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Synthesis and characterization of a triazine containing three phthalocyanines

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Abstract

A new trimeric-s-triazine containing three amino zinc(II) phthalocyanines has been prepared by following the multistep reactions of unsymmetrical substituted phthalocyanines. The zinc(II) phthalocyanine containing an unsymmetrical substituted nitro group was synthesized by means of the well-known statistically mixing method of two different phthalonitriles. 4-Nitrophthalonitrile and 4,5-bis(hexylthio)phthalonitrile were tetramerized in DMF in the presence of zinc acetate at elevated temperature to give a zinc(II) complex, which was then separated by column chromatography on silica gel. The nitro compound was reduced to the amine form by using sodium sulfide as the reducing agent and its ammonium salt was obtained by reaction with gaseous HCl. This compound was then reacted with cyanuric chloride in the presence of potassium carbonate as a base in THF and an interesting trimeric-s-triazine, containing three amino zinc(II) phthalocyanines, was synthesized. The separation of the product was carried out by column chromatography on silica gel. The new compounds were characterized by elemental analysis and UV/VIS, IR, NMR spectra.

Keywords: Phthalocyanine; Unsymmetrical; Substituted; Trimeric; Metal complex; s-Triazine

1. Introduction

Thanks to the rich coordination chemistry of phthalocyanine (pc) compounds, it has been possible for researchers to synthesize various compounds with specific properties that are required for high technology applications. The increasing importance and use of phthalocyanines (pcs) as advanced materials have created an attractive force on chemists to play for design variables of the central metal ion and the peripheral substituents to reach the planned interesting properties.

The metallopcs have been used as pigments since their invention. Beside this, the interesting catalytic, photovoltaic and electrochromic properties have been worth to study them extensively. The intense interest in soluble pcs originates from the suitability of these compounds as materials with novel electrical, optical, catalytic and mesogenic properties. These properties are strongly dependent on peripheral and axial substitution.

Unsymmetrical substituted pcs have become the subject of great interest for chemists for the last few years. These compounds possess very interesting nonlinear optical properties [1] and are important for Langmuir–Blodgett films [2]. Moreover, their zinc and aluminum derivatives are appropriate for application in photodynamic therapy of cancer [3]. The isolation of unsymmetrical substituted pcs is a very delicate task. The polymer support route, the subphthalocyanine route and the statistical condensation route are the methods to synthesize them. The last route requires well-developed chromatographic methods as well as definite structural preconditions of the precursor molecules.

Starting from simple monofunctional substituents, more complex structures such as crown ethers, tetraaza, diazadioxa, diazatrioxa, tetraaza-crown ether double layer and tetrathia macrocycles have been introduced to the periphery of the pc nucleus [4]. Beside the crown ethers, long alkyl or alkoxy groups as substituents give

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the pcs liquid crystal behavior [5–7]. The bulky substituents, like long alkyl chains, increase the solubility of pcs in common organic solvents [8,9].

Octakis(hexylthio)-substituted symmetrical pcs were reported in the literature [10]. Dabak et al. [11] synthesized an unsymmetrical metal-free pc carrying one nitro and three hexakis(alkylthio) groups by the ring enlargement reaction of the subphthalocyanine [12,13]. In this work, we report the zinc(II) complex of the same unsymmetrical pc prepared by using statistically mixed tetramerization of two different dinitriles and describe the synthesis of an interesting s-triazine carrying three phthalocyaninato zinc(II) macrocycles through amino groups.

2. Experimental

2.1. General

The starting compounds 4-nitrophthalonitrile [14] and 4,5-bis(hexylthio)phthalonitrile [10] were prepared according to the reported procedures. All reactions were carried out under dry argon atmosphere unless otherwise noted. IR and UV/VIS spectra were recorded on an ATI Unicam-Mattson 1000 FTIR spectrophotometer using KBr pellets and an ATI Unicam UV/VIS spectrometer UV2, respectively. Elemental analyses were performed in the instrumental analysis laboratory of the TUBITAK Marmara Research Center. ^{1}H NMR spectra were obtained by using a Bruker AC-250 MHz spectrometer.

