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SYNTHESIS, CHARACTERIZATION AND PHOTOPHYSICAL PROPERTIES OF EUROPIUM(III) PHTHALOCYANINES BEARING [4-(thiophen-3yl)-phenoxy]

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ABSTRACT

In this study, two novel phthalonitriles (1,4) and their corresponding metal-free (2,5) and Eu(III) phthalocyanine derivatives (3,6) bearing 4-(thiophen-3yl)-phenoxy groups were synthesized. These novel compounds were characterized by elemental analysis, FTIR, H NMR, UV-Vis, fluorescence, and mass spectroscopy. The aggregation behavior of these compounds was investigated in different solvents and concentrations. The effects of the substituent and the nature of the europium on the photophysical parameters are also reported.

Keywords: Phthalocyanine, fluorescence, aggregation, europium.

[4- (TİYOFEN-3İL) -FENOKSİ] GRUBU İÇEREN EUROPİYUM (III) FTALOSİYANİNLERİN SENTEZİ, KARAKTERİZASYONU VE FOTOFİZİKSEL ÖZELLİKLERİ

ÖZ

Bu çalışmada, iki yeni ftalonitril bileşiğinden hareket ile (1,4), bunların metal içermeyen bileşiği (2,5) ve Eu (III) ftalosiyanin bileşiği (3,6) olarak 4-(tiofen-3-il)-fenoksi grubunu içeren bileşikler sentezlendi. Sentezlenen yeni bileşikler, element analiz, FTIR, H NMR, UV-Vis, floresans ve kütle spektroskopisi ile karakterize edildi. Bu bileşiklerin agregasyon davranışı farklı çözücüler ve konsantrasyonlarda incelendi. Bağlı olan grubun ve Eu(III)'un metalinin fotofiziksel etkisi araştırıldı.

Anahtar Sözcükler: Ftalosiyanin, fluoresans, agregasyon, europium.

1. INTRODUCTION

Phthalocyanines have been widely used as organic dye stuffs since their first synthesis early last century because of their intense absorption of light in the visible and ultra-violet regions and their high chemical and thermal stabilities[1-2]. Sandwich-type phthalocyaninato complexes, in which two or three tetrapyrrole ligands are held by rare earth, actinide, and early transition metal or main group metals in close proximity, have been intensively studied over several decades in both fundamental academic and applied fields [3].

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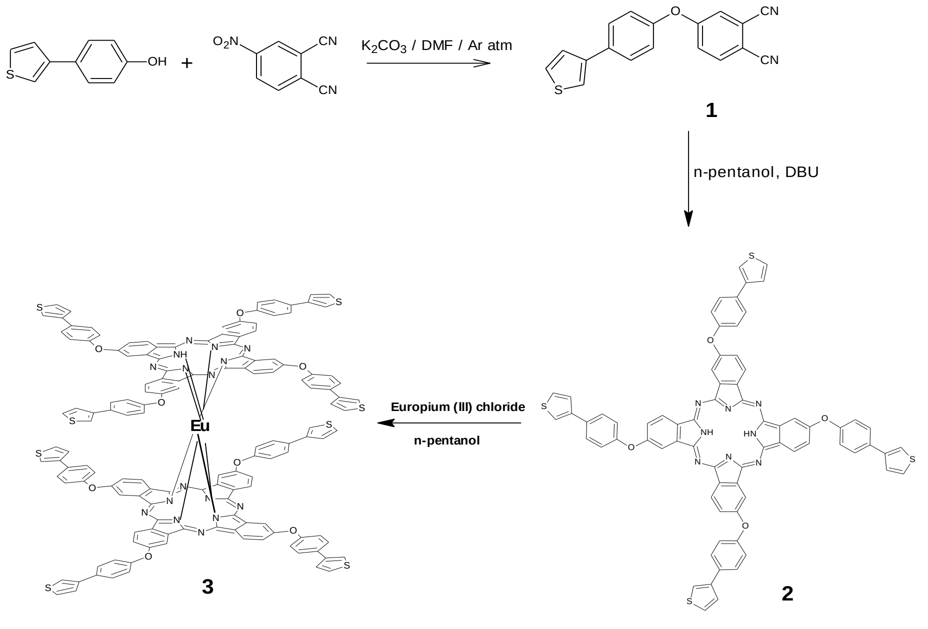
They are chemically robust and therefore have been used as dyes, pigments, catalysts for the removal of sulfur in oil, and more recently expanding in many fields such as xerography, photovoltaics, electrochromism, thermochromism, optical discs, laser dyes, liquid crystals, molecular metals, electro-catalysis, chemical sensors, magnetic materials, field effect transistors, photochemical hole burning, solar cell and photodynamic cancer therapy [4-9].

