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Research Article

Synthesis, Characterization and Spectroscopic Properties of Novel Mono-Lutetium(III) Phthalocyanines

Yeni Mono-Lutesyum(III) Ftalosiyaninlerin Sentezi, Karakterizasyonu ve Spektroskopik Özellikleri

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Abstract

In this study, the novel highly soluble and non-aggregated peripherally /non-peripherally tetrakis-2,6-dimethoxyphenoxy substituted mono-lutetium(III) acetate phthalocyanine complexes have been synthesized for use in different technological applications. The newly synthesized phthalocyanine complexes have been characterized by elemental analysis, FT-IR, ^{1}H NMR, UV–*vis*, fluorescence spectroscopy and MALDI-TOF Mass spectra. The effects of the positions (peripheral or non-peripheral) of the substituents on the spectroscopic properties of 2,6-dimethoxyphenoxy substituted mono-lutetium(III) phthalocyanines have also been reported.

Keywords: Lutetium(III) acetate, Mono-lutetium phthalocyanine, Non-aggregated, Non-peripheral, Peripheral, Soluble

Öz

Bu çalışmada çeşitli teknolojik uygulamalarda kullanılması amacıyla yeni, oldukça çözünür ve agregasyon yapmayan ftalosiyanin halkasına periferal ve non-periferal pozisyonlardan 2,6-dimetoksifenoksi gruplarıyla tetrasübstitüe lutesyum(III) asetat metalli ftalosiyanin bileşikleri sentezlenmiş ve yapıları elemental analiz, FT-IR, 1H NMR, UV–vis spektroskopisi ve MALDI-TOF Kütle analiz metotları kullanılarak karakterize edilip aydınlatılmıştır. Ayrıca bu bileşiklerin periferal ve non-periferal pozisyonlardan 2,6-dimetoksifenoksi gruplarıyla sübstitüe edilmesiyle spektroskopik özelliklerindeki değişiklikler rapor edilmiştir.

Anahtar Kelimeler: Lutesyum(III) asetat, Mono-lutesyum ftalosiyanin, Agregasyon yapmayan, Non-periferal, Periferal, Çözünür

1. Introduction

Metallophthalocyanines (MPcs) are organometallic macrocycles that typically comprise the usually planar organic ligand and a metal ion or metalloid within the central cavity of the ring. MPcs have attracted considerable attention in solar cells, photodynamic therapy, gas sensors, liquid crystal, and electrochoromic displays because of their remarkable optical and electrical properties, the conjugated system, as well as chemical and thermal stability (Simon and Andre 1985, Leznoff and Lever 1989, 1993, 1996, Simon and Bassoul 2000). Complexes of lanthanide metallated Pcs (LnPcs) are also highly interesting owing to their physical, electrical, optical, and electrochemical properties originated from their extensive electron delocalization and their thermal and chemical stability (Gould 1996, Kudrevich and vanLier 1996, Rosenthal 1996). They have found wide application in technological areas such fluorescence materials (Buono-Core et al. 1990, Wu et al. 2008), electroluminescence (Edward et al. 1997), and as fluorescence probes and labels in a variety of biological systems (Meares et al. 1984, Kukhta et al. 2006, Wu and Zhang 2002). Lutetium phthalocyanine complexes of (LuPcs) have been studied owing to their rich electrochromic and gas-sensing properties and high intrinsic conductivity (Nicholson et al. 1993, Zugle et al. 2011, Weiss and Fischer 2003, Besbes et al. 1987, Petty 1992). Their properties can be tuned by depending on the substituents at peripheral or non-peripheral positions onto the macrocycle ring (Yılmaz et al. 2003). Therefore, it is important to know electrochemical and spectroelectrochemical properties of these complexes to be used in various technological applications. Moreover, solubilities of phthalocyanines, which play key role for their application areas, can be enhanced substi-

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tution with suitable groups at peripheral or non-peripheral positions of the Pc ring (Friedrich and Haarer 1984, Takahashi et al. 1995, Wöhrle et al. 1993). Our aim in this study is to synthesize novel soluble non-aggregated substituted lutetium(III) acetate metallated mono-phthalocyanines (Lu(OAc)Pcs) for use in various technological applications. Herein, we report the synthesis, characterization and spectroscopic properties of Lu(OAc)Pcs tetra-substituted at the non-peripheral (**3**) and peripheral (**4**) positions with 2,6-dimethoxyphenoxy groups (Figure 1).

2. Material and Methods

All used chemicals were of reagent grade quality. 3-Nitrophthalonitrile, 4-Nitrophthalonitrile, 2,6-dimethoxyphenol and metal salt were purchased from Sigma-Aldrich and used as received. The solvents were purified, dried and stored over molecular sieves (4Å). All reactions were carried out under dry nitrogen atmosphere unless otherwise noted. 3-(2,6-dimethoxyphenoxy)phthalonitrile (**1**) and 4-(2,6-dimethoxyphenoxy)phthalonitrile (**2**) compounds were synthesized and purified according to the literature (Pişkin 2016). Column chromatography was performed on silica gel 60 for a proper purification of the pure compound. Melting points of the Pc complexes were found to be higher than 300 °C. The purity of the products was tested in each step by thin layer chromotography (Silicagel F-254 coated TLC plate). FT-IR Spectra and electronic spectra were recorded on a Shimadzu FTIR-8300 (ATR) and a Shimadzu UV–1601 spectrophotometer, respectively. Elemental analyses carried out using a LECO CHN 932 was performed by the Instrumental Analysis Laboratory of TUBITAK Ankara Test and Analysis Laboratory. ^{1}H-NMR spectra were recorded on a Varian Mercury 400 MHz spectrophotometer in DMSO-d_6 and chemical shifts were reported (δ) relative to Me_4Si as internal standard. MALDI-MS of newly synthesized complexes were obtained in 2,5-dihydroxybenzoic acid as MALDI matrix using nitrogen laser accumulating 50 laser shots using Bruker Microflex MALDI-TOF mass spectrometer.

