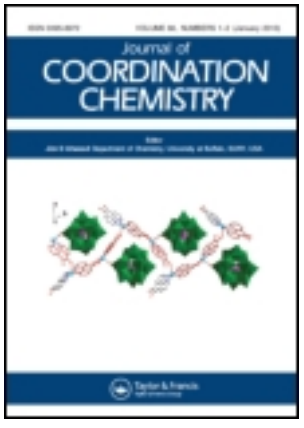

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis and characterization of soluble porphyrazines bearing octakis 2-anthraquinonylmethylthio substituents

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Published online: 18 Feb 2011.

To cite this article: Tuğba İpek & Ergün Gonca (2011) Synthesis and characterization of soluble porphyrazines bearing octakis 2-anthraquinonylmethylthio substituents, Journal of Coordination Chemistry, 64:5, 795-804, DOI: 10.1080/00958972.2011.555539

To link to this article: http://dx.doi.org/10.1080/00958972.2011.555539

Journal of Coordination Chemistry
Vol. 64, No. 5, 10 March 2011, 795–804

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Synthesis and characterization of soluble porphyrazines bearing octakis 2-anthraquinonylmethylthio substituents

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(*Received 29 September 2010; in final form 3 December 2010*)

By cyclotetramerization of 1,2-*bis*(2-anthraquinonylmethylthio)maleonitrile in the presence of magnesium butanolate, magnesium porphyrazinate carrying eight (2-anthraquinonylmethylthio) functional groups on peripheral positions has been synthesized. The metal-free derivative was obtained by treatment with trifluoroacetic acid; reaction of this product with copper(II) acetate, zinc(II) acetate, and cobalt(II) acetate led to the metal porphyrazinates [M = Cu(II), Zn(II), and Co(II)]. These new compounds have been characterized by elemental analysis, together with FT-IR, ^{1}H-NMR, ^{13}C-NMR, UV-Vis, and mass spectral data.

Keywords: 2-(Chloromethyl)anthraquinone; Porphyrazine; Maleonitrile; Copper; Zinc

1. Introduction

Tetrapyrrole macrocycles such as porphyrins, tetraazaporphyrins, phthalocyanines, and tetrabenzoporphyrins, modified by the attachment of peripheral substituents, receive extensive attention because of theoretical studies and applications in advanced materials science [1]. Porphyrins are important not only from biological aspects but also for coordination chemistry, catalysis, and materials science. Peripherally functionalized porphyrazines have the potential to exhibit novel optical, magnetic, and electronic properties. The transition metal ion in the inner core offers new ways to induce, modify, and control molecular properties. Metalloporphyrazines exhibit optical limiting effects comparable with phthalocyanine and naphthalocyanine derivatives [2].

Phthalocyanines are used in electrophotography, optic data collection, gas sensors, liquid crystals, laser technology, and photodynamic therapy of tumors as well as in their classical fields as pigments and dyes. Tuning properties of phthalocyanines has been generally achieved through changes in the nature and bonding of the substituents [3–6].

Although the number of metal ions taking part in the inner core of tetrapyrrole derivatives reaches 70, derivatization of porphyrazines has been generally achieved by addition of various substituents (e.g. alkyl-, aryl-, ether-, sulfanyl-, amino-, quaternized amino-groups, etc.) onto the peripheral positions [7–15]. These substituents mainly

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ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958972.2011.555539

enhance the solubility of the products and provide additional functionalities, such as interaction with alkali or transition metal ions, mesophase formation, etc.

Our group has been interested in the preparation of new porphyrazines in parallel with phthalocyanine analogs [16, 17]. Substitution of various groups on peripheral positions of porphyrazines has been accomplished either starting with an unsaturated dinitrile precursor with this group attached at the beginning (e.g. dimethylaminoethylthio [18], tosylaminoethylthio [19], 1-naphthylmethylthio [20], 9-anthracenylmethylthio [21], 4-*tert*-buthylphenylthio [22], (*p*-tolylmethylthio), (*o*-tolylmethylthio) [23], (3,5-*bis*-trifluoromethyl-benzylthio) [24], etc.) or a porphyrazine with reactive functional groups has been prepared first and then additional groups (e.g. ferrocene [25], benzo-15-crown-5 [26], quaternizable amino groups [27], triphenylphosphine [28], etc.) have been incorporated by further condensation. We have also synthesized new *seco*-porphyrazines substituted with 1-naphthyl [29], 4-biphenyl [30], *p*-tolyl and *o*-tolyl [31], and (4-*tert*-butylphenyl) [32] on the peripheral positions as encountered by Barrett, Hoffman, and coworkers, with peripheral amino derivatives [33, 34].

