Turkish Journal of Chemistry
http://journals.tubitak.gov.tr/chem/
Research Article

Turk J Chem
(2014) 38: 1056 – 1063

doi:10.3906/kim-1406-46

Synthesis and characterization of tetra-substituted titanium(IV) phthalocyanines with axial ligand

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Received: 18.06.2014 • **Accepted:** 09.09.2014 • **Published Online:** 24.11.2014 • **Printed:** 22.12.2014

Abstract: In this paper, the synthesis and characterization of peripheral tetra-2-(2-ethyloxyethyloxy)ethyloxy substituted oxo-titanium phthalocyanines (TiOPcs) are reported. The reaction of 2,2,3,3-tetrafluoropropoxy substituted and [2-(2-ethoxyethoxy)ethoxy] substituted TiOPcs (**1** and **3**) with 4-[(6-hydroxyhexyl)oxy]benzene-1,2-diol as a strongly chelating oxygen donor ligand is described. Compounds **1a** and **3a** bearing the hydroxyl group as an axial ligand of the bulky group are converted into a thiol group (**1c** and **3c**). The new compounds are characterized by elemental analysis, FT-IR, ^{1}H NMR, and mass spectrometry. While the fluoropropoxy substituted TiOPc has good solubility in polar solvents such as acetone and THF, the other TiOPc is soluble in chloroform.

Key words: TiOPc, titanium phthalocyanines, axial substitution

1. Introduction

The semiconducting properties of phthalocyanine (Pc) compounds are exploited for applications such as photoconductors,[1–3] solar cells,[4,5] and gas sensors,[6–9] while their electrochemical properties[10–15] are utilized for electrochemical applications such as electrocatalytic,[16,17] electrosensing,[18,19] photodynamic therapy (PDT),[20–23] and electrochromic fields.[24] Various phthalocyanines have been investigated for the relevant applications.[25–27] However, the insolubility of unsubstituted Pcs in almost all kinds of common solvent restricts their widespread applications. However, substituents on the Pc ring usually enhance the solubility of Pcs in solvents.

Recently, all transition metals were coordinated to Pc ligands; only a few of them (Zn, Ti, etc.) could form highly photoactive complexes, such as titanyl phthalocyanine, owing to the closed shell nature of the electronic configuration of Ti(IV).[28,29] In particular, tetra-substituted Pcs are usually more soluble than the corresponding octa-substituted phthalocyanines due to the formation of constitution isomers and high dipole moment that results from the unsymmetrical arrangement of the substituents at the periphery.[30–32] In addition, the physico-chemical properties such as color and solubility of titanium-oxo-phthalocyanines are strongly affected by introducing axial ligands to the titanium ion and the new compounds show different asymmetry. Catechol-like ligands are well-known axial substituents for Ti(IV) complexes in general.[33–38] Axial substitution with bulky groups of TiOPcs can reduce aggregation between phthalocyanine molecules.[39,40]

In this paper, we describe the synthesis and characterization of TiOPcs having different peripheral groups

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such as polyoxyethane and fluorinated groups. 4-[(6-Hydroxyhexyl)oxy]benzene-1,2-diol (**2**) was used to enhance the solubility. For this purpose, 4-[(6-hydroxyhexyl)oxy]benzene-1,2-diol is attached to TiOPcs and then the hydroxyl group of the bulky group is converted into a thiol group. The synthesis and chemical characterization of this novel compound are described in detail. Our aim was to investigate the formation of a self-assembly monolayer of TiOPc having a thiol-linker group attached to the quartz crystal microbalance (QCM) gold electrode.

