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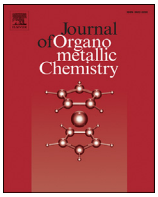

New electropolymerizable metal-free, metallophthalocyanines and their electrochemical, spectroelectrochemical studies

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ABSTRACT

The synthesis, characterization of newly synthesized metal-free **4** and metallophthalocyanine complexes **5**–**7** (MPcs, M = Ni, Co, Cu) have been presented in this work. All the new phthalocyanine compounds are characterized by a combination of IR, ^{1}H and ^{13}C NMR, mass and UV–Vis spectroscopy techniques. Voltammetric and spectroelectrochemical analyses of phthalocyanines supported the proposed structure of the synthesized complexes. All complexes were oxidatively electropolymerized on the working electrode during the repetitive anodic potential scans. Formation of thin film of the complex as a result of electropolymerization, and controlling the film characters by altering the excitation signals of the voltammetry, changing the working electrode and metal center of the complexes affects the polymerization mechanisms.

Introduction

Metal-free and metallophthalocyanines are very important compounds because they have been used in very different areas of technology and medical applications for example photodynamic therapy of cancer [1,2], chemical sensors [3], photoconductors [4], electrochromic display [5], catalysis [6–9], liquid crystal [10] and nanotechnology [11,12]. Despite many inherent chemical advantages of phthalocyanine complexes their one of the most important disadvantage is insolubility in common organic solvents. Substituents can bound on phthalocyanine ring its periferal or non-periferal positions and depending on the polarity of the substituents, substituted phthalocyanines become more soluble in apolar or polar solvents [13–18].

Metallophthalocyanines exhibit interesting electrochemical and spectroelectrochemical properties just because their properties may be remarkably affected by the chemical character of central metal ions and the nature of (electron-withdrawing or electron-donating) and position (peripheral or non peripheral) of substituent on the phthalocyanine ring [19–22]. Spectroelectrochemical studies of metallophthalocyanines are also important with regard to their possible usage as electrochromic materials, where several colors are displayed based on the potential applied to the electrode surface [23–25]. Therefore, in this paper we have investigated electrochemical and spectroelectrochemical properties of these newly synthesized complexes. We have also aimed to prepare modified electrodes with electropolymerization of the complexes.

Experimental

Materials

2-{2-[3-(Diethylamino)phenoxy]ethoxy}ethanol **1** [26], 4-nitrophthalonitrile **2** [27], 4-(2-{2-[3-(diethylamino)phenoxy]ethoxy}ethoxy)phthalonitrile **3** [28] were prepared according to the literature procedure. All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego [29].

Equipment

The IR spectra were recorded on a Perkin Elmer 1600 FT-IR spectrophotometer, using KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 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

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Quatro LC/ULTIMA LC–MS/MS spectrometer. MALDI–MS of complexes were obtained in dihydroxybenzoic acid as MALDI matrix using nitrogen laser accumulating 50 laser shots using Bruker Microflex LT MALDI–TOF mass spectrometer. Optical spectra in the UV–Vis region were recorded with a Perkin Elmer Lambda 25 spectrophotometer. Melting points were measured on an electrothermal apparatus and are uncorrected.

Electrochemical and spectroelectrochemical measurements

Cyclic voltammetry (CV) and square wave voltammetry (SWV) measurements were carried out with Gamry Reference 600 potentiostat/galvanostat. 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. Electrochemical grade tetrabuthylammonium perchlorate (TBAP) in extra pure dichloromethane (DCM) or dimethyl sulfoxide (DMSO) was employed as the supporting electrolyte.

An OceanOptics QE65000 diode array spectrophotometer was used for UV–Vis absorption spectra and chromaticity diagram measurements. *In-situ* spectroelectrochemical measurements were carried out by utilizing a three-electrode configuration of thin-layer quartz thin-layer spectroelectrochemical cell consisting a Pt tulle working electrode, a Pt wire counter electrode, and an SCE reference electrode.

Synthesis

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

A mixture of 4-(2-{2-[3-(Diethylamino)phenoxy]ethoxy}ethoxy)phthalonitrile (**3**) (0.350 g, $9,2 \times 10^{-4}$ mol), 4 drops of 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU) in n-pentanol (3.5×10^{-3} L) was heated to 160 °C with stirring for 24 h under N_2 gas atmosphere. After the reaction mixture was cooled at room temperature and precipitated by adding ethanol. The crude solid product was filtered and washed with ethanol, water and diethyl ether. Finally, pure metal-free phthalocyanine was obtained by column chromatography which is placed aluminium oxide using $CHCl_3$:CH_3OH (100:1) as solvent system.Yield: 0.079 g (23%). IR (KBr tablet) ν_{max}/cm^{-1}: 3291 (N–H), 3072 (Ar–H), 2967–2869 (Aliph. C–H), 1603, 1569, 1497, 1469, 1394, 1373, 1344, 1323, 1274, 1211, 1129, 1092, 1009, 819, 745, 716, 686. ^1H NMR. ($CDCl_3$), (δ:ppm): 8.28-8.26 (m, 4H, Ar–H), 7.42-7.24 (m, 12H, Ar–H), 6.74-6.64 (m, 4H, Ar–H), 6.36-6.35 (s, 8H, Ar–H), 4.32-4.14 (m, 32H, CH_2–O), 3.47-3.32 (m, 16H, CH_2–N), 1.15 (s, 24H, CH_3). ^{13}C NMR. ($CDCl_3$), (δ:ppm): 165.99, 149.94, 149.46, 138.22, 131.42, 130.85, 130.25, 130.21, 109.99, 105.59, 105.55, 101.09, 101.04, 99.45, 70.52, 67.53, 44.62, 12.90. UV–Vis (chloroform): λ_{max}, nm (log ε): 342 (4.84), 387 (4.55), 607 (4.46), 641 (4.64), 669 (5.00), 704 (5.06). MALDI–TOF–MS *m/z*: 1520 $[M+H]^+$.