2.1. Synthesis

2.1.1. General Procedure for the Synthesis of Metallo-Phthalocyanines (3 and 4)

3-(2,6-Dimethoxyphenoxy)phthalonitrile (**1**) or 4-(2,6-dimethoxyphenoxy)phthalonitrile (**2**) (0.200 g, 0.72 mmol), anhydrous lutetium(III) acetate (0.063 g, 0.18 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.12 mL, 0.80 mmol) used as a catalyst and *N,N*-dimethylformamide (DMF) (1.75 mL) were mixed and refluxed with stirring under argon atmosphere for 24 h. After cooling to room temperature, the solution was dropped in the hot methanol and then filtered off. The green solid products were precipitated and collected by filtration and washed with hot methanol, ethanol, n-hexane, acetone, diethyl ether and then dried in vacuum at 50°C. The products were purified by passing through a silica gel column using chloroform as the eluting solvent.

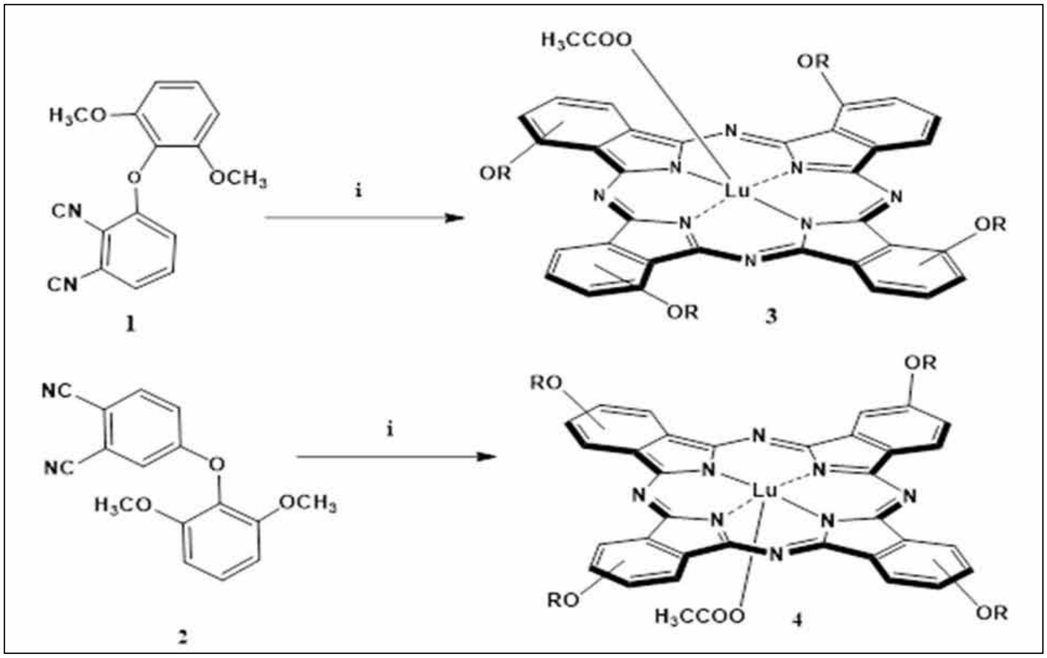

Figure 1. Synthesis of tetra-substituted lutetium (III) acetate mono-phthalocyanines (**3–4**). Reagents and conditions: (i) N_2, $Lu(CH_3COO)_3$, DMF, DBU, reflux, 24 hour.

2.1.1.1. 1(4),8(11),15(18),22(25)-Tetrakis-(2,6-dimethoxyphenoxy)phthalocyaninato lutetium(III) acetate (3)

The non-peripherally substituted Lu(OAc)Pc complex (**3**) is soluble in chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), tetrahydrofurane (THF), toluene, acetonitrile, DMF and dimethylsulfoxide (DMSO). Mp>300° C. Yield: 66.96 mg (25.48 %). Calculated for $C_{66}H_{51}LuN_8O_{14}$: C, 58.50%; H, 3.79%; N, 8.27%; found C, 58.66%; H, 3.63%; N, 8.45 %. FT-IR (ATR) ν_{max}/cm^{-1}: 743, 802, 823, 879, 970, 1077(C–C str.), 1108(C–N str.), 1182(C–N str.), 1338 (C–O str.), 1478(C–H bend.),1594(C=C str.), 1652(C=N str.), 1731(C=O str.), 2922(–CH_3 str.), 3007(=C–H str.), 3078(=C–H str.). UV–*vis* (DMSO, 1x10^{-5} M): λ_{max}(nm), (log ε): 320 (4.40), 375 (4.36), 635 (4.12), 675 (4.24), 704 (5.08). MS (MALDI-TOF) m/z: calc.: 1355.14; found: 1450.68 $[M–OAc+DHB]^+$. ^1H NMR (400MHz, DMSO-d_6, ppm): d = 8.88–8.07 (m, 4H, Ar–H), 8.06–6.79 (m, 20H, Ar–H), 3.82 (s, 24H, -OCH_3), 1.42 (s, 3H, acetate-CH_3)

2.1.1.2. 2(3),9(10),16(17),23(24)-Tetrakis-(2,6-dimethoxyphenoxy)phthalocyaninato lutetium(III) acetate (4)

