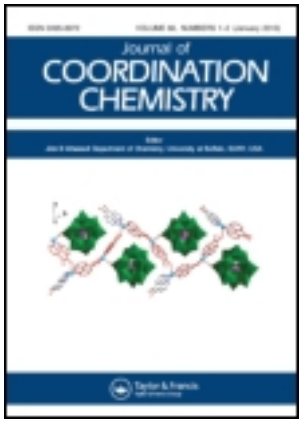


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis, spectral and photophysical investigation of porphyrazines with eight 3-quinolinecarboxy esters

Fatma Aytan Kiliçarslan[a], Alı Erdoğmuş[a], Nacıye Yılmaz Coşkun[a], Sabıha Manav Yalçın[a] & Ahmet Gül[b]

[a] Department of Chemistry, Yildiz Technical University, Esenler, Istanbul, Turkey

[b] Department of Chemistry, Technical University of Istanbul, Maslak, Istanbul, Turkey

Published online: 10 Dec 2013.

To cite this article: Fatma Aytan Kiliçarslan, Alı Erdoğmuş, Nacıye Yılmaz Coşkun, Sabıha Manav Yalçın & Ahmet Gül (2013) Synthesis, spectral and photophysical investigation of porphyrazines with eight 3-quinolinecarboxy esters, Journal of Coordination Chemistry, 66:24, 4316-4329, DOI: 10.1080/00958972.2013.867035

To link to this article: http://dx.doi.org/10.1080/00958972.2013.867035

Journal of Coordination Chemistry, 2013
Vol. 66, No. 24, 4316–4329, http://dx.doi.org/10.1080/00958972.2013.867035

Synthesis, spectral and photophysical investigation of porphyrazines with eight 3-quinolinecarboxy esters

FATMA AYTAN KILIÇARSLAN*†, ALİ ERDOĞMUŞ†, NACİYE YILMAZ COŞKUN†, SABİHA MANAV YALÇIN† and AHMET GÜL‡

†Department of Chemistry, Yildiz Technical University, Esenler, Istanbul, Turkey
‡Department of Chemistry, Technical University of Istanbul, Maslak, Istanbul, Turkey

(*Received 27 September 2013; accepted 14 November 2013*)

In this study, the syntheses and characterization of [2,3,7,8,12,13,17,18-octakis [2′-(3-quinolincarboxy)ethylhio] porphyrazinato $N^{21}N^{22}N^{23}N^{24}$] magnesium(II), quaternized [2,3,7,8,12,13,17,18-octakis [2′-(3-quinolincarboxy)ethylhio] porpyrazinato $N^{21}N^{22}N^{23}N^{24}$] magnesium(II), [2,3,7,8,12,13,17,18-octakis[2′-(3-quinolinecarboxy)-ethylthio]21H23H $N^{21}N^{22}N^{23}N^{24}$ porphyrazine and [2,3,7,8,12,13,17,18-octakis[2′-(3-quinolinecarboxy)-ethylthio]porphyrazinato $N^{21}N^{22}N^{23}N^{24}$} zinc are described. The new compounds have been characterized by elemental analysis, FT-IR, ^{1}H-NMR, and mass spectra. General trends are described for fluorescence quantum yields of these compounds in dimethylsulfoxide (DMSO). In this study, the effects quaternization of the substituents on the photophysical and spectroscopic properties are also reported.

Keywords: Porphyrazines; Quinoline; Esterification; Quaternized; Fluorescence; Photophysics

1. Introduction

In the last few years, a growing interest in studying porphyrazines has been developed because of their high flexibility and their interesting chemical and physical properties [1]. Porphyrazines are molecules with high delocalized electronic structures in which the four aza bridges are present between four pyrrole moieties. The electronic spectrum of these molecules has been analysed from a theoretical point of view only in few works [2–5]. Porphyrazines have been investigated as sensitizers for photodynamic therapy [6], metal ion probes [7], precursors to optical, magnetic, and conductive materials for nanotechnology, electrophotography, optical data recording systems, electronic devices, photovoltaic cells, fuel cells, and electrochromic displays [8–12]. Metalloporphyrazines (MPzs) with an extended delocalized 18 π-electron conjugated macrocyclic system, which exhibit high thermal stability, chemical reactivity, and unique electrochemical performance, are usually used as photo- and electro-catalysts [13, 14]. Peripherally functionalized porphyrazines have the potential to exhibit novel optical, magnetic, and electronic properties; also, the intense color of porphyrazines maintains some additional features superior to the values met in related

*Corresponding author. Email: faytank@hotmail.com

materials. The transition metal ion in the inner core offer new ways to include modification and control molecular properties. Cationic tetraazaporphyrins, or porphyrazines, represent an alternative and highly underdeveloped class of cationic porphyrinic compounds. Macrocycles based on the porphyrazine core, including phthalocyanines, exhibit many of the same properties as porphyrins, but the replacement of the *meso*-methylene carbons of porphyrins with nitrogen in porphyrazines creates profound differences [15, 16].

The synthesis, properties, and application of porphyrazines have received increasing attention in recent years [17–19], especially due to their potential role as photosensitisers in photodynamic therapy [20–24]. A continuing problem in photodynamic therapy is selectivity of uptake of the photosensitiser by cancerous tissue, for which a potential solution is functionalization of the photosensitiser with a biological moiety (e.g. a carbohydrate) to assist its selective uptake and improvement in solubility. Substituted amphiphilic and hydrophilic porphyrazines bearing both hydrophilic and hydrophobic moieties have been shown to be potent photosensitisers in photodynamic therapy [25–28]. Such pigments should be sufficiently hydrophilic to be administered as aqueous solutions so as to ensure that they quickly reach the target tumor tissues once administered and are rapidly eliminated from the body post clinic. Worth emphasizing, water solubility is an advantage for application in, for example, photodynamic theraphy (PDT). Studies on the peripherally functionalized porphyrazines in the literature indicate that these tetrapyrole derivatives should be considered as alternatives to the phthalocyanines [29]. There are many studies on photophysical and photochemical features of phthalocyanines. However, those studies on porphyrazine complexes are still very limited.

We have recently reported the synthesis of the new magnesium porphyrazines substituted with eight naphthalenecarboxy groups on the peripheral positions [30]. In this study, we report on the synthesis, characterization, and photophysical and spectroscopic properties of a new porphyrazine with eight quinoline-3-carboxylic acid groups on the peripherial location and a new water-soluble cationic magnesium(II) porphyrazine for the first time.

2. Experimental

2.1. *Materials*

All chemicals were reagent grade from Merck and Fluka. Solvents in reactions were distilled from appropriate drying agents prior to use and commercially available reagents were used without further purification unless otherwise stated. Flash column chromatography was carried out using silica gel 60(0.04–0.063 mm) from Merck. Dithiomaleonitrile disodium salt, 1,2-bis(thio)maleonitril ethane salt and 2,3,7,8,12,13,17,18-octakis(ethylsulfanyl) 5,10,15,20 porfirazinato magnesium(II) were prepared according to the previously reported procedures [31–33].

