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Newly Soluble and Non-Aggregated Copper(II) and Tin(II) Phthalocyanines: Synthesis, Characterization and Investigation of Photophysical and Photochemical-Responsive

Yeni İyi Çözünür ve Agregasyon Yapmayan Bakır(II) ve Kalay(II) MetallibFtalosiyaninler: Sentez, Karakterizasyon ve Fotofiziksel ve Fotokimyasal Duyarlılığın Araştırılması

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Abstract

This work presents the synthesis and characterization of non-aggregated and highly soluble copper(II) and tin(II) phthalocyanines substituted with 2,6-dimethoxyphenoxy groups at the non-peripheral (alpha) and peripheral (beta) positions. The phthalocyanines have been characterized by common spectroscopic techniques. They show excellent solubility and non-aggregated species in common organic solvents such as dimethylsulfoxide, dimethylformamide, tetrahydrofuran, toluene, acetonitrile, chloroform and dichloromethane, which make them candidates to use for many applications in different fields of science and technology. The effects positions of substituent on the phthalocyanine skeleton and the variety of central metal ions on the phthalocyanine of aggregation and on their spectroscopic properties were determined in different solvents as mentioned above. The novel synthesized copper phthalocyanines were not evaluated for fluorescence, photophysical and photochemical properties due to transition metal and paramagnetic behavior of central metal in the phthalocyanine cavity. The effects of substituent and their positions on the tin(II) phthalocyanines' on their photophysical (fluorescence quantum yields and lifetimes) and photochemical properties (singlet oxygen generation and photodegradation under light irradiation) were also investigated and reported in dimethylsulfoxide for the first time.

Keywords: Copper(II), Non-aggregated, Photochemical, Photophysical, Phthalocyanine, Soluble, Tin(II)

Öz

Bu çalışma, non-periferal (alfa-) ve periferal (beta-) pozisyonlarda 2,6-dimetoksi gruplarıyla sübstitüe edilen agrege olmayan oldukça çözünür bakır(II) ve kalay(II) metalli ftalosiyanin bileşiklerinin sentezini ve karakterizasyonunu sunar. Bu ftalosiyaninler bilinen spektroskopik tekniklerle karakterize edilmiştir. Dimetilsülfoksit, dimetilformamit, tetrahidrofuran, toluen, asetonitril, kloroform ve diklorometan gibi bilinen organik çözücülerde mükemmel çözünürlük ve agregasyon yapamayan türler göstermiştir. Orijinal ftalosiyanin bileşiklerinin yüksek çözünürlük özellikleri ve agregasyon yapmayan türler içermesi onları bilim ve teknolojinin farklı alanlarında pek çok uygulamalarda kullanılmaları amacıyla aday yapar. Bu orjinal ftalosiyaninlerin spektroskopik özellikleri hakkında üstte bahsedilen farklı çözeltilerde ftalosiyanin merkezindeki farklı metal iyonlarının ve ftalosiyanin iskeleti üzerinde sübstitüentin pozisyon etkileri ve agregasyon özellikleri belirlenmiştir. Ayrıca, bileşiklerin dimetilsülfokit çözeltisinde farklı konsantrasyonlardaki agregasyon özellikleri de incelenmiştir. Yeni sentezlenen bakır metalli ftalosiyaninler, ftalosiyanin çekirdeğinde merkez metalinin paramagnetik davranışı ve geçiş metalinden dolayı floresans, fotofiziksel ve fotokimyasal özellikleri değerlendirilmedi. Alfa ve beta-sübstitüentli kalay(II) metalli orijinal ftalosiyanin bileşiklerinin fotofiziksel (floresans kuantum verimleri ve ömürleri) ve fotokimyasal özellikleri (singlet oksijen kuantum verimleri, fotobozunma kuantum verimleri) hakkında ftalosiyanin iskeleti üzerindeki sübstitüent ve sübstitüentin pozisyonlarının etkileri de ilk defa bu çalışmada incelenmiş ve rapor edilmiştir.

Anahtar Kelimeler: Bakır(II), Agregasyon yapmayan, Fotokimyasal, Fotofiziksel, Ftalosiyanin, Çözünür, Kalay(II)

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1. Introduction

Phthalocyanines (Pcs) are composed of 18 π-electron conjugated macrocyclic compounds, and their derivatives generally are non-toxic. Moreover, they have also very good structural and chemical stability, and interesting electrical, optical sensitives (Leznoff and Lever 1989, 1993, 1996). Pcs have been proposed and used in various technological areas such as liquid crystals, electronic devices, gas and chemical sensors, electrochromic and electroluminescent displays, non-linear optics, photovoltaics, semiconductors (Leznoff and Lever 1989, 1993, 1996, Ince et al. 2011, Cicoira et al. 2011, Bohrer et al. 2011, Nagel et al. 2011, Shirk et al. 2000, Şahin et al. 2015), nanotechnology (Durmuş and Nyokong 2007), and photosensitizers for photodynamic cancer therapy (PDT) of tumors (Tekdaş et al. 2012, Camerin et al. 2010, Çakır et al. 2014, Çakır et al. 2015). They are also the presence of a highly conjugated 18 π-electron system, intense absorption in the red/near-IR (Q band) region (Reddy et al. 2007), capability to exhibit changeable conductivity and photocatalytic effects (Lokesh et al. 2009, Al-Sohaimi et al. 2016). Pcs exhibit a tendency in solution to form the dimer and higher oligomeric species therefore, many phthalocyanines have been restricted in application areas owing to their lower solubility in common organic solvents due to aggregation (Göl and Durmuş 2012). To prepare soluble Pc, the peripheral of Pc ring is attached functional groups such as bulky, crown ether groups, amide or carboxylic acid groups (Wierzchowski et al. 2013, Al-Sohaimi et al. 2016, Ghanem et al. 2015, Zheng et al. 2013) and so forth. As for obtained non-aggregation and soluble phthalocyanine attached both axial positions of the trivalent and tetravalent central metal ions in the Pc cavity (Jiang et al. 2006, Pişkin et al. 2011, Alamin Ali et al. 2016). All the properties of Pcs are influenced and enhanced both by the nature of central metals and the substituent (electron donating or electron withdrawing) and substituent's position [non-peripheral (alpha-) or peripheral (beta-)] in the Pc ring (Pişkin et al. 2011, Akçay et al. 2013, Nas et al. 2014, Demirbaş et al. 2013, Aktaş et al. 2014). The significant aim of the present research was to synthesize non-aggregated, highly soluble and capable of long wavelength absorption maximum alpha-(α-) and beta-(β-) substituted copper(II) (CuPcs) and tin(II) (SnPcs) phthalocyanines to investigate the effects of α- or β- substituent on their spectroscopic for the Pcs (**3-6**), photochemical and photophysical properties for the SnPcs (**5** and **6**). In this study, α- and β-tetra-2,6-dimethoxyphenoxy substituted CuPcs and SnPcs (**3-6**) have been synthesized (Figure 1) and characterized by elemental analysis, IR, UV-*vis*, fluorescence spectral data, ^{1}H-NMR (for the SnPcs **5** and **6**), and MALDI-TOF mass spectroscopies. The aggregation behaviors of the studied Pcs (**3-6**) were investigated both at different concentration in DMSO and different solvents such as dimethylsulfoxide (DMSO), dimethylformamide (DMF), tetrahydrofuran (THF), toluene, acetonitrile, chloroform ($CHCl_3$) and dichloromethane (DCM). The effects of the substituents and their positions on the Pc core on the spectroscopic for the novel Pcs (**3-6**), photophysical and photochemical properties of α- and β-substituted SnPcs (**5** and **6)** were also investigated and described in DMSO. The α- and β-substituted tin(II) Pcs (**5** and **6**) may be a potential candidate as photosensitizer for photocatalytic applications such as photodynamic therapy of cancer.

