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Synthesis and Characterization of New Unsymmetrically Substituted Phthalocyanines

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Summary. Unsymmetric metallophthalocyanines (*M* = Zn, Co, Ni) carrying alkylthio and acetyloxyethylthio groups on peripheral positions were prepared from 4,5-*bis*-alkylthio-phthalonitrile, 4,5-*bis*-(acetyloxyethylthio)-phthalonitrile, and the corresponding anhydrous metal salts $Zn(CH_3COO)_2$, $NiCl_2$, and $CoCl_2$. The extremely soluble compounds were characterized by their IR, ^1H NMR, and UV/Vis spectra. Their long wavelength absorption band was found to be bathochromically shifted; their solubility is superior to that of symmetrical phthalocyanines.

Keywords. Phthalocyanines; Unsymmetrical substituents; Alkylthio derivatives.

Introduction

Although phthalocyanines are still extensively used as dyestuffs and pigments, interest in these materials for more subtle applications has grown dramatically in recent years. The use of phthalocyanines as photoconducting agents in photocopiers is now well established, and the bulk of research in the field currently concentrates on phthalocyanines as sensors [1], catalyst, reagents for photodynamic therapy [2], display devices (electrochromic and liquid crystal) [3], data storage and laser dyes [4,5], semiconductors [6], and materials for non-linear optics [7].

Among the classical phthalocyanines, unsymmetrical ones are important for the development of new methods of synthesis and separation. Although the synthesis of symmetrical tetra- or octasubstituted phthalocyanines by cyclotetramerization of a suitable phthalonitrile as the single precursor can be accepted as a relatively straightforward method, unsymmetrical phthalocyanines containing different substituents on the benzo groups are extremely difficult to obtain [6].

Our group has been heavily engaged in the synthesis of novel phthalocyanines carrying macrocyclic substituents such as crown ether [8], diaza-dioxa [9,10], or dithia-dioxa [11] groups; some unsymmetrical structures have also been acquired by making use of the boronsubphthalocyanines [12,13]. The immediate consequence of peripheral substituents is enhanced solubility in common organic solvents and additional donor sites for alkali or transition metal ions.

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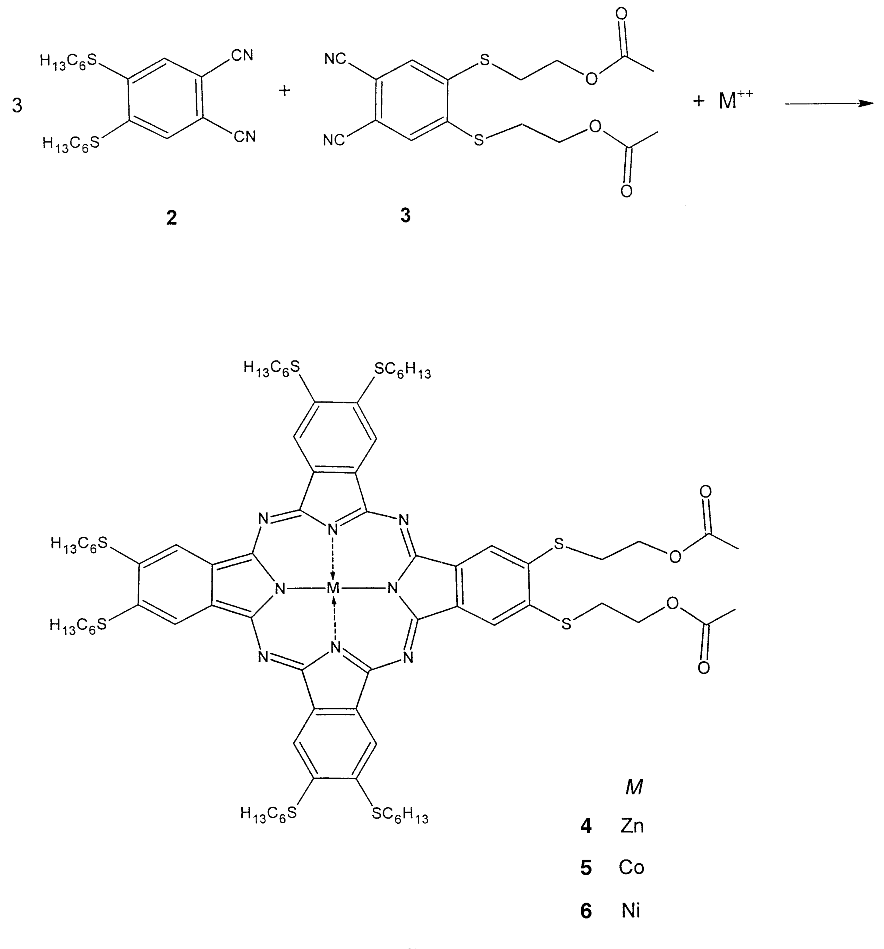
In the present work, soluble phthalocyanines peripherally substituted with three alkylthio groups and one acetyloxyethylthio group are presented. Elemental analysis and spectroscopic data (^{1}H NMR, IR, UV/Vis) were used to acess the structures of the new products.

