Graphical Abstract

ARTICLE TYPE

Non-Aggregated Axially Disubstituted Silicon Phthalocyanines Bearing Electropolymerizable Ligands and Their Aggregation, Electropolymerizaton, Thermal Properties

₅ **Zekeriya Bıyıklıoğlu[a*], Hüseyin Baş[a], Hakan Alp[a]**

A novel series of axially disubstituted silicon(IV) phthalocyanines bearing electropolymerizable ligand were designed and synthesized for the first time. Silicon(IV) phthalocyanines were also characterized by ₁₀ various spectroscopic techniques as well as elemental analysis. Aggregation behavior of SiPcs were examined in different solvents and concentrations in dimethyl sulfoxide. In all studied solvents and concentrations, SiPcs were non-aggregated. Thermal behavior of the silicon(IV) phthalocyanines were also studied. Electropolymerization properties of silicon(IV) phthalocyanines were investigated by cyclic and square wave voltammetry. This study is the first example of electropolymerization of axially ₁₅ disubstituted silicon phthalocyanines. The type of the axial ligand on phthalocyanine ring did not show any effect on the absorption and thermal properties but influenced the electropolymerization of phthalocyanines.

1. Introduction

Phthalocyanines are well-known 18π-electron aromatic ₂₀ molecules. Phthalocyanines are very important compounds owing to thier blue-green color and electronic properties. Phthalocyanines also have many potential applications in many areas such as solar cell,[1,2] sensors,[3,4] nonlinear optics,[5] electrochromic display,[6,7] liquid crystals,[8,9] semiconductor ₂₅ devices,[10] dyes,[11] optical data storage,[12,13] catalysts[14,15] and photodynamic therapy.[16-18] However, the poor solubility and aggregation of phthalocyanines limits their application. As known, phthalocyanines show high trend of aggregation in solution to form dimers and higher oligomers species owing to ₃₀ attractive π-π stacking interactions of their extended π-system.[19] Also, aggregation is an unfavourable property of phthalocyanines.[20] For this reason, one of the strategies employed to prevent the formation of aggregates is the introduction of substituents on the axial position of phthalocyanines. Recent ₃₅ years, in order to improve solubility of phthalocyanines, many axially disubstituted silicon phthalocyanine complexes have been synthesized.[21-26]

Axial substitution of phthalocyanines can strongly influence of essential parameters of a phthalocyanine, such as its solubility, ₄₀ aggregation behavior, electronic absorption, photophysical, photochemical, electrochemical properties.[27] On the other hand, axially disubstituted silicon phthalocyanines display very attractive electrochemical properties. Although a substantial number of electrochemical properties of silicon phthalocyanine ₄₅ derivatives have been reported rare,[28-34] to date, electropolymerizable axially disubstituted silicon phthalocyanine complexes has not been reported in the literature. Electropolymerization is a desired property for preparation of composite electrode, which has potentials for the usage in ₅₀ different electrochemical technologies such as, electrocatalytic, electrochromic and electrosensing applications. Electrochemical cycling can induce the dimethyl and diethylamino groups of phthalocyanines containing amines to undergo anodic oxidation, leading to the electropolymerization of the phthalocyanine.[35] For ₅₅ these reasons, in this article, we designed and synthesized a novel series of axially disubstituted silicon(IV) phthalocyanines bearing electropolymerizable ligand for the first time. The effect of axial groups on the the absorption, thermal and electrpolymerization properties were investigated.