Structural control of their properties is possible by varying the nature of the center metal ion and the substituents on the phthalocyanine rings[10]. The electronic and steric effects of substituents can influence the orbital and molecular structure of the metallophthalocyanine (MPc) complexes, and thus affect intrinsic physicochemical properties. The presence of electron donating oxygen and sulfur groups on Pcs caused shifting of the Q-band to the longer wavelengths, which directly alter the electrochemical responses[11-14].

Our previous papers have described a series of symmetric Pcs carrying various substituents. An essential shortcoming of the Pcs remains in their low solubility and spectroscopic measurements in organic solvents which hinders their application in solution. Although mono and bis- phthalocyanines have frequently been described, comparison of those bearing different number of substituents at different positions have not been extensively studied, especially those bearing tetra- and octa- substituents. Thus in this study, we report on the effects of the position of substituent and europium. Also, we report on comprehensive investigation of solvents effects on the aggregation behaviors of phthalocyanine derivatives in different solvents.



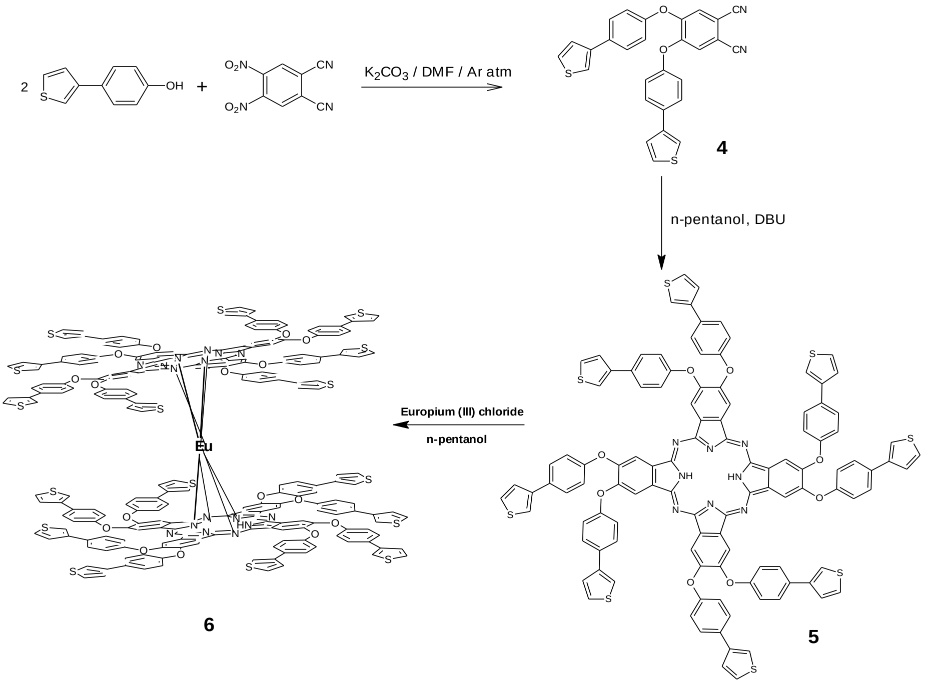
Schema 1. Synthetic pathway of tetra-[4-(thiophen-3yl)-phenoxy] substituted phthalonitriles and their metal-free and Eu(III) phthalocyanines derivatives

2. EXPERIMENTAL

2.1. Materials

All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. 4-(thiophen-3yl)-phenoxy was purchased from Aldrich. 4-Nitrophtalonitrile and 4,5-

Nitrophtalonitrile were synthesized and purified according to well-known literature. Flash column chromatography was carried out using silica gel 60 (0.04-0.063 mm) from Merck. All solvents were dried and purified as described by Perrin and Armarego[15].



Schema 2. Synthetic pathway of octa-[4-(thiophen-3yl)-phenoxy] substituted phthalonitriles and their metal-free and Eu(III) phthalocyanines derivatives

2.2. Equipment

The FT-IR spectra were recorded on a spectrum one Perkin Elmer 1600 FT-IR spectrophotometer, using ATR. ^{1}H NMR spectra were recorded on a Bruker Avance III 500 MHz spectrometer in $CDCl_3$, and chemical shifts were reported (δ) relative to Me_4Si as internal standard. Absorption spectra were recorded with an Agilent 8453 UV-Visible spectrophotometer. The elemental analyses and Bruker Microflex LT MALDI-TOF mass spectra were determined in the TUBITAK Laboratory (Center of Science and Technology Research of Turkey). Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectra fluorometer using 1 cm path length cuvettes at room temperature.

