Direct Amination of *meso*-Tetraarylporphyrin Derivatives – Easy Route to A_3B-, A_2BC-, and A_2B_2-Type Porphyrins Bearing Two Nitrogen-Containing Substituents at the *meso*-Positioned Phenyl Groups

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meso-Tetraarylporphyrinato complexes **1a**–**g** (Zn^{II}, Cu^{II}, and Ni^{II}) bearing one or two nitro-substituted aryl moieties react with 1,1,1-trimethylhydrazinium iodide in the presence of ^{t}BuOK in THF at 0–5° or in the presence of KOH in DMSO at 60–70° according to a nucleophilic substitution of an H-atom, thus affording porphyrins **2a**–**g** and **3f**,**g** with amino-functionalized *meso*-positioned aryl substituents in yields up to 73% (*Scheme 1* and *Table*). The products obtained are attractive intermediates for further derivatization of porphyrins and may be of potential use as sensitizers in photodynamic cancer therapy.

Introduction. – The selective derivatization of easily available *meso*-tetraarylporphyrins (= 5,10,15,20-tetraaryl-21*H*,23*H*-porphines) is of significant importance due to their potential use as photosensitizers in photodynamic therapy [1], molecular-based multi-bit memory storage [2], bis-faced substituted building blocks [3], and electron-donor parts in artificial photosynthetic models [4].

In the past decade, much attention has been focused on the preparation of well-defined 5,10,15,20-tetraarylporphyrin derivatives, substituted by various aryl groups. Finally, a fully controlled stepwise cyclocondensation process was achieved, and a large spectrum of the desired porphyrins was synthesized, from the A_4-type to the ABCD-type (A,B,C,D = different aryl groups) [5]. However, in some cases, a serious limitation of this methodology is a low total yield of the final product.

An alternative route to this type of compounds is an easy straightforward synthesis of symmetrical *meso*-tetraarylporphyrins followed by selective derivatization of their aryl substituents. In this approach, the synthesis is usually limited to the introduction of one type of substituent into either one or into all four *meso*-positioned aryl substituents[1]). An additional possibility could be the manipulation of the already existing groups by their transformation or replacement by other ones (*e.g.*, *via* an aromatic nucleophilic substitution (S_NAr) [7]).

We have recently extended this latter methodology to the introduction, in a fully controlled processes, of up to 10 various substituents in *meso*-positioned aryl groups [8]. This allows the preparation of highly substituted Cl-, N-, O-, and C-substituted synthetic porphyrins.

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[1]) For nitration, see [6a–c]; for sulfonation, see [6d,e]; for chlorosulfonation, see [6f]; for deuteration, see [6g]; for alkylation, see [6h].

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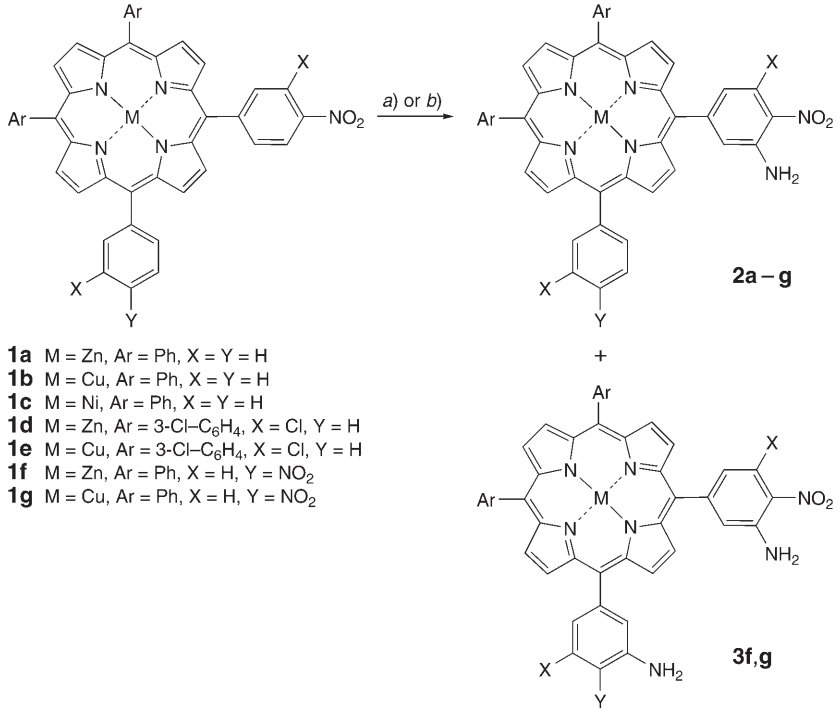
In continuation of our studies in this field, we were also planning to investigate the introduction of the very attractive amino group. It is known from the recent literature that the presence of a nitro group in an aromatic ring gives an opportunity for further amination of the system by the so-called 'vicarious nucleophilic substitution of hydrogen' (VNS) [9] (for a review, see [9d]). The products of such a reaction in porphyrin systems could be very versatile intermediates because porphyrins bearing water-solubilizing groups, such as $-NMe_3^+$, exhibit increased photodynamic efficacy [10]. On the other hand, nitro-substituted aromatic moieties have been found to be effective electron-affinity radiosensitizers [11].

