Research Article

SYNTHESIS, CHARACTERIZATION, SPECTRAL, AGGREGATION AND FLUORESCENCE AND IMPROVED PHOTOPHYSICAL PROPERTIES OF (ethylsulfanyl) PORPHYRAZINES CONTAINING β-THIOETHER APPENDED [(bpy)₂RuCl₂]

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ABSTRACT

In this study, (ethylsulfanyl) porphyrazines have been modified with one peripheral ruthenium bipyridine groups. These compounds possess (bpy)₂Ru^{II} moieties directly attached to the β position in the (ethylsulfanyl) porphyrazines through thioether chelation. The new compounds have been characterized by elemental analysis, FT-IR, ^{1}H-NMR spectroscopy and mass spectra. The spectral properties such as electronic spectra, aggregation and fluorescence of compounds have been studied in THF. Insertion of (bpy)₂Ru^{II} moiety on the porphyrazines structure have been investigated photophysical properties of the complexes.
Keywords: Porphyrazines, bipyridine, ruthenium, fluorescence, photophysics.

1. INTRODUCTION

Porphyrazines share structural similarities with porphyrins and phthalocyanines. They have diverse applications such as biomedical agents for diagnosis and therapy, precursors to new conducting materials, chemical sensors, ladder polymers and dyes [1]. Of much interest to this class of compounds is the role they play as potential photosensitisers in the treatment of tumors, a process known as photodynamic therapy (PDT) [2-5]. Porphyrazines have been synthesized by the template cyclization of maleonitrile derivatives [6,7].

Transition metal porphyrazines peripherally substituted with thioether groups are a new interesting class of complexes. They conjugate, indeed, the peculiar electronic and structural properties of porphyrazines with the peripheral coordinating capability of the (alkylS)₈ cage [8]. The transition metal ion in the inner core offers new ways to induce, modify and to control molecular properties [9].

Ruthenium(II) complexes have attracted a great deal of attention due to their unique spectroscopic and electrochemical properties [10–13]. Ruthenium polypyridyl complexes have

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received special attention due to their strong metal to ligand charge transfer (MLCT) absorption, their unique emission characteristics, the perturbance of which could be exploited to study their DNA binding properties [14–16]. The di- and oligomeric metalloporphyrins and polypyridylruthenium(II) complexes and their molecular arrays are acquiring particular research attention as potential candidates for device application in photovoltaic's, rectifiers, switches, logic gates, circuits and sensors etc. [17, 18]. These hybrid systems are specifically suitable because of their characteristic photo physical properties such as long lived MLCT excited states, intense absorption in the visible region and redox stability of the individual molecular units [19, 20]. Over the past few years Prasad and coworkers have been engaged in synthesis and study of metallo-tetraazaporphyrin/polypyridylruthenium(II) linked molecular arrays [21–22]. Prasad and coworkers have also fabricated metallo-tetraazaporphyrin based potentiometric sensors for a few cations and anions [22–24].

Chelating bidentate N-donor ligands such as 2,2'-bipyridine to ruthenium(II) have also proven effectiveness in catalysis [25]. In their investigations, they found that the catalytic properties in this reaction was dependent on the 2,2'-bipyridine structure. Thus, introducing dendritic bipyridine ligands in such systems should improve the stability, solubility, efficiency and recyclability of the catalyst [26].

In this study, four new dinuclear complexes were synthesized. These complexes possess $(bpy)_2Ru^{II}$ moieties directly attached to the β position in the (ethylsulfanyl) porphyrazines through thioether chelation. The new compounds have been characterized by elemental analysis, FT-IR, ^{1}H-NMR spectroscopy and mass spectra. Photophysical properties were examined by performing fluorescence spectrophotometer and we investigated that the $(bpy)_2Ru^{II}$ structure was effects on the fluorescent properties for the first time. Insertion of $(bpy)_2Ru^{II}$ moiety on the porphyrazines structure (**1,2,3,4**) were improved photophysical properties of the complexes (**5,6,7,8**).