2.2. *Equipment*

FT-IR Spectra were recorded On a Spectrum One Perkin–Elmer FT-IR spectrophotometer using KBr pellets. ^{1}H-NMR spectra were recorded on a Varian, Unity Inova 500 MHz spectrometer in Sabanci University. Elemental analyses were performed at the Instrumental Analysis Laboratory of İstanbul University. The mass spectra were acquired on a Bruker

Daltonics (Bremen, Germany) Micro-TOF mass spectrometer equipped with an electron-spray ionization (ESI) in the TUBITAK Laboratory (Center of Science and Technology Research of Turkey). The instrument was operated in positive ion mode using an *m/z* range of 50–3000. Absorption spectra in the UV–Vis region were recorded with a Shimadzu 2001 UV spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorimeter using 1 cm pathlength cuvettes at room temperature.

2.3. *Photophysical parameters*

2.3.1. Fluorescence quantum yields. Fluorescence quantum yields (Φ_F) were determined by the comparative method using equation 1 [34],

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

where F and F_{Std} are the areas under the fluorescence emission curves of the samples (**4, 5, 6,** and **7**) 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 DMSO) (Φ_F = 0.20) [35] was employed as the standard. Both the samples and standard were excited at the same wavelength.

2.4. *Synthesis*

2.4.1. {2,3,7,8,12,13,17,18-Octakis[2′-(3-quinolinecarboxy)-ethylthio]porphyrazinato N^{21} $N^{22}N^{23}N^{24}$}magnesium (4). A mixture of dried porphyrazine precursor **3** (0.206 g, 0.217 mM), dicyclohexylcarbodiimide (DCCI) (0.907 g, 4.40 mM), 3-quinolinecarboxylic acid (0.766 g, 4.40 mM) and toluene-*p*-sulfonic acid (0.041 g, 0.217 mM) was stirred in dry pyridine (50 mL) under argon at room temperature for 10 days. The suspension was filtered and the filtrate was evaporated. To separate excess 3-quinolinecarboxylic acid, the product was washed subsequently with hot water and EtOH. The residue was dissolved in CH_2Cl_2 (100 mL) and washed first with aqueous 10% Na_2CO_3 solution (100 mL) and then with water. The resulting solution was filtered through celite to remove N,N-dicyclohexyl-urea and then the organic layer was dried over anhydrous Na_2SO_4 and finally the solvent was evaporated in vacuum. The blue residue was washed with EtOH and then eluted by chromatography on silica (first with only CH_2Cl_2, then adding a gradually increasing amount of MeOH). Yield: 0.134 g (28%). Calcd for $C_{112}H_{80}MgN_{16}O_{16}S_8$: C 61.52, H 3.69, N 10.25%. Found: C 60.94, H 3.27, N 10.63%. FT-IR (KBr), υ/cm^{-1}: 3050 (aromatic CH), 2940 and 2851 (aliphatic CH_2), 1714 and 1283 (COO). ^{1}H-NMR($CDCl_3$): δ (ppm) 8.93 (s, 8H, Ar–H), 8.92 (s, 8H, Ar–H), 7.8–7.0 (m, 32H, Ar–H), 4.95 (m, 16H, –OCH_2), 4.25 (m, 16H, –SCH_2). ^{13}C NMR($CDCl_3$): δ (ppm) 32.9, 35.0, 63.3, 121.2, 122.5, 127.7, 127.8, 128.9, 129.9, 132.1, 138.9, 147.5, 150.6, 152.2, 165.8. UV–Vis (CH_2Cl_2) λ_{max}/nm (log ε/dm^3 M^{-1} cm^{-1}): 375 (4.6), 670 (4.78). MS (ESI-MS) *m/z:* Calcd 2186.75. Found: 2187.4 $[M + H]^+$.

2.5.2. Quaternized [2,3,7,8,12,13,17,18-octakis [2′-(3-quinolincarboxy)ethylthio] porpyrazinato $N^{21}N^{22}N^{23}N^{24}$]magnesium(II) (5). The procedure reported by Smith *et al.* [36, 37] was used to quaternize the porphyrazine **4**. Compound **4** (0.200 g, 0.09 mM) was heated to 120 °C in freshly distilled DMF (5 mL) and excess dimethylsulphate (0.1 mL) was added dropwise. The mixture was stirred at 120 °C for 12 h. After this time, the mixture was cooled to room temperature and the product was precipitated by addition of warm acetone and collected by filtration. The green solid product was washed successively with hot ethanol, ethyl acetate, THF, chloroform, n-hexane and diethylether. The resulting hygroscopic product was dried over phosphorous pentoxide. Yield: 0.16 g (64%).

Calcd for $C_{120}H_{104}MgN_{16}O_{32}S_{12}$ (+4H_2O): C 62.47, H 4.08, N 8.11. Found: C 61.58, H 4.17, N 8.48%. FT-IR (KBr), υ/cm^{-1}: 3050 (aromatic CH), 2945 and 2853 (aliphatic CH_2), 1714 and 1283 (COO). ^{1}H-NMR (D_2O): δ (ppm) 8.93 (s, 8H, Ar–H), 8.81 (s, 8H, Ar–H), 8.2–7.3 (m, 32H, Ar–H), 4.95 (m, 16H, –OCH_2), 4.32 (m, 24H, –CH_3), 4.25 (m, 16 H, –SCH_2). ^{13}C NMR (DMSO): δ (ppm) 32.9, 35.2, 50.8, 63.3, 117.4, 121.2, 127.1, 128.6, 131.7, 134.6, 135.5, 140.1, 144.3, 146.9, 150.6, 152.2, 165.8. UV–Vis (DMSO) λ_{max}/nm (log ε/$dm^3\,M^{-1}\,cm^{-1}$): 372 (4.20), 674 (4.15).