Results and Discussion. – We present herein a direct amination of *meso*-tetraarylporphyrinato complexes (Zn^{II}, Cu^{II}, Ni^{II}) bearing NO_2-substituted aryl groups by VNS with the use of 1,1,1-trimethylhydrazinium anion as nucleophilic amino species. It was found that the reaction of [5-(4-nitrophenyl)-10,15,20-triphenylporphyrinato]-zinc(II) complex **1a** with 1,1,1-trimethylhydrazinium iodide (TMHI) in the ^{t}BuOK/THF system at 0–5° (*Procedure A*) led to the product **2a** by nucleophilic substitution of a H-atom in the yield of 45% (*Scheme 1*, *Table*). Similar results were obtained for copper and nickel complexes (formation of **2b** and **2c** in 40 and 51% yield, resp.). The main product in the reactions of the Zn^{II} and Cu^{II} complexes **1a**,**b** was accompanied by

Scheme 1. *Direct Amination of* meso-*Tetraarylporphyrinato Chelates*



1a M = Zn, Ar = Ph, X = Y = H
1b M = Cu, Ar = Ph, X = Y = H
1c M = Ni, Ar = Ph, X = Y = H
1d M = Zn, Ar = 3-Cl–C_6H_4, X = Cl, Y = H
1e M = Cu, Ar = 3-Cl–C_6H_4, X = Cl, Y = H
1f M = Zn, Ar = Ph, X = H, Y = NO_2
1g M = Cu, Ar = Ph, X = H, Y = NO_2

a) *Procedure A*: 1. $H_2N-NMe_3^+$, ^{t}BuOK, THF, 0–5°, 6–8 h; 2. H^+. *b*) *Procedure B*: 1. $H_2N-NMe_3^+$, KOH, DMSO, 60–70°, 8–10 h; 2. H^+.

Table. *Products and Yields of the Amination of* meso-*Tetraarylporphyrin Derivatives*

Starting porphyrin	*Procedure*	Products (yield [%])			Total yield [%]
		2	**3**	Others	
1a	*A*	**2a** (45)		**4a** (4)	49
	B	**2a** (66)			66
1b	*A*	**2b** (40)		**4b** (16)	56
	B	**2b** (63)			63
1c	*A*	**2c** (51)			51
	B	**2c** (13)			13
1d	*A*	**2d** (27)		**8** (19)	46
	B	**2d** (11)		**8** (22)	33
1e	*A*	**2e** (41)			41
	B	**2e** (< 1)			< 1
1f	*A*	**2f** (16)	**3f** (5)	**9** (12)[a])	33
	B	**2f** (18)	**3f** (55)		73
1g	*A*	**2g** (15)		[b])	15
	B	**2g** (19)	**3g** (49)		68

[a]) Traces of **10** were detected. [b]) Traces of **11** were detected.

small amounts of a by-product, in which one phenyl group is substituted by a *tert*-butoxy and an amino group. For these by-products, the structures **4a** and **4b** were assigned (*Figure*).

Formation of compounds **4a**,**b** can be explained by oxidative nucleophilic substitution of a H-atom by the ^{t}BuO$^-$ anion ($\rightarrow$ **5**; ONSH process [12]) followed by reduction of the nitro to the amino group (*Scheme 2*). It can take place as an intramolecular or intermolecular red-ox process. In the latter, the σ^H-adduct **5** could be oxidized by O_2 or by the NO_2 group of another molecule. The intramolecular transformation is more likely in this case (*Path A*, *Scheme 2*) because we always observed a ^{t}BuO-substituted product bearing concomitantly a NH_2 group at the same ring, and we never could isolate a corresponding ^{t}BuO/NO_2-substituted intermediate from the post-reaction mixtures. The alternative reaction course (amination of **1a**,**b** to **6**, then S_NAr substitution of the NO_2 group by the ^{t}BuO$^-$ anion) should lead to the possible product **7** with the inverted substitution pattern of these groups. However, the NH_2 substituent strongly deactivates the *ortho*-position for S_NAr replacement. Thus, this pathway was *a priori* excluded from the consideration (*Path C*).

The heterogeneous KOH/DMSO system at 60–70° (*Procedure B*) was also successfully applied to the amination process **1** $\rightarrow$ **2** and gave, in most of the investigated instances, higher yields of **2** and better selectivity (see *Table*). Thus we never observed the ONSH by-products of type **4**.

In the case of a 3-chloro-4-nitro-substituted aryl group of the porphyrin moiety (substrate **1d**), the reaction partially took a different course, and a considerable amount of S_NAr compound was isolated as a by-product. For the product obtained from **1d**, on the basis of the MS ($[M+H]^+$ at m/z 839; isotope pattern in accord with the expected one) and ^{1}H-NMR investigations, structure **8** was proposed (*Fig*). This mode of reactivity can be rationalized by the strong NO_2 activation of the *ortho*-Cl substituent

