Polyhedron 38 (2012) 218–223

Contents lists available at SciVerse ScienceDirect

Polyhedron

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

Synthesis and characterization of novel metal-free and metallo-porphyrazines with eight 3-thiopropylpentafluorobenzoate units

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ARTICLE INFO

Article history:
Received 28 December 2011
Accepted 5 March 2012
Available online 21 March 2012

Keywords:
Porphyrazine
Pentafluorobenzoic acid
Esterification
Magnesium
Cobalt
Zinc

ABSTRACT

Metal-free and metallo-porphyrazines (M = 2H, Mg, Cu, Zn or Co) with eight polyfluorinated groups appended on the periphery through flexible alkylthio-bridges have been synthesized through esterification of octakis(hydroxypropylthio)porphyrazinato magnesium with 2,3,4,5,6-pentafluorobenzoic acid in the presence of dicyclohexylcarbodiimide (DCCI) and toluene-*p*-sulfonic acid. The symmetrically functionalized porphyrazines with eight ester units are soluble in common organic solvents, such as $CHCl_3$, CH_2Cl_2, THF, acetone and toluene, and are insoluble in water and *n*-hexane. The newly synthesized compounds were characterized by FT-IR, UV–Vis, mass, ^1H, ^{13}C and ^{19}F NMR, together with elemental analysis.

1. Introduction

Tetrapyrrole macrocycles, such as phthalocyanines, porphyrines and porphyrazines, possess a conjugated system of 18 π-electrons. The presence of a π-electron system is essential for charge-carrier transport, so they exhibit a number of unique properties which attribute them great interest in several scientific and technological areas ranging from nanotechnology to medicine [1–3]. There has been growing interest in the use of tetrapyrrole macrocycles in a variety of new high technology fields including energy conversion, electrophotography, gas sensors, liquid crystals, infrared dyes for laser technology, optical data storage, semiconductor devices, Langmuire–Blodgett films, electrochromic display devices, non-linear optics, organic light emitting diodes (OLED), photodynamic cancer therapy and various catalytic processes [4–14]. They have also been of considerable interest to theoretical chemists owing to their high symmetry, planarity, thermal stability and electronic delocalization [15,16]. A significant amount of work has been carried out on their magnetic and catalytic properties and also on their role in biomolecular processes [17,18].

During the last decade, intensive research interest on peripherally functionalized porphyrazines has shown that these tetrapyrrole derivatives should be considered as alternatives to phthalocyanines [19]. Substitution of different various groups (e.g. 4-tert-buthylphenylthio [20], *o*-tolylthio and *p*-tolylthio [21], tosylaminoethylthio [22], 3-methylbutylthio [23], 1-naphthylmethylthio [24], 9-anthracenylmethylthio [25], 3,5-bis-trifluoromethyl-benzylthio [26], etc.) on the peripheral positions of the porphyrazines has been accomplished by either starting with an unsaturated dinitrile precursor or a preformed porphyrazine with reactive functional groups that can be subsequently modified (e.g. crown ethers [27], ferrocenes [28], triphenylphosphine [29], acetoxy [30], etc. have been incorporated by further condensation reactions).

Solubility is an important property for porphyrazines and most of their treatments are best determined in the soluble form. Because the parent unsubstituted metal-free, metallo-porphyrazines and most of the metal polymeric porphyrazine structures are less or insoluble in common organic solvents, the synthesis of a new porphyrazine system should be essentially designed in such a way that the final porphyrazine derivatives are sufficiently soluble to perform the desired activities. Compared to the unsubstituted parent metal porphyrazines, ester-containing porphyrazines are highly soluble in chlorinated hydrocarbons, such as dichloromethane and chloroform [27–32]. A further step for porphyrazine esters is the possibility of forming supramolecular structures with donor groups on the ester moiety. The applications of ester-containing tetrapyrrole compounds are very variable. For example, some esters [33] showed a gas-sensor response against NO_x gases, whereas some showed characteristics of liquid crystals with glassy transitions [34,35]. Furthermore, some patents and publications reported that ester-containing tetrapyrroles could be used as tumor growth suppressors [36], electro-photographic photoconductors [37], optical storage agents [38] and photosensitizers in photo-dynamic therapy [39,40].

