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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

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ABSTRACT

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,

* 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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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≡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≡N), 115.05 (C≡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 ε) 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) (logε) 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 ε) 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 ε) 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,