In this study, we report new soluble porphyrazines with eight (2-anthraquinonylmethylthio) substituents appended to the peripheral positions. Magnesium porphyrazinate has been synthesized by the cyclotetramerization of 1,2-*bis*(2-anthraquinonylmethylthio)maleonitrile in the presence of magnesium butanolate. The metal-free derivative was obtained by its treatment with trifluoroacetic acid and further reaction of this product with copper(II) acetate, zinc(II) acetate, and cobalt(II) acetate led to metal porphyrazinates [M = Cu(II), Zn(II), Co(II)]. These new compounds have been characterized by elemental analysis, FT-IR, ^{1}H-NMR, ^{13}C-NMR, UV-Vis, and mass spectral data.

2. Experimental

IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer and electronic spectra on a Unicam UV2 spectrophotometer. Elemental analyses were recorded on a Thermo Finnigan Flash EA 1112 instrument. ^{1}H- and ^{13}C-NMR spectra were taken in $CDCl_3$ solutions at 400 and 100.6 MHz, respectively, recorded on a Bruker Ultra Shield Plus 400 MHz spectrometer. Chemical shifts refer to TMS (^{1}H- and ^{13}C-NMR) as the internal standards. Mass spectra were recorded on Bruker Daltonics Micro-TOF and MALDI-TOF mass spectrometers using the electrospray ionization (ESI) method. The instrument was operated in positive-ion mode. All starting materials were purchased from major suppliers and used without purification. The homogeneity of the products was tested in each step by TLC.

The disodium salt of dithiomaleonitrile (**1**) was prepared according to previously reported procedures [35].

2.1. *Synthesis of 1,2-bis(2-anthraquinonylmethylthio)maleonitrile (2)*

Disodium salt of dithiomaleonitrile (**1**) (2.80 g, 15 mmol) was mixed with 2-(chloromethyl)anthraquinone (9.63 g, 37.5 mmol) in methanol (75 mL) and refluxed

under nitrogen for 24 h. When MeOH was evaporated, the remaining product was treated with $CHCl_3$ to remove insoluble salts by filtration. The $CHCl_3$ solution was extracted several times with 15% Na_2SO_4 solution and then dried over anhydrous Na_2SO_4 overnight. After evaporation of the solvent, the colored product was extracted by refluxing *n*-hexane to remove excess 2-(chloromethyl)anthraquinone. The product was brown and very soluble in chloroform, dichloromethane, THF, benzene, and acetone, but insoluble in *n*-hexane. Yield: 7.43 g (85%). FT-IR, $\nu_{max}/(cm^{-1})$: 3070 (CH, aromatic), 2978–2867 (CH, aliphatic), 2218 (C≡N), 1674 (C=O), 1612 (C=C, aromatic), 1588, 1557, 1445, 1365, 1312, 1271, 1165, 1128, 1027, 981, 845, 760, 728, 712, and 654. ^{1}H-NMR (δ, ppm) 7.82–7.68 (m, 6H, Ar–H), 7.58–7.32 (m, 8H, Ar–H), 4.66 (s, 4H, S–CH_2). ^{13}C-NMR (δ, ppm) 40.2, 113.6, 115.8, 129.2, 130.2, 131.4, 132.2, 132.4, 133.8, 143.2, and 182.4. MS (ESI): (m/z): 582.1 $[M]^+$.