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 ethane thio maleonitril salt were prepared according to the previously reported procedures [27,28]. 2,3,7,8,12,13,17,18- octakis(ethylsulfanyl)- 5,10,15,20 porfirazinato magnesium(II) was prepared according to ref. 29. 2,3,7,8,12,13,17,18- octakis(ethylsulfanyl)-5,10,15,20-21*H*,23*H* porphyrazine was prepared according to ref. 30. 2,3,7,8,12,13,17,18- octakis(ethylsulfanyl)-5,10,15,20 porfirazinato nickel(II) was prepared according to the procedure reported in ref. 30 for the synthesis of similar nickel(II) (alkylsulfanyl)porphyrazines. 2,3,7,8,12,13,17,18-octakis(ethylsulfanyl)- 5,10,15,20 porfirazinato zinc(II) was prepared according to ref. 31.

2.2. Equipment

FT-IR spectra were recorded on a spectrum one Perkin Elmer FT-IR spectrophotometer using ATR. ^{1}H NMR spectra were recorded on a Bruker Avance III 500 MHz spectrometer. Absorption spectra were recorded with an Agilent 8453 UV-visible spectrophotometer. Elemental analyses were obtained with a Thermo Flash EA 1112 Series. The mass spectra were acquired on a 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 spectrofluorometer using 1 cm path length cuvettes at room temperature.

All chemicals used were of an analytical grade. Solvents were purified with conventional methods.

2.3. Photophysical parameters

2.3.1. Fluorescence quantum yields

Fluorescence quantum yields (Φ_F) were determined by the comparative method using Eq. 1 [32],

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

where F and F_{Std} are the areas under the fluorescence emission curves of the all samples 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) ($\Phi_F = 0.20$) [33] was employed as the standard. Both the samples and standard were excited at the same wavelength.

2.4. SYNTHESIS

2.4.1. Synthesis of [MgPz{Ru(bpy)$_2$}][PF$_6$]$_2$ complex, (5)

0.0817 g (0.1mmol) MgPz (**1**) and 0.052 g (0.1 mmol) [(bpy)$_2$RuCl$_2$].2H$_2$O in benzene/MeOH (1:2) mixture were stirred and reflux for 18 h. The resulting solution was filtered and volume was reduced to *ca.*2 mL by evaporation. To this was added a few drops of concentrated NH$_4$PF$_6$ in MeOH and the solid that separated out was filtered and purified by passage through cellulose column, eluting with CH$_2$Cl$_2$/petroleumether (3:1).

Yield: 0.092 g (60.5%). Calc. for C$_{52}$H$_{56}$F$_{12}$MgN$_{12}$P$_2$RuS$_8$: C 41.06, H 3.71, N 11.05 %; Found: C 40.67, H 3.32, N 11.45. FT-IR (ATR), υ/cm^{-1}: 2958 and 2920 (aliphatic CH$_2$), 1442 (bipyridine), 840 ([PF$_6$]$^-$): ^{1}H NMR(CDCl$_3$) : δ (ppm) 7.40-6.70 (m, 16 H, bpy-CH), 4.40-3.60 (m, 16 H, -SCH$_2$), 2.20-1.20 (m, 24 H, -CH$_3$): UV-Vis (THF) λ_{max}/nm (logε/dm^{3}mol^{-1}cm^{-1}) : 280 (5.00), 375 (4.80), 672 (4.70). MS (MALDI-TOF) m/z: Calc. 1520.91; Found: 1644.28 [M + 3AN]

2.4.2. Synthesis of [H$_2$Pz{Ru(bpy)$_2$}][PF$_6$]$_2$ complex, (6)

0.0795 g (0.1mmol) H$_2$Pz (**2**) and 0.052 g (0.1 mmol) [(bpy)$_2$RuCl$_2$].2H$_2$O in benzene/MeOH (1:2) mixture were stirred and reflux for 18 h. The resulting solution was filtered and volume was reduced to *ca.*2 mL by evaporation. To this was added a few drops of concentrated NH$_4$PF$_6$ in MeOH and the solid that separated out was filtered and purified by passage through cellulose column, eluting with CH$_2$Cl$_2$/petroleumether (3:1).