2.2. Synthesis of compounds (Scheme 1)

2.2.1. Zinc(II)-2-nitro-9,10,16,17,23,24-hexa(hexylthio)phthalocyanine (*1*)

Compound **1** was prepared from two different dinitriles by using the method of statistically mixed condensation [15]. A well-powdered mixture of 4-nitrophthalonitrile [14] (0.173 g, 1 mmole) and 4,5-bis(hexylthio)phthalonitrile [10] (1.442 g, 4 mmole) was dissolved in dry DMF. Zinc(II) acetate [$Zn(CH_3COO)_2 \cdot 2H_2O$] (0.878 g, 4 mmole) was added to this solution and the reaction was carried out in DMF at 170 °C for 6 h to give an unsymmetrical substituted pc. The reaction mixture was cooled down to room temperature and precipitated by adding 70-ml ethanol. After filtration, the dark green product was washed with cold ethanol and isolated by two successive column chromatographic separations [silica gel; THF:chloroform 1:1 (v/v) and THF:carbon tetrachloride 3:7 (v/v)].

Yield: 1.202 g (91%). *Anal*. Calc. for $C_{68}H_{87}N_9O_2S_6Zn$: C, 61.86; H, 6.64; N, 9.55; Found: C, 61.54; H, 6.72; N, 9.42%; UV/VIS ($CHCl_3$) λ, nm (log ε): 710 (5.269), 638 (4.613), 440 (sh) (4.263), 363 (4.860) and 337 (4.780); IR (KBr pellet) ν, cm^{-1}: 2979, 2928, 2877, 1600, 1549, 1472, 1370, 758; ^{1}H-NMR ($CDCl_3$) δ, ppm: 8.2–6.7 (br, 9H, Ar–H), 2.62 (br s, 12H, $-SCCH_2-$), 2.22 (br s, 12H, $-SCH_2-$), 1.92–1.26 (m, 36H, $-CCH_2C-$), 0.89 (s, 18H, $-CH_3$).

2.2.2. Zinc(II)-2-amino-9,10,16,17,23,24-hexa(hexylthio)phthalocyaninehydrochloride (*2*)

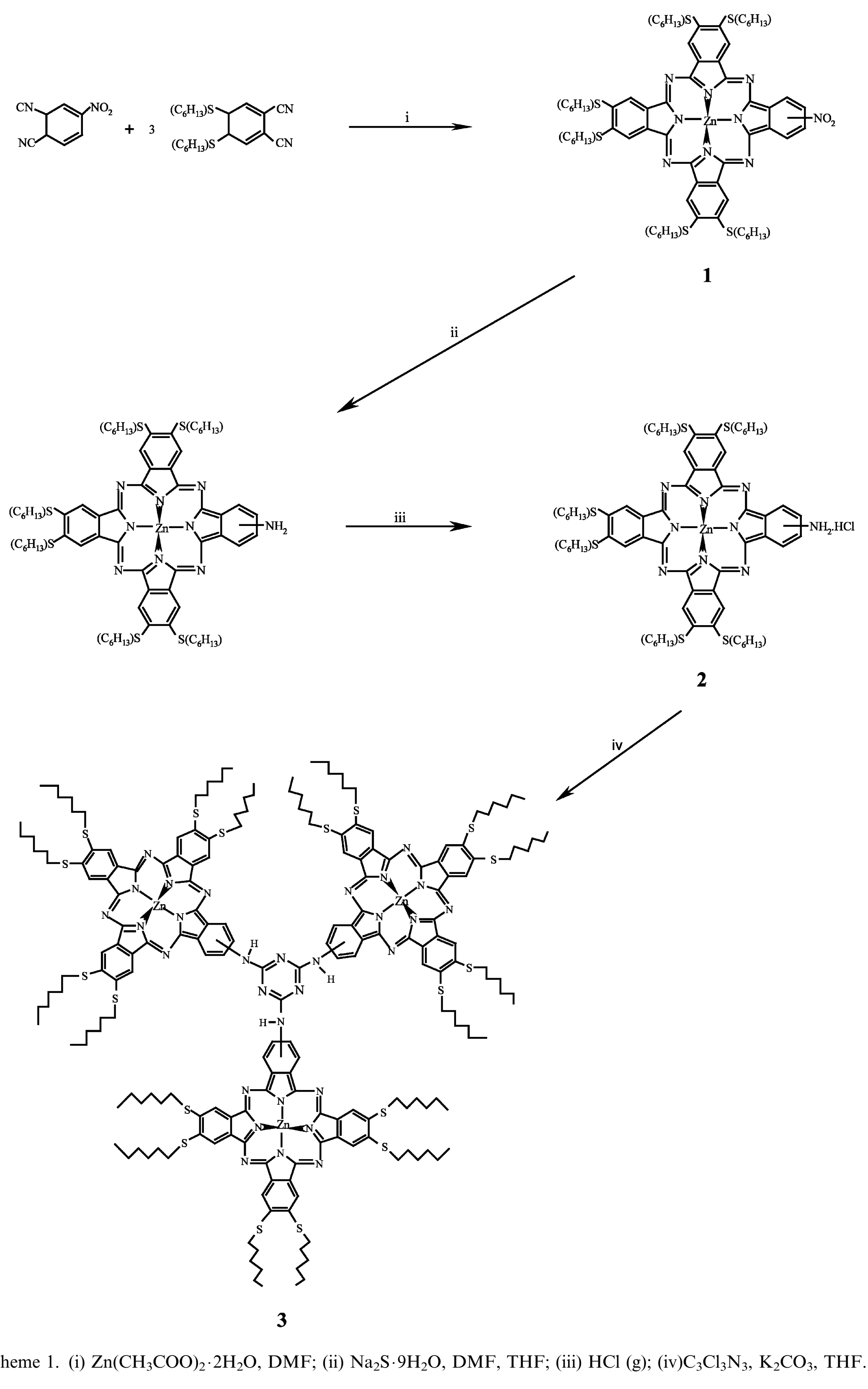
Compound **1** was reduced to amine form **2**. Dry DMF and THF (1.5 ml each, THF:DMF 1:1 v/v) were mixed under argon atmosphere. Compound **1** (0.100 g, 0.076 mmol) and sodium sulfide [$Na_2S \cdot 9H_2O$] (0.0545 g, 0.227 mmole) as reducing agent were dissolved in this solvent mixture. The reaction was carried out at 100 °C for 8 h [14,15]. The mixture was cooled down to room temperature and gaseous hydrochloric acid was passed through. The dark green precipitate was filtered and the product was obtained as the ammonium salt of compound **1**.