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

Mg turnings (6 mg, 0.25 mmol) and a small I_2 crystal were refluxed in *n*-BuOH (20 mL) for 8 h to obtain $Mg(BuO)_2$. Derivative **2** (291 mg, 0.5 mmol) was added to this solution and the mixture was refluxed for 12 h. The blue-green product was filtered, washed with ethanol and water, and dried in a vacuum. The crude product was dissolved in $CHCl_3$ and filtered. The $CHCl_3$ solution was dried over anhydrous Na_2SO_4. When the solvent was evaporated, a dark blue-green product was obtained. Finally, pure porphyrazine was obtained by chromatography on silica gel using methanol/chloroform (1 : 50) mixture as eluent. The product was soluble in chloroform, dichloromethane, acetone, and toluene, but insoluble in *n*-hexane. Yield: 200 mg (68%). FT-IR, $\nu_{max}/(cm^{-1})$: 3075 (CH, aromatic), 2982–2872 (CH, aliphatic), 1678 (C=O), 1615 (C=C, aromatic), 1590, 1559, 1448, 1367, 1310, 1269, 1166, 1125, 1028, 984, 846, 762, 730, 710, and 656. ^{1}H-NMR (δ, ppm) 7.85–7.64 (m, 24H, Ar–H), 7.54–7.28 (m, 32H, Ar–H), 5.49 (s, 16H, S–CH_2). ^{13}C-NMR (δ, ppm) 40.4, 113.4, 115.6, 129.1, 130.1, 131.3, 132.2, 132.4, 133.6, 143.0, and 182.0. MS (ESI): (m/z): 2353.2, 2354.2, and 2355.2 $[M]^+$.

2.3. *[2,3,7,8,12,13,17,18-octakis(2-anthraquinonylmethylthio)H^{21}, H^{23}porphyrazine] (3b)*

Derivative **3a** (235 mg, 0.1 mmol) was dissolved in minimum trifluoroacetic acid (~4 mL) and stirred for 3 h at room temperature. When the reaction mixture was added dropwise to ice and neutralized with 25% ammonia solution, precipitation occurred, and the precipitate was collected by filtration. The precipitate was extracted into chloroform and the chloroform solution was extracted with water twice. After drying over anhydrous Na_2SO_4, the solvent was evaporated to obtain a purple, metal-free porphyrazine. The crude product (**3b**) was purified by chromatography on silica gel using methanol/chloroform (1 : 50) as eluent. Yield: 145 mg (62%). FT-IR, $\nu_{max}/(cm^{-1})$: 3335 (N–H), 3065 (CH, aromatic), 2945–2863 (CH, aliphatic), 1674 (C=O), 1608 (C=C, aromatic), 1592, 1557, 1446, 1369, 1313, 1267, 1165, 1128, 1025, 986, 848, 764, 732, 712, and 658. ^{1}H-NMR (δ, ppm) 7.88–7.66 (m, 24H, Ar–H), 7.57–7.30 (m, 32H, Ar–H), 5.45 (s, 16H, S–CH_2), −1.10 (br s, 2H, NH). ^{13}C-NMR (δ, ppm) 40.4, 113.3, 115.5, 129.1, 130.0, 131.4, 132.3, 132.5, 133.5, 143.1, and 182.1. MS (ESI): (m/z): 2333.2 $[M]^+$.

2.4. *General procedure for metallo-porphyrazines (3c–3e)*

Derivative **3b** (233 mg, 0.1 mmol) in $CHCl_3$ (10 mL) was stirred with the metal salt [$Cu(OAc)_2$ (181.6 mg, 1 mmol), $Zn(OAc)_2$ (183.4 mg, 1 mmol), or $Co(OAc)_2$ (177 mg, 1 mmol)] in ethanol (15 mL) and refluxed under nitrogen for 6 h. Then, the precipitate, composed of the crude product and the excess metal salt, was filtered. The precipitate was treated with $CHCl_3$ and the insoluble metal salts were removed by filtration. The filtrate was reduced to the minimum volume under reduced pressure and then added into *n*-hexane (100 mL) drop by drop to realize precipitation. Finally, pure porphyrazine derivatives were obtained by chromatography on silica gel using methanol/chloroform (1 : 100) as eluent.

2.4.1. [2,3,7,8,12,13,17,18-octakis(2-anthraquinonylmethylthio)porphyrazinato]Cu(II) (3c).

Yield: 115 mg (48%). FT-IR, $\nu_{max}/(cm^{-1})$: 3072 (CH, aromatic), 2984–2870 (CH, aliphatic), 1676 (C=O), 1618 (C=C, aromatic), 1592, 1557, 1450, 1369, 1312, 1271, 1168, 1126, 1026, 986, 846, 761, 733, 711, and 655. MS (ESI): (*m*/*z*): 2394.9, 2395.9 [M]+.