2. Experimental Section

The used materials, equipment, photophysical and photochemical formulas and parameters were supplied as supplementary information.

2.1. Synthesis

2.1.1. General Procedure for the Synthesis of Metallo-Phthalocyanines (3-6)

0.25g (0.89 mmol) 3-(2,6-dimethoxyphenoxy)phthalonitrile 1 or 4-(2,6-dimethoxyphenoxy)phthalonitrile **2** and 0.46 mmol metal salts (0.06 g $CuCl_2$ or 0.09 g $SnCl_2$) were powdered in a quartz crucible and transferred in a reaction tube. 0.20 mL of DMF and 0.20 mL 1,8-diazabicyclo-[5.4.0] undec-7-ene (DBU) as a catalyst were entrained to this reaction mixture, and then the mixture was heated at 360° C in a sealed glass tube for 25 minutes under dry nitrogen atmosphere. The reaction mixture was precipitated by adding n-hexane. The green products were filtered and washed with n-hexane, distilled water, methanol, ethanol and acetone for 15 hours in the Soxhlet apparatus. After drying under vacuum, the products were purified by column chromatography with silica gel eluting with $CHCl_3$.

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

The CuPc (3) is very soluble in DMSO, DMF, THF, toluene, acetonitrile, $CHCl_3$ and DCM. Mp:>300° C. Yield: 94.02 mg (30.33%). Calculated for $C_{64}H_{48}CuN_8O_{12}$: C, 65.77%; H, 4.14%; N, 9.59%; found C, 65.66%; H, 4.26%; N, 9.72 %. IR (ATR) υ_{max}/cm^{-1}: 741, 801, 891, 981, 1085(C–C str.), 1105, 1132(C–N str.), 1202 (C–N str.), 1302, 1334 (C–O str.), 1403 (C–H bend.), 1434, 1478 (C–H bend.), 1596 (C=C str.), 1650 (C=N str.), 1735 (C=O str.), 2843 (>CH_2 str.), 2928 (>CH_2 str.), 3007 (=C–H str.), 3074 (=C–H str.). UV–*vis* (DMSO, 1×10^{-5} M): λ_{max}(nm), (log e): 315 (4.51), 369 (4.26), 632 (4.19), 670 (4.26), 702 (5.02). MS (MALDI-TOF) m/z: calc.: 1184.68; found: 1185.59 $[M+H]^+$.

2.1.1.2. 2(3),9(10),16(17),23(24)-Tetrakis-(2,6-dimethoxyphenoxy)phthalocyaninato copper(II) (4)

The CuPc (4) is very soluble in soluble in DMSO, DMF, THF, toluene, acetonitrile, $CHCl_3$ and DCM. Mp:>300° C. Yield: 99.70 mg (32.16%). Calculated for $C_{64}H_{48}CuN_8O_{12}$: C, 65.77%; H, 4.14%; N, 9.59%; found C, 65.63%; H, 4.28%; N, 9.74 %. IR (ATR) υ_{max}/cm^{-1}: 658, 701, 726, 745, 771, 816, 865, 892, 948, 97 (C–C str.), 1029, 1048, 1084 (C–C str.), 1106 (C–N str.), 1184 (C–N str.), 1300, 1342 (C–O str.), 1387, 1400 (C–H bend.), 1477, 1493 (C–H bend.), 1601 (C=C str.), 1667 (C=N str.), 1725 (C=O str.), 2838 (>CH_2 str.), 2933 (>CH_2 str.), 3003 (=C–H str.), 3071 (=C–H str.). UV–*vis* (DMSO, 1×10^{-5} M): l_{max}(nm), (log e): 349 (4.57), 613 (4.27), 632 (4.19), 652 (4.31), 683 (5.05). MS (MALDI-TOF) m/z: calc.: 1184.68; found: 1185.97 $[M+H]^+$.

2.1.1.3. 1(4),8(11),15(18),22(25)-Tetrakis-(2,6-dimethoxyphenoxy)phthalocyaninato tin(II) (5)

The SnPc (**5**) is very soluble in DMSO, DMF, THF, toluene, acetonitrile, $CHCl_3$ and DCM. Mp:>300° C. Yield: 72.86 mg (21.43%). Calculated for $C_{64}H_{48}N_8O_{12}Sn$: C, 62.81%; H, 3.95%; N, 9.16%; found C, 62.93%; H, 3.78 %; N, 9.33 %. IR (ATR) υ_{max}/cm^{-1}: 670, 706, 736, 801, 878, 951, 962 (C–C str.), 1020, 10701 (C–C str.), 1129 (C–N str.), 1159 (C–N str.), 1303, 1336 (C–O str.), 1437 (C–H bend.), 1479 (C–H bend.), 1595 (C=C str.), 1669 (C=N str.), 1725 (C=O str.), 2837 (>CH_2 str.), 2913 (>CH_2 str.), 3012 (=C–H str.), 3067 (=C–H str.). UV–*vis* (DMSO, 1×10^{-5} M): λ_{max}(nm), (log e): 327 (4.75), 365 (4.60), 668 (4.39), 705 (4.52), 744 (5.07). ^{1}H-NMR (600MHz, DMSO-d_6, ppm): 8.17-7.96 (m, 8H), 7.95-6.80 (m, 16H), 3.86 (s, 24H). MS (MALDI-TOF) m/z: calc.: 1239.84 $[M]^+$; found: 1258.26 $[M + H_2O]^+$.