2.5.3. {2,3,7,8,12,13,17,18-Octakis[2′-(3-quinolinecarboxy)-ethylthio]21H23H $N^{21}N^{22}$ $N^{23}N^{24}$ porphyrazine (6). Compound **4** (0.2 g, 0.0914 mM) was dissolved in 5 mL CH_2Cl_2 and after addition of trifluoroacetic acid (~2 mL) the mixture was stirred for 24 h at room temperature. When the reaction mixture was added to ice drop-by-drop and then neutralized with 25% ammonia solution, precipitation occurred and it was filtered. The precipitate was dissolved in chloroform and the organic phase was washed with water twice. After drying over anhydrous Na_2SO_4, $CHCl_3$ was evaporated to obtain dark blue-purple colored metal-free porphyrazine. The crude product was purified by thin layer chromatography on silica gel using CH_2Cl_2/MeOH (100 : 1) as eluent. Yield: 0.12 g (60.9%). Calcd for $C_{112}H_{82}N_{16}O_{16}S_8$: C 62.15, H 3.82, N 10.35%; Found: C 61.83, H 3.45, N 10.78%. FT-IR (KBr), υ/cm^{-1}: 3286 (NH), 3055 (aromatic CH), 2930 and 2855 (aliphatic CH_2), 1713 and 1277(COO). ^{1}H-NMR ($CDCl_3$): δ (ppm) 8.93 (s, 8H, Ar–H), 8.10 (s, 8H, Ar–H), 7.51–7.04 (m, 32H, Ar–H), 5.05 (m, 16H, –OCH_2), 4.50 (m, 16H, –SCH_2), –1.85 (s, 2H, NH). ^{13}C NMR($CDCl_3$): δ (ppm) 31.5, 34.3, 36.3, 63.5, 63.8, 116.2, 122.5, 125.2, 127.5, 127.7, 128.7, 129.5, 132.5, 138.7, 141, 147.5, 150.5, 164.1, 165.6. UV–Vis. (CH_2Cl_2) λ_{max}/nm (log ε/$dm^3\,M^{-1}\,cm^{-1}$): 361 (4.52), 647 (4.33) and 708 (4.43). MS (ESI-MS) *m/z*: Calcd 2164.46. Found: 2165.9 $[M + H]^+$.

2.5.4. {2,3,7,8,12,13,17,18-Octakis[2′-(3-quinolinecarboxy)-ethylthio]porphyrazinato N^{21} $N^{22}N^{23}N^{24}$} zinc (7). A solution of $Zn(CH_3COO)_2$ (0.125 g, 0.680 mM) in 10 mL EtOH was added to metal-free porphyrazine **6** (0.150 g, 0.068 mM) in 10 mL $CHCl_3$ and refluxed under argon for 2 days. After cooling to room temperature, insoluble excess $Zn(CH_3COO)_2$ was separated by filtering. The filtrate was evaporated and the residual oily substance was dissolved in a minimum amount of chloroform and was added into 30–35 mL hexane dropwise with stirring. The precipitate was separated by filtration. The color of compound **6** was blue-green. Yield: 0.134 g (87%). Calcd for $C_{112}H_{80}N_{16}O_{16}S_8$ Zn: C 60.38, H 3.62, N 10.06%. Found: C 59.84, H 3.23, N 10.45%. FT-IR (KBr) υ/cm^{-1}: 3049 (aromatic CH), 2930 and 2845 (aliphatic CH_2), 1713 and 1278 (COO). ^{1}H-NMR ($CDCl_3$): δ (ppm) 8.90 (s, 8H, Ar–H), 8.10 (s, 8H, Ar–H), 7.50–7.00 (m, 32H, Ar–H), 5.10

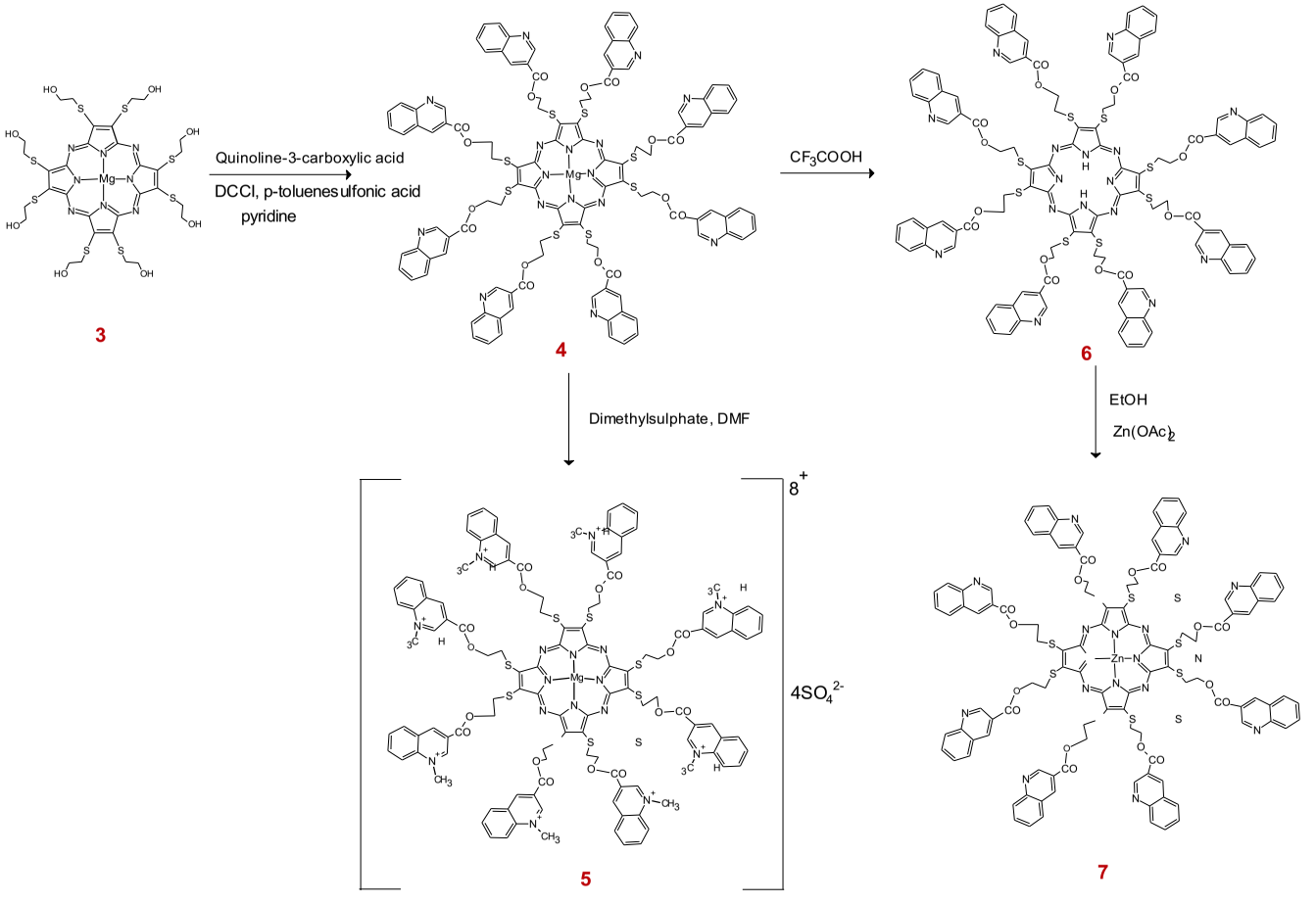
(m, 16H, –OCH_2), 4.55 (m, 16H, –SCH_2). ^{13}C NMR($CDCl_3$): δ (ppm) 32.9, 35.1, 63.3, 121.1, 122.5, 127.7, 127.8, 128.7, 129.8, 132.2, 138.9, 147.6, 150.6, 152.2, 165.8. UV–Vis. (CH_2Cl_2) λ_{max}/nm ($\log \varepsilon$/dm^3 M^{-1} cm^{-1}): 378 (4.5), 674 (4.62). MS (ESI-MS) *m/z*: Calcd 2227.8. Found: 2228.9 $[M + H]^+$.