Yield: 0.967 g (96%). *Anal*. Calc. for $C_{68}H_{90}N_9ClS_6Zn$: C, 61.56; H, 6.84; N, 9.50; Found: C, 61.91; H, 6.80; N, 9.46%; UV/VIS ($CHCl_3$) λ, nm (log ε): 712 (5.219), 640 (4.581), 439 (sh) (4.507), 363 (4.892) and 337 (4.911); IR (KBr pellet) ν, cm^{-1}: 3081, 2979, 2928, 2877, 2800, 1600, 1472, 1370, 758; ^{1}H-NMR ($CDCl_3$) δ, ppm: 9.49 (br s, 3H, $-NH_3^+$), 8.6–7.0 (br, 9H, Ar–H), 3.23 (br s, 12H, $-SCCH_2-$), 2.72 (s, 12H, $-SCH_2-$), 2.17–1.26 (m, 36H, $-CCH_2C-$), 1.00 (s, 18H, $-CH_3$).

2.2.3. 2,4,6-Tris[2-amino-9,10,16,17,23,24-hexa(hexylthio)phthalocyaninatozinc(II)]-s-triazine (*3*)

Cyanuric chloride (2,4,6-trichloro-1,3,5-triazine, $C_3Cl_3N_3$) (0.0117 g, 0.063 mmole) was dissolved in 80 ml THF under argon. Compound **2** (0.2516 g, 0.190 mmole) and K_2CO_3 (0.1253 g) were added and the reaction was realized at 70 °C for 24 h. KCl was filtered at the end of the reaction and the solvent was evaporated. The dark green product was separated by two column chromatographic separations carried out successively [silica gel; THF:chloroform 1:10 (v/v) and methanol:chloroform 1:10 (v/v)]. Compound **3** is in wax form and readily soluble in chloroform, diethyl ether, toluene, DMF, THF.

