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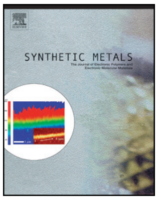

New electropolymerizable metal-free and metallophthalocyanines bearing {2-[3-(diethylamino)phenoxy]ethoxy} substituents

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ABSTRACT

In this work, metal-free and metallophthalocyanines (Ni, Co, Cu) bearing peripherally tetra substituted 4-{2-[3-(diethylamino)phenoxy]ethoxy}groups were synthesized by cyclotetramerization of the corresponding phthalonitrile derivative and their electrochemical, spectroelectrochemical properties were investigated. Phthalocyanines were characterized by a combination of IR, ^{1}H-NMR, UV–vis and MS spectral data. Diethylamino groups on the substituents of the complexes cause electropolymerization of the complexes on the working electrode during the oxidation reactions. Changing the potential window of the voltammetric cycles alters the electropolymerization mechanisms. Types of the metal center of the complexes also affect the electropolymerization mechanism. Spectroelectrochemical measurements were performed to assign the redox processes and spectroscopic responses of the electropolymerization processes.

1. Introduction

Metal-free and metallophthalocyanines are one of the most useful heterocyclic materials. They show a wide range of technological applications in different scientific areas for example solar cells [1], electronic devices [2], liquid crystals [3], gas and chemical sensors [4], photo dynamic therapy (PDT) [5–9], electrochromic and electroluminescent displays [10], non-linear optics [11], semiconductors [12], photovoltaics [13] and their electrochemical properties [14,15] are utilized for electrochemical applications such as electrocatalytic [16,17], electrosensing [18], electrochromic fields [19]. Electrochromism is an electrochemically produced stable and reversible color changes due to changing the optical responses of the electro-chromophores in the visible region of the light spectrum. Electrochromic materials which include electropolymerizable phthalocyanines [20] are used in different applications, such as various display technologies, energy-saving smart windows, sensors and data storage [21,22]. However, the applications of metal-free and metallophthalocyanines is limited by their low solubility in common organic solvents and water. Because of this, one of the goals of research on the phthalocyanines is to increase their solubility in common organic solvents and water. The solubility of metal-free and metallophthalocyanines can be enhanced by introducing different kinds of substituents such as alkyl, alkoxy, phenoxy, macrocyclic groups [23–26] in common organic solvents and amino, sulfo or carboxyl groups leads to phthalocyanine derivatives soluble in water [27–30].

Metallophthalocyanines (MPcs) are intensely studied as electrochemically functional materials due to the excellent redox properties [31–33]. Their electrochemical properties are easily arranged by changing the metal center and types, number and position of substituents. It is well documented that functional materials should be coated on a substrate for their practical applications [34–38]. Although many film coating techniques were studies for the preparation of composite electrodes, preparation of modified electrodes with electropolymerization is one of the most preferred techniques [39–43]. Since it is easy to control many of the film characters, such as morphology, thickness, conductivity, and polymer structure of the films [44,45]. Although numerous different conjugated polymers, such as polythiophene [46–49], polyaniline [50–52], polypyrrole [50–52], were studied for different applications, nowadays metal-containing conjugated polymers, especially polymerized MPcs have taken condensed attentions [53–59] Some examples of porphyrin and phthalocyanine-containing conjugated polymers have been also reported [60–67]. Applications of modified electrodes based on electropolymerization of functional materials canalized our studies to synthesis of MPcs bearing electropolymerizable substituents.

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For this purpose we reported different MPcs bearing thiophene [68,69], amino [70], and quinolin [71] moieties. Now in this paper, we have synthesized new MPcs bearing electropolymerizable 4-{2-[3-(diethylamino)phenoxy]ethoxy}groups and then we have investigated electrochemical and spectroelectrochemical properties of these novel complexes. Finally we aimed to prepare modified electrodes with electropolymerization of the MPcs for the possible applications of the complexes in different electrochemical technologies.

2. Experimental

2.1. Synthesis

2.1.1. Synthesis of metal-free phthalocyanine (**4**)

4-{2-[3-(Diethylamino)phenoxy]ethoxy}phthalonitrile **3** (0.4 g, 1.19×10^{-3} mol) and five drops of 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU) in 0.004 L of dry n-pentanol was heated and stirred at 160 °C for 12 h under N_2. After cooling to room temperature the product was precipitated with ethanol and then dried in vacuo. Lastly, pure metal-free phthalocyanine was obtained by column chromatography which is placed aluminum oxide using $CHCl_3$:CH_3OH (100:1) as solvent system. Yield: 0.175 g (44%). IR (KBr tablet) ν_{max}/cm^{-1}: 3292 (N—H), 3073 (Ar—H), 2965 – 2868 (Aliph. C—H), 1610, 1571, 1499, 1481, 1450, 1356, 1276, 1213, 1142, 1096, 1071, 1014, 951, 823, 748, 686. ^1H-NMR. ($CDCl_3$), (δ: ppm): 7.28 – 7.14 (m, 12H, Ar—H), 6.50 – 6.23 (m, 16H, Ar—H), 4.38 (m, 16H, —CH_2—O), 3.43 (m, 16H, —CH_2—N), 1.27 (m, 24H, —CH_3) –5,38 (bs, 2H, N—H). UV–vis (chloroform): λ_{max}, nm (log ε): 338 (4.85), 608 (4.43), 643 (4.61), 667 (4.90), 704 (4.95). MALDI-TOF-MS (2,5-dihydroxy benzoic acid as the matrix) *m/z*: 1344 $[M+H]^+$.

