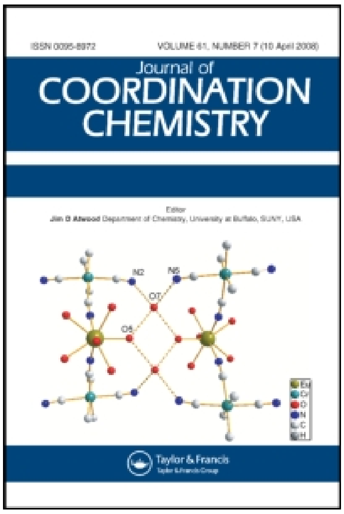

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SYNTHESIS AND PROPERTIES OF NEW PHTHALOCYANINES WITH TERTIARY OR QUATERNARIZED AMINOETHYLSULFANYL SUBSTITUENTS

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Metal-free- and metallo-phthalocyanines (M = Ni or Zn) carrying four dimethylaminoethylsulfanyl– or trimethylaminoethylsulfanyl– groups on peripheral positions have been synthesized from the corresponding phthalonitrile derivatives in the presence or the absence of the anhydrous metal salt [$NiCl_2$ or $Zn(CH_3COO)_2$]. The new compounds have been characterized by elemental analyses, IR, NMR, and electronic spectroscopy and mass spectra. Phthalocyanines with quaternarized amino groups are soluble in aqueous solution over a wide pH range and these molecules are present as aggregated species in solution as confirmed by the blue shift of Q bands in their electronic spectra.

KEYWORDS: phthalocyanines, aminoethylsulfanyl groups, nickel(II), cobalt(II), synthesis.

INTRODUCTION

In addition to their well known high thermal and chemical stabilities, phthalocyanines (pcs) have become noted recently for their special optical and electrical properties such as electrical conductivity, photovoltaic effects and electrochromism.[1,2] Also, their use as efficient photosensitizers in obtaining singlet oxygen is becoming especially important in photodynamic therapy (PDT) of tumours.[3] A common requirement in all these applications is enhanced solubility of the phthalocyanine core which is known for its insolubility in most common solvents in the case of unsubstituted derivatives. In this context solubility in aqueous media should be considered as a prerequisite in PDT.

Our previous contributions describing a series of pcs with oxa– and/or aza-macrocycles reported enhanced solubility of products with these bulky macrocycles on the periphery.[4–7] By quaternarizing aza groups of the substituents, soluble products in a wide pH range of aqueous solutions were acquired.[5] A consequence

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of incorporating a sulphanyl function on the periphery has been a shift of Q-band absorption to longer wavelengths;[8,9] this is preferred for number of applications such as with IR absorbers and photosensitizers. In the present paper we describe results on the synthesis and electronic spectra of a new group of pcs carrying both sulfanyl and quaternary ammonium functions simultaneously in order to make use of their solubilizing effect in aqueous media and their shift of the Q band to the near IR range.

EXPERIMENTAL

4-Nitrophthalonitrile was synthesized according to the reported procedure.[10] IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer in KBr pellets and electronic spectra on a Varian DMS 90 spectrophotometer. Elemental analyses were performed by the Instrumental Analysis Laboratory of TUBITAK Gebze Research centre. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 200 MHz spectrometer. Mass spectra were recorded on a VG Zabspec GC-MS spectrometer.

4-(2-Dimethylaminoethylsulfanyl)phthalonitrile (1)

To a solution of 4-nitrophthalonitrile (12 g, 69 mmol) in anhydrous DMSO (150 cm^3) under argon was added 2-dimethyaminoethanethiol hydrochloride (10.8 g, 76 mmol). After stirring for 10 mins, finely ground anhydrous K_2CO_3 (14.3 g, 104 mmol) was added in portions during 2 h with efficient stirring. The reaction mixture was stirred at room temperature for 72 h, after which time the solvent was evaporated under reduced pressure. Water (100 cm^3) was added and the aqueous phase was extracted with dichloromethane (3 × 50 cm^3). The combined extracts were treated first with a solution of $NaHCO_3$ (5%), then with water, and dried over Na_2SO_4. Recrystallization from ethanol (150 cm^3) gave the pure product. Yield: 11.3 g (71%), m.p. 110–2°C. ^{1}H NMR ($CDCl_3$): δ 7.72–7.27 (d, Ar-H, 3H), 3.17–3.01 (t, S-CH_2, 2H), 2.78–2.61 (t, N-CH_2, 2H), 2.30 (s, CH_3, 6H). IR (ν_{max}/cm^{-1}): 2880–2800 (CH_2), 2240 (C≡N), 1600, 1480, 1300, 1020, 900, 820, 520. ^{13}C NMR ($CDCl_3$): δ 147.27, 133.11, 130.11, 130, 129.86,116.11, 115.47, 115.09, 110.65, 57.15 (*S*-CH_2), 45.17 (CH_3), 30.27 (*N*-CH_2). MASS (EI) *m/z*: 232 (31% M + 1), 187 (57%, M-$(CH_3)_2N$), 131.9.