Yield: 0.078 g (52.07%). Calc. for C$_{52}$H$_{58}$F$_{12}$N$_{12}$P$_2$RuS$_8$: C 41.68, H 3.90, N 11.22 %; Found: C 41.43, H 3.49, N 11.65 %. FT-IR (ATR), υ/cm^{-1}: 3284 (NH), 2962 and 2924 (aliphatic CH$_2$), 1442 (bipyridine), 830 ([PF$_6$]$^-$):^{1}H NMR(CDCl$_3$) : δ (ppm) 7.50-6.60 (m, 16 H, bpy-CH), 4.45-3.90 (m, 16 H, -SCH$_2$), 2.20-1.10 (m, 24 H, -CH$_3$), -1.05 (s, 2H, NH). : UV-Vis (CHCl$_3$) λ_{max}/nm (logε/dm^{3}mol^{-1}cm^{-1}) : 294 (4.56), 350 (4.36), 657 (4.12), 712 (4.14). MS (MALDI-TOF) m/z: Calc. 1498.62; Found:1245.75 [M – 2[PF$_6$]+ AN]$^{4-}$

2.4.3. Synthesis of [NiPz{Ru(bpy)$_2$}][PF$_6$]$_2$ complex, (7)

0.012 g (0.014 mmol) NiPz (**3**) and 0.0073 g (0.014 mmol) [(bpy)$_2$RuCl$_2$].2H$_2$O in benzene/MeOH (1:2) mixture were stirred and reflux for 18 h. The resulting solution was filtered and volume was reduced to *ca.*2 mL by evaporation. To this was added a few drops of concentrated NH$_4$PF$_6$ in MeOH and the solid that separated out was filtered and purified by passage through cellulose column, eluting with CH$_2$Cl$_2$/petroleumether (3:1).

Yield: 0.0092 g (42.01%). Calc. for C$_{52}$H$_{56}$F$_{12}$N$_{12}$NiP$_2$RuS$_8$: C 40.16, H 3.63, N 10.81 %; Found: C 40.27, H 3.70, N 11.15 %. FT-IR (ATR), υ/cm^{-1}: 2958 and 2920 (aliphatic CH$_2$), 1442 (bipyridine), 840 ([PF$_6$]$^-$): ^{1}H NMR(CDCl$_3$) : δ (ppm) 7.50-6.70 (m, 16 H, bpy-CH), 4.40-3.50 (m, 16 H, -SCH$_2$), 2.20-1.10 (m, 24 H, -CH$_3$): UV-Vis (THF) λ_{max}/nm (logϵ/dm^{3}mol^{-1}cm^{-1}) : 280 (4.93), 343 (4.10), 662 (4.06). MS (MALDI-TOF) m/z: Calc. 1555.29; Found: 1646.1 [M – [PF$_6$] + DHB + AN]

2.4.4. Synthesis of [ZnPz{Ru(bpy)$_2$}][PF$_6$]$_2$ complex, (8)

0.1715 g (0.20 mmol) ZnPz (**4**) and 0.104 g (0.20 mmol) [(bpy)$_2$RuCl$_2$].2H$_2$O in benzene/MeOH (1:2) mixture were stirred and reflux for 18 h. The resulting solution was filtered and volume was reduced to *ca.*2 mL by evaporation. To this was added a few drops of concentrated NH$_4$PF$_6$ in MeOH and the solid that separated out was filtered and purified by passage through cellulose column, eluting with CH$_2$Cl$_2$/petroleumether (3:1).

Yield: 0.23 g (73.72%). Calc. for C$_{52}$H$_{56}$F$_{12}$N$_{12}$P$_2$RuS$_8$Zn: C 39.98, H 3.61, N 10.76 %; Found: C 39.57, H 3.79, N 11.18 %. FT-IR (ATR), υ/cm^{-1}: 2959 and 2921 (aliphatic CH$_2$), 1443 (bipyridine), 840 ([PF$_6$]$^-$): ^{1}H NMR(CDCl$_3$) : δ (ppm) 7.50-6.70 (m, 16 H, bpy-CH), 4.40-3.50 (m, 16 H, -SCH$_2$), 2.20-1.10 (m, 24 H, -CH$_3$): UV-Vis (THF) λ_{max}/nm (logϵ/dm^{3}mol^{-1}cm^{-1}) : 282 (5.13), 393 (4.61), 671 (4.57). MS (MALDI-TOF) m/z: Calc. 1562.01; Found: 1275.11 [M – 2[PF$_6$]]$^{3+}$