2.3. Photophysical Parameters

2.3.1. Fluorescence quantumields

Fluorescence quantum yields (Φ_F) were determined by the comparative method using Eq.1 [16],

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

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_{Std}^2 are the refractive indices of solvents used for the sample and standard, respectively. Unsubstituted ZnPc (in DMSO) (Φ_F = 0.20) [17-18] was employed as the standard. The complexes and the standart were excited at the same appropriate wavelength.

2.4. Synthesis

2.4.1. 4-[4-(thiophen-3-yl)phenoxy]phthalonitrile)(1)

4-Nitrophthalonitrile (1.2 g, 6.94 mmol was dissolved in 20 mL dry DMF under N_2 atmosphere, and of 4-(thiophen-3yl)-phenoxy (1.1 g, 6.94 mmol) was added to mixture. After stirring for 30 min. at 60 ^oC, finely ground anhydrous K_2CO_3 (3.83 g, 27.76 mmol) was added portion wise within 1 h [16-17]. The reaction mixture was stirred under N_2 at 60 ^oC for 2 days. At the end of this time, the reaction mixture was poured into ice-water (150.0 g) and stirred at room temperature for 1 h to yield a crude product. Aqueous phase was extracted with chloroform (4x30 mL). The combined extracts were dried over anhydrous sodium sulfate. The crude product was further purified by chromatography over a silica gel column a mixture of $CHCI_2$: MeOH (10:1 by volume) as eluents. Yield: 0.75 g, 64.32 %. Calc. for $C_{18}H_{10}N_2OS$: C, 71.50; H, 3.33; N, 9.27; S, 10.61 %; Found: C, 71.44; H, 3.38; N, 9.11; S, 10.53 %. FT-IR (ATR), υ/cm^{-1}: 3080-3040 (aromatic-CH), 2965-2847 (aliphatic-CH_2), 2225 (C≡N), 1244-1170 (C-O-C), 1032-781 (C-S-C). ^1H NMR ($CDCl_3$): δ (ppm) 5.70-6.78 (t, 2 H, S-CH_2), 6.92 (s, 1H, S-CH), 7.2-8.6 (m, 7 H, aromatic): ESI-MS (m/z): 303.27 $[M+H]^+$

2.4.2. 2(3),9(10),16(17),23(24)-[4-(thiophen-3yl)-phenoxy] phthalocyanine (2)

A mixture of *4-[4-(thiophen-3-yl)phenoxy]phthalonitrile* **(1)** (0.25 g, 0.80 mmol) and catalytic amount of 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU) in 2.5 ml of dry n-pentanol was heated and stirred at 160 ^oC in a sealed glass tube for 8 h under N_2. After cooling to room temperature the green crude product was precipitated with ethanol, filtered and washed first with ethanol then hexane and then dried in vacuum. Finally, pure metal-free phthalocyanine was purified by chromatography over a silica gel column using $CHCl_{3:}$ THF (10:1) as eluents. Yield: 0.10 g, 40.32 %. Calc. for $C_{72}H_{42}N_8O_4S_4$: C, 71.32; H, 3.46; N, 9.24; S, 10.56 %; Found: C, 71.39; H, 3.49; N, 9.25; S, 11.02 %. FT-IR (ATR), υ/cm^{-1}: 3285 (N-H), 3085-3037 (Aromatic C-H), 2962 (aliphatic -CH_2), 1220 and 1166 (C-O-C), 1080 and 773 (C-S-C). MALDI-TOF (m/z): 1211.1 $[M]^+$

2.4.3. 2(3),9(10),16(17),23(24)-[4-(thiophen-3-yl)-phenoxy]phthalocyaninato Europium(III) (3)

The phthalocyanine compound (**2**) (0.02 g, 0.01 mmol) and anhydrous $EuCl_3$ (0.001 g, 0.005 mmol) in n-pentanol (1.0 mL), in the presence of a drop of 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU) was heated and stirred at 140 ^oC for 4 h under N_2. Yield: 0.013 g, 52%. FT-IR (ATR), υ/cm^{-1}: 3090-3050 (Aromatic C-H), 2965 (aliphatic -CH_2), 1217 and 1090 (C-O-C), 1063 and 742 (C-S-C). MALDI-TOF (m/z): 2576.81 $[M+ 4H]^+$

2.4.4. 4,5-bis[4-(thiophen-3-yl)phenoxy]phthalonitrile (4)

