Polyhedron 100 (2015) 1–9

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Metal ion sensing soluble α or β tetrasubstituted gallium and indium phthalocyanines: Synthesis, characterization, photochemistry and aggregation behaviors

Ahmet T. Bilgiçli [a], Merve Durdaşoglu [a], Erkan Kırbaç [b], M. Nilüfer Yarasir [a,*], Mehmet Kandaz [a,*]

[a] Department of Chemistry, Sakarya University, TR54187 Serdivan, Sakarya, Turkey
[b] Department of Chemistry, Yildiz Technical University, 34210 Istanbul, Turkey

ARTICLE INFO

Article history:
Received 10 May 2015
Accepted 13 July 2015
Available online 22 July 2015

Keywords:
Phthalocyanine
Metal sensor
Gallium and indium
Photochemistry
Photophysical

ABSTRACT

This paper reports on the synthesis and characterization of peripherally and non-peripherally tetrasubstituted gallium and indium phthalocyanines (**3**, **4**, **5** and **6**) containing 6-hydroxyhexylthio group. Synthesized compounds have been characterized by elemental analysis, FT-IR, ^{1}H NMR, ^{13}C NMR, MALDI-TOF and UV–Vis spectral data. Atomic force microscopy was also used as complementary techniques to investigate the morphology. Absorption spectral changes of the functional MPcs during addition of Ag(I) and Pd(II) soft-metal ions were evaluated by UV–Vis spectroscopy with monomer–dimer formation. All the same, photochemical properties and photophysical properties (Fluorescence quantum yields and flouresans behavior) of these phthalocyanines were performed. General trends focus on fluorescence, photodegradation and singlet oxygen quantum yields of these compounds in dimethylformamide. The nature of the substituent and solvent effect on the photophysical and photochemical parameters of the substituted phthalocyanines (**3**, **4**, **5** and **6**) are also reported.

1. Introduction

Phthalocyanines are planar aromatic macrocycles consisting of four isoindole units [1]. Due to their excellent stability in a wide variety of chemical environments chemical and thermal stability and flexible preparation methods, substituted phthalocyanines (Pcs) has been studied for especially recent years [2]. Metalphthalocyanines (MPcs) have received a great deal of attention due to their interesting electrical, optical and structural properties, followed by numerous application for example chemical sensors [3,4], photoconductors [5], electrochromic display [6], catalysis [7], liquid crystal [8], nanotechnology [9] and especially, photosensitizers for photodynamic cancer therapy (PDT) [10,11]. Phthalocyanines (Pc) have been proved as highly promising photosensitizers for PDT (photodynamic therapy) due to their intense absorption in the red region of the visible light [12]. PDT technique based on the administration of a photosensitiser that must be condense more tumor tissues than regular tissues. This is followed by illumination of the tumor with visible light in a wavelength range matching the absorption spectrum of the photosensitizer [13]. The resulting photodynamic reactions give rise to singlet oxygen ($^1O_2$) and to other active oxygen species that lead to tumor destruction. The PDT efficiency can be improved with the use of photosensitizers that absorb strongly red light above 700 nm, where tissue exhibits optimal transparency. Up to now, several new generation of potential sensitisers for PDT have been developed and investigated; among these phthalocyanines have been found to be as highly promising due to high absorbance coefficient in the region of 650–680 nm [10].

Unsubstituted phthalocyanines are insoluble and tend to aggregate (π–π stacking interactions) in common organic solvents. this insolubility is restricted its very well research. Nevertheless, phthalocyanines can be modified in a number of ways by incorporation of substituents in their peripheral (β) and non-peripheral (α) positions and solubility of phthalocyanines can be improved. This modification increases the π-electron density and makes solvation easier [14]. Due to low solubility of unsubstituted phthalocyanines are not investigated in chemical and physical properties very well, Therefore, the solubility of Pcs is very important and soluble phthalocyanine synthesis are main purpose [15]. These type approaches to increase solubility, reduce aggregation, increasing its excited state lifetimes and improving its cellular uptake in aqueous media are of extremely importance in PTD studies [16]. Tetra substituted phthalocyanines are usually more soluble than

---

* Corresponding authors. Tel./fax: +90 (264) 295 60 42, +90 (264) 295 59 50.
E-mail addresses: nyarasir@sakarya.edu.tr (M.N. Yarasir), mkandaz@sakarya.edu.tr (M. Kandaz).

http://dx.doi.org/10.1016/j.poly.2015.07.035
0277-5387/

octa-substituted phthalocyanines because of the formation of constitutional isomers and the high dipole moment that results from the unsymmetrical arrangement of the substituents at the periphery [17].

Phthalocyanines have a high trend to aggregate in aqueous solutions particularly [18]. The peripheral and/or nonperipheral substituted phthalocyanines could be form two types of aggregations which affect on electronic and optical properties. One type is face-to-face *H*-aggregation [19] and other type is side-to-side *J*-aggregation [20]. Generally, phthalocyanine aggregation results in a decrease in intensity of the Q-band corresponding to the monomeric species, simultaneously a new, broader and blueshifted or red-shifted band is seen to increase in intensity. This shift to lower wavelengths indicates to H-type aggregation among the phthalocyanine molecules. In rare cases, red-shifted bands have been observed corresponding to J-type aggregation of the phthalocyanine molecules [20].

Phthalocyanines bearing thia-oxo functionalities show optical changes when they bind Ag (I) and Pd (II) ions, while crown-attached phthalocyanines are well suited to bind alkaline and alkaline earth metal ions [21].

Substitution at non-peripheral positions gives rise to red shifting of the Q-band of MPcs according to the substitution at the peripheral positions [22,23] and the presence of electron donating sulfur groups on Pc leads to the red shifting of the Q-band to more longer wavelengths as a result of the electron-donating thioether substituents when compared with those of unsubstituted and alklyl or O-substituted derivatives [24].

Due to their heavy diamagnetic nature and axially substituted capacity Ga(III) and In(III) metals have been chosen as central atoms. It is known that axial substitution can introduce a dipole moment perpendicular to macrocycle, and via steric effect it can alter the spatial relationship between neighboring molecules [25]. Also are known that photophysical properties of the phthalocyanine are influenced by the presence and nature of the central metal ion. Phthalocyanine complexes with diamagnetic ions, such as Zn^{2+}, Al^{3+}, and Ga^{3+}, both high triplet yields and long lifetimes have [26].

First of all this paper is concerned with the synthesis of ligand 4-(6-hydroxyhexylthio)-phthalonitrile and 3-(6-hydroxyhexylthio)-phthalonitrile were prepared according to the procedure reported in the literatüre [27,28] and then, its peripherally and nonperipherally β- α-substituted MPcs, $M[Pc(\beta\text{-}SC_6H_{12}OH)_4]$ {M = Ga(III)(**3**), In(III)(**4**)}, $M[Pc(\alpha\text{-}SC_6H_{12}OH)_4]$ {M = Ga(III)(**5**), In(III)(**6**)} are described, and also their soft metal ions (Ag(I) and (Pd(II)) binding properties are investigated and evaluated. In addition, Surface morphologies of novel type phthalocyanines were performed by AFM without interaction and after interaction with soft metal ions (Ag(I) and (Pd(II). Finally, photochemical properties (Singlet oxygen quantum yields and photodegradation quantum yields) and photophysical properties (Fluorescence quantum yields and flouresans behavior) of α or β tetra-substituted phthalocyanines were investigated.

2. Experimental

2.1. Materials and methods

Chloroform ($CHCl_3$), tetrahydrofuran (THF), 4-nitrophthalonitrile, 3-nitrophthalonitrile, $GaCl_3$, $InCl_3$ were purchased from Merck and Alfa Aesar and used as received. All other reagents were obtained from Fluka, Aldrich and Alfa Aesar Chemical Co. and used without purification. The purity of the products was tested in each step by TLC(SiO_2, $CHCl_3$/MeOH and THF/MeOH). FT-IR spectrophotometer recorded on Perkin Elmer Two FT-IR spectrophotometer where samples were dispersed in KBr. Chromatography was performed with silica gel (Merck grade 60) from Aldrich. All reactions were carried out under a dry N_2 atmosphere. Elemental analysis (C, H and N) was performed at the instrumental analysis laboratory of Marmara University. Time- and applied-resolved UV–Vis array spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker 300 spectrometer instruments. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra (MS) were measured using a Bruker Autoflex III mass spectrometer equipped with a nitrogen UV-Laser operating at 337 nm. The MALDI matrice, α-cyano-4-hydroxy-cinnamic acid (CHCA) was chosen as the best one.