4-(2-Trimethylaminoethylsulfanyl)phthalonitrile iodide (2)

1 (1 g, 4.3 mmol) was dissolved in abs. ethanol and methyliodide (0.613 g, 4.3 mmol) was added. The mixture was refluxed for 3 h and after cooling to room temperature, precipitation occurred. The white product was filtered off, washed with dichloromethane and dried in vacuo. Yield: 1 g (62%), m.p. 245–9°C. ^{1}H NMR (DMSO-d_6): δ 8.15–7.85 (d, Ar-H, 3H), 3.63 (t, *S*-CH_2, 2H), 3.24 (t, *N*-CH_2, 2H), 3.16 (s, CH_3, 9H) IR (ν_{max}/cm^{-1}): 3100-2960(-CH_2-, -CH_3), 2240 (C≡N), 1580, 1480, 1390, 1190, 1070, 980, 920, 850, 520. ^{13}C NMR (APT) (DMSO-d_6): δ 143.72, 133.82, 131.34, 130.87, 115.8, 115.44, 115.20, 110.66, 62.75 (*S*-CH_2), 52.36 (CH_3), 23.73 (*N*-CH_2).

Tetrakis(2-dimethylaminoethylsulfanyl)phthalocyanine (3)

A solution of 1 (0.25 g, 1.08 mmol) in dry 2-(dimethylamino)ethanol was refluxed under argon for 15 h. After cooling, the green product formed was dissolved in ethanol (10 cm^3) and the solution was added dropwise into acetone (20 cm^3) with stirring to precipitate the solid, which was filtered and then washed with acetone. Yield: 0.080 g (32%), m.p. >200°C. ^1H NMR ($CDCl_3$): δ 7.38–6.84 (m, Ar-H, 12H), 3.17–3.14 (t, *S*-CH_2, 8H), 2.79–2.76 (t,*N*-CH_2, 8H), 2.46 (s, CH_3, 24H), -7.0 (br s, NH, 2H). IR (ν_{max}/cm^{-1}): 3280(NH), 2880-2800 (CH_2), 1600, 1480, 1300, 1020, 900, 820, 740. ^{13}C NMR ($CDCl_3$): δ 145.56, 138.77, 134.36, 130.61, 126.93, 120.90, 116.23, 58.32 (*S*-CH_2), 45.52 (*N*-CH_2), 30.74 (CH_3). Mass (FAB) *m/z*: 927 (18%, M^+).

Tetrakis[(2-dimethylaminoethylsulfanyl)phthalocyaninatonickel(II) or zinc(II)] (4 or 5)

A mixture of 1 (0.5 g, 2,16 mmol), anhydrous quinoline (1.2 cm^3) and anhydrous $NiCl_2$ (0.08 g, 0.6 mmol) or $Zn(CH_3COO)_2$ (0.10 g, 0.54 mmol) was heated and stirred at 155–160°C for 5 h under Ar in a round-bottomed flask. The resulting green suspension was cooled and the product was precipitated by addition of acetone (20 cm^3). The dark-green precipitate was dissolved in methanol (40 cm^3) and added dropwise into ethyl acetate (50 cm^3) with stirring. The resulting dark-green product was filtered off, washed first with ethyl acetate and then with diethyl ether and dried. 4: Yield: 0.08 g (15%), m.p.>200°C; ^1H NMR ($CDCl_3$): δ 7.25-6.83 (m, Ar-H, 12H), 3.03 (t, *S*-CH_2, 8H), 2.69 (t, *N*-CH_2, 8H), 2.37 (s, CH_3, 12H). IR (ν_{max}/cm^{-1}): 2880–2800 (CH_2), 1600, 1460, 1300, 1120, 920, 740. 5: Yield 0.04 g (7%), m.p. >200°C. ^1H NMR ($CDCl_3$): δ 8.54–7.35 (m, Ar-H, 12H), 2.39 (t,*S*-CH_2, 8H), 1.60 (t, *N*-CH_2, 8H), 1.24 (s, CH_3, 12H). IR (ν_{max}/cm^{-1}): 2880-2800(CH_2), 1600, 1460, 1380, 1300, 1100, 920, 900, 740. Mass (FAB) *m/z*: 990 (7%, M^+).

