Unsymmetrically Substituted Phthalocyanine Derivatives via a Modified Ring Enlargement Reaction of Unsubstituted Subphthalocyanine

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Chlorosubphthalocyanine (**1**), obtained by an improved synthesis in a yield of 64%, was reacted with the 1,3-diiminoisoindolenines **2** or **3** of 4-*tert*-butylphenoxy-1,2-benzenedicarbonitrile (**6**) and 2,3-naphthalenedicarbonitrile (**7**) according to previously reported conditions of the ring enlargement reaction for the synthesis of monosubstituted phthalocyanines. As proven by DCI-MS and HPLC the product mixtures contain the expected 2-(4-*tert*-butylphenoxy)- and 2,3-dimethylphthalocyanines **4** and **5** as main reaction products. In addition, all other possible substituted phthalocyanines and chlorinated derivatives were found. The yields of monosubstituted phthalocyanine derivatives were improved by reacting the subphthalocyanine **1** with substituted aromatic dicarbonitriles in the presence of zinc(II) acetate. From the reaction of **1** with **6** or 6-*tert*-butyl-2,3-naphthalenedicarbonitrile (**7**) the zinc(II) chelates **4Zn** and **8Zn** were obtained in yields of 22 and 17% after chromatographic separation from unsubstituted and other substituted ring chelates.

Phthalocyanines (Pc) and related macrocycles like naphthalocyanines have found increasing interest as conductors and photoconductors, in photovoltaic and photoelectrochemical devices, as catalysts and photocatalysts and in the photodynamic therapy of cancer.[1,2] Unsubstituted and symmetrically tetra- or octasubstituted phthalocyanines have been employed for these investigations. Recently, monosubstituted phthalocyanines have attracted attention in the field of nonlinear optics, liquid crystalline properties, and thin film formation.[3,4] Monofunctional Pc's with one reactive functional group have the advantage of polymer binding without the disadvantage of crosslinking reactions, and they are, after binding to biomolecules like monoclonal antibodies, an interesting new group of photosensitizers for the photodynamic therapy of cancer (PDT).[5-7] Therefore, it is necessary to find pathways for the synthesis of monosubstituted Pc's. While symmetrical phthalocyanines are easily available by tetramerization of substituted 1,2-benzenedicarbonitriles, the synthesis of pure unsymmetrically substituted Pc's remains a difficult problem. The simplest and most used way is the statistical tetramerization of two different substituted 1,2-benzenedicarbonitriles,[8] always resulting in a mixture of different substituted phthalocyanines. Another way uses the polymer-supported route.[9-11] In addition to a several-step procedure, this route has the main disadvantage that only low amounts can be obtained due to the low capacity of the polymeric carrier.

At the beginning of this decade a new method, the ring enlargement reaction of subphthalocyanines, was described as a very promising route for the preparation of unsymmetrically substituted phthalocyanines.[12-16] Reaction of chloro[7,12;14,19-diimino-21,5-nitrilo-5*H*-tribenzo-[*c*,*h*,*m*][1,16,1]triazacyclopentadecinato-(2-)-N^{22},N^{23},N^{24}]-boron (chloro-SubPc, **1**) with substituted 1,3-diiminoisoindolenines resulted in monosubstituted metal-free phthalocyanines (see Scheme 1) without formation of unsubstituted, di-, tri-, and tetrasubstituted Pc's.[13,14] Chloro-SubPc (**1**) was described first by Meller and Ossko in 1971[17] by trimerization of 1,2-benzenedicarbonitrile in the presence of BCl_3. Tris-(1,1-dimethylethyl)-substituted subphthalocyanines bromo-substituted at the boron are also described.[12,15] A hexakis(hexylthio)-substituted chloro-SubPc was mentioned recently.[16]

Due to our current interest in monosubstituted phthalocyanines we investigated the ring enlargement reaction of unsubstituted chloro-SubPc (**1**) (obtained by an improved synthesis) in more detail. This compound was reacted with two different diiminoisoindolenines or two different dicarbonitriles in the presence of a metal salt. The obtained reaction mixtures were characterized by

