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Polymeric Bound Porphyrines and Their Precursors
2*. Solid Phase Synthesis of a Monosubstituted Phthalocyanine

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SUMMARY

The solid state synthesis of a monosubstituted phthalocyanine 6 is described . 4-(4'-Hydroxyphenoxy)-1,2-benzenedicarbonitrile is polymer bound to a chloromethylated macroreticular polystyrene, yielding polymer 3. Reaction of 3 with 4-phenoxy-1,2-benzenedicarbonitrile in the presence of zinc salt results in the formation of covalently bound polymeric phthalocyanine 5. 6 is obtained by cleavage with HBr/acetic acid.

INTRODUCTION

Numerous papers on phthalocyanines (Pc) report on their syntheses and properties (Ref. 2-6). Also, various symmetrically tetra- or octasubstituted Pc's are described (literature cited in Ref. 7-9). Only one paper concerns details on the preparation of a monosubstituted Pc (Ref. 10). Monosubstituted derivatives are important for preparing covalently bound polymeric Pc's without crosslinking occuring during polymer binding at linear polymers. The immobilization enhances the solubility of the chelate in various organic solvents and water. Pc's exhibit excellent photocatalytic properties (Ref. 11,12). Polymer binding of a sensitizer (Ref. 13) can enhance the photocatalytic properties due to hindered intermolecular interaction of Pc molecules and the stabilizing effect of the surrounding polymer. Furthermore, combined polymer binding of different sensitizers and stabilization of Pt as catalyst for H_2 evolution from water may be possible. Additionally, it must be mentioned that a controlled synthesis of chemically modified electrodes is possible with monosubstituted compounds (Ref. 14).

This paper now describes a simple solid phase synthesis of a monofunctional Pc in a few steps using easily available starting materials. Large-scale chromatographic techniques are avoided.

SYNTHESIS

In general, one of two pathways for preparing a monosubstituted Pc may be chosen:

(a) A statistical synthesis requires the cyclotetracondensation of two different 1,2-benzenedicarbonitriles and results in the formation of a mixture of un-, mono-, di-, tri-, and tetrasubstituted Pc's. This method was successfully used for the preparation of unsymmetrically substituted tetraarylporphyrines in low yield (Ref. 15). Our experiments for preparing monosubstituted Pc's by a statistical synthesis were

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* Part 1: Ref. 1

** To whom offprint requests should be sent unsuccessful till now because chromatographic techniques for the purification were insufficient.

(b) Solid phase synthesis at a crosslinked polymer followed by cleavage of the monosubstituted compound was once successfully used for Pc and porphyrines (Ref. 10, 16). Therefore this way was also selected in our case.

The preparation requires in the first step a covalently bound polymeric 1,2-benzenedicarbonitrile followed by the synthesis of the Pc at the polymer. Undesired low molecular reaction products or starting materials are easily separated. The polymer bound Pc must contain a cleavable group in order to separate the Pc and the carrier from each other. Macroreticular chloromethylated divinylbenzene-styrene copolymer 1 was employed as carrier. The macroreticular structure ensures excellent accessibility for the reacting materials. 4-(4'-Hydroxyphenoxy)-1,2-benzenedicarbonitrile (2) was prepared by the reaction of 4-nitro-1,2-benzenedicarbonitrile with a high excess of hydroquinone in a yield of 20 %. 2 was then reacted with 1 in DMA in the presence of $NaOCH_3$. Approximately 33 % of the CH_2-Cl groups were converted to the polymer bound dinitrile 3.