2.4.2. [2,3,7,8,12,13,17,18-octakis(2-anthraquinonylmethylthio)porphyrazinato]Zn(II) (3d).

Yield: 125 mg (52%). FT-IR, ν_{max}, cm^{-1}: 3062 (CH, aromatic), 2966–2875 (CH, aliphatic), 1675 (C=O, aromatic), 1618 (C=C, aromatic), 1595, 1553, 1455, 1366, 1315, 1274, 1170, 1129, 1024, 985, 844, 765, 736, 714, and 658. ^{1}H-NMR (δ, ppm) 7.84–7.60 (m, 24H, Ar–H), 7.56–7.25 (m, 32H, Ar–H), 4.75 (s, 16H, S–CH_2). ^{13}C-NMR (δ, ppm) 40.2, 113.6, 115.8, 129.2, 130.3, 131.0, 132.0, 132.2, 133.8, 143.3, and 182.4. MS (ESI): (*m*/*z*): 2394.8, 2396.8, 2397.8, 2398.8, and 2400.8 $[M]^+$.

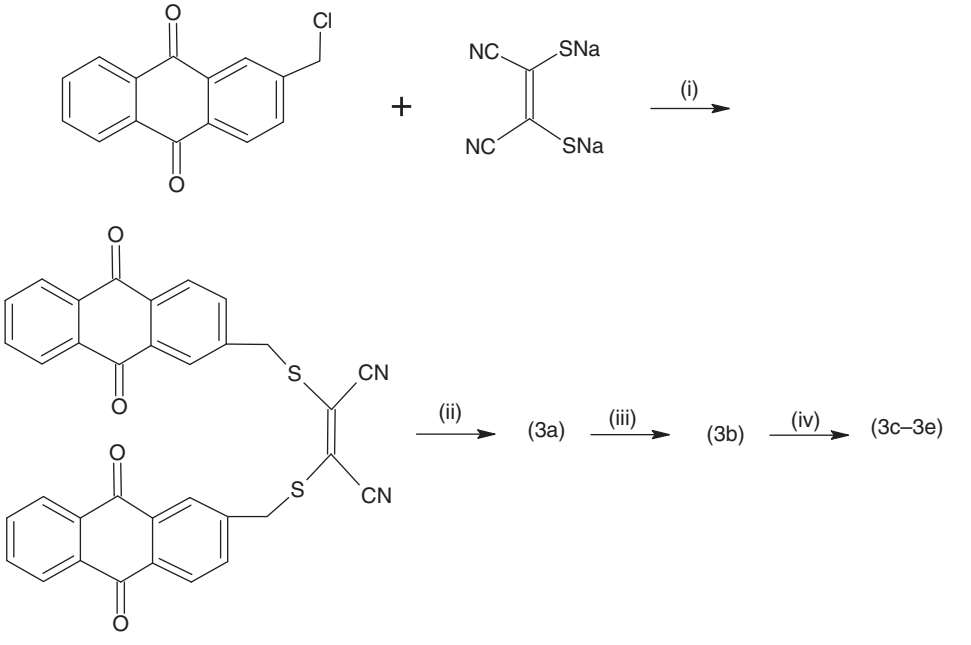
2.4.3. [2,3,7,8,12,13,17,18-octakis(2-anthraquinonylmethylthio)porphyrazinato]Co(II) (3e).

Yield: 131 mg (55%). FT-IR, ν_{max}, cm^{-1}: 3066 (CH, aromatic), 2968–2870 (CH, aliphatic), 1675 (C=O, aromatic), 1612 (C=C, aromatic), 1595, 1552, 1455, 1364, 1315, 1272, 1170, 1127, 1024, 984, 844, 767, 736, 712, and 658. MS (ESI): (*m*/*z*): 2390.2 $[M]^+$.

3. Results and discussion

New soluble porphyrazines with eight (2-anthraquinonylmethylthio) substituents appended to the peripheral positions have been synthesized and characterized. The starting point for these new porphyrazine structures with eight (2-anthraquinonylmethylthio) functional groups is 1,2-*bis*(2-anthraquinonylmethylthio)maleonitrile (**2**), which was obtained from the disodium salt of dithiomaleonitrile (**1**) and I_2. The brown **2** was obtained in 85% yield.