The peripherally substituted Lu(OAc)Pc complex (**4**) is soluble in $CHCl_3$, dichloromethane (DCM), THF, toluene, acetonitrile, DMF and DMSO. Mp>300° C. Yield: 59.55 mg (22.68%). Calculated for $C_{66}H_{51}LuN_8O_{14}$: C, 58.50%; H, 3.79%; N, 8.27%; found C, 58.71%; H, 3.62%; N, 8.43 %. FT-IR (ATR) ϖ_{max}/cm^{-1}: 736, 763, 823, 886, 940, 1040(C–C str.), 1074(C–C str.), 1105(C–N str.), 1182(C–N str.), 1330(C–O str.), 1388(C–H bend.), 1471(C–H bend.), 1601(C=C str.), 1655(C=N str.), 1717 (C=O str.), 2934(–CH_3 str.), 3005(=C–H str.), 3060(=C–H str.). UV–*vis* (DMSO, 1x10^{-5} M): λ_{max}(nm), (log ε): 338 (4.71), 359 (4.71), 618 (4.19), 688 (5.02). MS (MALDI-TOF) m/z: calc.: 1355.14; found: 1451.15 $[M–OAc+DHB]^+$. ^1H-NMR (400MHz, DMSO-d_6, ppm): d= 9.47-9.24 (m, 2H, Ar-H), 8.61-8.26 (m, 2H, Ar-H), 7.99–6.89 (m, 16H, Ar-H), 7.96–6.80 (m, 4H, Ar-H), 3.90 (s, 24H, -OCH_3), 1.33 (s, 3H, acetate-CH_3).

3. Results and Discussion

3.1. Syntheses and Characterization

The non-peripherally and peripherally substituted phthalonitriles synthesized from 3-nitrophthalonitrile, 4-nitrophthalonitrile and 2,6-dimethoxyphenol through base catalyzed nucleophilic aromatic displacement according to the literature (Pişkin 2016). Figure 1 shows the synthetic route involved for the formation of the novel phthalocyanines (**3** and **4**). The non-peripherally and peripherally substituted Lu(OAc)Pcs (**3** and **4**) were formed by cyclotetramerization of the compounds **1** and **2** in the presence of anhydrous $Lu(CH_3COO)_3$ and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a strong base in DMF at reflux temperature. The obtained Pcs (**3** and **4**) washed several times with different organic solvents (hot methanol, ethanol, n-hexane, acetone, diethyl ether) and then purified by column chromatography with silica gel using chloroform as eluenting solvent. The Lu(OAc)Pcs (**3** and **4**) exhibited excellent solubility in organic solvents such as $CHCl_3$, DCM, THF, toluene, acetonitrile, DMF and DMSO. It was observed that both introduction of 2,6-dimethoxyphenoxy groups as substituent on the Pc ring and lutetium(III) acetate metal ion in the Pc cavity increase the solubility. The newly synthesized phthalocyanine complexes (**3** and **4**) were fully characterized by spectroscopic techniques such as FT-IR, ^1H-NMR, MALDI-TOF mass, UV–*vis* and elemental analyses as well. The obtained results were in accordance with the proposed structures. The strong –C≡N bands of **1** and **2** were appeared at 2231 and 2227 cm^{-1} in the Fourier Transform Infrared (FT-IR) spectra (Pişkin 2016) and these bands were disappeared after conversion to the Lu(OAc)Pcs derivatives (**3 and 4**). In the FT-IR spectra of the Lu(OAc)Pcs, weak bands were observed above 3000 cm^{-1} due to aromatic C–H stretching. The aliphatic C–H stretching vibrations of synthesized complexes were observed at around 2838-2934 cm^{-1}. The $[M–OAc+DHB]^+$ peaks of the Lu(OAc)Pcs (**3** and **4**) were identified easily with 2,5-dihydroxybenzoic acid (DHB) as MALDI matrix in the reflectron mode using a MALDI-TOF mass spectrometry. These peaks (**3** and **4**) were observed at 1450.68 for **3** and 1451.15 Da for **4** (Figure 2 for **3** and Figure 3 for **4**). The MALDI-TOF mass spectra of **3** and **4** confirmed the proposed structures.

^1H-NMR data and spectra were consistent with the structures for **3** and **4** (Figure 4 for **3** and Figure 5 for **4**). All the protons were observed in their respective regions. The Pc ring protons integrated for 12 and 2,6-dimethoxyphenoxy for 36 as expected. In addition, protons due to the acetate axial ligand were observed. The isomeric nature of the molecules only results in the broadening of the NMR spectra. Elemental analysis results were in agreement with the proposed structure. A mixture of four possible structural isomers is expected for the complexes. In this study, synthesized Lu(OAc)Pc complexes (**3** and **4**) are obtained as isomeric mixtures as expected and no attempt was made to separate them.

3.2. Ground State Electronic Absorption Spectra

The best evidence the formation of phthalocyanine macrocycle is their UV–*vis* spectra in solution. The ground state electronic absorption spectra of the Pc complexes **3** and **4** are shown in Figure 6. The UV–*vis* absorption spectra of the Pc complexes **3** and **4** indicate the characteristic intense Q bands at 704 and 688 nm, respectively in DMSO solution. In addition, an intense peaks of B bands (B1 and B2 bands) at 320 nm for (**3**), 338 nm for (**4**) a relatively weak and broad absorption around 375 nm for (**3**) and 359 nm for (**4**) as shoulders (B bands) were monitored in DMSO, due to the superimposition of the B1 and B2 bands (Figure 6). For the lutetium(III) acetate phthalocyanine bearing 2,6-dimethoxyphenoxy moieties on the non-periphery and periphery, the Q band is shifted to the longer wavelength as a result of the electron-donating ability of 2,6-dimethoxyphenoxy substituents as shown in Figure 6. Red-shifted 16 nm between non-peripheral substituted Lu(OAc)Pc **3** and peripheral substituted Lu(OAc)Pc **4** (Figure 6) were typical of non-peripheral substituted

