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Synthesis, electrochemical, in-situ spectroelectrochemical and in-situ electrocolorimetric characterization of new phthalocyanines containing macrocyclic moieties

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ABSTRACT

In this work, we synthesized new phthalocyanine compounds containing optically active 1,1′-binaphthyl crown ethers units. The metal-free phthalocyanine **(3)** was synthesized by the cyclotetramerization of dinitrile derivative **(2)** in dry n-pentanol by a classical method. However, metal phthalocyanines complexes **(4, 5, 6)**, were synthesized by the reaction of dinitrile derivative **(2)** in DMAE. The structure of the new compounds were characterized by using spectroscopic data and elemental analysis. Electrochemical properties of Co (II) and Zn (II) phthalocyanines were investigated by using cyclic voltammetry and differential pulse voltammetry techniques. They exhibited two reversible Pc ring-based one-electron reduction couples. The Co (II) and Zn (II) phthalocyanines gave very similar voltammetric responses with slight potential shift due to different metal center.

1. Introduction

Metal-free phthalocyanine and its metal complexes have been intensively investigated since the early-1930s [1]. They play an important role in many advanced applications and modern technologies, mostly by virtue of their characteristic optical absorption and high chemical stability. The functions of phthalocyanine, its derivatives and phthalocyanine metal complexes are almost based on a redox or electron transfer reaction [2–4].

Much attention has been paid to preparation of new phthalocyanine derivatives because of their application as colorants, chemical sensors, electrochromic compounds, liquid crystalline materials and organic conductors [5–8]. They are generally insoluble in common organic solvents, although their solubility can be improved by incorporation of substituents such as phenoxy, alkyl or alkoxy of different chain lengths [9,10] or branched system at peripheral positions [11–16].

Another interesting class of alkoxy- and aryloxy- substituted phthalocyanines are 1:25, 11:15- and 2:24,10:16- bridged phthalocyanines first explored by Leznoff and Kobayashi research groups [17]. The precursors phthalonitriles can be prepared by aromatic nucleophilic substitution of 3- or 4- nitrophthalonitrile with appropriate diols in DMF using K_2CO_3 as a base. The resulting bisphthalonitriles can be cyclotetramerized into corresponding symmetric bridged phthalocyanines. Their low yields can be explained by the expected formation of oligomeric products.

Chirality is one of the most fascinating and complicated features commonly found in nature [18]. Inspired by the elegance of natural chiral structures with biological activity, numerous artificial chiral compounds including optically active porphyrins and phthalocyanines have been developed depending on various asymmetric synthetic methods [19].

Up to now, few reports have explored the process of combining chiral binaphthol groups with a phthalocyanine core [20]. Since the first report on the use of chiral binaphthy-based crown ethers as hosts for molecular recognition, chiral binaphthol has attracted much attention. Chiral macrocycles, metal complexes, linear oligomers and polymers based on the 1,1′-binaphthyl structure have been synthesized for use in molecular recognition, asymmetric catalysis and as new functional materials [21].

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In the last decade, microwave energy has attracted interest as an alternative to traditional heating, because microwave-assisted synthesis can result in increased yields and lowered reaction times [22–25].

Electrochemical and spectroelectrochemical measurements show that while copper phthalocyanine gives only ring-based electron transfer reactions, incorporating redox active metal centers, Co^{II}, Fe^{III}Ac, and Mn^{III}Ac, into the phthalocyanine core extends the redox richness of the phthalocyanine ring with the metal-based reduction and oxidation couples of the metal centers in addition to the common phthalocyanine ring-based electron transfer processes. *In-situ* electrocolorimetric measurements of the complexes allow quantification of color coordinates of each electrogenerated anionic and cationic redox species. Presence of O_2 in the electrolyte system influences the redox couples of the complexes due to the interaction between O_2 and metallophthalocyanines having redox active metal center.

In our previous papers, we reported electrochemical and spectroelectrochemical properties of metallophthalocyanines synthesized by our research groups [26–32]. Electrochemical and spectroelectrochemical responses of the complexes were used propose application of the complexes in different electrochemical application fields, such as, electrocatalysts for H^+ reduction [33–35], electrochemical oxygen reduction reaction [27,36,37], electrochemical metal ion sensor [38–42] and electrochromism [31–43]. In this work, we have investigated the electrochemical and spectroelectrochemical properties of these newly synthesized complexes and proposed possible application fields.

2. Experimental

2.1. Materials

1,1′-binaphthalene-2,2′-diol was purchased from Aldrich. 4,5-dichloro-1,2-dicyanobenzene was synthesized according to the procedure reported in the literature [44–46]. All solvents were dried and purified as described by Perrin and Armarego [47].

2.2. Equipment

The IR spectra were recorded on a Perkin Elmer 1600 FT-IR Spectrophotometer, using KBr pellets. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in $CDCl_3$, and chemical shifts were reported (δ) relative to Me_4Si as internal standard. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC-MS/MS spectrometer. The elemental analyses were performed on a Costech ECS 4010 instrument. Melting points were measured on an electrothermal apparatus and are uncorrected. The cyclic voltammetry (CV) and square wave voltammetry (SWV) measurements were carried out with Gamry Reference 600 potentiostat/galvanostat controlled by an external PC and utilizing a three-electrode configuration at 25 °C. The working electrode was a Pt disc with a surface area of 0.071 cm^2. A Pt wire served as the counter electrode. Saturated calomel electrode (SCE) was employed as the reference electrode and separated from the bulk of the solution by a double bridge.

