Cumhuriyet Dental Journal, 25(Suppl/2): 32-37, 2022
DOI: https://doi.org/10.7126/cumudj.1203684

Cumhuriyet Dental Journal

| cdj.cumhuriyet.edu.tr | Founded: 1998 Available online, ISSN: 1302-5805
e-ISSN: 2146-2852 Publisher: Sivas Cumhuriyet Üniversitesi

New Dyestuff Production to Sensitively Determine the Sealing Capacity of the Implant Abutment Connection

Ebru Yabaş[1-a*], Mehmet Şimşir[2-b*], Mustafa Çetin[3-c], Fatih Özaydın[3-d]

[1] *Advanced Technology Application and Research Center, Sivas Cumhuriyet University, Sivas, Türkiye.*

[2] *Faculty of Engineering, Metallurgical and Materials Engineering, Sivas Cumhuriyet University, Sivas, Türkiye*

[3] *ESTAŞ Eksantrik Sanayi ve Ticaret A.Ş., Sivas, Türkiye*

**Corresponding author*

Research Article

Acknowledgment
This study was presented as an oral presentation at the ''Sivas Cumhuriyet University 2st International Dentistry Congress'' held between 22-24 September 2022.

History

Received: 14/11/2022
Accepted: 22/12/2022

ABSTRACT

Aim: In this study, it was aimed to synthesize a new dyestuff with fluorescent active properties, which can be easily produced and water-soluble, to be used in sealing tests.

Materials and Methods: In this study, oxo-titanium phthalocyanine compound, which has dyestuff properties and is soluble in water, was obtained as a result of the tetramerization reaction of substituted phthalonitrile derivative. The synthesis of the compound was carried out in closed glass tubes resistant to temperature and pressure under an argon atmosphere. The synthesized crude product was purified by washing from solubility differences and using column chromatography. The sealing capacities of the implant abutment connection of the dental implant systems manufactured by ESTAŞ were determined spectroscopically by UV-Vis spectrophotometer using the synthesized dyestuff in the first stage. Thanks to the fluorescent active property of the dyestuff, the emission spectra were measured with the fluorescent spectrometer, which is highly sensitive to changes, and the sealing capacities could be determined, depending on time. In addition, the gap between the implant and the abutment connection was determined using a Scanning Electron Microscope (SEM), and the sealing capacities were evaluated from a different perspective. In addition, sealing tests of the same implant systems were also performed with methylene blue dyestuff and the results were compared. The efficiency of our synthesized dyestuff was determined.

Results*:* The dyestuff to be used in the sealing tests of the implants was synthesized and characterized in a short time in our laboratory. The phthalocyanine compound from the porphyrin class was obtained as a result of the tetramerization reaction of the synthesized phthalonitrile derivative. The dyestuff, which can be synthesized in a short time like 10 minutes, was purified by taking advantage of the solubility difference and chromatographic methods. The obtained dyestuff was characterized by NMR, FTIR, UV-Vis, and MALDI-TOF MS. The results obtained are in harmony with the structure of the molecule. The produced dyestuff is water soluble and was especially used to determine the sealing capacity of the implant abutment connection of dental implant systems produced by ESTAŞ. The sealing properties of the implant were determined by spectroscopic methods such as UV-Vis and fluorescence. In addition, sealing capacities were evaluated with SEM. According to the results obtained, we can say that the synthesized dyestuff is a dye that can give spectroscopically more sensitive results than methylene blue.

Conclusions: Dental implants, which are artificially placed in the mouth to support dental prostheses, have changed dental treatment methods to a large extent and become the most preferred successful technique. However, infection risks may occur during the treatment due to the formation of a gap between the abutment cap and the implant resulting from both the production and adaptation of the abutment cap, which is a part of the implant. For this reason, it is important that the implants produced are routinely sensitively checked for sealing and put into use. In addition, sealing control will contribute to the control and shaping of the process from the manufacturing stage of the implant.