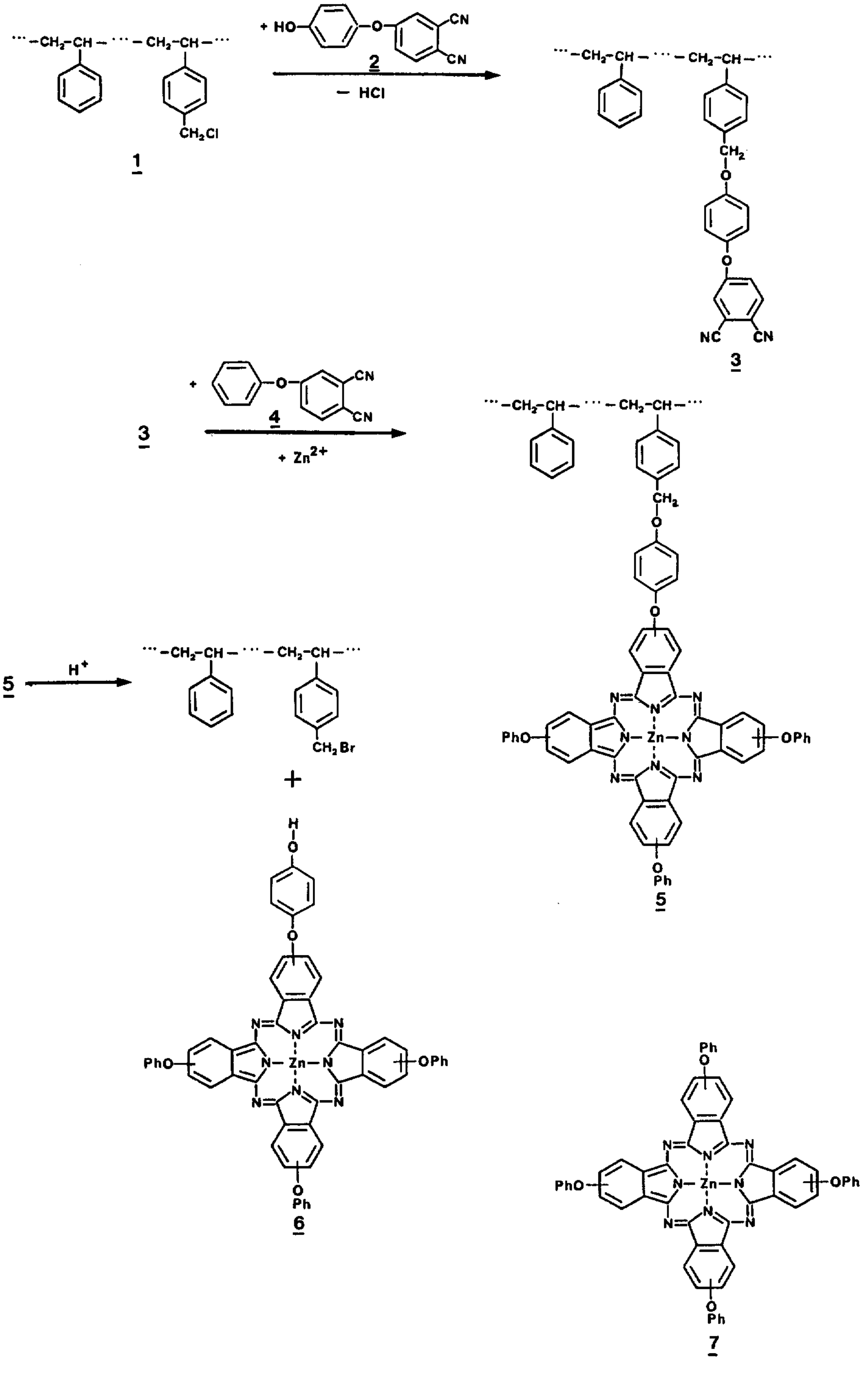
3 and the low molecular 4-phenoxy-1,2-benzenedicarbonitrile (4) gave the covalently bound polymeric Pc 5. Both dinitriles 3, 4 exhibit analogous reactivity as a result of the electron donating effect of the phenoxy substituent. Reaction of 3 and 4 with a zinc salt as templating agent in N,N-dimethylaminoethanol under ammonia bubbling results in the quantitative formation of polymer 5 and the low molecular tetraphenoxyphthalocyanine (7) (both as zinc complexes). For comparison, 7 was also prepared separately. 7 could be separated from 5 by extraction. The dark-green colored polymer 5 contains 0.227 mmole Pc groups/g polymer. The reaction of 4 with a dinitrile polymer bound to a linear polystyrene 4 in the presence of a zinc salt leads to insoluble polymers crosslinked by Pc units.

Cleavage of the polymer-Pc bond of 5 in order to obtain the monohydroxy-substituted Pc 6 was easily carried out with HBr/glacial acetic acid. Dark green 6 was obtained in a yield of 22 %. The acid treatment results in partial demetallization, rendering subsequent treatment with a zinc salt necessary. 6 was purified by washing with NaOH. Small amounts of Pc with a higher degree of hydroxy substitution are soluble in NaOH in contrast to 6.