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http://dx.doi.org/10.1016/j.poly.2012.03.015

Metal phthalocyanines bearing fluorine atoms are currently receiving a great deal of attention due to their high thermal and chemical stability, interesting electron-transporting characteristics, hydrophobicity, lipophobicity and decreased intermolecular attractive forces in comparison to their hydrocarbon analogs [41–44]. It has been reported that the position and the number of pentafluorophenyl groups on the macrocycle ring has a marked effect on the stability and catalytic activity [45,46]. Placing stronger electron-withdrawing fluorine atoms on the Pc ring results in both the valence and conduction band energies being further lowered. Thus, $MPcF_n$ (n: number of fluorine atoms) exhibits n-type behavior, while unsubstituted phthalocyanines possess p-type behavior due to doping with electron-accepting molecules [47]. These unusual properties of $MPcF_n$ have led scientists to expose their chemistry for use in a number of different industrial applications [48].

In the present work, the reactivity of hydroxypropylsulfanyl groups of metal-free and metallo-porphyrazines, which are novel compounds (**4–8**), has been demonstrated by the esterification with carboxylate groups such as pentafluorobenzoic acid. They are highly soluble redox-active compounds; therefore, they might be used in catalytic applications. The novel compounds have been characterized by FT-IR, UV–Vis, mass, ^{1}H, ^{13}C and ^{19}F NMR, together with elemental analysis.

2. Experimental

IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer, electronic spectra on a Unicam UV2 spectrophotometer. Elemental analyses were recorded on a Thermo Scientific 2000 instrument. ^{1}H, ^{13}C and ^{19}F NMR spectra were taken in $CDCl_3$ solutions at 400.000, 100.577 and 376.308 MHz, respectively, recorded on a Bruker Ultra Shield Plus 400 MHz spectrometer. Chemical shifts refer to TMS (^{1}H and ^{13}C NMR) and fluorotrichloromethane (^{19}F NMR) as the internal standards. By using the electrospray ionization (ESI) method, mass spectra were recorded on a Bruker Daltonics Micro-TOF and MALDI-TOF mass spectrometer. The instrument was operated in the positive ion mode. All reactions were carried out under a nitrogen atmosphere in dried solvents. All chemicals were used with sufficient chemical purity. 2,3,4,5,6-Pentafluorobenzoic acid, 3-chloro-1-propanol, *N,N*-dicyclohexylcarbodiimide (DCCI), toluene-*p*-sulfonic acid, *N,N*-dimethylformamide, chloroform, dichloromethane, pyridine, sodium sulfate and sodium carbonate were purchased from Aldrich, Merck or Alfa Aesar. Silica gel 60 (63–200 μm, Merck) was used for column chromatography. Analytical thin-layer chromatography (TLC) was performed using Merck 60 F_{254} silica gel (precoated sheets, 0.2 mm thick). The disodium salt of dithiomaleonitrile (**1**) was prepared according to the previously reported procedures [49].

2.1. 2,3-Bis(3-hydroxypropylthio)maleonitrile (*2*)

To a vigorously stirred suspension of the disodium salt of dithiomaleonitrile (5.59 g, 30.0 mmol) in abs. EtOH (250 mL) under N_2, a solution of $ClCH_2CH_2CH_2OH$ (5.67 g, 60.0 mmol) in abs. EtOH (10 mL) was added dropwise. After stirring for 72 h, the mixture was filtered and the filtrate was concentrated under vacuum. The reddish-brown oily residue was extracted several times with anhydrous *t*-BuOMe and after evaporation of the solvent in vacuum, a reddish-brown highly viscous product was obtained, which was recrystallised from cold Et_2O as white crystals. Yield: 5.81 g (75%). FT-IR, $\nu_{max}/(cm^{-1})$: 3350 br (OH), 2985–2883 (CH, aliphatic), 2227 (C≡N), 1650 (C=C), 1055 (C—O). ^{1}H NMR (δ, ppm): 4.72 (2H, t, OH), 3.61 (4H, t, O—CH_2), 3.27 (4H, t, S—CH_2), 2.42 (m, 4H, —CH_2—). 13C NMR (δ, ppm): 26.4, 30.0, 62.2, 115.9, 122.2. MS (ESI) *m/z*: 258.8 $[M]^+$.

2.2. [2,3,7,8,12,13,17,18-Octakis(3-hydroxypropylthio)porphyrazinato] Mg(II) (*3*)