In line with all obtained data, it has been determined that the implant types produced by ESTAŞ have a sealing capacity below the acceptable limits. In addition, it was observed that our newly synthesized dyestuff spectroscopically gave sensitive results in the sealing tests of implant systems.

Keywords: Phthalocyanine, synthesis, sealing, spectroscopy, dental implant.

[a] *eyabas@cumhuriyet.edu.tr* *https://orcid.org/0000-0001-7163-3057*
[b] *msimsir@cumhuriyet.edu.tr* *https://orcid.org/0000-0002-8895-7821*
[a] *mustafa.cetin@estas.com.tr* *https://orcid.org/0000-0003-1772-9837*
[b] *fatih.ozaydin@estas.com.tr* *https://orcid.org/0000-0002-0089-373X*

How to Cite: Yabaş E, Şimşir M, Çetin M, Özaydın F. (2022) New Dyestuff Production to Sensitively Determine the Sealing Capacity of the Implant Abutment Connection, Cumhuriyet Dental Journal, 25(Suppl/2):32-37.

Introduction

Dental implants, which are increasingly used for the treatment of tooth loss, are commercially produced materials from titanium alloys used to support dental prostheses.[1-3] Implants are produced by manufacturers with different standards and consist of a body and a changing head. Implants are produced by manufacturers with different standards and consist of a body and a changing head. During the production phase, it is important to ensure that the body and the abutment head are well interlocked. Because infection risks from dental implants may occur during the treatment. This is one of the most important problems that reduces the sustainability of the process. For this reason, it is important to routinely check the sealing tests between the body and the abutment head of the dental implants produced before the treatment. In the literature, commercial dyestuffs such as methylene blue or toluidine blue are generally used in dental implant sealing tests and their sealing capacity is determined spectroscopically (UV-Vis).[1,4-7] The development of new dyestuffs with effective properties in performing dental implant sealing tests, which is important in the treatment process, will be interesting in terms of the sensitivity of the tests.

Phthalocyanines are aromatic macromolecules composed of isoindole groups bonded with nitrogen atoms. Phthalocyanine and its derivatives are widely used as colorants due to their blue and green colors. This macromolecule contains 18 delocalized π-electrons and can host transition metals in the core constituting metal complexes making them very useful in many applications. Phthalocyanine compounds were first synthesized by chance in 1907 by researchers named Braun and Tcherniac by heating o-cyanobenzamide at high temperature.[8] The structure of phthalocyanine was elucidated by X-ray diffraction analysis by Robertson in 1936.[9] In addition, phthalocyanines have high thermal stability and sublimate without melting, usually around 550°C. Unsubstituted derivatives of phthalocyanines, which are a versatile and stable compound class, are extremely poorly soluble in water and organic solvents. However, the solubility of phthalocyanines can be noticeably increased by attaching substituents to the ring. These fluorescence-active macromolecules can be used in many applications due to their superior spectroscopic, electronic and optical properties.[8, 10-14]

In this context, we propose that our newly synthesized water-soluble oxo-titanium phthalocyanine compound can produce spectroscopically sensitive results in the sealing control of dental implants. We propose that oxo-titanium phthalocyanine might be a promising candidate in promising candidate in terms of showing more effective dyestuff activity than the currently used methylene blue.

Materials and Methods

Materials

4- (2-Trimethylaminoethylsulfany) phthalonitrile iodide, which was used as the starting material in the synthesis reaction, was prepared according to previous reports.[15] All chemical reagents and solvents used in the study were purchased from Merck. The implants used in the study were produced by ESTAŞ and their properties are described in below.

