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Synthesis and electrochemistry of non-aggregated silicon phthalocyanines bearing unsaturated functional groups

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ABSTRACT

This paper describes the synthesis, characterization, aggregation and electrochemical behavior of new silicon phthalocyanines with 6-({(1*E*)-[4-(diethylamino)phenyl]methylene}amino)hexan, 2-[2-({(1*E*)-[4(diethylamino)phenyl]methylene}amino)ethoxy], 6-({(1*E*)-[4-(dimethylamino)phenyl]methylene}amino)hexan groups as axial ligands. The aggregation behavior of these complexes was examined at different concentration and solvents. In all studied organic solvents, silicon phthalocyanine complexes were non-aggregated. Electrochemical properties of silicon phthalocyanine complexes **3**, **5** and **7** were determined by cyclic and square wave voltammetry. Voltammetric studies reveal that while complex **3** showed two reduction and two oxidation couples, complex **5** showed three reduction and one oxidation couples, on the other hand, complex **7** showed two reduction couples and one oxidation couples.

1. Introduction

Phthalocyanines and their metal complexes (MPcs) are the most studied classes of compounds that have attracted care owing to their potential usage in catalysts [1,2], optical data collection [3,4], liquid crystals [5–7], chemical sensors [8–10], semiconducting devices [11] and photodynamic therapy [12–15].

The electrochemical properties of phthalocyanines depends on diverse factors such as the solvent, axial ligands and type of metal center. The industrial application of phthalocyanines is related to their redox properties [16–20]. In order to determine redox properties of phthalocyanines, generally voltammetric methods such as cyclic voltammetry, square wave voltammetry are used.

Applications of phthalocyanine complexes have been limited owing to their low solubility in common organic solvents. Recent years, in order to improve solubility of phthalocyanines, many axially substituted phthalocyanine complexes have been synthesized [21–25]. Along with improving solubility, the nature of axial ligands vigorously influences the aggregation behavior, electronic absorption, spectral and electrochemical properties of phthalocyanines [26]. For these purposes the strategy of this study has focused on combining axial ligands with phthalocyanine. Thus, in this study, we have synthesized new axially disubstituted silicon phthalocyanine complexes and invesjom_18302_gr10_3c.tif -tigated of their aggregation and electrochemical properties.

2. Experimental

2.1. Synthesis

2.1.1. Synthesis of 6-({(1E)-[4-(diethylamino)phenyl]methylene}amino)hexan-1-ol (2)

4-(Diethylamino)benzaldehyde (4 g, 22.6 × 10^{-3} mol) was added to ethanol (0.07 L) and nitrogen gas was bubbled through this mixture for 10 min. 6-aminohexan-1-ol (2.64 g, 22.6 × 10^{-3} mol) was added this solution with stirring for 30 min and 18 drop of CH_3COOH was added in this mixture. The reaction mixture was refluxed under nitrogen for 24 h. After the mixture was cooled, the solvent was removed under vacuum, and resulting crude product was dissolved in chloroform. The mixture was washed with water. The organic phase was dried over $MgSO_4$, filtered and rotary evaporated. The obtained oily crude was purified by column chromatography which is placed in aluminum oxide using $CHCl_3$: CH_3OH (100:5) as a solvent system. Yield: 5.12 g (82%). IR (KBr pellet), ν_{max}/cm^{-1}: 3391 (O–H), 3060 (Ar–H), 2971–2856 (Aliph. C–H), 1635, 1602, 1557, 1525, 1468, 1404, 1356, 1270, 1215, 1155, 1076, 970, 815, 710. ^{1}H NMR, (DMSO-d_6), (δ:ppm): 8.06 (s, 1H, CH=N), 7.45 (d, 2H, Ar–H), 6.60 (d, 2H, Ar–H), 4.36 (t, 1H, O–H), 3.38 (t, 2H, CH_2–O), 1.53 (m, 6H, –CH_2–N), 1.39–1.27 (m, 6H, CH_3), 1.13–1.03 (m, 8H, –CH_2–CH_2). MS (ESI), (m/z): 276 $[M]^+$.

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*2.1.2. Synthesis of 2-[2-({(1E)-[4(diethylamino)phenyl]methylene}amino)ethoxy]ethanol (**4**)*

Compound **4** was prepared as described for the **2** using 4-(diethylamino)benzaldehyde (5 g, 28.2 × 10^{-3} mol) and 2-(2-aminoethoxy)ethanol (2.96 g, 28.2 × 10^{-3} mol). Yield: 6.85 g (92%). IR (KBr pellet), ν_{max}/cm^{-1}: 3376 (O–H), 3044 (Ar–H), 2970–2869 (Aliph. C–H), 1662, 1637, 1592, 1554, 1523, 1405, 1354, 1314, 1270, 1242, 1173, 1155, 1075, 900, 816, 710. ^{1}H NMR, (DMSO-d_6), (δ:ppm): 8.09 (s, 1H, CH=N), 7.48 (d, 2H, Ar–H), 6.59 (d, 2H, Ar–H), 3.43 (m, 6H, CH_2–O), 3.33 (m, 6H, –CH_2–N), 1.04 (m, 6H, CH_3). MS (ESI), (*m*/*z*): 264 $[M]^+$.