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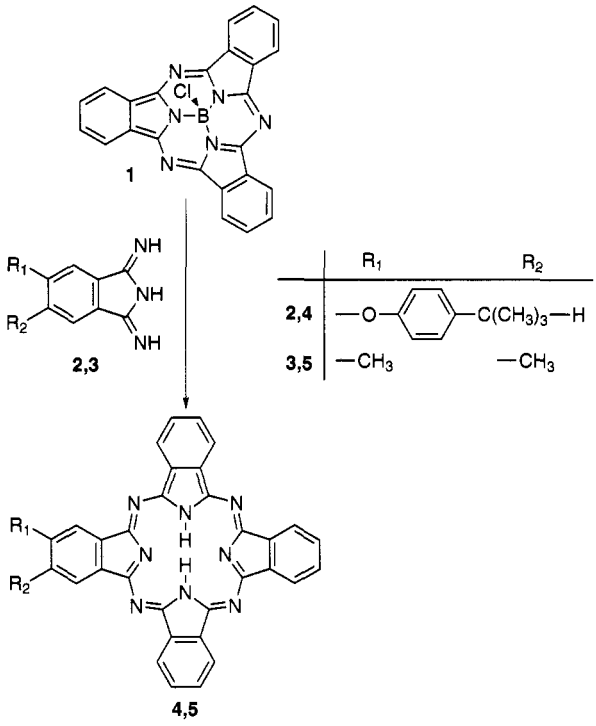
Scheme 1



(and other substituted compounds, see text)

HPLC and DCI-MS. Two new monosubstituted phthalocyaninezinc(II) complexes **4Zn** and **8Zn** were separated from the obtained product mixtures by preparative HPLC.

Results and Discussion

According to the literature,[17] chloro-SubPc (**1**) is synthesized from 1,2-benzenedicarbonitrile after condensing gaseous BCl_3 into the reaction vessel and heating to 250 °C. By employing BCl_3 in *n*-hexane we obtained **1** by an easier procedure in higher yield (64%, literature 40%) (see the Experimental Section). For the synthesis of the diiminoisoindolenines **2** and **3** a known method was used.[18,19]

In analogy to the previously reported general conditions of the ring enlargement reaction,[12-16] SubPc **1** and the diiminoisoindolenines **2** or **3** (molar ratio 2:3) were heated in a mixture of freshly distilled DMSO and 1-chloronaphthalene (2:1 v/v) at 80–90 °C for 24 h, in order to synthesize 2-(4-*tert*-butylphenoxy)phthalocyanine (**4**) and 2,3-dimethylphthalocyanine (**5**) (Scheme 1).

The reaction products were characterized by DCI-mass spectroscopy. The spectra indicate that the reaction products are not the expected pure **4** and **5** but a mixture of unsubstituted, different substituted, and various chlorinated phthalocyanines (see Figure 1 and Experimental Section) whereas in the literature under the same reaction conditions only the formation of pure monosubstituted Pc's was reported.[13,14] This was also described for the ring enlargement employing other subphthalocyanine derivatives.[12,15,16] The presence of chlorinated Pc's is not surprising because **1** also contains ring-chlorinated SubPc's as side products (visible in the MS spectrum) which was already mentioned by Meller and Ossko.[17] Also, in the case of substituted SubPc's, the occurrence of chlorinated side products was reported recently.[20] It was not possible to remove the chlorinated SubPc's by recrystallization or column chromatography. The product mixture obtained from **1** and **2** was metalated (in DMF with an excess of zinc(II) acetate dihydrate at 40 °C for 24 h) to the corresponding zinc compounds and then investigated by HPLC analysis in order to determine the amount of the different compounds. The metalation was necessary because the metal-free phthalocyanines show low solubility in common organic solvents. The chromatography was carried out in toluene/DMF (98:2) on silica Si 60. The peaks 1, 4, and 6 of the HPLC diagram (Figure 2) were identified as tetra(*tert*-butylphenoxy)-ZnPc,[21] monosubstituted **4Zn**, and unsubstituted ZnPc by comparing their retention times with those of the pure compounds and by MS spectroscopy. As seen from the mass spectra of the isolated fraction of analytical HPLC peaks 2 and 3 contain tri- and disubstituted ZnPc's and chlorinated side products and peak 5 contains different chlorinated unsubstituted ZnPc. The percentage of each compound in the mixture can be estimated from the peak areas. Taking the following extinction coefficients the composition of the product mixture was calculated as listed in Table 1 (ZnPc 3.84×10^4 ϵ/dm^3 mol^{-1} cm^{-1}, monosubstituted **4Zn** 5.58×10^4 ϵ/dm^3 mol^{-1} cm^{-1}, and tetrasubstituted ZnPc 6.32×10^4 ϵ/dm^3 mol^{-1} cm^{-1} (all extinctions were measured at 350 nm in toluene/DMF (98:2). The extinction coefficients of di- and trisubstituted ZnPc were calculated to approximately 5.8×10^4 and 6.1×10^4 ϵ/dm^3 mol^{-1} cm^{-1}).