Properties of implants

The implants produced by ESTAŞ were made from Ti6Al4V ELI (ASTM F136 Grade 23) material and Grade 23 was used to increase biocompatibility. The connection types of the products are explained below and shown schematically in Figure 1. The implant-healing head was inserted into the implant by screwing method. The products were mounted to each other in such a way that there was a forehead contact. The angular position within the implant was fixed with the implant-abutment hex region, and the implant was mounted with a 10° conical connection. The implant-abutment screw was mounted using the screw method. The abutment-abutment screw was mounted with a 45° conical connection. The carrying part-implant connection was mounted to each other in such a way that the products were in contact with the forehead. Flexible wings on the carrying part were placed inside the implant to fix the products. The implant-closure screw was inserted into the implant using the screwing method. The products were mounted to each other in such a way that there was a forehead contact.

Technical information on the implant parts produced by ESTAŞ and used in this study are given in Table 1.

Synthesis of Dyestuff

The synthesis procedure described below is schematized in Figure 2.

Tetrakis [(2-trimethylaminoethylsulfanyl) phthalocyaninato oxo-titanium(IV)] tetraiodide

A solid mixture of finely powdered 4-(2-trimethylaminoethylsulfany)phthalonitrile iodide (1.0 g, 2.69 mmol) and titanium(IV) butoxide (0.23 mg, 0.67 mmol) was heated at 300°C in the presence of DBU under nitrogen atmosphere. The mixture was then cooled and dissolved in DMF. The insoluble part was removed by filtration. The solvent of the solution was removed in the evaporator and the residue was dried in vacuum. The crude product was purified by column chromatography on alumina using $CHCl_3$:Methanol (4:1). The resulting dark green solid was soluble in water. Yield: 43%. M.p.: >300°C. ^{1}H-NMR (400 MHz, DMSO-d_6, 25°C) δ= 7.78-6.90 (Ar-H, 12H), 3.66 (t, S-CH_2, 8H), 3.50 (N-CH_2, 8H), 3.12 (N-CH_3, 36H). UV-Vis (DMSO) λ_{max}/nm (logε, $dm^3mol^{-1}cm^{-1}$): 687, 640, 345. IR (KBr pellet) υ (cm^{-1}): 2908-2800, 1605, 1463, 1305, 1100, 740. MS (MALDI-TOF) m/z: 1557 $[M+H]^+$.

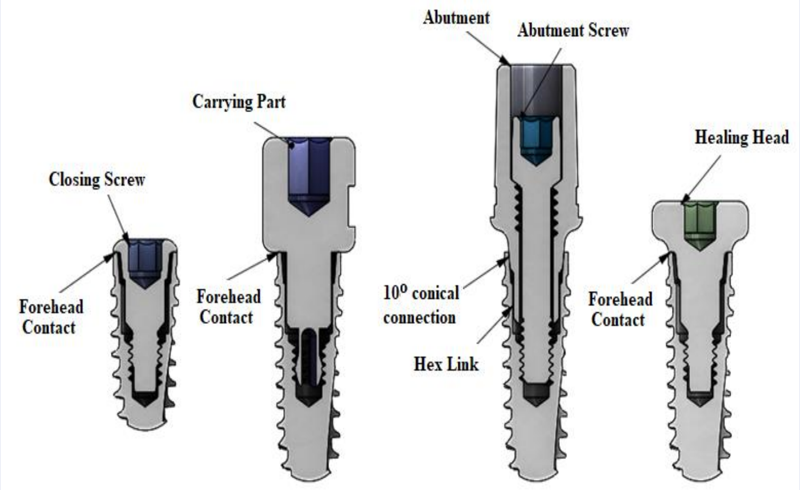

Figure 1. Connection types of implants manufactured by ESTAŞ.

Table 1. Technical characteristics of implant parts used in this study.