3. Results and discussion

3.1. *Synthesis and characterization*

The synthetic route followed in this work is shown in scheme 1. The oily octakis (2-hydroxyethylthio) porphyrazinato magnesium (**3**) is blue-green and it is soluble in MeOH, EtOH but insoluble in $CHCl_3$, CH_2Cl_2, and hexane. In order to convert this porphyrazine into totally esterified products, esterification of all the hydroxyethyl substituents of porphyrazine with 3-quinolinecarboxylic acid was achieved by using DCCI, p-toluenesulfonic acid in dry pyridine for 10 days [31, 38–45]. This product is soluble in $CHCl_3$ and CH_2Cl_2, but insoluble in MeOH and EtOH. The synthesized magnesium complex **4** showed characteristic vibrations of ester groups (–COO) at 1714 and 1283 cm^{-1}, aromatic CH stretching at ca. 3000 cm^{-1}, and aliphatic CH stretching at ca. 2940 cm^{-1}. After conversion into magnesium porphyrazine, the characteristic C≡N stretch at ~2200 cm^{-1} of compound **3** disappeared. Removal of the magnesium ion was accomplished by treatment with trifluoroacetic acid and free-base porphyrazine **6** was purified by column chromatography. In the FT-IR spectra of the purple-colored metal-free porphyrazine **6**, the N–H stretching vibration of the inner core and ester peaks were observed at 3286 and 1713 cm^{-1}, respectively. The zinc(II) metal porphyrazine with blue-green color was easily prepared by insertion of the anhydrous zinc(II)acetate in a mixture of $CHCl_3$ and EtOH. The zinc(II) porphyrazine **7** was also soluble in $CHCl_3$, CH_2Cl_2, but insoluble in MeOH and EtOH. Quaternization of the magnesium porphyrazine compound **4** was achieved by reaction with excess dimethylsulphate (DMS) as quaternization agent in DMF at 120 °C. Yield of the product was 64% for **5**. After reaction with DMS, the quaternized complex is extremely soluble in water. There are no major changes in the FT-IR spectrum after quaternization, just S=O stretching at 1260 cm^{-1} and 1180 cm^{-1}, S–O stretching at 600 cm^{-1} for **5** are indicative of quaternization formation.

Ar–H protons for peripherally octa-substituted complexes were observed in the 9.57–7.00 ppm range for **4**, **5**, **6**, and **7**, integrating for 48 protons. The S–CH_2 protons for complexes were observed in the 3.58–4.55 ppm range for **4**, **5**, **6**, and **7**, integrating for 16 protons. The N–CH_3 protons for complexes were observed at 4.66 ppm for **5**, integrating for 24 protons. Metal-free derivative **6** of protons in the inner core of porphyrazines are screened by aromatic π electrons of the macrocycle, so they appeared at –1.85 ppm in the ^{1}H-NMR. In addition to these, verifying results for the structures, the mass spectra of compounds (**4, 6, 7**) gave the characteristic molecular ion peaks at *m/z*: 2187.4 $[M]^+$, 2165.9 $[M]^+$, 2228.9 $[M]^+$, respectively, confirming the proposed structures. The most intense peaks of **4** at *m/z* 1852.3 and 2014.4 correspond to the fragments $[C_{92}H_{70}MgN_{14}O_{14}S_8 + Na]^+$ and $[C_{102}H_{75}MgN_{15}O_{14}S_8]^+$. The most intense peaks of (**7**) at *m/z* 1918.8 and 2074.9 correspond to the fragments $[C_{92}H_{70}N_{14}O_{14}S_8Zn]^+$ and $[C_{102}H_{75}N_{15}O_{15}S_8Zn]^{2+}$. The isotopic peak distribution of complexes **4** and **7** ion peaks were observed at 2186.4, 2187,4, 2188.4 for **4** and 2227.1, 2228.8, 2229.7 for **7** (figure 1, using complex **4** as an example). The structures of newly synthesized compounds were verified by FT-IR, ^{1}H-NMR, UV–Vis, and



Scheme 1. Synthetic route of a new porphyrazine with eight quinoline-3-carboxylic acid group on the peripheral location and a new water-soluble cationic magnesium(II) porphyrazine.

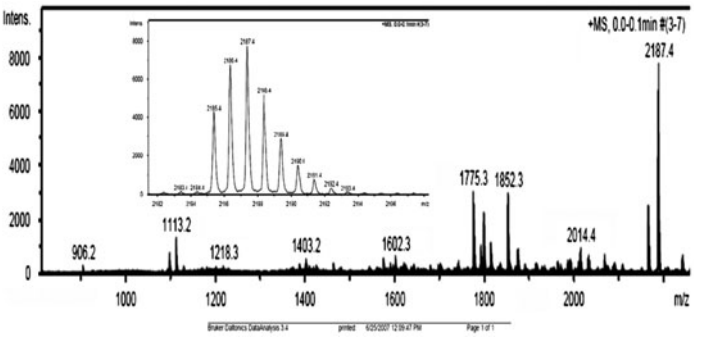


Figure 1. Micro-TOF mass spectra of **4**. Inset shows the experimental isotopic mass distrubution of the protonated ion peak.

MALDI-TOF MS spectroscopic methods, as well as by elemental analysis. The characterization data of the new compounds are consistent with the assigned formula as shown in the experimental section.

3.2. *Ground state electronic absorption*

Electronic spectra are especially useful to establish the structure of the porphyrazines. UV–Vis spectra of the porphyrazine core are dominated by two intense bands, the Q band around 660 nm and the B band in the near UV region of around 355 nm, both correlated to $\pi \rightarrow \pi^*$ transitions [46, 47]. The presence of an electron donating group on the periphery causes a bathochromic shift on Q bands. UV–Vis spectra of metallo-porphyrazine (**4** in $CHCl_3$) prepared in the present work exhibited intense single Q-band absorption of the $\pi \rightarrow \pi^*$ transitions around 670 nm and B bands in the UV region around 375 nm. For the metal-free derivative (**6** in $CHCl_3$), the Q band is split into two peaks at 647 and 708 nm as a consequence of the change in the symmetry of the porphyrazine core from D_{4h} (in the case of metallo derivatives) to D_{2h} and B bands in the UV region 361 nm. In the case of the Zn(II) derivative, the UV–Vis spectrum of zinc-coordinated derivative **7** in chloroform showed a single band at 674 nm and B bands at 378 nm as expected from D_{4h} symmetry, which was more intense than the metal-free derivative of porphyrazine, as is also observed for other peripherally macrocyclic substituted porphyrazines. The electronic spectra of porphyrazine compounds **4**, **6** and **7** are shown in figure 2. The broadening observed in Q and B bands of the both metal-free and metalloporphyrazines is attributed to $n \rightarrow \pi^*$ transition of the non-bonding electrons associated with peripheral S and N atoms [48]. This result also seems to be related to the presence of the sulfur substituents connected to the porphyrazine skeleton. The electronic spectrum of water-soluble derivatives (**5** in DMSO) exhibits absorption maxima at 674 and 372 nm (figure 3). The electronic spectrum of water-soluble derivatives (**5** in H_2O) exhibits absorption maxima at 320 nm (figure 3). Because of the advanced degree of water aggredation, Q and B bands appear extremely weak, $\pi \rightarrow \pi^*$ transitions of kinoline are seen as a single strong band.