When the results of HPLC (Table 1, Figure 2) with the DCI-MS spectra (Figure 1, Experimental Section) of the product mixture resulting from the reaction of **1** with **2** are compared, DCI mass spectroscopy is seen to be useful for the determination of the approximate composition of the product mixture. Both methods show that the monosubstituted Pc **4** is the main reaction product followed by the unsubstituted Pc and low amounts of various other substituted phthalocyanines. The product mixture from the reaction of **1** with **3** mainly consists of 2,3-dimethylphthalocyanine (**5**) according to the DCI mass spectrum and HPLC analysis, but the unsubstituted Pc and other substituted macrocycles could also be detected (see the Experimental Section).

IR and UV/Vis spectroscopy are not helpful to determine the composition of the product mixtures because they show only mean spectra of all compounds. Elementary analysis was not carried out because the calculated values for the mixture from Table 1 are C = 68.8, H = 3.6, N = 16.1, and O = 1.8. This is close to the calculated values of the pure monosubstituted compound **4Zn** with C = 69.5, H = 3.9 , N = 15.5 and O = 2.2 and very different from those calculated for higher substituted phthalocyanines and ZnPc.

^{1}H-NMR spectroscopy is only partially suitable for the characterization of the product mixtures because peaks are broadened due to aggregation, and therefore, it is difficult to differentiate between the distinct proton groups. Also the ratio of aromatic to methyl protons can appear to show that the mixture consists of the monosubstituted Pc only. For the pure metalated monosub-

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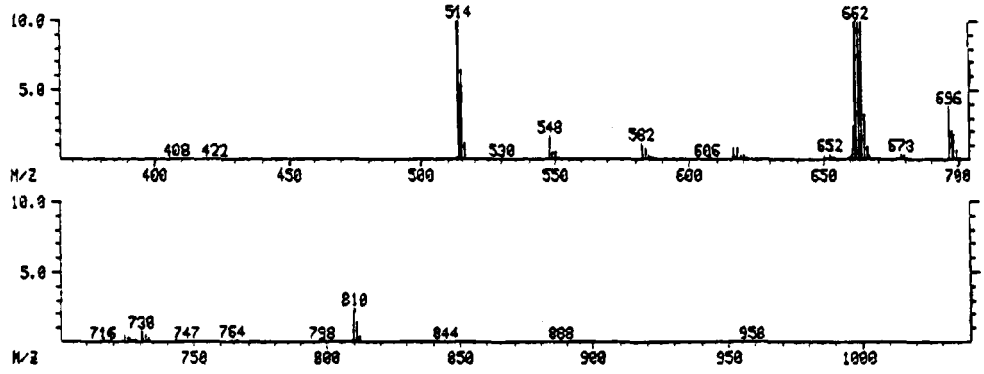

Figure 1. DCI-MS spectrum of the product mixture obtained from the reaction of **1** with **2**, m/z 662 = 100% (for correlation of m/z peaks, see the Experimental Section), 514 m/z = unsubstituted Pc, 548 m/z = unsubstituted Pc + Cl, 662 m/z = monosubstituted Pc **4**, 696 m/z = monosubstituted Pc **4** + Cl, 730 m/z = monosubstituted Pc **4** + 2Cl, 810 m/z = disubstituted Pc, 958 m/z = trisubstituted Pc (for other peaks see the Experimental Section).

