents prepared *in situ* often form rubber-like precipitates that tend to stick to the walls of the reaction vessel. Thus, the cooled solution of the porphyrin was added to the vigorously stirred solution of RLi and not the other way around. After removal of the cold bath the reaction mixture was stirred for another 1 hour (TLC control). The color of the reaction mixture changed from purple to brown within 30 min (if the color does not change, slow heating to reflux is necessary), subsequently a mixture of 5 ml of water in 5 ml of tetrahydrofuran (THF) was added for the hydrolysis. After stirring of the mixture for 20 min, a solution of 10–15 equivalents of DDQ in dichloromethane (≈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 the organic solvent was removed under vacuum. In order to remove residual bromide or hydrolyzed RLi, the residue was dried under high vacuum or washed with enough *n*-hexane during the column chromatography described below. Final purification was achieved by column chromatography on neutral alumina (Alfa) or silica gel (Merck) followed by recrystallization from CH_2Cl_2–methanol or CH_2Cl_2–*n*-hexane.

5-(*p*-Aminophenyl)-10,20-diphenylporphyrin 4

n-Butyllithium (6 ml of a 2.5 M solution in *n*-hexane, 15 mmol) was slowly added (*ca*. 1 h) under an argon atmosphere to a 250 ml Schlenk flask charged with a solution of *p*-bromoaniline (1 g, 5 mmol) in 15 ml of dry diethyl ether at 0 °C. After addition of *n*-butyllithium the cold bath was removed and the mixture was stirred for another 1 h at room temperature. The solution became yellow-brown and at the bottom of the flask a viscous material was observed. To the vigorously stirred mixture was added rapidly a solution of 5,15-diphenylporphyrin **2** (200 mg, 0.43 mmol) in 80 ml of dry THF under an argon atmosphere. The mixture changed from deep purple to brown within 30 min. Further work-up followed the general procedure as described above. Chromatography and elution with dichloromethane–*n*-hexane (5 : 1, v/v) on silica gel yielded compound **4** (196 mg, 82%) as purple crystals (Found: C, 80.08; H, 4.78; N, 11.88. $C_{38}H_{27}N_5{\cdot}1H_2O$ requires C, 79.83; H, 5.12; N, 12.26%), mp >300 °C (from CH_2Cl_2–*n*-hexane); λ_{max} (CH_2Cl_2)/nm 408 (log ε/dm^3 mol^{-1} cm^{-1} 5.21), 514 (4.18), 556 (3.97), 590 (3.82), 646 (3.69); δ_H (250 MHz; $CDCl_3$: $SiMe_4$) −2.85 (2 H, s, 2 × NH), 3.90–4.00 (2 H, s, NH_2), 6.96 (2 H, d, *J* 7.5, H_{Ph}†), 7.70–7.80 (6 H, m, H_{Ph}), 8.00 (2 H, d, *J* 7.5, H_{Ph}), 8.25 (4 H, m, H_{Ph}), 8.85 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 9.05–9.15 (4 H, m, 4 × $H_{\beta\text{-pyrrole}}$), 9.30 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 10.20 (1 H, s, H_{meso}); *m*/*z* (EI, 80 eV) 553.2261 (M^+, 100%. $C_{38}H_{27}N_5$ requires *M*, 553.2267), 277 (M^{2+}, 11).

5-(*p*-Hydroxyphenyl)-10,20-diphenylporphyrin 5

n-Butyllithium (4 ml of a 2.5 M solution in *n*-hexane, 10 mmol) was added under an argon atmosphere to a 250 ml of Schlenk flask charged with a solution of *p*-bromophenol (0.87 g, 5 mmol) in 15 ml of dry diethyl ether at 0 °C. After addition of *n*-butyllithium the cold bath was removed and stirring was continued for 16 h at room temperature. The solution slowly became white opaque. To this vigorously stirred mixture was added rapidly a solution of 5,15-diphenylporphyrin **2** (200 mg, 0.43 mmol) in 80 ml of dry THF under an argon atmosphere. The color of the mixture changed from deep purple to brown within 30 min. The further work-up followed the general procedure described above. Chromatography and elution with dichloromethane–*n*-hexane (3 : 1, v/v) on silica gel yielded 179 mg (75%) of porphyrin **5** as purple crystals (Found: C, 80.85; H, 4.50; N, 9.68. $C_{38}H_{26}N_4O{\cdot}0.5H_2O$ requires C, 80.96; H, 4.83; N, 9.95%); mp >300 °C (from CH_2Cl_2–*n*-hexane); λ_{max} (CH_2Cl_2)/nm 413 (log ε/dm^3 mol^{-1} cm^{-1} 5.21), 509 (3.81), 544 (3.12), 584 (3.05), 639 (2.42); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) −3.01 (2 H, s, NH), 6.85 (2 H, d, *J* 7.5, H_{Ph}), 7.75–7.80 (6 H, m, H_{Ph}), 8.00 (2 H, d, *J* 7.5, H_{Ph}), 8.25 (4 H, m, H_{Ph}), 8.85–9.10 (4 H, m, 4 × $H_{\beta\text{-pyrrole}}$), 9.15 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 9.40 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 10.20 (1 H, s, H_{meso}); *m*/*z* (EI, 80 eV) 554.2152 (M^+, 100%. $C_{38}H_{26}N_4O$ requires *M*, 554.2107), 277 (M^{2+}, 37).

5-(*m*-Hydroxyphenyl)-10,20-diphenylporphyrin 6

n-Butyllithium (4 ml of 2.5 M solution in *n*-hexane, 10 mmol) was added under an argon atmosphere to a 250 ml Schlenk flask charged with a solution of *m*-bromophenol (0.87 g, 5 mmol) in 15 ml of dry diethyl ether at 0 °C. After addition of *n*-butyllithium the cold bath was removed and stirring was continued for 16 h at room temperature. Further steps followed the general procedure described above. Chromatography and elution with dichloromethane–*n*-hexane (3 : 1, v/v) on silica gel yielded 66 mg (30%) of porphyrin **6** from 5,15-diphenylporphyrin **2** (200 mg, 0.43 mmol) as purple crystals, mp >300 °C (from CH_2Cl_2–*n*-hexane); λ_{max} (CH_2Cl_2)/nm 412 (log ε/dm^3 mol^{-1} cm^{-1} 5.31), 509 (4.06), 548 (3.42), 580 (3.25); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) −3.00 (2 H, s, NH), 7.25 (1 H, m, H_{Ph}), 7.50–7.60 (1 H, m, H_{Ph}), 7.70–7.75 (1 H, m, H_{Ph}), 7.70–7.80 (6 H, m, H_{Ph}), 8.00 (1 H, s, H_{Ph}), 8.25 (4 H, m, H_{Ph}), 8.85 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 8.90 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 9.00 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 9.30 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 10.20 (1 H, s, H_{meso}); *m*/*z* (EI, 80 eV) 554.2139 (M^+, 100%. $C_{38}H_{26}N_4O$ requires *M*, 554.2107), 277 (M^{2+}, 25).