2.2. Synthesis

2.2.1. 4-(6-hydroxyhexylthio)-phthalonitrile (**1**)

The compound was prepared according to the procedure reported in the literature [22].

2.2.2. 3-(6-hydroxyhexylthio)-phthalonitrile (**2**)

The compound was prepared according to the procedure reported in the literature [28].

2.2.3. [Ga] 2(3),9(10),16(17),23(24)-tetrakis-(6-hydroxyhexylthio) phthalocyanine (**3**)

A well-powdered mixture of compound **1** (0.5 g, 1.92 mmol), and $GaCl_3$ (0.08 g, 0.44 mmol) were refluxed in 1-hexanol (1 cm^3) and 1,8-diazabicyclo [5.4.0.] undec-7-ene (DBU, 0.05 ml) (0.05 cm^3) under argon sealed glass tube. The temperature of the reaction mixture was raised to 150–160 °C and kept for 8 h. The deep green-blue product was cooled tort, and the solid was washed successively with hot-heptane, copious of the mixture of isopropanol and water, and cold acetonitrile to remove impurities until the filtrate was clear. The green–blue product was isolated by silica gel column chromatography with THF-MeOH (50/2 v/v) and then dried in vacuum. The complex **3** is highly soluble in $CHCl_3$, CH_2Cl_2, THF, *i*-PrOH, MeOH, EtOH, DMF, DMSO, DMAA, and pyridine. Yield 0.174 g (34.80%), mp > 200 °C. *Anal.* Calc. for $C_{56}H_{64}N_8O_4S_4GaCl$ (1145.2 g/mol): C, 58.66; H, 5.63; N, 9.77. Found: C, 59.12; H, 5.75; N, 9.58%. FT-IR (KBr): ν, cm^{-1} 3350 (br, OH), 3040 (Ar–H), 2952, 2873 (Aliph–H), 1726 (w, H–O…H, weak), 1660, 1599, 1584, 1465, 1433, 1338, 1255, 1214, 1068, 912, 870, 835, 745. ^1H NMR (DMSO-d6): δ, ppm 8.13–7.75 (m, br, 12H, phenyl H3, H5, H6), 5.08 (s, t, br, 4H, $-CH_2-\mathit{OH}$, D_2O exchangeable), 3.48 (t, br, 8H, $\mathit{CH_2}OH$), 3.30 (DMSO), 2.80 (m, 8H, $CH_2\mathit{CH_2}\text{-}S-$), 1.62 (m, 8H,$\mathit{CH_2}CH_2-S-Ar$), 1.46 (m, 8H, $CH_2\mathit{CH_2}CH_2-OH$), 1.35 (m,8H, $\mathit{CH_2}CH_2CH_2-OH$) ^{13}C NMR (300 MHz, DMSO-d6): δ, ppm 148.25 (S–Ar–*C4*), 132.75 (Ar–*C6*), 129.80 (Ar–*C5*), 128.16 (Ar–*C3*), 115.11 (Ar–*C2*), 114.10 (Ar–*C1*), 144.98(Ar–CN), 144.01 (Ar–CN), 67.31 ($-CH_2OH$), 40.85 (DMSO), 36.98 (S–CH–), 37.56($\mathit{CH_2}CH_2OH$), 35.26 ($-SCH_2CH_2CH_2-$), 22.30 ($-CH_2CH_2-$), 14.08 ($-CH_2CH_2-$).UV–Vis (THF): λ_{max}, nm 704 (Q), 632 ($n-\pi^*$, sh), 331 (B). MS (MALDI-TOF-MS, α-cyano-4-hydroxycinnamic acid (CHCA) as matrix): 1146.8 $[M+H]^+$.

2.2.4. [In] 2(3),9(10),16(17),23(24)-tetrakis-(6-hydroxyhexylthio) phthalocyanine (**4**)

A well-powdered mixture of compound **1** (0.5 g, 1.92 mmol), and anhydrous $InCl_3$ (0.06 g, 0.26 mmol) were refluxed in 1-hexanol (1 cm^3) and 1,8-diazabicyclo [5.4.0.] undec-7-ene (DBU, 0.05 ml) (0.05 cm^3) under argon sealed glass tube. The temperature of the reaction mixture was raised to 150–160 °C and kept for 8 h. After cooling to room temperature and diluting with 2-propanol, it was filtered. The dark green–blue crude product formed during the reaction was treated with 2-propanol several times and filtered off. It was then successively washed with CH_3CN, and dried. Further purification by silica gel chromatography ($\mathrm{CHCl_3/MeOH}$ as a eluent (5/100%) and dried in vacuo. Blue phthalocyanine **4** is soluble in THF, MeOH, EtOH, DMF, DMSO. Yield 0.14 g (27.30%), mp > 200 °C. *Anal.* Calc. for $\mathrm{C_{56}H_{64}N_8O_4S_4InCI}$ (1190.6 g/mol): C, 56.44; H, 5.41; N, 9.40; Found: C, 57.12; H, 5.63; N, 9.61%. FT-IR (KBr): ν, $\mathrm{cm^{-1}}$ 3227 (H-bonded, OH), 2958 (Ar–H), 2950, 2851 (Aliph–H), 1645, 1573, 1463, 1364, 1261, 1109, 1025, 984, 798, 720, 615. ^{1}H NMR (DMSO-d6): δ, ppm 8.11–7.76 (m, br, 12H, phenyl H3, H5, H6), 4.80 (s, t, br, 4H, $\mathrm{-CH_2-}OH$, $\mathrm{D_2O}$ exchangeable), 3.42 (t, br, 8H, $CH_2\mathrm{OH}$), 3.30 (DMSO), 2.82 (m, 8H, $\mathrm{CH_2}CH_2\mathrm{\text{-}S-}$), 1.65 (m, 8H,$CH_2\mathrm{CH_2-S-Ar}$), 1.47 (m, 8H, $\mathrm{CH_2}CH_2\mathrm{CH_2-OH}$), 1.30 (m,8H, $CH_2\mathrm{CH_2CH_2-OH}$) ^{13}C NMR (300 MHz, DMSO-d6): δ, ppm 146.25 (S–Ar–*C4*), 135.78 (Ar–*C6*), 130.80 (Ar–*C5*), 128.16 (Ar–*C3*), 116.78 (Ar–*C2*), 114.10 (Ar–*C1*), 144.98 (Ar–*C*N), 144.01 (Ar–*C*N), 68.31 ($\mathrm{-}C\mathrm{H_2OH}$), 40.80 (DMSO), 36.90 (S–*C*H–), 36.56 ($CH_2\mathrm{CH_2OH}$), 35.12 ($\mathrm{-SCH_2}C\mathrm{H_2CH_2-}$), 21.40 ($\mathrm{-}CH_2\mathrm{CH_2-}$), 14.12 ($\mathrm{-CH_2}CH_2\mathrm{-}$). UV–vis (THF): λ_{max}, nm 710(Q), 636(n–π^*, sh), 341 (B). MS (MALDI-TOF-MS, α-cyano-4-hydroxycinnamic acid (CHCA) as matrix): 1191.5 $[\mathrm{M+H}]^+$.

2.2.5. [Ga] 1(4),8(11),15(18),22(25)-tetrakis-(6-hydroxyhexylthio) phthalocyanine (5)

A well-powdered mixture of compound **2** (0.25 g, 0.96 mmol), and anhydrous $\mathrm{GaCl_3}$ (0.02 g, 0.22 mmol) were refluxed in 1-hexanol (1 $\mathrm{cm^3}$) and 1,8-diazabicyclo [5.4.0.] undec-7-ene (DBU, 0.05 ml) (0.05 $\mathrm{cm^3}$) under argon sealed glass tube. The temperature of the reaction mixture was raised to 150–160 °C and kept for 5 h. The color of the mixture turned green–blue over this time. After heating for an additional 3 h, the green–blue product was cooled to room temperature. The crude product formed was washed several times, successively with hexane, *i*-PrOH and then cold $\mathrm{CH_3CN}$, to remove impurities. Finally, the product was further purified by silica gel chromatography $\mathrm{CHCl_3/MeOH}$ (100:4 v/v). After washing the resulting oily product with copious amounts of hexane, diethylether and i-PrOH, finally it was dried in vacuum. This product is soluble in MeOH, THF, DMF, DMSO, pyridine and insoluble in diethylether.