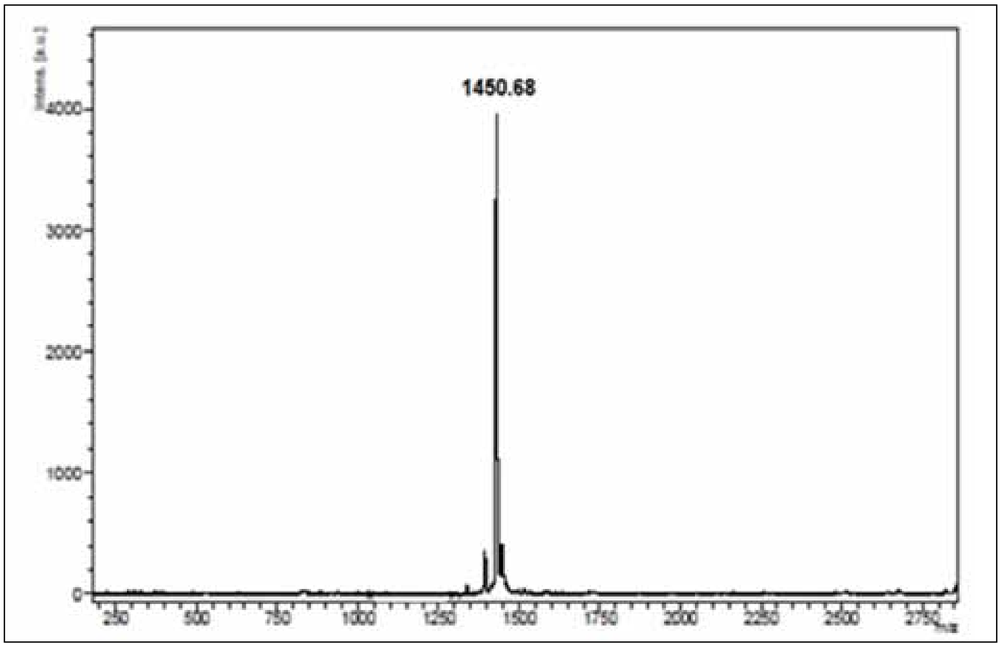

Figure 2. Mass spectrum of non-peripherally substituted Lu(OAc) Pc (**3**).

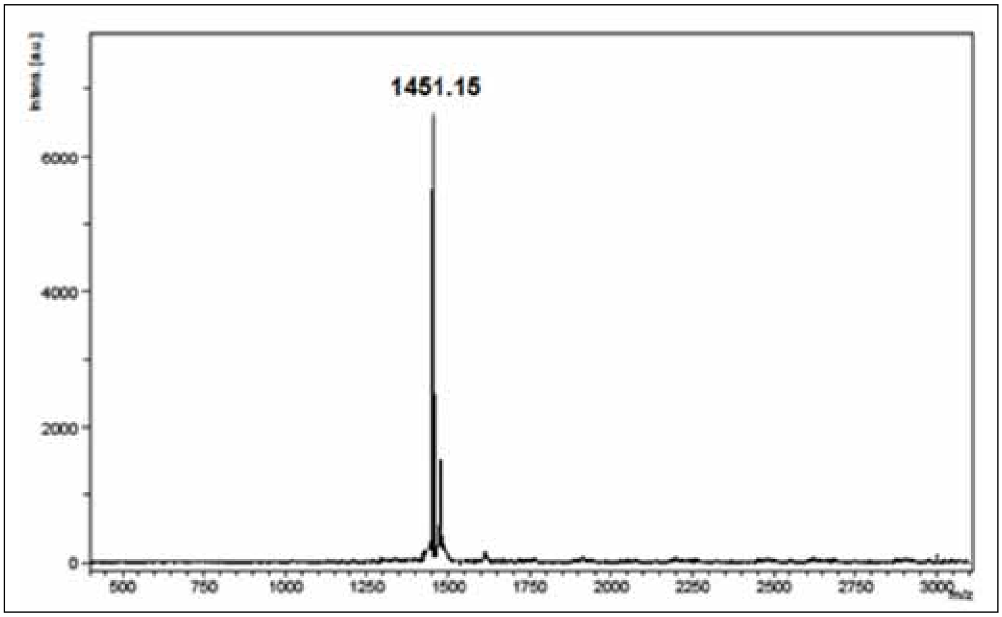

Figure 3. Mass spectrum of peripherally substituted Lu(OAc) Pc (**4**).

Pcs due to their linear combination of the atomic orbitals (LCAO) coefficients at the non-peripheral positions of the highest occupied molecular orbital (HOMO) being greater than those at the peripheral positions as explained in the literature (Anderson et al. 1985, Konami et al. 1990, Mack and Kobayashi 2011).