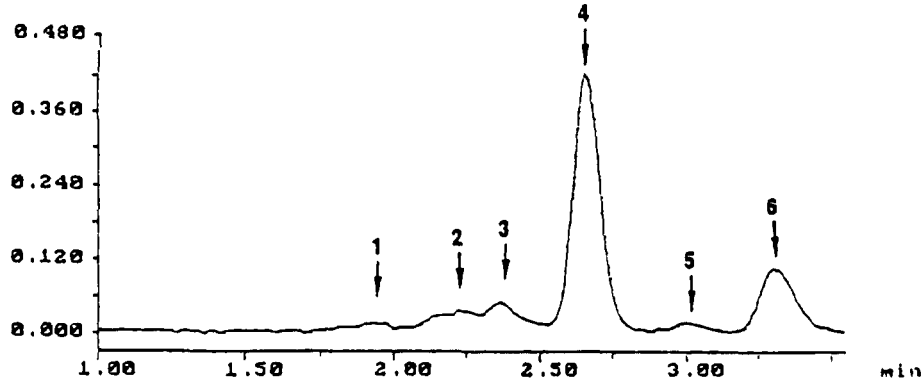

Figure 2. HPLC chromatogram of *tert*-butylphenoxy-substituted zinc phthalocyanines obtained by the ring enlargement reaction with diiminoisoindolenine **2** followed by metalation. Peaks are identified as follows: 1 = tetrasubstituted ZnPc, 2 = trisubstituted ZnPc, 3 = disubstituted ZnPc and chlorinated ZnPc **4**, 4 = monosubstituted ZnPc **4**, 5 = chlorinated unsubstituted ZnPc, 6 = unsubstituted ZnPc.

Table 1. Composition of the Metalated Product Mixture from the Reaction of 1 with 2 According to HPLC Analysis

compd (formula)	mol %	compd (formula)	mol %
tetrasubstituted ZnPc ($C_{72}H_{64}N_8O_4Zn$)	1	monosubstituted 4Zn ($C_{42}H_{28}N_8OZn$)	54
trisubstituted ZnPc ($C_{62}H_{52}N_8O_3Zn$)	6	chlorinated ZnPc ($C_{32}H_{12-15}Cl_{1-4}N_8Zn$)	4
disubstituted ZnPc ($C_{52}H_{40}N_8O_2Zn$)	7	ZnPc ($C_{32}H_{16}N_8Zn$)	28

stituted product **4Zn** the ratio of the aromatic protons to methyl protons is 19:9, and the ratio obtained from the mixtures is 19:8.4. But the presence of more than the expected aromatic signals indicate that the obtained products by the reaction of chloro-SubPc **1** with either **2** or **3** are not the expected pure **4** and **5**.

In order to explain the formation of product mixtures under these reaction conditions several additional experiments were carried out. Under the conditions reported in the literature, **1** (which contains no 1,2-benzenedicarbonitrile as proven by IR, MS, and ^{1}H-NMR spectroscopy) is stable in chloronaphthalene/DMSO at the reaction temperature for ring expansion of 80–90 °C. Chloro-SubPc and 1,2-benzenedicarbonitriles do not react to give phthalocyanines under these reaction conditions. The diiminoisoindolenines **2** or **3** produce only traces (yields < 0.1%) of metal-free tetrasubstituted Pc's only visible in the UV/Vis spectrum. Special care has been taken that the diiminoisoindolenines contain no sodium methanolate or water because this may catalyze phthalocyanine formation. Under the influence of the weak base zinc(II) acetate dihydrate SubPc was converted into unsubstituted ZnPc, whereas no reaction occurs with $ZnCl_2 \cdot H_2O$. All these experiments led to the assumption that SubPc does not undergo a concerted reaction with diiminoisoindolenine but a multistep reaction. The first step is supposed to be a base catalyzed decomposition of SubPc. The second step may be the reaction of the activated fragments with each other or diiminoisoindolenines followed by ring closure to differently substituted Pc's and also polynitriles. Brown-colored polynitriles can be seen in the UV/Vis spectra and can be isolated and characterized as described.[22] Further indications for these suppositions are the low yields of phthalocyanines (8–20% from literature and in the case of the reported compounds only 4–6%) which are not explicable by a concerted ring enlargement reaction.