In order to convert 1,2-*bis*(2-anthraquinonylmethylthio)maleonitrile (**2**) into porphyrazine (**3a**) (scheme 1), we have made use of its template reaction in the presence of magnesium butanolate, the typical method applied in cyclotetramerization of tetrapyrrole derivatives [36–38]. The dark green **3a** was obtained with a yield of 68% (figure 1). Derivative **3a** was soluble in chloroform, dichloromethane, acetone, and toluene, but insoluble in *n*-hexane.

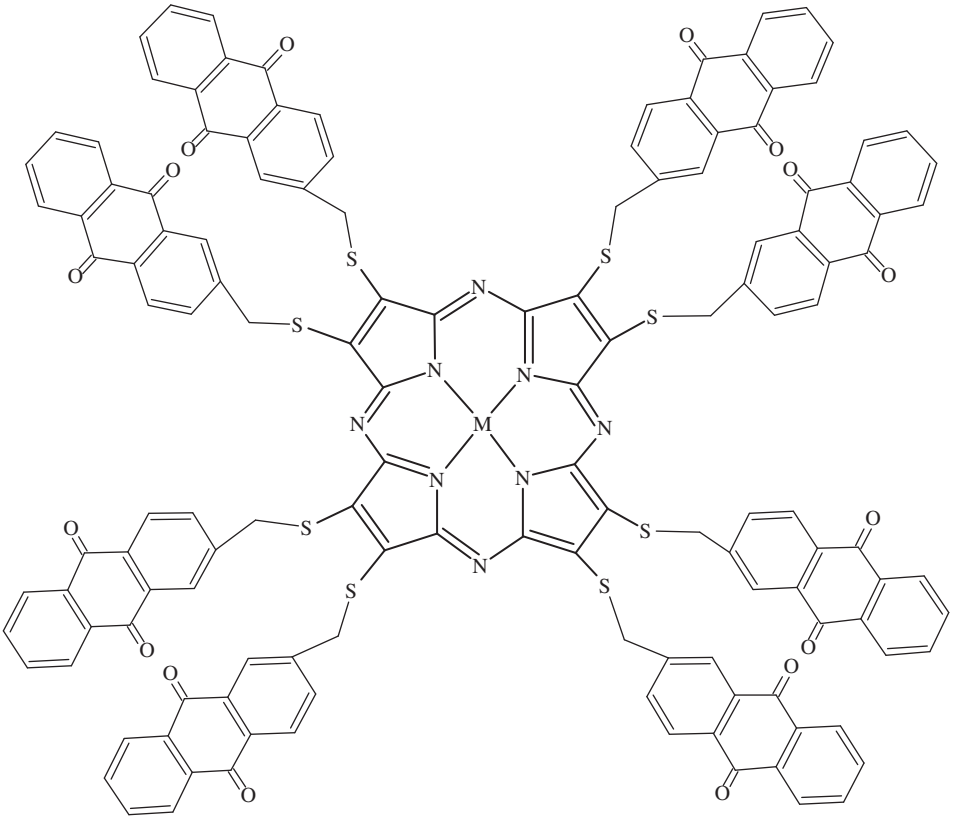


Scheme 1. (i) Methanol; (ii) Mg turnings, I_2, *n*-BuOH; (iii) CF_3CO_2H; (iv) EtOH and $Cu(OAc)_2$, $Zn(OAc)_2$, or $Co(OAc)_2$.

The conversion of **3a** to metal-free **3b** was achieved by treatment with trifluoroacetic acid followed by neutralization with ammonia and aqueous precipitation. The mass spectral results (figure 2) clearly indicate the change of the structure from magnesium porphyrazinate (**3a**) to the demetalated porphyrazine (**3b**). Incorporation of transition metal ions into the inner core of porphyrazine (**3c–3e**) was achieved by treatment of the demetalated porphyrazine (**3b**) with metal acetates [i.e. $Cu(OAc)_2$, $Zn(OAc)_2$, or $Co(OAc)_2$]. The metallation reactions were completed by refluxing under nitrogen for 4 h in a chloroform–ethanol mixture. Elemental analyses correspond closely with the values calculated for **2** and **3a**–**3e** (table 1).