3.3. Aggregation Studies

Aggregation is usually depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes. It is dependent on the concentration, nature of the solvent, nature of the substituents, complexed metal ions and temperature (Enkelkamp and Nolte 2000). In the aggregated state the electronic structure of the complexed phthalocyanine rings are perturbed resulting in alternation of the ground and excited state electronic structures (Dominquez 2001). In this study, the aggregation behaviors of non-peripheral and peripheral 2,6-dimethoxyphenoxy substituted lutetium(III) acetate Pc complexes were examined in DMSO, toluene and DCM (Figure 7a for Pc **3** and Figure 7b for Pc **4**). The Lu(OAc)Pcs (**3** and **4**) did

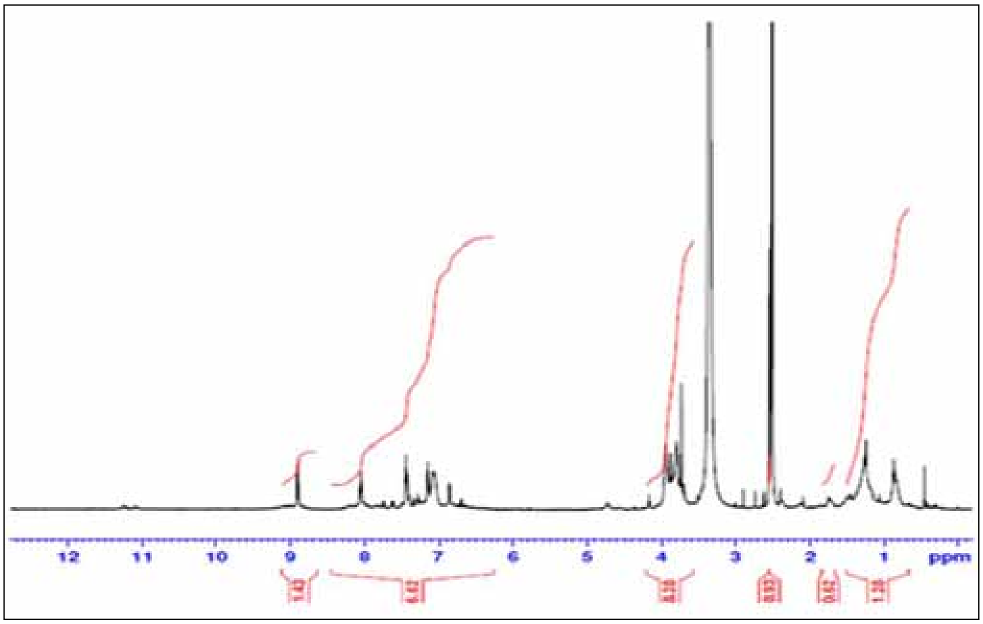

Figure 4. ^{1}H-NMR spectrum of non-peripherally substituted Lu(OAc)Pc (**3**) in DMSO-d_6.

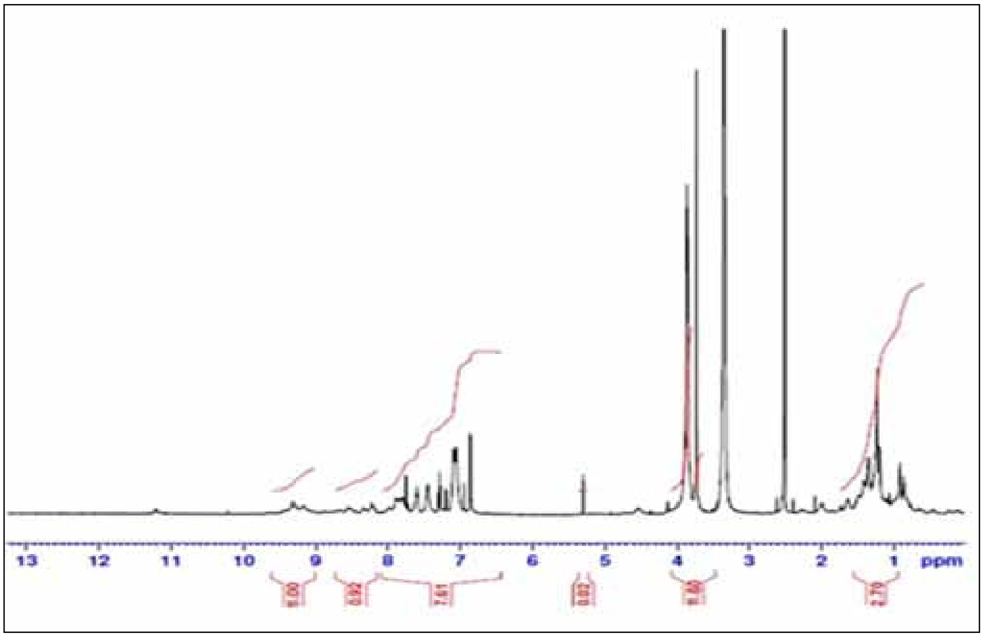

Figure 5. ^{1}H-NMR spectrum of peripherally substituted Lu(OAc)Pc (**4**) in DMSO-d_6.

not demonstrate any aggregation behaviors in the solvents (Figure 7).

The shoulder peak at 750 nm in chloroform solution was occured for the Lu(OAc)Pc (**3**) (Figure 7a). The peak can be protonation of the nitrogen atoms on the Pc core instead of J type aggregation because chloroform contains a little amounts of acidic impurities (generally HCl) (Gürel et al. 2015, Gürel et al. 2016). Moreover, the absorption intensity of this extra peak increased by adding trifluoroacetic acid and decreased by adding potassium carbonate (Figure 8 for **3** in chloroform) as in the literature (Gürel et al. 2015, Gürel et al. 2016). This obtained result substantiated the protonation of inner nitrogen atoms in the Pcs in chloroform asidic solvent.

The aggregation behaviors of non-peripherally and peripherally substituted lutetium(III) acetate phthalocyanines (**3** and **4**) were also investigated at different concentration in DMSO. As the concentration was increased, the intensity of absorption of the Q band also increased and there were no new bands (normally blue shifted) due to the aggregated species. Beer-Lambert law was obeyed for the complexes in DMSO in the concentration ranging from 2 × 10^{-6} to 1.20 × 10^{-5} M (Figure 9).