Bromo-substituted subphthalocyanines as employed for the ring enlargement reaction[12,15] were not investigated in detail but seem to react comparably.

In a new approach, the ring enlargement reaction was carried out in the presence of zinc(II) acetate dihydrate as template in order to provide selectivity for the formation of monosubstituted Pc's and to get metalated Pc's in a one-step procedure. The reaction of SubPc with substituted diiminoisoindolenines in the presence of a zinc salt results in higher percentages of tetrasubstituted Pc's because diiminoisoindolenines undergo cyclotet-

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Scheme 2

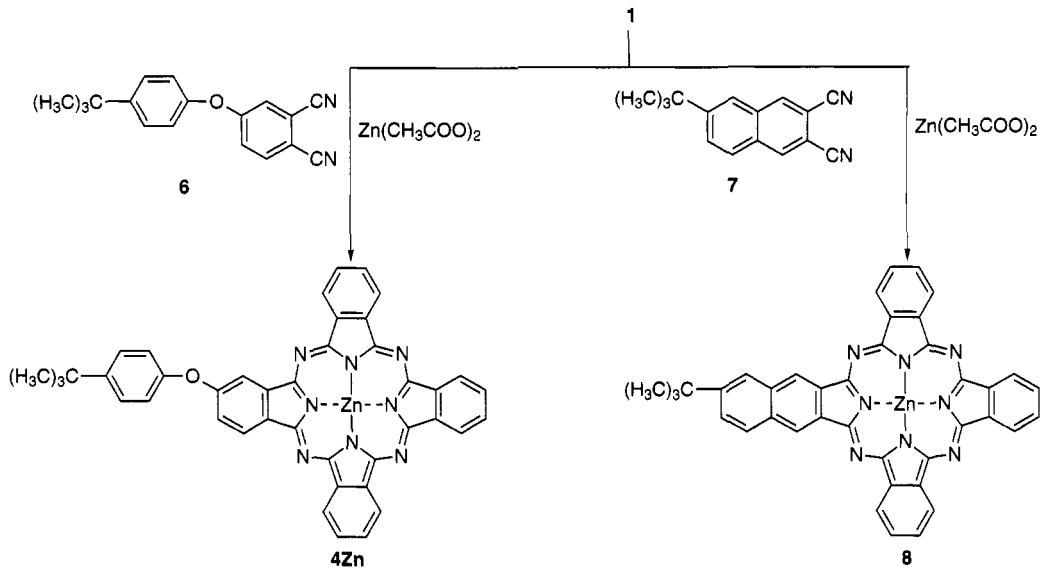

Table 2. Composition (%) of the Product Mixture Obtained from the Reaction of 1 and the Dinitriles 6 or 7 in the Presence of Zinc(II) Acetate According to HPLC

compd	ZnPc	mono-ZnPc	di-ZnPc	tri-ZnPc	tetra-ZnPc	total yield of Pc
4Zn	27	63	8	2	0	40
8Zn	48	45	3	0	0	32

ramerization with the zinc salt. Therefore, the less reactive 1,2-benzenedicarbonitrile **6** was used instead of the diiminoisoindolenine **2** (Scheme 2). The reaction of **1** with **6** and the zinc salt leads to much higher yields of Pc's in total (40%) but also to a relatively high amount of di-, tri-, and tetrasubstituted Pc's. Their formations can be reduced by use of catalytic amounts of DBU and pentanol and higher reaction temperatures because this increased the rate of the ring-opening reaction of **1**. By this procedure we obtained the best yields of the monosubstituted **4Zn** in the product mixture as determined by HPLC (Table 2). The new pathway was also applied to the reaction of 6-*tert*-butyl-2,3-naphthalenedicarbonitrile (**7**) with SubPc. In the case of **7** nearly no higher substituted macrocycles are found because 2,3-naphthalenedinitriles do not react as fast as 1,2-benzenedicarbonitriles in cyclotetramerization reactions. The product mixtures of **4Zn** and **8Zn** were separated by preparative HPLC on silica Si 60. While ^{1}H-NMR spectra (after several chromatographic cycles) indicate that the separated compounds are the pure monosubstituted **4Zn** and **8Zn** (Figure 4), DCI mass spectra show that there are still very small amounts of chlorinated phthalocyanines left (see the mass spectrum of compound **4Zn**, Figure 3). The UV/Vis spectra of compound **4Zn** and **8Zn** are characterized by the typical Q-band transition at 667 nm for **4Zn** and due to the presence of one annelated naphthalene residue at 685–700 nm for **8Zn** (see the supplementary material).