₆₀ ## 2. Experimental Section

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Journal Name

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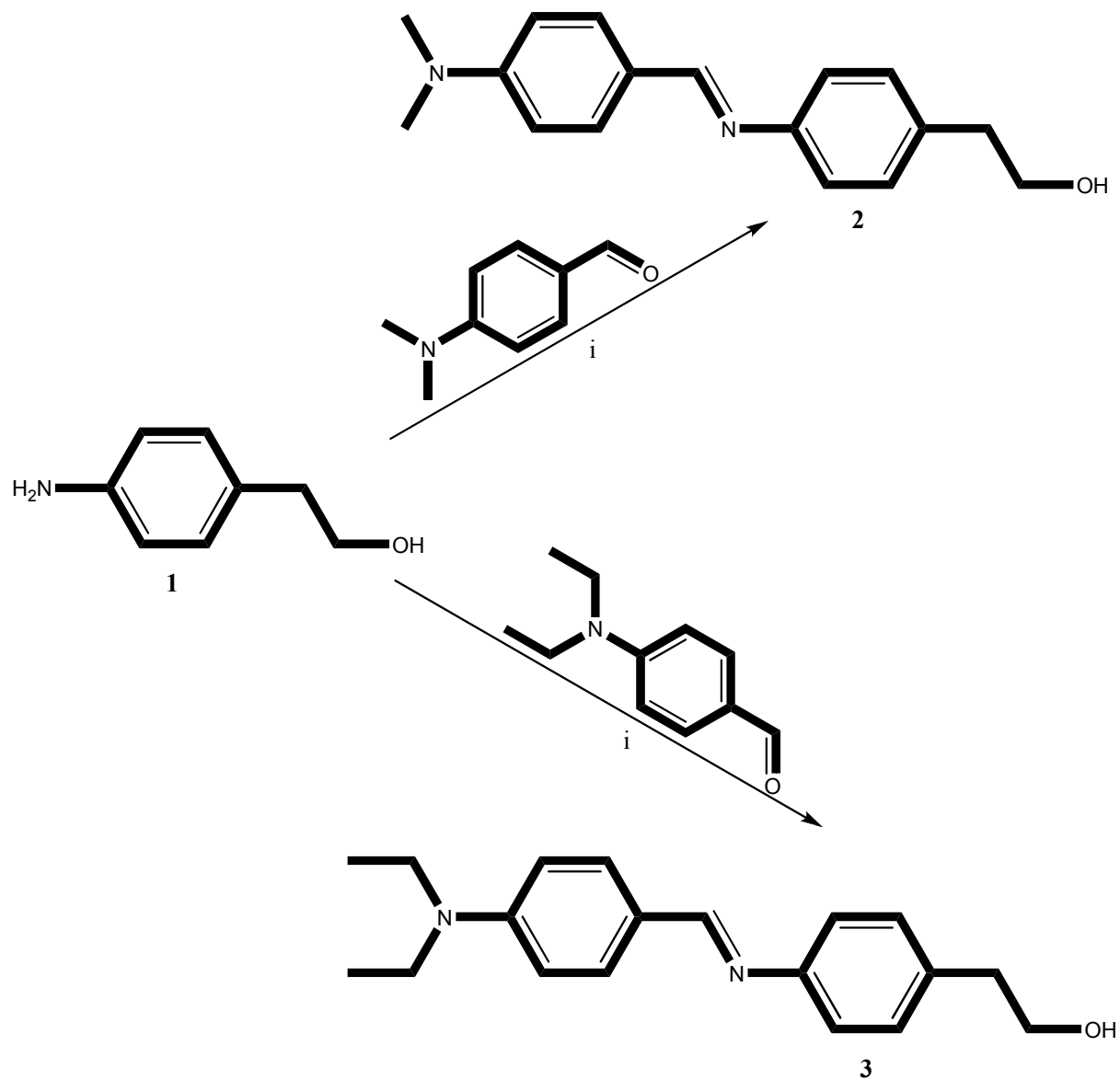
Scheme 1. The synthesis of compounds **2** and **3**. (i) EtOH, 85 ℃.
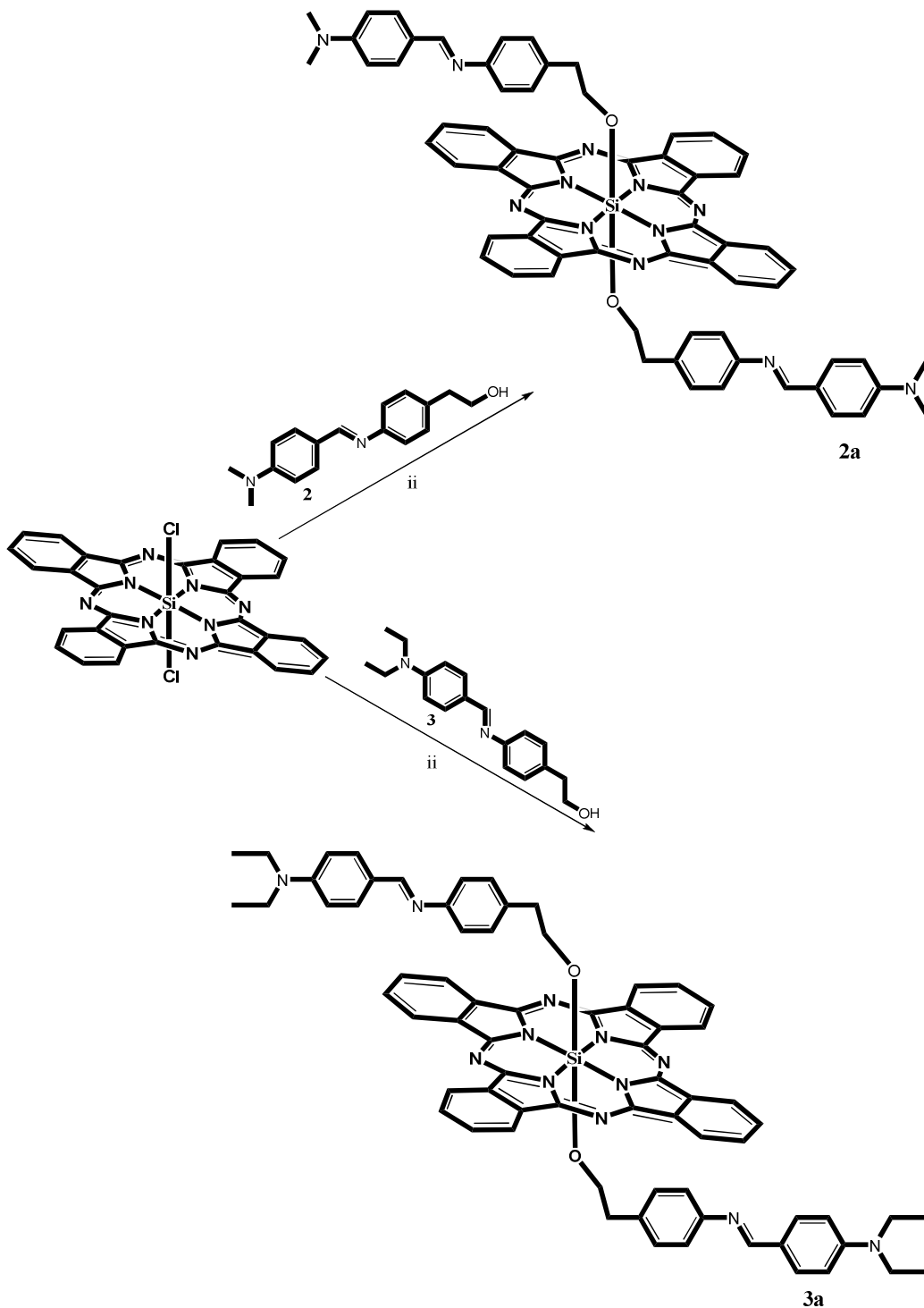
Scheme 2. The synthesis of axially disubstituted silicon phthalocyanines. (ii) Toluene, NaH, 120 °C.

2.1. Materials and methods

The used materials, equipments and the electrochemical measurements were supplied as supplementary information.

2.2. Synthesis

2.2.1. 2-[4-({(1E)-[4-(Dimethylamino)phenyl]methylene}amino)phenyl]ethanol (2)

A mixture of 4-aminophenethyl alcohol **1** (1 g, 7.30x10⁻³ mol), 4-dimethylaminobenzaldehyde (1.09 g, 7.30x10⁻³ mol) and four drops of acetic acid were added to ethanol (0.06 L) in two-necked round-bottom flask equipped with a reflux condenser. The reaction mixture was stirred in oil bath at 85 °C under an nitrogen

atmosphere. After stirring for 1 day, the solvent was evaporated under reduced pressure to near dryness. The crude product was purified by recrystallization from ethanol. Yield: 1.27 g (65%), m.p. 135-136 °C. IR (KBr), v/cm^{-1} : 3284 (O-H), 3035 (Ar-H),
5 2996-2867 (Aliph. C-H), 1607, 1578, 1503, 1443, 1412, 1366, 1318, 1231, 1167, 1122, 1061, 979, 944, 895, 815, 724. ^{1}H-NMR (400 MHz, CDCl$_3$), (δ:ppm): 8.33 (s, 1H, CH=N), 7.79 (d, 2H, J= 8.8, Ar-H), 7.23 (d, 2H, J= 8.2, Ar-H), 7.15 (d, 2H, J= 8.2, Ar-H), 6.76 (d, 2H, J= 8.8, Ar-H), 3.88 (t, 2H, J= 6.5, CH$_2$-O), 3.07 (s,
10 6H, CH$_3$), 2.89 (t, 2H, J= 6.5, Ar-CH$_2$), 1.66 (bs, 1H, OH). ^{13}C-NMR (100 MHz, CDCl$_3$), (δ:ppm): 160.00, 152.50, 151.39, 135.15, 130.42, 129.66, 124.46, 121.15, 111.59, 63.74, 40.17, 38.74. MS (ESI), (m/z) calcl. 268.35; found: 269.25 [M+H]$^+$. Elemental Analysis : (Found: C 76.18, H 7.38, N 10.58%,
15 C$_{17}$H$_{20}$N$_2$O (268.35) requires C 76.09, H 7.51, N 10.44%).