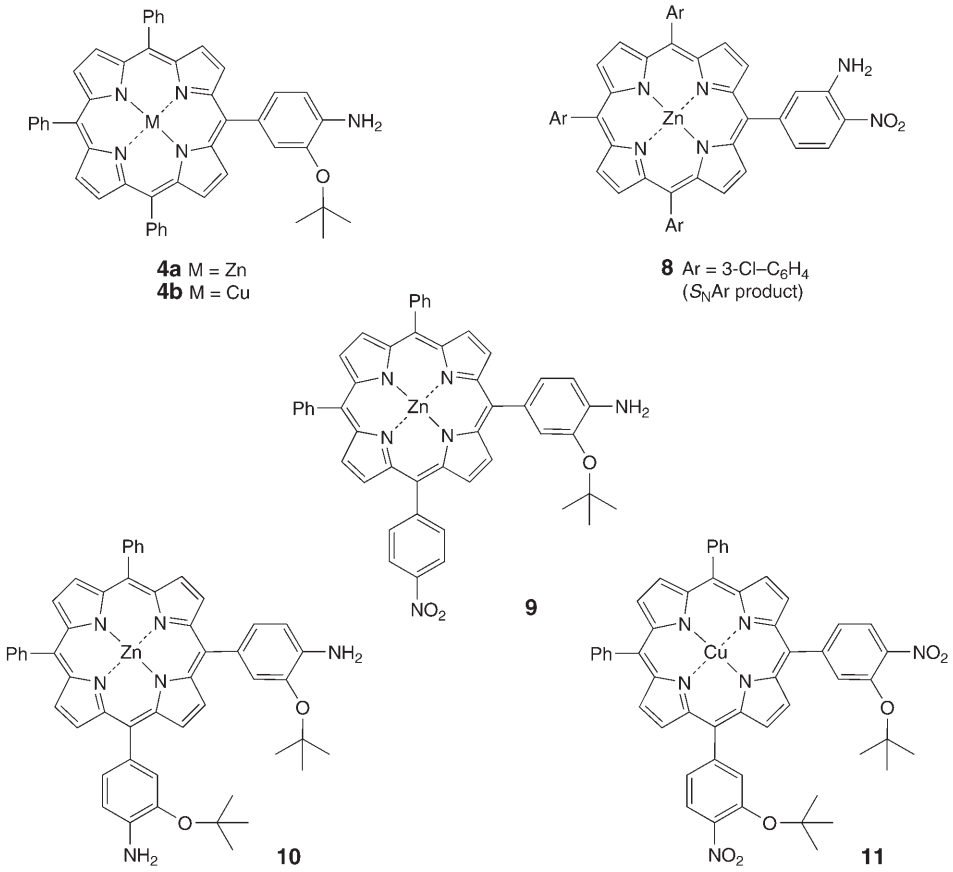


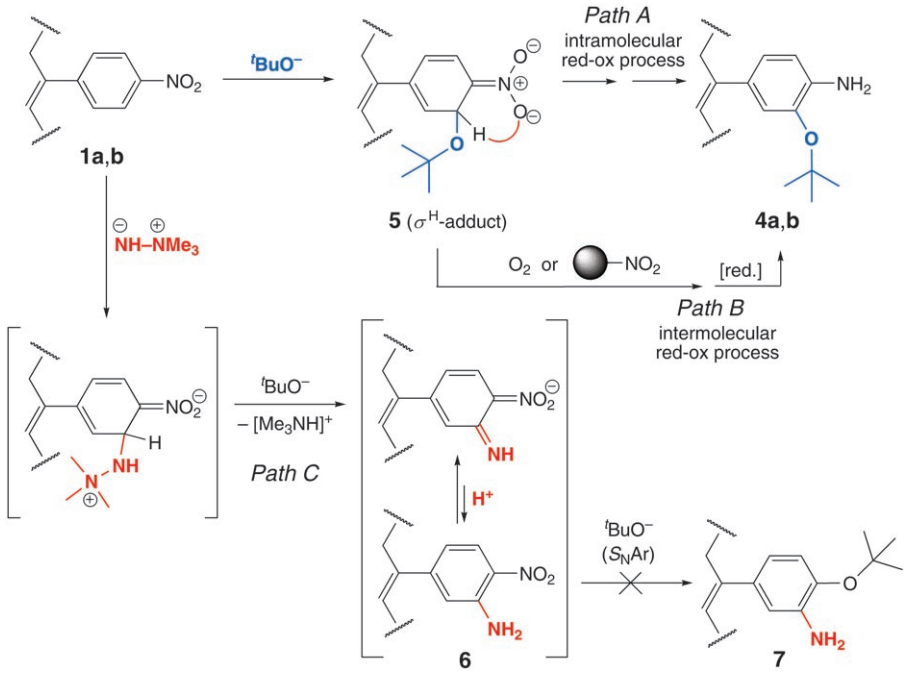
Figure. *Other products*

for an S_NAr process (herein, substitution by the hydrazinium anion). However, the subsequent conversion of the $NHNMe_3^+$ group into NH_2 is rather a more complicated process.

The dinitro-substituted porphyrins **1f** and **1g** can lead to mono-amination (→ **2f**,**g**), as well as to bis-amination (→ **3f**,**g**). However, the preferences for substitution in both rings is more pronounced with the KOH/DMSO system at 60–70°, thus affording the dinitro diamino derivatives **3f**,**g**.

On the other hand, with the *t*BuOK/THF system at 0–5°, in the reaction of [5,10-bis(4-nitrophenyl)-15,20-diphenylporphyrinato]zinc(II) complex **1f**, the formation of small amounts of the 'ONSH/reduction' product **9** was observed (12%). Additionally, traces of the disubstituted 'ONSH/reduction' compound **10** were identified in the post-reaction mixture (ESI-MS: $[M+H]^+$ at *m*/*z* 851). Under the same reaction conditions, **1g** yielded a small amount (< 5%) of compound **11** as by-product, which was observed in the crude post-reaction mixture (MS: M^+ at *m*/*z* 909).