2. Results and discussion

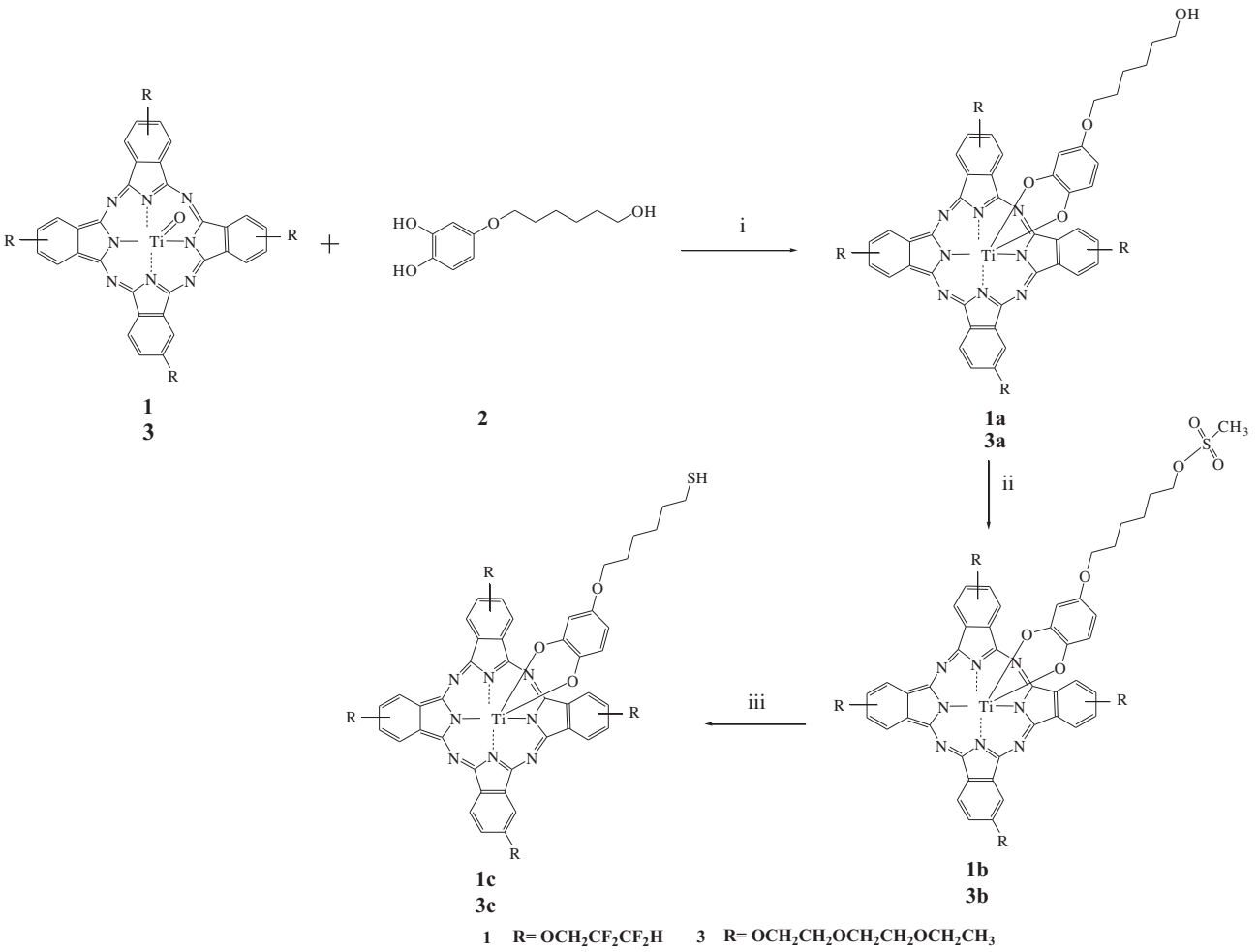
2.1. Synthesis and characterization

The synthesis and characterization of compound **1** have been previously reported in the literature.[41] Compound **3** was also prepared by the reaction of 4-[(2-(2-ethoxyethoxy)ethoxy] phthalonitrile with 4-nitrophthalonitrile according to the literature.[42–44] Compound **1** was reacted with titanium(IV) n-butoxide at 155 °C for 7 h in a Schlenk tube[45] and tetra-substituted phthalocyanine was obtained as an isomer mixture as expected. However, no attempt was made to separate these isomers. The mixture of isomeric TiOPc derivative was separated from impurities by column chromatography with silica gel 60 (0.63–0.200 mm) using a mixture of dichloromethane and ethanol (60:1) as eluent. Axially substituted **1a** and **3a** were obtained by refluxing a mixture of **1** and **3** and 4-[(6-hydroxyhexyl)oxy]benzene-1,2-diol (**2**) in THF and DMSO, respectively (Scheme).[36,41,46,47] While compound **1** exhibited excellent solubility in THF, compound **3** was very soluble in DMSO. Hence, 2 different solvents were used for these reactions. The purification procedure of all phthalocyanine derivatives was completed by preparative chromatography over silica gel using CH_2Cl_2:MeOH as eluent. The terminal hydroxyl group on complexes **1a** and **3a** was converted into its mesylate counterparts using triethylamine (TEA) followed by the addition of methanesulfonyl chloride to give the substituted phthalocyanines **1b** and **3b**. Finally, the terminal thiol functional group was obtained under an inert atmosphere in a previously degassed THF-ethanol solvent mixture containing complexes **1b** and **3b.** The product was then hydrolyzed using 20% NaOH solution. The inert atmosphere inhibits the formation of complexes **1c** and **3c**.[48] However, these types of phthalocyanines (**1c** and **3c**) were obtained in low yields (4% and 1.6%, respectively).

The characterization of the new products involved a combination of methods including elemental analyses, IR, UV-Vis, ^{1}H NMR, and MALDI-TOF mass spectroscopy. Elemental analysis results and the spectral data of the new synthesized compounds **1a**–**c** and **3a**–**c** are consistent with the proposed structures.