4,5-Dinitrophthalonitrile (1.20 g, 6.94 mmol was dissolved in 20 mL dry DMF under N_2 atmosphere, and of 4-(thiophen-3yl)-phenoxy (2.23 g, 13.02 mmol) was added to mixture. After stirring for 30 min. h at 60 ^oC, finally ground anhydrous K_2CO_3 (3.83 g, 27.76 mmol) was added portion wise within 1 h [16-17]. The reaction mixture was stirred under N_2 at 60 ^oC for 24 h. At the end of this time, the reaction mixture was poured into ice-water (150.0 g) and stirred at room temperature for 1 h to yield a crude product. Aqueous phase was extracted with chloroform (4x30 mL). The combined extracts were dried over anhydrous sodium sulfate. The crude product was further purified by chromatography over a silica gel column a mixture of $CHCI_2$: MeOH (10:1 by volume) as eluents. Yield: 1.19 g, 64.32 %. Calc. for $C_{28}H_{16}N_2O_2S_2$: C, 70.57; H, 3.38; N, 5.88; S, 13.46 %; Found: C, 70.25; H, 3.37; N, 5.31; S, 13.84 %. FT-IR (ATR), υ/cm^{-1}: 2962 (aliphatic-CH_2), 2853 (O-CH_2), 2212 (C≡N), 1280 and 1125 (C-O-C_{ether}), 781 (C-S-C). ^{1}H NMR ($CDCl_3$): δ (ppm) 5.90-6.82 (t, 4 H, S-CH_2), 6.96 (s, 2H, S-CH), 7.6-8.8 (m, 10 H, aromatic): ESI-MS (m/z): 477.66 $[M]^+$

2.4.5. 4,5-bis[4-(thiophen-3-yl)phenoxy]phthalocyanine (5)

A mixture of 4,5-bis[4-(thiophen-3-yl)phenoxy]phthalonitrile**(4)** (0.25 g, 0.52 mmol) and catalytic amount of 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU) in 2.5 mL of dry n-pentanol was heated and stirred at 160 ^oC in a sealed glass tube for 10 h under N_2. After cooling to room temperature the green crude product was precipitated with ethanol, filtered and washed first with ethanol then hexane and then dried in vacuum. Finally, pure metal-free phthalocyanine was purified by chromatography over a silica gel column using $CHCl_3$:THF (10:1) as eluents. Yield: 0.17 g, 54.10 %. Calc. for $C_{112}H_{66}N_8O_8S_8$: C, 70.44; H, 3.45; N, 5.87; S, 13.40 % ; Found: C, 70.49; H, 3.47; N, 5.89; S, 13.44 %. FT-IR (ATR), υ/cm^{-1}: 3294 (N-H), 3080-3050 (Aromatic C-H), 2926 (aliphatic -CH_2), 1208 and 1170 (C-O-C), 1012 and 776 (C-S-C). MALDI-TOF (m/z): 1908.55 $[M]^+$

2.4.6. 4,5-bis[4-(thiophen-3-yl)phenoxy] phthalocyaninato Europium (III) (6)

The phthalocyanine compound (**5)** (0.02 g, 0.01 mmol) and anhydrous $EuCl_3$ (0.001 g, 0.005 mmol) in n-pentanol (1 mL), in the presence of a drop of 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU) was heated and stirred at 140 ^oC for 4 h under N_2. Yield: 0.007 g, 70%. FT-IR (ATR), υ/cm^{-1}: 3080-3055 (Aromatic C-H), 2964 (aliphatic -CH_2), 1240 and 1166 (C-O-C), 1062 and 777 (C-S-C). MALDI-TOF (m/z): 3965.41 $[M + 8H]^+$.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization

Schema 1 and 2 show the synthetic route involved for the formation of the phthalonitriles and their metal-free and Eu(III)phthalocyanines derivatives **1-6**. Tetra- and octa-substituted phthalocyanines have been obtained from 2,3-dinitrile derivative with desired substituents. Synthesis of metal-free phthalocyanine **2** and **5** were formed by cyclotetramerization of compounds **1** and **4**. The Europium phthalocyanines (**3** and **6**) were formed by the **2** and **5** in the presence of anhydrous $EuCl_3$. Purification of the complexes was achieved by column chromatography.

FTIR, UV-vis, H-NMR and mass spectroscopies, as well as elemental analysis performed the characterizations of metal-free and Europium (III) phthalocyanines. FTIR spectroscopies have been proved the nature of phthalonitrile ligands and conversion to the metal-free and complexes.