*2.1.3. Synthesis of 6-({(1E)-[4-(dimethylamino)phenyl]methylene}amino)hexan-1-ol (**6**)*

Compound **6** was prepared as described for the **2** using 4-(dimethylamino)benzaldehyde (4 g, 27 × 10^{-3} mol) and 6-aminohexan-1-ol (3.2 g, 27 × 10^{-3} mol). Yield: 5.3 g (79%). IR (KBr pellet), ν_{max}/cm^{-1}: 3400 (O–H), 3093 (Ar–H), 2930–2855 (Aliph. C–H), 1662, 1606, 1555, 1528, 1501, 1443, 1371, 1314, 1231, 1166, 1063, 945, 815, 728. ^{1}H NMR, (DMSO-d_6), (δ:ppm): 8.08 (s, 1H, CH=N), 7.49 (d, 2H, Ar–H), 6.66 (d, 2H, Ar–H), 4.43 (bs, 1H, O–H), 3.39 (m, 2H, CH_2–O), 2.92 (s, 6H, –CH_3–N), 1.54 (m, 2H, CH_2–N), 1.39–1.29 (m, 8H, –CH_2–CH_2). MS (ESI), (*m*/*z*): 249 [M + H]+.

*2.1.4. Synthesis of silicon phthalocyanine (**3**)*

A mixture of dichloro(phthalocyaninato) silicon **1** (0.2 g, 0.32 × 10^{-3} mol) and [6-({(1*E*)-[4-(diethylamino)phenyl]methylene}amino)hexan-1-ol **2** (0.085 g, 0.64 × 10^{-3} mol) in toluene (0.02 L) was stirred and then sodium hydride (0.014 g, 0.58 × 10^{-3} mol) was added to this mixture. After refluxing under nitrogen 24 h, the reaction mixture was cooled to room temperature, and then the solvent was evaporated to dryness under reduced pressure. The crude product was purified by column chromatography which is placed in aluminum oxide using $CHCl_3$: CH_3OH (100:3) as a solvent system. Dark blue product was obtained. Yield: 0.105 g (29%). IR (KBr tablet) ν_{max}/cm^{-1}: 3053 (Ar–H), 2965–2852 (Aliph. C–H), 1736, 1638, 1594, 1519, 1333, 1289, 1171, 1120, 1078, 909, 758, 731. ^{1}H NMR, ($CDCl_3$), (δ:ppm): 9.61–9.59 (m, 8H, Pc–H_α), 8.34–8.32 (m, 8H, Pc–H_β), 7.72–7.68 (m, 4H, Pc–H), 7.45–7.43 (m, 2H, CH=N), 6.70–6.65 (m, 4H, Pc–H), 3.40–3.35 (m, 12H, CH_2–N), 1.35–1.32 (m, 12H, –CH_3), 1.11–1.06 (m, 16H, –CH_2–CH_2), –1.75 (m, 4H, Si–O–CH_2). UV–vis (chloroform): λ_{max}, nm (log ε): 674 (5.15), 641 (4.33), 606 (4.26), 341 (4.79). MALDI-TOF-MS *m*/*z*: 1113 $[M + H]^+$.

*2.1.5. Synthesis of silicon phthalocyanine (**5**)*

Silicon phthalocyanine **5** was prepared as described for the **3** using 2-[2-({(1*E*)-[4(diethylamino)phenyl]methylene}amino)ethoxy]ethanol **4** (0.169 g, 0.64 × 10^{-3} mol). Yield: 0.07 g (20%). IR (KBr tablet) ν_{max}/cm^{-1}: 3060 (Ar–H), 2970–2867 (Aliph. C–H), 1725, 1654, 1595, 1520, 1353, 1335, 1266, 1184, 1121, 1079, 1053, 953,739. ^{1}H NMR, (DMSO-d_6), (δ:ppm): 9.62–9.60 (m, 4H, Pc–H), 8.46–8.44 (m, 4H, Pc–H), 7.83 (m, 10H, Ar–H), 7.71 (m, 4H, Pc–H), 6.64 (m, 4H, Pc–H), 3.36 (m, 8H, CH_2–O), 2.52 (m, 12H, CH_2–N), 1.09 (m, 12H, –CH_3), –2.07 (m, 4H, Si–O–CH_2). UV–vis (chloroform): λ_{max}, nm (log ε): 676 (5.30), 645 (4.54), 609 (4.53), 352 (4.97). MALDI-TOF-MS *m*/*z*: 1066 $[M]^+$.

