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Synthesis of New Metal-Free and Metal-Containing Phthalocyanines with Tertiary or Quaternary Aminoethyl Substituents

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Summary. A novel phthalodinitrile derivative carrying dimethylaminoethylsulfanyl groups at positions 4 and 5 was synthesized from 2-dimethylaminoethanethiol hydrochloride and 1,2-dichloro-4,5-dicyanobenzene. Its cyclotetramerization in the presence of 2-dimethylamino-ethanol or metal salts ($CoCl_2$, $Zn(OAc)_2$) gave metal-free or metal-containing phthalocyanines ($M = Co$ or Zn). These phthalocyanines were converted into water soluble quaternized products by reaction with methyl iodide. The new compounds were characterized by elemental analysis, IR, NMR, and electronic spectra.

Keywords. Phthalodinitrile; Cyclotetramerization; Phthalocyanines; Quaternary amonium salts.

Introduction

In addition to their well-known high thermal and chemical stability, phthalocyanines 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 for singlet oxygen production is becoming important in photodynamic therapy [3]. However, their insolubility in common organic solvents causes difficulties for many applications, rendering the synthesis of soluble derivatives an important task. Whereas peripheral substitution with bulky groups [4] or long alkyl chains [5] leads to phthalocyanine products soluble in apolar solvents, the introduction of sulfonyl [6], carboxyl [7], or amino [8] groups results in water soluble derivatives, at least within certain *pH* ranges. Quaternized ammonium groups are especially useful, providing solubility within a wide *pH* range [9–11]. In previous contributions describing a series of phthalocyanines with oxa- and/or aza-macrocycles or acyclic substituents, enhanced solubility of phthalocyanines with bulky groups on the periphery has been demonstrated [12–26]. By quaternizing aza groups or amino groups of the substituents, products soluble in water over a wide *pH* range were obtained [19, 20]. In addition, a shift of the Q-band absorption to longer wavelengths has been observed as a consequence of incorporating a sulfanyl function on the periphery [10, 11, 27–31]. This effect is important for a number of applications (*e.g.* as IR absorbers and photosensitizers).

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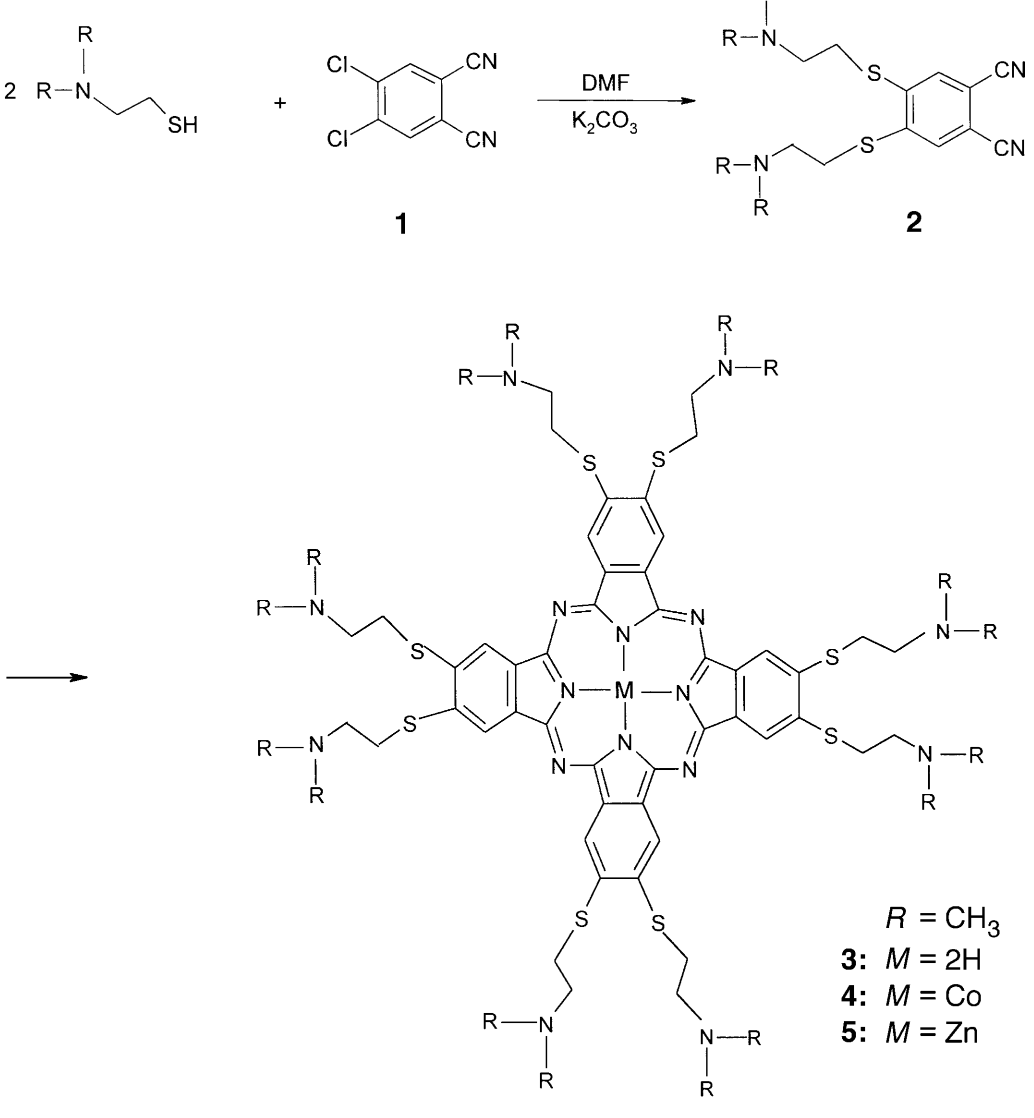
This paper describes the preparation of novel soluble phthalocyanine compounds which carry eight 2-dimethyl- or 2-trimethylaminoethylsulfanyl substituents on their periphery, providing extensive solubility in water over a wide *pH* range.