Results and Discussion

The cyclotetramerization of substituted phthalonitrile derivatives is normally used to prepare phthalocyanines with the same substitution pattern on all four benzenoid groups [1]. Various strategies have been employed in efforts to achieve products with different substituents on each of the benzo units. The most common route to unsymmetrical phthalocyanines involves a mixed phthalonitrile cyclotetramerization, but then the result is a statistical mixture of phthalocyanine derivatives. In order to isolate the unsymmetric phthalocyanine by column chromatography, two different types of substituents having different polarities need to be chosen. In this work the statistical method was used to synthesize the unsymmetrical metallophthalocyanines **4**–**6**.



Scheme

Two different precursors (**2** and **3**) with different polarities were used to prepare these unsymmetrical metallophthalocyanines. The starting point for both precursors was 1,2-dichloro-4,5-dicyanobenzene which could undergo base-catalyzed nucleophilic aromatic displacement [14,15]. This route was applied to prepare 1,2-*bis*-(hexylthio)-4,5-dicyanobenzene (**2**) from hexanethiol and 1,2-dichloro-4,5-dicyanobenzene according to Ref. [16]. The second precursor, 1,2-*bis*-(2-acetyloxyethlylthio)-4,5-dicyanobenzene (**3**), was prepared by acetylation of 1,2-*bis*-(hydroxyethylthio)-4,5-dicyanobenzene (**1**) with acetylchloride in dry pyridine.

The unsymmetric metalphthalocyanines were synthesized by cyclotetramerization of three equivalents of **2** and one equivalent of **3** in the presence of the anhydrous metal salts $NiCl_2$, $CoCl_2$, and $Zn(CH_3COO)_2$ in anhydrous *DMF* under reflux (Scheme).

Characterization of the new unsymmetric phthalocyanines **4**–**6** had to verify the condensation of the two precursers **2** and **3** in a 3:1 ratio. The elemental analysis results, ^1H NMR, and mass spectra agreed with the proposed structures. In the ^1H NMR spectrum of the unsymmetrical phthalocyanines **4** and **6** the aromatic protons appeared as a singlet at 7.55 and 7.57 ppm, respectively. The methyl protons of the phthalocyanines were observed at two different chemical shift values. Methyl end groups of the two different substituents could be used to identify the ratio of these groups on the periphery with respect to each other. Aliphatic CH_3 protons were

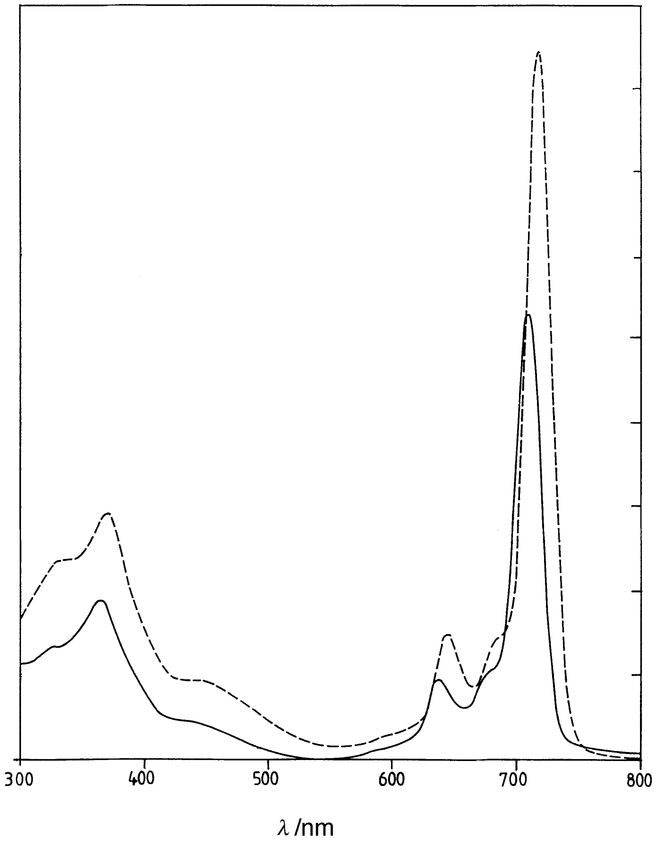


Fig. 1. UV/Vis spectra of *octakis*-(alkylthio)-phthalocyanines (–) and **4** (–) in $CHCl_3$

