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Synthesis, characterization, electropolymerization and aggregation properties of axially diethyl-dimethylaminophenoxypropanoxy substituted silicon phthalocyanines and their water soluble derivatives

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ABSTRACT

In this study, the synthesis of non-ionic and ionic soluble axially disubstituted silicon phthalocyanines has been reported. Aggregation behavior of the silicon phthalocyanines was investigated in different solvents and concentrations. In all studied solvents and concentrations, silicon phthalocyanines were non-aggregated. Electrochemical and electropolymerization properties of the silicon phthalocyanines were studied by cyclic and square wave voltammetry. Electrochemistry of silicon phthalocyanines bearing polymerizable dimethylamino and diethylamino groups were introduced. Silicon phthalocyanines displayed only phthalocyanine ring based reduction redox processes during the cathodic potential scans. However, the silicon phthalocyanine complexes during the anodic potential scans were coated on the working electrode owing to the oxidative electropolymerization of dimethylamino and diethylamino groups on the substituents of the complexes.

1. Introduction

Metallophthalocyanines (Pcs) are one of the important types of tetrapyrrole compound. In addition to multifunctional dyes, phthalocyanine has received great attention for applications in different areas, such as liquid crystals [1,2], catalysts [3], solar cells [4–6], chemical sensors [7,8], material devices [9], nonlinear optical materials [10,11], photovoltaic cells [12], electrocatalytic systems [13,14], organic semiconductors [15] and photodynamic therapy (PDT) [16–19].

Unsubstituted phthalocyanines show very limited solubility in most organic solvents and water, a feature which restricts their applications in several areas. However, the introduction of various substituents such as diethylaminophenoxyethoxy, benzyloxy, alkyne, 6-hydroxyhexylthio onto the ring system can increase the solubility of phthalocyanines in water or common organic solvents [20–29]. On the other hand, owing to the hydrophobic nature of the phthalocyanine ring, phthalocyanines have a strong tendency to aggregate in solution, which also limits their applications. However axially disubstituted silicon phthalocyanines are non-aggregated due to the non-planar substituents issuing from the center metal atom [30]. In order to increase the solubility of silicon phthalocyanines in water and common organic solvents and applications in different areas, we have synthesized a new series of axially substituted non-aggregated silicon phthalocyanines.

In the last few years, we have focused our research on the synthesis and electrochemical properties of axially disubstituted silicon phthalocyanines. Compared to the peripheral or non-peripheral substituted phthalocyanines, axially disubstituted silicon phthalocyanines and their electrochemical properties are still scarce in the literature [31–34]. On the other hand, we chose axially 3-(dimethylamino)phenoxy]propanoxy) and 3-(diethylamino) phenoxy]propanoxy) groups as substituent on the phthalocyanine framework because these substituents bearing dimethylamino and diethylamino in their structure. These structure allow electropolymerization after axially substitution on the phthalocyanine core and results electropolymerizable phthalocyanine complexes. Modifications of phthalocyanines with functional polymerizable substituents extend the versatility of their electrochemical

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applications. On the other hand, axially-substituted silicon phthalocyanines (SiPcs) are of marvelous interest to scientists because they are generally not able to aggregate due to their special structural features [35]. For these reasons, the aim of this study is to synthesize axially 3-diethyldimethylaminophenoxypropanoxy substituted silicon phthalocyanines and investigate of their electropolymerization properties. We have reported that 3-diethyl- or dimethylaminophenoxypropanoxy substituted silicon phthalocyanines had an electropolymerization tendency [36] and this feature has an advantage for possible usage in different electrochemical technologies, such as electrocatalysis [37], electrosensing [38] and electrochromic applications [39].

2. Experimental

2.1. 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 Bruker Avance III 400 MHz spectrometers in $CDCl_3$, DMSO-d_6 and chemical shifts were reported (δ) relative to Me_4Si as internal standard. Mass spectra were measured on a Micromass Quattro 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 Bremen, Germany). 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. The elemental analyses were performed on a Costech ECS 4010 instrument.

2.2. Electrochemical measurements

The cyclic voltammetry (CV) and square wave voltammetry (SWV) measurements were carried out with Gamry Interface 1000 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 was employed as the supporting electrolyte at a concentration of 0.10 mol dm^{-3}.