Results and Discussion

1,2-Dichloro-4,5-dicyanobenzene (**1**) has been used recently to prepare 4,5-disubstituted phthalonitrile derivatives by base-catalyzed nucleophilic aromatic displacement [29–31]. The same route was applied to prepare 1,2-*bis*-(2-dimethylaminoethylsulfanyl)-4,5-dicyanobenzene (**2**) from 2-dimethylaminoethanethiol and **1** (Scheme 1). The reaction was carried out in dry *DMF* at 50°C under a nitrogen atmosphere. During the reaction, an excess of K_2CO_3 was added to completely



Scheme 1. Synthetic route **2** and the corresponding metal-free and metal-containing phthalocyanines

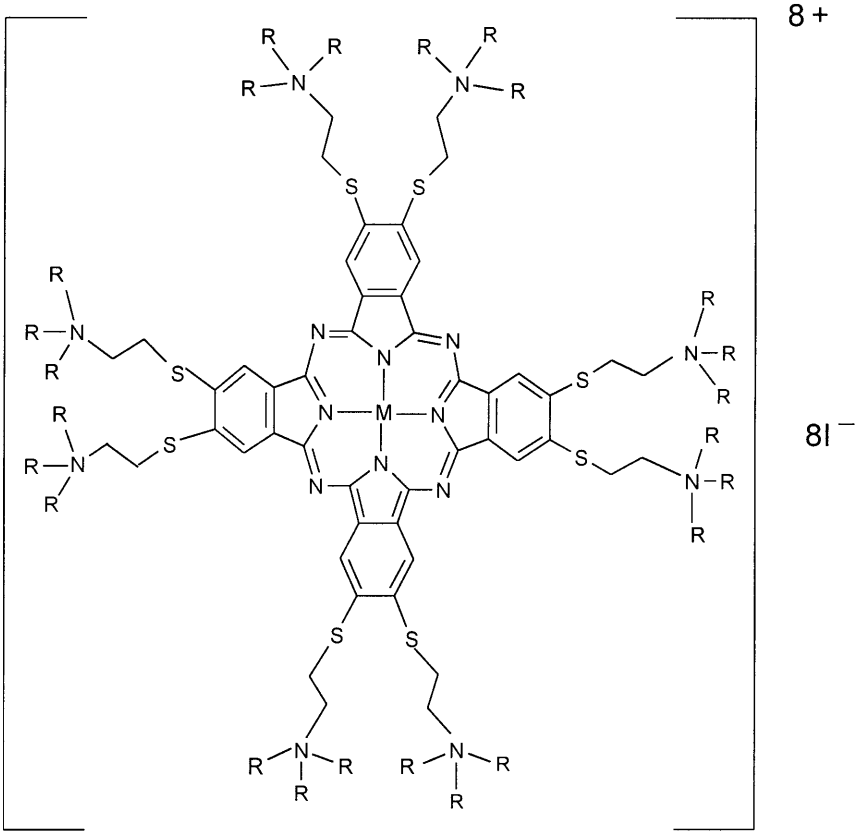
neutralize the amino group. In the IR spectrum of **2**, stretching vibrations of CN, CH_3, and CH_2 groups were observed at 2238, 2723, and 2953 cm^{-1}. These values are in agreement with those reported for similar compounds [10]. In the ^{1}H NMR spectrum of **2** ($CDCl_3$), the aromatic protons appear as a singlet at 7.48 ppm, the aliphatic protons as triplets at 3.13 and 2.67 ppm. The CH_3 protons of **2** are observed as a singlet at 2.30 ppm. As a consequence of the symmetrical structure, the ^{13}C NMR spectrum of **2** shows four different signals for unsaturated carbon atoms, one of them arising from CN (115.34 ppm). The aliphatic carbon atoms also give three different signals at 57.34, 45.11, and 31.29 ppm for SCH_2, NCH_2, and CH_3, respectively.