Yield: 0.195 g (78%). *Anal*. Calc. for $C_{207}H_{264}N_{30}S_{18}Zn_3$: C, 63.01; H, 6.74; N, 10.65; Found: C, 62,97; H, 6.99; N, 9.83%; UV/VIS ($CHCl_3$) λ, nm (log ε): 710 (5.221), 638 (4.568), 439 (sh) (4.272), 363 (4.816) and 335 (4.750); IR (KBr pellet) ν, cm^{-1}: 3489–3413, 2979, 2928, 2877, 1600, 1472, 1370, 758; ^{1}H-NMR ($CDCl_3$) δ, ppm: 8.0–7.0 (br, 27H, Ar–H), 2.70 (br s, 36H, $-SCH_2-$), 3.12 (br s, 36H, $-SCCH_2-$), 1.73 (s, 3H, $-NH-$), 1.58–1.31 (m, 108H, $-CCH_2C-$), 0.92 (s, 54H, $-CH_3$).



Scheme 1. (i) $Zn(CH_3COO)_2 \cdot 2H_2O$, DMF; (ii) $Na_2S \cdot 9H_2O$, DMF, THF; (iii) HCl (g); (iv)$C_3Cl_3N_3$, K_2CO_3, THF.

3. Results and discussion

The first step of the synthesis route outlined in Scheme 1 is the formation of a metallopc carrying an unsymmetrical substituted nitro group, namely compound **1** (pc **1**). Starting from 4-nitrophthalonitrile and 4,5-bis(hexylthio)phthalonitrile as two different dinitriles and using zinc(II) acetate, the reaction in DMF gave zinc(II) pc by the method of statistically mixed condensation. In our early publication [11], the compound **1** was described as metal-free pc by the ring enlargement reaction of subphthalocyanine [12]. However, the yield of the reaction was rather low. Therefore, the preparation of the desired compound **1** was accomplished by the mixed method that resulted in zinc(II) pc at a yield of 91%. The pc **1** was reduced with $Na_2S \cdot 9H_2O$ to the amine form and the pc **2** was separated as its ammonium salt by passing gaseous hydrochloric acid through the mixture. By the reaction of pc **2** with $C_3Cl_3N_3$ in THF and using K_2CO_3 as a base, an s-triazine containing three unsymmetrical metallopcs, namely pc **3**, was synthesized. All new compounds were sufficiently pure and gave satisfactory analytical results.

The elemental analyses; UV/VIS, IR and NMR spectra agreed well with the proposed structures of the synthesized compounds.

The spectroscopic data of the new compounds were in accordance with the structures. IR spectra taken with KBr pellets showed an aromatic –C=C peak at 1600 cm^{-1}, an aromatic –CH peak at 3081 cm^{-1}, and a substituted benzene peak at 758 cm^{-1} for all of the compounds. The stretching peaks at 2979, 2928, 2877 cm^{-1} and the bending peaks at 1472, 1370 cm^{-1} showed the structure of –CH and $-CH_3$, respectively in the substituents again for all of the compounds. The peak at 1549 cm^{-1} in the spectrum of pc **1** indicated the presence of a $-NO_2$ functional group that disappeared in the case of the amine-substituted pc **2**. To the stretching peaks of aliphatic –CH at 2979, 2928, 2877 cm^{-1}, the additional peak at 2800 cm^{-1} which was not present in the spectrum of nitro pc **1** indicated ammonium formation of pc **2**. The presence of –NH– in the structure of pc **3** was observed at 3489–3413 cm^{-1} as a doublet that is characteristic for the –NH– group. The peak at 2800 cm^{-1} for NH_3^+ in the spectrum of pc **2** also disappeared in the spectrum of pc **3**.