2.1.1.4. 2(3),9(10),16(17),23(24)-Tetrakis-(2,6-dimethoxyphenoxy)phthalocyaninato tin(II) (6)

The SnPc (6) is very soluble in DMSO, DMF, THF, toluene, acetonitrile, $CHCl_3$ and DCM. Mp:>300° C. Yield: 80.48 mg (23.67%). Calculated for $C_{64}H_{48}CuN_8O_{12}$: C, 62.81%; H, 3.95%; N, 9.16%; found C, 62.97%; H, 3.81%; N, 9.29 %. IR (ATR) υ_{max}/cm^{-1}: 675, 724, 736, 771, 825, 869, 891, 949 (C–C str.), 1043 (C–C str.), 1106 (C–N str.), 1181 (C–N str.), 1337 (C–O str.), 1394 (C–H bend.), 1477 (C–H bend.), 1603 (C=C str.), 1660 (C=N str.), 1714 (C=O str.), 2835 (>CH_2 str.), 2934 (>CH_2 str.), 3003 (=C–H str.), 3082 (=C–H str.). UV–*vis* (DMSO, 1×10^{-5} M): λ_{max}(nm), (log e): 352 (4.78), 405 (4.41), 641 (4.31), 682 (4.55), 714 (5.06). ^{1}H-NMR (600MHz, DMSO-d_6, ppm): 9.26-8.98 (m, 8H), 8.67-8.26 (m, 4H), 7.78–7.38 (m, 8H), 7.10–6.80 (m, 8H), 3.84 (s, 24H). MS (MALDI-TOF) m/z: calc.: 1239.84 $[M]^+$; found: 1258.92 $[M + H_2O]^+$.

3. Results and Discussion

3.1. Syntheses and Characterization

The preparation of 2,6-dimethoxyphenoxy substituted phthalonitriles (**1** and **2**) were achieved by the reaction of 2,6-dimethoxyphenol with 3-nitrophthalonitrile or 4-nitrophthalonitrile (Figure 1) through base catalysed nucleophilic aromatic displacement reaction (Pişkin 2016). The novel α- and β- tetrakis-substituted copper(II) and tin(II) Pcs (**3–6**) were prepared by cyclotetramerization of 2,6-dimethoxyphenol substituted phthalonitriles (**1** and **2**) (Figure 1). To synthesize the novel substituted copper(II) (**3** and **4**) and tin(II) Pcs (**5** and **6**), a mixture of compound **1** (or **2**), metal salts ($CuCl_2$ or $SnCl_2$) in dried DMF was heated at approximately 360 °C for 25 minutes. The four probable isomers can be designed by their molecular symmetry as C_{4h}, C_{2v}, C_s and D_{2h}. In this study, the Pcs (**3-6**) are obtained as isomer mixtures as expected. No attempt was made to separate the isomers mixture. The elemental analysis, IR, UV–*vis*, ^{1}H-NMR, fluorescence spectral data and the MALDI-TOF mass spectroscopic data confirmed the proposed structures of these novel Pcs. In the IR spectra of the starting phthalonitrile compounds **1** and **2** the disappearance of the NO_2 peak nearby 1350 cm^{-1} and the appearance of new peaks at 1260, 1274 for **1**, **2**, respectively belonging to Ar–O–Ar indicated the formation of phthalonitrile compounds. The sharp peak for the –C≡N vibrations of bands at 2231 cm^{-1} for **1** and 2237 cm^{-1} for **2** disappears after phthalocyanine formation in the IR spectrum.

The protonated molecular ion peaks $[M+H]^+$ peaks of the copper(II) (**3** and **4**) and water adducted molecular peaks $[M+H_2O]^+$ of the tin(II) Pcs (**5** and **6**) were identified easily with dihydroxybenzoic acid (DHB) MALDI matrix in the reflectron mode using a MALDI-TOF mass spectrometry. We observed these peaks (**3**-**6**) at m/z: 1185.59, 1185.97, 1258.26 and 1258.92 Da, respectively (Figure 2a for the CuPc **4** and Figure 2b for the SnPc **5** as examples). Elemental analysis results and mass spectra of the studied phthalocyanines were also well agreement with proposed structure.

The ^{1}H-NMR spectra of **3** and **4** could not be determined because of the presence of paramagnetic copper atom in the cavity (Kulaç et al. 2007, Bayrak et al. 2012). ^{1}H-NMR spectra of α- and β-substituted tin(II) Pcs (**5** and **6**) were also obtained and the proton atom numbers of the SnPcs (**5** and **6**) were matched the desired complexes (d$_6$-Dimethyl sulfoxide).

3.2. UV-*vis* Absorption Spectra

The electronic spectra of the Pcs showed a monomeric behaviour evidenced by a single (narrow) Q band for α- and β-substituted copper(II) and tin(II) phthalocyanines (**3–6**) up to ~1x10^{-5} mol dm^{-3} in DMSO (Figure 3a and 3b). The UV-*vis* spectra of α- and β- tetra-2,6-dimethoxyphenoxy substituted CuPcs and SnPcs (**3-6**) observed characteristic absorption in the Q band region at around 683-744 nm in DMSO, as typical of metallo Pc complexes (Kobayashi et al. 2003, Pişkin et al. 2012) (Table 1). When strongly electron donating substituents, such as phenoxy groups in this study,