The characteristic vibrations corresponding to $C\equiv N$ were observed at 2230 cm^{-1} and 2234 cm^{-1} for **1** and **4** in the FTIR spectra, respectively. The strong CN vibrations of **1** and **4** were disappeared after conversion to the metal-free and complexes **2, 3, 5 and 6**. The ether (C-O-C) and the tiofen (C-S-C) vibrations for compounds **1, 4** were observed at 1244 cm^{-1} and 781 cm^{-1} at 1280 cm^{-1} and 782 cm^{-1}, respectively. In complexes, the characteristic vibrations corresponding the ether (C-O-C) and thiophen (C-S-C) were observed at 1217 cm^{-1} and 742 cm^{-1} for **3**, 1240 cm^{-1} and 777 cm^{-1} for **6**. Metal-free derivatives **(2, 5)** of protons in the inner core of phthalocyanine are screened by aromatic π electrons of the macrocyclic, so they appeared at -1.20 **(2)** and -1.10 **(5)** ppm in the ^{1}H NMR. In addition to these verifying results for the structures, the mass spectra of compounds **(1-6)** gave the characteristic molecular ion peaks at m/z: 303.27 [M + H]$^{+}$, 1211.1 [M]$^{+}$, 2576.81 [M $^{+}$+ 4H^{+}], 477.66 [M^{+}], 1908.55 [M^{+}], 3995.41 [M^{+} +8 H^{+}] respectively, confirming the proposed structures **Schema 1**-**2**, and mass spectrum of the **(2)** and **(4) fig.1.**

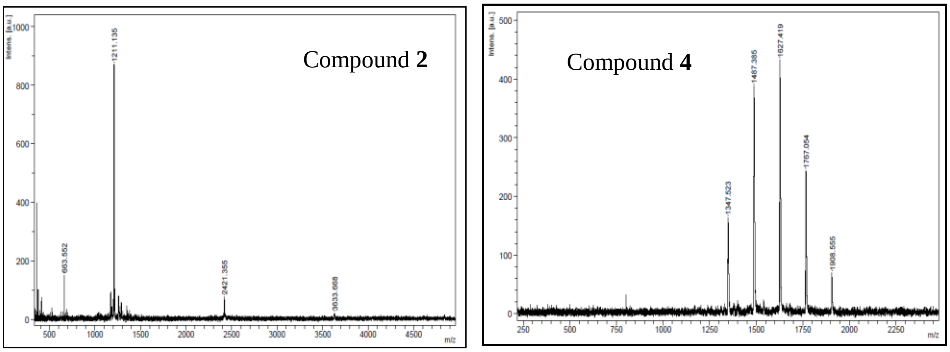


Figure 1. Mass spectra of compounds **2** and **4**.

3.2. Ground state electronic absorption

Electronic spectra are especially useful to establish the structure of the phthalocyanine. The ground state electronic absorption spectra of the metal-free **(2,5)** and Europium (III) phthalocyanines **(3,6) fig. 2**-**3**, respectively.

The UV-Vis absorption spectrum of metal-free phthalocyanines **(2,5)** showed characteristic two absorption bands at Q band region around 670-674 nm due to peripheral substitution and 698-704 nm due to non-peripheral substitution in different solution. The typical UV-Vis absorption spectrum of europium(III) phthalocyanines **(3, 6)** exhibited a characteristic by a single Q band in the visible region at 690 nm and 670 nm. It is attributed to the $\pi\rightarrow\pi^*$ transitions from the highest occupied molecular orbital **(HOMO)** to the lowest unoccupied molecular orbital **(LUMO)** of the Pc^{2-} ring. Compounds **3** and **6** show an additional band centered at 610 nm and 630 nm, respectively, as a result of aggregation through excitation coupling of the Pc units. The B-bands are broad due to the superimposition of the B_1 and B_2 bands in the 340-360 nm region for the metal-free and Europium(III) phthalocyanines. The broadening observed in Q and B bands of the both metal-free and europium phthalocyanines is attributed to $\pi\rightarrow\pi^*$ transition of the non-bonding electrons associated with peripheral S and O atoms.

The Q bands of the non-peripheral substituted Europium(III) phthalocyanines are red-shifted when compared to the corresponding peripheral tetra- and octa- substituted complexes in $CHCl_3$. The observed red spectral shifts are typical of Pcs with substituents at the non-peripheral position and have been explained in literature.