2.2.2.   *2-[4-({(1*E*)-[4-(Diethylamino)phenyl]methylene}amino)phenyl]ethanol (3)*

Synthesized similarly to 2 by using 4-diethylaminobenzaldehyde instead of 4-dimethylaminobenzaldehyde. Yield: 1.34 g (62%),
20 m.p. 107-108 °C. IR (KBr), v/cm^{-1} : 3425 (O-H), 3021 (Ar-H), 2975-2863 (Aliph. C-H), 1608, 1582, 1551, 1523, 1448, 1433, 1353, 1277, 1196, 1182, 1077, 1041, 984, 889, 814, 784. ^{1}H-NMR (400 MHz, CDCl$_3$), (δ:ppm): 8.31 (s, 1H, CH=N), 7.76 (d, 2H, J= 8.9, Ar-H), 7.22 (d, 2H, J= 8.3, Ar-H), 7.14 (d, 2H, J= 8.3,
25 Ar-H), 6.72 (d, 2H, J= 8.9, Ar-H), 3.87 (t, 2H, J= 6.6, CH$_2$-O), 3.45 (q, 4H, J= 7.0, CH$_2$-N), 2.88 (t, 2H, J= 6.6, Ar-CH$_2$), 1.90 (bs, 1H, OH), 1.24 (t, 6H, J= 7.0, CH$_3$). ^{13}C-NMR (100 MHz, CDCl$_3$), (δ:ppm): 159.97, 151.46, 150.11, 135.09, 130.73, 129.65, 123.63, 121.14, 111.06, 63.73, 44.52, 38.75, 12.60. MS
30 (ESI), (m/z) calcl. 296.40; found: 297.34 [M+H]$^+$. Elemental Analysis : (Found: C 77.15, H 8.01, N 9.52%, C$_{19}$H$_{24}$N$_2$O (296.40) requires C 76.99, H 8.16, N 9.45%).

2.2.3. *Synthesis of SiPc (2a)*

The SiPc(Cl)$_2$ (0.1 g, 0.16x10^{-3} mol) was dissolved in dry toluene
35 (0.015 L) under inert nitrogen atmosphere. Then 2-[4-({(1*E*)-[4-(dimethylamino)phenyl]methylene}amino)phenyl]ethanol **2** (0.086 g, 0.32x10^{-3} mol) and dry NaH (0.008 g, 0.32x10^{-3} mol) were added. The reaction mixture was heated and stirred under reflux at 120 °C for 24 h. After evaporating the solvent in vacuo,
40 the residue was purified by column chromatography over a aluminum oxide using a mixture of CHCl$_3$:MeOH (100:4) as solvent system. Yield: 0.092 g (53%), m.p. > 250 °C. IR (KBr) v_{max}/cm^{-1}: 3063 (Ar-H), 2977-2841 (Aliph. C-H), 1588, 1555, 1518, 1472, 1426, 1353, 1333, 1231, 1163, 1118, 1072, 977, 909,
45 816, 731. ^{1}H-NMR. (400 MHz, CDCl$_3$), (δ:ppm): 9.63-9.61 (m, 8H, Pc-H$_\alpha$), 8.35-8.31 (m, 8H, Pc-H$_\beta$), 8.21 (s, 2H, CH=N), 7.88 (d, 4H, J= 8.5, Ar-H), 6.85 (d, 4H, J= 8.6, Ar-H), 6.19 (d, 4H, J= 8.0, Ar-H), 4.88 (d, 4H, J= 7.9, Ar-H), 3.12 (s, 12H, CH$_3$), -0.37 (t, 4H, J= 6.0, Si-O-CH$_2$), -1.90 (t, 4H, J= 6.0, Ar-CH$_2$). ^{13}C-
50 NMR (100 MHz, CDCl$_3$), (δ:ppm): 158.79, 152.36, 149.14, 136.01, 135.94, 130.61, 130.25, 127.44, 123.66, 123.61, 119.57, 114.16, 111.72, 56.62, 40.26, 35.47. UV-Vis (chloroform): λ_{max}, nm (log ε): 674 (5.42), 644 (4.59), 606 (4.66), 356 (5.11). MALDI-TOF-MS m/z calc. 1075.30; found: 1076.59 [M+H]$^+$.
55 Elemental Analysis : (Found: C 73.91, H 4.90, N 15.84%, C$_{66}$H$_{54}$N$_{12}$O$_2$Si (1075.30) requires C 73.72, H 5.06, N 15.63%).

2.2.4. *Synthesis of SiPc (3a)*

The synthesis of SiPc 3a procedure was applied according to the compound   2a   by   using   2-[4-({(1*E*)-[4-
60 (diethylamino)phenyl]methylene}amino)phenyl]ethanol 3. Yield: 0.083 g (45%), m.p. > 250 °C. IR (KBr) v_{max}/cm^{-1}: 3059 (Ar-H), 2970-2846 (Aliph. C-H), 1609, 1589, 1515, 1427, 1333, 1288, 1178, 1120, 1075, 909, 817, 758, 728. ^{1}H-NMR. (400 MHz, CDCl$_3$), (δ:ppm): 9.64-9.62 (m, 8H, Pc-H$_\alpha$), 8.36-8.33 (m, 8H,
65 Pc-H$_\beta$), 8.19 (s, 2H, CH=N), 7.85 (d, 4H, J= 8.7, Ar-H), 6.81 (d,

4H, J= 8.8, Ar-H), 5.70 (d, 4H, J= 8.2, Ar-H), 4.89 (d, 4H, J= 7.8, Ar-H), 3.21 (m, 8H, CH$_2$-N), 1.28 (m, 12H, CH$_3$), -0.55 (t, 4H, J= 6.6, Si-O-CH$_2$), -1.94 (t, 4H, J= 6.6, Ar-CH$_2$). ^{13}C-NMR (100 MHz, CDCl$_3$), (δ:ppm): 158.76, 149.14, 143.07, 136.07,
70 130.54, 128.29, 127.68, 127.44, 123.62, 123.57, 119.59, 114.17, 111.14, 56.91, 44.56, 35.18, 12.67. UV-Vis (chloroform): λ_{max}, nm (log ε): 674 (5.52), 644 (4.78), 606 (4.84), 357 (5.14). MALDI-TOF-MS m/z calc. 1131.40; found: 1131.85 [M]$^+$. Elemental Analysis : (Found: C 74.48, H 5.39, N 14.98%,
75 C$_{70}$H$_{62}$N$_{12}$O$_2$Si (1131.40) requires C 74.31, H 5.52, N 14.86%).