5-(*o*-Methoxyphenyl)-10,20-diphenylporphyrin 7

n-Butyllithium (2.2 ml of 2.5 M solution in *n*-hexane, 5.5 mmol) was added under an argon atmosphere to a 250 ml Schlenk flask charged with a solution of *o*-bromoanisole (1 g, 5.4 mmol) in 15 ml of dry THF at −78 °C. After addition of *n*-butyllithium the cold bath was removed and the mixture was stirred for 1 h at room temperature. Further steps followed the general procedure described above. Chromatography and elution with dichloromethane–*n*-hexane (1 : 1, v/v) on silica gel gave 188 mg (83%) of porphyrin **7** from 5,15-diphenylporphyrin **2** (200 mg, 0.43 mmol) as purple crystals, mp >300 °C (from CH_2Cl_2–*n*-hexane); λ_{max} (CH_2Cl_2)/nm 412 (log ε/dm^3 mol^{-1} cm^{-1} 5.27), 508 (3.97), 547 (3.37), 580 (3.18); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) −2.85 (2 H, s, NH), 3.50 (3 H, s, OCH_3), 7.35–7.45 (2 H, m,

† In this paper H_{Ph} signifies all types of aromatic protons.

H_{Ph}), 7.70–7.80 (7 H, m, H_{Ph}), 8.02 (1 H, d, *J* 8.1, H_{Ph}), 8.25–8.35 (4 H, m, H_{Ph}), 8.80 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 8.90 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 9.05 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 9.40 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 10.20 (1 H, s, H_{meso}); *m*/*z* (EI, 80 eV) 568.2229 (M^+, 100%. $C_{39}H_{28}N_4O$ requires *M*, 568.2263), 283 (M^{2+}, 6).

5-[*p*-(Dimethylamino)phenyl]-10,20-diphenylporphyrin 8

n-Butyllithium (1 ml of 2.5 M solution in *n*-hexane, 2.5 mmol) was slowly added (*ca*. 1 h) under an argon atmosphere to a 100 ml Schlenk flask charged with a solution of *p*-(dimethylamino)bromobenzene (0.5 g, 2.5 mmol) in 10 ml of dry diethyl ether at 0 °C. After addition of *n*-butyllithium the cold bath was removed and stirring was continued for another 1 h at room temperature. The solution became bright yellow and opaque. To the vigorously stirred mixture was added rapidly a solution of 5,15-diphenylporphyrin **2** (100 mg, 0.22 mmol) in 40 ml of dry THF under an argon atmosphere. The color changed from deep purple to brown within 30 min. Further work-up followed the general procedure described above. Chromatography and elution with dichloromethane–*n*-hexane (5 : 1, v/v) on silica gel yielded 100 mg (78%) of porphyrin **8** as purple crystals (Found: C, 81.70; H, 5.28; N, 11.53. $C_{40}H_{31}N_5{\cdot}0.5H_2O$ requires, C, 81.32; H, 5.46; N, 11.86%), mp >300 °C (from CH_2Cl_2–CH_3OH); λ_{max} (CH_2Cl_2)/nm 412 (log ε/dm^3 mol^{-1} cm^{-1} 5.22), 513 (4.05), 553 (3.60), 587 (3.45), 643 (3.10); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) −2.95 (2 H, s, 2 × NH), 3.20 (6 H, s, CH_3), 7.00 (2 H, d, *J* 7.5, H_{Ph}), 7.75–7.80 (6 H, m, H_{Ph}), 8.15 (2 H, d, *J* 7.5, H_{Ph}), 8.25 (4 H, m, H_{Ph}), 8.80 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 9.05–9.15 (4 H, m, 4 × $H_{\beta\text{-pyrrole}}$), 9.25 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 10.15 (1 H, s, H_{meso}); *m*/*z* (EI, 80 eV) 581.2547 (M^+, 96%. $C_{40}H_{31}N_5$ requires *M*, 581.2579), 566 ($M^+ - CH_3$, 39), 291 (M^{2+}, 100).

5-[*p*-(1,3-Dioxolan-2-yl)phenyl]-10,20-diphenylporphyrin 9

n-Butyllithium (1 ml of 2.5 M solution in *n*-hexane, 2.5 mmol) was slowly added (*ca*. 1 h) under an argon atmosphere to a 100 ml Schlenk flask charged with a solution of 2-(*p*-bromophenyl)dioxolane (0.5 g, 2.2 mmol) in 10 ml of dry diethyl ether at 0 °C. After addition of *n*-butyllithium the cold bath was removed and the solution was stirred for another 1 h at room temperature. To this vigorously stirred mixture was added rapidly a solution of 5,15-diphenylporphyrin **2** (100 mg, 0.22 mmol) in 50 ml of dry THF under an argon atmosphere. The color of the mixture changed from deep purple to brown within 30 min. Further work-up followed the general procedure described above. Chromatography and elution with dichloromethane–*n*-hexane (2 : 1, v/v) on silica gel yielded 116 mg (86%) of porphyrin **9** as purple crystals, mp >300 °C (from CH_2Cl_2–CH_3OH); λ_{max} (CH_2Cl_2)/nm 411 (log ε/dm^3 mol^{-1} cm^{-1} 5.23), 508 (4.01), 544 (3.60), 584 (3.61), 636 (3.45); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) −3.02 (2 H, s, NH), 4.20, 4.35 (4 H, each m, OCH_2CH_2O), 6.15 (1 H, s, C*H*OCH_2CH_2O), 7.75–7.85 (8 H, m, H_{Ph}), 8.25–8.35 (6 H, m, H_{Ph}), 8.80–8.90 (4 H, m, 4 × $H_{\beta\text{-pyrrole}}$), 9.05 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 9.40 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 10.20 (1 H, s, H_{meso}); *m*/*z* (EI, 80 eV) 610.2329 (M^+, 100%. $C_{41}H_{30}N_4O_2$ requires *M*, 610.2369), 566 ($M^+ - CH_2CH_2O$, 13), 538 [$(M + H)^+ - CH(OCH_2)_2$, 16].