3. RESULTS AND DISCUSSION

3.1. Synthesis and characterization

Precursor complexes [(ethyl sulfanyl)porphyrazines] (**1, 2, 3, 4**) were synthesized according to the procedure reported in ref. [29-31]. These complexes upon reaction with equimolar amount of [Ru(bpy)$_2$Cl$_2$].2H$_2$O yielded peripherally coordinated complexes **5**, **6**, **7** and **8**.
The synthetic route followed in this work is shown in Schema 1.
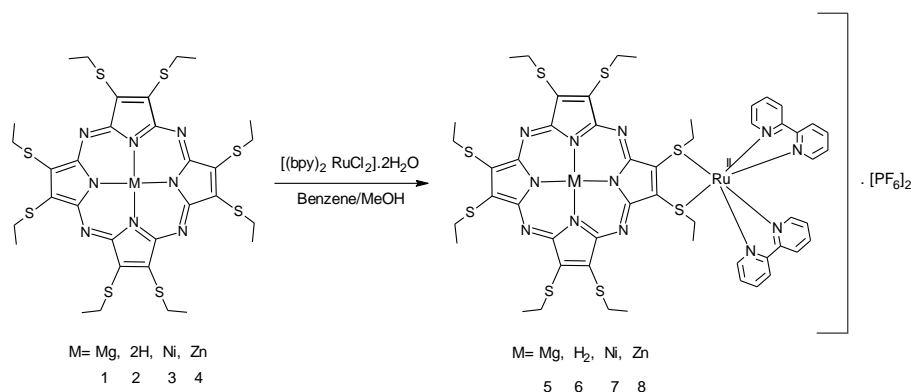
Schema 1. Synthetic route of a new dinuclear porphyrazines.

In the FTIR spectra they all exhibited the characteristic fingerprint of the constituent units. The dinuclear complexes **5**, **6**, **7** and **8** showed characteristic aliphatic C-H stretching at between 2961-2920 cm^{-1}. These complexes exhibited one strong band around 1443 cm^{-1}, due to the vibration of the bipyridine rings and a very strong band around 840 cm^{-1} due to [PF$_6$][-]. In the FTIR spectra of the purple-coloured metal-free porphyrazine **2**, the N-H stretching vibration of the inner core peaks were observed at 3282 cm^{-1}.

The dinuclear complexes possessing (bpy)$_2$Ru[II] units exhibited bpy-CH signals between 7.50-6.60 ppm integrating for 16 protons. The S-CH$_2$ protons for complexes were observed at 4.40-3.50 ppm range for **5**, **6**, **7** and **8** integrating for 16 protons. The -CH$_3$ protons for complexes were observed at 4.66 ppm for **5**, **6**, **7** and **8** 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 -1.05 ppm in the ^{1}H NMR.

In the MALDI-TOF mass spectra, in a matrix consisting of 2,5-dihydroxy benzoic acid (DHB) dissolved in acetonitrile (AN), complex **5** mass peaks were exhibited peak at *m/z* 1644.28 due to formation [M + 3AN], complex **6** mass peaks were observed peak at *m/z* 1245.75 due to [M – 2[PF$_6$]+ AN][4-], complex **7** mass peaks were observed peak at *m/z* 1646.10 due to [M – [PF$_6$] + DHB + AN] and complex **8** mass peaks were observed peak at *m/z* 1275.11 due to [M – 2[PF$_6$]][3+] (Fig.1. using complex **5** as example).
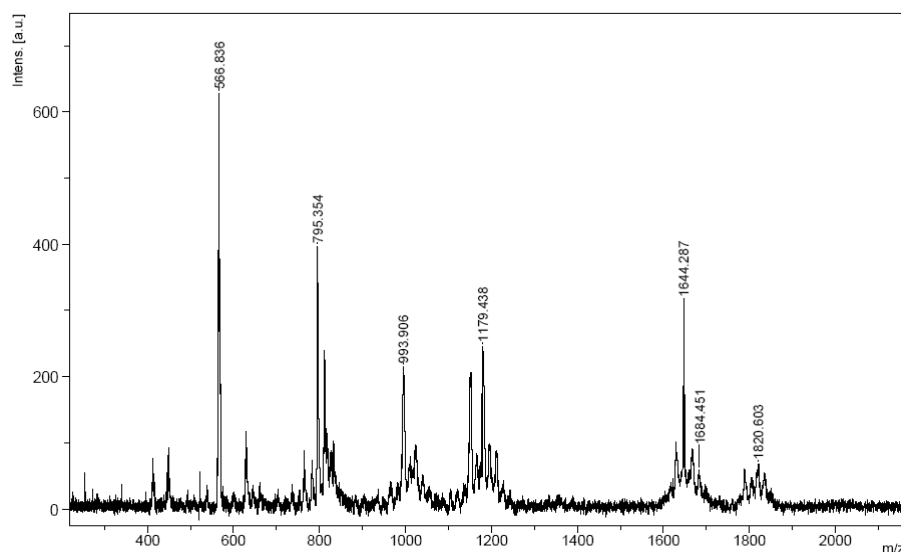