Conclusion

In contrast to previously reported results, we obtained, by the ring enlargement reaction with unsubstituted chlorosubphthalocyanine, different substituted Pc's and unsubstituted Pc which could be separated by analytical and preparative HPLC. The amounts of the monosubstituted compounds in the mixtures were substantially increased by the use of zinc(II) acetate dihydrate with 1,2-benzene- or 2,3-naphthalenedicarbonitriles instead of 1,3-diiminoisoindolenines. As an additional result it has to be pointed out that chlorinated side products which are always formed from chlorinated SubPc's are difficult to separate and remained as impurities even in the samples of monosubstituted ZnPc's purified by HPLC. Traces of chlorinated Pc's may negatively influence the properties of monosubstituted phthalocyanines, in particular, in the case of medical applications like PDT.

Experimental Section

Chloro[7,12;14,19-diimino-21,5-nitrilo-5*H*-tribenzo[*c*,*h*,*m*]-[1,16,1]triazacyclopentadecinato-(2−)-N^{22},N^{23},N^{24}]-boron (SubPc) (1). Dried 1,2-benzenedicarbonitrile (5.0 g, 0.04 mol) was suspended in freshly distilled 1-chloronaphthalene (12 mL) under nitrogen. The suspension was cooled to −3 °C. BCl_3 (20.5 mL, 0.02 mol, 1 M solution in *n*-hexane) was added slowly through an injection syringe to the suspension. The yellowish green solid was heated slowly to 120 °C under vigorous stirring. The color of the liquid changed to black. *n*-Hexane was distilled off, and then heating was continued at 250 °C for 10 min. The color changed to violet. Then the solvent was removed and the resulting violet product was extracted for 24 h with petroleum ether (80–100 °C) and then for 2 h with toluene. The obtained brown product was recrystallized from ethanol and washed with petroleum ether and sublimed at 350 °C to give 3.57 g (64%) of **1** as a brown powder: UV (DMF) λ_{max} 562, 302 nm; IR (KBr) 1692, 1611, 1452, 1384, 1280, 1195, 1130, 950, 878, 753, 695, 629 cm^{-1}; ^{1}H NMR (360 MHz) (DMSO-d_6) δ 8.85 (6H, dd), 7.90 (6H, dd); MS (EI 70 eV, 260 °C) *m*/*z* 464 (M^+ + Cl − H, 4), 431 (M^+, 20), 430 (55), 429 (18), 396 (20), 395 (70), 267 (10), 256 (8), 215 (5), 197.5 (35), 139 (15).

4-*tert*-Butylphenoxy-1,2-benzenedicarbonitrile (**6**),[21] 4,5-dimethyl-1,2-benzenedicarbonitrile,[19] and 6-*tert*-butyl-2,3-naphthalenedicarbonitrile (**8**)[23] were prepared according to the literature. The 5-[4-(1,1-dimethylethyl)phenoxy]-1-imino-1*H*-isoindol-3-amine (**2**)[18] and 1-imino-5,6-dimethyl-1*H*-isoindol-3-amine (**3**)[19] were synthesized from **6** and 4,5-dimethyl-1,2-benzenedicarbonitrile after a known procedure.