CHARACTERIZATION

The reaction steps were monitored by elemental analysis and IR spectroscopy. The IR spectra of the covalently bound polymeric dinitrile show absorptions at 2225 (ν(C≡N)), 1230 ($\nu(C_{Ar}\text{-O-}C_{Ar})$), 1195 ($\nu(C_{Ar}\text{-O-}C_{benzyl})$) and 670 cm^{-1} (ν(C-Cl), remaining CH_2-Cl groups) besides such typical of polystyrene. The band of ν(C≡N) at 2225 cm^{-1} vanishes through the reaction leading to the covalently bound polymeric Pc 5 while the absorptions at 1230 and 1195 cm^{-1} remain.

Pc formation is shown through absorptions at 3060 (ν(Ar-H)), 1501/1471/1453 (ν(C-C)), 1368 (δ(C-H)), 1223 (ν(C-O)), 1090 (pyrrol ring), 1041(β (C-H)), 750/702/545 (ϕ(C-C)). The monohydroxy substituted Pc 6 exhibits the same absorptions compared to the tetraphenoxy Pc 7 (Fig. 1). 6 has only one additional band at 1387 cm^{-1} which belongs to δ(COH) i.p.


1
2
− HCl
3
4
+ Zn²⁺
5
H⁺
6
7

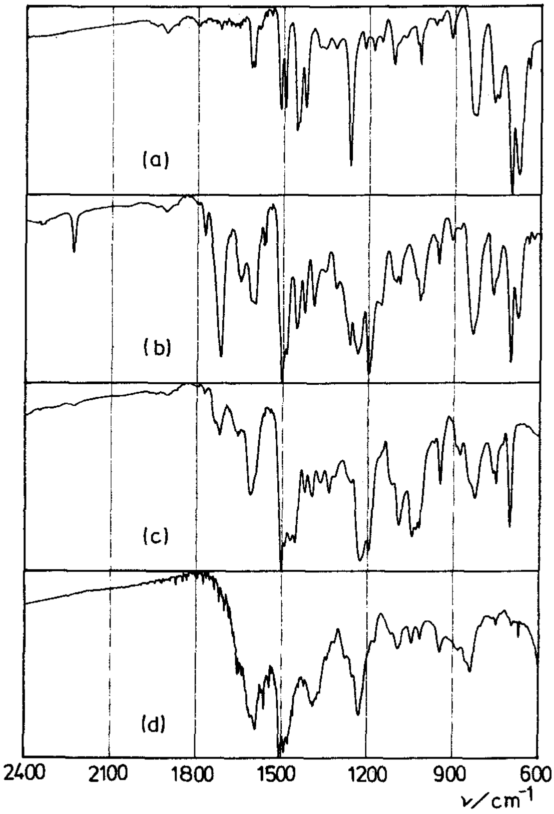


Fig. 1. IR spectra (in KBr) of 1(a), 3(b), 5(c), and 6(d)

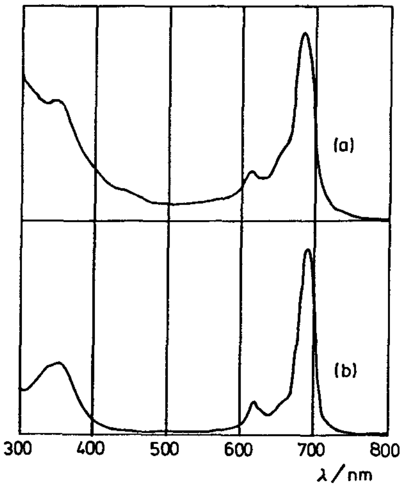


Fig. 2. UV/VIS spectra (in DMSO) of 6(a), 7(b)

The Q-bands of 6, 7 are typical for metal containing Pc with D_{4h} symmetry (Ref. 8). Therefore, the ligand contains Zn(II).
Additionally, the electronic spectra of 6 and 7 show the same transition in the long-wave region >500 nm (Q-band transition) and <400 nm (B-, N-, L-band transition) (Ref. 8) (Fig. 2). 6 was converted into its acyl derivative 8 with acetic anhydride. 8 shows an additional band at 1770 cm^{-1} (ν(C=O, Ar-O-CO-CH_3)) in its IR spectrum. The MS (70 eV) of 6, 7 show molepeaks at m/z 961 (M^+) resp. 945 (M^+).