3. RESULTS AND DISCUSSION

3.1. Characterization

The   synthesis   of   2-[4-({(1*E*)-[4-(dimethylamino)phenyl]methylene}amino)phenyl]ethanol   **2**, 2-
80 [4-({(1*E*)-[4-(diethylamino)phenyl]methylene}amino)phenyl]ethanol **3** and axially di-substituted silicon phthalocyanines (SiPcs) **2a** and **3a** are respectively shown in Scheme 1 and 2. 4-Aminophenethyl alcohol **1** was respectively treated with the 4-dimethylbenzaldehyde, 4-
85 diethylaminobenzaldehyde in ethanol in the presence of a few drops of acetic acid led to compounds **2** and **3.** Then, silicon phthalocyanines were synthesized by using compounds **2**, **3** in the presence of SiPc(Cl)$_2$ and NaH in toluene at 120 °C. All the new compounds were characterized by IR, ^{1}H-NMR, ^{13}C-NMR, UV-
90 Vis (only for SiPcs), MS spectroscopic methods

In the IR spectra, the formation of compounds **2** and **3** were clearly confirmed by disappearance of the NH$_2$ and C=O band and the appearance of the OH and HC=N band at 3284 and 1607 cm^{-1} for **2**, 3425 and 1608 cm^{-1} for **3**, respectively. ^{1}H-NMR
95 spectra were also in good agreement with the structures of compounds **2** and **3**. The molecular ion peaks of **2** and **3** were found at m/z 269 [M+H]$^+$, 297 [M+H]$^+$, respectively.

The formation of SiPcs **2a** and **3a** were clearly confirmed by disappearance of the OH bands at 3284, 3425 cm^{-1}, respectively.
100 In the ^{1}H-NMR spectrums, H$_\alpha$ protons of SiPcs **2a** and **3a** were observed between 9.63-9.61, 9.64-9.62 ppm, H$_\beta$ protons of SiPcs **2a** and **3a** were observed between 8.35-8.31, 8.36-8.33 ppm, respectively. Also, H protons of Si-O-CH$_2$ at -0.37 for **2a** (Figure 1), -0.55 ppm for **3a** and H protons of Ar-CH$_2$ at **-**1.90 for **2a, -**
105 1.94 ppm for **3a** have shifted negative area due to magnetic anisotropy of silicon phthalocyanine ring.[36] ^{13}C-NMR spectra were also in good agreement with the structures of compounds **2a** and **3a.** Final evidence of silicon phthalocyanines **2a** and **3a** were given by MALDI-MS where molecular ion peaks at m/z: 1076
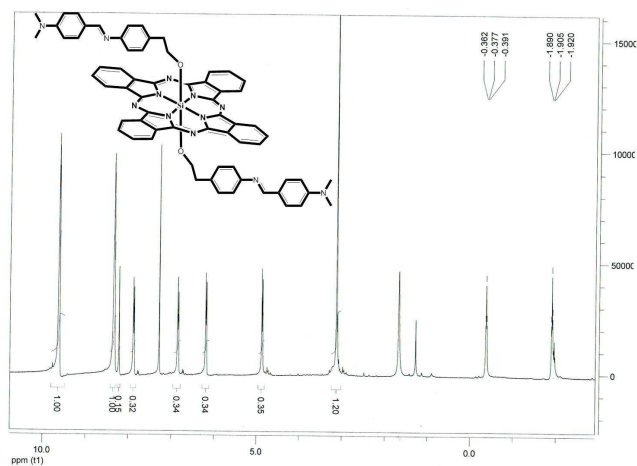110 [M+H]$^+$ (Figure 2), 1131 [M]$^+$, respectively is in accordance with the expected values.

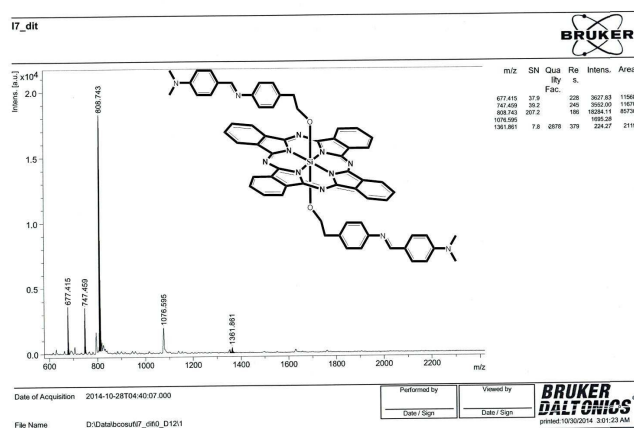**Fig. 1** ^{1}H-NMR spectrum of complex **2a** in CDCl$_3$.

5 **Fig. 2** MALDI-TOF mass spectrum of complex **2a**.