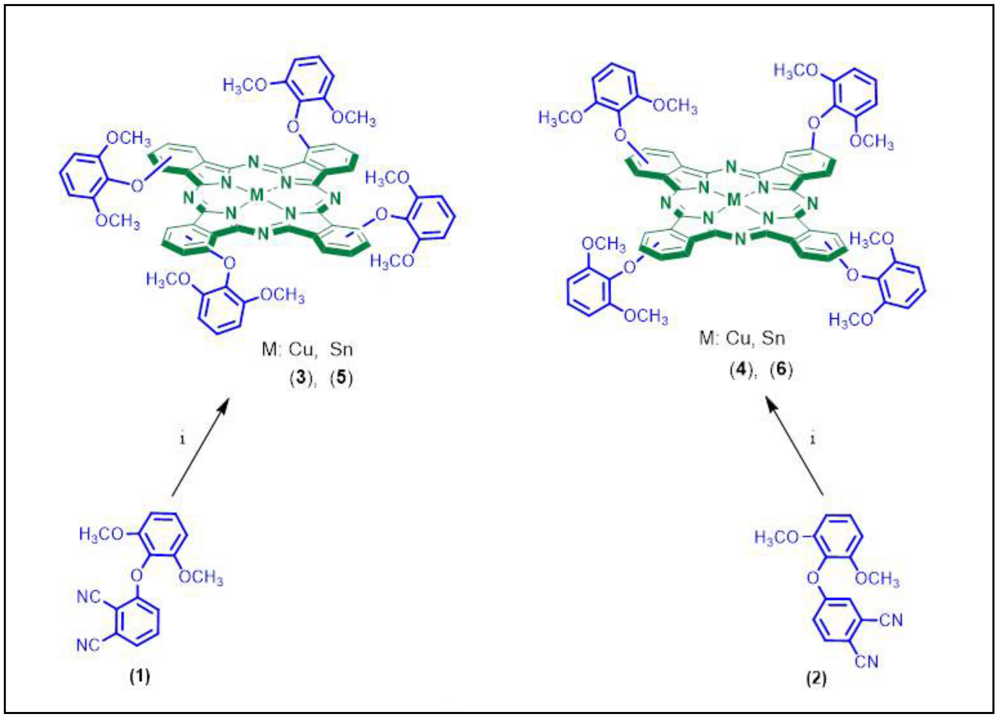

Figure 1. Synthesis of α- and β-substituted copper(II) and tin(II) phthalocyanines (**3–6**). Reagents and conditions: (i) N_2, Copper(II) chloride ($CuCl_2$) or Tin(II) chloride ($SnCl_2$), DMF, DBU, 360 °C, 25 min.

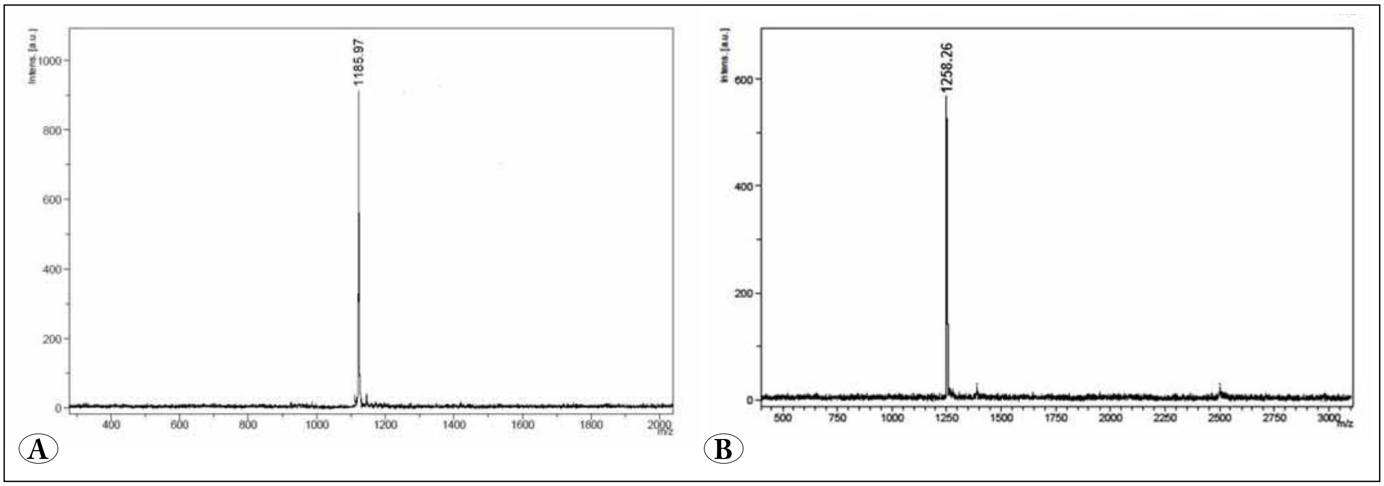

Figure 2. Mass spectra of **(A)** CuPc (**4**) and **(B)** SnPc (**5**).

the Q bands highly shift to the red region of the spectra (Kobayashi et al. 2003, Pişkin et al. 2012, Gürel et al. 2015). The Q bands of the alpha-substituted phthalocyanines (**3** and **5**) were red-shifted when compared to the beta-counterparts (**4** and **6**) in DMSO (Fig 3a and 3b). The observed red-shifts were 19 nm between **3** and **4**; 30 nm between **5** and **6** within the typical range for metallophthalocyanines in DMSO (Nyokong 2007).

It is known that alpha-substituted metallophthalocyanine complexes are more liable to non-planar distortion than their beta-substituted counterparts due to linear combinations of the atomic orbitals (LCAO) coefficients at the peripherally alpha positions of the HOMO being greater than those at the peripherally positions. As a result, the HOMO level is destabilized more at the peripherally α- position that it is at the peripherally position. Essentially, the energy gap (ΔE) between the HOMO and LUMO becomes smaller, resulting in a bathochromic shift (Anderson et al. 1985, Kobayashi et al. 2001, Gürel et al. 2016).

The Q bands of the α- and β-substituted tin(II) Pcs (**5** and **6**) were red-shifted when compared to the copper(II) Pcs (**3** and **4**) in DMSO, suggesting that the non-planar effect of the bigger tin as central metal atom (Kulaç et al. 2007, Bayrak et al. 2012). While the B bands of the α-substituted CuPc (**3**) , α- and β-substituted SnPcs (**5** and **6**) were broad due to the superimposition of the B1 and B2 bands, the B band of beta-substituted CuPc (**4**) were observed at 349 nm in DMSO (Figure 3a for the CuPcs and Figure 3b for the SnPcs).