Yield 0.087 g (32.80%), mp > 200 °C. *Anal.* Calc. for $\mathrm{C_{56}H_{64}N_8O_4S_4GaCI}$ (1145.2 g/mol): C, 58.66; H, 5.63; N, 9.77. Found: C, 59.85; H, 5.69; N, 9.82%. FT-IR (KBr): ν, $\mathrm{cm^{-1}}$ 3358 (br, OH), 3042 (Ar–H), 2950, 2870(Aliph-H), 1725 (w, H–O…H, weak), 1660, 1599, 1586, 1460, 1430, 1335, 1252, 1213, 1070, 913, 875, 837, 742. ^{1}H NMR (DMSO-d6): δ, ppm 8.10–7.70 (m, br, 12H, phenyl H4, H5, H6), 5.12 (s, t, br, 4H, $\mathrm{-CH_2-}OH$, $\mathrm{D_2O}$ exchangeable), 3.42 (t, br, 8H, $CH_2\mathrm{OH}$), 3.30 (DMSO), 2.79 (m, 8H, $\mathrm{CH_2}CH_2\mathrm{\text{-}S-}$), 1.65 (m, 8H,$CH_2\mathrm{CH_2-S-Ar}$), 1.38 (m, 8H, $\mathrm{CH_2}CH_2\mathrm{CH_2-OH}$), 1.32 (m,8H, $CH_2\mathrm{CH_2CH_2-OH}$) ^{13}C NMR (300 MHz, DMSO-d6): δ, ppm 147.15 (S–Ar–*C3*), 133.16 (Ar–*C6*), 130.20 (Ar–*C5*), 126.16 (Ar–*C4*), 118.20 (Ar–*C2*), 115.30 (Ar–*C1*), 145.78(Ar–*C*N), 145.01 (Ar–*C*N), 68.20 ($\mathrm{-}C\mathrm{H_2OH}$), 40.80 (DMSO), 38.70 (S–*C*H–), 37.15($CH_2\mathrm{CH_2OH}$), 36.26 ($\mathrm{-SCH_2}C\mathrm{H_2CH_2-}$), 21.42 ($\mathrm{-}CH_2\mathrm{CH_2-}$), 13.76 ($\mathrm{-CH_2}CH_2\mathrm{-}$). UV–vis (THF): λ_{max}, nm 734 (Q), 658 (n–π^*, sh), 346 (B). MS (MALDI-TOF-MS, α-cyano-4-hydroxycinnamic acid (CHCA) as matrix): 1146.5 $[\mathrm{M+H}]^+$.

2.2.6. [In] 1(4),8(11),15(18),22(25)-tetrakis-(6-hydroxyhexylthio) phthalocyanine (6)

A well-powdered mixture of compound **1** (0.5 g, 1.92 mmol), and anhydrous $\mathrm{InCl_3}$ (0.06 g, 0.26 mmol) were refluxed in 1-hexanol (1 $\mathrm{cm^3}$) and 1,8-diazabicyclo [5.4.0.] undec-7-ene (DBU, 0.05 ml) (0.05 $\mathrm{cm^3}$) under argon sealed glass tube. The temperature of the reaction mixture was raised to 150–160 °C and kept for 5 h. The color of the mixture turned green–blue over this time. After heating for an additional 3 h, the green–blue product was cooled to room temperature. The crude product formed was washed several times, successively with hexane, i-PrOH and then cold $\mathrm{CH_3CN}$, to remove impurities. Finally, the product was further purified by silica gel chromatography $\mathrm{CHCl_3/MeOH}$ (20:1 v/v). After washing the resulting oily product with copious amounts of hexane, diethylether and i-PrOH, finally it was dried in vacuum. This product is soluble in MeOH, THF, DMF, DMSO, pyridine and insoluble in diethylether.

Yield 0.12 g (23.40%), mp > 200 °C. *Anal.* Calc. for $\mathrm{C_{56}H_{64}N_8O_4S_4InCI}$ (1190.6 g/mol): C, 56.44; H, 5.41; N, 9.40; Found: C, 56.10; H, 5.78; N, 9.48%. FT-IR (KBr): ν, $\mathrm{cm^{-1}}$ 3355 (br, OH), 3043 (Ar–H), 2950, 2872 (Aliph–H), 1726 (w, H–O…H, weak), 1663, 1599, 1587, 1462, 1435, 1338, 1252, 1214, 1070, 912, 876, 837, 745. ^{1}H NMR (DMSO-d6): δ, ppm 8.30–7.75 (m, br, 12H, phenyl H4, H5, H6), 4.18 (s, t, br, 4H, $\mathrm{-CH_2-}OH$, $\mathrm{D_2O}$ exchangeable), 3.38 (t, br, 8H, $CH_2\mathrm{OH}$), 3.32 (DMSO), 2.80 (m, 8H, $\mathrm{CH_2}CH_2\mathrm{\text{-}S-}$), 1.64 (m, 8H,$CH_2\mathrm{CH_2-S-Ar}$), 1.32 (m, 8H, $\mathrm{CH_2}CH_2\mathrm{CH_2-OH}$), 1.29 (m,8H, $CH_2\mathrm{CH_2CH_2-OH}$) ^{13}C–NMR (300 MHz, DMSO-d6): δ, ppm 146.20 (S–Ar–*C3*), 135.18 (Ar–*C6*), 130.16 (Ar–*C5*), 125.10 (Ar–*C4*), 118.32 (Ar–*C2*), 115.28 (Ar–*C1*), 145.10 (Ar–*C*N), 145.12 (Ar–*C*N), 67.32 ($\mathrm{-}C\mathrm{H_2OH}$), 40.05 (DMSO), 38.75 (S–*C*H–), 37.65 ($CH_2\mathrm{CH_2OH}$), 36.24 ($\mathrm{-SCH_2}C\mathrm{H_2CH_2-}$), 20.80 ($\mathrm{-}CH_2\mathrm{CH_2-}$), 12.96 ($\mathrm{-CH_2}CH_2\mathrm{-}$). UV–vis (THF): λ_{max}, nm 740 (Q), 660 (n–π*, sh), 345 (B). MS (MALDI-TOF-MS, α-cyano-4-hydroxycinnamic acid (CHCA) as matrix): 1191.5 $[\mathrm{M+H}]^+$.

2.3. Photophysical and photochemical studies

2.3.1. Fluorescence quantum yields

Fluorescence quantum yields (Φ_F) were determined by the comparative method (Eq. (1)) [29],

$$\Phi_F = \Phi_{F(\mathrm{Std})} \frac{F.A_{\mathrm{Std}}.n^2}{F_{\mathrm{Std}}.A.n^2_{\mathrm{Std}}} \tag{1}$$

where F and F_{Std} are the areas under the fluorescence emission curves of the samples (**3**, **4**, **5** and **6**) and the standard, respectively. A and A_{Std} are the respective absorbances of the samples and standard at the excitation wavelengths, respectively. n^2 and n^2_{Std} are the refractive indices of solvents used for the sample and standard, respectively. Unsubstituted ZnPc (in DMF) ($\Phi_F = 0.17$) [30], was employed as the standard. Both the samples and standard were excited at the same wavelength. The absorbance of the solutions at the excitation wavelength ranged between 703 and 732.

2.3.2. Singlet oxygen quantum yields

Singlet oxygen quantum yield (Φ_Δ) determinations were carried out using the experimental set-up described in literature [31–33]. Quantum yields of singlet oxygen photogeneration were determined in air (no oxygen bubbled) using the relative method with ZnPc as reference and DPBF as chemical quencher for singlet oxygen, using formula (2),

$$\Phi_\Delta = \Phi_\Delta^{\mathrm{Std}} \frac{R.\mathrm{I}^{\mathrm{Std}}_{\mathrm{abs}}}{R^{\mathrm{Std}}.\mathrm{I}_{\mathrm{abs}}} \tag{2}$$

where Φ_Δ^{Std} is the singlet oxygen quantum yields for the standard ZnPc ($\Phi_\Delta^{Std} = 0.56$) for ZnPc in DMF [34]. R and R_{Std} are the DPBF photobleaching rates in the presence of the respective samples (**3**, **4**, **5** and **6**) and standard, respectively. I_{abs} and I_{abs}^{Std} are the rates of light absorption by the samples (**3**, **4**, **5** and **6**) and standard, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen [35], the concentration of quencher (DPBF) was lowered to $\sim 3 \times 10^{-5}\ \mathrm{mol\ dm^{-3}}$ Solutions of sensitizer (containing DPBF) were prepared in the dark and irradiated in the Q band region using the setup described above. DPBF degradation at 417 nm (in DMSO) were monitored. The light intensity of 7.05×10^{15} photons $\mathrm{s^{-1}\ cm^{-2}}$ was used for Φ_Δ determinations.