2.3. Synthesis

2.3.1. 3-[3-(Diethylamino)phenoxy]propan-1-ol (**2**)

3-Diethylaminophenol (4.00 g, 24.24 mmol) was dissolved in ethanol (35 mL). NaOH (1.21 g, 30.3 mmol) was then added and dissolved by stirring at 50 °C for 1.5 h. 3-Chloro-1-propanol (2.86 g, 30.3 mmol) in ethanol (5 mL) was added dropwise to this solution with stirring for 30 min. This mixture was refluxed under nitrogen for 24 h. After the mixture was cooled, the solvent was removed under vacuum, residue was dissolved in chloroform (75 mL). The mixture were washed with 10% NaOH (2.1 mL) and with water (100 mL). The organic phase was dried over $MgSO_4$, filtered and rotary evaporated. The crude product was purified by passing through an aluminum oxide column using $CHCl_3$ as a solvent. Yield: 3.40 g (63%), b.p.: 156 °C. IR (KBr pellet) ν (cm^{-1}): 3369 (O–H), 3089 (Ar–H), 2968–2874 (Aliph. C–H), 1611, 1573, 1500, 1470, 1374, 1356, 1284, 1215, 1177, 1142, 1064, 1026, 823, 748, 687. ^{1}H NMR (400 MHz, $CDCl_3$), (δ): 7.13 (t, 1H, $J = 8.4$, Ar–H), 6.35 (d, 1H, $J = 7.7$ Ar–H), 6.25–6.24 (m, 2H, Ar–H), 4.13 (t, 2H, $J = 4.9$, Ar–CH_2–O), 3.87 (t, 2H, $J = 5.8$, CH_2–O), 3.36 (q, 4H, $J = 7.0$, CH_2–N), 2.17 (bs, 1H, OH), 2.05 (m, 2H, –CH_2–), 1.18 (t, 6H, $J = 7.0$, –CH_3). ^{13}C NMR (100 MHz, $CDCl_3$), (δ): 160.13, 149.24, 129.93, 105.33, 100.75, 98.90, 65.74, 60.76, 44.40, 32.10, 12.63. MS (ESI), (m/z) calc. 223.31; found: 224.16 $[M + H]^+$. Elemental Analysis: (Found: C 70.12, H 9.30, N 6.41%, $C_{13}H_{21}NO_2$ (223.31) requires C 69.92, H 9.48, N 6.27%).

2.3.2. Bis ([3-(dimethylamino)phenoxy]propanoxy) phthalocyaninato silicon (IV) (**3**)

Silicon phthalocyanine dichloride [40] (150 mg, 0.24 mmol), 3-[3-(dimethylamino)phenoxy]propan-1-ol (**1**) (94 mg, 0.48 mmol) were mixed in dry toluene (15 mL). This mixture was stirred under N_2 atmosphere for 10 min and sodium hydride (11.52 mg, 0.48 mmol) was added. The mixture was refluxed for 24 h. After cooling, the solvent was evaporated to dryness under reduced pressure. The product was purified by column chromatography on aluminum oxide using $CHCl_3$:CH_3OH (100:2) as eluent system. Yield: 0.13 g (57%), m.p. >300 °C. IR (KBr pellet) ν (cm^{-1}): 3063 (Ar–H), 2941–2874 (Aliph. C–H), 1614, 1568, 1499, 1471, 1427, 1331, 1289, 1240, 1165, 1120, 1106, 1078, 1055, 908, 813, 735, 682. ^{1}H NMR (400 MHz, $CDCl_3$), (δ): 9.58–9.56 (m, 8H, Pc-H_α), 8.31–8.29 (m, 8H, Pc-H_β), 6.88–6.86 (m, 2H, Ar–H), 6.22–6.20 (m, 2H, Ar–H), 5.28–5.26 (m, 2H, Ar–H), 5.19–5.17 (m, 2H, Ar–H), 2.80 (s, 12H, CH_3), 1.08 (m, 4H, Ar–O–CH_2), −0.99 (m, 4H, CH_2–CH_2), −1.93 (m, 4H, Si–O–CH_2). ^{13}C NMR (100 MHz, $CDCl_3$), (δ): 159.08, 151.42, 149.24, 135.96, 130.67, 129.09, 123.63, 105.04, 101.46, 99.07, 62.17, 51.10, 40.57, 28.64. UV–vis (DMSO) λ_{max} nm (log ε): 677 (5.31), 643 (4.50), 609 (4.57), 356 (4.85). MALDI-TOF-MS m/z calc. 929.10; found: 930.57 $[M + H]^+$. Elemental Analysis: (Found: C 69.96, H 5.02, N 15.29%, $C_{54}H_{48}N_{10}O_4Si$ (929.10) requires C 69.81, H 5.21, N 15.08%).