EXPERIMENTAL

Used instruments: FT-IR (Nicolet 5 DX), UV/VIS (Perkin Elmer 544), MS (Varian CH 7 A).

Starting resin: Macroreticular divinylbenzene-styrene copolymer with 20 % crosslinking; pore diameter 800 Å, pore volume unknown, 22-55 mesh (Aldrich Nr. 9003-53-6). Chloromethylation to resin 1 was carried out with chloromethylmethylether/$ZnCl_2$ in tetrachloroethylene (Ref. 17). The resin contains 4.8 mmole Cl/g after chlorine analyses. 4-Nitro-1,2-benzenedicarbonitrile is a gift from Tokyo Inc. MFG. Co. LTD, Tokyo and can be prepared with slight modifications as described in Ref. 10.

All reactions were carried out in dry, distilled solvents under nitrogen.

4-(4'-Hydroxyphenoxy)-1,2-benzenedicarbonitrile (2): 2.75 g (25 mmole) hydroquinone and 1.7 g (12.5 mmole) dry K_2CO_3 were dissolved in 30 ml DMSO with intensive stirring. A solution of 5 g (25 mmole) 4-nitro-1,2-benzenedicarbonitrile in 50 ml DMSO was added dropwise over a special dropping funnel (Normag) under stirring for 24 h at RT. 2 was separated from the tetracyano-derivate by precipitation with water, washing with dilute NaOH and water. Then the product was dissolved in acetone with an excess of activated charcoal under stirring for 30 min. After filtration the solvent was evaporated and the product dried at 323 K i.vac. The white product 2 was isolated in a yield of 1.2 g (20 %).

IR (KBr, cm^{-1}): 3400 (ν(OH)), 3030, 3060 (ν(Ar-H)), 2230 (ν(C≡N)), 1595/1495/1480 (ν(Ar-H)), 1380 (δ(C-OH)), 1280/1245 (ν(C-O)), 1190/840/780 (δ(Ar-H)).
MS (70 eV): m/z 236 (M^+).

Covalently bound polymeric 1,2-benzenedicarbonitrile 3: 0.5 g 1 (containing 2.4 mmole CH_2Cl groups) were suspended in 30 ml DMA with slow stirring. After adding a solution of 1.7 g (7.2 mmole) 2 and 0.39 g (7.2 mmole) sodium methoxide in 70 ml DMA the mixture was stirred for 6 h at 323 K. The filtered resin was washed with DMA, water, treated in a Soxhlet apparatus with acetone and dried at 323 K i.vac. Conversion of CH_2Cl group according to N analysis of 3: 27.9 %. 3 contains 0.67 mmole benzenedicarbonitrile groups/g polymer.

$$(C_8H_8)_{0.65}(C_9H_9Cl)_{3.22}(C_{23}H_{16}N_2O_2)_{0.67}(C_{10}H_{10})_{1.54\ n} \qquad (2295.68)_n$$

Calc.:	C 78.08	H 6.08	N 1.88
Found:	C 78.4	H 6.05	N 1.87

IR (KBr, cm^{-1}): 2225 (ν(C≡N)), 1230/1195 (ν(C-O-C)), absorptions for polystyrene.

4-Phenoxy-1,2-benzenedicarbonitrile (4): The dinitrile was prepared as described in Ref. 18 (Yield 83 %).

Covalently bound polymeric phthalocyanine 5: 0.5 g 3 (containing 0.335 mmole benzenedicarbonitrile groups) were suspended in 30 ml N,N-dimethylaminoethanol (DMAE) with gentle stirring. The solvent was saturated with dry ammonia by bubbling for 15 min. A solution of 0.45 g (2 mmole) 4 in DMAE and 0.11 g (0.5 mmole) zinc acetate·$2H_2O$ was added. Then the mixture was heated for 24 h at 413 K under low ammonia bubbling. The color of the mixture turns to dark green after 2-3 h reaction time. The isolated resin was washed with DMAE and acetone followed by intensive treating with acetone in a Soxhlet apparatus till colorless solvent is obtained. The dark green polymer 5 was dried at 343 K i.vac. and contains 0.227 mmole phthalocyanine groups/g polymer (quantitative conversion).