3.3. Aggregation Studies

In this study, the aggregation behavior of the phthalocyanine complexes (**3-6**) were investigated in various commonly known organic solvents DMSO, DMF, THF, toluene,

Table 1. Absorption spectral data for the studied Pcs (**3-6**) and unsubstituted zinc(II) Pc in DMSO.

Complex	Q band (log ε)	B band (log ε)	λ_{Ex}	λ_{Em}	Δ_{Stokes}
3	702 (5.02)	315; 369 (4.51; 4.26)	-	-	-
4	683 (5.05)	349 (4.57)	-	-	-
5	744 (5.07)	327; 365 (4.75; 4.60)	746	756	12
6	714 (5.06)	352; 405 (4.78; 4.41)	716	729	15
ZnPc[a]	672 (5.14)	353 (4.36)	672	682	10

[a] *Data from Ref. Gürol et al. 2007.*

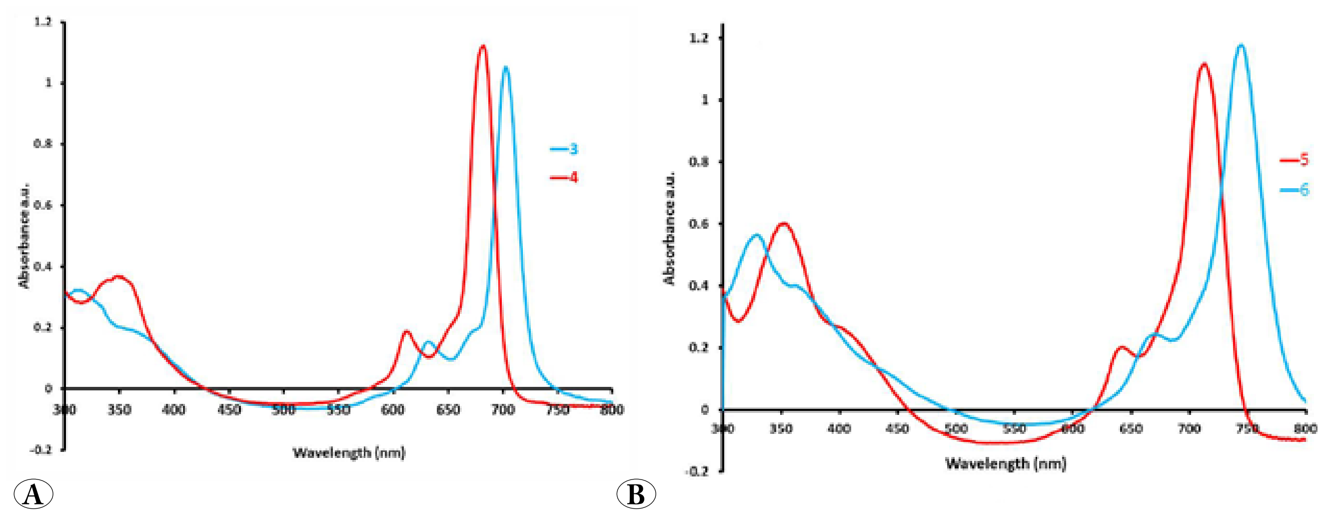

Figure 3. Electronic absorption spectra of **(A)** the CuPcs (**3** and **4**) and **(B)** SnPcs (**5** and **6**) in DMSO at ~1.0×10^{-5} M.

acetonitrile, $CHCl_3$ and DCM (Figure 4 for the CuPcs **3** and **4** and Figure 5 for the SnPcs **5** and **6**, respectively). The novel phthalocyanine complexes (**3-6**) did not form aggregates in these solvents (Figure 4 and Figure 5).

The aggregation behaviors of the novel Pcs (**3-6**) were also studied in DMSO at concentrations ranging from 1.20×10^{-5} M to 2.00×10^{-6} M. In DMSO, when the concentrations of the Pcs (**3-6**) increased, the intensity of absorption of the Q-band also increased, and new blue or red shifted band formation did not observe. It is known that the formation of new band is an evidence for the generation of aggregated species (Figure 6 for the Pc **4** and α-substituted SnPc 5 as an example). The Lambert–Beer law was obeyed and any new band formation was not observed [Figure 6 (a) for the β-CuPc **4** as an example].

3.3. Fluorescence Spectra

The fluorescence emission, absorption and excitation spectra of the β-substituted SnPc **6** in DMSO were showed in Figure 7 as an example. Fluorescence emission and excitation maximum peaks of the substituted SnPcs (**5** and **6**) in DMSO were listed in Table 1 and typical of metallophthalocyanines (Stillman and Nyokong, 1989). The fluorescence emissions of the SnPcs (**5** and **6**) were low intense peaks in DMSO. This behavior may be due to the fact that tin is metal with large atomic number that can be displaced from the core of the Pc ring on excitation hence, resulting into a loss of symmetry.

The SnPcs (**5** and **6**) had long the Stokes shifts in DMSO and these results for novel SnPcs (**6-9**) were characteristic