observed around 0.9 ppm, those of the acetyl group around 2.17 ppm. The ratio of these two methyl protons shows that alkyl chains with two different substituents are present in a 3:1 ratio as expected. Formation of the unsymmetric zinc phthalocyanine **4** was verified by the M^+ peak at $m/z = 1510$ which was obtained by fast atomic bombardment (FAB) mass spectroscopy. The characteristic intense absorption of the $C{\equiv}N$ groups in the spectra of **2** and **3** disappeared after phthalocyanine formation. The acetyl groups of the phthalocyanines **4**–**6** were characterized by intense carbonyl bands around 1727 cm^{-1}.

The phthalocyanines display typical electronic spectra with two strong absorption regions, one of them in the UV region at about 300–350 nm (B band) and the other one in the visible region at 600–700 nm (Q-band). The unsymmetrical phthalocyanines **4**–**6** show intense Q absorption bands at about 700 nm (Fig. 1). When compared with *octakis*-(alkyl or alkoxy)-substituted phthalocyanines, the shift of this intense band is especially important and will receive further attention for various near-IR applications.

In conclusion, the results of the present work show that alkylthio substituents enhance the solubility of phthalocyanines and cause Q-bands to shift to the red region. Some initial reactions with unsymmetric phthalocyanines showed that the unsymmetric part of the compound is sensitive to replacement reactions. Thus, further substitution reactions can be performed. The electric conductivity and mesogenic properties of the novel compounds will be investigated in due course.

Experimental

Routine IR spectra were recorded on a Mattison 1000 FTIR spectrophotometer using KBr pellets, electronic spectra on a Unicam UV2 spectrophotometer. Elemental analyses were performed by the Instrumental Analysis Laboratory of the TÜBİTAK Marmara Research Centre; the results agreed favorably with the calculated values (C,H,N). ^{1}H NMR spectra were recorded on a Bruker 200 MHz spectrometer using *TMS* as internal reference. 1,2-*Bis*-(hydroxyethylthio)-4,5-dicyanobenzene (**1**, [11]) and 1,2-di-(hexylthio)-4,5-dicyanobenzene (**2**, [16]) were synthesized according to published methods.

1,2-Bis-(2-acetyloxyethylthio)-4,5-dicyanobenzene (**3**; $C_{16}H_{16}N_2O_4S_2$)

0.56 g 1,2-*bis*-(hydroxyethylthio)-4,5-dicyanobenzene (**1**, 2 mmol) were dissolved in 5 cm^3 dry pyridine under nitrogen, and 0.345 g acetylchloride (4.39 mmol) were added dropwise over 2 h to the stirred and ice-cooled solution. Stirring was continued for 12 h at room temperature. The mixture was poured onto 100 g ice-water. The yellow precipitate was filtered off and washed with water. Recrystallization from ethanol gave a lightly yellow colored product. This compound was soluble in *THF*, acetone *DMF*, and *DMSO*.

Yield: 0.51 g (78%); m.p.: 89–90°C; ^{1}H NMR ($CDCl_3$, δ, 200 MHz): 7.67 (s, $2H_{arom}$), 4.33 (t, $J = 6.81$ Hz, $2OCH_2$), 3.31 (t, $J = 6.69$ Hz, $2SCH_2$), 2.08 (s, $2CH_3$) ppm; IR (KBr): $\bar{\nu}_{max} = 3055$, 2950, 2875, 2238, 1727, 1570, 1470, 1425, 1250, 1125, 1070, 1000 cm^{-1}.