Reaction of 1 with 2. **1** (100 mg, 0.23 mmol) and **2** (101 mg, 0.35 mmol) were dissolved in a mixture of DMSO/1-chloronaphthalene (20 mL, 2:1, v/v) and stirred under nitrogen at 80–90 °C for 24 h (according to the literature procedure). The solvent was removed under reduced pressure, and the

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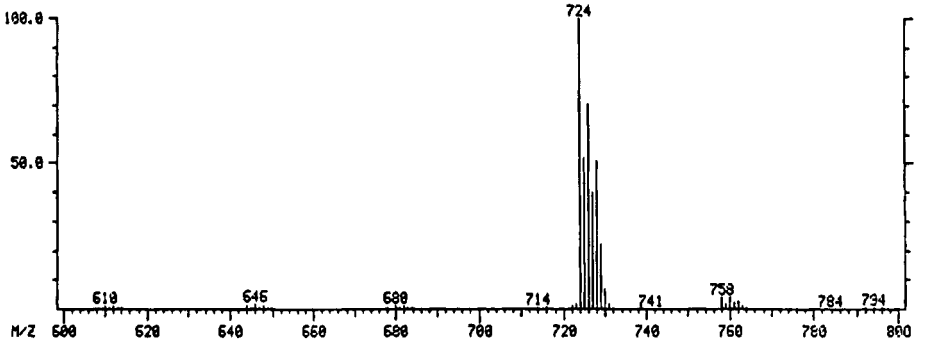

Figure 3. DCI-MS spectrum of **4Zn** purified three times by preparative HPLC.

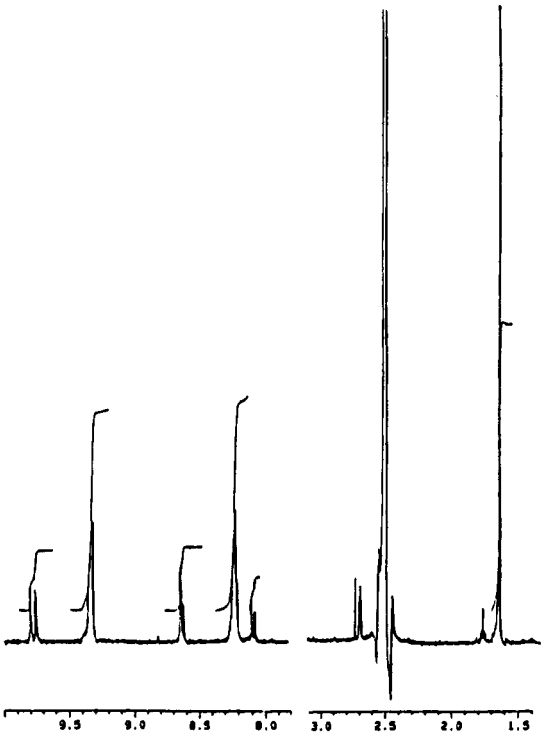

Figure 4. ^{1}H-NMR spectra in DMSO-d_6 of compound **8Zn** purified three times by preparative HPLC.

residue was washed with hot methanol several times: total yield of phthalocyanines 9 mg; UV (DMF) λ_{max} 688, 652, 633, 593, 334 nm; MS (DCI) m/z 958 (<1%, trisubstituted Pc), 844 (<1, disubstituted Pc + Cl), 810 (3, disubstituted Pc), 798 (<1, monosubstituted Pc **4** + 4Cl), 764 (<1, monosubstituted Pc **4** + 3Cl), 730 (1, monosubstituted Pc **4** + 2Cl), 696 (4, monosubstituted Pc **4** + Cl), 662 (100, 2-(4-*tert*-butylphenoxy)-phthalocyanine, **4**), 650 (<1, unsubstituted Pc + 4Cl), 616 (1, unsubstituted Pc + 3Cl), 582 (1, unsubstituted Pc + 2Cl), 548 (2, unsubstituted Pc + Cl), 514 (10, unsubstituted Pc) (see Figure 1).

Reaction of 1 with 3. For synthesis see the reaction of **1** with **2**: UV (DMF) 687, 652, 627, 592, 337 nm; MS (DCI) m/z 626 (1, octamethyl − Pc), 610 (4, dichlorodimethyl − Pc), 598 (5, hexamethyl − Pc), 576 (12, chlorodimethyl − Pc), 570 (5, tetramethyl − Pc), 548 (7, chloro − Pc), 542 (2,3-dimethyl-phthalocyanine **5**, 100), 514 (58, H_2Pc).