Conversion of **2** into metal-free phthalocyanine **3** was accomplished by refluxing it in 2-dimethylaminoethanol. The metal phthalocyaninates **4** and **5** (M = Co(II), Zn(II)) with eight tertiary aminoethylsulfanyl substituents were synthesized by cyclotetramerization of **2** in the presence of the corresponding anhydrous metal salts in *DMF*. Column chromatography on silica gel or alumina was employed to obtain the pure products from the reaction mixture. The intensely green products are easily soluble in various solvents such as chloroform, dichloromethane, *THF*, acetone, ethanol, methanol, *DMF*, and *DMSO*.

Elemental analyses as well as IR, ^{1}H NMR, ^{13}C NMR, and UV/Vis spectra confirmed the proposed structures of **3**, **4**, and **5**. Thus, in the IR spectrum of **3** the NH groups in the inner core give an absorption at 3310 cm^{-1}. These protons are also well characterized by the ^{1}H NMR spectrum, which shows a peak at -3.05 ppm as a result of the ring current of the 18π electron system of the phthalocyanine ring. A distinct difference encountered in the ^{1}H NMR spectra of **3** and **4** when compared with previously obtained macrocycle substituted compounds are the sharp peaks, which indicate a lower tendency to aggregate even at the concentrations used for NMR measurements [9, 15]. The phthalocyanines **3**–**5** show intense Q absorption bands above 700 nm. When compared with *octakis*-alkyl or -alkoxy substituted derivatives, the shift of this intense band is typical for phthalocyanines with peripheral thia substituents; this might be important for various near-IR applications. The characteristic Q-band absorption of metal phthalocyaninates with D_{4h} symmetry is observed as a single band of high intensity in the visible region. The D_{2h} symmetry of the metal-free phthalocyanine **3** is verified by two absorptions in the visible region (700–731 nm).

The addition of sulfonium or quaternary ammonium groups on the periphery led to phthalocyanines derivatives soluble in water. When phthalocyanines **3**–**5** were treated with methyl iodide in chloroform, the hygroscopic phthalocyanine products **3a**, **4a**, and **5a** with eight quaternary ammonium groups were obtained in high yields (~84%). No major changes in the IR spectra were found after quaternization. Their UV/Vis spectra in aqueous solution, however showed some differences. First, the shift of the Q-band absorbtions to shorter wavelengths is a result of solvent effect. Second, a single intense Q-band at 669 nm for the metal-free phthalocyanine **3a** is interesting, because commonly the D_{2h} symmetry of these compounds is expected to give rise to the formation of two bands in the low energy region. This result is indicative of molecular association in polar media.

In conclusion, the results of the present work show that the dimethylaminoethylsulfanyl substituents enhance the solubility of phthalocyanines in common



$R = CH_3$

3a: $M = 2H$

4a: $M = Co$

5a: $M = Zn$

Fig. 1. Formula of **3a–5a**

organic solvents, whereas the trimethylaminoethylsulfanyl residues enhance their solubility in water.

Experimental

IR spectra were recorded on a Mattison 1000 FT-IR spectrometer (KBr pellets), electronic spectra on a Unicam UV2 spectrophotometer. Elemental analyses were performed by the instrumental analysis laboratory of the TÜBİTAK Marmara Research Centre; their results agree with the calculated values within experimental error. ^1H NMR spectra were recorded on a Bruker 250 MHz spectrometer using *TMS* as internal standard. 1,2-Dichloro-4,5-dicyanobenzene (**1**) was prepared according to a reported procedure [31].