In the FT-IR spectrum of **2**, the C≡N stretch is at 2218 cm^{-1}, the aliphatic and aromatic C–H peaks in the range 2867–3070 cm^{-1}, C=O at 1674 cm^{-1} and C=C (aromatic) at 1612 cm^{-1}. These values comply with those reported for similar compounds [18–24]. After conversion of **2** to **3a**, the sharp C≡N vibration at 2218 cm^{-1} disappeared. The N–H stretches of the inner core of the demetalated porphyrazine (**3b**) were observed at 3335 cm^{-1}. FT-IR spectra of all porphyrazine derivatives (**3a–3e**) showed aliphatic and aromatic C–H peaks at 2863–3075 cm^{-1} [19–22, 29–32].

In ^{1}H-NMR spectra of **2**, **3a**, **3b**, and **3d**, chemical shifts corresponding to (2-anthraquinonylmethylthio) groups are at the expected values. The N–H protons of metal-free porphyrazine (**3b**) were identified as a broad peak at $\delta = -1.10$ ppm, with typical shielding of inner core protons, common for metal-free porphyrazines [20, 23, 26, 39]. In ^{1}H-NMR spectra of **3a**, **3b**, and **3d**, two types of protons are clearly seen as a multiplet in the range 7.25–7.88 ppm corresponding to anthraquinonyl-protons and a



M = Mg (**3a**); 2H (**3b**); Cu (**3c**); Zn (**3d**); Co (**3e**)

Figure 1. Octakis (2-anthraquinonylmethylthio) substituted porphyrazines (**3a–3e**).

singlet at 5.49 ppm (**3a**), 5.45 ppm (**3b**), or 4.75 ppm (**3d**) for methylene protons. The ratio of the integral values 7 : 2 confirms the proposed structure. In the ^{13}C-NMR spectra of diamagnetic porphyrazines **3a**, **3b,** and **3d**, 11 different chemical shifts for carbon atoms are clearly seen.

UV-Vis spectra establish the structure of the porphyrazines (**3a**–**3e**). The electronic spectra of **3a**, **3c**, **3d**, and **3e** exhibit a strong absorption at 632–644 nm due to a π–π^* transition, commonly referred to as the Q-band. A second intense and broad π–π^* transition at 340–368 nm is called B band, also characteristic of porphyrazines. The demetalated porphyrazine (**3b**) shows a split Q-band because of the change in symmetry from D_{4h} in **3a** to D_{2h} in **3b**. Here, for porphyrazines with appended (2-anthraquinonylmethylthio) substituents in addition to these absorptions of the porphyrazine core, an intense absorption due to $\pi \rightarrow \pi^*$ transition of anthraquinone appeared for **3a**–**3e** at 284–288 nm (table 2). UV-Vis spectra of (**3a–3e**, 1×10^{-5} M) in chloroform are shown in figure 3. An absorbance *versus* concentration study indicated that due to (2-anthraquinonylmethylthio) units, the UV-Vis spectrum of the free ligand with broad and low intensity Q-bands does not exclude the presence of aggregation.