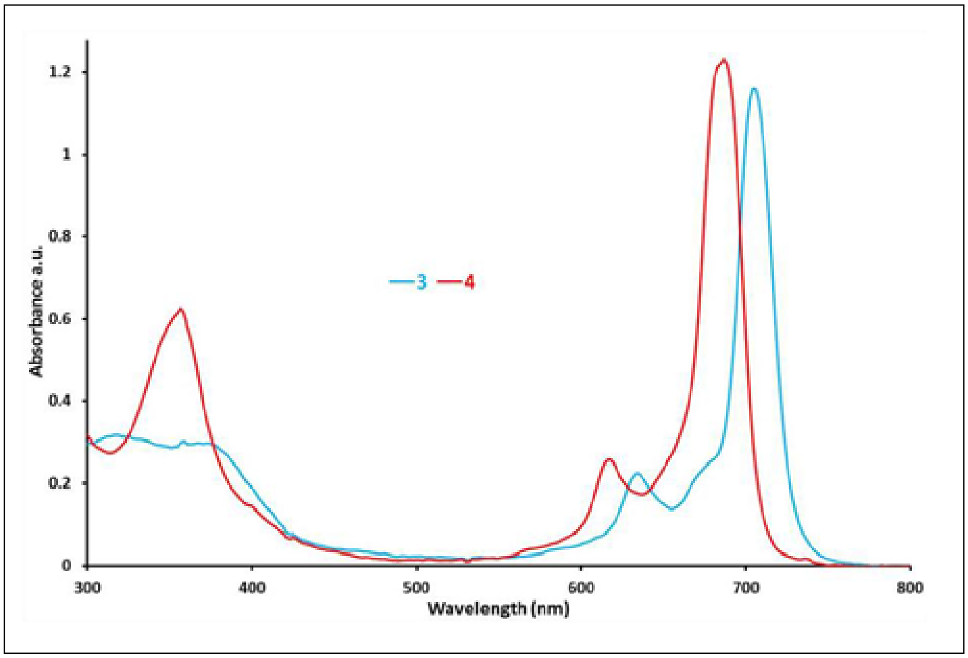

Figure 6. Electronic absorption spectra of non-peripheral and peripheral substituted Lu(OAc)Pcs (**3 and 4**) at 1.0x10^{-5} M in DMSO.

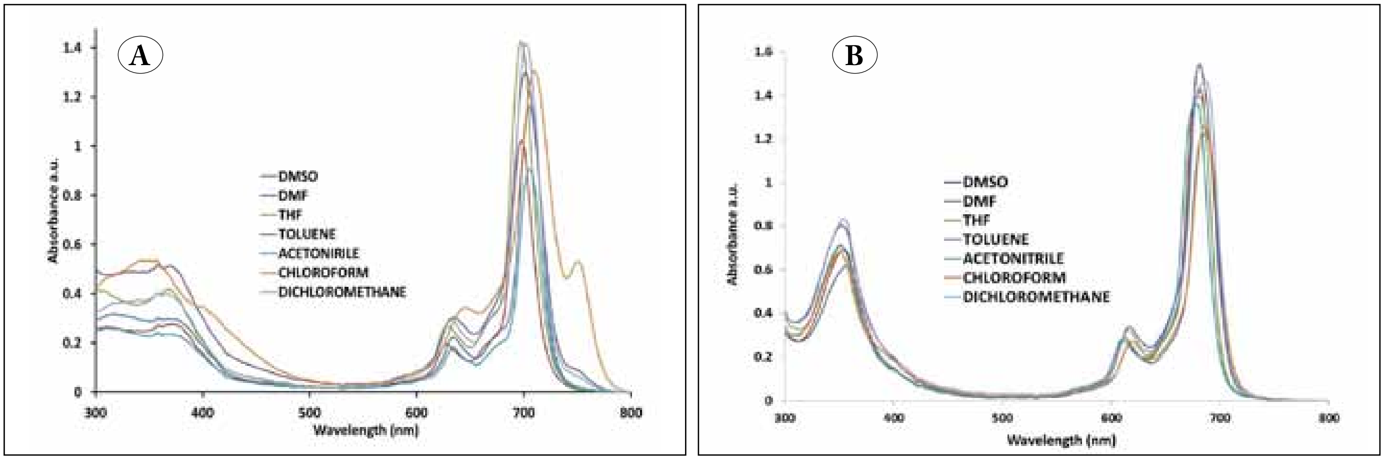

Figure 7. Electronic absorption spectra of **(A)** non-peripheral substituted Lu(OAc)Pc (**3**) and **(B)** peripheral substituted Lu(OAc)Pc (**4**) in different solvents.

4. Conclusions

The synthesis and characterization of non-peripherally and peripherally 2,6-dimethoxyphenoxy substituted lutetium (III) acetate Pcs were presented in this study. The elemental analyses, FT-IR, ^{1}H NMR, UV–*vis*, fluorescence spectroscopy and MALDI-TOF-MS spectra confirmed the proposed structures of the novel Pc complexes. The Lu(OAc)Pcs showed high solubility in common solvents such as chloroform, DCM, toluene, THF, acetonitrile, DMSO and DMF. In solution, the absorption spectra of the studied lutetium(III) acetate Pc complexes showed monomeric behavior evidenced by a single (narrow) Q band, typical of metallated phthalocyanine complexes in DMSO. The spectroscopic properties of 2,6-dimethoxyphenoxy substituted Lu(OAc)Pcs in DMSO were examined for comparison of the effects of the substituent positions on the Pc framework and aggregation behavior as well. The Lu(OAc)Pcs showed non-aggregated species above mentioned solvents.