Tetrakis[(2-trimethylaminoethylsulfanyl)phthalocyanine]tetraiodide (3a):

3 (0.050 g, 0.054 mmol) was dissolved in absolute ethanol (2 cm^3) and methyl iodide (0.031 g, 0.216 mmol) was added to this solution. After refluxing for 2 h, the mixture was cooled and the resulting green precipitate was filtered off, washed with ethanol and dried. Yield: 0.045 g (56%), m.p. > 200°C. IR(ν_{max}/cm^{-1}): 3260 (NH), 3020-2880(CH_2), 1600, 1460, 1020, 1080, 900, 740. $^1H_{NMR}$ (DMSO): δ 9.13 (Ar-H, 12H), 3.98 (*S*-CH_2, 8H), 3.92 (t, *N*-CH_2, 8H), 3.35 (s, CH_3, 36H), -2.0 (br s, NH, 2H).

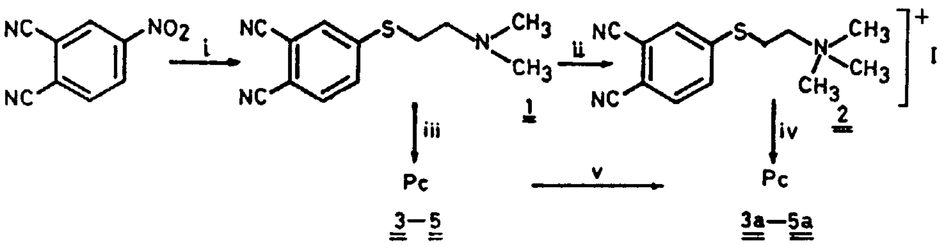
Tetrakis[(2-trimethylaminoethylsulfanyl)phthalocyaninatonickel(II) or zinc(II)] tetraiodide (4a or 5a)

A mixture of 2 (0.70 g, 1.88 mmol), anhydrous quinoline (0.85 cm^3) and $NiCl_2$ (0.060 g, 0.47 mmol) or $Zn(CH_3COO)_2$ (0.086 g, 0.47 mmol) was heated and stirred at 155–160°C for 6h under argon. The resulting green suspension was cooled to room temperature and treated with acetone (20 cm^3) to complete precipitation.

After filtration, the raw product was dissolved in methanol (20 cm^3) or dimethylformamide (10 cm^3) and reprecipitated by adding dropwise into ethyl acetate (30 cm^3) with stirring. The dark green precipitate was chromatographed on neutral Al_2O_3 and eluted with dichloromethane-ethanol (5:1). 4a: Yield 0.04 g (55%); m.p. >200°C. IR(v/cm^{-1}): 2880–2800 (CH_2), 1600, 1460, 1300, 1120, 920, 740. 5a: Yield 0.06 g (8%); m.p. >200°C. IR (v/cm^{-1}): 2880–2800 (CH_2), 1600, 1460, 1380, 1300, 1100, 900, 740.

RESULT AND DISCUSSION

The synthetic procedure, as outlined in the Scheme, starts with the synthesis of a hitherto unreported phthalonitrile, namely 4-(2-dimethylaminoethylsulfanyl)-phthalonitrile(1), from 4-nitro-phthalonitrile by displacement of the nitro group with the -SH function of 2-dimethylaminoethanethiol in the presence of anhydrous K_2CO_3 in dimethylsulfoxide.[11,12] Its quaternarized derivative 2 is obtained in relatively high yield (62%) by treating 1 with methyl iodide (Table I).