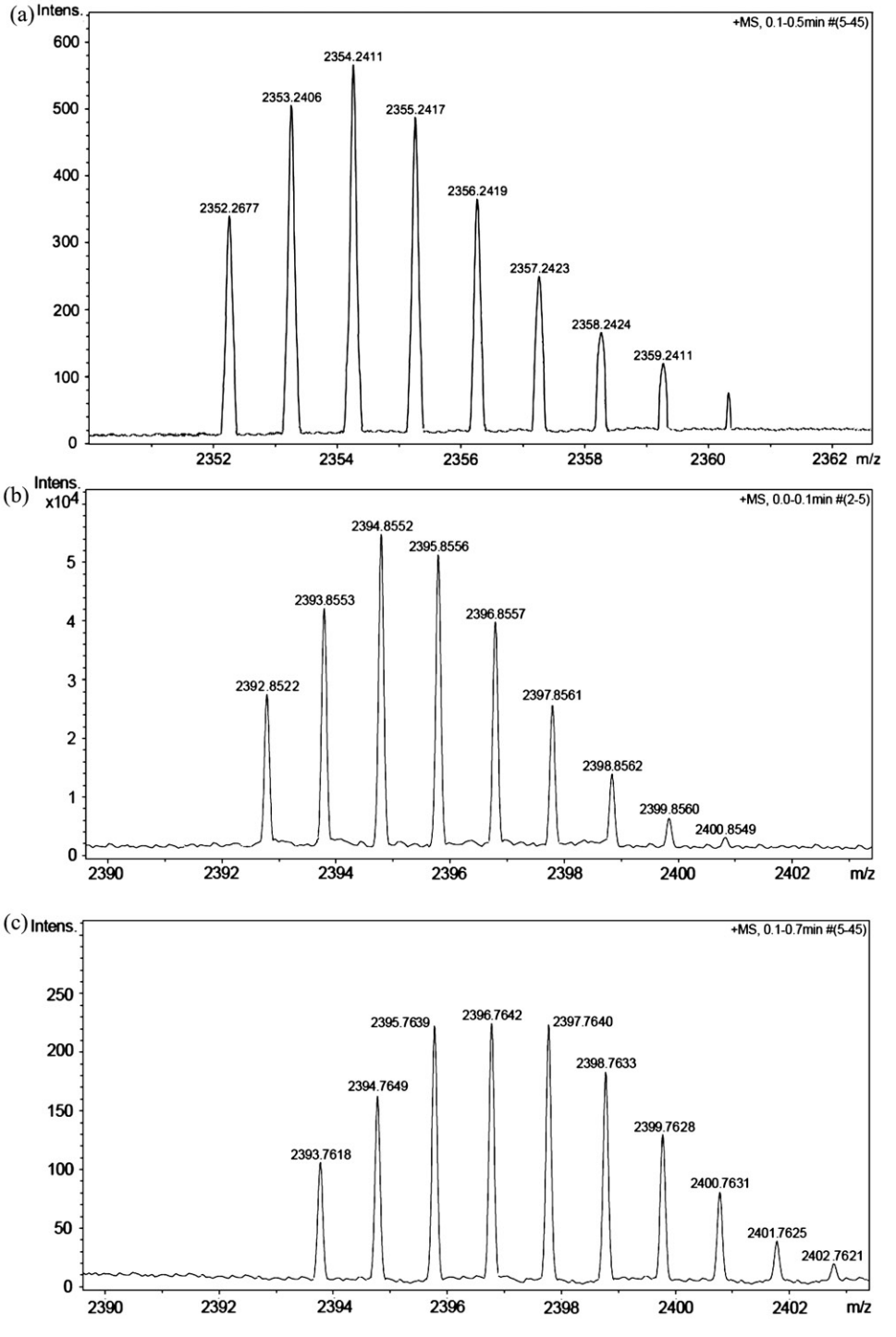


Figure 2. High-resolution mass spectra of: (a) **3a**, (b) **3c**, and (c) **3d**.

Table 1. Elemental analyses of **2** and **3a–3e**.[a]

Compound	C	H	N
2	70.20 (70.09)	3.21 (3.11)	4.70 (4.81)
3a	69.48 (69.36)	3.00 (3.08)	4.86 (4.76)
3b	70.14 (70.03)	3.11 (3.20)	4.69 (4.80)
3c	68.32 (68.23)	3.13 (3.03)	4.58 (4.68)
3d	68.09 (68.18)	3.12 (3.03)	4.79 (4.68)
3e	68.47 (68.36)	3.16 (3.04)	4.58 (4.69)

[a]Required values are given in parentheses.

Table 2. UV-Vis data for **3a–3e** in chloroform.

Compound	$\lambda\,nm^{-1}$ ($\log \varepsilon/dm^3\,mol^{-1}\,cm^{-1}$)			
3a	284 (4.88)	368 (4.64)	644 (4.45)	
3b	284 (4.99)	348 (4.81)	620 (4.25)	676 (4.32)
3c	284 (4.96)	344 (4.79)	632 (4.39)	
3d	288 (4.97)	344 (4.88)	644 (4.65)	
3e	288 (4.94)	340 (4.82)	640 (4.47)	