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. In this study, the aggregation behavior of the porphyrazine compounds is investigated in different

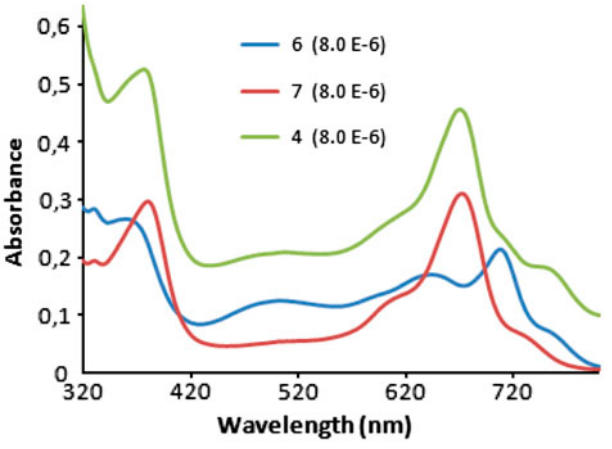


Figure 2. Absorption spectra of **4**, **6** and **7** in chloroform. Concentration: 8×10^{-6} M/L.

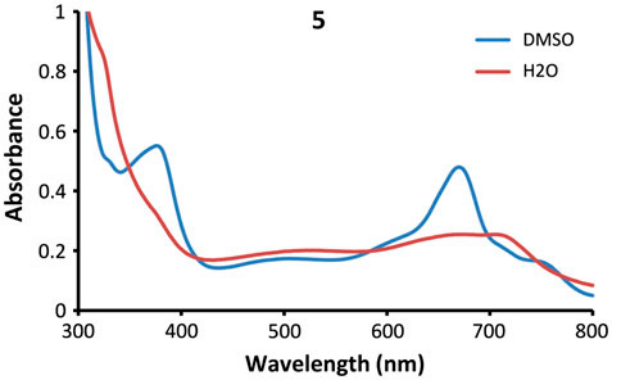


Figure 3. Absorption spectra of **5** in DMSO and water.

solvents (DMSO, DMF, chloroform, toluene, and THF). For complexes, as the concentration was increased, the intensity of absorption of the Q band also increased in parallel and there were no new bands (normally blue shifted), which might be attributed to aggregated species, observed in DMSO. Also, the Beer–Lambert law was obeyed for all of the compounds in the concentrations ranging from 2×10^{-6} to 12×10^{-6} M/L (figure 4 as example for complexes **4**(a), **6**(b) and **7**(c) in DMSO). Aggregation behavior of the studied water-soluble derivatives (**5**) in water and DMSO at different concentrations (figure 5 as example for complexes **5**).

3.3. *Photophysical properties*

3.3.1. Fluorescence spectra and quantum yields. The fluorescence behavior of the magnesium (**4**), metal free (**6**), zinc (**7**), and quaternized (**6**) porphyrazine complexes were studied in DMSO. The fluorescence emission of porphyrazines synthesized is characterized with so-called S1 and S2 emission (figure 6) [49]. The stimulated fluorescence spectra of