Figure 1. MALDI-TOF Mass Spectra of **5**.

3.2. Ground state electronic absorption

Electronic spectra are especially useful to establish the structure of the porphyrazines. UV-Vis spectra of 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 π→π* transitions [21,22]. The oligomeric complexes also exhibit a new medium intensity band between 450-480 nm attributable to the MLCT [dπ (Ru) → π*(bpy)] transitions and a strong band at around 294 nm due to intra ligand π→π*(bpy) transition [24]. The presence of an electron donating group on the periphery causes a bathochromic shift on Q bands. The electronic spectra of porphyrazine compounds **1** and **5** are shown in Fig. 2.

The Q band in complex **1** at λ_{max}= 669 nm and complex **5** observed a bathochromic shift to λ_{max}= 672 nm. UV-Vis spectra of Mg-porphyrazine (**5**) in THF prepared in the present work exhibited intense single Q band absorption of the $\pi\rightarrow\pi^*$ transitions 672 nm, B bands in the UV region 375 nm and $\pi\rightarrow\pi^*$(bpy) transition 280 nm (Fig. 3). For metal-free derivative (**6**) in CHCl$_3$, Q band is splitted into two peaks at 657 and 712 nm as a consequence of the change in the symmetry of porphyrazine core from D$_{4h}$ (in the case of metallo derivatives) to D$_{2h}$, B bands in the UV region 352 nm and $\pi\rightarrow\pi^*$(bpy) transition 294 nm (Fig. 4). The electronic spectrum of Ni-porphyrazine (**7**) in THF exhibits absorption maxima at 662, 343 and 280 nm. UV-Vis spectrum of Zn-porphyrazine (**8**) in THF showed a single band at 672 nm, B bands at 374 nm as expected from D$_{4h}$ symmetry and $\pi\rightarrow\pi^*$(bpy) transition 282 nm. 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 [17].
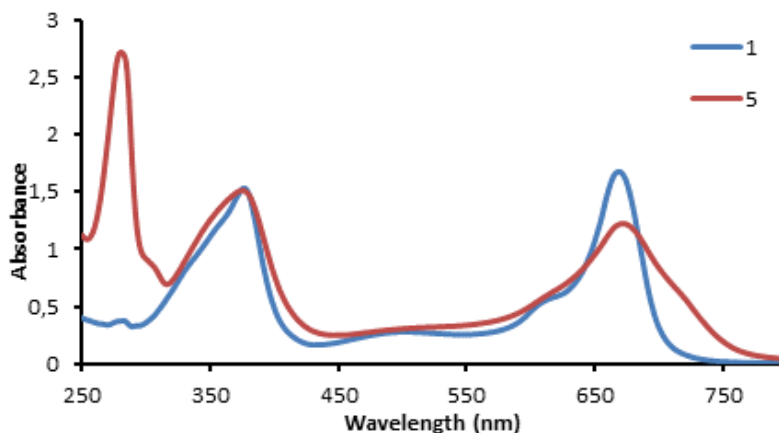

Figure 2. Optical spectra of **1** and **5** in THF at 2,25x10-6 mol/L.