2.3.3. Photodegradation quantum yields

The study of degradation of the molecules intended for use as photo catalysts is especially important. Thus, Photodegradation quantum yield (Φ_d) determinations were carried out by the experimental set-up described in literature [35–37]. Photodegradation quantum yields were determined using formula (3),

$$\Phi_d = \frac{(C_0 - C_t).V.N_A}{I_{\mathrm{abs}}.S.t} \qquad (3)$$

where "C_0" and "C_t" are the sample (**3**, **4**, **5** and **6**) concentrations before and after irradiation respectively, "V" is the reaction volume, "N_A" the Avogadro's constant, "S" the irradiated cell area and "t" the irradiation time, "I_{abs}" is the overlap integral of the radiation source light intensity and the absorption of the samples (**3**, **4**, **5** and **6**). A light intensity of 2.50 × 10^{16} photons s^{-1} cm^{-2} was employed for Φ_d determinations.

3. Results and discussion

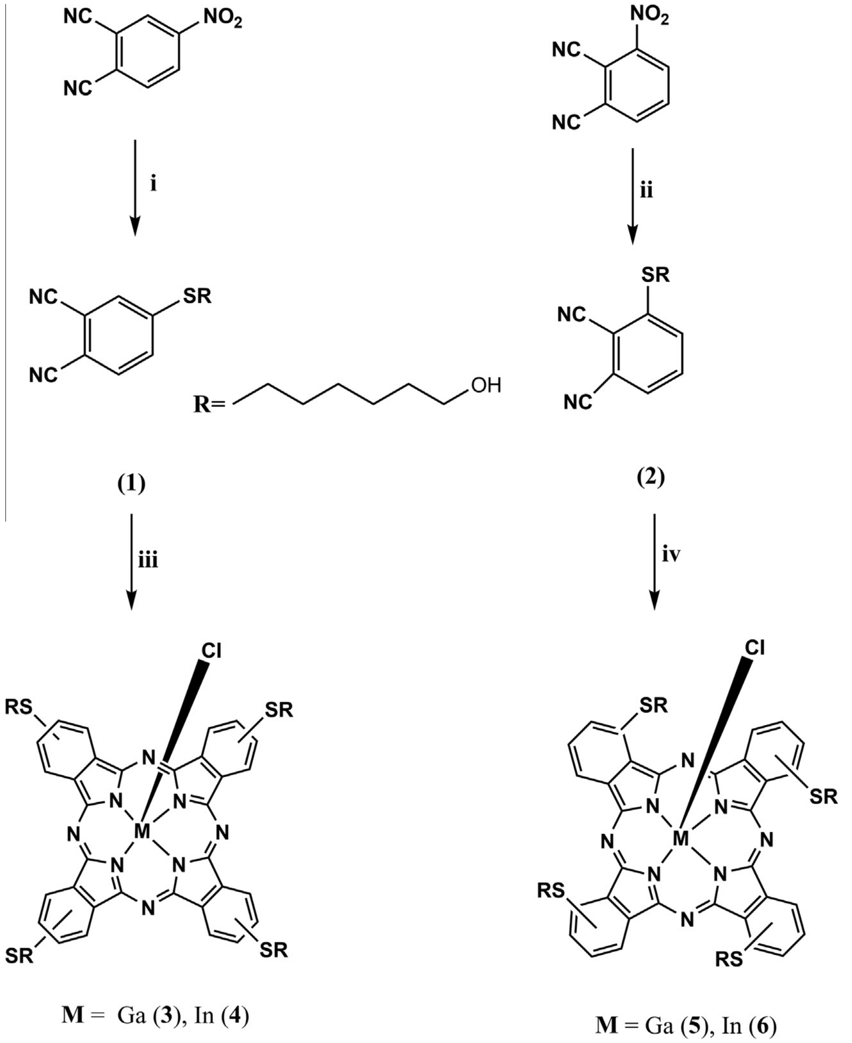
3.1. Synthesis and characterization

In common, substituted phthalocyanines are prepared by cyclotetramerization of α or β substituted 1,3-diimino-1H-isoindoles or phthalonitriles. 2(3),9(10),16(17),23(24)-Tetra-substituted phthalocyanines can be synthesized from β-substituted phthalonitriles on the other hand 1(4),8(11),15(18),22(25)-tetra-substituted phthalocyanines are synthesized from α-substituted analogues [27,28].

In this study, ligands, 4-(6-hydroxyhexylthio)-phthalonitrile (**1**) and 3-(6-hydroxyhexylthio)-phthalonitrile (**2**), their metal ion sensor gallium(III) and indium(III) phthalocyanines, **3**, **4 5** and **6**, were prepared. Related Pcs, **3–6**, were accomplished by heating a pulverized mixture of 4-(6-hydroxyhexylthio)-phthalonitrile and 3-(6-hydroxyhexylthio)-phthalonitrile with anhydrous $GaCl_3$, $InCl_3$ metal salt at *ca.* 150–160 °C under N_2 atmosphere in the presence of 1-hexanol and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) for 8 h (Scheme 1).

Generally, phthalocyanine complexes are insoluble in general organic solvents. If you are added suitable functional group on the ring from α or β positions, solubility of phthalocyanines can be increased. All of newly synthesized α or β substituted metallophthalocyanines **3–6** have excellent solubility in $CHCl_3$, MeOH, THF, DMF, DMSO.

The structure of phthalocyanines (**3–6**) were verified by standard method elemental analysis, FT-IR, ^{1}H NMR, ^{13}C NMR, MALDI-TOF, UV–Vis, fluorescence spectral data and AFM as complementary techniques. All the analytical spectral data are consistent with the predicted structures.



Scheme 1. Synthetic route of 2(3), 9(10), 16(17), 23(24)-tetrakis-(6-hydroxyhexylthio) phthalocyanine M{Pc[S-$C_6H_{12}OH$)]$_4$} (M = Ga(III) (3), In(III) (4)} and Synthetic route of 1(4),8(11),15(18),22(25)-Tetrakis-(6-hydroxyhexylthio) phthalocyanine M{Pc[S$C_6H_{12}OH$)]$_4$} (M = Ga(III) (5), In(III) (6) (i and ii) K_2CO_3, 6-mercapto-1-hexanol, DMF, 40 °C, 2 days. (iii and iv) anhydrous $GaCl_3$, $InCl_3$, 160–170 °C, for 8 h, DBU.

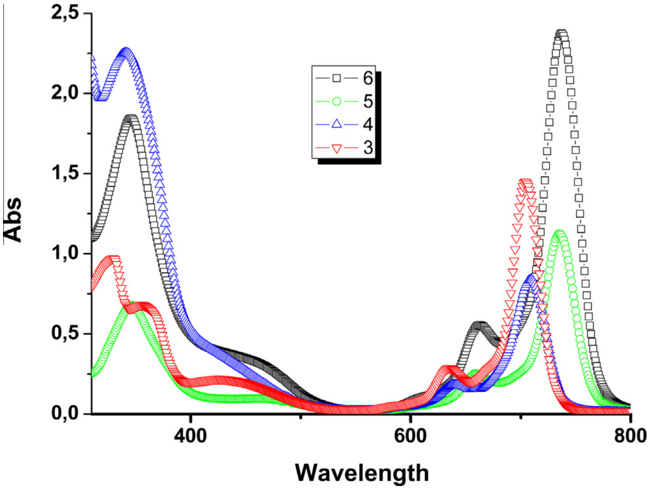


Fig. 1. UV–Vis spectra of **3**, **4**, **5** and **6** in THF.