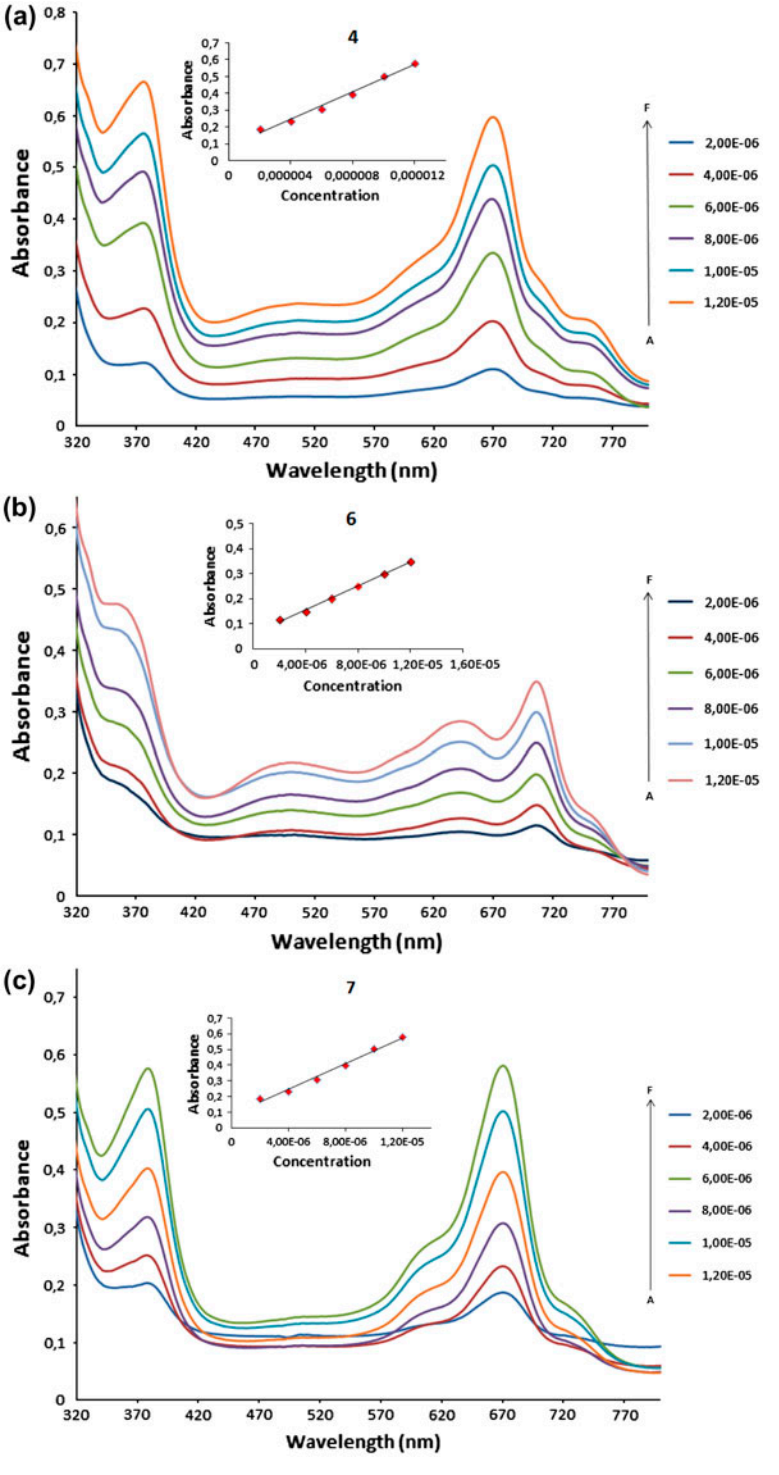


Figure 4. Absorption spectral changes of **4**(a), **6**(b) and **7**(c) in $CHCl_3$ at different concentrations: 2×10^{-6} (A), 4×10^{-6} (B), 6×10^{-6} (C), 8×10^{-6} (D), 10×10^{-6} (E), 12×10^{-6} (F) M/L.

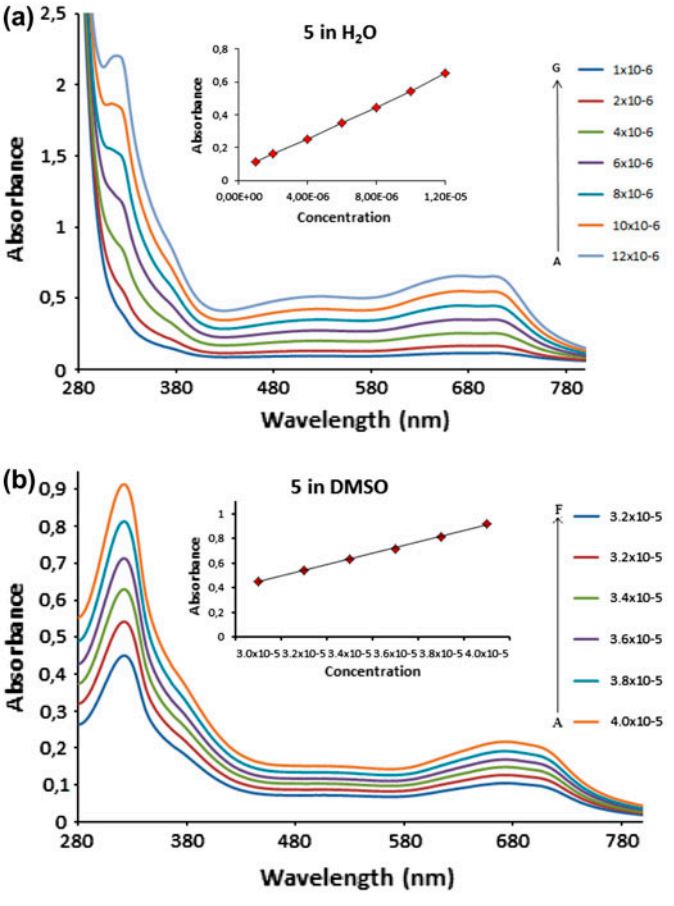


Figure 5. Aggregation behavior of **5** in water (a) and DMSO (b) at different concentrations.

all complexes were obtained at 350 and 620 nm and showed similar fluorescence properties. Figure 6 shows the fluorescence spectra for complexes in DMSO. Fluorescence emission peaks were observed at 701 nm for **4** (the most intense emission), 702 nm for **7** (low-emission), 681 nm for **6** (low-emission), and 681 nm for **5** (low-emission). Between 420 and 440 nm, all complexes showed a more severe and broader emission S2 than S1, except complex **4**. The magnesium porphyrazine (**4**) showed larger S1 emission than S2 emission.

The absorption and fluorescence emission and excitation spectra of **4** to **7** are similar in DMSO (except **5**). Figure 7 shows the absorption, fluorescence excitation, and emission spectra of **4** as an example in DMSO. The excitation spectra were narrower when compared to absorption spectra probability aggregation [50, 51] and both were mirror images of the fluorescent spectra for all complexes synthesized. The proximity of the wavelength of each component of the Q-band absorption to the Q band maxima of the excitation spectra for both complexes suggests that the nuclear configurations of the ground and excited states are similar and not affected by excitation [52–55]. Emission spectra of **4** showed a red shift and narrowing compared to the "mirror image" absorption spectrum. Fluorescence emission peaks were observed at 701 nm for **4**, 680 nm for **5**, 681 nm for **6**, and 702 nm for **7** in DMSO. The Stokes' shifts range from 10 to 30 nm.

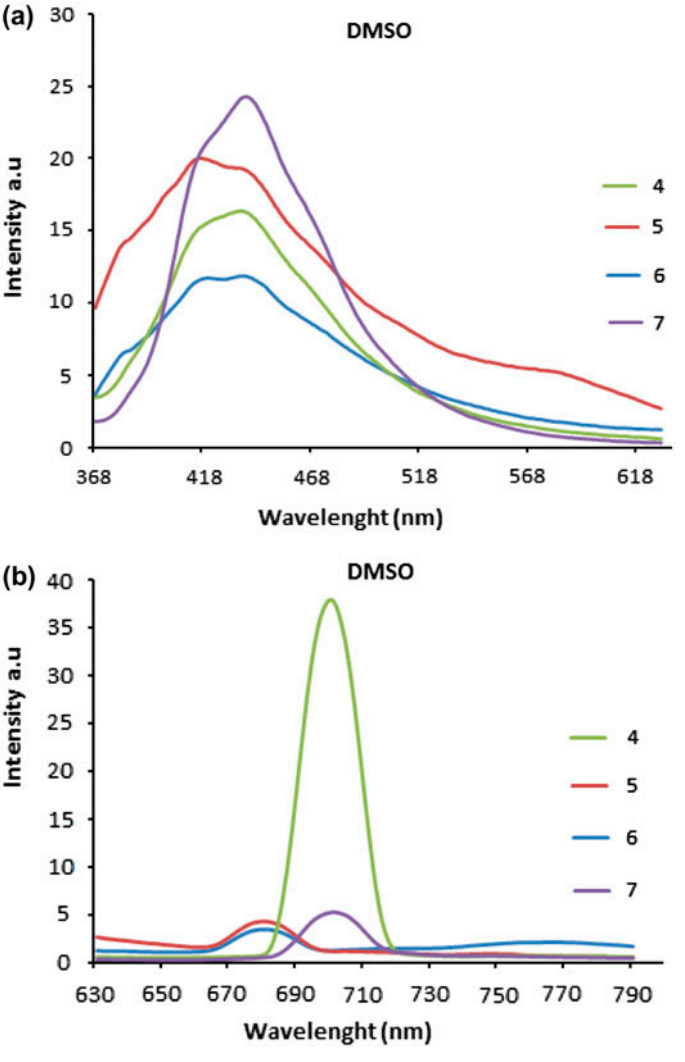


Figure 6. Fluorescence spectrum of all compounds in DMSO. Wavelength = 350 nm (a) and 620 nm (b).