5-(*p*-Ethynylphenyl)-10,20-diphenylporphyrin 10

n-Butyllithium (4 ml of 2.5 M solution in *n*-hexane, 10 mmol) was slowly added (*ca*. 1 h) under an argon atmosphere to a 100 ml Schlenk flask charged with a solution of *p*-bromophenylethyne (0.91 g, 5.0 mmol) in 15 ml of dry diethyl ether at −70 °C. The reaction mixture was then warmed to −40 °C and THF was added dropwise until the aryllithium was formed as a white–bright pink suspension. To this vigorously stirred mixture was added rapidly a solution of 5,15-diphenylporphyrin **2** (200 mg, 0.43 mmol) in 80 ml of dry THF under an argon atmosphere. The color of the mixture changed from deep purple to brown within 30 min. Further work-up followed the general procedure described above. Chromatography and elution with dichloromethane–*n*-hexane (1 : 5, v/v) on silica gel yielded 205 mg (85%) of porphyrin **10** as purple crystals (Found: C, 84.86; H, 4.90; N, 9.35. $C_{40}H_{26}N_4{\cdot}0.35H_2O$ requires, C, 84.43; H, 4.73; N, 9.85%), mp >300 °C (from CH_2Cl_2–CH_3OH); λ_{max} (CH_2Cl_2)/nm 413 (log ε/dm^3 mol^{-1} cm^{-1} 5.21), 509 (4.01), 544 (3.51), 585 (3.48), 639 (3,16); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) −3.15 (2 H, s, 2 × NH), 3.40 (1 H, s, HC≡C), 7.75–7.80 (6 H, m, H_{Ph}), 7.90 (2 H, d, *J* 7.4, H_{Ph}), 8.20 (2 H, d, *J* 7.4, H_{Ph}), 8.25–8.35 (4 H, m, H_{Ph}), 8.80 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 8.90 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 9.10 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 9.40 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 10.20 (1 H, s, H_{meso}); *m*/*z* (EI, 80 eV) 562.2152 (M^+, 100%. $C_{40}H_{26}N_4$ requires *M*, 562.2158), 281 (M^{2+}, 8).

5-[3-(Dimethylamino)propyl]-10,20-diphenylporphyrin 11

To a suspension of granular lithium (0.5 g, 0.07 mol) in dry diethyl ether (40 ml) was added freshly distilled 3-(dimethylamino)propyl chloride (3.7 g, 0.025 mol) under argon by means of a dropping funnel. After gentle heating to initiate the reaction, the reagent was added dropwise, so that reflux continued. After complete addition, stirring was continued for 1 h. The resulting solution was cooled to room temperature and used for the reaction following the general procedure described above. Chromatography and elution with neat dichloromethane on silica gel yielded 82 mg (75%) of porphyrin **11** as purple crystals from 5,15-diphenylporphyrin **2** (100 mg, 0.21 mmol), mp 276 °C (from CH_2Cl_2–*n*-hexane); λ_{max} (CH_2Cl_2)/nm 413 (log ε/dm^3 mol^{-1} cm^{-1} 5.21), 509 (3.86), 545 (3.03), 586 (2.97), 640 (2.02); δ_H (500 MHz; $CDCl_3$; $SiMe_4$) −3.05 (2 H, s, NH), 2.35 (6 H, s, CH_3N), 2.75 [2 H, t, *J* 7.5, $CH_2CH_2CH_2N(CH_3)_2$], 2.95 [2 H, q, *J* 7.5, $CH_2CH_2CH_2N(CH_3)_2$], 5.10 [2 H, t, *J* 7.5, $CH_2CH_2CH_2N(CH_3)_2$], 7.70–7.80, 8.15–8.25 (10 H, m, H_{Ph}), 8.90–8.95 (4 H, m, 4 × $H_{\beta\text{-pyrrole}}$), 9.25 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 9.55 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 10.10 (1 H, s, H_{meso}); *m*/*z* (EI, 80 eV) 547.2762 (M^+, 17%. $C_{37}H_{33}N_5$ requires *M*, 547.2736), 489 ($M^+ - C_3H_8N$, 100), 476 [$(M + H)^+ - C_4H_{10}N$, 11], 463 [$(M + 2H)^+ - C_5H_{12}N$, 27].

{5-[2-(1,3-Dioxan-2-yl)ethyl]-10,20-diphenylporphyrinato}-nickel(II) 12

A solution of 5 ml (≈2 mmol) of freshly synthesized 2-(1,3-dioxan-2-yl)ethyllithium[45] in THF was added dropwise under an argon atmosphere to a Schlenk flask charged with a solution of (5,15-diphenylporphyrinato)nickel(II) **3** (100 mg, 0.22 mmol) in 50 ml of THF at −70 °C. Further work-up followed the general procedure described above. Chromatography and elution with dichloromethane–*n*-hexane (3 : 1 v/v) on silica gel yielded 92 mg (73%) of porphyrin **12** as purple crystals, mp 283 °C (from CH_2Cl_2–CH_3OH); λ_{max} (CH_2Cl_2)/nm 408 (log ε/dm^3 mol^{-1} cm^{-1} 5.27), 523 (4.22); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) 2.15–2.40 (2 H, m, $OCH_2CH_2CH_2O$), 2.75–2.85 [2 H, q, *J* 7.5, $CH_2CH_2CH(OCH_2CH_2CH_2O)$], 4.20–4.30 (4 H, m, OCH_2-CH_2CH_2O), 4.55 (1 H, t, *J* 7.5, CH_2CH_2CH), 4.75 (2 H, t, *J* 7.6, CH_2CH_2CH), 7.70–7.85, 7.95–8.15 (10 H, m, H_{Ph}), 8.80 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 8.85–8.95 (4 H, m, 4 × $H_{\beta\text{-pyrrole}}$), 9.45 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 9.50 (1 H, s, H_{meso}); *m*/*z* (EI, 80 eV) 632.1768 (M^+, 100%. $C_{38}H_{30}N_4O_2Ni$ requires *M*, 632.1722), 531 ($M^+ - C_5H_9O_2$, 51).

