Dyes and Pigments 89 (2011) 162–168

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Preparation of heterogeneous phthalocyanine catalysts by cotton fabric dyeing

Altuğ Mert Sevim, Cidal Ilgün, Ahmet Gül*

Department of Chemistry, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey

A R T I C L E I N F O

Article history:
Received 16 August 2010
Received in revised form
13 October 2010
Accepted 16 October 2010
Available online 23 October 2010

Keywords:
Phthalocyanine
Thioglycolic acid
Cotton fabric
Dyeing
Fastness
Cyclotetramerisation

A B S T R A C T

Metal-free (**2**) and metallo-phthalocyanines (**2a**–**d**) bearing four thioglycolic acid groups on the periphery were prepared by cyclotetramerization of a new precursor, namely 4-(carboxymethylsulfanyl) phthalonitrile (**1**) in the presence of the corresponding divalent metal salts (Zn(II), Co(II), Ni(II), Cu(II)). The new compounds were characterized by elemental analyses, IR, UV–Vis, mass, ^{13}C-NMR and ^{1}H-NMR techniques. All these newly synthesized water-soluble metallo-phthalocyanine derivatives were supported on cationic cotton fabrics and the washing and water fastnesses of these novel dyed fabrics were investigated. Washing and water fastness data suggested that cationic cotton fabrics are superior to the others when dyed with these metallo-phthalocyanines.

1. Introduction

Among tetrapyrrole compounds, phthalocyanines (Pc) which are full-aromatic planar molecules due to their 18-π electron structure can be substituted with a great deal of functional groups. In addition to their extensive use as pigments and dyes, this versatility gives rise to many applications, such as catalysts, liquid crystals, electrochromic and photochromic substances, data storage systems, photodynamic cancer therapy agents, photoactive units, chemical sensors, and nonlinear optical devices [1–3].

The main restricting factor of phthalocyanines is a rather low solubility in organic solvents. Peripheral and axial substitution of phthalocyanines with alkyl, alkoxy, alkythio chains or bulky groups drastically enhances their solubility [4–11]. The introduction of carboxy or amino groups gives water-soluble products [7]. Soluble phthalocyanines with enhanced optical, electronic, redox and magnetic properties are expected to increase their possible application fields [12–14].

Catalytic activities of metallo-phthalocyanines derived from their structural similarity to metallo-porphyrin complexes have been widely studied because of their rather cheap and facile preparation in a large scale and of their chemical and thermal stability [15]. One drawback of metallo-phthalocyanine derivatives in heterogeneous catalysis is to obtain high surface area. If they are fixed onto a suitable supporting material, this drawback can be overcome. For such a material, suitable supports tested include charcoal [16,17], organic polymers [18,19], silica [20] and zeolites [21]. Comparing to these materials, fabrics may be the preferable candidate because not only it is easy to handle, it can also be manipulated structurally by means of well-established chemical and physical methods.

A large amount of effort has been directed towards the elimination of undesired atmospheric odours, particularly within buildings. Approaches adopted include sensory, chemical, biological and physical techniques [22–25]. Sensory techniques cannot provide an ultimate solution for the elimination of bad-smelling compounds, which only change our perception of the smell by using different smelling compounds. Physical deodorization eliminates smelling compounds through physical adsorption. Therefore, deodorizing capacity is rather limited and also the adsorbed compounds can be desorbed depending on the conditions. Chemical and biological methods can make these smelling compounds be converted into odourless end products. Various materials have been used as deodorants in those methods. The gases which are not effectively adsorbed using traditional air-purifying methods can be removed by oxidation if a suitable catalyst is available. Among them, metallo-phthalocyanine derivatives have received special attention [26].

In this study, a novel phthalonitrile derivative was prepared from a single step reaction. By using this phthalonitrile derivative,

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* Corresponding author. Tel.: +90 212 285 68 27; fax: +90 212 285 63 86.
E-mail address: ahmetg@itu.edu.tr (A. Gül).

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doi:10.1016/j.dyepig.2010.10.008

metal-free and metallo-phthalocyanines (M = Ni(II), Zn(II), Cu(II), Co(II)) carrying thioglycolic acid substituents on the periphery were synthesized. Spectral results such as FT-IR, UV–Vis, EI-MS, ^{13}C-NMR and ^{1}H-NMR for the newly synthesized compounds are in good agreement with the proposed structures. Last part of this work dealt with the cotton fabric which was modified with a cationic auxiliary and converted to cationic cotton fabric for dyeing process. The cationic cotton fabric was then dyed with the metallo-phthalocyanines (**2a**–**d**) in the presence of sodium carbonate. Finally, washing and water fastness tests were performed and evaluated according to ISO criteria.