Scheme 2. *Alternative Substitution–Reduction Pathways of* **1a** *and* **1b**



Conclusions. – We have described a method for the direct amination of tetraarylporphyrins in their nitro-substituted *meso*-positioned aryl groups. The type of products obtained demonstrate the general character of the presented methodology. It allows the synthesis of porphyrins bearing two *N*-substituents at the same aryl group, which are potentially attractive and versatile intermediates for the further derivatization of porphyrins designed as photosensitizers in photodynamic therapy.

Moreover, as the syntheses of A_3B, A_2BC, and A_2B_2-type *meso*-tetraarylporphyrins (A,B,C = different aryl groups) are possible the method may well receive future attention in the area of porphyrin skeleton modifications.

Experimental Part

1. *General*. The nitroporphyrinato complexes **1a**, **1b**, and **1f** were obtained in 89, 92, and 40% yield, resp., from 5-(4-nitrophenyl)-10,15,20-triphenylporphyrin or 5,10-bis(4-nitrophenyl)-15,20-diphenylporphyrin according to procedures described in [13]. The remaining nitroporphyrinato complexes were prepared according to the above procedures with the corresponding inorganic salts ($Zn(OAc)_2 \cdot 2\,H_2O$, $Cu(OAc)_2 \cdot H_2O$, or $Ni(OAc)_2 \cdot 4\,H_2O$); *i.e.*, [5-(4-nitrophenyl)-10,15,20-triphenylporphyrinato]nickel(II) **1c** (40 h, reflux; 70%), [5-(3-chloro-4-nitrophenyl)-10,15,20-tris(3-chlorophenyl)porphyrinato]zinc(II) **1d** (47%), [5-(3-chloro-4-nitrophenyl)-10,15,20-tris(3-chlorophenyl)porphyrinato]copper(II) **1e** (62%), and [5,10-bis(4-nitrophenyl)-15,20-diphenylporphyrinato]copper(II) **1g** (39%). The 1,1,1-trimethylhydrazinium iodide (TMHI) was prepared in 87% yield from commercially available 1,1-dimethylhydrazine (*Sigma-Aldrich*) by alkylation with MeI in CH_2Cl_2. TLC: aluminium-foil plates precoated with silica gel (*60F 254*, *Merck*). Column chromatography (CC): silica gel 230–400 mesh (*Merck*

AG). UV/VIS Spectra: *Beckman DU-68* spectrophotometer; in λ_{max} (log ε). ^{1}H-NMR Spectra: *Varian Gemini-2000BB* spectrometer, at 200 MHz; chemical shifts δ in ppm rel. to $CHCl_3$ (= 7.26 ppm); coupling constants *J* in Hz. MS: *Mariner* (*PerSeptive Biosystems*) spectrometer in the ESI-TOF mode; in *m*/*z* (rel. int. %).

2. *Data of* **1c**–**g**. *[5-(4-Nitrophenyl)-10,15,20-triphenyl-21*H,*23*H-*porphinato(2 –)-*κN^{21},κN^{22},κN^{23},κN^{24}*]nickel* (**1c**). M.p. > 300°. UV/VIS ($CHCl_3$): 529.0 (4.32), 414.0 (5.38, *Soret* band), 324.5 (4.13). ^{1}H-NMR (200 MHz, $CDCl_3$): 8.79 (*d*, *J* = 5.0, 2 H$^{\beta}$ (pyr)); 8.76 (*s*, 4 H$^{\beta}$ (pyr)); 8.62 (*d*, *J* = 5.0, 2 H$^{\beta}$ (pyr)); 8.56, 8.20 (*AA′XX′*, $NO_2C_6H_4$); 8.05–7.96 (*m*, 6 arom. H); 7.78–7.61 (*m*, 9 arom. H). ESI-MS: 721 (4), 720 (5), 719 (10), 718 (25), 717 (60), 716 (100), 715 (34) (isotope M^+ and $[M + H]^+$). HR-ESI-MS: 715.1541 (M^+, $C_{44}H_{27}N_5NiO_2^+$; calc. 715.1518).

*[5-(3-Chloro-4-nitrophenyl)-10,15,20-tris(3-chlorophenyl)-21*H,*23*H-*porphinato(2 –)-*κN^{21},κN^{22},κN^{23},κN^{24}*]zinc* (**1d**). M.p. > 300°. UV/VIS ($CHCl_3$): 585.0 (3.56), 547.5 (4.45), 510.0 (3.63), 419.5 (5.67, *Soret* band), 348.0 (4.16), 310.5 (4.29). ^{1}H-NMR (200 MHz, $CDCl_3$): 8.99 (*d*, *J* = 4.7, 1 H$^{\beta}$ (pyr)); 8.96 (*s*, 4 H$^{\beta}$ (pyr)); 8.95–8.81 (*m*, 2 H$^{\beta}$ (pyr)); 8.88 (*d*, *J* = 4.7, 1 H$^{\beta}$ (pyr)); 8.43 (*d*, *J* = 1.5, H–C(2) of $NO_2C_6H_3(Cl)$); 8.31 (part of *AB*, *J* = 8.1, H–C(5) of $NO_2C_6H_3(Cl)$); 8.27 (part of *AB* coupled with another proton, *J* = 8.1, 1.5, H–C(6) of $NO_2C_6H_3(Cl)$); 8.21 (br. *s*, H–C(2) of 3 ClC_6H_4); 8.11 (*d*, *J* = 7.1, 3 H of 3 ClC_6H_4); 7.86–7.63 (*m*, 6 H of 3 ClC_6H_4). ESI-MS: 868 (3), 867 (6), 866 (10), 865 (24), 864 (31), 863 (58), 862 (58), 861 (100), 860 (52), 859 (91), 858 (24), 857 (47) (isotope M^+). HR-ESI-MS: 856.9875 (M^+, $C_{44}H_{23}Cl_4N_5O_2Zn^+$; calc. 856.9897).