5-(*p*-Aminophenyl)-15-butyl-10,20-diphenylporphyrin 13

A Schlenk flask was charged with the porphyrin **4** (100 mg, 0.18 mmol) dissolved in 50 ml of dry THF under an argon atmosphere. Within 15 min the butyllithium (1.5 mmol, 0.6 ml of a 2.5 M solution in *n*-hexane) was added dropwise. Further

steps followed the general procedure described above. Chromatography and elution with dichloromethane–*n*-hexane (3 : 1, v/v) yielded 97 mg (80%) of porphyrin **13** as purple crystals, mp 272 °C (from CH_2Cl_2–CH_3OH); λ_{max} (CH_2Cl_2)/nm 420 (log ε/dm^3 mol^{-1} cm^{-1} 5.25), 518 (3.92), 556 (3.71), 594 (3.46), 649 (3.47); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) −2.65 (2 H, s, 2 × NH), 1.20 (3 H, t, *J* 7.5, $CH_2CH_2CH_2CH_3$), 1.80–1.90 (2 H, m, $CH_2CH_2CH_2CH_3$), 2.45–2.55 (2 H, m, $CH_2CH_2CH_2CH_3$), 3.05 (2 H, s, NH_2), 4.95 (2 H, t, *J* 7.8, $CH_2CH_2CH_2CH_3$), 6.75, 7.90 (4 H, each d, *J* 8.2, H_{Ph}), 7.75–7.85, 8.20–8.30 (10 H, each m, H_{Ph}), 8.75, 8.80, 8.85, 9.45 (8 H, each d, *J* 4.9, 8 × $H_{\beta\text{-pyrrole}}$); *m*/*z* (EI, 80 eV) 609.2888 (M^+, 100%. $C_{42}H_{35}N_5$ requires *M*, 609.2893), 566 ($M^+ - CH_2CH_2CH_3$, 28), 304 (M^{2+}, 8).

5-Butyl-15-{*p*-[(−)-2,3:4,6-di-*O*-isopropylidene-L-*gulo*-hex-2-ulofuranosonamido]phenyl}-10,20-diphenylporphyrin 14

DCC 0.1 g (0.48 mmol) was added in portions to a solution of (−)-2,3:4,6-di-*O*-isopropylidene-L-*gulo*-hex-2-ulofuranosonic acid (140 mg, 0.48 mmol) and porphyrin **13** (50 mg, 0.08 mmol) in CH_2Cl_2 (50 ml) at room temperature. The reaction mixture was stirred for 3 h and then washed with distilled water (3 × 100 ml) until the water phase became colorless. The organic phase was dried with Na_2SO_4 and evaporated to dryness on a rotary evaporator. Chromatography and elution with dichloromethane–*n*-hexane (3 : 1, v/v) on silica gel yielded 46 mg (70%) of porphyrin **14** as bright purple crystals, mp 216 °C (from CH_2Cl_2–CH_3OH); λ_{max} (CH_2Cl_2)/nm 418 (log ε/dm^3 mol^{-1} cm^{-1} 5.23), 516 (3.82), 552 (3.45), 593 (3.03); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) −2.70 (2 H, s, 2 × NH), 1.20 (3 H, t, *J* 7.5, $CH_2CH_2CH_2CH_3$), 1.45, 1.48, 1.63, 1.80 [12 H, each s, 2 × $OC(CH_3)_2$], 1.80–1.90 (2 H, m, $CH_2CH_2CH_2CH_3$), 2.45–2.55 (2 H, m, $CH_2CH_2CH_2CH_3$), 4.20 (2 H, m, $OCH_2CHCHOCHOC$), 4.30, 4.50, 4.80 (3 H, each s, $OCH_2CHCHOCHOC$), 5.05 (2 H, t, *J* 7.8, $CH_2CH_2CH_2CH_3$), 7.70–7.80, 7.95–8.05, 8.20–8.30 (14 H, each m, H_{Ph}), 8.85–8.90 (4 H, m, 4 × $H_{\beta\text{-pyrrole}}$), 8.95 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 9.45 (1 H, s, NHCO), 9.50 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$); *m*/*z* (EI, 80 eV) 865.3854 (M^+, 100%. $C_{54}H_{51}N_5O_6$ requires *M*, 865.3839), 850 ($M^+ - CH_3$, 6), 822 ($M^+ - CH_2CH_2CH_3$, 14), 635 ($M^+ - C_{11}H_{18}O_5$, 10), 592 ($M^+ - CH_2CH_2CH_3 - C_{11}H_{18}O_5$, 19).

5-Butyl-15-[*p*-(3-carboxyacrylamido)phenyl]-10,20-diphenylporphyrin 15

Maleic anhydride (63 mg, 0.64 mmol) was added in portions to a solution of porphyrin **13** (100 mg, 0.16 mmol) in dry THF (50 ml). The reaction mixture was stirred for 30 min at room temperature and then poured into 100 ml of 0.1 M NaOH. The porphyrin **15** was extracted with CH_2Cl_2 (3 × 50 ml) until the water phase became colorless. The combined extracts were dried with Na_2SO_4 and evaporated to dryness on a rotary evaporator. Chromatography and elution with CH_2Cl_2–MeOH (3 : 1, v/v) on silica gel yielded 104 mg (92%) of bright purple crystals; mp >300 °C (from CH_2Cl_2–CH_3OH); λ_{max} (CH_2Cl_2)/nm 420 (log ε/dm^3 mol^{-1} cm^{-1} 5.25), 517 (3.87), 552 (3.56), 594 (3.08), 648 (2.92); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) −2.30 (2 H, s, 2 × NH), 1.20 (3 H, t, *J* 7.5, $CH_2CH_2CH_2CH_3$), 1.80–1.90 (2 H, m, $CH_2CH_2CH_2CH_3$), 2.55–2.65 (2 H, m, $CH_2CH_2CH_2CH_3$), 5.05 (2 H, t, *J* 7.8, $CH_2CH_2CH_2CH_3$), 6.25–6.45 [2 H, m, $NHCO(CH)_2COOH$], 7.70–7.80, 7.95–8.15, 8.20–8.25, 8.30–8.35 (14 H, each m, H_{Ph}), 8.75–9.90 (6 H, m, 6 × $H_{\beta\text{-pyrrole}}$), 9.40 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 13.90 (1 H, s, COOH); *m*/*z* FAB(+) 708 ($M + H^+$, 100%. $C_{46}H_{38}N_5O_3$ requires *m*/*z*, 708); 609 [$(M + H)^+ - C_4H_3O_3$, 20].