In the FT-IR spectra, compound **3** gave a clear characteristic vibrations peak at around 3040 cm^{-1} corresponding to the aromatic CH stretching bands. C=C groups are observed around 1609 and 1613 cm^{-1} and a C–O group at around 1086 cm^{-1}. For **1a** and **3a**, while aliphatic CH stretching bands were observed at around 2963–2852 cm^{-1} due to axial substitution of **2**, the characteristic C–F and C–O bands were observed as strong peaks at 1086 and 1075 cm^{-1}, respectively. When compound **2** was added to compounds **1** and **3**, the characteristic Ti=O stretching vibration peaks at 945 and 948 cm^{-1} disappeared. This confirmed the formation of compounds **1a** and **3a**. Hence, the broad peaks at 3193 and 3216 cm^{-1} were assigned to the hydroxyl groups for compounds **1a** and **3a**, respectively. The disappearance of the hydroxyl groups and the observing of the new peaks at around 1172 cm^{-1} belonging to the O=S=O group confirmed the formation of compounds **1b** and **3b**.

In the ^{1}H NMR spectra, the substituents and ring protons of compound **3** were observed in their expected regions. It is likely that the broadness is due to both chemical exchange caused by aggregation–disaggregation



Scheme. Synthesis of TiPcs(IV) with axial ligand. i: DMSO or THF; ii: Methanesulfonyl chloride, triethylamine, dichloromethane; iii: Thiourea, ethanol, THF, (2) NaOH (20%).

equilibrium and, as far as the tetra-substituted complexes are concerned, the fact that the product obtained in this reaction is a mixture of 4 positional isomers that are expected to show chemical shifts differing slightly from each other. While in the spectra of compound **1a** the OH of group the axial ligands was observing at 2.34 ppm, for compound **3a** the OH signal was not observed clearly. The protons of the axial ligand give upfield-shifted signals due to the phthalocyanine magnetic anisotropy.[37,41,49] For compound **1a**, the peaks attributed to the Ar-CH group of the axial ligand were observed at 5.60 and 4.84 ppm. The SH groups of the target compounds (**1c** and **3c**) appeared at 5.62 and 2.98 ppm, respectively.

The mass spectra of all compounds gave the characteristic molecular ion peaks and supported the expected chemical structures, but molecular ion peaks of **1c** and **3c** were not observed. Intense molecular ion peaks of **1a**, **1b**, **3a**, and **3b** were observed in all cases in the MALDI-TOF technique without using a matrix (Figure 1).