2. Experimental

2.1. Materials

All reactions were carried out under nitrogen atmosphere in dried solvents. All reagents and solvents were of reagent grade quality obtained from commercial suppliers. Rucogen FWS from Rudolf was used as wetting and degreasing agent. Slipper from Mega-Teknoloji, Inc. was used for fracture-prevention purposes. Catalase was used under Sera Zyme C-SX brand name from Dystar. Cationizing chemical used was Mordiente DEL from Asutex. The homogeneity of the synthesized products was tested in each step by TLC. Analytical thin-layer chromatography (TLC) was performed using Merck 60 F 254 silica gel (precoated sheets, 0.2 mm thick). All solvents were dried and purified as described by Perrin and Armarego [27]. The solvents were stored over molecular sieves. 4-Nitrophthalonitrile [28] was synthesized according to published methods.

UV measurements were done with Scinco SD-1000 double beam UV-visible spectrophotometer. A Perkin–Elmer Spectrum One FTIR spectrophotometer with ATR sampling accessory was used for IR data collection. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker 200 MHz FT-NMR spectrometer. Mass spectra were obtained with a Perkin Elmer Clarus 500 GC/MS in EI^{+} mode. Dyeing of the fabrics was performed in Ahiba sample dyeing apparatus.

*2.2. Synthesis of phthalocyanine derivatives (**2**, **2a**–**d**)*

*2.2.1. 4-(Carboxymethylsulfanyl)phthalonitrile (**1**)*

4-Nitrophthalonitrile (0.5 g, 2.89 mmol) and an excess thioglycolic acid (0.5 mL, 5.8 mmol) were dissolved in 15 mL of dry DMF. Anhydrous K_2CO_3 (1.59 g, 11.56 mmol) was added in small portions over 2 h and the mixture was stirred vigorously at room temperature under N_2 stream for 1 h. The reaction mixture was poured into ice-water mixture (100 mL) and the pH of the solution was adjusted to 1 by addition of 1:1 HCl solution. The precipitate was filtered, washed with water until the filtrate was neutral, then washed with successively with hexane and diethyl ether, and dried. Finally, a pale beige product was crystallized from acetone–hexane. Yield: 0.396 g, 62.9 %, MA = 218.2 g/mol, M.p. = 132 °C. IR υ_{max}/(cm^{-1}): 3500 (carboxylic acid OH), 3096–3028 (Ar-H), 2935 (Aliphatic CH), 2229 ($C{\equiv}N$), 1709 ($C{=}O$), 1584–1479 (Ar $C{=}C$), 1213, 1171, 1067, 902, 872, 830, 717, 675. ^{1}H NMR ($CO(CD_3)_2$, δ ppm): 8.01 (s, 1H, Ar-H), 7.97 (d, 1H Ar-H), 7.85 (d, 1H Ar-H), 4.12 (s, 2H, CH_2); ^{13}C NMR (*d*-DMSO, δ ppm): 169.91 ($C{=}O$), 116.27 ($C{\equiv}N$), 115.05 ($C{\equiv}N$), 146.06 (Ar-C), 135.22 (Ar-C), 132.47 (Ar-C), 131.87 (Ar-C), 129.18 (Ar-C), 110.11 (Ar-C), 33.54 (Aliphatic C). MS (GC-MS, Scan EI^{+}): *m/z:* 218 [M^{+}]. For $C_{10}H_6N_2O_2S$ Anal. Calc.: C, 55.04; H, 2.77; N, 12.84; S, 14.69%. Found: C, 55.02; H, 2.75; N, 12.83; S, 14.67%.

*2.2.2. 2,9,16,23-Tetrakis(4-carboxymethylsulfanyl)-phthalocyanine (**2**)*

4-(Carboxymethylsulfanyl)phthalonitrile (**1**) (0.50 g, 2.291 mmol) was dissolved in 6 mL of dry 1-pentanol and heated at 140 °C under N_2. After addition of elemental lithium (0.122 g, 16.05 mmol) a green colour appeared in a few seconds. The suspension was stirred under reflux for 1 h. Then the mixture was cooled to room temperature, acidified with HCl and the resulting precipitate was centrifuged and the supernatant discarded. The precipitated blue-green solid was filtered and washed first with water, then successively with cold methanol, hexane and diethyl ether, and finally dried *in vacuo*. This compound is soluble in polar solvents especially DMF, THF, DMSO and pyridine. Yield: 0.165 g, 32.9%. M.p. > 200 °C. IR υ_{max}/(cm^{-1}): 3600–2500 (carboxylic acid OH), 3281 (N–H), 3058 (Ar-H), 2920–2855 (aliphatic CH), 1703 ($C{=}O$), 1598, 1500, 1448, 1385, 1298, 1134, 1010, 895, 816, 736, 663. ^{1}H NMR (*d*-DMSO, δ ppm): 13.21 (br s, 4H, COOH), 8.32–7.41 (m, 12H, Ar-H), 4.18 (s, 8H, CH_2), −6.54 (br s, 2H, N–H); UV–Vis λ_{max} (nm) ($\log \varepsilon$) in THF: 708 (4.41), 676 (4.43), 340 (4.39); Anal. Calc. for $C_{40}H_{26}N_8O_8S_4$: C, 54.91; H, 3.00; N, 12.81; S, 14.66%. Found: C, 54.90; H, 2.99; N, 12.80; S, 14.61%.