5-[*p*-(Carboxyethynyl)phenyl]-10,20-diphenylporphyrin 17

n-Butyllithium (4 ml of 2.5 M solution in *n*-hexane, 10 mmol) was slowly added (*ca*. 1 h) under an argon atmosphere to a 100 ml Schlenk flask charged with a solution of *p*-bromophenylethyne (0.91 g, 5.0 mmol) in 15 ml of dry diethyl ether at −70 °C. The reaction mixture was then warmed to −40 °C and THF was added dropwise until the aryllithium was formed as a bright pink suspension. To this vigorously stirred mixture was added rapidly a solution of 5,15-diphenylporphyrin **2** (200 mg, 0.43 mmol) in 80 ml of dry THF under an argon atmosphere. After removal of the cold bath, the color of the mixture changed from deep purple to brown within 30 min. The reaction mixture was then cooled again to −40 °C and excess of solid CO_2 was added in portions. Further work-up followed the general procedure described above. Chromatography and elution with dichloromethane–methanol (2 : 1, v/v) on silica gel yielded 112 mg (43%) of porphyrin **17** as purple crystals, mp >300 °C (from CH_2Cl_2–*n*-hexane); λ_{max} (CH_2Cl_2)/nm 413 (log ε/dm^3 mol^{-1} cm^{-1} 5.29), 509 (4.78), 545 (4.75), 582 (4.75), 634 (4.74); δ_H (250 MHz; DMSO; $SiMe_4$) −3.20 (2 H, s, 2 × NH), 7.75–7.90 (8 H, m, H_{Ph}), 8.15–8.30 (6 H, m, H_{Ph}), 8.80–8.90 (4 H, m, 4 × $H_{\beta\text{-pyrrole}}$), 8.95 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 9.60 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 10.55 (1 H, s, H_{meso}); *m*/*z* FAB (+) 607 ($M + H^+$, 100%. $C_{41}H_{27}N_4O_2$ requires *m*/*z*, 607), 563 [$(M + H)^+ - CO_2$, 52%]; (EI, 80 eV) 562.2198 ($M^+ - CO_2$, 100%. $C_{40}H_{26}N_4$ requires *m*/*z*, 562.2157).

{5-[*p*-(*p*-Iodobenzamido)phenyl]-10,20-diphenylporphyrinato}-zinc(II) 19

p-Iodobenzoyl chloride (0.2 g, 0.73 mmol) was added in portions to a solution of porphyrin **4** (100 mg, 0.18 mmol) in dry THF (50 ml). The reaction mixture was stirred for 30 min at room temperature and then poured into 100 ml of 0.1 M NaOH. The porphyrin solution was extracted with CH_2Cl_2 (3 × 50 ml) until the aqueous phase became colorless. The combined extracts were dried with Na_2SO_4 and evaporated to dryness on a rotary evaporator. The residue was then resolvated in 50 ml of dry CH_2Cl_2. Zinc acetate (0.24 g, 1.1 mol) was added and stirring was continued for 30 min. The reaction mixture was washed with distilled water (3 × 30 ml), and the organic phase was dried with Na_2SO_4 and evaporated to dryness on a rotary evaporator. Chromatography and elution with dichloromethane–*n*-hexane (3 : 1, v/v) on silica gel yielded 130 mg (86%) of porphyrin **19** as bright purple crystals, mp >300 °C (from CH_2Cl_2–CH_3OH) λ_{max} (CH_2Cl_2)/nm 414 (log ε/dm^3 mol^{-1} cm^{-1} 5.25), 542 (3.82); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) 7.45–7.55, 7.75–8.05, 8.25–8.35 (18 H, m, H_{Ph}), 8.85 (4 H, m, 4 × $H_{\beta\text{-pyrrole}}$), 9.05 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 9.40 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 10.20 (1 H, s, H_{meso}); *m*/*z* (EI, 80 eV) 845.0615 (M^+, 100%. $C_{45}H_{28}IN_5OZn$ requires *M*, 845.0629), 614 ($M^+ - C_7H_4OI$, 11), 231 ($C_7H_4OI^+$, 31).

5-[*p*-(3-Carboxyacrylamido)phenyl]-10,20-diphenylporphyrin 20

Maleic anhydride (63 mg, 0.64 mmol) was added portionwise to a solution of porphyrin **4** (100 mg, 0.18 mmol) in dry THF (50 ml). The reaction mixture was stirred for 30 min at room temperature and then poured into 100 ml of 0.1 M NaOH. Porphyrin **20** was extracted with CH_2Cl_2 (3 × 50 ml) until the aqueous phase became colorless. The combined extracts were dried with Na_2SO_4 and evaporated to dryness on a rotary evaporator. Chromatography and elution with CH_2Cl_2–MeOH (2 : 1, v/v) on silica gel yielded 110 mg (95%) of porphyrin **20** as bright purple crystals, mp >300 °C (from CH_2Cl_2–CH_3OH); λ_{max} (CH_2Cl_2)/nm 413 (log ε/dm^3 mol^{-1} cm^{-1} 5.28), 509 (3.99), 544 (3.53), 584 (3.46), 637 (3.19); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) −3.02 (2 H, s, NH), 6.40 [2 H, m, $NHCO(CH)_2COOH$], 7.70–7.80, 8.05–8.15, 8.25–8.35 (14 H, m, H_{Ph}), 8.80–8.95 (4 H, m, 4 × $H_{\beta\text{-pyrrole}}$), 9.10 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 9.35 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 10.20 (1 H, s, H_{meso}), 13.60 (1 H, s, COOH); *m*/*z* FAB(+) 652 ($M + H^+$); FAB(−) 650 ($M - H^+$). $C_{42}H_{29}N_5O_3$ required *M*, 651; (EI, 80 eV) 634.2259 ($M^+ - OH$, 11%. $C_{42}H_{28}N_5O_2$ requires *m*/*z*, 634.2243), 553 ($M^+ - C_4H_2O_3$, 100).