3.2. Aggregation studies

Phthalocyanines are known to form aggregation, which is due to the strong coupling between the molecules that causes either a 10 red shift or a blue shift in the absorption band of the aggregate[37,38]. Aggregation is dependent on the nature of solvent, concentration, nature of substituents, complex metal ions and temperature. In this study, aggregation behavior of the SiPcs **2a** and **3a** were investigated in different solvents such as CHCl$_3$, 15 CH$_2$Cl$_2$, THF, EtOAc, DMF, DMSO (Figure 3 for complex **2a**, Figure 4 for complex **3a**). SiPc **2a** having a Q band maxima at 674 nm in CH$_2$Cl$_2$, 674 nm in CHCl$_3$, 672 nm in THF, 675 nm in DMF, 677 nm in DMSO, 670 nm in EtOAc and SiPc **3a** having a Q band maxima at 672 nm in CH$_2$Cl$_2$, 674 nm in CHCl$_3$, 671 nm 20 in THF, 674 nm in DMF, 676 nm in DMSO, 670 nm in EtOAc (Table 1) did not show any aggregation in these solvents suggesting that the substitution effect of the groups as axial substituent on the phthalocyanine ring for silicon phthalocyanine. We also examined aggregation behavior SiPcs **2a** and **3a** in 25 different concentration in CHCl$_3$. As the concentration was increased, the intensity of absorption of the Q band also increased and there were no new bands due to the aggregated species.
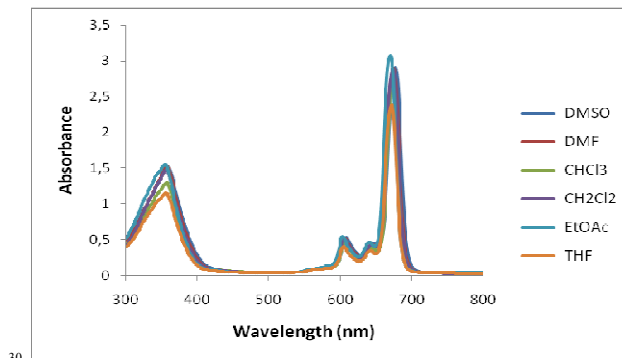

30 **Fig. 3** UV-Vis spectrum of **2a** in different solvents.
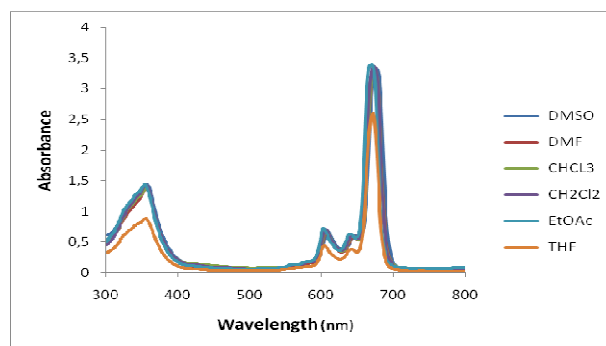

Fig. 4 UV-Vis spectrum of **3a** in different solvents.

35 **Table 1.** UV-Vis spectral data for Pcs **2a** and **3a** in various solvents at a concentration of 10×10^{-6} moldm^{-3}.

Solvent	Pcs	Q-Band, λ_{max}, (nm)	log ε	B-Band, λ_{max}, (nm)	log ε
CHCl$_3$	**2a**	674, 644, 606	5.42, 4.59, 4.66	356	5.11
CH$_2$Cl$_2$	**2a**	674, 644, 606	5.46, 4.63, 4.70	356	5.17
DMF	**2a**	675, 645, 606	5.46, 4.65, 4.71	357	5.18
DMSO	**2a**	677, 647, 608	5.46, 4.65, 4.72	358	5.18
EtOAc	**2a**	670, 640, 603	5.49, 4.66, 4.74	355	5.19
THF	**2a**	672, 643, 605	5.43, 4.59, 4.67	356	5.06
CHCl$_3$	**3a**	674,	5.52,	357	5.14

		644, 606	4.78, 4.84		
CH₂Cl₂	**3a**	672, 644, 606	5.53, 4.79, 4.85	356	5.16
DMF	**3a**	674, 645, 606	5.51, 4.75, 4.81	356	5.14
DMSO	**3a**	676, 647, 608	5.52, 4.77, 4.83	357	5.16
EtOAc	**3a**	670, 640, 603	5.53, 4.80, 4.86	354	5.16
THF	**3a**	671, 642, 604	5.53, 4.79, 4.85	355	5.13

3.3. Electrochemical studies

Voltammetric studies of SiPcs **2a** and **3a** were carried out in dichloromethane (DCM) / tetrabutylammoniumperchlorate (TBAP) electrolyte system on a Pt working electrode with CV and SWV techniques. Basic redox parameters were derived from the voltammetric analyses and they are listed in Table 2.

Axially disubstituted silicon phthalocyanine complexes **2a** and **3a** show similar voltammetric responses in DCM/TBAP electrolyte system. All of these complexes give two reductions reactions. CV and SWVs of silicon phthalocyanine **2a** are represented in Fig. 5a and 5b. Axially disubstituted silicon phthalocyanine **2a** gives two reductions, R₁ at -0.66 V (ΔE_p = 98 mV and $I_{p,a}/I_{p,c}$ = 0.94), R₂ at -1.09 V(ΔE_p = 95 mV and $I_{p,a}/I_{p,c}$= 0.91) within the potential window of DCM/TBAP electrolyte system. Two reduction reactions (R₁ and R₂) are both electrochemically and chemically reversible with respect to ΔE_p and $I_{p,a}/I_{p,c}$ values. SWV of the complex **2a** illustrate these analyses results more clearly as shown in Fig 5b.

Table 2. Voltammetric data of the SiPcs. All voltammetric data were given versus SCE.

Complexes		Polymerization Waves	Reductions	
SiPc 2a	$^{a}E_{1/2}$	1.30^{d} (1.01)^{e}	-0.66	-1.09
	$^{b}\Delta E_p$ (mV)	-	98	95
	$^{c}I_{p,a}/I_{p,c}$	-	0.94	0.91
SiPc 3a	$^{a}E_{1/2}$	1.19^{d}(0.96)^{e}	-0.67	-1.13
	$^{b}\Delta E_p$ (mV)	-	103	105
	$^{c}I_{p,a}/I_{p,c}$	-	0.89	0.88

ᵃ: $E_{1/2}$ values (($E_{pa}+E_{pc}$)/2) were given versus SCE at 0.100 Vs⁻¹ scan rate. **ᵇ:** $\Delta E_p= E_{pa}-E_{pc}$. **ᶜ:** $I_{p,a}/I_{p,c}$ for reduction ,$I_{p,c}/I_{p,a}$ for oxidation processes. ᵈ: E_{pa} of first CV cycle; ᵉ: E_{pc} of first CV cycle.
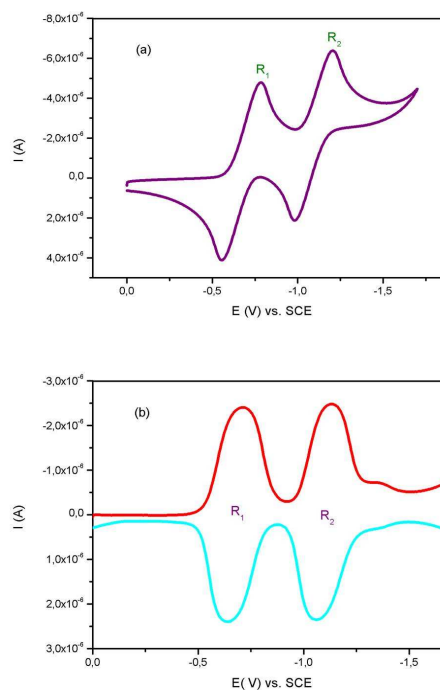
Fig. 5 (a) CVs of SiPc **2a** at 0.100 V.s⁻¹ in TBAP/DCM. (b) SWV of SiPc **2a** at 0.100 V.s⁻¹ in TBAP/DCM**.**