*2.2.3. General procedure for the 2,9,16,23-Tetrakis(4-carboxymethylsulfanyl)- phthalocyaninatometal derivatives (**2a**–**d**)*

4-(Carboxymethylsulfanyl)phthalonitrile (**1**) (0.50 g, 2.291 mmol) was dissolved in 6 mL of dry 1-pentanol and anhydrous metal salt [Zn $(AcO)_2$ 2,5 g (13.6 mmol), $CoCl_2$ 1.75 g (13.48 mmol), $NiCl_2$ 1.75 g (13.50 mmol) or $CuCl_2$ 1.80 g (13.40 mmol)] and heated at 140 °C under N_2. The suspension was stirred under reflux for 48 h. Then, the mixture was cooled to ambient temperature. The reaction mixture was acidified with HCl and the resulting precipitate was centrifuged and the supernatant discarded. The precipitated green coloured solid was filtered and washed first with water, then with methanol, hexane and diethyl ether, finally dried *in vacuo.*

*2.2.3.1. 2,9,16,23-Tetrakis(4-carboxymethylsulfanyl)-phthalocyaninatozinc(II) (**2a**).* This is soluble in polar solvents especially DMF, THF, DMSO and pyridine. Yield: 0.145 g, 27%. M.p. > 200 °C. IR υ_{max}/(cm^{-1}): 3600–2500 (carboxylic acid OH), 3058 (Ar-H), 2926–2861 (aliphatic CH), 1714 ($C{=}O$), 1598, 1485, 1455, 1380, 1259, 1132, 1037, 975, 908, 885, 822, 761, 741, 681. ^{1}H NMR (*d*-DMSO, δ ppm): 7.73–7.25 (m, 12H, Ar-H), 4.10 (s, 8H, CH_2); UV–Vis λ_{max} (nm) ($\log\varepsilon$) in THF: 684 (4.53), 345 (4.56); Anal. Calc. for $C_{40}H_{26}N_8O_8S_4Zn$: C, 51.20; H, 2.58; N, 11.94. Found: C, 51.19; H, 2.56; N, 11.93%.

*2.2.3.2. 2,9,16,23-Tetrakis(4-carboxymethylsulfanyl)-phthalocyaninatocobalt(II) (**2b**).* This is soluble in polar solvents especially DMF, THF, DMSO and pyridine. Yield: 0.181 g, 34%. M.p. > 200 °C. IR υ_{max}/(cm^{-1}): 3600–2500 (carboxylic acid OH), 3053 (Ar-H), 2956–2861 (aliphatic CH), 1717 ($C{=}O$), 1600, 1521, 1381, 1296, 1133, 1069, 1042, 932, 892, 819, 742,685 ; UV–Vis λ_{max} (nm) ($\log \varepsilon$) in THF: 679 (4.36), 325 (4.25); Anal. Calc. for $C_{40}H_{26}N_8O_8S_4Co$: C, 51.56; H, 2.60; N, 12.02; Found: C, 51.54; H, 2.62; N, 12.04%.

*2.2.3.3. 2,9,16,23-Tetrakis(4-carboxymethylsulfanyl)- phthalocyaninatonickel(II) (**2c**).* This is soluble in polar solvents especially DMF, THF, DMSO and pyridine. Yield: 0.168 g, 31.5%. M.p. > 200 °C. IR υ_{max}/(cm^{-1}): 3600–2500 (carboxylic acid OH), 3058 (Ar-H), 2921–2850 (aliphatic CH), 1709 ($C{=}O$), 1601, 1531, 1454, 1399, 1262, 1086, 1039, 934, 893, 816, 765, 747, 690; ^{1}H NMR (*d*-DMSO, δ ppm): 7.51–7.25 (m, 12H, Ar-H), 4.06 (s, 8H, CH_2) UV–Vis λ_{max} (nm) ($\log \varepsilon$) in THF: 680 (4.62), 360 (4.53); Anal. Calc. for $C_{40}H_{26}N_8O_8S_4Ni$: C, 51.57; H, 2.60; N, 12.03. Found: C, 51.55; H, 2.61; N, 12.05%.

*2.2.3.4. 2,9,16,23-Tetrakis(4-carboxymethylsulfanyl)- phthalocyaninatocopper(II) (**2d**).* This is soluble in polar solvents especially DMF, THF, DMSO and pyridine. Yield: 0.157 g, 29.3%. M.p. > 200 °C. IR υ_{max}/(cm^{-1}): 3600-2500 (carboxylic acid OH), 3057 (Ar-H), 2902–2840 (aliphatic CH), 1714 (C═O), 1602, 1506, 1384, 1315, 1242, 1162, 1031, 973, 922, 896, 824, 744, 677; UV–Vis λ_{max} (nm) (log ε) in THF: 685 (4.30), 340 (4.18); Anal. Calc. for $C_{40}H_{26}N_8O_8S_4Cu$: C, 51.30; H, 2.58; N, 11.97. Found: C, 51.32; H, 2.56; N, 11.95%.