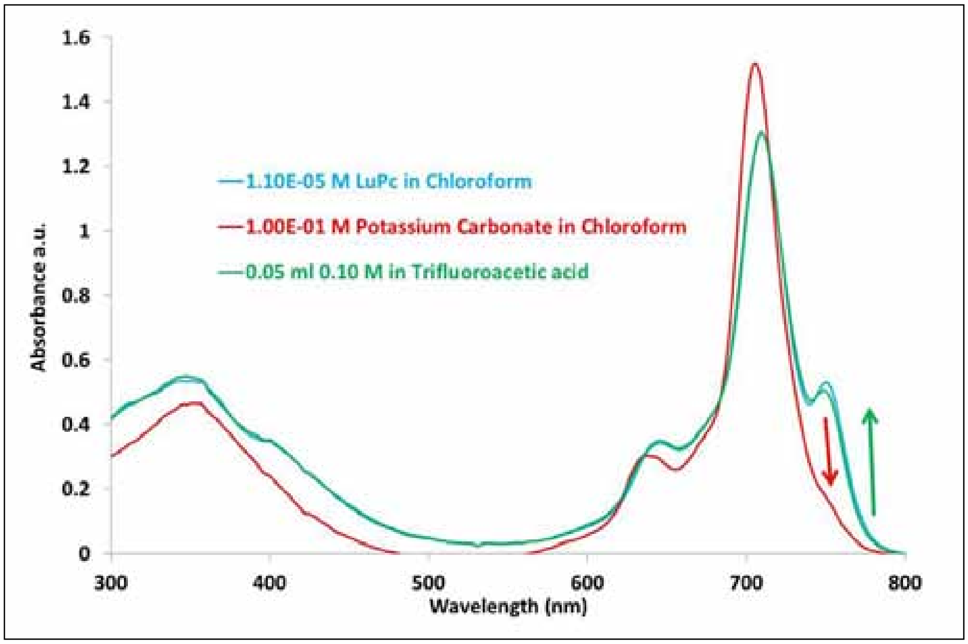

Figure 8. UV-*vis* spectral changes of the Lu(OAc)Pc (**3**) in chloroform by addition of potassium carbonate, trifluoroacetic acid solution, respectively.

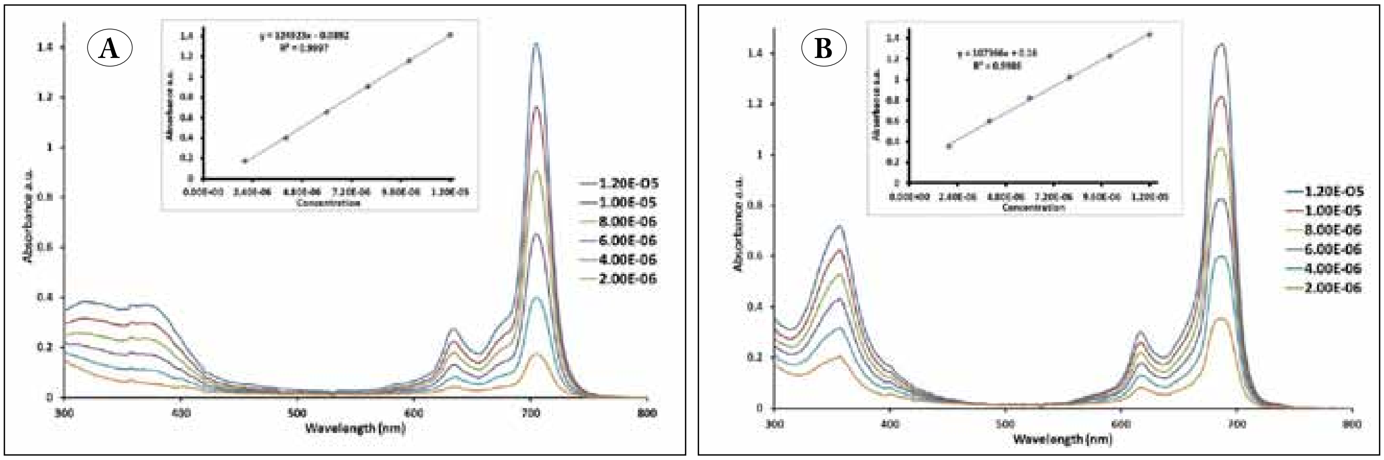

Figure 9. Aggregation behaviours of **(A)** non-peripheral substituted Lu(OAc)Pc (**3**) and **(B)** peripheral substituted Lu(OAc)Pc (**4**) in DMSO at different concentrations: (2 × 10^{-6} to 1.20 × 10^{-5} M).

5. References

Simon, J., Andre, JJ. 1985. Photoelectrical Properties and Solar Cells In: Molecular Semiconductors. J.M. Lehn, Ch.W Rees [eds.], Springer-Verlag, Berlin, pp-73-147.

Leznoff, CC., Lever, ABP. 1989. Phthalocyanines, Properties and Applications Vol.1, Wiley–VCH, New York, pp-341–392.

Leznoff, CC., Lever, ABP. 1993. Phthalocyanines, Properties and Applications Vol.3, Wiley–VCH, New York, pp-119–167.

Leznoff, CC., Lever, ABP. 1996. Phthalocyanines, Properties and Applications Vol.4, Wiley–VCH, New York, pp-79–181.

Simon, J., Bassoul, P. 2000. Design of Molecular Materials: Supramolecular Engineering, John Wiley & Sons, Chichester, pp 197-291.

Gould, RD. 1996. Structure and electrical conduction properties of phthalocyanine thin films. *Coordın. Chem. Rev.*, 156: 237-274.

Kudrevich, SV., Van Lier, JE. 1996. Azaanalogs of phthalocyanine: syntheses and properties. *Coordın. Chem. Rev.*, 156:163-182.