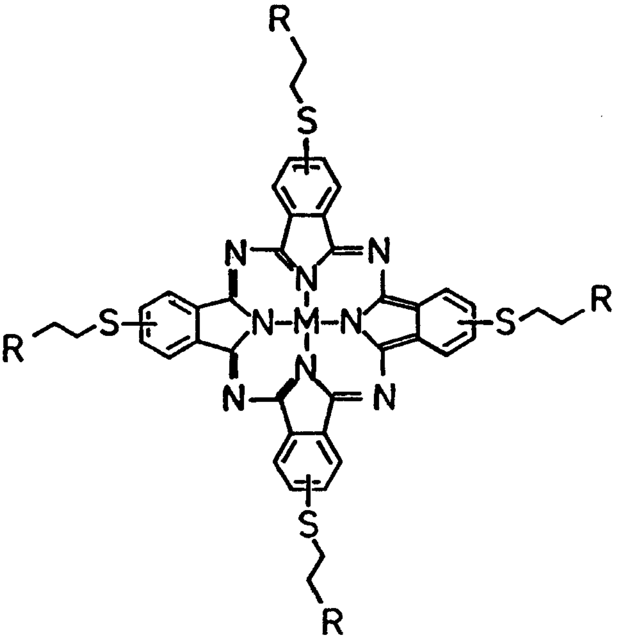
Scheme (i) Dimethylaminoethanethiolhydrochlorid/DMSO/K_2CO_3; (ii) MeI/EtOH; (iii) Dimethylaminoethanol or metal salt/quinoline; (iv) Metal salt/quinoline; (v) MeI/EtOH.

TABLE I Analytical[a] data for the starting materials and the phthalocyanines.

		Analysis (%)		
Compound	Formula	C	H	N
1	$C_{12}H_{13}N_3S$	619 (62.3)	5.6 (5.6)	18.3 (18.2)
2	$C_{13}H_{16}IN_3S$	42.0 (41.8)	4.3 (4.3)	11.4 (11.2)
3	$C_{48}H_{54}N_{12}S_4$	61.9 (62.2)	5.6 (5.9)	17.9 (18.1)
4	$C_{48}H_{52}N_{12}NiS_4$	58.4 (58.6)	5.0 (5.3)	16.8 (17.0)
5	$C_{48}H_{52}N_{12}ZnS_4$	58.0 (58.2)	4.9 (5.2)	16.7 (16.9)
3a	$C_{52}H_{66}I_4N_{12}S_4$	42.1 (41.8)	4.7 (4.4)	11.3 (11.2)
4a	$C_{52}H_{64}I_4N_{12}NiS_4$	40.7 (40.3)	4.3 (4.1)	10.9 (10.8)
5a	$C_{52}H_{64}I_4N_{12}S_4Zn$	39.8 (40.0)	3.9 (4.1)	10.9 (10.8)

[a] Calculated values are given in parenthesis.

Conversion of 1 into a metal-free Pc 3 is accomplished directly by refluxing this reagent in a suitable high-boiling solvent (*i.e.*, *N*,*N*-dimethylaminoethanol) to realize the cyclotetramerization.[13] The metal-free phthalocyanine with quaternarized amino group on the peripheral substituent (3a) has been prepared by treatment of 3 with methyl iodide as in the case of phthalonitrile derivative (1).



R \ M	2H	Ni	Zn
$-N(CH_3)_2$	3	4	5
$-N(CH_3)_3^+I^-$	3a	4a	5a

Formula

The metal phthalocyaninates (M = Ni^{II} or Zn^{II}) with four tertiary (4,5) or quaternary aminoethylsulfanyl substituents (4a, 5a) are synthesized directly by cyclotetramerization of the corresponding dicyano compounds (1 or 2) in the presence of the anhydrous metal salt in a high-boiling *N*-donor solvent (*e.g.* quinoline).[1] It should be pointed out that in the case of quaternarized metal phthalocyaninates 4a and 5a reproducible results are acquired when the quaternarized phthalonitrile derivative 2 is directly used. As expected from a singly substituted phthalonitrile, the phthalocyanines 3–5 and 3a–5a are a mixture of four structural isomers and our attempts to isolate each of them have been unsuccessful.[14] The finger-print regions of the IR spectra observed for 3–5 and 3a–5a are typical of phthalocyanines and do not show appreciable change by quaternarization of the latter. CH stretching vibrations observed at 2880–2800 cm^{-1} are due to methyl and ethyl groups of the peripheral substituents. Characteristic intense absorptions of C≡N groups at 2220 cm^{-1} in the spectra of phthalonitrile derivatives 1 and 2 disappear after Pc formation. Although the weak absorption bands for sulfanyl groups are normally expected in the 600-700 cm^{-1} region, they could not be observed in the spectra of either dinitriles (1,2) or the Pcs (3–5).