Parts of the product used in the study	Code
Dental Implant Ø3,3-13,0 mm	DNT-MTI-33130
Closing Screw, 0,5 mm	DNT-CS-3305
Implant Carrying Part AA2,0	DNT-İMT-20
Healing Head, Ø4,7x2,0 mm	DNT-HC-3320
Flat Abutment, Post 6,0 mm, Ø4,5-2,0 mm	DNT-ABST-4562
Abutment Screw, M1,6-6,0 mm	DNT-AS-1606

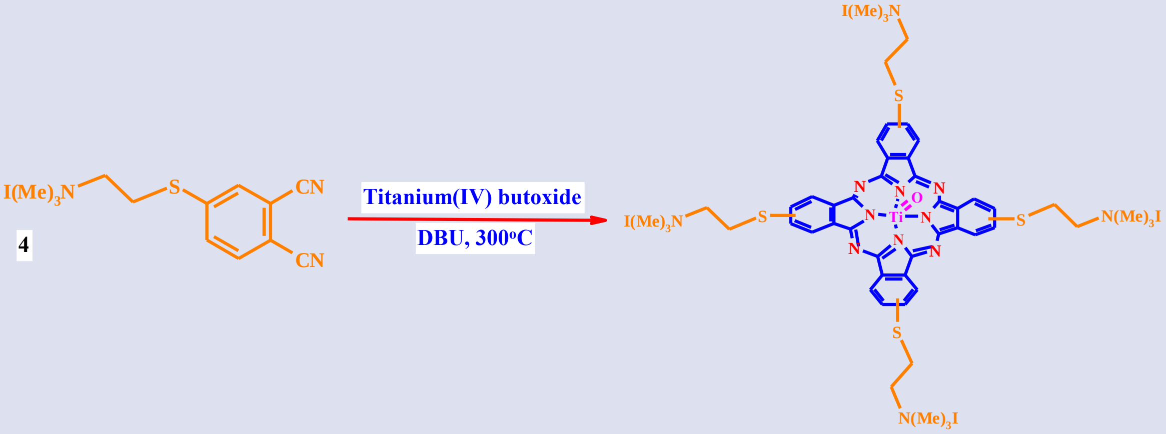

Figure 2. Synthesis of the dyestuff

Results and Discussion

The water-soluble oxo-titanium phthalocyanine compound was obtained by the tetramerization reaction of the quaternized phthalonitrile compound. The dyestuff was synthesized with high yields as a result of heating the solid mixture of phthalonitrile compound and metal salt in the presence of DBU in a short time like 10 minutes without using solvent. The synthesized oxo-titanium phthalocyanine compound was purified by washing from solubility differences and using column chromatography. The purified product was characterized by UV-Vis, FT-IR, ^{1}H-NMR and MALDI-TOF MS.

In the UV-vis spectrum of the water-soluble oxo-titanium phthalocyanine compound, typically a single absorption peak was observed between 600 and 700 nm in the Q-band region for metallophthalocyanines due to the D_{4h} symmetry. The Q-band absorptions of phthalocyanine compounds represent the $\pi \rightarrow \pi*$ transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the ring. The B-band absorptions observed between 300 and 350 nm indicate a transition from deeper π levels to the LUMO.[8, 16-19] In the UV-Vis spectrum of the synthesized dyestuff measured in DMSO, characteristic Q- and B-bands were observed at 687 nm and 345 nm, respectively. This result showed that the phthalocyanine compound was formed.

In the FT-IR spectrum of the synthesized phthalocyanine compound, it was observed that the -C≡N peak of the phthalonitrile derivative at 2240 cm^{-1}.[16, 20] disappeared. This result showed that the tetramerization reaction took place. Aliphatic C-H peaks of the phthalocyanine compound were also observed between 2908-2800 cm^{-1}. In addition, peaks in the FT-IR spectrum were observed for the stretching vibration of C=C and the substituted benzene ring at 1605 cm^{-1} and 740 cm^{-1}, respectively.[16, 20]

In the ^{1}H-NMR spectrum of the oxo-titanium phthalocyanine compound taken in DMSO-d$_6$ at room temperature, aromatic protons and aliphatic protons appeared in the range of 7.78-6.90 ppm and 3.66-3.12 ppm, respectively.[15, 21] It was observed that the integral ratios of the peaks in the spectrum were also compatible with the structure of the compound. This result confirms the structure of the compound we synthesized.