5-{*p*-[(−)-2,3:4,6-Di-*O*-isopropylidene-L-*gulo*-hex-2-ulofurano-sonamido]phenyl}-10,20-diphenylporphyrin 21

DCC 0.11 g (0.54 mmol) was added in portions to a solution of (−)-2,3:4,6-di-*O*-isopropylidene-L-*gulo*-hex-2-ulofuranosonic acid (0.16 g, 0.54 mmol) and porphyrin **4** (50 mg, 0.09 mmol) in CH_2Cl_2 (50 ml) at room temperature. The reaction mixture was stirred for 3 h at room temperature and then washed with distilled water (3 × 100 ml) until the aqueous phase became colorless. The organic phase was dried with Na_2SO_4 and evaporated to dryness on a rotary evaporator. Chromatography and elution with dichloromethane on silica gel yielded 55 mg (76%) of porphyrin **21** as bright purple crystals, mp >300 °C (from CH_2Cl_2–CH_3OH); λ_{max} (CH_2Cl_2)/nm 413 (log ε/dm^3 mol^{-1} cm^{-1} 5.26), 509 (4.07), 545 (3.56), 585 (3.54), 639 (3.24); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) −3.00 (2 H, s, 2 × NH), 1.45, 1.50, 1.65, 1.70 [12 H, each s, 2 × OC(CH_3)$_2$], 4.15 (2 H, m, OCH_2CH), 4.20, 4.50, 4.80 (3 H, each s, OCH$_2$C*H*C*H*OC*H*OC), 7.70–7.80, 7.95–8.05, 8.20–8.30 (14 H, each m, H_{Ph}), 8.85–8.90 (4 H, m, 4 × $H_{\beta\text{-pyrrole}}$), 9.00 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 9.40 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 10.20 (1 H, s, H_{meso}); *m*/*z* FAB (+) 810 (M + H$^+$, 100%), $C_{50}H_{44}N_5O_6$ required *m*/*z*, 810, 580 [(M + H)$^+$ − $C_{11}H_{18}O_5$, 12]; (EI, 80 eV) 809.3255 (M$^+$, 1%. $C_{50}H_{43}N_5O_6$ requires *M*, 809.3213), 536 (M$^+$ − $C_{12}H_{19}NO_6$ 17), 511 (M$^+$ − $C_{14}H_{20}NO_6$, 100).

[5,10,15-Triphenyl-20-(4-phthalimidobutyl)porphyrinato]-nickel(II) 24

Potassium phthalimide (0.1 g, 0.53 mmol) was added portion-wise to a solution of [5-(4-iodobutyl)-10,15,20-triphenylporphyrinato]nickel(II) **23** (100 mg, 0.12 mmol) in DMF (50 ml). The reaction mixture was heated overnight under reflux and then poured into 100 ml of distilled water. Porphyrin **24** was extracted with CH_2Cl_2 (3 × 50 ml) until the aqueous phase became colorless. The combined extracts were dried with Na_2SO_4 and evaporated to dryness on a rotary evaporator. Chromatography and elution with dichloromethane–*n*-hexane (3 : 1, v/v) on silica gel yielded 73 mg (71%) of the title compound as purple crystals, mp 260 °C; λ_{max} (CH_2Cl_2)/nm 415 (log ε/dm^3 mol^{-1} cm^{-1} 5.21), 530 (3.95); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) 1.85–2.00 (2 H, m, $CH_2CH_2CH_2CH_2$), 2.25–2.45 (2 H, m, $CH_2CH_2CH_2CH_2N$), 3.75 (2 H, t, *J* 7.6, $CH_2CH_2CH_2$-CH_2N), 4.65 (2 H, t, *J* 7.8, $CH_2CH_2CH_2CH_2N$), 7.55–7.75, 7.95–8.05 (19 H, each m, H_{Ph}), 8.65 (4 H, m, 4 × $H_{\beta\text{-pyrrole}}$), 8.80, 9.35, (4 H, each d, *J* 4.9, 4 × $H_{\beta\text{-pyrrole}}$); *m*/*z* (EI, 80 eV) 795.2184 (M$^+$, 100%. $C_{50}H_{35}N_5NiO_2$ requires *M*, 795.2144), 648 (M$^+$ − $C_8H_5NO_2$, 7), 608 [(M + H)$^+$ − $C_{11}H_{10}NO_2$, 60].

5-Butyl-15-{[4-(diethylamino)butyl]-10,20-diphenylporphyr-inato}nickel(II) 25

Diethylamine (5 ml, 48 mmol) was added dropwise to a solution of [5-butyl-15-(4-iodobutyl)-10,20-diphenylporphyrinato]-nickel(II) **22** (100 mg, 0.13 mmol) in THF (50 ml). The reaction mixture was stirred at 50 °C for 2 h and then poured into 100 ml of distilled water. Porphyrin **25** was extracted with CH_2Cl_2 (3 × 50 ml) until the aqueous phase became colorless. The combined extracts were dried with Na_2SO_4 and evaporated to dryness on a rotary evaporator. Chromatography and elution with dichloromethane–*n*-hexane (3 : 1, v/v) on silica gel yielded the target porphyrin (48 mg, 53%) as purple crystals, mp >300 °C (from aq. MeOH); λ_{max} (CH_2Cl_2)/nm 416 (log ε/dm^3 mol^{-1} cm^{-1} 5.13), 533 (3.97); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) 1.05 [9 H, m, CH_3CH$_2$CH$_2$CH$_2$, (CH_3CH_2)$_2$N], 1.45–1.55 (2 H, m, $CH_3CH_2CH_2CH_2$), 2.20–2.40 [6 H, m, (C_2H_5)$_2$NCH$_2$CH_2-CH_2CH$_2$, $CH_3CH_2CH_2CH_2$], 2.45–2.60 [6 H, m, (CH_3CH_2)$_2$-NCH_2CH$_2$CH$_2$CH$_2$], 4.50–4.55 [4 H, m, (CH_3CH_2)$_2$NCH$_2$-$CH_2CH_2CH_2$, $CH_3CH_2CH_2CH_2$], 7.65–7.75, 7.95– 8.05 (10 H, m, H_{Ph}), 8.70, 9.35 (8 H, each m, 8 × $H_{\beta\text{-pyrrole}}$); *m*/*z* (EI, 80 eV) 701.3073 (M$^+$, 16%. $C_{44}H_{45}N_5Ni$ requires *M*, 701.3028), 587 (M$^+$ − $C_7H_{16}N$, 6), 575 [(M + 2H)$^+$ − $C_8H_{18}N$, 33], 544 (M$^+$ − $C_7H_{16}N$ − C_3H_7, 14), 351 (M^{2+}, 7).

