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Non-aggregated axially naphthoxazin group substituted silicon phthalocyanines: Synthesis and electrochemistry

Hüseyin Baş, Zekeriya Biyiklioglu*

Department of Chemistry, Faculty of Science, Karadeniz Technical University, 61080 Trabzon, Turkey

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ABSTRACT

In this study, the new 2-[2-(1*H*-naphtho[1,2-*e*][1,3]oxazin-2(3*H*)-yl)ethoxy]ethanol, 6-(1*H*-naphtho[1,2-*e*][1,3]oxazin-2(3*H*)-yl)hexan-1-ol have been synthesized. Then, novel axially naphthoxazin substituted two silicon(IV) phthalocyanines (SiPcs) have been synthesized and characterized. The aggregation behavior of SiPcs were examined in different solvents and concentrations in DMSO. In all studied solvents and concentrations, SiPcs were non-aggregated. The reduction and oxidation behavior of the axially disubstituted SiPcs were established by cyclic (CV) and square wave (SWV) voltammetry. Axially naphthoxazin substituted silicon(IV) phthalocyanines were observed to display phthalocyanine ring-based redox processes.

1. Introduction

Phthalocyanines (Pcs) are important compounds due to not only their blue–green color but also their electronic properties. They have been proposed and used in various technological areas such as liquid crystals, electronic devices, gas and chemical sensors, electrochromic and electroluminescent displays, non-linear optics, photovoltaics and semiconductors [1–6]. Also usage of their efficient photosensitizers in obtaining singlet oxygen is becoming especially important in photodynamic therapy (PDT) of tumors [7,8]. These properties may be modulated by central metals and huge variety of substitutions attached to the Pc cores [9–14].

The main limitation in the applications of phthalocyanine complexes is their low solubility in common organic solvents [15]. The solubility of phthalocyanines alter of their chemical, physical and electrochemical properties. A common mean for preparing soluble phthalocyanines is to attach functional groups like tertiary butyl, amide or carboxylic acid groups [16,17] or bulky, crown ether groups [18–23], azo groups [24], etc. to the peripheral of phthalocyanine ring and/or axial positions of the trivalent and tetravalent central metal ions [Al(III), Mn(III), In(III), Ga(III), Ti(IV) and Si(IV)]. Recent years, in order to improve solubility of phthalocyanines, many axially substituted phthalocyanine complexes have been synthesized [25–32].

The nature of substituents on axially positions can strongly influence essential parameters of a phthalocyanine, such as its solubility, aggregation behavior, electronic absorption, photophysical, photochemical, electrochemical properties [33]. For these reasons, in this study we have synthesized non-aggregated axially disubstituted silicon phthalocyanines bearing naphthoxazin substituents and investigated aggregation and electrochemical properties of these newly synthesized SiPcs.

2. Experimental

2.1. Synthesis

2.1.1. 2-[2-(1H-naphtho[1,2-e][1,3]oxazin-2(3H)-yl)ethoxy] ethanol (**1**)

Paraformaldehyde (0.8 g, 27.6 mmol), 2-naphthol (2 g, 13.8 mmol) and 2-(2-aminoethoxy)ethanol (1.45 g, 13.8 mmol) were stirred at 110 °C for 1 days under an nitrogen atmosphere. Then, reaction mixture was diluted with chloroform (100 mL) and washed successively 4 times with 0.1 N NaOH and diluted AcOH solution. It was neutralized with distilled water. Organic layer was dried over anhydrous $MgSO_4$ and then filtered. Solvent was

* Corresponding author.
E-mail address: zekeriya_61@yahoo.com (Z. Biyiklioglu).