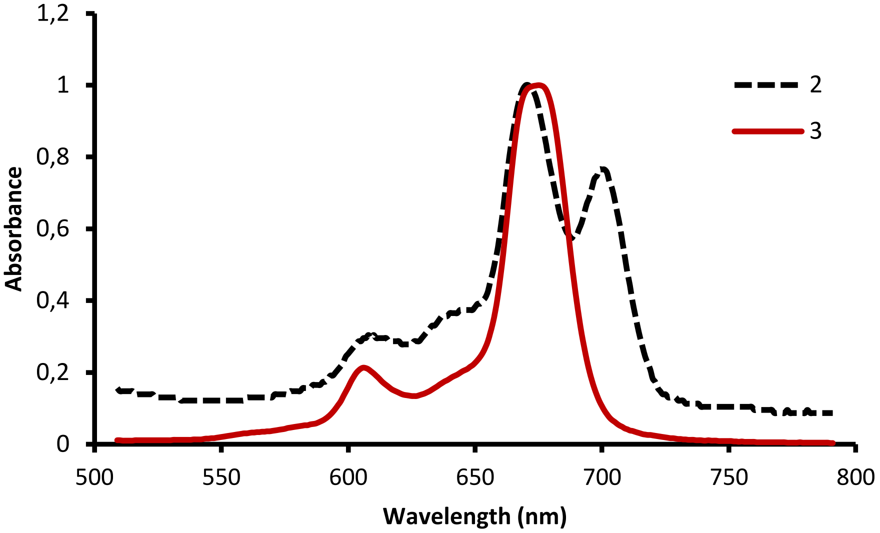


Figure 2. UV-Vis spectra of compound **2,3** in DMSO

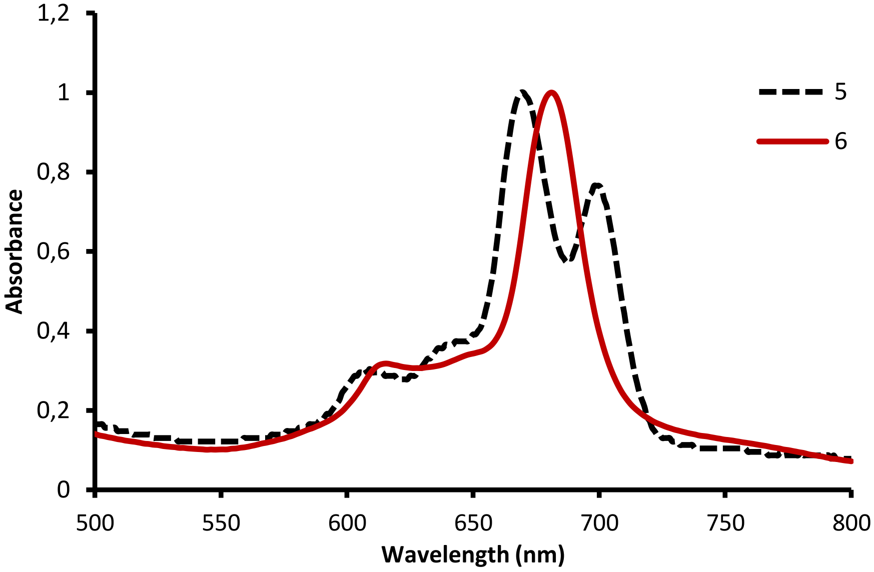


Figure 3. UV-Vis spectra of compound **5,6** in DMF

3.3. Aggregation Studies

Aggregation is usually depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes. It is dependent on the concentration, nature of the solvent, nature of the substituents, complexes metal ions and temperature. It has been established that Pcs can form H- and J-aggregates depending on the orientation of the induced transition dipoles of their constituent monomer. In H-aggregates, the component monomers are arranged into a face-to-face conformation, and transition dipoles are perpendicular to the line connecting their centers.

In this study, the aggregation behavior of 4-(thiophe-3yl)-phenoxy substituted metal-free and Europium phthalocyanines were investigated in different solvents such as $CHCl_3$, CH_2Cl_2, DMF, THF and DMSO. Aggregation is usually depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes. As the concentration was increased, the intensity of absorption of the Q band also increased and there were no new bands due to the aggregated species. Beer-Lambert law was obeyed for all of these compounds at concentration ranging from $2x10^{-6}$ to $12x10^{-6}$ M. Metal-free and Europium phthalocyanines did not show aggregation at these concentrations in $CHCl_3$ **fig.4.**