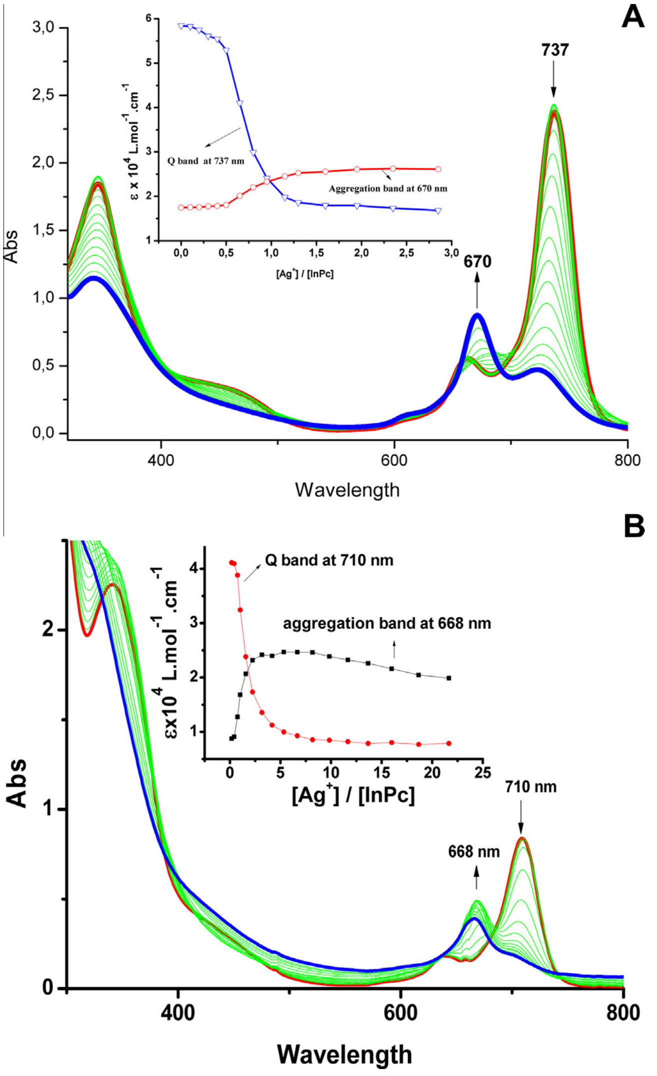


Fig. 2. UV–Vis spectra of **6** in THF during titration with Ag(I) (A) ions and UV–Vis spectra of **4** in THF during titration with Ag(I) (B) ions in THF.

Cyclotetramerization of 4-(6-hydroxyhexylthio)-phthalonitrile (**1**) and 3-(6-hydroxyhexylthio)-phthalonitrile (**2**) to the phthalocyanines (**3–6)** were confirmed by the disappearance of the sharp –C≡N vibration at 2223 cm^{-1}. The FT-IR spectra of phthalocyanines (**3–6**) are very similar with the exception of small stretching shifts.

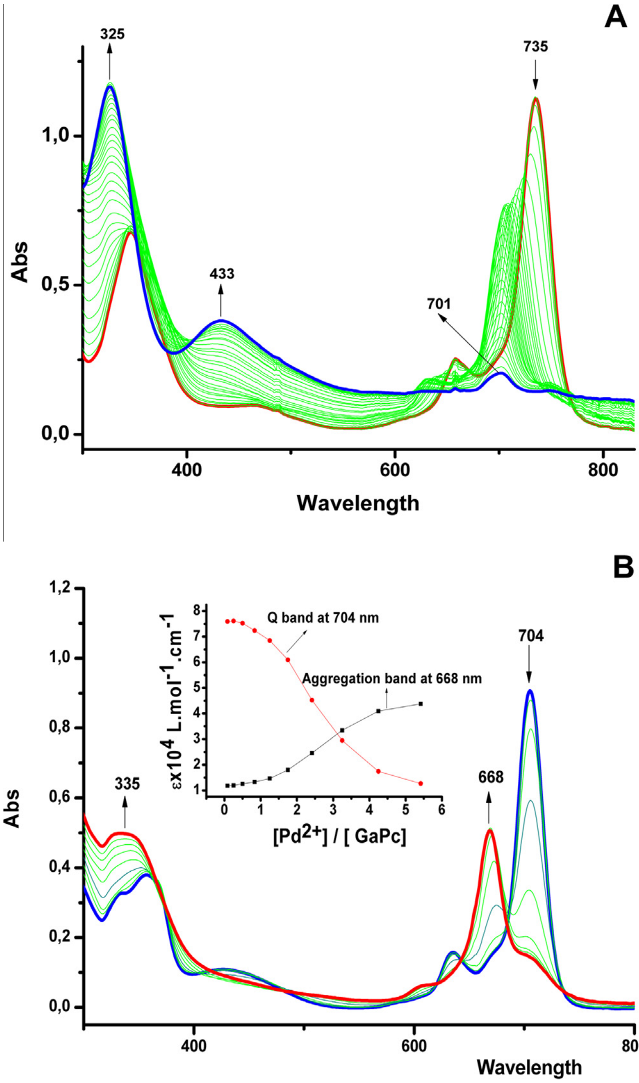


Fig. 3. UV–Vis spectra of **5** in THF during titration with Pd(II) (A) ions and UV–Vis spectra of **3** in THF during titration with Pd(II) (B) ions in THF.

^{1}H NMR investigations of compounds **3–6** provide the characteristic chemical shifts for the structures as expected. The ^{1}H NMR spectra of **3**, **4**, **5** and **6** are broader than the corresponding signals in the starting 4-(6-hydroxyhexylthio)-phthalonitrile (**1**) and 3-(6-hydroxyhexylthio)-phthalonitrile (**2**) derivative. This broadening is likely due to chemical exchange caused by aggregation-disaggregation equilibria and the fact that the product obtained in these reactions is a mixture of positional isomers which are expected to show chemical shifts that differ slightly from each other. The peripheral –OH proton at 4.50–4.70 ppm in **3–6** were easily identified in the ^{1}H NMR spectrum with a broad chemical shift especially in the case of **3–6** and this signal disappears on deuterium oxide, D_2O exchange [27,28]. The other resonances related to OCH_2, CH_2, SCH_2 and Ar–H protons in the ^{1}H NMR spectra of **3–6** are very similar to that of 4-(6-hydroxyhexylthio)-phthalonitrile (**1**) and 3-(6-hydroxyhexylthio)-phthalonitrile (**2**).

UV/Vis spectra of the phthalocyanine complexes (**3–6**) exhibited characteristic absorptions in the Q-band region at around 650–700 nm, attributed to the π–π^* transition from the HOMO

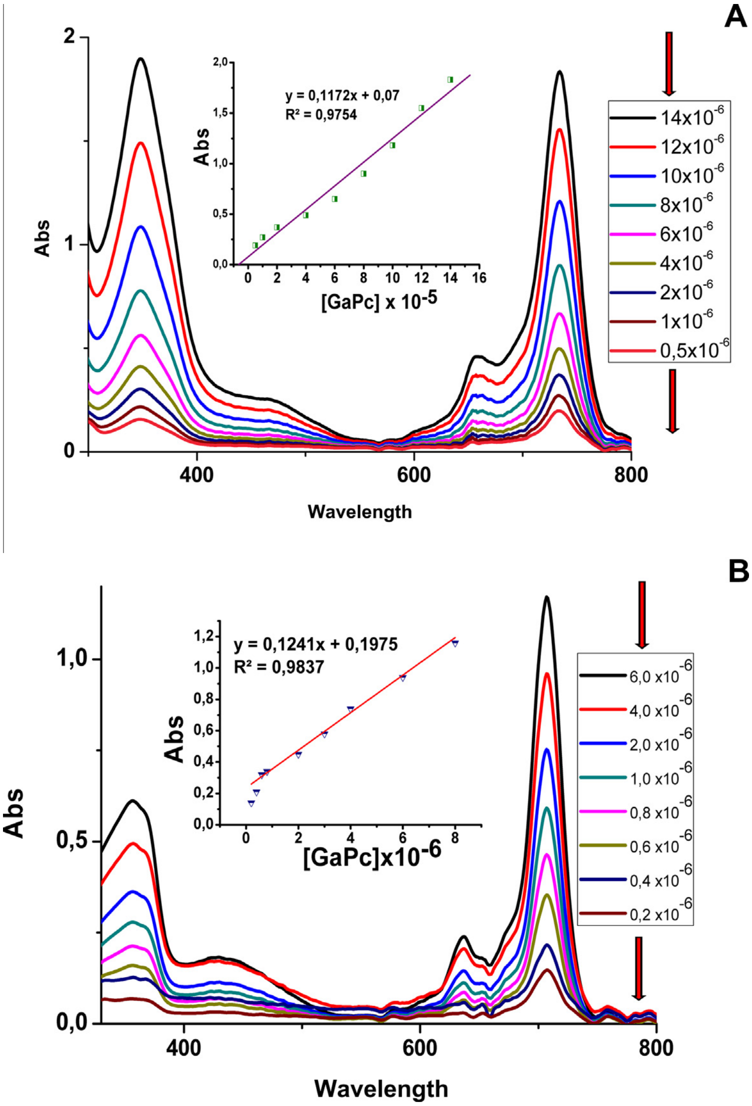


Fig. 4. Absorption spectra of **5** (A) and **3** (B) in THF at different concentrations (inset: plot of absorbance versus concentration).