2.1.2. General procedures for metallophthalocyanine derivatives (**5–7**)

A mixture of 4-{2-[3-(diethylamino)phenoxy]ethoxy}phthalonitrile **3** (0.3 g, 0.89×10^{-3} mol), four drops of 1.8-diazabicyclo-[5.4.0]undec-7-ene (DBU) in 0.003 L of n-pentanol and anhydrous metal salts [$NiCl_2$ (0.057 g), $CoCl_2$ (0.058 g), $CuCl_2$ (0.060 g)] were heated and stirred at 160 °C for 12 h under N_2. After cooling to room temperature, the reaction mixture was precipitated by adding it drop-wise into ethanol. The precipitated green solid product was filtered off, and then dried in vacuo over P_2O_5. Finally, pure metallophthalocyanines were obtained by column chromatography which is placed aluminum oxide using $CHCl_3$:CH_3OH (100:2) as solvent system.

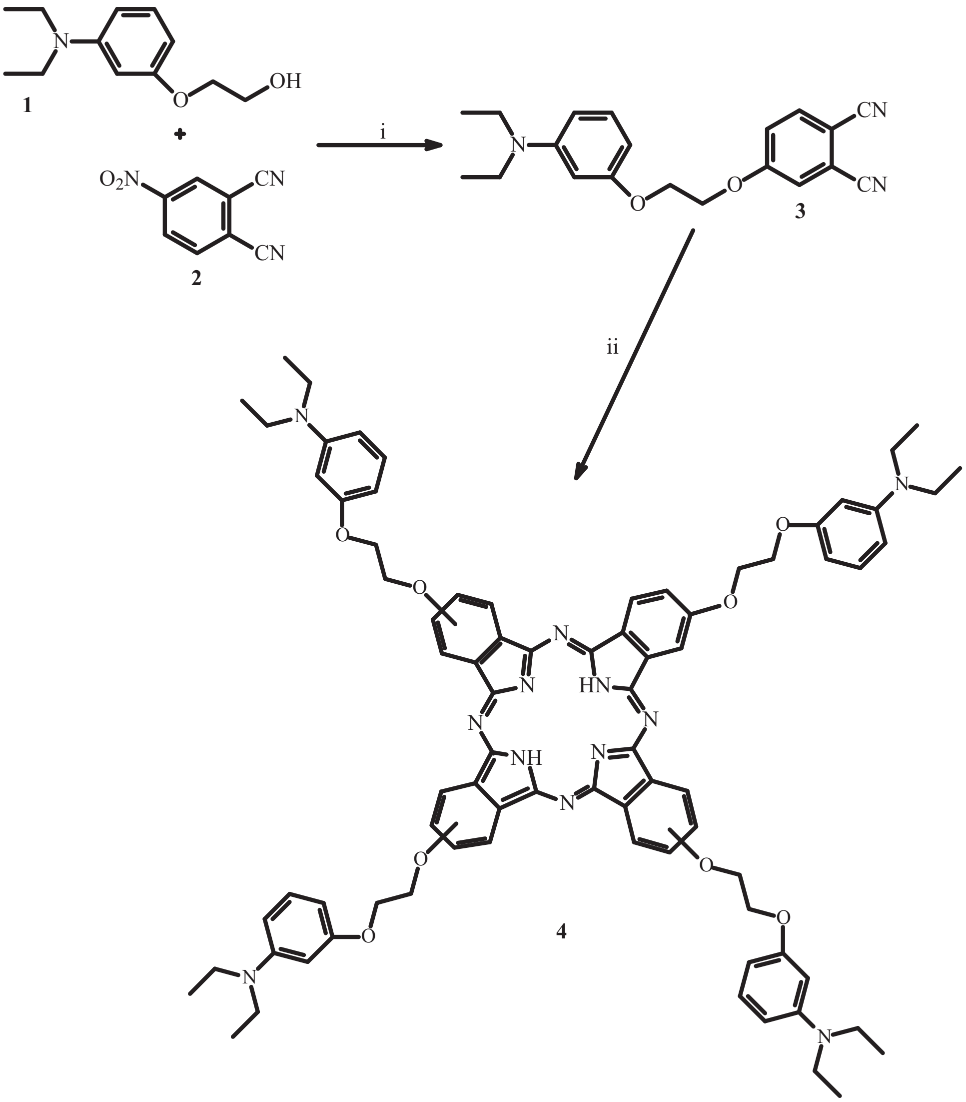

Fig. 1. The synthetic route of the metal-free phthalocyanine. Reagents and conditions: (i) dry DMF, K_2CO_3, 50 °C, 96 h; (ii) n-pentanol, DBU, 160 °C.