Fig. 6a and 6b show the CV and SWV responses of axially disubstituted silicon phthalocyanine complex **3a** in DCM/TBAP electrolyte system. The cyclic voltammogram of complex **3a** gives two one-electron reduction processes (Fig. 6a). It displays
5 two reversible reduction reactions labeled as **R₁** ($E_{1/2}$ = -0.67 V; ΔE_p = 103 mV; $I_{p,a}/I_{p,c}$ = 0.89), **R₂** ($E_{1/2}$ = -1.13 V; ΔE_p = 105 mV; $I_{p,a}/I_{p,c}$ = 0.88). All electron transfer processes are both electrochemically and chemically reversible with respect to ΔE_p and $I_{p,a}/I_{p,c}$ values. On the other hand, SVWs of the complex **3a**
10 clearly support these reversible characters of the processes, since these couples show symmetric cathodic peaks with the same peak currents (Fig. 6b). Also, the peak currents increased linearly with the square root of the scan rates for scan rates ranging from 25 to 500 mV.s⁻¹ for these complexes **2a** and **3a** (Fig. 7a and Fig. 7b),
15 respectively. This linearity was confirmed by the graphic of square root of scan rate versus peak current (Figure 8a for **2a** and Figure 8b for **3a**).
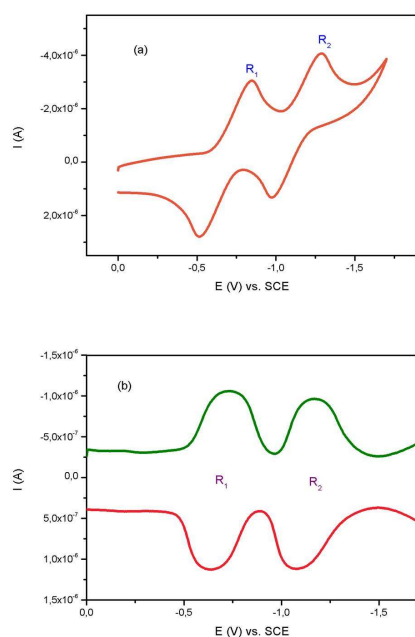

Fig. 6 (a) CVs of SiPc **3a** at 0.100 V.s⁻¹ in TBAP/DCM. (b) SWV of SiPc
20 **3a** at 0.100 V.s⁻¹ in TBAP/DCM**.**

Axially disubstituted silicon phthalocyanines **2a** and **3a** show different redox responses during the oxidation reactions. While the complexes **2a** and **3a** gave common reduction reactions
25 during the cathodic potential scans, they were electropolymerized on the working electrode. Figure 9 shows repetitive CVs of silicon phthalocyanine **2a** recorded at 0.100Vs⁻¹ scan rate within positive potential window of DCM/TBAP. During the first anodic CV cycle, a big wave is observed at 1.30 V which triggers
30 polymerization of the complex. Also during the first cycle cathodic couple is recorded at 1.01 V. During second to eleven CV cycles, the anodic wave increases with a potential shift at 1.39 V and cathodic wave increases with a potential shift at 0.99 V. After this point, it decreases in current intensity until the 15.
35 cycle. These voltammetric responses indicate electropolymerization of the axially disubstituted silicon phthalocyanine **2a** on the working electrode.

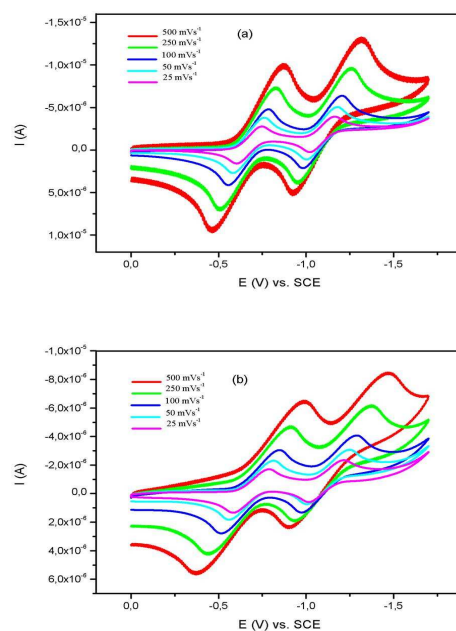**Fig. 7** (a) CV of silicon phthalocyanine **2a** at various scan rates (ranging
40 from 25 to 500 mV.s⁻¹) on a Pt working electrode in DCM/TBAP. (b) CV of silicon phthalocyanine **3a** at various scan rates (ranging from 25 to 500 mV.s⁻¹) on a Pt working electrode in DCM/TBAP.
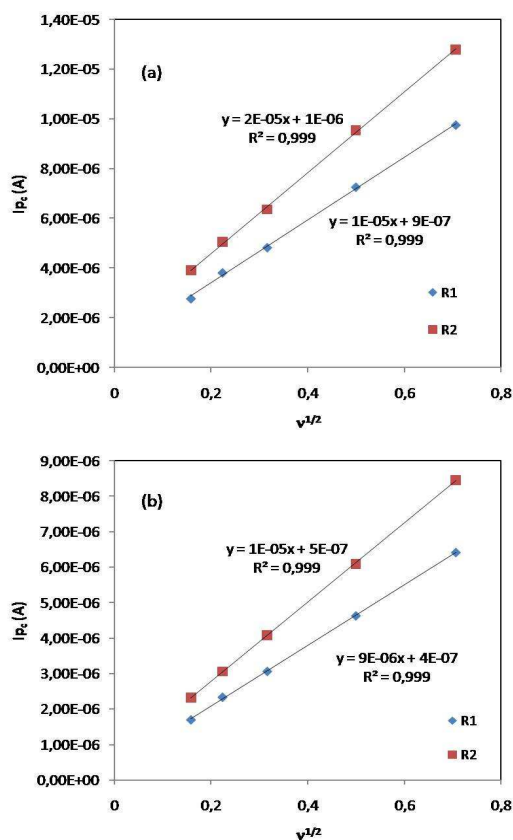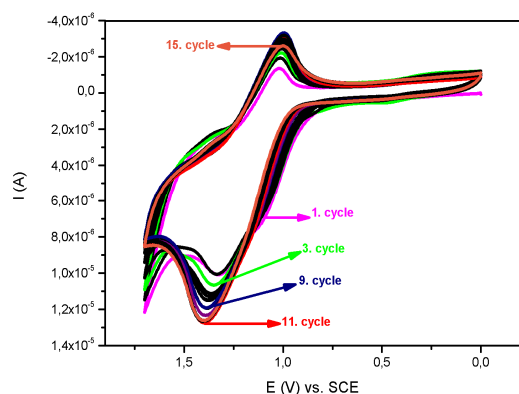