*[5-(3-Chloro-4-nitrophenyl)-10,15,20-tris(3-chlorophenyl)-21*H,*23*H-*porphinato(2 –)-*κN^{21},κN^{22},κN^{23},κN^{24}*]copper* (**1e**). M.p. > 300°. UV/VIS ($CHCl_3$): 572.0 (3.31), 539.5 (4.20), 499.5 (3.39), 415.5 (5.48, *Soret* band). ESI-MS: 865 (3), 864 (8), 863 (14), 862 (29), 861 (34), 860 (75), 859 (59), 858 (100), 857 (27), 856 (57) (isotope M^+). HR-ESI-MS: 855.9925 (M^+, $C_{44}H_{23}Cl_4CuN_5O_2^+$; calc. 855.9902).

*[5,10-Bis(4-nitrophenyl)-15,20-diphenyl-21*H,*23*H-*porphinato(2 –)-*κN^{21},κN^{22},κN^{23},κN^{24}*]zinc* (**1f**). M.p. > 300°. UV/VIS ($CHCl_3$): 588.0 (3.70), 548.5 (4.42), 511.0 (3.61), 421.0 (5.49, *Soret* band), 349.0 (4.12). ^{1}H-NMR (200 MHz, $CDCl_3$): 9.07–8.77 (*m*, 8 H$^{\beta}$ (pyr)); *ca.* 8.65 and 8.41 (*AA′XX′*, 2 $NO_2C_6H_4$); 8.28–8.10 (*m*, 4 arom. H); 7.88–7.66 (*m*, 6 arom. H). ESI-MS: 773 (5), 772 (11), 771 (30), 770 (51), 769 (49), 768 (74), 767 (58), 766 (100) (isotope M^+). HR-ESI-MS: 766.1296 (M^+, $C_{44}H_{26}N_6O_4Zn^+$; calc. 766.1307).

*[5,10-Bis(4-nitrophenyl)-15,20-diphenyl-21*H,*23*H-*porphinato(2 –)-*κN^{21},κN^{22},κN^{23},κN^{24}*]copper* (**1g**). M.p. > 300°. UV/VIS ($CHCl_3$): 576.0 (4.04), 540.5 (4.79), 501.5 (4.08), 418.5 (5.75, *Soret* band). ESI-MS: 769 (13), 768 (37), 767 (68), 766 (62), 765 (100) (isotope M^+). HR-ESI-MS: 765.1275 (M^+, $C_{44}H_{26}CuN_6O_4$; calc. 765.1312).

3. *Amination of Porphyrin Derivatives. Procedure A* (^{t}BuOK/THF system). To a stirred soln. of ^{t}BuOK (16.8 mg, 0.15 mmol) in anh. THF (0.5 ml), a soln. of 5,10,15,20-tetraarylporphyrinato complex **1** (0.03 mmol) and 1,1,1-trimethylhydrazinium iodide (TMHI; 18.2 mg, 0.09 mmol) in THF (0.5 ml) was added dropwise at 0–5° within 10 min, and the mixture was stirred under Ar in a light-shielded flask. Upon addition of the reagents, the soln. immediately changed from red to deep-green (Zn^{II} complexes) or to red-orange (Cu^{II} and Ni^{II} complexes). After 2 h of stirring, new portions of ^{t}BuOK (10.1 mg, 0.09 mmol) and TMHI (12.1 mg, 0.06 mmol) were added. After an additional 2 h of stirring, another portion of ^{t}BuOK (6.7 mg, 0.06 mmol) and TMHI (6.1 mg, 0.03 mmol) was added. The reaction was continued for 2–4 h, and then the mixture was poured into 3% aq. HCl soln. containing ice (10 ml). The acidified soln. was extracted with $CHCl_3$ (5 × 10 ml), the combined org. layer washed with H_2O (3 × 50 ml), dried (Na_2SO_4), and evaporated, and the residue subjected to CC ($CHCl_3$/hexane 2:1, then 3:1, then $CHCl_3$) to give the desired product (for yields, see *Table*).

Procedure B (KOH/DMSO system). To a vigorously stirred suspension of powdered KOH (77.3 mg, 1.38 mmol) and porphyrinato complex **1** (0.069 mmol) in anh. DMSO (1 ml) in a light-shielded flask, TMHI (42.4 mg, 0.21 mmol) was added at 60–70° under Ar. Upon addition of TMHI, the odor of Me_3N was noted. After 4 h of stirring at 60–70°, additional portions of KOH (38.1 mg, 0.68 mmol) and TMHI (14.1 mg, 0.07 mmol) were added. The reaction was continued for 4–6 h, and then the mixture was poured into 3% aq. HCl soln. containing ice (30 ml) and worked up as described for *Procedure A*.