The MALDI-TOF MS result is also in agreement with the proposed structure of the compound.

All characterization results confirm that the oxo-titanium phthalocyanine compound shown in Figure 2 was successfully synthesized.

At the same time, the synthesized oxo-titanium phthalocyanine compound is a fluorescent active compound and gives a sharp and intense emission peak at 689 nm in DMSO. We investigated the usability in the sealing experiments of the implants by taking advantage of these superior spectroscopic properties of the water-soluble oxo-titanium phthalocyanine compound. Also, we can say that the synthesized compound also has a very intense dyestuff feature.

In this study, we aimed to evaluate the sealing capacity of the dental implant systems, especially the implant abutment connection, with the paint we produced. Dental implant systems were produced by the ESTAŞ manufacturer and their properties were defined in the experimental part.

In the literature, we see that methylene blue is generally used in sealing trials in implant systems. We performed the sealing tests on the same implant systems using both methylene blue and the dyestuff we synthesized. In this way, we were able to compare the activity of the dyestuff we produced with superior spectroscopic properties.

In these studies, each experiment was repeated three times in order to see the reproducibility of the experiments. In these studies, each experiment was repeated three times in order to see the reproducibility of the experiments. In the sealing experiments, solutions of the oxo-phthalocyanine compound in the first step were prepared at different concentrations in water. The absorption and emission intensities of these prepared solutions were separately measured by using UV-Vis and fluorescence spectrophotometers, respectively. Calibration curves giving peak intensity versus concentration were drawn with the obtained data. Afterwards, the volume of the cavity between the deepest part of the inner screw and its inner base was determined by using a micropipette with precision volume measurement. For implant systems produced by the manufacturer, this cavity volume was determined as 2 µL. Thanks to the very thin tips of the micropipettes, the dye solution we prepared in water at a concentration of 10^{-1}M was sensitively added into the implants and the implant heads were closed using torque under the same conditions. Each implant with closed caps was placed in the water-filled (the same volume) eppendorf tubes as seen in Figure 3. Spectrophotometric analyzes were performed with UV-Vis and fluorescence spectrophotometers for each sample at room temperature at incubation times of 1, 3, 6, 24, 48, 72, 96 and 144 hours. Concentrations corresponding to incubation times were determined with the help of measured spectroscopic data and standard curves. The same trials were performed on the same implants and under the same conditions, using methylene blue as a dye.

In implant systems, no color change was observed in the water in eppendorf until the 144-hour incubation period in the sealing tests with methylene blue, and no absorption/emission peak was observed in the spectroscopic measurements of the water. However, weak absorption/emission peaks were observed in the spectroscopic measurements of water after the incubation period of 96 hours in the experiments performed with the dyestuff we synthesized. No discernible change was observed in the color of the water in the Eppendorf. As a result of our experiments, it was determined that there was approximately 3% leakage in the implant systems after 96 hours of incubation period.

Figure 3. Solution of dyestuff in water (left) and symbolic representation of sealing experiments.

At the same time, the images of the implant systems, whose sealing tests were performed and whose heads were closed with torque, were taken with scanning electron microscopy (SEM). As seen in Figure 4, the cavity between the head and body of the implant is micron size and completely symmetrical. This SEM images are evidence why there is little to no spectroscopic sealing in implant systems.

In addition, we cut the implant systems with the bakelite method and examined their inner surfaces with SEM. We observed that the head and body parts of the implants were symmetrically connected to each other (Figure 5). The SEM images in Figure 5 are also evidence of impermeability in implant systems.