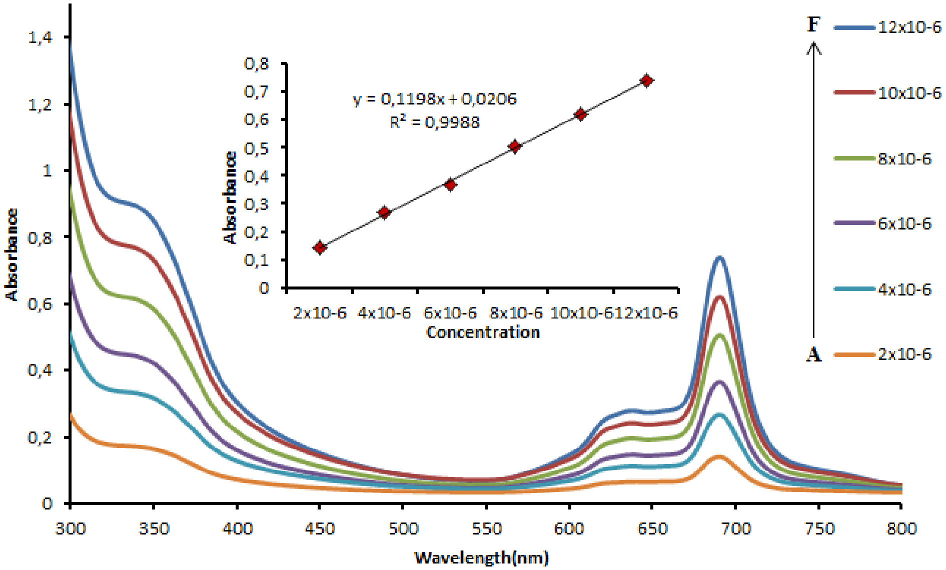


Figure 4. UV-vis spectra of compound **6** in $CHCl_3$ at different concentration.

3.4. Fluorescence spectra

Photophysical studies were carried out in $CHCl_3$, DMF and DMSO. The complexes and the standart were excited at the same appropriate wavelength. All spectral and fluorescence data are given in **Table 1**.

Fig.5 and **fig.6** shows fluorescence emission and excitation spectra of Europium phthalocyanines **3** in DMF and **6** in DMSO. 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 suggest that the nuclear configurations of the ground and excited states are similar and not affected by excitation[18-19]. The Stokes' shifts range from 3 to 19 nm, which is usual for ZnPc derivatives [20].

The proximity of the wavelength of each component of the Q-band absorption to the Q-band maxima of the excitation spectra for phthalocyanines **3** suggests that the nuclear configurations of the ground and excited states are similar and not affected by excitation in $CHCl_3$. For the octa substituted bis-Europium (III) phthalocyanine complex **6**, the shape of excitation spectrum was different from the absorption spectrum when compare to **3**. This suggests that there are changes in the molecule following excitation most likely due to loss of symmetry [17-19]. The observed Stokes shifts were within the region observed for metal-free and Europium phthalocyanines.

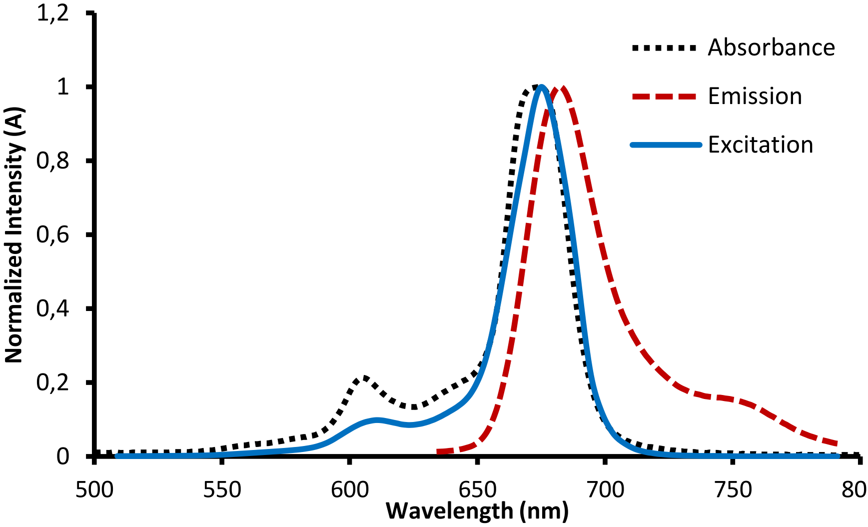


Figure 5. Absorption, excitation and emission spectra of the compounds **3** in DMF