4. *Data of Products. [5-(3-Amino-4-nitrophenyl)-10,15,20-triphenyl-21*H,*23*H-*porphinato(2 –)-*κN^{21},κN^{22},κN^{23},κN^{24}*]zinc* (**2a**). M.p. > 300°. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.98, 8.96 (2*s* (atypical),

8 H^{β} (pyr)); 8.45 (*d*, *J* = 8.7, H–C(5) of $NO_2C_6H_3(NH_2)$); 8.26–8.17 (*m*, 6 arom. H); 7.82–7.72 (*m*, 9 arom. H); 7.62 (*dd*, *J* = 8.7, 1.7, H–C(6) of $NO_2C_6H_3(NH_2)$); 7.55 (*d*, *J* = 1.7, H–C(2) of $NO_2C_6H_3(NH_2)$); 6.15 (br. *s*, NH_2). ^{1}H-NMR (200 MHz, (D_6)DMSO): 8.95 (*d*, *J* = 4.8 (typical), 2 H^{β} (pyr)); 8.80 (*d*, *J* = 4.8 (typical), 2 H^{β} (pyr)); 8.79 (*s* (typical), 4 H^{β} (pyr)); 8.34 (*d*, *J* = 8.7, H–C(5) of $NO_2C_6H_3(NH_2)$); 8.25–8.14 (*m*, 6 arom. H); 7.90–7.72 (*m*, H–C(2) of $NO_2C_6H_3(NH_2)$, 9 arom. H); 7.49 (*dd*, *J* = 8.7, 1.7, H–C(6) of $NO_2C_6H_3(NH_2)$); NH_2 undetected. For UV/VIS, MS, and HR-MS, see [14].

*5-(3-Amino-4-nitrophenyl)-10,15,20-triphenyl-21*H,*23*H-*porphinato(2–)-*κN^{21},κN^{22},κN^{23},κN^{24}*]copper* (**2b**). M.p. >300°. UV/VIS ($CHCl_3$): 572.0 (3.83), 540.0 (4.66), 501.5 (3.94), 423.5 (5.45, *Soret* band). ESI-MS: 739 (4), 738 (20), 737 (49), 736 (50), 735 (100) (isotope M^+). HR-ESI-MS: 735.1592 (M^+, $C_{44}H_{28}CuN_6O_2^+$; calc. 735.1570).

*[5-(3-Amino-4-nitrophenyl)-10,15,20-triphenyl-21*H,*23*H-*porphinato(2–)-*κN^{21},κN^{22},κN^{23},κN^{24}*]nickel* (**2c**). M.p. >300°. UV/VIS ($CHCl_3$): 555.5 (3.85), 530.0 (4.32), 416.5 (5.35, *Soret* band). ^{1}H-NMR (200 MHz, $CDCl_3$): 8.78 (*s*, 4 H^{β} (pyr)); 8.75 (*s*, 4 H^{β} (pyr)); 8.42 (*d*, *J* = 8.6, H–C(5) of $NO_2C_6H_3(NH_2)$); 8.05–7.95 (*m*, 6 arom. H); 7.74–7.62 (*m*, 9 arom. H); 7.45 (*dd*, *J* = 8.6, 1.8, H–C(6) of $NO_2C_6H_3(NH_2)$); 7.40 (*d*, *J* = 1.8, H–C(2) of $NO_2C_6H_3(NH_2)$); 6.28 (br. *s*, NH_2). ESI-MS: 737 (3), 736 (4), 735 (6), 734 (10), 733 (24), 732 (53), 731 (54), 730 (100) (isotope M^+). HR-ESI-MS: 730.1641 (M^+, $C_{44}H_{28}N_6NiO_2^+$; calc. 730.1627).

*[5-(3-Amino-5-chloro-4-nitrophenyl)-10,15,20-tris(3-chlorophenyl)-21*H,*23*H-*porphinato(2–)-*κN^{21},κN^{22},κN^{23},κN^{24}*]zinc* (**2d**). M.p. >300°. UV/VIS ($CHCl_3$): 582.5 (3.67), 548.0 (4.60), 510.0 (3.77), 420.0 (5.83, *Soret* band), 347.5 (4.32), 311.0 (4.40). ^{1}H-NMR (200 MHz, $CDCl_3$): 9.02–8.81 (*m*, 8 H^{β} (pyr)); 8.30–8.02, 7.86–7.61 (2*m*, 12 H of 3 ClC_6H_4, 2 H of $NO_2C_6H_2(Cl)(NH_2)$); 5.37 (br. *s*, NH_2). ESI-MS: 883 (5), 882 (7), 881 (15), 880 (30), 879 (34), 878 (63), 877 (62), 876 (100), 875 (67), 874 (95), 873 (35), 872 (50) (isotope M^+). HR-ESI-MS: 872.0006 (M^+, $C_{44}H_{24}Cl_4N_6O_2Zn^+$; calc. 872.0006).

*[5-(3-Amino-5-chloro-4-nitrophenyl)-10,15,20-tris(3-chlorophenyl)-21*H,*23*H-*porphinato(2–)-*κN^{21},κN^{22},κN^{23},κN^{24}*]copper* (**2e**). M.p. >300°. UV/VIS ($CHCl_3$): 570.0 (3.66), 539.5 (4.50), 499.5 (3.75), 416.0 (5.84, *Soret* band), 309.0 (4.13). ESI-MS: 881 (2), 880 (4), 879 (6), 878 (12), 877 (27), 876 (34), 875 (83), 874 (54), 873 (100), 872 (29), 871 (47) (isotope M^+). HR-ESI-MS: 871.0064 (M^+, $C_{44}H_{24}Cl_4CuN_6O_2^+$; calc. 871.0011).