2-(4-*tert*-Butylphenoxy)phthalocyanatozinc(II) (4Zn). **6** (0.25 g, 0.92 mmol) was dissolved in a mixture of freshly distilled DMSO/1-chloronaphthalene (4 mL/2 mL), and DBU (0.1 g, 0.65 mmol) was added. The mixture was heated to 130 °C. A suspension of **1** (0.2 g, 0.46 mmol) and zinc(II) acetate dihydrate (0.11 g, 0.5 mmol) in a solvent mixture of DMSO/1-chloronaphthalene/pentan-1-ol (13 mL/6.5 mL/0.5 mL) was added dropwise over a period of 1 h. After the first drops the color of the mixture immediately changed to blue. After cooling, glacial acetic acid (0.04 g,0.65 mmol) was added and the solvents were evaporated nearly to dryness. Afterwards, methanol (50 mL) was added. The product was centrifuged off and purified by flash chromatography with THF/DMF (95:5) on silica Si 60. Total Pc yield was 135 mg (40%). For the product ratios see Table 2. Then the monosubstituted Pc **4Zn** was separated from the mixture by preparative HPLC on silica Si 60 with toluene/DMF (98:2) as eluent (for comparison see analytical HPLC chromatogram Figure 2). The fraction containing the monosubstituted Pc **4Zn** had to be chromatographed three times (each time for recycling cycles) in order to reduce the amount of chlorinated side products. Due to chromatography loss the yield of **4Zn** was reduced to 22%: UV (DMF) λ_{max} 667, 602, 341 nm; IR (KBr) 3085, 2955, 1601, 1485, 1403, 1330, 1284, 1232, 1088, 724 cm^{-1}; ^{1}H NMR (360 MHz) (DMSO-d_6) δ 9.07−8.78 (7H, m), 8.35 (1H, s), 8.15−8.00 (6H, m), 7.70 (2H, d), 7.65 (1H, d), 7.50 (2H, d), 1.4 (9H, s); MS (DCI) m/z 758 (5, M^+ + Cl), 724 (100, M^+), 714 (0.5, unsubstituted ZnPc + 4Cl), 680 (1, unsubstituted ZnPc + 3Cl), 646 (1, unsubstituted ZnPc + 2Cl), 610 (1, unsubstituted ZnPc + Cl). Anal. Calcd for $C_{42}H_{28}N_8OZn$: C, 69.61; H, 3.89; N, 15.47; O, 2.21; Zn, 8.82. Found: C, 69.40; H, 3.79; N, 15.22; O, 2.14; Zn, 8.56.

3-*tert*-Butyltribenzomononaphthoporphyrazin−zinc(II) (8Zn). This compound was prepared from **1** and **7** and purified according to the procedure described for **4Zn**. Total Pc yield 32%. For the product ratios see Table 2. After preparative HPLC on silica Si 60 with toluene/DMF (98.2) as eluent the yield of monosubstituted **8Zn** was 17%: UV (DMF) 700 (shoulder), 685, 619, 340 λ_{max}; IR (KBr) 3056, 2961, 2933, 2864, 1661, 1485, 1332, 1090, 730 cm^{-1}; ^{1}H NMR (360 MHz) (DMSO-d_6) δ 9.79 (1H, s), 9.75 (1H, s), 9.33 (6H, m), 8.63 (2H, m), 8.23 (6H, m), 8.10 (1H, dd), 1.65 (9H, s); MS (DCI) m/z 716 (1, M^+ + Cl), 682 (M^+, 100), 646 (0.5, 8Zn + 2Cl), 610 (0,5, 8Zn + Cl). Anal. Calcd for $C_{40}H_{26}N_8Zn$: C, 70.38; H, 3.84; N, 16.42; Zn, 9.36. Found: C, 70.07; H, 3.71; N, 16.23; Zn, 9.09.

Supporting Information Available: UV/Vis spectra of compounds **4Zn** and **5Zn** and mass spectrum of compound **5Zn** (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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