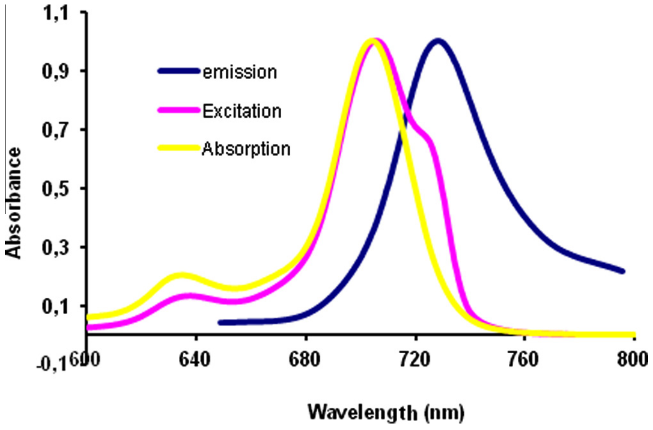


Fig. 5. Absorption (▬), excitation (▬) and emission (▬) spectra of the compound **6** in DMF.

(highest occupied molecular orbital) to the LUMO (lowest unoccupied molecular orbital) of the Pc^{2-} ring, and in the B band region (UV region) at around 300–400 nm, arising from the deeper π–π^* transitions. The Q-band absorptions of π–π^* transition for all phthalocyanines (**3**–**6**) in THF were observed as a single band of high intensity at 704 nm for **3**, 710 nm for **4**, 734 nm for **5**, 740 nm for **6**. There was also a shoulder at the slightly higher energy side of the Q band for each phthalocyanine. B band absorptions of the metallophthalocyanines **3**–**6** were observed at 331, 341, 346, 345 nm respectively (Fig. 1).

Table 1
Spectral parameters of **3**, **4**, **5** and **6** in DMF.

Comp. in DMF	Q band λ_{max} (nm)	log ε	Excitation λ_{Ex} (nm)	Emission λ_{Em} (nm)	Stokes Shift Δ_{Stokes} (nm)
3	704	4.09	705	722	17
4	706	4.49	690	733	43
5	733	4.06	732	754	22
6	704	4.47	706	728	22

3.2. Metal ion binding titration studies

Sulfur atoms on the periphery of the metallophthalocyanine complexes (MPcs) are know that optically sensitive to soft metal ions, such as Ag(I) and Pd(II). Thus, The metal binding properties of α or β tetrasubstituted phthalocyanines were investigated. In order to show metalion binding capability of the MPcs was used

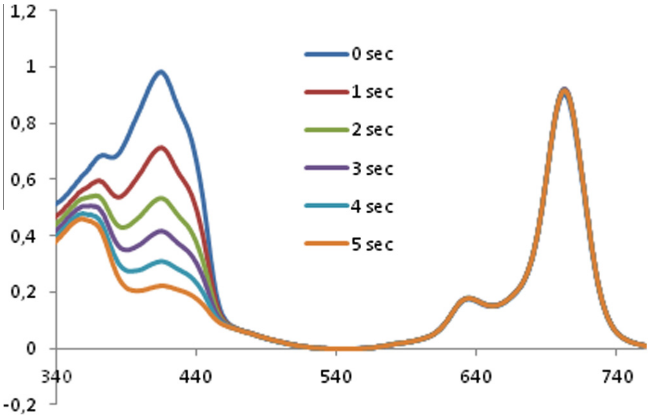


Fig. 6. A typical spectrum for the determination of singlet oxygen quantum yield for complex **3** in DMF at a concentration 6 × 10^{-6} mol dm^{-3}.

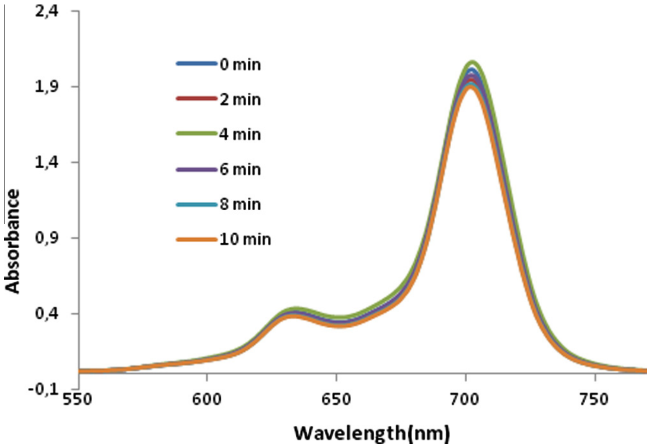


Fig. 7. A typical spectrum for the determination of photodegradation for complex **3** in DMF.

UV–Vis spectroscopy. Each titration experiment was carried out using a MeOH/THF solution of the MPcs (10/90, v/v) to ensure complete dissolution of the analyte salt in MeOH. The concentration of the metal salt (ca. 10^{-3} mol cm^{-3}) was kept higher than those of the MPc (ca. 10^{-5} mol cm^{-3}) to diminish the absorption decreases of the bands due to dilution. Gradual addition of Ag(I) to the solutions of **3**–**6** at room temperature caused a gradual color change, from green to blue, which suggests that the complexes coordinate with Ag(I) to form aggregated species Interaction of Ag(I) with these complexes decreases the solubility of the dimer, trimer, tetramer complexes formed, which results in the little observation of an intractable little product at the end of the titration due to polymer. As shown in Fig 2A (**6**) and Fig 2B (**4)** Ag(I) binding to the donor atoms of the complexes results in pronounced effects on the Q-, B- and shoulder band absorptions (n–π^* transitions: attributed to the non-bonding sulfur electron (n) to the π^* phthalocyanine orbital [24]. During the titration of **3**, **4**, **5** and **6** with Ag(I) the intensity of the Q and B-bands decreases and increase in the intensity of the dimeric H-type aggregates.

The gradual addition of Na_2PdCl_4 in MeOH (in μl portions) to **3**, **4**, **5** and **6** in THF at room temperature caused a similar gradual color change {Fig. 3A (**5**), Fig. 3B (**3**)}, suggesting H-type complex formation in the case compound **3**–**6**. These distinctive changes could be attributed to the increase in the intensity of the dimeric H-type aggregates and a decrease in the intensity of the monomers in **3**–**6**. During the titration, the intensity of the B-bands in **3**–**6** between 320–360 nm increased and somewhat shifts to shorter wavelengths (the CT region). These figures show that the binding of Ag(I) or Pd(II) to the donor atoms of **3**–**6** results in pronounced effects on the B- and especially Q-bands and on the n–π^* transitions in the UV/Vis spectrum. Also binding ratios (Insets in Figs. 2 and 3) of **4**, **6** to Ag (I) and **3**, **5** Pd(II) ions were found to be 3:1, 1:1, 3:1 respectively.

In this study, the aggregation behavior of synthesized α or β tetrasubstituted phthalocyanine complex (**3**–**6**) were investigated at different concentrations and solvent. Because aggregation behavior of phthalocyanines are important both investigation of photophysical and photochemical and to perform of sensor properties **(**as a example **5** (Fig 4A) and **3** (Fig 4B) were given in THF). As shown in the figure, the Q band increases in intensity with increasing in the concentration of **3** and **5** any new band were observed due to the aggregated species.

3.3. Fluorescence spectra and quantum yields

In this study, fluorescence properties of synthesized α or β tetrasubstituted phthalocyanine were investigated the effect of solvent used (DMF). Fig. 5 shows the absorption, fluorescence excitation and emission spectra of **3**, **4**, **5** and **6** in DMF. Fluorescence emission peaks were observed at: 754 nm for **5**, 728 nm for **6**, 723 nm for **3**, 734 nm for **4** in DMF (Table 1). The Stokes's shifts range from 5 to 15 nm in DMF, which is usual for ZnPc derivatives [38]. The observed Stokes shifts were typical of MPc complexes. As has been observed before, there is a increase Φ_F on going from ZnPc ($\Phi_F = 0.17$ [39], in DMF) to derivatives $\Phi_F = 0.2295$ (**5**), 0.0692 (**6**), 0.2666 (**3**) and 0.0551 (**4**). The fluorescence quantum yields were more observed in gallium metallophthalocyanines (**3** and **5**) than typical of MPc complexes, although indium metallophthalocyanines (**4** and **6**) were lower observed, Because of indium is a very heavy metal.