{5-Butyl-10,20-diphenyl-15-[4-(triethylammonio)butyl]porphyr-inato}nickel(II) iodide 26

Triethylamine (1 ml, 7 mmol) was added dropwise to a solution of [5-butyl-15-(4-iodobutyl)-10,20-diphenylporphyrinato]-nickel(II) **22** (100 mg, 0.13 mmol) in DMF (30 ml). The reaction mixture was stirred at 60 °C for 3 h and then poured into 100 ml of distilled water. Porphyrin **26** was extracted with CH_2Cl_2 (3 × 50 ml) until the aqueous phase became colorless. The combined extracts were dried with Na_2SO_4 and evaporated to dryness on a rotary evaporator. Chromatography and elution with CH_2Cl_2–MeOH (2 : 1, v/v) on Celite after recrystallization from aq. MeOH gave 78 mg (83%) purple crystals of **26** (Found: C, 63.62; H, 6.11; N, 8.10. $C_{46}H_{50}IN_5Ni$·0.5H_2O requires C, 63.72; H, 5.93; N, 8.08%), mp >300 °C (from aq. MeOH); λ_{max} (CH_2Cl_2)/nm 416 (log ε/dm^3 mol^{-1} cm^{-1} 5.27), 533 (3.99); δ_H (250 MHz; D_6-DMSO; $SiMe_4$) 0.85 (3 H, t, *J* 7.8 CH_3CH$_2$CH$_2$CH$_2$), 1.25 [9 H, t, *J* 7.5, (CH_3CH_2)$_3$N$^+$], 1.30–1.45 [2 H, m, $CH_3CH_2CH_2CH_2$], 1.90–2.10 [2 H, m, (CH_3CH_2)$_3$-N$^+$CH$_2$CH_2CH$_2$CH$_2$], 2.20–2.30 (2 H, m, $CH_3CH_2CH_2CH_2$), 2.35–2.60 [2 H, m, (CH_3CH_2)$_3$N$^+$CH$_2$CH$_2$CH_2CH$_2$], 3.20–3.30 [8 H, m, (CH_3CH_2)$_3$N$^+$CH_2CH$_2$CH$_2$CH$_2$], 4.60–4.75 [4 H, m, (CH_3CH_2)$_3$N$^+$CH$_2$CH$_2$CH$_2$CH_2, $CH_3CH_2CH_2CH_2$], 7.75–7.85, 7.95–8.10 (10 H, m, H_{Ph}), 8.60 (4 H, m, $H_{\beta\text{-pyrrole}}$), 9.45 (2 H, d, *J* 5.0, 2 × $H_{\beta\text{-pyrrole}}$), 9.60 (2 H, d, *J* 5.0, $H_{\beta\text{-pyrrole}}$); *m*/*z* FAB(+) 731 (M + H$^+$, 100%. $C_{46}H_{51}N_5Ni$ requires *m*/*z*, 731), 629 [M$^+$ − N(CH_2CH_3)$_3$, 30]; FAB(−): 127 (I$^-$, 100%. I requires *M*, 127).

[5-Butyl-15-(4-hydroxybutyl)-10,20-diphenylporphyrinato]-nickel(II) 27

0.4 g KOH in 5 ml H_2O was added to a solution of [5-butyl-15-(4-iodobutyl)-10,20-diphenylporphyrinato]nickel(II) **22** (50 mg, 0.065 mmol) in DMF (30 ml). The reaction mixture was stirred at 100 °C for 4 h and then poured into 100 ml of distilled water. Porphyrin **27** was extracted with CH_2Cl_2 (3 × 50 ml) until the aqueous phase became colourless. The combined extracts were dried with Na_2SO_4 and evaporated to dryness under vacuum. Chromatography and elution with ethyl acetate–*n*-hexane on neutral alumina (Alfa) (1:1, v/v) yielded 34 mg (80%) of porphyrin **27** as purple crystals. The spectroscopic data were identical with those given in our earlier work.[11]

{5-[4-(*N*-Acetyl-L-cystein-5-yl)butyl]-10,15,20-triphenylpor-phyrinato}nickel(II) 28

DBU (0.5 ml) was added dropwise to a solution of *N*-acetyl-L-cysteine (0.2 g, 1.3 mmol) and [5-(4-iodobutyl)-10,15,20-triphenylporphyrinato]nickel(II) **23** (50 mg, 0.06 mmol) in DMF (50 ml) at room temperature. The reaction mixture was stirred for 3 h and then poured into 200 ml of distilled water. Porphyrin **28** was extracted with CH_2Cl_2 (3 × 50 ml) until the aqueous phase became colorless. The combined extracts were washed with water (3 × 100 ml), dried with Na_2SO_4 and evaporated to dryness on a rotary evaporator. Chromatography and elution with CH_2Cl_2–MeOH (5 : 1, v/v) on silica gel yielded 27 mg (55%) of compound **28** as purple crystals; mp 225 °C (from CH_2Cl_2–CH_3OH); λ_{max} (CH_2Cl_2)/nm 415 (log ε/dm^3 mol^{-1} cm^{-1} 5.25), 529 (4.22); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) 1.75–1.85 (2 H, m, $CH_2CH_2CH_2CH_2S$), 2.10 (3 H, s, HNCOCH_3), 2.25–2.40 (2 H, m, $CH_2CH_2CH_2CH_2S$), 2.60 (2 H, m, $CH_2CH_2CH_2$-CH_2S), 3.10 (2 H, m, NHCHCH_2S), 4.40 (1 H, m, NHC*H*-CH_2S), 4.55 (2 H, t, *J* 7.8, CH_2CH$_2$CH$_2$CHS), 7.55–7.75, 7.85–7.95 (15 H, each m, H_{Ph}), 8.65 (4 H, m, 4 × $H_{\beta\text{-pyrrole}}$), 8.70, 9.35 (4 H, each d, *J* 4.9, 4 × $H_{\beta\text{-pyrrole}}$); *m*/*z* [FAB(+)] 812 (M + H$^+$, 100%. $C_{47}H_{40}N_5NiO_3S$ requires *m*/*z*, 812), 650 [(M + H)$^+$ − $SCH_2CHNHCOCH_3COOH$, 70].