Mg turnings (6 mg, 0.25 mmol) and a small I_2 crystal were refluxed in *n*-BuOH (20.0 mL) for about 8 h to obtain $Mg(BuO)_2$. 2,3-Bis(3-hydroxypropylthio)maleonitrile (**2**) (129 mg, 0.50 mmol) was added to this solution and the mixture was refluxed for about 12 h. The resulting blue-green suspension was filtered while hot, and the precipitate was washed with *n*-BuOH. The combined filtrates were evaporated and the residue was washed with aqueous 10% Na_2CO_3 solution (100 mL). The suspension was centrifuged and washed with distilled H_2O. The blue-green highly viscous product was dissolved in MeOH, filtered, and finally the solvent was evaporated in vacuum. Purification of the product was accomplished by column chromatography with silica gel using methanol/chloroform (1:20) as the eluent. The colored product was soluble in methanol, ethanol, *n*-propanol, DMF, DMSO and THF, but insoluble in *n*-hexane. Yield: 95 mg (72%). FT-IR, $\nu_{max}/(cm^{-1})$: 3330 (OH), 2955–2825 (CH, aliphatic), 1065 (C—O). ^{1}H NMR (δ, ppm): 4.55 (8H, t, OH), 4.38 (16H, t, O—CH_2), 3.66 (16H, t, S—CH_2), 2.48 (m, 16H, —CH_2—). 13C NMR (δ, ppm): 26.2, 29.6, 61.7, 115.5, 121.7. MS (ESI) *m/z*: 1057.2 $[M]^+$.

2.3. [2,3,7,8,12,13,17,18-Octakis(3-thiopropylpentafluorobenzoate) porphyrazinato] Mg(II) (*4*)

Octakis(3-thiopropylpentafluorobenzoate)porphyrazinato magnesium (**4**) was prepared by the reaction of **3** (0.529 g, 0.5 mmol), 2,3,4,5,6-pentafluorobenzoic acid (2.545 g, 12 mmol), dicyclohexylcarbodiimide (DCCI) (2.208 g, 12 mmol) and toluene-*p*-sulfonic acid (0.086 g, 0.5 mmol) in dry pyridine (30 mL) under N_2 at ambient temperature for 72 h. The suspension was filtered and the solvent was evaporated in a vacuum. The residue was treated with $CHCl_3$ (100 mL) and the clear solution was extracted with 10% Na_2CO_3 solution (100 mL) and then with distilled water. The extraction was repeated several times with distilled water until the pH was neutral. The chloroform phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated in a vacuum. The colored product was stirred in cold CH_2Cl_2, filtered and the solvent was evaporated in a vacuum. The residue was treated with acetone. The purification of the product was accomplished by column chromatography (SiO_2, CH_3OH:$CHCl_3$, 1:50 v/v). The colored product was soluble in $CHCl_3$, CH_2Cl_2, THF, acetone and toluene, and insoluble in distilled water and *n*-hexane. Yield: 757 mg (58%). FT-IR, $\nu_{max}/(cm^{-1})$: 2940–2855 (CH, aliphatic), 1720 and 1255 (COO), 1650 (C=C, aromatic), 1328, 1157, 1126, 628. ^{1}H NMR (δ, ppm): 4.66 (16H, t, O—CH_2), 4.10 (16H, t, S—CH_2), 2.52 (m, 16H, —CH_2—). ^{13}C NMR (δ, ppm): 26.4, 29.9, 61.9, 110.2, 115.8, 121.9, 137.4, 146.8, 147.9, 166.2. ^{19}F NMR (δ, ppm): −142.6 (*o*-fluoro), −152.8 (*p*-fluoro), −161.4 (*m*-fluoro). MS (ESI) *m/z*: 2610.8 $[M]^+$.

2.4. [2,3,7,8,12,13,17,18-Octakis(3-thiopropylpentafluorobenzoate) H^{21}, H^{23} porphyrazine] (*5*)

Compound **4** (106 mg, 0.1 mmol) was dissolved in a minimum amount of trifluoroaceticacid (~3.00 mL) and stirred for 3 h at room temperature. The reaction mixture was then added to ice dropwise and neutralized with 25% ammonia solution. Precipitation occurred and this precipitate was filtered. The precipitate was extracted into chloroform and the chloroform solution was extracted with distilled water twice. After drying over anhydrous Na_2SO_4, the solvent was evaporated to obtain a violet colored metal-free porphyrazine. Compound **5** was obtained by column chromatography (SiO_2, CH_3OH:$CHCl_3$, 1:50 v/v). Yield: 176 mg (68%). FT-IR, $\nu_{max}/(cm^{-1})$: 3285 (N—H), 2985–2850 (CH, aliphatic), 1727 and 1265 (COO), 1652 (C=C, aromatic), 1324, 1152, 1120, 622.

^{1}H NMR (δ, ppm): 4.44 (16H, t, O—CH_2), 4.15 (16H, t, S—CH_2), 2.55 (m, 16H, —CH_2—), −1.55 (br s, 2H, NH). ^{13}C NMR (δ, ppm): 26.5, 29.8, 61.8, 109.8, 115.9, 121.7, 137.0, 146.5, 147.7, 165.9. ^{19}F NMR (δ, ppm): −142.4 (*o*-fluoro), −151.2 (*p*-fluoro), −154.6 (*m*-fluoro). MS (ESI) *m*/*z*: 2587.2 $[M]^+$.