Fig. 8. (a) The plot of square root of scan rate versus peak current for
45 SiPc **2a.** (b) For SiPc **3a.**

Fig. 9 Repetitive CVs of complex **2a** recorded at anodic potential windows of DCM/TBAP electrolyte system at 0.100 Vs^{-1} scan rate on a Pt
5 working electrode.

Figure 10 shows repetitive CVs of silicon phthalocyanine **3a** recorded at 0.100Vs^{-1} scan rate within positive potential window of DCM/TBAP. Axially disubstituted silicon phthalocyanine
10 complex **3a** illustrate completely different electropolymerization responses. During the first anodic CV cycle, anodic redox couple was recorded at 1.19 V and its cathodic couple was recorded at 0.96 V. Electropolymerized film gives two couples at 0.52 and 0.83 V during the third CV cycle. These new couples
15 continuously increase in current intensity with negative potential shifts until the 15th CV cycle. Also, during the second CV cycle, an anodic wave at 0.80 V is observed. This new couple increase in current intensity until the 9. CV cycle with positive potential shifts and disappear finally after the 11th CV cycle. All of these
20 electrochemical signals are in agreement with the electropolymerized film on the working electrode. In previous papers, authors reported electropolymerization of peripherally tetra-substituted metallophthalocyanines bearing various amino moieties,[39,40] ethylenedioxythiophene,[41] hydroquinoline groups.[42]
25 But this study is the first example of electropolymerization of axially disubstituted silicon phthalocyanines.
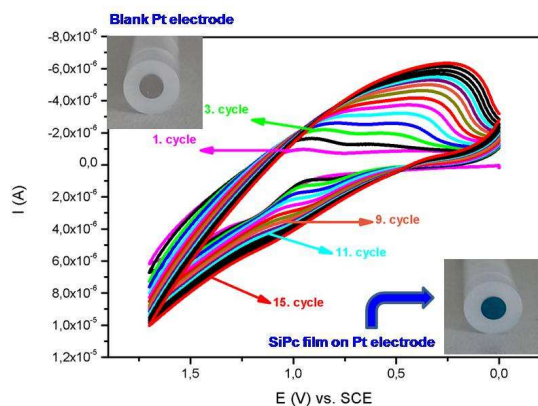
Fig. 10 Repetitive CVs of complex **3a** recorded at anodic potential windows of DCM/TBAP electrolyte system at 0.100 Vs^{-1} scan rate on a Pt
30 working electrode.

3.4. Thermal Properties of Silicon Phthalocyanines

The thermal behavior of the synthesized axially disubstituted silicon phthalocyanine complexes were studied by TGA/DT in N$_2$ atmosphere and as flow rate was set up to 20 ml/min.
35 Temperature rate was set up to 20 °C/min.

Generally, phthalocyanines are known as compounds which have high thermal stability.[43] Although the thermal stabilities of phthalocyanines is well known, axially disubstituted silicon phthalocyanine complexes are not stable above 264 ºC. The
40 initial and main decomposition temperatures are given in Table 3. The initial decomposition temperature decreased in the order: **2a** > **3a**. DTA curves exhibited exothermic changes for two axially disubstituted silicon phthalocyanine complexes (**2a** and **3a**) in the region investigated, the curves do not show melting points.
45

4. Conclusion

In conclusion, in this work synthesis, spectral characterization, aggregation, thermal and electropolymerization properties of novel axially disubstituted silicon phthalocyanine complexes
50 were presented. The silicon phthalocyanine complexes are easily soluble in common organic solvents. The effects of concentration and solvent (CHCl$_3$, CH$_2$Cl$_2$, THF, EtOAc, DMF, DMSO) on the aggregation behavior of the novel compounds were investigated. Aggregation studies of the axially disubstituted silicon
55 phthalocyanine complexes show that non-aggregated species for the compounds were formed because of the existence of the axial substituent on the phthalocyanine ring for silicon phthalocyanine. The thermal gravimetric analysis of the phthalocyanines was performed by TG/DTA system. Axially disubstituted silicon
60 phthahalocyanine complexes showed thermal stability until the 264 ºC. Electrochemical measurements indicate that axial substitution of the complexes with dimethylamino)phenyl]methylene}amino)phenyl]ethanol, diethylamino)phenyl]methylene} amino)phenyl]ethanol groups
65 supply electropolymerization of the complexes on the working electrode. As a result, this study is the first example of electropolymerization of axially disubstituted silicon phthalocyanines. Electropolymerization behaviors of the complexes are the desired properties of the electrochemical
70 applications, especially, electrocatalytic, electrochromic and electrosensing applications.