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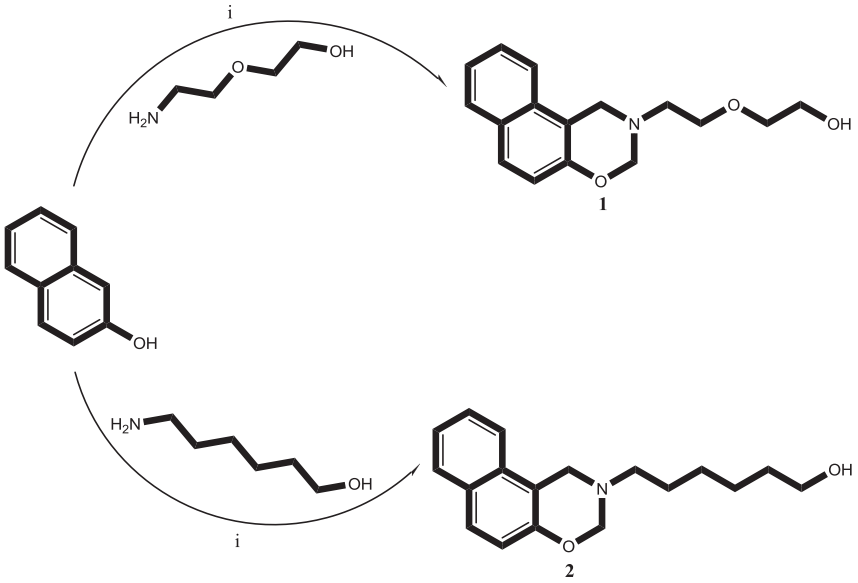

Fig. 1. The synthesis of compounds **1** and **2**. (i) Paraformaldehyde, 110 °C.

evaporated and the product was purified by column chromatography with basic alumina as column material and $CHCl_3$: as solvent. Yield: 1.36 g (36%). IR (ATR), ν/cm^{-1}: 3392 (O–H), 3060 (Ar–H), 2928–2864 (Aliph. C–H), 1624, 1598, 1515, 1471, 1435, 1354, 1264, 1227, 1125, 1069, 992, 944, 900, 813, 748. ^{1}H NMR ($CDCl_3$), (δ:ppm): 7.79 (d, 1H, Ar–H), 7.67–7.60 (m, 2H, Ar–H), 7.50 (t, 1H, Ar–H), 7.39 (t, 1H, Ar–H), 7.05 (d, 1H, Ar–H), 4.98 (s, 2H, N–CH_2–O), 4.40 (s, 2H, Ar–CH_2–N), 3.75–3.72 (m, 4H, CH_2–O), 3.63 (t, 2H, –CH_2–O), 3.06 (t, 2H, CH_2–N). ^{13}C NMR ($CDCl_3$), (δ:ppm): 151.72, 131.81, 129.02, 128.69, 128.17, 126.63, 123.58, 120.96, 118.50, 111.53, 82.28, 72.49, 69.28, 61.81, 51.69, 48.11. MS (ESI), (*m*/*z*): 274 $[M+H]^+$.

*2.1.2. 6-(1H-naphtho[1,2-e][1,3]oxazin-2(3H)-yl)hexan-1-ol (**2**)*

Synthesized similarly to **1** by using 6-amino-1-hexanol instead of 2-(2-aminoethoxy)ethanol. Yield: 2.48 g (63%). IR (ATR), ν/cm^{-1}: 3367 (O–H), 3061 (Ar–H), 2932–2857 (Aliph. C–H), 1625, 1598, 1514, 1471, 1434, 1401, 1227, 1139, 1056, 983, 945, 901, 812, 747, 681. ^{1}H NMR ($CDCl_3$), (δ:ppm): 7.80 (d, 1H, Ar–H), 7.67–7.63 (m, 2H, Ar–H), 7.50 (t, 1H, Ar–H), 7.37 (t, 1H, Ar–H), 7.06 (d, 1H, Ar–H), 4.94 (s, 2H, N–CH_2–O), 4.34 (s, 2H, Ar–CH_2–N), 3.64 (t, 2H, CH_2–O), 2.82 (t, 2H, –CH_2-N), 1.85 (bs, 1H, OH), 1.65–1.59 (m, 4H, CH_2–CH_2), 1.65–1.41 (m, 4H, CH_2–CH_2). ^{13}C NMR ($CDCl_3$), (δ:ppm): 151.88, 131.90, 128.97, 128.67, 127.98, 126.52, 123.44, 121.01, 118.54, 111.87, 82.21, 62.83, 51.91, 47.84, 32.70, 28.18, 27.03, 25.64. MS (ESI), (*m*/*z*): 286 $[M+H]^+$.