1,2-Bis-(2-dimethylaminoethylsulfanyl)-4,5-dicyanobenzene (**2**; $C_{16}H_{22}N_4S_2$)

2-Dimethylaminoethanethiol hydrochloride (3.36 mmol, 0.662 g) was dissolved in 15 cm^3 of dry *DMF* at 50°C under N_2 atmosphere, and 1 g **1** (7.05 mmol) was added. After stirring for 15 min, 2 g finely ground anhydrous K_2CO_3 (20 mmol) were added portionwise during 2 h with efficient stirring. The reaction mixture was stirred under nitrogen at 50°C for 20 h. Then the mixture was poured into 200 cm^3 of ice-water. The resulting yellow solid was collected by filtration and washed with H_2O until the washings were neutral. The wet solid was dissolved in CH_2Cl_2, and the solution was dried over Na_2SO_4. The solvent was evaporated under reduced pressure, and the crude residue was recrystallized from diethyl ether. The compound was soluble in $CHCl_3$, CH_2Cl_2 EtOH, MeOH, *THF*, *DMSO*, and *DMF*.

Yield: 0.500 g (45%); m.p: 102–103°C; ^{1}H NMR ($CDCl_3$, δ, 250 MHz): 7.48 (s, 2H, Ar–H), 3.14 (t, $J = 2.8$ Hz, 4H, S–CH_2), 2.67 (t, $J = 6.9$ Hz, 4H, N–CH_2), 2.30 (s, 12H, CH_3) ppm; ^{13}C NMR ($CDCl_3$, δ, 62.5 MHz): 144.49 (C–CN), 128.93 (CH), 115.34 (CN), 111.42 (C–S, 57.34 (CH_2–S), 45.11 (N–CH_3), 31.29 (N–CH_2) ppm; IR (KBr): $\nu = 3080$ ($\nu_{\text{CH-arom}}$), 2953–2851 ($\nu_{\text{CH-aliph}}$), 2238 (ν_{CN}), 1600, 1574, 1472, 1421, 1293, 1140, 936, 782, 553 cm^{-1}.

Oktakis-(2-dimethylaminoethylsulfanyl)-phthalocyanine (**3**; $C_{64}H_{90}N_{16}S_8$)

A solution of 0.2 g **2** (0.59 mmol) in 0.5 cm^3 2-(dimethylamino)-ethanol was refluxed under N_2 for 12 h. After cooling, the green product was filtered off, washed with hot H_2O, and dried *in vacuo*. The product was purified by column chromatography with neutral alumina (eluent: EtOH:$CHCl_3$ = 1:10).

Yield: 0.030 g (14.9%); ^{1}H NMR ($CDCl_3$, δ, 250 MHz): 8.80 (s, 8H, ArH), 3.74 (t, $J = 6.7$ Hz, 16H, SCH_2), 2.98 (t, $J = 6.9$ Hz, 16H, NCH_2), 2.52 (s, CH_3, 24H), −3.05 (s, 2H, NH, exchangeable) ppm; IR (KBr): $\nu = 3310$ (ν_{NH}), 3050 ($\nu_{\text{CH-arom}}$), 2953–2825 ($\nu_{\text{CH-aliph}}$), 1600, 1473, 1421, 1370, 1344, 1320, 1038, 961, 757, 706, 655 cm^{-1}; UV/Vis ($CHCl_3$): $\lambda_{\max}(\varepsilon) = 330$ (12620), 700 (22340), 731 (23490) nm.

Octakis-(2-dimethylaminoethylsulfanyl)-phthalocyaninato cobalt(II) (**4**; $C_{64}H_{88}N_{16}S_8Co$)

A mixture of 0.25 g **2** (0.74 mmol), 0.5 cm^3 anhydrous *DMF*, and 0.033 g anhydrous $Zn(CH_3COO)_2$ (0.185 mmol) was heated and stirred at 140–145°C for 8 h under N_2 in a round-bottomed flask. The resulting green suspension was cooled to room temperature, and the crude product was precipitated by addition of H_2O. The product was purified by column chromatography on silica gel (eluent: EtOH:$CHCl_3$ = 1:20).