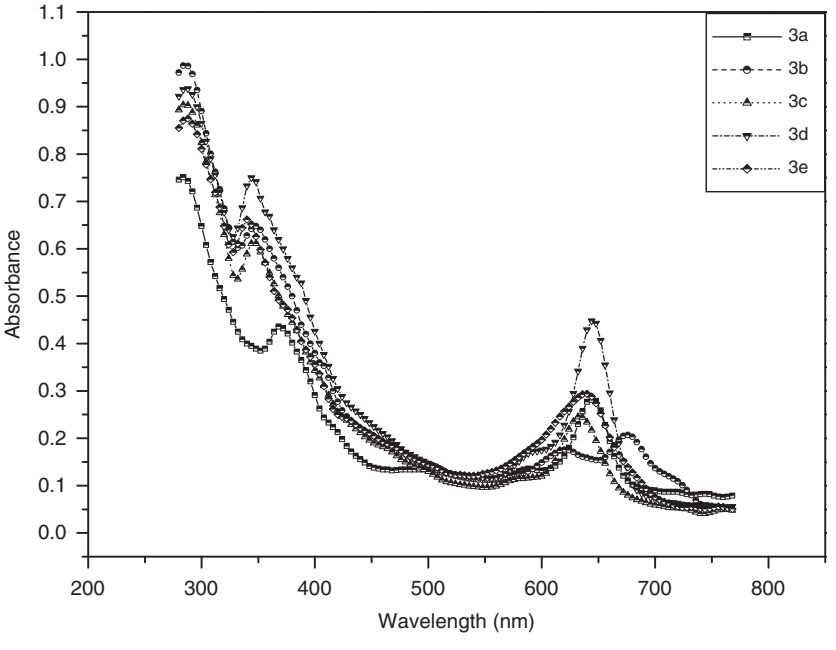


Figure 3. UV-Vis spectra of **3a–3e** in chloroform.

UV-Vis spectra of **3a** in solvents of different polarities (chloroform, dichloromethane, acetone, and toluene) are given in figure 4. There is almost no difference with respect to change in the nature of the solvent.

In conclusion, we have described the synthesis and the spectral characterization of new porphyrazines surrounded with eight bulky (2-anthraquinonylmethylthio) groups

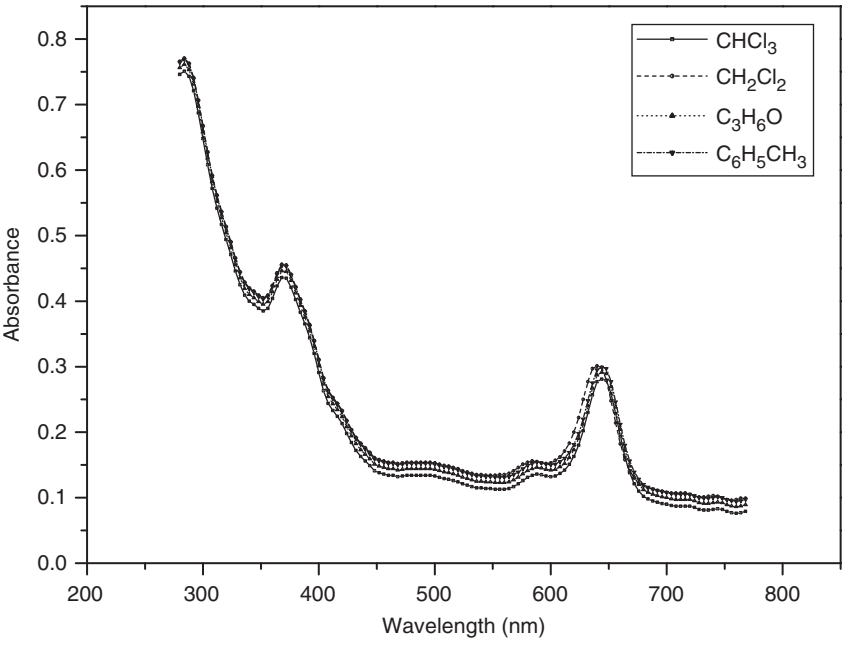


Figure 4. UV-Vis spectra of **3a** in various solvents.

on the periphery. High electron density on the substituents results in a second absorption in the ultraviolet region of comparable intensity to the intense B-band of porphyrazines.

Acknowledgments

This work was supported by the Scientific Research Fund of Fatih University under the project number P50020901_1.

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