The optical spectra of the soluble compounds (**1**, **1a**, and **3**) were measured in DMSO (1×10^{-5} M) and exhibited characteristic absorptions in the Q-band region at around 695, 701, and 704 nm respectively. The UV-Vis spectra of compounds **1** and **1a** are given in Figure 2. In the case of compound **1a**, the absorption maximum is red shifted about 6 nm compared to compound **1**.

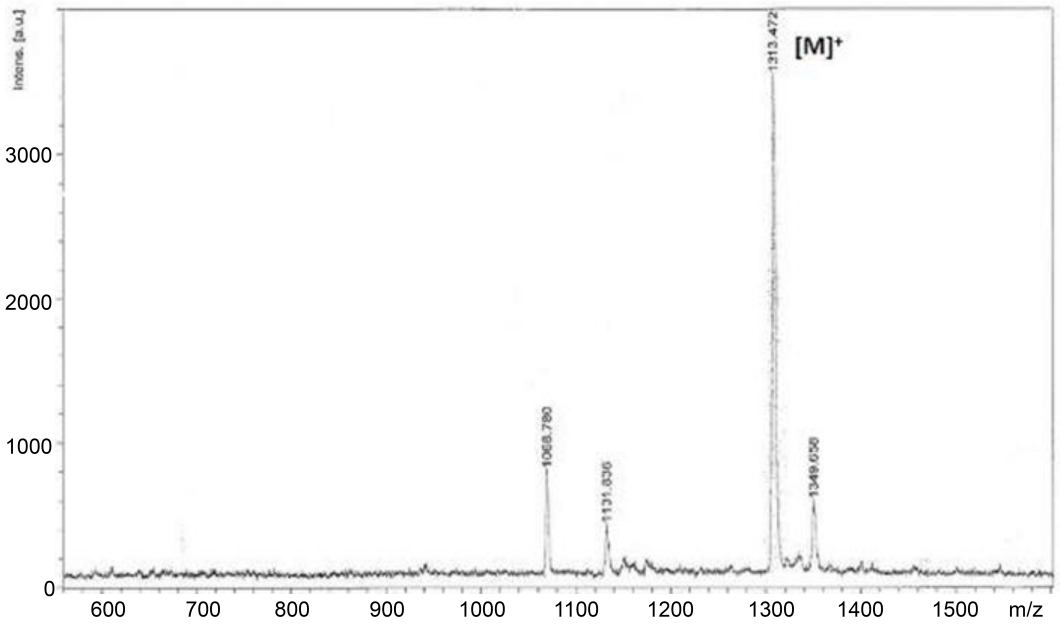


Figure 1. The mass spectrum of compound **3a**.

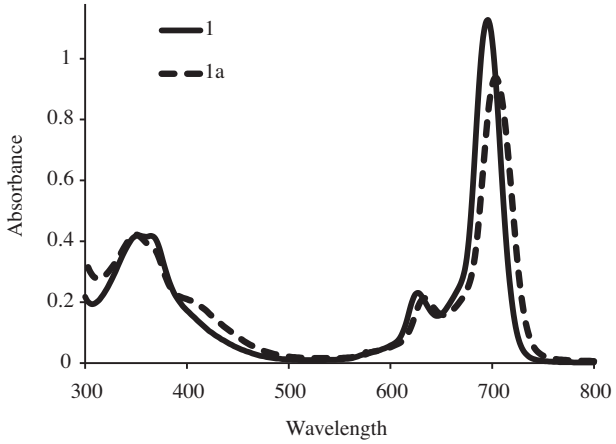


Figure 2. UV-Vis spectra of compounds **1** and **1a**.

3. Experimental

3.1. Material

Anhydrous titanium(IV) butoxide, 1,8-diazabcycloundec-7-ene (DBU), and 6-bromo-1-hexanol were purchased from Fluka. All solvents (dichloromethane, chloroform, methanol, ethanol, THF, triethylamine, and dimethylsulfoxide (DMSO)), K_2CO_3, and silica gel for column chromatography were purchased from Merck. 2,2,3,3-Tetrafluoropropoxy substituted oxo-titanium phthalocyanine was synthesized as reported in the literature.[41]

3.2. Equipment

Elemental analyses were performed using a Thermo Finnigan Flash 1112 Instrument. Infrared spectra were recorded on a PerkinElmer FT-IR System Spectrum BX. ^{1}H NMR spectra were recorded in acetone-d_6 and

$CDCl_3$ solution on Bruker and Varian 500 MHz spectrometers. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) measurements were performed on a Bruker Daltonics MicrOTOF.