2.5. General procedure for metallo-porphyrazines (**6**–**8**)

Compound **5** (124 mg, 0.05 mmol) in $CHCl_3$ (10.0 mL) was stirred with the metal salt [$Cu(OAc)_2$ (91 mg, 0.5 mmol), $Zn(OAc)_2$ (92 mg, 0.5 mmol) or $Co(OAc)_2$ (89 mg, 0.5 mmol)] in ethanol (15.0 mL) and refluxed under nitrogen for about 6 h. The precipitate thus obtained was composed of the crude product and excess metal salt. The precipitate was treated with $CHCl_3$ and the insoluble metal salts were removed by filtration. The filtrate was reduced to a minimum volume under reduced pressure and then added to *n*-hexane (150 mL) dropwise to ensure precipitation. Finally, the pure porphyrazine derivatives (**6–8**) were obtained by the column chromatography (SiO_2, CH_3OH:$CHCl_3$, 1:20 v/v).

2.5.1. [2,3,7,8,12,13,17,18-Octakis(3-thiopropylpentafluorobenzoate) porphyrazinato] Cu(II) (**6**)

Yield: 61 mg (46%). FT-IR, ν_{max}/(cm^{-1}): 2980–2858 (CH, aliphatic), 1722 and 1262 (COO), 1648 (C=C, aromatic), 1320, 1155, 1122, 625. MS (ESI) *m*/*z*: 2649.8 $[M]^+$.

2.5.2. [2,3,7,8,12,13,17,18-Octakis(3-thiopropylpentafluorobenzoate) porphyrazinato] Zn(II) (**7**)

Yield: 72 mg (54%). FT-IR, ν_{max}/(cm^{-1}): 2985–2855 (CH, aliphatic), 1720 and 1265 (COO), 1655 (C=C, aromatic), 1326, 1158, 1132, 621. ^{1}H NMR (δ, ppm): 4.64 (16H, t, O—CH_2), 4.12 (16H, t, S—CH_2), 2.50 (m, 16H, —CH_2—). ^{13}C NMR (δ, ppm): 26.6, 29.7, 61.8, 110.1, 115.9, 121.7, 137.1, 146.5, 147.4, 166.1. ^{19}F NMR (δ, ppm): −142.9 (*o*-fluoro), −152.6 (*p*-fluoro), −161.6 (*m*-fluoro). MS (ESI) *m*/*z*: 2651.9 $[M]^+$.

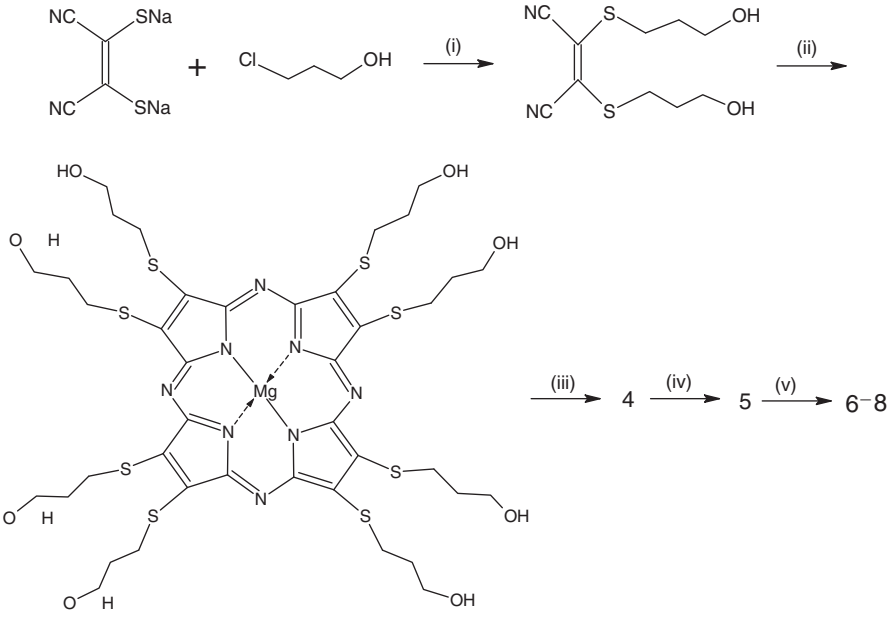
2.5.3. [2,3,7,8,12,13,17,18-Octakis(3-thiopropylpentafluorobenzoate) porphyrazinato] Co(II) (**8**)

Yield: 56 mg (42%). FT-IR, ν_{max}/(cm^{-1}): 2986–2854 (CH, aliphatic), 1725 and 1260 (COO), 1648 (C=C, aromatic), 1316, 1165, 1135, 629. MS (ESI) *m*/*z*: 2644.2 $[M]^+$.