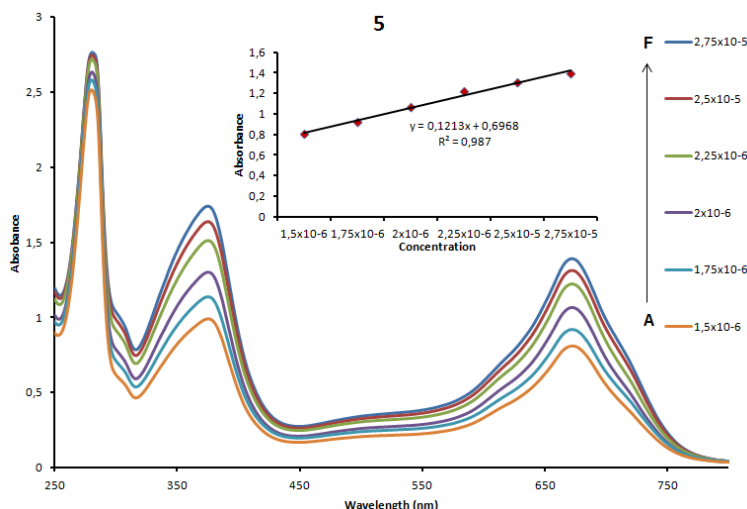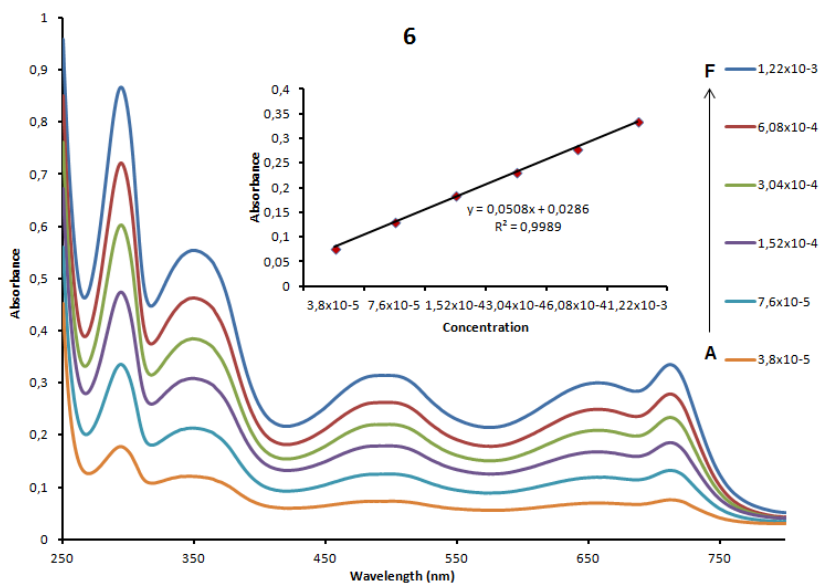**Figure 3.** Absorption spectral changes of **5** in THF at different concentrations: 1.50x10^{-6} (A), 1.75x10^{-6} (B), 2.00x10^{-6} (C), 2.25x10^{-6} (D), 2.50x10^{-6} (E), 2.75x10^{-6} (F) mol/L

Figure 4. Absorption spectral changes of **6** in $CHCl_3$ at different concentrations: 3.80×10^{-5} (A), 7.60×10^{-5} (B), 1.52×10^{-4} (C), 3.04×10^{-4} (D), 6.08×10^{-4} (E), 1.22×10^{-3} (F) mol/L.

3.2.1. Aggregation Studies

Aggregation is mostly described as a coplanar association of rings progressing from monomer to dimmer and higher order complexes. It is dependent on the concentration, nature of the solvent, nature of the substituents, complexed metal ions and temperature. High aggregation tendency of phthalocyanine and porphyrazine compounds due to the interactions between their 18 π-electron systems often cause weak solubility or insolubility in many solvents. The spectroscopic, photo physical, photochemical and electrochemical properties of the phthalocyanines and porphyrazines were seriously affected by the aggregation [34].