Yield: 0.050 g (16%); IR (KBr): $\nu = 3046$ ($\nu_{\text{CH-arom}}$), 2978–2877 ($\nu_{\text{CH-aliph}}$), 1600, 1472, 1321, 1140, 1114, 985, 961, 808, 757, 706, 578 cm^{-1}; UV/Vis ($CHCl_3$): $\lambda_{\max}(\varepsilon) = 364$ (14710), 710 (15200) nm.

Octakis-(2-dimethylaminoethylsulfanyl)-phthalocyaninato zinc(II) (**5**; $C_{64}H_{88}N_{16}S_8Zn$)

5 was prepared following the procedure described for **3**, starting from 0.250 g **2** (0.74 mmol), 0.5 cm^3 anhydrous *DMF*, and 0.024 g anhydrous $ZnCl_2$ (0.190 mmol). For purification by column chromatography, neutral alumina was used as the stationary phase and EtOH:$CHCl_3$ = 1:10 as the eluent.

Yield: 0.068 g (26%); ^{1}H NMR ($CDCl_3$, δ, 250 MHz): 8.54 (s, 8H, ArH) 3.38 (t, $J = 6.4$ Hz, 16H, SCH_2), 2.99 (t, $J = 6.7$ Hz, 16H, NCH_2), 1.98 (s, 24H, CH_3) ppm; IR (KBr): $\nu = 3038$ ($\nu_{\text{CH-arom}}$), 2928–2825 ($\nu_{\text{CH-aliph}}$), 1625, 1497, 1472, 1421, 1293, 1191, 1140, 961, 757, 706, 578 cm^{-1}; UV/Vis ($CHCl_3$): $\lambda_{\max}(\varepsilon) = 371$ (10640), 715 (11930) nm.

Oktakis-((2-trimethylaminoethylsulfanyl)-phthalocyanine) octaiodide (**3a**; $C_{72}H_{114}N_{16}S_8I_8$)

3 (0.050 g, 0.035 mmol) was dissolved in 2 cm^3 $CHCl_{31}$ and 0.052 g CH_3I (23 mm^3, 0.373 mmol) were added. After refluxing for 3 h, the mixture was cooled to room temperature, and resulting green precipitate was filtered off, washed with $CHCl_3$, and dried *in vacuo*.

Yield: 0.073 g (84%); IR (KBr): $\nu = 3260$ (ν_{NH}), 3030 ($\nu_{CH\text{-arom}}$), 2953–2872 ($\nu_{CH\text{-aliph}}$), 1625, 1497, 1421, 1395, 1293, 1217, 1089, 1038, 910, 757, 680 cm^{-1}; UV/Vis (H_2O): $\lambda_{max}(\varepsilon) = 321$ (15820), 669 (20300) nm.

Octakis-((2-trimethylaminoethylsulfanyl)-phthalocyaninato-cobalt(II)) octaiodide (**4a**; $C_{72}H_{112}N_{16}S_8I_8Co$)

4a was prepared following the procedure described for **3a**, starting from 0.05 g **4** (0.035 mmol) in 2 cm^3 $CHCl_3$ and, 0.044 g CH_3I (22 mm^3, 0.315 mmol).

Yield: 0.075 g (84%); IR (KBr): $\nu = 3030$ ($\nu_{CH\text{-arom}}$), 2910–2850 ($\nu_{CH\text{-aliph}}$), 1600, 1460, 1300, 1120, 920, 740 cm^{-1}; UV/Vis (H_2O): $\lambda_{max}(\varepsilon) = 370$ (7970), 678 (15340) nm.

Octakis-((2-trimethylaminoethylsulfanyl)-phthalocyaninato zinc(II)) octaiodide (**5a**; $C_{72}H_{112}N_{16}S_8I_8Zn$)

5a was prepared following the procedure described for **3a**, starting from 0.05 g **5** (0.035 mmol) in 2 cm^3 $CHCl_3$ and 0.044 g CH_3I (22 mm^3, 0.315 mmol).

Yield: 0.076 g (84.8%); IR (KBr): $\nu = 3030$ ($\nu_{CH\text{-arom}}$), 2928–2825 ($\nu_{CH\text{-aliph}}$), 1676, 1625, 1497, 1421, 1293, 1191, 961, 757, 706 cm^{-1}; UV/Vis (H_2O): $\lambda_{max}(\varepsilon) = 365$ (14500), 668 (11100) nm.

Acknowledgements

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