3. Results and discussion

As proposed by Linstead, an unsaturated 1,2-dinitrile derivative should be prepared as the starting material [49,50]. The disodium salt of dithiomaleonitrile (**1**), obtained from the simple reactants sodium cyanide and carbondisulfide in two steps, was referred to as the starting point. Alkylation of the disodium salt of maleonitrile with 3-chloro-1-propanol in absolute ethanol gave 2,3-bis (3-hydroxypropylthio)maleonitrile (**2**), which was in the *cis*-form and easily soluble in chloroform, dichloromethane and acetone (Scheme 1). The reddish-brown colored product (**2**) was obtained in 75% yield. The presence of bulky electron-donating S-groups is expected to enhance the chemical stability and optical properties of porphyrazines [51]. Octakis(3-hydroxypropylthio)porphyrazinato magnesium (**3**) is obtained by cyclotetramerization of 2,3-bis (3-hydroxypropylthio)maleonitrile in a high-boiling solvent, like *n*-butanol, at high temperatures for 12 h [52–54]. Under normal conditions, the porphyrazine core has a −2 charge, so divalent metal ions give neutral porphyrazine complexes. Compound **3** was very soluble in most common solvents, such as methanol, ethanol, *n*-propanol, DMF and DMSO, but insoluble in *n*-hexane (Scheme 1). Octakis(3-thiopropylpentafluorobenzoate)porphyrazinato magnesium (**4**), with eight polyfluorinated groups appended on the periphery through flexible alkylthio-bridges, has been synthesized through esterification of **3** with 2,3,4,5,6-pentafluorobenzoic acid in the presence of dicyclohexylcarbodiimide (DCCI) and toluene-*p*-sulfonic acid.

The aim of the esterification was to enhance the overall solubility in common organic solvents. The parent hydroxy-terminated porphyrazines [55] are not practically soluble in solvents like chloroform or tetrahydrofuran; therefore, in order to be used more efficiently in some organic transformations or in some technological applications, these compounds must be converted into a more soluble form. Ester groups are known to provide good solubility, and they were selected because of the ease of their synthesis [27–32]. The most efficient route for this condensation reaction of carboxylic acid and the —OH groups on porphyrazines was to carry out the reaction at room temperature in the presence of a strongly dehydrating agent, such as dicyclohexylcarbodiimide (DCCI). The by-product, dicyclohexylurea, was eliminated by



Scheme 1. (i) Abs. EtOH; (ii) Mg turnings, I_2, *n*-BuOH; (iii) 2,3,4,5,6-pentafluorobenzoic acid, DCCI, toluene-*p*-sulfonic acid and dry pyridine; (iv) CF_3CO_2H; (v) EtOH, $CHCl_3$ and $Cu(OAc)_2$, $Zn(OAc)_2$, or $Co(OAc)_2$.

filtering the reaction mixture after treatment with cold dichloromethane. By referring to mass spectrometric data, the usage of the DCCI-mediated esterification system for octakis(hydroxypropylsulfanyl)porphyrazines ensured that all of the available —OH groups reacted in the process. The choice of reaction time was based on routine TLC tests and changed with different conditions. Another aim of this study was to see the effect of different esterification conditions on the reaction yield. Our results show that the best condition was to utilize DCCI:OH group in a 9:1 M ratio. Other procedures involved the usage of DCCI with toluene-*p*-sulfonic acid and the —OH group in a molar ratio like 24:1 [27–30,56,57]. The yield of **4** was of a sufficient level (58%) (Scheme 1). The symmetrically functionalized porphyrazine with eight ester units was soluble in common organic solvents, such as $CHCl_3$, CH_2Cl_2, THF, acetone and toluene, and insoluble in water and *n*-hexane. The conversion of **4** into **5** was achieved by the treatment with relatively strong acids (e.g. trifluoroacetic acid). Further reaction of **5** with copper(II) acetate, zinc(II) acetate and cobalt(II) acetate has led to the metal porphyrazinates (M = Cu, Zn, Co) (**6–8**) (Fig. 1).