The aggregation behavior of metallo porphyrazines **5** (Fig.3.), **7** and **8** (in THF) and the metal-free porphyrazine **6** (in $CHCl_3$) (Fig.4.) and were also studied at different concentrations for determination of the aggregation depends on concentration. These studied porphyrazines did not show any aggregation concentration ranges. 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 were observed.

3.3. Photophysical properties

3.3.1. Fluorescence spectra and quantum yields

The fluorescence behavior of all the complexes was studied in THF. The fluorescence emission of porphyrazines synthesized is characterized with so-called S1 and S2 emission [35, 36]. All complexes excited same wavelength (257 nm) and stimulated fluorescence spectra of compounds were obtained at 311 (S2) and 605 (S1) nm respectively, and showed similar fluorescence properties. Fig. 5 shows the fluorescence spectra compounds **1** and **5** in THF.

Fig. 6 shows the fluorescence spectra compounds **2** and **6** in THF. The excitation spectra were narrower when compare to absorption spectra probability aggregation and both were mirror images of the fluorescent spectra for all complexes synthesized [37]. 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 [38]. Dinuclear complexes (**5-8**) studied in this work showed similar fluorescence behavior in THF. Fluorescence emission peaks for 1, 2, 3, 4, 5, 6, 7 and 8 were observed 308, 308, 309, 308, 311, 310 and 312 nm respectively in THF. The Stokes' shifts range from 17 to 30 nm. Table 1 shows UV-Vis spectral and photophysical parameters of **5-8** compounds studied in this work.
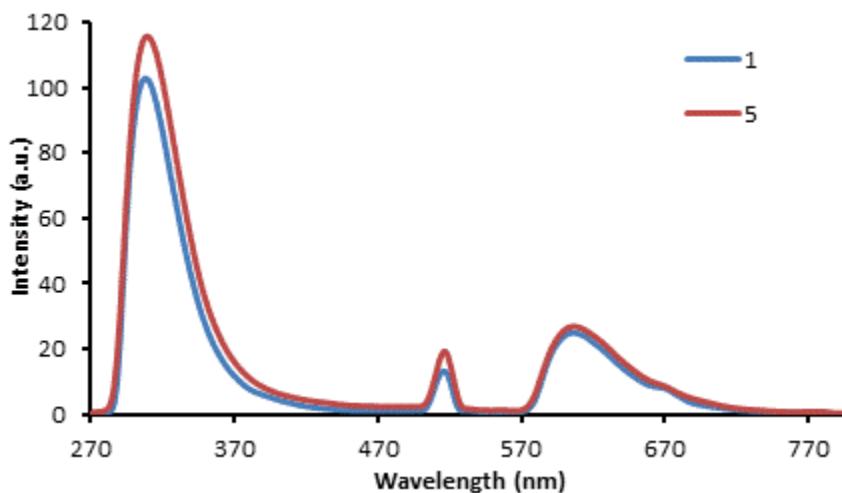

Figure 5. Fluorescence spectrum of compounds **1** and **5** in THF. λ_{emis} = 257 nm
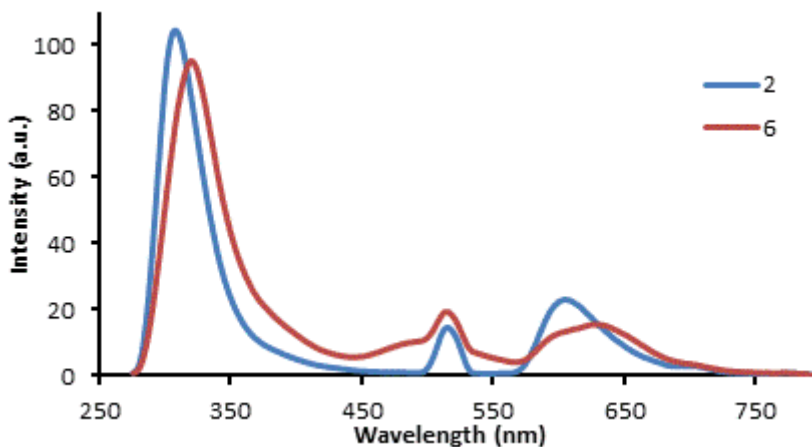