2,3,9,10,16,17-Hexakis-(hexylthio)-23,24-acetyloxyethylthio-phthalocyaninato-zinc(II) (**4**; $C_{76}H_{100}N_8O_4S_8Zn$)

A mixture of 0.296 g **2** (0.824 mmol), 0.100 g **3** (0.274 mmol),0.034 g anhydrous $Zn(CH_3COO)_2$ (0.274 mmol), and 2.5 cm^3 anhydrous *DMF* was heated at 170°C in a sealed tube under nitrogen for

12 h. After cooling to room temperature, the reaction mixture was diluted with 10 cm^3 ethanol, and the product was filtered off. The dark green compound was purified by column chromatography on silica gel (first with CCl_4:*THF* = 1:10, then with $CHCl_3$). The compound is soluble in $CHCl_3$ (2.3×10^{-2} mol dm^{-3}).

Yield: 0.064 g(15%); ^{1}H NMR ($CDCl_3$, δ, 200 MHz): 7.55 (s, 8H_{arom}), 4.21 (t, $J = 6.85$ Hz, 2OCH_2), 3.42 (t, $J = 6.78$ Hz, 2SCH_2), 3.02 (t, $J = 7.48$ Hz, 6SCH_2), 2.17 (s, 2CH_3), 1.85 (dd, $J_1 = 7.07$, $J_2 = 7.60$ Hz, 3SCH_2CH_2), 0.90–1.02 (t, $J = 6.83$ Hz, 6CH_3) ppm; IR (KBr): $\nu_{max} = 3020$, 2959, 2855, 1727, 1550, 1460, 1370, 1260, 1150, 1000 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 709 (27100), 675 (5000), 635 (4800), 440 (2700), 364 (9900) nm.

2,3,9,10,16,17-Hexakis-(hexylthio)-23,24-acetyloxyethythio-phthalocyaninato-cobalt(II)
(**5**; $C_{76}H_{100}N_8O_4S_8Co$)

A mixture of 0.296 g **2** (0.824 mmol), 0.100 g **3** (0.274 mmol), 0.036 g anhydrous $CoCl_2$ (0.274 mmol), and 3 cm^3 anhydrous *DMF* was heated and stirred at 170°C in a sealed tube for 18 h under nitrogen. After cooling to room temperature, the reaction mixture was treated several times with hot ethanol and filtered. The residue was chromatographed on silica gel (first with CCl_4:*THF* = 10:1, then with *THF* as eluents), and the green fraction was recrystallized from *THF*/methanol. After a second column chromatography (silica gel, $CHCl_3$) the pure compound was obtained. It is soluble in $CHCl_3$ (4.3×10^{-2} mol dm^{-3}).

Yield: 0.025 g (6%); IR (KBr): $\bar{\nu}_{max} = 2930$, 2990, 1727, 1650, 1540, 1470, 1430, 1370, 1250, 1200, 1070, 950, 810, 700 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 699 (14200), 625 (5000), 415 (3100), 324 (13300) nm.

2,3,9,10,16,17-Hexakis-(hexylthio)-23,24-acetyloxyethylthio-phthalocyaninato-nickel(II)
(**6**; $C_{76}H_{100}N_8O_4S_8Ni$)

A mixture of 0.296 g **2** (0.824 mmol), 0.100 g **3** (0.274 mmol), 0.036 g anhydrous $NiCl_2$ (0.274 mmol), and 3 cm^3 anhydrous *DMF* was heated at 170°C in a sealed tube for 24 h under nitrogen. The resulting green suspension was cooled to room temperature and diluted with 10 cm^3 ethanol. The crude product was washed with hot ethanol several times to remove the unreacted organic materials. The green compound was dried and chromatographed on silica gel (first with CCl_4:*THF* = 10:1 then with *THF*). Recrystallization from *THF*/methanol gave the pure green product which is soluble in $CHCl_3$ (2.7×10^{-2} mol dm^{-3}).

Yield: 0.037 g (9%); ^{1}H NMR ($CDCl_3$, δ, 200 MHz): 7.57 (s, 8H_{arom}), 4.25 (t, $J = 6.88$ Hz, 2OCH_2), 3.46 (t, $J = 6.82$ Hz, 2SCH_2), 3.20 (t, $J = 7.29$ Hz, 6SCH_2), 2.21 (s, 2CH_3), 1.90 (dd, $J_1 = 7.05$, $J_2 = 7.55$ Hz, 3SCH_2CH_2), 0.89–1.01 (t, $J =$ Hz, 6CH_3) ppm; IR (KBr): $\nu_{max} = 3030$, 2960, 2880, 1727, 1620, 1560, 1450, 1360, 1270, 1130, 1010 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 700 (13600), 660 (5800), 620 (4000), 421 (3000), 319 (9300) nm.

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