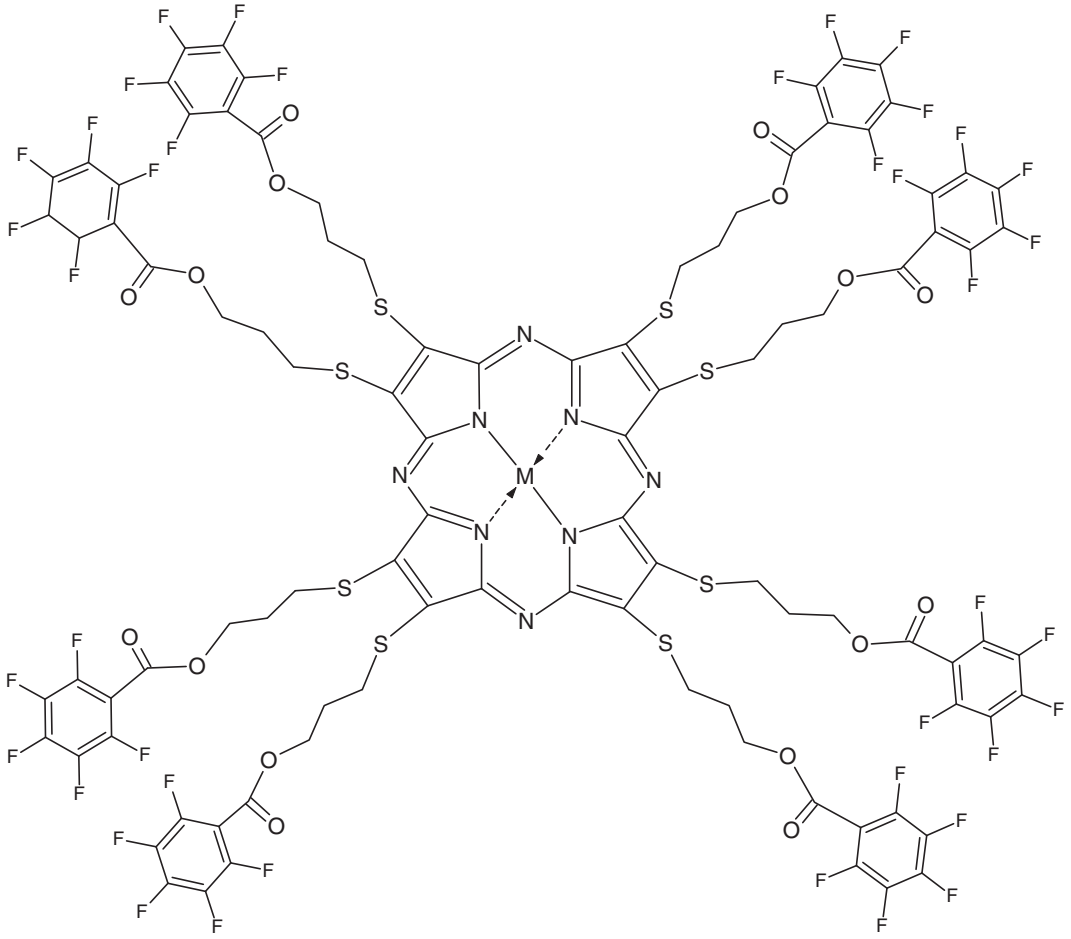
The newly synthesized compounds were characterized by FT-IR, UV–Vis, mass, ^1H, ^{13}C and ^{19}F NMR, together with elemental analysis. Spectral investigations for all new products were consistent with the assigned structures. The elemental analyses corresponded closely with the values calculated for **2–8** (Table 1).

Table 1
Elemental analyses results of **2–8**.*

Compound	C	H	N	S
2	46.61 (46.49)	5.59 (5.46)	10.72 (10.84)	24.70 (24.82)
3	45.54 (45.42)	5.23 (5.34)	10.69 (10.59)	24.37 (24.25)
4	44.28 (44.17)	1.96 (1.85)	4.18 (4.29)	9.72 (9.83)
5	44.66 (44.55)	1.82 (1.95)	4.44 (4.33)	9.80 (9.91)
6	43.64 (43.52)	1.72 (1.83)	4.34 (4.23)	9.81 (9.68)
7	43.59 (43.49)	1.71 (1.82)	4.34 (4.23)	9.58 (9.68)
8	43.71 (43.60)	1.71 (1.83)	4.36 (4.24)	9.58 (9.70)

* Required values are given in parentheses.

Comparison of the FT-IR spectra at each step gave some insights on the nature of the compounds. The FT-IR spectrum of **3** provided valuable information, as the C≡N vibration at 2227 cm^{-1} disappears with cyclotetramerization of **2**. This peak can be used to monitor the conversion, and to detect any ligand impurities in the porphyrazine **3**. In the FT-IR spectra for **4–8**, aliphatic C—H peaks around 2850–2986 cm^{-1}, C=O peaks around 1720–1727 cm^{-1}, O—C=O peaks at 1255–1265 cm^{-1}, the aromatic C=C peaks at 1648–1655 cm^{-1}, the disappearance of the O—H peak around 3330 cm^{-1} for **3** and the N—H vibrations around 3285 cm^{-1} for **5**, together with the high solubility in chloroform and tetrahydrofuran acquired after this reaction, are all evidences for the formation of **4–8**.



M = Mg(4); 2H(5); Cu(6); Zn(7); Co(8).

Fig. 1. 2,3,7,8,12,13,17,18-Octakis(3-thiopropylpentafluorobenzoate) substituted porphyrazines (**4–8**).

The ^{1}H NMR spectrum of **3** gave chemical shifts belonging to O—H (triplet), O—CH_2 (triplet), S—CH_2 (triplet) and —CH_2— (multiplet) at 4.55, 4.38, 3.66 and 2.48 ppm, respectively. In the ^{1}H NMR spectrum of **4**, protons of the O—CH_2, S—CH_2 and —CH_2— groups come out around 4.66, 4.10 and 2.52 ppm, respectively. ^{1}H NMR spectrum of **5** showed a chemical shift belonging to the porphyrazine ring protons (singlet) at −1.55 ppm [27–30,56,57]. In the ^{13}C NMR spectra of the diamagnetic porphyrazines **4**, **5** and **7**, ten different single chemical shifts for carbon atoms were clearly seen.

^{19}F NMR spectroscopy has been a very useful technique for investigating fluorinated compounds. The ^{19}F NMR spectrum of **4** showed three different peaks at −142.6, −152.8 and −161.4 ppm, relating to the fluorine atoms in the *ortho*, *para* and *meta* positions of the phenyl substituents, respectively, and the spectrum showed the expected signals for the five fluorine atoms attached to the aromatic ring [58,59]. Integration of the peaks gave a 2:1:2 ratio as expected.

In addition to these supportive results for the structures, mass spectrometry results of the pentafluorobenzoate substituted magnesium, metal-free, copper, zinc and cobalt porphyrazines (**4–8**) confirmed the complete esterification of —OH groups by the presence of molecular ion peaks, at *m/z*: 2610.8 $[M]^+$, 2587.2 $[M]^+$, 2649.8 $[M]^+$, 2651.9 $[M]^+$ and 2644.2 $[M]^+$, respectively.

UV–Vis spectra of **3**, **4**, **6–8** (Table 2) show two sharp bands as a result of $\pi \rightarrow \pi^*$ transitions of the macrocycles. The one around 300–400 nm is called the "B" or Soret band, while the one at 600–700 nm is called the "Q" band. The presence of an electron donating group on the periphery causes a bathochromic shift of the Q bands (**4**, **6–8**). These two bands are present in all the kinds of porphyrazine (**3**, **4**, **6–8**). UV–Vis spectra of **4**, **6–8** in chloroform are shown in Fig. 2. The UV–Vis spectra of **3** in solvents of different polarity (chloroform, ethanol, dichloromethane and pyridine) are given in Fig. 3. There is almost no difference with respect to the changes in the nature of the solvent. As expected for a porphyrazine core (**3**), there are two intense absorptions: one of them is in the UV-range around 368 nm and the other one is at the lower energy side of the visible region (668 nm). In most tetrapyrrole derivatives, the Q band absorption is more intense than the B band absorption, although both of them correspond to a $\pi \rightarrow \pi^*$ transition [52,60,61]. When we compare the absorbance values in these two peaks, the one in the UV-range is higher. The reason for this controversy is the combination of π–π^* transitions of pentafluorobenzoate units with the B band of the porphyrazine core. For the metal-free derivative (**5**), the Q band is split into two peaks at 650 and 710 nm as a consequence of the change in the symmetry of the porphyrazine core from D_{4h} (in the case of the metallo derivatives) to D_{2h}.

The aggregation treatment of porphyrazines in solution, which can be followed effectually by absorption works, is a good explanation of the interactions between the aromatic macrocycles of the porphyrazines. Aggregation, which is usually indicated as a coplanar association, is affected by the concentration, nature of the solvent, nature of the substituents, complexed metal ions and temperature [62–64]. The aggregation behavior of **6** was searched at several concentrations in chloroform (Fig. 4). In chloroform, as the concentration was increased, the intensity of the Q-band

Table 2
UV–Vis data for the porphyrazines **3–8** in chloroform.