Figure 6. Fluorescence spectrum of compounds **2** and **6** in THF. λ_{emis} = 257 nm

Table 1. UV-Vis spectral and photophysical parameters of **5-8** compounds

Compound in THF	λ_B (Abs) / nm (Logε)	λ_B (Ems) / nm	λ_B (Exc) / nm	$\Delta\lambda_{Stokes}$/ nm	Φ_F
5	280 (5.00)	309	293	29	0.351
6	294 (4.56)	311	298	17	0.245
7	280 (4.93)	310	293	30	0.223
8	282 (5.13)	312	302	30	0.328

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 [39]. The fluorescence quantum yields (Φ_F) of all porphyrazines were determined using **ZnPc** as a standard using the comparative method [33] in THF. Fig. 7 shows the absorption and fluorescence emission spectra of **8** in THF. All compounds fluorescence quantum yields are given in Table 2 comparatively. 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 [40-43]. This is contrary to what would be expected based on heavy atom effect where Zn would be expected to show low Φ_F values since it encourages intersystem crossing to the triplet state. The fluorescence quantum yield (Φ_F) for metal free (**2**) showed a larger Φ_F value (0.344) compared to complex (**4**) containing Zn central metal (Φ_F = 0.279). The highest fluorescence quantum yield (Φ_F) in dinucle complexes showed compound (**5**). The dinuclear complexes possessing (bpy)2Ru^{II} units exhibited highest quantum efficiency according to porphyrazines complex, except complex (**6**).
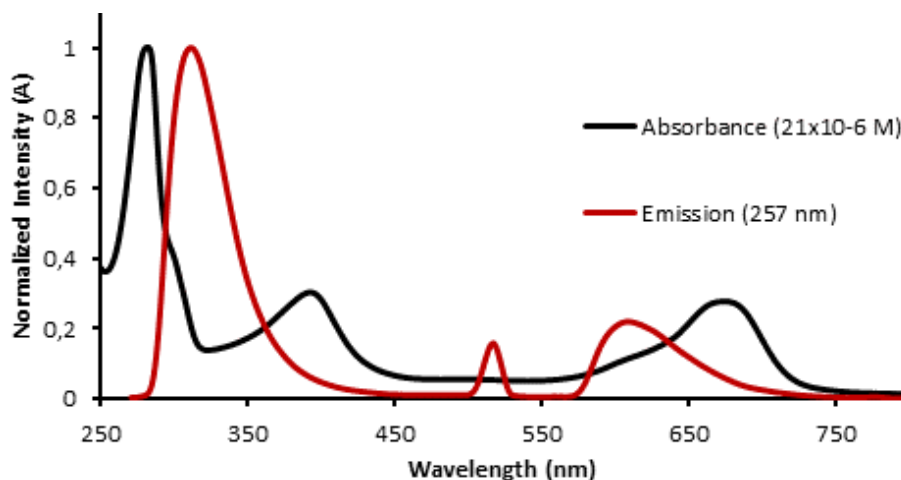
Figure 7. The absorption and emission spectra of **8** complex in THF

Table 2. Fluorescence quantum yields (Φ_F) of all compounds

Compound in THF	1	5	2	6	3	7	4	8
Φ_F	0.302	0.351	0.344	0.245	0.216	0.223	0.279	0.328

4. CONCLUSION

This work has described the synthesis, spectral and photophysical properties of free-base and metallo (ethylsulfanyl) porphyrazines has been modified with one peripheral ruthenium bipyridine groups. Solubilities of porphyrazine derivatives in common organic solvents such as THF, DMF, CHCl₃ are very good with a large concentration range. The new compounds have been characterized by elemental analysis, FT-IR, ^{1}H-NMR spectroscopy and mass spectra. The spectral and fluorecence properties of the porphyrazines were investigated in THF. Porphyrazines synthesized show the usual B (Soret) and Q-band absorptions. All porphyrazines did not show any aggregation different concentration. Fluorescence emission peaks were observed all the complexes feature similar fluorescence emission. The addition of (ethylsulfanyl) porphyrazines has been modified with one peripheral ruthenium bipyridine groups on the ring caused high florescence quantum yields.

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