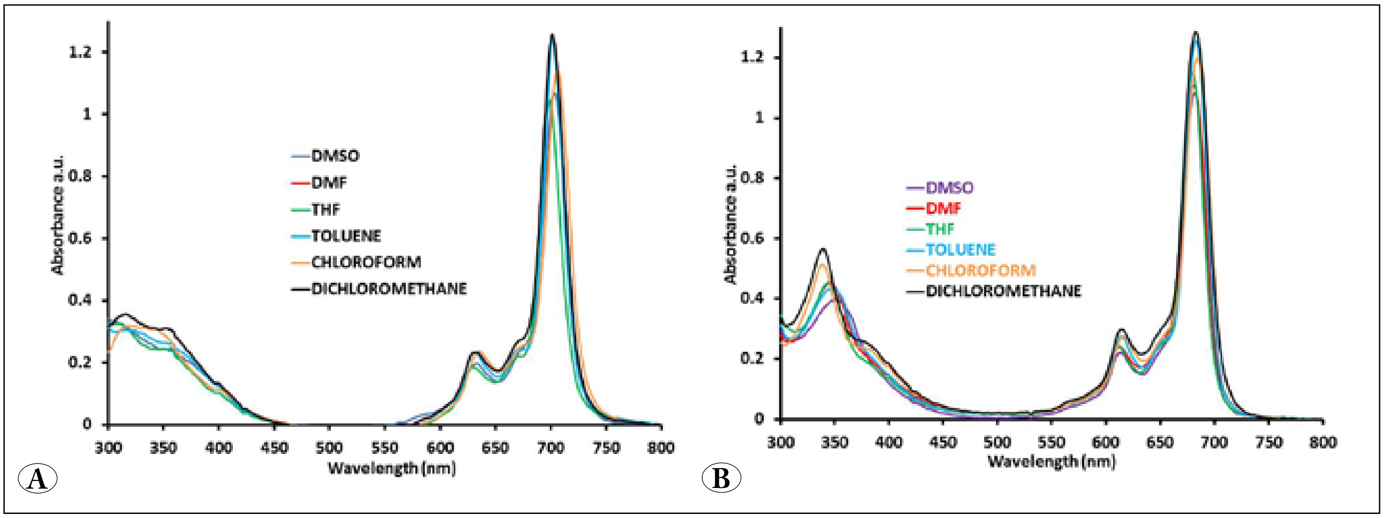

Figure 4. Electronic absorption spectra of **(A)** α-substituted CuPc (**3**) and **(B)** β-substituted CuPc (**4**) in different solvents.

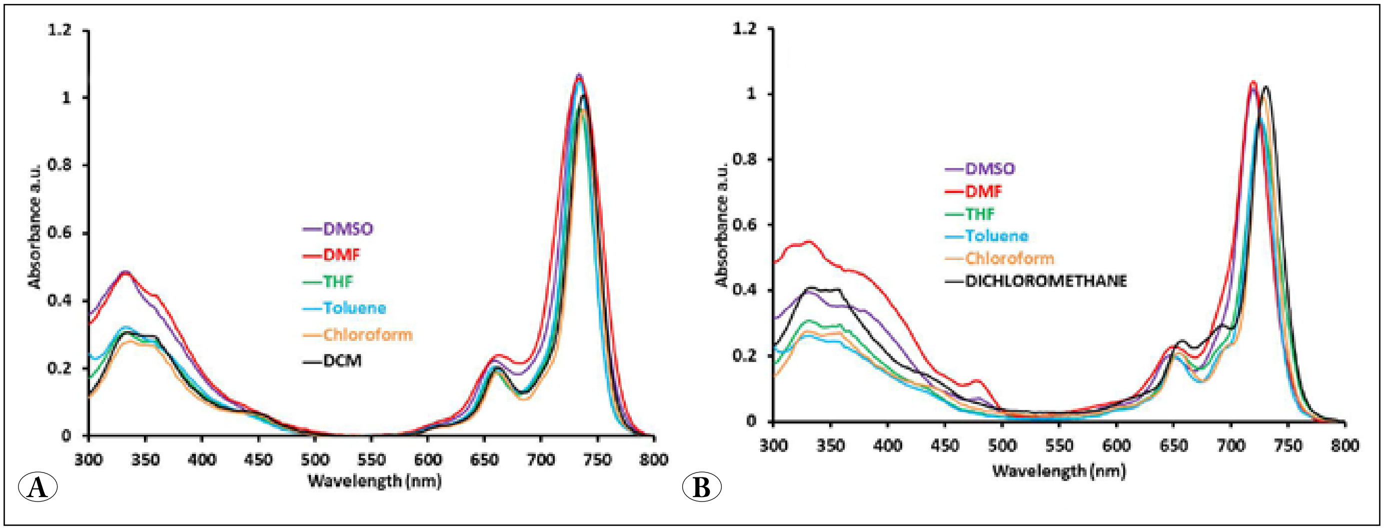

Figure 5. Electronic absorption spectra of **(A)** α-substituted SnPc (**5**) and **(B)** β-substituted SnPc (**6**) in different solvents.

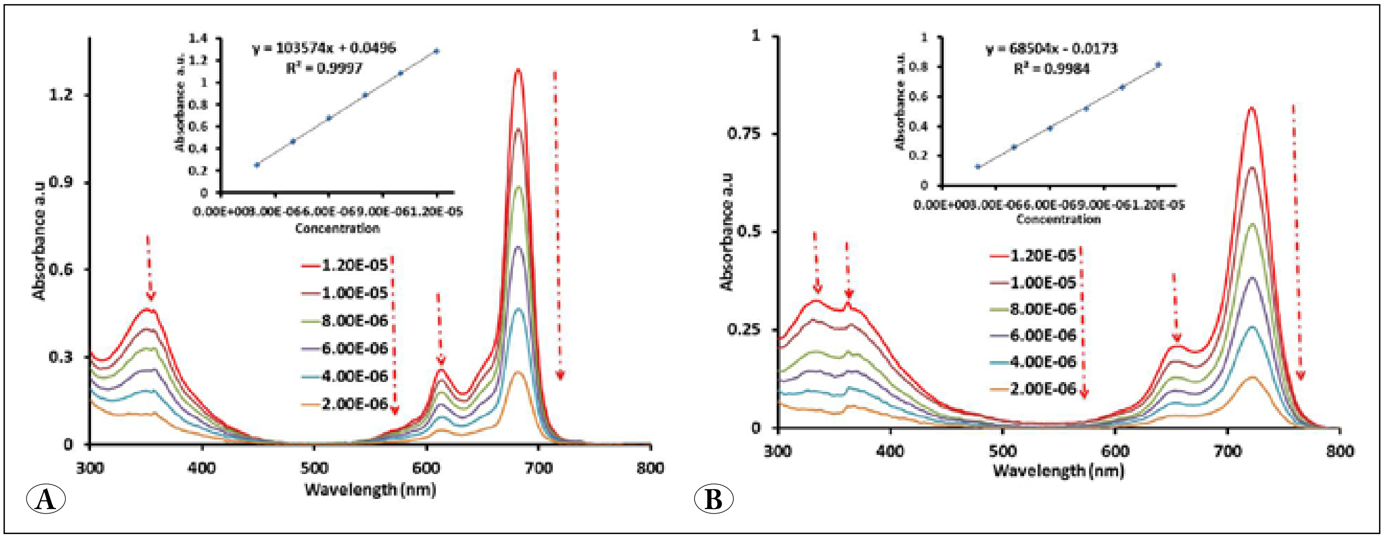

Figure 6. Absorption spectra of **(A)** beta-substituted CuPc (**4**) and **(B)** alpha-substituted SnPc (**5**) in DMSO at different concentrations (inset: plot of absorbance vs. concentration).

