Inorganic Chemistry Communications 55 (2015) 60–64

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Electrochemical and aggregation properties of newly synthesized dendritic axially morpholine-disubstituted silicon phthalocyanine, mono-substituted subphthalocyanine and their quaternized derivatives

Zekeriya Biyiklioglu

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

ARTICLE INFO

Article history:
Received 30 January 2015
Received in revised form 4 March 2015
Accepted 9 March 2015
Available online 11 March 2015

Keywords:
Phthalocyanine
Silicon
Axial
Synthesis
Electrochemistry
Aggregation

ABSTRACT

In this study, the new [3,5-bis(2-morpholin-4-ylethoxy)phenyl]methanol **3** has been synthesized. Then novel axially di-substituted silicon phthalocyanine **3**, axially mono-substituted subphthalocyanine **5** and their quaternized derivatives **4a** and **5a** have been synthesized using a convenient route starting with the [3,5-bis(2-morpholin-4-ylethoxy)phenyl]methanol. The complexes are obtained in high yield and are soluble in many organic solvents. The aggregation behavior of axially di-substituted silicon phthalocyanine **3**, axially mono-substituted subphthalocyanine **5** and their quaternized derivatives **4a** and **5a** was examined in different solvents. The effect of solvents on absorption spectra was studied in various solvents. In all studied solvents, these complexes were non-aggregated. The electrochemical properties of axially di-substituted silicon phthalocyanine **3** and axially mono-substituted subphthalocyanine **5** were also investigated by cyclic voltammetry and square wave voltammetry techniques. Cyclic voltammetry revealed two reduction couples and one oxidation couple for **4** and **5**.

Phthalocyanines are very important compounds owing to their blue-green color and electronic properties. Phthalocyanines have many potential applications in different areas such as chemical sensors [1], solar cell [2], liquid crystals [3], optical data storage [4,5], electrochromic display [6], non-linear optics [7], photodynamic therapy (PDT) of cancer [8,9]. Aggregation lowers the use of phthalocyanines in technological applications. Also, aggregation is an unfavorable property of phthalocyanines that causes difficulties in purification and characterization. In order to overcome this problem, the introduction of substituents at the axial positions of phthalocyanines is preferred, because the axial positions can strongly influence some properties of phthalocyanines such as its solubility and aggregation behavior. For example substitution on axial ligands with long alkyl chains [10], crown ethers [11,12], and bulky groups [13] leads to phthalocyanine soluble in common solvents and with amino groups [14,15] leads to phthalocyanine soluble in water. Silicon(IV) phthalocyanines carrying two axial ligands generally show reduced aggregation, enhanced water solubility and high photodynamic efficacy. For this reason, non-aggregating and water soluble axially disubstituted silicon phthalocyanines can be used as potential PDT agents.

Subphthalocyanines which have 14 π-electron system are nonplanar core-shaped aromatic macrocycles consisting of three diiminoisoindoline units N-fused around a boron center [16]. In contrast with planar phthalocyanines, subphthalocyanines possess a peculiar conical structure, which provides them with relatively high solubility and low tendency for aggregation [17].

Besides improving solubility, the nature of axial ligands influences the spectral and electrochemical properties of phthalocyanines and subphthalocyanines. On the other hand, axially disubstituted silicon phthalocyanines and axially substituted subphthalocyanines display very attractive electrochemical properties. Silicon phthalocyanine and subphthalocyanine derivatives have been reported rare [18–25]. But investigation of electrochemical properties of axially disubstituted silicon phthalocyanines and subphthalocyanines remains extremely rare in the literature [26–32]. For this reason, in this work, we have synthesized a new class of dendritic axially morpholine disubstituted silicon phthalocyanine, subphthalocyanine and their quaternized derivatives. Also we have examined their aggregation behavior in different solvents and electrochemical properties by using cyclic voltammetry (CV) and square wave voltammetry (SWV) techniques.