{5-[4-(Acetylthio)butyl]-5-butyl-10,20-diphenylporphyrinato}-nickel(II) 29

Potassium thioacetate (50 mg, 0.4 mmol) was added portionwise to a solution of {5-butyl-15-(4-iodobutyl)-10,20-diphenylporphyrinato}nickel(II) **22** (50 mg, 0.07 mmol) in THF–acetone (30 ml; 1 : 1, v/v). The reaction mixture was stirred for 12 h at room temperature and then poured into 100 ml of distilled water. Porphyrin **29** was extracted with CH_2Cl_2 (3 × 30 ml) until the aqueous phase became colorless. The combined extracts were dried with Na_2SO_4 and evaporated to dryness on a rotary evaporator. Chromatography and elution with dichloromethane–*n*-hexane (3 : 1, v/v) on silica gel yielded porphyrin **29** 45 mg (91%) as purple crystals, mp 240 °C (from CH_2Cl_2–*n*-hexane); λ_{max} (CH_2Cl_2)/nm 416 (log ε/dm^3 mol^{-1} cm^{-1} 5.15), 532 (4.04); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) 0.85 (3 H, t, *J* 7.8, C*H*$_3$CH$_2$CH$_2$CH$_2$), 1.45–1.55 (2 H, m, CH$_3$C*H*$_2$CH$_2$CH$_2$), 1.70–1.80 (2 H, m, SCH$_2$C*H*$_2$CH$_2$CH$_2$), 2.20–2.30 (7 H, m, CH$_3$CH$_2$C*H*$_2$CH$_2$, SCH$_2$CH$_2$C*H*$_2$CH$_2$, CH$_3$COS), 2.90 (2 H, t, *J* 7.8, SC*H*$_2$CH$_2$CH$_2$CH$_2$), 4.50–4.60 (4 H, m, SCH$_2$CH$_2$-CH$_2$C*H*$_2$, CH$_3$CH$_2$CH$_2$C*H*$_2$), 7.75–7.85, 7.95–8.10 (10 H, m, H_{Ph}), 8.65–8.75 (4 H, m, 4 × $H_{\beta\text{-pyrrole}}$), 9.20–9.30 (4 H, m, 4 × $H_{\beta\text{-pyrrole}}$); *m*/*z* (EI, 80 eV) 704.2164 (M^+, 100%. $C_{42}H_{38}N_4$-NiOS requires *M*, 704.2120), 661 ($M^+ - CH_2CH_2CH_3$, 42), 587 [$(M + H)^+ - CH_2CH_2CH_3 - SCOCH_3$, 72], 544 ($M^+ - CH_2CH_2CH_3 - CH_2CH_2CH_2SCOCH_3$, 63).

5-[4-(Acetylthio)butyl]-15-butyl-10,20-diphenylporphyrin 30

A solution of boron tribromide in CH_2Cl_2 (10 ml; 0.1 M) was added dropwise to a solution of porphyrin **29** (50 mg, 0.07 mmol) in CH_2Cl_2 (30 ml) at −70 °C under an argon atmosphere. After removal of the cold bath the reaction mixture was stirred at room temperature for 2 h and then cooled again to −70 °C. A solution of 1 ml of water in 5 ml of THF was added dropwise to the vigorously stirred reaction mixture. After the hydrolysis the solution was stirred for a further 30 min at room temperature and then poured into 100 ml of 0.1 M NaOH. Porphyrin **30** was extracted with CH_2Cl_2 (3 × 30 ml) until the aqueous phase became colorless. The combined extracts were dried with Na_2SO_4 and evaporated to dryness on a rotary evaporator. Chromatography and elution with dichloromethane–*n*-hexane (1 : 3, v/v) on silica gel gave 32 mg (57%) of porphyrin **30** as purple crystals, mp 234 °C (from CH_2Cl_2–CH_3OH); λ_{max} (CH_2Cl_2)/nm (log ε/dm^3 mol^{-1} cm^{-1} 5.22), 518 (3.91), 557 (3.68), 594 (3.43), 650 (3.21); δ_H (250 MHz; $CDCl_3$; $SiMe_4$) −2.60 (2 H, s, NH), 1.15 (3 H, t, *J* 7.8, C*H*$_3$CH$_2$CH$_2$CH$_2$), 1.80 (2 H, sext, *J* 7.8, CH$_3$C*H*$_2$CH$_2$CH$_2$), 2.05 (2 H, quint, *J* 7.8 SCH$_2$C*H*$_2$CH$_2$CH$_2$), 2.30 (3 H, s, CH$_3$COS), 2.45–2.75 (4 H, m, CH$_3$CH$_2$C*H*$_2$CH$_2$, SCH$_2$CH$_2$C*H*$_2$CH$_2$), 3.05 (2 H, t, *J* 7.8, SC*H*$_2$CH$_2$CH$_2$CH$_2$), 4.95 (4 H, m, SCH$_2$CH$_2$CH$_2$C*H*$_2$, CH$_3$CH$_2$CH$_2$C*H*$_2$), 7.75–7.85, 8.20–8.30 (10 H, m, H_{Ph}), 8.85–8.95 (4 H, m, 4 × $H_{\beta\text{-pyrrole}}$), 9.35–9.45 (4 H, m, 4 × $H_{\beta\text{-pyrrole}}$); *m*/*z* (EI, 80 eV) 648.2965 (M^+, 100%. $C_{42}H_{40}N_4OS$ requires *M*, 648.2923), 605 ($M^+ - CH_3CH_2CH_2$, 30), 574 [$(M + H)^+ - SCOCH_3$, 11], 531 [$(M + H)^+ - CH_3CH_2CH_2 - SCOCH_3$, 36], 517 [$(M + H)^+ - CH_3 - C_5H_9SO$, 12].

Acknowledgements

This work was supported by grants from the Deutsche Forschungsgemeinschaft (Se543/5-1 and Heisenberg fellowship /3-2) and the Fonds der Chemischen Industrie. We also acknowledge a gift of chemicals from Schering AG (Berlin).

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