2.3.3. Bis ([3-(diethylamino)phenoxy]propanoxy)phthalocyaninato silicon (IV) (**4**)

Compound **4** was synthesized similarly to **3** by using 3-[3-(diethylamino)phenoxy]propan-1-ol **2** instead of 3-[3-(diethylamino)phenoxy]propan-1-ol **1**. Yield: 0.149 g (62%), m.p. >300 °C. IR (KBr pellet) ν (cm^{-1}): 3061 (Ar–H), 2967–2867 (Aliph. C–H), 1613, 1571, 1500, 1428, 1335, 1288, 1220, 1163, 1119, 1075, 1031, 910, 823, 758, 730, 702. ^{1}H NMR (400 MHz, $CDCl_3$), (δ): 9.59–9.57 (m, 8H, Pc-H_α), 8.31–8.29 (m, 8H, Pc-H_β), 6.83–6.81 (m, 2H, Ar–H), 6.14–6.12 (m, 2H, Ar–H), 5.24–5.22 (m, 2H, Ar–H), 5.09–5.07 (m, 2H, Ar–H), 3.18–3.16 (m, 8H, CH_2–N), 1.27 (m, 4H, Ar–O–CH_2), 1.05 (t, 12H, $J = 6.7$, CH_3), −1.01 (m, 4H, CH_2–CH_2), −1.94 (m, 4H, Si–O–CH_2). ^{13}C NMR (100 MHz, $CDCl_3$), (δ): 159.33, 149.24, 148.58, 135.96, 130.67, 129.25, 123.63, 104.31, 100.08, 98.25, 62.26, 51.22, 44.17, 29.71, 12.63. UV–vis (DMSO) λ_{max} nm (log ε): 677 (5.41), 645 (4.61), 609 (4.67), 356 (4.96). MALDI-TOF-MS m/z calc. 985.21; found: 986.27 $[M + H]^+$. Elemental Analysis: (Found: C 70.92, H 5.60, N 14.39%, $C_{58}H_{56}N_{10}O_4Si$ (985.21) requires C 70.71, H 5.73, N 14.22%).

2.3.4. Axially bis ([3-(trimethylmethylamino)phenoxy]propanoxy) phthalocyaninato silicon (IV) iodide (**5**)

Compound **3** (35 mg, 0.038 mmol) was dissolved in $CHCl_3$ (4 mL) and stirred with iodomethane (2 mL) at room temperature for 2 days. The precipitate was filtered off, washed with chloroform, acetone and diethyl ether. The precipitate was dried in vacuo. Yield: 34 mg (75%), m.p. >300 °C. IR (KBr pellet) ν (cm^{-1}): 3015 (Ar–H), 2935–2898 (Aliph. C–H), 1611, 1588, 1519, 1498, 1471, 1427, 1334, 1290, 1249, 1164, 1113, 1079, 1016, 972, 909, 838, 791, 744. ^{1}H NMR (400 MHz, DMSO-d_6), (δ): 9.60 (br, 8H, Pc-H_α), 8.30 (br, 8H, Pc-H_β), 6.75–6.70 (m, 4H, Ar–H), 5.81–5.76 (m, 4H, Ar–H), 3.22 (s, 18H, CH_3), 1.15 (m, 4H, Ar–O–CH_2), −0.87 (m, 4H, CH_2–CH_2), −1.99 (m, 4H, Si–O–CH_2). ^{13}C NMR (100 MHz, DMSO-d_6), (δ): 161.22, 153.33,