3.3. Synthesis

3,4-Dibenzyloxybenzaldehyde[50] was oxidized with m-chloroperbenzoic acid and the compound 3,4-dibenzyloxyphenol was prepared according to the procedures given in the literature.[51,52]

6-[3,4-Bis(benzyloxy)phenoxy]hexan-1-ol: 1 g (3.26 mmol) of 3,4-diphenoxyphenol was dissolved in 5 mL of dry DMSO. After 1.57 g (11.4 mmol) of K_2CO_3 was added portionwise, the reaction was stirred under argon at 60 °C for 3 h. Next 1.18 g (6.52 mmol) of 6-bromo-1-hexanol dissolved in 3 mL of dry DMSO was added dropwise. The reaction mixture was stirred under argon at 100 °C for 72 h. The reaction was poured into ice-cooled water and extracted with CH_2Cl_2. The organic phase was dried with anhydrous Na_2SO_4. The product was purified by column chromatography (silica gel) with CH_2Cl_2 as eluent.

Yield: 1.26 g (95%). FT-IR (cm^{-1}): 3385, 3064, 2934, 1592, 1453, 1379, 1259, 1212, 1169, 1015, 832, 733. GC-MS: 407 $[M]^+$. Calc. for $C_{26}H_{30}O_4$ (407): C 76.82; H 7.44; Found: C 76.78; H 7.41.

4-[(6-Hydroxyhexyl)oxy]benzene-1,2-diol (2): 0.406 g (1 mmol) of 6-[3,4-bis(benzyloxy)phenyloxy] hexan-1-ol was dissolved in 25 mL of dry EtOH under argon. After about half an hour 0.083 g (0.6 mmol) of $Pd/(OH)_2$ was added and then the reaction was stirred at room temperature for 10 min under argon. The reaction mixture was stirred under H_2 in a reactor at room temperature for 24 h. The product was filtered under argon and purified by column chromatography (silica gel) with 5:2 CH_2Cl_2:*n*-hexane as eluent.

Yield: 178 mg (79%). FT-IR (cm^{-1}): 3248 (OH), 3059, 2939, 2861, 1606, 1516, 1463, 1367, 1244, 1157, 1112, 1009, 841, 789. ^{1}H NMR (500 MHz, acetone-d_6) ppm: 6.75 (1H, d, J_{HH} = 8.6 Hz ArCH), 6.47 (1H, d, J_{HH} = 2.9 Hz ArCH), 6.26 (1H, dd, J_{HH} = 8.6 Hz, J_{HH} = 2.9 Hz ArCH), 4.88 (3H, s, OH), 3.89–3.84 (2H, m, CH_2-O), 3.60–3.53 (2H, m CH_2-OH), 1.75–1.11 (8H, m, CH_2). MS (ESI): 225 $[M\text{-}H]^+$, 124 $[M\text{-}C_6H_{12}O]^+$. Calc. for $C_{12}H_{18}O_4$ (226): C 63.70; H 8.02; Found: C 63.69; H 7.98.

Compound 1a: 0.2 g (0.19 mmol) of compound **1** and 0.043 g (0.19 mmol) of 4-[(6-hydroxyhexyl)oxy] benzene-1,2-diol (**2**) were stirred in 2 mL of DMSO under argon at 60 °C for 24 h. The reaction mixture was poured into ice-water solution and filtered. The green product was dissolved in acetone and purified by column chromatography (silica gel) with 100:1 CH_2Cl_2:MeOH as eluent.