2.3. Preparation of cationic cotton fabric (CCF)

30/1 cotton supreme fabric needs to be processed with a cationic chemical prior to the dyeing application. The first step is to apply carbonate with a bath of 1/10 ratio (also known as bleaching). The following chemicals were used in the bleaching process:

Rucogen FWS (Wettening-degreasing agent): 0.5 g L^{-1}
Slipper (Fraction preventer): 1.0 g L^{-1}
Na_2CO_3: 3.0 g L^{-1}
H_2O_2 (50%): 1.0%

After the chemicals were added to the bath and kept for 30 min at 95 °C, the bath was removed, and the fabric was washed with tap water. The excessive peroxide was removed in a 1/10 bath by using the following chemicals:

Formic acid (85%): 1.0 g L^{-1}
Sera Zyme C-SX (Catalase): 0.4%

Chemicals were added to the bath and kept 15 min at 50 °C (controlling the pH between 5.0–5.5 is essential). The bath was then drained and the cationic chemical was applied to the fabric. The following chemicals were used:

Acetic acid (80%): 0.5 g L^{-1}
Mordiente DEL (cationic agent): 5%

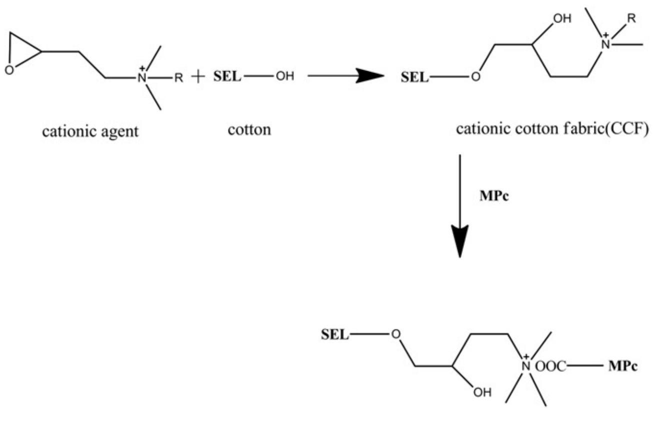
The pH was first set to 5.0 with acetic acid. Then, cationic agent was added to the medium and kept for 20 min at 60 °C. The fabric was removed, washed with tap water, and dried at 60 °C for 10 min. Cationization of cotton, which mainly contains cellulose, is depicted in Scheme 1.

2.4. Dyeing of cationic cotton fabric (CCF) with MPcs

A dyeing bath of 1/10 ratio and 5 g of CCF was used. Phthalocyanines were applied at 1% concentration. Sodium carbonate was preferred as the alkaline medium. 0.05 g of phthalocyanine (**2a**–**d**), 3 mL of 0.14 M sodium carbonate solution and 47 mL of water was added to a dyeing tube. After waiting for 45 min at 80 °C, 5 g of CCF was added and kept for a further 90 min. After this procedure, the fabric was removed and washed with tap water. The fabric was subjected to another bath, whose pH was set to 3.5–4.0 with acetic acid, and kept for 10 min at that temperature. The fabric was then removed, and dried at 60 °C for 10 min in an oven. Scheme 1 shows the binding of phthalocyanines to CCF. The uptake of dye was calculated by using Eq. (1):

$$\text{Dye uptake }(\%) = [(A - B)/A]100 \tag{1}$$

where A is the absorbance at nearly 670 nm (Q band of the MPcs) of the initial dye bath and B is its absorbance after dyeing [29].



Scheme 1. Preparation of the cationic cotton fabric (CCF) and dyeing with MPc.

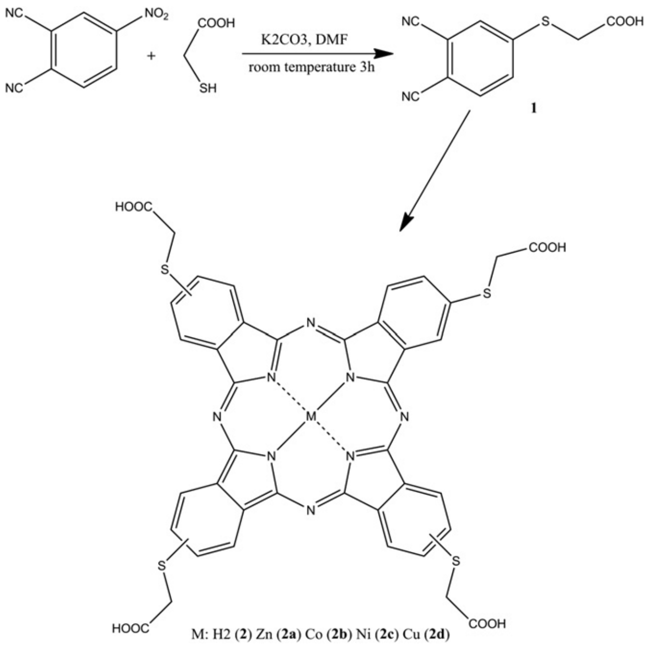
3. Results and discussion

3.1. Synthesis and characterization

Scheme 2 shows the synthesis of the target phthalocyanines (**2**, **2a**–**d**). The first step in the synthetic procedure was to obtain 4-(carboxymethylsulfanyl)phthalonitrile (**1**). **1** was prepared from 4-nitrophthalonitrile and thioglycolic acid in DMF. K_2CO_3 was used as the base for this nucleophilic aromatic displacement [30].