Electrochemical grade TBAP in extra pure DCM and DMSO was employed as the supporting electrolyte at a concentration of 0.10 mol dm^{-3}. For each measurement, the reference electrode tip was moved as close as possible to the working electrode so that uncompensated resistance of the solution was a smaller fraction of the total resistance and therefore the potential control error was low. Moreover, IR compensation was also applied to the voltammetric measurements to minimize the potential control error. UV-Vis absorption spectra and chromaticity diagrams were measured by an Ocean Optics QE65000 diode array spectrophotometer.

In-situ spectroelectrochemical measurements were carried out by utilizing a three-electrode configuration of thin-layer quartz thin-layer spectroelectrochemical cell at 25 °C. The working electrode was a semipermeable Pt sheet. Pt wire counter electrode separated by a glass bridge and a SCE reference electrode separated from the bulk of the solution by a double bridge were used. *In-situ* electrocolorimetric measurements, under potentiostatic control, were obtained using an Ocean Optics QE65000 diode array spectrophotometer at color measurement mode by utilizing a three-electrode configuration of thin-layer quartz spectroelectrochemical cell. Prior to each set of measurements, background color coordinates (x, y and z values) were taken at open-circuit, using the electrolyte solution without the complexes under study. During the measurements, readings were taken as a function of time under kinetic control, however only the color coordinates at the beginning and end of each redox process were reported.

2.3. Synthesis

2.3.1. Synthesis of 2,2′-[1,1′-Binaphtalene-2,2′-diyl bis(oxy)] diethanol (1)

1,1′-Binaphthalene-2,2′-diol (10 g, 35 mmol) was dissolved in 60 mL absolute ethanol under a N_2 (g) atmosphere and NaOH (35 g, 87.5 mmol) was added. The mixture was heated at 50 °C, and 2-chloroethanol (6 mL, 87.4 mmol) and 17 mL absolute ethanol were added dropwise for 15 min. Then it was refluxed for two days under N_2 (g) atmosphere. The mixture was controlled with chloroform/methanol (9.5:0.5) solvent system and then the synthesis was completed. The cream-like mixture was cooled to room temperature, filtered and evaporated to dryness under vacuum and finally a viscous liquid product was obtained. This product was redissolved in chloroform (200 mL), and then washed with 10% NaOH and water, respectively. The combined organic extracts were dried with anhydrous $MgSO_4$ and evaporated to dryness. The product was isolated as a cream-like solid following recrystallization of the crude residue from ethanol. Yield: 7 g (54%). m.p.: 100–102 °C. Anal. Calcd for $C_{24}H_{22}O_4$: C: 77.01; H: 5.88. Found: C: 77.20; H: 5.76%. IR (KBr tablet), νmax/cm^{-1}: 3516–3240 (OH), 3055(Ar–H), 2917 (Alif. C–H), 1619, 1456, 1242 (Ar-O-C),1141–1047 ($-OCH_2$), 972. ^1H NMR ($CDCl_3$), (δ:ppm): 8.06–7.87 (m, 4H, ArH), 7.47–7.11 (m, 8H, ArH), 4.19–4.03 (m, 4H, $O-CH_2$), 3.57 (br s, 4H, $O-CH_2$), 2.29 (s, 2H, OH). ^{13}C NMR ($CDCl_3$), (δ:ppm): 155.03, 134.02, 130.12, 129.87, 127.66, 126.92, 124.44, 123.69, 117.84, 111.14, 71.96, 61.46. MS (FAB) (m/z): 374 $[M]^+$.

2.3.2. Synthesis of 6,7,22,23-Tetrahydrobenzo[e]dinaphtho [1,2-m:2′,1′- k][1,4,7,10] tetraoxacyclotetradecine-2,3-dicarbonitrile(2)

Compound **2** was prepared as follows: 2,2′-[1,1′-Binaphtalene-2,2′-diyl bis(oxy)]diethanol (3 g, 8.16 mmol), 192 mL dry acetonitrile, anhydrous K_2CO_3 (5.58 g, 40.08 mmol), anhydrous NaI (6.12 g, 40.08 mmol) and 4,5-dichloro-1,2-dicyanobenzene (1.6 g, 8.16 mmol) were refluxed under N_2 (g) atmosphere for 7 days. The reaction system was controlled with chloroform/methanol (9.5:0.5) solvent system and then the procedure was completed. The resultant mixture was evaporated to dryness under vacuum and finally a viscous liquid product was obtained. This cream-like product was redissolved in chloroform (200 mL) and washed with water. The combined organic extracts were dried with anhydrous $MgSO_4$ and evaporated to dryness. The product was isolated as a cream-like solid following recrystallization of the crude residue from ethanol. Yield: 2.4 g (60%). m.p.: 94–96 °C. Anal. Calcd for $C_{32}H_{22}N_2O_4$: C: 77.10; H: 4.41; N: 5.62. Found: C: 77.00; H: 4.37; N: