



Research Article

Synthesis and investigation of thermal properties of octakis (ethylsulfanyl) porphyrazine

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ABSTRACT

Between tetrapyrrole macrocycles, porphyrazines show both special physical and chemical properties as metal free and transition metal complexes. Many new studies have demonstrated effective coordination chemistry, great chemical, thermal, and photochemical stability, as well as technological applications to this macrocycle. In the work, it has been planned to synthesize asymmetric porphyrazine having seven ethylsulfanyl groups and one bromine by using a different method. In this way, asymmetric(ethylsulfanyl) porphyrazines were synthesized by replacing one ethylsulfanyl-alkyl chain on macrocycle with a hydrogen atom. The bromination of this product has resulted monobromoporphyrazine derivative. Thermal analysis of the compounds were done by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) (between 50–1200°C). The structures of these compounds were characterized by using UV, FT-IR, MS, ¹H NMR, elemental analysis.

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INTRODUCTION

Porphyrazines can be viewed as porphyrin analogues, with meso nitrogen atoms replacing the meso carbon atoms [1]. Porphyrazines are molecules with high delocalised electronic structure 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 catalyst [13].

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Porphyrazines are molecules with a highly delocalized electronic structure in which the four pyrrole units are linked each other by four aza bridges. Porphyrazine systems and their metal complexes are known to exhibit adaptable physical (e.g. electronic, optical, magnetic and redox) properties for construction of various molecular architectures [14–18]. If the starshaped functionalization of the central core is required for molecular construction, those symmetrical octakis planar tetrapyrrole derivatives with eight peripheral positions are well known candidates. Functional groups fused to the peripheral positions of porphyrazines are investigated more intensely because of their high solubilities in many organic solvents than those of phthalocyanines [19,20].

The octakis(alkyl)sulfanylporphyrazine ring may be easily modified by synthetic means, allowing the arrangement of the structural and optical properties of the azaporphyrin ring. Such structural flexibility makes these derivatives appropriate to research in detail the molecular self-organizing phenomena of tetrapyrroles with the intent to find the relationship between the molecular structure and the occurrence of mesophases, with possible applications in opto-electronic technology [21].

The International Confederation for Thermal Analysis and Calorimetry (ICTAC) defines thermal analysis (TA) as a group of techniques that vary the physical or chemical properties of a sample with monitor time subject to a temperature program.

Thermogravimetric analyzers (TGA) monitor and record sample mass, time, and temperature. The temperature program can include heating, cooling, isothermal holds, or a combination of them [22]. The analyzer consists of a temperature programmer and control-thermo-balance, a precision micro-balance connected to a sample pan in an oven. The balance weighs the sample in a closed furnace [23].

The most widely used techniques are DTA (Differential Thermal Analysis), TGA (Thermogravimetric Analysis) and DTG (Derivative Thermogravimetry), which give the most accurate results on the composition of the substance. TGA is a simple analytical technique that measures the temperature of the material as a loss of mass in function, taking the measurement of its weight. Based on the TGA curves it is possible to determine how the weight of the sample changes with the effect of thermal energy. There are generally three regions in TGA curves: the weight gain region, the weight decrease region, and the horizontal region where weight remains constant. In terms of thermoanalytical application, the horizontal regions of the TGA curves are the most important parts, especially when controlling the stability of a compound.

In the work, it has been planned to synthesize symmetric and asymmetric (ethylsulfanyl) porphyrazine by using a different method. In this way, asymmetric(ethylsulfanyl) porphyrazines synthesized by

replacing one ethylsulfanyl-alkyl chain on the macrocycle with a hydrogen atom. The bromination of this product has resulted the synthesis of monobromoporphyrazine derivative (8). Thermal analysis of the compounds were done by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) was performed between 50–1200°C. The structures of these compounds were characterized with UV, FT-IR, MS, ¹H NMR, elemental analysis [24, 25].

MATERIAL AND METHODS

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 [26]. 2,3,7,8,12,13,17,18- octakis(ethylsulfanyl)- 5,10,15,20 porfirazinato magnesium(II) was prepared according to ref. [27]. 2,3,7,8,12,13,17,18- octakis(ethylsulfanyl)-5,10,15,20-21*H*,23*H* porphyrazine was prepared according to ref. [28]. 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. [29] 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. [30, 31].

EQUIPMENT

FT-IR spectra were recorded on a spectrum one Perkin Elmer FT-IR spectrophotometer using KBr pellets. Absorption spectra in the UV-Visible region were recorded with a Shimadzu 2001 UV spectrophotometer. ¹H NMR spectra were recorded in CDCl₃ solutions on a Varian 500 MHz spectrometer. Elemental analyses were obtained with a Thermo Flash EA 1112 Series. The mass spectra were acquired on a Bruker Daltonics (Bremen, Germany) MicroTOF mass spectrometer equipped with an electrospray ionization (ESI) source. The instrument was operated in positive ion mode using a *m/z* range of 50–3000. GC/MS spectra were acquired on a Agilent Technologies 6890 N Network GC System, Agilent 5973 inert Mass Selective Detector. TGA-DSC spectra were recorded on a TA SDT 600 Series.

SYNTHESIS

1,2-Bis ethane thio maleonitril (2):

1.6 g (15 mmol) of dithiomaleonitrile disodium salt are dissolved in methanol. It was cooled in an ice bath

at 0°C. Methanol containing bromoethane (1.28 mL) is dropped onto it. Remove the ice bath and stir at 25°C for 24 h. It is kept at -20°C for 24 h. The dark brown substance formed by the removal of methanol is dissolved in chloroform. Wash with distilled water and filter over Na₂SO₄. It is left to stand again for CHCl₃ to be removed. The product obtained is purified by column chromatography. Yield: 1.60 g, 47.0%. C₈H₁₀N₂S₂ FT-IR (KBr), ν/cm^{-1} : 2872 (aliphatic CH₃), 2969 (aliphatic CH₂), 2209 (C≡N). GC-MS: 198.3 g/mol.

2,3,7,8,12,13,17,18- Octakis(ethylsulfanyl)- 5,10,15,20 porfirazinato magnesium(II):

Mg turnings (0.0388 g, 1.58 mmol) and a small I₂ crystal were refluxed in n-propanol (20 ml) for about 12 h to obtain Mg(BuO)₂. 1,2-bis(ethane thio)maleonitrile (0.47 g, 2.37 mmol) was added to the this solution and the mixture was refluxed for about 24 h. The blue-green product was filtered, washed with ethanol and water and dried. The crude product was dissolved in CHCl₃ and filtered. The CHCl₃ solution was dried over anhydrous Na₂SO₄. When the solvent was evaporated, dark bluegreen product was obtained. Finally, pure porphyrazine was obtained by chromatography on silica gel using methanol/chloroform (1:50) mixture as eluent. The product was very soluble in chloroform, soluble in dichloromethane, acetone and toluene, but insoluble in nhexane and methanol. Yield: 4.1 g (% 62) Calc. for C₃₂H₄₀MgN₈S₈: C 47.01, H 4.93, N 13.71%; Found: C 46.77, H 4.56, N 13.35%. FT-IR (KBr), ν/cm^{-1} : 2963 and 2923 (aliphatic CH₂), 1626 (C-N-C): UV-Vis (CHCl₃) $\lambda_{\text{max}}/\text{nm}$ (log $\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$): 376 (4.73), 672 (4.72).

2,3,7,8,12,13,17,18- Octakis(ethylsulfanyl)-5,10,15,20-21H,23H porphyrazine:

Pure solid magnesium porphyrazine (3)(0.78 g, 0.96 mmol) was dissolved in the minimum amount of CF₃COOH and carefully poured onto ice. The solution was then neutralized with concentrated ammonia. The dark product was then filtered. The solid obtained was washed in a separating funnel with water until the wash was completely neutral. The solid was then dissolved in CHCl₃ and after removal of the solvent, the crude product was chromatographed on silica gel using chloroform as stripping fluid.

Yield: 0.45 g (59.3%). Calc. for C₃₂H₄₂N₈S₈: C 48.33, H 5.32, N 14.09, S 32.26%; Found: C 47.82, H 5.24, N 13.78, S 31.55%. FT-IR (KBr), ν/cm^{-1} : 3281 (N-H), 2950 and 2918 (aliphatic CH₂), 1572, 1518 (C-N-C), 1384, 1365 (C-CH₃), ¹H NMR (CDCl₃): δ 4.00 (q, 16 H, SCH₂), 1.50 (t, 24 H, CH₃) and -1.38 (s, 2 H, NpyrrolicH). UV-Vis (CHCl₃): λ/nm (log ϵ): 359 (4.71) Soret; 641 (4.51), 710 (4.64) Q bands.

General procedure for metallo porphyrazines (5–6)

0.24 g (0.13 mmol) of the free-base porphyrazine was dissolved in CHCl₃ and added to the solution of 0.23 g (1.3

mmol) Ni(OAc)₂, 0.24 g (1.3 mmol) Zn(OAc)₂ in EtOH. The mixture was refluxed under argon for 1h. After cooling to room temperature, insoluble excess metal salt was separated by filtering. The filtrate was evaporated and the resulting deep blue solid was purified by chromatography on silica gel using CHCl₃.

2,3,7,8,12,13,17,18- octakis(ethylsulfanyl)- 5,10,15,20 porfirazinato nickel(II) (5):

Yield: 0.053 g (73.0%). Calc. for C₃₂H₄₀NiN₈S₈: C 45.11, H 4.73, N 13.15, S 30.11%; Found: C 44.59, H 4.87, N 12.69, S 28.87%. FT-IR (KBr), ν/cm^{-1} : 2927 and 2861 (aliphatic CH₂), 1520 (C-N-C): UV-Vis (CHCl₃) $\lambda_{\text{max}}/\text{nm}$ (log $\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$): 665 (4.18).

2,3,7,8,12,13,17,18- Octakis(ethylsulfanyl)- 5,10,15,20 porfirazinato zinc(II) (6):

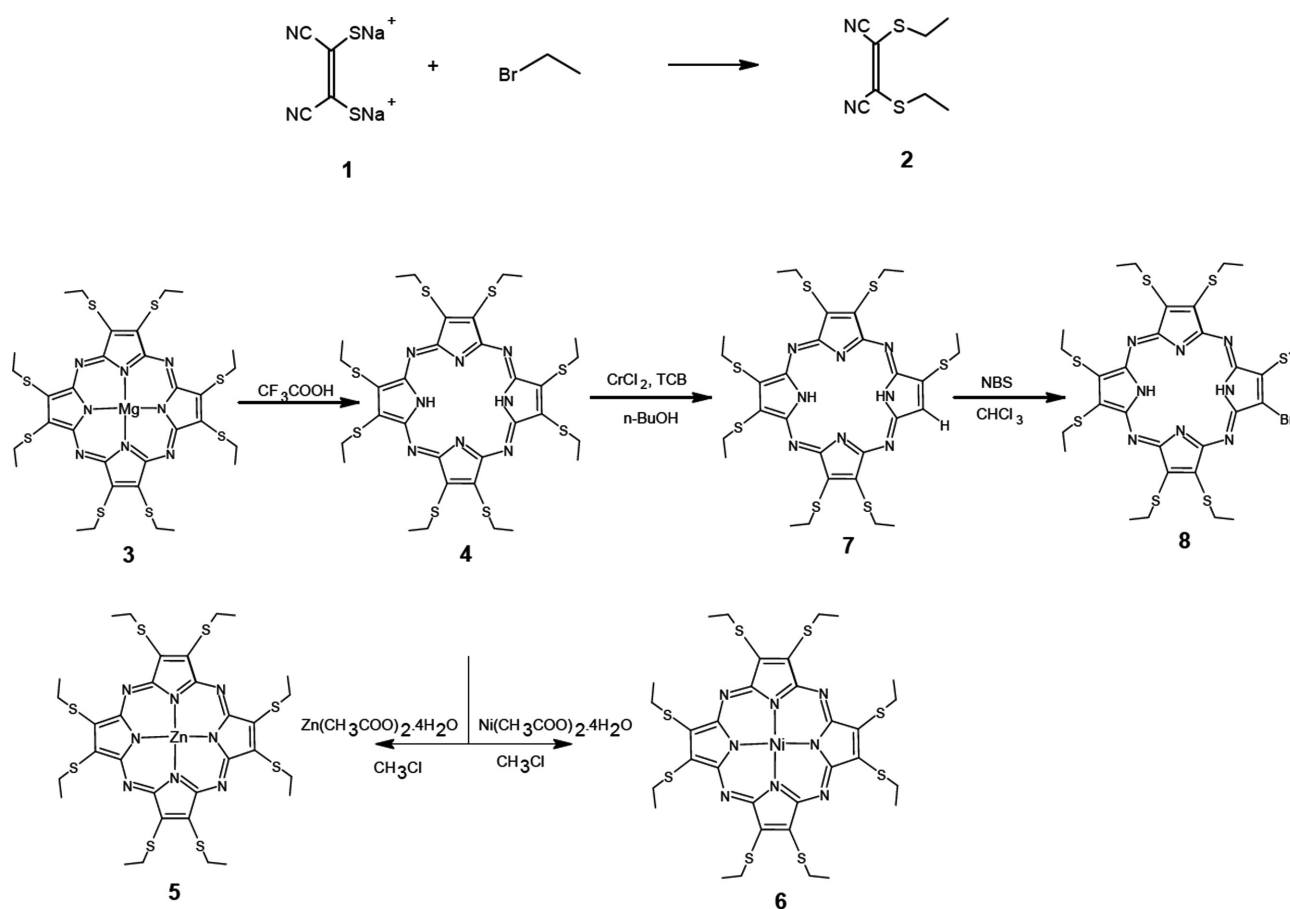
Yield: 0.036 g (42%). Calc. for C₃₂H₄₀ZnN₈S₈: C 45.09, H 4.73, N 13.14, S 32.04%; Found: C 45.55, H 4.24, N 13.48%. FT-IR (KBr), ν/cm^{-1} : 2927 and 2854 (aliphatic CH₂), 1525 (C-N-C): UV-Vis (CHCl₃) $\lambda_{\text{max}}/\text{nm}$ (log $\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$): 334 (4.32), 645 (4.45).

2H-3,7,8,12,13,17,18- Heptakis(ethylsulfanyl) 5,10,15,20-21H,23H porphyrazine (7):

Metal free porphyrazine (4) (0.30 g, 0.38 mmol) and CrCl₂ (0.120 g, 0.98 mmol) were refluxed in 5:1 (v/v) 1,2,4-trichlorobenzene (TCB)-n-BuOH (18 cm³) under N₂. The dark blue colored product first turns into red and dark green after 2 hours. After 7 hours of reflux, the solvent is removed in vacuo and purified by gradient technique by column chromatography. With an initial (1:1) CH₂Cl₂-n-hexane mixture as eluent a blue band was collected corresponding to unchanged H₂OESPz. The next slow moving green band, containing the desired compound, was collected using (7:3) CH₂Cl₂-n-hexane as eluent. The solvent is removed and the product crystallized with (9:1) CH₃OH-CH₂Cl₂. Yield: 0.15 g (23%). Calc. for C₃₀H₃₈N₈S₇: C 49.01, H 5.21, N 15.24, S 30.53%; Found: C 47.82, H 5.04, N 14.78, S 29.35%. FT-IR (KBr), ν/cm^{-1} : 3278 (N-H), 2921 and 2866 (aliphatic CH₂), 1572, 1518 (C-N-C), 1384, 1446 (C-CH₂), ¹H NMR (CDCl₃): δ 4.20-3.50 (q, 16 H, SCH₂), 1.49 (t, 24 H, CH₃) and -1.29 (s, 2 H, NpyrrolicH). UV-Vis (CHCl₃): λ/nm (log ϵ): 352 (4.69) Soret; 637 (4.45), 703 (4.55) Q bands. Calc. 735.13 g / mol; Found: 735.16 g / mol.

2-Bromo -3,7,8,12,13,17,18- heptakis(ethylsulfanyl) 5,10,15,20-21H,23H porphyrazine (8):

0.1 g of (7) (0.075 mmol) is dissolved in CHCl₃ at room temperature. 0.02 g dry N-bromosuccinimide (0.11mmol) dissolved in CHCl₃ is added. The reaction is stopped after 15 minutes and the solvent is removed in vacuo. The product formed is purified by column chromatography 1: 1 CH₂Cl₂-n Hexane (product first band). Again, the solvent is



Scheme 1. Synthetic route of a new porphyrazine with eight ethylsulfanyl group on the peripheral location.

removed in vacuo and crystallized by applying the solvent mixture $\text{CH}_3\text{OH}-\text{CH}_2\text{Cl}$ (9: 1).

Yield: 0.028 g (70.0 %). Calc. for $\text{C}_{30}\text{H}_{37}\text{BrN}_8\text{S}_7$: C 44.22, H 4.58, N 13.76, S 27.57 %; Found: C 43.91, H 4.17, N 13.25, S 26.95. FT-IR (KBr), ν/cm^{-1} : 3282 (N-H), 2921 and 2865 (aliphatic CH_2), 1572, 1518 (C-N-C), 1438 (C- CH_2), ^1H NMR (CDCl_3): δ 4.01 (q, 16 H, SCH_2), 1.49 (t, 24 H, CH_3) and -2.0 (s, 2 H, NpyrrolicH). UV-Vis (CHCl_3): λ/nm (log ϵ): 358 (4.52) Soret; 637 (4.37), 704 (4.22) Q bands. Calc. 814.13 g / mol; Found: 815.2 [M+].

RESULTS AND DISCUSSION

Synthesis and characterization

The synthetic route followed in this work is shown in **Scheme 1**. Starting from disodium salt of dithiomaleonitrile **1** in MeOH, addition of bromoethane afforded the corresponding maleonitrile derivative, **2**. Cyclotetramerization of **2** on $\text{MgII}(\text{n-Obu})_2$ for 5 h afforded the ethylsulfanyl thio-porphyrazine, **3**. This product is blue-green and it is

soluble in CHCl_3 , CH_2Cl_2 but insoluble in MeOH, EtOH. The synthesized magnesium complex **3** showed characteristic aliphatic CH stretching at ca. 2963 cm^{-1} . The characteristic $\text{C}\equiv\text{N}$ stretch at 2209 cm^{-1} of compound **3** disappeared after conversion into magnesium porphyrazine. Magnesium ion removal was accomplished by treatment with trifluoroacetic acid and free-base porphyrazine **4** was purified by column chromatography. FTIR spectra of the purple-coloured metal-free porphyrazine **4** are seen at 3231 cm^{-1} of the N-H stretching vibration of the inner core.

The metallo porphyrazine was easily prepared by insertion of the anhydrous metal salts in a mixture of CHCl_3 and EtOH. Compounds **5** and **6** was also soluble in CHCl_3 , CH_2Cl_2 , but insoluble in MeOH and EtOH.

Peripherally octa-substituted complexes were observed of S- CH_2 protons for complexes were observed at 4.00 ppm range for **3** and **4** integrating for 16 protons. The CH_2 protons for complexes were observed at 1.15 ppm for **3** and **4** integrating for 16 protons. Metal-free derivative **4**, of protons in the inner core of porphyrazines

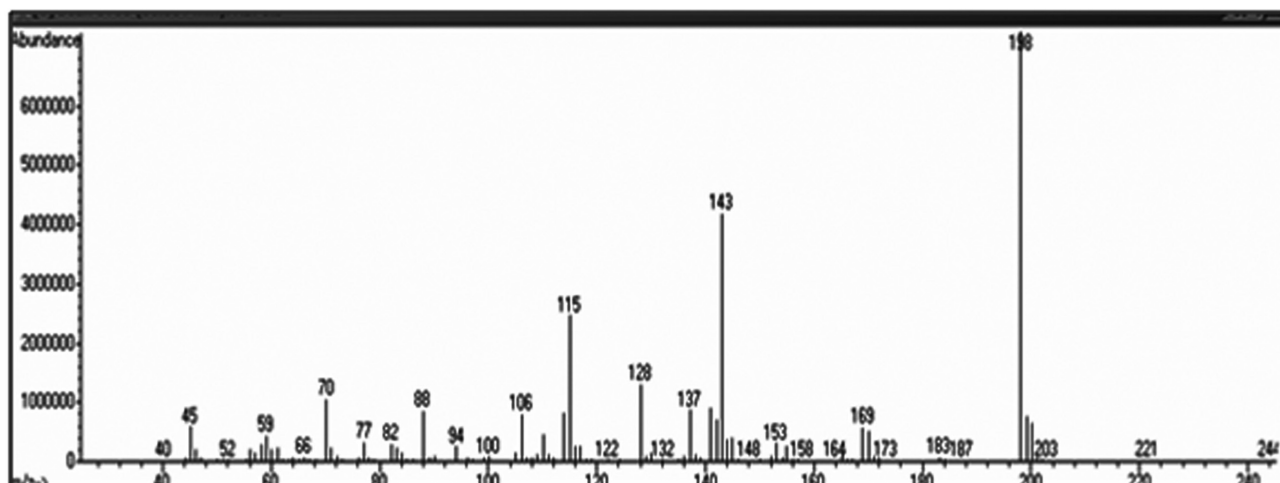


Figure 1. Mass Spectrum of Compound 2.

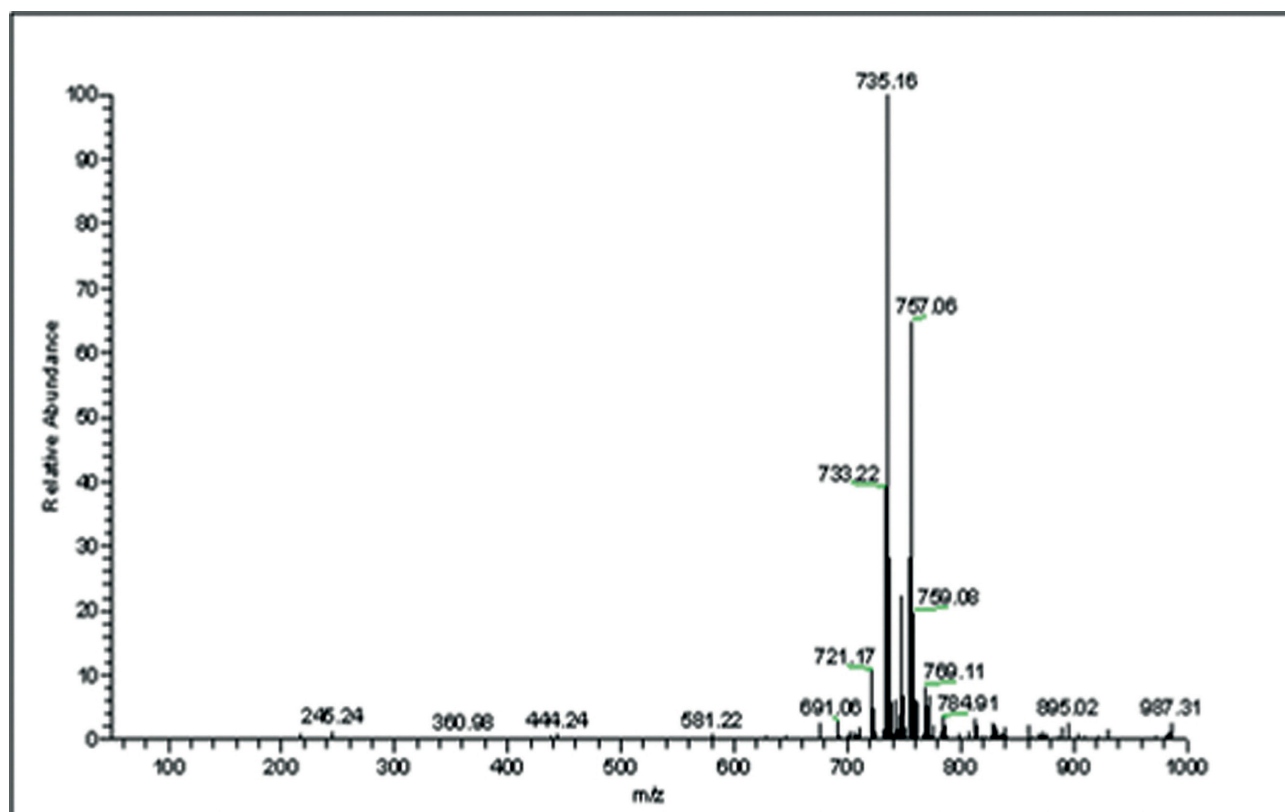


Figure 2. Mass Spectrum of Compound 7.

are screened by aromatic π electrons of the macrocycle, so they appeared at -1.38 ppm in the ^1H NMR. The mass spectra of compounds 1 and 7 gave the characteristic molecular ion peaks at m/z : 198.3 [M] and 735.16 [M] respectively, confirming the proposed structures (Figure 1 and Figure 2) using Compound 2 and 7 as example).

The structures of newly synthesized compounds were verified by FTIR, ^1H NMR, UV-Vis and MALDI-TOF MS spectroscopic methods, as well as by elemental analysis. The characterization data of compounds are consistent with the assigned formula as shown in the experimental section.

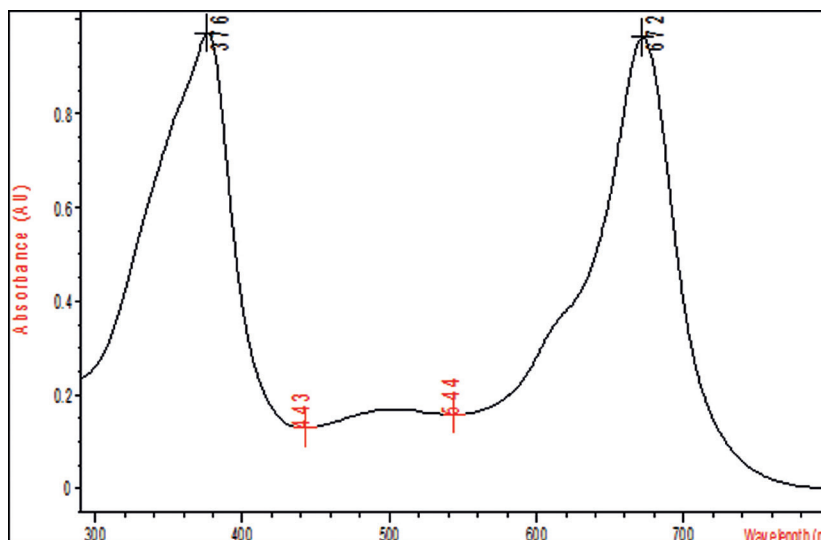


Figure 3. UV-Vis Spectrum of Compound 3.

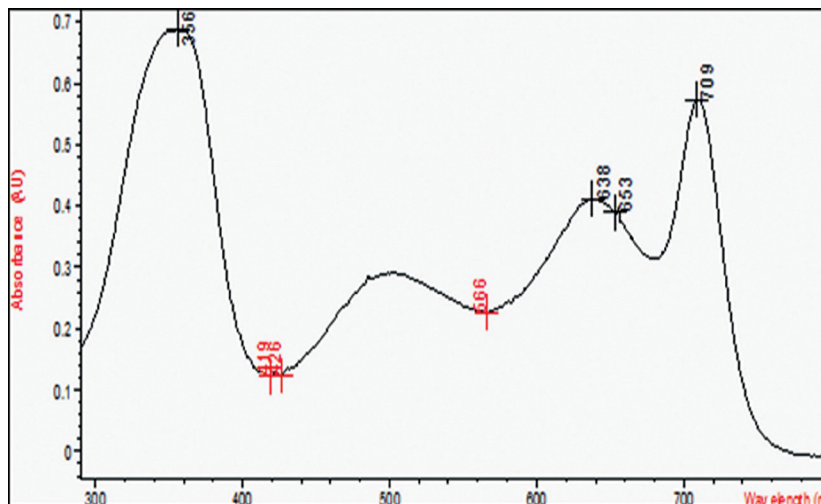


Figure 4. UV-Vis Spectrum of Compound 4.

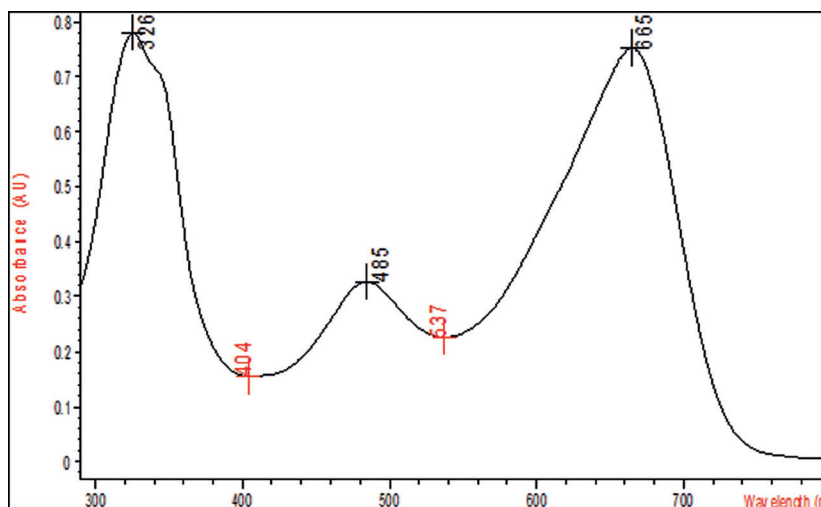


Figure 5. UV-Vis Spectrum of Compound 6.

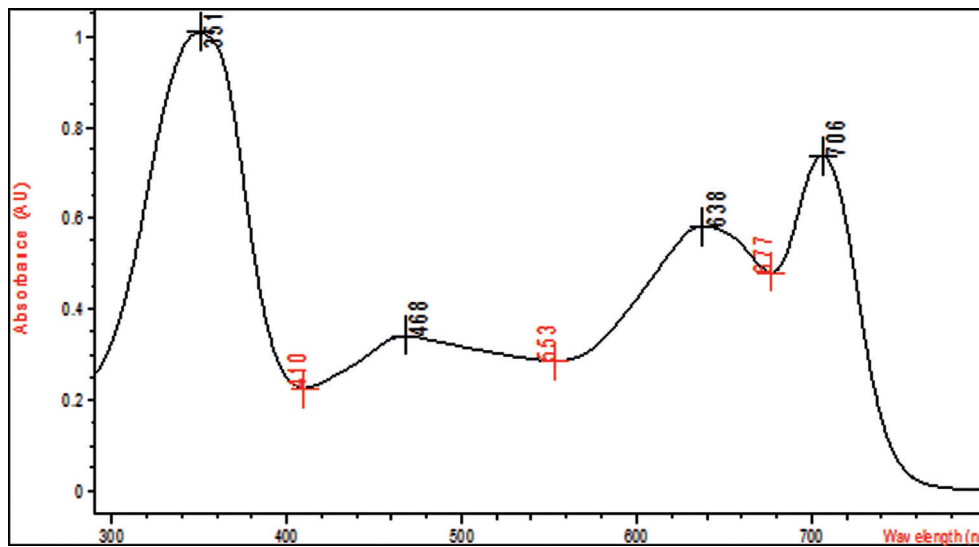


Figure 6. UV-Vis Spectrum of Compound 7.

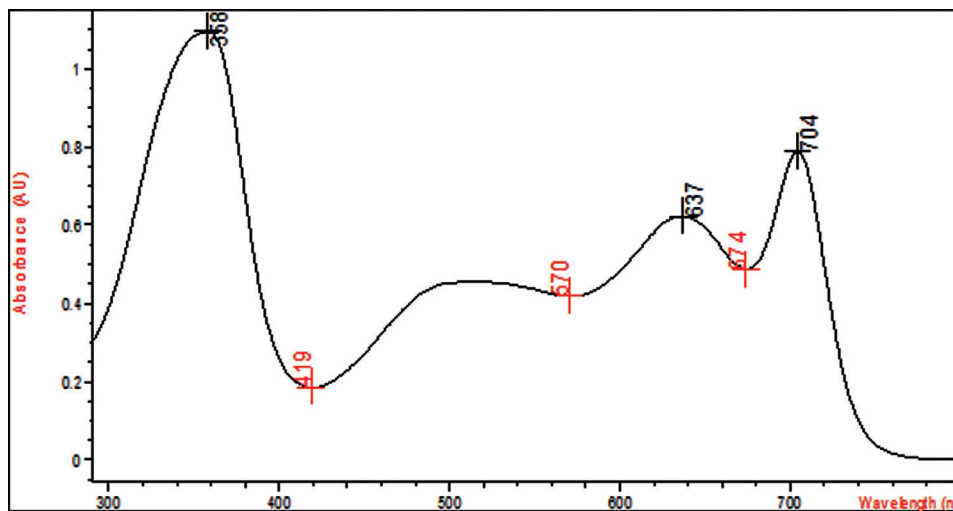
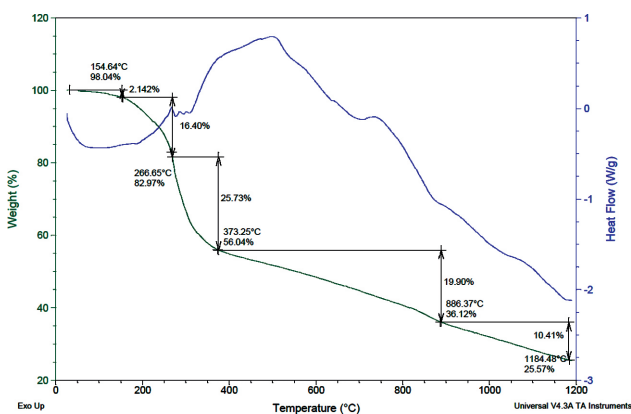
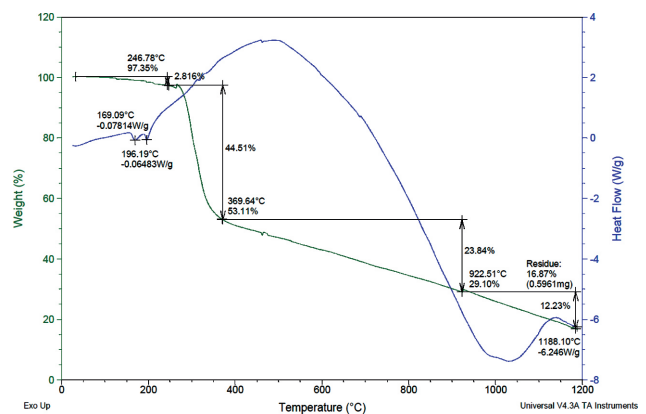


Figure 7. UV-Vis Spectrum of Compound 8.



Graphic 1. TGA thermograms of compound 3.



Graphic 2. TGA thermograms of compound 4.

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 $\pi^*\pi^*$ transitions [32, 33]. The presence of an electron donating group on the periphery causes a bathochromic shift on Q bands. UV-Vis spectra of Mg-porphyrazine (**3** in CHCl_3) prepared in the present work exhibited intense single Q band absorption of the $\pi^*\pi^*$ transitions around 672 nm and B bands in the UV region around 376 nm. For metal-free derivative (**4** in CHCl_3), Q band is splitted into two peaks at 641 and 710 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} and B bands in the UV region 359 nm. The electronic spectra of porphyrazine compounds **3**, **4**, **6**, **7** and **8** are given in Figure 3, Figure 4, Figure 5, Figure 6 and Fig. 7 respectively. The broadening observed in Q and B bands of the both metal-free and metalloporphyrazines is attributed to $n\pi^*$ transition of the non-bonding electrons associated with peripheral S and N atoms [34].

DSC-TGA ANALYSIS

Thermal properties of the compound **3**, **4**, **5**, **6**, **8** were investigated by TGA-DSC. Thermo gravimetric (TGA) and differential scanning calorimetric (DSC) curves for the compounds are presented in Graphic. 1-5. Compounds were heated from 50°C up to 1200°C.

Compound of 3 DSC-TGA analysis:

The TGA curve of the compound **3** shows five decomposition steps in the temperature range from 50-1200°C and is thermally stable up to 154°C. Compound **3** start to decompose at 154°C. The first step shows to the loss of the one water (% 2.14, endothermic) molecule within the

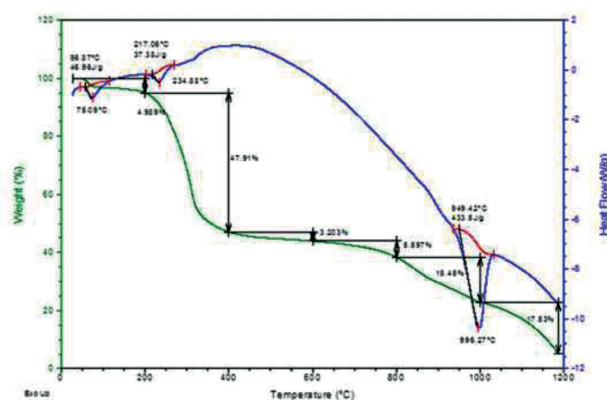
temperature range 50-154°C. The later three decomposition steps within the temperature range 154-886°C corresponds to the loss of $\text{C}_{16}\text{H}_{40}\text{S}_8$ (% 62, exothermic). The mass loss of fifth step within the temperature range 886-1200°C is % 10.41 (exothermic). Total mass loss is %74.58 from the beginning, there only remained organic moiety at the end (Residue: % 25.57).

Compound of 4 DSC-TGA analysis:

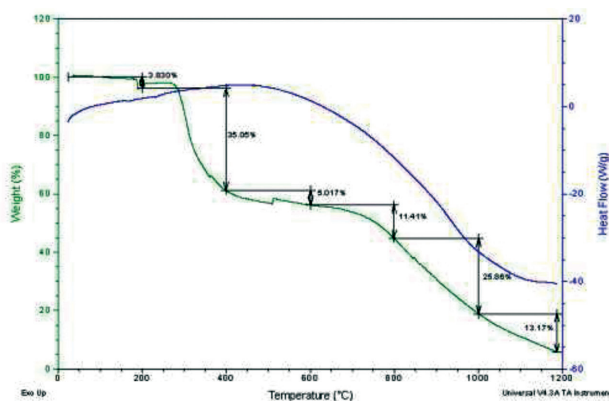
The TGA curve of the compound **4** shows four decomposition steps in the temperature range from 50-1200°C and is thermally stable up to 246°C. Compound **4** start to decompose at 246°C. The first step shows to the loss of the hydrated water (% 2.81, endothermic) molecule within the temperature range 150-246°C. The later two decomposition steps within the temperature range 246-922°C corresponds to the loss of $\text{C}_{16}\text{H}_{40}\text{S}_8$ (% 68, exothermic). The mass loss of fourth step within the temperature range 922-1200°C is % 12.23 (endothermic). Total mass loss is %83.39 from the beginning, there only remained organic moiety at the end (Residue: % 16.87).

Compound of 5 DSC-TGA analysis:

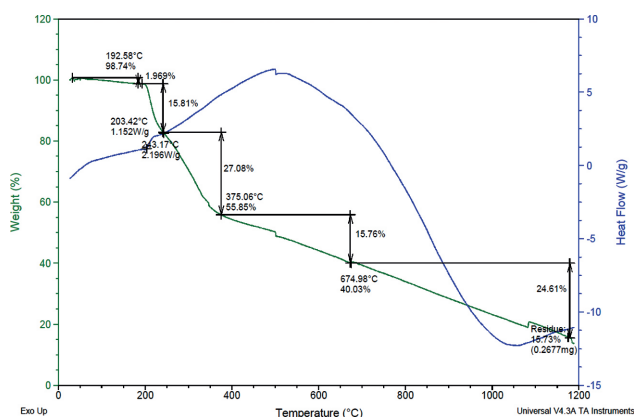
The TGA curve of the compound **5** shows six decomposition steps in the temperature range from 50-1200°C and is thermally stable up to 217°C. Compound **5** start to decompose at 217°C. The first step shows to the loss of the two hydrated water (% 4.93, endothermic) molecules within the temperature range 50-217°C. The later three decomposition steps within the temperature range 217-800°C corresponds to the loss of $\text{C}_{16}\text{H}_{40}\text{S}_8$ (% 56,71 exothermic). The decomposition two steps within the temperature range 800-1200°C correspond to the mass loss % 15.45 (endothermic) and % 17.53 (exothermic) respectively. The total mass losses of the decomposition steps are found to be % 94.62. The final product at 1200°C consist of organic moiety (Residue: % 5.38).



Graphic 3. TGA thermograms of compound 5.



Graphic 4. TGA thermograms of compound 6



Graphic 5. TGA thermograms of compound 8.

Compound of 6 DSC-TGA analysis:

The TGA curve of the compound 6 shows six decomposition steps in the temperature range from 50–1200°C and is thermally stable up to 250°C. Compound 6 start to decompose at 250°C. The first step shows to the loss of the two hydrated water (% 3.83, endothermic) molecules within the temperature range 100–250°C. The later three decomposition steps within the temperature range 250–800 °C corresponds to the loss of $C_{16}H_{40}S_8$ (% 51,41 exothermic). The decomposition two steps within the temperature range 800–1200°C corresponds to the mass loss % 25.86, and % 13.17 (exothermic) respectively. The total mass losses of the decomposition steps are found to be % 94.36. The final product at 1200 °C consist of organic moiety (Residue: % 5.64)

Compound of 8 DSC-TGA analysis:

The TGA curve of the compound 8 shows five decomposition steps in the temperature range from 50–1200°C and is thermally stable up to 192°C. Compound 8 start to decompose at 192°C. The first step shows to the loss of the one water (% 1.97, endothermic) molecule within the temperature range 50–192°C. The later three decomposition steps within the temperature range 192–675°C corresponds to the loss of $C_{14}H_{35}S_7Br$ (% 58,57, exothermic). The mass loss of fifth step within the temperature range 675–1200°C is % 24.61 (endothermic). Total mass loss is % 85.25 from the beginning, there only remained organic moiety at the end (Residue: % 15.73).

CONCLUSION

Magnesium porphyrine 3 substituted with eight ethylsulfanyl groups on the peripheral positions have been synthesized. The metal-free derivative 4 was obtained by treatment with trifluoroacetic acid and its reaction with zinc (II) and nickel (II) acetate to give products containing the respective metal ions in the porphyrine core 5–6. The

compounds have been characterized by elemental analysis, FT-IR, 1H -NMR spectroscopy and mass spectra. The porphyrines derived from this precursor do not show any tendency for aggregation independent of the polarity of the solvents used.

Thermal properties of compounds 3 and 4 were investigated by determining the weight loss of a sample onto linearly increasing the temperature by conventional TGA from room temperature to 1200°C under nitrogen atmosphere.

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The authors dedicate this publication for the retirement memory of Prof. Dr. Sabiha MANAV YALÇIN for her valuable contributions.

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AUTHORSHIP CONTRIBUTIONS

Authors equally contributed to this work.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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