*5-(3-Amino-4-nitrophenyl)-10-(4-nitrophenyl)-15,20-diphenyl-21*H,*23*H-*porphinato(2–)-*κN^{21},κN^{22},κN^{23},κN^{24}*]zinc* (**2f**). M.p. >300°. UV/VIS ($CHCl_3$): 587.0 (3.84), 549.0 (4.60), 513.0 (3.78), 421.5 (5.70, *Soret* band), 350.0 (4.36). ^{1}H-NMR (200 MHz, $CDCl_3$): 9.00 (*d*, *J* = 4.7, 1 H^{β} (pyr)); 8.98–8.93 (*m*, 3 H^{β} (pyr)); 8.91 (*d*, *J* = 4.9, 1 H^{β} (pyr)); 8.88–8.81 (*m*, 3 H^{β} (pyr)); 8.69–8.57 (*m*, 2 H of $NO_2C_6H_4$); 8.47–8.35 (*m*, 2 H of $NO_2C_6H_4$); 8.31 (*d*, *J* = 8.8, H–C(5) of $NO_2C_6H_3(NH_2)$); 8.28–8.12 (*m*, 4 arom. H); 7.86–7.69 (*m*, H–C(2) of $NO_2C_6H_3(NH_2)$, 6 arom. H); 7.56 (*dd*, *J* = 8.8, 1.7, H–C(6) of $NO_2C_6H_3(NH_2)$); 5.27 (br. *s*, NH_2). ESI-MS: 788 (3), 787 (8), 786 (19), 785 (45), 784 (39), 783 (76), 782 (51), 781 (100) (isotope M^+). HR-ESI-MS: 781.1409 (M^+, $C_{44}H_{27}N_7O_4Zn^+$; calc. 781.1416).

*[5-(3-Amino-4-nitrophenyl)-10-(4-nitrophenyl)-15,20-diphenyl-21*H,*23*H-*porphinato(2–)-*κN^{21},κN^{22},κN^{23},κN^{24}*]copper* (**2g**). M.p. >300°. UV/VIS ($CHCl_3$): 569.5 (3.94), 535.5 (4.72), 500.0 (3.99), 418.5 (5.48, *Soret* band). ESI-MS: 784 (8), 783 (32), 782 (54), 781 (58), 780 (100) (isotope M^+). HR-ESI-MS: 780.1483 (M^+, $C_{44}H_{27}CuN_7O_4^+$; calc. 780.1421).

*[5,10-Bis(3-amino-4-nitrophenyl)-15,20-diphenyl-21*H,*23*H-*porphinato(2–)-*κN^{21},κN^{22},κN^{23},κN^{24}*]zinc* (**3f**). M.p. >300°. UV/VIS ($CHCl_3$): 587.5 (3.76), 548.5 (4.52), 510.5 (3.71), 422.5 (5.64, *Soret* band), 354.5 (4.33). ^{1}H-NMR (200 MHz, $CDCl_3$): 9.01–8.79 (*m*, 8 H^{β} (pyr)); 8.34–8.13 (*m*, H–(5) of 2 $NO_2C_6H_3(NH_2)$, 4 arom. H); 7.85–7.67 (*m*, H–C(2) of 2 $NO_2C_6H_3(NH_2)$, 6 arom. H); 7.62–7.46 (*m*, H–C(6) of 2 $NO_2C_6H_3(NH_2)$); 5.24, 5.07 (2 br. *s*, 2 NH_2 of atropisomers). ESI-MS: 802 (9), 801 (26), 800 (49), 799 (47), 798 (79), 797 (65), 796 (100) (isotope M^+). HR-ESI-MS: 796.1502 (M^+, $C_{44}H_{28}N_8O_4Zn$; calc. 796.1525).

*[5,10-Bis(3-amino-4-nitrophenyl)-15,20-diphenyl-21*H,*23*H-*porphinato(2–)-*κN^{21},κN^{22},κN^{23},κN^{24}*]copper* (**3g**). M.p. >300°. UV/VIS ($CHCl_3$): 573.5 (3.42), 540.5 (4.27), 500.5 (3.53), 418.5 (5.40, *Soret* band). ESI-MS: 800 (4), 799 (10), 798 (31), 797 (75), 796 (61), 795 (100) (isotope M^+). HR-ESI-MS: 795.1583 (M^+, $C_{44}H_{28}CuN_8O_4^+$; calc. 795.1530).