Compound	λ/nm (log ε/dm^3 mol^{-1} cm^{-1})		
3	368 (4.94)	668 (4.79)	
4	379 (4.65)	675 (4.91)	
5	338 (4.85)	650 (4.65)	710 (4.68)
6	340 (4.95)	679 (4.99)	
7	352 (4.93)	683 (4.97)	
8	345 (4.65)	676 (4.72)	

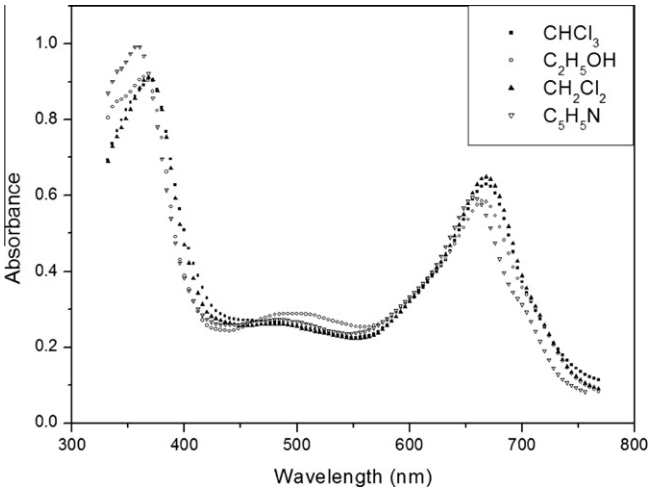


Fig. 3. UV–Vis spectra of **3** in various solvents.

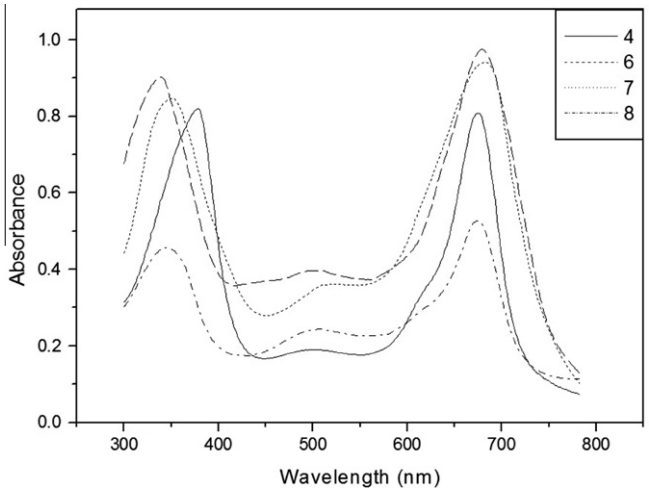


Fig. 2. UV–Vis spectra of **4**, **6–8** in chloroform.

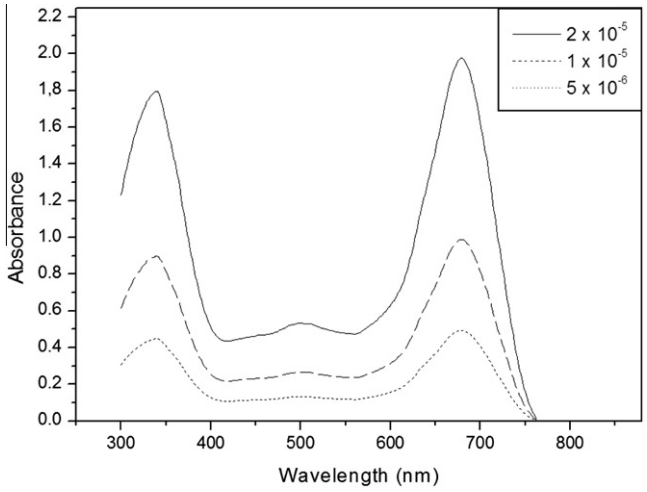


Fig. 4. UV–Vis spectra of **6** in chloroform at different concentrations.

absorption increased in parallel, and there were no new bands because of the aggregated species [23]. It is seen that the Beer–Lambert law was obeyed for compound **6** for concentrations ranging from 2×10^{-5} to 5×10^{-6} mol dm^{-3} (Fig. 4).

4. Conclusions

In conclusion, this study shows that a poorly soluble porphyrazine derivative containing reactive groups can be used as a framework for subsequent reactions, such as esterification. We believe that some of the synthesized compounds might be utilized as catalysts, soluble dyes and optical recording agents. Meanwhile, fluorinated metallo porphyrazines have currently been receiving a great deal of attention due to their interesting electron transport characteristics. Also, fluorocarbons display enhanced hydrophobicity, chemical resistance, thermal stability and lipophobicity in comparison to their hydrocarbon counterparts. Therefore, the products can be candidated for use in these areas.

Acknowledgement

This work was supported by the Scientific Research Fund of Fatih University under the Project No. P50021101_Y.

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