Yield: 143 mg (11%). FT-IR (cm^{-1}): 3040, 2963, 2852, 1609, 1485, 1456, 1397, 1339, 1283, 1231, 1200, 1099 (C-F), 1075 (C-O), 945. ^{1}H NMR (500 MHz, acetone-d_6): ppm 7.82–7.75 (8H, d, J_{HH} = 8.0 Hz ArCH), 7.48–7.43 (7H, dd, J_{HH} = 10.5 Hz, J_{HH} = 2.5 Hz ArCH), 6.67–6.45 (4H, t, $^2J_{HF}$ = 52.4 Hz, $^3J_{HF}$ = 5.5 Hz CF_2-CH), 5.60 (4H, s, CH_2-O) 4.84–4.79 (8H, t, J_{HH} = 11.9 Hz CH_2-O), 2.34 (1H, b, OH), 1.29–1.27 (8H, m, CH_2). MS (MALDI-TOF): m/z (%): 1305 $[M+H]^+$, 1095 $[M\text{-}C_{12}H_{16}O]^+$. Calc. for $C_{56}H_{40}F_{16}N_8O_8Ti$ (1305): C: 51.58; H: 3.09; N: 8.59; Found: C: 51.60; H: 2.99; N: 8.52. UV-Vis (DMSO): λmax, nm (log ε) 701 (4.97), 632 (4.20), 353 (4.90).

Compound 1b: 0.225 g (0.17 mmol) of compound **1a** was dissolved in 40 mL of dry CH_2Cl_2 in the presence of 8 mL (56 mmol) of triethylamine at 0 °C under argon. Next 8 mL (104 mmol) of methanesulfonyl chloride was added dropwise into the reaction mixture at the same temperature. Then the reaction was carried out at room temperature for 24 h under argon; the reaction mixture was poured into an ice-water solution and extracted with CH_2Cl_2. The organic phase was dried with anhydrous Na_2SO_4. The remaining product

was boiled with n-hexane several times to remove impurities. The green product was purified by column chromatography (silica gel) with 20:1 CH_2Cl_2:MeOH as eluent.

Yield: 150 mg (64%). FT-IR (cm^{-1}): 3071, 1618, 1489, 1361, 1300, 1230, 1200, 1068, 1034, 955. Calc. for $C_{57}H_{42}F_{16}N_8O_{10}STi$ (1383): C: 49.50; H: 3.06; N: 8.10.; Found: C: 49.98; H: 2.99; N: 8.12.

Compound 1c: 0.15 g (0.11 mmol) of **1b** was refluxed in 10 mL of THF and 3 mL of EtOH mixture for 30 min. Next 0.054 g (0.0603 mmol) of thiourea was added to the reaction mixture. After the reaction was refluxed for 24 h, aqueous NaOH solution (20%, 6.5 mL) was added and then the reaction was refluxed for 24 h. The reaction mixture was poured into ice-water solution and was added dropwise into 1.2 M 10 mL of HCl solution and extracted with CH_2Cl_2. The organic phase was dried with anhydrous sodium sulfate.

Yield: 5.8 mg (4%). ^{1}H NMR. (500 MHz, acetone-d_6): ppm 8.05–7.25 (15H, m, ArCH), 6.66–6.47 (4H, t, $^2J_{HF}$: 52.4 Hz, CF_2-CH), 5.62 (H, s, SH), 4.76–4.72 (8H, t, $^3J_{HF}$: 12.6 Hz, CH_2-O), 4.17–4.15 (2H, t, J_{HH}: 5.0 Hz, CH_2-O), 2.46 (2H, b, CH_2_ SH), 1.31–1.28 (8H, m, CH_2).

Compound 3a: 0.1 g (0.09 mmol) of 4-(2,9,16,23-[2-(2-ethyloxyethyloxy)ethyloxy]) phthalocyaninato titanium(IV) (**3**) and 0.02 g (0.19 mmol) of 4-[(6-hydroxyhexyl)oxy]benzene-1,2-diol (**2**) were refluxed in 2 mL of THF under argon at 66 °C for 48 h. After the reaction, the solvent was evaporated and the crude product was treated with n-hexane. The green product was purified by column chromatography (silica gel) with 20:1 CH_2Cl_2:MeOH as eluent.