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

A mixture of $SiPc(Cl_2)$ (0.1 g, 0.16 mmol), 2-[2-(1*H*-naphtho[1,2-*e*][1,3]oxazin-2(3*H*)-yl)ethoxy]ethanol **1** (0.087 g, 0.32 mmol) and NaH (0.008 g, 0.32 mmol) in toluene (10 mL) was refluxed for 24 h at 120 °C. After evaporating the solvent in vacuo, the residue was subjected to column chromatography which is placed silicagel using $CHCl_3$:CH_3OH (100:4) as solvent system. Yield: 0.076 g (43%). IR (ATR) ν_{max}/cm^{-1}: 3059 (Ar–H), 2962–2854 (Aliph. C–H), 1622, 1595, 1518, 1470, 1427, 1333, 1289, 1259, 1225, 1163, 1119, 1075, 1015, 938, 909, 806, 732. ^{1}H NMR. ($CDCl_3$), (δ:ppm): 9.59–9.58 (m, 8H, Pc-H_α), 8.26–8.24 (m, 8H, Pc-H_β), 7.79 (d, 2H, Ar–H), 7.65 (d, 2H, Ar–H), 7.47 (t, 2H, Ar–H), 7.38–7.37 (m, 4H, Ar–H), 6.97 (d, 2H, Ar–H), 4.29 (s, 4H, N–CH_2–O), 3.73 (s, 4H, Ar–CH_2–N), 1.89 (t, 4H, CH_2–O), 1.72 (t, 4H, –CH_2-O), 0.46 (t, 4H, CH_2–N), –1.84 (t, 4H,

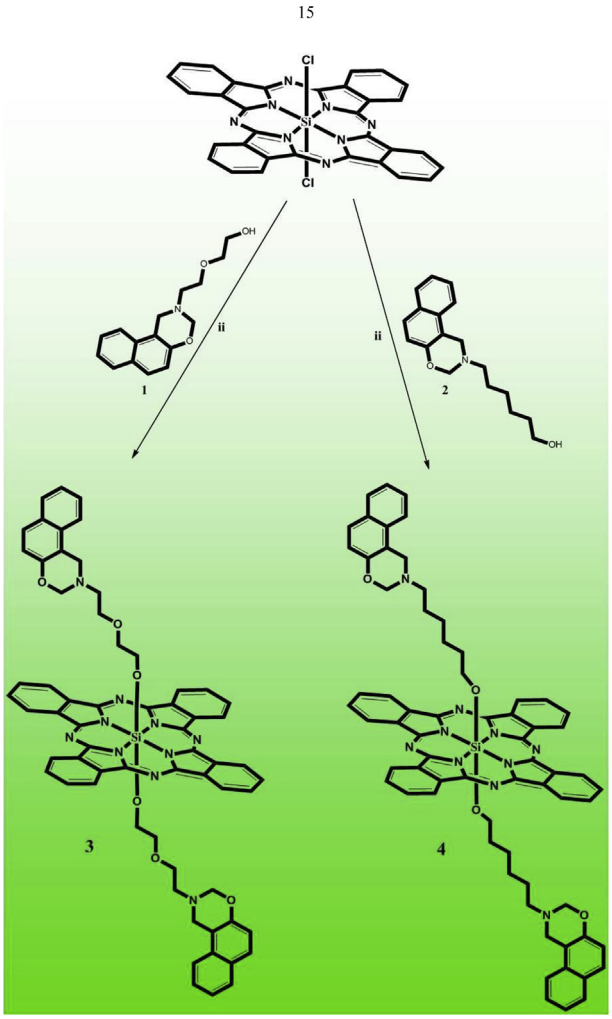

Fig. 2. The synthesis of axially disubstituted silicon phthalocyanines. (ii) Toluene, NaH, 120 °C.