The most usual method to prepare metal-free phthalocyanines is the cyclotetramerisation of a phthalic acid derivative such as a phthalonitrile or diiminoisoindoline. A practical way of achieving this goal is the treatment of a phthalonitrile with lithium alkoxide, giving rise to the corresponding alkali metal phthalocyanine which can be subsequently demetallated to the metal-free phthalocyanine with a mineral acid. In this study, the lithium route was chosen for synthesizing the metal-free phthalocyanine **2**. Lithium Pcs can be labile towards water and acid and can easily be converted to the metal-free phthalocyanine [31].

The metallo Pc derivatives were prepared from the same phthalonitrile precursor and corresponding metal salt *e.g.* zinc acetate, cobalt (II) chloride, nickel(II) chloride and copper(II)



Scheme 2. Synthesis of 4-(carboxymethylsulfanyl)phthalonitrile (**1**) and it's phthalocyanine derivatives.

chloride to obtain zinc phthalocyanine **2a**, cobalt phthalocyanine **2b**, nickel phthalocyanine **2c**, copper phthalocyanine **2d**, respectively. Insoluble products were encountered frequently as a result of complexation between the COOH groups and the metal ions [32]. After treatment of the product with HCl, desired metallo-phthalocyanines with free carboxy groups are obtained. As expected, all the phthalocyanines synthesized during this work are a mixture of positional isomers due to the usage of phthalonitrile precursor **1** with a single substituent [1]. However, our attempts to separate these isomers by chromatography were not successful.

The phthalocyanines **2a**–**d** are soluble in polar solvents such as THF, DMSO, and DMF owing to four polar peripheral substituents. The products were obtained in sufficient purity after successive washing with different solvents.

Characterizations of the products involved a combination of methods including elemental analysis, ^{1}H and ^{13}C-NMR, UV/Vis, FT-IR and mass spectroscopy. The spectroscopic data of the new compounds confirmed the proposed structures.

Comparison of the IR spectra at each step gave some insights on the nature of the compounds. When IR spectrum of 4-nitrophthalonitrile is compared with that of **1**, a distinct difference is the disappearance of the aromatic $-NO_2$ bands at 1355 cm^{-1} and 1535 cm^{-1} and the appearance of a new absorption at 1709 cm^{-1} attributable to carbonyl group of the acid. [33]. In the IR spectrum of **1** the presence of C≡N and C=O groups is indicated by the intense stretching bands at 2226 and 1709 cm^{-1}. ^{1}H-NMR spectrum of **1** exhibited the aromatic protons around 7.85–8.01 ppm and alkyl protons at 4.12 ppm. The ^{13}C-NMR spectral data are in harmony with the expected structure. The ^{13}C-NMR spectrum of **1** indicated the nitrile carbons at 116.27 and 115.05 ppm as expected [34]. Protonated aromatic and unsaturated carbon atoms appeared in the range at δ 146.06–110.11 ppm. Also the carbon atom of carboxylic acid group was observed at the lowest field at δ 169.91 ppm. The electron impact mass spectrometry result of **1** confirmed the complete nucleophilic aromatic displacement of the phthalonitrile's $-NO_2$ group by the presence of molecular ion peak at m/z 218 [M^{+}].

A diagnostic feature of the phthalocyanine formation from **1** is the disappearance of the C≡N peak of the reactant. This peak can be used to monitor the conversion and to detect any ligand impurities in the macrocycle. The IR spectra of metal-free **2** and metallophthalocyanines (**2a**–**d**) are very similar. The significant difference is the presence of N–H vibrations of the inner phthalocyanine core which are assigned to a weak band at 3281 cm^{-1} in the metal-free molecule. In the ^{1}H-NMR spectrum of **2**, aromatic protons appeared at 8.32–7.41, central core N–H protons at −6.54, CH_2 protons at 4.18 and COOH proton at 13.21 ppm. ^{1}H NMR spectrum of **2a** showed the aromatic protons at 7.73–6.96 and CH_2 protons at 4.13 ppm (see the ^{1}H NMR spectrum in supporting information).