Yield: 412 mg (31%). FT-IR (cm^{-1}): 3193 (OH), 2963, 2873, 1605, 1596, 1485, 1418, 1356, 1314, 1241, 1086 (C-O), 1055, 948, 746. ^{1}H NMR (500 MHz, $CDCl_3$) ppm: 9.12–7.29 (15H, m, ArCH), 4.30–3.54 (41H, m, CH_2-O), 1.62–1.30 (24H, m, CH_2-O, CH_2, CH_3). MS (MALDI-TOF), m/z (%): 1313 $[M]^+$. Calc. for $C_{68}H_{80}N_8O_{16}Ti$ (1313): C: 62.19; H: 6.14; N: 8.53; Found: C: 62.16; H: 5.99; N: 8.32. UV-Vis (DMSO): λmax, nm (log ε) 705 (4.72), 636 (4.14), 350 (4.83).

Compound 3b: 0.24 g (0.18 mmol) of compound **5a** was dissolved in 44 mL of dry CH_2Cl_2 in the presence of 9 mL (63 mmol) of triethylamine at 0 °C under argon. Next 9 mL (117 mmol) of methanesulfonyl chloride was added dropwise to the mixture at the same temperature. The reaction was stirred at room temperature for 24 h under argon. The reaction was poured into an ice-water solution and extracted with CH_2Cl_2. The organic phase was dried with anhydrous Na_2SO_4. The remaining crude product was boiled with n-hexane several times. The green product was purified by column chromatography (silica gel) with 50:1 CH_2Cl_2:MeOH as eluent.

Yield: 200 mg (80%). FT-IR (cm^{-1}): 2963–2873, 1615, 1488, 1447, 1363, 1241, 1172 (O=S=O), 1102, 1042, 956, 748. Calc. for $C_{69}H_{82}N_8O_{18}STi$ (1391): C: 59.56; H: 5.94; N: 8.50; Found: C: 49.48; H: 5.99; N: 8.52.

Compound 3c: 0.20 g (0.14 mmol) of compound **3b** was refluxed in a mixture of THF and 4 mL of EtOH for 30 min. Then 0.069 g (0.077 mmol) of thiourea was added to the reaction mixture. After the reaction was refluxed for 24 h, aqueous NaOH solution (20%, 8.61 mL) was added and the reaction was refluxed for another 24 h. The reaction mixture was poured into an ice-water solution and was added dropwise to 1.2 M 10 mL of HCl solution and extracted with CH_2Cl_2. The organic phase was separated and dried with anhydrous sodium sulfate.

Yield: 0.003 g (1.6%). FT-IR (cm^{-1}): 3040, 2963, 2852, 2572 (SH), 1606, 1485, 1453, 1399, 1339, 1240, 1107, 1073 (C-O), 958, 821, 748. ^{1}H NMR (500 MHz, acetone-d_6) ppm: 8.27–7.07 (15H, m, ArCH), 4.35–3.44 (44H, m, CH_2-O), 2.98 (H, s, SH) 1.31–1.10 (20H, m, CH_2, CH_3). Calc. for $C_{68}H_{80}N_8O_{15}STi$ (1329, 3466).

4. Conclusions

The synthesis and characterization of peripherally tetra-substituted TiOPc compounds (**1** and **3**) and axially substituted with 4-[(6-hydroxyhexyl)oxy]benzene-1,2-diol (**2**) were successfully accomplished. Compounds **1a** and **3a** having hydroxyl groups at the end of the bulky group were converted into a thiol group by using methanesulfonyl chloride and thiourea in ethanol. All compounds were characterized by ^{1}H NMR, FT-IR, elemental analysis, and mass spectroscopy. The results are in accordance with the proposed structures. Because of the low yields of compounds **1c** and **3c**, UV spectra could not be recorded. UV-Vis spectra of compounds **1** and **1a** are given in Figure 2. In the case of compound **1a**, the absorption maximum was red shifted about 6 nm compared to compound **1**.

Our next goal is going to be investigation of the SAM formation onto the QCM surface by using new axial groups.

Acknowledgment

This work was supported by the Scientific and Technological Research Council of Turkey (TÜBİTAK) (Project Nr: TBAG-109T442).

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