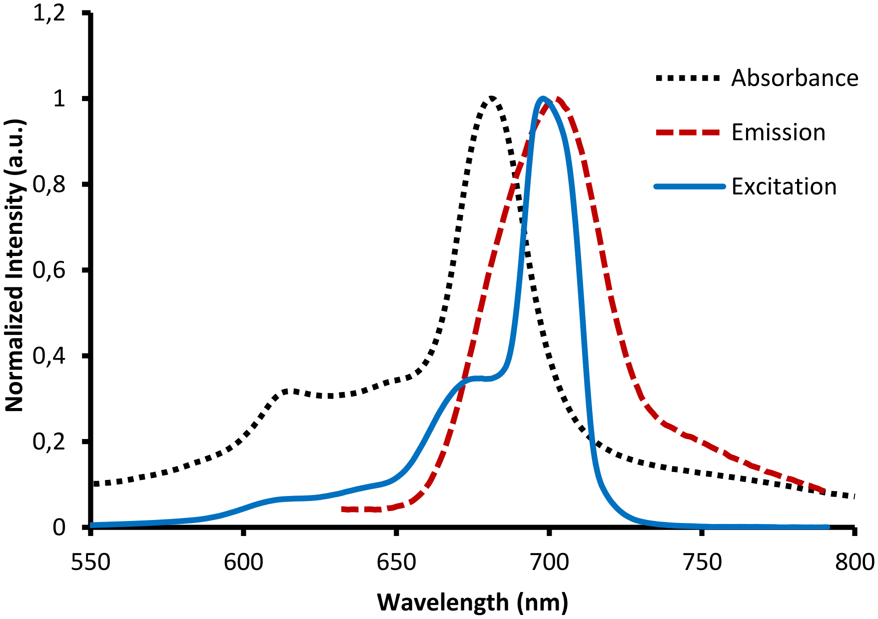


Figure 6. Absorption, excitation and emission spectra of the compounds **6** in DMSO

The small stokes shifts suggest that the structural change between the ground and excited states are small. The Q bands of all the excitation spectra suggests that following excitation, there were some changes in the molecule, presumably due to loss of symmetry. This loss of symmetry may be the cause of the slight broadening of the fluorescence spectra stated above [20-22].

Fluorescence quantum yield (Φ_F) values can be affected by a number of factors that include temperature, molecular structure and solvent parameters, such as polarity, viscosity, refractive index, and the presence of heavy atoms in the solvent molecule [23-24]. **Table 1** shows Φ_F values of Pc derivatives studied in this work. DMF, yielded the highest Φ_F values of 0.2202 for complex **2** and CH_2Cl_2, yielded the lowest Φ_F values of 0.0051 for complex **5**. Φ_F values in the three solvents demonstrate that fluorescence is influenced by the environment of the fluorescing molecule, e.g., solvent parameters.

Table 1. UV-vis spectral and photophysical parameters for all compounds

Sample	**Solvent**	**λ_B (Abs)/ nm**	**λ_B (Ems) / nm**	**λ_B (Exc) / nm**	**$\Delta\lambda_{Stokes}$/ nm**	**Φ_{Φ}**
2	$CHCl_3$	674(4.13) 704(4.03)	710	703	6	0.0887
	DMF	670(4.11) 700(4.21)	708	701	8	0.0751
	DMSO	670(4.25) 700(4.49)	706	691	6	0.0753
3	$CHCl_3$	690(4.75)	709	670	19	0.0478
	DMF	670 (4.63)	679	688	9	0.0263
	DMSO	674(4.55)	682	686	8	0.0301
5	$CHCl_3$	672(4.31) 701(4.14)	693	706	5	0.0107
	DMF	669(4.82) 698(4.03)	689	703	5	0.0716
	DMSO	670(4.11) 700(4.10)	693	706	6	0.0051
6	$CHCl_3$	690(4.79)	693	705	3	0.0093
	DMF	681(4.87)	691	698	10	0.0137
	DMSO	684(4.85)	693	686	9	0.0136

4. CONCLUSION

In conclusion, we have described the synthesis, spectral characterization and photophysical properties of new tetra and octa substituted metal-free and Europium phthalocyanines with bulky 4-(thiophen-3yl)-phenoxy groups on the periphery. Bulky 4-(thiophen-3yl)-phenoxy groups enhancive solubility of these metal-free and Europium phthalocyanines derivatives in polar organic solvents. The spectral and fluorescence properties of the phthalocyanines were investigated in $CHCl_3$, DMF and DMSO. All phthalocyanines did not show any aggregation concentration ranges between $2x10^{-6}$ M and $12x10^{-6}$ M. Fluorescence emission peaks were observed all the complexes feature similar fluorescence emission.

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