Phthalocyanines show typical electronic spectra with two absorption regions, the Q band around 600–700 nm and the B band in the near UV region around 300–350 nm 3[35]. The Q band of all the compounds are attributed to the $\pi-\pi^*$ transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the phthalocyanine ring. B band of all the phthalocyanines arise from the deeper π levels → LUMO transitions [36,37]. The split form of Q band for **2**, which is characteristic for metal-free phthalocyanines, is observed at λ_{max} 708 and 676 nm. The B or Soret absorption band for **2** at near UV region is observed at λ_{max} 340 nm. The Q band absorption of metallo-phthalocyanines is observed as a single band of high intensity in the visible region. The metallo-phthalocyanines **2a**–**d** showed the expected absorptions of the Q bands at 684, 679, 680, 685 nm and B bands at 345, 325, 360, and 340 nm, respectively in THF. UV spectra of phthalocyanines **2** in THF, **2a** and **2d** in DMSO were given in Fig. 1.

In many Pcs weaker absorptions on the higher energy side of the Q bands which indicate the presence of aggregated species are generally observed together with the main Q bands essentially responsible for the intense absorption occurring due to the monomeric ones [3]. The metallo-derivatives (**2a**–**d**) show these intense Q band absorptions for the $\pi-\pi^*$ transitions at around 679–685 nm with weaker absorptions at around 620–645 nm. When the electronic spectra of the metal-free phthalocyanine (**2**), zinc, nickel, cobalt and copper phthalocyanines (**2a**–**d**) were carefully examined, a clear difference from the usually encountered spectra for phthalocyanines could be easily observed. Because of aggregation, Q band of **2** was split into three peaks and the Q band

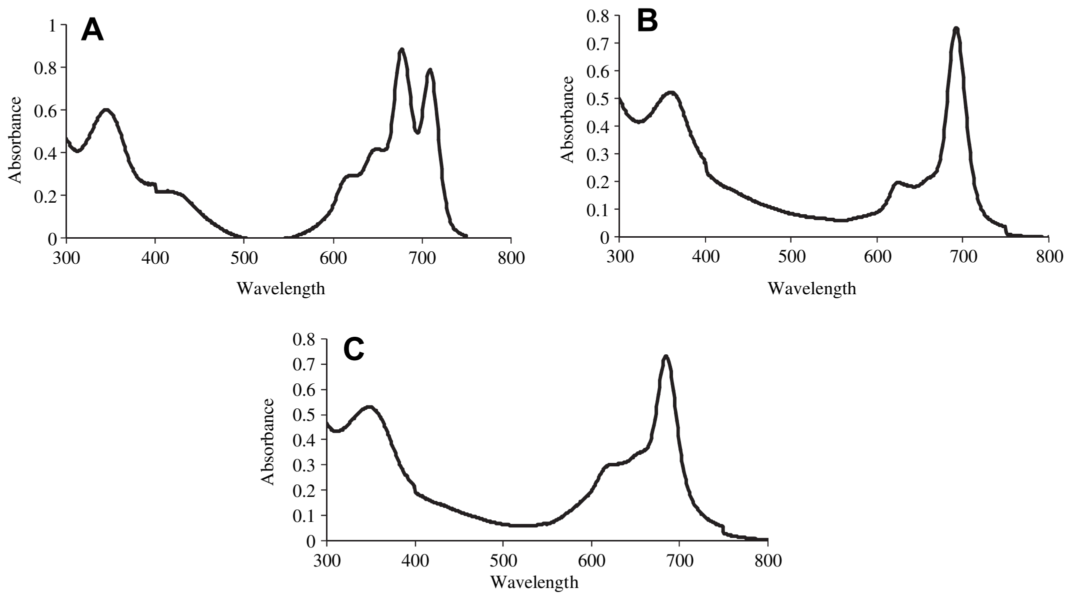


Fig. 1. UV spectra of compounds **2** (A), **2a** (B) and **2d** (C). A in THF, B and C in DMSO.

of the nickel, cobalt and copper phthalocyanines was nearly split into two peaks. The polarity of the solvent also effects the aggregation of the phthalocyanine molecules. In polar solvents, aggregation was observed to increase [38]. This is shown in Fig. 2 for metal-free and metallo-phthalocyanines with different solvents.

3.2. Results of dyeing and fastness

Due to their low solubility in water, some being practically insoluble, phthalocyanines are disadvantageous as dyes. Since phthalocyanines substituted with carboxylic acid moieties are still not very soluble in water, a solubilization step is required in order to start their dyeing process. For this purpose, an alkali (ammonia, sodium hydroxide or sodium carbonate) is preferred. After treating the phthalocyanine with one of these, the resulting carboxylate is highly soluble in water. It is adequate to use a cationized textile fabric to facilitate the dyeing process with electrostatic interactions.

As a natural fibre, cotton was preferred in the experiments. 30/1 cotton supreme fabric was used. After bleaching and cationizing steps, the epoxide group undergoes ring opening under aqueous acidic conditions, yielding $HO-CH_2CH-OH-N^+R_3$ moiety. The OH group from cellulose binds to the CH_2 group from the cationizing agent and removal of the OH group on the agent leads to cationic cotton fabric (CCF).