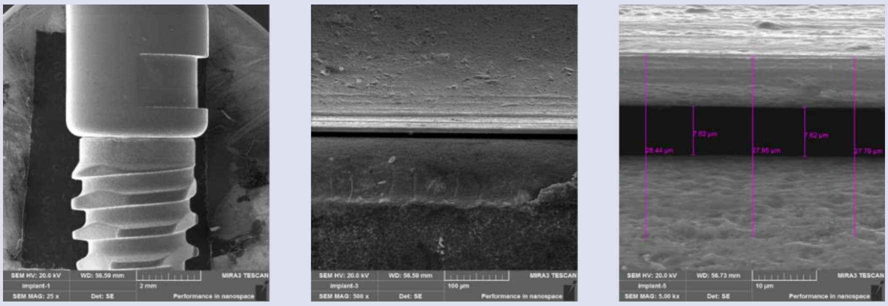

Figure 4. SEM image of the outer surface of the implant system.

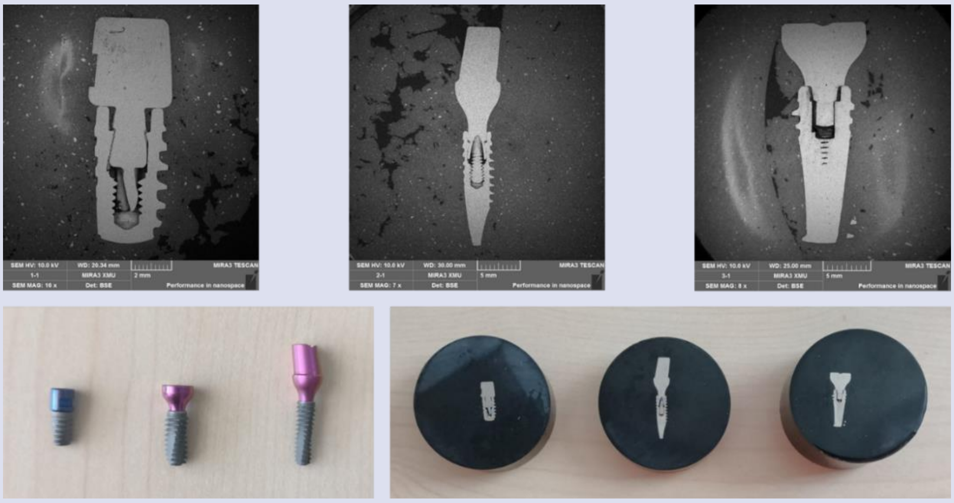

Figure 5. Implants cut with bakelite method and their SEM images.

Conclusions

In this study, we synthesized a new oxo-titanium phthalocyanine compound as a result of the tetramerization reaction of the phthalonitrile derivative. This compound, which is a water-soluble and intense green colorant, was obtained in a very good yield in a short reaction time of 10 minutes. The newly synthesized dyestuff was characterized by UV-Vis, FT-IR, ^{1}H-NMR and MALDI-TOF MS and its molecular structure was confirmed. By using this obtained dyestuff, the sealing tests of the implant systems produced by the ESTAŞ manufacturer were carried out. The sealing capacities of the implants were examined by spectroscopic methods (UV-Vis, fluorescence) and SEM. It was determined that the produced implant systems had a sealing capacity below acceptable limits. At the same time, sealing tests were repeated with methylene blue dyestuff to see the activity of our synthesized dye in the same implant systems. As a result, it was determined that our synthesized dye was a spectroscopically more sensitive marker than methylene blue.

Conflicts of Interest Statement

There are no conflicts to declare.