^{1}H-NMR spectra were also in good correlation with the structures of the synthesized compounds. The spectrum of pc **1**, which was taken in d-chloroform, showed aromatic protons at 6.7–8.2 ppm as a broad peak due to the aggregation. The aromatic protons moved to the higher region because of the electron attracting property of the $-NO_2$ group in the structure. The $-CCH_2C-$ protons in the long aliphatic chain appeared at 1.26–1.92 ppm and the $-CH_3$ at the end of the chain at 0.89 ppm. The peaks at 2.22 and 2.62 ppm indicated the presence of a $-SCH_2-$ group neighboring an aromatic ring and a $-SCCH_2-$ group in the structure, respectively [11]. The ^{1}H-NMR spectrum of pc **2** was similar to that of pc **1**. The aromatic protons were found at 7.0–8.6 ppm, the $-CCH_2C-$ protons in the long aliphatic chain at 1.26–2.17 ppm, the $-CH_3$ at the end of the chain at 1.00 ppm, the $-SCH_2-$ group neighboring an aromatic ring at 2.72 ppm and the $-SCCH_2-$ group at 3.23 ppm. The only difference was the peak at 9.49 ppm which disappeared with D_2O exchange. This confirmed the existence of $-NH_3^+$ in the synthesized compound. In the spectrum of pc **3** the aromatic protons appeared at 7.0–8.0 ppm, the $-CCH_2C-$ protons in the long aliphatic chain at 1.31–1.58 ppm, the $-CH_3$ at the end of the chain at 0.92 ppm, the $-SCH_2-$ group neighboring an aromatic ring at 2.70 ppm and the $-SCCH_2-$ group at 3.12 ppm. The disappearance of the peak at 1.73 ppm with D_2O exchange confirmed the –NH– group in the structure of the compound.

The Zn pcs **1**–**3** exhibited typical electronic spectra with Q and B (soret) bands (Fig. 1). The alkylthio substitution of the unsymmetrical pcs was responsible of a shift of the Q band to lower energy. Generally, a polar nitro substituent causes a drastic change in the Q band absorption that is extremely sensitive to the solvent used [5,11,16]. While the monomeric species with D_{2h} symmetry, i.e. metal-free derivative, show two intense absorptions of comparable intensity around 600–700 nm, those having D_{4h} symmetry give only a single band in this region. A small distortion in the case of pc **2** was a consequence of changing the nitro substituent to an amino group. The band around 710 nm (Q) of all compounds was attributed to the $\pi \rightarrow \pi^*$ transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the pc^{2-} ring. The other bands in the UV region at 363 nm (B_1) and 337 nm (B_2) arose from the deeper π levels $\rightarrow$ LUMO transition [16,17]. The origin of the band at around 440 nm absorption is unclear, because it has been found in a similar envelope of bands for several pcs containing peripheral crown ether complexes with

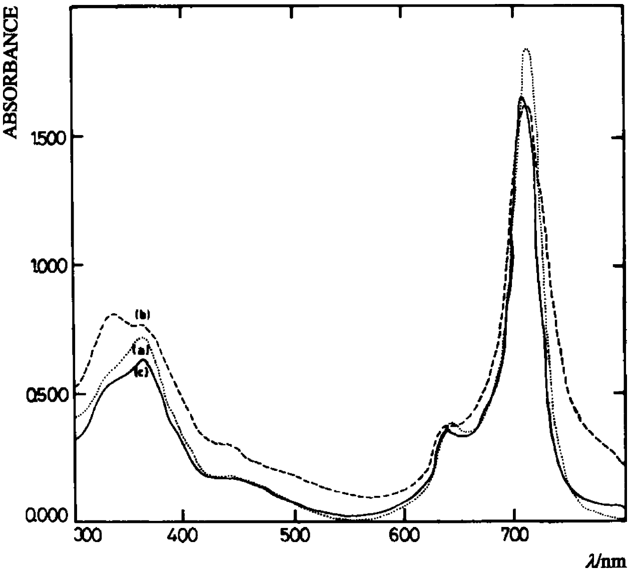


Fig. 1. UV/VIS Spectra of (a) **1**, (b) **2**, (c) **3** in $CHCl_3$.

Co(II), Cu(II), Ni(II) and Zn(II). Either the peripheral groups perturb the π system such that transitions which normally exhibit a low extinction coefficient become allowed, e.g. $n \rightarrow \pi^*$, or this absorption is related to the peripheral crown ether attachment itself. A similar broad absorption is not observed for unsubstituted pcs [16–19].

Usually aggregation of pcs results in a spectral effect that extends from band broadening to blue shifts of the Q and B bands. The shoulder at around 640 nm indicated the aggregation of all three pcs **1**–**3**. Aggregation occurs readily at low concentrations making the spectral data more difficult to interpret for many peripherally substituted pc complexes. It is also known that aggregation is enhanced by the solvent polarity and the presence of aliphatic side chains [16–19].

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