Prior to dyeing process, solubilities of the phthalocyanines were tested with 3% NH_3, 1 M NaOH and 0.14 M Na_2CO_3 solutions and it was found that the compounds were soluble in all of them. As a less hazardous reagent, sodium carbonate has been chosen for our study as the preferred alkali. Known amounts of dye, alkali and water were put into the dyeing tube, and kept at 80 °C for 45 min for completion of dyeing process. The fibres were taken out of the tube, and washed with tap water; the remaining baths were stored for analysis. In order to convert the carboxylate groups to the corresponding carboxylic acids, a dilute solution of acetic acid was added until the pH was 3.5–4.0. The finishing pH of the solutions was 10.60.

Examining the fibres shown in Fig. 3 led to the conclusion that **2b**, **2c** and **2d** yielded homogeneous and effective dyeing, but **2a** did not as obviously seen from the texture. The failure of the zinc compound **2a** might be explained with its sparingly soluble nature. Copper and nickel phthalocyanines, **2d** and **2c**, respectively, yielded the best dyeing performance in terms of colour deepness and homogeneity. Dyeing uptake of metallo-phthalocyanines have been calculated according to Eq. (1) and yielded 71%, 75% and 81% for CoPc, NiPc and CuPc, respectively. These results conform to similar studies from literature under these conditions [29]. From the colour perspective, the central atoms did not change the characteristic green hue.

Washing and water fastnesses of the metallophthalocyanines were also tested. After dyeing, tests for water and washing fastness were performed according to BS EN ISO 105-A03 and BS EN ISO 105-E01, respectively. Colour leaching at the gray scale was

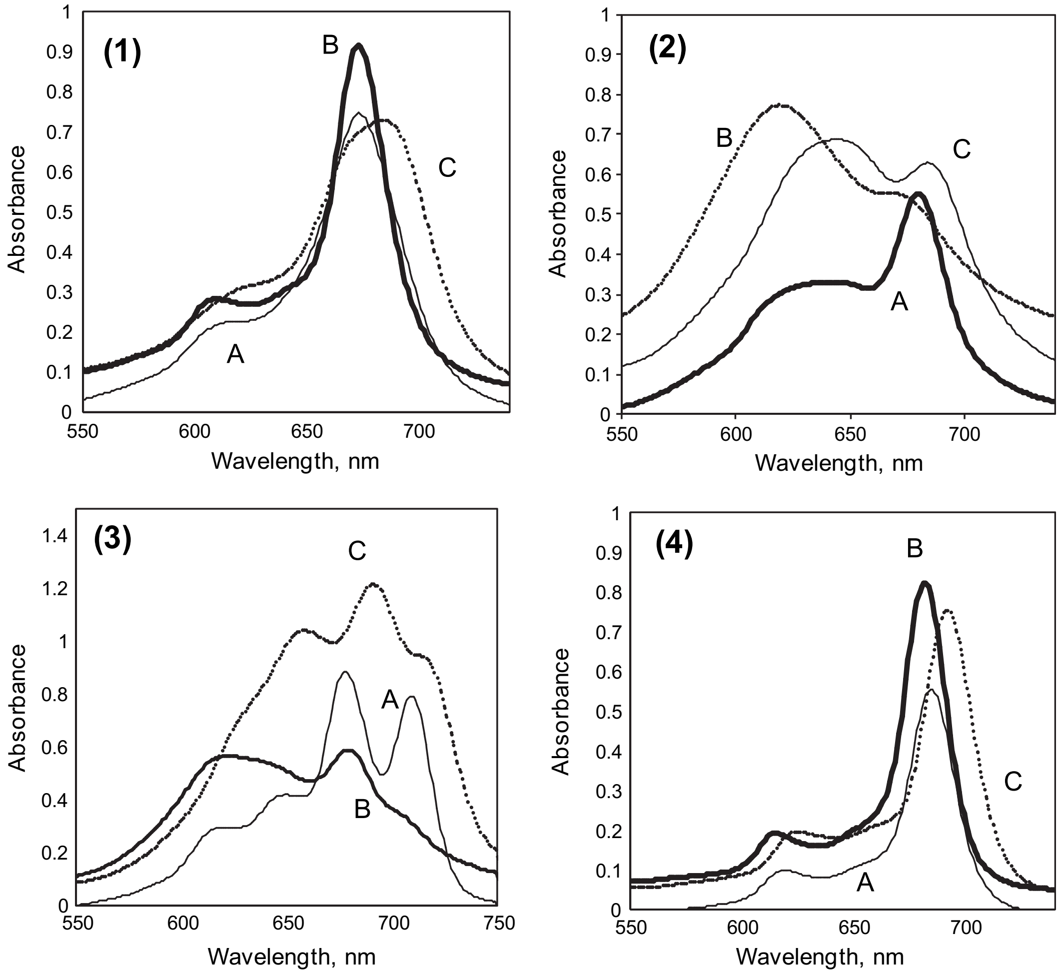


Fig. 2. Progress of aggregation in A:THF, B:Acetone and C:DMSO for corresponding phthalocyanines, 1:CoPc , 2:NiPc , 3:H_2Pc, 4:ZnPc.