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

A mixture of **3** (0.350 g, $9,2 \times 10^{-4}$ mol), n-pentanol (4×10^{-3} L), anhydrous metal salt ($4,6 \times 10^{-4}$ mol; 0.061 g $NiCl_2$, 0.060 g $CoCl_2$, 0.062 g $CuCl_2$) and 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU) (5 drops) was refluxed under N_2 for 24 h. After cooling to room temperature, ethanol was added in order to precipitate the product. The green product was filtered off and washed ethanol, water and diethyl ether. Finally, pure metallophthalocyanines were obtained by column chromatography which is placed aluminium oxide using $CHCl_3$:CH_3OH (100:1) as solvent system.

*Nickel(II) phthalocyanine (**5**)*

Yield: 0.100 g (27%). IR (KBr tablet) ν_{max}/cm^{-1}: 3070 (Ar–H), 2966-2869 (Aliph. C–H), 1603, 1569, 1532, 1497, 1467, 1411, 1373, 1351, 1272, 1215, 1120, 1090, 1063, 1021, 988, 964, 819, 783, 749, 686. ^1H NMR. ($CDCl_3$), (δ:ppm): 7.87-7.69 (m, 4H, Ar–H), 7.36-7.18 (m, 12H, Ar–H), 6.72-6.62 (m, 4H, Ar–H), 6.36-6.35 (s, 8H, Ar–H), 4.29-4.13 (m, 32H, CH_2–O), 3.45-3.33 (m, 16H, CH_2–N), 1.16 (s, 24H, CH_3). ^{13}C NMR. ($CDCl_3$), (δ:ppm): 160.56, 149.81, 149.46, 132.97, 131.13, 130.74, 130.23, 130.17, 105.53, 105.51, 105.48, 101.11, 101.07, 99.48, 70.43, 67.42, 44.64, 12.93. UV–Vis (chloroform): λ_{max}, nm (log ε): 326 (4.79), 380 (4.54), 608 (4.54), 675 (5.07). MALDI–TOF–MS *m/z*: 1576 $[M]^+$.

*Cobalt(II) phthalocyanine (**6**)*

Yield: 0.085 g (23%). IR (KBr tablet) ν_{max}/cm^{-1}: 3067 (Ar–H), 2967-2872 (Aliph. C–H), 1604, 1589, 1498, 1464, 1374, 1355, 1273, 1216, 1122, 1092, 1063, 1022, 988, 965, 819, 751, 686. UV–Vis (chloroform): λ_{max}, nm (log ε): 376 (4.70), 611 (4.59), 674 (5.01). MS (ESI), (*m/z*): 1598 $[M+Na]^+$

*Copper(II) phthalocyanine (**7**)*

Yield: 0.100 g (27%). IR (KBr tablet) ν_{max}/cm^{-1}: 3074 (Ar–H), 2966-2869 (Aliph. C–H), 1603, 1569, 1467, 1396, 1374, 1342, 1273, 1216, 1118, 1090, 1057, 1021, 988, 960, 819, 783, 745, 685. UV–Vis (chloroform): λ_{max}, nm (log ε): 338 (4.77), 380 (4.40), 615 (4.53), 683 (5.04). MALDI–TOF–MS *m/z*: 1581 $[M]^+$.

Results and discussion

Synthesis and characterization

The general synthetic route of new metal-free and metallophthalocyanines (**5**–**7**) is given in Fig. 1. The metal-free phthalocyanine **4** was accomplished in n-pentanol in the presence of a few drops of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a strong base at reflux temperature under N_2 gas atmosphere. The novel nickel(II), cobalt(II) and copper(II) phthalocyanines (**5**–**7**) were prepared by the templated cyclotetramerization reaction from 4-(2-{2-[3-(diethylamino)phenoxy]ethoxy}ethoxy)phthalonitrile **3** and metal salts ($NiCl_2$, $CoCl_2$, $CuCl_2$) in n-pentanol and DBU at 160 °C. Metal-free and metallophthalocyanines were purified by column chromatography. The structures of the target compounds were confirmed using UV–Vis, IR, ^1H NMR, ^{13}C NMR, MS spectroscopic data. The analyses are consistent with the predicted structures as shown in the experimental section.

In the IR spectrum of metal-free phthalocyanine (**4**), the peak at 3291 cm^{-1} is characteristic peak for the metal-free phthalocyanine N–H stretching vibration band (see the "Supplementary Information" file). The ^1H NMR spectra of compound (**4**) was in agreement with the proposed structure. The ^1H NMR spectra of metal-free phthalocyanine (**4**) showed aromatic protons between 8.28 and 6.35 ppm with the aliphatic protons observed between 4.32 and 1.15 ppm for the complex (see the "Supplementary Information" file). The NH protons of compound **4** could not be observed owing to the probable strong aggregation of the molecules [30]. The ^{13}C NMR spectra of the compound **4** indicated 18 carbon atoms between at 165.99–12.90 ppm. In general, phthalocyanines show typical electronic spectra with two strong absorption regions, one in the UV region at about 300–500 nm related to the B band and the other in the visible region at 600–700 nm related to the Q band. UV–Vis spectrum of metal-free phthalocyanine (**4**) in chloroform, the characteristic split Q bands were observed with absorptions at 704 and 669 nm which can be attributed $a_{1u} \rightarrow e_g$ transition [31]. UV–Vis spectrum of the metal-free phthalocyanine (**4**) in chloroform showed a B band region at