The fluorescence quantum yields (Φ_F) of the magnesium (**4**), metal free (**6**), zinc (**7**), and quaternized (**5**) porphyrazines were determined using **ZnPc** as a standard using the comparative method [35] in DMSO. The fluorescence quantum yield (Φ_F) for metal-free (**6**) was low at Φ_F = 0.007. Similarly metal-free porphyrazine like phthalocyanines have been reported to give low Φ_F values depending on the substituents, with the values actually improving on insertion of the Zn central metal [56]. This is contrary to what would be expected based on the heavy atom effect where Zn would be expected to show low Φ_F values since it encourages intersystem crossing to the triplet state. Thus, unmetallated **6** gave Φ_F = 0.007 compared to **7** with Φ_F = 0.011. Complex **4**, containing Mg in the central cavity, showed a larger Φ_F value (0.039) compared to complex **6**, containing Zn central metal (Φ_F = 0.011). The latter is expected to encourage intersystem crossing to the triplet state,

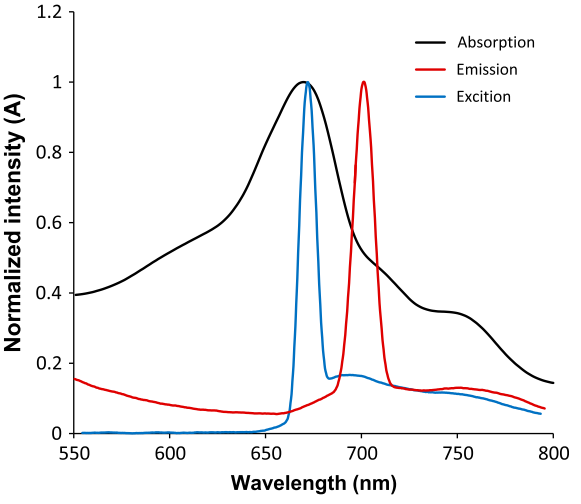


Figure 7. Absorption and fluorescence spectrum of MgPz in DMSO (λ_{exc} = 620 nm).

hence resulting in low Φ_F values. MgPcs have been found to give high fluorescence quantum yield values [57]. The same effect was observed for porphyrazines in this study. Quaternized complex **5** has a lower Φ_F (0.010) value than **4** in DMSO due to aggregation.

The fluorescence quantum yields (Φ_F) of metal-free (**6**), and the metallo complexes are lower than typical of phthalocyanines complexes in DMSO [58]. The fluorescence quantum yield (Φ_F) of zinc porphyrazine complex **7** (Φ_F = 0.011) is lower than for unsubstituted ZnPc (Φ_F = 0.20) [35] in DMSO.

5. Conclusion

Magnesium porphyrazines substituted with eight 3-quinolinecarboxy groups on the peripheral positions have been synthesized by esterification of octakis(hydroxyethylthio) derivative with 3-quinolinecarboxylic acid. The magnesium derivative **4** was converted into quaternized product **5** by reaction with dimethylsulphate. The metal-free derivative **6** was obtained by treatment with trifluoroacetic acid and its reaction with zinc(II) acetate led to the zinc derivative **7**. The new compounds have been characterized by elemental analysis, FT-IR, ^{1}H-NMR spectroscopy, and mass spectra. The spectral and photophysical properties of the porphyrazines were investigated in DMSO. Porphyrazines synthesized show the usual B (Soret) and Q-band absorptions. While complex **4** has the strong red emission from the lowest excited singlet state (S1), a broad and weak violet emission from S2 is also observed in the case of Soret band excitation, complex **7** and metal-free (**6**) show opposite fluorescence behavior. Water soluble complex **5** has the lower fluorescence quantum yield than complex **4** because of aggregation tendency.

Acknowledgements

This study was supported by Yildiz Technical University (Project No: 2011-01-02-GEP04 and project No: 2012-01-02-KAP03).