3.4. Photochemical properties

3.4.1. Singlet oxygen quantum yields

Singlet oxygen generation is very importance in PDT and the singlet oxygen quantum yield (Φ_Δ) gives an indication of how well a photosensitizer is able to generate it. Thus, Singlet oxygen quantum yields of the substituted Pcs in DMF solution were determined by using 1,3-diphenylisobenzofuran (DPBF) as a quencher. The Φ_Δ values were obtained using Eq. (2). Fig. 6 shows spectral changes observed during photolysis of complex **3** in DMF the presence of DPBF. The disappearance of DPBF was monitored using UV–Vis spectroscopy. The rate at which the DPBF degrades is related to the production of singlet oxygen. There were no changes in the Q band intensities during the Φ_Δ determinations, confirming that complexes are not degraded during singlet oxygen studies [38]. The Φ_Δ values for **3**, **4**, **5** and **6** ($\Phi_\Delta = 0.4287$, 0.1323, 0.4214, 0.1355, in DMF). This results consistent with literature [40,41]. When compared to Φ_Δ of ZnPc to α or β tetrasubstituted phthalocyanine complex (**3**–**6**) were found lower than expect in 0.56 for ZnPc in DMF. The results of gallium metallophthalocyanines were observed as close to zinc phthalocyanines but, the results of indium metallophthalocyanines were lower observed.

Table 2
Photophysical and photochemical properties of **3**, **4**, **5** and **6** in DMF.

Comp.	Solvent	Φ_F	Φ_d	Φ_Δ
3	DMF	0.2666	0.0036	0.428
4	DMF	0.0551	0.0031	0.132
5	DMF	0.2295	0.003	0.421
6	DMF	0.0692	0.0022	0.135

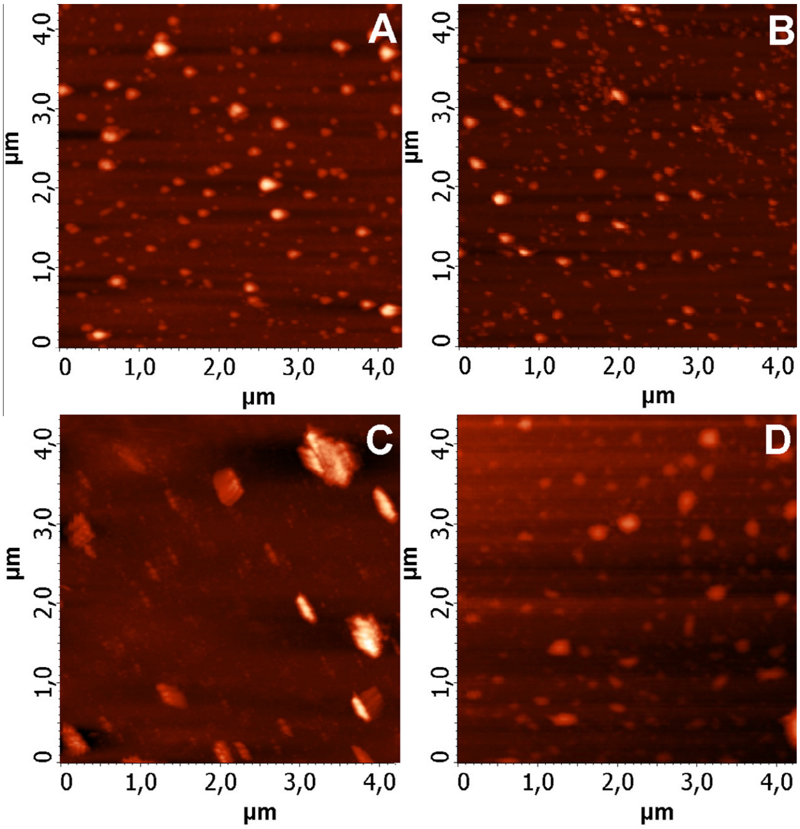


Fig. 8. (A) AFM images of **6**, (B) AFM images of **4**, (C) AFM images of **6**+Ag(I), (D) AFM images of **4**+Ag(I) were prepared from THF.

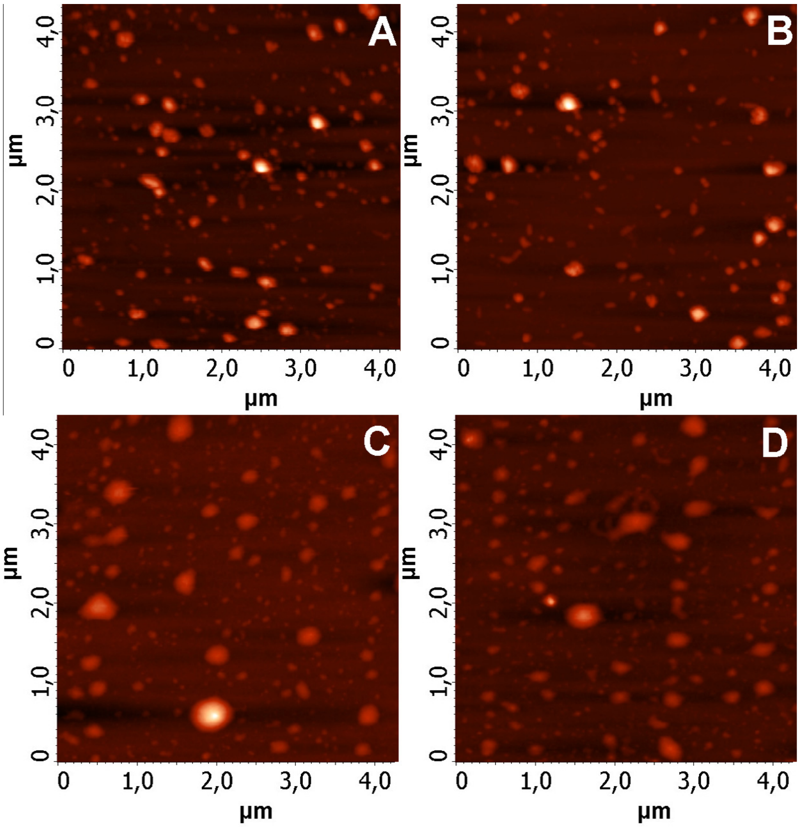


Fig. 9. (A) AFM images of **5**, (B) AFM images of **3**, (C) AFM images of **5**+Pd(II), (D) AFM images of **3**+Pd(II) were prepared from THF.

3.4.2. Photodegradation (photobleaching) quantum yields

Photobleaching is a process where phthalocyanine as photosensitizer is degraded under light irradiation owing to singlet oxygen attack which also import for photocatalytic studies in PDT. MPcs stability is especially important in the bod at a suitable under light. The photobleaching stabilities of complexes **3**, **4**, **5** and **6** were determined in DMF by monitoring the decrease in the intensity of the Q band under irradiation with increasing time (Fig 7 as a example of **3**). The photodegradation quantum yield (Φ_d) values for the complexes are listed in Table 2 are of the order of $10^{-4.}$ Stable ZnPc molecules show values as low as 10^{-6} and for unstable molecules, values of the order 10^{-3} have been reported [42].

3.5. Morphology of the phthalocyanines

As known, the investigation of surface areas of thin films are especially important for high technological applications. The thin films that have nanostructure and regular morphology are also important [43–45]. Atomic force microscopy (AFM) was also used to investigate the nano morphology of **3**–**6** in THF. The samples were prepared by drop-casting a concentrated solution of **3**–**6** in THF (6 mg/mL) onto a SiO_2 substrate. In the AFM images, was observed uniform particle structures between 10 and 20 nm (Fig 8 and Fig 9) In addition, thin films have regular morphology. AFM imafes of **6** and **4** without interaction with Ag(I) ions were given in Fig 8A and B, respectively. In addition, AFM imafes of **5** and **3** without interaction with Pd (II) ions were given in Fig 9A and B, respectively.

AFM morphologies of **3**–**6** in the case of Ag(I) and Pd(II) were given [**6**-Ag(I) (Fig 8C), **4**-Ag(I) (Fig 8D) and **5**-Pd(II) (Fig 9C), **3**-Pd(II) (Fig 9D)]. Morphologies formed from soft acid (Ag(I) or Pd(II)) soft base (Pcs) interactions also clearly reflect in the self-assembly processes of **3**–**6** including molecular packing conformations and morphologies.