$(C_8H_8)_{0.65}(C_9H_9Cl)_{1.67}(C_9H_{11}10)_{1.77}(C_{64}H_{38}N_8O_5Zn)_{0.227}(C_{10}H_{10})_{1.54}$ n
$(999.66)_n$

Calc.: C 79.4 H 6.4 N 5.0 Zn 1.48
Found: C 77.7 H 6.23 N 4.91 Zn 1.5

IR (KBr, cm^{-1}): 3060 (ν(Ar-H)), 1501/1471/1453 (ν(C-C)), 1368 (δ(C-H)), 1223 (ν(C-O)), 1090 (pyrrol ring), 1043 (β(C-H)), 750/702 (ϕ(C-C)) and absorptions of polystyrene.

2-[4-(4'-Hydroxyphenoxy)]-9,16,23-triphenoxyphthalocyanine zinc complex (6): 0.5 g 5 (containing 0.114 mmole phthalocyanine groups) were suspended with slow stirring in 30 ml HBr glacial acetic acid (47 %) for 15 min. After adding 50 ml water, the solid was filtered and washed with water to pH 7. A dark green solution of 6 could be extracted from the solid with hot methanol. 6 was isolated by precipitating with water, washing with dilute NaOH and water. The dark green 6 was dried at 423 K i.vac., yield 32 mg. After-treatment with zinc salt could be carried out by dissolving 30 mg of the phthalocyanine in 30 ml DMF and heating with 15 mg zinc acetate·$2H_2O$ under reflux for 0.5 h. The totally metallized 6 was obtained in the UV/VIS-spectrum and isolated by addition of water, washing with water after isolation and drying at 423 K i.vac. Yield 24 mg (21.9 % corresponding to the employed phthalocyanine groups of 5).

$C_{56}H_{32}N_8O_5Zn$ (961.4)

Calc.: C 69.89 H 3.33 N 11.65 O 8.32 Zn 6.8
Found: C 66.65 H 4.16 N 8.44 O 8.5 Zn 4.8

IR (KBr, cm^{-1}): like 7 and an additional band at 1387 (δ(C-OH)).

UV/VIS (DMSO): λ_{max}/nm (ε/l $mole^{-1}cm^{-1}$)= 678 (105 300).

MS (70 eV): m/z 961 (M^+).

2,9,16,23-Tetraphenoxyphthalocyanine zinc complex (7): 0.88 g (4 mmole) 4 were dissolved in 50 ml N,N-dimethylaminoethanol with slow stirring. The solvent was saturated with dry ammonia by bubbling for 15 min. A solution of 0.4 g (2 mmole) zinc acetate·2H_2O was added and the mixture was heated for 6 h at 413 K under slow ammonia bubbling. The color of the mixture turns to dark green after 20 min reaction time. After evaporation of most of the solvent, 7 was precipitated in H_2O and extracted in a soxhlet apparatus with methanol until colorless solvent is obtained. 7 was dried at 423 K i.vac. Yield 0.53 g (62 %).

IR (KBr, cm^{-1}): 3060 (ν(Ar-H)), 1590/1500/1480 (ν(Ar-H)), 1230 (ν(C-O-C)), 1090 (pyrrol ring), 1045/945/835 (β(C-H)), 750/702/545 (ϕ(C-C)).

UV/VIS (DMSO): λ_{max}/nm (ε/l $mole^{-1}cm^{-1}$)= 678 (170200).

UV/VIS (H_2SO_4): λ_{max}/nm (ε/l $mole^{-1}cm^{-1}$)= 825 (140202).
MS (70 eV): m/z 945 (M^+)

2-[4-(4'-Acyloxyphenoxy)]-9,16,23-triphenoxyphthalocyanine zinc complex (8): 0.1 g (0.1 mmole) 6 and a mixture of 9.9 ml acetic acid anhydride and 19.8 ml dry pyridine were heated under stirring for 12 h at 373 K. The solution was evaporated and water was added. After filtration and intensive washing with water the green product was dried at 423 K i.vac. Yield 92.3 mg (92 %).

IR (KBr, cm^{-1}): like 7 and an additional band at 1760 (ν(C=O))

UV/VIS (DMSO): λ_{max}/nm (ε/l $mole^{-1}cm^{-1}$)= 677 (92400)

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