The synthetic pathway of the silicon phthalocyanine **4**, subphthalocyanine **5** and their quaternized derivatives **4a** and **5a** is shown in Figs. 1 and 2. [3,5-Bis(2-morpholin-4-ylethoxy)phenyl]-methanol **3** [33] was synthesized from 3,5-dihydroxybenzyl alcohol **2** with 4-(2-chloroethyl)morpholine **1** in the presence of K_2CO_3 and 18-crown-6, in acetone at reflux temperature. Reaction of $SiPcCl_2$ with compound **3** in the presence of NaH in toluene led to silicon phthalocyanine **4** [34]. Axially mono-substituted subphthalocyanine **5** [35] was synthesized in the presence of Cl[B(SubPc)] in toluene at 120 °C by using compound **3**.

E-mail address: zekeriya_61@yahoo.com.

http://dx.doi.org/10.1016/j.inoche.2015.03.011
1387-7003/

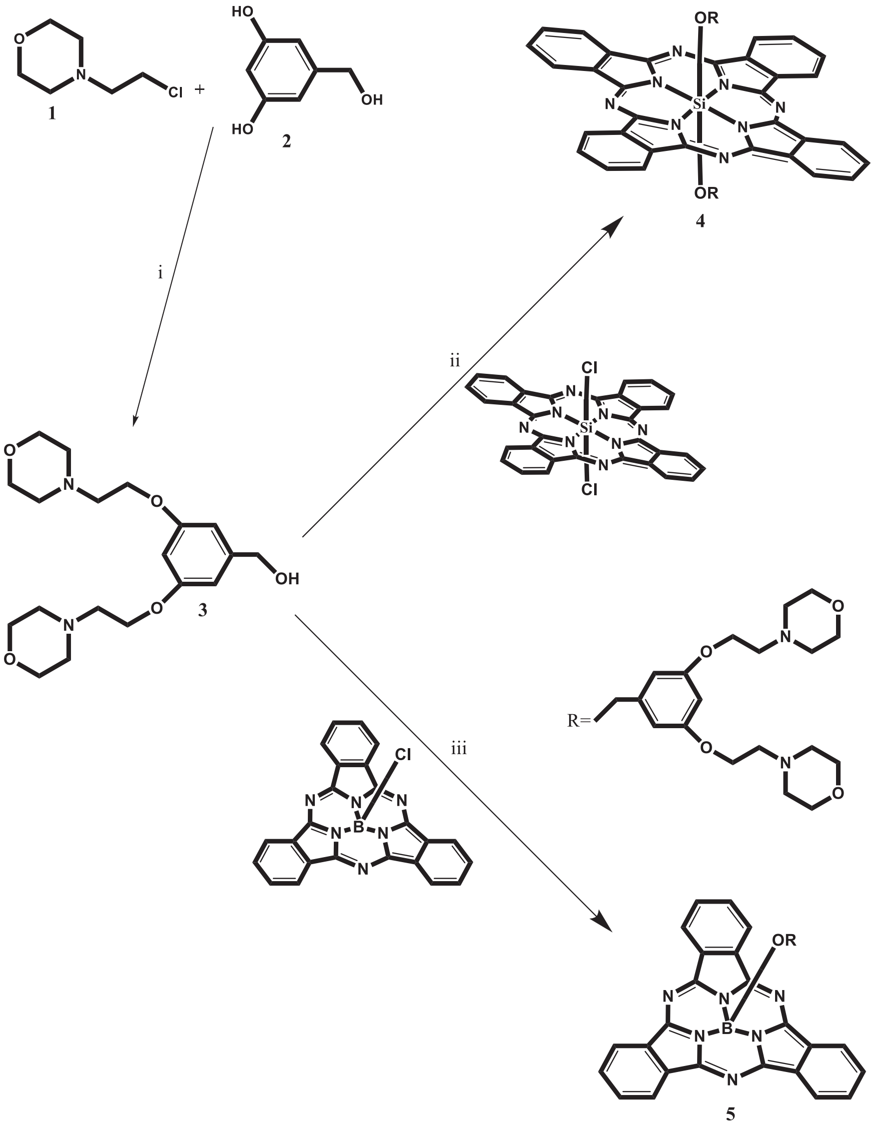

Fig. 1. The synthesis of compound **3**, axially di-substituted silicon phthalocyanine **4**, and axially mono-substituted subphthalocyanine **5**. (i) 18-Crown-6, acetone, reflux. (ii) Toluene, NaH, 120 °C. (iii) Toluene, 120 °C.

Lastly, quaternized silicon phthalocyanine **4a** [36] and subphthalocyanine **5a** [37] were prepared from the reaction of corresponding compounds **4** and **5** with iodomethane as quaternization agent in chloroform. After reaction with iodomethane, the quaternized silicon phthalocyanine **4a** is very soluble in water, DMF, and DMSO, but the quaternized subphthalocyanine **5a** is not soluble in water. IR, ^{1}H NMR, ^{13}C NMR, MALDI-TOF-MS, UV–vis and elemental analyses confirmed the proposed structures of the synthesized compounds.

In the FT-IR spectrum of compound **3**, OH vibrations disappeared and appeared –CH_2–OH peak at 3422 cm^{-1} as expected. In the IR spectrum, the formation of silicon and subphthalocyanines **4** and **5** was clearly confirmed by disappearance of the OH band at 3422 cm^{-1}. In the IR spectrum of quaternized silicon and subphthalocyanines **4a** and **5a**, no major change was found after quaternization. In the ^{1}H NMR spectrum of compound **3** phenolic OH