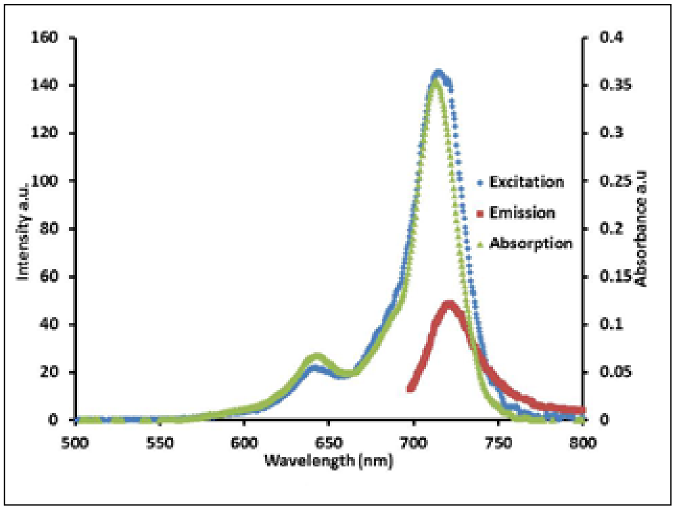

Figure 7. Absorption, excitation and emission spectra of β-substituted SnPc (**6**) in DMSO. Excitation wavelength: 670 nm. Concentration = 2.00×10^{-6} M.

for metallophthalocyanines (Nyokong 2007, Idowu and Nyokong 2008, Moeno and Nyokong 2009). However, the Q-band maxima of the absorption and excitation spectra are different for the SnPcs (**5** and **6**), the differences in the maxima of the absorption and excitation spectra were 2 nm, suggesting that the nuclear configurations of the ground and excited states are similar and are not affected by excitation in DMSO. This could be explained by the fact that the bulky 2,6-dimethoxyphenoxy substituent on the periphery of the SnPcs (**5** and **6**) may shield the central metal from displacement on excitation, for the SnPcs (**5** and **6**).

3.4. Fluorescence Quantum Yields and Lifetimes

The fluorescence quantum yield (Φ_F) values of the substituted SnPcs (**5** and **6**) in DMSO are presented in Table 2.

The Φ_F values for the substituted SnPcs (**5** and **6**) were highly lower than unsubstituted zinc(II) phthalocyanine in DMSO could be due to heavy metal effect of tin. The decrease in fluorescence intensity could be caused by the presence of the heavy atom effect of tin atom in the cavity of Pc, which increases the number of the triplet state species and causes quenching of the fluorescence. The Φ_F value of the beta substituted SnPc **6** was higher than the α-substituted SnPc **5** due to the substituent position effect on the Pc ring. This result implies that the β-substituted Pc has less quenching of the excited states. Although the studied SnPcs (**5** and **6**) had short the fluorescence lifetime (τ_F) values in DMSO due to heavy metal effect of tin as mentioned above (Table 2), these obtained values were typical of metallophthalocyanines (Nyokong 2006, Idowu and Nyokong 2008, Moeno and Nyokong 2009). Thus should be accompanied by corresponding very lower fluorescence quantum yield values of the SnPcs. On the other hand, the τ_F value of the β-substituted SnPcs **6** was longer than the α-substituted SnPc **5**. This result shows the position effect of Pc on fluorescence properties. The rate constants for fluorescence (k_F) and the natural radiative life time (τ_0) values of the substituted tin(II) Pcs (**5** and **6**) were also determined in DMSO and obtained results are presented in Table 2. While k_F value of the α-substituted SnPc (**5**) was found higher than the β-substituted SnPc (**6**),

Table 2. Photophysical and photochemical parameters for substituted SnPcs (5 and 6) and unsubstituted zinc(II) phthalocyanine in DMSO.

Complex	Φ_F	τ_F (ns)	[a]k_F (s^{-1}) ($\times 10^8$)	τ_0 (ns)	Φ_d ($\times 10^{-5}$)	Φ_Δ
5	0.008	0.18	0.44	22.50	3.84	0.75
6	0.012	0.29	0.41	24.17	3.09	0.70
ZnPc	0.200[b]	1.22[c]	1.47[c]	6.80[c]	2.61[d]	0.67[d]

[a] *k_F is the rate constant for fluorescence. Values calculated using $k_F = \Phi_F/\tau_F$.*

[b] *Data from Ref. (Ogunsipe et al. 2004)*

[c] *Data from Ref. (Gürol et al. 2007)*

[d] *Data from Ref. (Kuznetsova et al. 2000)*

τ_0 value of the α-substituted SnPc (**5**) was found shorter than the β-substituted SnPc (**6**) because of the substituents' position on the Pc ring.

3.5. Singlet Oxygen Generation

Singlet oxygen quantum yields (Φ_Δ) were determined in DMSO using decomposition of its chemical scavenger, 1,3-diphenylisobenzofuran (DPBF). The evanescence of DPBF at 417 nm was monitored using UV–*vis* spectral changes. No changes were observed in the intensities of Q-band of the SnPcs during the Φ_Δ determination confirming that the SnPcs were not degraded during singlet oxygen studies (Figure 8 as an example for the Pc **6**). The Φ_Δ values of the SnPcs (**5** and **6**) were given in Table 2. These were determined alike resultants including substituent like phenyl groups in the literature (Nyokong 2006, Idowu and Nyokong 2008, Moeno and Nyokong 2009). Moreover; the α- and β-substituted SnPcs (**5** and **6**) had high the Φ_Δ values due to large atom in the Pc cavity in DMSO. Study of substituent position effect showed that the Φ_Δ value of the α-substituted SnPc **5** was higher than the β-substituted SnPc **6** in DMSO.