*2.1.6. Synthesis of silicon phthalocyanine (**7**)*

Silicon phthalocyanine **7** was prepared as described for the **3** using 6-({(1*E*)-[4-(dimethylamino)phenyl]methylene}amino)hexan-1-ol **6** (0.16 g, 0.64 × 10^{-3} mol). Yield: 0.075 g (22%). IR (KBr tablet) ν_{max}/cm^{-1}: 3056 (Ar–H), 2918–2849 (Aliph. C–H), 1728, 1667, 1595, 1519, 1427, 1334, 1289, 1164, 1121, 1078, 909, 758, 733. ^{1}H NMR. ($CDCl_3$), (δ:ppm): 9.59–9.57 (m, 8H, Pc–H_α), 8.33–8.30 (m, 8H, Pc–H_β), 7.75–7.72 (m, 2H, CH=N), 6.73 (m, 4H, Pc–H), 5.55–5.51 (m, 4H, Pc–H), 3.09–3.05 (m, 12H, CH_3–N), 2.46 (m, 4H, –CH_2–N), 1.60–1.51 (m, 16H, –CH_2–CH_2), –0.81 (m, 4H, Si–O–CH_2). UV–vis (chloroform): λ_{max}, nm (log ε): 675 (5.44), 644 (4.67), 608 (4.66), 344 (5.00). MALDI-TOF-MS *m*/*z*: 1036 $[M + H]^+$.

3. Results and discussion

3.1. Syntheses and characterization

The synthesis of compounds **2**, **3**, **4**, **5**, **6**, and **7** are shown in Figs. 1 and 2. $SiPc(Cl)_2$ **1** [27] was synthesized according to previously published method. The first step is the synthesis of 6-({(1*E*)-[4-(diethylamino)phenyl]methylene}amino)hexan-1-ol **2**, 2-[2-({(1*E*)-[4(diethylamino)phenyl]methylene}amino)ethoxy]ethanol **4** and 6-({(1*E*)-[4-(dimethylamino)phenyl]methylene}amino) hexan-1-ol **6**. Second step is the synthesis of axially disubstituted silicon phthalocyanines **3**, **5**, **7**. These phthalocyanines were synthesized by using compounds **2**, **4**, **6** in the presence of $SiPc(Cl)_2$ **1** and NaH in toluene. These axially substituted silicon phthalocyanines showed high solubility in many common organic solvents. IR, ^{1}H NMR, MALDI-TOF-MS, UV–Vis analyses confirmed the proposed structures of the synthesized compounds.

In the IR spectra, the formation of compounds **2**, **4** and **6** were clearly confirmed by disappearance of the NH_2 and C=O band and the appearance of the OH and HC=N band at 3391 and 1635 cm^{-1} for **2**, 3376 and 1637 cm^{-1} for **4**, 3400 and 1606 cm^{-1} for **6**, respectively. ^{1}H NMR spectra were also in good agreement with the structures of compounds **2**, **4** and **6**. The molecular ion peaks of **2**, **4**

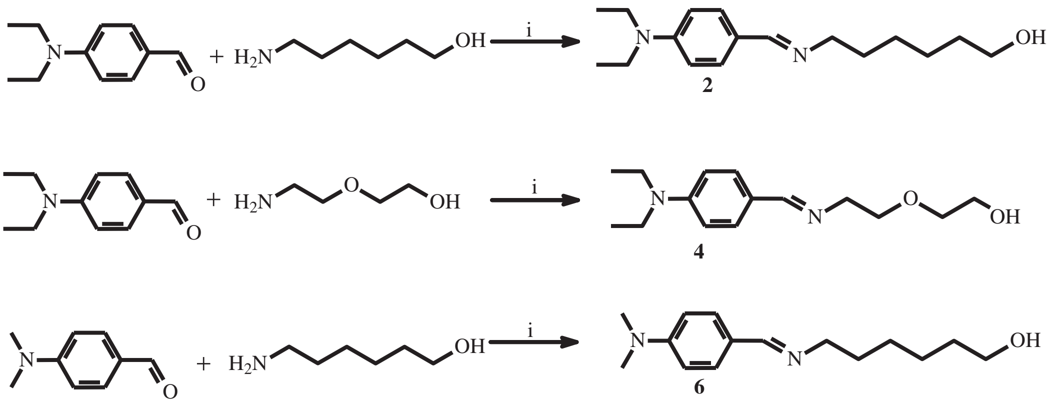

Fig. 1. The synthesis of the compounds **2**, **4** and **6**. (i) EtOH, CH_3COOH, reflux.