References

1. Meffert R M, Langer B, Fritz Michael E. Dental Implants: A Review. J Periodontol 1992; 63:859-870.
2. Nicholson J W. Titanium Alloys for Dental Implants: A Review. Prosthesis 2020; 2: 100-116.
3. McCracken M. Dental Implant Materials: Commerciallv Pure Tita&um and Titanium Alloys, Journal afl'msthodontics 1999; 8: 40-43.
4. Coelho P G, Sudack P, Suzuki M, Kurtz K S, Romanos G E, Silva N R F A. In vitro evaluation of the implant abutment connection sealing capability of different implant systems. J Oral Rehabilit 2008; 35: 917-924.
5. Lorenzoni F C, Coelho P G, Bonfante G, Carvalho R M, Silva N R F A, Suzuki M, Silva T L, Bonfante E A. Sealing Capability and SEM Observation of the Implant-Abutment Interface. Hindawi Publish Corpor Int J Dent 2011; 1-6.
6. Kawahara H, Kawahara D, Mimura Y, Takashima Y. Morphologic Studies on the Biologic Seal of Titanium Dental Implants. Report II. In Vivo Study on the Defending Mechanism of Epithelial Adhesion/ Attachment Against Invasive Factors. Int J Oral Maxillofac Implants 1998; 13: 465-473.
7. Duarte A R C, Rossetti P H O, Rossetti L M N, Torres S A, Bonachela W C. In Vitro Sealing Ability of Two Materials at Five Different Implant-Abutment Surfaces. J Periodontol 2006; 77: 1828-1832.
8. Lenzoff C C, Lever A B P. Phtalocyanines Properties and Applications. Cilt 1, VCH publishers 1993.
9. Kobayashi N. Phthalocyanines. Solid State Mater Sci 1999; 4: 345.
10. McKeown N B. Phthalocyanine-Containing Dendrimers. Adv Mater 1999; 11: 67.
11. Brewis M, Hassan B M, Li H, Makhseed S, McKeown N B, Thompson N. The synthetic quest for 'splendid isolation' within phthalocyanine materials. J Porphyrins Phthalocyanines 2000; 4(5): 460.
12. Kameyama K, Morisue M, Satake A, Kobuke Y. Highly Fluorescent Self Coordinated Phthalocyanine Dimers. Angew Chem Int Ed 2005; 44: 4763-4766.
13. Nyokong T. Electronic Spectral and Electrochemical Behavior of Near Infrared Absorbing Metallophthalocyanines. Struct Bond 2010; 135: 45-88.
14. Nyokong T. Effects of Substituents on The Photochemical and Photophysical Properties of Main Group Metal Phthalocyanines. Coord Chem Rev 2007; 251: 1707-1722.
15. Dabak S, Gümüş G, Gül A, Bekaroğlu Ö. Synthesis And Properties Of New Phthalocyanınes With Tertiary Or Quaternarized Aminoethylsulfanyl Substıtuents, J Coor Chem 1996; 38(4): 287-293.
16. Yabaş E, Sülü M, Saydam S, Dumludağ F, Salih B, Bekaroğlu Ö. Synthesis, characterization and investigation of electrical and electrochemical properties of imidazole substituted phthalocyanines. Inorg Chim Acta 2011; 365: 340-348.
17. Durmuş M, Nyokong T. Synthesis and Solvent Effects on The Electronic Absorption and Fluorescence Spectral Properties of Substituted Zinc Phthalocyanines. Polyhedron 2007; 26: 2767-2776.
18. Tau P, Nyokong T. Synthesis, Electrochemical and Photophysical Properties of Phthalocyaninato Oxotitanium(IV) Complexes Tetra-Substituted at The A and B Positions with Arylthio Groups. Dalton Trans 2006; 4482-4490.
19. Wöhrle D, Eskes M, Shigehara K, Yamada A. A simple Synthesis of 4,5-Disubstituted 1,2-Dicyanobenzenes and 2,3,9,10,16,17,23,24-Octasubstituted Phthalocyanines. Synthesis 1993; 2: 194-196.
20. Yabaş E, Sülü M, Dumludağ F, Salih B, Bekaroğlu Ö. Imidazole octasubstituted novel mono and double-decker phthalocyanines: Synthesis, characterization, electrical and gas sensing properties. Polyhedron 2018; 153: 51-63.
21. Polat M, Gül A. Synthesis of new porphyrazines with tertiary or quaternized aminoethyl substituents. Dyes Pigments 2000; 45: 195-199.