References

[1] S. Belviso, G. Ricciardi, F. Lelj. *J. Mater. Chem.*, **10**, 297 (2000).
[2] E.J. Baerends, S.J.A. van Gisbergen, A. Rosa, G. Ricciardi. *J. Phys. Chem. A*, **105**(13), 3311 (2001).
[3] K.A. Nguyen, R. Pachter. *J. Chem. Phys.*, **114**, 10757 (2001).
[4] L. Guo, D.E. Ellis, B.M. Hoffman, Y. Ishikawa. *Inorg. Chem.*, **35**, 5304 (1996).
[5] K. Deng, Z. Ding, D.E. Ellis, S.L.J. Michel, B.M. Hoffman. *Inorg. Chem.*, **40**, 1110 (2001).
[6] E.G. Sakellariou, A.G. Montalban, H.G. Meunier, G. Rumbles, D. Phillips, R.B. Ostler, K. Suhling, A.G.M. Barrett, B.M. Hoffman. *Inorg. Chem.*, **41**, 2182 (2002).
[7] S.J. Lange, J.W. Sibert, A.G.M. Barrett, B.M. Hoffman. *Tetrahedron*, **56**, 7371 (2000).
[8] T. Goslinski, C. Zhong, M.J. Fuchter, C. Stern, A.J.P. White, A.G.M. Barrett, B.M. Hoffman. *Inorg. Chem.*, **45**, 3686 (2006).
[9] S.L.J. Michel, D.P. Goldberg, C. Stern, A.G.M. Barrett, B.M. Hoffman. *J. Am. Chem. Soc.*, **123**, 4741 (2001).
[10] D.H. Hochmuth, S.L. Michel, A.J.P. White, D.J. Williams, A.G.M. Barrett, B.M. Hoffman, *Eur. J. Inorg. Chem*., 593 (2000).
[11] A. Koca, M. Şahin, A. Gül, R.Z. Uslu. *Monatsh. Chem.*, **133**, 1135 (2002).
[12] B.J. Vesper, K. Salaita, H. Zong, C.A. Mirkin, A.G.M. Barrett, B.M. Hoffman. *J. Am. Chem. Soc.*, **126**, 16653 (2004).
[13] K.M. Kadish, E. Van Caemelbecke, G. Royal. In *The Porphyrin Hand book*, K.M. Kadish, K.M. Smith, R. Guilard (Eds), Vol. 8, pp. 1–114, Academic Press (2000).
[14] K.M. Kadish, K.M. Smith, R. Guilard (Eds.). *The Porphyrin Hand book*, Vol. 8, pp. 17–114, Academic Press (2000).
[15] M. Gouterman. In *The Porphyrins*, D. Dolphin, (Ed.), Vol. III, p. 1, Academic Press, New York (1978).
[16] A.H. Jackson. In *The Porphyrins*, D. Dolphin, (Ed.), Vol. I, p. 365, Academic Press, New York (1978).
[17] J.P. Fitzgerald, B.S. Haggerty, A.L. Rheingold, L. May, G.A. Brewer. *Inorg. Chem.*, **31**, 2006 (1992).
[18] P.A. Stuzhin, M. Hamdush, U. Ziener. *Inorg. Chim. Acta*, **236**, 131 (1995).
[19] Y. Ni, J.P. Fitzgerald, P. Carroll, B.B. Wayland. *Inorg. Chem.*, **33**, 2029 (1994).
[20] B. Cosimelli, G. Roncucci, D. Dei, L. Fantetti, F. Ferroni, M. Ricci, et al. *Tetrahedron*, **59**, 10025 (2003).
[21] P. Kubát, J. Mosinger, J. Photoch. Photobio. A, *Chemistry*, **96**, 93 (1996).
[22] G. Li, S.K. Pandey, A. Graham, M.P. Dobhal, R. Mehta, Y. Chem, et al. *J. Org. Chem.*, **69**, 158 (2004).
[23] A.G. Montalban, W. Jarrell, E. Riguet. QJ. McCubbin, ME. Anderson, AJP. White, et al, *J. Org. Chem.*, **65**, 2472 (2000).
[24] W. Freyer, S. Flatau. *Tetrahedron Lett.*, **37**, 5083 (1996).
[25] E.G. Sakellariou, A.G. Montalban, S.L. Beall, D. Henderson, H.G. Meunier, D. Phillips, et al. *Tetrahedron*, **59**, 9083 (2003).
[26] E.G. Sakellariou, A.G. Montalban, H.G. Meunier, R.B. Ostler, G. Rumbles, A.G.M. Barrett, et al. *J. Photochem. Photobiol., A*, **136**, 185 (2000).
[27] A.G. Montalban, H.G. Meunier, R.B. Ostler, A.G.M. Barrett, B.M. Hoffman, G. Rumbles. *J. Phys. Chem. A*, **103**, 4352 (1999).
[28] E.G. Sakellariou, A.G. Montalban, H.G. Meunier, G. Rumbles, D. Phillips, R.B. Ostler, et al. *Inorg. Chem.*, **41**, 2182 (2002).
[29] P.A. Stuzhin, C. Ercolani. In *The Porphyrin Handbook*, K.M. Kadish, K.M. Smith, R. Guilard (Eds.), Vol. 15, p. 263, Academic Press (2003).
[30] N.Y. Coskun, O. Atak, F.A. Kılıçarslan, S.M. Yalçın, A. Gül. *Polish J. Chem.*, **82**, 2039 (2008).
[31] H. Akkuş, A. Gül. *Transit. Metal Chem.*, **26**, 689 (2001).
[32] A. Erdoğmuş, A. Koca, U. Avciata, A. Gül. *Polish J. Chem.*, **82**, 1541–1551 (2008).
[33] A. Erdoğmuş, A. Koca, U. Avciata, A. Gül. *Z. Anorg. Allg. Chem.*, **634**(14), 2649–2654 (2008).
[34] S. Frey-Forgues, D. Lavabre. *J. Chem. Educ.*, **76**, 1260–1264 (1999).
[35] A. Ogunsipe, J.Y. Chen, T. Nyokong. *New J. Chem.*, **28**, 822–827 (2004).
[36] T.D. Smith, J. Livorness, H. Taylor, *J. Chem. Soc. Dalton Trans.*, 1391–1400 (1983).
[37] A. Erdoğmuş, T. Nyokong. *J. Mol. Struc.*, **977**, 26–38 (2010).
[38] E. Gonca, A. Gül. *Inorg Chem Commun.*, **8**(4), 343–346 (2005).
[39] B. Akkurt, E. Hamuryudan. *Dyes Pigm.*, **79**(2), 153–158 (2008).
[40] İ. Özçeşmeci, O. Güney, Aİ. Okur, A. Gül, *J Porphyrins Phthalocyanines*, **13**, 753–759 (2009).
[41] İ. Özçeşmeci, O. Güney. Aİ. Okur, A. Gül, J, *Dyes Pigm.*, **75**, 761–765 (2007).
[42] H. Kunt, E. Gonca. *Polyhedron*, **38**(1), 218–223 (2012).
[43] T. Şimşek, E. Gonca. *Trans Met Chem*, **38**(1), 37–43 (2013).
[44] E. Gonca. *J Coord Chem.*, **66**, 1720–1729 (2013).
[45] E. Gonca. *Polyhedron*, **63**, 103–110 (2013).
[46] C.F. van Nostrum, R.J.M. Nolte, *Chem. Commun.*, 2385 (1996).
[47] A.E. Pullen, C. Faulmann, P. Cassoux, *Eur. J. Inorg. Chem.*, 269 (1999).
[48] (a) C.F. van Nastrum, F.B.G. Benneker, H. Brussaard, H. Kooijman, N. Veldman, A.L. Spek, et al. *Inorg. Chem*., 35, 959 (1996). (b) I. Yılmaz, A.G. Gürek, V. Ahsen, *Polyhedron,* **24**, 791 (2005).

[49] Q. Gan, F. Xiong. S. Li., S. Wang, *Inorg. Chem. Commun.*, **8**, 285–288 (2005).
[50] A. Erdoğmuş, T. Nyokong. *Dyes Pigm.*, **86**, 174–181 (2010).
[51] G. Gümrükçü, G.K. Karaoğlan, A. Erdoğmuş, A. Gül, U. Avcıata. *Dyes Pigm.*, **95**, 280–289 (2012).
[52] G. Yaşa, A. Erdoğmuş, A.L. Uğur, M.K. Şener, U. Avcıata, T. Nyokong. *J. Porphyrins Phthalocyanines*, **16**, 845–854 (2012).
[53] A. Erdoğmuş, T. Nyokong. *Dyes and Pigments*, **86**, 174–181 (2010).
[54] A. Erdoğmuş, S. Moeno, C. Litwinski, T. Nyokong. *J. Photochem. Photobiol., A*, **210**, 200–208 (2010).
[55] A. Erdoğmuş, T. Nyokong, *Inorg. Chim. Acta*, **362**, 4875–4883 (2009).
[56] T. Nyokong, E. Antunes. In K.M. Kadish, K.M. Smith, R. Guilard, *The Handbook of Porphyrin Science*, (Eds.), Vol. 7, Chap. 34, p. 247, Academic Press/World Scientific, New York/Singapore (2010).
[57] M. Canlica, T. Nyokong. *Inorg. Chim. Acta*, **363**, 3384 (2010).
[58] A.J.R. Williams. *Analyst*, **108**, 1067 (1983).