Rosenthal, I. 1996. In: Phthalocyanines - Properties and Applications, Leznoff, C.C.; Lever, A.B.P. [eds.], Wiley VCH: New York, Vol. 4,; pp. 486-514.

Buono-Core, GE., Li, H., Marciniak, B. 1990. Quenching of Excited States by Lanthanide Ions and Chelates in Solution. *Coordın. Chem. Rev.*, 90: 55-87.

Wu, W.-N., Tang, N., Yan, LJ. 2008. Syntheses, Characterization and Fluorescent Properties of Six Novel Lanthanide Complexes with *N,N*-diphenyl-2-(quinolin-8-yloxy)acetamide. *J. Fluoresc.*,18:101-107.

Edward, A., Chu, TY., Claude, C., Sokolik, I., Okamoto, Y., Dorisinville, R. 1997. Synthesis and characterization of electroluminescent organo-lanthanide (III) complexes. *Synth. Met.,* 84: 433-434.

Meares, CF.,Wense TG. 1984. Metal chelates as probes of biological systems. *Acc. Chem. Res,* 17: 202-209.

Kukhta, A., Kolesnik, E., Grabchev, IJ. 2006. Spectral and luminescent properties and electroluminescence of polyvinylcarbazole with 1,8-naphthalimide in the side chain. *J.Fluoresc.,* 16:375-378.

Wu, FB., Zhang C. 2002. A new europium beta-diketone chelate for ultrasensitive time-resolved fluorescence immunoassays, *Anal Biochem*, 311:57-67.

Nicholson, M., Leznoff, CC., Lever. ABP. 1993. The Redox Chemistry of Metallophthalocyanines in Solution. In: Leznoff, CC., Lever ABP [eds.], Phthalocyanines, Properties and Applications, Vol. 3, VCH, Publications, New York, pp.119–167.

Zugle, R., Litwinski, C., Nyokong, T. 2011. Photophysical characterization of dysprosium, erbium and lutetium phthalocyanines tetrasubstituted with phenoxy groups at non-peripheral positions. *Polyhedron*, 30 (9):1612-1619.

Weiss, R., Fischer, J. 2003. Lanthanide Phthalocyanine Complexes. In: Kadish K.M., Smith K.M., Guilard R. [eds.], The Porphyrin Handbook, Vol. 16, Academic Press, New York, pp.171-246.

Besbes, S., Plichon, V., Simon, J., Vaxiviere, J. 1987. Electrochromism of octaalkoxymethyl-substituted lutetium diphthalocyanine. *J. Electroanal. Chem.,* 237: 61–68.

Petty, M. 1992. Possible applications for Langmuir-Blodgett films. *Thin Solid Films,* 210: 417–426.

Yılmaz, İ., Nakanishi, T., Gürek, AG., Kadish, KM. 2003. Electrochemical and spectroscopic investigation of neutral, oxidized and reduced double-decker lutetium(III) phthalocyanines. *J. Porphyr. Phthalocya.*, 7: 227–238.

Friedrich, J., Haarer, D. 1984. Photochemical Hole Burning: A Spectroscopic Study of Relaxation Processes in Polymers and Glasses. *Angew. Chem. Int. Edit,* 23:113–140.

Takahashi, K., Kawashima, M., Tomita, Y., Itoh, M. 1995. Synthesis, spectral and electrochemical properties of 2,3,9,10,16,17,23,24-octabutylthiophthalocyaninato zinc(II). *Inorg. Chim. Acta.,* 232: 69–73.

Wöhrle, D., Eskes, M., Shigehara, K., Yamada, A. 1993. A simple synthesis of 4,5-disubstituted benzenes and octasubstituted phthalocyanines. *Synthesis*, 2:194–196.

Pişkin, M. 2016. The novel 2,6-dimethoxyphenoxy substituted phthalocyanine dyes having high singlet oxygen quantum yields. *Polyhedron*, 104: 17-24.

Anderson, AB., Gordon, TL., Kenney M.E. 1985. Electronic and redox properties of stacked-ring silicon pthalocyanines from molecular orbital theory. *J. Am. Chem. Soc.,* 107: 192-195.

Konami, M., Hatano, M., Tajiri, A. 1990. Inter-ring overlap integrals in dimer complexes of phthalocyanines and porphyrins. *Chem. Phys. Lett.*, 166 (5): 605-608.

Mack, J., Kobayashi, N. 2011. Low Symmetry Phthalocyanines and Their Analogues. Chem. Rev., 111 (2):281-321.

Enkelkamp, H., Nolte, RJM. 2000. Molecular materials based on crown ether functionalized phthalocyanines. *J. Porphyr. Phthalocya.*, 4(5): 454-459.

Dominquez, DD., Snow, AW., Shirk, JS., Pong, RGS. 2001. Polyethyleneoxide-capped phthalocyanines: limiting phthalocyanine aggregation to dimer formation. *J. Porphyr. Phthalocya.*, 5:582-592.

Gürel, E., Pişkin, M, Altun, S., Odabaş, Z., Durmuş, M. 2015. Synthesis, characterization and investigation of the photophysical and photochemical properties of highly soluble novel metal-free, zinc(II), and indium(III) phthalocyanines substituted with 2,3,6-trimethylphenoxy moieties. *Dalton Trans.*, 44: 6202–6211.

Gürel, E., Pişkin, M, Altun, S., Odabaş, Z., Durmuş, M. 2016. The novel mesityloxy substituted metallo-phthalocyanine dyes with long fluorescence lifetimes and high singlet oxygen quantum yields. *J. Photochem. Photobiol. A.*, 315: 42–51.