group of 3,5-dihydroxybenzyl alcohol vanished as expected. ^{13}C NMR spectra were also in good agreement with the structure of compound **3**. In ^{1}H NMR spectrum of silicon phthalocyanine **4**, Si–O–CH_2 has shifted negative area (−0.74 ppm) because of magnetic anisotropy of phthalocyanine ring. In ^{1}H NMR spectrum of silicon phthalocyanine **4**, the shifts between 9.62–9.60 ppm belong to H_α and the shifts between 8.36–8.34 ppm belong to H_β. Also the ^{1}H NMR measurements of subphthalocyanine **5** showed the expected total number of aliphatic and aromatic protons confirming the purity of compound **5** as shown in experimental part. The molecular ion peak of compound **3** found at m/z 367 $[M + H]^+$ supports the proposed structure. In the mass spectrum of compounds **4**, **5**, **4a** and **5a** which was obtained by using the MALDI-TOF method, the molecular ion peak of compounds **4**, **5**, **4a** and **5a** were observed at 1227 $[M\text{-}C_2H_4O]^+$, 760 $[M]^+$, 1809 $[M\text{-}2CH_3]^+$, 943 $[M\text{-}C_6H_{13}O]^+$, respectively.

The electronic absorption spectrum of the subphthalocyanine is similar to that of the metallophthalocyanine, it gives two intense bands, the Q-band observed at ca. 560 nm, and the Soret (B) band observed at around 300 nm. Q and B bands are blue-shifted compared to those of metallophthalocyanine (Q band observed at ca. 700 nm, the Soret (B) band observed at ca. 350 nm) [38] counterparts owing to the 14π conjugated system of subphthalocyanines compared to the 18π conjugated systems for phthalocyanines. The UV–vis spectra of silicon and subphthalocyanines **4** and **5** in $CHCl_3$ at room temperature are shown in Fig. 3a. The electronic spectra of the silicon and subphthalocyanines **4** and **5** showed characteristic absorptions in the Q band region at 677, 565 nm, approving the monomeric structure, respectively. B bands of silicon and subphthalocyanines **4** and **5** were observed at around 345 and 302 nm, respectively. Quaternized silicon and subphthalocyanines