*{5-[4-Amino-3-(*tert*-butoxy)phenyl]-10,15,20-triphenyl-21*H,*23*H-*porphinato(2–)-*κN^{21},κN^{22},κN^{23},κN^{24}*]zinc* (**4a**). M.p. >300°. UV/VIS ($CHCl_3$): 589.5 (3.48), 549.0 (4.14), 513.0 (3.49), 419.5 (5.42,

Soret band), 347.5 (3.94). ^{1}H-NMR (200 MHz, $CDCl_3$): 8.99, 8.96 (2*s*, 8 H^β (pyr)); 8.28–8.18 (*m*, 6 arom. H); 8.16 (*d*, *J* = 8.2, H–C(5) of ^{t}BuOC$_6$H$_3$(NH$_2$)); 7.89 (*d*, *J* = 1.6, H–C(2) of ^{t}BuOC$_6$H$_3$(NH$_2$)); 7.85–7.72 (*m*, 9 arom. H); 7.71 (*dd*, *J* = 8.2, 1.6, H–C(6) of ^{t}BuOC$_6$H$_3$(NH$_2$)); 1.28 (*s*, ^{t}BuO); NH_2 undetected. ESI-MS: 770 (1), 769 (6), 768 (29), 767 (24), 766 (74), 765 (46), 764 (100) (isotope $[M + H]^+$), 394 (2), 393 (21). HR-ESI-MS: 764.2395 ($[M + H]^+$, $C_{48}H_{38}N_5OZn^+$; calc. 764.2368).

*{5-[4-Amino-3-(*tert*-butoxy)phenyl]-10,15,20-triphenyl-21*H*,23*H*-porphinato(2–)-*κ*N^{21},*κ*N^{22},*κ*N^{23},*κ*N^{24}}copper* (**4b**). M.p. >300°. UV/VIS ($CHCl_3$): 578.0 (3.68), 541.0 (4.37), 414.0 (5.56, *Soret* band). ESI-MS: 768 (4), 767 (10), 766 (29), 765 (59), 764 (64), 763 (100) (isotope $[M + H]^+$), 394 (7), 393 (22), 309 (15). HR-ESI-MS: 763.2316 ($[M + H]^+$, $C_{48}H_{38}CuN_5O^+$; calc. 763.2372).

*{5-(3-Amino-4-nitrophenyl)-10,15,20-tris(3-chlorophenyl)porphinato(2–)-*κ*N^{21},*κ*N^{22},*κ*N^{23},*κ*N^{24}}zinc* (**8**). M.p. >300°. UV/VIS ($CHCl_3$): 587.0 (3.26), 548.0 (4.10), 509.0 (3.27), 419.0 (5.33, *Soret* band), 350.0 (3.86), 309.5 (3.95). ^{1}H-NMR (200 MHz, $CDCl_3$): 8.97 (part of *AB*, *J* = 4.7, 1 H^β (pyr)); 8.97–8.91 (*m*, 7 H^β (pyr)); 8.47 (*d*, *J* = 8.5, H–C(5) of $NO_2C_6H_3(NH_2)$); 8.22 (br. *s*, H–C(2) of 3 ClC_6H_4); 8.11 (*d*, *J* = 7.3, 3 H of 3 ClC_6H_4); 7.99 (*d*, *J* = 1.7, H–C(2) of $NO_2C_6H_3(NH_2)$); 7.87 (*dd*, *J* = 8.5, 1.7, H–C(6) of $NO_2C_6H_3(NH_2)$); 7.84–7.64 (*m*, 6 H of 3 ClC_6H_4); NH_2 undetected. ESI-MS: 849 (6), 848 (10), 847 (18), 846 (25), 845 (45), 844 (47), 843 (82), 842 (56), 841 (100), 840 (28), 839 (41) (isotope $[M + H]^+$). HR-ESI-MS: 839.0439 ($[M + H]^+$, $C_{44}H_{26}Cl_3N_6O_2Zn^+$; calc. 839.0474).

*{5-[4-Amino-3-(*tert*-butoxy)phenyl]-10-(4-nitrophenyl)-15,20-diphenyl-21*H*,23*H*-porphinato(2–)-*κ*N^{21},*κ*N^{22},*κ*N^{23},*κ*N^{24}}zinc* (**9**). M.p. >300°. UV/VIS ($CHCl_3$): 610.5 (3.31), 578.0 (3.72), 541.0 (4.47), 419.5 (5.33, *Soret* band). ^{1}H-NMR (200 MHz, $CDCl_3$): 9.03–8.81 (*m*, 8 H^β (pyr)); 8.69–8.58, 8.49–8.36 (2*m*, $NO_2C_6H_4$); 8.26–8.08 (*m*, H–C(5) of ^{t}BuOC$_6$H$_3$(NH$_2$), 4 arom. H); 7.85–7.51 (*m*, H–C(2) and H–C(6) of ^{t}BuOC$_6$H$_3$(NH$_2$), 6 arom. H); 5.34 (br. *s*, NH_2); 1.25 (*s*, ^{t}BuO). ESI-MS: 816 (14), 815 (19), 814 (48), 813 (66), 812 (62), 811 (100), 810 (80), 809 (94) (isotope $[M + H]^+$). HR-ESI-MS: 809.2280 ($[M + H]^+$, $C_{48}H_{37}N_6O_3Zn^+$; calc. 809.2219).

*{5,10-Bis[4-amino-3-(*tert*-butoxy)phenyl]-15,20-diphenyl-21*H*,23*H*-porphinato(2–)-*κ*N^{21},*κ*N^{22},*κ*N^{23},*κ*N^{24}}zinc* (**10**). Identified in the crude post-reaction mixture by its ESI-MS: 851 (15, $[M + H]^+$).

*{5,10-Bis[3-(*tert*-butoxy)-4-nitrophenyl]-15,20-diphenyl-21*H*,23*H*-porphinato(2–)-*κ*N^{21},*κ*N^{22},*κ*N^{23},*κ*N^{24}}copper* (**11**). Identified in the crude post-reaction mixture by its ESI-MS: 909 (73, M^+).

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