Table 3. Thermal properties of the axially disubstituted silicon phthalocyanines

75

Complexes	Initial decom. temp. (°C)	Main decom. temp. (°C)
2a	266	278
3a	264	274

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80 ## Notes and references

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[1] M. Han M, X. Zhang, C. Liao, B. Zhu, Q. Li, *Polyhedron*, 2015,
10 **85**, 864-873.
[2] L. Martin-Gomis, F. Fernandez-Lazaro, A. Sastre-Santos, *J. Mat. Chem. A*, 2014, **2**, 15672-1582.
[3] H. Xu, J. Xiao, B. Liu, S. Griveau, F. Bedioui, *Biosen. Bioelect.*, 2015, **66**, 438-444.
15 [4] K. Hou, L. Huang, Y. Qi, C. Huang, H. Pan, M. Du, *Mat. Sci. Eng. C*, 2015, **49**, 640-647.
[5] K. E. Sekhosana, E. Amuhaya, T. Nyokong, *Polyhedron*, 2015, **85**, 347-354.
[6] S. Nagel S, M. Lener, C. Keil, R. Gerdes, L. Lapok, S. M. Gorun,
20 D. Schlettwein, *J. Phy. Chem. C*, 2011, **115**, 8759-8767.
[7] M. L. Rodriguez-Mendez, J. Antonio De Saja, *J. Porphy. Phthalocyan.*, 2009, **13**, 606-615.
[8] B. S. Erdoğan, D. Atilla, A. G. Gürek, V. Ahsen, *J. Porphy. Phthalocyan.*, 2014, **18**, 139-148.
25 [9] M. M. Ayhan, M. Durmuş, A. G. Gürek, V. Ahsen, *Syn. Met.*, 2014, **195**, 83-90.
[10] L. Wang, Y. Li, X. Song, X. Liu, L. Zhang, D. Yan, *App. Phy. Lett.*, 2013, **103**, 243302-243304.
[11] T. Hihara, Y. Okada, Z. Morita, *Dyes Pigm.*, 2001, **50**, 185-201.
30 [12] M. Emmelius, G. Pawlowski, H. W. Vollmann, *Angew Chem. Int. Ed.*, 1989, **28**, 1445-1471.
[13] L. Tao, G. Fuxi, *Appl. Optics*, 1994, **33**, 3760-3763.
[14] Z. Huang, H. Bao, Y. Yao, W. Lu, W. Chen, *App. Cat. B Environ.*, 2014, **154-155**, 36-43.
35 [15] R. M. Wang, H. Wang, Y. Wang, H. R. Li, Y. F. He, E. X. Hao, *Col. Tech.*, 2014, **130**, 32-36.

[16] D. Çakır, V. Çakır, Z. Bıyıklıoğlu, M. Durmuş, H. Kantekin, *J. Organomet. Chem.*, 2013, **745-746**, 423-431.
40 [17] K. Plaetzer, B. Krammer, J. Berlanda, F. Berr Kiesslich, *Lasers Med. Sci.*, 2009, **24**, 259-268.
[18] D. Çakır, V. Çakır, M. Göksel, M. Durmuş, Z. Bıyıklıoğlu, H. Kantekin, *J. Photochem. Photobiol. A Chem.*, 2015, **299**, 138-151.
[19] A. Günsel, A. T. Bilgiçli, M. Kandaz, E. B. Orman, A. Özkaya,
45 *Dyes Pigm.*, 2014, **102**, 169-179.
[20] X. Chen, D. Ma, K. Cai, S. Pan, Y. Wang, T. Zhang, Z. Huang, H. Yang, Y. Peng, *J. Coord. Chem.*, 2015, **68**, 732-740.
[21] P. C. Lo, J. D. Huang, D. Y. Cheng, E. Y. Chan, W. P. Fong, W. H. Ko, D. K. P. Ng, *Chem. A Eur. J.*, 2004, **10**, 4831-4838.
50 [22] Z. Bıyıklıoğlu, *Col. Tech.*, 2012, **128**, 459-463.
[23] J. T. Lau, P. C. Lo, W. P. Fong, D. K. P. Ng, *Chem. A Eur. J.* 2011, **17**, 7569-7577.
[24] Z. Bıyıklıoğlu, D. Çakır, *Spectrochim. Acta Part A: Mol. Biomol. Spect.*, 2012, **98**, 178-182.
55 [25] Z. Bıyıklıoğlu, A. Aktaş, *Col. Tech.*, 2013, **129**, 425-430.
[26] C. Uslan, K. T. Oppelt, L. M. Reith, B. S. Sesalan, G. Knör, *Chem. Commun.*, 2013, **49**, 8108-8110.
[27] M. D. Maree, T. Nyokong, *J. Porphy. Phthalocyan.*, 2001, **5**, 555-563.
60 [28] A. Aktaş, Z. Bıyıklıoğlu, *J. Organomet. Chem.*, 2014, **749**, 364-9.
[29] Z. Li, M. Lieberman, *Inorg. Chem.*, 2001, **40**, 932-939.
[30] J. J. Bergkamp, B. D. Sherman, E. Marino-Ochoa E, R. E. Palacios, G. Cosa, T. A. Moore, D. Gust, A. L. Moore, *J. Porphy. Phthalocyan.*, 2011, **15**, 943-950.
65 [31] Z. Bıyıklıoğlu, H. Baş, *Inorg. Chim. Acta*, 2015, **427**, 293-298.
[32] Z. Bıyıklıoğlu, O. Bekircan, *Syn. Met.*, 2015, **200**, 148-55.
[33] Z. Bıyıklıoğlu, *Dyes Pigm.*, 2013, **99**, 59-66.
[34] Z. Bıyıklıoğlu, *Polyhedron*, 2013, **63**, 1-8.
[35] H. Li, T.F. Guarr, *Chem. Commun.* 1989, **13**, 832-834.
70 [36] D. Demirkapı, A. Şirin, Z. P. Turanlı Yıldız Çakar, B. Ş. Sesalan, *Syn. Met.*, 2014, **187**, 152-159.
[37] B. Zhu, X. Zhang, M. Han, P. Deng, Q. Li, *J. Mol. Struc.*, 2015, **1079**, 61-66.

[38] Z. S. Wang, K. Hara, Y. Dan-Oh, C. Kasada, A. Shinpo, S. Suga,
75 H. Arakawa, H. Sugihara, *J. Phys. Chem. B*, 2005, **109**, 3907-3914.
[39] Z. Bıyıklıoğlu, *Syn. Met.*, 2014, **196**, 48-55.
[40] V. Çakır, F. Demir, Z. Bıyıklıoğlu, A. Koca, H. Kantekin, *Dyes Pigm.*, 2013, **98**, 414-421.
[41] H. K. Yildiz, S. E. Korkut, A. Koca, M. K. Sener, *Sync. Met.*, 2011,
80 **161**, 1946-1952.
[42] D. Arıcan, A. Aktaş, H. Kantekin, A. Koca, *J. Electrochem. Soc.*, 2014, **161**, 670-676.
[43] R. Bayrak, H. T. Akçay, F. Ş. Beriş, E. Şahin, H. Bayrak, Ü. Demirbaş, *Spectrochim. Acta Part A Mol. Biomol. Spect.*, 2014,
85 **133**, 272-280.