The mass spectroscopy studies by the fast atom bombardment technique[4] on the newly synthesized compounds gave molecular ion species only for 1, 3 and 5. Values of the molecular ions show good agreement with the calculated values for metal-free 3 (*m/z* 927) and zinc phthalocyanines 5 (*m/z* 990); in the case of dinitrile derivative 1, M + 1 peak (*m/z* 232) has been observed.

The electronic spectra of the dimethylaminoethylsulfanyl substituted pcs (3–5) were measured in organic solvents and those with quaternarized amino substituents (4a, 5a) in aqueous solutions (Table II). Although the symmetry of the pcs are lowered by a single substituent on each benzene group, the metal-free pcs 3 and 3a still show split Q band absorptions of D_{2h} symmetry in organic solvents.[1] In aqueous solutions of 3a, a single intense Q band at 642 nm is observed, indicative of molecular association in polar media.[15] The aggregation of pc units in metallophthalocyanines is clearly observed by following the changes occurring in the Q band region. In the spectra of 4 and 5 in DMSO, there is an intense band around 685 nm corresponding to monomeric species and a shoulder around 645 nm indicating aggregated ones.[16] For the water-soluble quaternarized pcs (4a and 5a), the appearance of the spectra is vice versa; *i.e.*, the longer wavelength absorption is less intense and appears as a shoulder while the absorption of the aggregated species around 630 nm is the main peak.

The high solubility of quaternarized pcs in aqueous solutions enabled us to record their electronic spectra over the wide pH range of 2-9 (Table III). For this purpose, buffer solutions were prepared from AcOH-AcONa ($2 \leq pH \leq 7$) and NH_4Cl-NH_4OH ($7 < pH \leq 9$) systems. Examination of these data reveals that no perceptible shift of the band maxima in the Q band region occurs with varying pH of solution. A gradual decrease of absorption intensity is observed will increase pH, although this might be a consequence of changes in ionic strength. The general appearance of these spectra indicates that aggregated Pc species dominate monomeric ones at all pH values measured.

In conclusion, the results of the present work show that dimethylaminoethylsulfanyl or trimethylaminoethylsulfanyl substituents enhance the solubility of pcs and the latter enables solution studies over a wide pH range.

TABLE II Electronic spectra details of the phthalocyanines 3-5 and 3a-5a.

Compound	$\lambda_{max}(\varepsilon.10^{-4})$
3^a	714(10.2), 680(9.60), 651(4.79), 616(3.12),
4^b	686(6.6), 640(3.1)
5^b	685(1.99), 642(1.52)
$3a^b$	713(14.0), 684(13.32), 654(4.73), 623(4.25)
$3a^c$	642(6.16), 398(2.0), 332(5.75)
$4a^c$	688(1.27), 625(2.40)
$5a^c$	678(2.49), 644(3.81)

[a] In $CHCl_3$; [b]in DMSO; [c]in water.

TABLE III Q band absorption data for quaternarized metallo-pcs 4a and 5a in aqueous solution at different pH values.

	$\lambda_{max}(\varepsilon.10^{-4})$	
pH	4a	5a
2	687(1.80);630(3.93)	690(3.13);642(5.07)
3	683(1.63);630(3.67)	685(3.27);642(5.13)
4	688(1.46);630(3.53)	685(3.10);640(4.87)
5	690(1.37);628(3.40)	680(2.50);644(3.76)
6	688(1.30);625(3.26)	690(1.90);642(3.27)
7	688(1.13);620(2.31)	680(2.33);644(3.41)
8	680(0.83);620(2.40)	690(2.07);644(3.01)
9	690(0.90);620(2.69)	680(2.09);644(2.96)

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