3.6. Photodegradation Studies

Photodegradation (Φ_d) is used to determine the photostability of metallo-phthalocyanine molecules and identified by a decrease in the intensity of the absorption spectra without the appearance of any new bands. The absence of significant spectral changes except for decreasing Q and B band intensities during the irradiation of the studied phthalocyanines confirms that no phototransformation occurred during measurements. The photobleaching stabilities of the SnPcs (**5** and **6**) were evaluated in DMSO. The UV-*vis* spectral changes for during light irradiation were shown in Figure 9 for the SnPc **6** as an example. The Φ_d values of the SnPcs (**5** and **6**) in DMSO were presented in Table 2. These Φ_d values demonstrated that the SnPcs (**5**

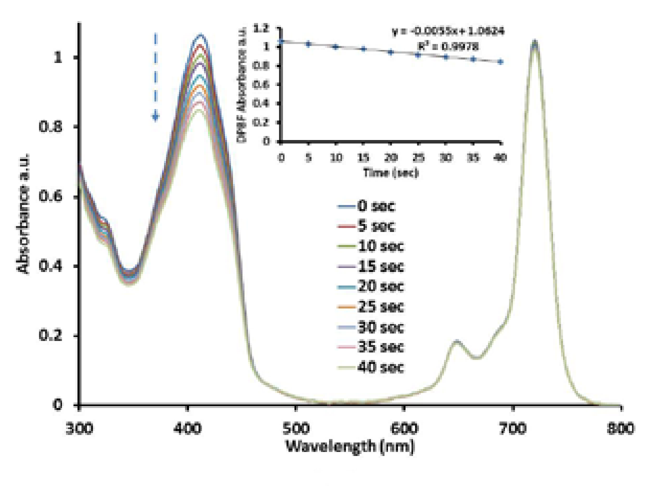

Figure 8. A typical spectrum for the determination of singlet oxygen quantum yield of the SnPc (**6**) in DMSO using DPBF as a singlet oxygen quencher. Concentration= 1.00×10^{-5} M. (Inset: plots of DPBF absorbance versus time).

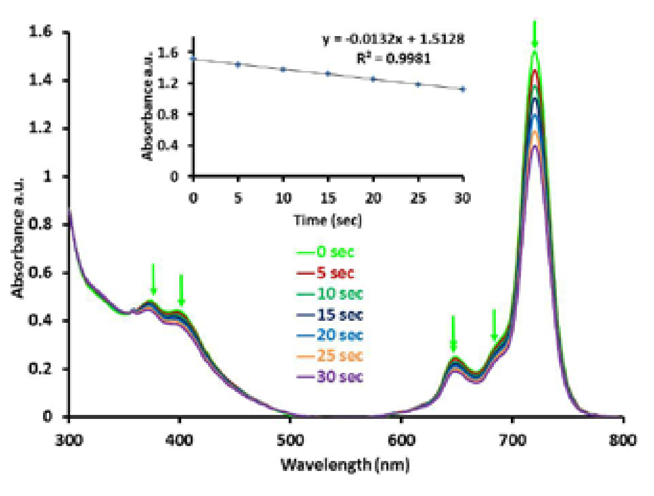

Figure 9. A typical spectrum for the determination of the photodegradation quantum yield of the SnPc (**6**) in DMSO (inset: plot of Q-band absorbance versus time).

and **6**) were less stable to degradation under light irradiation due to the larger tin metal being more displaced from the core of the Pc ring. For stable and unstable Pc molecules, Φ_d values have been reported to be of the order of 10^{-6} and 10^{-3}, respectively (Nyokong 2007). It is believed that the singlet oxygen formed is a decisive species which is responsible for the photodegradation of phthalocyanines. The higher Φ_d values of alpha substitution can be explained the HOMO of the Pc π-system has large molecular orbital coefficients at alpha positions and is destabilized by electron-donating substituents, resulting in a narrowing of the HOMO-LUMO gap and a decrease in the first oxidation potential (Mack and Kobayashi 2011).

4. Conclusions

The highly soluble, non-aggregated novel non-peripheral (alpha-) and peripheral (beta-)-tetrakis-2,6-dimethoxyphenoxy substituted copper(II) and tin(II) phthalocyanines (**3–6**) were synthesized and characterized by elemental analysis and different spectroscopic techniques such as IR, UV-*vis*, ^{1}H-NMR [for the tin(II) phthalocyanines **5** and **6**], fluorescence spectral data and MALDI-TOF mass spectroscopies. All the studied metallo-phthalocyanines (**3-6**) were quite soluble and non-aggregated in general organic solvents such as DMSO, DMF, THF, toluene, acetonitrile, chloroform, and DCM. Aggregation behaviors of the studied copper(II) and tin(II) phthalocyanines (**3-6**) were investigated in DMSO at concentrations ranging from 1.20×10^{-5} M to 2.00×10^{-6} M. The spectra showed monomeric behavior evidenced by a single (narrow) Q band, typical of metallo- phthalocyanine complexes (**3-6**) at the same concentration range mentioned above. The Q bands of the tin(II) phthalocyanines (**5** and **6**) were red-shifted in DMSO due to the non-planar effect of the bigger tin as central atom. Moreover; the influences of the positions (peripheral or non-peripheral) of the substituents on the photophysical and photochemical properties of the alpha- and beta-tetrakis-substituted tin(II) phthalocyanines (**5** and **6**) were also investigated and reported in DMSO. A difference in the nuclear configuration of the ground and excited states was observed in the tin(II) phthalocyanines (**5** and **6**) due to the central metal (tin) with large atomic number leading to a displacement of the metal from the core of the Pc ring, hence a loss of symmetry, which is more pronounced on excitation. The fluorescence lifetime values of the tin(II) phthalocyanines (**5** and **6**) were very short in DMSO because of the tin is heavy metal atom. The values of singlet oxygen quantum yield ranging from 0.70 [for the beta-substituted tin(II) phthalocyanine **6**] to 0.75 [for the alpha-substituted tin(II) phthalocyanine **5**] in DMSO indicate the potential of the tin(II) phthalocyanines as photosensitizers for photocatalytic applications such as PDT of cancer where singlet oxygen is required (Type II mechanism). It was observed that the substitution of the Pc framework with 2,6-dimethoxyphenoxy group as a substituent and the larger tin metal being more displaced from the core of the Pc ring decrease the photostability of the studied tin(II) phthalocyanines in DMSO.

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