4. Conclusion

We have presented the synthesis and characterization of peripherally or nonperipherally (β- or α-) substituted $M[Pc(\beta\text{-}SC_6H_{12}OH)_4]$ {M = Ga(III)(**3**), In(III)(**4**)}, $M[Pc(\alpha\text{-}SC_6H_{12}OH)_4]$ {M = Ga(III)(**5**), In(III)(**6**)} metallopthalocyanines. Structures of the new compounds were characterized by elemental analysis, FT-IR, ^1H NMR, ^{13}C NMR, MALDI-TOF, UV–Vis spectral data as standart method and also AFM was used as complementary techniques to investigate of surface morphology. The soft metal ions (Ag(I) and (Pd(II)) binding properties and binding ratios of α- β- or substituted metallophtalocyanines are investigated and evaluated by UV–Vis spectroscopy. In the same time, photochemical and photophysical properties of novel type phthalocyanines have been determined. According to photochemical and photophysical results, Singlet oxygen quantum yields of gallium metallophthalocyanines (**3** and **5**) were found to be about 4 times more than indium metallophthalocyanines (**4** and **6**). Similar results were obtained to fluorescence and quantum yields. Fluorescence and quantum yields of gallium metallophthalocyanines (**3** and **5**) were found higher than indium metal phthalocyanines (**4** and **6**).

Photodegradation (photobleaching) quantum yields of α- β-substituted phthalocyanines were investigated due to required to be stable to UV light of complexes. The singlet oxygen quantum efficiency gives indication of the potential of the complexes as photosensitizers in applications where singlet oxygen is required (Type II mechanism). Although the novel gallium phthalocyanines (**3** and **5**) can exhibit Type II photosensitizer properties on PDT applications. The novel type indium metallophthalocyanines (**4** and **6**) cannot exhibit Type II photosensitizer properties on PDT applications.

Acknowledgment

We thanks, The Research Fund of Sakarya University (Project no: 2013-02-04-049 and 2014-02-04-011) and TUBİTAK (Project no: 114Z448).

References

[1] N.B. McKeown, Phthalocyanine Materials: Synthesis, Structure and Function Cambridge University Press, Cambridge, 1998.
[2] C.C. Leznoff, A.B.P. Lever, Phthalocyanines Properties and Applications, vols. 1–4, VCH, Weinheim, 1996.
[3] W. Wu, S. Ji, H. Guo, X. Wang, J. Zhao, Dyes Pigm. 89 (2011) 199.
[4] M. Brumbach, D. Placencia, N.R. Armstrong, J. Phys. Chem. C 112 (2008) 3142.
[5] F. Yakuphanoglu, M. Kandaz, M.N. Yarasir, F.B. Şenkal, Physica B 393 (2007) 235.
[6] Y.S. Krasnov, G.Y. Kolbasov, I.N. Tretyakova, L.A. Tomachynska, V.Y. Chernii, S.V. Volkov, Solid State Ionics 180 (2009) 928.
[7] A. Kalilur Rahiman, K. Rajesh, K. Shanmuga Bharathi, S. Sreedaran, V. Narayanan, Inorg. Chim. Acta 362 (2009) 1491.
[8] T.V. Basova, R.G. Parkhomenko, I.K. Igumenov, A. Hassan, M. Durmus, A.G. Gürek, V. Ahsen, Dyes Pigm. 111 (2014) 58.
[9] M. Durmuş, T. Nyokong, Inorg. Chem. Commun. 10 (2007) 332.
[10] K.L. Dao, R.N. Hanson, Bioconjugate Chem. 23 (2012) 2139.
[11] K. Ishii, M. Shiine, Y. Shimizu, S. Hoshino, H. Abe, K. Sogawa, N. Kobayashi, J. Phys. Chem. B 112 (2008) 3138.
[12] E. Kirbaç, G.Y. Atmaca, A. Erdoğmuş, J. Organomet. Chem. 752 (2014) 115.
[13] M.N. Sibata, A.C. Tedesco, J.M. Marchetti, Eur. J. Pharma. Sci. 23 (2004) 131.
[14] E.N. Kaya, M. Durmus, M. Bulut, J. Organomet. Chem. 774 (2014) 94.
[15] A. Günsel, M.N. Yaraşır, M. Kandaz, A. Koca, Synthesis, Polyhedron 29 (2010) 3394.
[16] N. Saydan, M. Durmus, M.G. Dizge, H. Yaman, A.G. Gürek, E. Antunes, et al., J. Porphyrins Phthalocyanines 13 (2009) 681.
[17] Z. Biyiklioglu, Synth. Met. 196 (2014) 48.
[18] H. Li, N. Nguyen, F.R. Fronczek, M.G.H. Vincente, Tetrahedron 65 (2009) 3357.
[19] M. Sevim, M.N. Yaraşır, M. Kandaz, A. Koca, Dyes Pigm. 111 (2014) 190.
[20] A.T. Bilgiçli, A. Günsel, M. Kandaz, A.R. Özkaya, Dalton Trans. 41 (2012) 7047.
[21] M. Kandaz, I. Yılmaz, O. Bekaroglu, Polyhedron 19 (2000) 115.
[22] X.A. Micó, S.I. Vagin, L.R. Subramanian, T. Ziegler, M. Hanack, Eur. J. Org. Chem. (2005) 4328.
[23] D. Arican, M. Arici, A.L. Ugur, A. Erdogmus, A. Koca, Electrochim. Acta 106 (2013) 541.
[24] M.N. Yarasir, M. Kandaz, B.F. Senkal, A. Koca, B. Salih, Polyhedron 26 (2007) 5235.
[25] M. Hanack, T. Schneider, M. Barthel, J.S. Shirk, S.R. Flom, R.G.S. Pong, Coord. Chem. Rev. 219 (2008) 235.
[26] H. Ali, J.E. van Lier, Chem. Rev. 99 (1999) 2379.
[27] M.N. Yarasir, M. Kandaz, A. Koca, B. Salih, Polyhedron 26 (2007) 1139.
[28] M. Kandaz, M.N. Yarasir, A. Koca, Polyhedron 28 (2009) 257.
[29] S. Frey-Forgues, D. Lavabre, J. Chem. Edu. 76 (1999) 1260.
[30] A. Ogunsipe, J.Y. Chen, T. Nyokong, New J. Chem. 28 (2004) 822.
[31] J.H. Brannon, D. Madge, J. Am. Chem. Soc. 102 (1980) 62.
[32] A. Ogunsipe, T. Nyokong, J. Photochem. Photobiol. A: Chem 173 (2005) 211.
[33] I. Seotsanyana-Mokhosi, N. Kuznetsova, T. Nyokong, Photochem. Photobiol. A: Chem 140 (2001) 215.
[34] W. Spiller, H. Kliesch, D. Wohrle, S. Hackbarth, B. Roder, G. Schnurpfeil, J. Porp, Phthalocyan 2 (1998) 145.
[35] D. Çakır, M. Göksel, V. Çakır, M. Durmuş, Z. Biyiklioglu, H. Kantekin, Dalton Trans. (2015), http://dx.doi.org/10.1039/C5DT00747J.
[36] A. Ogunsipe, T. Nyokong, J. Photochem. Photobiol. A: Chem 173 (2005) 211.
[37] A. Ogunsipe, D. Maree, T. Nyokong, J. Mol. Struct. 650 (2003) 131.
[38] M.O. Senge, M.W. Renner, W.W. Kalisch, J. Fajer, Dalton Trans. (2000) 381.
[39] M. Durmus, T. Nyokong, Spectrochim. Acta A 69 (2008) 1170.
[40] M. Durmus, T. Nyokong, Tetrahedron 63 (2007) 1385.
[41] M. Durmus, T. Nyokong, Photochem. Photobiol. Sci. 6 (2007) 659.
[42] S. Maree, T. Nyokong, J. Porphyrins Phthalocyanines 5 (2001) 782.
[43] N. Akkaya, A.T. Bilgiçli, A. Aytekin, M.N. Yarasir, M. Kandaz, Polyhedron 85 (2015) 857.
[44] A. Günsel, M. Kandaz, F. Yakuphanoglu, W.A. Farooq, Synth. Met. 161 (2011) 1477.
[45] A.T. Bilgiçli, A. Günsel, M. Kandaz, A. Altindal, H. Cömert, J. Org. Chem. 785 (2015) 112.