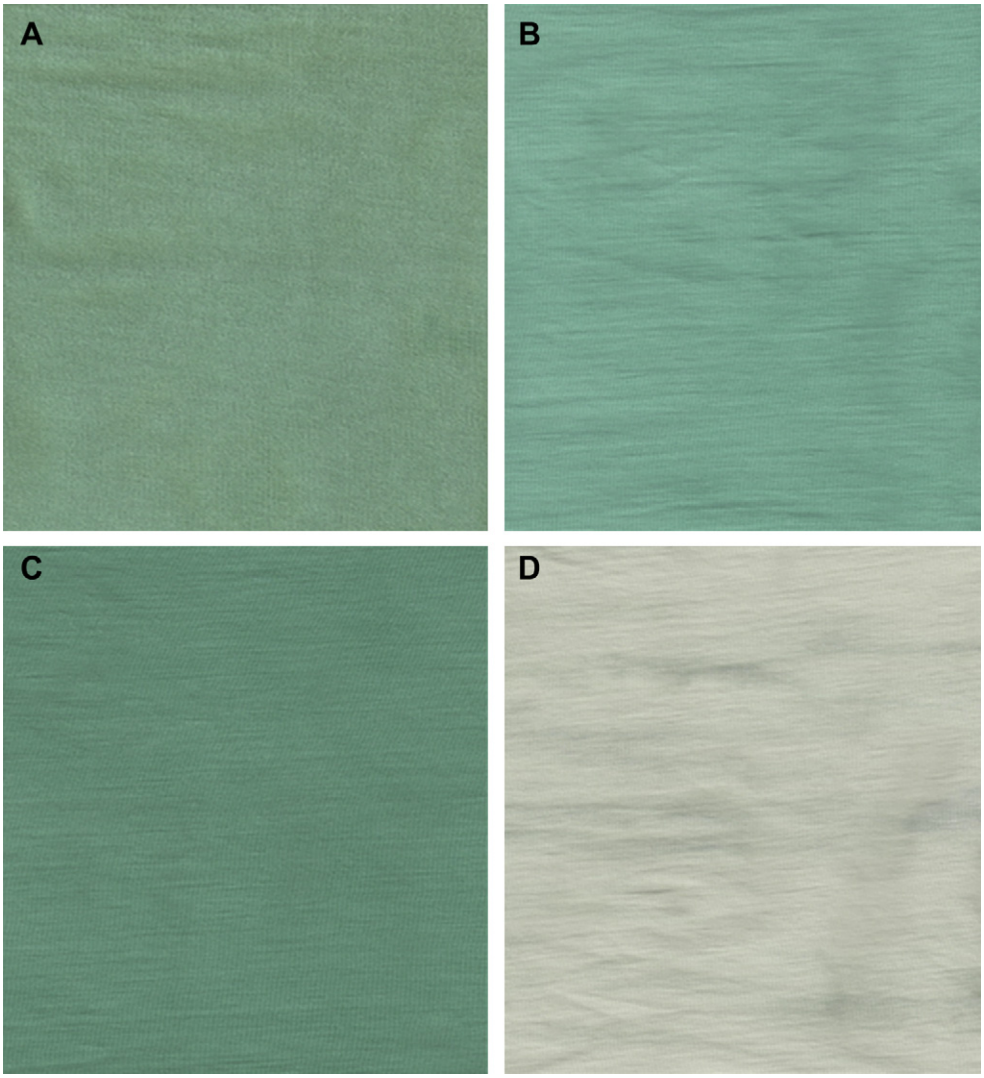


Fig. 3. Cationic cotton fibres dyed with metallophthalocyanines, namely CoPc (A), CuPc (B), NiPc (C) and ZnPc (D).

Table 1
The results of water and washing fastness of cotton fibres dyed with NiPc, CoPc or CuPc (The results are the same for all metallophthalocyanines.).

	Type of fibre	Wool	Acrylic	Polyester	Nylon (6,6)	Cotton	Acetate
Multifibre assessment procedure	Water fastness	4/5	4/5	4/5	4/5	4/5	4/5
	Washing fastness	4/5	4/5	4/5	4/5	4/5	4/5

evaluated according to BS EN ISO 105-A03. The results of fastness tests as given in Table 1 indicate that these values were best in the series (4 out of 5).

4. Conclusion

New phthalocyanine compounds having thioglycolic acid moieties were synthesized and their structures were elucidated with several spectroscopic techniques. In addition, cationic cotton fibre (CCF) was found to be a good choice for dyeing due to the electrostatic enhancement of the dyeing process. Dyeing performances were sufficient for copper, nickel and cobalt derivatives in terms of dyeing efficiency, homogeneity and fastness. Further studies on the use of these novel heterogeneous phthalocyanine catalysts in textile industry and especially as air-purifying materials are on progress.

Acknowledgement

This work was supported by the Research Fund of the Technical University of Istanbul.

Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.dyepig.2010.10.008.

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